with both lead bromide and lead chloride is described in the following paper.

We are very greatly indebted to the Carnegie Institution of Washington for generous assistance in pursuing this investigation.

CAMBRIDGE, MASS.

# A REVISION OF THE ATOMIC WEIGHT OF LEAD. THE ANALYSIS OF LEAD BROMIDE AND CHLORIDE.

### [THIRD PAPER.]

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## Introduction.

The outcome of the investigation described in the preceding paper, that the atomic weight of lead is nearly 207.2, rather than 207.1 as previously found by Baxter and Wilson,[1] led us to pursue the subject further with the greatest care, in order if possible to discover the cause of the difference, and at any rate to come to a definite conclusion as to the real value of the constant in question. In the first place, it was conceivable, in spite of the evidence obtained, that the lead bromide which had been fused in hydrobromic acid was slightly basic. In the second place, recently the apparent relationship of lead to radioactive change has aroused interest as to the identity of lead from different sources, and suggested the possibility that the lead material used by Baxter and Thorvaldson was different from that used earlier by Baxter and Wilson. These points were carefully tested. In the first place, lead bromide was prepared with even greater pains than before, and analyzed. Since this work yielded evidence in accord with the results given in the preceding paper, lead chloride was then investigated anew, with the outcome that essentially the same result was obtained as with the bromide, namely, 207.2.

While this investigation was in progress, the exact value of the atomic weight of lead became of considerable importance in connection with the theory of atomic disintegration of the radioactive elements. According

[1] *Proc. Amer. Acad.*, 43, 365 (1907); THIS JOURNAL, 30, 187 (1908).

to the hypothesis of Fajans[1] and Soddy[2] at least two lead "isotopes" exist, one resulting from the expulsion of five α-particles from radium with an atomic weight 206, the other resulting from the expulsion of eight α-particles from thorium with an atomic weight of about 208.3. If ordinary lead is composed of, or contains, these isotopes, in proportions varying with its origin, then its atomic weight might be expected to vary according to its source. Richards and Lembert[3] found that, in accordance with this hypothesis, radioactive lead extracted from radioactive minerals possesses an atomic weight different from that of ordinary lead, and differing also according to the mineral from which it is extracted, a result confirmed by Hönigschmid,[4] M. Curie[5] and Soddy.[6] In order to find out whether ordinary lead is subject to similar variations, seven varieties of inactive lead material from known widely different geographical sources were examined. Not the slightest difference between any of these specimens could be detected so far as analysis of the chloride is concerned. Furthermore these specimens were found to be spectroscopically identical and none of them were radioactive, so far as could be determined While the evidence thus obtained is by no means final as to the origin of ordinary lead, it certainly is striking that, if common lead is composed either wholly or in part of isotopes, its composition should be essentially constant.

## PART I. THE ANALYSIS OF LEAD BROMIDE.

### Purification of Reagents.

General reagents were purified by methods found amply satisfactory in the past.

**Water.**—All the pure water used in this work was prepared by double distillation, once from alkaline permanganate, and once from very dilute sulfuric acid. The condensers were block-tin tubes, fitted to Jena flasks with constricted necks, which served as stills. The connection was made by a water seal, no rubber or cork being used. The water was collected in Jena flasks or non-sol bottles, generally just previous to use.

**Ammonia.**—The concentrated C. P. reagent was gently boiled in a ground-stoppered flask, and the gas conducted through a glass tube to the surface of the purest water.

**Nitric Acid.**—Concentrated C. P. nitric acid was distilled through either a quartz or platinum condenser, with rejection of the first two-thirds of the distillate. The last third was collected in a quartz flask. The purity of nitric acid distilled through either platinum or quartz

[1] *Ber.*, 46, 422 (1913).
[2] *Chem. News*, 107, 97 (1913).
[3] THIS JOURNAL, 36, 1329 (1914).
[4] *Compt. rend.*, 158, 1786 (1914): *Z. Elect.*, 20, 319.
[5] *Ibid.*, 158, 1676 (1914).
[6] *Proc. Chem. Soc.*, 30, 134 (1914).

has been several times investigated in the past, but recently we made this matter the subject of a special investigation,[1] and found no evidence that well cleaned platinum vessels are affected by nitric acid.

Bromine.—Crude bromine was subjected to the following treatment in order to remove chlorine, iodine, and organic matter. Special pains were taken to eliminate the last impurity, because of the difficulty met by Baxter and Thorvaldson in preparing lead bromide free from organic matter. The treatment used was essentially that employed by Baxter, Moore, and Boylston[2] in an investigation upon the atomic weight of phosphorus.

The crude material was first subjected to distillation from aqueous potassium bromide in order to remove chlorine. About 600 cc. of a 50% solution of commerical potassium bromide were placed in a one-liter distilling flask with a ground stopper, and in the solution was dissolved somewhat over 400 g. of bromine. The side tube of the flask was inserted for some distance in one end of a glass condenser, while the other end of the condenser tube delivered into a Jena flask cooled with ice. With this apparatus the bromine could be distilled from the solution with minimum loss. Three portions of bromine were distilled from the same potassium bromide solution.

Next, one-fourth of the product was converted into potassium bromide by addition to recrystallized potassium oxalate, and the remaining three-fourths of the bromine was distilled from solution in this potassium bromide in the fashion described above. This second distillation, from a bromide which already must have been nearly free from chloride, has in the past been found amply sufficient to remove chlorine. Nevertheless, as will be described, the bromine later received still a third distillation from even purer potassium bromide.

In order to remove organic matter, the bromine was next changed to potassium bromide and fused. All of the twice-distilled bromine was converted into potassium bromide by addition to aqueous potassium oxalate, which had been recrystallized until free from chloride, and the solution was freed from iodine by boiling, with occasional addition of small amounts of the pure bromine. Then the solution was evaporated to dryness, and the salt was fused in a platinum dish. During the fusion a small amount of recrystallized potassium permanganate was added in order completely to oxidize organic matter. Material which had been fused with permanganate had no perceptible odor even while warm, whereas, if the addition of the permanganate was omitted, the salt had a distinct "organic" odor. The treatment with permanganate also must have eliminated any residual iodine. The purification of much of the

[1] This Journal, 36, 1088 (1914); Z. anorg. Chem., 87, 353 (1914).

[2] Proc. Amer. Acad., 47, 585 (1912); This Journal, 34, 1644 (1912).

bromine, up to this point, was performed by Mr. M. R. Grose. From this potassium bromide, bromine was prepared as needed by dissolving in water and adding twice-recrystallized potassium permanganate and sulfuric acid which had been heated to fuming with a small amount of permanganate. Only about four-fifths of the bromine was freed from the bromide, so that the product thus received still a third distillation from a very pure bromide. The bromine was always employed in the form of hydrobromic acid.

**Hydrobromic Acid.**—Hydrobromic acid was used either in the gaseous form, or in solution. It was always synthesized from the purified bromine and pure hydrogen, since this method seemed to offer fewest possibilities for contamination during the process of manufacture. Pure hydrogen was generated electrolytically in a series of cells, each of which consisted of zinc amalgam—hydrochloric acid—platinized platinum[1] (see figure). Hydrogen gas prepared in this way is free from arsine and hydrocarbons.[2] It contains, of course, hydrochloric acid and water vapor, but these were easily removed by passing the gas through tubes containing fused potassium hydroxide. The gas was charged with bromine in a small bulb, and then was conducted over either platinized asbestos or platinized pumice in a hard glass tube heated to dull redness. The pumice seemed to retain its catalytic power longer than the asbestos. In order to produce the maximum yield, the bromine was kept at about $44°$ by means of a water bath, since at that temperature the vapor pressure of bromine is about one-half atmosphere. Usually a very slight excess of hydrogen was maintained, so that the resulting gas mixture was nearly, if not quite free from bromine. To prepare hydrobromic acid solution, the gas was conducted into water until acid of nearly constant-boiling composition was obtained. Then the solution was subjected to three distillations through a quartz condenser, the first runnings being discarded in each distillation.

**Silver.**—Silver was prepared by methods which have frequently been used in the Harvard Laboratories for the purpose. Since the purification of silver has been many times described in some detail, it is necessary only to outline the processes employed. Crude metallic silver was dissolved in nitric acid, and the chloride was precipitated in strongly acid solution with an excess of hydrochloric acid. The precipitate was thoroughly washed, dissolved in concentrated ammonia, and reprecipitated with an excess of nitric acid. Reduction of the chloride by means of sodium hydroxide and sugar followed, and the product, after thorough washing, was fused on charcoal before a blowpipe. The buttons of metal were cleaned by scouring and etching. Then they were dissolved in redistilled nitric acid,

[1] Cooke and Richards, *Proc. Amer. Acad.*, **23**, 149 (1887).
[2] See also Baxter and Hoover, THIS JOURNAL, **34**, 1657 (1912).

and the metal was again precipitated from neutral solution with ammonium formate, which had been made from redistilled materials. Prolonged washing was necessary before the wash waters were free from ammonia. The product was dried and again fused before a clean blast lamp, in a porcelain crucible lined with very pure lime. This lime was made from calcium oxide and nitrate, both of which had been very carefully freed from foreign metals by crystallization of the nitrate. After being etched with nitric acid, the buttons were purified electrolytically in a cell in which a piece of the purest silver served as cathode, one or more of the buttons as anode, and a nearly neutral solution of one of the buttons as electrolyte. The washed electrolytic crystals were finally fused upon lime boats in a current of pure hydrogen. In order completely to remove adhering lime, the buttons were etched with dilute nitric acid, thoroughly washed with dilute ammonia and water, and then dried by heating in a vacuum to about 400° in a hard glass tube. This specimen of silver is designated Sample I. In many of the experiments, specimens of silver prepared in an identical fashion for other investigations were employed. Sample II was purified by Mr. W. H. Whitcomb,[1] Sample III by Mr. A. C. Boylston,[2] and Sample IV by Dr. H. C. Chapin.[3] Sample I was used in Analyses 6, 7, 9, 10, 11, 12, 16, 32, 34, 35, 36, 37, 38, 39, 40, 42, 44, 45, and 47; Sample II in Analyses 5, 8, 14, 15, 19, and 33; Sample III in Analyses 17, 41, 46, and 48; and Sample IV in Analyses 18 and 43. In Analyses 1, 2, 3, 4, and 13 it is uncertain whether Sample I or II was employed. So far as could be determined by the results of the analyses these four samples of silver were exactly alike. This matter is further considered on page 1058.

## Purification of Lead Nitrate.

Since the lead bromide was always made by precipitation from a nitrate solution, the preparation of pure lead nitrate was one of the most important operations. Several methods were used for the purification of the salt: first, electrolysis with a dissolving anode; second, simple recrystallization of the nitrate; and third, precipitation of sulfate or chloride. In fact the second method was used also in conjunction with the first and third.

For the electrolytic purification a cell was used consisting of an anode of crude sheet lead, a platinum cathode, and, as electrolyte, a nearly saturated slightly acid solution of lead nitrate. The crystals of metallic lead which formed on the cathode during electrolysis were frequently removed by means of a glass rake, washed thoroughly, and centrifugally

[1] For an investigation upon the atomic weight of neodymium, not yet published.

[2] Baxter, Moore and Boylston, *Proc. Amer. Acad.*, 47, 585 (1913); THIS JOURNAL, 34, 1644 (1912).

[3] Baxter and Chapin, *Proc. Amer. Acad.*, 46, 213 (1910); THIS JOURNAL, 33, 116 (1911).

drained in porcelain Gooch crucibles. The crystals rusted rapidly, hence they were subsequently reduced by fusion in a current of illuminating gas. Unglazed porcelain boats were filled with the crystals, and placed in an electrically heated porcelain tube. The illuminating gas was scrubbed with wet glass wool, and partially purified and dried by concentrated sulfuric acid and fused sodium hydroxide. Since the metal adhered strongly to the porcelain, the boat was then heated in the air, and the metal poured into a wooden mould.

The progress of the purification of this material was followed by photographing the ultraviolet spectrum of the lead spark by means of a Féry quartz spectrograph. In order to produce electrodes, the lead was melted in a hard glass tube or porcelain crucible, and drawn up into glass capillary tubes. The original sheet lead was found to contain a small amount of copper and a trace of silver. After the first electrolysis the copper and silver lines appeared in the spectrum in almost undiminished intensity. A second electrolysis followed. In this case the cathode was a small piece of the once electrolyzed lead, and the anode larger pieces of the same material. The electrolyte was made from the once purified lead by solution in nitric acid and crystallization of the nitrate. Since the greater part of the copper was contained in the mother liquor, the crystals were dissolved to form the electrolyte. During this second electrolysis, but not during the first, the anode was enclosed in a clean cotton bag to prevent the anode slime from contaminating the crystal deposit. The product of the second electrolysis was washed, dried and fused, as described above. Spectrographic examination of the twice electrolyzed material showed that copper and silver were still contained in the metal, although the proportions of these impurities may have diminished slightly.

With the hope that the transfer of silver and copper from anode to cathode would proceed less readily with a chloride electrolyte, a portion of the once electrolyzed material was subjected to a second electrolysis through a hot saturated solution of lead chloride containing a small amount of hydrochloric acid. The electrolytic crystals were somewhat larger than those obtained from the cold nitrate process. They were washed and dried as before, and spark electrodes were made from a portion of the product. While silver and copper lines were still plainly visible in the spectrum, the diminution in the proportions of these metals was greater than in the nitrate electrolysis. Since, however, the electrolytic purification seemed, on the whole, unsatisfactory, no further attempts were made to purify the material in this way.

None of this electrolyzed material was used directly for the preparation of lead bromide, but it was first subjected to crystallization as nitrate. About 170 g. of lead which had been twice electrolyzed from nitrate were dissolved in nitric acid, which had been distilled in quartz, and the excess

of acid was removed by evaporating almost to dryness. The residue was dissolved in water and evaporated in a platinum dish on an electric stove nearly to the saturation point. Instead of allowing the salt to crystallize by cooling, it was precipitated by adding a large quantity of redistilled nitric acid to the hot solution, which was then allowed to cool. The relatively pure crystals were centrifugally drained in platinum Gooch crucibles, and were washed with several portions of concentrated nitric acid. The salt was then recrystallized twice more in the same way. In order to determine whether purification was effected in this process, metallic lead was made from a portion of the nitrate by electrolysis upon a platinum cathode, and the electrolytic crystals were washed and converted into spark electrodes. In the ultraviolet spectrum of this metal no copper or silver lines could be seen, nor were there any other lines visible which were not observed in all of the lead samples which we prepared. This sample of lead nitrate is designated Sample A.

Sample B of lead nitrate was made in exactly the same way from metal which had been electrolyzed once through the nitrate, once through the chloride. In order to obtain some evidence as to the proportions of impurities in the original lead, the mother liquors from the three crystallizations of the nitrate of Sample A were freed from the greater part of the lead by evaporating with an excess of sulfuric acid, diluting, and adding alcohol. To the filtrate from the lead sulfate, ammonia was added in excess, and the very slight precipitate, apparently iron in large part, was removed by filtration. The filtrate was evaporated to small bulk, and after precipitation with an excess of potassium hydroxide, the copper and silver oxides were collected on a filter paper, ignited, and weighed. From the original 170 g. of lead nitrate, 0.0088 g. of copper oxide and silver were obtained, which indicates a percentage of silver and copper together of only 0.004. The electrolytic metal from which Sample B was made was found in the same way to contain less than 0.003% of silver and copper.

Another sample of lead nitrate was purified simply by repeated crystallization. About one kilogram of commercial salt was dissolved in water and the solution was filtered through a platinum-sponge Gooch crucible. Then the solution was evaporated, and the salt was crystallized four times in Jena vessels with addition of a large excess of redistilled nitric acid, as previously described. After the fourth crystallization, the material was transferred to platinum vessels, and recrystallized three times more, with a second filtration through platinum-sponge between the sixth and seventh crystallizations. All the nitric acid was distilled in quartz, and the crystals were centrifugally drained and rinsed with nitric acid. This material is designated Sample C.

Sample D of lead nitrate was purified first by Dr. J. W. Shipley, by precipitating lead chloride from a solution of the commercial nitrate,

converting the thoroughly washed lead chloride into sulfide by suspending the chloride in water and saturating with well scrubbed hydrogen sulfide gas, and finally dissolving the sulfide in nitric acid. The nitrate was crystallized once in glass, and then was subjected to three additional crystallizations in platinum. The solution of the nitrate was filtered through platinum sponge after the first crystallization.

The ultraviolet spark spectra of Samples C and D were found to be identical with those of Samples A and B. The geographical origin of these samples of lead is unknown to us, but it is highly probable that the sheet metal, at any rate, is of American origin, although the nitrate may have been either American or European material. This question of origin will be discussed more fully in a later portion of this paper (page 1048).

## Preparation of Lead Bromide.

To prepare lead bromide, pure lead nitrate was dissolved in water in a quartz dish, and a slight excess of the purest hydrobromic acid solution was added. The precipitated bromide was collected on platinum Gooch crucibles without mat of any sort, before any free bromine appeared in the mother liquors, and was centrifugally drained and washed. On account of the low solubility of lead bromide, crystallization of the product from water was avoided by the device described in the preceding paper, of dissolving the lead bromide in hot constant-boiling hydrobromic acid in a quartz dish, and reprecipitating the salt by the addition of water and cooling. During the solution of the lead bromide in hydrobromic acid for the first time, bromine was set free, presumably by traces of included nitric acid. Therefore, before draining the crystals in platinum, they were thoroughly washed by decantation with ice-cold water. All of the lead bromide analyzed was recrystallized in this way at least three times, and Sample CD, which was a mixture of Samples C and D, was further crystallized three times more, that is, six times in all. The purified material was preserved in platinum over fused potassium hydroxide in a desiccator. Since lead bromide darkens in the light,[1] the salt was protected from light so far as possible. The various preparations of lead bromide are designated by the letter corresponding to the nitrate samples from which they were made.

## Drying of Lead Bromide for Analysis.

The lead bromide was prepared for analysis by fusion in an atmosphere charged with hydrobromic acid gas, after the salt had been dried as far as possible in a vacuum desiccator over fused potassium hydroxide. Lead bromide which has been fused in this way, when treated with water yields a considerable amount of insoluble basic salt. Evidence that the salt which has been fused in hydrobromic acid is initially neutral,

[1] Norris, *Ann. Chem.*, 117, 189 (1861).

and that the basic salt is formed by hydrolysis during solution has already been presented in the preceding paper, and in our work with lead bromide no new evidence contradictory to this point of view was obtained. In fact, in two experiments (Analyses 5 and 11) where the lead bromide was initially very moist when the drying commenced and hydrolysis therefore was to be expected if it occurs at all during the drying, the fused material proved identical in composition with the other specimens. The difficulty was avoided in the analytical work by dissolving the salt in water which had been made slightly acid with nitric acid. Even under these conditions no evidence could be obtained of loss of either hydrobromic acid by evaporation, or of bromine by oxidation. As in the previous research, the agreement of the analyses of different preparations is valuable confirmation of the claim that the fused material was strictly neutral.

Another possibility which we considered was that of dissociation of the salt into either metal or sub-bromide with loss of bromine. A decomposition apparently occurs when lead bromide is exposed to light, although heating or even fusion in a neutral atmosphere gives no evidence of dissociation. The point was tested, however, by experiments in which the lead bromide was fused in hydrobromic acid containing free bromine, as well as in hydrobromic acid containing considerable hydrogen. So far as the appearance of the preparations and the results of the analyses are concerned, absolutely no difference could be detected.

The apparatus for fusing in hydrobromic acid gas was modified considerably from that used previously, enough so that it seems worth while to show a detailed diagram of the apparatus (see figure). Hydrogen was evolved by means of electrolytic generators, A, each consisting of the cell zinc amalgam—hydrochloric acid—platinized platinum (see page 1030). These generators were constructed entirely of glass. The gas was purified and dried by passing through several tubes containing fused potassium hydroxide B, and was then partly saturated with the purest bromine in a flask C, which was kept at a temperature of 44° or below. The hydrogen and bromine were combined in a hard glass tube D, containing either platinized asbestos or platinized pumice, heated electrically to dull redness, and the resulting hydrobromic acid was collected in constant-boiling hydrobromic acid solution in the flasks G and H, until the solutions in the two flasks were saturated at room temperature. As the saturation point was approached, the hydrobromic acid gas which escaped from the flask unabsorbed, was collected by being conducted into water through the outlet I. The small amount of bromine, which occasionally accompanied the hydrobromic acid, and which was dissolved in the fuming solution, was eliminated by introducing a small amount of very pure iron into the flasks G and H through the side arms. The resulting solution of ferrous bromide retains very effectively every trace of free bromine,
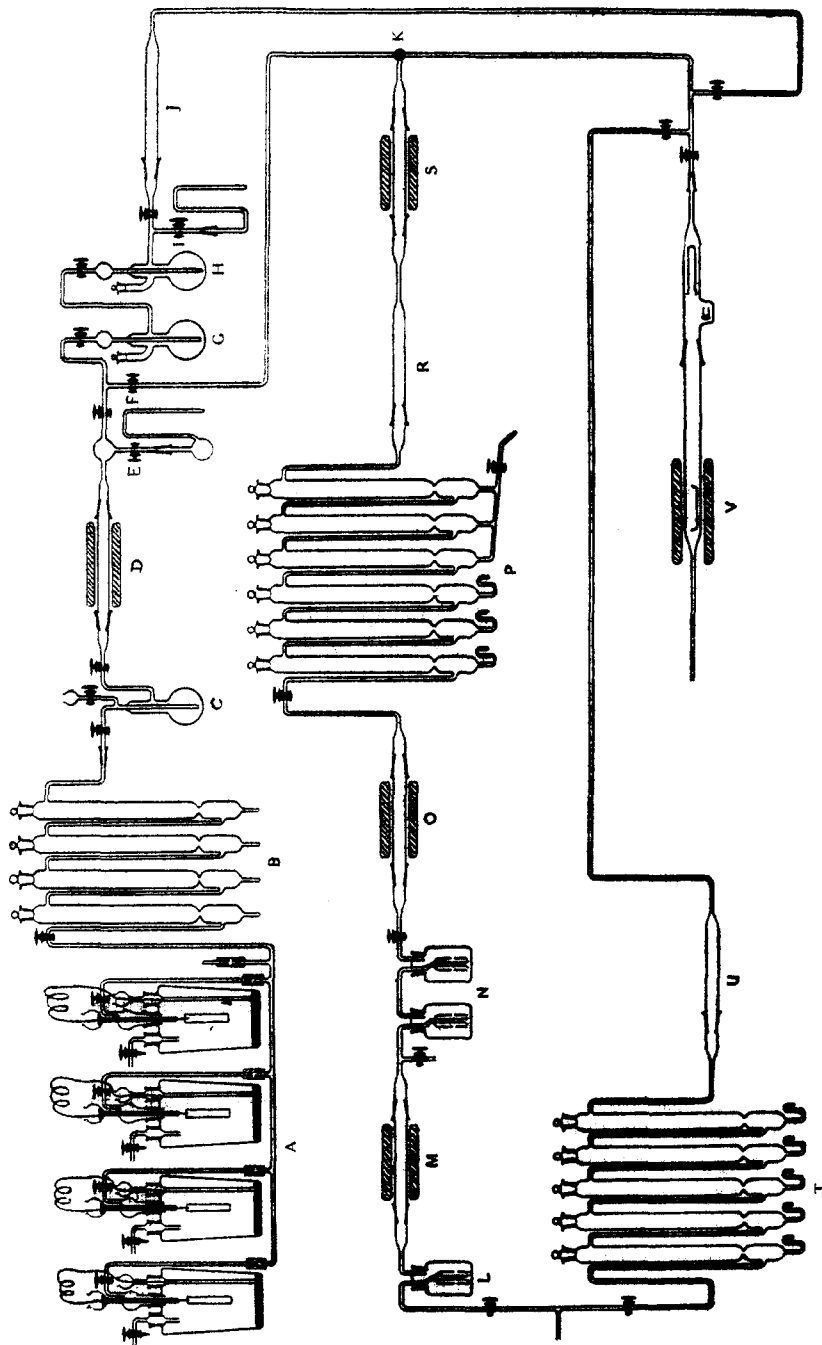
and is far more effective than a tube of dry ferrous bromide. The iron used for the purpose was free from every impurity except possibly platinum. It was obtained by reduction of the purest ferric oxide by Baxter and Hoover[1] in a determination of the atomic weight of iron in this way. Nitrogen was charged with hydrobromic acid gas by passing through the fuming solution, through the stop-cock F, and the gas mixture was dried by means of fused calcium bromide in the tube J, before being led into the fusion apparatus V. While fused calcium bromide is not a perfect drying agent, Baxter and Warren[2] have found that a liter of gas passed over this substance at 25° retains only 0.0002 g. of moisture. A current of hydrogen charged with hydrobromic acid could be produced by passing hydrogen through the cold bromine, then over hot platinum, and finally through the fuming hydrobromic acid solution and the calcium bromide tube, while a current of hydrobromic acid and bromine was obtained by warming the bromine flask considerably above 44°, at which temperature the bromine has a vapor pressure of one-half atmosphere, then through the catalysis tube, and through a drying tube containing calcium bromide. This latter arrangement, which was used only a few times, is not shown in the diagram.

Nitrogen was made by the Wanklyn process, by charging air with ammonia in a gas washing bottle, L, filled with concentrated ammonia solution (sp. gr. less than 0.92). In order to reduce the oxygen, the gas mixture was passed through an electrically heated tube, M, filled with copper gauze, and the excess of ammonia was absorbed in dilute sulfuric acid in the two gas washing bottles N. The hydrogen formed by dissociation of the excess of ammonia was oxidized in the tube O, containing hot copper oxide. The nitrogen was now purified and dried in the six towers P. The first one contained beads wet with a concentrated solution of potassium hydroxide. The other five contained concentrated sulfuric acid, which had previously been heated to fuming with a very small amount of potassium dichromate. Residual moisture was absorbed in a tube, R, containing phosphorus pentoxide which had been resublimed in a current of oxygen. Finally, last traces of oxygen were absorbed by hot copper in the hard glass tube S.

Air was purified and dried in the towers T, two of·which contained beads wet with silver nitrate solution, one, fused potassium hydroxide, and two, concentrated sulfuric acid, and in the phosphorus pentoxide tube U.

The hydrogen, nitrogen, hydrobromic acid, and air apparatus was constructed entirely of glass. Joints were either fused or ground, the necessary flexibility for detaching the different parts being afforded by numerous glass grids. The ground joints and stopcocks through which the bromine

or hydrobromic acid passed were kept clean and dry, but many of those used for nitrogen, air, and hydrogen were lubricated with a small amount of soft paraffin.

When the lead bromide was fused in either nitrogen or hydrogen charged with hydrobromic acid, either a platinum or a quartz boat was used, but when the fusion atmosphere contained bromine, of course a quartz boat was employed. The boat containing the partially dried lead bromide was placed in a quartz tube which formed part of the usual form of "bottling apparatus"[1] (V in figure). After the air had been swept out with a slow current of pure nitrogen, and this in turn by the fusion atmosphere containing hydrobromic acid, the salt was gently heated with an electric coil or with an aluminum block furnace, in order to drive off as much as possible of the residual moisture before fusion. The temperature was then raised by means of a "Ni-chrome" sleeve, until the salt was fused. As soon as the salt had solidified, the fusion atmosphere was displaced with pure nitrogen, and this finally with pure dry air, and the boat and contents were transferred to the weighing bottle, in which they were to be weighed, without exposure to the outside air. While the hydrobromic acid was being displaced by nitrogen and air, a portion of the gas was sent back through the tube I, in order to prevent possible contamination of the atmosphere of the bottling apparatus with hydrobromic acid while the boat was being transferred to the weighing bottle. The weighing bottle with its contents was then placed in a desiccator, and left near the balance for some time before being weighed. Neither the platinum nor the quartz boat was appreciably attacked in these experiments.

### Analysis of the Lead Bromide.

The fused and weighed lead bromide was dissolved and first compared with a weighed, very nearly equivalent, quantity of the purest silver, then the precipitated bromide was collected, dried, and weighed. This process is identical with the one which has been found very successful, both in the Harvard and in other laboratories. Very few deviations from the ordinary method of procedure were made. This method gives a comparison of the atomic weight of lead with those of silver and bromine, but any subsequent change in the standard of comparison, silver, will necessitate a change in the same proportion in that of lead.

Although lead bromide is not so soluble in water as lead chloride, yet a liter of water at ordinary temperatures will dissolve about 9 g. of salt. Solution of the fused material, however, takes place slowly, and we found it highly desirable to conduct the solution in nearly boiling water, as has been explained in the previous paper. When neutral lead bromide is dissolved in water, the salt is partially hydrolyzed, with precipitation of a basic bromide. In the earlier work by Baxter and Thorvaldson,

[1] Richards and Parker. *Proc. Amer. Acad.*, **32**, 59 (1896).

this hydrolysis was prevented by adding a considerable amount of acetic acid. Since, however, lead acetate is a slightly dissociated substance, we were somewhat concerned for fear this salt might be occluded by the silver bromide, and therefore we decided to substitute for acetic acid a quantity of a strong acid of equivalent acidity. At first, an exactly known amount of hydrobromic acid was used, but very shortly we discovered that a small amount of even nitric acid could be employed without the loss of a perceptible amount of either hydrobromic acid or bromine. The latter point was tested very carefully by distilling solutions of lead bromide containing nitric acid, collecting the distillate in alkali, and after evaporation, testing the solution for bromide.

In one experiment about 4 g. of lead bromide were dissolved in a liter of water, and 0.2 cc. of concentrated nitric acid was added. The solution was boiled in a Jena flask, fitted to a quartz condenser, and the distillate was collected in dilute ammonia. After 300 cc. of distillate had passed over, the ammoniacal solution was evaporated upon an electric stove to a volume of about 10 cc., and the solution was tested for bromide by adding a small amount of silver nitrate. Comparison with a standard solution of bromide in a nephelometer showed only 0.01 mg. of bromide in the solution. A repetition of the experiment, using 5 g. of lead bromide and 2.0 cc. of concentrated nitric acid, yielded a distillate containing 0.03 mg. During the solution of lead bromide for analysis the conditions were far less favorable for the liberation of hydrobromic acid and bromine, because, in the first place, much less nitric acid was found necessary to prevent formation of basic salt, and in the second place, while the solution occasionally was heated barely to boiling, very little vapor actually escaped from the solution flask. Additional experiments were made in order to find out how much nitric acid really was necessary in order to liberate an appreciable amount of bromine. For this purpose, the above experiments were repeated, using gradually increasing amounts of nitric acid. To a solution of 4 g. of lead bromide in 1200 cc. of water, nitric acid was added in successive portions, and the solution was distilled into a solution of halogen-free sodium carbonate. Each portion of distillate consisted of 25 cc., and before the succeeding distillation was carried out, the liquid distilled was replaced by an equal amount of water. The separate distillates were acidified with nitric acid, and after silver nitrate solution had been added, nephelometric comparisons were made with solutions of known bromide content.

| Nitric acid added (cc.) | 0.10 | 0.60 | 2.10 | 4.65 | 9.65 |
|---|---|---|---|---|---|
| Bromide found (mg.) | 0.000 | 0.000 | 0.005 | 0.015 | 0.150 |

These figures show conclusively that error from evaporation of either hydrobromic acid or bromine could not possibly have taken place during the solution of the lead bromide for analysis.

The method of carrying out the solution was as follows: The boat containing the weighed sample of lead bromide was transferred to a two-liter Jena glass Erlenmeyer flask, containing about one liter of the purest water. The weighing bottle was rinsed with hot water and the rinsings added to the flask. A column of seven bulbs, ground into the neck of the flask, was inserted to catch any possible spray if the solution happened to boil, and to serve as a reflux condenser. Finally two drops (0.10 cc.) of redistilled nitric acid were added. The flask and its contents were then heated over an electric stove, until solution was complete. This required several hours. In fact, the solution was generally heated over night.

Even after the lead bromide was dissolved, there still remained, usually floating on the surface of the solution, a small amount of black material. Preliminary investigation, both by Dr. Thorvaldson and ourselves, showed that the residue contained neither platinum nor lead. Furthermore, the platinum boat itself remained practically constant in weight. In a few preliminary experiments, this residue was neglected, but in most of the experiments, the weight of the black residue was determined by filtration upon a weighed platinum-sponge Gooch crucible. Similar material was found by Baxter and Thorvaldson, as described in the previous paper, and the nature of the residue has been discussed in a recent paper by Baxter and Hartmann,[1] where evidence is presented which shows it to consist of carbon and silica. In the course of our experiments we were able to make a quantitative analysis of a portion of material. The Gooch crucible containing the residue from several analyses was gently ignited. The black appearance of the residue disappeared with obvious combustion (sparks), confirming the conclusion that a portion of the residue is carbon. A white residue, presumably of silica, could still be seen. This was carefully removed by gently rubbing with a clean finger, and the crucible was carefully dried and reweighed.

| | |
|---|---|
| Original weight of crucible...................... | 24.05098 |
| Weight of crucible + residue.................... | 24.05200 |
| Weight of residue.............................. | 0.00102 |
| Weight of crucible after ignition................. | 24.05167 |
| Weight of carbon............................... | 0.00035 |
| Weight of cleaned crucible...................... | 24.05100 |
| Weight of silica................................ | 0.00067 |

It is interesting to see that about one-third of the residue was carbon, and two-thirds silica. The carbon undoubtedly originated largely in dust and lint from the room, but possibly in part in residual organic matter in the reagents in spite of the pains taken to prevent the difficulty. It seems likely that the silica resulted from attacking of the quartz dish in which the lead bromide was recrystallized. Whatever the origin of

[1] THIS JOURNAL. **37**, 113 (1915).

the residue, it could have had little effect upon the final result, because the weight was determined in each separate experiment, and because the proportion of residue was very small. In thirty-six experiments with lead bromide and chloride, we found on an average only 0.004% of residue. The method of determining the residue in each separate experiment seemed far preferable to applying an average correction to the results, because the percentage varied from almost nothing to nearly 0.01% in a few experiments. In Analyses 1 and 2 there was no visible residue, and no filtration was therefore carried out. These two analyses, nevertheless, gave results essentially identical with those in which the residue was considerable. Since the silver bromide has very nearly the same weight as the lead bromide from which it is obtained, and since the black residue, if not determined, would be collected and weighed with the silver bromide, neglecting the residue would affect the comparisons with silver only, which would then yield results a little more than 0.01 unit too high for the atomic weight of lead.

In filtering the solution of lead bromide, the thistle-tube holding the weighed platinum-sponge crucible was inserted in the upper tubulature of a large bell-jar, and the solution was caught in a three-liter precipitating flask. The solution came in contact only with glass, and was caught in such a way that spattering could not possibly have taken place. After the filtration of the solution, the platinum mat was very thoroughly washed with a large volume of warm water, and the crucible was dried over an electric stove at about 250° for half an hour. It was easily shown that the carbon residue did not oxidize during the drying, by reheating the crucible over a long period and reweighing. Furthermore, the platinum mat remained undissolved by the slightly acid solution of lead bromide. One crucible showed a gain in weight after cleaning of 0.00007 g. during six filtrations, and another a gain of 0.00002 g. during five filtrations.

Before precipitation, the solution of lead bromide was diluted until less than 0.02 $N$. Usually this concentration was reached during the washing of the crucible. When the corrected weight of the lead bromide had been found, a quantity of pure silver, very nearly equivalent to the lead bromide, was carefully weighed out. This silver consisted almost entirely of one or two large buttons, but the final adjustment of the weight was secured with tiny electrolytic crystals which had been heated to 500° in a vacuum. The silver was dissolved in a flask provided with a column of bulbs to prevent loss by spattering, but effervescence during solution was prevented by using a fairly concentrated solution of nitric acid, and by heating very gently. As soon as the metal had disappeared, the solution was diluted to about 200 cc., and heated until the nitrous acid formed during the solution of the silver had been destroyed. Then

the solution was further diluted in the dissolving flask until the concentration was no higher than 0.03 $N$.

In precipitating the silver bromide, generally, because of convenience, the silver solution was added to the bromide solution, although in a few instances the reverse method was employed, in order that if occlusion of either bromide or silver occurred it might be detected. That slight occlusion was likely to take place was obvious from the fact that during the early precipitations, where the concentrations of the solutions were somewhat higher than those given above, material apparently was extracted from the precipitate by long standing. For this reason, too, especial pains were taken during precipitation to agitate the mixed solutions thoroughly.

The silver nitrate solution was added to the bromide solution slowly with continual gentle agitation. At the end of the precipitation the flask was closed with its glass stopper, and gently shaken for a very short time. Then it was allowed to stand with occasional shaking for a week, before the supernatant liquid was tested in a nephelometer for excess of bromide or silver. Portions of 25 cc. of the clear liquid were transferred to test tubes, and treated, in one case, with a cubic centimeter of 0.01 $N$ bromide; in the other, with the same amount of 0.01 $N$ silver nitrate. After thorough stirring, they were occasionally examined in the nephelometer until the ratio of the opalescence in the two tubes became constant. If an excess of either bromide or silver was found, and this was usually the case, the deficiency was made up by adding 0.01 $N$ solutions to the main solution in the flask, and the solution was shaken and again allowed to stand before being tested. The process was continued until the solution contained equivalent amounts of bromide and silver. At this point, owing to the slight solubility of silver bromide, the test portions remained very nearly clear after the addition of the bromide and silver solutions. In a few analyses the end point seemed to change very slightly with time, indicating that occluded or entangled matter was being slowly leached from the precipitate. This change in the end point was at the worst only a matter of a few tenths of a mg., and came to an end within two or three weeks. In all the analyses testing was continued until we were sure that no further change was occurring.

As stated above, in three analyses, Nos. 10, 11, and 13, the bromide solution was poured into the silver nitrate solution. The results of these analyses were no different from the results of those precipitated in the reverse fashion.

The precipitation of the silver bromide was made in a room illuminated only with red light, and during the subsequent manipulations even diffused white light was never allowed to fall upon the precipitate for more than an instant.

As soon as the exact end point had been determined, 0.02 g. of dissolved silver nitrate were added for each liter of solution, and after standing for a short time, the supernatant liquid was poured through a large weighed platinum-sponge Gooch crucible.  The precipitate was washed ten times by decantation with a solution containing 0.01 g. of silver nitrate per liter, and once or twice with chilled water; and was transferred quantitatively to the crucible with ice-cold water.  The crucible and contents were dried at 160° for about 15 hours in a well ventilated electric oven, and then, after being allowed to reach the temperature of the balance room in a desiccator, were weighed.  The main mass of precipitate was transferred to a small porcelain crucible, which was weighed with its cover, and then, after being heated above the fusing point of the silver bromide, was weighed again.  The loss in weight was assumed to represent moisture retained by the silver bromide.  In accordance with the results of previous similar experiments by others, the silver bromide was never found to contain more than 0.006% of residual moisture, the average proportion being 0.003%.  The filtrate and the silver nitrate wash water were assumed to contain no dissolved silver bromide, since the solubility of silver bromide, even in pure water, is only 0.1 mg. per liter at room temperature.  Furthermore, since the pure water used in the rinsing and transference of the precipitate was previously chilled, the amount of silver bromide thus lost must have been very small indeed, judging from the diminution in the solubility of silver chloride with the temperature.  Since the volume of the aqueous washings was only a few hundred cc., no correction is applied for dissolved silver bromide.

The precipitating flask was rinsed with a small amount of distilled ammonia.  These rinsings were diluted to 250 cc., and the bromide content was determined in a nephelometer by adding silver nitrate solution, and comparing with standard solutions of bromide.  As a rule, about 0.1 mg. was found in this way.

All weighings were made upon a No. 10 Troemner balance, used only for exact work.  The atmosphere of the balance case was partially dried by solid potassium hydroxide.  In order to dissipate electrostatic charges upon the objects weighed, the balance case also was provided with a small amount of crude radium bromide.

The gold plated weights were standardized to hundredths of a milligram by the Richards[1] method.

All weighings were made by substitution for counterpoises as nearly as possible like the objects weighed in shape, volume, and material, except in the case of the small platinum crucible used in collecting the black residue, which was substituted for weights.

[1] THIS JOURNAL, 22, 144 (1900).
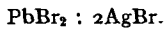
## SERIES I.—THE ATOMIC WEIGHT OF LEAD.

### PbBr$_2$ : 2Ag.

Ag = 107.880.                                                                 Br = 79.916.

| Number of analysis. | Sample of PbBr$_2$. | Fusion atmosphere. | Wt. of PbBr$_2$ in vacuum. Grams. | Wt. of residue. Gram. | Corr. wt. of PbBr$_2$ in vacuum. Grams. | Wt. of Ag in vacuum. Grams. | Wt. of Ag added. Gram. | Corr. wt. of Ag in vacuum. Grams. | Ratio PbBr$_2$ : 2Ag. | At. wt. of Pb. |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | C | HBr + H$_2$ | 5.27845 | . . . . . | 5.27845[1] | 3.10275 | —0.00004 | 3.10271 | 1.70124 | 207.23 |
| 2 | C | HBr + H$_2$ | 2.65094 | . . . . . | 2.65094[1] | 1.55869 | —0.00047 | 1.55822 | 1.70126 | 207.23 |
| 3 | C | HBr + N$_2$ | 4.08449 | 0.00039 | 4.08410 | 2.40152 | —0.00048 | 2.40104 | 1.70097 | 207.17 |
| 4 | D | HBr + N$_2$ | 4.97508 | 0.00040 | 4.97468 | 2.92493 | —0.00020 | 2.92473 | 1.70090 | 207.15 |
| 5 | CD | HBr + N$_2$ | 4.05573 | 0.00032 | 4.05541 | 2.38423 | —0.00025 | 2.38398 | 1.70111 | 207.20 |
| 6 | CD | HBr + N$_2$ | 3.44158 | 0.00019 | 3.44139 | 2.02322 | —0.00036 | 2.02288 | 1.70123 | 207.23 |
| 7 | CD | HBr + N$_2$ | 5.17416 | 0.00029 | 5.17387 | 3.04178 | —0.00020 | 3.04158 | 1.70105 | 207.19 |
| 8 | CD | HBr + N$_2$ | 3.84522 | 0.00025 | 3.84497 | 2.26058 | —0.00036 | 2.26022 | 1.70115 | 207.21 |
| 9 | CD | HBr + H$_2$ | 4.30542 | 0.00029 | 4.30513 | 2.53089 | —0.00003 | 2.53086 | 1.70105 | 207.19 |
| 10 | CD | HBr + H$_2$ | 4.53467 | 0.00022 | 4.53445 | 2.66542 | +0.00007 | 2.66549 | 1.70117 | 207.21 |
| 11 | A | HBr + N$_2$ | 5.78467 | 0.00030 | 5.78437 | 3.40050 | —0.00006 | 3.40044 | 1.70107 | 207.19 |
| 12 | A | HBr + N$_2$ | 4.87104 | 0.00025 | 4.87079 | 2.86350 | —0.00013 | 2.86337 | 1.70107 | 207.19 |
| 13 | A | HBr + N$_2$ | 6.28465 | 0.00019 | 6.28446 | 3.69427 | +0.00020 | 3.69447 | 1.70104 | 207.19 |
| 14 | B | HBr + N$_2$ | 4.74644 | 0.00005 | 4.74639 | 2.78996 | +0.00015 | 2.79011 | 1.70115 | 207.21 |
| 15 | B | HBr + N$_2$ | 6.82444 | 0.00020 | 6.82424 | 4.01203 | —0.00055 | 4.01148 | 1.70118 | 207.21 |
| 16 | B | HBr + N$_2$ | 6.53721 | 0.00032 | 6.53689 | 3.84278 | —0.00004 | 3.84274 | 1.70110 | 207.20 |
| 17 | B | HBr + Br$_2$ | 4.10128 | 0.00030 | 4.10098 | 2.41073 | +0.00015 | 2.41088 | 1.70103 | 207.18 |
| 18 | B | HBr + Br$_2$ | 2.64271 | 0.00015 | 2.64256 | 1.55327 | +0.00025 | 1.55352 | 1.70101 | 207.18 |
| 19 | A | HBr + Br$_2$ | 6.30717 | 0.00034 | 6.30683 | 3.70759 | —0.00041 | 3.70718 | 1.70125 | 207.23 |
|  |  |  |  |  |  |  |  | Average | 1.70111 | 207.20 |

[1] No visible residue. Solution not filtered.

SERIES II.—THE ATOMIC WEIGHT OF LEAD.

PbBr$_2$ : 2AgBr.

Ag = 107.880.                                                                 Br = 79.916.

| Number of analysis. | Sample of PbBr$_2$. | Fusion atmosphere. | Wt. of PbBr$_2$ in vacuum. Grams. | Wt. of residue. Gram. | Corr. wt. of PbBr$_2$ in vacuum. Grams. | Wt. of AgBr in vacuum. Grams. | Loss on fusion. Gram. | Dissolved AgBr from flask. Gram. | Corr. wt. of AgBr in vacuum. Grams. | Ratio PbBr$_2$ : 2AgBr. | At. wt. of Pb. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 20 | CD | HBr + N$_2$ | 4.05573 | 0.00032 | 4.05541 | 4.15023 | 0.00016 | 0.00010 | 4.15017 | 0.97717 | 207.18 |
| 21 | CD | HBr + N$_2$ | 3.44158 | 0.00019 | 3.44139 | 3.52230 | 0.00015 | 0.00009 | 3.52224 | 0.97705 | 207.14 |
| 22 | CD | HBr + N$_2$ | 5.17416 | 0.00029 | 5.17387 | 5.29504 | 0.00011 | 0.00005 | 5.29498 | 0.97713 | 207.17 |
| 23 | CD | HBr + N$_2$ | 3.84522 | 0.00025 | 3.84497 | 3.93464 | 0.00025 | 0.00007 | 3.93446 | 0.97726 | 207.22 |
| 24 | CD | HBr + H$_2$ | 4.30542 | 0.00029 | 4.30513 | 4.40622 | 0.00014 | 0.00008 | 4.40616 | 0.97707 | 207.15 |
| 25 | CD | HBr + H$_2$ | 4.53467 | 0.00022 | 4.53445 | 4.64054 | 0.00013 | 0.00007 | 4.64048 | 0.97715 | 207.18 |
| 26 | A | HBr + N$_2$ | 5.78467 | 0.00030 | 5.78437 | 5.91986 | 0.00020 | 0.00010 | 5.91976 | 0.97713 | 207.17 |
| 27 | A | HBr + N$_2$ | 4.87104 | 0.00025 | 4.87079 | 4.98473 | 0.00017 | 0.00011 | 4.98467 | 0.97715 | 207.18 |
| 28 | A | HBr + N$_2$ | 6.28465 | 0.00019 | 6.28446 | 6.43137 | 0.00023 | 0.00010 | 6.43124 | 0.97718 | 207.19 |
| 29 | B | HBr + N$_2$ | 4.74644 | 0.00005 | 4.74639 | 4.85720 | 0.00019 | 0.00007 | 4.85708 | 0.97721 | 207.20 |
| 30 | B | HBr + N$_2$ | 6.82444 | 0.00020 | 6.82424 | 6.98385 | 0.00014 | 0.00009 | 6.98380 | 0.97715 | 207.18 |
| 31 | B | HBr + Br$_2$ | 4.10128 | 0.00030 | 4.10098 | 4.19799 | 0.00018 | 0.00010 | 4.19791 | (0.97691) | (207.09) |

Average, omitting Analysis 31,                          0.97715   207.18

Average of Series I and II,                                          207.19

The following vacuum corrections are applied:

|  | Specific gravity. | Vacuum correction per gram. |
|---|---|---|
| Weights........................ | 8.3 | ...... |
| Ag......................... | 10.49[1] | —0.000031 |
| AgBr........................ | 6.473[2] | +0.000041 |
| PbBr$_2$........................ | 6.659[3] | +0.000036 |

## Results and Discussion.

Before the results recorded in the preceding table were obtained a preliminary series of determinations was carried out. In these analyses no attempt was made to collect and determine the black residue. Furthermore, several were subject to other uncertainties. The results varied from 207.08 to 207.22, with an average of 207.16. Since these determinations were comparable with those made by Dr. Thorvaldson, whose results are recorded in the preceding paper, it seems unnecessary to give further details. After the procedure had been mastered and various sources of error had been discovered and eliminated, the foregoing "final" series was carried out with the purest materials. All analyses which reached the stage of precipitation are recorded.

The agreement of the various determinations in each series is very satisfactory, when the high atomic weight of lead is taken into consideration. In the comparisons with silver the extreme values differ by 0.08 unit, corresponding to 0.0006 g. of silver for a five gram portion of lead bromide, but except for Analyses 3 and 4, the difference is 0.05 unit, corresponding to 0.0004 g. of silver. In the determination of the silver bromide the agreement is almost as good. Analysis 31 diverges widely from all the others in the series, but, since in this experiment contamination of the silver bromide with glass chips was suspected, the result of this experiment is omitted in computing the average.

In comparing the two series, it can be seen that the titrations against silver give a slightly higher result than the experiments where the silver bromide was weighed. This indicates that for a given amount of silver used, too much silver bromide was obtained, as the following table shows:

| Analyses. | Ag : AgBr. | Analyses. | Ag : AgBr. |
|---|---|---|---|
| 5 and 20 | 0.57443 | 12 and 27 | 0.57444 |
| 6 and 21 | (0.57432) | 13 and 28 | 0.57446 |
| 7 and 22 | 0.57443 | 14 and 29 | 0.57443 |
| 8 and 23 | 0.57447 | 15 and 30 | 0.57440 |
| 9 and 24 | 0.57439 | 17 and 31 | (0.57431) |
| 10 and 25 | 0.57440 | | |
| 11 and 26 | 0.57442 | Average, | 0.57443 |

[1] Richards and Wells, Pub. Car. Inst., 28, 11 (1905); THIS JOURNAL, 27, 466.
[2] Baxter and Hines, Am. Chem. Jour., 31, 224 (1904).
[3] Determined in this laboratory by Mr. C. F. Hawkins. Not yet published.

Baxter[1] has already found the probable value of the ratio Ag : AgBr to be 0.57445.

This apparent excess in weight of the silver bromide may have been due either to occlusions by the precipitated silver bromide or to contamination from the ground stoppers of the precipitating flasks, which necessarily were opened several times. The former explanation is less probable, for several of the silver bromide precipitates were very carefully tested for lead with negative results, by solution and reprecipitation, and examination of the mother liquor. With regard to the latter difficulty, every precaution was taken to avoid grinding during the insertion and removal of the stopper, and before using the flask the ground surfaces were made as smooth as possible by wet grinding. In any case the uncertainty in the average of Series I and II is no greater than 0.01 unit.

It is also interesting to compare the results obtained with different specimens of lead bromide, as well as the effect of varying the fusion atmosphere.

| Sample of PbBr₃. | PbBr₃ : 2Ag. | PbBr₃ : 2AgBr. | Average. |
|---|---|---|---|
| A................. | 207.20 | 207.18 | 207.19 |
| B................. | 207.20 | 207.19 | 207.20 |
| C................. | 207.21 | .... | 207.21 |
| D................. | (207.15) | .... | (207.15)[2] |
| CD................ | 207.20 | 207.18 | 207.19 |
| Average............ | 207.20 | 207.18 | 207.19 |

| Fusion atmosphere. | PbBr₃ : 2Ag. | PbBr₃ : 2AgBr. | Average. |
|---|---|---|---|
| N₂ + HBr......... | 207.19 | 207.18 | 207.19 |
| H₂ + HBr......... | 207.21 | 207.17 | 207.19 |
| Br₂ + HBr......... | 207.20 | .... [3] | 207.20 |
| Average............ | 207.20 | 207.18 | 207.19 |

So far as can be told the variations in these results are wholly accidental.

## PART II. THE ANALYSIS OF LEAD CHLORIDE.

Because the outcome of the foregoing work as well as of that of Baxter and Thorvaldson indicates a distinctly higher figure for the atomic weight of lead than the value obtained by Baxter and Wilson by the analysis of lead chloride, it became highly important to repeat the work upon lead chloride. At about this time we were informed of the results of Richards and Lembert's analyses of radioactive lead chloride, which indicate a considerably lower value for the radioactive material than for ordinary lead. Thus the question as to whether common lead always possesses the same atomic weight immediately became a vital one. We decided

[1] Proc. Amer. Acad., **42**, 201 (1906); THIS JOURNAL, **28**, 1322 (1906).

[2] This is the result of one analysis only.

[3] In the only analysis in which the silver bromide was collected, contamination of the precipitate was suspected (Analysis 31).

therefore to combine with the investigation of lead chloride the comparison of lead material from different geographical sources. Lead ores were secured from different parts of the United States, from Germany, and from New South Wales, and from these minerals pure material was prepared in essentially the same way in every case. The ores were either nearly pure galena or cerussite in all but one instance. Radioactive minerals in particular were avoided in order to eliminate uncertainty from the possible presence of radioactive lead.

### The Purification of Lead Nitrate.

In order to provide a cross connection with the bromide work, one specimen of lead nitrate which had been used in preparing the bromide was also employed as a source of lead chloride. This specimen was Sample D, which had been made from commercial lead nitrate by precipitation of lead chloride and many crystallizations as lead nitrate (see page 1033).

Sample E was prepared from large pieces of clear cerussite from the British Broken Hill Mine, New South Wales, Australia. After solution of the mineral in an excess of nitric acid, an insoluble residue was removed by filtration through an asbestos mat, and the filtrate was evaporated until lead nitrate began to separate. As soon as the solution was cold the mother liquor was poured off and the crystals were centrifugally drained and washed several times with nitric acid. The product was then four times crystallized in quartz, by solution in hot water and precipitation with nitric acid as previously described (see page 1033). Again the crystals were dissolved, and the solution was filtered through a platinum sponge crucible, held in a platinum thistle tube, into a platinum dish, and the salt was three more times crystallized in platinum. Evidence that the material was amply pure before the process was complete was obtained by preparing metallic electrodes from a portion of the five times crystallized material and photographing the spark spectrum. No lines could be seen which were not produced also by the pure specimens of lead prepared previously.[1]

A well crystallized specimen of galena from Joplin, Missouri, U. S. A., served as the source of Sample G. A few adherent crystals of zinc blende were mechanically dislodged and the galena was crushed in a large iron mortar. The powder was then digested hot with an excess of 5 $N$ nitric acid, and the residue of sulfur, lead sulfate and undecomposed galena was removed by filtration. Since the supply of material was ample the residue was rejected. The filtrate was evaporated until lead nitrate began to separate, and was allowed to cool. After centrifugal separation and rinsing, the crystals were dissolved in water and the solution was filtered

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[1] Although Richards and Lembert found the spectrum of radioactive lead to be indistinguishable from that of common lead, there is no reason to expect that ordinary impurities could not be detected in this way.

through an asbestos mat to remove traces of lead sulfate.   Four crystallizations in quartz and two in platinum, with intermediate filtration through platinum sponge, followed.   The spectrum of metal prepared from the four times crystallized salt was found to show no sign of foreign metals.

A second specimen of cerussite from Wallace, Idaho, U. S. A., was purified exactly as Sample E, except that the nitrate was crystallized four times in platinum vessels, instead of seven times.   At this point a spectrographic examination failed to bring to light any metallic impurity.   This was designated Sample H.

The three foregoing minerals were all obtained from the Harvard Mineralogical Museum.

Through Dr. F. Krantz of Bonn, Germany, a third specimen of cerussite and one of galena, of guaranteed German origin, were secured.   The cerussite was obtained from Commern in the Eifel Mountains, Rhenish Prussia.   It was purified exactly as Sample H and the final product was tested for impurities spectrographically with negative results.   This specimen is designated Sample I.

Argentiferous galena from Grube Holzappel, Nassau, was converted to nitrate by digestion with nitric acid and the nitrate was four times crystallized in platinum.   When metal prepared from this purified nitrate was tested spectrographically, the two strong silver lines of wave lengths 3280 and 3383 were visible, although faint, showing that where lead is badly contaminated with silver even more prolonged purification by crystallization of the nitrate is necessary than was here employed.   In order to obtain some idea of the proportion of the impurity, about 1 g. of this nitrate was dissolved in water and, after the addition of a small amount of bromide, the solution was examined in a nephelometer.   The very slight opalescence was estimated by comparison with a standard to represent about 0.001 mg. of silver, i. e., 0.0002%, an entirely negligible proportion.   This nitrate was not further crystallized, but after it had been converted to chloride and the chloride three times crystallized, electrodes prepared from the final material gave not the slightest indication of silver.   This was Sample F.

Dr. M. L. Hartmann very kindly furnished material for Sample J. The mineral consisted of yellow wulfenite ($PbMoO_4$) and red vanadinite ($Pb_5(VO_4)_3Cl$), and had been collected by Dr. Hartmann in the Tucson mountains, Arizona, U. S. A.   The crushed mineral was boiled with 6 $N$ nitric acid for some hours and a curdy, yellow precipitate together with an insoluble residue was removed by filtration.   When the filtrate was evaporated to small volume and allowed to cool, lead nitrate and a curdy precipitate separated.   The latter was removed in suspension by washing the lead nitrate with concentrated nitric acid.   The nitrate was dissolved, filtered and crystallized twice in Jena glass and, after filtration through

platinum sponge, three times in platinum. No impurities could be detected spectrographically.

Through the kindness of Professor E. P. Kohler a specimen of galena was obtained from Metalline Falls, Washington, U. S. A., where it occurs in glacial boulders. During the treatment of the mineral with nitric acid so much lead sulfate was produced that the latter substance was recovered by boiling with sodium carbonate and solution in nitric acid. The combined material was crystallized once in glass and four times in platinum. In the spectrum of this material the silver lines were very faintly visible, although when tested with bromide in a nephelometer, no opalescence could be detected. Judging from our experience with Sample F, the proportion of silver could not have been as much as 0.0001%, a proportion which surely must have been eliminated during the three crystallizations as chloride. This specimen is Sample K.

### The Radioactivity of the Minerals.

All seven minerals were carefully tested for radioactivity in a quantitative gold leaf electroscope. The natural leak of this electroscope was increased forty times by the black oxide of uranium, while no one of the substances examined increased the leak by an amount that could be detected. Since Richards and Lembert found the radioactive chloride to be several times as active as uranium oxide where the difference in atomic weight amounted to about half a unit, the sensitiveness of the tests for radioactivity was ample for the purpose.

### The Purification of Lead Chloride.

Lead chloride was prepared from the purified lead nitrate by precipitation with hydrochloric acid and crystallization of the product. The latter process served to remove not only traces of nitrate included during the precipitation, but also any metallic impurities which might have escaped elimination in the nitrate crystallization. The difficulties due to isomorphism make it desirable in the preparation of salts of a pure metal to crystallize in at least two different forms. As has already been stated, the traces of silver retained by the nitrate of Samples F and K were effectually eliminated in the chloride crystallization.

About 75 g. of nitrate were dissolved in water and the solution was filtered through platinum sponge into a quartz dish. Constant boiling hydrochloric acid which had been freshly distilled through a quartz condenser was then slowly added, with constant stirring, until an excess was present. Chlorine was never freed in the mother liquor. After the precipitate had settled, it was thoroughly washed by decantation with chilled water and was drained in a platinum centrifugal apparatus. The last wash waters, when tested with diphenylamine, were found to be essentially free from nitrate  The salt was next recrystallized either from water or,

because salt crystallized from water was subsequently found to be basic, from very dilute (0.006 $N$) hydrochloric acid, in platinum vessels. The salt was heated to boiling with the solvent in a large platinum still, and, when the solution was nearly saturated, it was poured into a large platinum dish and was cooled with ice. The mother liquor was used to dissolve fresh portions of the salt until all had been recrystallized. Every sample was three times recrystallized except Samples $D_2$ and $E_2$, which were twice recrystallized.

### The Drying of Lead Chloride.

After preliminary drying in a vacuum desiccator over fused potassium hydroxide the salt was finally fused in a current of dry hydrochloric acid gas. Experiments described later showed that in the desiccator the moisture content was reduced to a few hundredths of a per cent.

The apparatus for fusing the salt has been used for some years for a similar purpose. Hydrochloric acid gas was generated by dropping concentrated sulfuric acid into fuming hydrochloric acid solution, and was scrubbed and dried by passing through five towers containing beads moistened with concentrated sulfuric acid. All the sulfuric acid previous to use was heated to fuming. Nitrogen was prepared by the Wanklyn process as previously described in this paper, except that the small amount of hydrogen resulting from the catalytic decomposition of the ammonia was not removed. Air also was purified and dried as previously described.

The fusion of the salt was conducted in a platinum or quartz boat in a quartz tube which formed part of a bottling apparatus. After the salt had been gradually heated in a current of hydrochloric acid gas up to the melting point, the acid gas was then displaced by nitrogen and this finally by air. Then the boat and contents were transferred to the weighing bottle in which the boat had been initially weighed, and the system was reweighed.

### The Neutrality of Fused Lead Chloride.

In the earlier investigations by Baxter and Wilson, since the lead chloride which had been fused in hydrochloric acid was found to give a clear solution, the assumption was made that the fused salt was neutral. In preliminary experiments in this research, however, upon attempting to dissolve the fused salt in hot water a considerable quantity of white insoluble material separated as soon as the concentration of the solution became high. Similar insoluble material was eventually found to be soluble in acid and to contain chlorine and therefore to be basic chloride. A marked difference between the two cases exists, however. In Baxter and Wilson's experiments the total concentration of salt was never more than half as great as in these preliminary experiments. So far as analysis

of the salt was concerned no difficulty was introduced, for if the water in which the salt is dissolved is acidified slightly at the outset, no insoluble material separates. In these respects lead chloride resembles the bromide very closely. The question is so important, however, that much time was spent in proving that the fused salt really is neutral, and that the basic salt is formed by hydrolysis during solution.

In the first place we established the fact that unfused lead chloride which has been crystallized from dilute hydrochloric acid solution, and which therefore must have been either neutral or possibly slightly acid, when dissolved in water to yield a nearly saturated solution at room temperature, is slightly hydrolyzed to give a precipitate of basic salt. Lead chloride, which has been crystallized from water solution, behaves in the same way, but this is due in part to the fact that such material is already basic at the outset, as will presently be shown. Thus it was proved that the basic salt resulting from solution of fused lead chloride in water was at least in part due to hydrolysis during solution.

The second question as to whether a *portion* of the insoluble material was originally contained in the fused salt was more difficult to settle. The problem was finally solved by the method already employed by Richards[1] to determine the neutrality of fused barium chloride. The procedure was as follows: Two portions of lead chloride which had been crystallized from very dilute hydrochloric acid and dried for some time in a vacuum desiccator, were weighed out simultaneously. These crystals had been ground in an agate mortar during the drying in order to break open inclusions of mother liquor. One portion was dissolved in water with the addition of a trace of nitric acid and was analyzed by comparison with silver in the usual fashion, the details of which will be given shortly. The second portion was carefully fused in hydrochloric acid gas, bottled and weighed. A small quantity of material which sublimed from the boat into the tube was dissolved in water and, after evaporation of the solution in a weighed platinum crucible, the weight of residue was determined. This sublimate was kept as small as possible by taking care to heat the salt barely to the fusion point in a slow current of gas. From the loss in weight during fusion, corrected for the weight of the sublimate, the percentage of moisture in the original material could be ascertained. The fused specimen also was dissolved and compared with silver. Obviously, if no hydrolysis occurs during fusion of the chloride, the ratio of the fused chloride to silver should be the same as the ratio of the unfused after correction for moisture content.

The data for two parallel pairs of experiments are given below. The analyses of the fused salt appear also in the final tables.

[1] *Proc. Amer. Acad.*, **29**, 55 (1893).

| | I.<br>Fused salt. | II.<br>Fused salt. |
|---|---|---|
| Wt. unfused PbCl$_2$................... | 5.26117 g. | 4.17817 g. |
| Wt. fused PbCl$_2$...................... | 5.25898 | 4.17472 |
| Loss on fusion....................... | 0.00219 | 0.00345 |
| Wt. sublimate....................... | 0.00111 | 0.00180 |
| Wt. water........................... | 0.00108 | 0.00165 |
| Percentage of water.................. | 0.0206 | 0.0396 |
| Wt. black residue.................... | 0.00016 g. | 0.00027 g. |
| Corrected wt. PbCl$_2$................ | 5.25882 | 4.17445 |
| Wt. Ag.............................. | 4.07933 | 3.23862 |
| PbCl$_2$ : 2Ag........................ | 1.28914 | 1.28896 |
| | Mean, 1.28905.[1] | |
| | Unfused salt. | Unfused salt. |
| Wt. unfused PbCl$_2$................... | 5.82713 g. | 5.65341 g. |
| Wt. moisture (calculated)............. | 0.00120 | 0.00224 |
| Corrected wt. unfused PbCl$_2$........... | 5.82593 | 5.65117 |
| Wt. Ag.............................. | 4.51915 | 4.38382 |
| PbCl$_2$ : 2Ag........................ | 1.28917 | 1.28910 |
| | Mean, 1.28914. | |

The difference between the mean ratio of fused and unfused salt to silver corresponds to an excess of chlorine of 0.0001 g. in the fused salt or an equal deficiency in the unfused material. Because of some uncertainty in the correction for residual moisture in the unfused salt, closer concordance could hardly be expected. The results prove, as far as the method allows, that lead chloride which has been carefully fused in a current of dry hydrochloric acid gas contains no appreciable amount of basic salt.

In connection with the foregoing experiments similar ones were carried out with lead chloride which had been crystallized from water solution. Since these experiments showed first that the salt thus prepared contains basic material, and second that this basic chloride is converted to the neutral salt by fusion in hydrochloric acid gas, the experiments are discussed below in detail. The method of procedure was exactly similar to that described above.

A complication in computing the percentage of water in the unfused salt from the change in weight during fusion is introduced by the fact that when the basic salt contained in the unfused material is fused in hydrochloric acid, hydroxyl (or possibly oxygen) is replaced by chlorine. Thus the water content of the salt is equal to the loss in weight during fusion plus the gain in weight due to replacement of hydroxyl by chlorine. A first approximation to the latter increase in weight was calculated from the apparent deficiency of chlorine found in the comparison of the unfused chloride with silver. Then a more nearly correct value for the water

[1] This happens also to be the mean of 17 experiments, including these two, subsequently recorded.

content was calculated. The whole process of approximation was eventually repeated three times in order to find the water content of the unfused basic chloride to 0.01 mg.

| | I. Fused salt. | II. Fused salt. |
|---|---|---|
| Wt. unfused $PbCl_2$ | 6.26260 g. | 3.80729 g. |
| Wt. fused $PbCl_2$ | 6.25929 | 3.80525 |
| Loss on fusion | 0.00333 | 0.00204 |
| Wt. sublimate | 0.00108 | 0.00106 |
| Gain from replacement of OH by Cl | 0.00050 | 0.00056 |
| Water content | 0.00273 | 0.00154 |
| Percentage of water | 0.0437 | 0.0405 |
| Wt. black residue | 0.00045 g. | |
| Corrected wt. $PbCl_2$ | 6.25884 | |
| Wt. Ag | 4.85584 | |
| $PbCl_2 : 2Ag$ | 1.28893[1] | 1.28908[2] |

Mean of four analyses, 1.28904.

| | Unfused salt. | Unfused salt. |
|---|---|---|
| Wt. unfused $PbCl_2$ | 6.14944 g. | 6.34462 g. |
| Wt. water (calculated) | 0.00268 | 0.00257 |
| Corrected wt. unfused $PbCl_2$ | 6.14676 | 6.34205 |
| Wt. Ag | 4.76557 | 4.91435 |
| $PbCl_2 : 2Ag$ | 1.28983 | 1.29052 |

Mean, 1.29017.

In the four analyses in which the original salt had been crystallized from water previous to fusion, (Analyses 32, 33, 34 and 35) the average ratio of fused salt to silver is 1.28904, a value essentially in agreement with the average of experiments where the salt was crystallized from dilute hydrochloric acid, 1.28905.

These results indicate: first, that owing to hydrolysis lead chloride which has been crystallized from water contains roughly 0.1% less chlorine than the neutral salt and, second, that during fusion in hydrochloric acid gas, material originally basic becomes neutral, a result which cannot be attained with many chlorides such as those of zinc and magnesium.

## The Analysis of Lead Chloride.

After the lead chloride had been fused and weighed, the boat and contents were placed in a two liter Erlenmeyer flask, the neck of which was provided with a column of bulbs to catch spray and to serve as a condenser, and was covered with about a liter of distilled water to which 0.1 cc. concentrated nitric acid had been added to prevent the precipitation of the basic salt. The flask and contents were then heated upon an electric stove until the salt was dissolved.

By actually distilling a lead chloride solution of concentration similar

[1] Analysis 35, page 1057.

[2] The salt which was used in the water determination was lost. This value is the average from three other specimens of similar material (Analyses 32, 33 and 34).

to the analyses (5 g. per liter) with different amounts of nitric acid, it was found that even 4 cc. of nitric acid did not cause an appreciable loss of chlorine.

A slight black insoluble residue of carbon and silica was left floating upon the surface of the solution, as in the case of the bromide. This was collected upon a platinum sponge crucible and determined as described on p. 1041. The average proportion of insoluble residue in twenty-one analyses was 0.004%. The weight of the residue was subtracted from the weight of salt.

The comparison of the lead chloride solutions with silver was effected almost exactly as in the analysis of the bromide (see p. 1041). The concentration of the chloride solution at the time of precipitation was nearly 0.03 $N$, that of the silver solution 0.05 $N$. In Analyses 34 and 36 the chloride solution was poured into the silver solution; in all the others the reverse method of precipitation was employed. No attempt was made to collect the silver chloride in the experiments for comparing the lead chloride with silver.

In the first eight analyses, after the solutions had stood in contact with the precipitated silver chloride for nearly a week with occasional shaking, they were cooled to 0° previous to testing in a nephelometer for excess of chloride or silver, and maintained at that temperature until equivalence of chloride and silver had been reached. Richards and Willard[1] found that the diminution in the solubility of silver chloride thus produced is an assistance in the determination of the end point. In the subsequent analyses this cooling was omitted, since we found that the accuracy of our experiments was not perceptibly increased by the process, which is somewhat troublesome. Needless to say, in the comparison of tubes in the nephelometer, readings were taken until they became constant, and each analysis was tested several times on successive days after the end point had been reached. In the last six analyses two pairs of tubes were always prepared and examined at the same time. Even at the large volume of the analyses the effect of the addition of 0.1 mg. of silver could be detected without cooling to 0°.

During the first two weeks very slight variations in the end point sometimes took place, probably owing to the extraction of occluded chloride or silver. At the end of three weeks no perceptible change was occurring and Analyses 32 and 48 were allowed to stand six weeks without the production of any alteration in the end point from the one found at the end of the third week.

In four separate experiments the silver chloride precipitated by adding an excess of silver nitrate to the solution of the salt was collected and weighed. The lead chloride solution was prepared as previously described

[1] *Pub. Car. Inst.*, **125**, 15 (1910); THIS JOURNAL, **32**, 16 (1910).

and was precipitated by adding a solution of a weighed, very nearly equivalent amount, of very pure silver nitrate containing several cubic centimeters of nitric acid. In Analyses 49 and 52 the silver nitrate solution was added to the chloride solution; in Analyses 50 and 51 the reverse method of precipitation was followed. The precipitate was left in contact with the mother liquor for two weeks, with occasional shaking, in order to allow occluded material to be extracted. Then an excess of 0.05 g. silver nitrate for each liter of mother liquor was added, and after a day's standing the precipitate was washed and collected upon a large weighed platinum-sponge crucible. The precipitate was washed twelve times with silver nitrate solution containing 0.05 g. per liter and once with chilled water before transference to the crucible with ice cold water.

The crucible and contents were dried at 235° for sixteen hours in an electrically heated porcelain air bath before they were weighed. In order to determine how much moisture was retained by the dried chloride, it was transferred to a small porcelain crucible and weighed, then heated to fusion inside a larger crucible and again weighed. The loss in weight, which represents the moisture expelled, was never more than 0.002% of the weight of the salt. Although the dried, unfused salt was superficially very slightly discolored, the fused material was colorless.

A correction of 0.05 mg. per liter was applied for silver chloride dissolved in the mother liquor and silver nitrate wash waters. This correction is calculated from the solubility product of silver chloride at 20° as determined by Kohlrausch,[1] $1.0 \times 10^{-10}$. The silver chloride dissolved in the aqueous washings together with that dissolved from the precipitation flask by rinsing with ammonia was estimated by nephelometric comparison in each experiment. This never amounted to more than 0.75 mg. per liter.

Vacuum corrections for lead chloride and silver chloride were applied by adding 0.000060[2] and 0.000071 g., respectively, for each apparent gram of substance.
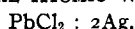
## Results and Discussion.

It is obvious that there is no evidence of dissimilarity in the various samples of chloride. The extreme difference in Series III, 0.04 unit, corresponds to less than 0.0006 g. of silver or 0.0007 g. of lead chloride, with a 5 g. portion of chloride. In Series IV, with larger quantities of lead chloride the extreme difference is half as large, corresponding to 0.0005 g. of silver chloride and to the same amount of lead chloride. The agreement of the averages with different specimens of lead chloride is even better.

[1] Z. physik. Chem., 64, 147 (1908).

[2] Computed from the density 5.89. recently found in this laboratory at 25° by Mr. C. F. Hawkins.
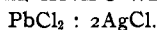
## SERIES III.—THE ATOMIC WEIGHT OF LEAD.
### PbCl₂ : 2Ag.

Ag = 107.880.                                   Cl = 35.457.

| Number of analysis. | Sample of PbCl₂. | Wt. of PbCl₂ in vacuum. Grams. | Wt. of residue. Milligram. | Corr. wt. of PbCl₂ in vacuum. Grams. | Wt. of Ag in vacuum. Grams. | Wt. of Ag added. Milligram. | Corr. wt. of Ag in vacuum. Grams. | Ratio PbCl₂ : 2Ag. | At. wt. of Pb. |
|---|---|---|---|---|---|---|---|---|---|
| 32 | D₂ | 5.63594 | 0.27 | 5.63567 | 4.37235 | —0.35 | 4.37200 | 1.28904 | 207.21 |
| 33 | D | 5.58758 | 0.28 | 5.58730 | 4.33467 | —0.40 | 4.33427 | 1.28910 | 207.22 |
| 34 | D | 6.86348 | 0.29 | 6.86319 | 5.32382 | +0.20 | 5.32402 | 1.28910 | 207.22 |
|  |  |  |  |  |  |  | Average, | 1.28908 | 207.22 |
| 35 | E₂ | 6.25929 | 0.45 | 6.25884 | 4.85564 | +0.20 | 4.85584 | 1.28893 | 207.19 |
| 36 | E | 5.25898 | 0.16 | 5.25882 | 4.07968 | —0.35 | 4.07933 | 1.28914 | 207.23 |
|  |  |  |  |  |  |  | Average, | 1.28904 | 207.21 |
| 37 | F | 5.73451 | 0.17 | 5.73434 | 4.44877 | —0.20 | 4.44857 | 1.28903 | 207.21 |
| 38 | F | 4.17472 | 0.27 | 4.17445 | 3.23837 | +0.25 | 3.23862 | 1.28896 | 207.19 |
|  |  |  |  |  |  |  | Average, | 1.28900 | 207.20 |
| 39 | G | 4.70784 | 0.14 | 4.70770 | 3.65198 | +0.25 | 3.65223 | 1.28899 | 207.20 |
| 40 | G | 4.20234 | 0.12 | 4.20222 | 3.25965 | +0.03 | 3.25968 | 1.28915 | 207.23 |
|  |  |  |  |  |  |  | Average, | 1.28907 | 207.22 |
| 41 | H | 7.04713 | 0.25 | 7.04688 | 5.46697 | —0.06 | 5.46691 | 1.28901 | 207.20 |
| 42 | H | 5.88935 | .... | 5.88935[1] | 4.56888 | —0.20 | 4.56868 | 1.28907 | 207.22 |
|  |  |  |  |  |  |  | Average, | 1.28904 | 207.21 |
| 43 | I | 6.57246 | 0.30 | 6.57216 | 5.09849 | 0.00 | 5.09849 | 1.28904 | 207.21 |
| 44 | I | 5.66347 | 0.17 | 5.66330 | 4.39340 | 0.00 | 4.39340 | 1.28905 | 207.21 |
|  |  |  |  |  |  |  | Average, | 1.28905 | 207.21 |
| 45 | J | 4.90098 | 0.15 | 4.90083 | 3.80188 | —0.17 | 3.80171 | 1.28911 | 207.22 |
| 46 | J | 5.79313 | 0.13 | 5.79300 | 4.49404 | 0.00 | 4.49404 | 1.28904 | 207.21 |
|  |  |  |  |  |  |  | Average, | 1.28908 | 207.22 |
| 47 | K | 5.43992 | 0.27 | 5.43965 | 4.21992 | 0.00 | 4.21992 | 1.28904 | 207.21 |
| 48 | K | 5.74557 | 0.53 | 5.74504 | 4.45584 | +0.90 | 4.45674 | 1.28907 | 207.22 |
|  |  |  |  |  |  |  | Average, | 1.28906 | 207.21 |

Average of individual analyses,    1.28905    207.21

[1] Undetermined, but wholly negligible.

## SERIES IV.—THE ATOMIC WEIGHT OF LEAD.
### PbCl₂ : 2AgCl.

Ag = 107.880.                                   Cl = 35.457.

| Number of analysis. | Sample of PbCl₂. | Wt. of PbCl₂ in vacuum. Grams. | Wt. of residue. Milligram. | Corr. wt. of PbCl₂ in vacuum. Grams. | Wt. of AgCl in vacuum. Grams. | Loss on fusion. Milligram. | Dissolved AgCl. Milligram. | Corr. wt. of AgCl in vacuum. Grams. | Ratio PbCl₂:2AgCl. | At. wt. of Pb. |
|---|---|---|---|---|---|---|---|---|---|---|
| 49 | H | 6.96405 | 0.35 | 6.96370 | 7.17708 | 0.14 | 0.60 | 7.17754 | 0.97021 | 207.22 |
| 50 | H | 6.89063 | 0.17 | 6.89046 | 7.10147 | 0.08 | 0.92 | 7.10231 | 0.97017 | 207.21 |
|  |  |  |  |  |  |  |  | Average, | 0.97019 | 207.21 |
| 51 | E | 7.33259 | 0.32 | 7.33227 | 7.55609 | 0.10 | 1.33 | 7.55732 | 0.97022 | 207.22 |
| 52 | E | 6.51730 | 0.31 | 6.51699 | 6.71604 | 0.14 | 1.00 | 6.71690 | 0.97024 | 207.23 |

Average,    0.97023    207.23
Average of individual analyses,    0.97021    207.22
Average of Series III and IV,                207.21

[1] In this experiment the residue was so small that it was not determined.

The average of Series III is very slightly lower than that of Series IV. The difference, 0.01 unit, indicates a slight deficiency in the weight of silver chloride or a slight excess in the weight of silver or both. However, at the most the discrepancy corresponds to less than 0.0003 mg. of substance.

In the following table a more complete comparison of the different specimens of material is made:

| Sample of PbCl₂. | Mineral. | Source. | Series III. PbCl₂:2Ag. | Series IV. PbCl₂:2AgCl. | Average. |
|---|---|---|---|---|---|
| D | | Commercial nitrate | 207.22 | | 207.22 |
| E | Cerussite | New South Wales, Australia | 207.21 | 207.23 | 207.22 |
| F | Cerussite | Eifel Mts., Germany | 207.20 | | 207.20 |
| G | Galena | Joplin, Mo., U. S. A. | 207.22 | | 207.22 |
| H | Cerussite | Wallace, Id., U. S. A. | 207.21 | 207.21 | 207.21 |
| I | Galena | Nassau, Germany | 207.21 | | 207.21 |
| J | {Vanadinite {Wulfenite | Tucson, Ariz., U. S. A. | 207.22 | | 207.21 |
| K | Galena | Metalline Falls, Wash., U. S. A. | 207.21 | | 207.21 |
| | | Average, | 207.21 | 207.22 | 207.21 |

In comparing the analyses of the bromide and chloride, variations are found of the same order of magnitude as in the separate series.

| | | Ratio. | Number of analysis. | At. wt. |
|---|---|---|---|---|
| Series I | PbBr₂ : 2Ag | 1.70111 | 19 | 207.20 |
| Series II | PbBr₂ : 2AgBr | 0.97715 | 11 | 207.18 |
| Series III | PbCl₂ : 2Ag | 1.28905 | 17 | 207.21 |
| Series IV | PbCl₂ : 2AgCl | 0.97021 | 4 | 207.22 |
| | Average | | | 207.20 |

Average, weighted according to number of analyses......    207.20

In all four series the results vary between essentially the same limits, so that the safest method of combining the four series is to compute the arithmetical mean. Weighting the average of each series according to the number of analyses does not alter the value of the mean. Of the four series, those in which the lead halides are compared with silver, Series I and III, are probably, on the whole, less subject to error. These two series agree almost exactly, both with each other and with the average of all four series. This final average, therefore, 207.20, seems to us to represent fairly the result of our work.

One more comparison may very well be made at this point, between the different silver samples. Since it is uncertain whether in the first five analyses Sample I or II of silver was used, these experiments are not included in the table.

| Sample of Ag. | PbBr₂ : 2Ag. | PbCl₂ : 2Ag. | Average of individual experiments. |
|:---:|:---:|:---:|:---:|
| I..................... | 207.20 | 207.21 | 207.20 |
| II..................... | 207.21 | 207.22[1] | 207.21 |
| III................... | 207.18[1] | 207.21 | 207.20 |
| IV................... | 207.18[1] | 207.21[1] | 207.20 |
| Average, | 207.19 | 207.21 | 207.20 |

Here again evidence of dissimilarity in material is lacking.

In comparing the present work with the earlier work of Baxter and Wilson, it is obvious that the discrepancy, 0.1 unit, is larger than the experimental error in either research. We are unable to offer any certain explanation of this difference. It is improbable that in the earlier work the silver chloride was contaminated with occluded material, for the precipitate was carefully examined for lead salts with negative results.[2] Furthermore, if lead chloride were occluded by the silver chloride, it would have raised the apparent atomic weight of lead, whereas the difference is in the opposite direction. On the whole, less difficulty was experienced in the earlier work than in the later from insoluble residue in the fused salt, for the final material left no visible residue upon solution. It might be suggested that the lead material used in the earlier work actually possessed an atomic weight different from that of any used in the present investigation. This seems unlikely, since no difference could be detected between any of the varied materials examined later. Unfortunately none of the material remained from the first investigation, so that comparison was impossible. Another possibility is that in Baxter and Wilson's experiments, during the fusion of the lead chloride in a current of hydrochloric acid in a glass tube, sufficient alkali chloride sublimed from the glass into the lead salt, or on the boat, to produce the difference. Only 0.025% of sodium chloride or 0.035% of potassium chloride would have been necessary, which represent about a milligram of impurity with a 4–5 gram portion. This seems on the whole the most probable explanation. It must be remembered, however, that because of the high atomic weight of lead, it is far more sensitive to experimental error than is an atomic weight of lesser magnitude. Because of the far larger number of experiments, and the more complete treatment, we feel that the present work should supersede the earlier research, even though the cause of the difference is not wholly certain.

With regard to the bearing of our work upon the theories of atomic disintegration, it is evident that no far-reaching conclusion may be drawn. If lead is a product of radioactive change, it might reasonably be expected to vary in atomic weight according as it originates in uranium or thorium, or both. This seems to be the case only with material extracted from

[1] This is the result of one analysis only.

[2] *Loc. cit.*, p. 367.

uranium and thorium ores.   But this material differs from common lead in still possessing radioactivity, even though spectroscopically the radioactive and common material seem to be identical.[1]   It still remains to be finally determined whether it is possible to separate radioactive lead into constituent parts, one of which may be ordinary lead.[2]   It certainly is remarkable, however, if common lead is composed wholly or in part of isotopes of different atomic weights, that the proportions should be as constant in geographically and mineralogically different specimens of material as the constancy in the atomic weight indicates.

It is not at all certain, however, that during the expulsion of the $\alpha$-particle the weight of the atom undergoes no other change, for as Hönigschmid[3] has pointed out, the difference between his own recent determinations of the atomic weights of uranium and radium is not an even multiple of the atomic weight of helium.   Possibly, after all, ordinary lead is the end product of the disintegration of uranium or thorium, or both.

At present we are engaged in an attempt to discover a comparative method for the determination of the atomic weight of lead as different as possible from the one employed here.

## Summary.

1.   Eleven specimens of lead salts from many different geographical and mineralogical sources were purified by various methods, and were found to be identical so far as could be determined by spectroscopic examination and by analysis of the chloride and bromide.   None of these specimens were found to be radioactive to an appreciable extent.

2.   Electrolytic deposition with a dissolving anode through nitrate or chloride electrolyte was found to be an unsatisfactory method of purifying lead from small amounts of silver and copper.   Crystallization of the nitrate proved to be an efficient method.

3.   Neutral lead bromide and chloride were found to hydrolyze upon solution in water, with precipitation of basic salts.   Lead chloride which had been crystallized from water was found to be basic, although when crystallized from very dilute hydrochloric acid it is neutral.

4.   Lead bromide and chloride which had been fused in an atmosphere of dry hydrobromic and hydrochloric acid gases, respectively, were found to be neutral.

5.   By the analysis of both lead bromide and lead chloride the atomic weight of common lead was found to be 207.20, if $Ag = 107.880$, or 207.18, if $Ag = 107.870$.

[1] Richards and Lembert, Loc. cit., p. 1341.

[2] Ibid., p. 1343.

[3] Z. Electrochem., 20, 457 (1914).   See also Whytlaw-Gray and Ramsay, Z. physik. Chem., 80, 275 (1912).

6. No evidence was found that common lead is composed either wholly or in part of isotopes of different atomic weight.

We are very greatly indebted to the Carnegie Institution of Washington for generous assistance in the pursuit of this investigation.

CAMBRIDGE, MASS.

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## THE VAPOR PRESSURE OF IODINE BETWEEN 50° AND 95°.

BY GREGORY PAUL BAXTER AND MERRITT ROY GROSE.

Some years ago the vapor pressure of iodine was determined in the Harvard Laboratory[1] by the "air current" method throughout the temperature range 0° to 55°. This earlier research was interrupted by the end of the college year during attempts to continue the work at still higher temperatures. In the present investigation the difficulties met at the close of the earlier work were overcome and the method has been extended to cover the temperatures up to 95°.

The procedure in general was to pass a measured volume of pure, dry air, first over the pure iodine, and then into a solution of sodium carbonate to absorb the volatilized iodine. From the carbonate solution, after acidification and reduction of the liberated iodine by means of hydrazine, the iodine was precipitated as silver iodide, which was collected and weighed. In the experiments below 55°, sodium sulfite was used to absorb the iodine, but at higher temperatures this proved too easily oxidized by the oxygen of the air current. An aqueous solution of hydrazine did not reduce the iodine rapidly enough, while sodium hydroxide, attacked the glass apparatus very rapidly.

The purification of the iodine was carried out by methods which have been found effective in earlier researches.[2] Commercial iodine was dissolved in aqueous potassium iodide and distilled from a retort into a Jena flask cooled with running water. The product was several times rinsed with water, and was then suspended in water and reduced to hydriodic acid by means of well scrubbed hydrogen sulfide gas. After being boiled for some time to remove hydrocyanic acid which might have had its source in cyanogen impurity in the iodine, the solution was filtered to remove coagulated sulfur, and was then oxidized in a retort with a slight excess of potassium permanganate. In the latter process there is set free only five-eighths of the iodine, which was then distilled from the solution of potassium and manganous iodides as before. Although this second distillation from an aqueous iodide must have eliminated every trace of

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[1] Baxter, Hickey and Holmes, THIS JOURNAL, 29, 127 (1907).

[2] THIS JOURNAL, 26, 1577 (1904); 27, 876 (1905).