

CONTRIBUTIONS TO THE CHEMISTRY OF TIN SULPHIDES
AND THEIR USE IN PROCESSING OF TIN ORES

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by

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ABSTRACT

Known reactions utilised in the extraction of tin from its ores are reviewed, and particular attention is given to "sulphidising" reactions in which tin ore (usually cassiterite, SnO_2) is converted directly into a tin sulphide or a thiostannate for further processing. It is shown that a sulphidising gas effective in this conversion (consisting of carbonyl sulphide, carbon disulphide vapour, carbon monoxide, and smaller proportions of sulphur vapour and carbon dioxide) is readily obtained by reducing sulphur dioxide with carbon.

The use of this new sulphidising reaction to convert tin oxide into a sulphide has been examined experimentally, and suitable conditions defined. X-Ray study of the products has permitted close correlation of the results with the quite complex stability relationships of phases in the tin-sulphur system.

Similar sulphidising of a mixture of tin oxide and sodium sulphate (which is reduced to sodium sulphide in the sulphidising gas) provides a convenient method of direct conversion of tin oxide into sodium thiostannates. This reaction has also been studied, and X-ray powder techniques used to define the compositions and stability ranges of thio-salts obtained as products.

As an alternative route to soluble thio-salts of tin, reactions of tin compounds with melts of sodium carbonate and sulphur have also been investigated. Knowledge gained in the preceding studies has allowed these reactions to be characterised more closely than before, and the work has led to formulation of a relatively convenient low-temperature method for melt attack of tin oxides and other tin compounds.

The bearing of the reactions studied on possible methods for industrial processing of tin ores is considered, and tests carried out on typical low-grade concentrates and tin-containing slags, providing a searching test of the principles developed, are described.

ACKNOWLEDGEMENT

I offer my sincere thanks to Dr A.J.E. Welch for his guidance and valuable advice without which this work would not have been carried out.

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Introduction

The Chemistry of Tin Sulphides and Thiostannates

Various solid phases have been postulated to exist in the tin-sulphur system; they include the alleged sulphides SnS_2 , Sn_2S_3 , Sn_3S_4 , Sn_4S_5 and SnS . Gerasimov et al. (1937) formulated the course of thermal decomposition of stannic sulphide as: $\text{SnS}_2 \rightarrow \text{Sn}_2\text{S}_3 \rightarrow \text{Sn}_4\text{S}_5 \rightarrow \text{SnS}$. Clair et al. (1954) disputed the existence of compounds other than SnS_2 and SnS and stated that complete solid solution exists between SnS_2 and SnS at temperatures up to 900°C . Bok et al. (1957) reported the existence of a tetragonal sulphide, Sn_3S_4 , formed by heating the elements at 600°C . Albers et al. (1961) reported the synthesis of a phase under a sulphur partial pressure of more than 100 mm. Hg, with X-ray data different from those reported by Bok et al., and stated that this phase is non-cubic.

Volynskii and Sevryakov (1956) reported a phase analysis of the dissociation products of SnS_2 using thermographic and microscopic methods and X-ray analysis. SnS_2 dissociates to form Sn_2S_3 at 520°C ; this, in turn, dissociates to form SnS at 640°C . Sevryakov et al. (1959) reported the results of experiments on the dissociation pressure of SnS_2 at 350° , 400° , 450° and 500°C .; their values were represented by the equation:

$$\log P_{\text{S}_2} (\text{mm Hg}) = - \frac{19,280}{T} + 16.66$$

Karakhanova et al. (1966) studied the tin-sulphur system by DTA and X-ray methods. SnS_2 , Sn_2S_3 , Sn_3S_4 , and SnS were prepared by heating tin-sulphur mixtures for long periods of time (400 - 500 hours) at 500°C . in evacuated quartz ampoules. Table I shows crystallographic data for the sulphides prepared.

Mootz et al. (1967) confirmed the existence of a tin sulphide, Sn_2S_3 , besides the well-known compounds SnS and SnS_2 , and its crystal structure was determined by three-dimensional single-crystal X-ray diffraction analysis. It is orthorhombic, with:

Table I

Crystallographic Data for Tin Sulphides reported by Karakhanova et al. (1966).

Formula	Wt % Sulphur	Crystallographic Data
SnS	21.27	Orthorhombic; $a = 4.340 \pm 0.004$ kX $b = 3.980 \pm 0.001$ kX $c = 11.180 \pm 0.002$ kX
SnS ₂	35.08	Hexagonal; $a = 3.650 \pm 0.001$ kX $c = 5.973 \pm 0.002$ kX
Sn ₂ S ₃	28.84	Orthorhombic; $a = 8.863 \pm 0.003$ kX $b = 3.754 \pm 0.001$ kX $c = 42.060 \pm 0.002$ kX
Sn ₃ S ₄	26.48	Tetragonal; $a = 7.473 \pm 0.001$ kX $c = 33.064 \pm 0.001$ kX

$$\begin{aligned}
 a &= 8.864 \text{ \AA} \\
 b &= 14.020 \text{ \AA} \\
 c &= 3.747 \text{ \AA} \\
 z &= 4
 \end{aligned}$$

The crystal structure consists of infinite double rutile strings of $\text{Sn}^{\text{IV}}\text{S}_6$ octahedra parallel to the c -axis, with Sn^{II} atoms attached laterally. This sulphide can be regarded as tin(II) thioannate ($\text{Sn}^{\text{II}}[\text{Sn}^{\text{IV}}\text{S}_3]$).

Recently, Moh (1969) reported a detailed study of the tin-sulphur system using quenching, high-temperature X-ray diffraction, and DTA, with silica tubes as reaction vessels. Three main phase regions exist at approximate compositions, SnS_2 , Sn_2S_3 , and SnS ; these all give rise to polymorphic forms, several of which cannot be retained by quenching. The use of a high-temperature camera in Moh's study has disclosed the true structural complexity of the system. Phases reported by Moh are listed below.

1. SnS : two forms

β - SnS : Stoichiometric and stable below 600°C .

α - $\text{Sn}_{(1-x)}\text{S}$: Non-quenchable form, stable above 600°C .

2. Sn_2S_3 : Four forms

δ - Sn_2S_3 : Low-temperature stable phase up to 675°C ; quenchable and stoichiometric or nearly so.

γ - $\text{Sn}_{(2-x)}\text{S}_3$: Non-quenchable, a high temperature polymorph.

β - $\text{Sn}_{(2+x)}\text{S}_3$: Non-quenchable; forms at $715 \pm 6^\circ\text{C}$ from γ - Sn_2S_3 .

α - $\text{Sn}_{(2+x)}\text{S}_3$: Non-quenchable, and stable above $744 \pm 3^\circ\text{C}$.

3. SnS_2 : Two forms

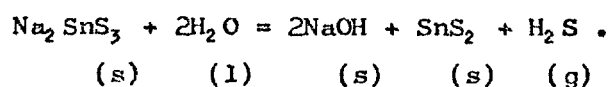
β - SnS_2 : Stoichiometric; golden yellow crystals; inverts to the α -phase at 692°C . Quenchable.

α - $\text{Sn}_{(1+x)}\text{S}_2$: Quenchable, dark reddish-brown to bronze-colored crystals. Stable in the presence of excess sulphur above 692°C .

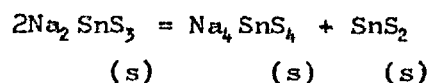
This brief account on the tin-sulphur system shows that it is a complex one structurally. It should be noted that in the various techniques adopted for the study of this system, or in the synthesis

of the individual sulphides; there is one feature in common: composition has been the main variable considered in the system. Temperatures, and in particular the effective pressures of sulphur vapour in which particular phases are stable, have received little attention. Probably this is the main reason for the lack of accurate information and apparently conflicting data. It is of extreme importance to give full consideration to composition, temperature, and sulphur vapour pressure, as variables in the system in order to draw useful conclusions. The stability of any metal sulphide is governed by the sulphur vapour pressure over the solid phase at the specified temperature; unless the sulphur vapour pressure is specified, decomposition or transformation temperatures are meaningless.

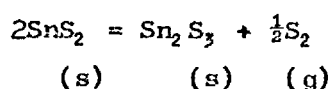
The sodium thioannates (the metathioannate, Na_2SnS_3 , and orthothioannate, Na_4SnS_4), were studied by Sevryukov (1960). The two salts were prepared in solution and isolated as hydrates, $\text{Na}_2\text{SnS}_3 \cdot 8\text{H}_2\text{O}$ and $\text{Na}_4\text{SnS}_4 \cdot 15\text{H}_2\text{O}$. Samples were dried in vacuo to about 1 mole H_2O , and then the thermal decomposition was studied in a dry, purified argon atmosphere. The dehydration of the Na_2SnS_3 hydrate was accompanied by an exothermic effect at 170°C ., possibly as a result of the hydrolysis reaction:



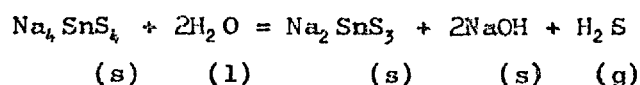
Upon further heating, Na_2SnS_3 decomposed to Na_4SnS_4 and SnS_2 , and formed a melt with the products of decomposition at 575°C .



An exothermic effect was observed at 525°C . and probably due to the decomposition of SnS_2 .



The dehydration of the Na_4SnS_4 hydrate had an endothermic hydrolysis at 150°C . At $650 - 695^\circ\text{C}$ the salt melted with



the decomposition products. An insignificant decomposition with the formation of SnS and sulphur began at about 900°C.

It is important to note that thioannates with S:Sn atomic ratio less than three were not observed. According to these results, Sevryukov concluded that the only thioannate stable at high temperature, e.g. 850°C., is Na_4SnS_4 . The most complete sulphidisation of cassiterite is therefore likely to lead to formation of Na_4SnS_4 .

In published papers, many methods have been described for the preparation of thioannates. Na_4SnS_4 can be obtained by melting or sintering tin dioxide with sodium sulphide, with a mixture of soda ash and sulphur, with a mixture of sodium sulphate and coal, or with sodium thiosulphate. The melt or agglomerate is leached in water and $\text{Na}_4\text{SnS}_4 \cdot 1.5\text{H}_2\text{O}$ crystallized from the solution (Murach, 1964).

When concentrated Na_2SnS_3 solutions are heated with tin and sulphur, polythioannates are formed, e.g. $\text{Na}_2\text{Sn}_3\text{S}_7$, which can be written as $\text{Na}_2\text{S} \cdot 3\text{SnS}_2$. A similar salt with the composition, $\text{Na}_2\text{S} \cdot 2\text{SnS}_2$, i.e. $\text{Na}_2\text{Sn}_2\text{S}_5$, was not obtained (Murach, 1964).

Thioannates of most other metals, such as Fe_2SnS_4 and CuSnS_3 , are insoluble in water. The tin mineral stannite is a thioannate of copper and iron, viz. $\text{Cu}_2\text{FeSnS}_4$. Mellor (1927) gave a short account of the formation of the base-metal thioannates and their synthesis.

The Chemistry of Extraction of Tin from Its Ores

The principal tin mineral of economic value is cassiterite (SnO_2). The complex sulphide minerals have been exploited only to a limited extent and, of these, stannite ($\text{Cu}_2\text{S}, \text{FeS}, \text{SnS}_2$) and franckeite ($5\text{PbS}, 2\text{SnS}_2, \text{Sb}_2\text{S}_3$), have had some significance in Bolivian production. The traditional methods of concentration of cassiterite are based on the exploitation of its physical properties, principally its high specific gravity (6.5 - 7.0), to separate it from the other minerals. Thus the low-density gangue minerals are generally separated from cassiterite by gravity concentration techniques, which include heavy-media separations and tabling. Sulphides are almost invariably removed by flotation with xanthates, though sulphidic ores may be oxidized in a roasting procedure for which rotating kiln-type furnaces or multi-hearth furnaces fitted with revolving rabbles have been used. Though gravity and flotation procedures predominate among the various concentration methods available, a wide variety of modifications and alternative procedures have been explored, often to cope with conditions imposed by the identities and concentrations of mineral species present in the ore.

The flotation of cassiterite is known to be unselective. The major problem in the concentration of cassiterite ores by flotation, especially the disseminated ores, is the effect of slimes. The polydispersed character of cassiterite dissemination (all ores contain grains of various sizes and aggregates of fine grains) is the main cause of high slime formation and low extraction values in flotation of tin from such sources.

A notable property of cassiterite is that it is very resistant to any chemical attack at room temperature, and this necessitates treatment of cassiterite concentrates at high temperatures to achieve any appreciable chemical reaction. Apart from the well-known smelting process which is applied mainly to high-grade concentrates, the processes applied to low-grade concentrates, and with which this project is concerned, can be classified broadly into four types:

1. Sulphidization: Conversion of cassiterite into the sulphide.
2. Chloridization: Conversion of cassiterite to the chloride.
3. Reduction: Conversion of cassiterite to the metal.
4. Thiostannate Formation: Conversion of cassiterite to the water-soluble thiosalt.

1. Sulphidization

The process of sulphidization of cassiterite to convert it into the sulphide seems to be a fairly simple one, and numerous patents were taken out many years ago (Wright, 1966). The sulphidizing agent is usually a sulphur carrier used with or without a reducing agent. The following are some of the sulphidizing agents used: pyrite (FeS_2), metal sulphides (ZnS or CaS), elemental sulphur, hydrogen sulphide, carbon disulphide, and sulphur dioxide. Reducing agents used are: carbon (coke or coal), carbon monoxide, and hydrogen. The technique and the working conditions depend mainly on the intended treatment of the sulphidized charge. Three types of treatment have been proposed:

- (1) Sulphidization at low temperatures, $300 - 600^\circ\text{C}$., followed by flotation. In this case, coating of cassiterite particles with sulphide is sufficient for high flotation recovery (Balberyszski et al., 1968).
- (2) Sulphidization at moderate temperatures, $600 - 800^\circ\text{C}$., followed by leaching. In this case, complete conversion of cassiterite to the sulphide is necessary, and therefore more effective conditions are used. Leaching can be carried out by means of acid or alkaline polysulfide solution (Sulman and Picard, 1928).
- (3) Sulphidization at high temperatures, $800 - 1000^\circ\text{C}$., with simultaneous volatilization of the tin sulphide formed (Klushin et al., 1962).

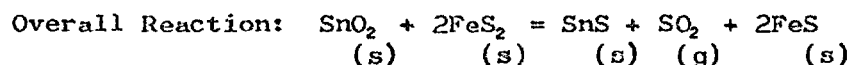
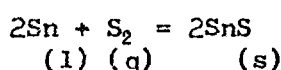
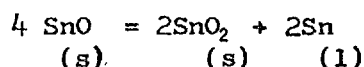
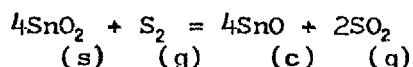
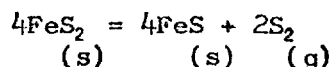
Table 2 summarises the reported work on the sulphidization of cassiterite.

Table 2

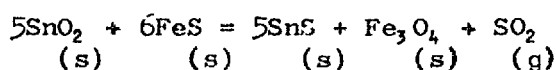
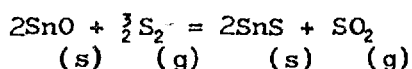
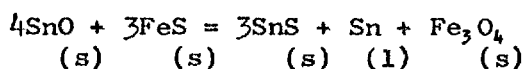
Reported Work on the Sulphidization of Cassiterite

Method	Sulphide Formed	Reference
1. Sulphidization of cassiterite by H_2S at low temperatures, 100-500°C, followed by flotation.	SnS , SnS_2 and Sn_2S_3	Balberyszski et al., (1968)
2. Sulphidization of cassiterite by SO_2 in a reducing atmosphere (CO or H_2) at low temperatures, 400-600°C, followed by flotation.	SnS	Vaschetti (1968)
3. Sulphidization of cassiterite using pyrite and a reducing agent at moderate temperatures, 750-850°C., followed by leaching.	SnS	Sulman and Picard (1928)
4. Volatilization of tin sulphide from cassiterite concentrates in a fluidized-bed roaster at 900-930°C., using pyrite and carbon	SnS	Klushin et al., (1962)
5. Volatilization of tin sulphide from cassiterite concentrates in a two-layer fluidized-bed reactor using pyrite at 900°C.	SnS	Wells et al. (1952)
6. Volatilization of tin sulphide from cassiterite concentrates using sulphur vapour at high temperatures	SnS	St Clair et al., (1954)
7. Volatilization of tin sulphide from cassiterite concentrates by using H_2S or CS_2 diluted with about three volumes of CO_2 or steam at 800°C	SnS_2	Burdick (1926)

The sulphidization of cassiterite by pyrite in the absence or presence of carbon was studied thoroughly by the Russian workers. In the 600 - 800°C range, conversion of SnO_2 into SnS is claimed to proceed by way of formation of SnO and SO_2 , decomposition of SnO with liberation of the metal, and reaction of metal with elemental sulphur:

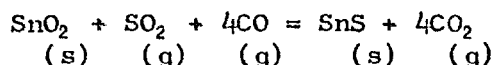
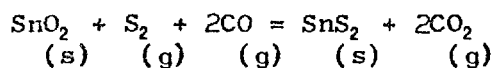
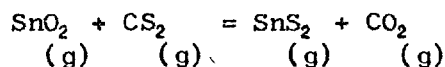
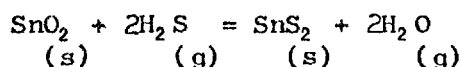


At high temperatures, the tin sulphide is believed to be formed both by the mechanism outlined above and by direct reaction of SnO and SnO_2 with FeS , and of SnO with sulphur (Klushin et al., 1961):



In the presence of a reducing agent, the sulphidizing action of FeS increases sharply with rise of temperature, starting at 700°C. The rate of conversion of SnO_2 into the sulphide in presence of a reducing agent is 2 - 6 times that observed in the absence of a reducing agent. The optimum tin to sulphur and tin to carbon atomic ratios in the mixture are (1:2.0 - 2.5) and (1:1) respectively (Klushin et al., 1962).

The sulphidization of cassiterite with sulphurous gases, e.g. H_2S , CS_2 ... etc, can be represented as follows:

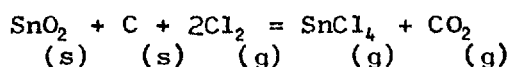
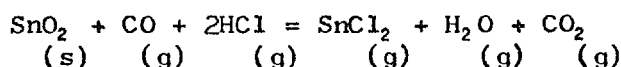
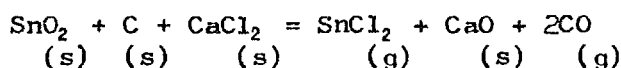


Recently, Welch (1970) has applied a novel technique for the sulphidization of metal oxides. This utilizes a powerful and effective sulphidizing gas mixture composed principally of CS_2 , COS , S_2 , CO_2 , and CO . This gas mixture is the reduction product of sulphur dioxide with carbon in the temperature range $700 - 1000^\circ\text{C}$ (Owen et al., 1951). The major advantages of this technique are:

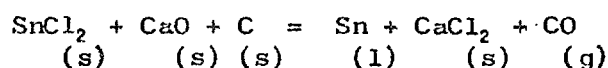
1. The sulphidizing gas is potentially cheap and easily prepared.
2. A powerful sulphidizing action is obtained, because the sulphidizing gas contains three sulphurous gases in a reducing atmosphere.
3. Complete control of the composition of the sulphidizing gas is possible with respect both to the sulphurous gases, and to the reducing agent, over a wide range of temperature. This is very convenient in practice. The sulphidizing gas has a known and constant sulphur vapour partial pressure at any given temperature; this determines the type of sulphide formed.

2. Chloridization

This technique involves the conversion of cassiterite into a volatile tin chloride, using a chlorine carrier in the presence of a reducing agent. Chloridizing agents used may be solids like CaCl_2 , NaCl , FeCl_3 etc, or gases like hydrogen chloride, chlorine, carbon tetrachloride etc. Reducing agents used are carbon, carbon monoxide, and hydrogen. The following reactions represent some of the equilibria involved in chloridization:



Recently, Fletcher and Wilson (1967) have found a promising method for recovering tin metal from tin chloride by heating it with lime and carbon; this reaction recovers calcium chloride to be recycled for the chloridization stage. This reaction is promising, if the technical

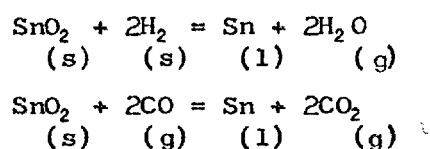


difficulties can be solved. The conventional methods used for recovering the metal from the chloride are the conversion of the chloride into the oxide for smelting or the direct electrolysis of the chloride in a fused salt bath.

The results reported by Fletcher et al. show that smelting of the chloride is the superior way of producing the metal. On the other hand, a possible disadvantage of chloridizing with calcium chloride is that in the presence of water vapour a hydrolytic reaction takes place which tends to reduce the degree of chloride conversion and volatilization. According to Shelton (1970), the solution to the problem of recovering tin from low-grade concentrates could be this chloridization-smelting process.

3. Reduction

The reduction of cassiterite to the metal, followed by acid leaching,



is interesting if it can be made selective, so that iron is prevented from going into solution. Wright (1966) has concluded, after a thermodynamic analysis and a thorough study of this problem, that an iron-free solution cannot be obtained. Alkaline leaching, on the other hand, will not take iron into solution, but will dissolve silica. Colloidal silica will then make the residue almost impossible to filter.

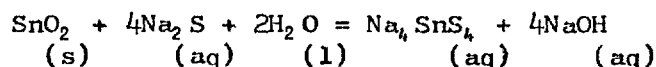
The most recent work in this field is the Geo-Met process, in which a finely ground concentrate (25% Sn) is allowed to fall through an externally heated tube containing a reducing gas. Hydrogen or carbon monoxide can be used, but hydrogen is preferable because it is easy to

remove water vapour by condensation, and inexpensive hydrogen production by electrolysis or from hydrocarbons is well established (Wright, 1966).

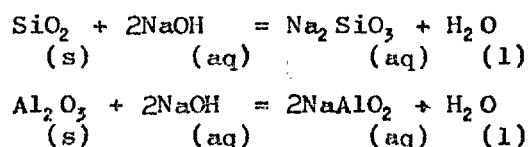
4. Thiostannate Formation

Recently, aqueous leaching of tin from low-grade concentrates has received much attention, because of its simplicity and the cheapness of the reagents used. This technique involves the conversion of cassiterite into a water-soluble thio-salt through the reaction with alkali salts in a reducing atmosphere at high temperatures (Vonstein, 1971). In some cases, sulphur is added to the charge (American Cyanamid Co., 1941).

Direct leaching of cassiterite concentrates with alkali sulphide or alkali sulphide-hydroxide solutions in an autoclave at high pressure and at a temperature of 400 - 500°C., has also been reported (Jangg et al., 1958). Other metals, including antimony, arsenic, tungsten, and molybdenum also go into solution as thio-salts.



Direct leaching of cassiterite concentrates with alkali sulphide-hydroxide solutions at high pressures is a promising process for high-grade concentrates; its disadvantage is the lack of selectivity. The dissolution of silica and alumina becomes serious in the case of low-grade concentrates.



The problem of selectivity could probably be solved in the recovery stage; selective reduction at a mercury cathode or by means of sodium amalgam has been proposed (Gladyshev et al., 1970).

Unfortunately, there is little information about melt reactions responsible for the formation of sodium thiostannate, or its identity, under working conditions. At high temperature, the only stable thio-salt reported to exist is the ortho-thiosalt, Na_4SnS_4 (Sevryukov, 1960). In a fused mixture of cassiterite concentrate, alkali salt, carbon, and sulphur, in which a thiostannate is undoubtedly formed, it is not easy to predict the types of reaction responsible for the formation of the

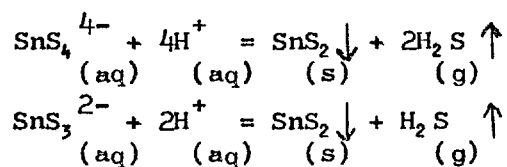
thio-salt. The main problems in formulating the participating reactions are:

1. The complexity of the reduction reactions of the alkali sulphate with carbon.
2. The possibility of direct interaction of cassiterite with alkali compounds.
3. The possibility of reduction of cassiterite to form SnO or tin metal, and their interactions in the system.
4. The possibility of sulphidization of any tin species (SnO_2 , SnO, or Sn) and the exact role of the formed sulphide in the system.
5. The role and effect of the presence of base-metal compounds in the system.

In this context it may be noted that related (but probably simpler) reactions may be formulated using, as a reducing gas and source of sulphide sulphur, the products of reduction of sulphur dioxide with carbon. If this gas is allowed to react with a mixture of cassiterite and sodium sulphate, the gaseous sulphur compounds are available to sulphidise the tin, and the high carbon monoxide content is adequate to reduce the sodium sulphate to sulphide. The tin and sodium sulphides then combine to form the thio-salt. Work to verify this new reaction is described later in this Thesis. This work provided a good chance to characterise the water-soluble thiostannate on the basis of a fuller understanding of the tin-sulphur system.

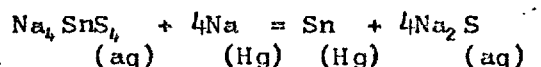
The final step in the process of "aqueous leaching" of tin concentrates is the recovery of the metal values from the leach solution. Three methods are known:-

1. Treatment of the leach solution with an acid to precipitate stannic sulphide:



This method is very simple, efficient, and cheap. But the product, stannic sulphide, is undesirable, and has to be roasted to convert it into the oxide for reduction.

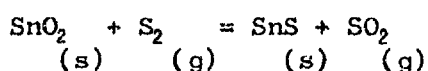
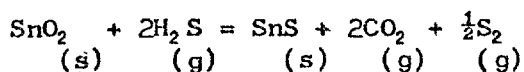
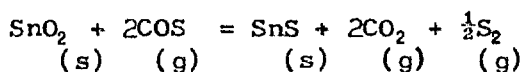
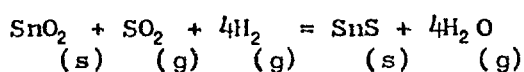
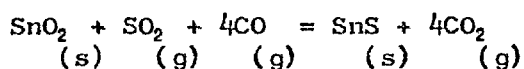
2. Precipitation of tin metal by sodium amalgam:



This is a very simple process, but costly and awkward to use on the large scale.

3. Electrolysis: The recovery of tin from the leach solution can be achieved by electrolysis. This process is recommended when a clean leach solution can be obtained. Trace amounts of arsenic present in solution greatly affect the current efficiency, and the presence of free alkali and polysulphides is also harmful (Sevryukov, 1958). Other likely impurities (silica and aluminate from direct leaching of cassiterite with alkali sulphide-hydroxide; colloidal or dissolved iron sulphides from the high-temperature treatment with alkali salts) make the electrolysis complicated and inefficient. The formation of sulphur at the anode and its dissolution as polysulphide necessitate the separation of the catholyte and the anolyte by a diaphragm.

The SO_2/CO or SO_2/H_2 sulphidization system reported by Vaschetti (1968) is interesting because of the low working temperatures employed, 400 - 600°C. Unfortunately, this system is a sulphur-producing system. Vaschetti reported that cassiterite was totally transformed to SnS . It was difficult to decide whether sulphidization was due to direct action of sulphur dioxide and carbon monoxide or hydrogen (primary sulphidization) or through the action of sulphurous gases formed from reduction of sulphur dioxide (secondary sulphidization):



Formation of large quantities of the sulphurous gases (carbonyl sulphide, hydrogen sulphide, and sulphur vapour) was observed at the exit of the reactor.

A thorough investigation of this system is worthwhile because industrial roaster gases contain 6 - 15% of SO_2 in nitrogen. The sulphidizing gas used by Vascetti contained:

SO_2 8%, CO or H_2 28%, and N_2 64% by volume.

Recently, a process was developed for extraction of tin from low-grade cassiterite concentrates by making a glass at high temperatures and leaching it with 9.0M sulphuric acid at 80°C . for two to three hours (Nixon, 1970). The metal values can be recovered from the leach solution by electrolysis. The potential technical problems are currently being investigated.

Work to be described in this Thesis

It is clear from this brief account of the various reported processes for the treatment of low-grade cassiterite concentrates that reliable information on the tin-sulphur system and the water-soluble thiostannates at various temperatures is lacking in the literature. Such information is important for further examination and planning of a potentially cheap process for the extraction of tin from low-grade tin sources. Therefore, it was decided to investigate:

Firstly

The reactions of stannic oxide with sulphurous gases (CS_2 , COS , and S_2) in a reducing atmosphere (CO/CO_2).

Secondly

The reactions of stannic oxide with sodium sulphate in a sulphidizing-reducing atmosphere.

Thirdly

The tin-sulphur system, and the conditions of formation of sodium thiostannates.

Fourthly

Reaction tests on low-grade tin concentrates under optimum conditions.

Chapter I

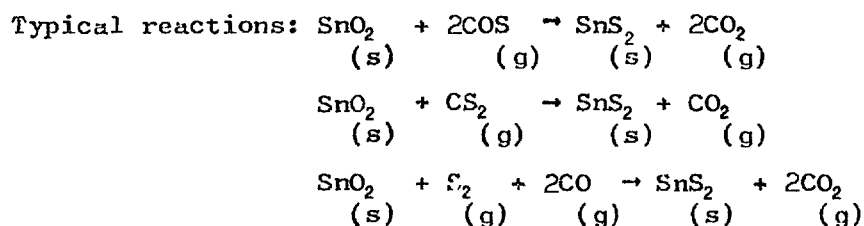
Sulphidization of Stannic Oxide with Carbonyl
Sulphide, Carbon Disulphide, and Sulphur Vapour
in a Reducing Atmosphere

The Sulphur dioxide-Carbon system has been studied extensively. Some workers were interested in the production of elemental sulphur, and others in the production of carbon disulphide. The complicated solid-gas reaction between carbon and sulphur dioxide involves a large number of equilibria (Siller, 1948). It is expected, and it has already been found experimentally and by thermodynamic calculations, that the composition of the gas mixture resulting from this reaction is temperature dependent. The reduction of sulphur dioxide by carbon at high temperatures is practically complete; the partial pressure of sulphur dioxide in the gas mixture resulting from reduction is less than 10^{-7} atm. at 727°C . (Owen et al., 1951). Figure 1 gives the distribution of sulphur in reaction products from reduction of sulphur dioxide with carbon.

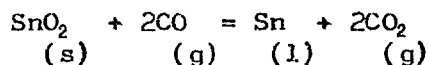
Recently, Welch (1970) has utilized the reduction products, without separation, for sulphidization of metal oxides. The useful temperature range of interest in the reduction reaction is $700 - 1000^{\circ}\text{C}$.

In the sulphidization of stannic oxide in a reducing gas mixture, two major reactions are important:

1. Sulphidization:



2. Reduction:



The incidence of reduction to the metal at a certain temperature will clearly depend on the CO/CO_2 ratio in the sulphidizing gas. The sulphidization of the oxide, in presence of reducing gas, may result in the formation of SnS , SnS_2 , Sn_2S_3 , or any other sulphide phase according to the working temperature and the gas composition.

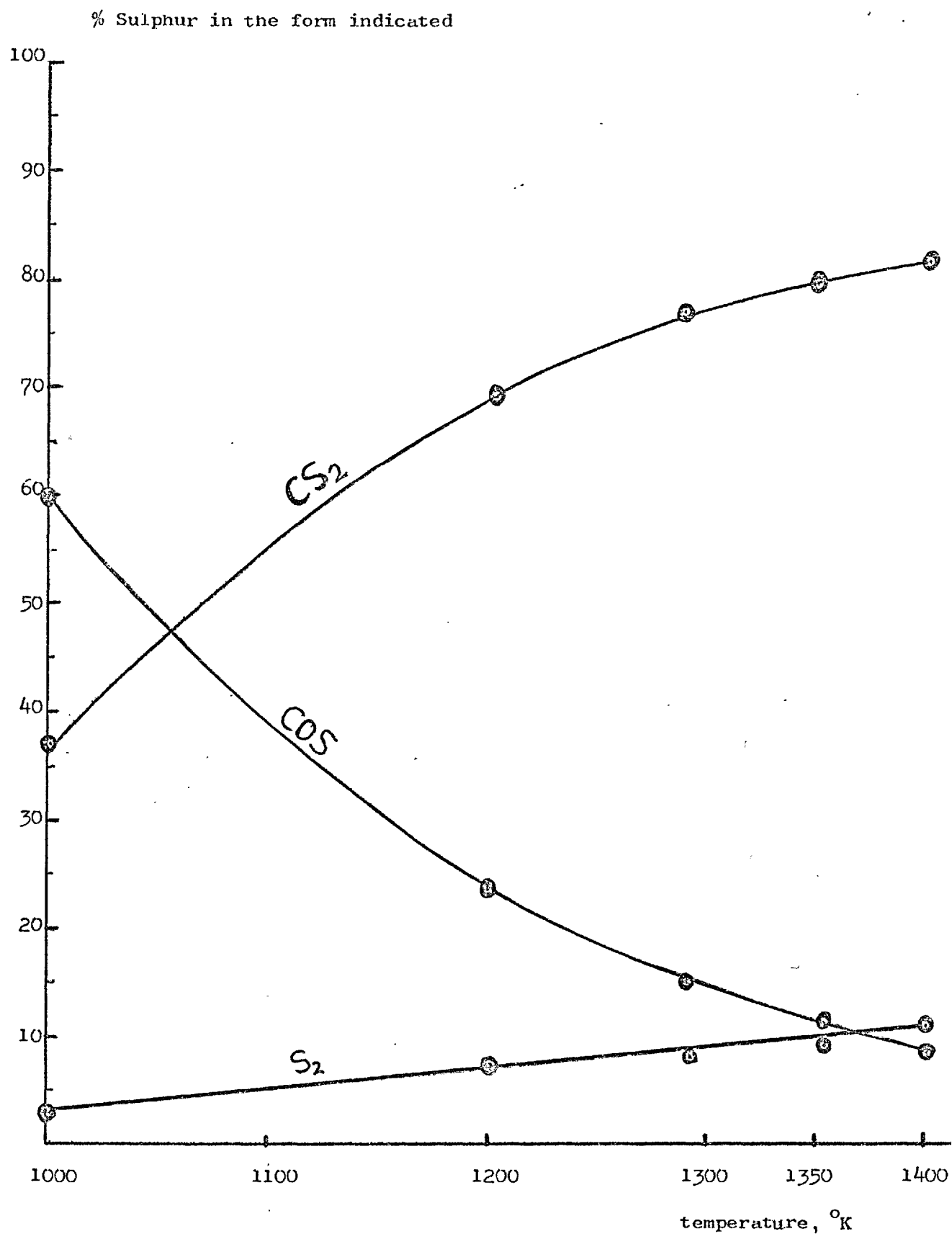
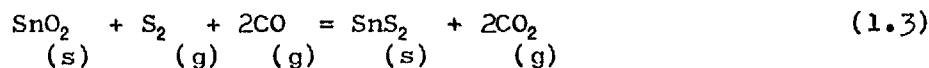
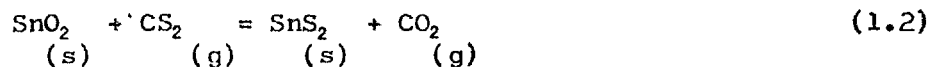
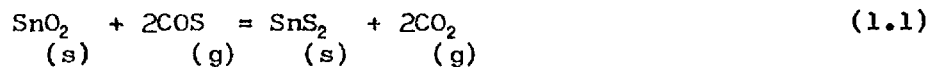


Figure 1: Distribution of Sulphur in Reaction Products from Reduction of Sulphur Dioxide with Carbon.

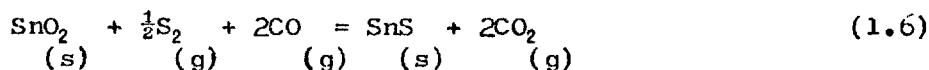
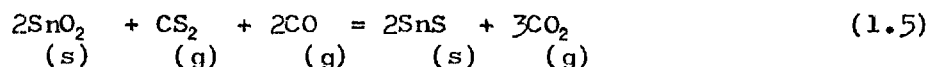
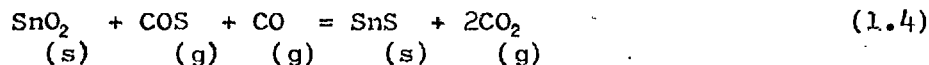
1.1. Thermodynamic Considerations

1.1.1. Sulphidization:

The conversion of stannic oxide into the sulphide (SnS_2 or SnS) through the reaction with carbonyl sulphide, carbon disulphide, and sulphur vapour can be represented as follows:



(In writing reactions with sulphur vapour, the presence of carbon monoxide is assumed.)



Similar reactions can, of course, be written to provide for formation of any other tin sulphide phase.

The set of equilibria predominating depends on the reducing power (in the present case, the CO/CO_2 ratio) of the sulphidizing gas, which (in the case of products from the sulphur dioxide and carbon reaction) is a function of the temperature of reduction. According to calculations by Owen et al. (1951) the $P_{\text{CO}}/P_{\text{CO}_2}$ ratio in the gas at 727°C . is 4.27, whereas at 927°C . it is 83.46. Thus, at lower reduction temperatures in the working range, reactions (1.1) to (1.3) are expected to predominate, because the gas has a relatively low reducing power, whereas at higher reduction temperatures reactions (1.4) to (1.6) involving reduction of tin to the bivalent state, should predominate.

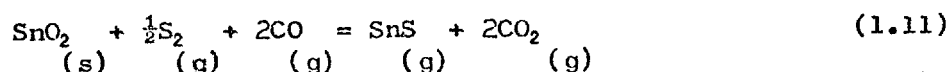
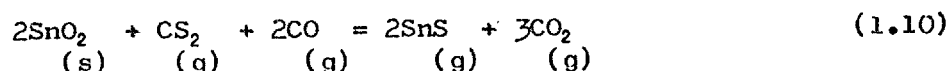
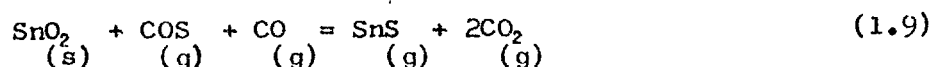
The type of tin sulphide formed is also a function of the temperature of sulphidization, which obviously may differ from the temperature of sulphur dioxide reduction. Stannic sulphide is not stable at higher temperatures, where it dissociates to give lower sulphides:



The only tin sulphide known to be stable at high temperatures under workable sulphur pressures is SnS. A detailed discussion on the tin-sulphur system will be presented in Chapter 3.

It is therefore expected that in the reaction system now envisaged stannic oxide could be converted into SnS, SnS₂, or Sn₂S₃, by appropriate control of the temperature of sulphur dioxide reduction with carbon, and the temperature of the sulphidizing reactor. The working system comprises two reactors, the "reducer", in which reduction of sulphur dioxide by carbon takes place, and the "sulphidizer" in which the products from the reducer are used to sulphidize tin oxide.

The standard free energy change for each of the reactions (1.1) to (1.6) was calculated for the temperature range 600 K - 1100°K, by using values of standard free energy of formation, compiled in Table 3. The results obtained are given in Table 4. All the reactions have negative ΔG_R° values in the temperature range considered, and they are therefore thermodynamically feasible. At temperatures above 1100°K, where SnS is the stable tin sulphide, the formation of gaseous SnS also requires to be considered as shown in reactions (1.9 - 1.11).



The possible formation of SnS₂ in the vapour state may also call for consideration at the higher temperatures (Burdick, 1926).

The formation of stannous sulphide at high temperatures, where reduction of SnO₂ would take place, is possible not only through reactions of SnO₂ with the sulphidizing gas, but also through sulphidization of SnO or tin metal previously formed by reduction of SnO₂ by carbon monoxide; however, the total reaction is the same whichever route is adopted, and the alternative mechanism does not require separate consideration in assessment of standard free-energy changes.

Table 3

Standard Free-Energy of Formation of Tin, Carbon, and Sulphur Compounds involved in
Sulphidization Equilibria. (in kcal/mole)

Temperature °K	SnO ₂ (s)	SnS [*] (s,l)	SnS [*] (g)	SnS ₂ [*] (s)	Sn ₂ S ₃ [*] (s)	SO ₂ (g)	CS ₂ (g)	COS (g)	S ₂ [*] (g)	SnO (s)	CO ₂ (g)	CO (g)
400	-119.30	-33.519	+2.15	-52.35	-87.20	-79.56	-3.87	-50.48	+15.42	-59.00	-94.05	-35.00
500	-114.50	-31.693	+0.78	-47.86	-79.72	-77.83	-4.01	-50.72	+11.67	-56.80	-94.40	-37.10
600	-109.30	-29.523	-0.35	-43.07	-72.24	-76.08	-4.17	-50.97	+8.01	-54.20	-94.45	-39.35
700	-104.30	-27.368	-1.41	-38.30	-64.76	-74.32	-4.32	-51.22	+4.46	-51.60	-94.50	-41.55
800	-99.20	-25.242	-2.42	-33.57	-57.28	-72.57	-4.50	-51.47	+1.02	-49.10	-94.50	-43.70
900	-94.20	-23.253	-3.41	-28.87	-49.80	-70.81	-4.67	-51.71	-2.32	-46.50	-94.55	-45.85
1000	-89.20	-21.112	-4.37	-23.68	-42.32	-69.06	-4.83	-51.95	-5.54	-43.90	-94.60	-47.95
1100	-84.20	-19.083	-5.29	-	-34.84	-67.33	-5.02	-52.21	-7.22	-41.30	-94.60	-50.10
1200	-79.30	-16.558	-6.19	-	-	-65.58	-5.16	-52.53	-10.155	-38.80	-94.65	-52.15
1300	-74.40	-	-7.07	-	-	-63.83	-5.39	-52.67	-12.98	-36.30	-94.70	-54.35
1400	-69.50	-	-7.92	-	-	-62.08	-5.53	-52.91	-15.70	-	-94.75	-56.25

* Values are calculated

Table 4

Standard Free-Energy Change of the Sulphidization Reactions
 (1.1) to (1.6) in the Temperature Range 600 - 1100°K
 (in kcal/mole Sulphide)

Temperature °K	Reaction (1.1) (COS)	Reaction (1.2) (CS ₂)	Reaction (1.3) (S ₂)	Reaction (1.4) (COS+CO)	Reaction (1.5) (CS ₂ +CO)	Reaction (1.6) (S ₂ +CO)
600	-20.73	-24.05	-51.98	-18.81	-20.47	-30.42
700	-20.57	-24.18	-44.36	-19.30	-21.11	-28.97
800	-20.43	-24.37	-37.09	-19.87	-21.84	-27.64
900	-20.35	-24.55	-29.75	-20.59	-22.68	-26.45
1000	-19.72	-24.25	-21.24	-21.21	-23.45	-25.21
1100	-	-	-	-21.77	-24.18	-23.88

The values of S_{298}° , ΔS_{298}° and ΔH_{298}° used in calculating the standard free-energy of formation of some of the compounds in Table 3 are listed in Table 5. The following thermodynamic relation was used:

$$\Delta G_f^{\circ} = \Delta H_{298}^{\circ} (\text{compound}) + [(H_T - H_{298})_{\text{comp.}} - \Sigma(H_T - H_{298})_{\text{elements}}] - T[\Delta S_{298}^{\circ} (\text{compound}) + \{(S_T - S_{298})_{\text{comp.}} - \Sigma(S_T - S_{298})_{\text{elements}}\}] \quad (1)$$

$(H_T - H_{298})_{\text{comp.}}$, $(H_T - H_{298})_{\text{elements}}$, $(S_T - S_{298})_{\text{comp.}}$ and $(S_T - S_{298})_{\text{elements}}$ values used in calculating ΔG_f° at various temperatures for $\text{SnS}_{(s,1)}$, $\text{SnS}_{(g)}$, and $\text{SnS}_{2(s)}$, were taken from Kelley (1960). The ΔG_f° values for $\text{Sn}_2\text{S}_3(s)$ were calculated using the relation:

$$\Delta G_f^{\circ} = \Delta H_{298}^{\circ} - T\Delta S_{298}^{\circ}.$$

For $\text{S}_{2(g)}$ the following relation (Kelly, 1962) was used:

$$\Delta G_f^{\circ} = + 31,360 - 1.36 T \log T + 5.80 \times 10^{-3} T^2 - 38.62 T.$$

The ΔG_f° values of $\text{SnO}_{2(s)}$, $\text{SnO}_{(s)}$, $\text{CO}_{2(g)}$ and $\text{CO}_{(g)}$ were taken from Wicks et al. (1963); those of $\text{COS}_{(g)}$ and $\text{CS}_{2(g)}$ from Kelley (1962) and those of $\text{SO}_{2(g)}$ from Coughlin (1954).

Table 5

S_{298}° , ΔS_{298}° , and ΔH_{298}° of some Carbon, Tin and Sulphur Compounds used in the calculation of values of standard Free-Energy.

Substance	S_{298}° (cal/mole.deg.)	ΔS_{298}° (cal/mole.deg.)	ΔH_{298}° (kcal/mole)	Reference
$\text{Sn}_{(s)}$	12.32	-	0	Wagman et al. (1965)
$\text{SnS}_{(s)}$	18.40	-19.18	-25.87	Rau (1966) and Wagman et al. (1965)
$\text{SnS}_{(g)}$	55.60	+16.03	+24.00	Rau (1966)
$\text{SnS}_2_{(s)}$	20.90	-45.93	-40.00	Kupaschewski (1967)
$\text{C}_{(\text{graphite})}$	1.37	-	0	Wagman et al. (1965)
$\text{S}_2_{(g)}$	54.51	-	+30.68	Wagman et al. (1965)
$\text{Sn}_2\text{S}_3_{(s)}$	31.60	-74.81	-71.10	Rau (1966)

1.1.2. Reduction:

It has been confirmed experimentally that sulphidization of stannic oxide with sulphidizing agents, e.g. FeS_2 or sulphur, is more effective in the presence of a reducing agent (Klushin et al., 1962). Sulphur reacts slowly with SnO_2 at 750°C ., provided that enough excess sulphur is present (St. Clair et al., 1954). On the other hand, the reduction of the oxide to the metal is likely to become important at high temperatures. Reduction to the metal by the sulphidizing gas used in this work depends on the CO/CO_2 ratio in the gas phase.

The following reactions require consideration:



the equilibrium constants and the $p_{\text{CO}}/p_{\text{CO}_2}$ ratios were calculated and are tabulated in Table 7; the ΔG_R° values of the reactions (1.12) and (1.13) in Table 6 were used for these calculations. Although it may form as a labile product, stannous oxide, SnO , is unstable, and decomposes as follows:



$$\Delta G_R^\circ = -880 + 3.12T$$

As the temperature increases, SnO becomes slowly less stable relative to $\text{Sn}_{(\text{l})} + \text{SnO}_{2(\text{s})}$ (Wright, 1966). The reduction of SnO_2 to the metal is expected to be competitive with sulphidization above 700°C ., where the equilibrium $p_{\text{CO}}/p_{\text{CO}_2}$ ratio in the gas is fairly large.

Table 6

Standard Free-Energy change of Reactions (1.12) and (1.13)
in the Temperature range 600 - 1400°K. (in kcal/mole)

Temperature °K	Reaction (1.12) $\text{SnO}_2 \rightarrow \text{SnO}$ (s) (s)	Reaction (1.13) $\text{SnO}_2 \rightarrow \text{Sn}$ (s) (l)
600	zero	-0.90
700	-0.25	-1.60
800	-0.70	-2.40
900	-1.00	-3.20
1000	-1.35	-4.10
1100	-1.60	-4.80
1200	-2.00	-5.70
1300	-2.25	-6.30
1400	-	-7.40

Table 7

Equilibrium Constant Values and the $p_{\text{CO}}/p_{\text{CO}_2}$ ratios for
 Reactions (1.12) and (1.13). ($\Delta G_R^0 = -2.303 \times 1.987T \log K_{\text{equ.}}$)

Temperature °K	Reaction (1.12)	Reaction (1.12)	Reaction (1.13)	Reaction (1.13)
	$K_{\text{equ.}}$	$p_{\text{CO}}/p_{\text{CO}_2}$	$K_{\text{equ.}}$	$p_{\text{CO}}/p_{\text{CO}_2}$
600	1.00	1.00	2.13	0.69
700	1.20	0.84	3.16	0.56
800	1.55	0.64	4.53	0.47
900	1.75	0.57	5.98	0.41
1000	1.97	0.51	7.87	0.36
1100	2.08	0.48	8.99	0.33
1200	2.31	0.43	10.89	0.30
1300	2.39	0.42	11.46	0.30
1400	-	-	14.29	0.27

1.2. Experimental

1.2.1. Apparatus and Materials:

The apparatus is illustrated in outline in Figure 2.

1. The Reducer is a tube-furnace with a silica tube packed with granular activated charcoal (6-12 mesh), closed with rubber bungs, and connected with glass and polythene tubes with the gas supply unit on one side and with the sulphidizer on the other side. In the reducer, the reduction of sulphur dioxide with heated carbon takes place, and the resulting gas mixture passes to the sulphidizer through the connecting tubing at ambient temperature. The temperature of the reducer was heat-regulated by means of a Variac in its power supply, and measured by a Pt/Pt-Rh thermocouple connected to a properly compensated temperature indicator.
2. The Sulphidizer is a horizontal tube-furnace, the temperature of which was automatically controlled by an electronic controller operating from a Pt/Pt-Rh thermocouple. The exhaust gases (which are toxic on account of their carbon monoxide and carbonyl sulphide content) were vented into an efficient fume offtake. Sulphur dioxide was taken from small aluminium cylinders, supplied by B.D.H. Ltd. Oxygen-free nitrogen was used from 110 cu.ft. cylinders, fitted with needle valves and pressure gauges. When the apparatus was in use, routine tests for gas-tightness were carried out before each run. Silica or alumina boats were used to contain the samples. Pure chemical-grade stannic oxide, previously sintered at 800°C. for several hours, and kept in a desiccator, was used in this investigation.

1.2.2. Procedure:

All experiments were carried out in the following manner:

1. The reducer tube was packed with granular charcoal and maintained continuously at the desired temperature with a slow nitrogen stream passing through.
2. About five grams of stannic oxide were weighed into a boat, and introduced into the sulphidizer tube. The furnace was switched on while the slow stream of nitrogen passed through the whole apparatus.
3. When the required temperature of the sulphidizer was reached, the nitrogen stream was stopped, and sulphur dioxide was passed into the reducer at a constant flow-rate.

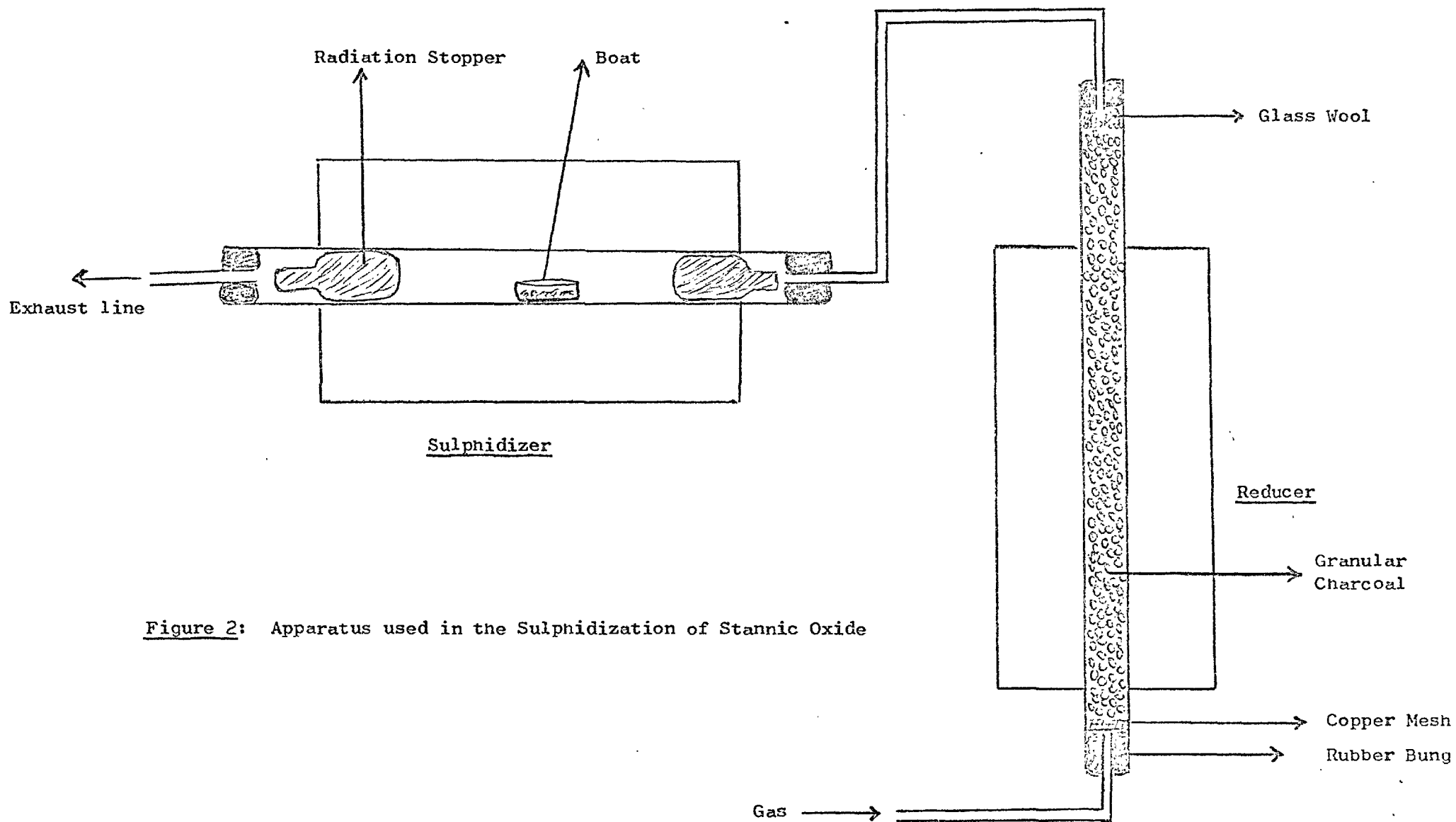


Figure 2: Apparatus used in the Sulphidization of Stannic Oxide

4. At the end of the reaction period, the reverse procedure was carried out, and the sample was left to cool to room temperature in a nitrogen atmosphere.

5. The boat was pulled out from the sulphidizer and weighed. The product was finely ground and stored for examination.

Acid Leaching of SnS:

To assess the extent of conversion of the tin oxide into sulphide, products containing SnS as the only sulphide product were leached with hot hydrochloric acid as follows (SnO₂ has an insignificant solubility in hydrochloric acid):

1. A sample of 1.00 g. to 2.00 g. was weighed.
2. 25 ml. of hydrochloric acid were added, and the suspension stirred on a hot plate for about 30 minutes. Stannous sulphide reacted quickly with the acid.
3. The solution was filtered; the unreacted oxide was collected on the filter paper, and carefully washed with dilute acid.
4. The residue was left to dry and the filter paper was burned off in a porcelain crucible and the residual oxide ignited and weighed. The percentage conversion of the original oxide was calculated.

Leaching of Higher Sulphides with Bromine and Carbon Tetrachloride:

When higher tin sulphides, not readily soluble in hydrochloric acid, were present, the tin sulphides were extracted with a mixture of bromine and carbon tetrachloride, in which tin sulphides (but not tin oxide) are soluble (Zverev et al., 1957). The procedure was as follows:

1. A sample of 0.20 g. to 0.50 g. of product was weighed.
2. 25 ml. of carbon tetrachloride, 10 ml. of bromine, and one gram of elemental sulphur were added. (In the case of products with a high percentage of sulphides, the quantities of reagents were doubled.
3. The mixture was stirred (with a magnetic stirrer) for 2.5 - 3.0 hours, without heating.

4. After filtration and thorough washing with carbon tetrachloride, the residue was left to dry. The filter paper containing the residue was then burned off and the unreacted oxide was ignited and weighed. The percentage conversion of the original oxide taken was calculated, as before.

1.3. Results and Discussion

The effects of gas composition, reaction period, and the gas flow-rate were studied with the sulphidizer in the temperature range 400 - 750°C.

1.3.1. Effect of Gas Composition (Reducer Temperature):

The temperature range of the reducer of interest is 600 - 950°C., which covers a considerable change in the gas composition with respect to the sulphurous gases (carbonyl sulphide, carbon disulphide, and sulphur vapour and the reducing power p_{CO}/p_{CO_2} ratio). In these experiments the reaction period was four hours, and a low flow-rate (75 ml./minute) of sulphur dioxide was used (3.0 g. SO_2 /g. SnO_2); the percentage conversion of stannic oxide to the sulphide in the sulphidizer temperature range 400 - 750°C. was investigated at various reducer temperatures.

1. Reducer at 600°C:

At this temperature, no sulphidizing reaction was observed. Large quantities of sulphur collected at the exit of the reducer and sulphidizer. The reducer was clogged and it had to be opened, cleaned, and re-packed.

2. Reducer at 650°C:

Again, as at 600°C., no reaction took place.

3. Reducer at 700°C:

The reaction of stannic oxide with the sulphidizing gas was first observed at this reducer temperature. The results obtained in the sulphidizer temperature range 400 - 750°C. are shown in Table 8. X-ray diffraction studies of the products showed that at 600°C sulphidizer and lower temperatures, stannic sulphide, SnS_2 , alone was present. As the temperature increased, other tin sulphides, Sn_2S_3 and SnS , formed. At 750°C., the product consisted of grey-black shining flakes of SnS (see photograph No.1). Elemental sulphur collected at the exit of the

sulphidizer in all the runs at above 600°C . The formation of elemental sulphur at low reducer temperatures, 600°C . and 650°C ., at which no reaction took place in the sulphidizer, is probably due to a change in the equilibrium composition of the gas on cooling.

4. Reducer at 750°C :

The results obtained are given in Table 9. It is interesting to see that the tin sulphide formed was SnS only, at all sulphidizer temperatures. This sudden change in the reaction product due to a 50°C . change in the reducer temperature is evidently due to the considerable change in the composition and reducing power of the sulphidizing gas. The sulphidization reactions responsible for the formation of SnS are (1.4), (1.5), and (1.6). No sulphur was observed at the exit of the sulphidizer at any temperature.

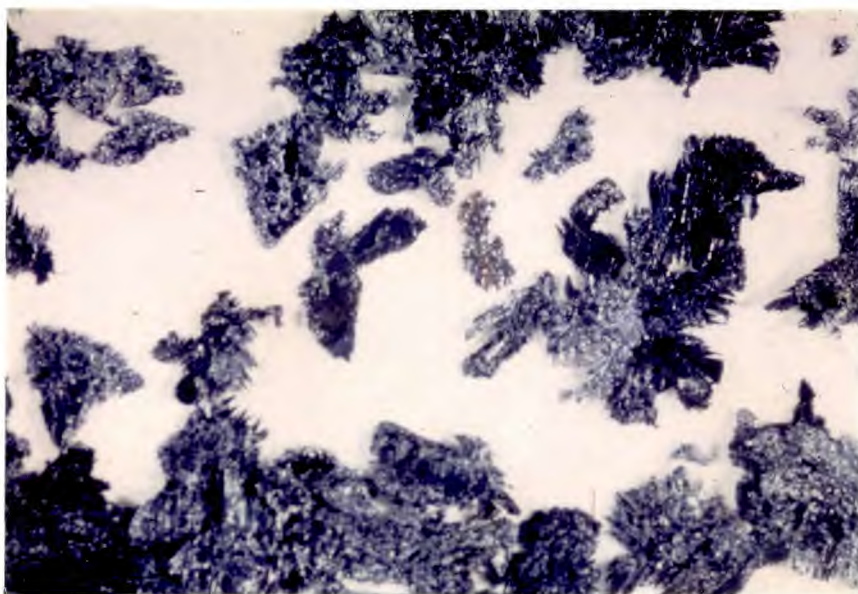
With the sulphidizer at 750°C ., small tin metal beads were observed on the surface of the product in the boat. The loss in weight of the sample (4.43%) corresponds with the formation of some tin metal.

5. Reducer at 800°C :

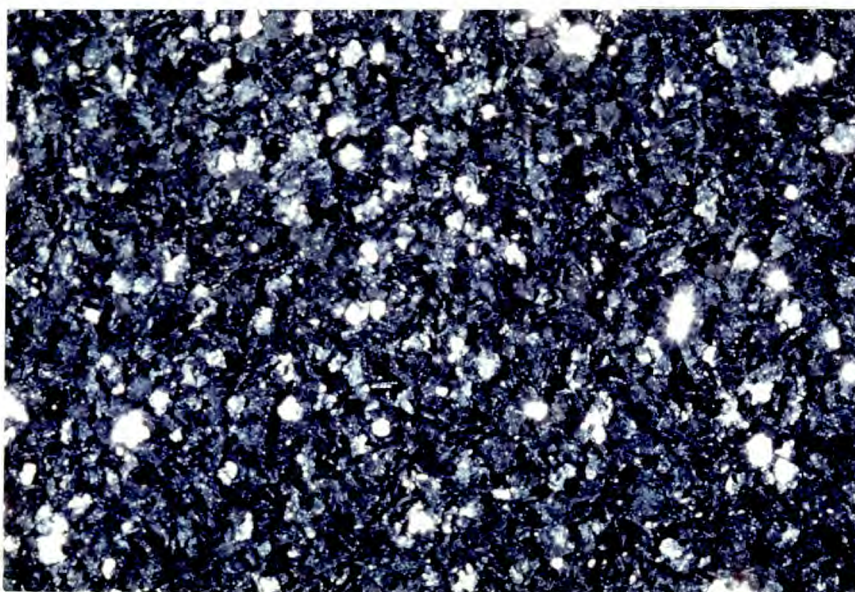
The results obtained are given in Table 10. Only stannous sulphide (with some metallic tin in some cases) was detected in the products at all sulphidizer temperatures. Almost pure, grey-black, coarsely crystalline SnS with a metallic lustre was obtained with the sulphidizer at 730°C . (see photograph No.2). Some reduction to the metal took place at 750°C . The loss in weight of the sample was 7.31%, again in accordance with some tin formation. The sulphidizer temperature range $600 - 700^{\circ}\text{C}$. appears to be promising for practical application because high conversion to sulphide is possible. The sulphidization reactions taking place at this reducer temperature are those of the three sulphurous gases (carbonyl sulphide, carbon disulphide, and sulphur vapour) in the presence of carbon monoxide, reactions (1.4), (1.5) and (1.6).

6. Reducer at 900°C :

The results obtained are given in Table 11; they are similar to those obtained with the reducer at 800°C . and for this reason the reducer



Photograph No.1: Flakes of Stannous Sulphide, SnS , obtained at 750°C .
Sulphidizer with the reducer at 700°C ., slow gas
flow-rate and four hours reaction period. (Mag. = $4\times$)



Photograph No.2: Coarse crystalline Stannous Sulphide, SnS , obtained
at 730°C . Sulphidizer with reducer at 900°C . using slow
gas flow-rate, and four hours reaction period. (Mag. = $4\times$)

the reducer was not tested at 850°C . The sulphidization reactions are also similar to those at 750°C . and 800°C . Some reduction to tin metal took place on sulphidization at 750°C .; the loss in weight (8.16%) was close to that obtained with the reducer at 800°C . The only tin sulphide detected was stannous sulphide.

7. Reducer at 950°C .:

The results obtained are given in Table 12. The only difference observed from the results obtained at somewhat lower reducer temperatures was the degree of reduction to tin metal with the sulphidizer at 750°C . The loss in weight of the sample was more than two times that with the reducer at 900°C . This means that at this temperature the partial pressure of carbon monoxide in the sulphidizing gas has, as expected, increased considerably. Table 13 compares the % loss in weight of the sample after sulphidization at 750°C . with various reducer temperatures.

Table 13

Percentage loss in Weight of Sample with Sulphidizer at 750°C .
and Various Reducer Temperatures ($700 - 950^{\circ}\text{C}$.)

Temperature, $^{\circ}\text{C}$.	% loss in Weight
700	1.65 (No Sn metal
750	4.43
800	7.31
900	8.16
950	18.44

Table 8

Results of Sulphidization of Stannic Oxide in the temperature range 400 - 750°C, with:

Reducer = 700°C.
 Time = 4 hours
 Flow-Rate = 75 ml./minute (3 g SO₂/g SnO₂)

Run Number	Temperature °C	Weight of SnO ₂ sample (g)	Weight of product (g)	Change in weight (g)	% Conversion to Sulphide	Type of Sulphide Formed	Remarks
1	400	4.9657	5.3126	+0.3469	33.91	SnS ₂ only	product is a yellow powder
2	450	5.0444	5.8219	+0.7775	70.34	SnS ₂ only	product is a yellow powder
3	500	5.1735	6.0921	+0.9186	85.08	SnS ₂ only	product is a yellow powder
4	600	5.1386	5.7506	+0.6120	58.20	SnS ₂ only	product is light brownish yellow powder.
5	700	5.2909	5.5585	+0.2675	75.11	SnS + Sn ₂ S ₃ + SnS ₂	product has some grey-black crystalline part and a yellow powder.
6	730	5.0330	5.2308	+0.1978	88.90	SnS + Sn ₂ S ₃ + SnS ₂	Similar to the product at 700°C, with the yellow powder part decreased.
7	750	5.0275	4.9445	-0.0830	95.83	SnS only	grey-black star-like flakes with metallic lustre.

Table 9

Results of Sulphidization of Stannic Oxide in the Temperature Range 400 - 750°C, with:

Reducer = 750°C.
 Time = 4 hours
 Flow-Rate = 75 ml./minute (3 g SO₂/g SnO₂)

Run Number	Temperature °C	Weight of SnO ₂ sample (g)	Weight of product (g)	Change in weight (g)	% Conversion to Sulphide	Type of Sulphide Formed	Remarks
1	400	5.0050	5.1130	+0.1080	25.14	SnS only	product is light grey powder
2	450	4.9960	5.1005	+0.1045	39.20	SnS only	product is light grey powder
3	500	5.2467	5.2914	+0.0447	60.62	SnS only	product is grey-black powder
4	600	5.0820	5.0414	-0.0106	90.06	SnS only	product is fine crystalline grey-black in colour
5	700	5.1132	5.0930	-0.0202	95.30	SnS only	product is fine crystalline grey-black in colour
6	730	5.0644	5.0331	-0.0313	97.40	SnS only	product is fine crystalline grey-black in colour
7	750	5.1033	4.8770	-0.2263	-	SnS + Sn metal	grey-black crystalline product with small tin metal beads on surface

Table 10

Results of Sulphidization of Stannic Oxide in the Temperature range 400 - 750°C., with:

Reducer = 800°C
 Time = 4 hours
 Flow-Rate = 75 ml./minute (3 g SO₂/g SnO₂)

Run Number	Temperature °C	Weight of SnO ₂ sample (g)	Weight of product (g)	Change in weight (g)	% Conversion to Sulphide	Type of Sulphide Formed	Remarks
1	400	5.0960	5.2011	+0.1051	32.57	SnS only	product is light grey powder
2	450	5.0612	5.1644	+0.1032	44.38	SnS only	product is light grey powder
3	500	5.1015	5.1373	+0.0358	63.37	SnS only	product is grey-black powder
4	600	5.1685	5.1560	-0.0125	91.47	SnS only	product is grey-black crystalline
5	700	5.2021	5.1787	-0.0234	96.52	SnS only	product is grey-black crystalline
6	730	5.0018	4.9600	-0.0418	98.00	SnS only	product is grey-black crystalline
7	750	5.0273	4.6594	-0.3679	-	SnS with tin metal	grey-black crystalline product with tin metal.

Table 11

Results of Sulphidization of Stannic Oxide in the Temperature Range 400 - 750°C., with:

Reducer = 900°C
 Time = 4 hours
 Flow-rate = 75 ml./minute (3 g SO₂/g SnO₂)

Run Number	Temperature °C	Weight of SnO ₂ sample (g)	Weight of product (g)	Change in weight (g)	% Conversion to Sulphide	Type of Sulphide Formed	Remarks
1	400	5.0001	5.0832	+0.0831	38.90	SnS only	product is light grey powder
2	450	5.0719	5.1308	+0.0589	64.36	SnS only	product is grey-black powder
3	500	5.2068	5.2323	+0.0255	75.07	SnS only	product is grey-black powder
4	600	5.1287	5.1293	-0.0005	90.00	SnS only	product is grey-black crystalline
5	700	5.2082	5.1985	-0.0097	95.03	SnS only	product is grey-black crystalline
6	730	4.8903	4.8409	-0.0494	97.59	SnS only	product is grey-black crystalline
7	750	5.0701	4.6597	-0.4142	-	SnS with tin metal	grey-black crystalline product with tin metal

Table 12

Results of Sulphidization of Stannic Oxide in the Temperature Range 400 - 750°C., with:

Reducer = 950°C
 Time = 4 hours
 Flow-Rate = 75 ml./minutes (3 g SO₂/g SnO₂)

Run Number	Temperature °C	Weight of SnO ₂ sample (g)	Weight of product (g)	Change in weight (g)	% Conversion to Sulphide	Type of Sulphide Formed	Remarks
1	400	5.0010	5.0665	+0.0655	40.13	SnS only	product is a grey powder
2	450	4.9985	5.0335	+0.0350	69.20	SnS only	product is a grey powder
3	500	5.0206	5.0332	+0.0126	86.03	SnS only	product is grey-black powder
4	600	5.1134	5.1046	-0.0088	91.65	SnS only	product is grey-black crystalline
5	700	4.9688	4.9428	-0.0260	94.60	SnS only	product is grey-black crystalline
6	730	5.1896	5.1352	-0.0544	95.00	SnS only	product is grey-black crystalline
7	750	5.0931	4.1541	-0.9390	-	SnS and tin metal	grey-black crystalline product with tin metal.

The relation between the percentage conversion and the reducer temperature, as shown in Figure 3, clearly shows that the optimum temperature of the reducer is $800 - 950^{\circ}\text{C}$ with the sulphidizer in the temperature range $600 - 700^{\circ}\text{C}$. The tin sulphide forming under these conditions is stannous sulphide.

1.3.2. Effect of Time:

To study the effect of time on the percentage conversion of the oxide to the sulphide, a moderate reducer temperature, 900°C ., was chosen, with the sulphidizer at 730°C ., and a slow gas flow-rate, 75 ml./minute (3 g. SO_2 /g. SnO_2). Results obtained with reaction periods of one, two, three and four hours are given in Table 14. It is interesting to see that the reaction was slow in the first hour, and the rate increased considerably in the second hour. In the last two hours the rate of the reaction dropped, probably because the rate-controlling step is the rate of diffusion of the gas through the sulphide coating of the oxide. This also explains why a small residue of unconverted oxide was recorded. For this purpose, the product would need to be ground and resulphidized.

The reduction of sulphur dioxide with carbon under the conditions of the experiments is complete and independent of the gas flow-rate within the limits used. An increase of flow-rate increases the rate of sulphidization (rate of exchange of sulphur between the solid and the gas). The effect of the reaction time at low sulphidizer temperatures, e.g. 500°C was examined using high gas flow-rate. The results obtained, with the reducer at 900°C ., and 150 ml./minute (6 g. SO_2 /g. SnO_2) flow-rate at various time intervals are given in Table 15.

The results of sulphidization of stannic oxide obtained at various conditions show a close relationship between the weight changes and the percentage conversion to the sulphide. Conversion of the oxide to stannous sulphide (when no appreciable weight change is expected) took place when the reducer temperature was at above 700°C .; the percentage change in weight of sample was never more than $\pm 2.2\%$. Under these conditions, reactions 1.4 - 1.6 took place. In the conversion of the oxide into the higher sulphides, e.g. SnS_2 or Sn_2S_3 , with the reducer at 700°C ., the percentage change in weight agrees well in each case

Table 14

Results of Sulphidization of Stannic Oxide at 730°C at Various Time Intervals, with:

Reducer = 900°C

Flow-Rate = 75 ml./minute (3 g. SO₂/g. SnO₂)

Run Number	Time (hours)	Weight of SnO ₂ sample (g)	Weight of product (g)	Change in weight (g)	% Conversion to Sulphide	Type of Sulphide Formed	Remarks
1	1	5.0719	5.0497	-0.0222	13.76	SnS	product is light grey and white powder
2	2	4.9000	4.8777	-0.0223	85.54	SnS	product is grey-black crystalline with metallic lustre
3	3	4.8515	4.8294	-0.0221	94.46	SnS	product is grey-black crystalline with metallic lustre
4	4	4.8903	4.8409	-0.0494	97.59	SnS	product is grey-black crystalline with metallic lustre

Table 15

Results of Sulphidization of Stannic Oxide at 500°C at Various Time Intervals, with:

Reducer = 900°C

Flow-Rate = 150 ml./minute (6 g. SO₂/g. SnO₂)

Run Number	Time (hours)	Weight of SnO ₂ sample (g)	Weight of product (g)	Change in weight (g)	% Conversion to Sulphide	Type of Sulphide Formed	Remarks
1	0.5	5.0287	5.0639	+0.0352	17.60	SnS (coating)	product is light greyish powder
2	1.0	4.9848	5.0108	+0.0260	57.13	SnS	product is grey-black powder
3	2.0	5.0332	5.0558	+0.0226	79.20	SnS	product is grey-black powder
4	4.0	5.1236	5.1502	+0.0266	91.18	SnS	product is grey-black powder

with the percentage conversion to the sulphide. Under these conditions, reactions 1.1 - 1.3 took place. Both the percentage change in weight and the percentage conversion into the sulphide were in accord with the X-ray photographs which clearly showed the type of phases present and their relative proportions in the products.

1.3.3. Sulphidization of Stannic Oxide with Diluted Sulphur Dioxide:

The possible need to use sulphur dioxide extensively diluted with nitrogen (roaster gases) made it desirable to test such gas as a sulphur source. Experiments were therefore carried out on the sulphidization of the oxide at the low sulphidization temperatures. With a total gas flow-rate of 150 ml./minute, a four-hour reaction period, and the reducer at 900°C ., the results obtained with pure sulphur dioxide, 75% SO_2 by volume, 50% SO_2 , 25% SO_2 , and 10% SO_2 , are given in Table 16. Dilution to 50% SO_2 did not show any appreciable effect. However, considerable change was observed with 25% SO_2 , and almost no reaction occurred with 10% SO_2 even when the temperature was increased to 600°C .. In a run carried out at 700°C . with 10% SO_2 , reaction took place only on the surface of the oxide towards the gas entry of the sulphidizer.

1.3.4. Volatilization of Stannous Sulphide at High Temperatures:

Sulphidization of stannic oxide with pure sulphur dioxide at high temperatures was investigated by using the high flow-rate, a four-hour reaction period, and the reducer at 900°C .. One experiment was carried out as shown below.

<u>Experiment:</u>	Reducer	= 900°C ..
	Sulphidizer	= 930°C .,
	Time	= 4 hours,
	Flow-rate	= 150 ml./minute (6 g. SO_2 /g. SnO_2)
1-	Weight of boat empty	= 45.8641 g.
2-	Weight of boat + SnO_2	= 48.4451 g.
3-	Weight of SnO_2 sample	= 2.5810 g.
4-	Weight of boat + product	= 45.9813 g.
5-	Weight of product in boat	= 0.1272 g. }
6-	Weight of collected SnS	= 2.4517 g. } 2.5789 g.

Table 16

Results of Sulphidization of Stannic Oxide with Diluted Sulphur Dioxide at low sulphidizer temperatures,

with : Reducer = 900°C
 Time = 4 hours
 Flow-rate = 150 ml./minute (6 g. SO₂/g. SnO₂)

Run Number	Temperature °C	% SO ₂ in nitrogen	Weight of SnO ₂ sample (g)	Weight of product (g)	Change in weight (g)	% Conversion to Sulphide	Type of Sulphide Formed	Remarks
1	500	100%	5.1236	5.1170	-0.0066	91.18	SnS	product is grey-black powder
2	500	75%	5.0003	5.0194	+0.0191	89.73	SnS	product is grey-black powder
3	500	50%	5.0339	5.0302	-0.0037	89.81	SnS	product is grey-black powder
4	500	25%	4.9360	4.9500	+0.0140	63.19	SnS	product is grey-black powder
5	500	10%	4.9935	5.0067	+0.0132	-	-	-
6	600	10%	4.9527	4.9538	+0.0011	-	-	-

Only two small crystals (flakes) of SnS were left in the boat. Volatilized SnS collected on the cool end of the sulphidizer near the exit. The effective yield of volatilized SnS =

$$\frac{2.4517}{2.5810} \times 100 = 95.07\%.$$

This experiment was satisfactory. It means that volatilization of SnS from low-grade cassiterite concentrates might be successful. A fluid-bed technique for the carrying out of the reaction would probably be effective.

1.3.5. X-Ray Diffraction Studies:

X-Ray diffraction photographs confirmed the type of tin sulphide formed under various conditions. The photographs were taken by means of a Guinier camera using copper target, with 50 kV., 10 mA., and 6 - 8 hours exposure time. Films were processed, measured, and interpreted to give d-spacings by conventional methods.

The previously recorded d-spacings for the tin compounds relevant to the present work are given in Table 17. Two sets of data are given for SnS₂, namely data on the ASTM Index Card No. (1 - 1010), (Hanawalt et al., 1938), and the recently reported data by Moh (1969). The d-spacings of SnS, SnS₂, and Sn₂S₃ obtained from the sulphidization of stannic oxide under various conditions mentioned previously are given in Table 18. The X-ray pattern for crystalline SnS, grey-black SnS powder, and that collected from volatilization were identical. It is in good agreement with literature data, with only one difference, which has to do with the intensities of the strong lines. The second strong line reported, 1.399 (70), was detected as a very weak line, and in fact has never been detected in the present work with SnS as grey-black powder.

The X-ray pattern of SnS₂ is that taken for the orange-brown powder obtained with the sulphidizer below 600°C. It is in good agreement with literature values. The weak lines: 3.36 (2), 2.638 (2), 1.762 (2), and 1.666 (15), were not included simply because they coincide with the strongest lines of tin oxide: 3.351 (100), 2.644 (81), 1.765 (63), and 1.675 (63). These lines evidently resulted from traces of unconverted tin oxide.

Table 17

X-Ray Diffraction Data for Tin Compounds

Sn ASTM (4-0673)		SnO ASTM (6-0395)		SnO ₂ ASTM (5-0467)		SnS ASTM (14-620)		SnS ₂ ASTM (1-1010)		SnS ₂ (Mon, 1969)		Sn ₂ S ₃ ASTM (14-619)		Sn ₃ S ₄ ASTM (14-538)	
d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I
2.915	100	2.85	10	3.351	100	4.04	5	5.90	50	5.90	100	7.00	40	6.95	18
2.793	90	2.989	100	2.644	81	3.421	10	3.15	40	3.36	2	5.50	75	5.45	45
2.062	34	2.688	35	2.369	24	3.243	15	2.78	100	3.15	20	4.43	10	4.41	6
2.017	74	2.418	14	2.309	5	2.929	5	2.14	50	2.942	10	4.13	100	4.10	55
1.659	17	1.901	14	2.120	2	2.831	25	1.82	50	2.780	40	3.74	35	3.72	20
1.484	23	1.797	25	1.765	63	2.793	100	1.74	40	2.638	2	3.35	15	3.35	4
1.458	13	1.604	25	1.675	63	2.305	15	1.66	13	2.152	35	3.26	30	3.23	10
1.442	20	1.494	12	1.593	8	2.123	1	1.57	6	1.963	15	3.22	25	3.20	20
1.304	15	1.484	12	1.498	13	2.024	10	1.52	20	1.822	18	3.10	5	3.08	4
1.292	15	1.382	4	1.439	17	1.988	10	1.472	2	1.762	2	2.89	25	2.86	18
1.205	20	1.344	6	1.415	15	1.874	5	1.391	13	1.741	16	2.86	5	2.78	100
		1.225	4	1.322	7	1.778	5	1.334	10	1.666	15	2.80	15	2.74	35
		1.209	4	1.215	11	1.721	1	1.302	4	1.570	2	2.75	35	2.66	25
		1.179	6	1.184	3	1.713	5	1.192	4	1.548	1	2.67	45	2.49	12
		1.169	8	1.155	8	1.694	1	1.170	13	1.524	10	2.65	5	2.36	12
		1.152	2	1.117	3	1.689	5	1.146	8	1.474	10	2.50	5	2.33	6
		1.102	4			1.622	5	1.105	10	1.392	8	2.46	5	2.25	16
						1.454	5					2.37	20	2.21	4
						1.451	5					2.33	5	2.18	2
						1.403	1					2.26	25	2.10	10
						1.399	70					2.24	10	2.06	6
						1.320	1					2.22	5	1.995	6
						1.286	1					2.11	10	1.946	6
						1.262	5					2.07	10	1.928	6
						1.195	5					2.00	10	1.819	2
						1.145	5					1.95	10	1.747	6
												1.93	10	1.652	4
												1.87	5	1.556	2
												1.84	5	1.493	4
												1.75	5	1.469	4
												1.657	5	1.395	16
												1.581	10	1.373	10
												1.562	5		
												1.477	10		
												1.377	10		

Table 18

d-spacings of SnS , SnS_2 and Sn_2S_3 Formed from the Sulphidization of Stannic Oxide (Intensities are estimated)

SnS (greyish-black crystal- line)		SnS ₂ (orange-brown powder)		Sn ₂ S ₃ (greyish-black powder)	
d	I	d	I	d	I
4.049	40	5.906	100	7.025	5
3.427	50	3.159	50	5.505	20
3.255	50	2.959	10	4.137	60
2.940	70	2.788	90	3.742	20
2.840	100	2.157	50	3.263	20
2.801	20	1.969	10	3.215	5
2.308	30	1.826	80	3.095	20
2.127	40	1.745	60	2.905	5
2.026	20	1.581	10	2.868	5
1.994	50	1.553	10	2.757	5
1.874	50	1.526	30	2.673	5
1.786	20	1.475	10	2.246	20
1.723	40	1.393	20	1.996	20
1.694	20	1.337	30	1.938	40
1.625	20			1.875	40
1.454	40			1.840	5
1.396	5			1.745	5
1.363	10				
1.3541	5				
1.261	20				

The d-spacings assigned to Sn_2S_3 are those detected in the product from sulphidization at 700°C . The full pattern of this product also contained lines due to admixed SnS , SnS_2 , and SnO_2 . The intention here is only to report the d-values which confirmed the presence of Sn_2S_3 in the product.

The effect of sulphidization temperature on the phase composition of the reaction products is evidently quite complex and is examined in more detail in Chapter 3.

1.4. Conclusions

From what has been done, the following conclusions are noteworthy.

1. The sulphidizing gas from the reduction of sulphur dioxide with carbon is highly effective.
2. The type of tin sulphide obtained from sulphidization of stannic oxide depends on the reaction temperature, and on the composition of the sulphidizing gas.

Chapter 2

Sulphidization of a Disseminated Tin Ore

2.1. Types of Tin Ore

There are two broad types of tin deposits:

1. Alluvial deposits, in which insoluble metallic oxides such as cassiterite, SnO_2 , are dispersed (usually in relatively small quantities) in silicone sands, clays etc. When found in firm ground, these can be worked by mechanical excavators or by hydraulic mining; in the case of a submerged mud they can be worked by dredging, as in Malaysia.

2. Primary deposits of two types:

- a. Highly dispersed, but relatively clean cassiterite deposits, which often contain a high percentage of pyrite, as in Cornwall.
- b. Complex sulphide deposits in which tin is combined with the sulphides of base metals, as in Bolivia.

The usual methods of treatment of cassiterite ores containing base-metal sulphides (pyrite, chalcopyrite, sphalerite, etc.) involve three major steps:

1. Flotation of sulphides with xanthates.
2. Gravity concentration by tabling to produce a high-grade concentrate.
3. Flotation of cassiterite from table tailings to produce a low-grade concentration. If the tin ore contains a high percentage of iron compounds (oxides or silicates), magnetic separation precedes cassiterite flotation. Figure 4 shows the flow-sheet for a low-grade tin ore (1.5% Sn) with a high percentage of sulphides; Figure 5 shows the flow-sheet for the cassiterite flotation, in detail.

The above treatment has the following disadvantages:

1. The loss of tin is very high, especially in the slimes. Furthermore, when the cassiterite is polydispersed in the metal sulphides, the loss increases, unless the sulphide flotation concentrate is reground to liberate cassiterite and enable the sulphides to be refloated.

2. The cassiterite flotation is costly, because the reagents used are expensive, and large quantities are needed.
3. The product of cassiterite flotation is a low-grade concentrate (10-20% Sn) which is unattractive to smelters and unprofitable. It is interesting to note that the recovery of cassiterite in the flotation operation does not exceed 40%.
4. The plant cost is high.

It would therefore be of interest to treat such ores directly by sulphidization to convert cassiterite to stannous sulphide, which could be leached out with hydrochloric acid or alkali polysulphide solutions. Some tests were carried out on a "Mount Wellington" ore containing disseminated cassiterite with a high percentage of base-metal sulphides. The particle size of cassiterite in this ore is about 30 - 35 μ . Two specific problems arise:

- (1) The effect of pyrite and chalcopyrite on the sulphidization of cassiterite.
- (2) The effect of the cassiterite particle size.

2.2. Experimental

2.2.1. Apparatus and Procedure: The apparatus and procedure used were those described in Chapter 1.

2.2.2. Materials: The materials used in this investigation were:

1. Pure chemical grade stannic oxide.
2. Pure pyrite crystals (Dr J.A. Kitchener, Min. Tech. Dept., R.S.N.).
3. An impure chalcopyrite sample containing some silica.
4. Mount Wellington Ore: sample contained 0.75% of tin.

2.3. Results and Discussion

2.3.1. Effect of Pyrite on the Sulphidization of Stannic Oxide: The effect of the presence of pyrite on the tin sulphidization reaction could not readily be predicted; a test of sulphidization in presence of pyrite, using tin dioxide as reactant, was therefore performed.

Two experiments were carried out with the sulphidizer at 700°C. and the reducer at 800°C. The gas flow-rate was slow (75 ml./minute SO₂), and the reaction period four hours.

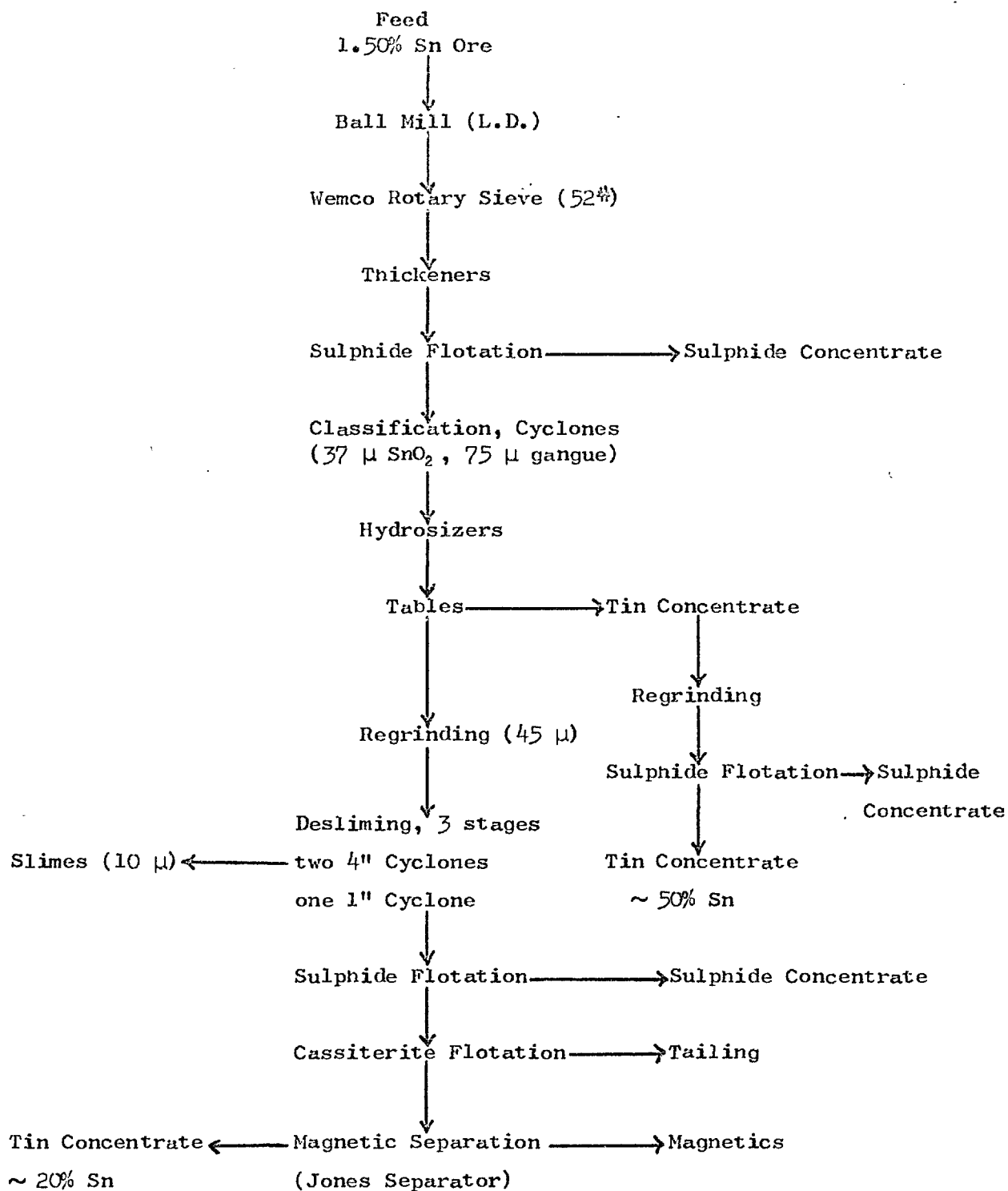


Figure 4. Flow-Sheet of Wheal-Jane Tin Ore (Cornwall)

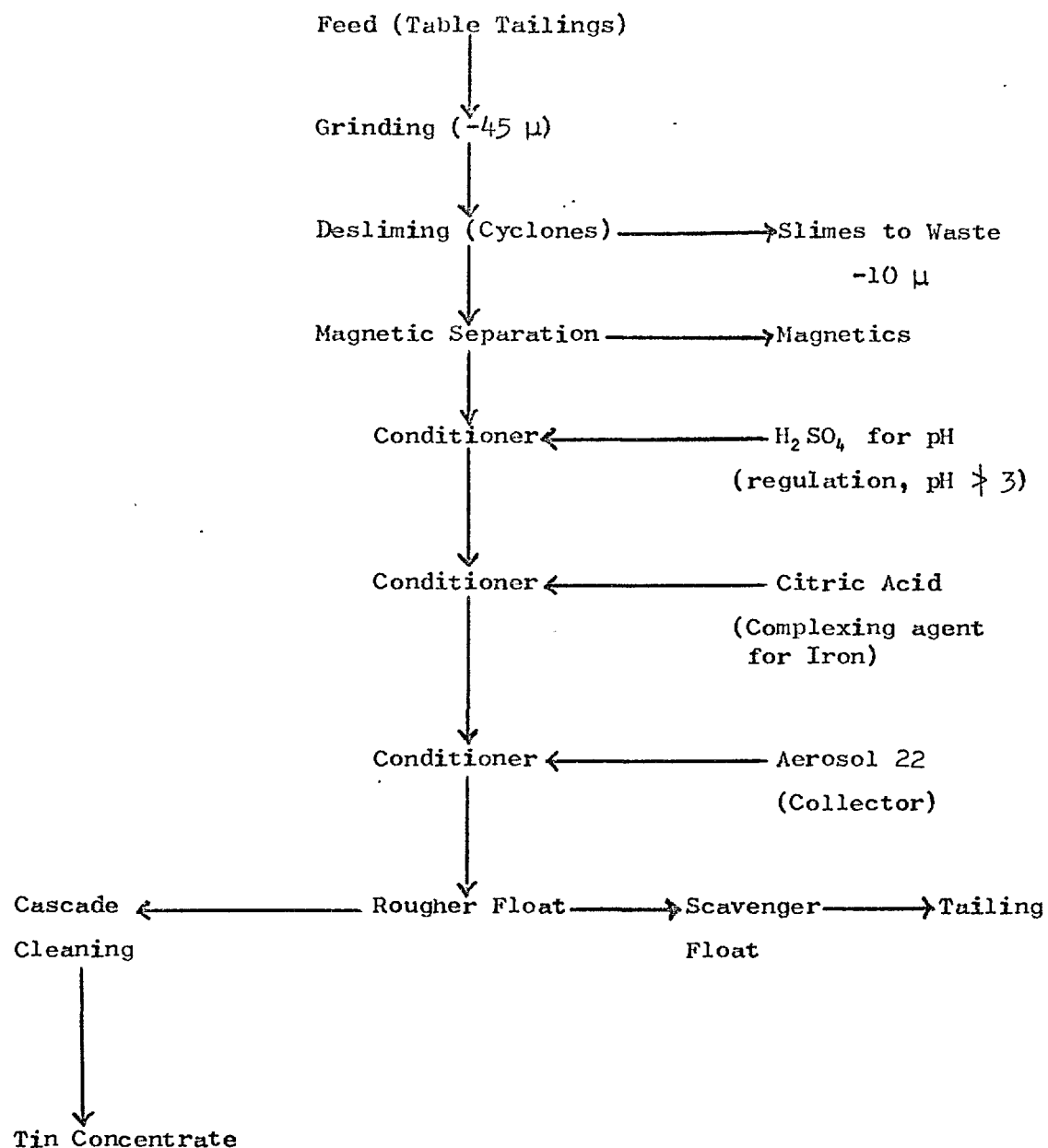


Figure 5. Flow-Sheet of Cassiterite Flotation

Experiment No.1: (SnO_2 to FeS_2 weight ratio, 2:3)

1.	Weight of boat empty	= 47.3800 g.
2.	Weight of SnO_2 taken	= 2.0000 g.
3.	Weight of FeS_2 taken	= 3.0000 g.
4.	Weight of boat + mixture	= 52.3512 g.
5.	Weight of Sample	= 4.9712 g.
6.	Weight of boat + product	= 51.7084 g.
7.	Change in weight	= -0.6428 g.

The product was grey-black and crystalline, with a metallic lustre. It was strongly magnetic and dissolved in hydrochloric acid quickly.

Experiment No.2: (SnO_2 to FeS_2 weight ratio, 1:4)

1.	Weight of boat empty	= 46.1386 g.
2.	Weight of SnO_2 taken	= 1.0000 g.
3.	Weight of FeS_2 taken	= 4.0000 g.
4.	Weight of boat + mixture	= 51.1281 g.
	(SnO_2 and FeS_2 mixed in mortar)	
5.	Weight of Sample	= 4.9895 g.
6.	Weight of boat + product	= 50.2411 g.
7.	Weight of product	= 4.1025 g.
8.	Change in weight	= -0.8870 g.

The product was similar to that from the previous test.

According to the chemical evidence from these two experiments, stannic oxide was totally converted into stannous sulphide; this is in good agreement with the results reported in Chapter 1. The sulphidization conditions used were, in fact, the optimum conditions. On the other hand, pyrite had decomposed to ferrous sulphide ($\text{Fe}_{0.88}\text{S}$). The observed loss in weight is approximately in agreement with this conclusion. (With the 2:3 ratio the theoretical loss is 0.8002 g., and with the 1:4 ratio it is 1.0670 g.).

The pyrite sample used in the investigation and the products of the two experiments were examined by X-ray diffraction; a diffractometer

was used in this case. The data obtained, given in Table 19, confirmed that stannic oxide was converted into stannous sulphide, and pyrite into ferrous sulphide, $\text{Fe}_{0.88}\text{S}$ (ASTM, Card No.17-200). The d -spacings obtained for the pyrite sample were in excellent agreement with the literature (ASTM, Card No.6-0710).

2.3.2. Effect of Chalcopyrite on the Sulphidization of Stannic Oxide:

Similar tests were performed to establish the influence of added chalcopyrite on the sulphidization reaction.

Two experiments were carried out with the sulphidizer at 700°C . and the reducer at 800°C . The flow-rate was slow (75 ml./minute SO_2), and the reaction period four hours.

Experiment No.1: (SnO_2 to CuFeS_2 weight ratio, 2:3)

1. Weight of boat empty = 47.3803 g.
2. Weight of SnO_2 taken = 2.0000 g.
3. Weight of CuFeS_2 taken = 3.0000 g.
4. Weight of boat + mixture = 52.3656 g.
(SnO_2 and CuFeS_2 mixed in mortar).
5. Weight of Sample = 4.9853 g.
6. Weight of boat + product = 52.2617 g.
7. Weight of product = 4.8814 g.
8. Change in weight = -0.1039 g.

The product was brownish-black and partly crystalline. It was not magnetic, and not completely soluble in hydrochloric acid.

Experiment No.2: (SnO_2 to CuFeS_2 , weight ratio, 1:4)

1. Weight of boat empty = 46.1389 g.
2. Weight of SnO_2 taken = 1.0000 g.
3. Weight of CuFeS_2 taken = 4.0000 g.
4. Weight of boat + mixture = 51.1367 g.
(SnO_2 and CuFeS_2 mixed in mortar)
5. Weight of Sample = 4.9978 g.
6. Weight of boat + product = 50.9261 g.
7. Weight of product = 4.7872 g.
8. Change in weight = -0.2106 g.

The product was similar to that of experiment No.1.

Table 19

X-Ray Diffraction Data from Pyrite Sample and Related
Sulphidization Products

Pyrite Sample FeS ₂	FeS ₂ ASTM (6-0710)	Product of Experiment No.1	Product of Experiment No.2	SnS ASTM (14-620)	Fe _{0.88} S ASTM (17-200)
d I	d I	d I	d I	d I	d I
3.117 32	3.128 35	5.739 5	5.739 8	-	5.75 20
2.703 100	2.709 85	4.022 25	5.231 6	4.04 5	5.67 20
2.419 71	2.423 65	3.413 50	4.022 15	3.421 10	5.24 10
2.207 44	2.2118 50	3.237 50	3.413 22	3.243 15	-
1.913 59	1.9155 40	2.969 25	3.237 24	-	-
1.631 48	1.6332 100	2.929 40	2.969 46	2.929 5	2.969 90
1.562 10	1.560 14	2.829 75	2.922 18	2.831 25	-
1.501 13	1.5025 20	2.793 100	2.829 44	2.793 100	-
1.447 13	1.4448 25	2.638 20	2.793 100	-	-
1.242 16	1.2427 12	2.302 50	2.637 30	2.305 15	2.647 30
1.211 10	1.2113 14	2.120 13	2.302 18	2.123 1	2.635 90
		2.064 15	2.120 10	-	2.621 80
		2.053 18	2.064 30	-	2.064 40
		2.049 22	2.053 38	-	2.057 100
		2.021 30	2.049 44	2.024 10	2.047 90
		1.986 20	2.021 14	1.988 10	2.042 30
		1.871 20	1.986 10	1.844 5	-
		1.776 15	1.871 10	1.778 5	-
		1.717 20	1.776 8	1.721 1	-
		1.711 12	1.717 30	1.713 5	-
		1.687 15	1.711 8	1.689 5	1.714 80
		1.622 10	1.687 10	1.622 5	+ many weak
			1.621 6		lines with
					intensities
					of 5 and 10

The chalcopryrite sample used in the investigation, and the products of the two experiments were examined by X-ray diffraction (in diffractometer). The data obtained are given in Table 20. Three phases are present: stannic oxide, and γ -chalcopryrite and stannite (Cu-Fe-Sn sulphide). The d -spacings of γ -chalcopryrite (ASTM Card No.11-0570) and of $\text{Cu}_2\text{FeSnS}_4$ (ASTM Card No.11-062) together with those of stannic oxide are present. The X-ray pattern obtained for the chalcopryrite sample is in agreement with the literature (ASTM Card No.9-0423). Chalcopryrite has transformed the γ -chalcopryrite, a sulphur-deficient modification. It seems that once stannic oxide undergoes sulphidization, a secondary reaction between the tin sulphide and chalcopryrite or γ -chalcopryrite gives stannite, $\text{Cu}_2\text{FeSnS}_4$; the stannite coating on the oxide particles probably impedes the sulphidization.

2.3.3. Sulphidization of Mount Wellington Ore:

This ore contains tin as finely disseminated cassiterite with a high percentage of pyrite and chalcopryrite. A sample assaying 0.75% of tin was treated with the sulphidizer at 700°C . and the reducer at 800°C . The sulphur dioxide flow-rate was 75 ml./minute and the reaction period three hours. The results obtained are given in Table 21. The products were leached with 25% hydrochloric acid and the leach residues were analysed by atomic absorption spectrometry. A fusion method, using sodium carbonate and sodium peroxide, was used to prepare the solutions for analysis (Mantell, 1949). The results obtained are given in Table 21. It is quite clear that the sulphidization was not very effective; this is probably due to the fact that the cassiterite is not liberated. With -300 mesh ore ($53\ \mu$), the degree of sulphidization is still low. A cassiterite particle interlocked with gangue particles cannot be sulphidized completely because of lack of access by the sulphidizing gas. The formation of stannite in the presence of chalcopryrite may well be an important inhibiting factor in the sulphidization of such cassiterite ores. The treated sample contained about 1.0 - 2.0% of chalcopryrite, and part of the cassiterite was known to be polydispersed with pyrite and chalcopryrite, supporting the above idea. Because the ore contained low values of tin, it was impossible to detect the formation of stannite in the sulphidized ore by X-ray diffraction.

Table 20

X-Ray Diffraction Data for the Chalcopyrite Sample and the Related Sulphidization Products.

Chalco- pyrite Sample		CuFeS ₂ ASTM (9-0423)		Product of Experiment No.1		Product of Experiment No.2		γ-CuFeS ASTM (2-x) (11-0570)		Stannite (Cu ₂ FeSnS ₄) (ASTM,11-062)	
d	I	d	I	d	I	d	I	d	I	d	I
3.348	9	3.03	100	5.418	3	9.261	8	7.79	20	5.37	5
3.039	100	2.63	5	3.823	3	7.437	4	5.38	10	4.85	5
2.769	4	1.865	40	3.347	100	5.398	3	4.38	10	3.12	100
2.642	5	1.854	80	3.127	84	4.235	21	3.76	35	2.71	30
2.605	4	1.591	60	3.066	26	3.806	4	3.07	100	2.46	5
1.870	20	1.573	20	2.917	2	3.342	83	2.843	10	2.38	5
1.857	45	1.518	5	2.827	1	3.119	87	2.679	25	2.21	5
1.593	24	1.323	10	2.712	5	3.066	100	2.643	45	1.922	70
1.575	10	1.303	5	2.636	70	3.820	3	2.608	10	1.642	40
1.543	5	1.214	10	2.416	2	2.696	4	2.346	10	1.626	30
1.323	3	1.205	30	2.366	23	2.638	60	2.260	15	1.570	10
1.303	2			2.308	5	2.45	3	2.168	25	1.368	20
1.212	3			2.210	2	2.360	33	1.880	90	1.346	20
1.205	4			2.116	2	2.302	4	1.634	55		
				1.913	24	1.911	21	1.597	70		
				1.875	14	1.879	32	1.535	30		
				1.809	1	1.814	5	1.418	5		
				1.763	45	1.760	35	1.389	5		
				1.674	10	1.672	8	1.343	35		
				1.633	13	1.630	8	1.323	55		
				1.604	4	1.604	12				
				1.593	6	1.591	4				
				1.563	2	1.496	8				
				1.498	10	1.437	7				
				1.438	9	1.413	9				
				1.414	11	1.321	3				
				1.353	1						
				1.322	5						

Table 21

Results of Sulphidization and Acid Leaching of Mount Wellington Tin Ore

Reducer = 800°C

Sulphidizer = 700°C

Time = 3 hours

Flow-Rate = 75 ml./minute

(Products were grey-black powders)

Run Number	Particle Size	Weight of Sample	Weight of Product	% Loss in Weight	Weight of Sample Leached	Weight of Leach Residue	% loss in Weight	% Sn in Leach Residue	% Extrac-tion
1	-100 mesh	18.2100	17.2783	5.12	10.00	7.20	28	0.60	35.3
2	-200 mesh	20.0158	18.9159	5.50	10.00	7.90	21	0.64	32.6
3	-300 mesh	17.2793	16.2687	5.85	10.00	7.60	24	0.43	56.4

2.4. Conclusions

The three tests briefly reported here indicate the kind of difficulty always likely to be encountered in processing low-grade ores by chemical methods. The reaction used to attack the ore values is inhibited, possibly by insufficient release of ore particles to chemical attack, or alternatively by complicating reactions in which minor gangue components interfere. More research will be needed to determine whether the direct sulphidization process is applicable to particular low-grade ores or concentrates. It is of interest, however, that the best recovery obtained in the preliminary tests just described is comparable with the levels of recovery often reported for flotation methods.

Chapter 3

The Tin-Sulphur System

3.1. Introduction

The use of a simple gas-phase sulphidizing reaction in which the solid product is held in contact with a gas of constant sulphur vapour pressure affords opportunity to verify existing general information on the relative stabilities of participating tin-sulphide phases. The results already shown in Table 8 (Chapter 1) disclosed a dependence of product composition on reaction temperature and sulphidizing gas composition; it was appropriate, therefore, to carry out a few carefully planned experiments, at more closely-spaced reaction temperatures, to confirm the conditions for stability of the established product phases (SnS_2 , Sn_2S_3 , and SnS). The determination of the decomposition temperatures of tin sulphides under specified and constant sulphur vapour partial pressures has not been reported previously.

With the reducer at 700°C ., a convenient working optimum in this system, the sulphidizing gas has a sulphur vapour partial pressure equal to 5.32 mm Hg. This is readily established from existing information on the carbon - sulphur - oxygen system, and corresponding values can be derived for other reducer temperatures. It is important to note, however, that when the reactor temperature (at which the sulphidizing equilibrium is maintained) is different from the reducer temperature (at which the sulphidizing mixture of sulphur compounds is formed), a readjustment of gas composition will normally occur between the reducer and sulphidizer. Calculations of this readjustment would be very difficult. As a first step to provide data of practical value, tests were carried out at a constant reducer temperature of 700°C . and reactor temperatures between 400° and 720°C .

3.2. Experimental

3.2.1. Apparatus and Materials: Same as given in Chapter 1.

3.2.2. Procedure:

All experiments were carried out exactly as described in Chapter 1. All the runs were done with the reducer maintained at 700°C ., and the carbon column was kept full. A high sulphur dioxide flow-rate of

150 ml./minute, equivalent at a 4-hour reaction time to 6.0 g. SO_2 /g. SnO_2 , was used. All products were characterised by X-ray diffraction (Guinier) photographs.

The effect of the reaction temperature was first examined in detail; later, the effects of reaction time and of certain aspects of sulphidizing gas composition were studied more briefly.

3.3. Results and Discussion

3.3.1. Effect of Reaction Temperature:

Sulphidization of stannic oxide using a four-hour reaction period, and a sulphidizing gas with a sulphur vapour partial pressure in the reducer of 5.32 mm Hg (reducer at $700^\circ\text{C}.$), was investigated in the temperature range $400 - 720^\circ\text{C}.$ The results obtained are given in Table 22. Stannic oxide was converted to stannic sulphide at all temperatures below $600^\circ\text{C}.$ At $570^\circ\text{C}.$ and $600^\circ\text{C}.$, brown crystalline stannic sulphide formed (see photograph No.3). As the reaction temperature was increased, a grey-black powder (photograph No.4) appeared in the products. At $660^\circ\text{C}.$ and $670^\circ\text{C}.$ the whole product was grey-black and finely crystalline, and stannic sulphide no longer appeared. The X-ray pattern of this product was that of tin sesquisulphide, Sn_2S_3 (ASTM Card No.14-619). At $680^\circ\text{C}.$ stannous sulphide appeared in the product; stannous sulphide alone was found, as grey-black crystals with metallic lustre at $720^\circ\text{C}.$ Large quantities of elemental sulphur collected at the exit of the sulphidizer tube in all runs above $600^\circ\text{C}.$ In fact, at $720^\circ\text{C}.$, the exit was almost clogged with sulphur. This condensed sulphur arises from shifts in the sulphidizing gas equilibria due to changes in temperature. The percentage changes in weight agreed well with the theoretical values for the formation of a single phase, (at $600^\circ\text{C}.$, stannic sulphide; at $660 - 670^\circ\text{C}.$, tin sesquisulphide; and at $720^\circ\text{C}.$, stannous sulphide) (see Table 23). The percentage conversion of the oxide to the sulphide was highest at temperatures where one single sulphide was present in the products, i.e. at $600^\circ\text{C}.$, $660 - 670^\circ\text{C}.$, and $720^\circ\text{C}.$



Photograph No.3: Crystalline Stannic Sulphide, SnS_2 , obtained at 600°C . in sulphidizer with reducer at 700°C . using high gas flow-rate and four hours reaction period (Magnification = $4\times$).



Photograph No.4: Tin Sesquisulphide, Sn_2S_3 , obtained at 620°C . (Magnification = $4\times$).

Table 22

Results of Sulphidization of Stannic Oxide in the temperature range 400 - 720°C.

Reducer at 700°C.

Time = 4 hours

Flow-Rate = 150 ml./minute SO₂ (6 g. SO₂/g. SnO₂)

Run Number	Temperature °C	Weight of sample(g)	Weight of product (s)	Change in weight(g)	% Change in weight	% Conversion to Sulphide	Type of Sulphide Formed	Remarks
1	400	5.0085	5.5225	+0.5140	+ 10.26	53.91	SnS ₂ only	Yellowish-orange powder
2	450	4.9821	5.7633	+0.7812	+ 15.68	78.75	SnS ₂ only	Orange powder
3	500	5.1954	6.0912	+0.8958	+ 17.24	90.68	SnS ₂ only	Brownish-orange powder
4	550	5.0127	5.9914	+0.9787	+ 19.52	94.17	SnS ₂ only	Dark brown powder
5	570	5.0071	5.9880	+0.9809	+ 19.59	96.03	SnS ₂ only	Dark brown crystalline
6	600	4.9634	5.9738	+1.0104	+ 20.36	97.96	SnS ₂ only	Light brown-bronze crystalline
7	610	5.0789	6.0837	+1.0048	+ 19.78	96.00	SnS ₂ + trace of Sn ₂ S ₃	Light brown bronze crystalline
8	620	5.1609	5.8239	+0.7630	+ 14.78	90.03	SnS ₂ + Sn ₂ S ₃	Mixed brownish flakes and grey-black powder
9	640	5.0386	5.7547	+0.7161	+ 14.21	92.00	Sn ₂ S ₃ + SnS ₂	Grey-black powder with some golden flakes

Table 22 (continued)

Run Number	Temperature °C	Weight of sample(g)	Weight of product (s)	Change in weight(g)	% Change in weight	% Conversion to Sulphide	Type of Sulphide Formed	Remarks
10	650	5.0341	5.6700	+0.6359	+ 12.63	93.47	$\text{Sn}_2\text{S}_3 + \text{SnS}_2$	Grey-black powder with some golden flakes
11	660	5.0553	5.6056	+0.5503	+ 10.88	96.40	Sn_2S_3 only	Grey-black very fine crystalline powder
12	670	5.1524	5.7089	+0.5565	+ 10.80	96.70	Sn_2S_3 only	Grey-black very fine crystalline powder
13	680	5.0070	5.3799	+0.3729	+ 7.45	92.06	Sn_2S_3 + trace of SnS	Grey-black very fine crystalline powder
14	690	5.1371	5.3426	+0.3055	+ 5.95	90.83	$\text{Sn}_2\text{S}_3 + \text{SnS}$	Grey-black crystalline with some grey powder
15	700	5.0383	5.1289	+0.0906	+ 1.80	96.14	SnS + trace of Sn_2S_3	Grey-black crystalline (metallic) with traces of grey powder
16	720	5.0134	5.0011	-0.0123	- 0.25	97.68	SnS only	Grey-black crystalline product

Table 23

Percentage Change in Weight of Sample in Relation to
the Type of Sulphide Formed at Various Temperatures

Tin Sulphide	Temperature °C	% Change in weight Observed value	% Change in weight Theoretical value
Stannic Sulphide: SnS_2	600	+ 20.36	+ 21.31
Tin Sesquisulphide: Sn_2S_3	660	+ 10.89	+ 10.68
	670	+ 10.80	
Stannous Sulphide: SnS	720	- 0.25	+ 0.04

X-Ray diffraction data obtained for the products at various temperatures showed no evidence for the formation of the tin sulphides, Sn_3S_4 and Sn_4S_5 , reported by some earlier workers. The d -spacings of stannic sulphide, SnS_2 , tin sesquisulphide, Sn_2S_3 , and stannous sulphide, SnS , agree well with published data (see Chapter 1). The flakey character of the product no doubt introduced some preferred orientation into the X-ray specimen, and this may have introduced observed intensity relationships among lines in the photographs.

3.3.2. Effect of Time:

The results of studying the effect of time on the percentage conversion at 600°C . are given in Table 24. The fine crystalline grey product ($\text{SnS} + \text{Sn}_2\text{S}_3$) obtained after one hour is a product, clearly, of incomplete sulphidization. Experiments were repeated at 500°C . to confirm the broad pattern of sulphide formation; the results obtained are given in Table 25. These results prove that lower sulphides, e.g. stannous sulphide and tin sesquisulphide, occur as intermediate products in sulphidization.

3.3.3. Effect of the Composition of the Sulphidizing Gas:

Accentuated formation of lower sulphides at low temperatures was observed when the carbon column of the reducer was freshly packed with charcoal. Table 26 shows some of the results observed. Reproducible results were obtained only after the third run, after the column had been packed with fresh charcoal. Initially it was thought that the reason for this was the presence of desorbed water vapour, which would introduce some hydrogen sulphide into the sulphidizing gas. Therefore the column was packed with fresh charcoal, and heated at 900°C . for 48 hours in a stream of nitrogen to desorb water and ensure a water-free atmosphere. Four successive runs were then carried out at 600°C . The results obtained are given in Table 27. The formation of a grey-black, fine crystalline product from the first run, and of a brown crystalline product from the fourth run is noteworthy. The composition of the gas obtained from the reduction of sulphur dioxide with carbon at 700°C . does not reach equilibrium quickly, and the equilibrium partial pressure of the sulphur is not quickly established. This fact no doubt arises from the need to remove a chemisorbed layer from the carbon granules before equilibrium can be attained rapidly.

Table 24

Results of Sulphidization of Stannic Oxide at 600°C at various reaction intervals

Reducer at 700°C

Flow-Rate = 150 ml.SO₂/minute

Run Number	Time (mins.)	Weight of Sample (SnO ₂)	Weight of Product (Sulphide)	Change in Weight of Sample	% Change in Weight	% Conversion to Sulphide	Type of Sulphide Formed	Remarks
1	15	5.0425	5.0390	-0.0035	-0.07	5.03	Superficial coating	product is brownish violet powder
2	30	5.0238	5.0938	+0.0700	+1.39	17.10	Superficial coating (SnS)	product is greenish-grey powder
3	60	5.0568	5.3227	+0.2659	+5.26	74.80	SnS + Sn ₂ S ₃	product is grey-black fine crystalline
4	120	5.0869	5.8071	+0.7202	+14.16	90.18	SnS ₂ + Sn ₂ S ₃	product is brownish-grey crystalline
5	240	5.0010	6.0112	+1.0102	+20.20	97.10	SnS ₂ only	product is brown crystalline

Table 25

Results of Sulphidization of Stannic Oxide at 500°C at Various Time intervals

Reducer at 700°C

Flow-Rate = 150 ml.SO₂/minute

Run Number	Time (mins.)	Weight of Sample (SnO ₂)	Weight of Product	Change in Weight	% Change in Weight	% Conver- to Sulphide	Type of Sulphide Formed	Remarks
1	15	5.1205	5.2095	+0.0890	+1.74	4.23	Superficial Coating	Product is light brownish powder
2	30	5.1635	5.3630	+0.1995	+3.86	12.11	SnS + Sn ₂ S ₃	Product is light grey powder
3	60	5.1140	5.5646	+0.4506	+8.81	46.03	Sn ₂ S ₃ + SnS ₂	Greenish-yellow with some grey powder
4	120	5.1745	6.0637	+0.8892	+17.18	88.12	SnS ₂ + Sn ₂ S ₃	Yellowish-orange with some grey powder
5	240	5.1041	6.0578	+0.9537	+18.68	91.20	SnS ₂ only	Brownish-orange powder
6	360	5.1156	6.0845	+0.9689	+18.94	91.80	SnS ₂ only	Brownish-orange powder

Table 26

Results of sulphidization of Stannic Oxide observed when Reducer Column was freshly packed with Charcoal.

Reducer at 700°C

Time = 4 hours

Flow-Rate = 150 ml.SO₂/minute

Run Number	Temperature °C	Weight of Sample (SnO ₂)	Weight of product	Change in weight	% Change weight	% Conversion to Sulphide	Type of Sulphide formed	Remarks
1	570	4.9672	4.9638	+0.0034	+ 0.07	92.00	SnS only	Product is grey-black fine crystalline
2	550	5.0013	5.3826	+0.3813	+ 7.62	90.10	Sn ₂ S ₃ +SnS	Product is grey-black powder
3	550	5.0874	5.8645	+0.7771	+14.27	94.00	SnS ₂ +Sn ₂ S ₃	Product is brown crystalline with some grey powder
4	570	5.0602	6.0338	+0.9736	19.24	96.00	SnS ₂ only	Product is brown crystalline

Table 27

Results of Sulphidization of Stannic Oxide observed when Reducer was freshly packed with Charcoal with a water-free atmosphere.

Reducer at 700°C

Time = 4 hours

Flow-Rate = 150 ml.SO₂/minute

Run Number	Temperature °C	Weight of sample	Weight of product	Change in weight	% Change in weight	Type of Sulphide Formed	Remarks
1	600	5.1671	5.4327	+0.2656	+ 5.14	SnS+Sn ₂ S ₃	Product is grey-black fine crystalline
2	600	5.1393	6.1050	+0.9657	+18.79	SnS ₂ +trace of Sn ₂ S ₃	Brown crystalline with some grey powder
3	600	5.1563	6.1669	+1.0106	+19.60	SnS ₂ only	Brown crystalline product
4	600	5.0360	6.0744	+1.0384	+20.62	SnS ₂ only	Brown crystalline product

3.4. Conclusions

The following conclusions relating to the tin-sulphur system may be drawn for experiments reported in this chapter:

1. The solid phases arising in the tin-sulphur system under the conditions of the experiments are SnS_2 , Sn_2S_3 , and SnS . There is no evidence for the occurrence of Sn_3S_4 or Sn_4S_5 .
2. The technique described is quite suitable for the synthesis of crystalline SnS_2 , Sn_2S_3 , or SnS . Stannic sulphide can be obtained at $570 - 600^\circ\text{C}$., tin sesquisulphide at $660 - 670^\circ\text{C}$., and stannous sulphide at $720 - 730^\circ\text{C}$.; when using a four-hour reaction period, a high gas flow-rate (6 g. SO_2 /g. SnO_2), and a reducer temperature of 700°C ., with the carbon column kept full.

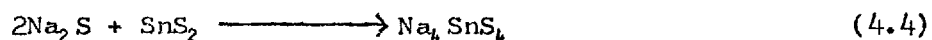
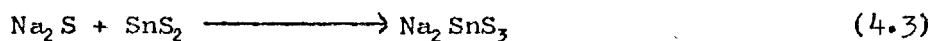
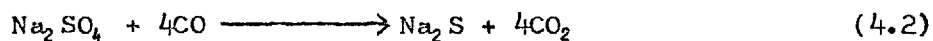
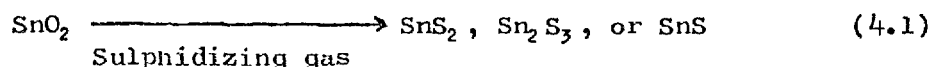
Chapter 4

Sulphidization of Stannic Oxide in the Presence of Sodium Sulphate

4.1. Introduction

Thiostannates are readily formed by combination of stannic sulphide with an alkali-metal sulphide (e.g. $\text{SnS}_2 + \text{Na}_2\text{S} \rightarrow \text{Na}_2\text{SnS}_3$; $\text{SnS}_2 + 2\text{Na}_2\text{S} \rightarrow \text{Na}_4\text{SnS}_4$). The sulphidization of stannic oxide with the sulphurous gases produced from reduction of sulphur dioxide by carbon has proved to be effective in the temperature range $600 - 750^\circ\text{C}$., with high conversion values ($> 90\%$). It should therefore be possible to prepare a thiostannate (e.g. the sodium salt) in a single operation by sulphidizing stannic oxide in admixture with sodium sulphide. Furthermore, the sulphidizing gas obtained by carbon reduction of sulphur dioxide is strongly reducing on account of its high carbon monoxide content, and this reserve of reducing power can be used to form sodium sulphide "in situ" from sodium sulphate. Sulphidization of a suitably proportional mixture of stannic oxide and sodium sulphate is therefore expected to yield sodium thiostannate directly.

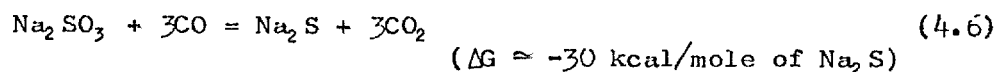
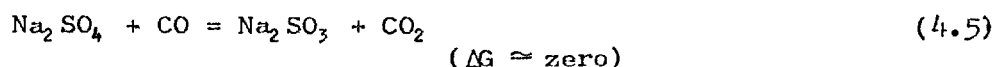
Sulphidization of stannic oxide at the higher temperatures in the working range has been shown to yield sulphides containing bivalent tin. This might indicate the possibility of obtaining corresponding thio-salts also containing tin in the bivalent state. However, previous work on thiostannates (although not extensive) shows that the quadri-valent thio-salts are very stable, but that existence of bivalent thio-salts is questionable. It was therefore realised that the thio-salt formation step (equation 4.3 and 4.4 below) might change the stability relationships between the tin sulphides and favour thio-stannate formation even at temperatures too high for stannic sulphide alone to be stable.



The sodium thiostannates alleged to exist, and introduced into equations 4.3 and 4.4 above, are the meta-thiosalt, Na_2SnS_3 , and the ortho-thiosalt, Na_4SnS_4 . The meta-thiosalt is not stable at high temperatures, above 600°C ., at which it decomposes to give the ortho-thiosalt and stannic sulphide or a lower sulphide and sulphur. The

complete extraction of tin from cassiterite concentrates can be achieved only through the formation of the ortho-thiosalt (Sevryukov, 1962).

The reduction of sodium sulphate with carbon monoxide is very slow at low temperatures; but in the temperature range 600 - 750°C., it proceeds with moderate speed. The "activity effect" introduced by its consumption in the secondary reaction favours sulphide formation in the case now under consideration. The rate-determining step of the reduction is the initial formation of sulphite, which is thermodynamically unfavourable (Fortiev, 1962). The reactions can be represented as follows:



The sodium sulphate-sodium sulphide system has a eutectic which lies in the temperature range 680 - 740°C. (Fortiev, 1962). This eutectic may interfere with the reactions in this temperature range by introducing a liquid phase, especially at high molar ratios of sodium sulphate to stannic oxide.

4.2. Experimental

4.2.1. Apparatus and Materials: The apparatus described in Chapter 1 was again used.

4.2.2. Procedure:

Five grams of pure stannic oxide were always used for one run. It was mixed in an agate mortar with the necessary quantity of anhydrous sodium sulphate. The mixture was transferred to a weighed porcelain boat, which was re-weighed and introduced into the sulphidizer. At the end of the experiment, the boat was pulled out and weighed. The product was then ground and stored for X-ray diffraction and leaching tests.

Leaching with water was carried out by taking 1-2 g. of sample in a small beaker with about 50 ml. of water and stirring with a glass rod for several minutes. After filtration and washing, the residue

was left to dry on the filter paper and weighed. This weight gave, with sufficient accuracy, the percentage of soluble material in the product. The filter paper was then burned off and the residue of tin oxide ignited and weighed so that the percentage conversion of tin into soluble thio-salt could be estimated. This value was confirmed by analysing the leach solution; a known aliquot of this was taken and acidified to precipitate stannic sulphide, which was ignited to stannic oxide and weighed.

4.3. Results and Discussion

The sulphidization of stannic oxide in the presence of sodium sulphate was investigated in the temperature range $600 - 800^{\circ}\text{C}$. This temperature range was chosen for three main reasons:

1. Reduction of sodium sulphate is not effective at temperatures below 600°C .
2. The degree of conversion of stannic oxide into sulphide is high ($> 90\%$) above 600°C .
3. The decomposition of thiostannates and volatilization of stannous sulphide become serious at temperatures above about 800°C .

Initial work was carried out with the reducer at 800°C ., the experimental variables were planned as follows:

1. Two molar ratios (1:1 and 2:1) of sodium sulphate to stannic oxide were first studied in the temperature range $600 - 800^{\circ}\text{C}$., with a four-hour reaction period and high gas flow-rate. Later other ratios (1.3:1, 1.6:1, 2.3:1, 2.6:1, and 3:1) were tested under the conditions found to approximate to the optimum.
2. A high gas flow-rate (6 g. SO_2 /g. SnO_2) was used in all initial runs. Later the effect of a slow flow-rate (3 g. SO_2 /g. SnO_2) was tested.
3. Initially a four-hour reaction period was used in all runs. Later the effect of time was studied under the optimum working conditions.
4. Finally, the effect of changing the temperature of the reducer (i.e. changing sulphidizing gas composition) on the percentage conversion was studied with optimum values for the other variables.

The sulphidization of tin metal in the presence of sodium sulphate was also tested.

4.3.1. Effect of Molar Ratio:

Results obtained when using the 1:1 and 2:1 molar ratios of sodium sulphate to stannic oxide, with the reducer at $800^{\circ}\text{C}.$, a four-hour reaction period, and high gas flow-rate, in the reaction temperature range $600 - 800^{\circ}\text{C}.$, are given in Tables 28 and 29, respectively.

With 1:1 ratio, the eutectic temperature in the sodium sulphate-sodium sulphide system did not have any evident effect. The product obtained below $700^{\circ}\text{C}.$ was greyish-black in colour, and melting had occurred. At $720^{\circ}\text{C}.$, the product was a green melted mass, clearly showing that a change in product phase had taken place; this change was supported by the X-ray diffraction pattern obtained. A completely soluble product could not be obtained even at $780^{\circ}\text{C}.$ The results show that increase in temperature did not cause any appreciable change in the percentage conversion.

With the 2:1 molar ratio, there was no significant melting below $700^{\circ}\text{C}.$ The products were greyish-green in colour and in the form of a porous cake. The product obtained at $700^{\circ}\text{C}.$ was a greyish crumbled block clearly showing the effect of some melting at the eutectic. The percentage conversion dropped considerably, and the leach residue was mainly stannic oxide. At $720^{\circ}\text{C}.$, the product was a melted mass forming two distinct regions: the middle part was greyish-green, and a yellowish zone surrounded it. Both areas had obviously melted. This clearly shows a change in the product phases, which was confirmed later by X-ray diffraction.

As the temperature was increased above $720^{\circ}\text{C}.$, the proportion of the yellowish product zone increased until, at $780^{\circ}\text{C}.$, a uniform slightly greenish-yellow melted mass, completely soluble in water, was obtained. At $800^{\circ}\text{C}.$, some decomposition was noticeable indicating that the optimum reaction temperature is quite critical.

4.3.2. Effect of Gas Flow-Rate

The effect of using a low flow-rate (3 g. SO_2 /g. SnO_2) was investigated with the reducer at $800^{\circ}\text{C}.$, a 2:1 molar ratio, and a four-hour reaction period. The results obtained are given in Table 30.

Table 28

Results of Conversion of Stannic Oxide to Sodium Thiostannate. Molar Ratio 1:1,
 Reducer at 800°C; Time = four hours; High Gas Flow-Rate

Run Number	Temperature °C	Weight of Sample (Na ₂ SO ₄ + SnO ₂)	Weight Loss in Weight of Product	% Soluble Material	% Conversion of SnO ₂ to Thiostannate	Water-Soluble Phases Detected	Remarks
1	600	9.6966	9.6790 0.0176	48	-	-	No reaction; product grey crystalline.
2	630	9.7029	9.5515 0.1514	56	15.01	Phase A	Little reaction; product grey crystalline.
3	650	9.6961	9.1440 0.5521	85	72.57	Phase A	Product is grey-black with little melting.
4	670	9.7054	8.9682 0.7272	87	76.38	Phase A	Product is grey-black melted mass.
5	680	9.7270	8.9540 0.7730	88	78.58	Phase A	Product is grey-black melted mass.
6	700	9.7014	8.8920 0.8094	88	80.00	Phase A	Product is grey-black melted mass.
7	720	9.7013	8.7059 0.9954	91	84.82	Phases A and B	Product is greenish melted mass.
8	740	9.7022	8.5361 1.1661	92	86.58	Phases A and B	Product is greenish melted mass.
9	760	9.7023	8.5843 1.1180	95	91.95	Phases A and B	Product is dark greenish melted mass.
10	780	9.7004	8.5872 1.1132	95	91.41	Phases A and B and traces of phase C	Product is dark greenish melted mass.

Table 29

Results of Conversion of Stannic Oxide to Sodium Thiostannate. Molar Ratio 2:1

Reducer at 800°C; Time = four hours; High Flow-Rate.

Run Number	Temperature °C	Weight of Sample (Na ₂ SO ₄ + SnO ₂)	Weight of Product	Loss in Weight	% Soluble Material	% Conversion of SnO ₂ to Thiostannate	Water-Soluble Phases Detected	Remarks
1	600	14.4178	14.3910	0.0268	65	-	-	No reaction, product is grey crystalline.
2	620	14.4150	14.3069	0.1081	67	-	-	No reaction, product is grey crystalline.
3	630	14.4272	13.7249	0.7023	93	81.42	Phases A and B	Product is greyish porous cake, no melting.
4	650	14.4260	13.4394	0.9866	94	84.30	Phases A and B	Product is greyish green porous cake, no melting.
5	660	14.4223	13.4178	1.0045	95	87.60	Phases A and B	Product is greyish green porous cake, no melting.
6	670	14.4208	13.1933	1.3275	98	93.81	Phases A and B	Melting just started. Product is greenish porous cake.
7	680	14.4264	13.2555	1.1709	95	85.00	Phases A and B	Like the previous result. Melting increased.

Table 29 (continued)

Run Number	Temperature °C	Weight of Sample (Na ₂ SO ₄ + SnO ₂)	Weight of Product	Loss in Weight	% Soluble Material	% Conversion of SnO ₂ to Thiostannate	Water-Soluble Phases Detected	Remarks
8	690	14.4241	13.0489	1.3752	91	75.30	Phases A and B	Like the previous result. Melting increased.
9	700	14.4211	13.4190	1.0050	85	60.15	Phase B only	Product is a light grey crumbled round piece.
10	720	14.4211	13.0279	1.3932	82	52.00	Phase B and traces of Phase C	Product is a melted mass greyish in the middle surrounded by a light greenish yellow coloured zone.
11	740	14.4195	13.0143	1.4052	83	55.70	" "	" " " "
12	760	14.4209	12.7219	1.6990	90	73.20	Phases B and C	Product is light greenish yellow coloured melted.
13	780	14.4195	12.0555	2.3640	100	100.00	Phases B and C	Product is light yellowish coloured melted mass.
14	800	14.4240	12.3232	2.1007	99	99.40	Phases B and C	" " " "

It is quite clear that a high flow-rate is important to achieve high extraction. It seems that sulphidization of oxide, reduction of sodium sulphate, and formation of a thiosalt are all slow when the flow-rate is low, even at high temperatures.

4.3.3. Effect of Time:

The effect of reaction period on the percentage conversion was investigated while using a 2:1 molar ratio, sulphidizer at 780°C ., high flow-rate, and the reducer at 800°C .. Results obtained are given in Table 31. These results show that the reaction is relatively slow, and a minimum of four hours' reaction period is necessary. This is important in connection with treatment of cassiterite, which is less reactive than the chemically prepared oxide. The product after two hours was a greenish grey melted mass; as the reaction time increased a yellowish phase started to form at the sides. Finally, a uniform yellowish melted mass, soluble in water, was formed after four hours.

4.3.4. Effect of Gas Composition (Reducer Temperature):

The effect of changing the reducer temperature (i.e. sulphidizing gas composition) on the percentage conversion of stannic oxide into the thio-salt was studied at the optimum conditions (sulphidizer at 780°C ., four hours' reaction period, high gas flow-rate, and 2:1 molar ratio). The results obtained are given in Table 32. At all reducer temperatures (750° , 900° , and 950°C .), completely water-soluble product was obtained, but with the reducer at 700°C . the reaction did not go to completion; the product was a greenish-grey melted mass in the middle surrounded by a yellowish zone. Some minor differences in the weight losses at different reaction temperatures were traced to slight traces of mixture in gas from the reducer, which were absorbed by the products during cooling. Careful desorption of water from the charcoal in the reducer column, ensuring a water-free atmosphere, led to consistent weight changes in runs 5, 6, and 7, which were carried out successively.

4.3.5. Effect of Molar Ratio at the Optimum Conditions:

Effect of the sodium sulphate to stannic oxide molar ratio at the optimum conditions was investigated by using 1:1, 1.3:1, 1.6:1, 2:1, 2.3:1, 2.6:1, and 3:1 ratios. The results obtained are given in Table 33.

Table 30

Results of Conversion of Stannic Oxide into Sodium Thiostannates. Slow Gas

Flow-Rate (3 g. SO₂/minute).

(Reducer at 800°C.; Time = four hours; 2:1 Molar Ratio)

Run Number	Temperature °C	Weight of Sample (Na ₂ SO ₄ + SnO ₂)	Weight of Product	Loss in Weight	% Soluble Material	% Conversion to Thiostannate	Water-Soluble Phases Detected	Remarks
1	670	14.4233	13.5393	0.8840	88	66.00	Phases A and B	No melting; product is light greenish grey porous cake.
2	720	14.4139	13.2509	1.1630	86	61.80	Phase B only	Product is light greenish melted mass.
3	780	14.4259	13.3694	1.0565	81	48.80	Phases B and C	Product is light greenish melted mass with some yellowish colour.
4	820	14.4277	13.2120	1.2157	85	59.30	Phases B and C	Product is light greenish-yellow melted mass.

Table 31

Results of Conversion of Stannic Oxide into Sodium Thiostannates at Various Time Intervals under Optimum Conditions.

(Reducer at 800°C; Molar Ratio = 2:1; High Flow-Rate)

Run No.	Time (mins.)	Weight of Sample ($\text{Na}_2\text{SO}_4 + \text{SnO}_2$)	Weight of Product	Loss in Weight	% Soluble Material	% Conversion to Thiostannate	Water-Soluble Phases Detected	Remarks
1	15	14.4235	14.4009	0.0226	65	-	-	No reaction tookplace
2	30	14.4250	14.1888	0.2362	68	9.65	Phase A only	Reaction started only on the surface. It has a light brownish-green colour.
3	60	14.4232	14.0020	0.4212	72	22.60	Phase A only	Reaction took place on surface. It is greyish-black in colour.
4	120	14.4230	13.3914	1.0316	82	51.00	Phases A and B	Product is a melted mass, greyish-green in colour.
5	180	14.4257	12.8257	1.6000	90	73.30	Phases B and C	Product is a melted mass with greenish colour in the middle and yellowish on the sides.
6	240	14.4195	12.0555	2.3640	100	100.00	Phases B and C	Product is a melted yellowish mass.

Table 32

Results of Conversion of Stannic Oxide to Sodium Thiostannates at Various Reducer Temperatures
(2:1 Molar Ratio; Four-Hour Reaction Period; High Gas Flow-Rate; Sulphidizer
at 780°C)

Run No.	Reducer Temperature °C	Weight of Sample (Na ₂ SO ₄ + SnO ₂)	Weight of Product	Loss in Weight	% Soluble Material	% Conversion to Thiostannate	Water-Soluble Phases Detected	Remarks
1	700	14.4195	12.7316	1.6879	95	86.50	Phases B and C	Product is a melted mass, greenish in the middle and yellowish green on the sides.
2	750	14.4213	12.0352	2.3861	100	100.00	Phases B and C	Product is a light greenish yellow melted mass.
3	800	14.4195	12.0555	2.3640	100	100.00	Phases B and C	" " "
4	900	14.4216	11.8410	2.5806	100	100.00	Phases B and C	" " "
5	950*	14.4174	11.4690	2.9481	100	100.00	Phases B and C	" " "
6	900*	14.4200	11.4270	2.9930	100	100.00	Phases B and C	" " "
7	800*	14.4190	11.4320	2.9870	100	100.00	Phases B and C	" " "

* These runs were carried out with careful exclusion of moisture during cooling.

Table 33

Results of Conversion of Stannic Oxide to Sodium Thiostannate at Various Molar Ratios
(Reducer at 800°C; Four-hours Reaction Period; High Gas Flow-Rate;
Sulphidizer at 780°C.)

Run No.	Molar Ratio of Na ₂ SO ₄ to SnO ₂	Weight of Sample (Na ₂ SO ₄ + SnO ₂)	Weight of Product	Loss in Weight	% Soluble Material	% Conversion to Thiostannates	Water-Soluble Phases Detected	Remarks
1	1:1	9.7004	8.5872	1.1132	95	91.41	Phases A and B and traces of phase C.	Product is a greenish melted mass.
2	1.3:1	11.1201	9.3857	1.7344	97	93.85	Phases B, A and C	Greenish product with some crystalline part
3	1.6:1	12.5341	10.1912	2.3429	99	97.58	Phases B and C	Light yellowish melted mass.
4	2.0:1	14.4195	12.0555	2.3640	100	100.00	Phases B and C	" "
5	2.3:1	15.8370	13.4722	2.3648	100	100.00	Phases B and C	Light greenish yellow melted mass.
6	2.6:1	17.2420	14.7305	2.5115	98	95.32	Phase B and C	Product is greenish yellow melted mass, greyish at the bottom of the boat.
7	3.0:1	19.1314	16.6932	2.4382	95	83.70	Phases B and C	Product is greenish yellow melted mass; greyish part at the bottom of the boat

Almost completely soluble product was obtained with the 1.6:1 molar ratio, which indicates that both thiosalts have formed; this was later confirmed by X-ray diffraction. At higher ratios (2.6:1 and 3:1) the products were not completely soluble; the leach residue was stannic oxide and not a sulphide. This may disclose the effect of the eutectic temperature in the sulphate-sulphide system.

4.3.6. Reactions of Tin Metal:

3.9382 g. of tin metal (powder) were used in all runs; this is the quantity of tin metal equivalent to five grams of the oxide. The powder was mixed with the necessary quantity of sodium sulphate. Results obtained are given in Table 34. The result obtained at 670°C shows that the sulphidization of tin metal is slow at low temperatures. At high temperatures the degree of conversion to the thiostannate is in agreement with the results obtained when using the oxide.

4.4. X-Ray Diffraction Studies

Products from all experiments were examined by X-ray diffraction. The Guinier camera was employed. The results are summarised below.

1. With 1:1 molar ratio, and at all temperatures below 700°C. the powder photograph appeared to show the presence of a single product phase. This phase is called "phase A" tentatively. Above 700°C. a second phase appeared; this second phase may be called "phase B". The proportion of this phase increased as the temperature increased. Phase A is greyish-black, whereas phase B is greenish. All products obtained above 700°C were greenish in colour. The change in weight above 700°C. clearly corresponds with this change in the phase composition of the products.

2. With the 2:1 molar ratio, phase A and phase B were detected in all products obtained below 700°C.; phase B is present in the highest proportion. The proportion of phase A decreased considerably as the temperature increased, and at 700°C. phase B was present alone. Above 700°C., a third phase appeared, referred to as "phase C", and its proportion increased as the degree of conversion increased. At 780°C., two phases were present in the product, phase B and phase C. Phase C appears to have a light yellowish colour (see Table 29).

Table 34

Results of Conversion of Tin Metal to Sodium Thiostannates. Reducer at 800°C.;
Four-hour Reaction Period; High Gas Flow-Rate

Run No.	Temperature °C	Molar Ratio of Na ₂ SO ₄ to Sn	Weight of Sample (Na ₂ SO ₄ + Sn)	Weight of Product	Change in Weight	% Soluble Material	% Conversion to Thiostannate	Water-Soluble Phases Detected	Remarks
1	670	2:1	13.3710	13.6571	+0.2861	89	70.28	Phases A and B	Product is dark greyish green melted mass.
2	780	2:1	13.3694	13.3694	-0.9516	99	97.36	Phases B and C	Product is light greenish yellow melted mass.
3	800	2:1	13.3712	12.5275	-0.8437	99	99.52	Phases B and C	Product is light greenish yellow melted mass.
4	760	1:1	8.6485	8.5457	-0.1028	93	88.00	Phases A and B, and traces of phase C	Product is a dark green melted mass.

3. Changing the molar ratio of reactants at the optimum conditions showed that phase A was present with phases B and C at a molar ratio less than 1.6:1, at which it disappeared; the product was almost completely soluble. The loss in weight changed considerably from 1.1132 g. at a ratio of 1:1 to 2.3429 g. at a ratio of 1.6:1. The X-ray photographs of products showed that the proportion of phase C increased as the molar ratio increased (see Table 35).

When the 2:1 and 2.3:1 molar ratios were used, the products were completely soluble in water and the losses in weight were 2.3670 g. and 2.3648 g. respectively. It is noticeable that there was no appreciable change in the loss in weight when the molar ratio was increased from 1.6:1 to 2.3:1. Only phases B and C were detected. As the molar ratio was increased to 3:1 the percentage conversion dropped considerably, and the physical appearance of the product clearly showed that the reaction took place at the surface only. The part of the sample at the bottom of the boat, greyish in colour, did not have access to the sulphidizing gas.

The same product phases (A, B and C) were obtained under corresponding conditions when tin metal was used as starting material.

A preliminary selection of X-ray diffraction d-spacings characteristic of the three phases is given in Table 35. The data are subject to revision and extension on account of the difficulty in associating particular diffraction lines with specific phases in the diffraction photograph of a mixture. It should be noted that phase C was never obtained in a reasonably pure state.

The compositions of the thiostannate phases are difficult to assess accurately. With a 1:1 molar ratio the data indicates that phase A is the meta-thiostannate, Na_2SnS_3 . This phase also predominates below 700°C . with a 2:1 ratio, and the losses in weight are satisfactorily in support of the view advanced above. As the temperature increased, the loss in weight increased; this corresponds with an increase in the amount of sodium sulphate reduced to sulphide. Phases B and C then predominate and phase A gradually disappears. These two phases therefore contain a higher relative proportion of sodium sulphide than the meta-thiosalt. The fact that phase C could not be obtained in even reasonable

Table 35

Characteristic d -spacings of the Three Water-Soluble
Sodium Thiostannates.

Phase A 1:1 Molar Ratio, and 700°C. Sulphidizer		Phase B 1:1 Molar Ratio and 780°C Sulphidizer		Phase C 1:1 Molar Ratio and 780°C. Sulphidizer		Phase C 2:1 Molar Ratio and 780°C. Sulphidizer	
d	I	d	I	d	I	d	I
6.65	70	6.84	100	11.71	2	11.71	60
5.75	10	5.97	90	7.90	10	7.90	90
3.770	5	5.28	2	7.50	2	7.50	80
3.275	40	4.23	80	5.41	2	5.41	70
3.155	30	3.604	90	4.05	5	4.05	75
2.764	100	3.541	70	3.323	5	3.323	40
2.550	5	3.395	10	2.903	20	2.903	60
2.159	30	3.273	60	2.803	10	2.803	40
1.992	50	3.181	80	2.675	40	2.675	50
1.916	70	2.990	60	2.625	20	2.625	50
1.842	30	2.942	55	2.557	20	2.557	60
1.658	20	2.840	30				
1.577	30	2.714	90	(limit 2.40)		(limit 2.40)	
1.379	10	2.406	80				
1.254	30	(limit 2.40)					
1.216	30						

purity, and the difficulty encountered in associating phases B and C with any simple composition relationship make it inadvisable to predict exact chemical composition for these two phases. Phase C may well be the alleged ortho-thiosalt, Na_4SnS_4 .

The Na-Sn-S system has not been reported on in detail in the literature. The $\text{Na}_2\text{S-SnS}_2\text{-H}_2\text{O}$ system was investigated by Sevryukov (1960), and the hydrated meta-thiosalt, $\text{Na}_2\text{SnS}_3 \cdot 8\text{H}_2\text{O}$, and ortho-thiosalt, $\text{Na}_4\text{SnS}_4 \cdot 15\text{H}_2\text{O}$ were allegedly prepared. By studying the thermal stability of these salts, Sevryukov concluded that the ortho-salt is the only stable species at high temperatures (e.g., 850°C .), and that this is the phase likely to form in a mixture of a cassiterite concentrate, sodium sulphate, carbon, and sulphur at such temperatures. This identification of the high-temperature-stable compound with the simple composition Na_4SnS_4 may well be subject to review on the basis of more direct evidence.

4.5. Treatment of a Cassiterite Concentrate (35.70% SnO_2)

In order to test the reactions described above in their possible application to tin, a cassiterite concentrate assaying 35.70% SnO_2 , with quartz as the major gangue mineral, was treated. The concentrate was ground to pass 85 mesh. A 10.00 g. sample was used in all runs, and mixed with 10.00 g. (1:1 by weight) of anhydrous sodium sulphate. The effect of reaction temperature and the reaction period were investigated with the reducer at 900°C ., and using a high gas flow-rate. The apparent percentage extraction was determined by leaching one to two grams of the product with water; the leach solution was acidified, and the precipitated stannic sulphide was filtered off, left to dry, and then ignited in a silica crucible to convert it into the oxide, which was weighed. The results obtained are given in Table 36. These results show that the optimum reaction time is six hours, and the optimum temperature is $670 - 780^\circ\text{C}$. These conclusions are in good agreement with the results obtained when using tin oxide, with the difference that cassiterite is less reactive, and requires a higher reaction time for complete attack. It seems that the use of the lower temperatures in the range given would be preferable because of the melting problem and slagging of the charge at high temperatures.

The product obtained at 840°C. was a brownish-black melted mass, so hard that it was difficult to remove, even by breaking the boat. The product obtained by reaction at 670°C. was a porous cake, and no detectable melting took place. The percentage extraction can be increased by the use of some excess of sodium sulphate. A test was carried out using a 4:1 molar ratio of sodium sulphate to cassiterite; 10.00 g. of concentrate were mixed with 13.46 g. of sodium sulphate; and the sulphidization reaction was carried out at 670°C. for six hours, with high gas flow-rate. The percentage extraction was 99.63%. The product was dark greenish in colour, and no melting took place.

The effect of the reaction time was studied at 780°C. , with a 1:1 weight ratio and a high gas flow-rate. The results obtained are given in Table 37; they confirmed that cassiterite is less reactive than the oxide used in earlier work.

The effect of the reaction temperature on the percentage extraction was also studied in runs using a six-hour reaction period, a 1:1 weight ratio, and a high gas flow-rate. The results (Table 38) confirmed that it is better to avoid high reaction temperatures by working in the temperature range $630 - 680^{\circ}\text{C.}$ and to use a somewhat increased excess of sodium sulphate to achieve high extraction values. These results also confirmed those obtained when using the pure oxide.

X-Ray diffraction studies on products and leach residues have confirmed that the water-soluble phases formed are in agreement with the proposed reactions, and in good agreement with those observed using tin oxide. Examination of the stannic oxide product from extraction experiments showed that it is the pure oxide. Tests on the leach residues confirmed that stannous sulphide and stannic oxide were present in products obtained at 800°C. and 840°C. , showing that high temperatures introduce difficulty, probably on account of instability of the thiosalts and slagging of the charge. At 780°C. and lower temperatures stannic oxide was the only detectable tin-containing phase in the residue after extraction of the soluble salts. The small percentage of iron present in the concentrate was converted into ferrous sulphide.

Table 36

Results of Treatment of the Cassiterite Concentrate (35.70% SnO₂), 1:1 by Weight Ratio,
Reducer at 900°C., High Gas Flow-Rate.

Run No.	Temperature °C	Time (hours)	Weight of Sample (Concentrate+Na ₂ SO ₄)	Weight of Product	Loss in Weight	% Apparent Extraction	Water-Soluble Phases Detected	Remarks
1	670	5	19.9800	16.9580	3.0220	78.20	Phases A and B	Product is dark greenish porous cake. No melting took place.
2	670	6	19.9884	16.5883	3.4001	93.42	Phases B and A	" " "
3	700	6	19.9990	16.6595	3.3390	77.00	Phases B and A	Product is greenish black melted mass.
4	780	4	19.9764	16.6565	3.3199	66.26	Phases B and C	" " "
5	780	5	19.9969	16.5207	3.4762	79.72	Phases B and C	" " "
6	780	6	19.9808	16.1752	3.7056	97.50	Phases B and C	Product is dark green melted mass.
7	800	6	19.9777	17.2337	2.7440	51.32	Phases B and C.	Product is dark black melted mass.
8	840	4	19.9860	16.6223	3.3637	31.89	Phases B and C.	Product is brownish black melted mass.

Table 37

Results of Treatment of the Cassiterite Concentrate
(35.70% SnO_2) at Different Time Intervals.

Sulphidizer at 780°C ; Reducer at 900°C .; Weight Ratio 1:1,
High Flow-Rate.

Time (hours)	% Apparent Extraction
1.0	15.00
2.0	32.47
4.0	66.26
5.0	79.72
6.0	97.50

Table 38

Results of Treatment of Cassiterite Concentrate
(35.70% SnO_2) at Various Temperatures.

Reducer at 900°C .; Weight Ratio 1:1; High
Flow-rate.

Temperature $^\circ\text{C}$	% Apparent Extraction
630	90.60
670	93.42
700	77.00
750	89.90
780	97.50
800	51.32

4.6. Treatment of a Tin Slag

A tin slag sample assaying 1.0% Sn was treated under a range of conditions of reaction temperature, reaction period, and weight ratios. The most important problems involved in this case are the following:

1. The slag contains tin values in the form of stannate and alloyed metal, which in the presence of much gangue may appear to be less reactive than cassiterite.
2. The slag contains a fairly high percentage of iron (about 25% FeO).
3. The slag also contains an economically useful percentage of niobium (2.8 - 3.0% Nb₂O₅).

The procedure used in the treatment of products was similar to that used for the cassiterite concentrate; one difference was that filtration was preceded by buffering with ammonium chloride to flocculate ferrous sulphide. The pH was then 9.0 - 9.5. The results of a series of tests, planned in the usual manner, are given in Tables 39 and 40. 15.00 g. of the slag sample contain 0.19 g. SnO₂ and a maximum of 0.45 g. of Nb₂O₅. By using these figures, and by estimating the proportions of recovered oxides from the X-ray diffraction patterns, the apparent percentage extraction of tin and niobium were estimated. The results are summarised in Table 40. The X-ray pattern obtained for recovered niobium oxide was in good agreement with the literature (Hann, 1951). Efficient extraction of tin from slags was seen to be possible by using a moderate quantity of sodium sulphate at low temperatures, e.g. 670°C. These results in general confirmed those obtained in the treatment of the cassiterite concentrate and the pure oxide. The co-extraction of valuable metals such as niobium, if present in the slag, is a potentially useful feature.

4.7. Behaviour of Iron Compounds

The experiments carried out on the cassiterite concentrate and the tin slag, and the X-ray data obtained, lead to the following conclusions:

1. Iron oxides and silicates undergo sulphidization to give ferrous sulphide.

Table 39

Results of Treatment of the Tin Slag. Reducer at 900°C.; using High Gas Flow-Rate

Run No.	Temperature °C	Weight Ratio	Time (Hrs)	Weight of Sample (Na ₂ SO ₄ +slag)	Weight of Product	Loss in Weight	Weight of oxides recovered per 15.00g. slag	Remarks
1	670	1:2	4	22.4785	20.4165	2.0620	0.1807	Product is greenish black melted mass.
2	670	1:2	6	22.4804	21.0531	1.4273	0.3158	" " " " "
3	670	1:1	4	19.9737	17.4144	2.5593	0.3710	Product is brownish melted mass.
4	670	1:1	6	19.9800	17.3166	2.6634	0.5014	Product is greenish brown melted mass.
5	700	1:1	6	19.9870	17.1613	2.8257	0.5856	" " " " "
6	740	1:1	6	19.9936	17.3521	2.6415	0.5726	" " " " "
7	780	1:3	4	19.9875	18.8994	1.0881	0.1890	Product is black melted mass.
8	780	1:2	4	22.4742	20.4551	2.0191	0.5134	Product is greenish black melted mass.
9	780	1:2	5	22.4816	20.7796	1.7820	0.2262	Product is dark greenish melted mass.
10	780	1:2	6	22.4844	20.9324	1.5520	0.2184	" " " " "
11	780	1:1	4	19.9762	17.3478	2.6284	0.4584	" " " " "
12	780	1:1	6	19.9790	17.3820	2.5970	0.4954	Product is light brownish melted mass.

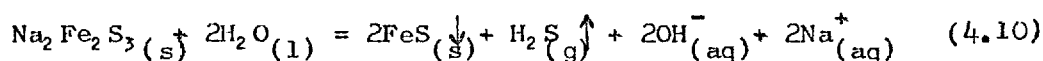
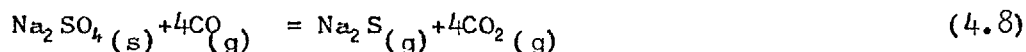
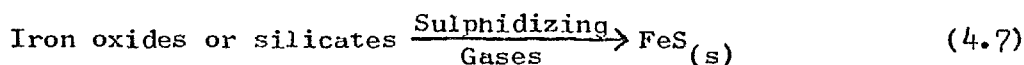
Table 40

Apparent Percentage Extraction of Tin and Niobium from the
Slag Sample (Reducer at 900°C.; High Gas Flow-Rate).

Run Number	Weight of Recovered Oxides (g)	Main constituents of Oxides	% Apparent Extraction of Tin	% Apparent Extraction of Niobium
1	0.1807	tin oxide	95	-
2	0.3158	very rich in tin oxide	100	28
3	0.3710	rich in tin oxide	100	40
4	0.5014	rich in both tin oxide and niobium oxide	100	69
5	0.5856	rich in both tin oxide and niobium oxide	100	88
6	0.5726	very rich in niobium oxide	65	100
7	0.1890	tin oxide	99	-
8	0.5134	very rich in niobium oxide	33	100
9	0.2262	mainly tin oxide	100	8
10	0.2184	mainly tin oxide	100	6
11	0.4584	rich in niobium oxide	65	75
12	0.4954	rich in both tin oxide and niobium oxide	100	68

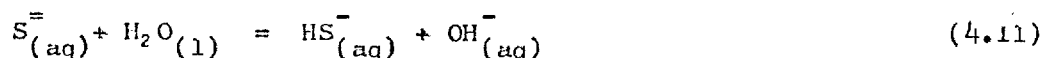
2. Iron sulphide reacts with sodium sulphide to form double sulphide complexes. Stromeyer (1858) reported the formation of an iron double sulphide with the formula $\text{Na}_2\text{Fe}_2\text{S}_3$.
3. The iron double sulphides rapidly decompose in moist air, and an odour of hydrogen sulphide rapidly develops from the action of moisture on such products. The slag products turned black during grinding in the mortar, and a very strong smell of hydrogen sulphide was observed. The products crumbled to powder in a short time in the specimen tubes. The formation of the double sulphides of iron is probably the main reason behind using a moderate excess of sodium sulphate (ratio of 1:1 by weight) to achieve high extraction in the treatment of the slag.
4. When a small quantity of one of the slag products was put in a beaker and a few drops of water added, vigorous reaction took place with the evolution of hydrogen sulphide and the formation of ferrous sulphide. When the slag products were leached a dark greenish-black solution resulted which was very difficult to filter. This filter contained colloidal ferrous sulphide which settled on standing or on centrifuging. When this colloidal ferrous sulphide was precipitated, an increase in the pH of the solution was observed. Therefore, in the treatment of slag products, the leached solution was buffered with ammonium chloride to a pH of about 9.0 - 9.5, at which ferrous sulphide flocculated, and a clear leach solution, greenish in colour, was obtained. Even this clear solution apparently contains some dissolved iron complex.

These observations might be explained as follows:



These reactions show that the ferrous sulphide will cause more trouble in the presence of excess sodium sulphide, which makes the resultant leach solution highly alkaline owing to the hydrolysis of

the sulphide ion (equations (4.11) and (4.12)):



The major problems involved in treating tin-bearing materials with a high content of iron are hydrogen sulphide poisoning in the plant, filtration, and the possible contamination of the leach solution with some iron. Vonstein (1971) reported in parallel cases that iron and other base metal sulphides, (e.g. of lead, copper, and zinc) remained in the water-insoluble residue after leaching of the product with water.

4.8. Conclusions

The following general conclusions may be drawn from the work described in this chapter.

1. Three water-soluble thiostannate phases exist in the Na-Sn-S system. The meta-thiosalt, Na_2SnS_3 , is greyish-black in colour, and melts above $600^{\circ}C$.; under the conditions prevailing in the present series of experiments it undergoes decomposition above $700^{\circ}C$. to give the ortho-thiosalt, probably Na_4SnS_4 . Complete conversion of stannic oxide to thiostannate cannot be achieved with a 1:1 molar ratio of sodium sulphate to stannic oxide, even at high temperature.

The ortho-thiosalt, provisionally formulated as Na_4SnS_4 , is greenish-yellow in colour, melts above $700^{\circ}C$., and is stable in the temperature range $600 - 800^{\circ}C$.; it appears to be converted into another phase (possibly another crystalline form of the same compound, or another compound of slightly different composition) above $700^{\circ}C$. Complete conversion of stannic oxide into thiostannate was achieved with a 2:1 molar ratio at $780^{\circ}C$.

2. The eutectic temperature of the sodium sulphate-sodium sulphide system appears to lie in the range $680 - 740^{\circ}C$., in good agreement with the literature. The effect of melting on the efficiency of conversion of the oxide to the thio-salt was observed when the 2:1 molar ratio was used.

3. High extractions from low-grade cassiterite concentrates can be achieved by using a moderate excess of sodium sulphate over the required stoichiometric value. In the treatment of tin slags with low tin content, an excess of sodium sulphate is necessary because of the high iron content. On the other hand, this excess is justified through the extraction of other values, such as niobium, in the slag. Optimum conditions for the treatment of tin slags would be a 1:1 weight ratio of sodium sulphate to slag and a six-hour reaction period at 700 - 740°C.

Chapter 5

The Reactions of Tin and its Compounds with Sulphur and Sodium Carbonate

The reactions of tin compounds with sulphur and sodium carbonate were reported many years ago. Mellow (1927) reported that A. Berg prepared sodium thioannate by melting a mixture of metallic tin with 6 or 8 times its weight of a mixture of equal parts of sodium carbonate and sulphur, at a dark red heat. H. Rose used stannic oxide in place of tin; and A. Hüring used stannous sulphide. It is quite clear that the intention of these experiments was to synthesize the thiosalts.

The American Cyanamid Company (1941) patented a process for the recovery of antimony and tin metals from refractory ores which are not amenable to ordinary metallurgical methods. This patent claimed the use of sodium carbonate and sulphur in an anhydrous reducing atmosphere using carbonaceous materials (coal) at high temperatures. Sufficient reducing agent (coal) is necessary to combine with the oxygen of the antimony or tin oxide in the ore. Data are given only for tests on an antimony ore assaying 10.27% antimony present as oxides. Three examples are reported:

Example No.1

The ore was crushed to -20 mesh and roasted for 30 minutes at 1400°F with 10% by weight each of sulphur and soda ash, and 2.5% by weight of coal. The roasted ore was quenched in water, and the solution boiled and filtered. The filtrate contained 76.3% of the antimony, which was removed in the usual manner by precipitation.

Example No.2

The ore was roasted as described, but the weight of sulphur and sodium carbonate used was increased to 15% of each. The recovery of antimony was 81.2%.

Example No.3

The ore was treated with an amount of sodium sulphide equivalent to 15% each of soda ash and sulphur. Recovery of antimony was substantially the same as in Example 2.

It seems that this work was carried out on an empirical basis without an adequate understanding or application of the chemical principles involved. No data were given for the treatment of a tin ore. In this connection it is important to remember that the chemistry of the Na-Sb-S system is far more complicated than that of the Na-Sn-S system. Sodium thiosalts and oxythiosalts which are sparingly soluble in water were

reported to exist in this system. Fridman et al. (1956) reported the formation of sodium oxythioantimonate, NaSbOS , from the reaction of antimony trisulphide, Sb_2S_3 , with sodium carbonate or sodium sulphate. Berul et al. (1971) reported that three phases exist in the Na-Sb-S system, namely: NaSbS_2 , which is dark grey in color and insoluble in water; $\text{Na}_6\text{Sb}_4\text{S}_9$, which is brown in color, unstable in air, and soluble in water; and Na_7SbS_3 , which is yellowish pink in color, unstable in air, and soluble in water. No X-ray diffraction data were reported.

In general, there is little information about the chemistry of the extraction of tin into aqueous media through the formation of thiosalts. The main reason for this no doubt lies in the complication of phase relationships in the systems used. The work reported in the previous chapter is, in fact, the first so far known to give a clear picture of the Na-Sn-S system at high temperatures (600 - 800°C).

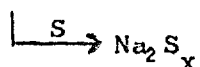
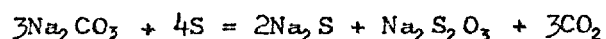
A detailed study of the reactions of tin or tin compounds with sodium carbonate and sulphur is not available in the literature. It was therefore decided to investigate this system to establish the participating chemical equilibria, and if possible to develop a process for extraction of tin from low-grade concentrates. The following questions are of importance in connection with this reaction system:

1. Is it necessary to use high temperatures to achieve complete reaction of the tin species with sodium carbonate and sulphur?
2. Is it necessary to use disproportionately large quantities of sodium carbonate and sulphur to achieve complete conversion of the tin species to the thiostannate?
3. Is it necessary to use equal quantities of sodium carbonate and sulphur, each not less than the weight of metal oxide in the ore (see American Cyanamid Co. Patent, 1941)? Does this have any scientific basis?
4. Is it necessary to conduct the reaction in a reducing atmosphere in order to render stannic oxide reactive?
5. What are the participating chemical reactions?
6. How do the gangue minerals in the ore (in particular, iron compounds) behave?

Some of the problems involved in the various processes reported in the literature are of interest in the planning of the project:

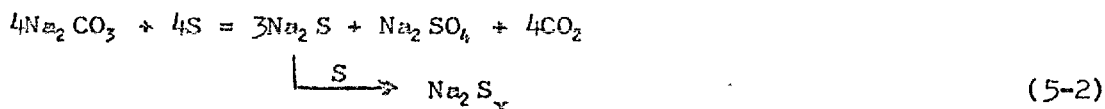
1. Troublesome reactions of the gangue minerals arise with sodium salts, in particular, sodium sulphide. In the common case of iron, the formation of alkali sulphide-iron sulphide complexes has a serious effect on the process, especially at high temperatures and in a reducing atmosphere, where iron is in the divalent state. The complexes $x\text{Na}_2\text{S}, y\text{FeS}$ and $x\text{Na}_2\text{S}, y\text{FeO}$ are known to form (see Chapter 4). By working at low temperatures, $400 - 500^\circ\text{C}$, using sodium carbonate and sulphur, iron should be convertible into FeS_2 , which is unlikely to cause difficulty even if it wastes some sulphur. Iron in silicates is expected not to react at all. At high temperatures, even silica and alumina are expected to react with sodium carbonate and sodium sulphide. Any application of the reaction possible at low temperatures will have clear advantages.
2. The possible formation of insoluble base-metal thiostannates (Fe_2SnS_4 , Cu_2SnS_3 , and $\text{Cu}_2\text{FeSnS}_4$) is another problem. Murach et al (1964) reported the existence of these compounds. Stannite, $\text{Cu}_2\text{FeSnS}_4$, was detected at 700°C , in the sulphidization of stannic oxide in the presence of chalcopyrite (see Chapter 2).
3. The instability of sodium meta-thiostannate, Na_2SnS_3 , at high temperatures, means that complete conversion of cassiterite can take place only through the formation of ortho-thiostannate, Na_4SnS_4 ; this requires a larger proportion of reagents. It is important to know that both thiostannates melt at high temperature (see Chapter 4).
4. Working at high temperatures and using sodium carbonate and sulphur complicates the chemistry of the process. Sodium stannate is a possible product in addition to the thiosalts. Loss of sulphur by volatilization is, of course, much increased.
5. A serious practical problem in industrial working at high temperatures and in a reducing atmosphere will be corrosion of plant.

Pearson et al. (1930), Macallum (1948), and Lenz et al. (1959) reported that the reaction of alkali carbonates with sulphur gives alkali sulphide as a primary product. The reaction commences slowly at 200°C . At 350°C , it proceeds with moderate speed as follows:

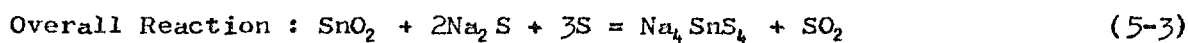
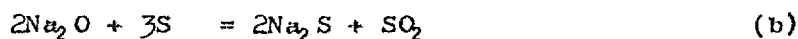
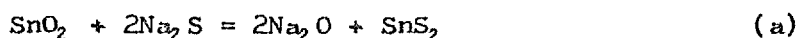


(5-1)

At 640°C, the reaction proceeds at high speed as follows:



On the other hand, the reactions of a tin compound with sodium carbonate and sulphur, at low temperatures (200 - 600°C) are not known. Sodium carbonate does not react with stannic oxide below 600°C, and sulphur alone does not convert this oxide into sulphide. St. Clair et al. (1954) reported that the reaction of sulphur with stannic oxide proceeds slowly at 750°C, providing enough excess sulphur is available; about 10 moles of sulphur per mole stannic oxide. It seems probable that a tin compound (e.g., stannic oxide) will react primarily with sodium sulphide to form a tin sulphide, which afterwards reacts with more sodium sulphide to give a thio-salt:



The formation of the meta-thiostannate, Na_2SnS_3 , is also possible in the case of the oxide; reaction (5-4) would then apply. However, on the basis of the work reported in Chapter 4 the predominant phase is expected to be the ortho-thiostannate, Na_4SnS_4 .



The proportion of each of the thiosalts in the product will also depend on the quantity of sodium sulphide available in the system, excess of sodium sulphide favouring formation of the ortho-salt, reaction (5-5):



It is to be noted that conversion of tin oxide into sodium thio-salts is, on the basis of the reactions proposed above, scarcely possible apart from the presence of sulphur (as well as sodium sulphide) in the reaction system.

In the presence of an adequate excess of sodium carbonate, sulphur dioxide formed as a co-product with sodium sulphide will, of course, be combined as an oxy-salt, which according to temperature and prevailing sulphur pressure could be sulphite, thiosulphate or sulphate. The

reactions are clearly very complex, but the participating steps considered above appear adequate to explain the general features of this reaction system.

5.1 Experimental:

The reactions of stannic oxide with sodium carbonate and sulphur were studied in a nitrogen atmosphere in the temperature range 200 - 650°C, to provide a complete picture, reactions with metallic tin and with stannous sulphide were also examined. The extraction of tin from some typical low-grade concentrates was investigated. Such an approach was expected to define the chemistry of the system and the technical feasibility of a related process for tin extraction.

5.1.1. Materials:

The following materials were used in the investigation:

1. Pure chemical-grade stannic oxide previously sintered at 800°C for several hours.
2. Pure tin metal powder.
3. Crystalline, grey-black stannous sulphide (97% SnS), obtained from the sulphidization of stannic oxide with sulphurous gases.
4. Pure antimony oxide (Sb_2O_3).
5. A tin concentrate containing 40.00% SnO_2 and a silicate matrix, obtained from Mount Wellington ore by gravity and flotation methods.
6. A low-grade tin ore sample obtained from Mount Wellington ore with pyrite, chalcopyrite and other sulphides removed by flotation, assaying 1.90% SnO_2 .
7. A series of artificial low-grade tin concentrates prepared by diluting the 40% SnO_2 concentrate with the tin ore (1.90% SnO_2).
8. A sulphide concentrate prepared by mixing SnS (97%), pyrite, and pure quartz (2.00 g SnS + 2.00 g FeS_2 + 16.00 g SiO_2).
9. Pure anhydrous sodium carbonate, and pure sulphur powder.

5.1.2. Procedure:

In the treatment of the pure tin and tin compounds in a nitrogen atmosphere the following procedure was used:

In the case of stannic oxide, the required stoichiometric proportions of the reactants were weighed out and mixed in an agate mortar; the mixture was then introduced into a small silica tube closed at one end; and the open end was plugged with asbestos wool. Such plugs are not completely gas-tight but nearly so. The silica tube with the reactants was introduced into a temperature-controlled furnace having a slow nitrogen stream passing through the working tube.

In the case of tin metal and stannous sulphide, a small porcelain boat was used instead of the small silica tube.

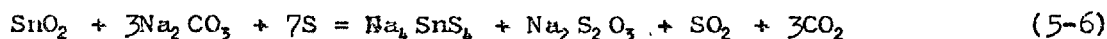
The product was examined by X-ray diffraction and the percentage material soluble in water was determined (see Chapter 4).

In the case of the treatment of low-grade tin concentrates, a covered beaker was used as a reaction vessel and heating was done in a muffle furnace at $430 \pm 10^\circ\text{C}$ for four hours. 20 g of concentrate were used, with the sodium carbonate and sulphur at a molar ratio 3:7. The product was then leached with hot water. After filtration, a 50 ml aliquot was taken and acidified with hydrochloric acid to precipitate stannic sulphide, which was filtered off, left to dry, and then ignited to convert it to the oxide, which was weighed. The apparent percentage extraction on the basis of the original ore analysis was calculated (see Chapter 4).

5.2 Results and Discussion:

5.2.1. Reactions of Stannic Oxide:

Reaction (5-6) was considered; it is an overall reaction of (5-1) and (5-3). Thus, one mole of stannic oxide needs three moles of sodium carbonate and seven atomic proportions of sulphur.



3.000 g SnO_2 with 6.3310 g Na_2CO_3 and 4.4680 g sulphur were used. The results obtained at various temperatures with four hours' reaction period are given in Table 41. At 350°C , the product was not completely soluble in water. This result was expected, because, according to the literature, the reaction between sodium carbonate and sulphur does not go to completion at 350°C , and some unreacted material remains (Pearson et al. 1930).

It is not easy to explain the loss in weight observed because of the complexity of the system at high temperatures. In all runs at above 450°C , sulphur was observed at the exit of the furnace tube. Such sulphur

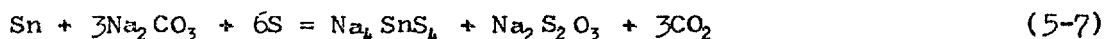
loss corresponds with the sudden change in the loss in weight. Also, above 450°C , the reaction of sodium carbonate and sulphur according to reaction (5-2) would take place. The products from all the runs are yellowish in color, dry, and easily powdered. X-Ray diffraction studies of these products showed two phases to be present. They are in agreement with those obtained from the sulphidization of stannic oxide and sodium sulphate. The ortho-thiosalt is the predominant phase, while the meta-thiosalt is only present in small proportion. The insoluble leach residue from the run at 350°C was examined by X-ray diffraction and was found to be a mixture of both stannic oxide and stannic sulphide in almost equal proportions. This result confirmed that reaction (5-3) is in fact an overall reaction in which initial formation of stannic sulphide is one step. As the temperature increases above 450°C , the proportion of the meta-thiosalt, Na_2SnS_3 , in the products decreases; at 600°C it is only present in trace amounts. As the temperature increases, reaction (5-2) evidently takes precedence, and the quantity of sodium sulphide available increases favouring the formation of the ortho-thiosalt, Na_4SnS_4 , by reaction (5-5). The decrease in the loss in weight as the temperature increases supports the above idea.

5.2.2. Reactions of Tin Metal and Stannous Sulphide:

Only one run was done with tin metal and one with stannous sulphide. The reactions were carried out at 450°C for four hours using the porcelain boat to contain the reactants.

Tin Metal

According to reaction (5-7), each mole of tin metal needs three moles of sodium carbonate and six atomic proportions of sulphur for complete conversion into the thiostannate:



1.000 g of tin therefore needs 2.6792 g of sodium carbonate and 1.6177 g of sulphur.

Experiment: Temperature: 450°C , time: 4 hours

1. Weight of boat alone	= 46.1303 g
2. Weight of boat + sample	= 51.4351 g
3. Weight of boat + product	= 50.0780 g
4. Weight of product	= 3.9477 g
5. Loss in weight	= 1.3571 g

Table 41

Results of Reactions of Stannic Oxide with Sodium Carbonate and Sulphur in a nitrogen atmosphere for four hours at various Temperatures

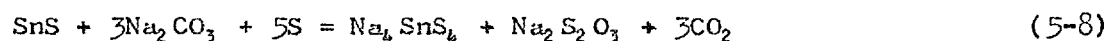
Run Number	Temperature °C	Weight of Reactants (SnO ₂ + Na ₂ CO ₃ + S)	Weight of Product	Loss in Weight	% Soluble Material in the Product
1	350	13.7945	10.6785	3.1160	91.91
2	400	13.7920	10.2750	3.5170	100
3	450	13.7923	10.1260	3.6663	100
4	500	13.7910	9.0301	4.7609	100
5	550	13.7908	9.2355	4.5553	100
6	600	13.7900	9.4010	4.3890	100
7	640	13.7908	9.5690	4.2218	100

The product was a yellowish-green dry powder; completely soluble in water, and giving a yellowish-green clear leach solution.

% Extraction = 100%.

Stannous Sulphide:

According to reaction (5-8), each mole of stannous sulphide needs three moles of sodium carbonate and five atomic proportions of sulphur:



2.0000 g of stannous sulphide needs 4.2208 g of sodium carbonate and 2.1237 g of sulphur.

Experiment: Temperature: 450°C ; time = 4 hours

1.	Weight of boat alone	= 46.1310 g
2.	Weight of boat + sample	= 54.4695 g
3.	Weight of boat + product	= 52.3090 g
4.	Weight of product	= 6.1780 g
5.	Loss in weight	= 2.1605 g.

The product was a yellowish-green dry cake which was easily powdered. It was completely soluble in water.

% Extraction = 100%.

The products from the oxide, metal, and sulphide dissolve in cold water in a very short time on stirring. This shows that the thio-stannates dissolve rapidly even in cold water.

X-Ray diffraction studies on the products from tin metal and stannous sulphide confirmed that they are exactly similar. Two phases are present, but the ortho-thiosalt, Na_4SnS_4 , is present in only small proportion and the meta-thiosalt, Na_2SnS_3 , is the predominant phase. When the reaction of stannous sulphide was tested at 350°C , the insoluble residue was found to be stannous, not stannic, sulphide.

Treatment of a Sulphide Concentrate

A sulphide concentrate containing 10% of SnS , 10% of FeS_2 , and 80% of SiO_2 was treated. 5.0000 g of this sample needs 1.0500 g of sodium carbonate and 0.5250 g of sulphur for complete conversion of the stannous sulphide in the sample into the thio-salt. Double the stoichiometric values were taken in order to give the pyrite the chance to react. 5.0009 g of sample, 2.1088 g of sodium carbonate and 1.0558 g of sulphur were therefore used.

Experiment: Temperature: 450°C ; time = 4 hours.

1. Weight of boat alone	= 46.1311 g
2. Weight of boat + sample	= 54.3007 g
3. Weight of boat + product	= 53.4010 g
4. Weight of product	= 7.2699 g
5. Loss in weight	= 0.8997 g.

The product was a light yellowish-green cake, dry and easily powdered. It leached very fast and gave a clear leach solution with very quick filtration.

% Apparent extraction = 100%.

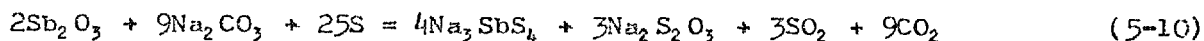
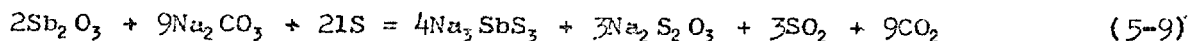
Iron sulphide evidently did not react at all. X-Ray diffraction of the leach residue confirmed the presence of pyrite and silica only. This experiment explained some of the difficulties encountered previously in working at high temperatures and in a reducing atmosphere.

Vonstein (1971) reported the following experiment.

1.0 kg concentrate with 12.6% SnS_2 , 0.43% CuS , 1.88% PbS , 24.26% FeS , and 3.5% by weight of sulphur; was mixed with 2.0 kg of sodium sulphate and 1.4 kg of coal. Heating was at 850°C , and the melt formed was poured off and cooled. The cooled material (2.2 kg) was extracted with water at $25 - 35^{\circ}\text{C}$ for one hour and then filtered. Analysis showed that 99.5% of the tin was in solution as sodium thioantimonate. Almost all copper, lead, and iron impurities were present in the residue as water-insoluble sulphides. It would be interesting to treat such a concentrate using sodium carbonate and sulphur at low temperatures, $400 - 450^{\circ}\text{C}$, in order to know how the base metal sulphides behave in relation with reagent consumption.

5.2.3. Reactions of Pure Antimony Oxide (Sb_2O_3):

The reactions of antimony oxide with sodium carbonate and sulphur are expected to be similar to those of tin compounds with one important difference, namely that antimony thiosalts or oxythiosalts which are insoluble in water are highly probable products. Some tests were carried out on the reactions of antimony oxide to clarify what has been reported in the literature (American Cyanamid Company, 1941). Antimony has two series of thiosalts known exemplified by the trivalent thiosalt, Na_3SbS_3 , and the pentavalent thiosalt, Na_3SbS_5 . Therefore, two reactions can be written as follows:



Similar reactions can be written introducing sodium sulphite or sulphate (instead of thiosulphate) as the sulphur oxy-salt co-product. Both reactions were tested using 3,0000 g of antimony trioxide and the calculated (stoichiometric) weights of sodium carbonate and sulphur; these were 4.9088 g of sodium carbonate with 3.4642 g of sulphur for reaction (5-9), and 4.9088 g of sodium carbonate with 4.1241 g of sulphur for reaction (5-10) respectively. The reactions were carried out at 450°C for four hours in small silica tubes, as in earlier experiments with tin oxide. The products from both experiments appear to be identical; they are dry, and easily powdered, with a light brownish- and grey-black color. The grey-black crystals could be seen distinctly with the naked eye in the light brownish cake. Losses in weight in the two experiments were 2.6340 g and 3.4120 g, respectively. These weight changes suggest that the surplus of sulphur used in the second reaction was volatilized out of the reaction zone, leaving a product similar to that of the first reaction. X-Ray diffraction showed that the two products were, in fact, identical. The photographs showed more than one phase to be present. Data are given in Table The products were leached with cold water as usual. A grey-black residue remained in both cases. The percentages of soluble material in the two products were 82.20% and 84.95%, respectively. The leach residue was examined by X-ray diffraction; lines of antimony sulphides or oxides or sodium oxy-salts or thio-salts of antimony for which X-ray data are available, could not be detected. The pattern appears to be from a single phase, which may well be the insoluble thiosalt, NaSbS_2 , or the insoluble oxy-thiosalt, NaSbOS , or a solid solution of the two. The residue reacted very quickly and vigorously with hydrochloric acid, some hydrogen sulphide being evolved. Semi-quantitative XRF analysis of the residue showed that it is an antimony compound and contains sulphur as a major element, and sodium as a minor element with about 5% Na maximum. (Analytical Services, R.S.M., Imperial College).

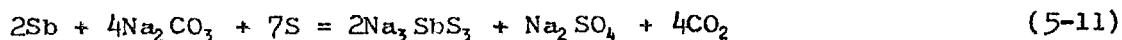
A third experiment was done using reaction (5-10) at 500°C with the same reactant weights, with closely similar results. The loss in weight was 3.4120 g and the percentage of soluble material in the product was 84.65 %. Thus, the increase of temperature did not have any appreciable effect.

A fourth experiment was carried out at 450°C using weights of sodium carbonate and sulphur about 29% in excess of those indicated by reaction (5-9), namely 3.0000 g of antimony trioxide, 6.3310 g of sodium carbonate, and 4.4687 g of sulphur. The product was a yellowish dry cake with some brownish shade, which was easily powdered. It was completely soluble in water and gave a clear light greenish-yellow solution. The loss in weight was 3.3353 g. The X-ray diffraction pattern obtained for this product is given in Table 42. Close examination of the X-ray data in Table , revealed that three water-soluble antimony thio-salts exist, which may be phase A ($\text{Na}_6\text{Sb}_4\text{S}_9$), phase B (Na_3SbS_3), and phase C (Na_3SbS_4). The partially water-soluble products contained phases A and B only, while the completely soluble product contained the three phases. Phase C appeared in the presence of excess sodium carbonate and sulphur in the completely soluble product. X-Ray diffraction d-spacings characteristic of these three phases are given in Table 43. It is worth noting that the completely soluble product showed a change in color on standing in air, it turned to light brownish-grey, which shows that the water-soluble antimony thio-salts decompose in air.

The antimony thio-salt reported by Robinson (1948), which has the formula $\text{Na}_2\text{Sb}_4\text{S}_7$ was not detected.

It is now of interest to re-examine procedures described in the American Patent (American Cyanamid Co., 1941). 100 g of ore assaying 10.27% of antimony present as oxide, means we have 10.27 g of antimony metal which is equivalent to 12.295 g of antimony trioxide.

1. Example No.1: 2.5% by weight of coal was used. This is more than enough to reduce all the antimony oxide to the metal. In addition 10% by weight of each of soda ash and sulphur were used, i.e. 10 g of soda ash and 10 g of sulphur, to extract 76.3% of the contained antimony into solution. The reaction:



requires 17.88 g of sodium carbonate and 9.45 g of sulphur to combine with the antimony present. The trivalent thiosalt is believed to have formed because the reaction was carried out in a reducing atmosphere and at high temperature. The amount of soda ash used was, in fact, less than the required amount for the reaction given, and the low recovery (76.3%) may be due to this deficiency. The statement in the patent that equal weights of soda ash and sulphur should be used has no scientific grounds at all.

Table 42

X-Ray Diffraction Data of the Products of Reactions of
Antimony Trioxide

Product from Sb_2O_3 using stoichiometric weights of Na_2CO_3 and S at 450°C				Water-Insoluble Leach Residue				Product from Sb_2O_3 using excess of Na_2CO_3 and S at 450°C (Completely soluble)			
<u>d</u>	<u>I</u>	<u>d</u>	<u>I</u>	<u>d</u>	<u>I</u>	<u>d</u>	<u>I</u>	<u>d</u>	<u>I</u>	<u>d</u>	<u>I</u>
8.525	50	1.996	50	5.268	90 _b	1.512	40	8.522	20	2.257	30
7.121	20	1.964	50	5.111	80	1.497	40	7.127	95	2.217	40
6.873	95	1.939	50	4.127	80	1.482	30	6.927	50	2.181	10
5.934	100	1.924	20	3.404	50	1.456	70	6.794	50	2.149	10
5.454	10	1.884	5	3.333	80	1.412	50	5.926	100	2.129	80
5.340	70	1.868	90	3.251	50	1.398	20	5.488	90	2.088	50
5.222	70	1.845	90	3.209	30	1.381	10	5.126	5	2.070	5
5.117	40	1.821	30	3.116	80	1.374	10	4.720	70	2.049	5
4.888	50	1.782	60	2.912	100 _b	1.343	50	4.651	5	2.023	50
4.745	5	1.763	30	2.855	95	1.334	30	4.500	70	2.000	5
4.495	10	1.742	40	2.560	30	1.320	30	4.274	20	1.982	50
4.220	95	1.707	60	2.534	50	1.312	40	4.205	20	1.959	80
4.127	50	1.690	60	2.510	30	1.301	50	4.146	40	1.942	20
3.986	80	1.667	20	2.328	40	1.287	70	4.053	70	1.928	40
3.926	20	1.643	40	2.190	20	1.276	30	3.934	30	1.911	10
3.878	20	1.627	80	2.159	40	1.254	70	3.862	50	1.886	80
3.794	70	1.607	10	2.129	50	1.234	50	3.778	30	1.858	40
3.739	20	1.583	20	2.100	30	1.219	20	3.734	30	1.845	40
3.597	80	1.558	20	2.085	10	1.201	40	3.651	90	1.833	40
3.523	5	1.531	40	2.059	95 _b	1.190	40	3.530	50	1.825	40
3.447	90	1.499	5	1.994	90	1.166	80	3.493	10	1.811	50
3.404	10	1.484	70	1.923	60			3.459	10	1.796	10
3.329	30	1.472	20	1.843	50			3.389	30	1.785	40
3.255	10	1.458	30	1.773	40			3.317	40	1.770	10
3.200	95	1.441	40	1.762	40			3.281	20	1.751	30
3.119	30	1.389	40	1.742	50			3.203	60	1.744	60
2.908	95	1.363	30	1.728	30			3.107	50	1.724	20
2.847	80	1.321	40	1.711	10			3.055	20	1.714	20
2.810	80	1.313	30	1.700	80			3.006	10	1.691	20

Table 43

X-Ray Diffraction d-Spacings Characteristic of the Water-Soluble Antimony Thio-salts

Phase A ($\text{Na}_6\text{Sb}_4\text{S}_9$)		Phase B (Na_3SbS_3)		Phase C (Na_3SbS_4)	
<u>d</u>	<u>I</u>	<u>d</u>	<u>I</u>	<u>d</u>	<u>I</u>
8.525	50	7.127	95	6.794	50
5.934	100	6.927	50	4.720	70
4.220	95	5.488	90	4.274	20
3.986	80	4.500	70	4.146	40
3.794	70	3.934	30	3.651	90
3.597	80	3.862	50	3.389	30
3.447	90	3.778	30	3.317	40
3.200	95	3.734	30	3.281	20
2.810	80	3.493	10	3.107	50
2.744	60	2.644	60	3.055	20
2.608	90	2.149	10	3.006	10
2.439	40	2.129	80	2.979	20
2.554	40			2.940	30
2.392	80			2.928	60
2.345	90	(Limit 2.00)		2.885	20
2.219	80			2.858	60
2.179	60			2.716	50
2.083	80			2.665	30
2.062	80			2.518	60
2.050	50			2.503	40
2.020	50			2.378	10
1.996	50			2.282	40
(Limit = 2.00)				2.257	30
				(Limit 2.00)	

2. Example No.2: 15% by weight was used of each of sulphur and soda ash, and 81.2% recovery was claimed. The amount of soda ash used in this example was, again, less than the required amount for the reaction given, and sulphur was used in large excess.

5.2.4. Treatment of the Tin Concentrate (40.00% SnO_2)

This concentrate, obtained from Mount Wellington ore, contains tin in the form of free cassiterite with a silicate matrix. The extraction of tin from this concentrate was carried out in a covered beaker, heated in a muffle furnace at $430 \pm 10^\circ\text{C}$ for four hours. Sodium carbonate and sulphur were used with a molar ratio of 3:7. By using 20 g samples from the concentrate, the effect of the Na:Sn atomic ratio on the apparent percentage extraction of tin was studied. Results obtained are given in Table 44. The percentage extraction increases as the Na:Sn atomic ratio increases.

X-Ray diffraction studies were done on products obtained with Na:Sn atomic ratios of: 1:1, 2:1, 3:1, 4:1, 6:1, and 7.2:1. The data obtained confirmed that the first new phase started to appear at a Na:Sn atomic ratio of 2:1. Nothing happened at the 1:1 ratio (sodium carbonate equal to 14.25% of sample weight); no extraction was observed. An experiment with 21.10% by weight of sodium carbonate gave 8.0% extraction. Thus, in general, we may say that 20% of the sample weight of sodium carbonate is lost. This problem will be discussed in more detail later. At a Na:Sn atomic ratio equal to 4:1, a second phase started to appear, and as the ratio increased the proportion of this phase increased. A high extraction value was achieved only by using about 20% by weight in excess of the stoichiometric value of sodium carbonate (7.2:1 ratio). The two phases detected are the meta-thiostannate, Na_2SnS_3 , and the ortho-thiostannate, Na_4SnS_4 , respectively. This result confirmed that the proposed reactions of stannic oxide with sodium carbonate and sulphur, reactions (5-1), (5-4) and (5-5) are taking place. The Na:Sn atomic ratio necessary to achieve high extraction value from this concentrate is in excellent agreement with that used in case of treatment of the concentrate with 35.70% SnO_2 with sodium sulphate and sulphurous gases (see Chapter 4).

5.2.5. Treatment of the Low-Grade Tin Ore (1.90% SnO₂)

This sample was obtained by crushing and grinding a sample from the original ore (Hand Specimen from M.P. Jones, Mineral Technology Department, R.S.M., Imperial College) to pass 72 mesh; pyrite, chalcopryrite and other metal sulphides were then floated by potassium ethyl xanthate and pine oil. Two experiments were carried out at $430 \pm 10^{\circ}\text{C}$. In the first experiment 32% by weight of sample of sodium carbonate was used and gave 22.84% extraction. In the second experiment 50% by weight of sodium carbonate was used, and gave 97.89% extraction. These results confirmed the previous observations on the concentrate, that sodium carbonate amounting to 20% by weight of the sample is lost and does not give any appreciable extraction. The main reason for this is probably oxidation of sodium sulphide and sulphur in the unsealed reaction system. X-Ray data did not show any change in the composition of the matrix. The leach residue was exactly similar to the treated sample.

5.2.6. Treatment of Low-Grade Tin Concentrates

Samples with varying tin content were prepared by diluting the tin concentrate (40% SnO₂) with the low-grade tin ore sample (1.90% SnO₂). Samples with 4.50, 6.30, 8.90, 10.30, 12.20, 14.10, 22.10, 26.10 and 32.20% of SnO₂ were prepared.

Treating these samples with 32% by weight of sodium carbonate gave the results in Table 45. The apparent percentage extraction increases as the percentage of SnO₂ increases in the sample up to 12.20% SnO₂; then it starts to decrease. Thus, it seems that the optimum reagent consumption would be in the treatment of samples with 7 - 15% SnO₂.

By using 50% by weight of sodium carbonate, results were obtained which are given in Table 46. Almost complete extraction of the tin was achieved with samples containing < 14% SnO₂; thereafter the percentage extraction started to drop. This suggests that high extractions can be obtained by using the optimum Na:Sn atomic ratio for every sample.

It is important to emphasize that the product obtained with samples containing less than 14% SnO₂ is a porous cake which can be dumped easily from the reaction vessel into the leaching vessel. It disintegrates and leaches very fast (in a few minutes) in hot water. Thus problems arising from melting and corrosion would not be serious. Pelletization of the reaction mixture, and use of a rotary calciner heated indirectly would give satisfactory results on the industrial scale.

Table 44. Results of Treatment of the Tin Concentrate (40% SnO_2)

Na/Sn Atomic Ratio	1.77	2.0	2.26	3.0	3.5	4.0	4.4	5.3	6.0	7.2
Apparent % Extraction	30	34	39	51	68	71	76	81	86	95

Table 45. Results of Treatment of the Tin Concentrates with different SnO_2 content, with 32% by weight sodium carbonate

% SnO_2 in sample	1.90	4.50	6.30	8.90	10.30	12.20	14.10	22.10	26.10	32.20
Apparent % Extraction	22.8	53.6	70.6	80.8	85.4	87.0	82.3	58.8	52.3	45.4

Table 46. Results of Treatment of the Tin Concentrates, with different SnO_2 content, with 50% by weight sodium carbonate

% SnO_2 in sample	1.90	4.50	6.30	8.90	10.3	12.2	14.10	22.10	26.10	32.20
Apparent % Extraction	97.9	100	99.6	99.6	99.7	99.7	95.0	80.6	76.7	68.0

5.2.7. Corrosion Studies:

These were brief studies carried out to test the suitability of stainless steel for plant designed to carry out the reactions described above.

A small piece of 316 stainless steel weighing 8.7500 g was used to test the effect of the reaction mixture on such material. The piece was put at the bottom of the beaker so that it would be covered by the reaction mixture. In several tests the surface became covered with a thin strongly adherent sulphide layer, grey-black in color. In experiments using 50% by weight of sodium carbonate or less, the attack was not serious; a loss of 18 mg was observed after 10 successive runs. This corresponds to loss of a metal surface layer about 10^{-4} cm in thickness. Much of this loss, no doubt, is due to the fact that the piece of steel was freshly cut. The corrosion problem became more serious when more aggressive conditions were used (100% of the sample weight of sodium carbonate). After 10 successive runs, the loss in weight was then 100 mg. In this case the charge had melted.

When the surface of the test piece was cleaned and polished, it was found that with 50% by weight reagent, the weight of the piece increased from 8.4060 g to 8.4124 g in one run. When the piece was then tested under more severe conditions (100% by weight reagent), no further change in weight was observed. Most probably, stainless steel with a high chromium content and sufficiently low in carbon would meet the requirements under the conditions needed for treating concentrates with a tin content less than 10%.

5.3 Some Economic Considerations:

The results obtained from the treatment of stannic oxide, tin metal, or tin sulphide in a nitrogen atmosphere proved the possibility of extraction of the tin metal values into aqueous media after roasting the tin-bearing material with optimum quantities of alkali carbonate and sulphur in the temperature range 400 - 450°C. High temperatures, or a reducing atmosphere in case of the treatment of stannic oxide, are not necessary when using this system. Increasing the temperature would no doubt increase the reaction rates, and a reducing atmosphere would make stannic oxide more reactive. The optimum molar ratio of alkali carbonate to sulphur is 3:7 in accordance with reaction (5-1) when

working at low temperatures; and probably a molar ratio of 4:7 according to reaction (5-2) when working at high temperatures.

In the treatment of cassiterite concentrates, it was found that an excess of sodium carbonate amounting to at least 20% by weight of sample should be used to achieve high extractions, when working in an oxidizing atmosphere. This excess of reagents is necessary because of the dilution factor, and the oxidation of sodium sulphide and sulphur. This needed excess would be less if the extraction was carried out in an inert atmosphere, and with the reaction mixture pelletized before introduction into the reaction vessel.

The metal values could be recovered from the leach solution by acid precipitation, reduction with sodium amalgam, or electrolysis. In the treatment of tin concentrates which contain antimony and arsenic compounds; it would be better to use sodium amalgam with which tin goes into the mercury phase; antimony and arsenic would remain suspended in solution, and are removable by filtration (Gladyshev et al., 1970).

The treatment of crude tin or hardhead from smelting with high contents of iron, copper, lead, zinc, antimony, arsenic, etc. would be very interesting to investigate, because tin should be separable in one step from the base metals, which would probably remain behind as insoluble sulphides for separate treatment. The tin metal could then be selectively recovered from the leach solution, with antimony and arsenic metals as by-products.

5.4 Conclusions

The important conclusions from work described in this chapter may be summarized as follows:

1. Tin and tin compounds (e.g. oxide or sulphide) have proved to be reactive at low temperatures in an inert atmosphere to form thio-salts, when present in an alkali carbonate-sulphur system.

The chemistry of an alkali hydroxide-sulphur system is known to be similar to that of a carbonate-sulphur system; therefore the alkali hydroxide-tin-sulphur system is expected to behave similarly, except that water formed in the reaction might hydrolyse the product thio-salt.

2. It is possible to achieve high extraction values of tin from cassiterite concentrates by using a relatively moderate excess of reagents over and above the stoichiometric values of sodium carbonate and sulphur, with a molar ratio 3:7, in the temperature range 400 - 450°C, without the use of a carbonaceous reducing agent.

3. The sodium carbonate-antimony-sulphur system has proved to be more complicated than the tin system owing to the formation of insoluble thio-salts or oxy-thiosalts. This system needs a thorough investigation.

If the tin-bearing material contains antimony and arsenic, it is expected that they will go into the leach solution. The selective separation of tin metal can be achieved, however, by reduction with sodium amalgam.

4. Base-metal compounds, e.g. compounds of iron, copper, lead and zinc, would be expected to form water-insoluble sulphides in the reaction and remain behind in the leach residue; their separation might then become possible, especially if they were present originally as oxides, silicates, or even metals.

5. The problem of formation of iron sulphide complexes with alkali sulphides can be solved by using the alkali carbonate-sulphur system. No pollution problem arises from hydrogen sulphide and no difficulty in filtration. Iron compounds appear to give pyrite, FeS_2 , which can be removed from the leach residue by flotation.

6. Treatment of a crude tin metal or a hardhead from smelting plants would have the advantage of separating all the base metals in one step, and in fact, aiding in their further separation and processing.

7. The procedures reported in the American Patent, 1941, have no scientific basis.

8. Since it is well-known that alkali carbonates react with sulphur to give alkali polysulphides at low temperatures (see reaction (5-1) and (5-2)), it would also be possible to use alkali polysulphides or alkali sulphides and sulphur, for the conversion of tin or antimony compounds into the thio-salts, and the subsequent extraction of the metal values into aqueous media from their ores or concentrates.

Chapter 6

General Discussion

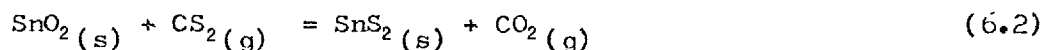
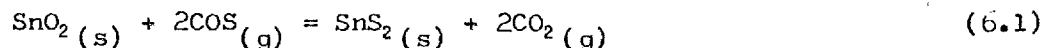
The project undertaken is mainly concerned with the study of the preparative chemistry and structural relationship of the tin sulphides, and of thioannates formed by a new reaction in which the necessary alkali-metal sulphide is formed "in situ" by reduction of the corresponding sulphate. The second part of the project deals with the chemistry of tin extraction from low-grade ores and concentrates by use of the sulphidization reactions previously described.

6.1. The Chemistry of Tin Sulphides:

6.1.1. Reactions of Stannic Oxide with Sulphurous Gases:

The new approach used in the preparation of tin sulphides introduces an effective sulphidizing gas obtained by the reduction of sulphur dioxide with carbon. This gas is composed principally of carbon disulphide vapour, carbonyl sulphide, sulphur vapour, carbon dioxide, and carbon monoxide, in proportions depending on the reduction temperature (see Chapter 1).

At relatively low reducer temperatures, e.g. 600 - 750°C., carbonyl sulphide predominates, and the gas has a relatively low reducing power; the reactions of interest are the following:



It is of interest to calculate K_p for the above reactions at 900°K (627°C) from the ΔG_R° values in Table 4, Chapter 1. The results obtained are:

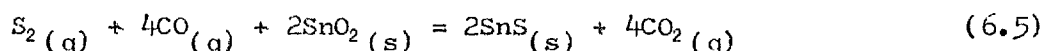
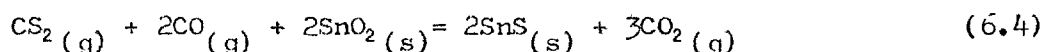
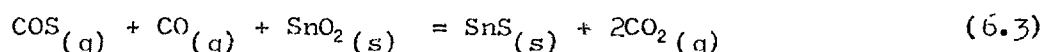
$$\text{Reaction (6.1): } K_p = \frac{P_{\text{CO}_2}^2}{P_{\text{COS}}^2} = 8.71 \times 10^{+4}, \text{ i.e. } \frac{P_{\text{CO}_2}}{P_{\text{COS}}} = 295$$

$$\text{Reaction (6.2): } K_p = \frac{P_{\text{CO}_2}}{P_{\text{CS}_2}} = 9.12 \times 10^{+5}$$

The complex nature of the inlet and outlet gas streams makes it difficult to calculate the precise equilibrium composition of the exhaust gas, but it is reasonable to infer from the very high values

of K_p shown above that at equilibrium very little carbonyl sulphide and carbon disulphide will remain unreacted. The reactions are therefore efficient in the utilisation of sulphur compounds from the gas supplied to the sulphidizer.

At relatively high reducer temperatures, e.g. 750 - 950°C., the distribution of sulphur in the gas changes considerably; the percentage of carbon disulphide increases and that of carbonyl sulphide decreases. The reducing power of the gas also increases considerably. Under such conditions, bivalent tin sulphide is formed at all reaction temperatures, and the reactions of interest are:



The equilibrium constants for these reactions were calculated at 900°K (627°C); the values obtained are as follows:

$$\text{Reaction (6.3): } K_p = \frac{P_{\text{CO}_2}^{+5}}{P_{\text{COS}} \cdot P_{\text{CO}}} = 1.0 \times 10$$

$$\text{Reaction (6.4): } K_p = \frac{P_{\text{CO}_2}^{+5}}{P_{\text{CS}_2} \cdot P_{\text{CO}}^2} = 3.2 \times 10$$

$$\text{Reaction (6.5): } K_p = \frac{P_{\text{CO}_2}^{+6}}{P_{\text{CO}}^4 \cdot P_{\text{S}_2}} = 2.6 \times 10$$

Although the expressions for K_p are now more complex, the values indicate that the partial pressures of the sulphurous gases at equilibrium in the exhaust gas are small and that utilisation of sulphur from the gas should again be satisfactory.

In the temperature range 400 - 750°C with the reducer at above 700°C., the changes in weight of the sample showed considerable variations. The percentage changes under various conditions are collected and tabulated in Table 47. The trend is that at any sulphidizer temperature the percentage gain in weight of the reacting material decreases as the

reducer temperature increases. At low reaction temperatures there is always a gain in weight, whereas at higher temperatures there is always a loss in weight. In general, as the reaction temperature increases, the loss in weight increases and it also tends to increase as the reducer temperature increases. Consequently the highest gain in weight is at the top left-hand corner of the table (sulphidizer at 400°C. and reducer at 750°C.), whereas the highest loss in weight is at the bottom right-hand corner (sulphidizer at 730°C. and reducer at 950°C.).

It may be visualised that two reaction mechanisms operate. At low reaction temperatures, sulphidization may take place through adsorption of the sulphurous gases on the tin oxide with the formation of a sulphide coating. It is likely that the stannous sulphide formed is non-stoichiometric, $\text{SnS}_{(1+x)}$, and this would account for the small observed variations of the gain in weight, the sulphur content of the non-stoichiometric sulphide falling as the reaction temperature increases.

At higher temperatures (above 600°C.), where extensive adsorption is not likely to take place, a different mechanism may be expected to operate. The percentage loss in weight is quite small and is of the order of magnitude expected from volatilization of stannous sulphide during the reaction; the partial pressure of stannous sulphide at 800°C. is 1.8 mm.Hg (Wright, 1966).

The objective of the experiments carried out at 500°C., 600°C., and 730°C., at various time intervals, was to establish the optimum reaction time for high conversions to the sulphide, a factor which is important in industrial operations. Incomplete sulphidization of stannic oxide by hydrogen sulphide at low temperatures (100 - 600°C.) leads to the formation of a mixture of tin sulphides (Balberyszski et al. 1968). Incomplete sulphidization was therefore tested with the reducer at 700°C (relatively low reducing power) and 900°C (relatively high reducer power). The results confirmed that incomplete sulphidization of stannic oxide at low temperatures and under relatively low reducing conditions gives a sulphide mixture. However, in the presence of a strong reducing atmosphere, stannous sulphide was the only sulphide detected at both low and high reaction temperatures (Figs. 4 and 5).

Table 47

The Percentage Changes in Weight of Tin Dioxide on conversion into SnS at Various Reducer and Sulphidizer Temperatures (low gas flow-rate and four-hour reaction period)

Reducer Temperature, °C		750	800	900	950
Sulphidizer Temperature °C		gain decreases →			
400	Gain decreases ↓	+ 2.16*	+ 2.06	+ 1.66	+ 1.31
450		+ 2.09	+ 2.04	+ 1.16	+ 0.70
500		+ 0.85	+ 0.70	+ 0.49	+ 0.25
600		- 0.21	- 0.24	- 0.01	- 0.17
700		- 0.40	- 0.45	- 0.19	- 0.52
730	Loss increases ↓	- 0.62	- 0.84	- 1.01	- 1.05 ⁺
		→ loss increases			

* Highest gain in weight

+ Highest loss in weight

(Theoretical % change for stoichiometric conversion into SnS is + 0.04%)

The optimum reaction time under the reaction conditions used seems to be four hours; it should be borne in mind that cassiterite is less reactive than the synthetic oxide. The reaction time is also important in sulphidization of stannic oxide in the presence of sodium sulphate to form thiostannates; in the four tests carried out, the sulphidization was quite slow in the first hour, but its rate increased considerably in the second hour.

The effect of increasing the gas flow-rate, with the reducer at 900°C . and the sulphidizer at 500°C . and a four-hour reaction interval was appreciable; on doubling of the flow-rate the percentage conversion increased from 75% to 91%.

6.1.2. The Tin-Sulphur System:

When the tin-sulphur system was studied more closely and narrow temperature changes were made with the reducer at 700°C . and a high gas flow-rate, the X-ray photographs revealed that three different solid products may occur, namely SnS_2 , Sn_2S_3 , and SnS . The changes in weight in the reactions, which agree well with theoretical values for the products indicated, are shown in Figures 6 and 7 for sulphidization temperatures of $400 - 600^{\circ}\text{C}$. and $600 - 720^{\circ}\text{C}$., respectively. As the temperature was increased towards 660°C ., the product contained an increasing proportion of Sn_2S_3 in addition to stannic sulphide. The X-ray diffraction pattern observed for Sn_2S_3 agrees well with that reported by Mosberg et al. (1961). A similar pattern reported by Bok et al. (1957) was interpreted by them to belong to a phase formulated as Sn_3S_4 , but no evidence of this phase has been obtained in the present work. At 680°C . lines of stannous sulphide started to appear, with several weak lines which could not be assigned to any known sulphide; these may prove to be superlattice lines due to a non-stoichiometric SnS . As the temperature was further increased the proportion of Sn_2S_3 decreased and that of SnS increased, and at 720°C . crystalline SnS alone was obtained. The percentage change in weight in each case agrees well with the estimated proportions of the phases in the products. It is quite possible that the Sn_2S_3 phase exists over an appreciable range of composition, and that the Sn_3S_4 phase reported by Bok et al. is in fact a superlattice structure formed in tin-rich Sn_2S_3 under other conditions.

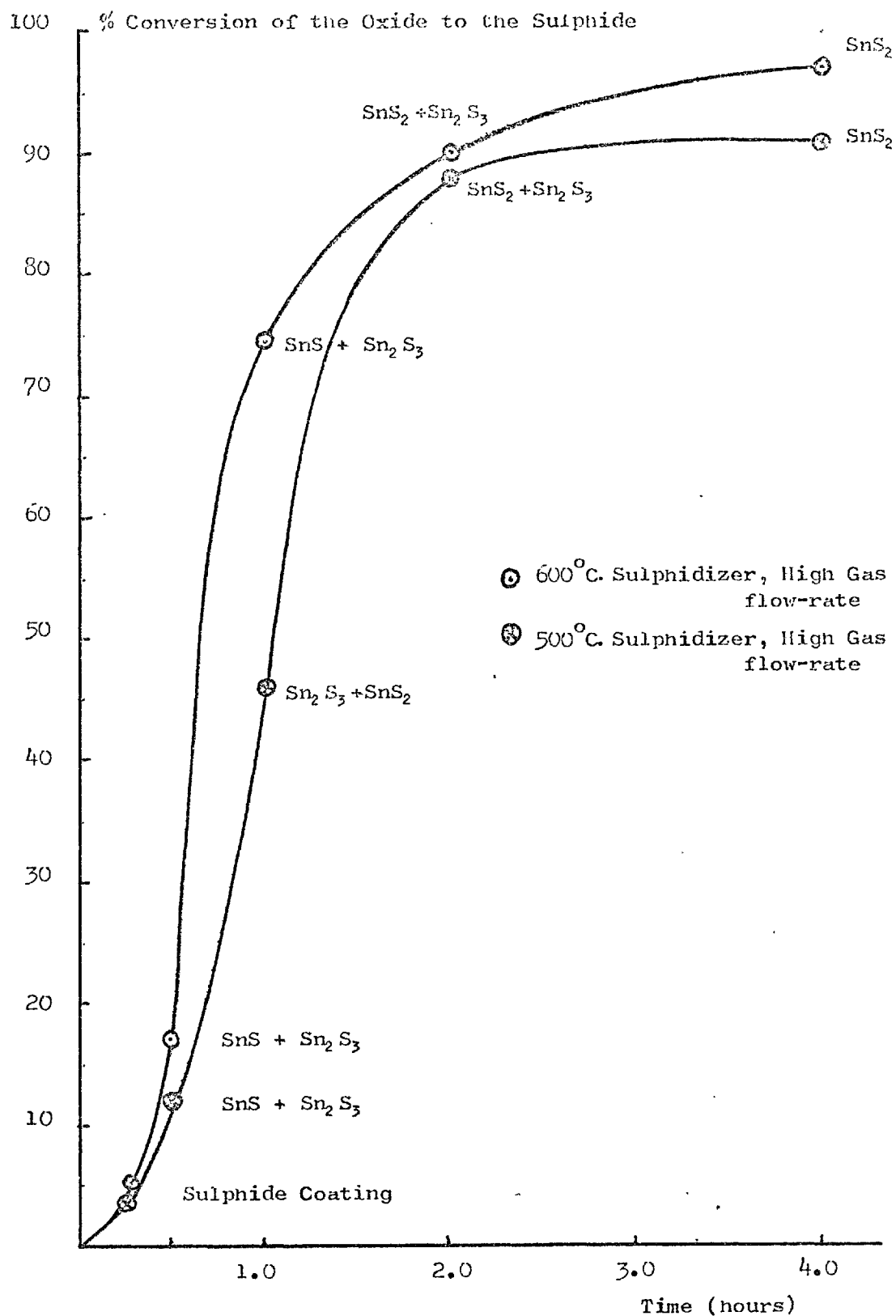


Figure 4: % Conversion of the Oxide to the Sulphide at Various Time Intervals (Reducer at 700°C.)

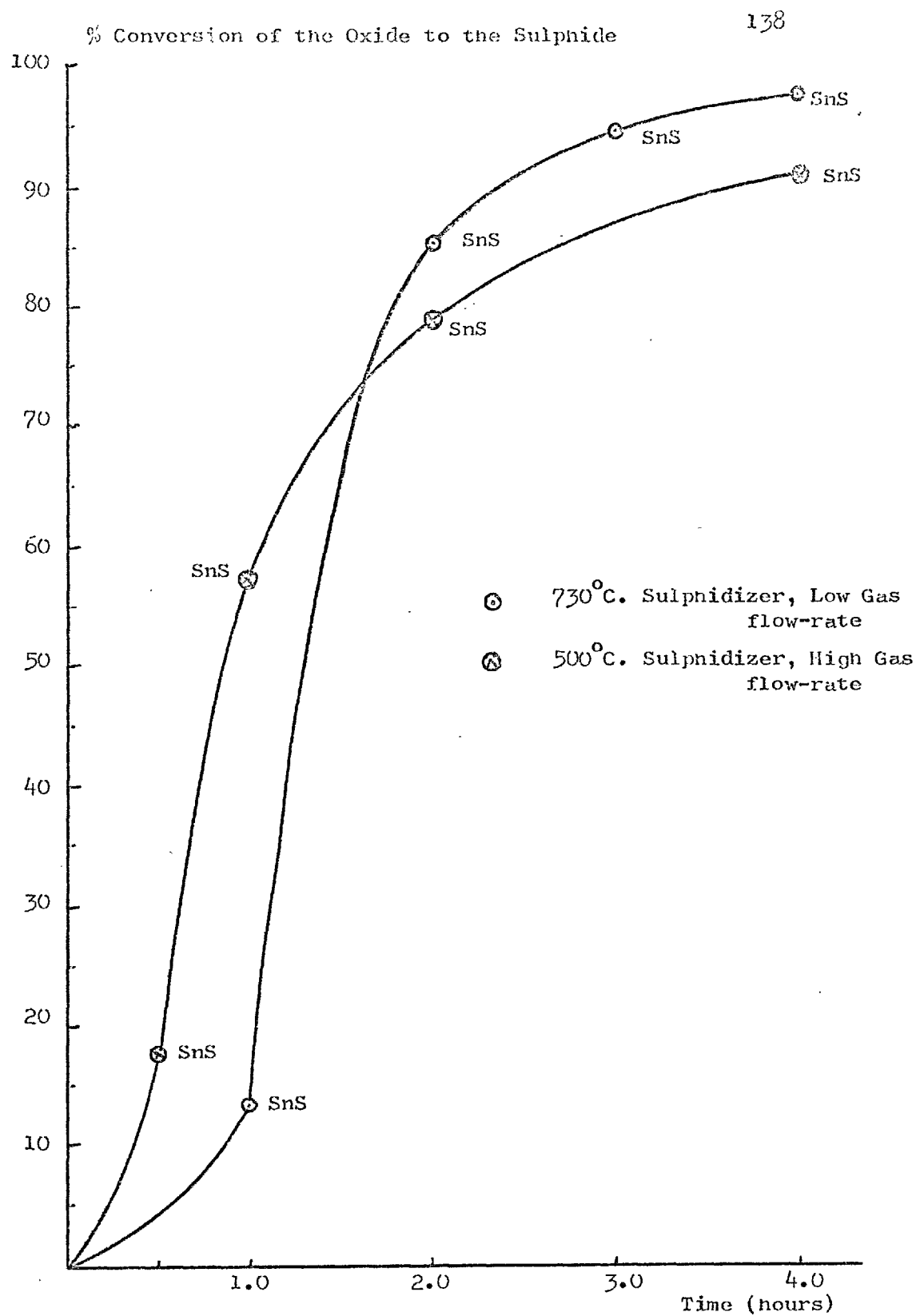


Figure 5: % Conversion of the Oxide to the Sulphide at Various Time Intervals (Reducer at 900°C)

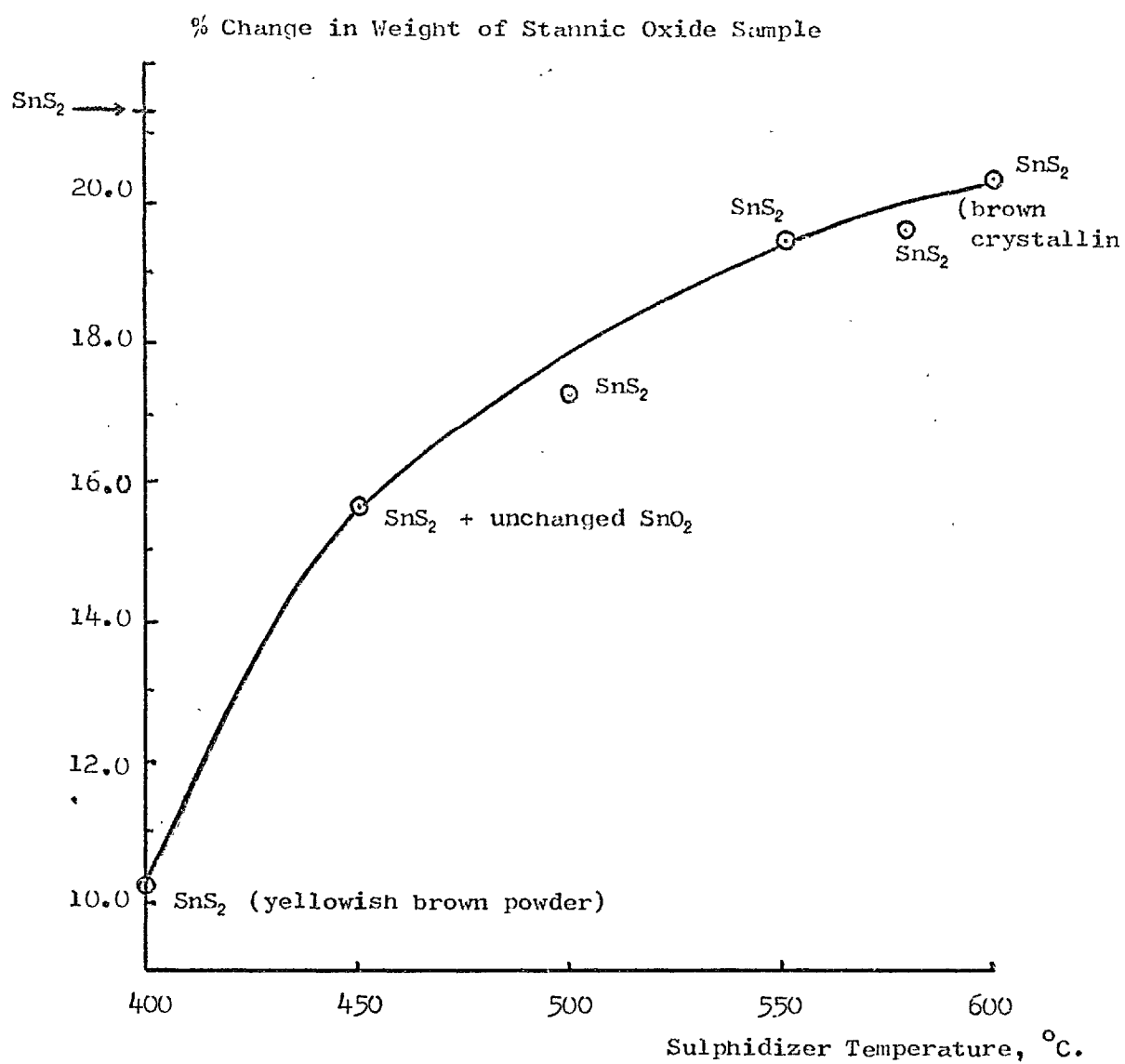


Figure 6: % Change in Weight of the Stannic Oxide Sample vs Sulphidizer Temperature in the Temperature Range 400 - 600°C.
(Reducer at 700°C.)

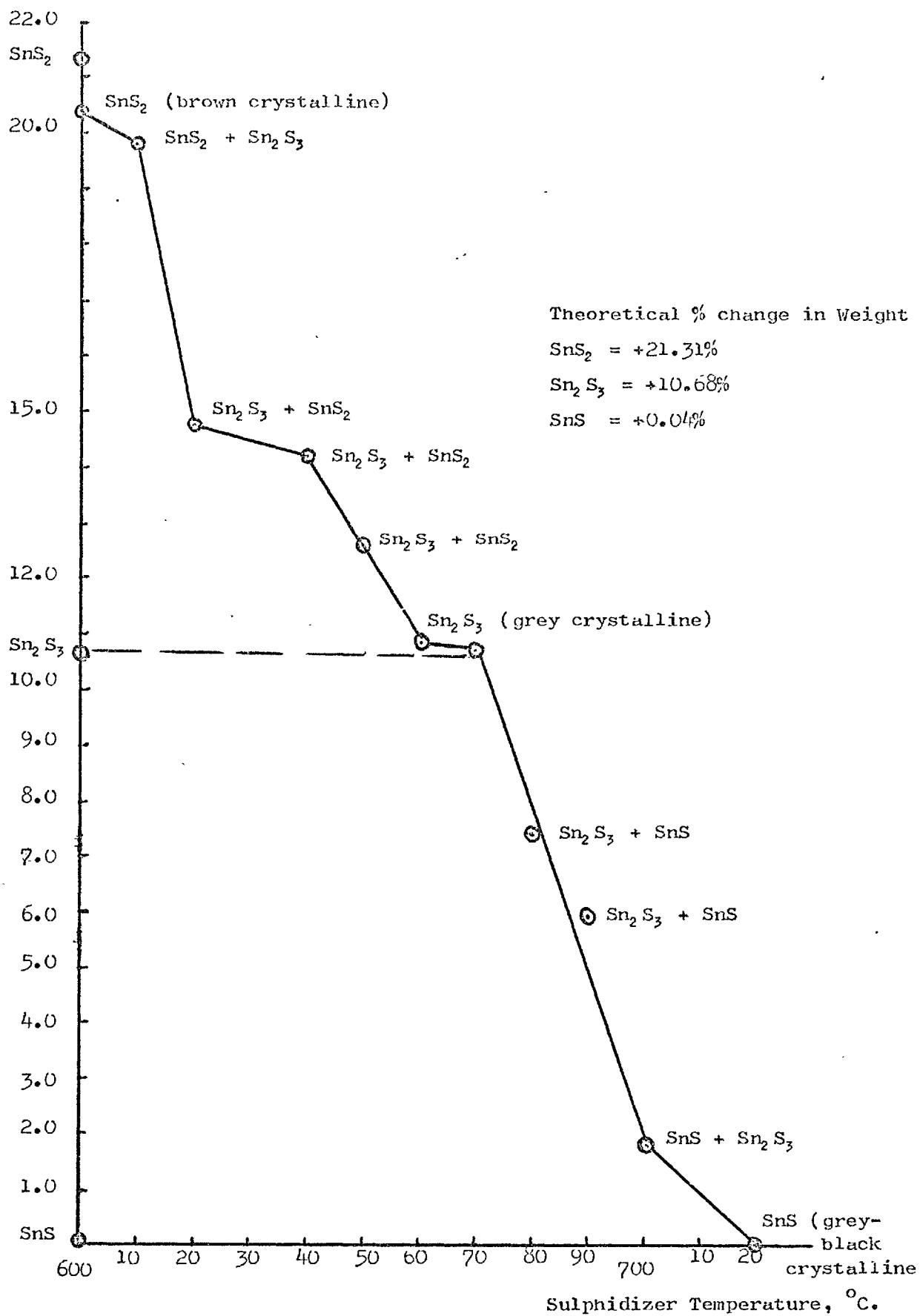


Figure 7: % Change in Weight of the Stannic Oxide sample vs. Sulphidizer Temperature in the Range 600 - 720°C. (Reducer at 700°C)

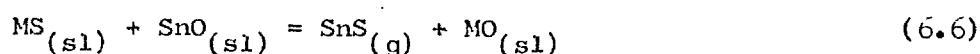
The existence of a non-stoichiometric composition range in Sn_2S_3 may explain some of the changes in weight in the temperature range $600 - 720^\circ\text{C}$.

Figure 7 shows the relation between the percentage change in weight and the reaction temperature in the range $600 - 720^\circ\text{C}$. It would be interesting to study selected compositions in the tin-sulphur system by single-crystal X-ray diffraction techniques in order to establish the nature of any superlattices that develop.

6.1.3. Volatilization of Stannous Sulphide:

Sulphidization of stannic oxide at high temperatures (above 900°C .) is likely to result in the volatilization of some, at least, of the sulphide formed. At such temperatures the vapour pressures of stannous oxide and stannous sulphide are quite high. The experiment carried out with the sulphidizer at 930°C . and the reducer at 900°C . (highly reducing atmosphere) confirmed the volatilisation of gaseous stannous sulphide, which condensed at the cool end of the reactor tube. Volatilisation of stannic sulphide was never observed; this is in good agreement with the proposed scheme of reactions.

In the "fuming process" employed industrially, in which the tin values are recovered by volatilization as sulphide, very high temperatures, e.g. $1200 - 1400^\circ\text{C}$. are needed. Solid sulphur carriers, e.g. pyrite (FeS_2) or zinc or calcium sulphide are used. The fundamental reaction involved can be formulated as follows (Wright, 1966):

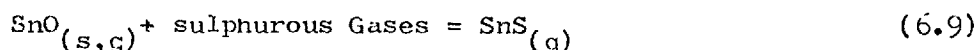
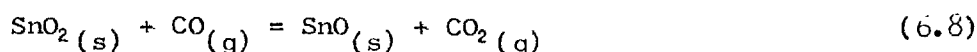


or, in the ionic form:



(the subscript (sl) means silicate solution).

Melting of the tin-bearing material, e.g. tin slag, is considered necessary. The use of sulphurous gases and of working temperatures which avoid melting of the charge is undoubtedly superior. The reactions of interest would be:



A continuous flow of a fresh sulphidizing gas is superior to the use of solid sulphidizing agents in allowing high reaction rates. The possibility that rich roaster gases could be used as a sulphur source in such operations gives the system industrial importance.

6.1.4. Sulphidization of Tin Oxide in presence of Copper and Iron Sulphides:

Tin ores usually contain an appreciable percentage of iron and copper sulphides, e.g. pyrrholite (FeS), pyrite (FeS_2), and chalcopyrite (CuFeS_2) (see Appendix). It is important, therefore, to establish whether the presence of these sulphides has any adverse effect in sulphidization of the tin content of the ore. Sulphidization of stannic oxide in the presence of pyrite and chalcopyrite was therefore tested. When pyrite was used, no reaction was observed between the tin sulphide formed and iron sulphides. The product was a mixture of stannous sulphide and ferrous sulphide. But when chalcopyrite was used the sulphidization of tin oxide was to some extent inhibited. The product consisted of three phases: γ -chalcopyrite, unreacted stannic oxide and stannite, $\text{Cu}_2\text{FeSnS}_4$. The formation of stannite in such cases must be borne in mind in any attempt to sulphidize tin ores containing appreciable quantities of copper.

6.2. The Chemistry of Sodium Thiostannates

The synthesis of sodium thiostannates was attempted in reactions of stannic oxide and sodium sulphate at moderate temperatures, $600 - 800^\circ\text{C}$. with the sulphurous gases previously mentioned. Three distinct water-soluble phases were detected. Lack of knowledge of the structures or X-ray diffraction patterns of possible thiostannates, including the alleged compounds Na_2SnS_3 and Na_4SnS_4 , made it impossible to establish accurately the chemical composition of these phases. The difficulties were increased by the fact that single-phase products could not be obtained, evidently because of complex phase relationships below the liquidus. Evidence obtained from reactant ratios and weight changes in the various experiments, confirmed by the X-ray powder photographs, indicates that the "meta"-thiosalt, Na_2SnS_3 , is the preferred product at low temperatures and with appropriate reactant molar ratios. As the temperature or the proportion of alkali-metal salt increases,

thiosalts with higher sodium sulphide content are favoured. Appropriate chemical tests confirmed in all cases the absence of bivalent tin.

One of the thiostannate phases may be the alleged "ortho"-thio salt, Na_4SnS_4 ; the other unidentified phase appears to be another thiostannate with a lower sodium sulphide content, in the range 30 - 46^o mol.-% Na_2S .

The results obtained with pure tin oxide and with the cassiterite concentrate are in good agreement with each other. The eutectic temperature of the sodium sulphate-sulphide system appears to be $710 \pm 20^\circ\text{C}$., which is in excellent agreement with the literature (see Figures 8 and 9). Complete conversion of stannic oxide into thiostannates took place in four hours, whereas in case of cassiterite six hours were needed (Figure 10). This confirmed that cassiterite is less reactive than the synthetic oxide. The considerable drop in the percentage apparent extraction at 800°C . (Figure 9) is interesting; probably the main reason for it is slagging of the charge, because thiostannate formation was satisfactory at this temperature when tin oxide was treated (Figure 8).

The techniques used in this investigation can be used to pursue the study of the Na-Sn-S system. The following points deserve attention:

1. It would be advisable to study the reactions of stannic sulphide with anhydrous sodium sulphide.
2. Separate experiments by other methods should be undertaken to characterise the individual sodium thiostannates and provide basic X-ray diffraction data. Rigid exclusion of moisture from the reacting systems would be very important.
3. The possible existence of oxy-thiostannates (e.g. $\text{Na}_2\text{SnO}_2\text{S}$, Na_2SnOS_2) needs investigation.

6.3. Melt Reactions

The reaction systems reported in the literature and concerned with aqueous leaching of tin from low-grade sources are based on mixing the tin-bearing material with an alkali salt, excess carbon, and sulphur, and heating the charge at high temperatures, ($800 - 950^\circ\text{C}$.). In all these systems, the formation of thiostannates was assumed. The most recent published work in this field is that of Vonstein (1971).

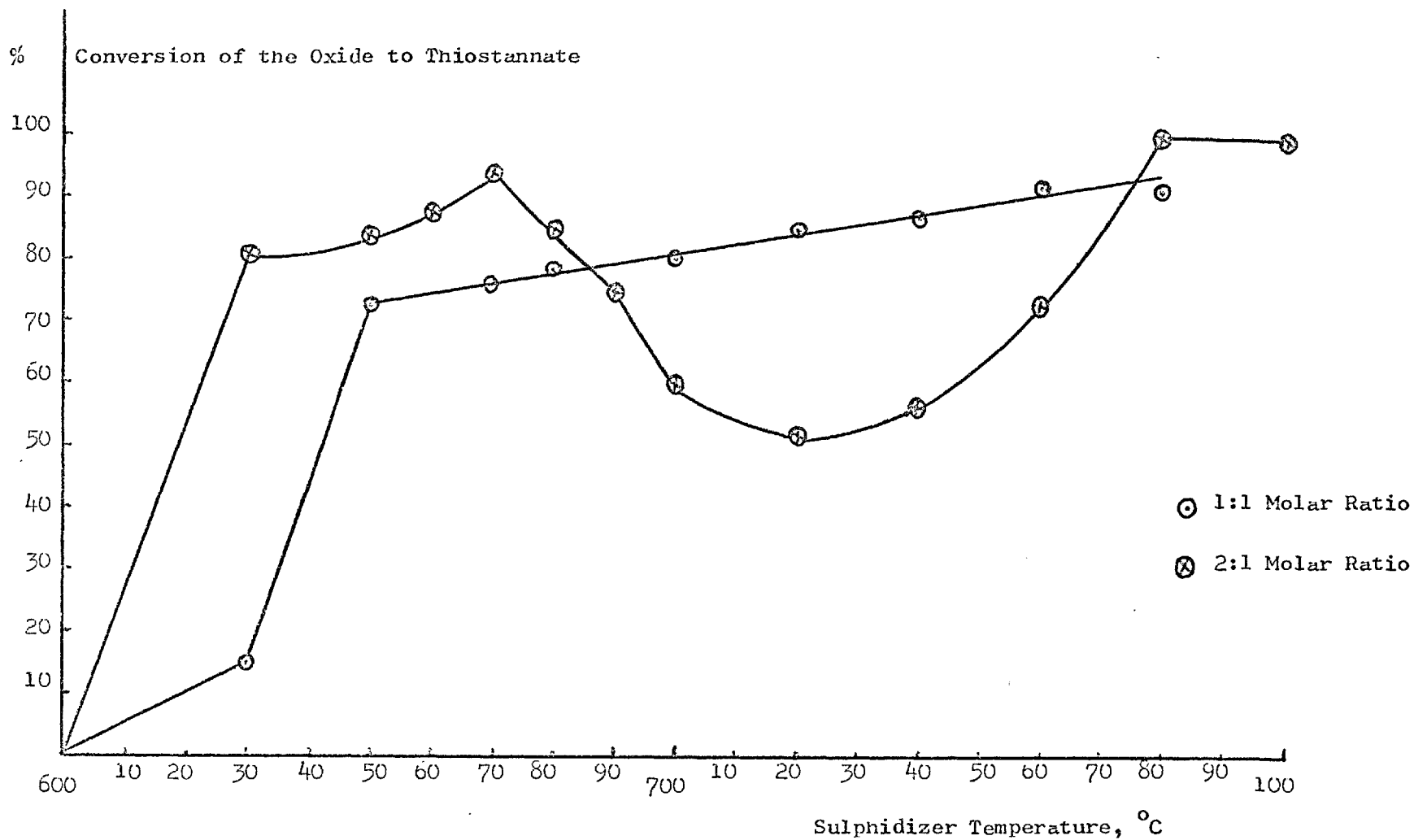


Figure 8: % Conversion of Stannic Oxide to Thiostannates vs. Sulphidizer Temperature.

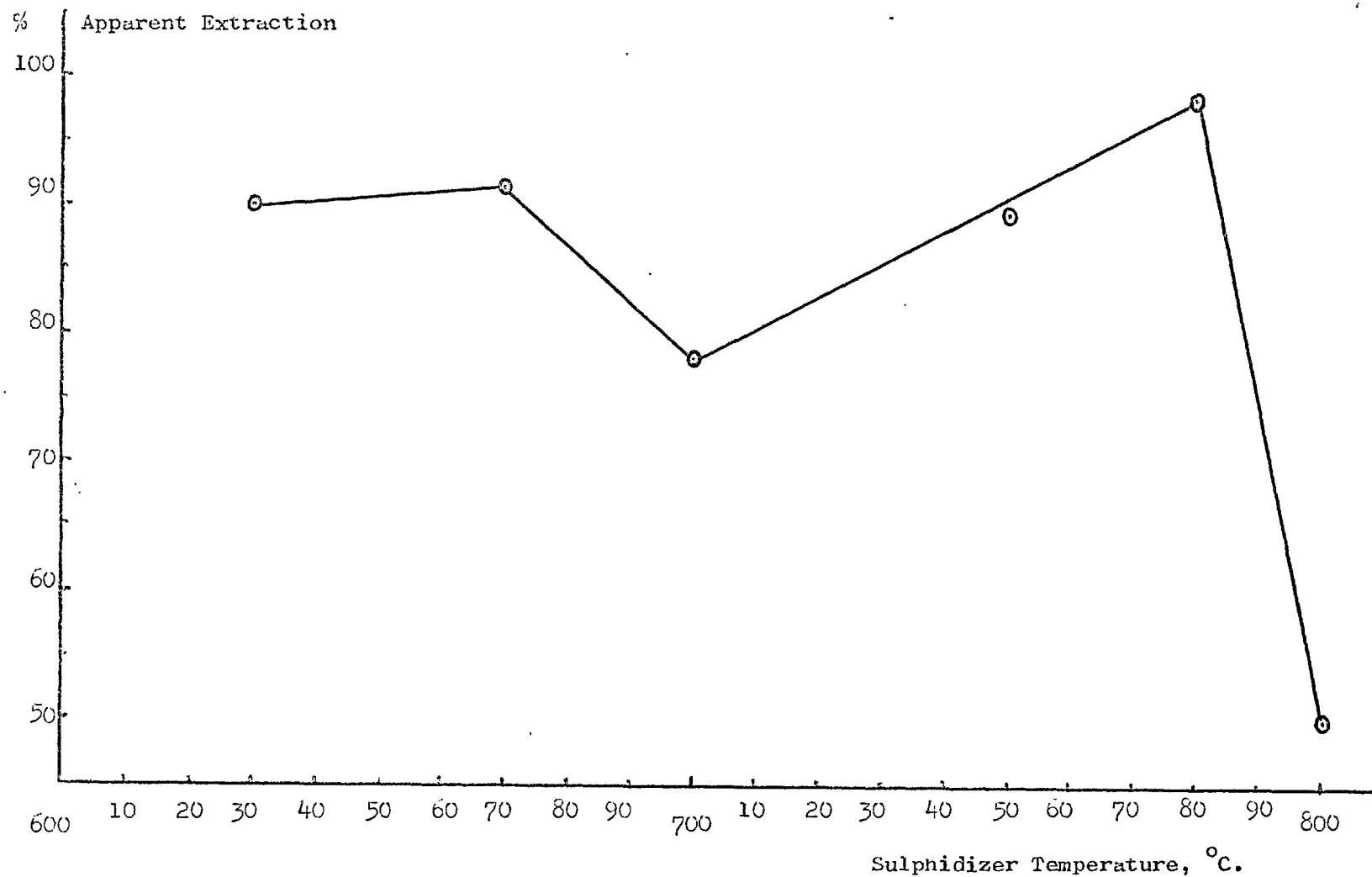


Figure 9: % Apparent Extraction of Cassiterite vs. Sulphidizer Temperature,
1:1 by Weight, 6 hours, High Gas flow-rate

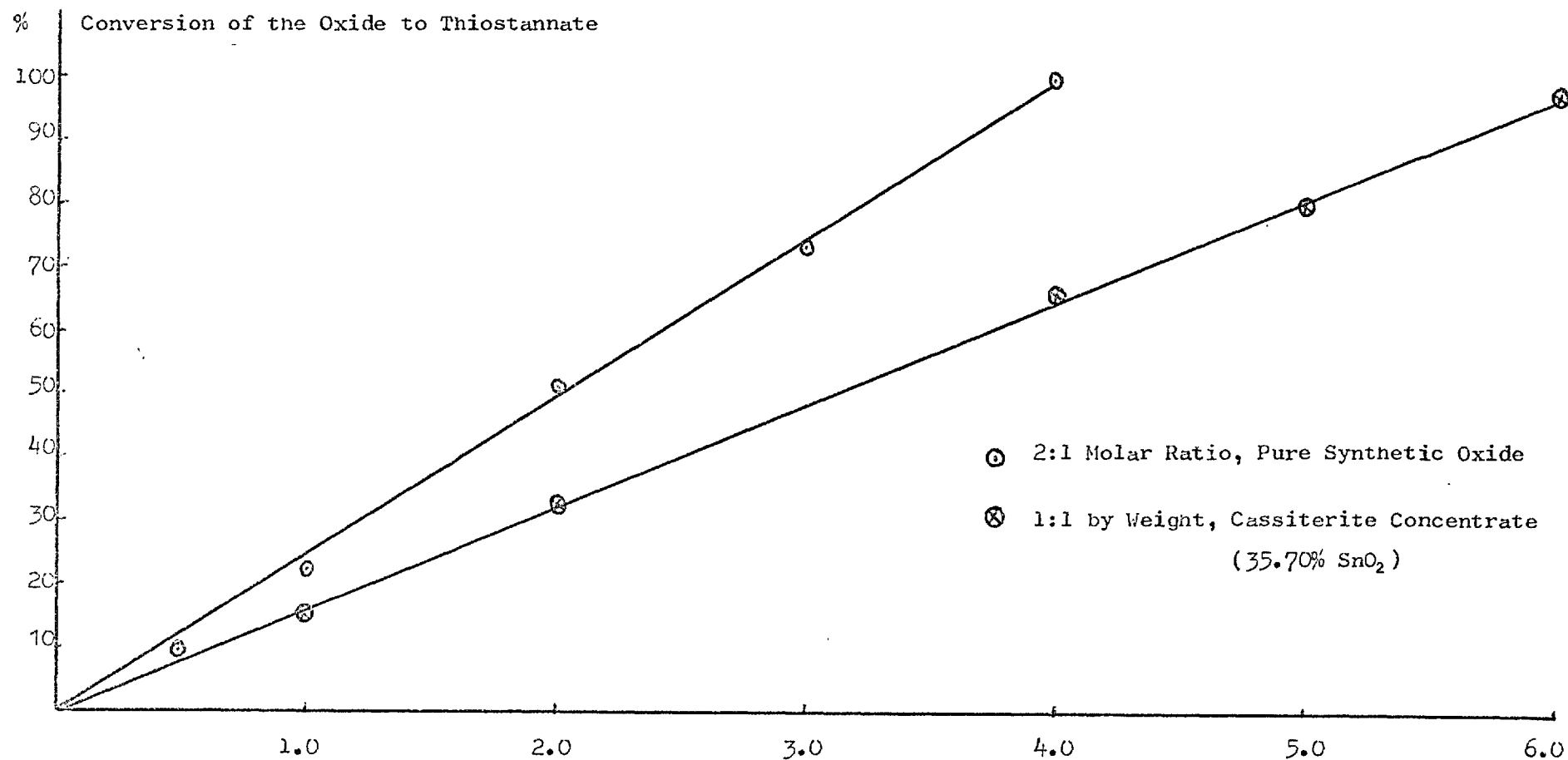
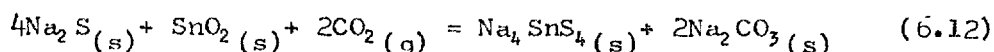
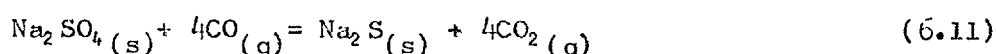


Figure 10: % Conversion of Stannic Oxide to Thiostannates vs. Time
(High Gas flow-rate)

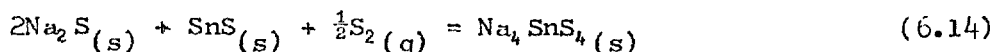
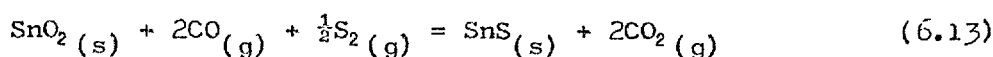
A mixture of stannic oxide, alkali sulphates, and charcoal was heated at 900°C. for one hour; the product was leached with water and 95% of the tin present was recovered as soluble thio-stannates.

The chemistry of these systems is not yet clear, but if the formation of thio-stannates is to be assumed under such conditions, the reactions below could be formulated. The ortho-thio-salt is assumed to be the thio-stannate product because of the presence of a large excess of alkali salt at a high working temperature:



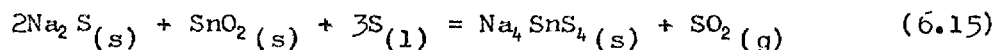
In the presence of free sulphur the sodium carbonate present would be converted into sulphide (e.g. $4NaCO_3 + 4S = 3Na_2S + Na_2SO_4 + 4CO_2$); probably this is one of the reasons why Sevryukov (1958) added elemental sulphur to the charge.

The reactions in the presence of a sulphur atmosphere could also be formulated as follows:



The formation of gaseous stannous sulphide is unavoidable at high temperatures. Sevryukov (1958) reported a maximum of 13% of the tin in the charge volatilized as stannous sulphide at 860°C.

In the presence of a sulphur atmosphere and the absence of a reducing agent, the reaction of interest would be:



and this means that sulphur is acting as a reducing agent to carry the oxygens of tin oxide, and therefore the presence of a reducing agent is probably not necessary. The reaction (6.12) leading to the formation of the thio-salt and the alkali carbonate might take place too.

The possible function of sulphur itself as a reducing agent encouraged testing of the reactions of stannic oxide with sodium carbonate and sulphur. The experiments carried out, although successful, are only exploratory and the system still needs further investigation.

The possibility is disclosed of converting any tin species to water-soluble thioannates at fairly low temperatures.

6.4. Applications

The sulphurous gases obtained by carbon reduction of sulphur dioxide could be utilized in various ways, some of which are enumerated below.

1. Sulphidization of the tin-bearing material at low working temperatures for a short period of time, followed by flotation of tin sulphides.
2. Sulphidization of the tin-bearing material at moderate temperatures, 600 - 800°C., to achieve high conversions to the sulphide, followed by leaching. If this were done, it would be advisable to remove the base-metal sulphides (e.g. pyrite, chalcopryrite, etc.) by flotation prior to sulphidization (see Appendix).
3. Sulphidization of the tin-bearing material at moderate temperatures in the presence of an alkali salt in order to form water-soluble thioannates, followed by leaching. The temperature range 650 - 700°C. would be favourable; a moderate excess of sodium sulphate is necessary to achieve high extractions while avoiding the formation of a melted mass.
4. Sulphidization of the tin-bearing material at high temperatures, 900 - 950°C., to effect volatilization of stannous sulphide, which could be condensed at the cool end of the reactor. This operation seems to be attractive because currently working plants using sulphidization operate at very much higher temperatures and use solid sulphidizing agents, e.g. pyrite.

The study of the melt reaction using sodium carbonate and sulphur to convert the tin species to the thiosalt has revealed that such system could be utilized effectively at low temperatures, 400 - 500°C., without

the use of a reducing atmosphere. This new approach to the problem of aqueous leaching of tin from low-grade sources has clear advantages over previously reported procedures using high temperatures and considerable amounts of reducer (Vonstein, 1971; American Cyanamid Co., 1941).

The industrial application of the sulphur dioxide and carbon system in mineral processing depends on three major factors:

1. The use of cheap coal or coke and roaster gases rich in sulphur dioxide content.
2. The cost of the heat energy input both in the reducer and sulphidizer.
3. The extent to which loss of sulphur in the exhaust gases can be avoided.

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APPENDIX

A Visit to Cornwall

The name "Cornwall" has been associated with the tin industry for many years. There is an extensive bibliography on Cornish Mining. Our concern, on the other hand, is the present status of "Tin Processing" in Cornwall. On April 17th, 1972, the Department of Mineral Technology arranged for a visit to the Industrial Plants in Cornwall, as is the case every year for the M.P.D. students. I am very much indebted to the Department for their help to enable me to join the trip.

In general terms, and according to what we could understand from the people we met, the following problems in tin processing are important:

1. In the case of a granitic type of bearing rock, the tin ore is processed by Heavy Medium Separation and Tabling. Usually such ores contain low values of base metal sulphides. Therefore, cleaning of the final concentrate to remove sulphides by flotation is necessary. Heavy Medium Separation could be very effective, if it were well designed; and big quantities of "barren rock" can be rejected at early stages of processing. If the tin ore contains high values of tin, e.g. = 1.5% Sn, most probably, a cascade arrangement of such technique with at least two units treating two different particle sizes, say -18 mm and -6 mm would produce a product with at least 2.0% Sn. This product may be considered as a low-grade concentrate, and could be treated by chemical processing. It is also possible to treat this product by gravity concentration methods in order to upgrade it to such tin content, say, 6 - 10% Sn, with optimum overall recovery and minimum cost, and would be suitable for chemical processing.

The purpose of this approach is to solve the problems of tin losses due to repeated treatment, and the removal of harmful elements, e.g. = iron, copper, arsenic ... etc. The presence of these elements give rise to a severe penalty on the price of the tin concentrate.

2. In case of a sulphidic type of bearing rock, where the ore contains very high values of metal sulphides, e.g.: pyrite, chalcopyrite and arsenopyrite, the removal of these sulphides by flotation is unavoidable, cheap and effective. Again, because

of the fact that almost all primary tin deposits are polydispersed, it would possibly be better to grind the ore to a finer size, say -150 mesh, at early stages to achieve removal of sulphides, and avoid repeated grinding and flotation. The tailing containing 1.5 - 2.0% Sn can be treated by chemical processing. In this case, we can be sure to have high overall recoveries of tin values, if the chemical treatment works well.

3. If the tin ore contains very low values, say 0.4% Sn, or even if we treat tailings or dumps, it seems that the purpose here is to recover as much as possible of the metal values with the minimum capital, and it appears that the solution might be to grind the material to a finer size, say -200 mesh, and treat on slime tables (Mozley and Holman Tables), keeping in mind that any product, even if it contains 5.0% Sn can be treated by chemical methods. This definitely would give the chance to the Mineral Processing Engineer to operate in that direction. In actual fact, by doing so, he is recovering, not only tin values, but also other metal values which are already present in the ore, e.g. = copper, tungsten, ... etc., which is the job of the Chemical Processing Engineer to handle, and thus increase the profitability of his process.

In some cases, it is possible that some of the cassiterite may be present in coarse size, and thus jigging at early stages would recover it.

4. One of the problems of some of the cassiterite deposits is the interlocking of cassiterite with wolframite. In such cases, the problem will remain until the final product, and even magnetic separation of wolframite from the final coarse tin concentrate would result in high losses of tin values into the wolframite concentrate, and at the same time decrease the value of the wolframite product. In this case, chemical processing may well be highly advantageous. This confirms the idea that it is better to treat the ore with simple flow-sheet to produce a low-grade tin concentrate, say 4 - 10% Sn, with high overall recoveries, and then treating the product by an efficient chemical process to selectively extract the cassiterite and leave the wolframite behind or vice versa. It should be possible to

extract the tin and tungsten values in one single process from the concentrate, and end up with two valuable products.

Such a combination of physical and chemical processing could probably lead to conservation of the Cornish Tin reserves which constitute a valuable national asset.