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The Entropy and Related Thermodynamic Properties
of Tetramethylgermane

by

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Doctor of Philosophy

Thesis Director's Signature:

A handwritten signature in cursive script, reading "John E. Kilpatrick". The signature is written in dark ink and is positioned above the text "Houston, Texas".

Houston, Texas

May, 1970

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I. INTRODUCTION

There are two possible goals to be attained in a research project which undertakes to measure the thermodynamic properties of a pure substance. The first goal is the addition of the measured and related thermodynamic properties of the substance to the tables of thermodynamic properties existing in the literature. The second goal is to use these thermodynamic properties in conjunction with existing spectroscopic data and the equations of statistical mechanics in order to calculate intramolecular parameters of the substance in question which cannot be determined by spectroscopic measurements alone.

Both goals have been attained in this research. The heat capacity from 15° to 300°K, the heat and temperature of fusion, the vapor pressure, and the heat of vaporization have been determined experimentally for tetramethylgermane, $(\text{CH}_3)_4\text{Ge}$. These measured properties allow the calculation of the entropy, the free energy function, and the enthalpy function.

Because of the absence of a permanent dipole moment in tetramethylgermane, it has no rotational spectrum and, therefore, the potential barrier hindering the internal rotations of the methyl groups cannot be obtained from spectroscopic data alone. The infrared and Raman spectra (19, 20, 21) of this compound have been studied and the assignment of fundamental vibrations made. The geometry of the molecule has been determined by an electron diffraction study (22). Enough information, then, exists so that we may calculate the entropy of tetramethylgermane in the ideal

gas state assuming free internal rotation. Because of this assumption, the calculated entropy will be different than the experimental value. The difference in these entropies allows calculation of the potential barrier hindering internal rotations (23).

In addition to the work on tetramethylgermane, the vapor pressure, the heat of vaporization, and the temperature of fusion of tetramethylstannane, $(\text{CH}_3)_4\text{Sn}$, have been determined. A large amount of work was done on the measurement of the heat capacity of this compound but reproducible results were not obtained. It was not possible, therefore, to obtain an entropy value for this compound.

II. EXPERIMENTAL

A. Apparatus

The apparatus used in this research has been previously described (1, 2, 3, 4, 5, 6). Modifications and major repairs are discussed below.

1. Cryostat

The calorimeter used throughout this research has the laboratory designation of Calorimeter B. It was built by Taylor (1). At the start of this research, the calorimeter was almost fifteen years old and some of the components had deteriorated severely. The glass vacuum line leading from the top of the calorimeter to the pumping system had been shattered, the wires in the electrical cables had become fatigued, and the inner can heater had come loose from the can.

The calorimeter was disassembled and all the wiring stripped out. The glass vacuum line was removed and replaced with a metal system. A stainless steel bellows was incorporated into the line to allow some degree of flexibility. The line terminated in a metal to glass seal and ball joint which could be connected to the pumping system.

The old heater winding was stripped from the can and the surface of the can was thoroughly cleaned. The can was then mounted on a lathe and a length of No. 22 B&S asbestos covered Chromel-A wire was wound on. As the winding was taking place, the

can surface was painted with red glyptal. After the winding was completed, it was given two coats of red glyptal. After overnight drying, the can was baked for two hours at 125°C . The resistance of the winding was 75 ohms.

A new inner cable was made by cutting 27 strands of copper wire and 7 strands of constantan wire to a length of 17 feet. Both types of wire were No. 30 B&S, enameled and cotton covered, and of thermocouple grade. The strands were strung out, painted with clear glyptal diluted 1 to 4 with chloroform, and allowed to dry overnight. The painting and drying were repeated. The strands were then bound into a cable and baked for two hours at 125°C . A new outer cable was made by cutting 3 strands of copper wire, 3 strands of constantan wire, both types of wire being No. 30 B&S of thermocouple grade, and 8 strands of No. 28 B&S copper magnet wire to a length of 11 feet. All three types of wire were enameled and cotton covered. The cable was painted, bound, and dried as above.

It was felt that the old method of attaching the inner cable to the spool, a random winding followed by painting with glyptal, could be improved upon. A small quantity of material from a Hysol Epoxy Patch Kit No. 0151 was quickly mixed and then placed in a vacuum chamber for 15 minutes in order to remove any volatile solvents or entrapped gases. A thin layer of the epoxy was then applied to the spool and the strands of wire from the inner cable were then given one tight winding around the spool. The wires were then held in place under slight tension for 24 hours. In this manner, good thermal contact between the wires and the spool was insured. The spool and cables were then mounted in the calorimeter.

The epoxy presented no problem with respect to obtaining a good vacuum; pressures of 10^{-6} mm were easily attained.

During the course of the thermometer calibration, the block heater failed. The block was removed from the calorimeter and the sheath over the block heater winding was unsoldered. The old winding was removed and the surface which had been under it was thoroughly cleaned. The surface was then painted with clear glyptal diluted 1 to 3 with chloroform. After allowing it to air dry several hours, it was baked 1 hour at 125°C . The painting and drying process was repeated. The block was then mounted on a lathe and wound with No. 24 B&S enameled and cotton covered constantan wire of such a length that the resistance was 78 ohms. While the winding was taking place, the block surface was painted with clear undiluted glyptal. When the winding was complete, the winding was painted with clear undiluted glyptal and allowed to air dry for 24 hours. The painting and drying process was repeated. The block was then baked 1 hour at 50°C and, finally, baked 3 hours at 125°C . The sheath was then resoldered in place and a new hermetic lead-through seal installed. The space under the sheath was filled with helium and then sealed up. No further difficulties were encountered with the block heater.

2. Sample Containers and Sample Heaters

The sample container used for the vapor pressure and heat of vaporization measurements carries the laboratory designation of sample container VI. It was built by Putnam (2) and partially rebuilt by Davis (3). Its associated sample heater was rebuilt

by Davis (3).

The sample container used for the heat capacity, temperature of fusion, and heat of fusion measurements carries the laboratory designation of sample container V. It was built by Putnam (2). Its associated sample heater had developed a low case to winding resistance and it was necessary to rebuild it. The procedure is thoroughly described by Davis (3).

3. Thermometers

The platinum resistance thermometer used for the vapor and heat of vaporization measurements carries the laboratory designation of 100-1. It was built by Johnson (4) and has been calibrated several times over the last 20 years, the most recent calibration being that of Davis (3).

The platinum resistance thermometer used for the heat capacity, temperature of fusion, and heat of fusion measurements carries the laboratory designation of 100-4. It was built and calibrated by McEachern (5). Since, at the start of this research, it had been seven years since the thermometer had been calibrated, recalibration was necessary.

Between the oxygen boiling point and the antimony freezing point, the International Temperature Scale is defined by the resistance of platinum. The relationship between the temperature, t , in degrees Centigrade and the resistance, R , is given by the well-known Callendar-Van Dusen equation:

$$t = \frac{1}{\alpha R_0} (R - R_0) + \left(\frac{t}{100} - 1\right)\left(\frac{t}{100}\right)\delta + \left(\frac{t}{100} - 1\right)\left(\frac{t}{100}\right)^3 \beta$$

where R_0 is the ice point resistance, α and δ are constants, and β is a constant which is set equal to zero for temperatures above the ice point.

In order to evaluate the four constants in this equation, it is necessary to calibrate the thermometer at four points of known temperature. The calibration points used in this laboratory are the benzoic acid freezing point, the water triple point, the nitrous oxide triple point, and the boiling point of oxygen.

The thermometer resistance at the benzoic acid melting point was determined in a cell calibrated by the National Bureau of Standards. The cell, designated No. 131, was certified to contain benzoic acid melting at 122.359°C . In 8 separate experiments during which 56 measurements were made, the resistance of the thermometer was found to be 115.7529 ± 0.0006 ohms.

The thermometer resistance at the water triple point, 0.010°C , was determined in a cell described by Johnson (4) and Weber (6). In 8 separate experiments during which 68 measurements were made, the resistance of the thermometer was found to be 78.2994 ± 0.0004 ohms.

The thermometer resistance at the nitrous oxide triple point, -90.809°C , is measured in a special sample container described by Weber (6). The nitrous oxide used was a clinical grade material which was further purified by several fractional distillations. In 4 separate experiments during which 38 measurements were made, the resistance of the thermometer was found to be 49.5543 ± 0.0003 ohms.

The thermometer resistance at the oxygen boiling point, -182.970°C , is also measured in the special sample container mentioned above. The oxygen used was prepared in the manner described by McDougall (7). The vapor pressure of the oxygen was measured at 11 points between -209° and -182°C . The temperatures corresponding to these vapor pressures were determined from the data of Hoge (8). The resistance of the thermometer at the normal boiling point was found to be 19.1971 ohms.

The temperatures of the calibration points and the thermometer resistances found in this research and in that of McEachern (5) are given in Table I. The Callendar-Van Dusen equation constants calculated in this research and in that of McEachern (5) are given in Table II.

Using the relationship between Centigrade temperature, t , and the thermodynamic temperature, T :

$$T = t + 273.15$$

and the Callendar-Van Dusen equation, a table of thermometer resistance versus thermodynamic temperature was constructed by the Rice University computer.

For the region below the oxygen boiling point, a temperature scale was established by the method suggested by Hoge and Brickwedde (9). This method compared the resistance of thermometer 100-4 against the resistance of a 25 ohm Leeds and Northrup platinum resistance thermometer which had been calibrated by the National Bureau of Standards. The comparison was made at 35 points

in the temperature range from 14.5° to 91° K.

In addition, at 6 of these points in the temperature range of 14.8° to 17.9° K, the temperature was checked by measuring the vapor pressure of hydrogen which had been condensed into the sample container. In the past, the hydrogen in the sample container was supplied by condensing "prepurified" hydrogen from cylinders. The hydrogen was of the high temperature equilibrium composition. A catalyst in the sample container was used to facilitate conversion over to the low temperature equilibrium composition. Vapor pressure data sometimes indicated that the conversion was not complete. In this research a different source of hydrogen was used. Liquid hydrogen is used to cool down the cryostat for this part of the calibration procedure. The hydrogen, while being liquified, is exposed to a catalyst so that there is no loss due to conversion during storage. It was decided, therefore, to use the hydrogen evaporating from the storage Dewar flask as the hydrogen source since it was already of the low temperature equilibrium composition. The temperatures corresponding to the measured vapor pressures were determined from the data of Woolley, et. al. (10). The vapor pressure temperatures agreed with those obtained from the Leeds and Northrup thermometer to within 0.009° K at 14.8° K and to within 0.002° K at 17.9° K.

The low temperature scale was constructed, smoothed, and printed out by the program written by Davis (3) on the Rice University computer.

TABLE I

Calibration Point Resistances of Thermometer 100-4

<u>Calibration Point</u>	<u>t °C</u>	<u>Resistance</u>	
		<u>This Research</u>	<u>Reference 5</u>
Benzoic Acid Melting Point	122.359	115.7529	115.7528
Water Triple Point	0.010	78.2994	78.2973
Nitrous Oxide Triple Point	-90.809	49.5543	49.5522
Oxygen Boiling Point	-182.970	19.1082	19.1037

TABLE II

Callendar-Van Dusen Constants of Thermometer 100-4

<u>Constant</u>	<u>This Research</u>	<u>Reference 5</u>
R_0	78.29629	78.29418
α	0.003922967	0.003923247
β	0.1119471	0.1137218
δ	1.504239	1.500284

B. Measurements

1. Electrical

The apparatus used for making potential measurements has been described by Taylor (1), Putnam (2), and Johnson (4). A new set of Eppley cells for use as standards of potential measurement was purchased for this research. The standardization of the cells is traceable back to the National Bureau of Standards.

2. Temperature

The temperature circuitry and the method of taking temperature measurements have been described by Taylor (1), Johnson (4), and McEachern (5).

3. Power

The power circuitry and the method of taking power measurements have been described by Taylor (1) and Johnson (4).

The resistors in the voltage divider circuit were recalibrated for this research. Agreement with previous calibrations was excellent.

One of the corrections made to the power measurements involves the resistance of certain leads in the calorimeter cables. Since new leads had been installed, it was necessary to calibrate their resistance as a function of temperature. The resulting correction factor to the power measurements ranged from 0.999704 at 15°K to 1.00000 at 300°K.

Another correction to the power measurements involves the

resistance of a pair of platinum leads which connect the block studs to the sample container heater. A new pair of leads was constructed and calibrated for this research. The resulting correction factor to the power measurements ranged from 0.999997 at 15°K to 0.998318 at 300°K.

The unit of energy for this research is the defined calorie (1 calorie = 4.1840 absolute joules).

C. Tetramethylgermane

1. Sample

The sample of tetramethylgermane used in this research was obtained from Alfa Inorganics, Inc. of Beverly, Massachusetts. According to the manufacturers, the material was better than 99% pure. The material was analyzed by vapor chromatography and was found to contain 0.2 mole % of impurities of lower boiling point than the tetramethylgermane and 0.7 mole % of impurities of higher boiling point than the tetramethylgermane.

2. Purification

145 grams of tetramethylgermane was placed in a 250 ml flask fitted with a jacketed 300 mm fractionating column packed with glass helices. The column head, condenser, and receiver were all fitted with greaseless stopcocks and connections. The material was then distilled over an eight hour period at a reflux ratio of 15 to 1. The first 5% and last 30% of the distillate were rejected. Vapor chromatography showed the middle fraction to contain a maximum of 0.02 mole % of impurities.

Since the sample container is constructed of tarnished copper, a compatibility test was run between tetramethylgermane and tarnished copper. A small amount of sample was placed in a vial with a small strip of tarnished copper. The vial was stored in the dark at 25°C. for a period of eight months. Vapor chromatography showed that no change had taken place in the tetramethylgermane during that period. Visual inspection showed

no change in the tarnished copper. However, when the heat capacity measurements were completed, the sample container was emptied of tetramethylgermane and washed with ether prior to drying and reweighing. The sample container was found to have lost 0.060 grams in weight and the ether wash was found to contain a soluble grey powder. The tetramethylgermane was found to be free of any dissolved solids. In addition, the temperature of fusion determinations showed that no change in purity had taken place between the start and the finish of the heat capacity measurements. Prior to the initial filling, the sample container had been carefully washed with water, then acetone, and finally with ether. The most reasonable explanation for the grey powder is that the tetramethylgermane had reacted with the solder in the sample container to form a material insoluble in the tetramethylgermane.

3. Heat Capacity

The in vacuo weight of tetramethylgermane taken for heat capacity measurements was determined by the initial filling weights to be 60.7117 grams. The molecular weight was taken to be 132.73 and, therefore, the sample consisted of 0.45471 moles of tetramethylgermane.

The precision of the heat capacity measurements is well within the limits stated by Putnam (2); i.e. within 1% below 30°K, within 0.3% above 230°K, and within 0.03% in the intermediate region. The exception to these limits is in the premelting region where precision is generally poor.

Several corrections must be made to the experimentally

determined heat capacity points. The first of these is the premelting correction which must be applied to the solid phase heat capacities. By using ideal solution theory and assuming only a solid insoluble-liquid soluble impurity, one can readily obtain:

$$C = \frac{n_2 R T_o^2}{(T_o - T)^2 - (\Delta T / 2)^2}$$

where:

- C = heat capacity correction to be subtracted
- n_2 = moles of impurity
- R = gas constant
- T_o = temperature of fusion
- T = mean temperature of heat capacity point
- ΔT = temperature interval of heat capacity point

By assuming that the heat capacity changes linearly with temperature immediately below fusion, an impurity content of 0.012 mole % was found to give the best fit to the experimental heat capacity data. The premelting correction is as large as 2.56 cal/mole. deg at 182.27°K but it drops off very rapidly with decreasing temperature.

The second correction which must be made is for the vaporization of the sample within the sample container over the temperature range where the sample is in the liquid state. The procedure outlined by Hoge (11) was used. This correction is only 0.062 cal/mole. deg at 304.69°K and, as in the case of the premelting correction, it drops off rapidly with decreasing temperature.

Although helium was used to fill the empty volume in the sample container in order to improve heat conduction, the amount added, 1.2×10^{-4} moles, contributes only an entirely negligible correction, 0.0007 cal/mole. deg, to the heat capacities.

The molar heat capacities of tetramethylgermane are presented in Table III in the order in which they were determined. Each series designated by a capital letter represents consecutive measurements during which the sample was not allowed to proceed through fusion. The temperature of fusion and heat of fusion determinations are designated by lower case letters and are listed in the order in which they were determined.

The molar heat capacity data is presented graphically in Figure I. In Table IV, the heat capacity, entropy, and the thermodynamic functions $(H - H_0)/T$ and $-(F - H_0)/T$ are tabulated at rounded temperatures from 15° to 300°K.

4. Temperature of Fusion

Three determinations of the temperature of fusion are summarized in Table V. Plots of the temperature versus the reciprocal of the fraction of the sample melted show a slight upward curvature. This would indicate the presence of at least one impurity which is soluble in both phases. Because of the small curvature, the low level of impurity, and the scatter in the data, the best fit was obtained by assuming a single liquid soluble-solid insoluble impurity and using the well-known equation:

$$T = T_0 - \frac{x_2 RT_0^2}{\Delta H} (f)^{-1}$$

TABLE III

Molar heat capacity of tetramethylgermane

Temp. (°K)	Heat capacity (cal/deg.mole)	Temp. (°K)	Heat capacity (cal/deg.mole)
Temp. of fusion a		Series E (liquid)	
Series A (solid)		188.64	40.90
95.47	23.64	196.82	41.18
102.32	24.76	204.98	41.50
109.87	25.91	213.38	41.86
118.42	27.15	223.47	42.34
153.75	31.83	232.61	42.83
158.55	32.42	241.82	43.38
163.96	33.11	250.92	43.92
169.63	33.82	257.36	44.23
175.45	34.53	266.64	44.91
180.84	35.33	276.11	45.57
Series B (solid)		286.22	46.20
81.86	21.09	295.41	46.80
89.37	22.62	304.69	47.34
97.50	23.99	Heat of fusion c	
105.83	25.30	Temp. of fusion b	
114.94	26.66	Series F (solid)	
124.08	27.96	45.01	11.77
133.59	29.23	49.11	12.97
142.88	30.43	53.80	14.34
151.85	31.57	60.06	16.08
158.66	32.45	67.14	17.90
163.86	33.07	Series G (solid)	
169.52	33.82	15.65	2.501
175.32	34.52	17.07	2.968
180.63	35.14	18.78	3.549
Series C (solid)		20.60	4.170
173.32	34.43	22.51	4.757
176.12	34.59	24.66	5.508
179.24	34.99	27.18	6.291
182.27	35.45	30.54	7.350
Heat of fusion a		34.14	8.473
Series D (liquid)		37.78	9.590
190.55	40.95	41.95	10.82
198.94	41.25	75.16	19.61
207.85	41.61	Temp. of fusion c	
217.27	42.05		
226.94	42.53		
236.46	43.04		
243.29	43.49		
252.57	44.03		
261.90	44.61		
Heat of fusion b			

TABLE IV

The thermodynamic properties of tetramethylgermane
at rounded temperatures

Temp. (°K)	C_p (cal/ deg.mole)	$\frac{(H-H_o)}{T}$ (cal/ deg.mole)	S (cal/ deg.mole)	$\frac{-(F-H_o)}{T}$ (cal/ deg.mole)
15	2.253	0.6152	0.8306	0.2154
20	3.967	1.2426	1.7170	0.4744
25	5.616	1.9548	2.7821	0.8273
30	7.182	2.6953	3.9442	1.2489
35	8.745	3.4477	5.1684	1.7207
40	10.25	4.2048	6.4353	2.2306
45	11.76	4.9603	7.7297	2.7694
50	13.24	5.7147	9.0458	3.3311
60	16.06	7.2073	11.713	4.5055
70	18.51	8.6575	14.384	5.7263
80	20.66	10.022	16.994	6.9723
90	22.73	11.324	19.552	8.2285
100	24.39	12.548	22.033	9.4856
110	25.93	13.695	24.431	10.736
120	27.38	14.776	26.750	11.974
130	28.77	15.799	28.997	13.198
140	30.07	16.772	31.177	14.405
150	31.34	17.701	33.295	15.594
160	32.60	18.593	35.358	16.765
170	33.88	19.455	37.373	17.918
180	35.14	20.291	39.345	19.054
190	40.94	30.617	51.078	20.461
200	41.30	31.141	53.187	22.045
210	41.70	31.634	55.211	23.577
220	42.17	32.103	57.162	25.059
230	42.68	32.551	59.047	26.496
240	43.27	32.985	60.876	27.891
250	43.86	33.409	62.655	29.246
260	44.48	33.822	64.387	30.564
270	45.15	34.230	66.078	31.848
280	45.81	34.632	67.732	33.100
290	46.45	35.028	69.351	34.323
300	47.06	35.419	70.936	35.516

FIGURE I. THE MOLAR HEAT CAPACITY OF TETRAMETHYLGERMANE

TABLE V

The temperature of fusion of tetramethylgermane
versus the reciprocal of the fraction melted

<u>Temp. of fusion ($^{\circ}\text{K}$)</u>	<u>(Fraction melted)$^{-1}$</u>
Determination a	
184.343	4.437
184.354	2.176
184.358	1.441
184.361	1.078
(184.366)	(Extrapolated to zero impurity)
Determination b	
184.340	4.938
184.358	2.228
184.367	1.440
184.374	1.065
(184.379)	(Extrapolated to zero impurity)
Determination c	
184.340	5.712
184.353	2.806
184.360	1.794
184.364	1.320
(184.370)	(Extrapolated to zero impurity)

Best value at zero impurity: $184.368 \pm 0.010^{\circ}\text{K}$
(95% confidence interval)

where:

- T = temperature of the sample
- x_2 = mole fraction of impurity
- R = gas constant
- T_0 = temperature of fusion at zero impurity
- ΔH = molar heat of fusion
- f = fraction of sample melted

The best value of the temperature of fusion at zero impurity was found to be $184.368^\circ \pm 0.010^\circ\text{K}$. (95% confidence interval). The pressure of helium in the sample container at this temperature was 229 mm. Its effect on the temperature of fusion should be negligible. The best value of the impurity content was found to be 0.020 mole %. This is in fair agreement with the 0.012 mole % impurity content determined from premelting corrections.

5. Heat of Fusion

Three determinations were made of the heat of fusion of tetramethylgermane. The results are summarized in Table VI.

Several corrections must be applied to the energy supplied to the sample. The first is simply the subtraction of the contribution due to the heat capacity of the sample and container over the temperature interval of the determination.

The second correction involves premelting; due to the presence of impurities, at any temperature below the fusion temperature, some amount of the sample is already melted. Consequently, the amount of heat necessary to melt this amount

of sample must be added to the heat input. The correction is given by:

$$Q \text{ (p.m.)} = \frac{n_2 R T T_0}{(T_0 - T)}$$

where T is the temperature at the start of the determination. The other symbols have the same meaning as before.

The third correction which must be made is the radiation correction. During a determination of the heat of fusion, the radiation shield surrounding the sample container is maintained at the temperature of fusion. In the early stages of the determination, then, heat is radiated to the sample container and in the later stages, from it. The temperatures of the radiation shield, T_s , and of the sample container, T_{sc} , are monitored during the determination. It is assumed that Newton's law of cooling is followed:

$$\frac{dQ}{dt} = k(T_s - T_{sc})$$

where Q is the heat radiated to the sample container and k is a constant. This equation is integrated graphically. The constant k is evaluated from the initial and final temperature drifts of the sample container and a knowledge of its heat capacity. The value of k at 184°K was found to be $0.0210 \text{ cal/deg. min.}$ Values of Q ranged from -0.21 to $+0.39$ calories and are incorporated into the "Heat Input" values in Table VI. The final value for the heat of fusion of tetramethylgermane is $1779.9 \pm 1.7 \text{ cal/mole}$ (95% confidence interval).

6. Heat of Vaporization and Vapor Pressure

The results of three determinations of the heat of vaporization of tetramethylgermane are summarized in Table VII. The apparatus used was built by Weber (6) and modified by Davis (3).

Because tetramethylgermane is a powerful solvent for stopcock lubricants, it was necessary to run the heats of vaporization at a temperature which was as low as possible but at which the vapor pressure was still high enough that the throttling valves could be properly adjusted. The temperature chosen was 285°K . Despite this precaution, of the 48.3403 grams of tetramethylgermane distilled into the calorimeter for the heat of vaporization determinations, 0.0262 gram were not recovered and are assumed to have been absorbed in the stopcock grease. The heats of vaporization are corrected for this loss.

As with the heat of fusion determinations, a radiation correction must be applied to the heat input. Experimentally, it is desirable to maintain the radiation shield at a slightly higher temperature than the sample container in order to preclude the possibility of condensation in the distillation tube where it passes through the radiation shield. For this reason, the radiation corrections are always positive. In addition, because of the higher temperature, the radiation constant is much larger than in the heat of fusion determinations: 0.123 cal/deg. min at 285°K versus 0.0210 cal/deg. min at 184°K . For these reasons, the radiation corrections are larger, ranging from +2.20 to +3.57 calories.

The heats of vaporization were calculated by the iterative

TABLE VI

The heat of fusion of tetramethylgermane

No.	Temp. interval (°K)	Heat input (cal)	$\int \text{CdT}$ (cal)	Premelting (cal/sample)	ΔH (cal/sample)
a	178.366-189.569	1088.13	274.46	0.42	814.09
b	180.842-186.754	957.44	143.76	0.74	814.42
c	177.474-186.042	1016.62	203.08	0.37	813.90

Average value: 814.14 ± 0.79 cal/sample

Equivalent to 1779.9 ± 1.7 cal/mole (95% confidence interval)

C is total heat capacity of sample and container

TABLE VII

The heat of vaporization of tetramethylgermane at 285°K

No.	Amount distilled (moles)	Temp. interval (°K)	Heat input (cal)	ΔH (cal/mole)
a	0.063384	284.673-284.631	424.78	6720.4
b	0.063519	284.813-284.645	423.99	6726.5
c	0.064020	284.901-284.545	424.54	6718.8

Average value: 6722 ± 10 cal/mole (95% confidence interval)

method of Weber (6) which treats the experimental data so as to produce a heat of vaporization which would have been obtained had the determination been run under constant temperature conditions. The final value for the heat of vaporization of tetramethylgermane at 285°K was found to be 6722 ± 10 cal/mole (95% confidence interval).

Vapor pressure measurements were made in the temperature range 189° to 296°K. by means of a large bore mercury manometer and a Wild cathetometer capable of measuring heights to an accuracy of ± 0.02 mm. The pressures are corrected for meniscus height according to the tables of Blaisdell (12), for temperature variations in the density of mercury, and for the value of the gravitational constant at the laboratory location. The data, summarized in Table VIII, was fitted to the following Antoine equation by the method of least squares:

$$\ln P_{\text{mm}} = 15.72198 - 2513.203/(T-41)$$

The measured pressures deviate from the equation with a root mean square deviation of ± 0.09 mm.

Dennis and Hance (13) report vapor pressure data for tetramethylgermane over the temperature range from -89° to 47°C. The data is presented as a table of pressures versus temperatures. An attempt to fit this data to an Antoine equation showed a root mean square deviation larger than ± 3 mm with individual deviations as large as 9 mm. Zablotna (14) measured the vapor pressure in the temperature range from 20° to 240°C. and fit the data to the

TABLE VIII

Measured vapor pressure of tetramethylgermane and
resulting heat of vaporization

No.	Temperature (°K)	P _{exptl} (mm)	P _{exptl} -P _{calc} (mm)
1	189.046	0.39	0.10
2	193.956	0.65	0.16
3	200.052	1.03	0.11
4	206.172	1.81	0.15
5	211.816	2.84	0.10
6	216.561	4.12	0.04
7	221.087	6.03	0.18
8	225.531	8.16	-0.03
9	229.680	10.96	-0.09
10	234.598	15.42	-0.07
11	239.830	21.71	-0.09
12	245.009	30.07	0.02
13	250.550	41.58	-0.04
14	256.193	56.98	-0.03
15	260.844	72.97	-0.01
16	265.679	93.39	0.05
17	270.818	119.87	0.01
18	275.643	150.13	0.04
19	280.641	187.72	0.06
20	284.680	223.25	-0.03
21	291.150	291.44	-0.11
22	296.314	357.30	0.06

Antoine equation: $\ln P_{\text{mm}} = 15.72198 - 2513.203/(T-41)$

Heat of vaporization: 6668.8 cal/mole $\pm$ 4.8 cal/mole
at 285°K

equation:

$$\log P_{\text{mm}} = 7.7721 - 1548.9/T$$

The equation is claimed to fit the data to within ± 1 mm. Both sets of data agree with the data of this research within the stated bounds of error.

The critical constants for tetramethylgermane were estimated by the method of Pitzer and Curl (15). The values obtained for the critical temperature and critical pressure were 476°K . and 28.1 atm., respectively. These values, when put into the Berthelot equation, give a value of the second virial coefficient at 298°K of -1.40 liter/mole. The second virial coefficients of neopentane (16) and tetramethylsilane (17) at this temperature are -1.09 and -1.21 liter/mole, respectively. The only gas data for tetramethylgermane given in the literature is the gas density (13) at 0°C . This yields a value of the second virial coefficient at 0°C of -0.28 liter/mole. Compressibility data calculated from the Berthelot equation and the estimated critical constants must be regarded as uncertain.

Solving the Clapeyron equation using calculated compressibility data and the vapor pressure equation of this research gives a heat of vaporization at 285°K of 6668.8 ± 4.9 cal/mole. The uncertainty figure reflects only the precision uncertainty in the vapor pressure equation. Agreement with the experimental value is not satisfactory and the experimental value must be accepted as the best value.

7. The Entropy

A Debye function of six degrees of freedom was found to best fit the experimental heat capacities from 15° to 28°K. The values of θ calculated for the heat capacity points in this temperature range are presented in Table IX. The average value of θ , 105.7°K, was used to calculate the entropy at 15°K.

A smooth plot was made of the heat capacity data from 15° to 305°K. The curve was integrated numerically using both Simpson's and Weddle's rules. The entropy of the solid at fusion is:

$$S (184.37^\circ\text{K, solid}) = 40.19 \pm 0.05 \text{ cal/deg. mole}$$

The entropy of fusion and the entropy contribution of the liquid from fusion to 285°K were added to this value to obtain the entropy of the liquid at 285°K:

$$S (285^\circ\text{K, liquid}) = 68.55 \pm 0.08 \text{ cal/deg. mole}$$

The entropy of vaporization at 285°K was calculated from the experimentally determined heat of vaporization.

If one assumes that the equation of state of the real gas may be adequately described by the Berthelot equation, then the correction for gas imperfection takes the form:

$$S (\text{ideal}) - S (\text{real}) = 27RT_c^3 P / 32T^3 P_c$$

This equation was used in conjunction with the previously

TABLE IX

The apparent Debye θ for six degrees of freedom for
tetramethylgermane as determined from
experimental heat capacities

<u>T ($^{\circ}$K)</u>	<u>θ ($^{\circ}$K)</u>
15.65	104.9
17.07	105.9
18.78	106.2
20.60	106.3
22.51	107.0
24.66	105.6
27.18	104.3
Average	105.7

estimated critical constants to calculate the gas imperfection correction.

The entropy contribution due to compression is simply $R \ln(P/760)$ where P is the vapor pressure of tetramethylgermane at 285°K as calculated from the vapor pressure equation.

The above calculations are summarized in Table X. The final value of the entropy of tetramethylgermane in the ideal gas state at 285°K and one atm pressure is:

$$S(285^\circ\text{K}, \text{ideal gas}, 1 \text{ atm}) = 89.81 \pm 0.15 \text{ cal/deg. mole}$$

8. Potential Barrier to Methyl Group Rotation

The potential barrier hindering the rotations of the methyl groups in tetramethylgermane may be calculated by comparing the experimentally determined entropy with the entropy calculated from spectroscopic data and molecular parameters.

The translational contribution to the entropy was calculated from the well known Sackur-Tetrode equation (Ref. 18, p. 420, eq. 27.2) and was found to be:

$$S(\text{translational}, 285^\circ\text{K}, 1 \text{ atm}) = 40.339 \text{ cal/deg. mole}$$

The infrared and Raman spectra of tetramethylgermane have been studied by several investigators (19, 20, 21). The frequency assignments of the most recent and complete work, that of Lippencott and Tobin (21), were used to calculate the vibrational contribution to the entropy. The contribution of each fundamental vibration was

TABLE X

The molar entropy of tetramethylgermane at 285°K

	S (cal/deg. mole)
0°-15°K, Debye ($\theta = 105.7$, six degrees of freedom)	0.831
15°-184.37°K, $\int C_p d(\ln T)$	39.363
Fusion, 184.37°K	9.654
184.37°-285°K, $\int C_p d(\ln T)$	18.697
S at 285°K (liquid)	68.545
Vaporization (Experimental, 285°K)	23.586
Gas imperfection	0.083
Compression	-2.407
S at 285°K (ideal gas)	89.81 $\pm$ 0.15

interpolated from a six place table of Einstein functions calculated on the Rice University computer. The calculations are summarized in Table XI. The large contributions of the skeletal distortions of symmetry types E and F_2 are noteworthy. The total vibrational entropy was found to be:

$$S \text{ (vibrational, } 285^\circ\text{K)} = 14.103 \text{ cal/deg. mole}$$

For a tetrahedral molecule of the type $M(\text{CH}_3)_4$, the moment of inertia, I, can be easily shown to be:

$$I = \frac{8}{3}\epsilon^2 m_c + (8\epsilon^2 + \frac{16}{3}\alpha\epsilon + 8\alpha^2)m_h$$

where:

ϵ = M-C bond length

α = C-H bond length

m_c = mass of a C atom

m_h = mass of a H atom

The Ge-C bond length in tetramethylgermane was determined by the electron diffraction studies of Brockway and Jenkins (22) to be $1.98 \overset{\circ}{\text{A}}$. Using this value and the widely accepted methyl C-H bond length of $1.093 \overset{\circ}{\text{A}}$ with the above equation, the moment of inertia of tetramethylgermane was found to be 296.27×10^{-40} gram. cm^2 . The overall rotational contribution to the entropy was calculated from the usual equation (Ref. 18, p. 428, eq. 27-32) using a symmetry number of 12, and was found to be:

TABLE XI

Vibrational entropy of tetramethylgermane.

Frequency assignments taken from Ref. 21

$$u = 1.4388 \text{ w/T} = 0.0050484 \text{ w at } 285^\circ\text{K}$$

<u>Vibrational description</u>	<u>Sym.</u>	<u>w. (cm⁻¹)</u>	<u>u</u>	<u>S/R</u>
CH ₃ stretching	A ₁	2907	14.676	0.0000
CH ₃ deformation	A ₁	1247	6.2954	0.0135
CH ₃ stretching	E	2978	15.034	0.0000
CH ₃ deformation	E	1400	7.0678	0.0137
CH ₃ rocking	E	825	4.1649	0.1627
CH ₃ stretching	F ₁	2978	15.034	0.0000
CH ₃ deformation	F ₁	1437	7.2536	0.0175
CH ₃ rocking	F ₁	825	4.1649	0.2441
CH ₃ stretching	F ₂	2978	15.034	0.0000
CH ₃ stretching	F ₂	2907	14.676	0.0000
CH ₃ deformation	F ₂	1437	7.2546	0.0175
CH ₃ deformation	F ₂	1234	6.2298	0.0428
CH ₃ rocking	F ₂	825	4.1649	0.2441
skeletal stretching	A ₁	558	2.8170	0.2408
skeletal distortion	E	175	0.8835	2.3116
skeletal stretching	F ₂	595	3.0038	0.6229
skeletal distortion	F ₂	195	0.9844	3.1653

$$\text{Total vibrational entropy} = 7.0965 \text{ R} = 14.103 \text{ cal/deg.mole}$$

$$S \text{ (overall rotation, } 285^{\circ}\text{K)} = 21.979 \text{ cal/deg. mole}$$

In calculating the entropy contribution of internal rotation, it was assumed that rotation was unhindered and uncoupled. The reduced moment of inertia was calculated to be 5.234×10^{-40} gram. cm^2 (Ref. 18, p. 440, eq. 27-58). Assuming a symmetry number of 3 for internal rotation, the partition function for free rotation, Q_f , (Ref. 18, p. 439, eq. 27-56) was calculated to be 3.5964 at 285°K . The entropy per methyl group was then calculated (Ref. 18, p. 424, eq. 27-15). This value was then multiplied by four to obtain the total entropy due to unhindered internal rotation:

$$S \text{ (free internal rotation, } 285^{\circ}\text{K)} = 14.145 \text{ cal/deg. mole}$$

By summing the contributions of translation, vibration, overall rotation, and free internal rotation, the total entropy was found to be:

$$S \text{ (} 285^{\circ}\text{K, ideal gas, 1 atm, calc.)} = 90.566 \text{ cal/deg. mole}$$

Comparing this value to the experimentally determined value, the entropy difference between the calculated and experimentally determined values per rotor was found to be 0.190 ± 0.038 cal/deg. mole. Referring to Table IV of the paper of Pitzer and Gwinn (23), we obtain for the potential barrier:

$$V = 750 \pm 90 \text{ cal/mole}$$

This value is surprisingly low. The potential barriers for ethane (24), propane (25), isobutane (26), and neopentane (27) are 2930, 3555, 3900, and 4200 cal/mole, respectively. The increasing barrier as the number of methyl groups increases is ascribed to coupling. The potential barriers for methylsilane (28), dimethylsilane (29), trimethylsilane (30), and tetramethylsilane (31) are 1670, 1647, 1830, and 1600 cal/mole, respectively. With the increase in length of the Si-C bond over that of the C-C bond, the effect of coupling seems to have become insignificant. It would seem reasonable that in the case of the methyl germanium compounds, where the Ge-C bond is longer than the Si-C bond, the potential barrier would be approximately constant as the number of methyl groups increases. The potential barriers for methylgermane (32), and dimethylgermane (33) are 1240 and 1180 cal/mole, respectively.

If one wishes to assume that the potential barrier in tetramethylgermane is 1200 cal/mole, then the difference between the calculated entropy assuming free rotation and the experimentally determined entropy should be 1.71 cal/deg. mole; i.e. the calculated entropy should be 0.95 cal/deg. mole higher or the experimentally determined entropy should be 0.95 cal/deg. mole lower. This figure is much greater than the uncertainty in the experimentally determined entropy and is too great to be explained by reasonable errors in the molecular parameters and vibrational assignments used in obtaining the calculated entropy.

D. Tetramethylstannane

1. Sample

The sample of tetramethylstannane, $(\text{CH}_3)_4\text{Sn}$, used in this research was obtained from Alfa Inorganics, Inc. of Beverly, Massachusetts. According to the manufacturers, the material was better than 99% pure. The material was analyzed by vapor chromatography and was found to contain 0.5 mole % of an impurity of about the same boiling point as the tetramethylstannane and 10 mole % of an impurity of a much higher boiling point than the tetramethylstannane.

2. Purification

145 grams of tetramethylstannane was fractionally distilled using the same apparatus as described in section II-C-2. The first 95 ml was distilled at a reflux ratio of 15 to 1 and was cut into 3 fractions of 25, 25 and 45 ml. Approximately 25 ml remained in the pot. Analysis by vapor chromatography showed that the high boiling impurity had been reduced to 0.1 mole % or less in all three fractions. The low boiling impurity was still present at the 0.1 mole % level in the third fraction. Because of this distribution of the low boiling impurity, fractional distillation alone was not a suitable means of purification.

Several attempts at purification by extraction or by reaction of the impurity were attempted but were unsuccessful.

Finally, fractional crystallization was found to be an effective means of removing the low boiling impurity. Prior to

proceeding with the fractional crystallization, the 95 ml of tetramethylstannane obtained from the first distillation was redistilled in the same apparatus in order to remove the last traces of the high boiling impurity. 5, 5, 30, and 40 ml fractions were distilled off leaving 15 ml in the pot. Fractional crystallization was accomplished by placing the tetramethylstannane in a stoppered test tube of such a size that the test tube was about half filled. The test tube was then suspended in a Dewar flask containing a small amount of liquid nitrogen. Although the bottom of the test tube was above the liquid nitrogen level, the gaseous nitrogen boiling off provided enough cooling to freeze the tetramethylstannane within 3 or 4 hours. When freezing was almost complete, the test tube was removed from the Dewar flask and the liquid phase was quickly decanted off. The process was repeated with the fractions being consolidated when analysis by vapor chromatography showed them to be of the same purity. Finally, 60 ml of tetramethylstannane was obtained in which analysis by vapor chromatography showed the content of high boiling impurity to be less than 0.001 mole % and the content of low boiling impurity to be 0.03 mole %.

3. Heat of Vaporization and Vapor Pressure

Vapor pressure measurements were made on tetramethylstannane in the temperature range from 220° to 294°K in the same manner as described in section II-C-6. The data, summarized in Table XII, was fitted to the following Antoine equation by the method of

TABLE XII

Measured vapor pressure of tetramethylstannane
and resulting heat of vaporization

No.	Temperature (°K)	P _{exptl} (mm)	P _{exptl} -P _{calc} (mm)
1	219.918	0.81	0.11
2	225.693	1.25	0.07
3	230.703	1.86	0.05
4	235.321	2.66	0.04
5	240.042	3.78	0.01
6	245.177	5.46	-0.03
7	250.328	7.78	-0.07
8	255.287	10.86	-0.04
9	260.212	14.87	-0.02
10	264.860	19.73	0.00
11	269.450	25.74	-0.03
12	274.704	34.54	0.01
13	279.498	44.60	0.00
14	284.292	57.05	0.03
15	289.128	72.43	0.05
16	293.848	90.47	-0.05

Antoine equation: $\ln P_{\text{mm}} = 16.32509 - 3000.302/(T-40)$

Heat of vaporization: 7861.5 ± 12.7 cal/mole at 298.15°K

least squares:

$$\ln P_{\text{mm}} = 16.32509 - 3000.302/(T-40)$$

The measured pressures deviate from the equation with a root mean square deviation of ± 0.05 mm.

Bullard and Haussmann (34) report vapor pressure data for tetramethylstannane over the temperature range from 0° to 80°C . The data from 0° to 35°C is represented by the equation:

$$\log P_{\text{mm}} = 7.8955 - 1747.8/T.$$

No estimate of error or standard deviation is reported. An attempt to fit their data to an Antoine equation showed a root mean square deviation of ± 0.33 mm. In addition, their only criterion for purity was a reported 0.5°C boiling range. Their results are lower than those of this research, the difference being 0.25 mm at 0°C and 1.87 mm at 20°C .

The critical constants of tetramethylstannane were estimated by the method of Pitzer and Curl (15). The values obtained for the critical temperature and critical pressure were 513°K and 27.4 atm, respectively. No equation of state data for tetramethylstannane exists in the literature. Compressibility data was calculated from the estimated critical constants and the Berthelot equation. This was used in conjunction with the Clapeyron equation and the vapor pressure equation of this research in order to calculate the heat of

vaporization. The value at 298.15°K was found to be 7862 ± 13 cal/mole. The uncertainty figure reflects only the precision uncertainty in the vapor pressure equation.

4. Heat Capacity

A large number of heat capacity determinations were made on tetramethylstannane over the temperature range from 15° to 300°K . It was discovered that although the heat capacities in a given series were quite smooth, a second series covering the same temperature range would give values differing from the first series by up to 3%. Heating and cooling curves were run. There was no trace of any solid-solid transitions. It appeared that there might be a correlation between heat capacity and thermal history in the solid phase. However, one series of heat capacities in the liquid phase was significantly different from other series in the liquid phase. It is difficult to explain this except in terms of a problem in the measuring circuitry of the apparatus. The circuitry was carefully examined but no malfunctions were discovered. Since the heat capacity values are not reproducible, for whatever reason, they are of no value in obtaining an entropy.

5. Temperature of Fusion

Three determinations of the temperature of fusion are summarized in Table XIII. Plots of the temperature versus the reciprocal of the fraction of the sample melted show a definite upward curvature for values of the reciprocal of the fraction

melted less than 3. This would indicate the presence of at least one impurity soluble in both phases. The scatter in the data prevented a meaningful determination of the concentration and distribution of the solid soluble impurity. The liquid soluble-solid insoluble impurity content was estimated from the linear portion of the plot and was found to be 0.068 mole %. The liquid soluble-solid insoluble impurity content estimated from premelting heat capacity data was found to be 0.063 mole %. The temperature of fusion at zero impurity, 218.070°K, and its probable uncertainty, $\pm 0.025^\circ\text{K}$, were estimated by graphical extrapolation. Staveley, et. al. (35) report a temperature of fusion for tetramethylstannane of 218.18°K.

TABLE XIII

The temperature of fusion of tetramethylstannane
versus the reciprocal of the fraction melted.

<u>Temp. of fusion (°K)</u>	<u>(Fraction melted)⁻¹</u>
Determination a	
217.891	5.175
217.954	2.321
217.981	1.495
218.006	1.102
Determination b	
217.812	8.790
217.925	3.667
217.970	1.961
217.992	1.338
Determination c	
217.696	13.515
217.936	2.852
217.975	1.650
217.990	1.160

Best value at zero impurity: 218.070 ± 0.025°K

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