THE SPECIFIC HEAT OF MANGANOUS SELENIDE

by

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TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>Apparatus and Material</td>
<td>2</td>
</tr>
<tr>
<td>Experimental Procedure</td>
<td>5</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>6</td>
</tr>
<tr>
<td>Conclusion</td>
<td>15</td>
</tr>
</tbody>
</table>
INTRODUCTION

The object of this investigation is to check the results of Kelley\(^1\), who has previously measured the specific heat of manganous selenide over the range of temperatures from that of liquid air to room temperature. The reason for checking these results is as follows. Squire\(^2\), Bizette and Tsai\(^3\), and Lindsay\(^4\) have made measurements of the magnetic susceptibility of manganous selenide versus temperature. Upon warming the manganous selenide after it had been cooled to liquid air temperature, Bizette and Tsai\(^3\) obtained a large temperature hysteresis effect. The curve of susceptibility versus temperature which they obtained when warming the sample exhibited a broad, low hump centering around 140\(^\circ\)K and a marked rise beginning about 250\(^\circ\)K. They correlated these portions of the curve with humps at 116\(^\circ\)K and 247\(^\circ\)K obtained in the specific heat versus temperature curve by Kelley\(^1\). The rise in the susceptibility at 250\(^\circ\)K corresponds rather closely with the hump in the specific heat curve at 247\(^\circ\)K, but the low plateau in the susceptibility curve around 140\(^\circ\)K does not agree so well with the hump in the specific heat curve at 116\(^\circ\)K.

Lindsay\(^4\) also obtained hysteresis effects when warming his specimen after having cooled it to liquid air temperature, but not so pronounced as that obtained by Bizette and Tsai\(^3\). Nor did he obtain a curve exhibiting the characteristics of that obtained by Bizette and Tsai\(^3\). He is at the present time attempting to check the results of Bizette and Tsai\(^3\). His investigation along with this one should, if both are successful, provide a check of both the specific heat and susceptibility measurements and determine which, if either, is in error.
It was originally intended that measurements of the specific heat be made from liquid air temperature to room temperature, but because of difficulties which will be given later this was not possible. Measurements were made only from 86.9°K to 120.8°K.

**APPARATUS AND MATERIAL**

The designs given by Gibson and Giauque and Millar were used in the construction of the apparatus. A diagram of the apparatus is given in Figure 1. The vacuum jacket A was made of brass tubing, 7 inches in length, of 2 3/4 inch outside diameter and 1/8 inch wall thickness. The top and bottom were brass plates 3/8 inch thick. The bottom plate was silver soldered on to the tubing; the top plate soldered with Wood's metal. Three screws spaced 120° apart around the top plate provided mechanical strength so that the Wood's metal joint would not have to support the weight of the vacuum jacket. The jacket was evacuated through a 7/16 inch stainless steel tube B which was hard soldered onto the top plate. The other end of this tube was waxed into the glass vacuum system and the whole apparatus was fastened rigidly by clamping around this tube.

From the top of the vacuum jacket was suspended by stout nylon threads a massive copper cylinder C which served as a thermal guard ring for the calorimeter. It was because of this guard ring that a Wood's metal joint was used at the top plate, for not even soft solder could have been used without getting the metal hot enough to burn the threads. The guard ring was turned down on a lathe to 2 inches outside diameter from a solid piece of copper 5 1/2 inches in length. A 1 1/4 inch hole was drilled into the solid rod to a depth of 5 inches. The top of the guard ring,
a copper plate of 3/4 inch thickness and 1 1/4 inch diameter, merely sat on the guard ring. Around the outside of the guard ring was wound a coil of no. 36 cotton and enamel insulated copper wire which served as both a resistance thermometer and a heater. The resistance of the coil at room temperature was about 120 ohms.

Hanging in turn from the top of the guard ring by finer nylon threads was the calorimeter D. It was made from 7/8 inch copper tubing 4 inches in length the wall of which was turned down to about .02 inch thickness in a lathe. The top and bottom of the calorimeter, of 1/32 inch copper sheet, were soft soldered onto the tubing. It was thought desirable to solder the top on before the manganese selenide was put in the calorimeter since it was feared that the heat might oxidize some of the substance. To this end a 1/8 inch hole was drilled in the top which was then soldered on. After the MnSe was introduced a 1/8 inch copper tube was soldered in the hole with Wood's metal. The calorimeter was then evacuated and filled with helium to a pressure of about 1 mm. of mercury whereupon the 1/8 inch tube was pinched off leaving the helium inside to aid in the distribution of heat. An even more rapid distribution of heat was obtained by the use of eight radial vanes of .004 inch copper foil inside the calorimeter.

Around the calorimeter, as around the guard ring, was wound a copper coil which was used both as thermometer and heater, but in this case no. 38 enamel coated wire was used. This type wire was used at first on the guard ring but after its having been twice completely rewound and in part several more times because of shorts and breaks which developed, the enamel coated wire was abandoned in favor of the cloth covered wire.
The wires from the coils were taken out of the vacuum jacket through Kovar seals which were soldered into the top of the jacket and in which the coil wires were soldered to the connecting wires. Lead storage cells were used as a source of current. When the coils were being used as thermometers they were put in series with 20,000 ohms. Hence the current remained fairly constant even though the resistance of the coils changed quite appreciably. The thermometer current was about 0.0003 amperes while the heating current was about 0.1 amperes for the calorimeter and up to about 0.75 amperes for the guard ring.

Electrical measurements were made on a Leeds and Northrup Type K potentiometer. These consisted of reading the potential drops across each of the coils and across a standard resistance in series with them. For measuring potential drops with the heater current a volt box had to be used, and since the total current was measured, a correction was made for the power lost in the parallel volt box resistance.

To cut down on the interchange of heat between the calorimeter and its surroundings, poorly radiating surfaces were needed. Consequently, all surfaces of the calorimeter, guard ring, and the inside of the outer jacket were polished. Also, highly polished aluminum foil was placed around the cloth covered coil on the guard ring.

The manganous selenide was prepared according to the method given by Kelley. It was made from selenium obtained from Johnson, Matthey and Company guaranteed to be 99.99% pure, and from manganese obtained from the Rice Institute Chemistry Department estimated to be 99.95% pure. An intimate mixture of the two which had been ground very thoroughly to a fine powder was introduced into a quartz tube about two feet long and one inch in diameter, sealed at one end. About 1/3 of its length from the
open end was a constriction. The open end was sealed onto the vacuum system and the tube was evacuated to a pressure of about $3 \times 10^{-5}$ mm. of Hg. The reaction was induced by heating the quartz tube with a Bunsen burner. To insure a complete reaction the quartz tube was sealed off from the vacuum system and placed inside an oven where it was heated for a period of about 24 hours during which the temperature was varied from 300°C to about 500°C.

An excess of selenium was used in the reaction and after the reaction was completed the excess was distilled into the portion beyond the constriction. The quartz tube was then broken open and the manganous selenide removed and ground into a coarse powder containing particles of perhaps 1 mm. in diameter or less.

**EXPERIMENTAL PROCEDURE**

To begin a series of measurements, the guard ring and calorimeter were first cooled to liquid air temperature. This was done by surrounding the vacuum jacket by a Dewar flask containing enough liquid air to completely cover the jacket. The system was then evacuated. Heating current was then passed through the guard ring heater until its temperature was somewhat above that of the calorimeter. The resistance of the calorimeter coil was measured and immediately after closing the switch sending heating current through the calorimeter coil the current was measured. The current was allowed to flow for a period of time (measured to the nearest tenth of a second on a stop watch) which would bring the temperature of the calorimeter somewhat above that of the guard ring. Just before the switch was opened the current was measured again and immediately after it was opened
the resistance of the calorimeter coil was measured. These measurements gave the average current and average resistance during the heating interval so that the energy input could be calculated.

Immediately after heating the calorimeter, the cooling rates of both the calorimeter and guard ring were measured for a period of about 10 to 15 minutes. Newton's law of cooling could then be used in calculating the heat interchange of the calorimeter with the surroundings during the time it was being heated. This procedure sufficed for a determination of the specific heat at one temperature. The procedure was repeated for the various temperatures.

RESULTS AND DISCUSSION

The results are tabulated in Table 1. A sample set of original data is given in Table 2 and a sample set of calculations in Table 3. A graph of the specific heat versus temperature together with a graph of Kelley's\textsuperscript{1} values is given in Figure 2. Curve A is a plot of Kelley's\textsuperscript{1} results and curve B a plot of the results of this experiment. The crosses represent Kelley's\textsuperscript{1} data, the dots the data of this experiment. The specific heat is plotted in units of calories per gram molecular weight per degree centigrade while the temperature is plotted in degrees Kelvin.

It will be noted that the points of curve B, although not differing by large amounts from those of curve A in magnitude, are somewhat scattered. This scattering is probably due to any or all of the following sources of error.

First, it was not possible to obtain as good a vacuum as desired. The difficulty lay in obtaining a joint at the top of the vacuum jacket which
<table>
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<tr>
<th>$T$, °K</th>
<th>$C_p$, Cal. per gm. molecular weight per degree</th>
</tr>
</thead>
<tbody>
<tr>
<td>86.9</td>
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<tr>
<td>90.3</td>
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<tr>
<td>93.7</td>
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<td>116.0</td>
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</tr>
<tr>
<td>120.8</td>
<td>10.69</td>
</tr>
<tr>
<td>304.2</td>
<td>14.22</td>
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### TABLE 2

SAMPLE SET OF ORIGINAL DATA

- **g** refers to guard ring cell
- **c** refers to calorimeter coil
- **s** refers to standard resistor

For Temperature Measurements

Before

\[ V_g = .005723 \text{ volts} \]

Heating **g**

\[ V_s = .030531 \text{ Volts (in series with g)} \]

After Heating **g**

\[ V_g = .059993 \text{ volts} \]

\[ V_s = .030428 \text{ volts (in series with g)} \]

Initial

\[ V_s = .030475 \text{ volts (in series with c)} \]

Heating current started in calorimeter

Initial \( V_s = 10.6526 \text{ volts} \)

Final \( V_s = 10.5158 \text{ volts} \)

Heating current stopped

Final \( V_o = .005276 \text{ volts} \)

\[ V_s = .030446 \text{ volts (in series with c)} \]

Time of heating interval = 10 minutes, 27.1 seconds

#### COOLING RATE

<table>
<thead>
<tr>
<th>Time</th>
<th>( V_g )</th>
<th>( V_o )</th>
<th>( V_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 min.</td>
<td>.005266</td>
<td>.030450</td>
<td></td>
</tr>
<tr>
<td>2 min. 10 sec.</td>
<td>.005930</td>
<td>.030454</td>
<td></td>
</tr>
<tr>
<td>3 min.</td>
<td>.005263</td>
<td>.030458</td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>$V_G$</td>
<td>$V_C$</td>
<td>$V_S$</td>
</tr>
<tr>
<td>--------------</td>
<td>----------</td>
<td>----------</td>
<td>----------</td>
</tr>
<tr>
<td>4 min., 20 sec.</td>
<td>0.005927</td>
<td></td>
<td>0.030461</td>
</tr>
<tr>
<td>5 min.</td>
<td></td>
<td>0.005261</td>
<td>0.030465</td>
</tr>
<tr>
<td>5 min., 40 sec.</td>
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<td></td>
<td>0.030469</td>
</tr>
<tr>
<td>7 min.</td>
<td></td>
<td>0.005259</td>
<td>0.030472</td>
</tr>
<tr>
<td>8 min.</td>
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<td></td>
<td>0.030476</td>
</tr>
<tr>
<td>9 min.</td>
<td></td>
<td>0.005255</td>
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</tr>
<tr>
<td>12 min.</td>
<td></td>
<td>0.005251</td>
<td>0.030484</td>
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TABLE 3

SAMPLE SET OF CALCULATIONS

g refers to guard ring coil

c refers to calorimeter coil

s refers to standard resistor

Initial $R_0 = \frac{\text{Initial } V_c \times R_3}{V_g}$

= $\frac{0.004896}{0.030475} \times 99.975 = 16.04$ ohms

Initial heating $I = \frac{V_g}{R_g} = \frac{10.6526}{99.975} = .10655$ amps

Final heating $I = \frac{10.5158}{99.975} = .10518$ amps

Final $R_0 = \frac{0.005276}{0.030446} \times 99.975 = 17.33$ ohms

Average $I = .10587$ amps

Average $R_0 = 16.68$ ohms

$I^2R$ in $R_0 = .1870$ watts

$I^2R$ in volt box resistor = $I^2R_0 \times \frac{R_0}{K}$

= $.1870 \times \frac{16.68}{20,000} = .0002$ watts

difference = .1868 watts

time of heating interval = 627.1 sec.

energy input = .1868 watts \times 627.1 sec. \times \frac{1 \text{ cal.}}{4,186.8} \text{ joules}

= 27.99 calories

Final $R_0 = 17.33$

Initial $R_0 = 16.04$
\[ \Delta R = 1.29 \text{ ohms} \]
\[ \Delta T_1 = \Delta R \left( \frac{\Delta T}{R} \right) = 1.29 \times 2.65 \]
\[ \Delta T_1 = 3.29 \text{ deg.} \]

At beginning of cooling period \( T_c = 91.8^\circ K \) from final \( R_e = 17.33 \text{ ohms} \)

Cooling Rate

1 min. \[ R_c = \frac{0.005266}{0.030450} \times 99.975 = 17.29 \text{ ohms} \]

2 min., 10 sec. \[ R_g = \frac{0.005930}{0.030454} \times 99.975 = 19.47 \text{ ohms} \]

3 min. \[ R_c = 17.28 \text{ ohms} \]

4 min., 20 sec. \[ R_g = 19.45 \text{ ohms} \]

5 min. \[ R_c = 17.27 \text{ ohms} \]

5 min., 40 sec. \[ R_g = 19.45 \text{ ohms} \]

7 min. \[ R_c = 17.25 \text{ ohms} \]

8 min. \[ R_g = 19.44 \text{ ohms} \]

9 min. \[ R_c = 17.24 \text{ ohms} \]

12 min. \[ R_c = 17.22 \text{ ohms} \]

At beginning of heating interval

\[ R_g = 16.04 \text{ ohms} \]

\[ R_g = 19.67 \text{ ohms} \]

\[ T_g = 90.2^\circ K \]

\[ T_c = 88.5^\circ K \]

\[ T_c - T_g = -1.7^\circ K \]
At end of heating interval

\[ T_c = 91.6^0K \]
\[ T_g = 89.7^0K \]
\[ T_c - T_g = 1.9^0K \]

Average \( T_c - T_g = \frac{2.1 - 1.7}{2} = .2^0K \)

During cooling interval

\[ T_c - T_g = 91.6^0K - 89.6^0K = 2^0K \]
\[ \Delta R_0 = 17.33 - 17.22 = .11 \text{ ohms} \]
\[ .11 \text{ ohms} \times 2.56 \frac{\text{deg}}{\text{ohm}} = .27 \text{ deg.} \]

\( \Delta T_2 = \text{correction for heat interchange during heating interval} \)

\[ \frac{.27 \text{ deg.}}{20^0K \times 12 \text{ min.}} = \frac{\Delta T_2}{20^0K \times 10.5 \text{ min.}} \]

\[ \Delta T_2 = .027 \times \frac{10.5}{12} = .023 \text{ deg.} \]
\[ \Delta T_1 = 3.29 \text{ deg.} \]
\[ \Delta T_2 = .02 \text{ deg.} \]
\[ \Delta T = 3.31 \text{ deg.} \]

Average \( T \) from average \( R_0 = 90.3^0K \)

Heat capacity of \( \text{MnSe} \) + calorimeter = \( \frac{\text{energy input}}{\Delta T} = \frac{27.99}{3.31} = 8.45 \frac{\text{Cal}}{\text{Deg}} \)

Heat capacity of empty calorimeter at 90.3^0K = 2.30 \frac{\text{Cal}}{\text{Deg}}

Heat capacity of \( \text{MnSe} = 6.15 \frac{\text{Cal}}{\text{Deg}} \)

Weight of \( \text{MnSe} = 85.507 \text{ gm.} \)

Sp. Heat = \( C_p \) of \( \text{MnSe} = \frac{6.15}{85.507} = .0725 \frac{\text{Cal}}{\text{gm. deg.}} \)

Molecular weight of \( \text{MnSe} = 133.89 \text{ gm.} \)

\[ C_p = .0725 \times 133.89 = 9.708 \frac{\text{Cal}}{\text{gm. mol. deg.}} \text{ at } 90.3^0K \]
would stay vacuum tight at liquid air temperature. An "O ring" rubber gasket was used at first but although a good vacuum was obtained at room temperature, when the vacuum jacket was immersed in liquid air a leak developed. At first it was thought that the leak may have developed in the wax joint between the stainless steel tube and the glass system. It was only about four inches from the top of the vacuum jacket and thus became quite cold. An extension was soldered onto the stainless steel tube and the wax joint moved some distance away so that it did not get cold at all. However the leak was still present.

After several more attempts to obtain a vacuum, the "O ring" was abandoned in favor of a soldered joint. As has been pointed out before, the fact that the guard ring was suspended from the top of the vacuum jacket by nylon thread prevented, because of the necessary heating, the use of ordinary solder. Wood's metal was the only possibility. Many attempts were made to obtain a satisfactory joint but the same difficulty still prevailed - a joint would be made which was vacuum tight at room temperature but which would not remain so at liquid air temperature.

The vacuum jacket was revised so that the top would fit completely down into the jacket as shown in Figure 1, which arrangement was thought perhaps to be more suitable than the previous one for soldering with Wood's metal. Finally, after several more attempts, a joint was made with which a pressure of $10^{-4}$ mm. of mercury, as indicated by an ionization gage, was obtained. A pressure as low as $10^{-5}$ mm. of mercury, however, is desirable to reduce the interchange of heat between the calorimeter and its surroundings and thus reduce the correction involving Newton's law of cooling. This law states that the rate of loss of heat of a body is proportional to the difference in temperature between the
body and its surroundings. The lack of a good vacuum becomes a source of error, because then the corrections are larger and, since they involve approximations, larger errors result in the final values obtained for the specific heat.

A second source of error was the fact that the resistance thermometers were not accurately calibrated. It was intended that this should be done after the measurements had been made, but lack of time prevented the accomplishing of this calibration. However, a rough calibration was made as follows. The resistances of the two coils were measured at room temperature from which the resistances were calculated at 0°C using tabulated values of the temperature coefficient of resistance of copper. Then, using the results of Cames and Tyna\(^7\) giving the fraction of its resistance at 0°C of a copper wire at different temperatures below 0°C, a calibration curve was made. This curve was used to obtain temperatures from the measured values of resistance.

In the third place a correction had to be made for the heat capacity of the empty calorimeter. This correction involved making measurements on the empty calorimeter. However, because of lack of time, this heat capacity was calculated as follows. Using the data of Rodebush and Rodebush\(^8\) for the specific heat of copper at low temperatures and knowing the mass of the calorimeter, a graph of the heat capacity of the calorimeter versus temperature was made which was used in making the corrections. There were probably errors in these corrections due to differences between the copper used and that of Rodebush and Rodebush\(^8\). Moreover, since it had not been planned to use this method of making this correction the calorimeter was not weighed again after the 1/8 inch copper tube had been soldered into the hole and then pinched off. Thus
The mass of the calorimeter was not known very accurately. The last two sources of error are not serious from the standpoint of getting relative values of the specific heat at different temperatures - one of the main objects of this experiment. The mean absolute value of the specific heat of the MnSe agrees remarkably well with Kelley's value in spite of the last two sources of error mentioned above.

A measurement at room temperature was also made and is included in Table 1. In this case a pressure of $10^{-5}$ atm. of mercury was obtained.

CONCLUSION

Because of the scattered nature of the points representing the results of this investigation, no positive conclusion can be drawn. However, it will be noted that in the vicinity of Kelley's 116° hump the points are much less scattered than in other places and, in fact, lie nearly on a smooth curve. They seem to indicate, if anything, the absence of a hump in this region. Hence the results of this experiment do not appear to indicate a specific heat anomaly at 116°K.
ACKNOWLEDGMENTS

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BIBLIOGRAPHY

Circuit Diagram

Figure 3