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.

37 EAST BRADLEY LANE RECEIVED DECEMBER 28, 1933
CHEVY CHASE, MARYLAND

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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).

thermal gradients in the calorimeter. This calorimeter showed extremely small temperature heads during energy input and continued to do so even after being cooled many times. We believe that the principal reason for this was the careful control of the temperature during the baking out of the varnish. Helium gas was used for heat conduction in the calorimeter.

The results have been collected in Tables I and II. The abnormally high value for the determination at 272.49°K. can be accounted for by the heat of fusion of less than 0.06% of water in the potassium iodate or on the walls of the calorimeter. Comparison of the two specific heat curves shows that from 15 to 37°K. the heat capacity of potassium bromate is lower than that of the iodate but that the reverse is the case between 37 and 85°K. From 85 to 300°K. the heat capacity of the bromate is again less than that of the iodate, as one would expect from mass consideration alone. This abnormal behavior is surprising. The forces between the ions must be greatly different in the two salts, which is further shown by the fact that potassium bromate crystallizes in the hexagonal system, while potassium iodate is monoclinic.[4]

TABLE I

MOLAL HEAT CAPACITY OF POTASSIUM BROMATE (167.01 G.)

T, °K.	C_p cal./mole/deg.	T, °K.	C_p cal./mole/deg.	T, °K.	C_p cal./mole/deg.
15.15	0.790	88.98	14.45	213.92	22.25
20.35	1.694	95.95	15.11	222.32	22.56
25.09	2.759	102.77	15.75	230.53	22.86
28.64	3.706	110.98	16.50	239.88	23.12
32.74	4.806	120.57	17.24	248.97	23.50
37.33	5.958	129.27	17.85	257.41	23.77
42.27	7.085	137.28	18.31	265.39	23.95
47.45	8.248	144.82	18.86	265.52	24.02
52.47	9.321	153.53	19.41	273.08	24.31
57.29	10.24	162.69	19.89	273.11	24.29
61.81	11.03	171.55	20.30	283.57	24.73
63.19	11.25	179.95	20.85	290.64	24.80
68.79	12.10	188.35	21.21	296.25	25.03
75.69	12.99	196.90	21.56		
82.46	13.83	204.72	22.02		

TABLE II

MOLAL HEAT CAPACITY OF POTASSIUM IODATE (214.03 G.)

T, °K.	C_p cal./mole/deg.	T, °K.	C_p cal./mole/deg.	T, °K.	C_p cal./mole/deg.
17.30	1.245	87.46	14.38	201.79	22.29
20.20	1.791	93.10	15.01	210.61	22.76
23.28	2.451	99.15	15.65	220.45	22.97
26.89	3.395	105.93	16.25	228.68	23.31
31.35	4.488	113.79	17.03	235.26	23.57
35.94	5.615	121.97	17.69	244.13	23.73
41.02	6.789	130.31	18.22	255.37	24.19
46.39	7.932	138.81	18.91	264.20	24.29
51.87	9.134	147.09	19.40	272.49	25.81
57.29	10.10	156.05	19.88	281.27	25.06
64.36	11.30	165.08	20.47	288.91	25.21
70.47	12.21	174.45	20.98	295.00	25.24
76.48	12.99	184.68	21.46		
81.96	13.73	193.15	22.03		

The Entropies of Potassium Bromate and Potassium Iodate.—The entropies of the two salts at 298.1°K. were evaluated from the integral $S = \int_0^{298.1} C_p \, d \ln T$. Graphical integration was used from the lowest temperatures at which measurements were made up to 298.1°K. Below the lowest temperatures analytical integrations were made, by employing the Debye specific heat equation. The results of these integrations are summarized in Tables III and IV.

TABLE III

ENTROPY OF POTASSIUM BROMATE

0–15.15°K. Debye extrapolation	0.25
15.15–298.1°K. Graphical from data	35.40 ± 0.1
Entropy of potassium bromate at 298.1°K.	35.65 E. U

TABLE IV

ENTROPY OF POTASSIUM IODATE

0–17.30°K. Debye extrapolation	0.43
17.30–298.1°K. Graphical from data	35.77 ± 0.1
Entropy of potassium iodate at 298.1°K.	36.20 E U.

In all of the above calculations we have taken the value of the calorie to be equal to 4.185 joules.

Entropies of Bromate and Iodate Ions.—The solubilities[5] of potassium bromate and of potassium iodate are 0.48 M and 0.43 M, respectively, at 298.1°K. At these concentrations their activity coefficients[6] are very likely not far different from those of silver nitrate. Therefore we assign the activity coefficients 0.50 and 0.52 to the two salts, respectively, at the concentrations which correspond to their saturated solutions and calculate their free energies of solution from the expression

$$\Delta F^\circ = -RT \ln (\gamma m)^2$$

The values which we find are +1690 and +1770 calories, respectively. We estimate that these values are accurate to within 100 calories.

The most accurate values for the heats of solution of the salts are those given by Stackelberg.[7] These measurements were made at about 288°K. and corrections for heats of dilution are necessary. Dr. F. D. Rossini[8] has recently calculated their heats of solution at infinite dilution at 298.1°K., using the values obtained by Stackelberg and recent heat capacity and heat of dilution

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(4) P. Groth, "Chemische Krystallographie," Wilhelm Engelmann, Leipzig, 1908, Vol. 2, pp. 92-93.

(5) Seidell, "Solubilities of Organic and Inorganic Compounds," D. Van Nostrand Co., N. Y., 1919.

(6) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923.

(7) Stackelberg, *Z. physik. Chem.*, **26**, 533 (1898).

(8) F. D. Rossini, personal communication.

data on similar salts. The values which Dr. Rossini obtains are +9540 and +6340 calories for potassium bromate and iodate, respectively. He estimates the uncertainties in the values for the heats of solutions at 298.1°K. to be ±140 and ±100 calories per mole, respectively. We may now calculate the entropies of solution from the relationship

$$\Delta S^\circ = (\Delta H^\circ - \Delta F^\circ)/T$$

We find that the entropy changes, in going from the salts to their respective hypothetical one molal solutions, are, respectively, 26.3 and 15.3 entropy units. These values, when added to the entropies of the respective salts, give the sum of the entropies of potassium and bromate ions, and potassium and iodate ions. Using the calculated value, 24.6 entropy units for the entropy of potassium ion,[9] we obtain the values 37.4 and 26.9 E. U. for the entropies of bromate and iodate ions, respectively. The values previously reported by Greensfelder and Latimer[10] from data on barium bromate and silver iodate have been recalculated, using revised values for the entropy of barium and silver ions:[9] these values are 38.7 and 27.7 E. U. The largest errors in all of these calculations are the heats of solution of the salts, and the direct calorimetric determinations of these heats of potassium bromate and iodate appear to be more reliable than the heats of solution obtained from temperature coefficients of solubility which were used in the case of barium bromate and silver iodate. We therefore are inclined to give more weight to our new values, and estimate their accuracy as about 1 E. U.

Since the entropy of iodate ion must be greater than that of bromate in the gaseous state, it follows that the entropy of hydration of iodate is from 10 to 15 E. U. greater than that of bromate. This is very surprising in view of the larger size of the iodate, and seems to indicate either that the iodate is much more polar so that the more negative oxygen atoms are producing greater polarization of the water molecules,[11] or that one or more water molecules have been definitely bonded to the ion to form $H_2IO_4^-$ or $H_4IO_5^-$ in the water solution.

The experimental work reported here was performed in the Chemical Laboratory of the University of California. The calculations involved were in great part completed at The Johns Hopkins University.

Summary

The specific heats of potassium bromate and of potassium iodate have been determined from the temperatures of liquid hydrogen to room temperature. The entropies of the two salts have been calculated at 298.1°K. These values have been used to calculate the entropies of bromate and iodate ions.

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[9] Latimer, Schutz and Hicks, *J. Chem. Phys.*, **2**, 82 (1934).

[10] Greensfelder and Latimer, THIS JOURNAL, **50**, 3286 (1928); **53**, 3813 (1931).

[11] See Latimer and Kasper, *ibid.*, **51**, 2293 (1929).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Dielectric Properties of Acetylenic Compounds. I. The Symmetrical Dialkyl Acetylenes

BY HERMAN H. WENZKE AND R. P. ALLARD

The zero moment found for acetylene is considered strong evidence against the existence of an appreciable portion of the acetylidene ($H_2C{=}C$) form of the compound. The very small P_{A+M} found by Sutton, New and Bently[1] for diiodoacetylene has been interpreted by them as indicating a zero moment for the molecule. Weissberger and Sängewald[2] showed that diphenylacetylene has a small value of P_{A+M} and this they assumed to indicate zero polarity for the compound. Both groups of investigators conducted their experimental work at one temperature which introduces an uncertainty in their conclusions as this method does not distinguish between atomic and orientation polarization. With the point of establishing more definitely the structure of symmetrically disubstituted acetylenes the authors selected two dialkyl substituted compounds, the normal dibutyl and the normal diamyl.

The polarizations of these compounds were determined at 25°, one in heptane and the other

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(1) Sutton, New and Bently, *J. Chem. Soc.*, 652 (1933).

(2) Weissberger and Sängewald, *Z. physik. Chem.*, **20B**, 145 (1933).