The Heat Capacities and Entropy of Dimethyl Sulphide and of Fluorotrichloromethane. The Preparation of Boron Trichloride

Thesis by

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1. Important information relative to the nature of potential barriers to internal rotation can be expected to emerge from the projected calorimetric studies of CH_3SH and CH_3CF_3.

2. A free energy decrease between 0 and 8000 calories accompanies the reaction,

$$6H_2 + 2BCl_3 \longrightarrow B_2H_6 + 6HCl. \quad \text{(gases at 298° K.)}$$

The search for a means to cause this reaction to proceed at a rate sufficiently great to permit the preparation of boroethane in quantities large enough for accurate calorimetric measurements would likely lead to an important contribution to the information concerning the nature of potential barriers to internal rotation. For example, the effect of finely divided palladium as a catalyst and the effect of hydrogen pressure might be investigated.

3. Although Schumann and Aston's calculation of the potential barrier for the C-O bond in ethyl alcohol (10,000 cal. mol^{-1}) is probably incorrect, structure considerations might lead one to expect the barrier for the C-O bond to be higher than that for the C-C bond. The value taken, in the calculation, for the barrier in the case of the C-C bond can reasonably be higher for ethyl alcohol than for ethane. The barrier in the case of the C-O bond might, from similar considerations, be expected to be higher for ethyl alcohol than for methyl alcohol; the barrier for methyl alcohol is roughly 7400 cal. mol^{-1}.

4. Rotation of the methyl groups in dimethyl sulfide is hindered.

5. The melting point of dimethyl sulfide should be revised downward from the present value of -83.2°C., determined by G. Carrara and A. Coppadoro (1903), to -98.27°C. This melting point would be a convenient secondary standard point for thermometer calibration.

6. The following merit investigation:
   (a) A slow reaction takes place between dimethyl sulfide and sodium at room temperatures. A reasonable guess as to the products, based upon the meager information available, is that they are sodium polysulfides and ethane.

   (b) During the preparation of boron trichloride from boron and chlorine, a sample having an intense yellow color was obtained. Apparently the treatment received by this sample differed from that received by the others only in the length of time (8 to 10 weeks in the case of the former) before the excess dissolved chlorine was removed by reaction with mercury. This sample had the properties of boron trichloride except for the yellow color, which was not diminished by standing over mercury (bright surface for a period of about two weeks) or by distillation (several times). A rough determination of the molecular weight (Dumas bulb) gave the result 101.

7. Some $POCl_3$ is probably formed in the preparation of BCl_3 by means of the reaction,

$$5B_2O_3 + 6PCl_5 \longrightarrow 10BCl_3 + 3P_2O_5 .$$

8. The chemical theory of conduction of nerve impulses across the synapse provides a more satisfactory explanation of the known facts than does the electrical theory.

9. The activity of certain reagents in solution is too often loosely attributed to gases in the atomic state.

10. More thought should be given to the improvement of the traditional system of academic marks on the collegiate level.

Summary

The heat capacities of dimethyl sulphide in the range from 13.4° to 291° K., the heat of fusion (1908 cal. mol^{-1}; m.p. 174.85° K.), and the heat of vaporization (6696 cal. mol^{-1}) at 291° K. were accurately measured. From these data the entropy of the ideal gas at 291.06° K. and 365.5 mm. was found to be 69.35 ± 0.1 cal. deg.^{-1} mol^{-1}. To bring the entropy calculated from molecular data to this value, it was necessary to assume a potential barrier of 2015 cal. mol^{-1} restricting the rotation of each methyl group, using the quantum statistical mechanical treatment of Crawford. The vapor pressure was found to be represented by the equation

$$\log_{10} p_{\text{mm.}} = 16.57356 - \frac{1878.16}{T} - 3.06733 \log_{10} T.$$

The heat capacities of fluorotrichloromethane from 54° to 292° K. and the heat of fusion (1647 cal. mol^{-1}; m.p. 162.68° K.) were measured. The difference between the entropy of the solid at 60° K. and that of the liquid at 296.94° K. was 41.86 cal. deg.^{-1} mol^{-1}.

Boron trichloride was prepared from boron trioxide and phosphorus pentachloride, this method being employed in order to obtain a very pure product, to be used for calorimetric measurements. Purification was accomplished by fractional distillation.

Introduction

There has been a growing interest in recent years in the problem of internal rotation in certain organic molecules. Differences between the molal entropies of the gaseous substances as determined by careful calorimetric measurements reaching almost to absolute zero and as calculated from spectroscopic and electron diffraction data provide means by which the relative freedom of rotation of methyl groups with respect to rigid frameworks in the molecules can be calculated. The thing that is actually determined calorimetrically is, of course, the difference in entropy between the crystalline substance at absolute zero (extrapolation being employed) and the substance in the state of a perfect gas at some much higher temperature, often near room temperature.

J. G. Aston and G. H. Messerly[1] found that the calorimetric entropy of tetramethylmethane was about 8 cal. deg.$^{-1}$ mol^{-1} below the spectroscopic entropy, and they attributed the difference to randomness of orientation in the crystals at very low temperatures, that is, to the failure to experimentally realize a pure quantum state at or near absolute zero. J. D. Kemp and K. S. Pitzer[2] found a similar but much smaller difference in the case of ethane. They assumed that the rotation of one methyl group with respect to the other is hindered, and by assuming a potential barrier of 3150 cal. mol^{-1}, they were able to obtain agreement among the following: the statistically calculated value of the entropy (by Kemp and Pitzer), the "third law" value of the entropy by Witt and

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[1] Aston and Messerly, "J. Chem. Physics", 4, 391 - 392 (1936).

[2] Kemp and Pitzer, "J. Am. Chem. Soc.", 59, 276 - 279 (1937).

Kemp, the heat capacity on the gas by Eucken and Parts, the values for the heat of hydrogenation of ethylene by Kistiakowsky, et. al., and by Rossini, and the numerous equilibrium measurements on the hydrogenation of ethylene. Pitzer[3] has treated the partition function for ethane-like molecules having restricted internal rotation. He claims that his expressions are reasonably accurate for most actual molecules, and he has given tables in which are presented the contributions of a single restricted rotational degree of freedom to the entropy, free energy, and heat capacity. Pitzer[4] has applied his theory in the consideration of the thermodynamics of ethane, ethylene, propane, propylene, butane, isobutane, tetramethylmethane, and others.

S. C. Schumann and J. G. Aston[5] have made calculations of the entropies of acetone and isopropyl alcohol on the basis, first, of free internal rotation, and second, of restricted rotation. Comparisons are made with the calorimetrically determined entropies. The values based upon restricted rotation are in better agreement with the values of the entropy change obtained from equilibrium data on the reaction.

$$(CH_3)_2CHOH\ (g) \rightleftarrows (CH_3)_2CO\ (g) + H_2\ (g),$$

than are those based upon free rotation. Schumann and Aston[6,7] have also calculated the entropy of ethyl alcohol on the bases of free and

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[3] Pitzer, "J. Chem. Physics", 5, 469 - 472 (1937).

[4] Pitzer, "J. Chem. Physics", 5, 473 - 479 (1937).

[5] Schumann and Aston, "J. Chem. Physics", 6, 485 - 488 (1938).

[6] Schumann and Aston, "J. Chem. Physics", 6, 480 - 484 (1938).

[7] Schumann and Aston, "J. Am. Chem. Soc.", 60, 985 - 986 (1938).

restricted internal rotation. Values of the entropy increase accompanying the reaction,

$$CH_2=CH_2\ (g) + H_2O\ (g) \rightleftarrows CH_3CH_2OH,$$

were thus obtained from both spectroscopic and calorimetric data. They showed that agreement with values of the entropy increase obtained from equilibrium data can be secured by assuming that the rotations about the C-C bond and C-O bond are restricted. The potential for the C-C bond is about 3000 cal. mol^{-1}, and that for the C-O bond is about 10,000 cal. mol^{-1}.

Experimental studies of methylamine and dimethylamine have been made by J. G. Aston, C. W. Siller, and G. H. Messerly[8] and by J. G. Aston, M. L. Eidinoff, and W. S. Forster[9] respectively. In the case of methylamine, the calorimetric entropy was found to be about 1.6 cal. deg.$^{-1}$ mol^{-1} below the spectroscopic entropy (assuming free rotation). In order to bring the value of the entropy of dimethylamine calculated from molecular data into agreement with the calorimetrically determined value, it was necessary to assume a potential of 3460 cal. mol^{-1} hindering the internal rotation of each methyl group.

Calculations made by L. S. Kassel[10] indicate that there is a difference of about 1.75 cal. deg.$^{-1}$ mol^{-1} between the calorimetric

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[8] Aston, Siller, and Messerly, "J. Am. Chem. Soc.", 59, 1743 - 1751 (1937).

[9] Aston, Eidinoff, and Forster, "J.Am.Chem.Soc.", 61, 1539 - 1543 (1939).

[10] Kassel, "J.Chem.Physics", 4, 493 - 496 (1936).

and spectroscopic (assuming free rotation) entropies of methyl alcohol, the former being the lower. At the time of publication, Kassel considered it impossible to reach a final decision regarding rotation about the C-O bond. He suggested that the entropy difference might be ascribed to lack of order in the actual crystal at absolute zero.

D. W. Osborne, C. S. Garner, and D. M. Yost[11] have determined the entropy of dimethylacetylene as a result of their calorimetric studies. By comparing the calorimetric and spectroscopic entropies, they have shown that rotation of the methyl groups is not hindered.

The present study of dimethyl sulphide has been undertaken in order to determine whether a potential barrier to free rotation of the methyl groups exists in the case of this molecule and to determine, if possible, the approximate height of the barrier. Another objective of the research is to contribute to the information concerning internal rotation through the addition of data on molecules in which the methyl group is attached to a kind of atom which has not heretofore been included in studies of this kind, namely sulphur. (It is planned that the thermal data shall include methyl mercaptan.) It is to be hoped that from the information accumulated by the various workers in this field may eventually come a clearer understanding of the exact nature of these potential barriers than is at present possible.

Another type of information that can be obtained from low temperature calorimetry is concerned with the states of crystals actually

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[11] Osborne, Garner, and Yost, "J. Chem. Physics", 8, 131 (1940).

attained at temperatures close to absolute zero. If the energy states of the molecule at elevated temperatures (e. g., at room temperature) are known, lack of uniform orientation in the crystal at absolute zero can be detected, that is, the amount of residual entropy at absolute zero can be determined. In many cases, such as those of carbon monoxide, nitrous oxide, and water,[12] the actual nature of the orientation can be worked out.

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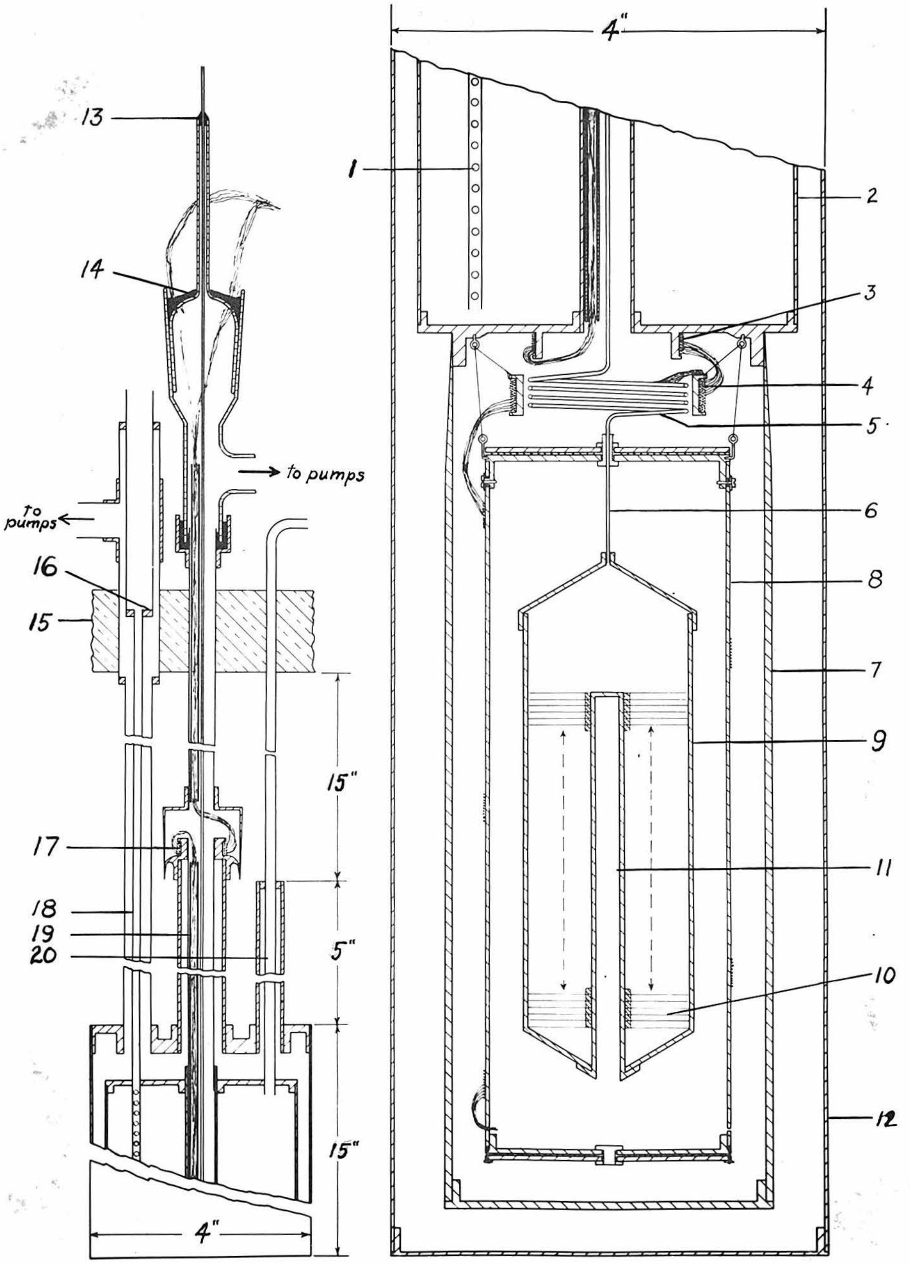
[12] Pauling, "J. Am. Chem. Soc.", <u>57</u>, 2680 - 2684 (1935).

Apparatus

Inasmuch as the writer did not construct the apparatus employed in the measurements, it might appear that a detailed description of the apparatus would be inappropriate. However, a detailed description has not as yet been written; hence, a large amount of specific information is given in the following account which would not otherwise be included, since it will probably be useful to others who will use the calorimeter. The figure on the following page shows the calorimeter and its surroundings, to scale. The calorimeter itself (9) has an average wall thickness of 0.05 cm. and is of copper. A platinum case containing a platinum resistance thermometer and a constantan heater fits into a reentrant tube (11), thermal contact being made by stop-cock grease. Forty-five perforated copper discs (10), 0.005 to 0.008 cm. thick, fit tightly on the central tube, spaced 0.020 cm. apart by means of copper rings, which are 1 cm. in diameter. The parts are soft-soldered together. The discs, spacers, and calorimeter, inside and outside, are gold plated. A filling tube (6) attached to the calorimeter consists of monel metal and has an inside diameter of 0.014 cm. and a wall thickness of 0.011 cm.

Surrounding the calorimeter is a chromium-plated copper radiation shield (8), approximately 0.1 cm. thick on the side. The calorimeter is suspended from the top of the radiation shield by means of the filling tube, the latter being attached to the top with bakelite cement. This cement has been baked on, good thermal contact but electrical insulation being thus provided. Where reference is made to bakelite cement hereafter, it should be understood that the cement has been baked on.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The side, top, and bottom of the shield are equipped with heaters fastened with bakelite cement. The three parts of the shield just mentioned are electrically insulated from each other. There are difference thermocouple junctions on the middle of the side of the calorimeter, the middle of the side of the shield, the top of the shield, and the bottom of the shield, soldered in place. There is also a difference thermocouple junction on a brass part called the "floating ring" (4), it being placed in a hole in the latter but electrically insulated by means of bakelite cement.

The leads from the calorimeter and difference thermocouples are wound on the shield underneath the heater windings, then around the floating ring, around a ring (3) on the bottom of a container used to hold liquid hydrogen, the "hydrogen can" (2), and around a third ring (17) where they are brought to the boiling point of liquid air. They are finally brought out through a picein joint (14) at the top of the apparatus. The leads are held in place by bakelite cement. The purpose of the various rings is to finally bring the leads to approximately the temperature of the shield before they reach it, in order to prevent the existence of a "hot spot" at the point where the leads make contact with the shield. The rings thus constitute "thermal dams". The shield and floating ring are suspended by means of fish line from the hydrogen can.

Surrounding the shield is a chromium-plated (inside and outside) copper sylinder (7), approximately 0.18 cm. thick, the upper rim of which is soldered to the hydrogen can. The hydrogen can is suspended by means of monel metal tubes (18, 19, and 20) from an outer brass cylinder (12), which completely encloses the apparatus described. In general, parts not plated are buffed up. The whole assembly is suspended in a three-foot Pyrex Dewar bulb from a wooden block (15) by means of three tubes used for evacuation. The wooden block is fastened to a kapok lined box, which holds the Dewar bulb. The copper cylinder is vacuum-tight, but the shield is not. The space between the brass cylinder and the copper cylinder, hereafter called the outer space, the space inside the copper cylinder, hereafter called the inner space, and the space inside the hydrogen can can be individually evacuated. Holes in the shield allow evacuation of the space between the shield and calorimeter when the space between the copper cylinder and shield is evacuated.

Thermal contact between a coil (5) in the filling tube (to reduce the temperature gradient) and the floating ring is made by heavy copper braid. The filling tube leaves the apparatus through a picein joint (13). Four thermocouple junctions are soldered to the filling tube at intervals.

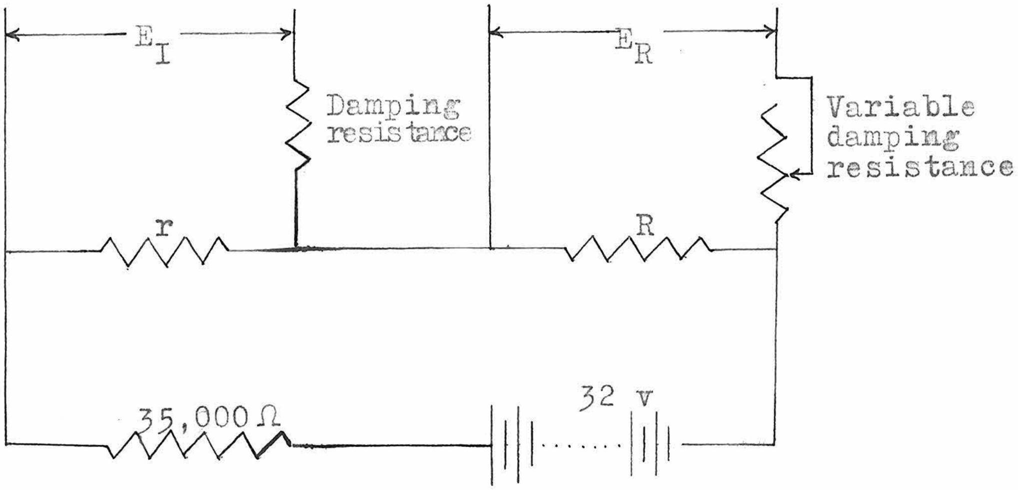
Liquid hydrogen is introduced into the hydrogen can through one of the monel metal tubes (18) supporting it, by means of a Dewar transfer tube, which fits against a shoulder (16). Air is excluded by a collar of rubber tubing. There are holes (1) in the inlet tube inside the hydrogen can.

Manipulation

It is evident from the foregoing description that the calorimeter is adapted to the measurement of the heat capacities of substances which boil near room temperature or below. In introducing material into the calorimeter, the following procedure is employed. Helium is admitted to the inner and outer spaces. Enough liquid air is poured into the large Dewar bulb to bring the whole contents to a temperature a few degrees above the melting point of the substance to be introduced. The substance is then distilled into the evacuated calorimeter. Following this, about one atmosphere of helium is admitted to the filling tube to drive any drops of liquid remaining in the tube down into the calorimeter. More liquid air is added to the Dewar bulb to cool the contents to the boiling point of liquid air. Next, the helium pressure in the calorimeter is reduced to (a known value of) a few centimeters, and lastly, the inner and outer spaces are evacuated.

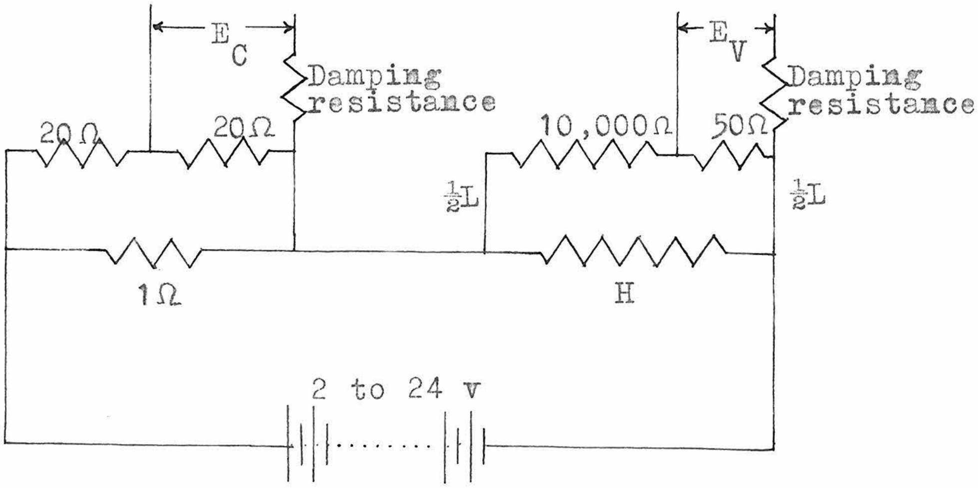
To cool the calorimeter to the temperatures attainable with liquid hydrogen, the liquid air level in the Dewar bulb is adjusted so that the outer brass cylinder is covered, the outer space is evaucated, helium is admitted to the inner space, and liquid hydrogen is introduced into the hydrogen can, slowly until the temperature reaches about 35° K., then more rapidly. After the temperature has fallen to about 20° K., the can is filled with liquid hydrogen. The transfer tube is then replaced with a stopper. The pressure at which the hydrogen is boiling is reduced by a high-capacity pump. When the hydrogen can reaches the minimum temperature attainable (about 12° K.), the inner space is evacuated with a pump <u>other</u> than that used for the outer space.

The resistance and energy input measurements are carried out with the use of a White Double Potentiometer in conjunction with standard resistances and cells. A calibration of the coils of the potentiometer has been made through intercomparison. The standard resistances and cells have been recently calibrated against standards of the Bureau of Standards in terms of international ohms and volts. The following is a diagram of the thermometer circuit:



The damping resistances are such that the galvanometer is critically damped. The resistance designated by r is fixed and has a value of very nearly 100 ohms; it has been accurately calibrated. The battery consists of Willard low discharge cells, which supply a very steady electromotive force under the conditions of use for which they are intended. The thermometer current flows continually except while the battery is being charged. For this reason, the current is practically constant. The resistance of the resistance thermometer (R) is determined by measuring the potentials E_I and E_R, and the temperature of the calorimeter is found through the use of a very accurate calibration. Since changes in r with the temperature of the room are sufficiently great to necessitate corrections, the room temperature must be known for each pair of potentials E_I and E_R.

The following is a diagram of the energy input circuit:



The numerical designations of resistances in this diagram are nominal, calibrations accurate to about 0.01% having been made. L denotes the potential lead resistance. It is measured under the conditions of the run by means of a Wheatstone bridge, and varies from about 3 to about 13 ohms. H denotes the heater.

The galvanometer used in measuring E_I, E_R, E_C, and E_V has a critical damping resistance of 450 ohms and a period of ten seconds. The telescope, scale, and length of optical path are such that the sensitivity is approximately 2.5 cm. per microvolt. Readings can be made to about 0.05 cm., so that it would seem possible to make measurements of potentials to about 0.02 microvolts. However, the results are not reproducible with this accuracy except for low potentials. At 14° K., 0.02 microvolts corresponds to 0.003°. Above 25° K. temperature measurements are reproducible to about 0.001°.

In measuring heat capacities, the temperature of the calorimeter and contents is first determined, readings being repeated at short intervals (usually 300 seconds) until it is apparent that thermal equilibrium has been reached. The potentiometer current is usually adjusted before each reading of E_R, but not between readings of E_R and E_I. The effective zero-point, or check reading of the galvanometer, and usually the sensitivity are determined for each reading. The principal quantities required for the determination of the energy input, E_C, E_V, and t, the time, are measured as follows. At a predetermined time, a switch is manually thrown which disconnects the heater battery from an "exercising" circuit of approximately the same resistance as the heater circuit and connects it to the latter. The exercising of the battery before the heating period prevents wide fluctuations in the current during this period. E_C is read at 0.211t and 0.789t, where t is the length of the heating interval, since it has been shown by Gibson and Giauque[13,14] that for a quantity which changes quadratically with time, the mean value of the quantity over a period t is equal to the arithmetic mean of the values at 0.211t

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[13] Gibson and Giauque, "J. Am. Chem. Soc.", <u>45</u>, 93 (1923).

[14] Giauque and Wiebe, "J. Am. Chem. Soc.", <u>50</u>, 101 (1928).

and 0.789t, regardless of the coefficients of the quadratic. It has been found that E_C can be represented by a quadratic expression with sufficient accuracy for this purpose for the heating intervals involved in heat capacity measurements. The change in the electromotive force of the battery is such that E_V can be taken as a linear function of the time without introducing an appreciable error; hence, E_V is read at the middle of the heating. As with readings of E_R and E_I, the check reading of the galvanometer is determined for each reading, but it is adequate to read E_C and E_V to about 1 microvolt. At the predetermined time of the close of the heating interval, the battery is switched back to the exercising circuit. The times are measured with both an electrical timing device and a calibrated stop-watch, the former being used principally as a matter of convenience in throwing the switch. Errors due to frequency irregularities are avoided by the use of the stop-watch. Following each heating period, the temperature of the calorimeter and contents is again determined, this being also the initial temperature for the next run. Equilibrium is usually attained within fifteen minutes except for temperatures just below the melting point of the substance, where the effects of premelting are observed.

During the run, the shield is kept within about 0.01° of the temperature of the calorimeter by a second operator, working at another switchboard. Control of the temperature is secured by the use of the difference thermocouples mentioned previously, in conjunction with a sensitive galvanometer (period about 5 seconds). At the beginning and end of the run, the deviation may exceed 0.01° by several times this amount, but experiments have shown that ordinarily no appreciable error is introduced thereby. This is evident from the following rates at which the calorimeter receives heat from the shield:

0.03 cal. per min. per degree at	175° K.
0.13	300

Under the conditions of the experiments, the sensitivity of the galvanometer is such that the deflections corresponding to 0.01° at various temperatures are as follows:

20° K.	0.25 cm.
100	0.8
300	1.6

Were it not for the helium in the calorimeter and the small diameter of the filling tube, distillation of material from the calorimeter into the filling tube might take place at the higher temperatures, where the vapor pressure of the substance becomes effective. The helium reduces diffusion. Also the temperature of the filling tube is kept not far below that of the calorimeter near the boiling point, by passing warm dry air into the Dewar bulb with helium in the outer space.

The energy input is equal to FE_CE_Vt, where F contains factors to take into account the constants of the energy input circuit, a conventional factor (1/4.1833) for converting international joules into defined calories, the potential lead resistance L, and a correction (about 0.06% at 0° C.) for the heat generated in the heater leads between the shield and calorimeter. In connection with the latter, the assumption is made that half of the heat generated is taken up by the calorimeter and half by the shield. The energy input, initial, and final temperatures being known, the heat capacity of the calorimeter and contents can be calculated. The molal heat capacity of the substance can be calculated from this gross heat capacity, the heat capacity of the empty calorimeter, the weight of the contents, and the molecular weight. Corrections must be made, however, for the heat capacity of the helium in the calorimeter and for the heat absorbed in vaporizing a portion of the substance into the gas space in the calorimeter during the run. In order to make this vaporization correction, the density of the liquid as a function of the temperature must be known so that the volume of the gas space can be calculated. The vapor pressure equation should be known, so that the vapor pressure and an approximate value of the heat of vaporization can be obtained. In the case of dimethyl sulphide, the maximum value of this correction (i.e., at the highest temperature involved) was about 0.25%.

In measuring the heat of fusion, the energy input is started at a temperature a few degrees below the melting point and stopped a few degrees above. The heating interval is divided into convenient periods, during each of which readings of E_C and E_V are made as in heat capacity measurements. The known heat capacities on either side of the melting point must be used to calculate the heat of fusion. Sometimes, it is impossible to avoid poor regulation of the shield at the end of the heat of fusion run, because of the difference between the temperature of the outside of the calorimeter at the time the heater current is shut off and the final equilibrium temperature; in that case, it may be necessary to make a small correction, for which the deflections at intervals and a heat transfer constant (cal. per min. per cm. defl.) must be determined. If there is appreciable premelting below the initial temperature, it may be necessary to apply a correction for this effect also.

As we have seen, information concerning the vapor pressures of the substance is required in making the vaporization correction to heat capacity measurements. Furthermore, a rather accurate knowledge of the vapor pressures is required for measurements of the heat of vaporization. A mercury manometer (1.9 cm. in diameter) enclosed in a wooden case with plate glass windows is used. The temperature inside the case is read from two calibrated mercury thermometers. Simultaneous readings of the calorimeter temperature and the mercury heights are made, the latter being found with a cathetometer, of precision about 0.005 cm. During the measurements, the calorimeter must be the coldest part of the system. No correction is necessary for capillary depression, but a correction is applied for the difference in meniscus heights. The acceleration of gravity is taken as 979.57 cm./sec.^{2}, as determined by the Coast and Geodetic Survey at this locality. Data used to correct the pressures to international centimeters of mercury were obtained from the "International Critical Tables"[15].

The diagram on the following page represents a portion of the vacuum bench connected with the calorimeter, which is used in the measurement of heat of vaporization. The procedure employed is given below. With helium in the outer space, warm dry air is blown into

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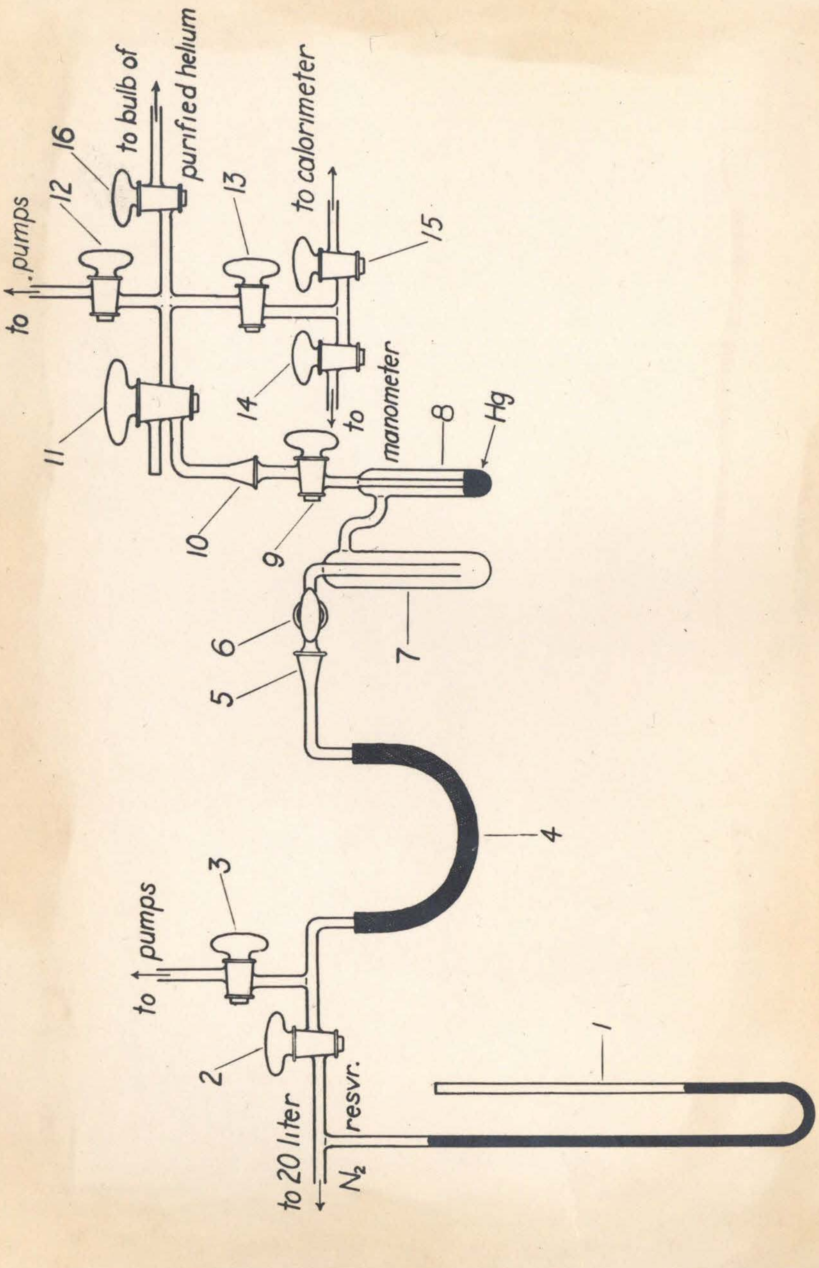
[15] "International Critical Tables", McGraw-Hill Book Co., New York, Vol.I (1926).


to 20 liter resvr.
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to pumps
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to bulb of purified helium
13
to calorimeter
15
14
to manometer

the Dewar bulb until the temperature of the hydrogen can and the Dewar bulb is about 4^{o} above that at which vaporization is to take place. (A thermocouple junction placed in the hydrogen can enables the operator to find its temperature.) Also, the temperature of vaporization must be at least several degrees below that of the room. The purpose of these precautions is to prevent condensation anywhere in the filling tube or other connections. A weighed and evacuated receiver, designated by numerals 6 to 9, is connected by means of ground-glass joints 5 and 10, and liquid air is placed around trap 7. The pressure in the nitrogen reservoir, read on the manometer designated by the numeral 1, is adjusted until it is equal to the vapor pressure at the desired temperature of vaporization minus the mercury immersion of the inlet tube in trap 8. After the space between stopcocks 9 and 15 is evacuated, stopcocks 12, 14, and 16 are closed; stopcocks 11 and 13 are left open. Stopcock 15 is then opened. The temperature of the calorimeter is now determined at intervals for a period of 30 to 45 minutes. The shield, meanwhile, is not regulated, but its temperature is always above that of the calorimeter, and the temperature difference is determined at frequent intervals. These data are used to find the rate at which the calorimeter receives heat per unit temperature difference. Following this period, stopcock 9 is opened, and a short time thereafter, the electrical energy input is started. Stopcock 9 is closed a few minutes after the close of the heating period, and the drift in calorimeter temperature is again followed for a period of 30 to 45 minutes, starting at about 10 minutes after the close of the heating period, this length of time being required for equilibrium to be established. Stopcock 6 is now closed, and the substance is barely allowed to melt; it is then frozen again, stopcock 6 is opened, and the nitrogen is pumped from the receiver. The purpose of this operation is to compact the sample. The substance initially condenses as a fine "snow", which perhaps would be swept out of the receiver when the nitrogen is pumped off. The receiver is disconnected, warmed to room temperature, and weighed. Stopcock 2 is closed when the two halves of the ground-glass joint 5 are separated, and stopcock 3 is open during the removal of the nitrogen. The numeral 4 designates a heavy rubber tube.

In making the calculations, it is assumed that the temperature of the vaporizing surface is that corresponding to the vapor pressure of the substance (given by the vapor pressure equation), which is equal to the pressure of the nitrogen plus the immersion of the inlet tube in the trap 8. The temperature of the main body of the liquid and calorimeter exterior are somewhat higher. The temperature differences between the shield and calorimeter are used not only to determine the heat received from the shield but also to find the temperature of the calorimeter exterior. It is assumed that the vapor is superheated to this temperature. Since the initial and final temperatures of the run are different, it is necessary to use the known heat capacities of the liquid and calorimeter to compute the amount of heat absorbed by these bodies in rising from the initial to the final temperature. Correction must also be made for the change in the amount of vapor in the calorimeter and line.

Experimental Results for Dimethyl Sulphide

A relatively pure sample of dimethyl sulphide was obtained by purifying the material supplied by the Eastman Kodak Company and specified as boiling between 38° and 39° C. The material was first refluxed over copper powder for 8 hours, then distilled over sodium through a total reflux column in a cold room. A second fractionation was made, with sodium absent (reflux ratio about 15 to 1). The sample was dried over sodium (a few hours only, since there is a very slow reaction between dimethyl sulphide and sodium at room temperature) before being distilled into the calorimeter.

The purity was estimated by observing the rise in the melting point as the sample was progressively melted and calculating the mol percent of impurity on the assumption that the impurity was soluable in the liquid but insoluble in the solid. The proportion of impurity which best fitted all the data was 0.0066 mol percent. The agreement can be appreciated by glancing at the following table:

Percentage Melted	Equilibrium Temperature	Calculated Temperature
4.4	174.807° K.	174.807° K.
42.0	174.849	174.850
79.6	174.851	174.852
98.4	174.854	174.853

The calculated temperature was found through the use of the familiar freezing-point lowering equation, which, with numerical values substituted, is

$$T = 174.855 - \frac{1.9871(174.86)^2}{1908.4} \frac{0.0066}{f}$$

where T = calculated temperature
f = percentage melted.

As this equation shows, the melting point of pure dimethyl sulphide is 174.855° K. (uncertainty 0.02).

The heat capacities are tabulated below. Each temperature is the average for the interval, ΔT.

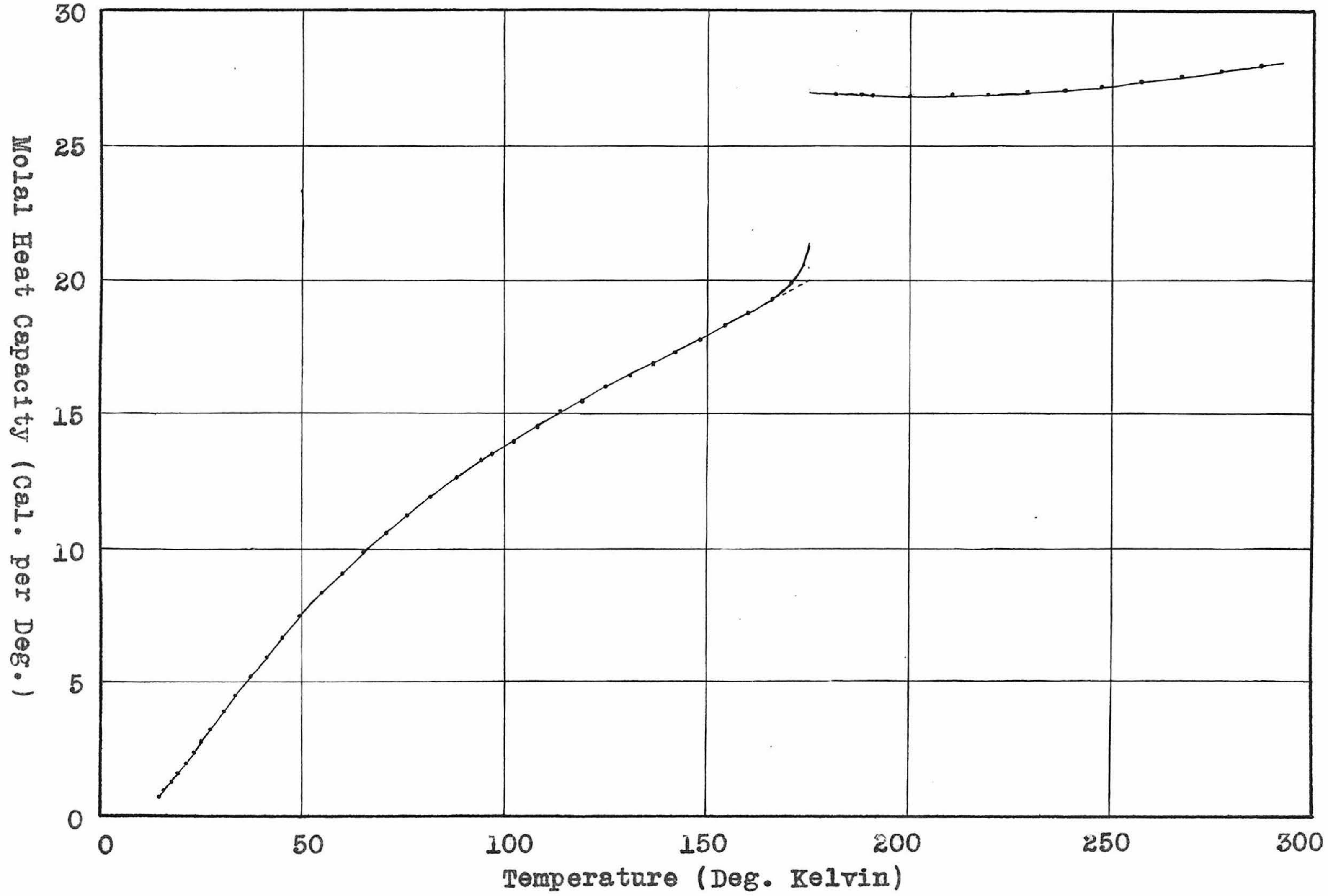
T	ΔT	$\widetilde{C}_p$
14.083° K.	1.453°	0.881 cal. deg.$^{-1}$
15.739	1.859	1.125
17.549	1.761	1.430
19.286	1.714	1.743
21.077	1.874	2.099
22.903	1.778	2.455
24.869	2.154	2.853
27.337	2.782	3.361
30.333	3.210	3.972
33.658	3.440	4.640
37.199	3.642	5.317
40.904	3.768	6.005
44.971	4.365	6.736
49.670	5.034	7.555
54.772	5.170	8.381
60.011	5.308	9.145
65.376	5.420	9.917
70.676	5.182	10.606
76.069	5.603	11.315
81.860	5.980	11.991
88.010	6.319	12.650
94.156	5.973	13.288
96.810	5.515	13.535
102.223	5.312	14.033
107.859	5.959	14.566
113.714	5.751	15.065
119.369	5.560	15.531
124.848	5.398	15.977
130.538	5.982	16.451
136.277	5.788	16.898
141.998	5.645	17.357
147.915	6.197	17.830
154.031	6.035	18.338
159.995	5.894	18.800
165.817	5.749	19.305)
170.557	3.731	19.910) Premelting
169.928	9.759	28.04)
174.855	Melting point	

T	Δ T	$\widetilde{C}_p$
181.210° K.	8.703°	26.899 cal. deg.$^{-1}$
181.304	6.658	26.893
187.943	6.620	26.873
190.432	9.742	26.842
200.126	9.646	26.841
209.736	9.574	26.866
219.276	9.506	26.889
228.741	9.424	26.966
238.122	9.337	27.058
247.413	9.245	27.178
257.063	10.053	27.337
267.063	9.947	27.513
276.941	9.809	27.706
286.687	9.683	27.929

These values are represented graphically on the following page. The graph is subject to inaccuracies, its principal purpose being to show the form of the curve. From a smooth curve through the experimental points, the heat capacities at regular intervals can be obtained. In the following table is presented such a series of heat capacities:

T	$\widetilde{C}_p$
15° K.	1.012 cal. deg.$^{-1}$
20	1.885
25	2.879
30	3.904
35	4.900
40	5.839
45	6.746
50	7.610
55	8.416
60	9.153
65	9.855
70	10.521
80	11.779
90	12.858
100	13.843
110	14.748
120	15.584
130	16.392

Molal Heat Capacity of Dimethyl Sulphide



T	$\widetilde{C}_p$
140° K.	17.198 cal. deg.$^{-1}$
150	18.005
160	18.811
170	19.618
180	26.905
190	26.856
200	26.841
210	26.856
220	26.901
230	26.975
240	27.080
250	27.217
260	27.386
270	27.569
280	27.777
290	28.007
300	28.238

Between 115° K. and the melting point, the curve is practically a straight line and can be represented by the equation,

$$\widetilde{C}_p = 13.972 + 0.08065(T - 100).$$

The values obtained from two heat of fusion runs were 1908.1 and 1908.7 cal. mol^{-1}. The average is 1908.4 cal. mol^{-1}.

The vapor pressures measured are given in the table below.

T	p
250.603° K.	52.53 mm. Hg
263.109	102.72
263.134	102.86
273.183	167.88
273.308	168.84
278.093	210.37
283.007	260.92
288.267	326.00
288.288	326.45
293.237	398.85

The vapor pressure equation,

$$\log_{10} p = 16.57356 - \frac{1878.16}{T} - 3.06733 \log_{10} T$$

(p in international millimeters of mercury, T in degrees Kelvin), represents the data to about 0.1 mm. at all points of the range covered by the experiments. The boiling point calculated from this equation is 37.34° C. The boiling point observed during the second distillation of the purification process, corrected for thermometer calibration, emergent stem, and barometric pressure, was between 37.3° and 37.4° C.

The values obtained for the molal heat of vaporization were as follows:

Run	T	$\Delta \tilde{H}_{vap}$
I	291.03° K.	6698 cal.
II	291.10	6694
Avg.	291.06	6696

The value calculated from the Clapeyron equation for 291.06° K. was 6689 cal. In making this calculation, it was assumed that the gas follows the Berthelot equation of state,

$$pv = RT \left[1 + \frac{9pT_c}{128p_cT}\left(1 - 6\frac{T_c^2}{T^2}\right) \right],$$

where p = pressure of the gas
v = volume of the gas
T = temperature of the gas
T_c = critical temperature
p_c = critical pressure.

The values taken for the critical constants[16] were $T_c = 503°$ K., $p_c = 54.6$ atm. The correction due to the use of Berthelot's equation rather than the perfect-gas equation was -123 cal. mol^{-1}.

In evaluating the integrals $\int_{15}^{174.855} \frac{\tilde{C}_p}{T} dT$ and $\int_{174.855}^{291.060} \frac{\tilde{C}_p}{T} dT$, the deviations of the experimentally determined heat capacities from

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[16] Berthoud and Brum, "J.Chem. Phys.", 21, 143 - 160 (1924).

conveniently placed straight lines were plotted against the logarithms of the temperatures. The areas under these curves were calculated by the use of the trapezoidal rule (intervals of $\log_{10}T$ were 0.025 for the first integral, 0.0125 for the second). In extrapolating below 15° K. to find the entropy at this temperature, a Debye function[17] (with three degrees of freedom) was used; $h\nu/k$ was 110.4. The accuracy with which the Debye function represents the heat capacities between 14° and 21° K. can be judged from the following table:

T	$\tilde{C}_{observed}$	$\tilde{C}_{calculated}$	$2.999 \times 10^{-4} T^3$
14.083° K.	0.881 cal. deg.$^{-1}$	0.867 cal. deg.$^{-1}$	0.838 cal. deg.$^{-1}$
15.000	1.012	(1.012)	(1.012)
15.739	1.125	1.133	1.169
17.549	1.430	1.438	1.621
19.286	1.743	1.735	2.151
21.077	2.099	2.035	2.808

The last column has been added to indicate the preferability of the Debye function over the "T^3 law" in this case. Before a comparison can be made between the calorimetric and spectroscopic entropies, it is necessary to apply a correction for the imperfection of the gas. Use is made of the thermodynamic equation

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$$

and of the Berthelot equation of state. The equation

$$S_{ideal} - S_{actual} = \frac{27RT_c^3 p}{32T^3 p_c}$$

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[17] Beattie, "J. of Math. and Phys.", 6, 1 - 32 (1926).

can be derived through the use of a conceptual process in which the gas is allowed to expand according to Berthelot's equation until its pressure is zero and is then compressed as a perfect gas until it is at the original pressure. In calculating the correction for the present case, T was taken as the temperature of vaporization, 291.06°K., p as the vapor pressure at this temperature, and the critical constants given above were used. The calorimetric entropy calculation is summarized below.

<u>Molal Entropy of Dimethyl Sulphide from Calorimetric Data</u>

0° to 15° K., Debye extrapolation, $h\nu/k = 110.4$	0.369	cal.deg.$^{-1}$ mol^{-1}
15° to 174.855° K., graphical	21.156	
Fusion, 1908.4/174.855	10.914	
174.855° to 291.060° K., graphical	13.821	
Vaporization, 6696/291.06	23.006	
Entropy of actual gas at 291.06° K. and 365.5 mm.	69.27 ± 0.1	
Correction for gas imperfection	0.08	
Entropy of ideal gas at 291.06° K. and 365.5 mm.	69.35	

Spectroscopic Entropy of Dimethyl Sulphide

From statistical mechanics[18] we have

$$S = k \ln Z + kT \frac{\partial \ln Z}{\partial T}$$

where Z is defined by the equation

$$Z = \sum_n e^{-\frac{E_n}{kT}}$$

and is called the sum-over-states. E_n is the energy eigenvalue for the nth steady state solution of the system, and k is Boltzmann's constant. The summation is carried over all the steady state solutions of which the system is capable. We make the assumption that

$$E_n = \epsilon_1 + \epsilon_2 + \dots + \epsilon_i + \dots$$

where ϵ_i is the energy of the ith molecule, and

$$\epsilon_i = \epsilon_{trans} + \epsilon_{elec} + \epsilon_{vib} + \epsilon_{rot}$$

where ϵ_{trans}, ϵ_{elec}, ϵ_{vib}, and ϵ_{rot} are the translational, electronic, vibrational, and rotational energies of the ith molecule, respectively. It can be shown that

$$\ln Z = N \left[\ln Q_{trans} + \ln Q_{elec} + \ln Q_{vib} + \ln Q_{rot} \right]$$

where N = Avogadro's number

$$Q_{trans} = \left(\frac{1}{N!} \right)^{\frac{1}{N}} \sum e^{-\frac{\epsilon_{trans}}{kT}}$$

$$Q_{elec} = \sum e^{-\frac{\epsilon_{elec}}{kT}}$$

$$Q_{vib} = \sum e^{-\frac{\epsilon_{vib}}{kT}}$$

$$Q_{rot} = \sum e^{-\frac{\epsilon_{rot}}{kT}} .$$

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[18] See, for example, Tolman, "The Principles of Statistical Mechanics", Oxford (1938).

The summations are carried out over all the translational, electronic, vibrational, and rotational states of the molecule, respectively. Then,

$$S = S_{trans} + S_{elec} + S_{vib} + S_{rot}$$

where $S_{trans} = R\left[\ln Q_{trans} + T\frac{\partial \ln Q_{trans}}{\partial T}\right]$ and the expressions for S_{elec}, S_{vib}, and S_{rot} are similar. The mathematical treatment results in the familiar Sackur-Tetrode equation,

$$\tilde{S}_{trans} = \frac{3}{2}R\ \ln M + \frac{5}{2}R\ \ln T - R\ \ln p + R\ \ln\frac{e^{5/2}(2\pi k)^{3/2}R}{N^{5/2}h^{3}}\ .$$

for the molal translational entropy. In this equation M is the molecular weight, h is Planck's constant, p is expressed in atmospheres, and R is expressed in cc. atm. deg.$^{-1}$mol^{-1}. The expressions[19] for $\tilde{S}_{vib}$ and $\tilde{S}_{rot}$ (rigid molecule) are

$$\tilde{S}_{vib} = R\sum_{i} g_i\left[\frac{\frac{hc\,\omega_i}{kT}}{e^{\frac{hc\,\omega_i}{kT}} - 1} - \ln\left(1 - e^{-\frac{hc\omega_i}{kT}}\right)\right]$$

(harmonic oscillators assumed)

$$\tilde{S}_{rot} = R\left[\frac{1}{2}\ln ABC + \frac{3}{2}\ln T - \ln\sigma + \frac{3}{2}\ln\frac{8\pi^{7/3}ek}{h^{2}}\right]\ .$$

g_i is the degeneracy of the ith vibration, c is the velocity of light, ω_i is the ith frequency in wave numbers, A, B, and C are the principal moments of inertia of the molecule, and σ is the "symmetry number", or number of equivalent orientations of the molecule. Gordon and Barnes[20]

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[19] Kassel, "J. Am. Chem. Soc.", 55, 1351 (1933).

[20] Gordon and Barnes, "J. Chem. Physics", 1, 297 (1933).

have given a table for the first of these two functions, in which $\tilde{S}_{vib}/R$ is listed for various values of $hc\omega/kT$. S_{elec} is usually zero, because the first excited electronic energy level is usually far above the electronic ground level, and the ground level is usually non-degenerate.

B. L. Crawford, Jr.[21] has offered a quantum statistical mechanical treatment of "pseudo-rigid" molecules (molecules with a rigid framework to which n symmetric tops are attached and the over-all moments of inertia of which are independent of the internal orientations of the tops). The partition function (product of Q's) for the external and internal rotations may be written in the form

$$Q = Q_R \prod Q_M\ (m)$$

where Q_R is the partition function for over-all rotation, and $Q_M(m)$ is the partition function for the internal hindered rotation of the m^{th} top. The effects of angular momentum couplings, etc., are all included in $Q_M(m)$, and hence, the thermodynamic contributions of the over-all rotations are the usual ones for a rigid molecule. Since the contributions of the internal hindered rotations are additive, it is adequate to describe $Q_M(m)$ for a single such motion. For the hindering potential, Crawford uses $(V_m/2)(1 - \cos \nu_m \alpha_m)$ where α_m is the angle of rotation of the top about its axis, ν_m is the number of minima encountered in one complete rotation, and V_m is the height of the maxima. This leads to the Mathieu equation,

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[21] Crawford, "J. Chem. Physics", 8, 273 - 281 (1940).

$$\frac{d^2\psi}{dx^2} \quad (a_{mr} + 20_m\cos 2x)\,\psi \;=\; 0,$$

where the quantities a_{mr} are the eigenvalues (depending upon the quantum number r) and Θ_m is a quantity which is essentially the hindering potential:

$$\Theta_m = V_m\frac{8\pi^2 A_m\Omega_m}{h^2\nu_m^2}$$

Here, A_m is the moment of inertia of the m^{th} top about its axis, and Ω_m is an important geometrical parameter:

$$\Omega_m = 1 - \sum_{i=1}^{3}\frac{A_m}{I_i}\lambda^2_{mi}$$

λ_{m1}, λ_{m2}, and λ_{m3} are the direction cosines of the top axis with respect to the principal axes of the molecule. $A_m\Omega_m$ may be regarded as a "reduced moment" for the top. The internal energy levels are vibrational in character for low values of the quantum numbers, r, and rotational for high values of r. The angular momentum interactions for these two types of level are different. The interactions can be included in summing over the energy levels if the sum is broken into two parts, one for the "vibrational" and one for the "rotational" levels, appropriate factors being used for the two. For the point of separation, $r = r_0$, $a_{mr_0} \approx 2\Theta$, and the energy is approximately V_m.

$$Q_M(m) = e^{-}\ q_m(\Omega_m^{\frac{1}{2}}G_R + G_V)$$

WHERE $q_m = \frac{V_m}{2RT}$

$$G_R = \sum_{r\geqq r_0} e^{-\frac{q_m\Omega_m}{2\Theta_m}a_{mr}}$$

$$G_V = \sum_{r<r_0} e^{-\frac{q_m}{2\Theta_m}a_{mr}}$$

$$S_M = \left[R\ \ln G + \frac{H}{G}\right]$$

where $G = (\Omega_m^{\frac{1}{2}} G_R + G_V)$

$$H = (\Omega_m^{\frac{1}{2}} H_R + H_V)$$

$$H_R = \sum_{r \geqq r_0} \Omega_m Y_{mr} e^{-\Omega_m Y_{mr}}$$

$$H_V = \sum_{r < r_0} Y_{mr} e^{-Y_{mr}}$$

$$Y_{mr} = \frac{h^2 \nu_m^2}{32\pi^2 A_m \Omega_m kT} a_{mr} .$$

For cases in which Ω_m may be taken as unity, the distinction between G_R and G_V vanishes, and the partition function, $Q_M(m)$, reduces to the simple sum-over-states for a Mathieu system. The corresponding thermodynamic contributions have been given in tables by K. S. Pitzer[3]. The "quantum effects" which require the introduction of the symmetry number in Q_R are easily taken into account in $Q_M(m)$. The result obtained by using only levels of a certain symmetry in the sums G_R, G_V, etc., gives a very good approximation, except at very low temperatures. No symmetry number factor is used. The required eigenvalues for the lower values of r are given in tables by Ince[22]. For finding values of a_{mr} higher than those given in the tables, the approximation indicated below is useful.

$$a_n \approx b_n \approx n^2 + \frac{\theta^2}{2(n^2 - 1)} \qquad \text{(Ince's notation)}$$

This equation is valid for small values of θ and large values of n.

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[22] Ince, "Proc. Roy. Soc. Edinburgh", 52, 355 (1931)

In making the calculations connected with this research, the following values of certain constants were used:

Ice point $T_0 = 273.16^{\circ}$ K.
Avogadro's number $N = 6.023 \times 10^{23}$ mol^{-1}
Planck's constant $h = 6.624 \times 10^{-27}$ erg sec.
Gas constant $R = 1.98707$ "defined calories" deg.$^{-1}$ mol^{-1}
$= 82.055$ cc. normal atm. deg.$^{-1}$ mol^{-1}
Boltzmann's constant $k = 1.3805 \times 10^{-16}$ erg deg.$^{-1}$
$\frac{hc}{k} = 1.4384$ cm. deg.

The following frequencies[23] were used in calculating the vibrational entropy:

284 cm.$^{-1}$
695
742
1030 (2)
1262 (2)
1323 (2)
1445 (4)
2900 (6)

Dimethyl sulphide is a pseudo-rigid molecule[24]. Hence, the over-all moments of inertia of the molecule can be calculated with the methyl groups in any convenient rotational orientation about their respective axes. The following molecular dimensions were used in calculating the principal moments of inertia:

Carbon-sulphur distance[25]	1.82 Å
Carbon-hydrogen distance	1.09 Å
Carbon-sulphur-carbon angle	102°
Angles of methyl groups	tetrahedral angle

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[23] Fonteyne, "J. Chem. Physics", 8, 60 (1940).

[24] Kassel, "J. Chem. Physics", 4, 277 (1936).

[25] Brockway and Jenkins, "J. Am. Shem. Soc.", 58, 2036 (1936).

The values obtained for the principal moments of inertia (about the center of gravity) were 45.49 x 10^{-40}, 116.1 x 10^{-40}, and 151.0 x 10^{-40} gm. cm.^{2} The value obtained for the moment of inertia of a methyl group (about its axis) was 5.303 x 10^{-40} gm. cm^2, that for Crawford's parameter was 0.9085, and that for the reduced moment of each methyl group was 4.818 x 10^{-40} gm. cm.^{2} The various contributions to the molal entropy of dimethyl sulphide in the state of a perfect gas at 291.06° K. and 365.5 mm. are tabulated below. The symmetry number 2 was used for the rigid molecule.

Molal Entropy of Gaseous Dimethyl Sulphide at 291.06° K. and 365.5 mm., from Molecular Data

S_{trans}		39.63 cal. deg.$^{-1}$mol^{-1}
S_{vib}	(harmonic)	2.31
S_{rot}	($V = 2015$ cal. mol^{-1})	27.41
Total entropy	($V = 2015$)	69.35
	($V = 1800$)	69.60
	($V = 0$)	71.03
	($V = \infty$)	64.08

Since Ω is nearly unity, the use of Pitzer's tables does not cause a large error at the temperature of interest. Thus, the entropy for $V = 2015$ cal. mol^{-1} calculated with the aid of Pitzer's tables is 69.28 cal. deg.$^{-1}$ mol^{-1}. We see that a potential barrier of about 2000 cal. mol.$^{-1}$ for each methyl group is required for dimethyl sulphide, provided that the values taken for the structural parameters and vibrational frequencies are not sufficiently inaccurate to invalidate the calculation. The fact that the barriers in ethane and the methyl amines are of about this same magnitude, while that in dimethyl acetylene is negligible, suggests that the restriction is mainly due to the proximity of the methyl groups rather than to the kind of atom to which the methyl groups are attached.

Experimental Results for Fluorotrichloromethane

In this section are presented the results which have been obtained up to the present time for fluorotrichloromethane. The work is still in progress, but the heat capacities between 55° and 290° K. and the heat of fusion have been determined. The material was purified by two distillations with a total reflux column in a cold room; the reflux ratio was about 15 to 1. The melting point data are given below.

Percentage Melted	Equilibrium Temperature	Calculated Equil. Temp.
24.7	162.613° K.	162.613° K.
47.8	162.644	162.645
64.8	162.654	162.653

The values in the last column were calculated through the use of the familiar freezing-point lowering equation, which here takes the form

$$T = 162.678 - \frac{1.9871(162.68)^2}{1646.9} \frac{0.050}{f}$$

where T = calculated temperature
f = percentage melted.

The agreement between the respective values in the last two columns indicates that the value of the mol percentage of impurity appearing in the equation, namely 0.050, is reasonably accurate. The equation also shows that the melting point of pure fluorotrichloromethane is 162.68° K. (uncertainty 0.02°).

The heat capacities are tabulated below. Each temperature is the average for the interval, ΔT.

T	ΔT	C_p	
56.78° K.	4.902°	11.30 cal. deg.$^{-1}$ mol^{-1}	
61.69	4.913	11.71	
66.76	5.232	12.14	
72.10	5.433	12.56	
77.79	5.962	13.06	
84.00	6.444	13.55	
90.65	6.853	14.12	
97.34	6.528	14.67	
103.72	6.246	15.21	
109.78	5.735	15.73	
115.42	5.537	16.24	
121.09	5.808	16.78	
126.81	5.619	17.34	
132.54	5.862	17.93	Premelting
138.51	6.068	18.62	
144.66	6.233	19.42	
150.77	5.990	20.36	
155.90	4.279	21.66	
162.68	Melting point		
170.55	9.518	26.19	
179.99	9.357	26.38	
189.61	9.892	26.58	
199.76	10.407	26.76	
210.10	10.264	26.98	
220.22	10.025	27.18	
230.19	9.902	27.41	
240.34	10.394	27.62	
250.34	9.620	27.83	
259.90	9.503	28.06	
269.33	9.361	28.31	
278.63	9.242	28.52	
287.82	9.121	28.77	

Correction has been made for vaporization, the vapor pressure equation of Garner and Osborne[26] and data of Ruff and Keim[27] on the density of the liquid being used. This correction amounted to 0.3% at 287.82° K. and was less at lower temperatures.

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[26] Garner and Osborne, Theses, Calif. Inst. Tech. (1938).

[27] Ruff and Keim, "Z. anorg. allgem. Chemie", 201, 245 (1931).

The heat of fusion data are given in the following table:

Temperature Interval	Heat Input	$\int \tilde{C}_p dT$ for Solid	$\int \tilde{C}_p dT$ for Liquid	Heat of Premelting	Molal Heat of Fusion
158.024° to 165.297° K.	1809.7 cal.mol^{-1}	100.6 cal.mol^{-1}	68.2 cal. mol^{-1}	5.5 cal. mol^{-1}	1646.4 cal. mol^{-1}
157.751 to 165.821	1834.3	110.0	81.9	5.0	1647.4
				Avg.	1646.9

The heat of premelting was calculated by means of the freezing-point lowering equation,

$$T = T_0 - \frac{RT_0T}{\Delta H}\,\frac{0.00050}{f} \qquad \text{(f the fraction melted)},$$

f ΔH being the quantity desired. In calculating $\int \tilde{C}_p dT$ for the solid, the heat capacities were corrected for premelting, and the corrected values were extrapolated. This procedure is somewhat arbitrary and introduces some uncertainty in the heat of fusion, but since the correction applied to the heat of fusion nearly counterbalances that applied to the heat capacities, the effect on the entropy is negligible.

The contributions to the molal entropy thus far determined are as follows:

60° to 162.68° K., graphical	15.32 cal. deg.$^{-1}$mol^{-1}
Fusion, 1646.9/162.68	10.12
162.68° to 296.94° K., graphical	16.42
	41.86 ± 0.05

The results obtained by Garner and Osborne[26] are given below in order to facilitate comparison.

Melting point 162.54 ± 0.05°K. (T_0 = 273.10°K.)

60° to 162.54° K., graphical	15.26 cal. deg.$^{-1}$ mol^{-1}
Fusion, 1641.8/162.54	10.10
162.54° to 296.88° K., graphical	16.34
	41.70 ± 0.17

Preparation of Boron Trichloride

It was originally planned to measure the heat capacities, heat of fusion, heat of vaporization, and thus the entropy of boron trichloride. Accordingly, a method was sought by which this compound could be prepared in a very pure state and in quantities sufficient for this type of experiments. The most convenient method, passing chlorine over a strongly heated mixture of boron trioxide and carbon, was not available, because phosgene is produced as the result of a side-reaction, and a satisfactory separation of this impurity is as yet impossible. The boiling points of boron trichloride and phosgene differ by only about 4°. For some months, an attempt was made to prepare the required quantity by burning boron in chlorine. It became evident that the boron could not be made in sufficiently large quantities nor pure enough to make the method practicable.

The method finally adopted makes use of the reaction

$$5B_2O_3 + 6PCl_5 \longrightarrow 10BCl_3 + 3P_2O_5.$$

The reagents are charged into a Carius tube, the tube is sealed, and the whole is kept at a temperature of approximately 150° C. for about 90 hours. For a Carius tube of 19 mm. inside diameter and 25 mm. outside diameter, 20 gm. of boron trioxide and 80 gm. of phosphorus pentachloride are convenient quantities. Reasonable precautions should be taken to see that the boron trioxide is dry (largely free from boric acid). Phosphorus pentachloride equivalent in grade to the Eastman Kodak Company's "practical" is satisfactory.

It is difficult to maintain a fairly constant temperature near

150° C. with an ordinary Carius furnace, heated by gas; hence, it is advantageous to use a pipe fitted with pipe-caps and an electrical heating element for heating the tube. For purposes of safety, holes should be drilled in the pipe-caps. The quantities mentioned above will yield about 25 gm. of the purified product.

When the number of tubes sufficient to yield the desired quantity of boron trichloride have been carried through the heating process, the product is purified by distillation. The end of each Carius tube opposite that to be opened is thoroughly chilled in a bath of alcohol containing dry ice, prior to the opening. As each tube is opened, it is connected to a trap immersed in an alcohol bath containing dry ice, by means of an adapter and tubes of glass. The exposed surfaces of the rubber connections should be kept as small as possible. The boron trichloride is distilled into the trap by allowing the Carius tube to warm up to room temperature; it is necessary to apply heat in the final stages of the distillation. A jacketed fractionating column, through the jacket of which cold alcohol is circulated, may be used for the purification of the product if better equipment is not available. In the apparatus employed, a "cold finger" was used, the cold alcohol passing through this before reaching the jacket. The alcohol runs down from a reservoir, through a copper coil in a bath of alcohol chilled with dry ice, and into the column. The return is accomplished through the use of an inverted air aspirator constructed of glass tubing (about 8 mm.); only a slow stream of air is necessary. The reflux can be regulated by adjusting the alcohol return. After the column has been cooled, the boron trichloride may be introduced directly into the boiler, from the trap in which it was collected. This should be done while the boron trichloride is still at the temperature of the alcohol-dry ice bath, since less phosphorus pentachloride will remain in solution at this temperature than if the boron trichloride were allowed to warm up somewhat. Care should, of course, be taken to avoid introducing any of the frozen out phosphorus pentachloride. A water bath around the boiler should be started at about 10° C. and gradually warmed. The distillation can be considered complete when condensation in the received has ceased after the temperature of the water bath has been raised to about 25° C. Redistillation will result in a purer product.

The distillate still contains hydrogen chloride. This can be largely removed as follows. The outlet tube of the receiver is provided with the male half of a ground-glass joint. The female half is connected to a vacuum system through a tube containing sodium hydroxide pellets. At the conclusion of the distillation, the tube joining the receiver to the fractionating column is sealed off, and the ground-glass joint is fitted together. The boron trichloride is frozen with liquid air and the vessel evacuated. The connection with the vacuum system is then shut off (between the vessel and the tube containing the sodium hydroxide) and the boron trichloride allowed to melt. The process is repeated several times. The sodium hydroxide prevents the hydrogen chloride reaching the vacuum pump. In this way, a product boiling at about 12.4° C. can be obtained.

A more detailed description of the preparation, accompanied by a figure, has been submitted for publication in "Inorganic Syntheses". Since boron trichloride attacks stopcock grease, certain changes would have to be made in the present apparatus before the calorimetric entropy could be measured. It was felt that it would be undesirable to make these changes at the present time, and the experiments await the construction of a new calorimeter.