It is quite obvious that the character of the alpha carbon atom in the hexanol (whether primary, secondary or tertiary) separates the isomers into three distinct groups. Also it is evident that further comparisons must be limited to compounds within these groups. Maximum solubility should exist in that isomer which has the most compact structure and which has the hydroxy group located as close to the center of the molecule as possible. In the tertiary group, the latter factor seems to dominate slightly (nos. 1 and 2). But in the secondary group, the former factor—compact structure—seems to prevail (nos. 4 and 5). Two of the isomers have almost identical solubilities of the alcohol in water (nos. 7 and 8) but even here the factor of compact structure seems to prevail slightly. In the two secondary isomers where the carbon chain remains constant (nos. 8 and 9), the solubility increases as the hydroxyl group is moved toward the center of the molecule, which is perfectly analogous to the behavior of the pentanols. Solubilities of all ten isomeric hexanols decrease as the temperature increases from 20 to 30°.

Experimental

All compounds were fractionally distilled from calcium oxide. Numbers 3 and 9 were Eastman best grade and were distilled using a short column. Number 7 was purified from Eastman practical grade by careful fractionation through a 1-m. column with a reflux ratio of about 10:1. All of the other compounds were prepared by some modification of the Grignard reaction with the usual procedure, and fractionally distilled through the 1-m. column. The following specific reagents were used: no. 1 from ethylmagnesium bromide and ethyl acetate; no. 2 from methylmagnesium iodide and *i*-propyl methyl ketone; no. 4 from *t*-butylmagnesium chloride and acetaldehyde; no. 5 from ethylmagnesium bromide and *i*-butyraldehyde; no. 6 from *s*-butylmagnesium bromide and acetaldehyde; no. 7 from *i*-butylmagnesium bromide and acetaldehyde; no. 8 from ethylmagnesium bromide and *n*-butyraldehyde; no. 10 from *t*-pentylmagnesium chloride and ethyl formate.

The procedure used for the measurement of the solubilities was essentially the same as that used in the work on pentanols. Any changes made were in the nature of slight refinements in technique. If details are desired, reference should be made to the article on pentanols. The results seem reliable to better than 0.1 weight per cent. and the authors feel that the validity of the results will approach this limit.

Summary

Aqueous solubilities of ten isomeric hexanols have been determined for 20, 25 and 30°. The three tertiary isomers are more soluble than any of the six secondary isomers which in turn are more soluble than the most compact primary isomer. Maximum solubility is obtained by having the hydroxyl group as close as possible to the center of a compact molecule. The solubility of all ten isomers decreases as the temperature increases from 20 to 30°.

GREENSBORO, N. C. RECEIVED MARCH 26, 2938

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

Sulfur Dioxide. The Heat Capacity of Solid and Liquid. Vapor Pressure. Heat of Vaporization. The Entropy Values from Thermal and Molecular Data

BY W. F. GIAUQUE AND C. C. STEPHENSON[1]

This paper presents the results of a low temperature investigation on sulfur dioxide. The data and the third law of thermodynamics have been used to calculate the entropy of sulfur dioxide gas. Cross[2] has calculated the entropy from molecular data and, while these data are not as complete as is desirable, it is possible to show that the entropy of crystalline sulfur dioxide does approach zero at the absolute zero of temperature.

The apparatus and methods used in this investigation are similar to those of previous investigations on condensed gases in this Laboratory. The calorimeter used has been referred to previously[3] as Gold Calorimeter II. A full description of a similar calorimeter has been given by Giauque and Egan.[4] The most recent calibration of the standard thermocouple has been described by Stephenson and Giauque.[5]

Preparation and Purity of Sulfur Dioxide.—The sulfur dioxide was prepared by the action of concentrated sulfuric acid on sodium sulfite. The evolved gas was bubbled through water to remove any traces of sulfur trioxide and then

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[1] Charles A. Coffin Fellow, Academic year 1934–1935.

[2] Cross, *J. Chem. Phys.*, **3**, 825 (1935).

[3] (a) Giauque and Wiebe, THIS JOURNAL, **50**, 101 (1928); (b) Blue and Giauque, *ibid.*, **57**, 991 (1935).

[4] Giauque and Egan, *J. Chem. Phys.*, **5**, 45 (1937).

[5] Stephenson and Giauque, *ibid.*, **5**, 149 (1937).

passed through tubes containing phosphorus pentoxide to remove water vapor. The sulfur dioxide was then collected in a large trap cooled by a salt and ice mixture and distilled several times, generous fractions being discarded at the beginning and end of each distillation. Finally the distillate was solidified by cooling with liquid air and subjected to a high vacuum by means of a mercury diffusion pump.

The heat capacity measurements showed no abnormal rise in the region below the melting point. The accuracy of this observation is sufficient to determine that the liquid soluble–solid insoluble impurity is not greater than one part in one hundred thousand. The constancy of the melting .point, measured as a function of the amount melted, provides additional although less precise evidence of the purity.

Vapor Pressure of Sulfur Dioxide.—The apparatus for the measurement of vapor pressures has been described previously.[4] The measurements were made by using a cathetometer as a comparison instrument. A standard meter was mounted in the manometer case. All of the observations are corrected to international cm. by means of data given in the "International Critical Tables."[6] The standard acceleration of gravity was taken as 980.665 cm./sec.^{2} and the gravitational acceleration for this location was taken as 979.973.[7]

The vapor pressure observations have been represented by the equation

Liquid SO_2, 197.64° to 263.5°K.

$$\log_{10}P_{\text{cm.}} = -\frac{1867.52}{T} - 0.015865T + 0.000015574T^2 + 12.07540$$

The observed and calculated values are given in Table I.

Melting Point.—The melting point was observed as a function of the percentage melted over a period of time. A summary of the results of two series of observations is given in Table II.

Table III contains a summary of measurements of the melting and boiling point temperatures for sulfur dioxide. The boiling point given for this research was calculated from the vapor pressure equation.

TABLE I

VAPOR PRESSURES OF SULFUR DIOXIDE

Melting point 197.64°K. Boiling point 263.08°K. 0°C. = 273.10°K. The temperatures in the table are given to 0.001° only because of the high relative accuracy.

T, °K.	P, cm. observed	P, obsd. − P, calcd.	T, obsd. − T, calcd.
197.64	1.256[a]	0.000	0.000
200.803	1.652	+ .002	− .014
205.142	2.358	− .001	+ .005
209.581	3.340	.000	.000
214.092	4.677	+ .003	− .009
218.602	6.437	+ .003	− .007
223.177	8.755	− .005	+ .009
228.290	12.157	+ .002	− .003
233.122	16.311	+ .003	− .003
238.110	21.762	+ .001	− .001
243.584	29.380	− .007	+ .004
249.637	40.227	.000	.000
256.375	55.897	+ .008	− .003
263.485	77.382	− .002	+ .001

[a] Triple point pressure.

TABLE II

MELTING POINT OF SULFUR DIOXIDE

Date and time		% melted	T, °K. Resistance thermometer	T, °K. Thermocouple	Pressure, cm.
		Series 1			
10/11/34	8:55 a.m.	Heated into melting point			
	2:40 p.m.	5	197.642	197.63	
	2:55 p.m.	Supplied heat			
	5:55 p.m.	15	197.631	197.63	
	7:15 p.m.	Supplied heat			
10/12/34	1:50 a.m.	25	197.643	197.66	
	2:00 a.m.	Supplied heat			
	5:20 a.m.	35	197.639	197.64	
	5:30 a.m.	Supplied heat			
	9:55 a.m.	50	197.643	197.64	
	11:50 a.m.	Supplied heat			
	3:40 p.m.	65	197.641		
		Series 2			
11/1/34	2:30 p.m.	Heated into melting point			
	7:55 p.m.	10	197.639	197.64	1.255
	8:15 p.m.	Supplied heat			
	10:30 p.m.	20	197.639	197.64	1.257
	10:45 p.m.	Supplied heat			
11/2/34	1:25 a.m.	45	197.641	197.64	1.256
			Accepted value	197.64	1.256

The Heat Capacity of Sulfur Dioxide.—The heat capacities were measured by the introduction of electrical energy and 1.00042 absolute joules were taken equal to one international joule and 4.185 absolute joules were taken equal to one calorie (15°). The procedure and method of correcting for heat leak have been described previously.[2] It is believed that for the region from 35°K. to the boiling point the smooth curve represents correct values of the heat capacity to within 0.2%. At 20°K. the error may be as large as 1% and at 15°K., 3%.

Table IV gives the observed heat capacities

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(6) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1926.

(7) Sternewarte, Landolt, Börnstein and Roth, "Physikalisch-chemische Tabellen," Verlag von Julius Springer, Berlin, 1923.

TABLE III

MELTING AND BOILING POINT TEMPERATURES OF SULFUR DIOXIDE

M. p., °K.	B. p., °K.	Observer
....	262.6 (744 mm.)	Bunsen[8] (1839)
194	....	Mitchell[9] (1841)
197	263	Faraday[10] (1845)
....	265	Drion[11] (1859)
....	263.2 (754 mm.)	Andreef[12] (1859)
....	263.02	Regnault[13] (1863)
....	265	Pierre[14] (1873)
...	263	Pictet[15] (1877)
....	263 (768 mm.)	Blümcke[16] (1888)
200.4	....	Walden and Centnerzwer[17] (1903)
....	263.0	Estreicher[18] (1904)
....	263.01	Gibbs[19] (1905)
200.8	....	Baume[20] (1909)
197.5	....	Smits and Mooy[21] (1910)
198.0	....	Van der Goot[22] (1913)
....	262.1	Burrell and Robertson[23] (1915)
....	263.11	Henning and Stock[24] (1921)
....	263.08	Bergstrom[25] (1922)
197.67	....	Seyler and Peck[26] (1930)
197.64	263.08	This research

TABLE IV

HEAT CAPACITY OF SULFUR DIOXIDE

Molecular weight, 64.06; 0 °C. = 273.10 °K.

T, °K.	ΔT	C_p, cal. deg.$^{-1}$ mole^{-1}	T, °K.	ΔT	C_p, cal. deg.$^{-1}$ mole^{-1}
15.20	1.514	0.860	135.83	5.031	13.15
17.32	2.293	1.155	140.92	4.802	13.32
19.73	2.385	1.621	146.19	5.344	13.63
22.59	3.179	2.211	151.72	5.115	13.94
25.67	2.900	2.864	156.98	4.915	14.15
28.96	3.524	3.570	162.03	4.707	14.46
32.44	3.408	4.311	167.29	5.218	14.69
34.87	4.380	4.821	172.67	4.996	14.92
39.25	4.411	5.672	177.84	4.796	15.25
43.29	3.615	6.325	182.82	4.600	15.64
47.16	3.690	6.930	188.23	4.441	15.93
51.28	4.493	7.535	192.82	4.324	16.16
55.75	4.369	8.106	197.64	Melting point	
60.85	5.839	8.727	201.74	5.305	20.97
66.34	5.760	9.252	207.26	5.160	20.95
71.68	4.867	9.687	212.60	5.026	20.91
76.98	5.560	10.11	217.82	4.917	20.90
83.08	6.525	10.54	222.97	4.807	20.85
88.84	5.001	10.86	228.05	4.708	20.83
93.10	5.432	11.05	235.09	4.577	20.79
98.30	5.027	11.36	240.09	4.470	20.79
103.82	5.921	11.68	245.22	4.904	20.71
109.50	5.355	11.98	250.51	4.797	20.72
114.74	5.092	12.21	255.72	4.680	20.69
120.37	6.066	12.42	260.86	4.602	20.69
124.56	5.922	12.55	263.08	Boiling point	
130.36	5.410	12.87			

which are shown in Fig. 1. Table V presents values taken from the smooth curve through the observations.

The amount of sulfur dioxide in the calorimeter was determined by condensing the material in a weighed, evacuated bulb which was then sealed and reweighed at room temperature. 2.419 moles was used for the measurements.

In the solid above 130°K., thermal equilibrium was established only after about thirty or forty minutes, whereas below this temperature equilibrium was reached in about five minutes. The results of the measurements above 130°K. are therefore not quite as accurate as those below this temperature.

At 175°K., about 20° below the melting point of sulfur dioxide, the resistance thermometer began to give slightly high values, and just below the melting point the abnormal increase in the resistance reached 0.1% of the total resistance. As soon as a portion of the sulfur dioxide was melted, the resistance returned to its normal

TABLE V

HEAT CAPACITY OF SULFUR DIOXIDE

Molecular weight, 64.06

T, °K.	C_p, cal. deg.$^{-1}$ mole^{-1}	T, °K.	C_p, cal. deg.$^{-1}$ mole^{-1}
15	0.83	130	12.83
20	1.66	140	13.31
25	2.74	150	13.82
30	3.79	160	14.33
35	4.85	170	14.85
40	5.78	180	15.42
45	6.61	190	16.02
50	7.36	197.64	Melting point
55	8.02	200	20.97
60	8.62	210	20.91
70	9.57	220	20.86
80	10.32	230	20.81
90	10.93	240	20.76
100	11.49	250	20.71
110	11.97	260	20.66
120	12.40		

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(8) Bunsen, *Pogg. Ann.*, **46**, 97 (1839).
(9) Mitchell, *Ann.*, **37**, 356 (1841).
(10) Faraday, *Phil. Trans.*, **135**, 170 (1845).
(11) Drion, *Jahresber.*, 18 (1859).
(12) Andreef, *ibid.*, 19 (1859).
(13) Regnault, *Mem. Acad.*, **26**, 526 (1863).
(14) Pierre, *Compt. rend.*, **76**, 214 (1873).
(15) Pictet, *Ann. Phys. and Chem. Biebl.* (Wiedermann), 629 (1883).
(16) Blümcke, *Wied. Ann.*, **34**, 10 (1886).
(17) Walden and Centnerzwer, *Z. physik. Chem.*, **42**, 432 (1903).
(18) Estreicher, *Bull. Acad. Cracovie*, **183** (1904).
(19) Gibbs, THIS JOURNAL, **27**, 851 (1905).
(20) Baume, *Compt. rend.*, **148**, 1322 (1909).
(21) Smits and Mooy, *Proc. Am. Acad.*, **13**, 339 (1910).
(22) Van der Goot, *Z. physik. Chem.*, **84**, 419 (1913).
(23) Burrell and Robertson, THIS JOURNAL, **37**, 2691 (1915).
(24) Henning and Stock, *Z. Physik*, **4**, 226 (1921).
(25) Bergstrom, *J. Phys. Chem.*, **26**, 358, 876 (1922).
(26) Seyler and Peck, THIS JOURNAL, **52**, 14 (1930).

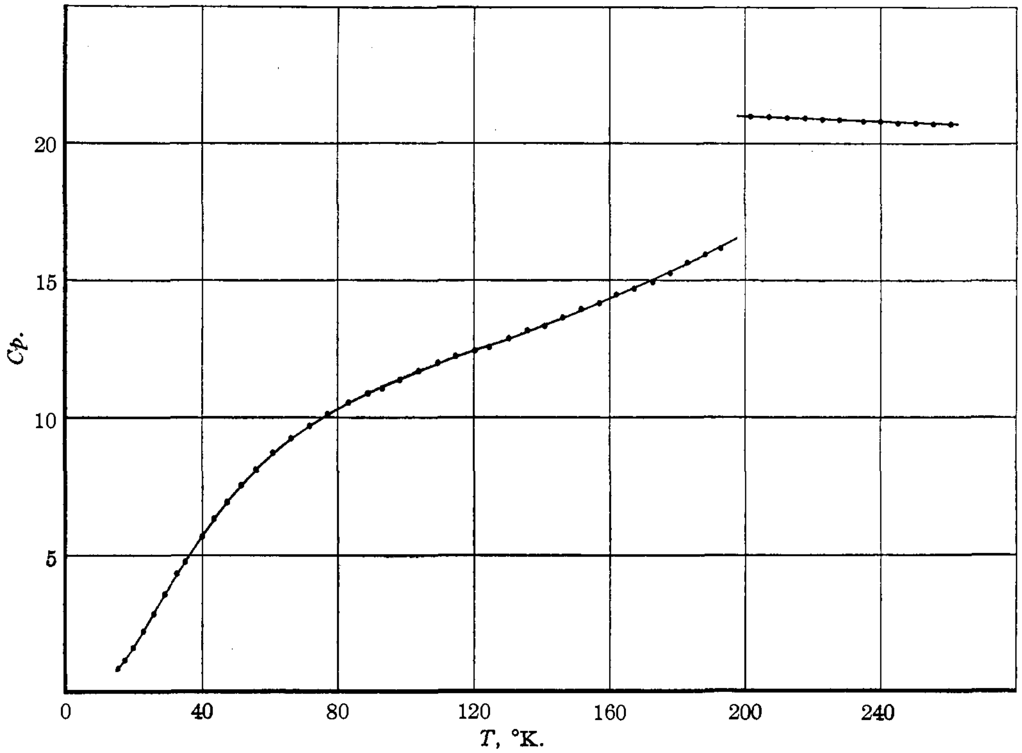

Fig. 1.—Heat capacity of sulfur dioxide in calories per degree per mole.

value. No completely satisfactory explanation of this stretching effect can be offered; none of the many other condensed gases investigated in this calorimeter have caused such a disturbance. The accuracy of the measurements was not appreciably impaired, because the resistance thermometer was calibrated before and after each measurement.

The form of the heat capacity curve above 100°K. indicates that an additional degree of freedom is being excited. This is presumably related to the slow equilibrium and possibly to the thermal expansion noted above.

Heat of Fusion.—The heat of fusion of sulfur dioxide was measured in the usual manner. Starting somewhat below the melting point heat was introduced until all of the material was melted and the liquid heated somewhat above the melting point. Correction was then made for the $\int C_p \, dT$. The data are given in Table VI.

TABLE VI

HEAT OF FUSION OF SULFUR DIOXIDE

Molecular weight, 64.06

Temperature interval	Corrected heat input/mole	$\int C_p \, dT$	ΔH, cal./mole
196.75–198.19	1795.1	26.2	1768.9
196.72–199.11	1815.0	46.0	1769.0
196.22–199.00	1821.1	51.8	1769.3
		Mean	1769 ± 2 cal.

Heat of Vaporization.—The heat of vaporization was measured by adding energy and absorbing the gas evolved in 4 *N* potassium hydroxide. A summary of the data obtained is given in Table VII.

TABLE VII

HEAT OF VAPORIZATION OF SULFUR DIOXIDE

Boiling point, 263.08°K.; molecular weight, 64.06

Moles vaporized	Time of energy input, min.	ΔH at 760 mm., cal./mole
0.18985	55	5965
.16562	45	5956
.14822	45	5963
.16420	50	5956
		Mean 5960 ± 4
From vapor pressure equation, assuming a Berthelot gas		5966

The value calculated from the vapor pressure data has been included in the table, but is given no weight in comparison to the more accurate calorimetric values. The calculated value includes a Berthelot correction of −136 cal. to the value calculated by assuming an ideal gas. The agreement of the two values justifies the use of Berthelot's equation to make a small entropy correction from the actual to the ideal gas state.[27]

The Entropy from Calorimetric Data.—The entropy was calculated in the usual way by graphical integration of $\int_0^T C_p \, d \ln T$ for the solid and liquid and adding to this the entropy changes due to fusion and vaporization. A Debye extrapolation was made for the entropy of the solid below 15°K. The correction for gas imperfection was made by combining the thermodynamic equation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ with Berthelot's equation of state to give

$$\Delta S = \frac{27RT_c^3P}{32T^3P_c}$$

T_c = 430.60°K.; P_c = 77.79 atm.[28] $\Delta S = S_{\text{ideal}} - S_{\text{actual}}$ = 0.09 e. u. at the boiling point. An itemized account of the entropy calculation is given in Table VIII.

TABLE VIII

THE ENTROPY OF SULFUR DIOXIDE

0–15°K., Debye function $h c\nu/k$ = 120	0.295
15–197.64°K., graphical	20.124
Fusion, 1769.1/197.64	8.951
197.64–263.08°K., graphical	5.959
Vaporization, 5960/263.08	22.655
Entropy of actual gas at boiling point	57.98 ± 0.10 e. u.
Correction for gas imperfection	0.09
Entropy of ideal gas at boiling point	58.07 ± 0.10 e. u.

Comparison of the Entropy Values from Calorimetric and Molecular Data.—From their electron diffraction measurements Cross and Brockway[29] found the S–O distance to be 1.46 ± 0.02 × 10^{-8} cm. and the O–S–O angle was estimated at 122 ± 5°.

Badger and Bonner[30] have considered the available spectroscopic data and give the fundamental vibrations as 525, 1152 and 1361 cm.$^{-1}$, respectively.

Cross[2] has used the above values to calculate the thermodynamic properties of sulfur dioxide gas. The entropy values are summarized in Table IX.

TABLE IX

COMPARISON OF THE ENTROPY VALUES FROM CALORIMETRIC AND FROM MOLECULAR DATA

Temperature, °K.	263.08	298.1
Experimental entropy		
Actual gas	57.98 ± 0.10	......
Ideal gas	58.07 ± 0.10	59.24 ± 0.10
Entropy from molecular data	58.23 ± 0.15	59.40 ± 0.15

The experimental value given for 298.1°K. was obtained by using the molecular data for the gas above the boiling point.

The agreement between the theoretical and experimental values shown in Table IX shows that the entropy of crystalline sulfur dioxide approaches zero entropy at 0°K.

Until the spectroscopic investigation and interpretation of the sulfur dioxide molecule is extended, the most reliable value of the entropy is the calorimetric one, SO_2, $S_{298.1^\circ K.}$ = 59.23 cal. deg.$^{-1}$ mole^{-1}. Since the above experimental entropy should be more reliable than that based on existing molecular data the values in the tables of Cross should be corrected as follows: 0.16 cal. deg.$^{-1}$ mole^{-1} should be subtracted from all entropy values and also from all values of $-(F^\circ - E_0^\circ)/T$. The values of heat capacity are unchanged.

By reversing the calculation the entropy may be used to obtain a more reliable value of the angle in the sulfur dioxide molecule.

$$S = \frac{3}{2} R \ln M + 4R \ln T - R \ln P + \frac{R}{2} \ln I_1I_2I_3 - R \ln \sigma + 265.349 + \Sigma S_{\text{vib.}}$$

σ, the symmetry number, has the value 2 for sulfur dioxide. At 263.08°K, $\Sigma S_{\text{vib.}}$ = 0.479 cal. deg.$^{-1}$ mole^{-1}. $S_{263.08}$ = 58.07.

The product of the principal moments of inertia is found to be $I_1I_2I_3 = 9.819 \times 10^{-116}$.

From the geometry of the SO_2 molecule the following relation is obtained

$$I_1I_2I_3 = \frac{8d^6M_0^3M_s \sin^2\Theta \cdot \cos^2\Theta \, [(2M_0 + M_s) \sin^2\Theta + M_s \cos^2\Theta]}{(2M_0 + M_s)}$$

M_0 and M_s represent the masses of oxygen and sulfur atoms, respectively. d represents the S–O distance and Θ refers to the half angle. Cross and Brockway[29] state that the electron diffraction

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(27) Since this paper was written a paper by A. Perlick (*Z. ges. Kälte-Ind.*, **44**, 201 (1937)) has come to our attention. He has measured the heat capacity of sulfur dioxide from 100 to 258°K. and the heats of fusion and vaporization. Perlick's heat capacity results are about 1% too high for the solid from 100°K. to the melting point. In the liquid range his results range from 1.5 to 4% high. Other comparisons with results of the present work are as follows:

(0°C. = 273.1 °K.)	Perlick	This research
Melting point	197.83 ± 0.05	197.64 ± 0.05
Heat of fusion	1789 ± 5	1769 ± 2
Heat of vaporization at b. p.	6095 ± 32	5960 ± 4

The entropy of sulfur dioxide gas estimated from Perlick's measurements is about one entropy unit or 2% larger than the known value referred to later.

(28) Cardoso and Fiorentino, *J. chim. phys.*, **23**, 841 (1926).

(29) Cross and Brockway, *J. Chem. Phys.*, **3**, 821 (1935).

(30) Badger and Bonner, *Phys. Rev.*, **43**, 305 (1933).

intensity curve is very insensitive to bond angle which they estimate as 122 ± 5°.

Using various values of d within the limits of 1.46 ± 0.02 Å. we have calculated the corresponding bond angles. The results are given in Table X.

TABLE X

DETERMINATION OF THE BOND ANGLE OF THE SULFUR DIOXIDE MOLECULE

$d \times 10^8$ cm.	$2\theta°$
1.44	125.2 ± 0.4
1.45	127.1 ± .4
1.46	128.9 ± .4
1.47	130.6 ± .4
1.48	132.1 ± .4

On the basis of the data in Table X the most reliable value of the bond angle is taken as 129 ± 4°.

We thank Dr. Roy Overstreet for assistance with the experimental measurements.

Summary

The heat capacity of solid and liquid sulfur dioxide has been determined from 15°K. to the boiling point.

The melting and boiling points were found to be 197.64 and 263.08°K., respectively.

The heats of fusion and vaporization were measured calorimetrically and found to be 1769.1 and 5960 calories per mole, respectively.

The vapor pressure of sulfur dioxide was measured from the melting point to the boiling point. The observations have been represented by the equation: liquid SO_2, 197.64 to 263.5°K. (0°C. = 273.10°K.).

$$\log_{10}P(\text{inter. cm. Hg}) = -1867.52/T - 0.015865T + 0.000015574T^2 + 12.07540$$

From the calorimetric measurements, the entropy of sulfur dioxide gas at the boiling point, 263.08°K., was calculated to be 58.07 cal. deg.$^{-1}$ mole^{-1}. $S^{\circ}_{298.1} = 59.23$. This value, which is the most reliable value to use in thermodynamic calculations, agrees with the value calculated by Cross from available molecular data. The agreement is sufficient to show that the entropy of sulfur dioxide approaches zero at the absolute zero of temperature.

The experimental entropy value has been used to obtain a more reliable value of the bond angle of sulfur dioxide. The angle was calculated to be 129 ± 4°.

BERKELEY, CALIF. RECEIVED MARCH 21, 1938

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

Optical Crystallographic Studies with the Polarizing Microscope. I. Identification and Semiquantitative Determination of Acetic and Propionic *p*-Bromoanilides in their Binary Mixtures

BY W. M. D. BRYANT

The following investigation of optical properties and melting points in the binary system of acetic and propionic *p*-bromoanilides, serves as the basis of a method for the identification of small amounts of acetic and propionic acids either individually or in mixture, and in the latter case supplies a means of estimating in a semiquantitative way the relative composition. *p*-Bromoanilides are highly satisfactory as derivatives for the identification of fatty acids,[1,2] and in this capacity excel many of the more recently described acid derivatives from the standpoints of stability, ease of preparation and convenient spacing of the melting points. The present research dealing with two compounds of this group has offered a favorable opportunity for the microscopic investigation of a system of organic mixed crystals by the methods of optical crystallography and has provided an illustration of the highly specific type of information that may be gained by this kind of research.

The binary system under consideration involves a number of distinct crystalline solid phases. Acet-*p*-bromoanilide exists in at least three crystal modifications,[3] a stable and two metastable forms, while the propionic derivative is dimorphous. In addition to the pure components, metastable propion-*p*-bromoanilide forms a continuous series of mixed crystals with one of the three acetic polymorphs, extending down to

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(1) Robertson, *J. Chem. Soc.*, **115**, 1210 (1919).

(2) Kuehn and McElvain, THIS JOURNAL, **53**, 1173 (1931).

(3) (a) Gossner, *Z. Krist.*, **38**, 110 (1904); (b) Chattaway and Lambert, *J. Chem. Soc.*, **107**, 1766 (1915). Both references mention only two forms.