The authors are glad to acknowledge assistance received from the Coffin Foundation in the form of a scholarship to one of us.

Summary

1. The chemical effects produced in gases by electrons from a Coolidge cathode-ray tube have been studied. The gases were enclosed in separate vessels not in contact with the window of the tube. The influence of time, voltage and space current has been studied.

2. Ozone was obtained from oxygen and the ozone was in turn decomposed. The rate of ozone formation was obtained by extrapolation to "zero time."

3. The chemical effects were expressed as the ratio of molecules produced per electron crossing the cathode-ray tube. These M/C ratios are as follows: nitric oxide decomposition 230, ozone from oxygen 100, ozone from air 44, nitric oxide from air 14, carbon dioxide decomposition 3.

4. The energy of the cathode rays was obtained with a small calorimeter and it varied from 3 to 16 calories per minute.

5. A calculation of the maximum number of ions was made using the energy input and the ionization potential of oxygen. This estimate gives a ratio of molecules to gas ions approximately the same as has been found with α-particles.

6. The close similarity in chemical behavior of cathode rays and α-particles has been emphasized. The yield depends on the ionization potential of the gas and the stoichiometrical reactions which follow ionization.

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[Contribution from the Chemical Laboratory of the University of California]

THE HEAT CAPACITY AND ENTROPY OF BARIUM BROMATE FROM 16 TO 300° ABSOLUTE. THE ENTROPY OF BROMATE ION

By Bernard S. Greensfelder and Wendell M. Latimer

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This work is a part of the program for the evaluation of entropy of aqueous ions as a means of facilitating the thermodynamic treatment of solutions. The general theory has been treated in previous papers by Latimer and coworkers.[1]

The present paper initiates work in the field of the halogenate ions, ClO_3^-, BrO_3^- and IO_3^-, and it is planned to use the entropy values obtained with experimental reaction heats in order to obtain the free energies of these ions. The experimental method follows the general plan of study

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[1] (a) Latimer and Buffington, This Journal, **48**, 2297 (1927); (b) Latimer, *ibid.*, **48**, 2868 (1926); (c) Latimer, *J. Phys. Chem.*, **31**, 1267 (1927); (d) Latimer and Greensfelder, This Journal, **50**, 2202 (1928); (e) Latimer and Kasper, unpublished material.

of cesium alum by Latimer and Greensfelder,[1d] wherein complete references to specific heat technique and laboratory technique are given.

Material.—Barium bromate monohydrate, $Ba(BrO_3)_2 \cdot H_2O$, was selected because of its low solubility, well-defined monoclinic crystal structure and purity. "C. P." material free from heavy metals, iron and bromide was obtained from the Mallinckrodt Company. A water determination gave 4.42% of water; theoretical, 4.38%. The specific heat measurements were made on a sample weighing 148.80 g.

Measurements.—The molal heat capacity values fall smoothly on a curve with two points of double inflection at 150°K. and at 190°K., too slight to be noticed on the accompanying diagram.

The gold resistance thermometer proved adequate to fix the temperature differences down to 13.92°K., the initial temperature of the first run. The calibrations continuously made against thermocouple No. 109 agreed exactly with two previous sets of comparisons, except in the range 30 to 105°K., wherein the resistance showed a regular deviation, reaching a maximum of 0.012 ohm/ohm at 37°K. This is, incidentally, the point of maximum deviation from rectilinearity of resistance as a function of temperature.

It was also noted that the thermocouple e.m.f. at the temperatures above 200°K. was altered by a change in the temperature of the surrounding block and radiation shield, necessitating the selection of a mean value corresponding to equal temperature of block and radiation shield with respect to the calorimeter. As a check, eight special calibrations were made with an average temperature difference between block and calorimeter of 0.05 degree. The resulting points accurately confirmed the previous mean values.

TABLE I

HEAT CAPACITY OF BARIUM BROMATE

Molecular weight of $Ba(BrO_3)_2 \cdot H_2O$ = 411.22

T, °K.	Sp. heat, cal./g./deg.	Molal heat cap., cal./mole/deg.	*T*, °K.	Sp. heat, cal./g./deg.	Molal heat cap., cal./mole/deg.	*T*, °K.	Sp. heat, cal./g./deg.	Molal heat cap., cal./mole/deg.
16.36	0.0052	2.15	94.24	0.0666	27.39	187.42	0.1038	42.70
19.57	.0077	3.15	99.63	.0692	28.47	193.33	.1052	43.27
23.65	.0116	4.77	103.82	.0718	29.54	202.51	.1069	43.98
28.06	.0160	6.57	109.30	.0748	30.77	209.79	.1096	45.07
33.12	.0212	8.71	114.58	.0775	31.87	217.41	.1113	45.77
37.42	.0257	10.56	119.87	.0795	32.71	229.40	.1144	47.02
41.49	.0294	12.08	138.11	.0868	35.68	237.35	.1160	47.69
47.34	.0343	14.17	145.05	.0884	36.35	245.19	.1184	49.13
58.57	.0421	17.30	151.70	.0910	37.41	252.67	.1205	49.57
63.67	.0480	19.74	156.76	.0925	38.05	269.19	.1236	50.83
69.80	.0530	21.76	162.71	.0956	39.30	280.97	.1255	51.60
77.91	.0573	23.55	168.33	.0974	40.07	288.24	.1270	52.20
83.68	.0609	25.03	174.28	.1014	41.69	295.88	.1294	53.21
88.91	.0638	26.25	181.06	.1016	41.76			

TABLE II

ENTROPY OF BARIUM BROMATE

0–3 °K.	Debye T^3 Rule	0.010 E. U.
3–10 °K.	Extrapolation	0.432 E. U.
10–298.1 °K.	Graphical	80.276 E. U.
		80.718 E. U.

Entropy of barium bromate at 298.1 °K. = 80.72 E. U.

Heat Capacity and Entropy of Barium Bromate

The experimental data are given in Table I, accompanied by a summary of the entropy calculations and illustrated by Figs. 1 and 2.

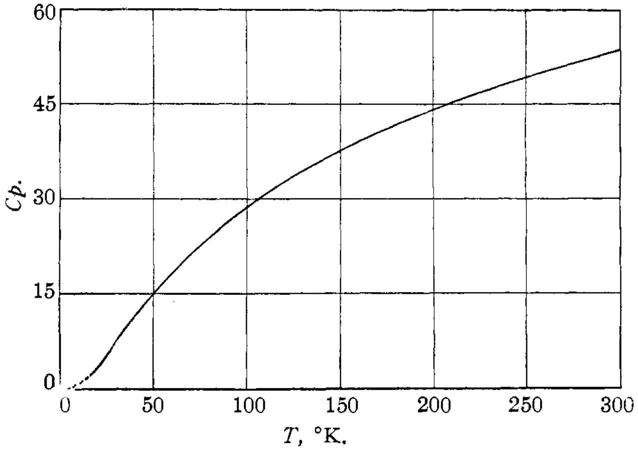

Fig. 1.—Molal heat capacity of barium bromate.

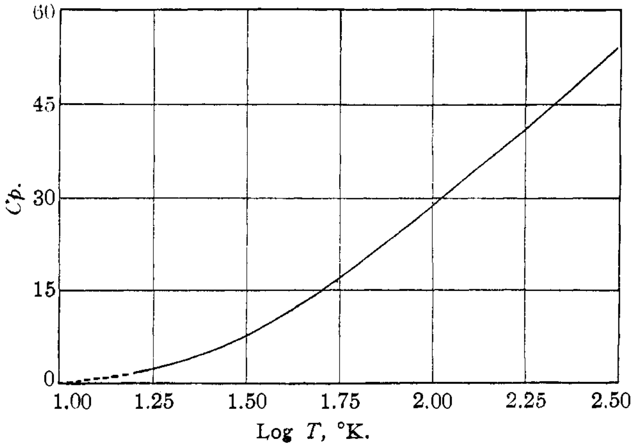

Fig. 2.—Molal entropy of barium bromate.

Heat of Solution.—The ΔH of solution of barium bromate may be calculated from the solubility–temperature coefficient as based on the solubility data of Trautz and Anschütz[2] and Harkins,[3] shown in Fig. 3. The single point of Harkins at 25° closely checks that of Trautz and Anschütz. The equation, originally applied by van't Hoff, may be given in the convenient form $\Delta H = -(R\,\mathrm{d}(\ln K)/\mathrm{d}(l/T))$.

The validity of the expression is dependent entirely upon the approximation of the given system to the laws of the ideal or perfect solution. In the absence of such complicating factors as hydrolysis and specific ion association, the ionic activity coefficients should accurately correct for the Debye-Hückel deviation. If such activities are then included in the equilibrium constant, K, ΔH will then presumably correspond to the true experimental value.

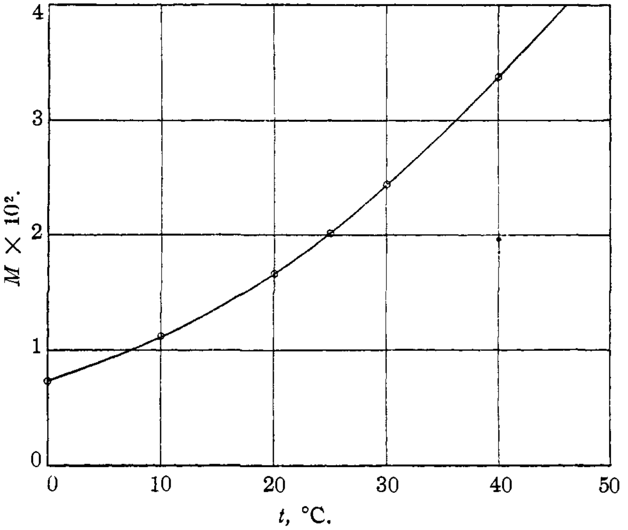

Fig. 3.—Solubility of barium bromate.

In the present case $Ba(BrO_3)_2 \cdot H_2O$ is considered free from hydrolysis or any ion association sufficient to exert perceptible influence on the heat of solution. The activity coefficients have been obtained with the aid of Professor M. Randall after a survey of similar ion types, and also from the data given by Lewis and Randall.[4]

It then follows that $\Delta H = -[4.5746\ \mathrm{d}\log(\gamma\, m)^3]/\mathrm{d}(l/T)$ and $\Delta H = +15{,}064$ calories.

From the solubility at 25°, we find $\Delta F = -RT\ln K = -1363.7\log 4 \times (0.550 \times 0.02023)^3 = +7171$ calories.

Then $\Delta S_{\mathrm{sol.}} = (\Delta H - \Delta F)/T = (15064 - 7171)/298.1 = 26.48$ E. U.

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[2] Trautz and Anschütz, *Z. physik. Chem.*, **56**, 236 (1906).

[3] Harkins, This Journal, **33**, 1815 (1911).

[4] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, p. 382.

Entropy of Bromate Ion.—Now $Ba(BrO_3)_2 \cdot H_2O = Ba^{++} + 2BrO_3^- + H_2O$. Using the value for Ba^{++} given by Latimer and Buffington,[1a] and that for water obtained by Latimer and Greensfelder[1d] from the data of Simon and others, we find $S^{\circ}_{BrO_3^-} = {}^1/_2(80.72 + 26.48 - 15.92 - 4) = +43.6$ E. U., and the entropy of BrO_3^- at 298.1°K. = +43.6 E. U., with respect to $S^{\circ}_{H^+} = 0$.

The greatest uncertainty is the value for the heat of solution and it is planned to check this value by a direct experimental determination.

The authors wish to thank Mr. J. Elston Ahlberg of this Laboratory for assistance in the experimental work and calculations.

Summary

The specific heat of $Ba(BrO_3)_2 \cdot H_2O$ has been measured from 16 to 300°K. These values, together with the heat and free energy of solution of barium bromate, have been used to calculate the entropy of bromate ion in hypothetical one molal aqueous solution.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

THE COMPRESSIBILITY OF THALLIUM, INDIUM AND LEAD[1]

BY THEODORE W. RICHARDS AND JOSEPH D. WHITE

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Introduction

Existing data on the compressibility of thallium are in apparent conflict. The first pertinent experimental work[2] on this metal (about twenty years ago) gives the value 2.85 × 10^{-6} for the cubic compressibility at 20° over the pressure range 100–500 megabars. Fifteen years afterwards, P. W. Bridgman published a determination[3] seeming to indicate that the cubic compressibility under the same conditions may be considerably larger—about 3.5 × 10^{-6}. This latter determination was based upon the linear compressibility, actually measured, which was multiplied by three on the assumption that thallium is isotropic. Bridgman pointed out that the large difference between his value and the earlier

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[1] *Note by the Editor.*—This research was completed in 1927 under the direction of Professor Theodore W. Richards but the present account of it was prepared after the death of Professor Richards by Dr. Lawrence P. Hall.

[2] Richards and Stull, *Carnegie Institution of Washington,* Pub. No. 76, **1907**, p. 65. The value there given, 2.6, after correction for the new compressibility of mercury, for slight errors in the pressure gage and to the megabar standard, becomes 2.85 × 10^{-6}. The value given on page 62 is wrong through typographical error—a misprint which has unfortunately been copied elsewhere (for example, THIS JOURNAL, **37,** 1646 (1915)).

[3] Bridgman, *Proc. Am. Acad. Arts Sci.,* **58,** 198 (1922).