

Wave length	Optic axial angle 2Ha, relative to cedar oil	Horizontal dispersion for interval λ -4600
4600	77.0 \pm 1	0
4916	73.5	6.0
5461	68.0	9.5
5780	66.0	10.5
6234	65.0	11.5
6908	64.0	11.5

Other optical crystallographic data for the five compounds discussed above are included in Table I.

Summary

1. Five crystalline organic compounds exhibiting measurable *crossed axial plane, inclined, horizontal* and *crossed* dispersion have been characterized optically. The compounds are *n*-butyl carbamate, 2,2'-dipyridyl, *o*-nitroacetanilide and

the picrates of guanylurea (dicyandiamidine) and 2-hydroxyethylamine (monoethanolamine).

2. The optic axial angles (2*E* or 2*Ha*) of these compounds have been measured for light of several different wave lengths. Refractive indices, optical character, optical orientation and other useful properties have also been measured.

3. An earlier technique for measuring optic axial angles has been placed on a photographic basis. Identification is facilitated by direct comparison of the negatives. Photographic measurements of the optic axial angles of *n*-butyl carbamate and 2,2'-dipyridyl for a wave length in the near ultraviolet (3650 Å.) have been made without the need of special optics.

WILMINGTON, DELAWARE RECEIVED SEPTEMBER 25, 1940

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

The Heat Capacity and Entropy of Silver Iodide and their Interpretation in Terms of Structure

BY KENNETH S. PITZER

A detailed investigation of the crystal structure of silver iodide, by Helmholtz,¹ showed certain peculiarities which might be expected to manifest themselves also in the thermal properties of the substance. With this in mind the heat capacity of silver iodide was measured from 15 to 300°K. The interpretation of the results will be discussed below.

Experimental Measurements.—The calorimeter and cryostat employed in this work were first described by Latimer and Greensfelder,² but have been modified in a manner discussed by Pitzer and Coulter.³ The sample was prepared by precipitation, using dilute solutions of c. p. silver nitrate and potassium iodide. After extensive washing it was dried at 150°C. for several days. The results are given in terms of calories defined as 4.1833 int. joules and temperatures based upon 273.10°K. for the ice point. Table I presents the measured heat capacities. Although many isolated heat capacity measurements have been made on silver iodide, only one extensive series of measurements has been reported in the literature. This is the work of Nernst and Schwerts⁴ in the

range 18–117°K., which is in reasonable agreement with the present results.

TABLE I
MOLAL HEAT CAPACITY OF SILVER IODIDE

<i>T</i> , °K.	<i>C_p</i> , cal. per degree	<i>T</i> , °K.	<i>C_p</i> , cal. per degree
15.09	2.89	97.05	10.93
18.01	3.33	105.79	11.19
21.00	3.82	116.56	11.44
24.23	4.36	126.53	11.60
27.52	4.79	136.49	11.79
30.53	5.23	145.67	11.92
33.67	5.77	158.80	12.05
37.84	6.43	170.86	12.15
42.70	7.09	184.65	12.33
47.32	7.67	198.89	12.49
52.15	8.20	213.13	12.63
57.70	8.76	228.34	12.76
64.44	9.36	244.24	13.02
72.38	9.84	258.79	13.05
75.19	9.99	273.23	13.26
81.67	10.32	287.42	13.48
88.58	10.60	301.37	13.64

The small wave in the heat capacity curve near 20°K. (see Fig. 1, log *T* = 1.3) is probably real. The heat capacity curves of the many other substances measured in the same calorimeter show no such irregularity.

Entropy Calculations.—Unfortunately it is not possible to obtain a very precise entropy for silver iodide from these heat capacity data be-

(1) L. Helmholtz, *J. Chem. Phys.*, **3**, 740 (1935).

(2) W. M. Latimer and B. S. Greensfelder, *THIS JOURNAL*, **50**, 2202 (1928).

(3) K. S. Pitzer and L. V. Coulter, *ibid.*, **60**, 1310 (1938).

(4) W. Nernst and F. Schwerts, *Sitzber. kgl. preuss. Akad. Wiss.*, **355** (1914).

cause of the difficulty of extrapolation to the absolute zero of temperature. The heat capacity at the lowest measured point is almost three cal. per degree and is by no means fitting a Debye function in this region. Figure 1 shows the latter situation clearly. However, if one assumes that the heat capacity curve below 15°K. must be reasonably smooth and qualitatively similar to a Debye curve, then fairly definite limits can be placed on the entropy. Table II summarizes the calculations.

0-15.0	Extrapolation	1.5 ± 0.3
15.0-298.1	Graphical integration from data	6.09 ± 0.1
$S_{298.1}^{\circ} = 27.6$ cal. per degree		

The entropy of silver iodide also has been calculated from the temperature coefficients of the e. m. f. of the cell: $2\text{Ag} + \text{PbI}_2 = 2\text{AgI} + \text{Pb}$. Kelley⁵ has surveyed the various data available and obtains the value 27.6 cal. per degree for the entropy of silver iodide at 298.1°K. The exact agreement between the two values is, of course, more than could be expected.

Discussion of Structure.—Below the transition at 146°C., silver iodide had been assigned the wurtzite structure by several authors.⁶ This structure for silver iodide may be described briefly as a hexagonal closest packing of iodide ions (or atoms) with silver ions at the centers of tetrahedra of iodides. The iodide ions are likewise at the centers of tetrahedra of silver ions. The sphalerite structure, which differs only in being based on cubic closest packing, also has been reported for some samples of silver iodide below 46°C. This structure is so similar that its properties might be expected to be almost identical to those of the wurtzite form. The stability relationships between these forms do not appear to be known with certainty.

Above the transition⁷ at 146°C. the iodide ions still form a closest packed lattice, now cubic, but the silver ions may be said to be molten. The crystal shows electrical conductivity. It is assumed that the silver ions can jump from one

cavity to another in the iodide ion lattice with relative ease.

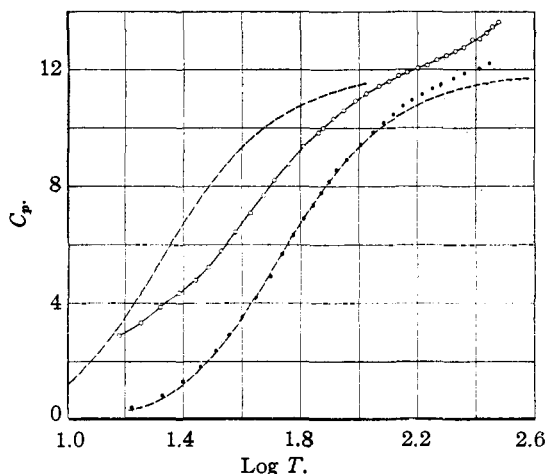


Fig. 1.—The molal heat capacity of silver iodide (open circles) in cal. per degree. The values of Southard and Nelson for potassium chloride (solid circles) and the Debye curves (dotted curves) are given for comparison.

In his detailed investigation of the low temperature form, Helmholtz¹ found that at the temperature of liquid air silver iodide has the ideal wurtzite structure. At room temperature, however, definite deviations have appeared, which may be described as a motion of the silver ions toward three and away from one of the four surrounding iodide ions. An extension of this motion leads eventually to the passage of the silver ion through the plane of the three iodide ions and on into the cavity on the other side. Thus this motion is in the direction consistent with the properties of the high temperature form.

Helmholtz suggested the possibility that there might be separate potential minima for the silver ions: one in the center of the tetrahedron of iodide ions, and four others, each near three and away from the fourth iodide. The center position would need to be lowest in energy so as to be preponderantly occupied at very low temperatures. If these positions were separated from one another by potential barriers, one would expect a marked hump in the heat capacity curve in the temperature range where the outer positions are first being occupied, *i. e.*, between liquid air and room temperatures. Actually the curve is very smooth and quite normal in this region. Consequently it seems probable that no potential barriers exist between the various positions within a tetrahedron, but rather

(5) K. K. Kelley, *U. S. Bur. Mines Bull.*, no. 350 (1932); *ibid.*, no. 394 (1936).

(6) "Strukturbericht" (*Z. Krist., Ergänzungsband*), 1928, pp. 112, 767.

(7) L. Strock, *Z. physik. Chem.*, **B25**, 441 (1934).

that the silver ions gradually take up larger and larger amplitudes of motion in the direction of the outer positions. The probable potential energy function can be described as having a single minimum at the center of the tetrahedron, but rising much more rapidly in the direction toward one iodide ion than in the opposite direction toward the hole between the other three. With the thermal energy of room temperature the amplitude of motion toward the hole is several tenths of an Ångström unit, and by 146°C. the silver ions have enough energy to pass through to the next cavity.

The somewhat peculiar shape of the silver iodide heat capacity curve below 100°K. (see Fig. 1) is probably caused by this peculiar potential function for the silver ions. Whether the small wave in the curve near 20°K. is to be explained in this way is difficult to decide definitely. Many other silver salts show one or more such waves in their heat capacity curves. Latimer, Hicks and Schutz⁸ mention such a situation in silver sulfate. Other examples, some less definite, include silver chlorite,⁹ silver nitrate,¹⁰ and silver chloride and bromide.¹¹ When one couples with this information the fact that silver shows a remarkably variable coordination number, it becomes not improbable that the two phenomena are related.

The color of silver iodide is also interesting. It changes gradually from white at very low temperatures through light yellow at room temperature to a darker yellow just below the transition. The high temperature form is orange and at still higher temperatures the substance becomes dark red.

If one compares these colors with the structural

(8) W. M. Latimer, J. F. G. Hicks and P. W. Schutz, *J. Chem. Phys.*, **1**, 424 (1933).

(9) W. V. Smith, K. S. Pitzer and W. M. Latimer, *THIS JOURNAL*, **59**, 2640 (1937).

(10) W. V. Smith, O. L. Brown and K. S. Pitzer, *ibid.*, **59**, 1213 (1937).

(11) E. D. Eastman and R. T. Milner, *J. Chem. Phys.*, **1**, 444 (1933).

data discussed above, the definite conclusion can be reached that the long wave length limit of intense absorption moves toward the red as the coordination number of the silver decreases. Probably this can be associated with greater deviation from pure ionic binding in the cases of smaller coordination number.

This connection between color, coordination number, and bond character appears to be a rather general one. These ideas involving color have developed from a series of discussions the writer has had with Professor J. H. Hildebrand. We hope to present a general discussion of the subject in the near future.

Summary

Experimental measurements of the heat capacity of silver iodide from 15 to 300°K. are presented. While the extrapolation of the heat capacity below 15°K. is somewhat ambiguous, a fairly reliable entropy value can be obtained which is in excellent agreement with a value obtained from other sources.

These data are combined with those available from other sources in a discussion of the structure of this substance. It is shown that the potential energy for a silver ion within the surrounding tetrahedron of iodide ions is lowest at the center of the tetrahedron but that it rises unsymmetrically in different directions. The potential energy rises relatively rapidly in the direction toward one iodide, but only very gradually toward the hole between three. The smoothness of the heat capacity curve, however, eliminates the possibility of distinct, separate potential minima within a tetrahedron.

It is noted that the increasing color of silver iodide with rise in temperature may be related to the decreasing average coordination number and probably to increasing deviation from pure ionic bond character.

BERKELEY, CALIFORNIA RECEIVED NOVEMBER 12, 1940