Dissociation Energy of the SbPb Molecule from Mass Spectrometric High Temperature Studies

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Z. Naturforsch. **36a**, 913–914 (1981);
received July 4, 1981

The observation of the gaseous BiPb molecule [1, 2] suggests the existence of heteronuclear diatomic molecules of lead with the group V-b elements. The present paper reports on the identification of the SbPb(g) molecule and the determination of its dissociation energy by mass spectrometric Knudsen-effusion method.

Experimental

The mass spectrometer and the general experimental technique have been described previously [3]. In the present investigation, the Knudsen cells were made of molybdenum and contained samples consisting of Sb(97%) and Pb(3%) placed in a stainless steel liner. The channel orifice of the cells was of 0.5 mm diameter and 0.5 mm length.

Results

During the vaporization in the temperature range from 800 to 1030 K, the ionic species Pb^+, Sb^+, Sb_2^+, Sb_3^+, Sb_4^+ and $SbPb^+$ were identified by their mass-to-charge ratio and isotopic patterns. The appearance potentials of Sb^+, Sb_2^+ and $SbPb^+$ ions were measured as 8.8, 8.5 and 7.5 eV, respectively, with reference to that of Pb^+ (7.4 eV) as a standard. The values of the appearance potentials of Sb^+ and Sb_2^+ ions, which are close to the previous measurements [4, 5], and of $SbPb^+$ indicate these ions to be parent.

The intensities (I_i) of the ions were measured at various temperatures at electron energies 2 eV above the respective appearance potentials and were used to calculate partial pressures of the corresponding neutrals by the equation

$$P_i = F I_i T / \gamma_i \sigma_i ,$$

where γ_i is the isotopic abundance and σ_i the ionization cross section of the ions i. The values of σ for Sb and Pb were taken from the tables of Mann [6], while those for Sb_2 and SbPb were estimated as the sums of the atomic cross sections multiplied by a factor of 0.75. The instrumental factor F was determined from the measured value of the equilibrium constant for the reaction $Sb_2(g) = 2\,Sb(g)$ and the known value of the dissociation energy of $Sb_2(g)$ [4, 5].

The partial pressures of the observed species were used to evaluate the equilibrium constants and then the enthalpy changes for the reactions

$$Sb(g) + Pb(g) = SbPb(g) , \qquad (1)$$

$$Sb_2(g) + Pb(g) = SbPb(g) + Sb(g) \qquad (2)$$

by the second and third law methods, according to the relations

$$\Delta H_T^\circ(\mathrm{II}) = -R\,\mathrm{d}\ln K/\mathrm{d}(1/T) ;$$
$$\Delta H_0^\circ(\mathrm{II}) = \Delta H_T^\circ(\mathrm{II}) - \Delta(H_T^\circ - H_0^\circ) ;$$
$$\Delta H_0^\circ(\mathrm{III}) = -RT\ln K + T\Delta\Phi_0^\circ .$$

The values of the thermodynamic functions $(H_T^\circ - H_0^\circ)$ and $\Phi_0^\circ = -(G_T^\circ - H_0^\circ)/T$ for $Sb(g)$, $Sb_2(g)$ and $Pb(g)$ were taken from the tables of Hultgren et al. [7], and those for $SbPb(g)$ were calculated by the statistical mechanical procedures for the harmonic oscillator and rigid rotator. The interatomic distance $r_e(SbPb) = 29.0$ nm was evaluated as the sum of the Pauling metallic radii of Sb and Pb; the vibration frequency $\omega(SbPb) = 500\ cm^{-1}$ was estimated from the Guggenheimer relation [8] for polar bonded diatomic molecules. The electronic contribution to the thermodynamic functions was computed using a ground state

Table 1. Estimated thermodynamic functions of $SbPb(g)$.

T/K	$H_T^\circ - H_0^\circ$ (kJ mol^{-1})	$-(G_T^\circ - H_0^\circ)/T$ (J mol^{-1} K^{-1})
298	9.26	241.44
700	23.70	269.18
800	27.38	273.73
900	31.07	277.78
1000	34.78	281.43
1100	38.49	284.75
1200	45.50	287.81
1300	45.92	290.63

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Table 2. Equilibrium constants and enthalpy changes for the reactions

$Sb(g) + Pb(g) = SbPb(g)$ (1) and

$Pb(g) + Sb_2(g) = SbPb(g) + Sb(g)$ (2),

$P_0 = 1.01325 \times 10^5$ Pa.

	T/K	$\ln(K_1P_0)$	$\ln K_2$	ΔH_1/kJ mol^{-1}	ΔH_2/kJ mol^{-1}
Run 1	957	10.095	− 13.984	− 159.4	133.1
	985	10.222	− 13.420	− 165.3	132.2
	968	10.034	− 13.491	− 160.7	130.5
	1005	9.647	− 13.044	− 163.8	131.8
	1030	9.243	− 12.528	− 164.4	130.5
		ΔH°_0 Average,	3rd law	− 162.7 ± 2.7	131.6 ± 1.1
			2nd law	− 91.5 ± 31.5	150.1 ± 18.2
Run 2	880	12.409	− 15.760	− 162.8	135.6
	900	10.765	− 16.161	− 154.4	141.4
	926	10.556	− 14.940	− 157.3	136.0
	954	9.881	− 14.890	− 156.9	139.7
	986	9.255	− 14.058	− 157.3	137.6
	1029	9.129	− 13.389	− 163.6	138.1
		ΔH°_0 Average,	3rd law	− 158.7 ± 3.6	138.1 ± 2.5
			2nd law	− 145.9 ± 30.5	134.7 ± 20.3
Run 3	1029	8.242	− 13.660	− 156.1	140.2
	1015	9.056	− 14.415	− 160.7	144.8
	995	9.377	− 14.956	− 159.8	146.4
	958	9.852	− 15.512	− 157.3	145.2
	950	10.435	− 15.633	− 160.7	145.2
	926	11.227	− 15.052	− 162.3	136.8
		ΔH°_0 Average,	3rd law	− 159.5 ± 2.3	143.1 ± 3.8
			2nd law	− 195.1 ± 23.3	116.6 ± 43.7

degeneracy $g_i = 2$ for SbPb(g), by analogy with the BiPb(g) molecule [1].

The numerical values of the thermodynamic functions of SbPb(g) are given in Table 1. The equilibrium constants and enthalpy changes for the reactions (1) and (2) from 3 different runs are listed in Table 2.

The uncertainties quoted were calculated as standard deviations from the mean. The uncertainties associated with the 2nd law treatment are considerably larger because of the rather limited temperature range of the measurements and small number of experimental points. The final mean values were calculated giving a weight of 2 to the 3rd law values.

The enthalpy change of the reaction (1) gives directly the dissociation energy of SbPb molecule:

$$- \Delta H^\circ_0(1) = D^\circ_0(\mathrm{SbPb}) = (154.9 \pm 10.4)\ \mathrm{kJ\ mol^{-1}}.$$

From the enthalpy change of the reaction (2), $\Delta H^\circ_0(2) = (136.4 \pm 10.8)$ kJ mol^{-1} and the known dissociation energy of $Sb_2(g)$, $D^\circ_0[Sb_2(g)] = (296.6 \pm 6.3)$ kJ mol^{-1} [4, 5], one obtains D°_0(SbPb) $= (160.2 \pm 10.8)$ kJ mol^{-1}, in good agreement with the value from reaction (1). A mean value of both results gives $D^\circ_0(\mathrm{SbPb}) = (157.6 \pm 10.6)$ kJ mol^{-1}.

The experimentally determined dissociation energy is considerably lower than the value (188.8 kJ · mol^{-1}) calculated by applying the Pauling rule for polar bonded diatomic molecules [9].

Acknowledgement

Support of this research from the funds for scientific cooperation between Germany and Yugoslavia through the International Bureau of the Kernforschungsanlage Jülich is acknowledged. Thanks are also due to Mrs. R. Jung for technical assistance.

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