TABLE II

HEAT CONTENTS (CAL./MOLE) AND ENTROPIES (CAL./DEG. MOLE) ABOVE 298.16°K.

	Al_2TiO_5		Fe_2TiO_5		Fe_2TiO_4		Zn_2TiO_4	
T, °K.	$H_T - H_{298.16}$	$S_T - S_{298.16}$	$H_T - H_{298.16}$	$S_T - S_{298.16}$	$H_T - H_{298.16}$	$S_T - S_{298.16}$	$H_T - H_{298.16}$	$S_T - S_{298.16}$
400	3,600	10.35	4,330	12.46	3,750	10.80	3,550	10.21
500	7,620	19.30	8,740	22.29	7,610	19.40	7,290	18.55
600	11,930	27.16	13,300	30.60	11,640	26.74	11,250	25.77
700	16,420	34.07	18,010	37.86	15,850	33.23	15,400	32.16
800	21,020	40.22	22,870	44.35	20,220	39.06	19,710	37.92
900	25,700	45.73	27,860	50.23	24,740	44.38	24,140	43.13
1000	30,450	50.73	32,960	55.60	29,400	49.29	28,660	47.89
1100	35,280	55.33	38,130	60.53	34,210	53.87	33,250	52.27
1200	40,180	59.59	43,330	65.05	39,180	58.20	37,890	56.30
1300	45,150	63.57	48,550	69.23	44,350	62.34	42,560	60.04
1400	50,180	67.30	53,800	73.12	49,160	66.35	47,250	63.52
1500	55,260	70.80	59,080	76.76	55,450	70.27	51,950	66.76
1600	60,370	74.10	64,400	80.20	61,460	74.15	56,680	69.81
1700	65,490	77.21	69,760	83.45			61,450	72.70
1800	70,620	80.14					66,270	75.46

magnetic inversion point at 900°K. which is absent for titanomagnetite.

Measurements of titanomagnetite beyond 1513°K. were hampered because the substance began to attack the platinum–rhodium capsule. Higher temperature results are considered unsound and therefore are not reported.

Table II gives smooth values of heat content and entropy increments above 298.16°K. at even 100° intervals, for use of those who make thermodynamic calculations by the tabular method. The entropy increments were calculated to match the heat content values by the method of Kelley.[13]

The heat content data are represented by the following equations. The temperature range of validity and average deviation from the measured values are indicated in parentheses.

$Al_2TiO_5(c)$

$$H_T - H_{298.16} = 43.63T + 2.65 \times 10^{-3}T^2 + 11.21 \times 10^5T^{-1} - 17{,}004$$
(298–1800°K.; 0.4%)

$Fe_2TiO_5(c)$

$$H_T - H_{298.16} = 46.03T + 2.63 \times 10^{-3}T^2 + 7.41 \times 10^5T^{-1} - 16{,}443$$
(298–1700°K.; 0.4%)

$Fe_2TiO_4(c)$

$$H_T - H_{298.16} = 33.34T + 7.54 \times 10^{-3}T^2 + 3.40 \times 10^5T^{-1} - 11{,}751$$
(298–1600°K.; 0.7%)

$Zn_2TiO_4(c)$

$$H_T - H_{298.16} = 39.82T + 2.77 \times 10^{-3}T^2 + 7.69 \times 10^5T^{-1} - 14{,}698$$
(298–1800°K.; 0.8%)

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[13] K. K. Kelley, U. S. Bur. Mines Bull. 476 (1949).

[CONTRIBUTION FROM THE LOW TEMPERATURE LABORATORY, DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

Arsine. Vapor Pressure, Heat Capacity, Heats of Transition, Fusion and Vaporization. The Entropy from Calorimetric and from Molecular Data[1]

BY R. H. SHERMAN AND W. F. GIAUQUE

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The heat capacity of arsine has been measured from 13°K. to its boiling point, 210.68°K. The heat of vaporization at this temperature is 3988 cal. mole^{-1}. The heat of sublimation at the absolute zero is $\Delta H_0^0 = 5090$ cal. mole^{-1}. The heat of fusion is 285.7 cal. mole^{-1} at the triple point, 156.23°K. The melting point at 1 atm. total pressure is 156.28°K. The heat of transition at 105.55°K. is 131.0 cal. mole^{-1}. 0°C. is taken as 273.16°K. A gradual transition of the type characteristic of restricted rotation occurs near 32°K. The entropy obtained from the third law of thermodynamics is 53.15 cal. deg.$^{-1}$ mole^{-1} at 298.16°K. This is in excellent agreement with the value 53.18 cal. deg.$^{-1}$ mole^{-1} calculated from spectroscopic data. This latter is the value to be used in ordinary thermodynamic calculations. Considering the nuclear spin contribution the absolute entropy is 60.07 cal. deg.$^{-1}$ mole^{-1}. The vapor pressure of the liquid has been measured and represented by the equation $\log_{10}P$ (int. cm. Hg) $= -1403.32T - 9.45935 \log_{10}T + 0.008037T + 28.82835$. The vapor pressure of the solid has been tabulated from 40°K. to the triple point. The second virial coefficient of arsine gas has been determined by two different methods which agree well. The accepted equation of state for low pressures is $PV = RT + bp/T^2$, where $b = -4.3 \times 10^5$ cal. deg.^{2} atm.$^{-1}$ $= -1.8 \times 10^7$ cm.^{3} deg.^{2}. The thermodynamic properties of solid, liquid and gaseous arsine have been tabulated.

This paper reports a low temperature calorimetric investigation of arsine. Its primary purpose was the comparison of the entropy of arsine gas obtained by means of the third law of thermodynamics with the value calculable from existing molecular data. It was also of interest to compare its properties with those of phosphine which has been

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(1) This work was supported in part by the Office of Naval Research, United States Navy, and by the United States Atomic Energy Commission.

found[2] to have, among its several crystalline forms, two which can be cooled to limiting low temperatures.

Calorimetric Apparatus.—The most recent description of rebuilt Gold Calorimeter IV, which was used for the low temperature measurements, and which we shall designate IVA, has been given by Hildenbrand and Giauque.[3] The gold resistance thermometer–heater was calibrated in terms of a standard copper–constantan thermocouple with the laboratory designation "W."[4,5] The thermocouple was checked against the triple (13.94°K.) and boiling (20.36°) points of hydrogen and the triple (63.15°) and boiling (77.34°) points of nitrogen. When allowance was made for the change of assumed ice point from 273.10° to 273.16°K., the thermocouple gave a temperature 0.04° too low at both the triple and boiling points of hydrogen, and 0.01° low at 63.15°K. and 0.04° low at the boiling point of nitrogen. Appropriate corrections were made. The above comparison shows good stability for a thermocouple which has been in use for 28 years. Other thermocouples made from the same wire have similar good records.

The physical constants used are those based on the evaluation by DuMond and Cohen[6] and recommended by Rossini, *et al.*[7] One defined calorie is taken equal to 4.1840 absolute joules.

The density of liquid arsine is given by the equation[8]

$$d = 2.074 - 1.241 \times 10^{-3}T - 4.321 \times 10^{-6}T^2$$

The density of the solid[9] is 1.96 at 103°K. on the basis of X-ray measurements.

Preparation and Purification of Arsine.—Calcium arsenide was prepared by treating C.P. calcium turnings with arsenic crystals taken from stock. A spectroscopic examination of the arsenic by Dr. John Conway showed the presence of Al, Ca, Fe, Mg and Ni, each to the order of 0.01%. Bi, Cr, Mn, Pb, Sb and Sn could not be detected. Since the spectroscopic analysis would probably not have detected small amounts of antimony in arsenic, its absence as noted above only indicates that it was probably not present in a concentration greater than 0.1%. The preparation of Ca_3As_2 was carried out in a piece of capped pipe which was heated to initiate the exothermic reaction.

The arsine was prepared in a vacuum tight glass system by means of the reaction

$$Ca_3As_2 + 6H_2O = 2AsH_3 + 3Ca(OH)_2$$

The arsine gas was bubbled through 3 *M* HCl to remove any ammonia which might have been formed. The gas was then passed through 6 *N* NaOH to remove acid fumes and given a preliminary drying with anhydrous calcium chloride.

At intervals the addition of water was stopped and the system was evacuated to remove hydrogen which accumulated presumably by arsine decomposition at the initially high temperature on the reacting surface.

One hundred and eighty ml. of liquid arsine was collected over P_2O_5 at 196°K. and allowed to dry for 6 days. Following this, two simple distillations were carried out. Small initial and final fractions were discarded until 130 ml. of liquid remained.

The change of melting point with fraction melted showed 0.04 mole % of liquid soluble-solid insoluble impurity. Premelting heat effects, just below the melting point, gave a result of 0.03 mole %. This sample was used for the heat capacity measurements.

A second preparation, distilled three times, was found to contain 0.01 mole % of impurity by both of the above methods. This sample was used for the vapor pressure determinations.

Since it has been reported that arsine decomposes in the presence of mercury,[10] it was decided to investigate the effect of having a mercury manometer in the system. A 1 liter Pyrex bulb, connected to a mercury manometer, was filled with doubly distilled arsine at a pressure of 439 mm. Hg to ascertain the rate of decomposition at room temperature. The bulb was not exposed to direct sunlight nor to any strong fluorescent light, but otherwise no special precautions were taken. At the end of 93 days there had been no evident change of pressure. There was a slight evidence of contamination of the mercury surface. Subsequently arsine gas was subjected to two other surfaces: (1) gold foil which had been used as a mercury vapor trap in other work and (2) a nitrogen cooled trap which had condensed mercury on its surface and which had been warmed to room

TABLE I

HEAT CAPACITY OF ARSINE

0°C. = 273.16°K., mol. wt. of AsH_3 = 77.947, 2.72502 moles in the calorimeter.

$T_{av.}$, °K.	C_p	$T_{av.}$, °K.	C_p	$T_{av.}$, °K.	C_p
Series 1					
15.35	2.905	62.72	11.731	28.44	7.356
16.38	3.212	66.92	11.830	30.13	8.239
17.60	3.583	70.85	11.903	33.04	10.387
18.78	2.985	75.25	12.012	34.64	10.374
19.99	4.374	80.12	12.014	36.15	10.459
21.78	4.982	85.40	12.053	37.58	10.557
23.84	5.688	91.07	12.104	39.76	10.727
25.97	6.417	97.09	12.174	42.54	10.916
28.14	7.219	101.93	12.229	45.08	11.076
29.99	8.110	111.55	11.231	47.45	11.213
32.66	10.450	117.37	11.187	50.45	11.371
34.11	10.353	123.66	11.180	53.99	11.476
35.70	10.436	130.84	11.165	57.23	11.611
37.52	10.560	Series 2		61.02	11.705
39.37	10.690	14.26	2.622	65.29	11.799
41.89	10.874	16.55	3.272	69.24	11.879
44.55	11.050	18.65	3.864	72.93	11.937
47.01	11.199	20.77	4.615	76.86	11.986
49.29	11.518[a]	22.81	5.444	81.24	12.025
52.20	11.448	24.80	6.007	85.59	12.053
55.69	11.572	26.69	6.674	90.36	12.094
58.89	11.682			95.50	12.135
100.26	12.208			Series 4	
111.87	11.185			100.38	12.259
118.37	11.170			111.16	11.287
125.17	11.202			115.76	11.165
131.97	11.180			122.05	11.183
138.86	11.224			128.45	11.190
145.91	11.258			135.32	11.190
150.98	11.564			142.40	11.316
Series 3		ΔT		148.90	11.473
30.560	8.352	0.492		Series 5	
30.977	8.830	.241		160.86	14.451
31.253	9.042	.235		166.46	14.430
31.517	10.914	.199		172.82	14.438
31.658	19.19	.0592		179.58	14.417
31.711	29.0	.0325		186.55	14.426
31.743	54.4	.0222		193.89	14.441
31.769	140	.0178		201.79	14.442
31.784	306	.0082		207.60	14.493
31.793	453	.0055			
31.801	285	.0088			
31.902	12.58	.177			
32.107	10.672	.203			

[a] Time of energy input uncertain.

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(2) C. C. Stephenson and W. F. Giauque, *J. Chem. Phys.*, **5**, 149 (1937).

(3) D. L. Hildenbrand and W. F. Giauque, THIS JOURNAL, **75**, 2811 (1953).

(4) W. F. Giauque, R. M. Buffington and W. A. Schulze, *ibid.*, **49**, 2343 (1927).

(5) W. F. Giauque, H. L. Johnston and K. K. Kelley, *ibid.*, **49**, 2367 (1927).

(6) J. W. M. DuMond and E. R. Cohen, *Phys. Rev.*, **82**, 555 (1951).

(7) F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling and G. W. Vinal, THIS JOURNAL, **74**, 2699 (1952).

(8) A. L. G. Rees and K. Stewart, *Trans. Faraday Soc.*, **45**, 1028 (1949).

(9) G. Natta and E. Cosazza, *Gazz. chim. ital.*, **60**, 851 (1930).

(10) (a) H. Rechleben, G. Lackemann and A. Eckhardt, *Z. anal. Chem.*, **46**, 671 (1927); (b) H. Kubina, *ibid.*, **76**, 39 (1929).

temperature. In the case of the gold foil which had condensed some mercury vapor the reaction was negligible. However, the finely divided mercury on the surface of the glass trap developed a brown coloration which indicated an appreciable reaction. There was no evidence of reaction with Apiezon stopcock grease.

Heat Capacity Measurements.—The heat capacity observations are given in Table I. Series 1 and 2, representing two runs starting at liquid hydrogen temperatures are in excellent agreement.

Series 3, covering a period of 8 hours, was run to determine the shape of the heat capacity curve in the region of the gradual transition near 32°K. The two observations on the high side of the maximum show that the heat capacity drops off gradually rather than discontinuously in this region. The gradual transition is presumably due to molecular rotation (including torsional vibration) in the solid. We know of no experimental or theoretical reason why the coöperative domains evidently associated with such effects should disintegrate at a definite temperature except as a highly improbable coincidence. The general evidence relating to this type of phenomenon indicates that residual domains persist into the region well above the maxima.

Series 4 covers the range of temperature in which the high temperature solid phase is stable, and series 5 gives the heat capacities of the liquid phase.

In both series 1 and series 2, total heat measurements were made through the region of high heat capacity near 32°K. For purposes of comparison the heat absorbed over the arbitrary interval 31.25–32.25°K. has been computed. The data are given in Table II. Figure 1 shows the details of the gradual transition.

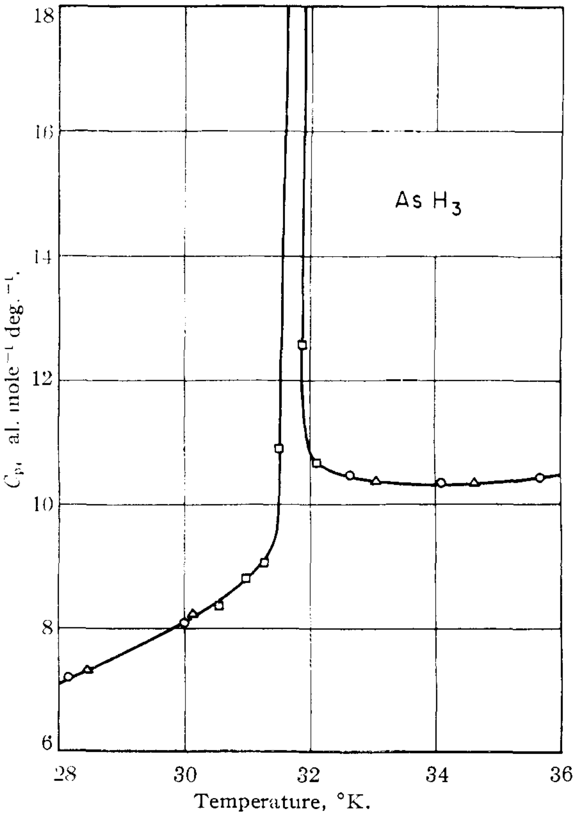

Fig. 1.—Region of high heat capacity near 32°K.

TABLE II

HEAT ABSORPTION IN ARSINE NEAR 32°K.

		Cal. mole^{-1}		
Series	$T_1 - T_2$, °K.	Cor. heat input	$\int C_p dT$	Cor. to 31.25–32.25°K.
1	30.848–32.021	25.31	−1.13	24.18
2	30.949–32.219	26.42	−2.35	24.07
			Average	24.13 ± 0.06

Search for a More Stable Low Temperature Phase of Arsine.—The low temperature properties of arsine and phosphine are very similar. Each has a gradual transition somewhat above 30°K. and each has a crystalline transition near 100°K. However, Stephenson and Giauque[2] found a more stable form of phosphine in the temperature range below 49.43°K. The rate of transition to this stable phase was very slow. The maximum rate was found near 40°K. and it decreased rapidly at either higher or lower temperatures. However, since the heat of transition in phosphine was 185.7 cal. mole^{-1}, a very slow rate could be detected in terms of heat evolution within a highly sensitive calorimeter.

Immediately after series 3, of arsine, the calorimeter was allowed to stand for 12 days while it slowly warmed from 35 to 64°K. The drift rates corresponded to the values expected on the basis of heat transfer between the calorimeter and its surroundings. This, of course, did not prove that a more stable form cannot exist. It is often difficult for a substance to surmount the potential involved in producing the first microscopic element of a new phase unless chance enters in the form of some impurity or other crystal defect.

A second attempt to find a more stable form of arsine was made with the second preparation. It was cooled to 20.4°K. and allowed to warm slowly to 75°K. over a total period of 10 days. No evidence of heat evolution within the calorimeter could be detected. All that can be said in the present case is that if a more stable form can exist, it failed to start or its rate of growth is excessively slow.

Phosphine also has a sharp change of phase at 30.29°K. from one metastable form to another. No evidence of such a transition was found in the case of arsine.

The Heat and Temperature of the Upper Transition of Arsine.—The transition at 105.55°K. was complicated by an extremely slow equilibrium. During energy input in the transition the calorimeter temperature was observed to rise 2° above the temperature of the transition. It is probably this slowness in equilibrium which caused Smyth and McNeight[11] to report a transition temperature of 106.6° on the basis of a "temperature–time curve."

Our observations on the transition temperature for both preparations of arsine are given in Table III as a function of the % transformed.

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(11) C. P. Smyth and S. A. McNeight, THIS JOURNAL, **58**, 1723 (1936).

TABLE III

TEMPERATURE OF THE UPPER TRANSITION OF ARSINE

Date		% Transformed	Temp., °K. Thermocouple	Resistance thermometer
		1st Preparation		
3/ 1/54	10:53 A.M.	Heat supplied		
	4:48 P.M.	20	105.62	105.610
	5:00 P.M.	Heat supplied		
3/ 2/54	10:58 A.M.	37	105.62	105.613
	11:17 A.M.	Heat supplied		
3/ 4/54	8:29 A.M.	56	105.67	105.698
3/ 5/54	11:11 A.M.	Heat supplied		
3/ 7/54	4:45 P.M.	61	105.82	.....
3/ 8/54	10:40 A.M.	Heat supplied		
3/11/54	3:00 P.M.	81	105.74	105.75
		2nd Preparation		
11/ 9/54	7:16 P.M.	Heat supplied		
11/10/54	9:35 A.M.	5	105.55	105.553
	9:58 A.M.	Heat supplied		
	4:20 P.M.	25	105.56	105.544
	4:47 P.M.	Heat supplied		
11/11/54	10:35 A.M.	63	105.63	105.612
11/12/54	10:25 A.M.	63	105.54	105.507
	1:42 P.M.	Heated out of transition		
	2:53 P.M.	Cooled into transition (97% upper form)		
11/13/54	10:35 A.M.	Equilibrium established	105.60	105.546
		Accepted value	105.55°K.	

One possibility of explaining the slow equilibrium could be the formation of microcrystalline regions during the phase change.

Thermal equilibrium during heat capacity measurements was attained somewhat more slowly than expected over the range 30° below the transition to the melting point 50° above it. From 50 to 65°K. the time required to reach substantial equilibrium was about 7 or 8 min. At 80°K. it was about 16 min.; at 95°K., 19 min.; and at 100°K. it was about 25 min. From 109°K. to the triple point, 156.23°K., the equilibrium time was about 30 min. Since the heat capacity curve appears to be normal the slow equilibrium may be due to excessively poor heat conductivity in these solids which have restricted molecular rotation. In any case the slow equilibrium within the transition seems to be of a different order of magnitude from that in the heat capacity measurements.

The Triple Point Temperature and the Heat of Fusion of Arsine.—The heat of fusion was measured in the usual manner of starting several degrees below the melting point and terminating heat input somewhat above. Small corrections of the order of one % were made for premelting below the starting temperature due to impurity. Since the substance had a vapor pressure of about 2 cm. in this region, a correction of about 0.02% was made for vaporization during the temperature increase.

The data are shown in Table IV. The values calculated apply to the triple point temperature 156.23°K.

The impurity produced a small lowering of the melting point, as may be seen from the trend in the results presented in Table V.

TABLE IV

HEAT OF FUSION OF ARSINE

Cal. mole^{-1}, triple point = 156.23°K.

T_1, °K.	T_2, °K.	Total heat (cor.)	$\int C_p dT$	ΔH
153.085	159.505	311.28	25.59	285.7
151.891	157.941	305.43	19.96	285.5
150.657	158.069	309.69	23.85	285.8
			Av.	285.7 ± 0.2

TABLE V

MELTING TEMPERATURE OF ARSINE

% melted	Thermocouple, °K.	Resistance therm., °K.
26.45	156.01	155.967
38.02	156.01	156.037
49.35	156.05	156.077
69.92	156.13	156.120
	Accepted T.P. = 156.23	

From a plot of T *vs.* $(1/x)$, where x = fraction melted, the triple point temperature was found as the intercept where $(1/x) = 0$. The points fell on a nearly straight line which extrapolated to 156.23°K.

Several recent determinations are: Smyth and McNeight,[11] 156.4°K.; Johnson and Pechukas,[12] 156.8°K.; and Nast,[13] 156.8°K.

The melting point at 1 atmosphere pressure may be calculated from the equation $dT/dP = T\Delta V/\Delta H$, to be 0.05° above the triple point temperature; thus, the melting point, at 1 atmosphere, is 156.28°K.

Heat of Vaporization of Arsine.—The method used was essentially the same as that employed for oxygen by Giauque and Johnston,[14] except that the 5 liter bulb which accepted the gas at constant pressure was not thermostated or calibrated. The amount of arsine was determined by later condensation and weighing in a monel pressure vessel. The 0.2 mole samples could be weighed within 0.01%. The standardized weights were corrected to vacuum and a small correction was applied for inequality of the balance arms. Small corrections were also made for changes of pressure and gas space in the line and calorimeter. The data are given in Table VI.

TABLE VI

HEAT OF VAPORIZATION OF ARSINE

Cal. mole^{-1}, b.p. = 210.68°K.

Moles evap.	Time of heat input, min.	ΔH
0.18832	50	3990
.20145	53	3991
.20604	52	3984
.20147	52	3990
.20180	51	3985
	Av.	3988 ± 3

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[12] W. C. Johnson and A. Pechukas, THIS JOURNAL, **59**, 2065 (1937).

[13] R. Nast, *Ber.*, **81**, 271 (1948).

[14] W. F. Giauque and H. L. Johnston, THIS JOURNAL, **51**, 2300 (1929).

Vapor Pressure and Gas Imperfection of Arsine.—The vapor pressure was measured from the triple point to the boiling point. A mercury manometer, 16 mm. in diameter, was compared with a standard meter bar, certified by the Bureau of Standards. A Société Génévoise Cathetometer which could be read to 0.02 mm. and interpolated accurately to 0.01 mm. was used to make the comparison.

Corrections were applied for the meniscus depression[15] and also for the weight of the column of arsine in the tube leading to the calorimeter. In correcting the data to international cm. g was taken as 979.973[16] for this location and g_0 = 980.665 cm. sec.$^{-2}$. The density of mercury was taken from the I.C.T.[17]

The vapor pressure observations are given in Table VII where they are compared with the empirical equation $\log_{10}P_{(\text{int. cm.})} = -1403.32/T - 9.43935 \log_{10}T + 0.008037T + 28.82835$,

TABLE VII

THE VAPOR PRESSURE OF ARSINE

P = inter. cm. Hg, 0°C. = 273.16°K.

T, °K.	Obsd.	Calcd.	$P_{\text{obs.}} - P_{\text{calc.}}$	$T_{\text{obs.}} - T_{\text{calc.}}$	Remarks
156.226	2.241				Triple point
	2.235				Tripe point
156.226	2.238	2.238	0.000	0.000	Av. value liquid
160.979	3.392	3.390	.002	− .007	Av. value liquid
166.824	5.459	5.446	.013	− .031	Av. value liquid
171.270	7.636	7.621	.015	− .027	Av. value liquid
175.278	10.171	10.154	.017	− .024	Av. value liquid
178.284	12.479	12.472	.007	− .008	Av. value liquid
181.783	15.697	15.693	.004	− .004	Av. value liquid
184.567	18.721	18.711	.010	− .010	Av. value liquid
190.397	26.542	26.546	− .004	.003	Av. value liquid
196.124	36.609	36.602	.007	− .004	Av. value liquid
199.802	44.509	44.509	.000	.000	Av. value liquid
206.010	60.849	60.854	− .005	.002	Av. value liquid
208.879	69.830	69.838	− .008	.002	Av. value liquid
210.837	76.544	76.541	.003	− .001	Av. value liquid

It will be observed that except for the triple point, $P_{\text{obs.}} - P_{\text{calc.}}$ is consistently slightly positive in the low pressure region. It is not difficult to obtain an empirical equation which runs through rather than above the low points; however, the utilization of the vapor pressure data and the third law of thermodynamics to obtain the second virial coefficient of the gas shows a small error in the above points. This method is so sensitive that errors of a few tenths of a percentage in a pressure measurement show up as rather glaring deviations. We are forced to conclude that the presence of a small amount of inert gas, presumably helium or possibly hydrogen, led to an error of one or two tenths of a millimeter pressure at low pressures. The triple point pressure is of much higher reliability as it was studied separately under conditions which minimized the possibility of inert gas. The deviations of the above points are shown in Fig. 2 and we feel certain that the empirical vapor pressure equation is more reliable than one passing through the several points at low pressures.

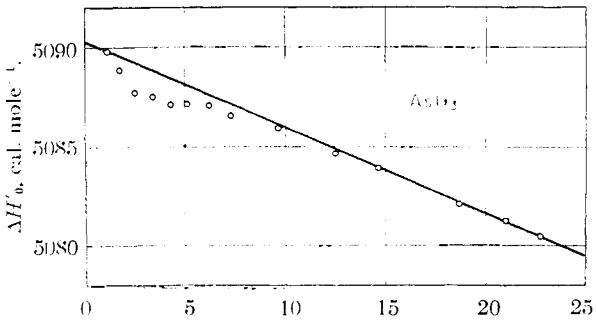

Fig. 2.—Heat of vaporization and gas imperfection of arsine.

Ordinarily the work on condensed gases in this Laboratory has made use of Berthelot's equation in making minor corrections for gas imperfection. Since the critical constants of arsine are unknown we have applied a method recently utilized by Busey and Giauque[18] in the case of mercury. This permits the evaluation of the second virial coefficient from the vapor pressure data when the free energy function is known for the condensed phase in its standard (P_{total} = 1 atm.) state and the gas in its standard (ideal gas P = 1 atm.) state. These quantities are tabulated in a later section. We will use the same symbols as Busey and Giauque. $PV = RT + bP/T^2$. $\Delta F^0/T = -R \ln f/a_{(1)} = -R \ln P - b'P/T^3 - V(1 - P)/T$. b' (cal. atm.$^{-1}$ deg.^{2}) corresponds to b(cm.^{3} deg.^{2}), $a_{(1)}$ refers to the activity of liquid arsine under its saturation pressure. The term $-V(1 - P)/T$ is required to correct for the change in free energy of liquid arsine when the pressure is increased from the saturation pressure, P, to 1 atmosphere to correspond to the usual standard state of thermodynamics.

$$\frac{\Delta F^0}{T} = \left(\frac{F^0 - H_0^0}{T}\right)_{(g)} - \left(\frac{F^0 - H^0}{T}\right)_{(l)} + \frac{\Delta H_0^0}{T}$$

Let

$$\frac{\Delta H'_0}{T} = \left(\frac{F^0 - H_0^0}{T}\right)_{(l)} - \left(\frac{F^0 - H_0^0}{T}\right)_{(g)} - R \ln P - \left(\frac{V_{(l)}(1 - P)}{T}\right)$$

where $\Delta H'_0$ is an approximate value for the heat of vaporization of arsine at the absolute zero, obtained by neglecting gas imperfection.

When $\Delta H'_0$ is plotted against P/T^2 the results are expected to fall on the straight line as shown in Fig. 2. The maximum deviation of about 1 cal. mole^{-1} occurs in the low pressure region, where, as mentioned above, a high percentage accuracy is not to be expected. All of the points above 0.25 atm. fall on the straight line within about one or two tenths of a cal. mole^{-1}. Thus the lower points are given little weight. However, the straight line went through the carefully measured triple point pressure. The fact that the more accurate points do fall on a straight line is taken as proof that the assumed temperature dependence of the second virial coefficient is correct within a small limit of error. The intercept, where P/T^2 = 0, gives the true ΔH_0^0 = 5090.3 cal. mole^{-1}.

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[15] W. Cawood and H. S. Patterson, *Trans. Faraday Soc.*, **29**, 514 (1933).

[16] Landolt, Bërnstein and Roth, "Physikalisch-chemische Tabellen," Verlag Julius Springer, Berlin, 1923.

[17] "International Critical Tables," Vol. 2, McGraw-Hill Book Co., New York, N. Y., 1926, p. 457.

[18] R. H. Busey and W. F. Giauque, This JOURNAL, **75**, 806 (1953).

The slope, $b' = -4.3 \times 10^5$ cal. atm.$^{-1}$ deg.^{2} mole^{-1}, $b = -1.8 \times 10^7$ cm.^{3} deg.^{2} mole^{-1}.

The measured heat of vaporization at the boiling point may be combined with the temperature coefficient of vapor pressure to give the second virial coefficient.

$$V_{(g)} = \frac{\Delta H}{T} \times \frac{dT}{dP} + V_{(l)} = \frac{RT}{P} + \frac{b}{T^2}$$

This gives $b' = -4.3 \times 10^5$ cal. atm. deg.^{2} mole^{-1}, $b = -1.8 \times 10^7$ cm.^{3} deg.^{2} mole^{-1}.

The values of b from the two methods happen to agree; however, in this case the value determined from the calorimetric heat of vaporization and dP/dT is the more reliable. The slope of the curve shown in Fig. 2 depends on the experimental value of the absolute entropy of the liquid. The slope of the straight line would be altered by about 5% for each change of 0.01 cal. deg.$^{-1}$ mole^{-1}, and considering the difficulty to be discussed below, in extrapolating the entropy below 15°K. in the present case, we can give no weight to the value of b determined from the slope in Fig. 2. However it should be realized that the positions of the points relative to the best straight line, as in Fig. 2, would not be altered by a small change in entropy and thus they support the form $BP = bP/T^2$ for the gas imperfection. Utilizing the value $b = -4.3 \times 10^{-5}$ cal. atm. deg.^{2} mole^{-1} the first method can be reversed to give the vapor pressure of solid arsine much more accurately than it could be measured directly. The values are given in Table VIII.

TABLE VIII

VAPOR PRESSURE OF SOLID ARSINE, INT. CM. Hg

T	P	T	P
40	6.0×10^{-21}	110	3.7×10^{-3}
50	2.8×10^{-15}	120	2.27×10^{-2}
60	1.6×10^{-11}	130	1.05×10^{-1}
70	7.3×10^{-9}	140	3.88×10^{-1}
80	7.0×10^{-7}	150	1.195
90	2.4×10^{-5}	T.P.	
100	3.9×10^{-4}	156.23	2.238

The Entropy of Arsine.—The calculation of the entropy of arsine from the calorimetric data is summarized in Table IX.

TABLE IX

THE ENTROPY OF ARSINE

CAL. DEG.$^{-1}$ MOLE^{-1}

0–15°K. (extrapolation)	1.26
15–31.25° (graphical integration)	3.794
31.25–32.25°, 24.13/Tav	0.760
32.25–105.55° (graphical integration)	13.608
Transition, 131.0/105.55	1.241
105.5—156.23° (graphical integration)	4.383
Fusion, 285.7/156.23	1.829
156.23-210.68° (graphical integration)	4.319
Vaporization, 3988/210.68	18.930
Entropy of arsine gas at b.p.	50.124
Correction to ideal gas, $\Delta S = -2b'P/T^3$	0.092
Entropy of ideal AsH_3 at b.p., 210.68°K.	50.22 ± 0.10
S^0 from molecular data at 210.68°K.	50.25

At 298.16°K., $S^0_{\text{mol. data}} = 53.18$ $S^0_{\text{exp.}} = 53.15$

The agreement shown in Table IX is very satisfactory and shows that arsine approaches zero entropy at limiting low temperatures in accordance with the third law of thermodynamics.

Arsenic consists of a single atomic species of mass 75, thus there is no entropy of isotopic mixing. Its nuclear spin is 3/2, thus the nuclear spin entropy of AsH_3 is $R \ln 4 + 3 R \ln 2 = 5 R \ln 2 = 6.89$ cal. deg.$^{-1}$ mole^{-1} and the absolute entropy is 60.07 cal. deg.$^{-1}$ mole^{-1} at 298.16°K.

The evaluation of the 1.26 cal. deg.$^{-1}$ mole^{-1} below 15°K. was exceptionally difficult because of the influence of the gradual transition near 32°K. on the heat capacities much below this temperature. The extrapolation was performed as follows. A family of Debye curves was subtracted, in turn, from the actual data and the residues were plotted. It was found that unless a Debye θ was selected within the range 68–73° it was impracticable to extrapolate the small residue. On this basis the total extrapolated entropy values ranged from 1.24 to 1.28 cal. deg.$^{-1}$ mole^{-1} and the value 1.26 was selected. This probably represents the major uncertainty in Table IX.

The entropy change between the actual and ideal arsine gas may be obtained by combining the experimentally evaluated equation of state with the thermodynamic equation

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad S^0 - S = -\frac{2b'P}{T^3}$$

cal. deg.$^{-1}$ mole^{-1}

The entropy from spectroscopic data was calculated in the usual manner[19] with the natural constants referred to above. The moments of inertia were taken from the work of Nielsen[20] $I_1 = I_2 = 7.516 \times 10^{-40}$ g. cm.^{2}, $I_3 = 7.963 \times 10^{-40}$ g. cm.^{2}. The molecule was assumed to be rigid since the small stretching correction has not been evaluated.

The vibrational frequencies used were those given by McConaghie and Nielsen[21]

	Cm.$^{-1}$	P
ν_1	2116.1	(1)
ν_2	2123.0	(2)
ν_3	904.4	(1/2)
	906.9	(1/2)
ν_4	1003	(2)

The Thermodynamic Properties of Arsine.—The thermodynamic properties of arsine, from 0°K. to the boiling point, have been computed from the observed data and are summarized in Table X. Since the standard state for condensed phases is taken at a total pressure of 1 atmosphere the following small corrections were made

$$S^0 - S = \int_P^1 \left(\frac{\partial V}{\partial T}\right)_P dP \simeq -\left(\frac{\partial V}{\partial T}\right)_P (1 - P)$$

$$\frac{(F^0 - H^0_0)}{T} - \frac{(F - H^0_0)}{T} = \int_P^1 V\, dP \simeq V(1 - P)$$

$$C_p{}^0 = C_{(\text{sat})} + T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_{(\text{sat})} - T\int_P^1 \left(\frac{\partial^2 V}{\partial T^2}\right) dP$$

The heat capacity corrections are very small,

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[19] W. F. Giauque, THIS JOURNAL, **52**, 4808 (1930).

[20] H. H. Nielsen, *J. Chem. Phys.*, **20**, 1955 (1952).

[21] V. M. McConaghie and H. H. Nielsen, *Phys. Rev.*, **75**, 633 (1949).

amounting to only 0.02 cal. deg.$^{-1}$ mole at 210°K., 0.01 at 200°K., and diminish rapidly.

TABLE X

THERMODYNAMIC FUNCTIONS OF SOLID AND LIQUID ARSINE, CAL. DEG.$^{-1}$ MOLE^{-1}

T, °K.	C_p^0	S^0	$(H^0 - H_0^0)/T$	$-(F^0 - H_0^0)/T$
15	2.795	(1.260)	(0.897)	(0.363)
20	4.370	2.276	1.565	0.711
25	6.078	3.433	2.296	1.137
30	8.100	4.705	3.081	1.624
35	10.406	6.664	4.407	2.257
40	10.748	8.075	5.217	2.858
45	11.084	9.361	5.851	3.510
50	11.350	10.543	6.388	4.155
55	11.534	11.635	6.849	4.786
60	11.676	12.645	7.246	5.399
70	11.906	14.463	7.896	6.567
80	12.018	16.061	8.405	7.656
90	12.092	17.480	8.810	8.670
100	12.207	18.760	9.144	9.616
105.55	12.281	19.421	9.300	10.121
105.55	11.175	20.662	10.541	10.121
110	11.176	21.124	10.584	10.540
120	11.178	22.096	10.633	11.463
130	11.180	22.991	10.675	12.316
140	11.182	23.820	10.712	13.108
150	11.184	24.591	10.743	13.848
156.23(s)	11.185	25.046	10.760	14.286
156.23(l)	14.465	26.874	12.595	14.279
156.28	14.465	26.878	12.596	14.288
160	14.451	27.219	12.637	14.582
170	14.428	28.094	12.742	15.352
180	14.422	28.919	12.833	16.086
190	14.436	29.700	12.916	16.784
200	14.464	30.441	12.991	17.450
210	14.511	31.148	13.060	18.087
210.68(l)	14.513	31.195	13.065	18.130

The molecular data given above have been used to tabulate the thermodynamic properties of arsine gas in the ideal state. The results are given in Table XI.

We thank M. N. Papadopoulos and Dr. E. W. Hornung for assistance with the low temperature measurements and Dr. J. Conway, of the Radiation Laboratory, for performing the spectroscopic analysis.

TABLE XI

THERMODYNAMIC FUNCTIONS OF ARSINE GAS, CAL. DEG.$^{-1}$ MOLE^{-1}

T, °K.	C_p^0	S^0	$(H^0 - H_0^0)/T$	$-(F^0 - H_0^0)/T$
20	7.949	31.469	7.949	23.520
25	7.949	33.243	7.949	25.294
30	7.949	34.692	7.949	26.743
35	7.949	35.917	7.949	27.968
40	7.949	36.979	7.949	29.030
45	7.949	37.915	7.949	29.966
50	7.949	38.752	7.949	30.803
55	7.949	39.510	7.949	31.561
60	7.949	40.202	7.949	32.253
70	7.949	41.427	7.949	33.478
80	7.949	42.488	7.949	34.539
90	7.949	43.424	7.949	35.475
100	7.950	44.262	7.949	36.313
110	7.953	45.020	7.949	37.071
120	7.955	45.712	7.950	37.762
130	7.966	46.349	7.950	38.399
140	7.978	46.940	7.952	38.988
150	7.998	47.491	7.954	39.537
160	8.026	48.008	7.958	40.050
170	8.066	48.496	7.963	40.533
180	8.108	48.958	7.970	40.988
190	8.163	49.397	7.978	41.419
200	8.226	49.818	7.989	41.829
210	8.299	50.221	8.002	42.219
220	8.382	50.608	8.017	42.591
230	8.469	50.983	8.035	42.948
240	8.564	51.347	8.056	43.291
250	8.617	51.697	8.077	43.620
260	8.770	52.040	8.103	43.937
270	8.880	52.372	8.129	44.243
280	8.993	52.698	8.159	44.539
290	9.112	53.015	8.189	44.826
298.16	9.207	53.176	8.122	45.054
300	9.228	53.326	8.222	45.104
310	9.348	53.630	8.259	45.374
320	9.469	53.929	8.292	45.637
330	9.593	54.222	8.329	45.893
340	9.717	54.510	8.368	46.142
350	9.840	54.794	8.408	46.386
400	10.447	56.147	8.629	47.518
450	10.985	57.379	8.840	48.539
500	11.617	58.607	9.111	49.496

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