"STUDIES OF THE THERMODYNAMIC BEHAVIOUR OF CUPROUS SULPHIDE AND ITS MIXTURES AT ELEVATED TEMPERATURES."

A Thesis

submitted for the degree of

Doctor of Philosophy

in the

University of London

by

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July, 1953.

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ABSTRACT

The thermodynamic behaviour of cuprous sulphide in three different states was studied by determining the hydrogen, hydrogen sulphide gas mixtures in equilibrium with it and a solid copper phase. Pure solid cuprous sulphide was investigated first over the temperature range 530°C - 1040°C. A standard free energy equation for its formation was obtained which was consistent with all previous work and can be considered the most accurate known at present. Secondly thin layers of cuprous sulphide approximately 0.003mm thick were grown on copper at three temperatures between 710°C and 840°C, and their stabilities found to be the same as those of bulk cuprous sulphide. In addition some interesting phenomena connected with their growth were observed, recorded and compared with similar results published for oxide layers. Lastly sodium sulphide - cuprous sulphide mixtures were investigated in both the solid and liquid states in the composition range 0 - 36 mole% sodium sulphide. Activities, partial molar free energies, heats and entropies of cuprous sulphide were obtained and

discussed from a chemical viewpoint. It was also possible from this last investigation to obtain a value of the heat of fusion of cuprous sulphide, and to correct the existing phase diagram for the sodium sulphide - cuprous sulphide system.

GENERAL INTRODUCTION

The majority of present day metallurgical extraction processes have been developed in a slightly "ad hoc" way, but the recent demand for new metals, the gradual exhaustion of high grade ores and the working of new ore deposits have made it necessary to put the subject of extraction metallurgy on a sounder theoretical basis. Thermodynamics has proved a very useful tool in this respect and there has therefore arisen a demand for accurate high temperature thermodynamic data on metals, alloys and metal compounds. The aim so far has been to study simple systems and then to apply the results obtained to the more complex systems and problems found in extraction processes. Previous work has been mainly concerned with metals, alloys and oxides and although there is still much to be done in this field an overall picture of the behaviour of these substances has been obtained. The position for sulphides is however much worse. Some sulphides have been thermodynamically investigated in their pure state but no accurate work has been published on sulphide mixtures. The abundance of sulphur in the earth's crust makes sulphides of extreme metallurgical importance and there is therefore an urgent need for data on these compounds.

To help him obtain and explain the necessary thermodynamic data the metallurgist now has the assistance of the chemist who until recently was not actively interested in the behaviour of inorganic substances at high temperatures. The chemist has now realized that besides being of metallurgical importance such data is also of chemical interest. The results for mixtures or solutions, both solid and molten, are of the greatest interest and it is hoped that they will provide information on the structures in the solid and liquid state and the effects of ionic size, charge and covalency character of the bonds. Furthermore new statistical mechanical treatments may have to be developed as most of the existing ones were worked out for mixtures of organic molecules and may not prove suitable for this type of work. To solve any of these problems it is necessary to have a large amount of accurate data on numerous systems. Sulphides have here a great advantage over other inorganic compounds as they are normally molten at low temperatures. Inaccuracy and experimental difficulties markedly increase with temperature and the type of information the chemist needs can therefore more easily be obtained using sulphides, although one great disadvantage in their use is that they can often have an appreciable range of composition.

Sulphides were therefore chosen for the present work in preference to any other type of inorganic compound,

because of the simplicity of the experimental technique and because the results could be applied to metallurgical as well as chemical problems. The main aim was to make an accurate study of a two component system, so that in later years when other systems had been studied all the results could be compared and a greater understanding of the factors determining the behaviour of inorganic salt mixtures could be obtained.

Cuprous sulphide was chosen as the centre-piece of the work, firstly because copper is of extreme industrial importance and cuprous sulphide occurs in almost every extraction process involving copper, and secondly because it is chemically suitable as it is stoicheiometric when solid and in equilibrium with copper and is sufficiently unstable at high temperatures for equilibrium measurements to be made on it. Before any results for mixtures can be interpreted the thermodynamics of the pure components has to be known. Unfortunately no reliable data existed for this sulphide in its solid state and a study of this compound therefore became the first task.

Upon the completion of the above work it was apparent that with only a slight modification of the apparatus thin films of cuprous sulphide grown upon copper could also be investigated. Alth ugh this was a little removed from the main objects of the research it was considered sufficiently importance to warrant investigation. Recently work has

been done on wustite in which it has been assumed that the thermodynamics of thin films is the same as that of the bulk phases (25). However there is experimental evidence which suggests that this assumption may be untrue (23.) It would be of fundamental importance in the theory of surfaces if it was found that the stabilities of thin films of cuprous sulphide on co per were different to those of bulk cuprous sulphide in equilibrium with copper, and the present work was therefore undertaken with the aim of helping the theoreticians as well as of assessing the validity of the above assumption.

The final and most interesting phase of the work was the study of the system cuprous sulphide - sodium sulphide. It has been known for many years in extraction metallurgy that there is a strong interaction between these two sulphides but no attempt until ~~not~~ now has been made to obtain a quantitative measure of this interaction. Such a system finds its main application in decoppering[12] processes. For example in the Orford process the sulphides of nickel and copper are separated by fusion with sodium sulphide, the copper enters the sodium sulphide slag leaving purified nickel sulphide. From a chemical viewpoint this system is an example of a mixture of two salts, between which there is a strong interaction and which have the same divalent anion but different univalent cations. In

addition the cation-anion bond has a greater covalent character for one of the components. It should be emphasized that the full importance of these characteristic properties cannot be assessed until several systems have been studied and all the various results and characteristic properties compared.

From this introduction it is apparent that the work can be divided into three separate sections.

1. Solid cuprous sulphide.
2. Thin films of cuprous sulphide grown on copper
3. Mixtures of cuprous sulphide and sodium sulphide

Although the last two sections are dependent upon the first, for the purpose of clarity in the present thesis all three sections will be considered separately each one having its own introduction and discussion of results etc.

SECTION I

"SOLID CUPROUS SULPHIDE"

INTRODUCTION

a) Chemical properties of cuprous sulphide.

The general chemical behaviour of cuprous sulphide is well known, but three properties will be mentioned as they were especially important in the present investigation.

Stoicheiometry

Buerger has found that solid stoicheiometric cuprous sulphide can take up sulphur to give a compound of variable composition called digenite (1). There is no evidence that solid cuprous sulphide is nonstoicheiometric when in equilbrium with copper.

Structure

The existence of a low (α) and high (β) temperature form of cuprous sulphide has been known for several years. The structure of the low temperature form has been accurately determined as orthorhombic. Until recently the high temperature form had been given an antifluorite structure. Buerger has shown however that this is incorrect, that the β form has hexagonal symmetry (2) and that only a slight displacement of certain atoms is involved in the transformation. From specific heat data Buerger pointed out that this transformation extended over a range of temperature. When a specimen of cuprous sulphide is slowly heated structural changes start at about 78°C and continue until

105°C when the complete transformation takes place. He deduced from this that the α to β transformation was from an ordered to a disordered structure. These terms are rather vague but a tentative explanation is that one or both of the copper atoms become progressively more free to move within a sulphur lattice, the final structure being similar in this respect to that of silver sulphide.

The copper cuprous sulphide phase diagram.

When a mixture of copper and cuprous sulphide is melted two liquid phases are formed, a copper rich and a sulphide rich phase.

Schuhmann and Moles (3) in 1951 determined the amount of copper in the sulphide phase by quenching and analysing samples which were in equilibrium with the metal phase. Their results are given in Table 1. It should be mentioned that their values, which can be considered the most reliable at present, for the amount of copper in excess of that for the stoicheiometric sulphide are less than those which were accepted previously.

Table 1

Temperature	wt % dissolved Cu
1150°	1.7
1250°	2.7
1350°	3.6

Rosenquist in 1951 (4) was able to deduce from his measurements and from those of Sudo (5) on the activity

of sulphur in liquid copper the composition of the copper rich phase. He found that there was approximately 1% by weight of sulphur present at 1200°C, which was less than was previously believed. Furthermore due to the melting point of pure copper being only 1083°C this sulphur solubility must increase only slightly with temperature.

b) Theory

No attempt here will be made to derive the fundamental thermodynamic equations as these can be obtained from any standard thermodynamic textbook. The notation adopted throughout this thesis will as closely as possible be that employed by Guggenheim in his book "Thermodynamics".

In a thermodynamic study of a pure compound the most interesting quantities are the standard free energy (ΔG°) heat (ΔH°) and entropy (ΔS°) of formation. That is the change in these functions when the elements combine to give the compound, both the reactants and products being in some fixed arbitrarily chosen standard state. In this type of work it is normal to choose the standard state for gases as one atmosphere pressure and for solids or liquids as the pure substance. For example, with sulphides the reactants are a pure metal in a solid or liquid state and sulphur in the form of diatomic sulphur gas at one atmosphere pressure; the product is a pure sulphide in a

solid or liquid state. No departure from this practice will be made here.

$$M + \tfrac{1}{2}S_2 \longrightarrow MS \quad \cdots\cdots \quad 1$$

The thermodynamic quantities can be obtained in several ways, one of which is to measure directly the diatomic sulphur pressure in equilibrium with the metal and sulphide as in a method employing a Knudsen cell. This entails placing the condensed phases in a cell or box having a small orifice. This cell is then placed in an evacuated chamber and heated to the required temperature. When equilibrium conditions are established the partial pressures of the various gaseous components, including diatomic sulphur, can be determined by collecting all the particles emerging from the orifice in a given time. The great disadvantage of the method is that the compositions and the relative amounts of all the gaseous components have to be known. It is often not possible to fulfil this condition because many sulphides are volatile and because various polyatomic molecules or sulphur may exist in the gas phase, and this method is therefore seldomly used.

From the law of mass action it follows that the equilibrium constant (K_1) for reaction 1 is given by

$$K_1 = \frac{a_{MS}}{p_{S_2}^{\frac{1}{2}} \, a_M} .$$

a = activity of the relevant substance.

p_{S_2} = equilibrium diatomic sulphur pressure.

If both the metal and the sulphide are in their pure and hence standard states their activities are equal to unity.

$$K_1 = \frac{1}{p^{\frac{1}{2}}_{S_2}} \quad \ldots\ldots\ldots\ldots \quad A$$

For any reversible reaction at constant temperature and pressure

$$\Delta G^{o} * = - RT \ln K$$

and $$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}.$$

It is therefore possible by studying the equilibrium at various temperatures, and then calculating the free energy changes at these temperatures, to evaluate both the heat and entropy terms.

A graph of free energy change against absolute temperature is normally an almost straight line but this does not mean that the heat and entropy changes are constant. They do in fact change slightly with temperature, but in such a manner that they partly compensate one another and an almost straight line results.

A more usual and convenient way to obtain the required quantities is to study the equilibrium between hydrogen, hydrogen sulphide, the metal and the sulphide. From the ratio of the partial pressures of the two gases it is then possible to calculate the equilibrium diatomic sulphur

* The suffice ^{o} signifies that the STANDARD change of the thermodynamic function is being considered.

pressure in equation A

$$H_2S + M \rightleftharpoons H_2 + MS \quad \ldots\ldots\ldots\ldots \quad 2$$

The equilibrium constant (K_2) for this reaction is given by

$$K_2 = \frac{a_{MS} \quad p_{H_2}}{a_M \quad p_{H_2S}} .$$

Strictly fugacities should be used instead of partial pressures but as hydrogen and hydrogen sulphide at the pressures used ($p_{H_2S} \approx 10^{-3}$ atms) are almost ideal no appreciable error will be introduced in using partial pressures.

Again the metal and sulphide can be considered pure and their activities taken as unity.

$$\therefore \Delta G^\circ_2 = - RT \ln \left(\frac{p_{H_2}}{p_{H_2S}} \right)$$

The free energy equation for the reaction between hydrogen and diatomic sulphur gas giving hydrogen sulphide is well known, a complete summary of the literature having been made by Richardson and Jeffes (6). The sulphur pressure in equilibrium with a given hydrogen, hydrogen sulphide gas mixture at a certain temperature can therefore be calculated.

$$H_2 + \tfrac{1}{2} S_2 \rightleftharpoons H_2S \quad \ldots\ldots\ldots\ldots \quad 3$$

$$K_3 = \frac{p_{H_2S}}{p_{H_2} \; p_{S_2}^{\frac{1}{2}}}$$

The required standard free energy change for equation 1 is now given by

$$\Delta G_1^o = -RT \ln K_2 K_3.$$

c) Previous work

The thermodynamic behaviour of solid cuprous sulphide at high temperatures has interested numerous investigators since 1925 but the results obtained were never satisfactory.

The first two studies were made by Jellinek and Zakowski (7) in 1925 and Britzke and Kapustinsky (8) in 1932. The method was to stream hydrogen over heated cuprous sulphide at various flowrates and to analyse the hydrogen, hydrogen sulphide gas mixtures formed. The gas compositions for no flowrate would be those in equilibrium with the condensed phases and to obtain them graphs of gas composition against flowrate were extrapolated to zero flowrate. No precautions were taken against thermal diffusion of the gases (see page 27), and the two sets of results are in marked disagreement with one another and with all subsequent work, the sulphur pressures obtained being too high. Results with similar inaccuracies were obtained for other sulphides these workers investigated (e.g. ferrous sulphide) and their work may therefore be disregarded.

Cox 'et al' (9) made the first investigation of any importance. Their apparatus consisted of a furnace, containing copper and cuprous sulphide, in a closed gas circuit which was initially filled with hydrogen. The gas was circulated at 60 cc/min* through a 1 inch bore reaction tube, sulphur being removed from the sulphide to form hydrogen sulphide, until the whole apparatus was filled with the equilibrium gas mixture which was then analysed chemically. The results were considered unsatisfactory because their reproducibility was bad and because similar measurements by the same workers on ferrous sulphide have since been shown inaccurate due to the presence of thermal diffusion (10).

Sudo's experiments (11) were the most recent being published during the course of the present work. A flow method similar to that employed by Jellinek and Zakowski was used, the main difference being that Sudo took adequate precautions against thermal diffusion. The results were not of the highest accuracy (internal consistency ± 3% of the equilibrium constant) and were obtained at only four temperatures within a two hundred degree range.

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* All flowrates mentioned in this thesis have been measured at room temperatures and pressures.

A standard free energy equation for the formation of cuprous sulphide can be obtained from thermal data compiled by Kelley. He has calculated (12) the standard free energy equation for the following reaction from specific heat data and from the heat of reaction measured by Von Wartenberg.

$$2Cu_{(s)} + S \text{ (rhombic)} \longrightarrow Cu_2S(\alpha)$$

$$\Delta G^\circ = -18440 + 11.70\ T \log T - 11.02 \times 10^{-2} T^2 - 32.76\ T$$

In the region of the α to β transformation this may be simplified to

$$\Delta G^\circ = -18880 - 5.60T. \quad \cdots\cdots\cdots\cdots\cdots \quad B$$

Kelley has in addition produced values of the heat and entropy changes for the α to β transformation (13) and a standard free energy equation for the conversion of rhombic sulphur to the diatomic gas (14).

$$Cu_2S\ (\alpha) \xrightarrow{376^\circ K} Cu_2S\ (\beta)$$

$$\Delta H^\circ = 1340 \frac{\text{cals}}{\text{mole}} \qquad \Delta S^\circ = 3.56 \frac{\text{cals}}{\text{mole}} \text{ deg.}$$

$$2\ S \text{ (rhombic)} \longrightarrow S_2$$

$$\Delta G^\circ = 31360 - 1.36T \log T + 5.80 \times 10^{-3} T^2 - 38.62T$$

When these data are combined with equation B the required equation is obtained

$$2Cu + \tfrac{1}{2} S_2 \longrightarrow Cu_2S\ (\beta)$$

$$\Delta G^\circ = -33220 + 0.68T \log T - 2.9 \times 10^{-3} T^2 + 10.1\ T$$

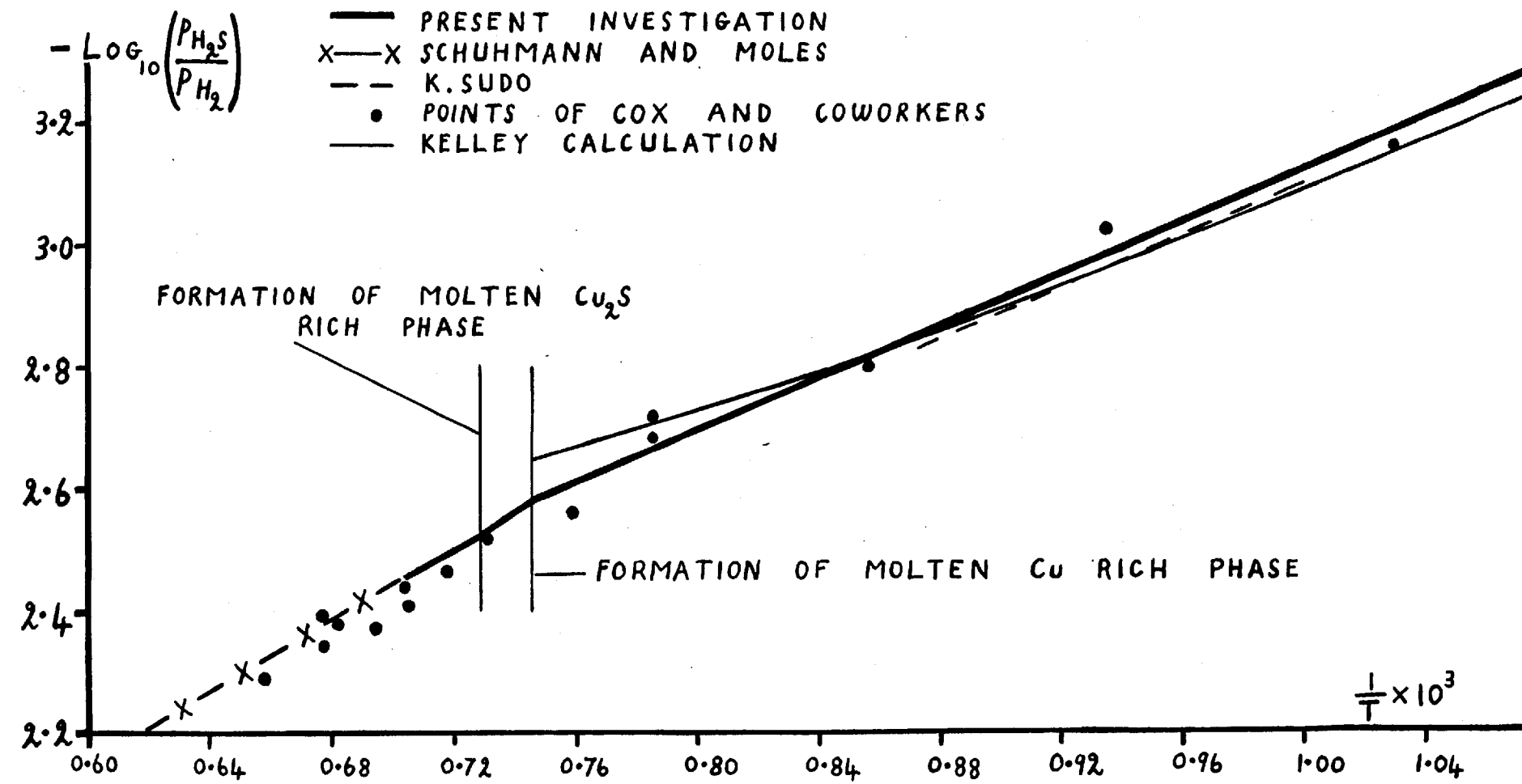
This type of calculation is useful as a guide but never gives results as accurate as the best experimental methods. This calculation can be considered especially unreliable for two reasons, firstly Von Wartenberg's heat of reaction (15) was determined in 1909 by bomb calorimetry without analyses being done to determine the compositions and quantities of the reaction products, and secondly when the calculated free energy changes are plotted against the absolute temperature a pronounced curve is obtained which implies that the specific heat data used in the equation for the conversion of rhombic sulphur to diatomic sulphur gas is inaccurate.

Schuhmann and Moles in a good piece of work in 1944 (3) determined the sulphur pressures, in equilibrium with the two molten phases (see pages 10, 11). They bubbled known hydrogen, hydrogen sulphide gas mixtures through the melts and analysed the resultant gas mixtures. The gas compositions in equilibrium with the melts were found by making the compositions of the entrant and exit gases the same. Precautions were taken against thermal diffusion, side reactions of hydrogen sulphide and faulty gas analysis; in addition the internal consistency of the results $\left\{ \pm 2\% \text{ of } p_{H_2S}/p_{H_2} \right\}$ was good considering the high temperatures at which the results were obtained.

FIG 1

PREVIOUS RESULTS FOR THE EQUILIBRIUM

$$2Cu + H_2S \rightleftharpoons Cu_2S + H_2$$



After analysing all the above data, the important parts of which are shown in Figure 1, it was decided to determine accurately the sulphur pressures in equilibrium with solid cuprous sulphide and copper over an extended temperature range, and to make a few measurements in the two liquid phase region so that a comparison with the results of Schuhmann and Moles could be made.

EXPERIMENTAL METHOD AND PROCEDURE

The method employed here was similar to that used by Cox and co-workers. A closed gas circuit was built, the components of which were a furnace, a gas circulating pump, a drying tube, a capillary gas flowmeter, a blow-off, a manometer and a gas sampling bulb (Fig.2).

Cuprous sulphide (2 gms) intimately mixed with an equal weight of copper was placed in a pure recrystallized alumina boat (Morgan Crucible Co.Ltd. Δ RR) in the furnace. The whole apparatus was filled with hydrogen and the sulphide specimen heated to a known temperature. The gas was then continuously circulated, at a flowrate sufficient to overcome thermal diffusion, until the whole apparatus contained the equilibrium hydrogen, hydrogen sulphide gas mixture($p_{H_2S}/p_{H_2} \approx 10^{-3}$). To determine the ratio of the partial pressures of the two gases the contents of the gas sampling bulb were analysed for sulphur. The standard free energy change for the formation of cuprous sulphide at this temperature was calculated and by repeating the experiments at various temperatures the standard heat and entropy changes were also obtained.

a) Apparatus

Furnace (Fig.3)

The furnace consisted of a 1¾ ins. bore mullite tube wound uniformly for 14 ins. of its length with Kanthal resistance wire (0.04 ins in diameter). In this tube was

FIG 2

GAS CIRCUIT

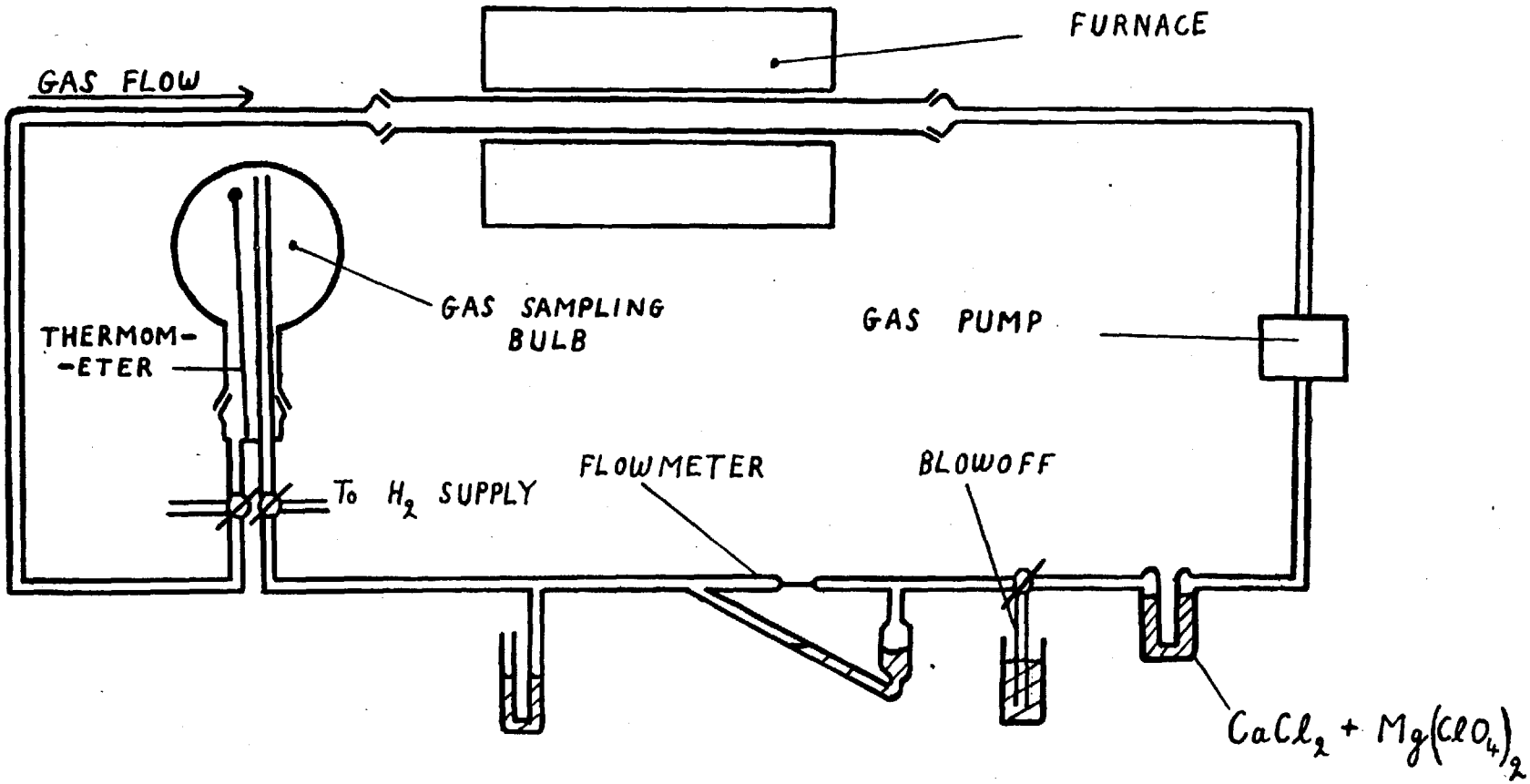
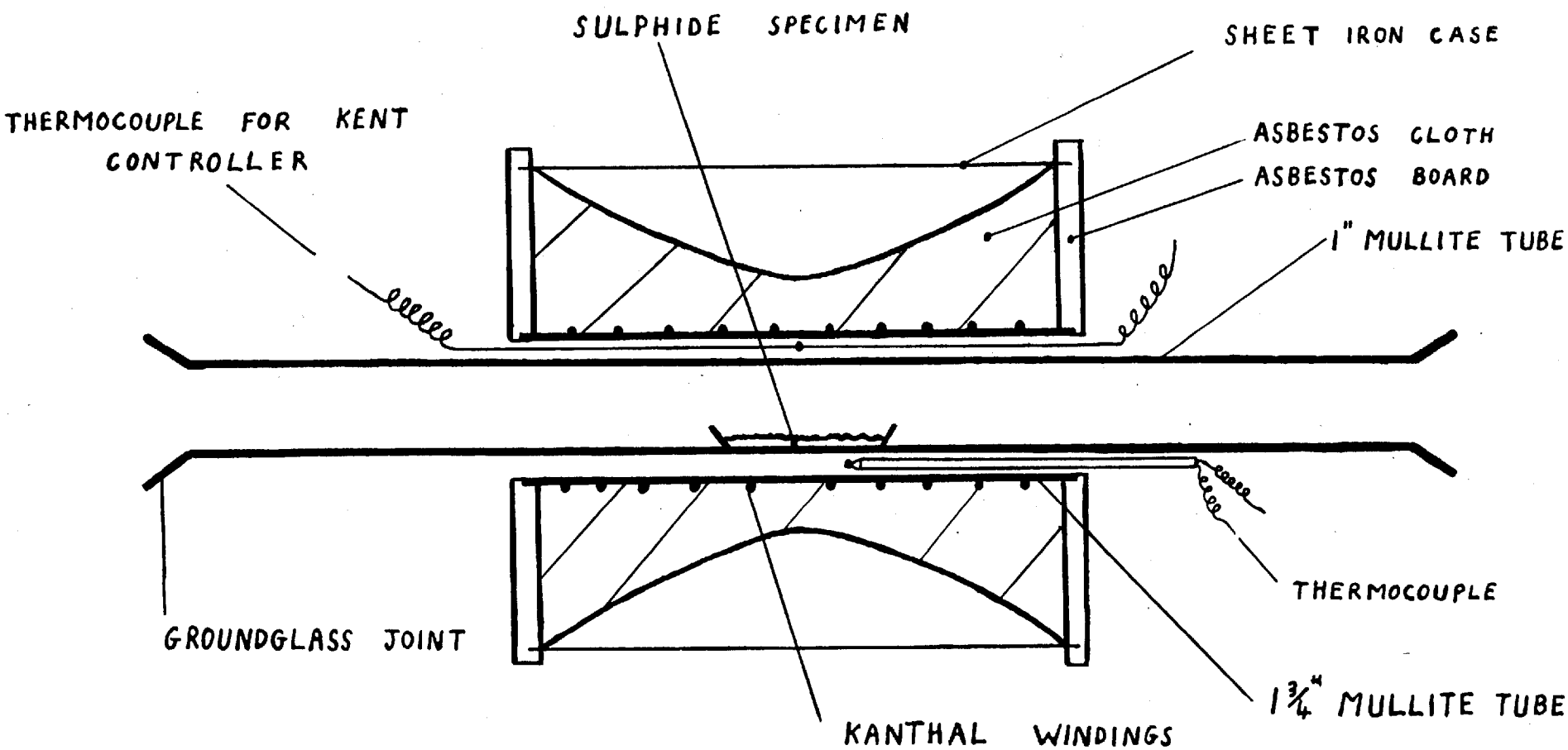


FIG 3

FURNACE



placed a 1 inch bore mullite reaction tube. Asbestos cloth was used as insulation and was wrapped round the winding tube differentially so as to improve the even temperature zone which was better than 2 ins of $\pm$ 2°C (i.e. the length of the sulphide specimen). The power to the furnace was controlled by means of a variac, a vacuum switch and a Kent controller. The Kent using a thermocouple in the furnace was able to keep the temperature to $\pm$ 1.5°C of the required value by proportioning one third of the power, the vacuum switch being used to make and break the circuit. This arrangement however did not always work satisfactorily and the temperature was then kept to the above limits by manual control.

Kanthal wire when it has been heated becomes brittle, and experimenters have found that when a kanthal wound furnace has been cooled to room temperature the wire may have fractured. The present furnace however was repeatedly heated and cooled to room temperature without this happening. This difference in behaviour is attributed to the fact that the wire used here(0.04 ins. in diameter) was thinner than that of the other experimenters.

On a similar furnace the author tried a modification, the above method to improve the even temperature zone, which proved more satisfactory. This was to wind the resistance wire differentially so that when the windings were lagged uniformly with asbestos cloth a dip was

obtained in the middle of the temperature distribution. This dip was then satisfactorily removed by increasing the lagging around the middle of the furnace. An even temperature zone of 3.5 ins of $\pm$ 1.3°C was obtained by this method.

The connections to the reaction tube were made by ground glass joints fastened to the ends of the mullite tube by the thermo-setting plastic "Araldite". Although "Araldite" is attacked by sulphur dioxide it is unharmed by hydrogen sulphide at a partial pressure of 10^{-2} atmospheres (16).

Temperature Measurement

The temperature measurement was made by means of a platinum-platinum 13% rhodium thermocouple* placed between the reaction and furnace tubes in a position which corresponded to a point halfway between the middle and trailing edge of the alumina boat.

The thermocouple was calibrated before and after the equilibrium measurements were made by placing a similar thermocouple in a corresponding position inside the reaction tube. The two calibrations agreed to within 1°C, and the

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* This was supplied by Johnson Matthey Co.Ltd. and was guaranteed to measure the temperature to $\pm$ 2°C of the true value in the temperature range investigated.

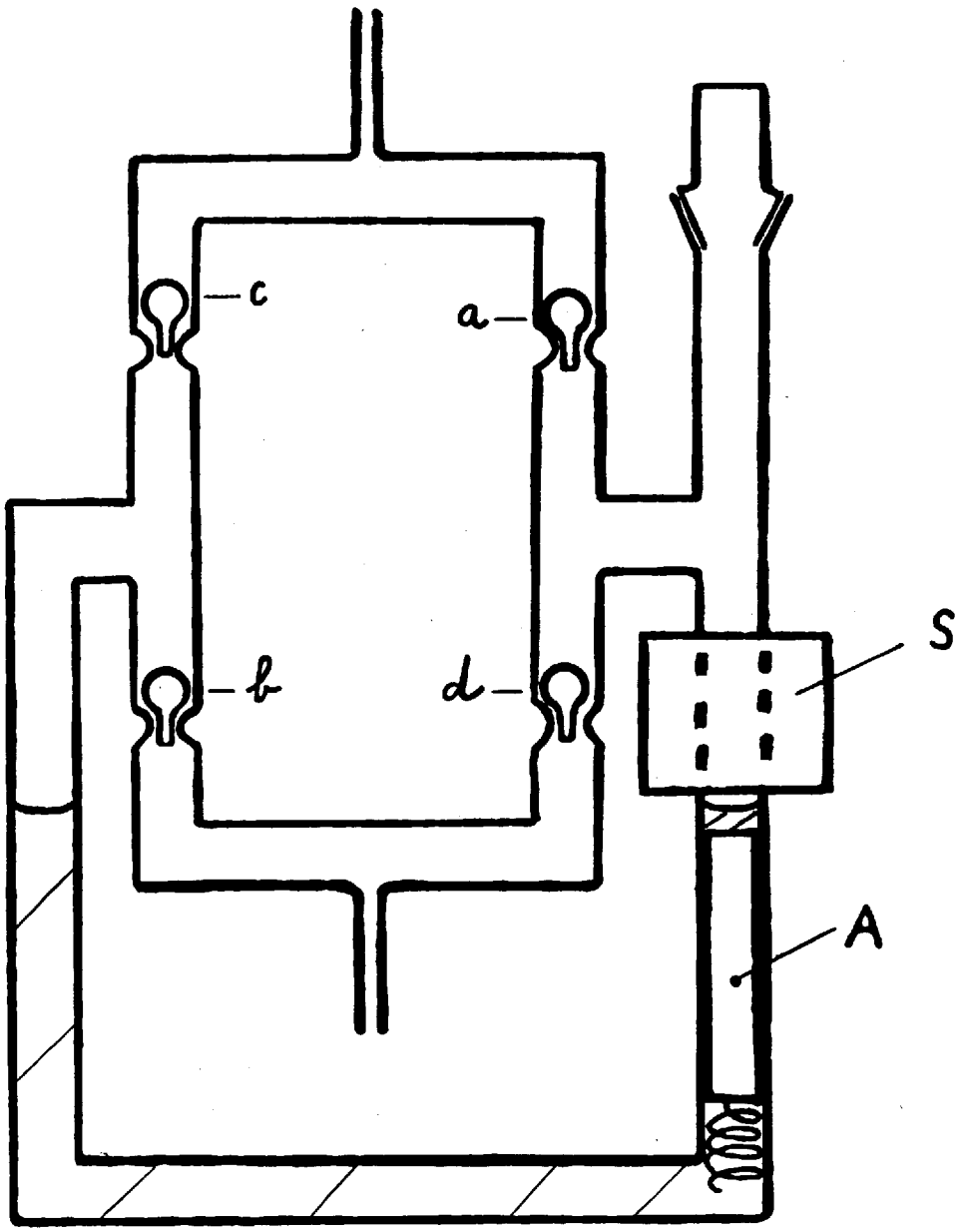
temperature drop across the reaction tube was less than 3°C. The effect of gas flowrate on the temperature was also studied. It was found that at 600°C the temperature given by a thermocouple inside the reaction tube did not alter when the flowrate of pure hydrogen was increased from zero to 600 cc/min.

Gas Pump

The gas pump was a copy of one used at the British Iron and Steel Research Association (B.I.S.R.A.) and was made by Mr. Leek of B.I.S.R.A. It was essentially a double acting pump utilizing four non-return values and is shown diagrammatically in Figure 4. The pumping power was derived from the solenoid S into which were fed a series of D.C. pulses (for the production of these pulses see Appendix I) which caused the iron armature A and hence the two columns of n - dibutyl phthalate (used because of its low vapour pressure and inertness to low partial pressures of hydrogen sulphide) to oscillate. When a D.C. pulse was passed the armature rose and gas was forced through valves (a) and (b), when the pulse was cut off the armature fell under gravity and gas was forced through valves (c) and (d). The valves were small glass bulbs blown on the ends of pieces of narrow bore tubing.

FIG 4

GAS PUMP



The valve seats were constructed pieces of glass tubing. It was important that the valve and its seat should be a good fit so that there was no leakage of gas back. Any flowrate between 0 and 500 cc/min could readily be obtained by altering the frequency of the D.C. pulses, but it was found that any impedance in the gas circuit such as narrow bore taps and capillary tubing greatly reduced the maximum obtainable flowrate.

Flowmeter (Fig.2)

A capillary gas flowmeter was constructed in such a manner that it offered little resistance to the pump. Instead of having a normal U-tube device to measure the pressure drop across a capillary, the limb used here to measure the position of a liquid (n - dibutyl phthalate) meniscus was inclined at an angle of 45° to the vertical. For a given displacement of this meniscus the pressure drop across the capillary was less, and hence the resistance offered to the pump was also less, than with the conventional type flowmeter.

Drying Tube

Calcium chloride and magnesium perchlorate (anhydrone) were used as drying agents after it was discovered that silica gel adsorbed hydrogen sulphide as well as water.

Initially some experiments were done with rubber bungs present in the system. The effect of these bungs on the hydrogen sulphide atmosphere was not known so they were replaced by ground glass joints and the previous results were then checked satisfactorily.

To ensure a little flexibility in the apparatus some joints were made with short lengths of polyvinyl chloride tubing.

Any small leak or pinhole in the apparatus which might have altered the gas composition was immediately detected, due to a reduction in pressure in the apparatus caused by the admittance of atmospheric oxygen which was converted to water vapour in the furnace and then absorbed by the drying tube. Any oxide present in the sulphide sample was also reduced in this manner.

b. Chemicals Used

Hydrogen

The hydrogen was commercial "oxygen free" hydrogen supplied by British Oxygen Co.Ltd. It was dried by calcium chloride and magnesium perchlorate before use. When dry it was guaranteed 99.95% pure (17.)

Copper

This was in the form of drillings which were

prepared from a piece of copper produced at the El Paso Refinery of the Phelps Dodge Co. The impurities* in this copper were silver

$< 0.001\%$, oxygen and sulphur combined $< 0.006\%$.

Cuprous Sulphide

Cupric sulphide was first prepared by passing hydrogen sulphide into an acidified (sulphuric acid) solution of "Analar" cupric sulphate. The precipitate was collected, dried, placed in a silica boat and heated in a slow stream of hydrogen for 1½ hours at 750°C. The product was cuprous sulphide together with a little copper which was easily removed as it was only formed at the leading edge of the sample. Chemical analysis** gave copper = 79.7% and sulphur= 20.2% (Theoretical values:- copper = 79.86% sulphur = 20.14%) The trace elements detected by spectrographic analysis** were silicon, lead and iron, all of which were present in quantities less than 0.03%.

c. Gas Analysis.

To determine the compositions of the gas mixtures the contents of the gas sampling bulb, which were at a known temperature and pressure, were analysed for sulphur by a method developed by Kitchener and co-workers (18). The gas samples were flushed out with hydrogen, into an standard

** These analyses were kindly done by the B.I.S.R.A. section of the Bragg Laboratory.

alkaline solution of sodium hypochlorite, which absorbed the hydrogen sulphide and at room temperatures oxidized some of the sulphide to sulphur giving the solution a turbid appearance. The solution was boiled for five minutes to convert all the sulphur to sulphate and then the quantity of sodium hypochlorite remaining was estimated iodimetrically. For these experiments the method was perfectly satisfactory and the results reproducible to ± 1%.

An indirect check on the method was obtained by a colleague who used the same standard solutions employed here (19). He estimated the quantity of sulphur in a slag by the hydrogen sulphide evolution method developed by Kitchener and co-workers for sulphur in iron (18) and obtained results concordant with those from combustion and gravimetric methods.

A seventeen hundred cc sampling bulb was used, the exact volume of which was determined by weighing it empty and full of water. To guarantee the removal of all the hydrogen sulphide from this bulb it was necessary to flush it out with hydrogen for 1½ hours at 150 cc/min.

d) Additional Precautions taken to ensure accurate results. Thermal Diffusion.

The existence of the phenomenon called thermal diffusion has been known for many years but only recently has its

importance in work using gas mixtures at high temperatures been fully realized.

If a gas mixture is left stagnant in an apparatus, parts of which are at different temperatures, the components of the mixture will partially separate, the heavier molecules concentrating in the colder parts of the system.

A theory for the phenomenon has been developed by Gillespie (20) from kinetic energy considerations; it predicts that the magnitude of the effect depends on the temperature gradient, the difference in the molecular weights and the relative amounts of the components and the average molecular weight of the mixture.

These thermal diffusion forces can be overcome by agitating the gas which for these experiments means a sufficiently high flowrate. Errors, however, can also by produced by fast flowrates if the gas is not given sufficient time to reach the equilibrium temperature before it comes into contact with the condensed phases. There is therefore a range of permissible flowrates which can be found if the gas composition is determined as a function of flowrate; a constant gas composition for a varying flowrate proves the absence of thermal diffusion.

Experimental studies relevant to the present investigation have been made by Darken and Gurry (21) and by Alcock and Richardson (22). Darken and Gurry used carbon dioxide,

carbon monoxide gas mixtures in a vertical furnace and found that thermal diffusion effects were much less apparent when the gas was passed up instead of down the furnace. Alcock and Richardson used hydrogen, hydrogen sulphide gas mixtures in an apparatus similar to the present one. They found that for a 1 inch bore reaction tube a gas mixture with $p_{H_2}/p_{H_2S} \approx 10^3$ and a temperature of 950°C, thermal diffusion was absent when a flowrate of 200 cc/min was used. Their results were verified for the present system with the aid of a sample of cuprous sulphide containing radioactive sulphur (isotope 35_S), and a Geiger Muller gas counter in the gas circuit. A continual record of the gas composition could then be kept whilst the flowrate was varied. No thermal diffusion was found with a temperature of 1000°C for flowrates between 270 and 550 cc/min. A complete description of these experiments is given in Appendix 2.

It was initially decided to use this radioactive tracer technique for all the work because of the simplicity of the gas analysis and because a continual record of the gas composition could be kept, but this decision was later reversed for the following reasons -

1) The electronic equipment available gave continual trouble, in addition to which the operator did not have a good knowledge of electronics (39 valves and 200 resistors and capacitors in a scaler) and the Harwell maintenance

service was not as efficient as it is at present.

2) The tracer technique had to be standardized by the chemical method and was therefore less accurate due to an additional counting error.

3) The time saved when the analyses were done by a tracer technique was less than the time taken to prepare the radioactive sulphide and to perform normal repairs on the counting mechanism.

Tracer techniques are only recommended where normal methods fail, for example, where it is impossible to take and analyse gas samples (e.g. when working with very low hydrogen sulphide pressures) or where a very large number of analyses have to be made.

The absence of thermal diffusion was further checked using stable sulphur. It was found that there was no appreciable difference between the equilibrium gas compositions obtained for flowrates of 275 cc/min and 530 cc/min at two temperatures one near each end of the temperature range investigated. The flowrates used for the rest of the experiments were between 325 and 500 cc/min.

<u>The presence of molecules other than hydrogen or hydrogen sulphide in the gas phase.</u>

At high temperatures hydrogen sulphide is in equilibrium with various gaseous polyatomic molecules or sulphur. The presence of diatomic sulphur gas, which would have been the most abundant decomposition product of hydrogen sulphide at the highest temperatures, might have been of importance.

When the equilibrium gas mixture was cooled leaving the furnace the diatomic sulphur would have combined with hydrogen to form additional hydrogen sulphide making the mixture from which samples were taken for analysis richer in hydrogen sulphide than that in equilibrium with the condensed phases. The greatest possible error however due to this cause was calculated to be less than 0.1% of the equilibrium constant.

At the high temperatures the silica in the mullite could have been reduced by hydrogen to give the gas silicon monoxide which could have contaminated the copper and cuprous sulphide and have altered the activities of these substances. The copper and the sulphide were therefore analysed separately after all the equilibrium measurements had been made. In both samples the percentages of silicon and of alumina were less than 0.1% and were therefore small enough to be ignored.

No attack whatever of the alumina boats by the solid or liquid sulphide could be seen which was confirmed by the analysis mentioned above. Equilibrium was approached from both sides (i.e. high and low sulphur pressures) and circulation continued for varying lengths of time to ensure that true equilibrium had been obtained. The approach to equilibrium was very fast, 1.5 hours circulation being sufficient for the majority of the experiments.

The experiments were done in a random order to ensure that any harmful effects which might have become gradually worse with time would be immediately detected.

To conclude and summarize this description of the work a detailed account of an equilibrium experiment will be given.

1. The apparatus was filled with hydrogen and the furnace adjusted to the required temperature.

2. Circulation was continued for 1.5 hours with a flowrate of approximately 400 cc/min. If it was required to approach equilibrium conditions from high sulphur pressures the furnace temperature was then lowered 50°C and circulation continued for another 1.5 hours.

3. The standardization of the sodium hypochlorite solution was checked.

4. Circulation was stopped and the temperature and pressure (a combination of atmospheric pressure, and of the difference between atmospheric pressure and the pressure inside the apparatus as measured by the manometer in the gas circuit) of the gas in the sampling bulb noted. The sample was then flushed out, using hydrogen at a flowrate of 150 cc/min for 1.5 hours, into a standard alkaline solution of sodium hypochlorite.

5. This solution was carefully boiled for 5 mins. excess 10% potassium iodide solution and 6N hydrochloric acid solution added, and the liberated iodine titrated with

standardized (by 'Analar' potassium iodate dried at 170°C overnight) sodium thiosulphate solution.

RESULTS

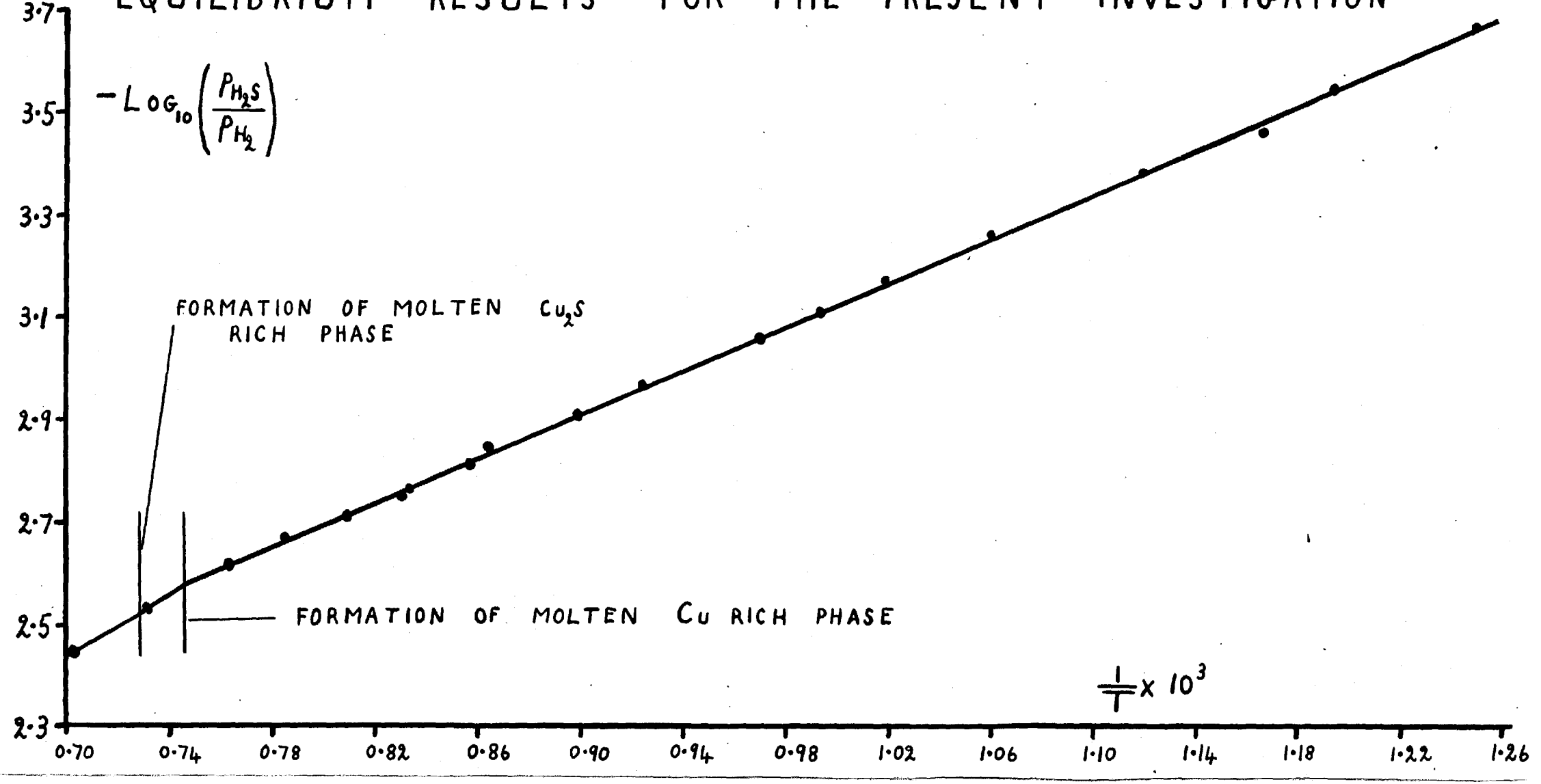
The results for the present investigation are most conveniently summarized in a graph of log $\left(\frac{p_{H_2S}}{p_{H_2}}\right)$ against $\frac{1}{T}$ (Fig.5). In regions where there are no phase changes this graph should be a straight line and therefore provides a useful check on the accuracy of the results. The results are presented in Table 2 (page 35); their order represents the order in which they were obtained. The flowrates for the experiments used to confirm the absence of thermal diffusion are shown in the fourth column, flowrates for all the other experiments were between 325 and 500 cc/min. The letters H and L in the last column indicate whether equilibrium was approached from high or low hydrogen sulphide pressures.

TABLE 2

Temperature in °C	$\frac{1}{T} \times 10^3$	$-\log \frac{(p_{H_2S})}{(p_{H_2})}$	flow-rate in $\frac{cc}{min}$	H or L
1001	0.785	2.672		L
708	1.019	3.170		L
1038	0.763	2.616	510	L
809	0.924	2.965		L
884	0.864	2.848		L
670	1.060	3.258	275	H
669	1.062	3.279		L
758	0.970	3.060		H
671	1.059	3.258	550	L
839	0.899	2.908		H
734	0.994	3.110		L
1040	0.762	2.614	275	L
963	0.809	2.711		H
930	0.831	2.751		L
1094	0.731	2.537		L
1094	0.731	2.530		L
1152	0.702	2.449		L
1149	0.703	2.443		L
926	0.833	2.765		L
894	0.851	2.816		L
893	0.858	2.812		L
620	1.120	3.381		L
564	1.195	3.542		L
527	1.250	3.659		L
584	1.167	3.460		H

FIG 5

EQUILIBRIUM RESULTS FOR THE PRESENT INVESTIGATION



Errors

In the experimental determination of the equilibrium constant there were only two main sources of error, firstly the gas analysis which could have caused an error in the equilibrium constant of ± 1%, and secondly the temperature measurement. The possible nonrandom errors in this are as follows:-

Calibration of the thermocouple by the makers ± 2°C

" " " " " " author ± 1°C

Even temperature zone in the furnace ± 2°C

The nonrandom error in the temperature measurement may therefore be ± 5°C which would give an error in the equilibrium constant of ± 3%. When this is combined with the error in the gas analysis the total nonrandom error becomes ± 4%. The internal consistency of the results was ± 2%. It is considered unlikely that all the above nonrandom errors exerted their maximum force in the same direction and it is therefore reasonable to conclude that an error of ± 3% of the average value of the equilibrium constant is a fair estimation of the accuracy of these results.

The graph of log (p_{H_2S}/p_{H_2}) against $\frac{1}{T}$ proved to be a straight line from which it was possible to calculate the standard free energy equation for the reaction

$$H_2 + Cu_2S(\beta) \longrightarrow H_2S + 2Cu.$$

$\Delta G^\circ = 9.84 + 0.00445T$ Kcals C

$(530^\circ C - 1040^\circ C)$

$\Delta H^\circ = 9.84 \pm 0.15$ Kcals/mole

$\Delta S^\circ = -0.00445 \pm 0.00018$ Kcals/mole deg

The standard free energy equation for the reaction between copper and diatomic sulphur gas can be obtained if equation C is combined with the standard free energy equation given by Richardson and Jeffes (6) for the dissociation of hydrogen sulphide into hydrogen and diatomic sulphur gas.

$$2\,Cu + \tfrac{1}{2}\,S_2 \longrightarrow Cu_2S\ (\beta)$$

$\Delta G^\circ = -31.42 + 0.00735T$ Kcals.

DISCUSSION OF RESULTS

All the previous work of any importance is summarized in Figure 1.

The data of Schuhmann and Moles is in good agreement (within 2% of the equilibrium constant) with the present investigation whilst that of Sudo and that of Cox and co-workers give slightly higher hydrogen sulphide pressures.

The disggreement of Sudo is only small (5% of the equilibrium constant) and can partially be explained by the experimental method he employed. This was to continuously pass pure hydrogen at various flowrates over a mixture of copper and cuprous sulphide and to analyse the hydrogen, hydrogen sulphide gas mixtures formed. The gas compositions for no flowrate would be those in equilibrium with the condensed phases (assuming thermal diffusion to be absent) and to obtain them graphs of $\frac{P_{H_2S}}{P_{H_2}}$ against flowrate (all the measurements for one graph having been made at one temperature) were extrapolated linearly to a flowrate of zero. It is possible that these graphs were not straight lines but curves with the gas compositions becoming almost constant at the lower flowrates, which would mean that the equilibrium hydrogen sulphide pressures obtained by Sudo were too high. The maximum error that could have arisen from this cause is

5% of the equilibrium constant, which would explain the discrepancy between the two sets of results, but an error of 2 or 3% is considered more probable. A difference of 2 or 3% still remains unexplained, but this is well within the limits of accuracy for the two sets of results and may be ignored.

Cox and co-workers' results are badly inconsistent at the lower temperatures. The present results lie within the scatter but at the higher temperatures Cox 'et al' definitely obtained higher sulphur pressures. The flowrate they used (60 cc/min through a 1 inch bore reaction tube) was much less than that in the present investigation and the discrepancy between the two sets of results could be explained if it was too low to overcome the thermal diffusion forces. Further support for this explanation is provided by the results of Alcock and Richardson and of Cox 'et al' for ferrous sulphide. Alcock and Richardson (10) have been able to show that a similar discrepancy between these two sets of results is due to thermal segregation of the gases in the experiments of Cox 'et al'.

The results presented here are consistent, therefore, with previous work, and it is considered that they, together with the results of Schuhmann and Moles provide at present the most accurate and complete picture for the thermodynamic behaviour of cuprous sulphide at elevated temperatures.

SECTION 2

"THIN FILMS OF CUPROUS SULPHIDE ON COPPER"

INTRODUCTION

The reasons for starting the present part of this research have already been explained in the General Introduction, and only a more detailed account of the relevant literature need now be given.

Thin films of wustite on iron

Gellner and Richardson (23) in 1951 studied the mechanism of the reduction by hydrogen of wustite layers grown on strips of polycrystalline iron. The layers were approximately 0.01 mm thick and were grown by oxidizing the iron with a hydrogen, water vapour gas mixture. They were reduced in a stream of pure hydrogen for various lengths of time at various temperatures between 600°C and 1000°C, and then quenched, sectioned, polished and examined under a microscope. At 900°C a thin layer of iron was first formed on the wustite surface, additional iron produced by the reduction was then deposited next to the substrate metal. At 700°C reduction proceeded, as would be expected, from the wustite surface inwards. At intermediate temperatures reduction proceeded simultaneously

inwards from the surface and outwards from the substrate metal. To explain these results, Gellner and Richardson suggested that the oxide in the immediate neighbourhood of the basis metal was less stable than the oxide on the surface, and that there was a gradation of stability across the wustite layer. An observation consistent with this hypothesis is that of Chipmann and Marshall (24) who observed that iron in slightly oxidizing atmospheres sometimes remained unattacked although once oxidation had commenced this passivity greatly diminished or disappeared.

Darken and Gurry (25) have recently tried to determine the thermodynamics of bulk wustite in equilibrium with iron by assuming that films of wustite grown upon iron behave in the same manner as the bulk phases. A strip of iron was suspended in a temperature gradient and in a gas mixture of fixed oxygen potential, which was adjusted so that only the hottest parts of the iron were oxidized. When the strip was removed from the furnace a sharp boundary was found between the unattacked iron and that having a surface layer of wustite. The temperature of this boundary was taken as the temperature at which bulk wustite was in equilibrium with iron at a known oxygen potential. In view of the work of Gellner and Richardson this appears a dangerous assumption. The present experiments were designed with the aim of determining the stability of cuprous sulphide films thinner than the wustite ones used by Gellner

and Richardson. They might therefore provide data which would support Gellner and Richardson's hypothesis and which would show the potential dangers of the experimental method employed by Darken and Gurry.

Bardolle and Benard (26) have recently done some work on the mechanism of the growth of wustite layers on iron. Their results were similar, in some respects, to those obtained by the author and were published after this section of the work had been completed. Bardolle and Benard grew their films at temperatures between 650°C and 850°C and at oxygen pressures of 10^{-1} to 10^{-3} atmospheres. At 650°C thin temper films of oxide were obtained which completely covered the iron surface. Their colour and hence thickness varied from one grain of iron to another; the grain boundaries were clearly defined by these different colours. At higher temperatures (850°C) the temper films were not formed, instead the surface was covered by small isolated patches of oxide which grew more readily on certain grains; the effect was sufficiently marked for phenomena connected with grain growth to be observed. In addition, it was noticed that the oxide had definite directions of preferred orientation which were different for different grains. This implied that the orientation of the oxide was dependent upon that of the basis metal. Mehl and McCandless (27) have

pointed out that the spacing of the iron atoms in α iron and in wustite is very similar, and that this similarity would give a film of oxide a preferred orientation with respect to a substrate of iron. The cube faces of the oxide and the metal would meet and be in the plane of the interface, and a (110) plane in the metal perpendicular to the interface would correspond to a (100) plane in the oxide. Bardolle and Benard took Laue X-ray photographs which confirmed this relationship for their films.

Gulbransen and Ruka (28) have been able to show that structural relationships between a film and its substrate can greatly influence the stability of the film. They grew thin films of magnetite on iron (unfortunately they did not mention the thickness of their films) and determined the transformation temperature for the reaction

$$Fe_3O_4 + Fe \longrightarrow 4\ FeO,$$

from electron diffraction photographs of the surface taken at various temperatures. From known thermodynamic quantities this temperature was predicted as 570°C for the bulk phases; Gulbransen and Ruka found however that for some of their thinnest films the transformation temperature was as low as 530°C, and that on increasing the thickness of the films this temperature rose to 570°C.

These results were explained by the fact that iron and wustite have the simple structural relationship shown by Mehl and McCandless whilst no such relationship exists for iron and magnetite. The wustite films were therefore preferentially stabilized which caused the transformation temperature to have been lowered. This work therefore provides additional evidence of the importance of structural relationships at the interface and still further emphasizes the need for accurate stability measurements on thin films.

Thin films of alkalie halides on various substrates

Schultz has published a series of papers in which he describes some qualitative results he obtained growing thin films of various alkalie halides on substrates of glass, mica, silver, sodium chloride, sodium nitrate and calcite (29). Most of the films were grown in two ways, firstly by crystallizing them from an aqueous solution, and secondly by the evaporation of the halide onto the substrate in vacuo. Schultz studied the films using various electron diffraction techniques and was able to determine their structure and orientation. The most interesting facts he observed were that:-

1) The final structures and orientations of the films were in most cases, although not all, the same when the two methods of preparation were used.

2) Polymorphism for some of the deposited halides was obtained where the crystal energies of the usual and unusual structures were similar. For example caesium chloride had the unusual sodium chloride structure on substrates of lithium fluoride, sodium chloride and mica. With a lithium fluoride substrate this unusual structure was obtained for crystals 100 - 200A high but for films with an average thickness greater than this, crystals were formed which were not in contact with the substrate and which had the normal body centred cubic structure.

3) Many of the films were strongly orientated. It was often possible to relate this orientation to atomic matching at the interface. For example, when caesium chloride was evaporated onto calcite it had the sodium chloride structure, but when crystallized from solution it had its normal body centred cubic structure. Different orientations were obtained for these two structures, but in both cases they were consistent with the best atomic matching at the interface.

4) When very thin films were grown by the evaporation method two different types of film were possible. If the atomic matching was bad the first few layers would migrate across the surface to give separate crystals. For example a layer of caesium chloride 10A thick on

lithium fluoride migrated to give discrete crystals 100 - 200A high. These crystals had the unusual sodium chloride type structure and were orientated with their axes parallel to those of the substrate. When the atomic matching was good (10% and 20% for substrates of mica and sodium chloride respectively) the first few layers were bound strongly to the substrate and separate crystals were not obtained until the films were thicker than 10A, when the bonds across the interface were presumably too weak to be effective.

Thermal etching

Chalmers in an excellent paper in 1948 (30) summarized all the previous work on the subject of thermal etching, presented some results for surfaces of silver and put forward some simple explanations for the phenomenon.

Striations have been produced on copper and silver surfaces when these metals have been maintained at a high temperature in an atmosphere containing oxygen, the higher the oxygen pressure the more pronounced the striations. Magnified these stations resembled a series of close, fine, parallel lines, their direction varied from grain to grain. They were unstable in inert atmospheres and disappeared in nitrogen for example, but repppeared with the same orientation, although the spacing between them differed in some cases, when the nitrogen was replaced by oxygen. Grooves were normally obtained at the grain boundaries but the photo-

micrographs of silver taken by Chalmers clearly show that the striations were not grooves but steps in the surface. Chalmers suggested that the presence of oxygen may have modified the equilibrium configuration of the surface, so that a stepped up structure in which specific crystallographic planes were developed resulted; the final state of the surface would have had less free energy than the original smooth surface of smaller area but of arbitrary orientation. Theoretically the oxygen could have produced this effect if it had been preferntially adsorbed on certain crystal planes (the developes ones) thereby lowering the energy of these planes. This explanation is consistent with the preferential attack of certain grains which has been observed in the oxidation of many metals including copper (31), and on which all etching processes depend. In addition Chalmers suggested that the most important mechanisms in the formation of these striations were the surface movement of metal atoms or ions, and the preferential attack by oxygen of certain crystal planes (the developed ones) followed by volatilization and condensation of the molecular oxide.

EXPERIMENTAL METHOD AND PROCEDURE

The principle of the method adopted here, to study the stabilities of thin films of cuprous sulphide on copper, was to determine the compositions of hydrogen, hydrogen sulphide gas mixtures which were in equilibrium with the films, and then to compare the values obtained with those obtained for the bulk phases in Section 1.

The apparatus was almost the same as that in Section 1, the only difference being that a small bulb was introduced into the gas circuit between the furnace and pump.

A piece of pure copper foil (4 cms x 5 cms x 0.01 ins) was placed in the furnace and heated in a stream of hydrogen for two hours at 900°C. This annealed the copper and reduced any oxide film. The small bulb was filled with hydrogen sulphide which was then dispersed throughout the rest of the gas circuit by circulation. All the hydrogen sulphide in excess of that necessary to form the equilibrium gas mixture reacted with the copper and formed a film of cuprous sulphide. The time necessary for the attainment of equilibrium conditions was taken as the same as that for the bulk phases in Section 1. Therefore after 1.5 to 2 hours circulation at 350 to 400 cc/min a gas sample was taken and analysed as in Section 1. The furnace was

then cooled and the copper foil removed and examined under a microscope.

The quantity of sulphur which combined with the copper was estimated from an approximate value of the volume of the apparatus and from a 'blank' partial pressure of hydrogen sulphide, obtained from a similar experiment in which there was no copper foil in the furnace. The volume of the small bulb was adjusted to give a film of approximately 400 atom layers providing the film was of uniform thickness. The final films obtained however were thicker than this and grew in patches (v.infra).

The experimentally determined 'blank' partial pressure of hydrogen sulphide ($p_{H_2S} = 1.5 \times 10^{-3}$ atms)was in excellent agreement with the theoretical value ($p_{H_2S} = 1.6 \times 10^{-3}$ atms) obtained from the volume of the small bulb and that of the apparatus. If in the equilibrium experiments described in Section 1 there had been a continual loss of sulphur from the gas phase, and hence the sulphide sample, the gas would never have been able to reach its equilibrium composition. The excellent agreement of the two values of this 'blank' partial pressure however prove this not to have been the case, and provides further evidence of the reliability of the results obtained in Section 1.

The exact manner in which the films had grown was not clear, all that was done was to examine the final state of the films. No measures were taken to throughly mix the hydrogen sulphide with the hydrogen in the rest of the gas circuit before the gas mixture came into contact with the copper specimen. Mixing effects will have been produced by the gas pump and large gas sampling bulb, but in spite of these effects the gas mixture in its first passage over the copper must have been inhomogeneous. This inhomogeneity can be thought of as a volume of gas, with a high hydrogen sulphide concentration, moving round the gas circuit. The speed of reaction shown by the bulk phases suggests that in the first passage of the gas most of the excess sulphur in the hydrogen sulphide rich part of the mixture reacted with the copper, and that the following gas deficient in hydrogen sulphide removed some of this sulphur to give the correct equilibrium gas composition. To express it in another way an excess of cuprous sulphide was initially formed and was later reduced back to copper. This fact could not have affected the equilibrium measurements, but in a qualitative discussion of the final state of the film it might be of importance.

Chemicals Used.

Copper

Johnson and Matthey Co.Ltd. "spectrographically pure" copper foil was used, the trace elements* in which were spectrographically determined as silver - 0.001%, lead - 0.001%, nickel - 0.0005%, iron-line just visible, galium - line barely visible.

Hydrogen Sulphide

A steady stream of hydrogen sulphide was generated by continually adding dilute sulphuric acid to a solution of sodium sulphide. The gas was dried by calcium chloride and magnesium perchlorate before use.

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* These values were kindly supplied by Johnson & Matthey Co. Ltd.

RESULTS

Three films were investigated each at a different temperature. The results obtained are summarized in Table 3. As the equilibrium times were different in each experiment they are given in the last column.

Table 3

Temperature in °C	$\left(\frac{p_{H_2S}}{p_{H_2}}\right)$ film	$\left(\frac{p_{H_2S}}{p_{H_2}}\right)$ bulk phases*	Equilibrium time in hours
713	7.05×10^{-4}	7.01×10^{-4}	2
790	9.79×10^{-4}	1.005×10^{-3}	1½
841	1.224×10^{-3}	1.241×10^{-3}	2½

The equilibrium gas compositions obtained for the films and for the bulk phases* are in agreement with one another within the limits of experimental error. It follows therefore that the standard free energies of formation and hence the stabilities of these films were very nearly the same or identical to those of the bulk phase.

It had been hoped that a uniformly thin film would be obtained but this was not the case. Instead it was found in all three experiments that the films grew in patches. An estimation of their thickness was obtained from the quantity of sulphur removed from the gas phase

* These values were obtained from Section 1.

and the area of copper surface covered, but a method using a microscope was found more satisfactory as this could be applied to any specific area of the surface. Here the vertical displacement of the microscope necessary in focusing on the copper surface and then on the film gave the thickness of the film.

Each film could be divided into three almost equal sections which were defined by the direction of gas flow i.e. one third which came into contact with the gas first, a middle third and a final third.

Sulphide formation was more abundant on the first third. Here nearly the whole copper surface was covered by a layer of dark grey sulphide, approximately 0.003 mm thick, which still contained however small specks of bright copper. Occasionally a single black crystal of sulphide would rise steeply to a height of 0.01 mm but these crystals only covered a very small part of the total surface.

The middle third was not so badly attacked; the areas of sulphide film and of bright copper were about equal. The average thickness of the films was still 0.003 mm. For this part of the surface all the films had a slightly different appearance as each one had grown in a characteristic way (v.infra).

The final third was only slightly attacked but still showed the characteristic properties of the middle third.

In addition to these properties whole grains were covered with thin temper films of different colours. These temper films were ignored because they could have been formed when the specimens were cooled to room temperature in a hydrogen sulphide rich atmosphere.

The characteristic properties shown by the last two thirds of the films will now be described. They are recorded in photomicrographs 1-6 which were taken without the surface being treated in any way (polished etc.)

The sulphide growth for the film grown at 713°C was more pronounced at the grain boundaries from which the sulphide grew with a dendritic structure. These dendrites had for a given copper grain several directions of preferred orientation (Photomicrographs 2,3,4). This effect was not so pronounced as for the wustite films of Bardolle and Benard but was sufficiently apparent to imply that there was some simple structural relationship between the metal and sulphide at the interface. Some grains were much more favourable to sulphide growth than others being completely covered, except for small specks of copper, whilst their neighbours were comparatively unattacked (Photomicrographs 1,2,3). This property is consistent with previous work, because similar effects were recorded by Bardolle and Benard for their wustite films and by Gwathmey and Benton for oxide films grown on a single crystal of copper in

oxygen (31).

For the film grown at 841°C the preferential growth away from grain boundaries and on certain grains was not pronounced. Patches of sulphide were obtained with an average height of 0.003 mm (Photomicrograph 5), but they nearly all had a small black crystal in their centre rising steeply to a height 0.01 mm. The dendritic nature of the sulphide crystals was less but the crystal size was greater for this film than for the films grown at lower temperatures. These differences could have been due to the slightly longer equilibrium time used in the formation of this film, but it is doubtful if this would have produced such large effects which are mainly attributed to the fact that this film was grown at a higher temperature. The most interesting effect observed for this film was that many of the copper grains appeared striated (Photomicrograph 6). These striated grains were not confined t o any part of the surface and were not found for the other two films. The striations were not thought to be slip planes, firstly because of the long annealing time given to the copper before use, and secondly because they did not look like slip planes being too close together. Instead they were thought to be similar to the striations obtained by Chalmers and co-workers (30) for silver and by other workers for copper when in the presence of oxygen (31) (32), and were therefore formed by a thermal etching process.

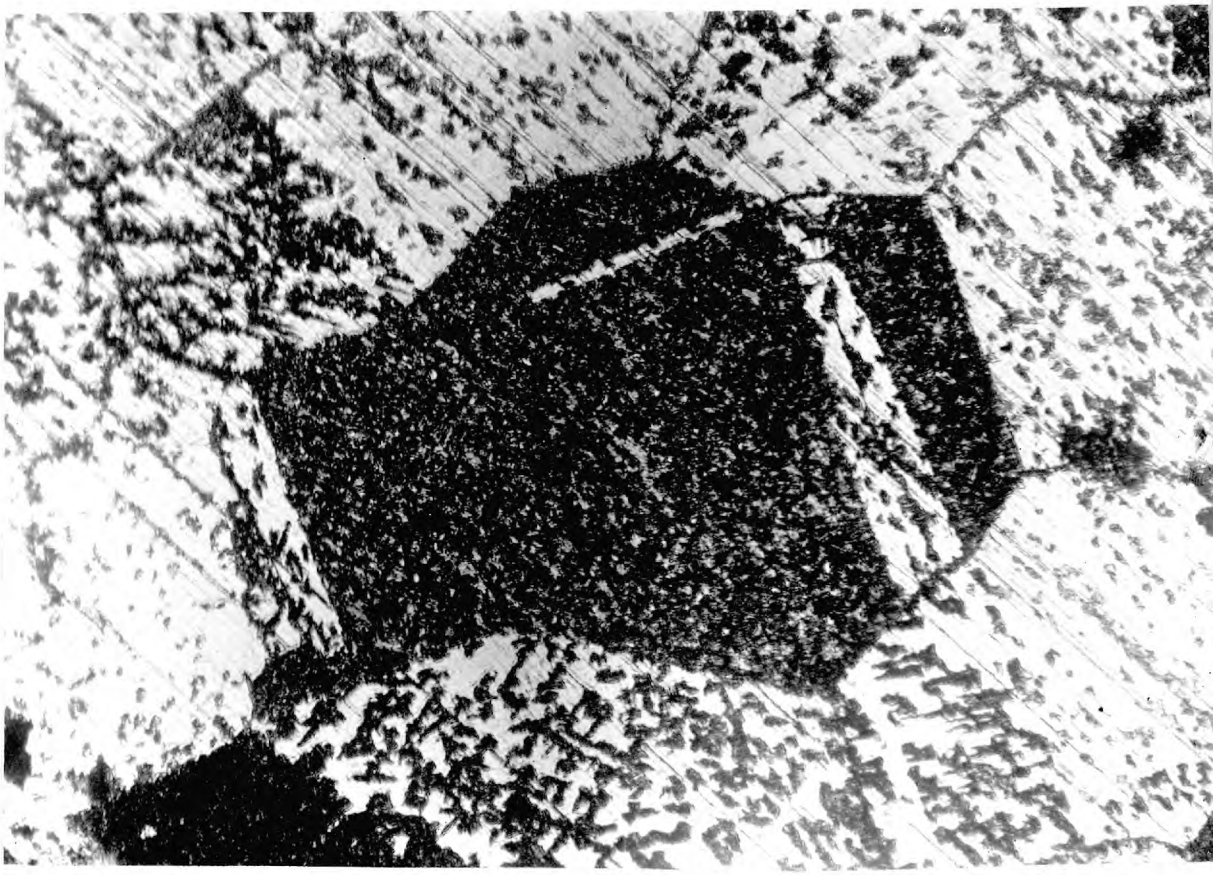
If the ideas of Chalmers are applied to this system the presence of sulphur should have altered the equilibrium state of the copper surface so that a stepped up structure resulted. This alteration in the equilibrium state would have been due to the sulphur being adsorbed preferentially on the developed crystallographic planes and would have produced a surface of lower ~~total~~ free energy. If this explanation was true sulphide growth should have been more favourable on certain crystal faces including the developed planes, but it has been pointed out that at the high temperatures at which striations were obtained preferential growth on certain grains was not prominent, although the dendrites in their initial stages of growth were usually parallel to the striations and hence may have grown on the developed planes. Further discussion on this point is however not justified because the ideas of Chalmers can only be treated as tentative suggestions not as established facts.

The characteristic properties of the third film grown at an intermediate temperature (790°C) were, as would be expected, similar to those for the two previously mentioned films and therefore need no further description.

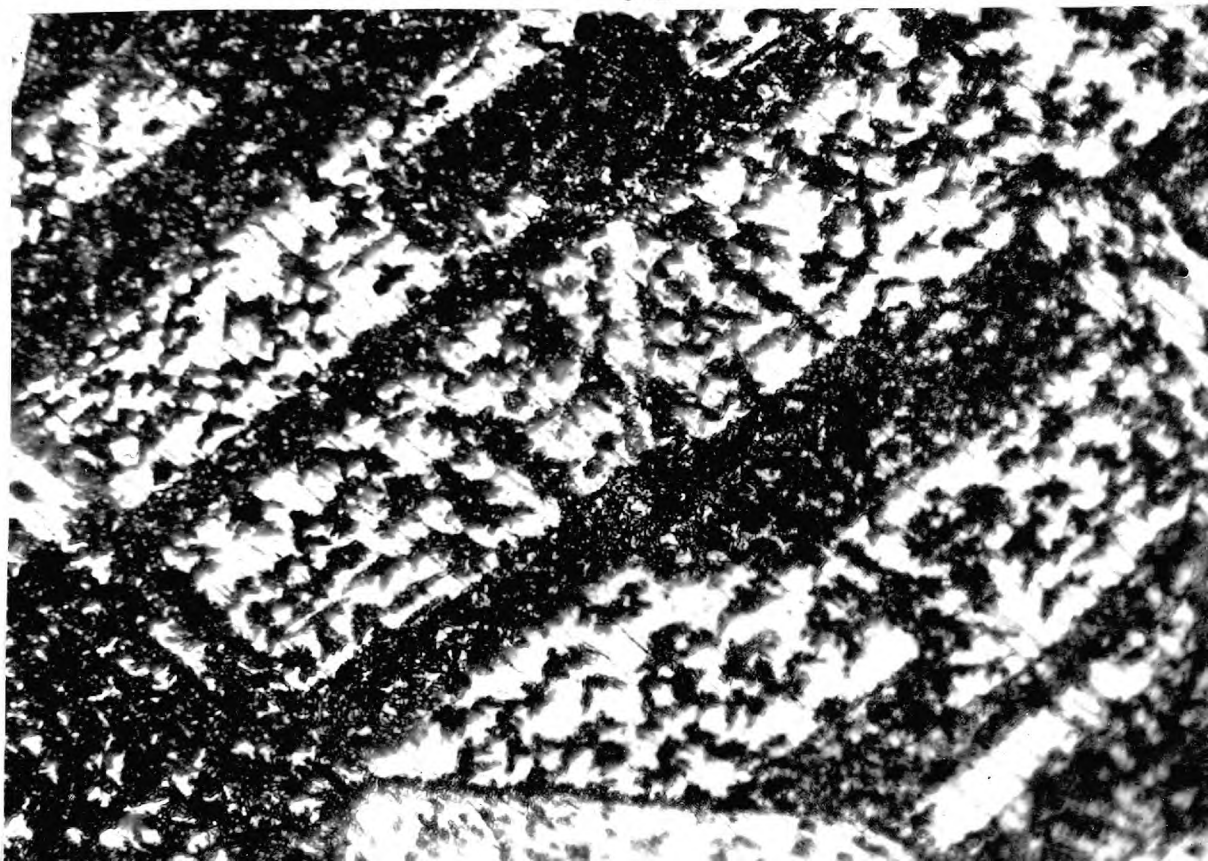
PHOTOMICROGRAPHS

1. The film was grown at 713°C Magnification = x 145
2. " " " " " 713°C " = x 250
3. " " " " " 713°C " = x 450
4. " " " " " 713°C " = x 1000
5. " " " " " 840°C " = x 145
6. " " " " " 840°C " = x 660

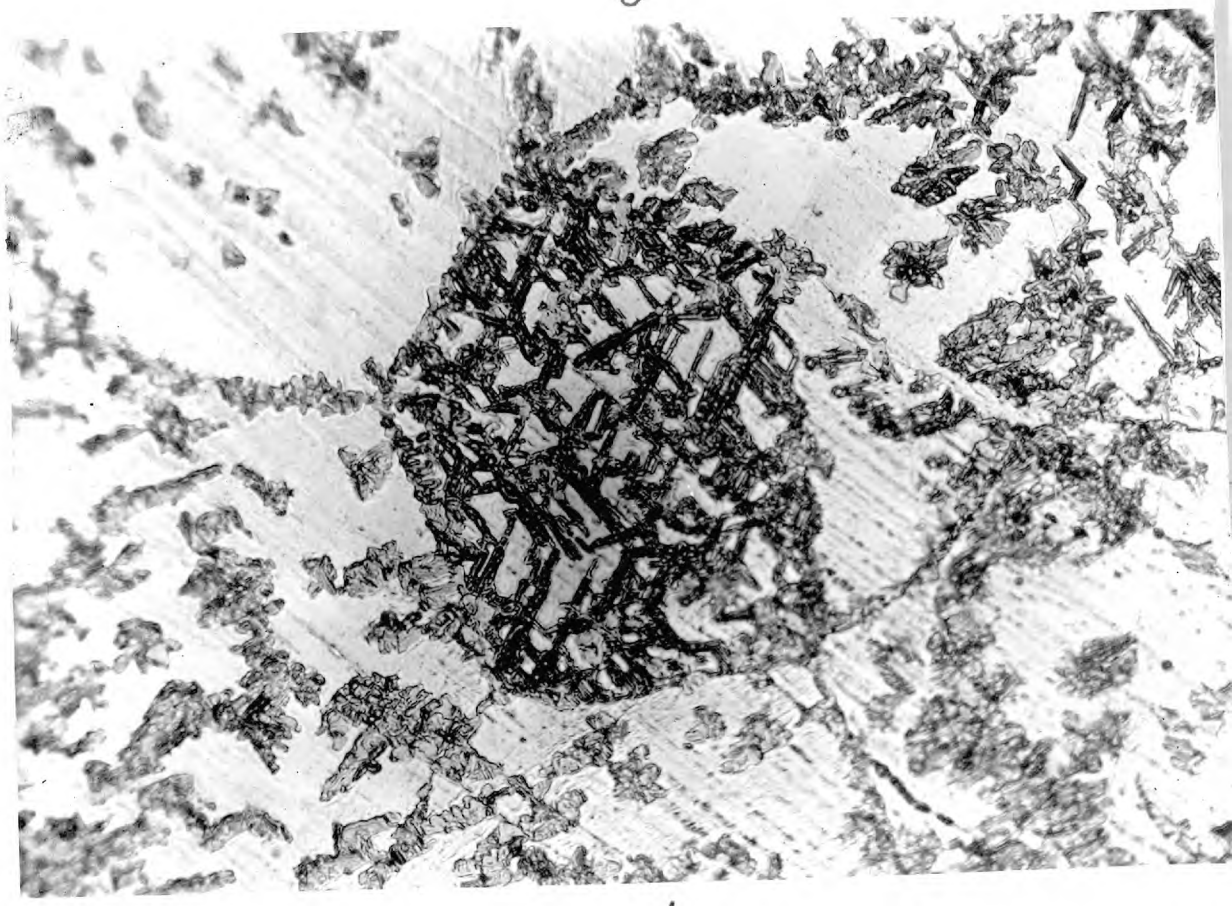
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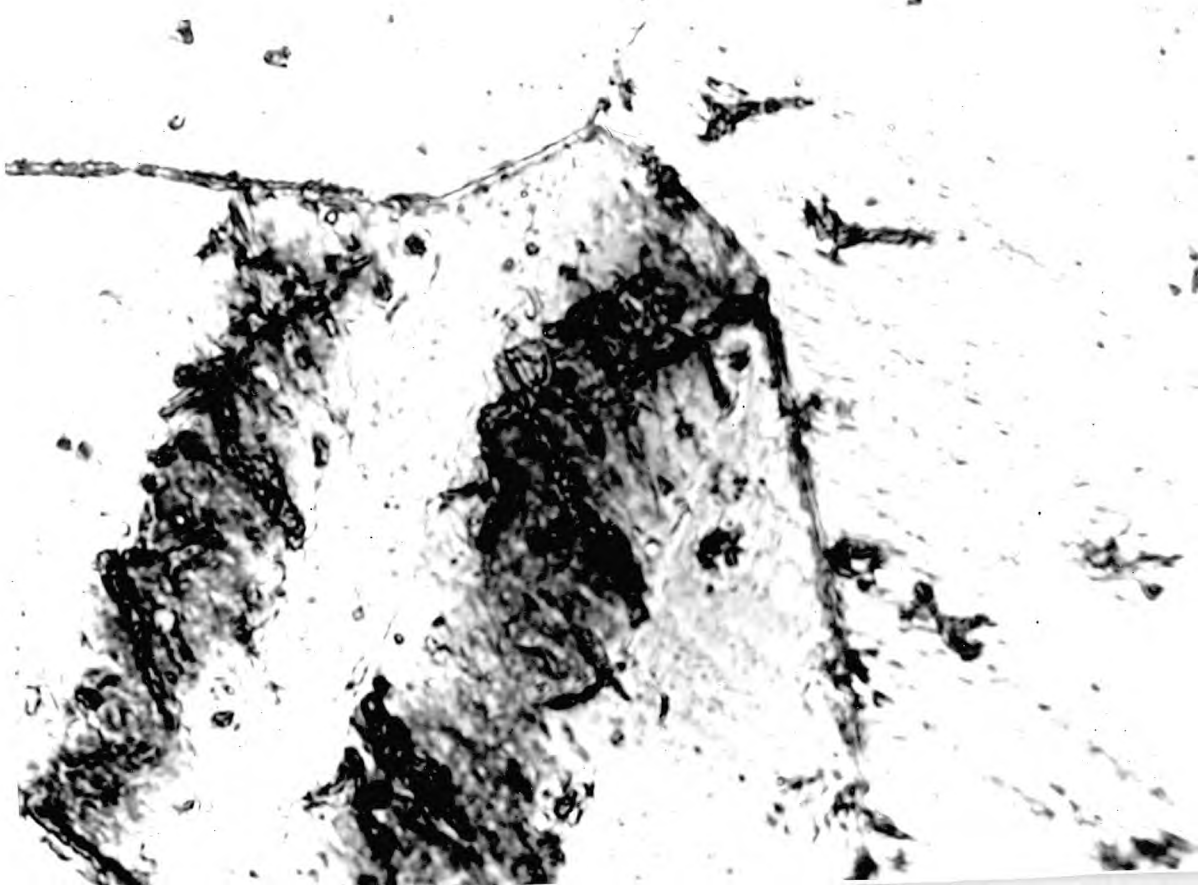
2



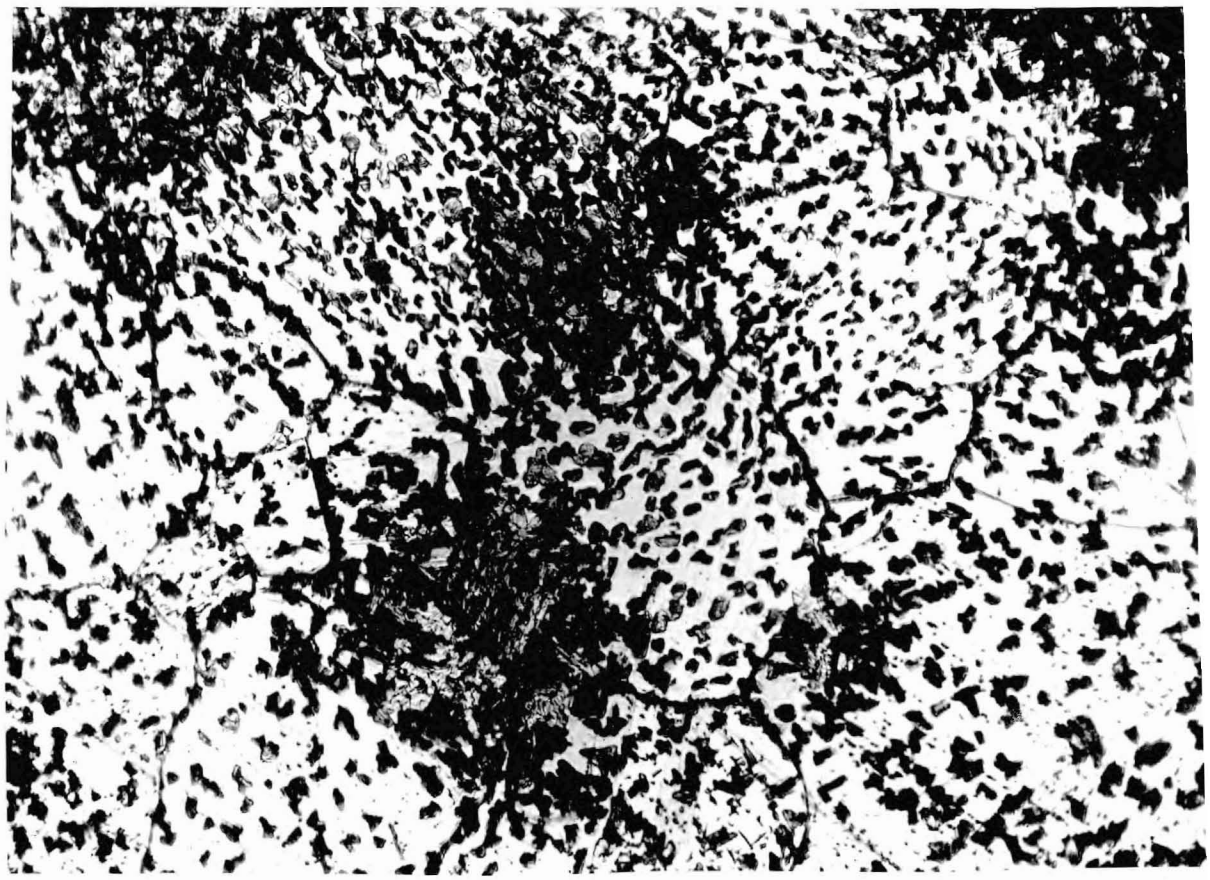
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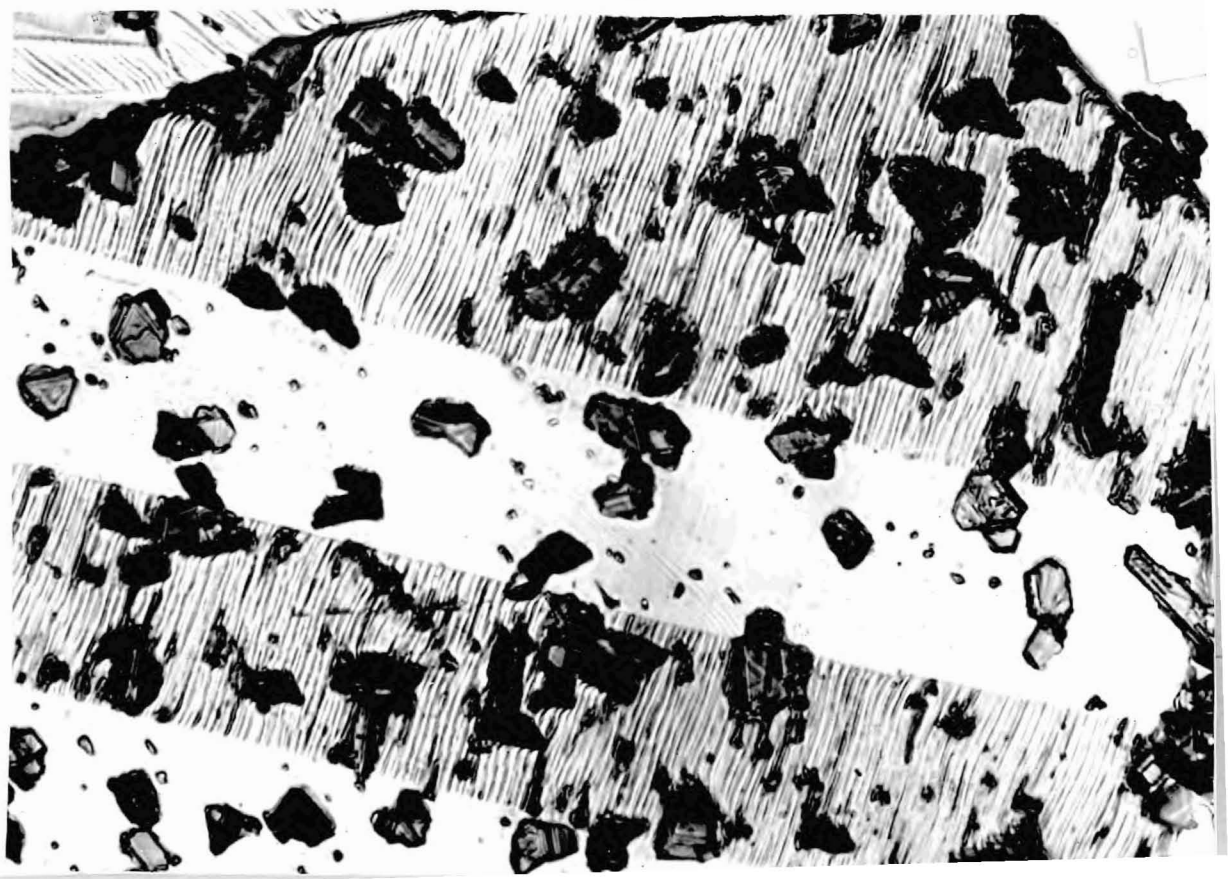
4



5



6



DISCUSSION OF RESULTS

The previously described phenomena and results are of interest in widely differing fields; an attempt will now be made to summarize them and to draw additional conclusions.

These films grew in patches which made them resemble in many ways the films of Schultz and of Bardolle and Benard, and they are therefore consistent with the present knowledge of surface behaviour. One anomaly however is that Gwathmey and Benton (31), who grew thin films of oxide on a single crystal of copper at various oxygen pressures (0.5 to 1 atms) and at various temperatures (room to 1000°C), did not report a patchy appearance for any of their films. The patchy state could have been formed in two ways. Firstly, if initial nucleation of the sulphide on the surface had been difficult, sulphide growth may have taken place by the diffusion of copper atoms through nucleated sulphide and then the reaction of these atoms with the sulphur in the gas, rather th an by the direct reaction between gas and metal. Secondly a uniform thin layer of sulphide may initially have covered the whole surface. If it had been more unstable than the films observed the thicker parts could have then grown at the expense of the others, either by the surface

movement of atoms or by the transport of sulphur via the gas phase, to give the observed results.

There is evidence that the sulphide films grown at the lower temperatures had a preferred orientation with respect to the basis metal which could have been due to some sort of structural relationship existing at the interface. Unfortunately no useful contribution to the determination of this relationship could be made from these experiments, because the crystal planes which formed the copper surface could not be identified and because the atomic positions in a cuprous sulphide crystal were not known.

The existence of preferential sulphide growth and of striations, imply that surfaces of copper in the presence of sulphur behave in a similar manner to copper and other metals in the presence of oxygen. This aspect of the work was considered of great interest and of possible importance if followed up, but the main object of the research was to obtain thermodynamic data on films thinner than those used by Gellner and Richardson. This had been achieved and therefore no further work was done on the qualititative aspect.

Cuprous sulphide films approximately 0.003 mm thick at temperatures between 700°C and 840°C behave in the same way from a thermodynamic viewpoint as bulk cuprous

sulphide. Gellner and Richardson postulated a gradation of stability across a layer of wustite 0.01 mm thick. If this was also true for a layer of cuprous sulphide the films investigated would have been unstable with respect to bulk cuprous sulphide. The results presented here do not disprove the hypothesis of Gellner and Richardson for wustite, but they do prove that such a hypothesis is not valid for cuprous sulphide. Also they do not invalidate the experimental method employed by Darken and Gurry but it should be used with care as surface behaviour is still not clearly understood.

SECTION 3

"MIXTURES OF CUPROUS SULPHIDE AND SODIUM SULPHIDE"

INTRODUCTION

The reasons for starting this research and the objects it was hoped to achieve have been explained in the General Introduction and they will not be enlarged upon further. All that is therefore necessary to introduce this section is a summary of previous work and a small chapter explaining the thermodynamic treatments applied to these mixtures.

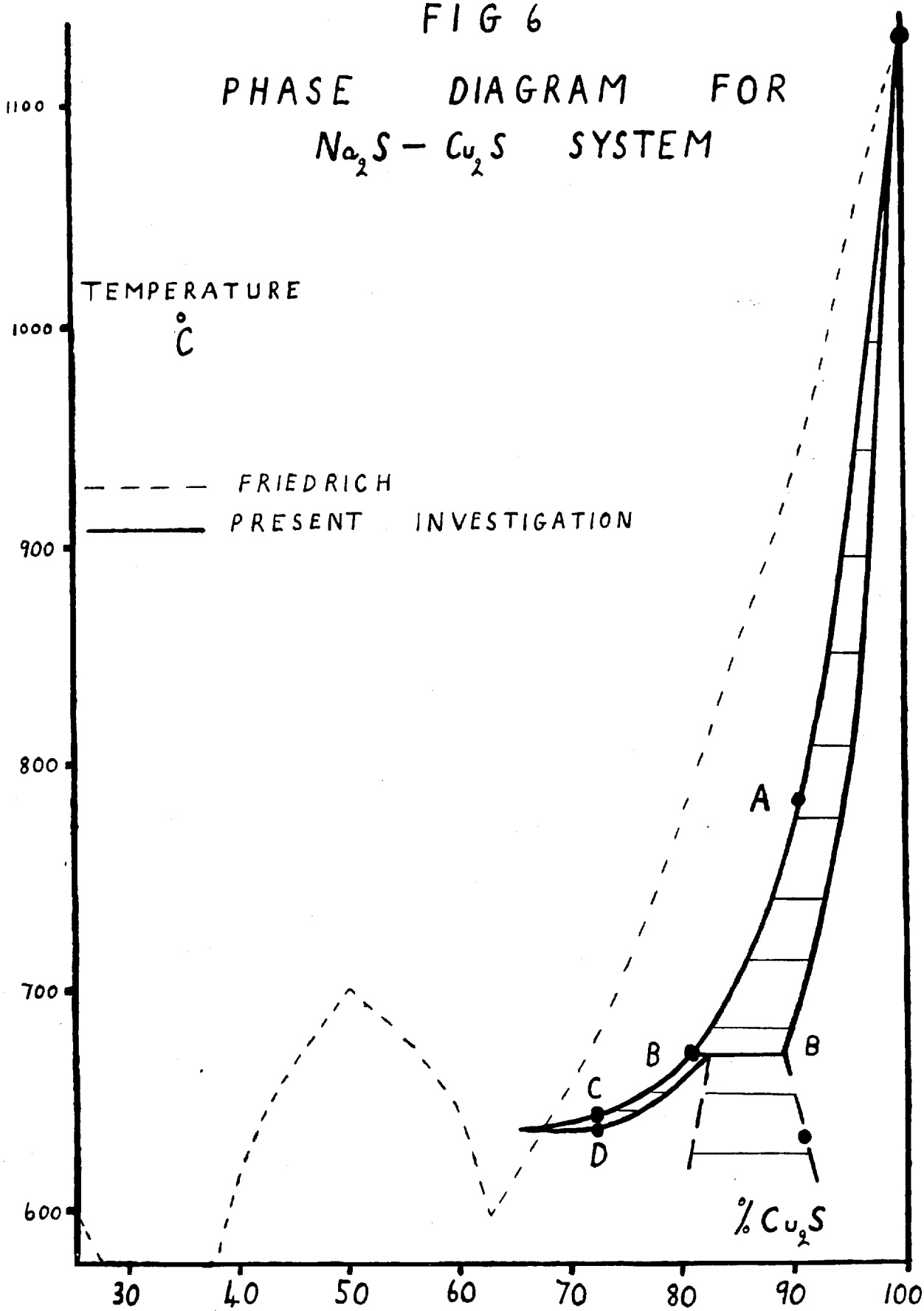
a) Previous work

Although there has been no work done on sulphides directly comparable with the present investigation two separate pieces of work are sufficiently important to be mentioned.

Phase diagram

Friedrich (33) in 1914 obtained a phase diagram for the cuprous sulphide-sodium sulphide system, part of which is shown in Figure 6. A maximum was obtained in the 50 mol% region from which it was deduced that a solid compound was formed of this composition. Further a rate of cooling technique was employed the curves for which showed two breaks one at the liquidus temperature and one at the relevant eutectic temperature. As these two breaks were obtained for numerous compositions it was concluded that there was no appreciable solid solution

FIG 6


PHASE DIAGRAM FOR
$Na_2S - Cu_2S$ SYSTEM
TEMPERATURE
°C
1100
1000
900
800
700
600
FRIEDRICH
PRESENT INVESTIGATION
A
B
B
C
D
% Cu_2S
30
40
50
60
70
80
90
100

for this system, but the work presented here has shown this conclusion to be wrong.

Conductivity Measurements

Some conductivity measurements for molten sulphide mixtures were made by Savelsberg (34) in 1940. The experiments were crude in that no attempt was made to use melts of high purity. Iron electrodes and iron and porcelain crucibles were sometimes used. They must have been attacked by the sulphide mixtures investigated and the results obtained can therefore only be considered reliable on a qualitative basis. A direct current arrangement was used which for electrolytic conductors caused a partial separation of the ions. This separation was investigated by having the cell divided into compartments and analysing the contents after all the conductivity measurements had been made. For molten mixtures which formed a compound in the solid state (Cu_2S. Na_2S; FeS2 Cu_2S) electrolytic conduction was obtained, and the more basic metal was transported towards the anode which implied that it was present in a complex anion. In ~~constant~~ contrast mixtures of cuprous sulphide and nickel sulphide, which do not form a solid compound, conducted electronically. Cuprous sulphide in a solid and liquid state also conducted electronically. With molten cuprous sulphide, sodium sulphide mixtures Savelsberg obtained, as mentioned above,

electrolytic conduction with the copper migrating towards, although no reference was made to it being deposited on, the anode. These results were reproducible and were well supported by the current potential curves and the analyses of the anode and cathode compartments. For example a current of 1 amp (at 6-7 volts) was passed for 25.5 hours through a molten 50 mole% cuprous sulphide mixture at 800°C. There was a loss of 1.0 gm (in 2 gms) of copper from the cathode compartment and a gain of 0.4 gms (in 16 gms) in the anode compartment. These results led Savelsberg to postulate the presence of Na^+ and CuS^- ions in the melts.

b. Theory

The main aim in a thermodynamic study of a series of mixtures is to obtain the activities of the components at as many temperatures and over as wide a composition range as possible. The experimental techniques for mixtures of organic molecules are normally simple, and the activities of each molecular component can be obtained directly by vapour pressure measurements for example. Mixtures of sulphides however need a different approach as these techniques are normally no longer applicable and the activities of the molecular sulphides have to be obtained from the activities of the constituent metals and sulphur. These can be determined by bringing the mixture to equilibrium with a gas and an alloy phase the compositions of which give

the activities of the sulphur and of the two metals respectively, providing the thermodynamic behaviour of these two phases is already known.

The experimental method employed in this work was to equilibrate a cuprous sulphide-sodium sulphide mixture with a metallic alloy phase and a gas mixture of hydrogen and hydrogen sulphide. After equilibrium had been established the compositions of the three phases were determined by analysis and the activities of the cuprous sulphide calculated. A similar calculation was not possible for the sodium sulphide because the activities of the sodium were too small to be determined from the compositions of the alloy phase.

The two condensed phases could have existed in a solid or molten state and have had numerous compositions. The alloy phase should have consisted mainly of sodium and copper, but it could have contained a little sulphur; whilst the sulphide phase should have consisted mainly of a mixture of the stoicheiometric sulphides, but it could have contained an excess of any of the constituent elements. The thermodynamic treatment for the present results was greatly simplified, because in practice the alloy phase was found to consistϕ of nearly pure solid copper and the sulphide phase of a mixture of the pure sulphides in a solid or liquid state (see page 79).

The structure of the sulphide phase was not known; the results of Savelsberg imply that ions were present but

the nature of the ions and the extent of their interaction was not clear. It is convenient in the following treatment to derive all the thermodynamic functions for cuprous sulphide molecules, but it should be emphasized that this does not mean that the mixtures consisted solely of molecules and did not contain ions. Any theories later developed concerning the structural composition of the mixtures could be used to calculate expected values of the thermodynamic functions for cuprous sulphide molecules, which could then be compared with the experimental ones. Thermodynamics can in this way help elucidate structures.

The above general thermodynamic thought behind the experiments will now be given a little more meaning as the mathematical treatments applied to the results to give exact values of the various thermodynamic functions will be given.

From the law of mass action the activity of cuprous sulphide ($a^1_{Cu_2S}$) in a mixture is given by

$$a^1_{Cu_2S} = k_1 a^2_{Cu} a_S$$

k_1 = a constant

a_{Cu} and a_S = the activities of copper and sulphur respectively.

As the condensed phases were in equilibrium with a gas mixture of hydrogen sulphide and hydrogen the sulphur activity is proportional to the ratio of the partial pressures of the two gases

$$a^{1}_{Cu_2S} = k_2 \, a^{2}_{Cu} \left(\frac{p_{H_2S}}{p_{H_2}} \right)$$

k_2 = another constant.

The alloy phases with which the mixtures were in equilibrium were found to be nearly pure solid copper and hence the copper activity can be taken as unity.

$$a^{1}_{Cu_2S} = k_2 \left(\frac{p_{H_2S}}{p_{H_2}} \right)$$

Similarly when the results for pure solid cuprous sulphide, here distinguished by the suffice ^{o}, are considered.

$$^{o}a^{1}_{Cu_2S} = k_2 \, \frac{^{o}p_{H_2S}}{^{o}p_{H_2}}$$

If the pure solid is taken as the standard state of cuprous sulphide the relative cuprous sulphide activity in a mixture is given by

$$a_{Cu_2S} = \frac{a^{1}_{Cu_2S}}{^{o}a^{1}_{Cu_2S}} = \frac{p_{H_2S}}{p_{H_2}} \, \frac{^{o}p_{H_2}}{^{o}p_{H_2S}}$$

The four partial pressures were determined experimentally and hence cuprous sulphide activities could be evaluated.

The partial molar heats, entropies and free energies are related to the activities by the following equations.

$$\overline{\Delta \, G_{Cu_2S}} = RT \ln a_{Cu_2S}$$

$$\overline{\Delta G_{Cu_2S}} = \overline{\Delta H_{Cu_2S}} - T\,\overline{\Delta S_{Cu_2S}}$$

The equilibrium measurements for each mixture were made at a series of different temperatures which meant that the partial molar free energies could be split into their more interesting heat and entropy terms.

The integral heat, entropy and free energy of mixing and the partial molar functions for sodium sulphide for a mixture with a composition of x mole % cuprous sulphide can be expressed by integrals containing the partial molar functions for cuprous sulphide. To evaluate these integrals it is necessary to know the partial molar functions for cuprous sulphide in the composition range x to 0 mole % cuprous sulphide. It was not possible to fulfil this condition in the present work because measurements could not be made on mixtures containing small amounts of cuprous sulphide and therefore no further space will be devoted to this subject. It should be emphasized before the work is described in detail, and the results discussed, that all the thermodynamic functions for the mixtures defined here have pure solid cuprous sulphide as their standard state.

APPARATUS AND EXPERIMENTAL METHOD

The apparatus was almost the same as that used in Section 1 the only difference being that for some of the experiments the furnace was vertical instead of horizontal.

The experimental procedure was also very similar to that in Section 1. A sodium sulphide-cuprous sulphide mixture and a piece of pure copper foil were held in a pure crystallized alumina boat or crucible (Morgan Crucible Co.Ltd. Δ RR) in the furnace. A hydrogen, hydrogen sulphide gas mixture was circulated at between 325 and 500 cc/min until it was in equilibrium with the melt; gas samples were then taken and analysed for sulphur. This was repeated at various temperatures until all the required equilibrium measurements had been made. The furnace was then cooled and the melt removed. The two condensed phases, which were easily separated, were then analysed to determine their exact composition. Seven mixtures were investigated, mostly in the liquid state, but a few results were also obtained for some of the mixtures in the solid state. The equilibrium times varied between 1.5 and 7 hours; they depended on whether the furnace was horizontal or vertical and whether the mixtures were solid or molten. The time required when the furnace was horizontal was 1.5 hours for both the solid

and liquid mixtures but when the furnace was vertical the time increased to 2 hours for liquid mixtures and between 2.5 and 7 hours for solid mixtures. The increase in the equilibrium times with the furnace in the vertical position was attributed to a bad contact between the gas and the mixture, caused by the fact that the gas was passed up through the furnace to mimimize the effects of thermal diffusion.

a) Chemicals used.

Copper

The copper was the same Johnson Matthey Co.Ltd. 'spectrographically pure' copper foil used in Section 2.

Cuprous Sulphide

This was from the same sample used in Section 1

Sodium Sulphide

Several methods were tried for preparing pure sodium sulphide from its elements but they were never satisfactory; the main difficulties were that sodium metal of guaranteed purity ('Analar') could not be bought, and that when sodium was melted in contact with sulphur a layer of sulphide almost impermeable to sulphur was formed round the sodium metal causing further reaction to proceed very slowly. The method finally chosen utilized sodium ethoxide as an intermediary. This was prepared by dissolving 10 gms of

reagent grade sodium obtained from British Drug Houses Ltd. in 50 cc of absolute alcohol, which had previously been distilled over lime to remove the last traces of water. The solution of sodium ethoxide in alcohol was left to stand overnight so that the undissolved impurities present in the sodium settled to the bottom of the flask. It was then decanted and divided into two equal parts. One part was saturated with hydrogen sulphide to give sodium hydrogen sulphide to which the other portion of sodium ethoxide was added. Sodium sulphide was formed in solution; it was then precipitated by boiling off most of the excess alcohol and adding ether. The precipitate was quickly collected and placed in a desiccator, great care having been taken throughout the preparation to exclude water.

$$2\,Na + 2C_2H_5OH \longrightarrow 2C_2H_5ONa + H_2$$

$$C_2H_5ONa + H_2S \longrightarrow C_2H_5OH + NaHS$$

$$NaHS + C_2H_5ONa \longrightarrow C_2H_5OH + Na_2S$$

Spectrographic analysis* of the sulphide showed that the trace elements were lead, iron, nickel, silver, aluminium, magnesium and copper present in quantities less than 0.002%, and tin and calcium present in quantities less than 0.01%. Evidence was obtained that the product had a sulphur content greater than that of the pure monosulphide. This was however

* The B.I.S.R.A. section of the Bragg Laboratory kindly did this analysis.

unimportant in the present investigation and no analyses were done to confirm it.

b. Preparation and properties of the melts.

Approximately the required compositions were obtained by weighing out the two sulphide powders. This was very inaccurate and all compositions had to be checked by analysis. The powders were first premelted in an atmosphere of hydrogen which removed any excess sulphur or oxygen in the sodium sulphide. A piece of copper foil so shaped as to cover completely the bottom of the container used, was added and the mixture again melted, and equilibrium measurements then made. The average weights of the metal and mixture were 0.4 gms and 2 gms respectively.

No attack of the alumina containers was obtained, but a strong reaction was obtained in some preliminary experiments between silica and sodium sulphide at about 600°C.

Some important surface tension effects were observed for the melts because sodium sulphide acted as an extremely efficient wetting agent. A type of sessile drop was obtained for molten cuprous sulphide, but when sodium sulphide was added this drop tended to flatten out and the liquid started to wet the alumina surface. This effect became so pronounced that a 40 mole% sodium sulphide mixture crept out of a crucible 3.2 cms high and 2 cms in diameter. In an attempt to overcome this difficulty a

specially made, long, recrystallized alumina crucible (8 cms high and 2 cms in diameter) was obtained from Royal Worcester Porcelain Co.Ltd. A 49% mixture* was heated at a temperature just above its melting point for 1 hour in this crucible. The melt rose a height of 5 cms when it was considered to have crept out of the even temperature zone of the furnace and to have solidified. In addition it had soaked through the walls of the crucible, indicating that this alumina ware is inferior to that supplied by Morgan Crucible Co.Ltd. This difficulty combined with the fact that the limit of the gas analysis technique (equilibrium $p_{H_2S}/p_{H_2} \approx 10^{-4}$) was reached for 40% mixtures made further experiments using mixtures richer in sodium sulphide than 40% difficult and therefore none were done.

It is known that sodium has such a strong affinity for oxygen that the oxide cannot easily be reduced by hydrogen and small amounts of oxide might therefore have been expected in the melts. As none of the mixtures investigated contained less than 60 mole% cuprous sulphide the sulphur activity of the melts was kept well above that of pure sodium sulphide which meant that the lower reaction (right to left) was favoured in the following equilibrium.

$$Na_2S \text{ (in melt)} + H_2O \rightleftharpoons Na_2O \text{ (in melt)} + H_2S$$

Most of the sodium oxide was therefore reduced and the water formed absorbed by the drying tube in the gas circuit.

* Throughout the rest of this thesis a mixture with a composition of x mole% sodium sulphide will be referred to as a x% mixture

A simple calculation showed that the sodium oxide activity was less than 0.01% of that of the sulphide in all of the mixtures, and therefore no additional measures were necessary to remove oxygen from the hydrogen or from the prepared sodium sulphide.

During the course of the equilibrium experiments there were two ways by which the melts could have altered in composition. The first was by the continual removal of sulphur to form the gas mixture. A check however could be kept on this as the amount of sulphur removed in each equilibrium experiment was that used in the gas analysis. For a complete series of measurements on one mixture the total change in composition due to this cause was never allowed to be greater than 1 mole% of cuprous sulphide. Some of the mixtures were investigated more throughly than others and for these a vertical furnace was used because more melt could be held in a crucible than a boat, which allowed more equilibrium measurements to be made for the same change in composition.

The second method was by the volatilization of sodium sulphide from the melt. Evidence was found in the literature that pure sodium sulphide started volatilizing at about 800°C (35), but the extent of this volatilization for the mixtures was not known. This was first ascertained by studying the equilibrium for one particular melt at a

series of increasing temperatures. The point at which volatilization started was the point at which a graph of $\log (p_{H_2S}/p_{H_2})$ against $1/T$ ceased to be a straight line, due to the melt becoming richer in cuprous sulphide. The fact that volatilization had occurred was then confirmed by obtaining a sulphur pressure higher than the original value at a temperature which corresponded to a point on the straight part of the graph. Appreciable volatilization was obtained for a 36% mixture at temperatures above 850°C but none was detected for a 10% mixture at 900°C. No accurate equilibrium measurements were made at temperatures greater than these for the respective melts and volatilization can therefore be considered to have been absent.

c. Composition of the copper and sulphide phases

The copper foil used with the mixture having the highest percentage of sodium sulphide (36% mixture) should have contained the greatest amount of sodium. Spectrographic analysis showed that it contained less than 0.01% sodium and therefore the copper activity for all the mixtures could be taken as unity.

The sulphide phase could have differed from a mixture of the two stoicheiometric sulphides by containing, firstly an excess of copper, or secondly an excess of sulphur due to the formation of a higher sulphide of sodium caused by the high sulphur activity of the cuprous sulphide. The first possibility was considered very improbable because

molten cuprous sulphide at 1150°C only dissolves 1.7% copper (see page 10) and most of these experiments were done at about 800°C. The analyses described below however proved both these effects to have been absent.

The sulphide phase was analysed for both copper and sulphur, the sodium figure being obtained by difference. Approximately 1-2 gms of the sample were weighed and dissolved in a hydrochloric acid (one part), nitric acid (three parts), bromine (one part) mixture. The excess bromine was evaporated off on a water bath and the solution made up accurately to 250 cc; samples of this solution were then used for analyses of copper and sulphur.

Sulphur determination

25cc of the copper sulphate - sodium sulphate solution were taken and the sulphur determined as barium sulphate. Due to the noninterference of the small amounts of copper and sodium present (36) these metals were not removed before precipitation. The solution was evaporated to dryness, the residue was digested with concentrated hydrochloric acid which was then evaporated off. This was done twice to ensure the removal of all nitrate ions. The residue was dissolved in 100-200 cc of water, made neutral and 3 cc excess hydrochloric acid added. The sulphur was then

precipitated by adding a solution of 24 cc N barium chloride solution diluted to 100 cc, quickly to the boiling sulphate solution. The solution was heated for five minutes and left to stand overnight. The barium sulphate was collected using a porous porcelain crucible (supplied by Royal Worcester Porcelain Co.Ltd), dried at 140°C and weighed. A sample of pure cuprous sulphide was analysed to check the method; the absolute accuracy as well as the internal consistency of the results was found to be ± 1%.

Copper determination

50 cc of the copper sulphate-sodium sulphate solution were taken and the copper determined by an electrolytic method. The solution was evaporated to dryness, the residue was digested with 1 cc concentrated sulphuric acid which was then fumed off. This was done twice to ensure the removal of all chloride ions. The copper was then deposited from a 4.5% nitric acid and a 1% sulphuric acid solution overnight using an amperage of 0.5 amps at 2.5 - 3 volts. The method was found very accurate and reliable and was checked using a piece of pure copper foil. The absolute accuracy as well as the internal consistency of the results was better than ± 0.3%.

The mole fractions of sodium sulphide in the mixtures were calculated from the copper and sodium percentages and can be considered accurate to ± 1 mole%. Most of the mixtures were cooled slowly overnight to room temperature

in the furnace; and if, therefore, the mixtures had contained excess sulphur or copper only at higher temperatures they could have altered in composition when they were cooled t o room temperature. Two of the mixtures (27.5% and 18.8% mixtures) were therefore quenched from 720°C to room temperature in an atmosphere of nitrogen in under 10 minutes; the analyses of these mixtures agreed with the others in that the sulphur percentages, when taking into account the possible error in them of ± 1%, were consistent with only the existence of the stoicheiometric sulphides and therefore there were no appreciable amounts of excess copper or of a higher sulphide of sodium present in any of the mixtures.

d. Gas analysis

The gas analysis technique employed in Section 1 was not entirely suitable for the present experiments as it was designed by Kitchener and co-workers to analyse 3.0 mgms of sulphur; here it was required to analyse 0.3 mgms to ± 1%, and the original technique (see pages 26,27) had therefore to be modified.

The quantity of sulphur to be analysed is directly proportional to the difference between the volumes of sodium thiosulphate solution used in the standardization of the sodium hypochlorite solution and in the actual

analysis. Therefore to analyse a quantity of sulphur to ± 1% the corresponding volume of sodium thiosulphate solution has to be known to ± 1%. For very small amounts of sulphur this can be achieved if very dilute solutions or small volumes and a microburette are used. The latter method was chosen here as a clearer end point could be obtained.

For the smallest amounts of sulphur (0.2 - 0.6 mgms) the hydrogen sulphide was absorbed in 5 cc of $\frac{N}{20}$ sodium hypochlorite and $\frac{N}{5}$ sodium hydroxide solution which had previously been boiled to expel all dissolved oxygen. A small boiling tube was added and the solution boiled in a paraffin bath of 5 minutes, 1 cc of 6N hydrochloric acid solution and 2 cc of 10% potassium iodide solution were added and the liberated iodine titrated with $\frac{N}{20}$ sodium thiosulphate solution from a 10 cc microburette. For slightly larger amounts of sulphur (0.6 - 2.0 mgms) 25 cc of hypochlorite solution and a microburette were used, in other respects the method was the same as the original.

These modified techniques were compared with the original by placing cuprous sulphide in the furnace and two bulbs in the gas circuit, one large and one small. An equilibrium experiment was performed and the gas samples from the large and small bulbs were analysed by

the original and the modified techniques respectively. A summary of the results obtained (Table 4) shows that the modified techniques gave consistently lower results, which can be explained if there was a loss of 10^{-2} mgms of sulphur in each analysis. No further experiments were done to determine the cause of this discrepancy, because of the good consistency of the results and because the loss of sulphur was small. Instead all the results obtained using the modified techniques were adjusted so that they were consistent with those obtained using the original technique.

TABLE 4

Quantity of sulphur to be analysed in gms.	Percentage difference between to two techniques
2.9×10^{-4}	3.3 , 3.0
7.5×10^{-4}	1.7 , 1.7
2.3×10^{-3}	0.1
3.6×10^{-3}	0.1

During the course of these experiments it was found that if sodium hypochlorite with a strength greater than $\frac{N}{20}$ was used the oxidation of the sulphide was incomplete, the results being 3 to 5% low. During the boiling process some of the precipitated sulphur

coagulated and would not dissolve even with continued boiling. This was reproducible but did not occur if the same solution of hypochlorite was diluted with $\frac{N}{5}$ sodium hydroxide solution.

RESULTS

The equilibrium results are most clearly summarized as in Section 1 by a graph of log (p_{H_2S}/p_{H_2}) against $\frac{1}{T}$ (Fig.7). The values obtained together with the analyses for each mixture are given below; the order of the equilibrium results represents the order in which they were obtained. The letters H and L in the fourth column indicate whether the equilibrium was approached from high or low hydrogen sulphide partial pressures.

The equilibrium times used for the experiments are shown in the end column together with the letter V or H indicating whether the furnace was vertical or horizontal.

Equilibrium Measurements

Table 5

Mixture No.1 (36.8 mole% Na_2S)

temperature in ^oC	$\frac{1}{T} \times 10^3$	$-\log (p_{H_2S}/p_{H_2})$	H or L	equilibrium time in hours
1.	2.	3.	4.	5.
724	1.003	3.523	L	1.5 H
795	0.936	3.381	L	1.5 "
836	0.902	3.310	L	1.5 "
764	0.964	3.442	H	1.5 "

continued on next page

Table 5 - continued

1.	2.	3.	4.	5.	
	Mixture No.2 (18.9 mole% Na_2S)				
847	0.893	3.024	L	1.5	H
813	0.928	3.075	L	1.5	"
751	0.977	3.170	L	2.0	"
779	0.951	3.126	L	1.5	"
	Mixture No.3 (30.0 mole% Na_2S)				
723	1.004	3.408	L	1.5	"
751	0.977	3.351	H	1.5	"
787	0.943	3.276	L	1.5	"
840	0.899	3.187	L	2.0	"
816	0.918	3.224	L	1.5	"
726	1.001	3.386	L	1.5	"
	Mixture No.4 (9.7 mole% Na_2S				
898	0.854	2.866	L	2.0	H
950	0.818	2.807	L	1.5	"
969	0.805	2.789	L	1.5	"
895	0.856	2.867	H	1.5	"
786	0.944	3.020	L	1.5	"
849	0.891	2.931	L	1.5	"
749	0.979	3.098	L	1.5	"
810	0.923	2.984	L	1.5	"
700	1.028	3.214	L	1.5	"
604	1.140	3.477	L	1.5	"
656	1.076	3.345	L	2.0	"
	Mixture No.5 (27.5 mole% Na_2S)				
696	1.032	3.448	L	2.0	V
695	1.033	3.444	L	4.0	"
745	0.982	3.342	L	2.0	"
644	1.090	3.557	L	2.5	"
602	1.143	3.871	L	2.5	"
565	1.193	4.117	L	2.5	"
610	1.132	3.821	L	2.5	"

Table 5 - continued

1.	2.	3.	4.	5.	
	Mixture No.5 (27.5 mole% Na_2S) - cont'd.				
581	1.171	4.025	L	2.5	V
796	0.935	3.250	H	2.5	"
585	1.165	4.003	H	2.5	"
625	1.114	3.734	L	2.5	"
635	1.101	3.650	L	3.0	"
587	1.163	3.986	L	2.5	"
639	1.096	3.613	L	2.5	"
	Mixture No.6 (18.8 mole% Na_2S)				
727	1.000	3.213	L	7.0	V
691	1.037	3.282	L	2.5	"
821	0.914	3.063	L	2.5	"
594	1.153	3.497	H	7.0	"
597	1.149	3.494	L	7.0	"
625	1.114	3.418	L	7.0	"
650	1.083	3.376	L	5.0	"
767	0.961	3.149	L	4.0	"
650	1.083	3.375	H	7.0	"
690	1.038	3.387	H	6.0	"
661	1.071	3.351	L	7.0	"
563	1.196	3.584	L	3.5	"
676	1.054	3.320	L	4.0	"
838	0.900	3.045	L	7.0	"
633	1.104	3.402	L	7.0	"
	Mixture No.8 (8.1 mole% Na_2S)				
628	1.110	3.392	L	6.0	H
629	1.109	3.407	L	5.0	"
629	1.109	3.397	H	4.0	"
628	1.110	3.388	L	19.0	"

Analyses for the Mixtures

Table 6

	Mixture No.1				=	Mixture No.2				=
wt % Cu	62.5_3	62.3_6	62.3_6	= 62.4_2		71.6_9	71.5_2	71.5_2	= 71.5_8	
wt % S	24.3_4	24.5_3	= 24.4_4			22.3_6	22.9_5	= 22.3_6		
wt % Na			= 13.1_4					= 6.0_6		
mole% Na_2S			= 36.8					= 18.9		

	Mixture No.3				Mixture No.4			
wt% Cu	65.9_1	65.9_1	=	65.9_1	75.6_1	75.6_1	=	75.6_1
wt% S	23.8_8	23.9_1	=	23.9_0	21.5_9	21.3_0	=	21.4_5
wt% Na			=	10.1_9			=	2.9_4
mole% Na_2S			=	30.0			=	9.7

	Mixture No.5				Mixture No.6			
wt % cu	67.1_7	67.3_1	=	67.2_4	71.6_0	71.6_3	=	71.6_2
wt % S	23.5_3	23.5_9	=	23.5_6	22.2_3	22.5_4	=	22.3_8
wt % Na			=	9.2_0			=	6.0_0
mole% Na_2S			=	27.5			=	18.8

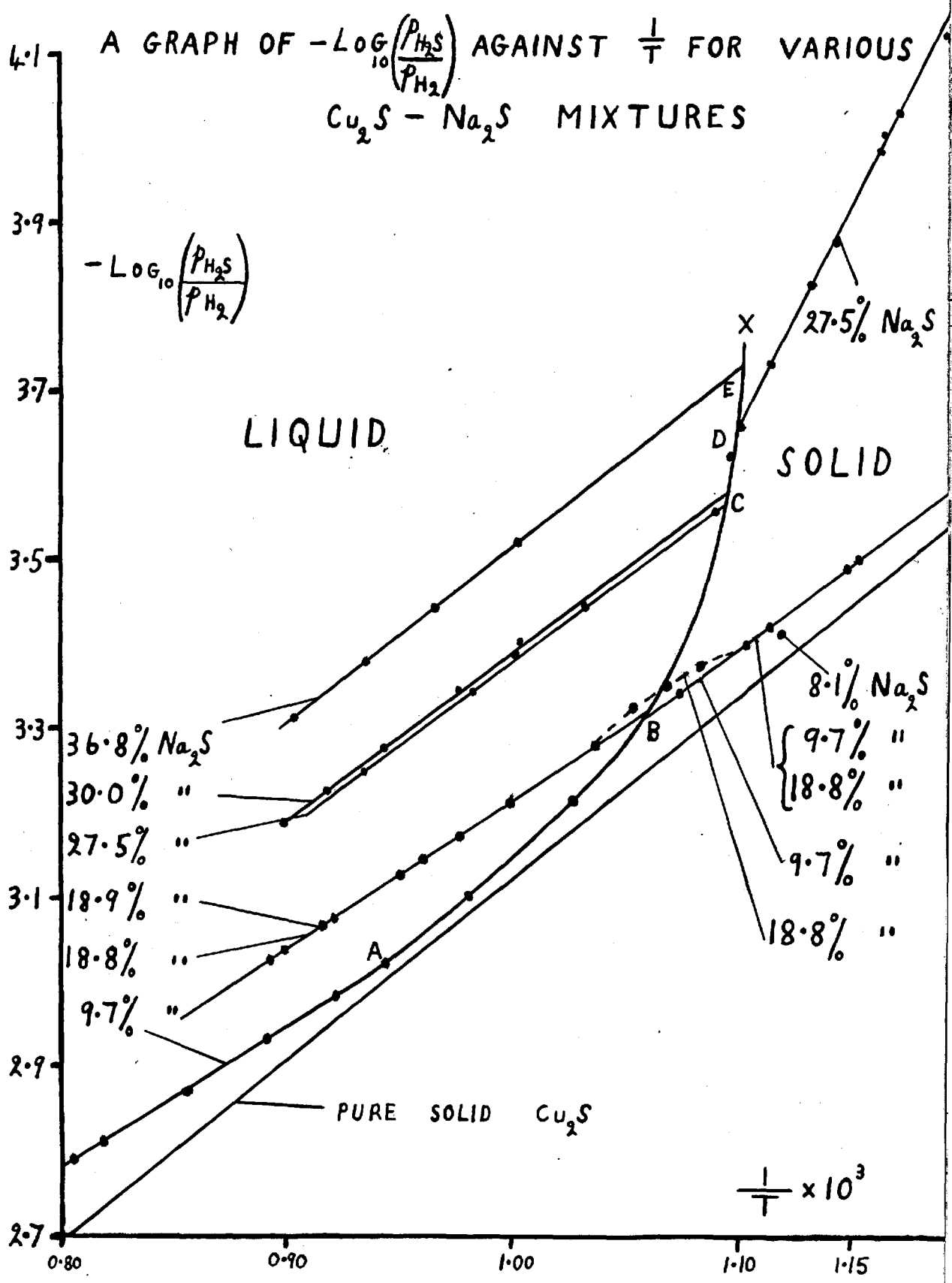
Mixture No.7

wt % cu	76.6_0	76.0_3	76.8_3	76.5_6	=	76.6_6
wt % S	20.8_5	20.9_0			=	20.8_8
wt % Na					=	2.4_6
mole% Na_2S					=	8.1

Errors

The internal consistency of these equilibrium results was ± 1% of (p_{H_2S}/p_{H_2}), which was better than that in Section 1 due to a general improvement in the experimental technique. The absolute accuracy however still cannot be considered better than ± 3% of (p_{H_2S}/p_{H_2}).

FIG 7


A GRAPH OF $-Log_{10}\left(\frac{P_{H_2S}}{P_{H_2}}\right)$ AGAINST $\frac{1}{T}$ FOR VARIOUS $Cu_2S - Na_2S$ MIXTURES
$-Log_{10}\left(\frac{P_{H_2S}}{P_{H_2}}\right)$
4·1
3·9
3·7
3·5
3·3
3·1
2·9
2·7
0·80
0·90
1·00
1·10
1·15
$\frac{1}{T} \times 10^3$
LIQUID
SOLID
X
E
D
C
B
A
27·5% Na_2S
36·8% Na_2S
30·0% "
27·5% "
18·9% "
18·8% "
9·7% "
8·1% Na_2S
9·7% "
18·8% "
9·7% "
18·8% "
PURE SOLID Cu_2S

DISCUSSION OF RESULTS

a) PHASE DIAGRAM FOR THE Cu_2S - Na_2S SYSTEM.

The main aim in this part of the discussion is to show the close relationship between the graph of log (p_{H_2S}/p_{H_2}) against $\frac{1}{T}$ (fig.7) and the phase diagram for the system (fig.6). It proved possible to obtain definite points on the phase diagram from this graph.

If Friedrich was correct and there is not appreciable solid solution for this system the mixtures investigated when solid should have had the same sulphur activity as pure solid cuprous sulphide. In fact they had a lower sulphur activity which means that an appreciable range of solid solution does exist. It follows that for each mixture Fig.7* should consist of two straight lines joined by a curve. A straight line represents a solid or a liquid phase and the curve (shown in Fig.7 as AX) represents a solid and a liquid phase, both of varying composition, in

---

* To avoid repetition the graph of log (p_{H_2S}/p_{H_2}) against $\frac{1}{T}$ will be referred to as Figure 7.

equilibrium. This type of graph was obtained for both the 9.7% and 27.5% mixtures.

The sulphur activities of the 9.7% and 18.8% mixtures were found to be the same in the solid phase, which implies that a two phase region containing these two mixtures must exist in the solid. There are two types of phase diagram which could include such a region. One where the two components (i.e. Cu_2S and Cu_2S Na_2S) are only partially miscible with one-another leaving a two phase region under the eutectic point. The other type is that containing a peritectic point; here there is an extended region of solid solution containing a small miscibility gap. From Fig.7 it is apparent that 20% to 30% mixtures in the solid at temperatures corresponding to points near the curve AX do not have the same cuprous sulphide activities as the 18.8% and 9.7% mixtures, and are therefore not in the two phase region. In addition the 20% to 30% mixtures can be considered to lie on the cuprous sulphide side of the eutectic point which means that the second alternative for the phase diagram, that containing a peritectic point, is the more probable.

The above general discussion can now be enlarged upon to show how it was possible to obtain definite points on the phase diagram.

Certain points on Figure 7 correspond to certain points on the phase diagram; for the purposes of clarity

corresponding points of special interest have here been identified by the same letter on the two diagrams.

When the straight lines for the mixtures in Figure 7 are extrapolated they cut the curve AX, the temperatures at the points of intersection (A,B,C,D) equal those for points (for the respective mixtures) on the solidus and liquidus curves in the phase diagram.

All the mixtures which are within the two phase region at the peritectic temperature cannot have a point corresponding to a point on the liquidus lying between BX on the curve AX (Fig. 7). An 18% mixture is the one richest in sodium sulphide which fulfils this condition, and it therefore follows that at the peritectic temperature the mixture at the sodium sulphide rich end of the two phase region cannot contain more, although it should be noted that it can contain less, than 18% sodium sulphide.

In the solid the 8.1% mixture had a higher sulphur pressure than the 9.7% mixture which means, assuming that the latter mixture was in the two phase region, that the cuprous sulphide rich end of the two phase region must lie between these two mixtures. From considerations of the differences between the sulphur pressures of the mixtures and of pure cuprous sulphide the cuprous sulphide rich end of the two phase region was fixed at 9.7% sodium sulphide at 629°C.

One point which is not clear is the shape of the graph in Figure 7 for the 18.8% mixture near the solidification temperature. No sharp breaks corresponding to the change in state of the mixture were obtained, instead there was a slight curve over an extended temperature ran ge. This curve was investigated very carefully and the points can be considered reliable. This mixture may be expected to have unusual properties as it should solidify at about the peritectic temperature. No simple explanation is available however and the effect has therefore been represented by a dotted line.

The various points on the phase diagram obtained from the previous reasoning are summarized in Figure 6 and in Table 7 below.

Table 7

Composition of mixtures in mole% Na_2S	Liquidus temp.in ^oC	Solidus temp. in ^oC	Temperature of a two phase boundary in ^oC
9.7	786	671	
18.8	670		
27.5	641	636	
9.7			629
less than 18			671

These results differ considerably from those of Friedrich in that the points on the liquidus, in some places, are 180°C lower than those on Friedrich's diagram and that positive evidence was obtained for an appreciable range of solid solution. There can be no doubt of this existing, and most of the liquidus points obtained here should be accurate to ± 20°C. Friedrich unfortunately did not publish any of his cooling curves and it is therefore impossible to assess the reliability of the two breaks he obtained in each curve, especially the second one at the eutectic temperature from which it was initially concluded that there was no solid solution for this system. If however both these breaks were clear there must have been a fault in his experimental method, because it is difficult to see how the present results could be so seriously in error.

b. Thermodynamic functions for the Liquid Mixtures

i) Conversion of the standard state for the thermodynamic functions from solid to liquid cuprous sulphide.

The calculation of the activities, partial molar free energies, heats and entropies of cuprous sulphide with solid cuprous sulphide as the standard state has been dealt with previously (pages 67-69); the values obtained are given in Table 8 (see page 93).

Thermodynamic functions for the liquid mixtures are of very little use unless the standard state of cuprous sulphide is taken as the pure liquid. Values of the functions having the liquid as the standard state can also be obtained for this system because these functions are related to those having the solid as the standard state by the heat of fusion of cuprous sulphide as shown by the following equations.*

$$\overline{\Delta H_l} = \overline{\Delta H_s} - H_f$$

$$\overline{\Delta S_l} = \overline{\Delta S_s} - H_f/T_f$$

$$\overline{\Delta G_l} = \overline{\Delta G_s} - H_f\left(1 - \frac{T}{T_f}\right)$$

$$a_l = \text{antilog}_e\left(\frac{\overline{\Delta G_l}}{RT}\right)$$

The subscript l denotes liquid cuprous sulphide as the standard state.

The subscript s denotes solid cuprous sulphide as the standard state.

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* It has been assumed that the specific heats of solid and supercooled liquid cuprous sulphide are the same.

H_f and T_f = the heat and absolute temperature of fusion of cuprous sulphide.

The thermodynamic functions $\overline{\Delta H_1}$, $\overline{\Delta S_1}$ and $\overline{\Delta G_1}$ must be zero for pure liquid cuprous sulphide. The terms dependent on the heat of fusion in the previous equations are therefore equal to the values that the functions having the solid as the standard state would have for the pure liquid, i.e. they equal the intercepts on the $\overline{\Delta H_s}$, $\overline{\Delta S_s}$, and $\overline{\Delta G_s}$ axes when graphs of $\overline{\Delta H_s}$, $\overline{\Delta S_s}$ and $\overline{\Delta G_s}$ against composition are extrapolated to pure cuprous sulphide. The values of the partial molar heat were considered the most suitable for the calculation of the heat of fusion. The graph used is shown in Figure 8 and a full discussion of the value obtained (2.5 ± 0.5 Kcals) is given in Appendix 3. Values of the functions having the liquid as the standard state were then calculated using this value; they are summarized in Figures 8,9, 10,11 and in Table 9.

ii) Values of the thermodynamic functions.

Table 8

Composition of the mixture in % Na_2S (mole)	$\overline{\Delta H_s}$ in cals/mole	$\overline{\Delta S_s}$ in cals/deg.mole	$\overline{\Delta G_s}$ at 820°C in cals/mole.
36.8	230	2.02	1980
30.0	740	1.96	1400
27.5	730	1.90	1340
18.9	1810	2.24	640
18.8	1890	2.29	620
9.7	2200	2.15	150

Table 9

Composition of the mixture in % Na_2S (mole)	$\overline{\Delta H_1}$ in cals/mole	$\overline{\Delta S_1}$ in cals/deg.mole	$\overline{\Delta G_1}$ at 820°C in cals/mole	a_1 at 820° C
36.8	- 2270	0.24	- 2530	0.31
30.0	- 1760	0.18	- 1950	0.41
27.5	- 1770	0.12	- 1900	0.42
18.9	- 690	0.46	- 1190	0.56
18.8	610	0.51	- 1170	0.58
9.7	300	0.37	- 700	0.72

FIG 8

A GRAPH OF $\overline{\Delta H}_{Cu_2S}$ AGAINST % Na_2S

FOR LIQUID $Cu_2S - Na_2S$ MIXTURES

□ LIMITS FOR RANDOM ERRORS

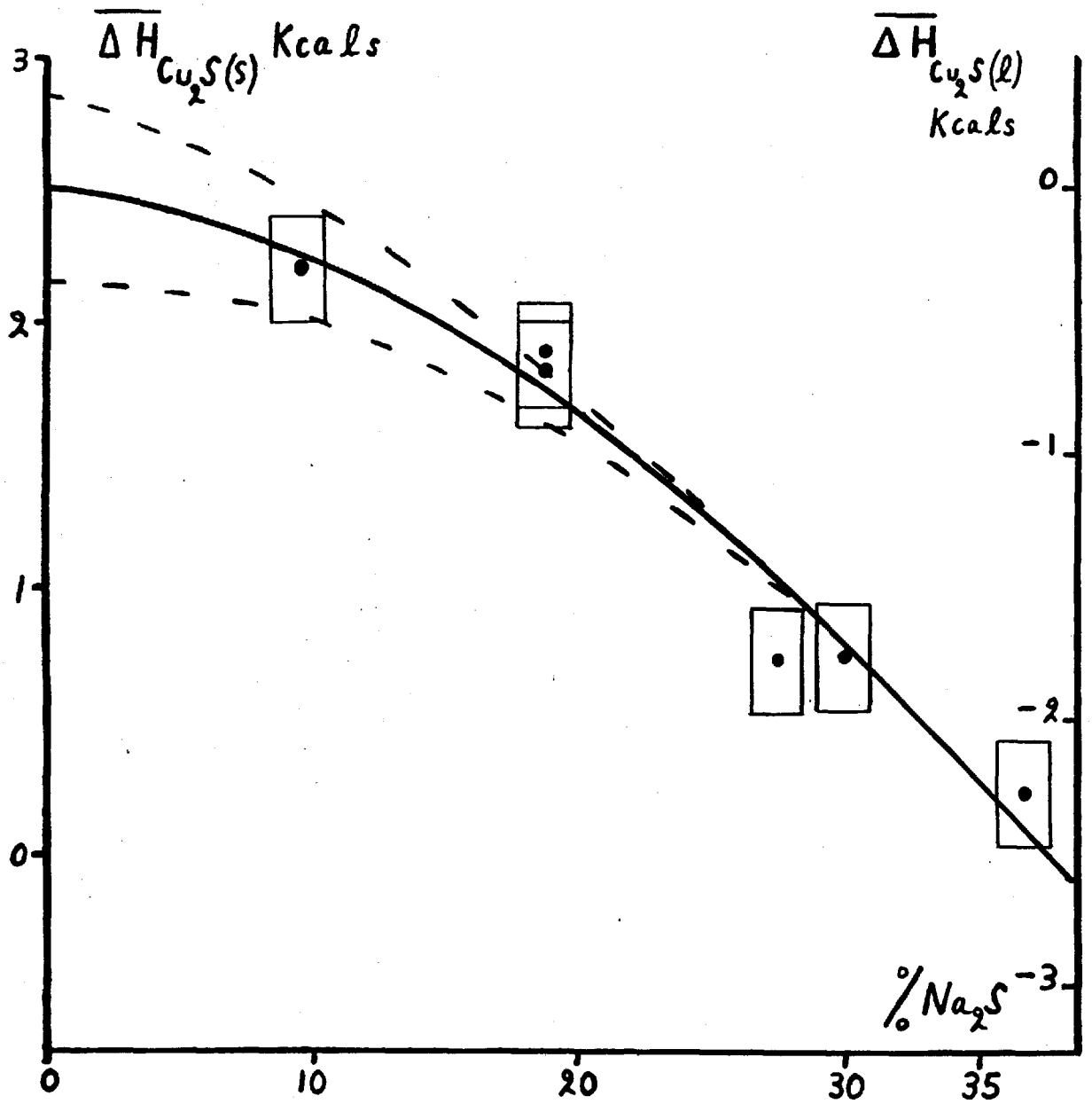


FIG 9

A GRAPH OF $\overline{\Delta S}_{Cu_2S}$ AGAINST % Na_2S FOR LIQUID $Cu_2S - Na_2S$ MIXTURES

□ = LIMITS FOR RANDOM ERRORS

[ ] = " " NONRANDOM "

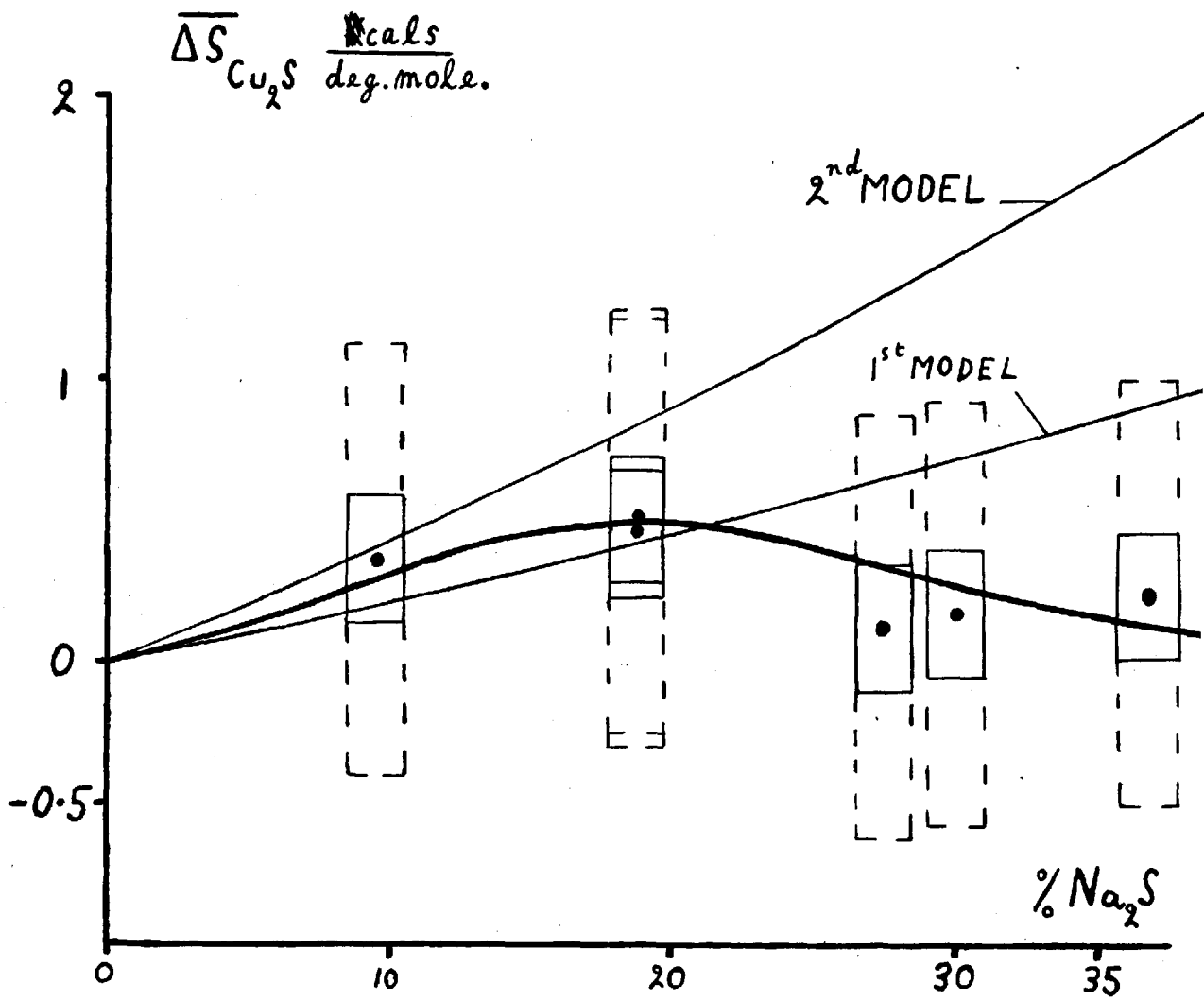


FIG 10

A GRAPH OF $\overline{\Delta G}_{Cu_2S(l)}$ AGAINST $\%Na_2S$ FOR LIQUID $Cu_2S - Na_2S$ MIXTURES AT 820°C

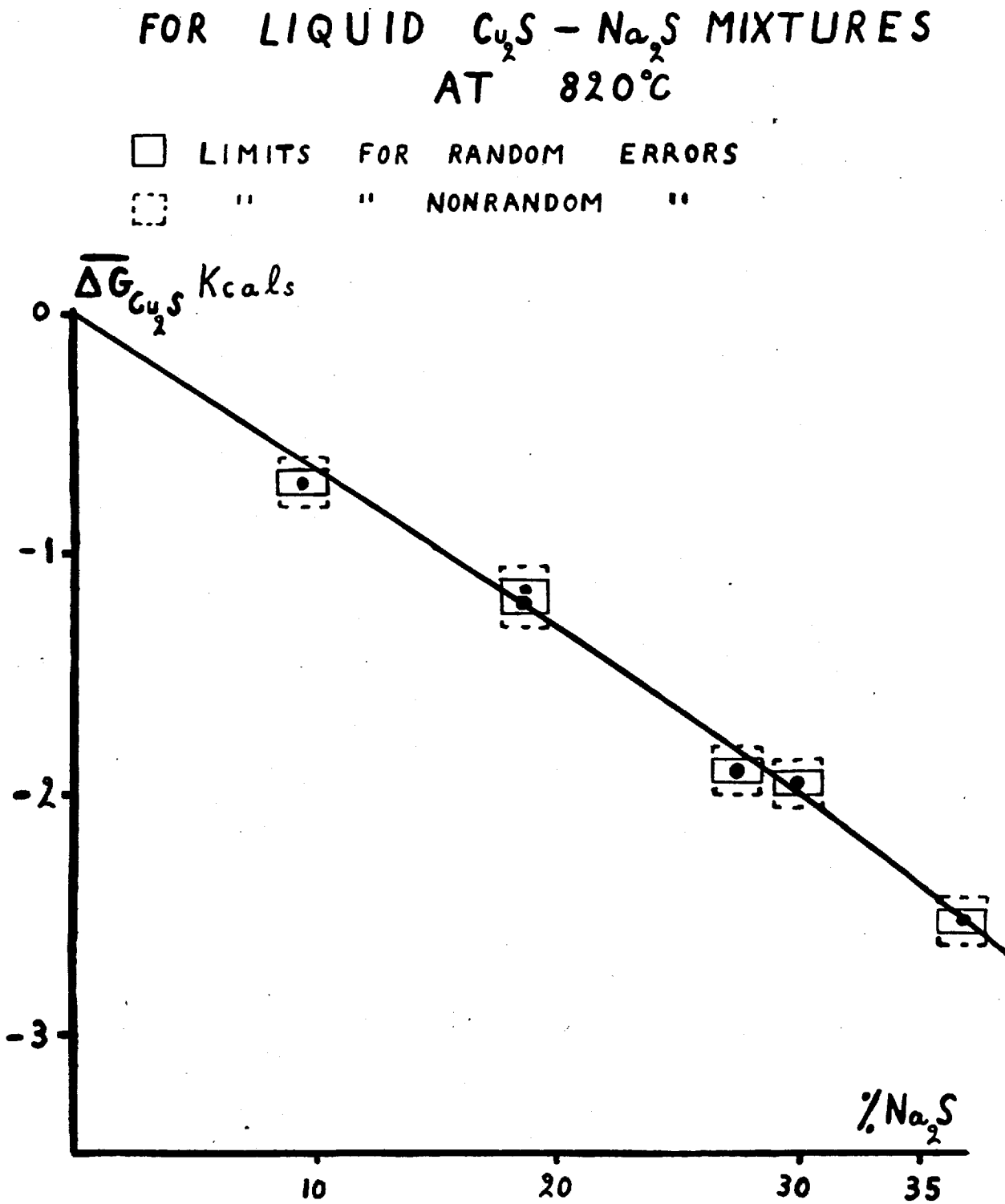
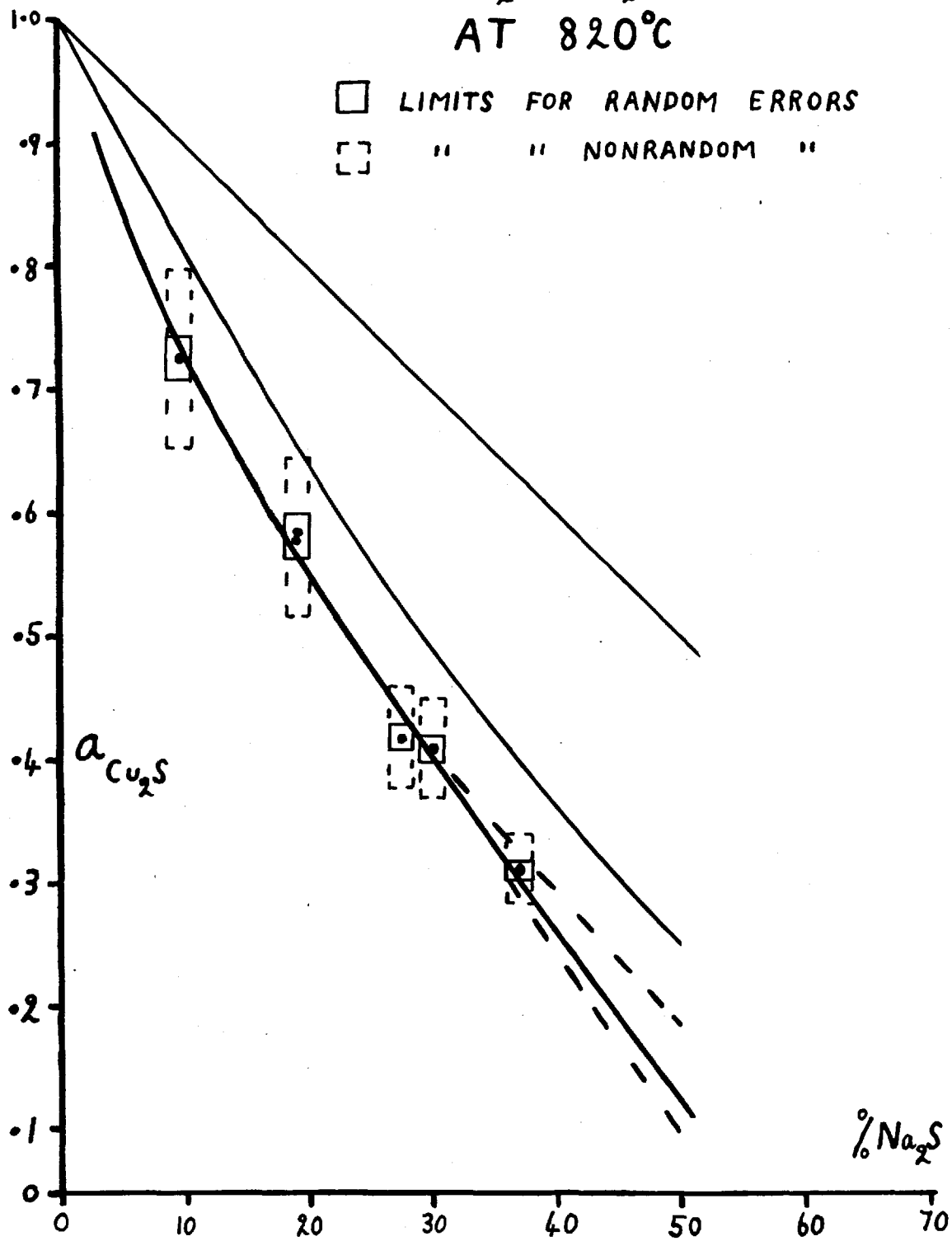


FIG 11

A GRAPH OF a_{Cu_2S} AGAINST % Na_2S FOR LIQUID $Cu_2S - Na_2S$ MIXTURES AT 820°C



Errors

Any errors in these functions could have originated from three different sources

1) The measurements on the mixtures

2) " " " " pure solid cuprous sulphide

3) " heat of fusion of cuprous sulphide

The probable values of the errors are shown in Table 10 below.

Table 10

Function	error from Source 1	error from Source 2	error from Source 3
$\overline{\Delta H}$	± 200 cals/mole	± 150 cals/mole	± 350 cals/mole
$\overline{\Delta S}$	± 0.22 cals/deg. mole	± 0.18 cals/deg. mole	± 0.35 cals/deg. mole
$\overline{\Delta G}$	± 50 cals/mole	± 50 cals/mole	± 110 cals/mole

The errors for the last two sources were considered nonrandom because they were ~~constant~~ the same for each mixture whilst those for the first source varied and they have therefore been classified as random. To obtain a fair estimation of the accuracy of the results the two types of error have been separated in the graphs of the thermodynamic functions plotted against composition (Figs. 8,9,10,11). The random errors are shown in solid lines whilst the nonrandom ones are superimposed in broken lines. The good consistency of the results is shown very clearly by these graphs because in all cases the curves drawn lie within the random error limits.

iii) Discussion

If the values of these functions were only required for thermodynamic calculations there would be no need for any further discussion, but it is desirable to relate them to the general chemical behaviour of the system and to obtain from them some qualitative information concerning the structure of the melts. However, before this can be done clearly it is necessary to make some general remarks on:-

1. The modern ideas concerning the liquid state.
2. The dependence of the heat and entropy terms on structure.
3. The possible ideal configurations for the present system.

α) The modern ideas concerning the liquid state.

Ideally a mixture of this type should have a random distribution of the constituent particles. In practice a certain amount of ordering may occur in pure liquids as well as in mixtures. Pure liquids are considered to be similar to solids in that they have a similar type of ordering, but this ordering only extends over a very short range and lacks the rigid characteristics of a crystalline lattice. The nonrandomness for mixtures also only exists over a very short range and is in no way permanent. It is thought of as a constituent particle having a greater number of like or unlike atoms as next nearest neighbours than in a perfectly random mixture, or to express it in another way that one particle in a mixture stays for different lengths of time in the co-ordination shells of different particles depending upon the type of the particles.

β) The dependence of the heat and entropy terms on structure

If it is required to relate the thermodynamic functions to the structure of the melts it is necessary to formulate an ideal structural model for the system for which it is possible to calculate values of the thermodynamic functions. These values are then compared with the experimentally determined ones. It is normal when constructing these

models to assume that all heat effects are absent, that the vibrational entropy terms remain constant and that the various constituents are randomly distributed.

Any deviations from these ideal configurations show in the heat and entropy terms, which are very closely related to one-another, any change in one is normally accompanied by a change in the other. For example the true system may differ from the ideal model in having appreciable heat effects which means that all the bonds in the mixture are not energetically equal. This inequality produces endothermic or exothermic heat effects and tends to produce ordering so that the total energy of the system is a minimum. Heat effects are therefore accompanied by small configurational entropy changes. It should be mentioned here that it is possible for mixtures to have small heats of formation and random mixing. This concept was first put forward by Hildebrand who called such mixtures "regular", it has proved very useful for mixtures of organic molecules but considerable care should be used in its application because there is a tendency when theoretically treating results to explain heat effects in this way without sufficient evidence of random mixing.

Entropies of mixing can be divided into a configurational term which can only be less or equal to the ideal value and a vibrational term which can be positive or negative (ideally this is zero). This vibrational entropy term depends on the interatomic vibrations and is therefore related to the strength and type of the bonds. The relationship is most clearly demonstrated by considering the vibrational degree of freedom of a diatomic gas molecule. The contribution to the molar entropy from the vibrations, which are normally taken as Simple Harmonic, can be shown to be (37):-

$$-R \ln\left(1 - e^{-h\nu/kT}\right) + \frac{R h\nu}{kT\left(e^{h\nu/kT} - 1\right)}$$

where k = Boltzmann's constant.

h = Planck's constant.

ν = frequency of vibration

If the strength of the bonds is increased and hence also the frequency of vibration (ν) both the above terms decrease. Therefore an increase in the strength of a bond is associated with a decrease in the vibrational entropy. The converse is also true.

8) <u>The possible ideal configurations for the system.</u>

For the present system three different ideal configurations are of more interest than others; unfortunately it is only possible to calculate the

thermodynamic functions for two of them assuming that there are no heat effects and that any changes in the vibrational entropy may be ignored.

The first model is a random mixture of the molecules of the two constituent sulphides; for this model the activity curves of the molecular sulphides obey Raoult's Law.

$$a_{Cu_2S} = x_{Cu_2S}$$

and

$$\overline{\Delta S_{Cu_2S}} = -R \ln x_{Cu_2S}$$

x_{Cu_2S} = the mole fraction of cuprous sulphide.

The second model is a random mixture of sodium, copper and sulphur atoms or ions. Due to the two constituent sulphides possessing two cations to the molecule the partial molar entropy must be double that in the first case.

i.e.

$$\overline{\Delta S_{Cu_2S}} = 2R \ln x_{Cu_2S}$$

Now ideally

$$\overline{\Delta H_{Cu_2S}} = 0$$

$$\therefore \quad \overline{\Delta G_{Cu_2S}} = RT \ln a_{Cu_2S} = 2RT \ln x_{Cu_2S}$$

$$a_{Cu_2S} = x^2_{Cu_2S}$$

The third model follows from the results of Savelsberg. The covalent nature of the Cu - S bond suggests that ideally pure liquid cuprous sulphide can be considered to consist of separate sulphide molecules. Savelsberg's results indicate that each of the sodium sulphide molecules in a mixture combines with a molecule of cuprous sulphide to give $2Na^+$ and 2 CuS^- ions, which ideally should be randomly distributed throughout the melt. Unfortunately it is impossible to calculate the required thermodynamic functions for this model because there is no method by which the contribution to the activity of the cuprous sulphide by the CuS^- ions may be estimated.

δ) Partial molar heats.

All the partial molar heats determined here were exothermic and constant for a given mixture over the temperature range investigated. The relation between the partial molar heats and the chemical behaviour of the system is most clearly understood, when the contribution to this function by one molecule of cuprous sulphide is considered as the difference between the strengths of all the bonds to the two copper atoms and the one sulphur atom in pure supercooled liquid cuprous sulphide and in a mixture. This statement can be summarized by an equation providing only the atomic interactions between next nearest neighbours are considered.

$$\overline{\Delta H_{Cu_2S}} = N \left[\delta(-Z_{Cu-Cu} E_{Cu-Cu}) + \delta(-Z_{Cu-S} E_{Cu-S}) \right.$$

$$\left. -Z_{Cu-Na} E_{Cu-Na} - Z_{S-Na} E_{S-Na} \right] \cdot \cdot \cdot \cdot D$$

Z_{x-x} = the number of x-x bonds for one molecule of cuprous sulphide

E_{x-x} = the energy of the x-x bond. It has a positive value. The minus signs in the above equation follow from the fact that an increase in the bond energy decreases the heat content of a substance.

$\delta(-Z_{x-x}E_{x-x})$ = the change in - ZE on transferring one molecule of cuprous sulphide from the pure liquid to the sulphide mixture.

For all the ideal configurations of the melts it has been assumed that there are no heat effects and therefore ideally

$$\delta(-Z_{Cu-Cu} E_{Cu-Cu}) + \delta(-Z_{Cu-S} E_{Cu-S}) = Z_{Cu-Na} E_{Cu-Na} +$$

$$Z_{S-Na} E_{S-Na} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot E$$

The large exothermic heats obtained show that the mixtures were not ideal but this was predicted and can easily be explained by two facts, namely the possible existence of a compound in the solid (Cu_2S Na_2S) and the stronger affinity of sodium compared with copper for sulphur.

The first would have produced a certain amount of short range order in the melts with a strengthening of some or all of the bonds. In equation E this would make the values of the left hand terms less, and of the right hand terms greater, than those for the ideal mixtures. The second effect would have increased the strength of the S-Na bonds; and would cause the $Z_{S-Na}\ E_{S-Na}$ term to have a value greater than that required by Equation E. Both these effects would make the partial molar heats in equation D exothermic and the experimental results can therefore be considered in full agreement with expected behaviour.

€) Partial molar entropies

The experimental values of the partial molar entropy were less than those calculated for the ideal models. There are two possible explanations for this fact; firstly there may have been a negative vibrational entropy contribution which could have been caused by the bonds having a greater electrovalent character in the mixtures than in the pure cupercooled liquid. The electrolytic conduction obtained by Savelsberg and the exothermic partial molar heats are consistent with such a view. Secondly there may have been a considerable degree of

ordering in the melts which would be expected if a compound (Cu_2S Na_2S) exists in the solid phase. Both these explanations may apply but at present it is impossible to assess their relative importance.

3) Activities

The experimentally determined activities are almost equal to those calculated for the second ideal model. No constructuve conclusions regarding the structure of the melts can be made from this fact however, because the ideal activities are based on ideal entropies and no heat effects. Such assumptions for these melts have been shown definitely wrong and agreement with any of the ideal activities can only be considered coincidental. Theoretically, conclusions concerning the choice of an ideal model could be drawn from results ~~with~~ for dilute solutions (3 mole%) where the assumptions may be valid, but it was found that results with the necessary ~~accurately~~ accuracy could not be obtained in this region.

This system indicates that entropies and heats are more likely to lead to the correct choice of an ideal model than activities. This fact has been pointed out by Hildebrand and Scott (38) who proved mathematically that any small deviation from an ideal model was more apparent in the entropy and heat than in the activity or free energy. In addition the deviations in the heat and entropy often

tend to cancel when combined to give the free energy. This is true for the present system, the exothermic heats tend to balance the low entropies.

It should be emphasized at this stage that present knowledge does not allow a useful estimation of the magnitude of any change in the vibrational entropy and of an accompanying heat effect to be made. It is therefore theoretically possible that one of the structural models is correct and that there was ideal mixing, the deviations shown in the activities heats and entropies being due to vibrational entropy changes and accompanying heat effects.

η) Comparison of these results with those for molten oxide mixtures

A comparison with some simple slag systems can be made by assuming that:-

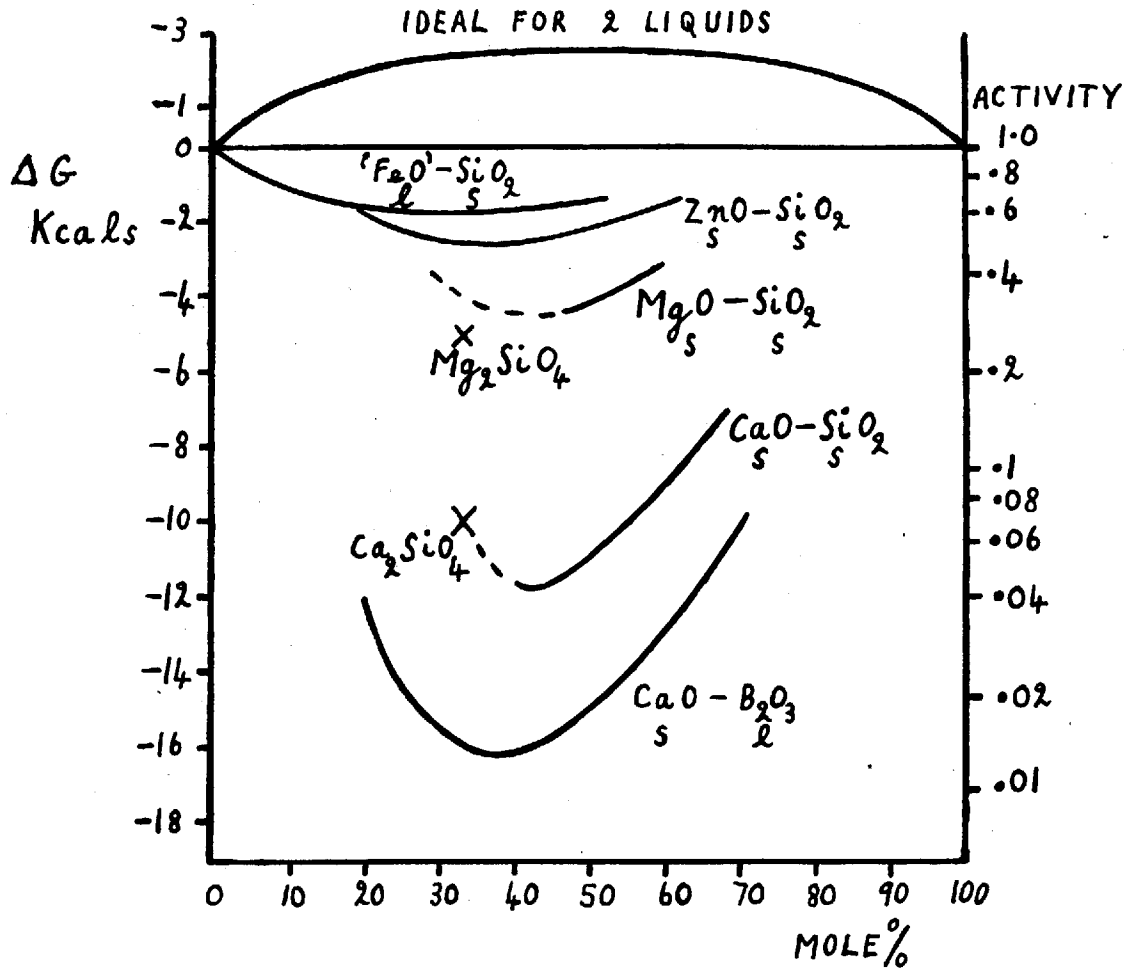
1) The activity curve has no pronounced inflexion enabling it to be extrapolated to the compound composition (Fig. 11)
2) The integral free energy of formation curve for this system has its minimum at the compound composition.

Due to the inaccuracy of the extrapolation the activity of cuprous sulphide in a 50 mole % mixture can have any value between the limits 0.1 and 0.2 at 820°C; the most likely value has been taken as 0.12. It follows from the second assumption that this value equals that of the activity of sodium sulphide in this mixture, and that

FIG 12

FREE ENERGIES OF FORMATION OF VARIOUS BINARY OXIDE MELTS AT 1600°C

SUBSCRIPT S OR ℓ DENOTES SOLID OR LIQUID AS STANDARD STATE



the minimum value for the integral free energy of formation curve is -4.6 Kcals at 820°C.

A summary of the important slag systems which have been investigated is shown in Figure 12.* It should be noted that the standard state of some of the components in this diagram was taken as the pure solid phase. This fact together with the inaccuracy in the present results makes a detailed comparison impossible; but it can be said that the activities are greater and the free energies of formation more positive for this sulphide system than for the CaO - SiO_2 and CaO-B_2O_3 systems, and that the converse is true when this system is compared with the 'FeO' - SiO_2 system.

c) SOLID MIXTURES

i) Thermodynamic study

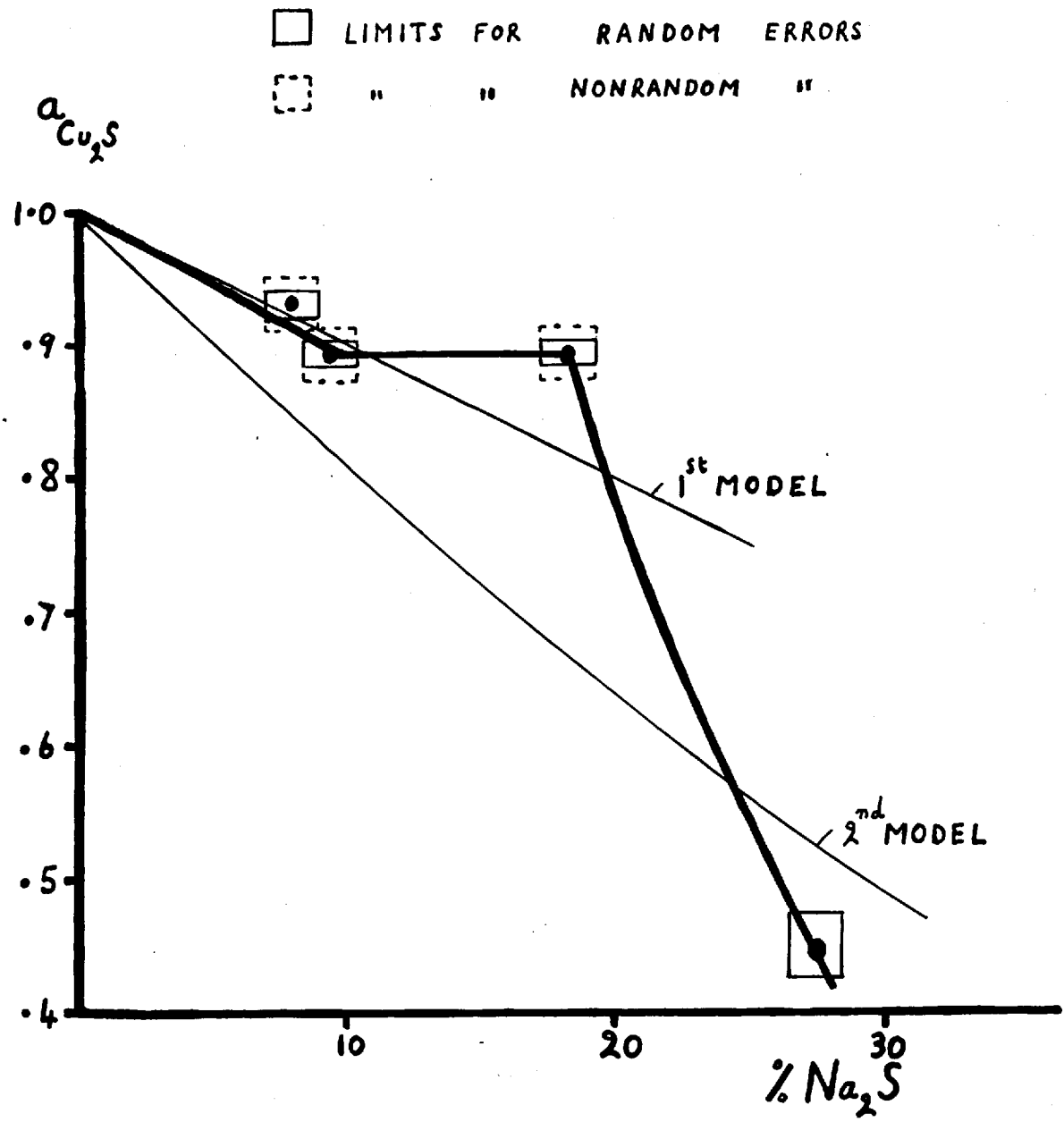
Thermodynamic measurements were made on four different mixtures in the solid state. Those on the 9.7% and 18.8% mixtures proved the existence of the two phase region, but unfortunately they could not be used to determine partial molar heats and entropies of cuprous sulphide because the two limiting compositions of the two phase region almost certainly changed with temperature. These functions, with the solid as the standard state, could however be calculated for the 27.5% mixture, the values obtained were - 13.6Kcals/

* This was reproduced from a paper given by Dr. F.D.Richardson at a Symposium on "The Nature of Molten Slags and Salts" held by the Nuffield Research Group in Extraction Metallurgy R.S.M. London 20th Feb.1952. Published by Inst.Min. and Met.

mole and -13.6 cals/deg mole. The heat term is considered reasonable when it is compared with the large exothermic heat of formation of solid sodium silicate (-56 Kcals/mole (39)), but the extreme negative value of the entropy can only be explained by a very large change in the vibrational entropy. Most of the partial molar entropies for the silicates are slightly positive and no other system having negative partial molar entropies of such a magnitude is known to the author. One possible source of error in the results for the 27.5% mixture is the equilibrium time used, the majority of the results were obtained by approaching the equilibrium from low hydrogen sulphide pressures the equilibrium time being taken as 2.5 hours; it was found subsequently that for different solid mixtures seven hours was necessary. This low value for the equilibrium time was checked by one experiment where the equilibrium was approached from high hydrogen sulphide pressures. The experiment was satisfactory and the equilibrium result was in good agreement with the others for this mixture but this was only one experiment which, now after all the results have been analysed, is considered inadequate proof of the attainment of equilibrium. The partial molar heats and entropies obtained for the 27.5% mixture have therefore been ignored, but the equilibrium results for this mixture at temperatures corresponding to points near the solidus curve cannot be in any great error and they have therefore been used to

FIG 13

A GRAPH OF a_{Cu_2S} AGAINST % Na_2S FOR SOLID $Cu_2S - Na_2S$ MIXTURES AT 628°C



calculate activities.

The cuprous sulphide activity curve is shown in Figure 13. The values obtained near the two phase region are much greater than those obtained for the liquids of the same composition. This higher activity in comparison with the liquid mixtures is to be expected because a two phase region is one within which there is a structural change and therefore in the neighbourhood of this region the lattice is under considerable strain resulting in high activities of the components. If these activities were divided into their heat and entropy terms it would probably be found that large endothermic partial molar heats had produced the increases in the activities and therefore no conclusions regarding the structures of the mixtures could be made from considerations of ideal models.

ii) X-ray powder photographs

When the above thermodynamic study had been concluded it was decided to take some X-ray powder photographs of the mixtures to verify the existence of solid solution and of the two phase region. The most satisfactory way to obtain these photographs was by means of a high temperature camera but unfortunately one was not available. A quenching technique had therefore to be employed; all

the mixtures were quenched from 500°C to room temperature in under 2 secs. A 9 cm camera and nickel filtered copper K radiation were used; the 'd' values obtained together with those used for reference purposes are presented in Table 11 (see page 110) and in Figure 14. All the patterns were complicated and had a heavy diffuse background, presumably due to secondary emission, which made the measurement of the lines difficult and therefore only the strongest most reliable lines were used.

In spite of the drastic quenching the low temperature form of cuprous sulphide was obtained. This is in agreement with Buerger (40) who believes that the transformation only involves a slight movement of certain atoms and is very rapid.

All the patterns of the 18.8 to 35% mixtures closely resembled one-another but there was a pronounced difference between these patterns and that of pure cuprous sulphide, when the patterns were examined closely it was found that two lines were common to both the 10.0% and 18.8% mixtures, and that both these lines did not appear for pure cuprous sulphide and the 27.5% and 35% mixtures. (d = 2.29 Å and d = 1.79 Å for the 10.0% mixture, d ≒ 2.28 Å and d = 1.80 Å for the 18.8% mixture). One of the lines was found in the pattern of pure cuprous sulphide and the other in the patterns of the 27.5% and 35% mixtures. These results indicate that a structure similar to that of cuprous sulphide may be present in a 10.0% and 18.8% mixture but

not in a 27.5% or 35% mixture, and that the structure of the 27.5% and 35% mixtures may be found in 10.0% and 18.8% mixtures but not in pure cuprous sulphide. These photographs therefore support the existence of a two phase region embracing both the 10% and 18.8% mixtures. In addition all the 'd' values obtained for the 18.8% to 35% mixtures steadily decreased whilst the order of the intensitites of the lines in each photograph remained the same with increasing sodium sulphide concentration, which is consistent with solid solution in this composition range.

Lastly a pattern completely different from any of the others was obtained for a 49% mixture and is probably that of the compound. A pattern similar to the one for the 35% mixture had been expected but the difference could be explained by another peritectic between these two compositions or by inadequate quenching and the existence of a two phase region at lower temperatures. This will not be discussed further because there is insufficient data from which to draw any definite conclusions.

The quenching technique which had to be employed means that the results cannot be treated in a quantitative manner (i.e. used to calculate lattice parameters) but qualitatively they are consistent with:-

1. The two phase region and the range of solid solution deduced from the equilibrium results.
2. The existence of a solid compound.

TABLE II

'd' values used for reference purposes

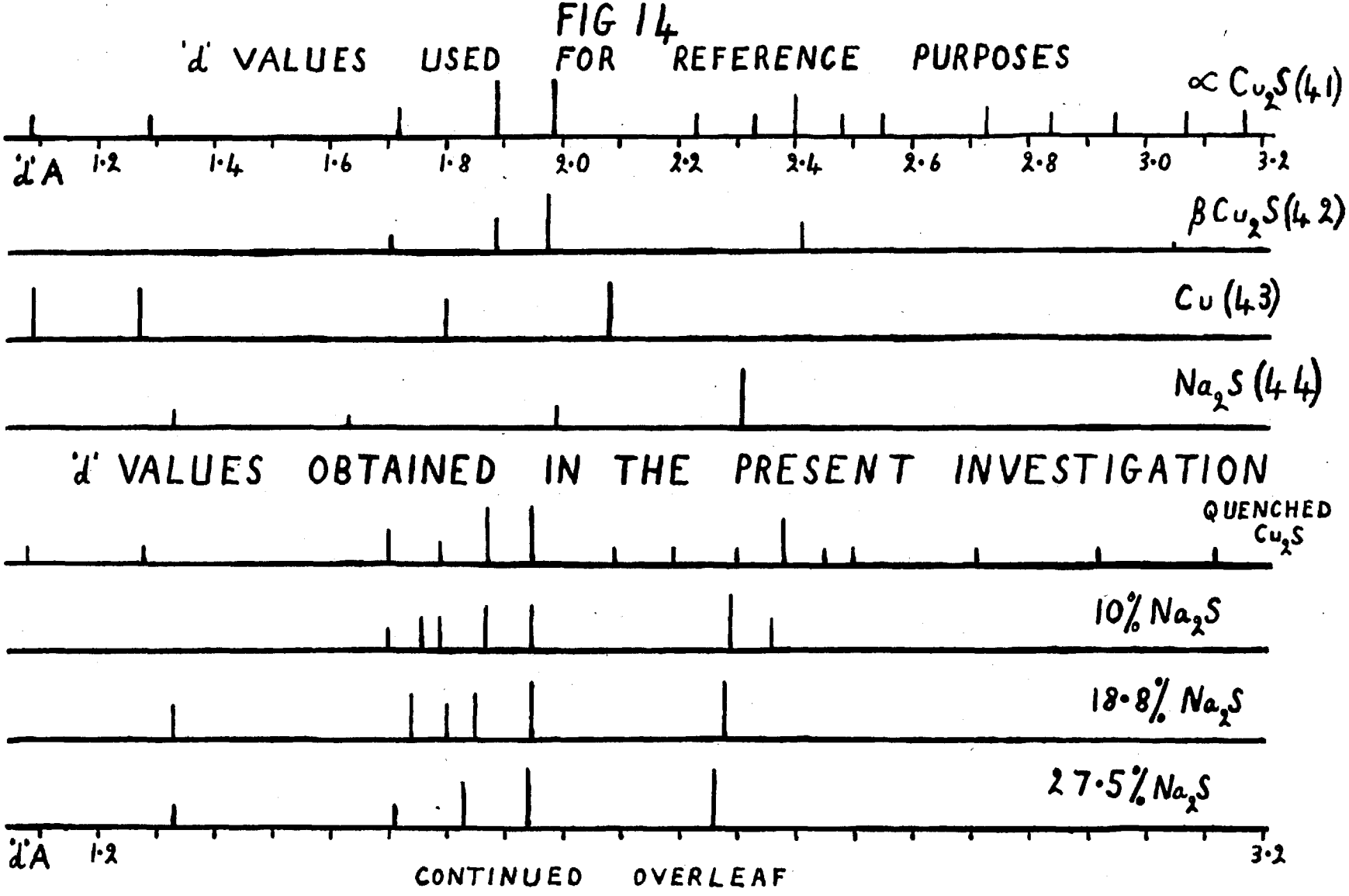
Substance	Reference	d	intensity
Cu_2S (α)	(41)	3.17	40
		3.07	40
		2.95	40
		2.84	40
		2.73	50
		2.55	40
		2.48	40
		2.40	70
		2.33	40
		2.23	40
		1.99	100
		1.89	100
		1.72	50
		1.29	40
		1.09	40
Cu_2S (β)	(42)	3.42	6
		3.40	6
		3.05	7
		2.412	50
		1.978	100
		1.975	100
		1.887	60
		1.708	36
		1.707	36
Cu	(43)	2.08	100
		1.80	70
		1.27	90
		1.09	90
		1.04	70
Na_2S	(44)	2.31 Å	100
		1.98	25
		1.63	20
		1.33	30

Table II - continued

'd' values obtained in the present investigation

Cu_2S (quenched)	3.12 Å	weak
	2.92	"
	2.71	"
	2.50	"
	2.45	"
	2.38	strong
	2.30	weak
	2.19	"
	2.09	"
	1.95	very strong
	1.87	"
	1.79	weak
	1.70	medium
	1.28	weak
	1.08	"
10% mixture	2.36	medium
	2.29	very strong
	1.95	strong
	1.87	"
	1.79	medium
	1.76	"
	1.70	weak
18.8% mixture	2.28	very strong
	1.95	"
	1.85	strong
	1.80	medium
	1.74	strong
	1.33	medium
27.5% mixture	2.26	very strong
	1.94	"
	1.83	strong
	1.71	weak
	1.33	"
35% mixture	2.24	very strong
	1.93	"
	1.82	strong
	1.70	medium
	1.32	weak

FIG 14



CONTINUED OVERLEAF

FIG 14 (CONTINUED)

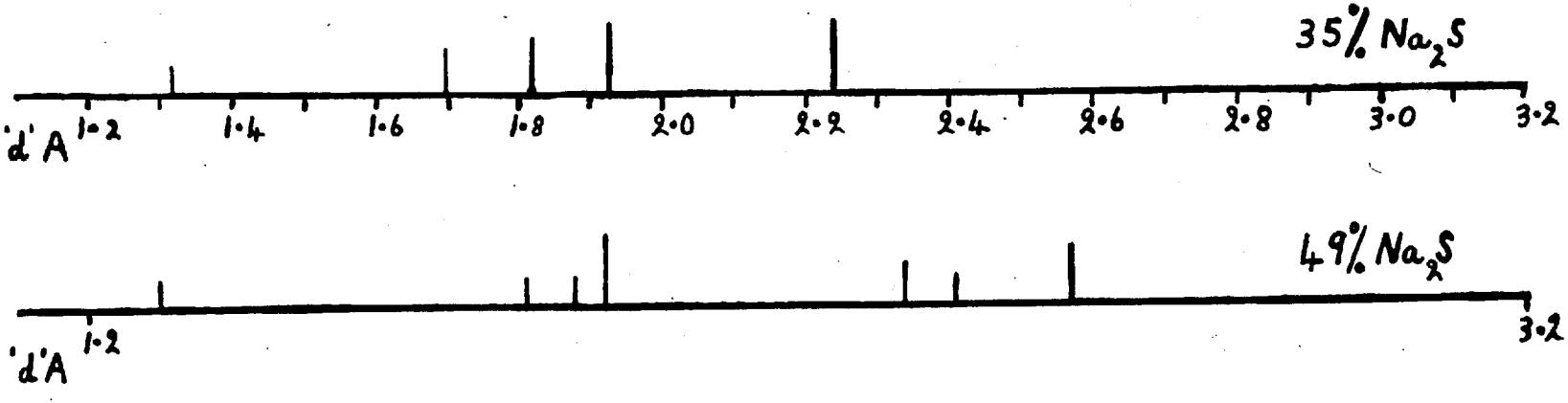


Table II - continued

49% mixture	2.57	strong
	2.41	weak
	2.34	medium
	1.92	very strong
	1.88	weak
	1.81	"
	1.30	"

No great accuracy is claimed for the above 'd' values due to the quenching technique employed. An error in them of $\pm$ 0.03 Å is considered possible. The intensities of the lines were estimated by eye; the values expressed diagrammatically in Figure 14, are only intended to show their relative order in e ach photograph and should not be taken as quantitatively accurate.

iii) Structure

This section of the work would be incomplete without a discussion of the structure of the solid solutions and therefore a few general remarks will be made on this subject.

General chemical knowledge supplies the following facts.

1) The sodium and cuprous ions are approximately the same size (Pauling's radii r_{Na+} = 0.95 Å r_{Cu+} = 0.96 Å (45))

2. The crystal symmetry of the high temperature form of cuprous sulphide is hexagonal and the Cu - S bonds are

largely covalent in character. Facts consistent with this last statement are the weak electronegative nature of the sulphide ion, the possible Sp and sp^3 hybridisation of the valence electrons of the cuprous ions and the electronic conduction of cuprous sulphide in the solid and liquid state.

3) The structure of sodium sulphide is antifluorite and the Na - S bonds are largely electrovalent in character due to the strong electropositive nature of the sodium ion.

The simplest structure for the solid solutions, consisting predominantly of cuprous sulphide, would be a cuprous sulphide lattice in which some of the cuprous ions have been replaced by sodium ions. The similar size of the two cations would suggest that no undue strains would be produced in the lattice. However another important factor to be considered is the covalent nature of the Cu - S bonds; this could give the bonds preferred orientations and could increase quite considerably the effective radius of the cuprous ion. For example, although its true ionic radius is 0.96 Å when combined with oxygen by sp hybridisation as in cuprous oxide its effective radius becomes 1.18Å (46). The sodium ion may therefore be replacing a much larger partide. More definite evidence of the importance of bond character is provided by the system lead sulphide - potassium chloride. Although these two compounds have the same structure and the corresponding ions are of similar size no appreciable

solid solution is obtained for this system (47) which must be attributed to the difference in bond type.

The two phase region could therefore be explained, if sodium ions in a cuprous sulphide lattice produce strains due to the difference in the character of the Na-S and Cu-S bonds. If the sodium concentration is gradually increased these strains should become progressively worse, until eventually the cuprous sulphide lattice breaks down. The new or modified structure should tend to remove the source of the strains. The similarity of the X-ray powder photographs of all the 18 to 35% mixtures indicate that this new structure exists over an appreciable composition range;,in addition it is probable that this structure becomes more stable the further away the composition is from the two phase region. This view is supported by the sudden decrease in the cuprous sulphide activity with increasing sodium sulphide concentration shown by mixtures richer in sodium sulphide than 19 mole%.

This discussion is necessarily inadequate due to the absence of comparable data but it should prove useful as a starting point when other sulphide systems have been investigated.

CONCLUSIONS

1) The points of importance in the corrected phase diagram are:-

a) The liquidus temperatures in the composition range 0 - 30% sodium sulphide are lower than those published by Friedrich.

b) There is an appreciable range of solid solution for the system which is inconsistent with the results obtained by Friedrich

c) There is a two phase region for the solid mixtures in the composition range 10 - 20% sodium sulphide.

2) The properties of the melts differ considerably from those of any simple ideal model because the melts have appreciable exothermic partial molar heats and low partial molar entropies of cuprous sulphide.

3) The heat of fusion of cuprous sulphide is 2.5± 0.5 Kcals/mole.

4. The free energy of formation of the molten compound (Cu_2S Na_2S) has a value between that of molten fayalite and the values of the molten caldium borates and silicates.

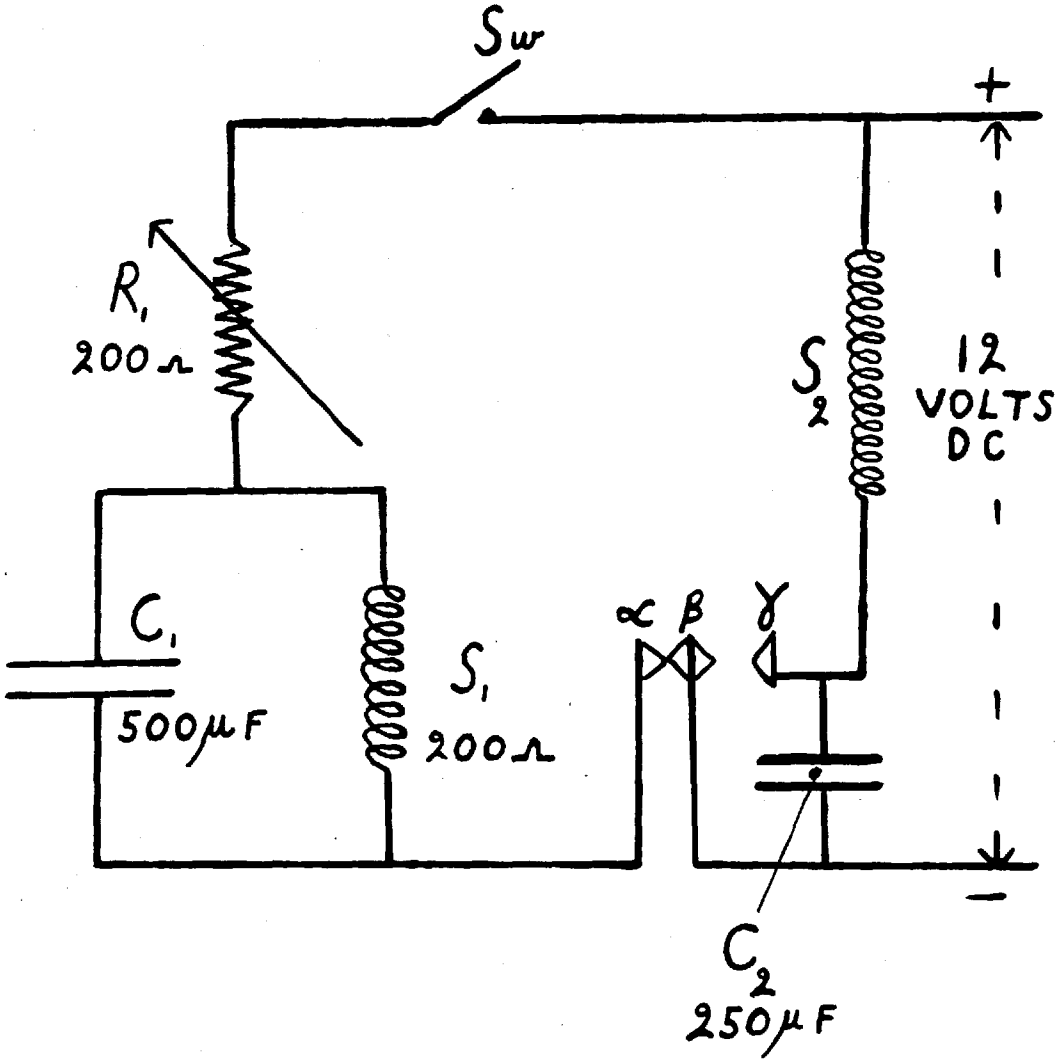
APPENDICES

APPENDIX 1

The D.C. Pulse Supply of the Gas Circulating Pump.

The D.C. pulse supply necessary for the operation of the gas circulating pump was a copy of one used by Mr.Alcock when at B.I.S.R.A. and is shown diagrammatically in Figure 15. The main component was a post office relay (contacts α β γ) which was used to make and break the current to the pump solenoid. When the supply was not in use contacts $\alpha-\beta$ were closed. To start the pump working switch Sw was closed; the condenser C_1 first became charged and current then flowed through the relay solenoid S_1 causing contacts $\alpha-\beta$ to break and $\beta-\gamma$ to make, which in turn caused current to flow through the pump solenoid S_2. The condenser C_1 then discharged through the relay solenoid S_1 which continued to keep contacts $\beta-\gamma$ closed, but once the charge was exhausted contacts $\beta-\gamma$ broke and $\alpha-\beta$ made which cut off the current to the pump solenoid S_2. Condenser C_1 again became charged and the process repeated. Condenser C_2 was used to eliminate any sparking across contacts $\beta-\gamma$. The frequency of the pulses and hence the gas flowrate was controlled by the rate of charge of condenser C_1 which could be regulated by the rheostat R_1.

FIG 15
DC PULSE SUPPLY



APPENDIX 2

Experiments which confirmed the absence of thermal diffusion with the aid of radioactive sulphur.

The principle of the method was exactly the same as in the experiments in which stable sulphur was used, i.e. a constant gas composition for a varying flowrate proved the absence of thermal diffusion. The experimental technique differed in that here a sample of cuprous sulphide containing radioactive sulphur was used and a gas counter was added to the gas circuit. The advantage gained was that a continual record of the gas composition could be kept.

Preparation of the cuprous sulphide containing ^{35}S.

Carrier-free radioactive sulphur was received from Harwell in the form of an aqueous solution of sodium sulphate. A sample of this solution containing 1 millicurie of radioactive sulphur was added to another solution containing 4.0 gms of stable sodium sulphate, and the liquid evaporated. The residue was transferred to an alumina boat and heated in a stream of hydrogen for 4 hours at 750°C. Most of the sulphate was reduced to sulphide. The product was dissolved in dilute acid and the hydrogen sulphide evolved passed into an acid solution of cupric

sulphate. The precipitated sulphide was collected, washed, dried and placed with an excess of copper in the furnace, which was heated slowly to 600°C whilst hydrogen was slowly circulated. Cupric sulphide is very unstable and therefore this reduction to cuprous sulphide was made to take one day so as to minimize the risk of sulphur deposition.

It was found in the sodium sulphate reduction stage that some of the resulting sulphide was always on the outside of the boat and in some cases had stuck the boat to the refractory tube. Due to this and to the general disadvantages of handling delinquescent sodium sulphide it is strongly recommended that this method is not used in any future work, instead that employed by Mr.Ignatowicz of B.I.S.R.A. should be tried, here the sodium sulphate is first converted to barium sulphate which is then reduced to the sulphide in hydrogen at about 1000°C.

Apparatus (Figure 16)

The gas counter consisted of an end window Geiger Müller tube (G.E.C. EHM2S) which was fastened by "Durofix" to the bottom of a glass hood through which the gas mixture continuously passed. Some of the soft β particles emitted by the sulphur passed through the mica window of the counter and caused a pulse to be produced at the

anode. This pulse passed through a probe unit and was recorded by a scaler. The rate of counting was a measure of the partial pressure of hydrogen sulphide in the gas.

The hood had to be painted black as the Geiger Müller tube was photosensitive, and a piece of cellophane had to be placed between the gas and the mica window, because mica strongly absorbs hydrogen sulphide. In these experiments a soda glass hood was used, but a high background count was obtained due to adsorption of hydrogen sulphide by the glass; 'pyrex' is therefore recommended for any future work.

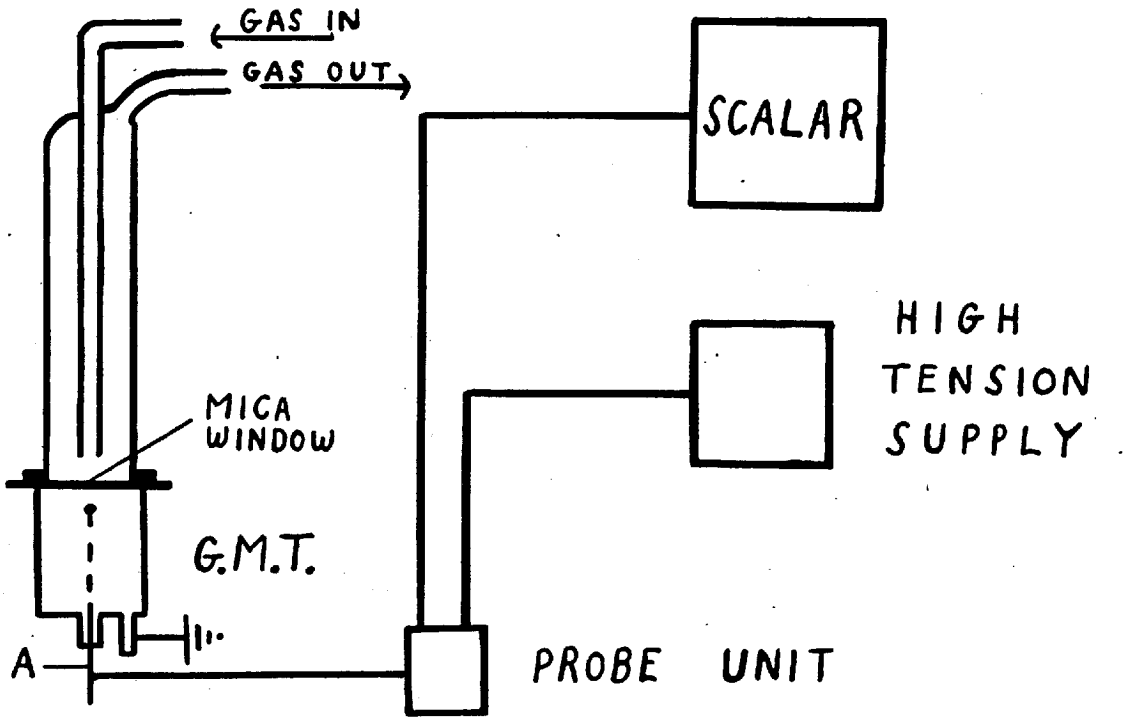
Due to the perfectly random manner of the radioactive decay of a given source a graph of the rate of counting against the total number of counts taken is a Gaussian curve, therefore for every measured counting rate there is a possible deviation from the average counting rate. It can be proved mathematically that if -

n = the average value of the number of counts recorded in a given time most of the individually measured values lie within $n \pm \sqrt{n}$

To obtain a reproducibility of ± 1% it was therefore necessary to take 10,000 counts and the activity of the sulphur was adjusted to give this number in a reasonable time (10 minutes).

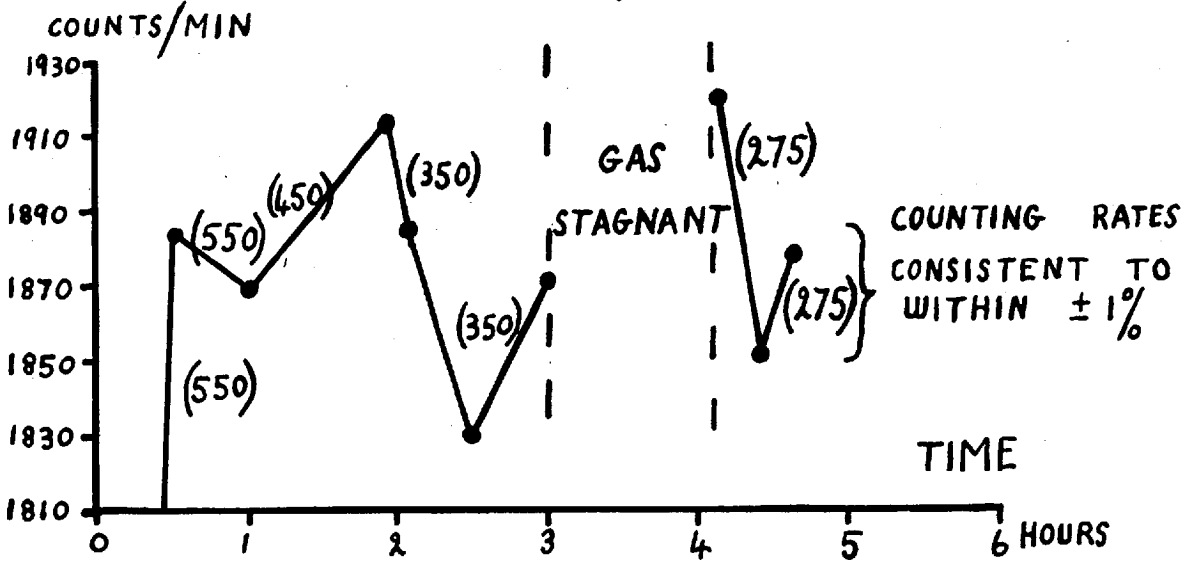
FIG 16

APPARATUS FOR EXPERIMENTS WITH ^{35}S



RESULTS PROVING THE ABSENCE OF THERMAL DIFFUSION USING ^{35}S

NUMBERS IN BRACKETS DENOTE GAS FLOWRATE IN C.C./MIN



Results

The results of an experiment in which the furnace was controlled at a temperature of 1016°C and the flowrate varied whilst a continual record of the gas composition was kept are shown in Figure 16. With a flowrate of 550 cc/min and no gas sampling bulb in the gas circuit equilibrium was reached in under half an hour, the flowrate was then reduced to 350 cc/min and at the end of an hour the counting rate was still constant. Circulation was discontinued for one hour; due to thermal diffusion an excess of hydrogen sulphide built up in the apparatus. When the gas was recirculated therefore at 270 cc/min a higher counting rate was initially obtained, but this later decreased to the original equilibrium value obtained with 550 cc/min. Thermal diffusion effects were therefore considered to have been absent when flowrates between 270 cc/min and 550 cc/min were used with the furnace at 1000°C.

APPENDIX 3

Heat of fusion of cuprous sulphide

The method by which the heat of fusion was calculated from the partial molar heats was explained on pages 90 - 92. It gave a value of 2.5 K cals/mole for the heat and 1.8 cals/deg mole for the entropy of fusion; these values are consistent with the partial molar free energies and entropies obtained because when the functions having the liquid as the standard state are plotted against composition the graphs extrapolate smoothly through the origin (Figs.9,10). In the calculation of the heat of fusion there are two sources of error to be considered firstly the extrapolation and secondly the uncertainty in the thermodynamics of pure solid cuprous sulphide. The two extreme possibilities of the extrapolation are shown in Figure 8 and the error due to this cause is not considered to be greater than ± 400 cals. The error due to the second cause is equal to that in the heat of formation of cuprous sulphide and may therefore be ± 150 cals. Lastly it should be mentioned that the heat obtained is strictly the heat required to convert the solid to the supercooled liquid at approximately 250°C below the true melting point. If the true heat of fusion was required, the difference between the specific heats of the solid and liquid would have to be taken into

account and a correction applied, but such a correction is probably small compared with the overall accuracy and it has therefore been ignored. The error in this value of the heat of fusion should therefore not be greater than ± 0.5 Kcals/mole.

The following table, reproduced from a paper given by Bockris (48), shows how the heat and entropy of fusion depend on the structure of a compound.

Table 12

	H_f in Kcals/mole	S_f in cals/deg.mole
Metals	0.5 - 5	1 - 5
Ionic substance	2 - 9	3 - 13
Molecular substance	0.02 - 2	2 - 9

It indicates that the values obtained here are reasonable but slightly lower than might have been expected.

Kelley gave the most likely values of the changes as 5.5 K cals/mole and 3.93 cals/deg mole (49). These values were based on freezing point data obtained from the phase diagrams for several binary systems (Cu_2S-Cu_2Cl_2, Cu_2S-Ni_2S etc.). This method is extremely unreliable because assumptions have to be made concerning the compositions and activities of the various molecular or ionic species present. In addition data was ignored which gave low values and therefore these figures need not be considered accurate.

Silver sulphide affords an interesting comparison with cuprous sulphide. Rosenquist (50) has calculated the heat and entropy of fusion of silver sulphide as 800 cals/mole and 0.7 cals/deg mole respectively. These values are very low and can be explained by the structure of solid silver sulphide which is thought to be a rigid sulphur lattice within which the silver atoms are free to move as in a liquid. It is possible therefore that in cuprous sulphide one or both of the copper atoms are free to wander within a sulphur lattice, a picture which would be consistent with the disordered state idea for the structure put forward by Buerger (see page 9,10) and the qualitative observation of Hideo Tazaki and Shigeya Kuwabara who noticed that copper has a high rate of diffusion through solid cuprous sulphide (51). They grew thick films of cuprous sulphide on copper and took electron diffraction photographs of the surface. For freshly formed films they obtained the patterns of copper and of cuprous sulphide, but after the films had been heated at 100°C for a short time only the pattern of copper was obtained, indicating that the copper had been sufficiently free to diffuse through the cuprous sulphide to form a thin layer on the surface.

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

I wish to express my gratitude to my supervisor Dr. F.D. Richardson for his constant guidance and advice during this work, which was made possible by a Department of Scientific and Industrial Research maintenance grant and the facilities provided by the Nuffield Research Group in Extraction Metallurgy in the Royal School of Mines.

Finally I wish to acknowledge the help received from the late Mr. O.H. Gellner, and in particular that from Mr. C.B. Alcock of the Nuffield Research Group who has always willingly offered advice, encouragement and criticism.

J. E. Antill.

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Royal School of Mines.

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