*p*H of 6, explaining why the height of the second wave is distinctly smaller than that of the first one. The rate of decomposition of hydrosulfurous acid increases with increasing hydrogen ion concentration, and also the $H_2S_2O_5$ formed (equation 8) decomposes with the formation of H_2SO_3

$$H_2S_2O_5 + H_2O \longrightarrow 2H_2SO_3 \qquad (9)$$

Therefore, the second wave disappears as the acidity increases. At *p*H values smaller than about 4 only one wave is found and the net reaction corresponds to a reduction to sulfoxylic acid (equations 5, 6, 8 and 9).

A polarographic investigation of various thionic acids at different acidities is planned in order to study the various involved reactions more in detail.

Summary

1. Sulfur dioxide in aqueous solutions can be determined polarographically in 0.1 to 1 *N* solutions of strong acids. The diffusion current is found proportional to the total sulfur dioxide concentration. The following reaction accounts quantitatively for the reduction: $SO_2 + 2H^+ + 2e \longrightarrow H_2SO_2$.

2. The diffusion coefficient of sulfur dioxide in aqueous medium was calculated to be 2.04×10^{-5} cm.,^{2} sec.$^{-1}$ at 25°.

3. Keeping the total sulfite concentration constant, the diffusion current decreases markedly when the *p*H becomes greater than 2. At a *p*H of 7 or greater than 7 no wave is found. This behavior is attributed to the facts that sulfurous acid exists in two tautomeric forms one of which is reducible, and that the speed of transformation of the oxidizible, strongly-acid form to the reducible, weakly-acid form is relatively small.

4. At a *p*H of 6 two small waves were found, the first one corresponding to a reduction to hydrosulfite, and the second to a reduction of the latter to thiosulfate.

MINNEAPOLIS, MINNESOTA RECEIVED JUNE 13, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Lead Amalgam–Lead Fluoride Electrode and Thermodynamic Properties of Aqueous Sodium Fluoride Solutions

BY REGINALD WILLIAM IVETT[1] AND THOMAS DE VRIES

The only use which has been made of electrodes whose reactions involve fluoride ions has been by Jahn-Held and Jellinek,[2] who measured the e. m. f. of the cells

Pb(5% amalgam), PbF_2 | HF(0.1 *N*) || KCl satd. || HF(1.0 *N*) | MF_2, M,

where M indicates copper, cadmium or zinc, as amalgams, or cobalt or nickel, as the powdered metal. They also measured the e. m. f. of the cell Pb(5% amalgam), PbF_2 | HF(1.0 *N*), H_2, Pt.

In this investigation further study was made of the reproducibility of the lead amalgam–lead fluoride electrode, using the cell Na(amalgam) | NaF(*m*) | PbF_2, Pb(amalgam). The free energy, heat content and entropy changes of the cell reaction, and the activity coefficients of the sodium fluoride were calculated from the e. m. f. measurements at 15, 25 and 35°, using 0.1 to 0.9 molal solutions. A saturated solution of sodium fluoride is 0.983*m* at 25°.

Materials

Sodium Amalgam.—Sodium amalgam was prepared by the electrolysis of a sodium carbonate solution using purified mercury as the cathode and a platinum foil as the anode. The sodium carbonate was recrystallized four times from conductivity water. The amalgam was washed repeatedly with water, then with acetone, and filtered through a small capillary into a flask filled with nitrogen.

Lead Amalgam.—Lead amalgam was prepared by using purified mercury as a cathode in a solution of Baker and Adamson reagent lead nitrate. The anode was a platinum foil in a solution of 1 *N* nitric acid, the two solutions being connected by means of an inverted glass U-tube filled with 1 *N* nitric acid. A current of about 0.2 ampere was passed until the concentration of the lead in the amalgam was about 5%. It was washed repeatedly with water, then with acetone, heated to 100° and filtered while hot through a small capillary into a container filled with nitrogen. A 5% amalgam consists of two phases at the highest temperature at which measurements were made, but can be changed to one phase by heating it to 100°.

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(1) Present address: Hercules Experiment Station, Wilmington, Del. This paper is an abstract of a thesis submitted by R. W. Ivett in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Jahn-Held and Jellinek, *Z. Elektrochem.*, **42**, 401 (1936).

Sodium Fluoride.—Merck reagent sodium fluoride was tested for the presence of sodium fluosilicate[3] and none was indicated. It was recrystallized by adding half as much redistilled isopropyl alcohol to an aqueous solution of the salt. The crystals were repeatedly washed on a sintered glass filter and dried in an air oven at 130°.

The sodium fluoride solutions were prepared by combining weighed amounts of the salt with conductivity water measured in a flask to give known weighed amounts of water at 25°. The solutions were stored in bottles lined with ceresin wax.

Lead Fluoride.—Lead fluoride was prepared by adding a solution of Merck reagent lead acetate in conductivity water to a slight molar excess of J. T. Baker Co. C. P. ammonium fluoride. The lead fluoride precipitate was washed on a sintered glass filter and dried at 110°.

Nitrogen.—Nitrogen was used to displace the air in the apparatus. It was passed over a heated copper gauze to remove traces of oxygen.

Analysis of Sodium Amalgam.—The sodium amalgam was analyzed by adding a slight excess of 0.05 N hydrochloric acid to about 10 g. of sample in an Erlenmeyer flask. The flask was shaken until the mercury broke up into small droplets. The solution was back-titrated with 0.02 N sodium hydroxide. The mercury was washed with water, then with acetone. It was weighed, and the composition of the amalgam calculated from the amount of acid used. In Table I are listed the compositions of the five amalgams used. Each one was analyzed four times and the consistency of the results is indicated. The potentials of the amalgams at 15, 25 and 35° as determined from results of other investigators are included. In the range of compositions of these amalgams a difference of 0.0005% sodium corresponds to a change of about 0.00015 volt in the potential.

Apparatus and Procedure

In order to prepare the dropping sodium-amalgam electrode the sodium-amalgam storage flask was sealed onto the apparatus at F (Fig. 1). The apparatus was alternately evacuated and filled with oxygen-free nitrogen, sufficient amalgam was introduced and the storage flask removed.

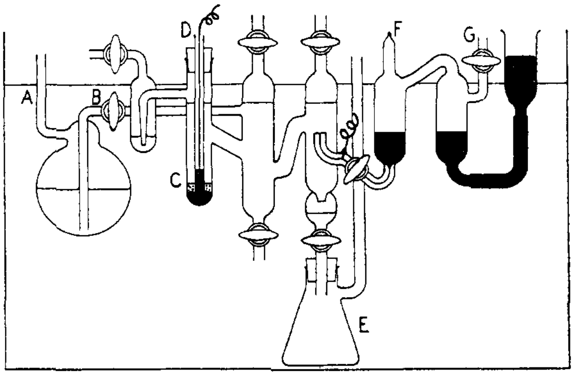

Fig. 1.—Diagrammatic sketch of cells.

To prepare the lead amalgam–lead fluoride electrodes the rest of the apparatus was filled with nitrogen, and while the nitrogen was flowing through the apparatus about 1 ml. of the lead amalgam, previously heated in a water-bath, and about 1 g. of lead fluoride was introduced into each of three electrodes, one of which is represented by C. Electrical connections to the lead amalgam were made by platinum wires sealed into the ends of tubes D. The sodium fluoride solution was introduced into the cell by forcing it over from the reservoir flask B. Dissolved oxygen had been removed by bubbling nitrogen for thirty minutes through a wash bottle containing some of the solution, then through the solution in flask B.

Measurements were made at the three temperatures 15, 25 and 35°, the water thermostat having a maximum deviation of ±0.02° in each case. In some determinations the sequence used was 25, 35, 15°; in others it was 35, 25, 15°. The temperature was changed through the sequence twice to observe any drift in the electromotive force. Readings were taken at the initial temperature after at least six hours. Subsequently, readings were taken two to three hours after a change of temperature.

The e. m. f. measuremets were made with a Rubicon Type B potentiometer. Since the voltages to be measured exceeded the range of the instrument, a Weston standard cell was used in series with the cell to reduce the voltage to a measured value. The voltage of this cell was checked periodically.

At each temperature the e. m. f. between one of the lead amalgam–lead fluoride electrodes and the sodium amalgam electrode was measured. The potential between the three lead amalgam–lead fluoride electrodes was measured to determine the reproducibility of that electrode. While the sodium amalgam was being used a drop of the amalgam was allowed to flow from the capillary every one to three seconds and the solution was allowed to flow through the cell at about three times that rate. The capillary of the sodium electrode was made to have a very small opening,[4] which made regulation of the amalgam flow easy and helped to reduce reaction of the amalgam with the solution while changing temperatures. The rate of flow was controlled by varying the pressure of nitrogen above the amalgam.

The e. m. f. readings of the cells, taken before and after a sequence of temperature changes, were in agreement to within 0.5 mv. when using solutions 0.1 m or more concentrated. For 0.5 m and 0.9 m solutions the agreement was to 0.1 mv. Any changes which occurred were decreases in the e. m. f. When using 0.05 m and 0.02 m solutions, although the readings at the initial temperature agreed reasonably, the e. m. f. decreased steadily at a rate of the order of 1 mv. per day for the former and 3 mv. per day for the latter concentration.

Calculations and Results

The potentials of dilute sodium amalgams have been determined by numerous investigators.[4-8]

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[3] Collins, *et al.*, *Ind. Eng. Chem.*, *Anal. Ed.*, **4**, 347 (1932).

[4] Richards and Conant, THIS JOURNAL, **44**, 601 (1922).

[5] Lewis and Kraus, *ibid.*, **32**, 1459 (1910).

[6] Allmand and Polack, *J. Chem. Soc.*, **115**, 1020 (1919).

[7] Michalek and Phipps, *J. Chem. Ed.*, **5**, 197 (1928). Bird and Hixon, *J. Phys. Chem.*, **34**, 1412 (1930). Philpot, Ross-Kane and Wolfender, *Phil. Mag.*, **13**, 765 (1932). Bent and Swift, THIS JOURNAL, **58**, 2216 (1936).

[8] Smith and Taylor, *Bur. Stand. J. Research*, **25**, 731 (1940).

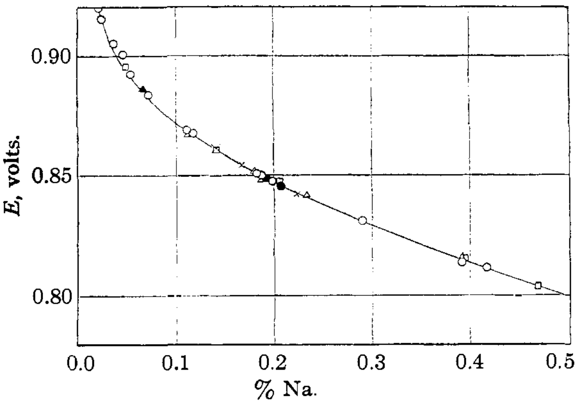

Fig. 2.—Potentials of sodium metal against sodium amalgams: ×, Allmand and Polack; □, Bent and Swift; ■, Bird and Hixon; ●, Lewis and Kraus; △, Michalek and Phipps; ○, Richards and Conant; ▲, Smith and Taylor.

A high degree of reproducibility makes them desirable for use as reference electrodes. The results of these investigators were used to calculate the potentials of sodium amalgams against sodium metal at 25° (Fig. 2). Some of these results were determined at temperatures other than 25°. Such data were used to calculate the corrections to be added to the potentials of sodium amalgams at 25° in order to obtain the values at 15 and 35° (Fig. 3).

TABLE I

POTENTIALS OF SODIUM AMALGAMS AGAINST SODIUM METAL

Amalgam	% Sodium	15°	25°	35°
A	0.2242 ± 0.0006	0.8418	0.8418	0.8422
B	.1337 ± .0004	.8613	.8618	.8628
C	.0866 ± .0004	.8764	.8774	.8788
D	.1184 ± .0003	.8654	.8660	.8671
E	.3284 ± .0003	.8235	.8230	.8230

The molal electrode potential of sodium has recently been determined by Smith and Taylor,[8] who measured the potential of a sodium amalgam against sodium metal and against a silver–silver chloride electrode at temperatures from 0 to 40°. Using the values of Harned and Ehlers[9] for the standard potential of the silver–silver chloride electrode, they calculated the potential of the sodium electrode to be given by the equation $E^0 = 2.71324 + 0.0007532\ (t - 25°) + 6.88 \times 10^{-7}\ (t - 25°)^2$. The E^0 at 25° may be compared with a value, 2.7139, calculated by MacInnes[10] from the potential difference between a 0.2062% amalgam and sodium metal, measured by Lewis and Kraus,[5] and the difference in potential between a 0.2062% amalgam and a normal calomel electrode, obtained by an interpolation between the results of Allmand and Polack.[6] The value of Smith and Taylor probably involves fewer uncertainties.

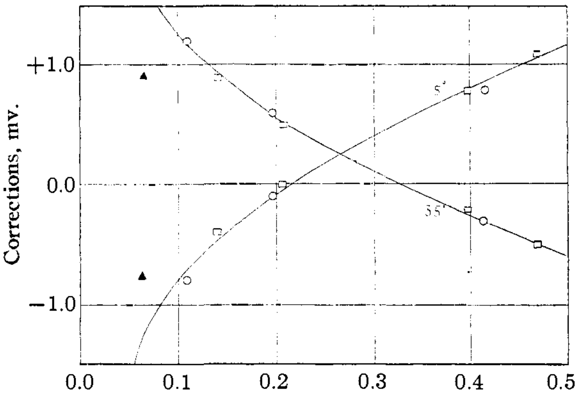

Fig. 3.—Sodium amalgam potentials at 15° and 35° calculated from the data of: □, Bent and Swift; ○, Richards and Conant; ▲, Smith and Taylor.

Molal Potential of Pb(Hg, 2 phase) | PbF_2 | F^- Electrode.—E. m. f. measurements were made of approximately 35 cells of the type Pb(Hg, 2 phase) | PbF_2(s) | NaF (0.05–0.90*m* | Na(Hg). In Table II are listed the average e. m. f. values (E) in millivolts for each of the sodium amalgams used with each concentration of sodium fluoride. The second column under each temperature gives E', the potential of the cells calculated with reference to a sodium metal electrode. These values are used to calculate the E^0 of the cell as follows.

The e. m. f. of the cell may be expressed by the Nernst equation

$$E^0 = E' + \frac{2RT}{F} \ln m\gamma = E'' + \frac{2RT}{F} \ln \gamma$$

According to the Debye–Hückel theory the activity coefficient of a uni-univalent electrolyte is given by the equation

$$\log \gamma = \frac{-A'\sqrt{m}}{1 + \beta' a_i \sqrt{m}}$$

in which A' and β' are constants at a given temperature and a_i is the "distance of closest approach" of the ions. Substituting this value for $\log \gamma$ and rearranging terms, the equation becomes

$$E'' - 4.6052\,\frac{RT}{F} A'\sqrt{m} = E^0 - (E'' - E^0)\beta' a_i \sqrt{m}$$

If the values on the left side of this equation, rep-

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(9) Harned and Ehlers, THIS JOURNAL, 55, 2183 (1933).

(10) MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corp., New York, N. Y., 1939, p. 197.

TABLE II

ELECTROMOTIVE FORCE OF CELLS

$Pb(Hg) \mid PbF_2(s) \mid NaF(m) \mid Na(Hg) = E$

$Pb(Hg) \mid PbF_2(s) \mid NaF(m) \mid Na \quad = E'$

Amalgam	15° *E*	15° *E'*	25° *E*	25° *E'*	35° *E*	35° *E'*
			0.05 *m* NaF			
B	1667.3 ± 0.2	2528.6	1672.1 ± 0.5	2533.9	1673.3 ± 0.4	2536.1
C	1653.7 ± .6	2530.1	1656.0 ± .3	2533.4	1657.4 ± .4	2536.2
			0.10 *m* NaF			
B	1636.4 ± .3	2497.7	1638.3 ± .4	2500.1	1639.5 ± .2	2502.3
D	1632.2 ± .4	2497.6	1633.5 ± .7	2499.5	1634.3 ± .5	2501.4
E	1675.1 ± .5	2498.6	1677.4 ± .1	2500.6	1678.8 ± .2	2501.8
			0.20 *m* NaF			
A	1625.8 ± .5	2467.6	1626.7 ± .4	2468.3	1627.7 ± .4	2469.9
B	1605.7 ± .2	2467.0	1606.4 ± .2	2468.2	1607.1 ± .2	2469.9
E	1643.8 ± .5	2467.3	1644.8 ± .5	2467.8	1645.9 ± .6	2468.9
			0.50 *m* NaF			
C	1550.2 ± .2	2426.7	1548.9 ± .2	2426.3	1547.1 ± .3	2425.9
D	1560.4 ± .4	2425.8	1559.4 ± .4	2425.4	1558.1 ± .3	2425.2
E	1601.7 ± .1	2425.2	1601.9 ± .3	2424.9	1601.6 ± .2	2424.6
			0.90 *m* NaF			
C	1524.5 ± .4	2400.5	1522.6 ± .3	2400.0	1519.7 ± .6	2398.5
D	1534.1 ± .3	2399.5	1532.1 ± .6	2398.1	1529.7 ± .5	2396.8
E	1576.9 ± .2	2400.4	1576.0 ± .1	2399.0	1575.0 ± .2	2398.0

resented by E''', are plotted against $(E'' - E^0)\sqrt{m}$, they should give a straight line in the range of concentration over which the Debye–Hückel equation holds.[11] By a series of approximations the values of E^0 at each of the three temperatures were obtained. The final extrapolations are shown in Fig. 4 and the results in Table III. The values are probably accurate to about 0.4 mv. The values for the potential difference between lead and two-phase lead amalgam were taken from the paper by Gerke.[12]

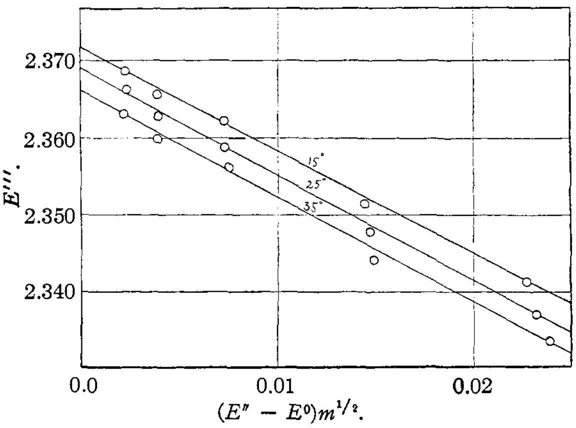

Fig. 4.—Extrapolation of data to obtain E^0.

TABLE III

POTENTIAL OF $Pb(Hg, 2\ PHASE) \mid PbF_2 \mid F^-$ ELECTRODE

	15°	25°	35°
E^0 of cell with Na electrode	2.3713	2.3688	2.3658
E^0 of $Pb(Hg, 2\ phase) \mid PbF_2 \mid F^-$ electrode	0.3345	0.3444	0.3550
Lead amalgam *vs.* lead	.0057	.0058	.0059
E^0 of $Pb \mid PbF_2 \mid F^-$ electrode	.3402	.3502	.3609

Mean Activity Coefficients of Sodium Fluoride.—Values of the mean activity coefficient of sodium fluoride were calculated for concentrations at which measurements were made by using the equation $2RT/F \ln \gamma = E^0 - E''$. At other concentrations the values were obtained by substituting the values of $\beta' a_i$, the slopes of the lines in Fig. 4, in the Debye–Hückel equation.

TABLE IV

ACTIVITY COEFFICIENTS OF SODIUM FLUORIDE

m	15°	25°	35°	At f. p. of solns.	25° (from vapor p.)
0.01	0.904	0.903	0.901	0.90	
.02	.873	.872	.870	.87	
.05	.816	.814	.813	.81	
.1	.778	.782	.773	.75	0.764
.2	.718	.725	.711	.69	.708
.3	.698	.697	.693		.675
.5	.663	.666	.656	.62	.631
.7	.638	.639	.633		.602
.9	.618	.621	.613		
.983[a]	.615	.617	.610		.572

[a] Saturated solution.

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[11] Hitchcock, THIS JOURNAL, 50, 2076 (1928); Brown and MacInnes, *ibid.*, 57, 1356 (1935).

[12] Gerke, *ibid.*, 44, 1695 (1922).

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. III, 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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