with the exception of dimerization, is identical to that proposed by Sworski[13] for the catalysis by Tl(I) of the photoreduction of Ce(IV). If one considers the difference in medium and experimental procedures, the value of k_2/k_3 of 0.021 obtained in this work is in amazingly good agreement with the values of 0.023, 0.024, and 0.026 determined by Sworski. One is tempted to conclude that this agreement argues that OH rather than NO_3 is the kinetic intermediate.

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(12) B. Krishna and B. P. Sinha, *Z. physik. Chem.*, **212**, 149, 177 (1959).

(13) T. J. Sworski, *J. Am. Chem. Soc.*, **79**, 3655 (1957); *Radiation Res.*, **4**, 483 (1956).

CONTRIBUTION FROM THE METALLURGICAL ENGINEERING DEPARTMENT, RESEARCH LABORATORIES,
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The Effect of Ultrahigh Pressure on the Melting Point of Bismuth Telluride

BY DONALD L. BALL

Received June 12, 1962

The effect of pressure up to 50 kb. on the melting point of Bi_2Te_3 has been determined. A maximum in melting point is indicated at approximately 610° and 15 kb. The Clapeyron–Clausius equation predicts that at one atmosphere the rate of increase of the melting point (585°) with increasing pressure is 3.3°/kb. However, above about 15 kb. the melting point was observed to decrease with pressure, reaching a value of about 535° at 50 kb. An effort is made to interpret this unusual dependence of melting point on pressure in terms of the structural changes in Bi_2Te_3 on fusion.

Introduction

In recent years the physical properties of bismuth telluride (Bi_2Te_3) have been investigated rather extensively. The particular interest in this substance has resulted from its relatively efficient performance capabilities in certain thermoelectric devices.

Conventional thermal analyses of the bismuth–tellurium system generally reveal only one intermediate phase,[1] the compound Bi_2Te_3, which displays only the rhombohedral, "Strukturbericht" type C33 structure.[2] However, the existence of three other intermediate phases, which form by peritectic reactions, has been reported.[3] One of these, containing approximately 50 atom % Bi and Te, forms at 540° by the reaction of solid Bi_2Te_3 with a bismuth-rich melt. The preparation of a compound BiTe by an evaporated film technique has been reported also[4]; its structure was investigated by electron diffraction and found to be of the B1 (rock salt) type with a lattice parameter of 6.47 Å. at room temperature.

Because of the wide interest in Bi_2Te_3 it was decided to investigate the effect of pressure and temperature on the condensed phase equilibria of the compound. The purpose was to demonstrate whether or not any new phase structures of Bi_2Te_3 are stable at elevated pressure and to determine the effect of pressure on the melting point. A more limited study was made of specimens containing 50 atom % Bi and Te.

Experimental

Sample Preparation.—Bi_2Te_3 was prepared by the reaction of the elements (99.999% purity) within evacuated Vycor capsules. Four separate preparations were employed in the high pressure experiments; each was made using stoichiometric amounts of the elements. Two additional preparations were used in the comparison experiments at one atmosphere. These preparations (designated as specimens I and II) originally were made as part of a program for the evaluation of thermoelectric materials. Specimen I contained Bi_2Te_3 + $^1/_8$ atom % Te; specimen II contained Bi_2Te_3 saturated with NaI (an amount less than $^1/_8$ atom %).

High Pressure Experiments.—These experiments were performed with a 600-ton tetrahedral anvil apparatus constructed at this Laboratory with the consultation of the inventor, H. Tracy Hall, Brigham Young University, Provo, Utah. The principal design and operation characteristics of the device are described elsewhere.[5] In

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(1) M. Hansen and K. Anderko, "Constitution of Binary Alloys," McGraw-Hill Book Co., Inc., New York, N. Y., 2nd Ed., 1958, p. 340.

(2) M. H. Francombe, *Brit. J. Appl. Phys.*, **9**, 415 (1958).

(3) M. Kh. Abrikosov and V. F. Bankina, *Zh. Neorgan. Khim.*, **3**, 659 (1958); *Chem. Abstr.*, **52**, 19377d.

(4) S. A. Semiletov, *Tr. Inst. Krist., Akad. Nauk SSSR*, **10**, 76 (1954).

(5) H. T. Hall, *Rev. Sci. Instr.*, **29** 267 (1958).

some respects, however, the techniques of this study differ sufficiently from previous practice to merit discussion.

The pressure calibration of the apparatus was obtained from the oil pressures (to the four hydraulic rams) required to produce phase transitions in specimens of bismuth and barium enclosed in silver chloride. In accordance with the customary practice, the transitions were revealed by changes in electrical resistance. The reference pressures employed are Bi (I–II) at 25.4 kilobars (kb.), Ba (I–II) at 60 kb., and Bi (VI–VIII) at 87 kb.[6] A linear dependence of specimen pressure (above 25.4 kb.) on oil pressure is indicated. The calibration for pressures below 25.4 kb. was provided by a line from the origin to the Bi (I–II) reference point; the slope of this line is about 50% greater than that connecting the three high pressure reference points. The importance and reliability of the low pressure branch of the calibration will be discussed below.

For the barium calibration, it was necessary (in order to maintain electrical contact) to restrict the oxidation of the ends of the specimen by ultrasonic tinning with a solder of InBi (m.p. 110°).

Specimens were enclosed within the center of pyrophyllite tetrahedra, the edges of which were 1.25 in. long. The matching triangular faces of the anvils (Carboloy 883) were 1.00 in. on the edge.

Electrical resistance of the Bi_2Te_3 samples proved to be the most reliable index of phase transformations. Specimens measuring $^1/_{16}$ in. in diameter and $^3/_8$ in. in length were enclosed in insulation tubes and centered within graphite tube heaters, $^1/_4$ in. long, $^1/_4$ in. outside diameter, and $^3/_{16}$ in. inside diameter. A variety of materials was used to insulate the sample, including quartz, pyrophyllite, boron nitride, and alumina. Two anvils afforded electrical contact to the heater through tantalum tabs; two anvils afforded electrical contact to the sample through copper tabs.

Temperature measurement was provided by two Pt–Pt + 10% Rh thermocouples. The two legs of each couple (30 gage wires) were inserted into 0.046 in. diameter, two-holed mullite insulation tubes and were welded at the junction. Holes were drilled from the mid-points of each of two edges directed toward the center of the tetrahedron. The thermocouples were inserted so that the junction was positioned at a point midway between the inner surface of the heater and the outer surface of the specimen. Two couples were used because occasionally one failed when the load was first applied to the tetrahedron. The two junctions always differed slightly in position relative to the hottest part of the specimen; the two output voltages usually differed by about 0.1–0.2 mv. The higher voltage always was selected for recording. It should be noted also that, at the points of emergence from the tetrahedron, each thermocouple insulating tube was cushioned by a 0.085 in. thick, $^1/_8 \times ^1/_8$ in. pyrophyllite pad in a manner similar to that first suggested by Dudley and Hall.[7]

Electrical power to the heater was provided by a 440/2.3 v. welding transformer; the primary voltage was regulated by a 440 v. Powerstat in series with a supplementary voltage of up to 36 v. The latter was provided by a 110/36 v. transformer powered by two cascaded Powerstats, one of which was adjusted manually and the other driven by a 1 r.p.m. reversible electric motor. The temperature of the specimen was raised to a value somewhat below the expected transition temperature by the adjustment of the 440 v. Powerstat; additional power to the heater was provided automatically and steadily by the motor-driven Powerstat. The temperature of the specimen thus was raised to a value above that of the phase transition and then returned to the original value by a reversal of the motor.

Electrical resistance of the sample proved to be the most reliable index of fusion. The resistance of the sample was determined with direct current. The observed resistance included, of course, the full length of the sample, the copper end tabs, and the associated junction resistances. The ends of the sample always were relatively cool (at 30–40°), but they inevitably differed somewhat in temperature and produced a slight thermoelectric voltage. The latter voltage never amounted to more than about 10% of the total and caused no interference.

The voltage drop through the specimen and one of the thermocouple voltages were simultaneously recorded on a two-channel null balance electronic recording potentiometer. A phase transition was indicated by abrupt, reversible changes in resistance during an automatic heating and cooling cycle. The resistance change was a reflection of an event occurring at the temperature of the hottest portion of the specimen; the thermocouple doubtlessly indicated a somewhat different temperature. The two temperatures are expected to be proportional to one another, however. The magnitude of the difference, which could be either positive or negative, must be considered in terms of the reproducibility of the data and a comparison experiment with lead which will be discussed below. Standard, one atmosphere, thermocouple conversion tables were used to determine the observed temperatures.

Indices of fusion other than resistance were investigated; they included thermoelectric power and certain temperature variations. Some description of these less satisfactory techniques will be given in the section on Results.

Experiments at One Atmosphere.—It was necessary to confirm that the abrupt resistance changes observed at high pressure could be accepted as evidence for fusion. For comparison, the electrical resistivity and thermoelectric power of two specimens of Bi_2Te_3 were measured, at atmospheric pressure, for temperatures extending up to and beyond the melting point.

The Bi_2Te_3 was enclosed in a Vycor tube under an argon atmosphere and positioned centrally in a vertical tube furnace. A bundle of the necessary two thermocouples (Pt–Pt + 10% Rh) and two current leads (Pt) was immersed in the molten sample after being assembled in the following manner. The individual wires were enclosed in snug fitting alumina insulation tubes. The wires were beaded with a gas–oxygen flame where they emerged from the insulation tubes to make contact with the sample. The flow of molten Bi_2Te_3 into the tubes was thereby restricted. The two thermocouple junctions were appropriately spaced between the ends of the current leads. Resistivity was determined during subsequent cooling of the sample; alternating current of 0.25 amp. was em-

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(6) G. C. Kennedy and P. N. LaMori, "Progress in Very High Pressure Research," John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 304–311.

(7) J. D. Dudley and H. T. Hall, *Phys. Rev.*, **118**, 1211 (1960).

ployed with the platinum legs of each thermocouple serving as voltage probes. The thermoelectric power was determined subsequently upon heating the sample.

Results

Experiments at One Atmosphere.—The temperature dependences of the electrical resistivity and thermoelectric power (relative to platinum) for two specimens (I and II) of Bi_2Te_3 are given in Fig. 1 and 2. The temperature range extends beyond the melting temperature (585°).

A discontinuous decrease in resistivity is observed upon fusion. During the experiments the resistance was observed to change for a period of about 5 min. at the temperature of melting. The value of the resistance at a given time was determined by the relative amounts of solid and liquid. Subsequent to the completion of these experiments, the author learned of similar observations on Bi_2Te_3 reported by Ioffe and Regel.[8] Their data also indicate an abrupt decrease in the resistivity upon fusion although no observation was made of solid–liquid mixtures.

Some difficulty was encountered in obtaining thermoelectric power measurements close to the melting point, but it is presumed that the observed change in this property is likewise discontinuous at that temperature. A measurement of the Peltier coefficient of solid Bi_2Te_3 relative to the melt has been reported.[9] It was determined from the rate of motion of a solid–liquid interface normal to which a direct current was passed. The observed value of -0.0166 v. corresponds to a thermoelectric power of -19.4 μv./deg. The relative difference between the solid and melt is of the same sign as that observed in the present investigation; the magnitude of the difference would be expected to vary for different specimens.

Data on the resistivity and thermoelectric power of specimen I are available which were obtained as part of a separate, earlier research program.[10] The data for the thermoelectric power are represented by the dark circles in Fig. 2. The data for resistivity are not shown in Fig. 1; they would each have to be reduced by about 20% to provide a smooth fit to the new data. This disparity is not considered excessive in view of the uncertainties in all the dimensional measurements used to calculate the two sets of resistivities. No knowledge of dimensions is required, of course, for the thermoelectric power determinations.

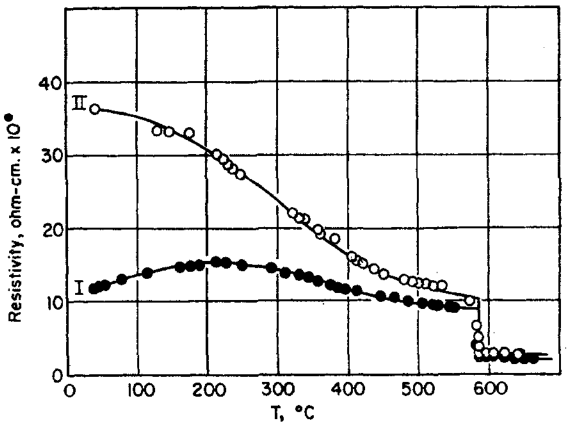

Fig. 1.—Effect of temperature on the electrical resistivity for two specimens of Bi_2Te_3 at atmospheric pressure. Discontinuities shown at the melting point, 585°.

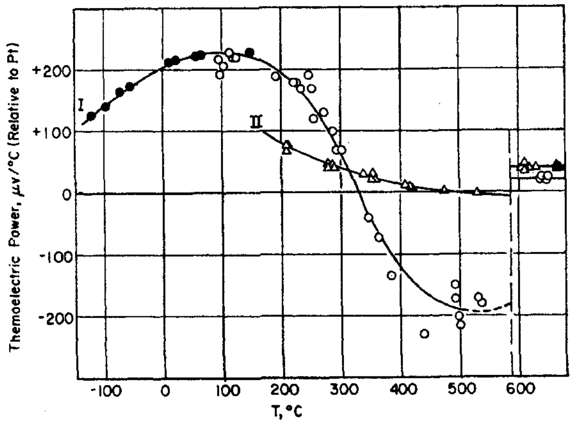

Fig. 2.—Effect of temperature on the thermoelectric power (relative to platinum) of two specimens of Bi_2Te_3. The vertical dashed line is placed at the melting point.

Platinum is known to react with tellurides at high temperature. However, only at 700° did the voltage measurements begin to appear erratic; otherwise stable voltages were observed. In addition, the data observed for specimen I agreed favorably with previous measurements. The reaction of platinum with the sample appears not to have been extensive enough to prevent a reliable determination of the effect of fusion on the observed electrical properties. A sufficient confirmation is provided for the indices of fusion employed for the high pressure experiments.

High Pressure Experiments with Bi_2Te_3.—Initially the regions of pressure and temperature up to 75 kb. and 900° were explored in an effort to determine the possible existence of any additional solid phases for Bi_2Te_3. The resistance of a sample enclosed in silver chloride was measured at pres-

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(8) A. F. Ioffe and A. R. Regel, "Progress in Semiconductors," Vol. 4, John Wiley and Sons, Inc., New York, N. Y., 1960, p. 272.

(9) S. A. Semenkovich, L. A. Kolomoets, and N. V. Kolomoets, *Soviet Phys.-Solid State*, **3**, 1159 (1961).

(10) E. J. Miller, unpublished experiments at the Research Laboratories, General Motors Corporation.

sures up to 75 kb. at room temperature. The resistance decreased smoothly from 0.040 ohm at 14 kb. to 0.007 ohm at 75 kb. There was no indication of a phase transformation. However, the entire series of measurements was completed in a period of 1 hr.; the possibility of sluggish transition cannot be excluded.

Figure 3 shows the dependence of the resistance of a specimen of Bi_2Te_3 on temperature at a pressure of 22 kb. The only phase transformation indicated is at 600°. The experiment represented extended to 900°, but frequently in similar experiments a pinching-off of the specimen was observed at temperatures as low as 700°. This observation suggests that the phase stable above the indicated transition temperature is liquid. Also, the change in resistance, which reveals the transition, is similar in form to that observed to accompany fusion at one atmosphere. The resistance change observed in the high pressure apparatus is less abrupt because of the temperature gradient along the specimen.

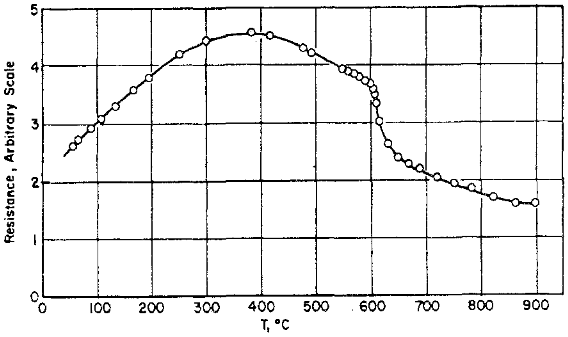

Fig. 3.—The effect of temperature on the resistance of Bi_2Te_3 at 22 kb.

Since no solid polymorphs of Bi_2Te_3 were encountered, the present investigation was principally restricted to a determination of the effect of pressure on the melting point. A series of five runs was made in which the resistance effect was used as an index of fusion at a series of constant pressures. Measurements of the type shown in Fig. 3 were made at each pressure. The individual sets of data (resistance and corresponding temperature) are taken from the chart on which the resistance and temperature are simultaneously recorded as functions of time. In the range of temperature just prior to melting the resistance decreased with time (and increasing temperature). Melting (or solidification) was revealed by an abrupt change in slope on the resistance trace. The observed change in slope usually was more abrupt and occurred at a lower temperature (by about 5°) for solidification than for fusion. These effects probably were due to a slight subcooling of the melt followed by a rapid solidification.

Figure 4 (upper curve) shows the results obtained for the melting temperature of Bi_2Te_3 as a function of pressure. A different symbol is used for each of the five runs. Each point is an average of three to four repeated determinations. The separate determinations were within ±1° of the average. The abruptness of the slope change (of the resistance trace) accompanying fusion decreased with increasing pressure. At pressures above 50 kb. a confident determination of the melting temperature no longer was possible. This condition persisted up to the maximum pressure investigated, about 70 kb. It is not considered possible to assign any specific significance to this phenomenon based on the information available.

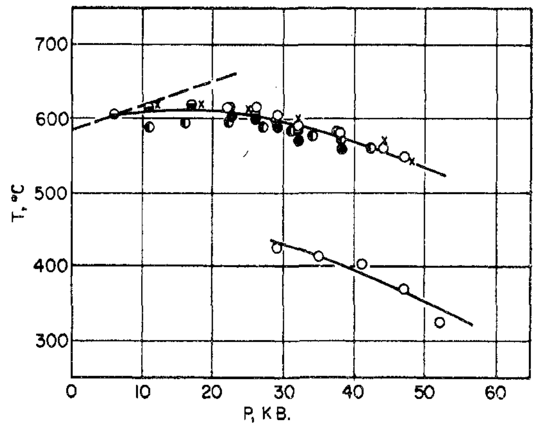

Fig. 4.—The dependence of the melting point of Bi_2Te_3 on pressure. The upper curve was determined from the measurement of sample resistance with indirect heating; each of five runs is represented with a different symbol. The dashed line extending from the one atmosphere melting point (585°) represents the limiting slope predicted by the Clapeyron–Clausius equation. The lower curve was obtained by the direct heating of the sample, which was separated from the thermocouple by circumferential insulation.

At this point, the reliability of the low pressure branch (below 25.4 kb.) of the pressure calibration must be discussed. When the resistance of Bi_2Te_3 (at room temperature) is plotted as a function of pressure (from 14 to 75 kb. using the indicated calibration) no unusual deviations in slope are apparent in the low pressure range. The calibration is, therefore, not considered to be violently in error, but certainly some caution must be employed in considering the lower pressure region of the upper curve in Fig. 4.

In Fig. 4, the straight dashed line extending from the one atmosphere melting point of Bi_2Te_3 is the limiting slope predicted by the Clapeyron–Clausius equation. The entropy of fusion (33.1 ± 0.9 cal./mole deg.) was reported recently by Bolling.[11] The change in molar volume accompanying fusion was measured in this Laboratory to be $+4.3 \pm 0.2\ \%$. The technique employed for determining the volume discontinuity and the results obtained are expected to be the subject of a separate publication.

The data obtained above 20 kb. show a decreasing melting temperature with increasing pressure in contrast with the low pressure limiting behavior predicted by the Clapeyron–Clausius equation. The data for pressures below 20 kb., despite their scatter, indicate a rather broad maximum in the melting point. As indicated above, there is some uncertainty in the pressure calibration in this region, but a maximum in the melting point would be shown regardless.

The over-all reliability of the cell configuration, the resistance technique, and the temperature measurements was confirmed by determination of the melting point of lead as a function of pressure. Lead was expected to display an uncomplicated behavior and melt in the same general temperature range as Bi_2Te_3. The data obtained (between 22 and 56 kb.) agree favorably with a previous determination.[12] The temperature measurements are in agreement to within less than 5°.

The lower curve in Fig. 4 presents data for the pressure dependence of the melting point of Bi_2Te_3 obtained by directly heating the sample. The middle section of the sample (where temperature was highest) was enclosed in a graphite tube. Electrical contact to the heater circuit was made to the ends of the sample, which extended 1/32 in. beyond the ends of the graphite tube. In effect, the total heater current was passed through the sample only because of the high junction resistance between Bi_2Te_3 and graphite. The thermocouple junction butted against the outside surface of the graphite at midspan. During the experiment, the a.c. voltage to the sample was increased automatically and the thermocouple output voltage recorded. The specimen resistance was the principal component of the total circuit resistance; when the specimen began to melt, the circuit resistance dropped and the power dissipated increased. Consequently, the record of temperature *vs.* time showed a sharp increase in slope. The temperatures at which the increase commenced (at a series of increasing pressures) are shown in Fig. 4.

In this case, the thermocouple junction was separated from the specimen along a severe radial temperature gradient; for this reason the observed temperatures were considerably below the true transition temperatures. In the previous technique the thermocouple junction and specimen were enclosed within a tubular heater. The radial temperature gradient within such an indirect heater is much less severe and more realistic data are provided. However, the temperatures shown in the lower curve of Fig. 4 are expected to be proportional to the actual transition temperatures; their dependence on pressure is similar to that observed with the technique used for the upper curve. Again it was not possible to extend the measurements to higher pressures; the index of fusion became too indistinct.

Some efforts also were made to use the thermoelectric power (of Bi_2Te_3 relative to Pt) as an index of fusion, but it is necessary to make a junction between sample and reference material in the hottest portion of the cell. The possibility of contamination is increased. Two experiments indicated a decreasing melting point with increasing pressure (from 22 to 32 kb.), but the measuring circuit opened in both cases and prevented continuance of the runs.

Efforts to Form the Compound BiTe at High Pressure.—It was attempted to form BiTe by quenching from melts of the 50 atom % composition both at 38 and 67 kb. However, subsequent Debye–Scherrer X-ray diffraction analysis of the two specimens revealed only Bi_2Te_3 plus a second bismuth-rich phase. There were no detectable diffraction lines corresponding to the reported structure for BiTe.

It had been hoped that elevated pressures would favor the formation of solid BiTe by quenching from the melt (at a rate of about 500°/sec.) because of the resulting lower diffusion rates. It is questionable whether the formation would be favored under equilibrium conditions at high pressure. The volume change for the reaction $3BiTe \rightarrow Bi + Bi_2Te_3$ was calculated to be about $+1\%$ at 25°. At 540°, the volume change probably is negative in sign principally because of the increase in density of bismuth on fusion. It is likely that increases in pressure would decrease

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(11) C. F. Bolling, *J. Chem. Phys.*, **33**, 305 (1960).

(12) V. P. Butuzov and M. G. Gonikberg, *Dokl. Akad. Nauk SSSR*, **91**, 1083 (1953).

the peritectic temperature relative to the liquidus temperature at the same composition. The congruent melting of BiTe would not be expected at any elevated pressure unless, possibly, it first transformed to a more compact crystal structure (*e.g.*, B2).

Discussion

Evidence has been provided for the existence of a maximum in the melting point of Bi_2Te_3 as a function of pressure. The data do not permit a precise assignment of the pressure at which the maximum occurs, but it appears to be in the neighborhood of 15 kb. and 610°. A melting point dependence of this type is unusual. It has been reported only for rubidium[13] and cesium.[14]

It is of interest that the occurrence of maxima in melting points once was hypothesized by Tammann[15] as the general behavior to be expected for all materials at high enough pressures. The validity of this suggestion was considered by Bridgman[16] in terms of available data on melting points and volume changes on fusion as functions of pressure. Based on the indicated trends in the data, Bridgman concluded that the hypothesis of Tammann would not be realized at any finite pressure.

It is necessary to consider the circumstances responsible for the exceptional behavior of Bi_2Te_3. The possibility of specimen contamination is regarded as unlikely. Four separate preparations of Bi_2Te_3 were used together with a variety of container materials. Inspection of one specimen after test by X-ray diffraction revealed only Bi_2Te_3. The over-all reliability of the techniques used was confirmed by the experiment with lead and the data for Bi_2Te_3 are considered to be reasonably reproducible.

A reversal in the dependence of melting temperature on pressure would not occur with the formation of a second solid phase (resulting in a triple point at the apparent maximum temperature). Such a new phase would have to be of higher density; its melting point would have to rise with pressure if that of the low pressure polymorph did. Also, as indicated, no evidence of a solid phase transition was provided by the resistance measurements.

The Clapeyron–Clausius equation, $dT_f/dP = \Delta V_f/\Delta S_f$, must hold at all pressures. Since the entropy change on fusion, ΔS_f, always must be positive, it is necessary to explain the observed maximum in terms of the pressure dependence of the volume change on fusion, ΔV_f, of the C33 structure of Bi_2Te_3. Whereas a volume expansion takes place on fusion at the lower pressures, a contraction must occur at higher pressure. The structural characteristics of Bi_2Te_3 which could be responsible for such a dependence will be considered.

Solid Bi_2Te_3 can be described in terms of an alternating sequence of layers each containing atoms of one element only. The layers are repeated in units of five (–Te–Bi–Te–Bi–Te–). Each atom within the inner three layers of a unit forms six bonds of almost octahedral symmetry to atoms in the adjacent layers only. Drabble and Goodman[17] have described the bonding in terms of sp^3d^2 hybridization and assigned two electrons to each of the octahedral bonds formed by the atoms of the three inner layers. It was assumed that the five layer units are joined by van der Waals bonds between the tellurium atoms in adjacent outer layers.

No direct evidence is available for the structure of liquid Bi_2Te_3. It is necessary to conclude, however, that the bonding of the liquid is significantly different from that of the solid because of the observed abrupt increase in electrical conductivity on fusion. More specifically, it is suggested that an effective increase in coördination number occurs (as in the case of bismuth). Although a precise description of the altered structure for the liquid cannot be given, it is possible that bonds between atoms of the same element are introduced. The increase in electrical conductivity might result from the excess of bond orbitals over the number of available valence electrons. Perhaps some higher d orbitals are involved.

Accompanying the proposed increase in coördination number on fusion, there also must occur a disappearance of long range order together with a marked increase in the number of vacancies (or voids). The coördination number increase and the new structural disorder are opposed in their contribution to the volume change on fusion. It is suggested that the effect of disorder dominates at

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[13] F. P. Bundy, *Phys. Rev.*, **115**, 274 (1959).

[14] R. C. Newton, A. Jayaraman, and G. C. Kennedy, *J. Geophys. Res.*, **67**, 2559 (1962).

[15] G. Tammann (R. F. Mehl, translator), "The States of Aggregation," D. Van Nostrand Co., New York, N. Y., 1925.

[16] P. W. Bridgman, "The Physics of High Pressure," G. Bell and Sons, Ltd., London, 1949, pp. 204–207.

[17] J. R. Drabble and C. H. L. Goodman, *J. Phys. Chem. Solids*, **5**, 142 (1958).

low pressure and produces a net increase in molar volume. The magnitude of the structural disorder (of the liquid relative to the solid) is expected to decrease with increasing pressure.[18] It is proposed that, above 15 kb., the effect of a coördination number increase is dominant and a net decrease in volume on fusion occurs.

A possible cause of the observed maxima in the melting points of cesium and rubidium has been proposed[14] involving an 'electronic collapse,' into empty inner orbitals, of the liquid under pressure. However, in the case of Bi_2Te_3, this sort of explanation appears less attractive.

[18] P. W. Bridgman, reference 16, pp. 132–133.

CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY,
RESEARCH AND ENGINEERING DIVISION, ST. LOUIS, MISSOURI

Hydrolysis of Sodium Pyrosulfate

BY HEINZ K. HOFMEISTER[1] AND JOHN R. VAN WAZER

Received April 6, 1962

Although sodium pyrosulfate is generally thought to hydrolyze almost instantaneously, it has a half-life in water at 25° of 1.7 min. In pure water, hydrolysis occurs according to first-order kinetics, and there is an activation energy of 11.3 kcal. Addition of dioxane reduces the hydrolysis rate much more rapidly than would be expected for uncomplicated second-order kinetics involving the water and pyrosulfate ion.

Introduction

Although the pyrosulfates have been described in the literature for well over a century,[2] it is generally believed that they hydrolyze almost instantaneously in aqueous solution. This instability of the pyrosulfate anion in aqueous solution has been emphasized by Glocker and Meland.[3] As part of a thorough study of inorganic macromolecules, we decided to investigate the rate of hydrolysis of sodium pyrosulfate in water in order to determine whether or not it would be possible, by working rapidly, to detect and prove the existence of the higher pyrosulfates in aqueous solution. We were pleasantly surprised to find that the pyrosulfate ion is moderately stable in water, as shown below.

Experimental

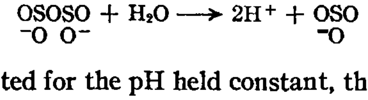
$Na_2S_2O_7$ was prepared by heating $NaHSO_4$ to 150–200° for 3 days. No loss of SO_3 occurred at these temperatures, as evidenced by pH titration of the hydrolyzed pyrosulfate. The X-ray diffraction powder pattern[4] and the infrared spectrum[5] are in accord with the data in the literature. The hydrolysis measurements were carried out with a Danish-made Radiometer Type TTT1 titrator, with Type SBR2/SBU1/TTA2 accessories. In measuring the kinetics, this instrument was used as a pH-stat to control the pH at various set values ranging from 1 to 10. The pH of the solution (made by dropping *ca.* 0.05 g. of the sodium pyrosulfate into 25 ml. of well stirred water in the titrimeter cup) was held constant by rapidly pulsed additions of 1 *N* sodium hydroxide.

Both finely powdered and moderately coarse sodium pyrosulfate were studied and it was found, with the thorough stirring employed, that after about 40 sec. the curves showing the rate of addition of sodium hydroxide merged. A first-order logarithmic plot evidenced only a slight diminution in the initial rate for the coarser particles. It was noted visually that when rate-of-addition curves for the sodium hydroxide merged, all of the particles of sodium pyrosulfate had dissolved. Careful inspection has led us to the conclusion that the rate process described herein is truly the hydrolysis of dissolved sodium pyrosulfate and is not confounded by the rate of dissolution.

The Radiometer titrator also was used to obtain pH titration curves of the sodium pyrosulfate.

Results and Discussion

The hydrolysis investigated in this study is described by eq. 1.



$$\begin{matrix} \text{O O} \\ \text{OSOSO} \\ {}^{-}\text{O O}^{-} \end{matrix} + H_2O \longrightarrow 2H^+ + \begin{matrix} \text{O} \\ \text{OSO} \\ {}^{-}\text{O} \end{matrix} \qquad (1)$$

As expected for the pH held constant, this process was found to follow first-order kinetics in dilute aqueous solution. The effect of temperature is

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[1] On leave of absence from Göttingen University, Germany, July, 1961–1962.

[2] *E.g.*, P. L. Geiger, *Mag. Pharm.*, **9**, 1251 (1825); H. Rose, *Ann. Physik* (Poggendorff), **38**, 122 (1836); D. A. Rosenstiehl, *Compt. rend.*, **53**, 658 (1861).

[3] G. Glockler and R. J. Meland, *Proc. Minn. Acad. Sci.*, **6**, 65 (1938).

[4] ASTM Powder Data File Card No. 1-0834.

[5] Y. Garnier and C. Duval, *J. Chromatog.*, **2**, 72 (1959).