Journal of the Less-Common Metals, *161* (1990) 93-99

THERMODYNAMIC PROPERTIES OF ZnTe

A. NASAR and M. SHAMSUDDIN

Department of Metallurgical Engineering, Institute of Technology, Banaras Hindu University, Varanasi 221 005 (India)

(Received October 6, 1989)

Summary

The free energy of formation of ZnTe has been determined by an electrochemical technique. From the open-circuit e.m.f. of the galvanic cell at different temperatures the following ΔG_f° *vs.* T relationships have been established

$$\Delta G_f^\circ = -119\,355 + 12.39T \text{ J mol}^{-1} \qquad (640 < T < 693 \text{ K})$$

$$\Delta G_f^\circ = -126\,870 + 23.18T \text{ J mol}^{-1} \qquad (693 < T < 723 \text{ K})$$

$$\Delta G_f^\circ = -145\,110 + 48.41T \text{ J mol}^{-1} \qquad (723 < T < 845 \text{ K})$$

The enthalpies of formation and fusion have been measured by differential thermal analysis. The combined investigations yield values of $\Delta G^\circ_{f,298K}$, $\Delta H^\circ_{f,298K}$, $\Delta S^\circ_{f,298K}$, S°_{298K}, ΔH^f and ΔS^f to be -115.2 ± 1.0 kJ mol^{-1}, -119.0 ± 2.0 kJ mol^{-1}, -12.75 J K^{-1} mol^{-1}, 78.4 J K^{-1} mol^{-1}, 63.0 ± 2.5 kJ mol^{-1} and 40.1 ± 1.6 J K^{-1} mol^{-1} respectively. The results are compared with the thermodynamic data available in the literature and discussed in terms of the structure and bonding of the compound.

1. Introduction

In the Zn–Te system [1, 2], there is only one intermetallic compound, *i.e.* ZnTe with a cubic (zinc-blende-type) structure, which melts congruently at 1570 K. ZnTe is a broad band gap (2.25 eV) semiconductor and has found applications in electronic devices [3] such as light-emitting diodes (LED) and photovoltaic detectors. The thermodynamic properties of ZnTe have been determined by various investigators using different techniques, *e.g.* electrochemical techniques [4, 5], calorimetry [6–8] and vapour pressure techniques [9, 10]. In order to check the consistency of data reported by different investigators a systematic investigation has been conducted to determine the free energy of formation, enthalpies of formation and fusion, and entropies of formation and fusion by two independent techniques, *i.e.* electrochemical techniques and calorimetry.

0022-5088/90/$3.50

2. Experimental details

2.1. Materials

High purity antimony, tellurium and zinc (99.99% pure) obtained from Bhabha Atomic Research Centre (India) and copper (99.999% pure) obtained from Johnson Matthey (U.K.), were used in this investigation. The following Analar grade salts were used for preparation of the electrolyte: LiCl (Sisco, India), KCl (Qualigens, India) and $ZnCl_2$ (Loba-Chemie, India).

ZnTe was prepared by heating (to 1300 K) the thoroughly mixed powders of zinc (150 μm) and tellurium (100 μm) in stoichiometric proportions under an argon atmosphere.

2.2. Electrochemical measurements

The standard free energy of formation of ZnTe was determined by measuring the open-circuit e.m.f. of the following galvanic cell

$$\mathrm{Zn(s,l)/LiCl{-}KCl + 5wt.\%ZnCl_2/ZnTe(s) + Te(s,l)} \tag{1}$$

The virtual cell reaction is

$$\mathrm{Zn(s,l) + Te(s,l) = ZnTe(s)} \tag{2}$$

The free energy of formation of ZnTe is calculated from the relation

$$\Delta G_f^\circ = -nFE \tag{3}$$

where n is the number of electrons transferred during reaction (2), E is the open circuit e.m.f. of the cell (1) and F is the Faraday constant.

A cell assembly made of borosil glass containing two lower limbs (8 mm inside diameter) below a tubular electrolyte compartment (35 mm inside diameter) was used in this investigation. At the bottom of each limb a tungsten wire of diameter 0.4 mm and length 20 cm was sealed. ZnTe with 10 at.% excess Te was formed in one limb by heating a thorough mixture of powders of ZnTe and tellurium under argon. In the other limb, 6 g of pure zinc was melted under argon. The cell attained equilibrium after 20 h and thereafter e.m.f. values remained constant for over 5 h. The e.m.f. measurements were made during both heating and cooling cycles. The cell e.m.f. was reproducible within ± 1 mV at any temperature whether approached from the higher or lower side. Three independent runs were performed to check the reproducibility of the results.

2.3. Differential thermal analysis (DTA) calorimetry

The enthalpies of formation and fusion of ZnTe were directly measured in a quantitative DTA calorimeter using a stainless steel block as a reference surrounding. The construction and operation of the calorimeter was as described by Shamsuddin and Misra [11]. A thorough mixture (7.26125 g) of fresh powders of zinc and tellurium in a stoichiometric proportion corresponding to the composition ZnTe was put in the graphite sample container of the calorimeter, which after evacuation and insertion of argon was heated at a constant and reproducible rate of 4 K min^{-1} using a thermal program controller (ULVAC, Sinku-Riku, Japan; model

HPC-7000). The temperature of the sample and differential temperature between the sample and the reference block were recorded with a four-pen recorder (BBC, Austria; model SE-460). During the exothermic pyrosynthesis of ZnTe, the value of ΔT showed a pronounced upward peak. The enthalpy of formation was calculated from the area of this peak. The calorimeter was calibrated by studying the fusion of pure tellurium and antimony under conditions identical with those of the runs with the powder mixture of zinc and tellurium. The mean calibration coefficient was employed to calculate the enthalpy of formation of ZnTe.

In the same DTA calorimeter, even after the formation of ZnTe was complete, heating of the product was continued beyond the melting temperature of ZnTe. A sharp endothermic peak was observed during the fusion of ZnTe. The enthalpy of fusion of ZnTe was calculated from the area of this peak. For this purpose the calorimeter was calibrated by studying the fusion of pure copper. Three independent runs were performed to check the reproducibility of the results.

3. Results and discussion

3.1. Free energy of formation

The plot of e.m.f. *vs.* temperature shown in Fig. 1 for the galvanic cell (1) is represented by three straight lines, intersecting at 693 and 723 K. In the lower temperature range of 640–693 K (Fig. 1A) solid zinc is in equilibrium with solid tellurium. In the temperature range 693–723 K (Fig. 1B) solid tellurium is in

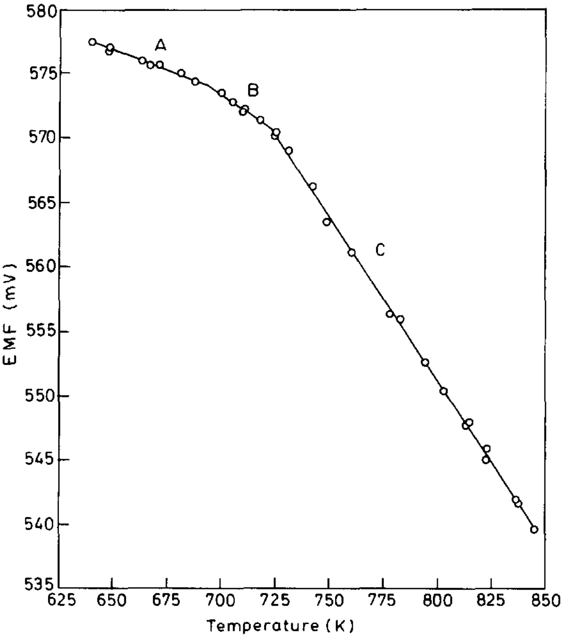

Fig. 1. E.m.f. *vs.* T plot of the galvanic cell (1).

equilibrium with liquid zinc. In the higher temperature range 723–845 K (Fig. 1C) liquid tellurium is involved. The following ΔG_f° *vs.* T relationships have been established from the e.m.f. values measured at different temperatures.

$Zn(s) + Te(s) = ZnTe(s)$ (Fig. 1A)

$$\Delta G_f^\circ = -119\,355 + 12.39T \text{ J mol}^{-1} \; (640 < T < 693 \text{ K}) \quad (4)$$

$Zn(l) + Te(s) = ZnTe(s)$ (Fig. 1B)

$$\Delta G_f^\circ = -126\,870 + 23.18T \text{ J mol}^{-1} \; (693 < T < 723 \text{ K}) \quad (5)$$

$Zn(l) + Te(l) = ZnTe(s)$ (Fig. 1C)

$$\Delta G_f^\circ = -145\,110 + 48.41T \text{ J mol}^{-1} \; (723 < T < 845 \text{ K}) \quad (6)$$

The standard free energy of formation of ZnTe has been determined by McAteer and Seltz [4] and Zabdyr [5] using a galvanic cell technique. Both have only studied the equilibrium between solid zinc and solid tellurium. Our result in the low temperature range (eqn. (4)) is comparable with the ΔG_f° *vs.* T relation reported by Zabdyr [5]. The following ΔG_f° *vs.* T expression calculated by Sharma and Chang [2] for the reaction between liquid zinc and liquid tellurium is in agreement with our ΔG_f° *vs.* T relation (eqn. (6))

$$\Delta G_f^\circ = -147\,400 + 53.62T \text{ J mol}^{-1} \quad (7)$$

Furthermore, the consistencies of eqn. (4) with (5) and eqn. (5) with (6) were checked by calculating the enthalpies of fusion of zinc and tellurium from these equations and were found to be 7.52 and 18.24 kJ mol^{-1} respectively. These values are in good agreement with the reported values [12] of 7.28 and 17.49 kJ mol^{-1} for the enthalpy of fusion of zinc and tellurium, respectively.

$\Delta G_{f,298\text{K}}^\circ = -115.2 \pm 1.0$ kJ mol^{-1} estimated from eqns. (4), (5) and (6) is in close agreement with the value of -114.5 kJ mol^{-1} obtained by McAteer and Seltz [4].

3.2. *Enthalpy of formation*

The enthalpy of formation of ZnTe at 812 K from liquid zinc and liquid tellurium obtained by DTA calorimetry is -146.1 ± 1.2 kJ mol^{-1}. This value of the enthalpy of formation is in excellent agreement with the value of -145.1 kJ mol^{-1} (in the temperature range 723–845 K), obtained by an electrochemical method (eqn. (6)). The standard enthalpy of formation of ZnTe at 298 K, $\Delta H_{f,298\text{K}}^\circ$ from the solid components, obtained by taking into account the enthalpies of fusion of zinc and tellurium and Kirchhoff's law correction [12] is -119.0 ± 2.0 kJ mol^{-1}. This value is in satisfactory agreement with the extrapolated value from eqns. (4), (5) and (6), and with the one determined by Pool [6] by liquid metal solution calorimetry and also with the value determined by McAteer and Seltz [4].

3.3. *Entropy of formation*

An accurate value of the entropy of formation may be calculated by combining the best value of the free energy of formation obtained by galvanic cell measurements and enthalpy of formation determined by calorimetry using the relation

$$\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ \qquad (8)$$

The value of $\Delta S_{f,298K}^\circ = -12.75$ J K^{-1} mol^{-1} obtained in this way is comparable with the value reported by McAteer and Seltz [4]. The entropy of ZnTe at 298 K, S_{298K}° calculated from these results, is in reasonable agreement with the values reported in the literature (Table 1).

The thermodynamic properties of ZnTe are summarized in Table 1.

3.4. Enthalpy and entropy of fusion

The enthalpy of fusion of ZnTe ΔH^f obtained in this investigation is 63.0 ± 2.5 kJ mol^{-1}, which is in excellent agreement with the value of 64.7 kJ mol^{-1} determined calorimetrically by Kulwicki [7] and also with the value of 63.9 kJ mol^{-1} estimated by Sharma and Chang [2]. Another value of 57.7 kJ mol^{-1} reported by Vigdrovich [8] is less endothermic.

The experimental value of entropy of fusion of ZnTe calculated by the expression

$$\Delta S^f = \Delta H^f / T^f \qquad (9)$$

is 40.1 ± 1.6 J K^{-1} mol^{-1}. A theoretical value of entropy of fusion of ZnTe may be estimated according to the procedure outlined by Kubaschewski and Alcock [12] by adding the entropy of mixing. Since the experimental value of entropy of mixing is not available, complete order in the solid and complete disorder in the liquid state may be assumed. The theoretical value of entropy of fusion is thus given by

$$\Delta S^f(\mathrm{ZnTe}) = \Delta S^f(\mathrm{Zn}) + \Delta S^f(\mathrm{Te}) - 4R(0.5 \ln 0.5) \qquad (10)$$

TABLE 1

Thermodynamic properties[a] of ZnTe

Investigators	$-\Delta G_{f,298K}^\circ$ (kJ mol^{-1})	$-\Delta H_{f,298K}^\circ$ (kJ mol^{-1})	$-\Delta S_{f,298K}^\circ$ (J K^{-1} mol^{-1})	S_{298K}° (J K^{-1} mol^{-1})	ΔH^f (kJ mol^{-1})
Sharma and Chang [2]					63.9
McAteer and Seltz [4]	114.5	118.0	11.9		
Zabdyr [5]		116.6 ± 0.6		82.3 ± 1.3	
Pool [6]		119.2[b]			
Kulwicki [7]					64.7
Vigdrovich *et al.* [8]					57.7
Goldfinger and Jeunehomme [9]		104.2		96.2	
Brebrick [10]		118.8[c]			
This investigation	115.2 ± 1.0	119.0 ± 2.0	12.75	78.4	63.0 ± 2.5

[a] The error limit is specified wherever available.

[b] Value at 273.15 K.

[c] Value calculated by Mills [1].

This yields a value of 46.3 J K^{-1} mol^{-1}. The smaller experimental value of the entropy of fusion indicates that full entropy is not generated during melting, that molten ZnTe may not be completely disordered and that the solid ZnTe may not be perfectly ordered. Some amount of non-configurational entropy may also be involved.

3.5. *Bonding*

The enthalpy of formation of ZnTe may be estimated on the basis of Pauling's equation [13] for ionic compounds:

$$\Delta H_f^\circ = -193\,016\,(x_A - x_B)^2 \text{ kJ mol}^{-1} \tag{11}$$

where x refers to the value of electronegativity. By substituting the values of electronegativity from Pauling's scale [13], ΔH_f° is found to be -48.3 kJ mol^{-1}, which is much smaller than the experimentally determined value. This indicates that the bonding in ZnTe is only partly ionic. The partial ionicity of the Zn–Te bond as estimated from Pauling's equation [13]

$$\text{per cent ionicity} = 100\{1 - e^{-1/4(x_A - x_B)^2}\} \tag{12}$$

is only 6%. The lattice parameters of ZnTe estimated on the basis of the covalent and ionic radii [14] of zinc and tellurium are 6.187 and 6.813 Å respectively. As the experimental value of 6.069 Å is close to the one calculated from covalent radii, it may be inferred that bonding in ZnTe is predominantly covalent.

Acknowledgments

The authors are thankful to Professor P. M. Prasad, Head of the Department for his keen interest in this investigation and for providing necessary facilities. Financial assistance from the Department of Science and Technology, Government of India, under sponsored research project 12(8)/84-STP-II is gratefully acknowledged.

References

1 K. C. Mills, *Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides*, Butterworths, London, 1974.
2 R. C. Sharma and Y. A. Chang, *Bull. Alloy Phase Diagrams*, *8* (1987) 14.
3 H. Hartmann, R. Mach and B. Selle, in E. Kaldis (ed.), *Current Topics in Materials Science*, Vol. 9, North-Holland, Amsterdam, 1982.
4 J. H. McAteer and H. Seltz, *J. Am. Chem. Soc.*, *58* (1936) 2081.
5 L. A. Zabdyr, *J. Electrochem. Soc.*, *131* (1984) 2157.
6 M. J. Pool, *TMS-AIME, 233* (1965) 1711.
7 B. M. Kulwicki, *Ph.D. Thesis*, The University of Michigan, 1963.
8 V. N. Vigdrovich, O. V. Pelevin and E. V. Ufimtseva, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, *8* (1972) 753.
9 P. Goldfinger and M. Jeunehomme, *Trans. Faraday Soc.*, *59* (1963) 2851.

10 R. F. Brebrick, *J. Electrochem. Soc.*, *116* (1969) 1274.
11 M. Shamsuddin and S. Misra, *J. Thermal Anal.*, *7* (1974) 309.
12 O. Kubaschewski and C. B. Alcock, *Metallurgical Thermochemistry*, Pergamon, Oxford, 5th edn., 1979.
13 L. Pauling, *The Nature of the Chemical Bond*, Cornell University, Ithaca, NY, 3rd edn., 1960.
14 W. B. Pearson, *The Crystal Chemistry and Physics of Metals and Alloys*, Wiley, New York, 1972.