orbital is generated which in part serves to bond hydrogen. Evaluation of the symmetry orbital coefficients in the first two cases, the most important in the present discussion, shows that those orbitals which contribute the principal positive overlap and hence bonding to these intermediate solutions are also those which have the greatest overlap with the s orbital. Addition of s to the basis set will thus be expected to increase the contributions of these symmetry orbitals in the strongly bonding solutions and therefore to lessen their contribution in and raise the energy of the middle eigenvalue, as observed. The prediction is weakest for the t_{2g} orbital in the cube as the t_{2u} and e_g solutions (where s does not mix) are only slightly lower in energy.[40] The lack of a change in the number of electrons in ground state for the two five-atom cages (D_{3h}) appears to result from the fact that the highest bonding solution (e'', no s) is more strongly bonding (Figure 4). In addition, a boron cation would be obtained if this were to go antibonding; the presence of carbon in the known $B_3C_2H_5$ may play an important role in increasing the electron affinity as well as in reducing the charge.

The presence of the large s–p and p–d separations in bismuth, *e.g.*, 9.5 and 10 ev to the lowest sp^3 (^5S) and s^2p^2d (^3D) states in Bi^+, respectively,[7] would appear to be of paramount importance for the existence of these compounds as well as for their remarkable resemblance to the polyborane anions just considered since this causes the bonding to be derived from substantially p orbitals only. The implications that certain bonding arrangements are preferred with such diverse elements is not entirely surprising. The relative surplus of orbitals over electrons with transition elements thus appears to require tight binding of anions as well.

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The Thermodynamic Properties of Bismuth(I) Bromide and Bismuth(III) Bromide[1]

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Literature data on the vaporization of $BiBr_3$ were reevaluated by a second-law method to derive the enthalpy and entropy of sublimation (27.56 kcal/mole and 43.36 eu, respectively, at 298°K). The absolute entropy of the solid (45.5 eu) was derived from the latter value and the absolute entropy of the gas as calculated from molecular constants. The free energy functions for the condensed phases up to 1000°K are tabulated. The enthalpy of formation of solid $BiBr_3$ was measured by solution calorimetry and found to be −66.0 kcal/mole at 298°K. This leads to a value of 168.1 kcal/mole for the enthalpy of atomization of gaseous $BiBr_3$ at 298°K. A second-law treatment of literature data on the equilibrium among $BiBr_3$, Bi, and BiBr led to a dissociation energy of 63.9 kcal/mole, for gaseous BiBr, in good agreement with the literature spectroscopic value. A value of 72 eu was derived for the absolute entropy of gaseous BiBr.

Introduction

The present work started as a reevaluation of our earlier study[2] of the equilibrium $^2/_3Bi(l) + {}^1/_3BiBr_3(g) = BiBr(g)$ similar to that made for the chloride system.[3] The vibration frequencies of $BiBr_3$ have recently been determined[4] and so have the enthalpy increment data[5] for the solid above room temperature. As the evaluation proceeded it became apparent that a measurement of the enthalpy of formation of solid $BiBr_3$ would serve as a check on the enthalpies of formation based only on the spectroscopic dissociation energy of BiBr. Accordingly, enthalpies of solution of Bi, Br_2, and $BiBr_3$ were measured in an aqueous Br_2–HBr solvent.

The Enthalpy of Formation of $BiBr_3$

Calorimeter.—A simple solution calorimeter was made from a 1-pint Pyrex dewar with a thermistor as a thermometer. The solution was stirred by a Teflon lift stirrer operated by a chain drive and constant-speed dc motor. The dewar top was closed by a cork which supported two 15-mm glass tubes, closed by rubber stoppers. The substances to be added to the solvent in the dewar were contained in those tubes, and the rubber stoppers were pushed out with glass rods when it was time to mix the components. The dewar as-

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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.

(2) D. Cubicciotti, *J. Phys. Chem.*, **64**, 1506 (1960).

(3) D. Cubicciotti, *ibid.*, **71**, 3066 (1967).

(4) T. R. Manley and D. A. Williams, *Spectrochim. Acta*, **21**, 1467 (1965). The molecular constants used were specified in Table I of this reference. No electronic contribution to the entropy was assumed.

(5) D. Cubicciotti and H. Eding, *J. Chem. Eng. Data*, in press.

sembly was encased in a wooden box to protect it from sudden changes in air temperature. Although the calorimeter was quite simple, the results have been found to be accurate to slightly more than 1%, as evidenced below.

The thermistor, which had a resistance of about 10,000 ohms, was obtained from YSI, Yellow Springs, Ohio. It was made one leg of a simple bridge energized by a mercury battery. The unbalance of the bridge was measured with a Leeds and Northrup K-3 potentiometer and a 1-mV span recorder. The sensitivity of this combination was approximately 0.003°/cm of recorder pen travel. The thermistor was calibrated from 19 to 26° against a mercury in-glass Parr thermometer. All measurements were made between 22 and 23°; however, the heat capacity differences of the substances involved in the reactions studied were all small enough that the enthalpy changes could be assumed to be the same as values at 298°K, within experimental error.

Calibrations.—The calorimeter constant was determined by two methods. Electrical calibrations were made at 0.5° intervals from 19 to 25° with 200 ml of pure water in the calorimeter. The second method was based on the heat of neutralization of 200 ml of 0.025 *N* HCl by 1.5 ml of 4.0 *N* NaOH (a 20% excess); 15 such calibrations were made. The enthalpy changes accompanying the neutralization reaction and the dilution of the excess NaOH were calculated from the data in NBS Circular 500.[6] The two calibration methods gave the same value for the calorimeter constant, which was 28.0 ± 1.0 cal/deg.

The heat capacities of the solutions used in the calorimeter must be known in order to evaluate the enthalpy change from the measured temperature change. These were determined by mixing 1.00 ml of 4.00 *N* NaOH with 200 ml of the acid solvent used. The enthalpy changes for the reactions, which included neutralization and dilution, were calculated from the data in Circular 500. For 2 *N* HBr (mole ratio of 1 HBr to 26.25 H_2O) the specific heat determined in this way was 0.804 ± 0.01 cal/g deg while the value calculated from Parker's evaluation[7] was 0.809 cal/g deg. This agreement indicates that the accuracy of our measurements was within about 1%. The solvent used in the experiments discussed below was 200 ml of 2 *N* HBr plus 2.00 ml of liquid Br_2. Four determinations of its specific heat gave 0.800 ± 0.007 cal/g deg.

A check on the over-all accuracy of the method was made by determining the heat of mixing 2.5 ml of $AgNO_3$ solution (1:94.13 mole ratio of $AgNO_3$ to H_2O) with 200 ml of 2 *N* HBr, corresponding to the reaction

$$AgNO_3\text{-}H_2O\ (1:94.13) + HBr\ (2\ N) = AgBr(s) + HNO_3\ (\text{in } 2\ N\ HBr) \qquad (1)$$

Two determinations of the enthalpy of mixing 2.5 ml of HNO_3 (1:95) with 200 ml of 2 *N* HBr were made, and the small temperature rise observed was subtracted from that of the $AgNO_3$–HBr reaction. The resulting enthalpy change for reaction 1 was found to be −20.4 ± 0.3 kcal/mole. The value calculated from the enthalpies of formation of Circular 500 and of dilution from Parker is −20.26, which also indicates that our over-all accuracy is within 1%.

Materials.—Reagent grade chemicals, except for the $BiBr_3$, were obtained from suppliers. The $BiBr_3$ was made by dissolving Bi_2O_3 in excess concentrated HBr. The slurry was dried in air and then heated in a slow N_2 stream in a quartz vessel until the water was removed; it was then distilled in a stream of dry N_2 into another quartz vessel. After the distillation the last vessel was sealed off and removed to an N_2-atmosphere box. The $BiBr_3$ product was ground to a fine powder and transferred to the calorimeter addition tubes in the N_2 box so that it would not be exposed to air until the moment of mixing in the calorimeter. Analysis of a sample for Bi by the phosphate method gave 46.68% Bi as compared with 46.75% (theoretical) for $BiBr_3$.

The Bi used was 99.999+% from American Smelting and Refining Co. In order to have it dissolved completely in a few minutes, in the Br_2–HBr solvent, it was pulverized and the fraction that passed through a screen of 30-μ nominal hole size was used.

The Br_2 was ACS Reagent grade from Allied Chemical Co. It was transferred quantitatively to the calorimeter with a 2-ml micrometer buret made of glass and Teflon. A literature value of the density was used to determine the weight from the volume.

Enthalpy Measurements.—The enthalpies of solution of Bi, Br_2, and $BiBr_3$ in the HBr–Br_2 solvent (200 ml of 2 *N* HBr + 2.00 ml of Br_2) were individually determined, and the enthalpy of formation of $BiBr_3$ was calculated from them. Four determinations were made of the enthalpy of solution of Bi, with sample weights ranging from 0.1 to 0.2 g. The average enthalpy of solution of Bi was −72.6 kcal/mole with a standard deviation of ±0.3. Three determinations of the enthalpy of solution of liquid Br_2 (0.50-ml samples) gave −2.79 ± 0.02 kcal/mole. Six determinations of the enthalpy of solution of $BiBr_3$, with sample weights ranging from 0.6 to 1.7 g, gave −10.73 ± 0.14 kcal/mole. Proper combination of these values gives for the formation reaction

$$Bi(s) + {}^3/_2Br_2(l) = BiBr_3(s) \qquad (2)$$

an enthalpy change of −66.0 ± 0.5 kcal/mole at about 295°K. The heat capacity difference of this reaction is small (less than 1 cal/deg) so that the enthalpy of formation at 298°K can be taken as the same value within experimental uncertainty. There are no other measurements of this quantity in the literature; however, Wilcox and Bromley[8] have estimated a value of −65 ± 5 kcal/mole from an empirical correlation of many heats of formation.

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[6] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., Feb 1, 1952.

[7] V. B. Parker, National Standard Reference Data Series, NSRDS-NBS-2, U. S. Government Printing Office, Washington, D. C., April 1, 1965.

[8] D. E. Wilcox and L. A. Bromley, *Ind. Eng. Chem.*, **55**, 32 (1963).

The Thermodynamics of Vaporization of $BiBr_3$

The vapor pressure of liquid $BiBr_3$ has been measured by Evnevich and Sukhodskii[9] by a boiling point method and by Cubicciotti and Keneshea[10] by a transpiration method. These two sets of data were subjected to a Σ-plot treatment using the method suggested by Cubicciotti.[11] The free energy function increments were evaluated for the gas from the entropy and enthalpy data of Manley and Williams[4] and for the liquid from the data of Cubicciotti and Eding.[5] The quantity $\Sigma' = R \ln p + \Delta\text{fef incr} = \Delta S^\circ_{298} - (\Delta H^\circ_{298}/T)$ was treated by a computerized least-squares method for the 76 vapor pressure points reported in ref 10 as ranges of values and the 26 data points of ref 9, as well as for all 102 points. The two sets of data were in good agreement. The values and their probable errors calculated for ΔH°_{298}(sublimation) were 27.52 ± 0.05 and 27.99 ± 0.11 kcal/mole from ref 10 and ref 9, respectively, and 27.56 ± 0.04 for all of the data. For ΔS°_{298}(sublimation) the values were 43.30 ± 0.07 and 43.96 ± 0.15 eu, respectively, and 43.36 ± 0.06 for all of the data. Since one set of measurements was sensitive to the total pressure of condensable species and the other to their vapor density, the agreement of the two sets of values indicates that the vapor species was $BiBr_3$ with negligible contributions from either decomposition products (*i.e.*, Br_2) or polymers (*i.e.*, Bi_2Br_6). (A fortuitous combination of gaseous Br_2 and Bi_2Br_6 in such a ratio as to make the vapor density the same as $BiBr_3$ may be possible but seems unlikely.) The enthalpy and entropy of sublimation at 298°K are taken to be 27.6 ± 0.2 kcal/mole and 46.4 ± 0.2 eu. The uncertainty assigned is slightly larger than the mean probable error of the less precise data.

The absolute entropy of gaseous $BiBr_3$ at 298°K was calculated from molecular constant data by Manley and Williams[4] to be 91.85 eu; therefore the absolute entropy of the crystal is 45.5 ± 0.2 eu at 298°K. The free energy functions at even temperatures for the condensed phase calculated from this entropy and the data of ref 5 are given in Table I, together with values for the gas phase from the data of ref 4.

The dissociation energy of gaseous $BiBr_3$ can be calculated from the data given above. The enthalpy changes for the pertinent reactions are given in Table II. The energy of dissociation of $BiBr_3(g)$ at 0°K to the completely separated atoms is equal to the enthalpy change at 298°K from Table II plus the following small enthalpy increments from 0 to 298°K: −1.5 kcal for Bi(g), −4.4 kcal for 3Br(g), and 4.9 kcal for $BiBr_3(g)$. The resulting dissociation energy is 167.1 ± 1 kcal/mole (7.26 ± 0.04 ev).

The Dissociation Energy and the Absolute Entropy of BiBr

The dissociation energy of BiBr can be derived from the data reported above together with the results of our earlier study[2] of the equilibrium

$$^2/_3\text{Bi(l)} + {}^1/_3\text{BiBr}_3\text{(g)} = \text{BiBr(g)} \qquad (3)$$

The enthalpy change for this reaction at 925°K was found by a second-law evaluation to be 21.3 ± 0.5 kcal/mole. With the enthalpy increments from 298 to 925°K for Bi(c) = 7.1 kcal,[12] BiBr(g) = 5.6 kcal, and $BiBr_3(g)$ = 12.4 kcal,[4] the second-law value for ΔH_{298} for the reaction

$$^2/_3\text{Bi(c)} + {}^1/_3\text{BiBr}_3\text{(g)} = \text{BiBr(g)} \qquad (4)$$

becomes 24.5 ± 0.5 kcal. By combination of this value with the data in Table II one obtains a ΔH_{298} of 64.5 ± 1 kcal for the dissociation reaction BiBr(g) = Bi(g) + Br(g). The dissociation energy of BiBr at 0°K is found by the addition of the following enthalpy increments from 0 to 298°K: 2.4 kcal for BiBr, −1.5 kcal each for Bi and Br. The dissociation energy so calculated is 63.9 ± 1 kcal or 2.77 ± 0.04 eV, which is within experimental error of the spectroscopic value, 2.74 ± 0.01 eV.[13,14]

TABLE I

ENTROPIES, ENTHALPY INCREMENTS, AND FREE ENERGY FUNCTIONS FOR $BiBr_3$

	Condensed phases			Gas phase		
Temp, °K	$H^\circ_T - H^\circ_{298}$, kcal/mole	S_T°, eu	$-(G^\circ_T - H^\circ_{298})/T$, eu	$H^\circ_T - H^\circ_{298}$, kcal/mole	S°_T, eu	$-(G^\circ_T - H^\circ_{298})/T$, eu
298	0	45.50	45.50	0	91.85	91.85
350	1.39	49.80	45.83	...	...	...
400	2.60	53.03	46.53	1.99	97.59	92.61
431(I)	3.28	54.68	47.07	...	...	...
431(II)	4.02	56.39	47.07	...	...	...
450	4.54	57.57	47.48	...	...	...
491.7(II)	5.34	58.95	48.09	...	...	...
491.7(l)	10.32	69.07	48.09	...	...	...
500	10.60	69.64	48.44	3.95	101.94	94.04
600	14.00	75.84	49.17	5.93	105.59	95.70
700	17.29	80.91	56.21	7.90	108.62	97.33
800	20.47	85.16	59.57	9.89	111.28	98.92
900	23.55	88.79	62.62	11.85	113.53	100.36
1000	26.52	91.93	65.41	13.85	115.65	101.80

TABLE II

ENTHALPY OF DISSOCIATION OF $BiBr_3$ GAS

Reaction	ΔH_{298}, kcal/mole	Ref
$BiBr_3(c) = BiBr_3(g)$	27.6 ± 0.2	This work
$Bi(c) + {}^3/_2Br_2(l) = BiBr_3(c)$	−66.0 ± 0.5	This work
$Bi(c) = Bi(g)$	49.5	*a*
$^1/_2Br_2(l) = Br(g)$	26.74	*b*
$BiBr_3(g) = Bi(g) + 3Br(g)$	168.1 ± 1	

[a] R. Hultgren, R. L. Orr, P. D. Anderson, and S. K. Kelley, "Thermodynamic Properties of Metals and Alloys," John Wiley and Sons, Inc., New York, N. Y., 1963. [b] D. D. Wagman, W. H. Evans, I. Halow, V. B. Packer, S. M. Bailey, and R. H. Schumm, National Bureau of Standards Technical Note 270-1, U. S. Government Printing Office, Washington, D. C., Oct 1, 1965.

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(9) E. V. Evnevich and V. A. Sukhodskii, *Zh. Russ. Fiz. Khim. Obshchestva*, **61**, 1503 (1929).

(10) D. Cubicciotti and F. J. Keneshea, *J. Phys. Chem.*, **62**, 999 (1958).

(11) D. Cubicciotti, *ibid.*, **70**, 2410 (1966).

(12) R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, "Thermodynamic Properties of Metals and Alloys," John Wiley and Sons, Inc., New York, N. Y., 1963.

(13) A. G. Gaydon, "Dissociation Energies," Chapman and Hall, Ltd., London, 1953.

(14) G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Princeton, N. J., 1950.

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]

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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.

[2] G. Herzberg, "Spectra of Diatomic Molecules," 2nd ed, D. Van Nostrand Co., Inc., Princeton, N. J., 1950.

[3] A. G. Gaydon, "Dissociation Energies," Chapman and Hall, Ltd., London, 1953.

[4] D. Cubicciotti, *Inorg. Chem.*, **7**, 208 (1968).

[5] D. Cubicciotti and H. Eding, *J. Phys. Chem.*, **69**, 3621 (1965).