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**Determining Vapor Density and Gaseous
Diffusion Coefficients of Sb_2S_3 Using
a Modified Transpiration Apparatus**

By B. W. Madsen, A. Adams, and P. A. Romans



UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cm	centimeter	mg	milligram
cm ²	square centimeter	mg/cm ³	milligram per cubic centimeter
cm ² /s	square centimeter per second	mg/mol	milligram per mole
cm ³ /min	cubic centimeter per minute	mg/s	milligram per second
cm ³ /s	cubic centimeter per second	min	minute
cm ³ ·torr ·mol ⁻¹ ·K ⁻¹	<u>centimeter cubed·torr</u> <u>mole·kelvin</u>	ml	milliliter
eV	electron volt	mm	millimeter
G	gauss	Pa	pascal
g	gram	pct	percent
g/mol	gram per mole	ppm	parts per million
h	hour	s	second
K	kelvin (absolute temperature)	torr	torr (milliliters of mercury)
kG	kilogauss	V	volt
		W	watt

DETERMINING VAPOR DENSITY AND GASEOUS DIFFUSION COEFFICIENTS OF Sb_2S_3 USING A MODIFIED TRANSPIRATION APPARATUS

By B. W. Madsen,¹ A. Adams,² and P. A. Romans³

ABSTRACT

A modified transpiration apparatus was devised by the Bureau of Mines to permit rapid and accurate measure of the vapor transport and vapor diffusion coefficients of antimony sulfide (Sb_2S_3) and other compounds at temperatures to 1,045 K. The apparatus was equipped with dual condensers and valves to switch the flow of vapor in a fraction of a second from one condenser to the other, thus allowing short-interval sampling under equilibrium conditions. Reliability of the technique was established by measuring the vapor pressure of $ZnCl_2$ as a function of temperature and comparing the results with published data.

As part of an investigation of the vapor concentrations and species of accessory element sulfides associated with copper and zinc smelting, the apparatus was used to measure the rate of vapor transport and diffusion coefficients of vapor over liquid Sb_2S_3 as a function of temperature between 870 and 1,045 K. The calculated vapor density was combined with published direct measurements of vapor pressure to calculate the average molecular weight of the gaseous species. Average molecular weight of the vapor in equilibrium with Sb_2S_3 ranged from 286 to 112 g/mol over the temperature range studied.

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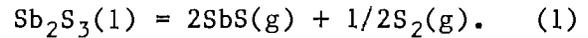
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INTRODUCTION

Emphasis on the environmental control of toxic materials has created a need for accurate vapor pressure and vapor species data covering smelter feeds, flue dusts, and associated products. The investigation of the vapor transport of Sb_2S_3 was undertaken as part of a Bureau of Mines program to identify and follow the distribution of accessory minerals in minerals processing. Although extensive information is available on the more common metal sulfides (2),⁴ there is a lack of reliable vapor pressure and vapor species data on Sb_2S_3 .

Previous vaporization studies of Sb_2S_3 were made with quartz manometers (5, 8) and transpiration apparatus (6). Analysis of these data (2) showed that vapor pressures reported are in disagreement with the assumption that

that Sb_2S_3 decomposes simply according to



In addition to the species Sb_2S_3 , Sb_2S_4 , Sb_4S_5 , and S, which are present in the vapor over Sb_2S_3 , recent investigations using mass spectrometry (1, 7) showed that other polymeric forms of SbS (SbS , Sb_2S_2 , and Sb_4S_4) are also likely present. A discussion of these studies is included later. The existence of compounds containing two or more Sb atoms is significant if other cations such as As and Bi are present. Substitution of As or Bi in these vapor compounds can substantially promote or suppress the vapor transport of Sb from complex mixtures. This investigation shows that the vapor composition over liquid antimony sulfide is a function of temperature.

DESCRIPTION OF METHOD

Transpiration techniques for the determination of vapor pressure require passing an inert gas over or through a sample at a rate sufficiently slow to assure saturation. Vapor from the sample is then condensed at some point downstream, and the vapor transport is calculated from the amount of the sample material collected in a known amount of carrier gas. If the average molecular weight of the gaseous species is known, the vapor pressure of the substance can be calculated. Application of the method to studies of vapor pressures of inorganic compounds at elevated temperatures was discussed by Merten (4). Certain aspects of the conventional and modified transpiration method are discussed in the following paragraphs.

⁴Underlined numbers in parentheses refer to items in the list of references preceding the nomenclature section at the end of this report.

CONVENTIONAL TRANSPIRATION METHOD

A typical experimental arrangement of the conventional transpiration apparatus is shown in figure 1. Carrier gas flows around a heat shield, over the sample, and into the condenser through a capillary tube.

The volume flow rate, V_1 ,⁵ of the total gas mixture at temperature T can be calculated if the saturated vapor pressure of the sample species, P_{sat} , at temperature T and the volume flow rate of the carrier gas, V_c , at temperature T_c are known according to

$$V_1 = \frac{V_c T}{T_c} \left[\frac{P_t}{P_t - P_{sat}} \right]. \quad (2)$$

⁵Symbols used in the equations are defined in the nomenclature section at the end of this report.

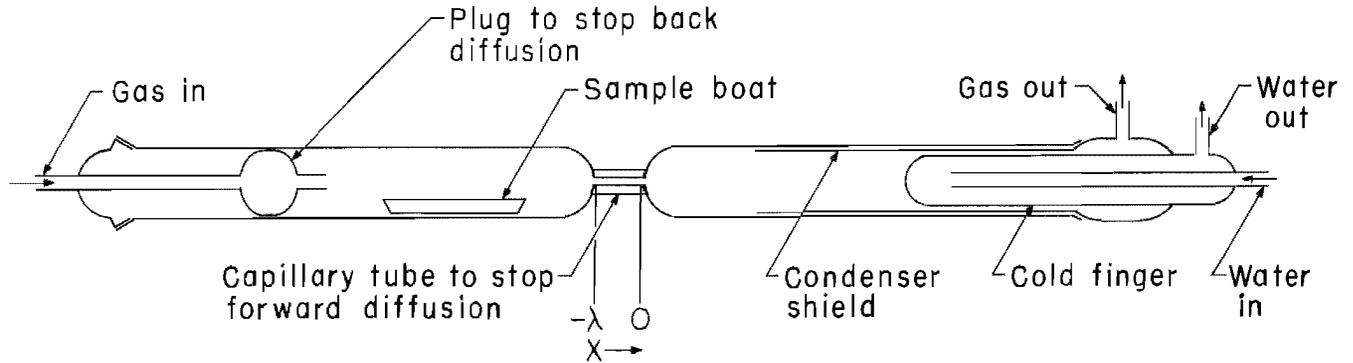


FIGURE 1. - Conventional transpiration apparatus.

The mass flow of sample vapor (F) is the sum of a slug-flow term and a diffusion term so that the mass of the vapor passing any point along the capillary per unit time is given by

$$F = V_1 C - AD \left[\frac{dC}{dX} \right]. \quad (3)$$

If condensation does not occur, F must be constant within the capillary at steady state. Therefore, equation 3 can be solved to obtain

$$C = \frac{F}{V_1} + B \exp \frac{V_1 X}{AD}, \quad (4)$$

where B is a constant of integration; we have assumed that there is no temperature or total pressure gradient along the capillary and that D is independent of concentration. Evaluating B for a capillary of length λ and assuming, for the present, that the vapor is condensed immediately as it leaves the capillary region ($C = 0$ at $X = 0$), we have

$$C_{sat} = \frac{F}{V_1} \left[1 - \exp \frac{-V_1 \lambda}{AD} \right], \quad (5)$$

where C_{sat} is the vapor density at the inlet end of the capillary where $X = -\lambda$. The vapor pressure corresponding to this vapor density can be calculated according to

$$P_{sat} = \frac{C_{sat} RT}{M}. \quad (6)$$

Merten (4) notes that the diffusion component (exponential term) in equation

5 becomes insignificant as the linear velocity of the gas mixture (V_1/A) increases, but that care must be taken to use flow rates low enough to insure saturation. For large V_1/A ,

$$C_{sat} = \frac{F}{V_1} \quad (7)$$

and

$$P_{sat} = \frac{FRT}{V_1 M}. \quad (8)$$

In the derivation of equation 5, we have assumed that the vapor concentration is zero at the exit end of the capillary and that the capillary is at uniform temperature. In an actual experiment, condensation will generally not occur until some distance downstream. Merten (4) showed that if the cross-sectional area of the exit tube is large compared with that of capillary, then the above assumptions are valid.

MODIFIED TRANSPIRATION METHOD

The modified transpiration apparatus designed and constructed by the Bureau of Mines is shown schematically in figure 2. The carrier gas is passed through or over the sample and leaves the sample region as with the conventional apparatus. However, a dual condenser is used for collecting the vapor after it exits the capillary. A separate gas flow is used in the condensers to provide a means of directing the flow of the vapor species to the desired condenser. This technique makes it possible to collect the

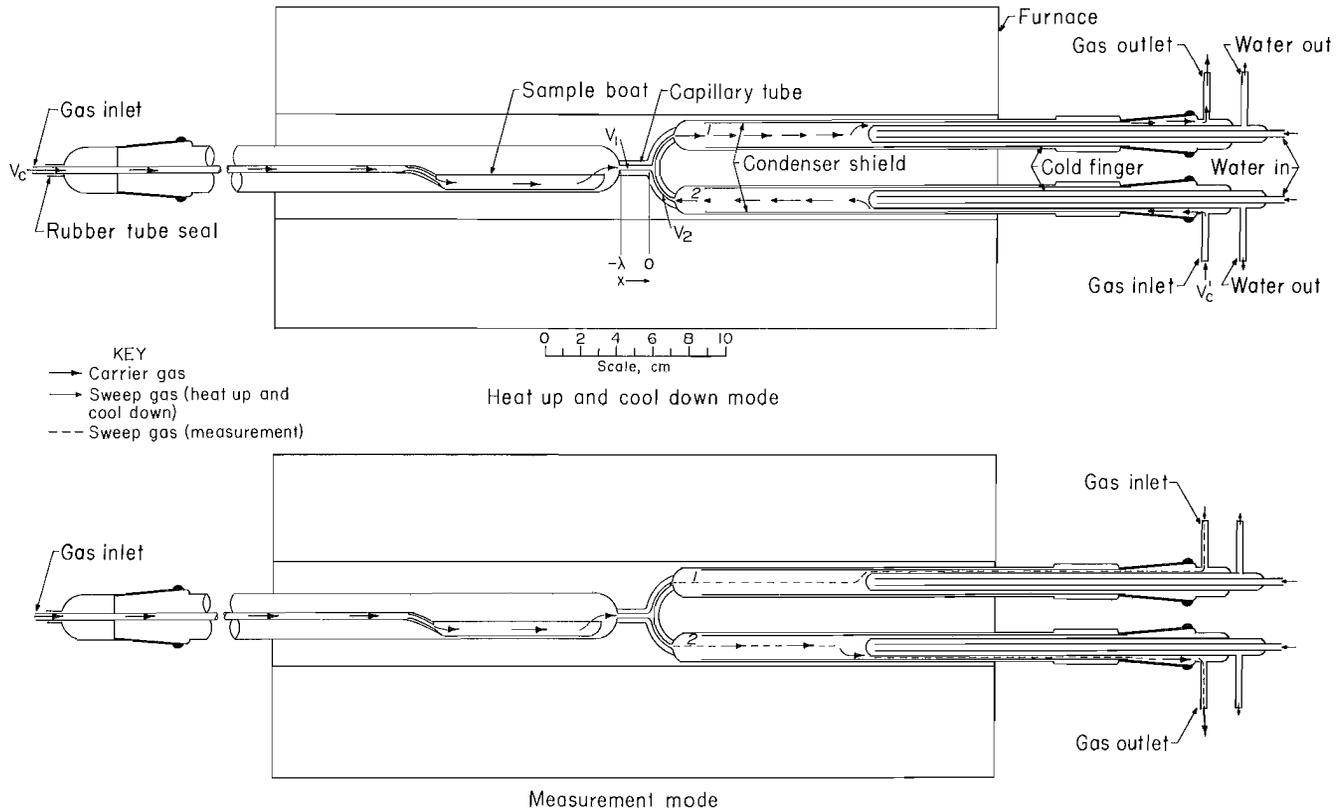


FIGURE 2. - Top view of modified transpiration apparatus, showing both unsteady state and measurement modes.

condensate on one condenser during the heat-up and cool-down periods and to collect a sample for measurement on the other condenser. By this means precise results may be obtained by collecting deposits during a time interval that is independent of the heat-up and cool-down periods. This allows shorter tests than with the conventional method since the sampling time does not have to be long compared to the heat-up and cool-down periods in order to minimize error.

A set of three-way valves enables the flow of the sweep gas through the condensers to be reversed quickly. If V_c' is the volume flow rate of sweep gas that is fed to one or the other condenser through the control valves, then $V_1 + V_2$ is the flow in the capillary leading to the analytical condenser where the sample is collected. Capillary connections to each condenser minimize back diffusion of the gases.

If the linear gas velocity (V_1/A) is great enough to minimize diffusion effects and V_1 is small enough to assure saturation, the C_{sat} and P_{sat} can be calculated according to equations 7 and 8, respectively. The concentration of the sample vapor in the y -intersection of capillaries can also be calculated according to

$$C_o = \frac{F}{V_1 + V_2}. \quad (9)$$

The modified transpiration apparatus also makes it possible to determine the interdiffusion coefficient D when V_c is zero. Then, according to equation 2, V_1 is also zero and the sample is transported by diffusion only. Since $C = C_{sat}$ at $X = -\lambda$ and $C = C_o$ at $X = 0$, equation 3 can be solved, giving

$$D = \frac{F\lambda}{A(C_{sat} - C_o)}. \quad (10)$$

Therefore, static tests ($V_c = 0$) can be performed and the value of D calculated if $C_{s_{at}}$ is obtained from dynamic tests at the same temperature. This type of test is valid if the flow of argon through the

condenser arms and the connecting capillary has no effect on the diffusion of gas in the capillary leading to the y-intersection.

APPARATUS

The modified transpiration apparatus developed in this investigation consists of a Vycor⁶ boat inside a Vycor reaction tube that is connected to two water-cooled condensers. Heat is applied to the reaction tube with an electric furnace, and argon gas is fed to the boat with a Matheson model 8240 mass flow controller and to the condensers through a micrometer-type valve. The reaction boat is depicted schematically in figure 3. A tube is connected to the boat to allow carrier gas to bubble through liquid samples. Tests, discussed later, show that the vapor concentration is constant over a wide range of gas flow rates, which demonstrates that the gas mixture is saturated with the sample vapor. The boat itself is 10 cm long and has tapered ends to allow for the expansion of solid samples while heating.

The reaction tube is 2.5 cm in diameter and 36 cm long. The two condensers are connected to the reaction tube with a y-intersection consisting of three capillaries. The capillary connecting the reaction tube and the y-intersection is 1 cm long and 2 mm in diameter. The two capillaries connecting the y-intersection with the condensers are approximately 2 cm long and 2 mm in diameter.

The condensers are water cooled and can be easily removed from the apparatus to facilitate dissolving of the sample. The condenser shields fit closely into the Vycor housing as shown in figure 2. The cold-finger portion of the condenser is placed 8 cm from the opening of the condenser tube. The reaction tube is fitted with ceramic ends to center the capillary intersection in the furnace and provide

insulation. The furnace is equipped with 10 heating element taps to provide control of the temperature profile within the heated tube. Four 150-W variable resistors are connected to various taps to provide the desired temperature profile.

Figure 4 shows temperature profiles obtained at different temperature levels. At a distance of 12 to 20 cm from the left end of the furnace, the profiles are constant to within 2 K. To the right of the y-intersection, the temperature increases 1 or 2 K to insure that the vaporized sample does not condense in the capillaries before entering the condensers. The condenser shield entrance is about 25 cm from the left edge of the furnace.

Temperature is monitored with a platinum 10-pct rhodium thermocouple located in a Vycor well 1 cm above the center of the reaction boat. An electronic digital



FIGURE 3. - Schematic of sample boat.

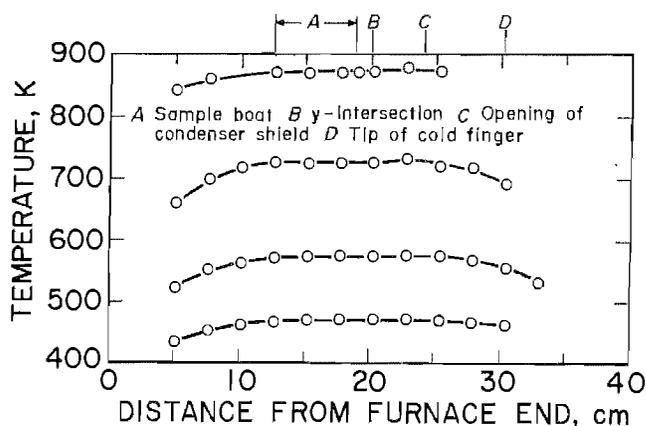


FIGURE 4. - Temperature profiles in reaction tube at different temperature levels.

⁶Reference to specific brand names is made for identification only and does not imply endorsement by the Bureau of Mines.

thermometer is used to convert the thermocouple electromotive force to degrees Celsius. Spot checks with a thermocouple placed directly in the molten sample revealed that the temperature in the well is 3 K higher than that of the sample. The temperatures presented in the tables have been corrected for this difference and therefore represent the true temperature of the sample.

Temperature is controlled by an electronic controller which keeps the sample within 1 K after a steady-state condition is achieved. A separate Chromel-Alumel thermocouple located in a well within the furnace itself is used as input to the temperature controller.

MASS FLOW CONTROLLER

A mass flow controller was used in all of the experimental measurements. The mass flow controller used was modified to accommodate a different range of flow rates. Because of this modification, the controller was carefully calibrated by displacing a known amount of argon in a given time using moving soap films in a buret. Although the vapor pressure of water is 19.8 torr (2,633 Pa) at 295 K (room temperature), the vapor pressure of water in equilibrium with the soap film

was not known and the possible small error (<2 pct) in calibration was neglected. Reproducible flow rates could be achieved in the range of 2 to 200 cm³/min at room temperature. The mass flow controller allowed for good control despite the variable pressures encountered in bubbling gas through a liquid melt.

REAGENTS

Reagent-grade ZnCl₂ and high-purity Sb₂S₃ were used in the study. The ZnCl₂ analyzed 47.8 pct Zn and 50.7 pct Cl after drying. The Sb₂S₃ analyzed 71.8 pct Sb and 30.2 pct S and gave an X-ray diffraction pattern that indicated less than 1 pct of antimony metal present. Theoretical amounts of zinc and chlorine in ZnCl₂ are 48.0 pct Zn and 52.0 pct Cl. Theoretical amounts of antimony and sulfur in Sb₂S₃ are 71.7 pct Sb and 28.3 pct S. Essentially the same X-ray diffraction pattern obtained for the starting material was also obtained on the Sb₂S₃ residue after all experiments were performed. This demonstrates that the vaporization itself is congruent. The carrier gas used in all experiments was reagent-grade argon, and flow rates are reported at ambient temperature and pressure.

EXPERIMENTAL PROCEDURE

Vapor transport determinations were begun by loading 25 to 40 g of sample into the boat and inserting it into the reaction tube. The system was purged with argon for at least 1,000 s before the flow rate of argon was reduced to the desired levels. Finally, the furnace and cooling water were turned on. During heat-up and while at a steady-state temperature for at least 1,800 s, the sample was collected in the "auxiliary" condenser. Then the valves were changed to reverse the flow of gas, and the sample was collected for a specific time in the "analytical" condenser. At the conclusion of the test period, the gas control valves were returned to their original position, thus stopping flow of vapor to the analytical condenser and

directing it once again to the auxiliary condenser. The furnace was then air-cooled, and the condensers were removed from the reactor.

Vapor transport measurements were made by determining the amount of material collected on the sample condenser. No attempt was made to determine the amount of weight lost from the sample boat. Deposits obtained when using Sb₂S₃ or ZnCl₂ were dissolved from the condenser with aqua regia, and the solutions were diluted to 100 ml for determination of antimony or zinc by atomic absorption methods. Analytical accuracy was within 2 pct, and concentrations of analyzed solutions were normally between 50 and 150 ppm. Before starting vapor density

determinations, the following preliminary experiments were conducted to establish the reliability of the apparatus:

1. The amount of material that diffuses upstream into the analytical condenser when the sample flow is directed into the auxiliary was determined. During heat-up and after attaining steady-state conditions at 870 K for 15 h, less than 0.005 mg of Sb was deposited on the analytical condenser when using Sb_2S_3 as the sample. Flow rates of 0.083 ± 0.002 and 0.417 ± 0.008 cm^3/s of argon were used as carrier and sweep gas respectively. Since 153 mg of Sb would have been deposited during a normal test, the error due to diffusion into the wrong condenser was considered negligible.

2. Particulate matter that may be carried past the analytical condenser by the gas stream was determined. An aqua regia trap was placed inline just beyond the

condenser. Antimony was not detected in the trap after running the test at 813 K for 3,600 s.

3. The error due to material being transferred from the auxiliary to the analytical condenser during a normal run was determined. Fourteen mg of condensate was deposited on the auxiliary condenser in the usual manner; then the reaction boat was removed and the reactor tube was cleaned. Next, the flow of sweep gas through the condensers was reversed, the furnace was heated, and a 1-h run at 870 K was performed without a sample in the reaction tube. After the run, only 0.07 mg of Sb_2S_3 was found in the analytical condenser. This test shows that only a 0.5-pct error would have occurred in a typical transpiration test from reverse deposit transfer. This possible small error was neglected in subsequent tests.

VAPOR PRESSURE OF ZINC CHLORIDE

Zinc chloride was chosen to study the reliability of the apparatus because it is a halide that can be obtained in pure form, its vapor pressure has been well established by Keneshea and Cubicciotti (3), and the temperature range for pressures of 1 to 100 torr (133 to 13,300 Pa) is near that of Sb_2S_3 . Reagent-grade ZnCl_2 was used in all tests. This material was used without prior treatment, although water evolved during the heat-up period and was carried out of the system by argon. Deposits collected on the condenser were analyzed for zinc by atomic absorption spectroscopy, as was done with the Sb_2S_3 deposits discussed earlier.

Several vapor pressure determinations were made in the temperature range of 667 to 883 K. Equilibrium pressures were calculated for each determination, assuming that the vapor was entirely monomeric. Pressures calculated on this basis are represented by a least-squares equation. The set of data obtained is presented in table 1 and is compared with the transpiration data of Keneshea and Cubicciotti (3) in figure 5. Both sets of data are plotted assuming the vapor is monomeric. Very close agreement was obtained between the two sets of data, showing the reliability of the modified transpiration technique.

TABLE 1. - Vapor pressure of ZnCl_2 assuming monomer only

Temperature, K	Time, s	Weight ZnCl_2 transported, mg^1	ZnCl_2 vapor density, mg/cm^3	Vapor pressure		Log_{10} vapor pressure	
				torr	Pa	torr	Pa
668.....	56,400	18.34	1.722×10^{-3}	0.527	70.3	-0.278	1.85
684.....	53,700	29.81	2.870×10^{-3}	.898	120	-.047	2.08
723.....	12,600	23.56	9.119×10^{-3}	3.01	401	.479	2.60
762.....	3,600	23.14	2.946×10^{-3}	10.27	1,369	1.01	3.14

¹Argon flow 0.083 ± 0.002 cm^3/s over boat and 0.417 ± 0.008 cm^3/s into noncollecting condenser.

VAPORIZATION OF ANTIMONY SULFIDE

Other vaporization studies of liquid Sb_2S_3 have been reported. Ryazantsev (5) and Ustyugov (8) used a quartz-membrane manometer to measure the pressure of Sb_2S_3 at 917 to 1,147 K. A transpiration method was used by Shendyapin (6) to determine the vapor pressure, assuming that $\text{Sb}_2\text{S}_3(l)$ decomposes into $\text{SbS}(g)$ as shown in equation 1. The data from these investigations were linearized and represented by

$$\log_{10} P(\text{torr}) = a + b/T. \quad (11)$$

In table 2 the coefficients derived from equation 11 are included for the three separate investigations. In all cases the uncertainty in the coefficients is shown as a standard deviation. The pressure data obtained by Shendyapin and Ustyugov show more uncertainty than the data obtained by Ryazantsev.

TABLE 2. - Comparison of vapor pressure equations, $\log_{10} P(\text{torr}) = a + b/T$

Reference	a	b
Ryazantsev (5).	8.219 ± 0.067	$-6,733 \pm 66.2$
Shendyapin (6).	$8.427 \pm .082$	$-7,445 \pm 102$
Ustyugov (8)...	$9.107 \pm .087$	$-7,818 \pm 95.3$

Shendyapin's vapor pressure data are much lower, as shown in figure 6. The

likely reason for this discrepancy is twofold: (1) Shendyapin assumed that Sb_2S_3 decomposes to SbS and S_2 according to equation 1, and (2) the experimental technique used by Shendyapin apparently did not allow for complete saturation of the gas with sample vapor.

Kaiser (2) recently reviewed vapor pressure and thermodynamic studies of antimony, arsenic, and bismuth sulfides and oxides. This review suggested that the work of Shendyapin was the best for the vapor pressure of liquid antimony sulfide when comparing the results of the three researchers mentioned. However, the results of the present study are most consistent with the work of Ryazantsev. Both studies using the quartz-membrane manometer report data that essentially agree except for the lower temperatures reported. At these temperatures Ustyugov's data bend toward lower values for vapor pressure, as shown in figure 6. This is probably due to a stiff membrane which is not sensitive to small pressure changes.

PRELIMINARY TESTS

Preliminary transpiration experiments were performed with Sb_2S_3 and using a flow rate of $0.417 \pm 0.008 \text{ cm}^3/\text{s}$ of argon

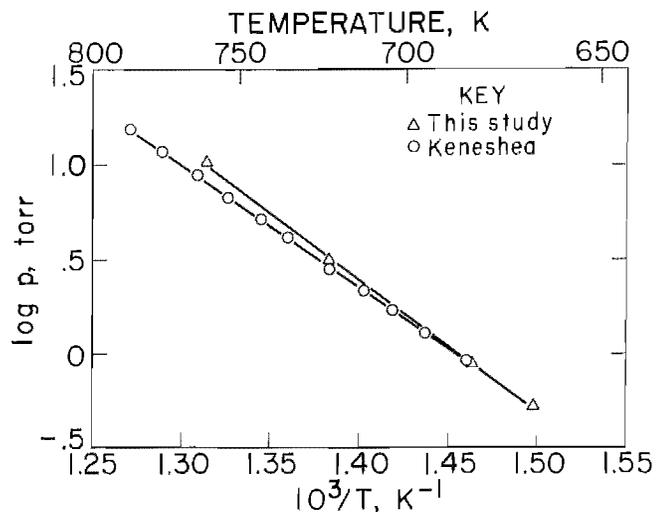


FIGURE 5. - Transpiration data calculated assuming monomer only for zinc chloride.

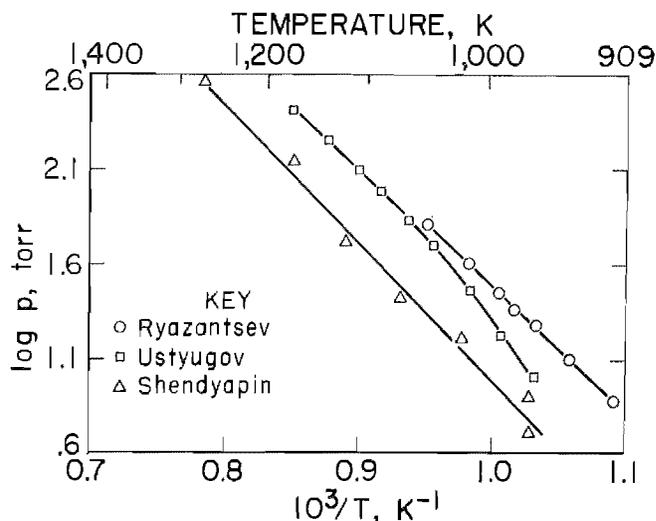


FIGURE 6. - Comparison of vapor pressure measurements made over liquid Sb_2S_3 by other investigators.

over the surface of the sample in an attempt to obtain vapor pressure data.

The reaction shown in equation 1 was assumed to occur, and vapor pressures were calculated according to equation 8. When the results were compared with data of previous investigations (5-6, 8), our data agreed more closely with those of Shendyapin (6). However, because of poor reproducibility, it was decided to modify the sample boat design to allow for bubbling the carrier gas through the molten sample.

Figure 7 shows the calculated vapor pressures (assuming equation 1 to be valid) for the present study along with those of Shendyapin. The vapor pressures obtained for tests in which the gas is bubbled through the molten sulfide are higher than those obtained when flowing the gas over the sample. Since the data for the unsaturated tests agree with those of Shendyapin, it can be concluded that Shendyapin's vapor pressure data are also low for the same reason.

A series of tests was conducted to determine the maximum flow rate that could be used to insure saturation of the gas stream with sample vapor. Figure 8 shows calculated vapor concentrations as a function of the flow rate of argon fed to the reaction tube. All tests

were conducted at 870 K with the boat design that allowed the gas to bubble through the sample. The data show that the vapor density was independent of flow, up to 0.833 ± 0.017 cm³/s. A value of 0.083 ± 0.002 cm³/s argon was chosen for use in subsequent tests in the investigation. This flow rate was low enough to insure saturation and high enough to make any effects due to diffusion extremely small.

VAPOR TRANSPORT MEASUREMENTS

The rate of vapor transport was measured as a function of temperature using the dual condenser apparatus previously described. Vapor pressures as measured by Ryazantsev (5) with a quartz manometer were used in equation 2 to allow calculation of V_1 and subsequent calculation of

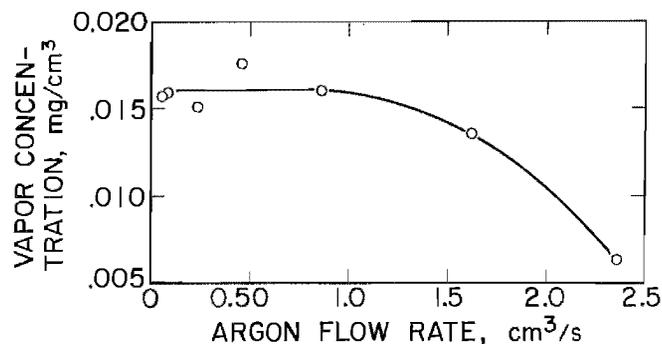


FIGURE 8. - Calculated vapor concentrations of Sb_2S_3 as a function of argon flow rate,

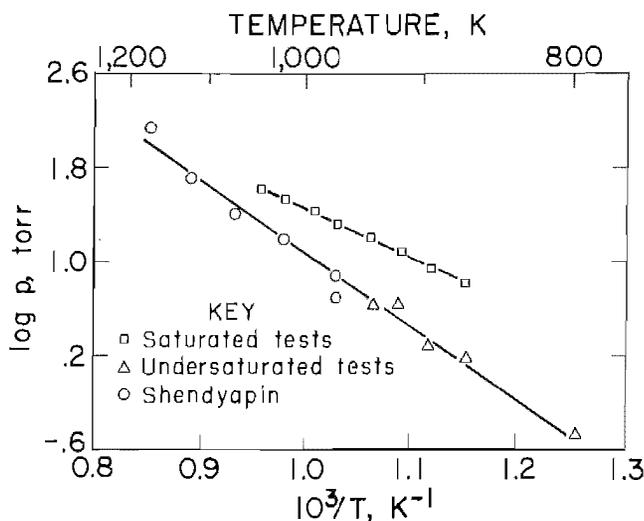


FIGURE 7. - Calculated vapor pressures for Sb_2S_3 assuming the reaction $Sb_2S_3(l) = 2SbS(g) + 1/2S_2(g)$.

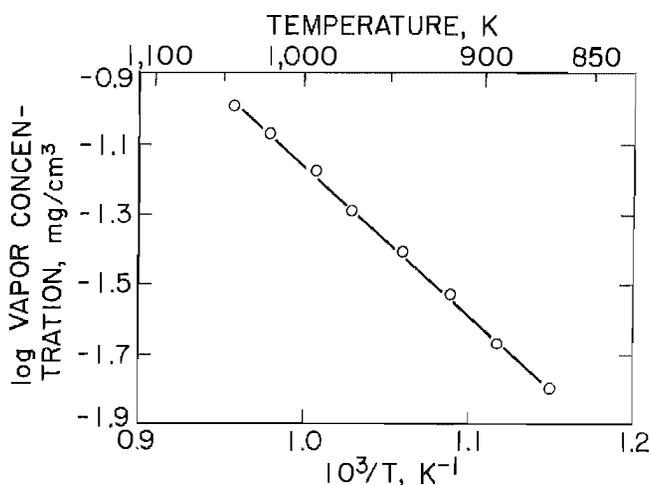


FIGURE 9. - Vapor concentration measurements of Sb_2S_3 as a function of temperature.

TABLE 3. - Vapor concentration of Sb_2S_3 as a function of temperature

Temperature, K	Time, s	Weight Sb_2S_3 transported, mg ^l	Sb_2S_3 vapor concentration (C_{sat}), mg/cm ³	$\log_{10} C_{sat}$, mg/cm ³
870.....	3,600	14.22	0.0160	-1.796
895.....	7,440	40.44	.0214	-1.670
918.....	6,900	53.82	.0298	-1.526
943.....	900	9.56	.0393	-1.406
972.....	600	8.64	.0511	-1.292
993.....	420	8.17	.0668	-1.175
1,021.....	300	7.75	.0846	-1.073
1,045.....	180	5.91	.1025	-.989

^lArgon flow was 0.083 ± 0.002 cm³/s over boat and 0.417 ± 0.008 cm³/s into noncollecting condenser.

C_{sat} according to equation 5. Table 3 shows the experimental data for the eight transpiration tests, and figure 9 is a plot of the logarithm of the vapor concentrations versus $1,000/T$.

The least-squares regression equation for data in table 3 is

$$\log_{10} C_{sat}(\text{mg/cm}^3) = (3.082 \pm 0.070) - (4,242 \pm 66.3)/T. \quad (12)$$

DIFFUSION COEFFICIENT MEASUREMENTS

As previously discussed, the modified transpiration apparatus makes it possible to determine the diffusion coefficients of compounds with the use of equation 10. Static tests were run with $V_c = 0$ at several different temperatures. A flow of 0.167 ± 0.003 cm³/s argon was used in the condenser. The values used for C_{sat} in equation 10 were computed by using the regression expression (equation 12), and C_o was calculated with equation 9.

Table 4 contains the diffusion data obtained in the static tests.

To demonstrate that diffusion effects were negligible for the transpiration measurements, a flow rate of 0.083 ± 0.002 cm³/s argon and the value for D at 1,020 K (0.31 cm²/s) were used in equations 2 and 5. The diffusion component (the exponential term) of equation 5 was found to be 3.98×10^{-14} , which is insignificant compared to unity. The use of equations 7 and 8 is therefore justified.

CALCULATION OF THE AVERAGE MOLECULAR WEIGHT

Combining our Sb_2S_3 vapor density data with the static vapor pressure measurements of Ryazantsev (5) permitted calculation of the average molecular weight of the vapor species at various temperatures. Average molecular weights were calculated by using the vapor density data in table 3 along with vapor pressures calculated with equation 11

TABLE 4. - Diffusion data for Sb_2S_3

Temperature, K	Time, s	Weight Sb_2S_3 transported, mg	F, mg/s	Concentration, mg/cm ³		D, cm ² /s
				C_{sat}	C_o	
870.....	7,200	0.39	5.42×10^{-5}	1.61×10^{-2}	1.10×10^{-4}	0.108
920.....	54,000	9.31	1.72×10^{-4}	2.96×10^{-2}	3.27×10^{-4}	.187
945.....	52,500	13.24	2.52×10^{-4}	3.92×10^{-2}	3.33×10^{-4}	.206
970.....	14,520	5.58	3.84×10^{-4}	5.11×10^{-2}	6.83×10^{-4}	.242
1,020.....	2,100	1.69	8.03×10^{-4}	8.38×10^{-2}	1.31×10^{-3}	.310

(using Ryazantsev's coefficients) according to a rearrangement of equation 6,

$$M' = \frac{C_{sat} RT}{P_{sat}} \quad (13)$$

Table 5 contains the average molecular weights calculated with equation 13.

TABLE 5. - Calculated average molecular weight as a function of temperature

Temperature, K	P _{sat}		C _{sat} , mg/cm ³	M, g/mol
	torr	Pa		
870.....	3.04	404	0.0160	286
895.....	4.99	664	.0214	239
918.....	7.71	1,025	.0298	221
943.....	12.08	1,607	.0393	191
972.....	19.53	2,597	.0511	159
993.....	27.47	3,654	.0668	151
1,021.....	42.40	5,639	.0846	127
1,045.....	59.63	7,931	.1025	112

The average molecular weight is plotted as a function of temperature in figure 10. A regression curve is plotted as the solid line in the figure and is represented by

$$M = 3,677 - 6.353T + 2.816 \times 10^{-3}T^2 \quad (870 \text{ K} < T < 1,045 \text{ K}). \quad (14)$$

Since the average molecular weight of the gaseous product in the reaction

MASS SPECTROMETRIC IDENTIFICATION OF SPECIES

Since this study shows that the average molecular weight of gaseous species in equilibrium with Sb₂S₃ (stibnite) is a function of temperature, a discussion of available mass spectrometric studies is helpful in understanding which vapor species may be present. While the mass spectrometry data available are at temperatures below the melting point of Sb₂S₃, the same species will exist in the vapor at temperatures above the melting point. Mass spectrometric analysis of the vapor species over stibnite has been performed by several researchers (1, 6-7). Two of these researchers (1, 7) concluded that the primary vapor species below the melting point of Sb₂S₃ are SbS

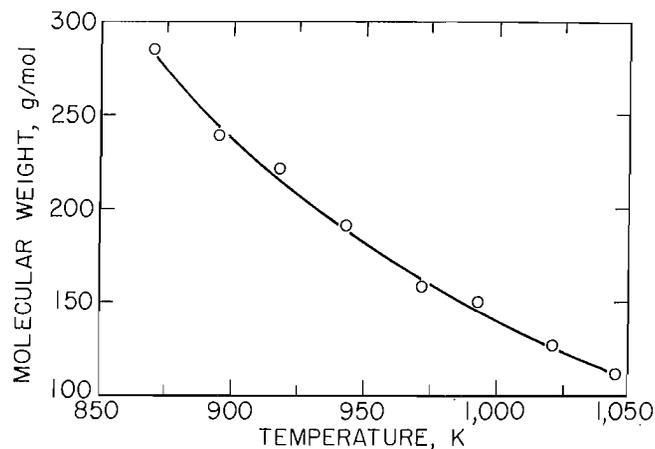


FIGURE 10. - Calculated average molecular weight of gaseous species in equilibrium with Sb₂S₃(l) at various temperatures.

expressed in equation 1 is 135.8 g/mol, and the molecular weight of Sb₂S₃ is 339.7 g/mol, it appears that Sb₂S₃ dissociates to a greater degree as temperature increases. This phenomenon was also observed qualitatively, as it was noted that more elemental sulfur was collected on the condensers as the temperature increased. Shendyapin also observed the higher amount of elemental sulfur at higher temperatures when doing transpiration experiments. The average molecular weights listed in table 5 should be useful in evaluating the results of mass spectrometry studies.

and S₂; the third (6) concluded the primary species to be Sb₂S₃. Analysis of the data in the literature indicates that there are several other species present in addition to SbS + S₂ and Sb₂S₃. All previous researchers acknowledged this but assumed a simple reaction in order to calculate vapor pressure values from their Knudsen cell and transpiration data.

Sullivan (7) reported appearance potentials for all the ions found. An evaluation of the appearance potentials allows a reasonable sorting of the ions into parents and fragments. The ionization of a molecule without fragmentation requires

TABLE 6. - Mass spectrometric identification of species

Species	Mass	Relative ionization cross section	Sullivan (7), 813 K, E = 20 V		Faure (1), ¹ 752 K, E = 35 V, relative intensity ²
			Relative intensity	Appearance potential, V	
S ⁺	32	12.8	NR	>20	140
S ₂ ⁺	64	25.6	64	9.9	83
Sb ⁺	121-123	26.1	21	16.4	41
SbS ⁺	153-155	38.9	100	8.4	100
SbS ₂ ⁺	185-187	51.7	64	10.6	6
Sb ₂ ⁺	242-246	52.2	11	11.8	12
Sb ₂ S ⁺	275-277	65.0	64	10.7	30
Sb ₂ S ₂ ⁺	306-310	77.8	44	8.8	11
Sb ₂ S ₃ ⁺	338-342	90.6	84	8.8	19
Sb ₂ S ₄ ⁺	370-374	103.4	12	8.6	NF
Sb ₃ ⁺	363-369	64.8	6.5	13.3	3.6
Sb ₃ S ⁺	395-401	77.6	11	10.7	3.6
Sb ₃ S ₂ ⁺	427-433	90.4	7.5	9.6	3.6
Sb ₃ S ₃ ⁺	459-465	116.7	29	9.5	5.4
Sb ₃ S ₄ ⁺	491-497	129.5	4.3	9.3	NF
Sb ₄ S ₃ ⁺	580-588	142.8	4.3	8.5	NF
Sb ₄ S ₄ ⁺	612-620	155.6	23	8.5	6.3
Sb ₄ S ₅ ⁺	644-652	155.6	1.6	8.5	NF

NF Sought but not found.

NR Not reported.

¹Magnetic field = 3.25 kG.

²Corrected for natural isotope percentage.

only enough energy to remove one electron, but when fragmentation occurs the energy must equal that needed to remove the electron and break the chemical bond. Parent ions will have a lower appearance potential than similar fragments.

From Sullivan's data, presented in table 6, it can be seen that SbS, Sb₄S₃,

Sb₄S₄, Sb₄S₅, Sb₂S₄, Sb₂S₂, and Sb₂S₃ are ions with the lower appearance potentials (<8.8 eV) and are likely to be the primary parent species at 813 K. As the temperature increases, the heavy species will disappear and will leave the light molecules like SbS and S₂ as the primary species.

SUMMARY

A modified transpiration apparatus was designed and constructed incorporating a two-condenser system. The apparatus was able to reproduce accepted vapor pressure data for ZnCl₂. This new device allows more accurate measurements of vapor transport, since it eliminates errors associated with the heat-up and cool-down periods when using a conventional

apparatus. The use of two condensers and gas valves makes it possible to allow the flow of sample to come to steady-state temperature before transporting vapor to the analytical condenser. It was also shown that the device could be used to obtain diffusion coefficient data by using zero flow of carrier gas through or over the sample.

The vapor concentrations over liquid antimony sulfide were measured with the modified transpiration apparatus in the temperature range of 870 to 1,045 K. Comparison of these data with previously published results disproves the hypothesis that Sb_2S_3 dissociates completely to SbS plus S_2 on vaporization. The present work indicates that the dissociation is incomplete and increases with temperature.

The average molecular weight for the gaseous species was calculated as a

function of temperature and was shown to decrease from 286 g/mol at 870 K to 112 g/mol at 1,045 K. Additional mass spectrometry work is needed to determine quantitatively the various gaseous species that exist as a function of temperature. Experiments conducted at higher temperatures should provide confirmation as to whether free antimony exists as a vapor. The average molecular weights obtained in this study should be useful in verifying the mass spectrometric results.

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NOMENCLATURE

- A = Capillary area, cm^2
- B = Constant of integration, mg/cm^3
- C = Concentration of sample vapor, mg/cm^3
- C_0 = Concentration of sample vapor at capillary exit ($X=0$), mg/cm^3
- C_{sat} = Saturated concentration of sample vapor, mg/cm^3
- D = Diffusion coefficient of sample vapor in carrier gas, cm^2/s
- F = Mass flow rate of sample vapor, mg/s
- M = Average molecular weight of the sample vapor, g/mol
- M' = Average molecular weight of the sample vapor, mg/mol
- P = Vapor partial pressure, torr
- P_{sat} = Saturated partial pressure of sample vapor, torr
- P_{t} = Total pressure, torr
- R = Gas constant, $62,363 \text{ cm}^3 \cdot \text{torr} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
- T = Temperature of sample in boat, K
- T_c = Calibration temperature of carrier gas, 295 K
- V_1 = Volume flow rate of carrier plus sample gas through or over boat, cm^3/s
- V_2 = Volume flow rate of sweep gas through condenser capillary only at reaction temperature, cm^3/s
- V_c = Volume flow rate of carrier gas at calibration temperature, cm^3/s
- V'_c = Volume flow rate of sweep gas through condenser only at calibration temperature, cm^3/s
- X = Distance in direction of gas flow measured from exit of the capillary, cm
- λ = Length of capillary tube, cm