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Atomization energies and enthalpies of formation of the SnBi$_n$ ($n=1-3$) gaseous molecules by Knudsen cell mass spectrometry

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The equilibria involving the gaseous species SnBi, SnBi$_2$, and SnBi$_3$ above the condensed system Bi–Sn contained in a graphite cell have been investigated by the Knudsen effusion technique combined with mass spectrometry. Third law enthalpies for the reactions SnBi$_n$(g)=Sn(cond) $+n$Bi(g), $n=1-3$, were evaluated. By combining the experimental reaction enthalpies with the appropriate thermodynamic data taken from literature, the following atomization energies, $\Delta_a H_0^o$, and enthalpies of formation, $\Delta_f H_{298.15}^o$, in kJ mol^{-1}, have been derived: SnBi, 191.1$\pm$12.0 and 317.5$\pm$12.0; SnBi$_2$, 415.2$\pm$15.0 and 303.0$\pm$15.0; SnBi$_3$, 603.4$\pm$18.0 and 323.0$\pm$18.0. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1461813]

I. INTRODUCTION

Inorganic polyatomic molecules have been extensively studied over the past years, both experimentally through various techniques[1–5] and theoretically employing several quantum chemistry methods.[6–9] Polyatomic molecules play an important role as intermediate state of matter. In fact, the formation of condensed phases is expected to be controlled by the properties of such molecules.

In particular, due to the environmental pollution caused by lead, in the last few years great attention has been directed toward the development of Pb-free electrically conducting materials, such as Sn–Bi alloys.[10] Among of the most promising alternatives to Pb-containing joining materials there is 42Sn–58Bi solder, a good candidate for low temperature applications such as flexible circuits and smart card assemblies, due to its low melting temperature.[11]

The presence of the SnBi and SnBi$_2$ intermetallic molecules in a mass spectrum was observed by Riekert *et al.*[12] during the determination of activities of the Sn–Bi alloys in the temperature range from 1023 to 1323 K. The only spectroscopic investigation on Sn–Bi molecules is that of SnBi by Bondybey and English.[13] Employing a laser to vaporize the metals followed by laser induced fluorescence of the products, they observed the SnBi gas phase spectrum, yielding the vibrational frequency and the bond distance of the ground state.

In the present investigation, we report our results derived from high-temperature mass spectrometric equilibrium measurements for the atomization enthalpies and enthalpies of formation of the SnBi(g), SnBi$_2$(g), and SnBi$_3$(g) molecules.

II. MASS SPECTROMETRIC MEASUREMENTS

The measurements were performed with a Nuclide Corporation 12-90 HT single focusing magnetic deflection-type mass spectrometer. Details of the instrument and the general experimental procedure have been described elsewhere.[14] A graphite Knudsen cell was charged with the eutectic mixture of tin–bismuth, and red phosphorus. The temperature of the Knudsen cell was measured using a Pt vs Pt–10% Rh thermocouple that was calibrated under *in situ* conditions against the solidification points of zinc and copper prior to the investigation. The thermocouple was enclosed in a ceramic sheath. The various species were identified by their mass to charge ratio, shutter effect, ionization efficiency curves, and, where possible, by their isotopic distribution. The ions were produced with 20 eV and 1.0 mA electron emission current. The acceleration voltage used was 4.5 kV, along with a voltage of 1.9 kV at the entrance shield of the electron multiplier.

At the time the measurements on the tin–bismuth species were begun, only trace amounts of phosphorus and of an apparent zinc impurity were present. The vaporization of the liquid tin–bismuth alloy was incongruent by predominant loss of bismuth.

The ionic species detected over the Sn–Bi mixture were Bi$^+$, Bi$_2^+$, SnBi$^+$, SnBi$_2^+$, and SnBi$_3^+$. Their measured ion currents are given in Table I. The ionization energy (IE), in eV, was estimated by the extrapolated voltage difference method[15] as 8.7$\pm$0.8 for the SnBi$_2$ molecule.

Indications for fragmentation were evident from the ionization efficiency curve of Bi$^+$. Rovner *et al.*[16] also observed a contribution of fragment ions to the measured intensities of Bi$^+$ during the evaporation of pure bismuth and of a 1:1 Bi–Pb alloy. They reported a 35% fragmentation contribution to Bi$^+$ intensity. Riekert *et al.*[12] during the determination of activities of the Sn–Bi alloys determined a 30% contribution to the ion current of Bi$^+$ essentially due to the fragmentation of Bi$_2$, using 20 V ionizing electrons. We took into account the fragment contribution to the Bi and SnBi molecules ion currents in the thermodynamic evaluation of the equilibria studied as explained in the Results and Discussion.

The ion intensities measured for the various ions were converted into partial pressures by using the relation p_i

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TABLE I. Measured ion currents,[a] in A, over the Sn–Bi–P system, and third-law values, in kJ mol^{-1}, of the $\Delta_r H_0^o$ for reactions (1), (2), (3).

T (K)	Bi$^+$	Bi$_2^+$	SnBi$^+$	SnBi$_2^+$	SnBi$_3^+$	$\Delta_r H_0^o$ reaction (1)	$\Delta_r H_0^o$ reaction (2)	$\Delta_r H_0^o$ reaction (3)
			Ion intensities					
903	$2.33E-08$	$1.35E-08$	$4.80E-13$	$2.80E-12$		-105.4	120.1	
884	$1.46E-08$	$8.05E-09$	$3.80E-13$	$1.82E-12$	$8.00E-14$	-99.82	121.0	312.0
922	$4.05E-08$	$2.20E-08$	$1.13E-12$	$6.60E-12$	$2.40E-13$	-105.1	120.6	310.3
941	$6.05E-08$	$3.29E-08$	$2.30E-12$	$1.15E-11$	$2.10E-13$	-102.7	121.3	306.2
952	$7.54E-08$	$4.00E-08$	$3.24E-12$	$1.69E-11$	$4.20E-13$	-103.1	122.3	309.9
969	$1.20E-07$	$6.29E-08$	$5.16E-12$	$2.44E-11$	$6.70E-13$	-103.7	120.0	307.9
984	$1.64E-07$	$8.58E-08$	$9.30E-12$	$4.23E-11$	$9.80E-13$	-102.5	121.4	308.2
						-103.2 ± 1.9[b]	121.0 ± 0.8	309.1 ± 2.1

[a]Measured ion currents without corrections for fragmentation (see text).
[b]The error terms are standard deviations.

$=(K/\sigma_i\gamma_i n_i)I_i T$, where K is the instrumental constant, σ_i, γ_i, n_i, and I_i are the cross section, the multiplier gain, the isotopic abundance, and the current intensity of the specific ion, respectively, and T is the temperature. The pressure calibration constants, $k_i=K/(\sigma_i\gamma_i n_i)$, were determined from the known $Bi_2(g)=2Bi(g)$ dissociation reaction. k_{Bi} was deduced by combining the ion intensities of Bi^+ and Bi_2^+, and the literature values of the dissociation enthalpy of $Bi_2(g)$, and the Gibbs energy functions (GEF$_0$) of $Bi(g)$ (Ref. 17) and $Bi_2(g)$. The dissociation enthalpy of $Bi_2(g)$ has been obtained from the formula $D_0^o=D_e^o-ZPE=(199.7\pm0.1)$ kJ mol^{-1}, where the value $D_e^o=(200.7\pm0.1)$ kJ mol^{-1} is from Ehret and Gerber,[18] and the zero-point energy (ZPE) of 1.03 kJ mol^{-1} was taken from Barrow et al.[19] The GEF$_0$ values of $Bi_2(g)$ have been computed according to statistical thermodynamic procedures, using the rigid-rotator harmonic-oscillator approximation[20] and the experimental molecular parameters; the vibrational frequency, $\omega_e=173.0$ cm^{-1},[19] the bond distance, $r_e=2.6597$ Å,[19] of the $Bi_2(g)$ $^1\Sigma_g^+$ ground state, and the transition energies of the first three low-lying excited states, $^3\Sigma_u^+$ (1_u) at 5480 cm^{-1}, $^3\Sigma_u^+$ (0_u) at 8245 cm^{-1}, and $^3\Delta_u$ (2_u) at 9900 cm^{-1} from Polak et al.[21] Table II lists the thermal functions of $Bi_2(g)$. For the calculation of k_{Bi}, the ionization cross section of $Bi_2(g)$ was assumed to be 1.5 times that of $Bi(g)$,[22] and the multiplier gains were measured as 10^5 times 2.67 and 2.30 for Bi^+ and Bi_2^+, respectively. The multiplier gains for $SnBi^+$, $SnBi_2^+$, and $SnBi_3^+$ were assumed equal to that of Bi_2^+. The isotopic abundance of the atomic species

was taken from Kiser,[23] and those of the molecular species were calculated from the isotopic abundance of the constituent elements. The relative ionization cross sections used, in 10^{-16} cm^2, were taken from experimental values reported in the literature for Bi, 7.61 (Ref. 22), and Sn, 9.04,[22] and those for SnBi (12.5), SnBi$_2$ (18.2), and SnBi$_3$ (23.9) were assumed as 0.75 times the sum of the atomic values. The resulting pressure constants, in bar A^{-1} K^{-1}, are 0.0269 for Bi, 0.0584 for SnBi, 0.0401 for SnBi$_2$, and 0.0305 for SnBi$_3$. The uncertainty of the k_i values is estimated to be about 30%.

III. THERMAL FUNCTIONS

The harmonic-oscillator rigid-rotator approximation[20] was used in the evaluation of the Gibbs energy functions, $(G_T^o-H_0^o)/T$ (GEF$_0$), and enthalpy increments, $H_T^o-H_0^o$ (HCF$_0$), of the SnBi(g), SnBi$_2$(g), and SnBi$_3$(g) molecules.

For the SnBi(g) thermal functions the experimental values for vibrational frequency (ω_e) of 183.06 cm^{-1} and bond distance (r_e) of 2.612 Å were taken from Bondybey and English.[13] Stoll[24] performed ab initio and density functional calculations on the SnBi$_n$ ($n=1-3$) molecules employing small-core pseudopotentials and valence $[6s6p4d3f2g]$ basis sets, and using the coupled cluster single and double excitations with the inclusion of perturbative triples [CCSD(T)] level of theory, and the Becke three parameter exchange functional and the Lee–Yang–Parr correlation functional

TABLE II. The Gibbs energy functions, $(G_T^o-H_0^o)/T$ (GEF$_0$), in J K^{-1} mol^{-1}, and the enthalpy increments, $H_T^o-H_0^o$ (HCF$_0$) in kJ mol^{-1}, for the SnBi, SnBi$_2$, and SnBi$_3$ molecules.

Species		298.15	600	700	800	900	1000	1100	1200
					Temperature (K)				
Bi$_2$	$-$GEF$_0$	237.9	262.5	268.0	272.8	277.1	280.9	284.4	287.6
	HCF$_0$	10.26	21.49	25.22	28.96	32.72	36.50	40.32	44.19
SnBi	$-$GEF$_0$	243.1	267.6	273.2	278.1	282.5	286.4	290.0	293.3
	HCF$_0$	10.22	21.58	25.48	29.43	33.44	37.50	41.58	45.68
SnBi$_2$	$-$GEF$_0$	300.6	340.2	349.3	357.1	364.1	370.4	376.1	381.4
	HCF$_0$	16.36	34.98	41.18	47.40	53.62	59.84	66.06	72.29
SnBi$_3$	$-$GEF$_0$	350.9	402.8	414.7	425.1	434.4	442.7	450.3	457.2
	HCF$_0$	21.16	46.06	54.35	62.64	70.94	79.24	87.54	95.85

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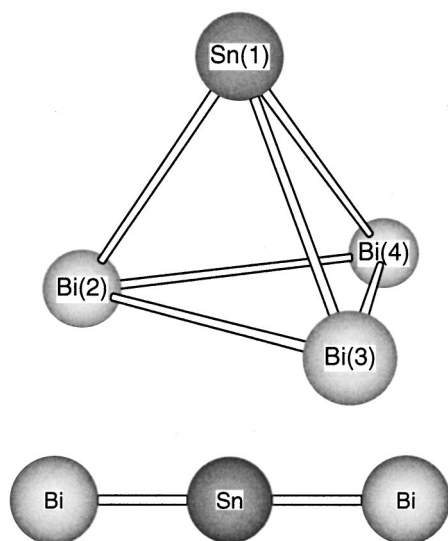
Enthalpies of formation of SnBi$_n$　6959

FIG. 1. Optimized computed geometries of the SnBi$_2$ and SnBi$_3$ molecules.

(B3LYP) method. In particular, including the spin–orbit (SO) coupling by complete active space self-consistent field (CASSCF) calculations Stoll obtained $^2\Pi_{3/2}$ as the SnBi(g) ground state. He also calculated two low-lying states, namely, $^2\Sigma_{1/2}$ and $^2\Pi_{1/2}$, at 2137 cm^{-1} and 8812 cm^{-1}, respectively, above the ground state. The molecular parameters of SnBi(g) for these states are $\omega_e = 194$ cm^{-1} and $r_e = 2.63$ Å for the $^2\Sigma_{1/2}$ state, and $\omega_e = 204$ cm^{-1} and $r_e = 2.66$ Å for the $^2\Pi_{1/2}$ state.

There are no experimental spectroscopic investigations on the SnBi$_2$(g) and SnBi$_3$(g) molecules. In order to calculate the thermal functions needed to evaluate the mass spectrometric equilibrium data of SnBi$_2$ and SnBi$_3$, we used the molecular parameters computed by Stoll.[24]
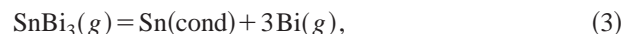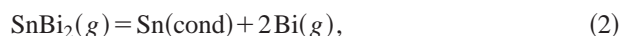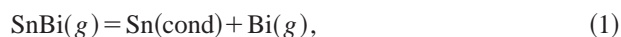
For the SnBi$_2$(g) molecule Stoll computed a linear symmetric $^3\Sigma^-$ ground state, Bi–Sn–Bi. Including the SO coupling, the r(Sn–Bi) bond distance was calculated as 2.68 Å, the symmetric vibrational stretching as 117 cm^{-1}, the antisymmetric vibrational stretching as 267 cm^{-1}, and the bending vibrational mode as 29 cm^{-1} (without SO coupling).

For the SnBi$_3$(g) molecule the calculations by Stoll were performed at the B3LYP level of theory. The ground state was found to be a doublet with a distorted pyramidal geometry, with symmetry reduction to C_s. The optimized geometries used in the thermal functions evaluation of SnBi$_2$ and SnBi$_3$ are shown in Fig. 1. The bond lengths, in Å, are r(Sn1–Bi2) $= r$(Sn1–Bi3) $= 2.956$, r(Sn1–Bi4) $= 3.285$, r(Bi2–Bi3) $= 3.126$, and r(Bi2–Bi4) $= r$(Bi3–Bi4) $= 2.950$. The vibrational frequencies, in cm^{-1}, are 71, 73, 92, 129, 139, and 170.

Table II lists the thermal functions calculated for the SnBi, SnBi$_2$, and SnBi$_3$ molecules.

IV. RESULTS AND DISCUSSION

The following heterogeneous equilibria:

$$SnBi(g) = Sn(cond) + Bi(g), \qquad (1)$$

$$SnBi_2(g) = Sn(cond) + 2Bi(g), \qquad (2)$$

$$SnBi_3(g) = Sn(cond) + 3Bi(g), \qquad (3)$$

were evaluated by the third-law method, using the standard relationship $\Delta_r H_0^o = -RT \ln K_p - T\Delta[(G_T^o - H_0^o)/T]$. Because of the few data and the short temperature range explored during the measurement it was not possible to perform a reliable second-law method analysis.

In order to evaluate the data, the ion currents of Bi$^+$ and SnBi$^+$ were corrected for fragmentation contributions. In particular, the correction applied to the ion intensity of Bi$^+$ was mainly due to fragmentation of Bi$_2$, approximately equal to 30%, meaning that only 70% of the measured ion current of Bi$^+$ is due to primary Bi$^+$. The ion intensities of SnBi$^+$ were corrected for a possible fragment contribution of 10% from the SnBi$_2^+$ intensity, or $I_{\text{correct}}(SnBi^+) = I_{\text{meas}}(SnBi^+) - 0.1 \times [I_{\text{correct}}(SnBi_2^+)]$, and $I_{\text{correct}}(SnBi_2^+) = I_{\text{meas}}(SnBi_2^+)/0.9$. In view of the smaller ion currents of SnBi$_3$ relative to that of SnBi and SnBi$_2$, the contribution from a possible fragment portion of SnBi$_3$ to the smaller mixed molecules is neglected. The activity of Sn in the eutectic Sn–Bi sample increased during the investigation, the sample becoming richer in Sn as Bi was vaporized (predominantly incongruent vaporization). According to Hultgren et al.,[25] Bi–Sn alloys show slightly positive deviations from ideality at 600 K. In the temperature range of the present investigation, they can be considered to obey ideal solution behavior, and hence the activity a_i can equated to the atom fraction χ_i. Therefore, at any temperature the partial pressure of Bi can be related to its activity by the relation $p_{\text{Bi}} = k_{\text{Bi}}I(\text{Bi}^+)T = a_{\text{Bi}}p_{\text{Bi}}^o$, where p_{Bi}^o is the partial pressure of pure bismuth ($a_{\text{Bi}} = 1$). Using this relationship we calculated the average activity of Bi as 0.346 ± 0.009. Consequently, the activity of Sn was obtained as 0.654. We used this value for a_{Sn} in the calculation of the equilibrium constants of reactions (1)–(3).

The reaction enthalpy, $\Delta_r H_0^o$, for reaction (1) was calculated as (-103.2 ± 1.9) kJ mol^{-1}. Using the enthalpy of formation of Sn(l), $\Delta_f H_0^o(\text{Sn},l) = (7.0 \pm 0.2)$ kJ mol^{-1},[17] the enthalpy of formation of Sn(g), $\Delta_f H_0^o(\text{Sn},g) = (301.3 \pm 1.5)$ kJ mol^{-1},[26] and the relation $\Delta_a H_0^o(SnBi_n,g) = \Delta_r H_0^o - \Delta_f H_0^o(\text{Sn},l) + \Delta_f H_0^o(\text{Sn},g)$, the atomization energy, $\Delta_a H_0^o(SnBi,g)$, was derived as (191.1 ± 12.0) kJ mol^{-1}. Here the uncertainty is the overall error, calculated as in Schmude et al.[27] The same thermodynamic relation has been employed in deriving the $\Delta_a H_0^o$ values for SnBi$_2$ and SnBi$_3$. For reaction (2) the $\Delta_r H_0^o$ was calculated as (121.0 ± 0.8) kJ mol^{-1}, and the $\Delta_a H_0^o(SnBi_2,g)$ was obtained as (415.2 ± 15.0) kJ mol^{-1}. From the calculated $\Delta_r H_0^o$ for reaction (3), (309.1 ± 2.1) kJ mol^{-1}, the $\Delta_a H_0^o(SnBi_3,g)$ was derived as (603.4 ± 18.0) kJ mol^{-1}.

The enthalpies of formation for SnBi, SnBi$_2$, and SnBi$_3$ have been obtained from the $\Delta_r H_0^o$ and the enthalpies of formation of Bi(g) and Sn(l), employing the relation $\Delta_f H_T^o(SnBi_n,g) = \Delta_f H_T^o(\text{Sn},l) + n\Delta_f H_T^o(\text{Bi},g) - \Delta_r H_T^o$, where T is 0 or 298.15 K. The thermodynamic properties for the SnBi, SnBi$_2$, and SnBi$_3$ molecules have been summarized in Table III.

It is interesting to compare trends in the dissociation energies of the Sn–Bi molecules with the homonuclear clus-

TABLE III. Thermodynamic properties for the SnBi, SnBi$_2$, and SnBi$_3$ molecules. All values are in kJ mol^{-1}.

Species	$\Delta_a H_0^o$	$\Delta_a H_{298.15}^o$	$\Delta_f H_0^o$	$\Delta_f H_{298.15}^o$
SnBi	191.1 ± 12.0	193.3 ± 12.0	320.0 ± 12.0	317.5 ± 12.0
SnBi$_2$	415.2 ± 15.0	417.4 ± 15.0	305.7 ± 15.0	303.0 ± 15.0
SnBi$_3$	603.4 ± 18.0	607.0 ± 18.0	327.3 ± 18.0	323.0 ± 18.0

ters of group 14 and 15 elements, Sn$_n$ and Bi$_n$ ($n = 2-4$). First of all, there is a systematic decrease in the dissociation energies of the homonuclear clusters from the top to the bottom within a group. A similar decrease also occurs in the ionization energy values, therefore these trends are quantitative in the framework of bond energy arguments. For instance, we can consider the D_0^o of SnBi as the average of the D_0^o of the homonuclear diatomics, Sn$_2$ and Bi$_2$. Employing $D_0^o(\text{Sn}_2,g) = 183.4$ kJ mol^{-1} from Pak *et al.*[28] and $D_0^o(\text{Bi}_2,g) = 199.7$ kJ mol^{-1} (see Mass Spectrometric Measurements), the average is 191.6 kJ mol^{-1}, the same as the experimental value of 191.1 kJ mol^{-1}. In an equivalent sense, the $\Delta_a H_0^o$ of triatomic SnBi$_2$ might be considered as the average of the homonuclear clusters $\Delta_a H_0^o$ values, two-thirds the atomization energy of Bi$_3$ (Ref. 16) plus one-third the atomization energy of Sn$_3$,[29] namely, 374.2 kJ mol^{-1}. The experimental value, approximately 10% larger than the average value, shows an increased stability for the SnBi$_2$ molecule. This can be explained in view of the presence of multiple bonds between Sn and Bi in the linear symmetric geometry, Sn–Bi–Sn, whereas Sn$_3$ and Bi$_3$, having bent structures, have somewhat smaller multiple bonds character. Sn$_3$ has been investigated by Balasubramanian[30] by using complete-active-space MCSCF (CASSCF) followed by multireference-singles and doubles configuration interaction (MRSDCI) calculations. He calculated the Sn$_3$ ground state as $^1A_1$ with a bond distance of 2.72 Å and an apex angle of 83°. Balasubramanian *et al.*[31] computed the optimized geometry of Bi$_3$ by CAS-MCSCF followed by MRCI calculations. They found a Jahn-Teller distorted $^2A_2$ ground state for Bi$_3$ with a bond distance of 2.94 Å and an apex angle of 65.6°. These bonds lengths are longer than that calculated for Sn–Bi in SnBi$_2$, 2.68 Å.

Averaging the $\Delta_a H_0^o$ for Sn$_4$ and Bi$_4$, one-fourth the $\Delta_a H_0^o(\text{Sn}_4,g)$ (Ref. 32) plus three-fourths the $\Delta_a H_0^o(\text{Bi}_4,g)$,[16] the value obtained as 630.0 kJ mol^{-1} is larger than the experimental $\Delta_a H_0^o(\text{SnBi}_3,g)$. This means a somewhat lower stability than that expected for SnBi$_3$. The structure of Sn$_4$ has been calculated by Jackson[33] as a planar rhombus (D_{2h}) with Sn–Sn bond distances of 2.86 Å, whereas the Bi$_4$ structure has been computed by Zhang and Balasubramanian[34] as a tetrahedron with Bi–Bi bond lengths of 3.12 Å, and the calculated geometry of SnBi$_3$ is a distorted pyramid.[24]

The relative thermodynamic stability of SnBi, SnBi$_2$, and SnBi$_3$ can be derived from the fragmentation energies, $\Delta_a H_0^o(\text{SnBi}_n,g) - \Delta_a H_0^o(\text{SnBi}_{n-1},g)$. The corresponding values are, in kJ mol^{-1}, 188.2, 224.1, and 191.1 for SnBi$_3$, SnBi$_2$, and SnBi, respectively. The values confirm the quali-

tative conclusion of the higher stability of SnBi$_2$ with respect to the other clusters here investigated.

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