[CONTRIBUTION FROM THE AMMONIA DEPARTMENT OF E. I. DU PONT DE NEMOURS & COMPANY, INC.]

Optical Crystallographic Studies with the Polarizing Microscope. III. Measurement of Several Types of Selective Dispersion in Organic Compounds

BY W. M. D. BRYANT

Optical methods of characterizing crystalline substances for purposes of identification are especially suitable for use in the organic field where examples of strong double refraction and dispersion are frequent. This is particularly true of the aromatic and heterocyclic classes in which directional differences in physical properties reach a maximum. Where these classes are involved it becomes possible to increase the number of well defined optical properties measurable with the polarizing microscope and thus greatly facilitate the identification of such difficult examples as isomers and adjacent homologs. The principal refractive indices and birefringences were almost the only numerical optical constants used for identification in the past. The value of optic axial angle in this connection has been demonstrated in earlier papers from this Laboratory.[1]

The present paper describes a group of organic compounds chosen to exemplify the various types of selective dispersion and includes a discussion of suitable measuring techniques for each type. Since these optical properties are rarely of measurable intensity among inorganic compounds, their importance in the organic field has been largely overlooked. However, cursory observations in this Laboratory covering a large number of organic compounds have shown that these supposedly rare dispersion phenomena are numerous, and are often of sufficient intensity for convenient measurement, and in certain series of aromatic compounds are present in almost every homolog, with significant differences from member to member.

Dispersion of the individual refractive indices has been employed to advantage in the inorganic field by Merwin[2] and later by Emmons.[3] The more complex types of dispersion designated as *selective dispersion*[4] include: axial, crossed axial plane, inclined, crossed, and horizontal dispersion (a sixth type, unsymmetrical or triclinic dispersion, is not discussed). These optical phenomena are the result of changes in the relative dimensions of the optical ellipsoid (indicatrix) and its orientation within the crystal lattice, resulting from a change in the wave length of light. Since an interference figure approximates an orthographic projection of the indicatrix for a given orientation, measurements of selective dispersion can be obtained from them. The principle of these measurements assuming the use of crystallographic rotation apparatus is outlined by Tutton.[5] Adaptation to the microscope proved simple and in most details analogous to optic axial angle measurement. In fact, axial and crossed axial plane dispersions are best represented by a table or curve of optic axial angle *versus* wave length of light, also noting in the latter case the plane in which the angle is measured. The remaining types of dispersion are measured by noting the angular displacement of one or both of the two bisectrices on varying the wave length of light. Obviously, a curve or tabulation of angular values over a range of wave lengths is a more critical characteristic of a particular substance than an observation at any single wave length would be.

Of the five compounds included in the present research only one seems to have been studied optically in the past. *o*-Nitroacetanilide was first examined by Jaeger[6] a number of years ago, but the dispersion of this compound was not correctly understood at that time. In the present investigation, this substance was recognized as an example of inclined dispersion.

The use of selective dispersion as an aid in identification appears very promising. After further study of structural requirements it should be possible to select reagents with the object of imparting strong dispersion to their derivatives. There is already evidence to indicate that benzenoid orthonitro compounds have this tendency.

Materials.—Eastman Kodak Co. *n*-butyl carbamate, 2,2′-dipyridyl and *o*-nitroacetanilide

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[1] (a) Bryant, THIS JOURNAL, **60**, 1394 (1938); (b) *ibid.*, **55**, 3201 (1933); (c) *Am. Mineral.*, **20**, 281 (1935); (d) Bryant and Mitchell, THIS JOURNAL, **60**, 2748 (1938).

[2] Posnjak and Merwin, *ibid.*, **44**, 1970 (1922).

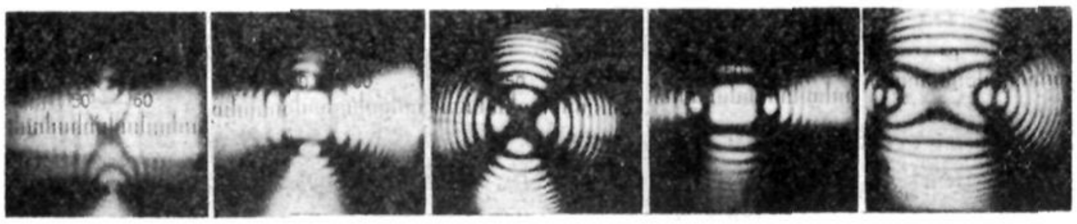
[3] Emmons, *Am. Mineral.*, **13**, 504 (1928); **14**, 414 (1929).

[4] Johannsen, "Manual of Petrographic Methods," 2nd ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1918, p. 442.

[5] Tutton, "Crystallography and Practical Crystal Measurement," 2nd ed., Macmillan & Co., Ltd., London, 1922, Vol. II, Ch. 48 and 49.

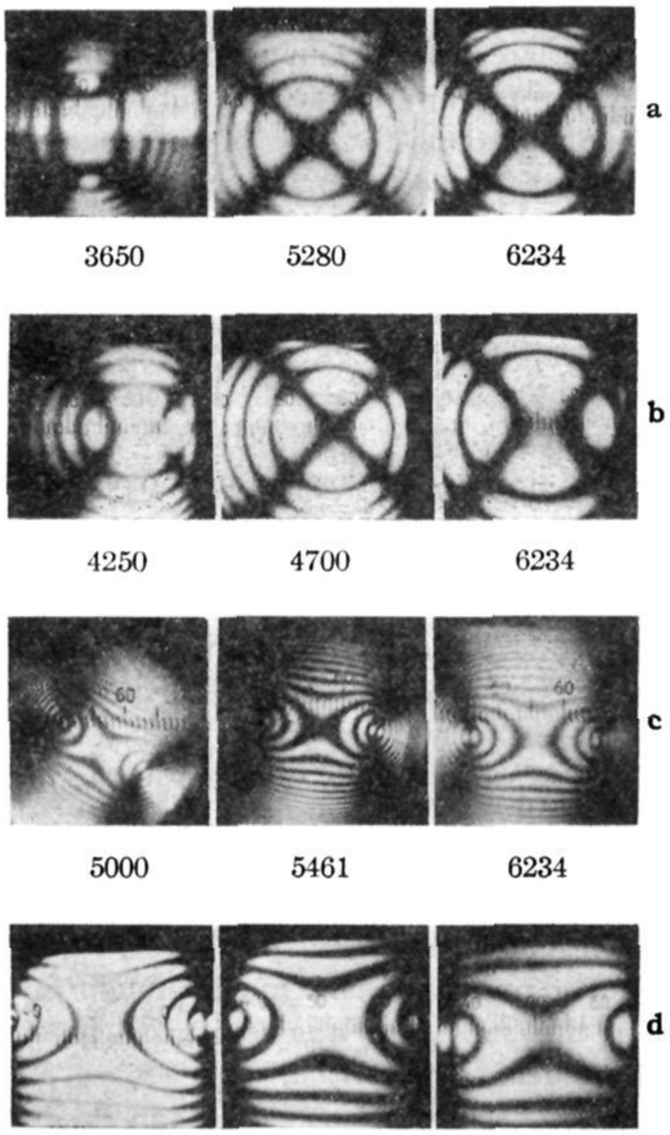
[6] Jaeger, *Z. Krist.*, **44**, 563 (1908).

melted sharply (at 53.2, 70.3 and 92.5°, respectively) and hence were used as received. Guanylurea (or dicyandiamidine) picrate was prepared by mixing aqueous methanol (50%) solutions of Eastman sulfate and picric acid in equimolecular quantities. The fine yellow precipitate of picrate was recrystallized from hot water and hot aqueous methanol. Compact yellow prisms were obtained from both solvents (m. p. 275° with decomposition). 2-Hydroxyethylamine (monoethanolamine) picrate was obtained similarly using dry ethanol solutions. The salt was recrystallized from hot ethanol (m. p. 161.0°).[7] The melting points were in good agreement with the values in the literature.



3650 4047 4150 4358 5461

Fig. 1.—Interference figures of 2,2′-dipyridyl in monochromatic light. Three types of dispersion are present: crossed axial plane, inclined (4150–5461 Å.) and horizontal (3650–4150 Å.).



3650 5280 6234

4250 4700 6234

5000 5461 6234

4700 4916 5461

Fig. 2.—Interference figures illustrating four types of selective dispersion in crystals: (a) *n*-butyl carbamate, crossed axial plane; (b) *o*-nitroacetanilide, inclined; (c) guanylurea picrate, crossed; (d) 2-hydroxyethylamine picrate, horizontal (wave length of light in Å. appears under each picture).

Optical Equipment and Technique.—The apparatus employed included a Bausch and Lomb LD petrographic microscope equipped as indicated in an earlier paper.[1a] Monochromatic radiation for the bulk of the work was obtained from a G. E. H-4 type mercury vapor lamp mounted in a Bausch and Lomb J-camera lamp carriage, equipped with a water cell and suitable Corning and Eastman Wratten filters. For work requiring specific wave lengths of the visible spectrum, a Bausch and Lomb monochromator and carbon arc were used. Appropriate clean-up filters to remove stray light were selected from a collection of Corning glasses. The wave length drum of the monochromator was adjusted to coincide with well-defined lines of the mercury spectrum. A Saylor constant-temperature stage[8] was used in the case of *o*-nitroacetanilide where the effect of temperature on the optic axial angle was marked.

The regular visual method of measuring optic axial angles and dispersion from interference figures[1a] was supplemented by a photographic technique. By simultaneously photographing the interference figure and ocular micrometer scale a permanent record of the observation is made available for future comparison by superposition. Comparisons of the negatives can be made directly by examination against an illuminated opal glass screen. A small fixed extension camera (Zeiss Miflex), magnification factor 0.5, proved adequate since interference figures appear sharper at lower magnifications. A Zeiss 17X orthoscopic micrometer ocular was used, care being taken to reverse the micrometer disk and adjust its focus sharply to the plane of the film holder. The microscope lens system was calibrated directly in angular units by recording the settings of an Abbe apertometer[1a] seen on the viewing screen.

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[7] Melting points were measured potentiometrically within ±0.3° using a Dennis melting point bar. The values given are corrected.

[8] Saylor, *J. Research Natl. Bur. Standards*, **15**, 97 (1935).

The optical system of the LD microscope was found to transmit sufficient of the near ultraviolet of the mercury arc to form well-defined interference figures. The 3650 Å. line isolated by Corning #586 (7 mm.) and #738 (2 mm.) filters produced good negatives after exposures of two to five minutes (Figs. 1 and 2a).

Refractive indices were determined by the immersion method as used in previous work. It was necessary, however, to employ the universal stage (Emmons model, Bausch and Lomb) to obtain the α index of *n*-butyl carbamate. Also refractive indices of 2,2′-dipyridyl could not be measured by immersion in liquids due to the extreme solvent action of all available liquids. Small amounts of the substance were therefore melted around fine grains of isotropic inorganic solids of known refractive index and the Becke line test used to determine the degree of match. Fortunately all three indices could be observed in the solidified melt.

Dispersion Measurements.—Measurement of axial and crossed axial plane dispersion depends directly upon the measurement of optic axial angles for a series of wave lengths by methods previously described.[1a] The evaluation of inclined and horizontal dispersion requires the same equipment but the procedure differs somewhat. Here the positions of the optic axes in the conoscopic field are measured for each wave length, and the angular displacement of the acute bisectrix relative to the section calculated from that of the optic axes. With inclined dispersion this is best accomplished by plotting the positions of the individual optic axes in the field, converting the linear (sine) scale to angular values, and finally plotting the bisector of the angle between the two optic axes corresponding to a given wave length of light as illustrated in Fig. 4. This angle is the apparent angle of dispersion in air and must be corrected to the value within the crystal by means of the refractive index β. To measure horizontal dispersion the preparation is set with the trace of the axial plane 90° to the linear scale and the displacement of the trace with varying wave length measured and converted to angular units and finally corrected to the true angle by means of β. Crossed dispersion is simpler from the experimental standpoint. Here no measurements are made in the conoscopic field but starting with the interference figure at extinction, the preparation on the stage is rotated to restore the interference figure to the extinction position (dark cross) after each change in the wave length of light. The necessary rotation of the stage is a direct measure of the crossed dispersion. This measurement can be made in parallel polarized light by simply measuring the extinction angles of the acute bisectrix section for various wave lengths. The conoscopic method is more convenient since the interference figure is a valuable guide to the correct orientation and the position of the isogyres is a sensitive indication of the extinction position in preparations exhibiting incomplete extinction in parallel light. Horizontal dispersion may also be obtained by measuring the crossed dispersion in the other bisectrix. The horizontal dispersion is numerically equal to the crossed dispersion in the section of the other bisectrix.

Dispersion and Other Optical Data

***n*-Butyl Carbamate.**—The stable modification of this substance[9] exhibits crossed axial plane dispersion as shown by the following optic axial angle values (see figure 2a).

Wave length, Å.	Optic axial angle, 2E	Plane of optic axes
3650	40 ± 1°[a]	(010)
4358	24.5 ± 1	(010)
4916	15 ± 2	(010)
5461	7 ± 3	⊥(010)
5780	13.0 ± 1	⊥(010)
6234	19.0 ± 1	⊥(010)
6908	23.0 ± 1	⊥(010)

[a] Photographic measurement.

The substance becomes uniaxial at 5250 ± 100 Å. This wave length could be determined to ±10 Å. in individual crystals but variations from one crystal to another were greater. No temperature sensitivity could be observed in the range 15–30°. The distribution of colors around the isogyres when viewed in white light showed that horizontal (for red) and inclined (for violet) dispersions are also present although not to a measurable degree.

2,2′-Dipyridyl.—Three types of dispersion, crossed axial plane, horizontal and inclined, are much more intense in this compound. Both visual and photographic measurements were made in obtaining the following data (Fig. 1).

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(9) One or two other modifications were observed but have not been measured.

Wave length	Optic axial angle 2Ha, relative to cedar oil[10]	Horizontal and inclined dispersion		Plane of optic axes
3650	38.0 ± 1°	6°	True horizontal dispersion 4150-λ	⊥(010)
4047	18.0	0		⊥(010)
4150(±10 Å.)	0.0	0		
4358	20.0	3	True inclined dispersion λ-4150	(010)
5461	41.5	7		(010)
5780	44.0	7		(010)
6234	46.5	9		(010)
6908	50.0	9.5		(010)

Figure 3 shows a plot of the relative positions of the optic axes and acute bisectrix for light of different wave lengths as observed conoscopically. The portion of the plot below 4150 Å. has of course been rotated 90° in the plane of the page. The apparent horizontal and inclined dispersions may be read from this figure. The true values follow from the relation: sine apparent angular displacement × 1.515/β = sine true angular displacement.

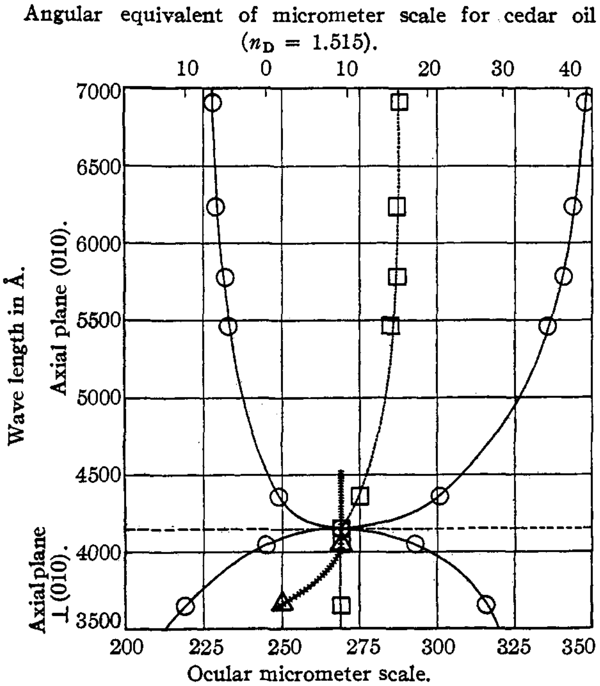

Fig. 3.—Three types of dispersion in 2,2′-dipyridyl: plot showing relative position of optic axes and acute bisectrix as function of wave length; full line curves—apparent loci of optic axes; broken line curve—apparent locus of acute bisectrix in (010) plane; hatch-marked curve—apparent lateral displacement of acute bisectrix.

***o*-Nitroacetanilide.**—This compound has strong inclined dispersion. The optic axial angle decreases rapidly on passing from yellow to a blue-green radiation, the change being confined almost entirely to one optic axis. After attaining a minimum at about 4650 Å. the angle begins to increase rapidly in the same plane without ever becoming uniaxial. In the blue, however, the motion is confined to the other optic axis (Figs. 2b and 4).[11] The numerical data are as shown.

Wave length	Optic axial angle 2E at 25°	Temp. coeff. d(2E)/dt	Inclined dispersion for intervals λ-4358
4358	26.5 ± 0.5°	−0.3°	0
4650	15.5	− .4	3.5
4916	18.5	− .4	5.5
5461	26.0	− .5	7.5
5780	29.0	− .5	8.0
6234	33.0	− .4	8.5
6908	35.5	− .4	9.0

The optic axial angle is temperature sensitive. The approximate temperature coefficients given above are for the range 15–35°.

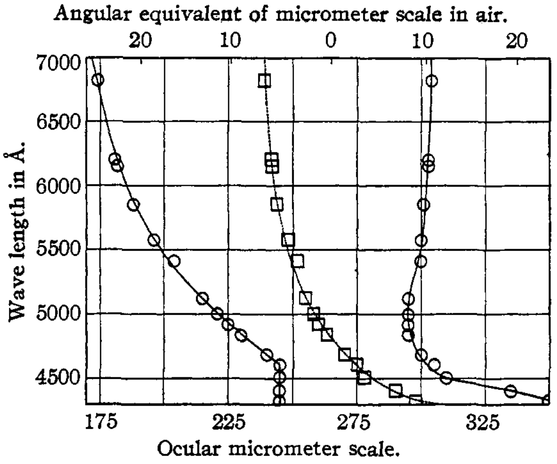

Fig. 4.—Inclined dispersion in *o*-nitroacetanilide showing relative position of optic axes and acute bisectrix *versus* wave length: full line curves, apparent loci of optic axes; broken line curve, apparent locus of acute bisectrix.

Guanylurea Picrate.—This salt has strong crossed dispersion. The crystal face presenting the acute bisectrix is the clino pinacoid (010). The entire interference figure rotates about Bx_a in this plane as the wave length of light is varied (Fig. 2c). The optic axial angle passes through a minimum at about 5050 Å. as shown in Fig. 5 and in the table.

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[10] As stated in ref. 1a, p. 1396, the dispersion of cedar oil has been neglected. The discrepancy introduced may reach ~1° for the extreme violet.

[11] Axial curves in agreement with Fig. 4 have been obtained photographically by E. E. Jelley (*J. Roy. Microsc. Soc.*, **66**, 101 (1936)) using his microspectrograph. Unfortunately this reference was not seen until after completion of the present research.

Wave length	2*E*	Crossed dispersion for interval 6908-λ
4710	89.0 ± 1	75
4750	83.0	63.5
4850	68.0	57.5
4950	62.0	49
5000	56.0	41
5050	54.5	34
5100	55.5	29.5
5150	56.0	24
5200	57.0	18.5
5250	58.5	17.5
5300	61.0	14
5350	62.0	11.5
5461	64.5	9
5780	71.0	4
6234	76.0	2
6800	78.0	0.5
6908	79.0	0

2-Hydroxyethylamine Picrate.—The final example deals with horizontal dispersion (Fig. 2d). This property has been observed less frequently in measurable intensity than the other forms, although weak horizontal dispersion distinguishable qualitatively by observations in white light is fairly common. The numerical results appear in the table.

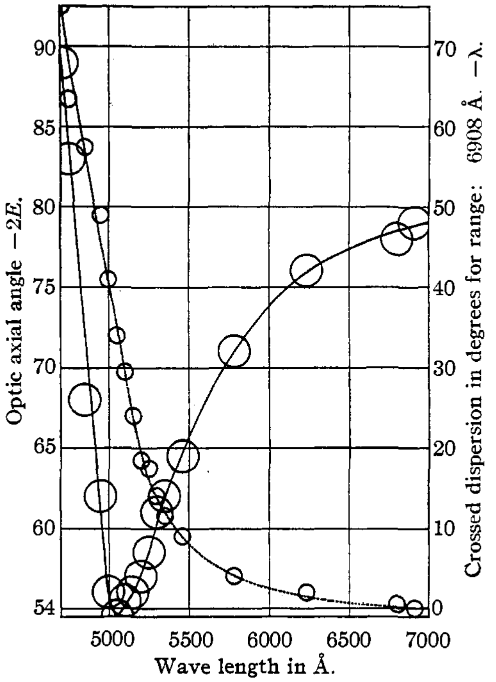

Fig. 5.—Crossed dispersion in guanylurea picrate: full line curve, optic axial angle; broken line curve, crossed dispersion.

TABLE I

OTHER OPTICAL CRYSTALLOGRAPHIC PROPERTIES

Compound	*n*-Butyl carbamate	2,2′-Dipyridyl	*o*-Nitroacetanilide	Guanylurea picrate	2-Hydroxyethylamine picrate
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Elongation[a]	//β(Bx_a) (red) //γ(Bx_a) (violet)	Inclined slightly from β(Bx_a) (red)	//β(Bx_a)	$\wedge \gamma = 22°$ (5461) (Bx_a)	//β(Bx_a)
Optical Orientation	$\gamma = b$ (red) $\beta = b$ (violet)	$\gamma = b$ (violet) $\beta = b$ (red)	$\beta = b$	$\alpha = b$	$\alpha = b$
Refractive indices at 25 ± 3° for λ = 5461[b]	α 1.435±.005[c] β 1.481 γ 1.482	1.63±.02[d] 1.77±.02 1.79±.02	1.626 1.629 1.840±.005	1.447 1.900±.005 1.97±.01	1.620 1.688 1.925±0.005
Birefringence λ = 5461	0.047	0.16	0.214	0.52	0.305
Optical character	Negative	Negative	Positive	Negative	Positive
Optic axial angle, 2V for λ = 5461	5°[e]	35°[e]	16°[e]	33°[e]; 34°[f]	62°[e,f]; 64°[g]
Crystal habit	Elongated plates from benzene; same habit from melt	Compact prisms; radial and parallel aggreg. of plates from melt	Thin elongated yellow prisms from EtOH–H_2O, same habit from melt but less regular	Deep yellow prismatic needles and roset-like aggregs. from hot 70% MeOH	Compact yellow prisms and thin plates from benzene MeOH mixture. Radial growths of plates and needles from melt

[a] Bisectrices in parentheses are the approximate normals to the sections for which elongations are given. [b] Refractive indices correct to ±0.003, except where noted. [c] This value obtained by means of universal stage. [d] Crystals fused with standard solids, matched after solidifying. [e] Calculated from 2*E*(or 2Ha) and β. [f] Calculated from α, β and γ. [g] Calculated from 2Ha and 2Ho.

Wave length	Optic axial angle 2Ha, relative to cedar oil	Horizontal dispersion for interval λ-4600
4600	77.0 ± 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 2Ha) 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.

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[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 Helmholz,[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 Schwers[4] in the range 18–117°K., which is in reasonable agreement with the present results.

TABLE I

MOLAL HEAT CAPACITY OF SILVER IODIDE

T, °K.	C_p, cal. per degree	T, °K.	C_p, 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-

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(1) L. Helmholz, *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. Schwers, *Sitzber. kgl. preuss. Akad. Wiss.*, 355 (1914).