

cation of this method the starting point was the difference in compression due to a change in concentration (at the same pressure), and it was necessary to measure this difference with an accuracy corresponding to less than 1 part in 2000 of the total compression at the highest pressure.

In appearance the equilibrium ( $P, x$ ) diagram resembles the more familiar melting ( $t, x$ ) diagram. The solubility curve of sodium chloride and the freezing pressure curve of ice<sub>VI</sub> meet at an invariant point, or pressure eutectic. There are two other invariant points in the system. These are analogous to incongruent melting points and are marked by abrupt changes in slope of the solubility curve.

Direct measurements confirmed the results of the indirect (thermodynamic) method. Attention is directed to the advantages of this method.

WASHINGTON, D. C.

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

## THE HEAT CAPACITY AND ENTROPY OF SILVER IODATE FROM 16 TO 300° ABSOLUTE. THE ENTROPY OF IODATE ION

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This work is a continuation of the program for the evaluation of the entropies of aqueous ions as a means of facilitating the calculation of the thermodynamic properties of solutions. The general theory, together with details of experimental and mathematical method, has been presented in earlier papers by Latimer and co-workers.<sup>1</sup>

In this investigation the entropy of iodate ion has been obtained from calorimetric measurements on silver iodate, AgIO<sub>3</sub>. The work is entirely similar to that done on barium bromate by Greensfelder and Latimer,<sup>1e</sup> and the same apparatus was used.

**Preparation of Silver Iodate.**—Silver iodate was prepared from c. p. silver nitrate and potassium iodate. Upon considering the methods in the literature, in particular that of Hill and Simmons,<sup>2</sup> a modified procedure was devised, which proved to be simple of execution.

Sufficient quantities of  $M/3$  solutions were prepared to yield two moles of silver iodate. On mixing, a finely divided white precipitate was formed. This was suction filtered and slowly washed with six liters of distilled water. The precipitate was then dissolved in c. p. concd. ammonium hydroxide. A very small quantity of a solid black substance remained, possibly an oxynitride of silver. This material was separated by a single filtration.

<sup>1</sup> (a) Latimer and Buffington, *THIS JOURNAL*, **48**, 2297 (1926); (b) Latimer, *ibid.*, **48**, 2868 (1926); (c) Latimer, *J. Phys. Chem.*, **31**, 1267 (1927); (d) Latimer and Greensfelder, *THIS JOURNAL*, **50**, 2202 (1928); (e) Greensfelder and Latimer, *ibid.*, **50**, 3286 (1928); (f) Latimer and Kasper, *ibid.*, **51**, 2293 (1929).

<sup>2</sup> Hill and Simmons, *ibid.*, **31**, 828 (1909).

The resultant clear solution was slowly evaporated during a period of four days, and the deposited crystals of silver iodate were removed at intervals. The first half of the crop (Lot 1) was tinged a very light silver gray. The second half (Lot 2) was pure white.

Thorough drying of Lot 1 was effected by heating for five days at 100° in a vacuum of 0.01 mm. The stability of the crystals was tested by exposure to direct sunlight for sixteen hours. No darkening was observed.

Lot 2 was dried for four days at 95° and barometric pressure in an electric oven. The crystals were then finely pulverized and heated for six days at 100° in a vacuum of 0.01 mm. on a water-bath. Exposure to sunlight produced no visible effect. The sample selected for the specific heat measurements was taken from Lot 2. Traces of moisture remained even after this rigorous drying, and a sample heated for twenty-four hours at 190° showed a weight loss of 0.029%. Decomposition according to the equation  $\text{AgIO}_3 = \text{AgI} + 3/2\text{O}_2$  is incipient at slightly higher temperatures; therefore, drying of the sample chosen for specific heat measurements was not made above water-bath temperature.

TABLE I  
HEAT CAPACITY OF SILVER IODATE  
Mol. wt.  $\text{AgIO}_3$ , 282.81

<i>T</i> , °K.	Sp. heat cal./g./deg.	Molal ht. cap., cal./mole/deg.	<i>T</i> , °K.	Sp. heat cal./g./deg.	Molal ht. cap., cal./mole/deg.
16.16	0.00526	1.5	156.5	0.06856	19.4
18.10	.00740	2.1	163.1	.06995	19.8
25.65	.01184	3.3	169.5	.07117	20.1
33.26	.01887	5.3	175.7	.07242	20.5
37.44	.02191	6.2	181.6	.07258	20.5
44.94	.02614	7.4	189.7	.07390	20.9
48.42	.02915	8.2	195.6	.07576	21.4
53.38	.03260	9.2	202.0	.07701	21.8
59.11	.03553	10.0	208.0	.07800	22.1
64.47	.03854	10.9	214.7	.07909	22.4
68.81	.04063	11.5	221.2	.07969	22.5
75.07	.04338	12.3	227.9	.07997	22.6
78.21	.04446	12.6	234.7	.08177	23.1
82.35	.04645	13.1	241.4	.08223	23.2
86.91	.04808	13.6	247.8	.08427	23.8
92.10	.04972	14.1	254.0	.08428	23.8
97.93	.05099	14.4	259.0	.08502	24.0
103.2	.05368	15.2	266.7	.08699	24.6
109.5	.05593	15.8	272.8	.08986	25.4
115.7	.05877	16.6	273.1	.08976	25.4
121.5	.05966	16.9	279.3	.08896	25.1
127.3	.06142	17.4	279.3	.08661	24.5
133.6	.06238	17.6	285.6	.08636	24.4
138.3	.06385	18.0	291.8	.08605	24.3
144.7	.06556	18.5	297.6	.08660	24.5
150.7	.06607	18.7			

Analysis of the product was made by reduction to silver iodide with sulfur dioxide. Two determinations gave: AgI, 82.96 and 83.12; average, 83.04%; theoretical, 83.05%.

**Apparatus.**—Complete description of the apparatus used for the specific heat measurements is given in Ref. 1d. The resistance thermometer

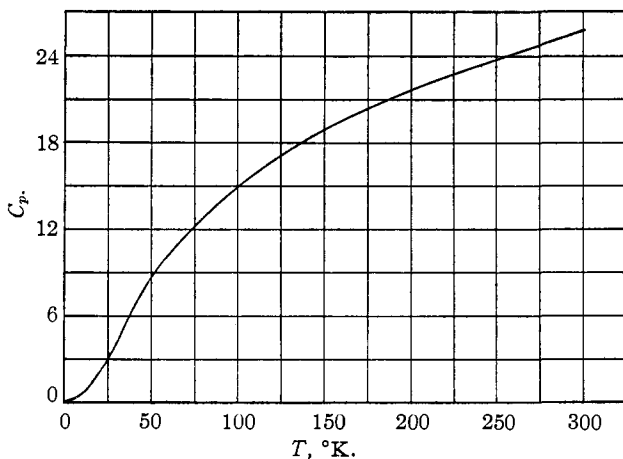


Fig. 1.—Molal heat capacity of silver iodate.

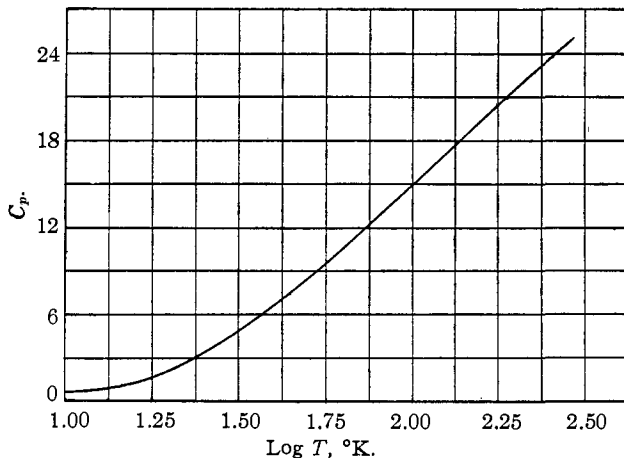


Fig. 2.—Molal entropy of silver iodate.

calibration duplicated that obtained for the barium bromate measurements (Ref. 1e), which differed only slightly from two previous calibrations.

**Results.**—The data are summarized in Table I and Figs. 1 and 2. All points fall on a smooth curve with an average deviation of less than 0.5%, excepting those in the vicinity of the ice-point, where the presence

of a few hundredths of a gram of water would account for the discrepancy. Approximately 0.07 g. of water was estimated as the moisture content of the specific heat sample (202.703 g.). Because of similar experience with cesium alum,<sup>1d</sup> check runs were made in this region. Those made at 273°K. show complete agreement, whereas those at 279°K. show a considerable difference, indicating the necessity for considering this important source of error. The final points on the curve are considerably influenced by large radiation corrections. However, if the actual areas involved in this deviation from the smooth curve are calculated in terms of entropy units, it is found that the positive error is +0.03 E. U., the negative error is -0.05 E. U., giving a difference of -0.02 E. U. This is only 0.05% of the total entropy of the salt.

The entropy calculations are shown in Table II.

The results below 30° may be in error by as much as 2% due to irregularities in the values obtained for the empty calorimeter over this range. However, it is believed that the total entropy of silver iodate at 298 Å. is correct to 1 per cent.

TABLE II  
ENTROPY OF SILVER IODATE

0-10°K.	Debye $T^3$ Rule	0.2 E. U.
10-298.1°K.	Graphical	35.8 E. U.
		<u>36.0 E. U.</u>

Entropy of silver iodate at 298.1°K. = 36.0 E. U.

**Heat and Free Energy of Solution.**—The heat and free energy of solution of silver iodate are derived from the solubility data<sup>3</sup> shown in Fig. 3.

The data of Kohlrausch, based on conductivity measurements, are the most complete. The analytical determination of Hill and Simmons at 25° is in agreement therewith. The low solubility of the salt, which is of the univalent type, indicates an activity coefficient approximating unity. Figures made available by the kindness of Professor Merle Randall give  $\gamma_{\pm} = -0.989$ . Then

$$\begin{aligned}\Delta F^{\circ}_{298.1} &= -RT \ln K = -1363.7 \log. (0.989 \times 0.00179)^2 \\ &= +10,233 \text{ cal./mole}\end{aligned}$$

Using the relation,  $\Delta H^{\circ} = -R d \ln K/d(1/T)$ , it is found that

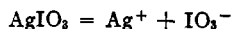
$$\Delta H^{\circ}_{298.1} = \frac{-4.5746 \times 2 \times 0.17812}{0.00011256} = +14,478 \text{ cal./mole}$$

whence

$$\Delta S^{\circ}_{298.1} = \frac{\Delta H - \Delta F}{T} = \frac{14,478 - 10,233}{298.1} = +14.2 \text{ E. U./mole}$$

<sup>3</sup> (a) Noyes and Kohr, *Z. physik. Chem.*, **42**, 336 (1903); (b) Böttger, *ibid.*, **46**, 521 (1903); (c) Kohlrausch, *ibid.*, **64**, 129 (1908); (d) Hill and Simmons, Ref. 2; (e) Whitby, *Z. anorg. Chem.*, **67**, 108 (1910).

**Entropy of Iodate Ion.**—Silver iodate forms an aqueous solution according to the equation



Since the molal entropy of the solid has been found to be 36.0 E. U., and the entropy of solution is +14.2 E. U., it follows that the entropy of a hypothetical one molal solution is  $36.0 + 14.2 = +50.2$  E. U.

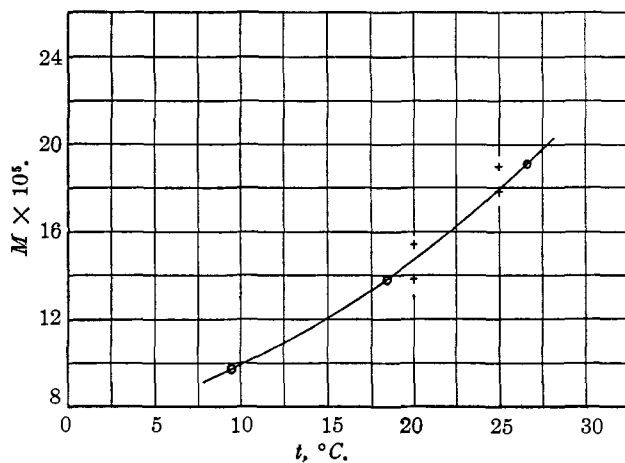


Fig. 3.—Solubility of silver iodate: O, Kohlrusch; +, others.

From the work of Latimer and Buffington<sup>1a</sup> the calculated molal entropy of  $\text{Ag}^+$  is +16 E. U.

Therefore, the molal entropy of  $\text{IO}_3^-$  at 298.1°K. = +34.3 E. U., with respect to  $S_{\text{H}^+}^\circ = 0$ .

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

### Summary

The specific heat of silver iodate has been measured from 16 to 300°K. By combining these values with the heat and free energy of solution derived from solubility data, together with the calculated entropy of silver ion, the entropy of iodate ion in a hypothetical one molal aqueous solution has been calculated to be +34.3 E. U.

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