For the M(IV) series the familiar increase in covalency (decrease of β) toward the end of the d block is again observed. Thus, the data of Jørgensen and Schwokau[39] for ReF_6^{2-} yield $\beta_{55} \approx 0.85$, as compared with our values of 0.74 and 0.72 for OsF_6^{2-} and IrF_6^{2-}, while for PtF_6^{2-} the data[40] require $\beta \approx 0.55$. In a similar way the optical electronegativity shows a progressive increase along the 5d series, the values of $\chi_{\text{opt(rel)}}$ for Re(IV) and Pt(IV) being approximately 1.9 and 2.6, respectively, so that the relationship between β and χ_{opt}, for which we have previously suggested a rationalization,[41] appears to hold in the 5d block as well as in the first transition series. This connection appears to be rather less exact in the 5d series than for the 3d complexes since the $\chi_{\text{opt(rel)}}$ value for Re(IV) is surprisingly low, but our own diffuse reflectance measurements confirm the σ_{obsd} value of 35.6 kK for $ReCl_6^{2-}$ and also show no indication of charge-transfer bands below 50 kK for ReF_6^{2-}. In fact, though, a fairly substantial difference in $\chi_{\text{opt(rel)}}$ between d^3 and d^4 systems is not altogether unexpected, since the relativistic corrections operate in a contrary sense in the two cases.

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The Enthalpies of Formation of Arsine and Biarsine[1]

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The enthalpies of formation of AsH_3 and As_2H_4 have been determined by the method of explosion in mixtures with SbH_3, and the thermochemical bond energies have been derived. Results are $\Delta H_f°(AsH_3(g)) = +14.9 \pm 0.4$ kcal mol^{-1}, $\Delta H_f°(As_2H_4) = +28.2 \pm 1.3$ kcal mol^{-1}, E(As–H) = 71.2 kcal mol^{-1}, and E(As–As) = 39.9 kcal mol^{-1}.

Introduction

As part of a continuing program of investigation of the enthalpies of formation and thermochemical bond energies of the binary[2–8] and ternary[9] hydrides of boron and the group IV–VI elements, the enthalpies of decomposition of arsine and biarsine have been measured. No previous calorimetric studies have been reported for biarsine, but a mass spectrometric appearance potential study exists.[10]

The method used was explosion of the gaseous hydride in mixtures with stibine, as in earlier studies.[2–6,8,9] The enthalpy of decomposition of arsine was previously measured by this method[2] but only at a single AsH_3:SbH_3 ratio. Since elemental arsenic and antimony form a continuous range of solid solutions, the enthalpy of mixing of the metals might have a significant effect upon the deduced enthalpy of formation. Accordingly, in the present work the measurements were performed over a range of AsH_3:SbH_3 ratios.

Experimental Section

Stibine and arsine were obtained from the Matheson Chemical Co.[11] The stibine cylinder was held at −78° while the gas was withdrawn into flasks at −196°; a middle fraction was used. The arsine was passed twice through a trap at −126°. A single flask of each gas was used for all of the calorimetric work; melting curve analysis[12] of both indicated the mole fraction of liquid-soluble, solid-insoluble impurities to be less than 2×10^{-5}.

Biarsine was prepared as described by Shriver and Jolly,[13] using an ozonizer-type discharge tube operated at 12.5 kV with arsine passed through at low pressure and without diluent gas. About 25 mmol of arsine was condensed in a U trap (without packing) at −196°. The surrounding dewar was removed and the liquid nitrogen was dumped out of it; when the discharge started, the cold, empty dewar was replaced around the trap and adjusted to a height such as to keep the trap at a temperature at which the vapor pressure of the arsine was barely adequate to maintain the discharge. About 30–45 min was required to pass the total batch of arsine; the rate of production of biarsine was roughly 0.15 mmol hr^{-1}. To a first approximation, this rate was unaffected by passing the arsine considerably more rapidly at a higher pressure.

Biarsine is fairly stable as a gas, even at somewhat elevated temperatures, but is extremely unstable in the condensed phase above *ca.* −100°. Accordingly, the biarsine was always condensed, in the preparation, purification, and calorimeter-loading vacuum lines, into special traps having electrically heated reentrant inlet tubes so that the gas went directly to a surface at −126° (methylcyclohexane slush), as described by Shriver and Jolly.[13] The biarsine was always volatilized rapidly from the trap by removing a surrounding dewar of liquid nitrogen and immediately replacing it with water at *ca.* 60°. The biarsine was purified by several trap-to-trap distillations at −126°. The volume of gas decreased 10–20% per pass, indicating this to be the amount decomposed at each volatilization.

The vapor pressure of biarsine is very difficult to determine because of the instability of the liquid; Shriver and Jolly[13] estimated 10 mm at room temperature. In the course of the present work, experiments were done wherein the pressure in a bulb was observed as the temperature of a surrounding bath was lowered.

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(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) S. R. Gunn, W. L. Jolly, and L. G. Green, *J. Phys. Chem.*, **64**, 1334 (1960).

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(6) S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **68**, 946 (1964).

(7) S. R. Gunn, *ibid.*, **68**, 949 (1964).

(8) S. R. Gunn and J. H. Kindsvater, *ibid.*, **70**, 1114 (1966).

(9) S. R. Gunn and J. H. Kindsvater, *ibid.*, **70**, 1750 (1966).

(10) F. E. Saalfeld and H. J. Svec, *Inorg. Chem.*, **2**, 50 (1963).

(11) Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U. S. Atomic Energy Commission to the exclusion of others that may be suitable.

(12) S. R. Gunn, *Anal. Chem.*, **34**, 1292 (1962).

(13) D. F. Shriver and W. L. Jolly, Report UCRL-5148, Lawrence Radiation Laboratory, Livermore, Calif., 1958.

The inflections of the pressure *vs.* temperature curves were rather indistinct but suggested a vapor pressure of *ca.* 12 mm at 10°.

The calorimeter used was an aneroid copper block type, designated 29C. It is similar to one previously described;[14] but to secure greater sensitivity it is less massive, the block being 1.375 in. in outer diameter and 9.00 in. long with a well 1.125 in. in diameter and 8.94 in. deep. The energy equivalent, including the glass explosion cell, is about 80 cal deg^{-1}. A Hewlett-Packard quartz thermometer was used; its sensor was mounted in a cup soldered to the copper block. Electrical calibration was performed following each reaction, using a heater of manganin wire wound on the glass cell.

The explosion cells were of Pyrex, 28 mm in outer diameter and 200 mm long. Tungsten electrodes lay in loose contact near the center of the cell; the explosion was initiated by discharging a 0.1-μF capacitor at 600 V across this spark gap. It was assumed that two-thirds of the 0.009 cal stored in the capacitor appeared as heat in the calorimeter. The cells for SbH_3 and SbH_3–AsH_3 mixtures had filling tubes that were sealed off after the weighed gases were condensed in the cell. These cells were fitted with glass break-seals through which the product gases were subsequently recovered for analysis. The cells for As_2H_4 and the comparison runs were fitted with axial glass capillary tubes extending from the center of the cell upward to a valve above the calorimeter.

The stibine for all runs was weighed in 50-ml bulbs fitted with greaseless Springham valves having Viton diaphragms. Arsine for the runs in sealed-off cells was weighed in the same manner. The accuracy was estimated at ±0.2 mg for the SbH_3 and SbH_3–AsH_3 runs in sealed-off cells; for the later SbH_3–As_2H_4 and comparison runs in the capillary cells, an improved procedure was estimated to be accurate to ±0.1 mg.

For the SbH_3–AsH_3 runs in sealed-off cells, the two gases were weighed in separate bulbs and were then condensed in the cell. The filling tube was sealed off and the cell was warmed and placed in the calorimeter. About 40 min later, after attaining a steady foredrift and with the calorimeter near 25°, the mixture was exploded. After the electrical heating calibration, the cell was attached to a vacuum line and the gas was transferred by means of a Toepler pump through a trap at −196° to a gas buret and measured to determine the amount of hydrogen produced. The trap was then warmed and the amount of condensable gas was measured.

The SbH_3–As_2H_4 runs and comparisons were done at 50° so that larger amounts of As_2H_4 might be used with assurance that the saturation vapor pressure would not be exceeded. The calorimeter thermostat was enclosed in an air thermostat, operated at 50°, which also housed part of the glass vacuum line used for leading the calorimeter. This line was fitted completely with greaseless Springham valves. Within the air thermostat the line included a trap for storing the As_2H_4, a detachable infrared cell, and connections to the calorimeter explosion cell. Other connections led outside the air thermostat to an oil manometer, to the SbH_3 weighing bulb, a bulb of xenon, and a mercury manometer, and to the vacuum pumps.

The sequence of operations was as follows. First, the As_2H_4 in the trap was volatilized into the line, the calorimeter cell, and the infrared cell. A valve was opened to the line connecting to the oil manometer, this line having previously been filled with argon at a pressure slightly lower than the anticipated pressure of As_2H_4, so that As_2H_4 would not pass outside the air thermostat nor contact the oil. The valve above the calorimeter cell was then closed, the line was reevacuated, and a valve to the line connecting to the SbH_3 weighing bulb, xenon bulb, and mercury manometer was opened. The SbH_3 bulb was warmed from −196° to room temperature, the valve at the top of the calorimeter cell was opened and closed again, and the SbH_3 in the line was recondensed at −196° in the bulb, which was later reweighed. The line was then filled with xenon to a pressure slightly higher than that of the As_2H_4 and SbH_3 combined in the cell, the valve at the top of the cell was again opened and closed, and the explosion was initiated. The xenon served to flush SbH_3 out of the valve at the top of the cell and out of the capillary tube; the amount of xenon used was 0.04–0.05 mmol. The time interval from volatilization of the As_2H_4 to explosion was about 7 min.

The comparison experiments were performed identically, except that AsH_3 or Xe was loaded into the trap in place of the As_2H_4.

The 25-ml infrared cell was fitted with a 50-ml bulb that was initially evacuated; before the cell was removed from the air thermostat, the valve connecting the two was opened to reduce the pressure.

A new capillary cell was used for each run. The volume of each was determined before use by placing it in the calorimeter, filling it with argon to a known pressure measured on the oil manometer, and then measuring the amount of argon on the Toepler pump–buret line. The hydrogen from each run in the capillary cells after being measured in the gas buret was analyzed by mass spectrometry to ensure that it contained no xenon or other contaminant.

Results

All results are expressed in terms of the defined thermochemical calorie, 4.184 J; and error limits are expressed as the uncertainty interval, twice the standard deviation of the mean, $\pm 2\sqrt{\Sigma d^2/n(n-1)}$, unless otherwise stated.

Five runs with SbH_3 only were performed in the sealed-off cells for comparison with the SbH_3–AsH_3 runs. The amount of SbH_3, n_1, ranged from 2.9 to 3.1 mmol; the values of $-\Delta E$ were 34.78, 34.80, 34.80, 34.81, and 34.82 kcal mol^{-1}, a mean of 34.80 ± 0.01 kcal mol^{-1}. From the last four of these runs, the measured hydrogen n_H was 99.94, 99.89, 99.94, and 99.92% of the theoretical $1.5n_1$. The values of ΔE are referred to n_1 as given by the weighing.

Five runs with SbH_3–AsH_3 mixtures were performed in sealed-off cells. Results are given in Table I. The numbers of millimoles of SbH_3 and AsH_3 used, as determined by the weighings, are designated n_1 and n_2. It is assumed that the amount of hydrogen produced by the SbH_3 is 99.92% of the theoretical $1.5n_1$, as for the SbH_3-only runs above; accordingly, the amount of AsH_3 decomposed, n_3, is taken to be $(n_H/1.5) - 0.9992n_1$, where n_H is the amount of hydrogen found. The amount of condensable gas found, n_4, is in good agreement with $n_2 - n_3$ and is assumed to be unchanged AsH_3. Accordingly, ΔE is taken to be $(q - 34.80n_1)/n_3$, where q is the observed heat less the firing energy. The ratio of antimony to arsenic in the solid product is designated r_1.

TABLE I

SbH_3–AsH_3 RUNS IN SEALED-OFF CELLS AT 25°

n_1 (SbH_3), mmol	n_2 (AsH_3), mmol	n_3,[a] mmol	n_4 (condensable gas found), mmol	q, cal	r_1, Sb:As	$-\Delta E$ (AsH_3), kcal mol^{-1}
3.281	1.348	1.342	0.006	135.94	2.445	16.22
2.992	1.357	1.348	0.006	125.88	2.219	16.15
2.737	1.664	1.650	0.013	121.58	1.659	15.97
2.492	1.923	1.894	0.029	116.69	1.316	15.82
2.235	2.241	2.153	0.084	111.59	1.038	15.70

[a] AsH_3 decomposed.

Results for runs in the capillary cells are given in Tables II–IV. In all cases, n_1 is the amount of SbH_3, determined by the weight loss of the weighing bulb to about ±0.0008 mmol; n_2 is the amount of Xe, AsH_3, or As_2H_4–AsH_3 mixture added to the cell from the loading trap, measured with the oil manometer to about ±0.0005 mmol; n_H is the amount of hydrogen found in the product gases, determined in the gas buret to ±0.0005 mmol; q_{obsd} is the observed heat, determined to about ±0.01 cal (neglecting some possible small systematic errors that would cancel out in comparing

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[14] S. R. Gunn, *Rev. Sci. Instrum.*, **35**, 183 (1964).

TABLE II

SbH_3–Xe RUNS IN CAPILLARY CELLS AT 50°

n_1 (SbH_3), mmol	n_2 (Xe), mmol	n_H,[a] mmol	n_H',[b] mmol	q_{obsd}, cal	q_{cor}, cal	r_2, SbH_3:Xe	$-\Delta E(SbH_3)$, kcal mol^{-1}
1.1328	0.0462	1.6971	0.0022	39.937	39.144	24.5	34.56
1.1208	0.0770	1.6760	0.0052	39.469	38.663	14.6	34.50
1.1123	0.0882	1.6633	0.0051	39.231	38.425	12.6	34.55
1.0396	0.1380	1.5546	0.0049	36.753	35.964	7.5	34.59

[a] H_2 found. [b] H_2 missing.

TABLE III

SbH_3–AsH_3 RUNS IN CAPILLARY CELLS AT 50°

n_1 (SbH_3), mmol	n_2 (AsH_3), mmol	n_H[a] (H_2), mmol	n_2',[b] mmol	n_H',[c] mmol	q_{obsd}, cal	q_{cor}, cal	r_1, Sb:As	r_2, SbH_3:AsH_3	$-\Delta E(AsH_3)$, kcal mol^{-1}
1.0945	0.0685	1.7395	0.0010	0.0035	39.674	38.891	16.21	15.98	15.94
1.1126	0.0757	1.7784	0.0010	0.0026	40.469	39.673	14.89	14.70	16.51
1.1123	0.0913	1.7988	0.0014	0.0045	40.630	39.825	12.37	12.18	15.52
1.1135	0.1015	1.8168	0.0016	0.0033	40.888	40.072	11.15	10.97	16.03
1.1078	0.1169	1.8306	0.0020	0.0034	40.903	40.078	9.64	9.48	15.70
1.0441	0.1352	1.7616	0.0026	0.0035	38.984	38.191	7.87	7.72	15.97

[a] H_2 found. AsH_3 not decomposed. [c] H_2 missing.

TABLE IV

SbH_3–As_2H_4 RUNS IN CAPILLARY CELLS AT 50°

n_1 (SbH_3), mmol	n_2 (AsH_3 + As_2H_4), mmol	n_H,[a] mmol	n_2',[b] mmol	n_5 (AsH_3), mmol	n_6 (As_2H_4), mmol	q_{obsd}, cal	q_{cor}, cal	r_1, Sb:As	r_2, n_1:n_2	$-\Delta E$ (As_2H_4), kcal mol^{-1}
1.1317	0.0368	1.7584	0.0003	0.0173	0.0192	40.742	39.956	20.32	30.75	30.2
1.1317	0.0452	1.7773	0.0007	0.0116	0.0329	41.013	40.221	14.62	25.04	28.4
1.1241	0.0507	1.7728	0.0011	0.0181	0.0315	40.888	40.098	13.86	22.17	30.8
1.1354	0.0519	1.7930	0.0008	0.0176	0.0335	41.255	40.460	13.42	21.88	28.4
1.1638	0.0538	1.8421	0.0012	0.0106	0.0420	42.458	41.640	12.30	21.63	30.0
1.1230	0.0536	1.7796	0.0012	0.0124	0.0400	40.986	40.196	12.15	20.95	30.0
1.1043	0.0678	1.7684	0.0016	0.0338	0.0324	40.501	39.709	11.20	16.29	31.4
1.1236	0.0891	1.8377	0.0023	0.0356	0.0512	41.813	40.999	8.14	12.61	31.5
1.1259	0.0845	1.8372	0.0022	0.0256	0.0567	41.835	41.019	8.10	13.32	30.2
1.1058	0.1220	1.8632	0.0032	0.0592	0.0596	41.902	41.076	6.20	9.06	32.3

[a] H_2 found. [b] AsH_3 not decomposed.

the three series of runs). The xenon flush, n_{Xe}, 0.04–0.05 mmol for all runs, was determined with the mercury manometer on the loading line to ±0.005 mmol. The heat effect corrected for the firing energy and compressional work of admitting the gases is tabulated as $q_{cor} = q_{obsd} - 0.006 - 0.642(n_1 + n_2 + n_{Xe})$. The AsH_3 in the condensable gas separated from the hydrogen after the run was determined by infrared spectrometry; it is designated n_2'. The total amount of condensable gas was measured and agreed with $n_{Xe} + n_2'$ (or $n_2 + n_{Xe}$ for SbH_3–Xe runs) within the accuracy of determination of n_{Xe}. The Sb:As ratio in the solid products is listed as r_1 and the ratio of admitted gases n_1:n_2 is listed as r_2.

In Table II, the missing hydrogen, n_H', is given by $1.5n_1 - n_H$; the average value is 0.0044 mmol. In Table III, it is given by $1.5(n_1 + n_2 - n_2') - n_H$; the average is 0.0035 mmol. This probably represents mainly a consistent loss of SbH_3 by adsorption and absorption in wax and valve diaphragms in the loading line and incomplete return of the excess in the line to the weighing bulb. In Table II, $-\Delta E(SbH_3)$ is given by q_{cor}/n_1; the average is 34.55 ± 0.04 kcal mol^{-1}, with no significant trend in ΔE *vs.* r_2. If the amount of hydrogen produced were used as the measure of reaction, the mean for $1.5q_{cor}/n_H$ would be 34.64. In Table III, $-\Delta E(AsH_3)$ is given by $(q_{cor} - 34.55n_1)/(n_2 - n_2')$; the mean is 15.94 ± 0.28 kcal mol^{-1}, with no significant trend in ΔE *vs.* r_1 or r_2.

In Table IV, n_2 represents the total amount of the mixture of AsH_3 and As_2H_4 that entered the calorimeter cell. To determine the individual amounts of AsH_3 and As_2H_4 that were decomposed, designated n_5 and n_6, respectively, the hydrogen measurement, n_H, was used together with n_1, n_2, and n_2'. It was assumed that the "missing hydrogen" was the same as for the SbH_3–AsH_3 runs, 0.0035 mmol. Since the decomposition of AsH_3 gives $1.5H_2$ and the decomposition of As_2H_4 gives $2H_2$, there result the simultaneous equations

$$1.5n_5 + 2n_6 = n_H + 0.0035 - 1.5n_1 \qquad (1)$$

$$n_5 + n_6 = n_2 - n_2' \qquad (2)$$

Solution of these equations gives n_5 and n_6. Then, $-\Delta E(As_2H_4)$ is given by $(q_{cor} - 34.55n_1 - 15.94n_5)/n_6$. If there had been any significant trend of $\Delta E(SbH_3)$ with r_2 or of $\Delta E(AsH_3)$ with r_1, the values of $\Delta E(SbH_3)$ and $\Delta E(AsH_3)$ corresponding to the particular values or r_2 and r_1 would have been used in calculating each SbH_3–As_2H_4 run. The mean value of $-\Delta E(As_2H_4)$ is 30.3 ± 0.8 kcal mol^{-1}, with no significant trend of ΔE *vs.* r_1 or r_2.

It is also possible to calculate the composition of the AsH_3–As_2H_4 mixture from the infrared spectrum, if it is assumed that the average composition of the gas streams going from the trap into the infrared cell and into the calorimeter cell are the same. This method is rather imprecise because the only usable AsH_3 absorption is a sharp peak at 2127 cm^{-1} superimposed on the broad As_2H_4 peak centered at 2110 cm^{-1}. In five of the ten runs, the amount of arsine, n_7, deduced from this peak agreed reasonably well with n_5 given in Table IV; in one run it was substantially less, and in the other four it was substantially more. For these latter four runs the missing hydrogen, $1.5n_1 + 1.5(n_7 - n_2') + 2(n_2 - n_7) - n_H$, ranged from -0.0005 to -0.0092 mmol, compared with the $+0.0035$ mmol assumed in the preceding calculations for SbH_3–As_2H_4 runs and found for the SbH_3–AsH_3 runs. However, if one ignores this and calculates $-\Delta E$ from $[q_{cor} - 34.55n_1 - 15.94(n_7 - n_2')]/(n_2 - n_7)$, the mean is 33.2 ± 3.6 kcal mol^{-1}.

Discussion

From the results for SbH_3-only runs in sealed-off cells, the value of $-\Delta E_{dec}$ referred to $n_H/1.5$ rather than n_1 is 34.83 ± 0.01 kcal mol^{-1}. The best previous value was 34.98.[2,5,14] This higher value is still preferred for SbH_3; it is probable that the slightly lower value in the present work is due to the calorimeter block being shorter, resulting in some loss of heat from the top of the glass explosion cell.

A plot of the values of $\Delta E_{dec}(AsH_3)$ from Table I *vs.* the Sb:As atom ratio in the solid product is nearly a straight line, extrapolating to 15.3 kcal mol^{-1} at Sb:As = 0. A plot of the same values *vs.* the atom fraction As:(As + Sb) is also nearly a straight line, extrapolating to 14.3 kcal mol^{-1} at As:(As + Sb) = 1. However, the former plot shows a small downward curvature and the latter a small upward curvature; a value of 14.9 ± 0.4 kcal mol^{-1} will be chosen. Converted to constant pressure, this gives for $\Delta H_f°(AsH_3)$ 14.6 ± 0.4 kcal mol^{-1}. The earlier value[2] of 16.17 kcal mol^{-1} for $-\Delta E(AsH_3)$ at Sb:As = 1.98 is in good agreement with the present results.

Using $C_p°$ data[15] at 25° and neglecting the change in ΔC_p between 25 and 50°, $-\Delta E_{dec}(SbH_3)$ at 50° is calculated to be 34.84 kcal mol^{-1}, assuming a value of 34.98 kcal mol^{-1} at 25°; the average from Table II is 34.55 ± 0.04 kcal mol^{-1}, which becomes 34.64 ± 0.05 kcal mol^{-1} if the amount of reaction is taken as $n_H/1.5$ rather than n_1. The discrepancy agrees within experimental error with that found in sealed-off cells at 25°.

The mean value of 15.94 ± 0.28 kcal mol^{-1} from Table III is taken as representing $-\Delta E_{dec}(AsH_3, 50°)$ to give $As_{0.08}Sb_{0.92}$. Using NBS data[15] for C_p and assuming ΔC_p for the heat of mixing of solid As and Sb to be zero, this corresponds to 16.10 kcal mol^{-1} for $-\Delta E_{dec}(AsH_3)$ at 25°. Extrapolation of a plot of the values of $-\Delta E$ from Table I *vs.* As:(As + Sb) to As:(As + Sb) = 0.08 gives a value of 16.75 kcal mol^{-1} if a straight line is used and a somewhat higher value if a curve is fitted.

However, the method of comparative measurements exploited in this work gives most directly, by comparison of the SbH_3–AsH_3 and SbH_3–As_2H_4 runs in Tables III and IV, a value of ΔE for the reaction

$$2AsH_3(g) \longrightarrow As_2H_4(g) + H_2(g) \qquad (3)$$

Since the range of Sb:As ratios in the two series is about the same, the uncertain heat of mixing of solid As and Sb is eliminated: subtracting $\Delta E_{dec}(As_2H_4, 50°)$ from $2\Delta E_{dec}(AsH_3, 50°)$ gives -1.6 ± 1.0 kcal mol^{-1} for $\Delta E_3(50°)$ and $\Delta H_3(50°)$. There are no heat capacity data available for As_2H_4; it will be assumed that ΔC_p for reaction 3 is the same as for the corresponding NH_3–N_2H_4–H_2 reaction. From the NBS tables, $\Delta C_p°$ for this reaction is only 1.98 cal deg^{-1} mol^{-1}, and so $\Delta H_3°$ at 25° is also -1.6 ± 1.0 kcal mol^{-1}. Thus $\Delta H_f°(As_2H_4(g))$ is $+28.2 \pm 1.3$ kcal mol^{-1}.

Using heats of formation of the gaseous atoms,[15] the thermochemical bond energies may be calculated: $E(As–H) = 71.2$ kcal mol^{-1} and $E(As–As) = 39.9$ kcal mol^{-1}. The energies are coupled in such a manner that an error of +1 kcal mol^{-1} in $\Delta H_f°(AsH_3)$ gives an error of -0.33 kcal mol^{-1} in E(As–H) and an error of -0.67 kcal mol^{-1} in E(As–As); an error of +1 kcal mol^{-1} in ΔH_3 gives an error of -1 kcal mol^{-1} in E(As–As). Also using the NBS data,[15] the corresponding values for nitrogen, phosphorus, and antimony compounds may be calculated (all in kcal mol^{-1}): E(N–H), 93.4; E(P–H), 76.7; E(Sb–H), 61.4; E(N–N), 37.8; E(P–P), 46.9. Thus E(M–H) decreases monotonically with increasing period number; but while E(As–As) is lower than E(P–P), E(N–N) is lower yet.

Saalfeld and Svec studied appearance potentials in the mass spectra of AsH_3[16] and As_2H_4[10] and calculated thermochemical bond energies and standard enthalpies of formation. The calculations are repeated here using ionization potentials and heats of atomization from the NBS compilation.[15] For the process

$$AsH_3 \longrightarrow As^+ + H_2 + H + e^- \qquad (4)$$

the appearance potential was 14.8 ± 0.2 eV; combined with IP(As) and $\Delta H_f°(H)$, this gives 72.6 ± 1.5 kcal mol^{-1} for E(As–H) and, combined with $\Delta H_f°(As)$, $+10.9 \pm 4.6$ kcal mol^{-1} for $\Delta H_f°(AsH_3)$. For the process

$$As_2H_4 \longrightarrow As^+ + As + 2H_2 + e^- \qquad (5)$$

the appearance potential was 14.3 ± 0.3 eV; combined with IP(As), $\Delta H_f°(H)$, and 72.6 ± 1.5 kcal mol^{-1} for E(As–H), this gives 20.1 ± 9.2 kcal mol^{-1} for E(As–As) and, combined with $\Delta H_f°(As)$, $+42.7 \pm 6.9$ kcal mol^{-1} for $\Delta H_f°(As_2H_4)$.

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[15] D. D. Wagman, *et al.*, *Nat. Bur. Stand.* (*U. S.*), *Tech. Note*, **No. 270-3** (1968).

[16] F. E. Saalfeld and H. J. Svec, *Inorg. Chem.*, **2**, 46 (1963).