

THE LOW TEMPERATURE
HEAT CAPACITY
OF SULFUR

By

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PREFACE

The primary purpose of the work described in this thesis was to obtain more accurate values for the thermodynamic properties of orthorhombic sulfur. Accurate measurements of its heat capacity from 12°K to 368°K were needed. Thermodynamic data for this material are particularly important, because they enter into so many calculations pertaining to the large number of sulfur compounds and their reactions.

Additional purposes were to obtain the heat capacity of monoclinic sulfur from 12°K to its melting point (particularly to check for a possible transformation at 374°K), to extend the measurements above the melting point to as high a temperature as possible, to assist with the design and construction of a new calorimeter and cryostat for heat capacity measurements, to verify the accuracy of the new system by measurements on n-heptane (a "standard" material for which the heat capacity is especially well known), and to discuss the theory pertaining to such phenomena as might be revealed or further explained by the sulfur measurements.

Given the rather ambitious scope of the study and the proclivity of sulfur for distorting its container upon repeated melting and freezing, one might have been tempted to select a "safer" and more predictable material for study,

so as to be guaranteed a minimum of problems and a clear-cut, easily defensible result. But "safe" topics add little to human knowledge, because of their very predictability. It was decided that the prospective utility and interest of the results of the sulfur study fully justified the greater risk. As the reader will see in the body and summary of this thesis, the primary goal was achieved, and a high degree of success was experienced in meeting the secondary goals.

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TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION	1
II. EXPERIMENTAL EQUIPMENT AND TECHNIQUES	3
Platinum Calorimeter and Associated Equipment	6
Verification of Accuracy	15
III. MATERIALS STUDIED	19
Material Sources and Handling	19
Discussion of Calorimeter Rupture	21
IV. MONOCLINIC (β) SULFUR	32
V. ORTHORHOMBIC (α) SULFUR	43
VI. THE ORTHORHOMBIC-MONOCLINIC TRANSFORMATION	47
VII. TRIPLE POINT, PURITY, AND HEAT OF FUSION	51
VIII. LIQUID SULFUR	54
IX. THERMODYNAMIC PROPERTIES OF EQUILIBRIUM SULFUR	57
Discussion of Precision	66
Other Corrections	70
Comparison With Other Data	72
BIBLIOGRAPHY	75
APPENDIX - ALUMINUM CALORIMETER DEVELOPMENT	77

LIST OF TABLES

Table	Page
I. Experimental Data for n-Heptane	17
II. Experimental Data for Monoclinic Sulfur	38
III. Thermodynamic Properties of Monoclinic Sulfur	40
IV. Experimental Data for Orthorhombic Sulfur	44
V. Experimental Data for Liquid Sulfur	56
VI. Thermodynamic Properties of Equilibrium Sulfur	58
VII. Thermodynamic Properties of Sulfur In Its Standard State	61
VIII. Other Corrections	71
IX. Comparison with Other Studies	73

LIST OF FIGURES

Figure	Page
1. Sketch of Calorimeter	7
2. Sketch of Cryostat	11
3. Sketch of Calorimeter and Shield in Position Inside the Cryostat	12
4. Electrical Circuits for Temperature and Power Measurement	14
5. Heat Capacity of Sulfur	63
6. Lambda Anomaly in Monoclinic Sulfur	64
7. Heat Capacity of Liquid Sulfur	65
8. Aluminum Calorimeter	79

CHAPTER I

INTRODUCTION

The first precise measurements of the heat capacity of sulfur at low temperatures were made by Eastman and McGavock (1). Further low-temperature measurements on orthorhombic sulfur were made by Mal'tsev and Demidenko (2), but these did not extend below 53°K. West (3) used modern techniques capable of high accuracy to determine the heat capacity of sulfur at 298°K and above. The work cited above supersedes the earlier results, summarized by Eastman and McGavock (1), West (3), and Mellor (4). Other work on liquid sulfur, summarized by Komarek, Miller, and Schick (5), did not determine the true heat capacities, because the techniques did not allow time for thermal equilibrium to be attained.

From existing data one can calculate the thermodynamic properties of orthorhombic and monoclinic sulfur below the melting point and those of liquid sulfur from the melting point to near the boiling point. However, the results of Eastman and McGavock are of lesser accuracy than is attainable today, and thermodynamic properties based on them are not accurate enough to answer such questions as whether the disordered structure of monoclinic sulfur at room temperature persists at lower temperatures (6). West (3) found

that the heat capacity of monoclinic sulfur decreased with increasing temperature and then rose sharply as in a change of phase. This behavior is surprising and should be rechecked, because it is generally believed that only one definite crystal form of monoclinic sulfur is stable.

The present investigation was undertaken to improve the accuracy of the low temperature heat capacities of orthorhombic and monoclinic sulfur and thus to improve the accuracy of the thermodynamic properties of sulfur. It was also desired to extend the measurements to as high a temperature as possible to recheck the results obtained by West, especially for monoclinic sulfur.

CHAPTER II

EXPERIMENTAL EQUIPMENT AND TECHNIQUES

The methods used in this study were those of adiabatic calorimetry as developed and applied by workers in low temperature calorimetry. In these methods, the calorimeter is a sample container equipped with an electrical heater, a resistance thermometer, and one junction of a difference thermocouple for temperature control. The calorimeter is surrounded by an adiabatic shield which is kept as close as is practicable to the temperature of the calorimeter. The apparatus is evacuated to eliminate convection effects and to reduce conduction of heat. When the calorimeter is not being heated or cooled deliberately (or by thermal changes in the sample) its temperature is very steady and can be measured accurately.

The calorimeter temperature is measured; then a known amount of electrical heat is supplied and the temperature is measured again. The energy divided by the temperature difference gives the average effective heat capacity of the calorimeter in the temperature interval over which it was heated. A number of measurements over different temperature intervals is made. A known amount of sample is then placed in the calorimeter and a similar set of measurements

is made, giving the average effective heat capacity of the calorimeter plus sample.

Corrections must be applied for the heat leak, that is, the heat exchanged between the calorimeter and its surroundings. During periods when no heat is being developed within the calorimeter, the heat leak can be calculated from the rate of temperature change and the effective heat capacity. The heat leak during periods when the calorimeter is being heated is not measurable; however, since the heat capacity of the sample is determined by difference, it is not necessary to correct for the absolute value of the heat leak, but only for changes in it. Factors which can change the heat leak when no heat is being supplied to the calorimeter should change the heat leak during heating periods by the same amounts. Among these factors are spurious thermal emfs in the lead wires, temperatures of the surroundings of the adiabatic shield, etc. A correction for these factors is obtained by determining temperature as a function of time during the "rating" periods before and after heating, and assuming that the heat leak during heating is the same as the average of the heat leaks during the rating periods before and after it. If, after correcting for heat leak, the effective heat capacity is still affected by some factor, then that factor must be the same during the measurements on the empty and full calorimeter, or the final result will be inaccurate.

The final result may also be inaccurate because of

changes in the heat leak depending upon the presence or absence of sample. If the presence of sample in the calorimeter causes heat to be conducted through the calorimeter in a different pattern, different temperature gradients may appear on the surface of the calorimeter, and therefore the heat leak may be different. Such differences in heat leak are minimized by low temperature (where radiation is little) and by good heat conduction through the calorimeter. For most low temperature work it has been sufficient to make the calorimeter from a good heat conductor like copper and to design it so that no part of the calorimeter is far from a good heat conductor. But when the calorimeter must be made from a poorer heat conductor (such as platinum for chemical resistance), and when the measurements are extended to relatively high temperatures, errors from variable temperature gradients may become appreciable. In high-temperature adiabatic calorimetry, such errors are avoided by making one or more outer radiation shields part of the calorimeter; heat reaches the shield primarily by a well-defined conduction path, and this path is independent of the sample in the calorimeter. We have adopted the outer shield as a method of extending low temperature calorimetric techniques to unusually high temperatures.

A modern cryostat to be used in the temperature range from the boiling point of helium to above room temperature will usually be equipped with two refrigerant tanks, a large upper tank with a radiation shield hanging from it, and a

smaller lower tank enclosed by the upper tank radiation shield (7, 8, 9). When hydrogen or helium is used as a refrigerant in the lower tank, the upper tank is filled with liquid or solid nitrogen and the radiation to the lower tank will come from a surface at the temperature of the nitrogen, not at room temperature. The adiabatic shield is inside a radiation shield suspended from the lower tank. A ring suspended between the lower tank and the adiabatic shield is used to adjust the temperature of the leads between the tank and the shield, preventing "cold spots" on the shield and possible direct conduction of heat from calorimeter to tank along the lead wires. One or more "economizers" is provided to use the effluent gas from the lower tank to cool the lead wires, and, sometimes, a radiation shield. The leads are placed so they make good thermal contact with the tanks, economizer, ring, and adiabatic shield. An arrangement is provided so that the calorimeter, ring, and shield can be pulled into good thermal contact with the lower tank by operating a windlass from outside the cryostat. Then it is not necessary to break the vacuum to cool the calorimeter.

Platinum Calorimeter and Associated Equipment

The platinum calorimeter (Figure 1) was of the same design and construction as those used previously at the Bartlesville Energy Research Center (7). It was calorimeter

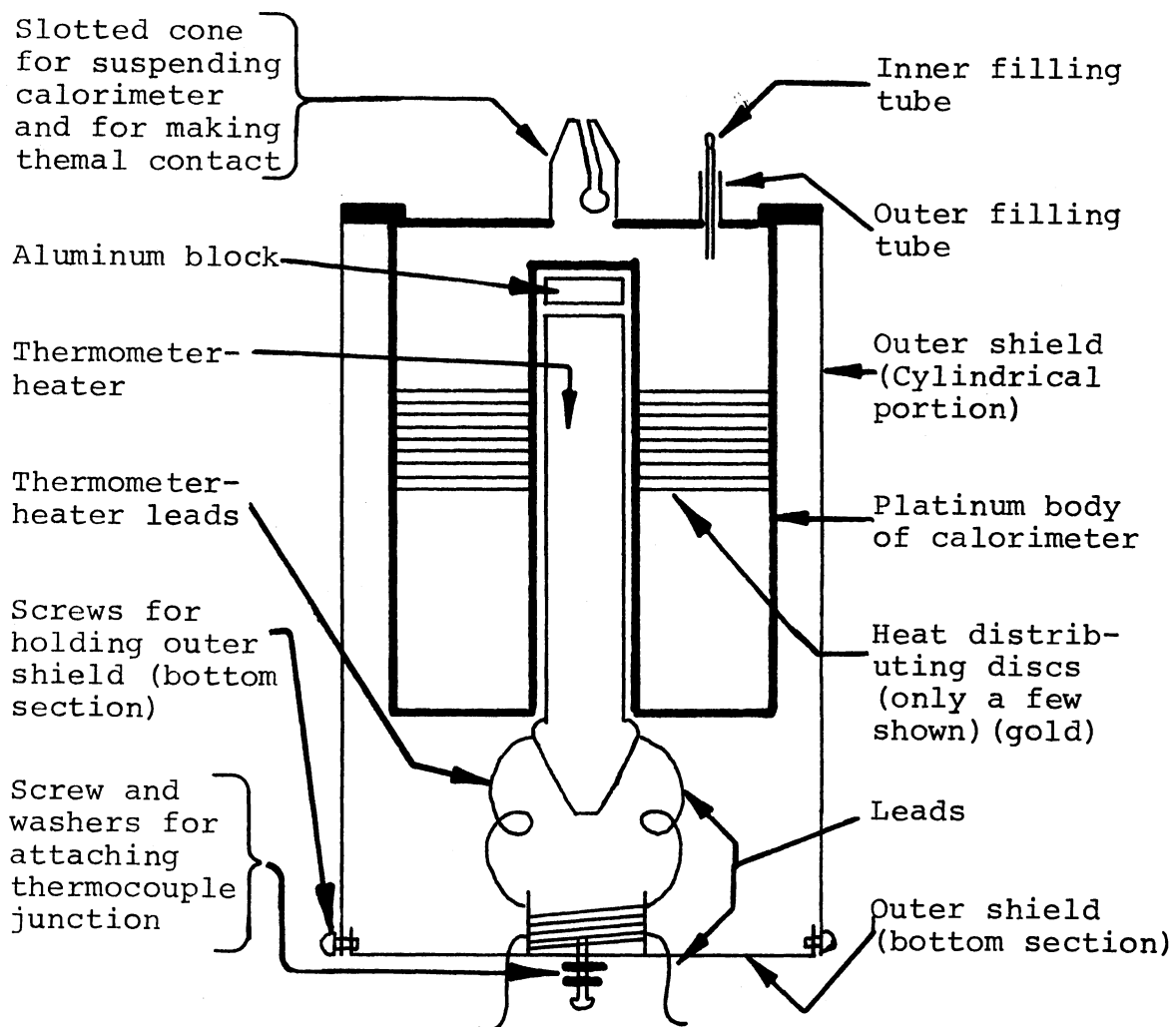


Figure 1. Sketch of
Calorimeter

number PT-5, rebuilt and modified by the addition of an outer shell. A removable shell was found to be unsatisfactory because of the difficulty of maintaining a constant thermal resistance at the junction between the calorimeter and the shell. The shell finally adopted consisted of a cylindrical portion silver soldered to the top of the calorimeter and a bottom section attached to the cylindrical portion with screws. The bottom section could be removed for access to the thermometer and heater. Copper leads soldered to the thermometer and heater leads with tin solder were wound around a tube on the inside of the bottom section and were brought out through small holes in the bottom. The outside of the shell was gold plated for low and constant emissivity. The shell itself was made of copper for good thermal conductivity.

The filling tube of the calorimeter was originally made from platinum. After the measurements of the heat capacity of the empty calorimeter, the tube was found to have become brittle because of the tin solder used on it, and therefore it was replaced by a monel tube. The entire tube weighed only about 0.1 gram out of a total calorimeter weight of over 200 grams; the change in heat capacity due to the change of tube material was estimated as no more than a few hundredths of a percent, and no correction for it was attempted. It is shown below that this change of material causes no significant error.

The thermometer-heater assembly used in this study was

designated C-1 and was of the same design and construction as thermometers used previously in the Bartlesville Energy Research Center (7, 10). It contained a platinum thermometer of about 50 ohm resistance at the ice point, and a constantan heater of about 200 ohm resistance. The thermometer was not on the International Temperature Scale, because it could not be annealed properly in the presence of constantan. However, it had been calibrated by direct comparison with a laboratory standard thermometer which was on the International Temperature Scale of 1948, and which conformed to the pre-1955 National Bureau of Standards Provisional Temperature Scale below the limits of the International Temperature Scale. The overall calibration was in $^{\circ}\text{K}$; in the range of the International Temperature Scale the value 273.16° was added to the values in $^{\circ}\text{C}$ to obtain $^{\circ}\text{K}$. The 1955 change in the absolute temperature used for the ice point makes the laboratory scale used for this study 0.01° higher than the best temperature values. The results in this thesis are given on the laboratory scale; the difference is of no consequence except for the triple point and the melting point derived from it, which were determined to within 0.01°K .

The initial calibration was extrapolated above 385°K . After the calorimetric measurements it was compared again with the laboratory standard thermometer from 263°K to 443°K to ensure that the resistance had not drifted and that the extrapolation had been correct. The differences were no

mote than a few thousandths of a degree, negligible for the purposes of this study.

The thermometer-heater was installed in the calorimeter with an aluminum foil shim and Apiezon H grease. A small block of aluminum was placed in the thermometer well with the thermometer to fill the well completely and avoid a possible air bubble, which would tend to push the thermometer-heater out of the well when the cryostat was evacuated.

The cryostat (Figures 2 and 3) was similar in general design to those used previously at the Bartlesville Energy Research Center (7, 8). Two economizers were provided, one of which cooled a radiation shield (9). The wires were Teflon covered and were laid in separate grooves on the tanks, economizers, ring, and adiabatic shield to provide good thermal contact and to make wires individually replaceable. Unfortunately, roughness of the grooves and variations of insulation thickness caused tearing of the Teflon insulation. The torn spots were insulated with enamel. Some of the tears were invisible and caused electrical leakage to the metal of the cryostat only under certain temperature conditions, so it was difficult to insulate all the torn spots.

The adiabatic shield was made in three sections, the top and bottom being larger than the middle. The temperatures of the shield, ring, and lower tank (which were provided with electrical heaters) were automatically controlled

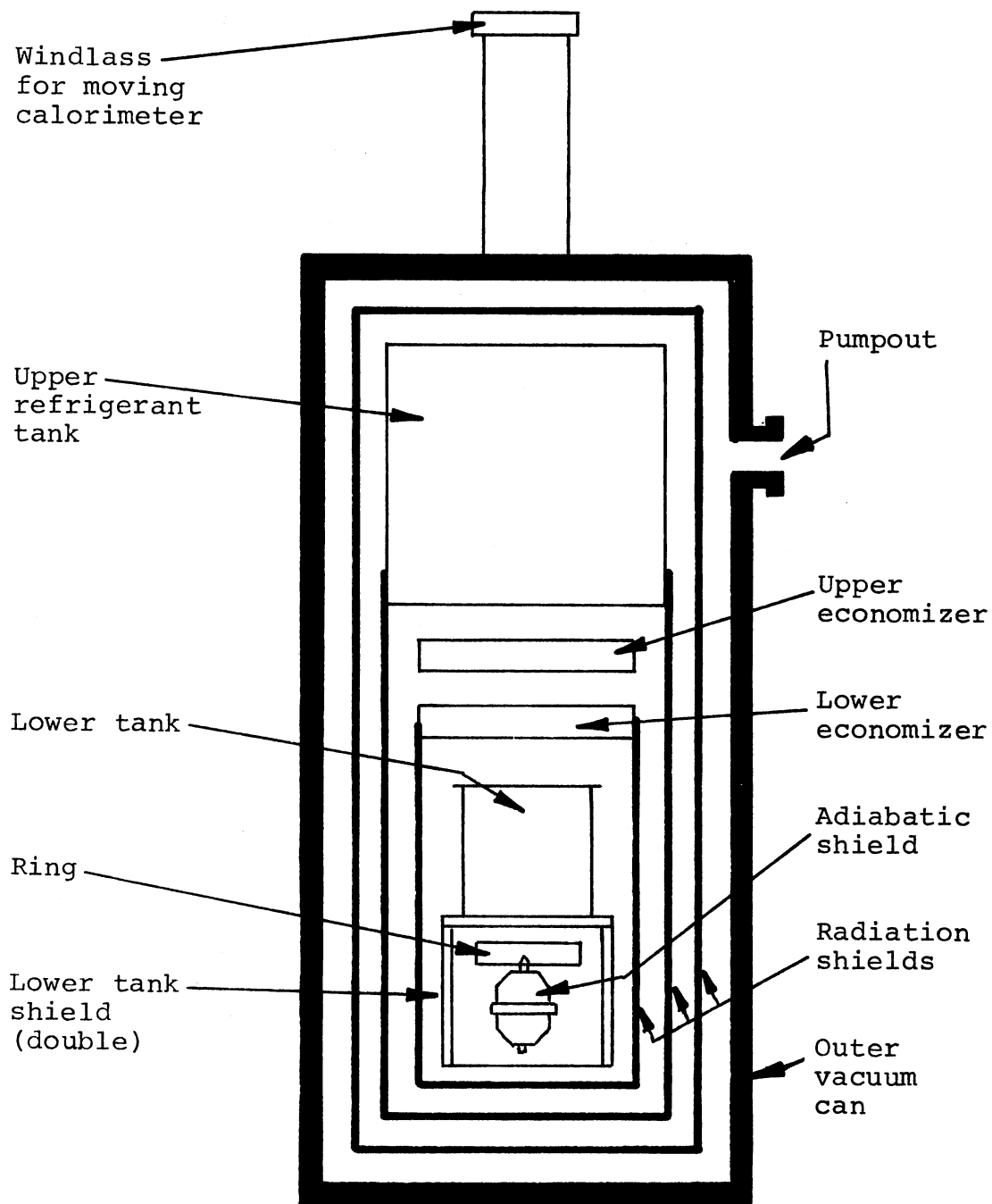


Figure 2. Sketch of
Cryostat

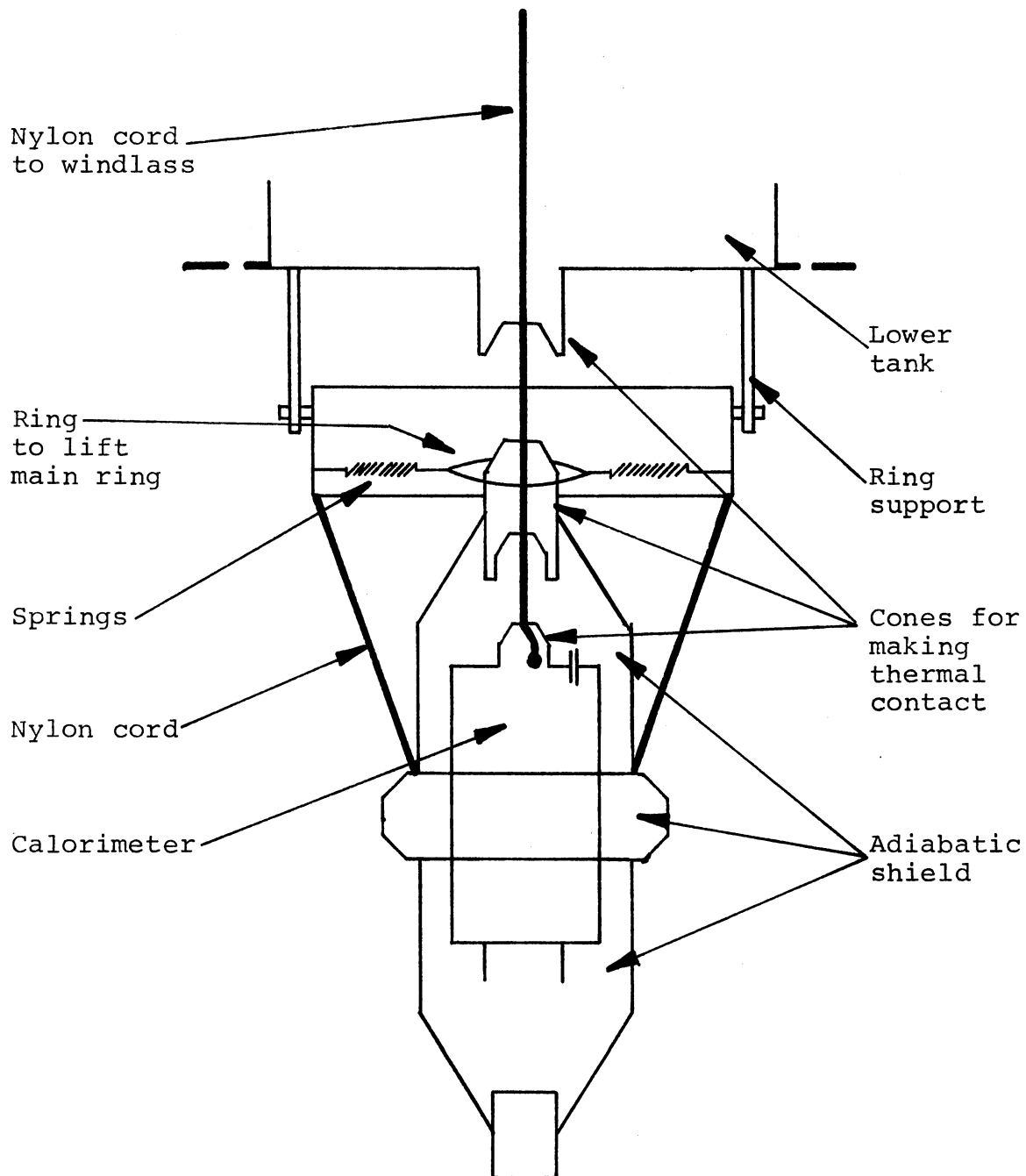
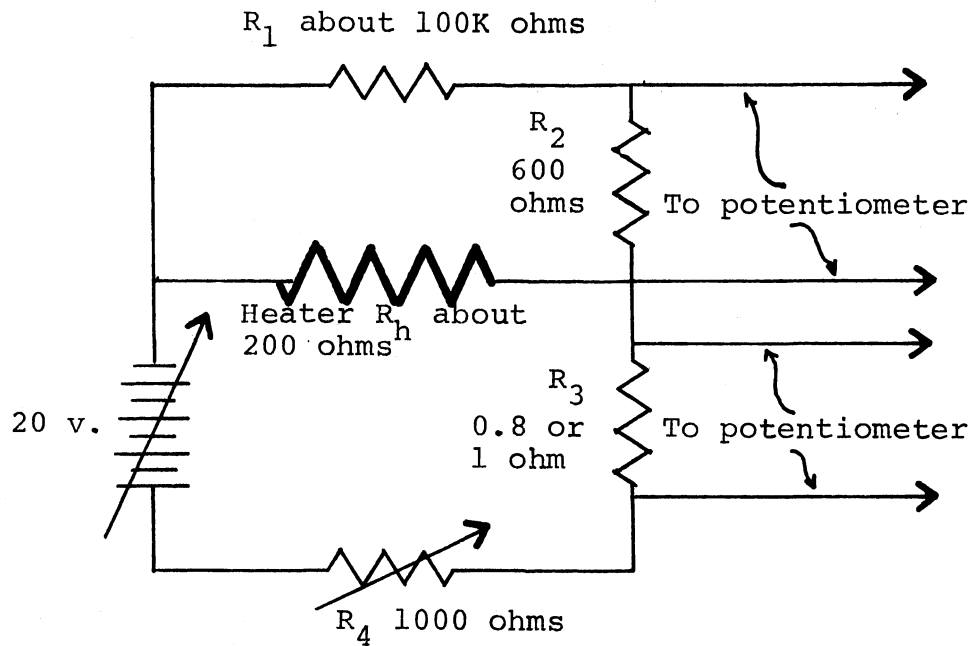


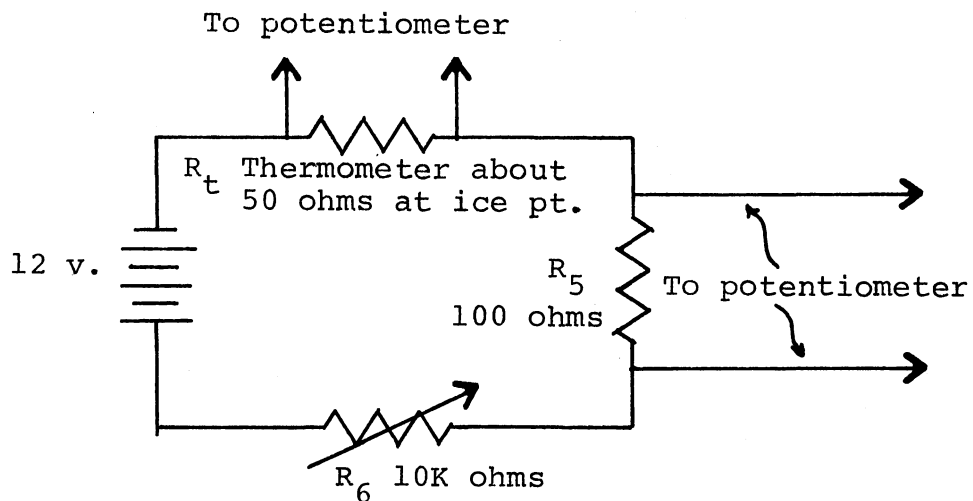
Figure 3. Sketch of Calorimeter and Shield in Position Inside the Cryostat

by Leeds & Northrup "C.A.T." units fed from the outputs of thermocouples and thermopiles. The shield middle temperature was controlled at the calorimeter temperature by a single junction thermocouple. The output of the couple was amplified with a Beckman Model 14 amplifier and a Speedomax. The top and bottom temperatures were controlled at the middle temperature by the outputs of six-junction thermopiles between them and the middle. The ring temperature was controlled at the middle temperature by a single junction thermocouple. The lower tank temperature could be controlled by the output of either of two thermocouples, one between the tank and the middle and the other between the tank and a junction outside the cryostat, which junction could be left at room temperature or placed in an ice bath. The outputs of these thermocouples and thermopiles were amplified by Leeds & Northrup null detectors. The lower tank null detector was equipped with an "offsetting circuit" to add any desired emf to that of the thermocouple so that the tank could be controlled at temperatures different from those of the other junctions of the lower tank couples.

The calorimeter temperature and electrical heat were measured with a double potentiometer of the White type, using the circuits shown in Figure 4. The "galvanometer" used to measure the unbalance of the potentiometer consisted of a Beckman Model 14 amplifier stabilized at a voltage gain of 1000 by negative feedback, a voltage-to-frequency converter, and an electronic counter, which together gave a



(a) Main features of heater circuit



(b) Main features of thermometer circuit

Figure 4. Electrical Circuits for Temperature and Power Measurement

digital indication of the unbalance voltage. The time of heating was measured with an electronic counter and crystal controlled oscillator operated by the heater on-off switch. Heat energies are reported as thermochemical calories (4.184 joules).

The techniques of measurement were as outlined above, and in detail were essentially the same as in previous work at the Bartlesville Energy Research Center, except that the lower tank temperature could be controlled to eliminate errors caused by drift of the lower tank temperature during measurements. Such errors were found to be appreciable only at high temperatures.

In setting up the control thermocouples it was found necessary to adjust the thermal "lags" so that the lags at the parts being controlled were shorter than those at the parts they were controlled against. This was necessary because although heat could be supplied easily, the rates of cooling available through radiation and conduction were sometimes very small, so that no overshoot of temperature during control was permissible. Although the lags cause the shield to depart from true adiabatic control during heating periods, the effect is the same whether the calorimeter contains sample or not, and thus causes no error.

Verification of Accuracy

Satisfactory operation of the cryostat at liquid helium temperatures was verified by measuring the effective heat

capacity of the calorimeter down to below 5°K with liquid helium in the lower tank. At higher temperatures a number of tests were made to determine the effects of changing the lower tank temperature, increasing the gas pressure in the cryostat, etc. Although the heat leak was affected greatly, the corrected effective heat capacity of the empty calorimeter was unaffected by the changes, as long as a reasonably good vacuum was maintained.

The absolute accuracy of measurement was checked by measuring the heat capacity of n-heptane and comparing it with selected values derived from previous measurements (11). The data are shown in Table I. The first column gives the average temperature \bar{T} in °K during the heating period; the second column gives the change in temperature ΔT during the heating period; the third column gives the average heat capacity \bar{C}_s of the n-heptane in cal.-g-atom⁻¹-°K⁻¹, corrected for heat leak, premelting, and vaporization. The subscript s on the heat capacity indicates that the effective pressure was the saturated vapor pressure of the n-heptane, with only a low pressure of helium added to provide heat conduction inside the calorimeter at very low temperatures.

The measurement marked "fusion" indicates the observed triple point (on the laboratory temperature scale) in the first column.

The fourth column gives the deviations of the observed heat capacities from the selected values as percentages.

TABLE I
EXPERIMENTAL DATA FOR n-HEPTANE

\bar{T}	ΔT	\bar{C}_s	dev., %	\bar{T}	ΔT	\bar{C}_s	dev., %
50.29	3.53	12.053	+0.19	172.00	7.42	32.928	-0.18
53.69	3.26	12.925	+0.22	182.560	---fusion---		+0.01
57.21	3.78	13.791	+0.12	193.04	10.18	48.25	+0.06
61.20	4.21	14.769	+0.18	203.19	10.12	48.17	+0.02
65.90	5.18	15.856	+0.21	213.20	10.01	48.34	+0.08
68.03	4.53	16.308	+0.20	223.01	9.86	48.64	+0.08
71.09	5.20	16.946	+0.18	232.82	9.75	49.05	+0.06
72.43	4.27	17.219	+0.19	239.32	3.74	49.33	-0.02
76.99	4.85	18.126	+0.10	242.50	9.63	49.56	+0.08
80.75	5.25	18.870	+0.08	245.90	9.43	49.71	-0.04
81.72	4.59	19.085	+0.23	255.42	9.62	50.31	-0.06
84.63	21.89	19.590	+0.21	263.20	31.78	50.95	+0.07
85.86	4.98	19.864	+0.19	265.45	10.45	51.06	+0.02
86.57	5.11	20.005	+0.26	275.82	10.29	51.87	+0.04
91.20	5.70	20.788	+0.12	283.62	9.07	52.52	+0.06
96.79	5.46	21.695	+0.12	286.02	10.14	52.70	0.00
99.17	7.18	22.083	+0.19	292.99	9.69	53.32	+0.04
102.58	6.13	22.603	+0.14	300.21	4.79	53.92	-0.06
106.19	6.86	23.164	+0.17	303.06	10.47	54.33	+0.22
109.01	6.72	23.587	+0.15	307.74	10.28	54.65	+0.02
112.85	6.44	24.164	+0.18	318.33	10.89	55.66	+0.07
119.18	6.21	25.056	+0.04	329.13	10.71	56.73	+0.06
125.30	6.03	25.947	+0.13	339.75	10.53	57.84	+0.19
131.25	5.87	26.768	+0.11	350.17	10.37	58.88	+0.12
137.52	6.66	27.631	+0.10	360.42	10.14	59.97	+0.05
144.08	6.48	28.544	+0.12	370.82	10.69	61.14	(0.00)
150.92	7.20	29.510	+0.09	381.40	10.49	62.36	(-0.10)
158.02	7.00	30.561	+0.02	389.74	6.21	63.37	(-0.19)
164.91	6.80	31.658	-0.03				

The value for the measurement marked "fusion" is the deviation of the observed heat of fusion from the selected value. The numbers in parentheses were for comparisons with extrapolated selected values.

The present values for liquid n-heptane agree well with the selected values. The present values for solid n-heptane are progressively higher at lower temperatures, being about 0.2 percent higher at 50°K, the lowest temperature of the present measurements. It is concluded that the present calorimeter, cryostat, and measuring techniques are accurate to within 0.2 percent.

CHAPTER III

MATERIALS STUDIED

Material Sources and Handling

The samples were introduced into the calorimeter from all-glass filling systems through a glass-to-platinum graded seal to a platinum tube soldered with tin to a monel inner filling tube soldered with tin to the inside of the calorimeter (outer) filling tube.

The n-heptane was a mixture of samples studied previously in the same laboratory. The break-off tip glass bulbs containing the material were sealed to the filling system, which was evacuated. The n-heptane was frozen by liquid nitrogen and the tips broken off. It was warmed to room temperature and distilled into a graduated bulb cooled in ice, until the desired amount had been collected. Then the material was forced from the bulb into calorimeter PT-5 with a low pressure of helium gas. The inner filling tube was pinched tightly, cut off in the pinched area, and sealed with a drop of tin solder. After the measurements were completed, the weight of the calorimeter plus sample was found to have remained constant within experimental error. A pinhole was made in the filling tube and the n-heptane was removed through the hole. The calorimeter plus plug (inner

filling tube and solder) was then weighed and the weight of n-heptane obtained by difference. During the measurements, the change of temperature during melting was determined, and it indicated 0.007 mole percent of liquid-soluble, solid-insoluble impurity.

The sulfur sample was obtained from the same source as that used by West for high-temperature calorimetric studies (Inorganic Chemistry Section, National Bureau of Standards). It was received dry, sealed in a glass bulb. The bulb was opened and immediately sealed upside down to the filling apparatus, which was immediately evacuated. The entire filling apparatus was enclosed in a heated box. The temperature of the box was gradually increased to about 135°C. As the sulfur melted, it flowed down through a funnel into a glass bulb. The position of the funnel was controlled by the action of an electromagnet on a steel bar sealed into the glass of the funnel. After a few milliliters of sulfur had collected in the bulb, the funnel was moved so that the sulfur flowed into a graduated bulb. When the desired amount of sulfur had collected in the graduated bulb, the funnel was moved back to drain the remainder of the sulfur into the other glass bulb. Then a low pressure of helium was admitted to the system to force the sulfur from the graduated bulb into calorimeter PT-5. The box was cooled slowly to freeze the sulfur, which crystallized in the monoclinic form in the glass bulb. The monel inner filling tube was pinched tightly, cut off in the pinched

area, and sealed with a drop of tin solder.

The amount of sulfur was estimated from the weights of the calorimeter before and after filling and the approximate plug weight. The volume calculated from the weight and Kellas' (12) density data agreed satisfactorily with the volume in the graduated bulb at 135°C, and indicated that there would be about 2 ml. vapor space in the calorimeter at the maximum temperature to be attained during measurements.

The filled calorimeter was tested for leaks with a helium leak detector "sniffer" and none was detected. It was heated to 159°C and cooled in vacuum but there was no significant change in weight. During handling the calorimeter was held so that the sulfur would not touch the filling tube. Preliminary tests had shown that monel is attacked only slowly by sulfur at the temperatures of this study, and corrosion of the monel should not affect the results. The amount of tin exposed to the sulfur vapor was quite small and should also have negligible effect on the results.

Discussion of Calorimeter Rupture

In order to guard against the loss of heat capacity data for solid sulfur due to rupture of the calorimeter by repeated melting and freezing of the sulfur, the sample was melted the minimum possible number of times before completion of the measurements on the solid. Direct evidence that the calorimeter might be expected to rupture eventu-

ally had been provided by the observation of West (3) that his aluminum calorimeter expanded 1.5% in diameter during his measurements on sulfur. This expansion wedged his calorimeter tightly into the apparatus so that it could not be removed for final weighing or final leak testing.

In the present study, the sulfur had to be melted once to load it into calorimeter PT-5. After it had been frozen in the calorimeter and cooled to room temperature, it was checked for leaks by the use of a helium gas leak detector "sniffer" and also by pumping out a vacuum desiccator containing the calorimeter and checking for changes in weight. If the helium gas had all escaped so that the leak detector could find no helium, the calorimeter would have shown changes in weight during the vacuum desiccator test, due to the entry and exit of air from the calorimeter. The tests, which involved heating to 432°K in vacuo, showed that the calorimeter was free of leaks.

A necessary part of the investigation was a verification of purity through the absence of the "melting point depression" which would be caused by impurities soluble in the liquid and insoluble in the solid. This required another melting and freezing of the sulfur. After this third melting, the sulfur was never again fully melted until the measurements on solid sulfur had been completed.

The heat capacity of monoclinic sulfur was measured in the temperature ranges where it was stable and where it was supercooled by only a few degrees. Next, the full set

of heat capacity data for orthorhombic sulfur was obtained. The heat capacity of supercooled monoclinic sulfur was then determined. The measurements were extended up to the temperatures where monoclinic sulfur was stable, and the heat of transformation was obtained. The heat of fusion and the heat capacity of liquid sulfur were the last quantities measured.

After the heat capacity of liquid sulfur had been obtained in the temperature range of the lambda anomaly, the calorimeter was cooled well below the freezing point, in preparation for another heat-of-fusion measurement and the determination of the liquid heat capacity just above the melting point. The calorimeter was then heated to the melting point, whereupon the calorimeter thermocouple indicated a rapid spontaneous warming of the calorimeter. The calorimeter was then removed from the cryostat for examination. The calorimeter (PT-5) was found to have bulged (primarily at the top and bottom) and had been distorted in shape. There was a crack at the bottom of the calorimeter, around the thermometer well, and sulfur had escaped through the crack. The inside (not gold plated) of the copper shell was heavily corroded and blackened by reaction with sulfur.

It appears that the calorimeter ruptured the last time it was cooled, and that the leak became apparent when the sulfur was beginning to melt again, so that liquid could run out through the leak. However, a close examination is necessary to verify that the leak did not begin earlier.

Heat capacity data obtained after the leak began would be inaccurate because of loss of the helium gas (which provides part of the heat transfer within the calorimeter), change in weight of the sample due to loss of sulfur through the leak, and spurious heat effects due to reactions between the sulfur and the materials of the calorimeter and cryostat.

The thermometer-heater was undamaged, but the calorimeter had deformed to the extent that it had to be cut away from the thermometer-heater to recover the latter. Inspection of the sulfur inside the calorimeter showed that it had wetted the top and bottom of the calorimeter and that it contained several large bubbles. In the process of returning the cryostat to service so as to calibrate the thermometer, sulfur was found to have condensed as fine crystals in several locations in the lower part of the cryostat.

The first necessary part of the consideration of the rupture of calorimeter PT-5 is an examination of possible causes. The outward bulging and distortion of the calorimeter show that internal pressure was responsible. This pressure might result from gas, liquid, or solid.

The pressure of the helium gas sealed into the calorimeter was quite small, well below atmospheric, and its thermal expansion should follow the ideal gas law closely. Therefore, helium pressure would not increase sufficiently to cause rupture. Outgassing of the sulfur would not

increase the pressure, because the sulfur was initially pure, it was introduced as a liquid free of visible bubbles, and the triple point study showed a high purity. The triple point was determined with a high degree of accuracy, and is only 0.006°K higher than the triple point determined accurately by West (3). If the pressure is increased, the triple point becomes a melting point affected by pressure through the equation

$$\frac{dT}{dP} = \frac{T\Delta V}{\Delta H}.$$

This equation predicts an increase in the melting point with increasing pressure at a rate of about 0.03°K per atmosphere. Experimental data of Tammann (13) quoted by Deaton and Blum (14) agree with this figure. The triple-point data thus indicate less than one atmosphere pressure inside the calorimeter at the melting point, which was not exceeded between the triple-point determination and the end of the solid state measurements.

Another argument similar to that used by West (3) does not make use of the absolute value of the triple point and is as follows: During the melting of the last half of the sulfur, the vapor space in the calorimeter was reduced by one-third. Therefore the pressure should have increased by 50%. The change of temperature during the last half of the melting was 0.0009°K. Even if this were all due to the change of pressure, the maximum possible pressure at the triple point would still be below one atmosphere.

These considerations eliminate increase of the gas pressure within the calorimeter as a cause of the rupture.

The sulfur was introduced in liquid form and was measured both by weight and by volume. The size of the sample was chosen such that the calorimeter would not be completely full below 573°K, which is 139 degrees higher than the maximum temperature reached during this study. The initial melting did not have any visible effect on the calorimeter, and the triple point did not show any temperature shift from high pressure. The heat is supplied from the thermometer-heater and should readily spread from there along the inside of the thermometer-heater well and throughout the network of heat distributing disks, preventing strictly local buildup of pressure from the expansion in melting. Additionally, local pressure buildup tends to retard further melting according to the shift of melting point with increasing pressure. For these reasons, expansion of the liquid and expansion of the sulfur during melting are ruled out as causes of the rupture.

The only possible causes remaining are changes of volume in the solid state. The calorimeter could not have shrunk down onto the solid sulfur and been damaged when the calorimeter was cooled, because the coefficient of expansion of solid sulfur is greater than that of platinum. Transformation of monoclinic to orthorhombic and back again is not likely to have been a cause, since the orthorhombic form is denser than the monoclinic, and one would expect

that both were in the form of many small crystals with a random average orientation, as is generally seen when one observes the transformation in the laboratory in glassware.

The remaining, and by far the most likely, possibility is that the liquid supercooled through the monoclinic sulfur temperature range and froze to orthorhombic sulfur while still in contact with the top and bottom of the calorimeter. Subsequent thermal expansion and conversion to the monoclinic form then developed enough force to bulge the top and bottom and cause a crack to develop in the calorimeter.

The most likely cause of the calorimeter rupture thus requires that it occurred after completion of the work on solid sulfur. However, a second necessary part of the discussion of the rupture is to consider the evidence for the presence or absence of a crack at the end of the solid sulfur measurements. If a crack had been present at that time, then sulfur would have escaped through it during the later measurements on liquid sulfur at temperatures up to 434°K. We would expect the following results:

- (1) Reaction of the sulfur with exposed copper, causing visible blackening by the formation of copper sulfide. This reaction takes place readily even at temperatures as low as 298°K.
- (2) Deposition of any unreacted sulfur in the cooler parts of the cryostat.
- (3) Heat effects due to the reaction between sulfur

and the clean bare copper surface on the inside of the shield of the calorimeter.

- (4) Loss of precision in the measurements on solid sulfur, due to the escape of sulfur and, possibly, helium when the sulfur was heated to the point of partial melting.

A search was made for evidence of these results. The cryostat had been opened and partially disassembled during the low temperature measurements to permit work to be done on the wiring. No copper blackening, evidence of corrosion, or deposition of sulfur was found. All these results were found after the known rupture later on.

Heat effects were searched for by comparing the "heat leak" of the empty calorimeter during its initial calibration at high temperatures with the "heat leak" of the filled calorimeter during the measurements on liquid sulfur. (The "heat leak" is indicated by the steady-state rate of change of temperature of the calorimeter when no heat is being supplied to it). This is an extremely sensitive test, yet no difference was found between the "heat leaks" of the empty and filled calorimeter.

The precision of measurement on solid sulfur was very good. In summary, then, no evidence was found for the effects we would have expected if the crack had been present during the low temperature measurements.

The third and final necessary part of the discussion of the rupture is consideration of the evidence for or

against the overall accuracy of the results for solid sulfur. Accurate results here imply the absence of a crack in the calorimeter, which would be expected to have adverse results. The entropy of monoclinic sulfur above the orthorhombic-monoclinic transformation temperature is the same (within an acceptably small error) whether found by integration of the heat capacity of monoclinic sulfur or by integration of the heat capacity of orthorhombic sulfur and addition of the entropy of transformation. The chance of such agreement occurring fortuitously with inaccurate data is remote, except for errors which affect both sets of data equally. A leak in the calorimeter would not be expected to fall into that category.

There are two sets of data for solid sulfur which were made with modern techniques in two different laboratories. Both agree quite well with the present data, except for West's data on monoclinic sulfur, which are already suspected of being erroneous (15). The chance of a fortuitous agreement between the present data and those of two other laboratories in widely separated temperature ranges is vanishingly small.

The conclusion of this discussion is that the leak developed at the time it was discovered and was not present during measurements on solid sulfur.

To determine the exact weight of sulfur in the calorimeter during the measurements it was necessary to determine the plug weight. After the calorimeter had been cut apart

to remove the thermometer, a visual inspection was made to ensure that no tin solder had run down into the calorimeter. Tin solder inside the calorimeter would produce errors from reaction with the sulfur and from an incorrectly calculated plug weight.

The top of the calorimeter was weighed after the sulfur had been removed from it. Then the plug was removed, and all the tin solder was removed by scraping; a small amount of the gold plate and platinum surface was removed with it. The top was weighed again. The difference in weight before and after removing the plug was 0.0981 gram, and is an upper limit on the true plug weight. The inner filling tube alone weighed 0.0406 gram, and sets a lower limit on the true plug weight. The estimated plug weight, 0.0704 gram, must therefore be correct to within 0.0298 gram, or about 0.03% of the total weight of sulfur (95.089 grams, corrected for buoyancy).

The uncertainty in energy measurement is estimated as 0.02%, and the uncertainty in the effective heat capacity of the empty calorimeter due to material changes is estimated as about 0.03%, which contributes about 0.02% to the overall uncertainty, since the calorimeter contributes about one-third of the total heat capacity.

The amount of sulfur in gram-atoms was calculated using the 1961 International Atomic Weight value of 32.064 for sulfur. Calculations were made using the initially estimated weight of sulfur in the calorimeter. This was

0.03% higher than the final estimated weight given above. The initial estimated weight assumes that only a very small amount of solder was used on the plug, and is probably closer to the true weight than the final estimate. The final estimate has the advantage that it cannot be in error by more than 0.03%. It is shown below that using the final estimated weight and applying a correction for the change of calorimeter material makes no significant difference in the final smoothed values for the heat capacity of sulfur.

CHAPTER IV

MONOCLINIC (β) SULFUR

The sulfur was received in the orthorhombic form. It was not heated above the polymer temperature (where the viscosity, heat capacity, etc., rise rapidly with increasing temperature) until after all the measurements on solid sulfur. The sample was melted during the initial triple point determination, cooled slowly to below the orthorhombic-monoclinic transformation point, and then annealed one day at 383.7°K before cooling slowly to 369.4°K to start measurements. In spite of this careful treatment, the results of the earlier heat capacity measurements were lower than those of later measurements, taken near the end of the measurements on solid sulfur. The earlier measurements showed a trend with time, gradually approaching the later measurements. As described below, the later measurements are consistent with the remainder of the heat capacity data, while the initial measurements are not. The heat leak of the calorimeter was normal during both the initial and the later measurements. For these reasons it was concluded that the sulfur had not reached equilibrium during the earlier measurements and they were discarded.

Molten sulfur has been observed to crystallize from the

liquid into forms other than orthorhombic and monoclinic (16). If the rates of conversion back to monoclinic are slow under the experimental conditions, pure monoclinic sulfur may not be obtained. The peculiar shape of the heat capacity versus temperature curve reported by West suggests that more than one form of sulfur was present, and West has interpreted it as pertaining to two forms of sulfur. One form may have been a non-equilibrium form. It has been suggested that the results obtained by West resulted from water present as an impurity, since his sulfur was supplied wet, and he may not have removed the last traces of water in filling the calorimeter. (15).

When monoclinic sulfur was cooled by the usual method of putting the calorimeter in contact with the shield and the shield and ring in contact with the lower tank full of liquid nitrogen, the sulfur transformed to orthorhombic. In this experiment the initial cooling rate was about 1°K per minute at the orthorhombic-monoclinic transformation temperature. When the initial cooling rate was increased to about 2°K per minute at the transformation point, lowering the temperature to 264°K in about one hour, there was only partial transformation to orthorhombic. When the monoclinic sulfur was partially melted and cooled slowly to a few degrees below the melting point, and then cooled at an initial rate of about 5°K per minute at the transformation point so that the temperature dropped below 264°K in about 20 minutes, the sulfur remained monoclinic. The lack

of conversion to orthorhombic was confirmed by the overall consistency of the heat capacity measurements and the reproducibility of the data each time the monoclinic was cooled, with different amounts melted and cooling rates each time. The necessary cooling rate was obtained by filling both tanks with liquid nitrogen, putting the calorimeter into contact with shield and tank, and admitting approximately 1 mm. helium gas pressure to the cryostat.

The heat capacity of supercooled monoclinic sulfur was measured from about 12°K to about 260°K, above which temperature it transformed to orthorhombic sulfur at a measurable rate. The only unusual feature of the heat capacity versus temperature curve was a lambda anomaly with its peak at 198.3°K. A Debye function did not fit the data well, so extrapolation to 0°K was made using a combination of the Einstein functions of the low frequency vibrations of the S_8 molecule (17), excluding translational motions, and a Debye function with 2.88 degrees of freedom per molecule and a characteristic temperature of 68.90°K.

The enthalpy of monoclinic sulfur over the temperature range where it reverted to orthorhombic sulfur rapidly enough to interfere with heat capacity measurements was determined in two experiments. In these experiments the monoclinic sulfur was heated from a temperature where it was changing only slowly to orthorhombic to a temperature where monoclinic sulfur was the stable form. Since the initial and final states of the sulfur were monoclinic,

even though it was partly orthorhombic during the heating period, the overall enthalpy is that of monoclinic sulfur.

The heat capacity of monoclinic sulfur was measured in the temperature range where it was stable; then the sulfur was cooled slightly below the transformation temperature and further measurements were made before transformation to orthorhombic sulfur began.

A smooth curve was drawn on a plot of heat capacity versus temperature, joining smoothly with smooth curves through the regions where the heat capacity could be measured and passing through the region where it could not be measured. This interpolated heat capacity curve was consistent with the enthalpies measured over the region. Thus, the interpolated curve probably corresponds very closely to the true heat capacity of monoclinic sulfur. The chance of an anomaly occurring in the unmeasured region without affecting the enthalpy is very small. Further evidence for the correctness of the interpolated curve is provided by the third law applied to the orthorhombic-monoclinic transformation as discussed below.

The present results do not show a decreasing heat capacity with increasing temperature (or a transformation) near 374°K, as reported by West. The behavior observed by West may have been caused by non-equilibrium conditions in the sulfur, or by impurity (as mentioned above). The latter seems unlikely in view of the results of his purity determination. A detailed comparison of the results with pre-

vious work is given below.

As is shown below, the third law applied to the orthorhombic-monoclinic transformation shows that both crystal forms have the same entropy at 0°K, and we follow the usual convention by defining that entropy as zero. The structure of monoclinic sulfur at room temperature has a randomness of orientation of some molecules which would lead to a zero-point entropy of $0.057 \text{ cal.-g-atom}^{-1}\text{-}^\circ\text{K}^{-1}$ if it persisted down to °K (6). The entropy change in the lambda anomaly of monoclinic sulfur can be compared with this in the following way: Both monoclinic and orthorhombic sulfur are structures formed from S_8 molecules and should show many similarities in heat capacity. In looking for a relationship between the heat capacities of the two forms, it is found that the smoothed heat capacity values from 70°K through 100°K and 250°K through 300°K can be fitted by the equation

$$C_{\text{monoclinic}} - C_{\text{orthorhombic}} = 5.11 \times 10^{-4} T - 0.0245$$

where C represents the heat capacity in $\text{cal.-g-atom}^{-1}\text{-}^\circ\text{K}^{-1}$ and T represents the temperature in °K. The algebraic average deviation from this equation is 0.000_0 ; the standard deviation is 0.001_2 , and the maximum deviation is 0.001_8 . By using the above equation to interpolate the heat capacity of monoclinic sulfur through the range of the lambda anomaly, one can find the heat capacity due to the anomaly alone (by subtracting the interpolated heat capacity from the observed

heat capacity). The entropy change in the lambda anomaly turns out to be $0.052 \pm 0.005 \text{ cal.-g-atom}^{-1}\text{-}^\circ\text{K}^{-1}$, which agrees with the theoretical value for the entropy due to the randomness observed at room temperature. Therefore the lambda transformation has been interpreted as due to the disordering of the structure of monoclinic sulfur on heating (18).

Experimental results for monoclinic sulfur are presented in Table II. The first column gives the number of the measurement in chronological order; the second column gives the average temperature \bar{T} in degrees Kelvin during the heating period; the third column gives the change of temperature ΔT during heating; the fourth column gives the average heat capacity \bar{C}_s over the temperature range through which it was heated; and the last column gives the deviation of \bar{C}_s from the smooth curve selected to represent the data. The heat capacity values are given in $\text{cal.-g-atom}^{-1}\text{-}^\circ\text{K}^{-1}$ and have been corrected for heat leak and premelting.

Graphical presentations of the smoothed heat capacity and some experimental data are given in Chapter IX below. The smoothed heat capacity data are given in Table III. The first column gives the temperature T in $^\circ\text{K}$; the second gives the smoothed heat capacity value C_s at temperature T in $\text{cal.-g-atom}^{-1}\text{-}^\circ\text{K}^{-1}$; the third gives $H - H^\circ$, the enthalpy less the enthalpy of orthorhombic sulfur (the standard state) at 0°K in cal.-g-atom^{-1} ; the fourth gives $S - S^\circ$, the entropy less the entropy of orthorhombic sulfur at 0°K , in cal.-g-

TABLE II
EXPERIMENTAL DATA FOR MONOCLINIC SULFUR

no.	\bar{T}	ΔT	\bar{C}_s	dev.	no.	\bar{T}	ΔT	\bar{C}_s	dev.
38	12.41	0.81	0.282	+0.006	71	145.34	4.15	3.986	0.000
50	13.12	0.95	0.317	+0.003	16	150.29	6.24	4.076	-0.001
39	13.38	1.15	0.331	+0.003	17	158.63	7.55	4.223	0.000
51	14.38	1.57	0.380	0.000	31	165.99	9.18	4.351	+0.001
40	14.54	1.16	0.388	0.000	18	166.08	7.36	4.352	0.000
41	15.92	1.62	0.456	-0.001	19	173.34	7.17	4.480	0.000
52	16.09	1.87	0.468	-0.001	2	176.82	21.24	4.542	-0.002
42	17.53	1.61	0.541	-0.001	1	177.06	21.35	4.548	0.000
53	18.03	2.01	0.566	-0.001	20	180.93	7.01	4.617	0.000
43	19.25	1.81	0.628	0.000	26	188.37	2.27	4.764	+0.002
54	20.37	2.68	0.685	+0.001	21	188.83	7.79	4.780	0.000
44	21.02	1.74	0.717	+0.001	27	190.62	2.25	4.828	+0.009
55	22.82	2.21	0.804	+0.001	28	192.86	2.22	4.887	+0.003
45	22.82	1.86	0.803	0.000	29	195.07	2.20	4.969	+0.002
46	25.03	2.57	0.908	+0.002	72	196.19	2.16	5.025	+0.002
56	25.18	2.51	0.915	+0.001	22	196.48	7.52	4.987	-0.010
47	27.56	2.49	1.020	+0.002	30	197.25	2.16	5.095	-0.011
57	27.87	2.87	1.032	+0.001	73	197.77	0.98	5.166	+0.010
48	30.11	2.59	1.122	-0.002	74	198.73	0.94	5.115	+0.007
58	31.14	3.66	1.165	-0.001	75	199.69	0.98	4.852	-0.031
49	33.11	3.40	1.241	-0.002	76	201.28	2.21	4.809	+0.001
32	33.95	2.50	1.275	0.000	77	203.16	2.21	4.807	+0.001
59	35.13	4.32	1.319	0.000	23	204.66	9.46	4.836	+0.016
33	36.55	2.70	1.371	+0.001	78	205.37	2.20	4.817	+0.003
60	39.60	4.63	1.476	0.000	79	207.57	2.20	4.830	0.000
34	39.72	3.64	1.480	0.000	80	211.75	6.17	4.868	+0.001
35	43.44	3.82	1.601	-0.001	24	213.55	8.31	4.883	0.000

TABLE II (Continued)

no.	\bar{T}	ΔT	\bar{C}_s	dev.	no.	\bar{T}	ΔT	\bar{C}_s	dev.
61	44.34	4.85	1.630	-0.002	81	218.88	8.09	4.928	-0.001
36	47.28	3.86	1.723	-0.001	82	225.59	8.03	4.987	0.000
37	51.32	4.23	1.846	-0.001	83	233.55	7.91	5.056	0.000
62	55.98	4.56	1.984	0.000	84	241.41	7.80	5.124	+0.001
63	60.78	5.03	2.122	0.000	85	249.15	7.70	5.187	-0.001
64	66.02	5.44	2.267	-0.002	86	256.79	7.58	5.250	0.000
65	71.27	5.08	2.401	0.000	87	264.80	8.45	5.308	-0.005
10	75.13	4.82	2.498	0.000	25	300.50	165.60	5.526	+0.002
11	79.83	4.58	2.616	-0.002	88	326.29	114.52	5.703	+0.003
12	84.74	5.23	2.739	+0.001	101	364.20	2.05	5.888	-0.014
13	90.25	5.81	2.869	+0.003	102	366.25	2.04	5.908	-0.003
3	94.93	5.58	2.967	-0.002	103	368.28	2.03	5.920	-0.001
66	99.39	41.01	3.059	0.000	104	370.29	2.02	5.941	+0.011
4	100.41	5.38	3.086	0.000	93	372.70	2.05	5.940	-0.002
5	105.70	5.19	3.199	0.000	94	374.75	2.05	5.948	-0.003
6	111.87	7.14	3.328	0.000	95	376.79	2.04	5.958	-0.003
14	116.97	47.62	3.427	0.000	96	378.82	2.04	5.965	-0.005
7	118.88	6.87	3.472	0.000	97	380.85	2.03	5.988	+0.008
67	123.83	7.87	3.572	0.000	89	380.93	1.02	5.980	0.000
8	126.26	7.91	3.620	0.000	90	382.46	2.04	5.999	+0.011
68	129.67	3.82	3.689	+0.002	98	382.85	2.02	5.993	+0.004
9	134.63	8.84	3.782	-0.001	91	384.49	2.04	6.001	-0.004
69	135.32	7.46	3.795	-0.001	99	384.85	2.00	5.997	-0.002
70	141.16	4.23	3.906	-0.002	92	386.51	2.03	5.883	-0.124
15	143.97	6.39	3.959	-0.002	100	386.83	1.98	5.785	-0.223

TABLE III
THERMODYNAMIC PROPERTIES OF MONOCLINIC SULFUR

T	C _S	H-H°	S-S°	$-\frac{F-H^\circ}{T}$	T	C _S	H-H°	S-S°	$-\frac{F-H^\circ}{T}$
0	0.000	59.53	0.007	-----	190	4.801	583.08	5.582	2.513
10	0.163	59.96	0.063	-5.933	192	4.858	592.74	5.632	2.545
12	0.257	60.37	0.101	-4.930	194	4.923	602.52	5.683	2.577
14	0.360	60.99	0.149	-4.207	196	5.009	612.50	5.734	2.609
16	0.464	61.81	0.203	-3.660	196.5	5.037	615.02	5.747	2.617
18	0.565	62.84	0.264	-3.227	197	5.073	617.55	5.760	2.625
20	0.666	64.07	0.329	-2.874	197.5	5.117	620.10	5.773	2.633
22	0.764	65.50	0.397	-2.580	198	5.184	622.67	5.786	2.641
24	0.860	67.13	0.467	-2.330	198.3	5.250	624.24	5.794	2.646
26	0.952	68.94	0.540	-2.112	198.4	5.215	624.76	5.796	2.647
28	1.037	70.93	0.613	-1.920	198.5	5.186	625.28	5.799	2.649
30	1.120	73.08	0.688	-1.748	199	5.044	627.83	5.812	2.657
32	1.200	75.40	0.763	-1.593	199.5	4.913	630.32	5.824	2.665
34	1.277	77.88	0.838	-1.453	199.7	4.854	631.30	5.829	2.668
36	1.351	80.51	0.913	-1.323	199.8	4.829	631.78	5.831	2.669
38	1.422	83.28	0.988	-1.204	199.9	4.821	632.27	5.834	2.671
40	1.490	86.19	1.062	-1.093	200	4.817	632.75	5.836	2.672
45	1.653	94.05	1.247	-0.843	200.2	4.812	633.71	5.841	2.676
50	1.808	102.70	1.429	-0.625	200.4	4.810	634.67	5.846	2.679
55	1.956	112.11	1.609	-0.429	201	4.808	637.56	5.860	2.688
60	2.101	122.26	1.785	-0.253	202	4.806	642.37	5.884	2.704
65	2.238	133.10	1.959	-0.089	203	4.806	647.17	5.908	2.720
70	2.369	144.62	2.130	0.064	204	4.808	651.98	5.932	2.736
75	2.495	156.78	2.297	0.207	205	4.812	656.79	5.955	2.751
80	2.622	169.57	2.462	0.342	206	4.817	661.60	5.978	2.766
85	2.744	182.99	2.625	0.472	208	4.833	671.25	6.025	2.798
90	2.862	197.00	2.785	0.596	210	4.852	680.94	6.071	2.828

TABLE III (Continued)

T	C _S	H-H°	S-S°	$\frac{F-H^\circ}{T}$	T	C _S	H-H°	S-S°	$\frac{F-H^\circ}{T}$
95	2.971	211.59	2.943	0.716	220	4.939	729.89	6.299	2.981
100	3.077	226.71	3.098	0.831	230	5.025	779.71	6.521	3.131
105	3.184	242.36	3.251	0.943	240	5.111	830.39	6.736	3.276
110	3.289	258.54	3.401	1.051	250	5.195	881.92	6.947	3.419
115	3.393	275.25	3.550	1.157	260	5.276	934.28	7.152	3.559
120	3.495	292.47	3.696	1.259	270	5.354	987.43	7.353	3.696
125	3.595	310.19	3.841	1.359	280	5.428	1041.34	7.549	3.830
130	3.694	328.41	3.984	1.458	290	5.498	1095.97	7.741	3.962
135	3.790	347.12	4.125	1.554	298.15	5.551	1140.99	7.893	4.066
140	3.886	366.31	4.265	1.648	300	5.563	1151.27	7.929	4.091
145	3.980	385.98	4.403	1.741	310	5.624	1207.21	8.111	4.217
150	4.072	406.11	4.539	1.832	320	5.682	1263.74	8.291	4.342
155	4.158	426.68	4.674	1.921	330	5.736	1320.83	8.467	4.464
160	4.247	447.70	4.808	2.010	340	5.786	1378.44	8.639	4.585
165	4.333	469.15	4.940	2.097	350	5.835	1436.54	8.807	4.703
170	4.421	491.03	5.070	2.182	360	5.882	1495.13	8.972	4.819
175	4.509	513.36	5.200	2.267	368.3	5.921	1544.11	9.106	4.913
180	4.599	536.13	5.328	2.350	370	5.929	1554.18	9.134	4.934
185	4.694	559.36	5.455	2.431	380	5.976	1613.71	9.293	5.046
188	4.753	573.53	5.531	2.480	388.34	6.015	1663.71	9.423	5.139

atom⁻¹-°K⁻¹; and the fifth gives the function $-\frac{1}{T}$ times the (free energy less the enthalpy of orthorhombic sulfur at 0°K). The results for orthorhombic sulfur have been anticipated in calculating columns 3, 4, and 5; the values of $H - H_0^\circ$ and $S - S_0^\circ$ at 0°K were chosen to make the values for orthorhombic and monoclinic consistent at the transformation temperature. Otherwise the values were obtained entirely by the integration of C_s from Column 2.

The precision and accuracy of these data are discussed below.

CHAPTER V

ORTHORHOMBIC (α) SULFUR

Orthorhombic sulfur was obtained very easily from monoclinic sulfur by cooling it to about 20° below the transformation temperature. The heat capacity versus temperature curve for orthorhombic sulfur was smooth, monotonically increasing and of normal shape. No unusual difficulties were encountered in the course of the measurements. The heat capacity was extrapolated down to 0°K with the same Einstein functions as those used for monoclinic sulfur plus a Debye function with 3.36 degrees of freedom per molecule and a characteristic temperature of 87.26°K.

Experimental data for orthorhombic sulfur are presented in Table IV. The first column gives the number of the measurement in chronological order; the second column gives the average temperature \bar{T} in degrees Kelvin during the heating period; the third column gives the change of temperature ΔT during the heating period; the fourth column gives the average heat capacity \bar{C}_s over the temperature range through which it was heated; and the fifth column gives the deviation of \bar{C}_s from the smooth curve selected to represent the data. The heat capacity values are given in cal.-g-atom⁻¹-°K⁻¹ and have been corrected for heat leak.

TABLE IV

EXPERIMENTAL DATA FOR ORTHORHOMBIC SULFUR

no.	\bar{T}	ΔT	\bar{C}_s	dev.	no.	\bar{T}	ΔT	\bar{C}_s	dev.
79	12.34	1.18	0.218	+0.005	17	126.04	6.32	3.561	0.000
70	12.56	0.97	0.227	+0.004	49	129.09	5.11	3.617	+0.001
80	13.69	1.54	0.284	+0.005	50	130.13	58.35	3.618	-0.002
71	13.80	1.52	0.288	+0.003	18	132.27	6.15	3.675	+0.002
81	15.59	2.26	0.381	0.000	19	138.33	5.98	3.777	-0.001
72	15.67	2.24	0.385	0.000	20	144.24	5.84	3.876	0.000
82	17.71	1.99	0.493	-0.002	21	151.30	7.46	3.989	0.000
73	17.78	1.98	0.496	-0.002	22	159.03	8.00	4.106	0.000
74	19.69	1.84	0.599	-0.001	51	164.53	10.45	4.183	-0.002
83	19.72	2.05	0.601	0.000	23	166.90	7.76	4.218	0.000
84	21.52	1.54	0.694	0.000	24	174.75	7.94	4.328	+0.005
75	21.57	1.93	0.698	0.000	52	174.81	10.10	4.325	+0.001
85	23.49	2.40	0.794	0.000	25	182.48	7.51	4.421	0.000
76	23.53	1.99	0.796	0.000	26	190.45	8.44	4.520	+0.001
77	25.57	2.10	0.895	+0.001	27	195.05	8.27	4.572	-0.003
86	25.86	2.33	0.908	0.000	28	203.24	8.12	4.663	0.000
78	28.45	3.64	1.023	-0.001	29	211.36	8.12	4.744	-0.004
87	28.75	3.45	1.036	-0.001	30	219.34	7.85	4.828	-0.002
88	31.81	2.68	1.164	-0.002	31	227.13	7.72	4.897	-0.003
65	32.35	3.43	1.187	-0.001	32	229.41	7.44	4.918	-0.002
66	35.75	2.65	1.320	0.000	33	236.80	7.36	4.984	+0.001
61	38.04	3.95	1.402	-0.001	34	244.54	8.20	5.046	-0.001
67	39.16	4.16	1.441	-0.002	5	248.39	5.73	5.075	-0.002
62	41.77	3.52	1.532	+0.002	35	253.17	9.00	5.117	+0.003
68	43.47	4.47	1.586	0.000	6	254.08	5.66	5.119	-0.002
63	45.88	4.71	1.663	-0.001	36	257.53	8.84	5.147	-0.001
69	48.06	4.70	1.731	-0.001	7	260.65	7.48	5.168	-0.004
64	50.35	4.23	1.804	0.000	37	266.30	8.70	5.214	+0.002

TABLE IV (Continued)

no.	\bar{T}	ΔT	\bar{C}_s	dev.	no.	\bar{T}	ΔT	\bar{C}_s	dev.
53	53.00	4.67	1.883	0.000	8	268.08	7.40	5.224	-0.001
54	57.95	5.25	2.027	-0.002	38	274.94	8.59	5.272	-0.002
55	63.38	5.61	2.182	0.000	9	275.89	8.24	5.282	+0.001
56	68.77	5.18	2.324	-0.001	39	283.46	8.47	5.330	-0.002
57	74.82	6.90	2.472	-0.005	40	291.86	8.34	5.385	-0.001
58	80.85	5.18	2.625	-0.001	41	300.14	8.23	5.436	-0.001
10	81.27	5.16	2.636	0.000	42	304.03	9.56	5.459	-0.001
59	85.95	5.01	2.749	+0.002	43	313.91	10.20	5.517	+0.001
11	91.51	5.49	2.872	0.000	44	324.02	10.04	5.571	0.000
60	91.64	6.38	2.875	0.000	45	333.98	9.89	5.625	+0.002
12	96.96	5.41	2.987	-0.002	46	343.75	9.66	5.677	+0.004
13	102.21	5.08	3.095	-0.002	1	345.40	7.70	5.681	-0.001
14	107.21	4.93	3.197	-0.001	3	346.57	9.21	5.686	-0.001
15	112.93	6.79	3.311	0.000	2	353.82	9.15	5.725	+0.001
16	119.60	6.55	3.440	0.000	4	355.73	9.12	5.732	-0.001
48	123.88	5.30	3.521	0.000	47	360.99	14.93	5.762	+0.003

The smoothed heat capacity curve for orthorhombic sulfur is given in Chapter IX. The discussion of the accuracy and tabulation of smoothed values and thermodynamic functions are also presented in Chapter IX.

CHAPTER VI

THE ORTHORHOMBIC-MONOCLINIC TRANSFORMATION

The equilibrium transformation temperature cannot be determined by letting the heat of transformation bring the calorimeter to the equilibrium temperature, because the rate of transformation near that temperature is too slow. Therefore a method such as West's (3), in which the equilibrium temperature is found by observing the rate of temperature change due to transformation as a function of temperature, had to be used. In this method, the heat leak of the calorimeter plays an important role. When the rate of transformation is zero, the rate of temperature change is that caused by the heat leak. When the rate of temperature change is zero, the heat leak is just enough to balance the rate of transformation. The temperature at which the rate of temperature change is zero may differ significantly from the equilibrium temperature if the rate of transformation is slow enough.

Experiments with pure orthorhombic and pure monoclinic sulfur were made to determine the heat leak in the absence of transformation, since the transformation does not usually initiate rapidly. The rates interpolated to 368.3°K ranged from -3×10^{-5} °K per minute up to almost zero, with a preponderance of rates close to zero.

Several experiments were then made on mixtures of the two forms ranging from about 25% orthorhombic to about 65% orthorhombic sulfur. They were heated to the desired temperatures and their rates of temperature change followed for periods of about one hour up to about two days. In addition, one observation was made after cooling to the desired temperature by temporarily lowering the temperature of the adiabatic shield. All the rates observed with mixtures of the two forms at 367.91°K and below were warming rates greater than 0.46×10^{-5} °K per minute. The cooling rates observed above that temperature were:

- (1) After heating: -3.2×10^{-5} °K per min. at 368.2940°K, gradually diminishing to -0.08×10^{-5} °K per min. at 368.2799°K.
- (2) After heating: -23×10^{-5} °K per min. at 369.0766°K, gradually diminishing to -5×10^{-5} °K per min. at 368.8316°K.
- (3) After cooling: -1.2×10^{-5} °K per min at 368.5424°K, gradually diminishing to -0.9×10^{-5} °K per min. at 368.5378°K.

The uncertainty in the heat leak and the slowness of transformation determine the uncertainty in the transformation temperature. We take the equilibrium transformation temperature to be 368.3 ± 0.3 °K. West reported 368.46 ± 0.01 °K, but the uncertainty estimate seems too small in view of the size of the heat leak and the rate of transformation, and the short times over which the rates were

measured.

The heat of transformation was obtained from measurements in which the orthorhombic sulfur was heated from a temperature at which it was stable or metastable to a temperature at which the transformation to monoclinic is extremely rapid. The heat required to warm the sulfur through this temperature range less the heat capacities of pure orthorhombic and monoclinic sulfur integrated over the temperature range in the regions where they are stable gives the heat of transformation. The results must be corrected for heat leak and for premelting. The corrected results were:

- (1) Initial 368.4431°K, final 383.3948°K, heat of transformation 95.68 cal.-g-atom⁻¹.
- (2) Initial 363.0828°K, final 384.5276°K, heat of transformation 95.75 cal.-g-atom⁻¹.

The average of these two results, 95.72 cal.-g-atom⁻¹, is taken as the heat of transformation; from it and the transformation temperature, the entropy of transformation is 0.2599 cal.-g-atom⁻¹-°K⁻¹, and we estimate the uncertainty as ± 0.0004 cal.-g-atom⁻¹-°K⁻¹. West's result is about 0.3% higher, and he estimated its uncertainty as about 0.5%.

When the third law is applied to this transformation by setting the difference in entropy calculated by direct integration of the heat capacities of the two forms equal to the entropy of transformation, the discrepancy is 0.007

cal.-g-atom⁻¹-°K⁻¹. We shall see below that this is less than the experimental uncertainty. Therefore, to within experimental error, both forms of sulfur have ordered structures at 0°K.

CHAPTER VII

TRIPLE POINT, PURITY, AND HEAT OF FUSION

Equilibrium at the triple point (strictly speaking, the melting point under a low pressure) was attained quite slowly. After each measured quantity of heat was supplied to the calorimeter, its temperature was observed as a function of time for a period of 3 to 4 days, until the rate of temperature change had become quite small and was changing linearly with temperature. The equilibrium temperature was then obtained by extrapolating to zero rate. These extrapolations were over temperature ranges of thousandths of a degree.

Results for the reciprocal of the fraction melted and the corresponding temperatures were: 7.81, 388.3354°K; 2.37, 388.3403 °K; and 1.35, 388.3413°K. A graph of the reciprocal of the fraction melted versus temperature is a straight line (to within 4×10^{-5} °K maximum deviation) with an intercept at 388.3425°K, the triple point (monoclinic-liquid-vapor). The slope of the line is -9.091×10^{-4} °K = $dT/d(F^{-1})$, where T represents temperature and F the fraction melted. It is necessary to consider the 0.01°K temperature difference between the laboratory scale and the modern temperature scales when using this triple point, since the

accuracy of measurement should be at least 0.01°K . The triple point is 0.0065°K higher than that reported by West, and the slope is about 0.72 times the slope he found.

The exact nature of the molecular species in liquid sulfur is unknown, but certainly liquid sulfur is mostly S_8 at the triple point. Assuming the formula S_8 , we can estimate the amount of impurity from the usual equation

$$N = \frac{-\Delta H}{RT^2} \frac{dT}{dF^{-1}} = 1.0 \times 10^{-5} \text{ mole fraction impurity.}$$

Here ΔH is the heat of fusion, T the triple point temperature, and N the mole fraction of liquid-soluble, solid-insoluble impurities.

The triple point is taken as $388.34 \pm 0.01^{\circ}\text{K}$, or $388.33 \pm 0.01^{\circ}\text{K}$ when the difference between the laboratory scale and the best estimate of temperature is taken into account. This agrees with West's determination.

The heat of fusion was obtained in the course of the triple point determination, but because of the long time required for the triple point study (about 12 days), the result, $412.04 \text{ cal.-g-atom}^{-1}$, is uncertain. The result of a separate direct measurement of the heat of fusion, which required about one day, was $411.45 \text{ cal.-g-atom}^{-1}$. This is about 0.2% higher than the value obtained by West. We take the heat of fusion to be $411.4 \pm 0.6 \text{ cal.-g-atom}^{-1}$. This was calculated using West's heat capacity data for the liquid.

For consistency, the heat of fusion was recalculated using the present liquid heat capacity data, extrapolated

down to the triple point. The result was 412.8 ± 1.5 cal.-g-atom⁻¹, which is the value used in this thesis for preparing the table of thermodynamic properties.

Because of the large uncertainty of the present data for liquid sulfur, they should be used with caution, and the heat of fusion value (411.4 ± 0.6) based on West's liquid heat capacity data is probably more accurate than the one used in this thesis.

CHAPTER VIII

LIQUID SULFUR

Liquid sulfur, which took several days to reach equilibrium near the triple point, took about one day at 404°K; as the temperature was increased, equilibration became more rapid until at temperatures near the polymer temperature, less than one hour was required. The precision of measurement was about as good as could be expected, considering the times required for equilibration and the short temperature intervals which had to be used near the peak of the lambda anomaly. This point is discussed below in more detail.

For the total entropy and enthalpy over the peak from 423.15°K to 434.15°K, the present results are 0.4% and 0.3% lower, respectively, than West's. The present results place the peak at $432.03 \pm 0.20^\circ\text{K}$; West reported $432.25 \pm 0.30^\circ\text{K}$.

To within experimental error, the present data for liquid heat capacity varied linearly with temperature below 420°K. They were extrapolated linearly to the melting point. The extrapolated data fell both above and below West's data; the maximum differences were about 2% in heat capacity but only about $1 \text{ cal.}\cdot\text{g}\cdot\text{atom}^{-1}$ in enthalpy and $0.003 \text{ cal.}\cdot\text{g}\cdot\text{atom}^{-1}\cdot^\circ\text{K}^{-1}$ in entropy over the extrapolated range.

On the basis of present theories of liquid sulfur, the lambda anomaly in liquid sulfur is caused by the polymerization of S_8 rings into long chains, which begins abruptly at a well-defined polymer temperature.

It is clear from the behavior observed after heating at temperatures below the polymer temperature (slow decrease of temperature to a final equilibrium temperature) that a slow endothermic process goes on in liquid sulfur as it is heated toward the polymer temperature. It is likely that the process could be described as an equilibration between sulfur species of low molecular weight.

The experimental data are given in Table V. The first column gives the number of the measurement in chronological order. The second gives the average temperature \bar{T} during the heating period in degrees K. The third column gives the change of temperature ΔT during heating. The fourth column gives the average heat capacity \bar{C}_s over the temperature range through which it was heated, in $\text{cal.}-\text{g}-\text{atom}^{-1}-\text{K}^{-1}$. The last column gives the deviation of \bar{C}_s from the smooth curve of heat capacity versus temperature selected to represent the data.

The data for liquid sulfur are presented graphically in Chapter IX.

TABLE V
EXPERIMENTAL DATA FOR LIQUID SULFUR

no.	\bar{T}	ΔT	\bar{C}_s	dev.
1	405.79	3.90	7.847	+0.029
2	410.35	5.56	7.897	-0.024
3	415.96	5.84	8.048	0.000
4	421.66	5.77	8.177	-0.024
7	426.91	1.29	8.459	-0.009
5	427.29	5.55	8.502	+0.029
8	428.43	1.75	8.620	-0.008
9	430.14	1.67	9.054	-0.028
10	431.43	0.90	10.872	-0.059
11	432.07	0.38	12.730	-0.002
12	432.13	0.19	12.754	-0.060
6	432.25	4.41	11.389	+0.006
13	432.41	0.38	12.696	+0.015
14	433.31	1.41	12.262	0.000

CHAPTER IX
THERMODYNAMIC PROPERTIES OF
EQUILIBRIUM SULFUR

The data for equilibrium sulfur obtained in the present study as described above have been summarized in Table VI. The first column gives the temperature T in degrees K. The second column gives the smoothed heat capacity C_s in cal.-g-atom⁻¹-°K⁻¹. This is effectively the constant pressure heat capacity at a low pressure (well below one atmosphere). The third column gives $H-H_0^\circ$, the enthalpy less the enthalpy of orthorhombic sulfur at 0°K, in cal.-g-atom⁻¹. The fourth column gives $S-S_0^\circ$, the entropy less the entropy of orthorhombic sulfur at 0°K, in cal.-g-atom⁻¹-°K⁻¹. The last column gives the function $-\frac{1}{T}$ times (free energy less the enthalpy of orthorhombic sulfur at 0°K). The last three columns were derived by integration of the data in the first two columns and addition of the heats of transformation and fusion where they occurred.

The tabulated properties are for very low pressure. Corrections of the heat capacities to atmospheric pressure are much smaller than experimental error and have not been attempted. However, the effect of pressure on melting and transformation temperatures is not necessarily negligible. Data of Tammann (13) quoted by Deaton and Blum (14) show

TABLE VI
THERMODYNAMIC PROPERTIES OF EQUILIBRIUM SULFUR

T	C _S	H-H°	S-S°	$-\frac{F-H^\circ}{T}$	T	C _S	H-H°	S-S°	$-\frac{F-H^\circ}{T}$
0	0.000	0.00	0.000	0.000	180	4.390	467.00	5.174	2.580
10	0.114	0.27	0.036	0.008	185	4.452	489.11	5.295	2.651
12	0.196	0.58	0.063	0.015	190	4.514	511.52	5.414	2.722
14	0.295	1.07	0.101	0.025	195	4.574	534.24	5.532	2.792
16	0.403	1.76	0.147	0.037	200	4.629	557.25	5.649	2.863
18	0.510	2.68	0.201	0.052	205	4.682	580.53	5.764	2.932
20	0.616	3.80	0.260	0.070	210	4.734	604.07	5.877	3.000
22	0.719	5.14	0.323	0.090	220	4.837	651.92	6.100	3.137
24	0.819	6.68	0.390	0.112	230	4.925	700.73	6.317	3.270
26	0.915	8.41	0.460	0.136	240	5.010	750.41	6.528	3.401
28	1.005	10.33	0.531	0.162	250	5.090	800.91	6.735	3.531
30	1.091	12.43	0.603	0.189	260	5.167	852.19	6.936	3.658
32	1.174	14.69	0.676	0.217	270	5.239	904.22	7.132	3.783
34	1.253	17.12	0.749	0.246	280	5.310	956.97	7.324	3.906
36	1.329	19.70	0.823	0.276	290	5.375	1010.39	7.511	4.027
38	1.402	22.43	0.897	0.307	298.15	5.425	1054.40	7.661	4.125
40	1.472	25.31	0.971	0.338	300	5.436	1064.45	7.695	4.147
45	1.636	33.08	1.154	0.419	310	5.495	1119.10	7.874	4.264
50	1.793	41.65	1.334	0.501	320	5.550	1174.33	8.049	4.379
55	1.943	50.99	1.512	0.585	330	5.602	1230.09	8.221	4.493
60	2.089	61.07	1.688	0.670	340	5.654	1286.37	8.389	4.606
65	2.226	71.86	1.860	0.755	350	5.705	1343.16	8.553	4.715
70	2.357	83.31	2.030	0.840	360	5.754	1400.46	8.715	4.825
75	2.482	95.41	2.197	0.925	368.3 (α)	5.795	1448.39	8.846	4.913
80	2.606	108.13	2.361	1.010	368.3 (β)	5.921	1544.11	9.106	4.913
85	2.725	121.46	2.523	1.094	370	5.929	1554.18	9.134	4.934
90	2.839	135.37	2.682	1.178	380	5.976	1613.71	9.293	5.046
95	2.948	149.84	2.838	1.261	388.34 (β)	6.015	1663.71	9.423	5.139
100	3.052	164.84	2.992	1.344	388.34 (1)	7.423	2076.51	10.486	5.139

TABLE VI (Continued)

T	C _S	H-H°	S-S°	$-\frac{F-H^\circ}{T}$	T	C _S	H-H°	S-S°	$-\frac{F-H^\circ}{T}$
105	3.154	180.35	3.144	1.426	390	7.461	2088.87	10.517	5.161
110	3.253	196.37	3.292	1.507	400	7.687	2164.61	10.709	5.297
115	3.352	212.88	3.439	1.588	410	7.913	2242.61	10.902	5.432
120	3.448	229.88	3.584	1.668	420	8.139	2322.87	11.095	5.564
125	3.542	247.36	3.727	1.748	422	8.185	2339.19	11.134	5.591
130	3.633	265.29	3.868	1.827	424	8.265	2355.64	11.173	5.617
135	3.721	283.68	4.006	1.905	426	8.390	2372.29	11.212	5.643
140	3.806	302.50	4.143	1.982	428	8.562	2389.25	11.252	5.670
145	3.888	321.73	4.278	2.059	429	8.702	2397.88	11.272	5.683
150	3.969	341.37	4.411	2.135	430	8.940	2406.70	11.292	5.695
155	4.046	361.41	4.543	2.211	431	9.560	2415.95	11.314	5.709
160	4.121	381.83	4.672	2.286	432	12.760	2427.11	11.340	5.721
165	4.192	402.61	4.800	2.360	432.03	12.860	2427.49	11.340	5.722
170	4.261	423.74	4.926	2.433	434	11.940	2451.92	11.397	5.747
175	4.326	445.21	5.051	2.507					

that the melting point increases by 0.03_1°K per atmosphere and that the $\alpha = \beta$ transformation temperature increases by 0.04_7°K per atmosphere. Therefore, the change in the melting point is not negligible, and it is 388.37°K at one atmosphere pressure. Enough density data exist for liquid sulfur to permit calculation of the changes in thermodynamic properties due to pressure (19). At the triple point,

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -0.001 \text{ cal.-g-atom}^{-1}\text{-}^\circ\text{K}^{-1}\text{-atm}^{-1}$$

and $\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V = -0.07 \text{ cal.-g-atom}^{-1}\text{-atm}^{-1}.$

These changes are negligible compared to experimental error.

Table VII gives the thermodynamic properties of sulfur in its standard state (one atmosphere pressure) using the best estimate of true thermodynamic temperature. The values are the same as in Table VI except at the melting point and the peak of the lambda anomaly in liquid sulfur.

The melting point of sulfur at one atmosphere pressure, taking into account the 0.01°K difference between the laboratory scale and the best estimate of temperature, is 388.36°K .

The smoothed heat capacity data are presented graphically in Figures 5, 6, and 7. In Figures 6 and 7, the horizontal bars indicate the experimental data. The vertical position of each bar shows the experimental average heat capacity and the length of each bar indicates the temperature range during the heating period.

TABLE VII
THERMODYNAMIC PROPERTIES OF SULFUR
IN ITS STANDARD STATE

T	C _p	H°-H° ₀	S°-S° ₀	$\frac{F^\circ-H^\circ}{T}$	T	C _p	H°-H° ₀	S°-S° ₀	$\frac{F^\circ-H^\circ}{T}$
0	0.000	0.00	0.000	0.000	180	4.390	467.00	5.174	2.580
10	0.114	0.27	0.036	0.008	185	4.452	489.11	5.295	2.651
12	0.196	0.58	0.063	0.015	190	4.514	511.52	5.414	2.722
14	0.295	1.07	0.101	0.025	195	4.574	534.24	5.532	2.792
16	0.403	1.76	0.147	0.037	200	4.629	557.25	5.649	2.863
18	0.510	2.68	0.201	0.052	205	4.682	580.53	5.764	2.932
20	0.616	3.80	0.260	0.070	210	4.734	604.07	5.877	3.000
22	0.719	5.14	0.323	0.090	220	4.837	651.92	6.100	3.137
24	0.819	6.68	0.390	0.112	230	4.925	700.73	6.317	3.270
26	0.915	8.41	0.460	0.136	240	5.010	750.41	6.528	3.401
28	1.005	10.33	0.531	0.162	250	5.090	800.91	6.735	3.531
30	1.091	12.43	0.603	0.189	260	5.167	852.19	6.936	3.658
32	1.174	14.69	0.676	0.217	270	5.239	904.22	7.132	3.783
34	1.253	17.12	0.749	0.246	280	5.310	956.97	7.324	3.906
36	1.329	19.70	0.823	0.276	290	5.375	1010.39	7.511	4.027
38	1.402	22.43	0.897	0.307	298.15	5.425	1054.40	7.661	4.125
40	1.472	25.31	0.971	0.388	300	5.436	1064.45	7.695	4.147
45	1.636	33.08	1.154	0.419	310	5.495	1119.10	7.874	4.264
50	1.793	41.65	1.334	0.501	320	5.550	1174.33	8.049	4.379
55	1.943	50.99	1.512	0.585	330	5.602	1230.09	8.221	4.493
60	2.089	61.07	1.688	0.670	340	5.654	1286.37	8.389	4.606
65	2.226	71.86	1.860	0.755	350	5.705	1343.16	8.553	4.715
70	2.357	83.31	2.030	0.840	360	5.754	1400.46	8.715	4.825
75	2.482	95.41	2.197	0.925	368.3(α)	5.795	1448.39	8.846	4.913
80	2.606	108.13	2.361	1.010	368.3(β)	5.921	1544.11	9.106	4.913
85	2.725	121.46	2.523	1.094	370	5.929	1554.18	9.134	4.934
90	2.839	135.37	2.682	1.178	380	5.976	1613.71	9.293	5.046
95	2.948	149.84	2.838	1.261	388.36(β)	6.015	1663.71	9.423	5.139

TABLE VII (Continued)

T	C_p	$H^\circ - H_0^\circ$	$S^\circ - S_0^\circ$	$\frac{F^\circ - H_0^\circ}{T}$	T	C_p	$H^\circ - H_0^\circ$	$S^\circ - S_0^\circ$	$\frac{F^\circ - H_0^\circ}{T}$
100	3.052	164.84	2.992	1.344	388.36 (1)	7.423	2076.51	10.486	5.139
105	3.154	180.35	3.144	1.426	390	7.461	2088.87	10.517	5.161
110	3.253	196.37	3.292	1.507	400	7.687	2164.61	10.709	5.297
115	3.352	212.88	3.439	1.588	410	7.913	2242.61	10.902	5.432
120	3.448	229.88	3.584	1.668	420	8.139	2322.87	11.095	5.564
125	3.542	247.36	3.727	1.748	422	8.185	2339.19	11.134	5.591
130	3.633	265.29	3.868	1.827	424	8.265	2355.64	11.173	5.617
135	3.721	283.68	4.006	1.905	426	8.390	2372.29	11.212	5.643
140	3.806	302.50	4.143	1.982	428	8.562	2389.25	11.252	5.670
145	3.888	321.73	4.278	2.059	429	8.702	2397.88	11.272	5.683
150	3.969	341.37	4.411	2.135	430	8.940	2406.70	11.292	5.695
155	4.046	361.41	4.543	2.211	431	9.560	2415.95	11.314	5.709
160	4.121	381.83	4.672	2.286	432	12.760	2427.11	11.340	5.721
165	4.192	402.61	4.800	2.360	432.02	12.860	2427.49	11.340	5.722
170	4.261	423.74	4.926	2.433	434	11.940	2451.92	11.397	5.747
175	4.326	445.21	5.051	2.507					

Figure 5. Heat Capacity of Sulfur

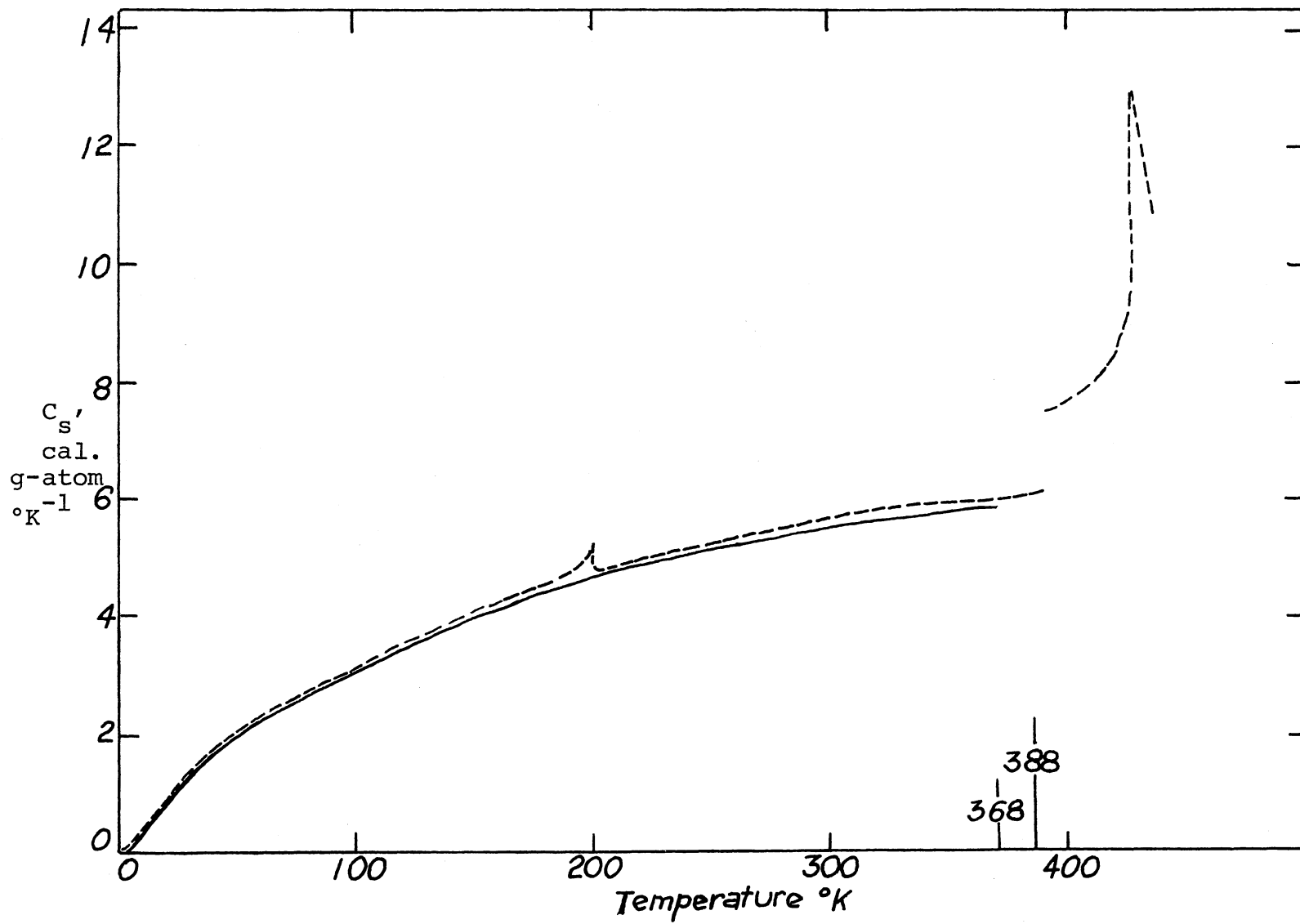
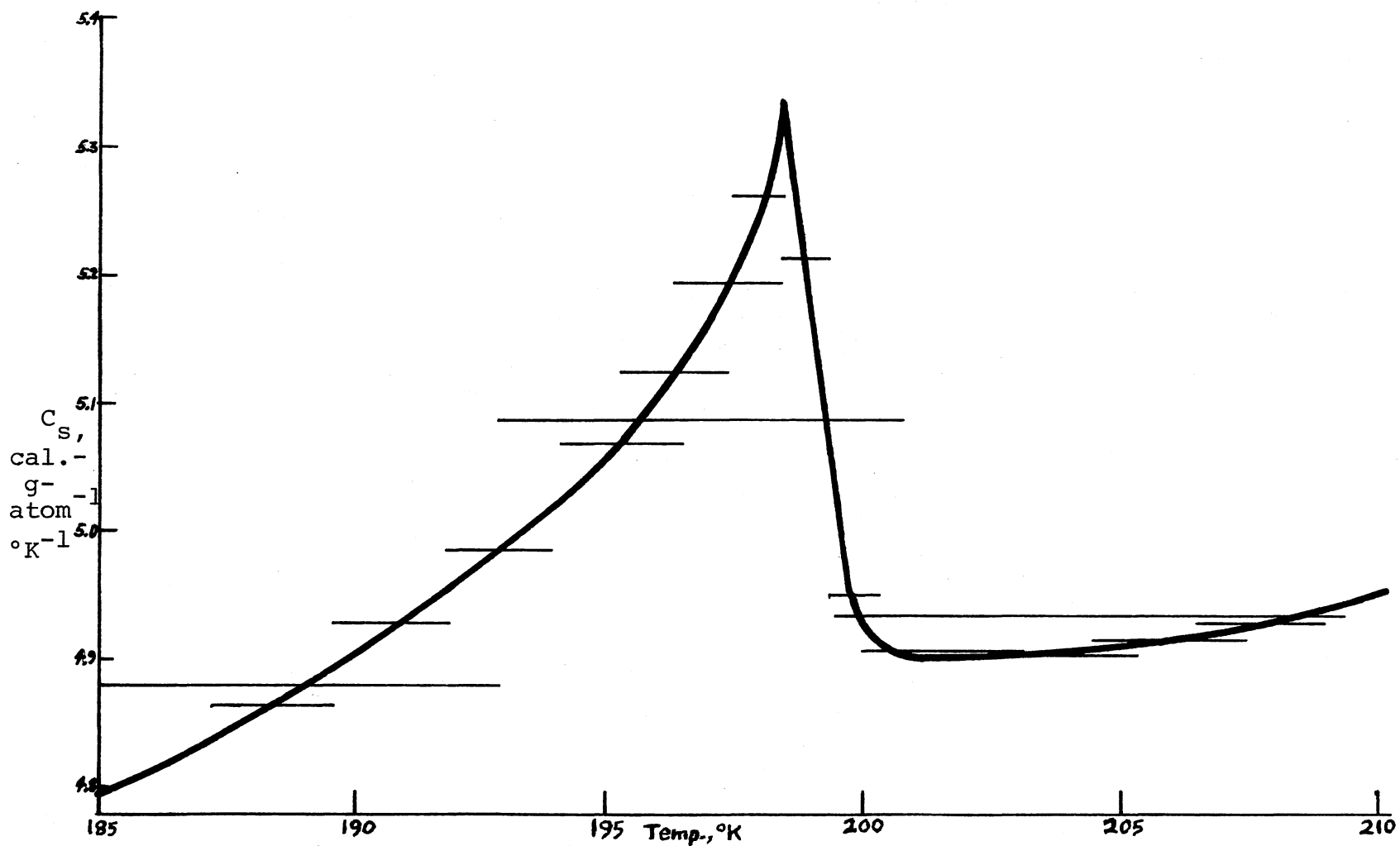


Figure 6. Lambda Anomaly in Monoclinic Sulfur



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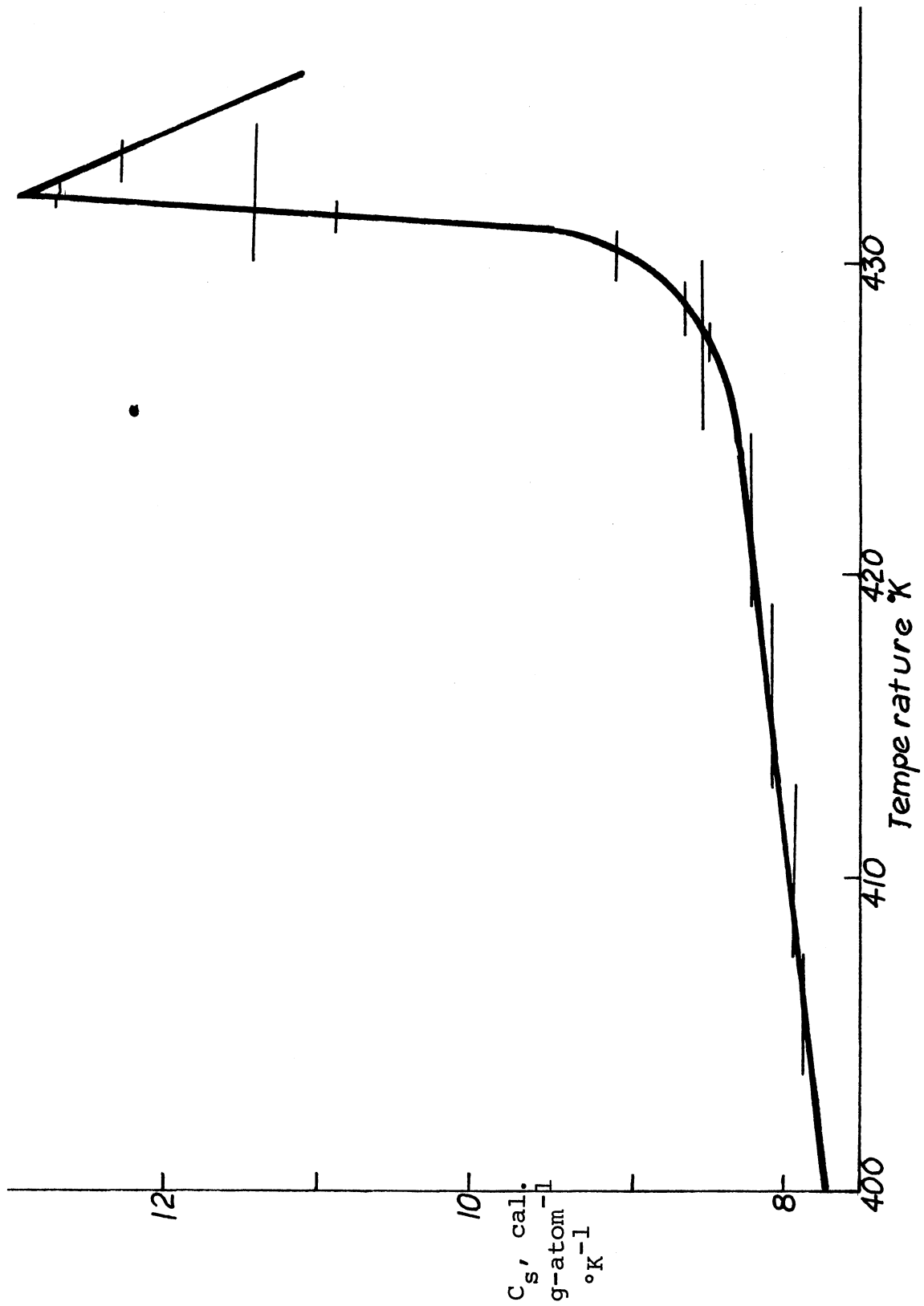


Figure 7. Heat Capacity of Liquid Sulfur

Discussion of Precision

The deviations of the experimental values from the smooth curves of heat capacity versus temperature provide a good indication of the experimental precision. In determining the precision, it is necessary to distinguish groups of experimental values which have different precisions and to treat them separately. All the precision data described below are in $\text{cal.} \cdot ^\circ\text{K}^{-1} \cdot \text{g} \cdot \text{atom}^{-1}$.

An examination of the data for orthorhombic sulfur shows that the precision is essentially constant except for the temperature range $12.34\text{--}13.80^\circ\text{K}$. In that range the deviations are greater because of the very small temperature changes and heat inputs, and the necessity for fitting the extrapolated curve. The four points in this range have an algebraic average deviation of $+0.004_2$ and a standard deviation of 0.005_0 . The remaining 84 "normal" points have an average deviation of -0.000_4 and a standard deviation of 0.001_7 .

In the case of monoclinic sulfur, the three points at the lowest temperatures ($12.41^\circ\text{--}13.38^\circ\text{K}$) have higher deviations than normal for the same reasons mentioned above. Their average deviation is $+0.004_0$ and their standard deviation is 0.005_2 . The point at 264.80°K deviates more than is normal because the transformation to orthorhombic was proceeding at a measurable rate. The points at 386.51°K and 386.83°K deviate more than is normal because the

premelting corrections were inaccurate; this may have resulted from the very slow equilibration in molten sulfur. The other fourteen points in the high temperature monoclinic range (364.20° - 384.85° K) deviate more than is normal because the temperature change during each measurement was smaller than normal. The small temperature changes were necessary in order to fully define the heat capacity at temperatures close to the anomaly reported by West. For these 14 points the average deviation is -0.000_2 and the standard deviation is 0.006_8 . The values in the lambda anomaly temperature range (188.37° - 208.57° K) also deviate more than is normal. This is because of the small temperature changes during measurements needed to define the heat capacity; the abnormally large deviations of the three measurements with normal large temperature changes may be ascribed to failure to allow sufficient time for equilibration before the presence of the anomaly was suspected. The 16 points in the lambda anomaly range have an average deviation of $+0.000_2$ and a standard deviation of 0.010_6 . If only the 13 points with the smallest temperature changes are considered, the standard deviation is still the same. There remain 68 "normal" points for monoclinic sulfur. They have an average deviation of $+0.000_1$ and a standard deviation of 0.001_2 .

The "normal" precisions for orthorhombic and monoclinic sulfur should be the same. However, a statistical F test indicates a 99% probability that they are different. This

discrepancy can be resolved by considering that the precision may well be a function of temperature, and monoclinic sulfur had few "normal" points at the higher temperatures. If the data for orthorhombic sulfur are divided into two groups (159.03°K and below, 164.53°K and above), we obtain the following results:

Low temperature, 48 points, average deviation -0.000_5 , standard deviation 0.001_3 .

High temperature, 36 points, average deviation -0.000_3 , standard deviation 0.002_1 .

A statistical F test applied to these results gives over 99% probability that the standard deviations are different in the two temperature ranges. A second F test applied to the low temperature range for orthorhombic sulfur vs. monoclinic sulfur shows no significant difference.

The error in liquid sulfur is expected to be much greater than for solid sulfur because of very slow equilibration and very small temperature changes during measurements. The 14 experimental points have an average deviation of -0.009_6 and a standard deviation of 0.029_2 .

It is concluded that the significant factors affecting the precision have been identified and that the standard deviations for each group of measurements are as given above. There is no difference between the precisions of measurement on the two solid forms of sulfur.

Although it is not permissible (strictly speaking) to pool the standard deviations for the low-temperature and high-temperature ranges of solid sulfur, these values are

not very different. A representative value for the precision of measurement on solid sulfur is convenient to have, and the standard deviation of 0.001_5 obtained by pooling the data for the "normal" ranges of solid sulfur will serve for approximate calculations.

The most important precision uncertainty to be calculated is that of the third-law test. The two questions to be answered are: Is the discrepancy of $0.007 \text{ cal.} \cdot \text{K}^{-1} \cdot \text{g-atom}^{-1}$ significant?, and, Is the precision good enough to establish that the entropy due to the disorder of the high-temperature monoclinic structure is absent at 0°K ?

The precision of the third-law test may be estimated by using the "representative" standard deviation 0.001_5 , multiplying by $\sqrt{2}$ to get the precision of the difference between two heat capacities, and multiplying by $\int_{12}^{368.3} d \ln T$ to get the standard deviation of the integral of the difference. The result is $0.007 \text{ cal.} \cdot \text{K}^{-1} \cdot \text{g-atom}^{-1}$. A more careful calculation taking into account the regions of greater uncertainty gives $0.010 \text{ cal.} \cdot \text{K}^{-1} \cdot \text{g-atom}^{-1}$.

Thus the zero-point entropy of monoclinic sulfur is the same as that of orthorhombic sulfur within experimental error, but the entropy of disorder of the high-temperature monoclinic form is much larger than experimental error and the absence of this entropy at 0°K is confirmed.

Although the absolute accuracy of measurement has already been determined from the data for n-heptane, a

statistical calculation can provide a little more information. For solid n-heptane there were 30 measurements with an average deviation of $+0.13_4\%$ and a standard deviation of $0.16_2\%$ from the selected values. The 26 measurements of liquid n-heptane had an average deviation of $+0.03_3\%$ and a standard deviation of $0.09_0\%$ from the selected values. A statistical F test gives a probability of over 99% that the standard deviations for liquid and solid are different. Since none of the individual sets of measurements in the selected values is expected to be accurate to better than 0.1%, our conclusions remain the same as before.

Other Corrections

Errors in the results may appear due to the change of calorimeter material and due to the use of the initially estimated weight of sulfur rather than the final. In order to test for these errors and to obtain a set of machine-computed thermodynamic properties for sulfur, the experimental data were subjected to analysis by an electronic computer. The final value for the weight of sulfur was used, and a correction was estimated for the change in calorimeter filling tube from platinum to monel.

Because of errors in the computation, the thermodynamic properties were not exactly correct as computed. They were compared with the calculated tables given in this thesis and permitted the elimination of all significant errors in smoothing and integration which had found their way into

those tables.

The experimental values from the machine computation were used to verify that the corrections introduced into the computation made no significant difference in the final smoothed results for heat capacity. In Table VIII the deviations of the machine computed points and the calculated points from the smoothed curves are presented. Since not all of the experimental points were used in the machine computation, an extra column labeled "Calculated, for comparison" was added, in which only the points used in the machine computation are included.

TABLE VIII
OTHER CORRECTIONS

Phase and temp. range	Quantity	Machine Computed	Calculated	Calculated, for comparison
Orthorhombic, 15.59°-360.98°	n	81	84	81
	avg. dev.	0.000 ₂	-0.000 ₄	-0.000 ₄
	std. dev.	0.001 ₆	0.001 ₇	0.001 ₆
Monoclinic, "normal" ranges	n	64	68	64
	avg. dev.	0.000 ₆	-0.000 ₁	-0.000 ₁
	std. dev.	0.001 ₇	0.001 ₂	0.001 ₂
Monoclinic, 18837°-20757°	n	11	16	11
	avg. dev.	0.001 ₅	0.000 ₂	0.000 ₀
	std. dev.	0.009 ₉	0.006 ₈	0.010 ₇
Monoclinic, 36420°-38485°	n	10	14	10
	avg. dev.	-0.000 ₃	-0.000 ₂	-0.001 ₉
	std. dev.	0.002 ₄	0.006 ₈	0.003 ₂

TABLE VIII (Continued)

Liquid	n	9	14	9
	avg. dev.	-0.009 ₁	-0.009 ₆	-0.010 ₄
	std. dev.	0.029 ₉	0.029 ₂	0.030 ₁

It is clear that the machine computed data are fitted very well by the smooth curve derived from the calculated data. Therefore the additional corrections introduced into the machine computation had no significant effect.

Comparison With Other Data

The present results are compared with other data in Table IX. The percentage deviation is the heat capacity given by the authors quoted minus the heat capacity obtained in the present study, expressed as a percentage of the value obtained in the present study. The estimated errors in Table IX are those estimated by the authors of the other studies quoted. In the case of monoclinic sulfur below 298°K, only a high-temperature error and a low-temperature error were quoted; we take a linear change of error for simplicity.

The agreement in Table IX is generally satisfactory, except that the peculiar behavior of the heat capacity of monoclinic sulfur near 374°K observed by West is not found.

The agreement near the peak heat capacity in liquid sulfur is reasonable, considering the difficulties of measurement.

TABLE IX
COMPARISON WITH OTHER STUDIES

T, °K	HEAT CAPACITIES BELOW 298°K					
	ORTHORHOMBIC				MONOCLINIC	
	Eastman & McGayock		Mal'tsey & Demidenko		Eastman & McGayock	
	dev., %	est'd error, %	dev., %	est'd error, %	dev., %	est'd error, %
15	-10.9	8.0	----	---	----	---
20	-1.8	1.5	----	---	----	---
25	-0.9	1.2	----	---	----	---
30	-1.5	1.0	----	---	----	---
40	-1.4	0.5	----	---	----	---
50	-1.2	0.4	----	---	----	---
60	-0.2	0.3	-1.2	0.2	-0.5	0.3
70	-0.2	0.3	-0.9	0.2	----	---
80	-0.1	0.3	-0.3	0.2	+0.1	0.4
90	0.0	0.3	-0.2	0.2	----	---
100	+0.3	0.3	0.0	0.2	+0.7	0.5
110	0.0	0.3	-0.2	0.2	----	---
120	-0.1	0.3	-0.1	0.2	+0.4	0.6
130	-0.2	0.3	+0.1	0.2	----	---
140	-0.3	0.3	0.0	0.2	-0.1	0.7
150	-0.1	0.3	0.0	0.2	----	---
160	0.0	0.3	+0.2	0.2	-0.3	0.8
170	+0.2	0.3	+0.4	0.2	----	---
180	+0.3	0.3	+0.4	0.2	-1.2	0.9
190	+0.3	0.3	+0.9*	0.2	----	---
200	+0.2	0.3	+0.1	0.2	-0.4	1.0
210	+0.2	0.3	+0.1	0.2	----	---
220	+0.1	0.3	+0.1	0.2	-0.4	1.1
230	0.0	0.3	+0.3	0.2	----	---
240	0.0	0.3	+0.3	0.2	+1.9	1.2
250	-0.1	0.3	+0.3	0.2	----	---

*If the "bump" in Mal'tsey & Demidenko's smoothed curve of heat capacity versus temperature is smoothed out by lowering their value at 190°K, the deviation becomes +0.2 at this temperature.

TABLE IX (Continued)

260	-0.3	0.3	+0.1	0.2	+1.8	1.3
270	-0.4	0.3	0.0	0.2	----	---
280	-0.5	0.3	-0.1	0.2	+1.7	1.4
290	-0.5	0.3	-0.1	0.2	----	---
298.15	-0.4	0.5	-0.1	0.2	+1.8	1.5

HEAT CAPACITIES ABOVE 298°K

T, °K	West		T, °K	West	
	dev., %	est'd error,* %		dev., %	est'd error,* %
298.15	-0.1	0.2	388.34(1)	(+2.1)	0.1
300	-0.2	0.2	390	(+1.9)	0.1
310	-0.2	0.2	400	(+0.6)	0.1
320	-0.2	0.2	410	-0.4	0.1
330	-0.2	0.2	420	-0.3	0.1
340	-0.2	0.2	422	0.0	0.1
350	-0.2	0.2	424	+0.2	0.1
360	-0.3	0.2	426	+0.6	0.1
368.3(α)	-0.3	0.2	428	+1.9	>0.7
368.3(β)	-0.3	0.5	429	+4.3	>0.7
370	-0.8	0.5	430	+8.2	>0.7
374.16	-3.6	0.5	431	+9.6	>0.7
374.16	+0.1	0.3	432	-10.4	>0.7
380	+0.3	0.3	434	-2.7	>0.7
388.34(β)	+0.6	0.3			

*The "est'd error" in this case is 2 times the observed estimated standard deviation. The systematic error is believed to be 0.1%.

Values enclosed in parentheses are extrapolated.

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APPENDIX

ALUMINUM CALORIMETER DEVELOPMENT

The slowness of equilibration in sulfur at the triple point and in the liquid as observed in the present study contrasted sharply with the observations of West (3), who found much more rapid equilibration at the triple point and noted equilibration in the liquid within a few hours at most. Alumina is reportedly a catalyst for the equilibration of sulfur vapor, and West's calorimeter was made from aluminum, which after exposure to air develops a thin oxide coat (20).

It was conjectured that the presence of the aluminum oxide coating on the aluminum metal of West's calorimeter was responsible for the rapid equilibration of liquid sulfur which he observed, and thus that more accurate measurements on liquid sulfur could be made in an aluminum calorimeter than in a platinum calorimeter. The oxide coating on aluminum also renders it inert to attack by many otherwise corrosive substances, including materials for which heat capacity data might later be desired. Aluminum has a higher heat conductivity than platinum; thus the temperature distribution on its surface should come to a steady state more rapidly than on a platinum

surface. With aluminum, the time during which unknown surface heat distributions (dependent upon the sample) exist on the calorimeter would be decreased, allowing a more accurate measurement. Finally, it was desired to avoid additional experimental difficulties, possibilities for contamination of the sample, and possibilities for slow equilibration after freezing from the molten state. These occur when materials for which solid state data are required must be melted for calorimeters designed to accept liquids only.

For these reasons a design and construction effort (in which the author was an active participant) was initiated to create a calorimeter similar to the platinum calorimeter, but made entirely of aluminum and suitable for loading with solid samples. The calorimeter which was constructed is shown in Figure 8.

The calorimeter body is made from a block of aluminum and is provided with a center hole in the bottom to accommodate the thermometer-heater. The outer shell forms a permanent part of the calorimeter body, but the bottom plate is removable for access to the thermometer-heater. The bottom plate is held in place by screws and is provided with leads wrapped around a cylinder, as in the platinum calorimeter.

The provision of heat distributing disks (as in the platinum calorimeter) would have been impracticable, not only because of the mechanical difficulties of providing

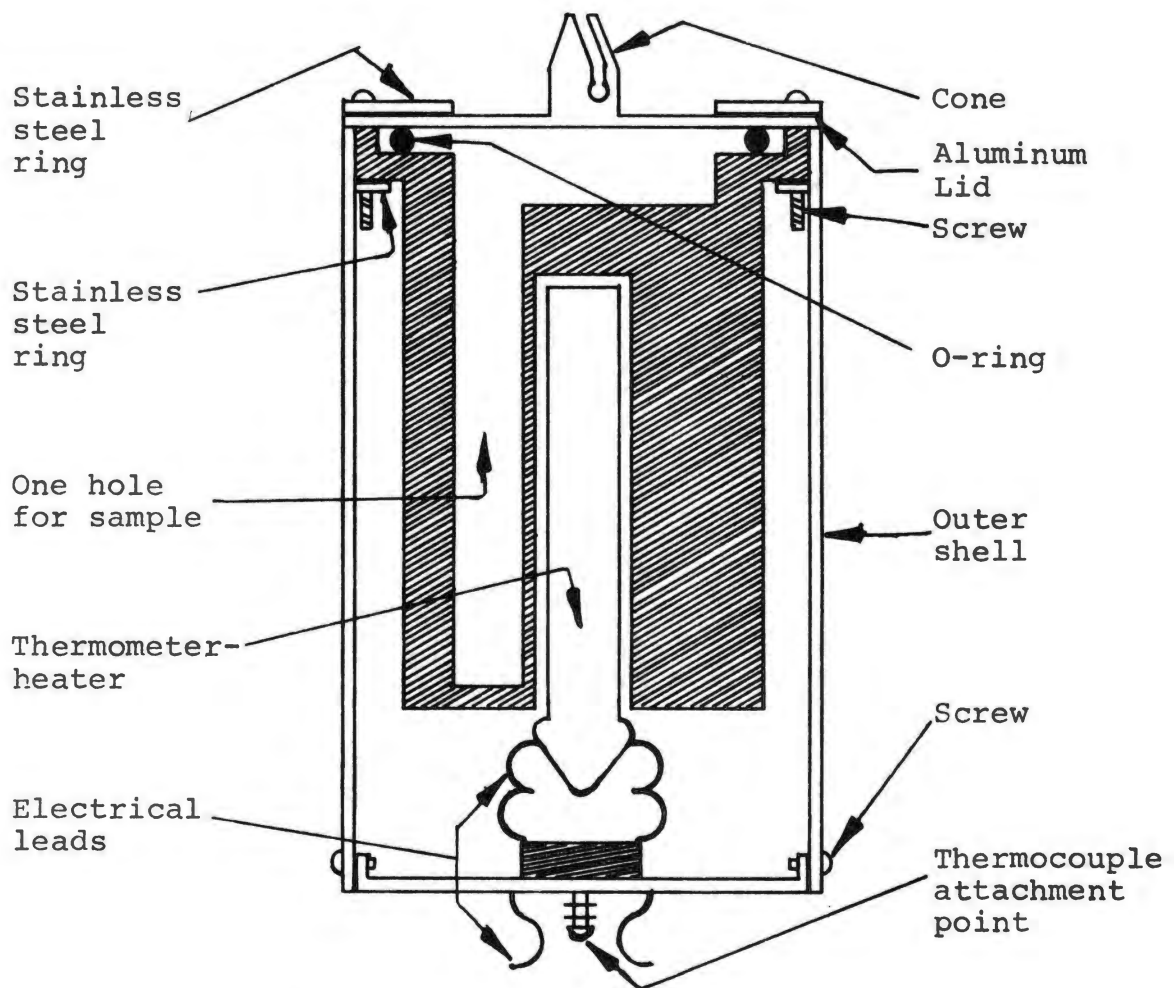


Figure 8. Aluminum Calorimeter

them, but because of the difficulty of filling a calorimeter containing them. It would not have been feasible to pack the calorimeter full of a solid sample, so the particles would not have been pressed into good thermal contact with each other and with the calorimeter. Additionally, the smaller sample would have had a lower heat capacity and required a smaller amount of energy to heat it. The smaller amount cannot be measured as accurately on a percentage basis as a larger amount, so the accuracy of measurement would have been impaired.

A method of maintaining the sample in good thermal contact with the calorimeter was essential in order to minimize the time during which the sample influences the heat distribution and the total time of measurement. The method chosen was to drill several vertical holes into the calorimeter body from above to accommodate the sample. No part of the sample is more than one-half the hole diameter from the metal of the calorimeter. The size and number of holes is determined by compromise between ease of filling and distance from the center of each part of the sample to the calorimeter metal.

The most difficult problem was the selection of a suitable method for sealing the calorimeter. The lid of the calorimeter needed to be made of aluminum, to be removable and resealable, and to withstand the mechanical stresses upon it without significant deformation. These requirements led to the choice of a bolted-on lid with a

gasket. Problems due to the relatively low mechanical strength of aluminum were solved by using a stainless steel ring with threaded holes below the outer flange of the calorimeter, and a wider stainless steel ring above it to distribute the forces from the screw heads and maintain force on the gasket. The lower ring allowed the screws to be tightened much more than if the aluminum itself had been threaded.

The choice of a gasket material was also difficult. It had to be chemically and thermally resistant up to 434°K and capable of maintaining a tight seal against the aluminum from 12°K to 434°K under pressures of about one atmosphere in either direction. Rubber gaskets do not have the necessary thermal and chemical resistance. Polytetrafluoroethylene (PTFE) does, but tests with PTFE were not satisfactory. The PTFE was tried in grooves in the calorimeter body and with grooves in the calorimeter body and matching raised areas on the calorimeter lid. No arrangement was found which would adequately confine the PTFE when sufficient pressure was applied to guarantee a tight seal under all conditions. The PTFE would always permanently deform and flow out through the slightest gap upon being subjected to an increase in pressure.

Gold was finally selected as the most promising gasket material. It was melted and cast in a round O-ring shape. Initial tests with the gold gasket at room temperature with one atmosphere inside and a vacuum outside showed that a

leak-tight seal was being maintained, even after flexing by applying and removing the vacuum. The calorimeter design and construction was essentially complete, subject to future testing for maintenance of a tight seal under repeated temperature and pressure cycling, and for overall accuracy in actual heat capacity measurement.

2
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