the bromate and crystallized four times, when the most soluble portion gave the thulium spectrum.

Dysprosium and holmium also separate from erbium with comparative ease, and as yttrium places itself between terbium and dysprosium, the latter element can be obtained terbium-free. The division between dysprosium and holmium is not so marked.

The absorption spectra and the colors of the various fractions show curious changes which are not altogether understood and may be simply due to the comparatively small amount of material under examination.

More material (15 kilos) is at present being fractionated and in the near future the less basic portion of earths derived from about 100 kilos of euxenite and 100 kilos of yttrotitanite, etc., will also be included. The bromate method will be further investigated and also applied to the cerium group and the results published at an early date.

NEW HAMPSHIRE COLLEGE,
Durham, N. H., November 18, 1907.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF LEAD.

Preliminary Paper—The Analysis of Lead Chloride.

GREGORY PAUL BAXTER AND JOHN HUNT WILSON.

Received December 2, 1907.

Although lead is one of the most common elements, its atomic weight has received comparatively little attention, the value at present accepted being based almost wholly upon the work of Stas.[1] Of the earlier determinations of this constant those of Döbereiner[2] and Longchamps[3] can hardly be considered as possessing other than historic interest. The first results which can lay claim to accuracy are those of Berzelius,[4] who obtained values ranging from 206.7 to 207.3 by reduction of litharge in a current of hydrogen. Berzelius also synthesized the sulphate from metallic lead with the result 207.0.[5] Shortly after, Turner[6] criticized

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[1] Earlier work on the atomic weight of lead has been carefully summarized by Clarke. Smithsonian Miscellaneous Collections, Constants of Nature, "A Recalculation of the Atomic Weights," 1897.

In recalculating the data of earlier determinations the following atomic weights have been used in this paper:

$$O=16.000;\ Ag=107.88;\ Cl=35.46;\ N=14.01;\ S=32.07$$

Richards and Wells, Pub. Car. Inst., No. 28 (1905); Richards and Forbes, *Ibid.*, No. 69, p. 47 (1907); Richards and Jones, *Ibid.*, No. 69, p. 69; Report of International Committe on Atomic Weights, This Journal, **29**, 110 (1907).

[2] Schweig. J., **17**, 241 (1816).

[3] Ann. chim. phys., **34**, 105 (1827).

[4] Pogg. Ann., **19**, 314 (1830).

[5] Lehrbuch, 5th ed., **3**, 1187 (1845).

[6] Phil. Trans., 527 (1833).

the first method employed by Berzelius and attributed the irregularity of his results to the action of lead oxide on the siliceous matter of the tube at the temperature employed in the reduction. By the conversion of both the metal and the oxide into sulphate Turner, in a painstaking research, deduced the values 207.0 and 207.6 respectively, and by converting the nitrate into sulphate, 204.2. Marignac[1] converted metallic lead into the chloride by heating in a stream of chlorine and obtained the result 207.42. Both Marignac[2] and Dumas[3] analyzed lead chloride. Marignac, who dried the salt at 200°, by titration against silver found the atomic weight of lead to be 206.81, and from the ratio of lead chloride to silver chloride, 206.85. Dumas subsequently showed that lead chloride, even when dried at 250°, retains moisture and is somewhat basic, and in one analysis in which corrections are applied for these errors, found a somewhat higher value, 207.07, as was to be expected. Chloride analyses by early investigators are, however, to be universally distrusted, owing to neglect of the very considerable solubility of silver chloride, thus producing too low results.

Stas's[4] work upon the syntheses of lead nitrate and sulphate from the metal is undoubtedly the most accurate contribution upon the subject, although a careful consideration of his work discloses minor defects, many of which he recognized himself. The metallic lead used in the syntheses was finally fused under potassium cyanide. Whether or not this treatment introduced impurities into the metal is uncertain. Stas himself suspected the presence of alkalies in the metal. Since the nitrate could not be dried above 150° without decomposition, it undoubtedly contained moisture, and Stas calls attention to this point. The sulphate was made by treatment of lead nitrate, resulting from the nitrate syntheses, with sulphuric acid. The sulphate was dried finally at dull redness, and was probably free, or nearly free, from moisture, although it may have contained traces of lead oxide resulting from occluded nitrate, as well as sulphuric acid. Most of these probable errors tend to lower the observed atomic weight, so that Stas's value from the series of nitrate syntheses, 206.81, and that from the sulphate series, 206.92, are to be regarded as minimum values. The reader of Stas's own account of his work upon lead cannot fail to be impressed with the fact that he was somewhat dissatisfied with the outcome of his research. Mention should also be made of the work of Anderson and Svanberg[5] on the conversion of lead nitrate into oxide, although the method was

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[1] Ann., **59**, 289 (1846).

[2] J. pr. Chem., **74**, 218 (1858).

[3] Ann., **113**, 35 (1860).

[4] Œuvres Completes, **1**, 383.

[5] Ann. chim. phys. [3], **9**, 254 (1843).

primarily employed in an endeavor to fix the atomic weight of nitrogen. Their results yield the value 207.37.

The discrepancies between the results of these various experiments only serve to emphasize the need of a redetermination of the value in question, and it was with this object in view that the work embodied in this paper was undertaken.

The search for a suitable method for determining the atomic weight of lead failed to reveal any more promising line of attack than those already employed for the purpose. With an element of so high an atomic weight as lead, in any method involving the change of one of its compounds into another, errors which may be insignificant with elements of small atomic weight are magnified in the calculations to undesirable proportions. Furthermore, during the following investigation, reduction of the chloride and oxide in hydrogen was investigated far enough to show that complete reduction of either compound was extremely difficult, if not impossible, without loss of material from the containing vessel by sublimation, aside from the fact that all available material for containing vessels is acted upon by either the fused salt or the reduced metal. The elimination of moisture from lead nitrate or lead sulphate without decomposition of the salts seemed likely to prove a stumbling block in the use of these substances. Finally, in spite of the slight solubility of lead chloride, the determination of the chlorine in this salt by precipitation with silver nitrate was chosen as presenting fewest difficulties. In the first place, the determination of a halogen can be effected with great accuracy. In the second place, the elimination of moisture from lead chloride is an easy matter, since the salt may be fused in a platinum vessel in a current of hydrochloric acid gas without attacking the platinum in the least and without the production of basic salts. In the third place, silver chloride, which has been precipitated from a dilute solution of lead chloride by means of silver nitrate, does not contain an amount of occluded lead salt large enough to be detected.

Purification of Materials.

Water.—All of the water used in either the purification or the analyses was distilled twice, once from an alkaline permanganate solution and once from very dilute sulphuric acid. Block-tin condensers were used in both distillations, and rubber and cork connections were avoided. Generally, receivers of Jena glass were employed, but in certain cases the water was collected in platinum or quartz vessels.

Hydrochloric acid.—Commercial C. P. hydrochloric acid was diluted with an equal volume of water and distilled with a quartz condenser, only the middle fraction being collected.

Nitric acid.—Nitric acid was distilled with a platinum condenser, until free from chlorine. Two distillations were invariably sufficient to accomplish this end, if the first third of each distillate was rejected.

Silver.—Pure silver was obtained by methods already many times employed in this laboratory. Silver nitrate was dissolved in a large volume of water and the silver was precipitated as chloride with an excess of hydrochloric acid. The precipitate was thoroughly washed and reduced with alkaline invert sugar. The reduced silver, after being washed, was dried and fused on charcoal in the flame of a clean blast lamp. After the buttons had been cleaned by scrubbing with sand and etching with nitric acid, they were dissolved in pure dilute nitric acid and the silver was precipitated as metal with ammonium formate.[1] This silver was washed and fused in the flame of a blast lamp on a crucible of the purest lime. The buttons were cleaned as before, and then electrolyzed.[2] Finally the electrolytic crystals were fused in a boat of the purest lime in a porcelain tube in a current of pure electrolytic hydrogen.[3] The bars of silver were cut in pieces with a fine steel saw, etched with dilute nitric acid until free from iron, washed, dried, and heated in a vacuum to 400°. The silver was kept in a desiccator containing solid potassium hydroxide.

Lead chloride.—Three samples of lead chloride from two entirely different sources were employed. Sample A was prepared from metallic lead. Commercial lead was dissolved in dilute nitric acid, and the solution, after filtration, was precipitated with a slight excess of sulphuric acid. The lead sulphate was thoroughly washed, suspended in water, and hydrogen sulphide was passed in until the sulphate was almost completely converted into sulphide. Next, the sulphide was washed with water, dissolved in hot, dilute nitric acid, and the solution was freed from sulphur and unchanged sulphate by filtration. The lead nitrate thus obtained was crystallized twice, dissolved in water, and precipitated in glass vessels with a slight excess of hydrochloric acid. The chloride was washed several times with cold water and then crystallized from aqueous solution eight times, the last five crystallizations being carried out wholly in platinum, with centrifugal drainage after each crystallization. In crystallizing the lead chloride the whole sample was not dissolved at one time, but the same mother liquor was used for dissolving several portions of the original salt. Needless to say, the chloride was not exposed to contact with the products of combustion of illuminating gas, lest lead sulphate be formed.

Sample B was prepared from commercial lead nitrate. This salt was dissolved and crystallized from dilute nitric acid once in glass and six

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[1] Richards and Wells, Pub. Car. Inst., No. 28, 19 (1905).

[2] Abrahall, J. Chem. Soc. Proc., 1892, p. 660.

[3] Baxter, Proc. Am. Acad., **39**, 249 (1903).

times in platinum vessels, with centrifugal drainage. Hydrochloric acid was then distilled into a large quartz dish, and the solution of the nitrate was slowly added with constant stirring with a quartz rod. The chloride was freed from aqua regia as far as possible by washing with cold water, and was once crystallized from aqueous solution in quartz dishes to remove last traces of aqua regia. Finally the salt was crystallized three times in platinum.

It could reasonably be expected that both of these samples were of a high degree of purity; nevertheless, upon heating the salt in an atmosphere of hydrochloric acid, the salt itself turned somewhat dark, and upon solution of the fused salt in water a slight dark residue remained. Although in a few preliminary experiments attempts were made to determine this residue by filtration and ignition, it was subsequently found that even a small filter paper adsorbs appreciable amounts of lead compounds from a solution of the chloride, which cannot be removed by washing with water. From three to thirteen hundredths of a milligram of residue were obtained in several blank experiments, by ignition of filters through which half per cent. solutions of lead chloride had been passed, with subsequent, very thorough washing. In order to avoid the uncertainty of this correction, further attempts were made to obtain a sample of the salt which would give a perfectly clear solution in water after fusion, and thus render filtration unnecessary. With this end in view a considerable quantity of Sample A was fused in a large platinum boat in a current of hydrochloric acid. The fused salt was powdered in an agate mortar, dissolved in water in a platinum vessel, and the solution was freed from the residue by filtration through a tiny filter in a platinum funnel into a platinum dish, where it was allowed to crystallize. This sample was then twice recrystallized with centrifugal drainage. Notwithstanding the drastic treatment to which it had been subjected, when a portion of this material was fused in hydrochloric acid, the same darkening as before was observed, and the same residue was obtained. The suspicion that the difficulty was due to dissolving of the filter paper by the solution of the salt[1] led to a second more successful attempt by crystallization from hydrochloric acid solution in platinum vessels. In this way it was found possible to prepare salt which showed no tendency to darken upon heating, and which, after fusion, left absolutely no residue upon solution in water. Portions of Samples A and B were thus recrystallized three times more. Since these two specimens of material gave identical results, for two final experiments portions from each of these samples were mixed and then subjected to three additional crystallizations. This last sample was designated Sample C.

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[1] Mr. P. B. Goode in this laboratory has recently found a similar difficulty with the chlorides of the alkaline earths.

Method of Analysis.

The lead chloride contained in a weighed platinum boat was first fused in a current of pure, dry hydrochloric acid gas. This gas was generated by dropping concentrated sulphuric acid into concentrated hydrochloric acid, and after being washed with a saturated solution of hydrochloric acid, was passed through five towers filled with beads moistened with freshly boiled, concentrated sulphuric acid, to dry the gas. It has already been shown that phosphorus pentoxide may not be used for this purpose.[1] After the salt had cooled, the hydrochloric acid was displaced by dry nitrogen, and this in turn by dry air. Nitrogen was prepared by passing air charged with ammonia over red-hot rolls of copper gauze, the excess of ammonia being removed by means of dilute sulphuric acid. The gas was passed over beads moistened with a dilute silver nitrate solution and over solid caustic potash to remove sulphur compounds and carbon dioxide respectively, and was finally dried by concentrated sulphuric acid and phosphorus pentoxide. The air was purified and dried in a similar fashion. The apparatus for generating the hydrochloric acid and for purifying the hydrochloric acid and nitrogen was constructed wholly of glass with ground-glass joints. The platinum boat containing the fused chloride was next transferred to a weighing bottle without exposure to moist air, by means of the bottling apparatus, which has frequently served for a similar purpose in many atomic weight investigations in this laboratory.[2] After standing some time in a desiccator in the balance room, the weighing bottle was weighed. In most of the analyses the lead chloride was dissolved from the boat by prolonged contact with boiling water in a Jena glass flask. In the last two analyses, in order to show that no error was introduced through solubility of the glass, the solution was prepared in a large platinum retort, and was not transferred to the precipitating flask until cold.

Very nearly the necessary amount of pure silver was then weighed out and dissolved in a redistilled nitric acid diluted with an equal volume of water in a flask provided with a column of bulbs to prevent loss by spattering. After the silver was all dissolved, an equal volume of water was added, and the nitrous fumes were expelled by gentle heating. The solution was then further diluted until not stronger than one per cent., and added slowly, with constant agitation, to the solution of lead chloride contained in the precipitating flask. The precipitation and handling of the silver chloride were conducted in a room lighted with ruby light. The flask was shaken for some time and allowed to stand for a few days, with occasional agitation, until the supernatant liquid had become clear. Thirty cubic centimeter portions of the solution were

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

[2] Richards and Parker, Proc. Am. Acad. Arts and Science, 32, 59 (1896).

then removed and tested with hundredth normal silver nitrate and sodium chloride, in a nephelometer,[1] for excess of either chloride or silver, and, if necessary, standard silver nitrate or sodium chloride was added, and the process of shaking and testing repeated until the amounts of silver and chloride were equivalent. The test solutions were always returned to the flask, since they contained appreciable amounts of silver chloride, and the weight of silver chloride subsequently obtained was corrected for the quantity thus introduced. Furthermore, if an excess of silver was found, a negative correction of an equivalent quantity of silver chloride was necessary.

After the exact end point had been obtained, about two tenths of a gram of silver nitrate in excess was added in order to precipitate the dissolved silver chloride, and the flask was thoroughly shaken, and allowed to stand again until the solution was perfectly clear. The silver chloride was washed, first several times with a very dilute silver nitrate solution containing four hundredths of a gram per liter, and then eight times with pure water. It was next transferred to a Gooch crucible and dried for several hours in an electric oven, the temperature being gradually raised to 180°, and was cooled in a desiccator and weighed. In every case the moisture retained by the precipitate was determined by fusion in a small porcelain crucible. The silver chloride, dissolved in the filtrate and washings, was determined by comparison with standard solutions in the nephelometer in the usual manner. Care was taken to treat both tubes in exactly the same manner, and final readings were taken only when the ratio had become constant. Before proceeding to the nephelometer tests, however, the filtrate and washings were passed through a very small filter in order to collect a small quantity of asbestos shreds mechanically detached from the Gooch crucible. The filter was ignited and weighed, the ash being treated with a drop of nitric and hydrochloric acids in order to convert any reduced silver into chloride. In order to find out whether lead or silver nitrates were appreciably adsorbed by the filter paper, a solution containing lead nitrate, silver nitrate, and nitric acid of the concentration of these filtrates, was passed through several small filter papers, which were then very carefully washed. In four cases, after incineration of the papers, there was found, —0.00001, +0.00002, +0.00003, +0.00001 gram of residue, exclusive of ash. This correction is so small that it is neglected in the calculations. In all the analyses the platinum boat behaved admirably, the loss in weight never amounting to more than a few hundredths of a milligram.

The balance used was a short arm Troemner, easily sensitive to a fiftieth of a milligram. The gold-plated brass weights were carefully standardized to hundredths of a milligram. All the weighings were

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[1] Richards and Wells, Am. Chem. J., **31**, 235 (1904); **35**, 510 (1906).

made by substitution with tare vessels as nearly like those to be weighed as possible.

Vacuum corrections: The values of the density of lead chloride as given by various observers range from 5.78 to 5.805,[1] the mean of the more accurate determinations being 5.80. This gives rise to a vacuum correction of +0.000062 for each apparent gram of lead chloride, the density of the weights being assumed to be 8.3. The other vacuum corrections applied were silver chloride +0.000071, and silver —0.000031.

All analyses which were carried to a successful completion are recorded in the tables.

THE ATOMIC WEIGHT OF LEAD.

Series I. $PbCl_2 : 2Ag$.

Number of analysis.	Sample of $PbCl_2$.	Weight of $PbCl_2$ in vacuum. Grams.	Weight of Ag in vacuum. Grams.	Weight of Ag added or subtracted. Gram.	Corrected weight of Ag. Grams.	Atomic weight of Pb. Ag=107.930. Cl=35.473.	Atomic weight of Pb. Ag=107.880. Cl=35.457.
1	A	4.67691	3.63061	—0.00074	3.62987	207.179	207.079
2	A	3.67705	2.85375	0.00000	2.85375	207.189	207.089
3	A	4.14110	3.21388	+0.00020	3.21408	207.173	207.073
4	A	4.56988	3.54672	0.00000	3.54672	207.185	207.085
5	B	5.12287	3.97596	—0.00028	3.97568	207.201	207.101
6	B	3.85844	2.99456	0.00000	2.99456	207.186	207.086
7	B	4.67244	3.62628	0.00000	3.62628	207.189	207.089
8	C	3.10317	2.40837	0.00000	2.40837	207.188	207.088
9	C	4.29613	3.33427	—0.00020	3.33407	207.202	207.102
Average						207.188	207.088

Series II. $PbCl_2 : 2AgCl$.

Number of analysis.	Sample of $PbCl_2$.	Weight of $PbCl_2$ in vacuum. Grams.	Weight of AgCl in vacuum. Grams.	Loss on fusion. Gram	Weight of asbestos. Gram.	Weight AgCl from wash waters. Gram.	Corrected weight of AgCl. Grams.	Atomic weight of Pb. Ag=107.930. Cl=35.473.	Atomic weight of Pb. Ag=107.880. Cl=35.457
10	A	4.67691	4.82148	0.00100	0.00021	0.00204	4.82273	207.188	207.088
11	A	4.14110	4.26848	0.00020	0.00008	0.00180	4.27016	207.192	207.092
12	B	5.12287	5.28116	0.00054	0.00013	0.00197	5.28272	207.181	207.081
13	B	3.85844	3.97759	0.00035	0.00033	0.00192	3.97949	207.136	207.036
14	C	3.10317	3.19751	0.00045	0.00014	0.00189	3.19909	207.261	207.161
15	C	4.29613	4.42730	0.00020	0.00004	0.00268	4.42982	207.204	207.104
Average								207.193	207.093
Average, rejecting the least satisfactory analyses, 13 and 14								207.191	207.091
Average of Series I and II								207.190	207.090

The close agreement of the averages of the two series is strong evidence that no constant error, such as occlusion, affects the results. Furthermore, in all, 19.55663 grams of silver produced 25.98401 grams of silver chloride, whence the ratio of silver to silver chloride is 132.865, a value in close agreement with the result 132.867 obtained by Richards

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[1] Landolt-Börnstein-Meyerhoffer, Tabellen.

and Wells.[1] The different samples, A, B, and C, all give essentially identical results.

It appears, then, that if the atomic weight of silver is taken as 107.93 (O = 16.000), the atomic weight of lead is 207.19, nearly three tenths of a unit higher than the value now in use. If the atomic weight of silver is 107.88, a value probably nearer the truth than 107.93, lead becomes 207.09, a number still much higher than that depending upon Stas's syntheses, as is to be expected.

We are greatly indebted to the Carnegie Institution of Washington for assistance in pursuing this investigation, also to Dr. Wolcott Gibbs and to the Cyrus M. Warren Fund for Research in Harvard University for many indispensable platinum vessels.

CAMBRIDGE, MASS.,
October 18, 1907.

CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE UNDER HIGH PRESSURES OF OXYGEN.[2]

BY E. B. SPEAR.

Received October 12, 1907.

Introduction.

The mechanism of catalysis by means of the metals in their different forms and especially their decomposing effect on hydrogen peroxide has been the subject of a great deal of very thorough experimental investigation. Since Bredig published his work on the preparation of colloidal solutions by electrical[3] means, the study of catalysis has had an additional impetus, and our knowledge of the subject has been greatly increased by the investigations of this author and his co-workers, Müller v. Berneck,[4] K. Ikeda,[5] W. Reinders,[6] Fortner,[7] Teletow[8] and v. Antropoff.[9]

It has been conjectured by several authors that the *dissolved* or *chemically* bound oxygen in the metal phase plays a necessary part in the catalytic decomposition of hydrogen peroxide. The experiments of Haber and S. Grinberg,[10] Euler,[11] and of Engler and Wöhler[12] indicate

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[1] *Loc. cit.*

[2] Dissertation, Heidelberg (1907).

[3] Z. angew. Chem., 1898, p. 951.

[4] Z. physik. Chem., **31**, 258.

[5] *Ibid.*, **37**, 2.

[6] *Ibid.*, **37**, 323.

[7] Ber., **37**, 798.

[8] Z. Elektrochemie, **12**, 581.

[9] *Ibid.*

[10] Z. anorg. Chem., **18**, 37.

[11] Oefers af. K Vetenskaps Förhandl., 1900, p. 267.

[12] Z. anorg. Chem., **29**, **1**.