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William L. Hallerberg

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ZINC SULFIDE - SULFATE
REACTION PRESSURES

by

William L. Hallerberg

A

Thesis

Submitted to the Faculty of the
University of Missouri School of Mines and Metallurgy
in partial fulfillment of the requirements for the
Degree of
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Approved by:

Andrew Larson Advisor   R. E. Moore

H. P. Leighly Jr.   W. P. Tappmeyer

ABSTRACT

A static manometric method was used to find the equilibrium reaction pressure as a function of temperature for the reaction:

$$11\ ZnSO_4 + ZnS \rightarrow 4\ (ZnO\cdot 2ZnSO_4) + 4\ SO_2$$

From the reaction pressures, the standard free energy of the reaction was found to be:

$$\Delta F^\circ = +51{,}320 - 36.68\ T$$

Using thermodynamic data for $ZnSO_4$, ZnS and SO_2 the standard free energy of formation of the basic salt $ZnO\cdot 2ZnSO_4$ was found to be:

$$\Delta F^\circ = -377{,}000 - 65.9\ T \quad \text{cal/mole}$$

in the temperature range 350 to 420° C.

Above 420° C. the reaction,

$$2\ ZnS + 3\ (ZnO\cdot 2ZnSO_4) \rightarrow 11\ ZnO + 8\ SO_2$$

proceeds.

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to Dr. A. H. Larson, Associate Professor of Metallurgical Engineering and to Dr. A. W. Schlechten, former Chairman of the Department of Metallurgical Engineering for their assistance and counsel during the course of this investigation.

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TABLE OF CONTENTS

LIST OF FIGURES

CHAPTER I

INTRODUCTION

Statement of the Problem.

The purpose of this investigation was to determine the reaction pressure as a function of temperature for the reaction:

$$11\ ZnSO_4 + ZnS \rightarrow 4\ (ZnO \cdot 2ZnSO_4) + 4\ SO_2$$

where $ZnO \cdot 2ZnSO_4$ is a stable intermediate phase in the sulfide-sulfate reaction mixture. From these data the standard free energy of formation of the intermediate basic sulfate phase can be calculated.

Organization of the Problem.

The problem was attacked experimentally by obtaining the pressure versus temperature relationship for the sulfide-sulfate reaction by a static manometric technique, incorporating the use of an all glass closed system with a glass spiral manometer. X-ray diffraction patterns were made to identify the solid reaction products.

Importance of the Study.

During the roasting of zinc sulfide ores the primary objective is the conversion of the ore to ZnO. However, deep in the bed of the roaster (hearth type), there may be a deficiency of oxygen and an excess of zinc sulfide. The question as to whether or not these conditions favor sulfate decomposition is of practical interest.

CHAPTER II

LITERATURE SURVEY

A substantial amount of information has been published concerning the decomposition of zinc sulfate both in the presence of zinc sulfide and in its absence. However, a few of the authors differ in their opinions as to whether a basic zinc sulfate is formed or not. Furthermore, those who advocate the presence of a basic sulfate in the decomposition reaction of zinc sulfate differ widely in their proposed stoichiometric formulae.

M. Trautz and S. Pakschwer[1] (1929), studying the general reaction, $MeS + 3\,MeSO_4 \rightarrow 4\,MeO + 4\,SO_2$ did some research on the Zn system. Their conclusion was that the existence of basic sulfates was doubtful, even though earlier literature suggested it.

This earlier literature may have been W. R. Ingalls[2] (1906) who said:

> "When the temperature is raised only to cherry red, neutral zinc sulfate, $ZnSO_4$, is split up into basic zinc sulfates and sulphuric and sulphurous anhydrides and oxygen. There is no record in chemical or metallurgical literature, so far as I have been able to discover, as to which of the several basic sulfates of zinc are produced during that process, except a remark in Plattner's ROSTPROZESSE that it is the tetrabasic sulfate ($ZnSO_4 \cdot 3ZnO$) which is formed."

About this same time H. O. Hofman[3] (1905) also mentioned Plattner's idea of the formation of $ZnSO_4 \cdot 3ZnO$. Hofman admited that a basic sulfate was formed but he did not commit himself as to the formula.

Later in a textbook, Hofman[4] (1922) stated that $ZnSO_4$ will decompose into SO_3 and $3ZnO \cdot 2SO_3$. His formula can also be represented as $ZnO \cdot 2ZnSO_4$.

I. P. Bardin[5] in his edited survey of metallurgy in the USSR mentioned sulfide-sulfate reaction rates but no mention whatsoever was made of any basic sulfate or intermediate phase. Bardin suggested the reaction mechanism for Cu, Pb, Cd, Fe and Zn as follows:

$$MeSO_4 + MeS \rightarrow 2\ Me + 2\ SO_4$$

$$MeSO_4 \rightarrow MeO + SO_2 + \tfrac{1}{2}\ O_2$$

Most of the more recent investigations mention the presence of the basic intermediate sulfate, although there is disagreement as to its composition.

Bui-Nam[6] (1959) proposed the existence of the basic sulfate $3ZnO \cdot 2SO_3$, ($ZnO \cdot 2ZnSO_4$), but he stated that to his knowledge it had never been found.

The work done in the USSR lead the investigators to different conclusions. V. V. Pechkovskii[7] (1957) says:

> "The thermochemical decomposition process of zinc sulfate, in the absence of admixtures, can be described by the following basic equations:
>
> $$ZnSO_4 \rightarrow ZnO + SO_3$$
>
> under these conditions we did not detect the presence of basic zinc sulfate among the solid calcination products."

Later on in his article, Pechkovskii stated that the major solid calcination products of zinc sulfate are zinc oxide, with oxygen, sulfur trioxide and sulfur dioxide present as the gaseous products.

J. S. Warner[8] (1961) suggested that any sulfate may or may not go through the intermediate basic sulfate phase.

In their investigations of the lead-sulfur-oxygen system, H. H. Kellogg and S. K. Basu[9] (1960) found cause to suggest the existence of the intermediate salts, $PbSO_4 \cdot PbO$, $PbSO_4 \cdot 2PbO$ and $PbSO_4 \cdot 4PbO$.

Using the static manometric method of analysis, incorporation a mercury manometer, Motoo and Toshiaki[10] (1947) studied the reaction pressure of $ZnSO_4$ and ZnS in combination. They contended that a basic sulfate was formed and that its formula is $3ZnO \cdot ZnSO_4$. Their reaction mechanism is as follows:

$$3\ ZnS + 13\ ZnSO_4 \rightarrow 4\ (3ZnO \cdot ZnSO_4) + 12\ SO_2$$

$$ZnS + 3\,(3ZnO\cdot ZnSO_4) \rightarrow 13\,ZnO + 4\,SO_2$$

In their investigation of the decomposition temperature of zinc sulfate, Ostroff and Sanderson[11] observed the formation of an intermediate phase, which, they said, was $3ZnO\cdot 2SO_3$. ($ZnO\cdot 2ZnSO_4$)

R. Schuhmann, Jr. reports in the chapter on the chemistry and physics of zinc technology which he wrote for Mathewson[12] (1959), "Some observers have considered the possible formation of basic zinc sulfates, such as $3ZnO\cdot 2SO_3$ ($ZnO\cdot 2ZnSO_4$) but evidence is not clear..."

Twidwell[13] (1962) investigated the influence of selected sulfides on the thermal decomposition rate of zinc sulfate. He found that the decomposition of $ZnSO_4$ in the presence of ZnS, CdS or Cu_2S yielded $ZnO\cdot 2ZnSO_4$. His reaction mechanism for $ZnSO_4$ and ZnS is as follows:

$$3\,ZnSO_4 + ZnS \rightarrow 4\,ZnO + 4\,SO_2$$

$$4\,ZnO + 8\,ZnSO_4 \rightarrow 4\,(ZnO\cdot 2ZnSO_4)$$

The overall initial reaction being:

$$11\,ZnSO_4 + ZnS \rightarrow 4\,(ZnO\cdot 2ZnSO_4) + 4\,SO_2$$

The final stage being:

$$4\,(ZnO\cdot 2ZnSO_4) + 8/3\,ZnS \rightarrow 44/3\,ZnO + 32/3\,SO_2$$

Adding the last two reactions, the overall reaction is found to be:

$$3\ ZnSO_4 + ZnS \rightarrow 4\ ZnO + 4\ SO_2$$

Twidwell identified the basic salt by X-ray diffraction analysis of various stoichiometric mixtures of ZnO and $ZnSO_4$.

T. R. Ingraham and H. H. Kellogg[14] (1962) presented a paper to the AIME in which they studied the zinc-sulfur-oxygen system. By thermogravimetric and X-ray analysis they identified an intermediate phase of $ZnO \cdot 2ZnSO_4$ upon the decomposition of pure $ZnSO_4$. Their reaction mechanism is:

Initial,

$$3\ ZnSO_4 \rightarrow (ZnO \cdot 2ZnSO_4) + SO_3$$

Final,

$$(ZnO \cdot 2ZnSO_4) \rightarrow 3\ ZnO + 2\ SO_3$$

Overall,

$$3\ ZnSO_4 \rightarrow 3\ ZnO + 3\ SO_3$$

Ingraham and Kellogg also calculated that for the reaction,

$$ZnO + 2\ ZnSO_4 \rightarrow (ZnO \cdot 2ZnSO_4)$$

$$\Delta H^\circ_{298} = -1650 \text{ cal.}$$

$$\Delta S^\circ_{298} = +1.13 \text{ eu.}$$

It is interesting to note that Ingraham and Kellogg's 'd' values from the X-ray diffraction of $ZnO \cdot 2ZnSO_4$ were very close to those of Twidwell.

The more recent investigations tend to point to the $ZnO \cdot 2ZnSO_4$ composition as the basic sulfate in the Zn-S-O system.

Perhaps this is but one of a number in that system. The question warrants further study.

CHAPTER III

THEORETICAL CONSIDERATIONS

Reaction Mechanism.

One approach to the study of the stability of the basic sulfate, $ZnO \cdot 2ZnSO_4$, or more specifically the free energy of formation of the salt, is to consider the overall reaction,

$$1/4\ ZnS + 3/4\ ZnSO_4 \longrightarrow ZnO + SO_2$$

The initial stage of this reaction is the formation of the basic sulfate:

$$11/4\ ZnSO_4 + 1/4\ ZnS \longrightarrow (ZnO \cdot 2ZnSO_4) + SO_2 \quad (1)$$

The final stage is the decomposition of the basic salt:

$$(ZnO \cdot 2ZnSO_4) + 2/3\ ZnS \longrightarrow 11/3\ ZnO + 8/3\ SO_2 \quad (2)$$

The occurrence of either stage is, of course, dependent upon the temperature and pressure of the system.

The pressure of the gaseous products are of such a magnitude that they can be measured at temperatures above 350° C. by the static manometric method.

It should be noted that SO_2 is not the only gaseous product in the formation of the basic salt. Some zinc sulfate will decompose by itself according to the reaction,

$$3\ ZnSO_4 \longrightarrow (ZnO \cdot 2ZnSO_4) + SO_3$$

releasing sulfur trioxide, which in turn decomposes into sulfur dioxide and oxygen by the reaction,

$$SO_3 \longrightarrow SO_2 + \tfrac{1}{2}\ O_2$$

making the total pressure of the system equal to the sum of the pressures of the sulfur trioxide, sulfur dioxide and oxygen, i. e.,

$$P_t = p_{SO_3} + p_{SO_2} + p_{O_2}$$

Using data for the equilibrium constant of the SO_2 - SO_3 reaction and the basic salt reaction, a calculation was made which showed that the percentages of oxygen and sulfur trioxide in the gas mixture are extremely small, ($2 \times 10^{-5}\%$ SO_3 and $5 \times 10^{-16}\%$ O_2 at 500° C. to $26 \times 10^{-5}\%$ SO_3 and $1.4 \times 10^{-12}\%$ O_2 at 700° C.) making P_t in the system equal to p_{SO_2}. Thus the pressure of SO_2 can be read from the manometer directly with no gas composition corrections.

To facilitate the attainment of equilibrium in the system, the reactants should be in a finely divided state and in intimate contact. This was accomplished by grinding the reaction mixture and pelletizing it in a small press.

Thermodynamics.

According to the law of mass action, the equilibrium constant for reaction (1) is;

$$K_{eq} = \frac{(a_{ZnO\cdot 2ZnSO_4})\ (a_{SO_2})}{(a_{ZnS})^{1/4}\ (a_{ZnSO_4})^{11/4}}$$

where, a represents activity. If it is assumed that the solid products and reactants are prue and in their standard states, then, a = 1, and,

$$K_{eq} = (a_{SO_2})$$

The change in the standard free energy associated with a chemical reaction is related to its equilibrium constant by the following expression;

$$\Delta F^\circ = -R\ T\ \ln(K_{eq})$$

where: R = gas constant
T = absolute temperature
ΔF° = standard free energy change for the reaction

Substituting the equilibrium constant for reaction (1) into this expression yields;

$$\Delta F^\circ = -R\ T\ \ln(p_{SO_2})$$

The Gibbs-Helmholtz equation is;

$$\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ$$

where: ΔF° = standard free energy change for the reaction.
ΔH° = standard enthalpy change for the reaction.
ΔS° = standard entropy change for the reaction.

Combining the Gibbs-Helmholtz equation with the standard free energy expression results in the following equation;

$$\log(p_{SO_2}) = \frac{-\Delta H^\circ}{4.58\ T} + \frac{\Delta S^\circ}{4.58}$$

which is in the form

$$\log(p_{SO_2}) = \frac{A}{T} + B$$

where:

$$A = \frac{-\Delta H^\circ}{4.58} = \text{slope}$$

$$B = \frac{+\Delta S^\circ}{4.58} = \text{intercept at } 1/T^\circ\ \text{K.} = 0$$

Consequently, the average change, over a small temperature change, in enthalpy and in entropy for the reaction can be found by plotting $\log(p_{SO_2})$ versus $1/T^\circ$ K., and from these the standard free energy of the reaction can be calculated. Using the standard free energy data for the other constituents of the reaction, the standard free energy of formation for $ZnO \cdot 2ZnSO_4$ can be calculated.

CHAPTER IV

THE APPARATUS

The Reaction System.

The experimental measurement of the reaction pressures consisted of measuring the pressure of the gas in equilibrium with the solid sulfide-sulfate charge by a static manometric technique, at various temperatures.

A schematic representation of the reaction system is presented in Figure 1. Figure 2 is a photograph of the system.

The pelletized charge of ZnS + 3 $SnSO_4$ was contained in a sealed Vycor bulb connected to a Kern-Springham glass spiral manometer. A graded seal, Vycor to Pyrex, allowed the Pyrex manometer to be sealed to the Vycor reaction tube without the use of rubber tubing.

The reaction tube was positioned in the center of a Type 70, Hevi Duty hinged electric furnace. To keep stray air currents from cooling the reaction tube, a sheet of asbestos was attached to one end of the tube furnace covering the opening.

Two chromel-alumel thermocouples were used in the furnace system. One, positioned adjacent to the furnace windings was connected to a Wheelco 402 automatic controller,

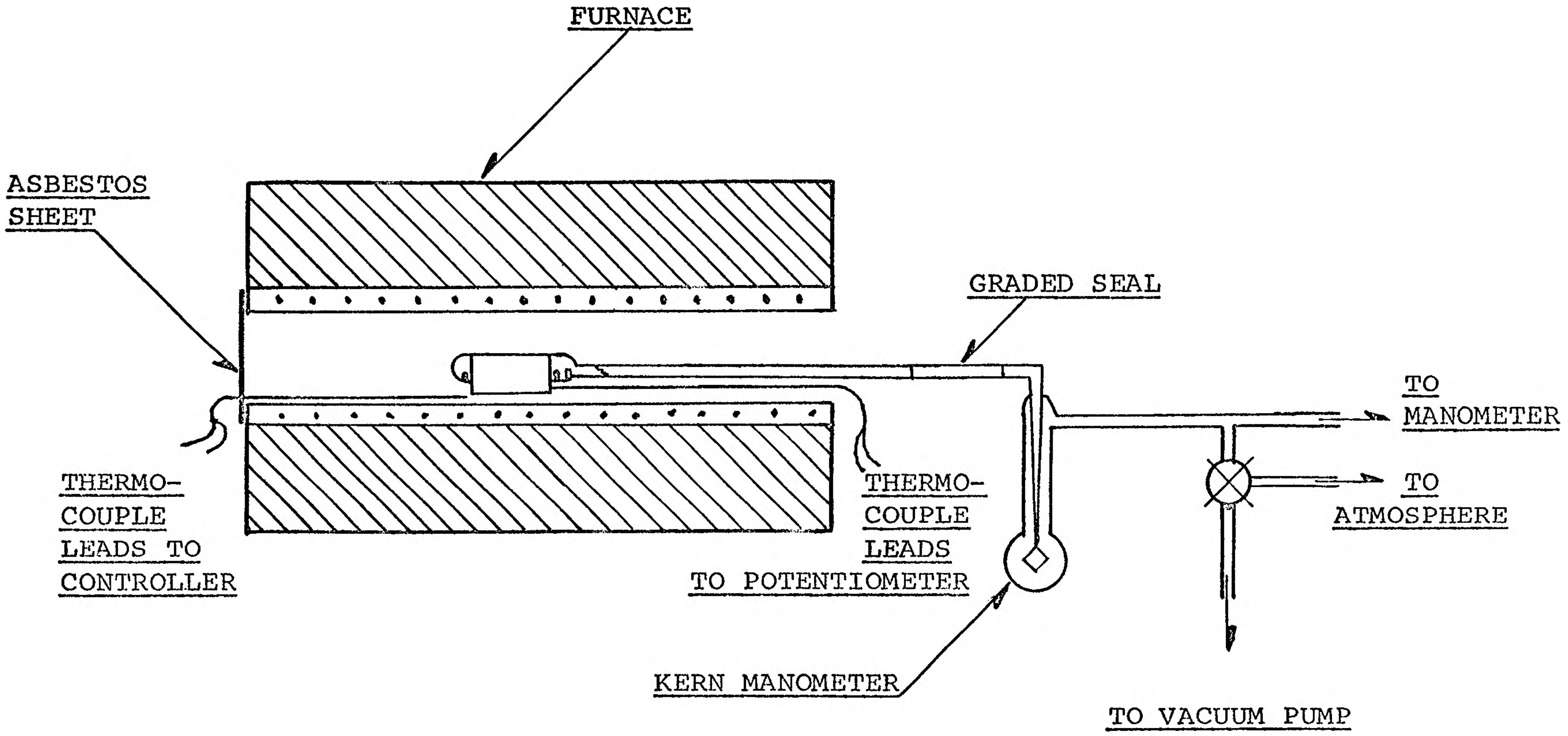

FIGURE 1

SCHEMATIC DIAGRAM OF REACTION SYSTEM

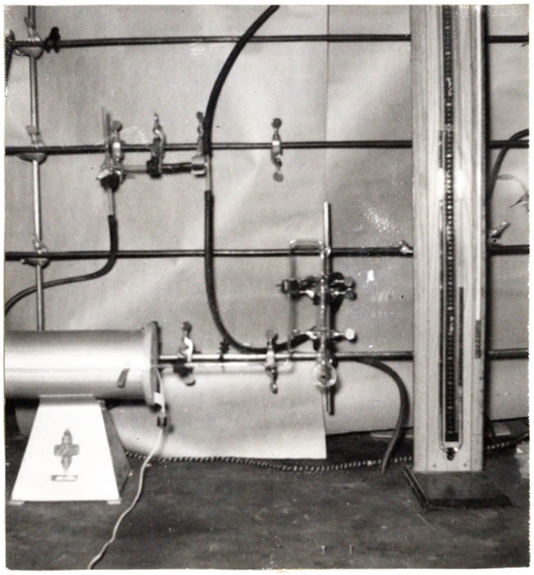

FIGURE 2

THE REACTION SYSTEM

which was connected in series with a powerstat for temperature control of the furnace. The second, held in contact with the reaction tube by silver foil, gave an accurate measurment of the reaction tube temperature. This measuring thermocouple was connected to a potentiometer. The temperature control was ± 1° C.

To charge the system, pellets of reaction mixture were placed in the reaction tube from the side which was not connected to the manometer. The system was evacuated, tested for leaks and sealed by welding the glass together, making a closed glass system. At no time did the reaction product gases come in contact with mercury, rubber tubing or vacuum grease, eliminating the chance of reaction with these substances.

It should be noted that an earlier system using a mercury manometer and incorporating a greased, ground glass stopcock failed to reach equilibrium even after a very long length of time at a given temperature. (more than four weeks at 450° C.) It was concluded that this was caused by reaction of the mercury in the manometer with the reaction product gases. Mellor[15] (1930) says: "F. C. Vogel showed that warm mercury is attacked by sulfur trioxide forming sulfur dioxide and mercuric sulfate."

The Kern-Springham spiral manometer shown in Figure 3, was designed to be used with a lamp and scale such as is used with a ballistic galvanometer, which after calibration, could be used to read the pressure directly. As the pressure changes within the hollow glass spiral of the manometer, the spiral twists, rotating a mirror attached to it. The amount of twist can be determined by the amount of movement of the spot of light reflected off the mirror onto the scale by a stationary light source. This is the optical lever principle.

However, it was found that in order to cover a range of one atmosphere change in pressure, the lamp and scale would have to be moved in relation to the manometer because the mirror would rotate more than 110° for 760 mm Hg. change in pressure. In one position the lamp and scale had a range of only ± 75 mm Hg.

The manometer was so constructed, however, that the atmospheric side of the pressure sensitive coil was completely enclosed except for a tap which normally led to the atmosphere. A vacuum pump, three-way stopcock and a mercury manometer were connected to this tap allowing the pressure on the atmospheric side of the coil to be varied and measured. Thus the glass manometer was used as a null

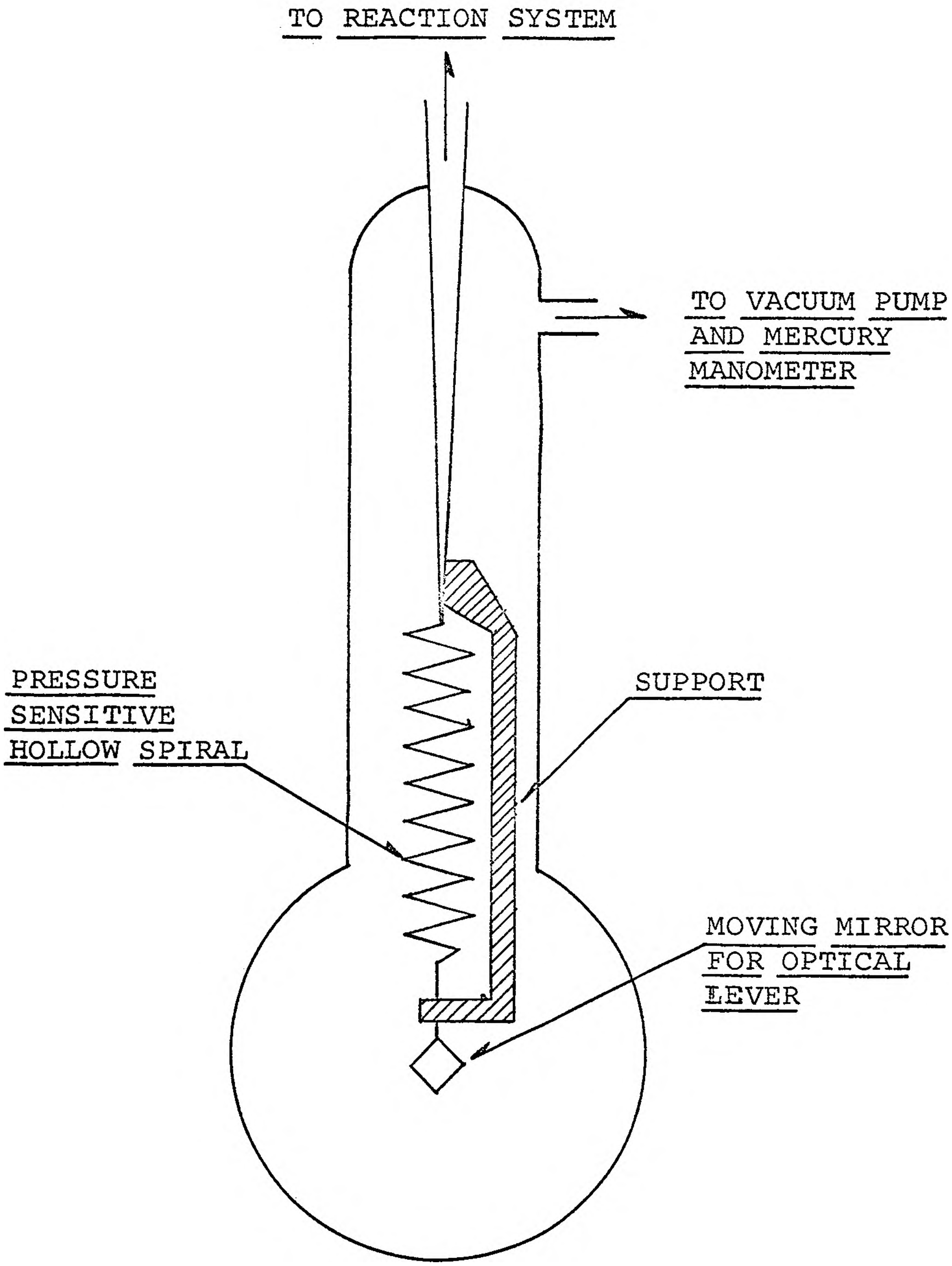

FIGURE 3

SCHEMATIC OF KERN-SPRINGHAM MANOMETER

point indicator to balance the pressure in the reaction system to that in a mercury manometer. When the glass manometer showed no pressure difference, the pressure reading on the mercury manometer was equal to that in the reaction system and was so recorded.

The use of the Kern-Springham manometer not only eliminated the presence of mercury, rubber tubing and vacuum grease, it also eliminated the volume change with pressure associated with mercury manometers.

The Drying System.

Because of the hygroscopic nature of $ZnSO_4$, it had to be dried before charging into the reaction tube.

The drying system consisted of a 30 mm diameter Pyrex tube in a Type 70 Hevi Duty electric furnace. Into the tube were put boats of $ZnSO_4$ and, separately, ZnS which was also dried. Argon was passed through $MgClO_4$ to dry it and was passed over the charge in the furnace to carry away the moisture evolved upon heating. The argon left the furnace through tygon tubing to a bubbler containing a solution of 3% H_2O_2 in distilled water with methyl red indicator, which would indicate any decompositon of $ZnSO_4$ in the drying furnace.

A chromel-alumel thermocouple in a Vycor protection tube was positioned adjacent to the boats containing the charge. The thermocouple was connected to a Wheelco 402 automatic controller, which connected in series with a powerstat controlled the temperature of the drying furnace. Figure 4 shows a schematic representation of the drying system. A photograph is shown in Figure 5.

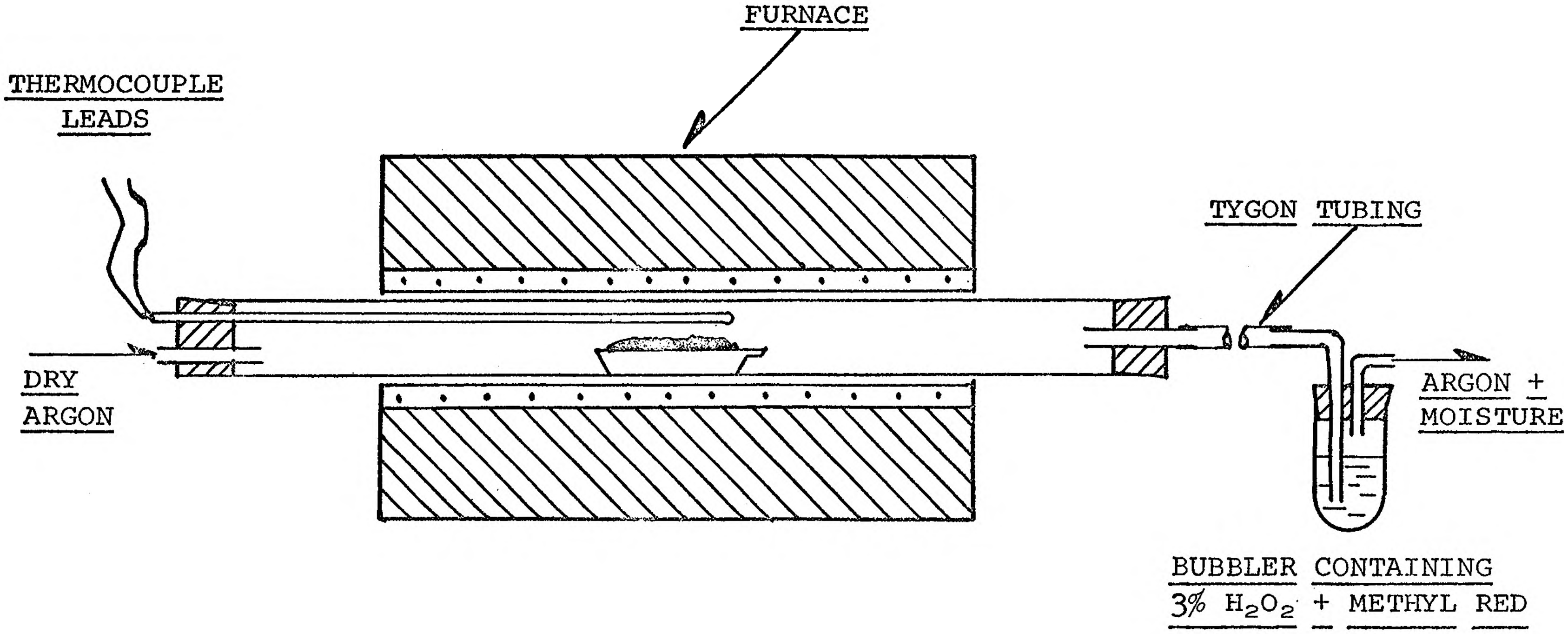

FIGURE 4

SCHEMATIC DIAGRAM OF DRYING SYSTEM

FIGURE 5

THE DRYING SYSTEM

CHAPTER V

PROCEDURE

The thermodynamic measurements of the reaction pressures were made by heating pelletized charges of $ZnS + 3 ZnSO_4$ to equilibrium at various temperatures in an originally evacuated reaction system, and recording the reaction pressures as a function of temperature. This is a static manometric technique.

Because of the hygroscopic nature of zinc sulfate, it can be present as $ZnSO_4 \cdot 7H_2O$. To avoid erroneous data in the pressure versus temperature relationship due to the pressure of this water of hydration, the water was removed.

Zinc sulfate heptahydrate was heated in a tube furnace at 400° C. for 24 hours. Argon was dried by passing it through $MgClO_4$ and was passed over the charge at about 10 cc/minute to remove the moisture present. The argon was exhausted from the system through a bubbler containing 3% H_2O_2 in distilled water and methyl red indicator. This solution was made slightly basic (yellow) to indicate any decomposition of $ZnSO_4$ by turning acidic (red) due to the formation of H_2SO_4 in the solution. If $ZnSO_4$ would decompose, SO_3 would be liberated. The SO_3 on contact with the solution would form H_2SO_4 making the solution acidic, turning the methyl red from yellow to red.

X-ray diffraction studies and weight loss calculations disclosed that the $ZnSO_4 \cdot 7H_2O$ dried at 400° C. for 24 hours contained extremely small amounts of $ZnSO_4 \cdot H_2O$, the bulk of the substance being $ZnSO_4$. If the $ZnSO_4 \cdot 7H_2O$ were dried at 425° C. for 24 hours, partial decomposition would result. From this, 400° C. was chosen as the optimum drying temperature.

Although zinc sulfide exhibits no hygroscopic properties, it was also dried in the same manner as the zinc sulfate.

After drying, the zinc sulfate and zinc sulfide were mixed in a mole ratio of 3 $ZnSO_4$ to 1 ZnS, ground in a mortar and pestle and pressed into pellets 1/8 inch in diameter by 3/16 inches in height. These pellets were kept in a vacuum desiccator over $MgClO_4$ to prevent hydration. A two gram charge of pellets was placed in the Vycor reaction tube and the tube was sealed to the Vycor side of the graded seal. The system was evacuated, sealed and tested for leaks. The temperature was then brought up to 350° C. for 24 hours. The reaction tube was allowed to cool, and the system was re-evacuated and permanently sealed. This was done to insure the absence of moisture in the system.

The reaction tube was then heated to 350° C. and held until equilibrium was attained. This was determined by recording the pressure of the system at various times during the day. It was assumed that equilibrium had been attained when the pressure remained constant over night or for a period of 12 hours. When equilibrium was reached the temperature was increased to obtain the next higher equilibrium temperature-pressure relationship. This was repeated until the necessary number of readings had been taken.

To determine the solid equilibrium phases present at the different temperatures, Vycor capsules containing pellets of the reaction mixture were evacuated, sealed and heated to the given temperature and held there until equilibrium was attained. It was assumed that equilibrium had been attained when the capsules had been heated for the same length of time necessary to equilibrate the reaction pressure system.

After heating, the capsules were air quenched, opened and the contents analyzed by X-ray diffraction methods.

CHAPTER VI

RESULTS AND CALCULATIONS

X-ray Diffraction Studies.

The X-ray diffraction determinations of the solid equilibrium products of the ZnS + 3 $ZnSO_4$ mixture from 350 to 450° C. showed that up to 420° C. the following chemical reaction takes place;

$$11\ ZnSO_4 + ZnS \rightarrow 4\ (ZnO \cdot 2ZnSO_4) + 4\ SO_2 \quad (1)$$

Above 420° C. the following reaction takes place;

$$3\ (ZnO \cdot 2ZnSO_4) + 2\ ZnS \rightarrow 11\ ZnO + 8\ SO_2$$

These two reactions are dependent upon the temperature and pressure of the system. The X-ray diffraction data are compiled on Table 1.

Reaction Pressures.

Table 2 shows, in tabulated form, the equilibrium reaction pressures for the given temperatures.

Figure 6, a plot of log p in atmospheres versus the reciprocal of the absolute temperature shows a linear relationship for these data. Using the least squares method of mathematical analysis, the slope and intercept of the straight line best representing these data was calculated. It is drawn in Figure 6.

From the discussion in Chapter III it is seen that the slope of the plot of log p in atmospheres versus 1/T° K. is equal to $-\Delta H°/4.58$ and the intercept of this line at 1/T° K. = 0 is equal to $+\Delta S°/4.58$. From this the standard free energy can be calculated for reaction (1).

Hence, from Figure 6,

$$\text{slope} = -2800$$

$$\text{intercept} = +2.0$$

Substituting these values in the Gibbs-Helmholtz equation, the following standard free energy equation for reaction (1) was obtained;

$$\Delta F° = +51{,}320 - 36.68\,T$$

Using the thermodynamic data of Ingraham and Kellogg[14] for $ZnSO_4$, ZnS and SO_2 the standard free energy of formation for the basic sulfate, $ZnO \cdot 2ZnSO_4$ was found to be;

$$\Delta F° = -377{,}000 - 65.9\,T \text{ cal/mole}$$

for the temperature range 350 to 420° C.

TABLE I

X-RAY DIFFRACTION DATA

Temperature ° C.	Phases Present		
350	$ZnSO_4$,	ZnS,	$ZnO \cdot 2ZnSO_4$
375	"	"	"
400	"	"	"
410	"	"	"
415	"	"	"
425	$ZnO \cdot 2ZnSO_4$,	ZnO,	ZnS
450	"	"	"

TABLE II

EXPERIMENTAL DATA

Temperature °C.	Time at Temperature Days	Reaction Pressures mm
350	0	0
	1	6
	2	6
380	1	12
	2	12
404	1	13
	2	19
	3	25
	4	25
429	22	462*

* Not equilibrated

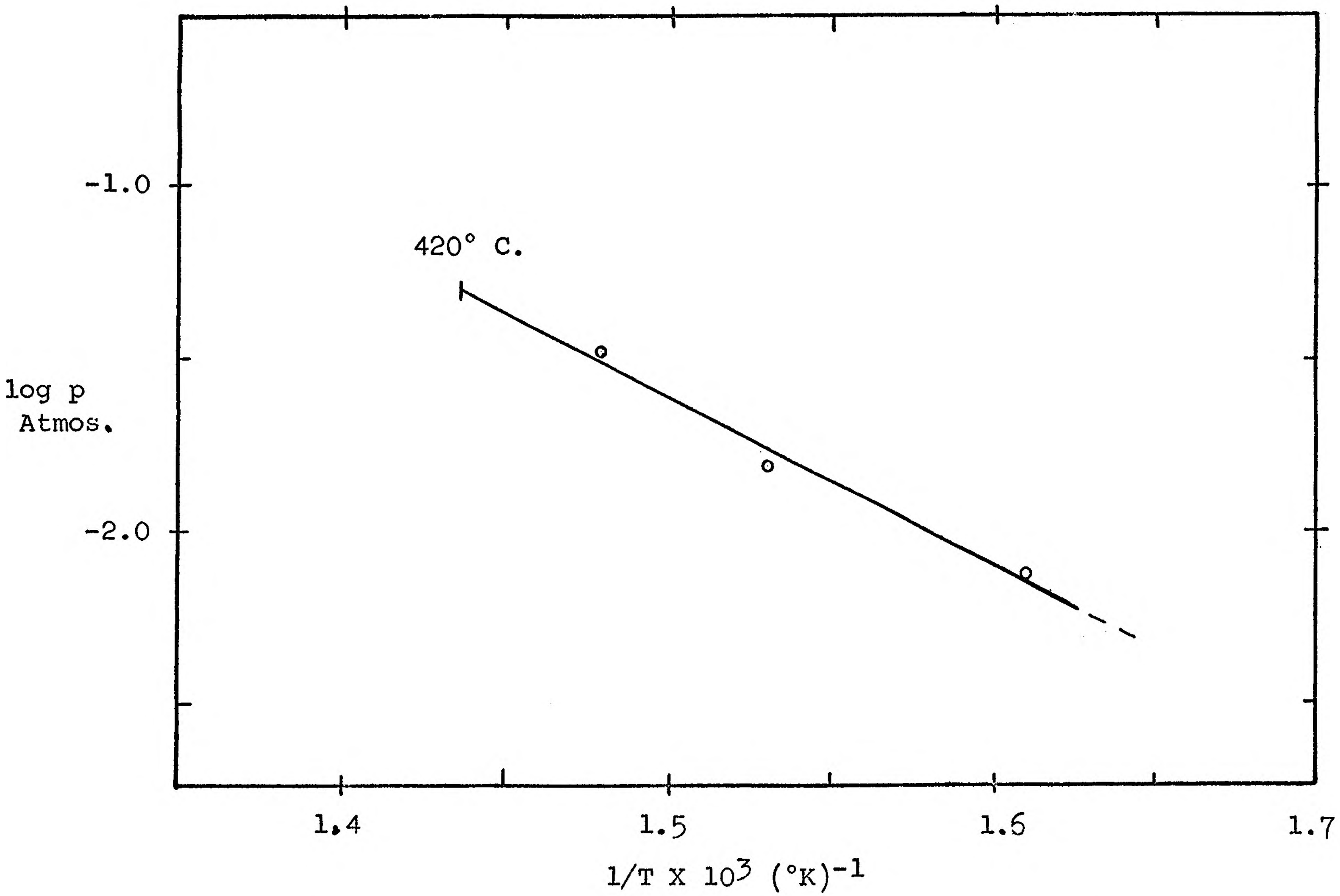

Fig. 6. log p vs. 1/T RELATIONSHIP FOR THE REACTION

$11\ ZnSO_4 + ZnS \longrightarrow 4\ (ZnO \cdot 2ZnSO_4) + 4\ SO_2$

CHAPTER VII

DISCUSSION OF EXPERIMENTAL ERRORS

The measurement of the reaction pressure of the $ZnS + 3 ZnSO_4$ mixture involved two variables, temperature and pressure, giving rise to two possible sources of error.

Although the temperature of the heating coils in the furnace fluctuated ± 3 degrees C. because of the on-off operation principle of the controller, the reaction tube, which was wrapped in silver foil, was held at a ± 1 degree C. tolerance. This minimized minute pressure fluctuations within the system. Random readings at various times during the day showed the temperature of the reaction tube to be well within this tolerance.

The pressure in the system was measured by balancing a mercury manometer against the Kern-Springham all galss manometer and reading the pressure directly from the mercury manometer. Readings were taken visually and rounded off to the nearest millimeter reading. This gave a tolerance of ± 0.5 mm to the pressure measurement. The atmospheric pressure was read at the same time as the system's, with the same technique, giving a ± 0.5 mm tolerance to the atmospheric pressure measurement also.

The pressure of the system was recorded when the

Kern-Springham manometer read zero. The readings on the scale of the glass manometer could only be taken to ± 1 mm because of the width of the image on the scale. However, a 1 mm movement of the image at the center of the scale corresponded to a 0.3 mm pressure change on the mercury manometer, making this error very small.

It was assumed that all the reactants were in their standard states of unit activity. The zinc sulfate and sulfide were reagent grade and were found to be pure, as far as it was possible to tell, by X-ray diffraction data. X-ray patterns were run both before and after drying of the ZnS and $ZnSO_4$ powders to substantiate the purity.

It was also assumed that the values of H° and S° do not vary with temperature in the range of 350 to 450° C.

CHAPTER VIII

DISCUSSION AND CONCLUSIONS

The static manometric method gave satisfactory data in this investigation, as long as no foreign materials (stopcock grease, rubber tubing or mercury) were in contact with the gaseous products. An all glass system, including an all glass manometer, was necessary for this.

In this investigation, it was found that for the reaction,

$$11\ ZnSO_4 + ZnS \longrightarrow 4\ (ZnO \cdot 2ZnSO_4) + 4\ SO_2$$

the standard free energy change could be expressed as;

$$\Delta F^\circ = +\ 51,320 - 36.68\ T$$

Further, the standard free energy of formation of the basic salt, $ZnO \cdot 2ZnSO_4$ was found to be;

$$\Delta F^\circ = -377,000 - 65.9\ T \quad \text{cal/mole}$$

over the temperature range 350 to 420° C.

It was also found that up to 420° C the reaction,

$$11\ ZnSO_4 + ZnS \longrightarrow 4\ (ZnO \cdot 2ZnSO_4) + 4\ SO_2$$

occurs. Above 420° C. the reaction,

$$2\ ZnS + 3\ (ZnO\cdot 2ZnSO_4) \rightarrow 11\ ZnO + 8\ SO_2$$

occurs.

Of interest to extractive metallurgists is the stability range of the basic sulfate, when not in contact with the sulfide, as a function of temperature and percent oxygen in the ambient atmosphere. Figures 7, 8 and 9 graphically show the stability ranges of the basic salt for the total pressures ($SO_2 + SO_3 + O_2$) of 1, 0.5 and 0.2 atmospheres, respectively. These data are of value for the determination of the conditions for a 'sulfating roast.' These plots were obtained using the thermodynamic data for $ZnSO_4$ and related compounds from 1000 to 1200° K. given by Ingraham and Kellogg[14] in the following manner.

For the reaction,

$$3\ ZnSO_4 \rightarrow (ZnO\cdot 2ZnSO_4) + SO_3 \qquad (3)$$

the equilibrium constant is;

$$K_3 = p_{SO_3}$$

For the reaction,

$$SO_2 + \tfrac{1}{2}\ O_2 \rightarrow SO_3 \qquad (4)$$

the equilibrium constant is;

$$K_4 = \frac{p_{SO_3}}{(p_{SO_2})\ (p_{O_2})^{\frac{1}{2}}}$$

Substituting K_3 into the expression for K_4, and rearranging, one obtains,

$$\frac{K_3}{K_4} = (p_{SO_2})\ (p_{O_2})^{\frac{1}{2}} \qquad (5)$$

From an earlier discussion (Chapter III) it is known that the total pressure of the system is;

$$P_t = p_{SO_3} + p_{SO_2} + p_{O_2}$$

So;

$$P_t - K_3 = p_{SO_2} + p_{O_2} \qquad (6)$$

Choosing a total pressure and solving equations 5 and 6 simultaneously will give values for p_{SO_2} and p_{O_2} for that pressure. From these values the percent oxygen versus temperature plot can be made for the formation of the basic salt.

The simultaneous solution of equations 5 and 6 can be performed either graphically or algebraically. In this case they were solved by the graphical method by plotting the equations on a graph of p_{SO_2} versus $(p_{O_2})^{\frac{1}{2}}$. This was done at 25° intervals from 1000 to 1200° K.

To find the temperatures at which the basic sulfate will decompose, the equilibrium constant for the following equation was substituted for K_3 and equations 5 and 6 were again solved simultaneously.

$$1/2\ (ZnO \cdot 2ZnSO_4) \rightarrow 3/2\ ZnO + SO_3 \qquad (7)$$

where,

$$K_7 = p_{SO_3}$$

From Figures 7, 8 and 9 it can be seen that as the temperature increases $ZnSO_4$ decomposes into $ZnO \cdot 2ZnSO_4$ and finally into ZnO for a given gas composition. It is also seen that as the total pressure decreases, the stability range of the basic salt shifts to lower temperatures.

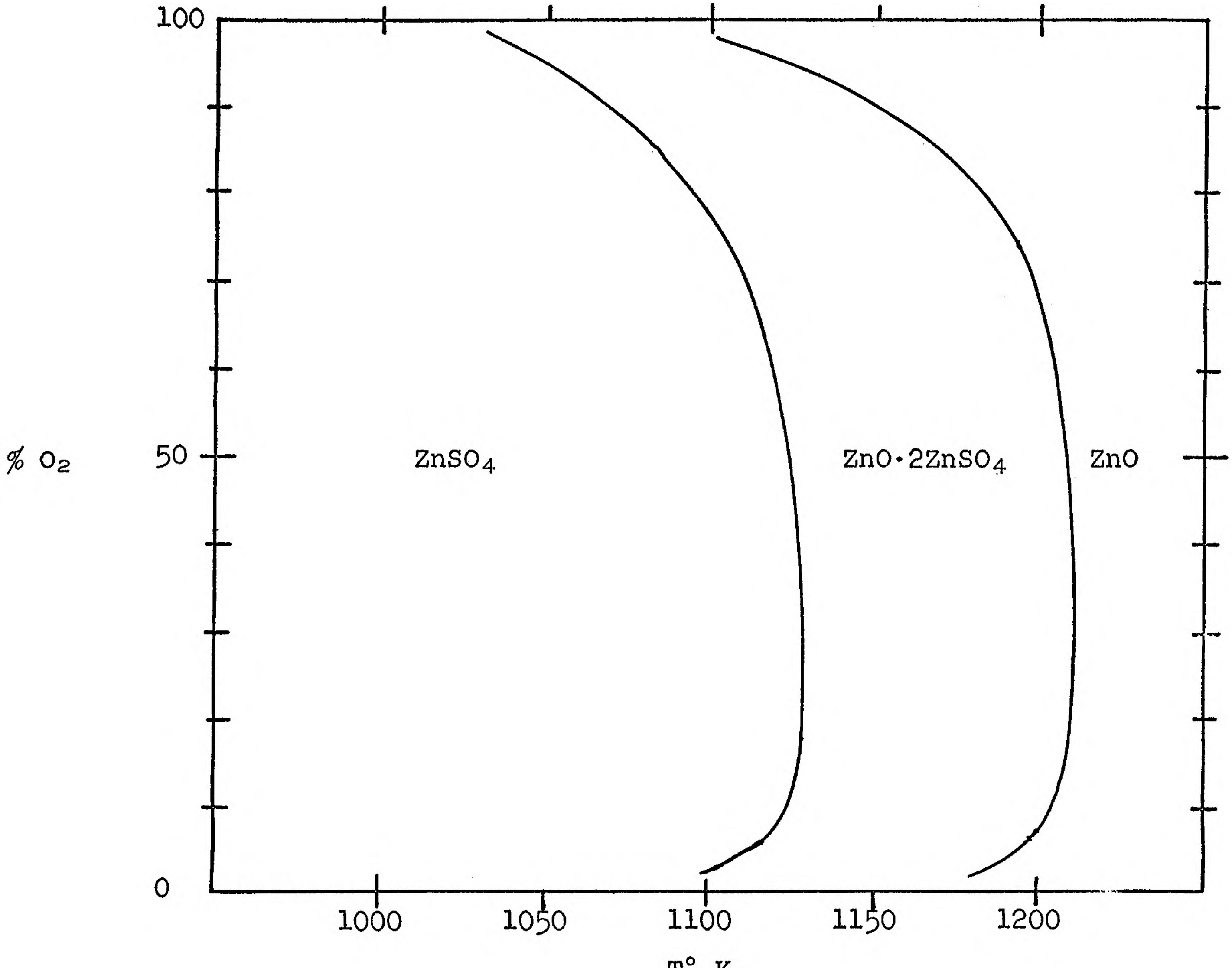

FIG. 7. EFFECT OF TEMPERATURE AND GAS COMPOSITION ON THE STABILITY OF BASIC ZINC SULFATE AT 1 ATMOSPHERE TOTAL PRESSURE

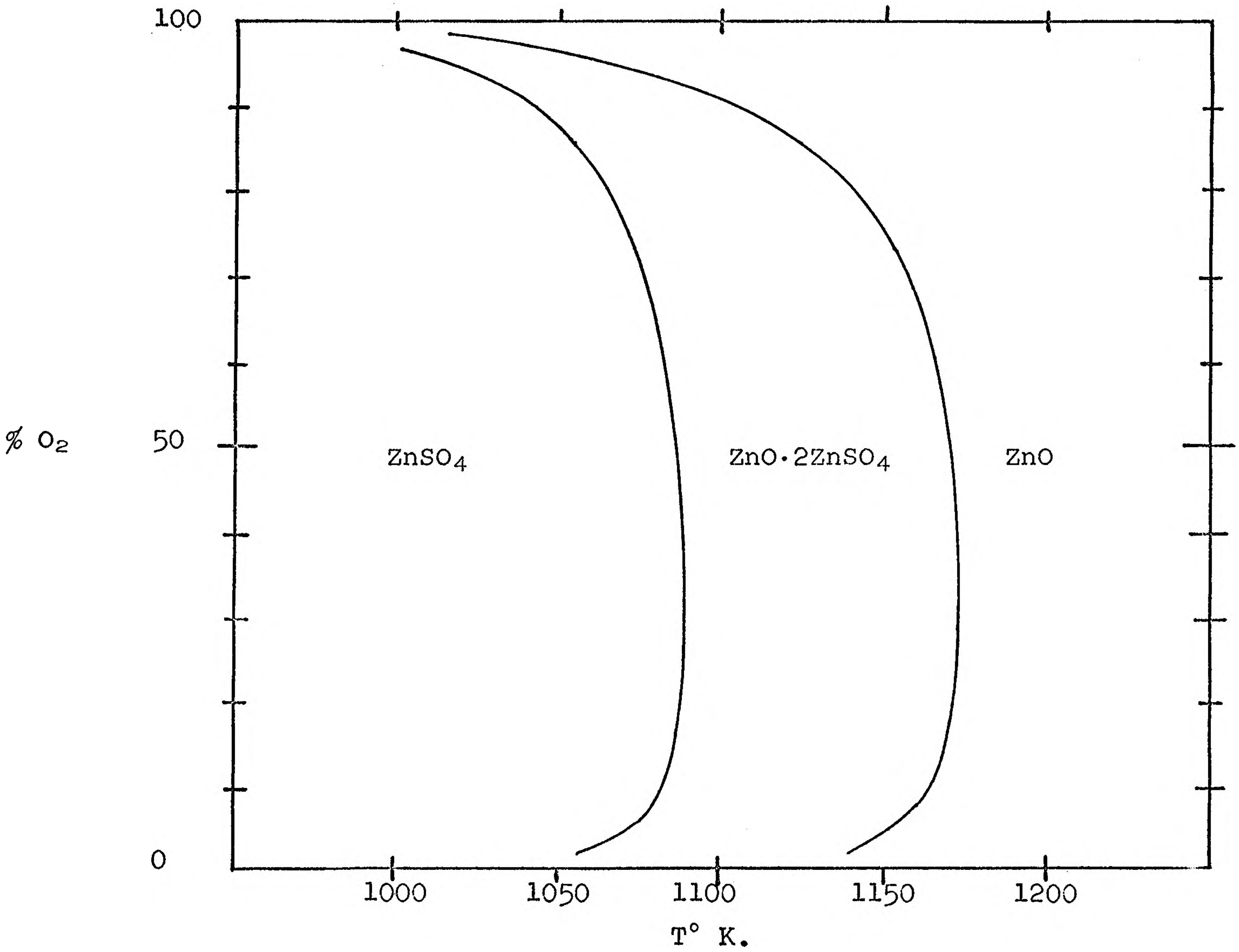

FIG. 8. EFFECT OF TEMPERATURE AND GAS COMPOSITION ON THE STABILITY OF BASIC ZINC SULFATE AT 0.5 ATMOSPHERES TOTAL PRESSURE

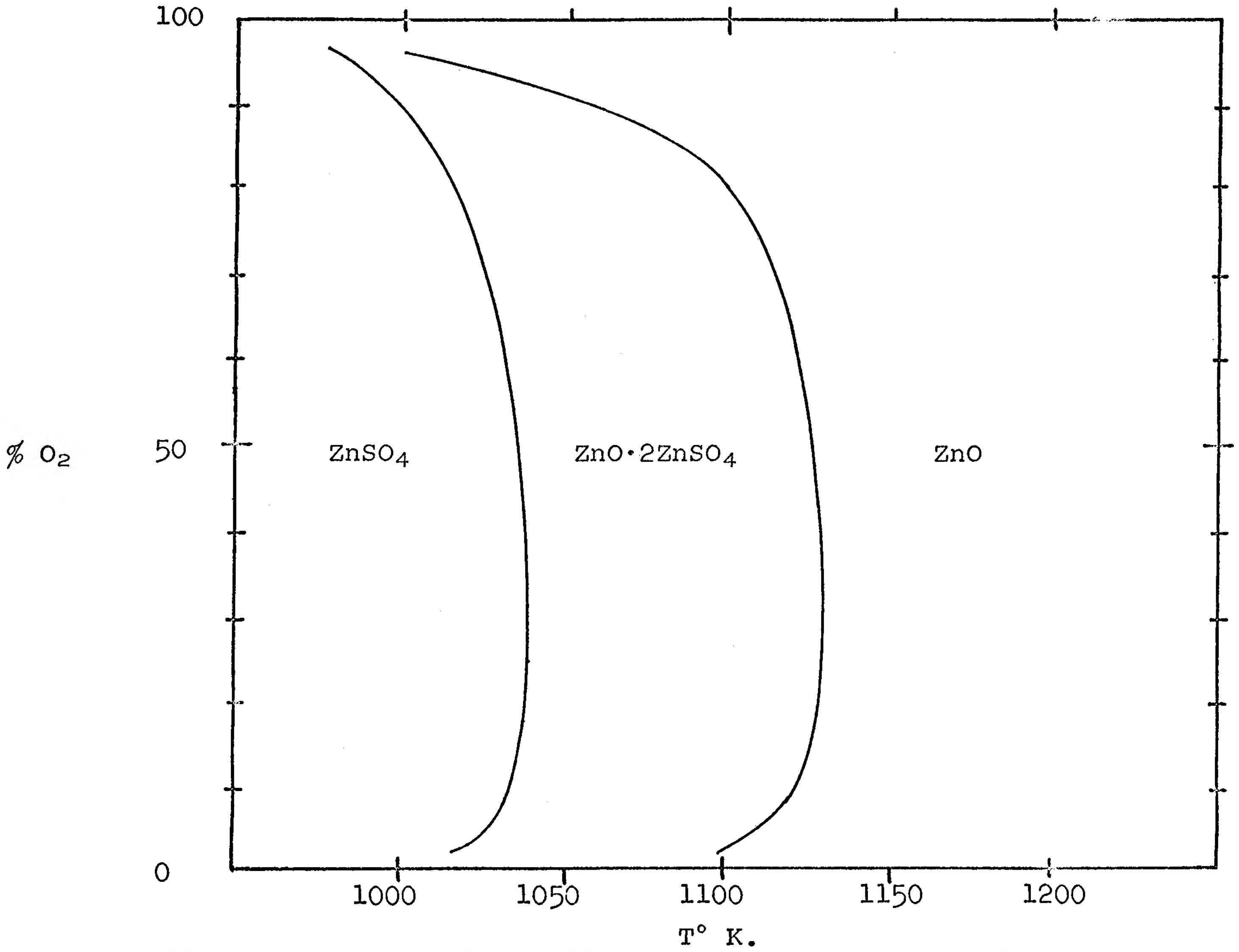

FIG. 9. EFFECT OF TEMPERATURE AND GAS COMPOSITION ON THE STABILITY OF BASIC ZINC SULFATE AT 0.2 ATMOSPHERES TOTAL PRESSURE

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VITA

The author was born on April 9, 1940 in Joliet, Illinois. He received his primary education in Lemont, Illinois and St. Louis, Missouri, and his secondary education in Kirkwood, Missouri. He received his college education from the University of Missouri School of Mines and Metallurgy where he received a Bachelor of Science Degree in Metallurgical Engineering, Nuclear Option, in May, 1962.

He has been enrolled in the Graduate School of the School of Mines since September, 1962, and has held the W. J. Kroll Fellowship for the period September, 1962 to August, 1963.