The values of γ are tabulated in Table IV, together with values obtained by Robinson[13] from vapor pressure measurements, and those calculated from freezing point measurements.[14]

Free Energy, Heat and Entropy Changes of the Reaction.—Calculated e. m. f. values for the cells at 25° with sodium and lead metal electrodes are compiled in Table V. The free energy changes for the reaction $2Na + PbF_2 = 2NaF\ (aq.) + Pb$ are shown. The heat changes of the reaction were calculated from the change of the e. m. f. with temperature, using the Gibbs–Helmholtz equation. The values of ΔS, equal to $-\ d(\Delta F)/dT$, are shown.

The partial molal free energy, heat and entropy changes resulting from a transfer of one mole of sodium fluoride from a given molality to a 0.1 *m* solution are tabulated in Table VI. The values of ΔF are accurate to about 20 cal., those of ΔH to about 150 cal. and the values of ΔS to about 0.5 cal. per degree.

TABLE V

ΔF, ΔH AND ΔS OF THE REACTION $2Na + PbF_2 = NaF(AQ.) + Pb$

m	$E_{25°}$	ΔF	ΔH	ΔS
0.05	2.5277	−116,650	−112,390	14.3
.10	2.4941	−115,100	−112,350	9.2
.20	2.4624	−113,640	−112,130	5.1
.50	2.4197	−111,670	−112,080	− 1.4
.90	2.3931	−110,440	−112,090	− 5.5

TABLE VI

ΔF, ΔH AND ΔS OF DILUTION OF NaF SOLUTIONS

m	ΔF, cal. $m \rightarrow 0.1\ m$	ΔH, cal. $m \rightarrow 0.1\ m$	ΔS, cal./deg. $m \rightarrow 0.1\ m$
0.9	4660	260	14.7
.5	3430	270	10.6
.2	1460	220	4.1
.05	−1550	− 40	− 5.1

The Activity Product Constant of Lead Fluoride.—By comparing the value of the molal electrode potential of the Pb | Pb^- electrode, 0.1263 v.,[15] with that of the Pb | PbF_2 | F^- electrode, the activity product constant for PbF_2 at 25° was calculated to be 2.69×10^{-8}. This corresponds to an activity of 0.0463 g. per 100 ml. of solution. The solubility of lead fluoride is reported to be 0.066 g. per 100 g. of water.[16]

Summary

Sodium amalgams have been used as reference electrodes in solutions of sodium fluoride to measure the potential of the Pb(Hg, 2 phase) | PbF_2 | F^- electrode. The standard molal electrode potential has been calculated for 15, 25 and 35° from the data. The mean activity coefficients of sodium fluoride from 0.01 *m* to saturation and the free energy, heat and entropy of dilution of sodium fluoride solutions have been calculated. The activity product constant of lead fluoride was calculated.

WEST LAFAYETTE, INDIANA RECEIVED JULY 17, 1941

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[13] Robinson, THIS JOURNAL, **63**, 628 (1941).

[14] Landolt–Börnstein, "Tabellen," 5th ed., Suppl. **111**, p. 2148.

[15] Lingane, THIS JOURNAL, **60**, 724 (1938).

[16] Carter, *Ind. Eng. Chem.*, **20**, 1195 (1928).

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 844]

The Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressure and Entropy of Arsenic Trifluoride

BY HORACE RUSSELL, JR., ROBERT E. RUNDLE* AND DON M. YOST

Introduction.—Arsenic trifluoride, AsF_3, is at room temperatures a clear, colorless, mobile liquid which hydrolyzes somewhat slowly when exposed to the atmosphere. When the liquid is frozen by means of liquid air or the solid allowed to warm up, a rather intense greenish-yellow luminescence is observed. It was considered of interest to determine whether this radiation is associated with a phase transition or results from purely mechanical causes. In addition to this the extensive use of arsenic trifluoride as a fluorinating agent makes a knowledge of its thermodynamic properties desirable. In the present paper there are described the results of a low temperature calorimetric study of arsenic trifluoride, together with a comparison of the experimentally determined entropy of the vapor with that calculated from molecular data.

Experimental.—All measurements except the heat of vaporization and vapor pressures were made using gold-plated adiabatic calorimeter I with a strain-free platinum resistance thermometer of laboratory designation CT-26. The heat of vaporization was measured in a specially designed non-adiabatic calorimeter using thermometer CT-4.

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The apparatus, the method of operation and the calibration of the thermometers are to be described in a forthcoming paper.[1]

Preparation and Purity of the Arsenic Trifluoride.—The material was prepared by the method of Ruff[2] from C. P. sulfuric acid and finely mixed reagent grade arsenious oxide and calcium fluoride. Hydrolysis of the crude product forms hydrogen fluoride which was removed by allowing the material to stand over sodium fluoride. Arsenic trifluoride treated in this manner does not attack glass. Further purification was carried out by distillation at atmospheric pressure in an all-glass system using a five-foot column packed with glass helices. Three fractions of 40, 70 and 60 cc. were collected from a 200-cc. sample. During the entire distillation the temperature did not vary more than 0.02°. The observed boiling point was 57.13° at 742.5 mm. (cor.). Premelting in the third fraction showed a liquid soluble, solid insoluble impurity of 0.04 mole per cent. A composite of the second and third fractions showed an impurity of only 0.02 mole per cent. The chief impurity in the arsenic trifluoride after treatment with sodium fluoride is thus probably high boiling. At no time was liquid arsenic trifluoride allowed to come into contact with stopcock grease. The vapor was found to attack Apiezon grease M rapidly but Apiezon L only very slowly. Nevertheless, stopcocks were eliminated from all steps except distillation into the calorimeter which was done at low pressure.

If solid arsenic trifluoride was either cooled or heated, sharp, cracking noises were heard. Near liquid air temperatures the noise was accompanied by flashes of light. The effect seemed to be associated with a high coefficient of expansion since traps frequently broke even when warmed with great care. Similar effects have been observed in hydrogen cyanide.[3] Here, as there, the light was probably due to static discharges since no heat effects were observed.

Vapor Pressure Measurements.—As liquid arsenic trifluoride supercools readily, measurements were made from slightly below the melting point to near room temperature. Arsenic trifluoride does not attack mercury so a mercury manometer was used. Measurements were made against a Gaertner steel meter bar suspended in the manometer case and read with a Hensen cathetometer. Values are given in Table I corrected to international mm. of mercury. As some trouble was experienced in attaining equilibrium, the values are reliable to only ±0.5 mm.

TABLE I

VAPOR PRESSURE OF ARSENIC TRIFLUORIDE

0°C. = 273.16°K.

T, °K.	$P_{\text{obs.}}$ (Int. mm. Hg)	$P_{\text{calcd.}}$[a] (mm. Hg)	$P_{\text{calcd.}} - P_{\text{obs.}}$ (mm. Hg)
265.019	28.90	29.00	+0.10
268.235	36.15	35.85	− .30
272.058	45.68	45.67	− .01
275.271	55.22	55.33	+ .31
280.182	74.20	73.88	− .32
288.055	112.70	113.10	+ .40
291.816	136.96	136.90	− .06
291.879	137.46	137.30	− .16

[a] $\log_{10} p_{\text{mm.}} = 61.3797 - (4149.78/T) - 18.2640 \log_{10} T$.

Heat Capacities.—The composite of fractions two and three with an impurity of 0.02 mole per cent. was used for the heat capacity measurements. One defined calorie was taken as equal to 4.1833 international joules. The results, not corrected for premelting, are given in Table II and Fig. 1. Table III gives values at even temperatures read from a smooth curve and corrected for premelting. Errors may be as high as 1% at the lowest temperatures but decrease rapidly until above about 30°K. they are 0.1%. A definite slowness in reaching equilibrium in the region 100–120°K. was noticed. This corresponded roughly to the temperature of maximum light emission. In the heat capacities correction was made for vaporization. The density data of Thorpe[4] were used; the densities may be somewhat low, but this would introduce no appreciable error.

TABLE II

THE MOLAL HEAT CAPACITY OF ARSENIC TRIFLUORIDE

0°C. = 273.16°K.; 1.7975 moles in calorimeter, molecular weight 131.91.

T, °K.	C_p cal./mole/deg.	T., °K.	C_p cal./mole/deg.
13.588	1.258	95.685	12.79
14.677	1.480	101.289	13.18
15.868	1.712	104.139	13.43
17.250	2.044	112.163	13.95
19.166	2.513	120.456	14.53
21.504	3.084	129.683	15.12
23.992	3.703	138.460	15.69
26.893	4.388	147.190	16.21
30.329	5.143	156.354	16.75
33.873	5.870	165.679	17.28
37.220	6.488	175.036	17.80
40.673	7.056	185.032	18.34
44.305	7.653	194.454	18.86
48.273	8.207	201.673	19.17
52.678	8.799	211.116	19.74
57.433	9.320	220.869	20.27
63.072	9.920	230.631	20.84
69.868	10.61	239.601	21.36
77.120	11.29	247.802	21.86
78.186	11.36	260.205	Melting point
84.407	11.89	276.203	29.96
87.074	12.12	280.091	30.02
92.365	12.54	283.958	30.07
		287.810	30.07

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(1) Yost, Garner, Osborne, Rubin and Russell, THIS JOURNAL, to appear.

(2) Ruff, "Die Chemie des Fluors," Verlag Julius Springer, Berlin, 1920.

(3) Giauque and Ruehrwein, THIS JOURNAL, 61, 2626 (1939).

(4) "International Critical Tables," Vol. III, 1929, p. 23.

TABLE III

THE MOLAL HEAT CAPACITY OF ARSENIC TRIFLUORIDE AT ROUNDED TEMPERATURES

0°C. = 273.16°K.; molecular weight 131.91

T., °K.	C_p cal./mole/deg.	T., °K.	C_p cal./mole/deg.
15	1.537	140	15.78
20	2.724	150	16.39
25	3.945	160	16.97
30	5.072	170	17.51
35	6.081	180	18.07
40	6.960	190	18.62
45	7.747	200	19.16
50	8.449	210	19.68
60	9.605	220	20.20
70	10.62	230	20.71
80	11.53	240	21.20
90	12.36	250	21.68
100	13.11	260.21	Melting point
110	13.81	270	29.88
120	14.50	280	30.01
130	15.15	290	30.14

The Heat of Vaporization.—The third fraction of material with an impurity of 0.04 mole per cent. was used for the heat of vaporization measurements. Although the runs were made at a pressure of 142.6 mm., quite satisfactory precision was obtained.

TABLE IV

HEAT OF VAPORIZATION OF ARSENIC TRIFLUORIDE

Heater	Moles vaporized	Time, sec.	ΔH at 292.50°K. and 142.6 mm. (cal./mole)
Wound on outside	0.04243	3300	8566
Inside thermometer	.04859	3000	8565
		Av.	8566

The Melting Point and Heat of Fusion.—Melting points determined in the two calorimeters with different thermometers agreed within 0.005°. Results with the adiabatic calorimeter are given in Table V. Ruff[2] gives −8.3° for the melting point. Only one accurate determination was made of the heat of fusion. The value found agreed within 0.3% with the less accurate value obtained in the determination of the premelting curve for the sample used for the heat of vaporization measurements.

TABLE V

THE MELTING POINT OF ARSENIC TRIFLUORIDE

0°C. = 273.16°K.

% melted	Equil. temp., °K.	Calcd. temp.,[a] °K.
17.5	267.143	267.141
35.9	267.173	267.174
60.3	267.190	267.187
86.5	267.192	267.192

M. p. this sample 267.19° ±0.02°K.

M. p. pure sample 267.21° ±0.02°K. (−5.95°C.)

[a] Assuming 0.02 mole per cent. impurity.

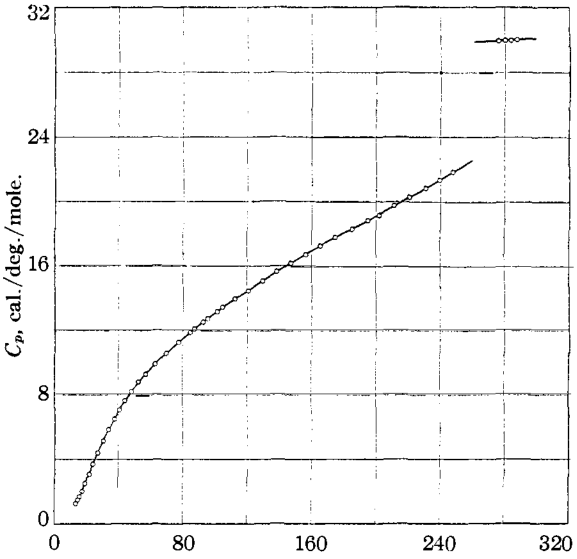

Fig. 1.—Molal heat capacity of arsenic trifluoride.

TABLE VI

THE HEAT OF FUSION OF ARSENIC TRIFLUORIDE

0°C. = 273.16°K.; molecular weight, 131.91

Temp. interval, °K.	Energy input, cal./mole	$\int C_p dT$ cal./mole	Premelting below 251.847°K.	ΔH, cal./mole
251.847–274.255	3218.0	736.7	5.1	2486

The Entropy from Calorimetric Data.—The calculation is summarized in Table VII. Critical constants for the gas are not known, so reasonable values were estimated for use in the Berthelot equation to correct for gas imperfections.

TABLE VII

THE MOLAL ENTROPY OF ARSENIC TRIFLUORIDE FROM CALORIMETRIC DATA

0°C. = 273.16°K.; molecular weight, 131.91

	ΔS cal./deg./mole
0–13.338°K. Debye extrapolation θ = 91.1°	0.454
13.338–267.205° graphical	30.272
Fusion 2486 (267.21°)	9.305
267.21–292.50° graphical	2.713
Vaporization 8566 (292.50°)	29.285
Real gas at 141.6 mm. and 292.50°K.	72.029 ±0.1
Correction for gas imperfections[a]	0.06
Ideal gas at 141.6 mm. and 292.50°K.	72.09 ± 0.15

[a] $S_{\text{ideal}} - S_{\text{actual}} = \frac{27}{32}\frac{T_c^3}{T^3}\frac{p}{p_c}R$; p_c = 50 atm., T_c = 570° K., assumed.

The Entropy from Molecular Data.—The entropy of arsenic trifluoride has previously been calculated by one of us.[5] A recalculation using new constants and slightly different structural parameters has been made; the two calculations agree to 0.1 cal./deg./mole. The constants used were 0°C. = 273.16°K., $R = 1.9871$ cal./deg./mole, $k = 1.3805 \times 10^{-16}$ erg/sec./molecule, $N = 6.023 \times 10^{23}$, $h = 6.624 \times 10^{-27}$ erg sec. The frequencies used were[6] 707, 341, 644(2), 274(2) cm.$^{-1}$. The moments of inertia were calculated from the results of a recent reinvestigation of the structure by electron diffraction.[7] The symmetry is C_{3v}, the As-F distance is 1.73 Å., and the F-As-F angle is 96.5 ± 2°. The results are summarized in Table VIII and compared with the calorimetric value of the entropy.

TABLE VIII

THE ENTROPY OF ARSENIC TRIFLUORIDE FROM MOLECULAR AND CALORIMETRIC DATA

	Spectroscopic entropy cal./deg./mole	Calorimetric entropy cal./deg./mole
Translational and rotational entropy	63.517	
Vibrational entropy	5.263	
Entropy at 1 atm. press. and 292.50°K.	68.78	
Entropy at 141.6 mm. press. and 292.50°K.	72.12 ± 0.10	72.09 ± 0.15
Entropy at 1 atm. press. and 298.16°K.	69.08 ± 0.10	69.05 ± 0.15

The calculated value should be very accurate; an error of 2° in the F-As-F angle makes an error of only 0.02 cal./deg./mole in the entropy; and an error of 0.02 Å. in the As-F distance corresponds to an error of 0.07 cal./deg./mole. The frequencies were measured with the liquid and may be shifted a few wave numbers in the gas, but the error should be less than 0.10 cal./deg./mole.

The excellent agreement between the calculated and observed entropies indicates that the entropy of crystalline arsenic trifluoride approaches zero at 0°K.

Summary

The heat capacity of arsenic trifluoride has been measured from 13 to 290°K. The melting point is 260.21 ± 0.02°K. with a heat of fusion of 2486 ±3 cal./mole. The heat of vaporization is 8566 ±8 cal./mole at 292.50°K. and 142.6 mm. The vapor pressure from 28 to 140 mm. of Hg is given by the equation $\log_{10} p = 61.3797 = (4149.78/T) - 18,2640 \log_{10} T$, where p is in intern. mm. of Hg.

The molal entropy from calorimetric data at 142.6 mm. pressure and 292.50°K. is 72.09 ± 0.15 cal./deg., compared with the value calculated from molecular data for the same conditions of 72.12 ± 0.10 cal./deg. The molal entropy at 1 atm. and 298.16°K. is 69.07 ± 0.10 cal./deg.

The strong luminescence noted when solid arsenic trifluoride is warmed or cooled near liquid air temperature is not associated with a change in phase.

PASADENA, CALIF. RECEIVED AUGUST 5, 1941

[5] Yost, *Proc. of the Ind. Acad. of Sci.*, **VIII**, 333 (1938).

[6] Howard and Wilson, *J. Chem. Phys.*, **2**, 630 (1934).

[7] Private communication from Dr. Verner Schomaker.

[CONTRIBUTION FROM NEWCOMB COLLEGE, TULANE UNIVERSITY]

An X-Ray Study of the Structure of Polyvinyl Alcohol*

BY ROSE C. L. MOONEY

An X-ray fiber diagram of polyvinyl alcohol, $(\text{—}CH_2CHOH\text{—})_n$, on which some fifteen reflections were recorded, was published by Halle and Hoffmann in 1935.[1] The extent of the work was a measurement of the periodicity along the fiber axis, given as 2.57 Å., and the calculation of interplanar spacings. In a fibrous substance such as this, "crystalline" orientation exists only along the fiber axis. Consequently, the amount of obtainable data, consisting, in general, of the equivalent of a rotation about a single axis, falls far short of that required for the best use of the X-ray methods. Usually, the determination of atomic positions is extremely difficult if not altogether impossible. Nevertheless, the vinyl alcohol fiber seemed to present an unusually favorable case for structure analysis, inasmuch as well oriented samples can be obtained, the fiber periodicity is short, and the chemical composition known and simple.

Experimental Data.—Two types of photographs were taken: one the usual fiber diagram, for which a beam of

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* Reported at Washington meeting of American Physical Society, April, 1941.

[1] Halle and Hoffmann, *Naturwiss.*, **45**, 770 (1935).