1. The method of adiabatic calorimetry as applied to combustion in the Berthelot bomb has been further improved in several directions, making more accurate determinations possible.

2. The agreement among the results with any substance is close enough to show that the method is capable of all the necessary refinement.

3. The relative heats of combustion of sugar, benzene, toluene, ethyl benzene, normal and isopropyl benzene, mesitylene, pseudocumene and cyclohexane have been determined.

4. The striking similarity between the heats of combustion of various isomers appears. Nevertheless, real differences exist, and will doubtless some time, when more data are available, be capable of reference to differences in molecular stability and configuration.

5. The boiling points of these liquids have been carefully studied, especially those of exceptionally pure toluene (110.31°) and cyclohexane (80.8°); and the melting point of benzene also has been determined as 5.484°, while that of cyclohexane was found to be 5.97°.

CAMBRIDGE, MASS., 1911-1912; 1915.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF LEAD. THE ANALYSIS OF LEAD BROMIDE.

[SECOND PAPER.]

BY GREGORY PAUL BAXTER AND THORBERGUR THORVALDSON.

Received March 8, 1915.

Since the work by Baxter and Wilson[1] on the atomic weight of lead by the analysis of lead chloride some years ago, which yielded the value 207.09 (Ag = 107.880), the atomic weight of lead has been under almost continuous investigation in the Harvard Laboratory. Attempts were made by Mr. W. A. Worsham to synthesize the sulfate from the metal, but serious difficulties were met in the production of lead sulfate free from occluded matter, and in the drying of the sulfate, so that this method was temporarily given up in favor of the analysis of lead bromide. The latter substance, in spite of the fact that it is somewhat less soluble than lead chloride, is, nevertheless, sufficiently soluble for the purpose. Preliminary experiments in the preparation of pure lead bromide were carried out by Mr. Worsham. The investigation was then continued by the present authors, and finally was taken up by Mr. F. L. Grover. This paper presents the results of Dr. Thorvaldson's experiments, while the following one describes the completion of the research by Mr. Grover.

The method employed was the usual one in the case of metallic halides, with special modifications made necessary by the idiosyncrasies of lead

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[1] *Proc. Amer. Acad.*, 43, 365 (1907); THIS JOURNAL, 30, 187 (1908); *Z. anorg. Chem.*, 57, 174 (1908).

bromide. Weighed amounts of the salt, which had been fused in an atmosphere containing hydrobromic acid, were dissolved in hot water which had been slightly acidified. To the solution after cooling was added a solution of a weighed, very nearly equivalent, amount of metallic silver. Any deficiency of bromide or silver was then added in the form of very dilute standard solutions, so that the exact amount of silver required could be accurately estimated. Finally, the silver bromide was collected and weighed.

The Purification of Materials.

Water, nitric acid and ammonia were purified by distillation in the usual fashion.

Hydrobromic Acid.—At first hydrobromic acid was prepared as explained in the paper by Baxter, Thorvaldson and Cobb upon the analysis of ferrous bromide.[1] This acid was made from bromine which had been freed from chlorine by distillation from aqueous potassium bromide (Sample I). The hydrobromic acid was synthesized by saturating hydrogen with bromine and conducting the mixed gases over hot platinum. The hydrogen was made from "hydrone" and was purified by scrubbing and passing over stick potassium hydroxide. The acid gas was collected in water and the solution was purified by distillation. Material produced in this way still gave evidence of containing organic matter,[2] so that for the later preparations steps were taken to free the bromine from such impurities by converting it to potassium bromide and fusing the salt with potassium permanganate, as described in detail in the following paper. From this potassium bromide, bromine was set free by adding three-fourths of the theoretical quantity of potassium permanganate and sulfuric acid. In this way the bromine received still a third distillation from a bromide (Sample II). The product was converted into hydrobromic acid by direct combination with pure hydrogen in contact with platinum. The gas was collected in the purest water, and the solution distilled, with rejection of the extreme fractions.

Lead Bromide.—This substance was prepared by precipitation of lead nitrate with hydrobromic acid solution, and crystallization of the product by solution in hot concentrated hydrobromic acid and reprecipitation by diluting the solution with water.

Sample A consisted of residues from earlier work by Mr. Worsham, which were recrystallized from hydrobromic acid solution, as above, with centrifugal drainage. The material was somewhat blackened at the outset but was pure white after crystallization.

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[1] THIS JOURNAL, **33**, 326 (1911); *Z. anorg. Chem.*, **70**, 329 (1911).

[2] This organic matter may have originated partly in the hydrogen made from hydrone. Baxter and Hoover, THIS JOURNAL, **34**, 1659 (1912); *Z. anorg. Chem.*, **80**, 203 (1913).

The source of Sample B was lead nitrate which had been purified by Dr. J. W. Shipley. The method of purifying the nitrate consisted in precipitating lead sulfate and washing this substance very thoroughly, converting it into lead sulfide by contact with a saturated solution of hydrogen sulfide, and solution in pure nitric acid. Three recrystallizations as nitrate followed, the mother liquors of the last two crystallizations being found free from sulfate. The nitrate was dissolved in water in a quartz dish and a slight excess of dilute hydrobromic acid was added. The crystals were separated from the mother liquor by centrifugal drainage in platinum Gooch crucibles, and were thoroughly rinsed with water. The lead bromide was dissolved in constant boiling hydrobromic acid in a quartz dish and again precipitated by dilution with water. Centrifugal drainage and rinsing followed. After a second recrystallization a portion of the material was reserved for analysis, Sample B_1. The remainder was once again recrystallized, Sample B_2.

Sample C was prepared from lead nitrate which, in turn, was obtained from precipitated lead chloride. The latter substance, after thorough washing, was changed to sulfide as above. The sulfide was washed and dissolved in nitric acid, and the lead nitrate was recrystallized three times. The preparation of lead bromide from this nitrate followed the lines indicated in the case of Sample B. Sample II of bromine was used.

Sample D. Lead nitrate for the preparation of this sample was obtained by recrystallizing the commercial product five times from nitric acid and once from aqueous solution. The bromide was prepared as above with Sample II of bromine.

The final crystallizations of the lead nitrate were carried out in platinum or quartz vessels, while the preparation and crystallization of the lead bromide was always conducted in quartz vessels. A quartz condenser was used for the distillation of the hydrobromic acid, and the distillate was collected in quartz vessels.

Silver.—Pure silver was prepared as frequently described in papers from the Harvard Chemical Laboratory. The particular specimen used in this work had already been used in the investigation upon ferrous bromide[1] (Sample A).

Preparation of Lead Bromide for Analysis.

The drying of lead bromide was effected by fusion in a dry atmosphere containing a considerable proportion of hydrobromic acid gas. In the earlier experiments the apparatus was identical with that used in the research upon ferrous bromide. Fuming hydrobromic acid gas was made by passing the synthetic gas into ice-cold water. A slight excess of bromine was removed by adding a small amount of ferrous bromide. Pure nitrogen was then bubbled through this solution, thereby acquiring a very consider-

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[1] Baxter, Thorvaldson and Cobb, *Loc. cit.*

able hydrobromic acid content, and the mixture was dried by passing it over fused calcium bromide.[1] The lead bromide, contained in a platinum boat, which in turn was placed in the quartz tube of a "bottling apparatus,"[2] was heated in a current of nitrogen and hydrobromic acid, gently at first, so that the greater part of the moisture in the salt was expelled at a low temperature, later at gradually increasing temperatures until finally fusion took place. The bottling apparatus and tube, after the salt had been allowed to cool, were then swept out with a current of pure nitrogen, and this in turn was displaced with dry air. Thereupon the boat and contents, by means of the bottling apparatus, were transferred to the weighing bottle, without exposure to moisture.

When lead bromide, fused as above, is treated with water, either cold or warm, a clear solution is never obtained. The horny mass of fused material whitens superficially, and if the solution is boiled, a white precipitate appears. At first the difficulty was ascribed to hydrolysis of the salt during fusion, but no precautions as to the preliminary drying of the salt before fusion, so as to insure fairly complete elimination of the water, produced any difference in the result, so that the conclusion was reached that the difficulty is caused by hydrolysis during solution. So far as obtaining a clear solution of the salt is concerned, a simple remedy was found in acidifying the solution slightly. In the experiments described in this paper, acetic acid was used for the purpose, although in the work described in the following paper a small amount of nitric acid was found to be equally satisfactory. It was necessary, however, to obtain further evidence as to the cause of the difficulty. This was done as follows: Neutral lead bromide, precipitated by the addition of a solution of recrystallized potassium bromide to a solution of recrystallized lead nitrate, was thoroughly washed by decantation and centrifugally drained. Three grams of this lead bromide when heated with about 600 cc. of water dissolved partially, leaving, however, a considerable amount of white insoluble matter, which did not dissolve when the solution was replaced by a liter of water. Fearing that the lead bromide which served as the starting point of this experiment might have been slightly basic, the experiment was repeated with material which had been crystallized from slightly acid solution. Even here the salt did not give a clear solution, a similar white insoluble residue remaining. Thus, material which surely must have been initially neutral or acid behaved, so far as we could tell, as the fused material behaved. In order to discover whether the insoluble matter is basic bromide or hydroxide, some of it was washed thoroughly, dissolved in nitric acid and treated with silver nitrate. A precipitate of

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[1] Baxter and Warren found calcium bromide to be a very efficient drying agent, THIS JOURNAL, **33**, 340 (1911).

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

silver bromide was produced, indicating the insoluble substance to be a basic bromide. In still another experiment some of the lead bromide which had been prepared from neutral potassium bromide and lead nitrate was dried in a current of hydrobromic acid at a temperature nearly as high as the fusion point. This material also yielded an insoluble residue. Since there seemed, therefore, to be reason to believe that lead bromide fused in an atmosphere containing hydrobromic acid is not basic, the analyses of the fused material were next carried out.

Before doing so, however, it was necessary to prove that during the solution of the bromide in the dilute acetic acid solution no volatile compounds of bromide are lost. About 4 g. of lead bromide were placed in a distilling flask with 400 cc. of water and 5 cc. of acetic acid, that is, ten times as much acetic acid was used as was ever used in an analysis. The solution was distilled and the distillate was collected and tested for bromide with silver nitrate. In the test portion about 0.004 mg. of bromine was found. Since the solution was more concentrated in lead bromide and since far more acetic acid was used than in any of the analyses, and since in practice the solution was never actually boiled while the lead bromide was dissolving, it seemed certain that the danger of losing bromine was negligible.

Even when the lead bromide was dissolved in acidulated water, there remained always a slight black residue, which was never observed when unfused material was dissolved. In later work by Mr. Grover and Dr. Hartmann in this laboratory it was found that this black residue consists in part of carbon formed by the charring of organic impurities, and in part of silicic acid, extracted probably from the quartz dishes. The proportion of this material was diminished when the hydrobromic acid was prepared from the purest bromine as previously described, but no specimen of fused material was ever obtained absolutely free from it. In this research the residue was very carefully examined for lead with negative results, and in the work described in the following paper evidence was obtained as to its real nature. From evidence obtained in the later research it seems probable that the weight of this black residue amounted to about 0.004%. This proportion would raise the observed atomic weight of lead by 0.015 unit in the comparisons with silver only, since it must have been collected and weighed with the silver bromide which is only slightly heavier than the lead bromide.

In order to dissolve the lead bromide, the boat after being weighed was transferred to a large Jena glass flask and was covered with nearly a liter of the purest water, to which about 0.5 cc. of glacial acetic acid was added. The solution was then heated almost to the boiling point until the lead bromide had dissolved. This required several hours. Next a quantity of the purest silver, very nearly equivalent to the lead bromide, was weighed out and dissolved in nitric acid and this solution also was diluted to a total volume of about a liter. The lead bromide solution was transferred quantitatively to a glass-stoppered precipitating flask, and, both solutions being cold, the silver nitrate solution was slowly poured into the lead bromide solution. The solutions were then thoroughly mixed by shaking and allowed to stand with occasional shaking for a few days. Next the liquid was examined in a nephelometer for excess of bromide or silver, and any deficiency of either was made up by the addition of 0.01*N* silver or bromide solution. Usually the comparison was completed within ten days of the time of precipitation, but in two analyses, 5 and 6, the precipitates were left under the solution for about four weeks longer. No perceptible alteration in end point during this period could be observed. As soon as the exact end point had been found, a slight excess of silver nitrate was added and the silver bromide was washed and collected upon a platinum-sponge Gooch crucible. After being dried for several hours at about 180° the silver halide was weighed. Residual moisture was determined by the loss in weight on fusion in a porcelain crucible, and a correction for solubility of the silver bromide in the wash-water of 0.1 mg. per liter of water was applied.

The silver bromide from one experiment was tested for occluded lead salts by solution in potassium cyanide, reprecipitation with hydrochloric acid, evaporation of the solution and addition of (A) hydrogen sulfide, (B) sulfuric acid. The evidence was negative.

In the first five analyses the hydrobromic acid gas mixture was produced as described above, but since we still feared that the fused salt might be basic, in subsequent analyses the concentration of hydrobromic acid was considerably increased. This was done by using synthetic gas produced as in the apparatus employed by Richards and Hönigschmid in their work upon the atomic weight of calcium.[1] This hydrobromic acid was formed by saturating hydrogen gas with the purest bromine at a temperature in the neighborhood of 44° and passing the mixed gases over hot platinum. The hydrobromic acid gas contained a slight excess of hydrogen. It was dried by fused calcium bromide. During the fusion of the lead bromide a small amount of nitrogen was passed into the apparatus, but even then the concentration of the hydrobromic acid must have been far greater than in the earlier experiments.

The effect of this change in procedure was not to increase, but, on the whole, to diminish slightly the apparent proportion of bromine in the salt, but it is by no means certain that the slight differences were really caused by the change in the process of fusion, since the earlier analyses were naturally subject to the uncertainties of preliminary determinations.

The platinum boat did not remain absolutely constant in weight, but

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[1] THIS JOURNAL, **32**, 1583 (1910).

lost by amounts varying from 0.1 to 0.3 mg. in each analysis. No correction was applied for the change, which averaged -0.14 mg.

Vacuum corrections were applied as follows:

	Specific gravity.	Vacuum correction.
Weights	8.3	......
Silver	10.49	-0.000031
Silver bromide	6.473	+0.000041
Lead bromide	6.66	+0.000035

SERIES I.

Ag = 107.880. $PbBr_2 : 2Ag$. Br = 79.916.

Number of analysis.	Sample of $PbBr_2$.	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	A	6.55858	3.85650	-0.00040	3.85610	1.70083	207.14
2	B_1	4.83285	2.84146	-0.00020	2.84126	1.70095	207.17
3	B_2	5.67758	3.33797	-0.00010	3.33787	1.70096	207.17
4	B_2	6.73361	3.95874	0.00000	3.95874	1.70095	207.16
5	B_2	5.93130	3.48710	-0.00050	3.48660	1.70117	207.21
6	B_2	5.01729	2.94948	+0.00020	2.94968	1.70096	207.17
7	C	5.89902	3.46810	-0.00080	3.46730	1.70133	207.25
8	C	7.71526	4.53568	-0.00070	4.53498	1.70128	207.24
9	C	7.40244	4.35147	+0.00010	4.35157	1.70110	207.20
10	D	7.01144	4.12204	-0.00050	4.12154	1.70117	207.21
11	D	6.91460	4.06454	+0.00030	4.06484	1.70108	207.19
12	D	8.12623	4.77699	-0.00020	4.77679	1.70119	207.22
					Average,	1.70108	207.19

SERIES II.

$PbBr_2 : 2AgBr$.

Number of analysis.	Sample of $PbBr_2$.	Wt. of $PbBr_2$ in vacuum. Grams.	Wt. of AgBr in vacuum. Grams.	Wt. of AgBr from wash waters. Gram.	Loss on fusion. Gram.	Corr. wt. of AgBr in vacuum. Grams.	Ratio $PbBr_2 : 2AgBr$.	At. wt. of Pb.
13	A	6.55858	6.71235	0.00024	0.00018	6.71241	0.97708	207.15
14	B_2	6.73361	6.89146	0.00015	0.00037	6.89124	0.97713	207.17
15	B_2	5.01729	5.13422	0.00017	0.00039	5.13400	0.97727	207.22
16	C	7.71526	7.89593	0.00015	0.00082	7.89526	0.97720	207.20
17	D	7.01144	7.17509	0.00013	0.00052	7.17470	0.97725	207.21
18	D	6.91460	7.07689	0.00022	0.00039	7.07672	0.97709	207.16
						Average.	0.97717	207.19
					Average of Series I and II,			207.19

It is obvious that the foregoing data indicate a value for the atomic weight of lead decidedly above the earlier one found by Baxter and Wilson, although that in turn was nearly 0.3 unit higher than the one commonly accepted at the time. Even in the case of an atomic weight as high as that of lead, the difference is larger than the experimental error. The investigation was therefore continued by Mr. F. L. Grover, whose work 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.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE.]

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

[THIRD PAPER.]

BY GREGORY PAUL BAXTER AND FRED LESLIE GROVER.

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CONTENTS.

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

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