3. The use of a Pyrex glass spiral manometer of the Johnson type as a null instrument in the measurement of vapor pressures of corrosive substances is discussed; constancy and reproducibility of readings, a lack of noticeable hysteresis and a degree of precision adequate for much work of this kind were noted with such an instrument.

CAMBRIDGE, MASS. RECEIVED DECEMBER 23, 1933

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY, HARVARD UNIVERSITY]

The Atomic Weight of Uranium Lead from Great Bear Lake, N. W. T., Canada, Pitchblende

BY JOHN PUTNAM MARBLE[1]

Introduction

The recent discovery of extensive deposits of high-grade pitchblende ore at LaBine Point, Echo Bay, Great Bear Lake, North West Territories, Canada, has aroused wide-spread general interest. As one part of a complete investigation, the atomic weight of the uranium lead therein contained has been determined, to assist in the calculation of the geologic age of the deposit. Heartiest thanks are due to the Mines Branch, Department of Mines, of the Canadian Government, who generously have furnished ample material, and especially to Mr. Hugh S. Spence, Mining Engineer, Mineral Resources Division, Mines Branch, who personally obtained the samples used, and who furnished much valuable information.

The geological, mineralogical and engineering relations of the occurrence have been discussed by C. W. Knight,[2] D. F. Kidd,[3] J. A. Reid,[4] among others, and most fully by H. S. Spence,[5] and H. S. Robinson.[6] These references include partial analyses, which show the ore to be a very high-grade thorium-free siliceous pitchblende. This should offer a favorable opportunity to obtain an uranium lead of minimum atomic weight, provided "ordinary" lead is absent. Petrographic studies by H. J. Fraser, L. C. Graton, W. Lindgren, and W. H. Newhouse[7] indicate that galena is present in exceedingly small amounts, visible only under the microscope, in specimens taken from the same portion of the same vein as the sample used in this investigation. Spence, in a personal communication, states that no macroscopically visible galena has been found in that part of the vein system from which he selected our material, though it is found at other places in the general vein system. This would suggest very slight contamination, if any. If the galena is due to the alteration of radiogenetic lead by sulfide solutions, its presence should not affect the atomic weight, but if it has been derived from "common" lead, the atomic weight should be raised above the value for a "pure" uranium lead.

Purification of Reagents

Water, silver, nitric, hydrochloric, hydrofluoric and sulfuric acids, sodium carbonate, hydrogen chloride, nitrogen and air were purified as described in previous papers from this Laboratory.[8] The silver used was taken from several lots, each of which had been used in acceptable determinations of other atomic weights in this Laboratory. Especial care was taken to see that all reagents and apparatus were lead free.

Preparation and Purification of Lead Chloride

The method for extracting and purifying the lead was based on that used by Baxter and Bliss[8] on Wilberforce uraninite, modified by differences between the two minerals and by subsequent experience. Five different preparations were made, but only one—Sample E—was used in the series of definitive analyses. About 50 g. of the coarsely powdered pitchblende, as received, was extracted with nitric acid in a Pyrex dish, which was not attacked, filtered, silica removed with hydrofluoric acid, residual fluorides converted to nitrates, and a trace of insoluble matter filtered off and rejected. To this was added lead chloride recovered from preliminary tests. Lead, etc., were precipitated from the three combined dilute nitric acid solutions with hydrogen sulfide, drawn from a cylinder and washed with purest water. The sulfides were filtered on

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(1) Research Associate, Committee on the Measurement of Geologic Time, Division of Geology and Geography, National Research Council.

(2) C. W. Knight, *Can. Min. J.*, **51**, 964 (1930).

(3) D. F. Kidd, *ibid.*, **53**, 5 (1932); *Can. Min. and Met. Bull.* No. 245, p. 512 (1932).

(4) J. A. Reid, *Can. Min. J.*, **53**, 61 (1932).

(5) H. S. Spence, Section III of Investigations in Mineral Resources and the Mining Industry, Department of Mines, Mines Branch, 1931, p. 55, Ottawa (1932).

(6) H. S. Robinson, *Can. Min. and Met. Bull.*, No. 258, p. 609 (1933).

(7) Private communications; see also Report of Committee on the Measurement of Geologic Time, Washington, 1932, pp. 44–46.

(8) *Vide inter alia* G. P. Baxter and A. D. Bliss, THIS JOURNAL **52**, 4848, 4851 (1930).

quantitative paper, washed with water saturated with hydrogen sulfide, rinsed from the paper, and dissolved in aqua regia. A slight excess of sulfuric acid was then added, the solution boiled to remove volatile acids, the lead sulfate filtered off on platinum sponge, washed repeatedly with very dilute sulfuric acid, boiled with excess sodium carbonate, filtered on platinum sponge, washed repeatedly with water, the carbonate dissolved from the filter with dilute nitric acid, and the lead nitrate evaporated to dryness in platinum. The lead was again precipitated as sulfide from dilute nitric acid solution, filtered off on platinum sponge, washed with water saturated with hydrogen sulfide, and dissolved in hydrochloric acid in platinum. The lead chloride was dissolved in water, filtered through platinum sponge, converted to nitrate in quartz, the nitrate crystallized from water once in quartz, and four times in platinum, with centrifugal draining and washing. The last crystals were dissolved in water, filtered through platinum sponge, converted to the chloride in quartz, and crystallized four times in platinum from water, with centrifugal draining and washing with very dilute hydrochloric acid. The solution was once more filtered before the last crystallization. The lead chloride was twice distilled in pure dry hydrogen chloride in a quartz tube, and cooled in nitrogen. Scarcely any residue remained after the first distillation, and none after the second.

Method of Analysis

The procedure was the same as that described in many other recent papers from this Laboratory on the determination of the ratio $PbCl_2/2Ag$, and details may be found elsewhere. Samples of distilled lead chloride were fused in an atmosphere of pure dry hydrogen chloride in a weighed clear fused quartz boat, standing in a quartz tube, care being taken that the fused mass was free from gas bubbles The fused salt was cooled in pure dry nitrogen, the last traces of hydrogen chloride being swept out by the time the salt had solidified, the nitrogen replaced by pure dry air, and the boat slid into its weighing bottle in the usual form of "bottling apparatus." After again weighing, the lead chloride was dissolved in warm purest water, containing a few drops of nitric acid, and the chloride precipitated in the dark-room by very nearly the equivalent weight of purest silver, which was dissolved in dilute nitric acid with precautions to prevent loss by spray or otherwise. The final concentration was less than 0.01 *N*. All weighings were made in duplicate by substitution on a No. 10 Troemner balance, sensitive to about 0.02 mg. Vacuum corrections of +0.000058 g. per gram of lead chloride and −0.000031 g. per gram of silver were applied. Temperature, pressure and humidity were observed at each weighing, but any corrections for changes therein would have been beyond the limits of weighing. The gold-plated brass weights were standardized at intervals by the method of Richards, with concordant results. After the precipitate had settled, 25 cc. portions of the clear liquid were examined in the nephelometer in the usual manner, and the exact equivalence point attained by small additions of a solution of silver containing 1 mg. per cc. or of an equivalent solution of purest potassium chloride. Further tests were then made over a period of at least three months. The silver chloride always remained colorless and the supernatant liquid clear. The flasks were shaken from time to time to aid attainment of equilibrium. No tendency of the end-point to drift with time was noted, once it had been reached. Results are noted in Table I.

TABLE I

ATOMIC WEIGHT OF LEAD FROM SILICEOUS PITCHBLENDE, GREAT BEAR LAKE, N. W. T., CANADA

Ag = 107.880 Cl = 35.457

Analysis No.	Sample No.	$PbCl_2$ *in vacuo*, g.	Ag *in vacuo*, g.	Ag added in soln., g.	$PbCl_2/2Ag$	Atomic weight Pb
VII	E	2.27721	1.77423	−0.00030	1.283709	206.059
VIII	E	2.22354	1.73254	− .00035	1.283658	206.048
IX	E	2.22397	1.72909	+ .00340	1.283681	206.054
				Average	1.283683	206.054

Total weight $PbCl_2$ = 6.72472 g. $PbCl_2/2Ag$ = 1.283684. Total weight Ag $\Leftrightarrow$ $PbCl_2$ = 5.23861 g. Atomic weight Pb = 206.054.

Discussion of Results

This value, 206.054, is interesting from several viewpoints. F. W. Aston[9] has studied the mass spectrum of lead tetramethyl prepared by A. von Grosse from the lead chloride used in this work, and from his percentages for the isotopes Pb^{206} 89.8; Pb^{207} 7.9; Pb^{208} 2.3, we may calculate a "mean mass-number" of 206.125[10], after correcting for "hydride effect," but without corrections for packing effect and for conversion to the chemical scale, for, as he points out, these may partly compensate each other.

The packing fraction correction is probably less than $+1 \times 10^{-4}$, and the conversion factor may be -2×10^{-4}. Should the former be 0, and the latter -2.2×10^{-4}, we may calculate a "mean mass-number" of 206.081. If the possible uncertainty of Aston's measurements ($\pm 1 \times 10^{-4}$) lies in the same direction, we would have a final value, on his basis, of 206.061, in better agreement with the present experiments. Such close agreement would probably be fortuitous.

Professor F. Allison and Dr. C. S. Piggot[11] have kindly tested samples of the lead chloride used in this work in the magnetoöptic apparatus, finding the same number of isotopes in the same general order of occurrence as in other radiogenetic leads known to be free from "common" or thorium lead. The presence of these other

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[9] F. W. Aston, *Proc. Roy. Soc.* (London), **A140,** 535 (1933).

[10] Aston's paper gives 206.102 as the value. This is apparently a misprint.

[11] C. S. Piggot, *Phys. Rev.*, **43**, 51 (1933).

isotopes would not alter the above calculated values significantly, as Aston has shown that in common lead they are present in extremely small amount.

If, however, since the mineral is apparently nearly if not quite free from thorium, we assume that the small amount of Pb^{208} reported in this material has been derived from "common" lead from some other source, using Aston's values of 2.3% of Pb^{208} in this lead and 49.5% of Pb^{208} in "common" lead, we may calculate 4.7% of "common" lead. Then

$$4.7 \times 207.21 + 95.3x = 206.05 \times 100$$

where $x = 205.99$ = atomic weight of "uranium" lead in this material, a value in fair agreement with those found by Baxter and Bliss and Baxter and Alter.[12] The difference between their results and those of Hönigschmid, Sachtleben and Baudrexler[13] material may perhaps be accounted for by the presence of a small amount of "common" lead in the material used by the latter. This presence of "common" lead is in accord with evidence from other vein-deposits of pitchblende. In view of the impossibility of estimating the quantity of galena with any great accuracy, calculations as to a "theoretical" atomic weight of this lead would appear to be of doubtful value.

Acknowledgments.—The kindness of Professor Gregory P. Baxter in permitting the use of the facilities of the T. Jefferson Coolidge Memorial Laboratory, his many helpful suggestions, and generous assistance are gratefully acknowledged. Professor Alfred C. Lane, Chairman of the Committee on the Measurement of Geologic Time, suggested the problem, and has aided greatly in the interpretation of the results. Mr. C. M. Alter and Mr. A. D. Bliss have kindly assisted in the preparation of apparatus and purification of reagents.

Summary

1. The atomic weight of lead extracted from Great Bear Lake, N. W. T., Canada, pitchblende is found to be 206.054.

2. This figure is slightly lower than the "mean mass-number" calculated from Aston's observations on identical material.

3. It is in accord with a value of approximately 206 for "pure" uranium lead, if Pb^{208} reported in the sample is derived from "common" lead.

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RECEIVED DECEMBER 28, 1933

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(12) (205.99) G. P. Baxter and C. M. Alter, THIS JOURNAL, **55**, 1445, 2785 (1933).

(13) O. Hönigschmid, R. Sachtleben and H. Baudrexler, *Z. anorg. allgem. Chem.*, **214**, 104 (1933).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heat Capacities and Entropies of Potassium Bromate and Iodate from 15 to 300° Absolute. The Entropies of Bromate and Iodate Ions[1]

BY J. ELSTON AHLBERG AND WENDELL M. LATIMER

The heat capacities of potassium bromate and iodate have been determined in order to evaluate more accurately the entropies of bromate and iodate ions in aqueous solutions.

Material.—Samples of "C. P." salts were recrystallized, washed four times and dried at 110° for several days. Analysis by thiosulfate and permanganate methods gave 100% purity within the experimental accuracy, about 0.1%.

Heat Capacity Measurements.—The measurements were made by the general method described by Latimer and Greensfelder.[2] These measurements were carried out, however, in a new calorimeter.

Previously we[3] reported that we had difficulty in making the gold wire of the combined heater and resistance thermometer adhere to the copper walls of the calorimeter. "Bakelite" varnish was applied to the outside walls of this calorimeter which had previously been roughened by sandpaper. Then rice paper was laid on this surface, and the gold wire was wrapped about the calorimeter. Rice paper was again laid over the gold wires. The rice paper was used since we believe it assists in binding the varnish to both the copper walls and gold wires. The calorimeter was next gradually heated to about 115° and kept a that temperature for fifty hours. Finally a thin coat of "Bakelite" varnish was applied and very thin gold leaf was used to cover the surface. We used gold leaf instead of foil since the metal must adhere snugly in order that the temperature of the radiating surface of the calorimeter will correspond to that of the wires; otherwise it is impossible to make accurate heat loss corrections because of

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(1) Presented at the 85th meeting of the American Chemical Society, Washington, D. C., March, 1933.

(2) Latimer and Greensfelder, THIS JOURNAL, **50**, 2202 (1928).

(3) Latimer and Ahlberg, *ibid.*, **54**, 1900 (1932).