

**THERMODYNAMICS AND PHASE EQUILIBRIA ON TIN CONTAINING
SULPHIDE SYSTEMS**

BY

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ABSTRACT

A study of phase relations and thermodynamic properties in iron, tin, sulphide system was conducted.

High temperature phase relations in the FeS-SnS system were established by quenching samples equilibrated in evacuated and sealed silica capsules. FeS-SnS phase diagram was drawn. The eutectic temperature is 815 °C with composition at $X_{SnS} = 0.767$. SnS activities were obtained at 1273, 1373, 1473 K by dew-point method and in accordance with the phase diagram positive deviations were observed.

Within the Fe-Sn-S ternary system, the boundaries of the immiscibility region together with the tie-line distributions were established at 1473 K also by quenching experiments. Activities of Fe, Sn and S along the miscibility gap were calculated by utilizing the bounding binary thermodynamics, phase equilibria and tie-lines.

ACHIEVEMENTS

FeS-SnS phase diagram was redrawn. Activities of SnS in FeS-SnS melts at 1000°, 1100°, 1200°C were measured and modelled.

Within the Fe-Sn-S ternary system, the boundaries of the ternary miscibility gap were found at 1200 °C. Activities of Fe, Sn, and S along the miscibility gap were calculated.

DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the Master of Science in Engineering at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

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CONTENTS

Abstract	i
Achievement	ii
Declaration	iii
Acknowledgments	iv
Contents	v
List of Tables	vi
List of Figures	vii
 1 INTRODUCTION	 1
2 REVIEW OF LITERATURE	4
2.1 PHASE RELATIONS	4
2.1.1 THE SYSTEM FeS-SnS	4
2.1.2 THE SYSTEM Fe-Sn-S	6
2.2 THERMODYNAMICS	15
2.2.1 THE SYSTEM FeS-SnS	15
2.2.2 THE SYSTEM Fe-Sn-S	20
3 EXPERIMENTAL METHODS AND PROCEDURE	25
3.1 GENERAL REMARKS ON EXPERIMENTAL PROCEDURE	25
3.2 DETAILS	25
3.3 STARTING MATERIALS	26
3.4 FURNACES AND TEMPERATURE CONTROL	27
3.5 PRINCIPLES OF DEW-POINT TECHNIQUE	32
3.6 PREPARATION OF DEW-POINT PROBES	33
3.7 MEASUREMENT OF DEW-POINT TEMPERATURE	34
3.8 PROCEDURE FOR QUENCHING EXPERIMENT	35
3.9 CHEMICAL ANALYSES PROCEDURE	37
4 EXPERIMENTAL RESULTS AND DISCUSSION	39
4.1 PHASE EQUILIBRIA	39
4.1.1 PRESENTATION OF RESULTS IN FeS-SnS SYSTEM ..	39
4.1.2 DISCUSSION OF RESULTS IN FeS-SnS SYSTEM	41
4.1.3 PRESENTATION OF RESULTS IN Fe-Sn-S SYSTEM ..	44
4.1.4 DISCUSSION OF RESULTS IN Fe-Sn-S SYSTEM	47
4.2 THERMODYNAMICS	48
4.2.1 PRESENTATION OF RESULTS IN FeS-SnS SYSTEM ..	48
4.2.2 DISCUSSION OF RESULTS IN FeS-SnS SYSTEM ...	59
4.2.3 PRESENTATION AND DISCUSSION OF RESULTS IN Fe-Sn-S SYSTEM	61
5 SUMMARY AND CONCLUSION	75
6 REFERENCES	77
7 APPENDIX	81

List of Tables

Table 1a	Experimental data of FeS-SnS Binary System	.. 40
Table 1b	SEM EDAX Results of FeS-SnS Binary System	... 40
Table 2a	Experimental Data on Tie-Lines of Fe-Sn-S System at 1200°C	45
Table 2b	Experimental Data on Tie-Lines of the Fe-Sn-S System at 1200°C on Fe Rich Side	45
Table 3a	Dew-Point Temperatures in FeS-SnS at 1200 °C	. 54
Table 3b	Dew-Point Temperatures in FeS-SnS at 1100 °C	. 54
Table 3c	Dew-Point Temperatures in FeS-SnS at 1000 °C	. 55
Table 4.	The results of activity calculations	70

List of Figures

Figure 1. FeS-SnS phase diagram	5
Figure 2. Sn-SnS Phase Diagram	7
Figure 3. Fe-S phase diagram	10
Figure 4. Fe-Sn Phase diagram	11
Figure 5. Fe-Sn-S liquidus projection	12
Figure 6. Fe-Sn-S isothermal section at 873 K	13
Figure 7. Fe-Sn-S isothermal section at 723 K	14
Figure 8. Activities in FeS-SnS system	18
Figure 9. Sn-SnS Activity Curves	21
Figure 10. Fe-Sn Activity Curves	23
Figure 11. Vertical Section of the Dew-point Furnace ..	28
Figure 12. Electrical Circuitry of the Dew-Point Furnace	30
Figure 13. Typical Temperature Profile of the DPF	31
Figure 14. FeS-SnS Phase diagram of Present Study	43
Figure 15. Tie-lines in Fe-Sn-S Melts	46
Figure 16. FeS-SnS Activity curves of present study ..	57
Figure 17. Alpha function of SnS versus mole fraction of SnS	58
Figure 18. Schematic of an isothermal section in A-B-C system	63
Figure 19. Activity coefficient of Fe versus mole fraction of Fe	68
Figure 20a Iso-activities of Fe in Fe-Sn-S melts at 1200 °C	71
Figure 20b Iso-activities of Sn in Fe-Sn-S melts at 1200 °C	72
Figure 20c Iso-activities of S in Fe-Sn-S melts at 1200 °C	73
Figure A.1a Integration Function for Fe activities ..	82
Figure A.2lb Integration function for Sn activities ..	83
Figure A.2lc Integration function for S activities ...	84

1 INTRODUCTION

Tin ores in the world are getting leaner in their tin contents. It is well known that tin smelting of oxide ores requires a two-stage operation due to the difficulties encountered in the separation of tin from iron. This is due to similar thermodynamic stabilities of both oxides SnO and FeO . As tin ores are getting leaner in tin, due to relative increases in Fe/Sn ratio, the above mentioned separation problem increases its magnitude. Here comes the advantage of sulphur containing systems. SnS is a relatively volatile compound, and thus tin can be separated from the bulk of the ore or concentrate by vaporization when favorable conditions are provided. This process is known as the fuming technique and involves first the sulphidization of tin oxides in the concentrate by pyrite additions at smelting temperatures. Thus an iron-tin matte is formed and subsequently SnS is evaporated. For this process to operate satisfactorily basic information, that is phase equilibria and thermodynamics of the FeS-SnS system should be known. For example if positive deviation exists in thermodynamic behavior of FeS-SnS mattes, this will help the fuming process. If negative deviation exists, special precautions must be devised. Afterwards the equilibrium of this matte system with the slag system should be delineated for actual process conditions because inevitably iron-tin mattes will not be stoichiometric sulphide solutions. They will probably dissolve oxygen in them and thus be sulphur deficient. This condition will mean that the composition of these mattes will end-up within the ternary field of the Fe-Sn-S system, on which no information exists. This is particularly important as Sn-SnS and Fe-Sn systems are characterized by large liquid miscibility gaps at smelting temperatures which will definitely extend to the ternary field and possibly join therein. The boundaries of immiscibility and thus phase relations should be determined as

this will have direct process implications. The distribution of tie lines within this two liquid region are also essential because these will give the compositions of sulphur deficient mattes in equilibrium with metallic phase containing both tin and iron. From a process point of view such an equilibrium may be favorable if the direction of conjugation lines dictate an acceptable level of iron dissolved in tin. If not, such an equilibrium may be avoided by careful control of fuming furnace atmosphere and proper adjustment of matte and slag composition.

It is apparent that SnS is one of the most critical constituents along with FeS in matte fuming operations to extract metallic tin from low grade ores. Almost equally important are the liquid systems containing Fe, FeS and Sn together with SnS for a better understanding of the extraction and refining processes.

The systems involving SnS and FeS are also of interest to researchers belonging to fields other than metallurgy. Geochemists, for example, contributed to much of the understanding of phase equilibria in such systems with the aim of establishing the rock formation behavior of sulphides. Materials Scientists, on the other hand, generated a substantial amount of solid state thermodynamic data with respect to semiconducting properties of sulphide compounds. The liquidus curves and pertinent phase equilibria data in binary and ternary metal-sulphur systems are also of particular interest to those concerned with the growth and perfection of these semiconducting compounds.

For a binary or ternary solution phase, many diverse sets of experimental thermodynamic data may be available. Activity of one or more components of various compositions and temperatures may have been measured by electromotive force, vapor pressure, mass spectrometric or other techniques. Enthalpies of mixing may have been determined calorimetrically. The experimental

data. If the standard Gibbs Free Energy of fusion of a stoichiometric component is known, for example, then the activity of this component in the liquid phase can be calculated even nonisothermally along its liquidus. Miscibility gap is also a source of thermodynamic data, since the activity of either component is the same at both ends of tie-line, even though the actual values of the activities may not be known.

The aim of this work is to generate thermodynamic data on Fe-Sn-S ternary and FeS-SnS pseudo-binary systems by using the Dew-Point and classical equilibration-quenching techniques of thermochemical research. The dew-point technique rely upon the high volatility of a component in a metallic or non-metallic solution. The measurements are conducted in a closed system where the advantage is taken from evaporation and condensation phenomena which become a problem in experiments using open systems.

The plan of work is designed to obtain specific information with respect to the following.

A) The direction of conjugation lines between the coexisting liquid sulphide and liquid metal phases by quenching experiments at 1200 °C and thus determine the boundaries of the immiscibility region (Phase Equilibria Study).

B) Activities of SnS in SnS-FeS melts at 1200 °C through the Dew-Point measurement (Thermodynamic Study).

C) Calculation and modelling of liquid solutions in the Fe-Sn-S system where results permit.

The information gathered in the steps described above would be applicable to the analysis of the thermodynamics of the Fe-FeS-SnS-Sn portion of the mother Fe-Sn-S ternary system.

2 REVIEW OF LITERATURE

2.1 PHASE RELATIONS

Many ternary systems of extractive metallurgical interest consist of two metals and one nonmetal such as oxygen or sulphur. In the liquid state, two metals are usually completely soluble in each other, while the miscibility gaps often form in the metal-oxygen or metal sulphur binaries, with the immiscibility region extending into the ternary compositions. Usually the composition of one of the liquid phases lies quite close to the pure metal component. For many of the systems, the only information available is that of the tie line distributions in the two liquid phase fields of the ternary systems.

The information available in literature on systems pertinent to the present study is presented in the following.

2.1.1 THE SYSTEM FeS-SnS

SnS-FeS Phase diagram was first constructed by Haan¹ in 1913. Secondly, phase diagram of this system, on the assumption of no solid solubility of either component and regular solution behavior of the liquid matte phase was constructed showing liquidus curves, from vapor pressure measurements by Davey and Joffe² in 1972. Both phase diagrams are reproduced in Figure 1. The FeS-SnS binary system is characterized by a single eutectic invariant at 797 °C and 18.4 weight percent FeS according to Davey and Joffe². At 1200 °C both sulphides form continuous homogeneous liquid solution. As seen in Figure 1, Haan's¹ experimental points tend to lie somewhat lower than Joffe and Davey's² calculated liquidus. The agreement can be

considered fairly good. The greatest deviation of Haan's¹ points from Dawey and Joffre's² calculated liquidus is around 50 to 60 percent FeS.

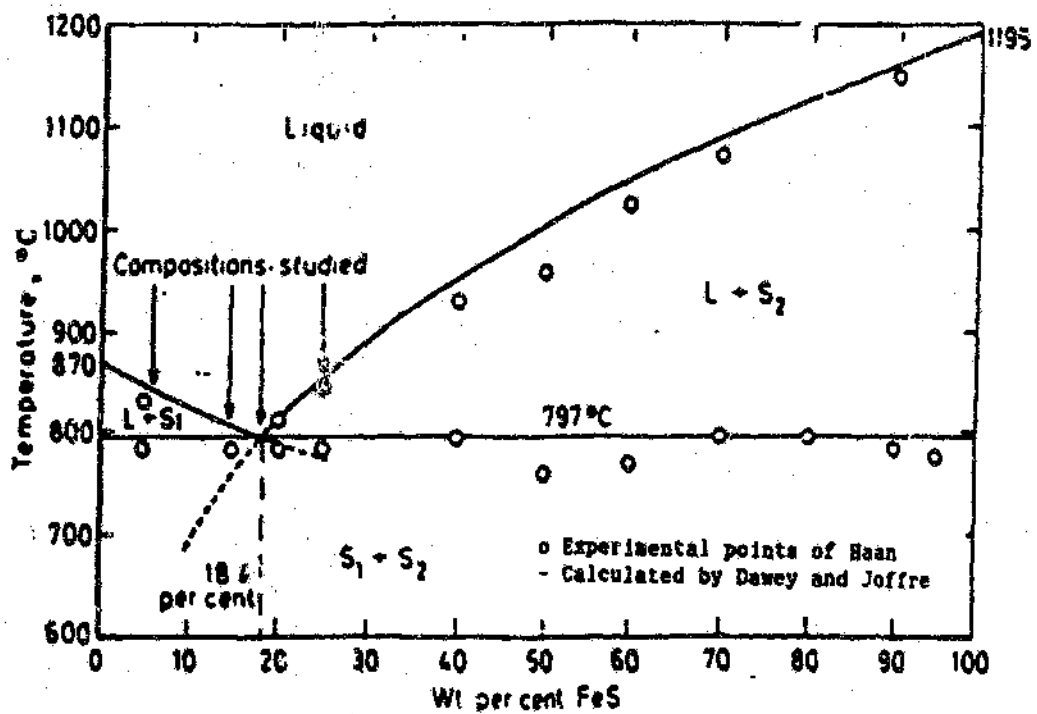


Figure 1. SnS-FeS Phase diagram from vapour measurements. L: liquid phase, S₁: SnS, S₂: FeS. After Haan¹ and Dawey and Joffre.²

2.1.2 THE SYSTEM Fe-Sn-S

In the Fe-Sn-S ternary system, the bounding binaries Fe-FeS, Fe-Sn are quite well known, whereas Sn-SnS have recently been established by Eric³ and Bilgin and Eric⁷.

The system Sn-SnS which is of interest in tin metallurgy is a part of the main Sn-S binary. Eric³ has applied the Regular Associate Solution model (RAS) to this binary system and constructed a model phase diagram. Sn rich eutectic is at 232 °C. The RAS model predicts a stable miscibility gap with a critical temperature of 1090 °C and a monotectic temperature of 860 °C. The liquidus data for this system was mainly from compilations of Hansen⁴ and Elliott⁵ but the solubility measurement of sulphur in Sn from Cheng and Alcock⁶, were also taken into consideration through the following equation, valid in the temperature range 500-600 °C.

$$\text{Log atom \%S in Sn(l)} = -3225/T + 3.40 \dots\dots(1)$$

Recently Sn-SnS system were examined experimentally by quenching technique by Bilgin and Eric⁷. The system was found to form a large miscibility gap above 860 °C. The phase diagram is reproduced Figure 2. The agreement between the two diagrams reported by Eric³ and Bilgin and Eric⁷ is quite good apart from the boundaries of the miscibility gap. The experimental diagram⁷ does not show a critical temperature for the closure of the gap where else the calculated one³ shows. This can be attributed to the inevitable assumptions inherit in the Regular Associated Solution model.

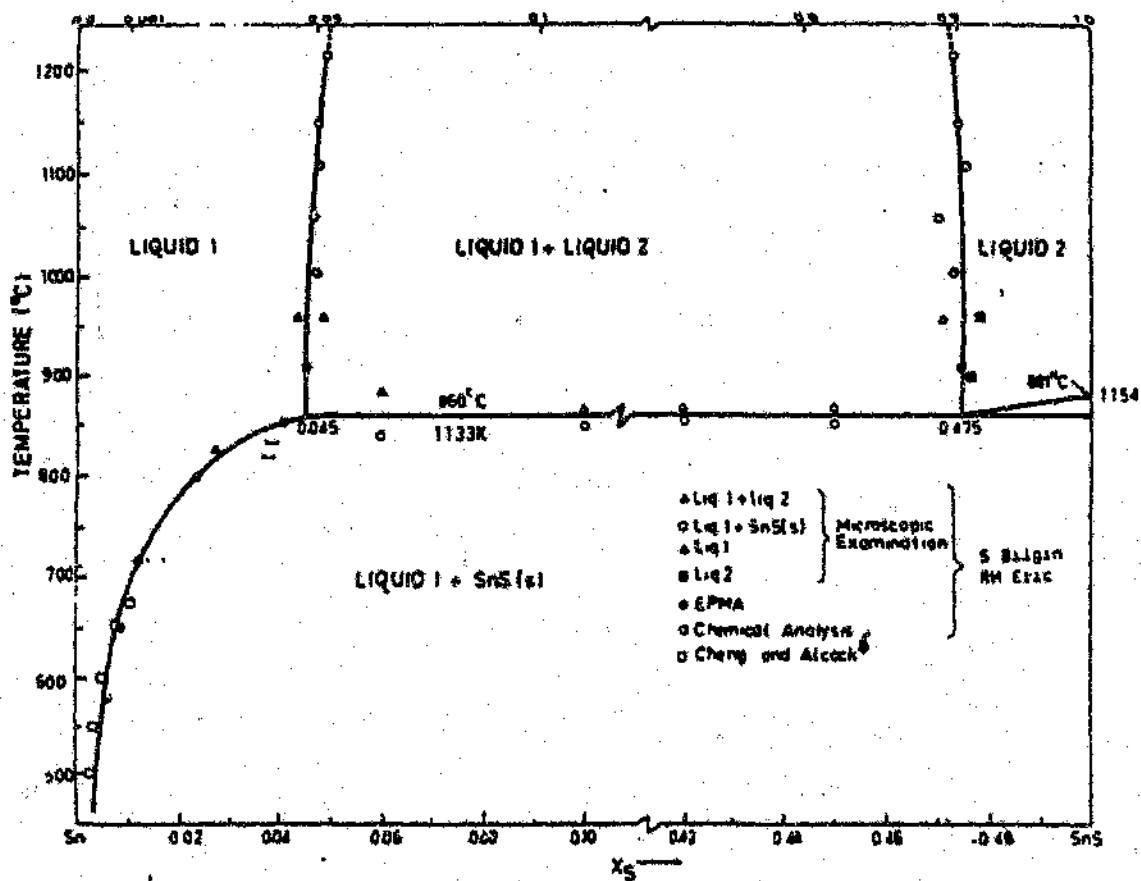


Figure 2. Sn-SnS phase diagram. After S Bilgin and RH Eric⁷.

The thermodynamic and phase equilibrium data of the subsystem Fe-FeS of the Fe-S binary were evaluated by Hillert and Staffanson⁸ taking pyrrhotite to be a stoichiometric compound at equal atomic fraction of the components Fe and S. Subsequently, the data for the entire system were evaluated by Sharma and Chang⁹ taking into consideration the homogeneity range of pyrrhotite. For the liquid phase, Sharma and Chang⁹ used an associated solution model in order to account for the rapid change of the component activities in the vicinity of equal atomic composition. Recently, Fernandez Guilermant, Hillert, Jansson, and Sundman¹¹ re-evaluated the Fe-S system using a two sublattice model for the liquid and pyrrhotite phases. Chuang, Hsieh, Austin Chang¹² also re-evaluated the Fe-S system, as shown in Figure 3, using the same models as Sharma and Chang⁹ for the liquid and pyrrhotite phase. This is an improvement of an earlier evaluation of Sharma and Chang.

The Fe-Sn phase diagram reviewed by O Kubaschewski¹⁰ is shown in Figure 4. There are ten invariant reactions in this system. At 1130 °C, a monotectic reaction occurs where liquid L decomposes to body centered iron and tin-rich liquid (Sn). The liquid miscibility gap closes at about 50 atom % (68 wt%) Sn and 1525 °C.

The liquidus projection in the Fe-FeS-SnS-S region of the Fe-Sn-S system was studied by MA Sokolova¹⁶. Figure 5 is partly adapted from his data. The primary regions of crystallization are α , γ , $Fe_{(1-x)}S$, SnS , ν , Fe_3Sn_2 , $FeSn$, $FeSn_2$ and Sn . The liquid miscibility gap in the Fe-Sn system, extends only slightly into the triangle and closes on itself at the lower critical point U' . On the other hand, the miscibility gap in the tin rich part of the Sn-S

binary systems extends deep into the ternary region. The eutectic line from e_2 of the FeS-SnS pseudobinary section meets the liquidus bounding this miscibility gap at around 750 °C, where the ternary monotectic reaction M occurs. The eutectic line from e_1 of the Fe-S system is postulated to meet the metatectic line from m_{e1} of the same system around 950 °C at U_1 . The composition of the product liquid from U_1 moves toward the tin corner with decreasing temperature. As many as six invariant reactions involving the tin rich liquid are needed at the tin corner, before the solidification is complete.

Approximate isotherms at 100 °C intervals are drawn in Figure 5 using the results of MA Sokolova¹⁶ and the binary data.

No data are available on the liquidus surface of the FeS-S-SnS region of the ternary system. A hypothetical surface for this region is included in Figure 5. The monotectic univariant lines from the Fe-S and SnS systems meet at U_4 around 800 °C. The final solidification of product liquid L is assumed to occur through a ternary eutectic reaction E_1 at about 700 °C

GH Moh¹⁷ gave two isothermal sections at 600 and 450 °C. Figure 6 and 7 give the isothermal sections at 600 °C and 450 °C, after slight modifications to match the binary data. At 450 °C, Sn, FeSn and FeSn₂ are in divariant equilibrium with $Fe_{(1-x)}S$. In Figure 6 and 7, all SnS compounds are the low temperature α forms. $Fe_{(1-x)}S$ is in divariant equilibrium with FeS₂, SnS₂, Sn₂S₃ and SnS. SnS₂ and FeS₂ are stable only with the most sulphur rich $Fe_{(1-x)}S$.

At the other extreme, almost stoichiometric FeS (troilite) coexists with SnS. Sn₂S₃ is in equilibrium with a range of compositions of $Fe_{(1-x)}S$.

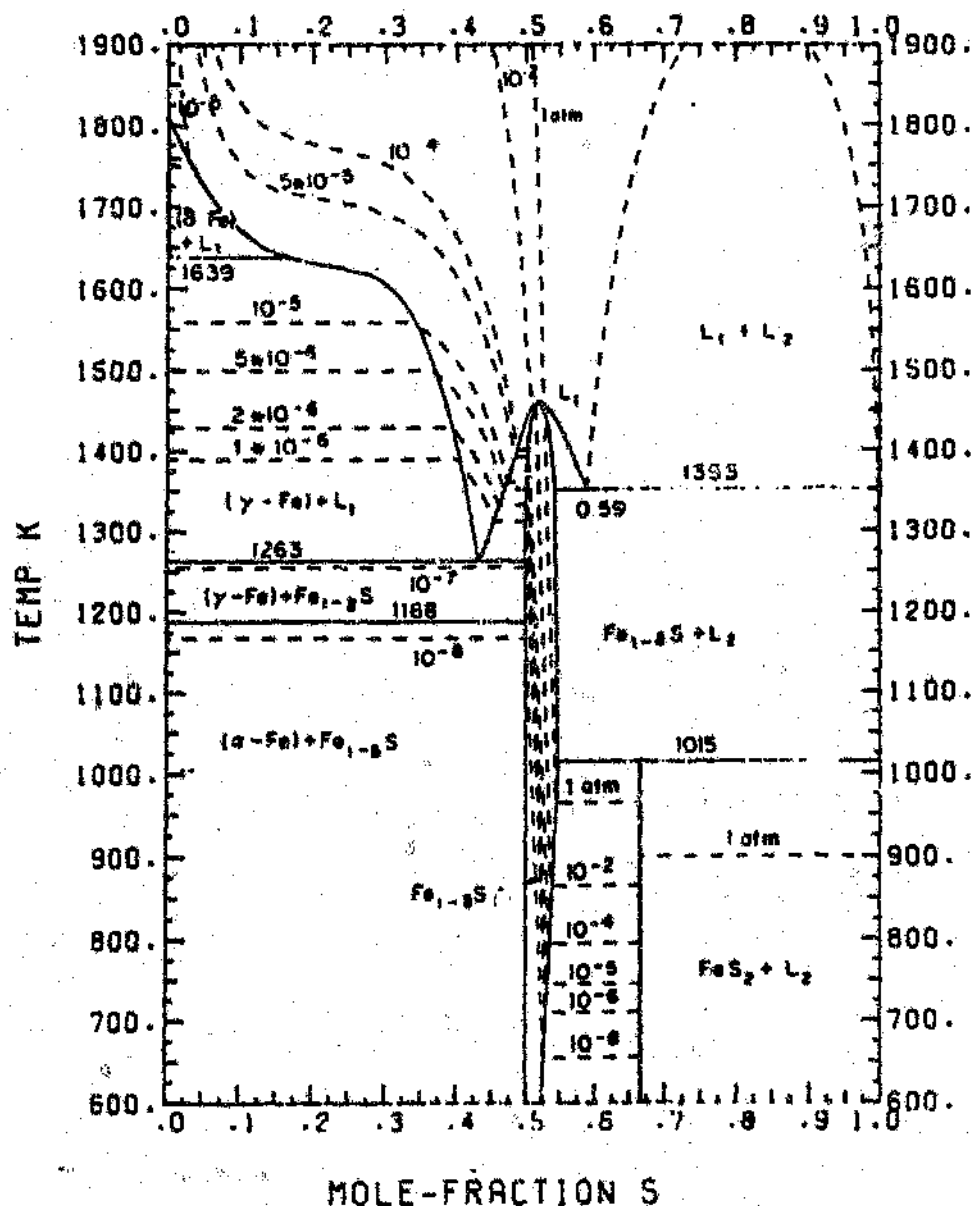


Figure 3. Fe-S phase diagram with isobar values of $S_2(g)$ up to $1 \text{ atm} = 1.01325 \times 10^5 \text{ pa}$. The critical temperature of pure S is 1313 K. After YY Chuang, KC Hsieh and YA Chang¹²

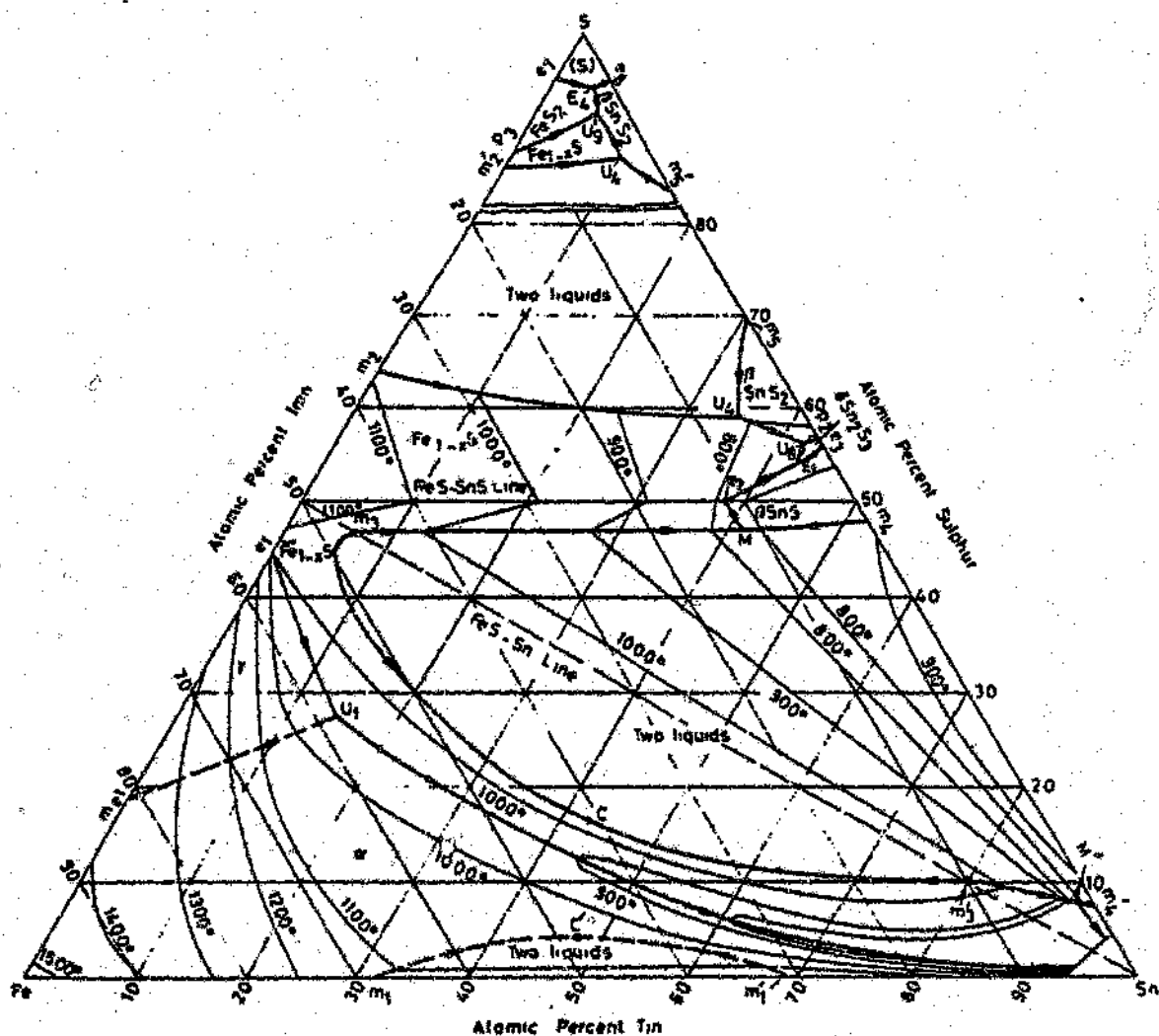


Figure 5. Fe-Sn-S liquidus projection in atomic percent
after MA Sokolova¹⁶

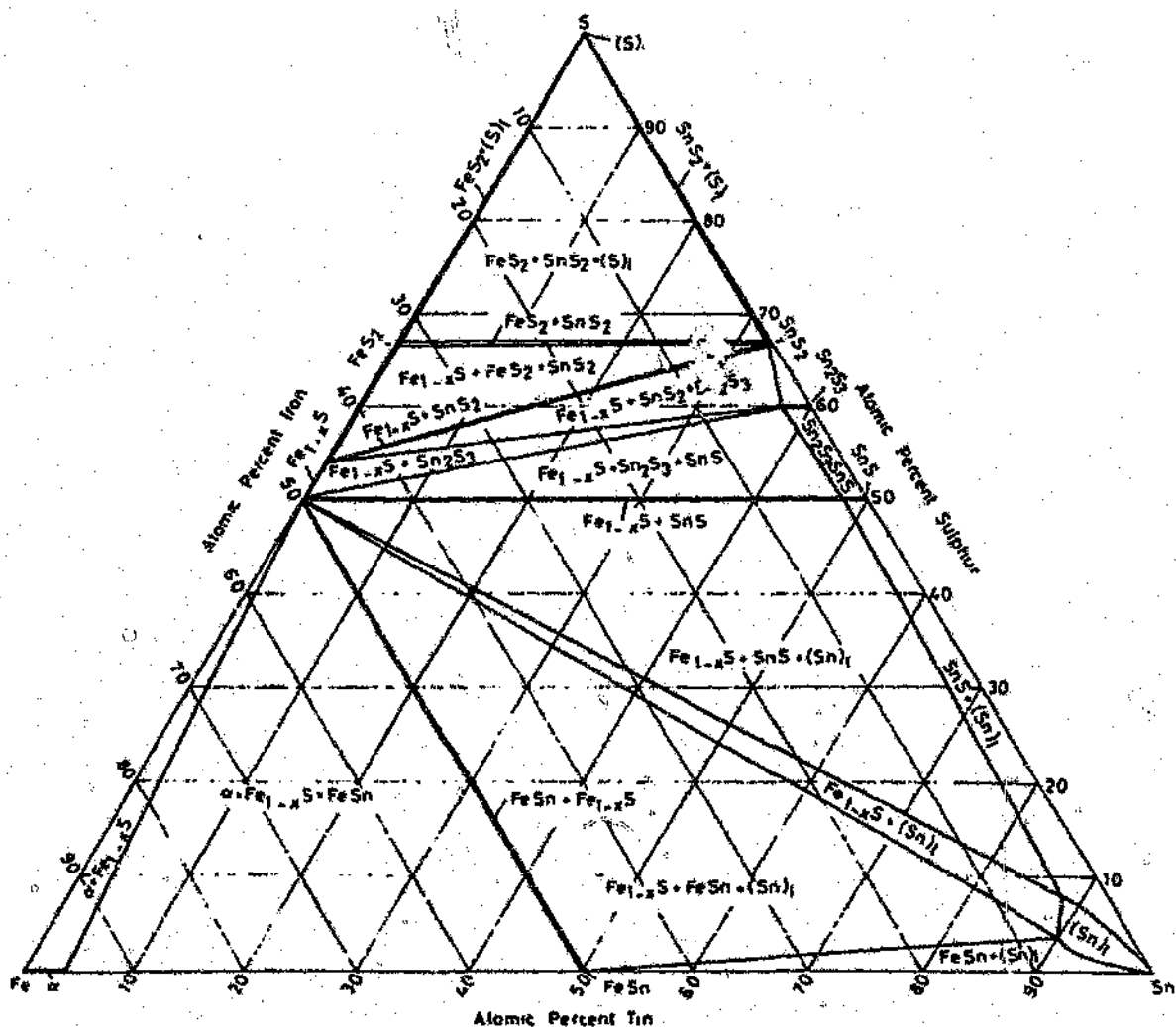


Figure 6. Fe-Sn-S isothermal section at 600 °C in atomic percent after GH Mohl¹⁷

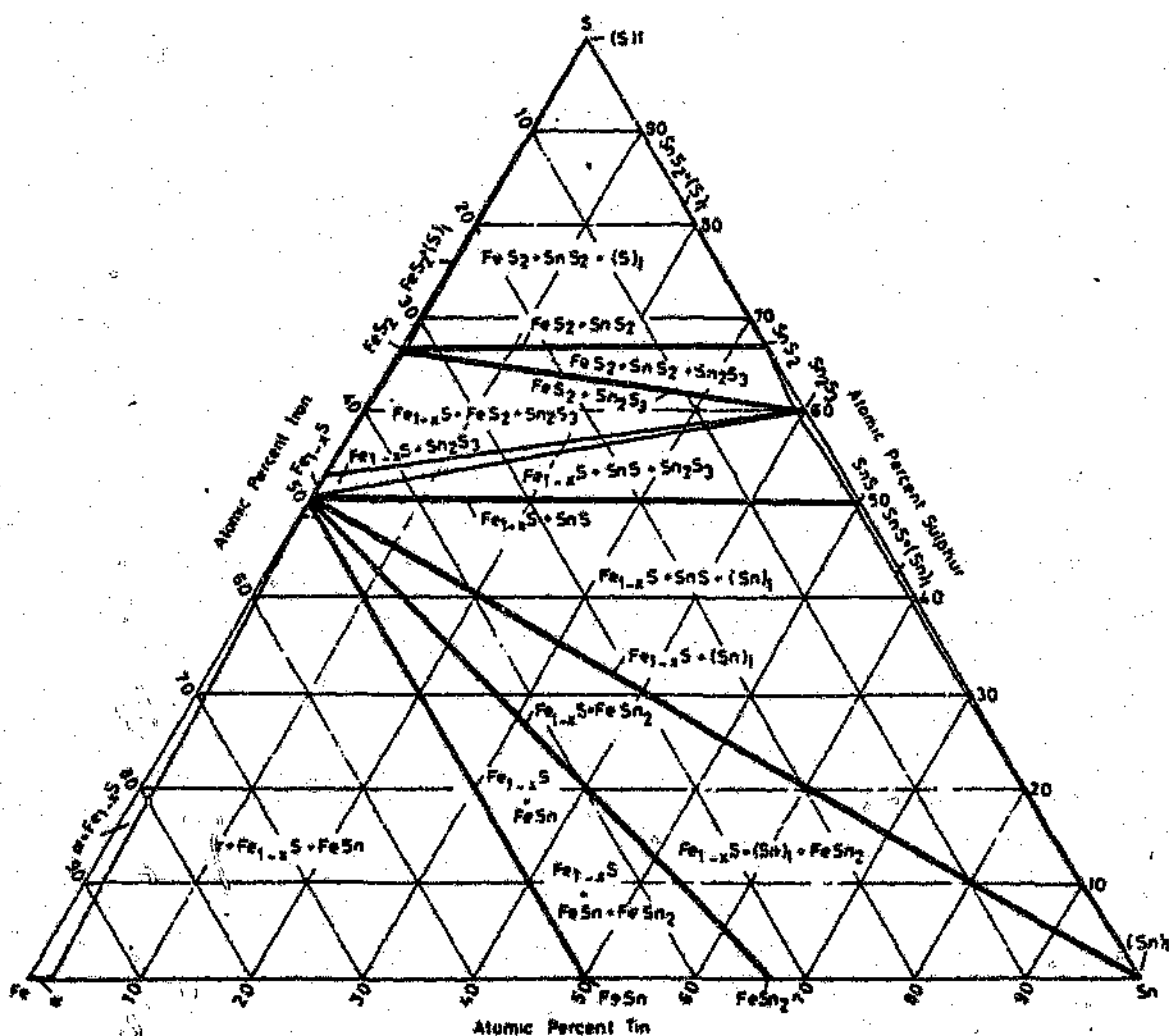


Figure 7. Fe-Sn-S isothermal sections at 450 °C in atomic percent after GH Moh¹⁷

2.2 THERMODYNAMICS

Since the knowledge of high temperature thermodynamic properties of Fe-Sn-S system is essential for a proper understanding of the extraction and refining processes of iron and tin, the available information pertinent to the present work is summarized in the following subsections.

2.2.1 THE SYSTEM FeS-SnS

Tin sulphide is highly volatile and this high volatility is maintained¹³ over a broad range of sulphur pressures. This behavior represents a challenge to the engineer searching for an effective means of separating tin from raw materials.

Davey and Joffre² have determined the vapor pressures of pure SnS, over both solid and liquid forms by the use of transportation method. Their equations are:

$$\log(P_{\text{SnS}}) = -10963/T + 7.64(\text{atm}) \dots (2)$$

$$\log(P_{\text{SnS}}) = -8877/T + 5.81(\text{atm}) \dots (3)$$

Equation 2 is for vaporization of pure solid SnS where else equation 3 is for vaporization of pure liquid SnS. Equations 2 and 3 are reported to be valid in the temperature ranges 975-1143 K and 1143-1500 K, respectively. Thus for the reaction:



The temperature dependence of the standard free energy change in the interval 800-1143 K was formulated as²

$$\Delta G^{\circ} = 209853 - 146.23T \text{ (J/mol)} \dots (5)$$

For the reaction:



The change in standard free energy, in the interval 1143-1500 K was given as²

$$\Delta G^{\circ} = 169921 - 111.21T \text{ (J/mol)} \dots (7)$$

For the same vaporization equilibria (reactions 4 and 6) the tabulated data reported by Kellogg¹³ was expressed after a linear regression analysis as

$$\Delta G^{\circ} = 212080 - 147.93T \text{ (J/mol)} (\text{solid SnS}) \dots (8)$$

and

$$\Delta G^{\circ} = 167787 - 109.26T \text{ (J/mol)} (\text{liquid SnS}) \dots (9)$$

The agreement between respective equations 5, 8 and 7, 9 were reported to be excellent.

Kellogg¹³ also reports that the vapor phase is composed of two tin sulphide bearing species, SnS and Sn₂S₂. However the concentration of the dimer Sn₂S₂ gas is very much less as compared to that of monomeric tin sulphide. Using the data given by Kellogg¹³ it can be calculated that, at 1400 K, the vapor pressure of SnS gas over liquid SnS is two orders of magnitude greater than vapor pressure of Sn₂S₂ gas.

The latent heat of fusion of SnS was calculated by Dawey and Joffre² by taking the difference in enthalpy terms of equations (5) and (7), as:

$$\Delta H^\circ_f = 209853 - 169921 = 39932 \text{ (J/mol)} \dots (10)$$

The melting point of SnS is equal to 881 °C. Thus the entropy of fusion is 34.60 J/K-mol, and for the equilibrium:



The standard free energy change can be given as:

$$\Delta G^\circ = 39932 - 34.60T \text{ (J/mol)} \dots (12)$$

Standard free energy change equation yields

$$\ln a_{\text{SnS}} = -\frac{4803}{T} + 4.162 \dots (13)$$

For melting of FeS²



$$\Delta G^\circ = 32310.7 + 22.01T \text{ (J/mol)} \dots (15)$$

$$\ln a_{\text{FeS}} = -\frac{3886.3}{T} + 2.647 \dots (16)$$

Dawey and Joffre² calculated activities of FeS and SnS in these liquid solutions at 800 °C and 1000 °C by using their data on SnS gathered by the transportation method. Their results are reproduced in Figure 8.

There are several expressions on the standard free energy of formation of pure solid and liquid SnS. For the equilibrium:

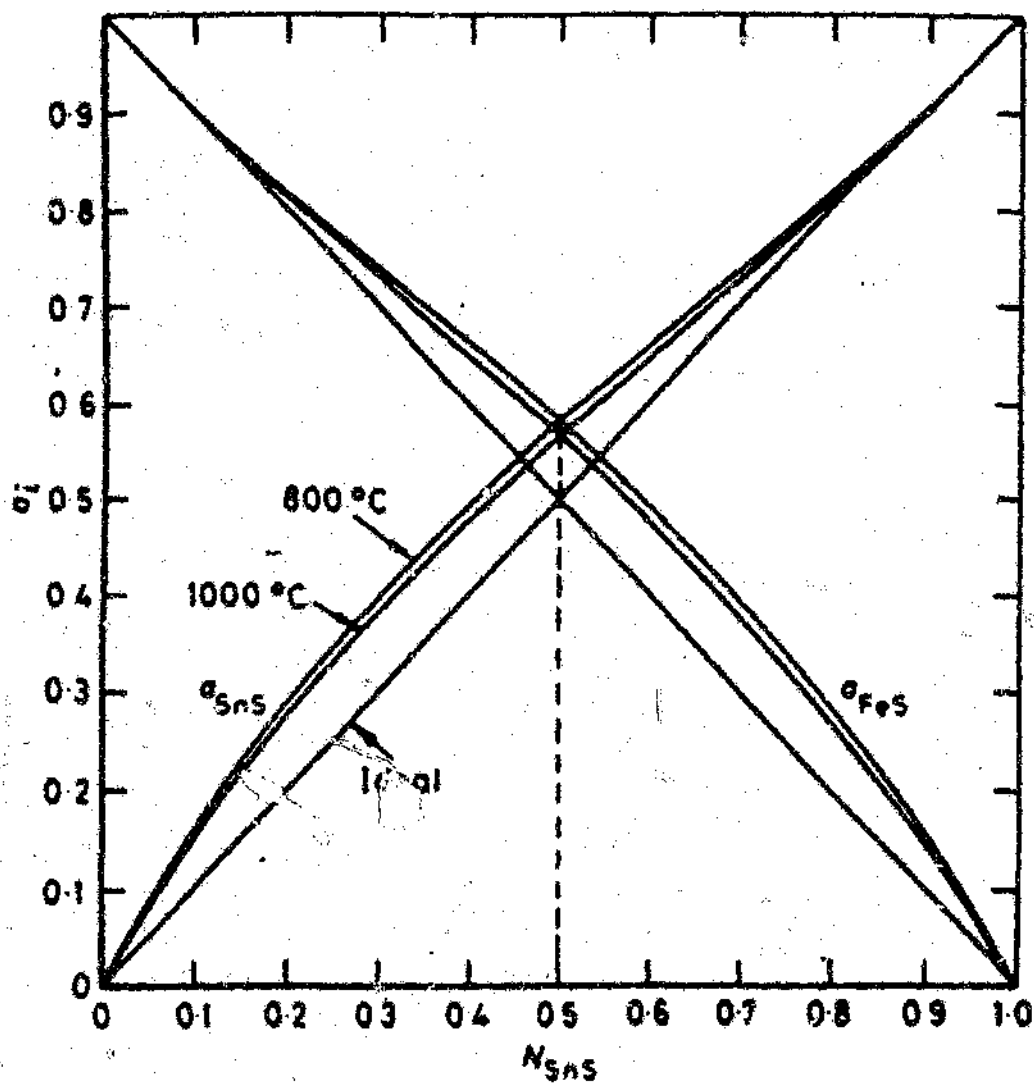
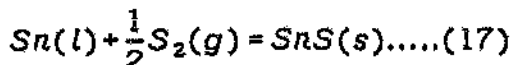


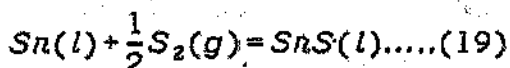
Figure 8. Activities in FeS-SnS system at 800 and 1000 °C after Dawey and Joffre²



The tabulated data given by Elliott and Gleiser¹⁸ when treated by regression analysis yields the following linear equation in the temperature range 505-1154 K:

$$\Delta G^\circ = -144139 + 94.22T (\text{J/mol}) \dots (18)$$

When reactions 11 and 17 and equations 12 and 18 are respectively combined, the standard free energy of formation of liquid SnS can be obtained as:



$$\Delta G^\circ = -104207 + 59.62T (\text{J/mol}) \dots (20)$$

On the other hand, when the tabular data of Kellogg¹³ is treated by regression analysis in temperature range 1200-1500 K, the standard free energy of formation of liquid SnS (for reaction 19) can be directly obtained as the following linear equation:

$$\Delta G^\circ = -133654 + 60.84T (\text{J/mol}) \dots (21)$$

This relationship is in good agreement with that reported by Barin and Knacke¹⁹ for liquid SnS:

$$\Delta G^\circ = -136398 + 59.92T (\text{J/mol}) \dots (22)$$

It can easily be seen that equation 20 predicts almost 27 kJ less values at 1423 K for the standard free energy of formation of liquid SnS than equations 21 and 22. It is estimated that the data given by Elliott and Gleiser¹⁸ are in error. That is because direct vapour pressure measurements of Dawey and Joffre² over pure solid and liquid SnS are in good agreement with the values given by Kellogg¹³.

Therefore their enthalpy of fusion value for SnS seems to be correct. This presumably shows possible errors in the tabulated data of Elliott and Gleiser¹⁸ for the standard free energy of formation of solid SnS. Throughout this investigation equation 12 was employed to calculate the standard free energy of fusion of SnS.

2.2.2 THE SYSTEM Fe-Sn-S

There are no experimentally measured or indirectly calculated activities of components within the ternary field or miscibility gap of the Fe-Sn-S system. In the Fe-Sn-S system, the bounding binaries Fe-FeS, Fe-Sn, Sn-SnS are quite well known.

In literature thermodynamic activities of components of Sn-SnS system is available from the experimental study of Bilgin and Eric⁷. They have measured SnS activities in the Sn-SnS subsystem by using the dew-point technique. This was possible because vapour pressure of Sn is more than three orders of magnitude smaller than the vapour pressure of SnS at temperature above 1000 °C. Their results are shown in Figure 9. Activities of both components of the Sn-SnS system show great positive departures from ideality in accord with the experimentally determined phase diagram. Eric³ has also calculated the activities of SnS and Sn by employing the Regular Associated Solution (RAS) model. The analytical calculations of Eric by RAS model also predict positive departures for activities of components but his values are considerably lower than the experimental values. The reason for this discrepancy lies in the RAS treatment which predicts a stable miscibility gap closing at temperature of 1090 °C.

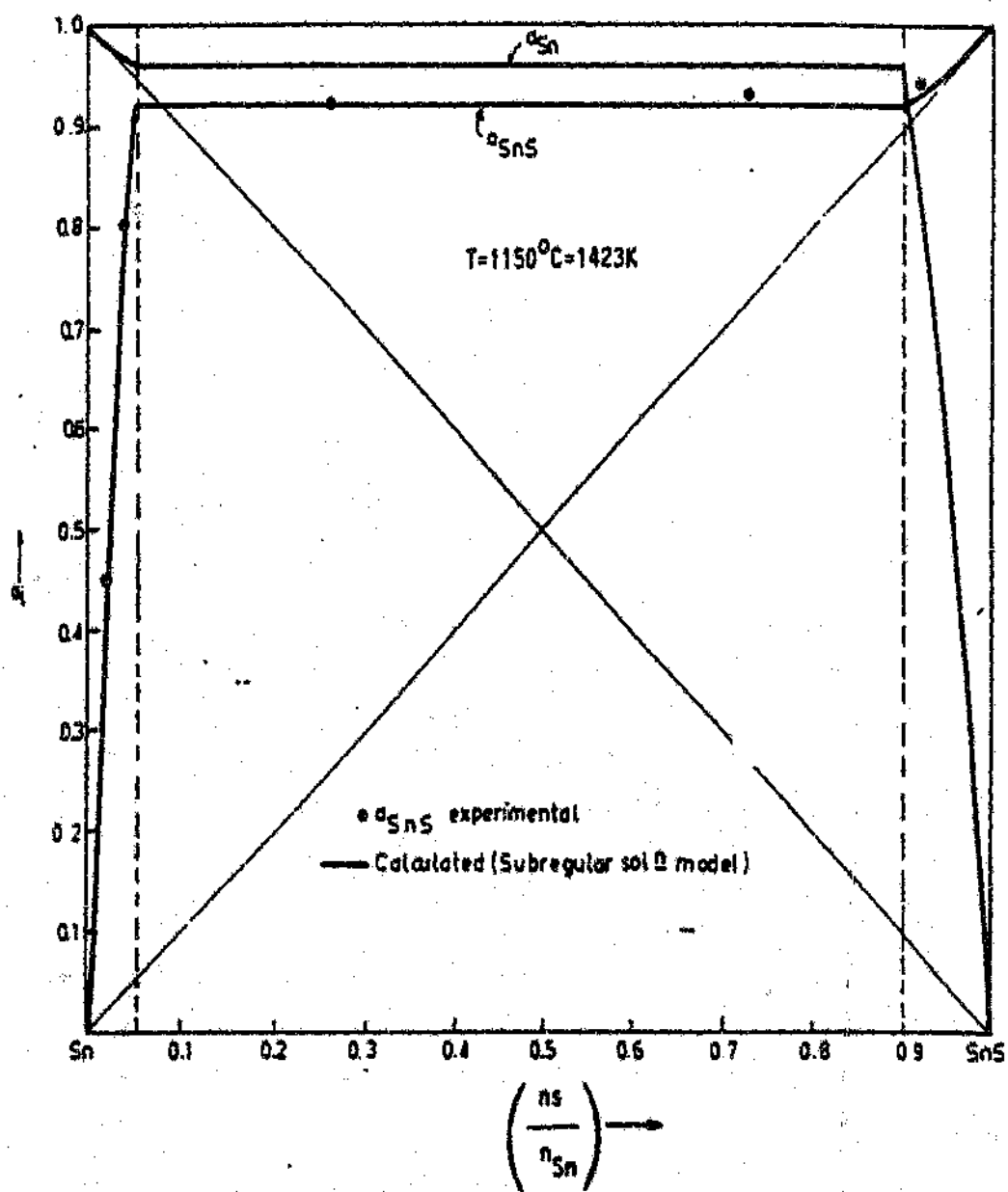


Figure 9. Activity data for Sn-SnS system at 1150°C after S Bilgin and RH Eric⁷

Activity data for the system Fe-Sn have been estimated from the phase diagram by Davey¹⁴. Davey has made calculations on the basis of several models. Davey proposed the following equations as a best estimate for the activity coefficient of iron in iron-tin liquid solution at 1401 K.

$$\log(\gamma_{Fe}) = 0.072 + 0.85N_{Sn}^2 \dots (23)$$

$$\log(\gamma_{Sn}) = 0.85N_{Fe}^2 \dots (24)$$

Above calculation was on the basis of regular solution behaviour at 1401 K. Davey has suggested that iron-tin solutions are regular with respect to the solvent tin and, although the relations for $\log(\gamma_{Sn})$ and $\log(\gamma_{Fe})$ suggest a constant alpha function, this does not prove regular behaviour. Strong positive deviations from ideality exhibited by the Fe-Sn solution and the existence of miscibility gap do not suggest random mixing of iron and tin atoms in the solution and regular behaviour would not be expected. The activity of tin and iron in liquid iron-tin alloys at 1438 K has been determined by vapour pressure measurements by SY Shiraishi and HB Bell¹⁵. The alloys show positive deviations from ideality as shown in Figure 10, as would be expected from the existence of a miscibility gap. The data can be summarized in the expressions:

$$\log(\gamma_{Sn}) = 0.613N_{Fe}^2 - 0.371N_{Fe}^3 \dots (25)$$

$$\log(\gamma_{Fe}) = 1.169N_{Sn}^2 - 0.371N_{Sn}^3 \dots (26)$$

Throughout this investigation, equations 25 and 26 were used.

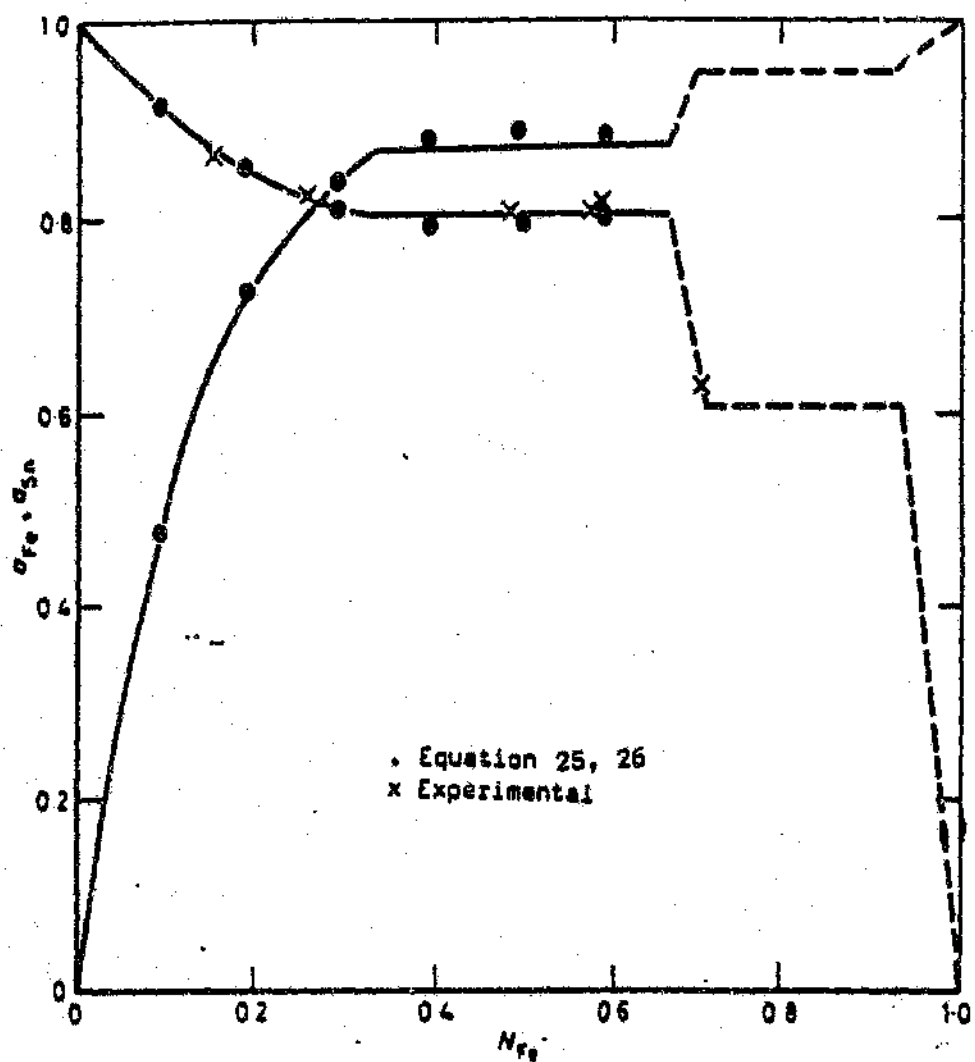


Figure 10. Activity data for Fe-Sn system at 1438 K after SY Shiraishi and HB Bell¹⁵.

The Fe-S binary is characterized by a congruent melting phase, pyrrhotite, at about 50 atomic percent S, an eutectic between Fe and pyrrhotite and a monotectic between pyrrhotite and $S^{20,21}$. The liquidus in equilibrium with Fe at about 20 atomic percent S is rather flat, suggesting a tendency toward immiscibility in the liquid. Pyrrhotite has an ordered NiAs structure ($B8_1$) and exists over a rather large range of homogeneity. The general features of the phase relationships in the Fe-S binary suggests a stable liquid solution around 50 atomic percent S and relatively weak solutions on either side of the equi-atomic composition. The activity data of sulfur in the liquid phase increases monotonously from pure Fe to about 50 atomic percent S and then increases rapidly with composition, similar to that of component in a highly stable solid phase^{22,23}.

3 EXPERIMENTAL METHODS AND PROCEDURE

3.1 GENERAL REMARKS ON EXPERIMENTAL PROCEDURE

Phase equilibrium studies in the systems FeS-SnS and Fe-Sn-S were performed by using the quenching method. For this purpose, samples belonging to these systems were contained in evacuated silica capsules and heated in a vertical tube furnace at selected temperatures until equilibrium phases have developed. The capsules were subsequently quenched into water, and the phases were examined metallographically. Portions of quenched samples were analyzed chemically and by Energy Dispersive Analyses of X Ray in order to ascertain the compositions of phases. The data obtained were used to delineate the liquidus lines in the FeS-SnS system, and the distribution of conjugation lines between co-existing liquids in the Fe-Sn-S system.

For activity measurements, the dew-point method was used. Other methods, like gas equilibration and emf measurements which operate well in open systems were inapplicable in the present study owing to the condensation of SnS vapors in cooler parts of the furnace tube.

In the course of activity measurements, activities of SnS in FeS-SnS binary system were determined by the dew-point method at 1000°, 1100° and 1200 °C.

3.2 DETAILS

Experimental details on furnaces, sample preparation, quenching, dew-point measurements and analyses are presented in the following.

3.3 STARTING MATERIALS

The primary starting materials were Sn, Fe, S. The source of iron was fine electrolytic powder of 99.9 % purity from South African Chemicals. Sulphur, from South African Chemicals had also 99.9 % purity. Analytical reagent grade granular tin was melted and solidified in small alumina boats under a flow of hydrogen gas at 500 °C in a horizontal tube furnace prior to use.

Tin sulphide was prepared by reacting a stoichiometric mixture of tin and sulphur step wise at temperatures 600 °C and 900 °C. Tin chips and sulphur pellets, forming a total mass of about 30 grams, were contained in a silica tube. The tube was evacuated to approximately 5×10^{-5} torr with the help of a rotary-diffusion pump unit. The tube so prepared was sealed by hydrogen torch and kept at 600 °C for a week and the temperature was increased up to 900 °C by 100 °C increments per week. The heating at 900 °C was for 2 hours. Tin and sulphur became molten in the first stage low temperature processing, forming solid SnS. At the last stage heating, SnS was melted for homogenizing the entire product. The SnS so formed and homogenized was cooled to room temperature, removed from the silica tube, and analyzed by X ray diffraction to verify that the final product was completely SnS.

Iron sulphide was synthesized from its elements by the same procedure described for the production of SnS, except that the initial heating was done at 600 °C for 3 weeks and final melting was accomplished at 1200 °C for 2 hours.

3.4 FURNACES AND TEMPERATURE CONTROL

Three different furnaces were employed throughout this investigation. Muffle furnace heated by silicon carbide elements was used during the syntheses of starting sulphides. This furnace could operate at temperatures up to 1200 °C; temperatures inside the muffle were maintained within ± 10 °C of their set values by Eurotherm on/off controller activated through a Platinum/Platinum-13% Rhodium thermocouple.

The second furnace was a vertical alumina tube furnace which could reach 1250 °C by wound kanthal wire heating element. This arrangement provided a 5 cm. long uniform hot zone over which the temperatures could be maintained constant to within ± 1 °C by means of thyristor coupled Eurotherm controller activated through a Platinum/Platinum-13% Rhodium thermocouple. This vertical type tube was used for the phase equilibrium studies in the FeS-SnS and Fe-Sn-S systems.

The last of the heating units which proved to be the major tool of experimentation for activity determinations was the Dew-Point furnace (DPF). Because of the fact that such furnaces has to be built according to specific needs for research, they are not manufactured commercially.

A vertical section through the midplane of the DPF used in present research is shown in Figure 11. The main mullite furnace tube, 46 cm long, 26 mm in diameter carried four different heating coils wound from 0.71 mm kanthal wire. The first three coils at the bottom were connected by the electrical circuit shown in Figure 12. The resistors in series with the second and third coils were adjustable so that the input power could be distributed between the three coils to obtain any desired temperature profile along the furnace tube. A typical temperature-distance curve is shown in Figure

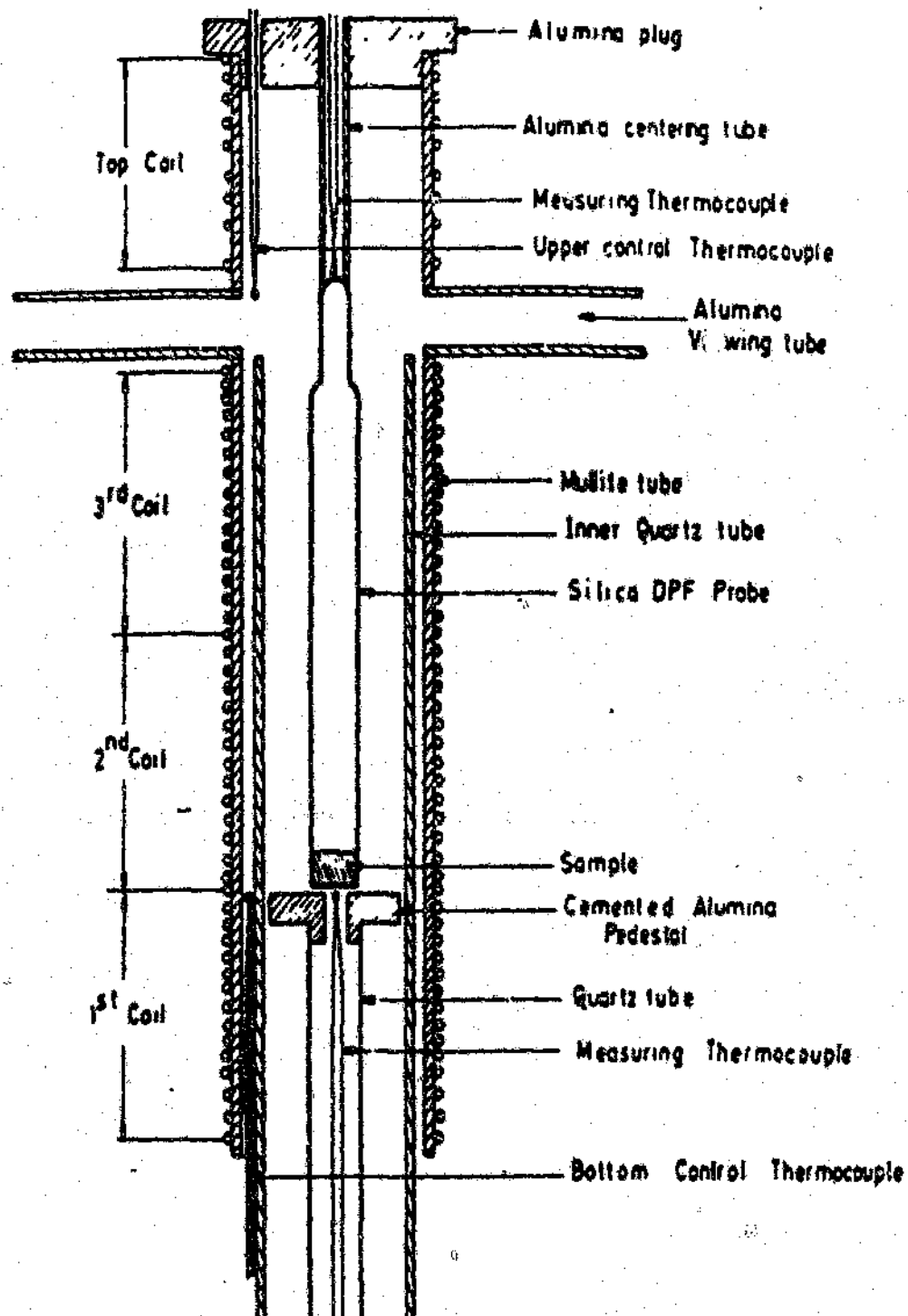


Figure 11. Part of the apparatus showing dew-point furnace, tube) windings sample tube arrangement and the thermocouples.

13. The control of temperature along these bottom coils was accomplished by a Eurotherm temperature controller coupled to a thyristor unit. The fourth and topmost coil was powered and controlled separately from the others with the aid of its own Eurotherm temperature controller. Both temperature controllers were activated by Pt-Pt 13% Rh thermocouples. This arrangement permitted to manipulate the temperatures at the tip of the silica sample tube to within $\pm 1/2$ °C of the set temperature values.

33 cm long 16 mm in diameter quartz tube was inserted into the DPF tube to help minimize the temperature gradients. Between the third and fourth coils two 7 mm in diameter alumina tubes were inserted in transverse position into the furnace tube for the purpose of viewing the tip of the sample tube. Each of these alumina tubes were 10 cm in length.

An alumina plug with a vertical alumina tube for sample tube positioning was used to cover the top of the DPF tube. A Pt-Pt 13% Rh thermocouple was suspended through the alumina tube of the plug to measure the temperature at the tip of the sample tube. The temperature of the liquid sample at the bottom of the sample were measured by means of a second Pt-Pt 13% Rh thermocouple led through the hole of the cemented alumina pedestal which was supported by a 13 mm in diameter quartz tube.

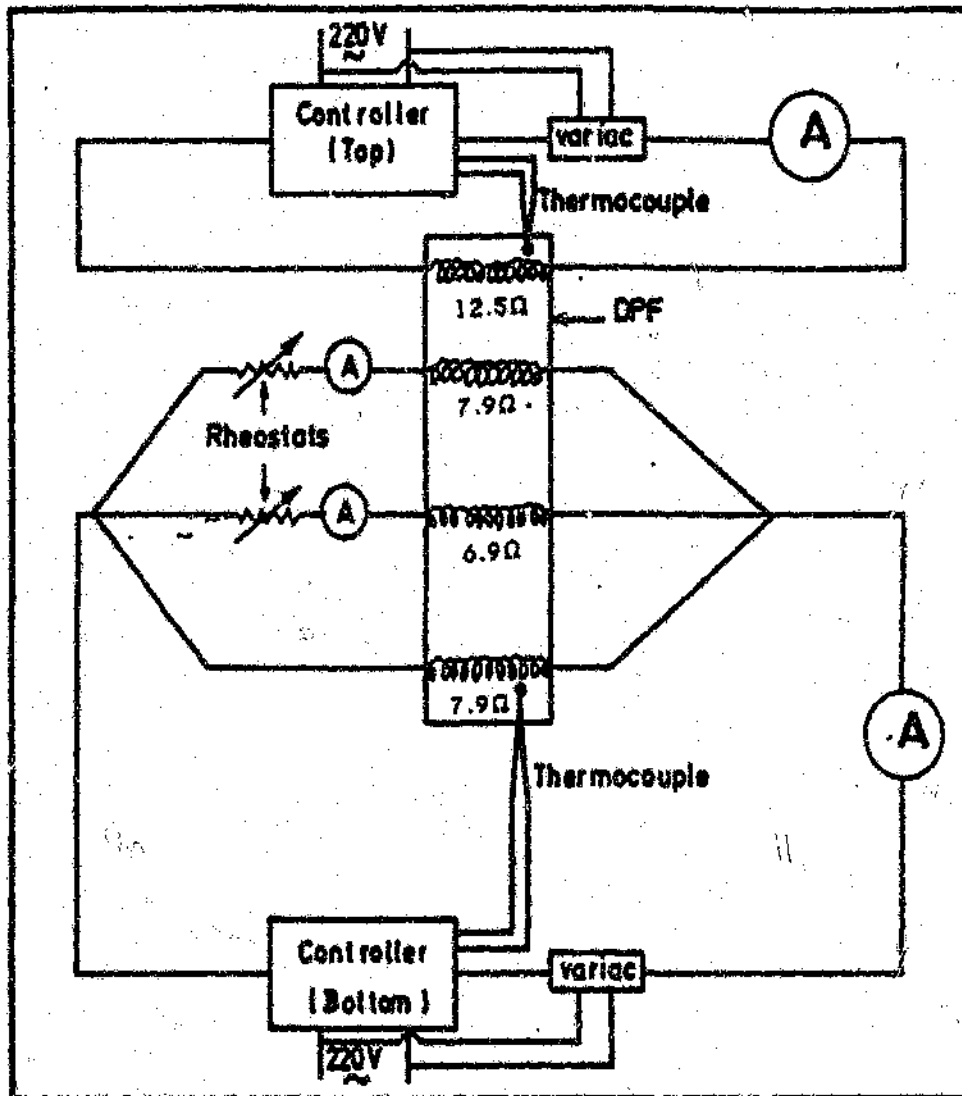


Figure 12. Schematic drawing of the electrical circuit of the dew-point furnace

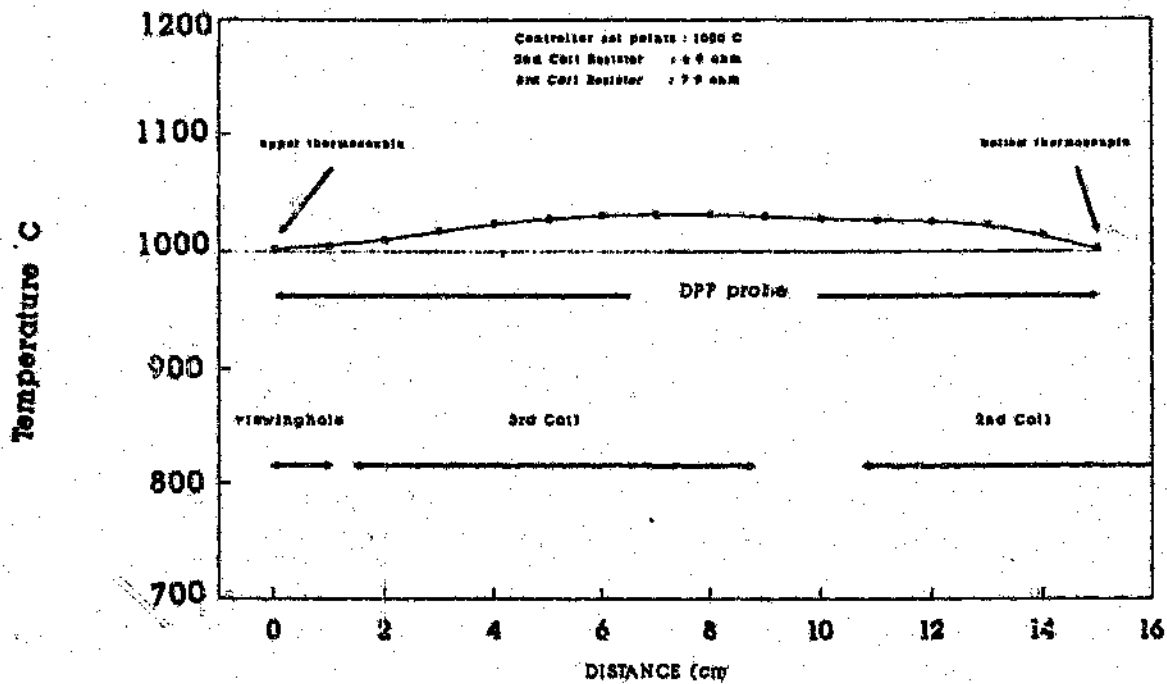


Figure 13. Typical temperature profile of the dew-point furnace

3.5 PRINCIPLES OF DEW-POINT TECHNIQUE

The Dew-Point technique of activity measurements takes advantage of the volatility of a component in the solution under consideration. In this method the pressure of the volatile component over a sample is determined from observations of the temperature at which condensation of the vapour occurs. The method is said to be applicable best when the vapour pressure of the components (in a binary system for example) would differ by at least three orders of magnitude¹⁷.

For dew-point measurements, the sample being studied is placed in an evacuated and closed long transparent silica tube. The tube is heated in DPT under a temperature gradient maintained between the bottom of the tube at temperature T and the top of the tube at temperature T' . The tube and its contents are heated for a sufficiently long time until a gaseous phase in equilibrium with the condensed phase at T develops. Then the top of the tube is cooled until condensation from the gas phase is observed. The temperature T_c at which the condensation occurs is called the dew-point of the volatile species. The vapour pressure of the condensing species above its pure reference condensed state at T_c is identical with the partial pressure of the condensing species above the condensed phase at T .

Temperatures at both ends of the silica tube are measured by thermocouples and by repeated heating and cooling, the dew-point temperature T_c can be determined precisely by observing the condensing particles through viewing holes down to within $\pm 1^\circ\text{C}$.

Once the dew-point temperature T_c is established, the activity of the volatile component at T can be calculated from the following equation:

$$a_i = P_i(T_c) / P^{\circ}_i(T) \dots (27)$$

Where $P_i(T_c)$ is the vapour pressure of component i at T_c , and $P^{\circ}_i(T)$ is the vapour pressure of i at T . Both $P_i(T_c)$ and $P^{\circ}_i(T)$ can be obtained from the vapour pressure equations of i available in literature. The method is quite fruitful in that, in a single sample numerous activities of i can be determined at various temperatures T by measuring the corresponding dew-point temperatures T_c .

3.6 PREPARATION OF DEW-POINT PROBES

The dew-point measurements involved the use of closed and evacuated transparent silica tubes for containing the samples. Furthermore, in order to avoid the oxidation of metallic tin and other sulphide components of the systems studied in this investigation, the samples were flushed and evacuated in the following manner.

One end of a long transparent silica tube of 10 mm in diameter was closed by a hydrogen torch. A sample of desired composition, weighing about 5 grams was placed in the tube. The tube was narrowed by the torch at a distance of 15 cm from the closed end to form nipple and neck. This distance was dictated by the temperature profile of the DPF. Then the silica tube was connected to the Edwards E1M5 combined outfit vacuum system and evacuated down to approximately 5×10^{-2} torr by means of the rotary pump. Commercially pure argon gas was allowed to flush the tube by means of a three-way stopcock connected to the vacuum system. This procedure of evacuation followed by flushing was repeated two times for

each sample. Then the gas train was closed and the tube was evacuated down to about 5×10^{-5} torr through the use of the diffusion pump. Afterwards, the tube was sealed at the neck under vacuum so that it was ready for use in the DPF.

3.7 MEASUREMENT OF DEW-POINT TEMPERATURE

The dew-point probes were introduced into the DPF from bottom slowly and stayed in place on a cemented alumina pedestal supported by quartz tube. This pedestal also served as a radiation shield. Through the inside of the quartz tube and a small hole in the centre of pedestal a Pt-Pt 13 %Rh thermocouple was introduced to measure the actual sample temperatures. The dew-point probe was centred with the help of the alumina tube of the alumina plug covering the top of the DPF tube, so that the tip of the probe was clearly visible through the viewing hole. A second Pt-Pt 13 %Rh thermocouple was suspended through the alumina tube from top for the measurement of dew-point temperatures at the tip of the probe.

At the beginning of each experiment, both ends of the DPF was kept at the same temperature (1200°C) for about 16 hours (Overnight) to ensure that equilibrium between the vapour and condensed phases has been reached⁷. Later, by means of temperature control devices of the fourth coil, the tip of the probe was cooled slowly until small condensing particles were observed through a telescope directed to the probe tip from the alumina viewing tubes.

The condensate was re-evaporated and re-condensed several times while decreasing continuously the temperature interval of the super heating and cooling. This procedure allowed to determine the dew-point temperatures of SnS within $\pm 1^{\circ}\text{C}$ to $\pm 4^{\circ}\text{C}$.

Upon completion of a dew-point experiment the probe was removed from the furnace. No reactions were observed between the liquid samples and the silica containers. Furthermore, the tubes remained un-collapsed throughout each experimental run.

The dew-point procedure was applied to determine the SnS activities in FeS-SnS system.

3.8 PROCEDURE FOR QUENCHING EXPERIMENT

The classical equilibration - quenching technique was used to establish the equilibrium relations between immiscible melts of the Fe-Sn-S system and the position of the liquidus in the FeS-SnS binary system, which resulted in the construction of the FeS-SnS phase diagram.

The distribution of the tie-lines in the ternary miscibility gap of the system Fe-Sn-S was ascertained by determining the compositions of sulphide saturated and sulphur saturated liquid phases which were in equilibrium with each other at 1200 °C. The samples for this study were prepared by mixing elements Fe, Sn, and S in such a manner that their gross composition would lie along the midrange of the miscibility gap. These samples, each weighing about 5 grams, were placed in silica tubes, each flushed with argon twice and evacuated down to 5×10^{-5} torr. Then they were sealed to a final length of 40 mm. These capsules again contained in silica crucibles were suspended by a platinum wire into the vertical tube furnace and heated at 1200 °C for a sufficiently long time to affect the melting of the charge, its separation into two liquids, and the attainment of equilibrium between these liquids. Time to reach equilibrium was established in initial experiments by chemical analysis of stratified liquids at

intervals of two hours for a total of eight hours. These analyses revealed that five hours would be a sufficient duration for equilibration, actual runs, however took at least six hours each, for sake of convenience.

During equilibration, the sulphide rich and metal rich phases formed two liquids which were virtually immiscible in each other; the sulphide melt floated on top of the metal melt because of its lower density. This stratification was preserved when the samples were quenched to room temperature by dropping the capsules carefully into water at the end of the equilibration run.

The quenched samples were removed from the capsules, the immiscible phases were separated readily from each other, and representative portions of these were analyzed chemically for their Fe, Sn and S in order to determine their composition. Tie-lines representing solid-liquid equilibria at the iron rich corner of the system were mainly determined by Energy Dispersive Analyses of X-rays (EDAX) coupled to a Scanning Electron Microscope.

The position of the liquidus and eutectic line in the FeS-SnS binary within the temperature interval 800-1200 °C were also determined by same technique as summarized above. Equilibration time for FeS-SnS was determined to be about twelve hours and after attainment of equilibrium the capsules were quenched to room temperature by carefully dropping them into water. The samples were removed and representative portions were analyzed chemically, metallographically and by EDAX where applicable. The position of the liquidus boundaries and eutectic line was established mainly by metallographic examination and EDAX. For metallography and EDAX, the

specimens were mounted in liquid epoxy resin which permeated the pores and cracks of the sample before hardening and greatly facilitated grinding and polishing.

Phase identification were made with a reflected light microscope. Samples quenched from above the liquidus line showed no solid phases but only the quenched dendritic liquid. On the other hand, samples quenched from below the liquidus curve evidenced the two phase region. Metallographic examination of such samples revealed existence of small globules of solid phase embedded in matrix of dendritic quenched liquid. Metallographic phase identification and results of EDAX analyses are in Table 1.

Error estimation in EDAX results is less than 0.070 wt% S, 0.697 wt% Fe and 0.275 wt% Sn. Effect of these results on mole fraction FeS and SnS were ± 0.1 and ± 0.032 .

3.9 CHEMICAL ANALYSES PROCEDURE

Chemical analyses for iron, tin and sulphur were performed at Mintek to determine the compositions of the samples obtained from quenching and occasionally from dew-point experiments.

For iron and tin determination; the sample would be fused in Na_2O and leached in water, then acidified, an internal standard (scandium) was added then made to volume. The elements requested were then determined using emission spectroscopy with an inductively coupled plasma source. The estimated error of tin and iron determination were less than 5%.

Sulphur determination; Sulphur was determined using a LECO Sulphur determinator. The principle of this apparatus is to burn the sulphur while passing oxygen over the sample so that SO_2 is formed. This gas is collected and titrated by iodine

and the sulphur content of the sample is directly read from instrument. The estimated error of sulphur determination reported to be less than 1% .

4 EXPERIMENTAL RESULTS AND DISCUSSION

The experimental results of this study are presented in two sections: (1) Data on phases present at the equilibration temperatures in the system FeS-SnS, and the data on compositions of co-existing liquids and solid liquid equilibria at 1200 °C in the system Fe-Sn-S are given in the section of "Phase Equilibria". (2) The results of measurements on dew-point temperatures for FeS-SnS system and activity calculations of Fe-Sn-S system are presented both in tabular and graphical forms in the section "Thermodynamics".

4.1 PHASE EQUILIBRIA

4.1.1 PRESENTATION OF RESULTS IN FeS-SnS SYSTEM

The phases present in various samples of the FeS-SnS at the equilibration temperatures as identified by the methods discussed earlier, are listed on Tables 1a and 1b. These data were obtained mainly with the purpose of delineating the liquidus lines, eutectic temperature, and solubility curves.

The data contained in Table 1a and 1b are summarized in Figure 14 showing the position of the liquidus, solid solubility curves and the eutectic line.

Occasionally chemical analyses were performed on equilibrated samples to check whether the overall composition of the samples have changed or not. The chemical analyses confirmed that the samples have kept their stoichiometric compositions within the error limits of the chemical analyses.

Table 1a; Experimental data of Quenching Experiments on FeS-SnS Binary system.

Composition of the samples (mole fraction)		Equilibrium Temperature T °C	Phase Identified
X _{SnS}	X _{FeS}		
0.16	0.84	1100	Solid+Liquid
0.26	0.74	1100	Liquid
0.31	0.69	1050	Solid+Liquid
0.41	0.59	1050	Liquid
0.42	0.58	1000	Solid+Liquid
0.53	0.47	1000	Liquid
0.55	0.45	950	Solid+Liquid
0.65	0.35	950	Liquid
0.61	0.39	900	Solid+liquid
0.71	0.29	900	Liquid
0.69	0.31	850	Solid+Liquid
0.77	0.46	850	Liquid
0.4	0.6	816	Solid+Liquid
0.4	0.6	812	Solid1+Solid2

Table 1b; SEM EDAX Results of Quenching Experiments on FeS-SnS Binary system.

Composition of the samples (mole fraction)		Equilibrium Temperature T °C	SEM EDAX RESULTS OF IDENTIFIED SOLID PHASES	
X _{SnS}	X _{FeS}		X _{SnS}	X _{FeS}
0.16	0.84	1100	0.005*	0.995*
0.31	0.69	1050	0.010*	0.990*
0.42	0.58	1000	0.010*	0.990*
0.55	0.45	950	0.015*	0.985*
0.61	0.39	900	0.015*	0.985*
0.69	0.31	850	0.021*	0.979*
0.40	0.60	812	0.025*	0.975*
0.40	0.60	786	0.020*	0.980*
0.40	0.60	767	0.015*	0.985*
0.40	0.60	812	0.985**	0.015**
0.40	0.60	786	0.990**	0.010**
0.40	0.60	767	0.990**	0.010**

* FeS rich solid solution

** SnS rich solid solution

It is well known that FeS is a non-stoichiometric compound with the actual formula $Fe_{1-x}S$ or FeS_{1-y} . However, the homogeneity range is very narrow and is a function of sulphur partial pressure. In the present case pure iron sulphide prepared by the method described earlier when analyzed for its iron and sulphur contents (63.28% Fe and 36.72% S) yielded the chemical formula $FeS_{1.01}$. Therefore in all the presentations and calculations iron sulphide was assumed to be a stoichiometric FeS.

SEM-EDAX analyses of solid phases in the equilibrated samples data of which is collected in Table 1b have permitted the construction of solid solubility curves at both ends of the diagram. In reality the solid phases were micro-analyzed by SEM-EDAX for their tin, iron and sulphur contents. In general, the analyses for the chemical constituents totalled 99.6 ± 0.8 percent. These were normalized to 100 % and converted to stoichiometric mole fractions of SnS and FeS. In these calculations an excess or deficiency of sulphur was not encountered within the error limits of microanalyses. This is a further proof of the soundness of experimental results.

4.1.2 DISCUSSION OF RESULTS IN FeS-SnS SYSTEM

The phase diagram of FeS-SnS binary system was constructed both by experiments and mathematical modelling of the activity data to be presented later. Eutectic temperature of FeS-SnS system was found as $815^{\circ}C$ and eutectic composition was obtained at $X_{SnS}=0.767$ by extrapolation of two liquid boundary curves obtained from the mathematical modelling of the liquidus curves. The experimental points

lie at both sides of the calculated liquidus lines confirming the soundness of the solution model. The melting points of both components were taken from literature^{2,7}.

The general shape of the phase diagram constructed in this investigation is slightly different when it is compared with the published diagram of Davey and Joffre². Their eutectic line is slightly lower than the present study indicating a eutectic temperature of 797 °C at $X_{\text{SnS}}=0.721$. They calculated liquidus curves at the FeS-SnS phase diagram on the assumption of no solid solubility of either component, and regular solution behavior of the liquid matte phase. The present findings through SEM-EDAX however, indicate small solid solubility ranges at both ends of the diagram.

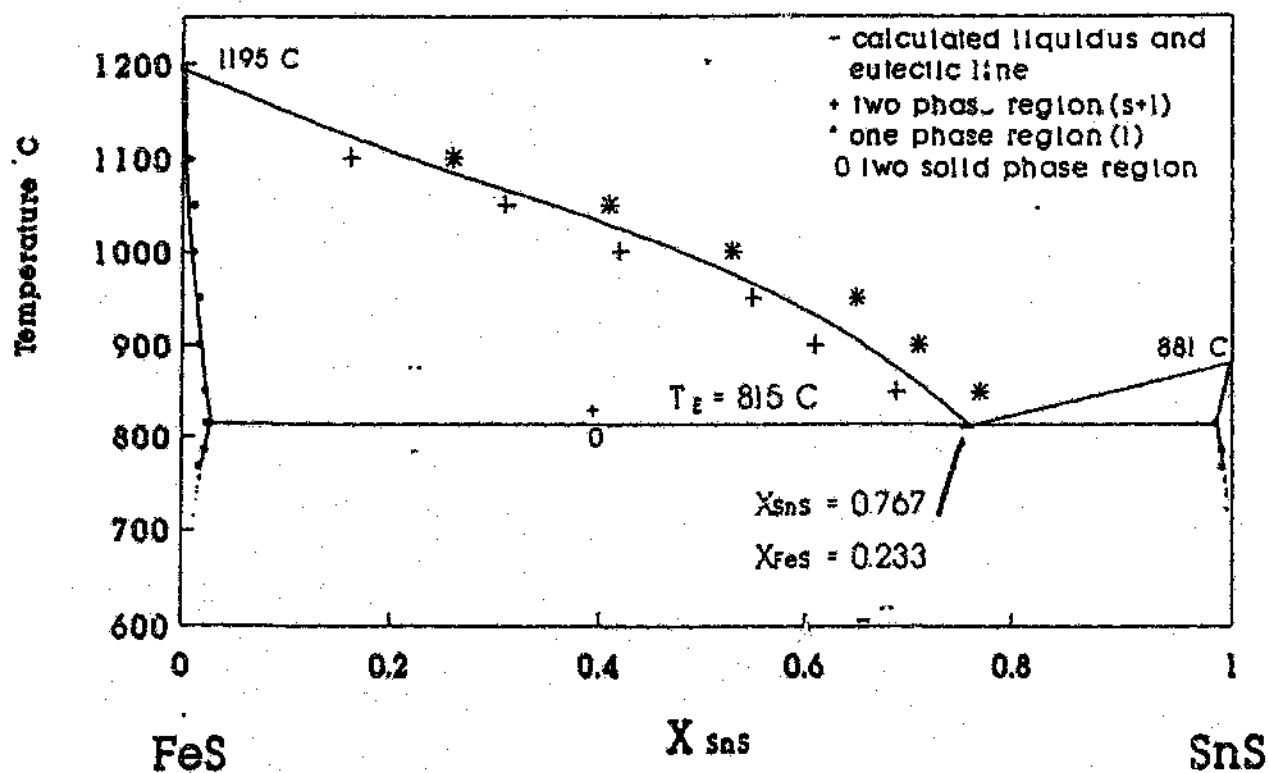


Figure 14. FeS-SnS phase diagram of the present study

4.1.3 PRESENTATION OF RESULTS IN Fe-Sn-S SYSTEM

In the total ternary Fe-Sn-S, the region of greatest metallurgical interest is that bounded by the compositions Fe-FeS-SnS-Sn. Within this field a large ternary liquid miscibility gap exists at 1200 °C originating from the Sn-SnS side⁷. There is another much smaller liquid immiscibility region originating from the Fe-Sn binary¹⁰. However, this miscibility gap does not penetrate much into the ternary field. Tie lines joining the equilibrium compositions of co-existing sulphur rich and metal rich liquid phases were determined at 1200 °C by the method described in section (3.8) and the boundaries of liquid immiscibility were redrawn based on the compositions of the end points of the tie lines. A sample belonging to the Fe-Sn binary was equilibrated to confirm the boundary of the liquid immiscibility region originating from the Fe-Sn side. The boundary of this small immiscibility region was however taken from literature¹⁰. The relevant data are given in Table 2 and Figure 15 is a graphical summary of the results. The liquidus curve running from about $X_{Fe} = 0.6$ on the Fe-FeS side to $X_{Sn} = 0.25$ on the Fe-Sn side was also determined mainly by SEM-EDAX analyses of equilibrated samples involving solid liquid equilibria.

Data on tie-lines representing $Fe(\gamma)$ -liquid and $Fe(\alpha)$ -liquid phase assemblages determined as explained above are given in table 2b and are shown in Figure 15. By making use of the available information on Fe-Sn phase diagram^{10,15}, and the tie line data it was possible to construct the complex phase equilibria at the iron rich corner of the Fe-Sn-S ternary. Two samples belonging to the three phase region, $Fe(\alpha) + \text{liquid} + Fe(\gamma)$ were also equilibrated at 1200 °C. The SEM-EDAX microanalyses of these three phases have permitted the construction of this triangular three phase region completing the phase relations at the iron rich corner of the diagram.

Table 2a; Experimental data on Tie-Lines of the Fe-Sn-S system at 1200 °C

Tie line number	Compositions (mole fraction)					
	Along metal rich boundary			Along sulphur rich boundary		
	X _{Fe}	X _{Sn}	X _S	X _{Fe}	X _{Sn}	X _S
1	0.005	0.950	0.045	0.013	0.527	0.460
2	0.010	0.952	0.038	0.027	0.513	0.460
3	0.020	0.930	0.050	0.045	0.500	0.455
4	0.034	0.910	0.056	0.070	0.460	0.462
5	0.050	0.904	0.046	0.110	0.430	0.460
6	0.070	0.870	0.060	0.160	0.380	0.460
7	0.107	0.821	0.072	0.223	0.312	0.465
8	0.126	0.798	0.076	0.310	0.223	0.467
9	0.164	0.750	0.086	0.380	0.150	0.470
10	0.204	0.696	0.100	0.450	0.080	0.470
11	0.250	0.640	0.110	0.505	0.090	0.405
12	0.290	0.597	0.113	0.500	0.210	0.290
13*	0.680	0.320	0.0	0.310	0.690	0.0

* Tie line on the iron-tin binary.

Table 2b; Experimental data on Tie-Lines of the Fe-Sn-S system at 1200 °C on Fe rich side

Tie line number	Compositions (mole fraction)								
	Along γ -Fe solid solubility curve			Along α -Fe solid solubility curve			Along liquid solubility curve		
	X _{Fe}	X _{Sn}	X _S	X _{Fe}	X _{Sn}	X _S	X _{Fe}	X _{Sn}	X _S
1	0.980	0.010	0.010	-	-	-	0.645	0.030	0.325
2	0.977	0.017	0.008	-	-	-	0.700	0.075	0.225
3	0.970	0.025	0.005	0.900	0.905	0.030	0.725	0.100	0.175
4	-	-	-	0.905	0.073	0.022	0.735	0.150	0.115
5	-	-	-	0.928	0.068	0.004	0.740	0.240	0.020

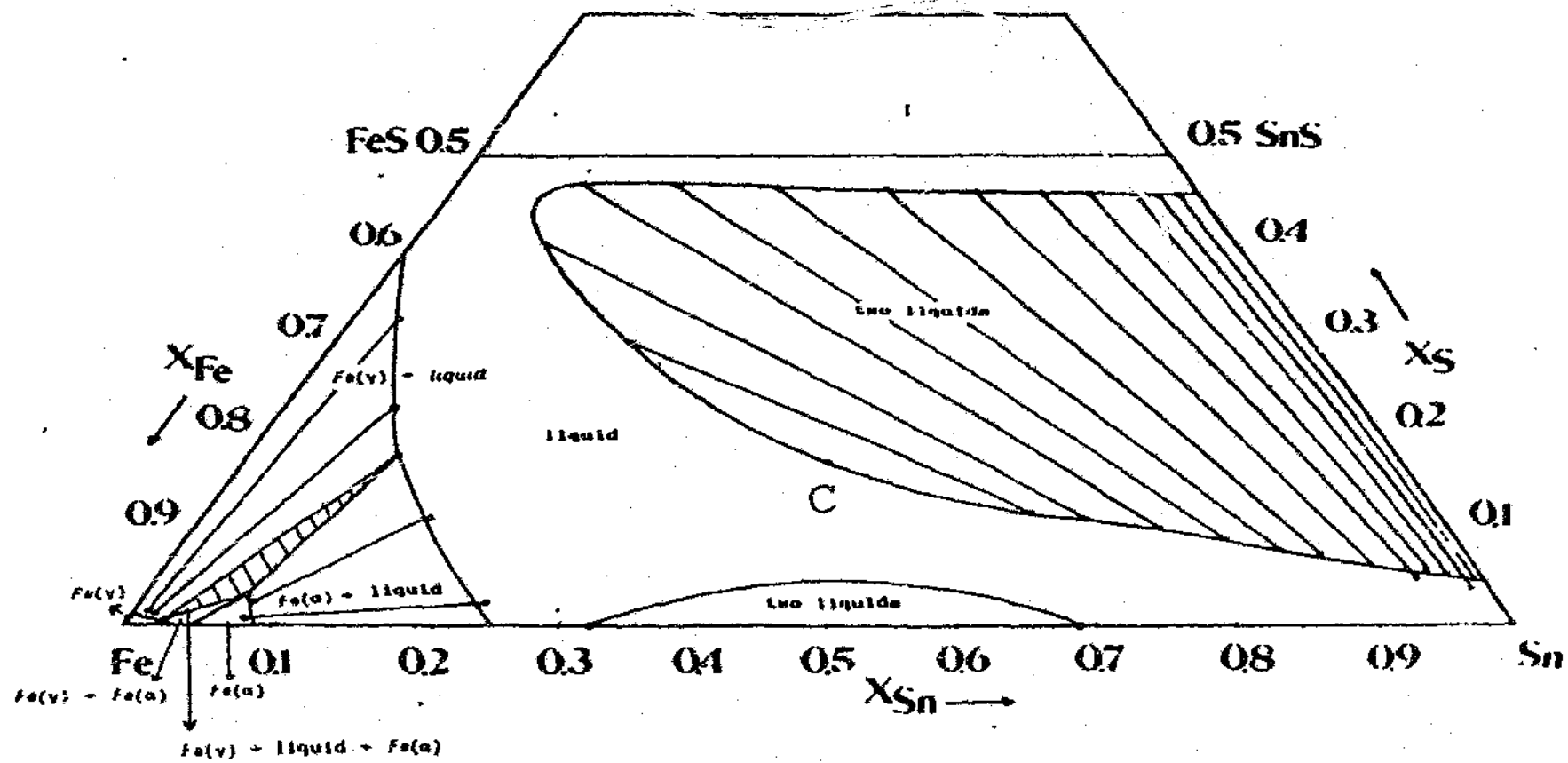


Figure 15. Experimentally determined tie-lines in Fe-Sn-S melts at 1200 °C

4.1.4 DISCUSSION OF RESULTS IN Fe-Sn-S SYSTEM

In literature there is no comparable ternary isothermal section of the Fe-Sn-S diagram at 1200 °C. Therefore, this is the first study revealing phase relations in this system at 1200 °C. However, the liquidus projection of Fe-Sn-S system available in literature although based on extrapolations rather than experimental findings predicts a large ternary immiscibility region which is in accord with the present findings. The predicted immiscibility region at 1200 °C from liquidus projection is quite similar in shape to the one drawn in Figure 15 with slight differences especially towards the tin corner of the diagram. The critical point of the miscibility gap shown as point C was actually taken from the literature. During experimental runs samples whose composition lied between point C and the small immiscibility region originating from the Fe-Sn side, did not separate into two liquids, always showing a quenched homogeneous single liquid phase structure.

The distribution of tie-lines at 1200 °C in the ternary miscibility gap, illustrated in Figure 15 cover the whole composition range from the Sn-SnS side upto almost critical point C. Again in literature there is no comparable information. The direction of tie-lines are closely related to soundness of chemical analyses. Especially at high tin containing regions of the miscibility gap small errors in the analyses may result in different orientations of tie-lines. In order to minimize the errors, during this investigation, each tie-line was determined by equilibrating more than one sample of the same initial composition. Chemical analyses of the stratified liquids of each of these samples for their iron, tin and sulphur

contents served to obtain an average composition value for the end points of each tie-line. In subsequent thermodynamic calculations end points of tie-lines were directly read from the boundary curves. Since Fe-Sn metallic melts exhibit positive deviations from ideality¹⁵, the distribution of tie-lines illustrated in Figure 15 is also an indication of possible positive deviations in FeS-SnS melts but at a less magnitude.

4.2 THERMODYNAMICS

The activity measurements in FeS-SnS melts were carried out by the dew-point technique at 1090°, 1100°, 1200 °C. The activities of tin, iron and sulphur were calculated employing the tie-line data and binary thermodynamic information. All these are presented in the following.

4.2.1 PRESENTATION OF RESULTS IN FeS-SnS SYSTEM

SnS activities of the binary SnS-FeS liquid samples at 1200 °C, 1100 °C, 1000 °C were determined by the dew-point technique described earlier in sections (3.5, 3.7). Equation 3, giving the vapour pressure of liquid SnS as a function of temperature was employed to convert the measured dew-point temperature into activity values. The dew-point temperatures of selected FeS-SnS samples were inserted into equation 3 and thus the ratio of calculated partial pressure of SnS to the vapour pressure of pure liquid SnS gave the required activities with pure liquid SnS as the standard state through:

$$a_{\text{SnS}} = P_{\text{SnS}} / P^{\circ}_{\text{SnS}} \dots (28)$$

Upon completion of a dew-point run the silica tube was quenched in air and the sample was removed for phase

identification and occasional chemical analyses. Microscopic examination of samples revealed the existence of one phase only in all the samples studied at all the temperatures in accord with the redrawn FeS-SnS phase diagram. The occasional chemical analyses for iron, tin and sulphur content of the samples revealed that there was no change in the composition of the samples within analytical error limits. The relevant data covering the compositions, dew point temperatures with their error ranges and activities are collected in Table 3 and Figure 16 all of which also include calculated SnS and FeS activities through a subregular solution model.

The α function for a species "i" is defined as follows:

$$\alpha_i = \ln \gamma_i / (1 - X_i)^2 \dots (29)$$

where γ_i is the activity coefficient ($\alpha_i = \gamma_i X_i$) and X_i is the mole fraction of species "i". The α function for SnS; α_{SnS} derived from the experimental activity data summarized in Tables 3 was found to vary linearly with composition at the three experimental temperatures. This is illustrated in Figure 17. This behavior was compatible with Hardy's²⁴ subregular solution model in which thermodynamic functions could be expressed by two constant equations. In the subregular solution model for binary systems the chemical potentials of the components are expressed as²⁴:

$$\mu_1 - \mu_1^\circ = RT \ln X_1 + X_2^2(2A_1 - A_2) + X_2^3(2A_2 - 2A_1) \dots (30)$$

$$\mu_2 - \mu_2^\circ = RT \ln X_2 + X_1^2(2A_2 - A_1) + X_1^3(2A_1 - 2A_2) \dots (31)$$

The chemical potential difference on the left hand side of equations 30, 31 are identical to the relative partial molar Gibbs free energy of components in solution; G_i^M , which is directly related to activities through:

$$G_i^M = RT \ln a_i = RT \ln X_i + RT \ln \gamma_i, \dots (32)$$

The first term after the second equality sign in equation 32 gives the ideal contribution to G_i^M and second term ($RT \ln \gamma_i$) shows the deviation from ideality by making use of activity coefficient. This term is also the definition of partial excess Gibbs free energy of component i in the solution; G_i^E . That is

$$G_i^E = RT \ln \gamma_i, \dots (33)$$

In other words G_i^M is made up of two terms as shown below:

$$G_i^M = G_i^{M_{id}} + G_i^E, \dots (34)$$

Thus by comparing equation 32 with the chemical potential equations 30, 31 it is obvious that partial excess Gibbs free energy of components in a binary subregular solution can be written as:

$$G_1^E = X_2^2(2A_1 - A_2) + X_2^3(2A_2 - 2A_1), \dots (35)$$

$$G_2^E = X_1^2(2A_2 - A_1) + X_1^3(2A_1 - 2A_2), \dots (36)$$

From the definition of partial excess free energy; equation 33 at constant temperature, the α functions for the components can be derived by making use of equations 35, 36. In order to incorporate the two constants; temperature, T (at constant temperature) and gas constant; R, two new constants are defined:

$$A = 2A_2/RT \dots (37)$$

$$B = 2A_1/RT \dots (38)$$

With these new constants, The α_1 and α_2 can be derived as:

$$\alpha_1 = A/2 + X_1(B - A) \dots (39)$$

$$\alpha_2 = B/2 + X_2(A - B) \dots (40)$$

These two general α function equations for subregular solutions clearly demonstrate the linearity of α with composition with two constants at constant temperature. As the experimental α_{SnS} function also behaved linearly with composition in the FeS-SnS liquid solution, it was decided to model the FeS-SnS liquid solution by the subregular technique. Since the data was available at three different temperatures, it was found justified that the α function could also be made a function of temperature. This would also be an improvement over the classical subregular solution model developed by Hardy²⁴. In order to do that with the limited temperature data at 1000°, 1100° and 1200 °C it was decided to express the non-compositional parameters of equations 39, 40 as linear equations of inverse absolute temperature. Thus:

$$A/2 = a/T + b \dots (41)$$

$$B/2 = c/T + d \dots (42)$$

These would yield α_{SnS} and α_{FeS} functions (taking component 1 as SnS and component 2 as FeS)

$$\alpha_{SnS} = \left(\frac{a}{T} + b \right) + X_{SnS} \left(\frac{e}{T} + f \right) \dots (43)$$

$$\alpha_{FeS} = \left(\frac{c}{T} + d \right) - X_{FeS} \left(\frac{e}{T} + f \right) \dots (44)$$

Where constant e and f are related to constant a, b, c and d through:

$$e = 2(c - a) \dots (45)$$

$$f = 2(d - b) \dots (46)$$

In order to conduct a multi-coefficient regression analyses to the data gathered on α_{SnS} as a function of composition and temperature the form of equation 43 was altered to take the form;

$$\alpha_{SnS} = aX_1 + fX_2 + eX_3 + b \dots (47)$$

Where the constants a, b, e and f have the same meaning and

$$X_1 = 1/T \dots (48)$$

$$X_2 = X_{SnS} \dots (49)$$

$$X_3 = X_{SnS}/T \dots (50)$$

The relevant regression analyses applied to experimental data gathered from dew-point experiments as a function of composition at temperatures 1000°, 1100° and 1200 °C resulted in the following equation for α_{SnS} with a correlation factor of 0.9595.

$$\alpha_{SnS} = 3583.5X_1 - 0.721X_2 - 359.9X_3 - 1.513 \dots (51)$$

This equation when converted to its proper form as in equation 43 became

$$\alpha_{SnS} = \left(\frac{3583.5}{T} - 1.513 \right) - X_{SnS} \left(\frac{359.9}{T} + 0.721 \right) \dots (52)$$

The corresponding α_{FeS} could then be easily obtained:

$$\alpha_{FeS} = \left(\frac{3403.5}{T} - 1.874 \right) + X_{FeS} \left(\frac{359.9}{T} + 0.721 \right) \dots (53)$$

Making use of the model α_{SnS} and α_{FeS} equations derived above, it was a matter of mathematical manipulation to express the activity coefficient and activity of both SnS and FeS analytically through basic definitions. Thus for SnS:

$$\ln \gamma_{SnS} = (1 - X_{SnS})^2 \left(\frac{3583.5}{T} - 1.513 - X_{SnS} \left(\frac{359.9}{T} + 0.721 \right) \right) \dots (54.a)$$

$$\ln a_{SnS} = \ln X_{SnS} + (1 - X_{SnS})^2 \left(\frac{3583.5}{T} - 1.513 - X_{SnS} \left(\frac{359.9}{T} + 0.721 \right) \right) \dots (54.b)$$

and similarly for FeS

$$\ln \gamma_{FeS} = (1 - X_{FeS})^2 \left(\frac{3403.5}{T} - 1.874 + X_{FeS} \left(\frac{359.9}{T} + 0.721 \right) \right) \dots (55.a)$$

$$\ln a_{FeS} = \ln X_{FeS} + (1 - X_{FeS})^2 \left(\frac{3403.5}{T} - 1.874 + X_{FeS} \left(\frac{359.9}{T} + 0.721 \right) \right) \dots (55.b)$$

The last two columns of Table 3 contain calculated activity values from equations 54.b and 55.b at 1200°, 1100° and 1000 °C respectively for comparison with experimentally measured values. In Figure 16, the full lines represented the activities calculated through model equations.

By the use of the equation 13 which gives the activity of SnS in equilibrium with solid SnS, it was possible to derive the liquidus temperature of SnS analytically. Combining equation 13 with equation 54.b and solving for temperature T, the position of the SnS liquidus was obtained. This is possible only when it is assumed that no solid solubility exists. Since the experimentally found solid solubilities of both ends of the diagram were very small, they were neglected in liquidus temperature calculations.

Table 3a; Data on Dew-Point temperatures and results of activity calculations in FeS-SnS System at 1200 °C

Sample Composition mole fraction		measured Dew-Point Temperatures	Experimental activities of SnS	Activities by subregular solution model	
X _{SnS}	X _{FeS}	T°C	a _{SnS}	a _{SnS}	a _{FeS}
0.1	0.9	1041.0 ±3.0	0.187	0.195	0.912
0.2	0.8	1087.0 ±3.0	0.317	0.320	0.839
0.3	0.7	1111.0 ±3.0	0.410	0.410	0.773
0.4	0.6	1126.0 ±4.0	0.483	0.487	0.706
0.5	0.5	1141.0 ±3.0	0.561	0.560	0.629
0.6	0.4	1151.5 ±2.5	0.624	0.635	0.539
0.7	0.3	1163.0 ±3.0	0.715	0.717	0.429
0.8	0.2	1177.0 ±2.5	0.803	0.805	0.301
0.9	0.1	1189.0 ±3.5	0.901	0.901	0.155

Table 3b; Data on Dew-Point temperatures and results of activity calculations in FeS-SnS system at 1100 °C.

Sample composition mole fraction		measured Dew-Point temperatures	Experimental activities of SnS	Activities by subregular solution model	
X _{SnS}	X _{FeS}	T°C	a _{SnS}	a _{SnS}	a _{FeS}
0.1*	0.9*	-	-	-	-
0.2	0.8	1014.0 ±3	0.369	0.358	0.847
0.3	0.7	1032.7 ±3	0.454	0.446	0.786
0.4	0.6	1043.4 ±3	0.527	0.517	0.727
0.5	0.5	1053.6 ±3	0.594	0.584	0.658
0.6	0.4	1061.7 ±2	0.652	0.652	0.574
0.8	0.3	1070.5 ±3	0.721	0.727	0.468
0.8	0.2	1081.0 ±3	0.809	0.811	0.336
0.9	0.1	1090.7 ±3	0.903	0.902	0.178

* solid + liquid two phase region

Table 3c; Data on Dew-Point temperatures and results of activity calculations in FeS-SnS system at 1000 °C.

sample composition mole fraction		measured Dew-Point temperatures	Experimental activities of SnS	Activities by sub-regular solution model	
X _{SnS}	X _{FeS}	T °C	a _{SnS}	a _{SnS}	X _{FeS}
0.1*	0.9*	-	-	-	-
0.2*	0.8*	-	-	-	-
0.3*	0.7*	-	-	-	-
0.4*	0.6*	-	-	-	-
0.5	0.5	962 ±3.0	0.610	0.613	0.693
0.6	0.4	968 ±2.5	0.664	0.654	0.618
0.7	0.3	976 ±2.5	0.736	0.740	0.517
0.8	0.2	984 ±1.5	0.818	0.817	0.382
0.9	0.1	992 ±3.0	0.904	0.904	0.209

* solid + liquid two phase region

In an exactly similar way combining equation 16 with equation 55.b and solving for temperature T, the position of the FeS liquidus was obtained with again no solid solubility assumption.

The solid lines in Figure 14 represent the calculated liquidus curves as explained above. The intersection of two liquidus curves, that for FeS and SnS yielded the eutectic temperature of 815 °C and its composition at $X_{SnS}=0.767$.

From equations 54.a and 55.a, it was also possible to obtain Henrian activity coefficient of for both SnS and FeS in an analytical form as a function of temperature in infinitely dilute solutions:

$$\ln \gamma^{\circ}_{SnS} = \frac{3583.5}{T} - 1.513 \dots (56)$$

$$\ln \gamma^{\circ}_{FeS} = \frac{3403.5}{T} - 1.874 \dots (57)$$

However, these equations must be used in the vicinity of the temperature regions where homogeneous liquid solutions exists.

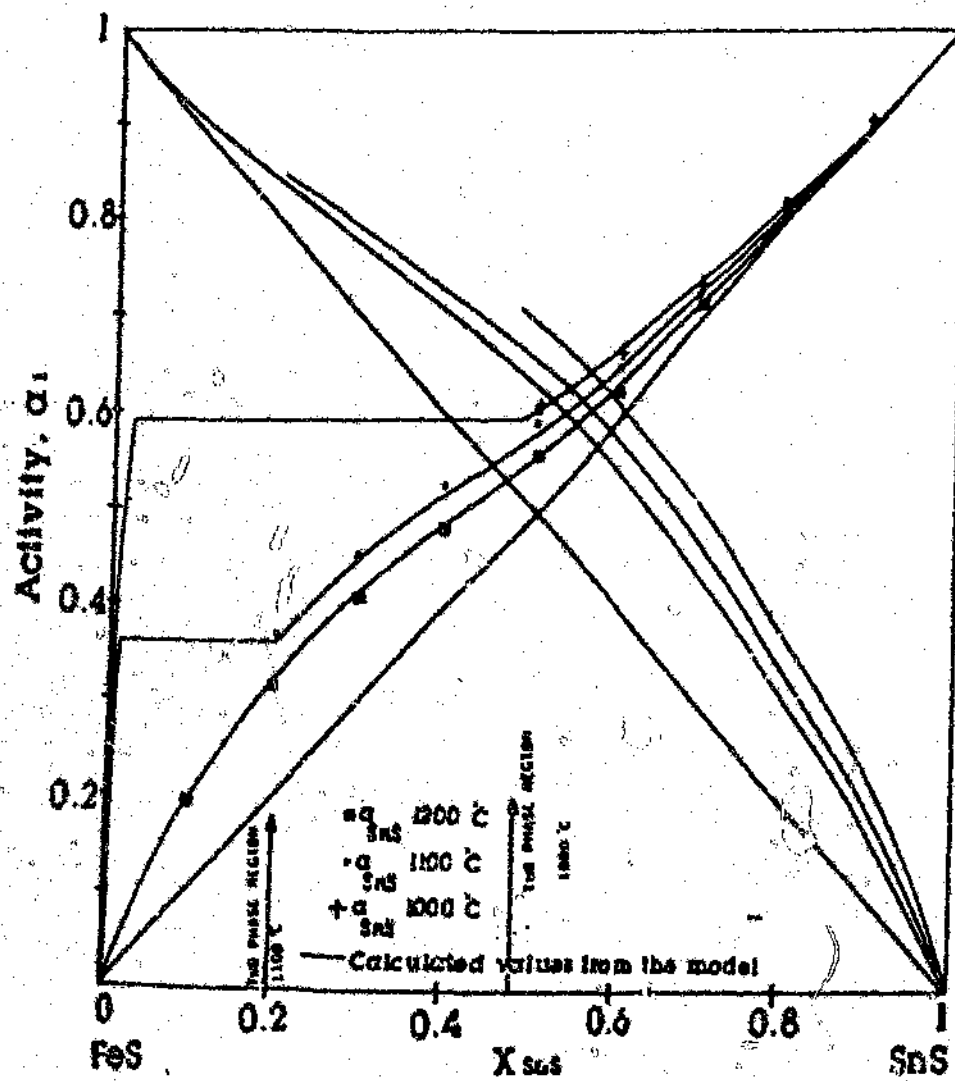


Figure 16 FeS-SnS Activity curves of present study

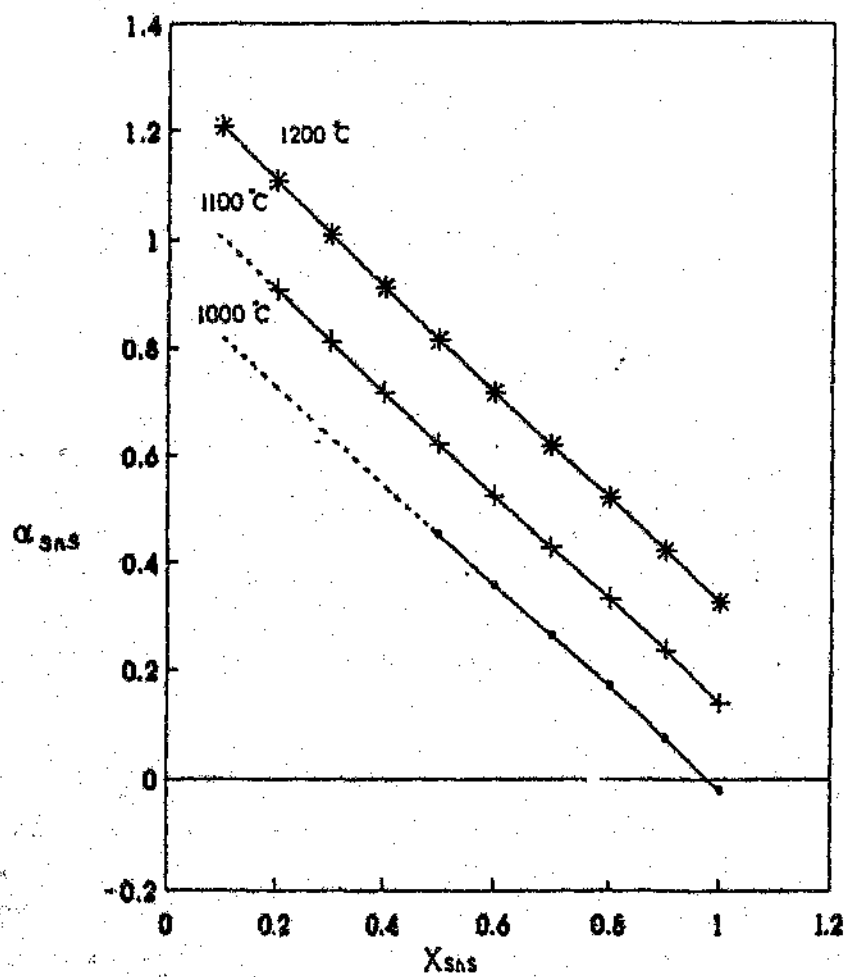


Figure 17 α function of SnS versus mole fraction of SnS in FeS-SnS system

4.2.2 DISCUSSION OF RESULTS IN FeS-SnS SYSTEM

Activities of both components of the FeS-SnS system show positive departures from ideality in accord with experimentally determined phase diagram as shown in Figure 16. Activities of FeS and SnS in these liquid solutions were calculated at 800 °C and 1000 °C by Davey and Joffre² by using their data on SnS gathered by the transportation method. Their results also show positive deviation as reproduced in Figure 8. Their values at 1000 °C are slightly lower than the experimental values of this investigation. However in their activity composition diagram, there is a serious fundamental error. This arises from the fact that their activity composition curves at both temperatures indicate that there is a homogeneous single liquid phase all throughout the composition range. As seen in the FeS-SnS phase diagram, for example at 1000 °C, for $0 < X_{SnS} < 0.5$, there are two phases in equilibrium, meaning that activities of both components should remain constant. Thus their activity data for compositions in the above interval at 1000 °C is completely unreliable. The situation is even worse at 800 °C.

An analysis of the errors involved in using the dew-point method of activity determination has been made by Eric²⁵ and Birchenall and Cheng³². The largest source of error is an incorrect measurement of the dew-point temperature. The reproducibility of the dew-point temperatures in this work, for the FeS-SnS system changed from 1 to 4 °C at 1200 °C. Hence starting from the highest value, the maximum error in a measured SnS activity can be estimated as follows: The temperature coefficient of SnS vapor pressure for pure SnS at 1200 °C from equation 3 is $dp/dT = 5.72 \times 10^{-3}$ atm/K. Hence a maximum error of 4 °C in dew-point temperature

corresponds to an error of $\Delta P^{\circ}_{\text{SnS}} = 5.72 \times 10^{-3}$ atm in measuring the value $P^{\circ}_{\text{SnS}} = 0.607$ atm for pure SnS. For this particular sample with maximum error, the activity is 0.483 and the equilibrium vapor pressure is $P_{\text{SnS}} = 0.292$ atm. The error in this P_{SnS} turns out to be $\Delta P_{\text{SnS}} = 1.2 \times 10^{-2}$ atm. The absolute error in the activity is related to the relative errors in pressures by the following equation²⁵.

$$\Delta a_i/a_i = (P^{\circ}_i \Delta P_i - P_i \Delta P^{\circ}_i) / (P_i (P^{\circ}_i + \Delta P^{\circ}_i)) \dots (58)$$

By inserting $\Delta P^{\circ}_{\text{SnS}}$, P_{SnS} , ΔP_{SnS} , P°_{SnS} values calculated above into equation 58, the absolute percentage error in determining of $a_{\text{SnS}} = 0.483$ for this particular sample becomes 0.325 %. By using the same method, in determining of $a_{\text{SnS}} = 0.805$ at 1100 °C and $a_{\text{SnS}} = 0.610$ at 1000 °C for these particular samples become 0.338 % and 0.031 %. The accuracy improves further for samples with less uncertainty in their measured dew-point temperatures. Thus it can be concluded that the contribution of uncertainties in dew-point temperatures to the reported activities are negligible.

The second source of error in dew-point measurements is the change of the original sample composition due to SnS vaporization into the specimen tube. In present study this type of error was also negligible, because from the ideal gas equation it was calculated that at 1200 °C 8.92 mg of SnS, at 1100 °C 2.3×10^{-2} mg of SnS, and 1000 °C 7.78×10^{-3} mg of SnS in the vapor phase would be sufficient to maintain the equilibrium tin sulphide vapor pressure over a sample of pure SnS. 8.92 mg of SnS represents the highest amount of SnS in the vapor phase among all samples. The total weight of the specimen in each run was about 5 to 6 grams, hence the SnS removed by vaporization would not cause a tangible change in the original composition of the

specimen. The changes in sample composition due to condensation of SnS at the tip of the dew-point probe were also negligible, because they were very small and not too much in number in many of the runs.

4.2.3 PRESENTATION AND DISCUSSION OF RESULTS IN Fe-Sn-S SYSTEM

Activities of iron, tin and sulphur were calculated along the miscibility gap of the Fe-Sn-S ternary system from the experimentally determined tie-lines and the knowledge on pertinent binary thermodynamic properties by the method developed by Choudary and Chang^{26,27}. This integration method is described in the following.

At constant temperature T, and pressure P, the generalized Gibbs-Duhem relation is:

$$\sum_i n_i d\bar{Q}_i = 0 \dots (59)$$

where n_i 's refer to number of moles of the component and $\bar{Q}_i$ is any partial molar thermodynamic property of the i th component. Following Chipman²⁸, the concentration variable n_i are changed to the new concentration variable y_i , henceforth referred to as the "atom ratio" of component i . The definitions of the atom ratios in ternary A-B-C system where A and B are metals and C is a non-metal, are given below:

$$y_A = n_A / (n_A + n_B) = 1 - y_B \dots (60a)$$

$$y_B = n_B / (n_A + n_B) \dots (60b)$$

$$y_C = n_C / (n_A + n_B) \dots (60c)$$

Expressing equation 59 in terms of activity coefficients and substituting n_i by y_i from equations 60 yields,

$$y_A d \ln \gamma_A + y_B d \ln \gamma_B + y_C d \ln \gamma_C = 0 \dots (61)$$

Figure 18 shows lines of constant y_C and y_A (or y_B), the miscibility gap along which equation 61 is to be integrated and the composition notations. $y_C = 0$ shows metallic A-B binary; $y_i = y_i^*$ shows compositions of non-metal saturated metallic phases in equilibrium with metal poor phases denoted by $y_i = y_i'$.

From equation 61 and following Wagner²⁹ an important relation was developed by Choudary and Chang^{26,27}, expressing the variation of $\ln(\gamma_B/\gamma_A)$ with y_C^* in terms of the change of $\ln \gamma_C$ with y_A . Knowing the tie line-distribution in the two liquid phase field and the boundary binary thermodynamics, this relationship may be utilized to compute all the pertinent thermodynamic data along the miscibility gap.

In derivation of this new equation y_B and y_C are independent variables with $y_A = 1 - y_B$. Thus from equation 61 the following relations are written:

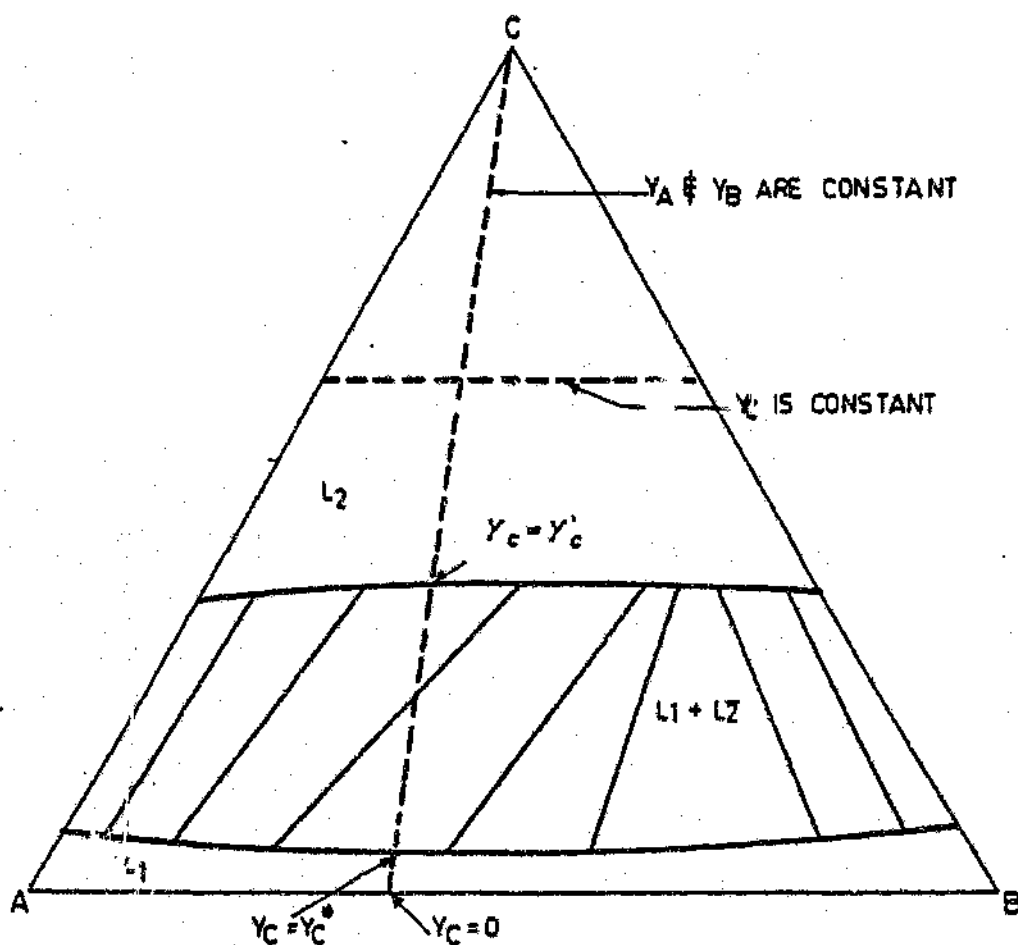


Figure 18. Schematic of an isothermal section showing a miscibility gap in a ternary system A-B-C.

$$(1-y_B)\left(\frac{d\ln\gamma_A}{dy_B}\right) + y_B\left(\frac{d\ln\gamma_B}{dy_B}\right) + y_C\left(\frac{d\ln\gamma_C}{dy_B}\right) = 0 \dots (62)$$

$$(1-y_B)\left(\frac{d\ln\gamma_A}{dy_C}\right) + y_B\left(\frac{d\ln\gamma_B}{dy_C}\right) + y_C\left(\frac{d\ln\gamma_C}{dy_C}\right) = 0 \dots (63)$$

Differentiation of equations 62 and 63 with respect to y_C and y_B respectively, and upon subtraction and subsequent rearrangement of the terms yields the above mentioned important relationship^{26,27}:

$$\left(\frac{d\ln(\gamma_B/\gamma_A)}{dy_C}\right) = \left(\frac{d\ln\gamma_C}{dy_B}\right) \dots (64)$$

Integrating equation 64 from $y_C = 0$ to $y_C = y_C^*$ along constant y_A and y_B yields the following equation for $\ln(\gamma_B/\gamma_A)$ along the metal-rich miscibility gap boundary as

$$\left(\ln \frac{\gamma_B}{\gamma_A}\right)_{\left(\begin{smallmatrix} y_B \\ y_C=y_C^* \end{smallmatrix}\right)} = \left(\ln \frac{\gamma_B}{\gamma_A}\right)_{\left(\begin{smallmatrix} y_B \\ y_C=0 \end{smallmatrix}\right)} + y_C^* \left(\frac{d\ln\gamma_C^0}{dy_B}\right)_{y_B} \dots (65)$$

Where γ_C^0 is the limiting activity coefficient of C at infinite dilution in A-B solutions. Equation 65 is strictly valid only if the variation $(d\ln\gamma_C/dy_B)$ with y_C is constant in the compositional range $0 < y_C < y_C^*$. This is a reasonable approximation provided that the metal rich boundary of the miscibility gap lies close to the metallic binary A-B. Thus the ratios of the activity coefficients and activities of B and A may be readily obtained from equation 65 by utilizing the thermodynamic properties of the metallic binary A-B and the limiting thermodynamic properties of the non-metallic C in the binary A-B.

Knowing the ratios of activity coefficients of B and A along the metal rich miscibility gap boundary as a function of metal atom ratio from equation 65, it is possible to calculate the activities of all three components by utilizing tie-line distribution data, through the following relations for coexisting liquid phases in the miscibility gap:

$$(1 - y_B^*) d \ln a_A + y_B^* d \ln a_B + y_C^* d \ln a_C = 0 \dots (66a)$$

$$(1 - y_B') d \ln a_A + y_B' d \ln a_B + y_C' d \ln a_C = 0 \dots (66b)$$

Subtracting equation 66b from equation 66a and rearranging the terms yield:

$$d(\ln a_C)_{y_B^*} = \left(\frac{y_B^* - y_B'}{y_C' - y_C^*} \right) d \ln(a_B/a_A)_{y_B^*} \dots (67)$$

Multiplying equation 66a by y_C' and 66b by y_C^* and upon subtraction and rearrangement of terms yield a relation for the activity of A as:

$$d(\ln a_A)_{y_B^*} = \left(\frac{y_B' y_C^* - y_B^* y_C'}{y_C' - y_C^*} \right) d \ln(a_B/a_A)_{y_B^*} \dots (68)$$

In the calculation of activities in Fe-Sn-S system equations 65, 67 and 68 were used with A for tin, B for iron and C for sulphur. Since the experimental values for the limiting activity-coefficient of sulphur in tin-iron melts were not available, they were calculated from the quasichemical relation of Jacob and Jeffes³⁰.

$$\ln \gamma_{S(Sn-Fe)}^\circ = y_{Sn} \ln \gamma_{S(Sn)}^\circ + y_{Fe} \ln \gamma_{S(Fe)}^\circ - \frac{2H^M}{RT} \dots (69)$$

Where H^M is the enthalpy of mixing for the Fe-Sn solutions. Equation 70 is reported²⁷ to predict good agreement between experimental values of γ° , and calculated values for the systems Cu-Ag-S, Ag-Pb-S and Ag-Sn-S. Thus the computed values of $\ln \gamma^\circ_{S(Fe-Sn)}$ were expected to be reasonable. With the quasichemical relationship of Jacob and Jeefes³⁰, equation 65 for Fe-Sn-S system takes the following form when expressed for activities²⁷:

$$\ln \left(\frac{\alpha_{Fe}}{\alpha_{Sn}} \right)_{\left(\frac{y_{Fe}}{y_{Fe}+y_S} \right)} = \left(\ln \frac{y_{Fe}}{y_{Sn}} \right)_{\left(\frac{y_{Fe}}{y_{Fe}+y_S} \right)} + \left(\ln \frac{y_{Fe}}{y_{Sn}} \right) + y_S \left(\ln \frac{(\gamma^\circ_{S(Fe)})}{(\gamma^\circ_{S(Sn)})} + \frac{2(H^M - H^M_{Fe})}{RT(1-y_{Fe})} \right) \dots (70)$$

The term H^M_{Fe} in the above relation represents the relative partial molar enthalpy of Fe in binary Fe-Sn solutions. The thermodynamic properties of Fe-Sn solutions, namely H^M and H^M_{Fe} as a function of composition were taken from S Wagner and GS Pierre³¹ which was reported at 1537 °C. In literature there is no available data at 1200 °C. Due to this reason, there was no choice but to assume that enthalpies were temperature independent and the 1537 °C data was directly used. This is not a bad assumption in the lack of data since enthalpies are slow functions of temperature. Henrian activity coefficient of sulphur at infinite dilution in liquid iron was obtained as $\gamma^\circ_{S(Fe)} = 1.83 \times 10^{-3}$ at 1200 °C from YY Chuang, KC Hsieh, YA Chang¹². The self interaction coefficient of iron; ϵ^{Fe}_{Fe} was calculated by applying the regression analyses to equation 26 developed by Shiraishi and Bell¹⁵. The natural logarithm of the activity coefficients calculated from equation 26 were plotted against mole fraction as shown in Figure 19 in the interval $0 < X_1 < 0.25$. The straight line of Figure 19 can be represented by the following linear

regression equation; $\log \gamma_{Fe} = -2.764X_{Fe} + 1.835$ The slope of this equation is the Gibbs energy self interaction coefficient of iron, $\epsilon_{Fe}^{Fe} = -2.764$.

Henrian activity coefficient of sulphur at infinite dilution in liquid tin; $\gamma_{S(Sn)}^\circ = 4.49 \times 10^{-2}$ at 1200 °C and self interaction parameter of sulphur in liquid tin: $\epsilon_S^S = -5.95$, the activities $a_{Sn} = 0.958$ and $a_S = 1.63 \times 10^{-3}$ along the binary immiscibility region and the boundaries of the immiscibility region of the Sn-SnS system; $X_S^{I1} = 0.0487$, $X_S^{I2} = 0.4738$ were all taken from AS Bilgin and RH Eric⁷. The interaction parameters ϵ_{Fe}^S and ϵ_{Sn}^S were assumed to equal zero in all calculations due to lack of the data in literature.

All the above mentioned thermodynamic information for the binaries were used in connection with the experimentally determined tie-line data (Table 2, Figure 15) to determine a consistent set of activities along the miscibility gap of the Fe-Sn-S system at 1473 K. Equation 70 permitted the calculation of the ratio $\ln a_{Fe}/a_{Sn}$ along the lower sulphur saturation boundary from which activities of sulphur, tin and iron were evaluated by the following integrated form of equations 67 and 68

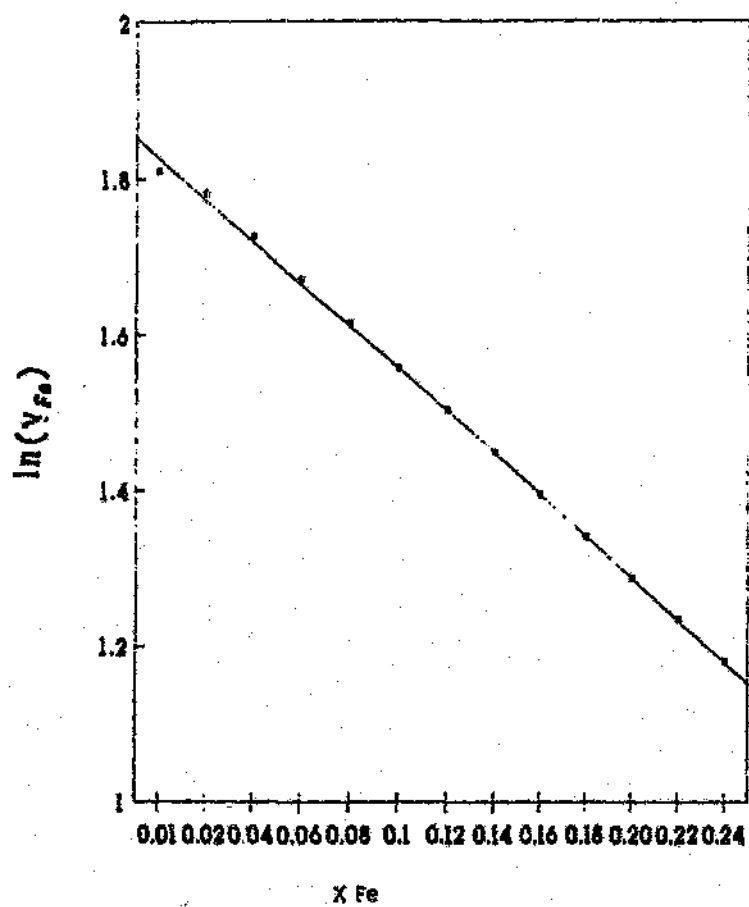


Figure 19 Activity coefficient of Fe versus mole fraction of Fe in Fe-Sn system

$$(\ln a_S)_{(y_{Fe}^*)} = (\ln a_S)_{(y_{Fe}^*=0)} + \int_0^{y_{Sn}^*} \Omega d\left(\ln \frac{a_{Fe}}{a_{Sn}}\right)_{(y_{Fe}^*)} \dots (71a)$$

$$(\ln a_{Sn})_{(y_{Fe}^*)} = (\ln a_{Sn})_{(y_{Fe}^*=0)} + \int_0^{y_{Fe}^*} \theta d\left(\frac{\ln a_{Fe}}{a_{Sn}}\right)_{(y_{Fe}^*)} \dots (71b)$$

$$(\ln a_{Fe})_{(y_{Fe}^*)} = (\ln a_{Fe})_{(y_{Fe}^*=0)} + \int_0^{y_{Fe}^*} \lambda d\left(\ln \frac{a_{Fe}}{a_{Sn}}\right)_{(y_{Fe}^*)} \dots (71c)$$

Where Ω , θ , λ are defined by:

$$\Omega = y_{Fe}^* - y_{Fe}' / y_S' - y_S^* \dots (72a)$$

$$\theta = (y_{Fe}' y_S^* - y_{Sn}^* y_S') / (y_S' - y_S^*) \dots (72b)$$

$$\lambda = (y_{Sn}' y_S^* - y_{Sn}^* y_S') / (y_S' - y_S^*) \dots (72c)$$

The integrals of equations 71 were evaluated graphically as the area under the curves θ , Ω , λ against $\ln(a_{Fe}/a_{Sn})$. These integration plots are shown, respectively in Figure 21 of Appendix. The results of integration are summarized in Table 4 giving the activities of all components on each tie-line.

All the thermodynamic data gathered with the procedure explained above, along the ternary miscibility gap of the Fe-Sn-S system were used to construct the diagrams shown in Figure 20 which show iso-activities of iron, tin and sulphur.

Since the tie-line distribution is known down to $y_{Sn}^* = 0.994$ (tie-line1) from the experimental work, the uncertainties in the lower integration limits obtained by extrapolation of the activity values of tin and sulphur from the Sn-SnS

Table 4. The results of activity calculations in the system Fe-Sn-S at 1473 K

Calculated activities along the metal rich boundary			
Tie-line number	a_{Fe}	a_{Sn}	a_S
1	0.047	0.950	1.59×10^{-3}
2	0.068	0.946	1.46×10^{-3}
3	0.097	0.941	1.36×10^{-3}
4	0.113	0.927	1.27×10^{-3}
5	0.176	0.918	1.21×10^{-3}
6	0.208	0.891	1.10×10^{-3}
7	0.270	0.858	9.87×10^{-4}
8	0.332	0.851	9.14×10^{-4}
9	0.416	0.822	7.87×10^{-4}
10	0.450	0.811	6.81×10^{-4}
11	0.487	0.801	6.33×10^{-4}
12	0.532	0.783	5.98×10^{-4}

binary are minimized. The value of a_{Sn} and a_S at $y_{Sn}^* = 0.994$ (tie-line 1) were taken as 0.950 and 1.50×10^{-3} , respectively by utilizing the available activity coefficients and self interaction parameter stated above. By using the same method, activity of iron was calculated from the iron-tin binary at y_{Sn}^* (tie-line 1) as $a_{Fe} = 0.047$.

In the calculation procedure, the end points of the tie-lines were read from the smooth miscibility gap boundaries to decrease the scatter of points.

The uncertainty in the derived activities can be readily assessed by analyzing the individual-uncertainties in various terms of equations 71. These equations are thermodynamically exact and the errors in the activities along the miscibility gap can be attributed to the uncertainties in a) the integration function Ω , θ and λ , b) the calculated activity ratio, and c) the integration procedure.

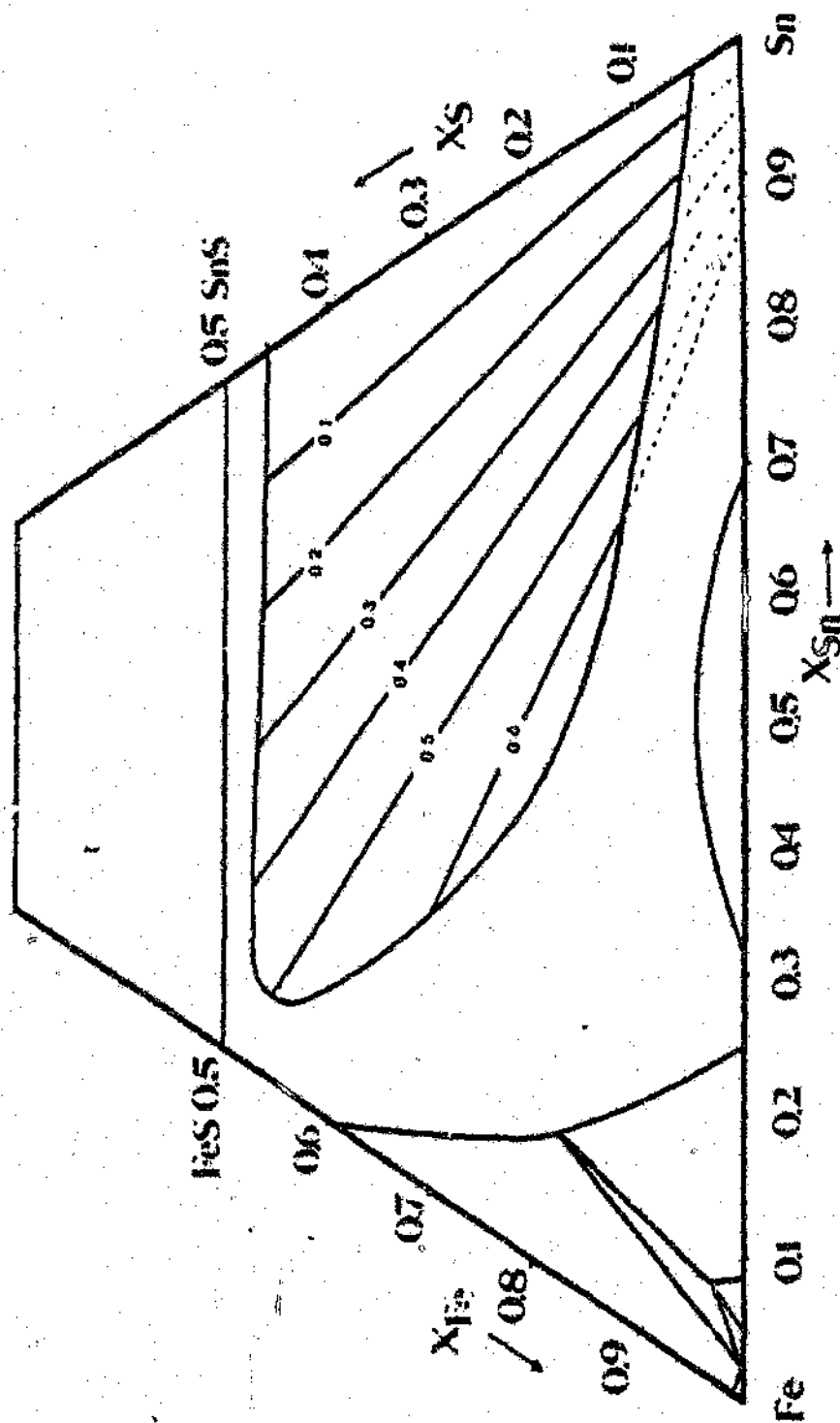


Figure 19a. Iso-activities of Fe in Fe-Sn-S melts at 1473 K

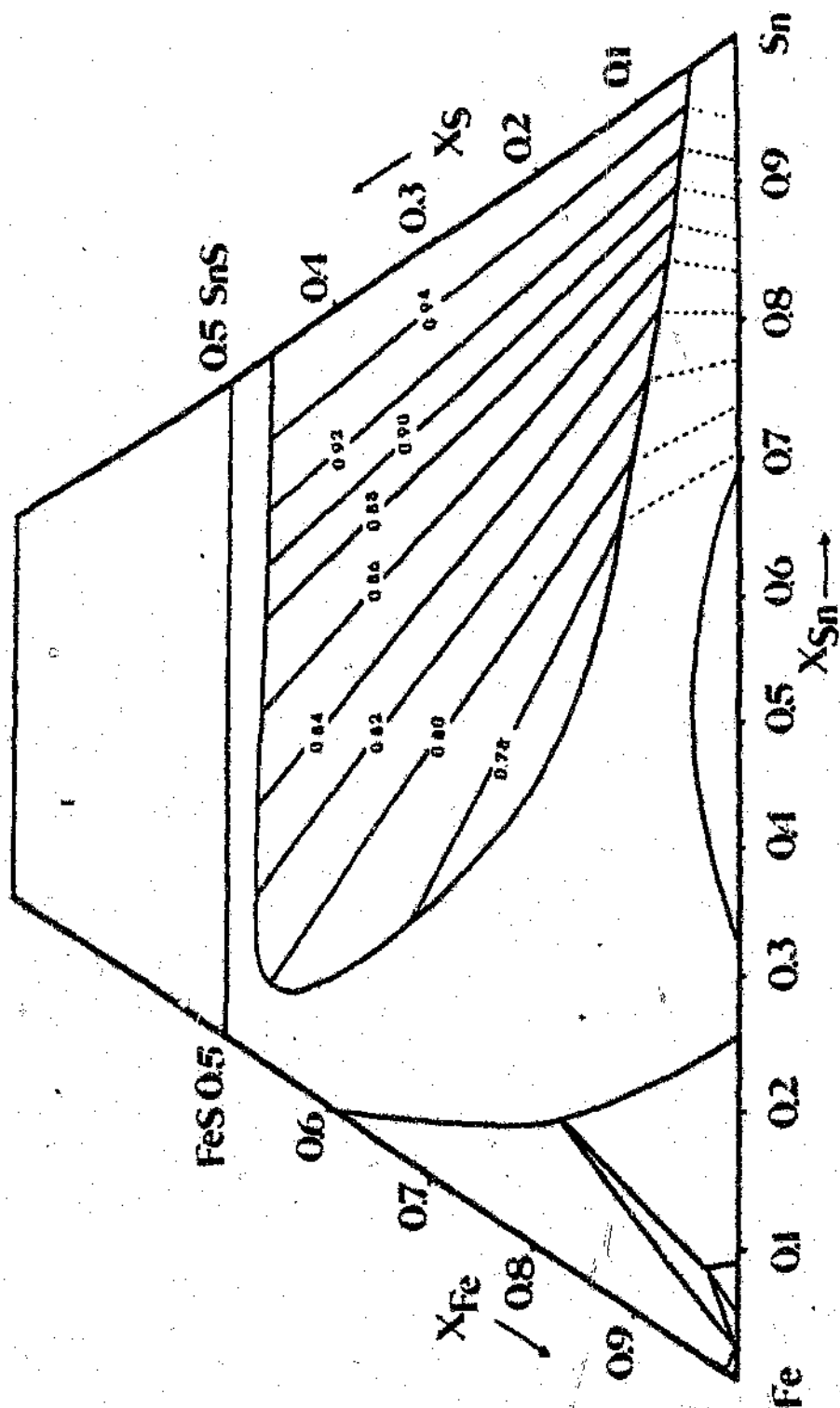


Figure 19b. Iso-activities of tin in Fe-Sn-S melts at 1473 K

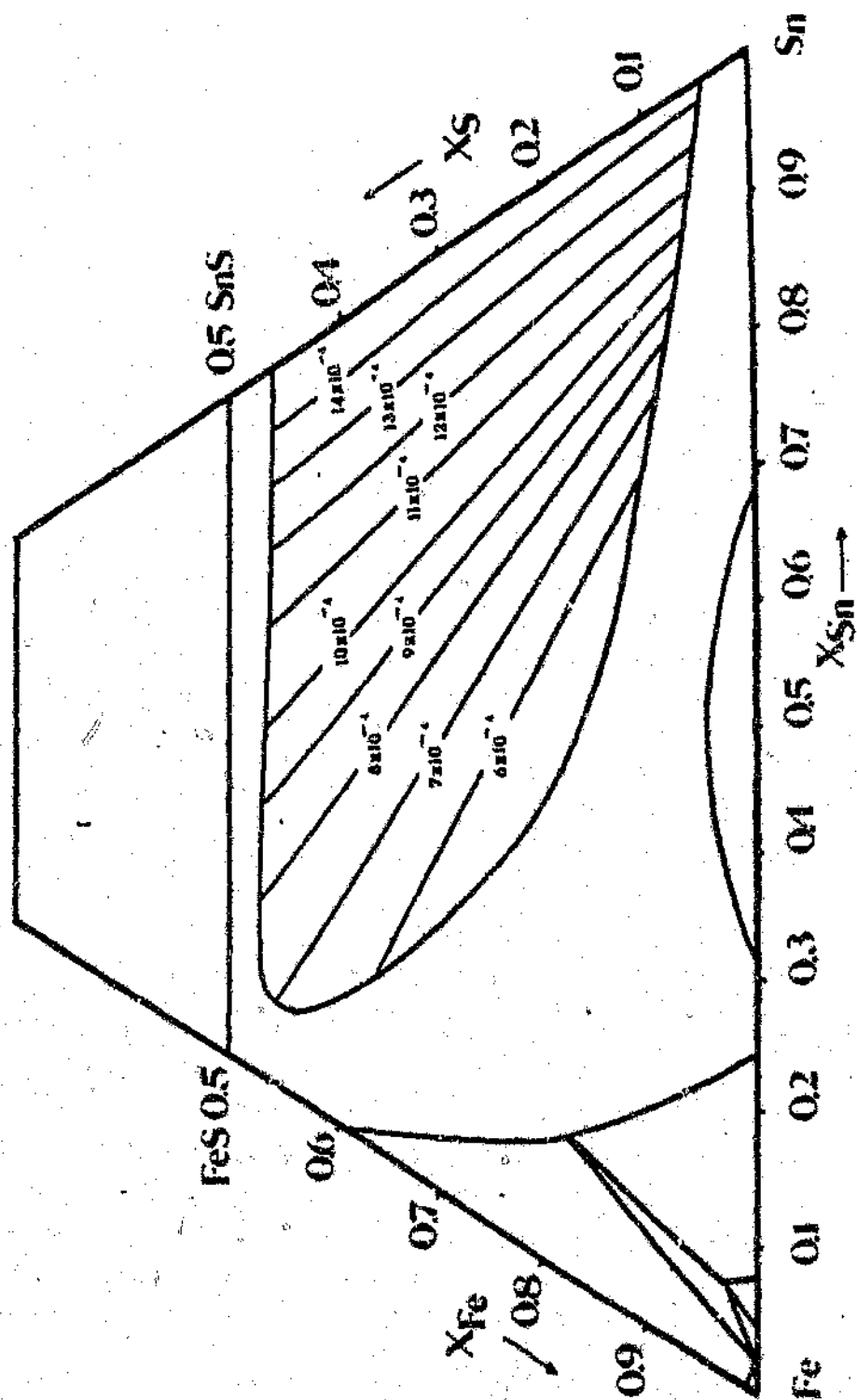


Figure 19c Iso-activities of S in Fe-Sn-S melts at 2473 K

From the tie-line data presented in Table 2 and Figure 15 the maximum error in the integration function Ω , λ and θ due to the error of chemical analysis is estimated to be ± 0.03 , ± 0.01 and ± 0.06 . Referring the equation 70, the uncertainty in the calculated $\ln(a_{Fe}/a_{Sn})$ values along the miscibility gap is due to a) the errors in the binary Fe-Sn activity data and b) the errors in the third term of the right hand side of equation 70 which consists of y_s^* and the term in the bracket. The term in the bracket was derived from the quasichemical model of Jacob and Jeffes³⁰. The derived values are reported by Chang et al²⁶ to have an uncertainty of $\pm 20\%$. Even if 40% uncertainty is assumed for the values of this term, with that of ± 0.05 in the values of $\ln(a_{Fe}/a_{Sn})$ in the Fe-Sn binary and of ± 0.03 in y_s^* , The derived values of $\ln(a_{Fe}/a_{Sn})$ along the miscibility gap will not be in error by more than ± 0.22 units.

However, as mentioned earlier all the thermodynamic data which were used for the calculation of $\ln(a_{Fe}/a_{Sn})$ were not at 1200 °C. In the calculation procedure for $\ln \frac{a_{Fe}}{a_{Sn}}$ the

activity data of Shiraishi and Bell¹⁵ was used. Their activity values at 1165 °C were extrapolated to 1200 °C by assuming regular solution behavior of Fe-Sn liquids within the small temperature range. Since the temperature range of extrapolation is quite small (35 °C), the error contribution from this source can be assumed negligible.

The last source of error is due to the graphical integration procedure. It can well be seen that the integration functions Ω , λ and θ result in very smooth curves in which integration errors would be negligible. Therefore, the total uncertainty in activity values is not expected to be greater than 10 %.

5 SUMMARY AND CONCLUSION

The objective of this work was to generate thermodynamic and phase equilibria data on tin containing sulphide systems by using the dew-point and quenching technique of thermochemical research. The specific systems selected for thermodynamic consideration during the present work were :

- 1.) The FeS-SnS binary
- 2.) The Fe-Sn-S ternary

The information gathered with respect to the above systems were the following.

1.) High temperature phase relations in the FeS-SnS system were examined by quenching technique. Eutectic temperature of this system was found at 815 °C. Activity measurements were carried out in this system at 1200°, 1100°, 1000 °C by measuring dew-point temperatures of SnS. Activities showed positive deviations from ideality. The SnS-FeS liquid solutions were modelled and SnS and FeS activities were calculated by applying the subregular solution model. This model permitted the calculation of liquidus lines, eutectic temperature and composition of the FeS-SnS phase diagram in excellent agreement with experimental determination.

2.) In Fe-Sn-S melts, the direction of conjugation lines between liquid matte and liquid metal phases at 1200 °C were found by quenching experiments. The activities of tin, iron and sulphur along the ternary miscibility gap of the Fe-Sn-S system were calculated through the recent method developed by Choudary and Chang^{26,27}, from the tie-line distributions and the thermodynamic information of the bounding binaries; Fe-Sn, Sn-SnS. The distribution of tie-lines were in concordance with the behavior of activity in both FeS-SnS and Fe-Sn melts.

The gathered information on high temperature thermodynamic properties and phase equilibria of Fe-Sn-S melts is essential for a proper understanding of the extraction and refining processes of tin. Further work is necessary for a better and efficient design of matte fuming process for tin. The equilibrium between FeS-SnS mattes and oxide slag phase should be investigated.

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7 APPENDIX

INTEGRATION FUNCTIONS OF Fe, Sn AND S IN Fe-Sn-S SYSTEM

The α , λ and Ω functions which were used in ternary Gibbs-Duhem integrations to derive Fe, Sn and S activities along the ternary miscibility gap of the system Fe-Sn-S at 1200 °C are illustrated in Figures A.21a, A.21b and A.21c respectively.

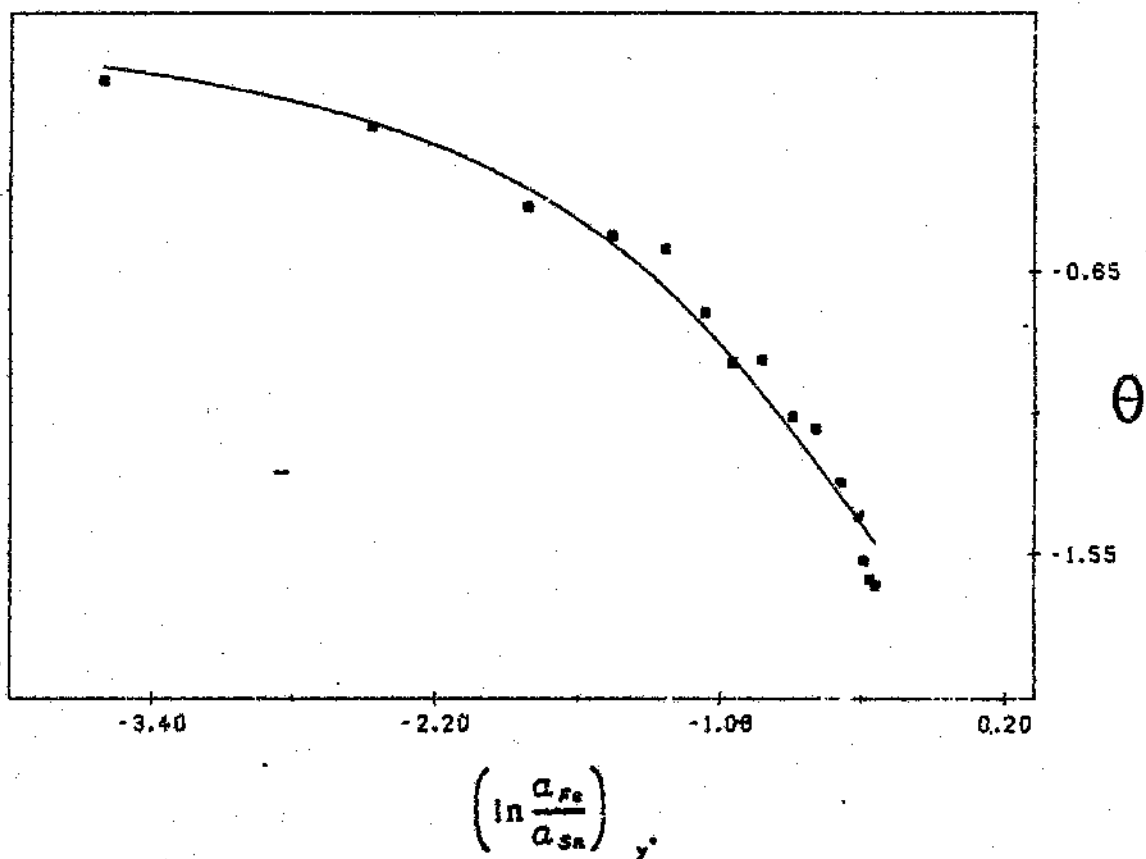


Figure A.21a The integration function θ against $\ln(a_{Fe}/a_{Sn})$ used to evaluate Fe activities in the system Fe-Sn-S at 1200 °C

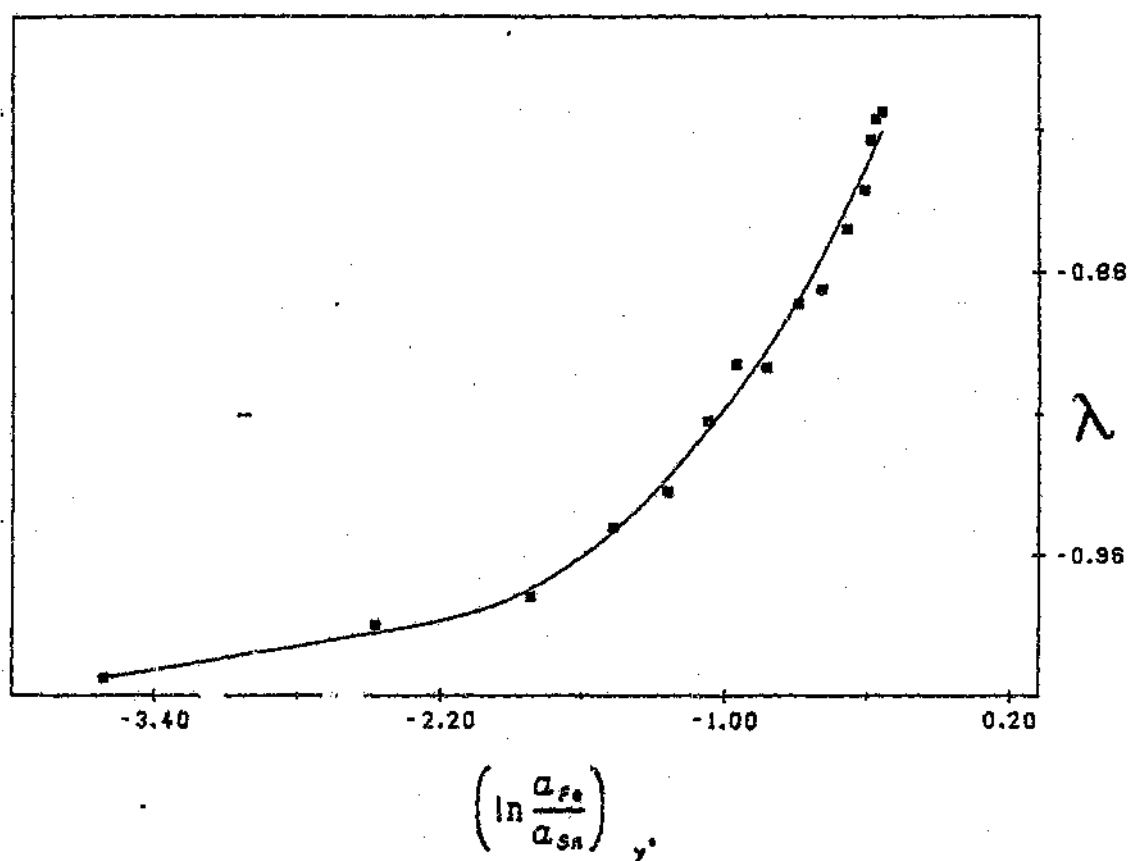


Figure A.21b The integration function λ against $\ln(a_{Fe}/a_{Sn})$ used to evaluate Sn activities in the system Fe-Sn-S at 1200 °C

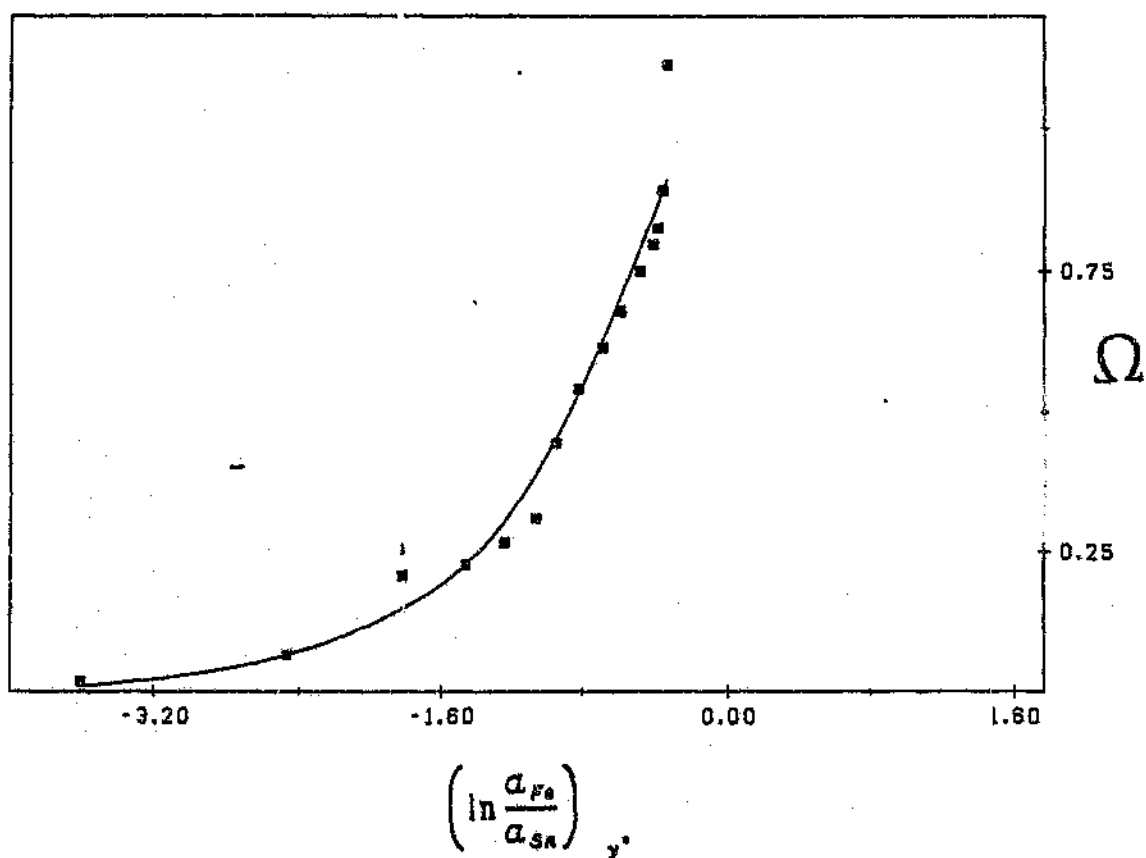


Figure A.21c The integration function Ω against $\ln(a_{Fe}/a_{Sn})$ used to evaluate S activities in the system Fe-Sn-S at 1200 °C

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