

ROASTING CONDITIONS for the RECOVERY of CADMIUM
from ZINC SMELTER FLUE DUSTS

By

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Metallurgical Engineering.

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ABSTRACT

Cadmium recovery from flue dusts in zinc smelters usually involves a sulfating roast followed by a water leach. This investigation is concerned with the sulfate - roasting conditions, i.e., temperatures and gas-phase compositions, for optimum separation and recovery of cadmium from zinc smelter flue dusts.

Free-energy data were used to construct stability diagrams for the Cd-S-O, Zn-S-O, and Pb-S-O systems. They were used to show the phases present at normal roasting temperatures and gas-phase compositions.

Roasting experiments performed under conditions that were thermodynamically favorable, demonstrated the validity of the stability diagrams. Then a sample of flue dust obtained from the St. Joseph Lead Company, Zinc Smelting Division, Monaca, Pennsylvania, was roasted under the conditions established from the previous studies. Additional experiments were made to determine the solubilities of zinc and cadmium basic sulfates.

TABLE OF CONTENTS

	Page
Abstract-----	iii
Contents-----	iv
List of Figures-----	vi
List of Tables-----	viii
List of Appendices-----	x
Acknowledgments-----	xii
INTRODUCTION-----	1
PHASE STABILITY CALCULATIONS-----	4
EXPERIMENTAL APPARATUS and PROCEDURE-----	14
Roasting Equipment-----	14
Drying Equipment-----	17
Temperature Control for Roasting Equipment-----	18
Flow Meters-----	20
EXPERIMENTAL RESULTS-----	21
Roasting Experiments-----	21

Table of Contents (Cont'd)

	Page
Cd-S-O System-----	23
Sublimation and Degree of Reaction-----	23
CdSO ₄ .2CdO Studies-----	25
Zn-S-O System-----	26
Pb-S-O System-----	26
Cd-Zn-Pb-S-O System-----	31
Flue Dust-----	31
Qualitative Analysis of the Flue Dust-----	32
Quantitative Analysis of the Flue Dust-----	33
Flue Dust Roast-----	34
Solubility of CdO, CdSO ₄ .2CdO, ZnO, and ZnO.2ZnSO ₄ -----	35
DISCUSSION-----	43
Stability Diagrams-----	43
Sulfation of CdS-----	43
Preparation of CdSO ₄ .2CdO in Evacuated Vycor Capsules-----	45
Cd-Zn-Pb-S-O System-----	46
Cadmium Recovery from Flue Dust-----	46
CONCLUSIONS-----	49
SUMMARY-----	51
APPENDICES-----	52
SELECTED BIBLIOGRAPHY-----	73
VITA-----	74

LIST OF FIGURES

Figure Number	Title	Page
1.	Effect of Temperature and Gas Composition on the Stability of Basic Cadmium Sulfate at 0.2 Atmosphere Pressure-----	9
2.	Effect of Temperature and Gas Composition on the Stability of Basic Cadmium Sulfate at 0.2 Atmosphere Pressure and Low Oxygen Potentials----	10
3.	Effect of Temperature and Gas Composition on the Stability of Basic Zinc Sulfate at 0.2 Atmos- phere Pressure-----	11
4.	Effect of Temperature and Gas Composition on the Stability of Basic Lead Sulfate at 0.2 Atmos- phere Pressure-----	12
5.	Effect of Temperature and Gas Composition on the Stability of Basic Zinc, Cadmium, and Lead Sulfates at 0.2 Atmosphere Pressure-----	13
6.	Roasting Apparatus-----	16
7.	Determination of Drying Time for the Flue Dust-----	19
8.	Experimental Positions on the $\text{CdSO}_4 \cdot 2\text{CdO}$ Stability Diagram for Sublimation and Degree of Reaction Tests-----	24
9.	Separation of Compounds in the Flue Dust for Qualitative Chemical Analysis-----	33

List of Figures (Cont'd)

Figure Number	Title	Page
10.	Roasting Operation Run #1-----	36
11.	Roasting Operation Run #2-----	37
12.	Roasting Operation Run #3-----	38
13.	$\text{CdSO}_4 \cdot 2\text{CdO}$ Solubility vs. pH in H_2SO_4 Solution-----	39
14.	CdO Solubility vs. pH in H_2SO_4 Solution-----	40
15.	$\text{ZnO} \cdot 2\text{ZnSO}_4$ Solubility vs. pH in H_2SO_4 Solution-----	41
16.	ZnO Solubility vs. pH in H_2SO_4 Solution-----	42

LIST OF TABLES

Table Number	Title	Page
1.	Efficiency of One-and Two-Furnace Operation-----	14
2.	Determination of Drying Temperature for the Flue Dust-----	18
3.	Equilibrium Partial Pressures and Total Pressure During Roasting-----	21
4.	Summary of the Experimental Conditions Set for the Roasting Tests-----	22
5.	Sublimation and Percent Conversion to CdSO_4 -----	27
6.	Phases Present for the Conversion of CdS to CdSO_4 ---	28
7.	Results of Basic Cadmium Sulfate Preparation-----	29
8.	"d" Spacing and Relative Intensities of the Low and High Temperature Form of $\text{CdSO}_4 \cdot 2\text{CdO}$ -----	30
9.	Composition of Mechanical Mixture Containing PbO , ZnO , and CdO -----	31
10.	Qualitative Analyses of Metals in the Flue Dust-----	32
11.	Qualitative Analyses of Compounds in the Flue Dust-----	33
12.	Quantitative Analyses of the Flue Dust for Zinc and Cadmium-----	34

List of Tables (Cont'd)

Table Number	Title	Page
13.	Change in Cadmium Distribution Due to Varying Roasting Conditions-----	47
14.	Change in Zinc Distribution Due to Varying Roasting Conditions-----	48

LIST OF APPENDICES

Number	Title	Page
I.	Summary of Free-Energy Equations Used for the Stability Diagrams-----	52
II.	Calculation of the Gas Composition Needed to Convert CdSO_4 to $\text{CdSO}_4 \cdot 2\text{CdO}$ -----	53
III.	Calculation of P_T for Determining the Shift in the $\text{CdSO}_4 \cdot 2\text{CdO}$ Stability Diagram-----	58
IV.	Variation of P_T with T at Constant % O_2 for the $\text{ZnO} \cdot 2\text{ZnSO}_4$ Stability Diagram-----	62
V.	Variation of P_T with T at Constant % O_2 for the $\text{CdSO}_4 \cdot 2\text{CdO}$ Stability Diagram-----	63
VI.	Shift in the $\text{ZnO} \cdot 2\text{ZnSO}_4$ Stability Diagram for Runs E and G-----	64
VII.	Shift in the $\text{CdSO}_4 \cdot 2\text{CdO}$ Stability Diagram for Runs G and H-----	65
VIII.	Thermocouple Standardization-----	66
IX.	Roasting Furnace Temperature Profile-----	67
X.	Calibration of Air Flow-Rate Meter-----	68
XI.	Calibration of SO_2 Flow-Rate Meter-----	69

List of Appendices (Cont'd)

Number	Title	Page
XII.	Sublimation and Degree of Reaction Calculation-----	70
XIII.	Standard Curve for Zinc Analysis with Atomic Absorption-----	71
XIV.	Standard Curve for Cadmium Analysis with Atomic Absorption-----	72

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INTRODUCTION

The only cadmium mineral of any importance is greenockite, CdS, which is not known in any isolated deposits, but is usually associated in small amounts with galena and sphalerite deposits. The cadmium content of these deposits is almost always under one percent. Thus, the recovery of cadmium is always in the form of a by-product in zinc and lead smelting.

In lead smelting, most of the cadmium is volatilized and caught in the flue system, particularly in bag houses or Cottrell treaters. It is sometimes present in sufficient quantity to warrant the treatment of the dust for its recovery.

In modern processes for roasting and sintering of zinc sulfide concentrates, it is possible to eliminate most of the cadmium in the fumes and recover it by treating the dust removed by Cottrell precipitators or bag houses. For optimum results, high temperatures are needed in the roasters and a high gas velocity must be maintained through the bed on the sintering machines. The addition of salt to the sinter mix assists in the removal of cadmium as a chloride.

The flue dusts from zinc smelters usually are complex mixtures of sulfides, oxides, basic sulfates, sulfates, and chlorides of zinc, lead, and cadmium. The usual method of cadmium recovery involves a sulfating roast, followed by a water leach, and cementation of cadmium with zinc dust.

This investigation is concerned with the sulfate - roasting conditions, i.e. temperatures and gas-phase compositions, for optimum separation and recovery of cadmium from zinc smelter flue dusts. One method to recover cadmium from these flue dusts would be to water leach the sulfates and chlorides of zinc and cadmium. This leaves as a residue the basic sulfates, oxides and sulfides of zinc, lead, and cadmium as well as lead sulfate. This procedure would eliminate difficulties in roasting due to the low melting temperatures of the chlorides. Roasting under suitable conditions should make it possible to convert the cadmium oxides and sulfides to a water-soluble sulfate, leaving insoluble compounds of lead and zinc. The effectiveness of this procedure depends, in part, on the solubilities of the basic sulfates of zinc and cadmium.

Consequently, this investigation, in general, involved the following studies:

- (1) Thermodynamic data were compiled from published and unpublished literature for the Cd-S-O, Zn-S-O, and Pb-S-O systems. Free-energy data were used to construct stability diagrams for phases present in these systems at normal roasting temperatures and gas-phase compositions.

- (2) Roasting experiments were performed under thermodynamically favorable conditions. Since the flue dust residue to be roasted is a complex mixture, experiments were made to determine the solubilities of zinc and cadmium basic sulfates.
- (3) A sample of flue dust obtained from the St. Joseph Lead Company, Zinc Smelting Division, Monaca, Pennsylvania, was leached, roasted, and leached again under the conditions determined from the previous studies.

As far as it is known by this author no study of this type has ever been attempted. Also, there was very little published data available that was useful. Private communication was the chief means of obtaining the needed information.

Mr. Dean Bangor of St. Joseph Lead Company provided a detailed description of their cadmium process. He indicated several areas where a more fundamental understanding would be highly desirable. Also he supplied an unpublished article by R. E. Lund and D. E. Warnes, entitled "An Early Commercial Application of Selective Sulfation", which helped with the background information by outlining the "state of the art" concerning cadmium roasting.

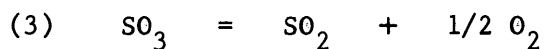
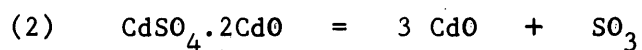
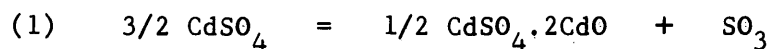
Mr. R. L. Nauert (1966, p. 15-17) described the cadmium process at Blackwell. Further communication with him has been helpful in learning about difficulties in their process.

Thermodynamic data was provided by Dr. H. H. Kellogg (1964, p. 1622-1634). Private communication with him has also yielded extremely useful thermodynamic data (unpublished) concerning basic cadmium sulfate.

PHASE STABILITY CALCULATIONS

With the application of the free-energy data from Appendix 1, graphs can be constructed to show how stability varies with temperature and percent oxygen.

The primary reactions during the sulfate roasting of cadmium oxide may be considered to be:



The equilibrium expression for reaction (1) is:

$$\frac{(\text{CdSO}_4 \cdot 2\text{CdO})^{1/2} (\text{SO}_3)}{(\text{CdSO}_4)^{3/2}} = K$$

On the assumption that flue dust is a mechanical mixture of pure solids (no solid solutions), the activity of $\text{CdSO}_4 \cdot 2\text{CdO}$ and CdSO_4 can be set equal to one. Furthermore, because the operating pressures found in a roaster are low, the activity of SO_3 can be set equal to P_{SO_3} .

Therefore rewriting of (1) gives:

$$(1) \quad \frac{(1) (P_{\text{SO}_3})}{(1)} = K_{(1)}$$

Similarly for equation (3):

$$(3) \quad \frac{(P_{\text{SO}_2}) (P_{\text{O}_2})^{1/2}}{(P_{\text{SO}_3})} = K_{(3)}$$

The combining of (1) and (3) gives:

$$(4) \quad (P_{\text{SO}_2}) (P_{\text{O}_2})^{1/2} = K_3 K_1$$

On the assumption that K_3 and K_1 could be found for a given temperature by using free-energy information, there would remain two unknowns and one equation. According to Gibbs' Phase Rule, both temperature and pressure must be fixed in order to define the state of the system. Hence, another equation is needed to fix the total pressure. A total pressure of 0.2 was chosen because this is approximately the sum of the partial pressures of SO_3 , O_2 , and SO_2 found during roasting.

$$(5) \quad P_T = P_{SO_3} + P_{SO_2} + P_{O_2} = .20$$

Therefore, on the basis of the following equations a diagram showing the stability regions of $CdSO_4$ and $CdSO_4 \cdot 2CdO$ can be constructed:

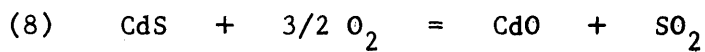
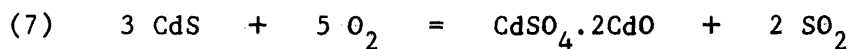
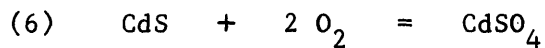
$$(1) \quad P_{SO_3} = K_{(1)}$$

$$(4) \quad (P_{SO_2}) (P_{O_2})^{1/2} = K_{(1)}K_{(3)}$$

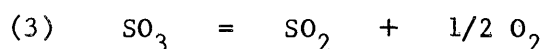
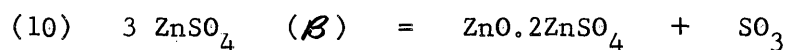
$$(5) \quad P_{SO_3} + P_{SO_2} + P_{O_2} = .20$$

A graphical or analytical approach could be used to solve this set of equations. The diagrams shown here were obtained by using a graphical method.

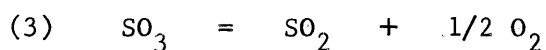
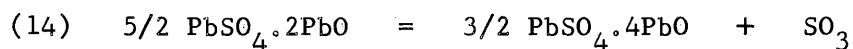
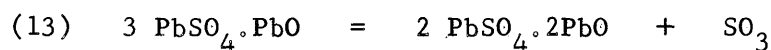
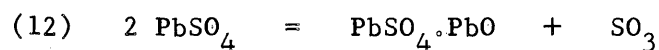
The same approach is used in developing the stability regions of CdO and $CdSO_4 \cdot 2CdO$, CdS and CdO , CdS and $CdSO_4$, and CdS and $CdSO_4 \cdot 2CdO$. The equations used are as follows:



The stability regions in the Zn-S-O system can be calculated using the free-energy data for the following reactions:



The stability regions in the Pb-S-O system can be calculated by using free-energy data for the following reactions:



The stability diagrams are shown in Figures 1 - 5.

In the construction of Figure 5, it was assumed that no inter-metallic compounds would form when a mixture of cadmium, lead, and zinc compounds were roasted together. Figure 5 was helpful in determining the thermodynamic-optimum-roasting conditions. Area A is

significant because ZnO and $PbSO_4$ are stable with water-soluble $CdSO_4$. Water leaching the roasted product would make it possible to separate cadmium from lead and zinc. In Area B, $CdSO_4$ and $PbSO_4$ are still stable, but ZnO would be converted to $ZnO \cdot 2ZnSO_4$. Water leaching would make some zinc join the cadmium because $ZnO \cdot 2ZnSO_4$ is partially soluble in water. However, the lower roasting temperature could reduce operating costs and might prove economical. If roasting was carried out so that $ZnSO_4$ was stable, no separation between zinc and cadmium could be expected. The roasting experiments were mainly carried out in Area A to demonstrate that separation of cadmium from lead and zinc was possible. An additional experiment was made in the $ZnSO_4$ stability region to show how ineffective this area was for cadmium separation.

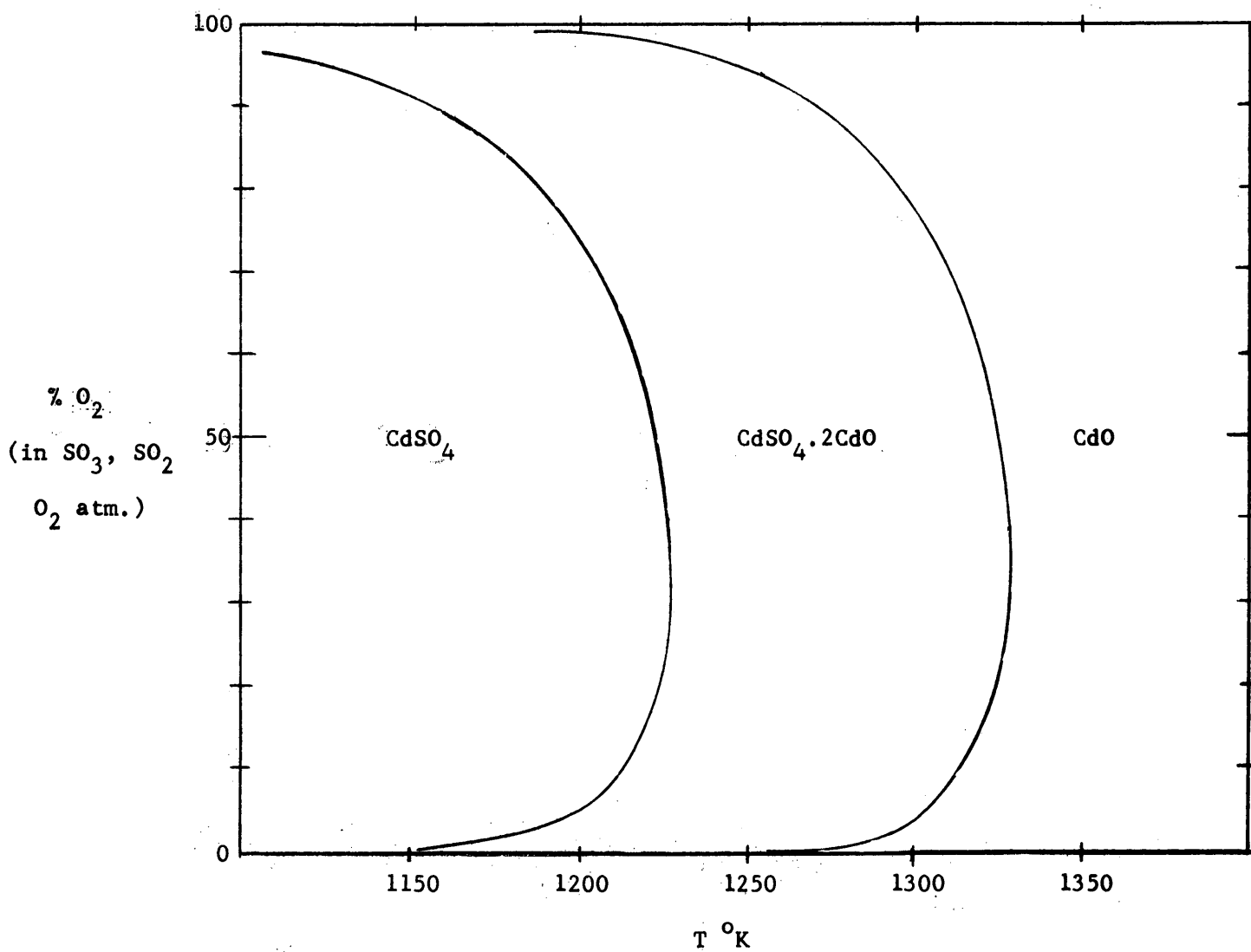


Figure 1. Effect of Temperature & Gas Composition on the Stability of Basic Cadmium Sulfate at 0.2 ATM Pressure

$$P_{SO_3} + P_{SO_2} + P_{O_2} = 0.2 \text{ ATM}$$

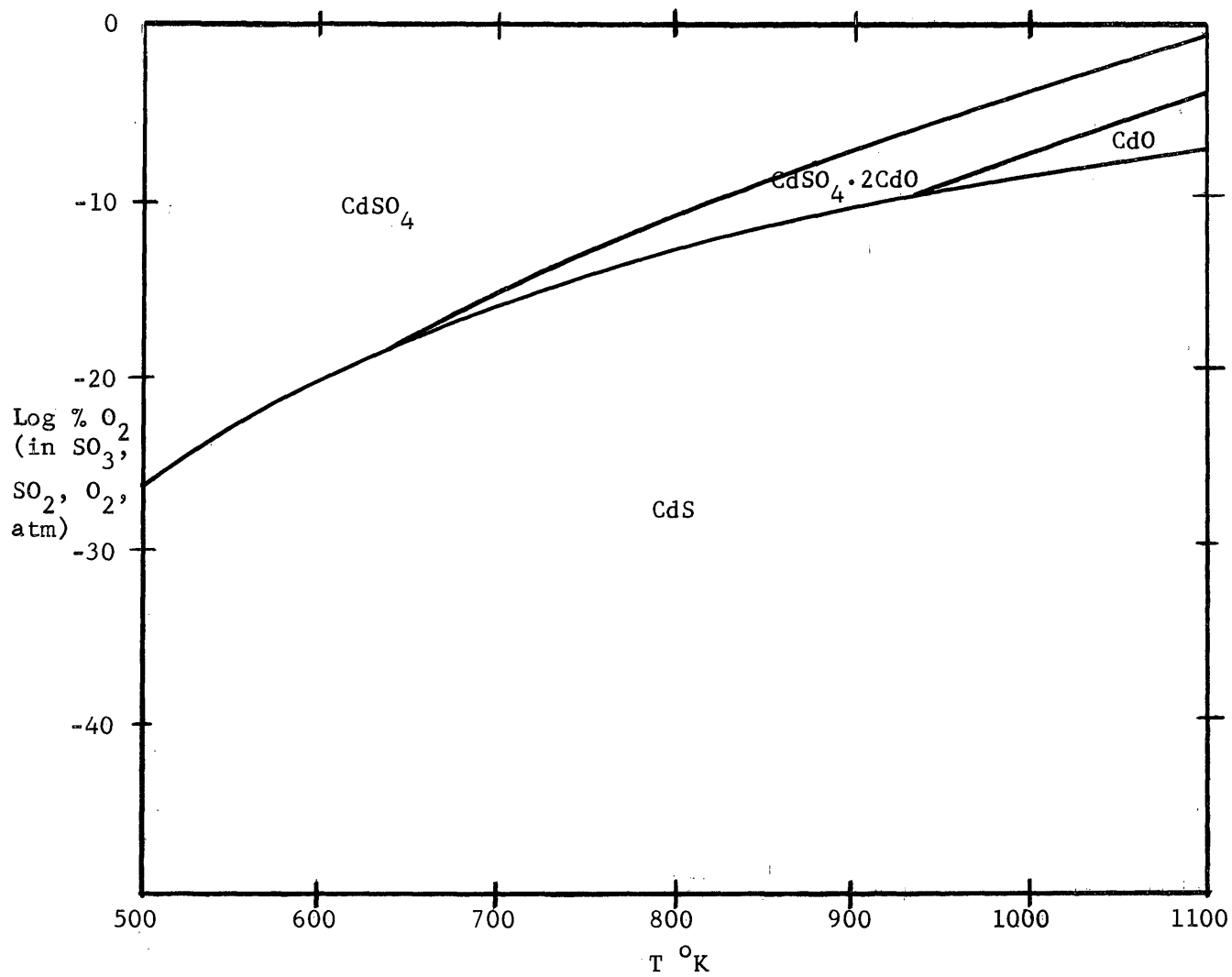


Figure 2. Effect of Temperature & Gas Composition on the Stability of Basic Cadmium Sulfate at 0.2 ATM Pressure & Low Oxygen Potentials

$$P_{\text{SO}_3} + P_{\text{SO}_2} + P_{\text{O}_2} = 0.2 \text{ ATM}$$

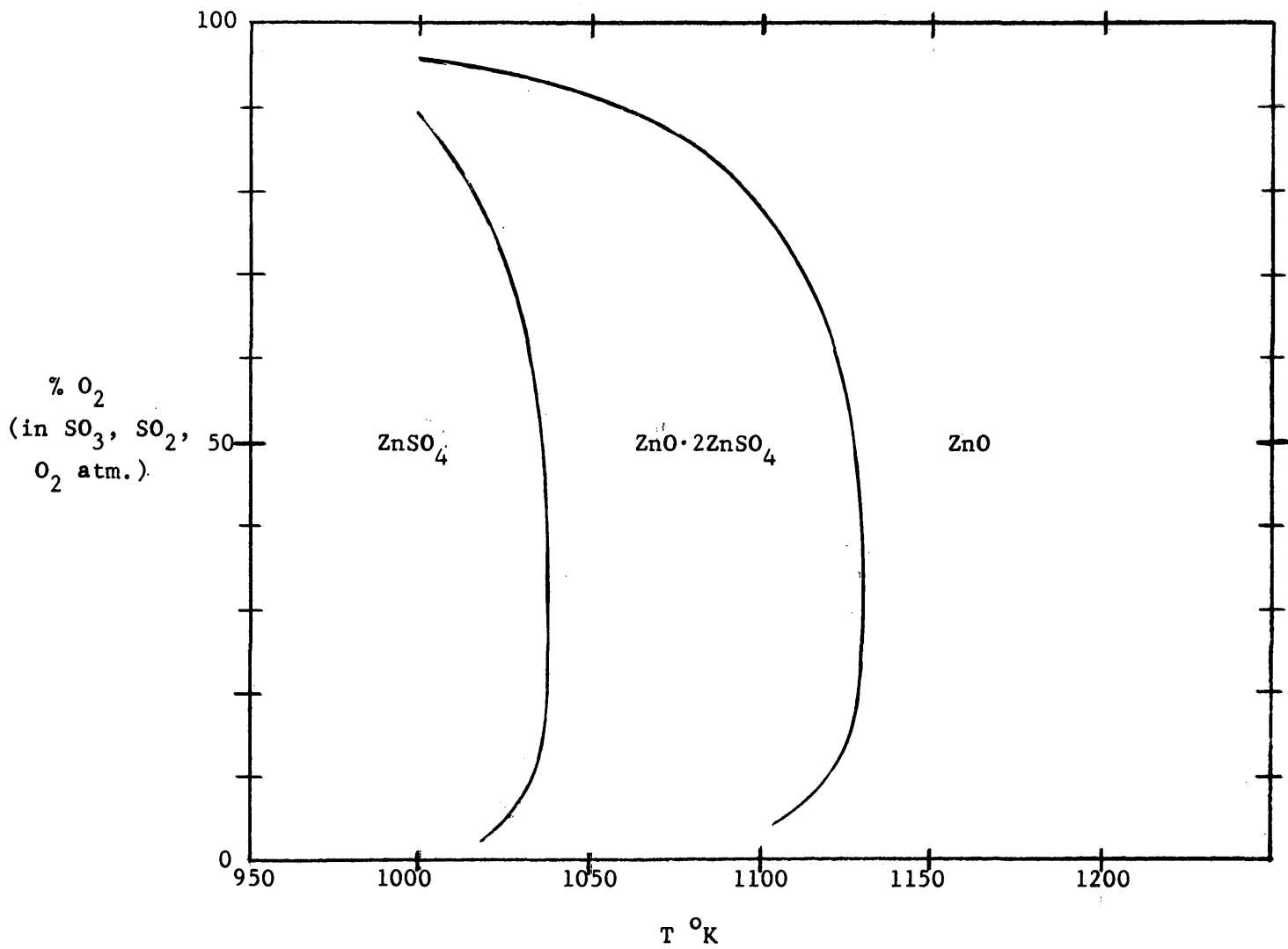


Figure 3. Effect of Temperature & Gas Composition on the Stability of Basic Zinc Sulfate at 0.2 ATM Pressure

$$P_{\text{SO}_3} + P_{\text{SO}_2} + P_{\text{O}_2} = 0.2 \text{ ATM}$$

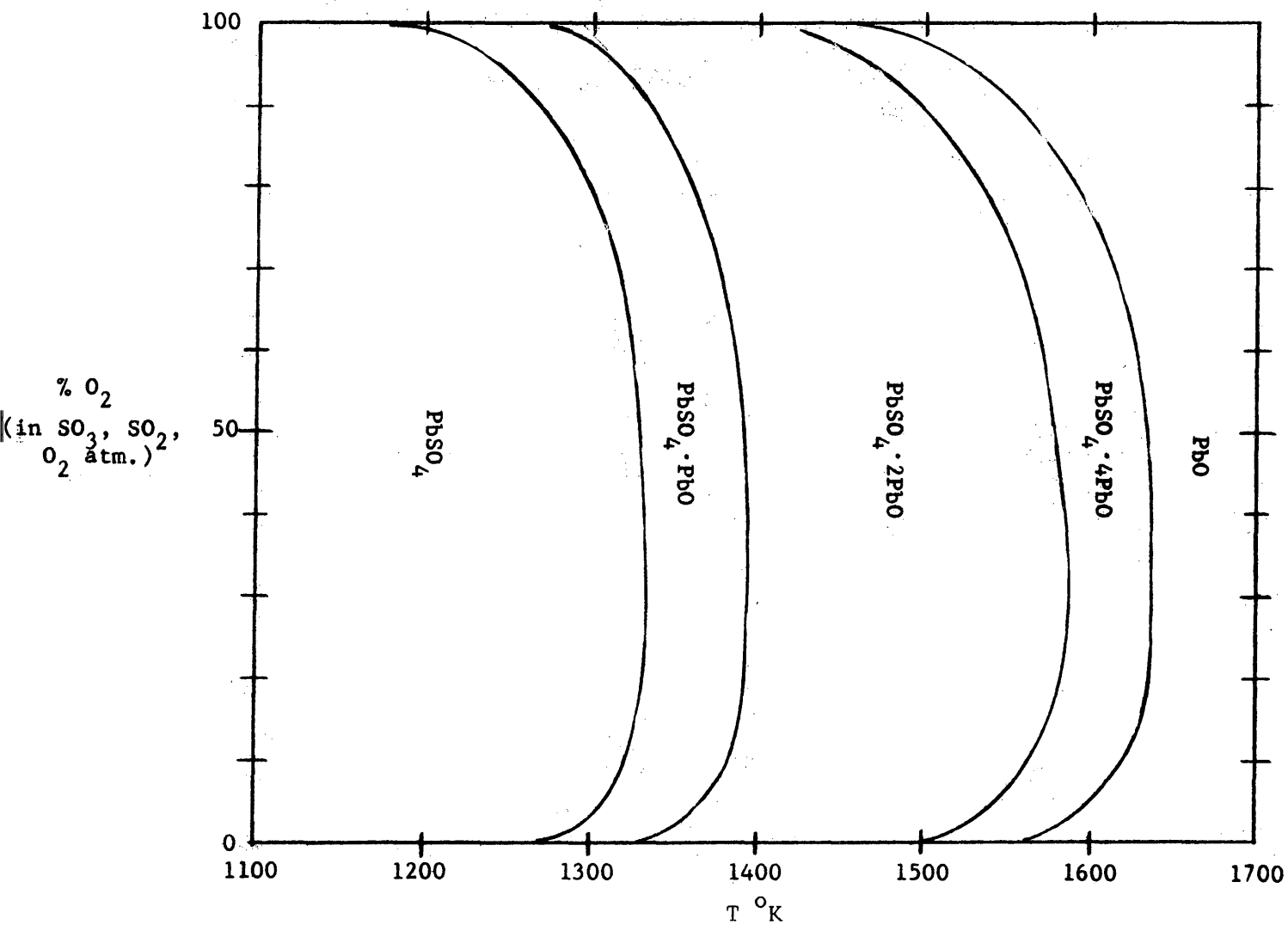


Figure 4. Effect of Temperature & Gas Composition on the Stability of Basic Lead Sulfate at 0.2 ATM Pressure

$$P_{SO_3} + P_{SO_2} + P_{O_2} = 0.2 \text{ ATM}$$

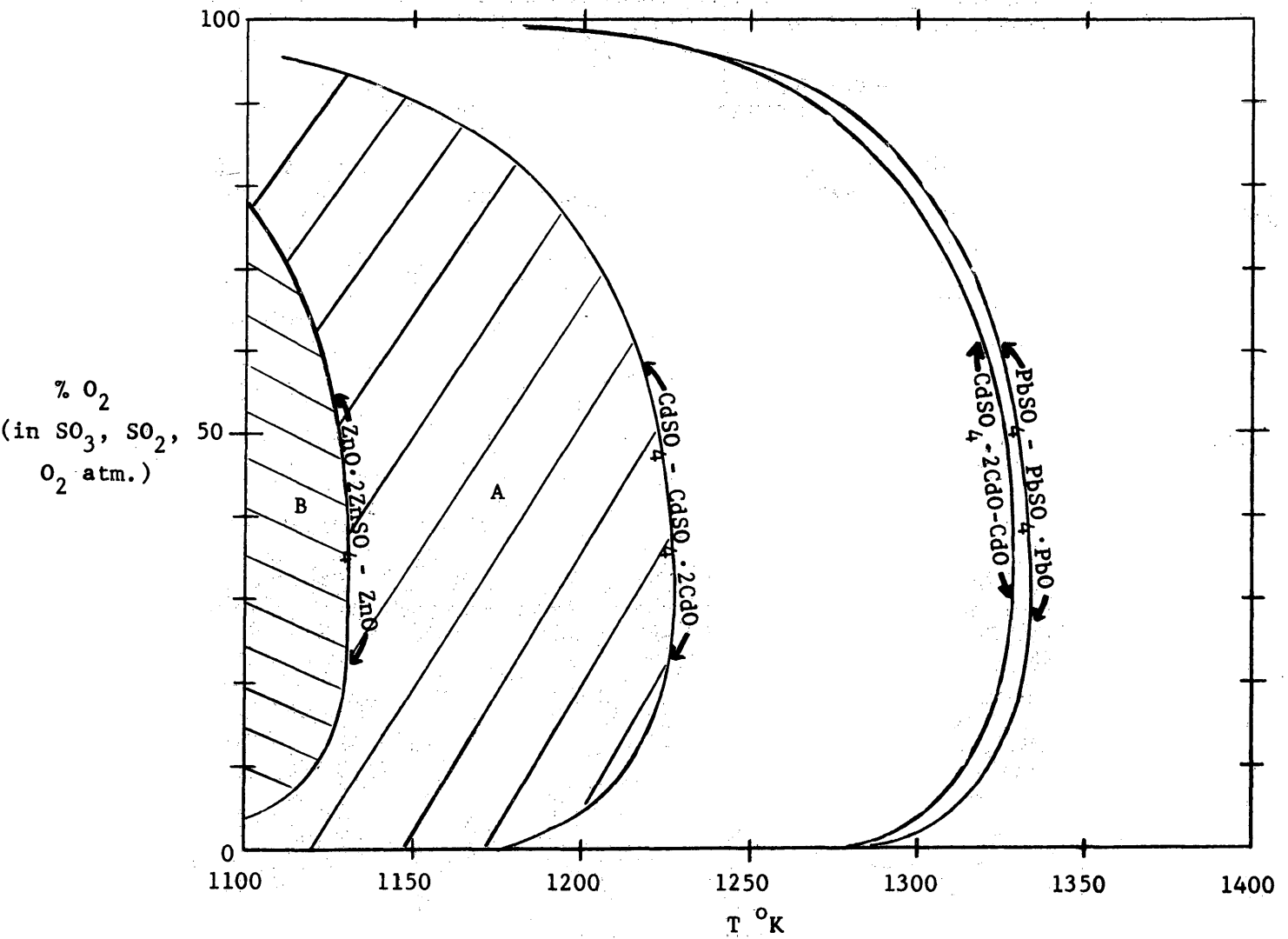


Figure 5. Effect of Temperature & Gas Composition on the Stability of Basic Zn, Cd, Pb Sulfates at 0.2 ATM Pressure

$$P_{SO_3} + P_{SO_2} + P_{O_2} = 0.2 \text{ ATM}$$

EXPERIMENTAL APPARATUS and PROCEDURE

Several tests were made to determine the best design and use of oven and roasting equipment.

Roasting Equipment

An experiment was made to determine whether one furnace would successfully roast CdO to CdSO₄ within a reasonable period of time. Table 1 gives the results of the test.

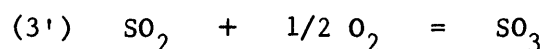
Based on the results of this test, two furnaces were used for roasting.

Table 1

EFFICIENCY of ONE-and TWO-FURNACE OPERATION

<u>Number of Furnaces</u>	<u>Starting Material</u>	<u>Desired Product</u>	<u>Temp. (°C)</u>	<u>Air SO₂ Ratio</u>	<u>Time (hrs)</u>	<u>Percent of Conversion</u>
1	CdO	CdSO ₄	917	6.46	6	75.2
2	CdO	CdSO ₄	917	6.46	6	99.8

The first furnace was used primarily to heat the incoming gas to promote the reaction:



Ceramic beads were placed in this furnace to further speed the reaction. The temperature of this furnace was always held close to the designated reaction temperature. The second furnace held the material to be roasted. A schematic diagram of the furnace apparatus is shown in Figure 6.

Material that sublimates during roasting condenses on the walls of the reaction tube. The condensate from the flue dust contains both water-soluble and water-insoluble compounds. Under normal conditions the addition of distilled water would remove only the water-soluble products. However, SO_3 also condenses (boiling point 44.8°C) on the reaction tube. When water comes in contact with SO_3 , sulfuric acid is formed. The pH of the water is now low enough to leach various otherwise water-insoluble compounds. So, if one desires to know whether there were any water-soluble compounds condensed on the reaction tube, the SO_3 must be removed before water is added. Figure 6 shows the apparatus used for the removal of the SO_3 from the reaction tube without altering the condensed material.

Insulating bricks were used to keep the temperature constant around the periphery of the tube. The hot plate was turned on at the beginning of a run. When the run was completed the furnaces were turned off, but the hot plate remained on. Argon was then used to flush out the remaining SO_3 gas and to prevent any chemical change in the condensed compounds. After a few hours the argon was turned off and the reaction tube was removed. Almost all of the SO_3 was eliminated.

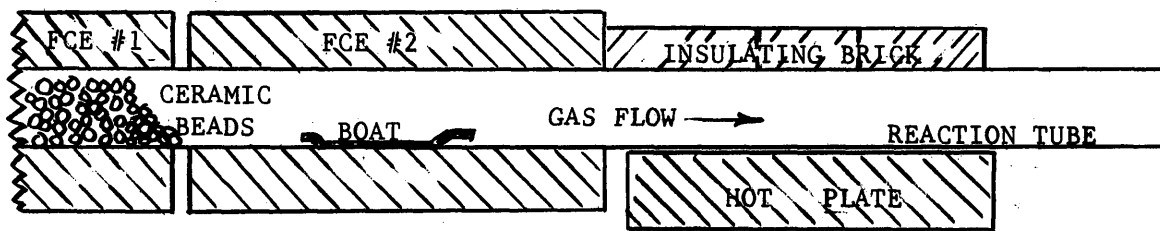


Figure 6. Roasting Apparatus

Drying Equipment

A drying furnace was used to remove water from the flue dust so that chemical analyses could be based on dry weight. Drying was also needed to remove water from hydrated compounds to facilitate x-ray analyses.

Boats containing the samples to be dried were placed inside a tube furnace and argon was allowed to pass over them to prevent oxidation. $\text{Mg}(\text{ClO}_4)_2$ was used to remove any H_2O vapor that might be present with the argon. A flask containing H_2O_2 mixed with methyl-red indicator was used to detect decomposition during drying. The H_2O_2 was needed to oxidize SO_2 to SO_3 . For instance, if $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was drying in the oven, the color of the H_2O_2 would indicate whether any ZnSO_4 decomposed to ZnO . This effect is obtained by making H_2O_2 slightly basic. When SO_2 is released from any decomposing ZnSO_4 , sulfuric acid is produced and the color of the indicator is changed.

The correct time and temperature for drying the flue dust were the next items investigated. Drying temperature was found by using water-leached flue dust that was kept in a desiccator for several months. When the flue dust was "dried" at various temperatures, any weight loss could be attributed to sublimation. What was aimed for was a high drying temperature with no decomposition or sublimation. Table 2 summarizes the results of the test.

On this basis an oven temperature of 291°C was chosen to dry water-leached flue dust. The raw flue dust was dried at 231°C because the melting point of ZnCl_2 is 283°C .

Table 2

DETERMINATION of DRYING TEMPERATURE for the FLUE DUST

<u>Material</u>	<u>Temp. (°C)</u>	<u>Time (hrs)</u>	<u>Percent Sublimation</u>
Flue Dust	258	26	0
Flue Dust	291	28	0
Flue Dust	332	20	2.47

Drying time was found by plotting percent weight loss of flue dust against time as shown in Figure 7.

Forty-eight hours at 291°C appeared to be adequate time to remove almost all H₂O and H₂SO₄. This drying time was also used when the temperature was reduced to 231°C for drying the raw flue dust.

Temperature Control for Roasting Equipment

Close temperature control was not necessary as long as the temperature range was within the intended region on the stability diagram (Figure 5). Nevertheless, a temperature controller, used on the roasting furnace (2nd furnace), allowed the temperature to be held within 1°C. Temperature measurements were made by using a platinum-platinum 13 percent rhodium thermocouple. The thermocouple was standardized (Appendix VIII) before it was put into operation to insure accurate temperature readings. In addition, several other corrections were needed. First, a temperature correction was made to adjust the measuring thermocouple temperature to that of the boat temperature. Second, a temperature profile of the roasting furnace was made

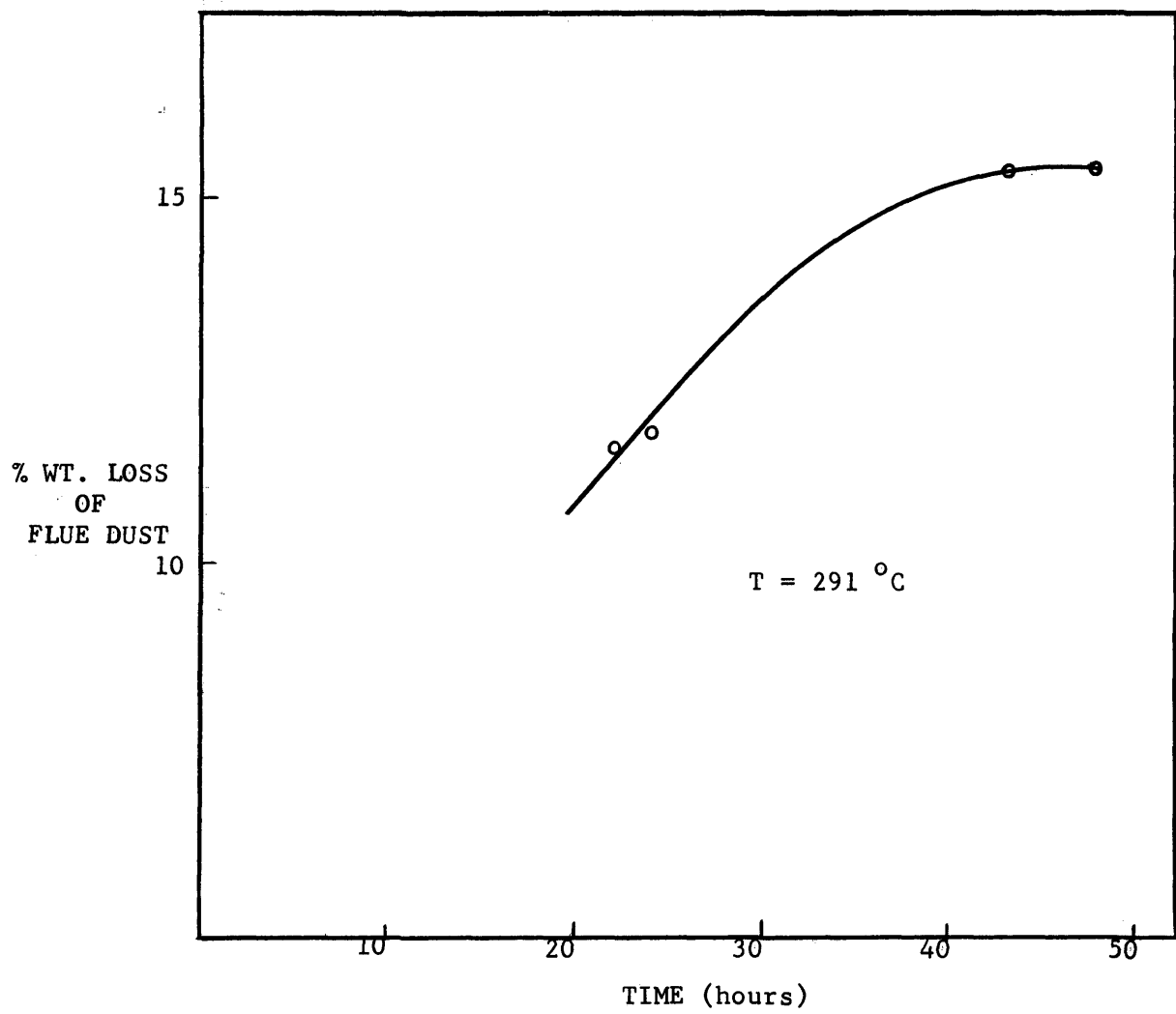


Figure 7. Determination of Drying Time for the Flue Dust

(Appendix IX) to find the region in the furnace that had the smallest temperature gradient. This profile also served to show the variation in boat temperature one could expect in the "flat" area of the furnace. This variation was 4°C . Therefore, temperature variation was 4°C , while temperature control was $\pm 1^{\circ}\text{C}$.

Flow Meters

The amounts of oxygen and SO_2 flowing to the roaster were regulated with manometric-type flow meters. An oil bubbler was installed to maintain a constant gas pressure to the flow-meter by allowing the gas to bubble constantly through the oil. Since the gas pressure was constant, the flow rate remained fixed. The flow rate could be regulated by altering the height of the bubbler in the oil.

The flow meters were calibrated by using a glass burette fitted with a rubber bulb. Squeezing the soap-containing rubber bulb brought a bubble at the gas outlet. The bubble would then be forced upward by the moving gas. The time it takes the bubble to displace x number of cubic centimeters would be the flow rate. The calibration curves for air and SO_2 are shown in Appendices X and XI.

EXPERIMENTAL RESULTS

The effect of temperature, atmosphere, initial material, and final product were studied in relation to the roasting process. In addition, the solubility of CdO, $\text{CdSO}_4 \cdot 2\text{CdO}$, ZnO and $\text{ZnO} \cdot 2\text{ZnSO}_4$ at different pH values was investigated.

Roasting Experiments

Table 3 gives the equilibrium gas composition for all the roasting tests made. Table 4 summarizes all the roasting experiments.

*Table 3

EQUILIBRIUM PARTIAL PRESSURES and
TOTAL PRESSURE DURING ROASTING

Run	P_{O_2}	P_{SO_2}	P_{SO_3}	P_{T}
A	0.1637	0.0260	0.0493	0.2390
B	0.1380	0.0484	0.0842	0.2706
C	0.0017	0.6236	0.1095	0.7349
D	0.1744	0.0516	0.0227	0.2486
E	0.1569	0.0915	0.0381	0.2865
F	0.0147	0.6410	0.0820	0.7378
G	0.1667	0.1138	0.0140	0.2945
H	0.1800	0.0714	0.0059	0.2573

* Pressures given in atmospheres

Table 4
SUMMARY of the EXPERIMENTAL CONDITIONS
SET for the ROASTING TESTS

Run	Initial Molar Ratio Air/SO ₂	Temp. (°C)	Mole Percent O ₂ in O ₂ , SO ₂ , SO ₃ atm.	Reaction Time (hrs)	Starting Material	Desired Product	cc/Min SO ₂	cc/Min Air
A 1	11.92	650	68.5	6	CdS	CdSO ₄	9.77	116.5
A 2	11.92	650	68.5	6	CdO	CdSO ₄	9.77	116.5
B 1	6.46	650	51.0	6	CdS	CdSO ₄	9.77	63.1
B 2	6.46	650	51.0	6	CdO	CdSO ₄	9.77	63.1
C 1	0.367	650	0.236	6	CdS	CdSO ₄	20.25	7.43
C 2	0.367	650	0.236	6	CdO	CdSO ₄	20.25	7.43
D 1	11.92	777	70.1	6	CdS	CdSO ₄	9.77	116.5
D 2	11.92	777	70.1	6	CdO	CdSO ₄	9.77	116.5
D 3	11.92	777	70.1	6	CdSO ₄	CdSO ₄	9.77	116.5
E 1	6.46	777	54.8	6	CdS	CdSO ₄	9.77	63.1
E 2	6.46	777	54.8	6	CdO	CdSO ₄	9.77	63.1
E 3	6.46	777	54.8	6	CdSO ₄	CdSO ₄	9.77	63.1
E 4	6.46	777	54.8	5	ZnSO ₄	ZnO.2ZnSO ₄	9.77	63.1
E 5	6.46	777	54.8	6	CdS + CdSO ₄	CdSO ₄	9.77	63.1
F 1	0.367	777	2.00	6	CdS	CdSO ₄	20.25	7.43
F 2	0.367	777	2.00	6	CdO	CdSO ₄	20.25	7.43
F 3	0.367	777	2.00	6	CdSO ₄	CdSO ₄	20.25	7.43
G 1	6.46	917	56.6	6	CdS	CdSO ₄	9.77	63.1
G 2	6.46	917	56.6	6	CdO	CdSO ₄	9.77	63.1
G 3	6.46	917	56.6	6	CdSO ₄	CdSO ₄	9.77	63.1
G 4	6.46	917	56.6	6	ZnO	ZnO	9.77	63.1
G 5	6.46	917	56.6	6	PbO	PbSO ₄	9.77	63.1
G 6	6.46	917	56.6	6	PbO, ZnO, CdO Mixture	CdSO ₄ , PbSO ₄ , ZnO	9.77	63.1
H	11.29	972	70.0	12	CdSO ₄	CdSO ₄ .2ZnO	9.77	110.2

Cd-S-O System. The degree of reaction and percent sublimation of CdS, CdO, and CdSO₄ for various temperatures and roasting atmospheres were sought. In addition, the number of different basic sulfates of cadmium, and their x-ray patterns, was investigated.

Sublimation and Degree of Reaction. It is important to know the degree to which cadmium and several of its compounds will sublime while being converted to CdSO₄ during roasting. A series of tests was made to measure the sublimation and degree of reaction of CdO, CdSO₄, and CdS at various temperatures and gas compositions. The CdSO₄ region was chosen as the area to be studied because cadmium compounds present in the flue dust must be converted to CdSO₄ in order to be removed by a water leach. The experimental positions chosen in the CdSO₄ stability region are shown in Figure 8.

The three different roasting atmospheres were chosen to see whether degree of sulfation was dependent upon oxygen potential. The temperature of 650°C was selected because this is the temperature that is currently being used for cadmium roasting. The second temperature, 777°C, was used because ZnO·2ZnSO₄ (which is only partially soluble in water) is stable along this isotherm within the gas compositions chosen. Rapid conversion (6 hours) of CdO to CdSO₄ at 917°C was responsible for choosing it as the final temperature.

Sublimation and degree of reaction were studied in the same experimental run. Suppose the sulfation and sublimation of CdS were to be studied at the roasting conditions specified by position 3 (Figure 8).

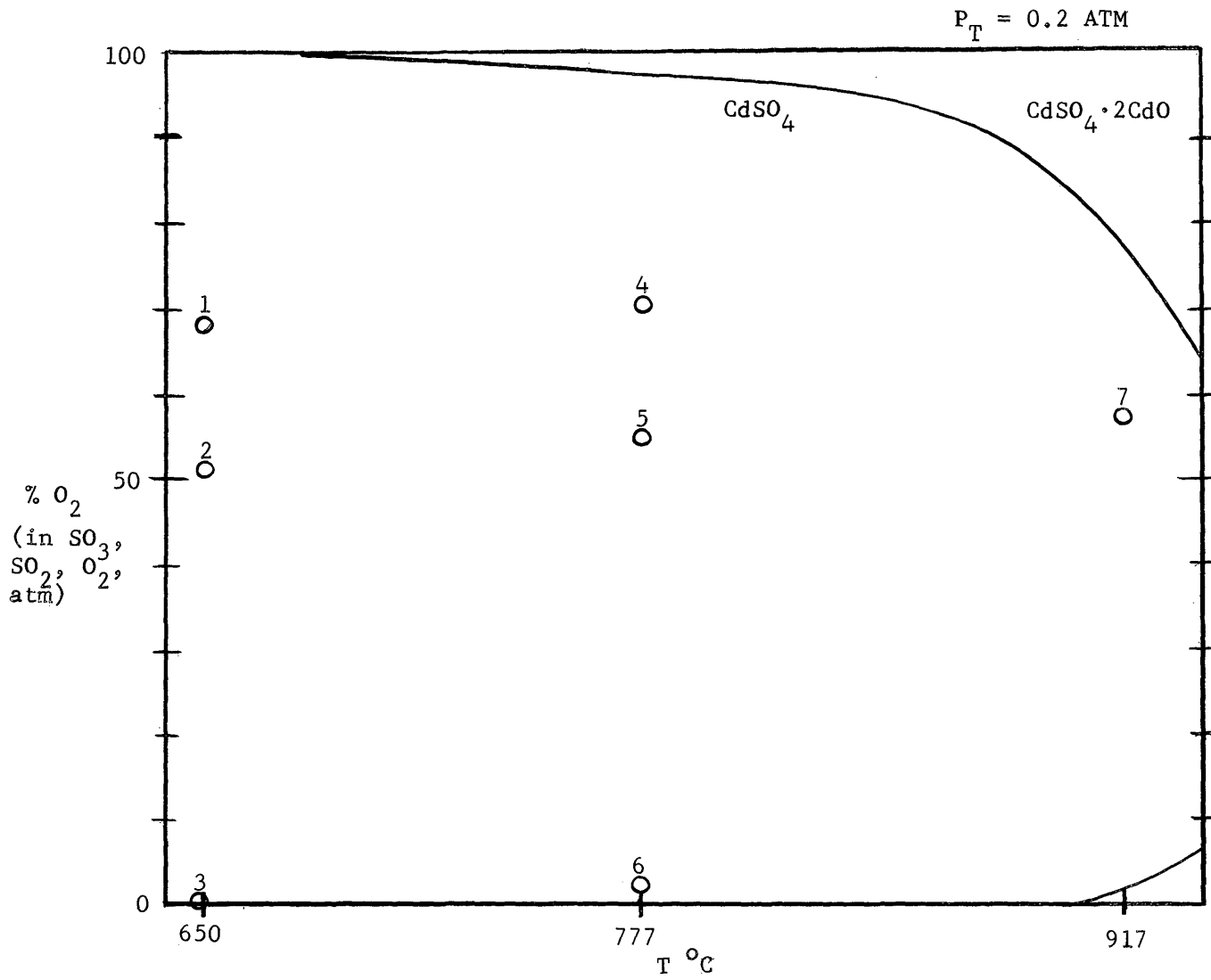


Figure 8. Experimental Positions on the $\text{CdSO}_4 \cdot 2\text{CdO}$ Stability Diagram for Sublimation and Degree of Reaction Tests

A weighed amount of CdS was placed in a boat and roasted at the conditions prescribed by position 3. Six hours were allowed for each run.

When the roasting was completed, the boat was immediately removed from the furnace and allowed to cool in a desiccator. After the material reached room temperature, it was allowed to dry in an oven at approximately 160°C for about 36 hours. It was then removed from the oven, allowed to cool, and re-weighed. The calculations necessary for finding the sublimation and degree of reaction are shown in Appendix XII.

Tables 5 and 6 give the results of these tests with CdO, CdSO₄, and CdS. Blank spaces indicate no test was made for that compound at that particular position on the stability diagram. When two insoluble phases were produced, the analytical method used did not permit a determination of the degrees of sublimation and reaction. In cases of this type the only information obtainable was the identification of the phases (plus their approximate relative amounts) present after roasting.

CdSO₄.2CdO Studies. Data concerning CdSO₄.2CdO is scarce. The possibility of having more than one basic sulfate of cadmium was not overlooked. Tests were made to determine whether more than one basic sulfate exists.

Evacuated Vycor capsules were used to hold pellets made of a mixture of CdO and CdSO₄. The initial proportion of CdO to CdSO₄ together with the results of each test is shown in Table 7.

Basic cadmium sulfate was also prepared by roasting CdSO₄ (Table 4 run H). An x-ray pattern showed that all CdSO₄ reacted to form the

desired product. However, the x-ray pattern of this basic sulfate (β) did not agree with the x-ray pattern of the basic sulfate (α) formed in the Vycor capsules; but when β was placed in an argon atmosphere at 400°C for 18 hours it was converted to α . Table 8 gives the "d" spacing and the relative intensities for the two forms.

Zn-S-O System. A check on the validity of the $\text{ZnO} \cdot 2\text{ZnSO}_4$ stability diagram was made by roasting ZnO at a temperature and in a roasting atmosphere where no chemical change of the compound should occur. Table 4, run G₄, gives the details of the test. A diffraction pattern indicated that ZnO had undergone no chemical change during roasting.

$\text{ZnO} \cdot 2\text{ZnSO}_4$ was prepared from ZnSO_4 . The roasted product was analyzed and found to be all $\text{ZnO} \cdot 2\text{ZnSO}_4$, as shown in Table 4, run E₄.

Pb-S-O System. A check on the validity of the basic lead sulfate stability diagram was made by roasting PbO at a temperature and gas composition where PbSO_4 should be stable. Table 4, run G₅, gives the details of the test. A diffraction pattern showed only PbSO_4 present after roasting.

Table 5
 SUBLIMATION and PERCENT CONVERSION to CdSO₄

Time - 6 Hours

Position	Time - 6 Hours						Total Gas Flow Rate cc/min
	1	2	3	4	5	6	
Starting Material	126.3	72.9	27.7	126.3	72.9	27.7	72.9
CdO	% Sublimation	0	0	0	0	0	1.3
	% Conversion	42.9	44.4	30.4	70.5	79.3	99.8
CdSO ₄	% Sublimation	--	--	--	1.17	0.87	1.09
	% Conversion	--	--	--	--	--	--
CdS	% Sublimation	0, 2.57	27.2	27.6	CdO	CdO	CdO
	% Conversion	62.2, 59.2	23.0	1.40	Cd	Cd	Cd
				CdSO ₄	CdSO ₄	CdSO ₄	CdSO ₄

*NOTE

- a Rerun
- b Major Product
- c Minor Product

* NOTE A great deal of sublimation on this run.
 CdS sublimed so rapidly it was not sulfated before leaving the furnace.

Table 6
 PHASES PRESENT for the
 CONVERSION of CdS to CdSO₄

Run	Molar Ratio of CdSO ₄ to CdS ⁴	Initial Gas atm.	Temp. (°C)	Time of Run	Final Products	
					Boat	Condensate
1	1	Argon	777	6 hrs	Cd CdS α CdS β CdO	CdS α Cd
2	1	$\frac{\text{Air}}{\text{SO}_2} = \frac{6.46}{1}$	777	6 hrs	CdO Cd CdS α	CdSO ₄
3	1	Argon	777	20 min	Cd CdO CdS α CdS β	CdS α Cd
4	2	Argon	777	10 min	CdSO ₄ CdS α CdS β CdSO ₄ · 2CdO α	CdS α
5	2	Argon	777	2½ min	CdSO ₄ CdS α CdS β	CdS α

Table 7

RESULTS of BASIC CADMIUM SULFATE PREPARATION

Run	$\frac{\text{CdO}}{\text{CdSO}_4}$ Initial Molar Ratio	Temp. (°C)	Reaction Time (hrs)	Results
1	3.24:1	700	121	Almost all CdO
2	0.811:1	700	83	Practically all CdO
3	8.11:1	700	83	CdSO ₄ .2CdO - High percent CdSO ₄ - Moderate percent CdO - Low percent
4	2:1	700	83	CdSO ₄ .2CdO - High percent CdO - Moderate percent
5	1.32:1	700	212	Almost all CdSO ₄ .2CdO
6	0.25:1	700	212	Almost all Hydrous CdSO ₄

Table 8
 "d" SPACING and RELATIVE INTENSITIES of
 the LOW and HIGH TEMPERATURE
 FORM of $\text{CdSO}_4 \cdot 2\text{CdO}$

α (Low Temperature Form)		β (High Temperature Form)	
d	I/I ₀	d	I/I ₀
2.84	100	2.79	100
3.13	58	3.59	34
2.79	55	4.41	25
2.55	48	1.796	16
4.90	20	1.888	14
2.16	15	3.76	13
6.07	12	1.665	13
1.831	11	2.41	12
7.19	10	1.643	12
6.88	10	4.06	11
2.18	10	2.69	10
1.760	8	2.13	9
		1.470	9
		1.442	9
		2.65	8
		2.00	7
		1.158	7

Cd-Zn-Pb-S-O System. A mechanical mixture was roasted (Table 4, run G₆) to find out whether any inter-metallic compounds would be found. The mixture had the following composition:

Table 9
COMPOSITION of MECHANICAL MIXTURE
CONTAINING PbO, ZnO, and CdO

PbO	16.26%
ZnO	70.70%
CdO	<u>13.04%</u>
Total	100.00%

Experimental conditions (run G₆) were kept the same as found on runs G₂, G₄, and G₅. The roasted product was water leached. An x-ray powder pattern was taken of the residue and the dried water-soluble product. No inter-metallic compounds were found. The mixture roasted exactly as did the individual reagents.

Flue Dust. A study of the flue dust was made to determine the type and relative amounts of metals and compounds present. After the major metallic elements were identified, an atomic absorption spectrometer was used for their quantitative analysis. The flue dust was then water leached and the residue and solution were similarly analyzed.

The water-leached flue dust was roasted under three separate roasting conditions. The product was again water leached, and the solution, sublimate, and residue analyzed.

Qualitative Analysis of the Flue Dust. An optical emission spectrograph was used to determine the metallic composition of the flue dust. The metals found together with their relative amounts are listed in Table 10.

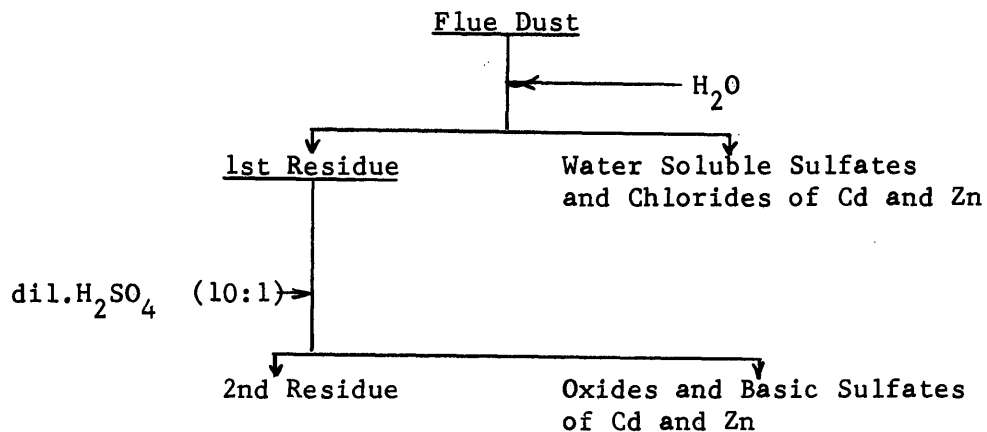
Table 10
 QUALITATIVE ANALYSIS of METALS
 in the FLUE DUST

<u>Major</u>	<u>Minor</u>	<u>Trace</u>	
Zn	Fe	Sn	Ag
Pb	Cu	Ti	Al
Cd	Mg	Ni	B
	Mn	Mo	Bi
		Ca	Cr
		Si	K

Powder x-ray diffraction patterns of the flue dust were made to determine which compounds were present. However, there were so many compounds in the flue dust that only those present in the greatest amounts could be identified. Figure 9 shows the method used to separate the various compounds so that an accurate analysis could be made.

Figure 9

SEPARATION of COMPOUNDS in the FLUE DUST
for QUALITATIVE CHEMICAL ANALYSIS



X-ray patterns were taken of each product. Table 11 shows the compounds found and their relative amounts.

Table 11
QUALITATIVE ANALYSIS of COMPOUNDS
in the FLUE DUST

<u>Major</u>	<u>Minor</u>
ZnO	CdS
[CdSO ₄ CdCl ₂]	ZnS
PbSO ₄	ZnSO ₄
	ZnO.2ZnSO ₄

Quantitative Chemical Analysis of the Flue Dust. The amount of cadmium and zinc in the flue dust was found by using an atomic

absorption spectrometer. For analysis with this instrument, the sample must first be put into solution. A 50:50 ratio (by volume) of concentrated HCl and HNO₃ was used to dissolve the zinc and cadmium. The solution was then diluted to parts per million because the instrument is most accurate at low concentration. Next, standard solutions of zinc and cadmium containing known parts per million of the respective element were run on the machine. The results were plotted against concentration. Two sample curves for zinc and cadmium are shown in Appendices XIII and XIV. Table 12 shows the analysis of the flue dust.

Table 12

QUANTITATIVE ANALYSIS of the
FLUE DUST for ZINC and CADMIUM

Run	Raw Flue Dust		H ₂ O	H ₂ O		
	Percent Zn	Percent Cd	Soluble Percent Zn	Insoluble Percent Cd	*Sample 1	Sample 2
1	36.7	10.51	5.28		0.583	0.551
2	36.6	10.77	5.35		0.494	0.552
3	36.5	10.59	5.38		0.497	0.556
4	36.7	10.57	5.19		0.488	0.553
Avg.	36.6	10.61	5.29		0.516	0.553

* Sample was not mixed before analysis.

Flue Dust Roast. The flue dust to be roasted was first leached to remove the water-soluble zinc and cadmium. A weighed amount

of dried (48 hours at 291°C under argon) residue was placed in a boat and roasted. Three roasting runs were made at different oxygen percentages and temperatures. The results of these tests are shown in Figures 10, 11, and 12.

Solubility of CdO, CdSO₄.2CdO, ZnO, and ZnO.2ZnSO₄

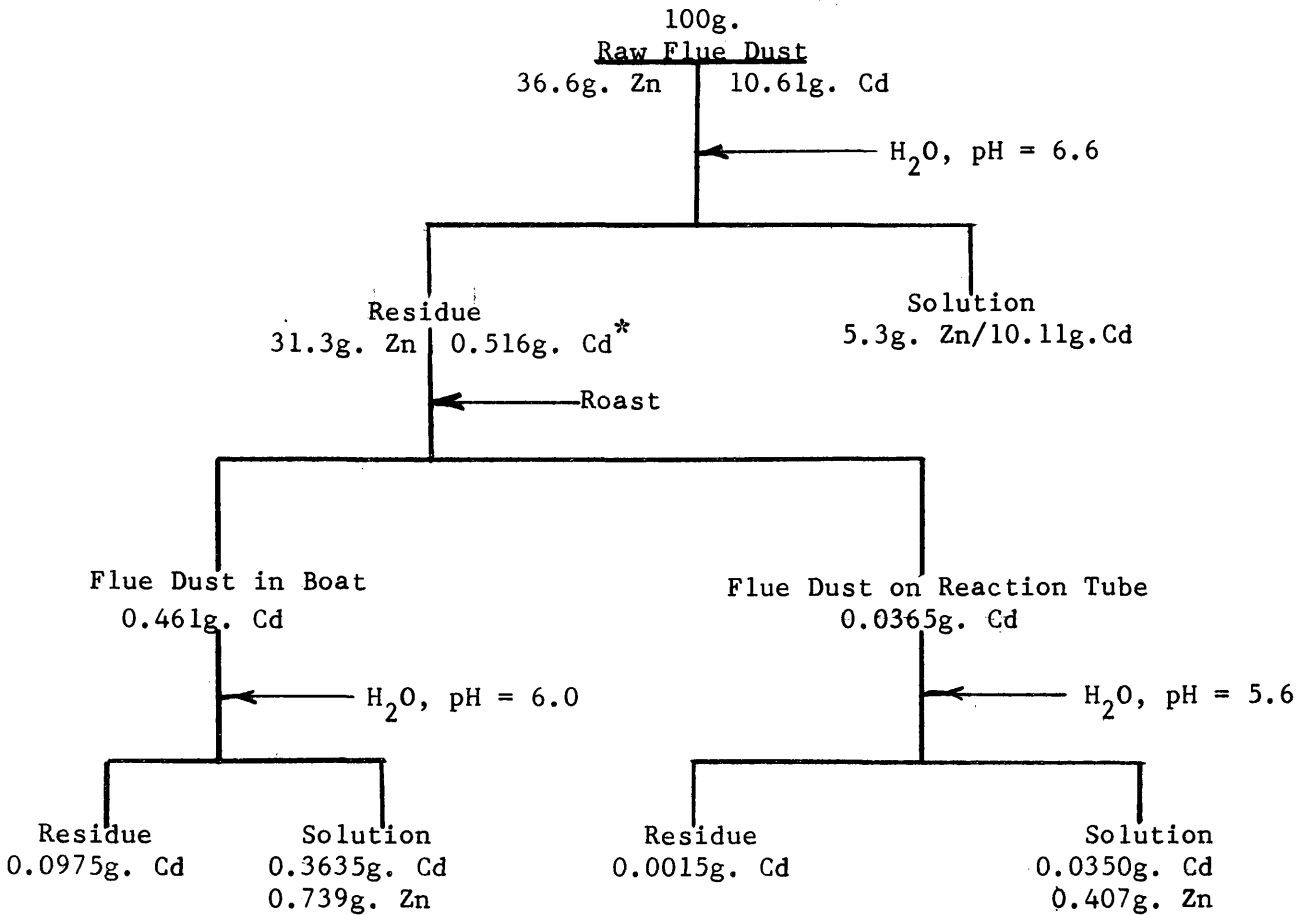
Under some conditions basic cadmium sulfate may be present in roasted or unroasted flue dusts. In such cases the solubility of CdSO₄.2CdO may be of interest, so this solubility was measured at several different pH values. The solubility of CdO was also measured to see whether any correlation could be made between the two compounds. The results of the tests are shown in Figures 13 and 14.

Solubility data of ZnO.2ZnSO₄ could be very useful if the flue dust was roasted in the stability region of the basic sulfate. In this case, knowledge of the amount of zinc one would expect to find with the water-soluble cadmium could be very helpful. The solubility measurements are shown in Figures 15 and 16.

Figure 10
ROASTING OPERATION RUN #1

Parameters: Position 5, Figure 8 - 1.27 hrs.
Position 7, Figure 8 - 6 hrs.

Initial Air/SO₂ = 6.46

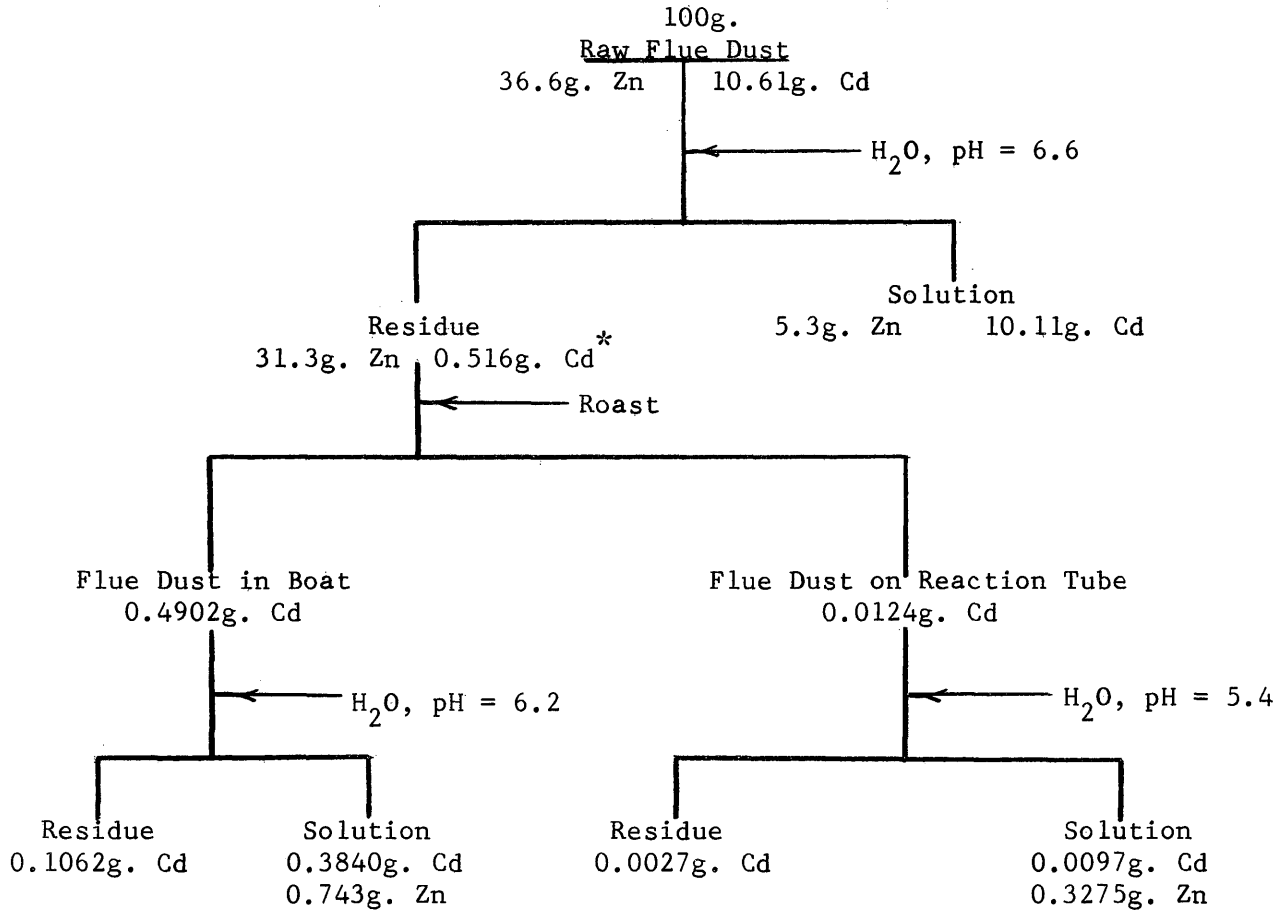


$$\text{Percent Recovery Cd} = \frac{10.61 - (0.098 + 0.0015)}{10.61} \times 100 = 98.9\%$$

*0.516g. arrived at by direct assay - sample #1

Figure 11
ROASTING OPERATION RUN #2

Parameters: Position 1, Figure 8 - 1.27 hrs. Initial Air/SO₂ : 11.92
Position 7, Figure 8 - 6 hrs. 6.46

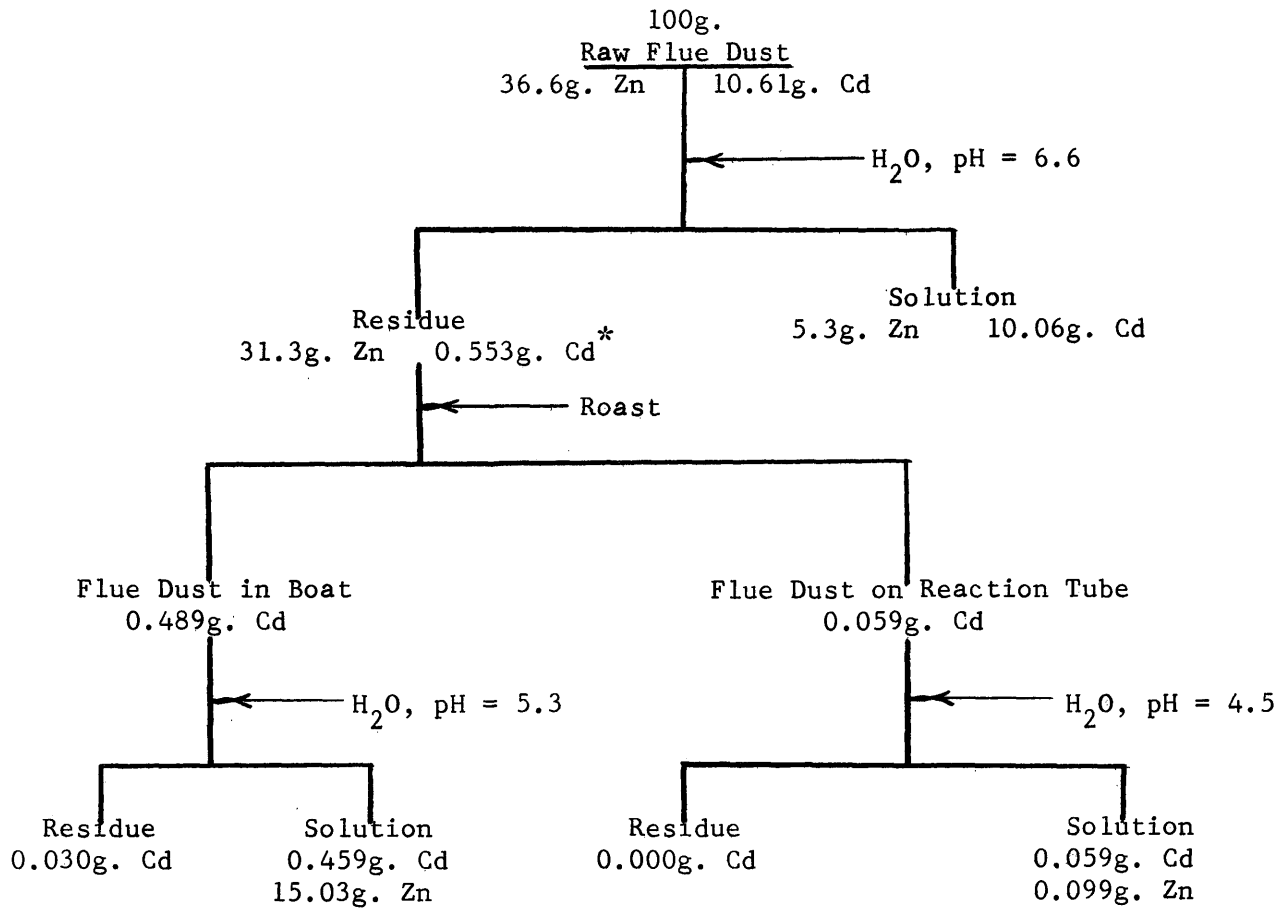


$$\text{Percent Recovery Cd} = \frac{10.61 - (0.1062 + 0.0027)}{10.61} \times 100 = 98.9\%$$

*0.516g. Cd arrived at by direct assay - sample #1

Figure 12
ROASTING OPERATION RUN #3

Parameters: Position 2, Figure 8 - 7.27 hrs. Initial Air/SO₂: 6.46



$$\text{Percent Recovery Cd} = \frac{10.61 - (0.03 + 0.00)}{10.61} \times 100 = 99.7\%$$

*0.553g. Cd arrived at by direct assay - sample #2

Figure 13 $\text{CdSO}_4 \cdot 2\text{CdO}$ Solubility vs. pH in H_2SO_4 Solution

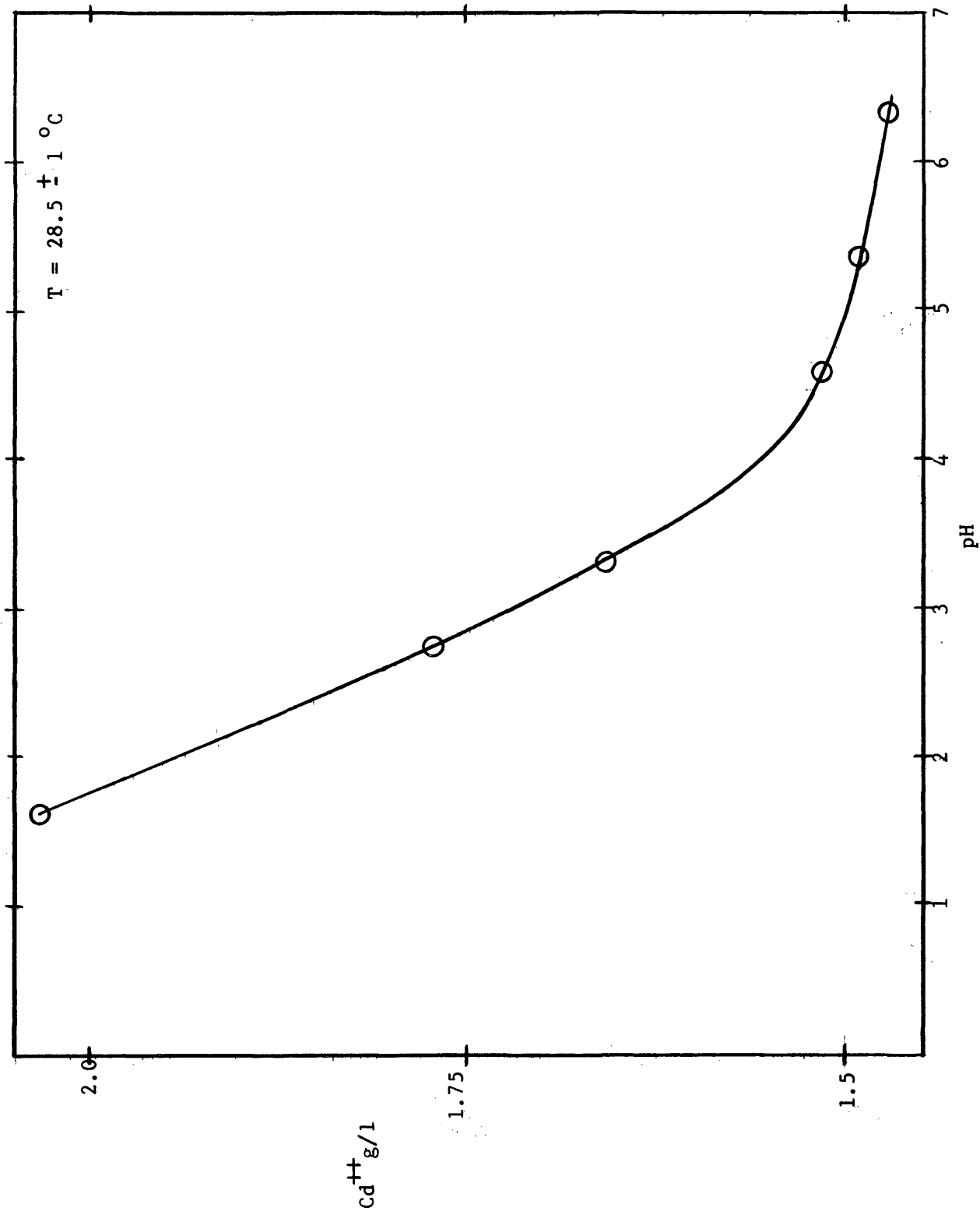


Figure 14 CdO Solubility vs. pH in H₂SO₄ Solution

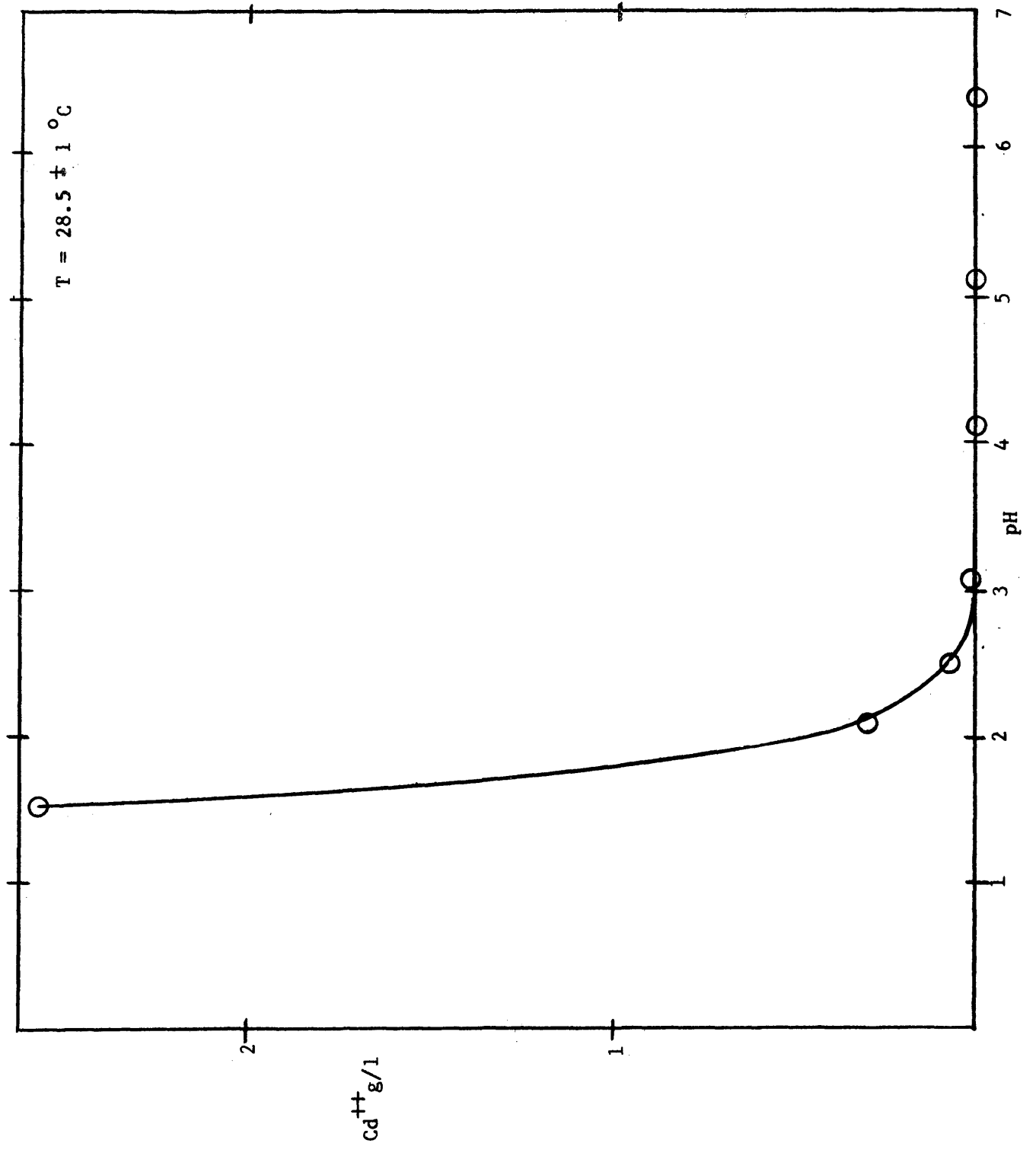


Figure 15 ZnO·2ZnSO₄ Solubility vs. pH in H₂SO₄ Solution

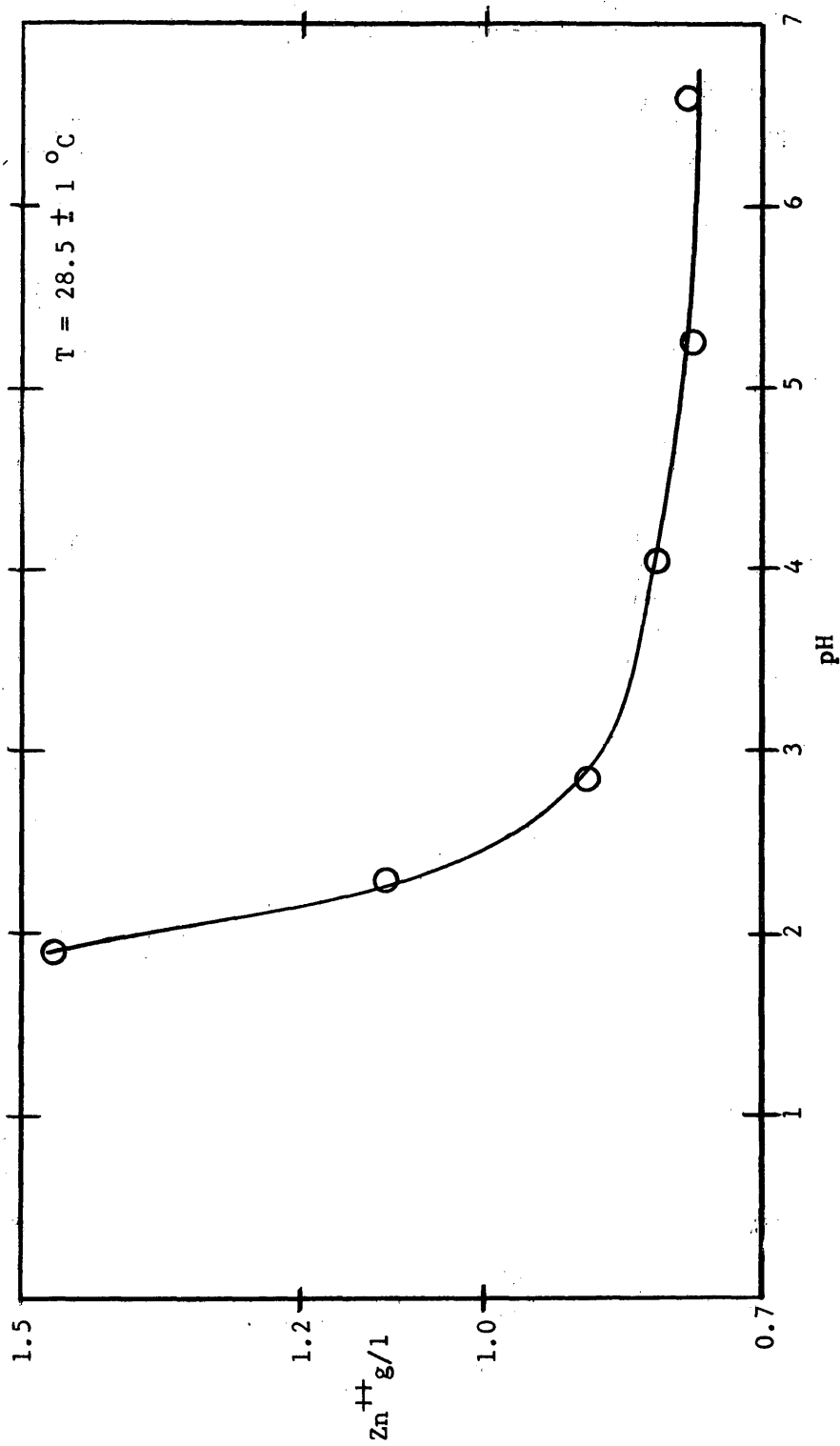
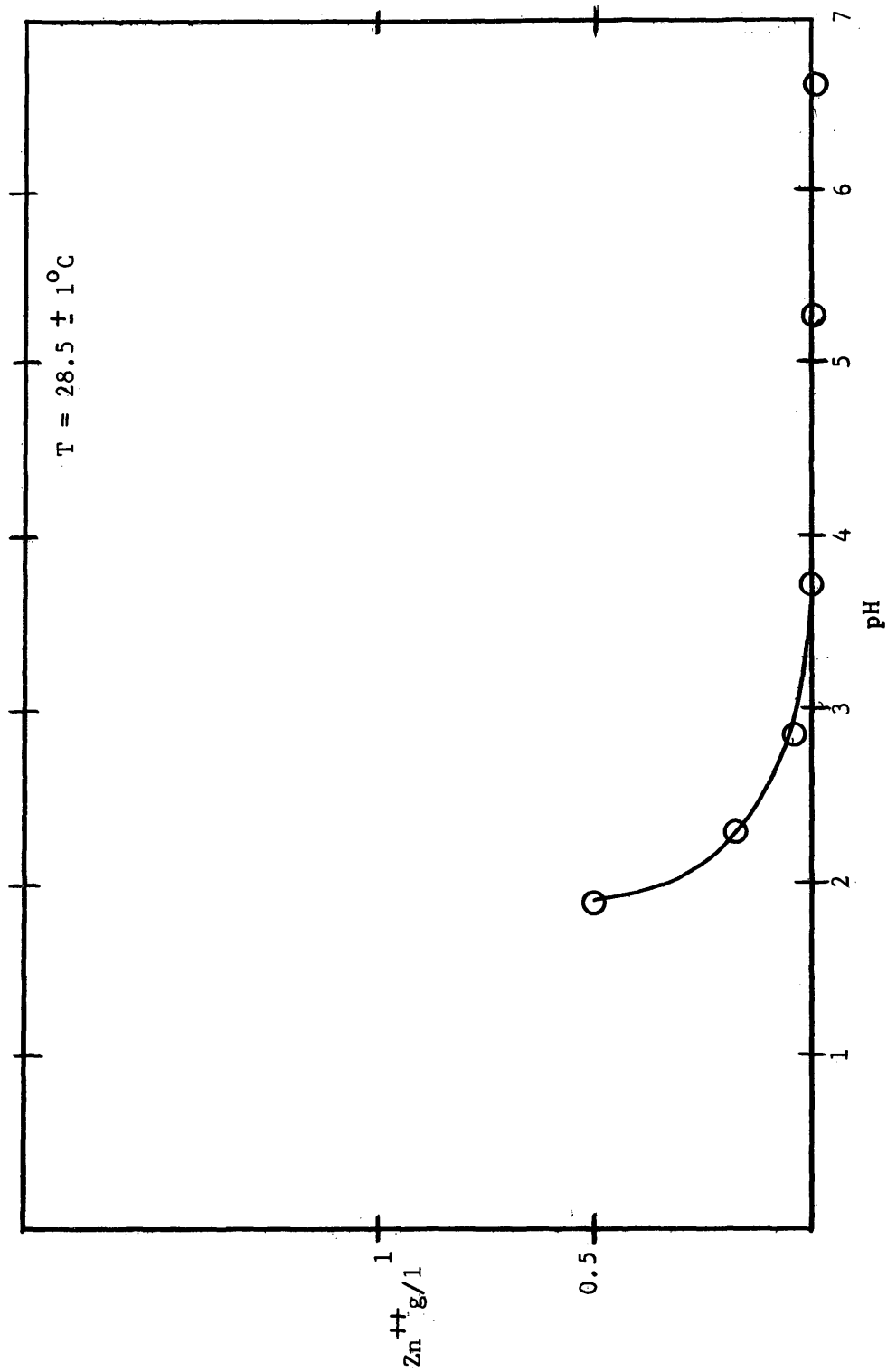


Figure 16 ZnO Solubility vs. pH in H₂SO₄ Solution



DISCUSSION

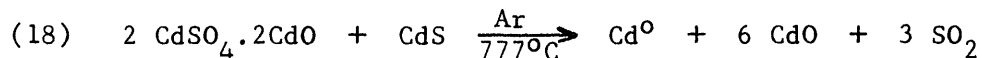
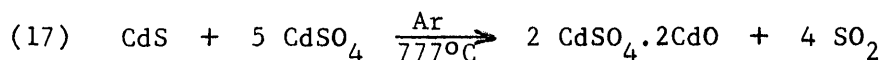
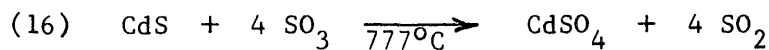
Stability Diagrams

The stability diagrams appear to be valid because they predicted the phases present after roasting. However, one must consider these diagrams (Figures 1 - 5) as only approximate for the roasting experiments in question (Table 4) because in no instance does the experimental total pressure (Table 3) equal the total pressure used to construct the stability diagrams. Appendices II through VII demonstrate how the stability diagrams can be corrected to accurately predict the phase present after roasting. Since only air and SO_2 were used it was impossible to reduce the total pressure of SO_3 , SO_2 , and O_2 to 0.2 atmospheres. Therefore the stability diagrams had to be corrected to match the total pressure for the roasting experiments in question.

Sulfation of CdS

The conversion of CdS to CdSO_4 is not easily accomplished at 777°C and above. Upon analyzing the product from positions 4, 5, and 7 (Figure 8), one finds Cd, CdSO_4 , and CdO. In order to investigate this occurrence, a mixture of CdS and CdSO_4 was roasted at 777°C . Table 6 gives the results of the tests.

From Tables 5 and 6 the following reaction mechanism is proposed:



If the product from reaction (18) is placed in a roasting atmosphere (run 2, Table 6), no sulfation of CdO occurs. However, if reagent grade CdO is roasted under the same conditions (Table 5, position 5), 79.3 percent of the CdO is converted to CdSO₄. Further x-ray studies of this product were made to learn more about the way Cd is deposited with CdO.

If a diffraction pattern of the product of reaction (18) is made without first grinding it in a mortar, the relative intensities of CdO to Cd are much closer than if the material is ground before it is analyzed. This fact could mean that Cd is a coating on CdO. Reactions (17) and (18) provide another clue. Since the CdSO₄·2CdO is formed first, the Cd will be deposited at the interface between the two reactive species. At this interface only the CdSO₄ part of the CdSO₄·2CdO is reacting. This reaction leaves behind CdO. Therefore, Cd should deposit on the surface of CdO. Further evidence for this occurrence was the absence of sulfation when this product was placed in a sulfating atmosphere even though there appeared to be much more CdO than Cd.

The coating of Cd hinders the sulfation of CdO because it prevents the sulfating atmospheres from reaching the CdO surface. This coating cannot be pure cadmium because it would volatilize within a short time.

It appears to be some type of chemical intermediate, made up of Cd and CdO that cannot be easily driven from the CdO surface even at high temperatures.

Preparation of $\text{CdSO}_4 \cdot 2\text{CdO}$ in Evacuated Vycor Capsules

Evacuated Vycor capsules were used to hold pellets made of a mixture of CdO and CdSO_4 . The proportion of CdO to CdSO_4 used during the runs is shown in Table 7.

There appears to be some discrepancy in runs 4 and 5. The high CdO percentage seems to be out of line with the other data. However, it is probably due to the decomposition of CdSO_4 during drying. While the capsules containing the pellets were being evacuated, heat was applied to drive off moisture. This heat might have seriously reduced the amount of CdSO_4 . Thus, a greater percentage of $\text{CdSO}_4 \cdot 2\text{CdO}$ was produced on run 5 than on run 4. Theoretically, run 4 should produce 100 percent $\text{CdSO}_4 \cdot 2\text{CdO}$ because the stoichiometric proportion of CdSO_4 to CdO was used. However, during drying some CdSO_4 was decomposed, so a complete conversion to $\text{CdSO}_4 \cdot 2\text{CdO}$ was impossible. Since run 5 started with a slight excess of CdSO_4 some decomposition would actually increase the amount of $\text{CdSO}_4 \cdot 2\text{CdO}$ found. Thus, run 5 could conceivably have more $\text{CdSO}_4 \cdot 2\text{CdO}$ than run 4.

The important point is that only one diffraction pattern was found for basic cadmium sulfate over the whole range of CdO and CdSO_4 molar ratios. Therefore, only one basic sulfate of cadmium exists, and it appears to be $\text{CdSO}_4 \cdot 2\text{CdO}$.

Cd-Zn-Pb-S-O System

Roasting the mechanical mixture of CdO, PbO, and ZnO produced the desired products with no inter-metallic compounds formed. Therefore, Figure 5 is a valid diagram.

Cadmium Recovery from Flue Dust

The raw flue dust contains about 95 percent water-soluble cadmium. It is present either as the chloride or the sulfate. The high percentage of water-soluble cadmium is unusual because this material is processed as though most of the cadmium was water-insoluble. By referring to Figures 10 and 11, one can see that all but approximately 5 percent of the cadmium can be removed by leaching with water. Although some zinc dissolves with the cadmium, there is still a 2:1 ratio of cadmium to zinc (raw flue dust has about a 4:1 ratio zinc to cadmium). The question of whether or not it is worthwhile to remove the final 0.5 percent cadmium is left unanswered.

The remaining cadmium could be present as a sulfide, basic sulfate, or an oxide. X-ray patterns of the flue dust showed only the sulfide present. Because it appeared that cadmium sulfide was the main source of residual cadmium, Table 5 was used to help provide a clue to the best roasting techniques. For run 1, position 5, and position 7 were chosen for roasting. The flue dust was held under the conditions of position 5 for 1.27 hours. The purpose of this position was to convert CdS to CdSO₄ without subliming too much of the sulfide. The flue dust was then placed under the conditions of position 7 for 6 hours to oxidize

any $\text{ZnO} \cdot 2\text{ZnSO}_4$ that may have formed to ZnO . The conditions for runs 2 and 3 are described in Figures 11 and 12. The loss of cadmium due to sublimation for runs 1, 2, and 3 (Figures 10, 11, and 12) is summarized in Table 13.

Table 13

CHANGE in CADMIUM DISTRIBUTION
DUE to VARYING ROASTING CONDITIONS

Run	Percent Cadmium Sublimed	Percent Water- Insoluble Cd in Boat	Percent Water- Soluble Cd in Boat
1	7.34	19.58	73.1
2	2.47	21.18	76.4
3	10.77	5.47	83.8

The results of Table 13 are in agreement with the findings shown on Table 5 for CdS . One would expect position 5 (run 1) to give worse results than run 2 because very little CdSO_4 was produced from CdS at this position (Table 5). Position 1 on Table 5 recorded the best conversion of CdS to CdSO_4 with very little sublimation. Similarly Table 13, run 2, shows a much lower percentage of sublimed cadmium than run 1. Run 3 (Table 13) illustrates that higher temperatures have a retarding effect on the conversion of CdS to CdSO_4 . This outcome agrees with the results found in position 2 for CdS on Table 5. However, the amount of zinc found with the water-soluble cadmium is greatly increased if it is roasted at position 2 for the entire roasting operation. This increase is shown in Table 14.

*Table 14
CHANGE in ZINC DISTRIBUTION DUE to
VARYING ROASTING CONDITIONS

<u>Run</u>	<u>Grams Soluble Cd in Boat</u>	<u>Grams Soluble Zn in Boat</u>	<u>Percent Overall Cd Recovery</u>
1	0.364	0.739	98.9
2	0.384	0.743	98.9
3	0.459	15.03	99.7

* Based on 100 grams of raw flue dust.

CONCLUSIONS

The stability diagrams not only were helpful in selecting the proper roasting conditions, but also proved to be accurate if the proper corrections were made.

The diagrams shown in Figures 10 through 12 record recoveries of at least 98.9 percent cadmium. If flow diagram 12 is used, a great deal of zinc will be found with the cadmium since roasting is carried out within the stability region of $ZnSO_4$. If, however, roasting is performed in the stability region of ZnO (Figures 10 and 11), very little of the total amount of zinc is found with the cadmium.

The roasting of CdO to $CdSO_4$ was straightforward and without complications. Almost complete conversion was obtained at $917^{\circ}C$. On the other hand, CdS was much more difficult to roast to the sulfate. If the roasting temperature was too high (greater than $777^{\circ}C$ for this study), cadmium metal would coat the surface of CdO formed from CdS , and prevent it from being sulfated. Apparently the only sulfation that occurred was when Cd or CdS volatilized and was sulfated in the gas stream. Nevertheless, this study shows that CdS can be converted

(slowly) to CdSO_4 at 650°C under the conditions of position 1, Table 5, with very little sublimation of the sulfide. However, it is doubtful that under these conditions equilibrium was obtained between SO_3 , SO_2 , and O_2 since no catalyst was used. According to Sommer and Kellogg (1959, p. 742-744), the rate of oxidation of ZnS is dependent upon the presence of SO_3 , and the amount of SO_3 available for reaction is controlled by the presence of a catalyst (V_2O_5). Further study concerning the conversion of CdS to CdSO_4 is necessary. Specifically, a study should be made of the reaction mechanism at 650°C that allows CdS to be converted to CdSO_4 with little sublimation of the sulfide at high oxygen potentials. A catalyst should be used to ensure an equilibrium amount of SO_3 present. Another study at 777°C for the same reaction would also be desirable in order to provide more information concerning the mechanism described in this paper.

Another area in which much information is needed is that of reaction kinetics. Reactor design might play a very important role in accelerating the conversion of CdS and CdO to CdSO_4 . For instance, a fluidized bed reactor might cut reaction time to only a fraction of the time required in a conventional hearth-type roaster.

The solubility information concerning $\text{ZnO}\cdot 2\text{ZnSO}_4$ might prove helpful in deciding the best operating temperature for roasting. Since the basic sulfate has a limited solubility, only a certain amount of Zn would be found with the Cd .

SUMMARY

Several roasting experiments were made to demonstrate the validity of the Cd-S-O, Zn-S-O, Pb-S-O, and Cd-Zn-Pb-S-O stability diagrams. Roasting tests were made concerning the ease with which CdS and CdO could be converted to CdSO_4 at various temperatures and gas-phase compositions. Also $\text{CdSO}_4 \cdot 2\text{CdO}$ was prepared using two different techniques.

Three separate roasting experiments were conducted with the flue dust. The effect of temperature and roasting atmosphere was demonstrated.

Experiments regarding the solubility of CdO, $\text{CdSO}_4 \cdot 2\text{CdO}$, ZnO, $\text{ZnO} \cdot 2\text{ZnSO}_4$ at various pH values were made. The pH was lowered using H_2SO_4 .

APPENDIX I. Summary of Free-Energy Equations used for the
Stability Diagrams

Equation Number	ΔG° (cal mole ⁻¹)
(1)	38,700 - 22.0 T
(2)	86,000 + 9.2 T log T - 87.0 T
(3)	25,010 + 5.562 T log T - 40.52 T
(6)	-168,000 - 4.70 T log T + 84.2 T
(7)	-375,000 - 2.9 T log T + 127 T
(8)	-96,330 + 2.10 T log T + 13.34 T
(9)	53,730 - 45.21 T
(10)	39,280 - 30.87 T
(11)	57,190 + 7.60 T log T - 65.63 T
(12)	74,000 + 16.81 T log T - 97.40 T
(13)	87,920 + 16.81 T log T - 104.08 T
(14)	71,380 + 16.81 T log T - 85.47 T
(15)	72,870 - 30.70 T

APPENDIX II. Calculation of Gas Composition Needed to Convert
 CdSO_4 to $\text{CdSO}_4 \cdot 2\text{CdO}$

Air was mixed with SO_2 to form an equilibrium mixture of O_2 , SO_3 , and SO_2 for roasting. For the conversion of CdSO_4 to $\text{CdSO}_4 \cdot 2\text{CdO}$, an equilibrium gas mixture must be used to render CdSO_4 unstable so that $\text{CdSO}_4 \cdot 2\text{CdO}$ would be formed. The gas mixture was selected in the following way:

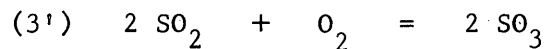
With the help of the $\text{CdSO}_4 \cdot 2\text{CdO}$ stability diagram, a temperature was selected within the stability region of $\text{CdSO}_4 \cdot 2\text{CdO}$.

$$T = 1245^\circ\text{K}$$

Next, for the determination of a point on the isotherm, a ratio between O_2 and P_T ($P_T = P_{\text{O}_2} + P_{\text{SO}_2} + P_{\text{SO}_3}$) was selected.

$$(19) \quad \frac{P_{\text{O}_2}}{P_{\text{O}_2} + P_{\text{SO}_2} + P_{\text{SO}_3}} = 0.7$$

Rewriting reaction (3) in reverse and defining condition (20), the author constructed the following table:



$$(20) \quad P_{\text{O}_2} + P_{\text{SO}_2} + P_{\text{SO}_3} + P_{\text{N}_2} = .9474$$

ORGANIZATION USED to SOLVE for EQUILIBRIUM

PRESSURES of SO_3 , SO_2 , and O_2

Gas	Initial		Final		
	Moles	Moles	X_i	P_i	
O_2	$.21a^*$	$.21a - x^{**}$	$\frac{.21a - x}{a + 1 - x}$	$\left[\frac{.21a - x}{a + 1 - x} \right]$	$[.9474]$
SO_2	1	$1 - 2x$	$\frac{1 - 2x}{a + 1 - x}$	$\left[\frac{1 - 2x}{a + 1 - x} \right]$	$[.9474]$
SO_3	0	$2x$	$\frac{2x}{a + 1 - x}$	$\left[\frac{2x}{a + 1 - x} \right]$	$[.9474]$
N_2	$.79a$	$.79a$	$\frac{.79a}{a + 1 - x}$	$\left[\frac{.79a}{a + 1 - x} \right]$	$[.9474]$
TOTAL		$a + 1 - x$			

Using this table to substitute into equation (3') and (20) "a" can be found:

$$(3') \quad \frac{\left[\frac{2x}{a + 1 - x} (.9474) \right]^2}{\left[\frac{.21a - x}{a + 1 - x} (.9474) \right] \left[\frac{1 - 2x}{a + 1 - x} (.9474) \right]^2} = K_3'$$

* a = moles of air
 ** x = moles reacted

$$(19) \frac{\frac{.21a - x}{a + 1 - x}}{\left[\frac{.21a - x}{a + 1 - x} + \frac{1 - 2x}{a + 1 - x} + \frac{2x}{a + 1 - x} \right]} = 0.7 \quad (.9474)$$

$$K_3 = \frac{(P_{SO_2}) (P_{O_2})^{\frac{1}{2}}}{(P_{SO_3})}$$

$$\log K_3 = 8.86 - \frac{5470}{T} - 1.216 \log T$$

$$K_{3'} = \frac{1}{K_3^2}$$

$$\log K_3 = 8.86 - 4.39 - 3.76 = 0.71$$

$$K_3 = 5.14 \quad ; \quad K_{3'} = (0.1946)^2$$

Taking the square root of both sides

$$(3') \quad \frac{P_{SO_3}}{P_{SO_2}} = (0.1946) \frac{0.21a - x}{a + 1 - x} \quad (.9474)^{\frac{1}{2}} = \frac{2x}{1 - 2x}$$

$$\frac{0.21a - x}{a + 1 - x} = \frac{4}{(0.1946)^2 (0.9474)} \frac{x^2}{(1 - 2x)^2} = (1.1115 \times 10^2) \frac{x^2}{(1 - 2x)^2}$$

$$(19') \quad \frac{.21a - x}{.21a - x + 1} = 0.7$$

$$0.21a - x = 0.147a - 0.7x + 0.7$$

$$0.063a = 0.3x + 0.7$$

$$a = 4.762x + 11.111$$

$$418.3 x^3 + 1346.6 x^2 = -9.332 x + 9.332 x^2 + 2.333$$

$$x^3 + 3.197 x^2 + 2.231 x \cdot 10^{-2} - 5.577 x \cdot 10^{-3} = 0$$

$$\underline{\underline{\text{SOLUTION: } x = 0.0382}}$$

Check

$$x_{O_2} = \frac{0.21 (11.29) - 0.0382}{12.29 - 0.0382} = \frac{2.33}{12.25} = 0.1902$$

$$x_{SO_3} = \frac{0.0764}{12.25} = 0.624 \times 10^{-2}$$

$$x_{SO_2} = \frac{0.9236}{12.25} = 0.0754$$

$$x_{N_2} = \frac{0.79 (11.29)}{12.25} = \frac{8.919}{12.25} = 0.7281$$

	$\Sigma X_i = 1$
	0.7281
	0.1902
	0.0062
	<u>0.0754</u>
	0.9999 = ΣX_i

$$\frac{P_{SO_3}}{P_{SO_2} P_{O_2}^{\frac{1}{2}}} = 0.1946$$

$$\frac{6.24 \times 10^{-3}}{7.54 \times 10^{-2}} (.1902 \times .9474)^{\frac{1}{2}} = 0.1946$$

$$\frac{8.276 \times 10^{-2}}{0.4249} = 19.46 \times 10^{-2} = .1946$$

•• Checks

$$\frac{\text{Air}}{SO_2} = \frac{11.29}{1} \quad \text{at} \quad \begin{array}{l} 1245^\circ\text{K} \\ \text{or} \\ 972^\circ\text{C} \end{array}$$

APPENDIX III. Calculation of P_T for Determining the Shift in the $\text{CdSO}_4 \cdot 2\text{CdO}$ Stability Diagram.

In no instance does P_T equal 0.2. However, all of the stability diagrams were made by using 0.2 as the total pressure. A correction must be made to show that these experimental runs still lie within the intended region.

As an example, run H was made at 972°C and $P_T = 0.2573$; therefore, the $\text{CdSO}_4 \cdot 2\text{CdO}$ stability line will move due to the change in P_T . The degree of shift in this stability line is found in the following way:

$$(4) \quad (P_{\text{SO}_2}) (P_{\text{O}_2})^{\frac{1}{2}} = K_{(1)}K_{(3)}$$

$$(21) \quad P_{\text{O}_2} + P_{\text{SO}_2} + P_{\text{SO}_3} = P_T$$

Run H was made at 70 percent O_2 . To calculate the shift in the curve:

$$(19') \quad P_{\text{O}_2} = 0.7 P_T$$

Combination of (19') and (21) gives:

$$P_T - 0.7 P_T = P_{\text{SO}_2} + P_{\text{SO}_3}$$

$$(22) \quad 0.3 P_T = P_{\text{SO}_2} + P_{\text{SO}_3}$$

A temperature must now be chosen so that P_T can be found because it is difficult to calculate ahead of time the temperature that corresponds exactly to the P_T in question. The method used was to approximate the temperature. Then plotting P_T against T at constant P_{O_2} (namely $P_{O_2} = 0.7$) makes it possible to find the shift of that point on the stability line.

The temperature chosen was: $T = 1220^\circ\text{K}$. With this information $K_{(1)}$ and $K_{(3)}$ can be determined, and equation (4) can be rewritten:

$$(4') \quad P_{SO_2} = \frac{K_1 K_3}{(0.7 P_T)^{\frac{1}{2}}}$$

This equation together with equations (22') and (3) can now be solved simultaneously.

$$K_3 = \frac{P_{SO_2} (0.7 P_T)^{\frac{1}{2}}}{P_{SO_3}} \quad \text{and at } T = 1220^\circ\text{K}$$

$$K_1 = 7.41 \times 10^{-3}$$

$$K_3 = 4.26$$

$$K_1 = P_{SO_3}$$

$$\text{Therefore } P_{SO_3} = 7.41 \times 10^{-3}$$

$$(4') \quad P_{\text{SO}_2} = \frac{4.26 \times 7.41 \times 10^{-3}}{(0.7 P_T)^{\frac{1}{2}}} = \frac{3.16 \times 10^{-2}}{(0.7 P_T)^{\frac{1}{2}}}$$

$$(22) \quad 0.3 P_T = P_{\text{SO}_2} + 7.41 \times 10^{-3}$$

$$(22') \quad P_T = \frac{P_{\text{SO}_2} + 7.41 \times 10^{-3}}{0.3}$$

$$(22'') \quad P_{\text{SO}_2} = 0.3 P_T - 7.41 \times 10^{-3}$$

$$(4''') \quad P_{\text{SO}_2}^2 = \frac{10^{-3}}{0.7 P_T}$$

Combination of (4''') and (22') gives:

$$(23) \quad P_{\text{SO}_2}^2 = \frac{10^{-3}}{0.7} \left[P_{\text{SO}_2} + 7.41 \times 10^{-3} \right]$$

$$0.3$$

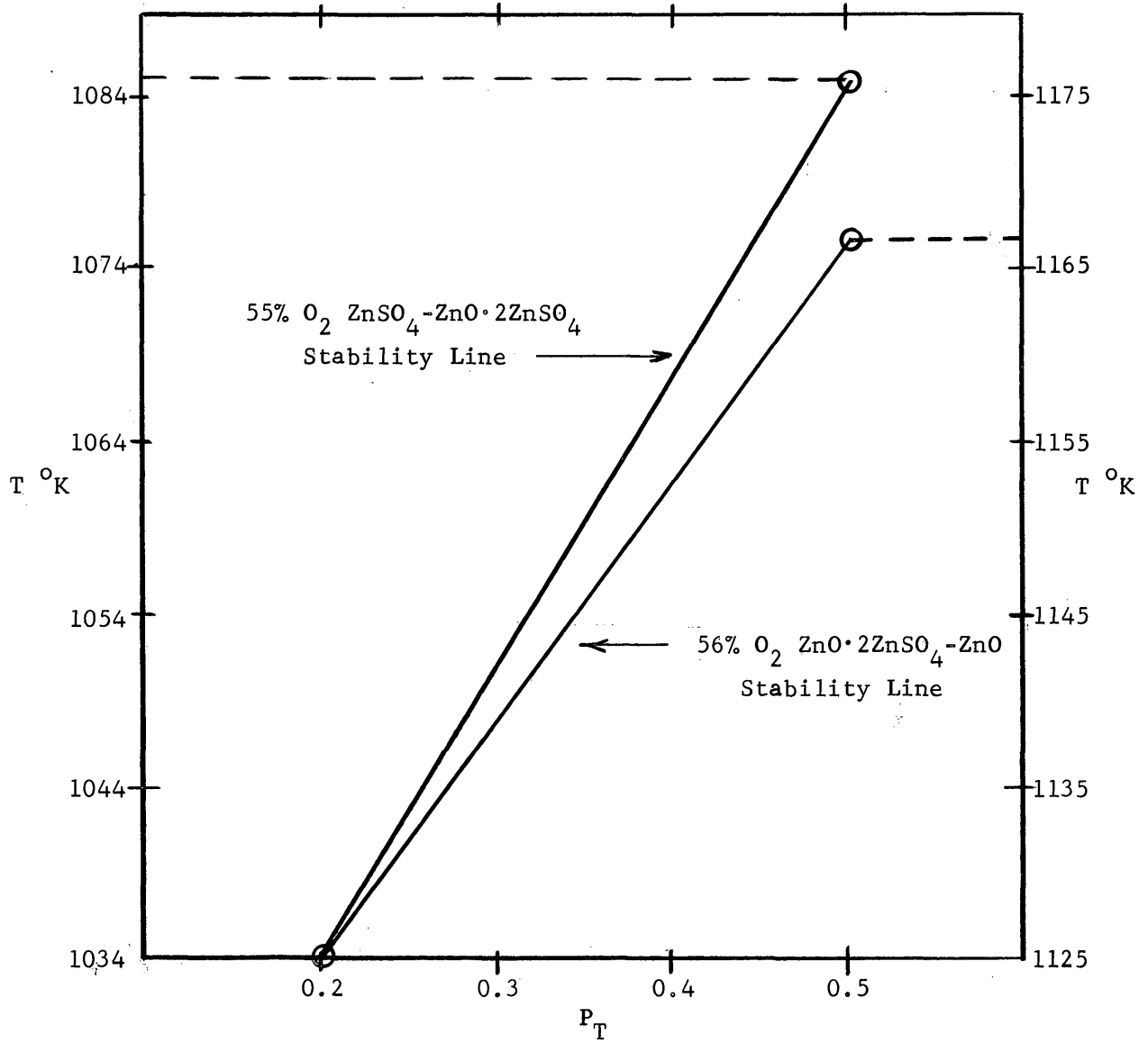
$$(23') \quad P_{\text{SO}_2}^3 + 7.41 \times 10^{-3} P_{\text{SO}_2}^2 - 1.429 \times 10^{-3} = 0$$

$$\text{SOLUTION: } P_{\text{SO}_2} = 7.303 \times 10^{-2}$$

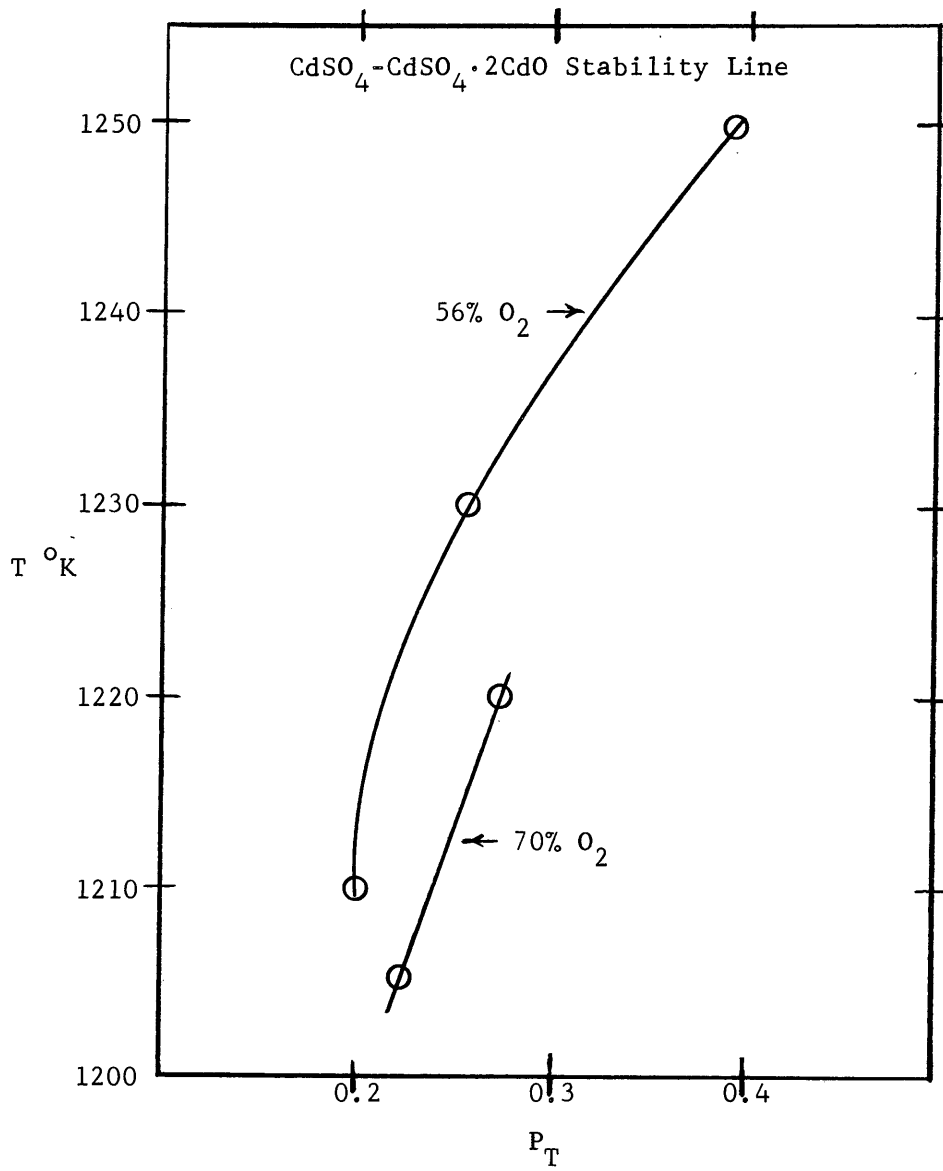
$$(4''''') \quad P_T = \frac{1.429 \times 10^{-3}}{(7.303 \times 10^{-2})^2} = \frac{1.429 \times 10^{-3}}{53.33 \times 10^{-4}} = .2680$$

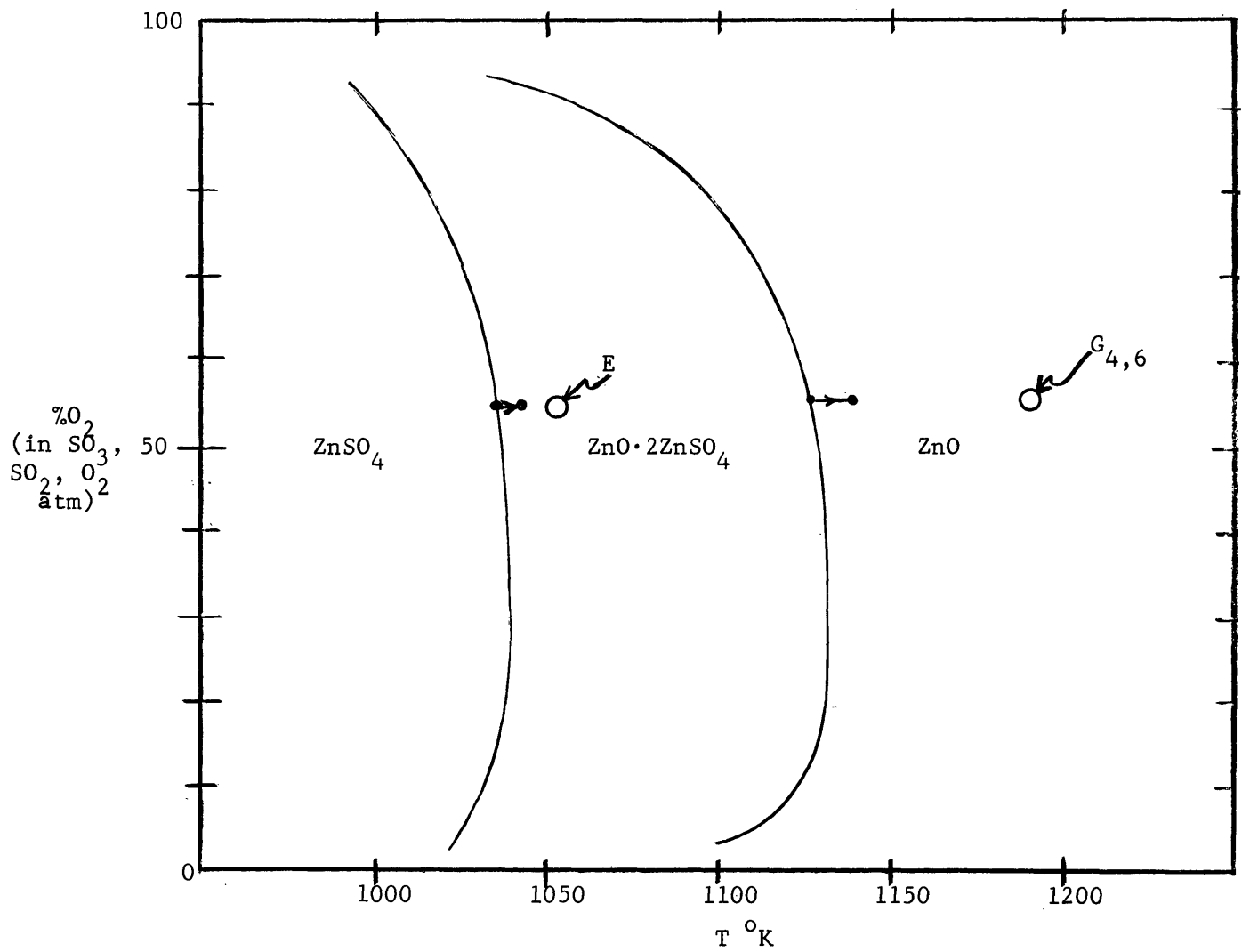
Once P_T is found (Appendix III) a plot is made (Appendices IV and V). Now, simply from the knowledge of P_T (Appendix II) for run H, a temperature is obtained. This temperature represents the change in the position of the CdSO_4 - $\text{CdSO}_4 \cdot 2\text{CdO}$ stability line at $P_{\text{O}_2} = 0.7 P_T$ (Appendices VI and VII).

APPENDIX IV. Variation of P_T with T at Constant Percent O_2 for the $ZnO \cdot 2ZnSO_4$ Stability Diagram

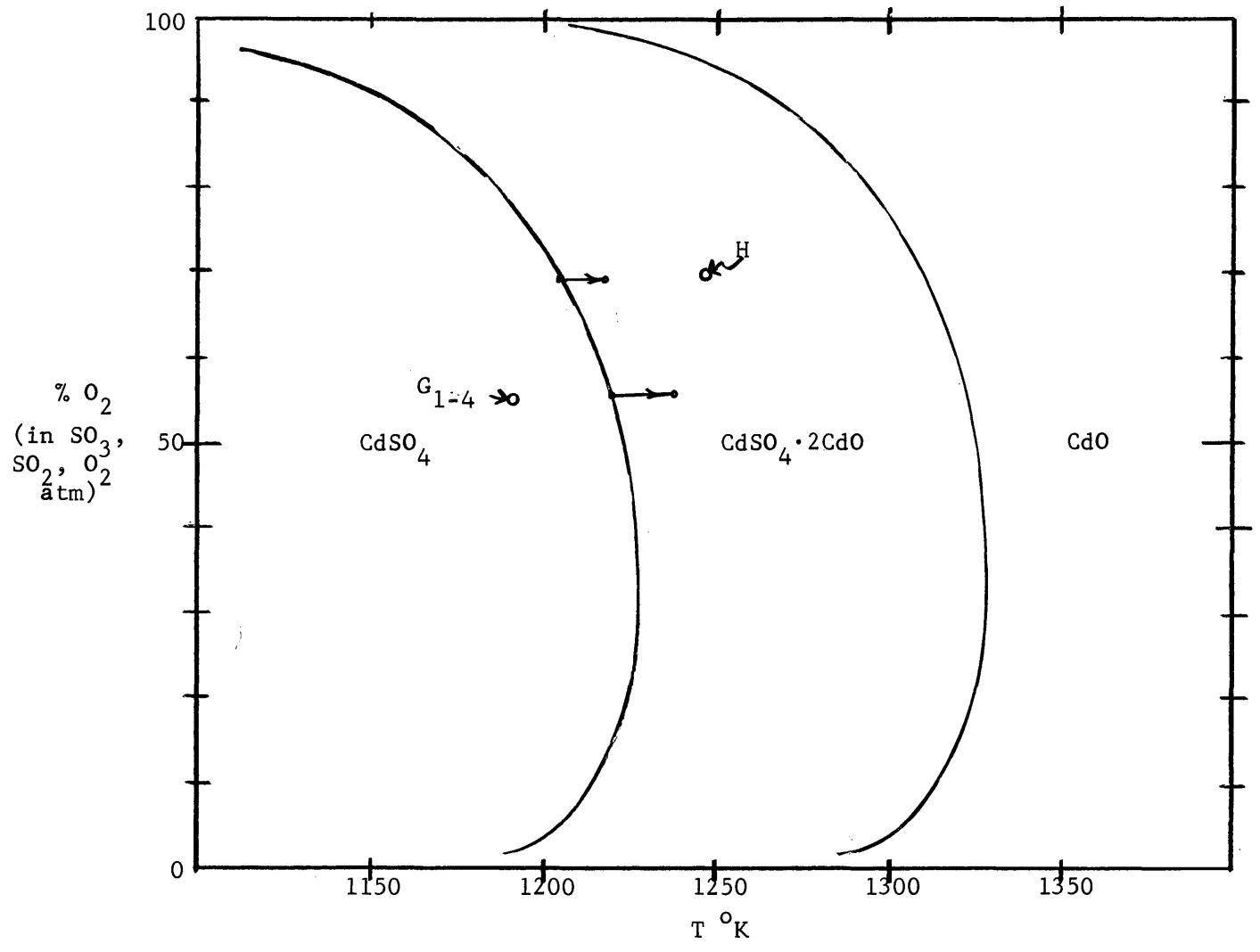


APPENDIX V. Variation of P_T with T at Constant Percent O_2 for the $CdSO_4 \cdot 2CdO$ Stability Diagram



APPENDIX VI. Shift in the $\text{ZnO} \cdot 2\text{ZnSO}_4$ Stability Diagram for Runs E & G

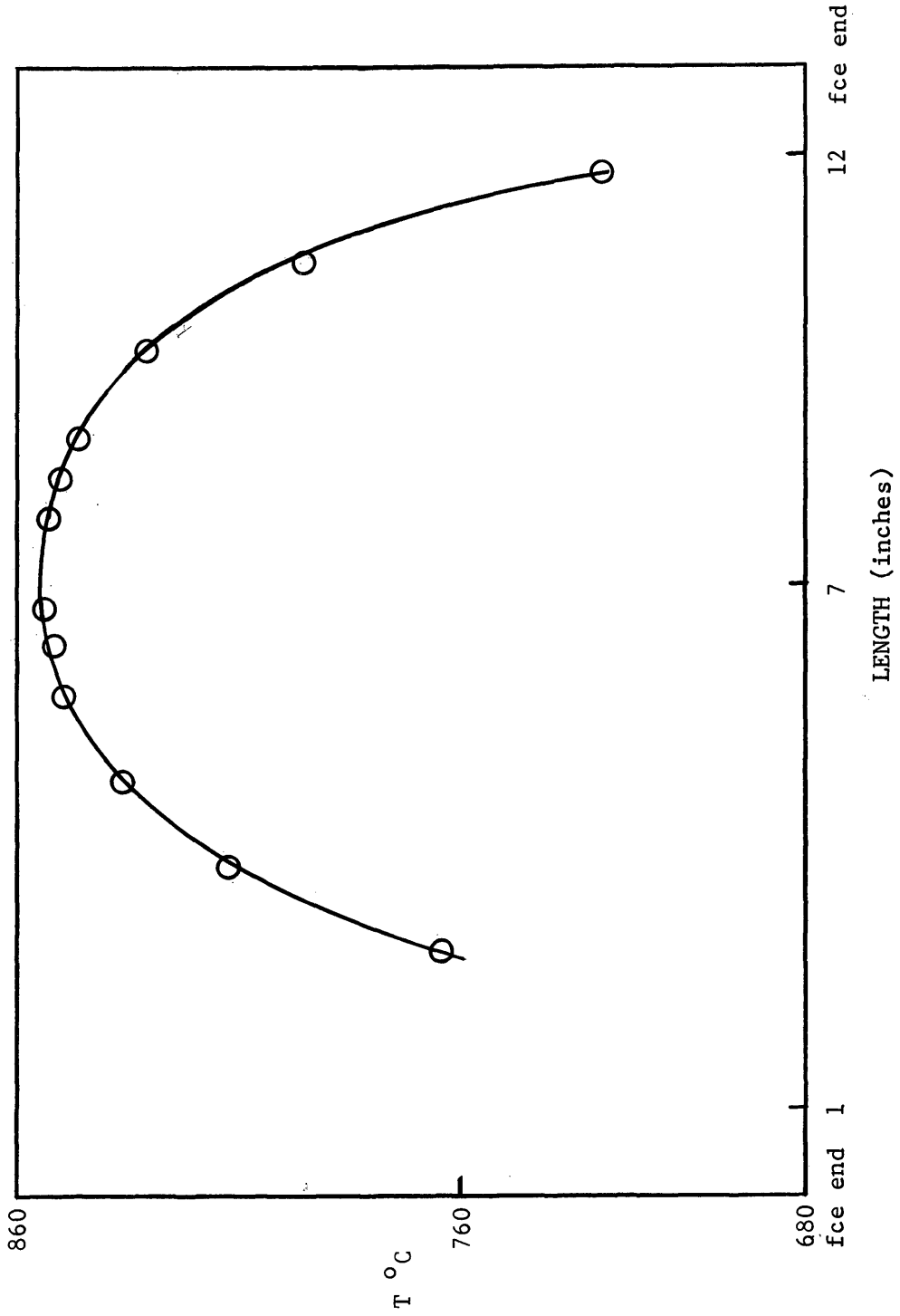
APPENDIX VII. Shift in the $\text{CdSO}_4 \cdot 2\text{CdO}$ Stability Diagram for Runs G & H



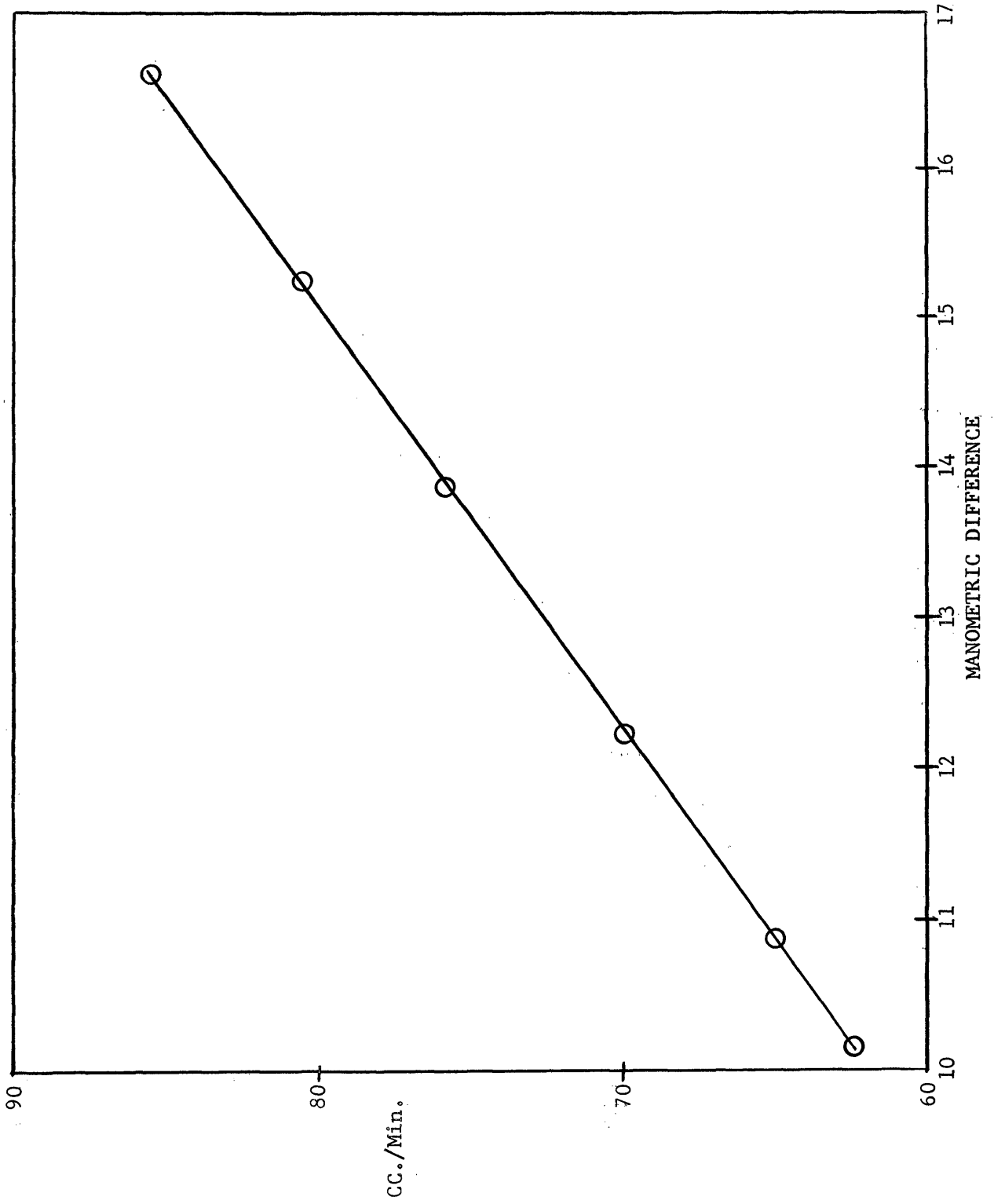
APPENDIX VIII. Thermocouple Standardization

Temp.	Millivolt Std.	Millivolt Pt-Pt, 13% Rb	
		Thermocouple	T
699	6.708	6.698	698
798	7.900	7.898	798
838	8.394	8.389	838
887	9.009	8.980	885
935	9.625	9.611	934
982	10.234	10.222	981

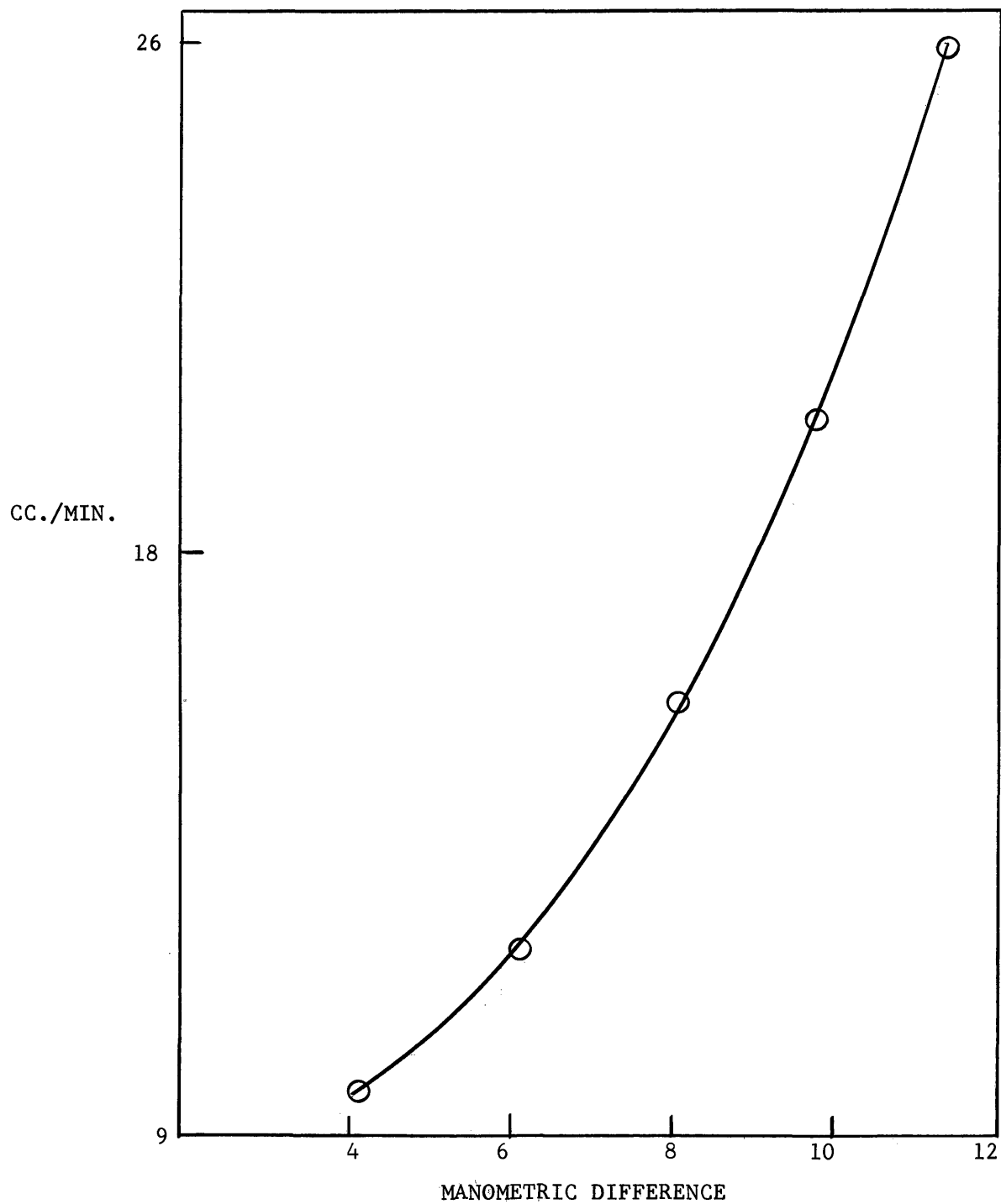
APPENDIX IX. Roasting Furnace Temperature Profile



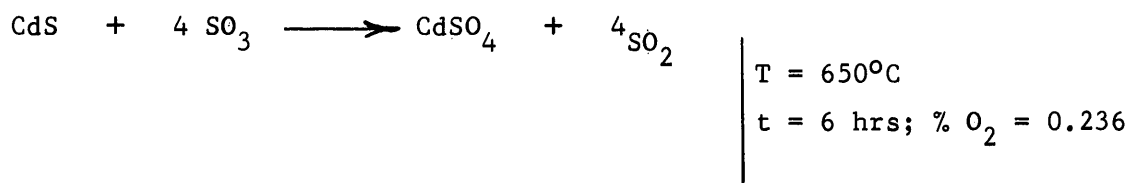
APPENDIX X. Calibration of the Air Flow-Rate Meter



APPENDIX XI, Calibration of SO₂ Flow-Rate Meter



APPENDIX XII. Sublimation and Degree of Reaction Calculation



wt. CdS = 4.21723 g. (initial wt)

wt. CdSO₄ expected = 6.08546 g.

wt. CdSO₄ found in boat = 0.08501 g.

MASS BALANCE

CdS reacted + CdS remaining + CdS subliming = CdS start

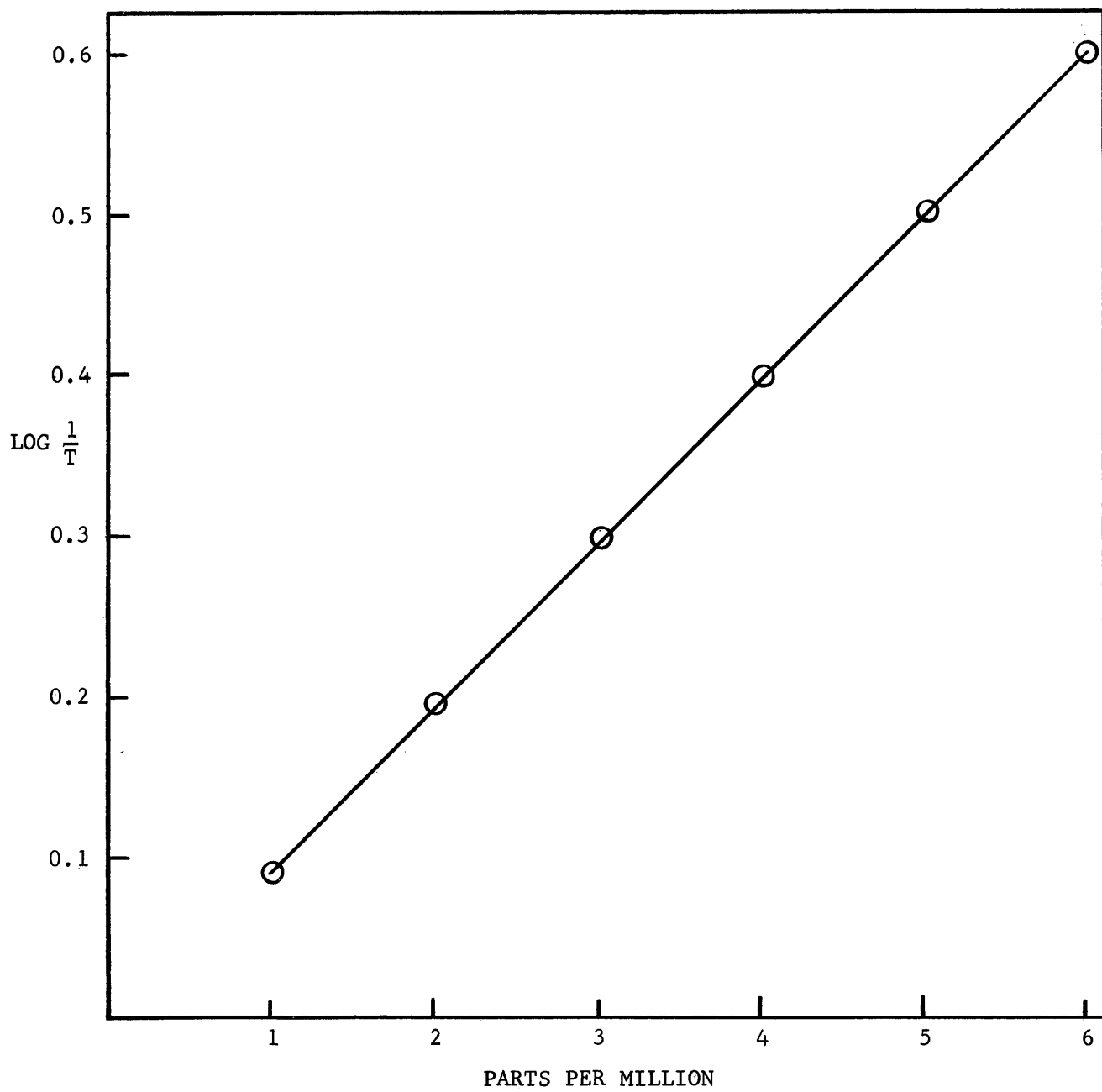
$$\begin{aligned} \text{CdS}_{\text{Subl.}} &= 4.21723 \text{ g.} - (.05891 \text{ g.} + 2.89657 \text{ g.}) \\ &= 1.16175 \text{ g.} \end{aligned}$$

$$\% \text{ Sublimation} = \frac{1.16175 \text{ g.}}{4.21723 \text{ g.}} \times 100 = 27.55\%$$

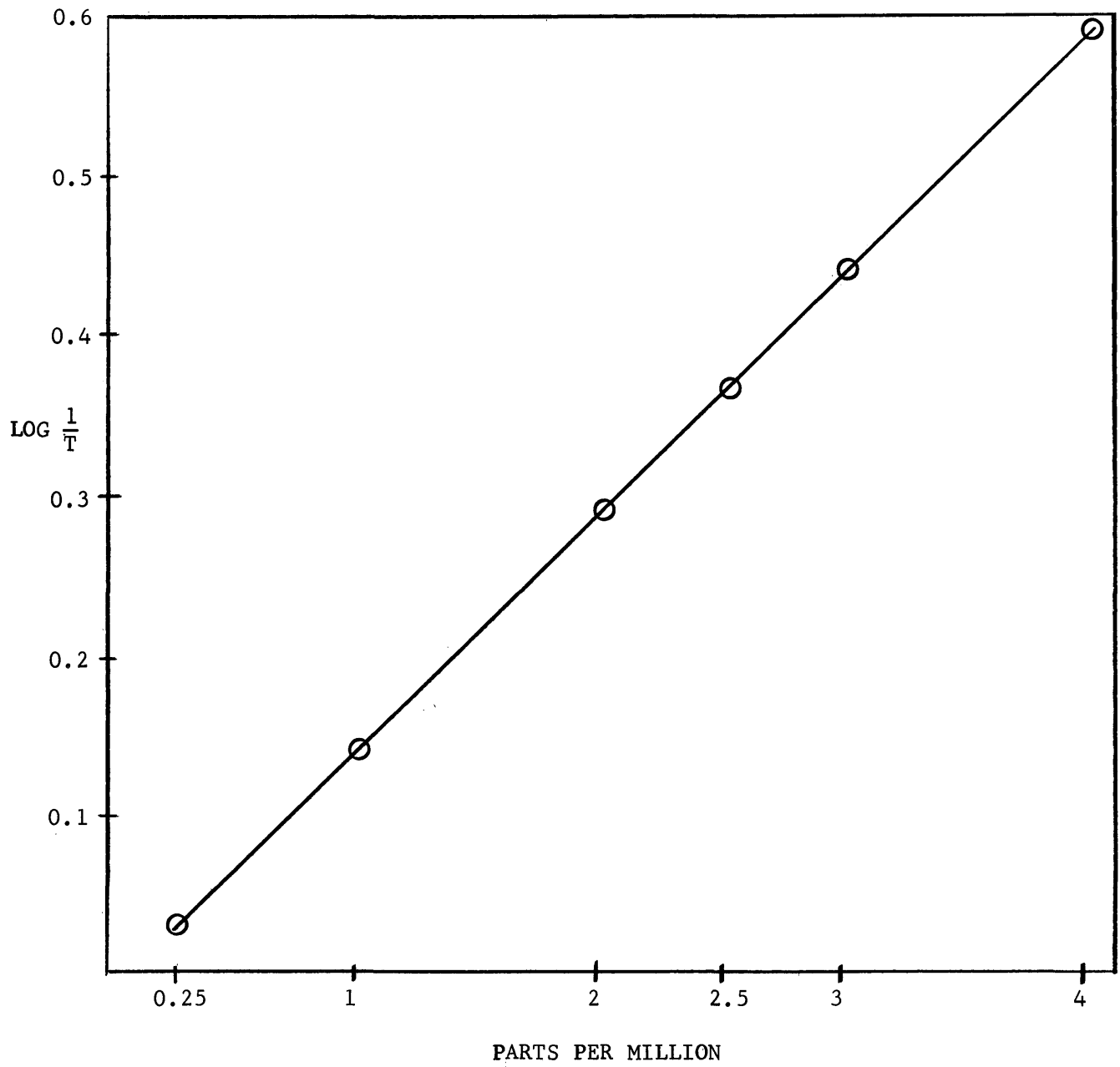
Degree of conversion in boat:

$$\frac{0.08501 \text{ g.}}{6.08546 \text{ g.}} \times 100 = 1.40\%$$

APPENDIX XIII. Standard Curve for Zinc Analysis with Atomic Absorption



APPENDIX XIV. Standard Curve for Cadmium Analysis with Atomic Absorption



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VITA

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