ΔV_c	molar volume contraction
m	mole fraction
S	association factor
$\Delta V(\mathrm{mix})$	maximum molar volume contraction
μ_g	dipole moment of pure substance in vapor state
μ	dipole moment of pure substance in liquid state
$\bar{\mu}$	dipole moment of the molecule and the induced moment
M	molecular weight
N	Avogadro's number
k	Boltzmann constant
T	temperature, K

Registry No. Acetic acid, 64-19-7; methyl alcohol, 67-56-1; ethyl alcohol, 64-17-5; propyl alcohol, 71-23-8; butyl alcohol, 71-36-3; isopropyl alcohol, 67-63-0; isobutyl alcohol, 78-83-1.

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Vaporization Study of Solid Bi_2Se_3

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The vaporization behavior of $Bi_2Se_3(s)$ and the vapor pressure over this compound were measured by torsion-effusion, thermogravimetric, and high-temperature Knudsen-effusion techniques in the temperature range 800-900 K. The gas phase in equilibrium with the solid Bi_2Se_3 in the first steps of its vaporization is practically composed of only $Se_2(g)$ and consequently, in the condensed phase Bi_4Se_5, a solid solution of BiSe-Se is formed. The practically null value of the heat of solution obtained for the process $4BiSe(s) + Se(s) \rightarrow Bi_4Se_5(s)$ shows the nearly ideal behavior of the solid solution Bi_4Se_5.

Introduction

The vaporization behavior of Bi_2Se_3 and its vapor pressure are not well-known. By employing static methods some authors (*1*, *2*) measured pressure data larger by about 2 orders of magnitude than those derived by using effusion techniques (*3*, *4*). The mass-spectrometric analysis of the vapor over Bi_2Se_3 at 1050 K carried out by Porter and Spencer (*5*) has shown that it is initially constituted of $Se_2(g)$ and of a small amount of BiSe(g) and Bi(g). After prolonged heating of the sample, with the consequent evaporation of selenium at constant temperature, these authors observed that the amount of $Bi_2(g)$ and BiSe(g) became larger than that of $Se_2(g)$. As part of a research program for investigation of the vaporization of bismuth compounds (*6*, *7*), also in view of the observed discrepancies between pressure values obtained with static and effusion methods and also within effusion experiments made by different authors (*3*, *4*), we were prompted to perform new, extensive, and more accurate pressure determinations for $Bi_2Se_3(s)$. The measurements were made with the effusion method using two different techniques and the results are reported below.

Experimental Section and Results

The Bi_2Se_3, 99.8 mol % pure, with impurities mostly due to selenium, was supplied by CERAC. Before the determination of the vapor pressures the samples of the compound were purified by heating at about 550 K, so that the selenium impurities were lost by vaporization. After this treatment the sample did not change weight up to about 750 K. The vaporization of Bi_2Se_3 was investigated by torsion- and Knudsen-effusion techniques, employing vitreous graphite crucibles. No interaction of the samples with the used crucibles was observed.

Torsion Effusion. The vapor pressure over $Bi_2Se_3(s)$ was measured by the torsion-effusion method. The technique and the assembly have been describe previously (*8*, *9*). From the torsion angle α of the effusion cell, at each experimental temperature the poressure value was derived by the relation $P = K\alpha$, where in K are included the torsion constant of the suspension tungsten wire, the geometrical constants of the used cell, and the correction factors (*10*) for the effusion orifice geometry. In this study the value $K = (1.72 \pm 0.25) \times 10^{-6}$ atm deg^{-1} was employed. In order to test the reliability of the assembly and of the temperature measurements, the vapor pressure of pure Zn, used as a standard, was measured. Vapor pressure values measured in the temperature range 685-751 K were treated by the second- and third-law methods. The second-law $\Delta H_v^\circ(298.15\ \mathrm{K}) = 133.8 \pm 0.8$ kJ mol^{-1} and the third-law $\Delta H_v^\circ(298.15\ \mathrm{K}) = 129.2 \pm 4.6$ kJ mol^{-1} values, where the associated errors are standard deviations, are in good agreement with the value selected by Hultgren (*11*), $\Delta H_v^\circ(298.15\ \mathrm{K}) = 130.3 \pm 4.2$ kJ mol^{-1}. The vaporization of

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Table I. Vapor Pressure of $Bi_2Se_3(s)$

method	run	temp range, K	no. of points	log *P* (atm) = *A* − *B*/*T*	
				A	*B*
torsion	71.0	801-899	8	7.74 ± 0.09	10 816 ± 76
	71.3	805-889	7	7.65 ± 0.33	10 818 ± 285
	71.5	805-875	12	7.99 ± 0.20	11 002 ± 169
	71.6	804-875	9	7.14 ± 0.54	10 291 ± 461
thermobalance	1	799-876	9	7.94 ± 0.24	10 840 ± 201
	2	859-898	6	8.42 ± 0.85	10 489 ± 749
	3	813-898	10	7.59 ± 0.45	10 770 ± 381
	4	813-876	11	7.05 ± 0.32	10 372 ± 276
HT[a] Knudsen	1	831-888	9	9.07 ± 0.53	11 745 ± 456

[a] HT = high temperature.

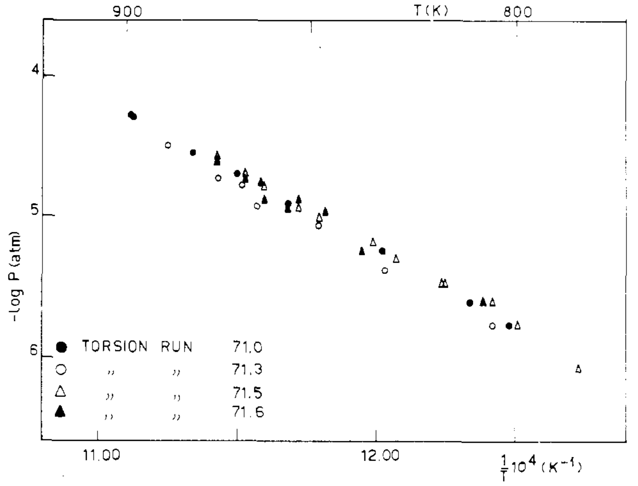

Figure 1. Vapor pressure of $Bi_2Se_3(s)$ measured by torsion method.

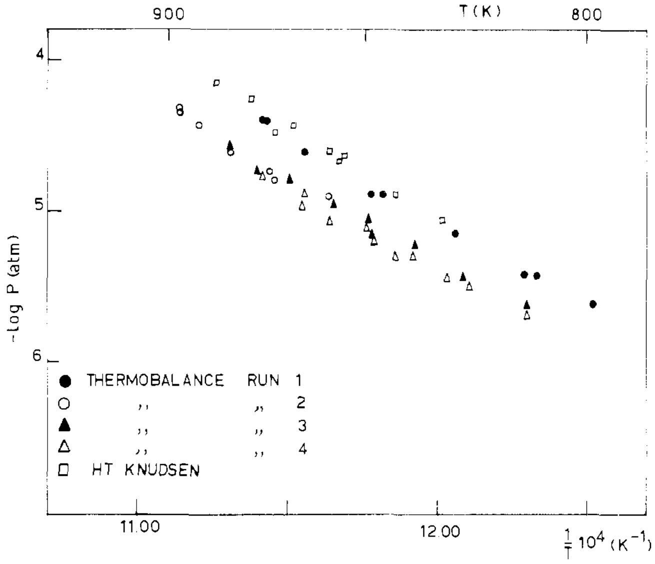

Figure 2. Vapor pressure of $Bi_2Se_3(s)$ measured by Knudsen method.

$Bi_2Se_3(s)$ was studied over four separate runs, in the temperature range 801–899 K, utilizing graphite cells. The results are plotted in Figure 1.

At temperatures higher than 900 K the pressure values tend to increase. Therefore, as explained later, only the initial points, measured when about 2–3% of the original mass of the sample was evaporated, were taken into account. Table I reports the constants of the Clausius–Clapeyron equation for each run, obtained by least-squares treatment of the experimental points. The errors associated are standard deviations.

***Knudsen Effusion*.** The vapor pressure of Bi_2Se_3 was also measured by the mass-loss effusion method employing the well-known equation (*12*)

$$P\,(\text{atm}) = [(2.256 \times 10^{-2})/S](T/M)^{1/2}(\Delta m/\Delta t)K^{-1} \quad (1)$$

where M is the molar mass of $Se_2(g)$, Δm the mass (in grams) of the sample evaporated in the time Δt (in seconds) at the constant absolute temperature T, from a conventional Knudsen cell through an effusion orifice well-known in its area S (in cm^2) and in the thickness of its edges, and K the Clausing's correction factor (*13*).

Experimentally, two different techniques based on this method were used; a thermobalance and a high-temperature Knudsen-effusion assembly.

***A. Thermobalance*.** Thermogravimetric measurements were carried out by using an Ugine-Eyraud Model B60 Setaram thermobalance.

The apparatus and the method have been described previously (*14*). The samples of Bi_2Se_3 were vaporized in crucibles suspended by means of a platinum chain at the center of the furnace. Four runs of vaporizations were carried out by this technique and in Table I are reported the corresponding Clausius–Clapeyron equations derived by the least-squares treatment of the data obtained in the first steps of the vaporizations. The associated errors are standard deviations. The results are also plotted as log P vs. $1/T$ in Figure 2.

***B. High-Temperature Knudsen*.** Vapor pressure measurement of Bi_2Se_3 were carried out by using the high-temperature Knudsen apparatus described previously (*15*). The results are reported ion Table I and plotted in Figure 2. This apparatus has also permitted us to condense the vapor effused from the Knudsen cell over a cold target. Scanning electron microscope (SEM) analysis of the condensed vapor showed that, during the first step of the Bi_2Se_3 vaporization carried out below 900 K, selenium was the only species present in it, whereas going on the vaporization, also the presence of bismuth was observed. This fact led us to suppose that, in the first step of the vaporization, the gas phase is composed practically of only $Se_2(g)$, whereas, subsequently, it is composed also of molecules involving bismuth. Bismuth was also observed in the vapor condensed during the first step of the vaporizations carried out at temperatures higher than 900 K. Consequently, also utilizing this technique, we have taken into account only the vapor pressure values measured when very small portions of the sample were vaporized.

Discussion

As shown in Figures 1 and 2 the vapor pressure data over $Bi_2Se_3(s)$ measured with the torsion- and Knudsen-effusion methods are reproducible and in agreement. By weighting the slopes and the intercepts reported in Table I, proportionally to the number of the experimental points, the following pressure–temperature equation, for the temperature range 800–900 K, was selected:

$$\log P\,(\text{atm}) = (7.81 \pm 0.50) - (10.87 \pm 0.64) \times 10^3/T \quad (2)$$

where the associated errors have been estimated by taking into

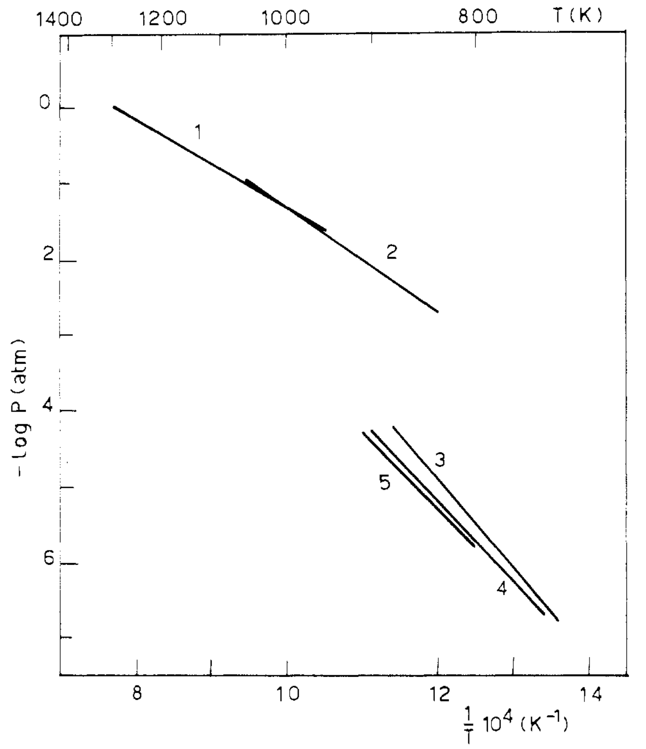

Figure 3. Comparison of the vapor pressure data of Bi_2Se_3(s): (1) Ustyugov (*1*); (2) Ohashi (*2*); (3) Boncheva-Mladenova (*4*); (4) Krestovnikov (*3*); (5) this work.

account the uncertainties in the temperature measurements and in the calibration factors. This equation is reported for comparison in Figure 3 with the data of the literature. Our vapor pressures are slightly lower than those measured by the effusion technique (*3*, *4*) but confirm furthermore the disagreement with the values obtained by utilizing static methods (*1*, *2*). On the basis of the results of the analysis of the condensed vapors, and of the very good agreement between the torsion data and those derived from the Knudsen experiments, involving the molecular weight of the effused vapor, one can deduce that the vapor is practically constituted of Se_2(g), so that, during the vaporization of Bi_2Se_3(s), the condensed phase becomes richer in bismuth. Unfortunately, the phase diagram of Bi–Se is not well-known. Hansen (*16*) reports that BiSe is the only compound poorer in selenium than Bi_2Se_3. On the other hand, Semiletov (*17*) points out the presence of another intermediate compound, Bi_3Se_4, for which he gives the crystallographic parameters. Abrikosov (*18*), lastly, by thermal analysis of the Bi–Se system, reports a region of solid solutions based on BiSe in the range 21–32 atom % in Se and the existence of a new compound, rich in bismuth, Bi_2Se. Consequently, the phase diagram of Abrikosov, also selected by Elliott (*19*), reports the boundary line of this region of solid solutions, corresponding to a ratio Bi:Se equal to 4:5 (Bi_4Se_5 or 4BiSe·Se). At this step of knowledge, the most probable initial vaporization process of Bi_2Se_3(s) occurs involving the formation of the solid solution Bi_4Se_5. Because in each experiment we have taken into account only the vapor pressure values measured during the first steps of the vaporizations, these values can be referred to the pressure of the vapor over the practically pure phase Bi_2Se_3.

The enthalpy change of the vaporization process

$$2Bi_2Se_3(s) \rightarrow Bi_4Se_5(s) + {}^1/_2Se_2(g) \qquad (3)$$

was derived from the slope of the selected equation 2, $\Delta H°(850\ K) = 104 \pm 6$ kJ. Another value of the enthalpy change of reaction 3, $\Delta H°(850\ K) = 114$ kJ, was obtained from the value $P_{Se_2}(g) = 1.05 \times 10^{-5}$ atm calculated with eq 2 at 850 K and from the value $\Delta S°(850\ K) = 87$ J mol^{-1} K^{-1} obtained by utilizing the standard entropy values reported in the literature for Se_2(g) (*11*) and Bi_2Se_3(g) (*20*) and the value $S°(850\ K) = 694$ J mol^{-1} K^{-1} for the solid solution Bi_4Se_5, estimated by the additivity rule. The good agreement between these enthalpy values can be taken as proof of the reliability of the hypothesized reaction of vaporization (eq 3). On this basis we propose as enthalpy change for reaction 3 the value $\Delta H°(850\ K) = 107$ kJ and we believe that the associated uncertainty should not exceed ±8 kJ. By using the heat capacities reported in the literature for Se_2(g) (*11*) and Bi_2Se_3(s) (*21*), and that estimated by the additivity rule for the solid solution, we calculated the standard enthalpy changes for the vaporization of Bi_2Se_3(s) $\Delta H°(298.15\ K) = 127 \pm 8$ kJ.

Considering Bi_4Se_5 as a solid solution of BiSe(s) and Se(s), we derived the standard heat of solution according to the reaction

$$4BiSe(s) + Se(s) \rightarrow Bi_4Se_5(s) \qquad (4)$$

Combining appropriately the standard enthalpy change of the vaporization reaction of Bi_2Se_3(s) with the standard sublimation enthalpy of Se(s) to Se_2(g) (*11*) and with the heats of formation of Bi_2Se_3(s), $\Delta H_f°(298.15\ K) = 140$ kJ mol^{-1} (*22*), and of BiSe(s), $\Delta H_f(298.15\ K) = 52 \pm 6$ kJ mol^{-1} (*23*), we estimated the value $\Delta H(298.15\ K) = -11$ kJ for reaction 4, where the associated error could be larger than 35 kJ. This value of −11 kJ, practically null, can be taken as a confirmation that the solid solution grows during the process of vaporization of Bi_2Se_3(s) and that this solution presents a nearly ideal behavior.

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Registry No. Bi_2Se_3, 12068-69-8.

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