Determinations of the Fractional Volume Changes on Fusion of Antimony Telluride and Lead Telluride

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The fractional volume increases associated with the melting of antimony telluride and lead telluride were observed to be 0.064 ± 0.001 and 0.045 ± 0.002, respectively.

EFFECTS OF pressure on the melting points of antimony telluride (Sb_2Te_3) and lead telluride (PbTe) were determined in this laboratory (2). For comparison, it was desirable to calculate the limiting slopes of the fusion curves as provided by the Clapeyron-Clausius equation. Consequently, it was necessary to measure the fractional volume changes associated with the fusion of these compounds (at effective zero pressure).

EXPERIMENTAL

The technique used in this investigation was described in detail in a previous publication (*1*). However, it is worthwhile to outline the essential features of the procedure, which is a refinement of the method of fed and unfed castings (*5*).

Pairs of tubular graphite crucibles are immersed in a melt of the substance of interest, which is contained in an evacuated glass capsule. The crucibles are stacked with the open ends opposite. The melt is slowly solidified in the direction parallel to the axes of the crucibles. Consequently, a shrinkage void naturally occurs with the contents of one crucible but not with the other. The unfed ingot is provided in the former case and the fed ingot in the latter.

Ideally, a comparison of the weights of the recovered ingots permits a calculation of the fractional volume change appropriate to fusion, $(V_l - V_s)/V_s = (W_f - W_u)/W_u$. The symbols, V_l and V_s, represent the molar volumes of the liquid and solid, respectively, at the equilibrium melting temperature; the symbols W_f and W_u represent the weights of the fed and unfed ingots, respectively.

The above relation requires that the capacities of the crucibles be equal, although the observed weights of the ingots may be corrected accordingly, if necessary. The data to be presented below were obtained with crucibles of the same effective capacities; the various ingot weights are directly comparable.

No corrections were imposed to compensate for the temperature gradient (about 20° C. per inch) along the crucibles during solidification. The necessary data for the coefficients of thermal expansion of solid and melt are not available. However, as discussed in the previous report for tellurium and bismuth telluride (*1*), the corrections for this deviation from the idealized basis for the calculations are expected to be no more than about 2% of the tabulated results. In all instances, the ingots were about 0.75 inch long.

The compounds investigated were synthesized by the reaction of stoichiometric amounts of the elements (99.99 wt. % purity) within evacuated fused quartz capsules.

RESULTS

Table I summarizes the data obtained for antimony telluride. The densities of the ingots were determined at room temperature by the Archimedean method; the results for the fed and unfed ingots are labeled d_f and d_u, respectively. For comparison, the density of this compound was observed elsewhere to be 6.488 grams per cc. (*4*). Thus, the soundness of the ingots is indicated. For the fed ingots, this is a necessary condition for the validity of the calculations. Table II summarizes the data obtained for lead telluride. The densities observed may be compared with a reported value of 8.25 grams per cc. (*3*).

Preliminary measurements with this system revealed evidence of pronounced subcooling of the melt. Visible internal voids were contained in the fed ingots. Four determinations yielded mean values of 5.678 grams for W_f and 8.17 grams per cc. for d_f. The unfed ingots would be expected to be somewhat too heavy as a result of subcooling; they would then be the result of the rapid solidification of a melt of higher density than that appropriate to the equilibrium solidification temperature. Accordingly, this was observed. Four determinations yielded mean values of 5.564 grams for W_u and 8.21 grams per cc. for d_u.

Table I. Antimony Telluride Determination

	W_f, Grams	d_f, Grams/Cc.	W_u, Grams	d_u, Grams/Cc.
	4.623	6.48	4.336	6.49
	4.625	6.49	4.359	6.50
	4.629	6.48	4.348	6.50
	4.630	6.48	4.353	6.49
Mean	4.627		4.349	

$(V_l - V_s)/V_s$, mean ± standard deviation: 0.064 ± 0.001

Table II. Lead Telluride Determination

	W_f, Grams	d_f, Grams/Cc.	W_u, Grams	d_u, Grams/Cc.
	5.756	8.24	5.498	8.25
	5.704	8.23	5.474	8.25
	5.713	8.24	5.475	8.23
	5.717	8.23	5.468	8.25
	5.730	8.24		
	5.734	8.24		
Mean	5.724		5.479	

$(V_l - V_s)/V_s$, mean ± standard deviation: 0.045 ± 0.002

The data in Table II were obtained after the procedure was altered to provide for the seeding of the melt and a slow, orderly solidification of the crucible contents. The details of the necessary modifications are contained in the earlier description (*1*) of experiments with the element tellurium, where a similar problem was encountered.

The data obtained clearly indicate that the melting points of Sb_2Te_3 and PbTe must initially increase as the pressure rises above one atmosphere. In contrast, above 15,000 atmospheres the melting points of both these compounds were observed (*2*) to decrease with increasing pressure. Thus, in each case, a maximum melting point must be encountered at some intermediate pressure. A direct measurement of these values was not possible since the high pressure equipment used (a tetrahedral anvil apparatus) does not provide sustained, reliable pressure below about 15,000 atmospheres.

LITERATURE CITED

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Received for review June 8, 1964. Accepted September 8, 1964.

Heat Capacity of β-Manganese

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The molar heat capacity of β-Mn has been measured from 14° to 300° K. in an adiabatic calorimeter. Both measured and smooth values of the data are presented.

THE ELEMENT MANGANESE has in recent years been a subject of considerable interest. In 1958, Weiss and Tauer published a paper (*6*) on the thermodynamics and magnetic structure of the allotropic modifications of this element. Additional thermal data on some of the allotropic forms were needed. More recently Arrott, Zimmerman, and coworkers have been engaged in a comprehensive study of the thermodynamics of α-, β-, and γ-manganese (*2*). As a contribution to this effort, the authors have undertaken to measure the specific heat of β-Mn between 14° and 300° K.

Previous thermal measurements on β-Mn have been made at low temperatures by Booth, Hoare, and Murphy (*3*) (12° to 20° K.) and Zimmerman (*2*) (1.6° to 19° K.). Heat capacity measurements were also made in the high temperature region (1000° to 1050° K.) by Armstrong and Grayson-Smith (*1*).

EXPERIMENTAL

The adiabatic calorimeter used in the investigation has been described (*4*). The sample container employed is one which had been used in heat capacity measurements on Cd and Mg. It consisted of a thin-walled copper can into which the sample could be sealed with a few cm. of He gas to promote heat exchange. It was designed to receive a sample machined to cylindrical form with a tapered hole along the axis. The tapered hole was intended to fit over a tapered pin, an integral part of the sample container, which contained the heater and Pt resistance thermometer so that good thermal contact could be established. The β-Mn sample, however, was in the form of small chunks and not readily adaptable to the customary method of loading. The β-Mn (262.401 grams) was simply sealed into the sample container, and reliance was placed upon the He exchange gas to maintain thermal equilibrium. The atomic weight of manganese was taken as 54.94 grams per mole.

The starting material was electrolytic α-Mn which was arc melted under argon and quenched to convert it to the β-allotrope. The principle impurities, shown by spectrographic analysis, and their approximate concentrations in per cent were Fe(0.2), Ni(0.04), Pb(0.05), and Si(0.05). X-ray diffraction patterns, obtained both before and after the heat capacity measurements, showed no α-Mn lines. The x-ray patterns did show evidence for the presence of MnO, however, and it was estimated that this substance might be present in the sample to the extent of about 2 mole % (*7*).

RESULTS AND DISCUSSION

The raw data are shown in Table I. As an index of the precision, the averages of the absolute values of the percentage deviations of the measured points from the smooth curve have been computed. Between 13° and 40° K. the average deviation is about 2.5%, between 40° and 100° K. the average deviation is about 0.3%, between 100° and 273° K. it is less than 0.1%, while between 273° and 300° K. the average deviation is about 0.2%. The precision obtained in these measurements is not as good as has been obtained in measurements on other metals in the calorimeter. The fact that the sample was in the form of pellets rather than a single solid piece may account for the difference in behavior.

A large scale plot of the raw data shows a slight deviation in the curve of C_p *vs.* T at about 125° K. The magnitude of the deviation is such that a smooth curve interpolated