

## A THERMOANALYTICAL INVESTIGATION OF THE THERMODYNAMIC PROPERTIES OF TIN TELLURIDE

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(Received July 13, 1973)

The heats of formation and fusion of SnTe were determined in a differential thermal analysis calorimeter. Its free energy of formation was calculated by the analyses due to Wagner and Jordan using this heat of fusion and liquidus data. The experimentally determined value of the heat of formation and the calculated free energy of formation were combined to obtain the entropy of formation. The thermodynamic properties were interpreted in terms of the structure and bonding of the compound.

The system Sn–Te, as shown in the phase diagram (Fig. 1) [1, 2], contains only one compound, SnTe. This melts congruently and has a narrow range of homogeneity (50.1–50.9 at. % Te). This compound has gained prominence as a material for generation and detection of infrared radiation [3] and thermoelectric energy conversion [4]. The thermodynamic properties of tin telluride have not been systematically investigated. The available data are limited and show wide disagreement. For example, the published values of its heat of fusion, based on two different techniques, are 7.9 and 10.8 kcal/mole, respectively [5, 6]. Hirayama [7] has compiled various thermodynamic properties of SnTe. McAteer and Seltz

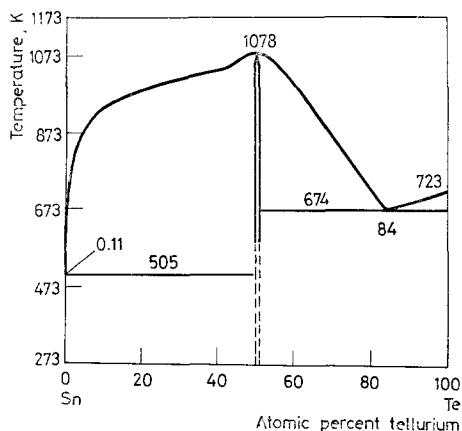


Fig. 1. Phase diagram of the system Sn–Te

[8] determined its free energy of formation in the temperature range 533–663 K by an EMF technique, using a  $\text{LiCl}-\text{KCl} + \text{SnCl}_2$  molten-salt electrolyte. Robinson and Bever [9] have determined the heat of formation in a liquid-metal solution calorimeter, using bismuth as a solvent.

In the present investigation the heats of formation and fusion of  $\text{SnTe}$  have been determined in a differential thermal analysis (DTA) calorimeter. From these results its free energy of formation at the melting point has been calculated by the analyses due to Wagner [10] and Jordan [11]. The entropy of formation of  $\text{SnTe}$  has been obtained by combination of the heat of formation and the free energy of formation. The results are correlated with the structure and bonding of the compound.

## Experimental

### Materials

High-purity tin, tellurium, bismuth and lead (each of 99.99% purity) obtained from the Bhabha Atomic Research Centre, Bombay, and analar grade sodium chloride (B.D.H.) were used in this investigation.

### DTA calorimeter

The differential thermal analysis calorimeter employed for the determination of the heats of formation and fusion is shown schematically in Fig. 2. It consists of a Kanthal-wound vertical furnace with a sillimanite muffle closed at the bottom.

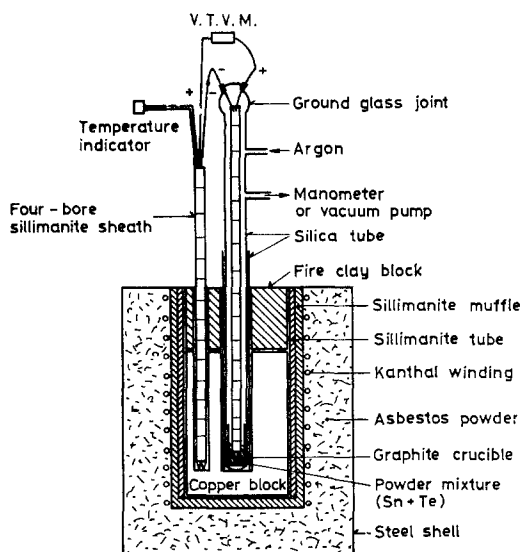


Fig. 2. Differential thermal analysis calorimeter

A cylindrical copper block (65 mm dia) is placed centrally in the furnace muffle. The block is insulated by another sillimanite tube. A central hole (22 mm dia) in the copper block contains a 12-mm I.D. silica well. This is surrounded by another silica tube. A sample container of graphite (7 mm I.D., 50 mm long) is placed in the silica well. There are arrangements at the top of the well for insertion of thermocouple wires, attachment of a manometer, evacuation and admission of inert gas. There are three pairs of chromel-alumel thermocouples in the calorimeter, one of which is embedded in the sample. The other two pairs are inserted in another cylindrical hole of 10 mm dia in the copper block, one pair of which is used to measure the temperature of the copper block, while the other pair is differentially connected to the sample thermocouple. The differential EMF is measured by a Philips Microvoltmeter (V.T.V.M.). The top of the copper block is insulated by a fireclay block having holes identical to that in the block.

*DTA calorimeter run with the mixture of tin and tellurium*

3.2225 g of a thorough mixture of fresh powders (–150 mesh) of tin and tellurium in stoichiometric proportion was taken in the graphite crucible with the thermocouple embedded in it. After insertion of the crucible, the silica well was evacuated and purged with purified argon three times. A slight negative pressure was maintained inside, to take care of the expansion of the gas during heating.

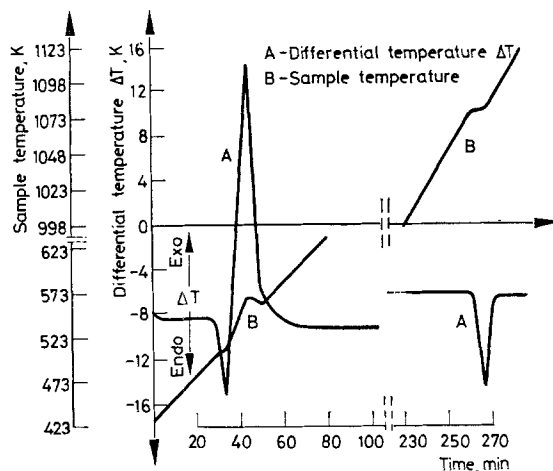


Fig. 3. Differential temperature and sample temperature vs. time

The furnace block was heated at the rate of  $2.5^{\circ}/\text{min}$  by controlling the input voltage through a voltage stabilizer and a dimmerstat. The temperature of the block and the differential temperature  $\Delta T$  between the sample and the reference surrounding (copper block) were noted at intervals of 30 seconds. As can be seen

in Fig. 3, the  $\Delta T$  values showed an endothermic peak (downward) corresponding to the melting point of tin (505 K), and thereafter began to increase rapidly, reaching an exothermic peak value of  $14.6^\circ$  corresponding to the sample temperature of 565 K. After this the  $\Delta T$  values started decreasing, and returned to the normal background value. This upward peak is due to the exothermic formation of tin telluride by the reaction between liquid tin and solid tellurium. The peak area related to the formation of SnTe was measured by counting the squares and by planimetry. Since the reaction between liquid tin and solid tellurium is accomplished between 505 and 565 K, the calorimeter was calibrated by studying the fusion of the pure elements tin, bismuth and lead (melting points 505, 544 and 600 K, respectively) under conditions identical to those of the runs with the mixture of tin and tellurium. The mean calibration coefficient was employed to calculate the heat of formation of SnTe. Three different runs were performed to check the reproducibility of the results.

In the same DTA calorimeter, even after the SnTe-compound formation, reaction was complete, the product was continued to be heated beyond the melting point of tin telluride. A sharp endothermic (downward) peak was observed during the fusion of SnTe (Fig. 3). The heat of fusion of the compound was calculated from the area of this second peak. For this purpose the calorimeter was calibrated by studying the fusion of sodium chloride, which has the same crystal structure and nearly the same melting point as tin telluride. Further details of the technique and theory of the DTA calorimeter for the determination of the heats of formation and fusion are published elsewhere [12, 13].

## Results and discussion

### *Heat of formation*

The first endothermic peak in Fig. 3, at 505 K, corresponds to the fusion of tin. This is confirmed by the independent calibration run with pure tin. The sudden increase in the value of  $\Delta T$  immediately after the melting of tin indicates that the exothermic synthesis reaction between the constituent elements takes place between liquid tin and solid tellurium. The completion of the synthesis reaction corresponding to this exothermic peak is checked by X-ray diffraction of the reaction product. The reflections of SnTe only, corresponding to the NaCl structure, are observed. The precise lattice parameter calculated by the Nelson – Riley extrapolation is 6.315 Å, and compares with the published value of 6.313 Å [14].

The heat of formation  $\Delta H$  obtained by this method is  $-16.0 \pm 0.4$  kcal/mole. This may be referred to the mean temperature 535 K in the temperature range 505–565 K for the reaction  $\text{Sn}(l) + \text{Te}(s) = \text{SnTe}(s)$ . The heat of formation from the solid components, obtained by adding the heat of fusion of tin, results in the value  $-14.3 \pm 0.4$  kcal/mole for  $\Delta H_{505}$ . This is in satisfactory agreement with the values reported in the literature [7–9], obtained by EMF and solution-calorimetric techniques.

*Heat and entropy of fusion*

The heat of fusion  $\Delta H^f$  of SnTe obtained in this investigation is  $8.1 \pm 0.3$  kcal/mole, which is in reasonable agreement with the value of 7.9 kcal/mole reported by Steininger [6]. The more endothermic value of 10.8 kcal/mole obtained by Brebrick and Strauss [5] with absorption spectrometry is only an approximate one, as it was derived indirectly from vapour pressure data: the limiting error involved was large,  $\pm 2$  kcal/g-atom.

The experimental value of the entropy of fusion,  $\Delta S^f = \Delta H^f(\text{experimental})/T_f$ , is 7.54 cal/deg · mole. The theoretical value of the entropy of fusion of SnTe may be estimated [15] by adding the entropies of fusion of the component elements to their entropy of mixing. Since the experimental value of the entropy of mixing is not available, complete order in the solid state and complete disorder in the liquid state may be assumed. The theoretical value of the entropy of fusion is thus given by

$$\Delta S_{\text{SnTe}}^f = \Delta S_{\text{Sn}}^f + \Delta S_{\text{Te}}^f - 4R (0.5 \ln 0.5) \text{ cal/deg} \cdot \text{mole} \quad (1)$$

where  $R$  is the gas constant. This yields a value of 11.87 cal/deg · mole, which is appreciably larger than the experimental value of the entropy of fusion. This indicates that molten SnTe may not be in a completely disordered state and solid SnTe may not be fully ordered. Brebrick and Strauss have suggested that the intrinsic atomic disorder in solid SnTe is extremely high [5]. The lack of complete disorder in the melt, to be discussed further below, indicates that the Sn–Te liquid system does not behave as an ideal solution.

*Free energy of formation*

Wagner [10] suggested a method for calculation of the free energy of formation of a congruently-melting line compound at its melting point from the known value of its heat of fusion and the liquidus of the phase boundary. The analysis which assumes the melt to be a regular solution, has been applied to a number of intermetallic compounds [16, 17]. The excess free energy of liquid SnTe, obtained from this analysis by using the value of  $\Delta H^f$  obtained in this investigation and the liquidus from the phase diagram (Fig. 1), is highly exothermic ( $-4.0 \pm 0.5$  kcal/mole), indicating thereby that the atomic distribution in the Sn–Te melt may be non-random. Calculations from Wagner's analysis yield a value for the free energy of formation,  $\Delta G[\text{Sn}(l) + \text{Te}(l) = \text{SnTe}(s), 1078 \text{ K}]$ , of  $-7.0 \pm 0.5$  kcal/mole. The corresponding value from McAteer and Seltz [8] extrapolated to 1078 K is  $-10.8$  kcal/mole. From the wide disagreement between these two values it may be concluded that the assumption of the regular behaviour of the melt adopted in Wagner's analysis may not be valid for the Sn–Te liquid alloy.

In the system Sn–Te, both the liquidus and the Guggenheim interchange energy (defined as  $\alpha = \left[ -\frac{1}{2} RT \ln 4(1-x_2)x_2 - \Delta H^f + T\Delta S^f \right] / (x_2 - 0.5)^2$ , where  $x_2$  is

at. % solute) show sharp peaks near the equiatomic composition. On analogy with the similar behaviour observed in Cd–Te and Zn–Te melts by Jordan [11], it may be postulated that the Sn–Te melt behaves as a regular associated solution. The free energy of formation of a compound in such a system at the melting point is given according to Jordan's analysis by the relation:

$$\Delta G(T_f) = \frac{1}{2} RT \ln \left( \frac{\bar{\beta}}{1 + \bar{\beta}} \right) + \frac{1}{4} \bar{\alpha} \quad (2)$$

where  $\bar{\alpha}$  and  $\bar{\beta}$  are the average values of the interchange energy  $\alpha$  and the degree of dissociation  $\beta$ , respectively, for the two different composition ranges Sn–SnTe and Te–SnTe. The values of  $\alpha$  and  $\beta$  are determined from the heat and entropy of fusion of the compound and liquidus data.  $\Delta G(T_f)$  of SnTe calculated by the above analysis as per the procedure in Ref. [11] is  $-10.6$  kcal/mole, which is in good agreement with the extrapolated value of  $-10.8$  kcal/mole from the data of McAteer and Seltz [8].

The regular associated behaviour of molten Sn–Te is also reflected in its activity–composition relationship. The activity of tellurium in a tellurium-rich melt of Sn–Te may be calculated from the depression in the melting point of tellurium (Fig. 1), according to the relationship [18]

$$\Delta \bar{G}_{\text{Te}}^1 = RT \ln a_{\text{Te}} = -\Delta S(T_{\text{Te}}^f - T) \quad (3)$$

where  $a_{\text{Te}}$ ,  $T_{\text{Te}}^f$  and  $\Delta S_{\text{Te}}^f$  stand for the activity, melting point and entropy of fusion, respectively, of tellurium and  $T$  is the liquidus temperature. The calculated activity values exhibit a negative deviation from Raoult's Law. This is consistent with the postulation of the existence of association in the melt as discussed in the preceding paragraph.

The standard free energy of formation of solid SnTe from the solid components at 298 K, calculated by integrating the Gibbs–Helmholtz relation between 298 K and the melting point 1078 K, is  $-14.5 \pm 1.0$  kcal/mole.

#### *Entropy of formation*

The standard entropy of formation of the solid compound SnTe may be calculated from the standard free energy of formation and the experimental value of the heat of formation, using the equation

$$\Delta S = (\Delta H - \Delta G)/T \quad (4)$$

The value is  $0.66$  cal/deg · mole. This low positive value of the entropy of formation of SnTe is consistent with its range of off-stoichiometry [2] and the lack of complete order as inferred earlier. The thermodynamic properties of SnTe are summarized in Table 1.

Table 1  
Thermodynamic properties of SnTe

Investigator	Heat of fusion ( $\Delta H_f$ ) kcal/mole	Free energy of formation ( $\Delta G_{298}^\circ$ ) kcal/mole	Heat of formation ( $\Delta H_{298}^\circ$ ) kcal/mole	Entropy of formation ( $\Delta S_{298}^\circ$ ) cal/deg · mole
Brebrick and Strauss [5]	10.8	—	—	—
Steininger [6]	7.9	—	—	—
Hirayama [7]	—	-14.2	-14.2	0.0
McAteer and Seltz [8]	—	-14.66	-14.65	0.0
Robinson and Bever [9]	—	—	-14.50	—
this investigation	$8.1 \pm 0.3$	$-14.5 \pm 1.0$	$-14.3 \pm 0.4$	+0.66

### Bonding

The estimated values of the lattice parameter of solid SnTe, based on the covalent and ionic radii [19] of tin and tellurium, are 6.232 and 5.84 Å, respectively. Since the experimental value 6.315 Å is close to the value calculated from the covalent radii, the bonding in SnTe appears to be essentially covalent. The covalency of tin in SnTe calculated in a manner analogous to that performed by Pauling [20] for PbS, is 1.2. The low energy gap of 0.18 eV [21] for SnTe further confirms that the bonding is covalent and that the ionicity is negligible. The percent ionicity of the Sn-Te bond in the compound, as estimated from Pauling's equation:

$$\% \text{ ionicity} = 100 [1 - e^{-\frac{1}{4}(X_{\text{Sn}} - X_{\text{Te}})^2}],$$

where  $X$  refers to the electronegativity value, is only 2.5%.

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The authors are grateful to Professors T. R. Anantharaman and S. L. Malhotra for their keen interest in this work and for providing necessary facilities. Our thanks are also due to Professor S. K. Bhattacharya of the Department of Chemistry for kindly going through the manuscript and for valuable comments. Financial assistance from the Department of Atomic Energy, Government of India, under sponsored research projects No. BRNS/C and M/15/70, is gratefully acknowledged.

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RÉSUMÉ — On a déterminé par analyse calorimétrique différentielle les chaleurs de formation et de fusion de SnTe. On a utilisé la méthode de Wagner et Jordan pour calculer l'énergie libre de formation à partir de la chaleur de fusion et des données relatives au liquide. On en a déduit l'entropie de la formation en combinant la valeur de la chaleur de formation obtenue par voie expérimentale et l'énergie libre de formation calculée. On a interprété les propriétés thermodynamiques du point de vue de la structure et des liaisons de ce composé.

ZUSAMMENFASSUNG — Die Bildungs- und Schmelzwärmen von SnTe wurden in einem Calorimeter zur Differentialthermoanalyse bestimmt. Die freie Energie der Bildung wurde mittels Analysen nach Wagner und Jordan unter Anwendung dieser Schmelzwärme und Flüssigkeitsdaten errechnet. Der auf dem Versuchswege bestimmte Wert der Bildungswärme und die errechnete freie Energie der Bildung wurden kombiniert, um die Bildungsentropie zu erhalten. Die thermodynamischen Eigenschaften wurden bezüglich der Struktur und Bindungen der Verbindung erörtert.

Резюме — Определена теплота образования и плавления SnTe с помощью дифференциального термоаналитического калориметра. Свободная энергия образования рассчитана по методу Вагнера и Йордана на основании данных о жидком состоянии и теплоте плавления. Сопоставлены величины теплоты образования, определенной экспериментальным путем, и рассчитанной свободной энергии образования с целью установления энтропии образования. Термодинамические особенности интерпретированы на основании строения и связей соединений.