A third-law treatment of the data for reaction 3 was made on the assumption that the entropy of BiBr could be calculated as a rigid-rotor harmonic oscillator in a triplet ground electronic state. (The internuclear distance was estimated to be 2.3 Å; the fundamental vibration frequency of 209 cm^{-1} was taken from Herzberg;[14] no contribution from excited electronic states was included because the first excited state[14]—20,000 cm^{-1}—is too high.) The ΔH_{298} from this calculation increased from 27.9 kcal, for the experimental equilibrium constant at 870°K, to 28.6 kcal for the 983°K constant. The large trend in values and their divergence from the second-law value (24.5 kcal) indicate some inconsistency. We presume that the inconsistency lies in the value used for the entropy of BiBr because the other quantities used in the calculation are known well enough that they could not give rise to so large an inconsistency.

Since BiBr is a heavy molecule of nonzero electron spin, the nuclear rotation and electronic motions couple in some fashion between Hund's cases b and c.[14] The rotational energy levels for such a molecule are seriously perturbed from those of case b and depend on the degree of coupling. The entropy depends, through the partition function, on the accessible energy levels and cannot be calculated accurately without further information about the energy levels.

We shall therefore use the second-law treatment of reaction 3 to derive the entropy of BiBr. At 935°K (the midtemperature of the measurements of ref 12). the enthalpy change was found to be 21.3 kcal and the equilibrium constant 3.3×10^{-2} $atm^{2/3}$, so the standard free energy change is 6.4 kcal and the standard entropy change 16 eu. (This method of evaluating the entropy change is probably more accurate than that used in ref 12.) The absolute entropies of Bi(l)[12] and $BiBr_3(g)$[4] at 935°K are 26.3 and 114.3 eu, respectively. These results give a value of 72 ± 2 eu for the absolute entropy of BiBr at 935°K. (A value of 73.6 eu at 935°K is calculated from the molecular constant data assuming a singlet electronic state obeying Hund's case b coupling and an internuclear distance of 2.3 Å.)

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The Enthalpy of Formation of Bismuth(III) Iodide and the Dissociation Energy of Bismuth(I) Iodide[1]

BY DANIEL CUBICCIOTTI

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The enthalpy of formation of solid BiI_3 was determined, by solution calorimetry of Bi, I_2, and BiI_3 in a solvent of $HBr-Br_2$, to be −36.0 kcal/mole at 298°K. Literature data on the vaporization of BiI_3 were used to evaluate the enthalpy of atomization of gaseous BiI_3 (129.9 kcal/mole at 298°K) and the absolute entropy of the solid (53.7 eu) from that calculated for the gas. The dissociation energy of gaseous BiI (51.5 kcal/mole at 0°K) and its absolute entropy (73.6 eu) were derived from literature data on the equilibrium among Bi, BiI_3, and BiI.

Until the present, there has been no reliable evaluation of the energy of the Bi–I bond. The spectroscopic value[2,3] for the dissociation energy of BiI is unreliable because it involves a long extrapolation from the low-lying vibrational levels to the dissociation limit. We have determined the dissociation energy by measuring the enthalpy of formation of $BiI_3(s)$ and then combining it with the enthalpy of vaporization of BiI_3 and the enthalpy of reduction of gaseous BiI_3 to BiI.

Enthalpy of Formation of BiI_3.—This quantity was evaluated by measuring the heat of solution of equivalent amounts of Bi and I_2 in a solution of Br_2 in HBr and, separately, the heat of solution of BiI_3 in the same solvent. The procedure is described in ref 4. This solvent will be referred to as "solution" in the equations below to simplify writing them. The Bi used was five nines grade from American Smelting and Refining Co. It was found that powder that passed a nominal 150-μ sieve dissolved rapidly enough. The iodine was Baker's Analyzed Reagent grade. It was simply granulated before use. The BiI_3 was made by the method described in ref 5.

Six determinations of the heat of solution of equivalent amounts of Bi and I_2 ranging from 0.1 to 0.23 g of Bi (and I_2 weights $^{381}/_{209}$ as large) in the solvent gave

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(1) This work was supported by the Research Division of the U. S. Atomic Energy Commission under Contract No. AT(04-3)-106.

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an enthalpy change of −82.1 ± 0.5 kcal/mole for the reaction

$$\mathrm{Bi(s)} + {}^{3}/_{2}\mathrm{I_2(s)} + \text{solvent} = \mathrm{BiI_3(soln)} \qquad (1)$$

Seven determinations of the heat of solution of BiI$_3$ were made and resulted in a value of −46.1 ± 0.5 kcal/mole for the enthalpy change of the reaction

$$\mathrm{BiI_3(s)} + \text{solvent} = \mathrm{BiI_3(soln)} \qquad (2)$$

Therefore, the enthalpy change for the formation reaction

$$\mathrm{Bi(s)} + {}^{3}/_{2}\mathrm{I_2(s)} = \mathrm{BiI_3(s)} \qquad (3)$$

is −36.0 ± 1.0 kcal/mole at 298°K. Wilcox and Bromley[6] have estimated the enthalpy of formation to be −26 ± 5 kcal and Brewer, *et al.*,[7] give a value of −24 kcal.

Thermodynamics of Vaporization of BiI$_3$.—The vapor pressure data reported in ref 8 were treated by the second-law method described by Cubicciotti.[9] Heat capacities were taken from ref 5. A least-squares treatment of the data gave the enthalpy and entropy of sublimation: $\Delta H^\circ_{298} = 32.09 \pm 0.13$ kcal/mole and $\Delta S^\circ_{298} = 43.85 \pm 0.19$ eu. (These values are in good agreement with those obtained graphically in ref 8.)

Manley and Williams[10] have determined the fundamental vibration frequencies for BiI$_3$ and estimated the molecular geometry. They reported a value of S°_{298} = 97.58 eu for the absolute standard entropy of the gas. This leads to a value of 53.73 ± 0.2 eu for the entropy of the crystal at 298°K—a value somewhat lower than that given in ref 5. Since the value from ref 5 was based on estimated vibration frequencies, it is less reliable than the present one. The entropies and free energy functions for solid BiI$_3$ given in ref 5 must be revised in the light of this new entropy. The corrected values are given in Table I.

TABLE I

CORRECTED ENTROPIES AND FREE ENERGY FUNCTIONS FOR CONDENSED PHASES OF BiI$_3$

Temp, °K	S°_T, eu	$-(G^\circ_T - H^\circ_{298})/T$, eu
298	53.7	53.7
400	61.0	54.7
500	66.5	56.5
600	71.3	58.6
681.8(s)	74.9	60.4
681.8(l)	88.6	60.4
700	89.6	61.1
800	94.4	65.0
900	98.6	68.4
1000	102.4	71.7

Dissociation Energies.—The enthalpy of dissociation of gaseous BiI$_3$ to the atoms in their ground states is evaluated in Table II. Addition of the enthalpy increment values ($H^\circ_{298} - H^\circ_0$) of BiI$_3$(g) (5.1 kcal/mole),[10] I(g) (1.5 kcal/mole),[11] and Bi(g) (1.5 kcal/mole)[11] allows one to evaluate the dissociation energy to atoms at 0°K, namely, 128.9 ± 1.1 kcal/mole (5.59 ± 0.05 eV).

TABLE II

ENTHALPY OF DISSOCIATION OF GASEOUS BiI$_3$ AT 298°K

Reaction	ΔH°_{298}, kcal/mole	Ref
$\mathrm{Bi(s)} + {}^{3}/_{2}\mathrm{I_2(s)} = \mathrm{BiI_3(s)}$	−36.0 ± 1.0	This work
$\mathrm{BiI_3(s)} = \mathrm{BiI_3(g)}$	32.1 ± 0.1	This work
${}^{1}/_{2}\mathrm{I_2(s)} = \mathrm{I(g)}$	25.5	11
$\mathrm{Bi(s)} = \mathrm{Bi(g)}$	49.5	13
$\mathrm{BiI_3(g)} = \mathrm{Bi(g)} + 3\mathrm{I(g)}$	129.9 ± 1.1	

The second-law treatment in ref 12 of the equilibrium

$${}^{2}/_{3}\mathrm{Bi(l)} + {}^{1}/_{3}\mathrm{BiI_3(g)} = \mathrm{BiI(g)} \qquad (4)$$

gave an enthalpy change of 21.1 ± 0.8 kcal/mole at the midtemperature of those studies (913°K). The enthalpy increments ($H_{913} - H_{298}$) for these reactants are: Bi, 6.9;[13] BiI$_3$, 11.9;[10] BiI, 5.4 kcal/mole.[14] Thus ΔH°_{298} for reaction 4, with Bi in the crystalline state, is 24.3 ± 0.8 kcal/mole. From this value and the data in Table II the enthalpy change of the dissociation reaction

$$\mathrm{BiI(g)} = \mathrm{Bi(g)} + \mathrm{I(g)} \qquad (5)$$

is 52.0 ± 1.1 kcal/mole at 298°K. The dissociation energy at 0°K (derived from this value and the enthalpy increments ($H_{298} - H_0$) of Bi(g), 1.5 kcal/mole;[11] BiI(g), 2.5 kcal/mole;[14] I(g), 1.5 kcal/mole[11] is 51.5 ± 1.1 kcal/mole (2.24 ± 0.05) eV. The spectroscopic values for the dissociation energy of BiI are not accurate because they rely on long extrapolations from low-lying vibrational states. Herzberg[2] has given 2.7 eV (doubtful) and Gaydon[3] reported 2.5 ± 1 eV. Our value is slightly smaller than these but within their range of uncertainty.

Entropy of BiI.—The absolute entropy of gaseous BiI can be derived from the second-law treatment of reaction 4. At 913°K, the enthalpy change was 21.1 ± 0.8 kcal/mole. From the equilibrium constant at 913°K, the free energy change, ΔG°_{913}, is 6.2 ± 0.01; hence, ΔS°_{913} is 16.3 ± 0.9 eu. The absolute entropies at 913°K for Bi(l)[13] and BiI$_3$(g)[10] are 26.1 and 119.6 eu. Therefore, the absolute entropy of BiI(g) by this second-law treatment is 73.6 ± 0.9 eu.

An exact calculation of the entropy from molecular constants is not possible at this time because the rotational constant is not known. One can estimate the internuclear distance to be 2.5 Å by comparing BiCl,

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[14] Calculated from molecular constant data. The vibration frequency used was 164 cm^{-1}, from ref 2; the internuclear distance was assumed to be 2.5 Å.

TlCl, and TlI. If one also assumes that the electronic and nuclear rotational motions couple according to Hund's case c[2] (and so the molecule is effectively in a singlet state), the entropy calculated is 75 eu at 913°K. This value is just outside the uncertainty range of the experimental value.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AND THE INORGANIC MATERIALS RESEARCH DIVISION OF THE LAWRENCE RADIATION LABORATORY, BERKELEY, CALIFORNIA 94720

Potassium Germyltrihydroborate

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Potassium germyltrihydroborate, KH_3GeBH_3, is formed by the reaction of diborane with potassium germyl. The salt melts with little decomposition at 98–99° and decomposes at 200° to germanium, germanium hydrides, hydrogen, and potassium hydroborate. Alkaline aqueous solutions are fairly stable, but addition of acid causes complete hydrolysis to germane, hydrogen, and boric acid. The infrared and nmr spectra are given.

Although many compounds containing carbon–boron bonds are known, only two compounds containing germanium–boron bonds have been characterized: $[(CH_3)_4N][(C_6H_5)_3GeB(C_6H_5)_3]$ and $[CH_3(C_6H_5)_3P][(C_6H_5)_3GeB(C_6H_5)_3]$.[1] The purpose of this study was to prepare and characterize an unsubstituted hydrogen analog of these compounds: potassium germyltrihydroborate, KH_3GeBH_3. A previous attempt to prepare the corresponding silicon compound, KH_3SiBH_3, had been unsuccessful.[2] Nevertheless, we had two reasons to be optimistic about the synthesis of the germanium compound. First, the carbon compounds LiH_3CBH_3,[3] $LiB(CH_3)_4$,[4] and $NaB(C_2H_5)_3H$[5] have been prepared and are apparently reasonably stable compounds, and many germanium compounds behave more like the analogous carbon compounds than the analogous silicon compounds.[6] Second, data from a study of the reaction of Ge_2Cl_6 with sodium hydroborate suggested that NaH_3GeBH_3 was formed as a stable intermediate.[7] In this study, the synthesis was accomplished by the direct reaction of potassium germyl ($KGeH_3$) with diborane.

Experimental Section

General Material.—Volatile materials were manipulated by standard vacuum-line techniques. Noncondensable gases were collected and measured using a Toepler pump and gas buret, respectively. Moisture- and air-sensitive solids were handled in a polyethylene glove bag flushed with dry argon or nitrogen.

Reagents.—The 1,2-dimethoxyethane was dried with a sodium–potassium alloy and degassed by distilling it into a −78° trap while pumping. Diethyl ether was dried with sodium diphenylketyl[8] and degassed by distilling it into a −196° trap while pumping. Potassium was distilled directly into the reactor *in vacuo*. Germane[9] and diborane[10] were prepared and purified by standard methods.

The identity and purity of volatile materials were determined by infrared spectrometry[11–15] with Perkin-Elmer Infracord spectrophotometers (Models 137B and 137), by mass spectrometry with a Consolidated Engineering Corp. mass spectrometer, Model 21-620, by molecular weight determinations, and by vapor pressure measurements.[16,17] Volatile mixtures were separated, when possible, by fractional condensation in appropriate cold traps. Mixtures of germane, digermane, trigermane, diborane, and 1,2-dimethoxyethane were analyzed for the first four constituents by the following procedure. The mixture was treated with excess 1 *M* aqueous HCl at room temperature for several minutes; the evolved hydrogen was separated and measured, and the equivalent amount of diborane was calculated. The remaining mixture was then separated by fractional condensation in traps cooled to −78° (solvent), −95° (trigermane), −160° (digermane), and −196° (germane).

Reaction Apparatus.—A typical reaction apparatus is illustrated in Figure 1. The apparatus was designed to permit the distillation of potassium from A into B, followed by the sealing off of tube A. Solvent and volatile reactants were distilled into vessel B, and, after reaction, the mixture was inverted and filtered through the fritted disk into C. In one experiment, a similar apparatus with a series of three fritted disks and receiving vessels was used, so that a sequence of reactions and filtrations could be carried out.

Potassium Germyl.—Potassium germyl was prepared[18] by the reaction (during about 36 hr) of excess germane with potassium in 1,2-dimethoxyethane at −63.5°

$$K + GeH_4 \longrightarrow KGeH_3 + {}^1/_2H_2 \tag{1}$$

In a typical synthesis, 0.435 mmol of germane was consumed, with the evolution of 0.226 mmol of hydrogen (theoretical, 0.218).

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