UCRL 8781

UNIVERSITY OF
CALIFORNIA
Ernest O. Lawrence
Radiation Laboratory

THE CHEMISTRY OF STIBINE

DISCLAIMER

UCRL-8781
Chemistry General

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory

Berkeley, California

Contract No. W-7405-eng-48

THE CHEMISTRY OF STIBINE

Ladislav Henry Berka

(M.S. Thesis)

June 1959

Printed for the U. S. Atomic Energy Commission

Printed in USA. Price $1.50. Available from the
Office of Technical Services
U. S. Department of Commerce
Washington 25, D.C.

THE CHEMISTRY OF STIBINE

Ladislav Henry Berka

Lawrence Radiation Laboratory
University of California
Berkeley, California

TABLE OF CONTENTS

TABLE OF CONTENTS

THE CHEMISTRY OF STIBINE

Ladislav Henry Berka

Lawrence Radiation Laboratory
University of California
Berkeley, California

ABSTRACT

Results of the study of the preparation of stibine by the reaction of aqueous borohydride with Sb(III) are given. The highest yield (based on BH_4^- assuming 3 $BH_4^- \longrightarrow$ 4 SbH_3) obtained was 23.6%.

The vapor pressure of stibine is given at six different temperatures, from -95° to -22°C. An equation of vapor pressure vs temperature is derived which represents the data. Temperature equations for the ΔH°, ΔF°, and ΔS° of vaporization are also derived.

THE CHEMISTRY OF STIBINE

Ladislav Henry Berka

Lawrence Radiation Laboratory
University of California
Berkeley, California

PREPARATION OF STIBINE BY BH_4^- REDUCTION OF Sb(III) SOLUTIONS

Introduction

The classical method for preparing stibine is to react a magnesium-antimony alloy with aqueous acid. The alloy is previously prepared by heating a mixture of magnesium and antimony metals in an atmosphere of hydrogen for several hours. By this method, Durrant and co-workers[1] obtained 10 grams of stibine from 250 grams of alloy containing a weight ratio of Sb/Mg = 0.667. With the advent of aluminum hydride and the borohydrides of sodium and potassium during recent years, has come their use in the preparation of various metallic hydrides.[2-4]

In an extensive study of sodium borohydride and its reactions, Kramer[5] studied reactions of aqueous borohydride (in excess) with solutions of antimony potassium tartrate. In basic solutions no stibine was evolved, whereas at pH 6.0, 5.5, and 4.0, Kramer obtained yields (based on the amount of antimony) of 3.21, 2.74, and 2.71%, respectively. The only experiments carried out below a pH of 4 were done in 6 N HClwhere the average yield was 7.7%. In all cases, 50 cc of 0.26 M $NaBH_4$ was added to 25 cc of approximately 0.033 M antimony solution.

These results of Kramer, along with some preliminary experiments performed in solutions of low pH, showed that the yields of stibine

obtainable by borohydride reduction in these solutions were large enough, not only to provide a means of preparing stibine for use in later experiments, but also to warrant a detailed study of this method, aimed at finding the optimum yield conditions.

Experimental

Antimony trichloride (Mallinckrodt Chemical Works) was used as the source of Sb(III). The samples available were not suitable for direct weighing because of a layer of liquid above the crystalline material. It was therefore necessary to devise some other scheme for determining the amount of Sb(III) being put into solution. This was done by collecting the liquid phase from a variety of samples, diluting a known volume of this to a liter with 4 M HCl, and analyzing aliquots for Sb(III) by titration with triiodide.[6] Thus, knowing the concentration of antimony in this liquid stock (8.74 M), desired amounts for each experiment could be added volumetrically to the reaction vessel. The stock solution, when analyzed in the same manner two months later, showed no appreciable change in Sb(III) concentration.

Most of the experiments were performed with antimony solutions in which the chloride ion concentration was 4 M. In such solutions, we had no difficulty in keeping the antimony in solution. The ionic strength of the solutions was maintained 4 M with hydrochloric acid and sodium chloride.

Both sodium and potassium borohydride (Metal Hydrides, Inc., Beverly, Massachusetts) were used. Since both hydrolyze slowly when dissolved in water at room temperature with the formation of hydrogen, fresh solutions of them were prepared in water at 0° C just prior to each experiment.

In all runs (with one exception) the solution of borohydride was added by means of a separatory funnel to the Sb(III) solution in the reaction vessel (see Fig. 1).

The reaction vessel was a three-necked flask, attached through a cold finger containing dry ice to a vacuum line. The cold finger served partially

to prevent water from passing on to the rest of the collection train.

The collection train consisted of three traps in series. The first was cooled to -78° C with a mixture of dry ice and acetone, and the second was cooled to -95° with a toluene slush in order to trap out the less volatile impurities. The crude stibine was collected in the third trap, which was immersed in liquid nitrogen. Beyond the liquid nitrogen trap, a stopcock (leading to the vacuum pump) provided the means for regulating the pressure in the system at 600 mm Hg.

The stibine was transferred to a manometer system and measured.

Some experiments were carried out in the following manner. The Sb(III) solutions were titrated by adding 0.50 M borohydride slowly, in increments, and measuring the stibine formed after each addition. This titration technique was used so that the yield could be followed as a function of the amount of borohydride added.

Upon first assembling the apparatus, the system was purged with hydrogen for at least five minutes, during which time the stibine collection trap was at room temperature. After each incremental addition of borohydride (during addition, there was no hydrogen flow from an external source, and the pressure in the system was kept at 600 mm), the entire system was purged again with hydrogen for at least two minutes in order to ensure that all the stibine in the system was driven into the liquid nitrogen trap. The flushing hydrogen passed over the Sb(III) solutions in these runs.

The reactions at 0° C were run by surrounding the reaction vessel with crushed ice. A magnetic stirrer stirred the Sb(III) solutions.

The procedure described above was modified somewhat in other studies. In a few runs, hydrogen was continually bubbled through the Sb(III) solution

during the borohydride additions by having the hydrogen delivery tube immersed well below the surface of the solution. In these runs, the bubbling was very vigorous and thus served to stir the solution. A modified separatory funnel was also necessary so that the borohydride could be added under the excess pressure in the system. Glass beads were placed in the stibine collection trap in order to provide a much greater area for stibine condensation, thus preventing stibine from being flushed out of the trap.

(Only one experiment was done in which an Sb(III) solution was added to 0.50 M borohydride. Hydrogen was not flushed through the system during the addition. The Sb(III) solution was added until all the borohydride had reacted as evidenced by a cessation of hydrogen evolution.)

Results

During the course of the reaction producing stibine, the formation of a deposit of antimony metal in the reaction vessel was noted. Also, hydrogen was continually evolved as the borohydride was added.

The over-all percentage yields of stibine formed based on the amount of borohydride added were calculated on the assumption that all four hydrogens of the BH_4^- ion are capable of appearing in the metal hydride product. The reaction assumed for stibine formation in HCl solution is:

$$4\ SbCl_4^- + 3\ BH_4^- + 9\ H_2O = 4\ SbH_3 + 3\ H_3BO_3 + 16\ Cl^- + 9\ H^+ \quad . \quad (1)$$

The reduction reactions of borohydride have not been sufficiently studied for us to know just how many hydrogens originating in the BH_4^- ion are incorporated in the metal hydride product. It is therefore to be noted that the true percentage yields may be greater than the values we have calculated. The yields represent crude stibine (all but 2% of a portion of one crude product decomposed to hydrogen when heated in a closed tube); the only pre-measurement purification was that provided by the collection train.

The results of a typical experiment are shown in Fig. 2. The over-all number of millimoles of stibine formed was plotted against the total number of millimoles of BH_4^- added, and, for the most part, were proportional to the first incremental amounts of borohydride.

Results obtained under varying conditions of stirring, H^+ concentration, Sb(III) concentration, reaction temperature, with or without constant hydrogen bubbling, are given in Table I. The "initial" percentage yields based on borohydride were calculated by multiplying the slope of the

linear portion of the over-all yield curve by 75 (3 BH_4^- ⟶ 4 SbH_3). The "endpoint" is defined as the point where the slope of the over-all yield curve is 1/4 of the initial slope. The total number of millimoles of BH_4^- added in getting to the endpoint divided by the number of millimoles of Sb(III) originally present is also tabulated in Table I for each run. The over-all percentage yields based on borohydride at the endpoint were calculated by multiplying by 75 the ratio of the total number of millimoles of SbH_3 produced to the total number of millimoles of BH_4^- added, both evaluated at the endpoint.

It will be sufficient for purposes of comparison to restrict ourselves to the "initial" percentage yield based on borohydride column of Table I. (The other quantities we have calculated and given in Table I will serve to enable the reader to construct approximate over-all yield curves for all the runs, and from these gain information more suited to his own purposes.)

Table I

Over-all Percentage Yields Obtained by Titrating Solutions of Sb(III) with 0.50 M KBH_4 Under Various Conditions

Expt No.	Initial M Sb(III)	Sb(III) soln. (cc)	M HCl	M NaCl	React temp(°C)	"Endpoint"[a] [mmoles BH_4^- per mmoles Sb(III)]	% Yield Based on borohydride[b] Initial	% Yield Based on borohydride[b] At "endpoint"	Remarks
1	0.10	300	1.0	3.0	R.T.	1.1	7.1	6.8	Magnetic stirrer
2	1.0	100	1.0	3.0	R.T.	1.9	4.8	3.8	"
3	0.10	300	4.0		R.T.	1.0	4.3	3.8	"
4	0.10	300	1.0	3.0	0°	1.3	11.8	10.7	"
5	1.0	100	1.0	3.0	0°	1.5	5.6	4.9	"
6[d]	0.20[c]	300	(c)		0°	1.3	6.3	5.9	"
7[d]	0.098	305	0.40	3.7	0°	1.4	10.4	7.6	"
8[d]	0.10	300	1.0	3.0	0°	0.93	1.6	1.0	Mech stirrer
9[d]	0.10	300	1.0	3.0	0°	0.95	14.1	11.7	H_2 bubbling
10	1.0	100	0.70		0°	0.80	14.4	10.3	"
11	1.0	100	1.0	3.0	0°	0.92	20.6	18.2	"

[a] The point where the slope of the yield curve (e.g., Fig. 2) is 1/4 of the initial slope.

[b] 75 times the SbH_3/BH_4^- ratio.

[c] Reaction carried out in 1.0 M tartaric acid.

[d] Titrated with 0.50 M $NaBH_4$.

First, let us consider the experiments in which the Sb(III) solution was magnetically stirred without continual hydrogen bubbling during reaction, namely, Experiments 1 through 7. In comparing the initial over-all percentage yields given by Experiments 1 and 2, we see that decreasing the Sb(III) concentration from 1.0 to 0.10 M improved the stibine yield by a factor of about 50%. In Experiment 3 this factor was in effect nullified by increasing the H^+ concentration from 1.0 to 4.0 M. Experiment 4 compared to 1 shows an even better yield when the reaction was held at 0° C. Experiment 5 confirms the improvement in yield by running the reaction at 0° C rather than room temperature. The temperature dependence of stibine yield does not seem to be as great with 1.0 M Sb(III) as it is when the Sb(III) concentration is 0.10 M.

From the results of these preliminary experiments, we may conclude that: (a) lower(H^+)(1.0 M vs 4.0 M), (b) lower (Sb(III)) (0.10 M vs 1.0 M), (c) and running the reaction at 0° C rather than room temperature, favor the formation of stibine when the Sb(III) solution is magnetically stirred and no hydrogen is flushed through the system during stibine formation. Furthermore, the optimum H^+ concentration seems to be about 1.0 M rather than 4.0 or 0.40. Experiment 7, compared with the other results, points this out.

All experiments were performed with HCl solutions except No. 6, in which 1.0 M tartaric acid was used instead. The effect of this change is hard to evaluate because of the "odd" Sb(III) concentration of 0.20 M. However, the large yield difference between Experiments 4 and 6 could hardly be attributed alone to the small change in Sb(III) concentration and probably rests quite appreciably in the different acid being present (there is also a large ionic-strength difference between the two solutions).

Now, let us consider the initial percentage yields of Experiments 8 through 11 in Table I, along with the pertinent initial yields of Experiments 1 through 7.

Experiments 8 and 9, each having identical initial Sb(III) solutions as in Experiment 4, show the effect of stirring rate and continual hydrogen flushing during reaction. Bubbling hydrogen through the solution continually during the borohydride addition increased the previously highest yield of 11.8% to 14.1%. Stirring the solution vigorously with a mechanical stirrer, on the other hand, decreased the yield eight fold.

From Experiments 11 and 9 we see that continual hydrogen flushing during stibine formation had an even greater effect in the case of the 1.0 M Sb(III) solution of Experiment 5, than in the case of the 0.10 M Sb(III) solution of Experiment 4. In fact, the yield order we had noted previously (i.e., 0.10 M Sb(III) > 1.0 M Sb(III), with magnetically stirred solutions) is in effect reversed when these same solutions react under hydrogen flushing conditions.

Having obtained the optimum conditions of those studied by the titration technique (i.e., 1.0 M Sb(III), 1.0 M HCl, 3.0 M NaCl, run at 0° C with continual hydrogen bubbling through the solution) a run was made employing these optimum conditions, 75 millimoles of 0.50 M borohydride being added in one increment to 100 cc of the Sb(III) solution. This run gave the best over-all percentage yield of stibine obtained by us in this study, 23.6%.

Finally, 45 millimoles of 0.50 M borohydride were added in one increment to each of two 600-cc solutions containing 0.10 M Sb(III), 1.0 M HCl, 3.0 M NaCl, run at 0°C with continual hydrogen bubbling. The average yield in these two runs was 18.9%.

[The only experiment in which an Sb(III) solution was added to 0.50 M BH_4^-, rather than in the reverse manner, gave the following result: 24 cc of 1.0 M Sb(III) solution -- with 1.0 M HCl and 3.0 M NaCl at 0° C -- was needed to react with 150 cc of the borohydride solution, giving a 6.8% yield based on BH_4^-. A white precipitate, most likely containing Sb(III), was found in the reaction flask along with antimony metal at the conclusion of the experiment.]

Discussion

The reaction [Eq. (1)] which produces stibine when borohydride is added to an acid solution of Sb(III) is undoubtedly only one of several taking place simultaneously in solution. Hence, any interpretation of the results of the study we have made must concern itself with a consideration of what the competing reactions are, and how varying conditions affect them along with the desired reaction taking place. With more detailed knowledge, of course, a complete interpretation would involve the specific kinetics of these reactions.

The formation of hydrogen during the addition of borohydride to an acid solution may be represented by the reaction:

$$BH_4^- + H^+ + 3\ H_2O = H_3BO_3 + 4\ H_2 \ . \qquad (2)$$

This explains the lower stibine yield at high concentrations of H^+. More of the borohydride is used up by Reaction (2) and less is available for stibine formation.

For the formation of antimony metal, at least two possible reactions are conceivable:

$$9\ H_2O + 3\ BH_4^- + 8\ SbCl_4^- = 8\ Sb + 3\ H_3BO_3 + 32\ Cl^- + 21\ H^+ \qquad (3)$$

or

$$SbCl_4^- + SbH_3 = Sb + 3\ H^+ + 4\ Cl^- \ . \qquad (4)$$

Reaction (3) involves the partial reduction of Sb(III) by BH_4^- to Sb. As a check on Reaction (4), an experiment was performed in which SbH_3 was passed through a trap containing an Sb(III) solution. A copious precipitate of antimony metal was formed. [A reaction analogous to (4) occurs to produce arsenic metal when arsine is passed through a solution

of $AsCl_3$.] On this basis, together with the observed yield results, Reaction (4) is probably the reaction producing antimony metal.

Hydrogen bubbling through the solution would remove the stibine from the solution and its vicinity as rapidly as it was being formed and thereby decrease the extent of Reaction (4). The higher yields obtained with hydrogen bubbling are evidence of this. The higher yields obtained with hydrogen bubbling would not be explicable on the basis of Reaction (3).

In addition, a high stirring rate unaccompanied by hydrogen flushing would distribute the stibine throughout the solution as it was formed and thereby increase the extent of Reaction (4). The very low yield in the mechanical-stirrer experiment bears this out.

The observed change in the percentage yield vs Sb(III) concentration, which was brought about by the introduction of continual hydrogen flushing through the system, is consistent with Equations (1), (2), and (4). Both Reactions (1) and (2) are in competition for the BH_4^- ion. Higher concentrations of Sb(III) favor the stibine reaction (1) at the expense of the hydrogen reaction (2). However, without hydrogen flushing, Reaction (4) is occurring quite appreciably, destroying a greater amount of SbH_3 at higher Sb(III) concentrations. Reaction (4) occurs to such an extent so as to give the result that 0.10 M Sb(III) gives a higher percentage stibine yield than does 1.0 M Sb(III). On the other hand, with continual hydrogen flushing, Reaction (4) may in effect be neglected and Reaction (1) controls the stibine yield.

Only a minute fraction of the total number of possible combinations of the several variables considered in this study have been explored by

the author. The problem involved in determining the optimum conditions for stibine formation by borohydride reduction of Sb(III) solutions is indeed complex. Rate studies on the aqueous BH_4^- + H^+ reaction and other BH_4^- reduction reactions, along with more information on the reactions of Sb(III) species and SbH_3, would be helpful in predicting the effect of changing variables.

STIBINE: VAPOR PRESSURE, THERMODYNAMIC FUNCTIONS OF VAPORIZATION, AND A VAPOR-PRESSURE EQUATION

Introduction

Until the present investigation, the only extensive study of the vapor pressure of stibine was that made by Durrant[1] and co-workers. Vapor pressures calculated from their empirical equation differed by more than 10% from those we observed with our samples. These discrepancies prompted us to measure the vapor pressure of stibine from -95° C, just below its melting point, to -23° C, just below its boiling point, in order to obtain a more accurate set of data on vapor pressure vs temperature than had been determined.

We thought it desirable to express our vapor-pressure data in terms of an equation having thermodynamic significance. The treatment of Brewer and Searcy[7] was applied (with some modification) to our measurements in order to obtain temperature expressions for ΔF°, ΔH°, and ΔS° of vaporization.

VAPOR PRESSURE

Experimental

Measurements were made on two samples of stibine (hereafter denoted by "A" and "B") prepared by borohydride reduction of Sb(III) solutions. Each sample was treated independently and agreed within experimental error.

Purification

Preliminary purification had been afforded by the collection train in the preparation of the stibine used (three traps in series: -78, -95, the stibine collecting in the third at -196° C).

A further purification was carried out by allowing the stibine to pass from a container, which was warming up slowly to room temperature from -196° C, through three traps in series maintained at -95°, -126°, and -196° C. After all the stibine (about 35 millimoles) had vaporized from the original container, another five minutes were allowed for further distribution of the stibine among the three traps. The major portion (about 90%) of the original sample condensed in the -126° trap and was kept for further work. The rest of the sample was distributed evenly between the other two traps with vapor pressures of 7.7 cm (-95° trap) and 12 cm Hg (-196° trap) when surrounded by a chloroform slush. These portions were discarded.

The stibine preparation having taken place from acid solution, a chemical purification to remove possible acid impurities was carried out. A small amount of dry ammonia (~ 2 mmoles) was mixed with the stibine at -78° C and allowed to remain in contact with it for about ten minutes. Much hydrogen was formed because of the catalytic effect of ammonia on the

decomposition of stibine. The ammonia-stibine-hydrogen mixture was then pumped from the trap at -78°, through a trap at 0°C containing $MgClO_4$ to absorb the ammonia, into a trap at -196° C to condense the stibine, the hydrogen going on to the vacuum pump. Any acid impurities such as CO_2 and HCl would be expected to remain in the -78° trap as $NH_4CO_2NH_2$ and NH_4Cl. About half the original amount of stibine remained after these purification procedures.

Evaluation of Purity

a. Tensiometric homogeneity: Two traps in series were used in the following procedure, one containing the stibine at the temperature of chloroform slush, the other cooled with liquid nitrogen. The stopcock between the two traps was opened momentarily, allowing about 0.05 millimoles of stibine to distill over into the liquid nitrogen trap. The cock was then closed and the stibine at -64° C allowed to equilibrate again. This process was repeated until about 10% (2 mmoles) of the stibine had distilled over. The remaining stibine was similarly fractionated until about 10% remained in the -64° trap as a residue. The vapor pressures of the initial and residual fractions were determined at the temperature of chloroform slush, the agreement between these vapor pressures giving a criterion of purity. The results obtained with the two samples, A and B, are given in Table II. The vapor pressures and temperature given in the table were obtained by methods to be described later. There was no appreciable difference between the vapor pressures of distillates and residues of either sample. The agreement in vapor pressure between the two samples is not nearly as good.

These distillates and residues were discarded and all further work was done using the remaining 12 mmoles of stibine.

Table II

Tests for Tensiometric Homogeneity (T = 209.21° K)

Sample	Fraction	Vapor Pressure (cm Hg)
A	1st distillate	8.08
	1st residue	8.05
	2nd distillate	8.07
	2nd residue	8.05
B	1st distillate	7.97
	1st residue	8.00
	2nd distillate	8.00

b. Melting point: Two procedures were used for determining the melting point. The first employed the standard melting-point apparatus described by Sanderson.[8] With the pinwheel raised in the apparatus by means of an external magnet, the stibine was distilled into the apparatus to form a solid ring just below the pinwheel. With the apparatus immersed in a dewar containing ethyl alcohol cooled to $\sim 5^{\circ}$ below the stibine melting point, the pinwheel was lowered so as to rest on the solid ring of stibine. The coolant was stirred constantly, and eventually the inner assembly dropped in the apparatus. The temperature shown by a CO_2 vapor-pressure thermometer (immersed in the coolant) when this drop occurred was taken to be the melting point.

A second method for determining the melting point involved following the vapor pressure of a sample of stibine originally at -196° C as a function of time. While pressure-time measurements were being made, the stibine was warming up in an empty dewar, which had been previously rinsed with liquid nitrogen. The pressure rose slowly, leveled off at the melting point, and increased again steadily. The observed pressure plotted against time is shown in Fig. 3. The temperature at this "melting-point pressure" was determined from the final pressure-temperature curve of stibine.

The melting point was checked at various times during the main vapor-pressure measurements in order to ensure that the melting point was remaining essentially constant. The resulting melting points given by the drop and pressure-time methods are given in Table III.

Table III

Melting Point of Stibine

Sample	P_{CO_2}(Obs) at m.p.	P_{CO_2}(cor) at m.p.	m.p. (°K)	Method	Where observed in course of regular v.p. measurements
A	18.56 cm Hg	18.47 cm Hg	178.9 ± 0.2	drop	middle
	18.72	18.62	179.0 ± 0.2	"	end
B	18.70	18.61	179.0 ± 0.2	"	start
	18.08	17.99	178.6 ± 0.2	"	middle
	---	---	(a) 178.8 ± 1.0	v.p.-time curve	middle

(a) Melting-point pressure of stibine, 0.86 cm Hg.

c. Analysis by decomposition into Sb and H_2 on heating: Stibine, when present at about 0.5 atmos, decomposes into Sb and H_2 on heating, accompanied by a small explosion (on heating the container with a bunsen burner, the reaction takes place within 10 seconds of initial heating; a bright yellow-orange flash travels along the decomposition tube from zone of heating, with simultaneous deposition of antimony metal). The amount of hydrogen formed is then a measure of the stibine present initially according to the equation:

$$SbH_3 = Sb + \frac{3}{2} H_2 \,. \qquad (5)$$

Portions of the samples used in the vapor-pressure work were decomposed as described, and the evolved hydrogen collected and measured by means of a Toepler pump. Results obtained with the two samples, A and B, are given in Table IV.

Table IV

Purity of Stibine by Decomposition According to Equation (5)

Sample	SbH_3 (mmoles)	H_2 (mmoles)	SbH_3 (%)
A	0.9146	1.359	99.1 ± 1.0
B	0.9162	1.376	100.1 ± 1.0
	0.9583	1.444	100.5 ± 1.0
B[a]	3.744	5.610	99.90
	4.330	6.485	99.85

[a]Determined by S. Gunn at the Lawrence Radiation Laboratory, Livermore

Temperature

All temperatures were determined by vapor-pressure thermometers. Very reliable equations of vapor pressure vs temperature are given in the literature for CO_2,[9] SO_2,[10] and NH_3,[11] which cover the complete temperature range studied.

Slight changes in the published equations had to be made to take into account the different temperature scales used by the various experimenters. Our work is based on 0° C = 273.15°K. When these changes are made, the equations become:

Solid CO_2[9] (273.10° K $\longrightarrow$ 273.15°K)

$$\log P_{cm} = 8.69903 - \frac{1354.446}{T} + .0015877\ T - 4.5090 \times 10^{-6}\ T^2; \quad (6)$$

Liquid SO_2[10] (273.10° K $\longrightarrow$ 273.15° K)

$$\log P_{cm} = 12.07540 - \frac{1867.86}{T} - 0.015862\ T + 1.5568 \times 10^{-5}\ T^2; \quad (7)$$

Liquid NH_3[11] (273.16° K $\longrightarrow$ 273.15° K)

$$\log P_{mm} = 9.95023 - \frac{1473.12}{T} - 0.0038604\ T; \quad (8)$$

Solid NH_3[11] (273.16° K $\longrightarrow$ 273.15° K)

$$\log P_{mm} = 9.98379 - \frac{1627.16}{T}\ . \quad (9)$$

Various temperatures were attained by using the following coolants: toluene, ethyl acetate, chloroform, chlorobenzene, and CCl_4 slushes, dry-ice and acetone (or methanol) mixture, and boiling ammonia.

Vapor Pressures

The apparatus in which all vapor-pressure measurements were made is shown in Fig. 4. The stibine was condensed into the apparatus with liquid nitrogen, and then, with the stopcock leading to the vacuum line closed, the condensation tube was immersed in the appropriate constant-temperature bath. The coolant was stirred for 5 minutes prior to each measurement of vapor-pressure and temperature, during which time the manometer and vapor-pressure thermometer were tapped repeatedly to prevent sticking of the mercury.

The vapor-pressure thermometer was placed as close as possible to the sample container. All measurements of mercury heights were made with a cathetometer (read to 0.01 cm).

Typical Data

Although the data are too extensive to be given here in their entirety, those obtained with Sample B at the temperature of CCl_4 slush are given in Table V (the experimentally measured quantities, i.e., raw data, in Table V are denoted by an asterisk). These data will serve to illustrate the typical data obtained and will be followed through to show how the data were treated to determine the final temperatures and pressures given in Table VI.

Treatment of Data

Various corrections had to be applied to the raw vapor-pressure data in order to convert these data to standard conditions (H_2 was formed during the process of a few of the vapor-pressure measurements and its partial pressure had to be subtracted from the total pressure as an added correction). The cathetometer used in this work was calibrated with a standard meter bar and was found to be accurate enough not to require a correction. The other

corrections, which were taken into account, follow in the order in which they were applied to our raw data.

a. Differences in heights of menisci. The capillary depression of mercury as a function of meniscus height and tube diameters is given by Weissberger.[12] The manometer and vapor-pressure thermometers used in our work had internal diameters of 0.8 and 0.6 cm, respectively. From the data given by Weissberger, the appropriate correction for each observed meniscus height was added to the corresponding "top of the meniscus reading."

As an illustration, let us consider the stibine data given in column No. 1 of Table V. The observed meniscus height, i.e. h'_{PM}, in one arm of the manometer is 0.12 cm. From the table in Weissberger,[12] we see that 0.07 cm (c_W) must be added to h'_P = 63.83 cm, the "top of the meniscus reading," giving 63.90 cm as h'_P (cor. men.). Similarly, the observed meniscus height in the other arm of the manometer, h_P = 1.37 cm, becomes 1.45 cm, as h_P (cor. men.). Thus, h'_P (cor. men.) - h_P (cor. men.) = 62.45 cm = Δh_P (cor. men.) is the stibine pressure as corrected for meniscus height difference only. A similar correction applies to the vapor-pressure-thermometer data, which are denoted by the subscript T in Table V.

b. H_2 evolution. An appreciable amount of hydrogen was evolved as a result of stibine decomposition during some of the vapor-pressure measurements, particularly those at the higher temperatures. After each set of vapor-pressure vs temperature data had been taken, the dewar containing the constant-temperature bath was replaced by one with liquid nitrogen. The heights of mercury in the arms of the manometer were then measured, along with the corresponding meniscus heights.

Table V

Stibine Vapor-Pressure Data, Sample B, at the Temperature of CCl_4 Slush, SO_2 Vapor-Pressure Thermometer (h'_P, h_P, ... are defined by the distances shown in Fig. 4, raw data denoted by asterisk, h in cm)

No.	1	2	3	4	5	6 (H_2 meas.)
* Time (min)	15	30	45	60	75	80
* R. T. (°C)	23.8	23.8	23.8	23.9	24.0	24.0
* h'_P	63.83	64.25	64.50	64.84	63.98	14.15
* h'_{PM}	0.12	0.12	0.13	0.13	0.12	0.11
c_W	0.07	0.07	0.07	0.07	0.07	0.07
h'_P (cor. men.)	63.90	64.32	64.57	64.91	64.05	14.22
* h_P	1.37	1.67	2.09	2.29	1.35	14.09
* h_{PM}	0.14	0.15	0.15	0.13	0.12	0.16
c_W	0.08	0.08	0.08	0.07	0.07	0.08
h_P (cor. men.)	1.45	1.75	2.17	2.36	1.42	14.17
Δh_P (cor. men.)	62.45	62.57	62.40	62.55	62.63	0.05
Δh_P(cor.men. + H_2)	62.44	62.54	62.36	62.49	62.56	
f_{dHg}	0.99569	0.99569	0.99569	0.99567	0.99565	
f_g	0.99929	0.99929	0.99929	0.99929	0.99929	
Final P_{SbH_3} (cor.)	62.127	62.226	62.047	62.175	62.244	
* h'_T	50.92	51.00	50.92	50.91	50.93	
* h'_{TM}	0.09	0.09	0.05	0.05	0.06	
c_W	0.11	0.11	0.06	0.06	0.08	
h'_T (cor.men.)	51.03	51.11	50.98	50.97	51.01	
* h_T	9.58	9.50	9.53	9.49	9.43	
* h_{TM}	0.08	0.07	0.06	0.07	0.06	
c_W	0.10	0.09	0.08	0.09	0.08	
h_T(cor.men.)	9.68	9.59	9.61	9.58	9.51	
Δh_T (cor.men.)	41.35	41.52	41.37	41.39	41.50	
Final P_{SO_2}	41.143	41.312	41.163	41.182	41.290	
Calc 1000/T	3.99790	3.99662	3.99775	3.99762	3.99678	

Table VI

Observed Vapor Pressure of Stibine at Various Temperatures

Temp (°K)	Thermometer	Observed Stibine Pressure (cm Hg) A	B	Average	Calc P[(a)] (cm)
250.18	SO_2	62.106	62.173	62.14	62.78
227.66	NH_3	22.330	22.353	22.34	22.27
221.73	NH_3	16.422	- -	16.42	16.32
209.21	NH_3	8.084	8.007	8.023	7.941
		7.979			
194.70	NH_3 CO_2	3.043	- -	3.043	3.029
192.49	NH_3 CO_2	- -	2.543	2.543	2.579
187.83	CO_2	1.818	1.785	1.802	1.812

(a) Calculated from final vapor-pressure equation, Eq. (26).

Column No. 6 in Table V gives the H_2 correction data for Sample B in the CCl_4 slush. In the table we see that hydrogen, to the extent of 0.05 cm Hg (correction for difference in meniscus heights, i.e. c_w, included) was present in the apparatus at the end of 80 minutes. When these hydrogen measurements were being made, one fourth of the gas volume was at -196° C, the rest at room temperature. Also, when the stibine vapor-pressure measurements were being made, one half of the gas volume was at the temperature of the CCl_4 slush. Therefore, the hydrogen pressure that was in the manometer system just before the liquid nitrogen replaced the CCl_4 is given by (derived from P V = P'V'):

$$\Delta P_{H_2} \text{ (80 min with } CCl_4) = \frac{1}{2}\left[\frac{3 + \frac{T_{room}}{T_{liq\ N_2}}}{1 + \frac{T_{room}}{T_{CCl_4}}}\right] (.05) . \qquad (10)$$

Substitution of the appropriate temperatures into Eq. (10) gives ΔP_{H_2} (80 min) = 0.079. The appropriate hydrogen correction for column No. 1, Table V, is therefore, 0.01 cm, i.e., $\frac{15}{80}$ x 0.079, taking into account that column No. 1 measurements were made at time = 15 min. Subtracting this from the stibine pressure of the preceding section, i.e. Δh_P (cor. men.) = 62.45 cm, we get Δh_P (cor. men. + H_2) = 62.44 cm.

Obviously, this H_2 correction did not apply to the vapor-pressure thermometers.

C. Density of mercury; gravity: Because of the change in the density of mercury with temperature, all pressure readings, both manometer and vapor-pressure thermometer, had to be corrected to the density of mercury[13] at 0°C. The density-of-mercury correction factor is

$$f_{dHg} = \frac{d_{Hg}\ (t^{\circ}\ C\ expt.)}{d_{Hg}\ (0^{\circ}\ C)} \quad . \tag{11}$$

The value of g for this area is 979.973 cm/sec^2, while g_o = 980.665 cm/sec^2. The gravity correction factor is:

$$f_g = \frac{979.973}{980.665} \tag{12}$$

The density-of-mercury factor, f_{dHg}, and the gravity factor, f_g, are given in Table V for the CCl_4 data on Sample B. The product of (f_{dHg} x f_g) times Δh_p (cor. men. + H_2) is the observed vapor pressure of stibine, corrected to standard conditions. Likewise, (f_{dHg} x f_g) times the corresponding Δh_T (cor. men.), is the vapor pressure of the material used in the vapor-pressure thermometer at the same temperature as that of the stibine.

At this point, the final corrected vapor-pressure thermometer data were converted to the corresponding 1/T's, using Eqs. (6), (7), (8), and (9). This was done by making numerous plots of log P vs 1/T, from Eqs. (6), (7), and (8), over the pressure intervals required and interpolating the experimental 1/T's from these plots. Eq. (9) may be solved directly for 1/T. The P_{SO_2} (final cor.) data in Table V were treated, using Eq. (5), giving the 1/T's indicated.

Finally, in order to obtain an average stibine pressure and temperature for each set of data as that in Table V, the log of the final corrected stibine pressure was plotted against the corresponding 1/T. This is shown in Fig. 5 for the Table V data. A line of best fit, having a slope of

-1150 (slope $= \frac{-\text{est } \Delta H_{vap}}{2.303\ R} \simeq \frac{(20\ T_{bp})}{(2.303)(1.987)} \simeq -1150$). One point on this line was chosen to represent the average of the data on Sample B (in processing the CCl_4 data on Sample A, the same 1/T was chosen).

Similar treatment of the rest of the data gave the final results given in Table VI.

The temperature 221.73° K, given in Table VI, was obtained when boiling ammonia was used as a coolant. Such a temperature, 18° below the normal boiling point of liquid ammonia, was surely not expected. No reason is offered for the low value.

The temperature 194.70° K was obtained with a dry-ice and methanol mixture, while that of 192.49° K was with dry ice and acetone, both mixtures consisting of finely ground dry ice mixed with the liquid phase for two hours before the vapor-pressure measurements were made. In both these cases it was found necessary to use two vapor-pressure thermometers, namely NH_3 and CO_2. The two gave temperatures differing by 0.08 to 0.36° K. The temperatures 192.49° K and 194.70° K, given in Table VI, were obtained by averaging the different temperatures indicated by the two thermometers before the final log P vs 1/T plot was made for choosing and average P and T for these data. Ammonia has the disadvantage at these temperatures of its low vapor pressure (3 - 4 cm). On the other hand, the small amount of solid CO_2 in equilibrium with its vapor in our CO_2 thermometer at these temperatures made the CO_2 temperatures open to question.

A plot was made of the log of the stibine pressure vs 1/T. Extrapolation of the data gave 254.8° K as the observed boiling point.

The results obtained at the temperature of the toluene slush are not included in Table VI. At this temperature (below the melting point of

stibine), solid stibine is in equilibrium with the vapor. Extrapolating data on phosphine and arsine,[14] we estimate the heat of melting of stibine as 350 calories. Adding this to the ΔH° of vaporization at the melting point calculated from Eq. (23), gives 5840 calories as the estimated ΔH° of sublimation at the melting point. The toluene data were plotted as in Fig. 5. A line of best fit with slope -1250 (slope = $\frac{-\Delta H^{\circ}_{subl}}{R\ T_{m\ p}} \simeq -1250$) was drawn through the data. At 177.87° K, Samples A and B gave average pressures of 0.839 and 0.794 cm Hg, respectively.

Discussion

Examples of melting points reported previous to our work are: -88°,[15] -90.0°,[1] and -91.5° C.[16] These melting points were of stibine prepared by the action of dilute acid on alloys of alkaline earth metals and antimony. The average melting point we observed, -94.3° C, is quite appreciably lower than those reported. Impurities (perhaps introduced via our unique method of preparation, i.e. reduction of Sb(III) solutions by BH_4^-) depressing the melting point of our stibine may be responsible for our low value.

The boiling point from our data, -18.4° C, is lower than Stock and Doht's[15] -17.0° C value.

THERMODYNAMIC FUNCTIONS AND A VAPOR PRESSURE EQUATION

Theoretical

Beginning with van der Waals' equation and by making various approximations, Brewer and Searcy[7] derive the following equation relating the fugacity, pressure, and temperature of a vapor:

$$\frac{f}{P} = 1 - 0.0158 \frac{P \bar{v}_l}{T}\left(7.78 \frac{T_b}{T} - 1 \right) , \qquad (13)$$

where:

$\bar{v}_l$ = molal volume of the liquid in cm^3

P = pressure in atmospheres

f = fugacity in atmospheres

T_b = normal boiling temperature in ^oK

T = temperature in ^oK.

The reader is referred to Brewer and Searcy's paper[7] for further details.

Having pressure-temperature data and knowing the molal volume of the liquid as a function of temperature, one is able to calculate the f/P ratio of a gas at various temperatures and pressures using this equation.

The change in T and $\bar{v}_l$ for stibine from T_{mp} to T_b is small compared to the corresponding change in P, and so Equation (13) may be approximated by:

$$\frac{f}{P} = 1 - k P , \qquad (14)$$

where k is a constant. The value of k may be calculated by plotting the previously determined f/P ratios against the corresponding values of P. The slope of the resulting curve will be equal to -k.

The fugacity of a gas is related to the change in the standard free energy of vaporization by the well-known thermodynamic equation:

$$- R T \ln f = \Delta F^{\circ} . \qquad (15)$$

Assuming ΔC_p° of vaporization to be constant, the thermodynamic functions ΔH°, ΔF°, and ΔS° may be given by:

$$\Delta H^{\circ} = \Delta H_o^{\circ} + \Delta C_p^{\circ} T \qquad (16)$$

$$\Delta F^{\circ} = \Delta H_o^{\circ} - \Delta C_p^{\circ} T \ln T + I T \qquad (17)$$

$$\Delta S^{\circ} = \Delta C_p^{\circ} + \Delta C_p^{\circ} \ln T - I , \qquad (18)$$

where ΔH_o° and I are constants.

Combining Equations (15) and (17) results in another well-known thermodynamic relationship:

$$\Sigma = - R \ln f + \Delta C_p^{\circ} \ln T = \frac{\Delta H_o^{\circ}}{T} + I . \qquad (19)$$

Equation (14) may be rewritten into the form:

$$f = P - k P^2 . \qquad (20)$$

After calculating the fugacity from the experimentally determined pressures using Equation (20) and the previously determined value of k, the value of Σ in Equation (19) may be calculated at the various corresponding experimentally determined temperatures. A plot of Σ against $1/T$ will be a straight line of slope ΔH_o° and intercept on the $1/T$ axis equal to I. Thus, temperature expressions for ΔH°, ΔF°, and ΔS° of vaporization result.

Taking the logarithm of Equation (14) and using the approximation $\ln (1 - k P) = -kP$ (valid, since k is small), we obtain:

$$\ln f = \ln P - kP. \qquad (21)$$

Finally, combining Equations (15), (17), and (21) we have:

$$\log P_{atm} = \left(\frac{k}{2.303}\right) P - \left(\frac{\Delta H_o^o}{2.303\ R}\right) \frac{1}{T} + \left(\frac{\Delta C_p^o}{R}\right) \log T - \frac{I}{2.303R} \quad (22)$$

It may be argued that an equation of vapor pressure vs temperature such as Eq. (22) is impractical since the pressure cannot be solved for explicitly. The pressure term on the right side of the equation may be neglected, however, and a good first approximation of the pressure may still be obtained at a given temperature. By successive approximations and substituting these approximate values for P on the right side of the equation each time, a very exact value of P may be determined for any given temperature.

Application of Theory to Stibine Data

From a plot of log P_{SbH_3} vs 1/T, various pressures and temperatures were chosen from which to calculate the corresponding f/P ratios. The molal volume of liquid stibine at these temperatures was calculated from liquid density data given by Durrant.[1] With $T_b = 254.8^\circ$ K, the f/P ratios were calculated using Equation (13) and are given in Table VII.

These f/P ratios given in Table VII were then plotted against the corresponding pressures as shown in Fig. 6, and k of Equation (14) was calculated to be 0.026 $atmos^{-1}$.

Putting this value into Equation (20), we calculated the fugacity at the various experimental pressures given in Table VI.

Although no C_p data are available for stibine, those for phosphine and arsine are given in the literature. From the data given by Stephenson and Giauque,[17] ΔC_p° of vaporization for phosphine at a temperature half-way between its melting and boiling points is -6.47 cal/deg mole. From the data given by Sherman and Giauque,[18] the corresponding ΔC_p° for arsine is -6.31 cal/deg mole. Extrapolating to stibine, we estimated the ΔC_p° of vaporization in the temperature range studied to be -6.2 cal/deg mole.

At this point, having calculated the fugacity at the various experimental temperatures and with our estimate of ΔC_p°, the function Σ was calculated as given by the first part of Equation (19). The results of these calculations are given in Table VIII.

Table VII

f/P of Stibine, Calculated Using Equation (14);

v_l Calculated from Data by Durrant,[1] T_b = 254.8° K

P (cm)	P (atmos)	T (°K)	$\bar{v}_l$ (cm^3)	f/P
70.8	0.9316	253.2	56.4	0.9776
47.87	0.6299	243.9	55.7	0.9838
35.48	0.4668	237.5	55.1	0.9874
25.12	0.3305	230.4	54.6	0.9907
12.59	0.1657	217.4	53.6	0.9947
7.08	0.0932	207.5	52.8	0.9968
3.16	0.0416	195.3	51.9	0.9984
1.95	0.0257	188.7	51.4	0.9990

Table VIII

$\Sigma = - R \ln f + \Delta C_p^o \ln T$, with $\Delta C_p^o = -6.2$ cal/deg mole;
f calculated from Equation (20), with $k = 0.026$ atmos^{-1},
and data from Table VI

P (cm)	T (^oK)	f (atmos)	$1/T \times 10^3$ ($^oK^{-1}$)	Σ
62.14	250.18	0.8002	3.99720	-33.8007
22.34	227.66	0.2917	4.39260	-31.2105
16.42	221.73	0.2149	4.5100	-30.4392
8.023	209.21	0.1053	4.7800	-28.6607
3.043	194.70	0.04000	5.1360	-26.2913
2.543	192.49	0.03343	5.1951	-25.8639
1.802	187.83	0.02370	5.3240	-25.0283

The method of least squares[19] was used to determine the best line through the data in obtaining the constants ΔH_o^o and I. Because of the uncertainty in the temperatures of the dry-ice baths, these points were assigned only one-half the weight of the other points in the least-squares calculation. The results of these calculations are:

$$\Delta H_o^o = 6619.2 \text{ cal/mole} \pm 1.0$$

$$I = -60.279 \text{ cal/deg mole} \pm 0.100.$$

The thermodynamic functions of vaporization, ΔH^o, ΔF^o, and ΔS^o, are:

$$\Delta H^o = 6619.2 - 6.2\,T \tag{23}$$

$$\Delta F^o = 6619.2 + 6.2\,T \ln T - 60.279\,T \tag{24}$$

$$\Delta S^o = 54.079 - 6.2 \ln T \,. \tag{25}$$

The vapor pressure of stibine is given by:

$$\log P_{atmos} = 0.011290\,P - \frac{1446.34}{T} - 3.11997 \log T + 13.17136 \,. \tag{26}$$

Discussion

The application of Equation (13) to stibine may be questioned in that stibine may show large deviations from the "average" vapor model, which Brewer and Searcy[7] assume in deriving that equation. Stock and Gutmann[20] have reported that at 15°C and 754 mm pressure, the density of stibine is 4.360 times that of air. These data supply a check on the applicability of Equation (13) to stibine near the temperature range of our work. Calculating the molal volume of liquid stibine at 15° C from data by Durrant[1] and taking T_b = 254.8°K, Equation (13) gives f/P = 0.9810 for stibine at 15°C and 754 mm pressure. Using the Lewis and Randall[21] equation $\frac{f}{P} = \frac{P V_g}{R T}$, where V_g is the molal volume of the vapor, Equation (13) gives 23,380 cc as the molal volume of stibine vapor at 15°C and 754 mm pressure. On the other hand, Stock and Gutmann's[20] data and the density of air,[13] substituted into the equation $V_g = \frac{\text{molecular wt}}{\text{density}}$, gives V_g = 23,540 cc. The small deviation (0.7%) between these two values of V_g indicates that Equation (13) very adequately represents stibine vapor near the temperature range of our work.

A check on the internal consistency of our results may be obtained by comparing our least-squares ΔH_o^o = 6619.2 cal/mole to those calculated by substituting the Σ's and corresponding T's given in Table VIII, along with the least-squares I = -60.279 cal/deg mole, into the equation

$$\Delta H_o^o = T \Sigma - I T . \qquad (27)$$

The ΔH_o^o's calculated in this manner are given in Table IX. The calculated values of ΔH_o^o are all within $\pm$ 0.1% of 6619.2, showing good agreement throughout the experimental temperature range.

From Equation (23), ΔH^{o}_{vap} at the boiling point (254.8°K) is 5039 cal, giving a Trouton's constant of 19.8 for SbH_3. This result appears high when compared to 18.8 and 18.9, calculated from data for PH_3[17] and AsH_3,[18] respectively.

In Table X, the vapor pressures calculated from Equation (26) are compared with those observed experimentally. It can be seen that the vapor pressure equation represents our experimental data to within 1%, with the only exception at 192.49°K, a point that was only "half weighted" in the least-squares fitting.

Table IX

Comparison of ΔH_o^o Calculated from $\Delta H_o^o = T\,\Sigma + 60.279\,T$ (Using data given in Table VIII) to the Least-Squares' $\Delta H_o^o = 6619.2$ cal

T (^oK)	ΔH_o^o (calc)	ΔH_o^o (calc) - 6619.2
250.18	6624.3 cal	+5.1
227.66	6617.7	-1.5
221.73	6616.4	-2.8
209.21	6614.9	-4.3
194.70	6617.4	-1.8
192.49	6624.6	+5.4
187.83	6621.1	+1.9

Table X

Pressures Calculated for Stibine from Equation (26)

Compared With the Pressures Observed Experimentally

T (^{o}K)	P_{obs} (cm)	P_{calc} (cm)	(P_{obs} - P_{calc})	% Deviation from P_{obs}
250.18	62.14	62.78	- 0.64	1.03
227.66	22.34	22.27	+ 0.07	0.31
221.73	16.42	16.32	+ 0.10	0.61
209.21	8.023	7.941	+ 0.082	1.02
194.70	3.043	3.029	+ 0.014	0.46
192.49	2.543	2.579	- 0.036	1.42
187.83	1.802	1.812	- 0.010	0.55

ACKNOWLEDGMENTS

The author wishes to thank Professor William L. Jolly, who suggested this research and who offered many helpful suggestions and criticisms during its progress.

The author is indebted to Mr. Leon M. Burright, a fellow graduate student, for having supplied some of the apparatus used in connection with this work.

The efforts of Mrs. Jane Waite in the final stages of this project are greatly appreciated.

Words do not permit an adequate expression of appreciation to the author's fiancee, Miss Barbara Schemmel, for all she has done in making this work possible. Her constant encouragement and moral support have been of invaluable assistance.

Gratitude is felt for financial support from the U. S. Atomic Energy Commission through the University of California Radiation Laboratory.

REFERENCES

1. A. A. Durrant, T. G. Pearson, and P. L. Robinson, J. Am. Chem. Soc. 730 (1934).
2. A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach, and H. I. Schlesinger, J. Am. Chem. Soc. 69, 2692 (1947).
3. G. W. Schaeffer and M. Emilius, J. Am. Chem. Soc. 76, 1204 (1954).
4. T. S. Piper and M. K. Wilson, J. Inorg. Nuclear Chem. 4, 22 (1947).
5. Sister M. E. Kramer, Thesis, St. Louis University (1954), "Reactions with Aqueous Sodium Borohydride."
6. L. F. Hamilton and S. G. Simpson, Quantitative Chemical Analysis, 10th ed. (Macmillan, New York (1952), p. 255.)
7. L. Brewer and A. Searcy, J. Chem. Educ. 26, 548 (1949).
8. R. T. Sanderson, Vacuum Manipulation of Volatile Compounds (John Wiley and Sons, New York (1948), p. 96.)
9. W. F. Giauque and C. J. Egan, J. Chem. Phys. 5, 45 (1937).
10. W. F. Giauque and C. C. Stephenson, J. Am. Chem. Soc. 60, 1389 (1938).
11. G. T. Armstrong, A Critical Review of the Literature Relating to the Vapor Pressure of Ammonia and Trideuterammonia, National Bureau of Standards, Report No. 2626.
12. A. Weissberger, Physical Methods of Organic Chemistry, 2nd ed., Vol I., Pt. II (Interscience Publishers, New York (1949), p. 153.)
13. Handbook of Physics and Chemistry, 35th ed. (Chemical Rubber Co., Cleveland (1953).)
14. R. E. Elson, H. C. Hornig, W. L. Jolly, J. W. Kury, W. J. Ramsey, and A. Zalkin, "Some Physical Properties of the Hydrides," UCRL-4519,6/56.
15. A. Stock and W. Doht, Chem. Ber. 35, 2270 (1902).

16. K. Olchewsky, Monatsh 7, 371 (1886).

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

18. R. H. Sherman and W. F. Giauque, J. Am. Chem. Soc. 77, 2154 (1955).

19. G. B. Thomas, Jr., Calculus (Addison-Wesley, Reading, Massachusetts, 1953, p. 432.)

20. A. Stock and O. Gutmann, Chem. Ber. 37, 885 (1904).

21. G. N. Lewis and M. Randall, Thermodynamics and the Free Energy of Chemical Substances (McGraw-Hill, New York (1923), p. 198.)

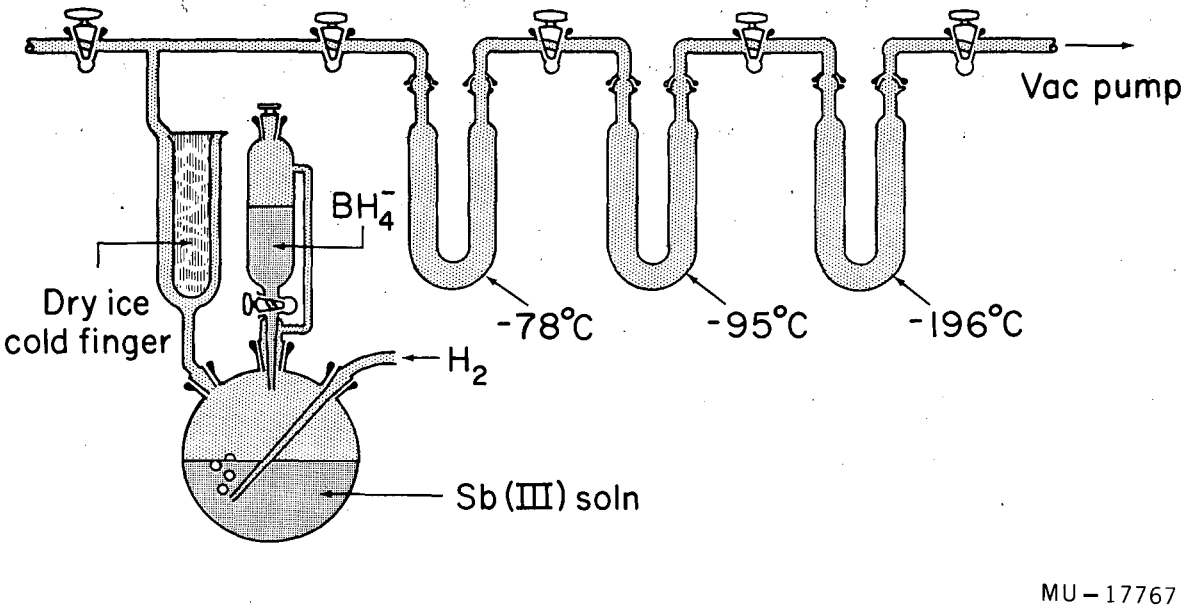

Fig. 1. Stibine preparation and collection apparatus.

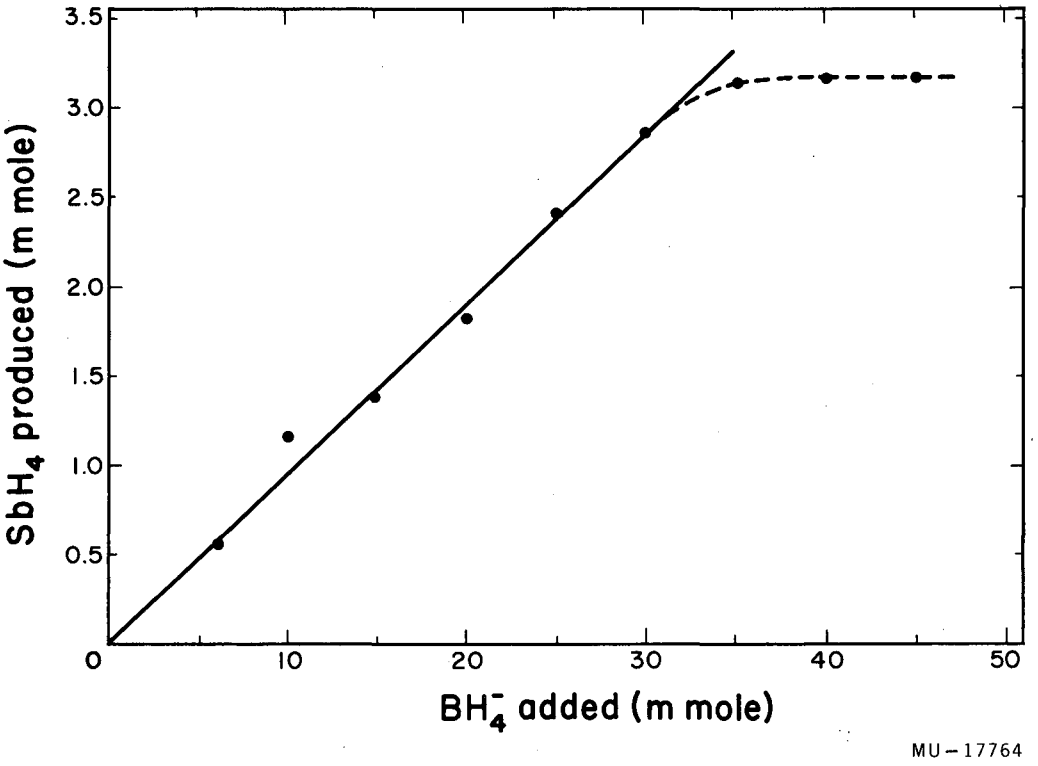

Fig. 2. 0.50 M KBH_4 added to 300 cc 0.10 M $SbCl_3$ in 1.0 M HCl and 3.0 M NaCl at room temperature.

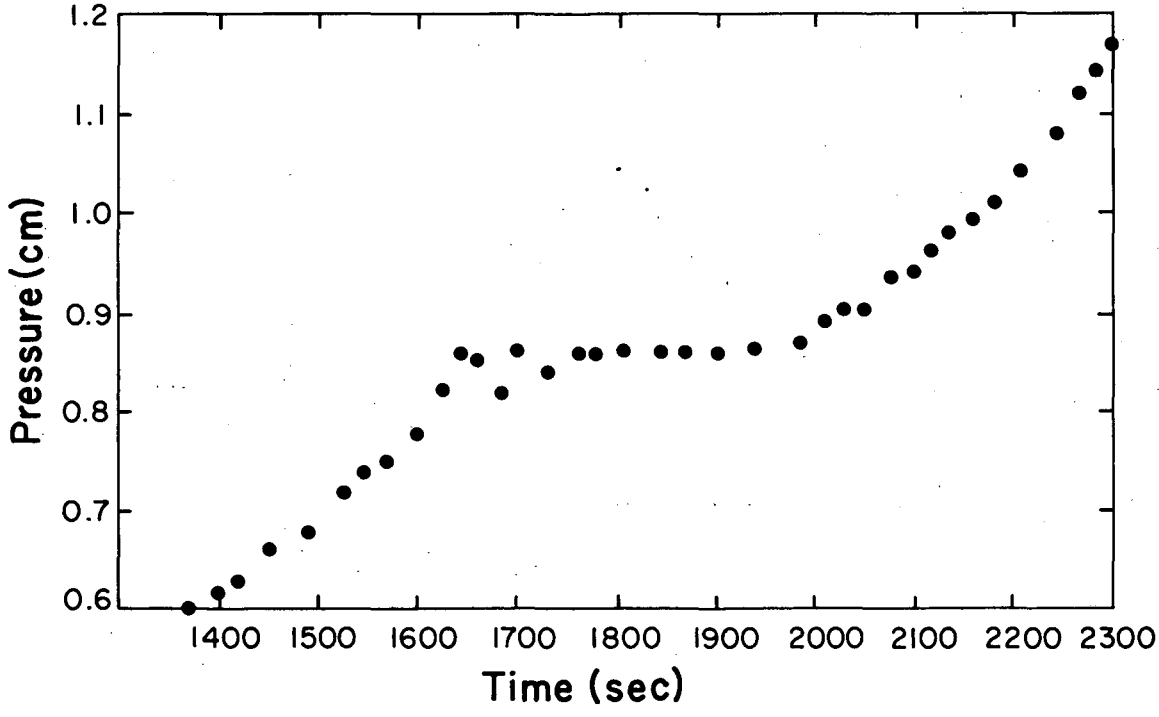

Fig. 3. Vapor pressure of stibine (sample B) versus time on warming from solid to liquid.

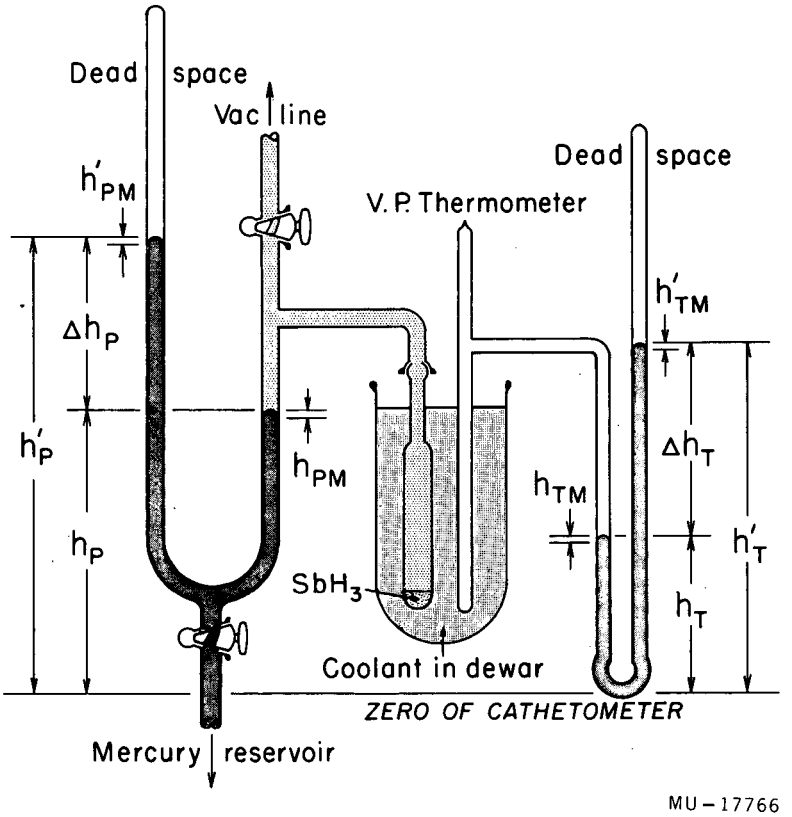

Fig. 4. Vapor-pressure apparatus

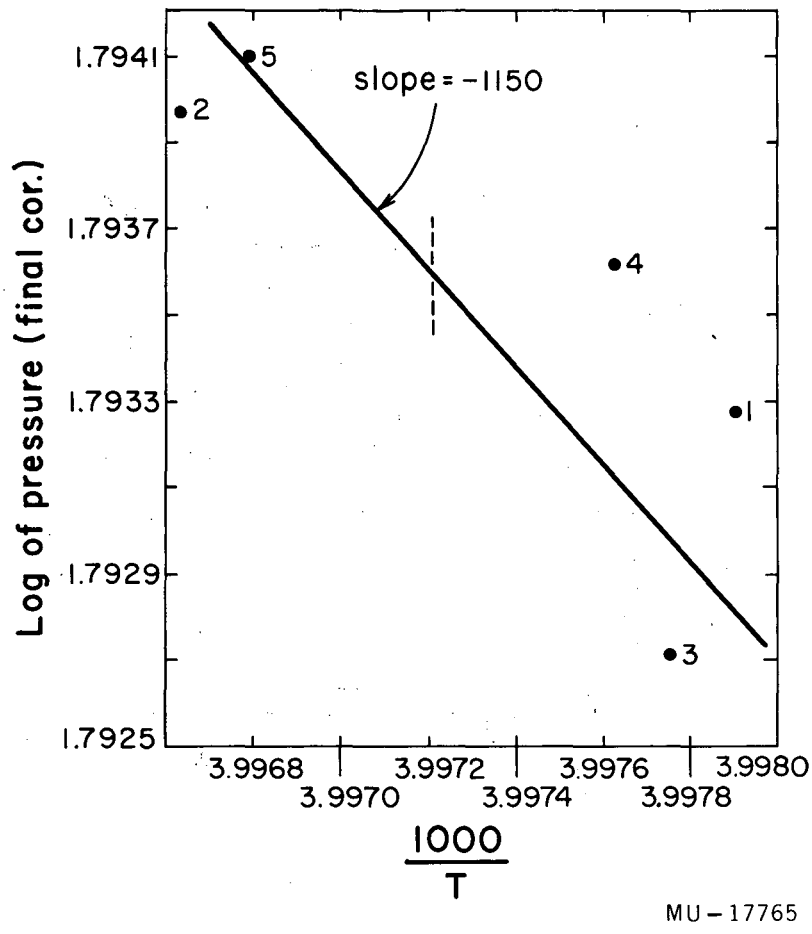

Fig. 5. Plot of Table-V data to obtain an average P_{SbH_3} with Sample B in CCl_4 slush.

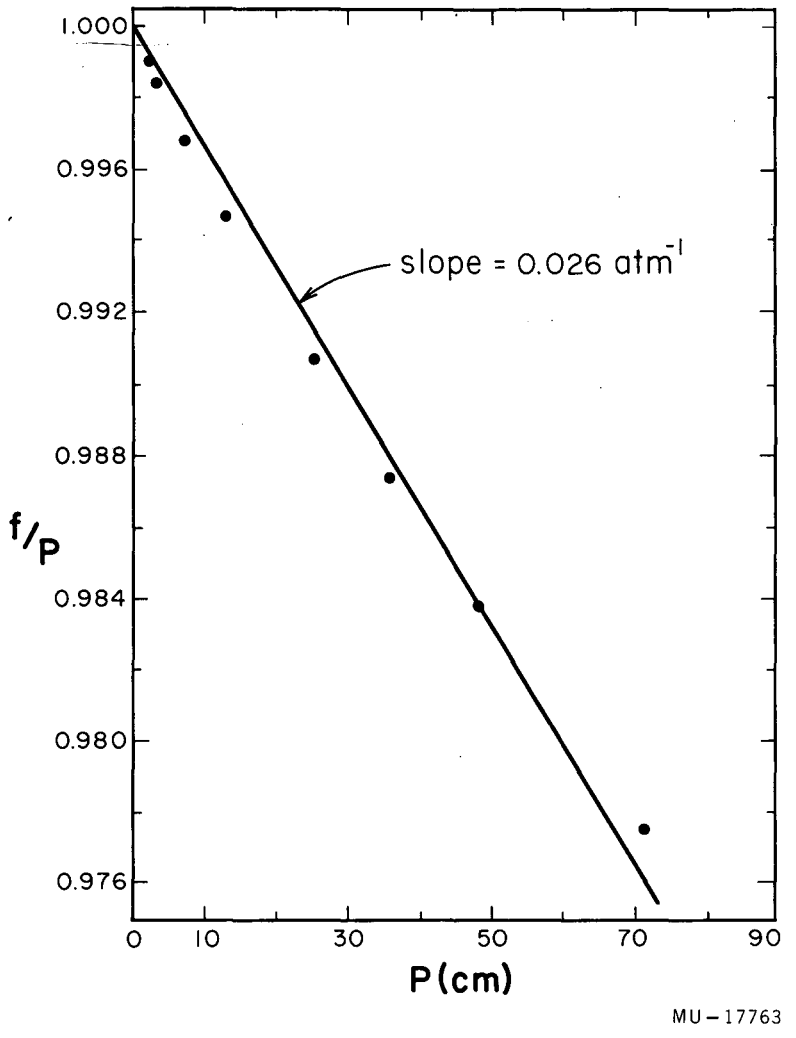

Fig. 6. Plot of f/P versus P_{cm} from data in Table VII to determine k in f/P = 1 - k P (14).