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THERMODYNAMIC PROPERTIES OF SULFURYL FLUORIDE
FROM 12°K TO ITS BOILING POINT. THE ENTROPY
FROM MOLECULAR AND SPECTROSCOPIC DATA

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-- ABSTRACT --

The heat capacity of sulfuryl fluoride has been measured from 12° to 218°K. A lambda transition was observed at 65.7°K. The heat of fusion at the triple point temperature, 137.34°K, was 1073 cal/mole. The heat of vaporization at the normal boiling point, 217.78°K, was 4594 cal/mole. The vapor pressure data are closely represented by the equation:

$$\log_{10} P_{\text{mm}} = 7.8323 - 1071.235/T - 0.01391 \log_{10} T$$

The liquid density from 182 to 204°K is closely represented by the equation:

$$d = 2.576 - 0.004044 T$$

The entropy of sulfuryl fluoride gas has been calculated from the calorimetric data and the third law of thermodynamics to be 62.63 E.U./mole at 217.78°K. The calculated spectroscopic entropy was 63.24 E.U./mole. The discrepancy, 0.61 E.U./mole is attributed to randomness in the solid at 0°K.

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Eight of the nine expected vibrational fundamentals for sulfuryl fluoride have been assigned from a study of the infrared spectrum¹, and six of these have been confirmed by an analysis of the Raman spectrum². The one remaining fundamental, attributed to a symmetric SF₂ bending, was estimated through an interaction of excited vibrational states in the microwave region³ to be $388 \pm 15 \text{ cm}^{-1}$, although neither the fundamental nor any of its expected overtones or combinations were observed in the infrared or Raman spectra. Since the SF₂ bending frequency is the lowest of the nine fundamentals for SO₂F₂, its contribution to calculated thermodynamic functions is the largest, and an independent experimental confirmation is desirable.

It was the purpose of this research to provide calorimetric measurements whose precision⁴ would allow the doubtful frequency to be determined within an error limit of $\pm 20 \text{ cm}^{-1}$. However, a third-law entropy comparison is complicated by the strong possibility of randomness at absolute zero, due to the nearly equal sizes of the fluorine and oxygen atoms and the nearly tetrahedral

⁺Department of Chemistry and Chemical Engineering, Fenn College, Cleveland, Ohio

¹W. D. Perkins and M. K. Wilson, J. Chem. Phys., 23, 1316 (1955)

²P. Bender and J. M. Wood, Jr., J. Chem. Phys., 23, 1316 (1955)

³D. R. Lide, Jr., D. E. Mann, and R. M. Fristrom, J. Chem. Phys., 26, 734 (1957)

⁴L. Pierce and E. L. Pace, J. Chem. Phys., 22, 1271 (1954)

symmetry³ of the sulfuryl fluoride molecule.

SAMPLE PREPARATION AND PURITY

Approximately one-half mole of sulfuryl fluoride was prepared by the reaction of sulfur dioxide with argentic fluoride⁵, and was purified by fractional distillation at atmospheric pressure. Remaining traces of sulfur dioxide and possible silicon tetrafluoride were removed by washing in neutral potassium permanganate solution. Analysis of the mass spectrum and infrared spectrum of the purified sample indicated the possibility of a very small amount of carbon dioxide as a remaining impurity.

The purity and triple-point temperature of the sulfuryl fluoride, prepared in the above manner, were determined in an adiabatic calorimeter previously described by Pace et al.⁶ The entire quantity, 53.951 g, of sample was transferred to the calorimeter by direct weighing, and equilibrium temperatures were determined for various fractions of sample melted. Temperatures were measured with a platinum resistance thermometer having an ice-point resistance of 25.5 ohms and calibrated by the National Bureau of Standards. The ice-point temperature is taken as 273.16°K.

The data are presented in Table I. Analysis of the data by usual methods⁷ yielded a triple-point temperature of 137.34°K. for pure sulfuryl fluoride, which is slightly higher than the value of 136.5°K reported by Yost and Russell⁸. The calculated mole

⁵H. J. Emeleus and J. F. Wood, J. Chem. Soc., 60, 2183 (1948)

⁶E. L. Pace, L. Pierce, K. S. Dennis, Rev. Sci. Instr., 26, 20 (1955)

⁷F. D. Rossini, "Chemical Thermodynamics", John Wiley and Sons, Inc. New York, 1950, p. 456

⁸D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry", Prentice-Hall, Inc., New York, 1944, p. 307

TABLE I

EQUILIBRIUM TEMPERATURES OF FUSION
OF SULFURYL FLUORIDE53.951 g.; $0^{\circ}\text{C} = 273.16^{\circ}\text{K}$

Equilibrium Temperature, T ($^{\circ}\text{K}$)	Fraction Melted, r	1/r
135.40	0.0123	81.3
136.81	0.182	5.49
137.01	0.336	2.98
137.12	0.522	1.91
137.22	0.709	1.41
137.34		0 (extrapolated)

fraction of impurity of the calorimetric sample was 0.0029.

LIQUID DENSITIES

Liquid densities at various temperatures were required for subsequent calorimetric calculations.

A specially designed density bulb, having a volume of 8.3 cc, was calibrated at various reference marks on its capillary neck by weighing contained volumes of mercury at known temperatures. In making density determinations, 15.683 g of sulfuryl fluoride were condensed into the bulb at 195°K. A bath of dry ice and acetone surrounding the bulb was subsequently cooled by successive additions of liquid nitrogen, and volume readings were taken at equilibrium. After cooling the bath and sample to 182°K, the system was allowed to warm very slowly, with continuous stirring, to 204°K, and additional readings were taken at intervals. Temperatures were measured with a toluene thermometer whose calibration was found to be accurate within 0.1°K at the carbon dioxide fixed point (194.7°K). A slight correction was made for expansion of the glass bulb. The correction for vapor weight of sulfuryl fluoride was negligible.

The variation of d , the liquid density of sulfuryl fluoride, in g/cc, with T , the absolute temperature in °K, from 182°K, as determined by the method of least squares, is closely represented by the equation:

$$d = 2.576 - 0.004044 T \quad (1)$$

Twenty points were observed with a mean absolute deviation of 0.001 g/cc from the values calculated from equation (1).

HEAT CAPACITY MEASUREMENTS

The adiabatic calorimeter used for these measurements has been previously described.⁶

The measured heat capacities, taking one calorie as 4.1858 joules, are listed in Table II and plotted in Figure 1. Saturated heat capacities were calculated from the equation:

$$C_s = M/n \left\{ (G - G_o) - T \frac{d}{dT} \left[(V - nv) \frac{dP}{dT} \right] \right\} \quad (2)$$

where G is the heat capacity of the calorimeter when it contains n grams of sample; G_o , the heat capacity of the empty calorimeter; V , the volume of the calorimeter in cc; v , the specific volume of the sample; M , the molecular weight of the sample; and P , the vapor pressure. Specific volumes were calculated from equation (1).

A 0.52859 gram-mole sample was used for all runs except Series 20. Due to loss of a portion of the sample on removal from the calorimeter, a final weight check on the sample could not be made. However, an indirect check was made by observing four separate heat capacities in the 80°K. to 97°K. range (Series 20) with a sample mass of 0.52765 gram moles. The mean deviation from the smooth heat capacity curve for the four check points was 0.06%. A comparison of this mean deviation (0.06%) with that of other C_s values from 80-97°K (0.08%) affords an excellent check on sample weight.

The mean deviation of the experimental points of Table II from a smooth curve is 0.09% above 50°K and 0.7% below 50°K.

Values of the saturated molar heat capacity taken from the smooth curve through the experimental points are presented in Table III. Due to extensive premelting, smoothed values from

TABLE II

THE MOLAR HEAT CAPACITY OF SULFURYL FLUORIDE
 Mol wgt 102.006; 0.52859 mole; 0°C = 273.16°K;
 1 cal = 4.1858 abs joules

Temp °K	C _g , cal/ °K/mole	Series	Temp °K	C _g , cal/ °K/mole	Series
12.29	1.879	11	80.36	11.93	5
12.91	2.049	10	80.71	11.98 ^a	20
15.12	2.722	11	81.25	12.01	7
15.75	2.915	10	81.33	12.00	4
18.96	3.848	11	84.50	12.26	6
19.81	4.175	10	85.06	12.28	5
23.49	5.106	11	86.13	12.36 ^a	20
24.67	5.466	10	86.42	12.39	4
28.45	6.415	11	86.76	12.44	7
29.68	6.705	10	90.20	12.67	5
33.28	7.284	11	91.28	12.76 ^a	20
34.99	7.821	10	92.31	12.84	7
38.47	8.421	11	95.14	13.06	5
38.79	8.525	10	96.76	13.22 ^a	20
42.86	9.069	10	97.92	13.32	7
43.74	9.151	11	100.13	13.51	5
48.37	9.743	10	103.27	13.85	7
49.17	9.898	11	105.49	14.09	5
53.76	10.67	6	108.70	14.51	7
54.16	10.71	4	110.89	14.78	5
57.84	11.12	8	114.16	15.24	7
58.29	11.19	8	116.07	15.54	5
58.73	11.24	8	121.01	16.35	5
59.17	11.28	8	124.45	17.01	7
59.61	11.36	8	125.98	17.30	5
60.04	11.41	8	128.35	17.98	7
61.31	11.64	8	131.10	19.24	7
61.72	11.71	8	137.34	Fusion	
62.13	11.81	8	142.34	25.82	18
62.53	11.88	8	143.13	25.80	16
62.62	11.87	9	147.28	25.80	16
62.93	11.95	8	149.80	25.79	19
63.27	12.02	9	152.54	25.72	16
63.33	12.09	8	155.76	25.71	19
63.73	12.13	8	158.11	25.67	16
63.90	12.29	9	164.02	25.56	16
64.12	12.30	8	167.54	25.45	19
64.51	12.45	8	169.89	25.39	16
64.53	12.47	9	173.39	25.33	19
65.02	12.74	8	175.74	25.24	16
65.15	12.81	9	177.08	25.20	17
65.7	Lambda transition		181.56	25.11	16
65.77	12.54	9	182.85	25.06	17
66.39	11.20	9	188.57	24.96	17
67.65	11.15	9	194.24	24.91	17
68.28	11.14	9	199.91	24.83	17
70.92	11.29	4	205.42	24.89	17
74.46	11.52	6	209.58	24.91	17
76.16	11.64	4	217.78	Vaporization (1 atm)	
79.51	11.87	6			

^a0.52765 mole

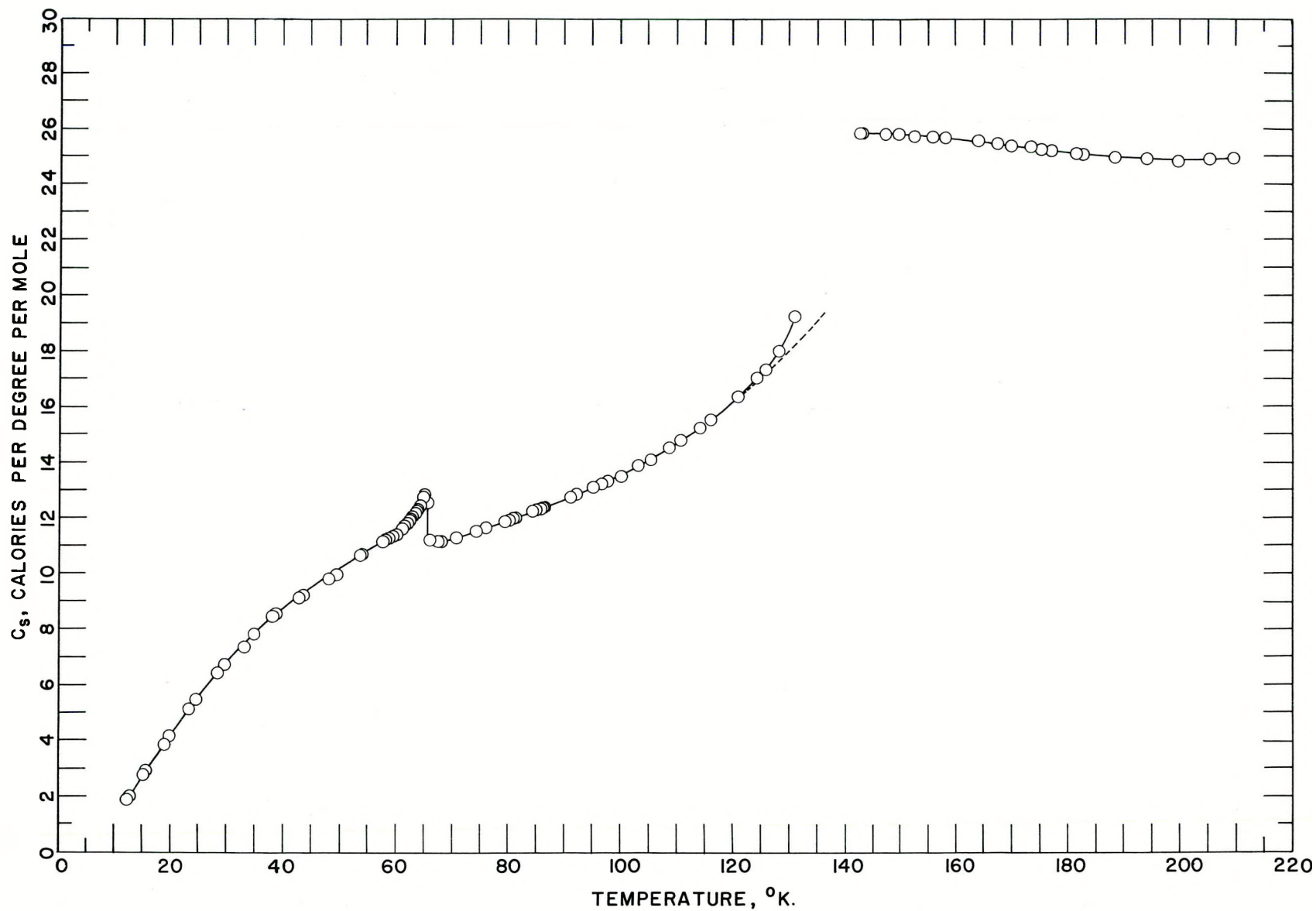


Fig. 1. The molar heat capacity of sulfuryl fluoride

124°K. to fusion (137.34°K) were taken from the dotted extrapolation of Figure 1.

HEAT OF TRANSITION AND TRANSITION TEMPERATURE

Careful heat capacity measurements, taken over small temperature intervals in the range from 58°K to 69°K, indicated a sharp peak in the heat capacity curve which appeared to extrapolate to an infinite value of C_p at 65.7°K. The heat capacity measurements gave no indication of a latent heat of transition. Based on the apparent absence of a latent heat of transition and the shape of the heat capacity curve⁹, the anomalous peak at 65.7°K was attributed to a lambda transition, which culminates on warming at 65.7°K.

Although the latent heat of the lambda transition was zero, an estimation of the heat involved in the transition, over a temperature range, was made by determining the area between the actual heat capacity curve and a curve interpolated between two smooth portions of the overall heat capacity curve. The two curves are shown in Figure 2. The approximate heat of the lambda transition, ΔH_λ , in the range from 38°K to 72°K, was graphically determined by the relation:

$$\Delta H_\lambda = \int_{38^\circ\text{K}}^{72^\circ\text{K}} (C_p - C_i) dT \quad (3)$$

where C_i was taken from the interpolated curve of Figure 2. The calculated value for ΔH_λ was 14.5 cal/mole.

⁹H. N. V. Temperly, "Changes of State", Cleaver-Hume Press, Ltd., London, 1956, pp. 232-240

TABLE III

THE MOLAR HEAT CAPACITY OF SULFURYL
FLUORIDE. VALUES TAKEN FROM SMOOTH
CURVE THROUGH OBSERVATIONS

Mol wgt 102.066; $0^{\circ}\text{C} = 273.16^{\circ}\text{K}$; 1 cal = 4.1858 abs joules

Temperature $^{\circ}\text{K}$	C_S , cal/ $^{\circ}\text{K}/\text{mole}$	Temperature $^{\circ}\text{K}$	C_S , cal/ $^{\circ}\text{K}/\text{mole}$
Crystal II		120	16.16
12	1.793	124	16.85 ^a
16	2.990	126	17.58 ^a
20	4.159	132	18.35 ^a
24	5.174	136	19.17 ^a
28	6.294	Liquid	
32	7.230	138	25.83
36	8.040	142	25.82
40	8.715	146	25.81
44	9.314	150	25.77
48	9.863	154	25.73
52	10.38	158	25.67
56	10.87	162	25.60
60	11.42	166	25.51
64	12.24	170	25.40
65	12.70	174	25.30
Crystal I		178	25.19
66	11.27	182	25.09
68	11.14	186	25.00
72	11.35	190	24.93
76	11.63	194	24.89
80	11.91	198	24.85
84	11.21	202	24.86
88	12.51	206	24.87
92	12.82	210	24.90
96	13.14	214	24.95
100	13.51	216	24.97
104	13.93	^a Extrapolated	
108	14.40		
112	14.93		
116	15.52		

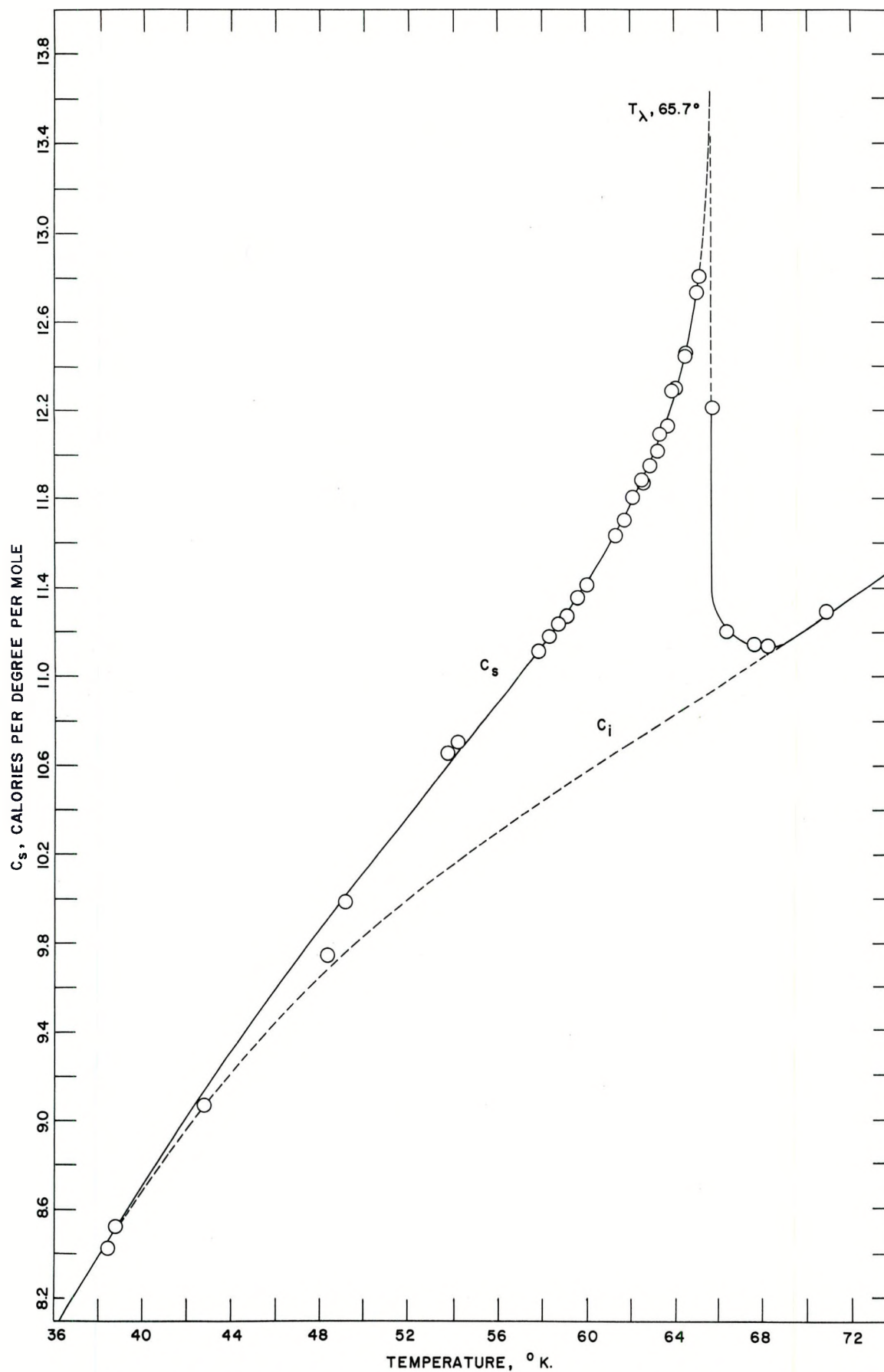


Fig. 2. Molar heat capacity of sulfuryl fluoride in the region of the lambda transition

HEAT OF FUSION

Data for the heat of fusion are listed in Table IV. Heat of fusion measurements were made by starting at a temperature below fusion and adding sufficient heat to raise the temperature of the calorimeter above that of fusion. A sensible heat correction was then made for temperature rise of the calorimeter and contents. A premelting correction was also required for one of the determinations.

VAPOR PRESSURE

Vapor pressure measurements for sulfuryl fluoride were obtained using a Gaertner precision cathetometer as a comparison instrument in conjunction with a standard meter bar. The data were fitted by the equation:

$$\log_{10} P_{\text{mm}} = 7.8323 - 1071.235/T - 0.01391 \log_{10} T \quad (4)$$

which was derived by the method of least squares. The observed and calculated pressures are listed in Table V. The usual gravity, meniscus, and temperature corrections were applied. The average absolute difference between observed and calculated vapor pressures was 0.38 mm. The last column of Table V gives the pressure observed in this research minus the pressure calculated from the equation given by Yost and Russell⁸. Agreement is better at pressures above 200 mm. than below and is excellent at 760 mm.

The normal boiling point, calculated from equation (4) is 217.78°K.

TABLE IV

HEAT OF FUSION OF SULFURYL FLUORIDE

Mol wt 102.066; 0.52589 mole; triple point 137.34°K;
 0°C = 273.16°K; 1 cal = 4.1858 abs joules

Temp Interval °K	Corr Heat Input cal/mole	Sensible Heat corr, cal/mole	Premelt Corr cal/mole	Heat of Fusion cal/mole
---------------------	-----------------------------	---------------------------------	--------------------------	----------------------------

123.93 - 141.04	1751.59	-676.39		1075.2
124.12 - 141.62	1767.39	-695.85		1071.5
133.36 - 140.74	1372.62	-311.80	12.55	1073.4

Average = 1073

TABLE V

THE VAPOR PRESSURE OF SULFURYL FLUORIDE
 Normal boiling pt. = 217.78°K; 0°C = 273.16°K

Temp °K	P _{obs} Int. mm Hg	P _{calc} ^a Int. mm Hg	P _{obs} - P _{calc}	
			This research	Yost & Russell
164.603	19.43	19.66	-0.23	+2.89
171.846	37.29	36.94	+0.35	+4.30
179.022	66.11	65.64	+0.45	+4.83
186.361	112.95	112.92	+0.03	+4.06
192.727	174.32	174.80	-0.48	+2.40
198.416	251.46	252.01	-0.55	+0.56
205.209	379.82	380.15	-0.37	-1.27
209.556	487.80	487.69	+0.11	-1.66
212.892	586.72	586.33	+0.39	-1.12
215.887	687.61	688.41	-0.80	-1.36
218.080	771.67	772.09	+0.42	+0.56

HEAT OF VAPORIZATION

Heat of vaporization measurements were made using the same heater as for all other calorimetric measurements. Since the resistance thermometer and heater were an integral unit, the thermometer could not measure the true temperature of the calorimeter while heat was being added to it. Thus, temperatures during vaporization were determined from vapor pressure readings in conjunction with the vapor pressure equation (4).

Vapor pressure measurements provided a very sensitive indication of temperature variation, particularly near the boiling point where dP/dT , the slope of the vapor pressure-temperature curve, was 39.5 mm/ $^{\circ}$ K. Using an auxiliary heater, independent of the resistance thermometer, Pierce and Pace⁴ have shown that the mean temperature of vaporization, as determined by the resistance thermometer, differed in the worst case by only 0.3 $^{\circ}$ K from that determined from vapor pressure measurements. Due to thermal gradients within the calorimeter during vaporization, the actual temperature of vaporization was probably somewhere between the value calculated from vapor pressure and that which would have been given by the resistance thermometer. The maximum uncertainty of 0.3 $^{\circ}$ K in the temperature of vaporization corresponds to an uncertainty of only four calories in the molar heat of vaporization.

The method of maintaining constant pressure during vaporization and the method of calculating heat of vaporization have been described.^{4,10} Corrections were made for heat leak to the surroundings and for temperature rise of the system (sensible heat correction). Pierce and Pace⁴ have shown that a correction for superheating of

¹⁰R. B. Scott, C. H. Meyers, R. D. Rands, F. G. Brickwedde, N. Bekkedahl, J. Research Nat'l. Bur. Standards, 35, 39 (1945)

the liquid due to hydrostatic head is negligible. In addition, calculations showed that no correction was necessary for pressure drop between the calorimeter and the manometer tap.

Table VI summarizes the data. The mean temperatures of vaporization were both close enough to the normal boiling point to obviate any correction in heat of vaporization to the normal boiling point.

THE ENTROPY FROM CALORIMETRIC DATA

The calculation of the entropy for the liquid and the gas at the normal boiling point are summarized in Table VII.

The gas imperfection correction, ΔS_i , assuming a Berthelot gas, is given by¹¹

$$\Delta S_i = \frac{27}{32} \frac{RT_c^3}{P_c T^3} \quad (5)$$

Solving the Berthelot equation of state for T_c/P_c , substituting in (5), and rearranging in terms of the compressibility factor at the boiling point, z_b , yields

$$\Delta S_i = \frac{12R (1 - z_b)}{6 - T_b/T_c} \quad (6)$$

where T_b is the normal boiling temperature. It is interesting to note that regardless of the method used for estimating the critical temperature, T_c , the error in ΔS_i will be small due to the form of the denominator of equation (6). Assuming that, for most compounds¹², T_b/T_c is equal to 0.62, and taking R as 1.987 cal.

¹¹I. M. Klotz, "Chemical Thermodynamics", Prentice-Hall, Inc., New York, 1950, p. 161

¹²S. Glasstone, "Thermodynamics for Chemists", D. Van Nostrand Co. Inc., New York, 1947, p. 502

TABLE VI

MOLAR HEAT OF VAPORIZATION OF SULFURYL FLUORIDE

Mol Wgt, 102.066; Normal boiling pt, 217.78°K;
 0°C = 273.16°K; 1 cal = 4.1858 abs joules

Series	I	II
Mean temp of Vaporization, °K	217.78	217.76
Moles vaporized	0.02603	0.03232
Total energy cal/mole	4645.2	4664.4
Heat leak correction, cal/mole	-34.6	-59.1
Sensible heat correction, cal/mole	-1.6	+7.2
Corr energy cal/mole	4609.0	4612.5
Heat of vaporization cal/mole	4592.4	4596.0
Average, cal/mole	4594	

TABLE VII

THE MOLAR ENTROPY OF SULFURYL FLUORIDES

Mol wgt, 102.066; $0^{\circ}\text{C} = 273.16^{\circ}\text{K}$; 1 cal = 4.1858 abs joules

0-13.00°K, Debye extrapolation, ($\theta = 94.2$, 6 degrees of freedom)	0.759 ± 0.04
13.00-65.70°K, $\int C_s \frac{dT}{T}$ (graphical)	10.903 ± 0.06
65.70-137.34°K, $\int C_s \frac{dT}{T}$ (graphical)	10.139 ± 0.01
Fusion, 1073/137.34	7.813 ± 0.01
Entropy of liquid at solid-liquid-vapor triple point	29.614 ± 0.12
137.34-217.78°K, $\int C_s \frac{dT}{T}$ (graphical)	11.678 ± 0.00
Entropy of liquid at normal boiling point	41.292 ± 0.12
Vaporization, 4594/217.78	21.095 ± 0.01
Gas imperfection correction	0.247 ± 0.02
Entropy of ideal gas at 217.78°K and one atmosphere pressure	62.63 ± 0.15

$\text{deg}^{-1} \text{ mole}^{-1}$, one obtains

$$\Delta S_i = 4.24 (1 - z_b) \quad (7)$$

where ΔS_i is given in E. U./mole. The molar vapor volume at the boiling point, used in determining z_b , was calculated from the Clapeyron equation.

THE ENTROPY FROM MOLECULAR AND SPECTROSCOPIC DATA

Translational and rotational entropy contributions S_t^0 and S_r^0 , in entropy units, were calculated from relations given by Wagman, et al¹³.

$$S_t^0 = 6.8635 \log M - 2.3141 + 11.4391 \log T \quad (8)$$

$$S_r^0 = 2.2878 (\log I_A I_B I_C \cdot 10^{117}) - 4.5757 \log s - 0.0332 + 6.8635 \log T \quad (9)$$

where M , the molecular weight, was taken as 102.066; T , the absolute temperature, was taken as 217.78°K; and s , the symmetry number, was taken as two. Values for I_A , I_B , and I_C , the moments of inertia, have been previously determined³.

The fundamentals used for the calculation of vibrational entropy contribution, with the exception of $\nu_4(A_1)$, the symmetric SF_2 bending frequency, were taken from the infrared data of Perkins and Wilson¹ and the Raman data of Bender and Wood². The $\nu_4(A_1)$ fundamental was taken, according to the microwave data of Lide et al³, as 388 cm^{-1} . The fundamental frequencies used in the calcula-

¹³D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, J. Research Nat'l. Bur. Standards, 34, 143 (1945)

tion of the vibrational entropy were:

$$\nu_4(A_1) = 388 \text{ cm}^{-1}$$

$$\nu_5(A_2) = 388 \text{ cm}^{-1}$$

$$\nu_9(B_2) = 539 \text{ cm}^{-1}$$

$$\nu_3(A_1) = 544 \text{ cm}^{-1}$$

$$\nu_7(B_1) = 533 \text{ cm}^{-1}$$

$$\nu_2(A_1) = 848 \text{ cm}^{-1}$$

$$\nu_8(B_2) = 883 \text{ cm}^{-1}$$

$$\nu_1(A_1) = 1269 \text{ cm}^{-1}$$

$$\nu_6(B_1) = 1502 \text{ cm}^{-1}$$

The entropy calculations are summarized in Table VIII.

DISCUSSION

The observed discrepancy of 0.61 E. U. per mole between the calorimetric entropy and the spectroscopic entropy is attributed to residual entropy at absolute zero, rather than to an incorrect assignment of the $\nu_4(A_1)$ fundamental. To provide good agreement between the calorimetric and spectroscopic entropies, the frequency of the $\nu_4(A_1)$ fundamental would have to be greater than 1000 cm^{-1} , which is extremely unlikely. On the other hand, randomness at absolute zero seems plausible due to the near symmetry³ of the sulfuryl fluoride molecule. If the molecule were considered entirely symmetrical, the residual entropy should be $R \ln 6$, or 3.56 E.U. per mole. The much lower observed value of 0.61 E.U. per mole implies a high degree of crystalline order based on six energy-equivalent positions for the molecule. Considering the slight asymmetry of the molecule and the partial crystalline ordering which occurs at the lambda transition, it appears that the number of equivalent molecular position is nearer to two.

TABLE VIII

THE MOLAR ENTROPY OF SULFURYL FLUORIDE
IN THE IDEAL GAS STATE FROM MOLECULAR
AND SPECTROSCOPIC DATA

1 atmosphere; 217.78°K

S_t° , E.U.	38.219
S_r° , E.U.	22.991
S_v° , E.U.	2.030
Total, E.U.	63.24
Calorimetric entropy, E.U.	62.63
Residual Entropy, E.U.	0.61

The results of the present work are insufficient in themselves to confirm the frequency of the symmetric SF_2 bending fundamental, $\nu_4(\text{A}_1)$, and the residual entropy value of 0.61 E.U. per mole is based on a ν_4 frequency of 388 cm^{-1} . Further gaseous heat capacity data would provide a confirmation of the ν_4 fundamental and allow the residual entropy to be determined more exactly.