SOME MOLECULAR DATA FROM RAMAN SPECTRA, ELECTRON DIFFRACTION AND LOW TEMPERATURE CALORIMETRY

Thesis by

Horace Russell, Jr.

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Dr. David P. Stevenson directed and aided in the electron diffraction experiments. Dr. Darrell Osborne is jointly responsible for the measurements on methyl mercaptan, except for the final heat of vaporization. In these measurements Dr. Thor Rubin assisted. The calibration of the resistance thermometers and the construction of the heat of vaporization apparatus was done in cooperation with Professor Don M. Yost and Dr. Rubin. Measurements on arsenic trifluoride were made jointly with Mr. Robert Rundle. Dr. C.S.Lu made the graphs and figures for this thesis. To all of these I am greatly indebted.

Especially do I wish to thank Professor Yost, under whom I have worked for the last three years. I hope my work can come up to his direction and example.

Horace Russell, Jr.

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INTRODUCTION

This thesis presents the results of molecular structure investigations carried out during the last three years by means of Raman spectra, electron diffraction, and low temperature calorimetry. The general aim of the work was the gaining of experience in several methods of structure determination as well as the accumulation and interpretation of data. Thus work was done in several fields, although the principle field of research was low temperature calorimetry. In this field valuable experimental training was gained in the calibration of a set of resistance thermometers and in the construction of an apparatus for the accurate measurement of heats of vaporization.

Three of the compounds treated are inorganic fluorine compounds; the data gained extend and in some cases verify previous knowledge of this type of compound--much of which originated in these laboratories. The methyl mercaptan is an interesting case in which restricted internal rotation occurs; it is the third of such cases examined in this laboratory.

The work is presented in essentially independent sections and in the chronological order of its performance. References are given at the close of each section.

PROPOSITIONS

1. Corrections from the real gas to the ideal gas may be made in entropy calculations by use of the experimentally derived quantities p, T, dp/dT, and $\widetilde{\Delta H}_v$. The accuracy is equal to that obtained using the Berthelot equation of state and it is not necessary to know critical constants for the gas.

2. A reinvestigation of the low temperature calorimetric work on methyl alcohol should be made before too much importance is attached to the discrepency between the barrier to internal rotation as calculated by Dennison and Kohler[1] and as calculated from calorimetric data by Crawford.[2]

   1. Dennison and Kohler, Phys. Rev. June 1940.
   2. Crawford, J. Chem. Phys. 8, 744 (1940).

3. The quantity actually measured in ordinary calorimetric work is the saturated heat capacity rather than the heat capacity at constant pressure as commonly assumed. Appreciable error may be made in liquid heat capacities near room temperature but the entropy is very little affected.

4. With the data now available, reasonable correlations can be made of the frequencies of simple inorganic molecules containing S-O and S-X bonds such as SOF_2, SO_3ClH, etc. Further polarization data are desirable.

5. An interesting program of research would be the experimental study of low temperature transitions in the solid using an automatically regulated adiabatic calorimeter. A design is proposed for the regulator.

6. In measuring heats of vaporization as described in this thesis the exact temperature of the vaporizing surface does not have to be known.

7. The sophomore course in analytical chemistry for physics majors could be more closely adapted to the needs and interests of the students. Two ways to do this are through outside reports on advanced topics and through special experiments.

8. Diffraction of slow electrons in a gas should be studied more thoroughly.

9. The sulfur point should be eliminated in the calibration of platinum resistance thermometers for low temperature work. It is desirable to find a good fixed point at about -120°C. for the calibration. If such a one cannot be found the mercury boiling point could be substituted for the sulfur point.

SUMMARY

Results of investigations by Raman spectra, electron diffraction, and low temperature calorimetry are given with calorimetry as the main field of research. The results are presented in five sections.

I. Sulfuryl fluoride was prepared and tested for purity. Although no evidence of impurity was found, a melting point of 135.9° K. was found instead of the previously reported 152° K. The Raman spectrum of both the gas and liquid were examined. Nine lines were found in the liquid, 388 (6), 456 (0), 544 (8), 845 (10), 885 (6b), 1109 (1b), 1262 (10), 1387 (0), and 1492 (5) cm^{-1} (intensities in parenthesis). Two lines were found in the gas, 859 (10), and 1279 (8) cm^{-1}. Assignments to normal vibrations of the frequencies of sulfuryl fluoride and chloride are made. The 1387 cm^{-1} frequency is assigned as a combination; the others as fundamentals. A frequency of about 350 cm^{-1} is suggested as the missing frequency.

II. Electron diffraction technique was used to investigate the structures of sulfuryl fluoride and thiophosphoryl fluoride. The interatomic distances and bond angles are: for sulfuryl fluoride, S-F=1.56±.02 A., S-O=1.43±.02 A., ∠F-S-O = 105±2°, and ∠ F-S-F = 100±10°; and for thiophosphoryl fluoride, P-F = 1.51±.02 A, P-S = 1.85±.02 A., ∠ F-P-F = 99.5±2°, and ∠ F-P-S = 118±2°.

III: A brief description of the adiabatic calorimeter and of the temperature scale of the laboratory is given. A detailed discussion of the calibration of three platinum resistance thermometers, CT 2, 4, and 7, for the international temperature scale range, and against the laboratory standard CT 26 in the

SUMMARY (con't)

range from 14° to 90° K.

Details of the construction of an improved heat of vaporization calorimeter and of the associated manometer are given next. Special features of the calorimeter are both internal and external heaters, two difference thermocouples to measure gradients on the calorimeter, a special absolute thermocouple to measure the temperature of the emerging gas, and close control over the temperature of the filling tube. The method of operation and of calculation are given.

IV. Calorimetric data on methyl mercaptan are presented including heat capacities from 15° to 279° K. A transition is found at 137.6±.15° with a heat of transition of 50.5±.5 cal/mole. The melting point is 150.162°±.02° K. with a heat of fusion of 1411.4 cal/mole. The heat of vaporization at the boiling point (279.11° K.) is 5872±4 cal/mole. The entropy from calorimetric data is 60.16±.1 e. u. at 1 atm. and 279.11° K. Comparison of this value with that calculated from spectroscopic and structual data shows a 2.02 e. u. contribution from the internal rotation in the molecule. A calculation using Pitzer's tables gives a barrier of 1460 cal.

V. Heat capacities and other data on arsenic trifluoride are given for the range from 14° to 292.50° K. Vapor pressures are also given. The melting point is 267.205°.02° K. with a heat of fusion of 2486 cal. The heat of vaporization is 8566 8 cal/mole at 292.50° K. The entropy from the data is 72.12±.1 e.u. at 141.6 mm. pressure and 292.50° K. The spectroscopic entropy is calculated as 72.13 at the same pressure and temperature. The entropy at 1 atm. and 298.1° K. is 69.08 e. u.

I

Preparations and Raman Spectrum of Sulfuryl Fluoride.

PREPARATION OF SULFURYL FLUORIDE.

The method of Trautz and Ehrman was used. Three separate operations are necessary: (1) The distillation of fluosulfonic acid from a mixture of fuming sulfuric acid and calcium fluoride, (2) the formation of the barium salt, and (3) the decomposition of the salt at 500° C. to get sulfuryl fluoride. The reactions are:

$$CaF_2 + 2SO_3 + H_2SO_4 = Ca\ SO_4 + 2\ SO_3FH$$

$$2\ SO_3FH + BaCl_2 = (F\ SO_3)_2\ Ba + 2HCl$$

$$(FSO_3)_2\ Ba = SO_2F_2 + BaSO_4$$

Iron reaction vessels were used except for the final trap. Chemicals were of C.P. grade thoroughly dried ($BaCl_2$ at 200°) except for the acid which was technical fuming 60% sulfuric acid. A number of runs were necessary to get the right technique and the yield in the last run was only about 30% based on the supposed SO_3 content of the fuming acid. This yield could be improved. It is essential that the fuming acid be of full strength (60% at least) and that the loss of SO_3 be small on the addition of the CAF_2. In the decomposition of $Ba(FSO_3)_2$ care must be taken not to heat the container too hot as SO_2F_2 reacts with red hot iron to give SO_2. A Monel container would probably be better.

The crude product was collected in a glass trap in liquid air. At -78° it was a yellow liquid smelling strongly of sulfur dioxide. This product was washed through water, then through silver nitrate solution to remove hydrogen chloride, and then through slightly acid saturated potassium permanganate solution to remove sulfur dioxide. Some hydrogen chloride passed through the silver nitrate solution (which was partly used up by precipitating silver sulfite) and was oxidized by the permanganate. The trace of chlorine was removed by washing the gas with a solution of sodium thiosulfate. Tests showed that thiosulfate removes chlorine quite completely with no formation of sulfur dioxide. After a second washing with permanganate, the gas was dried with phosphorus pentoxide. A faint pink color was observed on the P_2O_5 surface. About forty cubic centimeters of colorless liquid (at -78°) were received. The gas was colorless, odorless, and neutral to moist litmus paper. The material was frozen and pumped on, then melted and the process repeated. Finally it was distilled from a dry ice trap in an all glass system into the Raman tube, leaving about two cubic centimeters as a last fraction. A small flask fitted with a ground glass joint and stopcock, was filled with gas to 200 mm. pressure for the electron diffraction pictures. Later some material was lost when the dry ice bath level in the storage Dewar dropped, and another set of two runs was made. Raman plates and diffraction pictures were made with both preparations.

After most of the Raman plates were taken, the melting point was determined with a calibrated thermocouple. An approximate value was obtained of 135.2°K. although the result the result was not very satisfactory due to drift. The gas was washed again through permanganate solution and dried -- this time with magnesium perchlorate. It was distilled four times from a dry ice trap, leaving about one cc. the first three times as a last fraction. The last distillation was directly into the adiabatic calorimeter of Drs. Garner and Osborne. The melting point was determined to be 135.9°±.2° K. with a calculated liquid soluble, solid insoluble impurity of .5 mole per cent. After the determination, the liquid was distilled into a Raman tube, rejecting three cc. as a first fraction and 10 cc. as a last fraction. A good thirteen hour plate then obtained was one of three measured.

The melting point is in serious disagreement with the results of Trautz and Ehrman (151.7±.5° K.) and Moissan (152° K.) obtained with pentane thermometers. No sign of a transition was found at that temperature. Since our temperature scale is almost surely correct (See later section on calibration of resistance thermometers) and the adiabatic method well tested, the question of purity and identity must be examined.

The gas density was determined by weighing a 280 cc. flask, first evacuated and then filled with sulfuryl fluoride. The results are compared with those of Trautz :

		Observed	Calc. as perfect gas
This Thesis	$D^{24.7^\circ}_{741.7\text{ mm.}}$ =	4.05±.01 g/1	4.08 g/1
Trautz	$D^{16.6^\circ}_{754.6\text{ mm.}}$ =	4.23 g/1	4.27 g/1

About a gram of gas was absorbed in a basic solution, acidified, and oxidized, part with hot nitric acid and part with hot acid permanganate. Qualitative tests showed large amounts of sulfate and fluoride, but no trace of chloride or phosphate. A quantitative test for SO_2 showed less than .1% to be present. No Raman lines of any known , possible impurity are found. All plates have the same relative intensity for different lines as nearly as can be judged. The sulfuryl fluoride is thus believed to be about 99.5% pure, although a quantative analysis is projected to be sure.

The Raman Spectrum of Sulfuryl Fluoride.

Fifteen Raman plates were taken of the liquid with exposures of from three to thirteen hours. Three plates were taken using a sodium nitrite solution filter to prevent any ambiguity in assignment of the exciting line . About twenty cubic centimeters of the liquid were contained in a standard Pyrex Raman tube mounted in a dry ice-alcohol bath. The Dewar vessel holding the bath was unsilvered on one side and through this side the tube was illuminated by a water cooled Pyrex mercury arc. An iron arc was used as a comparison spectrum. The spectograph was a glass prism instrument with a dispersion of about 60Å per millimeter. The plates were measured on a comparator and a plot of deviation from linearity determined from the comparison iron spectrum used to fix positions of the lines. A five hour and a thirteen hour plate were used for the final measurements. Microphotometer traces aided in identifying the lines and in the intensity estimations. The lines found are listed in Table I.

TABLE I

Raman Frequencies of Liquid Sulfuryl Fluoride.

Frequency (cm.-1)	Intensity	No. of Exciting Lines Scattered from
388	6	4
544	8	3
456?	0	1
845	10	5
885	6b	3
1109	1b	1
1262	10	5
1387?	0	1
1492	5	2

Measurements are ± 1 $cm.^{-1}$ for the sharp lines and ± 3 $cm.^{-1}$ for the broad lines.

The Raman spectrum of the gas was photographed using the mercury resonance line from a quartz water-cooled arc and a quartz prism spectrograph. Mercury vapor inside the spectograph case absorbed much of the exciting line. The gas was contained in a quartz tube under ninety pounds gauge pressure. Four plates were taken with exposures of from ten to twenty hours. Longer exposures had excessive background. Only the two strongest lines could be found as shown in Table II.

TABLE II

Raman Frequencies in Sulfuryl Fluoride Gas.

Frequency (cm.-1)	Intensity
859	10
1279	8

Measurements are ± 1 $cm.^{-1}$

Discussion of Raman Spectrum.

The structure of the molecule is known from electron diffraction experiments (see next section of this thesis) to have symmetry C_{2v}. A normal coordinate treatment has never been made, but the vibrations, resolved into those of symmetry coordinates, are given by Sponer[2]. The characteristics and selection rules for the vibrations are easily computed from tables given by Kohlrausch[3]. The vibrations are pictured in Table III, together with the selection rules. Assignments for sulfuryl chloride and sulfuryl fluoride are given in Table IV. Sulfuryl chloride is included as it has not been previously done and as the polarization data and comparisons are necessary for the assignments.

These assignments are made on the basis of empirical rules and analogy and are not to be considered as final, although they are probably correct. Most doubtful are the $\delta^{(1)}\perp$ and the δ frequencies for sulfuryl fluoride. Much use was made of the data collected by Yost[5] on the Raman spectra of volatile fluorides. The empirical rule that $\frac{\nu_{M-F}}{\nu_{M-Cl}} = 1.7 - 2.0$ is seen to hold quite well. The $\delta^{(1)}\parallel$ frequency for sulfuryl fluoride is suggested from it and from ratios of what are presumably similar frequencies in thionyl chloride and fluoride. Polarization data for sulfuryl fluoride would aid considerably in the assignments. For example, the 1387 frequency, assigned as a combination, should be polarized. Since none of the vibrations are degenerate, calculations of thermodynamic functions would not be affected by interchange of assignments.

REFERENCES.

1. Trautz and Ehrman, Jour. fur prakt. Chem. <u>142</u>, 79 (1935).

2. Sponer, "Molekulspektren", Vol. II, p. 87 (1936).

3. Kohlrausch, "Der Smekal-Raman-Effekt", Erganzungsband, p. 37-52 (1938).

4. Cabannes and Rousset, Ann. phys. <u>19</u>, 229 (1933).

5. Yost, Proc. of the Indian Academy of Science, VIII, 333 (1938).

TABLE IV

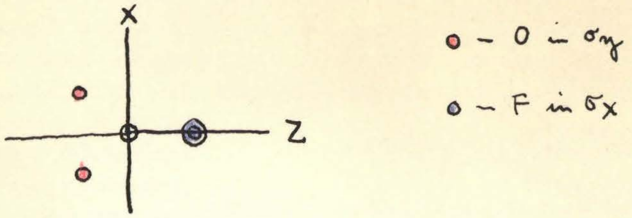
Vibration	Assignments	
	Sulfuryl Fluoride	Sulfuryl Chloride*
$\nu_t^{(1)} \parallel$	845 (10)	408 (10) P
$\nu_t^{(2)} \parallel$	1262 (10)	1190 (1) P
$\nu^{(1)} \perp$	885 (6b)	390 (5) D
$\nu^{(2)} \perp$	1492 (5)	1415 (0) D
$\delta^{(1)} \parallel$	[350] ?	214 (5) P
$\delta^{(2)} \parallel$	544 (8)	556-63 (5) P
$\delta^{(1)} \perp$	?456 (0)	280 (2) D
$\delta^{(2)} \perp$	388(6)	365 (1) D
δ	1109 (1b)	? 576 (0) D
$\nu_t^{1} \parallel + \delta_t^{2} \parallel$	1387 (0)	

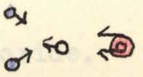
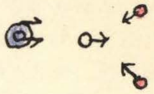
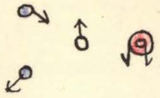
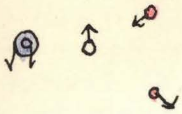
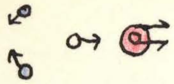
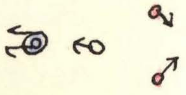
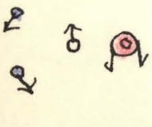
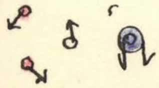
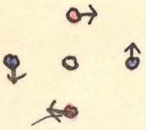
Estimated intensity in (). P means polarized; D depolarized.

*Measurements by Cabannes and Rousset, Ref. 4.

TABLE III

Vibrations of a Molecule of the
SO_2F_2 Type - Symmetry C_{2v}



Vibration	Movement of Atoms	Type (Placzek)	Section Rule	Description
$\nu_t^{(1)} \parallel$		A	P M_z	s-x ∥ stretching
$\nu_t^{(2)} \parallel$		A	P M_z	s-o ∥ stretching
$\nu^{(1)} \perp$		B	D M_y	s-x ⊥ stretching
$\nu^{(2)} \perp$		B	D M_x	s-o ⊥ stretching
$\delta_t^{(1)} \parallel$		A	P M_z	s-x ∥ bending
$\delta_t^{(2)} \parallel$		A	P M_z	s-o ∥ bending
$\delta^{(1)} \perp$		B	D M_y	s-x ⊥ bending
$\delta^{(2)} \perp$		B	D M_x	s-o ⊥ bending
δ		A	D ia	torsion bending

P means polarized; D, depolarized; M_x etc. indicates direction of electric moment produced; ia means inactive in infrared.

II

Electron Diffraction Studies On Sulfury Fluoride and Thiophosphoryl Fluoride.

[Reprinted from the Journal of the American Chemical Society, **61**, 3264 (1939).]

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 736]

The Molecular Structures of Sulfuryl Fluoride and Thiophosphoryl Fluoride

BY D. P. STEVENSON[1] AND HORACE RUSSELL, JR.

The relations between bond length and bond character in molecules containing bonds of the type sometimes called semipolar are not well understood. Among the compounds of phosphorus and sulfur there are a great number of such molecules, some of which have been investigated recently.[2,3,4] In this paper we give the results of an electron diffraction investigation of the structures of two such molecules containing fluorine atoms as well as semipolar double bonds.

Experimental.—The electron diffraction apparatus used in this investigation has been described by Brockway.[5] The camera distance was 10.84 cm., and the wave length of the electrons, determined in the usual fashion,[5] was 0.0611 Å.

Fifty cc. (S. T. P.) of pure thiophosphoryl fluoride was given to us by Professor H. S. Booth and Miss M. C. Cassidy of Western Reserve University, who have described the preparation and purification of the substance.[6] The sample was transferred to a bulb of about 150 cc. capacity which could be attached to the apparatus by means of a ground joint.

The preparation and purity of the sulfuryl fluoride used will be described in a separate paper on the Raman spectrum of this compound.[7] The pressure of the gas in the sample bulb was approximately 200 mm.

Interpretation.—Both the radial distribution method[8] and the correlation method[9] were used in interpreting the electron diffraction photographs. The modified radial distribution formula

$$D(l) = \sum_{\mathrm{n}} C_{\mathrm{n}} \frac{\sin s_{\mathrm{n}} l}{s_{\mathrm{n}} l} \quad C_{\mathrm{n}} = \mathrm{f}(I_{\mathrm{n}}, s_{\mathrm{n}}) \qquad (1)$$

has been discussed by Schomaker.[10]

It has been remarked in the literature[9,11] that the coefficients Z_iZ_j in the simplified theoretical scattering formula ordinarily used

$$I(s) = \sum\sum Z_i Z_j \frac{\sin l_{ij}s}{l_{ij}s} \qquad (2)$$

are not completely satisfactory when the atoms i and j are members of different rows of the periodic system, and that the more exact expression

$$I(s) = \sum\sum (Z_i - f_i)(Z_j - f_j)\ \frac{\sin l_{ij}s}{l_{ij}s} \qquad (3)$$

should be used. Since the corresponding coefficients in (2) and (3) differ by as much as 30% when $4 \leqslant s \leqslant 10$ for sulfuryl fluoride and thiophosphoryl fluoride, it was thought that it might be necessary to use (3) rather than (2) in the application of the correlation method to the interpretation of the photographs of these molecules. However, curves calculated according to (2) and (3) were found to be indistinguishable qualitatively and to have differences in the position of their maxima and minima of about 1% within the range of s indicated above. Since for $s \geqslant 12$ the coefficients of (2) and (3) are the same within 2%, it is thus satisfactory to use (2) rather than (3) in interpreting the photographs of sulfuryl fluoride and thiophosphoryl fluoride when $s > 12$. When $s < 12$ the photographs were compared with curves calculated according to (3).

Inasmuch as the two molecules under consideration are rather rigid, it was thought unnecessary to include a temperature factor[5] in the coefficients of the scattering formulas.

Sulfuryl Fluoride.—The photographs of this molecule show seven measurable maxima, six measurable minima, and two shelf-like features. The first shelf, designated *a*, is a shoulder on the inner side of the first maximum. The second shelf, feature *b*, is on the outside of the third maximum. The intensities of the maxima decrease uniformly from the first through the seventh. The only irregularity in the decreasing depth of the minima is that the fifth minimum is shallower than either

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(1) National Research Fellow.

(2) L. O. Brockway and J. Y. Beach, THIS JOURNAL, **60**, 1836 (1938).

(3) K. J. Palmer, *ibid.*, **60**, 2360 (1938).

(4) J. Y. Beach and D. P. Stevenson, *J. Chem. Phys.*, **6**, 75 (1938).

(5) L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

(6) H. S. Booth and M. C. Cassidy, Boston, A. C. S. meeting, September, 1939.

(7) Horace Russell, Jr., and D. M. Yost, to be published.

(8) L. Pauling and L. O. Brockway, THIS JOURNAL, **57**, 2684 (1935).

(9) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

(10) V. Schomaker, Baltimore, A. C. S. meeting, April, 1939.

(11) M. H. Pirenne, *J. Chem. Phys.*, **7**, 144 (1939).

the fourth or sixth minimum. The visually estimated relative intensities and the measured values of $s\left(s_0 = \frac{4\pi}{\lambda} \sin \frac{\vartheta}{2}\right)$ of the maxima and minima are given in columns 3 and 5 of Table I.

TABLE I

Max.	Min.	I_0	C_n	s_0	s^a	s^a/s_0	s^b	s^b/s_0
a		5	2	3.43	...	....	...	....
1		10	6	5.81	5.54	(0.954)[c]	5.57	(0.959)[c]
	2	−9	−7	7.22	7.24	1.003	7.22	1.000
2		8	8	8.80	8.92	1.014	8.92	1.014
b		4	5	11.21	...	....	...	....
	3	−6	−8	12.26	12.09	0.986	12.03	0.981
3		6	8	13.92	13.89	0.998	13.72	0.986
	4	−4	−6	15.41	15.48	1.005	15.42	1.001
4		4	6	16.77	16.94	1.010	16.91	1.008
	5	−2	−3	17.82	18.12	1.017	18.00	1.010
5		3	5	19.10	19.10	1.000	19.01	0.995
	6	−3	−6	20.51	20.49	0.999	20.50	1.000
6		2	4	22.09	21.89	.991	21.83	0.988
	7	−1	−2	23.25	23.22	.999	23.21	.998
7		1	2	25.02	24.55	(.981)[c]	24.49	(.979)[c]
Average of 11 features						1.002 ± 0.007		0.998 ± 0.008

[a] From curve for model with S − F/S − O = 1.56/1.43. F − O/S − O = 2.36/1.43. [b] From curve for model with S − F/S − O = 1.56/1.43, F − O/S − O = 2.38/1.43. [c] Omitted from average.

The radial distribution function (1), calculated with the coefficients C_n of column 4, Table I, is shown in Fig. 1, curve B. The first maximum at 1.48 Å. is an unresolved average of the sulfur–oxygen and the sulfur–fluorine distances. If one assumes the sulfur–oxygen distance to be 1.43 Å., the distance found in sulfuryl chloride,[4] one may estimate the sulfur–fluorine distance to be 1.52 Å. Since the term involving the fluorine–oxygen distance is four times as important in the scattering formula as the terms involving the fluorine–fluorine and oxygen–oxygen distances, the second peak at 2.37 Å. probably corresponds closely to the fluorine–oxygen distance.

If one assumes, as has been found to be the case for sulfuryl chloride,[4] that the sulfuryl fluoride molecule is a bisphenoid with symmetry C_{2v}, there are three parameters which determine the form of the intensity curves. These may be conveniently taken as ρ_1, the ratio of the sulfur–fluorine to sulfur–oxygen distance, ρ_2, the ratio of the fluorine–oxygen to sulfur–oxygen distance, and β, the fluorine–sulfur–fluorine angle.

The radial distribution function indicates that the value of ρ_1 is in the vicinity of 1.52/1.43 and the value of ρ_2 is near 2.37/1.43. Eighteen curves were calculated,[2] for models with the parameters ρ_1 and ρ_2 in the ranges $1.48/1.43 \leqslant \rho_1 \leqslant 1.60/1.43$ and $2.32/1.43 \leqslant \rho_2 \leqslant 2.44/1.43$.

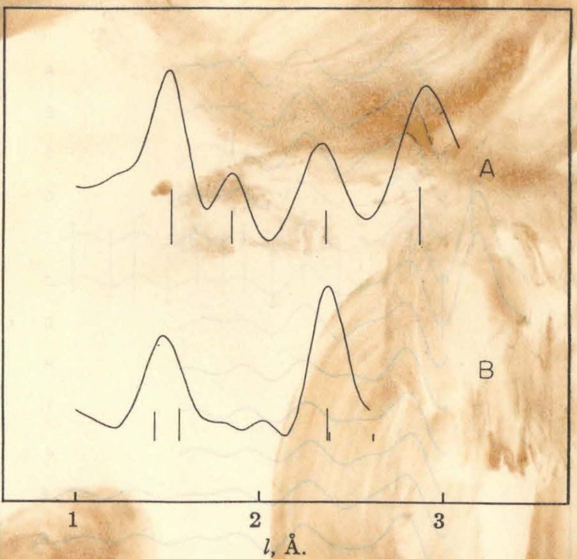


Fig. 1.—Radial distribution function, $D(l)$ vs. l: Curve A, thiophosphoryl fluoride; Curve B, sulfuryl fluoride. The vertical lines represent the internuclear distances found.

The parameter β was assumed to be 100° for all these curves. This is roughly the value found for the chlorine–sulfur–chlorine angle in sulfuryl and thionyl chlorides, and the qualitative and quantitative character of the theoretical curves is quite insensitive to variations in the value of this parameter. Some of these curves are shown in Fig. 2. Of these curves only the two with $\rho_1 = 1.56/1.43$ and $\rho_2 = 2.36/1.43$ or $2.38/1.43$ are in agreement with the appearance of the photographs. Curves were then calculated for models with these values of ρ_1 and ρ_2 with $\beta = 90$ and 110°. The curves with $\beta = 90°$ are unsatisfactory because feature b disappears while for $\beta = 110°$ the fifth maximum is too low. This is illustrated by curves E_1 and E_2 of Fig. 2.

Quantitative comparison of the photographs with the curves for $\rho_1 = 1.56/1.43$, $\beta = 100°$ and $\rho_2 = 2.36/1.43$ and $2.38/1.43$ is made in Table I, columns 7 and 9. The agreement is quite satisfactory. The final results for the structure of sulfuryl fluoride are

$$\begin{array}{ll} \text{S–F} = 1.56 \pm 0.02\ \text{Å.} & \angle\text{F–S–O} = 105 \pm 2° \\ \text{S–O} = 1.43 \pm 0.02\ \text{Å.} & \angle\text{F–S–F} = 100 \pm 8° \\ \text{F–O} = 2.37 \pm 0.02\ \text{Å.} & \angle\text{O–S–O} = 130 \pm 10° \end{array}$$

Thiophosphoryl Fluoride.—The photographs of thiophosphoryl fluoride were exceptionally clear, showing nine rings. The first and third maxima appear weaker than the second maximum, and the fifth maximum is weaker than the

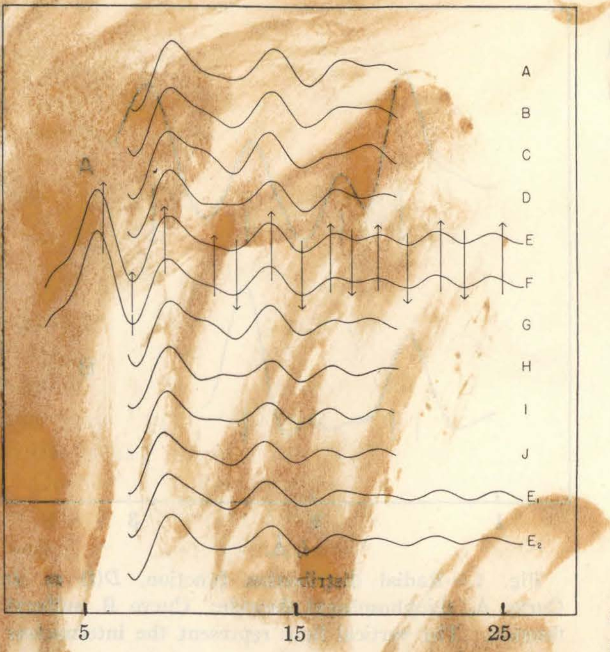


Fig. 2.—Theoretical scattering curves for sulfuryl fluoride:

Curve A, $\rho_1 = 1.52/1.43$; $\rho_2 = 2.32/1.43$; and $\beta = 100°$
Curve B, 2.36/1.43 100°
Curve C, 2.40/1.43 100°
Curve D, $\rho_1 = 1.56/1.43$ 2.32/1.43 100°
Curve E, 2.36/1.43 100°
Curve F, 2.38/1.43 100°
Curve G, 2.40/1.43 100°
Curve H, $\rho_1 = 1.60/1.43$ 2.32/1.43 100°
Curve I, 2.36/1.43 100°
Curve J, 2.40/1.43 100°
Curve E_1, $\rho_1 = 1.56/1.43$ 2.36/1.43 110°
Curve E_2, 2.36/1.43 90°

fourth and sixth maxima. The fourth minimum is deeper than the third minimum and the sixth minimum is slightly deeper than the fifth minimum. The visually estimated relative intensities are given in Table II along with the values of $s_{\text{obs.}}$.

The radial distribution function calculated according to (1), with the coefficients C_n, given in column 4 of Table II, has four maxima (see curve A, Fig. 1) at 1.50, 1.85, 2.33, and 2.90 Å. These correspond to the four distances, phosphorus–fluorine, phosphorus–sulfur, fluorine–fluorine and fluorine–sulfur. The fluorine–phosphorus–fluorine and fluorine–phosphorus–sulfur angles computed from these distances are 100 and 118°, respectively.

If this molecule has the symmetry C_{3v}, two structural parameters determine the shapes of

TABLE II

Max.	Min.	I_0	C_n	s_0	s_c[a]	s_0/s_c
1		5	2	2.95	..	..
	2	−9	−5	3.62	..	..
2		10	6	5.06	4.84	(0.957)[b]
	3	−2	−2	5.84	6.28	(1.075)
3		3	3	7.01	6.89	(0.983)
	4	−8	−9	7.67	7.71	1.005
4		8	9	9.17	9.09	0.991
	5	−5	−7	10.15	10.34	1.019
5		4	6	11.46	11.35	0.990
	6	−6	−9	12.36	12.42	1.005
6		6	10	13.89	13.73	0.988
	7	−4	−7	15.57	15.70	1.008
7		4	7	17.67	17.65	0.999
	8	−3	−5	19.36	19.13	0.988
8		3	5	21.73	22.00	1.013
	9	−1	−2	23.25	23.45	1.009
9		1	2	25.19	24.90	0.988
		Average of 12 features				1.001 ± 0.010

[a] From model with $\frac{P-F}{P-S} = \frac{1.52}{1.85}$ and $\angle F\text{–}P\text{–}F = 99°$.

[b] Values in parentheses omitted from average because of unreliability of measurements.

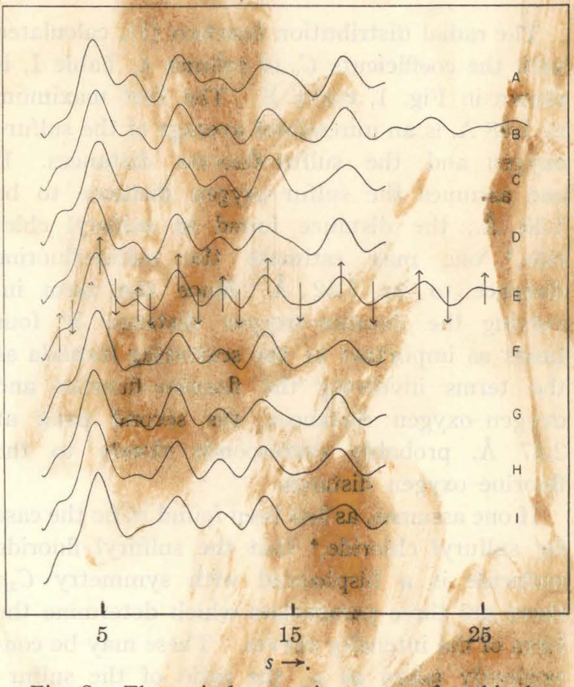


Fig. 3.—Theoretical scattering curves for thiophosphoryl fluoride.

Curve A, $\rho = 1.48/1.85$ $\alpha = 96°$
Curve B, 99°
Curve C, 102°
Curve D, $\rho = 1.52/1.85$ 96°
Curve E, 99°
Curve F, 102°
Curve G, $\rho = 1.54/1.85$ 96°
Curve H, 99°
Curve I, 102°

TABLE III

	P–F	P–Cl	P–Y	X–P–X	Reference
PF_3	1.52 ± 0.02 Å.			104 ± 4°	12 and 8
OPF_3	1.52 ± 0.02		1.56 ± 0.02 Å.	107 ± 2°	2
OPF_2Cl	1.51 ± 0.02	2.01 ± 0.02 Å.	1.55 ± 0.03	106 ± 3°	2
$OPFCl_2$	1.50 ± 0.03	2.02 ± 0.02	1.54 ± 0.03	106 ± 3°	2
$OPCl_3$	....	2.02 ± 0.02	(1.58)[a]	106 ± 1°	2
PCl_3	....	2.00 ± 0.02		101 ± 2°	12 and 8
SPF_3	1.51 ± 0.02		1.85 ± 0.02	99.5 ± 2°	This research
$SPCl_3$		2.01 ± 0.02	1.94 ± 0.03	107 ± 3°	4

[a] This distance was assumed.

appropriate models and the form of the theoretical intensity curves. These parameters are conveniently taken as the ratio ρ of the phosphorus–fluorine to the phosphorus–sulfur distance, and α the fluorine–phosphorus–fluorine angle.

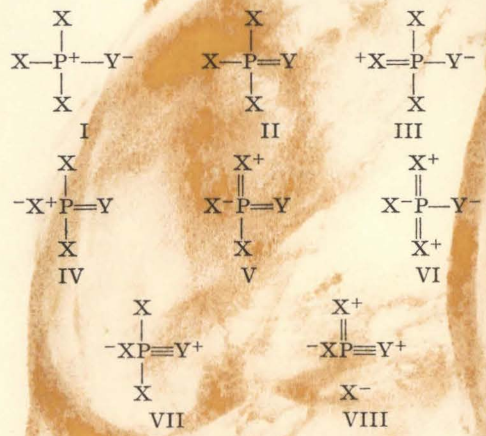
Curves were calculated for eighteen models, in which α was varied from 90–108° and ρ was varied from 1.54/1.85 to 1.46/1.85. A selection of these curves is shown in Fig. 3. All models with $96° \geqslant \alpha \geqslant 102°$ could be eliminated because the appearance of the third maximum on the curves is not that of the photographs and they show an asymmetry on either the outer side of the sixth maximum or the inner side of the seventh maximum while on the photographs these maxima appear quite symmetrical. The model with $\alpha = 99°$ and $\rho = 1.54/1.85$ is unsatisfactory because its fourth minimum is not deeper than its third and the sixth minimum is not deeper than the fifth. The curves for models with $\rho = 1.50/1.85$ and $\alpha = 99°$ show a shelf on the inner side of the ninth maximum and are unsatisfactory for this reason.

The curve calculated for the model $\rho = 1.52/1.85$ and $\alpha = 99°$ is in good qualitative agreement with the photographs. The quantitative comparison of this model with the photographs is shown in Table II. The final results for the structure of thiophosphoryl fluoride are P–F = 1.51 ± 0.02 Å., P–S = 1.85 ± 0.02 Å., ∠ F–P–F = 99.5 ± 2°, and ∠ F–P–S = 118 ± 2°.

Discussion.—Table III presents a summary of the structures found for molecules of the type X_3PY.

The distances predicted by the covalent radius table[13] are P–F (single bond) = 1.74 Å., P–Cl (single bond) = 2.09 Å., P–O (double bond) = 1.57 Å., and P–S (double bond) = 1.95 Å. The structure of thiophosphoryl fluoride presents two interesting differences from the structures of the other molecules in the group that have been studied, a decrease of 0.09 Å. in the phosphorus–sulfur distance and a small fluorine–phosphorus–fluorine angle.

An explanation for the first of these differences may be found from a consideration of the various resonating valence bond structures that may be written for molecules of this type.



The much greater shortening observed for the phosphorus–fluorine distance, 0.22 Å., than for the phosphorus–chlorine distance, 0.08 Å., has been explained by the assumption of a larger contribution of structures IV–VIII to the resultant structure of molecules containing fluorine, made possible by the larger electronegativity[14] of fluorine. Since the electronegativity of oxygen is so much larger than the electronegativity of phosphorus and sulfur, structures VII and VIII are unimportant in the molecules X_3PO. Thus we interpret the extra shortening of the phosphorus–sulfur bond in thiophosphoryl fluoride as due to considerable triple bond character made possible by the large electronegativity of fluorine and the small difference in the electronegativity between phosphorus and sulfur.

Although several explanations for the small fluorine–phosphorus–fluorine angle in thiophos-

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(12) L. O. Brockway and F. T. Wall, THIS JOURNAL, **56**, 2373 (1934).

(13) L. Pauling and L. O. Brockway, *ibid.*, **59**, 1223 (1937).

(14) L. O. Brockway, *J. Phys. Chem.*, **41**, 185 (1937).

phoryl fluoride present themselves, a satisfactory one cannot be advanced until more data have been acquired.

The sulfur–fluorine distance in sulfuryl fluoride, 1.56 Å., is 0.12 Å. less than the single bond distance predicted by the covalent radius table.[13] This shortening is not as great as is observed in the fluorine derivatives of phosphorus. A similar situation obtains for the corresponding chlorine compounds of sulfur and phosphorus.

It is of interest to note that, although there is much more shortening in the sulfur–halogen bond in sulfuryl fluoride than in sulfuryl chloride, the sulfur–oxygen distance in sulfuryl fluoride, 1.43 Å., is just that found for this distance in sulfur dioxide,[15] sulfur trioxide,[3] and sulfuryl chloride.[3]

In conclusion it should be remarked that the large uncertainty in the fluorine–sulfur–fluorine angle, ±8°, introduces an uncertainty of less than 0.1 E. U. into the calculation of the rotational entropy from the structure of the molecule.

Summary

The structures of sulfuryl fluoride and thiophosphoryl fluoride have been investigated by the electron diffraction technique. The interatomic distances and bond angles are: for sulfuryl fluoride, S–F = 1.56 ± 0.02 Å., S–O = 1.43 ± 0.02 Å., ∠ F–S–O = 105 ± 2°, and ∠ F–S–F = 100 ± 10°; and for thiophosphoryl fluoride, P–F = 1.51 ± 0.02 Å., P–S = 1.85 ± 0.02 Å., ∠ F–P–F = 99.5 ± 2°, and ∠ F–P–S = 118 ± 2°. The relationship between the structures found and the resonating valence bond structures is briefly discussed.

Pasadena, Calif. Received September 25, 1939

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[15] V. Schomaker and D. P. Stevenson, to be published.

III

Low Temperature Calorimetry

Introduction to the Calorimetric Work.

Description of Apparatus.

During the last five years calorimetric apparatus has been constructed in this laboratory for the accurate determination of vapor pressures, heat capacities, and heats of transition, fusion, and vaporization. The first apparatus built was a non-adiabatic calorimeter for the use to 60° K. described by Dr. Osborne [1] and Dr. Garner [2] in their theses in 1938. The calorimeter was used for preliminary measurements on trichlorofluoro-methane . In 1938-39 Professor Yost, Dr. Osborne and Dr. Garner constructed an adiabatic calorimeter for use from 15° K. to 300° K. This apparatus is described by Dr. Doescher [3] in his thesis and in a paper soon to be published.[4] The calorimeter was extremely satisfactory with advantages of a simple, reproducible temperature scale, freedom from heat leak corrections, and low liquid hydrogen consumption. The apparatus was used also for vapor pressures and heats of vaporization. With it measurements were made on dimethyl acetylene,[5] dimethyl sulfide [6] and trichlorofluoro-methane, [3,7] and methyl mercaptan [8] (listed in chronological order).

In July, 1940, at the close of the work on methyl mercaptan, failure to close a stopcock after vapor pressure measurements allowed mercury to flow into the calorimeter. It was consequently dismantled in the fall of 1940 and the calorimeter taken out. The apparatus was then reassembled for the thermometer calibration described in the next section of this thesis. Also a new and faster vacuum system was built using a three stage oil diffusion pump of R.C.A. design backed by a Cenco Megavac pump. About the same time work was started on the design and construction of the heat of vaporization apparatus described in a later section.

When the thermometer calibrations were completed, and after the construction of the heat of vaporization apparatus, the replated calorimeter was put in place with certain changes in the apparatus. A heater winding of a single layer of No. 30 constantin wire was put on the filling tube with No. 36 copper leads soldered on at 12 cm. intervals as both current leads and difference thermocouples. The lowest junction is 9 mm. above the top of the radiation shield and may be read absolutely. The heater leads from the shield to the calorimeter were made five cm. long instead of the six cm. previously.

On tests it was discovered that the filling tube was getting very cold and that heat leaked along it out the calorimeter. The thermal dam provided by a bakelite varnish joint at the shield was not good enough. The filling tube was then soldered to the top of the radiation shield and a foil radiation shield placed between the hydrogen can and the loops in the filling tube. The performance was much improved and the drifts were negligible. An interesting result of the improved vacuum system is that with the can constant at 15° K. almost no current is required to maintain the radiation shield at a fixed temperature anywhere in the range 15°-90° K. Both radiation and gas conduction losses are negligible.

The heat capacity of the empty adiabatic calorimeter was run in April, 1941, and measurements on arsenic trifluoride were made immediately afterward.

The Temperature Scale.

The first temperature scale of the laboratory was a copper-constantin thermocouple calibrated indirectly against the Berkeley temperature scale. This was replaced in January, 1939, by a scale based on a platinum resistance thermometer of laboratory designation CT 26, which has been used in all measurements in the adiabatic calorimeter through the arsenic trifluoride ones. This thermometer was constructed according to the designs of Meyers[9] and the specifications of the Bureau of Standards. The platinum case was .762 cm. in diameter and eight cm. long. It contained two separate coils, one of chemically pure annealed platinum wire (.0036 in. in diameter) and the other of No. 40 bare constantin wire (129Ω). Two platinum leads were gold soldered to the constantin coil, and, where they emerge through the glass head of the thermometer case, each was soft soldered to two copper wires which served as current and potential leads, respectively, to the heater. Each end ofthe platinum thermometer coil was welded to two platinum lead wires, the branch points in this case being inside the thermometer case.

The thermometer was calibrated for use with the Callender--Van Dusen formula :

$$t = \frac{R-Ro}{\alpha Ro} + \delta\left(\frac{t}{100} - 1\right)\left(\frac{t}{100}\right) + \beta\left(\frac{t}{100} - 1\right)\left(\frac{t}{100}\right)^3$$

The Ro was measured in an ice bath; then α was determined by comparison in a steam bath with a Leeds and Northrup resistance thermometer which had been calibrated three months previously by the

Bureau of Standards. The δ was determined at the mercury freezing point taken as -38.870° C.[10] The thermometer was then mounted in the adiabatic calorimeter and the oxygen fixed point used to determine β. With this calibration, it was believed the temperature scale did not differ more than .02° from the international temperature scale.[10]

Below 90° K. thermometer CT 26 was calibrated[4] by means of a helium gas thermometer (corrected to the thermodynamic scale) according to the procedure described by Hoge and Brickwedde.[11] The ice point is taken as 273.16° K. Forty-four points were measured with a maximum deviation of .02° and an average deviation of .007° . Accordingly it is believed that in the range of 14°K. thermometer CT 26 measures temperatures that probably do not differ by more than .02° from the thermodynamic scale. The complete calibration of CT 26 was carried out between December, 1938 and June, 1939, by Professor Yost, Dr. Osborne and Dr. Garner.

In June, 1940, through the courtesy of Dr. Huffman of the biology department we secured a set of three resistance thermometers made by Dr. Robert Ruehrwein in the same way as CT 26. These were given laboratory designations CT 2, CT 4, and CT 7. An all platinum thermometer, CT 22, had been sent to the Bureau of Standards in the fall of 1939 for calibration from 14° K. to 440° C. and it was hoped that all thermometers could be calibrated against it. However, the thermometer had not come back, so other calibrations were made. After an ice point measurement, constants and in the Callender--Van Dusen equation were determined by comparison with the same Bureau of Standard's certified resistance thermometer that was used for the determination of α for CT 26. Comparisons were made in baths of boiling water and boiling O-toluidine (200° C.) As a check the melting point of mercury was determined for the three new thermometers.

After those determinations five thermometers, CT 26, CT 2, CT 4, CT 7, and H 3, a thermometer belonging to Dr. Huffman and of the same type as the others, were mounted with stopcock grease in closely fitting holes in a cylindrical copper block, 3.8 cm. by 11 cm. with CT 26 in the center. The block was equipped with a heater and difference thermocouple and hung by fish line from the top of the radiation shield in the adiabatic calorimeter. Comparisons were made at the oxygen point (-182.97° C.) and the constant β fixed for CT 2, CT 4, CT 7 on the basis of the oxygen point of CT 26. A few comparisons were made in the international temperature scale range; then a complete set of comparisons, at intervals of a few degrees, were made from 14° K. to 90° K. In these as for all other calibrations discussed, the switch board coil in Room 13, Gates, was taken as standard, $R = 100.000 (1+9\times10^{-6} (t-25))$. A standard current of one milliampere was used. Measurements were made with an autocalibrated White potentiometer.

Results of the calibrations are given in Tables I to III. Below 90° K. smoothed tables for the thermometers CT 2 and CT 7 were prepared. A table for CT 4 has not been made although data is available. With the smoothed tables CT 2 and CT 7 give the same temperatures from 14° to 90° K. as CT 26 within at least .01° . The greatest uncertainty in the CT 2,4,7 calibrations is in the values of th δ's. There was a spread in values obtained of .015 unit corresponding to .039° at -117° C. The cause of the spread is unknown as a high degree of constancy of temperature was achieved during the determinations. The deviations at the mercury point and at -117° C. indicate the δ's are somewhat low. An error in δ would have its maximum effect (below 0° C.) at about -117° C. However the observed deviations are only slightly more than the uncertainty in the international scale,[14,15] so it is believed the δ's are probably correct to ±.007 unit. Thermometer CT 4 has a much higher δ than allowed by the international temperature scale and shows marked deviations. A plot was made of its deviations from the average of the other three thermometers (Figure 1) and from it a smoothed table constructed.

Table I

Constants of the Thermometers for the Callender-Van Dusen Formula.

Thermometer	CT 26	CT 2	CT 7	CT 22	CT 4
R_0 (Int. ohms)	26.2820	45.7725	45.1234	22.63930	46.0269
x 10^2	.39094	.391757	.391751	.391349	.390622
	1.509	1.499	1.494	1.5118	1.551
	.1264	.1211	.1233	.12143	.1336
Freezing Point Hg[a]	38.870°[b]	-38.871°	-38.872°		-38.888°

a The FP of Hg is -38.864° on the international scale.[12,13]
b Calibration point

Table II

Values of $\Delta T_n = t_{CT\ 26} - t_{CT_n}$ in °C.

Temp. °C.	23.8	-117.9	-180.8
2	.002°	.010	.001
7	.001°	.022	.001
4	.000°	.062	.004

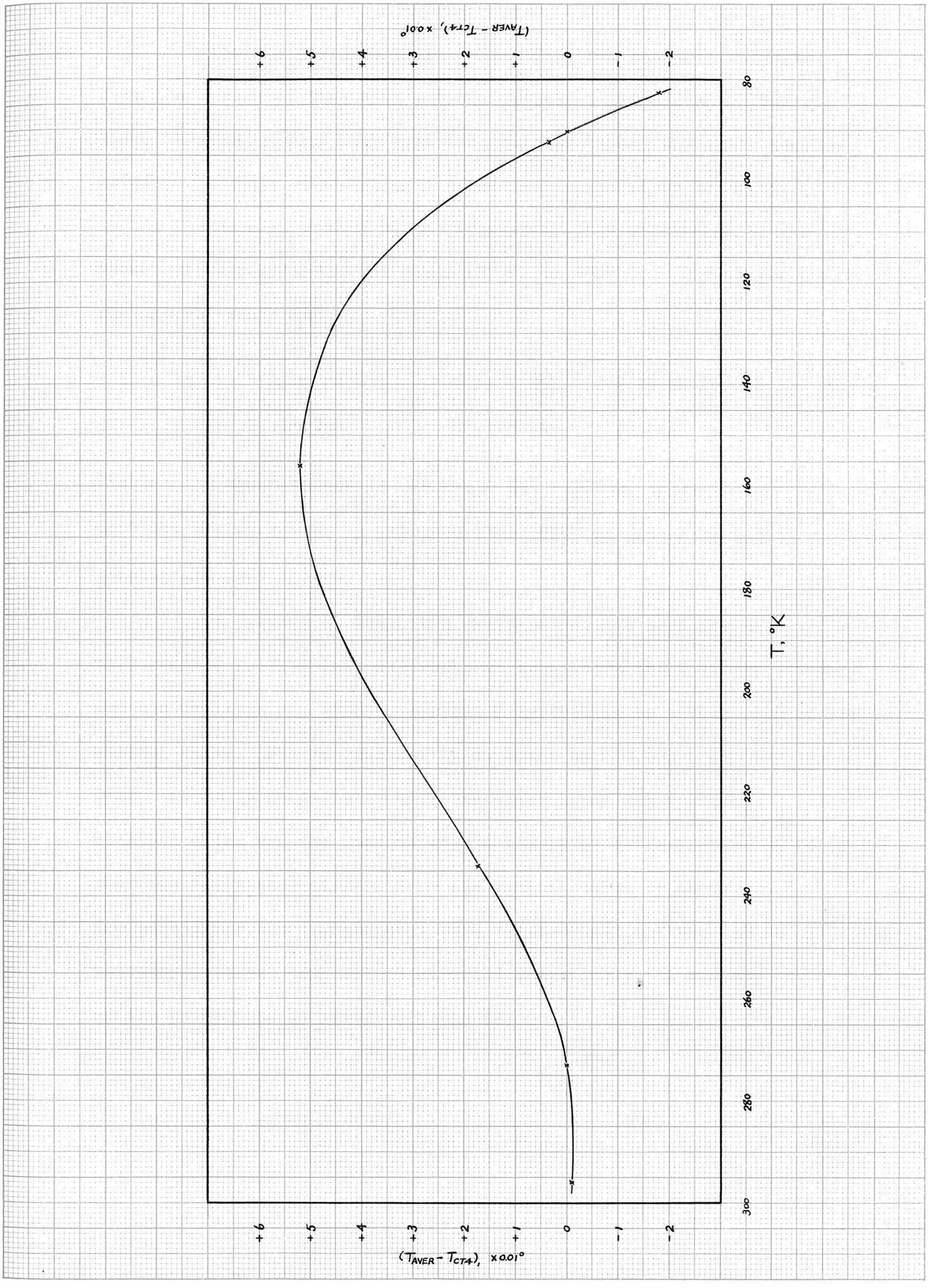
Table III

Values of $\Delta T = t^{a.}_{therm.} - t^{b}_{Cal-V.D.}$

Temp. °C.	-190.3°
2	- .044°
7	- .045°
26	- .040°
4	- .062

a. As determined by the corrected helium gas thermometer.
b. t calculated from the Callender--Van Dusen equation.

Figure 1


(T_AVER − T_CT4), x 0.01°
+6
+5
+4
+3
+2
+1
0
−1
−2
80
100
120
140
160
180
200
220
240
260
280
300
T, °K
(T_AVER − T_CT4), x 0.01°

The all platinum thermometer CT 22 has now been returned from the Bureau of Standards and its constants are listed in Table I also. No comparisons have been made between it and the other thermometers. Recently thermometer H 3 has been compared by Dr. Huffman, in his laboratory, with H 25, a thermometer just calibrated by the Bureau of Standards for the range 14° K. to 440° C. Our oxygen point was closely confirmed.

R/Ro of H 3	T by H 25	T by CT 26
.246796	90.664° K.	90.662° K.

Preliminary measurements in the range 36° - 90° K. indicate that the scales differ by not more than .025° at any point and in general are much closer.

On January 1, 1941, the switchboard coil used for all measurements to that date was replaced by a Leeds and Northrop standard 100 ohm resistor No. 288075, certified by them to be within .01% of its nominal value. For convenience it is taken as $100.000\ (1+(t-25)8\text{x}10^{-6})$ ohms. Accurate comparisons with two other Leeds and Northrop standard coils and the results of the ice point determination on CT 22 show the resistance differs from its nominal value by about .001%. Ice points for the thermometers were redetermined and the tables of resistance versus temperature adjusted accordingly. A summary of ice point data is given in Table IV.

Table IV

Ro for Resistance Thermometers in Int. Ohms.

Thermometer	CT 26	CT 2	CT 4	CT 7	CT 22
January, 1939	26.2820				22.6335[a]
August, 1940		45.7725[a]	46.0269[a]	45.1234[a]	
December, 1940					22.63930[b]
January, 1941	26.2829[c]	45.7734[c]	(46.0278)[d]	45.1240[c]	22.6396[c]

a. With switchboard coil Room 13, Gates.
b. Determined by the Bureau of Standards.
c. With Leeds and Northrup coil No. 288075.
d. Value assumed.

The temperature scale of this laboratory is seen to consist of two parts, one being the thermodynamic scale (14° - 90° K.) and the other being the international scale (above 90° K.). It is known that the international scale may differ by as much as .05° from the thermodynamic scale at some temperatures, but even the sign of the deviations is not agreed upon[14,15]. Data are therefore reported in terms of the international scale above 90° K. and in terms of the thermodynamic scale below 90° K.

Construction of a Heat of Vaporization Apparatus.

The adiabatic calorimeter is undoubtedly best suited for measurements of heat capacities and heats of transition and fusion. It was decided, however, that for the determination of vapor pressures and heats of vaporization the Nernst-Giauque [16] type of calorimeter offers definite advantages. In particular the massive copper block with its high heat capacity is more convenient to operate than a light radiation shield. By building a special calorimeter certain improvements of design for the particular measurement desired can be made. These are:

1) Heater windings on the filling tube with thermocouple junctions at frequent intervals;

2) Vertical vanes within the calorimeter so that the surface area does not change abruptly ;

3) A spray cap to prevent loss of unvaporized liquid and to insure heating of the gas to a known temperature as it leaves the calorimeter;

4) A calorimeter fairly small in capacity;

5) Internal and external heaters to check heat loss corrections and to see if the method of heating influences the result;

6) An absolute thermocouple at the top of the calorimeter to measure the temperature of the emerging gas.

Accordingly such a calorimeter was built.

Figure two shows the general plan of construction. The calorimeter is of gold plated copper with a wall thickness of .5 mm. and is provided with three separate heaters. The first, usually called

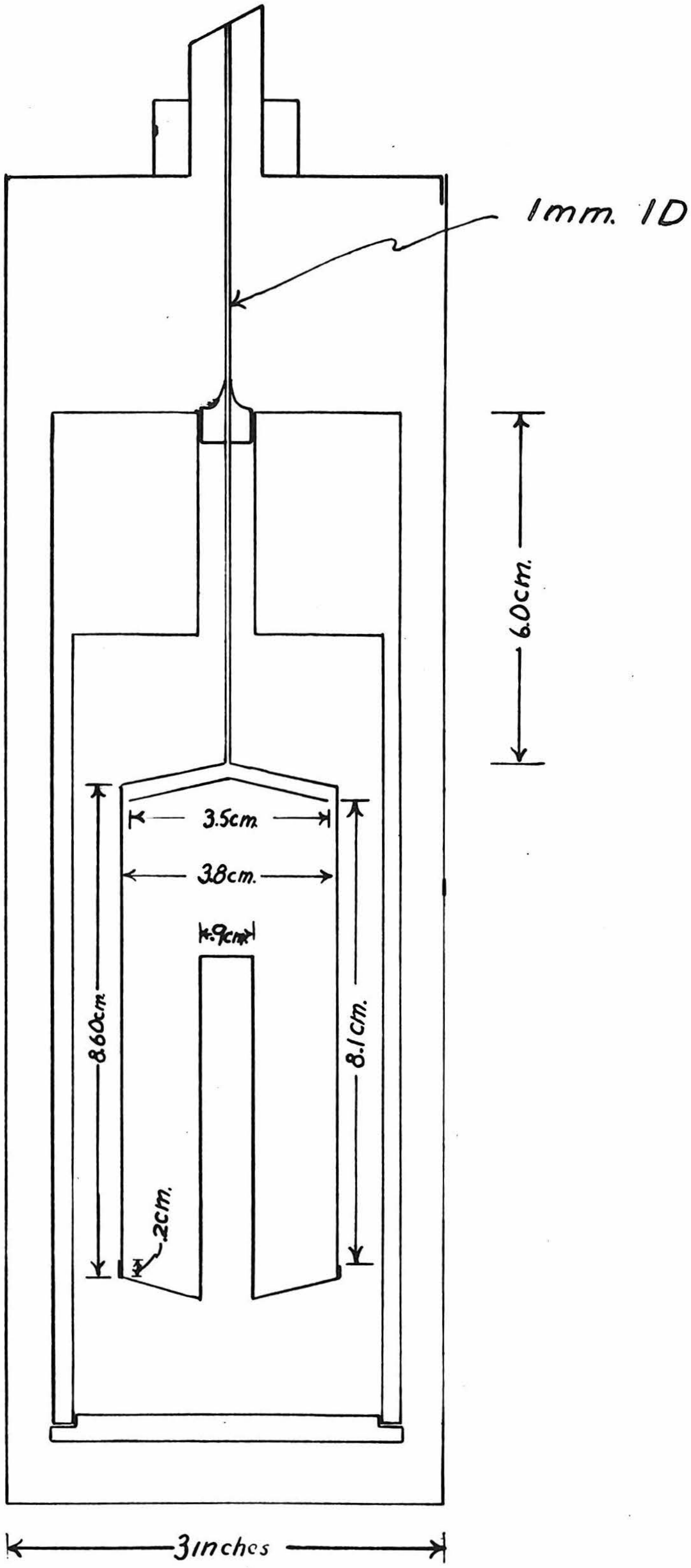


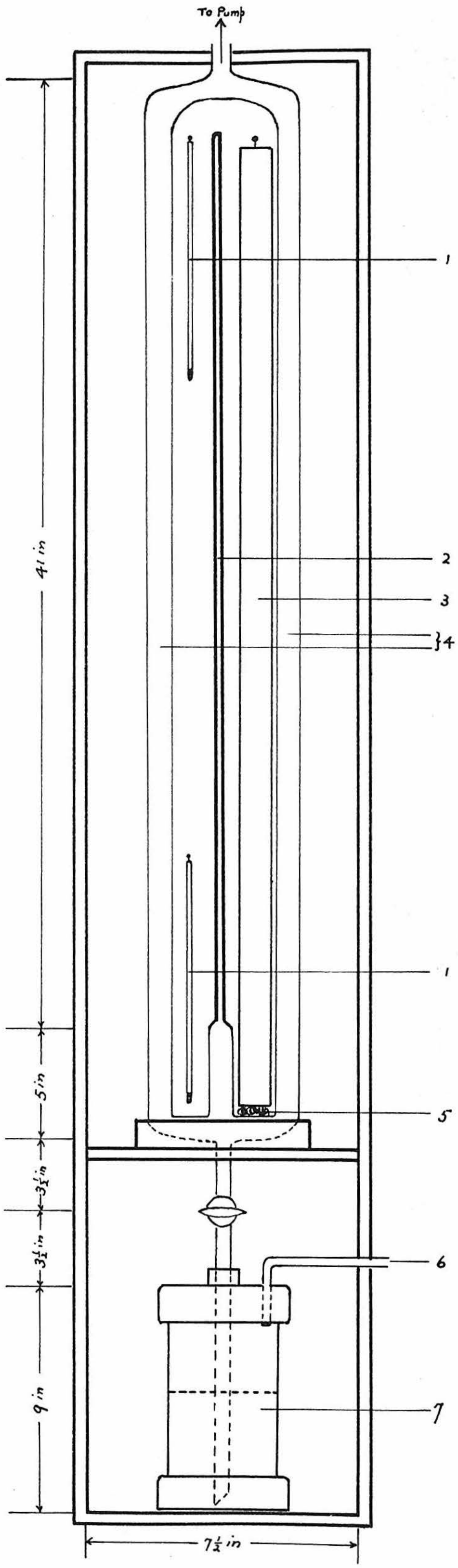
Figure 2

the inside heater, is of constantin (147.3Ω) wound inside the resistance thermometer case; the second, or bottom heater, is wound on the lower half of the calorimeter and the third is just above the second. A single layer of No. 26 bare copper wire is wound over these outer heaters and, after being impregnated with bakelite varnish and baked, was filed flat and smooth in a lathe. The junctions of two copper-constantin difference thermocouples are soldered to the smoothed surface, one at the center of each outside heater. The other junctions are joined and thermally anchored to the heavy (2 Kg.) silver plated copper radiation shield. An absolute thermocouple is soldered to the one mm. ID Monel filling tube at the point where it joins the calorimeter. With this arrangement of heaters and thermocouples, it is possible to vaporize the liquid in the calorimeter by means of internal or external heating and at the same time observe the temperature gradiants along the calorimeter. With the absolute thermocouple the temperature of the emerging vapor is measured.

The free volume of the calorimeter is 82 cc. It is provided with sixteen vertical copper vanes which are soldered to the reentrant tube holding resistance thermometer CT 4. Both the inside and outside of the calorimeter, including the vanes, are heavily gold plated. The Monel filling tube is covered by a single layer of No. 30 constantin wire to which is soldered at 25 cm. intervals No. 36 copper leads. The tube is soldered to the top of the block and below the block is a centimeter long winding on the tube of No. 30 constantin. This last winding is used only during the filling of the calorimeter. The filling tube can thus be heated in sections at will and the temperature determined at a number of points. Energy input and temperatures are measured as for the adiabatic calorimeter. Current leads from the block to the calorimeter are six inches of No. 36 copper wire. Correction for heat generated in the leads is made, assuming half goes to the calorimeter and half to the block. The maximum correction is .2% for the bottom heater and .15% for the inside heater. Other leads are from one foot to one and a half feet long.

Vapor pressure measurements are made by means of a manometer shown in Figure 3. The desired amount of mercury is raised through the stopcock into the manometer by atmospheric pressure or by compressed air and the stopcock closed. The pressure to be measured is applied in the middle arm with gold leaf in the line to protect the calorimeter from mercury. The double low pressure arms of the manometer are connected to a mercury diffusion pump and are used in the leveling of the Hensen cathetometer used for the readings. Measurements are made in terms of a standard Gärtner steel meter bar ruled in millimeters. Fractions of a millimeter are read with the fine adjustment screw of the cathetometer (100 divisions to the millimeter). Precision of reading is .05 mm. or better. A check of the total length of the meter bar scale against the scale of the cathetometer which had been calibrated against a standard decimeter from the Bureau of Standards showed it to be correct to .02 mm. The manometer and scale are enclosed in a wooden box with plate glass windows. The case temperature is measured with two calibrated mercury thermometers. Corrections are made to 0°C. to $g = 980.655$ from $g = 979.57$ for Pasadena, and for the meniscus height.

Figure 3



1. Mercury thermometers
2. Capillary tube to the calorimeter
3. Steel meter bar
4. Pyrex tubing, 13 mm. ID
5. Glass Wool damper
6. Inlet for compressed air
7. Iron reservoir for mercury

Operation of the Heat of Vaporization Apparatus.

About 70 cc. of the compound to be measured is weighed either in a bulb provided with a stopcock or in a bulb provided with a thin tube to be broken with a magnetic hammer. This last type of container is weighed first, then the compound distilled in through a ground joint, the joint sealed off and the container and joint weighed again. This method of handling liquids has proved quite satisfactory. A great advantage is that if delays make storage necessary, the compound is sealed in glass, avoiding slow attack on or solution of the stopcock grease and resultant leakage. The material is next distilled into the previously evacuated calorimeter. At the end of the distillation the filling tube is heated above room temperature to clear it of all liquid.

After the calorimeter is filled, it is cooled to about thirty degrees below the melting point and the percentage of impurity determined by heat capacity and melting point measurements. If the compound is satisfactorily pure, liquid heat capacity measurements are made over the range where the vaporization is to take place. About four points are necessary to fix the slope of the curve well. Heat capacity runs are made either adiabatically or by measuring the drift bfore and after the run. Tests have shown that the bottom and inside heaters give the same results. Calculation is more difficult with the bottom heater as two difference thermocouples must be read and a correction applied for their difference. The inside heater is thus generally used for heat capacities.

If vapor pressures are unknown, they are next determined, as the data is needed for heat of vaporization runs. At least two readings are made at each point with material being taken out betwean readings.

This must be collected and weighed if the runs are made at the beginning. If possible, therefore, the runs are left until last.

After the preliminary work the heat of vaporization run is made. The procedure is similar to that described by Doescher [3] but differs in many details. The calorimeter is heated to the desired temperature maintaining the block and filling tube hotter than the calorimeter. Current sufficient to give the desired rate of evaporation during the run is started through an exercising resistance. Good rates are .2 moles per hour at a pressure of 760 mm. and .08 moles per hour at 140 mm. A vaporization bulb is evacuated, weighed and put in place. Other methods of collecting the gas could be used, but the present method of allowing the vapor to bubble through a few millimeters of mercury into a trap cooled in liquid air is quite satisfactory. Constant pressure is provided by a twenty liter buffer jar of dry nitrogen connected to the trap. Trap and bubbler are a single unit equipped with two ground glass joints.

With the bulb in place the buffer pressure is adjusted to the correct value. The block is adjusted until it is hotter than the calorimeter by .2° to .8° and the difference maintained constant during a drift reading lasting about fifteen minutes. During the drift the absolute thermocouple is calibrated against the resistance thermometer if necessary. Near room temperature, thermocouple tables already available are found accurate. After a good linear drift is obtained, the energy input is started. About the same time the stopcock to the bulb is opened and alternate readings begun on the two difference thermocouples at half minute intervals. After the initial rapid change in temperature of the calorimeter, readings are made less frequently. During the heating readings are made of the electrical energy going in and of the absolute thermocouple at 100 to 300 second intervals. The approximate gas flow is noted. The temperature of the filling tube is checked occasionally and kept several degrees above that of the calorimeter. A selector switch automatically turns off the tube heater current when thermocouple readings are made.

At the end of the heating period, frequent readings are again taken of the difference thermocouples. The absolute thermocouple is read until the flow of gas has stopped. The stopcock on the vaporization bulb is closed when the flow of gas has slowed or stopped-- usually five to fifteen minutes after the heating has been stopped. After equilibrium is established a final set of drifts is taken. The vaporization bulb is carefully evacuated, the material melted and the bulb again evacuated. It is then weighed.

Calculation of Results.

The following resultant changes are assumed in going from the equilibrium state at temperature T_1 to the equilibrium T_2.

$M+C+M_g$ is heated under constant pressure from T_1 to T_2.

$m_1 + m_2$ is heated under constant pressure to T_s, there vaporized and the vapor heated under constant pressure to T_g.

m_3 is heated from T_1 to T_s there vaporized and the vapor heated under constant pressure to T_2.

m_1	is the moles of material collected in the vaporization bulb.
m_2	is increase in moles of material in the line from the calorimeter to the stopcock on the vaporization bulb.
m_3	is the increase in moles of gas in the calorimeter due to the removal of m and m and the pressure change.
M	is the moles of liquid finally present in the calorimeter.
M_g	is the moles of gas present in the calorimeter at T_1 .
C	is the calorimeter.
T_s	is temperature of vaporizing surface.
T_g	is temperature of emerging gas.

This listing of the changes is not entirely precise. $M + M_g + m_1 + m_2 + m_3$ are really heated from T_1 to T_s under the vapor pressure of the material rather than under constant pressure. However, the difference between the saturated heat capacities and the constant pressure heat capacities is very small. This, added to the fact that the heat used in this way is only a few per cent. of the total, makes the error less than .01%.

The chief question is whether the vaporization occurs under conditions approximating reversible ones. This can only be tested experimentally by varying the conditions of vaporization and is one of the chief reasons for the use of two different heaters in a set of runs. The agreement obtained in runs using different heaters, different amounts of material and different heating rates show the assumption of reversible conditions to be a good one.

In making the numerical calculations no single formula is used, only the basic changes listed above.

The quantities needed for the calculation and the methods of their determination are listed below:

T_1, T_2	direct measurement with the resistance thermometer.
Energy Added	from the known electrical power input plus the energy received from the shield. This energy is the average area under the readings of the two difference thermocouples times the average of the fore and after drift constants.
T_s	determined from the buffer pressure plus the mercury in the bubbler plus pressure drop due to gas flow in the filling tube .
T_g	determined by graphical averaging of the absolute thermocouple readings weighted by the rate of flow.
m_1	by weighing vaporization bulb.
m_2, M_g	by measuring volume and temperature of the line and knowing the vapor pressure.
m_3	by knowing the volume of the calorimeter and the amount and density of the material present.
M	by weighing material before it is put in the calorimeter.
Heat Capacities	determined experimentally for the calorimeter and liquid. Gas heat capacities are either calculated, found in the literature or guessed. They need be known only to 10% or so.

From these quantities we find the amount of heat needed to vaporize $m_1 + m_2 + m_3$ moles of material at temperature T_S . Agreement of runs made with different temperature gradients along the calorimeter show the heat leak corrections are made correctly.

From consideration of possible errors and from the experimental results obtained, we conclude that this is the most accurate method and apparatus available for determination of heats of vaporization. Under favorable conditions an error of less than .06% is made.

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IV

Calorimetric Data on Methyl Mercaptan.

Calorimetric Data on Methyl Mercaptan.

An accurate calorimetric value of the entropy of methyl mercaptan was desired so that a comparison could be made with the value calculated from spectroscopic and structural data. It was expected, and found, that evidence would be gained for the existance of a potential hindering rotation about the carbon-sulfur bond.

All calorimetric measurements, except the final heat of vaporization ones, were made in the adiabatic calorimeter using thermometer 26. The heat of vaporization was determined in the heat of vaporization apparatus using thermometer CT 4. The ice point is taken as 273.16° K. Resistance is in international ohms and energy is expressed in the defined calorie (1 calorie = 4.1833 int. joules). Vapor pressures are given in international millimeters of mercury. A description of the apparatus and methods of measurement is given in a previous section of this thesis. Correction of heat capacities for vaporization into the small gas space and for premelting were made when necessary. Heat capacities are accurate to 1% or better below 30° K. and to .1% above that temperature, except in the range between the transition point and melting point (137.6° - 150.2° K) where the error may be several per cent. In making corrections, the liquid densities of Ellis and Reid[1] were used to get the specific volume:

$$v = 1.11754\ (1 + .0016239t)$$

t in ° C.

Preparation of Material. For the purification of methyl mercaptan there was constructed a one and a half meter, helices-packed, vacuum jacketed column. The condenser, set just above the vacuum jacket, was an insulated metal can seven inches across and ten inches deep equipped with a stirrer. This condenser was filled with crushed ice. However, the stirrer did not hold the temperature at 0° C. It was found best to set the stirrer at a constant speed and merely add ice at the top to maintain a constant ice level. Under these conditions pressure fluctuations were reduced but a slow change was observed. The average distillation temperature was 3.5° C.

Two bottles of one hundred grams each of methyl mercaptan , obtained from the Eastman Kodak Company, were purified. The bottles were distilled separately; the procedure being first to pour the liquid into a glass trap equipped with stopcocks lubricated with Apiezon L grease as were all other stopcocks used. This was done under a hood. In fairly high concentrations methyl mercaptan smells like spoiled cabbage. In low concentrations the odor becomes more like that from a distant skunk and is quite persistant. With proper handling, however, the material is quite easy to work with. After the transfer, the glass trap was sealed to the pot of the still through a two foot P_2O_5 tube, the mercaptan frozen and the air pumped out. Frozen in liquid air the mercaptan was pink ; melted it was yellow. Upon distilling it into the pot, most of the yellow remained in a high boiling liquid. The first two sections of the P_2O_5 tube turned turned yellow; the mercaptan appeared to react with phosphoric acid slightly, but not with P_2O_5 . The distillation was made at a reflux ratio of 20:1. The first and main fractions were not pink when frozen in liquid air but the last one was. It was also observed that on breaking open one of the last fractions while frozen that a pink color quickly appeared in the upper layers of solid. The nature of the pink material is not known.

The middle fractions from both bottles were combined (115g) and distilled again at a reflux ratio of 30:1. About ninety-four grams (1.9462 moles)of purified material were received in a weighed bulb equipped with a fragile tip to be broken by a magnetic hammer. The bulb was then sealed off.

Purity of Material and Melting Point. The mercaptan was distilled into the adiabatic calorimeter and a premelting curve run on it. The results showed .052 mole per cent. impurity.

Per cent.melted	Equilibrium Temperature	Calculated Temp.
10.3	150.002° K.	150.002° K.
31.4	150.108	150.109
50.5	150.129	150.129
69.6	150.138	150.138
88.8	150.143	150.143

Melting point is 150.162 ± .02° K.

The calculated temperatures come from the freezing point lowering equation.

$$T = To - \frac{R\,T_o^2}{\Delta H_F}\;\frac{x}{\%\ \text{melted}}$$

x = mole per cent. impurity.

After these measurements the filling tube was cleared of vapor by admitting suddenly about an atmosphere of helium. After the calorimeter was cooled to 90° K. all but 8 mm. of the helium was pumped out.

Vapor Pressure Measurements. The vapor pressure of methyl mercaptan was measured after the heat capacity runs were finished with the results given in Table I.

TABLE I

T (^{o}K.)	Observed Pressure (int. mm. Hg)	Calculated Pressure (mm.)	Obs. - Calc. P (mm.)
221.880°	41.22	41.20	.02
249.288	201.64	201.48	.16
263.686	399.43	399.43	.00
273.189	399.47	599.63	-.16
279.137	760.74	760.73	.01

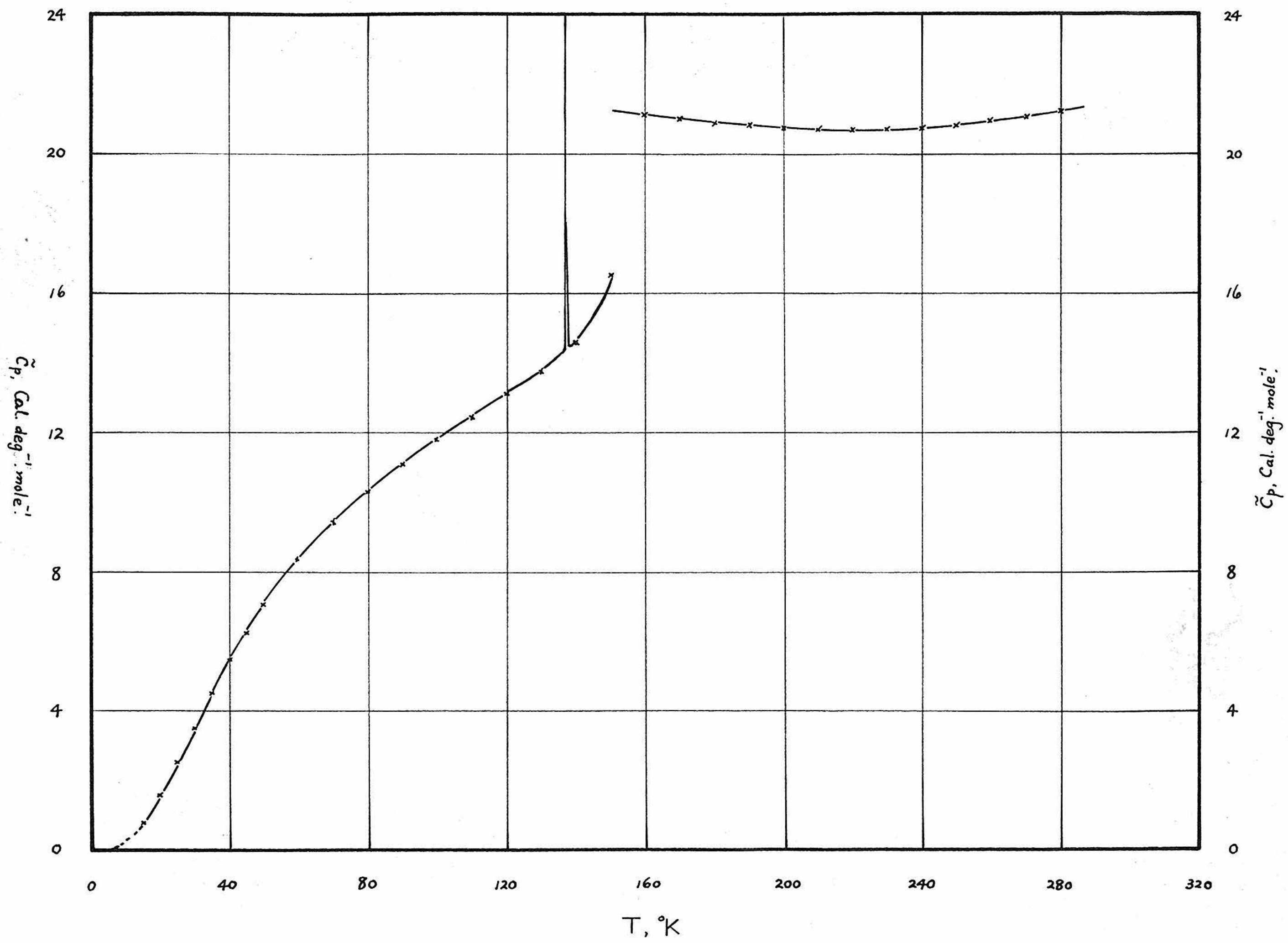
Calculated pressures are from the equation :

$$\log_{10} p\ \text{mm} = 18.27439 - \frac{1769.05}{T} - 3.70248 \log_{10} T$$

The calculated boiling point is 279.11° K.

Heat Capacities. Heat capacities were run from 15° K. to the boiling point, 279.11° K. The first points in a series of runs beginning at 90° K. were low due to supercooling of a few per cent. of the high temperature form of the solid. Care was then taken to hold the calorimeter just below the transition temperature for some time before cooling it farther. Results were then quite reproducible. Two other series of points were taken over the low temperature range (below 137° K.). The complete results, except for the low points first mentioned, are given in Table II. Table III shows the heat capacities as taken from a smooth curve. Figure 1 shows the shape of the curve.

The Transition Point. At about 137° K. a transition was found which went extremely slowly. Effects were complicated also by appreciable premelting in this region. Four series of runs were made in an effort to get equilibrium and to fix, if possible, the temperature of the transition. In investigations of such transitions as these an adiabatic calorimeter is especially desirable as the time of waiting for equilibrium



Heat Capacities of Methyl Mercaptan

TABLE II

Molal Heat Capacities

of Methyl Mercaptan.

Run No.	T °K.	ΔT °K. ~~Approx.~~	C_p cal/deg,/ mol.
55	14.97	1.461	0.773
72	15.82	1.490	0.885
56	16.47	1.522	0.983
73	17.48	1.823	1.126
57	17.98	1.515	1.226
74	19.35	1.912	1.453
58	19.49	1.499	1.476
59	21.17	1.855	1.773
75	21.50	2.388	1.835
60	23.26	2.327	2.168
76	23.94	2.502	2.300
61	25.63	2.419	2.641
77	26.57	2.747	2.831
62	28.17	2.655	3.155
78	29.37	2.861	3.396
63	30.97	2.950	3.719
79	32.51	3.409	4.022
64	33.86	2.827	4.285
80	35.96	3.495	4.690
65	37.09	3.627	4.902
81	39.61	3.813	5.352
66	40.73	3.655	5.555
82	43.61	4.191	6.038
67	44.40	3.688	6.170
83	48.08	4.751	6.763
68	48.30	4.107	6.798
69	52.64	4.572	7.435
84	53.04	5.165	7.486
35	56.72	5.155	7.948
70	57.46	5.076	8.038
36	61.86	5.134	8.548
71	62.53	5.061	8.625
37	67.00	5.139	9.106
38	72.15	5.175	9.600
39	77.34	5.206	10.094
40	82.58	5.272	10,510
41	87.89	5.336	10.925
11	88.84	5.405	10.994
42	93.26	5.402	11.332
12	94.12	5.151	11.384
13	99.38	5.376	11.738
14	104.87	5.594	12.099
15	110.37	5.408	12.466
16	115.70	5.248	12.811

TABLE II. Cont.

Molal Heat Capacities

of Methyl Mercaptan.

Run No.	T ° K.	ΔT °K ~~Approx.~~	C_p cal./deg.	mol.
25	117.20	5.169	12.890	
17	120.87	5.098	13.153	
26	122.29	5.009	13.231	
18	125.90	4.968	13.457	
27	128.06	4.873	13.614	
19	130.81	4.840	13.795	
45	133.03	4.711	13.949	
28	133.21	5.425	13.972	
49	133.22	5.344	13.963	
	137.6	Transition		
51	140.42	3.163	1487	not corr. for pre-melting
47	140.60	3.165	14.97	
30.	141.09	4.938	15.66	
52	143.45	2.902	16.62	
31	145.88	4.640	16.98	
53	146.57	3.340	17.47	
	150.16	M.p.		
85	154.16	6.350	21.27	21.27
33	155.62	6.457	21.27	21.27
86	160.50	6.317	21.17	21.17
34	162.07	6.449	21.12	21.12
87	166.80	6.293	21.07	21.07
88	174.47	9.033	20.97	20.97
89	184.11	10.248	20.87	20.87
90	194.31	10.235	20.80	20.80
91	204.51	10.164	20.75	20.75
92	214.63	10.083	20.71	20.71
93	224.68	10.003	20.70	20.70
94	234.63	9.903	20.74	20.73
95	244.48	9.798	20.82	20.81
96	254.23	9.709	20.89	20.88
97	263.89	9.599	21.02	21.00
98	271.06	4.752	21.15	21.13
	279.11	B.p.		

A few extra pts. are not included in this table.

TABLE III

Molal Heat Capacities of Methyl Mercaptan.

T ° K.	C_p cal.deg.$^{-1}$ mole^{-1} .	
15	0.777	
20	1.565	
25	2.515	
30	3.523	
35	4.508	
40	5.425	
45	6.265	
50	7.053	
60	8.333	
70	9.411	
80	10.300	
90	11.081	
100	11.785	
110	12.438	
120	13.080	
130	13.740	
137.6	transition	
140	14.54	Corrected for premelting.
150	16.58	
150.16	m.p.	
160	21.18	
170	21.03	
180	20.91	
190	20.83	
200	20.77	
210	20.73	
220	20.70	
230	20.72	
240	20.76	
250	20.85	
260	20.97	
270	21.13	
280	21.30	

is limited only by the patience and endurance of the operators. In this case as long as eight hours were spent at a single point without assurance of equilibrium. Examples of typical observations are given.

18% Transformed		89% Transformed.	
Time after Heating (hrs:min.)	T °K.	Time after Heating (hrs;min.)	T ° K.
:21	137.591	:05	138.017
:31	.561	:10	137.908
:41	.547	:30	.864
1:06	.528	1:00	.756
1:38	.519	1:30	.734
2:08	.512	2:30	.716
2:38	.509	3:14	.707
3:08	.506	4:27	.696
3:38	.503	5:00	.692
4:38	.499	5:30	.688
5:26	.497	6:00	.685

On the basis of these and other points the transition temperature was taken as 137.6±.15 ° K. The heat of transition is given in Table IV.

TABLE IV

Run No.	Temp. Interval	Heat Input Cal/mole	Cal/mole Incl.premelting	Cal/mole
29	135.925 - 138.618	91.04	38.38	52.64
46	135.382 - 139.021	104.19	51.91	52.28
50	135.887 - 138.833	94.57	42.04	52.53
			Average	52.5

Premelting at the upper temperature made this determination somewhat difficult.

Heat of Fusion. The heat of fusion determination is given in Table V, assuming the melting point as 150.162° K.

TABLE V

Temperature Interval	ΔH_F cal/mole
148.196 - 152.390	1411.2
148.238 - 153.519	1411.6
Average	1411.4

Heat of Vaporization. The heat of vaporization was determined as described previously in this thesis. Tests showed that no appreciable amount of mercaptan was absorbed in the stopcock grease. Rubber bands were used to hold the stopcocks in during the weighing of the liquid mercaptan. Two runs were made using the adiabatic calorimeter, but disagreed badly. When the new heat of vaporization apparatus was completed, five runs were made with excellent precision. The low run in the first set was given no weight in the average. Results are given in Table VI.

TABLE VI.

Heat of Vaporization of Methyl Mercaptan.

Run No.	Heater	Moles Vaporized	Time required	ΔH_v at 279.11°
1[a]	Inside	.17335	3000	5815[b]
2[a]	Inside	.19343	3600	5871
1	Inside	.17313	3600	5876
2	Inside	.17401	3600	5868
3	Bottom outside	.13943	4200	5869
4	Inside	.11630	3000	5874
5	Bottom outside	.11075	3000	5876
			Average	5872 ± 4

a using adiabatic calorimeter

b given no weight in average.

The heat of vaporization as calculated from the vapor pressure and Berthelot's equation of state is 5866 cal/mole including a Berthelot correction of 161 calories. Critical constants used were $T_c = 470^\circ$ K.[2] and $p_c = 71.4$ atms.

The Entropy of Methyl Mercaptan. Below 15° K. a Debye function was used for the extrapolation of the heat capacities. The fit with experimental points is shown below:

T °K.	C_p Cal. deg^{-1} mole^{-1} observed	$3 R \times D\left(\frac{122.8^\circ}{T}\right)$
14.97	.773	.773
15.82	.885	.889
16.47	.983	.981
17.48	1.126	1.128
17.98	1.226	1.203
19.35	1.453	1.412
19.49	1.476	1.433
21.17	1.773	1.691
21.50	1.835	1.741

The correction of the gas to the ideal gas state was made using the thermodynamic equation:

$$(\partial S/\partial P)_T = -(\partial V/\partial T)_p$$

and Berthelot's equation of state. The criticalconstants were taken as

$$T_c = 470^\circ \text{ K.}^2 \quad p_c = 71.4 \text{ atm.}^2 .$$

The correction is

$$S_{ideal} - S_{actual} = 27\, RT_c\, P/32\, T\, P_c \quad = .11 \text{ cal.deg}^{-1} \text{ mole}^{-1}$$

The entropy calculations are summarized in Table VII.

TABLE VII.

Entropy of Methyl Mercaptan.

0-15°K. Debye function 0 = 122.8°	.331
15° -137.6° K. graphical	14.679
Transition 52.5/137.6	.350
137.6-150.16° K. graphical	1.339
Fusion 1411.4/150.16	9.399
150.16° -279.11° graphical	12.968
Vaporization 5872/279.11	21.038
Entropy of actual gas at boiling point	60.047
Correction for gas imperfection	.112
Entropy of ideal gas at 760 mm. and 279.110 °K.	60.16 cal deg^{-1} mole^{-1}

Discussion of Transition. Data on a number of low temperature transitions in the solid phase have recently been obtained.[3] As yet no very general or satisfactory theory has been proposed.[3] It is of considerable interest to obtain information on a large number of such transitions to aid in the development of a better theory.

The transition in methyl mercaptan appears to be isothermal at 139.6° K., although it progresses very slowly. At most it extends over a range of a few tenths degree. The heat of transition is 50.5±.5 cal/mole. It is possible to supercool to 90°K. a few per cent., at least, of the high temperature form. No deliberate attempts were made to supercool the high temperature form. No further experimental information is available concerning the transition.

A transition has been found also in methyl alcohol. It has been investigated calorimetrically by Parks [6] and Kelley [4], and with dielectric constant measurements by Smyth and Mc Neight [5]. The calorimetric experiments found the transition to occur over a range of about 15° with a heat of transition of 154 cal/mole. Temperatures of 161.1° [6] and 157.4° [4] were picked as transition temperatures. The large range found was probably due to the non-adiabatic method used. Dielectric constant measurements show a sharp transition at 159.9° with rising temperature.[5] Hysteresis was observed with falling temperature. No transitions have been found in higher alcohols by either calorimetric or dielectric constant studies. Smyth and Mc Neight believe that those results exclude the possibility that the transition merely involves the rotation of the hydroxyl group. They postulate a rotation of the whole molecule about an axis along the C-O bond. The methyl mercaptan transition is believed to be quite similar to that in the methyl alcohol and no better explanation can be offered at present than that of Smyth and Mc Neight.

Spectroscopic Entropy. The spectroscopic entropy was calculated using the following constants:

$T_0 = 273.16^\circ$ K.

1 cal.= 4.1833 Int. joules

$R = 1.98708$ cal.deg.$^{-1}$ mole^{-1} .

$k = 1.3805 \times 10^{-16}$ erg deg^{-1} molecule^{-1} .

$N = 6.023 \times 10^{23}$

$h = 6.624 \times 10^{-27}$ erg sec.

$\frac{hc}{R} = 1.4384$ cm.deg.

The translational and vibrational contributions to the entropy are calculated by the standard formulae given below. The vibrational degree of freedom associated with the rotation of the methyl group is omitted, however, and its contribution calculated separately.

$$S_{trans} = 3/2\ R \ln M + 5/2\ R \ln T - R \ln p_{atm.} - 2.314$$

$$R \ln \frac{e^{5/2} (2\pi k)^{3/2} R}{N^{5/2} h^3} = - 2.314 \text{ cal.deg.}^{-1} \text{ mole}^{-1}$$

$$S_{vib.} = \ln Q + T \frac{\partial \ln Q}{\partial T}$$

$$Q = \sum_n e^{-(n+\frac{1}{2}) hcw/kT}$$

The vibrational contributions are given in tables by Gordon and Barnes [7] for various values of $hc\omega/kT$.

The calculation of the rotational contribution is more difficult. It is customary to calculate moments of inertia for the molecule as though it were rigid. The contributions to the entropy of the overall rotation is calculated by the usual formula using the symmetry number of the rigid molecule ($\sigma = 1$ for CH_3SH).

$$S_{rot} = 1/2\ R \ln I_x I_y I_z + 3/2\ R \ln T - R \ln \sigma - 5.385$$

where I's are in At.wt. units x Å .

The contribution of the internal rotation is then evaluated separately. In the case of free rotation methods of calculation have been given by Eidinoff and Aston [8] and by Kassel [9] . In the case of hindered rotation a special treatment is necessary. One has been given by Pitzer [10] who neglected angular momentum interactions between the rotating top and the framework. He gives tables of functions which are quite accurate for high potential barriers, but which may be in error for low barriers. Crawford [11] has presented a treatment for hindered rotation which includes angular momentum coupling effects and is suitable for molecules where the top axis does not pass through the center of gravity of the molecule. If the top is not too large relative to the rest of the molecule the treatment is quite satisfactory. In his method a parameter Ω is used which depends on the orientation of the top relative to the principle axes of the molecule and on the relative mass of the top to that of the framework. For $\Omega =$ 1 his treatment is the same as Pitzer's. For Ω small, approximations made in Crawford's method become serious and further investigation of them seems necessary. Both treatments use a cosine form of hindering potential.

The molecular weight of methyl mercaptan was taken as 48.102. The vibrational assignments of Thompson and Skerrett [12] were used. The frequencies and their degeneracies are 3000 (2), 2870, 1335, 1475 1430, 704, 1060. 957. 2597 and 803. Distances taken were S-C = 1.83 Å as determined by electron diffraction, S-H = 1.35 Å, $\angle$C - S- H = 100° and a tetrahedral methyl group with C-H = 1.09 Å. The parameter Ω = .34921 and a further investigation of Crawford's method seems desirable but has not been completed. A summary of calculations is given in Table VIII.

TABLE VIII

Entropy of Methyl Mercaptan

at 279.11° K. and 1 atmosphere.

Translational	37.207 e.u.
Rotational (omitting internal rotation)	20.338
Vibrational	.592
Total omitting internal rotation	58.137 e.u.
Experimental entropy	60.16
Contribution of hindered rotation as experimentally determined	2.02 e.u.
Contribution from free rotation	2.60 e.u.
Contribution if barrier potential of 1460 calories is taken (Pitzer's Tables.)	2.02 e.u.

The height of the barrier would be raised somewhat by using Crawford's treatment. We can thus say that the data presented adds to the experimental evidence for hindered rotation and that a lower limit to the barrier is about 1460 calories.

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V

Calorimetric Data on Arsenic Trifluoride.

Calorimetric Data on Arsenic Trifluoride.

Arsenic trifluoride was selected, for two reasons, as being an interesting compound to investigate. One was that it is a relatively simple molecule for which an accurate value of the entropy could presumably be calculated from electron diffraction and Raman spectrum data. The comparison with the calorimetric value would check to a certain extent both the frequency assignments and the experimental method. In such a molecule the entropy would be expected to approach zero at absolute zero. The other reason was that the solid had been observed to emit light on cooling to liquid air temperatures. The investigation would reveal whether any thermal effects were associated with the phenomenon.

Preparation of Material. Arsenic trifluoride was made according to the directions of Ruff[1] from C.P. sulfuric acid and finely mixed reagent grade arsenious oxide and calcium fluoride. The preparation was carried out in an all glass system. About fifty grams of dried sodium fluoride in the receiver served to remove hydrogen fluoride. After the collection of the crude product, the receiver, which was equipped with a fragile tip, was sealed off. It was allowed to stand for two or three days to allow the arsenic trifluoride time to react with possible water. The sodium fluoride was to remove the hydrogen fluoride formed. This procedure was quite successful and at no time have we had evidence of pressure being built up in a sealed bulb of arsenic trifluoride. Dry arsenic trifluoride does not attack glass.

The material was next distilled in an all glass system without stopcocks, through a two foot sodium fluoride tube into the pot of a five foot, glass helices packed column. The column was insulated and wound with heater wire. In order to get a variable reflux ratio without the use of a stopcock, the take-off tube was sloped up and equipped with a condenser, then sloped down and supplied with another condenser. Through the first condenser, water from a constant temperature bath (about 50°) was circulated by a small centrifugal pump. Through the second cold water was passed. The reflux ratio was varied either by changing the speed of the pump or the temperature of the bath. This system worked reasonably well, although it had to be watched carefully. Distillations were made at a reflux ratio of 10:1. A ground glass joint allowed receivers to be changed without admitting moist air. An inner tube joined by a ring seal above the joint prevented any liquid from coming into contact with the grease (on the outer third of the joint only). Apiezon M grease was early found to be appreciably attacked, but Apiezon L was only very slowly attacked and was used throughout. Distillations were made at atmospheric pressure with a series of drying tubes in the open line. During the course of the distillations the boiling point did not change more than .01°. There was no evidence of a more volatile impurity in the sodium fluoride treated material, but the high boiling portion left in the still had red-brown particles of solid in it.

The purified arsenic trifluoride was a colorless, very mobile liquid which froze to a white crystalline solid in a dry ice bath. On either freezing down to, or warming up from, liquid air temperatures loud, cracking noises are made and flashes of blue-green light emitted. Under proper conditions light is emitted also above -78° C. but not in general.

On trying to put the first purified sample obtained into the calorimeter, the trap broke while the solid was warming up.

Solid arsenic trifluoride has apparently a high coefficient of expansion and extreme care is necessary to prevent breakage. Even with care the trap broke—five in the course of the preparation. The recovered arsenic trifluoride plus more crude material was again distilled, this time cutting a first fraction of 30 cc., a second of 70 cc. and a third of 60 cc., leaving 40 cc. in the pot as a last fraction. The distillation proceded as before.

The Vapor Pressure of Arsenic Trifluoride. The weighed third fraction was distilled into the evacuated heat of vaporization apparatus without incident. A melting point curve gave a liquid soluble, solid insoluble impurity of .04 mole per cent. Vapor pressure measurements were then made. Considerable trouble was found in getting good reproducibility. Later a slight leak was found in the line, but as material was pumped out at each point, no serious error is thought to have been made. Results are in Table I.

TABLE I

Vapor Pressure of Arsenic Trifluoride.

T °K.	p obs. (Int.mm.H_g)	p calc. (mm)	p calc.- p obs. (mm)
265.019	28.90	29.00	.10
268.235	36.15	35.85	-.30
272.058	45.68	45.67	-.01
275.271	55.22	55.53	.31
280.182	74.20	73.88	-.32
288.055	112.70	113.10	.40
291.816	136.96	136.90	-.06
291.879	137.46	137.30	-.16

Calculated values are from the equation:

$$\log_{10} p_{mm} = 61.37969 - \frac{4149.784}{T} - 18.26403 \log_{10} T.$$

Calorimeter Data. Calorimeter work, except for the heat of vaporization, was done in the rebuilt adiabatic calorimeter using thermometer CT 26 measured with Leeds and Northrop coil # 288075. The heat of vaporization was measured in the special apparatus for that purpose. In all results $T_0 = 273{,}16^\circ$ and energy is expressed in the defined calorie (1 calorie = 4.1833 int. joules). Heat capacities are accurate to 1% or better below 30° K. and to .1% above that temperature, except for the liquid heat capacities which may be in error about .2%. Corrections were made when necessary for vaporization into the small gas space and for premelting. In these corrections, the density equation of Thorpe[2] was used.

$$d_4^t = 2.6659 - .003839\,t + .00000435t \qquad (0^\circ \text{ to } 60^\circ \text{ C.})$$

Some evidence indicates these densities are low[1,2], but no appreciable error in the entropy would result.

Heat of Vaporization. Four runs were made on the heat of vaporization. Results are in Table II.

TABLE II

Heat of Vaporization of Arsenic Trifluoride.

Run No.	Heater used.	Mole vaporized	Time sec.	ΔH_v at 292.50° K. cal/mole
1	Inside	.037722	3600	8531
2	Bottom	.042432	3300	8566
3	Bottom	.058841	2500	8529
4	Inside	.048593	3000	8565

The runs fall into two sets. The explanation is almost surely as follows:

Runs 1 and 2 were done one day and Runs 3 and 4 the next day. Only one container was used each day with the second sample being collected directly after the first. Due to the marked propensity of arsenic trifluoride to break traps, the collected material was not pumped on, melted, frozen and again pumped on, but only pumped on as it had collected. About a third of the nitrogen in the bulb was apparently trapped in the solid and weighed each time. The first sample weights were then high each day while the second were approximately correct as there was then nitrogen weighed in each weighing. The heat of vaporization is:

ΔH_v at 292.50° = 8566 ± 8 cal/mole of the arsenic trifluoride.

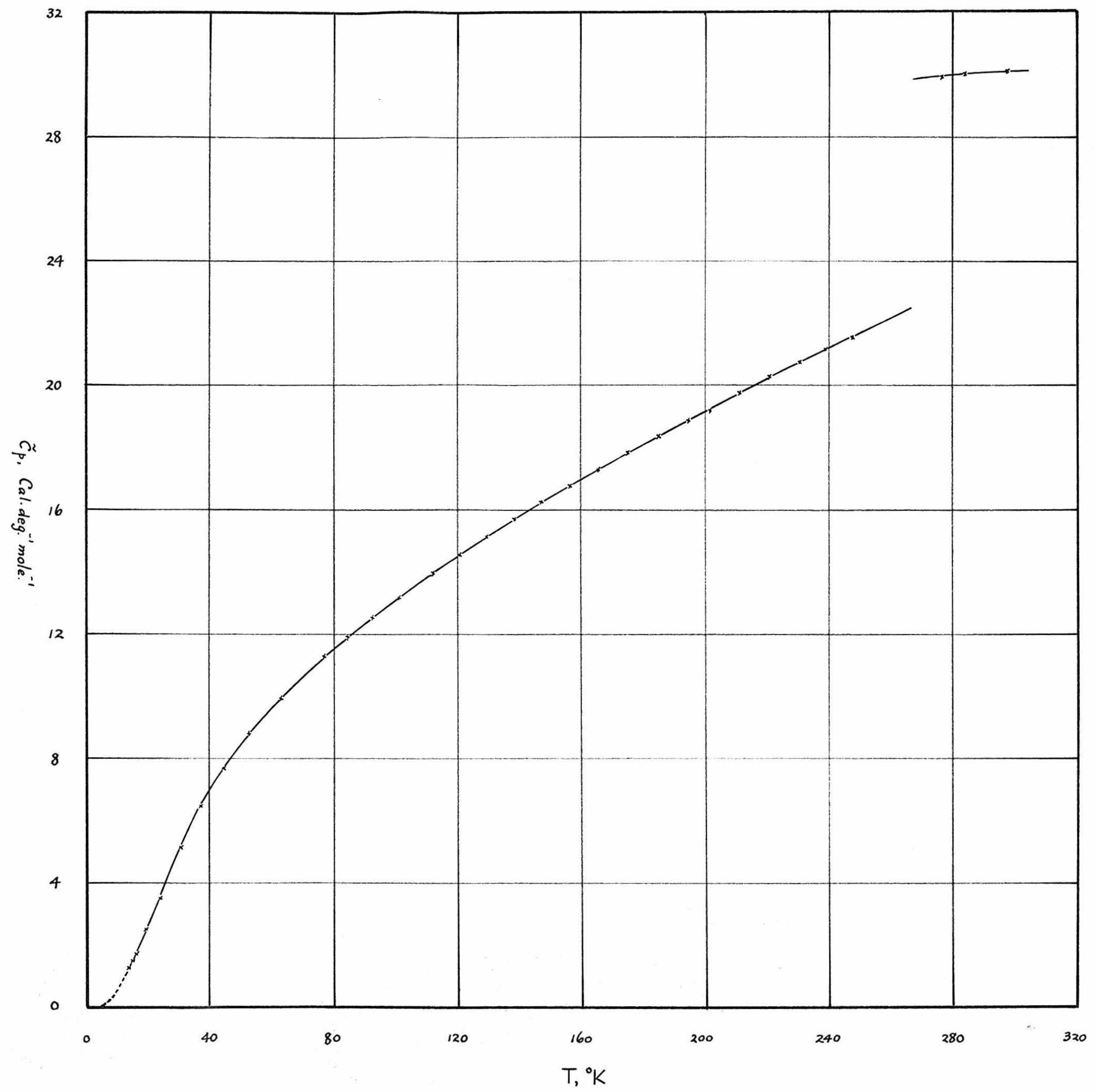
Heat Capacities. Fractions two and three of the arsenic trifluoride were combined and distilled into the adiabatic calorimeter (1.7975 moles) The filling tube was cleared of vapor with helium. A small amount of helium was left in to promote equilibrium of the solid. Suitable corrections were made. A melting point curve showed about .02 mole per cent. impurity.

Per cent. melted	Equilibrium Temperature °K.	Calculated Temp. °K.
17.5	267.143	267.141
35.9	267.173	267.174
60.3	267.190	267.187
86.5	267.192	267.192

Melting Point = 267.205° ± .02° K.

The calculated temperature came from the freezing point lowering equation using a mole per cent. impurity of .0195. The second fraction was thus purer than the third.

Heat capacities are given in Table III. No sign of a transition was observed. The only irregularity was that in the region 100° - 120° K. equilibrium was reached more slowly than at either higher or lower temperatures. The origin of the light observed is probably due static discharges caused by strain in the crystals on warming or cooling. A similar effect is observed for hydrogen cyanide.[6]



Heat Capacities of Arsenic Trifluoride

TABLE III

Heat Capacities of Arsenic Trifluoride

Run No.	T °K.	T (approx.)	C_p cal/mole
1	13.588	1.03	1.258
2	14.677	1.15	1.480
3	15.868	1.23	1.712
4	17.250	1.53	2.044
5	19.166	2.30	2.513
6	21.504	2.38	3.084
7	23.992	2.60	3.703
8	26.893	3.20	4.388
9	30.329	3.67	5.143
10	33.873	3.42	5.870
11	37.220	3.28	6.488
12	40.673	3.63	7.056
13	44.305	3.64	7.653
14	48.273	4.30	8.207
15	52.678	4.52	8.799
16	57.433	5.00	9.320
17	63.072	6.28	9.920
18	69.868	7.31	10.610
19	77.120	7.22	11.287
23	78.186	9.26	11.359
20	84.407	7.34	11.894
24	87.074	8.52	12.118
21	92.365	8.58	12.541
25	95.685	8.70	12.788
22	101.289	9.27	13.183
26	104.139	8.21	13.433
27	112.163	7.84	13.953
28	120.456	8.75	14.525
29	129.683	8.95	15.122
30	138.460	8.60	15.685
31	147.190	8.86	16.209
32	156.354	9.47	16.749
33	165.679	9.18	17.282
34	175.036	9.54	17.800
35	185.032	9.25	18.342
36	194.454	9.60	18.856
37	201.673	9.28	19.172
38	211.116	9.60	19.744
39	220.869	9.90	20.254
40	230.631	9.62	20.736
41	239.601	8.32	21.172
42	247.802	8.09	21.569
Melting Point260.205°			
44	276.203	3.90	29.96
45	280.091	3.88	30.02
46	283.958	3.86	30.07
47	287.810	3.85	30.07

The Heat of Fusion. Due to lack of time only one run was made on the heat of fusion. The less accurate value obtained during the impurity determination in the heat of vaporization apparatus agreed within .3% but is given no weight.

TABLE IV

Heat of Fusion of Arsenic Trifluoride.

Temperature Interval	ΔH_F cal/mole
251.847° - 274.255°	2486.4

The Entropy of Arsenic Trifluoride. The correction to the ideal gas is made by use of the relation

$$(\partial S/\partial P)_T = -(\partial v/\partial T)_P \quad ,$$

the Clapeyron equation,

$$\frac{dp}{dT} = \frac{\widetilde{\Delta H}_V}{T\,(v_g - v_L)} \quad ,$$

and the Berthelot equation of state

$$pv = RT\left[1 + \frac{9pT_c}{128p_cT} \quad \left(1 - 6\,\frac{T_c}{T}\right)\right]$$

From these equations we may derive

$$\frac{-27}{192} \quad \frac{R\,T_c\,p}{T\,p_c} \quad \left(1 - \frac{6\,T_c^2}{T^2}\right) = \frac{2\,p\,\widetilde{\Delta H}_V}{T^2\,\frac{dp}{dT}} - 2R + \frac{2p\,V_L}{T}$$

We might neglect the 1 compared to $6\,T_c^2/T^2$ which introduces an error of from 4 to 7 %. A mean correction of 5 %.is taken but may be made more accurately if desired. We may neglect also the $2pv_L/T$ term.

We then get

$$\Delta S = S_{ideal} - S_{actual} = \frac{27}{32} \frac{R T_c^3 p}{T p_c}$$

$$= -\left[\frac{2 p \tilde{\Delta} H_v}{T^2 \frac{dp}{dT}} - 2R \right] \qquad 1.05$$

The quantities of p, $\tilde{\Delta}H_v$, T, and dp/dT are all experimentally determined quantities. The least accurate term is probably dp/dT. If it is known to .4 % the ΔS would be given accurately to .016 e. u., assuming the Berthelot equation holds for the gas. Entropy calculations are summarized in Table V.

TABLE V

The Entropy of Arsenic Trifluoride

0° - 13.338° K. Debye function $\theta = 91.1°$	.454 e.u.
13.338° - 267.205° graphical	30.272
Fusion 2484.6 / 267.21	9.305
267.21° - 292.50° graphical	2.713
Vaporization 8566/292.50	29.285
Real gas at 141.6 mm. and 292.50° K.	72.029
Correction for gas imperfections	.09
Entropy of ideal gas at 141.6 mm. and 292.50° K.	72.12 e.u.

Entropy Comparisons The entropy of the molecule was calculated by standard statistical mechanical methods using the formular given in the methyl mercaptan section. For the calculations of moments of inertia the electron diffraction data of Pauling and Brockway [4] were used. The As - F distance is 1.72 Å and the F - As - F angle 100°. The angle is somewhat uncertain, but small changes in the parameters make but slight changes in the product of the moments of inertia and consequently in the entropy.

Effect of Parameter Changes on the Entropy of Arsenic Trifluoride.

As-F	1.72 Å	1.73 Å	173 Å
F-As-F	100°	100°	105°
$S_{298.1°}$	69.083 e u.	69.118 e.u.	69.173 e.u.

The frequency assignments of Wilson and Howard [5] are used. The frequencies and their degeneraces are 707, 341, 644 (2), and 274 (2) cm^{-1}. The frequencies were obtained from the Raman spectrum of the liquid and may be somewhat different from the frequencies in the gas. Results of the entropy calculation and comparisons with the experimental value are presented in Table VI. In view of the uncertainties in the structural and spectroscopic values, the perfect agreement is fortuitous.

TABLE VI

Comparison of Calculated and Observed Entropies for Arsenic Trifluoride.

T °K.	Actual Gas	Ideal Gas	Spectroscopic
292.50 (141.6mm)	72.03±.1	72.12	72.13
298.10 (1 atm.)		69.07	69.08

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