Percentage Volume Changes on Fusion of Bismuth Telluride and Tellurium

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A revised technique for calculating the percentage increase in volume on fusion was developed from the method of fed and unfed castings. Applications of the revised technique to bismuth telluride and tellurium provided values of 4.3 ± 0.2% and 5.4 ± 0.2%, respectively.

EXPERIMENTAL DETERMINATION of the effect of pressure on the melting points of bismuth telluride, Bi_2Te_3, (*1*) and tellurium (*2*) were recently completed in this laboratory. It was desired to compare the data obtained with the limiting dependences, at 1 atm., of the melting points on pressure as provided by the Clapeyron-Clausius equation—i.e., the ratio of the volume change on fusion to the corresponding entropy change. To make the desired calculation, it was necessary to determine the volume change on fusion of bismuth telluride. Tellurium is reported (*5*) to expand in volume by approximately 2% upon melting, but further measurements on this substance were considered to be worthwhile.

To obtain the desired data, a technique was developed which is a refinement of the method of fed and unfed castings (*11*). This method, in its original form, was applied to the determination of the solidification shrinkage of cast iron (*10*). Molten metal was poured into two molds of approximately the same capacities. However, one mold was provided with a riser from which extra melt was obtained to compensate for solidification shrinkage. The second mold was capped immediately after filling with liquid; shrinkage voids occurred upon the solidification of the contents. Ideally, the solidification shrinkage can be calculated from the weights of the two ingots obtained. Despite subsequent modifications (*9*), this technique never provided as accurate data as other methods did. In particular, the molds were filled with melt well above the solidification temperature, and the solidification process took place too rapidly to avoid the inclusion of a significant amount of internal shrinkage voids in the fed ingot.

Further refinements have now been developed which provide for the remote casting of the melt at a controlled and known temperature close to the melting point and for the slow, directional freezing of the melt. This modified procedure is regarded as accurate as other available methods, which in some instances are less convenient.

EXPERIMENTAL

Method. In brief, the revised method, as applied to substances that expand in volume on fusion, includes the following procedures. A solid charge of the desired material is sealed in an evacuated glass capsule together with at least one set of two crucibles of the design shown in Figure. 1. The two crucibles are firmly positioned at the bottom of the capsule, whose internal diameter is only slightly larger than the outside diameter of the crucibles. The lowermost crucible is inverted; the open end is directed toward the bottom of the capsule. The uppermost crucible is upright; the open end is directed toward the top of the capsule.

The capsule and its contents are hung in a vertical tube furnace. The charge melts and flows to the bottom of the capsule filling both crucibles. The charge is then directionally solidified according to the Bridgman technique for crystal growth; the capsule is lowered out of the hot central zone of the furnace at a rate of about 1 inch per hour. The entire assembly is shown diagramatically in Figure 2.

Once the bottom end of the inverted crucible is plugged with solid, the liquid contents are isolated from the bulk of the melt. Upon subsequent solidification of the contents, a shrinkage void is formed at the top. The charge in the upright crucible is continuously fed from the bulk of the melt until the entire contents are solidified; ideally, no shrinkage void can occur. Subsequently, the two ingots are removed from the crucibles and weighed.

The fractional change in volume on fusion is given by the relation

$$\frac{V_L - V_S}{V_S} = \frac{W_f - W_u}{W_u}$$

V_L and V_S are, respectively, the molar volumes of the liquid and solid at the melting point; W_f and W_u are, respectively, the weights of the fed ingot (from the upright crucible) and of the unfed ingot (from the inverted crucible). Four assumptions are necessary in the derivation of the above relation. First, the capacities of both crucibles are identical. Second, the entire liquid contents of the inverted crucible are at the equilibrium solidification temperature when they are first isolated from the bulk of the melt. Third, when the solidification of the entire contents of the upright crucible is first completed, all the material within is at the equilibrium solidification temperature.

In practice, the extent to which the four fundamental conditions are realized must be evaluated and appropriate corrections made where necessary. In this investigation, the pairs of crucibles were matched in capacity to within ±0.2% or less and the first condition was adequately fulfilled. In case of larger variations an obvious correction could be made. Slight corrections for deviations from the second and third conditions will be discussed. The soundness of the ingots is demonstrated by density measurements.

Procedures. High purity extruded graphite rod was used to manufacture the crucibles. Although the diameters and depths of the drilled holes varied somewhat for different batches of crucibles, the indicated consistency of volume was realized for the two members of a matched pair of crucibles. The capacities of the crucibles were checked either with a micrometer depth gage or by determining the weight of mercury required for filling. The latter technique was capable of a precision that was only barely sufficient, ±0.2%. The absorption of mercury by the graphite limited the precision of the volume check and necessitated a baking of the crucibles before subsequent use.

The crucibles had to be rigidly fixed in position after insertion into the 96% silica or borosilicate glass capsules by collapsing some of the glass wall into the conical holes in the sides of the crucibles. Otherwise the graphite crucibles would float in the molten charge. The flat sides of each crucible and the chamber at the closed ends were required to facilitate the flow of the molten charge to the bottom of the capsule.

After the capsule and contents were attached to a vacuum system, the crucibles were baked out for at least 1 hour at a temperature just below the melting point of the charge. The effective removal of gases absorbed by the graphite was indicated by a pressure below 10^{-5} Torr before the capsule was sealed off. The capsule was hung in the central zone of a vertical tube furnace, the temperature profile of which had been determined. The temperature along the entire length of the capsule contents was regulated at a temperature of 40° C. (or less) above the melting point of the charge. In no case was evidence encountered of the formation of gas bubbles within the contents of the crucibles. The temperature gradient in the furnace was 20° C. per inch at the position corresponding to the solidification temperature.

Materials. The bismuth telluride used was prepared by the reaction of stoichiometric amounts of the elements within evacuated 96% silica capsules; three separate preparations were employed. The elemental substances used in this study were of 99.99 wt. % purity.

RESULTS

Measurements on Tin. The over-all reliability of the technique was tested with tin. The change in volume on fusion for orthorhombic tin is reported (*6, 7*) to be +2.8%. The data obtained in the present work are presented in Table I.

The densities of the fed ingots (measured by buoyancy) were 7.30 grams per cc. in agreement with the handbook value (*7*). The densities of the unfed ingots were somewhat lower, 7.21 grams per cc., but the occurrence of internal voids in these ingots is not detrimental. The reproducibility of the method is indicated by a comparison of the ingot weights for runs 2 and 3; all four of the crucibles were from the same matched set. The crucibles used in run 1 were from a different set.

Although the agreement with the handbook value is considered adequate, it may be improved still further by the following correction. Since the chambers of the crucibles used were about 0.75 of an inch long, and because of the indicated temperature gradient within the furnace, the average temperature of the liquid contents in the inverted crucible was about 8° C. above the melting point when the entrance port was first plugged with solid. Similarly the solid contents of the upright crucibles were at an average temperature of about 8° C. below the melting point when solidification at the entrance port was completed. The fed ingots are, therefore, expected to be somewhat too heavy and the unfed ingots somewhat too light. At the melting point, the coefficients of the volume thermal expansion of solid and liquid tin are reported (*6*) to be 0.0095% per ° C. and 0.0115% per ° C., respectively. The indicated correction is −6% of the observed mean, yielding the value of 2.8% for the volume change on fusion for tin.

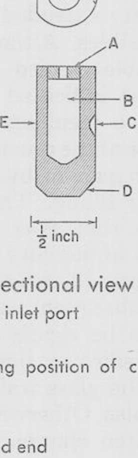

Figure 1. Sectional view of crucible

A. Press-fit cap with inlet port
B. Internal chamber
C. Recess for affixing position of crucible within glass capsule
D. Longitudinal flat
E. Chamber of closed end

In no case was a correction for the thermal expansion of the crucibles themselves considered necessary. The coefficient of thermal expansion of extruded graphite is at least an order of magnitude less than that of any substance investigated in this study (*3*).

The data obtained for tin indicate that no error resulted from the porosity of the graphite. Either no significant absorption of melt occurred or the process was completed before the solidification of the contents of the inverted crucibles began. The time during which the contents were molten varied between 3 and 6 hours for both the tin determination and those for bismuth telluride and tellurium.

Measurements on Bismuth Telluride. The results on tin demonstrated that the technique is sufficiently reliable to be applied to other substances. The data obtained for bismuth telluride are summarized in Table II. The densities of the fed ingots are designated as D_f.

The densities of the fed ingots from runs 3 and 4 deviate significantly from the average density of the other fed ingots (7.71 vs. 7.83 grams per cc.). Microscopic examination of polished ingot sections revealed sufficient internal voids to account for the discrepancy. It was considered proper, therefore, to make the indicated correction in the values of W_f for runs 3 and 4. The values for W_u are in

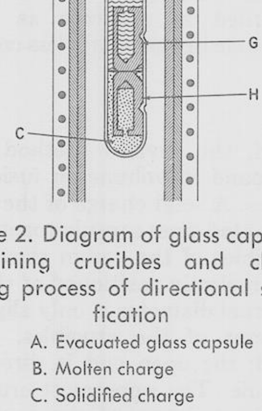

Figure 2. Diagram of glass capsule containing crucibles and charge during process of directional solidification

A. Evacuated glass capsule
B. Molten charge
C. Solidified charge
D. Support rod
E. Furnace thermocouple
F. Furnace
G. Upright crucible
H. Inverted crucible

reasonable agreement for all of the first four runs, which were conducted using crucibles of the same matched set.

Using available x-ray diffraction data (*4*), the density of bismuth telluride may be calculated to be 7.86 grams per cc. This value is somewhat larger than any of the values listed in Table II. But microscopic examination of sections of a representative ingot failed to reveal a sufficient amount of internal voids to account for the discrepancy. Adjustment of the values of W_f to conform with the calculated density would raise the volume change on fusion by 7% of the observed value. But, because of the apparent soundness of the ingots and possible error in the density measurments the correction can not be recommended.

The temperature gradient along the crucibles during the solidification process forms the basis of another correction. The coefficient of thermal volume expansion of bismuth telluride at 400° C. (taken from x-ray diffraction measurements (*4*) is 0.005% per ° C. If this value is applied to both the solid and liquid in the vicinity of the melting point, a correction of −2% of the observed value for the volume change on fusion given in Table II is indicated. However, since the correction is small and of some uncentainty (due to the extrapolation of the value for the coefficient of thermal expansion), it has not been applied.

Measurements on Tellurium. Four initial runs using the procedures outlined previously gave highly variable results for the volume change on fusion of tellurium: 1.8, 2.1, 5.1, and 5.7%. The variability may be assigned to the pronounced subcooling of the molten tellurium and subsequent rapid solidification. Internal pipes were present in some of the fed ingots resulting in low values for W_f. The reported (*5*) expansion of liquid tellurium upon subcooling below the equilibrium solidification temperature may have caused low values of W_u. Certainly no confidence can be assigned to any of the preliminary data.

It was necessary to seed the melt with solid tellurium to ensure a slow, continuous solidification process. The bottom, inverted crucibles in each run were placed on an eight-inch length of graphite rod which extended to the bottom of the glass capsule. Once the charge was melted, some of it flowed down along the rod until it solidified and subsequently seeded the melt. The bottom of the capsule was at a temperature at least 300° below the melting point of tellurium at the start of the experiment. Axial holes of 0.025-inch diameter were drilled in the bottom ends of the upright crucibles to ensure that the molten contents would be continuously seeded.

Table I. Tin Determination

Run	W_f, Grams	W_u, Grams	$(V_L - V_S)/V_S$, %
1	5.371	5.212	3.0
2	4.927	4.778	3.1
3	4.923	4.778	3.0
		Mean	3.0

Table II. Bismuth Telluride Determination

Run	W_f, Grams Obs.	W_f, Grams Corr.	D_f, Grams/Cc.	W_u, Grams	$(V_L - V_S)/V_S$, %
1	3.593		7.84	3.451	4.1
2	3.597		7.83	3.437	4.7
3	3.534	3.584	7.71	3.448	4.1
4	3.540	3.595	7.71	3.442	4.4
5	9.786		7.83	9.379	4.3
6	9.787		7.81	9.387	4.3
			Mean ± standard deviation:		4.3 ± 0.2

Table III. Tellurium Determination

Run	W_f, Grams	D_f, Grams/Cc.	W_u, Grams	D_u, Grams/Cc.	$(V_L - V_S)/V_S$, %
1	5.681	6.24	5.398	6.23	5.2
2	5.670	6.22	5.382	6.24	5.4
3	5.670	6.24	5.384	6.24	5.4
4	5.669	6.22	5.366	6.24	5.6
		Mean ± standard deviation:			5.4 ± 0.2

With the indicated modifications, consistent data were obtained, which are listed in Table III. The densities of both the fed and unfed ingots are included; all agree reasonable well with a handbook value (*8*), 6.24 grams per cc. The crucible capacities were matched to within ±0.1% for each run, but the variation between sets was somewhat greater, ±0.3%.

The thermal expansion coefficient of solid tellurium in the vicinity of the melting point is about 0.008% per ° C. (*5*). The thermal expansion of the liquid is unusually low and may be neglected. The maximum correction based on the temperature gradient along the axes of the crucibles during solidification is about −2% of the observed value.

DISCUSSION

The revised technique based on the method of fed and unfed castings appears to have provided satisfactory data on the percentage volume change characteristic of fusion. The apparent scatter in the data (about ±4%) is probably, for the most part, a reflection of the slight variation in the capacities of the crucibles. The variance could be reduced by the use of larger crucibles, which would permit a more accurate capacity determination. The correction for the temperature gradient (20° C. per inch) along the crucibles during solidification could be reduced by appropriate modifications in the furnace.

The principal advantage of the revised technique lies in the remote, slow performance of the essential processes. Reasonable estimates are possible for all corrections, which are small in magnitude. The technique shares one disadvantage with many of the other methods for the same determination. The quantities (weights) determined, the difference between which are used in the calculations, are comparable in magnitude. Rather demanding experimental accuracy is essential in the individual determinations in order to yield acceptable accuracy in the calculated quantity of interest.

The results on tellurium merit special consideration because of the large difference between the observed value, 5.4% for $(V_L - V_S)/V_S$ and the previously reported value of about 2%. The previous determination (*5*) was made by noting the change, upon fusion, of the level of a quantity of tellurium contained in a pycnometer. The resultant value of the volume change on fusion was described as uncertain and worthy of redetermination. It is possible that this lower value was the consequence of shrinkage voids within the solid.

A consideration of the procedure of this report does not reveal to the author sources of error adequate to explain the discrepancy. The measurements for tellurium are reasonably reproducible, although it was necessary to introduce modifications in the procedure to seed the melt and ensure slow, orderly solidification. The density measurements of the ingots, both fed and unfed, confirm the absence of a deleterious quantity of internal voids. The peculiarity of liquid tellurium in expanding in volume upon subcooling gives special importance to the measurements of the densities of the unfed ingots. Had subcooling occurred, followed by rapid solidification of the ingots, the density values would have been lower than the handbook value. In addition, the values of W_u would have then have been too low, and an improperly high value for the volume change on fusion would have resulted. Since the unfed ingots were sound, however, there is no reason to suspect the results.

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RECEIVED for review July 17, 1962. Accepted October 31, 1962.

Thermal Stability Studies of Pure Hydrocarbons in a High Pressure Isoteniscope

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Monsanto Research Coporation

Decomposition temperatures were determined in a high pressure isoteniscope for 80 naphthenic and 9 paraffinic saturated hydrocarbons. The effect of the number of rings, length of side chains, and number of side chains on the thermal stability was studied. The naphthenic compounds investigated were 14 cyclohexanes, 7 hydrindans, 17 decalins, 26 nonfused dicyclohexanes, and 16 nonfused polycyclic hydrocarbons. The paraffinic hydrocarbons ranged from C_{12} to C_{19}. The decomposition temperature can be estimated with a precision of ±12.5° F. as a function of the critical pressure by the equation: $T_d = C + 8.31\ P_c$, where C is a characteristic constant for each homologous series of hydrocarbons.

THERMAL stability of a number of saturated hydrocarbons was investigated in the course of this study. The stability was determined by measuring the pressure of the decomposition products in an isoteniscope (*1*, *2*, *4*, and *6*). This method gives quantitative information about the decomposition of hydrocarbons into gaseous products.

A semi-automatic isoteniscope was used in the present investigation. This high pressure isoteniscope was recently described in detail (*3*). By this instrument the vapor pressure of the sample is measured at incrasing temperatures until the sample begins to decompose. Then isothermal rates of pressure increase due to decomposition are measured, usually at three temperatures. To express the thermal stability by a single value the decomposition temperature is defined as that temperature at which the rate of decomposition is 1 mole %. The isoteniscope required only very small samples (3 ml.) and results were reproducible within ± 6° F.

The thermal decomposition temperatures of 89 paraffinic and naphthenic hydrocarbons were determined, and the results are given in Table I. The purity data given in the table are estimated values from vapor phase chromatographic data. Isomers were not separated in this investigation. The sources of the samples are given in Table I. The samples did not contain detectable quantities of peroxides. To prove this further, a number of hydrocarbons were deperoxidized with ferrous sulfate, and their decomposition temperature was determined. The results were within the experimental precision of the method.

EXPERIMENTAL

At temperatures below decomposition levels, the vapor pressure of the hydrocarbon under investigation was measured at a series of temperatures. If the pressure was constant for 15 minutes at a given temperature, the pressure was recorded, and the temperature was adjusted to the next higher value. At temperatures where decomposition occurred, the pressure increase was recorded for 20 to 60 minutes, usually at three temperature levels. Since only 1 to 2% of the material decomposed in each experiment, the rate of pressure increase was constant at a given temperature, and no correction was applied for any previous decomposition.

EVALUATION OF RESULTS

To correlate the results, the rate was assumed to be first order for the hydrocarbon—i.e.,

$$\frac{dn}{dt} = kn \qquad (1)$$

and it was assumed further that there was a 1 to 1 correspondence between moles of hydrocarbon decomposed and moles of gas produced:

$$dn = -d(n_{\text{gas}}) = -d\left(\frac{PV}{RT}\right) = -\frac{V}{RT}\,dP \qquad (2)$$