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# THE VAPOR PRESSURES OF
# $PbO-Sb_2O_3-SiO_2$ MIXTURES

BY

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A

THESIS

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Approved by

A W Schlechten (Advisor) W. J. James

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# CHAPTER I

## INTRODUCTION

The removal of antimony is one of the important steps in the production of pure lead. The process of removing antimony from impure lead bullion is called "lead softening". The most common method used is to blow air into a bath of impure molten lead.(1) The impurities, primarily antimony, arsenic and tin, if present, are oxidized and form a slag or "dross" which floats on the surface of the lead bath. A considerable amount of lead is oxidized in this step and joins the other oxidized compounds in the dross. This dross is skimmed from the bath of molten lead and the antimony, arsenic and lead are recovered in separate operations.

Recovery of the antimony from this slag is difficult and expensive. Therefore, the need for an efficient, cheap process by which the antimony can be recovered from the mixed oxide slag is apparent.

The present investigation was made to examine the possibility of recovering the antimony from the slag by use of a vacuum process. Antimony forms a volatile oxide, $Sb_2O_3$. The lead and lead oxide, PbO, are relatively nonvolatile.(2) Therefore, it should be possible to separate the antimony from the impure lead bullion by selectively volatilizing the antimony as antimony trioxide, $Sb_2O_3$.

(1) All references are in bibliography.

To determine if this selective volatilization process is possible, a study was made of the vapor pressures of **artificial** lead oxide - antimony trioxide mixtures. The antimony trioxide is the only highly volatile phase present in these mixtures, so the vapor pressure is due almost entirely to the antimony trioxide. The vapor pressures were determined for mixtures of $PbO - Sb_2O_3$ of several different compositions.

Additions of silica, $SiO_2$, were then made to the $PbO-Sb_2O_3$ mixtures to determine the effect of the silica on the vapor pressures of these mixtures. The silica was expected to form a lead silicate compound and thus prevent the formation of a lead antimonite compound. It was hoped that this would increase the vapor pressures of the $Sb_2O_3$ above the $PbO-Sb_2O_3-SiO_2$ mixtures.

The vapor pressures were measured by the inert gas saturation method. For comparison, the volatility of the $PbO-Sb_2O_3$ mixtures was measured directly by heating the sample under a vacuum.

# CHAPTER II

# REVIEW OF LITERATURE

The most extensive study of the lead oxide - antimony trioxide system was made by Maier and Hincke.(3) They determined the melting point of PbO - $Sb_2O_3$ mixtures containing from zero to one hundred percent PbO. This melting point diagram is shown in Figure 1 and shows a eutectic at 21.5 percent PbO.

Maier and Hincke(3) also made microscopic studies of the PbO-$Sb_2O_3$ mixtures. These studies indicated the formation of a compound, $PbO \cdot Sb_2O_3$, containing 43.3 percent PbO. The presence of this compound has been further substantiated by Tammann(4) and by Barthel(5). In the more recent work of Barthel(5), the complete phase diagram of Pb - Sb -$O_2$ is shown.

Maier and Hincke(3) measured the vapor pressures of PbO-$Sb_2O_3$ mixtures at 539°C. The results of their investigation are shown in Figure 2 and in Table 1. They show that the vapor pressures of the PbO-$Sb_2O_3$ mixtures containing up to 40 percent PbO are nearly the same as the vapor pressure of pure antimony trioxide, $Sb_2O_3$. For PbO-$Sb_2O_3$ mixtures containing more than 40 percent PbO, the vapor pressures drop very rapidly to nearly zero at about 60 percent PbO. It is concluded that the vapor pressure of the PbO-$Sb_2O_3$ mixtures is due entirely to the volatility of the $Sb_2O_3$ and not to the PbO phase or to the volatility of any PbO - $Sb_2O_3$ compounds. The related microscopic investigation showed that $Sb_2O_3$ exists as a primary phase in the PbO - $Sb_2O_3$ mixtures containing up to about 40 percent PbO.

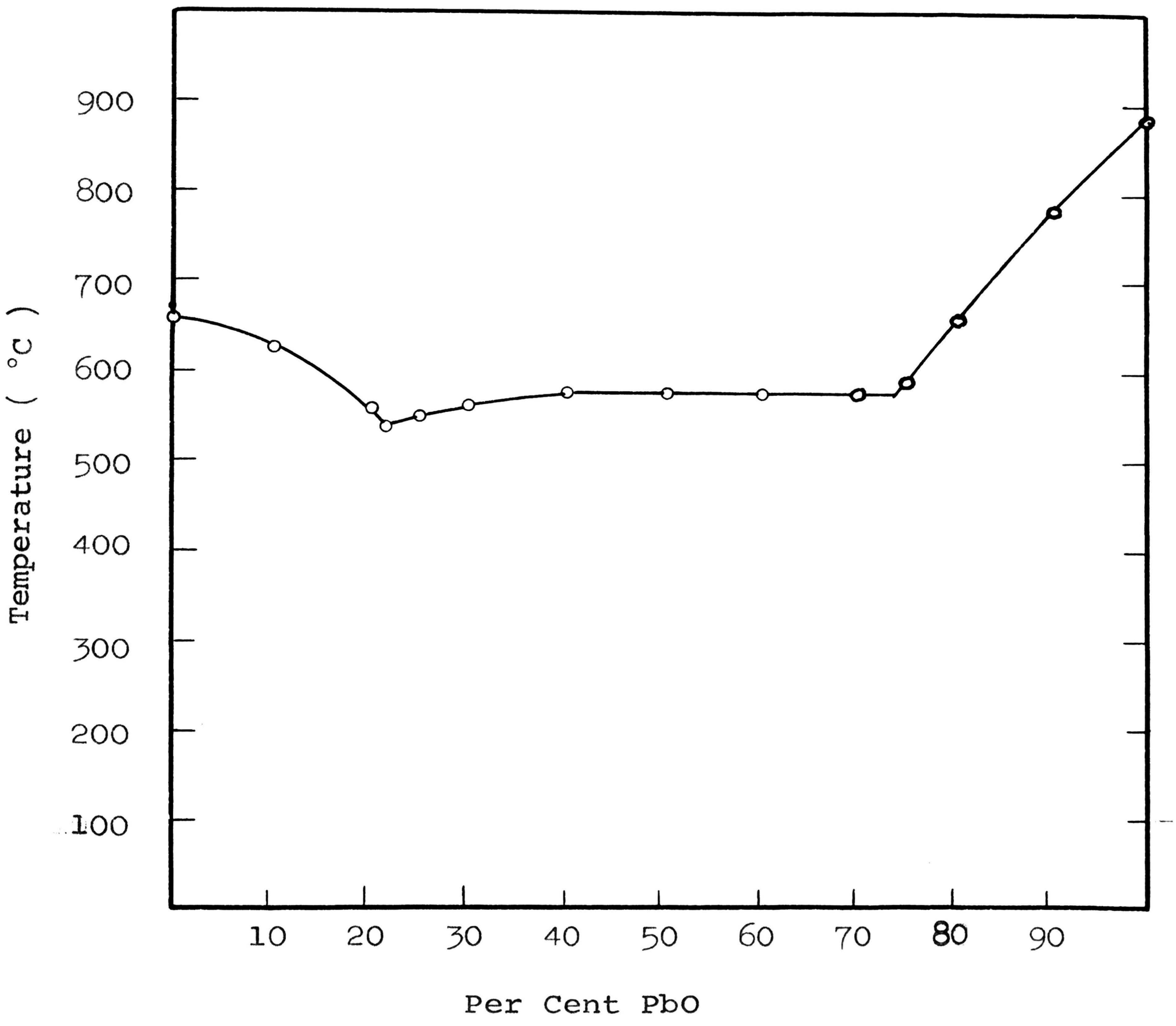


Figure 1. Melting point diagram for the system $PbO - Sb_2O_3$

## TABLE I

## VAPOR PRESSURES OF MIXTURES OF PbO-$Sb_2O_3$ AS MEASURED BY MAIER AND HINCKE

| PbO (Percent) | Vapor Pressure (at 539°C, mm.Hg) |
|---|---|
| 0 | 0.303 |
| 10 | 0.311 |
| 22 | 0.295 |
| 34 | 0.308 |
| 40 | 0.241 |
| 43.4 | 0.152 |
| 43.4 | 0.130 |
| 56 | 0.03 |
| 69 | 0.01 |
| 82 | 0.00 |

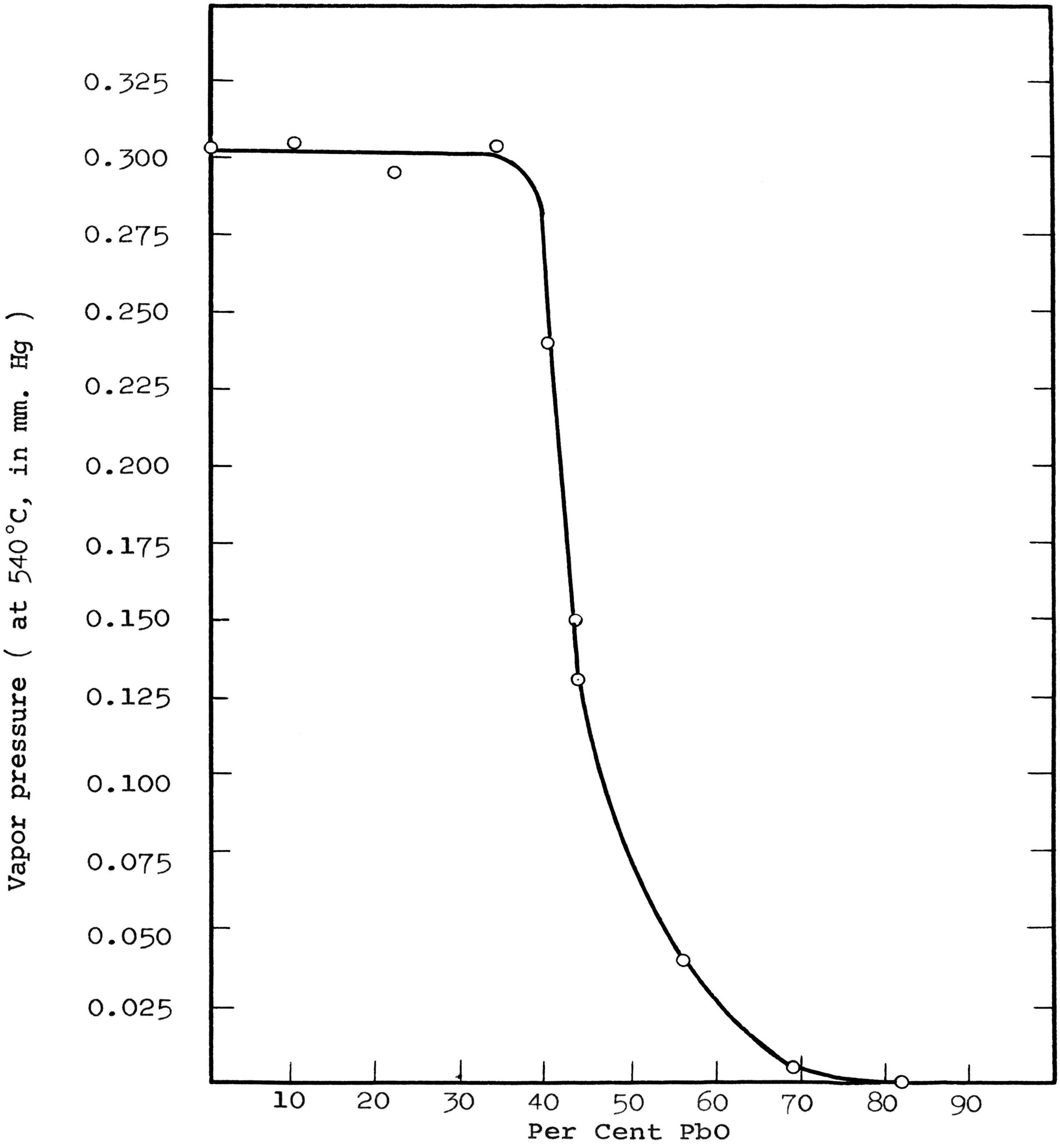


Figure 2. Vapor pressures of PbO - $Sb_2O_3$ mixtures as measured by Maier and Hincke.(3)

Above 40 percent PbO, the $Sb_2O_3$ is tied up as the $PbO.Sb_2O_3$ compound and therefore is in a nonvolatile form. This accounts for the sharp drop in the vapor pressure of the PbO - $Sb_2O_3$ mixtures above 40 percent PbO. For mixtures containing more than 40 percent PbO, the only $Sb_2O_3$ which volatilizes comes from the dissociation of the $PbO.Sb_2O_3$ compound.

In the lead softening process, the dross contains about 75 to 80 percent PbO(3). The vapor pressure of PbO - $Sb_2O_3$ mixtures containing this amount of PbO is essentially zero as seen in Figure 2. To allow the $Sb_2O_3$ to be removed from these drosses by volatilization, it is necessary to break down the $PbO.Sb_2O_3$ compound. The proposed method of doing this was to add silica, $SiO_2$, to the PbO - $Sb_2O_3$ mixtures. The $SiO_2$ should form a silicate compound, either $4PbO.Sb_2O_3$ or $PbO:Sb_2O_3$, as shown by Geller(6).

# CHAPTER III

# THE APPARATUS

## The Apparatus for Measuring Vapor Pressures.

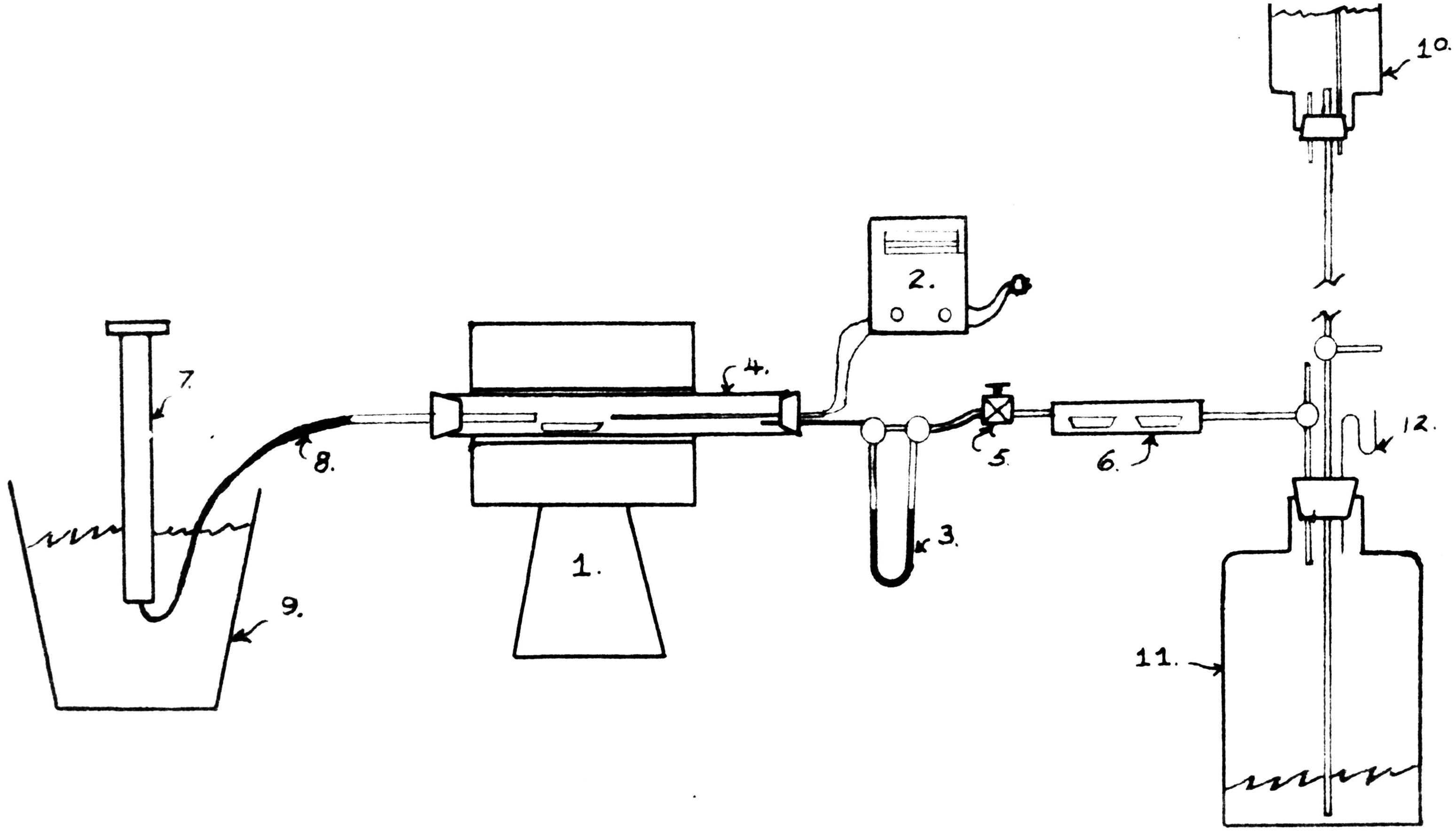
The inert gas saturation method was used to measure the vapor pressures. The apparatus used was similar to that of Maier and Hincke(3) which was described in detail by Eastman and Duschak(7). This apparatus is shown in Figure 3.

The principle parts of this apparatus are:

1. Reaction tube
2. Gas flow system
3. Furnace and controller

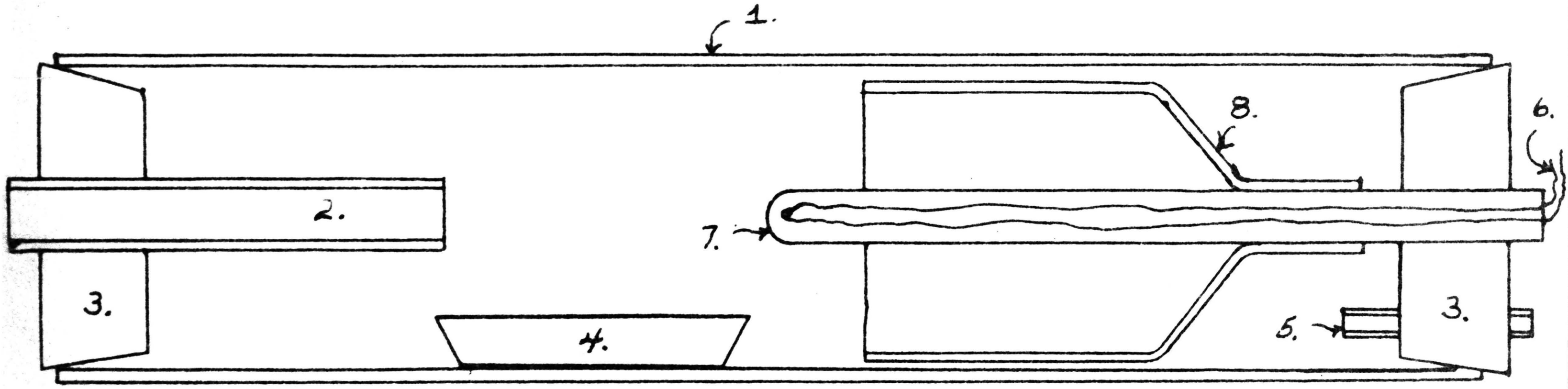
Reaction Tube. The reaction tube is shown in Figure 4. The inert gas passes in through the gas inlet tube, around the gas baffle, over the combustion boat containing the sample where it picks up the volatile material given off, and through the condensing tube where the volatile material condenses.

The reaction tube was made of pyrex which was adequate because the highest temperature reached was 540°C and there was no reaction between the $Sb_2O_3$ gas and the pyrex. The reaction tube was modified slightly from the one used by Maier and Hincke(3) to make the combustion boat easier to place in and remove from the tube and to eliminate some of the complicated glass blowing necessary in making the reaction tube.



1. tube furnace
2. temperature controller
3. flow meter
4. reaction tube
5. needle valve
6. $P_2O_5$ drying tube
7. graduated cylinder
8. rubber tube
9. water bucket
10. water reservoir
11. gas reservoir bottle
12. manometer

Figure 3. The arrangement of the apparatus for measuring vapor pressures.



1. pyrex reaction tube
2. condensing tube
3. rubber stopper
4. combustion boat
5. gas inlet tube
6. chromel-alumel thermocouple
7. thermocouple tube
8. gas baffle

Figure 4. The reaction tube in the apparatus for measuring vapor pressures.

The gas baffle was necessary between the gas inlet tube and the combustion boat to prevent counter-diffusion of the inert gas. The condensing tube is necessary to remove the volatile material from the saturated inert gas and to prevent it from recondensing in the combustion boat.

Gas Flow System. The inert gas must pass over the sample at a constant flow rate and under constant pressure. The apparatus used to establish these conditions is shown in Figure 5.

The gas flow system consists of:

(1) A large aspirator bottle (13 gal. Carboy) to serve as a gas reservoir.

(2) A gas inlet tube with a three way stopcock to allow fresh inert gas to be put into the gas reservoir bottle or to pass into the system.

(3) A water inlet tube with a three way stopcock, to allow water to flow into the gas reservoir bottle and force the gas out.

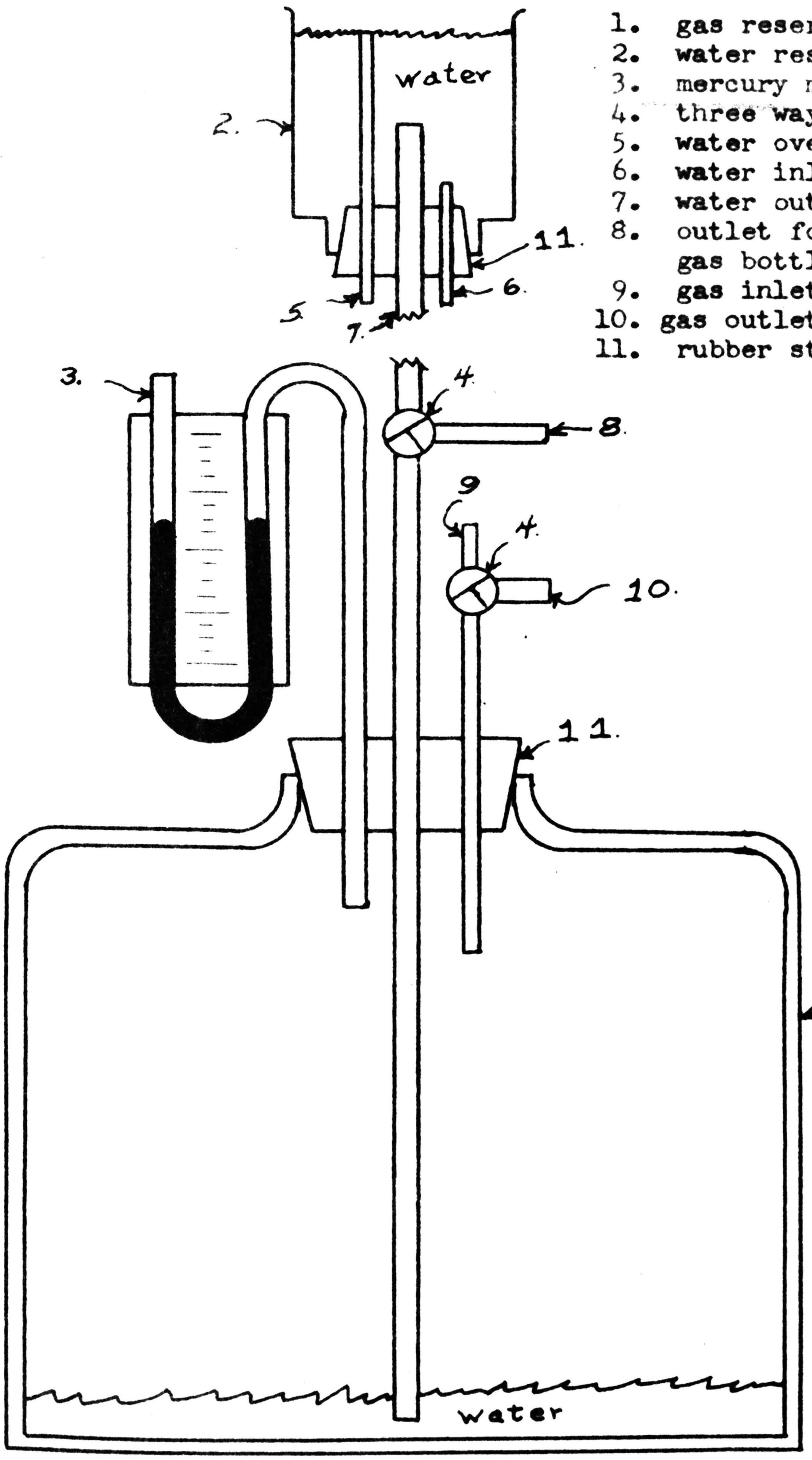
(4) A manometer for measuring the pressure of the gas in the system.

(5) A water reservoir to maintain a constant pressure head.

(6) A tube containing anhydrous phosphoric acid ($P_2O_5$) for drying the gas before it flows through the reaction tube.

(7) A needle valve for accurately regulating the flow of gas through the reaction tube.

(8) A flow meter for measuring the desired gas flow rate. Some initial attempts were made to measure the volume by a flow meter but these proved unsatisfactory.



1. gas reservoir bottle
2. water reservoir
3. mercury manometer
4. three way stopcock
5. water overflow to drain
6. water inlet
7. water outlet to gas bottle
8. outlet for draining water from gas bottle
9. gas inlet
10. gas outlet to system
11. rubber stopper

Figure 5. **The gas flow system used in the apparatus for measuring vapor pressures.**

(9) Two graduated cylinders to measure the gas volume by collecting the gas over water after it had passed through the reaction tube.

(10) A source of inert gas. A cylinder of commercial, water pumped Argon 99.9% pure was used.

Furnace and Controller. A wire wound electrical resistance tube furnace was used. This was capable of reaching temperatures up to 1100°C. The reaction tube fitted tightly into this furnace. The combustion boat was positioned in the center two inches of the furnace.

The furnace was connected in series with a Wheelco time proportioning capacitrol controller. A Chromel-Alumel thermocouple was used to measure the temperature in the furnace. The thermocouple was placed inside the pyrex protecting tube and directly over the end of the combustion boat.

## The Apparatus for Measuring Volatility under Vacuum.

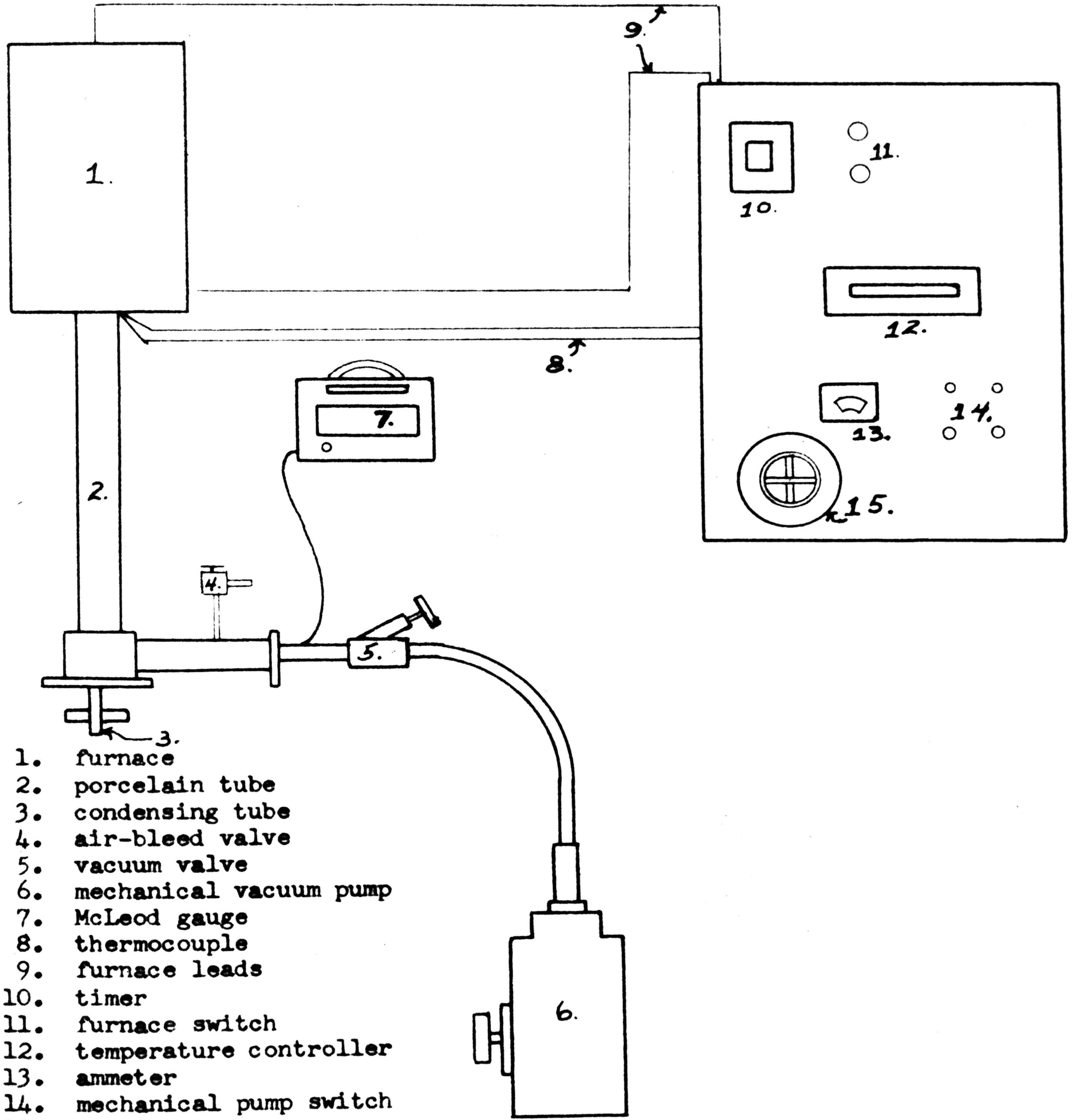
The apparatus used to measure the volatility of the PbO-$Sb_2O_3$ mixtures and the $Sb_2O_3$ - $SiO_2$ mixtures under vacuum was designed and built by Neumann(8). This apparatus is shown in Figure 6.

The apparatus consists of:

(1) A vacuum furnace capable of operating at temperatures up to about 1200°C.

(2) A vacuum pump.

(3) The necessary furnace and vacuum pump controls.



1. furnace
2. porcelain tube
3. condensing tube
4. air-bleed valve
5. vacuum valve
6. mechanical vacuum pump
7. McLeod gauge
8. thermocouple
9. furnace leads
10. timer
11. furnace switch
12. temperature controller
13. ammeter
14. mechanical pump switch
15. powerstat

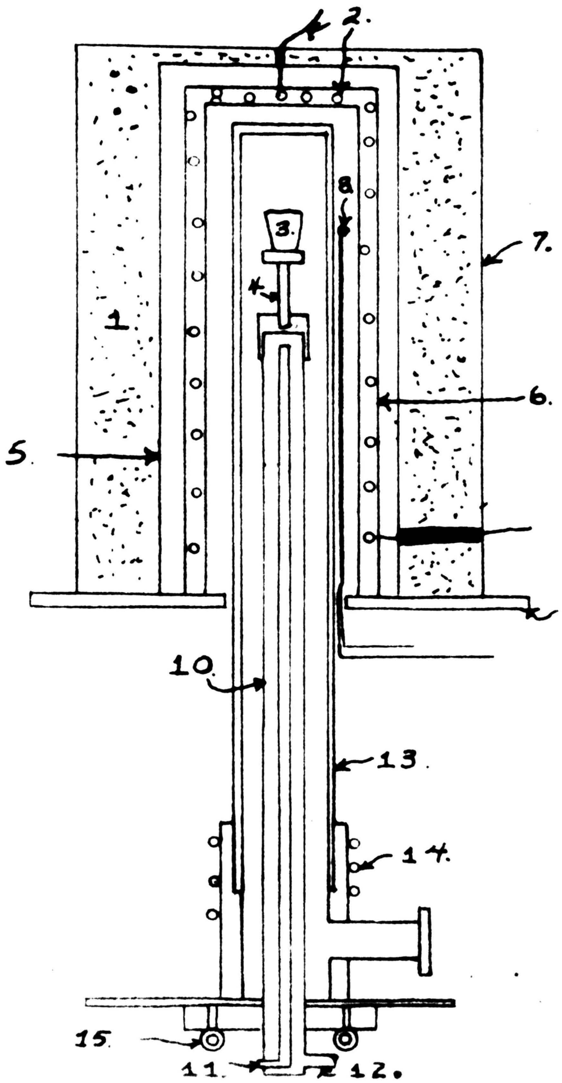
Figure 6. **The arrangement of the apparatus for measuring volatility under vacuum.**

(4) A condensing arrangement to remove the volatile material.

The furnace is shown in detail in Figure 7. The furnace is made of a 2 1/2 inch porcelain tube heated with windings of resistance wire. The porcelain tube is sealed at its lower end into a metal head with Pyseal. The socket into which the tube fits is cooled by circulating water to keep the Pyseal from melting. There is a temperature gradient in the tube from the working temperature to a temperature not far above room temperature in the bottom of the tube.

The temperature is measured with a Chromel - Alumel thermocouple which is placed in the furnace on the outside of the porcelain tube and near the crucible. A powerstat, capacity 7.5 kw, is used to adjust the voltage to the furnace. A Tork self starting clock is placed in the temperature controller circuit so the heating time can be preset.

The crucible containing the sample was supported by a special porcelain crucible support on top of the water cooled condensing tube. The crucible was placed into the hot zone of the furnace and removed by sliding the condensing tube through "O" rings mounted in the base of the furnace. This permitted placement of the sample in the furnace and removal of the sample without breaking the vacuum in the furnace.



1. insulating material
2. resistance wire
3. crucible
4. porcelain crucible support
5. alumina sleeve
6. alumina core
7. steel shell
8. thermocouple
9. asbestos plate
10. stainless steel condensing tube
11. water inlet tube
12. water outlet tube
13. porcelain tube
14. cooling coils
15. wing nuts

Figure 7. Construction of the furnace in the apparatus for measuring volatility under vacuum.

# CHAPTER IV

# EXPERIMENTAL PROCEDURE

## Preparation of Samples.

$PbO - Sb_2O_3$ Mixtures. Samples of lead oxide - antimony trioxide were prepared from analytical grade reagents of PbO and $Sb_2O_3$. The reagents were finely ground powder. The proper amount of each reagent was weighed out and mixed in the powder form. They were then tightly packed into a No. 2 Coors glazed porcelain crucible, a tight cover was attached and the crucible was heated to 700°C. in a small electric furnace. The samples were held at about 700°C for fifteen minutes to allow the PbO to dissolve in the molten $Sb_2O_3$. The molten mixture was then cast into a clean iron button dish and immediately covered to prevent loss of $Sb_2O_3$ during cooling. After cooling, the samples were ground in an agate mortar until the entire sample passed through a 65 mesh screen. Samples were made up containing from zero to 60 percent PbO.

$PbO - Sb_2O_3 - SiO_2$ Mixtures. These samples were prepared in a manner similar to the samples of $PbO - Sb_2O_3$ except that the mixed powder in the crucible was heated to 950°C instead of 700°C. This was necessary to fuse both the $Sb_2O_3$ and the PbO. PbO melts at 888°C and $Sb_2O_3$ melts at 656°C(9). It was necessary to have both phases molten so that the $SiO_2$ could go into solution. The $SiO_2$ used was pure ground quartz, ( -150 mesh). The $PbO - Sb_2O_3 - SiO_2$ mixtures were cast and ground in the same manner as the $PbO-Sb_2O_3$ samples.

Determination of Vapor Pressures.

All vapor pressure determinations for both PbO - $Sb_2O_3$ and PbO - $Sb_2O_3$ - $SiO_2$ were made at 540°C. This is the highest temperature at which the PbO - $Sb_2O_3$ samples would remain solid as determined by Maier and Hincke(3). There is a eutectic between $Sb_2O_3$ and PbO whose composition is about 21.5 percent PbO and which has a melting point of 539°C. It was desired to keep the samples below this temperature to avoid melting. Molten samples would greatly increase the corrosion of the crucibles in the time necessary to make the vapor pressure determinations.

The gas reservoir bottle was first filled with inert gas. This was done by opening the stopcock on the gas inlet tube to allow the air in the bottle to exhaust to the atmosphere. The water was then allowed to fill the gas reservoir bottle from the water reservoir. This forced all the air out of the bottle. The gas inlet tube was then connected to the argon tank. The stopcock on the water inlet tube was opened to allow the water from the gas reservoir bottle to be forced out. The argon was turned on and the pressure increased to force nearly all the water from the gas reservoir. This left the gas reservoir with a small amount of water in the bottom and the rest of the bottle filled with argon. The stopcock on the gas inlet tube was then shut and the connection to the argon tank was removed. The stopcock on the water inlet tube was opened to allow water to flow into the gas reservoir. The gas flow system was then allowed to come to equilibrium as shown by constant pressure on the manometer attached to the gas reservoir bottle. This pressure was a measure of the pressure head or the height of the water reservoir above the water level in the gas reservoir bottle.

When equilibrium had been reached, the stopcock on the gas inlet tube was turned to allow the gas to pass through the reaction tube. The needle valve was adjusted to the desired gas flow rate. The flow rate used was varied from about 15 to 40 cubic centimeters per minute. Usually four or five runs were made on each particular sample at different flow rates. Gas flow rates slower than 15 cubic centimeters per minute were tried but caused very erratic results due to counterdiffusion in the reaction tube and to small leaks in the gas flow system. Flow rates greater than 50 cubic centimeters per minute required very large volumes of gas to be passed over the sample to obtain a measurable weight loss.

The furnace and reaction tube were heated to about 540°C. After the gas flow had been started through the reaction tube, the tube was opened and the boat containing the sample was quickly placed in the reaction tube. The crucible plus sample had been previously weighed. The reaction tube was then closed and the rubber tube connected to the condensing tube was placed under the graduated cylinder containing water to measure the volume of gas passed through the reaction tube. The time at the start of the run and the initial pressure of the gas in the gas reservoir bottle were recorded. The barometric pressure and room temperature were also recorded to correct the volume of gas collected to standard temperature and pressure conditions.

During the run, the tube running to the graduated cylinders measuring the volume of gas was changed from one cylinder to the other as one of the cylinders became emptied. The volume of gas collected in each cylinder was recorded. From four to six liters of gas were passed over the samples during each run.

At the end of the run, the time and pressure of the gas were again recorded and the boat containing the sample was removed from the furnace and reweighed to determine the weight loss. This weight loss was a measure of the amount of $Sb_2O_3$ volatilized during the run. The weight loss depends on the vapor pressure of the sample, the volume of gas passed over the sample, the gas flow rate, and the total pressure in the system. The total pressure, as measured by the manometer attached to the gas reservoir, usually decreased by less than 5 centimeters of mercury during a run. This decrease in pressure was due to the slight rise in the level of the water in the bottle necessary to force out the gas passing over the sample.

The combustion boat containing the sample was cleaned and fired at 950°C to remove any volatile matter before reusing. All combustion boats and samples were kept in a desiccator when not in the furnace. The samples were dried for at least two hours at 110°C before using.

The vapor pressures calculated for each flow rate were plotted on a graph of vapor pressures versus flow rate. An example of those curves is shown for pure $Sb_2O_3$ in Figure 8. The function of

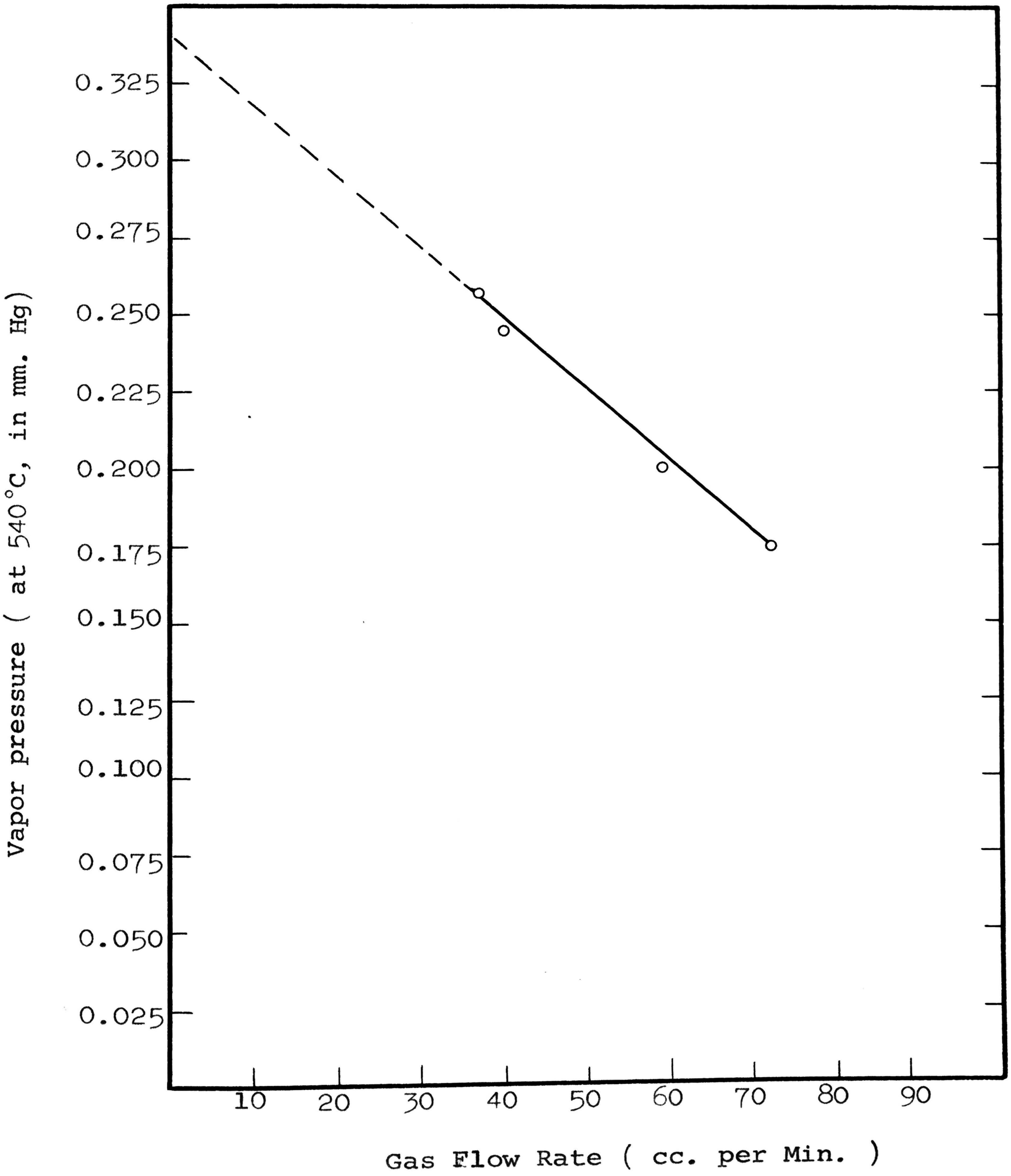


Figure 8. Example of curve for finding the equilibrium vapor pressure from experimental data.

flow rate versus vapor pressure is linear for low flow rates. Therefore, the data were extrapolated to zero flow rate and this value was taken as the equilibrium vapor pressure.

### Measurement of Volatility Under Vacuum.

To measure the volatility of the $Sb_2O_3$ - PbO and $Sb_2O_3$ - $SiO_2$ samples under vacuum, the furnace was first heated to the desired temperature. The crucible containing the sample to be run was accurately weighed. The crucible was then placed in the furnace with the condensing tube (Figure 7) in the lowered position so that the crucible was in the unheated part of the porcelain tube. The furnace system was then tightly closed, the vacuum pump was turned on and the valve between the vacuum pump and the furnace was opened. When the desired vacuum had been obtained, usually 40 to 60 microns of mercury, the condensing tube supporting the crucible was raised to the heated zone of the furnace. The crucible was left in the heated zone of the furnace for exactly one hour at which time the condensing tube was lowered and the crucible allowed to cool. The heating and cooling time was the same for all samples and therefore the amount of material volatilizing during heating or cooling was constant for all samples. The crucible was left in the unheated part of the furnace until it had cooled to nearly room temperature. The valve between the furnace and the vacuum pump was then closed and the pump was shut off. The furnace was then opened and the crucible removed and reweighed. The change in the weight of the crucible before and after heating in the furnace was a measure of the volatility of the sample. The condensing tube was cleaned and the furnace reloaded in preparation for another run.

## X-ray Analysis.

X-ray diffraction patterns were made of some of the samples to determine the phases present. The samples of the PbO-$Sb_2O_3$ mixtures and the condensate were analysed with a Norelco x-ray diffraction unit using copper radiation and a nickel filter. These x-ray patterns were recorded on photographic film. The samples of the PbO - $Sb_2O_3$ - $SiO_2$ mixtures were studied on the same x-ray unit but an x-ray spectrometer was used instead of the photographic film to record the diffraction patterns. The spectrometer was connected to an automatic recorder which showed the intensity of each diffraction line on the pattern. The intensity of the lines on the film patterns was estimated by eye.

In both cases, the diffraction angle $2\theta$ was measured from the film of spectrometer pattern. The diffraction angle was measured from 0 to 90° of $2\ \theta$. After measuring $2\theta$, either directly from the spectrometer pattern by knowing the chart factor or from the film by knowing the camera factor, the interplanar spacings (d values) were calculated from Bragg's Law $\lambda = 2d \sin \theta$. By referring to the ASTM x-ray index cards,(10) the principle phases could be identified.

X-ray analyses were also made on the $Sb_2O_3$ - $SiO_2$ samples to determine the existence of a compound formed between these two phases. This was done by running x-ray samples on all initial samples, condensate, and residue of the $Sb_2O_3$ - $SiO_2$ mixtures. All this work was done by use of an x-ray spectrometer to detect better any change in the intensity of the diffracted x-ray beam and to detect any shift in the poitions of the diffracted beam.

# CHAPTER V

# DISCUSSION

## Theoretical Background

Vapor Pressure Measurement. A study of the various methods available for measuring vapor pressures showed that the inert gas saturation method or transportation method was the best for the low vapor pressures expected with the $Sb_2O_3$ samples.(11) This method is described by Kubaschewski and Evans.(12) In this method of measuring vapor pressures, a steady stream of inert gas is passed over the substance whose vapor pressure is to be measured. The inert gas removes the vapors given off by the volatile substance. The material whose vapor pressure is being measured is kept at constant temperature throughout the time the inert gas is passed over it. The amount of material removed from the sample is dependent on the pressure of the inert gas, the vapor pressure of the substance, and the flow rate of the inert gas.

The inert gas is passed over the volatile substance at varying flow rates. Theoretically, saturation of the inert gas should occur at zero flow rate. The vapor pressure is measured for various flow rates and then extrapolated to zero flow rate. The vapor pressure at zero flow rate should be the same as the vapor pressure measured by static methods. The inert gas must be quite pure, particularly free of water vapor or oxygen and as heavy as possible. Most commercial gases such as argon, helium, or nitrogen are suitable for this purpose. It is necessary to dry the gas before passing it over the sample to remove any traces of water vapor. This may be done by passing the gas over any good drying agent such as activated alumina or anhydrous phosphoric acid. The total volume of gas passed over the sample is measured by volumetric methods and the time allowed for the gas to pass over the sample is recorded.

The sample is heated and cooled as rapidly as possible at the start and end of the run to reduce errors in the amount of volatile material given off when the substance does not have inert gas passing over it. The weight of volatile material given off is measured by weighing the sample before and after the run has been made. As can be seen from this discussion, the inert gas saturation method can be used only when the vapors given off by a volatile substance contain only one compound. If more than one type of vapor is given off it is impossible to measure how much of it is due to each substance and therefore to measure the vapor pressure of that substance. As will be shown in the calculations, it is also necessary to know the molecular weight of the vapors given off and therefore the molecular form of the gas given off by the volatile substance.

Measurement of Volatility Under Vacuum. The volatility measurements are based on the work of Langmuir(13) which shows that the maximum rate of evaporation of a volatile material is directly proportional to the vapor pressure of the material. The Langmuir method is applied by heating the volatile material in a vacuum and measuring the rate of evaporation. From the Langmuir equation:

$$W = P\sqrt{\frac{M}{2\,RT}}$$

where:

W = maximum rate of evaporation measured in grams per square centimeter per second.

P = vapor pressure in mm of mercury.

M = molecular weight in grams of vapors given off.

R = gas constant.

T = absolute temperature.

the rate of evaporation is shown to be proportional to the vapor pressure of the volatile substance.

To eliminate as many variables as possible, all samples were heated to the same temperature, for the same length of time, and under the same vacuum. Therefore, the weight loss of the sample during the run is a measure of the maximum rate of evaporation or the vapor pressure.

## Calculations

### Method of Calculating Vapor Pressures:

(1) From Boyle's law of gases:

$$p_V = n_V P_T$$

where:

$p_V$ = vapor pressure of volatile material

$P_T$ = total pressure in system

$n_V$ = mole fraction of vapors from volatile material.

$$n_V = \frac{\text{moles of vapor given off by volatile material}}{\text{Total moles of gas when inert gas is saturated}}$$

(2) $$\text{Vapor pressure} = \frac{\text{moles of substance removed}}{\text{total moles of gas}} \quad \text{total pressure}$$

(3) Number of moles of substances removed = weight loss  mol. wt.

The molecular weight of $Sb_2O_3$ in the gaseous phase is 583.0 because the gas molecules are of the form $Sb_4O_6$(14).

(4) Total number of moles of gas = moles of vapor from volatile material + moles of inert gas passed over the sample.

(5) Moles of inert gas passed over the sample = volume of dry inert gas at S.T.P. / 22.4.

(6) Volume of dry inert gas at S.T.P. =

$$\text{volume of gas measured} \times \frac{273}{670} \times \frac{P_1}{T_1} \times \frac{\text{density of dry air at room conditions}}{\text{density of moist air at room conditions}}$$

where: $T_1$ = temperature of gas

$P_1$ = total pressure of gas in system

(7) $$\text{Vapor Pressure} = \frac{\dfrac{(\text{weight loss})\,(\text{total pressure})}{(\text{density of moist air})}}{\text{volume of inert gas as measured}}$$

Method of calculating flow rate. The volume of gas passed over the sample was measured by collecting over water in a graduated cylinder as previously described. The time of each run was determined by recording the time at the beginning and end of each run. The volume of gas collected was considered to be completely saturated with water vapor because it had been collected by bubbling through water.

The flow rate of pure dry inert gas was calculated by dividing the total volume of dry gas by the time in minutes to make the run. To convert the volume of saturated gas to dry gas, the room temperature and barometric pressure were recorded and from this the density of saturated air could be found in the air density tables(15).

$$\left(\begin{array}{l}\text{Volume of}\\ \text{saturated gas}\\ \text{measured}\end{array}\right)\left(\frac{\begin{array}{l}\text{volume of dry}\\ \text{air at S.T.P.}\end{array}}{\begin{array}{l}\text{Volume of saturated}\\ \text{air at room conditions}\end{array}}\right) = \begin{array}{l}\text{volume of dry}\\ \text{gas at S.T.P.}\end{array}$$

$$\frac{\text{Volume of dry gas at S.T.P.}}{\text{total time in minutes of run}} = \begin{array}{l}\text{flow rate of dry gas in}\\ \text{cc. per min.}\end{array}$$

# CHAPTER VI

# EXPERIMENTAL RESULTS

## $PbO - Sb_2O_3$ Data.

The vapor pressure of the $PbO - Sb_2O_3$ mixtures were measured at 540°C by the method previously described. The results of these vapor pressures measurements are shown in Figure 9 and in Table II. The data from which these vapor pressures were calculated are shown in Table III.

Figure 9 shows that the vapor pressures of the $PbO - Sb_2O_3$ mixtures remain constant up to a composition of about 40 percent PbO. The vapor pressures of these mixtures are nearly the same as the vapor pressure of pure $Sb_2O_3$ at this temperature. As shown by Figure 10 and Table IV, the vapor pressure of pure $Sb_2O_3$ at 540°C is about 0.340 mm of mercury. These data were obtained from the published data for the vapor pressure of $Sb_2O_3$(16).

Beyond about 40 percent PbO, the vapor pressures of the $PbO - Sb_2O_3$ mixtures drops rapidly to nearly zero at about 60 percent. This agrees very closely with the results obtained by Maier and Hincke(3) as seen by comparing Figures 2 and 9. Maier and Hincke found the vapor pressures of the $PbO - Sb_2O_3$ mixtures to drop off very rapidly between 40 and 45 percent PbO. The slight deviation of the experimental data shown in Figure 9 from those of Maier and Hincke may be due to inaccuracies in chemical analysis and to the slight modifications made to the method in this investigation. The

## TABLE II

## VAPOR PRESSURES OF MIXTURES OF $PbO-Sb_2O_3$ AS MEASURED IN THIS STUDY

| PbO (percent) | Vapor Pressure (at 540°C., mm. Hg.) |
|---|---|
| 0 | 0.342 |
| 22.2 | 0.350 |
| 31.8 | 0.318 |
| 41.9 | 0.296 |
| 46.6 | 0.111 |
| 52.1 | 0.053 |
| 57.7 | 0.000 |

# TABLE III

## PbO-$Sb_2O_3$

## VAPOR PRESSURE AT VARIOUS FLOW RATES

| Sample | PbO (percent) | Flow Rate (cc/min.) | Vapor Pressure (mm.. Hg at 539°C) |
|---|---|---|---|
| $Sb_2O_3$ | 0 | 72.1 | 0.175 |
| | 0 | 59.1 | 0.202 |
| | 0 | 40.4 | 0.245 |
| | 0 | 37.3 | 0.258 |
| No. 2 | 22.2 | 47.0 | .231 |
| | | 33.3 | .255 |
| | | 27.2 | .288 |
| No. 3 | 31.8 | 33.3 | .226 |
| | | 37.5 | .218 |
| | | 46.6 | .182 |
| | | 59.1 | .157 |
| No. 4 | 41.9 | 36.4 | 0.085 |
| | | 34.8 | 0.101 |
| | | 26.3 | 0.146 |
| | | 22.0 | 0.169 |
| No. 5 | 46.6 | 49.1 | 0.046 |
| | | 48.1 | 0.049 |
| | | 38.9 | 0.062 |
| | | 24.4 | 0.095 |

### TABLE III (continued)

| | | | |
|---|---|---|---|
| No. 6 | 52.1 | 39.2 | 0.016 |
| | | 36.6 | 0.016 |
| | | 26.6 | 0.025 |
| | | 26.3 | 0.030 |
| No. 12 | 57.7 | 24.0 | 0.00 |
| | | 29.1 | 0.00 |

## TABLE IV

## VAPOR PRESSURE OF PURE $Sb_2O_3$ AT VARIOUS TEMPERATURES*

| Temperature (°C) | Vapor Pressure (mm. Hg) |
|---|---|
| 450 | 0.0075 |
| 469 | 0.0169 |
| 475 | 0.0224 |
| 483 | 0.0319 |
| 495 | 0.0528 |
| 500 | 0.0625 |
| 507 | 0.0802 |
| 525 | 0.1645 |
| 543 | 0.319 |
| 550 | 0.406 |
| 557 | 0.525 |
| 566 | 0.703 |

*From W. B. Hincke, "The Vapor Pressure of Antimony Trioxide", J. Amer. Chem. Soc., 52, 3869, (1930)

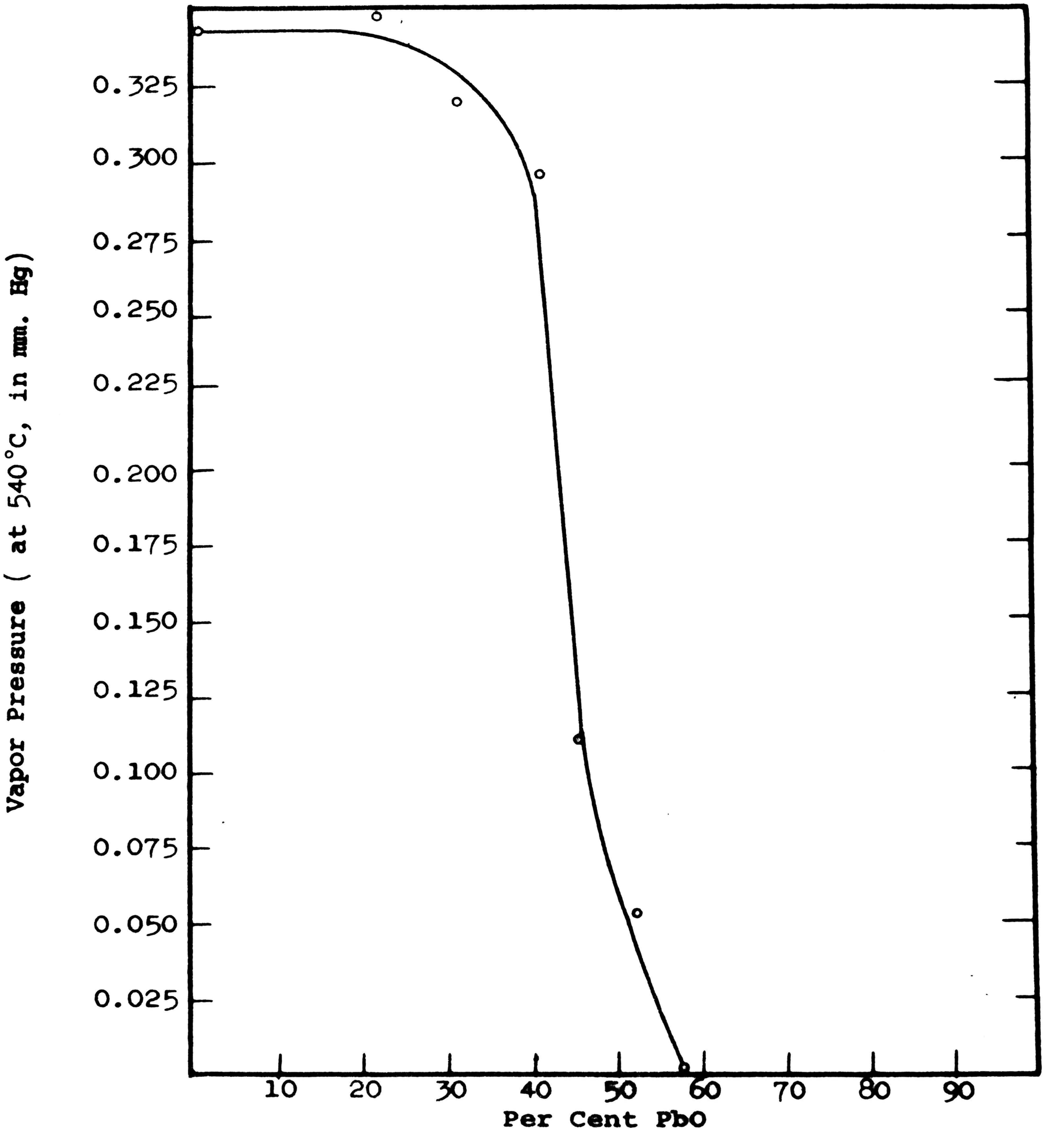


Figure 9. Vapor pressure of $PbO - Sb_2O_3$ Mixtures as measured in this study.

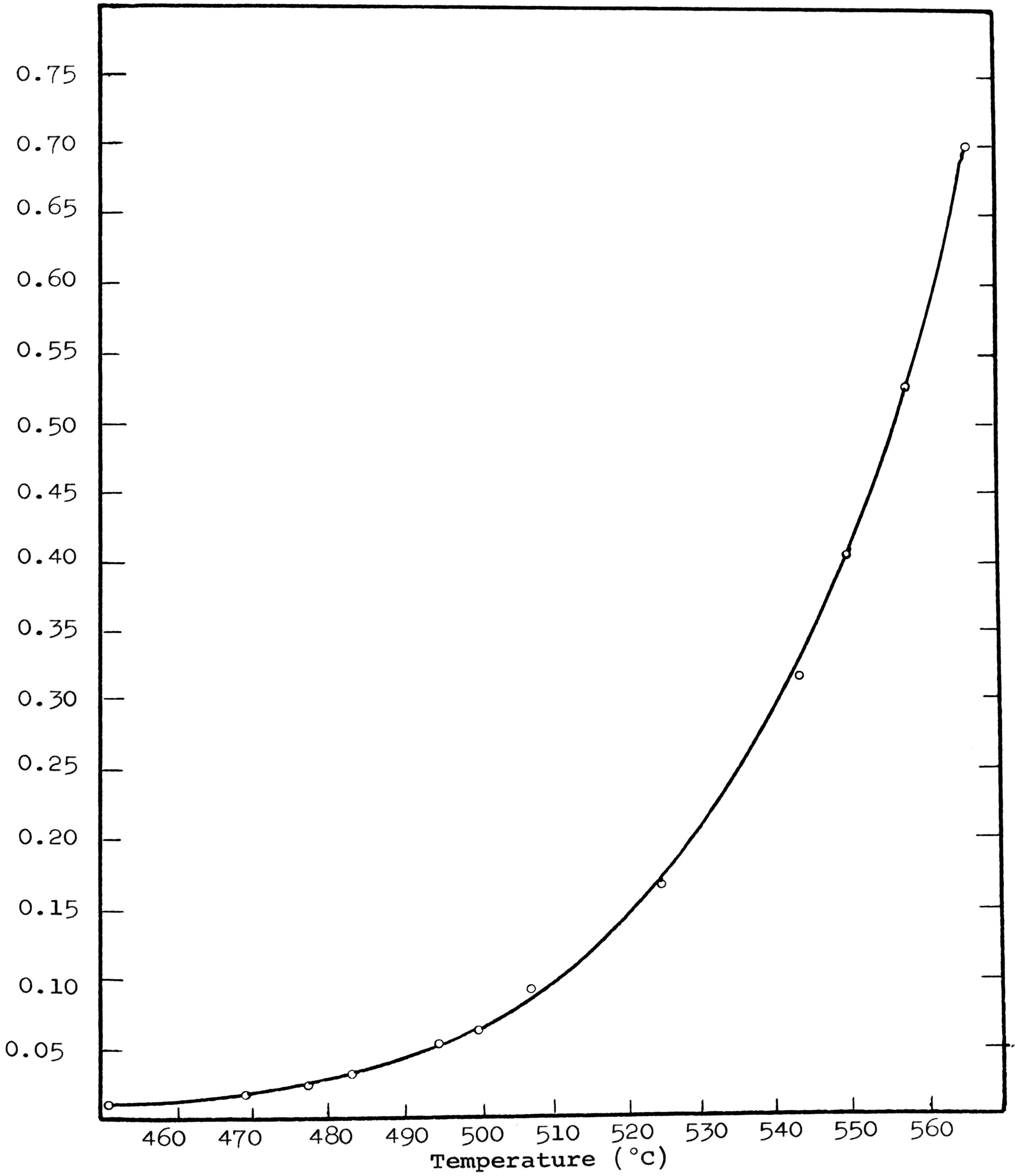


Figure 10. Vapor pressure of pure $Sb_2O_3$ as a function of temperature.

agreement of these two investigations confirms the work of Maier and Hincke and also establishes the validity of this method and the equipment which was used.

The reasons for the sharp change in the vapor pressures of the PbO-$Sb_2O_3$ mixtures can best be explained in a manner analogous to the explanation of Maier and Hincke(3). There is a compound formed between the PbO and the $Sb_2O_3$ which has the form PbO.$Sb_2O_3$. This compound has a composition of 43.4 percent PbO. For mixtures of PbO-$Sb_2O_3$ containing less than 40 percent PbO, the $Sb_2O_3$ exists as a primary phase surrounded by the PbO.$Sb_2O_3$ compound as the second phase. Therefore, the $Sb_2O_3$ is free to volatilize as readily as if it existed as pure $Sb_2O_3$ with no PbO present. As the PbO-$Sb_2O_3$ mixtures approach the composition of the PbO.$Sb_2O_3$ compound, 43.4 percent, the $Sb_2O_3$ becomes tied up in a nonvolatile phase. Therefore, the vapor pressures of the mixtures are greatly decreased due to the decreased amount of $Sb_2O_3$ that is free to volatilize.

The volatility of these samples was measured directly by heating them in a vacuum to compare this method with the method of measuring the vapor pressures. The samples were heated for exactly one hour under a vacuum of 40 to 50 microns of mercury. Most of the samples were heated to 540°C although the volatility of a few was measured at 510°C and at 480°C to determine if there was any significant temperature effect. The results of these volatility measurements are shown in Figure 11 and in Table V.

# TABLE V

## VOLATILITY OF MIXTURES OF $PbO-Sb_2O_3$ MEASURED UNDER VACUUM

| PbO (percent) | Temperature (°C) | Weight Loss (grams) |
|---|---|---|
| 0 | 540 | 2.7874 |
| 9.15 | 540 | 2.6852 |
| 20.0 | 540 | 1.1285 |
| 30.8 | 540 | 0.7689 |
| 40.0 | 540 | 0.6130 |
| 46.8 | 540 | 0.1219 |
| 57.7 | 540 | 0.0484 |
| 0 | 510 | 1.2584 |
| 10.3 | 510 | 0.9619 |
| 20.0 | 510 | 0.5852 |
| 33.4 | 510 | 0.3507 |
| 43.5 | 510 | 0.0280 |
| 0 | 480 | 0.5932 |
| 9.15 | 480 | 0.4644 |
| 20.0 | 480 | 0.2542 |
| 30.8 | 480 | 0.0915 |
| 37.0 | 480 | 0.0749 |

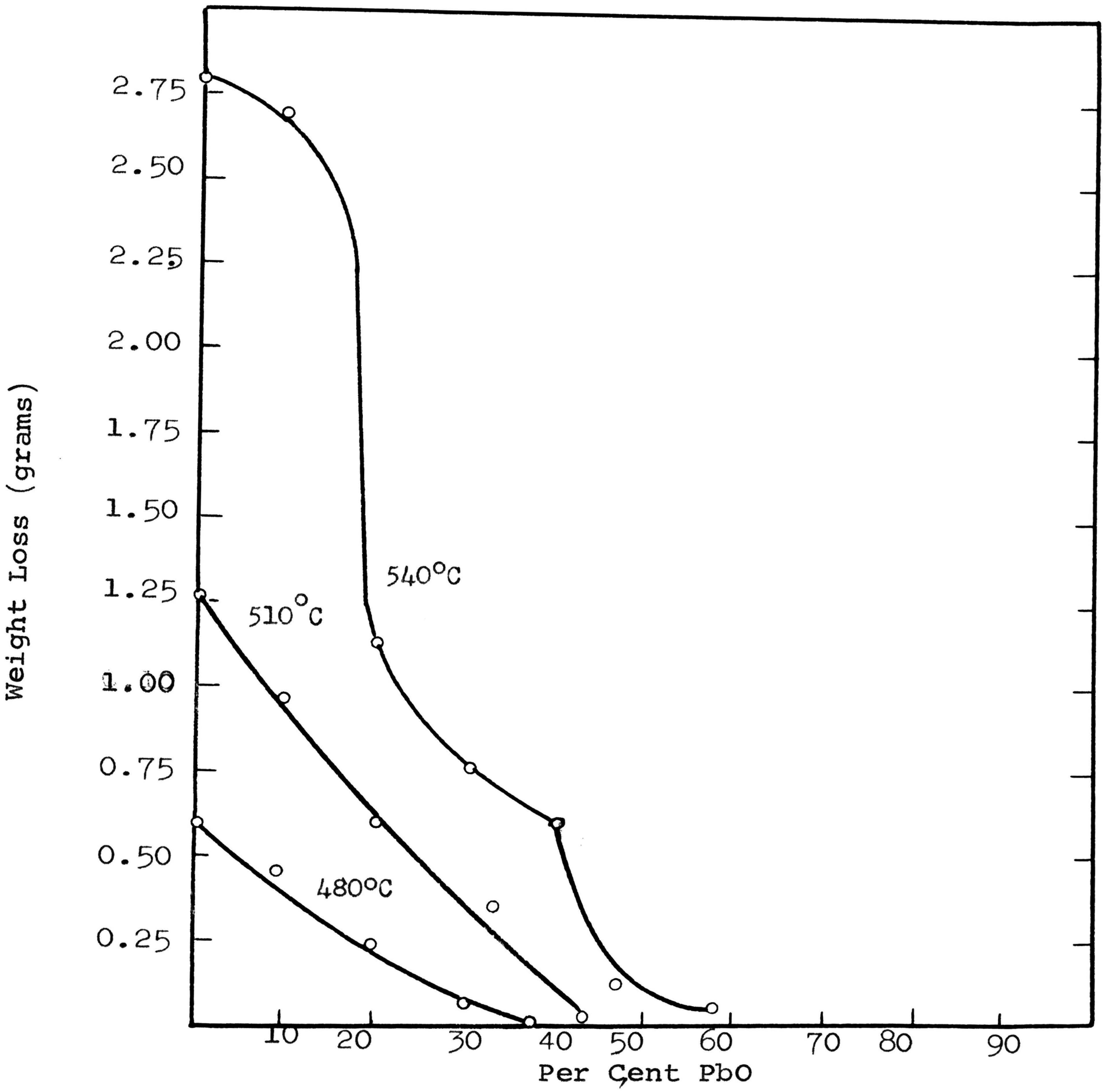


Figure 11. Volatility of mixtures of PbO - $Sb_2O_3$ measured under vacuum.

If the Langmuir equation is correct and if it is applicable to these conditions, the volatility should be directly proportional to the vapor pressure of the substance. If this is the case, the curve for the weight loss versus composition, Figure 11 should be of the same form as the curve for vapor pressure versus composition, Figure 9. A comparison of Figures 9 and 11 shows that this is not true. The vapor pressure versus composition shows a very sharp decrease between 40 and 45 percent PbO but the weight loss under vacuum versus composition shows a sharp decrease at about 15 to 20 percent PbO.

This lack of agreement may be due to the volatility under vacuum being measured under non equilibrium conditions. Therefore, the volatility will not be directly proportional to the vapor pressure but will be somewhat lower depending on how near the conditions were the vapor pressure because the vapor pressure is measured to equilibrium.

Although the method used to measure the vapor pressures was a dynamic method and therefore the vapor pressure was not measured under exactly equilibrium conditions as would be true for a static method of vapor pressure measurement, the vapor pressure measurements were made under more nearly equilibrium conditions than were the volatility measurements.

The error in the volatility measurements is most likely due to the effect of diffusion of the volatile $Sb_2O_3$ through the sample during heating under a vacuum. When the run is started, the first

$Sb_2O_3$ to be removed is from the top surface of the sample in the crucible. As the run continues, the upper surface of the sample is depleted of $Sb_2O_3$ due to its removal by volatilization. This in effect increases the percentage of PbO in the surface layer from which the material is volatilized. As the run continues, it is necessary for the $Sb_2O_3$ to diffuse through the solid sample of $Sb_2O_3$ - PbO from below the surface layer. This in effect will greatly decrease the rate of volatilization due to the slow rate of diffusion of the $Sb_2O_3$ through the sample. Hence, the measured rate of volatility is no longer the maximum rate of evaporation as predicted by the Langmuir equation, but some rate less than this maximum due to the diffusion effect. Therefore, the weight of material volatilized per square centimeter per second is not proportional to the vapor pressure but is considerably less than this.

In the method used for measuring the vapor pressures, the amount of material removed during the run is considerably less than the total weight of the sample but in the volatility measurements, the weight loss is maybe as much as half of the total weight to the sample. Therefore, there is less chance for the surface of the sample to be significantly depleted in $Sb_2O_3$ in the vapor pressure measurements than there is in the volatility measurements. Since the rate of flow of inert gas over the sample in the vapor pressure measurements is very low, the conditions are nearly those of equilibrium and therefore the vapor pressure measurements are less dependent on the rate of evaporation than the volatility measurements. Also the rate of removal of $Sb_2O_3$ is slow enough in the vapor pressure measurements that if diffusion of the argon through the sample in any way affected the vapor pressure, the rate of gas flow was nearly the same as the rate of diffusion and hence canceled out any diffusion effects. This was far from true in the case of the volatility measurements where the rate of volatilization was much greater than the rate of diffusion in which case the rate of diffusion would greatly affect the measured volatility. For these reasons the vapor pressure measurements are considered to be more accurate and indicate better the mechanism of volatilization than are the measurements made under vacuum. This is true even though the measurements of weight loss under vacuum are simpler and quicker and eliminate the extrapolation necessary with the dynamic method of vapor pressure measurement.

X-ray diffraction patterns were made of several of the samples before their vapor pressures were measured and of the condensate collected in the condensing tube after the run. These x-ray patterns showed the presence of PbO and $Sb_2O_3$ in all the initial samples. The amount of $Sb_2O_3$ decreased as the composition changed to more than 40 percent PbO which indicates that the $Sb_2O_3$ is no longer present as crystals of the pure phase. The compound $PbO.Sb_2O_3$ has not been indexed by x-ray diffraction techniques and so could not be confirmed due to the lack of data available for x-ray analysis. The condensate from all samples was also examined by use of x-ray diffraction and found to contain only $Sb_2O_3$. No evidence of PbO was found in the condensate which indicates conclusively that the vapor pressure of these samples was due only to the volatility of the $Sb_2O_3$ phase.

An attempt was made to determine if the decrease in volatility as measured under vacuum was just due to the effect of dilution of the sample by the PbO present. To determine this, a plot was made of the activity of the $Sb_2O_3$ in the PbO-$Sb_2O_3$ mixtures versus the mole fraction of $Sb_2O_3$. According to Raoult's law for ideal solutions, a plot of activity versus mole fraction will be a straight line for an ideal solution(17). This means that the only effect of a mixture of two substances which form an ideal solution is due to dilution of the solvent by the solute, in which case the activity of the solute is directly proportional to the mole fraction of the solvent.

To plot this curve from the volatility data obtained, the activity of pure $Sb_2O_3$ was taken as equal to 1.0. The activity of the PbO - $Sb_2O_3$ mixtures was calculated by dividing the weight loss for the samples by the weight loss of pure $Sb_2O_3$, all measurements being made at 540°C. The mole fraction was calculated in the usual manner:

$$N = \frac{\dfrac{\text{weight percent } Sb_2O_3}{\text{molecular weight } Sb_2O_3}}{\dfrac{\text{wt. \% } Sb_2O_3}{\text{mol. wt. } Sb_2O_3} + \dfrac{\text{wt. \% PbO}}{\text{mol. wt. PbO}}}$$

These results are shown in Figure 12 and in Table VI. As can be seen from this figure, the effect of the PbO on the $Sb_2O_3$ sample is not just due to dilutions. There is definite evidence of other heat

## TABLE VI

## ACTIVITY OF $Sb_2O_3$ IN $PbO-Sb_2O_3$ MIXTURES AS CALCULATED FROM VOLATILITY DATA

| Mole Fraction $Sb_2O_3$ | Activity of $Sb_2O_3$ |
|---|---|
| 1.00 | 1.00 |
| .877 | 0.963 |
| .754 | 0.404 |
| .633 | 0.261 |
| .526 | 0.179 |
| .465 | 0.044 |
| .359 | 0.017 |

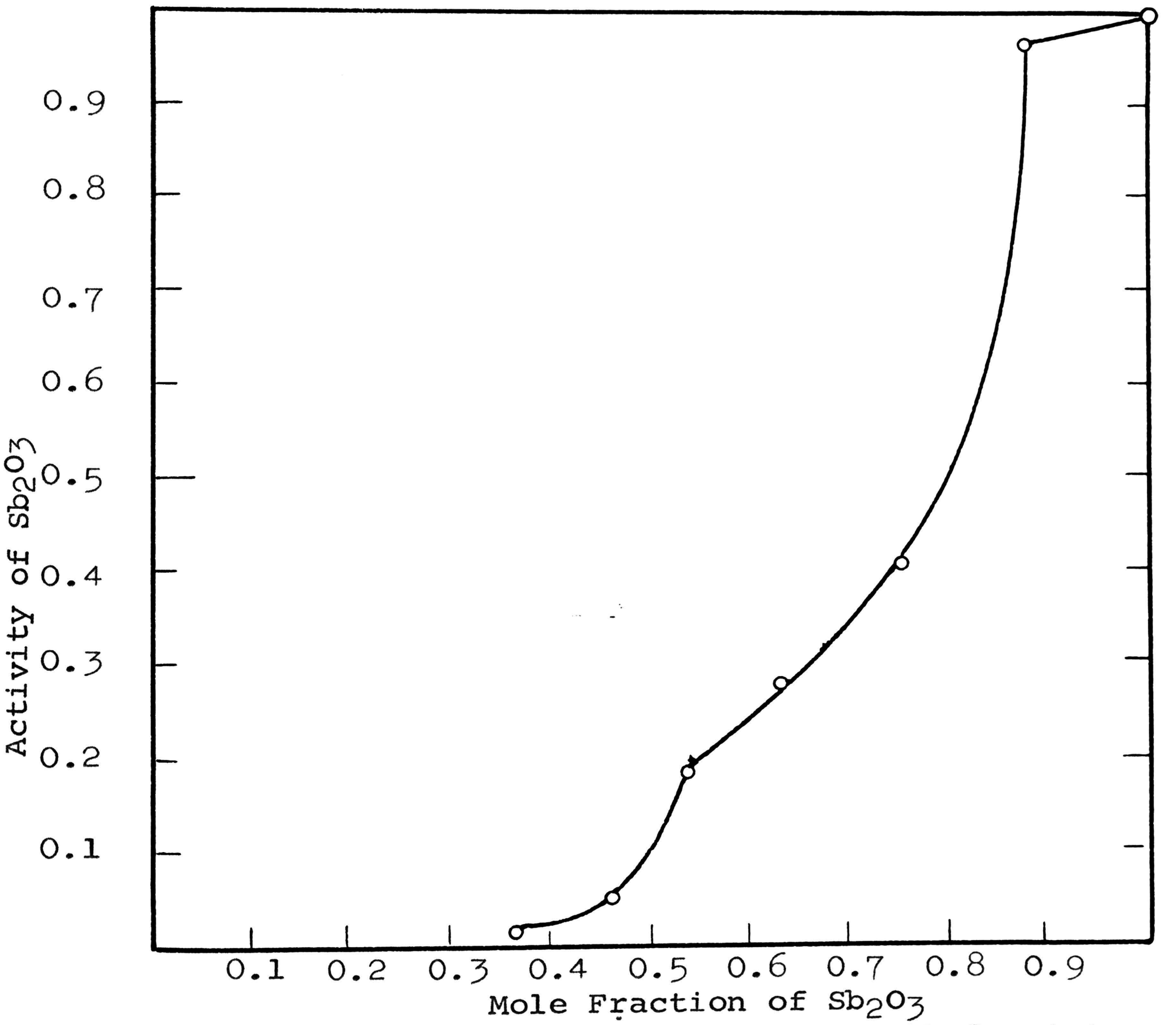


Figure 12. Activity of $Sb_2O_3$ in PbO - $Sb_2O_3$ mixtures as calculated from volatility data

effects than the heat of dilution. This is shown by the extreme deviation of the empirical curve for the PbO-$Sb_2O_3$ mixtures from the theoretical curve for ideal solutions.

This deviation from an ideal solution as indicated by the activity versus mole fraction curve, can best be explained as due to the formation of compounds between the PbO and the $Sb_2O_3$. This would contribute other heat effects which would prevent the activity from being directly proportional to the mole fractions.

The activity of $Sb_2O_3$ in the PbO-$Sb_2O_3$ mixtures was also calculated from the vapor pressures of these mixtures as shown in Figure 13 and in Table VII. This curve also deviates from the curve of Raoult's law for ideal solutions but has a different shape than the activity curve calculated from the volatility data, Figure 12.

# TABLE VII

## ACTIVITY OF $Sb_2O_3$ IN $PbO-Sb_2O_3$ MIXTURES AS CALCULATED FROM VAPOR PRESSURE DATA

| Mole Fraction $Sb_2O_3$ | Activity of $Sb_2O_3$ |
|---|---|
| 1.00 | 1.00 |
| .728 | 1.00 |
| .620 | 0.928 |
| .515 | 0.865 |
| .467 | 0.324 |
| .412 | 0.016 |
| .359 | 0.000 |

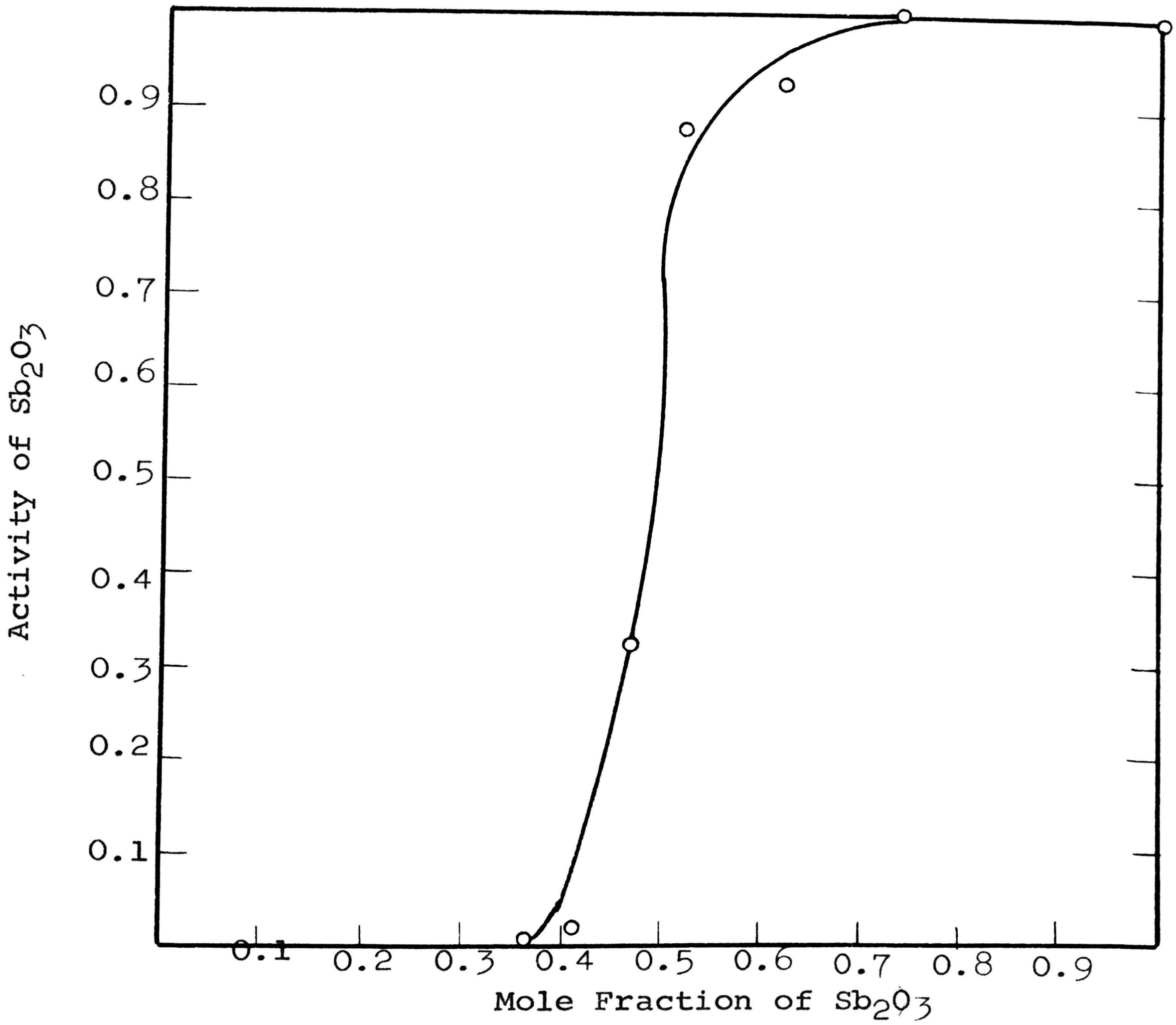


Figure 13. Activity of $Sb_2O_3$ in Pbo - $Sb_2O_3$ mixtures as calculated from vapor pressure data.

## $PbO - Sb_2O_3 - SiO_2$ Data

Samples were made up containing small amounts of $SiO_2$ in an attempt to tie up the PbO and make the $Sb_2O_3$ easier to remove from the mixtures. From the phase diagram for $PbO - SiO_2$, it was determined how much $SiO_2$ was necessary to tie up the PbO as $2PbO.SiO_2$(7). The vapor pressures of these samples were measured and the results are shown in Figures 14 and 15 and in Table VIII. The data from which these vapor pressures were calculated are shown in Table IX.

From Figures 14 and 15 it is seen that the addition of $SiO_2$ to the $PbO - Sb_2O_3$ mixtures has little effect on the shape or position of the vapor pressure versus composition curve. The samples containing $SiO_2$ do not seem to be significantly displaced from the vapor pressure of the samples containing no $SiO_2$. If anything, a slight lowering of the vapor pressure is noticed for the samples containing less than 50 percent PbO, but this is not generally enough to give any conclusive evidence of a significant lowering of the vapor pressures due to the addition of $SiO_2$. The samples containing 8 percent $SiO_2$ have slightly lower vapor pressures than those having 4 percent $SiO_2$. This indicates that possibly the $Sb_2O_3$ is tied up as a compound between $Sb_2O_3$ and $SiO_2$ instead of between PbO and $SiO_2$. The evidence of a compound between $Sb_2O_3$ and $SiO_2$ will be discussed later. The addition of $SiO_2$ definitely did not displace the rapid decrease in the vapor pressure versus composition curve as had been expected.

## TABLE VIII

## VAPOR PRESSURES OF MIXTURES OF $PbO-Sb_2O_3-SiO_2$

| PbO (percent) | $SiO_2$ (percent) | Vapor Pressure (at 540°C., mm. Hg) |
|---|---|---|
| 40.0 | 4.0 | 0.240 |
| 45.0 | 4.0 | 0.208 |
| 50.0 | 4.0 | 0.200 |
| 55.0 | 4.0 | 0.055 |
| 60.0 | 4.0 | 0.025 |
| 40.0 | 8.0 | 0.315 |
| 45.0 | 8.0 | 0.150 |
| 50.0 | 8.0 | 0.150 |
| 55.0 | 8.0 | 0.055 |
| 60.0 | 8.0 | 0.025 |

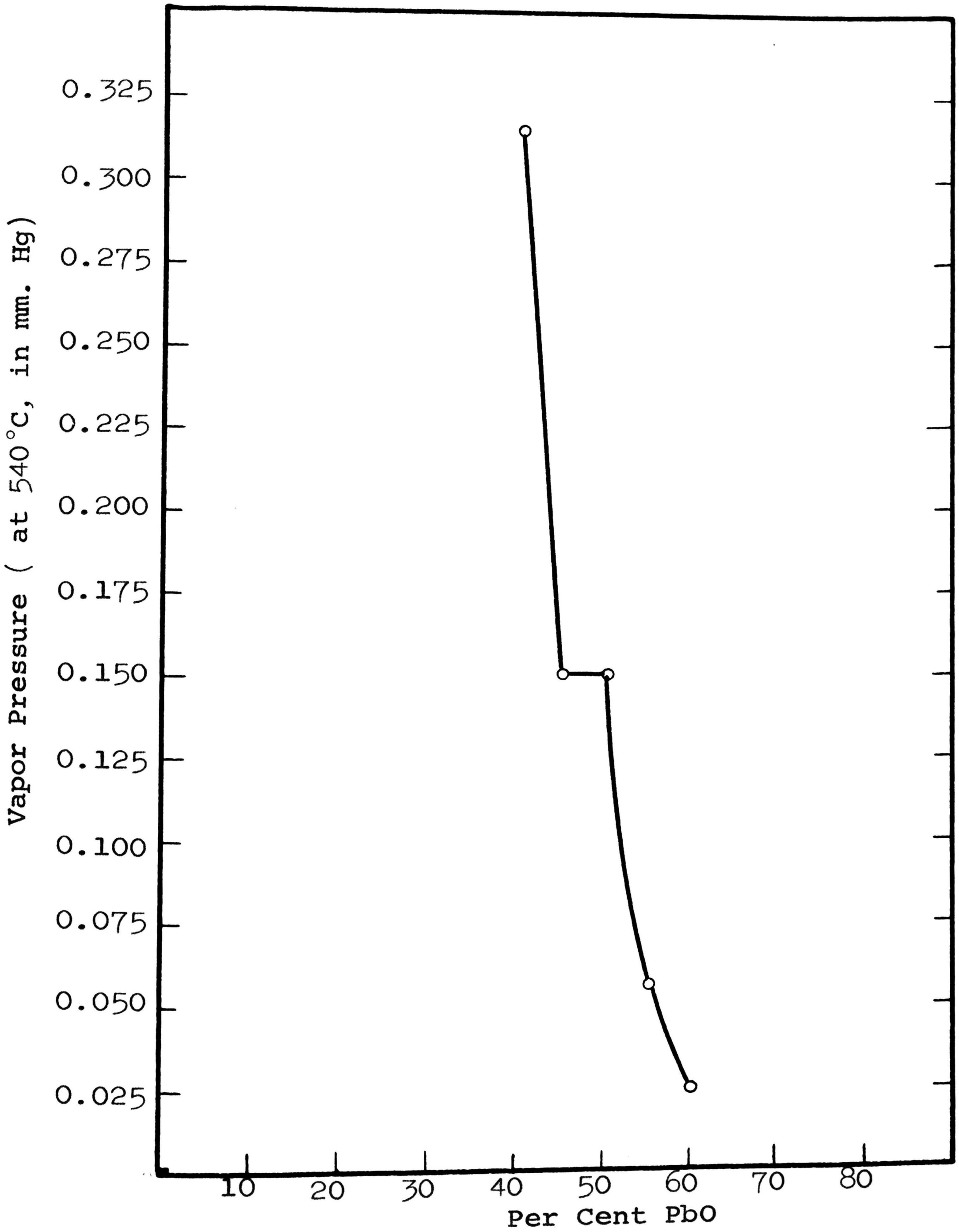


Figure 14. Vapor pressures of mixtures of $PbO - Sb_2O_3$ with addition of 4 per cent $SiO_2$

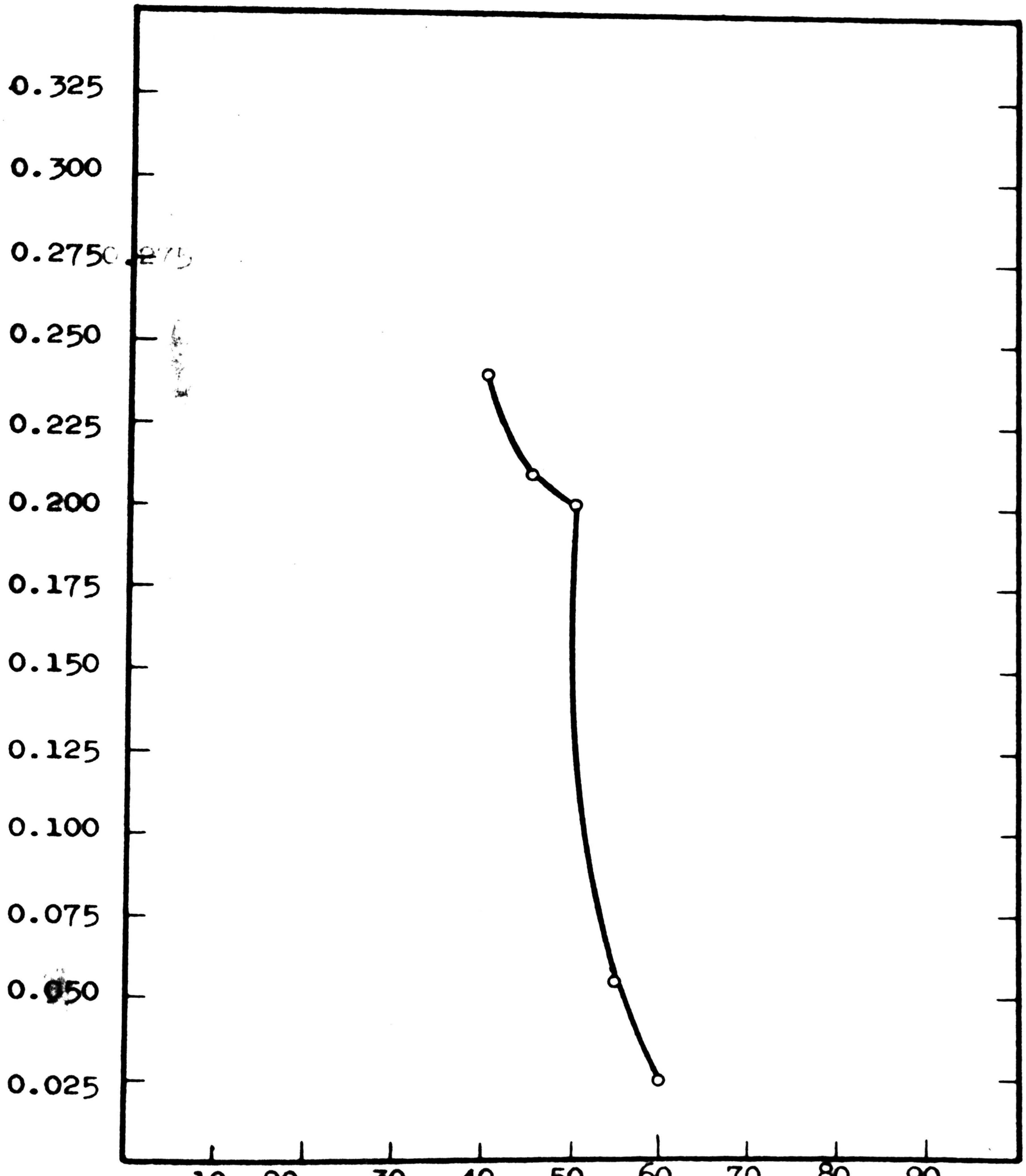


Figure 15. Vapor pressures of mixtures of PbO - $Sb_2O_3$ with addition of 8 per cent $SiO_2$

## TABLE IX

### VAPOR PRESSURES AT VARIOUS FLOW RATES
### $PbO-Sb_2O_3-SiO_2$ MIXTURES MEASURED AT 540°C

| Sample | PbO (percent) | $SiO_2$ (percent) | Flow rate cc / min. | Vapor Pressure (mm. Hg) |
|---|---|---|---|---|
| 36 | 40.0 | 4.0 | 31.6 | 0.159 |
| | | | 25.8 | 0.169 |
| | | | 21.2 | 0.184 |
| 37 | 40.0 | 8.0 | 28.7 | 0.189 |
| | | | 24.8 | 0.187 |
| | | | 18.7 | 0.233 |
| 38 | 45.0 | 4.0 | 31.0 | 0.109 |
| | | | 24.5 | 0.131 |
| | | | 22.9 | 0.136 |
| 39 | 45.0 | 8.0 | 28.9 | 0.145 |
| | | | 26.2 | 0.149 |
| | | | 22.9 | 0.136 |
| 40 | 50.0 | 4.0 | 29.0 | 0.061 |
| | | | 27.7 | 0.067 |
| | | | 24.7 | 0.090 |
| 41 | 50.0 | 8.0 | 29.5 | 0.102 |
| | | | 26.3 | 0.098 |
| | | | 19.9 | 0.116 |
| 42 | 55.0 | 4.0 | 29.4 | 0.062 |
| | | | 26.1 | 0.047 |
| | | | 22.2 | 0.056 |
| | | | 18.0 | 0.049 |

## TABLE IX (continued)

| Sample | PbO (percent) | $SiO_2$ (percent) | Flow rate cc /mm. | Vapor Pressure (mm. Hg) |
|---|---|---|---|---|
| 43 | 55.0 | 8.0 | 34.1 | 0.056 |
| | | | 30.3 | 0.057 |
| | | | 26.7 | 0.055 |
| | | | 23.7 | 0.052 |
| 44 | 60.0 | 4.0 | 26.7 | 0.021 |
| | | | 26.5 | 0.018 |
| 45 | 60.0 | 8.0 | 25.9 | 0.037 |
| | | | 20.3 | 0.026 |

Only a few of these samples were heated under a vacuum to measure the volatility. These data are not sufficient to draw any valid conclusions in comparison with the vapor pressure measurements.

The data for the PbO-$Sb_2O_3$-$SiO_2$ mixtures were according to Raoult's law of activity versus mole fraction as shown in Figure 16 and in Table X. Since there was definite evidence of compounds existing in these mixtures, these data do not obey Raoult's law.

### PbO - $Sb_2O_3$ - CaO Data

After the failure of the $SiO_2$ to form a compound with the PbO and tie up the PbO, an attempt was made to make samples containing CaO. It was thought that possibly the CaO which is a basic compound, might be more favorable for tying up the PbO in a compound than the highly acidic $SiO_2$. Unfortunately, the CaO did not go into solution with the PbO and the $Sb_2O_3$ even at 1000°C. Since a homogeneous mixture could not be produced, no vapor pressure masurements were made.

### $Sb_2O_3$ - $SiO_2$ Data

The decreased vapor pressure of some of the PbO-$Sb_2O_3$ samples after the addition of $SiO_2$ indicated the possibility of a compound formed between $Sb_2O_3$ and $SiO_2$. A check of the literature revealed that no compound of this nature had been reported. Therefore, an attempt was made to determine if such a compound does exist. Several samples of $Sb_2O_3$ - $SiO_2$ were made up containing from 0.5 to about 12 percent $SiO_2$. The volatility of these samples was measured as

## TABLE X

## ACTIVITY OF $Sb_2O_3$ IN MIXTURES OF $PbO$-$Sb_2O_3$-$SiO_2$

| $SiO_2$ (percent) | Mole Fraction $Sb_2O_3$ | Activity of $Sb_2O_3$ |
|---|---|---|
| 4.0 | 0.438 | 0.702 |
| 4.0 | 0.394 | 0.608 |
| 4.0 | 0.352 | 0.585 |
| 4.0 | 0.308 | 0.161 |
| 4.0 | 0.268 | 0.077 |
| 8.0 | 0.363 | 0.921 |
| 8.0 | 0.325 | 0.439 |
| 8.0 | 0.287 | 0.439 |
| 8.0 | 0.250 | 0.161 |
| 8.0 | 0.215 | 0.077 |

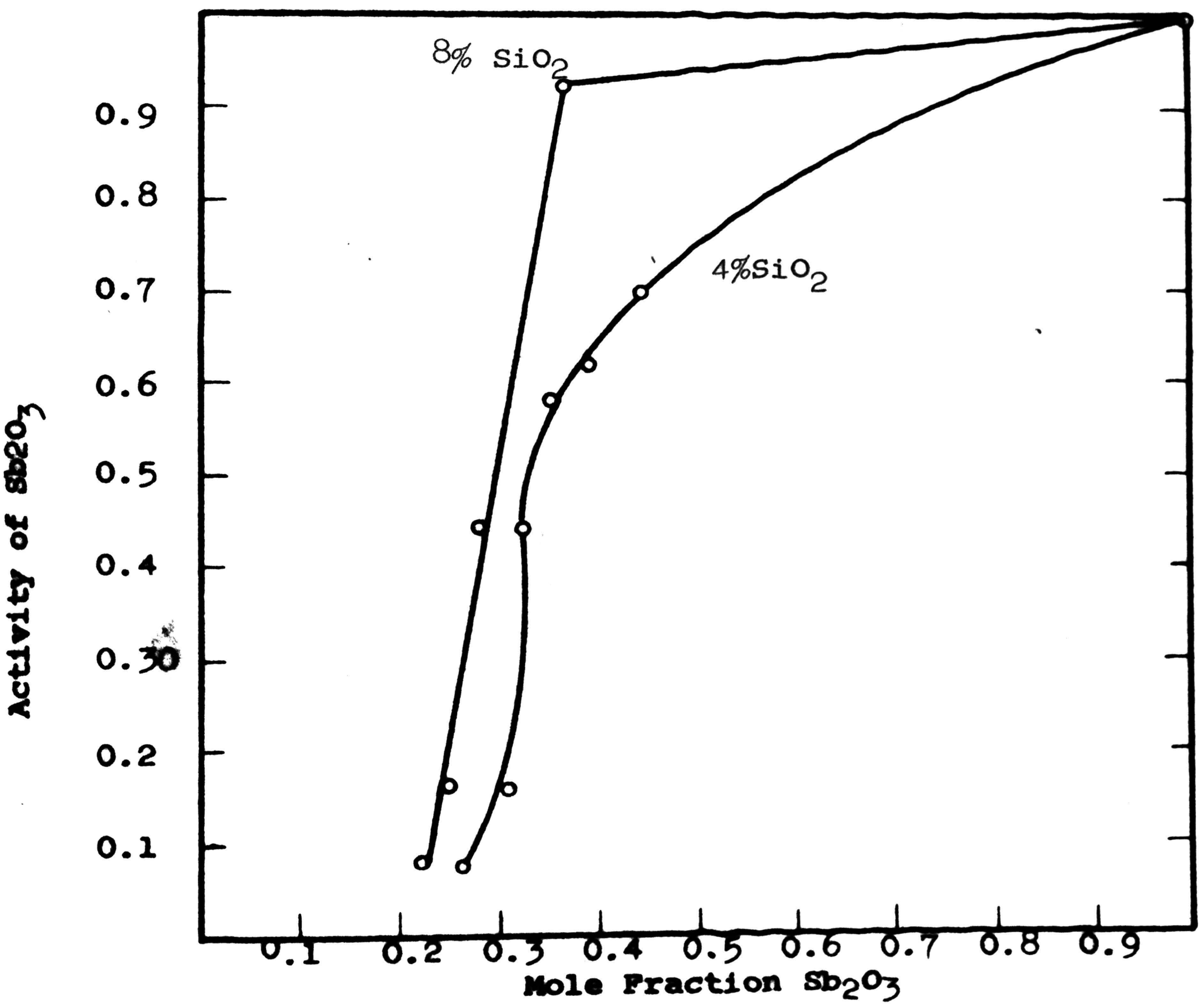


Figure 16. Activity of $Sb_2O_3$ in mixtures of $PbO - Sb_2O_3 - SiO_2$.

shown in Figure 17 and in Table XI and from these data the activity of the $Sb_2O_3$ in these mixtures was determined as shown in Figure 18 and in Table XII.

A short x-ray diffraction study was made of these samples in an attempt to detect the presence of a compound formed between $Sb_2O_3$ and $SiO_2$. This was done by determining the position and intensity of the major lines on the diffraction pattern for each sample. These lines did not correspond to the lines given in the ASTM index(10) for either $Sb_2O_3$ or for $SiO_2$. A comparison of the interplaner spacing, d values, of the various forms of $Sb_2O_3$ and $SiO_2$ and the $Sb_2O_3$ - $SiO_2$ fused mixtures is shown in Table XIII. This shows that there definitely is a new compound formed between the $Sb_2O_3$ and the $SiO_2$ because of the new lines which appear in the x-ray pattern of the fused mixture. The change in the position and intensity of the lines on the x-ray diffraction patterns is shown for the various sample of $Sb_2O_3$ and $SiO_2$ in Table XI. This indicates that possibly two compounds exist due to the change in the relative intensity of the lines as the composition of the samples changes from 0.5 to 12 percent. The possible compounds are: 2 $PbO.SiO_2$ and 3 $PbO.SiO_2$. No further work was done on the identification of these compounds but there is sufficient evidence for the existance of these compounds that at least some preliminary work on the $Sb_2O_3$ - $SiO_2$ system is warranted. Possibly a part of this system should be investigated by thermal and x-ray analysis techniques.

## TABLE XI

## VOLATILITY OF $Sb_2O_3$-$SiO_2$ MIXTURES MEASURED UNDER VACUUM AT 540°C

| $SiO_2$ (percent) | Weight Loss (grams) |
|---|---|
| 0 | 2.7874 |
| 0.50 | 2.1394 |
| 1.0 | 2.1908 |
| 2.0 | 1.9244 |
| 4.0 | 1.1542 |
| 10.0 | 1.0660 |
| 20.6 | 0.8901 |
| 48.0 | 0.0461 |

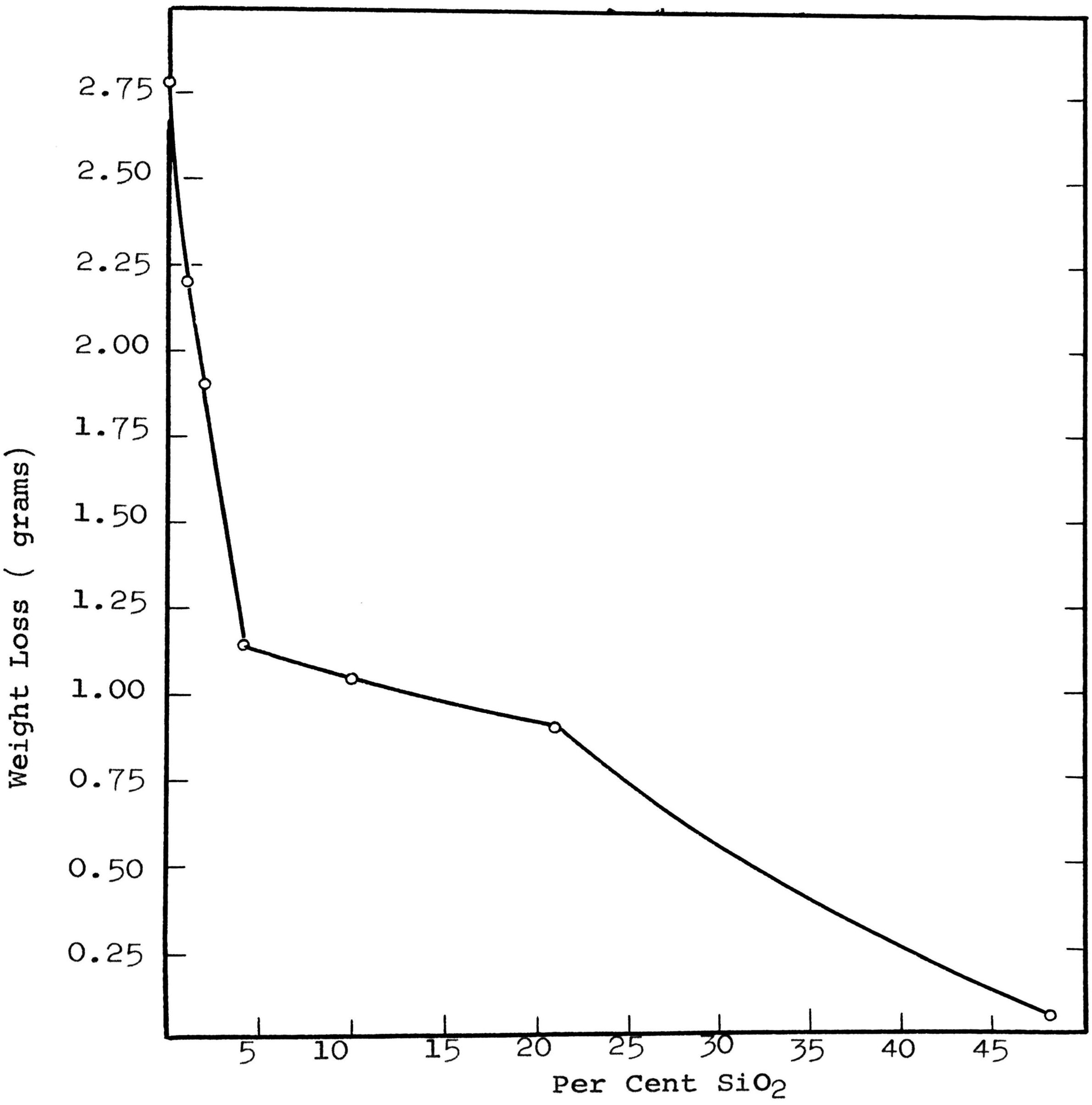


Figure 17. Volatility of $Sb_2O_3$ - $SiO_2$ mixtures measured under vacuum.

## TABLE XII

## ACTIVITY OF $Sb_2O_3$ IN $Sb_2O_3$-$SiO_2$ MIXTURES

| Mole Fraction $Sb_2O_3$ | Activity of $Sb_2O_3$ |
|---|---|
| 1.00 | 1.00 |
| 0.954 | 0.785 |
| 0.912 | 0.425 |
| 0.830 | 0.383 |
| 0.672 | 0.382 |
| 0.500 | 0.319 |
| 0.300 | 0.017 |

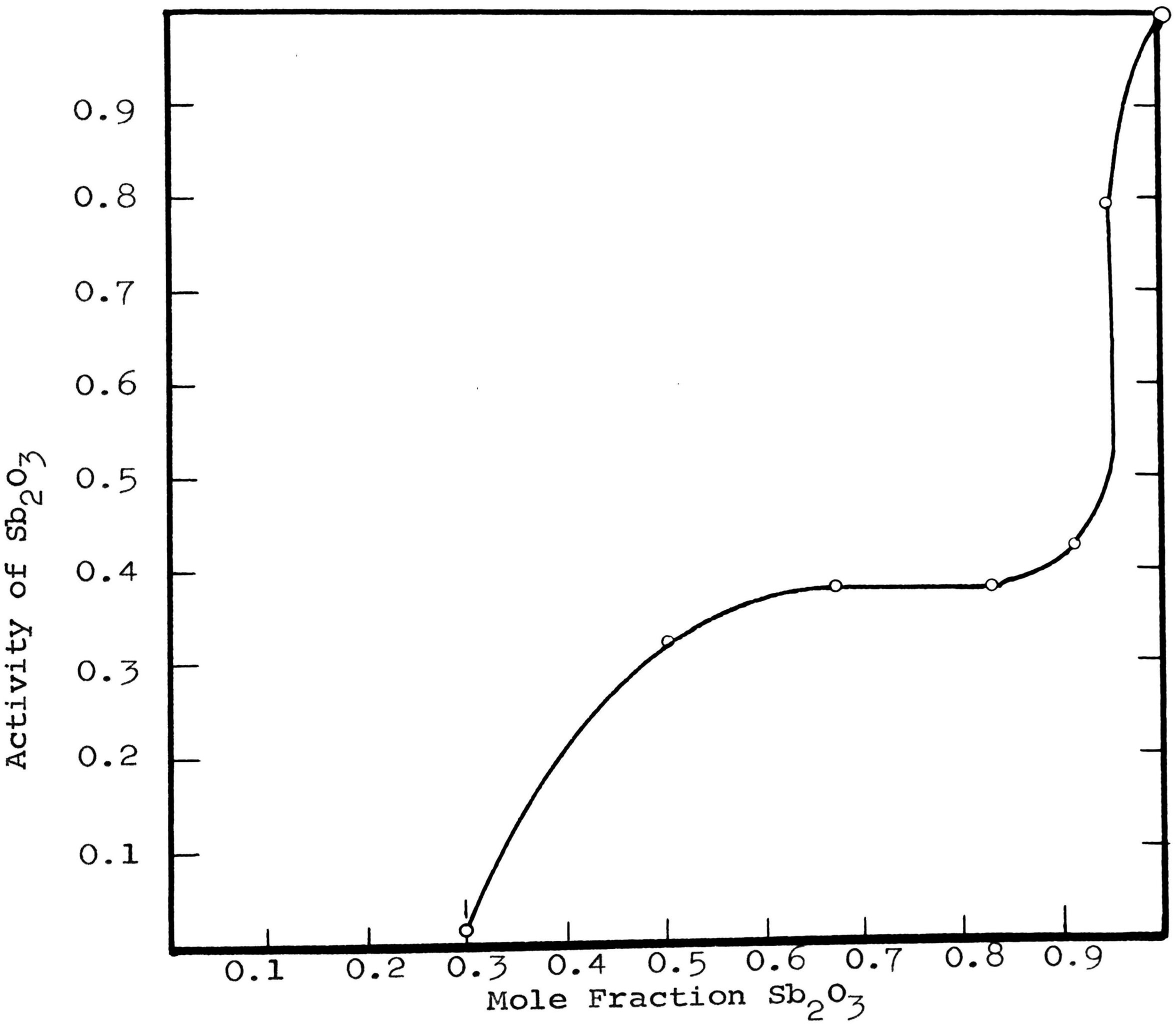


Figure 18. Activity of $Sb_2O_3$ in $Sb_2O_3$ - $SiO_2$ mixtures

## TABLE XIII

## X-RAY DIFFRACTION DATA OF $Sb_2O_3$-$SiO_2$ SAMPLES AND OF CONDENSATE

| A.S.T.M. Card No. 5-0534 $Sb_2O_3$ | | A.S.T.M. Card No. 7-346 $SiO_2$ | | Condensate from Vapor Pressure Run | | Sample 1% $SiO_2$ 99% $Sb_2O_3$ | | Sample 2% $SiO_2$ 98% $Sb_2O_3$ | |
|---|---|---|---|---|---|---|---|---|---|
| d (A) | $I/I_o$ | d (A) | $I/I_o$ | d (A) | $I/I_o$ | d (A) | $I/I_o$ | d (A) | $I/I_o$ |
| 3.21 | 100 | 4.43 | 60 | 3.19 | V.S. | 4.59 | 44 | 4.61 | 20 |
| 2.79 | 40 | 3.42 | 100 | 2.76 | M | 3.15 | 39 | 3.16 | 38 |
| 2.56 | 11 | 2.55 | 60 | 2.53 | V.W. | 3.12 | 42 | 3.14 | 34 |
| 1.97 | 42 | 2.30 | 40 | 1.95 | V.S. | 2.60 | 40 | 2.47 | 22 |
| 1.68 | 35 | 2.22 | 60 | 1.66 | V.S. | 2.36 | 64 | 2.36 | 59 |
| 1.61 | 11 | 2.05 | 60 | 1.60 | W | 2.04 | 52 | 2.04 | 51 |
| 1.28 | 12 | 1.85 | 90 | 1.27 | W | 1.81 | 19 | 1.94 | 20 |
| | | 1.71 | 40 | | | 1.52 | 14 | 1.81 | 16 |
| | | 1.57 | 80 | | | | | 1.52 | 11 |
| | | 1.42 | 80 | | | | | | |
| | | 1.39 | 80 | | | | | | |
| | | 1.29 | 60 | | | | | | |
| | | 1.28 | 60 | | | | | | |
| | | 1.23 | 40 | | | | | | |
| | | 1.20 | 60 | | | | | | |
| | | 1.19 | 40 | | | | | | |

NOTE: Intensity designation for film patterns V.S. Very strong, S - Strong, M - Medium, W- Weak, V.W. - Very Weak.

## TABLE XIII (continued)

| Sample<br>4% $SiO_2$<br>96% $Sb_2O_3$ | | Sample<br>10% $SiO_2$<br>90% $Sb_2O_3$ | |
|---|---|---|---|
| d (A) | $I/I_o$ | d (A) | $I/I_o$ |
| 4.60 | 22 | 2.36 | 81 |
| 3.51 | 17 | 2.04 | 60 |
| 3.15 | 81 | | |
| 3.13 | 58 | | |
| 2.48 | 17 | | |
| 2.36 | 66 | | |
| 2.04 | 44 | | |
| 1.93 | 24 | | |
| 1.81 | 29 | | |
| 1.52 | 12 | | |

The volatility of the $Sb_2O_3$ - $SiO_2$ samples was measured and these results are shown in Figure 17 and in Table XI. These data indicate that the $SiO_2$ definitely does decrease the volatility at the $Sb_2O_3$. The plot of activity of the sample versus mole fraction of $Sb_2O_3$, Figure 18 indicates that the effect of the $SiO_2$ is more than a dilutant which would be the case if the plot of activity versus mole fraction followed Raoult's law. This further indicates the presence of a compound between the $Sb_2O_3$ and the $SiO_2$.

# CHAPTER VII

## CONCLUSIONS AND SUMMARY

This investigation attempted to obtain the necessary data to determine if the direct removal of antimony oxide from lead oxide antimony oxide mixtures under a vacuum is possible.

The inert gas saturation method was used to measure the vapor pressures of mixtures of PbO - $Sb_2O_3$. An abrupt decrease in the vapor pressure of these mixtures was found at about 40 percent PbO. The vapor pressures of the PbO - $Sb_2O_3$ mixtures containing more than 50 percent PbO was nearly zero indicating that the $Sb_2O_3$ could not be removed from these mixtures by volatilization. The abrupt change in the vapor pressure of these mixtures was due to the formation of the compound PbO - $Sb_2O_3$ which ties up the $Sb_2O_3$ in a non volatile phase.

In order to remove antimony from commercial lead slags as $Sb_2O_3$, it is necessary that the vapor pressure of these slags be sufficiently high for mixtures of PbO - $Sb_2O_3$ containing more than 80 percent PbO. Since the vapor pressure of the normal PbO - $Sb_2O_3$ mixtures drops off very abruptly at about 40 percent PbO, it is necessary to attempt to displace the vapor pressure curve to the right so as to increase the vapor pressure of the slags containing a high concentration of PbO. This was attempted by adding $SiO_2$ to the PbO-$Sb_2O_3$ mixtures to form a PbO - $SiO_2$ compound which would effectively tie up the PbO and thereby raise the vapor pressure of the $Sb_2O_3$.

Instead of raising the vapor pressure of the PbO - $Sb_2O_3$ mixtures, the addition of $SiO_2$ caused either no change in the vapor pressure or even a slight lowering of the vapor pressure. This was probably due to the formation of a compound between the $Sb_2O_3$ and the $SiO_2$ either instead of or in addition to the formation of a PbO - $SiO_2$ compound.

It is quite possible that a compound could be formed between PbO and some other substance in such a way that the PbO.$Sb_2O_3$ compound could be broken down and the $Sb_2O_3$ freed to be removed by volatilization. The addition of various other compounds to the PbO-$Sb_2O_3$ should be attempted with this objective in mind.

This investigation has also brought forth the indication of compounds existing between $Sb_2O_3$ and $SiO_2$. It is suggested that this system be at least partially investigated and possibly the $Sb_2O_3$ - $SiO_2$ diagram determined. Although no direct commercial use can be predicted at this time for $Sb_2O_3$ - $SiO_2$ compounds this phase diagram may indicate some unusual properties of these compounds which would make them of value.

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