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ACTIVITIES OF SnS IN TIN - IRON MATTES

By

JUAN E. JOFFRE

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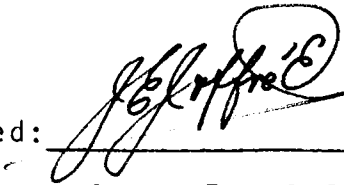
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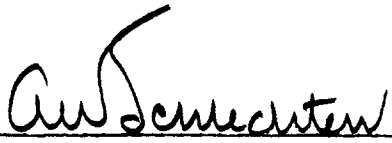
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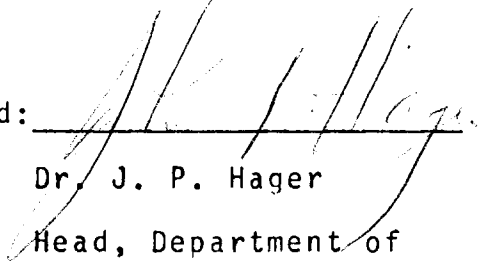
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ACTIVITIES OF SnS IN TIN - IRON MATTES.

By

Juan E. Joffre.

A B S T R A C T

The vapor pressure of SnS above pure SnS(c,l), and above tin - iron mattes was determined by means of the transportation method. It was confirmed that - apart from the other well known factors, such as a uniform temperature in the reaction zone, and a uniform flowrate - the influence of the geometry of the reaction chamber is very important for accurate determinations using this method. The carrier gas utilized for these determinations on tin and iron sulfides, should be able to control the sulfur potential to prevent errors due to decomposition and/or segregation.

The results obtained for SnS vapor above pure SnS(c,l) agree very well with the most reliable data in the literature. There are no available data on the tin-iron mattes. It was found that the SnS-FeS liquid solution behaves almost regularly, and can be represented by:

$$\text{Log } \gamma_{\text{SnS}} = \frac{260.8}{T} N_{\text{FeS}}^2 \quad ,$$

and,

$$\text{Log } \gamma_{\text{FeS}} = \frac{260.8}{T} N_{\text{SnS}}^2 \quad .$$

Thermodynamic relations were derived from this regular solution model and a practical application to an SnS - fuming operation is presented.

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## I. INTRODUCTION.

Tin ores are invariably associated with iron minerals. Concentration processes in general never lead to a clean separation of  $\text{SnO}_2$  (Cassiterite, the most commercial tin ore) from the iron minerals ( $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{FeS}_2$ ,  $\text{CuFeS}_2$ , etc.). Removal of iron from concentrates prior to smelting by magnetic separation is not possible in all cases because cassiterite is often firmly attached to, or coated with iron oxides. Leaching the concentrates with HCl dissolves iron oxides and amounts of As, Sb, Bi, Pb, Cu are also removed by this process. But when the concentrates contain much sulfur and arsenic as sulfides and arsenides, the effectiveness of leaching is reduced.

During smelting sulfur may form  $\text{FeS} - \text{Cu}_2\text{S} - \text{SnS}$  mattes which render difficult the recovery of tin. Furthermore, sulfur increases the loss of tin by volatilization as  $\text{SnS}$ . Every 1% S may cause volatilization of 3.72% Sn. Therefore, to prevent the negative action of sulfur and arsenic during smelting, the concentrates should be roasted.

### Tin Smelting Practice

Figure 1 gives a general flowsheet of the tin smelting process. Tin concentrates - which may have been roasted and/or leached - are mixed with coke (or coal) and limestone and fed to a reduction furnace (blast, reverberatory, or rotary).

Basically, tin smelting is practiced in two stages:

- a) Smelting of concentrates to produce crude tin (high grade tin) and a tin-rich slag which may contain from 10 to 25 % Sn.
- b) Smelting of the tin-rich slag under stronger reducing conditions to produce a tin-iron alloy or "hardhead" which contains about 80% Sn and 20% Fe

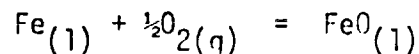
(miscibility gap composition) and a final slag to discard.

This second slag is frequently not low enough in tin to discard and may be treated again before being sent to waste.

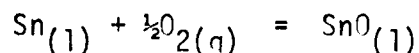
The crude tin from the first stage is drossed to produce pure metal and an iron-bearing dross. Iron drosses and hardheads from the second stage are recycled to the concentrate smelting stage where their iron content acts to reduce tin. All fumes (recovered as  $\text{SnO}_2$ ) are also recycled to the first stage.

### Distribution of Tin and Iron Between Metal and Slag

The free energies of formation of the lower oxides of iron and tin are very similar:



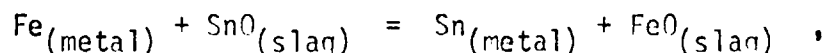
$$\Delta G_F^0 = -55,620 + 10.83T \quad , \quad \text{for } T = 1808 \text{ to } 2000^\circ\text{K}^{(1)}$$



$$\Delta G_F^0 = -69,336 + 25.7T \quad , \quad \text{for } T = 1143 \text{ to } 1873^\circ\text{K}^{(2)}$$

Therefore, a complete reduction of tin as fairly pure metal from the slag is impossible because reduction of iron occurs at the same time, so that an iron-tin alloy results.

The equilibrium distribution of tin and iron between metal and slag phases may be expressed by the following reaction:



for which the equilibrium constant  $K$  is given by:

$$K = \left[ \frac{a_{\text{Sn}}}{a_{\text{Fe}}} \right]_{\text{METAL}} \cdot \left[ \frac{a_{\text{FeO}}}{a_{\text{SnO}}} \right]_{\text{SLAG}}$$

and,

$$k = \left[ \frac{\text{wt\%Sn}}{\text{wt\%Fe}} \right]_{\text{METAL}} \cdot \left[ \frac{\text{wt\%Fe}}{\text{wt\%Sn}} \right]_{\text{SLAG}} \quad (\text{ref. 3})$$

where  $k$  is the distribution coefficient.

Practical experience (Refs. 2,3,4) indicates that  $k$  varies from about 50 for a hardhead of about miscibility gap composition to about 300 for crude tin.

To summarize; complete removal of tin metal from the waste slag, and the production of a metal with a low content of iron constitute a most difficult problem in tin metallurgy.

Tin is lost in slag not only by incomplete reduction from it, but there are also mechanical and physical losses.

Mechanical losses are caused by incomplete settling of tin droplets from slag to molten metal.

Physical losses can be caused by dispersion and formation of very fine suspensions of tin in the slag. According to Murach<sup>(5)</sup>, tin solubility in slags is not admitted as a true fact as yet.

The losses of tin in slag are influenced by the chemical composition of slag since it determines the degree of reduction of SnO to metal, the specific gravity, viscosity, melting point, and surface properties of slags.

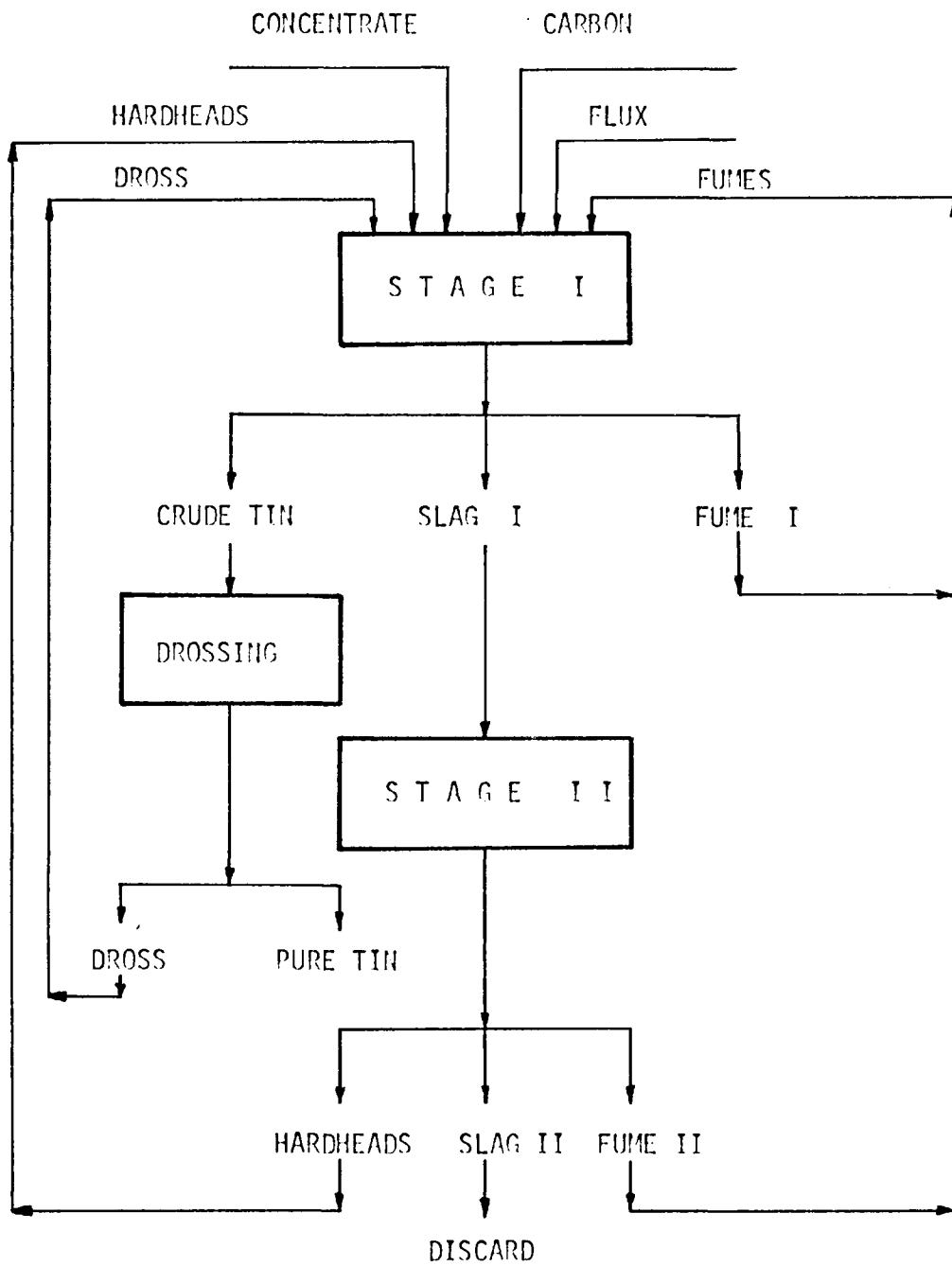


FIG. 1. TIN SMELTING FLOWSHEET.

### Recovery of Tin from Slags

Tin contents in slags from first-stage smelting vary from 3.5 to 25%Sn. This wide range depends on the methods and temperatures of smelting, composition of concentrates and slags, and on many other factors. This primary slag is re-smelted to produce a hardhead and a final slag, as was mentioned above.

Considering the high price of tin (around \$ 1.70/fine pound in the last five years), a loss of 3%Sn in slag is a considerable loss and the final tin concentration in waste slags is in many cases greater than in the ore from which it was extracted. Therefore, any effort towards the reduction of tin losses in slags is extremely important for tin-producing countries.

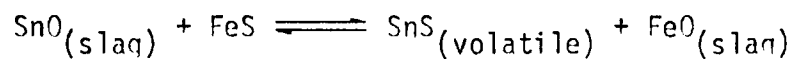
Tin can be recovered from slags by:

- a) resmelting the slag to produce hardhead and a slag lower in tin,
- b) mineral dressing methods,
- c) hydrometallurgical methods, and
- d) volatilization processes.

The first three methods are explained in detail by Murach<sup>(5)</sup>, Wright<sup>(6)</sup>, Belyayev<sup>(7)</sup>, and others. They all have some drawbacks or limitations as far as efficiency and cost are concerned. The fourth, recovery of tin from slags by volatilization, is assuming increasing importance and is based on the volatility of SnO and SnS.

### Purpose of this Investigation

Formation of SnS from stannous oxide contained in slags can be effected by exchange reactions with sulfides of the other metals, usually pyrites. The reaction presenting the final result is given below:



Along with the tin sulfide formation from SnO in the slag, an iron-tin matte is formed, principally when the FeS is in excess (as is usually the case). SnS solution in this matte is accompanied by a decrease in its activity, and there is a drop in vapor pressure of stannous sulfide which would reduce its volatility.

To what extent is this volatility reduced?

What would be the activity of tin sulfide in this liquid matte?

There is not a specific answer to these questions so far and only estimates can be made based on certain properties of the system.

The phase diagram of the SnS-FeS system is known<sup>(8)</sup>, but no information exists about the thermodynamic properties of SnS in tin-iron mattes.

Therefore, the purpose of this investigation was to obtain the answers to the above questions under the simplest assumptions and conditions possible, as a preliminary step toward more sophisticated studies for a better understanding of the thermodynamics of tin fuming from slags and mattes.

## II. L I T E R A T U R E S U R V E Y

### Tin - Sulfur System

The Sn - S system was studied by Albers and collaborators<sup>(9)</sup> and by G. Moh<sup>(10)</sup>.

Their results are summarized in table I.

Table I

Phase Relations in the Sn - S System

PHASE	SYMMETRY	CHARACTERISTICS
SnS	Orthorhombic	Occurs in nature as Herzenbergite (Potosi, Bolivia). Nearly stoichiometric phase. Melts at 870°C.
Sn <sub>2</sub> S <sub>3</sub>	"	Melts at 758°C to liquid Sn <sub>2</sub> S <sub>3</sub> and αSnS <sub>2</sub> . Possible existence of a high temperature polymorph.
βSnS <sub>2</sub>	Hexagonal	On heating inverts to αSnS <sub>2</sub> at 692°C.
αSnS <sub>2</sub>	Cubic	Melts at about 860°C.
Sn <sub>3</sub> S <sub>4</sub>	?	Reported by Albers (?)

Table II

Heats of Formation, Fusion, and Standard Entropies of Sn - S Species. (11,12)

SPECIES	$\Delta H_{298}^{\circ}$ cal/mol	$S_{298}^{\circ}$ cal/degm	MELTING PT., °C	$\Delta H_f^{\circ}$ cal/mol	$\Delta S_f^{\circ}$ cal/mol	$C_p$ , cal/mole	$H_T^{\circ} - H_{298}^{\circ}$ , cal	TEMP. RANGE °K
Sn(c) white	0	12.29 $\pm 0.06$	232	1720	3.64(c) 7.05(1)	$4.42 + 6.3 \cdot 10^{-3} T$	$4.42T + 3.15 \cdot 10^{-3} T^2 - 1598$ $\pm 0.08$	298-505
Sn(c) gray	-500	10.55 $\pm .06$	-	-	-	-	-	-
Sn( $\gamma$ )	-	40.25 $\pm .01$	-	-	-	$8.31 - .62 \cdot 10^{-3} T$ $- 2.7 \cdot 10^5 T^{-2}$	$8.31T - .31 \cdot 10^{-3} T^2 + 2.7 \cdot 10^{-5} T - 1.3356$	1400-5000
SnS(c) ( $\pm 1200$ )	-25100 $\pm .2$	18.4	880 (870) Sh.	-	-	-	-	-
SnS(c) $\alpha$	-	-	886	trans 160	-	$8.53 + 7.48 \cdot 10^{-3} T$ $+ 9 \cdot 10^5 T^{-2}$	$8.53T + 3.74 \cdot 10^{-3} T^2 - .9$ $105T - 1 - 2574$	298-875
SnS(c) $\beta$	-	-	-	7550	-	$9.78 + 3.74 \cdot 10^{-3} T$	$9.78T + 1.87 \cdot 10^{-3} T^2 - 2180$	1153-1250

cont.

Table II  
Continued.

SPECIES	$\Delta H_{298}^{\circ}$ cal/mol	$S_{298}^{\circ}$ cal/degm pt. °C	MELTING pt. °C	$\Delta H_f^{\circ}$ cal/mol	$\Delta S_f^{\circ}$ cal/mol	$C_p$ , cal/mole	$H_T^{\circ} - H_{298}^{\circ}$ , cal	TEMP. RANGE °K
SnS(l)	-25300*	-	-	-	-	17.9	$17.9T - 1510$	1153-1250
SnS( $\alpha$ )	-	57.9 $\pm .2$	-	-	-	$8.83 + .08 \cdot 10^{-3}T$ $-.55 \cdot 10^{-5}T^{-2}$	$8.83T + .04 \cdot 10^{-3}T^2 +$ $.55 \cdot 10^{-5}T^{-1} - 2821$	298-2000
SnS <sub>2</sub> (c)	-40000 ( $\pm 4000$ ) -70800** ( $\pm 4000$ )	20.9 $\pm .2$	-	-	-	$15.51 + 4.2 \cdot 10^{-3}T$	$15.51T + 2.1 \cdot 10^{-3}T^2 -$ 4811	298-1000

\* Freeman (ref. 13)

\*\* Elliott and Gleiser (ref. 14)

Since stannous sulfide (SnS) is the compound of interest to this investigation, a literature survey was conducted on the thermodynamic properties of this species. Table II gives the heat and standard entropies for the Sn-S species as given by Kelley<sup>(11,12)</sup>.

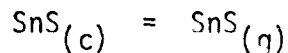
Hsiao and Schlechten<sup>(15)</sup> studied the volatility of SnS in a vacuum furnace. Their result is given in the following equation:

$$\text{Log } p_{\text{SnS}}, (\text{mm Hg}) = -8380/T + 6.728$$

Temperature range: 503° - 704°C (could be extended up to 870°C)

Pressure range, log  $p_{\text{SnS}}, (\text{mm Hg})$ : -4.09 to 1.91 .

A. W. Richards<sup>(16)</sup> studied the heat and free energy of formation and vaporization of stannous sulfide using the entrainment method. Based on this study, he made a new estimate of the entropy of SnS. His data are summarized as follows:



$$\text{Log } p_{\text{SnS}}, \text{ atm} = -10,470/T + 7.088 (\pm 0.02)$$

$$S_{298}^0(\text{SnS}_{(c)}) = 19.4 \pm 1 \text{ e.u.}$$

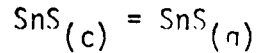
compared to 18.2  $\pm$  1.5 e.u. (Kireev<sup>(17)</sup>).

$$\Delta H_{f298}^0(\text{SnS}_{(c)}) = -24.34 \pm 1.1 \text{ Kcal/mole.}$$

compared to - 24.7 Kcal/mole (Sudo<sup>(18)</sup>).

St. Clair, Shibley, and Solet<sup>(19)</sup> obtained the vapor pressure of SnS by means of the transpiration method, and calculated the heat and free energy of vaporization above and below the melting point:

For



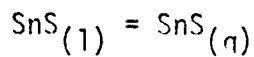
$$\Delta C_p = -1.06 - 3.6 \cdot 10^{-3} T \quad ,$$

$$\Delta H_{\text{subl.}}^0 = 51,355 - 1.06T - 1.8 \cdot 10^{-3} T^2 \quad (\text{cal/mole}) \quad .$$

$$\Delta G_{\text{subl.}}^0 = 51,355 + 2.44T \text{ Log } T + 1.8 \cdot 10^{-3} T^2 - 46.02T \quad (\text{cal/mole}) \quad .$$

$$\text{Log } p_{\text{SnS}} \text{ , atm} = - \frac{11,225}{T} - .533 \text{ Log } T - 3.93 \cdot 10^{-4} T + 10.059 \quad .$$

For



$$\Delta C_p = - 9.02 \quad ,$$

$$\Delta H_{\text{vap.}}^0 = 50,590 - 9.02T \quad , \quad (\text{cal/mole}) \quad ,$$

$$\Delta G_{\text{vap.}}^0 = 50,590 + 20.77T \text{ Log } T - 99.41 \quad (\text{cal/mole}) \quad ,$$

$$\text{Log } p_{\text{SnS}} \text{ , atm} = - \frac{11,060}{T} - 4.54 \text{ Log } T + 21.729 \quad .$$

The vapor pressure of SnS in equilibrium with molten SnS is, according to Klushin and Chernykh<sup>(20)</sup> (quoted by G. J. Janz<sup>(21)</sup>), expressed as follows:

$$\text{Log } p_{\text{SnS}} \text{ , (mm Hg)} = - \frac{9980}{T} + 9.551 \quad .$$

The existence of other gaseous species than SnS was uncertain until P. Colin and J. Drowart<sup>(22)</sup> made a thermodynamic study of SnS in 1964 using a mass spectrometer.

They found that the major components of the tin-sulfur vapor are gaseous SnS and Sn<sub>2</sub>S<sub>2</sub>, the latter in a very low proportion. Possible trimer Sn<sub>3</sub>S<sub>3</sub> and tetramer Sn<sub>4</sub>S<sub>4</sub> molecules, whose intensity relative to SnS was equal to, or smaller than 5 · 10<sup>-4</sup>, could not be detected. Their summarized data are given as follows:

Molecule	Temp. Range °K	$H_{\text{subl.},298}^0$ Kcal/mole	$D_0^0 = \text{Dissoc. energies}$
SnS	815 - 1005	$52.6 \pm 1.6$	$110.1 \pm 3$ Kcal/ mole
Sn <sub>2</sub> S <sub>2</sub>	815 - 1005	$56.5 \pm 5$	-

Thus, the thermodynamic data given by Richards<sup>(16)</sup>, St. Clair et al.<sup>(19)</sup>, and Klushin and Chernikh<sup>(20)</sup> are not referred to the partial pressures of SnS(g) but to the total vapor pressure of tin as a sulfide; i.e.

$$P_{T(\text{SnS})} = P_{\text{Sn}(g)} + P_{\text{SnS}(g)} + 2 P_{\text{Sn}_2\text{S}_2(g)}$$

It can be assumed, without introducing a significant error, that:

$$P_{\text{SnS}(g)} = P_{T(\text{SnS})}$$

as will be shown later.

Theoretical thermodynamic considerations, based mostly on Colin and Drowart's investigations<sup>(22)</sup>, were given by H. H. Kelloqq<sup>(23)</sup> in 1966.

The standard free energies for vaporization and related equilibria for the Sn - S system, are given in table III. These equations were calculated by a least-squares fit to the data tabulated in Kelloqq's paper.

The presence of SnS<sub>2</sub> in SnS samples is not harmful to SnS because SnS<sub>2</sub> decomposes at low temperatures to SnS and a complex mixture of polyatomic sulfur molecules. If, in turn, samples contain also SnO<sub>2</sub>, these are simultaneously reduced to SnS as shown by effusion of SO<sub>2</sub> molecules. These processes were observed in the mass spectrometer at about 500°K by Colin and Drowart<sup>(22)</sup>.

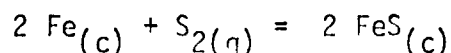
Table III

Sn - S System. Standard Free Energy for Vaporization and Related Equilibria<sup>(23)</sup>.

R E A C T I O N	$\Delta G_R^0 = A \cdot T + B$ (cal/mole)			
	A	B	Temp. Range, °K	$\pm x$ (cal)
Sn(l) = Sn( $\eta$ )	-23.83	+70,190	505 - 1500	6.05
Sn(l) + $\frac{1}{2}$ S <sub>2</sub> ( $\eta$ ) = SnS(c)	+24.7927	-43,704	493 - 1143	32.41
Sn(l) + $\frac{1}{2}$ S <sub>2</sub> ( $\eta$ ) = SnS(l)	+14.6092	-32,042	1143 - 1500	22.43
SnS(c) = SnS( $\eta$ )	-35.357	+50,671	493 - 1143	10.396
SnS(l) = SnS( $\eta$ )	-26.1126	+40,102	1143 - 1500	6.117
2SnS( $\eta$ ) = Sn <sub>2</sub> S <sub>2</sub> ( $\eta$ )	+37.96	-46,888	1100 - 1500	34.33

### Iron - Sulfur System

Rosenqvist<sup>(24)</sup> studied the iron - sulfur system based on data surveyed by Hansen<sup>(25)</sup> and the work on thermal analysis by Jensen<sup>(26)</sup>. The free energy of formation of FeS is given below:



$$\Delta G_F^0 = - 71,500 + 25.25 T \quad (\text{cal}) \quad (500 - 988^\circ\text{C}).$$

Which agrees very well with data obtained by Sudo<sup>(27)</sup>:

$$\Delta G_F^0 = - 71,250 + 24.62 T \quad (\text{cal}) ,$$

and by Alcock and Richardson<sup>(28)</sup>:

$$\Delta G_F^0 = -71,820 + 25.12 T \quad (\text{cal}) .$$

More accurate expressions, which take into consideration the specific heats, the latent heats of the phases, and the magnetic transformations of iron and iron sulfide are given by Kubaschewski, Evans, and Alcock<sup>(1)</sup>. These are reproduced in table IV.

Table IV

Free Energies of Formation of Iron Sulfide Species<sup>(1)</sup>

REACTION	$\Delta G_F^0 = A \cdot T + B \quad (\text{cal/mole})$		
	A	B	Temp. Range, °K
$2\text{FeS}_{\alpha}(\text{c}) = 2\text{Fe}_{\alpha}(\text{c}) + \text{S}_2(\eta)$	-31.18	+74,320	298 - 412
$2\text{FeS}_{\beta}(\text{c}) = 2\text{Fe}_{\beta}(\text{c}) + \text{S}_2(\eta)$	-25.12	+71,820	412 - 1179
$2\text{FeS}_{\beta}(\text{c}) = 2\text{Fe}_{\gamma}(\text{c}) + \text{S}_2(\eta)$	-25.48	+72,140	1179 - 1261
$2\text{FeS}_2(\text{c}) = 2\text{FeS}(\text{c}) + \text{S}_2(\eta)$	-90.0	+86,700	600 - 1100

Hsiao and Schlechten<sup>(15)</sup> give the following approximate expression for the FeS vapor pressure:

$$\text{Log } p_{\text{FeS}}, (\text{mm Hg}) = -10,850/T + 4.162$$

Temperature range: 804 - 1006°C.

Pressure range,  $\text{Log } p_{\text{FeS}}, (\text{mm Hg}) = -5.84$  to  $-4.26$

$$p_{\text{FeS}}, (\text{mm Hg}) = 1.44 \cdot 10^{-6} \text{ to } 5.49 \cdot 10^{-5}$$

which shows the extremely low pressure of this sulfide. To corroborate this, Rosenqvist<sup>(24)</sup> states that the vapor pressure of FeS is too low to be measured directly. Advantage of this fact is taken to study the vaporization of SnS in Fe-Sn mattes.

### Iron - Tin - Sulfur System

The ternary system was investigated by Murach and Likhnikaya<sup>(29)</sup> in 1938. According to these authors, the iron-tin matte contains less sulfur than could be expected in solutions of FeS and SnS. Therefore, they believed that tin in mattes is present also as dissolved metal. They showed a miscibility gap between 0%Fe and 50%Fe which, according to the now well established limits of the miscibility gap region in the iron-tin system, is wrong. The correct limits of that miscibility gap are 20%Fe and 50%Sn<sup>(3,4,30)</sup>.

Moh<sup>(10)</sup> investigated the phase relations in this system at 600°C by the rigid silica tube method and found that the stable phases at this temperature are: pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ) and pyrite ( $\text{FeS}_2$ ) on the Fe-S join; herzenberquite (SnS),  $\text{Sn}_2\text{S}_3$ , and  $\text{SnS}_2$  on the Sn-S join; and  $\alpha$ -Fe solid solution with up to 6at%Sn, hexagonal FeSn and liquid on the Fe-Sn join. No ternary compounds exist at 600°C.

Solid solutions between phases such as  $\text{FeS}_2$  and SnS,  $\text{SnS}_2$ ,  $\text{Sn}_2\text{S}_3$ , and FeS are restricted to less than 1%, whereas the mutual solubilities between SnS and FeS exceed 1%. The solubility of sulfur in either Fe or FeSn as well as that of the metals in liquid sulfur was reported too small to be detected<sup>(10)</sup>. There is no other account on this system in the literature.

## Iron Sulfide - Tin Sulfide System

The literature gives only one reference on this system. The phase diagram was studied by Haan<sup>(8)</sup> in Germany (1913). The graph obtained by Haan is given in Phase Diagrams for Ceramists<sup>(31)</sup> (1964) and there are no other data available.

The following data can be obtained from the phase diagram:

SnS melting point at 870°C,  
 FeS melting point at 1188°C .  
 Eutectic temperature at 785°C  
 at 15%FeS (85 wt%SnS).  
 No solid solubility has been detected.

Later, J.P. Coughlin<sup>(32)</sup> determined the melting point of FeS as 1195°C. This value is given by Kubashevski et al.<sup>(1)</sup>, and will be taken for calculations in this work since it is believed to be the most reliable.

Davey and Flossbach<sup>(33)</sup> made an estimation of the vapor pressure of SnS over tin-iron mattes based on this phase diagram and on data given by Kelloqq<sup>(23)</sup>. They give the following expression for the vapor pressures of SnS over Sn-Fe mattes:

$$\text{Log } p_{\text{SnS}} = -8650/T + 5.62 + \text{Log } N_{\text{SnS}} + 230.0 \cdot N_{\text{FeS}}^2 / T$$

for a temperature range of 1000 - 1500°K.

The value 230.0 corresponds to a constant (B) when assuming regular solution behavior of the liquid phase:

$$\text{Log } \gamma_{\text{FeS}} = \frac{B}{T} \cdot N_{\text{SnS}}^2 \quad ,$$

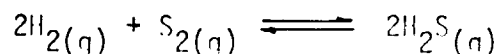
and to an eutectic composition of 18wt%FeS.

The following chapter will present some calculations based on Davey's estimates.

### Hydrogen - Sulfur System

Thermodynamic data on this system were required to calculate the  $H_2S/H_2$  ratios for the mixtures of these two gases acting as a carrier gas in the transpiration method, and in this manner maintain a controlled sulfur potential so as to prevent any decomposition of the sulfide mixtures during the process.

Kubaschewski et al.<sup>(1)</sup> list the following data for the formation of  $H_2S$  gas:



$$\Delta G_F^0 = -40,210 + 7.27T \text{ Log } T - 1.21T \quad (\pm 700 \text{ cal})$$

for  $T = 298$  to  $1750^\circ K$  ,

or:

$$\Delta G_F^0 = -43,160 + 23.61T \quad (\pm 1000 \text{ cal})$$

for  $T = 298$  to  $1800^\circ K$  .

Elliott and Gleiser<sup>(14)</sup> give for the same equation a table of values, from which a least-squares fit calculation gives:

$$\Delta G_F^0 = -43,006 + 23.407T \quad (\pm 21.2 \text{ cal})$$

for  $T = 900$  to  $1600^\circ K$ .

Hager<sup>(34)</sup> made a careful survey of the literature on the hydrogen-sulfur system and calculated equations of  $\Delta G_F^0$  of  $H_2S(g)$ ,  $HS(g)$ , and  $S(g)$  species at high temperatures based on values of  $\Delta G_F^0$  given in the JANAF tables<sup>(35)</sup> and gives the equations for  $\Delta G_F^0$  of  $S_6(g)$  and  $S_8(g)$  from Richardson and Jeffes<sup>(36)</sup>.

These equations, along with above given data are listed in Table V.

The reference states for sulfur and hydrogen are the ideal  $S_2(g)$  and ideal  $H_2(g)$  respectively in all the equations given in Table V.

It can be seen that for the formation of  $H_2S(g)$ , the agreement in all cases is good. The values given by Kubaschewski et al.<sup>(1)</sup> were taken for calculations in this work since they are based on most recent data.

Table V

Thermodynamic Properties of Hydrogen Sulfide and  
Sulfur Gases

SPECIES	$\Delta G_F^0$ , calories	Temp. Range, °K	SOURCE REFERENCE.
$H_2S(g)$	$-20,105 + 3.635T \text{ Log}T - .605T$ ( $\pm 350$ cal)	298 - 1750	1, 12
	$-21,580 + 11.805T$ ( $\pm 500$ cal)	298 - 1800	1, 36
	$-21,580 + 11.80 T$ ( $\pm 500$ cal)	298 - 1723	14, 37
	$-21,570 + 11.79 T$ ( $\pm 200$ cal)	900 - 1700	34, 35
$HS(g)$	$+20,070 - 3.70T$ ( $\pm 300$ cal)	900 - 1700	34, 35
$S(g)$	$+51,170 - 14.44T$ ( $\pm 1000$ cal)	900 - 1700	34, 35
$S_6(g)$	$-66,450 + 73.74T$ ( $\pm 3000$ cal)	298 - 1300	34, 35
$S_8(g)$	$-99,200 + 113.16T$ ( $\pm 4000$ cal)	298 - 1300	34, 35

### III. THE FUMING OF TIN FROM SLAGS AND MATTES

Apart from tin, slags from tin smelting contain considerable quantities of Pb, Zn, Cu; as well as rare metals which are valuable to the economy of the tin-producing countries.

As stated above (Ch. I), and as practical experience has shown, among all the existing processes to recover tin from second-stage slags, the most effective and economically advantageous is the slag fuming process.

#### Description of the Process

The essence of the process consists in the conversion of SnO in slags into the more volatile compound SnS, which is then recovered as a dust in the form of SnO<sub>2</sub>.

Studies on the volatility of SnS are not scarce; some of them (the important ones) were already cited in Chapter II.

Some of the works at a pilot plant or at industrial level given in the literature are mentioned below:

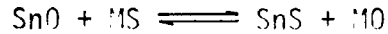
A development of a process of tin fuming applicable to the enrichment of low-grade Bolivian and German tin concentrates by Lange and Barthel<sup>(38)</sup>.

Belyayev<sup>(7)</sup>, Murach<sup>(5)</sup>, Kolodin<sup>(39)</sup> describe the fuming process in detail.

Wright<sup>(6)</sup> also quotes these authors in his book.

Wright himself conducted a pilot-plant investigation, using a modification of the Kolodin-type furnace, built by the Institute of Mining and Metallurgical Investigations at Oruro, Bolivia. There is no published account of this.

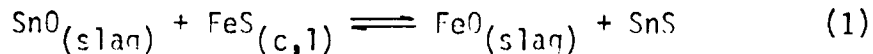
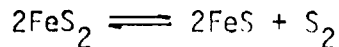
Formation of SnS from stannous oxide in slag can be effected by exchange reactions with sulfides of other metals:



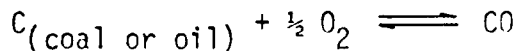
where MS could be  $\text{Al}_2\text{S}_3$ , CaS, ZnS, or FeS, the most effective and most expensive being  $\text{Al}_2\text{S}_3$ .

Since pyrite,  $\text{FeS}_2$ , transforms easily to FeS at temperatures above  $600^\circ\text{C}$ , and as it is the cheapest, it is most commonly used for tin sulfidization.

Slag from second-stage tin smelting is melted, or kept in the molten state, in a reverberatory or rotary furnace, and when in the molten state it is carried in steel ladles (batches of 6 - 8 tons) and poured into the fuming furnace where it is blown by a mixture of coal dust, or oil, air, and pyrite. The pyrite mixes with the slag and decomposes with formation of ferrous sulfide which extracts the tin from its silicates in the slag:



Zinc oxide in slag reacts with CO according to:



This reduced Zn vaporizes and is trapped as ZnO in the electrostatic precipitators when the exhaust furnace gases are cleaned.

Lead is removed from slag as PbO, PbS, and Pb vapor.

Rare elements that form volatile species are also removed as vapors from the slag and trapped as dust.

The furnace used in tin fuming is basically the same as for the zinc fuming process. It is a water-jacketed rectangular shaft-furnace, as shown in Fig. 2, with 12 converter-type tuyeres (6 on each short side of the furnace) through which the coal, or oil and pyrites are blown into the furnace by compressed air. The hearth of the furnace is a cast iron plate with 12 water-cooled steel pipes cast into it. It is installed on 6 cast-iron supports. Blowing begins at the time the slag is being poured into the furnace and continues for about 2 to 3 hours.

The process, according to Belyayev<sup>(7)</sup>, can be divided into three periods:

- a) Heating-up of the slag.
- b) Reduction and sulfidization.
- c) Reheating of the slag before tapping.

Slag temperatures are from 1150 to 1300°C.

The operating conditions, as summarized by Wright<sup>(6)</sup>, are:

Furnace charge	approx. 8.5 ton.
Duration of cycle	2 - 3 hours.
Coal consumption (When oil is not used)	18wt% of slag treated
Pyrite consumption	4.1wt% of slag.
Air supply	67% of theoretical for complete combustion.

Typical charge and product compositions are given in Table VI.

Private communication<sup>(40)</sup> gives the following recent data from a Russian and a Bolivian plant respectively:

Russian plant;	charge	avge. 1%Sn
	waste slag	0.1 - 0.09%Sn.
Bolivian plant:	charge	avge. 6%Sn
	waste slag	0.5%Sn.

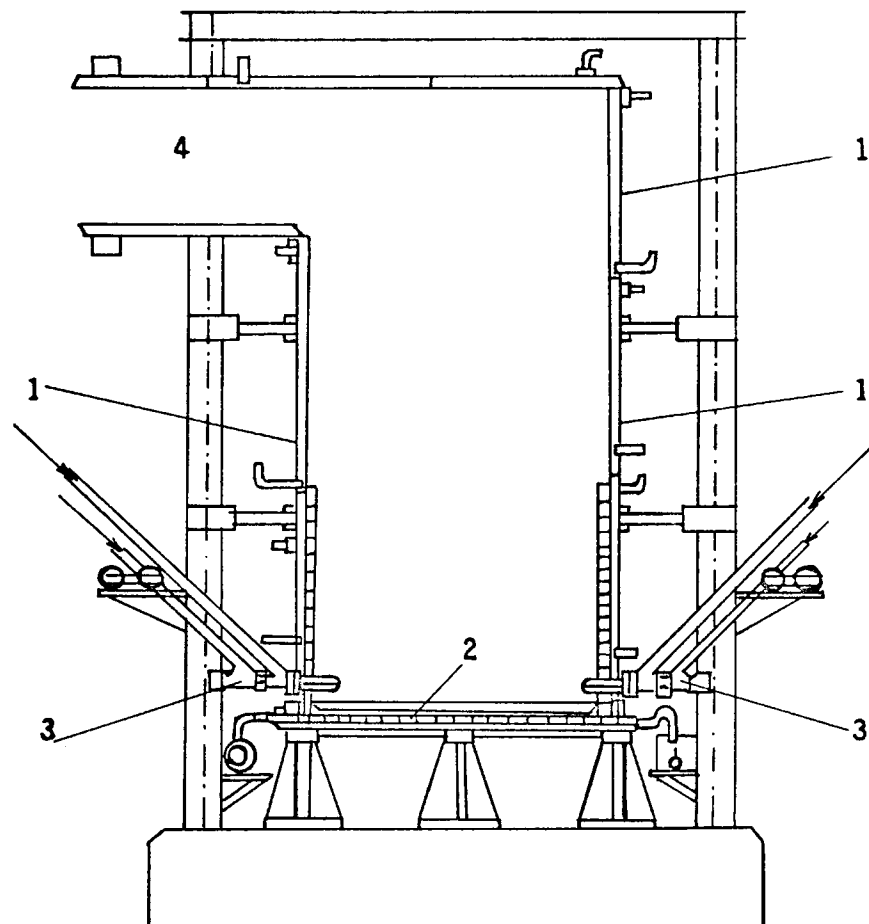


FIG. 2. SHAFT FURNACE FOR SLAG FUMING.  
1. COOLING PLATES      3. TUYERES  
2. HEARTH              4. FLUE.  
(Ref. 7)

Table VI.

Chemical Composition of Slags Treated at the Podols'k  
Smelter in Russia<sup>(6)</sup>.

% ELEMENT IN CHARGE	DUST PRODUCT (%)	WASTE SLAG (%)	RECOVERY (%)	
Sn	1.5 - 1.8	15 - 18	<0.2	90 -95
Pb	0.8 - 1.0	10 - 12	<0.1	90 -95
Zn	3.5 - 4.5	27 - 32	<2.5	60 -65
Cu	0.8 - 1.0	-	-	-
S	1.5 - 2.0	4 - 6	-	-
Fe	20.0 - 25.0	-	-	-
As	-	1.5 - 2.0	-	-

### Matte Formation

The use of excess pyrite or sulfur blown into the molten slag reduces the recovery of tin as the volatile Sn sulfide, because of the formation of an iron-tin matte due to undecomposed ferrous sulfide. This matte consists not only of FeS and SnS but also of the sulfides of the other metals present in slag (Pb, Cu, Zn, etc.).

Matte, being heavier than slag, collects under the latter in the hearth of the fuming furnace and is periodically tapped as it accumulates.

It is eventually treated again to volatilize the SnS, either separately, or mixed with new batches of slag.

It is of great interest to the tin metallurgist to know the extent to which SnS volatility is hampered by the solution of stannous sulfide in this matte, so as to determine the optimum conditions for this process.

It is advisable at this point to analyse in more detail the data available on the tin - sulfur system.

### Thermodynamic Evaluations

Figures 3 and 4 were obtained by calculations from data given in Table IV, Chapter II. Complete calculations are given in Appendix I. The stability regions, depending on the partial pressure of  $S_2$ , are indicated at the top of the two figures. It can be seen that, as the temperature increases, the partial pressures of  $Sn_2S_2$  gaseous species also increase in importance as do those of  $SnS_{(g)}$ , but the percentage of  $Sn_2S_2_{(g)}$  relative to that of  $SnS_{(g)}$  decreases.

The effective total pressure of Sn - S gaseous species is plotted against sulfur pressure in Fig. 5, and against  $1/T$  in Fig. 6. The partial pressures of  $SnS_{(g)}$  and  $Sn_2S_2_{(g)}$  versus  $1/T$  are also given in Fig. 6, to show the importance of  $p_{SnS}$  over the total pressure and the very small contributions of  $Sn_2S_2_{(g)}$  and of  $Sn_{(g)}$  to the effective total pressure, given as:

$$p_{T(SnS)} = p_{Sn_{(g)}} + p_{SnS_{(g)}} + 2 p_{Sn_2S_2_{(g)}} \cdot$$

Therefore,  $p_{Sn}$  and  $p_{Sn_2S_2}$  can be neglected without introducing any significant error to the thermodynamic properties of:

$$SnS_{(c,l)} = SnS_{(g)} \cdot$$

The stability zones of interest to this investigation are the zones to the right of the  $Sn(l) - SnS_{(c,l)}$  line, that is; the zones at which the vapor pressures of  $SnS_{(g)}$  and  $Sn_2S_2_{(g)}$  are independent of sulfur gas pressures since no decomposition of  $SnS_{(c,l)}$  is desired.

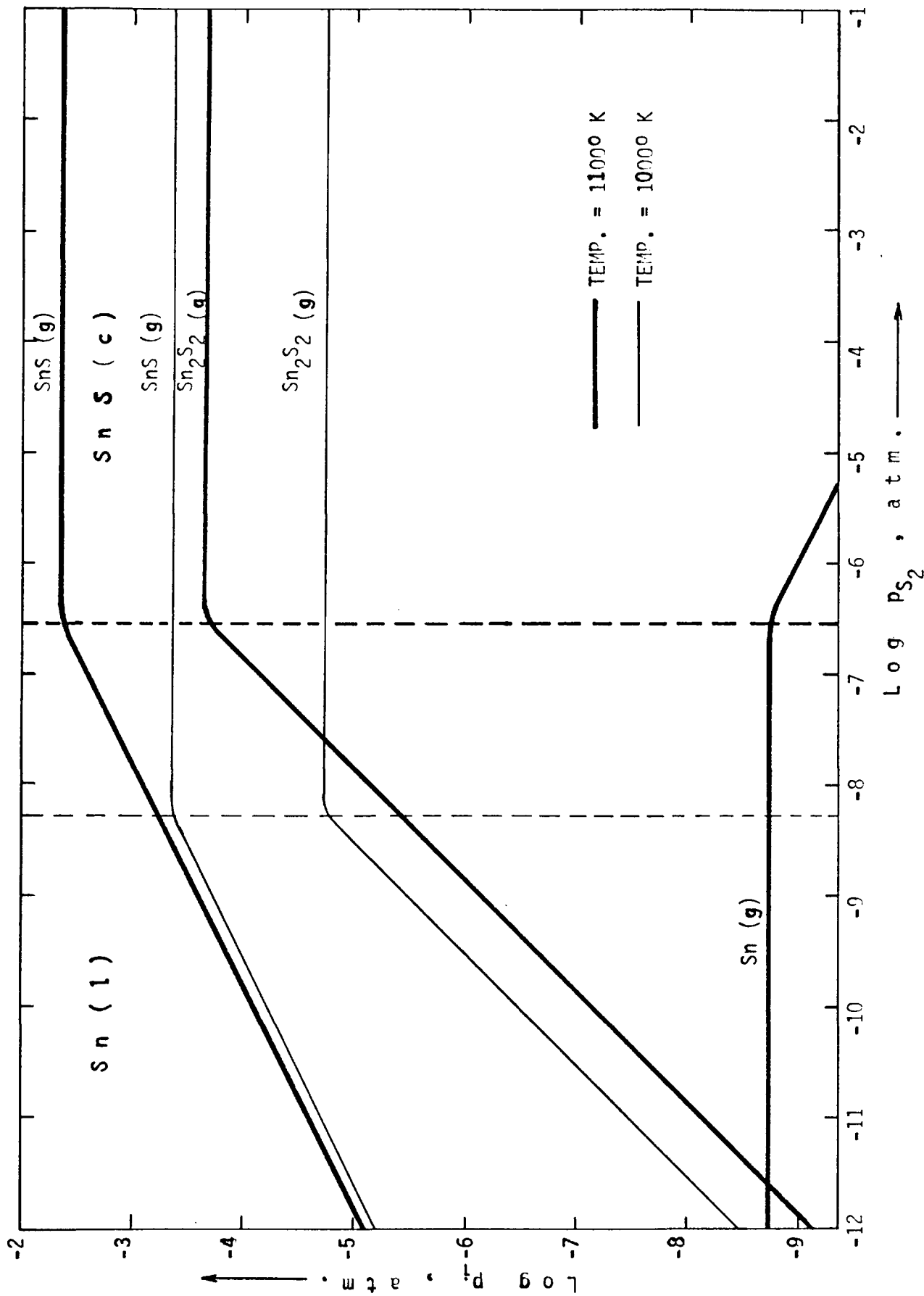


FIG. 3. VAPOR PRESSURES IN SYSTEM Sn - S.

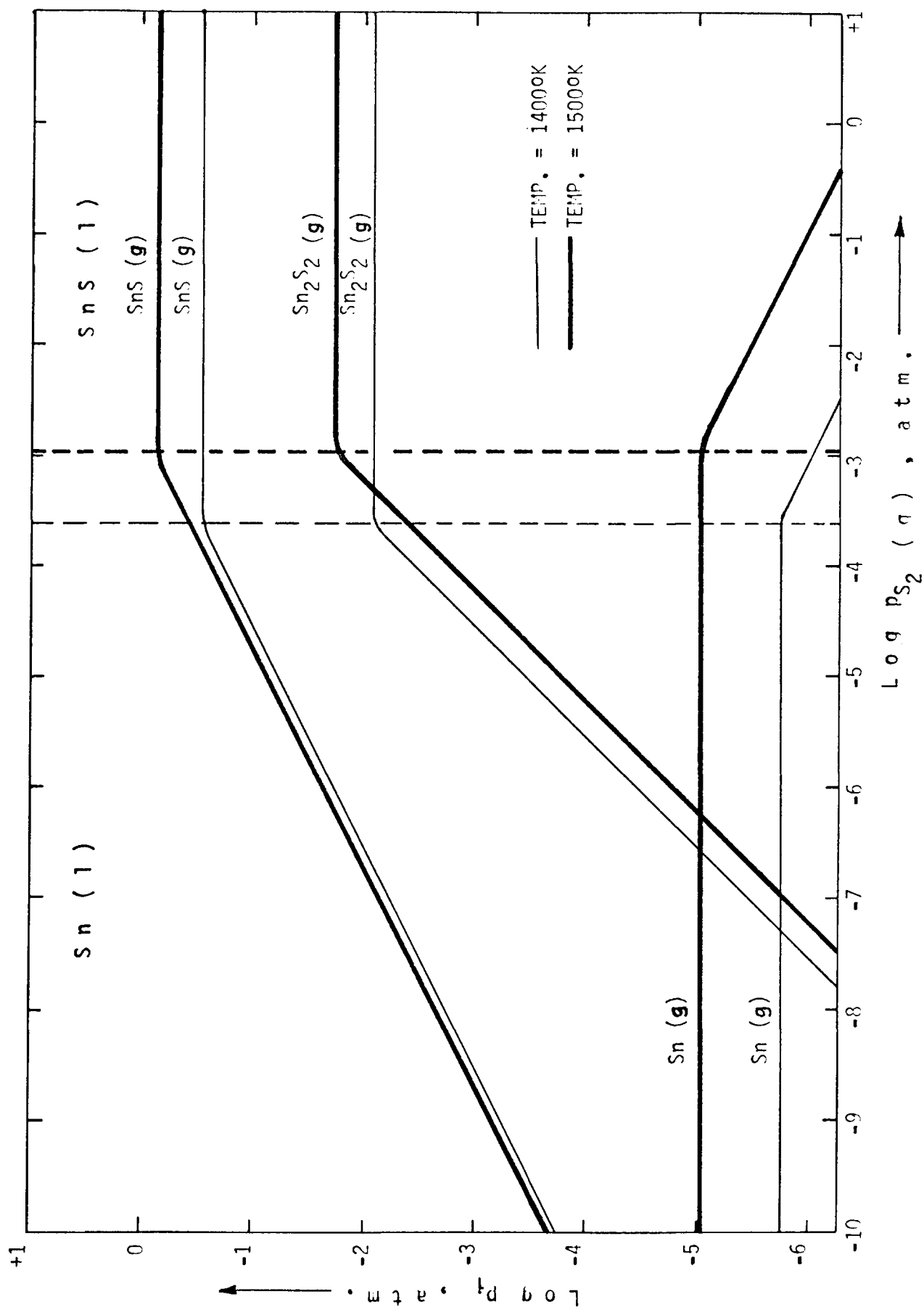


FIG. 4. VAPOR PRESSURES IN SYSTEM Sn - S.

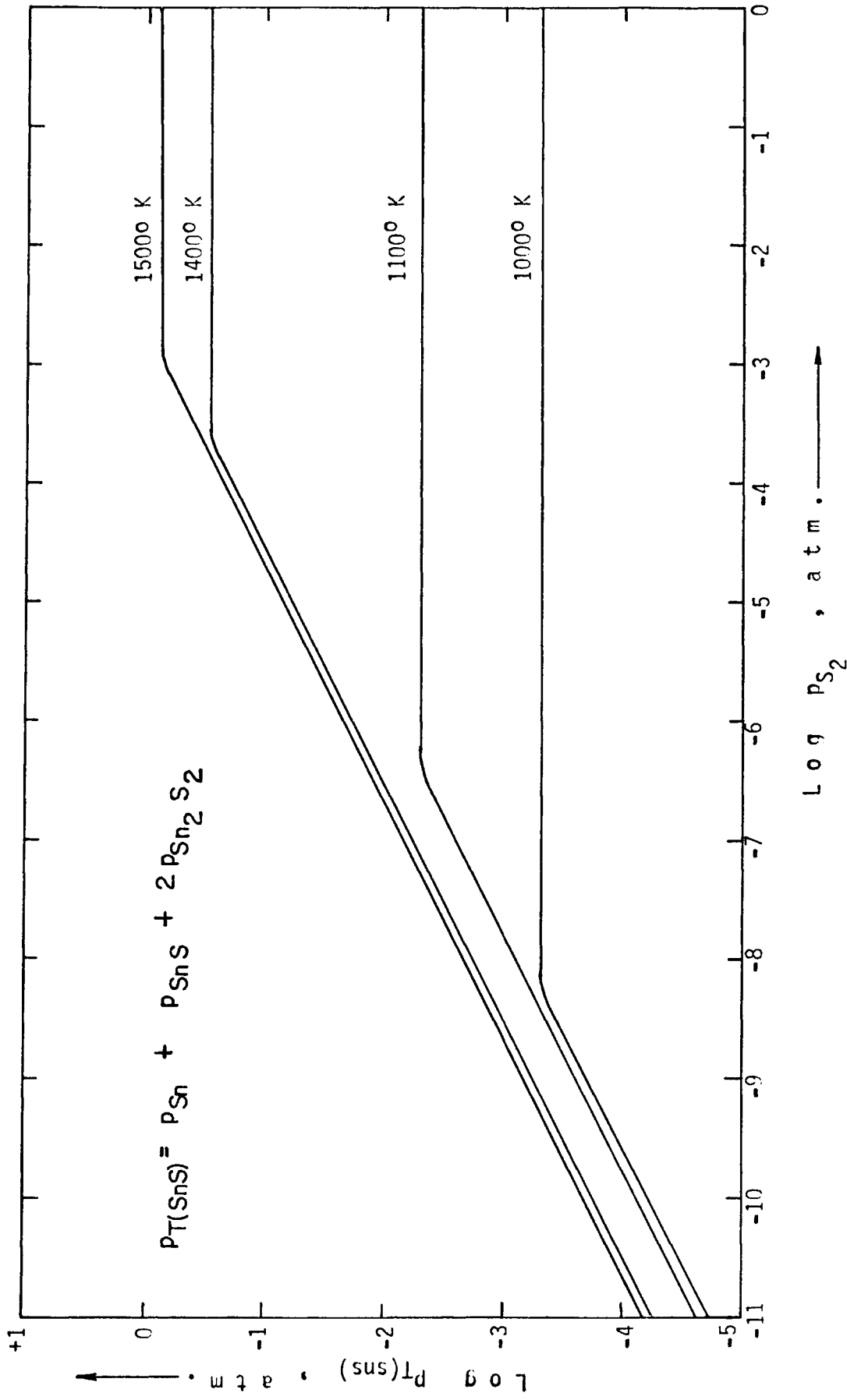


FIG. 5 . EFFECTIVE TOTAL VAPOR PRESSURE OF TIN IN SYSTEM Sn - S AS A FUNCTION OF SULFUR PRESSURE.

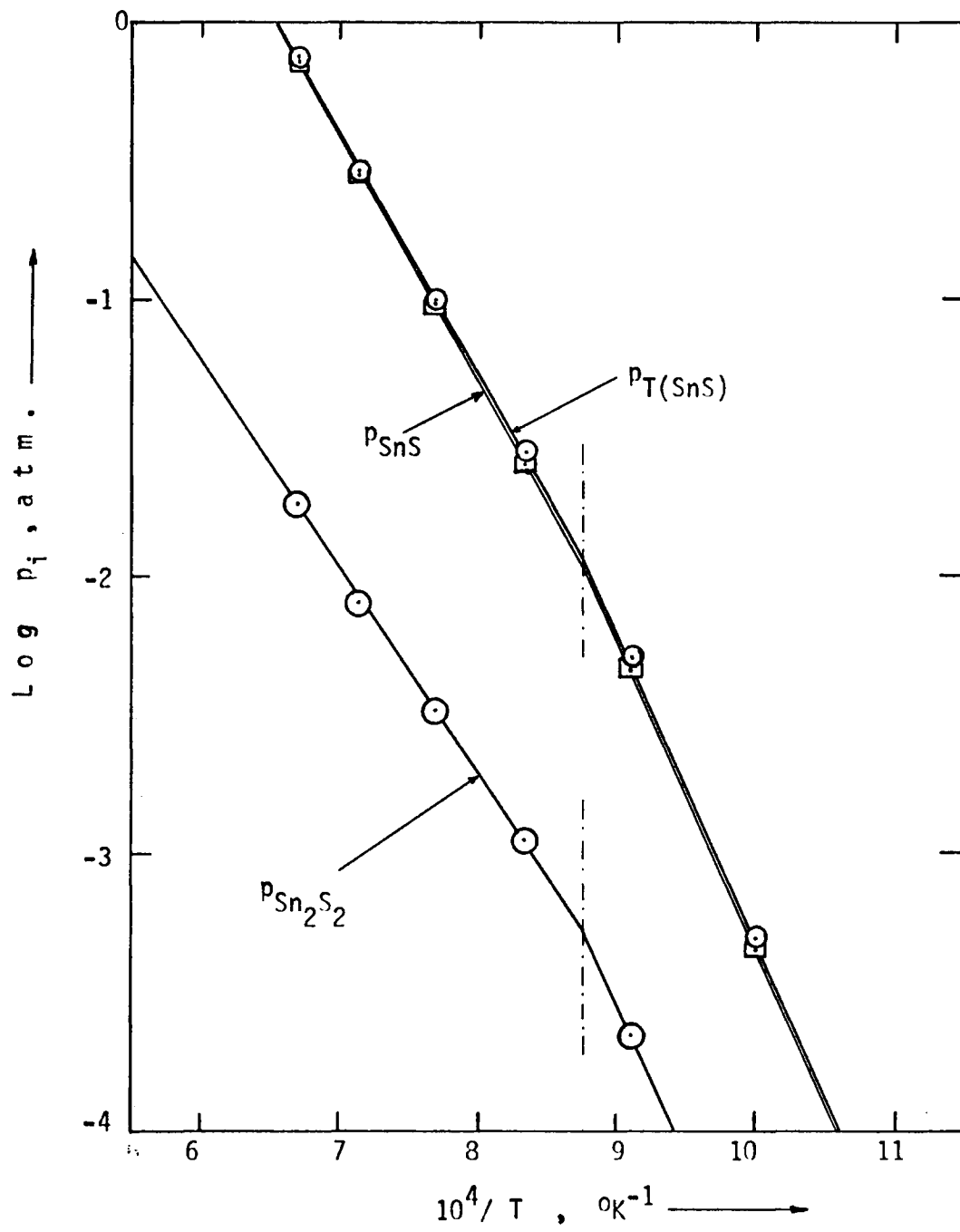


FIG. 6. TOTAL AND PARTIAL PRESSURES ABOVE SnS (c,1).

The percentage of  $P_{\text{Sn}_2\text{S}_2(g)}$  over the effective total pressure ranges between 2.4 to 4% (in the flat zones) at temperatures between 1500 to 1000°K in that order. In all cases  $P_{\text{Sn}_2\text{S}_2(g)}$  is less than 1% of the total pressure when it is dependent on the sulfur pressure (Figs. 3,4, and 5). Calculations are given in Appendix I.

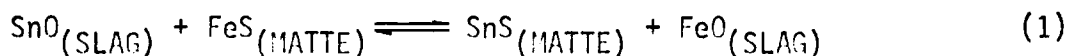
Therefore, for the present work, the total vapor pressure of SnS species will be considered as being the vapor pressure of  $\text{SnS}_{(g)}$  only, neglecting the other gaseous species.

Crude estimations based on the thermodynamic properties of FeS and SnS, and on the FeS-SnS phase diagram are presented below. The pressure of SnS vapor over the matte is proportional to its activity therein, say:

$$P_{\text{SnS}_{\text{MATTE}}} = c \cdot a_{\text{SnS}_{\text{MATTE}}} \quad (2)$$

where  $c = \text{constant at each temperature} = P_{\text{SnS}}^0$  :

Referring again to the sulfidizing reaction of SnS from slags, and applying it to the matte formation:



for which:

$$K = \left[ \frac{a_{\text{SnS}}}{a_{\text{FeS}}} \right]_{\text{MATTE}} \cdot \left[ \frac{a_{\text{FeO}}}{a_{\text{SnO}}} \right]_{\text{SLAG}} \quad (3)$$

Substituting (2) into (3):

$$a_{\text{SnS}_{\text{MATTE}}} = \frac{P_{\text{SnS}_{\text{MATTE}}}}{c} = K \cdot a_{\text{FeS}_{\text{MATTE}}} \cdot \left[ \frac{a_{\text{SnO}}}{a_{\text{FeO}}} \right]_{\text{SLAG}}$$

Therefore:

$$P_{\text{SnS}}_{\text{MATTE}} = K' \cdot a_{\text{FeS}}_{\text{MATTE}} \cdot \left[ \frac{a_{\text{SnO}}}{a_{\text{FeO}}} \right]_{\text{SLAG}}$$

Hence, the vapor pressure of pure SnS is higher, the higher the activity of SnO in the slag, and the lower the FeO content therein.

Now the vapor pressure of pure SnS can be calculated from data given in Table III (Ch. II), and the activity of SnS in iron-tin mattes can be obtained from the phase diagram given by Haan<sup>(8)</sup> and the enthalpy of fusion of FeS<sup>(1)</sup>. Thus, the partial pressure of SnS vapor over Sn-Fe mattes is estimated to be represented by the following equations:

$$\text{Log } P_{\text{SnS}} = - \frac{\Delta G_v^0}{RT} + \text{Log } N_{\text{SnS}} + \frac{338.225}{T} \cdot N_{\text{FeS}}^2 \quad (4)$$

$$\text{Log } P_{\text{SnS}} = - \frac{\Delta G_s^0}{RT} + \text{Log } N_{\text{SnS}} + \frac{338.225}{T} \cdot N_{\text{FeS}}^2 \quad (5)$$

Where  $\Delta G_v^0$  and  $\Delta G_s^0$  are the free energy of vaporization and sublimation respectively. Their expressions are given in Table III (Ch. II).

The complete derivation of these two equations is given in Appendix II, along with the calculation of the phase diagram knowing the temperatures of fusion, the eutectic temperature and composition, and the enthalpy of fusion of FeS assuming a regular solution behavior of the liquid phase and that there is no solid solubility in the system. The agreement of these results with the diagram in the literature appears to be good. Figure 7 shows the phase diagram as obtained by Haan<sup>(8)</sup>, and as calculated assuming the regular solution model for the liquid phase.

Figure 8 shows the variation of the partial pressure of SnS as a function of SnS content in the mattes for different temperatures as calculated from equations (4), and (5).

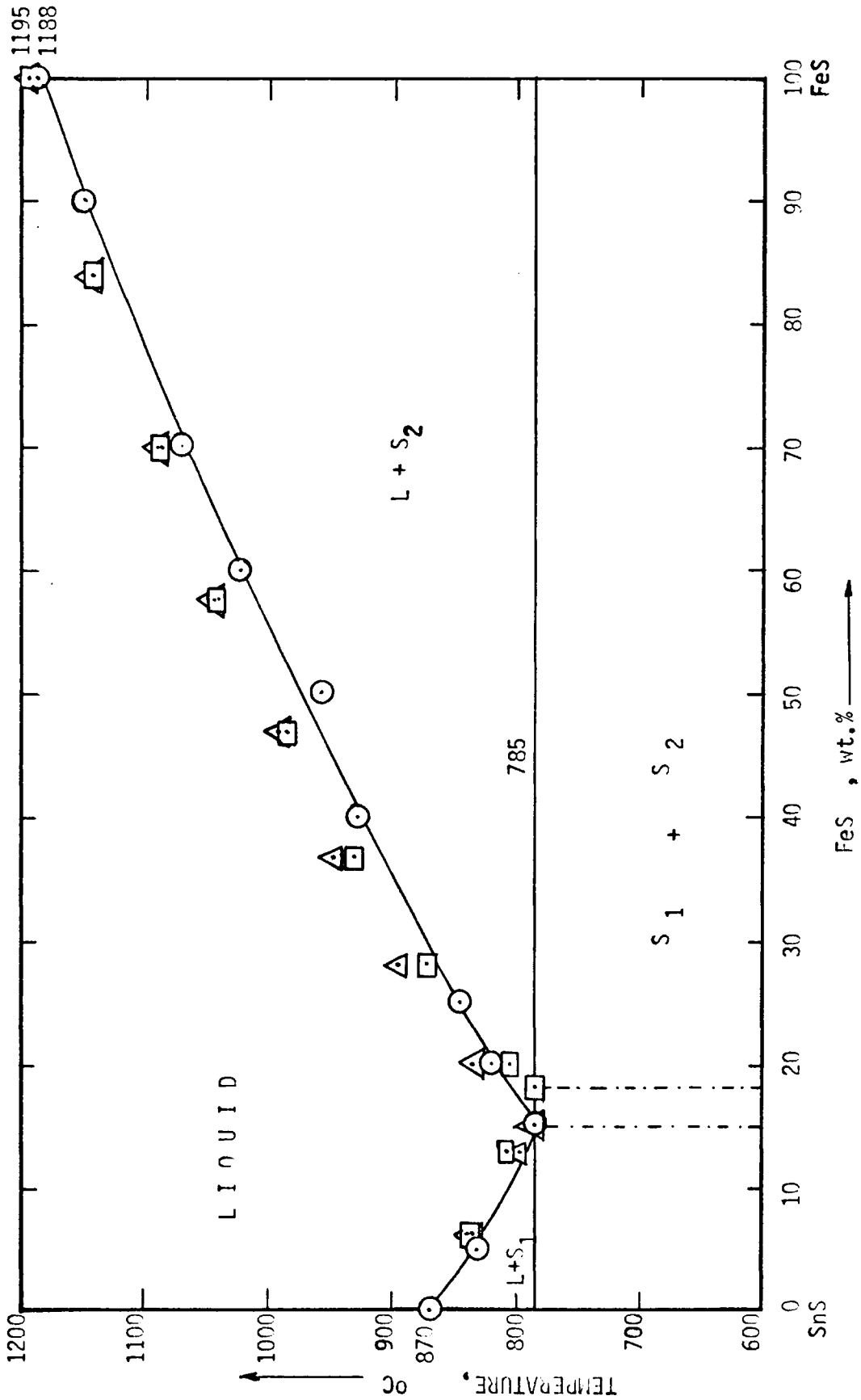
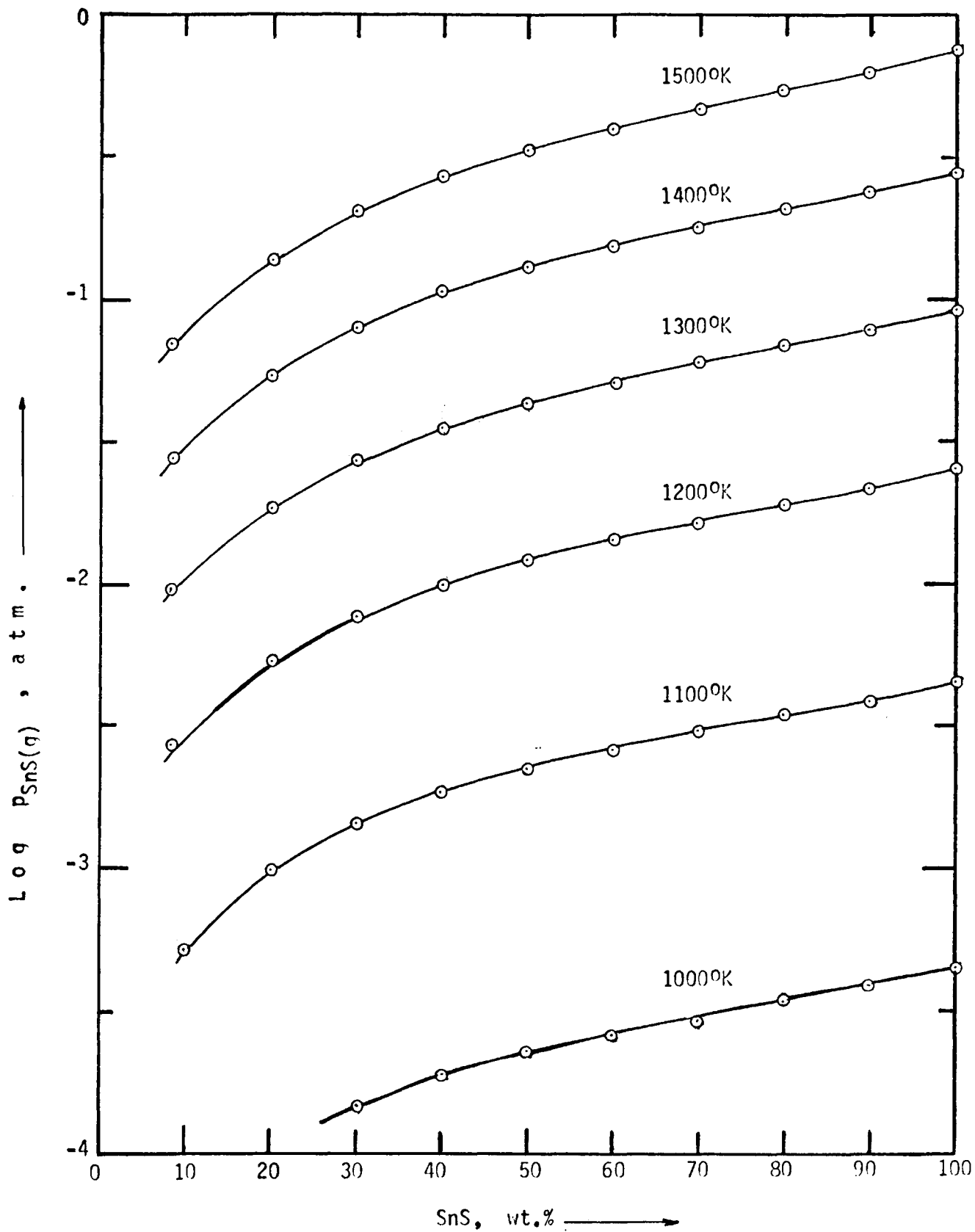


FIG. 7 . SnS - FeS PHASE DIAGRAM.  
 ○ EXPERIMENTAL, HAAN.  
 □ CALCULATED, DAVEY.  
 △ CALCULATED, THIS WORK.

FIG. 8 . VAPOR PRESSURE OF  $\text{SnS}(g)$  ABOVE IRON - TIN MATTES.

The accuracy of these estimates is dependent upon the accuracy to which the phase diagram was determined in 1913, and the validity of the regular solution assumption for the liquid phase. Therefore, the determination of the vapor pressures of SnS over Fe-Sn mattes in the laboratory is not only justified but necessary for a better control of the tin fuming process.

## IV. EXPERIMENTAL APPARATUS

### AND PROCEDURE

#### Choice of Method

The transportation (transpiration) method was selected because it requires a relatively simple design of apparatus and because it has proved to be successful in measuring vapor pressures of a number of elements, their halides, oxides, and sulfides, over a wide range of vapor pressures (between  $10^{-4}$  to  $10^2$  mm Hg). It has also been extensively used to determine the partial pressures of volatile components of an alloy over the liquid, or solid alloy.

The literature gives numerous accounts of investigations using this method. There are very many, and only the classical and most important to this study are listed here.

It is a dynamic method, by which a measured volume of an inert gas over the solid or liquid matte becomes saturated with tin sulfide vapors. This carrier gas is passed at a constant velocity over the substance in the saturation chamber, at a constant temperature, and carries away the volatile components. The vapor pressure is then determined from the loss in weight of the sample per unit volume of carrier gas.

The important conditions of the transportation method are:

- (i) A uniform temperature zone in the furnace, and
- (ii) the geometry of the reaction or saturation chamber.

These and other features are discussed in detail in Chapter VI.

## Apparatus

The transportation method to determine the vapor pressures of tin sulfide required an apparatus suitable to:

- a) determine the loss in weight of a sample in contact with a moving gas phase at constant flowrate, at a uniform, elevated temperature, and
- b) change flowrates and temperatures for different sets of experiments.

The apparatus utilized for this purpose is shown schematically in Fig. 9, and a photograph is given in Fig. 10. It consisted of two gas purification systems, a gas mixing system, a saturation, and a condensation system. Nitrogen was used at a high flowrate to purge the furnace F3 and the gas trains. It was also used as a carrier gas for measurements of SnS vapor pressures over pure SnS(c) to prove the reliability of the apparatus. Surface oxidation took place in the first experiments. Therefore nitrogen was passed over pure copper turnings at 500°C (furnace F1) and then through two drying chambers containing silica gel and anhydrous ( $\text{Hg}(\text{ClO}_4)_2$ ) respectively (D1, D2) to remove the water vapor. This procedure proved to be sufficient to prevent oxidation at the temperatures mentioned.

Nitrogen could be flushed from the opposite side of the reaction tube in furnace F3 by means of two stopcocks (T2 and S4 in Fig. 9) so as to make sure that air was evacuated as completely as possible.

The second gas purification system was used for the hydrogen. This gas was also passed over copper turnings at 500°C in furnace F2 to remove oxygen if present. From there, it passed through a conduit containing silica gel to remove moisture if still present. Since  $\text{H}_2$  gas had to be mixed with  $\text{H}_2\text{S}$  gas to act as the carrier gas at different  $\text{H}_2\text{S}/\text{H}_2$  ratios, and in order to prevent possible segregation due to differences in temperature and molecular weights during the mixing operation, hydrogen was passed through a pyrex glass spiral (SP) after leaving the purification furnace F2 and the drying tube. This allowed the hydrogen to cool down to room temperature before entering flowmeter F12.

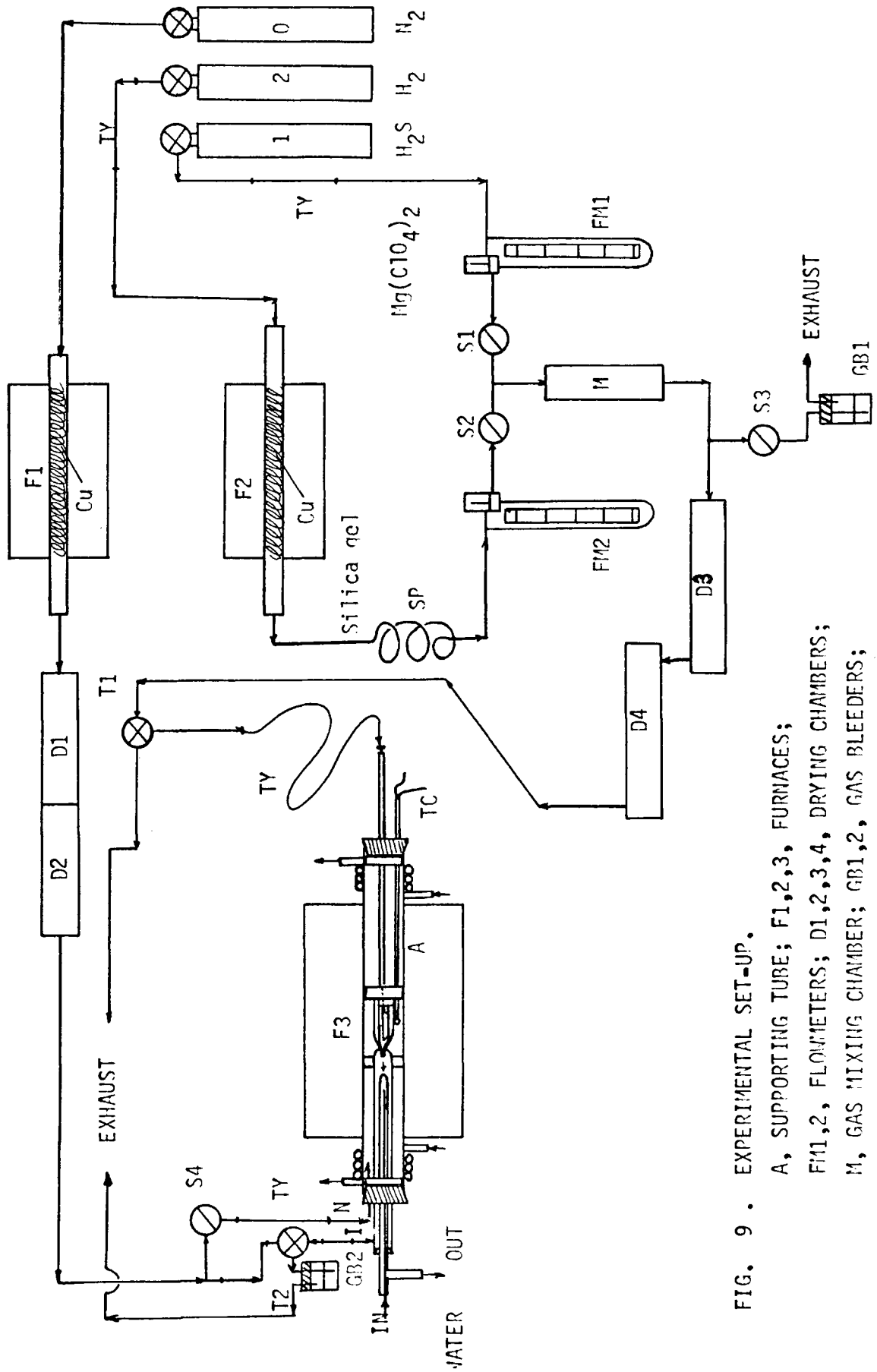


FIG. 9 . EXPERIMENTAL SET-UP.

- A, SUPPORTING TUBE; F1,2,3, FURNACES;
- FM1,2, FLOWMETERS; D1,2,3,4, DRYING CHAMBERS;
- M, GAS MIXING CHAMBER; GB1,2, GAS BLEEDERS;
- T1,2, THREE-WAY STOPCOCKS; S1,2,3,4, TWO-WAY STOPCOCKS;
- SP, COOLING SPIRAL; TC, THERMOCOUPLE; TY, TYGON CONNECTING TUBES.

Hydrogen sulfide gas was passed through a conduit containing magnesium perchlorate ( $Mg(ClO_4)_2$ ) before entering flowmeter FM1 to remove moisture (if present).

From their respective flowmeters,  $H_2S(g)$  and  $H_2(g)$  entered into the mixing chamber M which consisted of a 10-in. pyrex tube filled with glass beads. From the mixing chamber the gas mixture was passed through two drying chambers containing anhydrous ( $Mg(ClO_4)_2$ ) and connected in series to remove any moisture still present, and finally, through stopcock T1 into furnace F3 at different flowrates for each set of experiments.

Temperatures in furnaces F1 and F2 were measured by means of Chromel-Alumel thermocouples and controlled by a Leeds & Northrup 8686-2 potentiometer.

Most of the gas trains consisted of pyrex glass tubing and ground joints. The purification chambers in furnaces F1 and F2 were made of Vycor tubes, since they withstand temperatures of up to  $1000^{\circ}C$ .

Tygon tubing (TY in Fig.9) was used for some small connections in the purification systems and for all the exhaust trains.

It was seen that no constant-head tanks were needed for controlling the constant flow of  $H_2$  and  $H_2S$  gases because the gas tanks were provided with low pressure regulators and with an auxiliary needle valve each. Furthermore, the calibration of the two flowmeters was effected taking the inlet gases to the flowmeter calibrator after the gases passed through all the desiccators, right before entering the furnace, so as to eliminate the so-called "back pressure" effect.

The power for furnaces F1 and F2 was supplied by means of type 116 and type 2PF236B powerstats respectively, operating on 11V AC.

The saturation (reaction) system, shown schematically in Fig. 11, consisted of a three-zone gradient Lindberg/Hevi-Duty horizontal-tube furnace, model no. 54357. This is shown pictorially in Fig. 10a. All three zones were controlled by the automatic control system in the 59744 Lindberg/Hevi-Duty control console operating on 220V AC. The furnace was equipped with a platinum

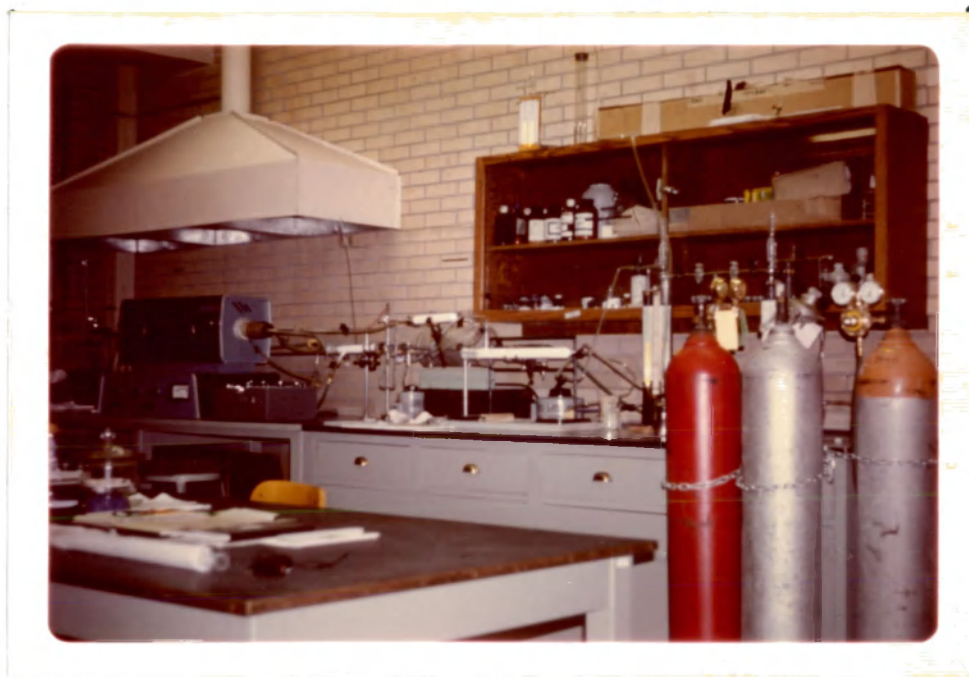


Fig. 10 PHOTOGRAPH OF THE EXPERIMENTAL APPARATUS.



Fig. 10a FURNACE USED FOR THE SnS VAPOR PRESSURE DETERMINATIONS.

thermocouple, and was capable of producing a flat zone of  $\pm 2^{\circ}\text{F}$  over a 12 in. of tube length at maximum operating temperature ( $2200^{\circ}\text{F}$ ), but a 4-in. flat zone in the center of the tube at experimental conditions (considering the temperature drop in the condensing zone), for which the maximum temperature gradient was  $\pm 1.3^{\circ}\text{C}$  at  $700^{\circ}\text{C}$ , and the minimum temperature gradient was  $\pm .15^{\circ}\text{C}$  at  $1000^{\circ}\text{C}$ .

A controlling Pt-Pt/10%Rh thermocouple was placed inside tube A in the center, right beside reaction chamber R, and connected to a Leeds & Northrup 8686-2 potentiometer.

Radial temperature gradient between sample and measuring thermocouple was determined and found to be less than  $2^{\circ}\text{C}$ .

The support tube used was a  $2\frac{1}{2}$  by  $2\frac{1}{2}$  by 42 in. Coors/Mullite tube, A. Inside this tube were placed the condensing chamber C, and the saturation chamber R, inside which the sample boat B was placed. The left side of the support tube was permanently sealed by means of a rubber stopper Z1, and Silicone-Seal super glue fabricated by the General Electric Company.

The pyrex glass condenser was inserted and removed as necessary by means of rubber stopper Z3. When this was in place, silicone-seal glue was also used there.

Transite discs were used as radiation shields, D ( $\frac{1}{2}$ -in. thick), inside tube A. Both ends of this tube were externally refrigerated (II) to prevent overheating of the rubber stoppers Z1 and Z2.

The mullite reaction tube R, having a total length of 7 in. and a diameter of  $\frac{9}{16}$  in. (I.D.), had one end reduced to an inside diameter of  $\frac{1}{32}$  in. (capillary) as shown in Fig. 11. This reduced end, in a 2-in. length, was fitted to the condensing system so as to allow the vapors to hit the condenser as soon as they left the reaction chamber.

The original interior diameter of the reaction chamber was  $\frac{7}{8}$ -in., and its total length was  $8\frac{1}{2}$  in. This was used for the measurements of the vapor pressure of SnS over pure solid SnS, when passing nitrogen as the carrier gas. Its dimensions were reduced afterwards to improve the results by decreasing the dead volume inside the chamber. This will be discussed later.

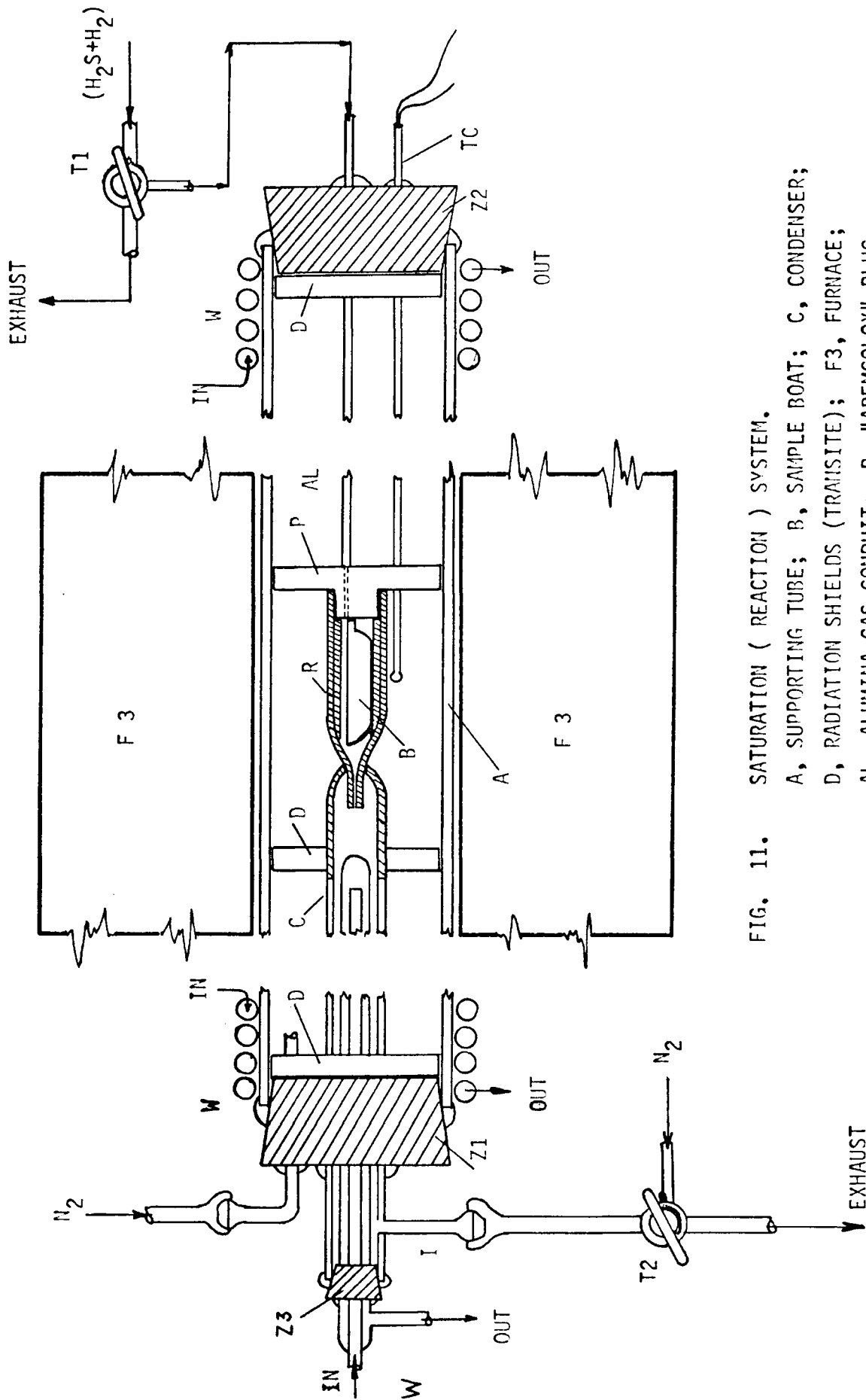


FIG. 11. SATURATION ( REACTION ) SYSTEM.

A, SUPPORTING TUBE; B, SAMPLE BOAT; C, CONDENSER;  
 D, RADIATION SHIELDS (TRAVISITE); F3, FURNACE;  
 AL, ALUMINA GAS CONDUIT; P, "AREMCOLOX" PLUG;  
 R, SATURATION CHAMBER; T1,2, THREE-WAY STOPCOCKS;  
 W, COOLING COIL; Z1,2, RUBBER STOPPERS.

The sample was placed in a 5/16-in. wide by 3-5/16-in. long by 3/16-in. deep Leco combustion boat. The right end of the reaction tube R was tightly closed with an Aremcolox no. 502-1300-Machinable-Ceramic plug, P, which was constructed to fit exactly with the inside walls of the mullite reaction tube, and a thin hole (capillary) was opened in the plug to allow the carrier gas into the chamber. This plug was connected to a 5/32-in. O.D. by 26-in. long Coors/AD-998 Alumina tube (AL) which, in turn, was connected to the gas-train system by means of ground joints and a short length of tygon tubing, TY.

## Experimental

### 1. Materials, Samples, and Matte Preparation

1.1 Gases. Pure nitrogen gas, type E (approx. 99%) for laboratory use, and high-purity hydrogen gas (99.99% $H_2$ ) were supplied by the National Cylinder Company. Both gases were passed through copper turnings at 500°C temperature for further purification. Moisture and/or oxygen in the hydrogen gas was practically undetectable, whereas the nitrogen appeared to contain oxygen, as the copper turnings absorbed this element at considerable rates. Hydrogen sulfide gas, C.P. grade (Purity: 99.6% min.) was supplied by the Matheson company. The main impurity in this gas was (apparently) moisture, which was removed by use of drying chambers containing magnesium perchlorate ( $Mg(ClO_4)_2$ ). It was planned to use silica gel, as recommended by the literature (41) but it was found, and confirmed by chemists, that silica gel absorbs  $H_2S$  as well as  $H_2O$ .

Dibutyl Phthalate (density 1.04 gm/cc) was used as manometer fluid for the flowmeters and as the gas bleeder's fluid.

1.2 Samples. Stannous sulfide ( $SnS$ ), 99.99% min., was supplied by A.D. Mackay, Inc. and by the Research Organic/Inorganic Chemical Corp. The compound was obtained by vacuum distillation and did not need further treatment.

Ferrous sulfide ( $FeS$ ), C.P. grade, was supplied by the Sargent Welch Company.

This material was ground and subjected to magnetic separation for further purification.

Samples for the determination of SnS vapor pressures over pure solid SnS were prepared directly from the stannous sulfide material.

1.3 Matte Preparation. Mattes of the different compositions studied were prepared by weighing the required amounts of SnS and FeS separately, mixing, and then thoroughly grinding them together before placing in sample boats (the same boats used for the experiments on transpiration technique). These were weighed again and the mattes were melted at temperatures varying according to their composition. After being melted, the samples were allowed to attain room temperature, then they were weighed. The weight losses were in all cases attributed to the vaporization of SnS, and since the melting operations were performed in a closed system under neutral conditions (loading and unloading operations are explained in point 5, Operating Procedure), these losses were in all cases very small (from 0% to 0.8% of the sample weight). The differences in weight were made up by addition of proper quantities of pure SnS to the samples. Then, the solidified mattes were ground and mixed properly, and stored in a desiccator, ready to be used.

The four mattes prepared were chemically analyzed by the Analytical laboratory of the Colorado School of Mines Research Institute. The calculated results are as follows:

Matte S1 -	5.81%FeS	,	balance SnS.
Matte S2 -	14.59228%FeS	,	" SnS.
Matte S3 -	18.1026%FeS	,	" SnS.
Matte S4 -	25.029%FeS	,	" SnS.

The analyses showed low values in SnS, but this is always the case due to the difficulty encountered in the chemical determination of tin. This was proved by the excess sulfur in all four cases after calculating for FeS and SnS taking the Sn values. Whereas when taking the sulfur values, calculating for FeS, and then for SnS, the balance gave very reasonable results within the limits of experimental error. The analysis report and the calculations are given in Appendix III.

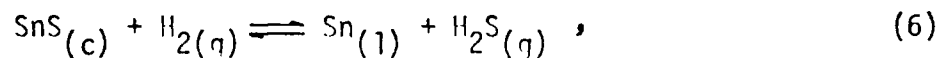
Since the analyses of mattes of known composition were so imprecise, analytical results on mattes after a run could not be used to check on the final composition.

## 2. Sulfur Potential Control

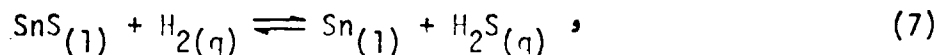
Mixtures of hydrogen sulfide and hydrogen were used as the carrier gas in order to control the sulfur potential in the system so as to prevent any decomposition of the sulfide samples at the temperatures studied.

The possible reactions considered within the temperature range of 700° to 1200°C are listed below:

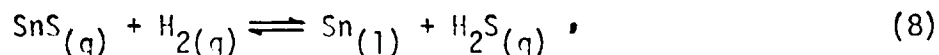
### 2.1 Stannous Sulfide. $\Delta G_R^0$ expressions from Ref. 23 (Kellong).



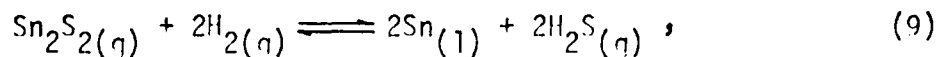
$$\Delta G_R^0 = +22,124 - 12.988T \quad (298^\circ - 1143^\circ\text{K})$$



$$\Delta G_R^0 = +10,460 - 2.804T \quad (1143^\circ - 1500^\circ\text{K})$$



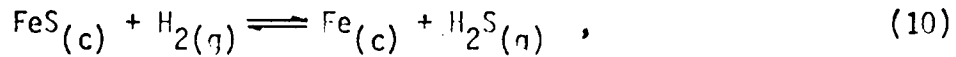
$$\Delta G_R^0 = -29,640 + 23.309T \quad (298^\circ - 1500^\circ\text{K})$$



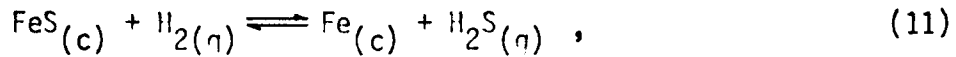
$$\Delta G_R^0 = -12,392 + 8.657T \quad (298^\circ - 1500^\circ\text{K})$$

All  $\Delta G_R^0$  expressions are in cal/mole.

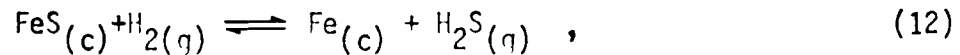
2.2 Ferrous Sulfide.  $\Delta G_R^0$  expressions from Ref. 1 (Kubaschewski et al.). Free energies are expressed in calories per mole.



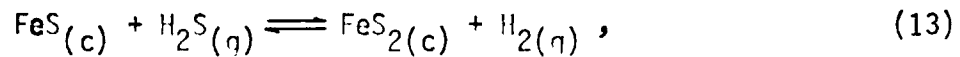
$$\Delta G_R^0 = +15,580 - 3.785T \quad (298^\circ - 412^\circ\text{K})$$



$$\Delta G_R^0 = +14,330 - 0.755T \quad (412^\circ - 1179^\circ\text{K})$$

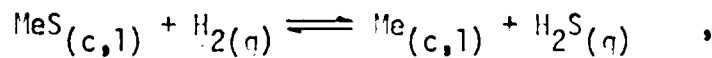


$$\Delta G_R^0 = +14,490 - 0.935T \quad (1179^\circ - 1261^\circ\text{K})$$



$$\Delta G_R^0 = -11,770 + 33.195T \quad (600^\circ - 1100^\circ\text{K}) .$$

All these equations ( but 8 and 9 ) can be expressed in a generalized form as:



for which the equilibrium constant is:

$$K = \frac{\cancel{a_{\text{Me}(c,l)}}}{\cancel{a_{\text{MeS}(c,l)}}} \cdot \frac{P_{\text{H}_{2\text{S}(g)}}}{P_{\text{H}_{2(g)}}}$$

1

since pure metal and pure sulfide are considered.

Therefore,

$$\Delta G_R^0 = -R T \ln \left[ \frac{p_{H_2S}(\eta)}{p_{H_2}(\eta)} \right]$$

and

$$\frac{p_{H_2S}(\eta)}{p_{H_2}(\eta)} = \exp \left[ \frac{-\Delta G_R^0}{R T} \right] \quad (14)$$

In case of equations (8) and (9) ;

$$K = \frac{1}{p_{Sn_i S_i}(\eta)} \cdot \frac{p_{H_2S}(\eta)}{p_{H_2}(\eta)}$$

$$\frac{p_{H_2S}(\eta)}{p_{H_2}(\eta)} = \left[ \exp \left[ \frac{-\Delta G_R^0}{R T} \right] \right] \cdot p_{Sn_i S_i}(\eta) \quad (15)$$

where  $i = 1$  for (8), and  $i = 2$  for (9).

Therefore, to prevent reactions (6) through (13) from proceeding to the right, the experimental values of the  $p_{H_2S}/p_{H_2}$  ratios should be higher than, or equal to the calculated equilibrium ratios; that is:

$$\left[ \frac{p_{H_2S}(\eta)}{p_{H_2}(\eta)} \right]_{\text{EXPTL.}} \geq \left[ \frac{p_{H_2S}(\eta)}{p_{H_2}(\eta)} \right]_{\text{EQUIL.}}$$

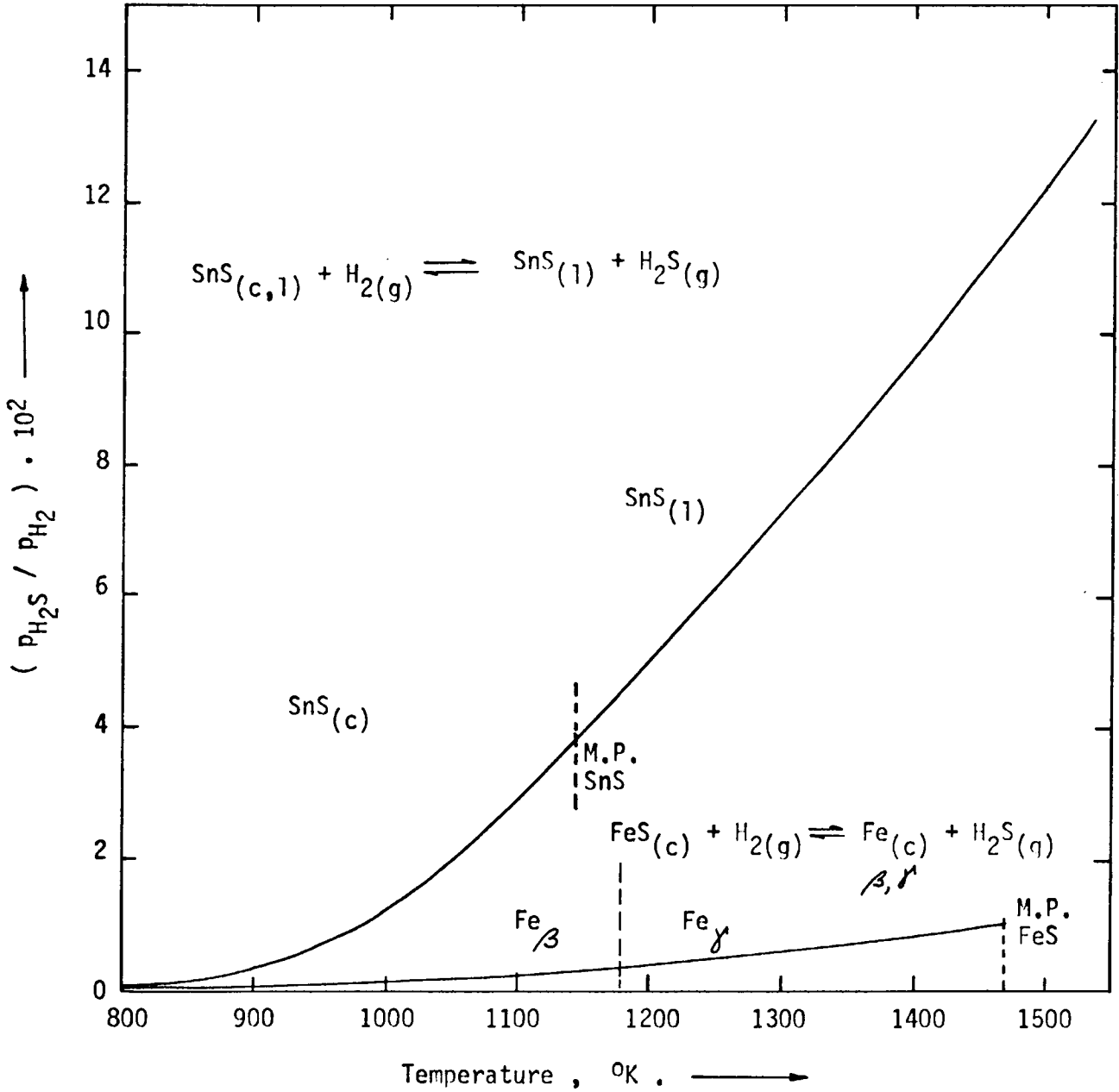


Fig. 12 SnS - FeS mattes.  $p_{H_2S} / p_{H_2}$  ratio versus temperature for the SnS and FeS dissociation reactions.

Figure 12 shows a plot of  $p_{\text{H}_2\text{S}} / p_{\text{H}_2}$  vs. temperature obtained from the above values of  $\Delta G_R^0$  for the most important reactions, which are also indicated in the figure. The other reactions are not indicated because they lie below the FeS line, and therefore are neglected.

The ratios which fulfil the required condition for different temperatures; i. e., to prevent FeS as well as SnS decomposition, are the highest of both equilibrium lines.

So then:

$$\left[ \frac{p_{\text{H}_2\text{S}}(\eta)}{p_{\text{H}_2}(\eta)} \right]_{\text{EXPTL.}} \geq \left[ \frac{p_{\text{H}_2\text{S}}(\eta)}{p_{\text{H}_2}(\eta)} \right]_{\text{EQUIL. (SnS(c))}} \quad (16)$$

A complete derivation of the above equations, and the  $p_{\text{H}_2\text{S}} / p_{\text{H}_2}$  calculations are given in Appendix IV.

### 3. Flowmeter Calibration

The two flowmeters used were calibrated by measuring the velocity of displacement of a soap bubble in a calibrated volumetric-glass tube. They were calibrated using both nitrogen and hydrogen. Since a stable soap bubble could not be formed during the direct calibration of flowmeter FM1 using hydrogen sulfide, this was theoretically calibrated based on the careful calibrations with nitrogen and hydrogen as follows:

Considering a laminar flow of gas in cylindrical tubes (capillaries), the volume rate of flow  $Q$  is the product of the cross-sectional area and the average velocity; thus:

$$Q = \frac{\pi \Delta P R^4}{8 \mu l} \quad (\text{Ref. 42}) \quad (17)$$

where  $Q$  = flowrate,  $V/T$  ( $L^3/T$ )  
 $\Delta P$  = pressure drop,  $M/LT^2$   
 $R$  =  $D/2$  = radius of capillary,  $L$   
 $\mu$  = viscosity of the fluid,  $M/LT$   
 $l$  = length of capillary,  $L$

Equation (17), expression of the Hagen-Poiseuille law, can also be represented by:

$$Q = \frac{K h}{\mu} \quad (18)$$

where  $K$  is a constant depending on the dimensions of each capillary and on the density of the fluid in the manometers; and  $h$  is the height in the manometers (proportional to the pressure drop).

Dibutyl Phthalate (density = 1.04 gm/cc) was used as manometer fluid.

The values of  $K_1$  and  $K_2$  for the two flowmeters, FM1 and FM2 respectively were determined by direct calibrations of the flowmeters with  $H_2(g)$  ( $\mu_{H_2} = 0.0177$  cp at 25°C) and with  $H_2(g)$  ( $\mu_{H_2} = 0.008853$  cp at 25°C), giving a double check for the constants, for which the average values are:

$$K_1 = 0.0058073 \quad (\text{for FM1})$$

$$K_2 = 0.00205428 \quad (\text{for FM2}) .$$

Flowmeter FM1 was then arbitrarily chosen for the  $H_2S(g)$  ( $\mu_{H_2S} = 0.0128$  cp at 25°C) and theoretically calibrated from equation (18), for which the following units were chosen:

$$\begin{aligned} Q & \text{ in ml/sec} && (L^3/T) \\ h & \text{ in cm} && (L) \\ \mu & \text{ in centipoises} && (1 \text{ cp} = \text{gm/cm sec} \cdot 10^2) \\ K_1 & \text{ constant.} \end{aligned}$$

Once the flowmeters were satisfactorily calibrated, the  $H_2S / H_2$  mixtures were adjusted as follows:

Consider 1 mole of  $H_2S(g)$  and 1 mole of  $H_2(g)$ , and that the ideal-gas law is obeyed, thus:

$p_{H_2S}$  is proportional to  $V_{H_2S(g)}$  , and

$p_{H_2}$  is proportional to  $V_{H_2(g)}$  .

Then:

$$\frac{p_{H_2S}}{p_{H_2}} = \frac{V_{H_2S(g)}}{V_{H_2(g)}} .$$

At the same time  $t$ , it follows that:

$$\frac{p_{H_2S}}{p_{H_2}} = \frac{Q_{H_2S(g)}}{Q_{H_2(g)}} = \frac{K_1 h_1}{K_2 h_2} \cdot \frac{\mu_{H_2}}{\mu_{H_2S}} \quad (\text{from (18)}) .$$

Let  $\frac{K_1 \mu_{H_2}}{K_2 \mu_{H_2S}} = C$  where  $C = \text{constant} = 1.955$  ,

then

$$\frac{p_{H_2S}}{p_{H_2}} = 1.955 \frac{h_1}{h_2} \quad (19)$$

where  $h_1$  and  $h_2$  are expressed in cm.

#### 4. Temperature Control

Temperature in the reaction furnace F3 was controlled by a platinum thermocouple placed above the supporting tube in the furnace and connected to the control console.

Temperature in the saturation (reaction) chamber was measured with a Pt-Pt/10%Rh thermocouple insulated in a 7/64-in.O.D., R.D.B., Alumina tube in the position shown in Fig. 11.

This thermocouple was calibrated against NBS Pt 27 by the Engelhard Company. The results are given in Table VII.

Table VII

Pt-Pt/10%Rh T. C. vs. NBS Pt27-Pt/10%Rh T. C.

TEMPERATURE OF	NBS T. C. °C	e.m.f. vs. Pt27 mV	(R/J 32°F) mV	DIFFERENCE $\mu V$	TOLERANCE $\mu V$
1000	537.24	4.596	4.594	- 2	+14 to -12
1600	870.24	8.110	8.118	+ 8	+21 to -18
2400	1314.24	13.325	13.333	+ 8	+35 to -29

Temperatures in the vapor pressure measurements ranged from 750°C to 930°C. Hence, from Table VII, the maximum difference in this range was + 8  $\mu V$ . Therefore, because of the negligible difference, the temperature of the controlling thermocouple (Pt-Pt/10%Rh) was determined directly from the standard conversion tables for thermocouples issued by the Leeds & Northrup Company (taken from the National Bureau of Standards - NBS - Circular 561).

The difference between the reaction chamber temperature and the furnace controlling temperature can be observed in Fig. 13. The points in this figure were determined from the difference between the temperature measured by the

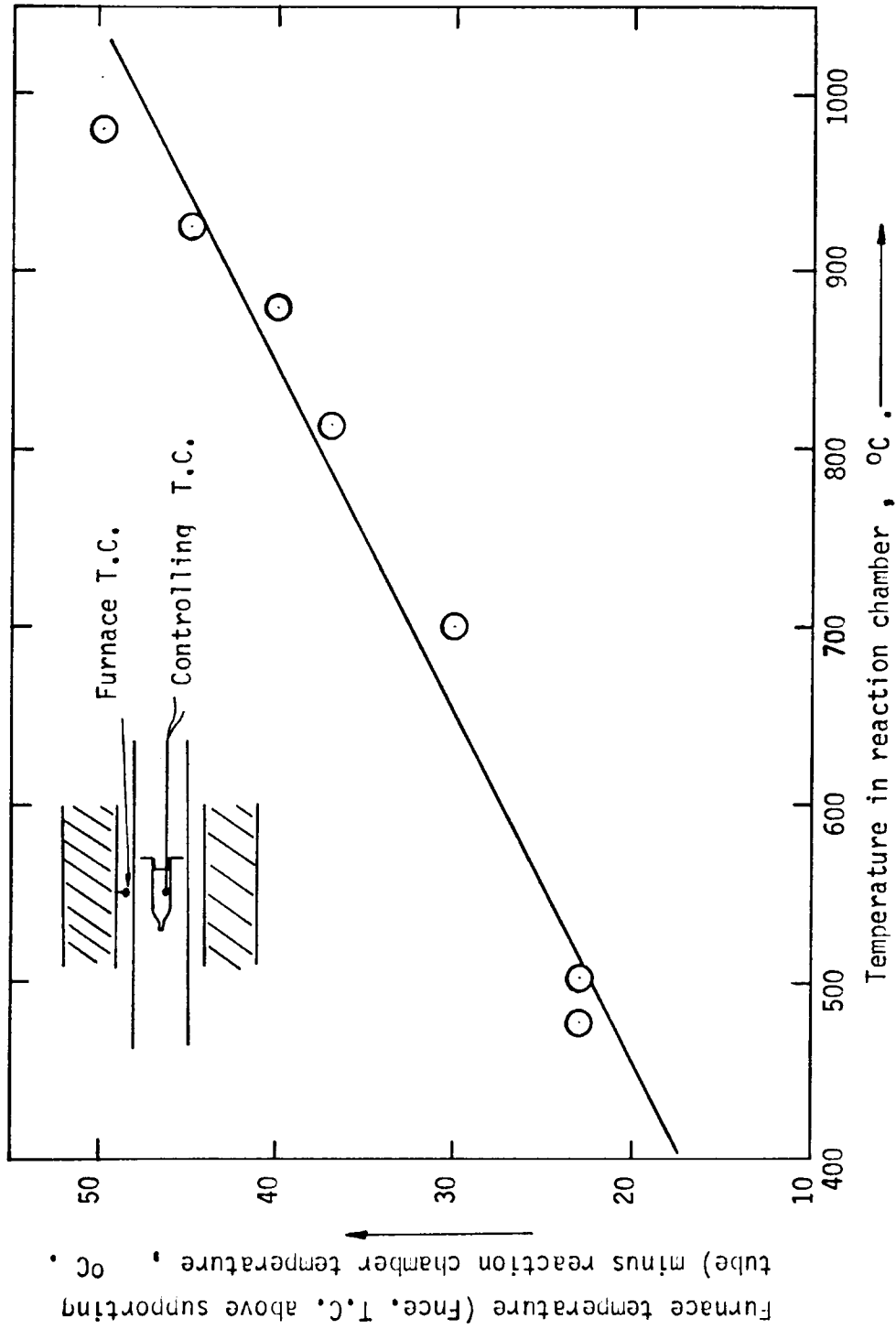


Fig. 13 Correlation between reaction chamber and furnace temperatures.

Pt-Pt/10%Rh thermocouple element placed in the middle and at about 10 mm from the center of the sample and the temperature measured by the platinum thermocouple element placed at about 40 mm above the center of the sample. The standard error of estimate for the temperature in the correction taken from the straight line in Fig. 13 was of  $\pm 2.27^{\circ}\text{C}$ .

Temperature was measured several times during the period of a test (15 to 40 min). A control of  $\pm .81^{\circ}\text{C}$  was obtained as an average during this period. The highest standard deviation in the emf reading during the course of a test was  $1.91 \cdot 10^{-2}$  and the lowest was  $7.974 \cdot 10^{-4}$ .

## 5. Operating Procedure

The experimental procedure for the vapor pressure determinations on pure stannous sulfide and on stannous sulfide in iron-tin mattes was as follows:

5.1 Carrier gas: Nitrogen. Pure SnS Samples. Valves T1, T2, and T3 (Fig. 9) were opened to permit passage of nitrogen gas from cylinder 0 into furnace F3 at relatively high flowrates to prevent contamination of the system with air. Meanwhile, the combustion boat containing the sample whose vapor pressure was to be determined was placed into the cold reaction chamber, outside of the supporting tube A, and the plug P was placed in position while nitrogen passed through it into the chamber. The latter was then placed into the cold end of the supporting tube A, the rubber stopper Z2 fitted tightly, and the system sealed.

The reaction chamber was kept in this position for from 5 to 8 minutes, depending on how high the temperature was. Nitrogen was still passing from the opposite side of the furnace, but at a much lower flowrate. Then the reaction tube was slid into the furnace through an "O" ring placed in the rubber stopper, to fit exactly in the opening of the condensing chamber inside the supporting tube as shown in Fig. 11.

At this moment the nitrogen flow was stopped and the closed system allowed to attain thermal equilibrium with the furnace. When this equilibrium was reached, valve T1 was opened and the nitrogen carrier gas was allowed to enter the reaction chamber at the desired flowrate. This was the starting time for the experiment. When the experiment was ended, the nitrogen flow was turned off, the reaction chamber was slid back to the cold part of the furnace, then removed from it and allowed to cool down.

After 3 to 5 minutes the sample boat was removed from the reaction chamber and placed inside a desiccator to reach room temperature.

When room temperature was reached, the sample boat was weighed and the total weight lost during the experiment was determined. A Mettler type H15 analytical balance, with an accuracy of  $\pm 0.0003$  gm, was used for weighing purposes.

5.2 Carrier gas:  $H_2S/H_2$  mixtures. Pure SnS samples and Matte Samples. The operation in this case was in general the same as when using nitrogen as the carrier gas. The only difference was that one end of the three-way stopcock T1 was connected to the suction of the fume hood fan, the second end to the gas mixing system, and the third one, as before, to the reaction chamber.

Nitrogen was flushed from the opposite side as before, but the  $H_2S/H_2$  mixtures passed from the right side during the loading operation.

When the reaction chamber was placed in the cold part of the supporting tube, and the system was sealed, valve T1 was connected to the suction of the fume hood fan, so as to give a slightly negative pressure to the system while nitrogen was still flowing from the opposite side.

After 5 to 8 minutes the reaction chamber was slid to the center of the furnace, as before, and all valves were closed until thermal equilibrium inside the tube was reached.

Meanwhile, the proper ratio of the two gases was adjusted in the mixing system by means of flowmeters F11 and F12, and the gas bleeder GB1. When equilibrium was attained in the furnace, valve T1 was opened and valve S3 closed to allow the mixture into the furnace at a determined flowrate. This was registered as the starting time. The withdrawal operation was performed as explained in point 5.1 of this chapter.

The period between the end of the loading operation and the attainment of thermal equilibrium, which from now on will be referred to as the "heating-up time", and the weight lost during this time, varied as the temperature increased, and as the samples changed from pure SnS to the various compositions of the mattes studied. Heating-up times varied from 17 to 30 minutes, and were determined for each set of samples and temperatures, using a Pt-Pt/10%Rh thermocouple, in a blank sample.

"Heating-up" weight losses were determined by running several blank samples at the temperature considered until thermal equilibrium was reached. At this time, the sample was withdrawn, allowed to cool down and weighed to determine the "heating-up" loss. An average of the various weight losses for each set was calculated. The actual weight loss was therefore:

$$\Delta W_A = \Delta W_T - \Delta W_{Hup.}$$

where

$$\begin{aligned} \Delta W_A &= \text{Actual weight loss for each run, (mg)} \\ &\quad \text{The weight losses were in all cases attributed} \\ &\quad \text{only to SnS as the only volatile species.} \\ \Delta W_T &= \text{Total weight loss, (mg)} \\ \Delta W_{Hup.} &= \text{"Heating-up" weight loss, (mg).} \end{aligned}$$

The loading and withdrawal operations were systematically performed in each case, as explained above, so as to avoid errors due to mechanical handling. Weight losses during heating-up times were in all cases less than 1% of the total weight of the sample.

Weight losses due to the heating of the sample boats themselves were completely eliminated by heating the empty boats for 6 to 8 hours at temperatures higher than 700°C. When cooled, they were kept inside a desiccator.

## V. EXPERIMENTAL RESULTS

The experimental results in this investigation are divided into two sets, according to the dimensions of the reaction chamber and the inert gas used to carry the vapor away from it.

The first set of experiments was made on pure solid stannous sulfide samples in order to prove the reliability of the apparatus constructed for this investigation, and to compare the results with the values given in the literature.

As explained above, the dimensions of the reaction chamber were reduced after measuring the vapor pressure of pure  $\text{SnS}_{(g)}$  over pure solid  $\text{SnS}$ , using nitrogen as the carrier gas.

The unmodified reaction tube (7/8-in. I.D. by 8-1/2-in. long) will be called from now on: Reaction chamber no. 1; and the modified tube (9/16-in. I.D. by 7-in. long): Reaction chamber no. 2.

The equilibrium value of sample weight loss per liter of carrier gas was found by drawing the best horizontal line through the experimental points in the flat zone of the wt. loss/liter vs. flowrate plots. That is, through the mean of the best points in this zero-slope zone. These plots for all the experiments on pure  $\text{SnS}_{(c,l)}$  and on the four mattes are shown in Figs. 14 through 20. An estimation was made of the random errors in each series of experiments by calculating the standard deviation from the mean point.

The lower standard deviation was found to be equal to 0.22893 (corresponding to a mean of 100.365), and the higher standard deviation was equal to 4.92207 (corresponding to a mean value of wt. loss/liter equal to 85.5201).

The relation:

$$\text{Log } p_{\text{SnS}} = -A/T + B$$

was chosen to represent the vapor pressure of SnS as a function of temperature because the latent heat of evaporation was assumed to be independent of temperature within the range studied. This expression is derived from the Clausius-Clapeyron equation (20) assuming that in the equilibrium:

$$MS_{(\text{cond})} = MS_{(\text{vapor})}$$

the vapor is a perfect gas and the specific volume of the gas is large compared to the volume of the condensed phase,

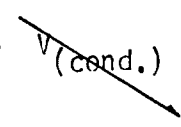
$$V_{(\text{vapor})} \gg V_{(\text{cond.})}$$

The Clausius-Clapeyron equation may be represented as:

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V} \quad (\text{Ref. 43}) \quad (20)$$

where  $dP/dT$  is the pressure change with temperature,  $\Delta H$  is the enthalpy change of the transition, and  $\Delta V$  is the change in volume defined as:

$$\Delta V = V_{(\text{vapor})} - V_{(\text{cond.})} = V_{(\text{vapor})}$$


  
 neglected cf.  $\rightarrow V_{(\text{vapor})}$

Since the pressures of the vapors of interest here are low (which means that little interaction occurs between the gas molecules because they are sufficiently far apart from one another) the perfect gas law can be applied and the molar volume of the vapor is given by;

$$V_{(\text{vapor})} = \frac{RT}{p} \quad (21)$$

where  $p$  is the partial pressure of the vapor.

Substituting (21) into (20) yields

$$\frac{dp}{dT} = \frac{p \Delta H}{R T^2} .$$

Separating variables,

$$\frac{dp}{p} = \frac{\Delta H}{R T^2} dT$$

or,

$$\frac{d(\ln p)}{d(1/T)} = - \frac{\Delta H}{R} \quad (22)$$

Integrating this, keeping  $\Delta H$  constant;

$$\ln p = - \Delta H / RT + B$$

where B is the integration constant.

Hence,

$$\text{Log } p = - A/T + B$$

The two sets of results are given in tables IIX and IX respectively.

The experimental data for all these results are tabulated in Appendix V. A sample calculation for the vapor pressure of SnS, and the least-squares fit, and standard deviation results are also given in Appendix V.

The standard deviation in the  $\text{Log } p_{\text{SnS}}$  calculations was found to lie between 0.1326 and 0.4777. The standard error of estimate for  $\text{Log } p_{\text{SnS}}$  (atm) expressions lies between 0.003462 and 0.0441.

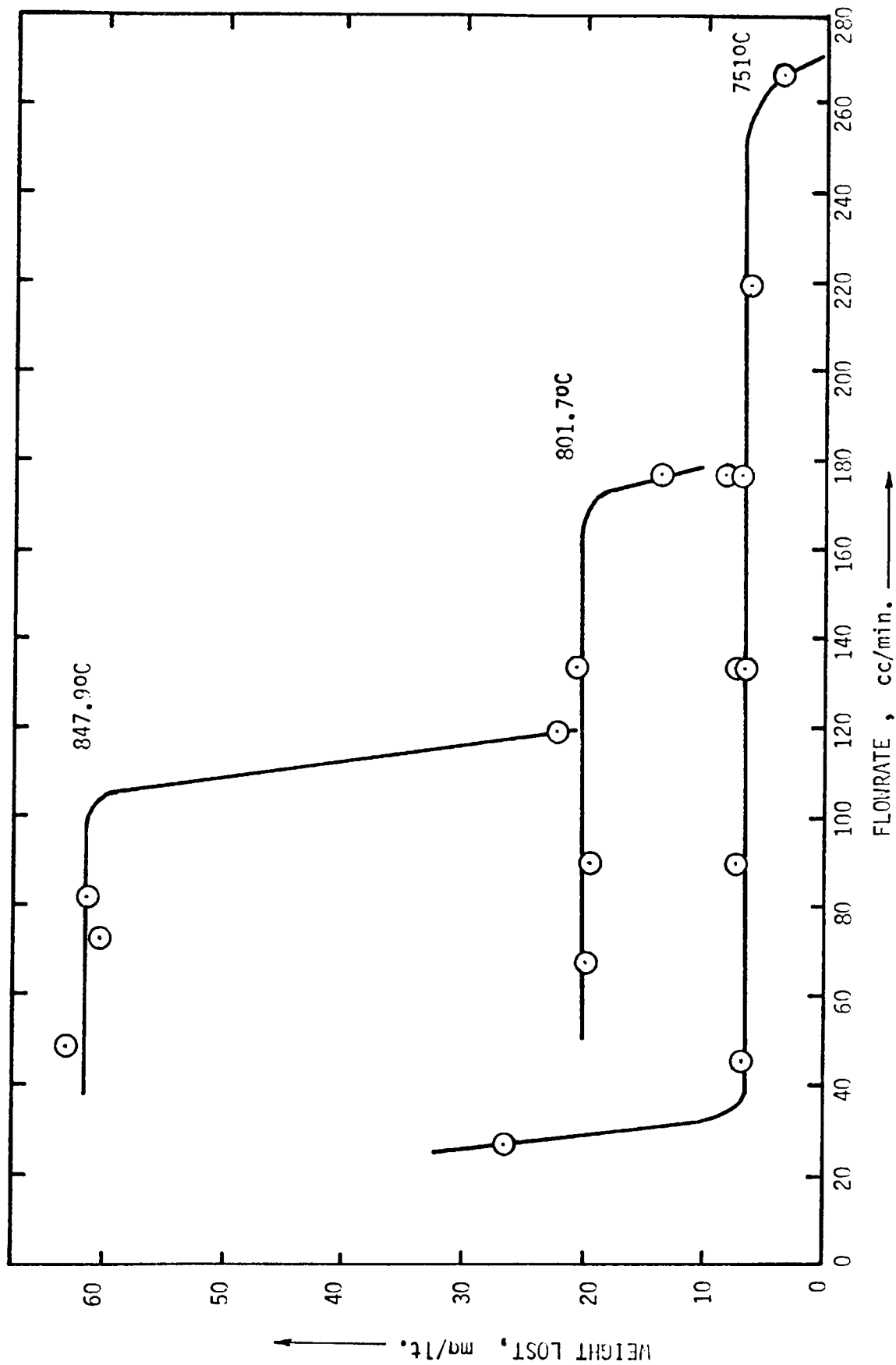


FIG. 14 WEIGHT OF SnS LOST PER LITER OF CARRIER GAS AS A FUNCTION OF FLOWRATE.

SAMPLE : PURE SnS (c).

CARRIER GAS : N<sub>2</sub>

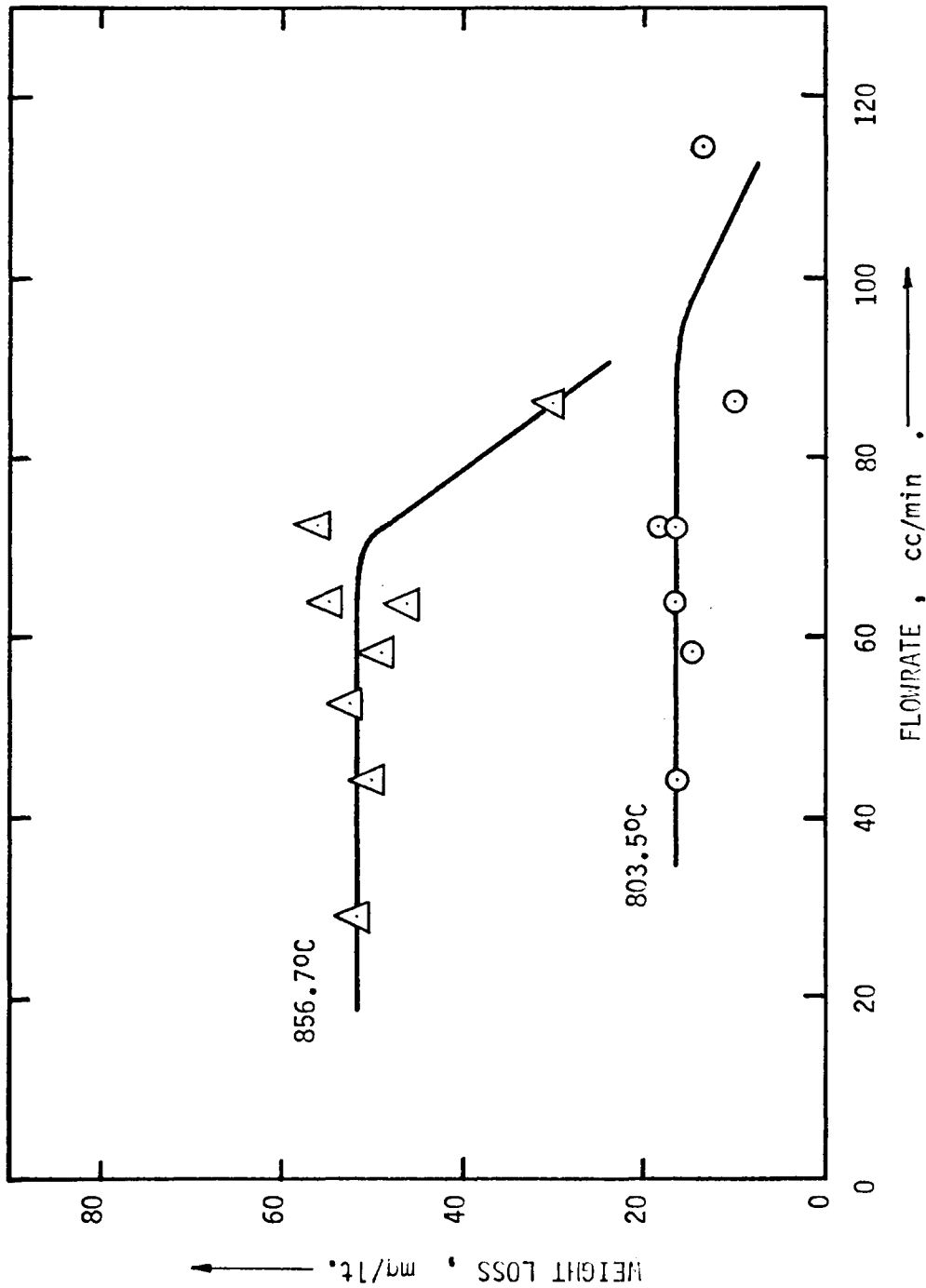


Fig. 15 WT. OF SnS LOST PER LITER OF CARRIER GAS AS A FUNCTION OF FLOWRATE.

SAMPLE: PURE SnS(c).

CARRIER GAS: (H<sub>2</sub>S + H<sub>2</sub>) MIXTURES.

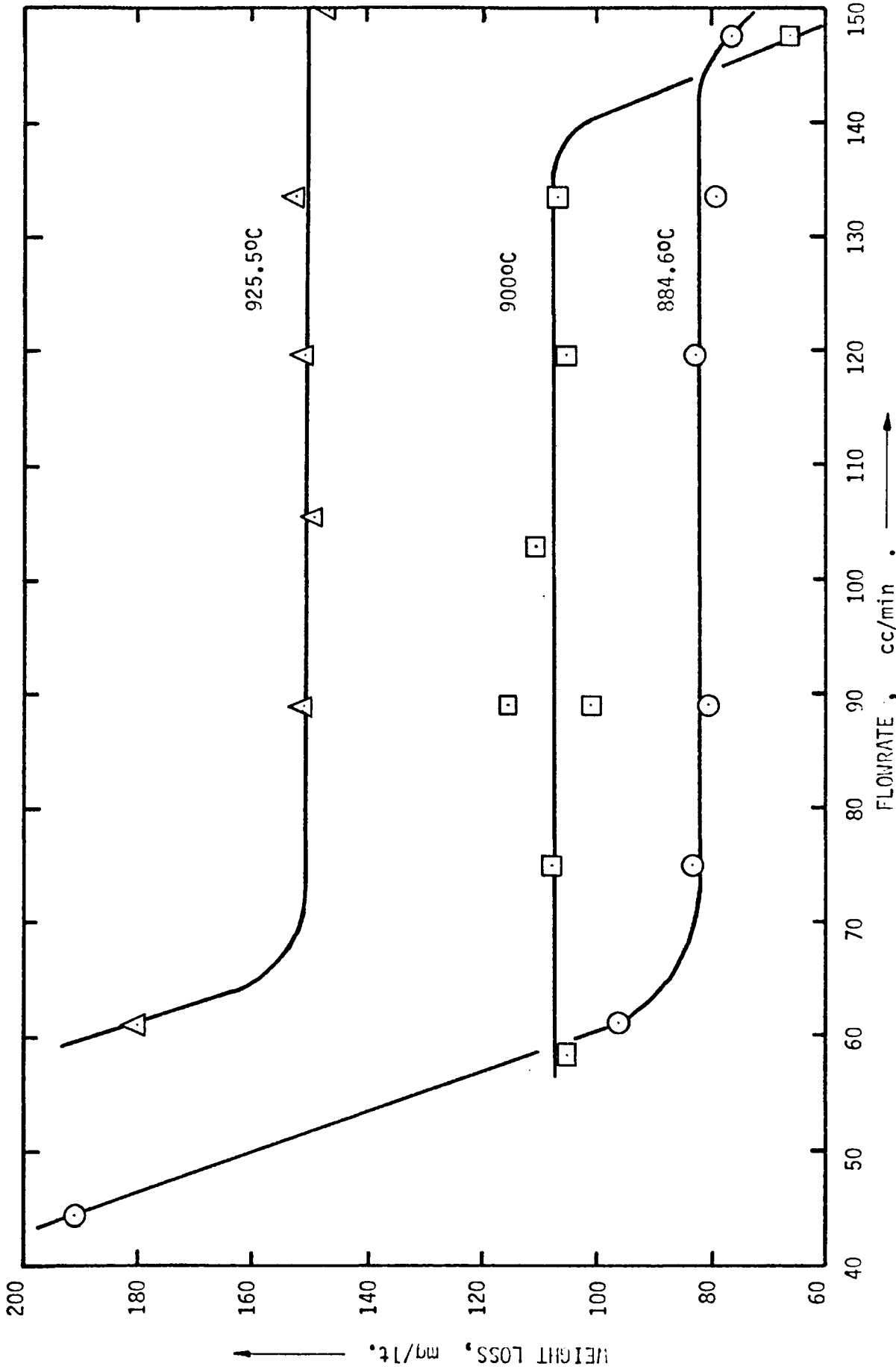


FIG. 16 WEIGHT OF SnS LOST PER LITER OF CARRIER GAS AS A FUNCTION OF FLOWRATE.

SAMPLE: PURE SnS(1). CARRIER GAS: (H<sub>2</sub>S + H<sub>2</sub>) MIXTURES.

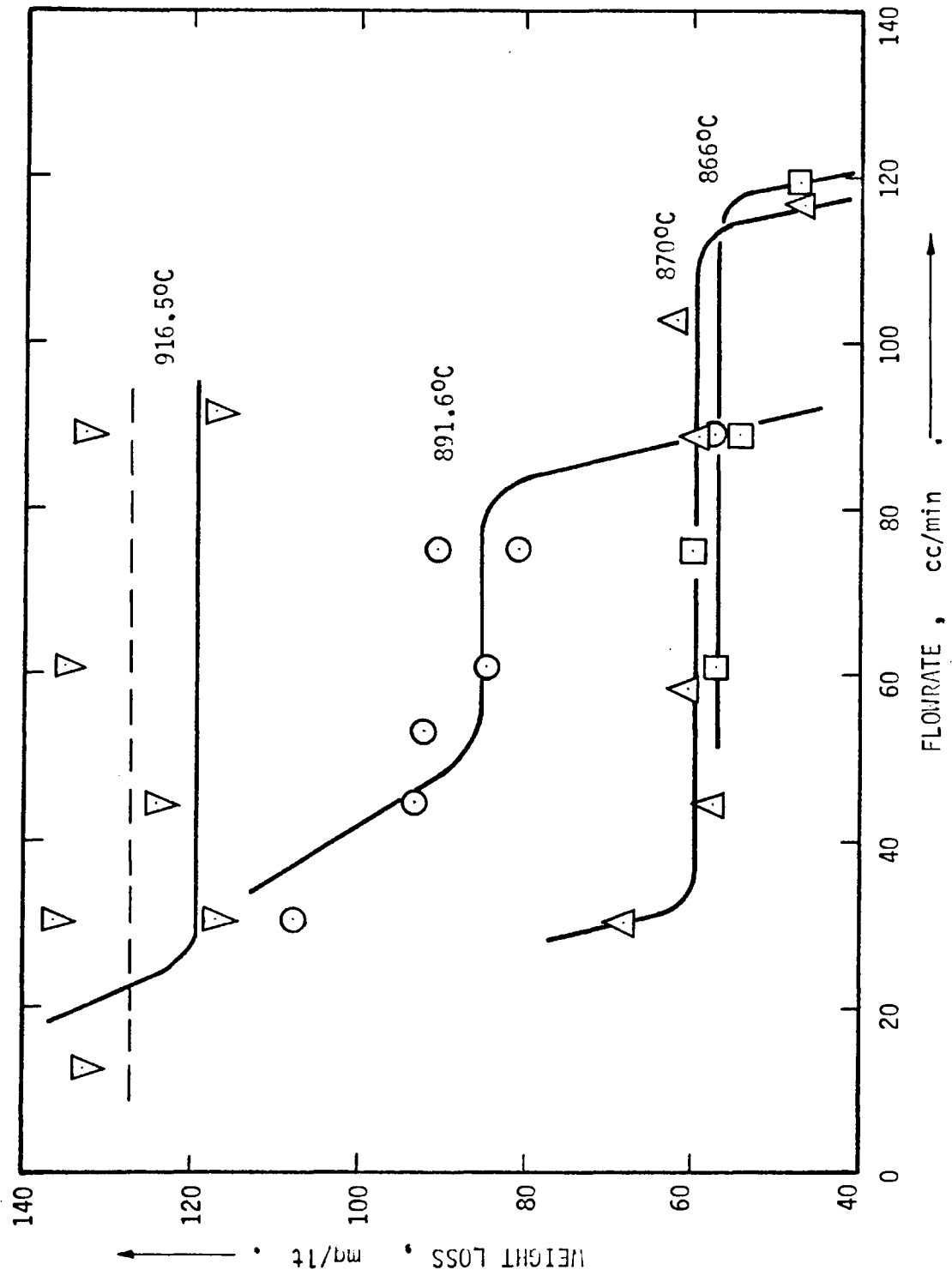


FIG. 17 WT. OF SAMPLE LOST PER LITER OF CARRIER GAS AS A FUNCTION OF FLOWRATE.

SAMPLE: SnS - 5.81%FeS MATTE. CARRIER GAS: (H<sub>2</sub>S + H<sub>2</sub>) MIXTURES.

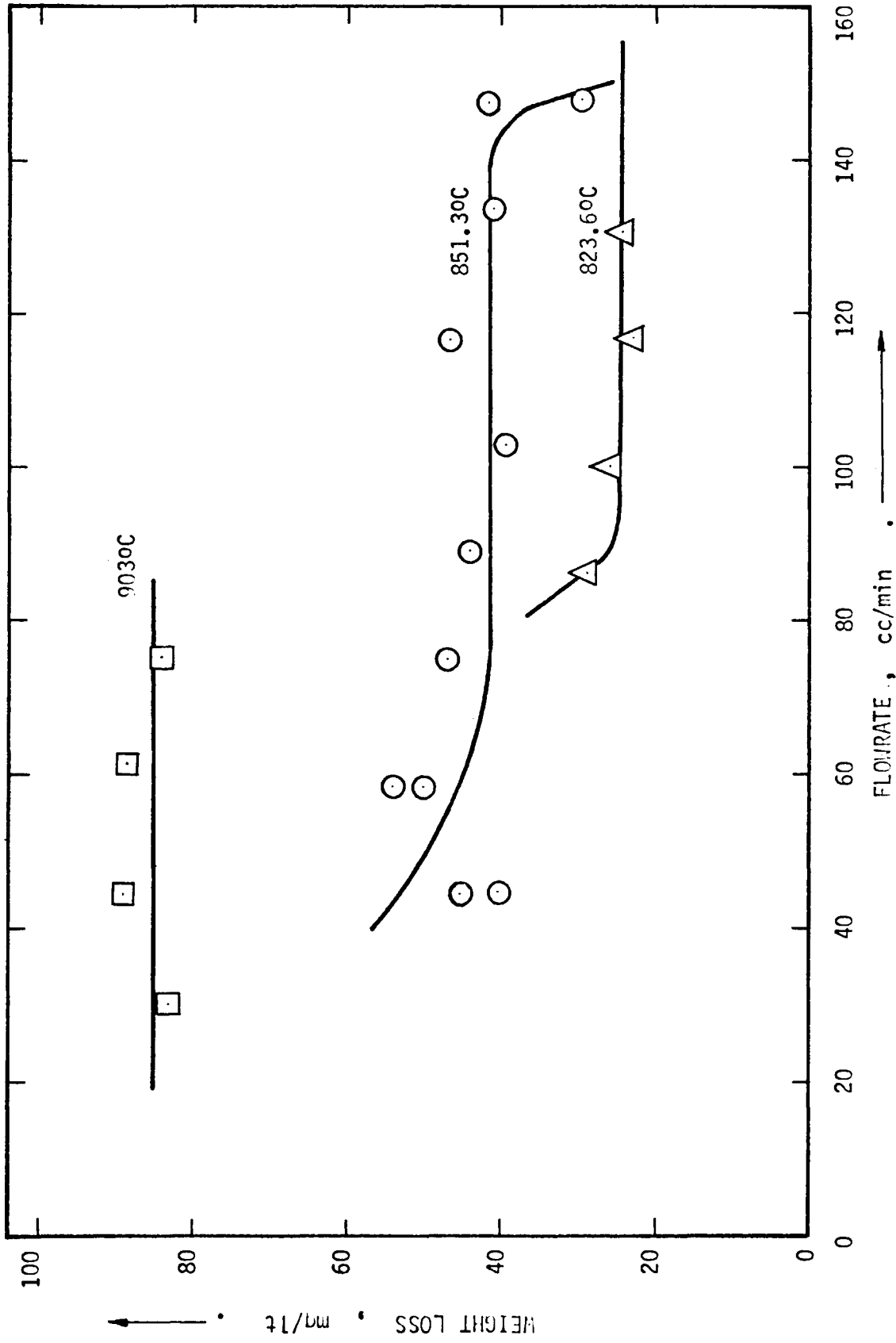


FIG. 18 WEIGHT OF SAMPLE LOST PER LITER OF CARRIER GAS AS A FUNCTION OF FLOWRATE.  
SAMPLE: SnS - 14.59%FeS MATTE. CARRIER GAS: (H<sub>2</sub>S + H<sub>2</sub>) MIXTURES.

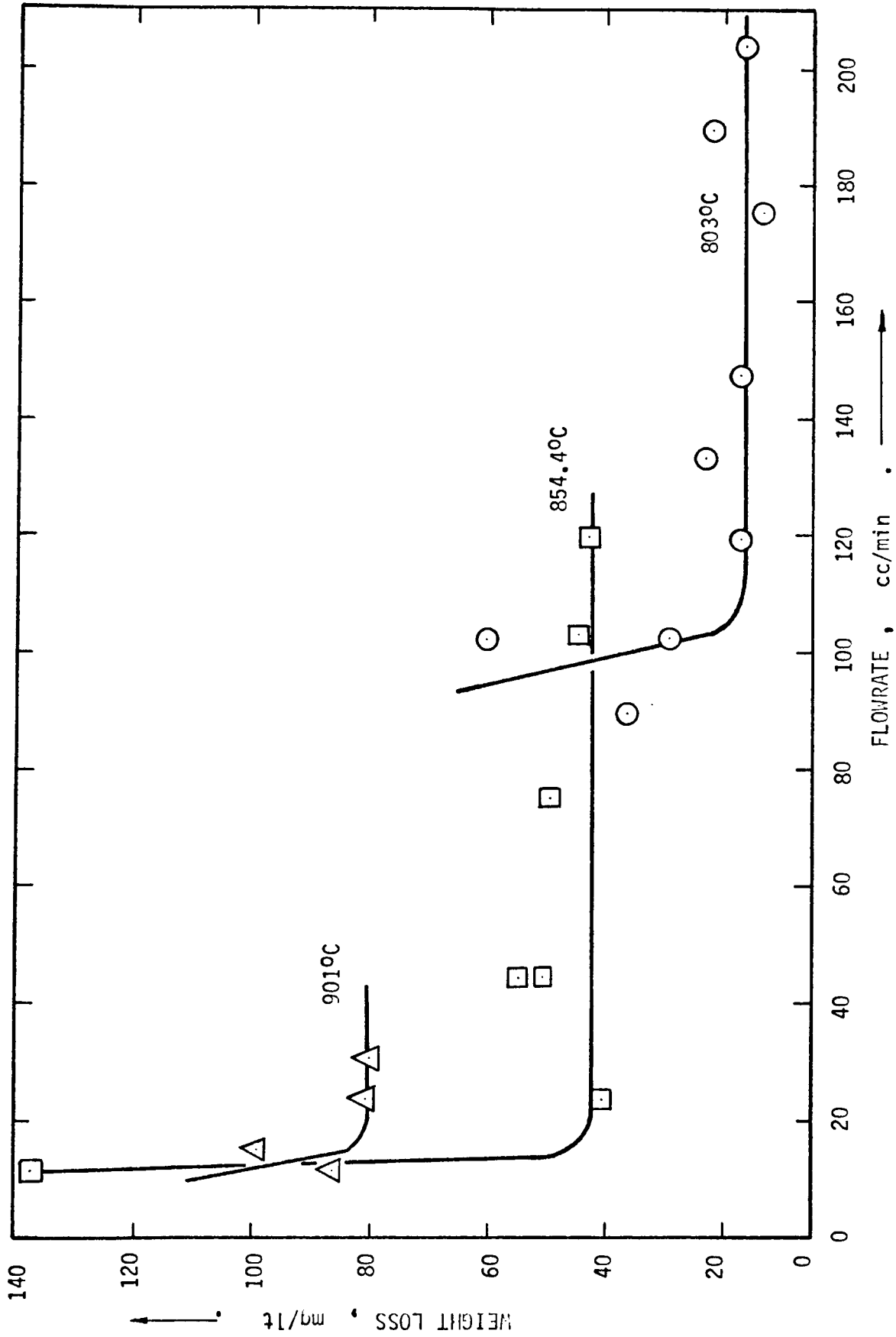


FIG. 19 WT. OF SAMPLE LOST PER LITER OF CARRIER GAS AS A FUNCTION OF FLOWRATE.  
SAMPLE: SnS - 18.103%FeS MATTE. CARRIER GAS: (H<sub>2</sub>S + H<sub>2</sub>) MIXTURES.

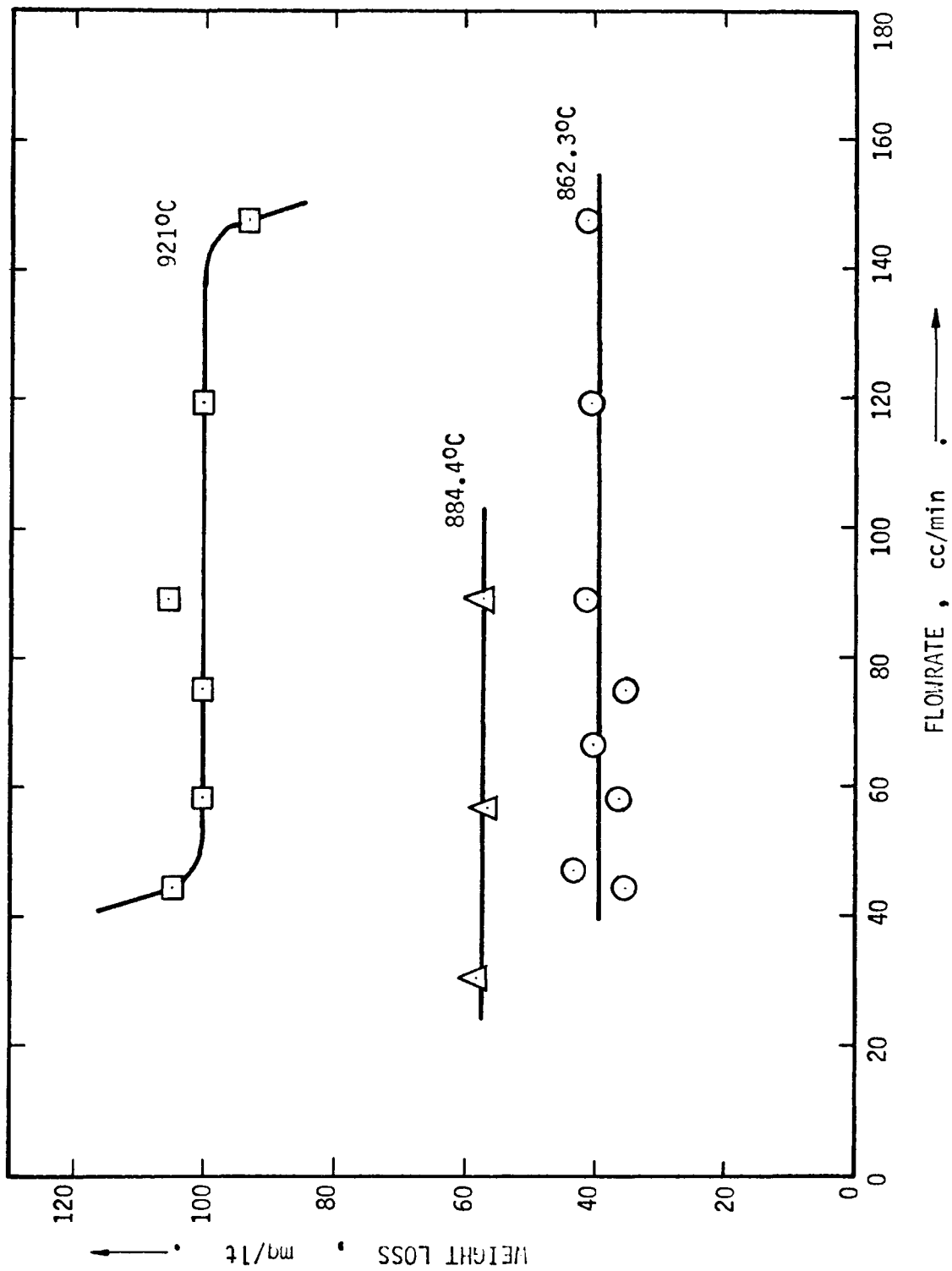


FIG. 20 WEIGHT OF SAMPLE LOST PER LITER OF CARRIER GAS AS A FUNCTION OF FLOWRATE.  
SAMPLE: SnS - 25.02%FeS MATTE. CARRIER GAS: (H<sub>2</sub>S + H<sub>2</sub>) MIXTURES.

Table IX

Vapor Pressure of SnS<sub>(n)</sub> Over Pure Solid SnS as a  
Function of Temperature

Reaction chamber: no. 1 - Carrier gas: H<sub>2</sub>

SAMPLE	TEMPERATURE, °C	p <sub>SnS</sub> <sup>0</sup> , atm	Log p <sub>SnS</sub> <sup>0</sup> (atm)
SnS <sub>(c)</sub>	751.52	0.001095	- 2.96058
"	801.40	0.003167	- 2.49935
"	848.00	0.009877	- 2.00537

Least-squares fit equation:

$$\text{Log } p_{\text{SnS}}^0 = - 11,336.5 / T + 8.0881 \quad (\pm 0.044) \quad (\text{atm})$$

for a temperature range of ~975 to 1143°K where

$$\text{Log } p_{\text{SnS}}^0 = -3.53908 \quad \text{to} \quad -1.8301 \quad (\text{atm})$$

Table IX

Vapor Pressure of  $\text{SnS}_{(g)}$  Over Pure  $\text{SnS}_{(c,l)}$ , and Over  
Sn - Fe Liquid Mattes as a Function of Temperature.

Reaction chamber: no. 2 - Carrier gas:  $\text{H}_2\text{S}/\text{H}_2$  Mixtures

SAMPLE	TEMPERATURE, °C	$p_{\text{SnS}}^0$ , atm	Log $p_{\text{SnS}}^0$ (atm)
$\text{SnS}_{(c)}$	803.5	0.002745	- 2.56150
"	856.8	0.008334	- 2.07915

Least-squares fit equation:

$$\text{Log } p_{\text{SnS}}^0 = - 11,002.5 / T + 7.65915 \quad (\text{atm})$$

Temperature range:  $\sim 975 - 1143^\circ\text{K}$

SAMPLE	TEMPERATURE, °C	$p_{\text{SnS}}^0$ , atm	Log $p_{\text{SnS}}^0$ (atm)
$\text{SnS}_{(l)}$	884.6	0.013201	- 1.87943
"	900.0	0.01740	- 1.75945
"	925.5	0.02428	- 1.61470

Least-squares fit equation:

$$\text{Log } p_{\text{SnS}}^0 = - 8876.3 / T + 5.79595 \quad (\pm 0.0145) \quad (\text{atm})$$

for a temperature range of  $1143 - 1500^\circ\text{K}$  where

$$\text{Log } p_{\text{SnS}}^0 = - 1.96984 \quad \text{to} \quad - 0.12158 \quad (\text{atm})$$

Table IX - Continued

SAMPLE	TEMPERATURE, °C	$p_{\text{SnS}}$ , atm	Log $p_{\text{SnS}}$ (atm)
SnS-5.810%FeS	866.0	0.0091876	- 2.03680
" - "	870.0	0.0096698	- 2.01460
" - "	891.6	0.0137850	- 1.86059
" - "	916.6	0.0205600	- 1.68698 *
" - "	916.5	0.0192560	- 1.71543

Least-squares fit equation excluding value corresponding to \* :

$$\text{Log } p_{\text{SnS}} = - 8686.69 / T + 5.58911 \quad (\text{atm})$$

Temperature range: ~1100 - 1500°K

SAMPLE	TEMPERATURE, °C	$p_{\text{SnS}}$ , atm	Log $p_{\text{SnS}}$ (atm)
SnS-14.592%FeS	823.6	0.0039924	- 2.39900
" - "	851.3	0.0066790	- 2.17347
" - "	903.0	0.0141485	- 1.84930

Least-squares fit equation:

$$\text{Log } p_{\text{SnS}} = - 8845.89 / T + 5.67853 \quad (\text{atm})$$

Temperature range: ~1080 - 1500°K

Table IX - Continued

SAMPLE	TEMPERATURE, °C	$p_{\text{SnS}}$ , atm	Log $p_{\text{SnS}}$ (atm)
SnS-18.103%FeS	803.0	0.0026456	- 2.57727
" - "	854.4	0.0068805	- 2.16273
" - "	901.0	0.0129400	- 1.88807

Least-squares fit equation:

$$\text{Log } p_{\text{SnS}} = -8964.39 / T + 5.7622 \quad (\text{atm})$$

Temperature range: ~1070 - 1500°K

SAMPLE	TEMPERATURE, °C	$p_{\text{SnS}}$ , atm	Log $p_{\text{SnS}}$ (atm)
SnS-25.029%FeS	862.4	0.006370	- 2.19586
" - "	884.4	0.009342	- 2.02956
" - "	921.0	0.016205	- 1.79035

Least-squares fit equation:

$$\text{Log } p_{\text{SnS}} = - 9340.54 / T + 6.03485 \quad (\text{atm})$$

Temperature range: ~1130 - 1500°K

## VI. DISCUSSION

### 1. The Transportation Method

There are many examples of the application of this method to vapor pressure measurements. But critical works, by which the reliability of the apparatus (the construction of which varies considerably as among different investigators) can be estimated, are relatively few.

Apparently, H. von Wartenberg<sup>(44)</sup> (1913) was the first one to use this method when he determined the silver vapor pressure.

Other investigators using this method have calculated an apparent vapor pressure from several flowrates of the transporting gas, and then obtained by extrapolation the vapor pressure at zero flowrate. These investigators have assumed that the carrier gas would become saturated only when the gas was stationary. The extrapolated pressure was assumed to be the equilibrium vapor pressure. A typical example of this, which is of interest to this investigation, is the work of H.W. St. Clair and collaborators<sup>(19)</sup>. This will be discussed later.

A mathematical analysis of the transportation method by Lepore and Van Hazer<sup>(45)</sup> has shown that extrapolation to zero flowrate is not always reasonable. They showed that the apparent vapor pressure plotted against the flowrate of the gas (Fig. 21) can be represented by curve 1 for a substance of high vapor pressure and by curve 2 for a substance of very low vapor pressure. Figure 21 is only illustrative. The actual, experimental figures are shown in Chapter V (Figs. 14 to 20).

According to curve 2 (Fig. 21) - low vapor pressure - the apparent vapor pressure is inversely proportional to the flowrate, a consequence of the fact that

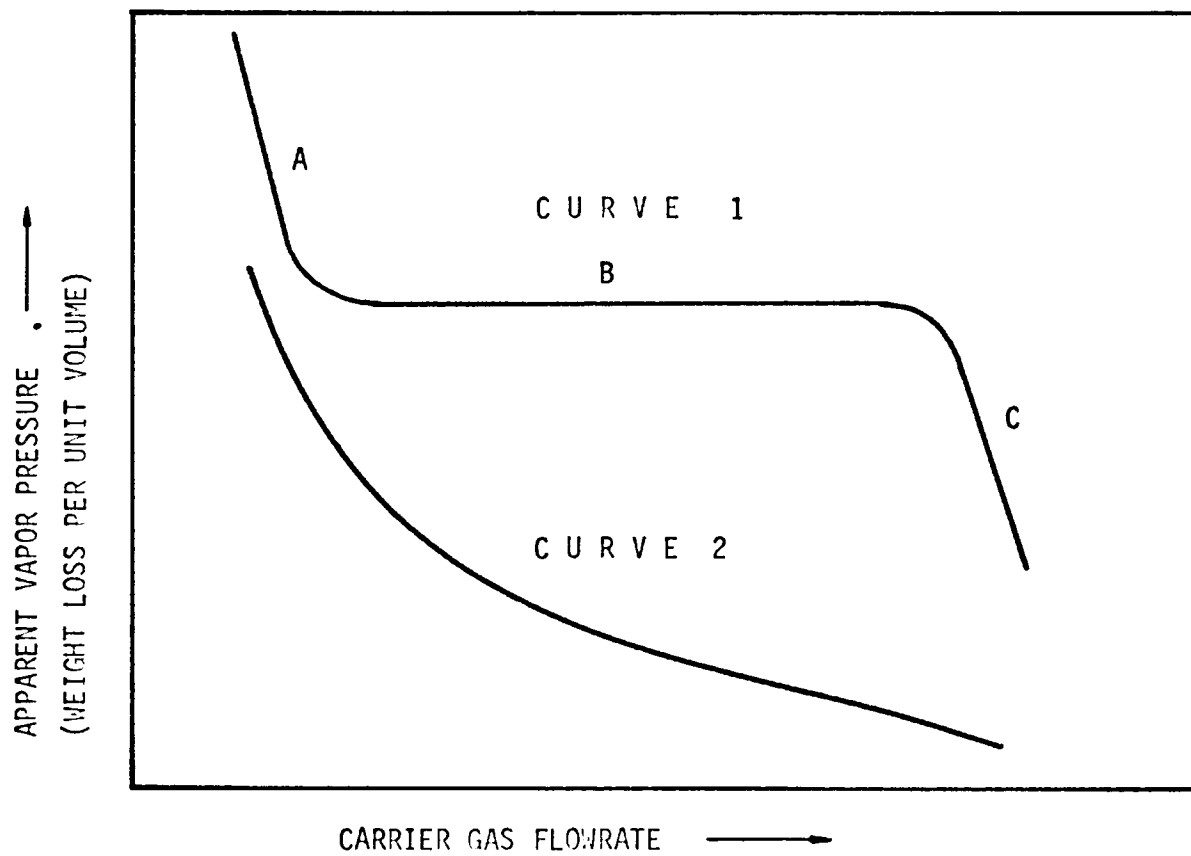


FIG. 21 THE APPARENT VAPOR PRESSURE PLOTTED AS A FUNCTION OF THE INERT ( CARRIER ) GAS FLOWRATE. ( SCHEMATIC ) .

the rate of diffusion through the inert gas is greater than the rate of evaporation. They have proposed for such cases (unsaturation) that, when plotting the weight loss per unit of time versus flowrate, the true vapor pressure could be obtained. The curve of such a plot should pass through the origin, because there should be no weight loss per unit time at zero flowrate, and the slope of this curve would be equal to the true vapor pressure. These authors have assumed that the errors due to thermal diffusion and segregation were dependent only on time and were not a function of flowrate; thus, they would be constant.

However, Alcock and Hooper<sup>(46)</sup> showed that it is not always possible to draw a straight line passing through the origin for this curve. The graph of weight loss per unit time is a straight line which can be extrapolated through the origin, only if the plot of weight loss per unit volume against flowrate contains a flat zone.

The vapor pressure calculated from both curves is exactly the same, which clearly indicates that the plot of weight loss per unit time versus flowrate would in this case be unnecessary.

Consequently, the transportation method should only be used in cases where the apparent vapor pressure is independent of flowrate.

Referring again to Fig. 21, curve 1 shows two other regions, A and C, besides the flat zone B.

Region A shows that at low flowrates the apparent vapor pressures are high. This is the region in which the so-called "back diffusion" occurs (diffusion of the vapors backward through the unsaturated inert gas). This can be called the "oversaturation zone".

According to Alcock and Hooper<sup>(46)</sup>, there can be two causes of these high weight losses:

a) A difference in molecular weight between the carrier gas and the vapor species could cause them to segregate ( It should be added that a difference in molecular weight between the components of the carrier gas - when a mixture of gases is used - and hence among the components of carrier gas and vapor species could cause the same phenomenon).

b) The existence of concentration gradients in the vicinity of the sample, particularly at the inlet and outlet of the reaction chamber, might cause the vapor molecules to diffuse from the reaction zone.

Another reason, as McClincy<sup>(47)</sup> points out, could be the existence of thermal gradients on either side of the sample, which may cause mass fluxes of one species relative to the other as a result of thermal diffusion. But considerable thermal gradients are not likely to occur, particularly if the apparatus is well designed and the temperature can be controlled in this region. McClincy also gives illustrative calculations on this matter and shows that, in fact, the abnormally high weight losses observed at low flowrates cannot be attributed to thermal diffusion.

Cause a) will be considered later, when discussing the use of nitrogen and  $H_2S/H_2$  mixtures as carrier gases.

Region B (curve 1, Fig. 21) is the region where the rate of evaporation is rapid enough to saturate the carrier gas so that the apparent vapor pressure is independent of the flowrate of the carrier gas. This region corresponds to the true vapor pressure of the sample.

Finally, there is a region C, where the flowrate of carrier gas is greater than the rate of evaporation. The carrier gas moves at too high a flowrate to be able to become saturated with vapor from the sample. Therefore, the weight loss per liter decreases as the velocity of the carrier gas is increased. This can be called the "unsaturated zone".

The design of the reaction chamber plays a very important role in achieving a series of values in which the weight loss of sample per unit volume is independent of flowrate. The existence of a large "dead volume" in this chamber should be avoided, and both the inlet and outlet should be as small as possible to minimize errors due to diffusion.

The chamber should be constructed in such a way as to provide maximum turbulence in the gas phase, to insure saturation of the gases before leaving it.

The reaction chamber designed for this study was different from the one used by Alcock and Hooper<sup>(46)</sup>. It was different in shape, but the main features were the same; i.e. the shape of the tube was chosen to provide turbulence, and the Aremcolox Machinable-ceramic plug was constructed so as to give as tight a seal as possible when inserted into the reaction chamber. A very small hole was opened in this plug to allow the entrance of the carrier gas into the chamber passing over the sample surface and not below it. Before leaving the reaction tube, the gases had to acquire more turbulence because the chamber was gradually reduced in the outlet direction (which gave it the shape of a funnel) and the outlet was also a very narrow hole (capillary). The shape of the reduced end of the reaction chamber conformed to the outside contours of the sample boat, and when the interior diameter was modified, the interior walls of the chamber were in actual contact with the outside walls of the reaction boat when this was positioned. Furthermore, the length of the sample boat was seven times its width. This insured enough "contact time" of the carrier gas with the sample (which completely filled the sample boat) by exposing a sufficiently great surface area of sample to the carrier gas.

It was hoped that these precautions would ensure a zero-slope zone in the wt. loss per unit volume vs. flowrate plots, from which the true vapor pressure of SnS could be calculated. The results have proved the merit of this. The existence of relatively large regions where the apparent pressure is independent of flowrate in almost all the cases studied confirmed that the design of the apparatus was satisfactory, in ensuring that the carrier gas was saturated with vapor. This is shown in Figs. 14 to 20 in Chapter V. It can be seen in most of these curves, by comparison, that the temperature is not the prime factor influencing the shape of the curve (especially when the slope changes at higher flowrates). Rather, the absolute magnitude of the vapor pressure is the main factor causing unsaturation to begin at lower flowrates, the higher the temperature.

This occurs because, when the vapor pressure is high, the carrier gas is forced to remove a greater concentration of volatile species than at lower pressures, for the same time of contact in the reaction chamber.

## 2. Interpretation of Results

2.1 Vapor Pressure of SnS Over Pure SnS<sub>(c,1)</sub> • The results of the vapor pressure measurements on pure solid SnS using nitrogen as the carrier gas and Reaction chamber no. 1 (unreduced diameter) are shown graphically in Figs. 14 (wt loss/liter vs. flowrate) and 22 (Log p vs. 1/T). The latter shows also the values obtained by other authors. Richards<sup>(16)</sup> used the "entrainment method", which is the same as the transpiration technique, but using the reaction tube in a vertical position. These values are considered to be low, although they are quoted by Kubaschewski, Evans, and Alcock<sup>(1)</sup>. Richards used nitrogen as the carrier gas, and the condensed stannous sulfide was dissolved out in hydrochloric acid, and tin was estimated iodometrically. This, along with the possibility of an impure SnS sample, might have been the reason for the low values obtained. The geometry of his reaction apparatus is not given.

St. Clair and collaborators<sup>(19)</sup> used the transportation method, with helium as the carrier gas, for their determinations. Their values were accepted, during the decade of 1950-60, as the basis for development of a fuming process by the U. S. Bureau of Mines. The agreement of the present results (using nitrogen as carrier gas, and a large reaction chamber) with St. Clair et al. is fairly good, but this will be discussed later.

Colin and Drowart<sup>(22)</sup> (1962) made a mass spectrometric investigation of the vapor in equilibrium with solid SnS in the temperature range of approximately 540 to 727°C. Their results for SnS<sub>(g)</sub> are very scattered but most points lie between the lines obtained by St. Clair et al. and by Richards. It is to be deplored that Colin and Drowart<sup>(22)</sup> failed to publish a data table for the p<sub>SnS</sub> values, which are very difficult to read from the small figure published (See Fig. 23). However, it is obvious that the best-fit line through all their experimental points lies between the lines of the other authors (Which are the lines for total SnS vapor pressure, but it was shown in Chapter III that the main species is SnS<sub>(g)</sub> and the other gaseous species

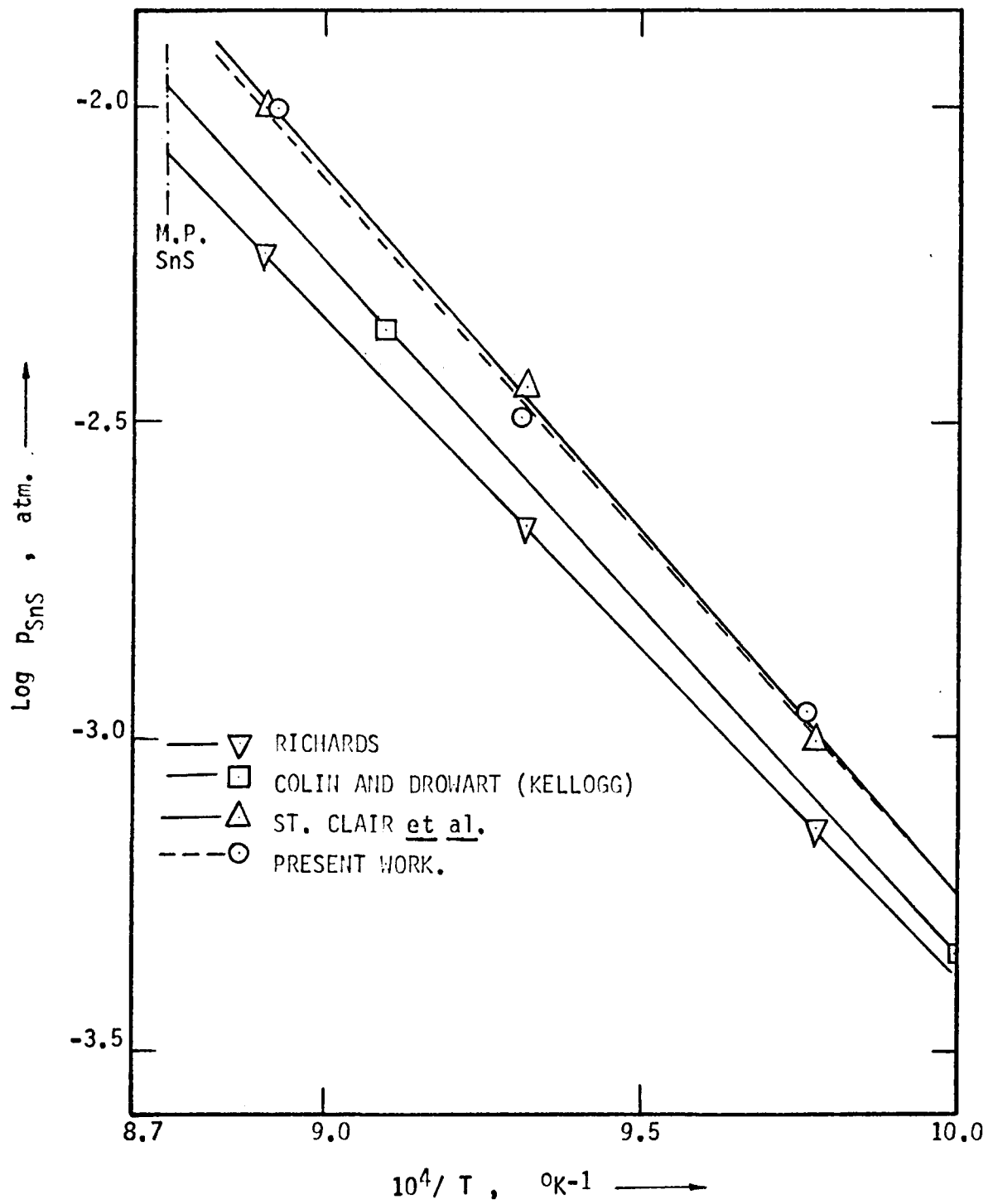


FIG. 22  $\text{LOG } p_{\text{SnS}(\eta)} \approx \text{LOG } p_{\text{SnS}_T}$  VERSUS  $1/T$  PLOT.

SAMPLE: PURE SnS(c).

CARRIER GAS:  $\text{N}_2$ .

REACTION CHAMBER: no. 1.

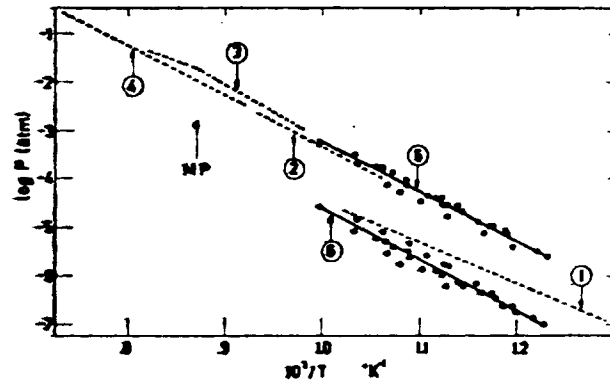


FIG. 1. Total and partial pressures above SnS. Total pressures: (1) Hsiao and Schlechten<sup>1</sup>; (2) Richards<sup>2</sup>; (3) St Clair, Shabler, and Solet<sup>3</sup>; (4) Klushin and Chernykh.<sup>4</sup> Partial pressures; this work: (5) gaseous SnS; (6) gaseous Sn<sub>2</sub>S<sub>3</sub>.

(\*)

FIG. 23 COLIN AND DROWART'S (REF. 22) PLOT OF  
Log P<sub>SnS</sub> VERSUS 1/T.

(\*) FIGURE AND REFERENCE NUMBERS CORRESPOND TO COLIN AND  
DROWART'S PAPER.

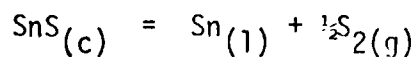
can be neglected).

H.H. Kellogg<sup>(23)</sup> calculated the thermodynamic relations for the vapor pressure of  $\text{SnS}_{(c,l)}$  and polymerization of  $\text{SnS}_{(g)}$  based on Colin and Drowart's work. The  $\text{SnS}$  vapor pressure line obtained lies almost mid-way between the lines of St. Clair et al. and Richards.

The fairly good agreement of the values obtained in the present work with those of St. Clair et al.<sup>(19)</sup> drew the attention of the author to the similarities and differences in experimental procedure and apparatus.

1. Helium ( $\mu_{\text{He}} = 0.0195$  cp at  $25^{\circ}\text{C}$ ) was used by St. Clair and collaborators as a carrier gas. Nitrogen ( $\mu_{\text{N}_2} = 0.0177$  cp at  $25^{\circ}\text{C}$ ) was used in this work. Both gases, because they are inert, did not control the sulfur potential in the reaction chamber.

Since in both cases contamination with oxygen was prevented, no surface oxidation occurred at the experimental temperatures (this would have yielded lower values rather than higher). Therefore the high values are attributed to the loss in weight of the sample not only by  $\text{SnS}$  volatilization but also by loss of sulfur, which would probably have been combined with some remnants of oxygen in the carrier gas. Or, as was evident in some cases when examining the condenser, sulfur vapor would leave the chamber by diffusion without oxidation. One possibility was the dissociation reaction:



$$\Delta G^{\circ} = + 43,704 - 24.793 T . \quad (\text{Ref. 23}) \quad (\text{cal/mole})$$

At  $850^{\circ}\text{C}$ , the value for  $\Delta G^{\circ}$  is:

$$\Delta G_{11230\text{K}}^{\circ} = + 15,861.6 \text{ cal/mole} ,$$

and

$$K = p_{\text{S}_2}^{\frac{1}{2}} = 8.18 \cdot 10^{-4} .$$

The free energy of sublimation of SnS at that temperature is:

$$\Delta G_s^0 = + 10,965 \text{ cal/mole}$$

for which

$$K = p_{\text{SnS}} = 7.276 \cdot 10^{-3}.$$

The sulfur pressure,

$$p_{\text{S}_2} = 7.00 \cdot 10^{-7}$$

accounts only for 0.01% of the SnS vapor pressure.

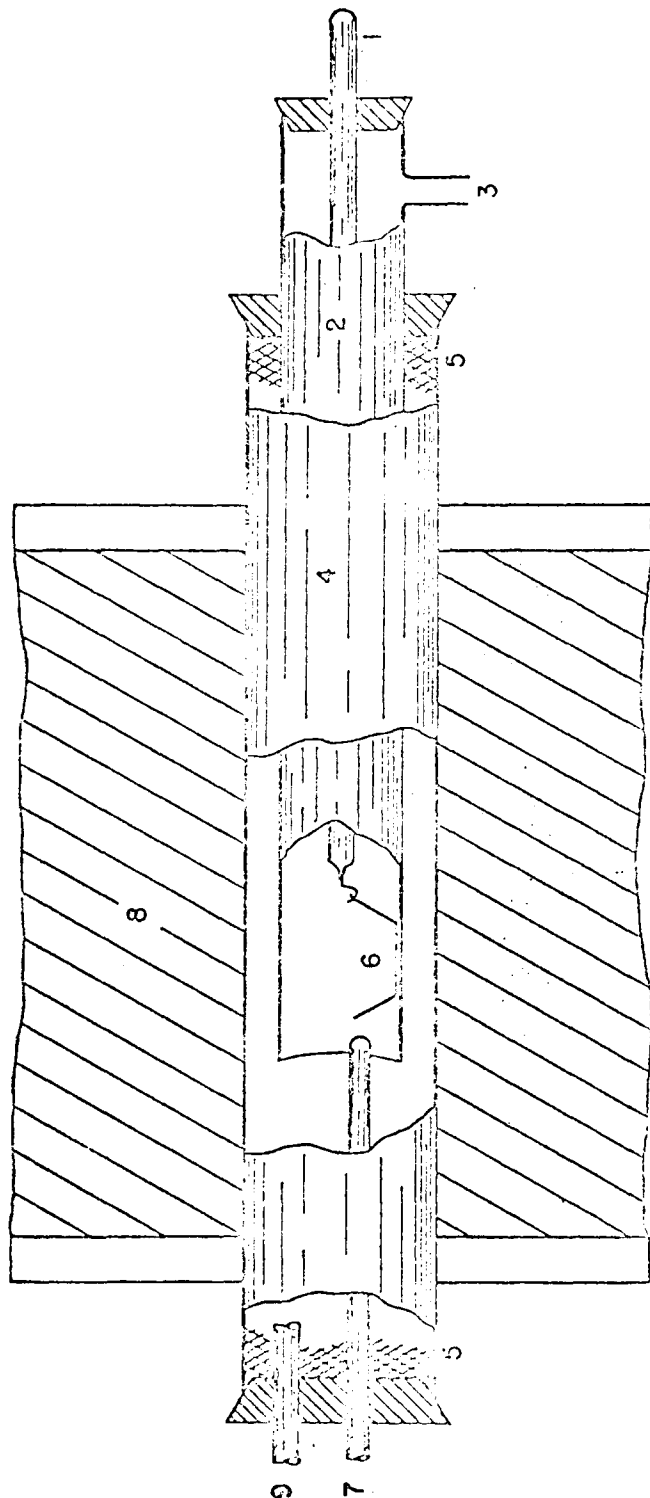
This analysis shows that, although this decomposition will occur under the conditions of the experiments, the increase in the apparent vapor pressure due to the dissociation reaction is not significant.

It should also be pointed out that in the present investigation, when using nitrogen as carrier gas at temperatures higher than 850°C, a tarnish of brown-yellow oxide film ( $\text{SnO}_2$ ) appeared on the sample surfaces, and this was a further reason for deciding to use  $\text{H}_2\text{S}/\text{H}_2$  mixtures instead of nitrogen. The boats which showed the surface oxidation were, of course, discarded. When there was doubt about whether or not a thin oxide film existed after a run, the sample was dissolved in concentrated hydrochloric acid. If indeed oxide existed, it would not dissolve in HCl, and the test would be discarded.

2. The geometry of the apparatuses was also compared. Fig. 24 shows the apparatus used by St. Clair et al.<sup>(19)</sup> for their experiments.

A careful observation of this, and the description given by the authors, show that the sample was placed inside tube 2, at the center of the furnace but no plugs or seals were provided, and the carrier gas entered the system through inlet 3 at low flowrates (0.03 to 0.3 lt/min) and left the system through outlet 9.

The "dead volume" existing around the sample was considerable and therefore saturation must have been difficult to achieve. Therefore, the vapors left the sample boat by other means than saturation.



- |                       |                      |
|-----------------------|----------------------|
| 1. POSITIONING ROD    | 6. BOAT              |
| 2. INNER FURNACE TUBE | 7. THERMOCOUPLE TUBE |
| 3. HELIUM INLET       | 8. FURNACE           |
| 4. OUTER FURNACE TUBE | 9. HELIUM OUTLET     |
| 5. ASBESTOS PACKING   |                      |

FIG. 24 APPARATUS USED BY ST. CLAIR AND COLLABORATORS FOR SnS VAPOR PRESSURE MEASUREMENTS.  
(REF. 19)

This diffusion through the carrier gas was probably caused by concentration gradients in the vicinity of the sample. The possibility of the existence of a thermal gradient in that region cannot be overlooked since the authors did not mention the existence of a constant temperature region in their apparatus.

The first reaction chamber used in the present investigation allowed for a "dead volume" comparable to St. Clair et al.'s apparatus. Although one might expect that saturation would be difficult to achieve, obviously saturation was achieved downstream from the sample boat as evidenced by the flat zone on the curves of weight loss per unit volume vs. flowrate.

The high values obtained must be attributed to the same causes as those of St. Clair and collaborators, i.e. segregation or back diffusion errors (as well as the use of an inert gas which did not control the sulfur pressure).

3. Finally, as a difference rather than as a similarity, it can be said that St. Clair et al.<sup>(19)</sup> calculated the vapor pressure of  $\text{SnS}_{(g)}$  by extrapolating the loss of weight per liter to zero flowrate. This, as proved by Alcock and Hooper<sup>(46)</sup>, and others, will always yield a vapor pressure which is high unless a zero-slope zone exists.

For all these reasons, although the values obtained in the first part of this investigation were within the limits of the available data in the literature, a check on the SnS vapor pressure measurements using a carrier gas able to control the sulfur atmosphere was desirable, before starting the measurements of SnS vapor pressures above the mattes. A mixture of Hydrogen sulfide and hydrogen was chosen as the carrier gas. Furthermore, as mentioned, the inside diameter of the reaction chamber was reduced to keep a minimum dead volume around the sample.

First, vapor pressure measurements were made above pure liquid SnS, to give a line ( $\log p$  vs.  $1/T$  plot) which must intersect the vapor pressure line for pure solid SnS at its melting point. If so, this would have proved that the vapor pressure of solid SnS had been correctly determined and thus that the old experimental technique was satisfactory.

It would then not have been necessary to run further experiments on pure solid SnS.

The results of these experiments are shown graphically in Figs. 16 and 25. It can readily be seen from Fig. 25 that it was worth while to make the modifications, and necessary to run a further series of tests on the pure solid SnS.

Tests were carried out at about 800°C and 860°C.

Figure 15 shows the weight loss per liter of carrier gas versus flowrate plot, and Fig. 25 shows also the new line for pure solid SnS. The line through the crosses shows the results obtained by Klushin and Chernikh<sup>(20)</sup> quoted by P. Wright<sup>(6)</sup> and Janz<sup>(21)</sup>. The method used by these authors was not stated. The discontinuous line shows the results of the present work under the new conditions and the dotted line shows the results of this work under previous conditions.

The agreement of the discontinuous line with the line calculated from Kellogg's data<sup>(23)</sup> (full line) can be considered extremely good, particularly at higher temperatures.

This demonstrates the important role played by the geometry of the reaction chamber in the determination of vapor pressures by means of the transportation method. A sulfur pressure-controlling gas, in the case of SnS and Sn-Fe mattes, prevents decomposition or segregation at different temperatures.

The effect of SnS decomposition is extremely low and the difference between values obtained by the old and the new method, about 23% (18% at 975°K and 27% at 1143°K), is due mainly to the effect of the geometry on back diffusion and segregation errors. (The effect of the nature of the carrier gas on segregation errors was not determined but it presumably accounts for some 2/23% of that difference).

Some of the curves in Figs. 16 through 20 do not show a systematic variation (with the absolute magnitude of vapor pressure) of the point at which unsaturation begins. This is attributed to the different compositions of the carrier mixtures used.

At higher temperatures, higher H<sub>2</sub>S/H<sub>2</sub> ratios were used, therefore changing in a sense the "nature" of the carrier gas - not in its ability to prevent

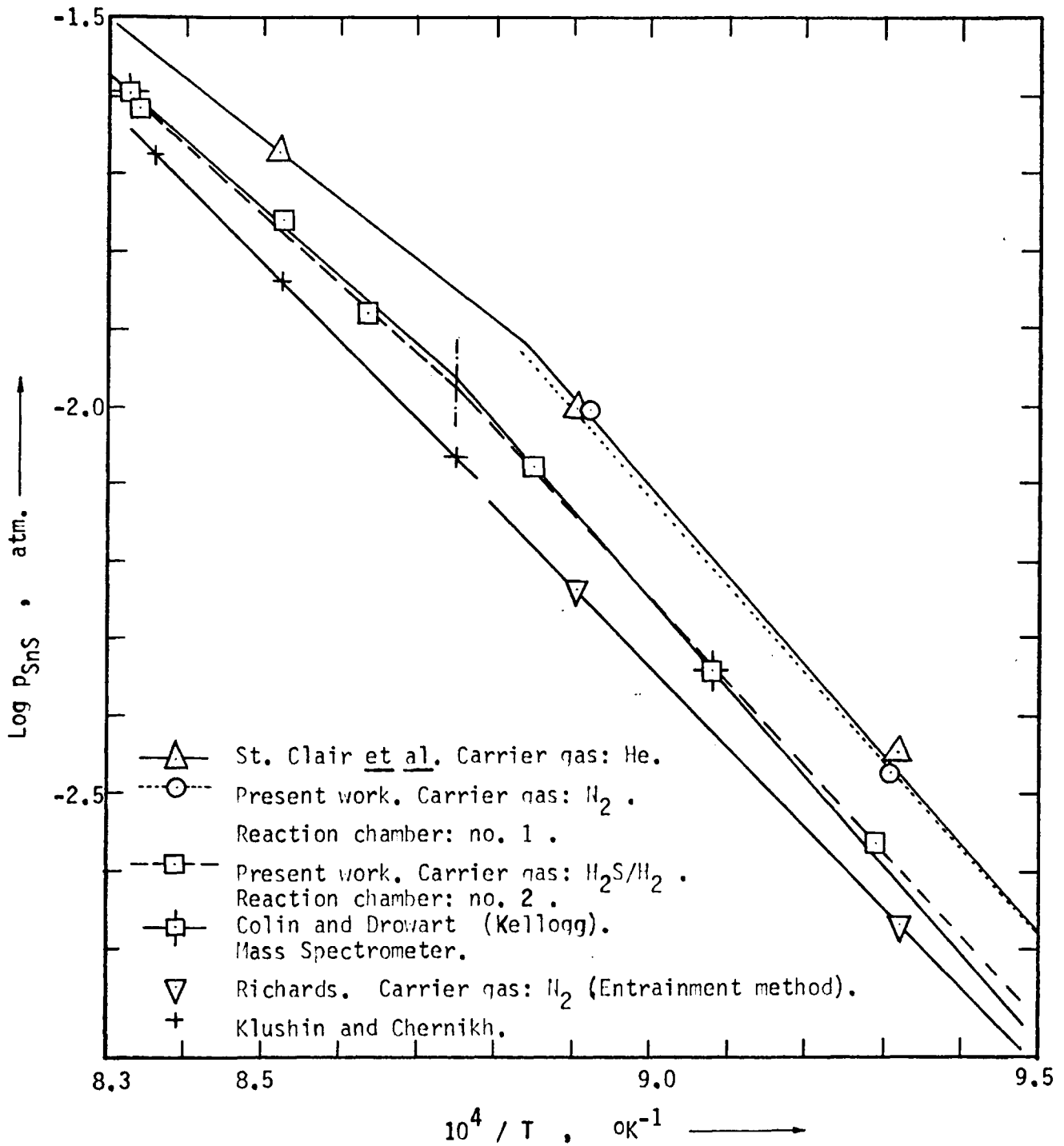


FIG. 25 INFLUENCE OF THE GEOMETRY OF THE REACTION CHAMBER AND OF THE NATURE OF CARRIER GAS ON THE VAPOR PRESSURE MEASUREMENTS OF PURE  $\text{SnS}(c,1)$  BY MEANS OF THE TRANSPORTATION METHOD.

decomposition, but probably in its capability of saturation, increasing it at higher temperatures.

Grjotheim, Herstad, and Toouri<sup>(48)</sup> showed, for instance, that the apparent pressure of magnesium was independent of the gas nature (Hydrogen and argon were used as carrier gases) but that the flat zone started at lower flow-rates for argon than for hydrogen. This same phenomenon occurs when using different  $H_2S/H_2$  mixtures in the same set of experiments, keeping the condition:

$$\left[ \frac{p_{H_2S(g)}}{p_{H_2(g)}} \right]_{EXPTL.} \geq \left[ \frac{p_{H_2S(g)}}{p_{H_2(g)}} \right]_{EQUIL. (SnS_{(c,1)})} \quad (16)$$

The only reason for doing this during the experiments was so as always to obtain a round even number (without decimal fractions) for  $h_1$  and  $h_2$ , the manometer altitudes in flowmeters F11 and F12 respectively, and in such way decrease the error due to gas volume measurements.

The composition of the  $H_2S/H_2$  mixtures can vary as long as it fulfils the desired conditions.

The agreement between the vapor pressure of SnS over pure  $SnS_{(c,1)}$  as obtained in this investigation and the results found by Colin and Drowart<sup>(22)</sup> by means of a mass spectrometric technique, taken by Kellogg as the most reliable so far, gives an indication of the reliability of the experimental apparatus and method used.

2.2 Vapor Pressures of SnS Over Tin - Iron Mattes. There are no available data with which the values obtained in this investigation could be compared. The results on the four mattes studied are tabulated in Chapter V and are graphically represented in Fig. 26. The apparent pressure vs. flowrate plots are given in Figs. 17 through 20 (Chapter V).

It is noticeable in these plots that there is scattering of the results in the zero-slope zone at higher temperatures, especially for the mattes with a higher content of SnS, as compared with the horizontal lines obtained for the mattes with higher contents of FeS, and with the lines at lower temperatures. This is most probably due to the difference in magnitude of the vapor pressure being measured. When the vapor pressure is high, saturation becomes more difficult at comparable flowrates.

Figure 26 shows each one of the points as calculated from the horizontal lines of the respective wt. loss/lit vs. flowrate plot. A simple least-squares fit for each experimental group gave the lines as shown in the figure.

Referring again to Fig. 17, the wt. loss/lit vs. flowrate plot for the SnS-5.81% FeS matte, and observing the results at 916.5°C - the experimental points are scattered, and the horizontal line can only be surmised. The mean point was calculated, as for all the other graphs, and through it the horizontal line (discontinuous line in Fig. 17) was traced. The vapor pressure calculated from this line is shown (Sn-5.81%FeS matte) in Fig. 26 as the broken-line circle (⊙).

Upon observation of all the other results and the path followed by the three other points in that particular line, that point (⊙) is undoubtedly high. As was discussed earlier in this chapter, when saturation is difficult to achieve and the horizontal line is not well defined, the lower values are more likely to be correct. Therefore the full line at 916.5°C in Fig. 17 was traced through the lower points, and the vapor pressure so calculated is given in Fig. 26 below the broken-line circle for that matte. It agrees well with the other points for the SnS-5.81%FeS matte.

It can be seen that the five lines in Fig. 26 are very close to parallel. The deviations of their slopes from that of the line for pure liquid SnS are not systematic (observe the slope values in table IX, Chapter V). Therefore, they

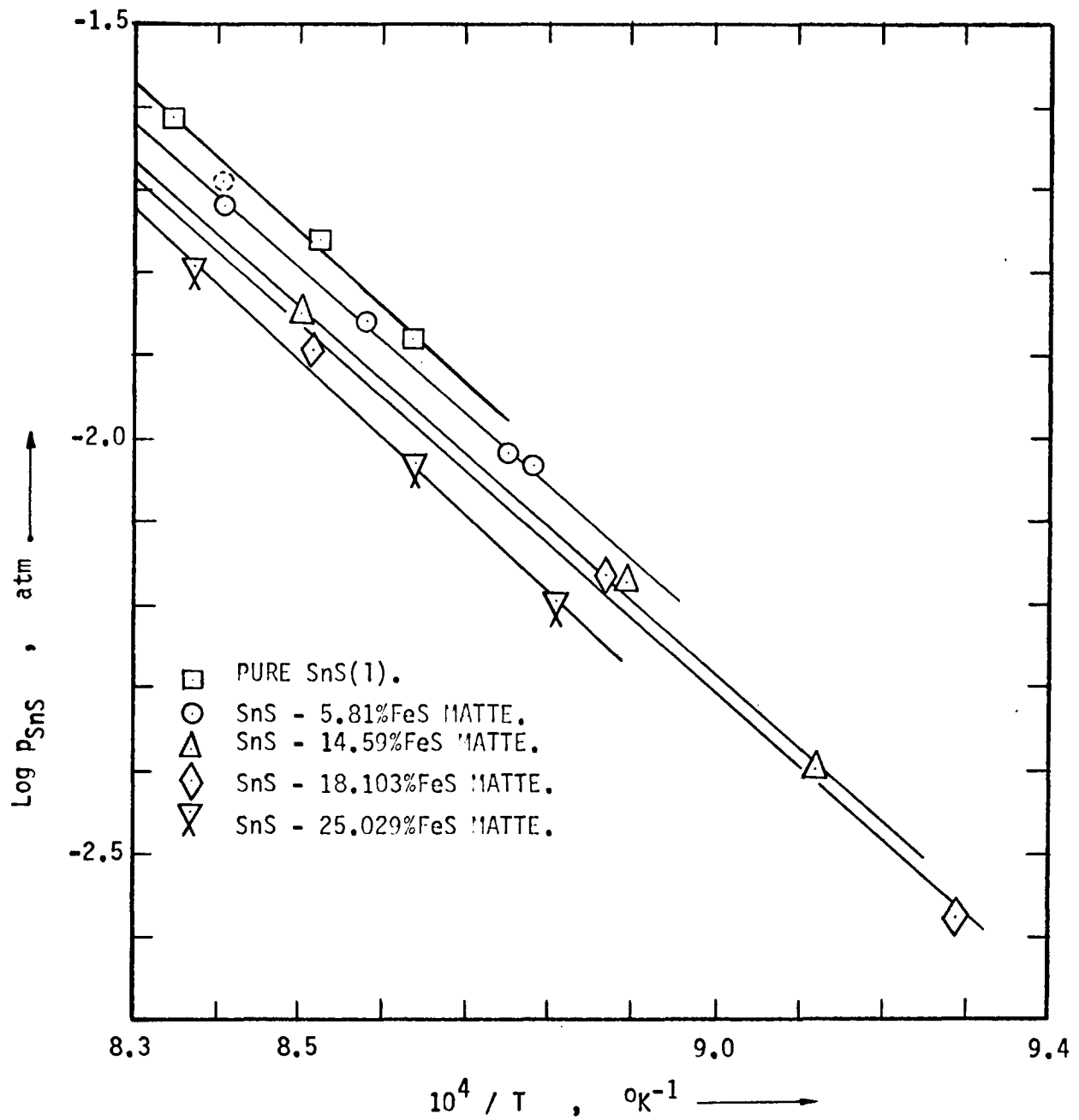


FIG. 26 VAPOR PRESSURE OF SnS( $\eta$ ) ABOVE IRON - TIN MATTES.  
 LINES CORRESPOND TO SIMPLE LEAST-SQUARES FITS FOR EACH GROUP  
 OF EXPERIMENTAL POINTS.

were attributed to random experimental errors. The measurements made on pure SnS, rather than those on the mattes, are undoubtedly less liable to error. The  $\alpha$ -function:

$$\alpha = \frac{R T \text{ Log } \gamma_{\text{SnS}}}{N_{\text{FeS}}^2} = \frac{R T}{N_{\text{FeS}}^2} (\text{Log } p_{\text{SnS}} - \text{Log } p_{\text{SnS}}^0 - \text{Log } H_{\text{SnS}})$$

was calculated for all the experimental points except those clearly not in harmony with the rest - eq. the SnS-14.59%FeS matte at 851.3°C, or the SnS-5.81%FeS matte at 916.5°C. The results are given in table X.

Figure 27 shows a plot of the  $\alpha$ -function vs. temperature. It can be seen that, within the experimental scatter, the  $\alpha$ -function is independent of temperature. The implications of this will be discussed later in this chapter.

Table X

Alpha - Function from Experimental Measurements of SnS Vapor Pressure.

MATTE COMPOSITION	TEMPERATURE °K	$10^4/T$	Log $p_{\text{SnS}}$ (atm) Exptl.	Log $\gamma_{\text{SnS}}$	$\alpha$
SnS-5.81%FeS	1139	8.780	- 2.0368	0.00398	2266.412
	1143	8.750	- 2.0146	-0.00109	- 622.881
SnS-14.59%FeS	1096.6	9.120	- 2.3990	0.01102	1076.728
	1176	8.503	- 1.8493	0.01421	1488.941
SnS-25.03%FeS	1135.3	8.808	- 2.19586	0.02324	910.664
	1194	8.375	- 1.79035	0.04438	1828.955
	1157.4	8.640	- 2.02956	0.04025	1607.906
SnS-18.10%FeS	1076	9.294	- 2.57727	0.01571	1023.635
	1174	8.518	- 1.88807	0.01629	1158.099
MEAN $\alpha$ =					1193.162

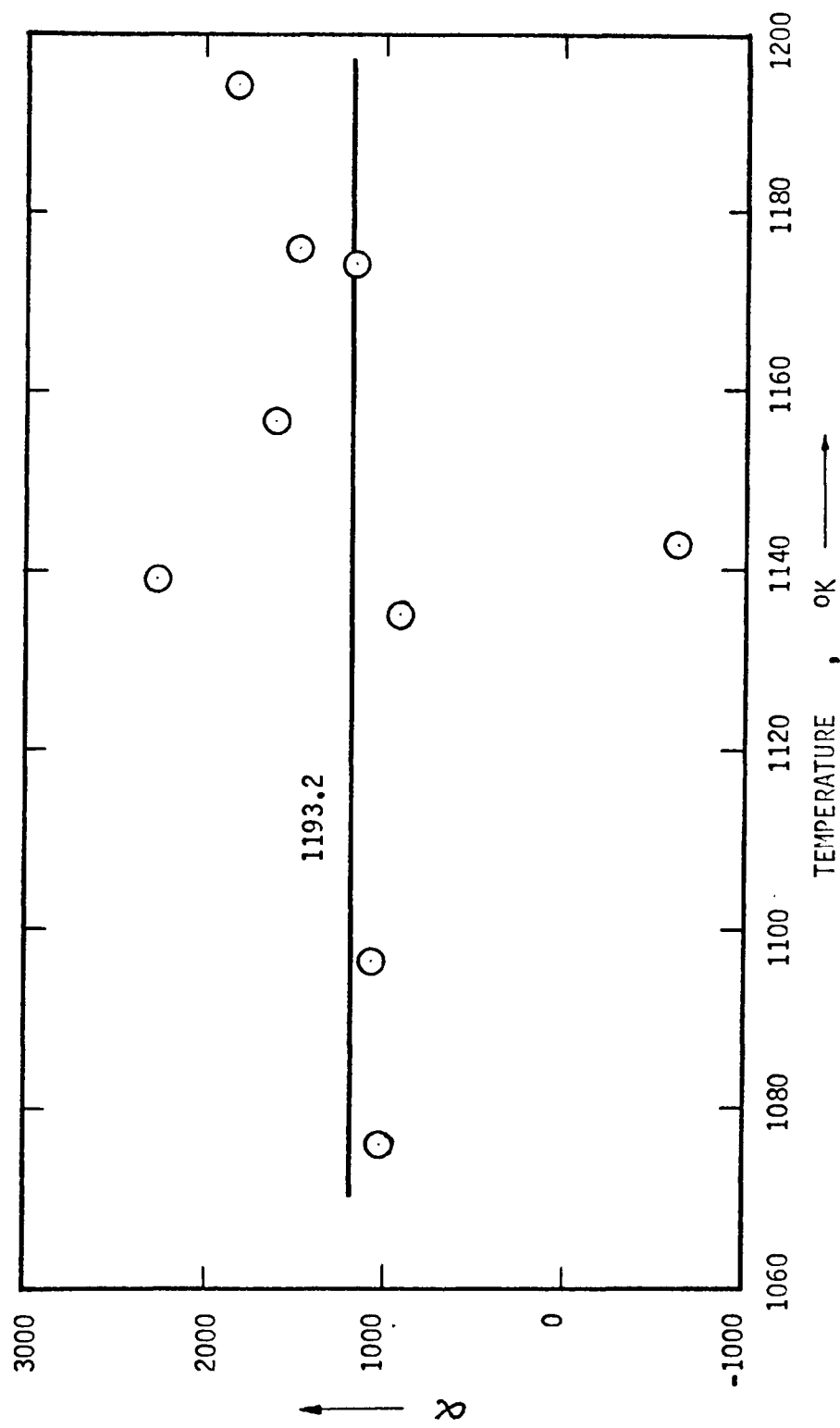


FIG. 27 ALPHA AS A FUNCTION OF TEMPERATURE.

$$\alpha = \frac{RT \log. \gamma_{SnS}}{N_{FeS}^2}$$

Now, taking the mean value of  $\alpha$ , the corresponding value for each experimental point was re-calculated and the corrected equations found for each of the four mattes (See Appendix VI).

These corrected equations, of the  $\text{Log } p_{\text{SnS}} = -A/T + B$  form, are shown in Table XI along with the equation for pure liquid SnS.

Figure 28 shows the corrected lines and the intersections of three of these lines with the line for pure solid SnS. The fourth line (Sn-25.03%FeS) should not intersect it, because it definitely lies on the FeS-rich side of the SnS - FeS phase diagram.

These intersections occur where the SnS vapor pressure over each liquid matte is at that particular point (the melting point of the matte in question) equal to the SnS vapor pressure over pure solid SnS. Hence the activity of SnS in the matte, at the liquidus (on the SnS-rich side of the diagram), with respect to pure solid SnS, is equal to 1.

Table XI

Expressions for the Vapor Pressure of SnS Over Pure Liquid SnS and Over Sn - Fe Mattes as Function of Temperature.

CONDENSED PHASE (liquid)	$\text{Log } p_{\text{SnS}} = -A/T + B$ , (atm)		TEMPERATURE RANGE, °K
	A	B	
Pure SnS <sub>(l)</sub>	8876.3	5.796	1143 - 1500
SnS-5.81%FeS	8859.2	5.740	1070 - 1500
SnS-14.59%FeS	8846.4	5.670	1070 - 1500
SnS-18.10%FeS	8843.0	5.646	1070 - 1500
SnS-25.03%FeS	8841.7	5.599	1070 - 1500

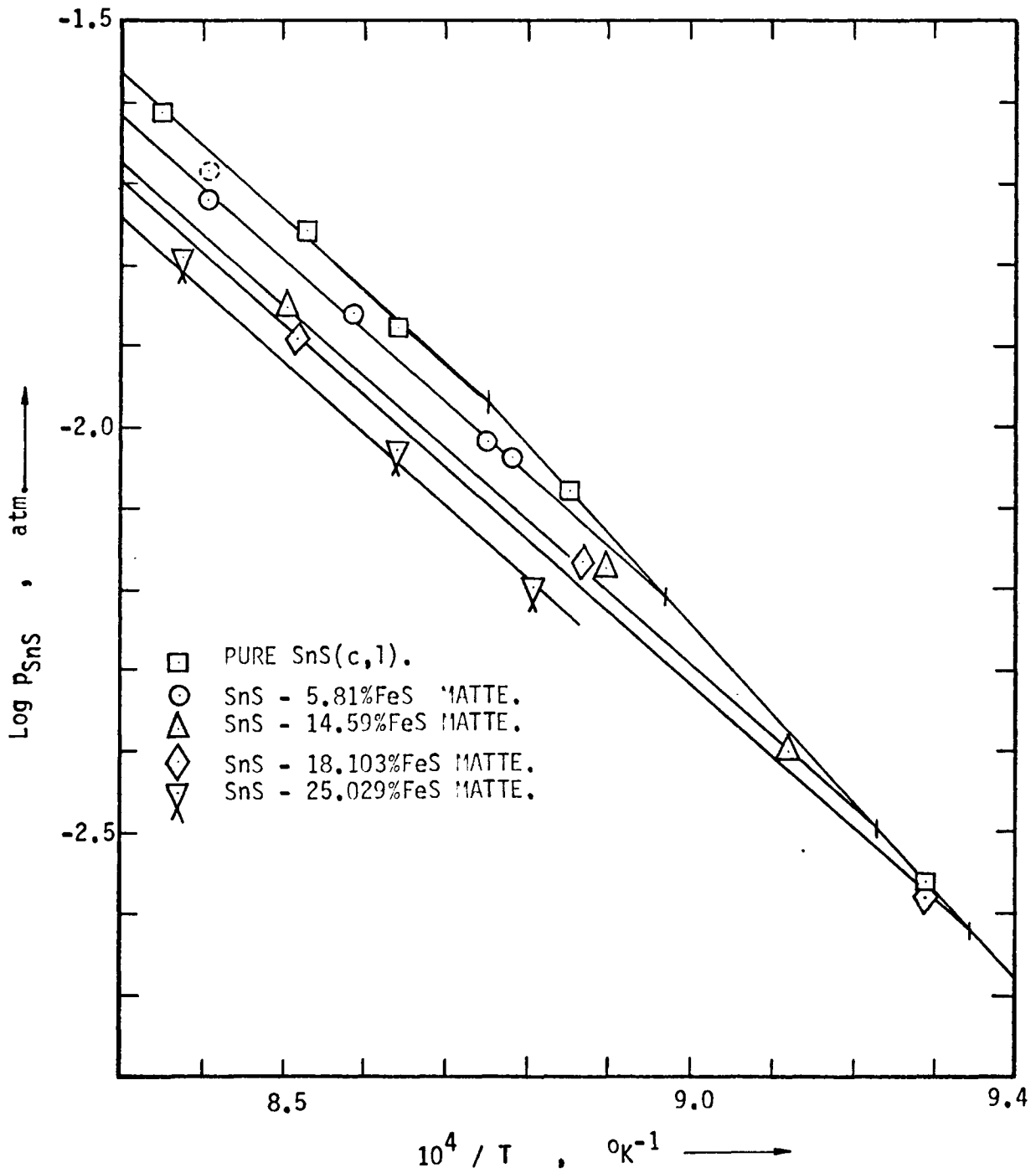
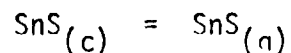


FIG. 28 VAPOR PRESSURE OF SnS ABOVE IRON - TIN MATTES.  
CORRECTED LINES.

### 3. Thermodynamic Considerations

Some useful properties can be derived from the results on the vapor pressure measurements on pure  $\text{SnS}_{(c,l)}$  and on the mattes.

3.1 Pure  $\text{SnS}_{(c,l)}$ . Consider the equilibrium:



for which,

$$\Delta G_S^0 = - R T \text{Log } p_{\text{SnS}}^0$$

Substituting the expression derived for the  $p_{\text{SnS}}^0$  in this investigation (Table IX), the free energy of sublimation can be represented by:

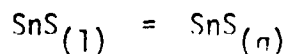
$$\Delta G_S^0 = - 35.041 T + 50,336 \quad (\text{cal}) .$$

This expression is in good agreement with Kellonq's data <sup>(23)</sup>:

$$\Delta G_S^0 = - 35.357 T + 50,671 \quad (\text{cal})$$

within the temperature range:  $\sim 800^\circ - 1143^\circ\text{K}$ .

The free energy of vaporization for the equilibrium:



using the  $\text{Log } p_{\text{SnS}}^0$  expression obtained experimentally (Table IX) is as follows:

$$\Delta G_V^0 = - 26.52 T + 40,610 \quad (\text{cal})$$

as compared with Kellonq's data <sup>(23)</sup>:

$$\Delta G_V^0 = - 26.113 T + 40,102 \quad (\text{cal})$$

for temperatures between 1143° and 1500°K.

The latent heat of fusion of stannous sulfide can be estimated from the slopes of the  $\log p_{\text{SnS}}$  vs.  $1/T$  plots in Fig. 25 as follows:

$\text{SnS}_{(l)} - \text{SnS}_{(g)}$  line; slope = - 8876.3

$$\frac{-\Delta H_v^0}{R} = - 8876.3 \quad (\text{from equation (22)})$$

$\text{SnS}_{(c)} - \text{SnS}_{(g)}$  line; slope = - 11,002.5

$$\frac{-\Delta H_s^0}{R} = - 11,002.5 \quad (\text{from equation (22)})$$

The difference in slopes, equal to - 2,126.2 gives  $-\Delta H_f^0 / R$ . Thus:

$$\Delta H_{f\text{SnS}}^0 = 9,727 \text{ cal/mole.}$$

Similar estimates can be made from St. Clair et al.'s. and Colin and Drowart's lines shown in the same figure (25). The results are:

$$\Delta H_f^0 = 16,992 \text{ cal/mole} \quad (\text{St. Clair } \underline{\text{et al.}})$$

$$\Delta H_f^0 = 10,529 \text{ cal/mole} \quad (\text{Kelloqq}).$$

The latter agrees fairly well with the estimate from the present work.

The free energy of fusion is zero at the melting temperature (equilibrium). Therefore;

$$\Delta H_f^0 = T \Delta S_f^0,$$

from which the entropy of fusion can be also estimated. Taking  $T = 1143^\circ\text{K}$  ( $\text{SnS}$  melting point):

$$\Delta S_{f\text{SnS}}^0 = 9,727/1143 = 8.51 \text{ e.u.}$$

This value is comparable to the first estimate by Davey<sup>(33)</sup> of 6.954 e.u.

3.2 Liquid Tin - Iron Mattes. The activity of SnS in liquid tin-iron mattes is, by definition, equal to the partial pressure of SnS above the liquid mattes, divided by the partial pressure of SnS above pure liquid SnS:

$$a_{\text{SnS}(l)} = \frac{p_{\text{SnS}(g)}^{\text{Matte}}}{p_{\text{SnS}(g)}^0} = \frac{p_{\text{SnS}(g)}}{p_{\text{SnS}(g)}^0}$$

Furthermore, for a given temperature:

$$a_{\text{SnS}(l)} = \gamma_{\text{SnS}} N_{\text{SnS}},$$

where  $\gamma_{\text{SnS}}$  is the Raoultian activity coefficient of SnS and  $N_{\text{SnS}}$  is its mole fraction.

It was seen that the experimental values of  $p_{\text{SnS}}$  on the different mattes varied randomly about  $p_{\text{SnS}}^0$  (pure SnS<sub>(l)</sub>). There was no systematic variation.

Figure 27 shows no dependence on temperature for  $\alpha$ , although there is appreciable scatter. It can be shown also that  $T \text{Log } \gamma_{\text{SnS}}$  varies linearly as a function of  $N_{\text{FeS}}^2$ . This is shown in Fig. 29 which is a plot of  $T \text{Log } \gamma_{\text{SnS}}$  versus  $N_{\text{FeS}}^2$ , the slope is equal to  $\alpha/R$ , a constant:

$$\alpha/R = B = 260.8.$$

Therefore the liquid solution of SnS and FeS has been shown to behave almost regularly, and the activity coefficients can be represented by:

$$\text{Log } \gamma_{\text{SnS}} = \frac{B}{T} N_{\text{FeS}}^2$$

$$\text{Log } \gamma_{\text{FeS}} = \frac{B}{T} N_{\text{SnS}}^2$$

where B is the "regularity" constant.

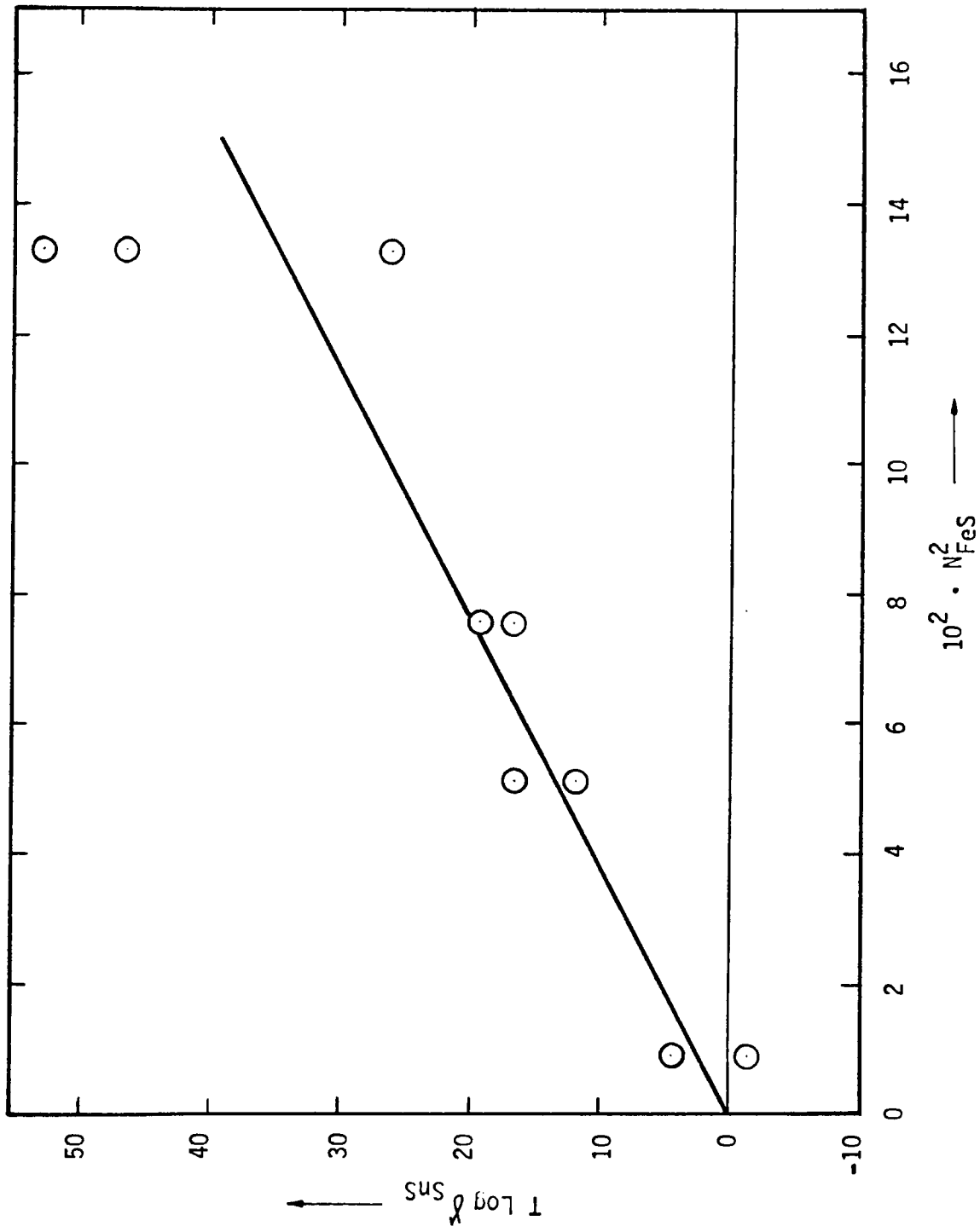


FIG. 29 T(Log δ<sub>SnS</sub>) VERSUS N<sub>FeS</sub><sup>2</sup> PLOT. SLOPE = α/R = B = 260.8

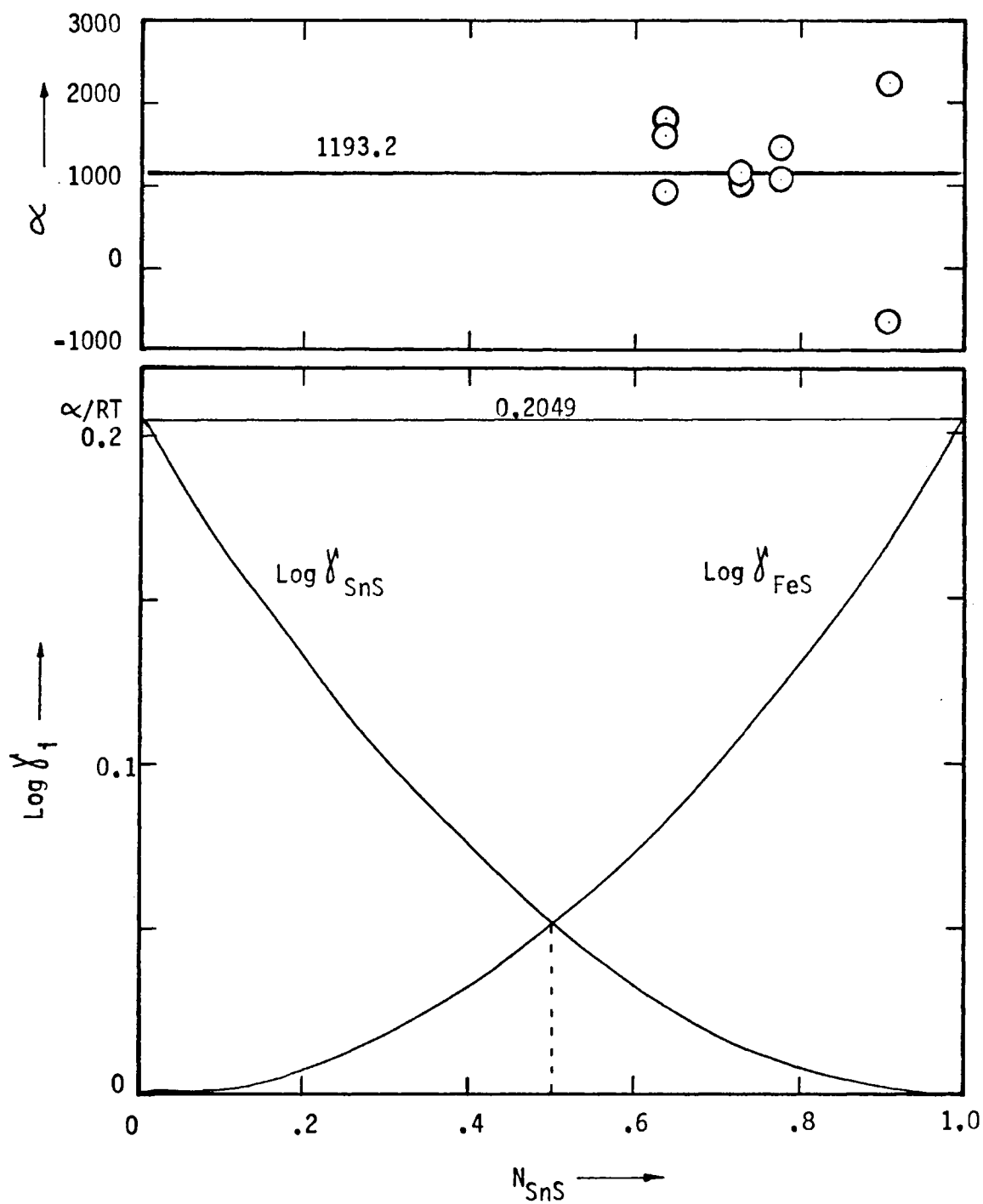


FIG. 30  $\alpha$  - FUNCTION FOR SnS - FeS SOLUTIONS , AND SYMMETRICAL LINES OF  $\text{Log } \gamma_i$  AT 1000°C AS A FUNCTION OF  $N_{SnS}$  .

Figure 30 shows a plot of  $\alpha$  as a function of composition indicating it to be approximately constant. The same figure shows a plot of  $\text{Log } \gamma_{\text{SnS}}$  as a function of composition at 1000°C calculated from the constant  $\alpha$  evaluated above it. So, the lines are symmetrical with respect to:

$$N_{\text{SnS}} = N_{\text{FeS}} = 0.5 \quad ,$$

and

$$\text{Log } \gamma_i = \frac{\alpha}{RT} \quad \text{for } N_i = 0 \quad .$$

These values are listed in table XII.

**3.3 Thermodynamic Relations Derived from the Regular Solution Model.** "A regular solution is defined as one for which the entropy of formation and hence the partial molar entropies are the same as for an ideal solution" (Darken and Gurry<sup>(49)</sup>).

The enthalpy of mixing of these solutions is different from zero:

$$\Delta H^M \neq 0 \quad (23)$$

The SnS-FeS liquid solution has been shown to approximate to regular. It is convenient therefore, to study how this regular solution behaves as a step away from ideality.

The entropy of mixing is given as follows:

$$\Delta S^M = -R (N_{\text{SnS}} \text{Log } N_{\text{SnS}} + N_{\text{FeS}} \text{Log } N_{\text{FeS}}) \quad (24)$$

It will be symmetrical about  $N_{\text{SnS}} = N_{\text{FeS}} = 0.5 \quad .$

The excess free energy of mixing in a binary solution is defined as:

$$\Delta G^{XS} = \Delta G^M - \Delta G_{\text{ideal}}^M \quad . \quad (25)$$

The free energy of mixing for the binary system,  $\Delta G^M$ , is by definition:

$$\Delta G^M = RT(N_{\text{SnS}} \text{Log } a_{\text{SnS}} + N_{\text{FeS}} \text{Log } a_{\text{FeS}}) \quad (26)$$

And for an ideal solution:

$$\Delta G_{\text{ideal}}^M = RT(N_{\text{SnS}} \text{Log } n_{\text{SnS}} + N_{\text{FeS}} \text{Log } n_{\text{FeS}}) . \quad (27)$$

Therefore, substituting (26) and (27) into (25) gives the excess free energy of mixing:

$$\Delta G^{\text{XS}} = RT(N_{\text{SnS}} \text{Log } \gamma_{\text{SnS}} + N_{\text{FeS}} \text{Log } \gamma_{\text{FeS}}) . \quad (28)$$

Also, 
$$\Delta G^M = \Delta H^M - T \Delta S^M . \quad (29)$$

Since 
$$\Delta H_{\text{ideal}}^M = 0 \quad ; \quad \Delta G_{\text{ideal}}^M = - T \Delta S_{\text{ideal}}^M . \quad (30)$$

Substituting (29) and (30) into (25):

$$\Delta G^{\text{XS}} = \Delta H^M - T(\Delta S^M - \Delta S_{\text{ideal}}^M) \quad (31)$$

↘ 0

Therefore,

$$\Delta G^{\text{XS}} = \Delta H^M . \quad (32)$$

Now, since

$$\alpha = \frac{R T \text{Log } \gamma_{\text{SnS}}}{N_{\text{FeS}}^2} = \frac{R T \text{Log } \gamma_{\text{FeS}}}{N_{\text{SnS}}^2} ,$$

$$\therefore \left. \begin{aligned} R T \text{Log } \gamma_{\text{SnS}} &= \alpha N_{\text{FeS}}^2 \\ R T \text{Log } \gamma_{\text{FeS}} &= \alpha N_{\text{SnS}}^2 \end{aligned} \right\} \quad (33)$$

Substituting (33) into (28):

$$\Delta G^{\text{XS}} = \alpha N_{\text{SnS}} N_{\text{FeS}} = \Delta H^M . \quad (34)$$

For a regular solution the excess free energy of mixing is equal to the enthalpy of mixing, and is a parabolic function of composition.

These thermodynamic functions were calculated at different temperatures for the SnS - FeS system. The results are given in table XII. Figure 31 shows a plot of the excess and mixing functions for the formation of 1 mole of liquid SnS-FeS matte at various temperatures as a function of composition. The partial molar quantities for FeS and SnS are obtained from these curves upon intersection of a tangent to the desired curve at any point with the ordinates at  $N_{\text{SnS}} = 0$  and at  $N_{\text{SnS}} = 1$  respectively.

The relatively small heat of mixing explains the absence of a significant effect of temperature on the present results.

Figure 32 is a plot of activities of SnS and FeS as a function of composition for different temperatures. Notice that the variation of activity at any composition as a function of temperature is in fact very little. The figure shows positive departures from ideality. These positive deviations are not large and they decrease with increasing temperature.

Krivsky and Schuhmann, as quoted by Oriani and Alcock<sup>(50)</sup>, found that the pseudobinary system  $\text{Cu}_2\text{S} - \text{FeS}$  could reasonably be described as ideal.

Rosenqvist and Hastig<sup>(51)</sup> showed that the activities of  $\text{Cu}_2\text{S}$  and FeS in the system Cu-Fe-S-O could be calculated to a good approximation by equations based on random mixing.

Davey<sup>(52)</sup> showed that the PbS- $\text{Cu}_2\text{S}$  system is regular.

These examples show that base metal mattes tend to be regular solutions which are not very far from ideal.

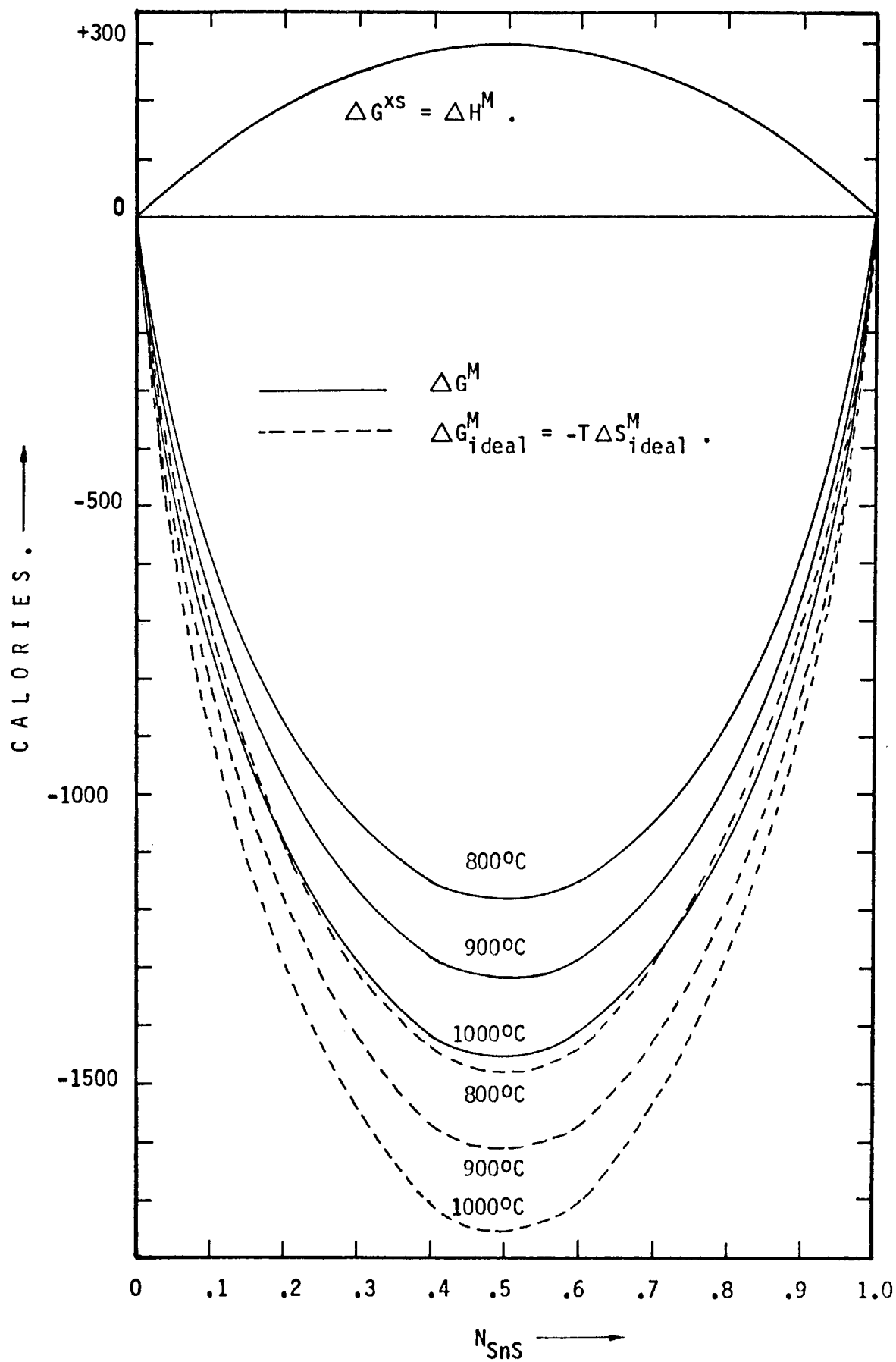


FIG. 31 EXCESS AND MIXING FUNCTIONS FOR THE FORMATION OF 1 MOLE OF LIQUID SnS - FeS MATTE AT VARIOUS TEMPERATURES.

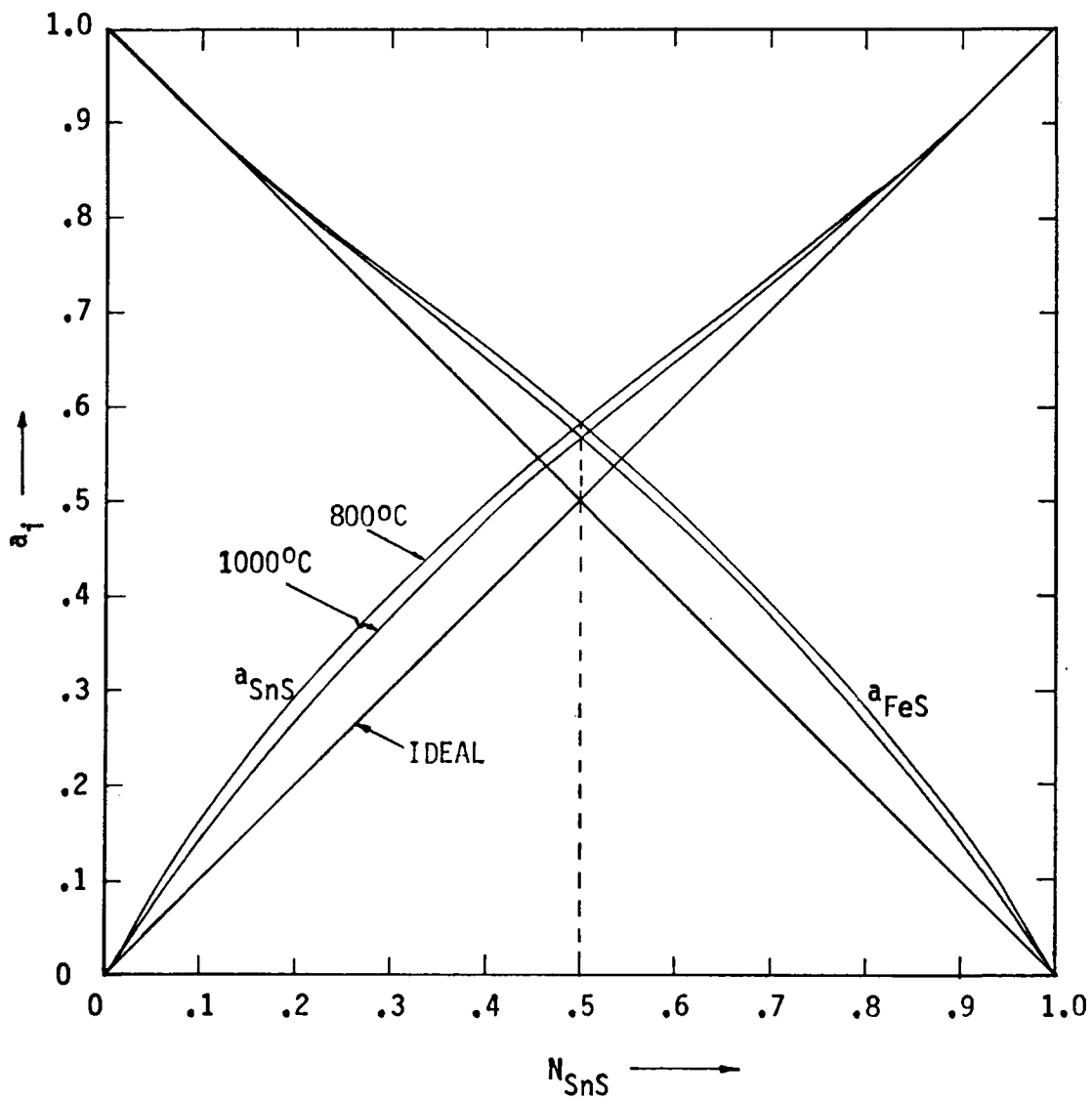


FIG. 32 ACTIVITIES IN THE SnS - FeS SYSTEM AT 800° and 1000°C.

Table XII

Thermodynamic Functions for the SnS - FeS Liquid System.  
 Regularity Constant B = 260.8

TEMP. °C	$N_{\text{SnS}}$	$\text{Log } \gamma_{\text{SnS}}$	$a_{\text{SnS}}$	$\text{Log } \gamma_{\text{FeS}}$	$a_{\text{FeS}}$	$\Delta G^M$ cal/mole	$\Delta G_{\text{ideal}}^M$ cal/mole	$\Delta G^{\text{XS}} = \Delta H^M$ cal/mole	$\Delta S^M$ cal/deg mole
800	0.1	0.19694	0.15739	0.00243	0.90505	-585.513	-692.933	107.420	0.64579
	0.2	0.15561	0.28620	0.00973	0.81812	-875.663	-1066.640	190.969	0.99407
	0.3	0.11914	0.39471	0.02188	0.73618	-1051.450	-1302.090	250.646	1.21351
	0.4	0.08753	0.48933	0.03890	0.65624	-1148.110	-1434.560	286.453	1.33696
	0.5	0.06078	0.57513	0.06078	0.57513	-1179.090	-1477.480	298.388	1.37696
	0.6	0.03890	0.65624	0.08753	0.48933	-1148.110	-1434.560	286.453	1.33696
	0.7	0.02188	0.73718	0.11914	0.39471	-1051.450	-1302.090	250.646	1.21351
	0.8	0.00973	0.81812	0.15561	0.28620	-875.668	-1066.640	190.969	0.99407
	0.9	0.00243	0.90505	0.19694	0.15739	-585.513	-692.933	107.420	0.64579
	1.0	0.0	1.0	0.24314	0.0	0.0	0.0	0.0	0.0

Table XXI - Continued

TEMP. °C	$N_{\text{SnS}}$	$\text{Log } \gamma_{\text{SnS}}$	$a_{\text{SnS}}$	$\text{Log } \gamma_{\text{FeS}}$	$a_{\text{FeS}}$	$\Delta G^M$ cal/mole	$\Delta G^M_{\text{ideal}}$ cal/mole	$\Delta G^{XS} = \Delta H^M$ cal/mole	$\Delta S^M$ cal/deg mole
900	0.1	0.18915	0.15142	0.00222	0.90462	-650.092	-757.512	107.420	0.64579
	0.2	0.14234	0.27759	0.00890	0.81656	-975.074	-1166.040	190.969	0.99407
	0.3	0.10898	0.38559	0.02002	0.73303	-1172.890	-1423.440	250.646	1.21351
	0.4	0.08907	0.48100	0.03559	0.65124	-1281.810	-1568.260	286.453	1.33696
	0.5	0.05560	0.56831	0.05560	0.56831	-1316.790	-1615.180	298.388	1.37696
	0.6	0.03556	0.65124	0.08007	0.48100	-1281.810	-1568.260	286.453	1.33696
	0.7	0.02002	0.73303	0.10898	0.38559	-1172.890	-1423.440	250.646	1.21351
	0.8	0.00890	0.81656	0.14234	0.27759	-975.074	-1166.040	190.969	0.99407
	0.9	0.00222	0.90462	0.18015	0.15142	-650.092	-757.512	107.420	0.64579
	1.0	0.0	1.0	0.22241	0.0	0.0	0.0	0.0	0.0
1000	0.1	0.16600	0.14657	0.00205	0.90426	-714.671	-822.091	107.420	0.64579
	0.2	0.13116	0.27053	0.00820	0.81525	-1074.480	-1265.450	190.969	0.99407
	0.3	0.10042	0.37806	0.01845	0.73038	-1294.150	-1544.790	250.646	1.21351
	0.4	0.07378	0.47408	0.03279	0.64706	-1415.500	-1701.960	286.453	1.33696
	0.5	0.05124	0.56262	0.05124	0.56262	-1454.490	-1758.880	298.388	1.37696
	0.6	0.03279	0.64706	0.07378	0.47408	-1415.500	-1701.960	286.453	1.33696
	0.7	0.01845	0.73038	0.10042	0.37806	-1294.150	-1544.790	250.646	1.21351
	0.8	0.00820	0.81525	0.13116	0.27053	-1074.480	-1265.450	190.969	0.99407
	0.9	0.00205	0.90426	0.16600	0.14657	-714.671	-822.091	107.420	0.64579
	1.0	0.0	1.0	0.20494	0.0	0.0	0.0	0.0	0.0

3.4 Calculation of the SnS - FeS Phase Diagram from Vapor Pressure Measurements Assuming the Regular Solution Model for the Liquid Phase and that there are no Solid Solubilities in the System. It was shown that:

$$\text{Log } \gamma_{\text{SnS}} = \frac{B}{T} N_{\text{FeS}}^2$$

where  $B = 260.8$  is the regularity constant.

Therefore, the SnS - FeS phase diagram can be calculated from the vapor pressure measurements and from the latent heat of fusion of FeS and the estimated latent heat of fusion of SnS.

The derivations of the equations for temperature as a function of composition for both the FeS- and the SnS-rich side of the simple eutectic phase diagram are given in Appendix II.

The derived equation (35) gives the temperature as a function of the fusion properties of SnS and FeS, where  $i = \text{FeS}$  at the FeS-rich side and  $i = \text{SnS}$  at SnS-rich side of the phase diagram.

$$T = \frac{\Delta S_{f_i}^0 \cdot T_{f_i} + B \cdot R \cdot (1 - N_i)^2}{\Delta S_{f_i}^0 - R \cdot \text{Log } N_i} \quad (35)$$

where,

$T$  = Temperature at a particular composition , °K  
 $\Delta S_{f_i}^0$  = Entropy of fusion of component  $i$  , e.u.

$T_{f_i}$  = Temperature of fusion of component  $i$  , °K

$B = 260.8$  = Regularity Constant

$R = 4.575$  = Gas Constant

$N_i$  = Mole Fraction of Component  $i$  .

The results are shown in Table XIII.

Figure 33 shows the calculated phase diagram. The experimental points of Haan<sup>(8)</sup> are also indicated (Haan's data are tabulated in Appendix II). The eutectic composition was found by intersection of the two liquidus lines at 18.4% FeS and 797°C.

Table XIII

The SnS - FeS Phase Diagram Calculated from Vapor Pressure Measurements.

Assumptions: Regular Solution Model for Liquid Mattes, and No Solid Solution in Either Component.

Data	SnS	FeS
$T_f$ , °K	1143	1468 *
$\Delta H_f^0$ , cal/mole	9727	7730 *
$\Delta S_f^0$ , e.u.	8.51	5.26

\* Kubaschewski et al. (Ref. 1)

FeS-rich arm

wt% SnS	$N_{SnS}$	Temp., °K	Temp., °C
10	0.06085	1434.85	1161.85
20	0.12724	1399.80	1126.80
30	0.19995	1362.40	1089.40
40	0.27993	1321.97	1048.97
50	0.36835	1277.36	1004.36
60	0.46659	1226.54	953.54
70	0.57639	1165.60	892.60
80	0.69993	1085.91	812.91
90	0.83996	962.55	689.55

Table XIII - Continued

SnS-rich arm			
wt% SnS	$N_{\text{SnS}}$	Temp. , °K	Temp. , °C
100	1.0	1143.00	870.
95	0.91722	1121.34	848.34
90	0.88996	1101.74	828.74
85	0.76768	1083.69	810.69
80	0.69993	1066.79	793.79
75	0.63629	1050.67	777.67
70	0.57639	1035.05	762.05

The melting points of the mattes used in the vapor pressure measurements, obtained from the calculated phase diagram are compared with the intersections of the Log p vs. 1/T plots of the mattes and the pure  $\text{SnS}_{(c)} - \text{SnS}_{(\eta)}$  line (Fig. 28) in table XIV.

Table XIV

## Melting Points of Mattes

Matte Composition %	$T_f$ from liquidus line (Fig. 33)	$T_f$ from intersec. with pure $\text{SnS}_{(c)}$ line		Difference	
	°C	°K <sup>-1</sup>	°C	°C	%
SnS-5.81%FeS	844.00	8.97	841.83	- 2.17	- 0.26
SnS-14.59%FeS	810.69	9.23	810.42	- 0.27	- 0.03
SnS-18.10%FeS	798.00	9.35	796.52	- 1.48	- 0.19
SnS-25.03%FeS	856.00*	-	-	-	-

\* This composition lies on the other side of the phase diagram (FeS-rich side).

The agreement is good.

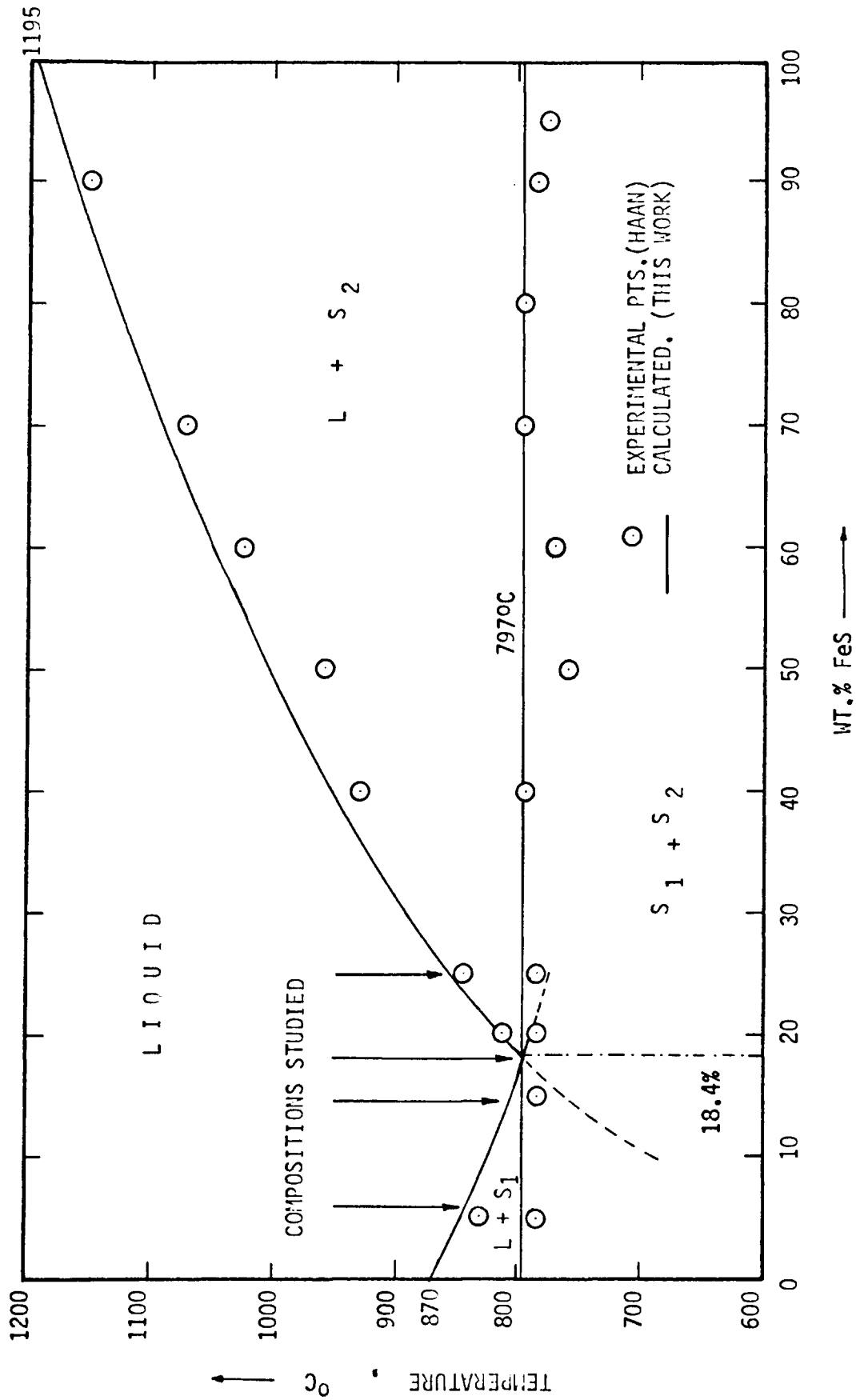


FIG. 33 THE SnS - FeS PHASE DIAGRAM FROM VAPOR PRESSURE MEASUREMENTS. LIQUID PHASE: REGULAR SOLUTION. NO SOLID SOLUBILITIES.

Referring to Fig. 33, the experimental values of Haan for the 50%FeS matte are definitely out of line with the rest of his experimental data.

The calculated line appears to be higher than Haan's experimental points but it must be considered that any impurity in the SnS and FeS used tends to lower the melting point of a matte.

To obtain a pure sample of SnS (99.99%) is rather difficult nowadays, and it must have been even more difficult 59 years ago. Haan did not give the composition of his "pure" compounds.

With these considerations in mind, it can be said that the agreement of the present work with Haan's work is fairly good, and there is no other work to confirm either Haan's investigation or the present work as yet.

### 3.5 The Sub - Regular Solution Model Applied to the SnS - FeS System.

Since the regular solution, a one-parameter model, appeared to be in fairly good agreement with the SnS-FeS phase diagram experimentally obtained by Haan<sup>(8)</sup>, it was assumed that the sub-regular solution model, with four parameters allowing for temperature variation, would represent a better fit to these experimental values.

This model can be represented by:

$$\text{Log } \delta_{\text{FeS}}^{\lambda} = (A_1 + B_1/T) N_{\text{SnS}}^2 + (A_2 + B_2/T) N_{\text{SnS}}^3 \quad , \quad (36)$$

and upon integration of the Gibbs-Duhem equation:

$$\text{Log } \delta_{\text{SnS}}^{\lambda} = - \int_{N_{\text{SnS}}=1}^{N_{\text{SnS}}} \frac{N_{\text{FeS}}}{N_{\text{SnS}}} d(\text{Log } \delta_{\text{FeS}}^{\lambda}) \quad ,$$

the following expression results:

$$\text{Log } \delta_{\text{SnS}}^{\lambda} = \left[ (A_1 + B_1/T) + 3/2(A_2 + B_2/T) \right] N_{\text{FeS}}^2 - (A_2 + B_2/T) N_{\text{FeS}}^3 \quad . \quad (37)$$

To find the numerical values of constants  $A_1$ ,  $A_2$ ,  $B_1$ , and  $B_2$ , four points of the phase diagram were chosen randomly and  $\text{Log } \delta_{\text{FeS}}^k$  calculated therefrom. The values are tabulated below (Table XV).

The activity was calculated for each composition using the following expression:

$$\text{Log } a_{\text{FeS}} = - \frac{\Delta S_{\text{f FeS}}^{\circ} (T_{\text{f}} - T)}{R T} ,$$

where  $\Delta S_{\text{f FeS}}^{\circ} = 5.26 \text{ e.u.}$  ,

and  $T_{\text{f}} = 1468^{\circ}\text{K}$ .

Table XV

SnS - FeS System. Sub-regular Solution Model

wt% FeS	$N_{\text{FeS}}$	Temp. , $^{\circ}\text{K}$	$\text{Log } N_{\text{FeS}}$	$\text{Log } a_{\text{FeS}}$	$\text{Log } \delta_{\text{FeS}}^k$
15	0.23235	1958	- 0.6339	- 0.44555	0.19335
25	0.36371	1119	- 0.4393	- 0.35858	0.08068
70	0.80005	1347	- 0.0969	- 0.10328	-0.00642
90	0.93915	1423	- 0.0273	- 0.03636	-0.00908

wt% FeS	$N_{\text{SnS}}^2$	$N_{\text{SnS}}^3$	$N_{\text{SnS}}^2 / T$	$N_{\text{SnS}}^3 / T$
15	0.58929	0.45237	0.0005570	0.0004276
25	0.40487	0.25761	0.0003618	0.0002302
70	0.03990	0.00799	0.0000297	0.0000059
90	0.00370	0.00023	0.0000026	0.0000002

Therefore four equations of the form (36), with four unknowns, were obtained. These were solved by means of a computer program using the Gaussian algorithm (See Appendix VI).

The following results were obtained:

$$A_1 = 527,245$$

$$B_1 = -773,589,000$$

$$A_2 = 119,697$$

$$B_2 = 154,857,000$$

It was found that:

$$T = \frac{-\Delta S_{f_i}^0 T_{f_i} / R}{\text{Log } \gamma_i + \text{Log } n_i - \Delta S_{f_i}^0 / R} \quad (38)$$

where  $i = \text{FeS}$  for the FeS-rich side, and  $i = \text{SnS}$  for the SnS-rich side of the phase diagram.

Substituting (36) for  $\text{Log } \gamma_{\text{FeS}}$  into (38) yields,

$$T = \frac{\Delta S_{f_{\text{FeS}}}^0 T_{f_{\text{FeS}}} / R + B_1 N_{\text{SnS}}^2 + B_2 N_{\text{SnS}}^3}{\Delta S_{f_{\text{FeS}}}^0 / R - A_1 N_{\text{SnS}}^2 - A_2 N_{\text{SnS}}^3 - \text{Log } N_{\text{FeS}}} \quad (39)$$

where  $\Delta S_{f_{\text{FeS}}}^0 = 5.26$  and  $T_f = 1468^\circ\text{K}$  for the FeS-rich side.

Substituting (37) for  $\text{Log } \gamma_{\text{SnS}}$  into (38) yields:

$$T = \frac{\Delta S_{f_{\text{SnS}}}^0 T_{f_{\text{SnS}}} / R + (B_1 + 3/2 B_2 - B_2 N_{\text{FeS}}) N_{\text{FeS}}^2}{\Delta S_{f_{\text{SnS}}}^0 / R - \text{Log } N_{\text{SnS}} - (A_1 + 3/2 A_2 - A_2 N_{\text{FeS}}) N_{\text{FeS}}^2} \quad (40)$$

where  $\Delta S_{f_{\text{SnS}}}^0 = 8.51$  and  $T_f = 1143^\circ\text{K}$  for the SnS-rich side.

Solving both (39) and (40) for T at different  $N_i$ , the liquidus line could be found. The results are listed in Table XVI.

Table XVI

SnS - FeS System . Sub-regular Solution Model

FeS-rich side.

wt% SnS	$N_{\text{SnS}}$	Temp. , °K	Temp. , °C
10	0.06085	1423.16	1150.16
20	0.12724	1388.67	1115.67
30	0.19995	1346.95	1073.95
40	0.27993	1302.14	1029.14
50	0.36835	1254.22	981.22
60	0.46659	1202.97	929.97
70	0.57639	1148.05	875.05
80	0.69993	1089.11	816.11
90	0.83996	1025.75	752.75

SnS-rich side.

95	0.91722	580.70	307.70
90	0.83996	789.28	516.28
85	0.76768	837.32	564.32
80	0.69993	869.95	596.95
75	0.63629	897.86	624.86

Comparing these with the experimental values of Haan, it can be seen that the fit to the liquidus line on the FeS-rich side is fairly good, but the values obtained for the SnS-rich side are completely wrong. Logically, this is not possible. A four-parameter equation should give a better fit than a one-parameter model.

This error must be attributed to the round-off system of the computer applied to the calculation of the four constants  $A_1$ ,  $A_2$ ,  $B_1$ , and  $B_2$ .

The PDP-10 computer in use at C.S.I. carries seven significant digits, and some coefficients (Table XV) in the four equations of the form (36) are significant only in the eighth place. As a consequence they are rounded-off to zero by the computer and incorrect values of T are found.

White<sup>(53)</sup> encountered the same problems while fitting solution models with more than four parameters to some well known systems.

This a drawback in the use of the computer. Computer calculations are applied to these models because they represent time savings and avoid complications, but in cases such as the present one the results can sometimes be in error.

3.6 Possibility of Complex Formation. The question arose whether iron could form a volatile complex with Sn and S, which would cause a greater weight loss than that due to SnS alone.

Analyses on two condensates were made; the condensates were the product of tests run on the 18.03%FeS mattes. The results for the iron concentration in the condensates are as follows:

Cond. 1	0.011% Fe
Cond. 2	0.028% Fe .

The very low Fe contents in the condensate indicate that any weight loss in the residue from iron volatilization can be neglected without introducing a significant error to the present results. It shows that Fe-Sn-S complex formation is improbable.

## VII PRACTICAL APPLICATION

The SnS vapor pressure over Sn - Fe liquid mattes may be evaluated as a function of composition at various temperatures as follows:

$$p_{\text{SnS}} = (\gamma_{\text{SnS}} N_{\text{SnS}}) p_{\text{SnS}}^0 \quad (41)$$

It was found that the vapor pressure of SnS over pure liquid SnS is represented by:

$$\text{Log } p_{\text{SnS}}^0 = - \frac{8876.3}{T} + 5.80 \text{ atm (Table IX) ,} \quad (42)$$

and the activity coefficient can be approximated by:

$$\text{Log } \gamma_{\text{SnS}} = \frac{260.8}{T} N_{\text{FeS}}^2 \quad (43)$$

Therefore, applying logarithms to both sides in equation (41), and substituting (42) and (43) into it yields:

$$\text{Log } p_{\text{SnS}} = - \frac{8876.3}{T} + 5.80 + \text{Log } N_{\text{SnS}} + \frac{260.8}{T} N_{\text{FeS}}^2 . \quad (44)$$

This equation can now be evaluated as a function of composition and temperature. The results of this evaluation are shown in Fig. 34 (Numerical results are tabulated in Appendix VIII).

The results show a sharp increase in vapor pressure for SnS contents in dilute mattes, increasing less sharply with SnS content.

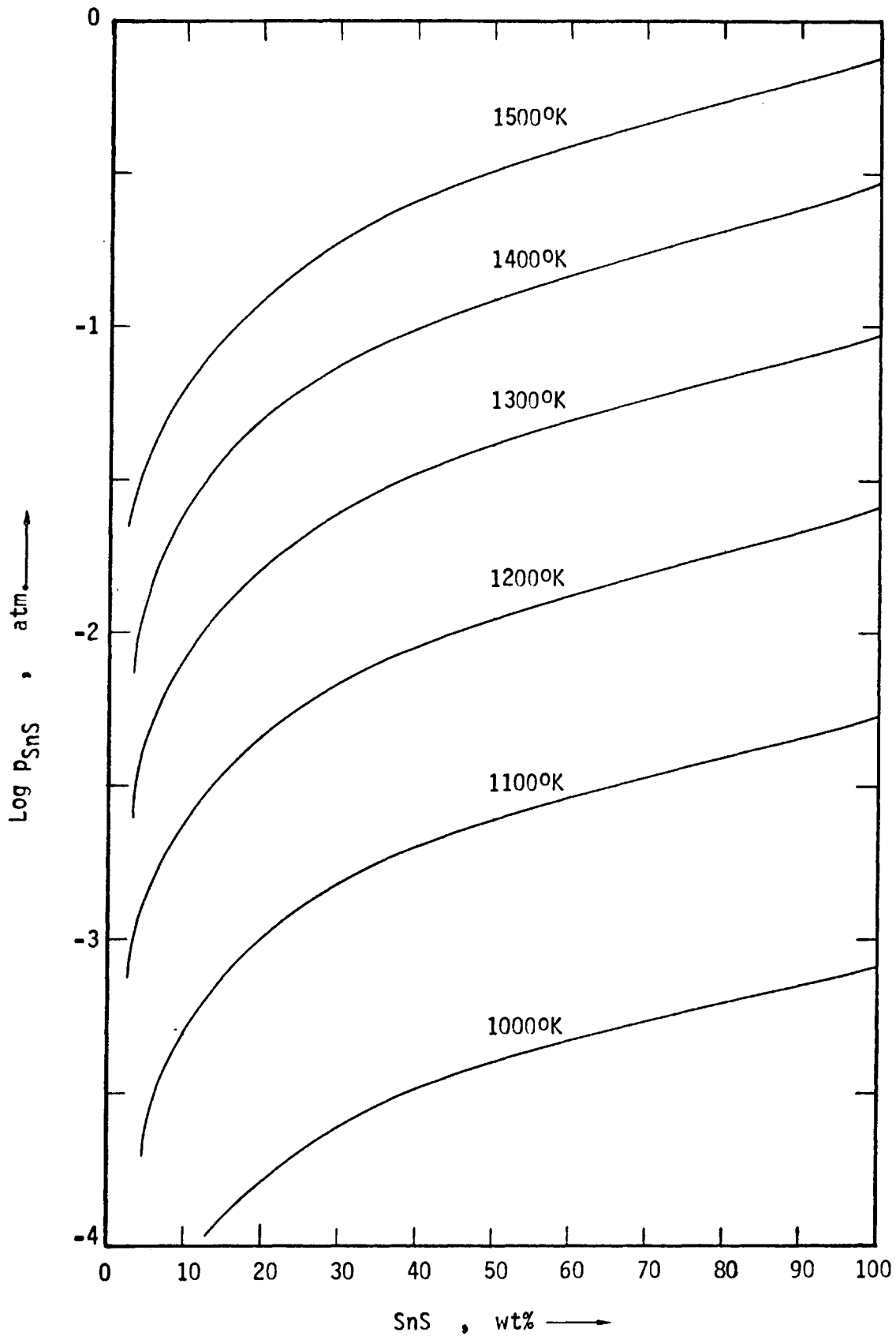


FIG. 34 VAPOR PRESSURE OF SnS(g) IN TiN - IRON MATTES AS A FUNCTION OF COMPOSITION AND TEMPERATURE.

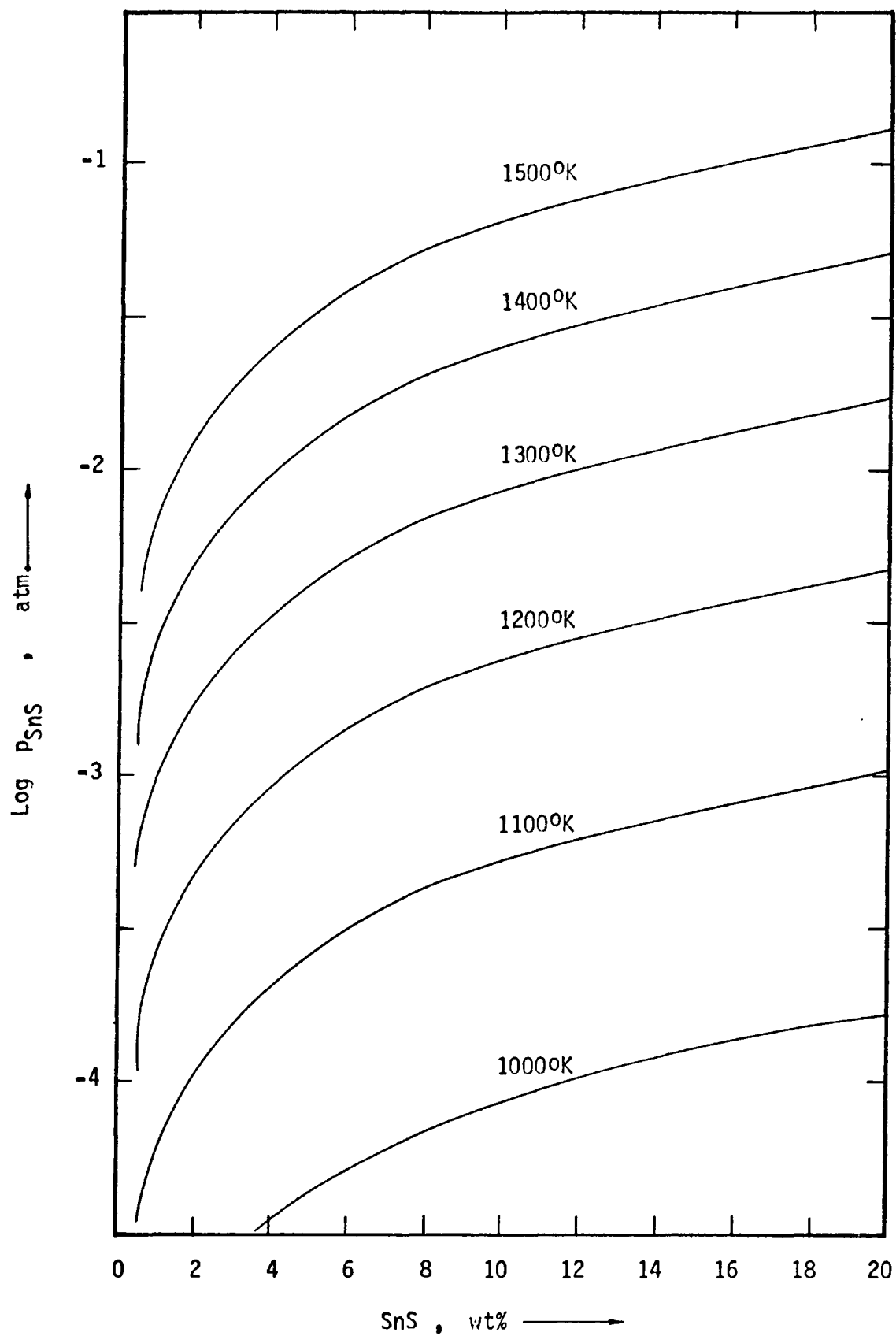


FIG. 35 VAPOR PRESSURE OF SnS IN TIN - IRON MATTES. EXTENDED SCALE FOR MATTES OCCURRING IN PRACTICE.

Since mattes contain up to about 20% SnS in practice, it is more appropriate to restrict the pressure vs. composition plots within, say 1% to 20% SnS. Figure 35 shows these evaluations for the same range of temperatures as before (Appendix VIII also contains these values tabulated).

Here, the dependence of vapor pressure upon composition and temperature is more noticeable since the scale has been reduced five times. This type of plot is useful because the quantity of carrier gas required to volatilize SnS from mattes can be estimated therefrom. This can be done by integrating the area under a curve at a particular temperature within the required limits, assuming that the gas is saturated with the SnS vapors.

Since a mathematical integration would lead to a complicated function, this estimation can be effected by integrating small sections of this curve under the assumption that  $p_{\text{SnS}}$  is constant over a small concentration range, and the total carrier gas required will be the sum of all these integrations.

A simple computer program was developed to calculate the theoretical volume of carrier gas required to fume tin from 1 ton of Fe - Sn matte containing initially S% Sn to a final matte containing J% Sn. The program calculates also the volume of oil required to be burnt to provide this carrier gas. The complete development of the program, and the results for a 15% Sn- and a 10% Sn-matte are given in Appendix VIII. The overall results are given in table XVII. Figure 36 shows graphically the variation of the required carrier gas as the temperature is increased, for two different mattes, removing the tin down to two different final compositions in both cases.

Figure 37 shows the oil required to be burnt as for Fig. 36.

The higher the temperature, the faster the fuming operation because the volume of gas required is less.

The highest temperature achieved during fuming operations (2-3 hrs per batch) is about 1300°K in practice.

As a matter of comparison, fuming operations at Oruro, Bolivia, had an oil consumption of 35 lt/hr when treating 2.5 tons of matte with 15% SnS at about 1325°K in 24 hours, to a final matte of about 0.7%Sn<sup>(54)</sup>. This amounts to 336 lt of oil per ton of matte. The extrapolated value from Fig. 37 gives for

Table XVII

Fuming SnS from Sn - Fe Mattes.

INITIAL % SnS	FINAL %SnS	TEMPERATURE °K	CARRIER GAS REQ'D. m <sup>3</sup>	OIL REQ'D. lt
10	1	1100	269,535.0	5411.97
		1200	65,162.0	1199.35
		1300	19,679.1	334.34
		1400	7,048.0	111.19
		1500	2,869.5	42.25
10	5	1100	86,766.4	1742.17
		1200	20,915.5	384.96
		1300	6,289.3	106.86
		1400	2,233.4	35.23
		1500	892.5	13.14
15	1	1100	325,023.0	6526.10
		1200	78,475.2	1444.39
		1300	23,654.8	401.89
		1400	8,440.5	133.16
		1500	3,408.9	50.19
15	5	1100	142,254.0	2856.31
		1200	34,228.7	630.00
		1300	10,265.1	174.40
		1400	3,625.9	57.20
		1500	1,431.9	21.08

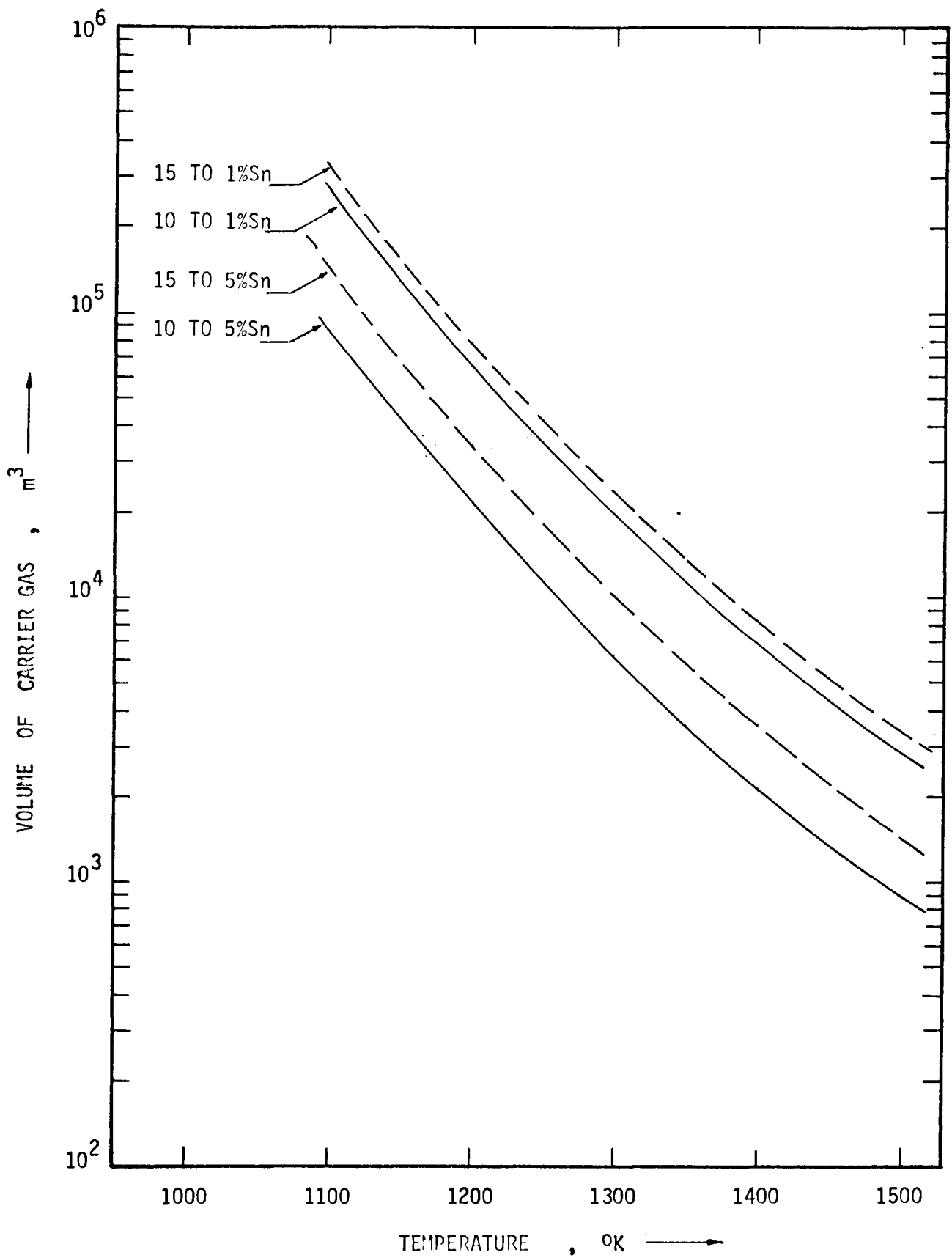


FIG. 36 THEORETICAL VOLUME OF CARRIER GAS REQUIRED TO FUME SnS FROM ONE TON OF Sn - Fe MATTE.

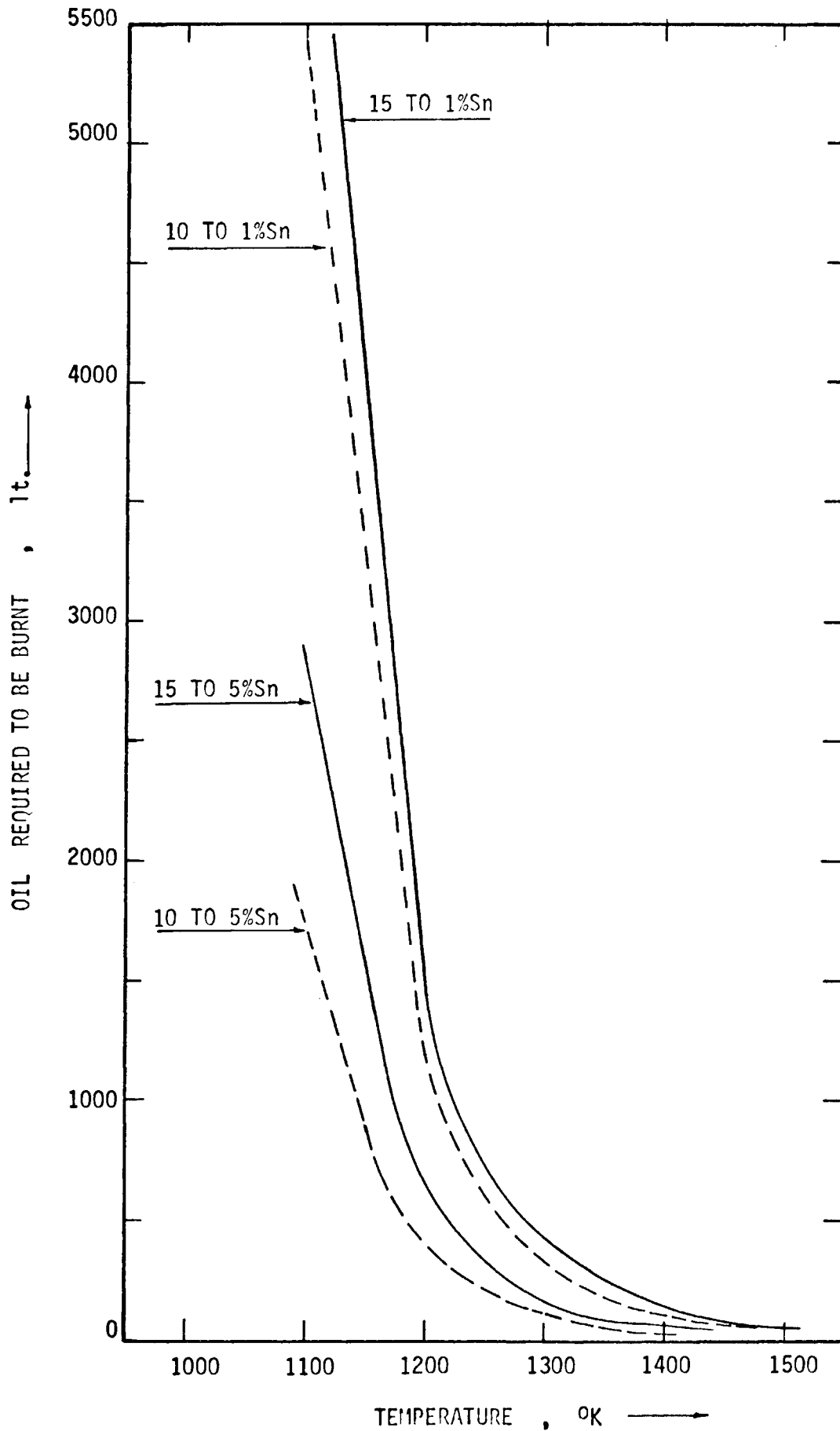


FIG. 37 THEORETICAL VOLUME OF OIL REQUIRED TO BE BURNT TO PROVIDE CARRIER GAS AS IN FIG. 36.

the 15%Sn - matte an oil consumption of 320 lt/ton when removing Sn to a final content of 1% in matte; and 80 lt/ton when removing only 10%Sn , leaving 5% Sn in the matte.

The calculated value of 320 lt/ton compares fairly well with the value of the practice, 336 lt/ton, so it can be assumed that the flue gases are 95% saturated with SnS vapor (320 lt/ton were calculated assuming complete saturation).

If the operating temperature is increased in practice, say to 1400°K, the residence time of the charge will decrease (vaporization will be faster), the oil consumption would decrease (from about 320 lt/ton at 1325°K) to about 133.2 lt/ton. This would correspond to:

$$\frac{133.2 \cdot 2.5 \text{ ton}}{0.95} = 350.53 \text{ lt.}$$

Approximately 117 lt/hr in a 3-hr batch.

Therefore it would appear advantageous to increase the fuming operating temperatures up to about 1500°K (1227°C) provided maintenance costs do not increase too much.

## VIII CONCLUSIONS

The conclusions derived from the present investigation are:

1. When measuring the vapor pressure of sulfides, it is usually advisable to use a carrier gas capable of controlling the sulfur potential in the reaction chamber, and so prevent decomposition of the sulfide, leading to too high an apparent vapor pressure. In the case of SnS vapor over solid or liquid tin sulfide or tin-iron mattes, the decomposition that would occur with an inert gas has been calculated to be negligibly small at the temperatures of the experiments, although visible deposits of sulfur appeared in the condenser.

The difference between the earlier (too high) determinations using  $H_2$  as the carrier gas, and the later determinations, with a modified reaction chamber and  $H_2S/H_2$  carrier gas, must be attributed entirely to the change in the chamber geometry.

This confirms the statement of Alcock and Hooper<sup>(46)</sup> that the geometry of the reaction chamber is extremely important for an accurate determination of vapor pressure by means of the transportation method.

2. The equilibrium vapor pressure of SnS over pure  $SnS_{(c)}$ , in the temperature range  $\sim 970 - 1143^{\circ}K$  can be represented by the equation:

$$\text{Log } p_{SnS}^o = - \frac{11,003}{T} + 7.66 \quad (\text{atm}),$$

and the equilibrium vapor pressure of SnS over pure  $SnS_{(l)}$ , in the temperature range  $1143 - 1500^{\circ}K$  can be represented by the equation:

$$\text{Log } p_{\text{SnS}}^0 = - \frac{8,876.3}{T} + 5.80 \quad (\text{atm}),$$

as determined by means of the transportation method.

3. The free energies of sublimation and vaporization of  $\text{SnS}_{(c,l)}$  can be represented by the following equations respectively:

$$\Delta G_S^0 = - 35.04 T + 50,336 \quad (\text{cal/mole})$$

$$\Delta G_V^0 = - 26.52 T + 40,610 \quad (\text{cal/mole})$$

4. The enthalpies of sublimation, vaporization, and fusion of pure  $\text{SnS}$  estimated from vapor pressure measurements are respectively:

$$\Delta H_S^0 = 50,336 \quad \text{cal/mole}$$

$$\Delta H_V^0 = 40,609 \quad \text{cal/mole}$$

$$\Delta H_f^0 = 9,727 \quad \text{cal/mole}$$

The entropy of fusion of  $\text{SnS}$  as estimated therefrom is:

$$\Delta S_f^0 = 8.51 \text{ e.u.}$$

5. The liquid solution of  $\text{SnS}$  and  $\text{FeS}$  exhibits behavior close to regularity. It can be represented by:

$$\text{Log } \gamma_{\text{SnS}} = \frac{260.8}{T} N_{\text{FeS}}^2,$$

and

$$\text{Log } \gamma_{\text{FeS}} = \frac{260.8}{T} N_{\text{SnS}}^2$$

6. The excess free energy of mixing in the binary system SnS - FeS can be represented by:

$$\Delta G^{XS} = 1193.2 N_{SnS} N_{FeS} = \Delta H^M \quad , \text{ cal/mole .}$$

7. The activities of both SnS and FeS in the liquid mattes calculated from the regular solution model show fairly small positive departures from ideality (Raoult's law). These departures slowly decrease with increasing temperature.
8. The amount of carrier gas and the oil required to be burnt to provide this gas to fume SnS from mattes containing S% Sn initially, to a final matte containing J% Sn , at different temperatures, can be estimated from the vapor pressure measurements performed in this work by use of a simple computer program (OILREQ) which, when the actual conditions of a plant and the costs of the various items are added, can be easily transformed into an Optimization Program.

## IX SUGGESTIONS FOR FURTHER WORK

Since the volatilization process for the recovery of tin, not only from slags and mattes but also from low grade ores, is acquiring increasing importance in the tin industry, it is necessary to provide a more adequate knowledge of the SnS-FeS system.

The only experimental data available are those given by Haan<sup>(8)</sup> in 1913. It is therefore suggested that a new experimental determination of this system should be carried out, to confirm Haan's data or to give a better approximation to the true values of the phase diagram boundary.

The thermodynamic properties derived therefrom should be compared with the values obtained in this work, and it would be established whether the new values agree or disagree with the present ones.

This work represents one of the first experimental attempts to give an account of the behavior of the Fe-Sn mattes, and as such it might have many defects.

It is also suggested that - based on the accurate SnS vapor pressure determinations over pure SnS<sub>(c,1)</sub> in this work - more determinations on the mattes, expanding the composition and temperature ranges considered in the present investigation, should be carried out by means of the same or other techniques.

This determinations would then be compared with other data.

A C K N O W L E D G E M E N T S

This work has been conducted under the direction of Dr. T.R.A. Davey and Dr. A.W. Schlechten.

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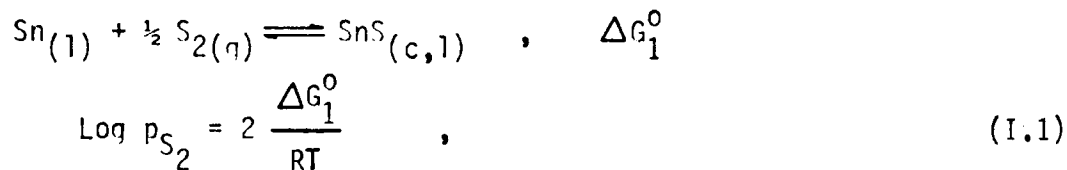
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APPENDIX I

Calculations of Vapor Pressures in the System Sn - S

Free energy of vaporization and related equilibria taken from Table III (Ch. III). All free energy values are given in cal/mole.

1. Equilibrium Sn(l) - SnS(c,l)

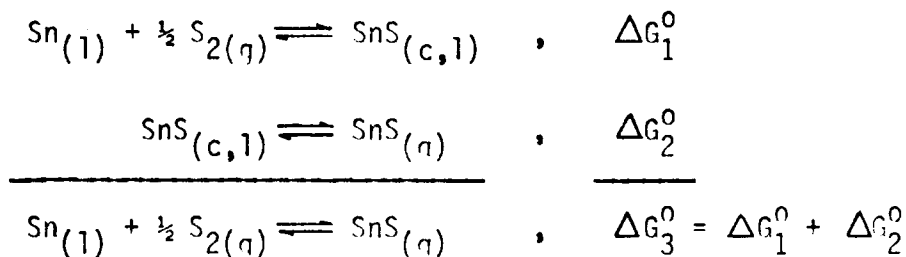


where;

$$\Delta G_1^0 = 24.793T - 43,704 \quad \text{for } 1000 \text{ and } 1100^\circ\text{K}$$

$$\Delta G_1^0 = 14.609T - 32,042 \quad \text{for } 1400 \text{ and } 1500^\circ\text{K}$$

2. Equilibrium SnS(\eta) - Sn(l)



Thus,

$$\text{Log } p_{\text{SnS}(\eta)} = \frac{-\Delta G_3^0}{RT} + \frac{1}{2} \text{Log } p_{\text{S}_2(\eta)} \quad , \quad (I.2)$$

where;

$$\Delta G_3^0 = -10.564T + 6,967 \quad \text{for } 1000 - 1100^\circ\text{K} \quad .$$

$$\Delta G_3^0 = -11.503T + 8,060 \quad \text{for } 1400 - 1500^\circ\text{K} \quad .$$

3. Equilibrium SnS(c,l) - SnS(g)

$$\begin{aligned} \text{SnS}_{(c,l)} &\rightleftharpoons \text{SnS}_{(g)} & , & \quad \Delta G_2^0 \\ \therefore \text{Log } p_{\text{SnS}(g)} &= - \frac{\Delta G_2^0}{R T} & . & \quad (I.3) \end{aligned}$$

For which:

$$\Delta G_2^0 = - 35.357T + 50,671 \quad \text{for } 1000 \text{ and } 1100^{\circ}\text{K}$$

$$\Delta G_2^0 = - 26.113T + 40,102 \quad \text{for } 1400 \text{ and } 1500^{\circ}\text{K}.$$

4. Equilibrium Sn(l) - Sn<sub>2</sub>S<sub>2</sub>(g)

$$\begin{aligned} 2\text{Sn}_{(l)} + \text{S}_{2(g)} &\rightleftharpoons 2\text{SnS}_{(c,l)} & , & \quad 2 \Delta G_1^0 \\ \underline{2\text{SnS}_{(c,l)} &\rightleftharpoons 2 \text{SnS}_{(g)} & , & \quad 2 \Delta G_2^0} \\ 2\text{Sn}_{(l)} + \text{S}_{2(g)} &\rightleftharpoons 2\text{SnS}_{(g)} & , & \quad 2 \Delta G_3^0 \\ \underline{2\text{SnS}_{(g)} &\rightleftharpoons \text{Sn}_2\text{S}_2(g) & , & \quad \Delta G_4^0} \\ 2\text{Sn}_{(l)} + \text{S}_{2(g)} &\rightleftharpoons \text{Sn}_2\text{S}_2(g) & , & \quad \Delta G_5^0 = 2\Delta G_3^0 + \Delta G_4^0 \end{aligned}$$

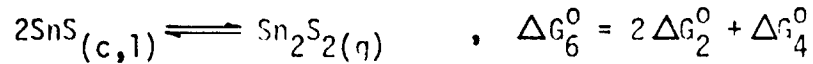
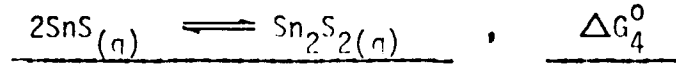
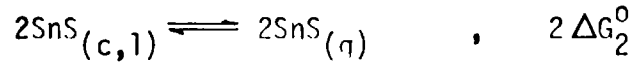
Thus,

$$\text{Log } p_{\text{Sn}_2\text{S}_2(g)} = - \frac{\Delta G_5^0}{R T} + \text{Log } p_{\text{S}_{2(g)}} \quad , \quad (I.4)$$

where:

$$\Delta G_5^0 = 16.831T - 32,954 \quad \text{for } 1000 \text{ and } 1100^{\circ}\text{K}$$

$$\Delta G_5^0 = 14.953T - 30,768 \quad \text{for } 1400 \text{ and } 1500^{\circ}\text{K}.$$

5. Equilibrium SnS(c,l) - Sn<sub>2</sub>S<sub>2</sub>(g)

$$\therefore \quad \text{Log } p_{\text{Sn}_2\text{S}_2(g)} = - \frac{\Delta G_6^0}{R T} \quad , \quad (I.5)$$

where:

$$\Delta G_6^0 = - 32.754T + 54,454 \quad \text{for } 1000 \text{ and } 1100^\circ\text{K}$$

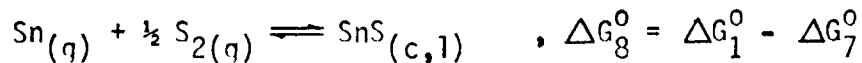
$$\Delta G_6^0 = - 14.265T + 33,315 \quad \text{for } 1400 \text{ and } 1500^\circ\text{K}$$

6. Equilibrium Sn(l) - Sn(g)

$$\text{Log } p_{\text{Sn}(g)} = - \frac{\Delta G_7^0}{R T} \quad (I.6)$$

where

$$\Delta G_7^0 = - 23.830T + 70,109 \quad \text{from } 1000 \text{ to } 1500^\circ\text{K} .$$

7. Equilibrium SnS(c,l) - Sn(g)

$$\therefore \quad \text{Log } p_{\text{Sn}(g)} = \frac{\Delta G_8^0}{R T} - \frac{1}{2} \text{Log } p_{\text{S}_2(g)} \quad (I.7)$$

where:

$$\Delta G_8^0 = 48.623T - 113,813 \quad \text{for } 1000 \text{ and } 1500^\circ\text{K}$$

$$\Delta G_8^0 = 38.439T - 102,151 \quad \text{for } 1000 \text{ and } 1500^\circ\text{K}.$$

The calculated equilibrium pressures (from I.1 to I.7) are given in table I.1, from which Figs. 3 and 4 (Chapter III) were obtained.

Appendix I. Table I.1Vapor Pressures in the System Sn - S

TEMPERATURE °K	EQUILIBRIUM No.	Phases	Log $p_{S_2(\eta)}$ , atm	Log $p_{i(\eta)}$ , atm i = gaseous phase
1000 ↓	1	Sn(l)-SnS(c)	- 8.267	-
	2	SnS( $\eta$ )-Sn(l)	-11.000	- 4.71
			- 9.000	- 3.71
	3	SnS(c)-SnS( $\eta$ )	-	- 3.35
	4	Sn(l)-Sn <sub>2</sub> S <sub>2</sub> ( $\eta$ )	-11.000	- 7.48
			- 9.000	- 5.48
	5	SnS(c)-Sn <sub>2</sub> S <sub>2</sub> ( $\eta$ )	-	- 4.74
6	Sn(l)-Sn( $\eta$ )	-	-10.116	
7	SnS(c)-SnS( $\eta$ )	- 6.000	-11.25	
		- 4.000	-12.25	
1100 ↓	1	Sn(l)-SnS(c)	- 6.53	-
	2	SnS( $\eta$ )-Sn(l)	-11.00	- 4.60
			- 8.00	- 3.10
	3	SnS(c)-SnS( $\eta$ )	-	- 2.34
	4	Sn(l)-Sn <sub>2</sub> S <sub>2</sub> ( $\eta$ )	-11.00	- 8.13
			- 8.00	- 5.13
	5	SnS(c)-Sn <sub>2</sub> S <sub>2</sub> ( $\eta$ )	-	- 3.66
6	Sn(l)-Sn( $\eta$ )	-	- 8.72	
7	SnS(c)-Sn( $\eta$ )	- 6.00	- 8.99	
		- 4.00	- 9.99	

Appendix I. Table I.1 - Continued

TEMPERATURE OK	EQUILIBRIUM No.	Phases	Log $p_{S_2(\eta)}$ , atm	Log $p_{i(\eta)}$ , atm i = gaseous phase
1400 ↓	1	Sn(1)-SnS(1)	- 3.619	-
	2	SnS( $\eta$ )-Sn(1)	- 9.000	- 3.240
			- 5.000	- 1.240
	3	SnS(1)-SnS( $\eta$ )	-	- 0.553
	4	Sn(1)-Sn <sub>2</sub> S <sub>2</sub> ( $\eta$ )	- 8.000	- 6.460
			- 5.000	- 3.460
	5	SnS(1)-Sn <sub>2</sub> S <sub>2</sub> ( $\eta$ )	-	- 2.083
6	Sn(1)-Sn( $\eta$ )	-	- 5.737	
7	SnS(1)-Sn( $\eta$ )	- 3.000	- 6.050	
			- 1.000	- 7.05
1500 ↓	1	Sn(1)-SnS(1)	- 2.952	-
	2	SnS( $\eta$ )-SnS(1)	- 9.000	- 3.160
			- 5.000	- 1.160
	3	SnS(1)-SnS( $\eta$ )	-	- 0.136
	4	Sn(1)-Sn <sub>2</sub> S <sub>2</sub> ( $\eta$ )	- 8.000	- 6.780
			- 5.000	- 3.780
	5	SnS(1)-Sn <sub>2</sub> S <sub>2</sub> ( $\eta$ )	-	- 1.740
6	Sn(1)-Sn( $\eta$ )	-	- 5.007	
7	SnS(1)-Sn( $\eta$ )	- 1.000	- 5.980	
			0.000	- 6.480

## Appendix I - Continued

Effective Total Pressure in the Sn - S System as a Function of  $p_{S_2(\eta)}$

The effective total pressure of tin in this system is given by the following expression:

$$p_{T(\text{SnS})} = p_{\text{Sn}(\eta)} + p_{\text{SnS}(\eta)} + 2 p_{\text{Sn}_2\text{S}_2(\eta)}$$

or,

$$\text{Log } p_{T(\text{SnS})} = \text{Log } p_{\text{Sn}(\eta)} + p_{\text{SnS}(\eta)} + 2 p_{\text{Sn}_2\text{S}_2(\eta)} \quad \cdot$$

Values of  $p_T$  are given in Table I.2 along with respective values from previous calculations. It can be seen that the difference between  $p_{T(\text{SnS})}$  and  $p_{\text{SnS}(\eta)}$  is in all cases very small.

Partial Pressures of Gaseous Species in the System Sn - S Over Pure  $\text{SnS}_{(c,1)}$

The partial pressures of gaseous species over pure  $\text{SnS}_{(c,1)}$ , that is; the values which are independent of sulfur pressure (to the right of equil. line Sn(l)-SnS(c,1) in Figs. 3, 4, and 5; chapter III), are obtained from equil. equations (I.3), (I.5), and (I.7) in this appendix. They are given in table I.3 for various temperatures (Fig. 6, chapter III).

Appendix I. Table I.2

Effective Total Pressure in System Sn - S as a Function of  $P_{S_2}(\eta)$ 

TEMP. OK	Log $P_{S_2}(\eta)$	$P_{Sn}(\eta)$	$P_{SnS}(\eta)$	atm		$P_T(SnS)$	Log $P_T(SnS)$
				Log $P_{SnS}(\eta)$	$P_{Sn_2S_2}(\eta)$		
1000	- 11.0	$7.66 \cdot 10^{-11}$	$1.95 \cdot 10^{-5}$	- 4.71	$3.312 \cdot 10^{-8}$	$1.956 \cdot 10^{-5}$	- 4.7086
	- 9.0	$7.66 \cdot 10^{-11}$	$1.95 \cdot 10^{-4}$	- 3.71	$3.312 \cdot 10^{-6}$	$2.016 \cdot 10^{-4}$	- 3.6955
	- 7.0	$1.8 \cdot 10^{-11}$	$4.47 \cdot 10^{-4}$	- 3.35	$1.82 \cdot 10^{-5}$	$4.83 \cdot 10^{-4}$	- 3.316
	- 4.0	$5.6 \cdot 10^{-13}$	$4.47 \cdot 10^{-4}$	- 3.35	$1.82 \cdot 10^{-5}$	$4.83 \cdot 10^{-4}$	- 3.316
1100	- 11.0	$1.9 \cdot 10^{-9}$	$2.5 \cdot 10^{-5}$	- 4.60	$7.40 \cdot 10^{-9}$	$2.50 \cdot 10^{-5}$	- 4.602
	- 9.0	$1.9 \cdot 10^{-9}$	$2.5 \cdot 10^{-4}$	- 3.60	$7.40 \cdot 10^{-7}$	$2.51 \cdot 10^{-4}$	- 3.600
	- 6.0	$1.02 \cdot 10^{-9}$	$4.6 \cdot 10^{-3}$	- 2.34	$2.20 \cdot 10^{-4}$	$5.04 \cdot 10^{-3}$	- 2.298
	- 4.0	$1.02 \cdot 10^{-10}$	$4.6 \cdot 10^{-3}$	- 2.34	$2.20 \cdot 10^{-4}$	$5.04 \cdot 10^{-3}$	- 2.998
1400	- 9.0	$1.80 \cdot 10^{-6}$	$5.75 \cdot 10^{-4}$	- 3.24	$3.47 \cdot 10^{-8}$	$5.77 \cdot 10^{-4}$	- 3.239
	- 5.0	$1.80 \cdot 10^{-6}$	$5.75 \cdot 10^{-2}$	- 1.24	$3.47 \cdot 10^{-4}$	$5.80 \cdot 10^{-2}$	- 1.236
	- 3.0	$8.90 \cdot 10^{-7}$	$2.8 \cdot 10^{-1}$	- 0.55	$8.26 \cdot 10^{-3}$	$2.97 \cdot 10^{-1}$	- 0.530
	0.0	$2.80 \cdot 10^{-8}$	$2.8 \cdot 10^{-1}$	- 0.55	$8.26 \cdot 10^{-3}$	$2.97 \cdot 10^{-1}$	- 0.530
1500	- 9.0	$9.86 \cdot 10^{-6}$	$6.92 \cdot 10^{-4}$	- 3.15	$1.66 \cdot 10^{-8}$	$7.02 \cdot 10^{-4}$	- 3.154
	- 5.0	$9.84 \cdot 10^{-6}$	$6.92 \cdot 10^{-2}$	- 1.16	$1.66 \cdot 10^{-4}$	$6.90 \cdot 10^{-2}$	- 1.160
	- 1.0	$1.05 \cdot 10^{-6}$	$7.30 \cdot 10^{-1}$	- 0.14	$1.82 \cdot 10^{-2}$	$7.66 \cdot 10^{-1}$	- 0.120
	0.0	$3.3 \cdot 10^{-7}$	$7.30 \cdot 10^{-1}$	- 0.14	$1.82 \cdot 10^{-2}$	$7.66 \cdot 10^{-1}$	- 0.120

Appendix I. Table I.3Total and Partial Pressures of Vapor Species Over Pure SnS<sub>(c,l)</sub>

TEMPERATURE °K	$10^4/T$	Log $p_{\text{Sn}}$	Log $p_{\text{SnS}}$	Log $p_{\text{Sn}_2\text{S}_2}$	Log $p_{\text{T}}(\text{SnS})$
		←————— atm —————→			
1000	10.0	- 10.12	- 3.35	- 4.74	- 3.31
1100	9.09	- 8.72	- 2.34	- 3.66	- 2.30
1200	8.33	- 7.56	- 1.60	- 2.95	- 1.56
1300	7.69	- 6.58	- 1.03	- 2.48	- 1.00
1400	7.14	- 5.74	- 0.55	- 2.08	- 0.53
1500	6.70	- 5.00	- 0.13	- 1.73	- 0.12

## Appendix II

### Calculation of the SnS-FeS Phase Diagram

The SnS-FeS phase diagram, as obtained by Haan<sup>(8)</sup>, shows no solid solubility. To express the properties of the liquid phase of this system in terms of the properties of the pure components, such as their melting points, and a known property of the mixture (the eutectic temperature and composition) a solution model can be assumed.

The simplest model would be that of an ideal solution. Empirically, very few solutions approach ideality, but many miscibility gap systems in addition to simple complete-solution systems, like the SnS-FeS system, are consistent with the regular solution model, which is characterized by a non-zero enthalpy of solution and an ideal entropy of mixing corresponding to perfect random mixing.

Therefore, this phase diagram is calculated assuming that the liquid phase behaves as a regular solution and that there is no solid solubility.

#### Data.

SnS melting temperature,  $T_f = 1143^\circ\text{K}$  ( $870^\circ\text{C}$ ),

FeS " " " ,  $T_f = 1468^\circ\text{K}$  ( $1195^\circ\text{C}$ ),

Eutectic temperature,  $T_e = 1058^\circ\text{K}$  ( $785^\circ\text{C}$ ) at 15% FeS (in weight).

$\Delta H_f^0(\text{FeS}) = 7730 \text{ cal/mole}$  ,  $\Delta S_f^0(\text{FeS}) = 5.26 \text{ e.u.}$

Thus,

$$\Delta G_f^0 = \Delta S_f^0 ( T_f - T ) = - R T \text{ Log } a_{\text{FeS}} \quad (\text{II.1})$$

This system can be represented by:

$$\text{Log } \gamma_{\text{FeS}} = \frac{B}{T} N_{\text{SnS}}^2 \quad , \quad (\text{II.2})$$

where B is the regularity constant.

The FeS activity at the eutectic temperature and composition ( $N_{\text{FeS}} = 0.2323$ ) is:

$$\text{Log } a_{\text{FeS}} = - 0.44555 \quad .$$

And:

$$\text{Log } \gamma_{\text{FeS}} = \text{Log } a_{\text{FeS}} - \text{Log } N_{\text{FeS}} = 0.18837 \quad (\text{II.3})$$

Solving (II.2) for B, and substituting values:

$$B = 338.225 \quad (\text{II.4})$$

Equating (II.1) and (II.3), substituting (II.1) and (II.4) in the resulting equation, and solving it for T, the following expression for the FeS-rich side of the phase diagram results:

$$T = \frac{\Delta S_f^0 T_f + \alpha (1 - N_{\text{FeS}})^2}{\Delta S_f^0 - R \text{Log } N_{\text{FeS}}} \quad (\text{II.5})$$

where:  $\alpha = B \cdot R = 1547.38$

Then, for the SnS-rich side:

$$\text{Log } \gamma_{\text{SnS}} = (338.225/1058)(0.2323)^2 = 0.017254 \quad \text{at } T_{\text{eut.}}$$

then;

$$\text{Log } a_{\text{SnS}} = -0.97556$$

Hence:

$$\Delta S_{f(\text{SnS})}^0 = \frac{\Delta G_{f(\text{SnS})}^0}{T_f - T_e} = 5.56 \text{ e.u.}$$

By analogy with (II.5):

$$T = \frac{\Delta S_f^0 T_f + \alpha (1 - N_{\text{SnS}})^2}{\Delta S_f^0 - R \text{Log } N_{\text{SnS}}} \quad (\text{II.6})$$

Calculated values using equations (II.5) and (II.6) are given in table II.1. The values calculated by Davey<sup>(33)</sup>, and the experimental values obtained by Haan<sup>(8)</sup> are also listed in table II.1.

Appendix II. Table II.1  
Calculated and Experimental (Haan) Values for the SnS - FeS Phase Diagram

CALCULATED (Ref. Sn.)			EXPERIMENTAL (Haan, 1913)				
$N_{FeS}$ FeS-rich side.	wt% FeS	TEMPERATURE, °C Present work	EXPT. No.	wt%SnS	wt%FeS	TEMPERATURE, °C I	TEMPERATURE, °C II
0.273	18.00	-	1	95	5	831	785
0.2323	15.00	785	2	85	15	Nothing	784
0.3	19.99	835	3	80	20	821	785
0.4	27.99	896	4	75	25	846	785
0.5	36.83	949	5	60	40	929	794
0.6	46.66	997	6	50	50	958	760
0.7	57.64	1044	7	40	60	1024	770
0.8	69.99	1092	8	30	70	1070	797
0.9	83.99	1142	9	20	80	not good	796
1.0	100.00	1195	10	10	90	1150	786
$N_{SnS}$ SnS-rich side.	wt% SnS	TEMPERATURE, °C Present work	11	5	95	not good	777
0.727	82.00	-	$T_f^{SnS} = 870^\circ C$				
0.7677	85.00	785	$T_f^{FeS} = 1183^\circ C$				
0.8	87.28	796					
0.9	93.92	831					
1.0	100.00	870					

Note. The calculation of the phase diagram from the experimental values of  $p_{\text{SnS}}$  obtained in this work was the same as this one. The only difference was that it was calculated from the estimated value of  $\Delta H_{\text{fSnS}}^{\circ}$  and the eutectic was not known.

### Estimation of the Vapor Pressure of SnS Over Sn-Fe Mattes

It was assumed that the FeS-SnS system can be represented by:

$$\text{Log } \gamma_{\text{SnS}} = \frac{B}{T} N_{\text{FeS}}^2 \quad (\text{II.7})$$

For the SnS(c,l) - SnS(g) equilibrium:

$$\text{Log } p_{\text{SnS}}^{\circ} = - \frac{\Delta G_{\text{s,v}}^{\circ}}{R T} \quad (\text{II.8})$$

where  $p_{\text{SnS}}^{\circ}$  is the vapor pressure of SnS over pure SnS(c,l), and subscripts s, v stand for sublimation and vaporization respectively.

The partial pressure of SnS in matte is:

$$P_{\text{SnS}} = \gamma_{\text{SnS}} N_{\text{SnS}} p_{\text{SnS}}^{\circ} \quad (\text{II.9})$$

Applying logarithms to both sides in equation (II.9) and substituting (II.7) and (II.8) in the resulting equation:

$$\text{Log } p_{\text{SnS}} = - \frac{\Delta G_{\text{s,v}}^{\circ}}{R T} + \text{Log } N_{\text{SnS}} + 338.225 N_{\text{FeS}}^2 / T \quad (\text{II.10})$$

From table III, Chapter II, the following expressions for  $\Delta G_{\text{s,v}}^{\circ}$  are obtained:

$$\Delta G_{\text{s}}^{\circ} = 50,671 - 35.357 T \quad (800 - 1143^{\circ}\text{K})$$

$$\Delta G_{\text{v}}^{\circ} = 40,102 - 26.113 T \quad (1143 - 1500^{\circ}\text{K}).$$

Figure 8 (Chapter III) was obtained from equation (II.10), for a range of compositions and temperatures.

Appendix IIIMatte Analysis Report

<u>Sample no.</u>	<u>Sn %</u>	<u>Fe %</u>	<u>S %</u>
S - 1	( 68.1 )	3.69	22.3
S - 2	( 63.1 )	9.27	22.5
S - 3	( 45.5 )	11.50	24.4
S - 4	( 45.0 )	15.90	26.4

Calculations.            M.W. SnS = 150.754    ,    M.W. FeS = 87.911

Sample S - 1.

$$\% S \text{ (for 3.69\%Fe)} = (3.69)(32.064)/(55.847) = 2.12$$

$$\therefore 2.12 + 3.69 = 5.81\% \text{ FeS}$$

$$22.3 - 2.12 = 20.18\% \text{ S left.}$$

$$\% \text{ Sn} = (20.18)(118.69)/(32.064) = 74.699$$

$$\text{so, } 20.18 + 74.699 = 94.879\% \text{ SnS.}$$

$$\text{Total: } 100.69\% \text{ Sample.}$$

Sample S - 2.

$$\% S \text{ (for 9.27\%Fe)} = (9.27)(32.064)/(55.847) = 5.3223$$

$$\therefore 9.27 + 5.3223 = 14.5923\% \text{ FeS}$$

$$22.5 - 5.3223 = 17.1777\% \text{ S left.}$$

$$\% \text{ Sn} = (17.1777)(118.69)/(32.064) = 63.586$$

$$\text{so, } 17.1777 + 63.586 = 80.764\% \text{ SnS.}$$

$$\text{Total: } 95.356\% \text{ Sample.}$$

Sample S - 3.

$$\% S \text{ (for 11.5\% Fe)} = (11.5)(32.064)/(55.847) = 6.6026$$

$$\therefore 6.6026 + 11.5 = 18.1026\% \text{ FeS}$$

$$24.4 - 6.6026 = 17.7974\% \text{ S left.}$$

$$\% \text{ Sn} = (17.7974)(118.69)/(32.064) = 65.88$$

so,  $17.7974 + 65.88 = 83.6774\%$  SnS.

Total: 101.7974% Sample.

Sample S - 4.

$$\% \text{ S (for 15.9\% Fe)} = (15.9)(32.064)/(55.847) = 9.129$$

∴  $9.129 + 15.9 = 25.029\%$  FeS

$$26.4 - 9.129 = 17.271\% \text{ S left.}$$

$$\% \text{ Sn} = (17.271)(118.69)/(32.064) = 63.932$$

so,  $17.271 + 63.932 = 81.203\%$  SnS.

Total: 106.232% Sample.

Therefore, considering the difficulty in the analysis of Sn, and the possible error in the analysis of sulfur, the matte composition is taken as follows:

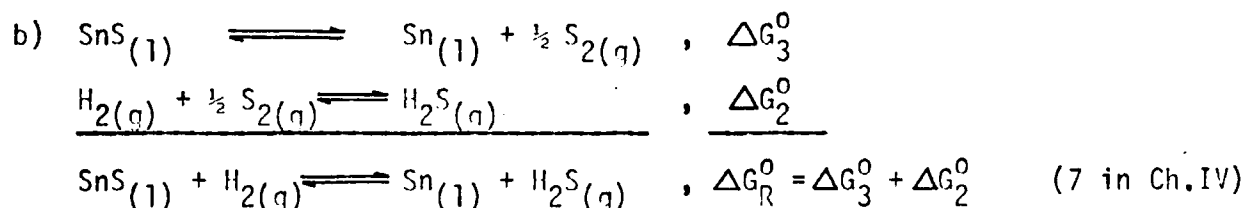
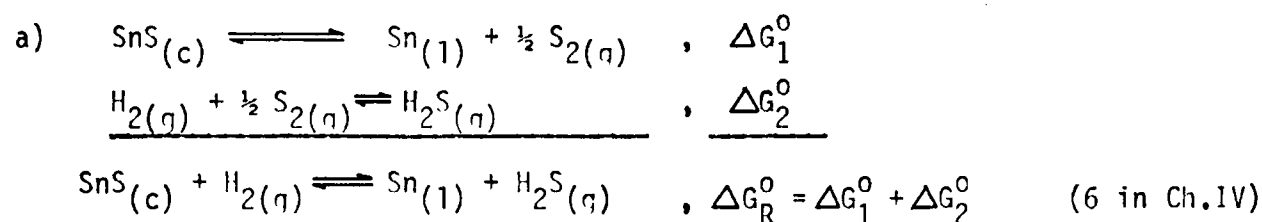
Matte prepared for _____%FeS	Chemical Analysis % FeS	Balance % SnS
6	5.81	94.89
15	14.5923	85.4077
18	18.1026	81.8974
25	25.029	74.971

Appendix IV

Sulfur Potential Control

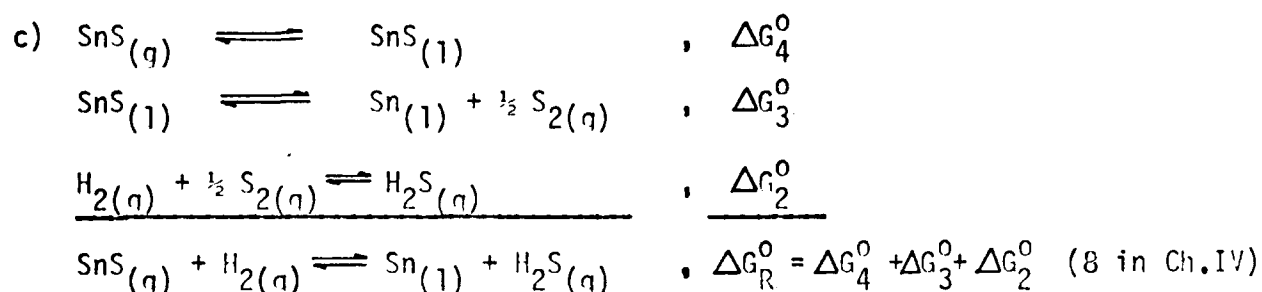
Derivation of the equations involved      See section 2., Chapter IV.

Interaction Between SnS<sub>(c,1)</sub> and H<sub>2</sub>S/H<sub>2</sub> Mixtures. Free energies (in cal/mole) of Sn - S reactions from Table III, Ch. II (Ref. 23). Free energies (in cal/mole) of H - S reactions from Table V, Ch. II (Ref. 1).

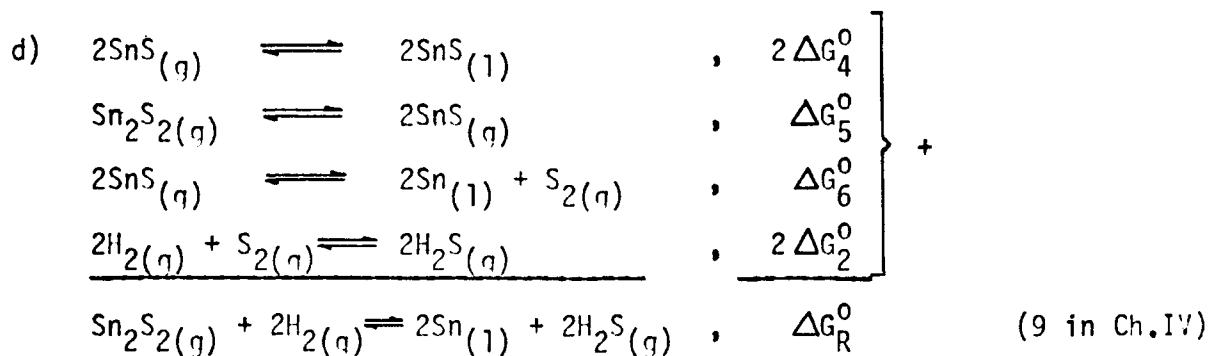


∴ For (6) and (7):

$$\frac{P_{\text{H}_2\text{S}(g)}}{P_{\text{H}_2(g)}} = \exp \left[ \frac{-\Delta G_R^0}{R T} \right] \quad (\text{IV.1})$$

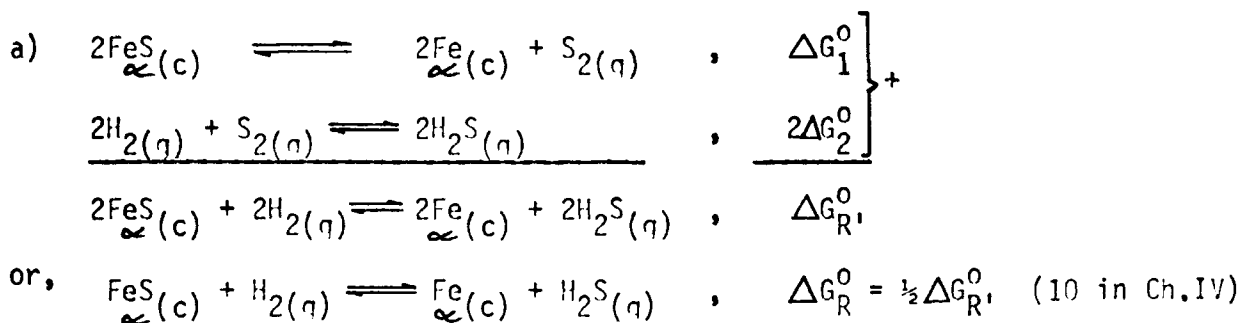


$$\therefore \frac{p_{\text{H}_2\text{S}(\eta)}}{p_{\text{H}_2(\eta)}} = \left( \exp \left[ \frac{-\Delta G_R^0}{R T} \right] \right) \cdot p_{\text{SnS}(\eta)} \quad (\text{IV.2})$$

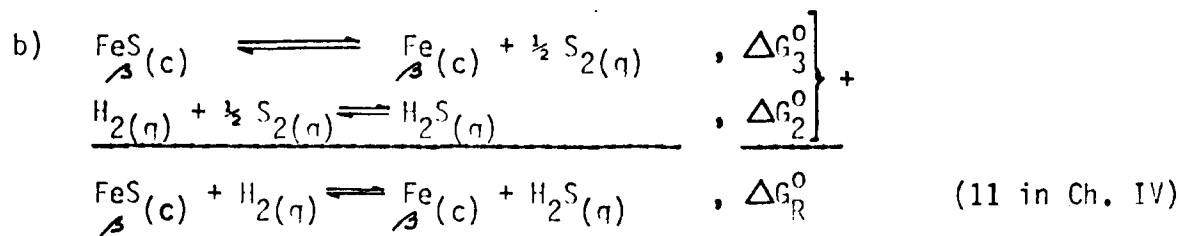


$$\therefore \frac{p_{\text{H}_2\text{S}(\eta)}}{p_{\text{H}_2(\eta)}} = \left[ \left( \exp \left[ \frac{-\Delta G_R^0}{R T} \right] \right) \cdot p_{\text{Sn}_2\text{S}_2(\eta)} \right]^{\frac{1}{2}} \quad (\text{IV.3})$$

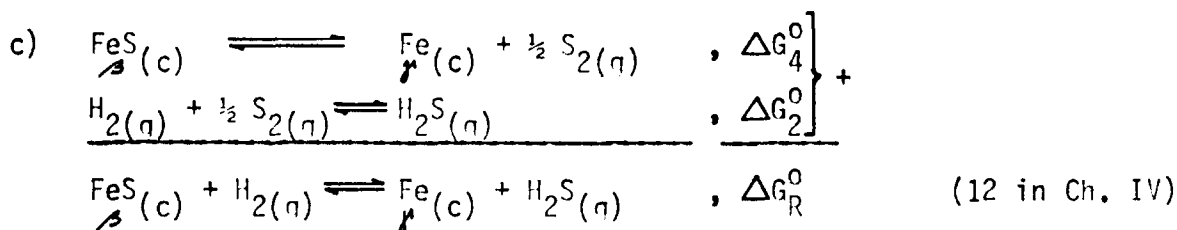
Interaction Between FeS<sub>(c.1)</sub> and H<sub>2</sub>S/H<sub>2</sub> Mixtures. Free energies of the Fe - S, and the H - S reactions from Tables IV and V respectively (Chapter II). All free energy expressions in cal/mole.



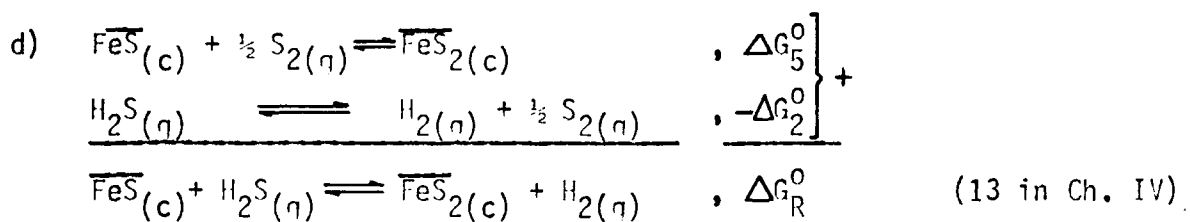
$$\therefore \frac{p_{\text{H}_2\text{S}(\eta)}}{p_{\text{H}_2(\eta)}} = \exp \left[ \frac{-\Delta G_R^0}{R T} \right] \quad (\text{IV.4})$$



and:  $p_{\text{H}_2\text{S}} / p_{\text{H}_2}$  same as (IV.4).



and:  $p_{\text{H}_2\text{S}} / p_{\text{H}_2}$  same as (IV.4).



$$\therefore \frac{p_{\text{H}_2\text{S}(\eta)}}{p_{\text{H}_2(\eta)}} = \exp \left[ - \frac{R T}{\Delta G_R^0} \right] \quad (\text{IV.5}).$$

The respective ratios were calculated from (IV.1) through (IV.5). The results are tabulated in this Appendix. Figure 12 in Chapter IV was obtained from these calculations.

Appendix IV. Table IV.1

SnS - H<sub>2</sub>S/H<sub>2</sub>, and FeS - H<sub>2</sub>S/H<sub>2</sub> Interactions. Sulfur Potential Control.

Equilibrium: SnS <sub>(c,l)</sub> + H <sub>2</sub> (g) ⇌ Sn(l) + H <sub>2</sub> S(g)		Equilibrium: FeS <sub>(c)</sub> + H <sub>2</sub> (g) ⇌ Fe(c) + H <sub>2</sub> S(g)	
TEMPERATURE, °K	ΔG <sub>R</sub> <sup>0</sup> , cal/mole	TEMPERATURE, °K	ΔG <sub>R</sub> <sup>0</sup> , cal/mole
	P <sub>H<sub>2</sub>S</sub> / P <sub>H<sub>2</sub></sub>		P <sub>H<sub>2</sub>S</sub> / P <sub>H<sub>2</sub></sub>
700	13,032.5	360	14,217.4
750	12,383.1	380	14,141.7
800	11,733.7	400	14,066.0
850	11,084.3		
900	10,434.9	500	13,952.5
950	9,785.5	600	13,877.0
1000	9,136.1	800	13,726.0
1050	8,486.7	1000	13,575.0
1100	7,837.1	1100	13,499.5
1150	7,237.0	1185	13,382.0
1200	7,096.8	1200	13,368.0
1250	6,956.6	1230	13,340.0
1300	6,814.4	1245	13,325.9
1350	6,676.2	1260	13,311.9
1400	6,536.0		
1450	6,395.8		

Note. Values for the most important equations are tabulated here. The others were neglected because all lay below the FeS-H<sub>2</sub>S/H<sub>2</sub> equilibrium lines.



Appendix V. Table V.1 - Continued

TEMPERATURE °C	TEST No.	ROOM TEMP. °C	FLOWRATE lt/min	REAC. TIME min	VOLUME lt	WEIGHT gm	LOSS mg/lt
801.4	B1	22.5	0.13260	20	2.65200	0.05328	20.09018
	B2 *	23.0	0.17595	15	2.63925	0.03623	13.72715
	B3 *	23.5	0.08924	15	1.33860	0.02613	19.52044
	B4 *	24.0	0.06750	15	1.01250	0.02003	19.78272
848.0	C1	25.0	0.11800	15	1.77000	0.03870	21.86441
	C2 *	26.0	0.07232	15	1.08500	0.06545	60.32000
	C3 *	26.0	0.08200	15	1.24350	0.07480	60.15300
	C4 *	26.0	0.04722	18	0.84096	0.05360	63.06200

Note. \* Indicates tests used to calculate the average vapor pressure.

Appendix V. Table V.2Experimental Data for the Vapor Pressure Determinations on Pure SnS(c,l)Carrier gas:  $H_2S/H_2$  mixtures - Reaction chamber: no. 2

TEMPERATURE °C	TEST No.	ROOM TEMP. °C	$H_2S/H_2$ RATIO $\cdot 10^2$	FLOWRATE lt/min	REAC.TIME min	VOLUME lt	WEIGHT gm	LOSS mg/lt
856.8	D1	26	4.443	0.06397	30	1.91910	0.0893	46.5320
	D2	27	3.910	0.07232	30	2.16960	0.1225	56.4620
	D3	26	3.258	0.08622	30	2.58660	0.0793	30.6580
	D4 *	25	4.880	0.05842	30	1.75260	0.0861	49.1200
	D5 *	23	6.500	0.04448	30	1.33440	0.0671	50.2840
	D6 *	24	5.400	0.05283	30	1.58490	0.0846	53.3781
	D7 *	24	4.443	0.06397	30	1.91910	0.1055	54.9740
	D8 *	24	4.890	0.02920	30	0.87600	0.0456	52.0540
803.5	E1	29	2.44	0.11412	35	3.9942	0.0552	13.890
	E2	30	3.26	0.08622	35	3.0177	0.0303	10.041
	E3 *	30	3.91	0.07232	40	2.8928	0.0484	16.730
	E4 *	30	3.91	0.07232	40	2.8928	0.0545	18.840
	E5 *	29	4.88	0.05842	40	2.3368	0.0349	14.935
	E6 *	30	6.52	0.04448	40	1.7792	0.0296	16.637
	E7 *	30.5	4.44	0.06397	40	2.5588	0.0428	16.748

Appendix V. Table V.2 - Continued

TEMPERATURE °C	TEST No.	ROOM TEMP. °C	H <sub>2</sub> S/H <sub>2</sub> RATIO·10 <sup>2</sup>	FLOWRATE lt/min	REAC.TIME min	VOLUME lt	WEIGHT gm	LOSS mg/lt
884.6	F1	28	6.517	0.04448	20	0.8896	0.1699	190.985
	F2 *	29	6.517	0.08894	20	1.7788	0.1424	80.054
	F3 *	26	7.330	0.11956	20	2.3912	0.1972	82.469
	F4	27	9.770	0.06114	20	1.2228	0.1179	96.418
	F5	26.5	5.865	0.14736	21	3.0946	0.2352	76.004
	F6 *	28	7.820	0.07504	25	1.8760	0.1570	83.690
	F7 *	28	6.520	0.13346	25	3.3365	0.2624	78.645
925.5	G1	26	9.770	0.03056	20	0.6112	0.1408	230.370
	G2	26	9.770	0.06114	20	1.2228	0.2209	180.651
	G3 *	26	6.517	0.08894	20	1.7788	0.2688	151.113
	G4 *	26.5	8.380	0.10556	20	2.1112	0.3151	149.252
	G5 *	26	7.330	0.11956	20	2.3912	0.3617	151.263
	G6 *	26	7.820	0.15009	20	3.3019	0.4878	147.740
	G7 *	26	6.517	0.13346	20	2.6692	0.4073	152.592

Appendix V. Table V.2 - Continued

TEMPERATURE °C	TEST No.	ROOM TEMP. °C	H <sub>2</sub> S/H <sub>2</sub> RATIO·10 <sup>2</sup>	FLOWRATE lt/min	REAC.TIME min	VOLUME lt	WEIGHT gm	LOSS mg/lt
900.0	H1 *	28	7.330	0.11956	25	2.9890	0.31420	105.120
	H2 *	27.5	6.520	0.13346	25	3.3365	0.35670	106.910
	H3 *	27.5	6.520	0.08894	25	2.2235	0.22445	100.940
	H4 *	27	6.520	0.08894	25	2.2235	0.25690	115.540
	H5 *	27	4.890	0.05842	25	1.4605	0.15340	105.033
	H6	27	5.865	0.14736	27	3.9787	0.26290	66.080
	H7 *	26	7.820	0.07504	20	1.4408	0.15520	107.720
	H8 *	26.5	5.590	0.10284	20	2.0568	0.22740	110.560

Note. \* Indicated tests used to calculate the average vapor pressure.

Appendix V. Table V.3Experimental Data for the Vapor Pressure Determinations of SnS Over Sn-Fe MattesCarrier gas:  $H_2S/H_2$  Mixtures - Reaction chamber: no. 2SnS - 5.81%FeS Matte

TEMPERATURE °C	TEST No.	ROOM TEMP. °C	$H_2S/H_2$ RATIO $\cdot 10^2$	FLOWRATE lt/min	REAC. TIME min	VOLUME lt	WEIGHT gm	LOSS mg/lt
866.0	I1-1 *	26	7.820	0.07504	33	2.4763	0.1484	59.928
	I2-1	23	7.330	0.11956	25	2.9890	0.1420	47.506
	I3-1 *	25	6.520	0.08894	30	2.6682	0.1442	54.044
	I4-1 *	25	7.820	0.06114	30	1.8342	0.1048	57.140
870.0	I1-2	21.5	4.887	0.11684	30	3.5052	0.1629	46.445
	I2-2 *	22	6.520	0.08894	30	2.6682	0.1577	59.137
	I3-2 *	25	4.887	0.05842	30	1.7526	0.1061	60.540
	I4-2 *	25.5	6.520	0.04448	30	1.3344	0.0761	57.030
	I5-2	26	9.770	0.03056	30	0.9168	0.0624	68.062
	I6-2 *	26	5.580	0.10284	30	3.0852	0.1914	62.038
891.6	J1	26	9.770	0.03056	25	0.7640	0.0825	107.984
	J2 *	26.5	7.820	0.07500	26	1.9510	0.1770	90.721
	J3 *	25	9.770	0.06114	28	1.7120	0.1076	84.905
	J4	26	6.520	0.08894	25	2.2235	0.1454	57.747
	J5	25	6.520	0.04448	26	1.1565	0.1284	93.387
	J6	25.5	4.890	0.05298	28	1.4830	0.1080	92.083
	J7 *	25	7.820	0.07504	30	2.2512	0.1366	80.935

Appendix V. Table V.3 - Continued

TEMPERATURE °C	TEST No.	ROOM TEMP. °C	H <sub>2</sub> S/H <sub>2</sub> RATIO·10 <sup>2</sup>	FLOWRATE lt/min	REAC.TIME min	VOLUME lt	WEIGHT gm	LOSS mg/lt
916.5	K1 *	25	9.770	0.03056	25	0.7640	0.1041	136.190
	K2 *	25	12.000	0.01256	25	0.3140	0.0417	132.800
	K3 *	26	6.520	0.08894	30	2.6682	0.3538	132.599
	K4 **	26	6.520	0.04448	28	1.2454	0.1548	124.300
	K5 **	27	9.770	0.03056	27	0.8251	0.0964	116.830
	K6 *	26	9.770	0.06114	30	1.8342	0.2480	135.180
	K7 **	25.5	7.330	0.09166	25	2.2915	0.2673	116.650
** Indicates the final choice for the average pressure (See Discussion).								
SnS - 14.59%Fes Matte								
823.6	L1 *	29	4.887	0.11684	30	3.5052	0.08040	22.910
	L2 *	29	3.260	0.08622	30	2.5866	0.07570	29.270
	L3	29	2.790	0.10012	30	3.0036	0.07830	26.070
	L4 *	29	4.340	0.13074	30	3.9222	0.09595	24.436
851.3	M1	25	4.887	0.05842	30	1.7526	0.09590	54.072
	M2 *	25.5	6.520	0.08894	30	2.6682	0.11760	44.075
	M3	25.5	6.520	0.04448	30	1.3344	0.05360	40.168
	M4	26	4.880	0.05842	30	1.7526	0.08750	50.040
	M5	26.5	7.820	0.07504	30	2.2512	0.10620	47.173

Appendix V. Table V.3 - Continued

TEMPERATURE °C	TEST No.	ROOM TEMP. °C	H <sub>2</sub> S/H <sub>2</sub> RATIO·10 <sup>2</sup>	FLOWRATE lt/min	REAC.TIME min	VOLUME lt	WEIGHT gm	LOSS mg/lt	
851.3 ↓	M6	23	6.520	0.04448	30	1.3344	0.0605	45.339	
	M7 *	24	5.600	0.10284	30	3.0852	0.1217	39.430	
	M8	28	4.880	0.11684	35	4.0894	0.1924	47.048	
	M9 *	28	6.520	0.13346	35	4.6711	0.1925	41.211	
	M10	28	5.860	0.14736	30	4.4208	0.1322	29.904	
	M11	28	5.860	0.14736	30	4.4208	0.1854	41.938	
	903.0 ↓	N1 *	26.5	6.520	0.04448	31	1.3789	0.1231	89.275
		N2 *	27	9.770	0.03056	30	0.9168	0.0762	83.115
		N3 *	27.5	9.770	0.06114	30	1.8342	0.1621	88.376
		N4 *	27	7.820	0.07504	30	2.2512	0.1844	81.912
	<b>SnS - 25.029%FeS Matte</b>								
862.3 ↓	O1 *	25	7.820	0.05842	25	1.8760	0.0678	36.141	
	O2 *	25.5	4.887	0.04448	30	1.7526	0.0626	35.718	
	O3 *	26	6.517	0.07504	31	1.3790	0.0488	35.391	
	O4 *	26	6.517	0.08894	30	2.6680	0.1107	41.489	
	O5 *	25.5	7.330	0.11956	30	3.5870	0.1467	40.900	
	O6 *	28	8.900	0.06669	25	1.6673	0.0672	40.306	
	O7 *	28	13.000	0.04720	20	0.9440	0.0409	43.320	
	O8 *	27	5.860	0.14736	20	2.9472	0.1217	41.293	

Appendix V. Table V.3 - Continued

TEMPERATURE °C	TEST No.	ROOM TEMP. °C	H <sub>2</sub> S/H <sub>2</sub> RATIO·10 <sup>2</sup>	FLOWRATE lt/min	REAC.TIME min	VOLUME lt	WEIGHT gm	LOSS mg/lt
921.0	P1 *	25.5	4.890	0.05842	25	1.4602	0.1468	100.514
	P2	26	6.517	0.04448	25	1.1120	0.1167	104.946
	P3 *	26	7.820	0.07504	25	1.8760	0.1885	100.480
	P4	24	6.517	0.08894	25	2.2235	0.2345	105.464
	P5 *	26	7.330	0.11956	25	2.9890	0.2992	100.100
	P6	26	5.860	0.14736	25	3.6840	0.3437	93.295
884.4	Q1 *	27	4.890	0.05842	30	1.7596	0.0997	56.661
	Q2 *	28.5	6.520	0.08894	25	2.2235	0.1270	57.120
	Q3 *	29	9.770	0.03056	25	0.7640	0.0448	58.640
SnS - 18.103%FeS Matte								
803.0	R1	25.5	4.510	0.18912	25	4.7280	0.1069	22.288
	R2	26	6.520	0.08904	30	2.6712	0.0968	36.253
	R3	26	5.586	0.10284	20	2.0568	0.1246	60.599
	R4	28	5.586	0.10284	20	2.0568	0.0610	29.677
	R5 *	26	7.300	0.11956	25	2.9890	0.0527	17.645
	R6	26	6.520	0.13346	25	3.3365	0.0786	23.570
	R7 *	25	4.190	0.20316	25	5.0790	0.0846	16.655
	R8 *	26	4.997	0.17516	25	4.3790	0.0609	13.916
	R9 *	24	5.865	0.14736	25	3.6840	0.0646	17.546

Appendix V. Table V.3 - Continued

TEMPERATURE °C	TEST No.	ROOM TEMP. °C	H <sub>2</sub> S/H <sub>2</sub> RATIO·10 <sup>2</sup>	FLOWRATE lt/min	REAC.TIME min	VOLUME lt	WEIGHT gm	LOSS mg/lt
854.4	S1	26	6.000	0.01144	30	0.3432	0.0472	137.650
	S2 *	25	6.000	0.02365	31	0.7332	0.0295	40.292
	S3	25.5	6.520	0.04448	31	1.3790	0.0758	54.996
	S4 *	24.5	7.300	0.11956	31	3.7064	0.1593	42.990
	S5	23	7.820	0.07504	31	2.3262	0.1154	49.623
	S6	24.5	6.520	0.04448	30	1.3344	0.0678	50.840
	S7 *	25	5.586	0.10284	30	3.0850	0.1388	44.990
901.0	T1 *	25	9.770	0.03056	25	0.7640	0.0611	79.908
	T2	25.5	9.770	0.01528	25	0.3820	0.0381	99.600
	T3	25	14.000	0.01110	26	0.2886	0.0251	86.800
	T4 *	24	6.00	0.02366	27	0.6389	0.0519	81.162

Note. \* Indicates tests used to calculate the average vapor pressure.

Sample Calculation for the Vapor Pressure of SnS  
Above Pure SnS(c,l), and Above Sn-Fe Mattes.

---

The partial pressure of SnS vapor can be represented by:

$$P_{\text{SnS}} = \frac{n_{\text{SnS}}}{n_{\text{SnS}} + n_{\text{Carrier gas}}} \cdot P_t \quad (\text{atm}) \quad (\text{V.1})$$

But since  $n_{\text{Carrier gas}} \gg n_{\text{SnS}}$ ,

then:

$$P_{\text{SnS}} = \frac{n_{\text{SnS}}}{n_{\text{Carrier gas}}} \cdot P_t \quad (\text{atm})$$

The perfect gas law can be applied to the carrier gas. Therefore the volume of the carrier gas is given by:

$$V_{(\text{Carrier gas})} = \frac{R T_r}{P_t} \cdot n_{\text{Carrier gas}}, \quad (\text{V.2})$$

where  $T_r$  is the temperature at which the volume of the carrier gas is measured ( $^{\circ}\text{K}$ ).

From (V.2):

$$n_{\text{Carrier gas}} = \frac{P_t V}{R T_r}, \quad (\text{V.3})$$

where  $R$ , the gas constant, is equal to 0.08205 lt atm/gmole  $^{\circ}\text{K}$ .

The number of moles of SnS is represented by:

$$n_{\text{SnS}} = \frac{\Delta W}{150.754} \quad (\text{V.4})$$

where  $\Delta W$  is the weight of sample lost during a test (in gm).  
Hence, substituting (V.3) and (V.4) into (V.1) yields:

$$P_{\text{SnS}} = \frac{\Delta W P_t T_r}{P_t V 150.754} \quad , \quad \text{atm} \quad (\text{V.5})$$

where  $V$  is in lt, and  $\Delta W$  in gm.

Since the weight loss during a test was in all cases a fraction of a gm, it is better to convert gm to mg in equation (V.5). Thus:

$$P_{\text{SnS}} = \frac{(\Delta W, \text{ gm})(0.08205)(T_r)}{(V, \text{ lt})(150.754)(1000 \text{ mg/gm})} \quad , \quad \text{atm}$$

Finally:

$$P_{\text{SnS}} = \frac{(\Delta W, \text{ mg})}{(V, \text{ lt})} (T_r, \text{ }^\circ\text{K})(5.4 \cdot 10^{-7}) \quad , \quad \text{atm} .$$

The values of  $T_r$  and  $\Delta W/V$  were taken from the third and last column respectively, from Tables V.1 through V.3 .

The equilibrium vapor pressure was obtained from the average of all the tests marked (\*), for each individual group.

The least-squares fit results for all the groups of tests run, are given in the following pages. The program itself is not listed here since it is a common program in use at C. S. M.

In these results:  $X = 10^4/T$  ,  
 $Y = \text{Log } P_{\text{SnS}}$  , and

STD ERROR OF  $Y$  = Standard deviation of  $\text{Log } P_{\text{SnS}}$ .

## PURE SOLID SNS .

CARRIER GAS: NITROGEN. - REACTION CHAMBER: NO. 1..

## LEAST - SQUARES POLYNOMIALS

NUMBER OF POINTS = 3  
 MEAN VALUE OF X = 9.3296  
 MEAN VALUE OF Y = -2.48843  
 STD ERROR OF Y = 0.477698

NOTE: CODE FOR WHAT NEXT? IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1 INDEX OF DETERM = 0.995738 WHAT NEXT?  
 ?2

TERM	COEFFICIENT			
0	8.0881			
1	-1.13365			

X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
9.7607	-2.96058	-2.97715	1.65674E-2	-0.556485
9.3075	-2.49935	-2.46338	-3.59742E-2	1.46036
8.92061	-2.00537	-2.02478	1.94068E-2	-0.958467

STD ERROR OF ESTIMATE FOR Y = 0.0441049

WHAT NEXT?  
 ?0

## PURE SOLID SNS.

CARRIER GAS: (H<sub>2</sub>S + H<sub>2</sub>) MIXTURES . - REACTION CHAMBER: NO. 2.

## LEAST - SQUARES POLYNOMIALS

NUMBER OF POINTS = 2  
 MEAN VALUE OF X = 9.0702  
 MEAN VALUE OF Y = -2.32033  
 STD ERROR OF Y = 0.341073

NOTE: CODE FOR WHAT NEXT? IS:

- 0 = STOP PROGRAM
- 1 = COEFFICIENTS ONLY
- 2 = ENTIRE SUMMARY
- 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1 INDEX OF DETERM = 1 WHAT NEXT?  
 ?2

TERM	COEFFICIENT				
0	7.65915				
1	-1.10025				
X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF	
9.2894	-2.5615	-2.5615	-6.55651E-7	0.0000255964	
8.851	-2.07915	-2.07915	5.66244E-7	-2.72344E-5	

STD ERROR OF ESTIMATE FOR Y = 0

WHAT NEXT?  
 ?0

## PURE LIQUID SNS.

CARRIER GAS: (H<sub>2</sub>S + H<sub>2</sub>) MIXTURES. - REACTION CHAMBER: NO. 2.

## LEAST - SQUARES POLYNOMIALS

NUMBER OF POINTS = 3  
 MEAN VALUE OF X = 8.50258  
 MEAN VALUE OF Y = -1.75119  
 STD ERROR OF Y = 0.132558

NOTE: CODE FOR WHAT NEXT? IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1 INDEX OF DETERM = 0.993979 WHAT NEXT?  
 ?2

TERM	COEFFICIENT				
0	5.79595				
1	-0.88763				
X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF	
8.6389	-1.87943	-1.87219	-7.23790E-3	0.3866	
8.3437	-1.6147	-1.61016	-4.53626E-3	0.281726	
8.52515	-1.75945	-1.77122	1.17741E-2	-0.664743	

STD ERROR OF ESTIMATE FOR Y = 0.0145463

WHAT NEXT?  
 ?0

SNS - 5.81%FES MATTE.

CARRIER GAS: (H<sub>2</sub>S + H<sub>2</sub>) MIXTURES. - REACTION CHAMBER: NO. 2.

LEAST - SQUARES POLYNOMIALS

NUMBER OF POINTS = 4  
 MEAN VALUE OF X = 8.62925  
 MEAN VALUE OF Y = -1.90686  
 STD ERROR OF Y = 0.149754

NOTE: CODE FOR WHAT NEXT? IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1 INDEX OF DETERM = 0.999644 WHAT NEXT?  
 ?2

TERM	COEFFICIENT			
0	5.58914			
1	-0.868673			
X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
8.58	-1.86059	-1.86407	3.48286E-3	-0.186842
8.407	-1.71543	-1.71379	-1.63749E-3	9.55477E-2
8.78	-2.0368	-2.03781	1.00735E-3	-4.94330E-2
8.75	-2.0146	-2.01175	-2.85283E-3	0.141808

STD ERROR OF ESTIMATE FOR Y = 3.46158E-3

WHAT NEXT?  
 ?0 .

SNS - 5.81%FES MATTE (UNCORRECTED)

CARRIER GAS: (H<sub>2</sub>S + H<sub>2</sub>) MIXTURES. - REACTION CHAMBER: NO. 2.

LEAST - SQUARES POLYNOMIALS

NUMBER OF POINTS = 4  
 MEAN VALUE OF X = 8.62905  
 MEAN VALUE OF Y = -1.89974  
 STD ERROR OF Y = 0.162047

NOTE: CODE FOR WHAT NEXT? IS:

- 0 = STOP PROGRAM
- 1 = COEFFICIENTS ONLY
- 2 = ENTIRE SUMMARY
- 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1 INDEX OF DETERM = 0.998941 WHAT NEXT?  
 ?2

TERM                    COEFFICIENT

0                    6.19243  
 1                    -0.937782

X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
8.58	-1.86059	-1.85374	-6.84573E-3	0.369292
8.4062	-1.68698	-1.69076	0.00377777	-0.223437
8.78	-2.0368	-2.0413	4.50078E-3	-0.220486
8.75	-2.0146	-2.01317	-1.43275E-3	7.11688E-2

STD ERROR OF ESTIMATE FOR Y = 6.45931E-3

WHAT NEXT?  
 ?0

SNS - 14.59%FES MATTE.

CARRIER GAS: (H<sub>2</sub>S + H<sub>2</sub>) MIXTURES. - REACTION CHAMBER: NO. 2.

LEAST - SQUARES POLYNOMIALS

NUMBER OF POINTS = 3  
 MEAN VALUE OF X = 8.83927  
 MEAN VALUE OF Y = -2.14059  
 STD ERROR OF Y = 0.276321

NOTE: CODE FOR WHAT NEXT? IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1 INDEX OF DETERM = 0.99746 WHAT NEXT?  
 ?2

TERM	COEFFICIENT			
0	5.67853			
1	-0.884589			

X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
9.12	-2.399	-2.38892	-1.00764E-2	0.421798
8.8944	-2.17347	-2.18936	1.58904E-2	-0.725801
8.5034	-1.8493	-1.84349	-0.00581387	0.315374

STD ERROR OF ESTIMATE FOR Y = 1.96937E-2

WHAT NEXT?  
 ?0

SNS - 25.029%FES MATTE.

CARRIER GAS: (H<sub>2</sub>S + H<sub>2</sub>) MIXTURES. - REACTION CHAMBER: NO. 2.

LEAST - SQUARES POLYNOMIALS

NUMBER OF POINTS = 3  
 MEAN VALUE OF X = 8.60773  
 MEAN VALUE OF Y = -2.00524  
 STD ERROR OF Y = 0.203871

NOTE: CODE FOR WHAT NEXT? IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1 INDEX OF DETERM = 0.999379 WHAT NEXT?  
 ?2

TERM                    COEFFICIENT

0                    6.03485  
 1                    -0.934054

X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
8.808	-2.19586	-2.1923	-3.56001E-3	0.162387
8.3752	-1.7903	-1.78804	-2.25864E-3	0.126319
8.64	-2.02956	-2.03538	5.81884E-3	-0.285885

STD ERROR OF ESTIMATE FOR Y = 7.18568E-3

WHAT-NEXT?  
 ?0

SNS - 18.103%FES MATTE.

CARRIER GAS: (H2S + H2) MIXTURES. - REACTION CHAMBER: NO. 2.

LEAST-SQUARES POLYNOMIALS

NUMBER OF POINTS = 3  
 MEAN VALUE OF X = 8.89027  
 MEAN VALUE OF Y = -2.20937  
 STD ERROR OF Y = 0.346962

NOTE: CODE FOR WHAT NEXT? IS:

- 0 = STOP PROGRAM
- 1 = COEFFICIENTS ONLY
- 2 = ENTIRE SUMMARY
- 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1 INDEX OF DETERM = 0.995545 WHAT NEXT?  
 ?2

TERM	COEFFICIENT			
0	5.76218			
1	-0.896439			

X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
9.2893	-2.5773	-2.5651	-1.21967E-2	0.475484
8.8702	-2.1627	-2.18941	2.67060E-2	-1.21978
8.5179	-1.8881	-1.87359	-0.0145094	0.774414

STD ERROR OF ESTIMATE FOR Y = 3.27489E-2

WHAT NEXT?  
 ?0

Appendix VI

Tin-Iron Mattes

Corrected Equations for the SnS Vapor Pressures

Taking the mean value of the  $\alpha$ - function (See Table X, Chapter VI):

$$\alpha = 1193.2 ,$$

and the equation obtained for  $p_{\text{SnS}}^0$  (Table IX, Ch. V),  $\text{Log } p_{\text{SnS}}$  can be recalculated as follows:

$$\text{Log } p_{\text{SnS}} = \text{Log } f_{\text{SnS}}^{\text{A}} + \text{Log } p_{\text{SnS}}^0 + \text{Log } N_{\text{SnS}} ,$$

where  $\text{Log } f_{\text{SnS}}^{\text{A}} = ( \alpha N_{\text{FeS}}^2 ) / ( R T ) .$

The corrected values are listed in table VI.1, and the least-squares fits are given thereafter.

Appendix VI. Table VI.1Corrected Values of Log  $p_{\text{SnS}}$ 

MATTE COMPOSITION	TEMPERATURE		Log $p_{\text{SnS}}$ , (atm)
	$^{\circ}\text{K}$	$10^4/T$	
SnS - 5.81%FeS	1139.0	8.780	- 2.03869
	1143.0	8.750	- 2.01142
	1164.6	8.587	- 1.86743
	1189.5	8.407	- 1.70792
Sn - 14.59%FeS	1096.6	9.120	- 2.39781
	1124.3	8.894	- 2.19869
	1176.0	8.503	- 1.85212
SnS - 18.103%FeS	1076.0	9.294	- 2.57250
	1127.4	8.870	- 2.19770
	1174.0	8.518	- 1.88630
SnS - 25.03%FeS	1135.3	8.808	- 2.18865
	1194.0	8.375	- 1.80578
	1157.4	8.640	- 2.03994

SNS - 5.81ZFES MATTE  
 \*\*\*\*\*

LEAST - SQUARES POLYNOMIALS

NUMBER OF POINTS = 4  
 MEAN VALUE OF X = 8.631  
 MEAN VALUE OF Y = -1.90636  
 STD ERROR OF Y = 0.152143

NOTE: CODE FOR WHAT NEXT? IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1 INDEX OF DETERM = 0.999997 WHAT NEXT?  
 ?2

TERM	COEFFICIENT			
0	5.74018			
1	-0.885939			
X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
8.78	-2.03869	-2.03837	-3.20077E-4	1.57026E-2
8.75	-2.01142	-2.01179	3.71724E-4	-1.84773E-2
8.587	-1.86743	-1.86738	-4.63277E-5	2.48089E-3
8.407	-1.70792	-1.70791	-5.31971E-6	3.11474E-4

STD ERROR OF ESTIMATE FOR Y = 3.48427E-4

WHAT NEXT?  
 ?0

SNS - 14.5923%FES MATTE  
 \*\*\*\*\*

L E A S T - S Q U A R E S P O L Y N O M I A L S

NUMBER OF POINTS = 3  
 MEAN VALUE OF X = 8.839  
 MEAN VALUE OF Y = -2.14954  
 STD ERROR OF Y = 0.276145

NOTE: CODE FOR WHAT NEXT? IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1 INDEX OF DETERM = .0.999998 WHAT NEXT?  
 ?2

TERM	COEFFICIENT			
0	5.66976			
1	-0.884636			
X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
9.12	-2.39781	-2.39812	0.000312775	-1.30425E-2
8.894	-2.19869	-2.19819	-4.95106E-4	2.25233E-2
8.503	-1.85212	-1.8523	1.82033E-4	-0.00982737

STD ERROR OF ESTIMATE FOR Y = 6.13265E-4

WHAT NEXT?  
 ?0

SNS - 18.1032FES MATTE  
 \*\*\*\*\*

LEAST - SQUARES POLYNOMIALS

NUMBER OF POINTS = 3  
 MEAN VALUE OF X = 8.894  
 MEAN VALUE OF Y = -2.21883  
 STD ERROR OF Y = 0.343588

NOTE: CODE FOR WHAT NEXT? IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1 INDEX OF DETERM = 1. WHAT NEXT?  
 ?2

TERM                    COEFFICIENT

0                    5.64584  
 1                    -0.884267

X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
9.294	-2.5725	-2.57254	3.99947E-5	-0.00155468
8.87	-2.1977	-2.19761	-8.90791E-5	0.00405345
8.518	-1.8863	-1.88635	4.89652E-5	-2.59577E-3

STD ERROR OF ESTIMATE FOR Y = 1.09235E-4

WHAT NEXT?  
 ?0

SNS - 25.029%FES MATTE  
 \*\*\*\*\*

L E A S T - S Q U A R E S P O L Y N O M I A L S

NUMBER OF POINTS = 3  
 MEAN VALUE OF X = 8.60767  
 MEAN VALUE OF Y = -2.01146  
 STD ERROR OF Y = 0.193018

NOTE: CODE FOR WHAT NEXT? IS:

0 = STOP PROGRAM  
 1 = COEFFICIENTS ONLY  
 2 = ENTIRE SUMMARY  
 3 = FIT NEXT HIGHER DEGREE

POLYFIT OF DEGREE 1 INDEX OF DETERM = 1. WHAT NEXT?  
 ?2

TERM	COEFFICIENT
0	5.59918
1	-0.884169

X-ACTUAL	Y-ACTUAL	Y-CALC	DIFF	PCT-DIFF
8.808	-2.18865	-2.18859	-6.47604E-5	2.95901E-3
8.375	-1.80578	-1.80574	-4.01586E-5	2.22394E-3
8.64	-2.03994	-2.04004	1.04696E-4	-0.00513202

STD ERROR OF ESTIMATE FOR Y = 1.29491E-4

WHAT NEXT?  
 ?0

Appendix VII

Program SUBREG

The Gaussian Algorithm to Calculate n  
Simultaneous Linear Equations

```

1 DIM I(50),J(50),A(50,50),B(50),X(50)
5 N=4
6 REM
7 REM   PROGRAM SUBREG CALCULATES N SYMULANEØS LINEAR EQUATIONS
8 REM   USING THE GAUSSIAN ALGORITHM.
10 REM
11 REM   A(1,1)X1 + A(1,2)X2 + A(1,3)X3 + ..... = B1
12 REM   ..... + ..... + ..... + ..... = ..
13 REM   A(N,1)X1 + A(N,2)X2 + A(N,3)X3 + ..... = B(N)
14 REM
15 FOR I=1 TO N
20 FOR J=1 TO N
30 READ A(I,J)
40 NEXT J
41 NEXT I
43 PRINT"SYMULANEØS LINEAR EQUATIONS: GAUSSIAN ALGORITHM"
45 PRINT"*****"
46 PRINT
51 PRINT"CØEFFICIENTS ARE:"
52 PRINT
53 FOR I=1 TO N
54 FOR J=1 TO N
55 PRINT A(I,J)
56 NEXT J
57 NEXT I
58 PRINT
60 FOR J=1 TO N
70 READ B(J)
80 NEXT J
81 PRINT"INDEPENDENT CØNSTANTS ARE:"
82 PRINT
83 FOR J=1 TO N
84 PRINT B(J)
85 NEXT J
86 PRINT
87 PRINT
90 FOR K=1 TO N
92 REM
93 REM   ROW NØRMALIZING LOOP STARTS.
100 FOR J=(K+1) TO N
110 A(K,J)=A(K,J)/A(K,K)
120 NEXT J
130 B(K)=B(K)/A(K,K)
132 REM

```

## Appendix VII - Continued

```

      REM          ROW NORMALIZING LOOP ENDS.
134 REM
135 REM
136 REM          SUBTRACTING MULTIPLES OF ROW K FROM ALL
137 REM          THE SUBSEQUENT ROWS STARTS.
138 REM
140 FOR I=(K+1) TO N
150 FOR J=(K+1) TO N
160 A(I,J)=A(I,J)-A(I,K)*A(K,J)
170 NEXT J
180 B(I)=B(I)-A(I,K)*B(K)
190 NEXT I
200 NEXT K
201 REM
202 REM          SUBTRACTING MULTIPLES OF ROW K FROM ALL
203 REM          THE SUBSEQUENT ROWS ENDS.
204 REM
205 REM
206 REM          THE BACK SOLUTION STARTS.
207 REM
210 FOR I=N TO 1 STEP (-1)
220 X(I)=B(I)
230 J=N
240 IF J<=I THEN 280
250 X(I)=X(I)-A(I,J)*X(J)
260 J=J-1
270 GO TO 240
280 NEXT I
282 REM          THE BACK SOLUTION ENDS.
283 REM
284 PRINT"NUMBER OF VARIABLES =";N
285 PRINT
286 PRINT"S O L U T I O N S : "
290 PRINT"*****"
300 PRINT
305 FOR I=1 TO N
308 PRINT"X(";I;") = ";X(I)
310 PRINT
320 NEXT I
330 DATA .58929,5.5698E-4,.4524,4.2756E-4,.4049,3.618E-4,.2576,2.3021E-4
331DATA .03998,2.968E-5,7.988E-3,5.93E-6,3.703E-3,2.6E-6,2.2253E-4
332 DATA 1.5E-7
340 DATA .188345,.080677,-.006419,-.009078
500 END

```

READY

## Appendix VII - Continued

SYMULTANEOUS LINEAR EQUATIONS: GAUSSIAN ALGORITHM  
 \*\*\*\*\*

COEFFICIENTS ARE:

0.58929  
 5.56980E-4  
 0.4524  
 4.27560E-4  
 0.4049  
 3.61800E-4  
 0.2576  
 2.30210E-4  
 3.99800E-2  
 0.00002968  
 7.98300E-3  
 5.93000E-6  
 3.70300E-3  
 2.60000E-6  
 2.22530E-4  
 0.00000015

INDEPENDENT CONSTANTS ARE:

0.188345  
 0.080677  
 -0.006419  
 -9.07800E-3

NUMBER OF VARIABLES = 4

S O L U T I O N S :  
 \*\*\*\*\*

X( 1 ) = 527.245  
 X( 2 ) = -773589.  
 X( 3 ) = 119.697  
 X( 4 ) = 154857.

Note. Data from table XV, Chapter VI.

Appendix VIIINumerical Results of Log  $p_{\text{SnS}}$  as a Function of  
Sn Content in Sn-Fe Mattes, and Temperature.

It was found that:

$$\text{Log } p_{\text{SnS}} = - \frac{8876.3}{T} + 5.80 + \text{Log } N_{\text{SnS}} + \frac{260.8}{T} N_{\text{FeS}}^2, \text{ (Eqn. 44, Ch. VII)}$$

This equation was programmed for a temperature range between 1000 and 1500°K, and from 0% to 100% Sn in matte.

The results are tabulated in the following pages.

```

100 PRINT
102 PRINT
103 PRINT
137 PRINT
138 PRINT
140 PRINT
141 PRINT"P(SNS) VS. WT%SNS IN MATTE - REGULARITY CONST. = 260.8"
142 PRINT"*****"
143 PRINT
144 PRINT"CALCULATION OF P(SNS) AS A FUNCTION OF COMPOSITION AND TEMP."
145 PRINT
146 PRINT
150 FOR T=1000 TO 1500 STEP 100
160 PRINT"TEMPERATURE = ";T;"DEG. K"
165 PRINT"*****"
170 PRINT
180 PRINT"WT% SN","WT%SNS","N(SNS)","LOG P(SNS)","P (SNS)"
185 PRINT
190 FOR A= 10 TO 100 STEP 10
195 S=A*110.7/150.754
200 N1=(A/150.754)/((A/150.754)+(100-A)/87.911)
210 N2=1-N1
220 P1=-8876.3/T+5.796+(LOG(N1))/2.303+260.8*(N2+2)/T
230 P2=EXP(P1*2.303)
235 PRINT S,A,N1,P1,P2
240 NEXT A
245 PRINT
250 PRINT
255 NEXT T
400 END

```

READY

P(SNS) VS. WT%SNS IN MATTE - REGULARITY CONST. = 260.8

\*\*\*\*\*

CALCULATION OF P(SNS) AS A FUNCTION OF COMPOSITION AND TEMP.

TEMPERATURE = 1000 DEG. K

\*\*\*\*\*

WT% SN	WT%SNS	N(SNS)	LOG P(SNS)	P (SNS)
7.87375	10	6.08508E-2	-4.06579	8.57983E-5
15.7475	20	0.127236	-3.77687	1.66897E-4
23.6213	30	0.199948	-3.61232	0.000243795
31.495	40	0.279934	-3.49792	3.17284E-4
39.3688	50	0.368345	-3.40991	3.88575E-4
47.2425	60	0.466585	-3.3371	4.59510E-4
55.1163	70	0.576391	-3.27274	5.32929E-4
62.99	80	0.699931	-3.21173	6.13320E-4
70.8638	90	0.839956	-3.14935	7.08081E-4
78.7375	100	1	-3.0803	8.30128E-4

TEMPERATURE = 1100 DEG. K

\*\*\*\*\*

WT% SN	WT%SNS	N(SNS)	LOG P(SNS)	P (SNS)
7.87375	10	6.08508E-2	-3.27976	5.24379E-4
15.7475	20	0.127236	-2.988	1.02675E-3
23.6213	30	0.199948	-2.82056	1.50983E-3
31.495	40	0.279934	-2.70328	1.97804E-3
39.3688	50	0.368345	-2.61243	2.43834E-3
47.2425	60	0.466585	-2.53691	2.90155E-3
55.1163	70	0.576391	-2.47006	0.00338451
62.99	80	0.699931	-2.40693	3.91412E-3
70.8638	90	0.839956	-2.34302	4.53479E-3
78.7375	100	1	-2.27336	5.32386E-3

TEMPERATURE = 1200 DEG. K

\*\*\*\*\*

WT% SN	WT%SNS	N(SNS)	LOG P(SNS)	P (SNS)
7.87375	10	6.08508E-2	-2.62474	2.37020E-3
15.7475	20	0.127236	-2.3306	4.66640E-3
23.6213	30	0.199948	-2.16076	0.00689998
31.495	40	0.279934	-2.04108	9.08985E-3
39.3688	50	0.368345	-1.94787	1.12662E-2
47.2425	60	0.466585	-1.87009	1.34764E-2
55.1163	70	0.576391	-1.80116	1.57949E-2
62.99	80	0.699931	-1.73626	0.018341
70.8638	90	0.839956	-1.67108	2.13118E-2
78.7375	100	1	-1.60092	2.50493E-2

P(SNS) VS. WT%SNS IN MATTE - REGULARITY CONST. = 260.8

\*\*\*\*\*

CALCULATION OF P(SNS) AS A FUNCTION OF COMPOSITION AND TEMP.

TEMPERATURE = 1300 DEG. K

\*\*\*\*\*

WT% SN	WT%SNS	N(SNS)	LOG P(SNS)	P (SNS)
7.87375	10	6.08508E-2	-2.07049	8.49439E-3
15.7475	20	0.127236	-1.77434	1.68013E-2
23.6213	30	0.199948	-1.60247	0.0249598
31.495	40	0.279934	-1.48075	3.30357E-2
39.3688	50	0.368345	-1.38555	4.11342E-2
47.2425	60	0.466585	-1.30585	4.94212E-2
55.1163	70	0.576391	-1.23516	5.81586E-2
62.99	80	0.699931	-1.16878	6.77662E-2
70.8638	90	0.839956	-1.10251	7.89352E-2
78.7375	100	1	-1.03192	0.0928733

TEMPERATURE = 1400 DEG. K

\*\*\*\*\*

WT% SN	WT%SNS	N(SNS)	LOG P(SNS)	P (SNS)
7.87375	10	6.08508E-2	-1.59542	2.53681E-2
15.7475	20	0.127236	-1.29755	0.0503757
23.6213	30	0.199948	-1.12393	0.0751387
31.495	40	0.279934	-1.00047	9.98502E-2
39.3688	50	0.368345	-0.903556	0.124819
47.2425	60	0.466585	-0.82222	0.150533
55.1163	70	0.576391	-0.750026	0.177762
62.99	80	0.699931	-0.682358	0.20774
70.8638	90	0.839956	-0.615173	0.242503
78.7375	100	1	-0.544214	0.285554

TEMPERATURE = 1500 DEG. K

\*\*\*\*\*

WT% SN	WT%SNS	N(SNS)	LOG P(SNS)	P (SNS)
7.87375	10	6.08508E-2	-1.1837	6.54771E-2
15.7475	20	0.127236	-0.884324	0.130472
23.6213	30	0.199948	-0.709202	0.195286
31.495	40	0.279934	-0.584229	0.260415
39.3688	50	0.368345	-0.48583	0.32665
47.2425	60	0.466585	-0.403072	0.395235
55.1163	70	0.576391	-0.329574	0.46813
62.99	80	0.699931	-0.260795	0.548477
70.8638	90	0.839956	-0.19281	0.641439
78.7375	100	1	-0.121533	0.755866

P(SNS) VS. WT%SNS IN MATTE - REGULARITY CONST. = 260.8

\*\*\*\*\*

CALCULATION OF P(SNS) AS A FUNCTION OF COMPOSITION AND TEMP.

TEMPERATURE = 1000 DEG. K

\*\*\*\*\*

WT% SN	WT%SNS	N(SNS)	LOG P(SNS)	P (SNS)
1.57475	2	0.0117609	-4.75481	1.75522E-5
3.1495	4	2.37212E-2	-4.4563	3.49060E-5
4.72425	6	3.58861E-2	-4.2827	5.20634E-5
6.299	8	4.82608E-2	-4.16023	6.90266E-5
7.87375	10	6.08508E-2	-4.06579	8.57983E-5
9.44851	12	0.0736618	-3.98906	1.02381E-4
11.0233	14	8.66997E-2	-3.92455	1.18779E-4
12.598	16	9.99705E-2	-3.86899	1.34995E-4
14.1728	18	0.113481	-3.82024	0.000151032
15.7475	20	0.127236	-3.77687	1.66897E-4

TEMPERATURE = 1100 DEG. K

\*\*\*\*\*

WT% SN	WT%SNS	N(SNS)	LOG P(SNS)	P (SNS)
1.57475	2	0.0117609	-3.97103	1.06722E-4
3.1495	4	2.37212E-2	-3.67196	2.12511E-4
4.72425	6	3.58861E-2	-3.4978	3.17375E-4
6.299	8	4.82608E-2	-3.37477	0.000421326
7.87375	10	6.08508E-2	-3.27976	5.24379E-4
9.44851	12	0.0736618	-3.20247	0.000626548
11.0233	14	8.66997E-2	-3.13739	7.27850E-4
12.598	16	9.99705E-2	-3.08126	8.28303E-4
14.1728	18	0.113481	-3.03194	9.27930E-4
15.7475	20	0.127236	-2.988	1.02675E-3

TEMPERATURE = 1200 DEG. K

\*\*\*\*\*

WT% SN	WT%SNS	N(SNS)	LOG P(SNS)	P (SNS)
1.57475	2	0.0117609	-3.31788	4.80313E-4
3.1495	4	2.37212E-2	-3.01834	9.57445E-4
4.72425	6	3.58861E-2	-2.84372	1.43144E-3
6.299	8	4.82608E-2	-2.72022	1.90234E-3
7.87375	10	6.08508E-2	-2.62474	2.37020E-3
9.44851	12	0.0736618	-2.54698	2.83508E-3
11.0233	14	8.66997E-2	-2.48143	3.29706E-3
12.598	16	9.99705E-2	-2.42481	3.75621E-3
14.1728	18	0.113481	-2.37502	4.21263E-3
15.7475	20	0.127236	-2.3306	4.66640E-3

P(SNS) VS. WT%SNS IN MATTE - REGULARITY CONST. = 260.8

\*\*\*\*\*

CALCULATION OF P(SNS) AS A FUNCTION OF COMPOSITION AND TEMP.

TEMPERATURE = 1300 DEG. K

\*\*\*\*\*

WT% SN	WT%SNS	N(SNS)	LOG P(SNS)	P (SNS)
1.57475	2	0.0117609	-2.76521	1.71511E-3
3.1495	4	2.37212E-2	-2.46528	3.42195E-3
4.72425	6	3.58861E-2	-2.29026	0.00512066
6.299	8	4.82608E-2	-2.16637	6.81141E-3
7.87375	10	6.08508E-2	-2.07049	8.49439E-3
9.44851	12	0.0736618	-1.99233	1.01698E-2
11.0233	14	8.66997E-2	-1.92638	1.18379E-2
12.598	16	9.99705E-2	-1.86936	1.34990E-2
14.1728	18	0.113431	-1.81916	1.51533E-2
15.7475	20	0.127236	-1.77434	1.68013E-2

TEMPERATURE = 1400 DEG. K

\*\*\*\*\*

WT% SN	WT%SNS	N(SNS)	LOG P(SNS)	P (SNS)
1.57475	2	0.0117609	-2.2915	5.10611E-3
3.1495	4	2.37212E-2	-1.99123	1.01955E-2
4.72425	6	3.58861E-2	-1.81587	0.0152686
6.299	8	4.82608E-2	-1.69164	2.03260E-2
7.87375	10	6.08508E-2	-1.59542	2.53681E-2
9.44851	12	0.0736618	-1.51692	0.0303956
11.0233	14	8.66997E-2	-1.45062	3.54093E-2
12.598	16	9.99705E-2	-1.39326	4.04099E-2
14.1728	18	0.113481	-1.34272	4.53984E-2
15.7475	20	0.127236	-1.29755	0.0503757

TEMPERATURE = 1500 DEG. K

\*\*\*\*\*

WT% SN	WT%SNS	N(SNS)	LOG P(SNS)	P (SNS)
1.57475	2	0.0117609	-1.88094	1.31437E-2
3.1495	4	2.37212E-2	-1.58039	2.62620E-2
4.72425	6	3.58861E-2	-1.40474	3.93561E-2
6.299	8	4.82608E-2	-1.28021	5.24273E-2
7.87375	10	6.08508E-2	-1.1837	6.54771E-2
9.44851	12	0.0736618	-1.10489	7.85072E-2
11.0233	14	8.66997E-2	-1.0383	9.15195E-2
12.598	16	9.99705E-2	-0.98064	0.104516
14.1728	18	0.113481	-0.929797	0.117499
15.7475	20	0.127236	-0.884324	0.130472

## Appendix VIII - Continued

Development of a Simple Computer Program to Calculate  
the Theoretical Volume of Carrier Gas and Oil Required  
to be Burnt to Provide the Gas to Fume SnS from a Tin-  
Iron Matte Containing Initially S% Sn to a Final Matte  
Containing J% Sn

---

The tin content of a matte is to be reduced from S% Sn to a final content of J% Sn. This reduction is to be performed assuming  $p_{\text{SnS}}$  to be constant within a small concentration range, say each 1%Sn in matte.

The addition of all these reductions together gives the total carrier gas and the oil required.

Consider, therefore, the reduction of tin in matte from S% Sn to (S-1)% Sn.

A loop with the desired limits will then solve the problem to achieve the reduction aimed at the temperature required.

S% Sn in matte corresponds to,

$$S \frac{150.754}{118.690} = S1 \% \text{ SnS in matte.}$$

Assume  $p_{\text{SnS}}$  constant from S% Sn to (S-1)% Sn, and call S2 the wt% SnS in matte after fuming 1% Sn.

$$\therefore S2 = (S-1) \cdot \frac{150.754}{118.690} .$$

The matte is assumed to consist only of FeS and SnS. Therefore, before fuming:

100 parts of matte contain S1 parts of SnS and (100-S1) parts of FeS.

After fuming, matte contains:

P parts of SnS and (100-S1) parts of FeS.

So,

$$\frac{P}{P + (100-S1)} = \frac{S2}{100}$$

$$\therefore P = \frac{S2 \cdot (100-S1)}{(100-S1)}$$

Thus SnS fumed:  $F = S1 - P$  (%).

Taking the mean value of the %SnS in matte before fuming, and the %SnS in matte after fuming (for which the  $p_{\text{SnS}}$  is assumed constant):

$$A = (S1 + P)/2 \quad (\%),$$

for which:

$$N_{\text{SnS}} = N1 = \frac{A/150.754}{\frac{A}{150.754} + \frac{(100 - A)}{87.911}},$$

$N_{\text{SnS}}$  is the SnS mole fraction.

It was found that:

$$\text{Log } p_{\text{SnS}} = - \frac{8876.3}{T} + 5.80 + \text{Log } N_{\text{SnS}} + \frac{260.8}{T} N_{\text{FeS}}^2, \quad (\text{Eqn. 44, Ch.VII})$$

or:

$$Q = - \frac{8876.3}{T} + 5.80 + \text{Log } N1 + \frac{260.8}{T} (1 - N1)^2$$

$$\therefore p_{\text{SnS}} = B = \text{EXP}(Q/2.303), \quad \text{atm.}$$

Consider 1 ton of matte, from which  $F/100$  tons of SnS must be fumed. The volume of SnS vapor will be:

$$V1 = \frac{(F/100) \cdot 10^6}{150.754} \cdot \frac{22.4}{1000} \text{ m}^3 \quad \text{at STP,}$$

or:

$$V2 = \frac{V1 \cdot T}{273} \text{ m}^3 \quad \text{at TOK.}$$

Therefore, the volume of carrier gas required will be:

$$V_3 = V_2 \cdot \frac{(1 - B)}{B} \quad \text{m}^3 \quad \text{at } T^{\circ}\text{K for each 1\% Sn reduction.}$$

And the total volume of carrier gas required will be:

$$V = V + V_3.$$

Now, consider an oil of the following composition:

86% C, 11% H, 3% O, and a S. G. of 0.9 .

One liter of oil contains:	86% C	774 gm C = 64.5 moles of C
	11% H	99 gm H = 49.5 moles of H
	3% O	27 gm O = 0.84 moles of O <sub>2</sub> .

The O <sub>2</sub> required respectively is:	64.5 moles O <sub>2</sub>
	24.75 " "
	(-0.84) " "

---

Total      88.41 moles O<sub>2</sub> required.

This oil is to be burnt, say with a 25% excess air (79%N<sub>2</sub>, 21% O<sub>2</sub> by volume).

∴ 88.41 moles + 25% excess O<sub>2</sub> = 415.74 moles N<sub>2</sub>.

Therefore, the total number of moles of flue gases is:

64.5 moles CO <sub>2</sub>
49.5 moles H <sub>2</sub> O
22.1 moles O <sub>2</sub>
415.74 moles N <sub>2</sub>

---

Total 551.8 moles.

The volume of these gases at  $T^{\circ}\text{K}$  is equal to:

$$W = \frac{551.8 \cdot 22.4}{1000} \frac{T}{273} \text{ m}^3$$

Hence, the oil required, burnt with 25% excess air, to fume Sn from S to (S - 1)% Sn in matte is:

$$\emptyset = V_3 / W \text{ lt at } T^{\circ}\text{K} ,$$

and the total volume of oil required is:

$$\emptyset_1 = V / W \text{ lt at } T^{\circ}\text{K}.$$

The program, OILREQ, is listed below followed by the results on a 10% Sn- and a 15% Sn- matte fumed to final contents of 1% Sn and 5% Sn in matte, each.

```

5 M=15
6 J=5
10 PRINT"      FUMING SNS FROM SN - FE MATTES"
12 PRINT"      *****"
14 PRINT
16 PRINT
18 PRINT"THEORETICAL VOLUME OF INERT GAS REQUIRED TO FUME TIN FROM"
20 PRINT"A TIN-IRON MATTE CONTAINING INITIALLY";M;"%SN TO A FINAL"
21 PRINT"      MATTE CONTAINING";J;"%SN."
22 PRINT
24 PRINT"THEORETICAL VOLUME OF OIL REQUIRED TO BE BURNT WITH 25%EXCESS"
25 PRINT"AIR TO PROVIDE THE CALCULATED VOL. OF INERT GAS REQD."
28 PRINT
30 PRINT"OIL ANALYSIS:  86%C , 11%H , 3%O , S.G..9"
32 PRINT" AIR COMP. :  21%OXYGEN , 79%NITROGEN BY VOLUME"
34 PRINT
36 PRINT
40 FOR T=1000 TO 1500 STEP 100
45 PRINT"TEMPERATURE = ";T;"DEG. K"
46 PRINT"*****"
48 PRINT
50 PRINT" INITIAL SN  CONTENT = ";M;"%"
52 PRINT
55 PRINT"FROM ABOVE","P(SNS) OF","SNS VAPOR","INERT GAS","OIL REQD."
56 PRINT"%SN TO... ","AVGE COMP","      ","REQUIRED","      "
57 PRINT"  %SN   ","  ATM   "," CU.METERS","CU.METERS","  LITERS "
60 PRINT
65 FOR S=M TO (J+1) STEP (-1)
70 S1=S*150.754/118.69
75 S2=(S-1)*150.754/118.69
80 P=S2*(100-S1)/(100-S2)
85 F=S1-P
90 A=(S1+P)/2
95 N1=(A/150.754)/(A/150.754+(100-A)/87.911)
100 Q=-8876.3/T+5.796 +(LOG(N1))/2.303+260.8*((1-N1)+2)/T
105 B=EXP(Q*2.303)
110 V1=F*224/150.754
115 V2=V1*T/273
120 V3=V2*(1-B)/B
125 V=V+V3
130 W=(551.8*22.4*T)/273000
135 Q=V3/W
140 PRINT S;"T";(S-1),B,V2,V3,Q
145 NEXT S
150 PRINT
155 PRINT"TOTAL VOLUME OF INERT GAS REQD. = ";V;"CU. METERS"
160 Q1=V/Q

```

READY

```

160 OI=V/W
165 PRINT"TOTAL VOLUME OF OIL REQUIRED      = ";OI;"LITERS"
166 V=0
170 PRINT
175 PRINT
180 NEXT T
185 PRINT
190 REM
191 REM
192 REM
193 REM   S=%SN IN MATTE , S1=%SNS IN MATTE
194 REM   S2=%SNS IN MATTE CONTAINING (S-1%)TIN
195 REM   P=%SNS CONTENT IN MATTE AFTER FUMING 1%TIN
196 REM   F=S1-P=TIN FUMED (%)
197 REM   A=%VOLUME COMPOSITION CONSIDERED AT A TIME (%)
198 REM   N1=N(SNS)
199 REM   Q=LOG P(SNS) ,   B=P(SNS) ATM.
200 REM   V1=VOLUME OF SNS VAPOR AT STP
201 REM   V2=VOLUME OF SNS VAPOR AT TEMP T(DEG. K)
202 REM   V3=VOLUME OF INERT GAS REQUIRED.   CU.METERS.
203 REM   V=TOTAL VOLUME OF INERT GAS REQUIRED.   CU.METERS.
204 REM   W=VOLUME OF FLUE GASES AT T(K)   CU.METERS.
205 REM   Q=OIL REQD. TO BE BURNT + 25%EXCESS AIR.   LITERS.
206 REM   OI=TOTAL VOLUME OF OIL REQUIRED.   LITERS.
207 REM
208 REM
209 REM
300 REM   TO CHANGE FEED AND FINAL MATTE COMPOSITION, CHANGE ONLY
301 REM   STATEMENTS 5 AND 6.
302 REM   STATEMENT 5: I , GIVES THE INITIAL CONTENTS OF SN IN MATTE
303 REM   STATEMENT 6: J , GIVES THE FINAL CONTENT OF TIN (%) IN MATTE.
304 REM
305 REM
400 END

```

READY

## FUMING SNS FROM SN - FE MATTES

\*\*\*\*\*

THEORETICAL VOLUME OF INERT GAS REQUIRED TO FUME TIN FROM  
A TIN-IRON MATTE CONTAINING INITIALLY 10 %SN TO A FINAL  
MATTE CONTAINING 1 %SN.

THEORETICAL VOLUME OF OIL REQUIRED TO BE BURNED WITH 25%EXCESS  
AIR TO PROVIDE THE CALCULATED VOL. OF INERT GAS REQD.

OIL ANALYSIS: 36% C , 11% H , 3% O , S.G..9  
AIR COMP. : 21% OXYGEN , 79% NITROGEN BY VOLUME

TEMPERATURE = 1000 DEG. K

\*\*\*\*\*

INITIAL SN CONTENT = 10 %

FROM ABOVE %SN TO... %SN	P(SNS) OF AVGE COMP ATM	SNS VAPOR CO. METERS	INERT GAS REQUIRED CO. METERS	OIL REQD. LITERS
10 TO 9	1.82259E-4	7.33533	76321.4	1635.7
9 TO 8	3.3330913317	7.69493	33736.4	1853.57
8 TO 7	3.13233E-5	7.5177	93269.6	2366.47
7 TO 6	3.623073747	7.43336	155769.	2336.1
6 TO 5	6.00675E-5	7.35136	122345.	2713.25
5 TO 4	4.93491E-5	7.2621	147570.	3257.43
4 TO 3	3.35312E-5	7.17693	136515.	4117.32
3 TO 2	2.76333E-5	7. 7326	258665.	3667.36
2 TO 1	1.66549E-5	7.33291	423429.	9285.3

TOTAL VOLUME OF INERT GAS REQD. = 1.49326E+6 CO. METERS  
TOTAL VOLUME OF OIL REQUIRED = 32979.9 LITERS

TEMPERATURE = 1100 DEG. K  
 \*\*\*\*\*

INITIAL SN CONTENT = 1.4 %

FROM ABOVE %SN TO... %SN	P(SNS) OF AVGE COEF ATM	SNS VAPOR CU.METERS	INERT GAS REQUIRED CU.METERS	OIL REQRD. LITERS
10 TO 9	6.25781E-4	6.55536	13711.6	275.315
9 TO 8	5.61511E-4	6.46447	15066.	302.509
8 TO 7	0.000496576	6.34647	16789.5	337.115
7 TO 6	4.31377E-4	6.23171	19052.1	382.545
6 TO 5	0.000366526	6.12037	22147.2	444.692
5 TO 4	3.30762E-4	6.01141	26629.1	534.662
4 TO 3	1.04691E-4	7.00502	33664.6	676.35
3 TO 2	1.63146E-4	7.60859	46897.5	931.611
2 TO 1	1.01253E-4	7.73821	76057.4	1527.15

TOTAL VOLUME OF INERT GAS REQRD. = 269535. CU. METERS  
 TOTAL VOLUME OF OIL REQUIRED = 5411.97 LITERS

TEMPERATURE = 1200 DEG. K  
 \*\*\*\*\*

INITIAL SN CONTENT = 1.6 %

FROM ABOVE %SN TO... %SN	P(SNS) OF AVGE COEF ATM	SNS VAPOR CU.METERS	INERT GAS REQUIRED CU.METERS	OIL REQRD. LITERS
10 TO 9	2.63158E-3	9.00809	3296.5	66.7111
9 TO 8	3.002539	9.23397	3127.62	66.7633
8 TO 7	0.00224521	9.10524	4046.31	74.475
7 TO 6	1.95316E-3	9.00005	4595.79	84.5036
6 TO 5	1.65335E-3	8.85326	5347.29	96.4204
5 TO 4	1.35626E-3	8.70770	6435.26	113.445
4 TO 3	1.05737E-3	8.62431	8147.74	149.955
3 TO 2	7.57167E-4	8.51192	11233.	226.751
2 TO 1	4.55659E-4	8.40241	16435.5	339.226

TOTAL VOLUME OF INERT GAS REQRD. = 65162. CU. METERS  
 TOTAL VOLUME OF OIL REQUIRED = 1199.35 LITERS

TEMPERATURE = 1300 DEG. K  
 \*\*\*\*\*

INITIAL SN CONTENT = 10 %

FROM ABOVE ZSN TO... ZSN	P(SNS) OF AVGE COMP ATM	SNS VAPOR CU.METERS	INERT GAS REQUIRED CU.METERS	OIL REQRD. LITERS
10 TO 9	1.01570E-2	10.1469	988.864	16.8006
9 TO 8	0.00910229	10.0035	1089.	18.502
8 TO 7	8.04439E-3	9.86431	1216.33	23.6853
7 TO 6	6.96323E-3	9.70139	1383.35	28.5334
6 TO 5	5.91577E-3	9.52744	1511.76	27.3036
5 TO 4	4.85096E-3	9.48503	1942.32	32.9997
4 TO 3	3.77976E-3	9.34301	2462.51	41.8376
3 TO 2	2.70515E-3	9.22124	3399.55	57.7519
2 TO 1	1.62706E-3	9.10261	5505.34	94.8941

TOTAL VOLUME OF INERT GAS REQRD. = 19679.1 CU. METERS  
 TOTAL VOLUME OF OIL REQUIRED = 334.344 LITERS

TEMPERATURE = 1400 DEG. K  
 \*\*\*\*\*

INITIAL SN CONTENT = 10 %

FROM ABOVE ZSN TO... ZSN	P(SNS) OF AVGE COMP ATM	SNS VAPOR CU.METERS	INERT GAS REQUIRED CU.METERS	OIL REQRD. LITERS
10 TO 9	3.73568E-2	10.9275	349.04	5.50656
9 TO 8	2.71910E-2	10.773	335.422	6.38854
8 TO 7	2.40159E-2	10.7126	431.645	8.00976
7 TO 6	2.06402E-2	10.4767	492.241	7.76574
6 TO 5	1.76547E-2	10.3346	575.039	9.07179
5 TO 4	1.44695E-2	10.1963	674.622	10.9617
4 TO 3	1.12630E-2	10.0617	803.252	13.9344
3 TO 2	8.05714E-3	9.93557	1222.59	19.2379
2 TO 1	4.84331E-3	9.80831	2013.96	31.7731

TOTAL VOLUME OF INERT GAS REQRD. = 7345.03 CU. METERS  
 TOTAL VOLUME OF OIL REQUIRED = 111.192 LITERS

TEMPERATURE = 1500 DEG. K  
 \*\*\*\*\*

INITIAL SN CONTENT = 10 %

FROM ABOVE ZEN TO... %SN	P(SNS) OF AUGE COMP AIR	SNS VAPOR CU. METERS	INERT GAS REQUIRED CU. METERS	OIL REqd. LITERS
13 TO 9	7.84058E-2	11.733	137.613	2.02635
9 TO 8	0.0701991	11.5425	152.662	2.25112
8 TO 7	6.19320E-2	11.3516	172.243	2.53619
7 TO 6	5.37566E-2	11.2251	197.567	2.90933
6 TO 5	4.55206E-2	11.2723	232.176	3.41660
5 TO 4	3.72739E-2	10.9046	282.167	4.15477
4 TO 3	2.90164E-2	10.7334	369.747	5.31134
3 TO 2	2.07473E-2	10.6399	502.13	7.39437
2 TO 1	1.24679E-2	10.553	631.9	12.2493

TOTAL VOLUME OF INERT GAS REqd. = 2569.5 CU. METERS  
 TOTAL VOLUME OF OIL REqd. = 42.252 LITERS

FUMING SNS FROM SN - FE MATTES  
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THEORETICAL VOLUME OF INERT GAS REQUIRED TO FUME TIN FROM  
 A TIN-IRON MATTE CONTAINING INITIALLY 10 %SN TO A FINAL  
 MATTE CONTAINING 5 %SN.

THEORETICAL VOLUME OF OIL REQUIRED TO BE BURNED WITH 25%EXCESS  
 AIR TO PROVIDE THE CALCULATED VOL. OF INERT GAS REQD.

OIL ANALYSIS: 86%C , 11%H , 3%O , S.G. .9  
 AIR COMP. : 21%OXYGEN , 79%NITROGEN BY VOLUME

TEMPERATURE = 1000 DEG. K  
 \*\*\*\*\*

INITIAL SN CONTENT = 10 %

FROM ABOVE %SN TO... %SN	P(SNS) OF AVGE COMP ATM	SNS VAPOR CU.METERS	INERT GAS REQUIRED CU.METERS	OIL REQD. LITERS
10 TO 9	1.02259E-4	7.59533	76321.4	1655.7
9 TO 8	2.0000913319	7.69496	33736.4	1550.57
8 TO 7	8.13263E-5	7.5677	93289.6	2569.47
7 TO 6	6.000073747	7.45331	105769.	2336.1
6 TO 5	6.000075E-5	7.35156	122345.	2713.25

TOTAL VOLUME OF INERT GAS REQD. = 402011. CU. METERS  
 TOTAL VOLUME OF OIL REQUIRED = 12646.1 LITERS

TEMPERATURE = 1100 DEG. K  
 \*\*\*\*\*

INITIAL SN CONTENT = 10 %

FROM ABOVE %SN TO... %SN	P(SNS) OF AVGE COMP ATM	SNS VAPOR CU.METERS	INERT GAS REQUIRED CU.METERS	OIL REQD. LITERS
10 TO 9	6.25761E-4	6.58336	13711.6	275.315
9 TO 8	5.01511E-4	6.48447	15266.	302.539
8 TO 7	3.000496876	6.34647	16739.5	337.115
7 TO 6	4.31377E-4	6.23171	19352.1	382.345
6 TO 5	6.000366536	6.12337	22147.2	444.692

TOTAL VOLUME OF INERT GAS REQD. = 60706.4 CU. METERS  
 TOTAL VOLUME OF OIL REQUIRED = 1742.17 LITERS

TEMPERATURE = 1200 DEG. K  
 \*\*\*\*\*

INITIAL SN CONTENT = 10 %

FROM ABOVE %SN TO... %SN	P(SNS) OF AVGE COMP ATM	SNS VAPOR CU.METERS	INERT GAS REQUIRED CU.METERS	OIL REQD. LITERS
10 TO 9	2.33155E-3	9.36639	3293.5	60.7111
9 TO 8	0.002539	9.23397	3027.62	66.7680
8 TO 7	0.00224521	9.10524	4046.31	74.475
7 TO 6	1.95016E-3	3.93005	4595.79	84.5336
6 TO 5	1.65385E-3	3.85326	5347.29	98.4204

TOTAL VOLUME OF INERT GAS REQD. = 20915.5 CU. METERS  
 TOTAL VOLUME OF OIL REQUIRED = 384.964 LITERS

TEMPERATURE = 1300 DEG. K  
 \*\*\*\*\*

INITIAL SN CONTENT = 10 %

FROM ABOVE %SN TO... %SN	P(SNS) OF AVGE COMP ATM	SNS VAPOR CU.METERS	INERT GAS REQUIRED CU.METERS	OIL REQD. LITERS
10 TO 9	1.01570E-2	11.1469	988.864	16.3006
9 TO 8	0.00913229	10.0035	1089.	13.502
8 TO 7	3.04439E-3	9.86401	1216.33	20.6653
7 TO 6	6.96323E-3	9.72839	1333.35	23.5034
6 TO 5	5.91577E-3	9.59644	1611.76	27.3636

TOTAL VOLUME OF INERT GAS REQD. = 6259.34 CU. METERS  
 TOTAL VOLUME OF OIL REQUIRED = 106.355 LITERS

TEMPERATURE = 1400 DEG. K  
 \*\*\*\*\*

INITIAL SN CONTENT = 10 %

FROM ABOVE %SN TO... %SN	P(SNS) OF AVGE COMP ATM	SNS VAPOR CU.METERS	INERT GAS REQUIRED CU.METERS	OIL REQD. LITERS
10 TO 9	3.03563E-2	10.9275	349.04	5.50656
9 TO 8	2.71913E-2	10.773	385.422	6.08354
8 TO 7	2.40189E-2	10.6220	431.645	6.80976
7 TO 6	2.06402E-2	10.4767	492.241	7.70574
6 TO 5	1.78547E-2	10.3346	575.039	9.07197

TOTAL VOLUME OF INERT GAS REQD. = 2233.39 CU. METERS  
 TOTAL VOLUME OF OIL REQUIRED = 35.2340 LITERS

TEMPERATURE = 1500 DEG. K

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INITIAL SN CONTENT = 10 %

FROM ABOVE %SN TO... %SN	P(SNS) OF AVGE COMP ATM	SNS VAPOR CU.METERS	INERT GAS REQUIRED CU.METERS	OIL REQRD. LITERS
10 TO 9	7.84058E-2	11.708	137.618	2.02635
9 TO 8	9.0701991	11.5425	152.882	2.25112
8 TO 7	6.19528E-2	11.3516	172.243	2.53019
7 TO 6	5.37568E-2	11.2251	197.587	2.90938
6 TO 5	4.55206E-2	11.0788	232.176	3.41868

TOTAL VOLUME OF INERT GAS REQRD. = 692.505 CU. METERS

TOTAL VOLUME OF OIL REQRD. = 13.1417 LITERS

FUMING SNS FROM SN - FE MATTES  
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THEORETICAL VOLUME OF INERT GAS REQUIRED TO FUME TIN FROM  
 A TIN-IRON MATTE CONTAINING INITIALLY 15 ZSN TO A FINAL  
 MATTE CONTAINING 1 ZSN.

THEORETICAL VOLUME OF OIL REQUIRED TO BE BURNT WITH 25%EXCESS  
 AIR TO PROVIDE THE CALCULATED VOL. OF INERT GAS REQD.

OIL ANALYSIS: 86% C , 11% H , 3% O , S.G..9  
 AIR COMP. : 21% OXYGEN , 79% NITROGEN BY VOLUME

TEMPERATURE = 1000 DEG. K  
 \*\*\*\*\*

INITIAL SN CONTENT = 15 Z

FROM ABOVE ZSN TO... ZSN	P(SNS) OF AVGE COMP ATM	SNS VAPOR CU.METERS	INERT GAS REQUIRED CU.METERS	OIL REQD. LITERS
15 TO 14	1.53266E-4	5.40003	54551.1	1211.49
14 TO 13	1.43213E-4	5.26732	57559.6	1276.53
13 TO 12	1.33066E-4	5.13463	61277.3	1353.42
12 TO 11	1.22835E-4	5.00351	65355.	1444.15
11 TO 10	1.12609E-4	4.87359	70313.6	1553.31
10 TO 9	1.02259E-4	4.74533	76321.4	1685.7
9 TO 8	9.190591631E-5	4.61945	83756.4	1855.57
8 TO 7	8.13253E-5	4.50577	93239.6	2083.47
7 TO 6	7.05373747E-5	4.39335	105769.	2386.1
6 TO 5	6.00575E-5	4.28155	122845.	2773.25
5 TO 4	4.93491E-5	4.17231	147576.	3259.48
4 TO 3	3.85312E-5	4.06493	186515.	4179.52
3 TO 2	2.76333E-5	3.95926	256655.	5669.36
2 TO 1	1.66549E-5	3.85551	423489.	9255.5

TOTAL VOLUME OF INERT GAS REQD. = 1.53263E+6 CU. METERS  
 TOTAL VOLUME OF OIL REQUIRED = 39513.5 LITERS

TEMPERATURE = 1100 DEG. K  
 \*\*\*\*\*

INITIAL SN CONTENT = 15 %

FROM ABOVE %SN TO... %SN	P(SNS) OF AVGE COMP ATM	SNS VAPOR CU. METERS	INERT GAS REQUIRED CU. METERS	OIL REQRD. LITERS
15 TO 14	9.41828E-4	9.24906	9811.07	196.996
14 TO 13	8.79310E-4	9.18835	12349.4	237.835
13 TO 12	8.16452E-4	8.97135	15979.9	225.484
12 TO 11	7.53247E-4	8.83939	11726.2	235.45
11 TO 10	6.89692E-4	8.71078	12621.2	253.421
10 TO 9	6.25781E-4	8.58556	13711.6	275.315
9 TO 8	5.61511E-4	8.46447	15066.	302.589
8 TO 7	5.000496675	8.34647	16789.5	337.115
7 TO 6	4.31877E-4	8.23171	19852.1	382.545
6 TO 5	3.70066516	8.1107	22177.2	442.692
5 TO 4	3.30762E-4	8.01141	26829.1	534.882
4 TO 3	2.84641E-4	7.92562	33684.6	676.35
3 TO 2	1.68148E-4	7.88259	46397.5	931.811
2 TO 1	1.01258E-4	7.78221	76857.4	1527.15

TOTAL VOLUME OF INERT GAS REQRD. = 323023. CU. METERS  
 TOTAL VOLUME OF OIL REQUIRED = 6526.1 LITERS

TEMPERATURE = 1200 DEG. K  
 \*\*\*\*\*

INITIAL SN CONTENT = 15 %

FROM ABOVE %SN TO... %SN	P(SNS) OF AVGE COMP ATM	SNS VAPOR CU. METERS	INERT GAS REQUIRED CU. METERS	OIL REQRD. LITERS
15 TO 14	4.27633E-3	11.0899	2649.38	43.824
14 TO 13	5.33398971	9.98835	2438.57	48.8585
13 TO 12	3.78194E-3	9.78747	2834.89	48.4882
12 TO 11	3.41313E-3	9.64897	8315.72	51.8252
11 TO 10	3.12888E-3	9.51237	3488.42	55.8221
10 TO 9	2.83155E-3	9.38889	3898.5	60.7111
9 TO 8	3.002589	9.28897	3227.62	66.7835
8 TO 7	3.30224581	9.17884	4848.31	74.475
7 TO 6	1.95118E-3	9.98835	4595.79	64.5556
6 TO 5	1.68885E-3	9.88128	5847.29	78.4204
5 TO 4	1.35826E-3	9.78747	6485.26	111.473
4 TO 3	1.05787E-3	9.68481	8147.74	149.965
3 TO 2	7.57187E-4	9.51192	11233.	206.751
2 TO 1	4.55689E-4	9.40221	18430.5	339.226

TOTAL VOLUME OF INERT GAS REQRD. = 76475.2 CU. METERS  
 TOTAL VOLUME OF OIL REQRD. INERT = 1047.89 LITERS

TEMPERATURE = 1300 DEG. K

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INITIAL SN CONTENT = 15 %

FROM ABOVE ZSN TO...	P(SNS) OF AVGE COMP ATM	SNS VAPOR CU. METERS	INERT GAS REQUIRED CU. METERS	OIL REQRD. LITERS
15 TO 14	1.53843E-2	10.9397	699.579	11.0057
14 TO 13	1.43478E-2	10.7644	739.642	12.5664
13 TO 12	0.0133023	10.6031	766.402	13.3622
12 TO 11	1.22569E-2	10.4466	841.35	14.3329
11 TO 10	1.12005E-2	10.2946	908.165	15.4296
10 TO 9	1.01570E-2	10.1469	968.064	16.6006
9 TO 8	0.00910209	10.0035	1009.	18.502
8 TO 7	0.004439E-3	9.86401	1216.33	20.6653
7 TO 6	6.98323E-3	9.72539	1333.35	23.5034
6 TO 5	5.91577E-3	9.59644	1611.76	27.3836
5 TO 4	4.15174E-3	9.47306	1748.02	32.9977
4 TO 3	3.77976E-3	9.37331	2462.51	41.0070
3 TO 2	2.70515E-3	9.22124	3399.55	57.7579
2 TO 1	1.62703E-3	9.10261	5585.34	94.8941

TOTAL VOLUME OF INERT GAS REQRD. = 23654.6 CU. METERS

TOTAL VOLUME OF OIL REQUIRED = 401.891 LITERS

TEMPERATURE = 1400 DEG. K

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INITIAL SN CONTENT = 15 %

FROM ABOVE ZSN TO...	P(SNS) OF AVGE COMP ATM	SNS VAPOR CU. METERS	INERT GAS REQUIRED CU. METERS	OIL REQRD. LITERS
15 TO 14	0.0460952	11.7715	243.603	3.84315
14 TO 13	4.29539E-2	11.5924	255.257	4.07434
13 TO 12	3.93171E-2	11.4167	275.36	4.34415
12 TO 11	3.66697E-2	11.2501	295.547	4.66263
11 TO 10	3.35163E-2	11.0864	319.892	5.04355
10 TO 9	3.03563E-2	10.9275	349.34	5.50058
9 TO 8	2.71910E-2	10.773	385.422	6.03004
8 TO 7	2.40109E-2	10.6220	431.645	6.63976
7 TO 6	2.08402E-2	10.4707	492.241	7.76574
6 TO 5	1.76547E-2	10.3346	575.339	9.07199
5 TO 4	1.44025E-2	10.1963	694.322	10.9617
4 TO 3	1.12633E-2	10.0617	852.252	13.9344
3 TO 2	0.05714E-3	9.93957	1222.59	19.2579
2 TO 1	4.34331E-3	9.8281	2013.90	31.7731

TOTAL VOLUME OF INERT GAS REQRD. = 3421.47 CU. METERS

TOTAL VOLUME OF OIL REQUIRED = 133.10 LITERS

TEMPERATURE = 1500 DEG. K

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INITIAL SN CONTENT = 15 %

FROM ABOVE ZSN TO... ZSN	PC(SNS) OF AVGE COMP ATM	SNS VAPOR CU. METERS	INERT GAS REQUIRED CU. METERS	OIL REQD. LITERS
15 TO 14	8.119313	12.6123	93.0954	1.37379
14 TO 13	8.111147	12.4205	99.3276	1.46255
13 TO 12	8.102974	12.2343	106.576	1.56928
12 TO 11	9.47927E-2	12.3537	115.105	1.69467
11 TO 10	3.66036E-2	11.8733	125.279	1.84468
10 TO 9	7.84353E-2	11.705	137.613	2.02625
9 TO 8	0.0701991	11.5425	152.882	2.25112
8 TO 7	6.19823E-2	11.3516	172.243	2.53619
7 TO 6	5.37563E-2	11.2251	197.537	2.90938
6 TO 5	4.55286E-2	11.0725	232.176	3.41865
5 TO 4	3.72739E-2	10.9246	282.167	4.15477
4 TO 3	2.93164E-2	10.7554	363.747	5.31134
3 TO 2	2.07475E-2	10.6399	532.13	7.39437
2 TO 1	1.24679E-2	10.533	831.9	12.2493

TOTAL VOLUME OF INERT GAS REQD. = 3408.55 CU. METERS  
 TOTAL VOLUME OF OIL REQUIRED = 55.1942 LITERS

FUMING SNS FROM SN - FE MATTES  
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THEORETICAL VOLUME OF INERT GAS REQUIRED TO FUME TIN FROM  
 A TIN-IRON MATTE CONTAINING INITIALLY 15 %SN TO A FINAL  
 MATTE CONTAINING 5 %SN.

THEORETICAL VOLUME OF OIL REQUIRED TO BE BURNT WITH 25%EXCESS  
 AIR TO PROVIDE THE CALCULATED VOL. OF INERT GAS REQD.

OIL ANALYSIS: 86%C , 11%H , 3%O , S.G. .9  
 AIR COMP. : 21%OXYGEN , 79%NITROGEN BY VOLUME

TEMPERATURE = 1000 DEG. K  
 \*\*\*\*\*

INITIAL SN CONTENT = 15 %

FROM ABOVE %SN TO... %SN	P(SNS) OF AIR COMP ATM	SNS VAPOR CO. METERS	INERT GAS REQUIRED CO. METERS	OIL REQD. LITERS
15 TO 14	1.53263E-4	6.47523	54351.1	1211.47
14 TO 13	1.48913E-4	6.29101	57639.3	1273.33
13 TO 12	1.33856E-4	6.18622	61277.3	1353.42
12 TO 11	1.22335E-4	6.05541	65335.	1444.13
11 TO 10	1.12609E-4	7.91759	70313.3	1533.31
10 TO 9	1.02259E-4	7.53333	77321.4	1633.7
9 TO 8	9.0000913319	7.00495	83736.4	1833.37
8 TO 7	8.13233E-5	7.5377	93239.6	2133.47
7 TO 6	8.330073747	7.40331	103769.	2333.1
6 TO 5	6.00075E-5	7.33133	122343.	2713.23

TOTAL VOLUME OF INERT GAS REQD. = 791643. CO. METERS  
 TOTAL VOLUME OF OIL REQUIRED = 17435. LITERS

TEMPERATURE = 1100 DEG. K  
 \*\*\*\*\*

INITIAL SN CONTENT = 15 %

FROM ABOVE ZSN TO... ZSN	P(SNS) OF AVGE COMP ATM	SNS VAPOR CU. METERS	INERT GAS REQUIRED CU. METERS	OIL REQD. LITERS
15 TO 14	9.41823E-4	9.24906	9811.37	196.996
14 TO 13	8.79318E-4	9.13335	10349.4	207.885
13 TO 12	8.16452E-4	8.97185	10979.9	220.464
12 TO 11	7.53247E-4	8.83939	11726.2	235.45
11 TO 10	6.89692E-4	8.71975	12621.2	253.421
10 TO 9	6.25741E-4	8.5952	13711.6	275.315
9 TO 8	5.61511E-4	8.47477	15066.	302.577
8 TO 7	4.98849E-4	8.34647	16789.5	337.115
7 TO 6	4.31877E-4	8.23171	19052.1	382.545
6 TO 5	3.60036E-4	8.12007	22147.2	444.692

TOTAL VOLUME OF INERT GAS REQD. = 142254. CU. METERS  
 TOTAL VOLUME OF OIL REQUIRED = 2356.31 LITERS

TEMPERATURE = 1200 DEG. K  
 \*\*\*\*\*

INITIAL SN CONTENT = 15 %

FROM ABOVE ZSN TO... ZSN	P(SNS) OF AVGE COMP ATM	SNS VAPOR CU. METERS	INERT GAS REQUIRED CU. METERS	OIL REQD. LITERS
15 TO 14	4.27633E-3	10.7399	2349.35	43.242
14 TO 13	3.90395E-3	9.98635	2480.57	45.6565
13 TO 12	3.78194E-3	9.75747	2634.59	48.4822
12 TO 11	3.41355E-3	9.64097	2815.72	51.5252
11 TO 10	3.12255E-3	9.53267	3033.42	55.6321
10 TO 9	2.83155E-3	9.36139	3293.5	60.7111
9 TO 8	2.50253E-3	9.23397	3627.62	66.7555
8 TO 7	2.20224E-3	9.13524	4046.31	74.475
7 TO 6	1.95316E-3	8.96625	4595.79	84.5356
6 TO 5	1.65335E-3	8.85326	5347.29	98.4254

TOTAL VOLUME OF INERT GAS REQD. = 34225.7 CU. METERS  
 TOTAL VOLUME OF OIL REQUIRED = 627.322 LITERS

TEMPERATURE = 1300 DEG. K

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INITIAL SN CONTENT = 15 %

FROM ABOVE ZSN TO...	P(SNS) OF AVGE COMP ATM	SNS VAPOR CU.METERS	INERT GAS REQUIRED CU.METERS	OIL REQRD. LITERS
15 TO 14	1.53543E-2	10.9337	699.579	11.3357
14 TO 13	1.43448E-2	10.7644	739.642	12.5664
13 TO 12	0.0133023	10.6031	786.482	13.3622
12 TO 11	1.22569E-2	10.4466	841.85	14.3029
11 TO 10	1.12085E-2	10.2946	908.165	15.4296
10 TO 9	1.11571E-2	10.1469	985.864	16.8006
9 TO 8	0.00911219	10.0035	1075.	18.4111
8 TO 7	8.04409E-3	9.86451	1216.33	20.2653
7 TO 6	6.96323E-3	9.72339	1383.38	23.5034
6 TO 5	5.91377E-3	9.59644	1611.76	27.3536

TOTAL VOLUME OF INERT GAS REQRD. = 10265.1 CU. METERS

TOTAL VOLUME OF OIL REQUIRED = 174.402 LITERS

TEMPERATURE = 1400 DEG. K

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INITIAL SN CONTENT = 15 %

FROM ABOVE ZSN TO...	P(SNS) OF AVGE COMP ATM	SNS VAPOR CU.METERS	INERT GAS REQUIRED CU.METERS	OIL REQRD. LITERS
15 TO 14	0.0460952	11.7715	243.633	3.84315
14 TO 13	4.29539E-2	11.5904	253.257	4.37434
13 TO 12	3.95171E-2	11.4187	273.36	4.84416
12 TO 11	3.66697E-2	11.2501	295.547	4.66203
11 TO 10	3.35163E-2	11.0804	319.092	5.14355
10 TO 9	3.03566E-2	10.9275	343.804	5.57056
9 TO 8	2.71910E-2	10.779	368.722	6.00554
8 TO 7	2.40109E-2	10.6225	431.645	6.30976
7 TO 6	2.08402E-2	10.4707	492.241	7.76574
6 TO 5	1.76547E-2	10.3246	575.009	9.07199

TOTAL VOLUME OF INERT GAS REQRD. = 3025.35 CU. METERS

TOTAL VOLUME OF OIL REQUIRED = 57.2024 LITERS

TEMPERATURE = 1500 DEG. K

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INITIAL SN CONTENT = 15 %

FROM ABOVE ZSN TO... ZSN	P(SNS) OF AVGE COMP ATM	SNS VAPOR CU.METERS	INERT GAS REQUIRED CU.METERS	OIL RECD. LITERS
15 TO 14	0.119313	12.6123	93.0954	1.37079
14 TO 13	0.111147	12.4235	99.3276	1.46255
13 TO 12	0.102974	12.2343	106.576	1.56923
12 TO 11	9.47927E-2	12.0537	115.105	1.69457
11 TO 10	8.66036E-2	11.8733	125.279	1.84483
10 TO 9	7.84055E-2	11.703	137.616	2.02635
9 TO 8	0.0701991	11.5425	152.882	2.25112
8 TO 7	6.19823E-2	11.3816	172.243	2.53619
7 TO 6	5.37563E-2	11.2251	197.587	2.93933
6 TO 5	4.55203E-2	11.0726	232.176	3.41363

TOTAL VOLUME OF INERT GAS RECD. = 1431.39 CU. METERS  
 TOTAL VOLUME OF OIL REQUIRED = 21.3607 LITERS