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Studies of Sulphides of Elements
of Groups Three and Four

by Alan Ivor Foster

A thesis submitted for the Degree of
Doctor of Philosophy

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ABSTRACT

A study was made of the possibility of synthesising sulphur analogues of the aluminosilicates, in which the oxygen in the framework was replaced by sulphur. From the basis of a consideration of the structures of the oxides and sulphides of the elements of Groups III b and IV b, stereochemical and radius ratio predictions suggest that such a substitution of sulphur for oxygen should be possible. Two approaches were adopted in testing this hypothesis. Firstly, attempts were made to sulphide 13X zeolite (chosen as a representative and stable framework aluminosilicate) with carbon disulphide at temperatures up to 700°C. The results indicated that replacement of structural oxygen by sulphur only occurred with a destruction of the framework lattice, which was not reformed. Secondly, hydrothermal systems were set up, in which synthesis of sulphides was attempted in a manner analogous to the hydrothermal preparation of zeolites. Two experimentally distinct methods were used, employing as solvent hydrogen sulphide and water respectively. The work with hydrogen sulphide was conducted in autoclaves under both sub-critical and super-critical conditions, the maximum temperature employed being 350°C. The aqueous reactions were conducted at atmospheric pressure below 100°C. The results in both cases were similar. Solution of the Group III b and Group IV b sulphides occurred in the basic solvent media, with the formation of ternary sulphides analogous to sodium silicate. However, no tendency was found for these ternary sulphides to interact in solution with the formation of more complex phases. The materials formed were characterised by chemical analysis, x-ray diffraction, infrared analysis, adsorption and surface area measurements and tests of catalytic activity. The results obtained confirmed the view that only low surface area ternary sulphides were formed, bearing little relationship to framework aluminosilicates.

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CHAPTER 1. INTRODUCTION

1.1 BACKGROUND AND OBJECT OF THE PROJECT

To a large extent the chemistry of the sulphides has developed independently, and in many cases to a lesser degree, than that of the oxides, it being usual to discuss the two families of compounds from the basis of their differences rather than their similarities. In part, this is due to the changes in the stereochemistry and chemical properties found between one element and another in the same group, and probably also partly due to the separate distribution of the two classes of compounds in nature, leading to their independent study and classification.

Mason's "Principles of Geochemistry" (1) lists the relative abundance of the elements, the three most commonly occurring being oxygen, silicon and aluminium (46.60, 27.72 and 8.13 wt % respectively). The preponderance of the earth's crust therefore consists of silicates, with smaller amounts of oxides of aluminium. When it is remembered that the sulphides of silicon and aluminium hydrolyse immediately and irreversibly in the presence of water, it is not surprising that they do not occur in nature, and that the study of their chemistry has not been developed to the same extent as that of the oxides.

Elements naturally occurring as sulphides are not normally found also as oxides; Goldschmidt (2) classified the elements that are 'chalcophile'-ie characterised by a strong affinity in nature for sulphur and arsenic, and 'lithiophile' - ie associated with oxygen, often in silicates. Considering the elements of

groups III b and IV b, silicon and aluminium, and to an extent gallium and tin, are generally found as oxides, while germanium, tin, lead, gallium, indium, and thallium occur as sulphides. These sulphides crystallise out quite separately from the main body of the silicates.

It is therefore not unreasonable that sulphides should be regarded separately from oxides, and even in the last few years the existence of thio-analogues of the simple oxides (ie silicates or aluminates) has been discounted by most texts on inorganic chemistry (eg 3 and 4). However, fresh work is continually furnishing new evidence to show that such distinctions are provided more by circumstance than by nature, and it is with this field of research that the present work is concerned.

Comment was made above of the instability of the sulphides of aluminium and silicon towards water; it is apparent therefore that any attempt to investigate the chemistry and structures of the oxides and sulphides must be restricted either to systems involving sulphides stable towards water, or otherwise to anhydrous systems. It was with this latter topic that the greater part of this work was concerned. If water is regarded as the parent of the oxides and the medium from which silicates and related structures are formed, then by direct analogy hydrogen sulphide may be regarded as the parent of the sulphide analogues of these compounds. It was a desire to find whether this material, whose solvent properties have received only scant attention, could form a medium from which sulphides could be crystallised in the same way that silicates and aluminosilicates crystallise from aqueous solutions, that was the starting point of this work. A

second aspect of interest was the inherent nature of materials formed by such a process. Almost without exception, sulphides have been prepared by heating the elements in a sealed tube; this leads to dense materials frequently based on close packed atoms - the 'conventional' sulphides of nature. These materials are very different from many of the silicates and related oxides that have crystallised from a solvent. The latter are characterised by more open, framework structures based on interconnected tetrahedra. The extreme case is found in zeolites, where channels and cavities of precisely defined dimensions are formed by the structural tetrahedra of SiO_4 and AlO_4 joining in clearly defined ways. No such structures are known in the sulphide systems, and it was thought that this might simply be a reflection on the methods of preparation previously adopted. The oxides only form these open framework structures containing channels and voids in the presence of a suitable 'mineralising' solvent, and it was thought that the duplication of these structures in the sulphide system would also require a solvent, and hydrogen sulphide would form the obvious first choice.

Besides the inherent interest of any such framework sulphides that might be formed, there is a strong industrial interest in zeolites and related oxides. Zeolites themselves have found widespread use as molecular sieves for the separation of materials according to molecular size, and aluminosilicates in general are widely used as catalysts. The acidic properties associated with these materials is rendered more useful in the case of zeolites by the location of the active sites within the molecular framework, and these materials have found widespread use as catalysts for

reactions demanding acidic conditions (ie cracking, isomerization). Besides the use of selective poisoning by sulphur as a well established means of enhancing catalyst selectivity, sulphided zeolites have been shown to have particularly beneficial properties. Therefore, great interest would be attached to the catalytic properties of sulphur analogues of these compounds, with especial regard to selectivity, resistance to poisoning by sulphur, and desulphurising activity.

An alternative approach in the comparative study of oxides and sulphides is to use sulphides which are stable under aqueous conditions, rather than hydrolysable sulphides under anhydrous conditions. Therefore, besides an examination of the sulphides of aluminium and silicon in liquid hydrogen sulphide, a further basis for comparison is the examination of the sulphides of gallium, indium, germanium and tin in aqueous media. These materials are stable with respect to hydrolysis under conditions similar to those in which silicates and aluminosilicates are formed. The known existence of oxides formed by these lower Group III b and IV b elements analogous to silicates and aluminosilicates offered incentive to the attempted preparation of analogous sulphides. The survey was ultimately completed by extending the anhydrous studies with hydrogen sulphide to also cover these elements.

A further approach in the preparation of sulphur analogues of the aluminosilicates is to take an oxide with the required structure and attempt to replace the oxygen atoms by those of sulphur. Such a process is known to be possible in

the case of simpler oxides, and partial or complete replacement of oxygen by sulphur has been reported for silica, alumina and certain aluminosilicates. High temperature reaction with hydrogen sulphide or carbon disulphide was used. Therefore, another aspect of the research was the extension of these techniques to more complex oxides in the form of zeolites.

Thus, the aims behind the project may be summarised as an examination of the possibilities of preparing sulphide analogues of the silicates and aluminosilicates by several methods, but with especial regard to the use of hydrogensulphide as a mineralising solvent.

The ultimate aim would be the formation of thiozeolites, which could have great intrinsic and commercial interest. During the course of this work, the general question of the interrelations of the sulphides and oxides, and their similarities and differences, was borne in mind, in the hopes of contributing to a more complete correlation between these two families of compounds.

An important aspect of any research project of this sort is the characterisation of the materials formed. Besides chemical analysis, X-ray powder diffraction was used as a quick and ready means of assessing the extent to which reactions had proceeded, and the type of material and crystallization obtained. In a project where formation of a specific type of crystal structure is desired, the importance of this technique as an analytical tool cannot be overestimated, although it does not by itself give a complete insight into the processes occurring. The formation of zeolitic materials, for example, leads to large unit cell structures, and the presence of lines corresponding to wide interplanar spacings

on the diffraction patterns serves as an indication of the formation of this type of material. However, zeolites are known which do not give rise to lines corresponding to particularly wide spacings, and conversely, widely spaced lines may be due to causes other than the presence of zeolites. Thus, additional means of characterization are required.

Measurement of the surface area, and data on pore size and shape, by nitrogen adsorption is a useful approach. Aluminosilicates and related materials have comparatively large specific surface areas, either on a macroscale (like certain aluminas), resulting from the mode of preparation, or as an inherent feature of the structure, as with zeolites. Furthermore, measurement of the adsorption capacity for molecules of graded sizes forms a convenient means of assessing the sieve properties characteristic of zeolites. Cation exchange and stability towards dehydration are further properties a material must possess to be regarded as zeolite-like.

The acidic properties associated with aluminosilicates may be measured by their reactivity towards mildly basic materials such as pyridine, using either chemisorption or infra-red techniques. These properties are also reflected in catalytic activity for reactions such as cracking or isomerization, whilst sulphide analogues of these compounds might be expected to show resistance to poisoning by sulphur or especial activity for desulphurization reactions. Whilst not all of these approaches were adopted in the work undertaken, they serve to illustrate the range of methods available for the characterization of the products obtained by the various preparative techniques used. In practice, chemical and x-ray analyses were backed up by measurement of the

surface area and catalyst activity for typically acid catalysed reactions, and other tests such as ion exchange were used as appropriate. In this way, the nature of the products obtained and the degree to which they resembled the corresponding oxides was assessed.

1.2 LAYOUT OF THESIS

From the foregoing discussions of the work undertaken, it will be appreciated that a large area was covered during the course of the investigation, and the following shows how it has been incorporated into the thesis.

Owing to the diverse nature of the topics studied, these have been presented separately as different sections (Chapters 3 - 7), each comprising (1) Introduction, including a survey of the background literature and objects of the work undertaken; (2) Experimental Section, with the results and discussion, and (3) Final Conclusions.

Following these chapters, a section of overall conclusions has been included (Chapter 8), wherein are discussed the significance of the results obtained in meeting the objectives set. Also included are suggestions for further work on the more interesting topics.

This is followed by the bibliography and an appendix consisting of tabulations considered too bulky to be conveniently incorporated within the text.

No matter how interesting and original a topic may be, time spent pursuing it will be wasted if the objectives are theoretically infeasible. For this reason the first main section

(Chapter 2) comprises a theoretical discussion of the chemistry involved, with especial regard to the comparative chemistry of the sulphides and oxides, and the types of structures encountered and their modes of formation. As the formation of zeolitic type materials was the ultimate objective, some thought as to their mode of formation in the hydrothermal system is given. The general question of analogue compounds is reviewed - the isomorphous replacement of one ion by another in a crystal lattice, and some mention is also made of the establishment of novel crystallization systems in recent years, and the development of new materials to serve as fluxes in such systems. In addition to the discussion of the fundamental chemistry, this section also includes a review of the relevant literature, fundamental to the project as a whole.

This section is followed by the first experimental section, comprising the work concerned with the sulphiding of conventional zeolites at elevated temperature (Chapter 3). The literature relating to the sulphiding of molecular sieves and the use of sieves in sulphide-containing systems is reviewed here.

Many of the materials required for the synthetic techniques investigated were not available commercially, and in some cases published methods for their preparation did not exist, or required investigation. Therefore, the next section (Chapter 4) is devoted to the preparation methods adopted for these materials. Especial regard is given to the use of aluminium alkyls as starting materials for the preparation of organo-aluminium sulphur compounds, and the properties of the materials obtained.

Next follows a description of the main hydrothermal experiments in hydrogen sulphide solvent (Chapter 5), and of the high pressure equipment used. The background literature relating to

hydrogen sulphide and its solvent properties is reviewed here. This is followed by a description of the reactions carried out under aqueous conditions (Chapter 6), and the final experimental section (Chapter 7) relates to the measurement of surface area and catalytic activity as a means of further characterizing the products obtained. The known catalytic properties of the sulphides and aluminosilicates are briefly reviewed here as a means of assessing the significance of the results obtained.

1.3 LITERATURE SURVEY

As the literature relating to the research topic is presented in the sections to which it is relevant, the following general remarks are made as an indication of the scope of the survey undertaken.

The retrospective survey was conducted using Chemical Abstracts, which was searched from its inception to date. The topics scanned included zeolites, ultramarines, thiols, all aspects of sulfur and sulphides, molecular sieves, mercaptides, hydrogen sulphide, crystallization and crystal growth, and catalysis, besides all elements considered in the work. As a further check on the completeness of this survey, Science Citation Index, published by the Institute for Scientific Information, has been used with leading references.

The current awareness search has been conducted using Chemical Abstracts as published, and in addition, for a more up to date survey, Current Chemical Papers, published by the Chemical Society (London), has been scanned as published. When this ceased publication at the end of 1969, Current Contents - Chemical and Physical Sciences section, was used. This is published by the Institute for Scientific Information.

Besides primary sources, reviews and text books have been widely used, and these are referred to in the various sections. In addition to the topics mentioned above, other references relate to the methods of analysis, equipment and other subsidiary subjects covered by the project.

CHAPTER 2 THEORETICAL BACKGROUND

2.1 COMPARATIVE SURVEY OF THE SULPHIDES AND OXIDES

It is usual for members of the first row of the Periodic Table to possess properties markedly different from lower elements in the same groups, and so it is that major differences exist between oxygen and sulphur. Nevertheless, it is hoped to illustrate in this chapter that these elements do have properties in common, and that differences are better represented as sharp transitions than impenetratable boundaries.

2.1.1 Fundamental Differences between Oxygen and Sulphur

Oxygen has the outer electronic structure $2s^2 2p^4$, and sulphur $3s^2 3p^4$. From this, many of the stereochemical and chemical features of the oxides and sulphides may be rationalised, and most modern text-books of inorganic chemistry contain a discussion of this sort. Especially useful have been found those by Wells (5) and Sanderson (3). Another text found invaluable is the comprehensive review on inorganic sulphur chemistry edited by Nickless (6).

Although the outer electronic configuration of the two elements is similar, there are fundamental differences, which may be summarised as follows. Firstly, there is the greater screening of the outer electrons in the case of sulphur, with ten underlying electrons, compared to only two in the case of oxygen. This reduces the closeness of interaction and multiple bond formation characteristic of oxygen compounds, and results in a preference for single bonds in the case of sulphur. This is witnessed by the multiply bonded oxygen molecule and the singly bonded ring of eight atoms constituting a sulphur molecule. This behaviour is also responsible for the formation of polysulphides containing chains of sulphur atoms, a situation never found in the case of oxides, and is reflected in the structures of many sulphides.

Another major difference between the two elements apparent from their electronic structures is their electronegativities. Sulphur has a considerably more diffuse electron field than oxygen, and possesses a lower electronegativity. Pauling (7) assigned electronegativities to oxygen, sulphur and selenium of 3.5, 2.5 and 2.4 respectively, and the difference between oxygen and the lower group VIb elements is immediately apparent. Bonds with sulphur therefore have considerably less ionic character than those with oxygen, having more tendency to become polarised, with structures tending more to those associated with co-valency. The sulphur atom therefore frequently has a more asymmetrical surrounding than oxygen, and layer structures are common with sulphides, while the corresponding oxides generally have simple ionic structures. The extreme is reached with those sulphides (particularly of the transition elements) which have properties more in common with metallic alloys, such as lustre, conductivity and reflectivity.

In general, the lower electronegativity of sulphur leads to compounds that are less polar, and possess corresponding features (eg, lower melting point, boiling point, dipole moment, and dielectric constant). Nowhere are these differences more marked than between water and hydrogen sulphide. The properties of hydrogen sulphide are fully considered in Chapter 5, but the unassociated, non-polar characteristics of this material may be cited here as resulting from the low electronegativity of sulphur compared to oxygen. Similarly, its low boiling point compared to that of water is attributed to the much lower degree of hydrogen bonding found in the sulphur system, a direct consequence of the lower electronegativity of sulphur. Similarly, the lower solute-solvent interaction through hydrogen bonding found in the sulphur system is apparent in the limited solubility of the alkali

metal salts of mercaptans in the parent mercaptan, compared to the ready solubility of the corresponding alcohol salts in the alcohols.

Until comparatively recently, such facts were taken as evidence that hydrogen bonding was not encountered in the sulphur system, but later work, based chiefly on spectroscopic measurements, has shown that it does occur to a limited degree with strong bases, where the -SH group acts as a proton donor. More recently still, it has been shown that hydrogen bonding can occur to sulphur (proton acceptor), although the effect is very weak, accounting no doubt for its supposed absence in such materials as thiols. Useful reviews exist on the topic (8, p 201 ;9). As a direct comparison to the strong hydrogen bonding observed in the oxygen system, and its effect on the solvent properties of water, the systems where sulphur acts as a proton acceptor are more interesting. Infra-red (10) and nuclear magnetic resonance (11) measurements of dilution shifts have shown this type of hydrogen bonding (SH S) in thiols, albeit very weak compared to that found in alcohols, where chains of molecules are found (8, p 19). The authors of (11) suggest that only monomers and dimers exist in thiols to an appreciable extent. The structure of water is typified by a three dimensional network of hydrogen-bonded molecules (8, p 17), and by analogy with the water/alcohol system, hydrogen sulphide would be expected to exhibit a greater degree of hydrogen bonding than do the thiols. Evidence (12) suggested that no interaction existed when hydrogen sulphide was dissolved in carbon disulphide, but more recent work on solid (13), liquid (14) and gaseous (15) hydrogen sulphide indicates weak intermolecular interactions. Monomer, dimer and polymer species are reported in the solid state from matrix isolation spectra (13), with a hydrogen bond strength of

approximately half that of water in a similar system. From gas phase measurements (15) the hydrogen bonding energy has been estimated as 1.7 ± 0.3 kcal/mole; this may be compared to the value of 4.5 kcal/mole quoted by Pauling (7, p 304) for water. Further evidence for the existence of (S-H S) hydrogen bonding was provided by a study of the solute-solvent interactions of the tetramethyl ammonium hydrosulphide/liquid hydrogen sulphide and triethyl ammonium hydrosulphide/liquid hydrogen sulphide systems (16) in which complexes (SH^- HS^-) with hydrogen bond energies of between 7 and 14 kcal/mole were encountered. This system is further considered in Chapter 5 in connection with the hydrothermal reactions in liquid hydrogen sulphide.

Another consequence of the lower electronegativity of sulphur is that, in general, oxygen can easily displace it from most of its compounds, and most sulphides soluble in water are readily hydrolysed. This is attributed to the reduced stability of the negative ions going down Gp.VIb, as witnessed by the ready hydrolysis of the S^{2-} ion in aqueous solution to form SH^- or even H_2S^- - evidence of the strong basic strength of the sulphide ion. A further consequence relevant to the present work is the formation of thiosalts. Just as acidic oxides can form compounds with basic oxides (ie aluminium hydroxide and sodium hydroxide form sodium aluminate), so similar compounds are found in the sulphur system, albeit to a more limited degree. Sanderson (3, pp 208 et seq) discusses this point, and cites a charge on sulphur of less than -0.09 electron as necessary for a sulphide to become the anionic portion of such a complex. The data he presents is reproduced in Table 2.1, and from this it is concluded that only gallium, carbon, germanium and tin are able to form complex sulphides analogous to silicates and aluminates, at least in aqueous solution. This proviso seems necessary, for, as the author points out, with the exception of

<u>Group IIIb</u>	B_2S_3	Al_2S_3	Ga_2S_3	In_2S_3	Tl_2S_3
Charge on Sulphur (e)	-0.13	-0.25	-0.09	-0.13	-0.11

<u>Group IVb</u>	CS_2	SiS_2	GeS	GeS_2	SnS	SnS_2
Charge on Sulphur (e)	-0.03	-0.13	-0.06	-0.04	-0.13	-0.09

Table 2.1 Charge carried by sulphur in Group IIIb and IVb Sulphides.

(3, p.208 et seq.)

Triangular	Tetrahedral	Octahedral	Cubic
Co-ord. No. 3	Co-ord. No. 4	Co-ord. No. 6	Co-ord. No. 8
0.155-0.225	0.225-0.414	0.414-0.732	≥ 0.732

Table 2.2 Radius Ratio of Cation to Anion for various structure types.

(5, p.72)

indium and thallium, all of the above 'forbidden' sulphides are hydrolysed in aqueous solution, and only exist in the anhydrous state. Under anhydrous conditions complex sulphides of these elements can be formed, and in fact under favourable conditions sparingly soluble NaInS_2 may be formed in aqueous solutions.

In spite of these limitations, this is a worthwhile criterion, and it explains why stannous sulphide is oxidised in aqueous sulphide solutions to form stannic thiosalts while germanous sulphide can form thiogermanites. Exceptions can often be explained as not being true thiosalts, but rather complex sulphides based on sulphur atom arrays. It is interesting to note that in the case of oxides the corresponding critical charge is about $-0.45e$, and is no restriction in the case of the oxides of groups IIb and IVb, whose charges on oxygen lie between -0.11 to $-0.36e$. The conclusion is that the lower negative charges found with the sulphides means that these compounds have little tendency to show the amphoteric properties associated with oxides such as alumina as they are unable to act as electron donors to more acidic sulphides.

Another important difference between the electronic structures of sulphur and oxygen is the availability for bonding participation of d-orbitals in the case of sulphur. Unlike oxygen, therefore, sulphur is not restricted to a co-valency of four, d-orbital participation frequently leading to structures impossible in the case of oxygen through more complex hybridisation schemes, with co-valency of five or six. Another way in which the d-orbitals in sulphur can modify the bonding schemes is by participating in back donation from a cation also possessing d-orbitals. For instance, this has been proposed as a reason for the stability with respect to hydrolysis of the thioanions of Ge^{4+} and Sn^{4+} (6, p 672); back donation of electrons is proposed from the filled d-orbitals of the cation to the empty d-orbitals of the anion.

2.1.2 Structures of Sulphides and Oxides

From these differences between sulphur and oxygen much may be learned about the types of structures encountered in the sulphides and oxides, and the differences between them. The most important factor is the nature of the bonding. The greater electronegativity of oxygen compared to sulphur leads to bonds to sulphur having more co-valent character than those to oxygen. Further, the higher polarisability of sulphur compared to oxygen frequently leads to asymmetric surroundings in the case of sulphides, while oxide ions generally occur in symmetrical environments. Oxides do not, for instance, form the layer structures found with the sulphides, to any appreciable extent, although such structures are known (eg MoO_3). Oxides range in bond type from the essentially ionic compounds of the less electronegative, generally metallic, elements, to the co-valent, molecular oxides of the non-metals with higher electronegativity. The electronegativity of the elements decreases in going from right to left in a period, and from top to bottom in a group, and Wells (5, p 481) uses this as a rough criterion for assessing bond type. Group IIIb may be considered as forming essentially ionic oxides, at least from aluminium downwards. In Group IVb, silicon is a border-line case, carbon forming co-valent, molecular CO_2 , and germanium, tin and lead becoming ionic in their oxides. From a theoretical standpoint, the corresponding sulphides may be regarded as possessing a more co-valent character than the oxides.

The only truly ionic sulphides are those of the alkali and alkaline earth metals, where the positive ions have low charge and polarising power. It is here that the only established close similarities between sulphides and oxides exist, and similar structures occur (eg Na_2O and Na_2S both have the anti-fluorite structure (5, p 458)).

With cations of higher charge, the sulphides show increasing tendency to co-valency, and in the type of structure adopted by pyrites, FeS_2 , discrete co-valent S_2 groups are found, a situation never encountered in oxide systems. In general, the sulphide ion is not found in the presence of cations of charge +4 or greater, such systems being effectively purely co-valent, although to describe them as exhibiting simple co-valency with no other bond-type contribution would doubtless be an over simplification. The high polarisability of the sulphide ion with cations of high field strength leads to bonds that are not only co-valent, but possess free electron character, leading to metallic properties such as high thermal and electrical conductivity, lustre, etc.

The same characteristics are found in the field of especial interest in the present work - complex sulphides. Whilst in the complex oxides such as the silicates, complex and discrete oxyions are formed, in complex sulphides the bonds are essentially co-valent, giving rise to a large variety of structures, many possessing semi-metallic properties. However, the silicate structures are not as ionic as other complex oxides with cations of lower electronegativity, where aggregates of ions governed by radius ratio considerations are formed rather than complex ions.

This leads to the concept of close packing and radius ratio control of coordination. These factors are discussed in texts concerned with structural chemistry (eg 5, pp 72 and 112), and are relevant as many of the oxides and sulphides may be regarded as close packed arrays. The structure adopted in a particular case is not necessarily related to the mode of bonding; for instance, galena has a sodium chloride type structure that is associated with ionic crystals, and yet some metallic character is found in the long bond distances, electric conductivity and metallic lustre. Thus many sulphides (and oxides) that are not predominantly

ionic adopt the simple structures of ionic crystals. Owing to the fact that the sulphide (and oxide) ion is considerably larger than the cations commonly encountered, many of the structures encountered may be regarded as close packed arrays of anions with the cations in the tetrahedral and octahedral holes. Replacement of one cation by another is common, (see Section 2.3). Considering the structure from the point of view of the cations, the type of coordination that is possible in a simple ionic crystal may be defined by the radius ratio between the cation and anion. Thus the type of site that a particular cation will occupy in a close packed lattice may be determined, or alternatively the possibility of a particular structure being adopted by a particular ion pair may be evaluated. The approach is discussed more fully by Wells, and the data in Table 2.2 (which shows the ranges of radius ratio for the different structural types) is taken from this source.

Many reviews of the sulphides and classifications of their structures have been published. A general discussion is included by Nickless (6, pp 669-747), whilst Wells (5, pp 510-539) includes structural details of the commoner materials. Useful compilations of crystal structures of mineral sulphides have been made by Dana (118) and Bragg and Claringbull (17). Much crystallographic data is to be found in Wyckoffs' comprehensive work (18). Ross (19) has classified mineral sulphides according to structural type, and Flahaut (20) and Hellner (21) applied the concepts of anion close packing and radius ratio control of the metal cation position. This has led to a better understanding of the non-stoichiometric sulphide phases. In general such reviews indicate the complex nature of sulphides, and the transitional nature of the bonding, ranging from ionic to co-valent and metallic. Many structures are based on close packing of the sulphur atoms, and much work has been conducted in this area (20, 108).

2.1.3 Sulphides and Oxides of Groups IIIb and IVb

The basis of the present work was the three dimensional type of structure adopted by aluminium and silicon in their oxides. Similar properties are found with gallium, indium, tin and germanium, but boron and carbon, being first period elements, differ markedly and are not considered in this work.

The area of interest is the relationship between the sulphides and complex sulphides of Groups IIIb and IVb with the corresponding oxides. As the work was primarily concerned with the formation of sulphide analogues of the silicates and aluminosilicates, the structures of silica and alumina may be taken as the starting point, and the other structures related to them.

Sulphides may be subdivided according to the number of elements other than sulphur that they contain. For the purpose of the present work, simple elemental sulphides (M_xS_n) are referred to as binary sulphides, sulphides with two elements other than sulphur ($M_x^1M_y^2S_n$) are referred to as ternary sulphides and sulphides with three or more additional elements are referred to as complex sulphides. Some authors refer to sulphides with two or more elements other than sulphur as complex sulphides or sulphosalts, and there is no universal system of nomenclature. In the present work the term sulphosalt is reserved for sulphides where there is evidence for discrete sulfo-anions.

2.1.3.1 SiO₂

There are three well established structures adopted by silicon dioxide in its crystalline state with various degrees of close packing, as witnessed by the densities. These are quartz, $\rho = 2.655$, tridymite, $\rho = 2.30$ and cristobalite, $\rho = 2.27$ g/cc (5, p 785). However, although most silicates consist of close packed oxygen atoms with the cations in the holes, it is possible to distinguish complex ions according to the

arrangements adopted by these cations, although there is no reason for supposing them necessarily to exist in solution. It is usual, therefore, in considering silicate structures, to regard these as being built up from SiO_4 tetrahedra linked together in different ways. From this point of view the three structures of silicon dioxide may be regarded as SiO_4 tetrahedra linked via corners, with every oxygen atom common to two tetrahedra, forming a three dimensional lattice. The different forms vary in the arrangement of tetrahedra adopted, and in addition α - and β - modifications of the individual structures may be distinguished (the β - form being the high temperature form with higher symmetry), having the same basic arrangement of tetrahedra, but suffering small displacements of the constituent atoms. The various structures are reviewed in detail by Wyckoff, volume 1 (18) and another useful account is included by Bragg and Claringbull (17, p 84).

The main points are summarised in Table 2.3, together with bond distances for the SiO_4 tetrahedra. Coesite and keatite are more recently discovered types, and the structure of the latter is not fully established. A very high pressure modification has also been reported (53), possessing octahedral coordination of silicon.

2.1.3.2 GeO_2

Germanium dioxide is found with two structures, that of quartz described above (22 - 24) exhibiting 4:2 coordination, and that of rutile (28), exhibiting 6:3 coordination. The quartz - like structure is of most interest in the present context. It is metastable below the transition point of 1033°C , and its structure is considerably distorted compared to true quartz. The greater size of the germanium ion gives rise to longer Ge-O bond lengths, but an irregular O-Ge-O angle produces better contact between the tetrahedrally dispersed oxygen atoms. The two distinct Ge-O lengths are 1.737 and 1.741 Å.

Type	Name	Symmetry	Z mol/unit cell	Parameter	Si-O Å	O-O Å
α	quartz	hexagonal	3	$a_o = 4.91304$ $c_o = 5.40463$	1.61	2.60 -2.67
β	quartz	hexagonal	3	$a_o = 5.01$ $c_o = 5.47$	1.62	2.60
α	tridymite	hexagonal	864	$a_o = 5.01.6$ $c_o = 8.18.8$		
β	tridymite	hexagonal	4	$a_o = 5.03$ $c_o = 8.22$	1.52	2.57
α	cristobalite	tetragonal pseudocubic	4	$a_o = 4.9733$ $c_o = 6.9262$	1.59	2.58 -2.63
β	cristobalite	cubic	8	$a_o = 7.16$	1.58 -1.69	
high pres. mod.	coesite	monoclinic	16	$a = b = 7.17$ $c_o = 12.38$ $\beta = 120^\circ$	1.60 -1.63	2.60 -2.67
	keatite	tetragonal		$a_o = 7.456$ $c_o = 8.604$	1.57 -1.61	

Table 2.3 Forms of Silica.

2.1.3.3 SnO_2 and PbO_2

The rutile modification of germanium dioxide is also the structure adopted by tin (cassiterite) and lead (Plattnerite) in their dioxides. The structures of these compounds are reviewed by Wyckoff (18, volume 1), and the parameters of the tetragonal unit cell ($Z = 2$) are given below:-

$$\begin{array}{llll} \text{GeO}_2 & a_o & = & 4.395 \text{ \AA} \quad c_o = 2.859 \text{ \AA} \\ \text{SnO}_2 & a_o & = & 4.737 \text{ \AA} \quad c_o = 3.186 \text{ \AA} \\ \text{PbO}_2 & a_o & = & 4.964 \text{ \AA} \quad c_o = 3.379 \text{ \AA} \end{array}$$

These structures exhibit octahedral coordination of six oxygen atoms around the metal atom, and cannot therefore be considered as being analogous to silica with its tetrahedral coordination. The rutile structure, increasingly adopted on going down the dioxides of Group IVb, represents an increasing tendency to form octahedral rather than tetrahedral hybridisation, consistent with increasing d -orbital contribution. It serves to indicate also the increasing ionic character of these elements in their dioxides from Si to Pb, the bonds of Si-O having appreciable co-valent character.

2.1.3.4 Al_2O_3 , Ga_2O_3 & In_2O_3

The most common structure adopted by aluminium oxide in its dehydrated state, Al_2O_3 , is the corundum (α -) form. This structure is reviewed by Wyckoff (18, volume 2), and is best regarded as a nearly perfect hexagonal close packed array of oxygen ions with aluminium ions occupying the octahedral holes. γ -alumina is a distorted metastable modification, assigned a defect spinel structure (25), and has a higher surface area and is more active chemically. α - Ga_2O_3 possesses a similar structure to α - Al_2O_3 , and the parameters for the rhombohedral unit cells ($Z = 2$) are:-

$$\begin{array}{llll} \alpha\text{-Al}_2\text{O}_3 & a_o & = & 5.128 \text{ \AA} \quad \alpha = 55^\circ 20' \\ \alpha\text{-Ga}_2\text{O}_3 & a_o & = & 5.320 \text{ \AA} \quad \alpha = 55^\circ 48' \end{array}$$

Gallium sesquioxide, Ga_2O_3 , is polymorphic, and the system is described by Roy et al (26), who compared it to the similar system formed by aluminium. Wyckoff reviews the established crystal structures (18, volume 2). Just as in Group IVb, where a departure from the silica type of structure is found in tin and lead dioxides, germanium dioxide being a borderline case, so here, in Group IIIb, one of the modifications of Ga_2O_3 , the so called 'C-rare earth' structure, is the only structure reported for In_2O_3 (and Tl_2O_3), and bears no relation to the corundum structure. Wells (5, p 465) includes a useful discussion of this structure. The structure is cubic, and the parameters for In_2O_3 are $a = 10.118\text{\AA}$ ($Z = 10$). It is characterised by an incomplete cubic close packed lattice of oxygen ions.

2.1.3.5 SiS_2

The structure of silicon disulphide, SiS_2 , is well established, and forms a well known example of a chain structure. It is similar to silica in that it is composed of tetrahedra of SiS_4 , but differs in that these tetrahedra are linked via edges to form infinite chains, and not, as in silica, via corners to form a three dimensional lattice. The chains of silicon disulphide are held together only by weak van der Waals forces, and the material is fibrous in nature. Details of the structure were first published by Zintl and Loosen (29) and Büssem, Fischer and Gruner (30), and are included in Wyckoff's compilation (18, volume 1). The unit cell is orthorhombic, with the following parameters ($Z = 4$)

$$\begin{aligned} a_o &= 9.55 \overset{a}{\text{\AA}} \\ b_o &= 5.65 \overset{b}{\text{\AA}} \\ c_o &= 5.54 \overset{c}{\text{\AA}} \end{aligned}$$

The adjacent tetrahedra are distorted, the shared S-S bond length

being either 3.24 or 3.58 Å, and the remaining (unshared) S-S bond length being 3.62 Å. The Si-S bond length is 2.14 Å, and the nearest approach of sulphur atoms between chains is 3.75 Å. These values are correspondingly larger than those found in the various forms of SiO₂, corresponding to the increased size of the sulphur ion. Pauling (7, p 398), discussing this structure, cited it as characterising the essentially co-valent bonding found in the sulphide as compared to the oxide, SiO₂.

More recently, a high pressure form of silicon disulphide has been reported in which the tetrahedra share corners to form the three dimensional network of cristobalite (31). Thus a direct analogy exists between the dioxide and disulphide of silicon. The material was prepared at 60 - 65 k bar and 1300°C. The parameters of the tetrahedral unit cell ($Z = 4$) may be compared to those of cristobalite alone (Table 2.3), when the greater size of the sulphide structure is apparent.

$$a_o = 5.420 \pm 0.004 \text{ Å}$$

$$c_o = 8.718 \pm 0.004 \text{ Å}$$

The Si-S length is 2.13 Å, and the S - S length 3.68 or 3.38 Å.

The same material was independently reported by Silvermann and Soulen (32), who, working under similar conditions, reported further (uncharacterised) glass-like structures, which hydrolysed only slowly. All the other forms of silicon disulphide hydrolyse immediately in the presence of water to form silicon dioxide and hydrogen sulphide.

2.1.3.6 GeS₂

The crystal structure of the disulphide of germanium was first elucidated by Zachariasen (33, 34), and details are included by Wyckoff (18, volume 1). The structure is essentially similar to the various forms of silica, and is thus of great interest in the present work. It consists of a three dimensional framework of corner linked GeS₄ tetrahedra.

It is similar to the structure adopted by quartz, although rather more complex due to distortion of the tetrahedra. Zachariasen discussed the structure in some detail (33), attributing an essentially co-valent character to the bonds, without the ionic contribution found in quartz. This he concluded from the distorted structure, the average Ge-S-Ge angle being 103° as against 144° in α -quartz. (these values may be compared to 80° for the SiS_2 low pressure structure discussed above (30)). The Ge-S distance is $2.19 \text{ \AA}$, only slightly larger than the Si-S distance in SiS_2 (see above). The parameters of the orthorhombic unit cell of GeS_2 ($Z = 24$) are:

$$\begin{aligned} a_o &= 11.66 \pm 0.05 \text{ \AA} \\ b_o &= 22.34 \pm 0.10 \text{ \AA} \\ c_o &= 6.86 \pm 0.03 \text{ \AA} \end{aligned}$$

The structure has been confirmed more recently (35), and this paper is useful in that it incorporates the powder diffraction data omitted by Zachariasen.

Recently, a high pressure form of germanium disulphide has been reported (31), exactly analogous to the high pressure form of silicon disulphide discussed above.

The parameters of the tetragonal unit cell ($Z = 4$) are:

$$\begin{aligned} a_o &= 5.48 \text{ \AA} \quad \text{Ge-S} = 2.21 \text{ \AA} \\ c_o &= 9.14 \text{ \AA} \quad \text{S-S} = 3.78 \text{ or } 3.52 \text{ \AA} \end{aligned}$$

Thus, there are two well established structures of germanium disulphide analogous to quartz and cristobalite, albeit somewhat distorted and with more co-valent character in the bonds, which form a firm basis for comparison of the sulphide and oxide systems of Group IVb. A further similarity is found in another high temperature modification of germanium disulphide recently discovered (36). Just as germanium dioxide can adopt both the structure of silicon dioxide (quartz) and

stannic oxide (rutile), so it was found that by high temperature vapour transport (up to 845°C) a further form of germanium disulphide could be formed having what the authors suggested to be a highly deformed modification of the cadmium iodide layer structure adopted by stannic sulphide (see below). The monoclinic crystals ($Z = 16$) have the following parameters:-

$$\begin{aligned} a_o &= 11.46 \pm 0.05 \text{ \AA} \\ b_o &= 16.1 \pm 0.5 \text{ \AA} \\ c_o &= 6.69 \pm 0.08 \text{ \AA} \\ \beta &= 90^\circ, 48' \pm 9' \end{aligned}$$

2.1.3.7 SnS₂

Silicon and germanium disulphides, like the respective oxides, exhibit 4:2 coordination, and just as the transition through germanium dioxide to stannic oxide (with the rutile structure) represents an increasing tendency for 6:3 coordination, so the cadmium iodide structure found in stannic sulphide represents a similar trend in the sulphur system. It may be represented as a hexagonal close packed matrix of sulphur atoms with the metal atoms occupying half the octahedral sites (ie those between every second pair of layers of sulphur atoms). The rutile structure adopted by stannic oxide is not related to close packing, but rather to a distorted body centred cubic type of arrangement with octahedral coordination of the metal atom by oxygen in a three dimensional framework. These structures represent the preference for co-valency and layered (asymmetrical) structures found in moving from oxide to sulphide. The structure of stannic sulphide is described by Wyckoff (18, volume 1) and was originally published by Oftedal (37, 38). The parameters of the hexagonal unit cell ($Z = 1$) are :-

$$\begin{aligned} a_o &= 3.639 \text{ \AA} \\ c_o &= 5.868 \text{ \AA} \end{aligned}$$

2.1.3.8 Al_2S_3

Al_2S_3 exists in three well established forms, α , β and γ .

The structures of these materials were first reported by Flahaut (39, 40, 41), and are mentioned by Wyckoff (18, volume 2). The α -form is the stable, low temperature modification, and possesses an ordered super-structure of the wurtzite type.

The parameters of the hexagonal unit cell ($Z = 6$) are:-

$$a_0 = 6.423 \text{ \AA}$$

$$c_0 = 12.27 \text{ \AA}$$

The structure is best regarded as a hexagonal close packed array of sulphur atoms, with aluminium occupying tetrahedral holes. The β -form, stable at high temperatures in the presence of carbon, consists of a similar distribution of sulphur atoms, with the aluminium atoms displaced to form a random wurtzite structure. The parameters of the hexagonal unit cell ($Z = 1$) are:-

$$a_0 = 3.579 \text{ \AA}$$

$$c_0 = 5.829 \text{ \AA}$$

The γ -form is obtained by heating α - Al_2S_3 over $\sim 1000^\circ\text{C}$, and may be retained by quenching. It is of most interest in the present work, as it possesses the corundum structure of α - Al_2O_3 , and may be regarded as a hexagonal close packed array of sulphur atoms with aluminium atoms occupying the octahedral holes. The parameters of the unit cell are:-

$$a_0 = 6.86 \text{ \AA}, \quad \alpha = 56.16^\circ$$

They are quite similar to those of α - Al_2O_3 (c f), allowing for the larger size of the sulphur atom, and Flahaut suggested appreciable ionic character in the bonds (41). More recently, a cubic modification of aluminium sulphide has been reported (42). Approximately two per cent of the aluminium is replaced by arsenic in this material, which was prepared by reaction of the elements at $450 - 650^\circ\text{C}$.

$$a_0 = 9.93 \pm 0.01 \text{ \AA}$$

2.1.3.9 Ga_2S_3

The various forms of gallium sulphide, Ga_2S_3 , are reviewed by Wyckoff (18, volume 2), and Sheka, Chaus and Mityurera (43 Chapter 5). The original structure determinations were by Hahn et al (44, 45 and 46). Like Al_2S_3 , three well defined structures are found, α , β and γ (46). The γ -form is the type obtained by normal preparation, and may be regarded as the low temperature modification. It possesses the zinc blende structure, and the parameter of the cubic unit cell ($Z = 4$) is:-

$$a_0 = 5.441 \text{ \AA}$$

It is best regarded as a cubic close packed array of sulphur atoms with gallium atoms in random occupation of the tetrahedral holes. Annealing at $\sim 1000^\circ\text{C}$ leads to the stable, α -form, which has an ordered super-structure of the wurtzite type, similar to $\alpha\text{-Al}_2\text{S}_3$. The parameters for $\alpha\text{-Ga}_2\text{S}_3$ are:-

$$a_0 = 6.389 \text{ \AA}$$

$$c_0 = 18.089 \text{ \AA}$$

$\beta\text{-Ga}_2\text{S}_3$, like $\beta\text{-Al}_2\text{S}_3$, has a random wurtzite structure, and is made by annealing $\gamma\text{-Ga}_2\text{S}_3$ at $550 - 600^\circ\text{C}$.

$$a_0 = 3.685 \text{ \AA}$$

$$c_0 = 6.028 \text{ \AA}$$

These structures characterised by random distribution of the cations in the close packed anion lattice are all unstable, and revert on heating sufficiently to the stable $\alpha\text{-Al}_2\text{S}_3$ and $\alpha\text{-Ga}_2\text{S}_3$ respectively.

In all three forms of Ga_2S_3 , the coordination of the metal is tetrahedral, and no structural modification has been reported possessing the octahedrally coordinated corundum structure of $\gamma\text{-Al}_2\text{S}_3$ and $\alpha\text{-Al}_2\text{O}_3$.

As a result of a fresh analysis of the structure of α -Ga₂S₃, using both single crystal and powder data, Goodyear et al (47) assigned monoclinic symmetry, and concluded that space group requirements ruled out the possibility of the wurtzite structure previously assigned to this material. However, in a reappraisal of the structure, these authors later assigned a modified monoclinic unit cell (48), based on wurtzite with shrinkage of sulphur tetrahedra leading to some departure from close packing. The parameters given to the unit cell ($Z = 4$) were:-

$$\begin{aligned} a_o &= 11.14 \text{ \AA} & \beta &= 121.22^\circ \\ b_o &= 6.41 \text{ \AA} \\ c_o &= 7.03 \text{ \AA} \end{aligned}$$

From the point of view of this discussion, the general conclusions of Hahn presented above may be regarded as essentially still valid.

2.1.3.10 In_2S_3

The crystal structure of In_2S_3 was also first elucidated by Hahn et al (49), and is reported by Wyckoff (18, volume 2). There are two modifications, α - and β -, corresponding to the low and high temperature forms respectively, with a transition temperature of ca 300°C. Both these structures Hahn considered were similar to those of γ -alumina (c f), being defect spinel structures. They are characterised by cubic close packed sulphur atoms, and instead of the ideal metal atom occupation of eight of the 64 available tetrahedral sites and 16 of the 32 available octahedral sites, as found in spinel, the α -form has metal atoms in 15 octahedral and 6 tetrahedral positions, and the β -form has the 21 metal atoms in completely random positions. These structures correspond to two distinct forms of γ -alumina (49). The α -form is metastable, and the transformation to

the β form is non-reversible. The parameters of the cubic unit cells are given as:-

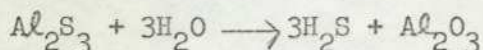
$$\alpha\text{-In}_2\text{S}_3; a_0 = 5.36 \text{ \AA}$$

$$\beta\text{-In}_2\text{S}_3; a_0 = 10.72 \text{ \AA}$$

However, more recent examination of the structures (50, 51, 52) have shown these proposals of Hahn to be incorrect and it is now fairly well established that the α -form has a random cation distribution in the close packed lattice, and the β -form has a tetragonal (ordered) superstructure of the spinel structure. Therefore $\alpha\text{-In}_2\text{S}_3$ and $\beta\text{-In}_2\text{S}_3$ are not isostructural with the two forms of $\gamma\text{-Al}_2\text{O}_3$.

2.1.3.11 Hydrolysis of the Sulphides of Groups III b and IV b

The sulphides of aluminium and silicon are immediately and irreversibly hydrolysed by water to liberate hydrogen sulphide:-



The lower sulphides of the two subgroups are more resistant to hydrolysis. Germanium disulphide is very slightly soluble in water, and is only slowly hydrolysed, with the liberation of hydrogen sulphide. It may in fact be precipitated from strongly acidic solutions of germanium salts by hydrogen sulphide. Stannic sulphide is quite stable in aqueous media, being insoluble and precipitated from solutions of tin(IV) salts by hydrogen sulphide. Similarly indium (III) sulphide may be precipitated from aqueous solutions of indium(III) salts, but gallium(III) sulphide is partially decomposed by water. However, the liberated hydrogen sulphide presents precipitation of $\text{Ga}(\text{OH})_3$, and the hydrolysis is incomplete.

No disulphide of lead, PbS_2 is known, and thallium sulphide Tl_2S_3 is only formed by high temperature reaction of the elements. Oxidation of hydrogen sulphide occurs in aqueous conditions.

2.1.4 More Complex Sulphides and Oxides of Groups III b and IV b

Having considered the structures of the simple (binary) oxides and sulphides of Groups III b and IV b, the relations these materials bear to the more complex sulphides and oxides will be considered. The main emphasis is placed on alkali metal salts of these materials, the classes of compounds of which the parents are the alkali metal silicates and aluminates.

Finely divided silica or alumina is readily soluble in alkaline solution to form silicates and aluminates. Complex ions exist in solution, and interaction of these ions leads to the formation of complex aluminosilicates. A consideration of the mechanism of formation of these compounds is given in the second part of this chapter, but an extended discussion of the types of material that are formed would be inappropriate. Many excellent reviews and classifications have been published, and the books by Wells (5) and Bragg (17) contain material of this sort.

2.1.4.1 Silicates and Aluminosilicates

Like the various forms of silica, silicates are generally classified according to the kind of silicon-oxygen framework they possess. These structures are built up, like silica, from SiO_4 tetrahedra, and the various types of structure encountered represent different arrangements of these tetrahedra. According to the net negative charge on the framework so formed, various other cations are present to ensure electrical neutrality.

Partial replacement of silicon by aluminium is another frequent cause of charge imbalance requiring the presence of additional cations in the lattice. The various categories of materials distinguished may be summarised, according to the arrangement of the SiO_4 tetrahedra:-

1. SiO_4 units discrete
2. SiO_4 units share one corner (ie two units only)
3. SiO_4 units share two corners (ring or chain formation)
4. Alternate SiO_4 units share two and three corners (double chains)
5. SiO_4 units share three corners (sheet structures)
6. SiO_4 units share four corners (three dimensional structures)

All these forms are characterised by the tetrahedral building blocks sharing corners, and it is apparent that this type of coordination is essential for a material to adopt this type of structure.

According to Pauling (7 p, 396), the existence of edges, and particularly faces, common to two anion polyhedra decreases the stability of the structure due to coulombic interaction between the cations.

Considering the edge sharing of SiS_4 tetrahedra in SiS_2 , Pauling suggests that this confirms the covalent character of this material.

From the point of view of the present work, the latter class of structure is of most interest, representing the three dimensional type of framework found in silica. The chief classes of compound of interest having this framework structure are the feldspars, zeolites and ultramarines, and these all possess relatively open structures. They are all characterised by up to one half of the silicon atoms being replaced by aluminium, in similar tetrahedral sites, and positive ions are present to neutralise the charge generated.

The feldspars have relatively compact structures (5, p 808), with the cations required to ensure electrical neutrality accommodated in holes running through the structure. The zeolites have much more open structures, however (5, p 810), containing large voids both within and between the complex structural units, often polyhedra, formed from the AlO_4 and SiO_4 tetrahedra. Up to 50 per cent substitution of aluminium for silicon may occur in the tetrahedral MO_4 units, and in the zeolites the positive ions necessary to neutralise the net charge on the framework are situated within the voids. In feldspars, on the other hand, these cations are far more closely surrounded by the framework. Also accommodated within the zeolitic cavities are loosely held water molecules, and the ultramarines (otherwise similar to the zeolites) contain in addition finite negative ions- eg S^{2-} , SO_4^{2-} , Cl^- . These voids are connected by channels, in one, two or three directions, and the volume of the cavities may be 50 per cent or more of the volume of the crystal. The water, which is only loosely held, may be removed without the structure becoming destroyed, and other molecules of appropriate size may enter the framework. This property has led to these materials being used as molecular sieves, for the channels have precisely defined dimensions, and only those molecules of a smaller size will become adsorbed from a mixture. Furthermore, these materials have a strong tendency to regain the water molecules if these are removed during 'activation', by heating, preferably under vacuum, and this gives them strong desiccating properties. Also, the cations present to ensure electrical neutrality are readily

exchanged by other cations, of similar or dissimilar charge (the number of ions present changing in the latter case), and this gives these materials a further use as ion exchanging media.

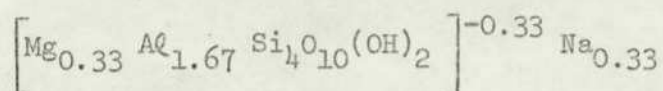
An extremely large amount of literature exists on these very important materials, and some key references are listed below.

The absorbent properties of zeolites were first studied in the early years of the present century, but not until the crystal structures of a few zeolites were determined in the early 1930's and Professor R.M. Barrer began his pioneering studies on these materials in the latter part of that decade, was their science properly established. Since then, many different zeolites have been synthesised and characterised, some not known in nature, and the full crystal structures of many elucidated. A review by Breck (54) gives a comprehensive introduction to all aspects of the subject. Barrer has reviewed the crystal structure (55) and molecular sieve properties (56) of these materials.

Much useful data, especially on the commercial and industrial side, is to be found in the book by Hersh (57). The book by Sokolova (58) gives data on the Russian work in this field. The proceedings of the first and second International Conferences on Molecular Sieves form a convenient compilation of recent information (60, 225). In a further discussion (59), Barrer has considered the degree of porosity found in aluminosilicates. At one extreme are the feldspars, with no intercrystalline voidage, and with the charge balancing cations immobilised within the framework. The crystalline silicas, containing no aluminium and therefore no cations, have a small

amount of voidage resulting from unoccupied interstices among the tetrahedra. Finally, the zeolites have a large degree of porosity resulting from the crystal structure and the fitting together of the structural units.

It is possible for some of the characteristics of porosity on a molecular scale to exist in other types of structure besides three dimensional lattices. For instance, layer type aluminosilicates have charge balancing cations situated between the layers which may be ion exchanged. An example is montmorillonite, represented as:-



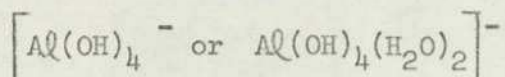
Besides exhibiting cation exchange, this material forms adsorption complexes with a variety of organic liquids, which penetrate between the structural sheets, forming 'two dimensional liquids' and expanding the structure (110).

2.1.4.2 Complex Oxides of the Lower Subgroup Elements of III b and IV b

As the present work was concerned with the formation of sulphide analogues of the aluminosilicates, the most important aspect of the structures of the oxides of the lower subgroup elements was the degree to which these elements may be substituted in the aluminosilicate frameworks. The concept of isomorphous substitution is considered in the final section of this chapter, but from the standpoint of their known oxide structures only germanium and gallium would be expected to undergo such a substitution. This is because, of the Group IV b elements, only high temperature

GeO_2 resembles silica with the quartz structure, and of the Group III b elements, only Ga_2O_3 possesses the corundum structure of $\alpha\text{-Al}_2\text{O}_3$.

A further area of comparison is the amphoteric properties of these oxides, and the formation of complex oxides analogous to the soluble silicates and aluminates. Aluminium dissolves readily in solutions of metal hydroxides, with the formation of complex anions such as



(3). Gallium and indium also possess similar amphoteric properties, but while Ga_2O_3 is more strongly acidic than Al_2O_3 , dissolving in ammonia, In_2O_3 is primarily a basic oxide, dissolving initially in base, but tending to precipitate out on standing (3).

Thallium oxide, Tl_2O_3 , shows no acidic properties.

Considering Group IV b, germanium dioxide is more acidic than silicon dioxide, and is readily soluble in bases to form germanates that are usually isomorphous with the corresponding silicates. Similarly, stannates and plumbates are obtained by dissolving the oxides in basic solution, but these materials, together with the indates, tend to octahedral coordination in such systems, and are not strictly analogous to the silicates and aluminosilicates. Therefore, the view is supported that in the light of their oxide structures, only gallium and germanium are capable of forming analogues of the silicates and aluminosilicates.

2.1.4.3 Ternary Sulphides of Aluminium

There is little direct similarity between the ternary oxides and the ternary sulphides of aluminium (aluminates and thioaluminates). As aluminium sulphide is hydrolysed by water, aqueous methods of preparation of ternary phases cannot be used,

and there have been few attempts to prepare thioaluminates by non-aqueous or high temperature methods. The only well characterised ternary sulphides of aluminium with the alkali metals are LiAl_5S_8 (61) and LiAl_2S_4 (62), obtained by high temperature reaction of the elements with sulphur or hydrogen sulphide. They have spinel structures, the former having two distinct modifications, above and below $\sim 1200^\circ\text{C}$. Many of the complex sulphides of Group III b have normal, inverse or disordered spinel structures, but unlike the corresponding oxides, simple structures with tetrahedral coordination of the M^{3+} cation are not found in complex sulphides of aluminium with the alkali metals. For instance, LiAlO_2 and NaAlO_2 have wurtzite structures, and the analogous K, Rb and Cs compounds the cristobalite structure, all with tetrahedral coordination of aluminium (63), but analogous sulphides are not reported. Such sulphides, with tetrahedral coordination of the aluminium, are found only with metals other than those of Group I. It has been reported, for instance, that $\text{M}^{\text{II}}\text{Al}_2\text{S}_4$ ($\text{M}^{\text{II}} = \text{Zn, Cd, Hg, Cu and Ag}$) have tetragonal, zinc blende structures, with tetrahedral coordination of the aluminium (64, 65), although earlier a normal spinel structure was assigned below 800°C (octahedral coordination of aluminium) and a wurtzite structure above this temperature (97). A similar view was published by Steigmann (98), although he proposed a type of layer structure as the high temperature form, based on a close packed network of sulphur atoms (exhibiting some distortion), with the M^{3+} cation occupying both octahedral and tetrahedral sites. No doubt, much of the confusion concerning this type

of system arises from the prevalence of non-stoichiometric phases, which can readily occur in structures based on a close packed anion array. Flahaut (100) discusses this point, with especial regard to the systems Al_2S_3 -ZnS and Ga_2S_3 -ZnS, which exhibit wide regions of homogeneity.

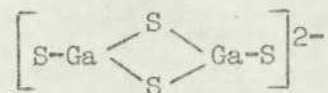
Other thioaluminates reported include those of the rare earths; Flahaut (103) describes the double sulphide $Ce_6Al_{10/3}S_{14}$, formed by the high temperature reaction between aluminium, Ce_2S_3 and H_2S . Two types of coordination of aluminium were found - tetrahedral, and distorted octahedral with 66 per cent occupation. The thioaluminates $CrAl_2S_4$ (104) and $CuAl_3S_8$ and $AgAl_5S_8$ (61) were found to possess spinel-type structures. Also mentioned in these works were analogous thiogallates and thioindates - $CrGa_2S_4$, $CrIn_2S_4$ (104) and $CuIn_5S_8$ and $AgIn_5S_8$ (61).

2.1.4.4 Ternary Sulphides of Gallium

Whilst there are no sulphur analogues reported of the simple ternary oxides MAO_2 (M = alkali metal), these are found if aluminium is replaced by gallium (63). Thus, $LiGaS_2$, $NaGaS_2$, $KGaS_2$; $LiAlO_2$, and β - $NaAlO_2$ all have wurtzite structures. The exact structure adopted in these ternary compounds is governed largely by ion size considerations, and it is likely, therefore, that the aluminium ion is too small to be stabilised within the tetrahedral holes of the close packed sulphur array. The larger gallium ion, (together with indium and thallium) is better able to fulfill this role.

It has been suggested (66) that these ternary sulphides formed by gallium should be represented as $M_2Ga_2S_4$ (M = alkali

metal). The existence of the thio-anion



was proposed in these compounds, the difference from aluminium being attributed to the electronic structures of the two metals.

In view of the resistance of gallium sulphide to hydrolysis, the possibility exists of preparing ternary sulphides of gallium with the alkali metals by reaction of the sulphides in aqueous media. However, materials reported to have been prepared by such a process are not well characterised, or free from the effects of hydrolysis (67). In general, the thiogallates described above are insoluble in water and non hygroscopic; this is in contrast to what would be expected from analogy from the simple ternary oxides. The only exception is the sodium salt, which forms the crystal hydrate, $\text{Na}_2\text{Ga}_2\text{S}_4 \cdot 2\text{H}_2\text{O}$, and hydrolyses in aqueous solution. The other thiogallates are only decomposed by strong acids.

2.1.4.5 Ternary Sulphides of Indium

The thioindates MInS_2 ($\text{M} = \text{Li}, \text{K}, \text{Rb}, \text{Cs}$) are reported by Hoppe (63), and, like their gallium counter-parts discussed above, all have the wurtzite structure.

The analogous oxides are also discussed in this paper - LiInO_2 has a superstructure of the NaCl type with octahedral coordination of the cations. The Na, K and Rb derivatives have similar structures. Therefore tetrahedral coordination of the In^{3+} ion is only found in the sulphide; this is a direct reflection on the larger size of the sulphide ion compared to the oxide, and the larger tetrahedral holes found in the sulphide close packed array.

NaInS_2 differs in structure from the Li, K, Rb and Cs analogues, and has the same structure as NaInO_2 , with octahedral coordination of the metal (68, 69). It has been reported that LiInS_2 also adopts this structure at $300^\circ - 400^\circ\text{C}$ under pressure (70). In general, other ternary sulphides of indium adopt a spinel structure (99).

These complex sulphides of indium are readily prepared by high temperature reaction of the sulphides, or the reaction of sulphur or hydrogen sulphide with suitable metal salts. However, indium sulphide In_2S_3 is not hydrolysed by water, and therefore, as in case of gallium, the possibility of aqueous preparations exist. It has been shown (71, 72) that reaction of a solution of an indium III salt with alkaline sulphides yields the sparingly soluble compounds $\text{M}(\text{InS}_2) \cdot x\text{H}_2\text{O}$, where $x = 4$ when $\text{M} = \text{Na}^+$ or K^+ , and $x = 0$ when $\text{M} = \text{NH}_4^+$. The system has been examined (73-77) as a function of composition and pH. In general, it was found that low ratios of $\text{M}_2\text{S}:\text{InCl}_3$ (1 to 1.5) led to the formation of In_2S_3 , and that over ratios of ~ 2.0 , MInS_2 was formed, redissolving in excess of the alkali metal sulphide. The stability of the ternary phase was found to decrease in the order $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$. The intermediate region with $\text{M}_2\text{S}:\text{InCl}_3$ ratios $\sim 1.5-2.0$ is characterised by surface reactions leading to products of uncertain composition. The use of alkali metal polysulphides in these systems was found to lead to polysulphide compounds of the type $\text{In}_2(\text{S}_x)_3$ and $\text{MIn}(\text{S}_x)_2$. Durrant (4, p 578) considers systems to be characterised by digonally hybridised indium ions: $(\text{S}-\text{In}-\text{S})^-$.

2.1.4.6 Ternary Sulphides of Silicon

Very little is known of the alkali metal thiosilicates. As silicon disulphide is hydrolysed by water, it would be expected that these compounds might only be formed by high temperature or non-aqueous methods. The formation of sodium sulphosilicate, Na_2SiS_3 (and also incidently the sulphoaluminates, $\text{Na}_6\text{Al}_2\text{S}_6$ and $\text{K}_6\text{Al}_2\text{S}_6$) is discussed by Mellor (78, 6, p 986 and 5, p 331). The thiosilicate was formed by melting the sulphides of sodium and silicon together, and the thioaluminates by heating the oxides or carbonates in an atmosphere of carbon disulphide. However, the products obtained were ill characterised, the original literature cited by Mellor dating from the last century, and they are not further discussed here. This type of system is considered in Chapter 3, in connection with the high temperature sulphiding of zeolites.

Li_2SiS_3 and Li_4SiS_4 (and also calcium and magnesium thiosilicates) were prepared by heating metal silicates in a sulphur atmosphere (79). They contain tetrahedrally coordinated SiS_4^{4-} groups, the latter as discrete groups and the former as chain anions. The selenium and tellurium analogues were also prepared.

With the exception of these compounds, the only well characterised thiosilicates reported are those with sulphides other than those of the alkali metals. In general, such compounds contain the tetrahedral SiS_4 group in a more or less distorted form, with Si-S bond lengths similar to those found in SiS_2 .

This grouping was established using X-ray techniques in, for instance, Mg_2SiS_4 , Ca_2SiS_4 (80), Mn_2SiS_4 (80, 81), and in the rare earth compounds $\text{Ln}_6\text{Si}_{2.5}\text{S}_{14}$, $\text{Ln}_4\text{Si}_3\text{S}_{12}$ and Ln_2SiS_5 (82, 105, 107).

Infra-red data gave similar results for the thiosilicates

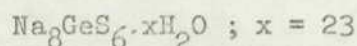
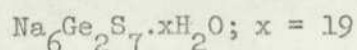
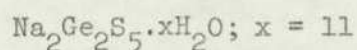
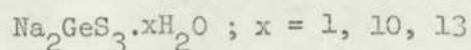
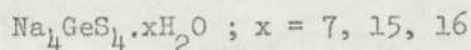
Cd_4SiS_6 , Hg_4SiS_6 (83) and Ba_2SiS_4 , Sn_2SiS_4 (461). This type of grouping is apparently typical of this class of compound. Other thiosilicates reported include Cu_8SiS_6 , Cu_6SiS_7 and Cu_4SiS_4 ; Ag_6SiS_7 , Ag_8SiS_6 and Ag_2SiS_3 (109).

2.1.4.7 Ternary Sulphides of Germanium

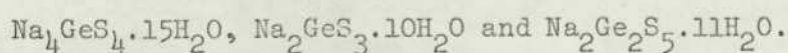
The alkali metal thiogermanates are quite well known compared to the thiosilicates, and one reason for this is undoubtedly that germanium disulphide is not appreciably hydrolysed by water. Ternary phases are therefore readily prepared by dissolving the sulphide in an aqueous solution of alkali metal sulphide, in direct analogy with the solution of amphoteric oxides in alkaline hydroxide solution. This leads to germanium disulphide, like the oxide, being regarded as primarily acidic in character.

Like many other ternary sulphides, those of germanium with the alkali metals may also be obtained by high temperature reaction of the sulphides or of the elements and sulphur. For instance, Maslov and Polyvyannyi(84) prepared Na_2GeS_2 from GeS_2 and Na_2S at 950° , and $\text{Na}_6\text{Ge}_2\text{S}_5$ at 100°C , by varying the proportions of the reactants. But by far the most common method of preparing this type of material is the aqueous technique, and these same authors obtained a further thiogermanate $\text{Na}_6\text{Ge}_2\text{S}_7 \cdot 5\text{H}_2\text{O}$, by this method. Schwarz and Giese (85) obtained crystals corresponding to $\text{Na}_6\text{Ge}_2\text{S}_7 \cdot 9\text{H}_2\text{O}$ (and its potassium analogue) by

dissolving the disulphide of germanium in sodium sulphide solution and evaporating the solution. By a rather more complicated process, involving precipitation with acetone, Willard and Zuehlke (86) were able to separate $K_2Ge_5S_5 \cdot xH_2O$ ($x \approx 3$). More recently, Sevrykov et al (87) carried out a more complete examination of these systems, using both high temperature reaction of the oxides with H_2S ($500^\circ C$), and also aqueous methods similar to those already described. The materials obtained corresponded to various compositions, but the following phases were indicated:-



The results of conductance measurements of aqueous solutions indicated the presence of GeS_3^{2-} ions (probably as $Ge_2S_6^{2-}$) in solution ; x-ray diffraction patterns confirmed the individuality of the different families of compounds, but no attempts at structure elucidation by x-ray techniques was made. The potassium compound was also prepared, $K_2Ge_2S_5 \cdot 4H_2O$ being obtained by a method similar to that of Willard and Zuehlke described above. More recently, Sevrykov and Salikova have published details of the isothermal solubility diagram for the aqueous $Na_2S:GeS_2$ system at $25^\circ C$ (93). From this data, they proposed confirmation of the phases:-



Nanobashvili et al have examined (92) the $M_2S:GeCl_4$ system by potentiometric titration, in a similar investigation to

to that described above with the analogous indium system. It was found that precipitated GeS_2 was soluble in excess M_2S , the solubility decreasing with change of M in M_2S ($\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$). The compound M_8GeS_6 was isolated by precipitation with acetone, and was found to possess cubic symmetry.

It is apparent that the chemistry of these materials is far from well defined, no doubt largely due to their very hygroscopic nature and the consequent reluctance to crystallise and lose non-stoichiometric water of crystallization. Moreover, these materials tend to be unstable in the solid form. However, more orderly attempts at the classification of this class of material have been made by Ribes et al (88, 89 and 90) and Krebs et al (91). The first paper of Ribes work comprises an account of the synthesis of Na_4GeS_4 , Na_2GeS_3 and $\text{Na}_2\text{Ge}_2\text{S}_5$ by high temperature reaction of the binary sulphides at 500°C , and presents infra-red and powder diffraction data of these materials. He stresses the ready hydrolysis of these materials in moist air, which are therefore less stable than GeS_2 . This is in contrast to the ternary sulphides of aluminium, which are considerably more resistant to hydrolysis than Al_2S_3 . The latter papers of Ribes work relate to the single crystal analysis of the structure of these materials. $\text{Na}_2\text{Ge}_2\text{S}_5$ possessed orthorhombic symmetry, and consisted of Na^+ and $\text{Ge}_4\text{S}_{10}^{4-}$ ions. These anions consist of four GeS_4 tetrahedra connected via three of their apexes (Figure 2.1) with a Ge-S bond length of between 2.137 and 2.240 Å. The other two ternary sulphides isolated were shown to possess monoclinic symmetry.

Krebs et al (91) used the aqueous methods of preparation, precipitating the ternary salts with an excess of acetone at pH 7.8.

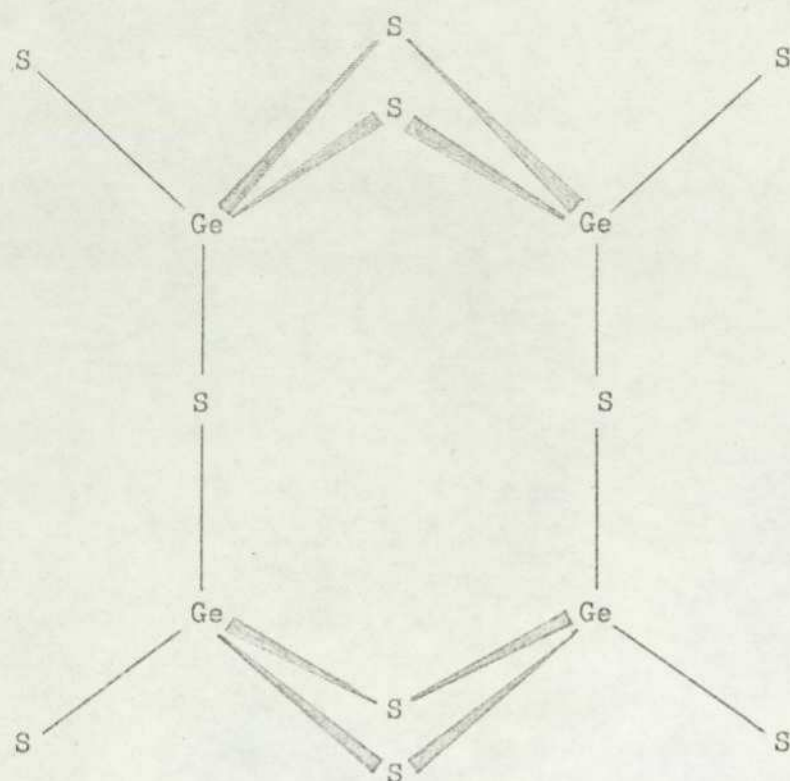


Fig. 2.1 The structure of the $(\text{Ge}_4\text{S}_{10})^{4-}$ ion. (89)

He obtained the material $\text{Na}_4\text{Ge}_2\text{S}_6 \cdot 14\text{H}_2\text{O}$, which was shown to have triclinic symmetry and to possess the anion $\text{Ge}_2\text{S}_6^{4-}$. This consists of two GeS_4 tetrahedra sharing edges in the manner of dimeric Al_2X_6 (X=halide). This is more in common with SiS_2 than GeS_2 .

In addition to the alkali metal thiogermanates, the materials Ca_2GeS_4 , Sn_2GeS_4 , Ba_2GeS_4 , BaGeS_3 and BaGe_2S_5 have been reported (101, 102, 464, 465), and found to possess tetrahedral GeS_4 groups. Ba_2GeS_4 was found to be isostructural with Ba_2SiS_4 , a continuous series of solid solutions existing (466). Similarly, the thiogermanates of the rare earths (82, 106, 107), of cadmium and mercury (83), and of manganese, calcium and magnesium (80, 81) were found to be isostructural with the corresponding thiosilicates.

2.1.4.8 Ternary Sulphides of Tin

The metathiostannate ion, SnS_3^{2-} (formulated as $\text{Sn}_2\text{S}_6^{4-}$) has a similar structure to $\text{Ge}_2\text{S}_6^{4-}$. The sodium salt was prepared (91) by a similar method to that used to prepare the thiogermanate. It was also found that the orthothiostannate ion (SnS_4^{4-}) possessed discrete SnS_4 tetrahedral ions. These materials are typified by $\text{Na}_4\text{Sn}_2\text{S}_6 \cdot 14\text{H}_2\text{O}$ and $\text{Na}_4\text{SnS}_4 \cdot 14\text{H}_2\text{O}$.

The presence of tetrahedrally coordinated tin in these compounds is especially interesting in view of the octahedral coordination found in SnS_2 . A different type of structure was found by LeBlanc (463), who reacted SnS_2 with solutions of alkali metals in liquid ammonia. MSnS_2 (M=Li, Na, K, Rb, Cs) was formed, where the alkali metal was intercalated and retained its high activity. This type of material was decomposed by water to form SnS_2 .

The chemistry of the alkali metal thiostannates is similar to that of the analogous germanium compounds, and similar methods of

preparation have been used. Early work of Jelley (94) has been largely superceded by the work of Krebs (91) discussed above. Babko and Liselskaya (95) examined the solubility of SnS_2 in alkali and alkaline sulphide solution, and found that in an alkaline solution not containing H_2S , the ion $[\text{SnS}_2\text{OH}]^-$ is formed. In the presence of H_2S or in alkaline sulphide solution the metathiostannate ion, $[\text{SnS}_3]^{2-}$ is formed. The system $\text{Na}_2\text{S}-\text{SnS}_2-\text{H}_2\text{O}$ was also examined by Sevryukov (96), who obtained two compounds, $\text{Na}_2\text{SnS}_3 \cdot 8\text{H}_2\text{O}$ and $\text{Na}_4\text{SnS}_4 \cdot 15\text{H}_2\text{O}$. These materials obviously correspond to the meta- and ortho-thiostannates obtained by Jelley and Krebs. Like the thiogermanates, the thiostannates are found in various degrees of hydration, no doubt explaining the rather contradictory nature of the literature relating to them.

Other thiostannates reported, besides those of the alkali metals, include those of calcium, strontium and barium (467, 468).

2.1.4.9 Complex Sulphides of Groups IIIb and IVb

Besides the ternary sulphides of Groups IIIb and IVb discussed in the preceding sections, more complex sulphides containing at least three elements besides sulphur have been reported. $(\text{M}_x^1 \text{M}_y^2 \text{M}_z^3 \text{S}_n)$. It is with this type of compound that one might expect to find analogues of the aluminosilicates (eg $\text{Na}_x \text{Al}_y \text{Si}_z \text{O}_n$), but very little such similarity exists. No direct analogues of the more open type of framework oxides have been reported, and most complex sulphides may best be described as ternary sulphides $(\text{M}_x^1 \text{M}_y^2 \text{S}_n)$ based on close packed sulphur atoms, where a certain amount of cationic substitution has occurred, some of M^1 or M^2 being replaced by M^3 .

Nevertheless, this process is very similar to the substitution of aluminium for silicon in the more densely packed aluminosilicates,

where alkali or alkaline earth metal ions are introduced to maintain electrical neutrality. For instance, a continuous phase exists between $YAlS_3$ and $YSiS_3$ as aluminium is replaced by silicon (20, 111, 112). The sulphur (close packed) framework is unaltered by this process, and the number of Y ions alters to maintain electrical neutrality.

Many of the complex sulphides exhibiting tetrahedral coordination of the cations are derived from the zinc blende or wurtzite structures, both of which are based on simple close packed sulphur lattices. Substitution of the zinc in zinc blende (ZnS) leads to $CuFeS_2$ (chalcopyrite) or Cu_2FeSnS_4 (stannite), with all the cations in the tetrahedrally coordinated sites occupied by zinc in ZnS. This type of structure is considerably more compact than those of the silicates, sulphur atoms being common to four tetrahedra. In the framework silicates, oxygen atoms are common to only two SiO_4 tetrahedra.

There have not been many reports of complex sulphides of aluminium and silicon, doubtless as a result of the reactive nature of SiS_2 and Al_2S_3 . Structures including other Group III b and IV b elements are also rare. Attempts were made (119) to introduce sulphur vapour into molten aluminium and aluminium-silicon alloys, but no composite phases were found. $Al_2(SiS)_3$ was reported (120) to result from the fusing together of Al_2S_3 and SiS_2 , but nothing is known of its structure. Similarly, the In_2S_3 -GeS system has been briefly examined (121), but no new phases were found.

The class of compounds represented by $In_6Cu_2Si_{12}S_{14}$ has been well characterised (113-116). This structure is based on a close packed array of sulphur atoms, the sites occupied by

copper being octahedral and those occupied by silicon tetrahedral. Substitution of Cu by Fe, Ag, Ti, V, Cr, Mn, Fe, Co, Ni, Mg, and Zn; of Si by Al, and of S by Se is known.

Other complex sulphides reported for the elements of Groups III b and IV b are of similar close-packed type. A family of compounds $\text{Cu}^{\text{I}}\text{M}^{\text{II}}\text{X}_4$ ($\text{M}^{\text{I}} = \text{Al, B, Ga, In}$; $\text{M}^{\text{II}} = \text{Si, Ge}$; $\text{X} = \text{S, Se, Te}$) is based on the sphalerite (zinc blende) structure (122). $\text{Cu}_2\text{CdGeS}_4$ has a wurtzite structure, and $\text{MnIn}_x\text{Cr}_{2-x}\text{S}_4$ has a spinel structure (124).

All these complex sulphides, if synthesised, were prepared either by high temperature reaction of the elementary sulphides, reaction of the elements with sulphur in sealed tubes, or reaction with hydrogen sulphide in a flow system. In general, it might be supposed that more open structures would only be formed in systems employing a solvent. No such system has been encountered.

2.1.4.10 Thioanions

A characteristic of many of the complex oxides of the groups under consideration is the formation of complex oxyanions. The ionic complex oxides may be regarded as aggregates of ions, and the more covalent materials may be regarded as possessing complex ions. The silicates are essentially borderline cases, although they are generally thought of as possessing complex anions. It was indicated above (2.1.4.1) how these materials may be classified according to the way in which the SiO_4^{2-} tetrahedra are linked together to form more complex anionic arrays. It must be remembered however, that there is no reason for supposing the such ions exist in solution, or that they are derived from hypothetical acids, notions that were widespread when complex oxides were first examined.

If such complex ions exist in the silicates, then it is to be expected that similar systems will be found among the analogous sulphides, where the bonds are considerably more covalent in character. The similarity between germanium disulphide, the high pressure modification of silicon disulphide and the various forms of silica has been noted above (2.1.3.5 and 2.1.3.6). The presence of various thioanions has also been noted in many of the complex sulphide structures discussed. The discrete SiS_4^{4-} groups found in Li_4SiS_4 , and the chain anions built from these groups in Li_2SiS_3 has also been noted (2.1.4.6). This is in direct analogy with the discrete SiO_4^{4-} ions found in the orthosilicates (eg olivine, M_2SiO_4 , $\text{M} = \text{Mg, Fe, Mn}$) and the various chain ions, $(\text{SiO}_3)_n$ found in the metasilicates (eg Na_2SiO_3 and Li_2SiO_3 (125-126)).

Although the germanium-sulphur system appears to bear a closer resemblance to the silicates than does the silicon-sulphur system, very recently structural analyses have shown that the thioanions formed are frequently different to the oxyanions found in the silicates. The structure of the discrete ions $[\text{Ge}_4\text{S}_{10}]^{4-}$ found in $\text{Na}_2\text{Ge}_2\text{S}_5$ (89) was illustrated above (2.1.4.7); there is no directly analogous finite ion found in the silicates (5, p 790). Similarly, the work of Krebs (91) showed the presence of the thioanion $[\text{Ge}_2\text{S}_6]^{4-}$ in $\text{Na}_4\text{Ge}_2\text{S}_6 \cdot 14\text{H}_2\text{O}$, consisting of two tetrahedra joined by their edges - a system more in common with low temperature SiS_2 than the silicates. The same structure was reported for the metathiostannate ion, and indeed, in some respects this aspect of the chemistry of germanium bears more resemblance to tin than to silicon. This illustrates the increased covalent character of the sulphides, and is reflected

in many complex sulphides adopting layer structures in which infinite thioanion layers are held together by ions of the opposite charge. However, the structures formed are not sufficiently open to permit exchange of these ions in the manner described for the layer type of aluminosilicate (2.1.4.1). For instance, the structure of KCu_4S_3 consists of double layers of CuS_4 tetrahedra interspersed by K^+ ions at the centre of a cube of eight sulphur atoms (127). A three-dimensional framework of composition $(\text{Cu}_7\text{S}_4)^-$ is found in $\text{NH}_4\text{Cu}_7\text{S}_4$ (128), in which cubic holes between eight sulphur atoms are occupied by the ammonium ions, in what is in effect a distorted CsCl lattice. This structure, like those of the other framework sulphides, is not developed to the extent that it takes on the character of the open framework aluminosilicates.

2.2 CRYSTALLIZATION AND FORMATION OF ALUMINOSILICATES AND SULPHIDES OF INTEREST

2.2.1 Aluminosilicates

A large impetus has been given to the study of crystallization processes in recent years by the need to produce single crystals of controlled purity for semiconductor technology and solid state research. Although the formation of single crystals was not an object of the project, nevertheless, many of the novel systems used with sulphides and other materials are worthy of consideration within the context of the present work, and could well be applied to crystallization in the wider sense of the word. As regards the oxide systems discussed in this section, the fundamental chemistry of the growth of amphoteric oxides from alkaline solutions is the same whether the ultimate aim is the production of new phases or the production of large

single crystals of an existing phase. The main difference is that in the latter situation the phase in question will generally be used (in a finely divided or amorphous state) as the starting material, while in the former case the starting materials will differ from the products, and one or more chemical reactions are an essential additional part of the process.

In a review of recent developments in crystal growth (129), distinction is made between the two processes most widely used. These are flux (high temperature solution) and hydrothermal (high pressure solution) processes. Many high temperature liquids have been used as fluxes. Included are borates, used as solvents for materials containing larger ions which occupy network modifying sites in the melt, and Bi_2O_3 and PbO which have been used to grow oxide materials in view of the presence of ionic bonds in the liquid state. Various halides have also been used as fluxes, but in general such techniques are not used for the crystallization of aluminosilicates, hydrothermal methods being well established here. This type of process is used widely, both for the growth of single crystals and the crystallization of new phases.

Hydrothermal processes generally involve operation in a region of temperature where the vapour pressure of the solvent (or flux) is such as to require a sealed system, when the vapour phase plays an essential part in the equilibria occurring. The term hydrothermal is taken almost without exception to imply the use of water as solvent, and in geology and mineralogy a

distinction is made between reactions below and above the critical point of the solvent. Reactions below critical are referred to as hydrothermal and above critical as pneumatolytic (130). However, there is little evidence for discontinuity at the critical point in terms of solubility, and for this reason the term hydrothermal in chemical texts is taken to imply any aqueous reaction conducted under conditions of elevated temperature and pressure. There is no fundamental reason why water should be regarded as the sole solvent permissible for such systems. Its extensive use stems from the fact that such techniques were originally used for the laboratory synthesis of naturally occurring minerals, where attempts were made to simulate the conditions under which such materials are formed in nature. However, for the synthesis of other types of material, water may well not be the most suitable solvent. True hydrothermal techniques employing non-aqueous solvents have not received much attention. Besides the few systems used for the preparation of sulphides, and described in the next section, the crystallization of selenium from supercritical ammonia (183) is a rare example of the more general application of the hydrothermal technique.

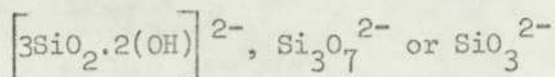
In this context it is slightly misleading to distinguish between hydrothermal and flux techniques. A flux may be regarded as a non aqueous hydrothermal solvent with a very low vapour pressure, and indeed, many supercritical hydrothermal syntheses may be run at temperatures approaching those of conventional molten salt 'flux' systems, although the types of ion present will obviously be very different.

Many reviews have been written in recent years on the hydrothermal technique in general (129, 130), and on the formation of single crystals (131, 132, 134). The basic operating factors of the method may be appreciated from a study of the systems used to prepare large single crystals, without the additional complication of chemical reaction involved when the hydrothermal technique is used as a means of preparing new phases. The main feature of hydrothermal systems is the mineralising solvent, by means of which the temperature for crystallization is reduced to less than that required for melt growth. Indeed, melt growth would not be possible for aluminosilicate materials containing water or hydroxyl groups, and even where it is possible, the hydrothermal technique will generally lead to better, strain free crystals.

The growth of large crystals of quartz serves to illustrate the hydrothermal technique whereby materials insoluble under ambient conditions are dissolved and recrystallized (131, 132). In general, the solubility in pure water is insufficient, and complexing agents are added to increase it. Alkali is the usual choice for silica and aluminosilicates, generally in the form of sodium hydroxide or carbonate. Temperatures of a few hundred degrees centigrade are established, a slight temperature gradient generally existing so that material is dissolved from the polycrystalline feedstock and deposited on the crystal being grown. In general, the solubility will increase with increasing temperature, but decrease in the solvent density may cause the weight percentage of solute dissolved to pass through a maximum. Thus, at 250 atm, the maximum solubility of quartz in water

occurs at 350°C (137), but at 1000 atm the solubility increases relatively uniformly with pressure. Therefore, a choice of operating conditions may be made which is of great importance, assuming such data is available.

Very little is known of the species existing in solution in these systems. Laudise and Kolb (131) propose ions of the type



Brady (133) considered that in water the predominant species over a few hundred atmospheres was $\text{Si}(\text{OH})_4$, a species of higher molecular weight (possibly $\text{Si}_2\text{O}(\text{OH})_6$) existing at lower temperatures.

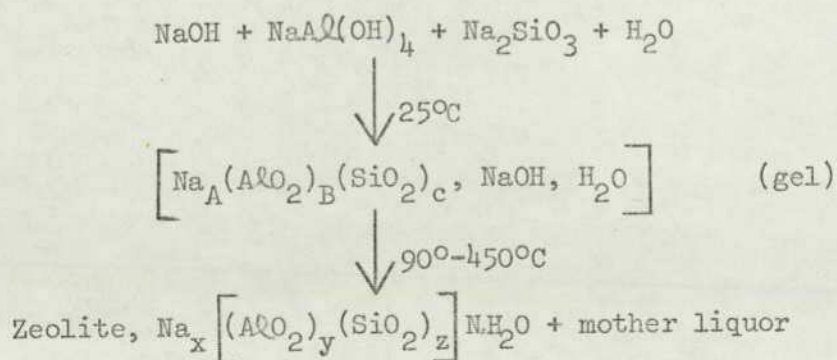
Many types of crystal have been grown in this type of system, not all simple oxides like SiO_2 . Garnets are examples of aluminosilicates crystals grown by both hydrothermal and flux methods (the latter employing lead oxide flux) (134).

The wider application of hydrothermal synthesis is in the preparation of new phases, generally oxides. Water with an added alkali is generally the solvent, and mixed oxide gels are frequently used as starting materials. Generally, only microcrystals result from such procedures, designed to produce either naturally occurring minerals or new compounds. Earlier work of this sort had generally employed melt growth (135). Various other low pressure processes have been developed for the synthesis of minerals, although such techniques are not relevant to the scope of the present work. Crystallization from the melt, sintering and the Verneuil flame fusion technique are examples. Spinel, rutile and sapphire are all examples of materials made by this latter technique (134),

which involves fusion of the reactants in an oxy-hydrogen flame, and was first used for the synthesis of corundum,

The hydrothermal technique as applied to the growth of large crystals has been discussed with reference to quartz, and the principles are essentially the same when the process is used to prepare new materials in polycrystalline form. The key factor is again the mineralizing solvent, usually a basic aqueous solution. In the formation of silicates, it is the presence of this solvent that gives rise to the more open type of structure. Water molecules may become incorporated, as in zeolites, or hydroxyl groups may enter the lattice as in clays.

Professor Barrer has written a useful review on mineral synthesis under hydrothermal conditions (136), in which he describes his own work in this field. Besides naturally occurring minerals, analogue compounds exhibiting isomorphous substitution have been formed, as well as some minerals with no naturally occurring counterparts. Types of materials formed include layer silicates, feldspars and zeolites. In general, such materials were formed from hydrous gels which occurred from interaction of the alkaline silicate and aluminate solutions:-



The species present in solution in this type of system have been considered by Barrer (136; 60, p 39). The essential feature of such systems is the mineralising solvent, and water is a good choice for several reasons. Firstly, being chemically reactive, it may alter the defect structures of crystal lattices, both on the surface through chemisorption, and in the internal structure through bond hydrolysis. Thus bonds may become reorganised and crystal growth nucleated. Secondly, the normally low concentration of hydroxyl groups in glassy silica phases is greatly increased under hydrothermal conditions, and a further beneficial property of water is its good solvent power which facilitates transport and mixing of the reagents.

A somewhat different role of water in these systems is that of stabilising the cavities of porous crystals such as zeolites. This type of structure will not form in the absence of a stabilising guest molecule, although this does not have to be water. Salts present in solution may fulfill this rôle (ie NaCl , Na_2SO_4), and in addition to this the salts themselves may be used as fluxes (in melt growth), when they must fulfill the dual rôle of solvent and stabilising (guest) molecule. Besides molten salts, it is suggested (60, p 39) that ammonia or even argon should be able to stabilise porous lattices of the type found in zeolites, in a similar situation to that found in clathrate gas hydrates.

The mode of growth of complex aluminosilicates in hydrothermal systems is also of interest. It is assumed (136) that the gel may become supersaturated with the phase precipitated, leading to a high nucleation rate and the observed preponderance

of small crystals. It is unlikely that crystallization proceeds through the linking together of single AlO_4 and SiO_4 tetrahedra, as this would not be likely to result in the open and elaborate structures of the zeolites. The formation of intermediate, polyhedral anions is a more plausible explanation. Such polyhedra may be distinguished in this type of structure - ie four-cornered rings on feldspars, cubes in Linde A zeolite, cubo-octahedra in faujasite, etc (136). Concrete evidence for the existence of such anions in solution prior to crystallization is not forthcoming, although the discrete polyhedral anions found, for instance, in beryl (six cornered ring) and osumulite (hexagonal prism) constitutes evidence for the presence of such ions in solution. Similarly, molecules based upon cubic and hexagonal prisms are known in the silsesquioxanes (138, 139), of which an example is $(RSi)_8O_{12}$ (R = alkyl or aryl group).

It has also been suggested by Zhdanov (60, p 39 and p 20) that the pore structure of zeolites is at least partially formed in the gel stage, as these gels possess ion exchange and adsorptive properties more in character with zeolites than silica or alumina gels. This view is also supported by spectroscopic evidence (344) and studies of crystallization from glasses (225, p 51).

Although the solubility of the solid feedstocks used in hydrothermal synthesis generally increases with temperature, it has been found that the most hydrated zeolites are formed at lower reaction temperatures. Indeed, many zeolites can

be prepared below 100°C, at atmospheric pressure. It must be remembered that most of the zeolites prepared are not true equilibrium phases in the systems from which they precipitate.

2.2.2 Sulphides

2.2.2.1 Solvent Methods

Many attempts have been made to extend the techniques for the hydrothermal growth of oxides to the growth of sulphide materials. Initial attempts were made during the last war when the processes for the growth of quartz crystals were being developed. It was shown by Smith (140, 141) that lead and tin sulphides could be crystallized from aqueous sodium polysulphide or sodium hydrosulphide solutions at 410°-425°C. This was quite a general technique, although only microscopic crystals were obtained, the starting materials generally being the metal halides. Other sulphides crystallized were FeS, Cu₂S, Ag₂S, Bi₂S₃, Au₂S, HgS, Sb₂S₃ and As₂S₃. It must be remembered that when sulphides are deposited from aqueous solutions, they are generally obtained as largely amorphous phases, exhibiting very little crystallinity, and therefore the demonstration that such materials could be crystallized in this way was of great importance as a means of understanding the crystalline sulphide deposits found in nature.

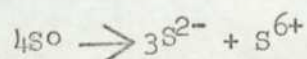
More recently, attempts have been made to grow single crystals of such phases by methods analogous to those already described for the growth of oxides. Thus Laudise and Ballman (142) grew both zinc oxide and zinc sulphide from 1M NaOH solutions. Little tendency was noted for the zinc sulphide to hydrolyse under these conditions, and in fact it was stable in hydroxide solution

of strengths up to 10 M. These authors also crystallized ZnS from sodium sulphide solution. This stability of zinc sulphide in hydroxide solutions is somewhat surprising, and it is by no means univervally found. For instance PbS hydrolyses under these conditions (132), and it was found necessary to use a solution of ammonium polysulphide to recrystallise this material. Conversely ZnS has been crystallized as $2\ \mu$ crystallites in water alone at 350°C and several hundred atmospheres (168).

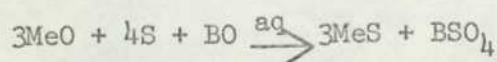
Since this work there have been many reports of similar processes, some with additional ions present, which it is claimed enhance solubility or promote crystallization. Unlike the analogous process for the crystallization of oxides, these methods do not always use the sulphide as starting material. Halides are sometimes preferred, alkali polysulphide furnishing the additional sulphur required. The crystallization of lead and zinc sulphides from aqueous polysulphide solutions containing sodium and lithium halides at 450° , was described (143). Laudise et al made a comprehensive study of the hydrothermal solubility and growth of sphalerite (ZnS), (144), from KOH and NH_4Cl solutions. They suggested $\text{Zn}(\text{SOH})^-$ to be the predominant species in alkaline solution, and confirmed earlier observation of the resistance to hydrolysis of this material. Concentrations up to 6 per cent w/w were used. This work has since been extended to an examination of the potentiality of using the hydrothermal technique for the preparation of single crystals of ZnSe, ZnTe, CdSe and CdTe. PbS and CdS hydrolysed under these conditions (145). Cadmium sulphide has been crystallized from

many solutions, including NH_4Cl , CaCl_2 and Na_2MoO_4 (146). Antimony sulphide (147) and molybdenum disulphide (158) have also been crystallized in this type of system.

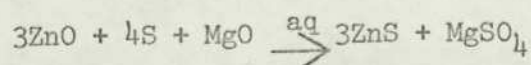
These examples serve to show the scope of the work in this field undertaken during recent years, and are not intended to be exhaustive in their coverage. In general, such processes have been used to crystallize sulphides rather than to form new phases by means of chemical reaction, although in cases where halides, etc are used as starting material a chemical reaction will obviously occur. A rather different approach to the hydrothermal synthesis of sulphides has been developed by Cambri et al, and is described in a comprehensive review (148). The technique, by which new phases and complex sulphides have been prepared, is based on the effect of sulphur in aqueous media on the related oxides, in the presence of base to neutralise the sulphuric acid developed by sulphur auto-oxidation:-



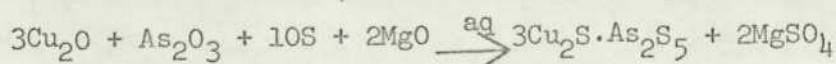
The conditions used were $180^\circ\text{--}343^\circ\text{C}$, at 10-150 atmospheres. The general process may be represented as:-



where MeO = heavy metal oxides and BO = base (NH_3 , MgO , Na_2CO_3 , ZnO , etc). Thus zinc sulphide has been formed:-



and the formation of complex phases is illustrated by:-



The authors believe that most of the sulphosalts of nature are formed by these processes. The sulphurization to thiogermanates and thioannates is very interesting from the point of view of the present work; although GeO_2 and SnO_2 are not transformed into sulphides by the process described, they are sulphided in the presence of metals able to form a sulphosalt (149) - eg Ag or Cu.

A more recent development in the use of acidic media for the growth of sulphide crystals (150-154). Many sulphides hydrolyse in basic hydroxide media and are insufficiently soluble in alkaline sulphide solution. Under these circumstances concentrated solutions of hydrohalic acids have been used as solvents at temperatures up to 500°C . Behind this approach was the known ability of many sulphides to dissolve in acids with the formation of H_2S , and the tendency of heavy metals to form complexes with halogens. As the reactions were conducted in autoclaves, loss of H_2S could not occur, which remained to take part in the equilibrium. CuS , Cu_9S_5 , CdS , Sb_2S_3 , HgS and PbS were grown in 2-12 M HCl or HBr , and the technique has been applied to other materials (eg halides, Te, Pt, As).

In all the hydrothermal preparations or crystallizations of sulphides discussed so far, complete analogy with the corresponding reactions with oxides is not obtained, as the 'oxide' solvent, water, is still used in the sulphide system. Therefore, the possibility of hydrolysis still exists even if alkali sulphide is used in place of the hydroxide as the basic complexing reagent. Admittedly such hydrolysis can be further suppressed by the use of excess sulphur in the form of polysulphide, but the main

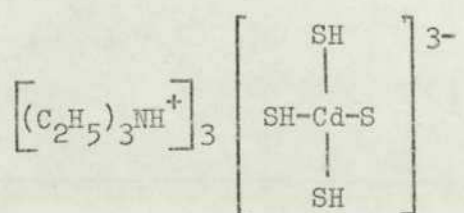
drawback still exists, and the technique cannot be used for sulphides unstable in the presence of water (eg, Al_2S_3 , SiS_2).

The true parent of sulphides, at any rate from a theoretical standpoint, is hydrogen sulphide, and the hydrothermal systems discussed above for the preparation of oxides can only be regarded as completely copied in sulphide systems when water is replaced by hydrogen sulphide as solvent. Scant attention has been given to such systems in the literature. The intermediate situation where a solution of H_2S in water forms the solvent was investigated by Popolitov and Litvin (155), who crystallized $SbSI$ at 250° - $300^{\circ}C$ and 400° - 600 atm from such a system. Only two attempts to use hydrogen sulphide alone as the solvent for such a system have been published. In 1963, Fredericks et al (156) attempted without success to grow potassium chloride from hydrogen sulphide at high temperatures and pressures. Measurements of the solubility of cadmium sulphide and zinc sulphide in this solvent indicated that the technique should be more successful with these materials, although results of such experiments were not reported. In 1968, the results of a detailed investigation into the crystal growth of the heavy metal sulphides from liquid hydrogen sulphide were presented by L.C. Lewis in the form of a thesis (157). This work is discussed in some detail in Chapter 5, and it will suffice to say here that limited success was obtained in the growth of silver sulphide, lead sulphide and stannic sulphide from supercritical H_2S at pressures up to 15,000 psi using seed crystals in a temperature gradient. The use of higher pressures was not beneficial. The feedstock was amorphous or polycrystalline sulphide, and although there was no appreciable growth of the seed crystals, crystallization

of the amorphous feed and the deposition of micro-crystals from solution was indicated in many of the experiments. There was no mineraliser present in the majority of these experiments. As will be seen in Chapter 5, the use of the simple analogues of the mineralisers used in comparable aqueous syntheses (eg sodium sulphide or sodium hydrosulphide) is of little use, as these materials possess very limited solubility in liquid hydrogen sulphide. Organic bases possess higher solubilities in this material, and salts may be formed by such reactions as



For this reason Lewis added various concentrations of triethylamine to a few of his crystal growth experiments to attempt to increase the solubility of the metal sulphide through complex formation. Although it was demonstrated that appreciable solubility of the metal sulphide could be obtained by this means (eg with cadmium sulphide), crystal growth in the supercritical system was not aided. From the results of conductivity measurements on the cadmium sulphide complex solution so formed, a high concentration of the hydrosulphide ion was indicated. From the amount of ethylamine required to completely complex a given amount of cadmium sulphide, the author proposed the following structure for the soluble species:-



Therefore, such results are encouraging for setting up more complex systems in which new phases might be formed in direct analogy to the formation of complex oxides from basic aqueous hydrothermal systems. Such systems would not suffer from the possibility of hydrolysis which is always likely to occur whenever sulphides are prepared in aqueous media.

2.2.2.2 Other Techniques

Beside hydrothermal techniques, there are many other non-aqueous processes that have been used to prepare sulphides in crystalline form. These include growth from the melt, sublimation, chemical transport, and the use of molten salt 'fluxes' in various systems. In general, only flux systems, where there is a 'mineralising solvent' present, could be expected to give rise to sulphides analogous to the more open aluminosilicates formed in hydrothermal systems.

Melt growth of crystals suffers from the disadvantage that relatively high temperatures are required, which can lead to crystal imperfections as well as operating difficulties. Nevertheless, the technique has been applied to the growth of large crystals - ie α -HgS (159) at 120 atm and 1100°C. ZnS was grown by controlled cooling of the melt (160), but the similar technique of vapour phase growth, involving sublimation rather than melting, has been more widely applied to sulphides. For instance, CdS and ZnS have been grown in an H_2/H_2S gas system. (161, 162), the metal or metal sulphide serving as starting material. A related technique (163) was used to grow the sulphides, selenides and tellurides of zinc, cadmium, gallium and indium. The sulphide was grown in a melt in the presence

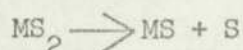
of CS_2 at 30-40 atmospheres, an autoclave being employed.

Another commonly used method of sulphide crystal growth is chemical transport. This relies on the presence of a substance that reacts reversibly with the compound to be crystallized, and which is used to transport it in a volatile form and redeposit it, generally on cooling. It is thus related to sublimation techniques. For instance, gallium sulphide crystals were grown at $800^\circ\text{--}950^\circ\text{C}$ in an H_2S stream containing iodine vapour (164), and zinc sulphide was grown by heating zinc chloride in an H_2S stream (165). Zinc sulphide has also been grown by iodine transport (166), and chlorine transport has been used to grow FeS_2 , CoS_2 and NiS_2 (167).

Chemical transport has also been used to prepare crystals of new phases of complex sulphides. Thus $\text{A}_2^{\text{I}}\text{B}^{\text{II}}\text{C}^{\text{IV}}\text{X}_4$ ($\text{A} = \text{Cu}$; $\text{B} = \text{Zn, Cd, Fe, Mn, Ni,; C} = \text{Si, Ge, Sn and X} = \text{S, Se}$) were grown by iodine transport (169). The structures of these phases were described as tetragonal superstructures of the wurtzite system. Similarly, Cd_4SiS_6 was prepared by iodine transport at $775^\circ\text{--}875^\circ\text{C}$ (170°C), and similar reactions employing aluminium chloride were used to produce XIn_2S_4 ($\text{X} = \text{Zn, Cd, Hg}$) (170); XCr_2S_4 ($\text{X} = \text{Zn, Cd, Mn, Ni}$) and related materials (171). In general, such systems used as starting materials a mixture of the elements.

Vapour-liquid transport has been used to grow CoCr_2S_4 and FeCr_2S_4 from CoS or CrCl_3 and FeS , in sealed tubes at 906°C (172). Similarly, ACr_2X_4 ($\text{A} = \text{Zn, Cd; X} = \text{S, Se}$) were grown from AX and CrCl_3 at 1000°C (173), and CdIn_2S_4 , ZnIn_2S_4 and CdGa_2S_4 have been grown from the gas phase (174).

These methods have been mostly used to produce well defined crystals rather than crystalline masses, and for purposes of comparison with oxides produced by hydrothermal methods, only techniques employing a mineralising solvent are likely to be of use. It is doubtful whether vapour, liquid or chemical transport methods could fulfill this rôle, and only techniques employing some sort of flux are likely to be applicable. Zinc chloride was used as flux in the attempted growth of zinc sulphide (175). The solubility was 0.344 M at 730°C and 0.0831 M at 530°C. Successful results were not obtained, but crystallization of pyrites and related disulphides occurred from fluxes of the metal bromide or lead chloride under an atmosphere of sulphur vapour (176). The presence of sulphur was necessary to prevent dissociation of the disulphide:-



Zinc sulphide has been grown from potassium chloride flux (177) or by slow cooling of a lead chloride melt (179). Mixed fluxes have also been used - ie KI-ZnCl₂ (178). The formation of complexes (ie 2KI.ZnS, KCl-KI-ZnS) is supposed to occur in this type of system.

A variation of this approach has been the use of molten metals as fluxes. Zinc sulphide and cadmium sulphide crystals have been grown from Ga, In, Tl and Sn melts (180). Two mole per cent solutions were obtained at 1180°C in vacuo. Tin has been widely used in this type of system (181), and the approach has been reviewed by Luzhnaya (184).

The use of flux growth techniques for the preparation of oxides has already been discussed (2.2.1). The use of lead borate and oxyfluoride fluxes to prepare garnets is in direct analogy with sulphide growth in this type of medium (182). As certain zeolitic materials (eg noselite, sodalite) contain salt molecules instead of water molecules in the structural voids, there seems a good chance that such materials could be prepared in molten salt media.

This is therefore a worthwhile line of approach that can readily be duplicated in the sulphide system. The use of non-aqueous hydrothermal systems for the preparation of complex sulphides is a relatively unexplored field. The use of hydrogen sulphide as a solvent in such systems is considered in Chapter 5, but unfortunately lack of time prevented the inclusion of molten salt and other high temperature flux techniques. Aqueous hydrothermal systems used for attempted preparation of complex sulphides are discussed in Chapter 6.

2.3 ANALOGUE COMPOUNDS AND THE SUBSTITUTION IN ALUMINOSILICATE LATTICES

In the first part of this chapter mention was made of the fact that many oxides and sulphides may be regarded as close packed arrays of either oxygen or sulphur anions, with the cations occupying interstitial spaces. This type of situation was then developed to include the more open type of framework structure typified by the zeolites. It is apparent that two types of isomorphous substitution may occur in such systems:-

- | | |
|--------------------------------|---|
| 1. Substitution of the cations |] by other ions of similar
size and charge |
| 2. Substitution of the anions | |

2.3.1 Cation Substitution

This is quite common among oxides and sulphides. Assuming the element in question is capable of forming a cation with charge

similar to that of the cation it is intended to replace (or that charge imbalance may be neutralised within the structure), the chief criterion for substitution to occur seems to be the radius of the ion formed. If this is similar to the radius of the ion it is intended to replace, then substitution is likely to be possible and frequently occurs. The concept of radius ratio has been considered above (2.1.2), and it is simple to predict from it whether a particular substitution is possible. Such calculations are included for the structures of interest in section 2.3.3.

Substitution of cations in oxides is an extremely common occurrence, and is responsible for the varying composition found amongst naturally occurring minerals. Besides replacement of, for instance, silicon in silicates, ion exchange of charge - balancing cations is generally possible, and forms a further type of substitution encountered in these materials. Cationic substitution may be illustrated by reference to hornblende, which has the ideal composition

$(\text{OH})_2 \text{Ca}_2 \text{Mg}_5 (\text{Si}_4 \text{O}_{11})_2$. A typical sample contained (5, p 789):-

Si 5.98	] 8.30	Ti 0.13	] 4.75	Na 0.37	] 2.87
A 2.32		Fe ^{III} 0.90		K 0.66	
		Mg 0.46		Ca 1.84	
		Fe ^{II} 3.16			
		Mn ^{II} 0.10			

The increase in overall negative charge resulting from substitution of aluminium for silicon is witnessed by the increase in the number of positive ions (Na, K, Ca) present. Thus apparently complex silicates may be explained in terms of cationic substitution, and materials may be prepared synthetically containing elements not found in the naturally occurring counterparts.

The general similarities between the oxides of silicon and germanium and of aluminium and gallium lead to substitution of both of these elements in synthetically prepared aluminosilicates. In the most complex aluminosilicates (eg, zeolites, feldspars) it is obvious that partial replacement of silicon by aluminium is an essential part of the system, and therefore cationic substitution in these compounds may be taken to imply further replacement of these ions. This type of substitution is not nearly so common as that found in the more compact type of structure (eg, hornblende, discussed above), where the more closely packed anion array is not so dependent upon the cations in the interstitial spaces for strength. Further, the degree of co-valent character present in the bonding of the silicates suggests that replacement of silicon will involve more than only size and charge considerations.

In 1950, Goldsmith (221, 222) reported the synthesis of feldspars and related minerals with gallium and germanium in place of aluminium and silicon. In 1959, Barrer (185) reported the hydrothermal crystallization of zeolites with similar substitutions. Slightly larger unit cells were found to result. An attempt (186) to replace silicon by phosphorus (similar ionic radius) was not successful although this has since been achieved (225, p 76). More recently, Barrer has extended (187) his work to include the synthesis of micas with gallium and germanium replacing aluminium and silicon, and there have been several later reports of zeolites exhibiting this type of substitution. Generally, such materials are prepared by incorporating the appropriate oxide in the gel, and the resulting materials differ from conventional zeolites only in small changes in lattice parameters and adsorption properties. The relevant data for well characterised zeolites is summarised in Table 2.4.

Substituted element	Reference
<u>Total replacement of aluminium</u>	
Ga	188, 189, 192, 193
Ti, Zr, Hf	194, 195
<u>Partial replacement of aluminium or silicon</u>	
Ga	190, 191
B	196
Cr	197, 198
P	199
V	202
Be, Mg	201
B, As, P, V	200

Table 2.4 Cationic Substitution in Zeolites.

The complete replacement of silicon is not common, as this would involve change of the basic structure of an aluminosilicate. Possibly germanium (as claimed by Barrer (185)) is the only element with properties sufficiently like those of silicon to fulfil this capacity.

A series of alkali metal germanates has been given considerable attention over the last 20 years (203 - 219), and as they possess zeolitic properties, they may be considered as zeolite analogues, although they are established materials in their own right and do not possess analogue compounds among the silicates. They may be represented as $M_3 H Ge_7 O_{16} \cdot 4H_2 O$, where M is an alkali metal atom. They were shown (208) to be isostructural with minerals of the Pharmacosiderite group (220), which includes $KFe_4 (AsO_4)_3 (OH)_4 \cdot 6-8H_2 O$, the parent compound. The two classes of material have analogous structural frameworks, with the alkali metal and water placed in channels running through the structure. NMR measurements of the germanates revealed that both alkali metal and water are capable of diffusional movement within the structure (216, 218), and the alkali metal may be ion exchanged (206, 214), showing these materials to be like zeolites in their properties. It is interesting to note that isomorphous substitution of germanium by silicon was found to be possible in these materials (207), up to ~5:1 Si to Ge atomic ratio being obtained before the structure became weakened sufficiently for side products to predominate. It was also found possible to substitute phosphorus for silicon in small amounts (212), the amount of hydrogen present decreasing to maintain electrical neutrality.

The substitution of cations in sulphides is very common, and the processes whereby many complex sulphides are built up by

cationic substitution of simple sulphides was outlined above (2.1.4.9). Whilst in oxides, ionic size is the chief criterion for substitution, the more co-valent character of the sulphides requires more consideration to be given to the chemical characteristics of the substituting elements. Thus, in the substitution of Cu, Fe and Sn in ZnS to form $\text{Cu}_2\text{FeSnS}_2$ with the ZnS (zinc blende) structure, Cu, Fe and Sn form similar numbers of bonds as Zn, besides having similar ionic radii. When As or Sb substitute into this type of structure (Cu_3AsS_3 , Cu_3SbS_3), only three quarters of the positions are occupied as Sb and As form only three bonds. This is in contrast to the replacement of, for instance, Na^+ in oxides. Substitution by Ca^{2+} is more frequent than substitution by K^+ as the calcium ion is more similar in size to the sodium.

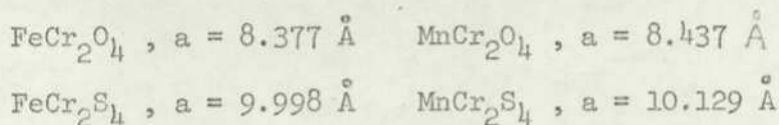
2.3.2 Anion Substitution

This is considerably less common than cation substitution, and does not occur in systems of any complexity. It is a fundamentally different process in that it involves replacement of the close packed anion array in the compact structures, or modification of the tetrahedral building blocks in the more open, framework, structures. It is the anions that form the basis of these structures, with the cations situated within the structural units. Therefore any change in the anion framework is likely to result in a drastic change in structure. Nevertheless, providing charge, radius ratio and possibly bonding characteristics are favourable, there seems no reason why substitution of this sort should not occur.

Within the context of the present work, anion substitution may be taken to mean the replacement of oxygen in an oxide by sulphur. This has not been reported in structures of any complexity. Only very

simple compounds have the same structures in both oxide and sulphide (eg alkali and alkaline earth oxides and sulphides). In so far as certain structural and chemical similarities exist between the binary sulphides and oxides of Groups IIIB and IVB (see 2.1.4.3 - 2.1.4.8), these materials may in certain cases be regarded as analogues. However, these similarities do not persist in the more complex sulphides (2.1.4.9).

The spinels form one of the few families of oxides with clearly defined sulphur analogues. These are compact materials based on close packed anion arrays (224, p 92). The sulphur analogues have larger unit cells:-



In principle, sulphur analogues of oxides may be formed by either direct sulphiding of the oxide, or alternatively by synthesis of the sulphide in a system analogous to that in which the oxide is formed. A few reports of partial sulphiding of ternary oxides do exist, and are discussed in Chapter 3. However, no reports have been encountered of the sulphiding of the more open structured materials such as zeolites. Wells remarks (5, p 794) on the stability of the SiO_4 tetrahedra in silicates, and indicates how, in the chondrodite series of minerals, $m[\text{Mg}_2\text{SiO}_4] \cdot n[\text{Mg}(\text{OH})_2]$, whilst anion substitution by F^- may occur, it is always the anion associated with Mg that is replaced (OH), never that associated with silicon.

A degree of similarity does exist between oxides and sulphides in chalcogenide glasses (223), where sulphide, selenide and telluride analogues of oxide species exist. No direct boundary occurs between the anionic species, and mixed oxychalcogenous glasses are known.

2.3.3 The Feasibility of the Formation of Sulphur Analogues of the Silicates

Throughout the foregoing discussions, emphasis has been placed on the tetrahedral coordination of the cations found in the silicates, and it is therefore apparent that for thio-analogues of these compounds to be formed a similar coordination scheme must be possible. It has been shown that this type of structure is in fact found for many of the simple sulphides of Groups IIIb and IVb, and it has been suggested that both geometrical and chemical considerations must be satisfied. Whilst it is not easy to predict exactly chemical effects, geometrical factors may be predicted with a fair degree of accuracy by the use of the concept of radius ratio. This has been described briefly above (2.1.2), where the limiting values for tetrahedral coordination (0.225 - 0.414) were stated. This means that if this ratio is less than 0.225, the cation becomes too small to be accommodated stably within the tetrahedral cavity formed by four anions (cation-anion contact is impaired), and the structure becomes triangular and an anion is eliminated. Similarly, if the radius ratio exceeds 0.414, anion contact is impaired by the large cation and extra anions are incorporated to yield octahedral coordination. It must be emphasised that this is not an exact law, and one of the main reasons for at least some of the exceptions is polarisation. This means that the larger and more diffuse ions become distorted by the electrical field of the counter ion, and no longer remain the theoretical size. This is quite common in sulphides (see 2.1), but nevertheless the concept of radius ratio is useful as a general guide in predicting the feasibility of structures.

The values of ionic radii of the relevant elements, and the radius ratio (radius of cation/radius of anion) for the Group IIIb and IVb sulphide and oxide ion pairs are included in Table 2.5. It

Ionic Radii ($\text{\AA}$)

C (+4)	0.15	B (+3)	0.20
Si (+4)	0.41	Al (+3)	0.50
Ge (+4)	0.53	Ga (+3)	0.62
Sn (+4)	0.71	In (+3)	0.81
Pb (+4)	0.84	Tl (+3)	0.95
	O (-2)	1.40	
	S (-2)	1.84	

Radius Ratios

	<u>Sulphides</u>	<u>Oxides</u>
C	0.082	0.107
Si	0.222 *	0.292 *
Ge	0.288 *	0.379 *
Sn	0.385 *	0.507
Pb	0.456	0.600
B	0.109	0.143
Al	0.272 *	0.357 *
Ga	0.337 *	0.443 **
In	0.440 **	0.579
Tl	0.515	0.679

* suitable for tetrahedral co-ordination,
 $0.225 \leq \text{radius ratio} \leq 0.414$

** see text

Table 2.5 Ionic Radii of the Elements of Groups IIIb and IVb and Radius Ratios for the sulphides and oxides of these Elements.

Ionic Radii taken from Greenwood (224, pp. 40 - 41), and are values for octahedral co-ordination.

is apparent that the criterion accounts for the observed ready substitution of germanium for silicon in many silicates, both ratios lying well within the range for tetrahedral coordination, as does aluminium. However, gallium is omitted, whilst structures with gallium replacing oxygen are quite well established. A possible source of error is change in ionic radii associated with the change of coordination number from +6 to +4. Greenwood (224, p 42) suggested a three per cent reduction in ionic radius is to be expected in going from octahedral to tetrahedral coordination.

The overall conclusion is that, from a geometrical standpoint, sulphur analogues of the aluminosilicates are feasible for silicon, germanium, tin, aluminium, gallium and indium. This latter element is included in view of the existence of gallium substituted silicates with similar radius ratio.

The chemical considerations are in general agreement with these conclusions. It has been shown above (2.1.3) how high pressure silicon disulphide and both low and high pressure germanium disulphide possess tetrahedral structures analogous to silica. Although stannic sulphide adopts octahedral coordination of tin, the ternary sulphides do possess tetrahedral coordination. Similarly, the ternary sulphides of aluminium, gallium and indium adopt tetrahedral coordination, and should therefore be able to replace cations in a Group IVb sulphide, to form a complex structure. The octahedral corundum structure of Al_2O_3 is also adopted by forms of Al_2S_3 and Ga_2S_3 , a further similarity between these two classes of compound. Indeed, the similarities between these sulphides and oxides are much more marked than those between similar pairs elsewhere in the periodic table (eg NiO, with the sodium chloride structure and NiS with the nickel arsenide structure).

Therefore, from a consideration of the structures adopted by the elements of Groups IIIb and IVb in their oxides and sulphides, it seems that the more co-valent character of the sulphide bonds does not prevent sufficient similarity existing between the two classes of compound to enable direct analogues to be formed.

In general terms, oxides or sulphides of a periodic group of elements become more ionic in character on descending the group (cf CS_2 and SnS_2). Therefore, some degree of compensation for the increasing co-valency experienced in replacing oxygen with sulphur may be obtained by using a cation from further down the periodic group. This is well illustrated by the greater similarity between GeS_2 and SiO_2 than between SiS_2 and SiO_2 . Radius ratio considerations also favour this. However, in view of the fact that the silicates possess a considerable degree of co-valent character, the presence of appreciable co-valency in the bonds of analogous sulphides is not sufficient reason to assume that thio-analogues of the aluminosilicates cannot exist.

Therefore, the formation of thio-analogues of the aluminosilicates would appear to be feasible from a theoretical point of view, and well worth the time expended in pursuing the topic experimentally. The points made concerning the synthesis of this type of material (2.2) must be observed in setting up experimental systems. The use of a mineralising solvent is essential, and lower temperatures should favour the formation of more open types of structure. The ability for gel formation is also highly desirable, as evidence suggests that this is an essential intermediate in the formation of complex phases. The use of hydrogen sulphide as a solvent enables the whole range of cations to be used, while germanium, tin and indium sulphides may also be used in aqueous systems.

CHAPTER 3 SULPHIDED ZEOLITES

3.1 INTRODUCTION AND LITERATURE

A few reports exist from the last century of the partial conversion of alumina to aluminium sulphide by high temperature treatment with carbon disulphide (227). Similarly, $\text{Na}_6\text{Al}_2\text{S}_6$ was reported to be formed when sodium carbonate and alumina were heated in carbon disulphide vapour to elevated temperatures (228). This literature is reviewed by Mellor (Ref: 78; 5, 331), and although the technique is of limited value for the synthesis of complex sulphides analogous to zeolites, as it does not employ a mineralising solvent, nevertheless it is potentially useful for the modification of existing structures. A few such preparations have been reported. For instance, Ba TiS_3 , Ba ZnS_3 and other alkaline earth thiozirconates were prepared in this way at temperatures over 700°C (229).

Thus, with the relatively compact oxides at least, there is good evidence for the practicality of direct sulphiding at elevated temperatures, and it was considered desirable to extend this type of reaction to zeolites. An extensive literature exists relating to the sulphiding of zeolites under a variety of conditions, although replacement of structural oxygen has not been reported.

3.1.1 Ultramarines

A possibility that must be considered when a zeolite is sulphided is that an ultramarine will be formed. These materials are based on aluminosilicate frameworks similar to zeolites, but contain in addition anions within the framework cavities. In the case of ultramarines sulphide ions are present, although other ions are found in related materials (eg sulphate or halide ions). The

net ionic charge must balance the framework charge, as in zeolites, and anion as well as cation exchange is possible.

It must be emphasised that the sulphur, whilst an essential part of the ultramarine, is not incorporated into the framework lattice, and remains a separate part of the structure. The established process for the preparation of ultramarine is well documented (230, 231, 241). A source of aluminosilicate (frequently china clay) is heated to $850^{\circ} - 900^{\circ}\text{C}$ with sulphur, sodium sulphate or sodium carbonate, and a reducing agent (frequently carbon). A pale green material results, and subsequent heating in air converts this to the blue ultramarine. It is suggested (232) that only about 30 per cent of the sulphur used appears in the product, the remainder being lost as sulphur dioxide, which plays an important part in the reaction.

Ultramarines have also been prepared from mixtures of silica and alumina with sodium carbonate and sodium sulphide (233). Various mechanisms have been proposed for the process that occurs in these reactions (234). Sodium aluminosilicate is first formed, which then reacts with either sodium sulphide to form the green ultramarine precursor, or with sodium polysulphide to form ultramarine blue directly. The structure proposed for ultramarine was $2[\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2] \text{Na}_2\text{S}_4$.

Further light was thrown on these reactions by a thermographic study of ultramarine formation (235). Polysulphides were formed from sulphur and sodium carbonate, and reacted with alumina/silica to form a yellow, sulphur containing aluminosilicate (pseudonepheline) between 400 and 750°C . This was converted to a more open (zeolitic) lattice at 720°C , when ultramarine green was formed. Heating in air between 350 and 450°C formed ultramarine blue, with a slightly larger crystal lattice. It is apparent that in these

preparations the salts present are serving as a flux for the formation of the zeolitic lattice. Further, the bulky anions present will help to stabilise this lattice as it forms around them.

In view of the close similarity between ultramarines and zeolites, it is not surprising that ultramarines have been formed by direct sulphiding of zeolites. Attempts at preparing ultramarines by boiling zeolites in sodium polysulphide solution were only partially successful (236). It was necessary (231, 237) to heat the zeolite with sulphur and sodium acetate at 850°C , and subsequently to calcine the product at 500°C in the presence of sulphur dioxide to form ultramarine blue. Reconstruction of the zeolite lattice occurred during the process, with formation of the framework around the polysulphide linkages. Thus the process does not simply involve the incorporation of sulphur into the zeolite structure.

Other workers have used (238-240) sulphur vapour and hydrogen sulphide atmospheres in the preparation of ultramarines from aluminosilicates, and found benefits to result. The presence of polysulphide seems an important factor, and it has been suggested (231) that the second (oxidation) stage in ultramarine formation involves removal of sodium oxide from the lattice, leaving a vacant space. Sulphur trioxide, formed by oxidation of sulphur dioxide was believed to promote this through the formation of sodium sulphate. Similarly, it has been found (242-245) that while sulphur-ultramarine bonds are strong, and resist oxidation even at 600°C , the polysulphide bonds are much weaker and sodium may be readily removed. It was found that ultramarine is stable to 1200°C in an inert atmosphere.

Whilst it is well established that the colour in ultramarines is due to sulphur, the specific nature of the species involved

has attracted a considerable amount of speculation. Colloidal sulphur (247) or the incompletely oxidised parent compound (246) were two early theories. This latter interpretation was in line with the observation that the colour depends on the degree of calcination employed (248). It was not found possible to produce ultramarines with a sulphur content less than about nine per cent (249). As a result of an examination of the decomposition of ultramarines by acid (250), the colour was also attributed to sulphur molecules containing several atoms.

The application of E.P.R. to ultramarines showed them to possess strong paramagnetism, attributed to sulphur radicals (251). g values between 2.028 and 2.029 were found. Dudzik (252), as part of a comprehensive study into catalysts containing free radicals (see 3.1.2), reported the g -values of ultramarines as 2.084, with 3.5 ± 0.5 sulphur atoms per spin. Many other reports of this nature have appeared, and the active species identified as S^- or S_3^- (255), or S_2^- (256). S_3^- is probably the correct interpretation, as the g -value of ultramarine was found to agree closely with that of alkali halide trapped S_3^- ions (257). This is in agreement with conclusions of Dudzik (252) based on U.V. fluorescence, and Raman spectra confirm this view. It has been suggested (303) that the oxidation step in ultramarine preparation consists of the conversion of S_2^- to S_3^- . Further details of these species are to be found in a recent review of homonuclear sulphur species (469).

Sulphur radical anions are also found in aqueous and organic polysulphide solutions (302, 308, 309), molten salt systems (303, 304, 310) and liquid sulphur (253). Sulphur cations (S_{16}^{2+} , S_8^{2+} ; S_4^{2+}) are found in highly acidic media containing strong oxidising agents (eg, oleum) (254, 297-301). These systems are discussed in more detail in the review mentioned above (469).

Analogues of ultramarines are known, similar to those discussed above under aluminosilicates (2.3.1). Germanium and boron containing ultramarines have been reported (258, 259), and the sulphur has also been replaced by selenium (233, 260) giving red-brown products. No report exists, however, of sulphur or selenium replacing oxygen in the structural lattice.

3.1.2 Sulphided Zeolites

Ultramarines may be regarded as a special class of sulphided zeolite, and a large amount of work has been published on the topic of sulphided zeolites in the wider sense. The work of Dudzik discussed above represents a comprehensive study of the nature and catalytic activity of this type of material. Reactions studied were the activity of ultramarine for the dehydrogenation of isopropanol and the hydrodesulphurization of thiophen (261, 262, 285, 286, 263), and the cracking of 2-3, dimethylbutane over both ultramarines (264) and sulphided zeolites (267, 268). Considerable enhancement of activity over that of unsulphided zeolites was obtained, and the activity was related to the paramagnetic strength rather than the sulphur content. A product distribution was obtained typical of a free-radical mechanism, and differing from the carbonium-ion mechanism found over a hydrogen Y-zeolite. In view of the diffusion controlled nature of the reactions observed, and a dependence on molecular size of the reagent, it appeared that the free-radical site was buried deep within the framework structure. The considerable high temperature stability of the free-radicals was considered to be added confirmation of this, the radical function being effectively locked within the aluminosilicate framework, and quite separate from the usual acidic function associated with these materials. Therefore it seems likely that the catalytic activity for the reactions studied is due to sulphur free radicals trapped within the aluminosilicate framework.

Zeolites impregnated with sulphur at temperatures over 300°C were found to be intensely paramagnetic (266) although the active centre was quite different to that found in ultramarines. The latter gave rise to a single line even at 4°K , while sulphided zeolites showed fine structure. Further, the 'sulphur atoms per spin' ratio was two orders of magnitude greater for the sulphided zeolites, and was attributed to chains of ca 600 sulphur atoms with a free radical at either end, frozen into the lattice. Stability on exposure to air decreased with increasing pore size, silicas with pores of $40 - 90 \text{ \AA}$ being considerably less stable than the zeolites, but otherwise similar in properties.

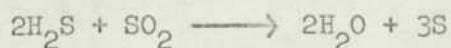
The ESR signal strength obtained from these compounds was dependent upon the mode of preparation and rate of cooling, confirming the concept of radicals frozen within the framework. However, the abnormal stability found for the smallest pored sulphided zeolite used (3A) was not accounted for. The pores will be large enough for easy access of the oxygen and water molecules which destroy the sulphur radicals in the larger pored sieves (4A, 5A). It is perhaps significant that stability was only achieved by completely saturating the zeolite with sulphur; partial blocking of the pores by sulphur is suggested. Catalytic activity of these materials was attributed to perturbation of the electric field on the catalyst surface rather than direct interaction of the reactant molecule with the free radical.

The stabilisation of free radicals by the zeolite framework is quite a general phenomenon. For instance, radicals generated by the thermal decomposition of dibenzoyl peroxide have been stabilised in this way (269). Conversely, aluminosilicates other than zeolites can give blue colourations with alkali sulphides or polysulphides (270), and the formation and stabilisation of sulphide radicals within aluminosilicate frameworks appears to be a well established phenomenon.

The adsorption of sulphur (and phosphorus) by various zeolites has been investigated by Barrer (271), who obtained evidence that the sulphur diffused as chains, no change being noted in the structure of the zeolite after sulphiding. The luminescence and tenebrescence of certain sulphur containing aluminosilicates (sodalites) was attributed to the presence of sodium polysulphide (272, 273), thus distinguishing them from ultramarines.

Several reports have appeared on the oxidation of hydrogen sulphide over zeolites, which are particularly active catalysts for this reaction. The types of reaction occurring are closely related to the reactions between sulphides and zeolites already described. Kerr and Johnson (274, 275) described how a stream of hydrogen sulphide ignited when passed over 13X zeolite in air at room temperature. Controlled oxidation at 245°C led to the formation of sulphur with very little sulphur dioxide. The zeolite became deep blue during the reaction, but the colour faded if the reaction was stopped, doubtless due to oxidation of the radicals responsible. X-ray diffraction did not indicate any structural modification of the zeolite. Direct oxidation of hydrogen sulphide to sulphur trioxide has been observed in zeolites at 100 - 200°C (276, 277).

Various zeolites have also been used to promote the oxidation of hydrogen sulphide by sulphur dioxide (Claus reaction), (278):



High surface area γ -alumina was also a good catalyst for this reaction, also developing sulphur radicals (with characteristic blue colouration) during the reaction. Zeolites have also been used to promote the formation of carbonyl sulphide from carbon monoxide and sulphur (279) and from carbon dioxide and carbon disulphide (280).

Many commercial applications of sulphided zeolites as catalysts have been reported, an increase in activity or selectivity

resulting from the sulphiding process. A five to tenfold increase in cracking activity has been reported (281, 282) to result from sulphiding a zeolite catalyst. Sulphiding may be achieved through the addition of hydrogen sulphide or methyl mercaptan to the feedstock (287), but more commonly the catalyst is presulphided, the zeolite being impregnated with sodium sulphide solution, molten sulphur, carbon disulphide or an organic sulphide (288). Besides cracking, reactions promoted include alkylation, isomerization and polymerization. A mixture of hydrogen and hydrogen sulphide has been found (289, 290) particularly useful for activating zeolites for hydrocracking, and ultramarines have also been used in this type of reaction (291). Dehydrogenation catalysts have been prepared by sulphur treatment of zeolites (292), and the hydration activity of silica-alumina has been enhanced by treatment with hydrogen sulphide (293). Selective poisoning by sulphur has also been reported - for instance the inhibition of olefin polymerization (294). In general, selenium treatment of zeolites produces similar effects to sulphur treatment, but tellurium treatment has been found (283, 284, 295, 311) to produce very selective dehydrocyclization catalysts for the conversion of *n*-hexane to benzene. It seems that the active species is tellurium in a negative oxidation state, coordinated to zeolitic cations in the supercages.

A large number of publications exist relating to the use of zeolites as adsorbents in sulphur-containing systems, where the sulphur compound is adsorbed from either gas or liquid phase. No permanent interaction is observed in most cases, and the subject is not further discussed here. Only occasionally has interaction, with the formation of radical species, been observed (296) in these systems.

There was therefore an extensive literature on which to base the present sulphiding experiments on zeolites. No report was encountered that might imply replacement of lattice oxygen to form a sulphide

structure, the chief reaction noted being the formation and stabilisation of sulphur radicals within the zeolite framework. However, there is no reason to rule out the possibility of replacing structural oxygen with sulphur. For instance, the liberation of hydrogen sulphide with acid treatment of ultramarines (250) is attributed to the presence of sulphide and polysulphide ions, although it could equally well be due to the hydrolysis of aluminium-sulphur or silicon-sulphur bonds.

The various processes used to prepare ultramarines are well documented (see Section 3.1.1), and it seemed unlikely that appreciable structural sulphiding could be achieved using this approach, which was therefore not investigated.

A series of experiments was set up in which direct sulphiding of 13X zeolite with carbon disulphide at elevated temperatures was attempted. 13X zeolite was used in view of its high reactivity towards sulphur, which was apparent from a study of the literature. Carbon disulphide was used in view of the reports that sulphiding of simple oxides had been achieved using this material.

3.2 EXPERIMENTAL SECTION

3.2.1 Dry Box Handling Techniques

As it was likely that many of the products formed by sulphiding zeolites would be reactive towards air, a glove box was assembled for handling these materials under dry nitrogen. The box was a commercial unit, measuring 3 foot 3 inch x 2 foot 3 inch x 2 foot, with a cylindrical entry port 1 foot in diameter and 1 foot long. It was manufactured by Lintott Engineering Limited, Horsham, Sussex, and mounted on a Dexion stand.

The gas purification system was arranged beneath the box, and was built in glass from standard Quickfit components. Vacuum

grade taps of wide bore were used throughout. The arrangement is shown in Figure 3.1. A re-cycling system was employed, a small electric diaphragm pump with a throughput of three litres per minute being used. This was arranged to draw the gas through the purification system, which was therefore slightly below atmospheric pressure. This avoided any tendency for the joints to ease open due to internal pressure.

Under normal operation, gas left the box through the upper tube and tap T1, the right angle limb of this three-way tap being isolated (as was that of T4, the return tap). It then passed through a cold trap, chilled with liquid nitrogen when solvents were being used in the box, and passed to the bulk drier. This consisted of 3 kg of Hopkin and Williams 'Drierite', (specially prepared anhydrous calcium sulphate) arranged in a large desiccator, the gas entering at the base of the bed, which was supported on metal gauze. From the top of this bed the gas passed to the oxygen removal unit, which consisted of a tube (2 foot x 1 inch) packed with copper wool and heated to 350°C by means of a thermostat controlled furnace. From this the gas passed to six 9 x 1 inch 'Drierite' tubes to remove final traces of moisture. The desiccant used in these tubes was the self-indicating variety available commercially, and the colour change indicated when the bulk drier was becoming exhausted. A final 9 x 2 inch 4A molecular sieve drier served to remove final traces of moisture, this material being an effective desiccant at low ambient moisture level. The gas then passed through the pump and was returned to the box through T3, T4 and the lower distributor. By rotating T1 and T4 through 90° and opening V2 and V3, the entry port atmosphere could be passed through the purifying system, although this mode of operation was not required in normal use. When taking articles into or out of the box, the entry port was filled with purified nitrogen,

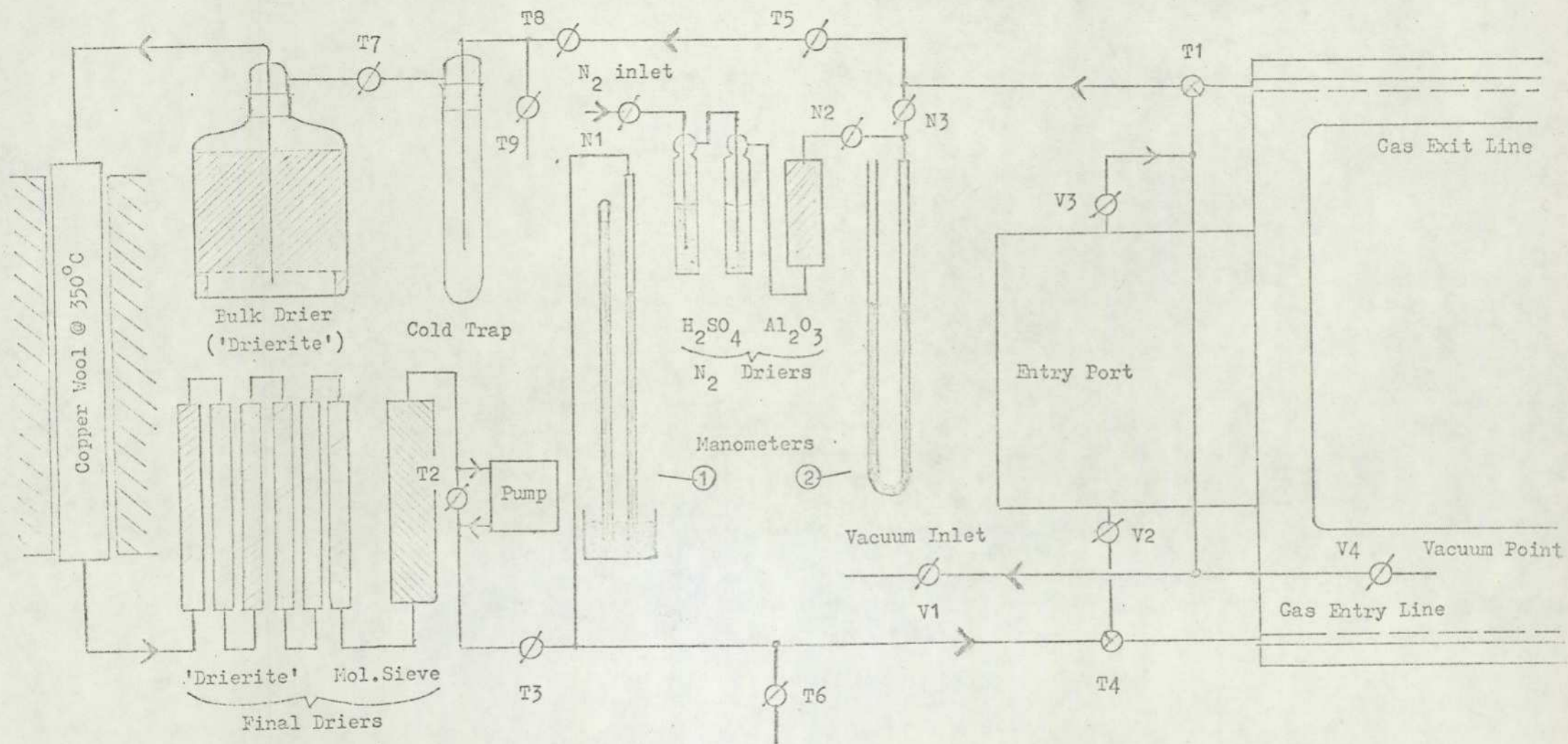


Fig. 3.1 Dry Box gas purification and circulating system.

before the inner door was opened. A Rotary Vacuum pump was connected to the vacuum inlet, and T1 was left in an intermediate position so that all the lines attached to it were shut off, V3 and V2 were opened, and T4 was rotated so that gas could pass to the manometer (1), but not to the box. T3 was closed so that the purification system was not evacuated, and T2 opened to render the circulating pump inoperative. Vacuum was then applied through V1, the pressure drop in the entry port being monitored on manometer (1); the barometric limb served to indicate the zero position. When the entry port was evacuated, V2 and V3 were closed, and nitrogen was allowed into the system through N3. Nitrogen (BOC 'White Spot' oxygen - free grade) was dried with two sulphuric acid bubblers and an alumina tower. The nitrogen passed through the main purifying system, T3 and T4 being opened again, and was bled into the entry port through V2, so that a slight pressure was maintained on the supply manometer (2).

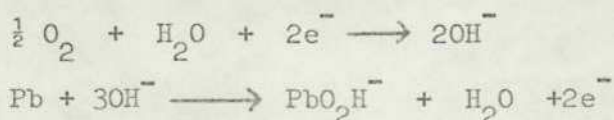
It was possible to conduct vacuum filtrations, etc, in the box by using the tap V4, which was connected directly to the vacuum pump. By conducting the entry port evacuation procedure with T3 open, the main purification system was evacuated and could then be refilled with nitrogen. This was the procedure adopted when the desiccant was changed. When taking solvents into the box, the entry port was purged with dry nitrogen rather than evacuated. Nitrogen entered via T4 and V2, and was vented through V3, V1 and the vacuum inlet. By rotating T4 when in this mode of operation, purging of the box with fresh nitrogen was possible. It was vented through T1 and V1. When emptying the cold trap, it was isolated by T7 and T8 and evacuated through T9 before being reconnected into the system.

A automatic balance reading to 0.1 mg was installed within the box. Moisture level was recorded with a Negretti and Zambra hair hygrometer (0-100 per cent relative humidity), zeroed in a dessicator over P_2O_5 . After purging the box with dry nitrogen for a week, and operating the atmosphere-circulating system for a further month, a reading of <1 per cent relative humidity was obtained. Desiccant life was about 6 months, but the much smaller volume (due to furnace size) of copper wool required renewing every 3 - 4 weeks.

Oxygen level in the atmosphere was monitored with a 'Hersch' cell (305) constructed in the laboratory (Figure 3.2). It was connected to T6, and T4 closed. Gas was pumped through the cell at 100 ml/min, being adjusted by the needle valve. It is reported that the scale reading is proportional to oxygen concentration in the range 0 - 100 ppm, although it was found possible to obtain an indication up to 500 ppm if accurate calibration was not required. BOC oxygen-free nitrogen was taken as the zero point, and the author's approximate calibration factor ($2.34 \text{ A/ppm } O_2$) used. This was felt to give sufficient accuracy for the purpose required. The oxygen level was 300 - 500 ppm during normal use.

The anode consisted of $\frac{1}{2}$ inch iron tube wrapped with lead foil. The electrolyte (KOH solution) was impregnated in porous PVC. (0.75 mm Porvic S, supplied by Pritchett and Gold and EPS Company Limited, 107a, Pimlico Road, London S.W.1) wrapped around the lead foil, and the anode consisted of silver gauze wrapped around this. A 1 mA f.s.d. ammeter in series with a 100 ohm resistor was connected across the cell.

The electrochemical reactions may be represented as:-



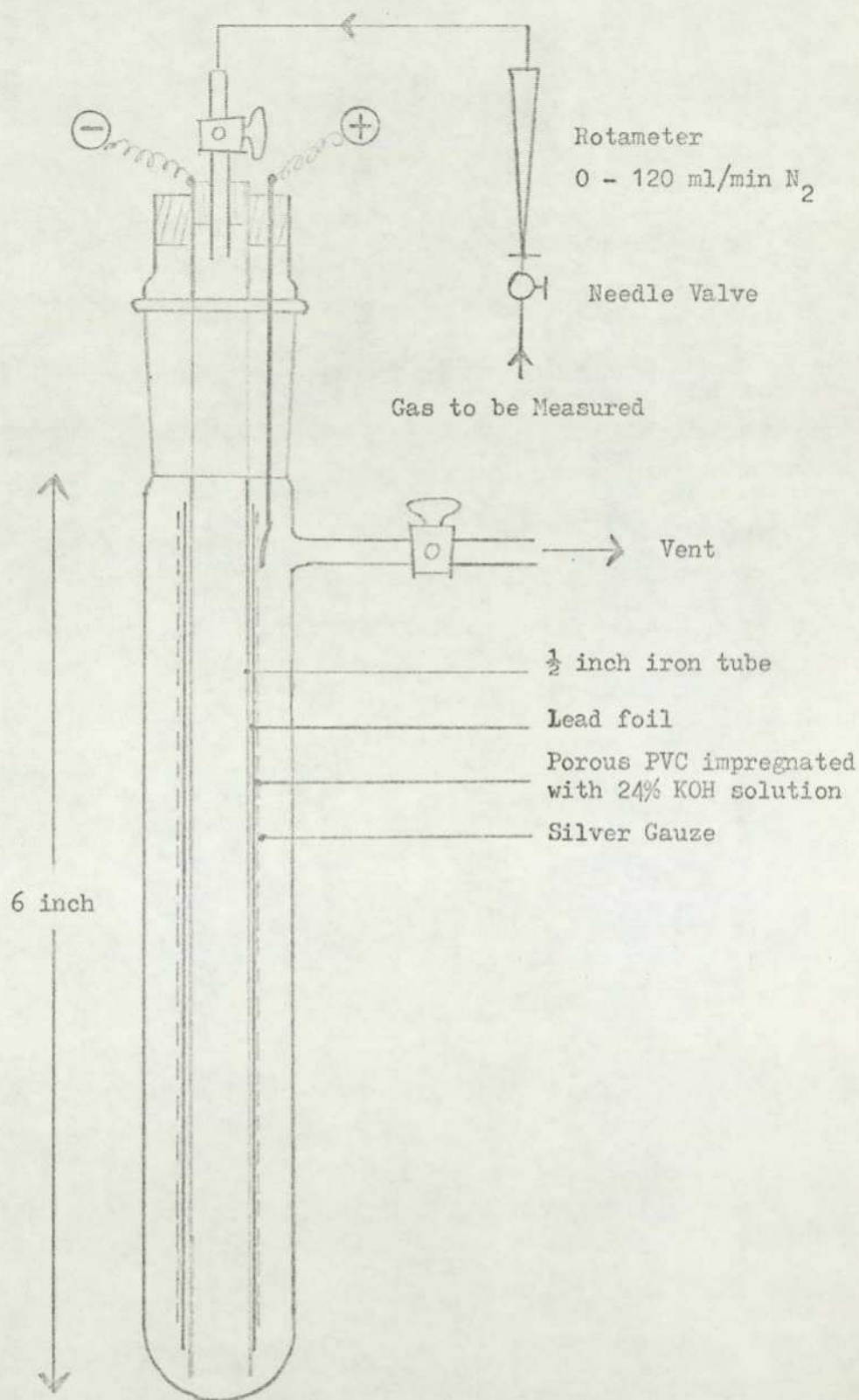


Fig. 3.2 Hersch cell for the measurement of the oxygen content of gases.

The silver cathode is partially in contact with both the KOH electrolyte and the surrounding atmosphere. The current flowing through the milli-ammeter is proportional to the oxygen concentration of the atmosphere, and the device may be described as a fuel cell for converting the free energy of oxidation of lead into a galvanic current.

The device proved a simple and effective way of checking oxygen levels at low concentration. The lead foil required periodic replacement, and this necessitated replacement of the PVC which became brittle during use.

3.2.2 Analysis for Sulphur

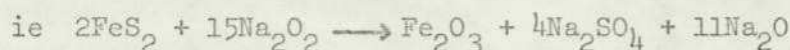
As a reliable and convenient method of quantitative analysis for sulphur was of basic importance to the project, various techniques were examined and tested. The initial experiments to test the validity of the methods were made on mixtures of sulphur and molecular sieve, as this was the type of system encountered in the work described in the present chapter, where the sulphur was likely to be in either elemental or sulphide form. Analysis of both these forms of sulphur is similar, and may be regarded as 'inorganic' sulphur. Analysis of the organic and organometallic sulphur compounds encountered in subsequent parts of the work is described in later chapters.

In considering analysis of sulphided zeolites, attempts were made to distinguish between

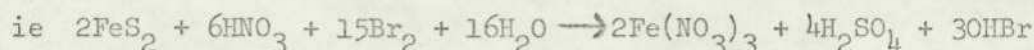
- (a) combined (sulphide) sulphur or strongly bound elemental sulphur.
- (b) adsorbed or loosely bound elemental sulphur.

The general method recommended for analysis of sulphur ores (306; p 573 and 466) involves oxidation of the sulphur (or sulphide) to sulphate, and the determination of this gravimetrically as barium sulphate. The conventional method of carrying out the oxidation is

by fusion with sodium peroxide and sodium carbonate;



Other methods employed involve liquid phase oxidation, for instance with bromine/carbon tetrachloride solution and nitric acid:-



The sodium peroxide fusion method was tested on synthetic mixtures of sulphur and the powdered (without binder) grade of 13X molecular sieve used for subsequent experiments. 0.5 g of a mixture of flowers of sulphur and zeolite (~5%) was heated with the fusion mixture (1 g sodium carbonate + 5 g sodium peroxide) in a nickel crucible for 30 minutes, and then boiled with water for 15 minutes to extract the sulphate. The solution was then boiled with bromine water to oxidise any sulphide present to sulphate, filtered and the residue evaporated to dryness. The residue was dissolved in dilute hydrochloric acid, and the sulphate precipitated with dilute barium chloride solution, and determined gravimetrically in the usual way (306). Low results were obtained by this technique, which was also extremely time-consuming, and not well suited to a routine procedure. The low results were probably due to a loss of sulphur during the fusion stage; the melt was coloured yellow for some time, and the elemental sulphur appeared slow to react and prone to loss as SO_2 .

Example

wt of sulphur = 0.0112 g (5% in 13X sieve)

wt of ignition crucible = 32.1457 g

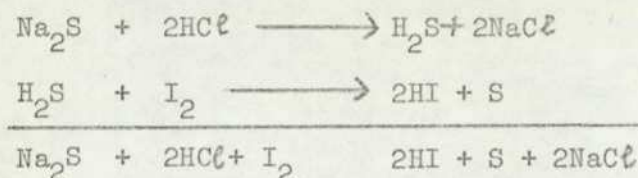
wt of ignition crucible + barium sulphate = 32.1978 g

wt of ignition crucible + barium sulphate = 32.2001 g
(2nd heating)

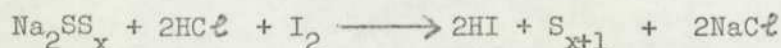
$\therefore$ wt of precipitate = 0.544 g

$\therefore$ % recovery of sulphur = $\frac{0.0544 \cdot 0.1374 \cdot 100}{0.0112} = \underline{\underline{66.7\%}}$

An alternative method was based upon the well-known qualitative test for organic sulphur compounds, involving fusion with metallic sodium to form sodium sulphide, and seemed well suited to materials likely to contain considerable quantities of elemental sulphur. The sodium sulphide is then determined by any of the standard methods for soluble sulphides. The application of this technique to quantitative analysis is discussed by Ingram (307). The method of sulphide analysis used was to extract the fusion product with water or dilute sodium hydroxide solution, and to determine the sulphide by reaction with excess of standard iodine in the presence of acid. The excess iodine was then determined by titration with thiosulphate.



It is generally recommended (306, p 370) that the sulphide is added to excess of acidified iodine solution so that loss of hydrogen sulphide does not occur. Another source of error is the formation of polysulphides that will not react quantitatively with the iodine:-



This error may be eliminated by estimating the sulphur remaining (6, p 215), although evidence suggests that, at least in the case of organic sulphides where carbon is present, complete reduction to monosulphide occurs (307).

The method was checked on mixtures of sulphur and 13X zeolite. A 0.2 g sample placed at the bottom of a tube made from 6 mm pyrex glass tube, sealed at one end and about 5 cm long. A pellet of sodium was placed on top of the sample and the tube heated just above the sodium until this melted and covered the sample. In this way, loss of sulphur was eliminated. The sample was then heated

strongly until red hot, allowed to cool slightly, and then plunged into water so that the glass was shattered and the sodium sulphide extracted. No improvement to the accuracy was found if the tube was totally sealed before the initial heating, and therefore this potentially more dangerous approach was not adopted. After extraction, the mixture was boiled, filtered, and made up to a convenient volume. Aliquots were then added to excess of acidified 0.1N iodine, and back-titrated with 0.1N sodium thiosulphate, employing starch solution as indicator. The technique is illustrated in the following examples, which were made on a ~5 per cent mixture of flowers of sulphur and 13X molecular sieve. A blank determination was found to be necessary, using molecular sieve only. The 0.1N iodine and thiosulphate solutions were prepared from BDH ampoules of concentrated volumetric solution.

Example

(1) Blank:- (0.20 g 13X molecular sieve).

Fused, extracted and made up to 100 ml. 25 ml aliquots added to 10.0 ml 0.1N I_2 acidified with 5 ml 20 per cent HCl. Excess iodine back-titrated with 0.1N thiosulphate.

(i) Excess iodine = 9.91 ml 0.1N thiosulphate

(ii) " " = 9.74 ml 0.1N "

∴ Iodine used = 10.00 - 9.82 = 0.18 ml 0.1N

$0.18 \times 0.001602 \text{ g S} = 0.000288 \text{ g}$

∴ wt sulphur in 100 ml = $4 \times 0.000288 = \underline{0.001152 \text{ g sulphur}}$

- (2) Synthetic Mixture of ~5 per cent Sulphur
+ 13X Molecular Sieve. Method as for blank.

$$\text{wt of sulphur} = 0.0055 \text{ g.}$$

$$\text{wt of molecular sieve} = 0.20 \text{ g}$$

$$(i) \text{ Excess iodine} = 8.96 \text{ ml } 0.1N \text{ thiosulphate}$$

$$(ii) \quad " \quad " \quad = 8.97 \text{ ml } 0.1N \quad "$$

$$\therefore \text{ Iodine used} = 10.00 - 8.97 = 1.03 \text{ ml}$$

$$= 1.03 \times 0.001602 \text{ g sulphur} = \\ 0.001668 \text{ g}$$

$$\therefore \text{ wt sulphur in } 100 \text{ ml} = 4 \times 0.001668 = \underline{0.006672 \text{ g}}$$

$$\therefore \text{ wt of sulphur in sample} = 0.006672 - 0.001152 \\ = \underline{0.005520 \text{ g}}$$

$$\therefore \% \text{ Recovery of sulphur} = \frac{0.005520 \times 100}{0.0055} = \underline{100.4\%}$$

It is apparent that this method is capable of giving quite accurate results for sulphur (and also sulphides), providing a reagent blank is subtracted, and was therefore made the standard procedure for determination of sulphur content of sulphided zeolites. Modification of parts of this procedure were also used for various analyses in later parts of the work; these are covered in subsequent chapters.

Experiments were also conducted on the use of solvent extraction to estimate adsorbed rather than combined sulphur in the products obtained. Although initial experiments were conducted with carbon disulphide, xylene was subsequently found to be a considerably more satisfactory solvent for elemental sulphur, a golden solution being readily obtained on warming. Attempts to measure the concentration of the dissolved sulphur colourimetrically were not very satisfactory as the absorption was found to border the solvent absorption and to change with the method of preparation of the solution. Interaction with the solvent, or modification of the dissolved species was indicated.

Chemical methods of estimating the dissolved sulphur were therefore investigated. A known solution of ~ 0.3 per cent w/w sulphur in xylene was therefore prepared, and various techniques used to analyse it so that their accuracy might be assessed. Initially, an aliquot was diluted 20 times, and the resulting solution refluxed over sodium pellets for ~ 30 minutes to promote reaction of the dissolved sulphur to form sodium sulphide. The xylene was then removed under vacuum, and the residue extracted with water for analysis titrimetrically, as described above. This technique was later modified, water being added directly to extract the sodium sulphide from the xylene mixture without removing the solvent under vacuum. The lower water layer was then run off and analysed as before. However, low results were obtained and it was suspected that a coating of sodium sulphide on the sodium pellets was preventing complete reaction. This difficulty was overcome by using the following technique. To the solution of sulphur in xylene an equal volume of water was added, followed by a few pellets of sodium. The xylene formed a layer over the water, and the sodium floated on the water surrounded by the xylene. The sodium reacted with the dissolved sulphur to form sodium sulphide, which dissolved in the water, keeping the surface of the sodium clean. Sufficient heat was generated by the water to keep the sodium molten, and the colour of the solution passed from the xylene to the water layer. When the reaction was complete, the water layer was run off, and the sulphide determined as previously. Reasonably accurate results were obtained by this procedure.

Example

(1) 0.3505 g flowers of sulphur dissolved in xylene by warming, and made up to 100 ml. 10 ml extracted with sodium, and made up to

100 ml with water. 25 ml of this solution were then added to 25 ml 0.1N iodine acidified with hydrochloric acid, and the excess iodine back-titrated with 0.1N thiosulphate.

$$(i) \text{ Excess iodine} = 19.37 \text{ ml } 0.1N \text{ thiosulphate}$$

$$(ii) \quad " \quad " \quad = 19.57 \text{ ml } 0.1N \quad "$$

$$\therefore \text{ Iodine used} = 25.00 - 19.47 = 5.53 \text{ ml } 0.1N$$

$$\therefore \text{ Sulphur in extract} = 4 \times 5.53 \times 0.001602 \text{ g} = 0.03542 \text{ g}$$

$$\therefore \text{ Sulphur in original solution} = 0.03542 \times 10 = \underline{0.3542 \text{ g}}$$

(2) Solvent Blank. 10 ml of the xylene treated as above

$$(i) \text{ Excess iodine} = 24.79 \text{ ml } 0.1N \text{ thiosulphate}$$

$$(ii) \quad " \quad " \quad = 24.87 \text{ ml } 0.1N \quad "$$

$$\therefore \text{ Iodine used} = 25.00 - 24.83 = 0.17 \text{ ml } 0.1N$$

$$\therefore \text{ Sulphur present in 100 ml} = 0.17 \times 4 \times 10 \times 0.001602 \text{ g} \\ = \underline{0.01091 \text{ g}}$$

$$\therefore \text{ wt of sulphur in sample} = 0.3542 - 0.0109 = 0.3433 \text{ g}$$

$$\therefore \% \text{ Recovery of sulphur} = \frac{0.3433 \times 100}{0.3505} = \underline{97.9\%}$$

This method was used to check for the presence of free sulphur in the products from the sulphiding of zeolites.

3.2.3 Sulphur Treatment of 13X Zeolite

This zeolite has been described in detail by Breck and Flanigen (60, p 47), and possesses a structure similar to that of faujasite. The framework is exceptionally rigid, being stable to at least 700°C after dehydration, and yet it possesses the largest voidage (51% v/v) of any known zeolite, with an effective pore diameter of 10 Å. It was obtained in powder form (without binder) from Hopkins and Williams, and its x-ray powder pattern (Figure 3.14, Appendix A1) was in good agreement with that published (60, p 47). The x-ray technique is described in section 3.2.3.5.

The equipment used to conduct the sulphiding is illustrated in Figure 3.3. A 1 inch silica tube fitted with a silica sinter (obtained from Quadrant Glass Blowers, Harlow) was heated by a tube furnace, controlled by an external thermocouple, with maximum temperature 1000°C . This furnace could be raised to enable the sample to be examined during reaction. A silica thermocouple pocket held within the reactor enabled the sample temperature to be measured. A preheater tube was employed, being operated at 500°C maximum. Temperature indication was by means of an external thermocouple and calibrated galvanometer. The carrier gas was BOC oxygen free nitrogen, dried over 3A molecular sieve. It could be passed either directly to the reactor, or via the carbon disulphide saturator. This was water jacketted at 25°C , the gas being assumed saturated at this temperature. The vapour pressure of carbon disulphide at 28°C is 400 torr, and the $\text{CS}_2:\text{N}_2$ mole ratio was therefore approximately 1:1. The carbon disulphide (Hopkins and Williams General reagent grade) was dried over anhydrous calcium sulphate.

In use, a tendency for the sinter in the reactor tube to block with sulphur was experienced, especially at the lower temperatures of operation, and a second reactor (without sinter) was obtained and used in some of the later experiments. The zeolite was then supported on a plug of quartz wool.

In all, some fifteen individual experiments were conducted, and these are described below. A flow rate of 85 ml/min (measured at the vent with a soap bubble flow meter) was employed throughout, and 1.0 g of zeolite was used.

The zeolite was activated in situ by connecting a vacuum pump to the effluent line, and heating it at 150°C in vacuo. In

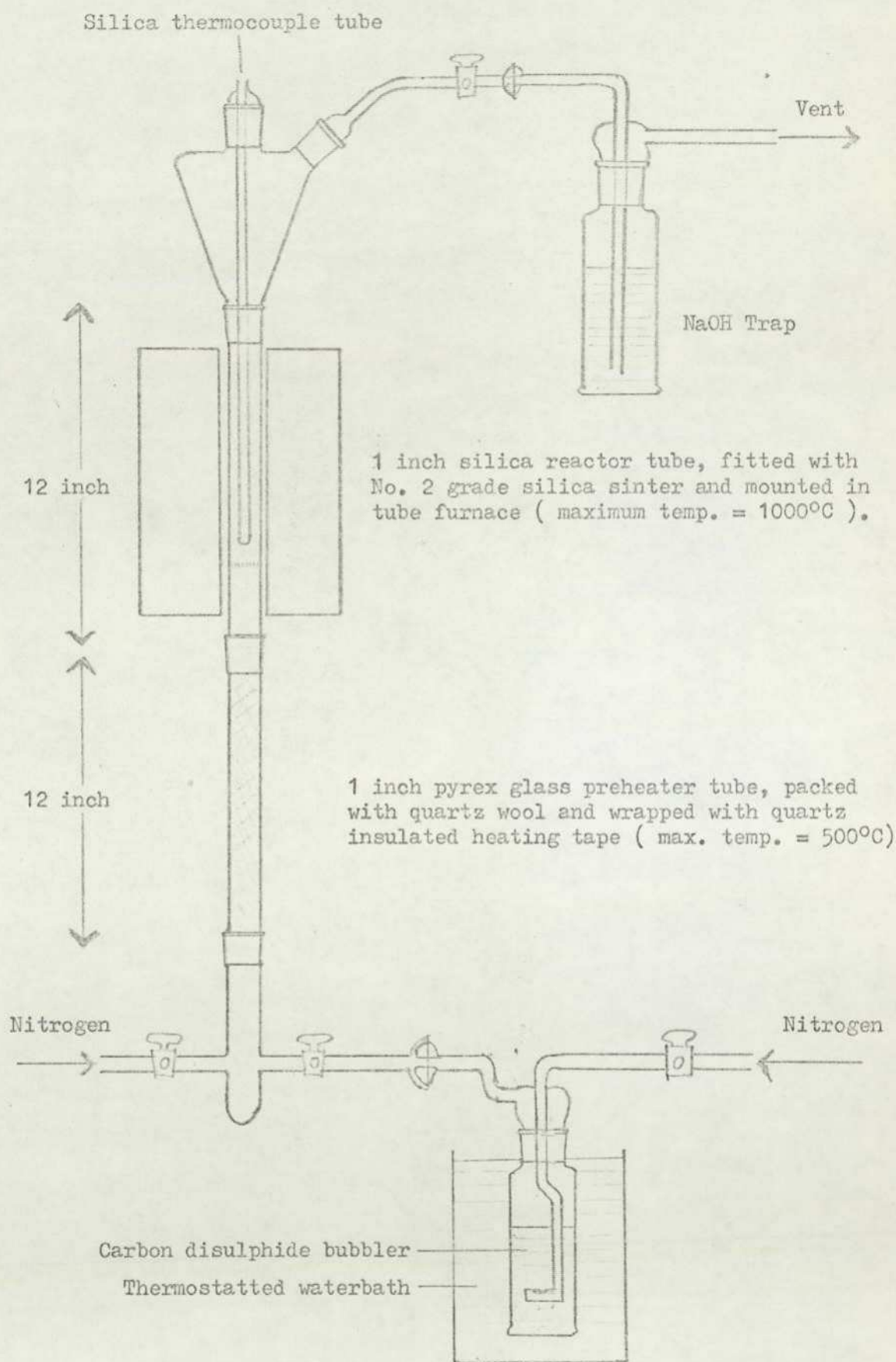
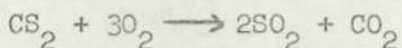
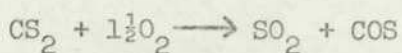
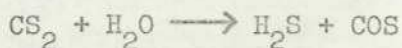
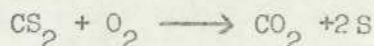


Fig. 3.3 Reactor for Zeolite Sulphiding.

normal operation a sodium hydroxide bubbler was attached to the effluent line to remove carbon disulphide and hydrogen sulphide from the gas stream.

3.2.3.1 Experiments 3.1 - 3.5

These constituted a series of experiments to enable the characteristics of the reaction system and products to be ascertained. They are summarised in Table 3.1. The first experiment (Experiment 3.1) was conducted at 500°C. An immediate yellow colour was observed in the zeolite bed on introduction of carbon disulphide, and sulphur slowly appeared in the cooler part of the reactor above the reaction zone. Both sulphur dioxide and hydrogen sulphide were suggested by smell to be present in the effluent entering the sodium hydroxide scrubber. If these gases were in fact present, together with sulphur they lead to interesting speculation as to possible reactions occurring:-



The above equations represent the kind of reactions that would be required to account for the presence of sulphur, SO_2 and H_2S in the effluent. Whilst no indication of the amount of the gaseous components was available, there was a considerable amount of sulphur formed during the course of the reaction, and unless this was formed from breakdown of carbon disulphide (when a considerable deposition of carbon would be expected), a source of oxygen within the zeolite was required.

Direct sulphiding of the oxide framework might occur but one would not expect free sulphur to be liberated as a result, and so insufficient degassing of the zeolite during activation seemed the most reasonable

Expt.	Temp. (°C)	Flow (ml/min)	Duration (hr)	Notes
3.1	500	85	1	Extended activation
3.2	500	85	1	
3.3	600	85	1	
3.4	600	85	2	No burn-off after reaction
3.5	600	85	1	

Table 3.1 Summary of Experiments 3.1 - 3.5

Expt.	Temp. (°C)	Flow (ml/min)	Duration (hr)	Notes
3.6	300	85	1	
3.7	400	85	1	
3.8	500	85	1	
3.9	600	85	1	
3.10	600	85	1	
3.11	600	85	3	
3.12	700	85	1	
3.13	600	85	4	
3.14	600	85	4	
3.15	600	85	4	

Table 3.2 Summary of Experiments 3.6 - 3.15

explanation. That zeolites in air are powerful oxidation catalysts has been indicated in the literature survey, and it therefore seemed likely that any oxygen remaining in the zeolite after activation at 150° would react in this way.

The reactor was cooled under nitrogen after one hour, and then opened to the air and the product removed as a grey powder. This rapidly turned deep blue on exposure to air, and considerable quantities of heat and sulphur dioxide were evolved. As the reaction died down, the blue colour faded rapidly to a very light violet. It is apparent that large amounts of sulphur had remained within the sieve, possibly as hydrogen sulphide or elemental sulphur, and that this was readily oxidised on exposure to air. The reactions are generally similar to those of Kerr and Johnson (274, 275), in that a blue colour develops during the oxidation, and suggest the presence of the radical species discussed in section 3.1.

This experiment was repeated with a longer activation time of two hours, (Experiment 3.2), in an attempt to remove more completely oxygen and water trapped within the zeolite framework. Considerably less sulphur appeared above the reactor during this experiment, confirming that insufficient outgassing had occurred in the first experiment. In an attempt to remove any free sulphur deposited on the zeolite (in case it was this causing the oxidation effects noted on exposure to air), the product was heated at the reaction temperature in N₂ for 30 minutes after the run before the reactor was cooled. In spite of this, the material formed was still highly reactive towards air, and differed little from the material formed in Experiment 3.1 in this respect. However, it possessed a yellow colour rather than the grey previously found, and this suggested that the subsequent heating may have removed sulphur from within the structure, and deposited it on the surface of the zeolite.

As it was felt that the presence of large amounts of free sulphur would mask the presence of any sulphide sulphur that might enter the zeolite lattice, the reaction was repeated at 600°C (Experiment 3.3) in an attempt to discourage the deposition of sulphur within the zeolite framework. The other conditions were the same as those used in the previous run, but the product was heated for one hour at 600°C after the reaction to remove deposited sulphur. As hydrogen sulphide was detected by its smell in the effluent during this subsequent heating, a further experiment was conducted at 600°C (Experiment 3.4) in which this final step was omitted. It was thought possible that moisture contamination present in the nitrogen could be hydrolysing metal sulphur bonds formed in this extended post-reaction time at elevated temperatures. The products from these two runs were found to be similar. The materials obtained at 600°C were not as reactive as those formed at 500°C, and oxidised much more slowly on exposure to air. However, the overall pattern of reaction was the same, and it was still apparent that sources of oxygen and hydrogen were present in the reactor throughout the experiment, resulting in reaction with the carbon disulphide to form sulphur, hydrogen sulphide and possibly sulphur dioxide. As the carbon disulphide and carrier nitrogen were carefully dried, it was suspected that the zeolite was still not completely degassed prior to the experiment. Therefore, activation was conducted for three hours at 250°C (Experiment 3.5). However, it was found that the material was just as reactive as those previously obtained, and it seemed that the more rigorous activation had not caused any further loss of oxygen or moisture from the framework.

3.2.3.2 Analysis of Products from Experiments 3.1 - 3.5

The products from these experiments were stored in the dry box, the reactor tube being removed from the sulphiding system and stoppered, under a nitrogen purge, before it was transferred to the entry port. The stopper at one end was then loosened and the port quickly evacuated and filled with nitrogen. This handling procedure still permitted slow decomposition of the material during subsequent storage, as witnessed by slow colour changes. It was hoped that only free-radical species were decomposing, and that any aluminium-silicon sulphide species would be more stable. By carrying out the various tests immediately after the reaction was complete, consistency in the results was obtained.

The material prepared at 600°C (Experiment 3.5) was chosen for further study in view of its slower rate of decomposition than materials prepared at 500°C, and the greater chance of metal-sulphur bond formation as against free-radical formation that this suggested.

Sulphur analysis (total)

A sample of the material was weighed out in the dry box, and some sodium pellets added and the tube stoppered. The stopper was not removed until the sodium melted, and in this way loss of sulphur was avoided. Analysis (including blank determination) was conducted as described above (Section 3.2.2).

Found (two samples):- 9.7, 8.9% sulphur

A sample of sulphided zeolite was deliberately exposed for 30 minutes in air before analysis, to determine what proportion of sulphur was lost as SO_2 or SO_3 on oxidation:-

Found: 4.3% sulphur

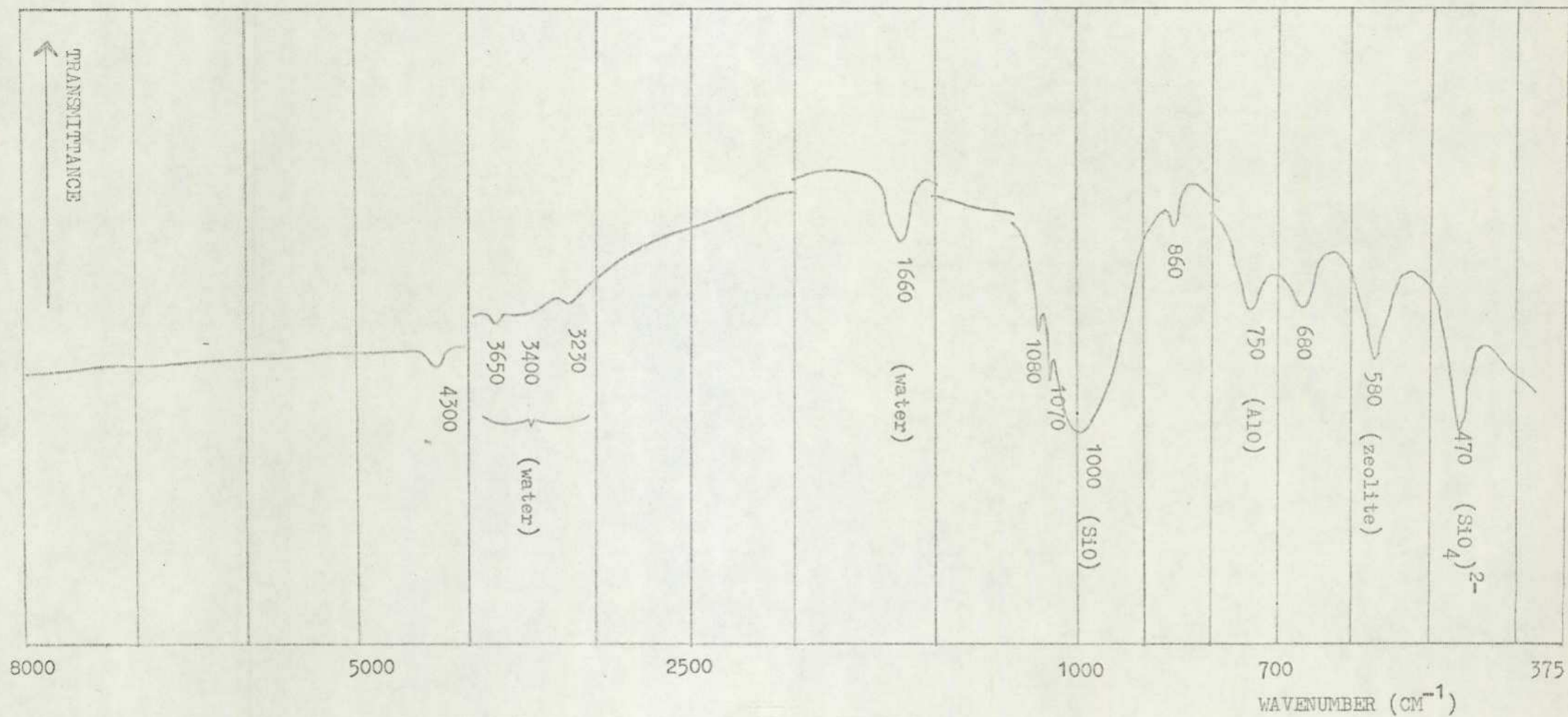
Sulphur analysis (free)

This was conducted using xylene extraction, as described in section 3.2.2. No free sulphur was found, readings of the same order as the solvent blank being obtained. It was therefore apparent that the sulphur present in these materials was firmly bound within the zeolite lattice.

Infra-Red Analysis

Infra-red analysis was made of the sulphided and untreated molecular sieve in an attempt to see whether structural modifications had occurred as a result of the sulphiding process. Spectra in the range 8850 cm^{-1} to 375 cm^{-1} were made on nujol or hexachlorobutadiene mulls, using a Unicam S.P.100 high resolution spectrophotometer. The mulls were prepared in the dry box, and were supported between potassium bromide plates. Spectra in the region 500 cm^{-1} to 200 cm^{-1} were obtained with a Grubb-Parsons DM4 far infra-red spectrophotometer. The sample was milled with a polythene powder/nujol paste and supported between plates of thin polythene, which is optically transparent in this range (see Figure 3.7).

Figure 3.4 is a reproduction of the infra-red spectra ($375 - 8000\text{ cm}^{-1}$) of the untreated zeolite 13X after activation under vacuum. It is combined from spectra taken with both nujol and hexachlorobutadiene mulls (prepared in the dry box), and is therefore free from mulling-agent bands. Some of the better characterised bands are labelled from assignments appearing in the literature (312, 313). The band at 580 cm^{-1} labelled 'zeolite' is characteristic of zeolites, and, together with that at 780 cm^{-1} , is sensitive to the Si:Al ratio (313). It was also found that the latter



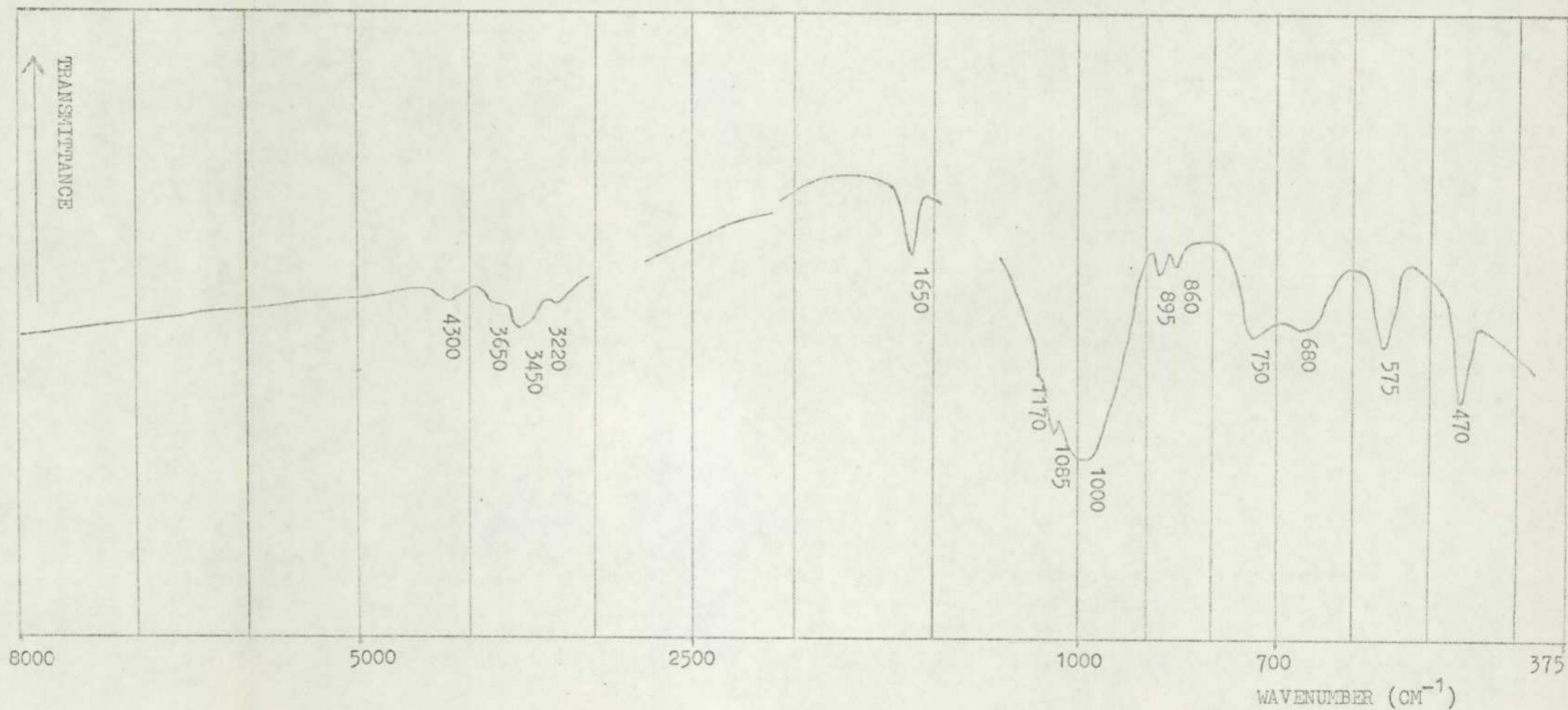
8000-4000 cm⁻¹; 2000-1500 cm⁻¹; 1300-375 cm⁻¹ Nujol mull.
 4000-2000 cm⁻¹; 1500-1300 cm⁻¹ Hexachlorobutadiene mull.

Fig. 3.4 Infrared Spectrum of 13X Zeolite, activated at 150°C under vacuum.

band was sensitive to cation exchange. These authors also assigned the water peak near 3230 cm^{-1} to easily removed water, that near 3400 cm^{-1} to strongly bound water present over 400°C , and that near 3650 cm^{-1} to water coordinated to the cation.

Retention of appreciable concentrations of water and hydroxyl groups can occur even after severe dehydration treatments. The spectra obtained in the present work, of which that reproduced in Figure 3.5 is typical, show considerable amounts of water to be present even after vacuum activation at elevated temperatures of 250°C or above. As the mulling agents were dried over molecular sieve, and all samples prepared in the dry box, contamination during sample preparation is unlikely. Further, as the spectrometer was fitted with a sealed sample chamber dried with desiccant, contamination during the time the spectra were being run is also unlikely. Similar findings have been reported by Zhdanov (314).

Spectra in the infra-red region $375\text{ cm}^{-1} - 8000\text{ cm}^{-1}$ were obtained from the material from Experiments 3.1 to 3.5. In general, no alteration was observed compared to the spectra of the untreated material. The spectra of the sulphided material were all essentially similar, and an example is reproduced in Figure 3.5; its similarity with Figure 3.4 is immediately apparent. It therefore seemed that no structural modification had occurred during the sulphiding process, and the zeolite framework was essentially unaltered. The formation of sulphide species within the framework structure was suggested, however, and



8000-4000 cm^{-1} ; 2000-1500 cm^{-1} ; 1300-375 cm^{-1} Nujol mull.
 4000-2000 cm^{-1} ; 1500-1300 cm^{-1} Hexachlorobutadiene mull.

Fig. 3.5 Infrared Spectrum of 13X zeolite treated with CS_2 at 500°C .

it is somewhat surprising that no modification to the spectra of 13X zeolite was observed. The low sensitivity available as a result of the high background scattering of the mulls is a possible explanation.

Certainly, however, any metal sulphur bonds formed would be expected to resist hydrolysis for sufficiently long under the experimental conditions used to permit their identification by infra-red techniques. Although the spectra so far presented do not reveal any noticeable loss of silicon-oxygen or aluminium-oxygen bonds, nevertheless the formation of the corresponding sulphide bonds in small amounts is not precluded. For this reason, far infra-red spectra were obtained of the sulphided zeolites, as it is in this part of the spectrum that metal sulphur vibrations would be expected to occur. There is very little reliable documented data on metal - sulphur infra-red frequencies in general, and silicon-sulphur and aluminium-sulphur frequencies in particular. The silicon-sulphur stretching frequency, $\nu(\text{Si-S})$ was determined by Fehér and Goller (315) for a number of organometallic compounds $\left[(\text{R}_3\text{Si})_2\text{S}_n; \text{R}_3\text{SiSR}' \right]$ and was found to occur in the $503\text{--}572\text{ cm}^{-1}$ range. Similar results were reported by Schumann and Schmidt (316) for germanium-, tin-, and lead-sulphur bonds. $\nu(\text{Ge-S}) = 400\text{--}404\text{ cm}^{-1}$, $\nu(\text{Sn-S}) = 355\text{--}365\text{ cm}^{-1}$ and $\nu(\text{Pb-S}) = 305\text{--}317\text{ cm}^{-1}$. The $\nu_{\text{asym}}(\text{M-S-M})$ vibrations ($\text{M} = \text{Ge}, \text{Sn}$ or Pb) were found at slightly higher frequencies. Frequencies for organometallic compounds of aluminium, gallium, and indium were reported by Coates and Mukherjee (317). $\nu(\text{Al-S})$ occurred between 310 cm^{-1} and 391 cm^{-1} in the range of compounds studied; $\nu(\text{Ga-S})$ was reported as being 314 cm^{-1} , and $\nu(\text{In-S})$ as 313 cm^{-1} . In an extensive examination of metal

sulphur vibrations, Adams and Cornell (318) examined thiourea complexes of many metals, and found ν (M-S) to lie in the range 205-298 cm^{-1} for transition metals, and to be as low as 170 cm^{-1} for group metals. Over a wider range of complexes, ν (M-S) was found up to 504 cm^{-1} for many metals (ie Ni, Co, Cu, Zn, Pd or Pt). Other studies of thiourea complexes have been reported by Flint and Goodgame (319). ν (M-S) was found between 216 cm^{-1} and 278 cm^{-1} for metals such as Co, Zn, Pd, Cd, Ni and Mn. Such evidence as exists suggests that metal-sulphur vibrations in sulphides occur at similar frequencies to those found in the complexes discussed above. Of especial relevance is an examination of the far infra-red spectra of metal sulphides and related minerals by Karr and Kovach (320). The spectra were obtained on thin discs of the powdered sulphide pelleted with polythene powder, and the sulphides examined were CaS, SnS, BaS, HgS, As_4S_4 and As_2S_3 . In general, the bands likely to be attributable to ν (M-S) were found between about 100 cm^{-1} and 380 cm^{-1} . Further data has been reviewed by Adams (362), and the overall conclusion from published results suggests that an examination of the infra-red spectrum down to 200 cm^{-1} (instrument limit) would reveal any metal sulphur bonds formed as a result of the sulphiding process.

Figure 3.6 shows the spectra obtained under different instrument and mulling conditions. For comparison, a blank spectrum of the polythene nujol paste used for mulling the samples is shown in Figure 3.7, and shows the useful instrument range when under these conditions of operation to be $\sim 210 \text{ cm}^{-1}$

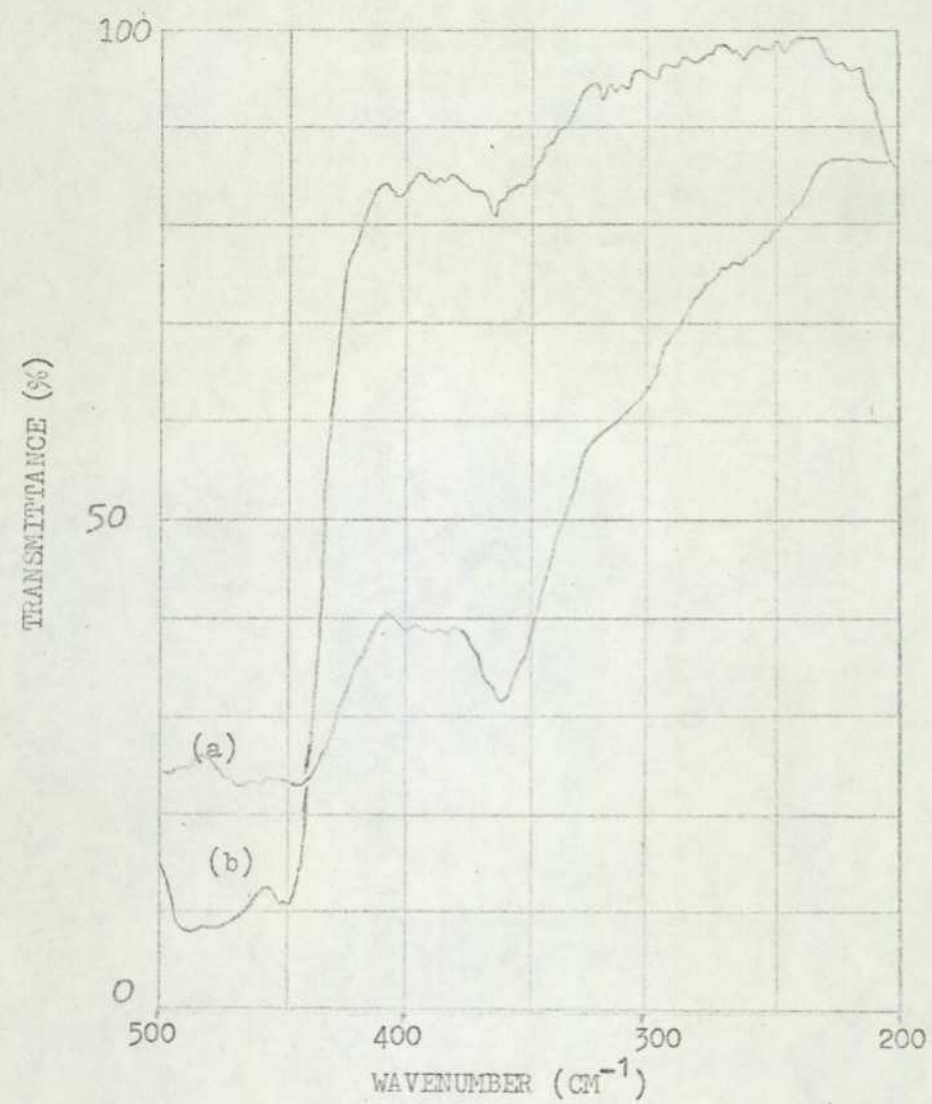


Fig. 3.6 Far-Infrared Spectrum of 13X zeolite. Polythene plates.

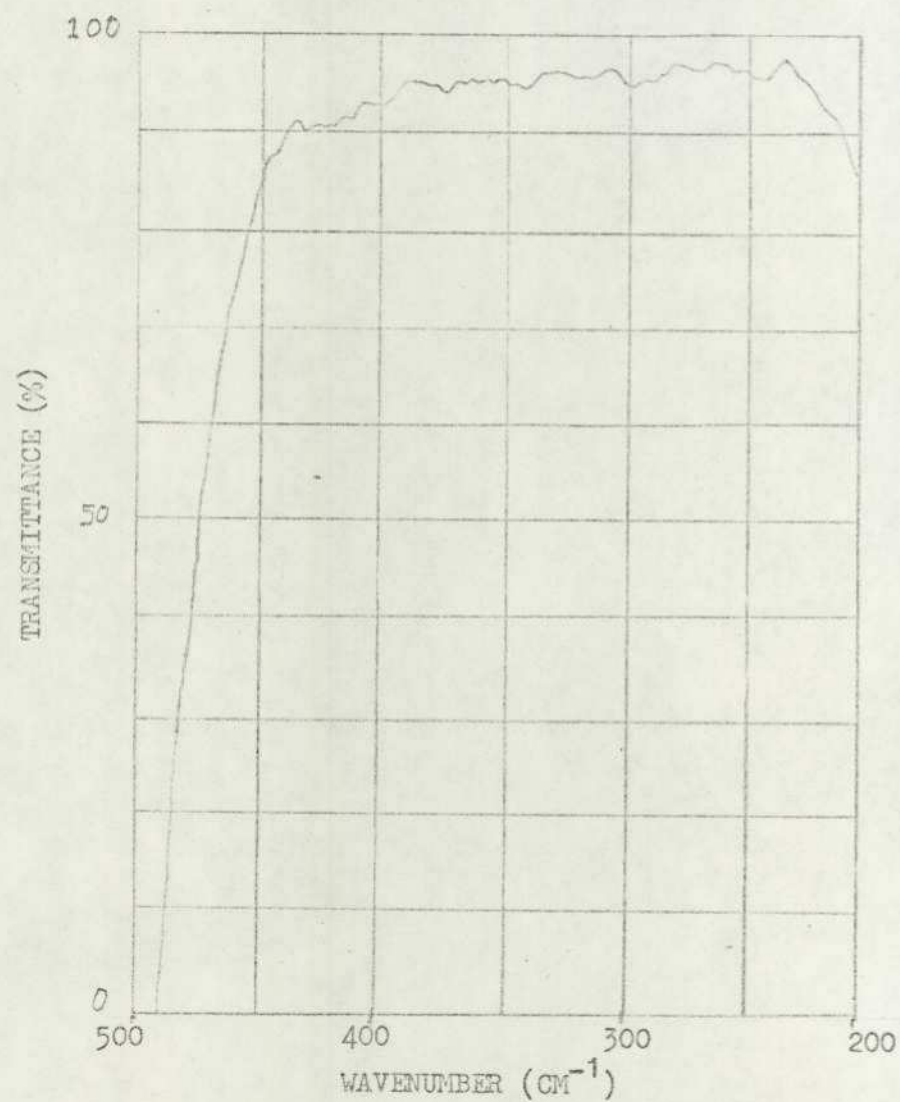


Fig. 3.7 Blank Far-Infrared Spectrum of the nujol and polythene mulling agent.

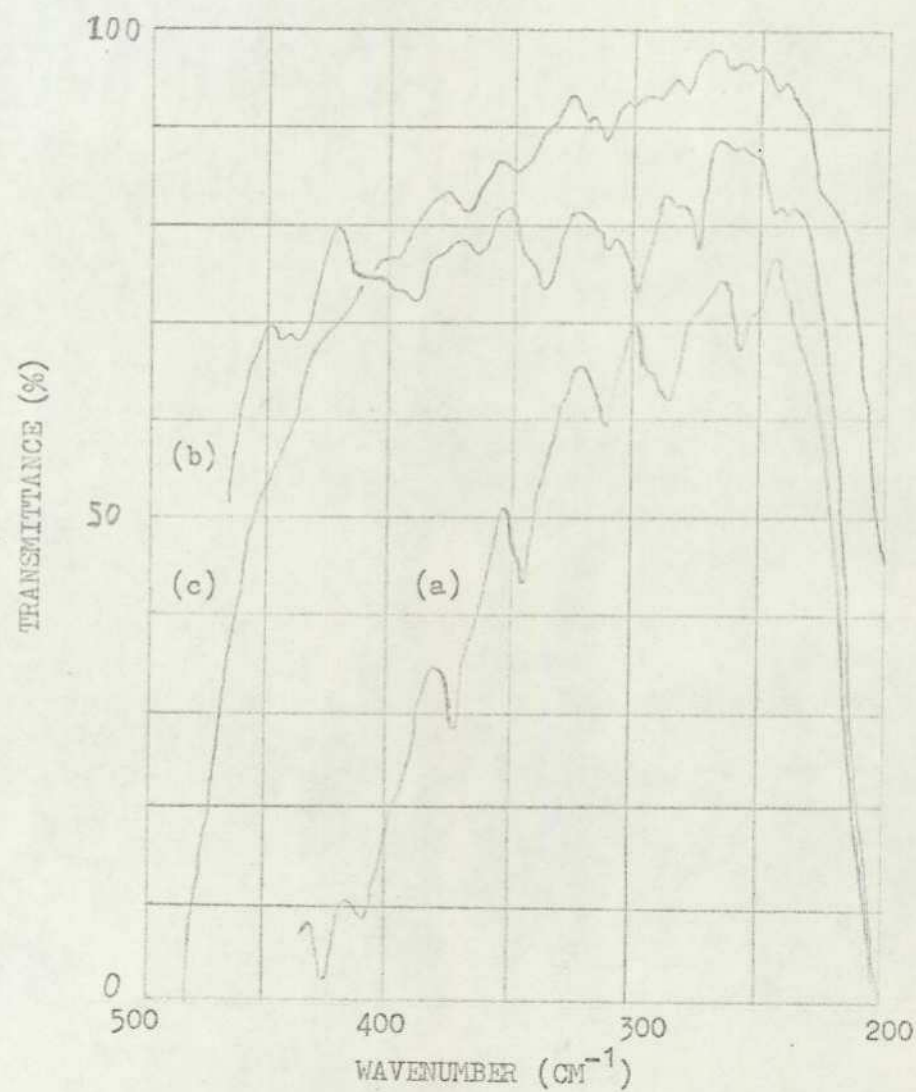


Fig. 3.8 Far-Infrared Spectrum of 13X Zeolite sulphided with CS₂ at 500°C. Polythene plates.

to 460 cm^{-1} . It also gives some idea of the noise due to the high sample scattering of the radiation. Referring to the spectra of the zeolite, besides the peak near 450 cm^{-1} (found at 470 cm^{-1} on the infra-red spectra described above), another peak near 360 cm^{-1} was found. Besides these two peaks, no other features were distinguished that could clearly be separated from instrument noise.

In Figure 3.8 are shown spectra typical of those obtained from sulphided zeolites. Very few features clearly distinguishable from instrument noise were observed, perhaps the most noteworthy being the loss of a peak near 360 cm^{-1} found with the untreated zeolite. Other possible features are of the same magnitude as the instrument noise, and no firm conclusions can be reached as to the presence of new peaks resulting from the sulphiding process. However, the absence of any strong bands attributable to metal sulphur vibrations can be taken as strong evidence against the substitution of appreciable amounts of sulphur into the zeolite framework.

3.2.3.3 Conclusions from Experiments 3.1 - 3.5

No definite conclusions were reached from this preliminary work concerning the exact nature of the reactions occurring during the sulphiding of 13X zeolite. However, it seemed apparent that although appreciable sulphiding was occurring, no modification of the zeolite framework was taking place even at 600°C . From the highly reactive products obtained, it may be tentatively concluded that free radical species of the type described in the literature were being formed, with sulphide radicals being trapped within the zeolite lattice, which remained

essentially unaltered.

In order to come to more definite conclusions and to gain a deeper insight into this system, a series of ten further experiments were undertaken (3.6-3.15).

3.2.3.4 Experiments 3.6-3.15

Experiment 3.6

This was the first of several experiments in which sulphiding over a wide range of temperature was investigated. It was conducted at 300°C for one hour, with one hour activation under vacuum at 300°C. The zeolite became a dark yellow colour on admitting the feed gas, darkening to a brown-yellow where the feed entered the bed after a few minutes. This colouration was probably attributable to a deposit of sulphur being adsorbed on the surface of the zeolite. Sulphur boils at 445°C, and so it is a reasonable postulate that free sulphur could be adsorbed on the surface of the zeolite at temperatures below this. Kerr and Johnson (274, 275) reported this same yellow colouration on passing a mixture of hydrogen sulphide and air over zeolite at 245°C. The yellow material obtained in the present work was relatively stable in air, oxidising only slightly.

Total sulphur content (Na fusion) = 2.8%

(method as described previously)

Experiment 3.7

This was conducted at 400°C for one hour, and was preceded by one hour activation under vacuum at 400°C. Otherwise the conditions were as Experiment 3.6. When the feed was admitted, the part of the bed where the feed entered became

bright yellow, while the latter part of the bed where the gas stream left became dark blue. This behaviour was quite different to that observed at 500°C, when the blue colour only developed when the sulphided zeolite was exposed to air, the bed being grey during the sulphiding. The blue colour suggested an ultramarine structure, but while ultramarines are stable in air, the material formed in the present instance rapidly lost its colour on contact with air, the blue and yellow fading to mauve, even in the dry box. In common with the materials prepared in the preliminary experiments, considerable quantities of heat and sulphur dioxide were generated on exposure to air. Similar yellow and blue colourations were observed by Kerr and Johnson (274, 275) in the oxidation of hydrogen sulphide over zeolites.

Total sulphur content (Na fusion) = 4.6%

(method as described previously)

Experiment 3.8

This was conducted at 500°C for one hour, and was preceded by one hour activation at 500°C in vacuo. Otherwise the conditions were as for Experiment 3.6. The zeolite was pale grey during the sulphiding. This is consistent with the yellow colour observed at 300° and 400°C being due to elemental sulphur. Over 445°C, the sulphur will exist as a vapour, and is presumably not so readily adsorbed. Only very slight blue colouration was observed during the reaction, and the material formed reacted with air in the manner already described.

Total sulphur content (Na fusion) = 5.7%

(method as previously described)

Experiment 3.9

This experiment was similar to 3.8, except that it was conducted at 600°C for one hour, with one hour activation at this temperature in vacuo. The overall reaction pattern was similar to that found at 500°C, except that no blue colour was observed and the material formed was very hard and granular. It was reactive towards air, although not to the same extent as the materials formed at 500°C.

Total sulphur content (Na fusion) = 11.2%

(method as described previously)

Experiment 3.10

This was a duplicate of Experiment 3.9, and a similar product was obtained.

Total sulphur content (Na fusion) = 8.7%

(method as described previously)

Experiment 3.11

As reaction at 600°C appeared to produce a material relatively free of adsorbed sulphur and somewhat less reactive towards air than material prepared at lower temperature, it was felt that these conditions were approaching the situation when direct sulphiding of the zeolite might be expected to occur. For this reason a prolonged time of three hours at 600°C was investigated, other conditions being similar to those employed in Experiment 3.9. The product was pale grey as before, and of similar reactivity towards air. However, it was somewhat more granular in nature.

Total sulphur content (Na fusion) = 13.9%

(method as described previously)

Experiment 3.12

This was conducted at 700°C, the highest temperature used. One hour reaction time was preceded by one hour activation at 650°C in vacuo. The zeolite became hard and granular during the reaction, and of a grey-green colour. The material formed did not decompose appreciably on contact with air, although a smell of hydrogen sulphide developed. Further hydrogen sulphide was formed on contact with moisture. This was strongly indicative of the formation of Si-S and Al-S bonds, and was the only material of those prepared found to react in this way. It therefore seemed likely that some structural sulphiding had been achieved, but it was a matter of speculation whether the product was zeolitic in nature as the reaction temperature used was approaching the breakdown temperature of the zeolite framework (60, p 47).

Total sulphur content (Na fusion) = 7.1%

(method as described previously)

Experiment 3.13

Hydrogen sulphide had been detected by its characteristic smell in the reactor off-gases from the previous experiments. Speculation existed as to whether this resulted from water remaining after activation, and to enable some idea to be obtained of the quantities of hydrogen sulphide liberated, the reactor off-gas in Experiment 3.13 was bubbled into acidified standard iodine solution:-



A second bubbler contained lead nitrate solution, the absence of darkening of which indicated complete extraction of the hydrogen sulphide with the iodine.

The zeolite was dried overnight at 130°C in vacuo, before being weighed out in the dry box. It was then transferred to the reactor, and activated and sulphided in the usual way at 600°C for four hours. The total sulphur content was 11.3 per cent.

At the end of the reaction time hydrogen sulphide was being only slowly liberated (effluent gas tested with lead nitrate solution). Excess iodine remaining in the bubbler was titrated with standard sodium thiosulphate solution:

Weight of zeolite used = 0.2056 g

100 mL of 0.079 N iodine used

Iodine unreacted = 60.3 mL 0.079 N thiosulphate

$$\therefore \text{Iodine used} = 100.0 - 60.3 = \underline{39.7 \text{ mL}}$$

Experiment 3.14

This constituted a blank on the previous experiment.

It was conducted under identical conditions except that no zeolite was present in the reactor. Hydrogen sulphide was detected in the reactor effluent gas by smell, which suggested that moisture might be entering the reactor with the feed stream due to insufficient drying of either the nitrogen or the carbon disulphide.

25 mL 0.079 N iodine used

Iodine unreacted = 3.9 mL 0.079 N thiosulphate

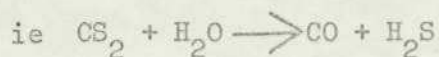
$$\therefore \text{Iodine used} = 25.0 - 3.9 = \underline{21.1 \text{ mL}}$$

$$\therefore \text{Iodine used in Experiment 3.13} = 39.7 - 21.1 \text{ mL}$$

$$= 18.6 \text{ mL (0.078 N)}$$

$$= \frac{18.6 \times 0.078}{0.10} = 14.6 \text{ mL 0.1 N}$$

Assuming the hydrogen sulphide to have been produced by reaction with water,

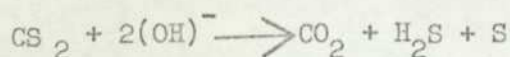


Weight of water to give rise to consumption of iodine observed

$$= 0.0009008 \times 14.6 \text{ g} = 0.01307 \text{ g}$$

$$\therefore \% \text{ water in zeolite} = \frac{0.01307 \times 100}{0.2056} = 6.35\%$$

Therefore the implication is that 6.35% water must have remained trapped within the zeolite during activation if it was reaction with water that had given rise to the hydrogen sulphide liberated. Another possibility is reaction with surface hydroxyl groups, and this is possibly more likely as it would account for the elemental sulphur observed in these reactions:-



Retention of surface hydroxyl groups by zeolites after high temperature activation has been reported (60, p 334). If this was indeed the source of hydrogen sulphide, then it is surprising that no loss of intensity of the infra-red peaks associated with these bands was observed after sulphiding (Figures 3.4 and 3.5). It is possible that sample contamination occurred during the time that the spectra were run. To clarify this situation, Experiment 3.13 was repeated, great care being taken to exclude moisture whenever possible.

Experiment 3.15

The conditions were similar to Experiment 3.13. One hour activation at 600°C in vacuo was followed by four hours reaction at 600°C. Freshly dried carbon disulphide was employed,

and at the end of the reaction period only very little hydrogen sulphide was detected in the effluent gas, it being necessary to bubble it through lead nitrate solution for several minutes before any darkening was observed. The total sulphur content of the product was 13.7 per cent.

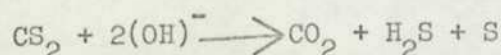
Weight of zeolite used = 0.7700 g

50 ml of 0.079 N iodine used

Iodine unreacted = 46.1 ml 0.079 N thiosulphate

∴ Iodine used = 50.0 - 46.1 = 3.9 ml

Considerably less hydrogen sulphide was liberated during this reaction (equivalent to 0.46 per cent water on the zeolite). Therefore it appeared that free water present during the reaction led to at least part of the hydrogen sulphide observed. It also appeared that less sulphur was deposited during the reaction than was found previously; this is consistent with a reduction in the concentration of hydroxyl groups on the zeolite surface if the reaction occurring is in fact:-



3.2.3.5 Analysis from Experiments 3.6-3.15

A summary of these experiments is presented in Table 3.2, and in Figures 3.9 and 3.10 the uptake of sulphur by the zeolite as function of temperature and time of sulphiding is shown. Figure 3.10 indicates that most of the sulphur uptake occurred during the first hour of reaction - indeed experimental observation suggests that most of the reaction occurred during the first few minutes. Accepting that most of the sulphiding

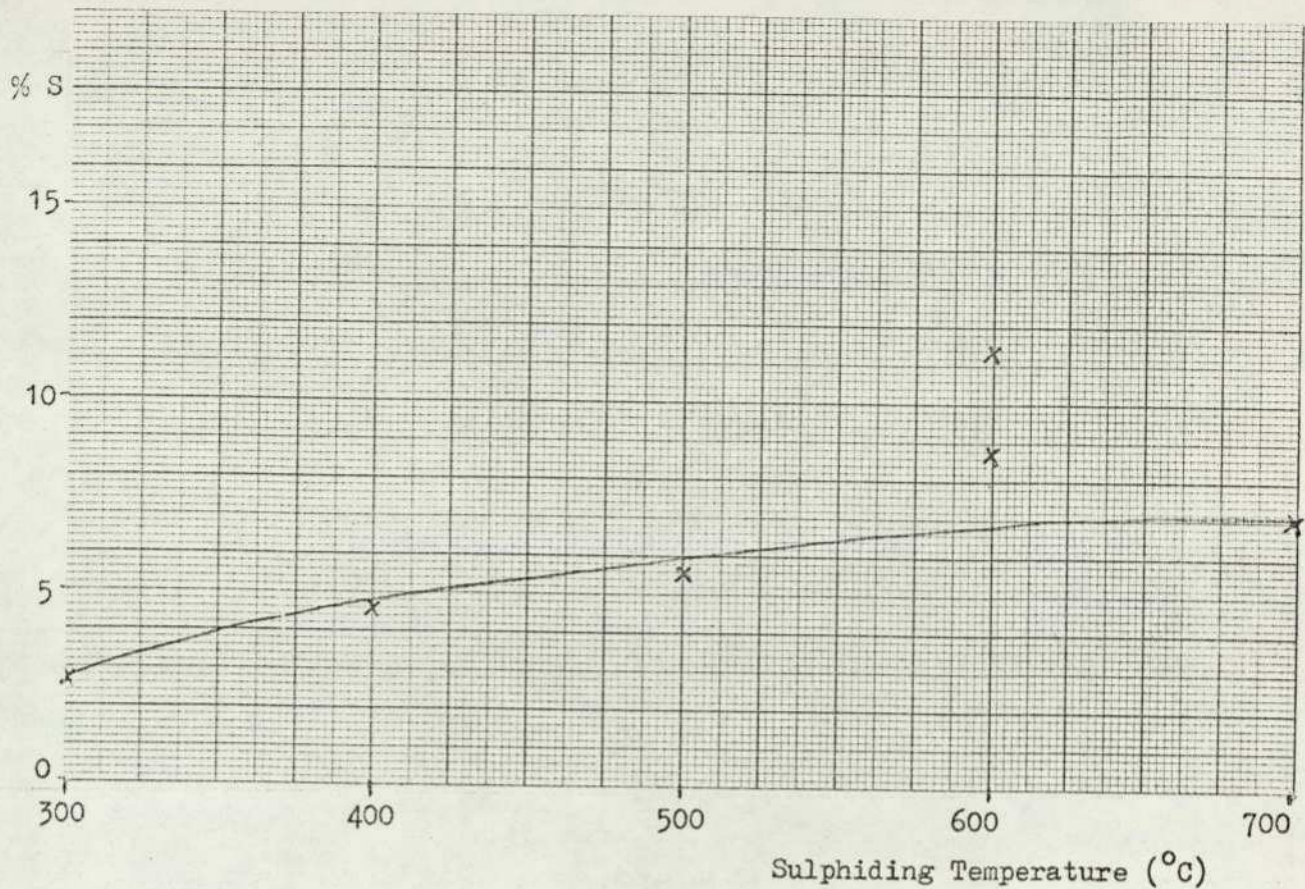


Fig. 3.9 Sulphur uptake vs. sulphiding temperature for CS_2 on 13X zeolite.

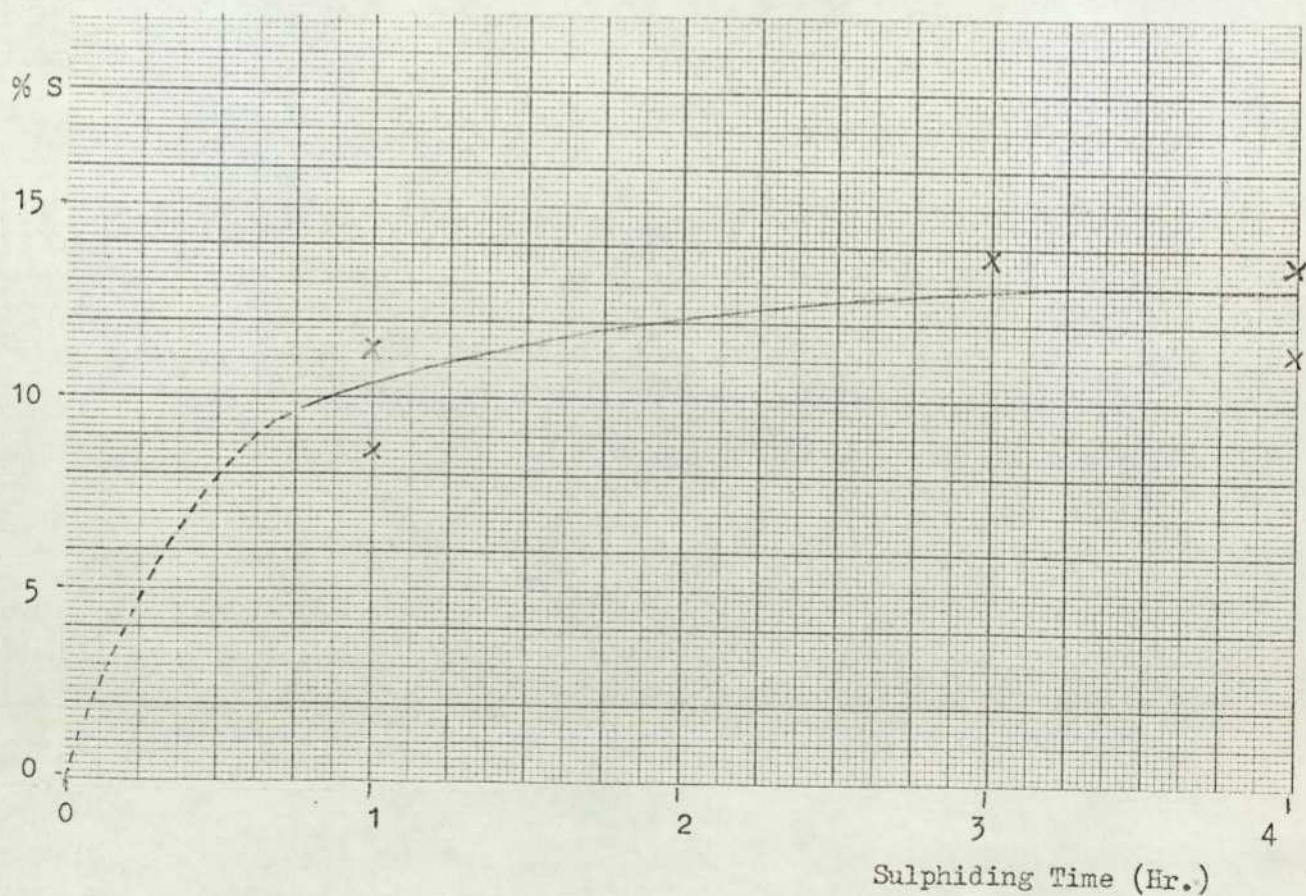


Fig. 3.10 Sulphur uptake vs. duration of reaction for CS_2 on 13X zeolite.

involved the formation of radical species, then any permanent sulphiding (ie replacement of structural oxygen) was probably represented by the slower reaction giving rise to a slight increase in sulphur content with time.

Figure 3.9 indicates that increasing the reaction temperature produced an almost linear increase in sulphur uptake up to 600°C, when the uptake was greater but more variable. Considering the more granular state of the product obtained with prolonged sulphiding at 600°C (or shorter periods at 700°C), it is implied that structural modification might be occurring under these conditions.

Far Infra-red Analysis

Far infra-red spectra were obtained of the products from Experiments 3.6 to 3.15. In general, these were similar to each other and to those obtained from the preliminary experiments. Typical spectra are presented in Figure 3.11, which is that of the product from Experiment 3.8 before and after oxidation. It was found that by taking care to exclude moisture from the sample, the peak near 360 cm^{-1} , previously attributed to the zeolite framework (Figure 3.8), was still present after sulphiding (Figure 3.11a). After oxidation, this peak was largely obscured by a very broad absorption between it and the zeolite peak near 460 cm^{-1} (Figure 3.11b).

In general, these spectra do not throw any additional light on the structures of the materials formed during the sulphiding, and tend to confirm the view that no structural sulphiding had taken place. It is possible that the strong zeolite absorption

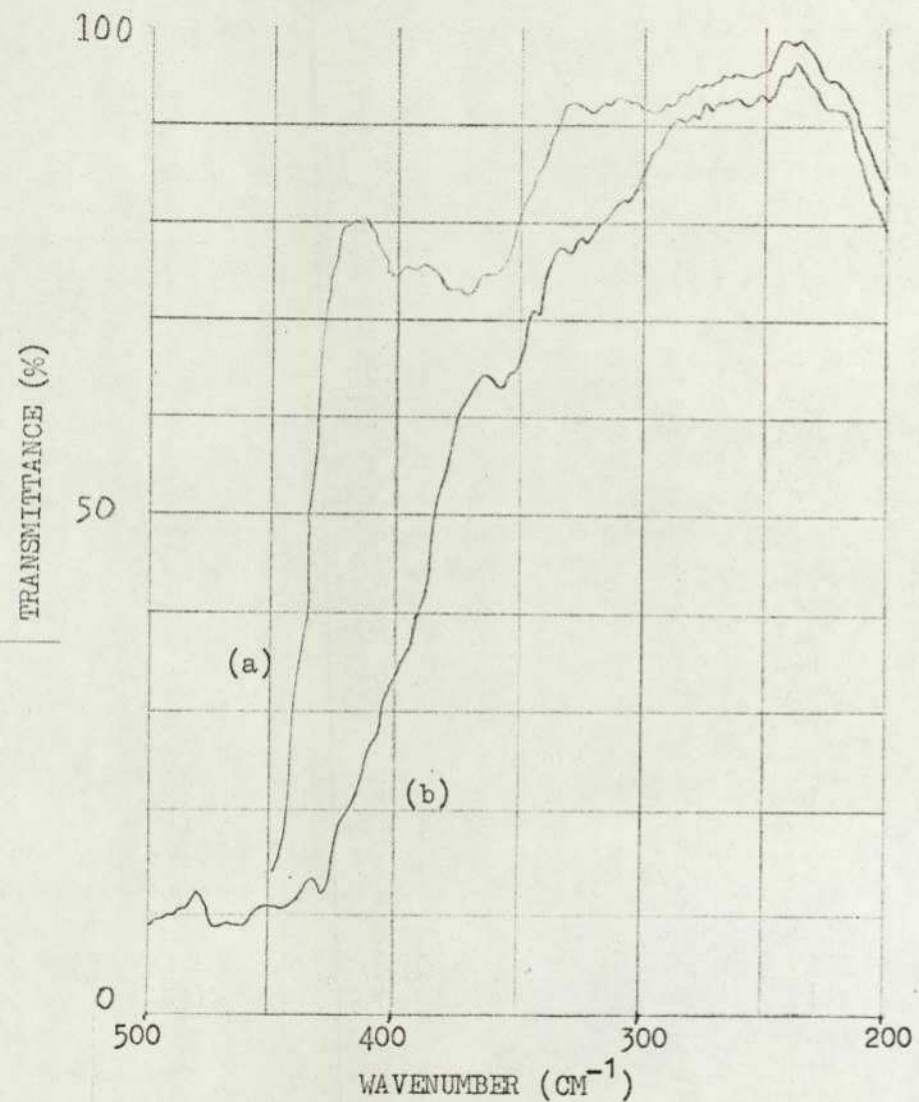


Fig. 3.11 Far-Infrared Spectrum of 13X zeolite sulphided with CS₂ at 500°C. (a), as prepared; (b), after contact with air. Polythene plates.

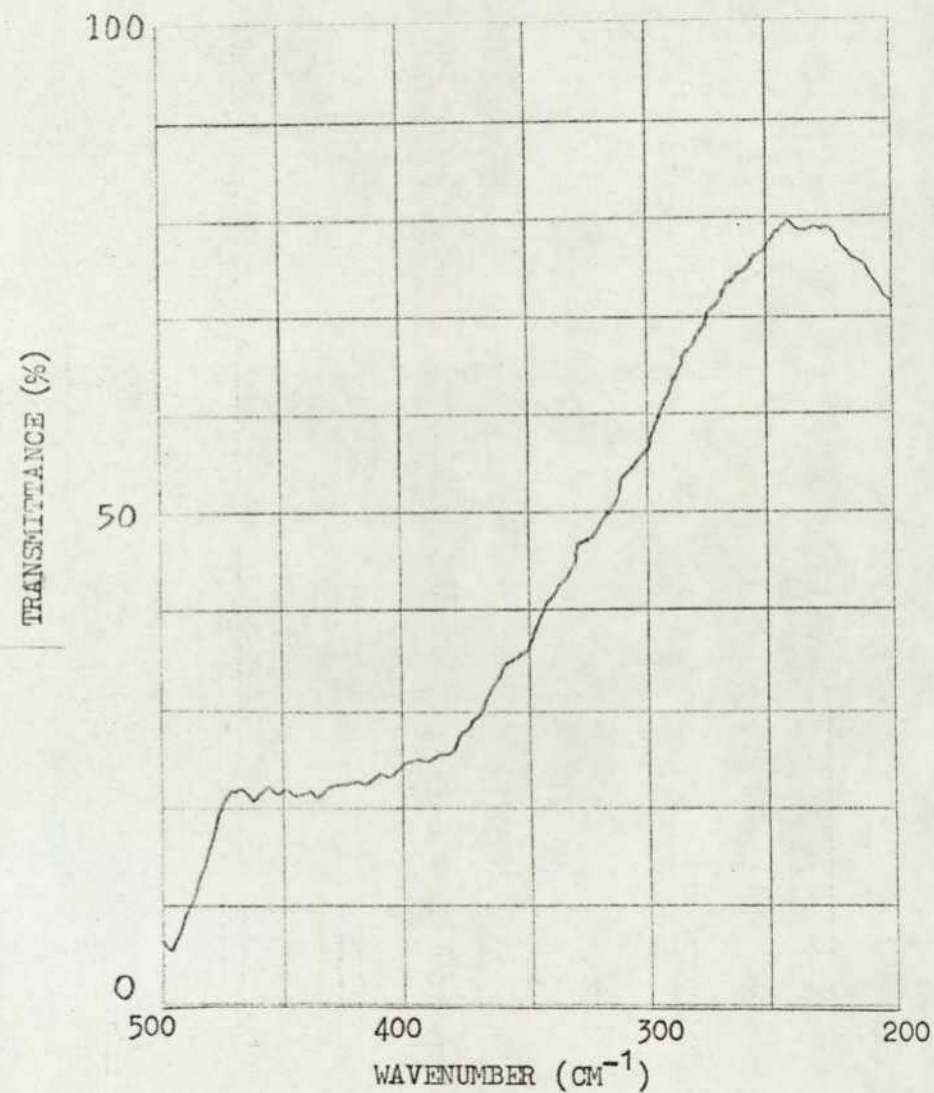


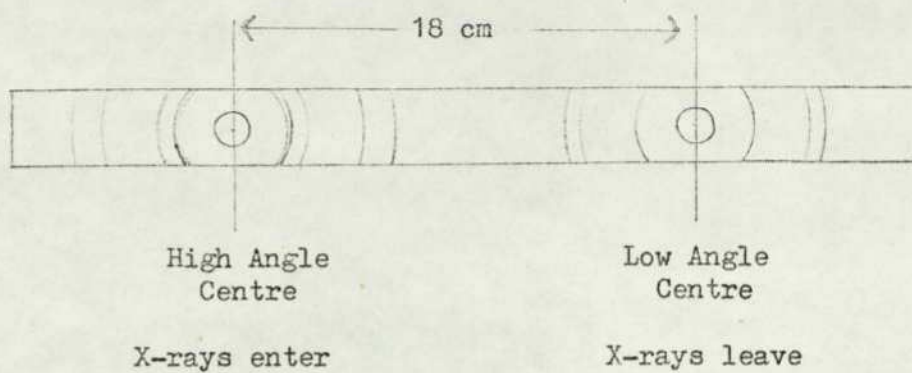
Fig. 3.12 Far-Infrared Spectrum of 13X Zeolite sulphided with CS₂ at 700°C. Polythene plates.

near 460 cm^{-1} was masking silicon-sulphur absorption. Literature suggests (Section 3.2.3.2) that $\nu(\text{Si-S})$ occurs near 500 cm^{-1} , and thus might well not be observed. However, $\nu(\text{Al-S})$ is reported to be somewhat lower, between 300 and 400 cm^{-1} , and is unlikely to be masked by the weaker zeolite band near 360 cm^{-1} . It therefore seemed fair judgement to infer that no appreciable concentration of metal-sulphur bonds had been formed.

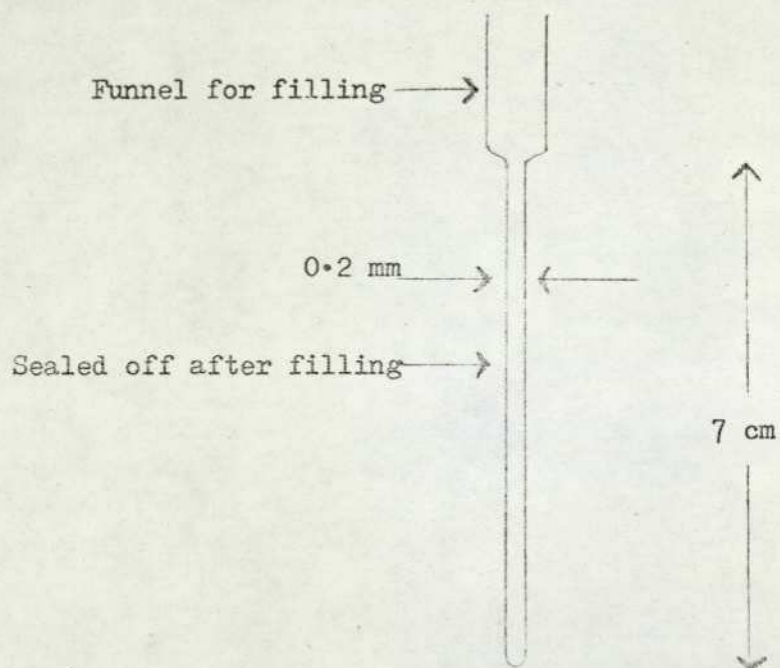
The material prepared at 700°C (Experiment 3.12) had a rather different spectrum (Figure 3.12). However, its resolution was not adequate to enable any assignments to be made.

X-ray Powder Patterns

In view of the rather inconclusive nature of the results obtained from the infra-red analysis of the sulphided zeolites, X-ray powder patterns were obtained of a range of these materials in an attempt to discover whether any structural modification was in fact taking place. The powder patterns were obtained on the unoxidised material, which was ground into a fine powder in the dry box and packed into 0.2 mm "Pantax" glass capillaries. These capillaries were constructed of a glass transparent to X-rays, and were supplied sealed at one end, and with the other end in the form of a funnel (Figure 3.13a). A little of the powder was transferred to the funnel end, and shaken down to the beginning of the narrow part of the tube. The end was then sealed with plasticine, and the tube removed from the dry box. The tube was then shaken to cause the powder to fall to the base of the narrow-section. When about 1 cm of the capillary tube was filled with powder, the tube was sealed off just above this level, using a microgas flame constructed from



(a)



(b)

Fig. 3.13 (a) Straumanis method of mounting X-ray film.
 (b) Glass Capillary used to obtain X-ray powder patterns without exposure of the material to the atmosphere.

a length of drawn-out 5mm glass tubing.

By this means it was possible to avoid contact of the sample with air at any time during the preparation or subsequent exposure in the X-ray camera. This camera (Phillips) used the Straumanis method of mounting, with a diameter of 11.74 cm; this led to a calibration factor of 1 cm line spacing for 5° Bragg angle (Figure 13b). When both high and low angle lines were obtained, it was possible to check this calibration by calculating the distance between the two centres. It was never found when this check was made that it differed significantly from the 18.00 cm assumed from the calibration factor. The centres were fixed by taking the mean of several pairs of lines around the centre in question. Measurements were made using a Hilger-Watts vernier calibrated to 0.05 mm. In use, the film was attached to the vernier, the low angle centre fixed, and the position of all lines measured (in cm) from this centre. The Bragg angle was then calculated for every line using the calibration factor, and the interplanar spacing 'd' (Å) obtained using the relationship due to Bragg:

$$\lambda = 2d \sin \theta$$

λ is the wavelength of the radiation used, in Å. In the present work, Cu K α was generally used ($\lambda = 1.5424$ Å), although Co K α ($\lambda = 1.7909$ Å) was used in one instance. An approximate calibration scale for measurements on the reproduced diffraction patterns is included (Figure 3.14a). This was calculated for Cu K α radiation, and some compensation was made for the pattern distortion that occurred during the reproduction process.

The results obtained are illustrated in Figure 3.14 (b-e) and Appendix A1. The four diffraction patterns reproduced show: (b) activated 13X zeolite; (c) zeolite sulphided at 400°C ; (d) zeolite sulphided at 500°C ; (e) zeolite sulphided at 600°C . Two factors are apparent from these patterns:-

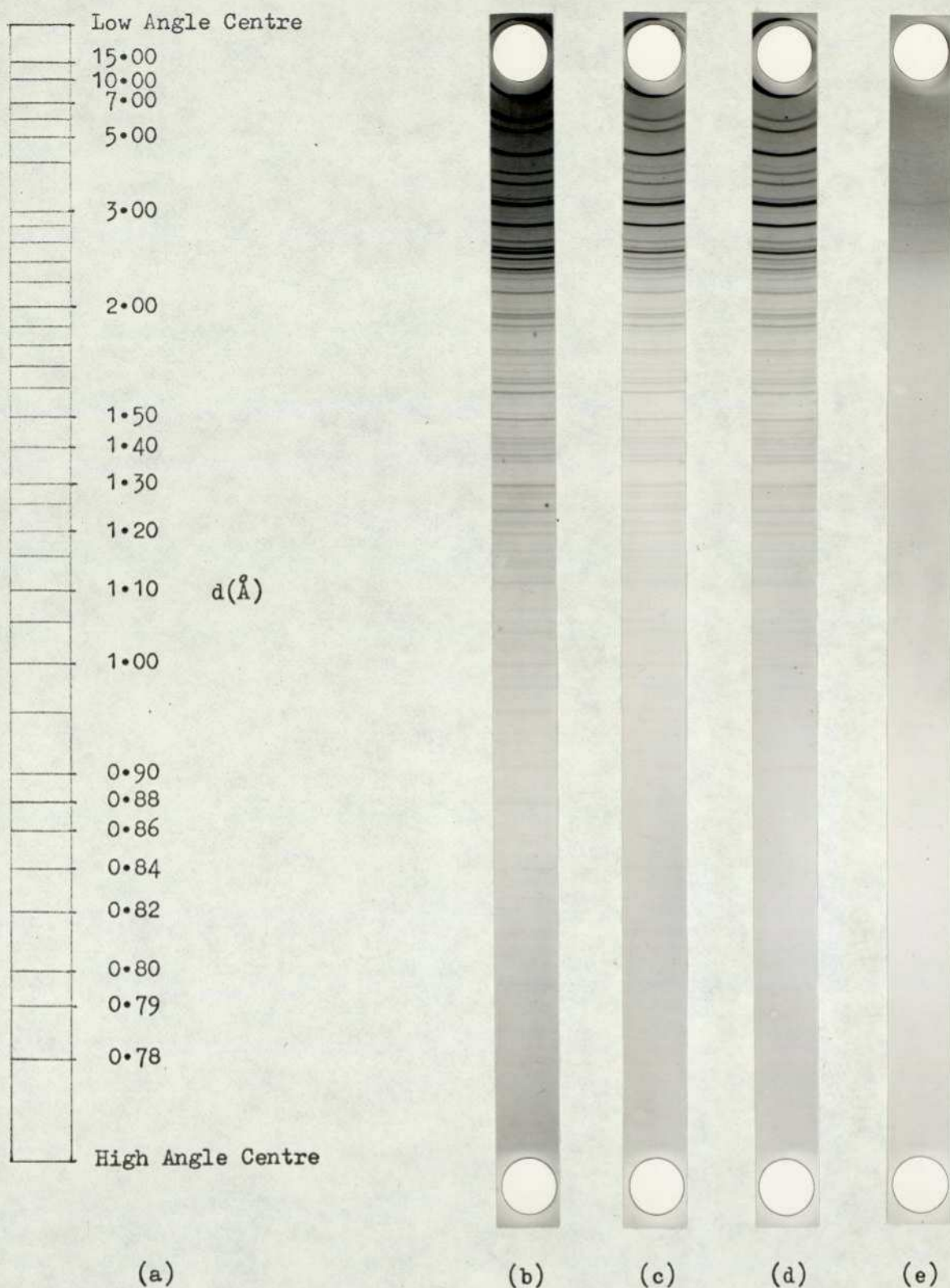


Fig 3.14 X-Ray Powder Patterns of 13X zeolite sulphided with CS_2 .

- (a) Scale calibrated in Interplanar Spacing (d) for making approximate measurements on Powder Patterns obtained with Copper $\text{K}\alpha$ Radiation. Pattern distortion during reproduction allowed for.
- (b) 13X zeolite after activation.
- (c) 13X zeolite sulphided at 400°C .
- (d) 13X zeolite sulphided at 500°C .
- (e) 13X zeolite sulphided at 600°C .

Copper $\text{K}\alpha$ Radiation

(1) No structural modification occurred during the sulphiding process. This is evident in the similar line spacings observed before and after sulphiding.

(2) With increasing temperature of reaction, the sample lost crystallinity. This was witnessed by an overall weakening of the diffraction pattern at 500°C, while at 600°C very little crystallinity remained. This corresponds with a granular product and rather erratic sulphur uptake. The material prepared at 700°C was completely non-crystalline, and gave a featureless diffraction pattern.

The X-ray powder patterns therefore indicate that sulphiding at temperatures up to 500°C had not modified the zeolite framework, and that reaction above this temperature led to a loss of crystallinity, complete at 700°C. Thus it may be stated that although appreciable sulphiding is likely to have occurred above 600°C, the products did not have the characteristic framework of the zeolite used, which was destroyed as sulphiding occurred.

Infra-Red Analysis of Reactor Off-Gas

Small quantities of hydrogen sulphide had previously been detected in the effluent gas stream during the sulphiding process (Experiments 3.13 to 3.15). A fuller analysis of the gaseous products leaving the reactor was made by obtaining their infra-red spectrum, and examining the peaks with a view to determining the components present. A Perkin-Elmer Infra-cord(670 - 4000 cm^{-1}) was used, and a sample of the gas stream was collected in a 10 cm cell with NaCl windows. The spectra were examined for the following components, using reference data from the Sadtler compilation:- CO_2 , COS, CO, CS_2 , SO_2 and H_2S .

A sulphiding experiment (similar to those already conducted) at 600°C was carried out, as X-ray and analytical data suggested that structural sulphiding without a total loss of crystallinity was encountered at this temperature. The spectrum obtained soon after admitting the feed stream is shown in Figure 3.15. A second spectra was taken 30 minutes after the start of the run (Figure 3.16), and a third after 90 minutes. This latter spectrum was identical to that obtained after 30 minutes, and is not reproduced.

A second experiment was conducted at 500°C , as X-ray data had suggested that very little structural modification occurred at this temperature, and a means was therefore afforded of examining the reaction of carbon disulphide to form the unstable species obtained when structural breakdown did not occur. A spectrum was obtained soon after admitting the feed (Figure 3.17), and is generally similar to that obtained at the same point during the previous run (Figure 3.15). Similarly, spectra obtained later in the experiment were identical to those from the previous experiment, and are not reproduced.

The peaks found in these spectra are listed in Table 3.3, together with assignments made. The two runs may be considered together as the results were so similar. The strong peaks at 1530 cm^{-1} and 2190 cm^{-1} were attributed to CS_2 , and the peak near 2320 cm^{-1} is the characteristic absorption due to CO_2 . The concentration of this component is too low to permit identification of the other weak adsorptions associated with it. Whilst the concentration of these components (CS_2 and CO_2) were not altered during the time that the reaction was monitored

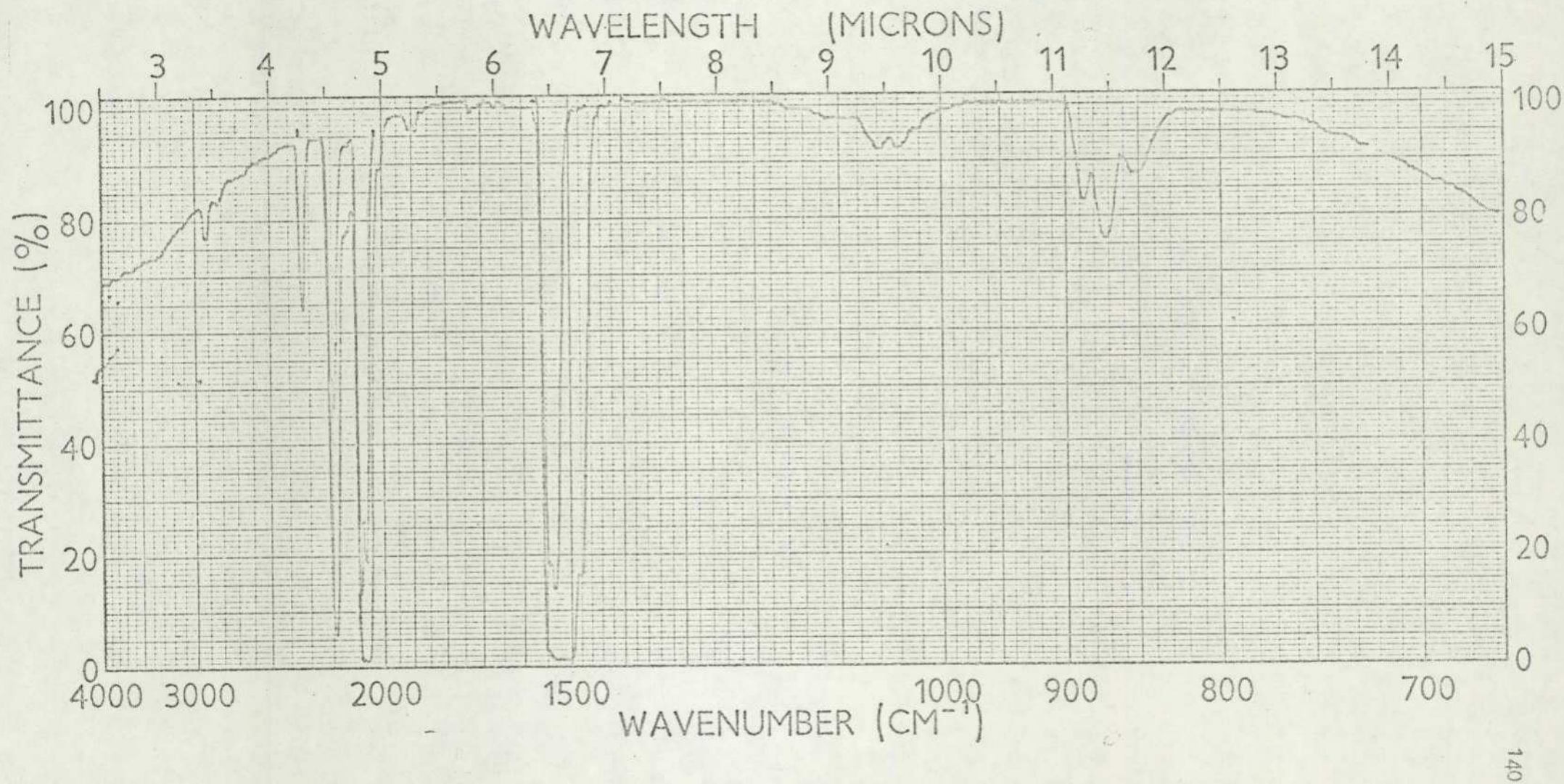


Fig. 3.15 Off-Gas I.R. Analysis of CS₂ treatment of 13X zeolite @ 600°C . Beginning of reaction.

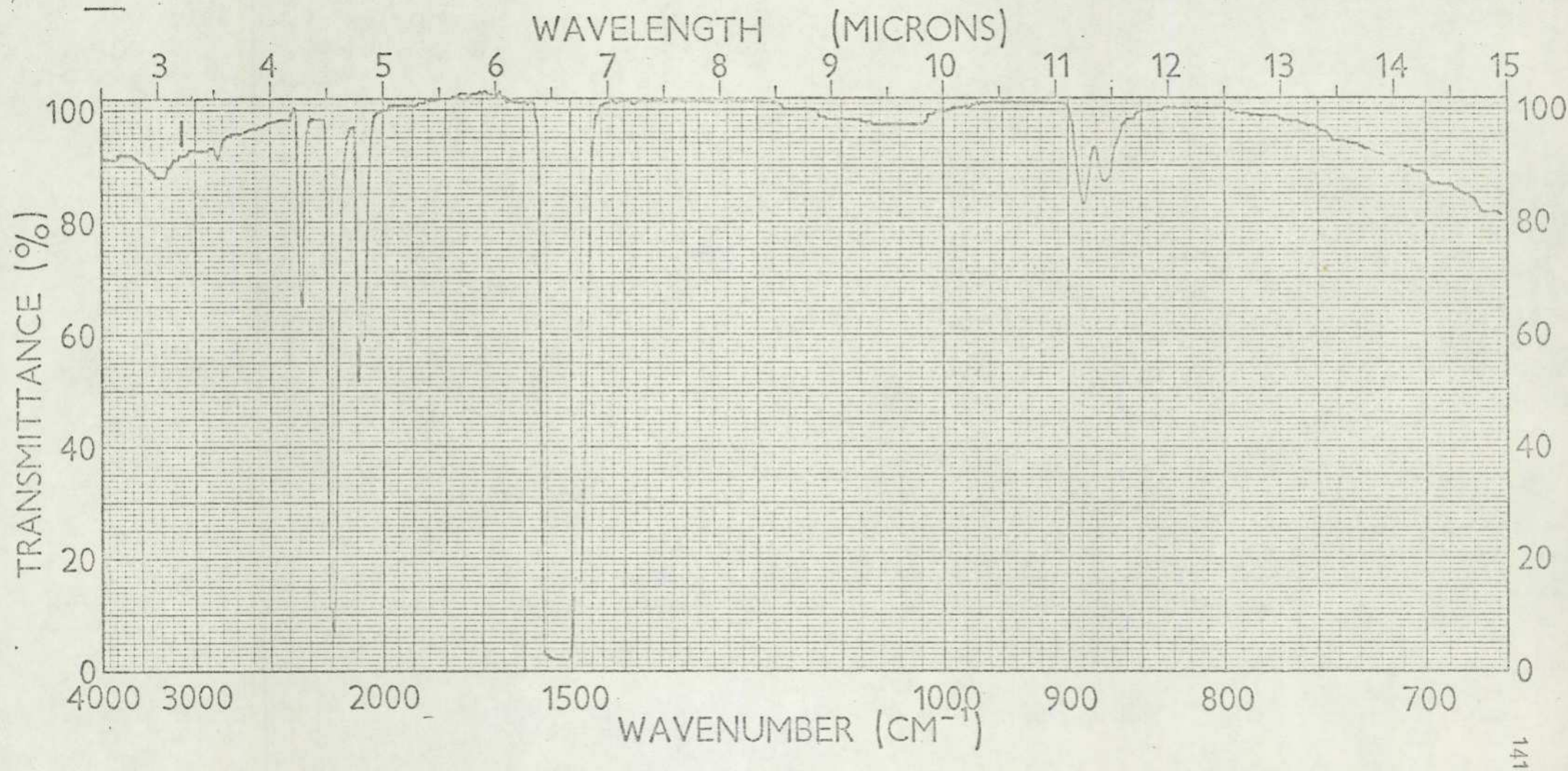


Fig. 3.16 Off-Gas I.R. Analysis of CS_2 treatment of 13X zeolite @ 600°C . After 30 minutes. (spectra similar after 90 minutes).

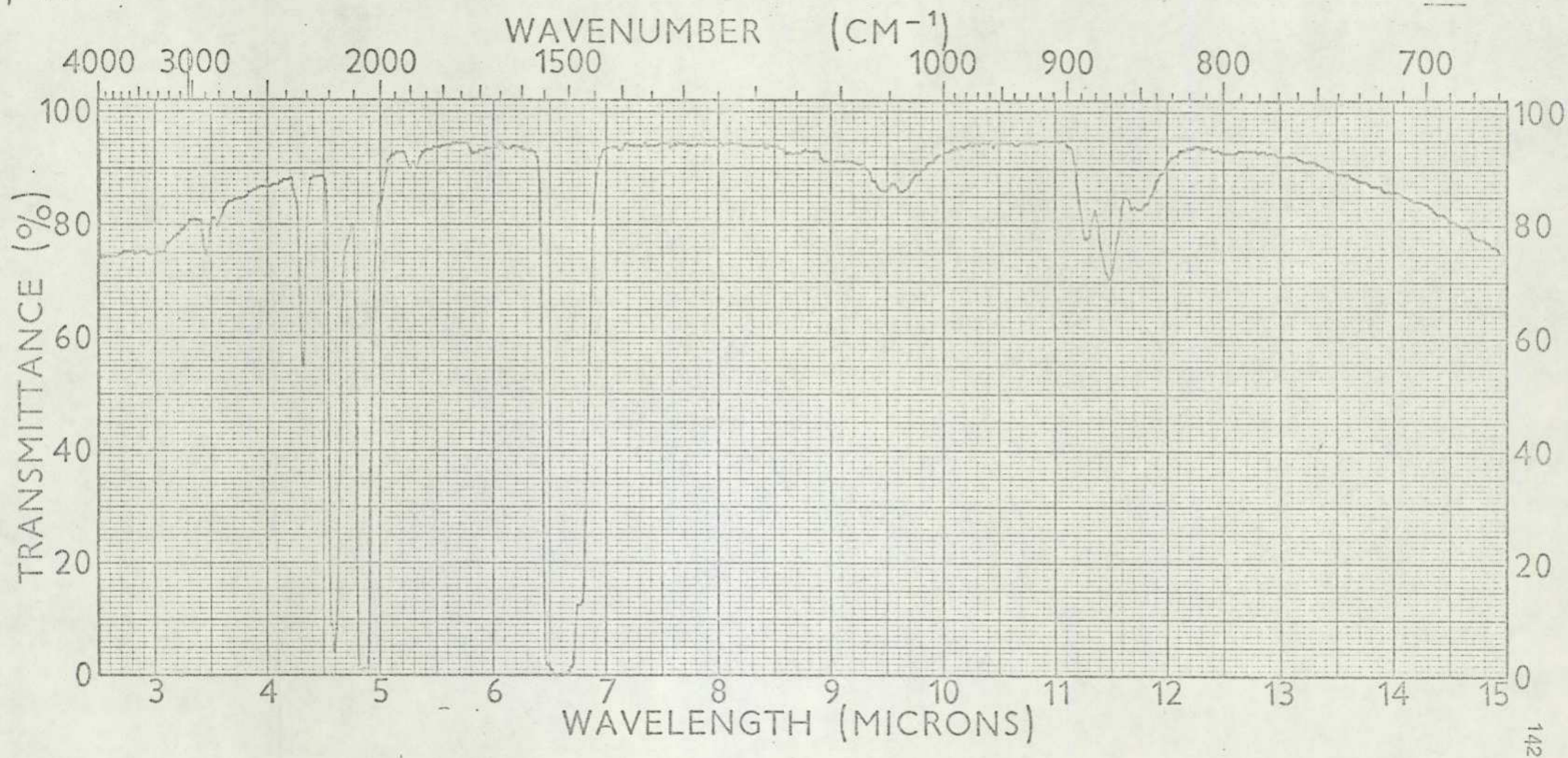


Fig. 3.17 Off-Gas I.R. Analysis of CS₂ treatment of 13X zeolite @ 500°C. Beginning of reaction.

Peak (cm^{-1})	Notes	Assignment	Literature
852 w.	1st. spec. only	COS	COS= 859 w.
871 w.		CS ₂	CS ₂ = several peaks
888 m.		CS ₂	
1040 w.	1st. spec. only	COS	COS= 1051 m.
1060 w.	1st. spec. only	COS	
1530 v.s.triplet		CS ₂	CS ₂ = 1523 s.
1730 v.w.	1st. spec. only	COS	COS= 1718 w.
1880 v.w.	1st. spec. only	COS	
1920 v.w.	1st. spec. only	COS	COS= 1895 w.
2080 v.s.doublet	weakened after	COS	COS= 2079 v.s.
2190 s.doublet	1st. spec.	CS ₂	CS ₂ = 2184 w.
2320 m.		CO ₂	CO ₂ = 2350 v.s.
2920 w.	1st. spec. only	COS	COS= 2904 m.

v.s.= very strong; s.= strong; m.= medium; w.=weak;

v.w.= very weak.

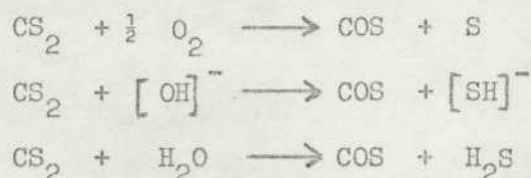
Table 3.3 Off - Gas Infrared data from the sulphiding of 13X Zeolite with CS₂.

	Toluene Adsorption, g/100g.
Activated 13X zeolite	
Sample 1	19.3
Sample 2	22.9
Material from	
Experiment 3.7	7.9
Material from	
Experiment 3.9	0.0

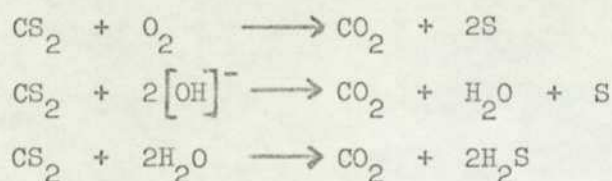
Table 3.4 Adsorption of Toluene on Activated and Sulphided 13X Zeolite at 25°C and 27 torr.

(cf Figure 3.16), the other strong peak in the spectra (2080 cm^{-1}) became considerably weaker during the first 30 minutes of the reaction. This peak is coincident with the strong adsorption of COS at 2079 cm^{-1} , and several other peaks in the spectrum which also lost intensity during the first 30 minutes may also be attributed to COS. This is illustrated in Table 3.3. Therefore, there is evidence that the initial sulphiding of the zeolite at all temperatures at which sulphur uptake occurred was accompanied by conversion of CS_2 to COS. The initial high evolution of COS is consistent with the observation that most of the sulphur uptake occurred in the early part of the reaction (Figure 3.10), whilst the almost steady low-concentration observed after this is consistent with the gradually increasing sulphur content found with prolonged reaction time. In the light of the X-ray-data presented above, it may be inferred that the reaction giving rise to the COS does not involve structural modification to the zeolite framework, as it occurred as readily at 500°C (when the crystal structure is essentially unchanged) as at 600°C (loss of crystallinity observed). It is also interesting to note that no H_2S was detected by the infrared spectra. This is consistent with the rather low total concentrations found in the quantitative estimation of this component discussed above. $\nu(\text{S-H})$, occurring at around 2500 cm^{-1} (2684 cm^{-1} in gaseous H_2S) is a weak vibration, and the other characteristic vibrations of H_2S (1290 cm^{-1} , 2240 cm^{-1} and 3788 cm^{-1}) are not strong enough to be detected in low concentrations. Therefore, it is apparent that COS was the chief product of the sulphiding process, together with a small amount of CO_2 , with H_2S present only as a trace constituent. No SO_2 was detected on any of the spectra.

It may therefore be suggested that the principal reaction occurring is that between CS_2 and oxygen, water or a surface hydroxyl group:-



Reaction with water is not likely, as it would involve liberation of an equimolar quantity of hydrogen sulphide, which was not found. An explanation of the observation of CO_2 , and of free sulphur during some of the experiments, and of the apparent presence of radical species spontaneously oxidised to SO_2 , is afforded by direct oxidation of CS_2 :-



Therefore, it seemed that the components formed during sulphiding of the zeolite were all attributable to the presence of oxygen, moisture and surface hydroxyl groups within the structure, incompletely removed on activation.

Adsorption Capacity of Sulphided Zeolites

To confirm the conclusions reached regarding the position in the zeolite structure occupied by the sulphur deposited in the sulphiding process, the adsorption capacity of the zeolite was measured before and after the CS_2 treatment. In this way it was possible to see whether the incorporation of sulphur occurred with a loss of pore volume, as would be expected if it was held within the pores and cavities rather than being incorporated into the structural framework.

The measurements were made on a micro quartz spring balance of the McBain type. This equipment is described in Chapter 7. The sample (20 - 50 mg) was placed in the glass bucket, the system evacuated and the sample heated at 150°C until constant weight was attained. This was taken as the sample weight. The system was then isolated from the pump, allowed to cool to room temperature, and toluene vapour admitted until the required pressure was registered by the main manometer. The system was then left until a constant weight was obtained, and the weight increase taken as the adsorption capacity at the temperature and pressure of measurement (25°C , 27 torr).

Toluene was chosen as adsorbate as its minimum kinetic diameter of 5.9 Å (60, p 47) was just small enough to allow it to pass freely through the 8 Å apertures between the 13 Å cages of 13X zeolite, providing that the pore structure was not obstructed. 13X zeolite has an adsorption capacity for toluene of 0.268 g/g under the conditions used (60, p 47). The results from the present work are summarised in Table 3.4.

The adsorption capacity for toluene was determined for activated 13X zeolite, and zeolite that had been sulphided at 400°C . (Experiment 3.7), and 600°C (Experiment 3.9). The experimental arrangements used necessitated the samples being briefly exposed to air, and the materials must therefore be regarded as oxidised. A blank experiment was conducted with no sample, but no weight increase was observed on admitting toluene in this case.

The up-take for the activated zeolite was 19.3 and 22.9 g toluene/100 g activated zeolite. This is somewhat less than the published results (60, p 47), which was 26.8 g/100 g, probably due

to different activation procedures. It was not felt advisable to activate at above 150°C in the present work in case loss of sulphur occurred from the sulphided samples.

The adsorption capacity of zeolite sulphided at 400°C was reduced from an average of 21 g toluene/100 g to 7.9 g toluene/100 g, and clearly demonstrated the blocking of much of the structural voidage by adsorbed sulphur. Taken in conjunction with the x-ray data, it was therefore apparent that the sulphur had entered the pores of the zeolite rather than the structural framework.

The zeolite sulphided at 600°C did not possess any adsorption capacity for toluene. This is consistent with the loss of crystallinity already suggested by the x-ray powder pattern of this material (Figure 3.14, d).

Therefore, adsorption measurements confirmed the view reached from other methods of examination of the sulphided zeolites. At temperatures up to about 500°C , the sulphur entered the lattice cages and not the framework structure. At temperatures higher than this, a loss of crystallinity occurred, and the material formed did not possess the characteristic zeolitic framework.

Thermal Stability of Sulphided 13X Zeolite

As it seemed well established that the main product from the high temperature treatment of 13X zeolite with carbon disulphide was unaltered zeolite containing elemental sulphur within its pores, some measure of the strength with which the sulphur was bound was of interest.

A simple apparatus was assembled (Figure 3.18), in which a sample of sulphided zeolite was heated under vacuum, the removed

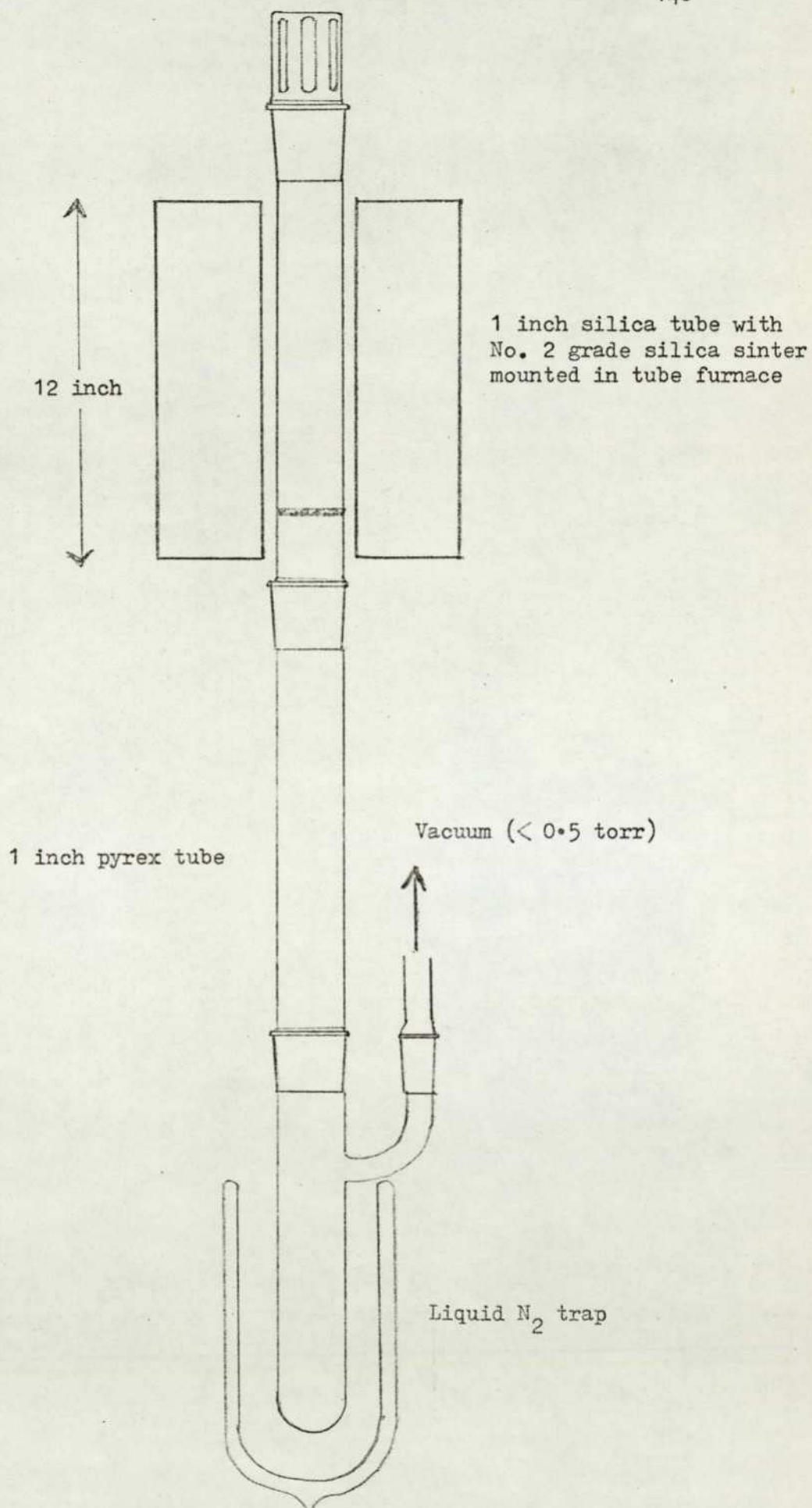


Fig. 3.18 Apparatus for testing the temperature stability of sulphided Zeolites.

sulphur being condensed in a cold trap. In practice, it was found that most of the sulphur removed from the zeolite condensed on the cooler part of the tube beneath the furnace.

(i) 13X zeolite sulphided at 500°C (Experiment 3.8)

This material, containing 5.7 per cent sulphur before exposure to air, was used for the first experiment. About 1 g was transferred to the quartz tube in the dry box. The tube was then quickly attached to the remainder of the system, and evacuated to avoid contact with air. The furnace was heated to 500°C for 6 hours. A loss of sulphur was observed, the sample becoming nearly colourless. At the end of this time, a sulphur analysis showed that most of the sulphur had been lost, only 1.5 per cent w/w remaining. Therefore, it was apparent that most of the sulphur was easily removed from the zeolite structure, already shown by x-ray diffraction to be essentially unaltered 13X framework.

(ii) 13X Zeolite Sulphided at 600°C

This material had a sulphur content before exposure to air of 12.3 per cent w/w. It was firstly heated at 400°C for 6 hours in vacuo. The initially colourless material became pale yellow during this time. A sample removed for analysis contained 10.8 per cent w/w sulphur. The temperature was then increased to 600°C for 6 hours. The colour became bright chrome yellow, and a further sample removed for analysis contained 10.1 per cent w/w sulphur. The temperature was then raised to 700°C for 6 hours. The colour became green-yellow, and the sulphur content was 6.5 per cent w/w.

As it was not possible to heat the sample above 750°C in the apparatus described, a Stanton direct-reading thermobalance was

used up to 1100°C . The design of this instrument made it inevitable that the sample was contacted with air.

The materials already examined were used for these tests - ie untreated zeolite, and zeolite sulphided at 500° and 600°C . The results, plotted from the thermobalance recorder outputs of temperature versus time and weight versus time, are shown in Figure 3.19.

The sample of untreated zeolite (lower curve) showed a water loss of 28 mg (7.6 per cent of the 0.3669 g sample) between 150° and 450°C . This is consistent with the fact that no activation procedures were adopted, the zeolite being used as supplied. No further weight change was recorded above 450°C .

The sample of zeolite sulphided at 500°C (central curve) showed a smaller weight loss in the 200° - 400°C range. The loss, of 8 mg, corresponded to 6.5 per cent of the 0.1238 g sample taken. Above this temperature range, the only weight loss recorded was 3 mg (2.4 per cent) between 800° and 1000°C . Therefore, of the 5.7 per cent sulphur initially present in this material, it is likely that 2.4 per cent was firmly bound within the zeolite, and not lost below 800°C , above which temperature the zeolite is likely to start to decompose. The remaining 3.3 per cent sulphur was lost fairly readily between 200° and 400°C , and the difference between this weight loss and the total weight loss of 6.5 per cent observed in this temperature range may be accounted for by water. This figure of 3.3 per cent sulphur lost below 500°C compares tolerably with that of 4.2 per cent obtained in the in vacuo

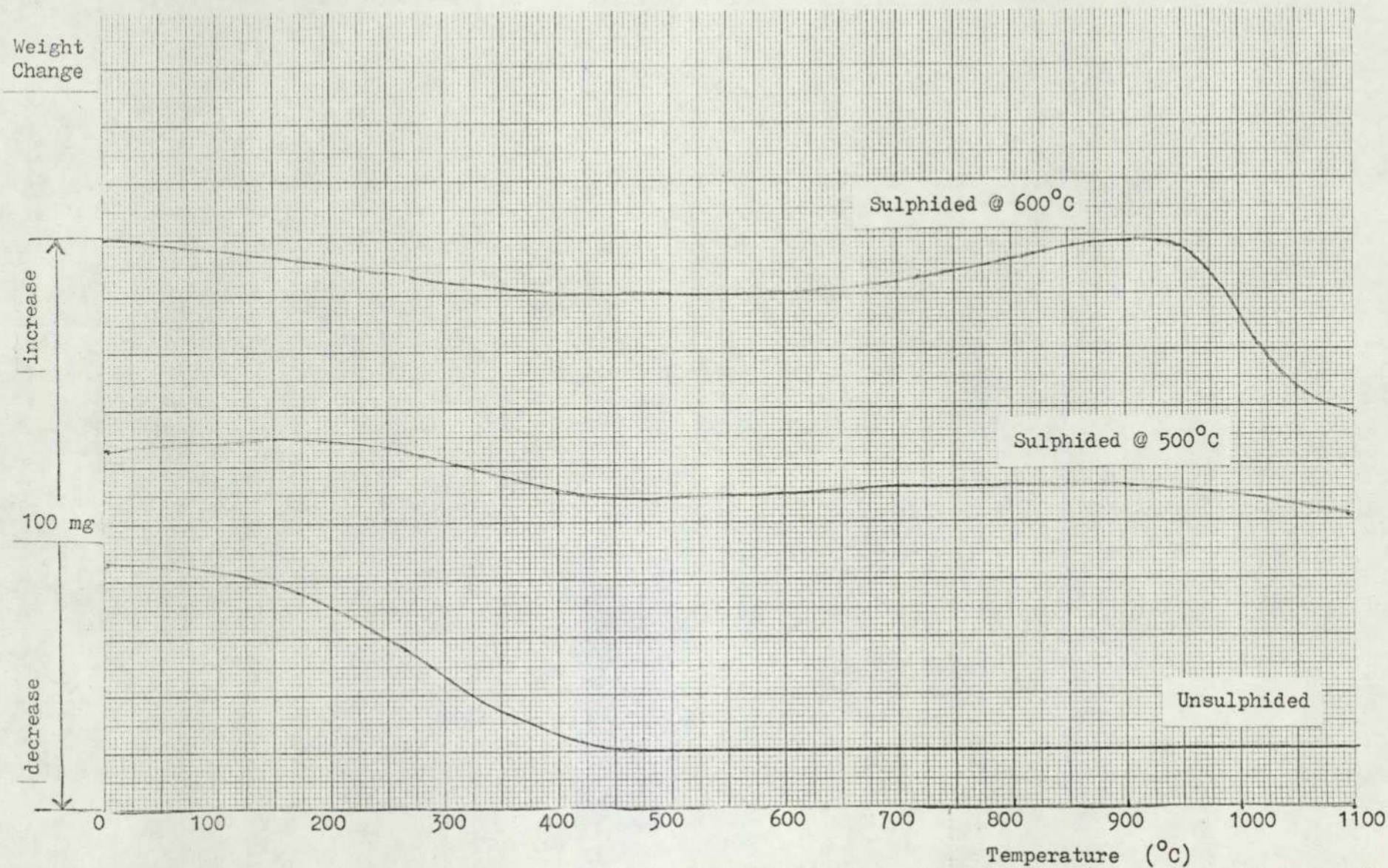


Fig. 3.19 Thermogravimetric analysis of sulphided and unsulphided 13X zeolite

experiments, bearing in mind that the sample in the thermogravimetric analysis must be regarded as oxidised. Therefore, the two approaches lead to the same conclusions - that the larger part of the sulphur in zeolites sulphided at 500°C is lost on heating below this temperature in air or vacuum demonstrating its ready removal from the practically intact zeolite lattice.

The curve obtained from the thermogravimetric analysis of 13X zeolite sulphided at 600°C (top curve, Figure 3.20) is somewhat different to the others. No clearly defined weight loss was recorded until nearly 1000°C , when a very sharp loss of weight was recorded over a narrow temperature range. The weight loss of 22 mg corresponded to 7.3 per cent of the 0.2989 g sample, and is in rough agreement with the 6.9 per cent sulphur remaining after the 700°C in vacuo treatment. The sample of sulphided zeolite used contained 12.3 per cent sulphur, and the remaining sulphur, lost below 700°C in the vacuum treatment, is not accounted for by the thermogravimetric data. It is likely that some was lost by oxidation during sample preparation, but it is unlikely that all the discrepancy could be accounted for in this way as the sample sulphided at 500°C did not exhibit this loss. It seems more likely that whereas the weight loss between 200° and 400°C observed for the zeolite sulphided at 500°C may be regarded as the loss of elemental sulphur, the weight loss at 1000°C observed for the zeolite sulphided at 600°C is best regarded as the oxidation of a sulphide. Oxidation of the 12.3 per cent sulphur present would involve the incorporation of :-

$$\frac{12.3 \times 16}{32} = 6.2\% \text{ oxygen}$$

Thus the overall weight loss during the oxidation would be:-

$$= 12.3 - 6.2 = 6.1\%$$

This is in approximate agreement with the 7.3 per cent recorded, and offers an alternative explanation to the loss of strongly bound elemental sulphur.

The results from these stability tests serve to confirm the earlier conclusions. Sulphiding at 500°C left an essentially unmodified zeolite framework containing elemental sulphur readily removed on heating. At temperatures above 600°C, the sulphur was much more strongly bound, and was only partially lost by heating at 700°C in vacuo. It is significant that the material became yellow-green during this treatment, suggesting decomposition and removal of sulphur in elemental form. Thus the overall conclusions were that reaction under conditions likely to cause substitution of sulphur into the zeolite lattice in fact caused a destruction of this lattice and the formation of non-crystalline sulphides.

3.3 CONCLUSIONS

The overriding conclusion was that permanent sulphiding of 13X zeolite with carbon disulphide at elevated temperatures was accompanied by a loss of the characteristic framework structure of this material. The zeolitic structure was not reformed under the conditions used. A dividing line may be drawn between products sulphided below and above 500°C. Materials formed below this temperature exhibited a virtually unchanged 13X zeolite lattice, with sulphur species incorporated within the channels and voids. Materials formed above 500°C exhibited more permanent

sulphiding. They hydrolysed slightly on contact with moisture, with liberation of hydrogen sulphide, and this was indicative of aluminium-sulphur and silicon-sulphur bond formation. The X-ray diffraction patterns indicated a substantial structural modification to have occurred, and this was confirmed by the physical appearance of the materials.

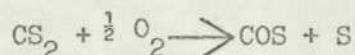
As material prepared at 600°C exhibited both the reactivity and crystal structure (albeit weakened) of the first category of product, together with evidence of partial change of structure, it is in this product range that sulphur analogues of zeolites might be expected to form. However, new crystalline (zeolitic) phases were not detected. X-ray data (Figure 3.14) indicated that the materials were non-crystalline, and adsorption measurements and thermogravimetric data (Figure 3.19) confirmed the loss of zeolitic properties.

The commencement of loss of crystallinity at 600°C was accompanied by the erratic sulphur uptake noted at this temperature (Figure 3.9). As 13X zeolite is normally regarded as being stable in air to at least 700°C (60, p 47), attack by carbon disulphide is clearly indicated.

The overall conclusion was therefore that structural sulphiding was only obtained with an accompanying loss of crystallinity, and sulphur analogues of the starting phase cannot be obtained by this means. However, the exact nature of the reactions occurring, and the products obtained at the lower reaction temperatures were not so clearly established.

Infra-red evidence (Figures 3.4 and 3.5) indicated that some adsorbed water was remaining after activation, and this

could account for the small quantities of hydrogen sulphide detected during reaction. The detection of elemental sulphur, accompanied COS formation is indicative of the partial oxidation of carbon disulphide:-



As it had been shown that careful activation of the zeolite reduced the quantity of sulphur formed, some adsorbed species, possibly oxygen, is likely to be responsible for at least part of this oxidation. Traces of contaminants in the feed stream are another possible source of oxygen and water.

It is interesting to note that the high initial concentration of COS in the off-gas, and subsequent low (steady) concentration is similar to the rate of uptake of sulphur with time (Figure 3.10). This suggests that at least part of the COS formation was associated with the sulphiding of the zeolite.

This leads to the question as to the exact nature of the sulphided species formed below 500°C. In view of the literature reports concerning the unstable nature of zeolites containing elemental sulphur in the form of radicals, and the observations of free sulphur in some of the present materials, it is tempting to attribute the reactivity of these materials to sulphur radicals of this type. Nevertheless, it is questionable whether the amount of sulphur deposited by the quantities of free oxygen likely to be available could account for the extreme reactivity of these materials towards air. The simpler explanation is that at least some of this activity was due to adsorbed carbon disulphide remaining after the reaction.

Zeolites are known to be powerful catalysts for the oxidation of hydrogen sulphide (274, 275), and it is possible that a similar reaction occurs with carbon disulphide. Oxidation of carbon disulphide to carbon dioxide and sulphur dioxide would then occur:-



As it was shown that only about one half of the total sulphur content was lost on oxidation, it is apparent that the remainder was left within the zeolite, probably as elemental sulphur. This is consistent with the oxidation of hydrogen sulphide, where nearly complete conversion to sulphur was obtained under suitable conditions.

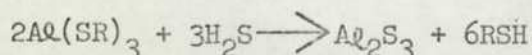
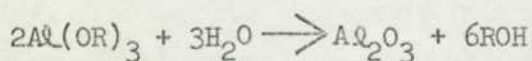
A further consideration is the development of blue and green colours during the oxidation, and also some of the sulphiding reactions. Similar effects have been reported in the literature (Section 3.1.2), and attributed to oxidation. From the present work it seemed evident that these effects were at least partially due to reaction of the sulphur compound (or free sulphur) with the zeolite, and the colouration is indicative of the free radical species generally held to be responsible for the formation of this colouration in sulphided zeolites and ultramarines. Ultramarine formation is precluded in the present work as the colouration was lost on oxidation, whereas the development of the colour in ultramarine formation is an oxidation process. Therefore, the formation of unstable sulphur radicals during both the sulphiding and oxidation was suggested.

Under no conditions was it found that modification of the zeolite framework occurred without loss of crystallinity, and the general conclusion was that the energy required to replace structural oxygen with sulphur is in excess of that required to destroy the zeolite lattice. Thus, while direct sulphiding of oxides may be a satisfactory means of synthesising sulphur analogues of the simpler, compact structures, it is not successful with the more open, framework compounds.

CHAPTER 4. PREPARATION OF INTERMEDIATES

4.1 INTRODUCTION

The hydrothermal techniques investigated for the preparation of crystalline complex sulphides required several materials not readily available, and this chapter describes the various methods adopted for their preparation. Two classes of compound were required - mercaptides and sulphides. The majority of original work carried out was in connection with the preparation of mercaptides. The Group III b derivatives, in particular, have been only poorly documented, with a number of somewhat contradictory publications. The mercaptide salts are sulphur analogues of the alkoxides (eg aluminium ethoxide, $\text{Al}(\text{OEt})_3$), and may be written as $\text{Al}(\text{SR})_3$, $\text{Si}(\text{SR})_4$, etc, where R is an alkyl or aryl group. Their purpose in the present work was as a source of finely divided, reactive, sulphide material for use with hydrogen sulphide. Just as the alkoxide may be hydrolysed in aqueous solution, with a greater or lesser degree of difficulty, so it was hoped that the mercaptides would be hydrolysed by hydrogen sulphide:-



The preparation and properties of metal alkoxides have been described by Bradley (321). Although hydrolysis to the oxide frequently occurs, formation of hydrated metal oxides is more common. The formation of intermediate, polymeric compounds is also common - ie $\text{MO}_x(\text{OR})_y$. The silicon alkoxides ('alkoxysilanes') have been described by Mehrotra (322). They

are sometimes stable with respect to hydrolysis because of their low solubility in water, but hydrolyse more readily when brought into solution by, for instance, alcohol.

Hydrolysis of alkoxides is encouraged by acidic or alkaline conditions, and the hydrolysis in basic solution of mixtures of the aluminium and silicon derivatives has been used as a source of finely divided co-gels for use in subsequent hydrothermal crystallization to form zeolites. 'Thiohydrolysis' of aluminium and silicon mercaptides in basic hydrogen sulphide solution presented possibly the most convenient route to suitable starting phases in the case of the aluminium and silicon sulphur system. The sulphides of these elements are difficult to prepare by low temperature, non-aqueous methods, and the high temperature techniques usually employed yield impure, crystalline products very different from the amorphous, gelatinous starting phases generally used in hydrothermal synthesis (Section 4.3.1). Further, some of the mercaptides of aluminium and silicon are readily soluble in non polar solvents (Section 4.2), and therefore offered a good means of obtaining a solution of aluminium and silicon sulphy-species in non-polar hydrogen sulphide (Chapter 5).

With the lower subgroup elements (gallium, indium, germanium and tin), hydrolysis of the mercaptides becomes more difficult. In view of this, and the fact that preparation of their sulphides in pure, finely divided states is comparatively easy, mercaptides of these elements were not investigated.

Therefore, the next section of this Chapter is concerned with the preparation and properties of the mercaptides of aluminium and silicon, $Al(SR)_3$ and $Si(SR)_4$.

The final section of this Chapter covers the preparation of the various sulphides required for the aqueous and non-aqueous hydrothermal techniques. The methods commonly used for the preparation of Al_2S_3 and SiS_2 are discussed, and the preparation of GeS_2 , SnS_2 and In_2S_3 described. As was indicated in Chapter 2, these latter elements should be capable of undergoing isomorphous substitution into the lattice of sulphur analogues of conventional aluminosilicates. Gallium was not used, as its chemical properties are intermediate between aluminium and indium, its sulphide being too readily hydrolysed to be prepared by the simple aqueous methods applicable to the other lower subgroup elements, and its mercaptides not being likely to be completely hydrolysed by hydrogen sulphide. Compounds such as $Ga_2S_2(OH)_2$ are formed from partial hydrolysis of gallium sulphide (43, Chapter 5), and prevent its precipitation from aqueous solution by hydrogen sulphide. Further, the preparation of gallium sulphide by high temperature, non-aqueous methods suffers the same disadvantages as the preparation of aluminium sulphide by these methods. Therefore, it was not thought worthwhile including this material in the programme of work to be undertaken, and experiments using the lower sulphides of Group III b employed indium sulphide, In_2S_3 .

Hydrothermal synthesis is conventionally conducted in basic media, generally an alkaline hydroxide solution (ie NaOH). However, organic bases have been used in the preparation

of zeolites. For example, with tetraalkylammonium hydroxide, the alkali metal cation is replaced with R_4N^+ . The organic base may totally replace the inorganic base (323), or a mixture may be used (324). Literature reports suggested (Chapter 5) that while inorganic bases (eg NaSH) are only sparingly soluble in liquid hydrogen sulphide, organic bases (ie $Et_4N^+SH^-$) possess considerable solubility in this material, and are therefore potentially more useful. The preparation of both classes of base are discussed in the latter part of this chapter. The organic base used was tetraethylammonium hydrosulphide, $Et_4N^+SH^-$, and the inorganic sulphide was sodium hydrosulphide, NaSH.

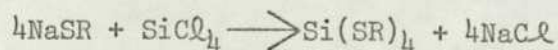
4.2 MERCAPTIDES

4.2.1 Introduction and Literature

4.2.1.1 Silicon and Germanium Mercaptides

The mercaptides of Group IVb, $M(SR)_4$ ($M = Si, Ge, Sn, Pb$; $R = \text{alkyl}$) are well documented. Abel and Armitage discuss them in a recent review (325), and the compounds were originally described by Backer et al between 1932 and 1951 (326-338).

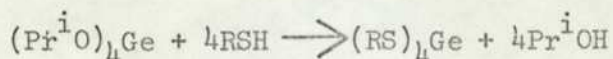
The silicon derivative was prepared by reaction of the sodium mercaptide and silicon tetrachloride in benzene as solvent (326):-



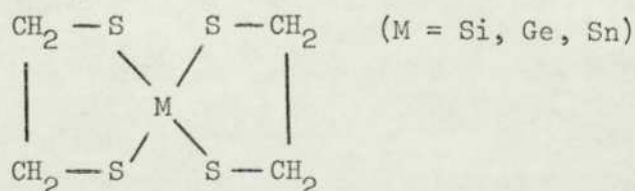
The sodium mercaptide was prepared from the reaction between metallic sodium and the mercaptan. It was not soluble in either the mercaptan or benzene, and was reacted with $SiCl_4$ as a suspension.

The mercaptide derivatives ('silicic acid tetrathioesters') were soluble in benzene, and were separated by vacuum distillation after the sodium chloride had been filtered off. They were obtained as oils of low volatility, insoluble in water and soluble in organic solvents. They were stable towards hydrolysis by both water and hydrochloric acid.

The initial report described the lower alkyl derivatives. Later reports (327-329) described the n-, sec- and iso-butyl derivatives, the phenyl and p-tolyl, and finally the t-butyl derivatives. The germanium derivatives $\text{Ge}(\text{SR})_4$, were also described (331). Unlike the silicon derivatives these did not react with alcohol, which was therefore used as solvent during the preparation. It is interesting to note that the germanium derivatives may be prepared directly from the mercaptan (379):-

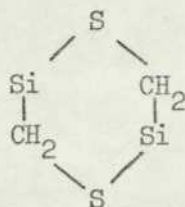


The physical data and crystallography have been summarised for these silicon and germanium derivatives (330, 332), and the tin and carbon derivatives have also been prepared (333-337) $[\text{Sn}(\text{SR})_4, \text{C}(\text{SR})_4]$. Spirocyclic derivatives were also reported (338), with the structure:-



Various other reports have since appeared on the preparation of Group IV b mercaptides, but they do not in general add any additional information. Partially substituted derivatives RSSiSR' have been reported (339), and various other organo-sulphur-silicon compounds have been prepared. For instance,

the cyclic compound:-



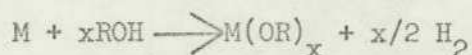
was prepared from $\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ and hydrogen sulphide (340), and silicon-sulphur compounds possessing the cage structure of adamantane have been reported (341).

For the purposes of the present work, it was important that the mercaptide derivative should be hydrolysed in solution in hydrogen sulphide. The stability of these materials towards water and hydrochloric acid (326) is probably due to their low solubility in aqueous solvents. In alcohol solution, silicon mercaptides are decomposed to the thiol and alkoxide (339), which is hydrolysed in solution (322). Silicon mercaptides will almost certainly be soluble in non-polar hydrogen sulphide, and if in addition basic media can be established, then the chances of hydrolysis seem good. In addition, thermal decomposition of silicon mercaptides leads to the formation of SiS_2 below 350°C (342, 343), and so the chances of obtaining finely divided SiS_2 in situ seemed favourable.

4.2.1.2 Aluminium Mercaptides

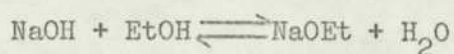
These materials have not been widely reported in the literature. Potential methods for their preparation may be devised by a consideration of the techniques used to prepare alkoxides (321). The simplest method is the reaction of a metal and alcohol, but this is restricted to the alkali metals, although beryllium, magnesium and aluminium react in the

presence of a catalyst that destroys the oxide film:-

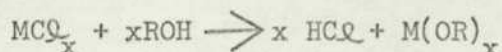


The formation of alkali metal mercaptides by reaction between the metal and the mercaptan is analogous to this, and suggests a possible method in the case of aluminium. This method is only applicable to lower, straight chain alkyl groups.

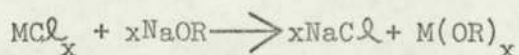
Another technique for the preparation of alkoxides involves reaction of the metal hydroxide with the alcohol:-



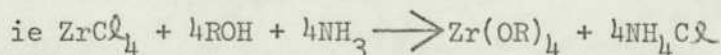
The most common method, however, involves reaction of the chloride:-



As the HCl formed tends to hydrolyse the alkoxide, some means of removing it is generally required. A convenient method is to introduce base by replacing the alcohol with its sodium salt:-

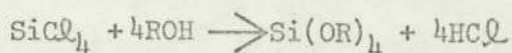


This is exactly analogous to the preparation of silicon mercaptides, and a similar method should be applicable to the preparation of aluminium mercaptides. Bases other than sodium alkoxides used in alkoxide preparation include anhydrous ammonia and pyridine.



Therefore, adequate scope existed for the formation of aluminium mercaptides. The preparation of silicon mercaptide derivatives already described is exactly analogous to the preparation of silicon alkoxides - 'alkoxysilanes' (322), and thus the close similarity between the sulphur and oxygen systems in

this respect was demonstrated. However, the preparation of $\text{Si}(\text{SR})_4$ demands reaction of NaSR with SiCl_4 while $\text{Si}(\text{OR})_4$ may also be prepared directly from the alcohol if required:-



Therefore, in view of the difficulty experienced in preparing aluminium alkoxides by direct reaction of the metal with the alcohol (370, p 834) it seemed unlikely that the mercaptide could be formed by an analogous route. Reaction of aluminium halide with the sodium salt of the mercaptan offered the greatest chance of success.

Very few publications have related to the formation of the mercaptide derivatives of aluminium, $\text{R}_x\text{Al}(\text{SR})_{(3-x)}$ and the few reports existing relate to their preparation from aluminium alkyls. There is no reported formation of these compounds by a route analogous to that used for the silicon derivatives (ie AlCl_3 and NaSR). Patent reports have claimed (345, 346) formation of $\text{Al}(\text{SPh})_3$ and $\text{Al}(\text{SCH}_2\text{Ph})_3$ by reaction of aluminium amalgam with the corresponding mercaptan.

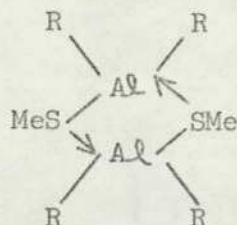
The reaction of the thiols with trialkyl aluminium was first investigated by Davidson and Brown (347) and reviewed by Coates (363). Two classes of compound are formed:-

(i) Coordination complexes with sulphur-containing ligands not containing active hydrogen - ie $\text{R}_3\text{Al} \leftarrow \text{SR}_2$, formed by dialkyl sulphide.

(ii) Coordination complexes with sulphur-containing ligands containing active hydrogen - ie R_2AlSR . It is this latter class of compound that is of interest in the present work. Its formation (from thiol) may be represented:-



This particular derivative was reported as a white solid melting at 103°C, with a dimeric structure (347):-



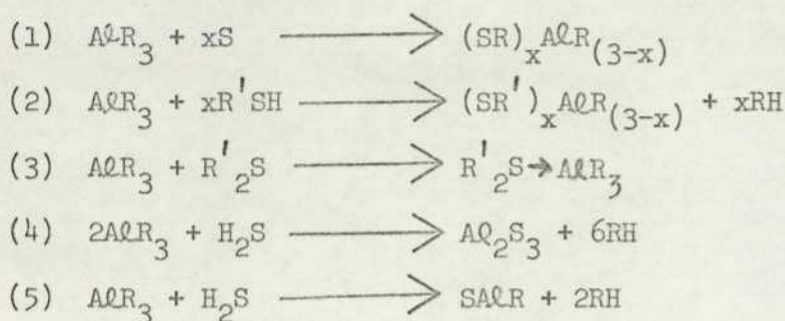
However, later work has found it to be a one dimensional infinite polymer in the solid state (350).

The formation of Et_2AlSEt has been claimed (348) from elemental sulphur and Et_3Al in hexane at 70°C, while the formation of $\text{R}'_2\text{AlSR}$, $\text{R}'\text{Al}(\text{SR})_2$ and $\text{Al}(\text{SR})_3$ from the appropriate molar ratios of $\text{R}'_3\text{Al}$ and RSH has been reported (349). Et_2AlSEt was reported to be a liquid, while $\text{EtAl}(\text{SEt})_2$, $\text{Al}(\text{SPh})_3$ and several other di- and tri- substituted derivatives were reported as white solids.

Attempts to prepare the trisubstituted derivatives, $\text{Al}(\text{SR})_3$, have generally been unsuccessful (351). An attempt to rationalise the formation of these compounds was made by Lalancette et al (352, 353). Reaction of CH_3SH with Et_3Al in pentane as diluent led only to the disubstituted product, $\text{CH}_3\text{Al}(\text{SCH}_3)_2$, but use of diethyl ether as diluent led to a quantitative yield of the trisubstituted derivative, $\text{Al}(\text{CH}_3)_3$. Both derivatives were insoluble in common solvents. The degree of polymerization of these materials was not established, but the disubstituted tertiary butyl derivative was unpolymerized and soluble in non-polar solvents. This was considered to be a steric effect.

By way of completion it may be noted that reaction of trimethyl aluminium (in vapour form) with hydrogen sulphide at 90°C led to 95-98 per cent Al_2S_3 , contaminated with SAlCH_3 (354, 355).

The reactions of aluminium alkyls with sulphur compounds reported in the literature may be summarized:-



The degree of substitution of SR' for R occurring in (1) and (2) is dependent upon conditions, especially the diluent used, and it seemed that the bridged, possibly polymeric structure of the monosubstituted material, $\text{R}_2\text{AlSR}'$ stabilises this material against further substitution. In general, it seemed that these materials were insoluble in common solvents, although the monosubstituted derivatives appeared to exist in a soluble (unpolymerized) form.

Replacement of the thiol in reaction (2) by Na_2S led to Et_2AlSNa (356), and restriction of the quantity of H_2S in reaction (5) led to $\text{Et}_2\text{-Al-S-Al-Et}_2$.

Mercaptides of the lower group III b elements have been briefly reviewed (358). Like the Group IV b derivatives, they are considerably more resistant towards hydrolysis than the aluminium compounds.

It was therefore apparent that while the mercaptide derivatives of silicon were well documented, there was less information available about the aluminium derivatives $Al(SR)_3$. There seemed no reason why this material should not be prepared from anhydrous aluminium halide and the sodium salt of the mercaptan, in a method analogous to that used to prepare $Si(SR)_4$. The only problem likely to be encountered was separation of the product, which was likely to be a solid material according to the information gleaned from the literature.

This technique was therefore investigated as experimentally easy to conduct. The reactions of triethyl aluminium with simple sulphur compounds were then investigated with a view to clarifying the literature on this class of reaction.

4.2.2 Experimental

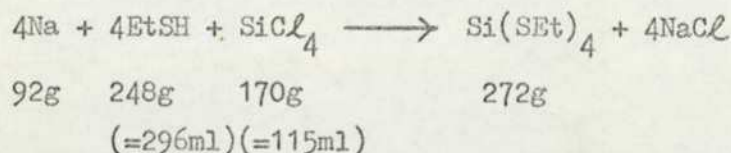
Infra-red spectra ($670-4000\text{ cm}^{-1}$) were obtained with a Perkin Elmer Infracord spectrophotometer. The far infra-red spectra ($500-200\text{ cm}^{-1}$) were obtained with a Grubb-Parsons DM4 instrument. High resolution spectra ($4000-250\text{ cm}^{-1}$) were obtained on a Perkin Elmer Model 457 grating spectrophotometer that became available towards the end of the preparative work.

Between 4000 and 600 cm^{-1} , samples contained between NaCl discs were used, and between 600 and 200 cm^{-1} polythene plates were used. Considerable background adsorption was present in the range $650-500\text{ cm}^{-1}$ (Figure 4.6), but unfortunately the costly caesium iodide plates transparent over the far infra-red region were not available. KBr discs prepared in the dry box, using a stainless steel die, were used for some of the spectra. Finely ground AR grade KBr was employed.

4.2.2.1 Si(SET)₄ and related compounds

This material was readily prepared by the published method (326), described in Section 4.2.1.1. Ethyl mercaptan was supplied by Koch-Light Ltd., and was distilled before use, the fraction boiling between 34.2° and 36.0°C being used. (Published BP = 34.7°C). Its infra-red spectrum is shown in Figure 4.2. The silicon tetrachloride was supplied by BDH Ltd., and distilled under a nitrogen purge before use. The fraction boiling between 50.0° and 53.0°C was used. (Published BP = 57.5°C). The rather low boiling point was attributed to the cooling effect of the nitrogen purge.

A yield of 47.5 per cent on the sodium used was obtained. The boiling range of the product collected was 130° - 150°C at 1 Torr, and $\eta_D^{25} = 1.5605$ (Published values are 169° - 171°C at 12 Torr, and $\eta_D^{25} = 1.5638$). In view of the rather lengthy procedure involved in this preparation (the NaSET being prepared and separated, and subsequently reacted with SiCl₄ in toluene), it was modified to include only a single step, using the apparatus illustrated in Figure 4.1. Sodium wire (15g) was reacted with EtSH (50 ml) in 125 ml of toluene.



SiCl₄ (20 ml) dissolved in toluene (20 ml) was then added for the second part of the reaction, and the mixture slowly heated to reflux.

Vacuum was applied after the mixture was subsequently cooled, and the solvent pumped into the cold trap. The product was then distilled under vacuum into the receiver. The boiling range of the fraction collected was 115° - 120°C at 0.05 Torr, and $\eta_D^{25} = 1.5612$. It had an identical infra-red spectrum to the earlier material (Figure 4.3). Carbon

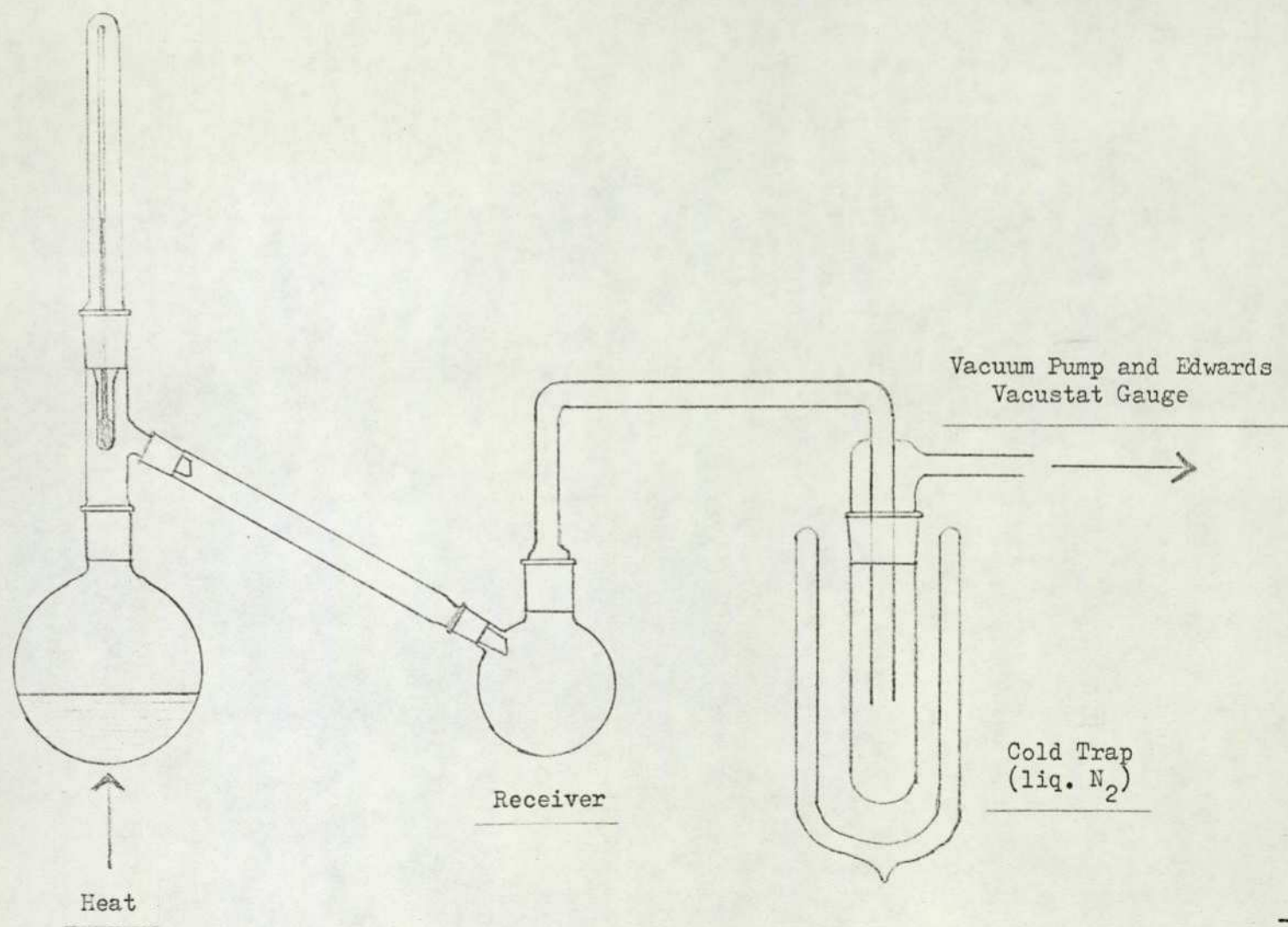


Fig. 4.1 Apparatus for the distillation of $\text{Si}(\text{SR})_4$.

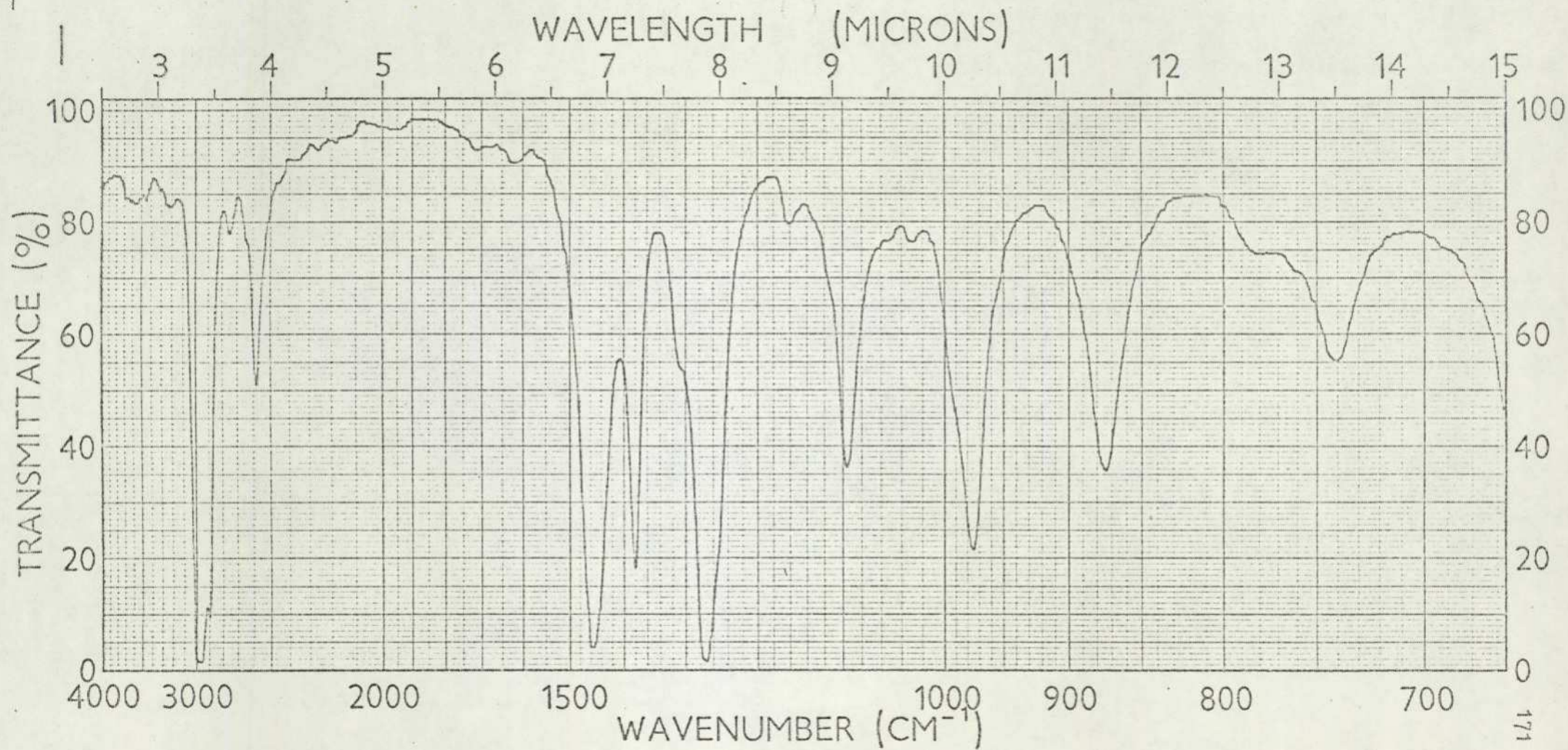


Fig. 4.2 Infrared Spectrum of Ethyl Mercaptan. 0.025mm NaCl cell.

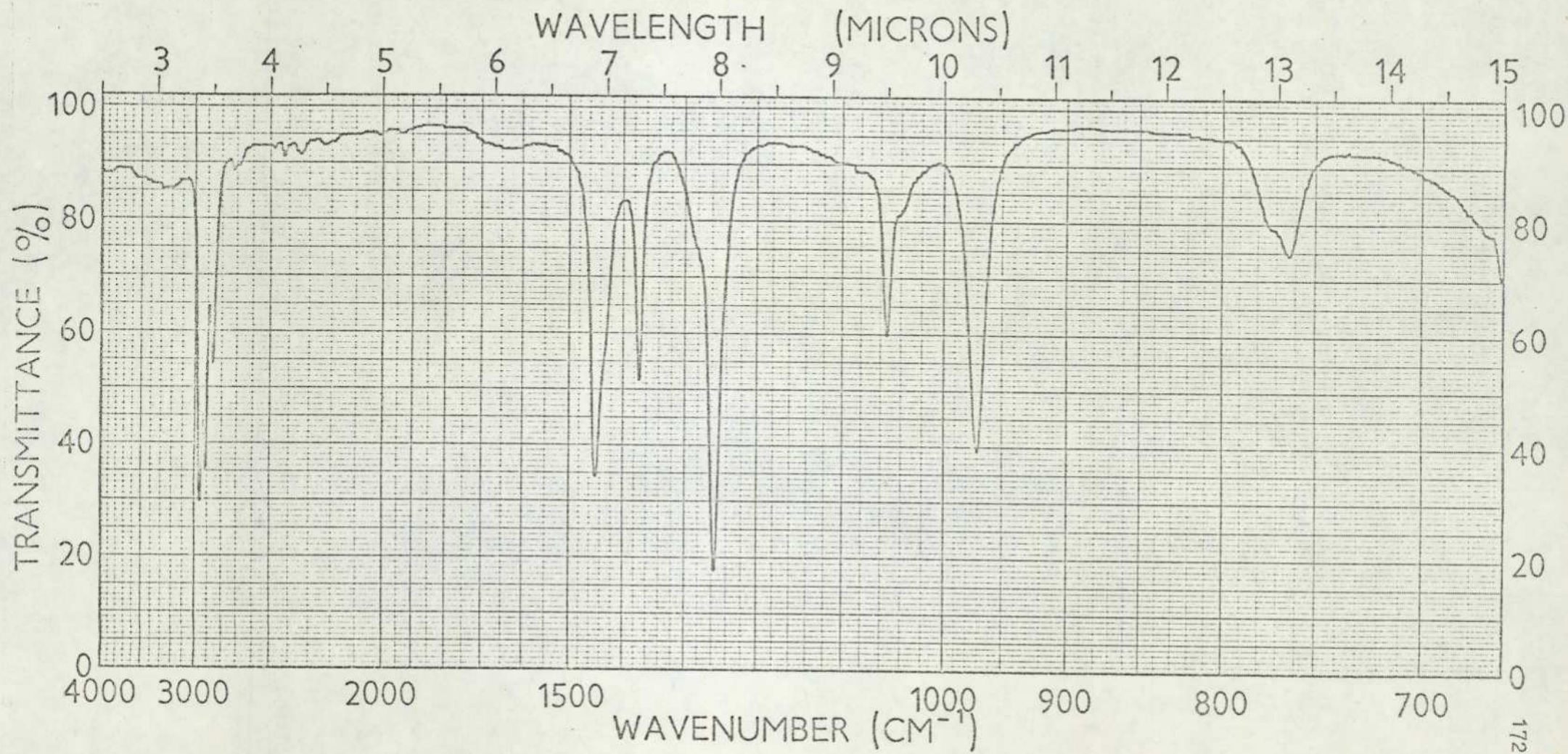


Fig. 4.3 Infrared Spectrum of $\text{Si}(\text{SEt})_4$, NaCl plates.

hydrogen and nitrogen analysis was obtained with an F and M Model 185 analyser. Found:- C, 33.9; H, 7.5%; required for $\text{Si}(\text{SEt})_4$:- C, 35.2; H, 7.4%. In accordance with published findings, the material was relatively stable in air, and did not decompose during handling. It had a strong smell resembling ethyl mercaptan.

In order to investigate changes in the properties of the silicon mercaptide with change of the alkyl group, a sample was prepared using *n*-butyl mercaptan. This was supplied by Koch-Light laboratories, and was distilled before used (BP = 97.9°C - published value = 98.0°C). The published technique was employed (326), toluene being used as diluent. The product boiling between 235° and 240°C at 5 Torr was collected. $n_{25}^D = 1.526$. Reported values (327) are 200°C at 2 Torr; $n_{25}^D = 1.529$. The infra-red spectrum of this material is reproduced in Figure 4.5, and its general properties were similar to those of the ethyl derivatives.

A comparison of the infra-red spectra of the silicon mercaptides with the parent mercaptans (Figures 4.2-4.5) shows a strong similarity. The $\nu(\text{S-H})$ present as a weak band at 2600 cm^{-1} in the mercaptan is replaced by a Si-S band at higher wavelength. This band does not occur within the range of the present spectra, and is discussed below. Apart from this, only minor shifts and changes in the 'fingerprint' region below 1500 cm^{-1} were noted. This demonstrated that the thioalkoxy group is substituted unaltered in the mercaptide.

The two wide range spectra (Figures 4.7 and 4.8) of $\text{Si}(\text{SBU}^n)_4$ and $\text{Si}(\text{SEt})_4$ cover the Si-S region of $500\text{--}575\text{ cm}^{-1}$

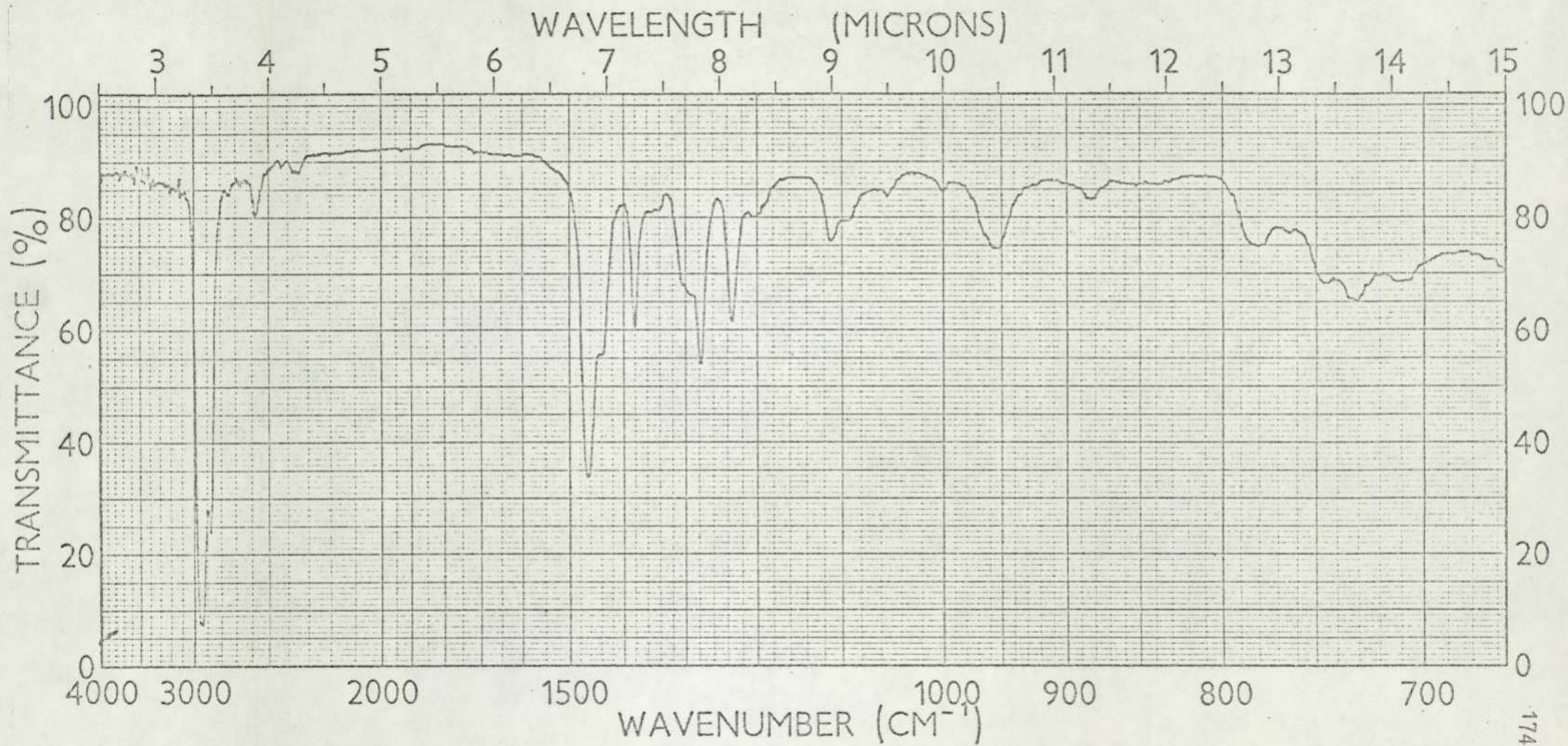


Fig. 4.4 Infrared Spectrum of n-Butyl Mercaptan. NaCl plates.

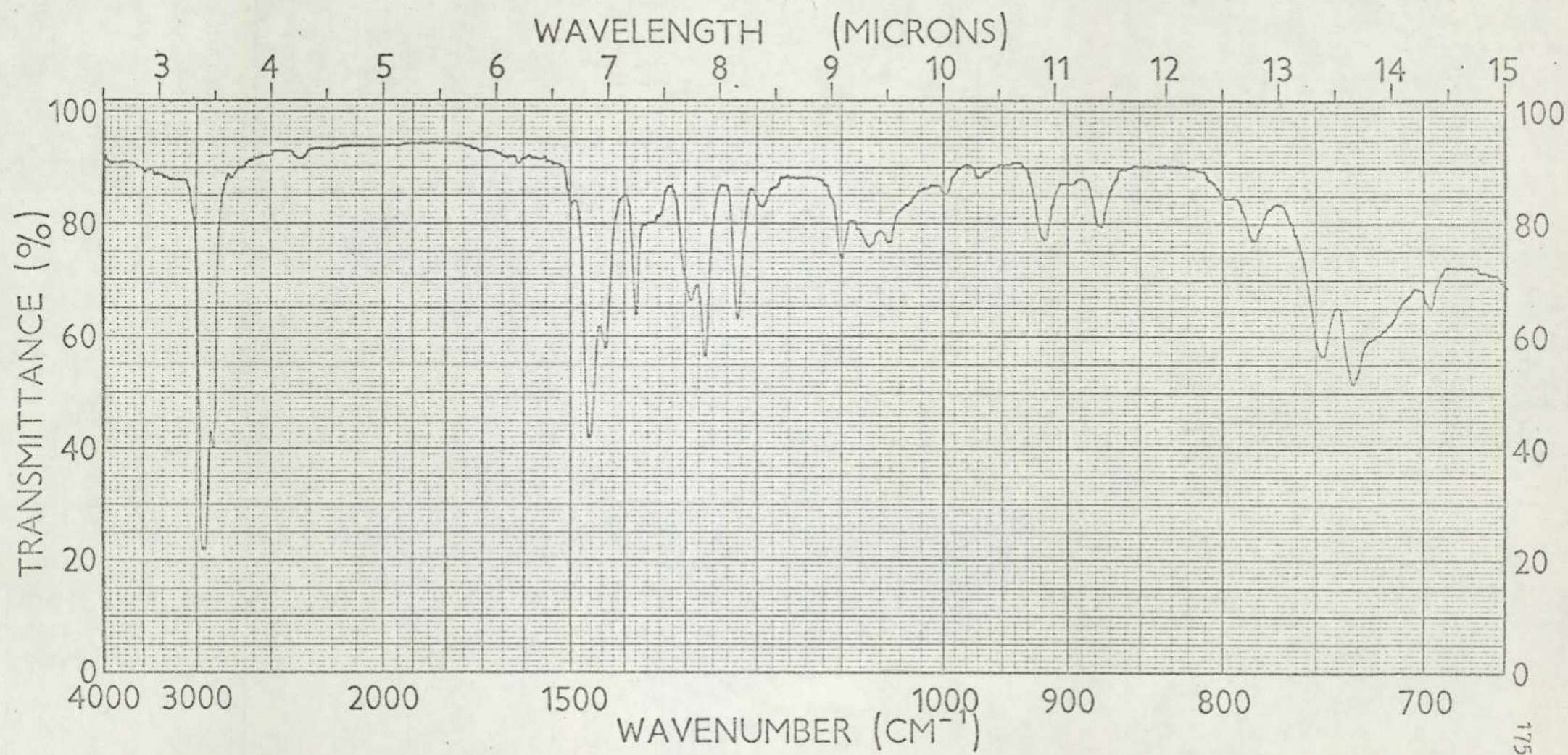


Fig. 4.5 Infrared Spectrum of $\text{Si}(\text{SBu}^n)_4$, NaCl plates.

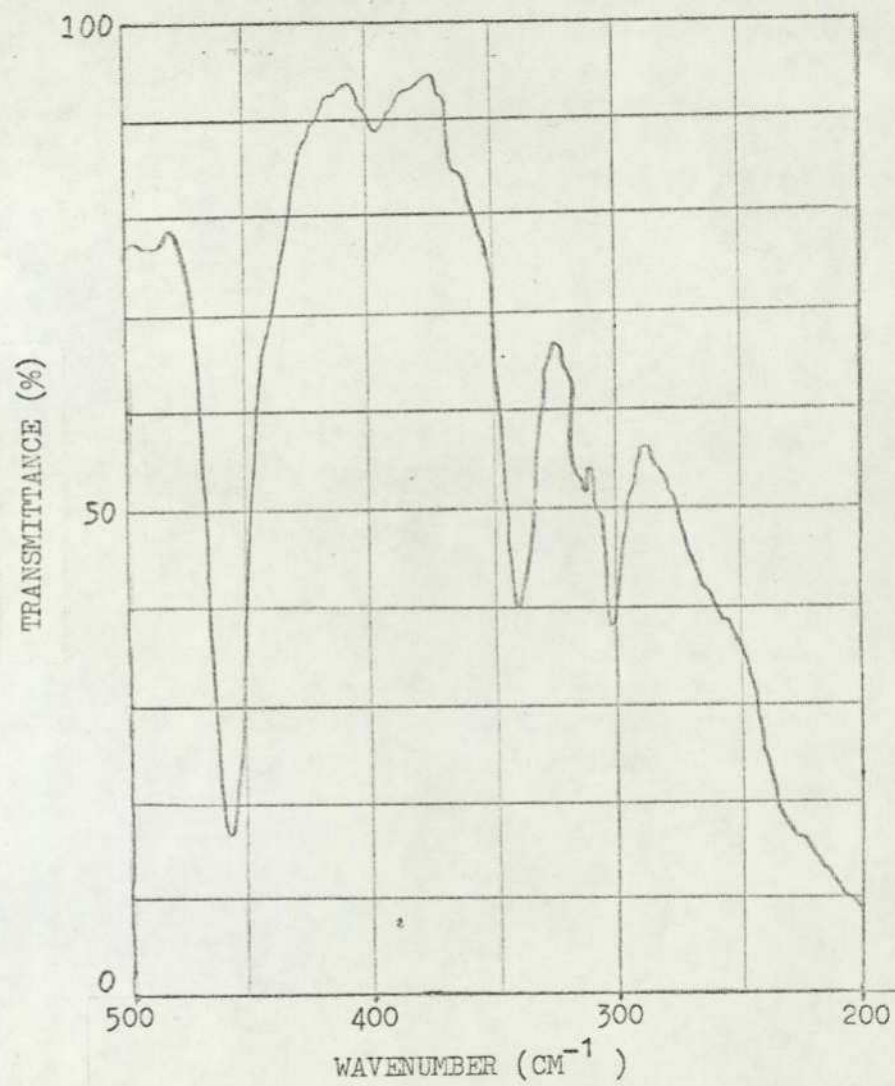
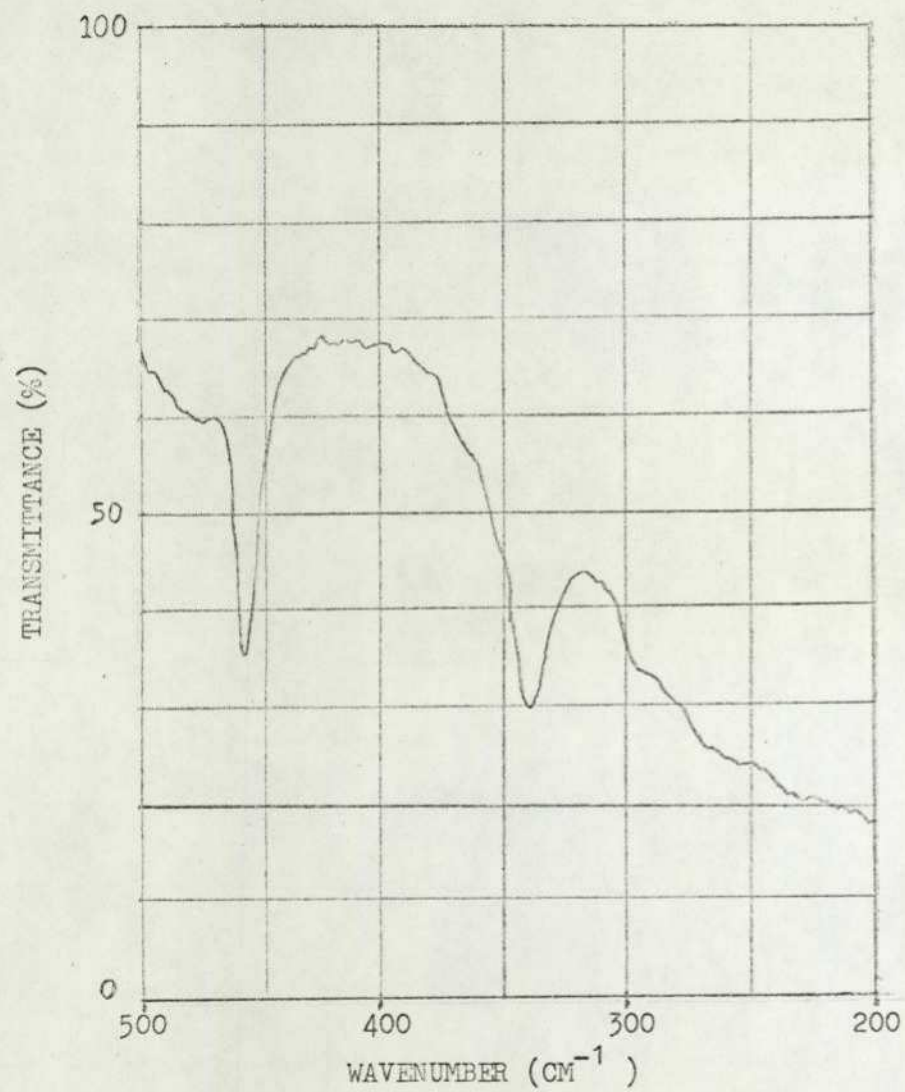
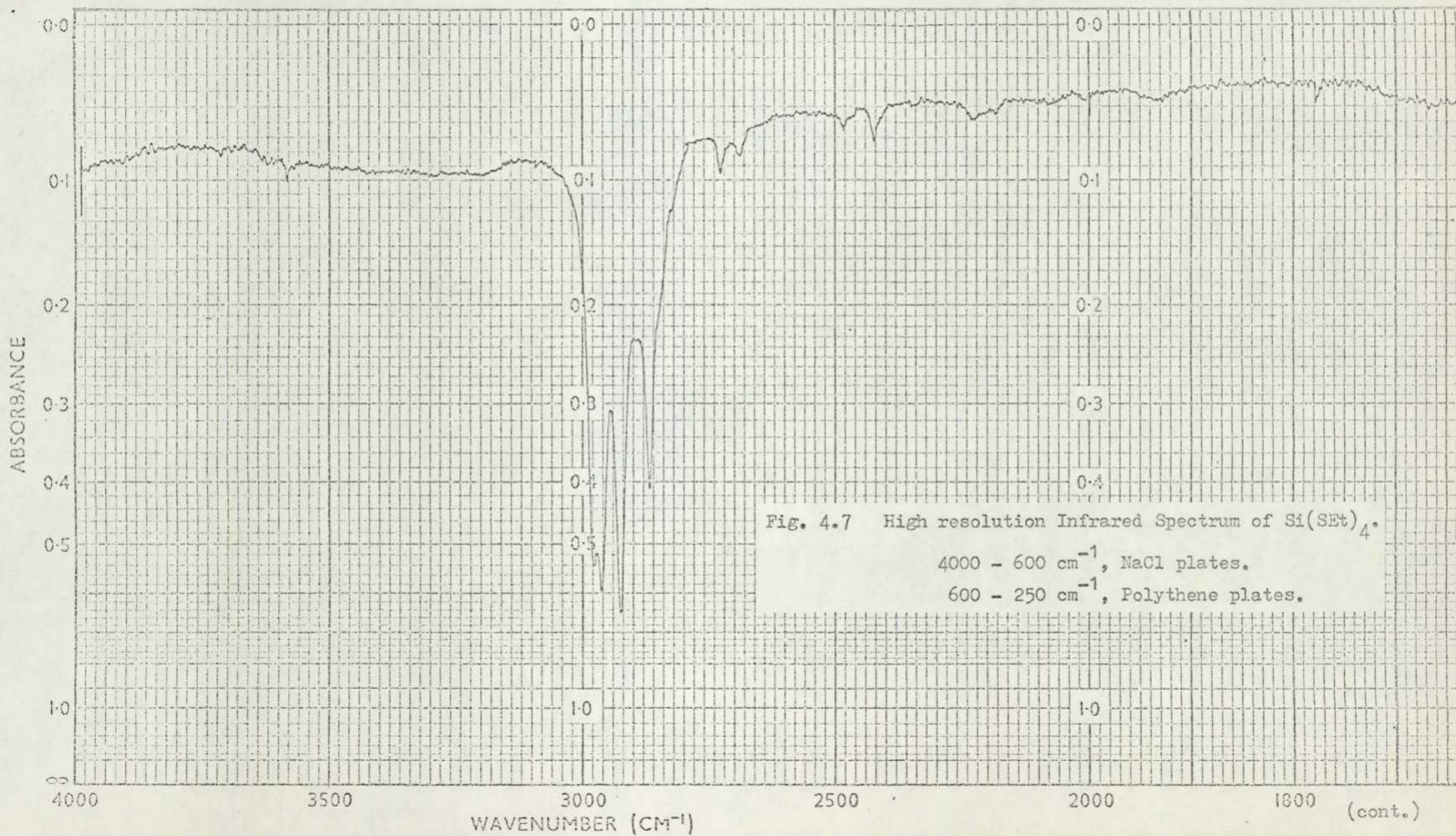
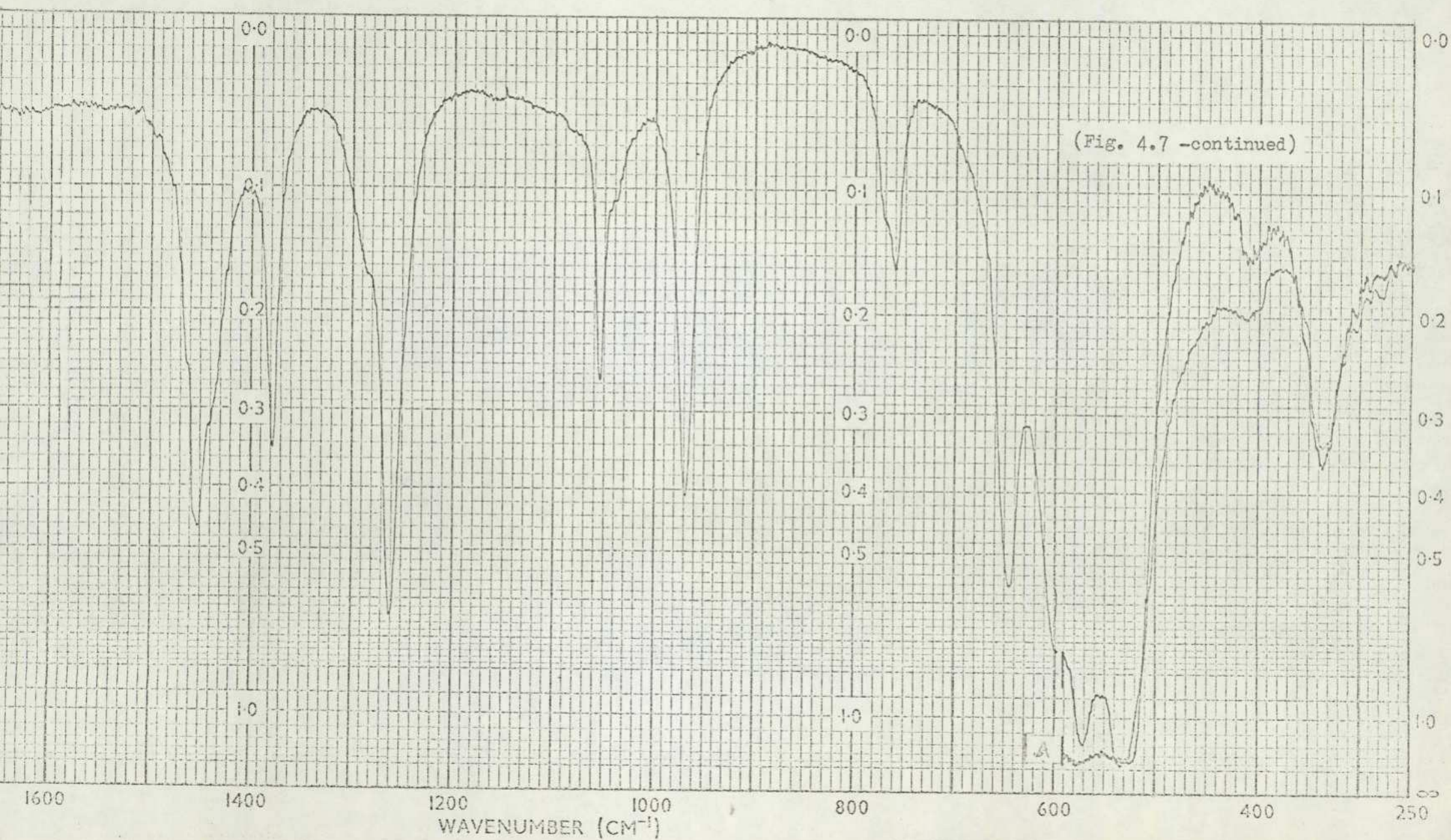
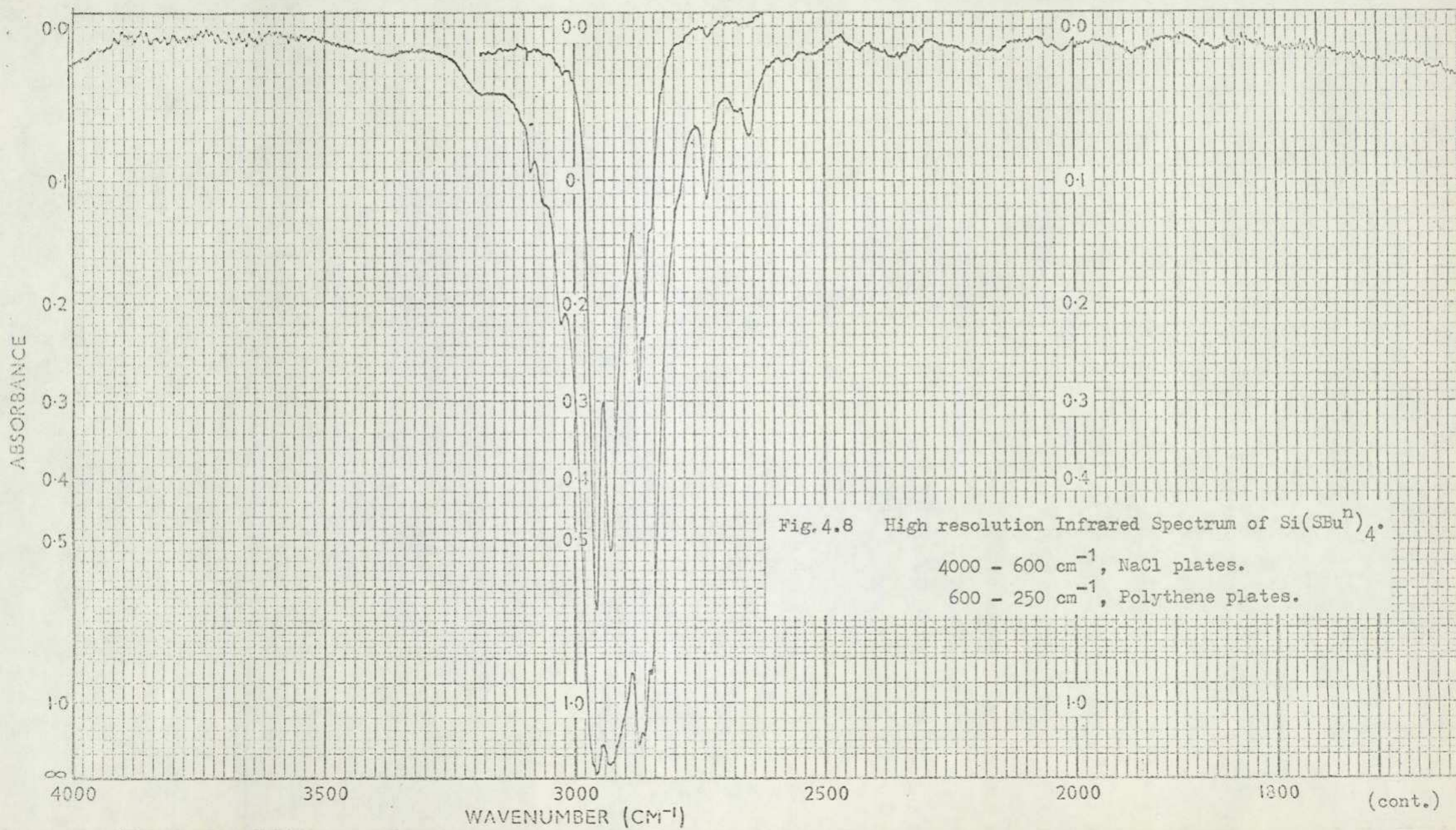
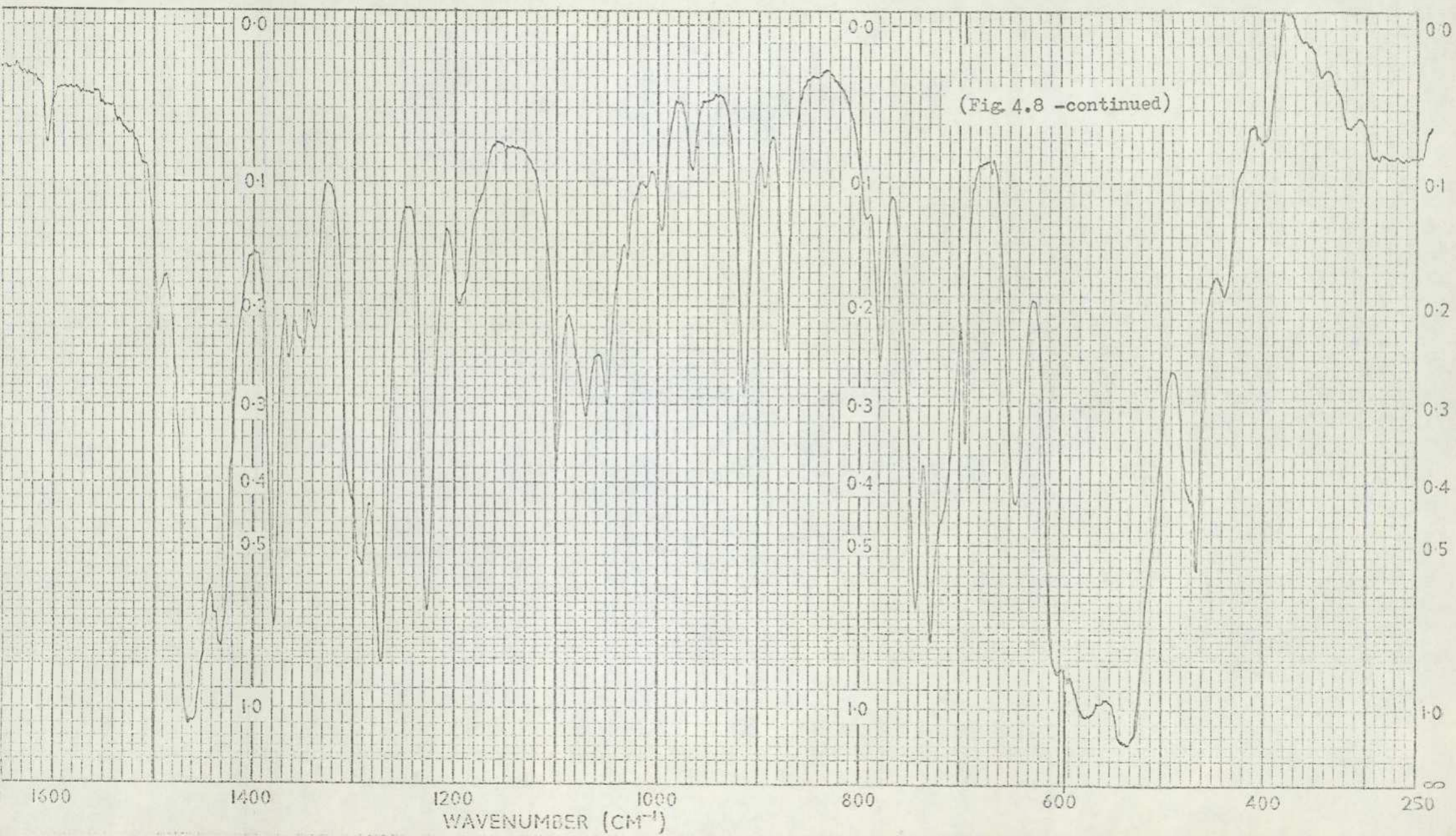


Fig. 4.6 Far-Infrared Spectra of (left) NaSEt and (right) NaSBuⁿ. Nujol mulls and polythene plates.









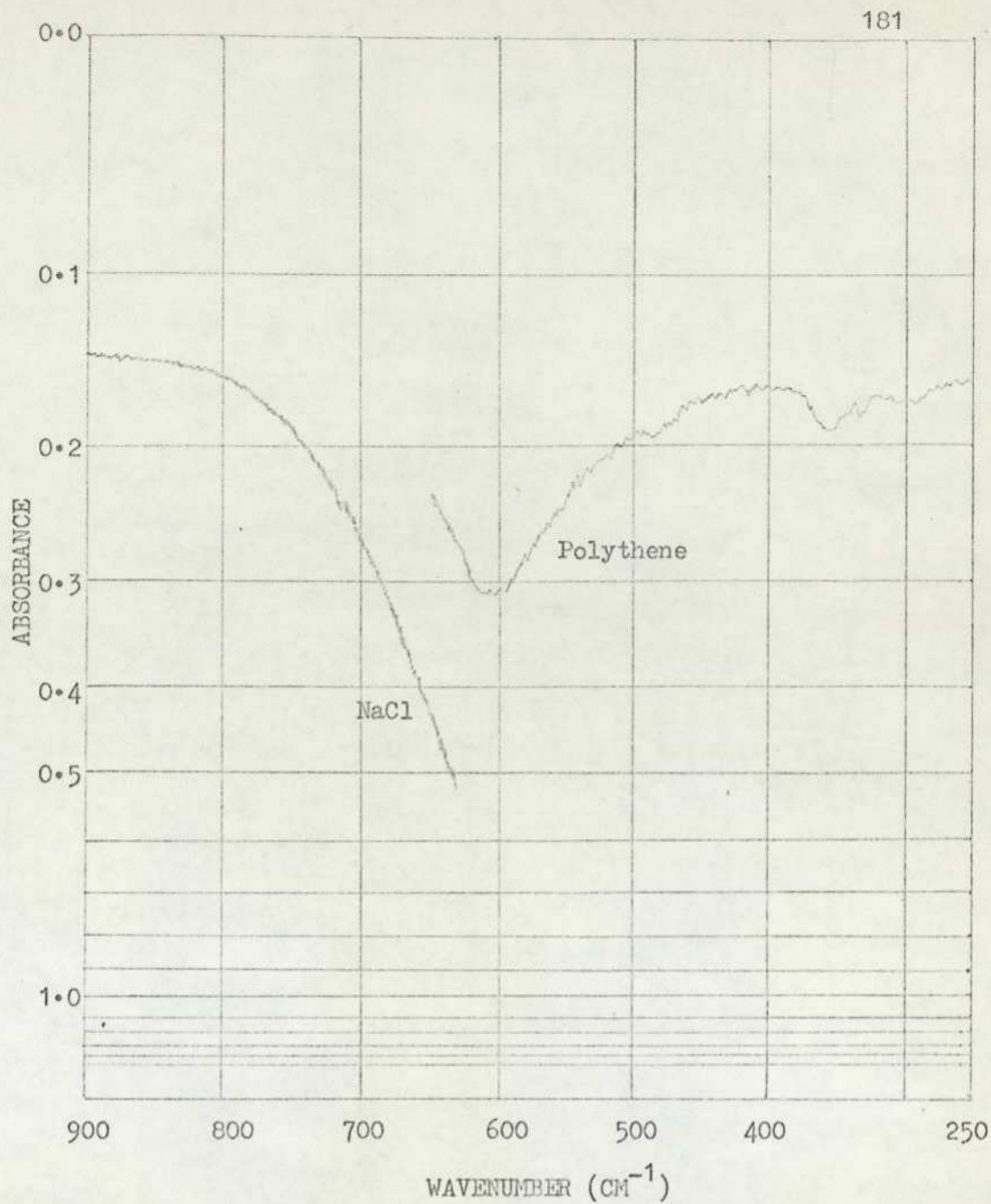


Fig. 4.9 Infrared absorption of NaCl and Polythene sample holder Plates between 900 and 250 cm⁻¹.

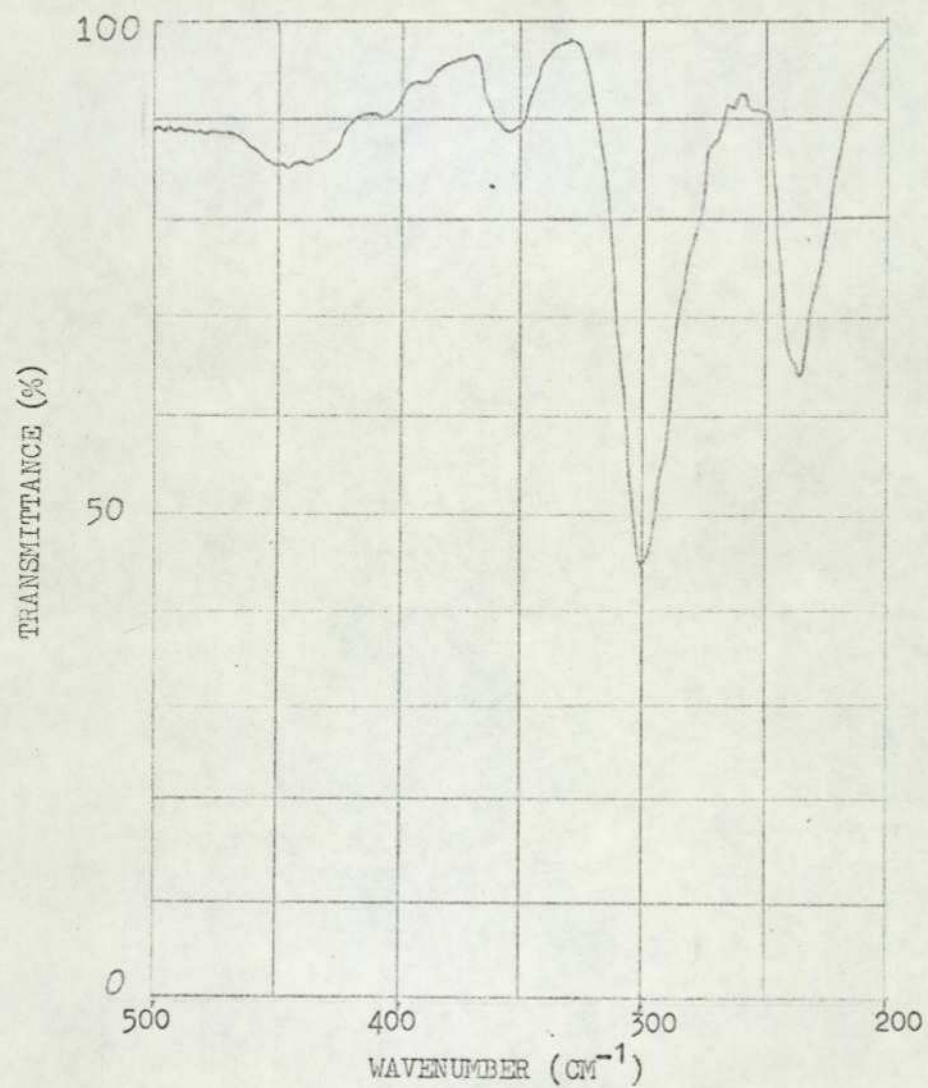


Fig. 4.10 Far-Infrared Spectrum of Copper n-butyl mercaptide, CuSBu^n . Nujol-polythene mull, polythene plates.

(see Section 3.2.3.2). A pair of strong absorptions at 530 cm^{-1} and 570 cm^{-1} in both compounds is probably attributable to this band being clearly visible over the broad polythene absorption at 555 cm^{-1} (Figure 4.9). Another band occurred in both mercaptide spectra at 645 cm^{-1} , and this is probably due to $\nu(\text{C-S})$ (359) or $\nu(\text{C-S-Si})$ (339). A strong band at 465 cm^{-1} occurred in the spectra of the *n*-butyl derivative, while the ethyl derivative exhibited a strong band at 335 cm^{-1} .

In an attempt to throw further light on the nature of these absorptions in the metal-sulphur region, the far infra-red spectra of the two sodium derivatives, NaSEt and NaSBu^n , were obtained (Figure 4.6). Strong absorptions near 460 cm^{-1} and 340 cm^{-1} were observed, and NaSBu^n also had a peak near 300 cm^{-1} . Either the 460 cm^{-1} or the 340 cm^{-1} band could be attributed to $\nu(\text{Na-S})$, but in view of the appearance of a band near 465 cm^{-1} in $\text{Si}(\text{SBu}^n)_4$, it is suggested that the 340 cm^{-1} absorption is best assigned to $\nu(\text{Na-S})$. $\nu(\text{S-S})$ is known to occur in the 460 cm^{-1} region (359), although it is generally found above 500 cm^{-1} (385). It is therefore suggested that the band at 465 cm^{-1} in the present spectra is due to oxidation of the sample during handling, with the formation of disulphide. The absence of this band in $\text{Si}(\text{SEt})_4$ is not explained, however, as this material would not be expected to be especially resistant to oxidation.

As a final approach to the understanding of these spectra, a sample of cuprous *n*-butyl mercaptide CuSBu^n , was prepared from Cu_2O and the thiol (360). This material is reported to be stable towards oxidation and moisture (361). Two bands

Band (cm^{-1})	Suggested Assignment	NaSEt	NaSBu ⁿ	CuSBu ⁿ	Si(SET) ₄	Si(SBu ⁿ) ₄
240	ν (Cu-S)			-		
300	-S-Bu ⁿ		-	-		-
340	ν (Na-S)	-	-		-	
460	ν (S-S)	-	-			-
530	} ν (Si-S)				-	-
570					-	-
645	ν (C-S)				-	-

Table 4.1 Summary of Far Infrared Correlations.

were observed in the far infra-red spectrum (Figure 4.10) at 240 cm^{-1} and 300 cm^{-1} . The absence of a band at 460 cm^{-1} , found in both the sodium and the silicon *n*-butyl mercaptides, adds confirmation to the assignment of this band to disulphide present as an impurity. The band at 240 cm^{-1} in Cu S Bu^n is probably attributed to $\nu(\text{Cu-S})$. The strong peak near 300 cm^{-1} in the spectra of both the copper and sodium *n*-butyl mercaptides, and several weak peaks in this region of the spectrum of the silicon derivative, are probably assigned to the S-Bu^n group.

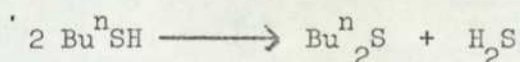
The tentative assignments made from these spectra are summarised in Table 4.1. As the (S-S), (C-S) and (S-H) bands are only strongly observed in the Raman spectrum (385), these assignments cannot be considered as conclusive.

4.2.2.2 Attempted Preparation of Aluminium Mercaptide Derivatives from Aluminium Halides or Metallic Aluminium

Reaction of AlCl_3 or SiCl_4 with Mercaptan

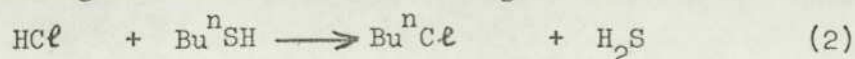
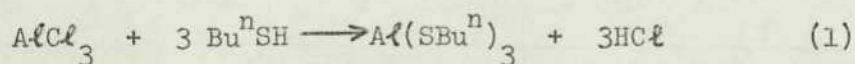
In the introduction to this chapter it was indicated that although Si(OR)_4 could be prepared by direct reaction of SiCl_4 and the alcohol, no analogous route was reported for the formation of Si(SR)_4 from SiCl_4 and the thiol. Instead, the sodium salt of the mercaptan was always used. In the study of the possible formation of Al(SR)_3 from AlX_3 ($\text{X} = \text{halogen}$), the direct reaction with thiol was initially investigated. For purposes of comparison, the reaction of thiol with SiCl_4 was also investigated at the same time. *n*-Butyl mercaptan was used for this work, as it possessed a sufficiently high boiling point (98.5°C) to permit a reasonably high reaction temperature.

In spite of prolonged refluxing under nitrogen, no reaction was observed with the silicon reaction, which remained colourless, and separated into its constituents on subsequent distillation. In the case of the aluminium reaction, the chloride appeared to dissolve in the thiol in the cold to give a yellow oily liquid. The mixture was then heated to reflux under nitrogen for a total of about 8 hours. During the heating, the mixture became dark in colour, and H_2S was liberated, being detected by its distinctive smell and action on lead acetate paper. The product from the reaction did not have the characteristic smell of the mercaptan, and its IR spectrum (Figure 4.11) was similar to that of the mercaptan (Figure 4.4) except that the (S-H) absorption at 2580 cm^{-1} was missing, and certain peaks around 1400 cm^{-1} were shifted slightly. This is consistent with the spectrum of 1-butyl sulphide or disulphide, and indicates a reaction of the type:



No H_2S was evolved in the absence of aluminium chloride, which apparently catalyzed the reaction. On attempting to distil the mixture, only a few drops of liquid were obtained, and this had the same IR spectrum as that obtained before distillation. The solid residue reacted violently with water with evolution of only HCl , and so was presumably aluminium chloride.

The only other apparent explanation for the liberation of hydrogen sulphide in this reaction would be interaction of the HCl formed in the main reaction with further mercaptan:-



This behaviour has been noted with the corresponding alkoxides, chiefly with the tertiary butyl group (321, 322). However, the

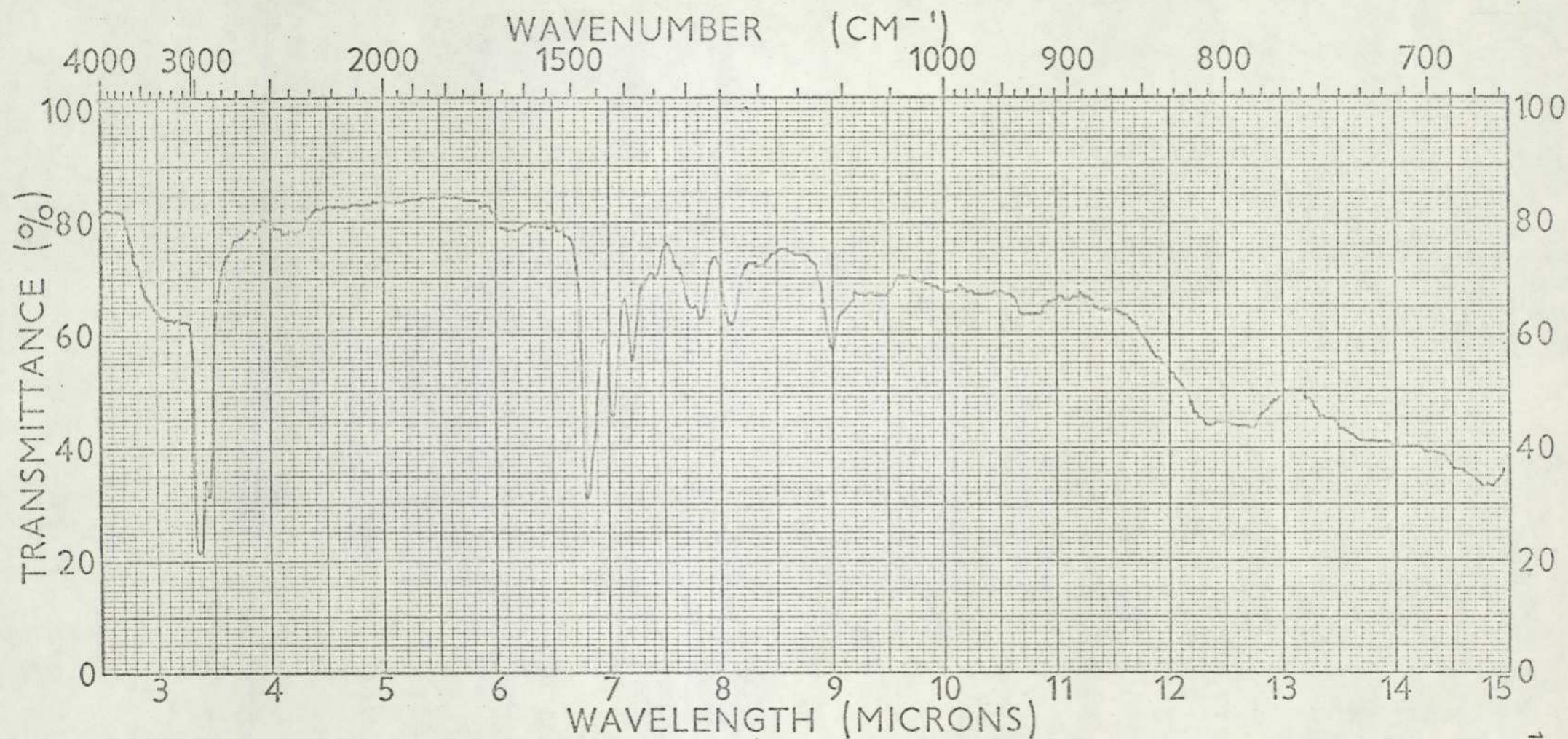
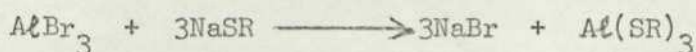


Fig. 4.11 Infrared Spectrum of the product from the reaction of AlCl_3 with Bu^nSH .
NaCl plates.

infra-red spectrum did not show any adsorption around $700\text{--}800\text{ cm}^{-1}$, corresponding to R-Cl , which discounts the possibility of this reaction.

Reaction of AlBr_3 with Sodium Mercaptide

As aluminium chloride did not react directly with mercaptan, further experiments employed the sodium salt of the mercaptan in the presence of an inert solvent.



Partial substitution to form $\text{Br}_x\text{Al}(\text{SR})_{(3-x)}$ must also be considered.

AlBr_3 was used rather than AlCl_3 , as it is more soluble in toluene, a suitable inert solvent. Literature solubilities (364) are:-

AlBr_3 , 42.5 g/100 g saturated solution (20°C) and AlCl_3 , 0.2 g/100 g saturated solution (17°C).

Initially, commercial (anhydrous) aluminium bromide supplied by B.D.H. was used. A saturated solution was prepared in the dry box, using sodium-dried toluene. It was dark green-brown in colour. 50 ml of this solution were refluxed with NaSEt (7 g) prepared as described in the preparation of $\text{Si}(\text{SEt})_4$ (Section 4.2.1.1). The experiment was conducted under nitrogen, and after 3 hours the liquid became colourless, and the character of the solid changed to a cream coloured powder from the flocculent white material used. Reaction to form insoluble sodium bromide was therefore indicated. The mixture was filtered in the dry box.

The liquid phase was distilled, and found to consist wholly of toluene, (bp 110°C), only a trace of oily residue remaining. The solid phase was extracted with dimethyl sulphide. Only very little extract was obtained, but it was possible to obtain its infra-red spectrum (Figure 4.12). Comparison with the spectrum of dimethyl

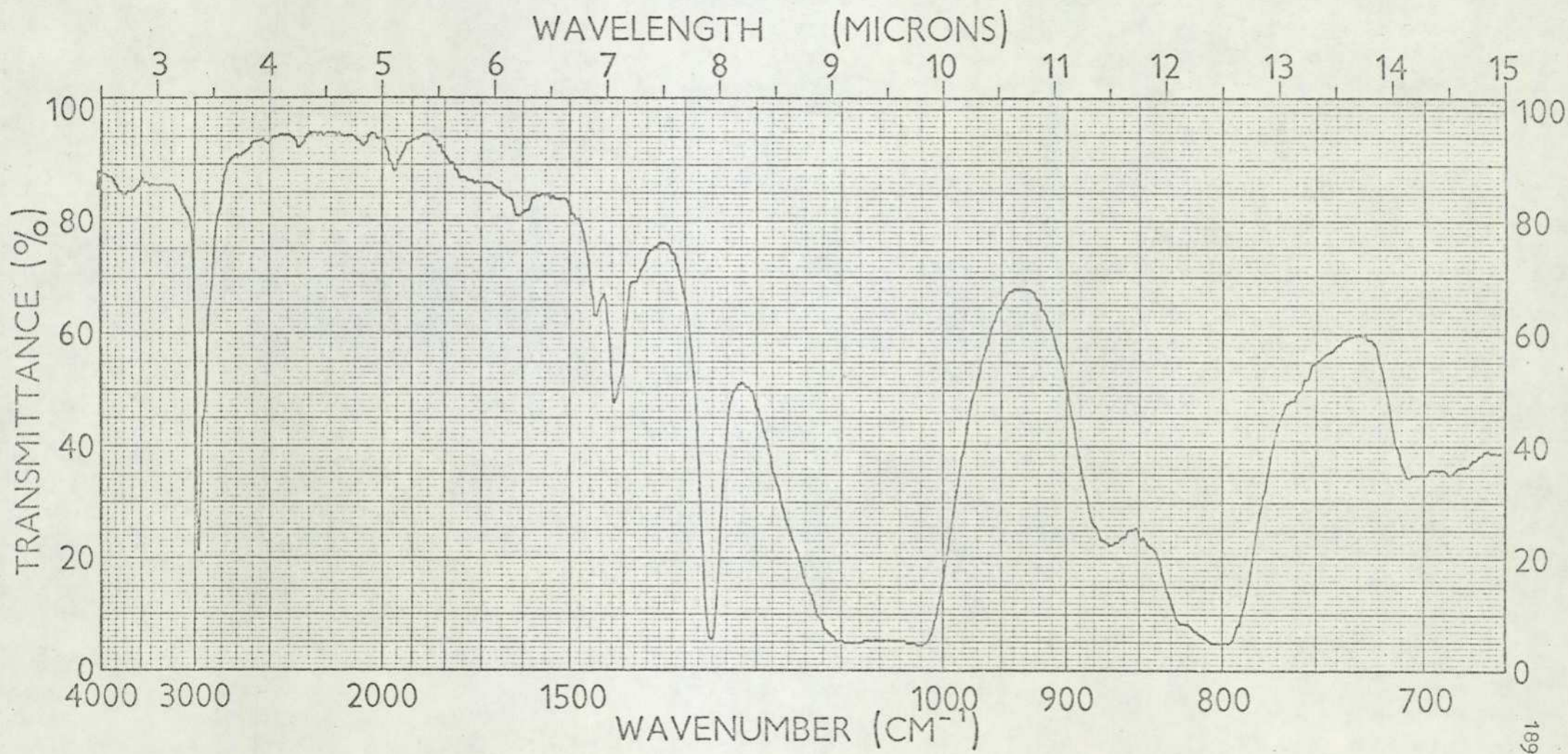


Fig. 4.12. Infrared Spectrum of the material isolated by extraction with dimethyl sulphide from the reaction between AlBr_3 and NaSEt in toluene. NaCl plates.

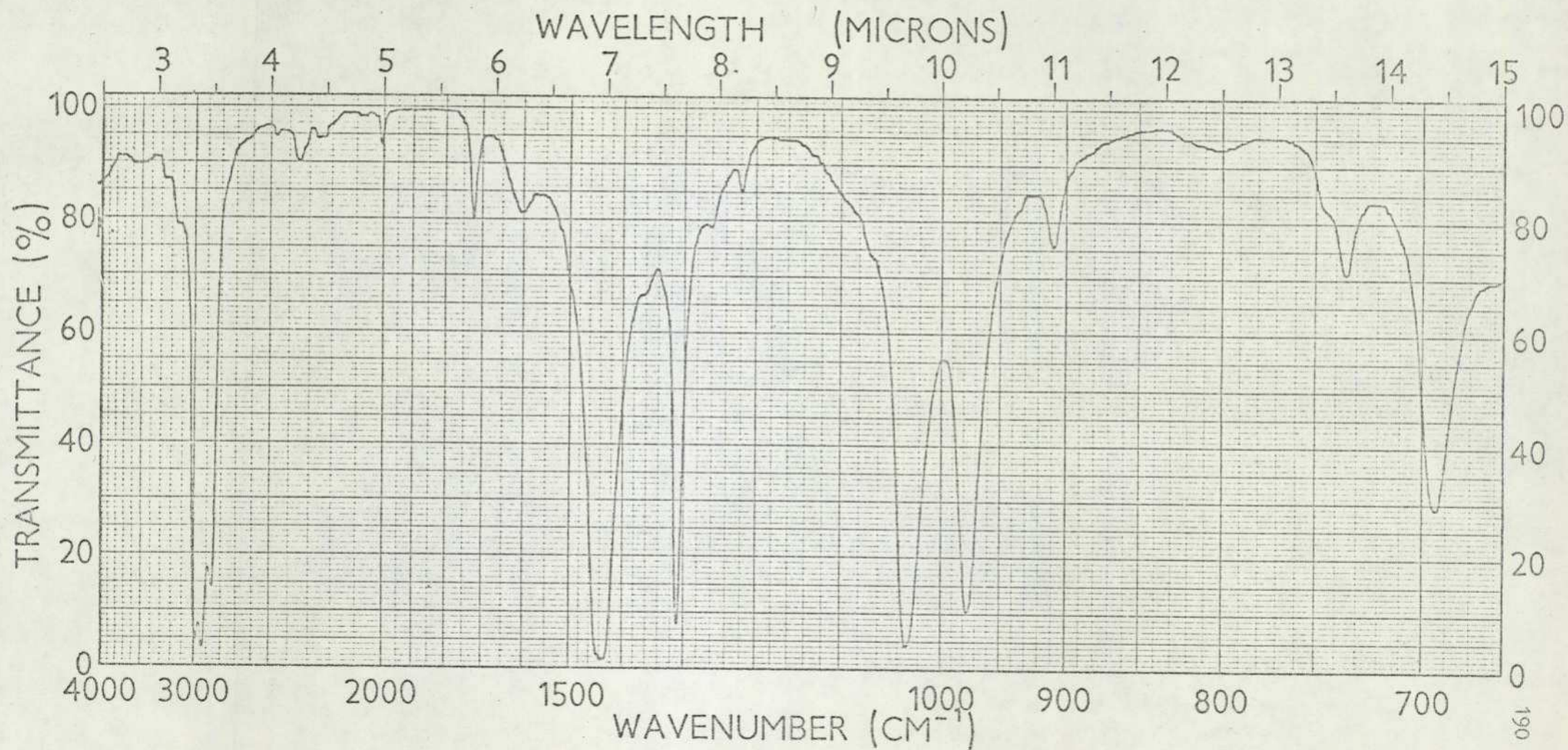


Fig. 4.13 Infrared Spectrum of dimethyl sulphide. NaCl plates.

sulphide (Figure 4.13) showed marked differences, notably the absence of strong peaks at 1310, 978 and 693 cm^{-1} , and the presence of strong absorptions near 810 cm^{-1} , 870 cm^{-1} and 1260 cm^{-1} , and the very broad absorption near 1060 cm^{-1} . Therefore, the organic residues in the product spectrum were not due to unremoved dimethyl sulphide. Certain similarities existed between the spectra of the product and those of ethyl mercaptan and $\text{Si}(\text{SEt})_4$ (Figures 4.2 and 4.3 respectively). Therefore, it is possible that the present material contained the S-Et group, although marked differences existed between this spectrum and that of Et_2AlSEt and $\text{EtAl}(\text{SEt})_2$ later obtained (Figure 4.19 and 4.21).

It was apparent, therefore, that whilst the results of this experiment were encouraging from the point of view of the ultimate feasibility of the reaction, insufficient product was obtained to enable a satisfactory evaluation to be performed, assuming that the oily residue extracted with dimethyl sulphide was the material required, $\text{Al}(\text{SEt})_3$. The reaction was repeated, using different solvents to extract the product from the reaction mixture, but with essentially similar results.

The effect of using freshly prepared aluminium bromide was investigated. It was prepared by a method based on that described by Brauer (370, p 213). The apparatus used is illustrated in Figure 4.14. Aluminium wire was placed in the flask, which was purged out with nitrogen after evacuating it to remove air and moisture. Sulphuric acid-dried bromine was added, and the mixture refluxed for three hours. The tube to the receiver was wrapped with heating tape, and the aluminium bromide distilled off and transferred to the dry box. When it was dissolved in toluene, a very dark green solution was formed that fumed in air.

The solution of AlBr_3 was reacted with NaSEt as before.

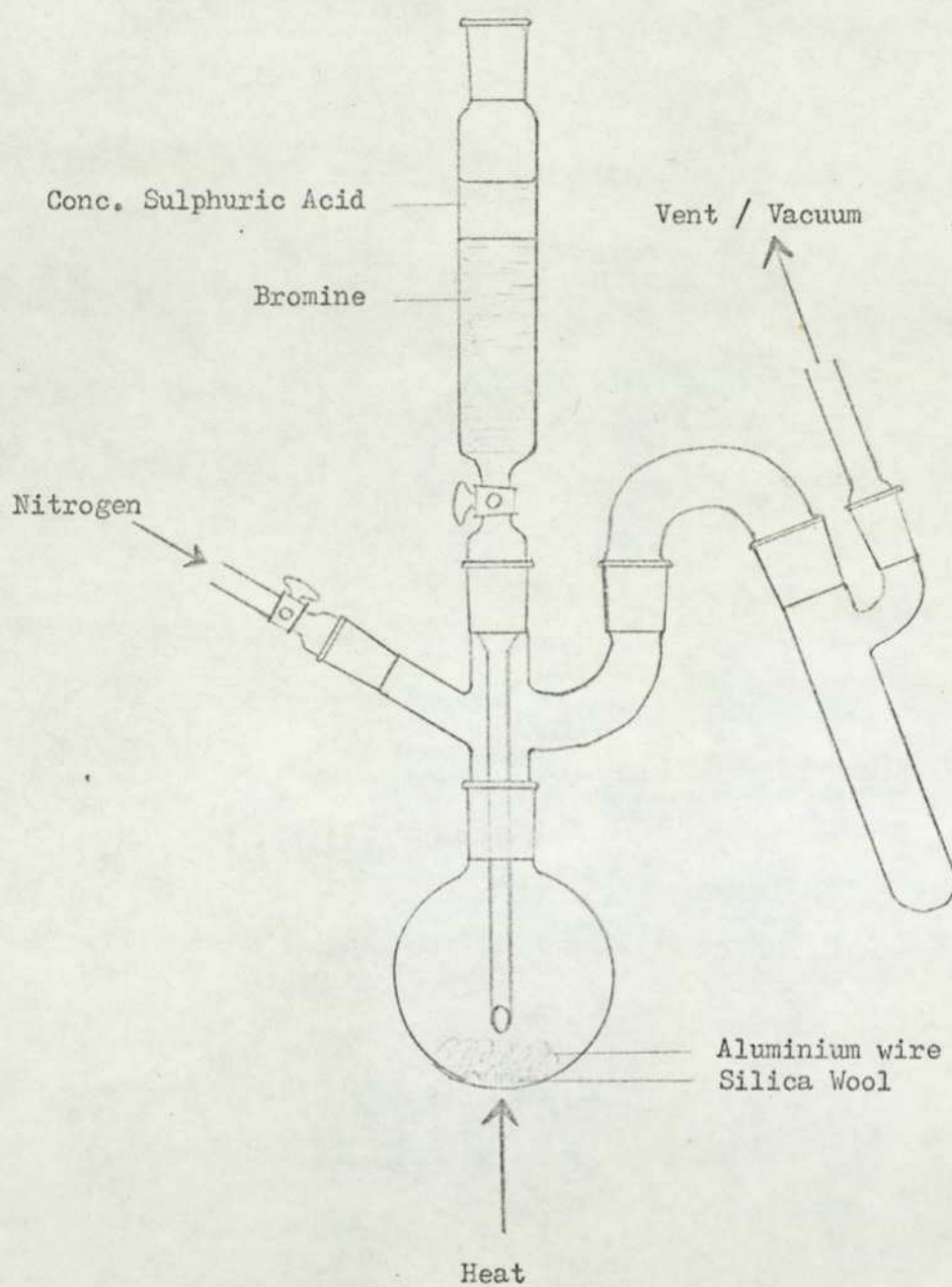


Fig. 4.14 Apparatus used to prepare AlBr_3 from the elements.

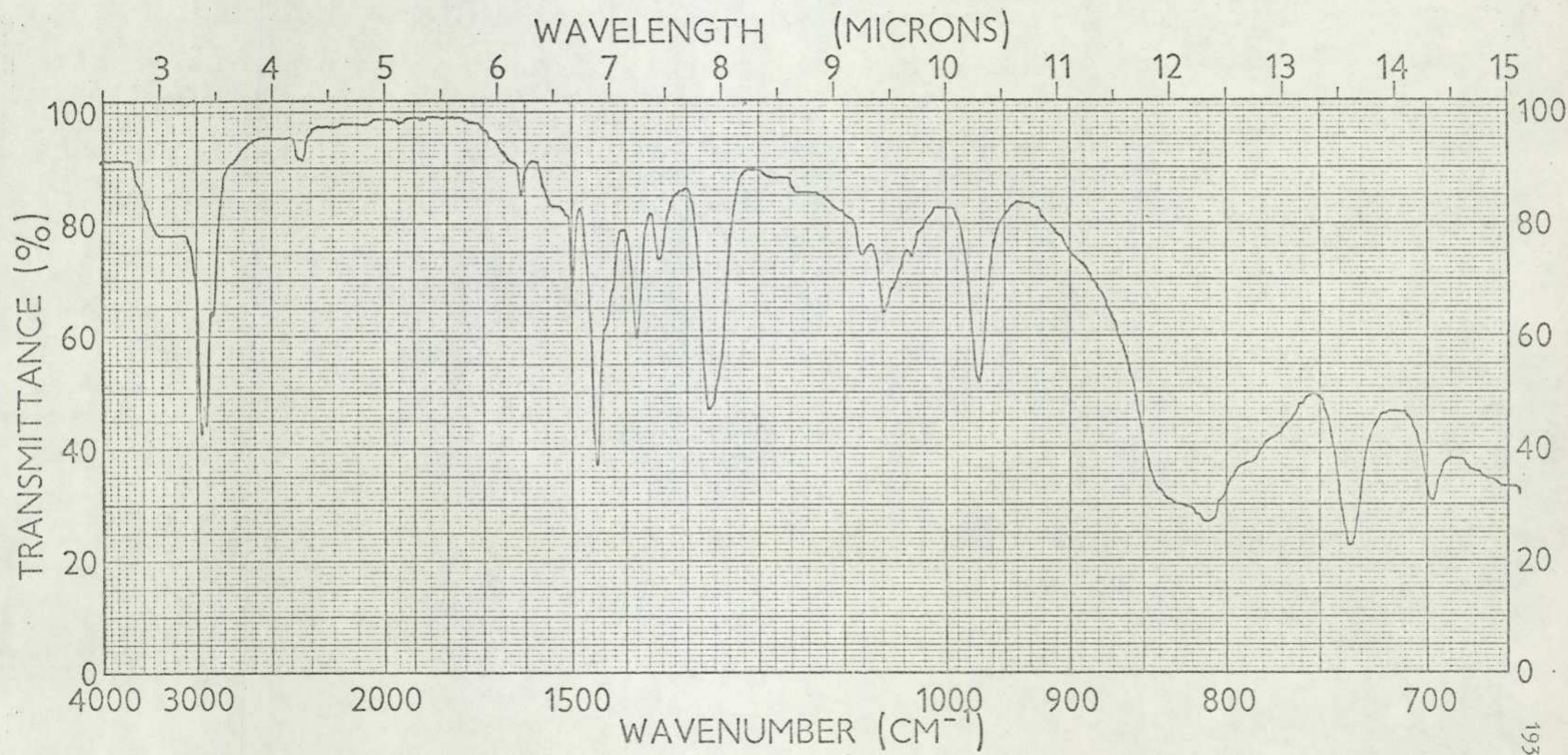


Fig. 4.15 Infrared spectrum of the product isolated from the liquid phase after reaction of AlBr_3 with NaSEt in toluene. NaCl plates.

As the materials were mixed, the colour of the AlBr_3 solution was removed, indicating reaction to be occurring. The AlBr_3 was added until just present in excess, and the mixture then refluxed under nitrogen for 60 minutes. It was then filtered in the dry box.

Only a trace of sulphur was detected in the solid phase, the bulk appearing in the toluene solution. A qualitative test employing sodium fusion was employed, the presence of sulphide in the fusion extract being detected by its intense purple colouration with sodium nitroprusside. The toluene solution was pumped down under vacuum to leave a few drops of oily residue. Its infra-red spectrum (Figure 4.15) showed peaks at 970 cm^{-1} and 1260 cm^{-1} , characteristic of EtSH and $\text{Si}(\text{SEt})_4$ (Figure 4.2 and 4.3), and similar peaks to those found in the spectrum of the dimethyl sulphide extract from the initial reaction (Figure 4.12). The spectrum also showed similarities to the spectra later obtained of Et_2AlSEt and $\text{EtAl}(\text{SEt})_2$ (Figures 4.19, and 4.21). The far infra-red spectrum (Figure 4.16) of the oily residue had a strong peak at 460 cm^{-1} , previously attributed to disulphide (Section 4.2.2.1).

It seemed therefore that only a very small amount of the required product, $\text{Br}_{(3-x)}\text{Al}(\text{SEt})_x$ (preferably with $x=3$) was formed in these reactions, and in view of the fact that it had appeared a substantial quantity of AlBr_3 was reacting, it was concluded that side reactions predominated. The infra-red spectra of the residue obtained from the latter reaction (Figure 4.15) was not identical to that of the dimethyl sulphide extract from the initial experiment (Figure 4.12), and a well characterized product was not therefore being obtained.

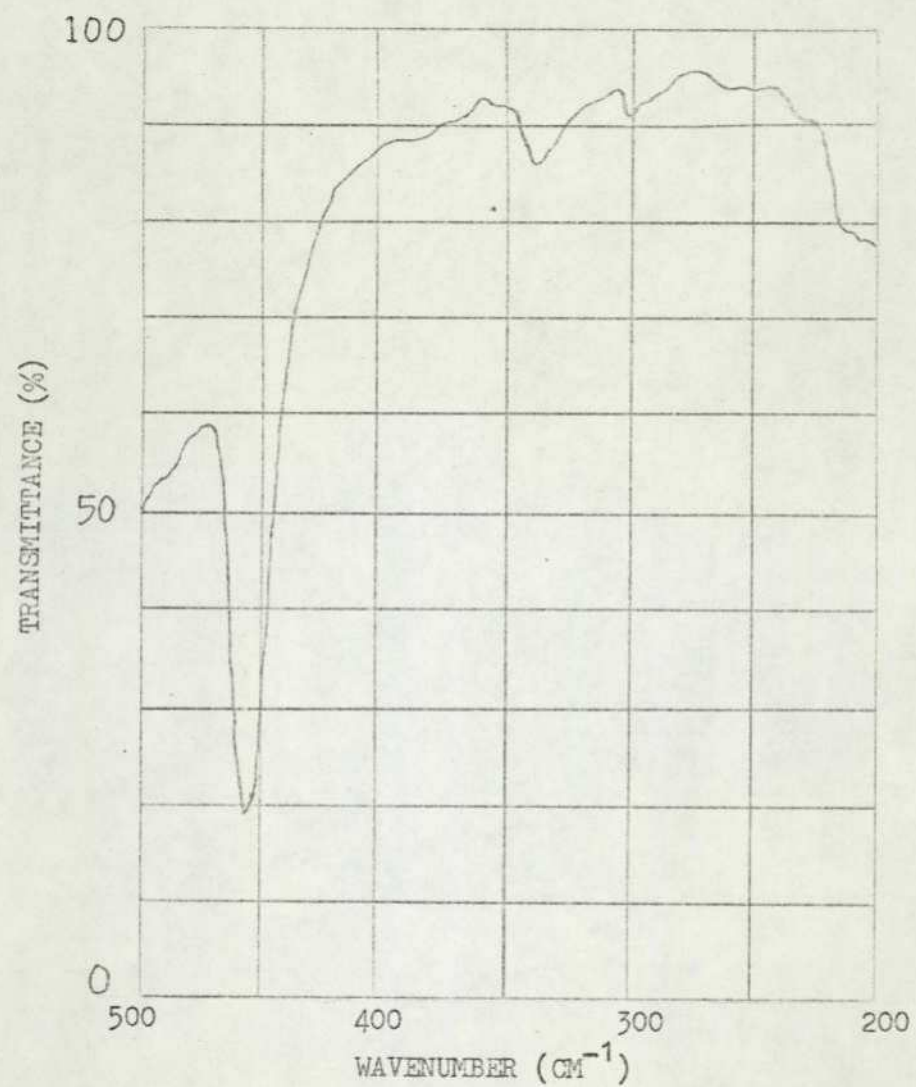


Fig. 4.16 Far-Infrared Spectrum of the product isolated from the liquid phase after reaction of AlBr_3 with NaSEt in toluene. Polythene plates.

Reaction of Aluminium Amalgam with Thiol

Reports exist (see Section 4.2.1.2) claiming that $Al(SR)_3$ may be prepared by the reaction of aluminium amalgam with a mercaptan:-



Several attempts were made at conducting this type of reaction, *n*-butyl mercaptan, ethyl mercaptan and thiophenol being the mercaptans used. They were carefully dried over calcium sulphate before use. Various techniques for amalgamating the aluminium were employed, using mercuric iodide or mercuric chloride, both before and during the reaction. In spite of the careful control of experimental conditions, with the strict exclusion of water, no tendency was observed for reaction to occur, the aluminium remaining unchanged. The possibility of obtaining aluminium mercaptides by direct reaction of aluminium with the mercaptan was therefore dismissed.

4.2.2.3 Preparation of Aluminium Mercaptide

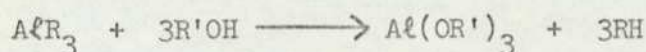
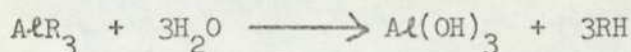
Derivatives from Triethyl Aluminium

In the investigation of the reactions of aluminium alkyls with sulphur compounds, triethyl aluminium, $AlEt_3$, was used. This material, in common with the other low carbon number homologues, is a highly reactive and pyrophoric colourless liquid. With increasing molecular weight, the trialkylaluminiums become less reactive and easier to handle. A further small decrease in activity accompanies replacement of one or two of the alkyl groups with halogen. In general, the most reactive compounds are the trimethyl, triethyl, tripropyl and triisobutyl derivatives. Spontaneous ignition in air does not normally occur with the longer chain-length derivatives, although ignition can occur from contact with flammable materials such as paper or cotton wool because of their large surface area and adsorbed moisture.

The highly reactive nature of these compounds is due to the high reactivity of the organometallic bond with oxygen and 'active hydrogen' compounds. During oxidation the oxygen enters between the carbon and aluminium atoms, with the formation of alkoxide bonds:-



Owing to their highly exothermic nature, such reactions must be carefully controlled. Of the reactions with 'active hydrogen' compounds, that with water is probably the most violent, being instantaneous and explosive in nature, although the reactions with alcohols are almost as severe:-



Therefore reaction with either sulphur or thiols would, by analogy with these reactions, be expected to lead to the required mercaptide derivatives, Al(SR)_3 . One of the more reactive alkyls would be required, which restricted the choice to either the trimethyl, triethyl or possibly the tripropyl derivative. Triethyl aluminium was used as it was readily available of purity >98 per cent through the British Petroleum Research Centre at Sunbury-on-Thames. Initially, a 25 per cent solution in benzene was obtained, as this was less dangerous to handle than the undiluted material. When handling techniques were well established, the undiluted material was obtained to permit greater control of reaction conditions.

The general background and safety aspects of this section of the work were obtained from two reports on the handling and nature of aluminium alkyls (366, 367). The material was obtained in three litre three-necked Pyrex flasks stored in boxes of sand, and transfer to reaction equipment was by means of all-glass syringes fitted with

stainless steel needles, using rubber septum caps at the withdrawal and injection points.

On receiving a fresh flask of alkyl, the first step was to fit the septum adaptor, shown fitted to a small flask in Figure 4.17(a). A supply of dry oxygen-free nitrogen was first arranged. BOC 'Oxygen-Free' grade was used, and dried by passing it through concentrated AR sulphuric acid. After passing through a glass wool tower to remove any acid spray it was passed up a tower containing finely divided potassium dispersed on sodium carbonate. A slow purge of nitrogen was passed through the side arm of the adaptor, both taps being open. A fine grade hypodermic needle was pushed through the septum to act as a bleed when the lower tap was closed, and the nitrogen flow left on for several minutes to ensure that all air and moisture were removed. A second nitrogen supply was then directed across one of the necks of the alkyl flask, its stopper quickly removed and the adaptor inserted, still with nitrogen issuing from it. Once fitted, the nitrogen supply to the adaptor was forced to leave via the hypodermic needle in the septum. The nitrogen supply tap was then closed, a few seconds allowed for the pressure in the alkyl container to fall to atmospheric, and then the flask tap was closed and the hypodermic needle removed.

When it was required to remove alkyl from the flask, a syringe (generally 50 ml) fitted with a 6 inch needle was used. The needle was inserted through the septum with the flask valve closed. Nitrogen was admitted through the side tube as before, and the syringe filled and removed several times until thoroughly purged. The flask tap was then opened and the needle pushed down until alkyl could be withdrawn. By keeping the nitrogen supply

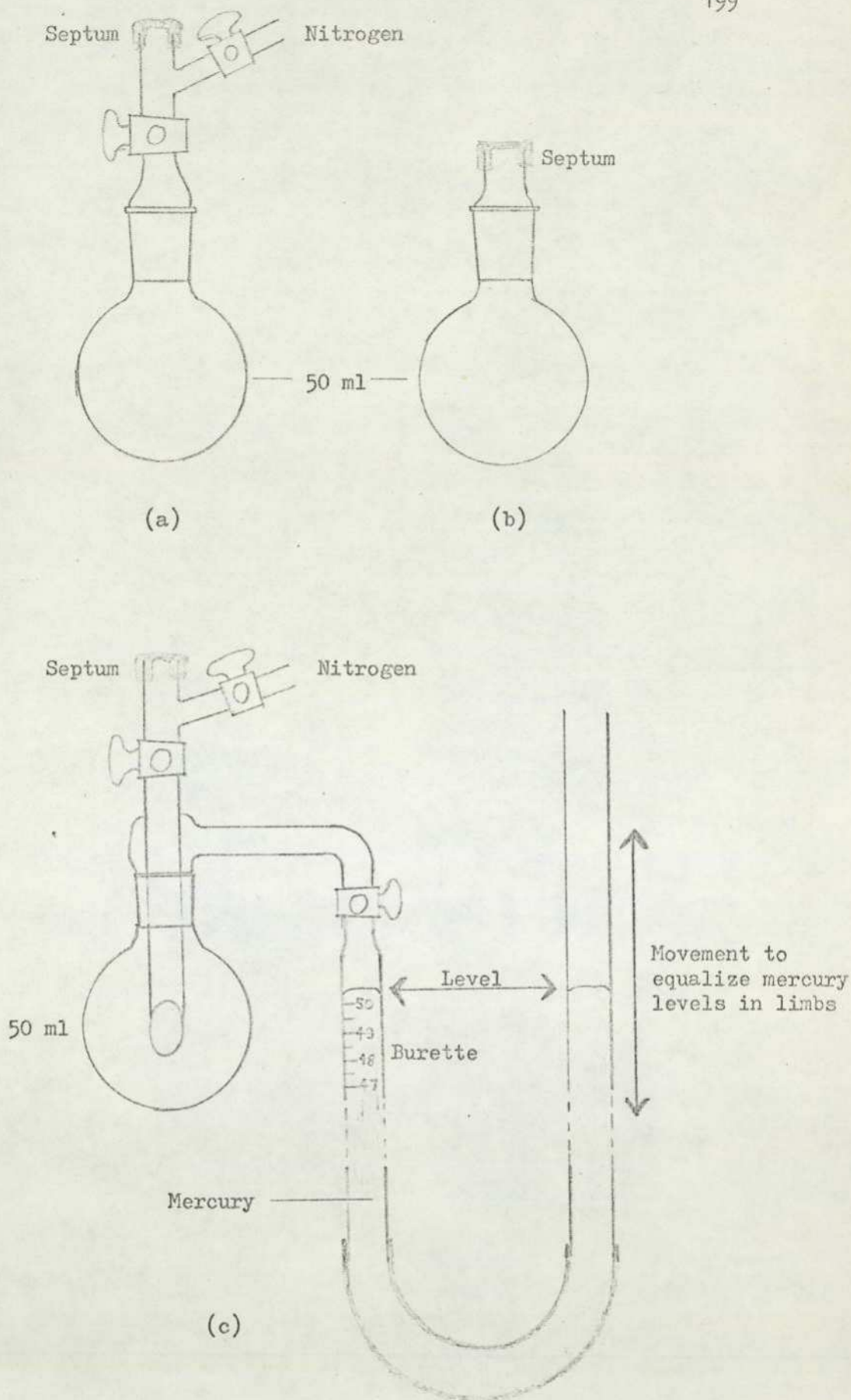


Fig. 4.17 Apparatus for small scale reactions of AlEt_3 .

pressure to 1 - 2 psig during this operation, a controlled removal of alkyl was effected. When the required quantity had been transferred to the syringe, the needle was withdrawn from the septum and the end quickly sealed with a rubber bung for transfer to the reaction equipment. The alkyl flask was then sealed as before.

This handling procedure was found to be quite satisfactory with the small quantities of alkyl involved. No fire or explosion was ever encountered. Contaminated equipment was washed out with a solution of 25 per cent isopropanol in di-n-butyl ether (366). All reactions involving alkyls were conducted in the fume cupboard, and the storage flasks kept separately. Dry powder fire extinguishers were on hand in case of accident, and face-shield and rubber gauntlets used when handling these compounds.

Two approaches were adopted in the examination of the reaction between triethyl aluminium and sulphur compounds. Initially, small scale reactions were carried out in a gas burette. This enabled the replacement of alkyl groups by thioalkyl groups on the aluminium to be followed by measurement of the volume of gas evolved:-



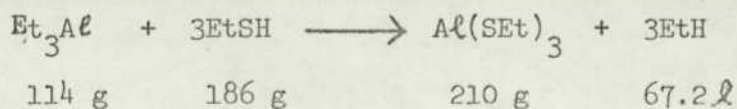
The apparatus used for this is illustrated in Figure 4.17c. Larger scale reactions were carried out in the apparatus shown in Figure 4.18. Thiols, sulphur and hydrogen sulphide were the sulphur compounds used in this study, the addition compounds formed with disulphides not being relevant to the present study.

Reactions in Gas Burette

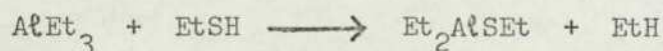
The burette scale was initially calibrated with water. To carry out a reaction in the burette, solutions of thiol and alkyl in the diluting solvent were prepared in the septum sealed flasks shown in Figure 4.17(a)-alkyl, and (b)-thiol. The alkyl was diluted in

flask (a) as follows. A syringe needle was inserted in the septum, and connected to a vacuum pump by means of a short length of rubber tubing pushed over the syringe fitting. The flask was then evacuated and filled with nitrogen through the side tap several times. The required amount of alkyl and diluting solvent was then injected through the septum. The syringe was used to remove the same volume of gas as liquid was injected to prevent a pressure build up. The required volume of the solution so prepared was then transferred to the gas burette by means of a syringe. Before use, the burette was filled with nitrogen in the same way as has been described for the alkyl diluting flask, the mercury having previously been levelled to the tap. When the alkyl solution had been injected into the flask, the syringe was removed with the plunger depressed, and a needle inserted through the septum briefly to equalise the pressure developed in the system with atmospheric pressure. Then the tap over the flask was closed, and the thiol solution injected into the upper part of the reactor over the tap. The pressure in this part of the system was then again equalised with atmospheric pressure by momentarily inserting a needle through the septum, and then the lower tap was opened so that the thiol ran into the flask and mixed with the alkyl. The tap was then closed, and the burette tap opened so that the volume of gas liberated could be recorded by levelling the mercury in the two limbs when the reaction mixture had attained room temperature.

Initially, reaction between ethyl mercaptan and triethyl aluminium was investigated. For complete reaction:-



$\text{Et}_3\text{Al}^\ell$ was obtained as a 25 per cent v/v solution in benzene. 2 ml of this were diluted to 22 ml with toluene, and 2 ml of this solution used in the experiment (0.03809 g alkyl). 1 ml of thiol was diluted with 20 ml of toluene, and 1.75 ml of this solution (10 per cent excess) used in the reaction. The reaction was conducted at high dilution and at room temperature in an attempt to prevent polymerization of the product with consequent incomplete replacement of the alkyl groups by thioalkyl groups. No evidence of reaction was observed on adding the thiol to the alkyl, although a slow liberation of gas occurred. After 20 hours, the flask was gently warmed to ensure completion of reaction. When the mixture had regained room temperature, it was observed that a further evolution of gas had occurred. At this stage, the reaction was taken to be complete. The product in the flask was a colourless liquid, indistinguishable from the starting material. A 2 ml sample of the gas was withdrawn for analysis by GLC, using a silicone oil column in a Perkin Elmer Model 800 chromatograph, with a flame ionization detector and nitrogen as carrier gas. Comparison with the chromatographs of benzene, toluene and ethyl mercaptan vapours showed the presence of one additional peak eluted immediately before the thiol. This was taken to be ethane. The volumetric data from this run is summarised in Table 4.2. It is apparent that only one replacement of (Et) by (-SEt) had occurred, even on warming the mixture, ie



It was considered possible that polymerization of Et_2AlSEt was occurring before further substitution of (-SEt) for (-Et) could occur, and that this was stabilising the Et_2AlSEt against further substitution. For this reason, the reaction was repeated, the mixture being warmed as soon as the thiol was added. The results are presented

Time (hr)	Temp ($^{\circ}\text{C}$)	Atm.Pres.(torr)	Volume (ml)	Vol.NTP (ml)
$\frac{1}{4}$	21.7	763.1	6.56	6.13
1	22.1	763.1	7.01	6.55
20	21.1	762.9	7.86	7.34
after warming	21.1	762.9	8.29	7.74

Table 4.2 Volumetric data for the reaction of EtSH with AlEt_3 in toluene at high dilution.

Time (hr)	Temp ($^{\circ}\text{C}$)	Atm.Press.(torr)	Volume (ml)	Vol.NTP (ml)
$\frac{1}{4}$	15.8	749.2	6.41	5.97
$\frac{3}{4}$	17.2	749.2	7.41	6.86

Table 4.3 Volumetric data for the reaction of EtSH with AlEt_3 in toluene at high dilution(heated).

Time (hr)	Temp ($^{\circ}\text{C}$)	Atm.Pres.(torr)	Volume (ml)	Vol.NTP (ml)
$\frac{1}{4}$	15.4	752.9	42.81	40.1
1	15.4	752.9	42.81	40.1

Table 4.4 Volumetric data for the reaction of EtSH with AlEt_3 in toluene in concentrated solution.

Time (hr)	Temp ($^{\circ}\text{C}$)	Atm.Pres.(torr)	Volume (ml)	Vol.NTP (ml)
$\frac{1}{4}$	20.6	758.4	5.71	5.31
1	20.6	758.4	6.93	6.44
5	20.2	758.4	9.91	9.21
20	18.8	756.1	11.91	11.12
$\frac{1}{4}$	17.2	762.0	13.51	12.72
5	17.2	762.0	13.51	12.72
20	17.0	761.3	13.51	12.72

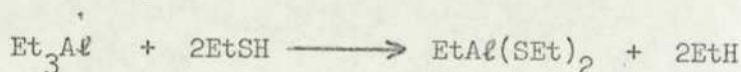
Table 4.5 Volumetric data for the reaction of PhSH with AlEt_3 in toluene. Above, dilute and below, concentrated solution.

Reference (calculated) data for Tables 4.2 - 4.5

Replacement of 1 alkyl group:	7.48	20.56	7.48	8.22 ml
" " 2 " "	: 14.97	41.12	14.96	16.44 ml
" " 3 " "	: 22.45	61.68	22.45	24.67 ml
	(4.2 &4.3)	(4.4)	(4.5 dil.)	(4.5 conc.)

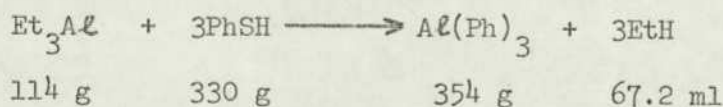
in Table 4.3. It was apparent that no further reaction had occurred, Et_2AlSEt again being the main product.

The next variable to be investigated was the concentration of the reagents. Dilute solutions had originally been used in an attempt to prevent polymerisation of the product, and the effect of using more concentrated solutions was next investigated. Et_3Al was used as supplied - ie 0.5 ml, 25 per cent v/v in benzene, equivalent to 0.1046 g. EtSH was diluted to a 50 per cent solution in toluene. 0.5 ml were used (20 per cent excess). The reagents were mixed as before, and the mixture warmed until nearly boiling. The product appeared as a flocculent white precipitate. The solution was cooled to room temperature, and after about one hour the contents of the flask had gelled, presumably due to polymerization. The results are summarised in Table 4.4, and it is apparent that two aluminium alkyl groups had been replaced:-



It therefore seemed that the more concentrated conditions were necessary for formation of the disubstituted product, although no tendency for replacement of the final aluminium alkyl group was observed.

The reaction of triethyl aluminium with thiophenol was next investigated, as patent reports (345, 346) had indicated $\text{Al}(\text{SPh})_3$ to be readily formed.



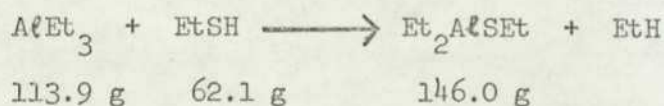
The reaction was conducted under both dilute and concentrated conditions, similar dilutions and quantities of reagents being employed as for the reactions with EtSH . The results of these reactions are summarised in Table 4.5. In both cases, the mixture was heated to near boiling soon

after mixing, and then left for 20 hours at room temperature. Although increasing the concentration increased the reaction rate, the eventual product was the same in both cases, and corresponded to between one and two aluminium alkyl groups being replaced by (SPh) groups. The product was obtained as a white, gelatinous solid, presumably a mixture of $\text{Et}_2\text{Al}(\text{SPh})$ and $\text{EtAl}(\text{SPh})_2$.

Reactions of AlEt_3 with Mercaptans

At this stage, the preparation of larger quantities of the ethyl aluminium-thiol derivatives was attempted, to enable a more complete characterization of these materials to be obtained. From the reactions carried out in the gas burette, existence of the compounds Et_2AlSET , $\text{EtAl}(\text{SET})_2$, Et_2AlSPh and $\text{EtAl}(\text{SPh})_2$ in various degrees of polymerization was suggested.

The apparatus used is illustrated in Figure 4.18. Initially ethyl mercaptan (1 mole) was reacted with triethyl aluminium (1 mole) in an attempt to prepare Et_2AlSET :-



25 per cent AlEt_3 in benzene (50 ml) was transferred by syringe to the funnel A (Figure 4.18) after the equipment had been flushed with dry nitrogen. The solution was run into the flask B, and then with the funnel tap closed, EtSH (9 ml) and toluene (9 ml) were injected into the funnel. This mixture was slowly run into the alkyl solution (under nitrogen purge) whereupon a violent reaction ensued, slowly subsiding as more thiol was added. When the addition was complete, nitrogen was bubbled through the solution for 30 minutes. At the end of this time, the liquid was quite clear, and there was no

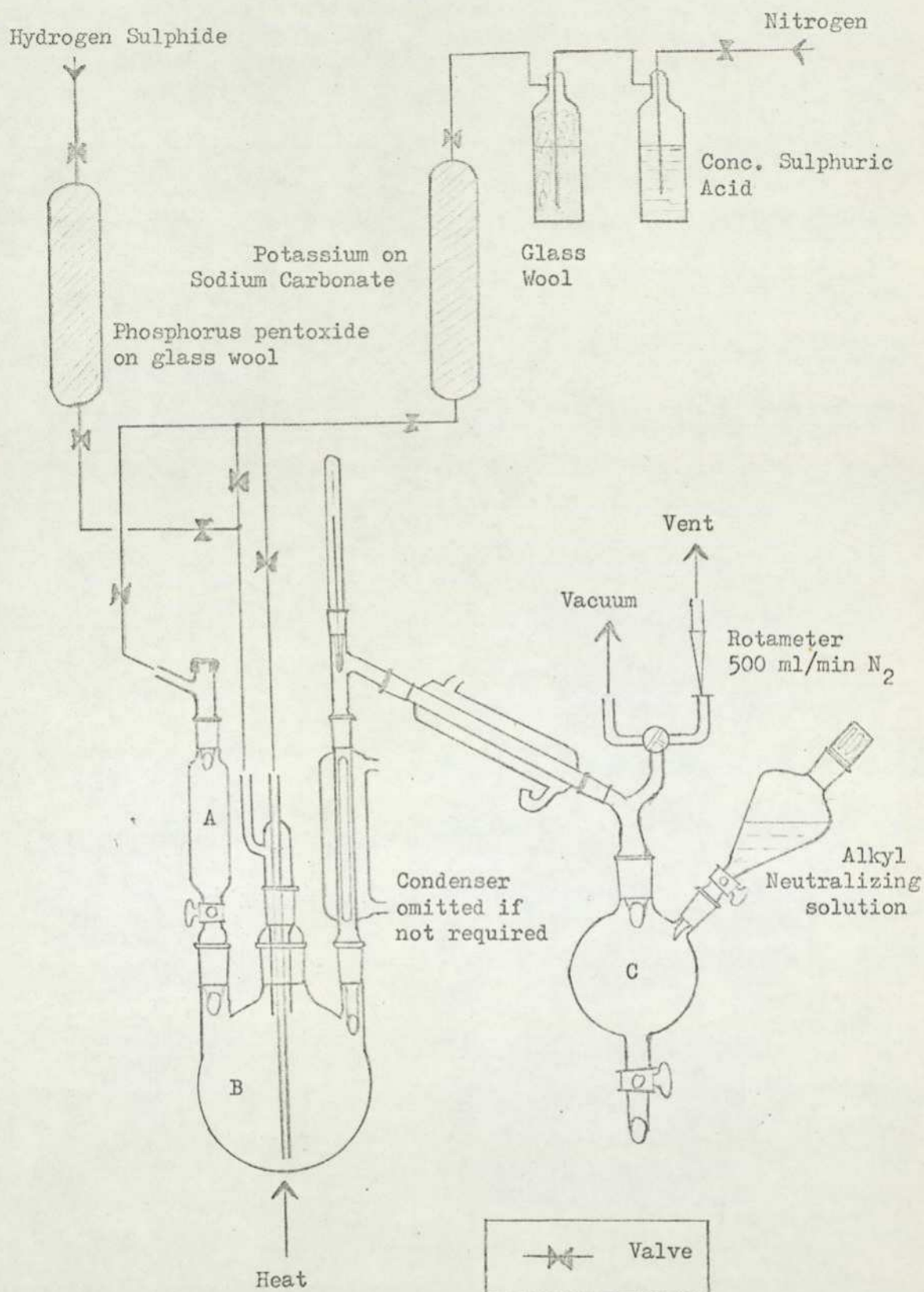
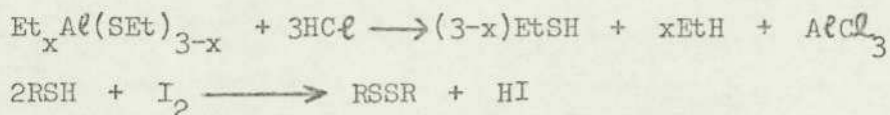


Fig. 4.18 Apparatus for reactions employing aluminium alkyls.

precipitate. The nitrogen purge leaving the apparatus no longer fumed in air, suggesting that no unreacted alkyl remained. The reaction mixture was left standing under nitrogen overnight, after which a white cloudiness had developed in the liquid and a gelatinous precipitate formed. The solvent was distilled under vacuum at room temperature into receiver (C) leaving a white gelatinous solid. The liquid was run off from the receiver (C), and the temperature of the flask (B) slowly raised. The solid product melted to a colourless liquid which distilled at $140^{\circ} - 150^{\circ}\text{C}$, 1 torr, and tended to solidify in the receiver. The water was removed from the condensers during this distillation. 7.43 g was obtained, corresponding to 46 per cent conversion to Et_2AlSET . The material smelt strongly of thiol when exposed to air, presumably due to hydrolysis, and charred paper even in the dry box. It was soluble in toluene and similar non-polar solvents. The infra-red spectrum was obtained by pressing a drop of the material between two sodium chloride plates in the dry box, and mounting these in their holder before bringing them into the air. A sample so prepared did not decompose appreciably in the time it took to run a spectrum (Figure 4.19). On standing in a sealed container for several days the material slowly solidified to a white material of pasty consistency, presumably through polymerization. Its infra-red spectrum was essentially unaltered, however, and it still remained soluble in non-polar solvents. Its sealed-tube melting point was not sharp, but about 95°C .

Quantitative analysis was obtained for sulphur and aluminium. An analysis for carbon and hydrogen was not carried out as the automated instrument available could not handle air-sensitive samples. Analysis

for sulphur involved hydrolysis in acid solution to liberate the sulphur as thiol, which was then determined by oxidation to disulphide with iodine:-



In practice, a sample of the material was weighed (in the dry box) into a stoppered phial. The phial was then brought into the laboratory, where the stopper was loosened, and the phial quickly dropped into a flask containing 25 ml of N/10 iodine and 10 ml of 20 per cent HCl. The flask was quickly stoppered, and shaken to promote reaction. By tilting the conical flask used, the phial of sample could be rested on the wall above the liquid until the stopper was replaced, thereby eliminating loss of the volatile EtSH. Excess iodine was then titrated with thiosulphate. 25 ml 0.130 g N iodine was used.

Sample 1.

$$\text{wt sample} = 0.1400 \text{ g}$$

$$\text{Excess iodine} = 22.53 \text{ ml } 0.1\text{N thiosulphate.}$$

$$25 \text{ ml } 0.1309 \text{ N } \text{I}_2 = 32.71 \text{ ml } 0.1\text{N thiosulphate}$$

$$\therefore \text{Iodine used} = 32.71 - 22.53 = 10.18 \text{ ml } (0.1\text{N})$$

$$\therefore \% \text{ sulphur} = \frac{10.18 \times 0.00316 \times 100}{0.1400} = \underline{22.95\%}$$

Sample 2.

$$\text{wt sample} = 0.0658 \text{ g}$$

$$\text{Excess iodine} = 27.67 \text{ ml } 0.1\text{N thiosulphate.}$$

$$\therefore \text{Iodine used} = 32.71 - 27.67 = 5.04 \text{ ml } (0.1\text{N})$$

$$\therefore \% \text{ sulphur} = \frac{5.04 \times 0.00316 \times 100}{0.0658} = \underline{23.98\%}$$

Analysis for aluminium was by EDTA. A sample of the material (0.4 g) was weighed in the dry box, and then dissolved in dilute hydrochloric acid. The solution was boiled to remove the thiol formed during hydrolysis, and then cooled and made up to 500 ml. 25 ml aliquots of this were reacted with 25 ml (excess) of 0.01M EDTA, and the solution neutralised to pH 7 - 8 with dilute ammonia, using narrow range pH paper. The solution was then boiled for a few minutes, cooled to room temperature, and the pH checked. A few drops of 'Erichrome T' indicator were added, and excess EDTA titrated with 0.01M zinc to a blue-red end point.

The zinc solution was prepared by dissolving the AR grade metal in 50 per cent HCl, nearly neutralising the resulting solution with sodium hydroxide and diluting to volume. This solution was also used to standardise the EDTA. 25 ml of 0.01M zinc were diluted with 100 ml of distilled water, 2 ml of pH 10 buffer added (14.2 ml conc ammonia and 1.75 g ammonium chloride), and a few drops of Erichrome Black in methanol (0.4%). This was then titrated with the nominally 0.01M EDTA to a blue-red end point.

$$\text{Zinc solution} = 0.6738 \text{ g/litre} = \underline{0.01032\text{M}}$$

Standardization of EDTA:-

$$(i) \quad 25 \text{ ml EDTA} = 23.50 \text{ ml zinc}$$

$$(ii) \quad 25 \text{ ml EDTA} = 23.58 \text{ ml zinc}$$

$$\therefore \text{Strength of EDTA} = \frac{23.54 \times 0.01032}{25} = \underline{0.00973\text{M}}$$

Sample 1.

$$\text{wt sample} = 0.1827 \text{ g}$$

$$\text{Excess EDTA} = 17.90 \text{ ml } 0.01032\text{M zinc} = 18.45 \text{ ml } 0.01\text{M}$$

$$25 \text{ ml } 0.00973\text{M EDTA} = 24.33 \text{ ml } 0.01\text{M EDTA}$$

$$\therefore \text{EDTA used} = 24.33 - 18.45 = 5.88 \text{ ml}$$

$$\therefore \% \text{ Al} = \frac{5.88 \times 2 \times 698.2}{0.1827 \times 10} = \underline{17.32\%}$$

Sample 2.

wt sample = 0.1548 g

Excess EDTA = 18.81 ml 0.01032M zinc = 19.42 ml 0.01M

∴ EDTA used = 24.22 - 19.42 = 4.91 ml

∴ % Al = $\frac{4.91 \times 2 \times 698.2}{0.1548 \times 10} = 17.10\%$

The analysis may be summarised:-

% S = 22.95 , 23.98%

% Al = 17.32 , 17.10%

Calculated data is:-

Et_2AlSEt ; 21.92 %S, 18.49% Al

Et Al(SEt)_2 ; 35.98 %S, 15.15% Al

Al(SEt)_3 ; 45.72 %S, 12.88% Al

The analysis corresponds most closely with that of Et_2AlSEt , the expected product.

This reaction was repeated several times during the course of the work. By removing the two condensers during the distillation of the product, wastage due to solidification was reduced, and up to 78 per cent of the theoretical conversion of ethyl aluminium was obtained. The infra-red spectra of the products were always identical to that shown in Figure 4.19 and Figures 4.20. These spectra are discussed below, together with those of the other derivatives prepared.

The reaction of one mole of ethyl aluminium with three moles of ethane thiol was next carried out, in an attempt to promote further replacement of alkyl by thioalkyl group on aluminium. The experiments in the gas burette had suggested that two such replacements

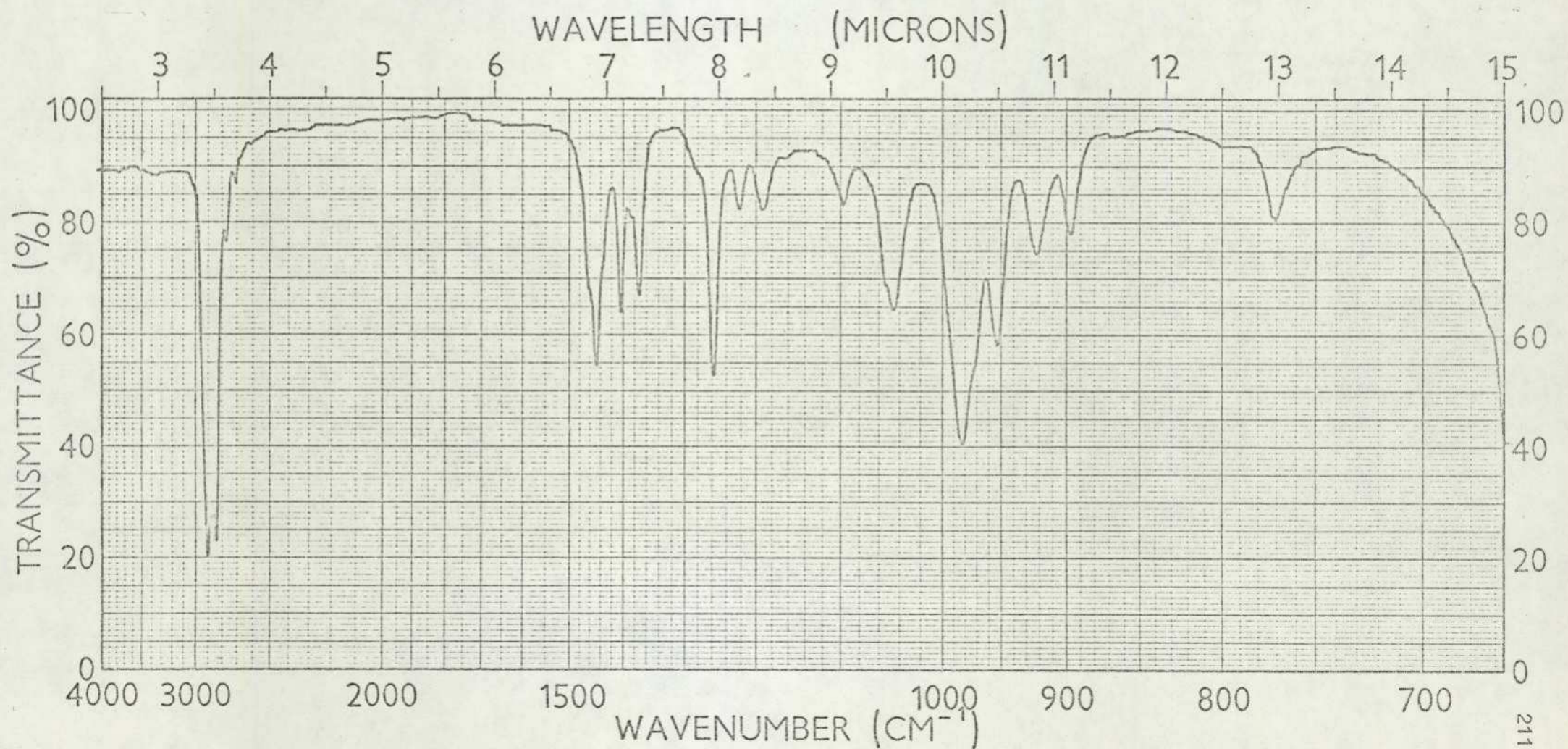
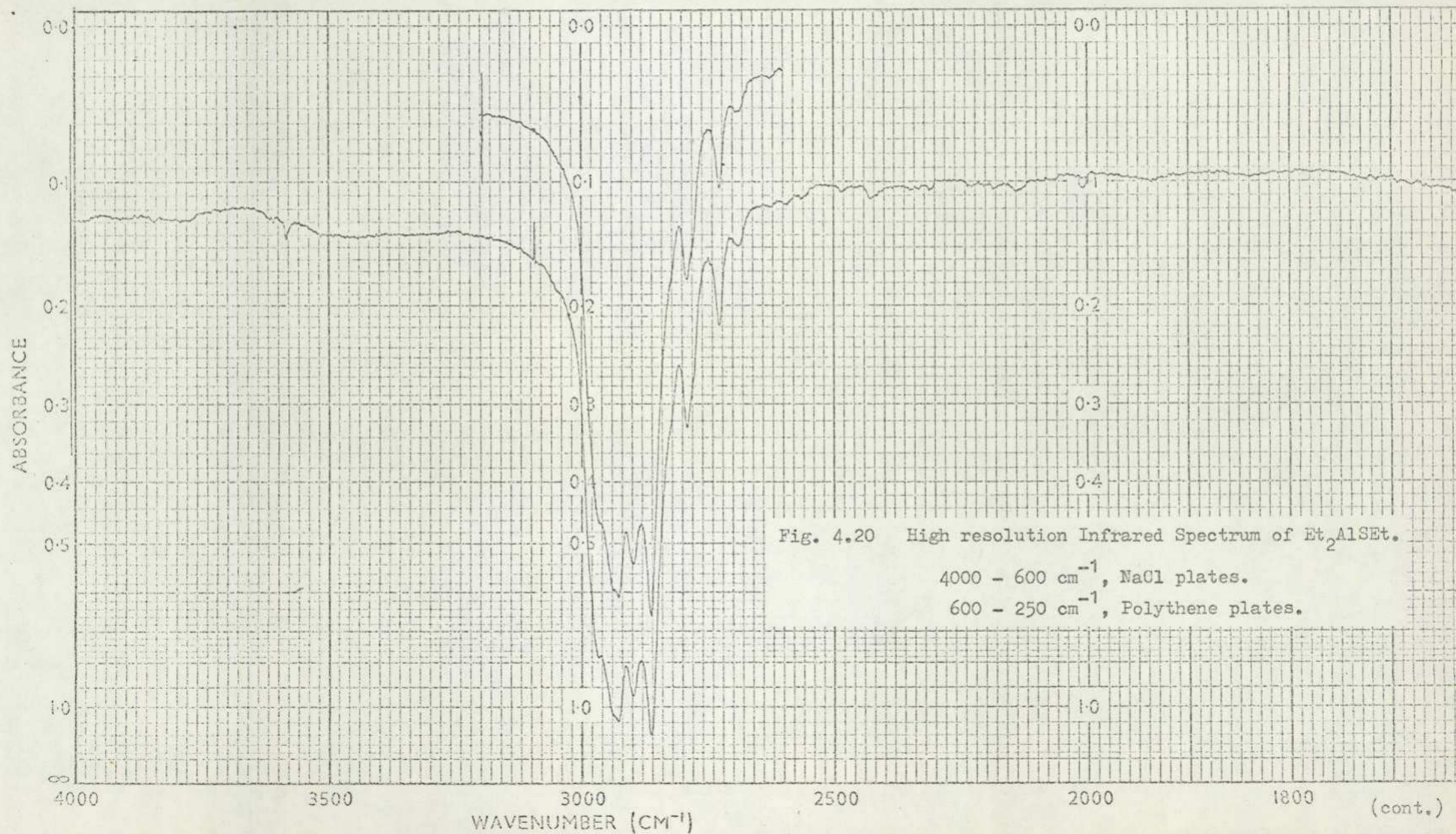
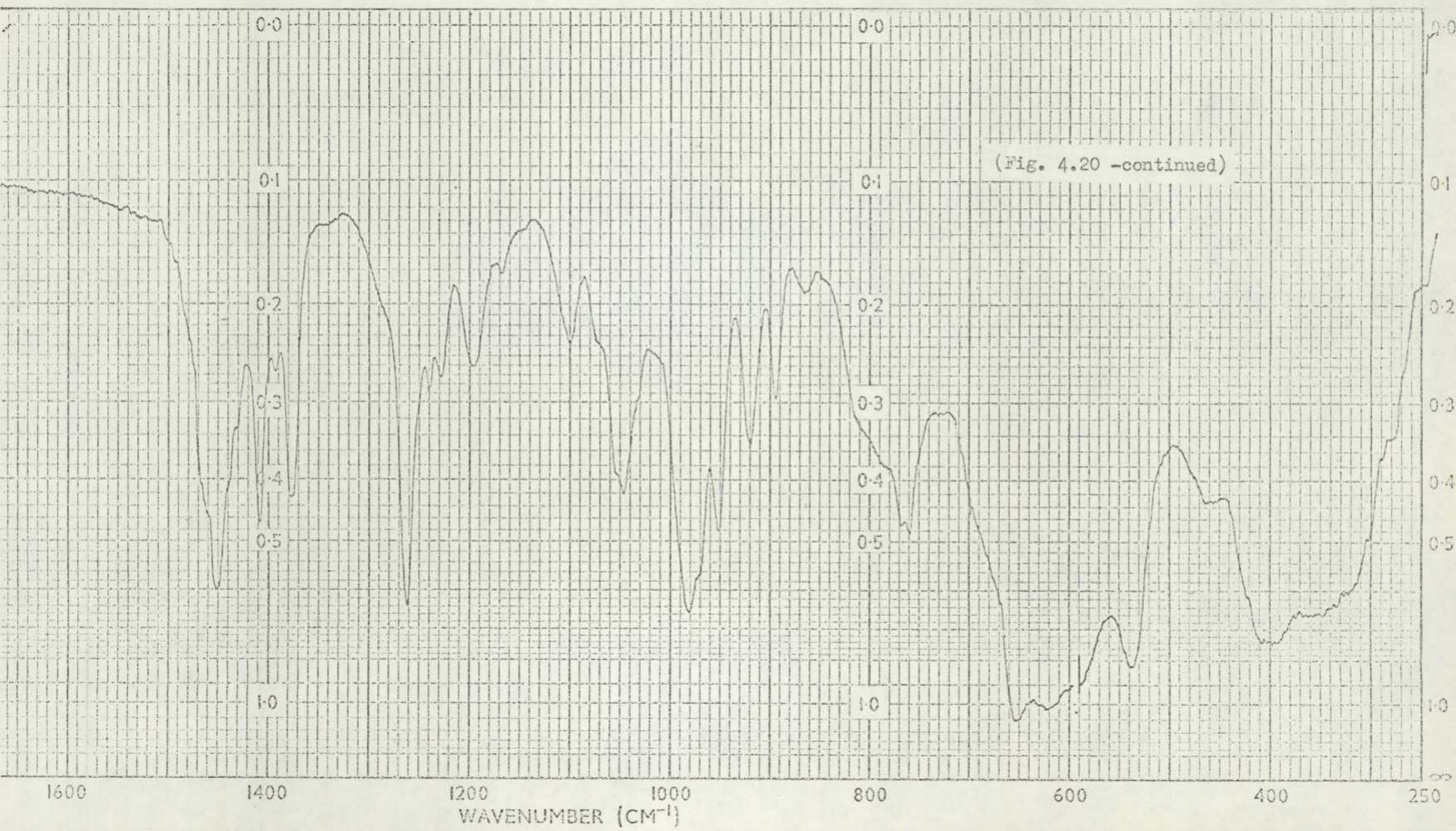


Fig. 4.19 Infrared Spectrum of Et₂AlSEt , NaCl plates.





could occur in concentrated reaction conditions to form $\text{EtAl}(\text{SEt})_2$. These were the conditions used in the present experiment. The equation for complete substitution is:-



The alkyl was placed in the reaction flask as before (25 ml of 25 per cent solution in benzene), and 12 ml of EtSH diluted with 12 ml of toluene run in from the funnel. An evolution of heat occurred during mixing, as previously, and when the resulting colourless liquid was heated to reflux, it quickly solidified to a white material. A period of several hours was allowed to elapse between mixing the reagents and refluxing, during which the flask was intermittently shaken. This was to encourage further reaction without the polymerization of the product likely to occur on heating.

The solid product was taken into the dry box and washed free of Et_2AlSEt with toluene. A tendency for the washings to gel on contact with air suggested that some Et_2AlSEt had been removed. The solid product was vacuum dried. It was not soluble in any of the common solvents tested, and did not melt below 325°C in a sealed tube. Its infra-red spectrum is shown in Figures 4.21 and 4.22. Small differences compared to that of Et_2AlSEt (Figure 4.19) are apparent. The material hydrolysed in dilute acid, and was analysed for sulphur and aluminium by the methods used for Et_2AlSEt .

Found:- % S (as SH) = 37.58%, 38.72%

% Al = 14.55%, 14.20%

Calculated:-

Et_2AlSEt ; 21.92% S , 18.49% Al

$\text{Et Al}(\text{SEt})_2$; 35.98% S , 15.15% Al

$\text{Al}(\text{SEt})_3$; 45.72% S , 12.88% Al

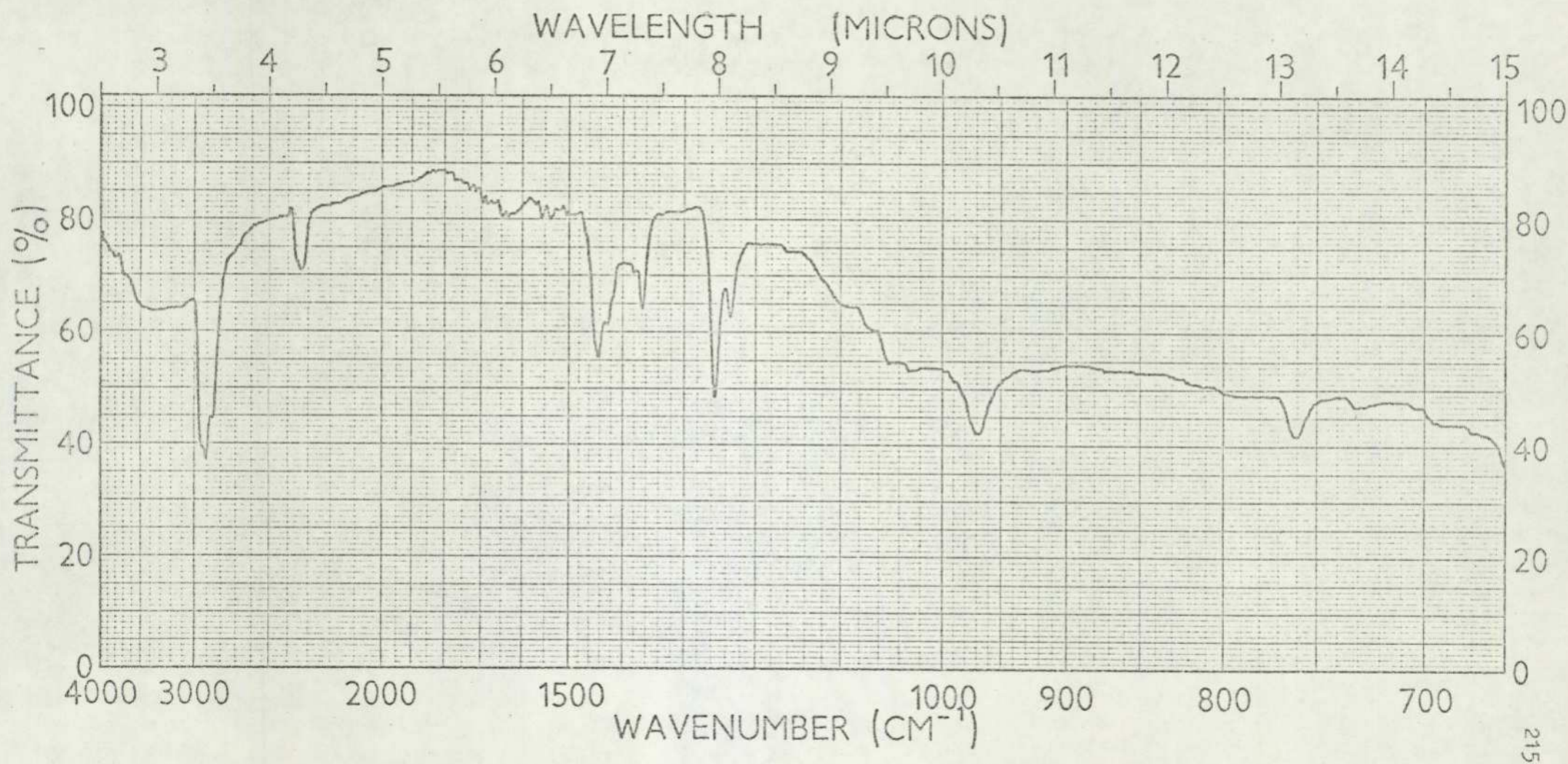


Fig. 4.21 Infrared Spectrum of Et Al(SEt)_2 , KBr disc.

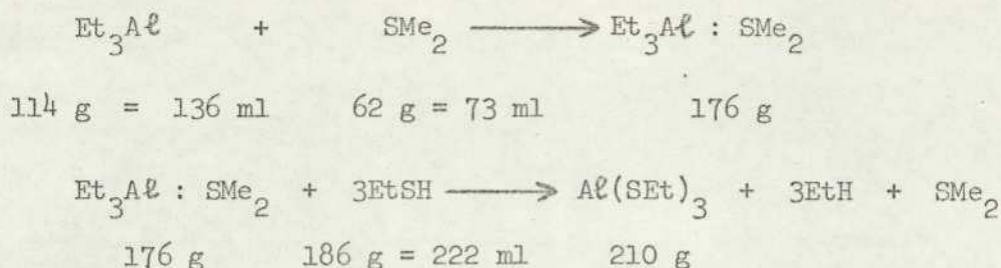




The chief product was therefore $\text{EtAl}(\text{SEt})_2$, although the figures suggested that a small amount of $\text{Al}(\text{SEt})_3$ was present. This was in general agreement with the results from the volumetric data, where two replacements of Et by SEt was the most achieved. The solid, insoluble nature of $\text{EtAl}(\text{SEt})_2$ compared to the gelatinous, soluble Et_2AlSEt , indicated a higher degree of polymerization, and implied that the material $\text{Al}(\text{SEt})_3$ would, if its formation were possible, be an insoluble polymer unlikely to be of much use in the subsequent hydrothermal studies.

Literature reports indicating that $(\text{MeS})_3\text{Al}$ may be prepared by reaction of MeSH with Me_3Al in diethyl ether appeared during the course of this work (352, 353). In this solvent, the alkyl will exist as the addition compound $\text{Me}_3\text{Al}:\text{O Et}_2$. Solvent effects will undoubtedly play an important part in controlling reaction rate and polymerization, and reaction in diethyl ether would be expected to proceed more slowly than in benzene. A similar addition compound is formed with dimethyl sulphide, $\text{Et}_3\text{Al}:\text{S Me}_2$, and reaction in both diethyl ether and dimethyl sulphide was investigated to obtain a measure of the effect of coordination complex strength. It was not felt that the use of EtSH and Et_3Al rather than MeSH and Me_3Al would appreciably alter the course of the reaction. Instead of the solution of 25 per cent alkyl in benzene previously employed, undiluted alkyl was obtained to permit the use of the required solvent.

Initially, reaction was conducted in dimethyl sulphide. 50 ml were transferred to the reaction flask, and Et_3Al (20 ml) added. EtSH (50 ml) and SMe_2 (50 ml) were transferred to the dropping funnel, and run into the alkyl,



Addition was over one hour, whilst stirring the mixture with a stream of nitrogen. The reaction was initially vigorous, but slowed after about half the thiol was added. A precipitate slowly formed, and the mixture was left overnight under a nitrogen purge. The solvent was removed under vacuum, and the product obtained as a hard, white solid. Its infra-red spectrum (Figure 4.23) was practically identical to that of $\text{Et Al}(\text{SEt})_2$ (Figure 4.22). Analysis for sulphur confirmed that this was in fact the identity of the product:

Found: S, 34.21, 34.06%

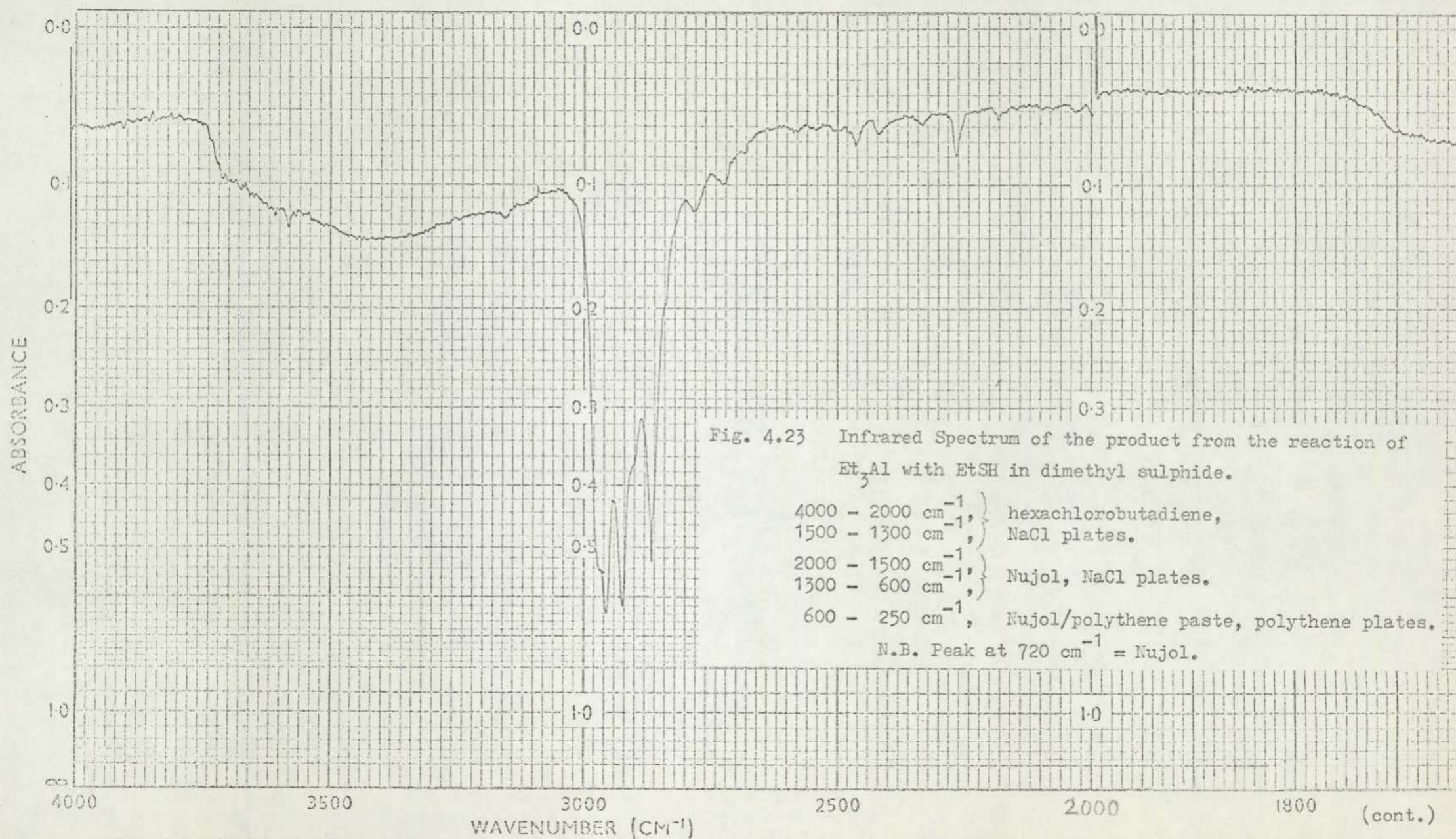
Calculated: Et_2AlSEt , 21.92% S : $\text{EtAl}(\text{SEt})_2$, 35.98% S;

$\text{Al}(\text{SEt})_3$, 45.72% S.

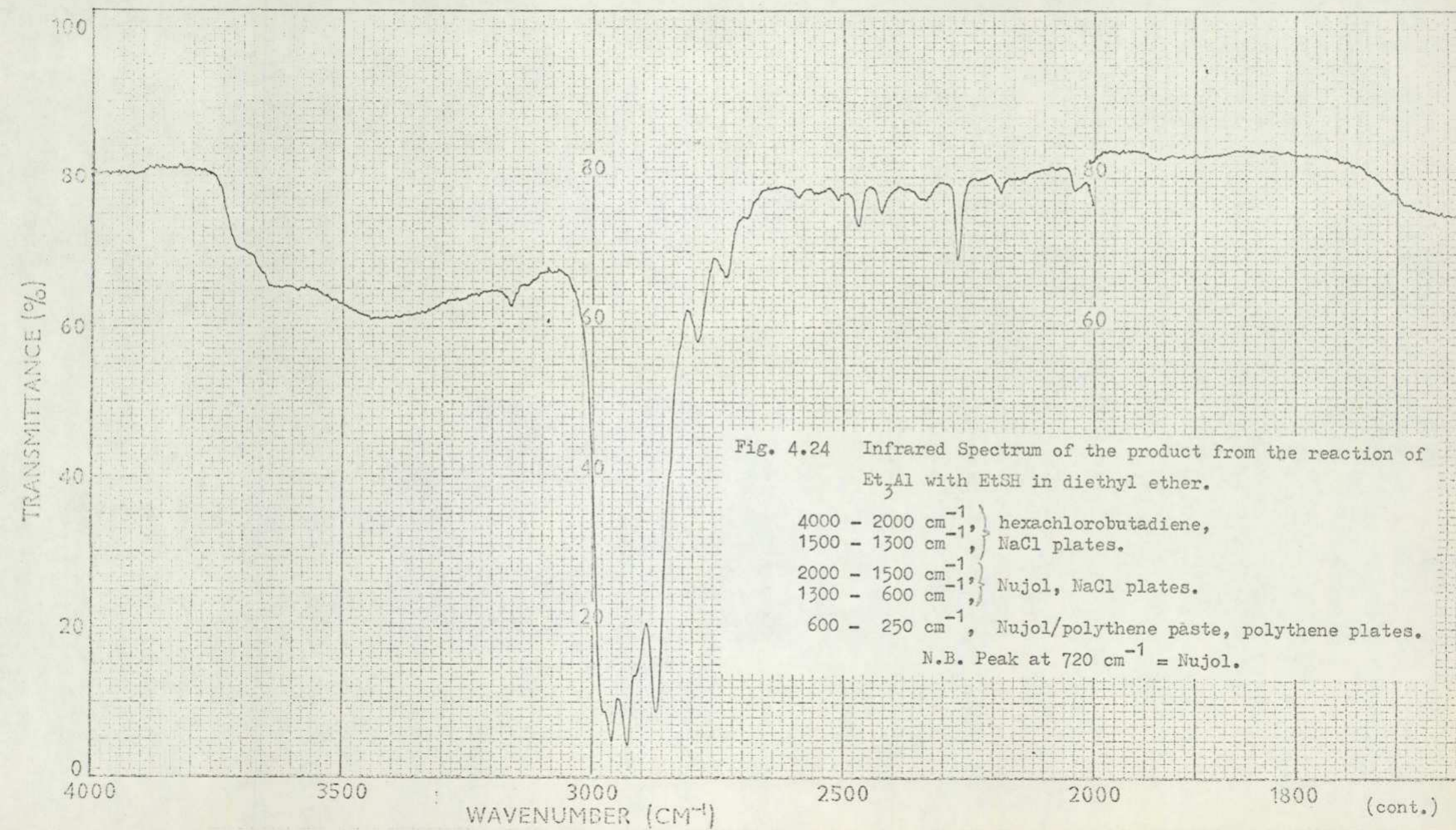
This experiment was repeated using diethyl ether as diluent, the conditions being otherwise identical. The reaction was much less vigorous than had been noted previously, and cautious warming of the flask was necessary to promote solidification of the product. The infra-red spectrum of the product (Figure 4.24) was similar to that from the previous reaction, and a similar sulphur analysis was obtained.

Found: S, 32.14, 32.00%.

It was therefore apparent that no promotion of reaction, with the formation of $\text{Al}(\text{SEt})_3$, had occurred as a result of using

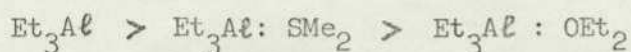






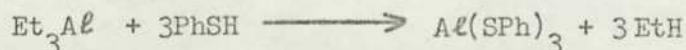


either diethyl ether or dimethyl sulphide as diluent. In both cases the product formed was $\text{EtAl}(\text{SEt})_2$, the same as that obtained in toluene. The reaction rates were found qualitatively to be inversely proportional to the coordinating power of the ligands in the complexes with the solvent:



The only real difference between the techniques used and the published method purported to lead to $\text{Al}(\text{SR})_3$ was the use of ethyl rather than methyl derivatives. It seemed most unlikely that this could alter the course of reaction, as steric effects could not play a part with such small alkyl groups. The matter was not pursued, however, as an aluminium-sulphur derivative soluble in non-polar solvents was required, and it was evident that both $\text{EtAl}(\text{SEt})_2$ and $\text{Al}(\text{SEt})_3$ (if prepared) could only be obtained as insoluble polymers. Therefore Et_2AlSEt , which was readily soluble in toluene and benzene, was used as the standard organoaluminium-thiol derivative in the subsequent hydrothermal work.

The study of the reactions of alkyl aluminium compounds with thiols was completed with the reaction of triethylaluminium with thiophenol.



$$114 \text{ g} = 136 \text{ ml} \quad 330 \text{ g} = 307 \text{ ml} \quad 354 \text{ g}$$

Et_3Al was used as 25 per cent solution in benzene. 20 ml were transferred to the reaction flask, and PhSH (15 ml) mixed with toluene (15 ml) slowly run in over one hour. (10 per cent excess of thiol). The contents of the flask remained clear until warmed, when a white solid precipitated. Eventually the contents of the flask had nearly

completely solidified. The mixture was left overnight and the solvent removed under vacuum.

The infra-red spectrum (Figures 4.25 and 4.26) was similar to that of thiophenol (Figure 4.27). Analysis was performed for aluminium and sulphur by the methods described at the beginning of this section.

Found: Al, 5.34, 5.29% S; 16.68, 16.90%

Calculated: $\text{Et}_2\text{Al}(\text{SPh})$; 16.50% S, 13.92. Al

$\text{EtAl}(\text{SPh})_2$; 23.38% S, 9.86% Al

$\text{Al}(\text{SPh})_3$; 27.12% S, 7.62% Al

$\text{Ph}_2\text{Al}(\text{SPh})$; 10.88% S, 9.18% Al

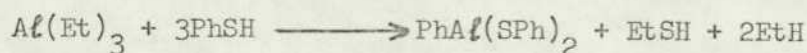
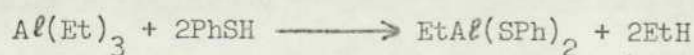
$\text{PhAl}(\text{SPh})_2$; 19.78% S, 8.34% Al

$\text{Et}_2\text{Al}(\text{SEt})$; 21.92% S, 18.49% Al

$\text{EtAl}(\text{SEt})_2$; 35.98% S, 15.15% Al

$\text{Al}(\text{SEt})_3$; 45.72% S, 12.88% Al

The aluminium figure is very low if the product was $\text{Et}_2\text{Al}(\text{SPh})$, as suggested by the sulphur figure. The aluminium analysis was later confirmed by atomic absorption when an instrument became available. The infra-red spectrum revealed little evidence for aliphatic residues in the molecule (vis weak C-H frequency absorption in the 2900 cm^{-1} - 3000 cm^{-1} region), and the material appeared to be predominantly aromatic in character. It is possible, therefore, that the product was $\text{PhAl}(\text{SPh})_2$, the calculated analysis of which corresponds most nearly with the values found. The volumetric measurement of ethane liberated had indicated that reaction had proceeded as far as $\text{EtAl}(\text{SPh})_2$; it could equally well account for the formation of $\text{PhAl}(\text{SPh})_2$ where a similar quantity of ethane is liberated:-



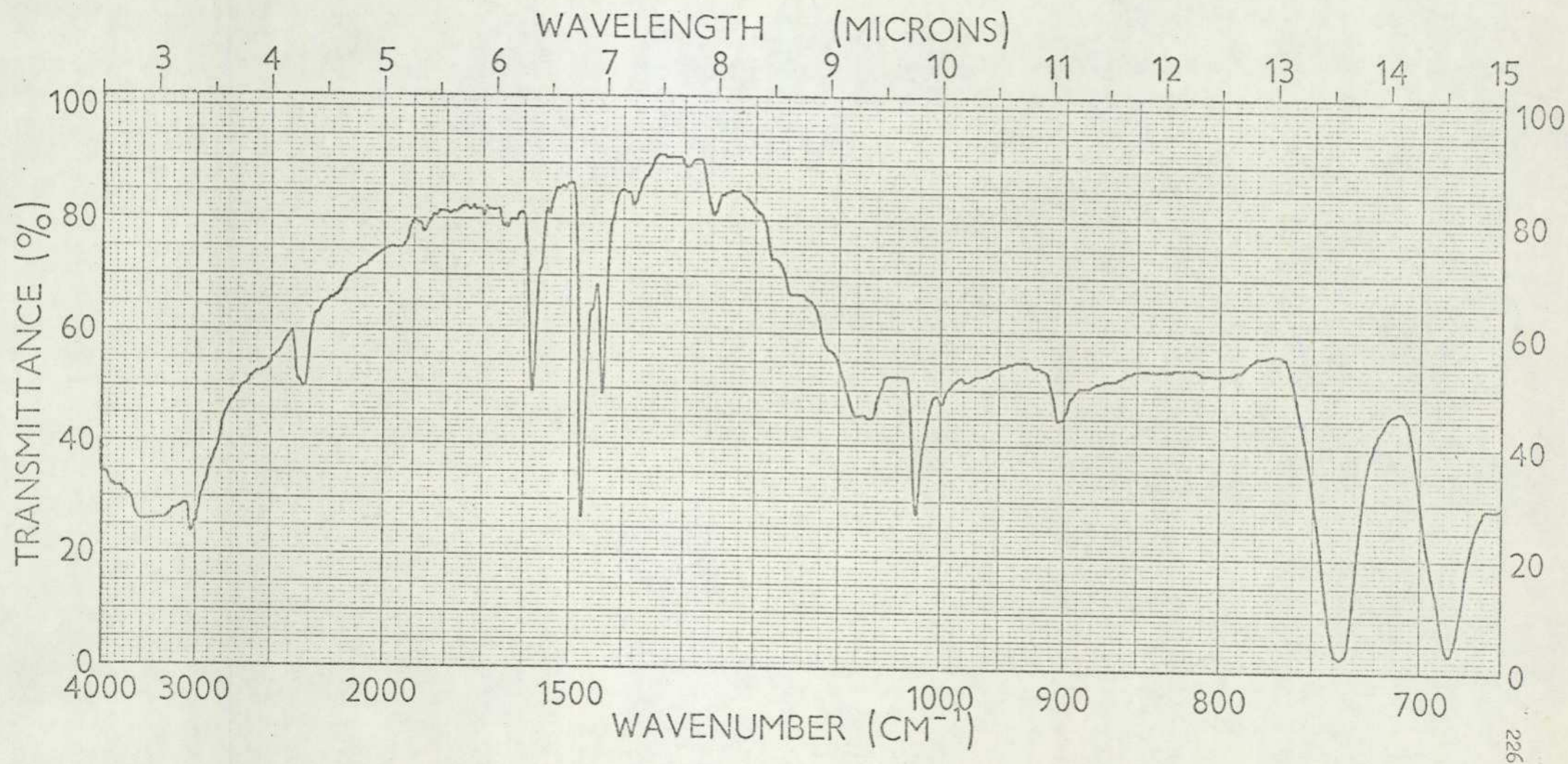
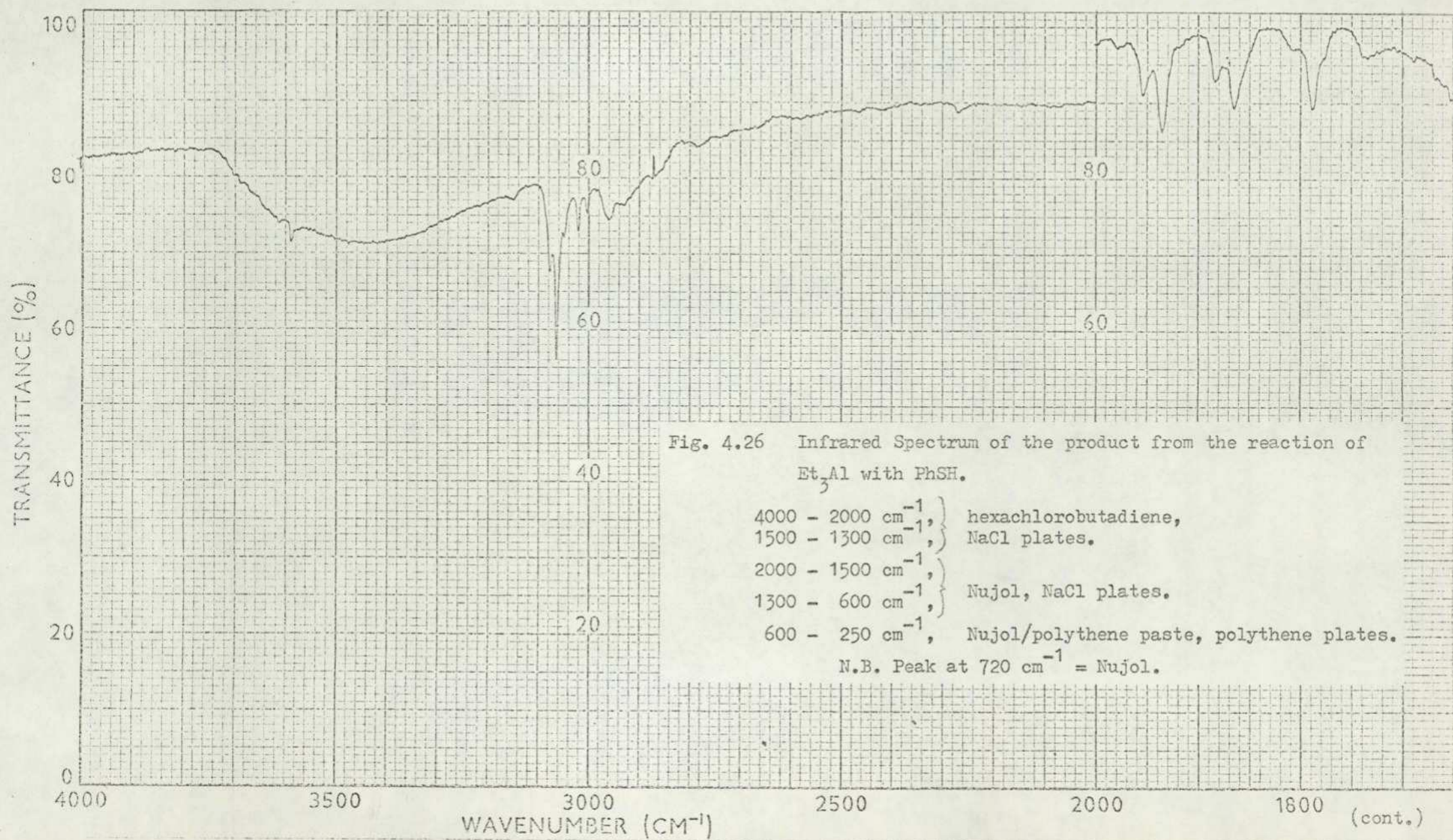


Fig. 4.25 Infrared Spectrum of the product from the reaction between Et_3Al and PhSH .
KBr disc.





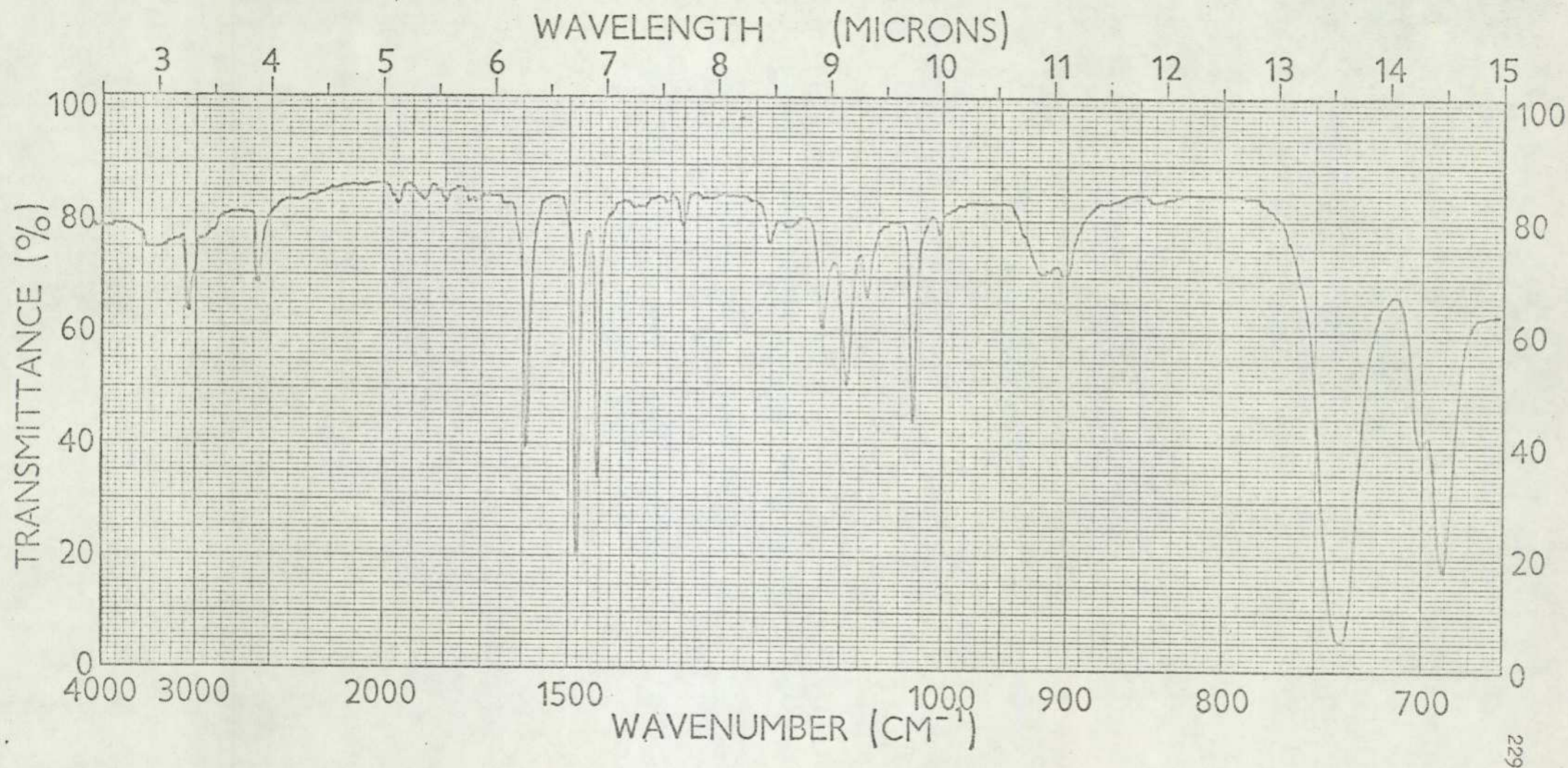
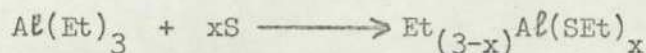


Fig. 4.27 Infrared Spectrum of Thiophenol, NaCl plates.

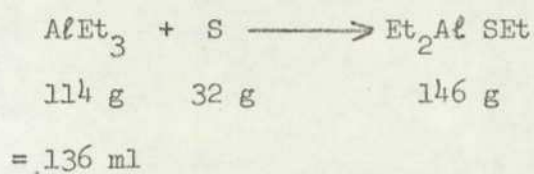
Such a reaction would seem somewhat unlikely, as it would involve rupture of all three Al-C bonds in AlEt_3 , and $\text{Al}(\text{SPh})_3$ would be expected as the most likely product if this occurred. In any case, it seemed that a mixture of products was formed during this reaction.

Reaction of $\text{Al}(\text{Et})_3$ with Sulphur

The reaction expected was:-



Literature reports (Section 4.2.1.2) suggested that insertion of more than one sulphur per alkyl molecule was not possible. Reaction was therefore initially restricted to one equivalent of sulphur. The apparatus used in the thiol reactions was employed for this work. Elemental (flowers of) sulphur (3.5 g) were dried under vacuum and put



in the reaction flask, and the equipment purged with nitrogen. Ethyl aluminium (50 ml, 25 per cent solution in benzene) was slowly run in, whereupon a vigorous reaction ensued. A white solid remained, together with a colourless liquid, and the equipment was left under a nitrogen purge overnight. The solvent was removed under vacuum, and a colourless oily liquid remained. This was distilled off under vacuum (124°C, 1 torr). Its infra-red spectrum (Figure 4.28) was identical to that of Et_2AlSET prepared earlier (Figure 4.19), although it did not solidify on standing, as did the earlier material. The identity was confirmed by elemental analysis for sulphur and aluminium, conducted as described previously.

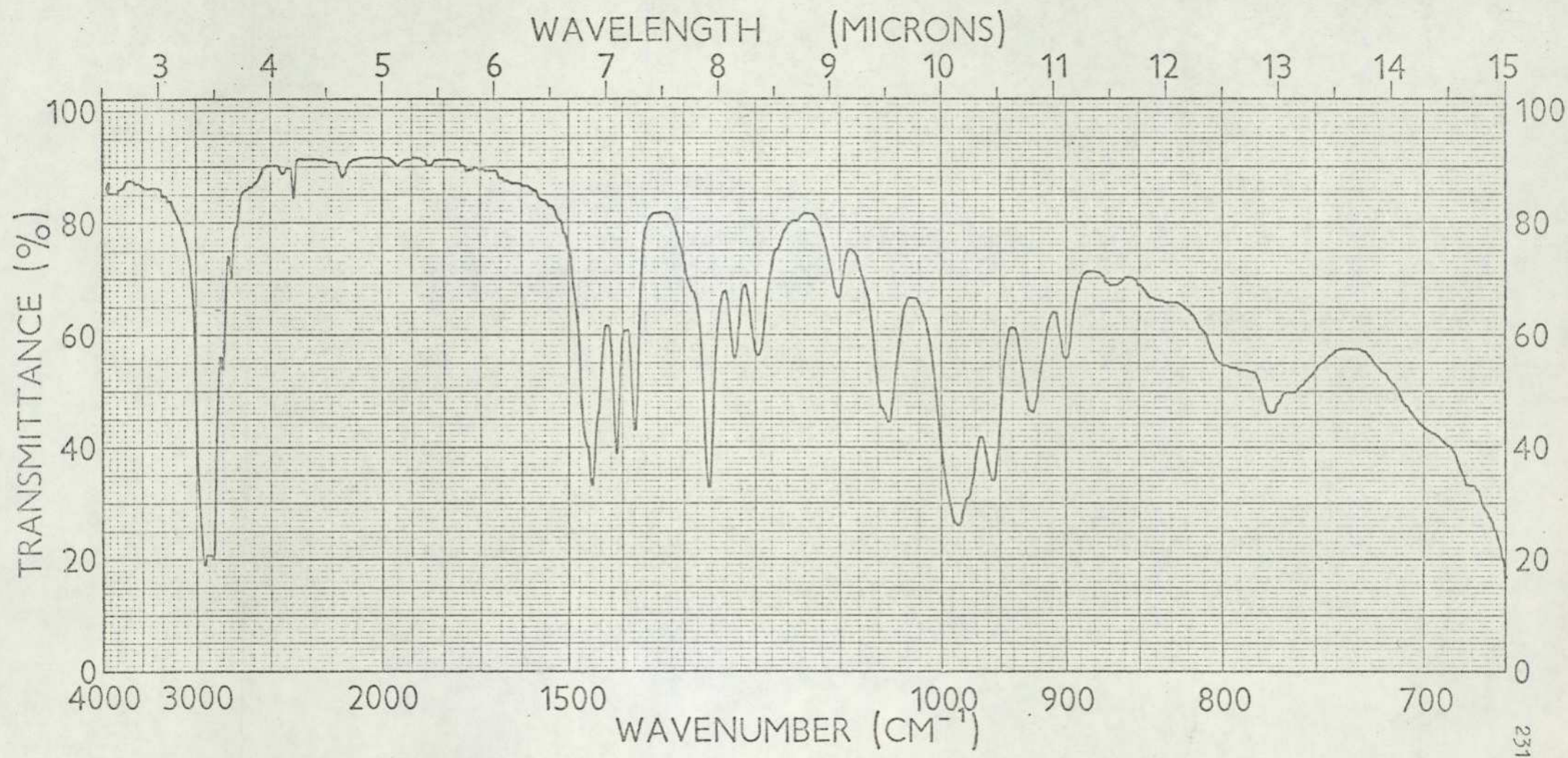


Fig. 4.28 Infrared Spectrum of product from the reaction between Et_3Al and elemental Sulphur. NaCl plates.

Found: S(thiol or mercaptide, by reaction with acidified iodine), 18.68%;

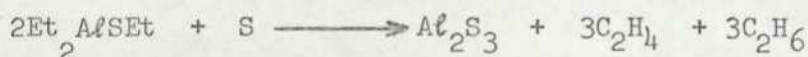
S(total, by sodium fusion), 20.12%; Al, 17.56%

Required for Et_2AlSET ; S, 21.92%, Al, 18.40%.

Therefore, it seemed that the material was not completely pure, which could account for the fact it did solidify on standing as did the earlier samples. Contamination with, for instance, $\text{Et}_3\text{Al}:\text{SET}_2$ (15.69% S), is possible.

The reaction between triethyl aluminium and sulphur was repeated using sulphur in excess of that required to form $\text{Al}(\text{SET})_3$, but with essentially similar results. Again, a solid residue remained after the reaction, together with a little Et_2AlSET (bp 120°C at 1.5 torr). Its infra-red spectrum was identical to Figure 4.28.

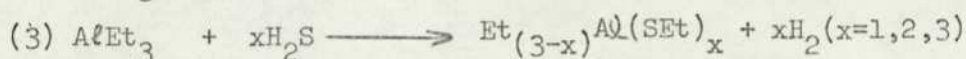
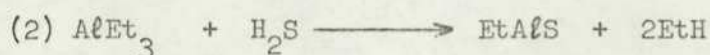
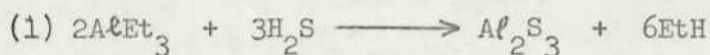
The infusible residue from these reactions reacted with water to liberate hydrogen sulphide (identified with lead acetate paper). Its infra-red spectrum showed no organic residues, and these factors indicated that it was mainly aluminium sulphide formed by a reaction such as



Although solvent washing of the residue rather than distillation to remove Et_2AlSET might have reduced decomposition to form Al_2S_3 , it seemed likely that most of the side reactions producing this material were occurring during the initial reaction. Earlier experiments had indicated that $\text{EtAl}(\text{SET})_2$ and $\text{Al}(\text{SET})_3$ were insoluble, infusible polymers, and therefore impossible to separate from Al_2S_3 which is also insoluble in common (non aqueous) solvents. For this reason, the reaction between Et_3Al and sulphur was not followed up as a potential source of $\text{Al}(\text{SET})_3$, the inference being that side reactions between the initially formed Et_2AlSET and further sulphur led to contamination of the higher substituted derivatives with Al_2S_3 .

Reaction of $\text{Al}(\text{Et})_3$ with H_2S

Literature reports (Section 4.2.1.2) suggested that vapour phase reaction of $\text{Al}(\text{Et})_3$ and H_2S at 90°C produced 95 - 98 per cent Al_2S_3 contaminated with SAlEt . At 125°C , pure SAlEt was formed. Vapour phase reaction was not considered feasible within the restriction of apparatus available in the present work, but the reaction of gaseous H_2S with liquid AlEt_3 was investigated with the equipment used for the previous experiments with aluminium alkyl. Possible reactions are:-



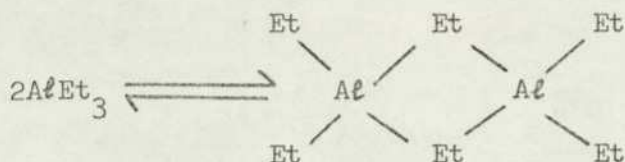
Published work suggested that reactions (1) and (2) were expected; analogy with the reaction of alkyl aluminiums with water suggested that reaction (3) is unlikely.

25 per cent AlEt_3 in benzene (50 ml) were transferred to the nitrogen purged reaction flask, and a mixture of 125 ml/min nitrogen and 125 ml/min H_2S (CP grade dried over P_2O_5 supported on glass wool) bubbled in. No reaction was observed, and so 250 ml/min of undiluted H_2S was bubbled in. A slight fuming was observed, and the liquid became warm. After about 30 minutes a white solid appeared. Reaction was continued for two hours, and the solvent then removed under vacuum. A little triethyl aluminium remained, and this was distilled off (bp = 80°C at 1 torr - published value (363) = $75-80^\circ\text{C}$ at 1 torr). A yield of 3.14 g of white solid material was obtained. It was analysed for sulphur (sodium fusion for total sulphur) and aluminium by the usual methods.

Found: S ; 33.72, 33.60%, Al; 29.05, 30.05%.

Calculated; Al_2S_3 ; 35.99% Al, 64.11% S; EtAlS ; 30.68% Al, 36.38% S.

The product therefore corresponded most closely to EtAlS . Taking into account the published results, it seemed that reaction at 90°C was essential for the formation of Al_2S_3 from AlEt_3 and H_2S . Reaction at room temperature and 125°C both lead to EtAlS . The presence of a solvent in the present work is likely to modify the reaction path further, and the monomer - dimer equilibrium in Et_3Al (368) will probably play a part here, ie



It is generally considered that the reactive species is the monomer, and that dimerization or coordination (ie with R_2O , R_2S , etc) leads to a reduction in reactivity. It therefore seemed likely that vapour phase reaction at 90°C led to complete reaction of Et_3Al as the monomer to form Al_2S_3 . A further complication is the possibility of polymerization of SAlEt , with consequent stabilization against further reaction to form Al_2S_3 . It is possible that this predominates at higher temperature, leading to the formation of only SAlEt at 125°C . Whilst these suggestions have no experimental or theoretical basis, they are offered as a possible explanation of observations made, and suggest that vapour phase reaction might be a worthwhile extension of attempts to prepare $\text{Al}(\text{SEt})_3$ from Et_3Al and EtSH .

Infra-Red Data

A comparison of the infra-red spectra of Et_2AlSET (Figure 4.20), EtAl(SET)_2 (Figure 4.22) and EtSH (Figure 4.2) reveals again the strong similarity between the derivatives and the parent mercaptan that was found for the silicon mercaptides (Section 4.2.2.1). Bands occur near 750 cm^{-1} , 980 cm^{-1} , 1280 cm^{-1} , 1380 cm^{-1} and 1460 cm^{-1} in all the thioethyl derivatives of aluminium and silicon, and show the strong family resemblance between these compounds and EtSH . The spectrum of the thiophenol derivative (Figure 4.26) shows a similar resemblance to the spectrum of thiophenol (Figure 4.27). The characteristic aryl $\nu(\text{C-H})$ between 3000 and 3100 cm^{-1} is present, besides very weak bands between 2900 and 3000 cm^{-1} , characteristic of the $\nu(\text{C-H})$ of the aliphatic alkyl component remaining in the molecule after reaction. The characteristic aromatic (C-H) frequency at 1600 cm^{-1} is present. as is the out-of-plane (C-H) bending mode at 730 cm^{-1} . These bands, together with many others in the fingerprint region, are present in both thiophenol and the aluminium derivative, showing the close similarity between these compounds. The bands expected from the alkyl substituent remaining in the molecule, if indeed it is EtAl(SPh)_2 , are surprisingly weak, as is witnessed by the very weak alkyl $\nu(\text{C-H})$ bands between 2900 and 3000 cm^{-1} . From this evidence, one is led to suppose that the molecule is predominantly aromatic in character (ie Al(SPh)_3 or PhAl(SPh)_2).

The other point of interest in these spectra is the assignment of the (Al-S) stretching frequency. This has been reported (317) as lying between 310 and 391 cm^{-1} . The spectra obtained in the present work all show bands in this region, although

there is no single band present in all three spectra that would enable unambiguous assignment to be made. Et_2AlSEt and $\text{EtAl}(\text{SEt})_2$ have moderately strong bands near 410 cm^{-1} , and there is a weak band near this frequency in the thiophenol derivative. There is also a broad shoulder near 350 cm^{-1} in Et_2AlSEt , and a stronger band at 320 cm^{-1} in $\text{EtAl}(\text{SEt})_2$. There is a corresponding band at 350 cm^{-1} of moderate intensity in the thiophenol derivative. Intensity variations of these bands with degree of substitution of $-\text{SR}$ for $-\text{R}$ are in the correct direction for either of these two groups of bands to be assigned to $\nu(\text{Al}-\text{S})$, and for this reason unambiguous assignment is not possible. Comparison with the published results leads to a preference for $320 - 350\text{ cm}^{-1}$ as the assignment of $\nu(\text{Al}-\text{S})$.

In discussing the far infra-red spectra of the silicon mercaptides (4.2.2.1), peaks in the vicinity of 645 cm^{-1} were attributed to $\nu(\text{C}-\text{S})$; the spectra of the aluminium mercaptides show peaks corresponding to this vibration, although somewhat weaker than the silicon derivatives. This reflects the presence of only one or two carbon-sulphur bonds per molecule in the aluminium derivatives compared to three in the silicon compounds.

Et_2AlSEt has a weak shoulder in its far infra-red spectrum near 460 cm^{-1} . This could be $\nu(\text{S}-\text{S})$ if the assignment of this vibration was correct in the case of the silicon derivatives. There is only the vague suggestion of a band near this frequency for $\text{EtAl}(\text{SEt})_2$; this would indicate a greater stability towards oxidation which is consistent with the polymeric nature of this material. There are several weak bands near 460 cm^{-1} in the spectrum of the thiophenol derivative, and no firm conclusion can

be reached in this case about the possibility of $\nu(\text{S-S})$ occurring in this spectrum.

The conclusions reached from an examination of these spectra are therefore in general agreement with those reached from the spectra of the silicon derivatives, and summarised in Table 4.1. To this data may be added the tentative assignment of $\nu(\text{Al-S})$ to the region of $320 - 350 \text{ cm}^{-1}$.

4.2.3 Conclusions

In the comprehensive study made of the reactions between the anhydrous halides of aluminium and silicon with thiols and their sodium salts, only the reactions between silicon tetrachloride and sodium mercaptides were found to give appreciable quantities of the expected mercaptide derivatives. No reaction was observed between aluminium or silicon halide with mercaptan, although the aluminium halide appeared to promote oxidation of the mercaptan to alkyl sulphide with liberation of hydrogen sulphide. Reaction of silicon tetrachloride with sodium mercaptides in an inert solvent led to the mercaptide derivatives of silicon, $\text{Si}(\text{SR})_4$, as colourless oils, relatively stable towards hydrolysis by water and acids. This is in agreement with previously published results.

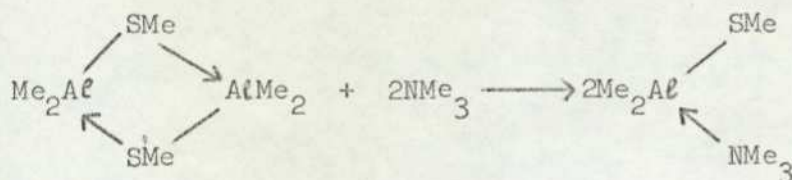
Successful results were not obtained from the analogous reaction between aluminium bromide and sodium mercaptide under similar conditions. If, as seemed likely from later work using aluminium alkyl as starting material, the product required was an insoluble, polymeric material, its separation from the reaction mixture would be difficult. Certainly, only very little soluble product was obtained, although reaction appeared to proceed, with formation of

sodium bromide. The resemblance of the infra-red spectra of the very small amount of soluble product formed to that of EtSH , $\text{Si}(\text{SEt})_4$ and subsequently prepared Et_2AlSEt and $\text{EtAl}(\text{SEt})_2$, suggests that the reaction might at least be considered feasible, although the bulk of the product appeared to remain in the solid phase. As its separation from the sodium halide would be difficult without risk of decomposition, this reaction cannot be regarded as a convenient pathway to $\text{Al}(\text{SR})_3$. Formation of soluble $\text{Al}(\text{SR})_3$ by this means was not possible, and in the light of subsequent work it seems highly unlikely that this derivative could be prepared in a soluble form. A useful extension of the study of the reaction between aluminium trihalide and sodium mercaptide would be to replace the basic sodium salt by an alternative base, for instance anhydrous ammonia or pyridine. This would eliminate the sodium halide from the reaction mixture, and lead to an easier separation of insoluble products.

However, it seemed from later experiments employing aluminium trialkyl that formation of the mercaptide of aluminium, $\text{Al}(\text{SR})_3$, was not possible owing to polymerization of the initially formed R_2AlSR and $\text{RAl}(\text{SR})_2$. This apparently stabilised the molecule against further replacement of alkyl by thioalkyl groups. Attempts to replace the final alkyl group to form $\text{Al}(\text{SR})_3$ were not successful despite the use of a wide range of conditions, and the question is raised as to whether this material is likely to be formed under any conditions. R_2AlSR polymerized slowly on standing, transforming from a clear liquid to a gel, and finally to a white solid. The complete solidification took about 24 hours, and the material remained soluble in non-polar solvents. In the case of $\text{RAl}(\text{SR})_2$ however, the polymerization took place during the preparation, and the resulting material was completely

insoluble under all conditions. Under these circumstances it is very unlikely that reaction to form $Al(SR)_3$ would occur, as the reagent $[Al(SR)_2]$ will be wholly in the solid phase.

Under these circumstances, the replacement of the final alkyl group of $Al(SR)_2$ will depend upon keeping this material in solution in an unpolymerized form. The use of a coordinating solvent is one way in which this might be achieved. Coordination of electron donors (eg R_2O , R_2S) with trialkyl aluminium is well known, and there was good reason for hoping that similar coordination with $EtAl(SET)_2$ would suppress polymerization. For instance, it was reported (347) that trimethylamine, a stronger donor to aluminium than sulphur, can split open cyclic $(Me_2AlSMe)_2$:-



However, these same authors reported that dimethyl ether did not react in this way, and in the present work $EtAl(SET)_2$ precipitated as readily from solution in diethyl ether or dimethyl sulphide as it did from toluene where such coordination is not encountered. The only effect found to result from the use of coordinating solvents was a reduction in the overall reaction rate.

It therefore seemed unlikely that $Al(SR)_3$ could be formed from $AlEt_3$ and RSH in diethyl ether as claimed in the literature. Examination of the reports where this reaction was claimed to have been performed (352, 353) show that in fact only an isolated preparation leading to the trisubstituted derivative was reported, and that this

material was never in fact used in subsequent reactions, all of which employed $\text{MeAl}(\text{SMe})_2$. As the only evidence presented for the formation of $\text{Al}(\text{SMe})_3$ was an elemental determination of aluminium, it is suggested that contamination of the sample (possibly with coordinated ether) led to reduction of the aluminium content from the 20.6 per cent expected for $\text{MeAl}(\text{SMe})_2$ to the 16.3 per cent expected for $\text{Al}(\text{SMe})_3$. It was in fact reported that this analysis was difficult because of a tendency for the material to retain solvent and thiol.

It was felt that the infra-red data presented in this work formed unambiguous proof that the products from reaction between Et_3Al and EtSH in coordinating solvents are identical to those formed in hydrocarbon solvents.

It is possible that reaction between aluminium bromide and sodium mercaptide would be more likely to lead to $\text{Al}(\text{SR})_3$ if the intermediates $\text{Br}_x\text{Al}(\text{SR})_{(3-x)}$ are soluble. However, aluminium halides are strongly associated like the alkyls, and it is by no means certain that this solubility would exist.

For the requirements of the present work, $\text{Si}(\text{SEt})_4$ and Et_2AlSEt possessed the required solubility in non-polar solvents, and were therefore suitable for reaction in liquid hydrogen sulphide. The presence of the alkyl groups in Et_2AlSEt was not considered likely to interfere with thiohydrolysis by hydrogen sulphide. Indeed, trialkyl aluminium reacts with hydrogen sulphide under suitable conditions to form Al_2S_3 (Section 4.2.2).

Of the other reactions with triethyl aluminium examined, that with elemental sulphur was found to proceed similarly to that with mercaptans, Et_2AlSEt being formed. This is exactly analogous

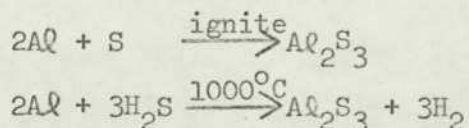
to the formation of $Al(OR)_3$ with oxygen. However, with sulphur the production of Al_2S_3 by side reactions was encountered, and further substitution to form $Al(SET)_3$ was not observed. The reaction between $AlEt_3$ and hydrogen sulphide was found to lead to $EtAlS$ at ambient temperature.

Contrary to patent reports (345, 346), no reaction was observed between aluminium amalgam and thiols. All the reactions performed between aluminium alkyl and sulphur compounds indicated reduced reaction rate compared to the corresponding reactions with the oxygen analogues. This reflects the important difference between the heat of formation of the $Al-O$ and $Al-S$ bonds (369) Al_2O_3 , $\Delta H^\circ = -399$ kcal/mole; Al_2S_3 , $\Delta H^\circ = -121$ kcal/mole. In view of the difficulty experienced in reacting aluminium with alcohols, the lack of any reactivity towards thiols is to be expected.

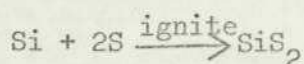
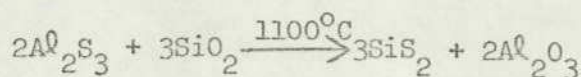
4.3 SULPHIDES

4.3.1 Al_2S_3 and SiS_2

These sulphides are hydrolysed to the oxide and hydrogen sulphide by water, and the only methods reported for their preparation involve high temperature techniques (370, p 823 and p 700). Al_2S_3 is prepared by igniting (with a strip of magnesium) a mixture of the elements, or alternatively by passing a stream of H_2S over aluminium at $1000^\circ C$:-



SiS_2 is prepared by heating a mixture of Al_2S_3 and silica to $1100^\circ C$ in nitrogen, or by igniting (with magnesium) a mixture of the elements (371):-



The chief drawbacks with these methods are the difficulties of purifying the products. Al_2S_3 is purified by removing excess aluminium in vacuo at 1150°C , while SiS_2 may be sublimed under nitrogen at 1200°C - 1300°C . To sublime Al_2S_3 , temperatures in excess of 1550°C are required.

There are few reports of low temperature (non-aqueous) methods for the preparation of these materials. Methods via $\text{Si}(\text{SR})_4$ and AlR_3 (R = alkyl) have been described in Section 4.2. A recent review of silicon-sulphur chemistry describes only classical (high temperature) techniques (372). Polymeric $(\text{SiS})_n$ with a layer structure may be formed by reaction of CaSi_2 and S_2Cl_2 (373), while it has been reported (374) that Al_2S_3 may be formed by heating a mixture of aluminium chloride and calcium sulphide at 60°C - 80°C . It has also been reported that Al_2S_3 may be formed from the reaction between hydrogen sulphide and a benzene solution of aluminium naphthionate (375).

Apparatus suitable for purifying the required quantity of Al_2S_3 and SiS_2 prepared by high temperature techniques was not available. In view of the availability of other starting materials it was not considered worthwhile purchasing suitable equipment. Samples of commercial silicon disulphide and aluminium sulphide were purchased for possible use in the hydrothermal syntheses in liquid hydrogen sulphide. Silicon disulphide was purchased from Cerac Incorporated, and aluminium sulphide

from K and K (distributed by Kodak). Neither material was found to be readily available, and were not available at all in this country, the above American suppliers being the only source discovered. The material was of 'commercial purity', which was taken to mean that no especial purification had been performed following the (high temperature) preparation. X-ray powder patterns were taken for comparison with standard ASTM data, and the results are shown in Figure 4.29 and in Appendix A4 and A6. The technique used to obtain these powder patterns was described in the previous chapter; the samples were ground to a fine powder in the dry box, and transferred to glass capillaries before removal to the laboratory. In this way, contact with the air was avoided, these materials hydrolysing readily on contact with moisture. The results of these examinations showed that the aluminium sulphide was quite pure, with strong diffraction lines (corresponding to the ASTM data for Al_2S_3) indicating a high degree of crystallinity (Appendix A6). Contamination by a small amount of alumina was suggested by comparison of diffraction lines not accounted for by Al_2S_3 with the standard ASTM data. The silicon disulphide was less pure, many diffraction lines not attributed to SiS_2 be observed. Many of these lines may be accounted for by the presence of SiO_2 in various modifications. It is impossible to arrive at a quantitative estimation of purity from this data, but from a rough comparison of impurity line intensity with the intensity of lines attributable to SiS_2 , the impurity level must amount to many percent.

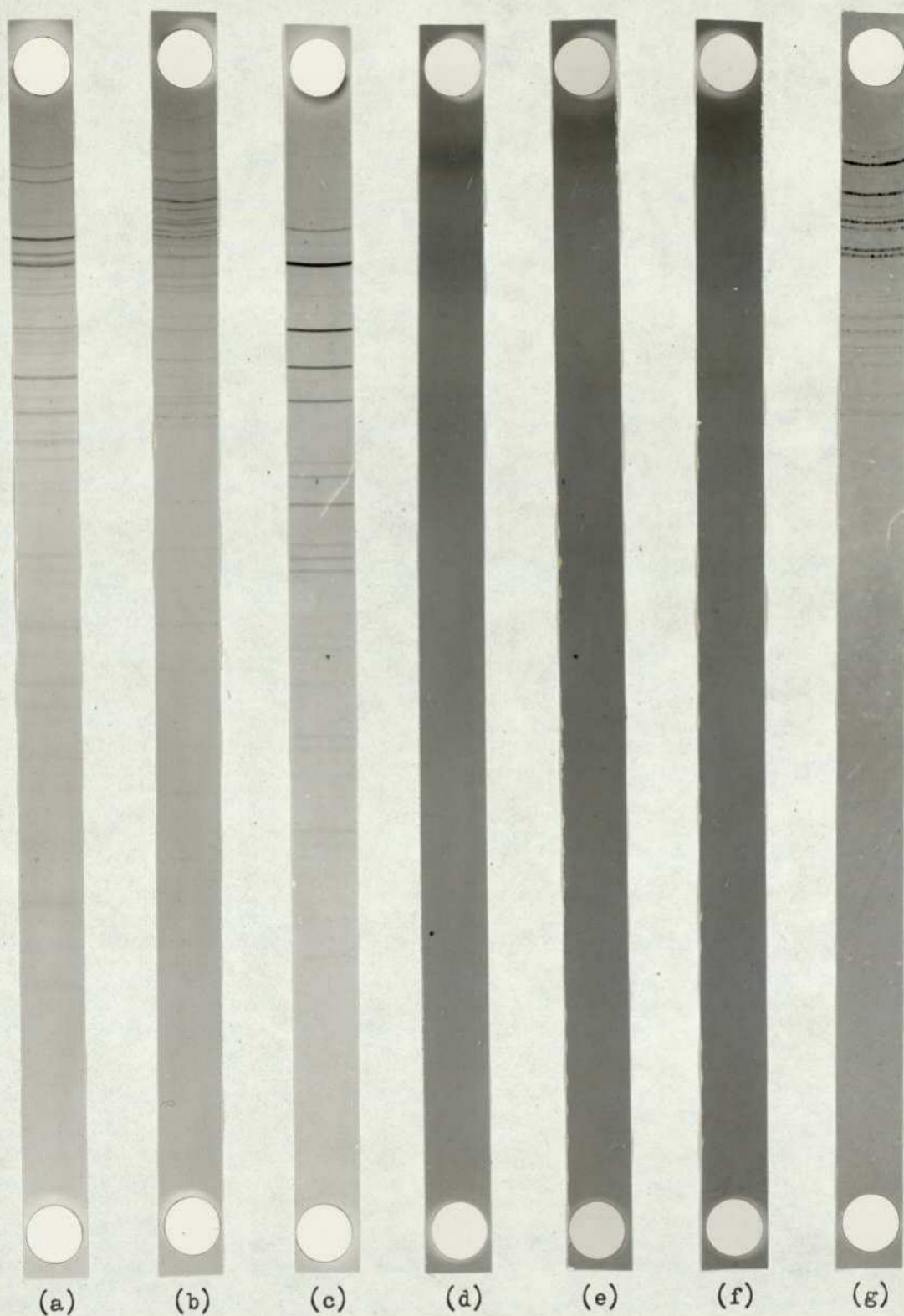


Fig. 4.29 X-Ray Powder Patterns of Feedstock Materials.

(a) Al_2S_3 .

(b) SiS_2 .

(c) NaSH .

(d) GeS_2 .

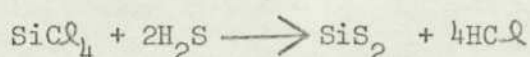
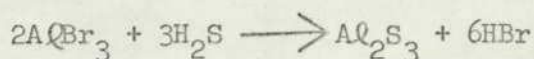
(e) SnS_2 .

(f) In_2S_3 .

(g) $\text{Et}_4\text{N}^+\text{SH}^-$.

Copper K α Radiation

A short investigation was carried out on possible low temperature, non aqueous routes to SiS_2 and Al_2S_3 . In view of the violent reaction of the anhydrous halides of silicon and aluminium with water, it might be supposed that thiohydrolysis would occur with hydrogen sulphide in a similar way:-



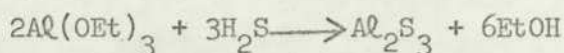
However, it appeared from published data that this is not the case, and these halides are very resistant to attack by hydrogen sulphide. Reaction between SiCl_4 and H_2S is well documented (376, 377). It occurs only over 500°C , and a range of products are formed, including SiCl_3SH , $(\text{SiCl}_3)_2\text{S}$, $\text{Si}_2\text{S}_2\text{Cl}_4$, $(\text{SiSCl}_2)_n$ as well as SiS_2 , which was only formed indirectly. The reaction of H_2S with aluminium halides has not been so well documented, but a range of addition compounds have been reported (378). Brauer (370, p 819) described preparation of $\text{AlBr}_3 \cdot \text{H}_2\text{S}$ in toluene solution. It crystallized out of solution as colourless, moisture sensitive crystals.

A short investigation was made of this reaction to see whether formation of Al_2S_3 was possible. A saturated solution of freshly prepared AlBr_3 in toluene (Section 4.2.2.2) was diluted with its own volume of toluene, and saturated with hydrogen sulphide (BDH, dried over P_2O_5) for two hours. When the H_2S stream was initially introduced, fumes attributed to HBr were observed, and the solution became warm. Heating the liquid until it refluxed produced copious white fumes, and the effluent gas stream produced dense white fumes with gaseous ammonia, confirming the presence of HBr . At the end of the

reaction, a small amount of precipitate had formed, and this was filtered off in the dry box and washed with toluene. Less than 0.1 g were obtained after drying, and therefore the material cannot be regarded as a major product. An analysis for aluminium and sulphur was performed, although in view of the small amount of sample available it cannot be regarded as very accurate. Found: Aluminium, 15.45 per cent; Sulphur (total, sodium fusion), 14.55 per cent. Required: Al_2S_3 , 64.2 per cent S, 35.4 per cent Al; $\text{AlBr}_3 \cdot \text{H}_2\text{S}$, 10.7 per cent S, 8.9 per cent Al; $\text{AlBr}_2(\text{SH})$, 14.6 per cent S, 12.3 per cent Al; $\text{AlBr}(\text{SH})_2$, 37.1 per cent S, 15.6 per cent Al. From these results, it seemed that $\text{AlBr}_2(\text{SH})$ was the most likely product. Unfortunately, insufficient sample was available to enable a bromine analysis to be carried out, but it seemed evident that stepwise replacement of bromine with sulphur had occurred. As with SiCl_4 , complete reaction to form the sulphide was apparently not encountered. The solution remaining from the reaction did not react so violently in air as did the AlBr_3 solution used, and both HBr and H_2S were produced by its reaction with water. It seemed likely, therefore, that an adduct (possible $\text{AlBr}_3 \cdot \text{H}_2\text{S}$) was present in solution, and it was possibly the formation of this that inhibited reaction to form the sulphide.

Attempts to conduct the reaction between AlBr_3 and H_2S in sulpholane (a solvent of high dielectric constant which it was hoped would promote dissociation and reaction of dimeric AlBr_3) were not successful. Attack on the solvent occurred, and reaction appeared to be only slightly enhanced.

The final approach investigated was the reaction of aluminium ethoxide with H_2S . This is analogous to the reaction between sodium ethoxide and H_2S used to prepare NaSH (Section 4.3.2), and it was considered as a possible route to Al_2S_3 (or the hypothetical $\text{Al}(\text{SH})_3$).

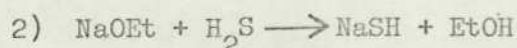
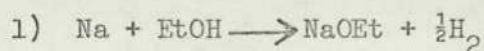


Ethanol was carefully dried with firstly calcium sulphate, and then by distillation over magnesium ethoxide. It was then reacted with carefully cleaned and dried aluminium wire in the presence of sodium-dried xylene. The solution of aluminium ethoxide obtained was saturated with H_2S at room temperature and subsequently heated. No reaction was observed. Diluting with diethyl ether caused precipitation of unreacted aluminium ethoxide, shown by analysis to contain no sulphur.

It was therefore apparent that compared to the violent hydrolysis observed between for instance, silicon tetrachloride and water, a surprising lack of thiohydrolysis was found with hydrogen sulphide in the systems examined. These conclusions are in agreement with the findings described in the previous section (4.2), where comment was made on the lesser reactivity of thiols than alcohols towards alkyl aluminiums and metallic aluminium.

4.3.2 NaSH

This material was prepared in an anhydrous state by the method described by Brauer (370, p 357). The apparatus used is illustrated in Figure 4.30.



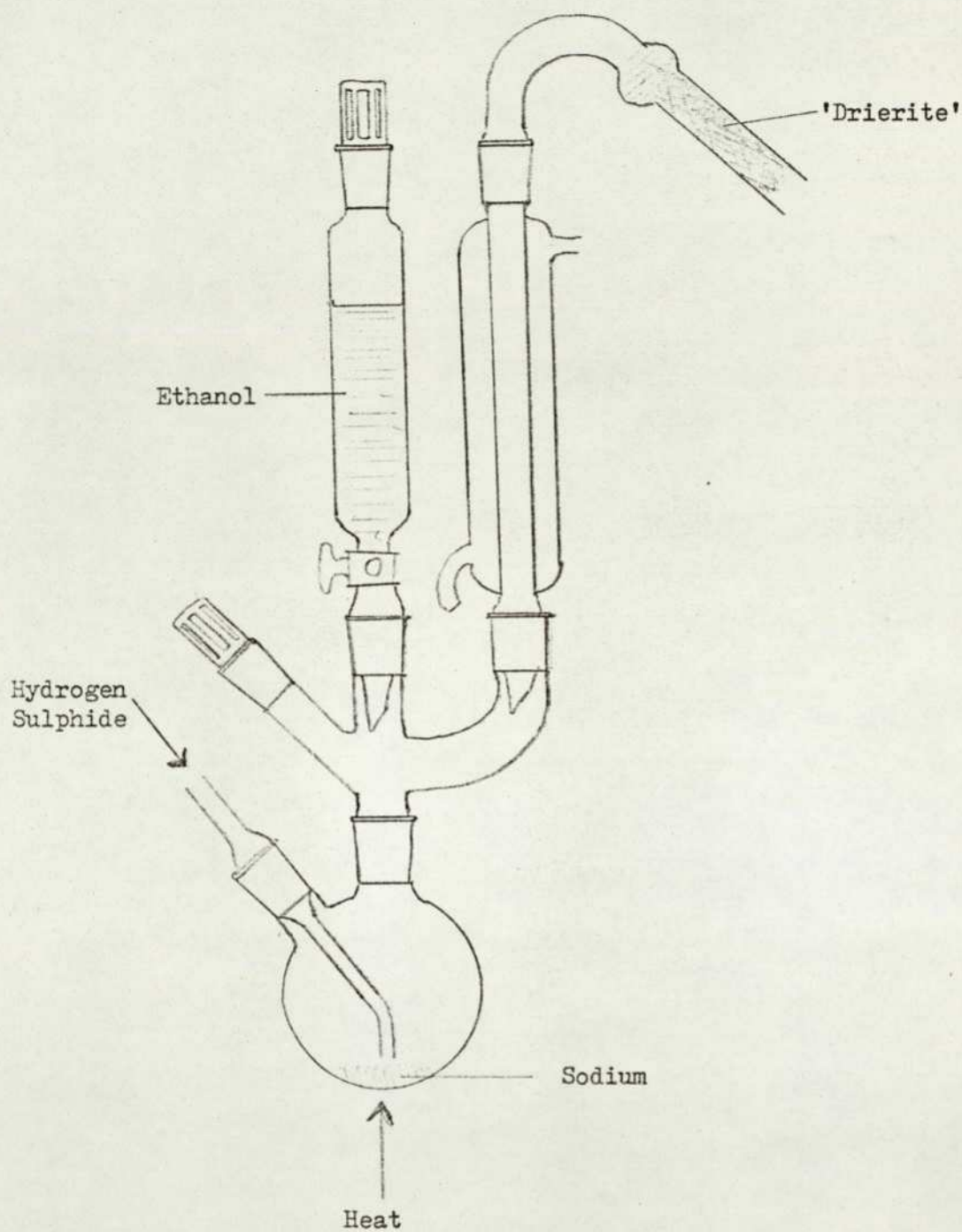


Fig. 4.30 Apparatus for the preparation of Sodium hydrosulphide, NaSH , free of moisture.

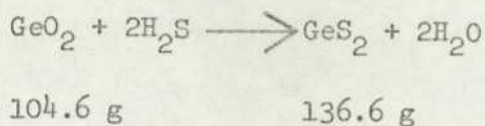
Ethanol was dried by refluxing over calcium sulphate, and 200 mL distilled into the separating funnel. It was then run onto the sodium (10 g, cut and weighed in the dry box), and when the initial reaction had subsided, the mixture was refluxed and ethanol added until all the sodium had dissolved. H_2S (BDH, dried over P_2O_5 supported on glass wool) was bubbled in until the liquid was saturated, and H_2S was issuing from the effluent tube. The solution was then transferred to the dry box, and an excess of sodium dried ether was added. The precipitate of NaSH immediately formed, and was filtered off and washed with sodium dried ether and dried under vacuum. Yield - 14.12 g, 58.4 per cent on sodium used. A sample was analysed for sulphur. It was dissolved in dilute sodium hydroxide solution and titrated with iodine as in the sodium fusion analysis. Found; S, 55.53 per cent; Required for NaSH, 57.10 per cent. An X-ray powder pattern was obtained of the material (Figure 4.29 and Appendix A4). All lines of intensity greater than about 20 per cent were accounted for by the ASTM data for NaSH (Appendix A6). The presence of very weak lines not listed in the ASTM data is not of direct relevance as it is by no means certain that all the diffractions it is possible to observe under favourable experimental conditions are included in the published data.

4.3.3 GeS_2

Germanium disulphide is precipitated as a white solid from strongly acid solutions of Ge IV compounds by H_2S (380). It may also be formed by heating GeO_2 with sulphur or in a

stream of H_2S , or by direct reaction of the elements at high pressure (31, 382). GeS_2 is slightly soluble in water, but the solution rapidly hydrolyses. It dissolves in alkaline sulphide solutions to form thiogermanates, and is reprecipitated when these solutions are acidified. A useful summary of the general properties of the material is included in Glockling's work (381).

GeS_2 was prepared from a solution of GeO_2 in 6NHCl . The technique was described by Brauer (370, p 723). GeO_2 supplied by



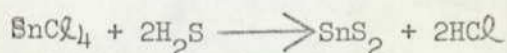
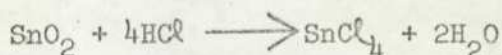
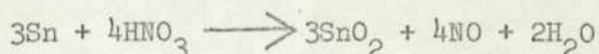
Koch Light (>99.999 per cent GeO_2) was employed, but difficulty was experienced in dissolving this in the hydrochloric acid. For this reason it was fused with a mixture of sodium peroxide and sodium carbonate in a nickel crucible. The residue readily dissolved in water on boiling, and the solution was then acidified with hydrochloric acid. H_2S (obtained from BDH) was bubbled into the solution for 30 minutes, and the solution then left over night under a positive pressure of H_2S . The precipitate of GeS_2 that appeared was filtered off, washed with water and dried under vacuum, and the solution resaturated with H_2S and refiltered. Up to 90 per cent conversion of the GeO_2 to GeS_2 was obtained.

An X-ray powder pattern was obtained of the product (Appendix A4; Figure 4.29), and revealed that it was almost completely non-crystalline. Only a few very weak lines were observed.

4.3.4 SnS₂

The usual method of preparing stannic sulphide involves reaction of the elements (370, p 741), but a simpler approach involves precipitation by H₂S from a solution of a SnIV salt. Material so prepared possessed the added advantage of being readily soluble in alkali sulphide solution (4, p 661), and therefore of more use for the present work.

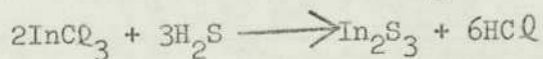
AR tin was dissolved in concentrated AR nitric acid, and the white precipitate of SnO₂ filtered off and dissolved in dilute (20 per cent) HCl by repeated evaporation to low volume. The resulting solution was filtered, diluted with four times its own volume of water and saturated with H₂S (BDH). The yellow precipitate of SnS₂ was filtered off, washed with water and dried under vacuum over P₂O₅.



Up to 80 per cent conversion of Sn to SnS₂ was obtained. The product was found by X-ray diffraction (Appendix A4; Figure 4.29) to be nearly completely non-crystalline.

4.3.5 In₂S₃

Indium sulphide was prepared by the method of Hahn and Klinger (383), and summarised by Brauer (370, p 864). It involved precipitation of the sulphide from weakly acidic aqueous solutions of In III salts by H₂S.



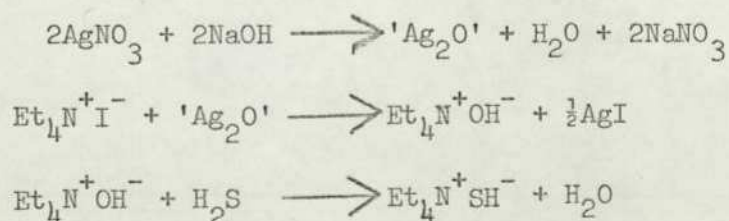
442.6 g

325.8 g

Indium chloride, InCl_3 , was used as the starting material. It was obtained from Koch Light (>99.999 per cent InCl_3) and dissolved in an acetic acid/sodium acetate buffer solution for saturation with H_2S . The yellow precipitate of In_2S_3 was filtered off, washed with water and dried under vacuum over P_2O_5 . 93.7 per cent conversion of InCl_3 to In_2S_3 was obtained in a typical preparation. It was shown by an X-ray powder pattern to be nearly totally non-crystalline (Appendix A4; Figure 4.29).

4.3.6 Tetraethylammonium Hydrosulphide, $\text{Et}_4\text{N}^+\text{SH}^-$

The preparation of the class of material represented by $\text{R}_4\text{N}^+\text{SH}^-$ was described by Cotton and Waddington (384), and the method described was used in the present work to prepare the ethyl derivative, $\text{Et}_4\text{N}^+\text{SH}^-$. The method involved reaction of a solution of tetra ethylammonium hydroxide with gaseous hydrogen sulphide. The tetra ethylammonium hydroxide was prepared by treatment of the iodide with silver oxide. The silver oxide was freshly prepared by precipitation from aqueous silver nitrate solution using dilute (5N) sodium hydroxide solution. The dark brown precipitate of silver oxide was filtered off, washed with water and methanol and dried under vacuum.



40 g of tetra ethylammonium iodide (obtained from BDH) was dissolved in AR grade methanol (400 ml), and silver oxide added until no iodide was detected in the liquid phase. The mixture was shaken for one hour, and the silver iodide and excess silver oxide filtered off. The solution was then saturated with H_2S . It rapidly became yellow in colour, and H_2S was passed in until it was issuing freely from the effluent line. The methanol was then removed under vacuum, and the residue slowly crystallized to a yellow solid. The crystals were then cautiously heated to 85°C in a water bath (still under vacuum). The colour of the solid gradually faded to white over six hours, as methanol of crystallization was lost.

The published method indicated that all reagents should be carefully dried before use; in view of the liberation of 1 mole of water in the final stage, this seemed somewhat unnecessary, although reasonable precautions were taken to avoid excessive contact of the materials with the atmosphere. A yield of 15.0 g $\text{Et}_4\text{N}^+\text{SH}^-$ was obtained, representing 61.2 per cent conversion of the iodide.

The infra-red spectrum of the product (Figure 4.31) exhibited a band due to ∇ (S-H) at 2550 cm^{-1} . The band at 3300 cm^{-1} is probably due to water absorbed during the time the spectrum was being run. The band at 1620 cm^{-1} is also attributable to moisture.

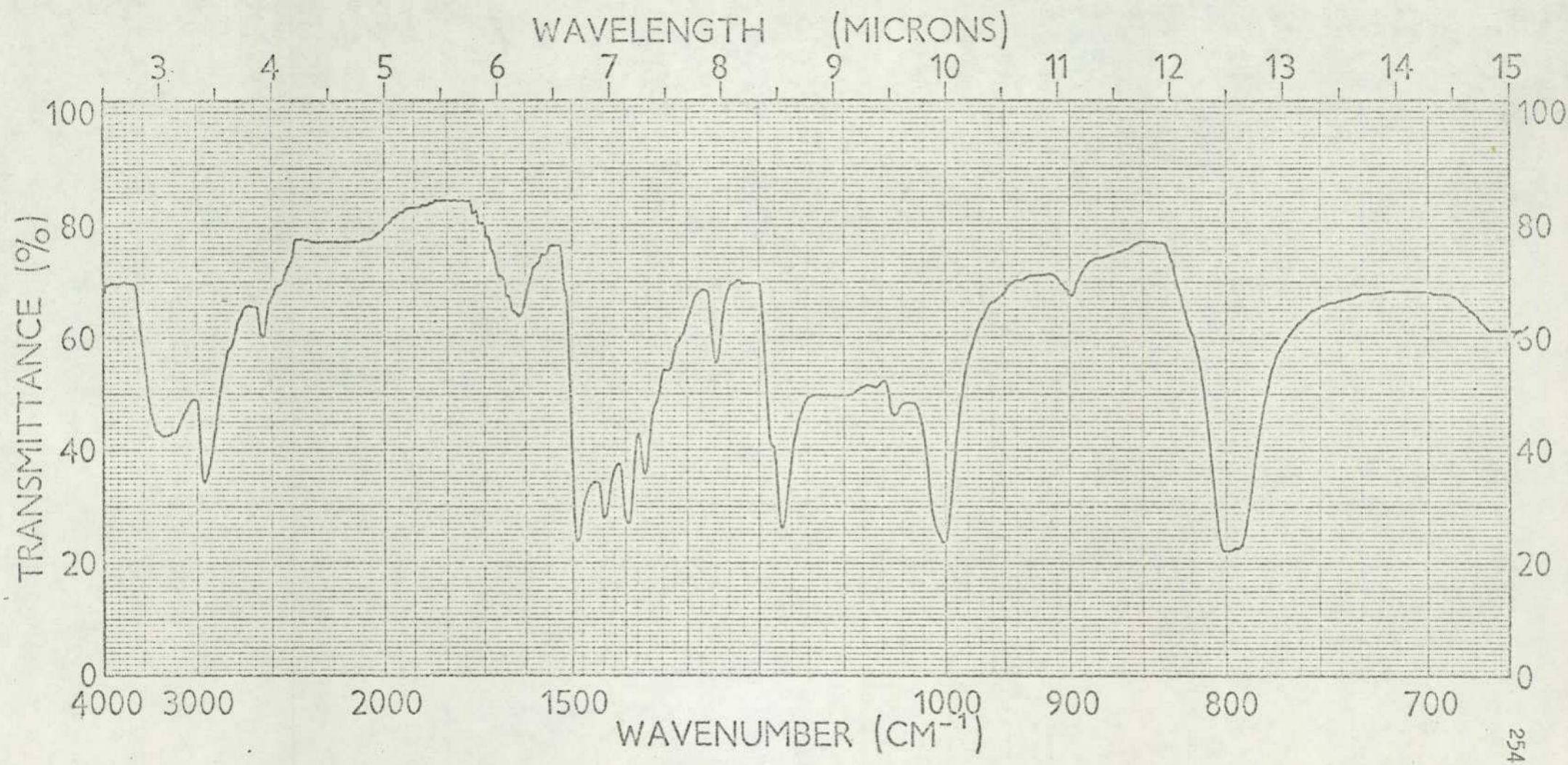


Fig. 4.31 Infrared Spectrum of $\text{Et}_4\text{N}^+\text{SH}^-$. KBr disc.

Analysis for sulphur, carbon, hydrogen and nitrogen was made to confirm the identity of the material. Sulphur was determined by reaction with acidified iodine, as described previously for the determination of thiol derivatives. Carbon, hydrogen and nitrogen were determined with an F and M model 185 analyser. Found: S; 20.03; 20.06 per cent; C: 55.7, 56.7 per cent; H: 12.76, 12.92 per cent; N: 8.04, 8.04 per cent. Calculated for $(C_2H_5)_4N^+SH^-$; S: 19.64 per cent; C: 58.80 per cent; H: 12.99 per cent; N: 8.57 per cent. An X-ray powder pattern was also obtained (Appendix A4; Figure 4.30), and indicated that the material was highly crystalline.

CHAPTER 5. HYDROTHERMAL PREPARATIONS IN LIQUID AND SUPERCRITICAL HYDROGEN SULPHIDE

5.1 INTRODUCTION AND LITERATURE

The preparation of minerals and other crystalline solids by hydrothermal methods is a well established technique, duplicating the processes by which these materials are formed in nature. In Chapter 2, the method was described, and it was indicated how water is generally the solvent used. Oxides are readily prepared under these conditions, and the technique is widely used either for the preparation of new phases in polycrystalline form, or for the growth of large crystals from polycrystalline feedstock.

The basis of the method is the transportation and reaction of solids in a fluid medium. The solid species in solution either react to form new (generally insoluble) phases, or alternatively are transported to a zone where they are precipitated from solution (in crystal growth). Solvents other than water that have been used in these systems were described in Chapter 2. An additional component will frequently be present to promote solubility of the starting materials. Thus oxides are prepared in the presence of a base, and the oxides dissolve as complex ions. Generally (but not invariably) such reactions are conducted under pressure, above 100°C. The critical factor is generally solubility of the starting phases, and it is not necessary for the solvent to be in liquid form; supercritical conditions may be used if this promotes solubility and is compatible with other factors.

As a model in the present work, the synthesis of zeolites was considered. The starting materials are silica and alumina (or silicates and aluminates), which are reacted in a basic medium (generally alkali hydroxide solution). The gels which form are crystallized to form zeolites under hydrothermal conditions, generally above 100°C .

The object of the work described in this and the following chapter was the duplication of this type of reaction in the sulphur system. By direct analogy with conventional aqueous systems, hydrogen sulphide would be used as solvent for the preparation of sulphides. Alumina and silica would be replaced by aluminium and silicon sulphides, and the base would become sodium hydro-sulphide or a similar sulphide. This type of approach forms the basis of the work described in the present chapter. However, there is a different approach which is described in the following chapter. In Chapter 2, it was described how certain metal sulphides may be crystallized in aqueous media in the presence of alkali sulphide. This type of approach could be applied to the formation of sulphur analogues of zeolites providing that the sulphides involved are not hydrolysed by water under the conditions used. Of the Group III b and IV b sulphides under consideration, those of indium, germanium and tin fulfil this condition and have been shown to be capable of undergoing isomorphous substitution into a thiozeolite lattice (Chapter 2). This approach forms the basis of the work described in Chapter 6.

The hydrothermal synthesis employing hydrogen sulphide as solvent formed the core of the work described in

this thesis, and continued over a large proportion of the time available for practical work. It formed a new and novel concept in sulphide chemistry, hydrogen sulphide having been only little used as a solvent owing to its toxic and corrosive nature, and the fact that it is necessary to work either at sub-zero temperatures or under elevated pressure. A large proportion of the funds available in the present work were invested in sophisticated high pressure equipment able to operate up to 400°C and 4000 psi. The ground work having been covered and suitable starting materials prepared, a start was made in investigating what was effectively a completely new type of system.

Only a few of the standard tests on non aqueous solvents mention liquid hydrogen sulphide. A brief review is included in the book by Charlot and Tremillon (386), whilst a more detailed account has been published by Fehér (387). By analogy with water, liquid hydrogen sulphide might be supposed a protonated solvent producing H_3S^+ ions. However, in general its properties lead to its classification as a non-polar, non-associated solvent, more like a hydrocarbon than water. The liquid is inactive when dry and pure, and it is a poor, non-dissociating solvent for salts, only covalent solids being appreciably soluble in it.

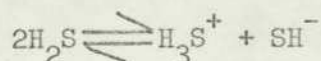
The boiling point of liquid hydrogen sulphide is -60°C and its freezing point is -85°C . Thus, besides requiring low reaction temperatures when experiments are conducted at

atmospheric pressure, the limited liquid temperature range of 25°C is a further drawback. Therefore, most useful experimental work is conducted in an autoclave, when the liquid phase is present up to the critical temperature of 100.4°C . The vapour pressure at this temperature is 88.9 atm.

Useful tabulations of the thermodynamic properties hydrogen sulphide have been made (388-390), and this data was invaluable for calculating reaction conditions. Sage and Lacey (389) reported pressure versus volume isotherms for liquid and supercritical hydrogen sulphide from 40°F (4.5°C) to 340°F (171°C), above which they considered it to decompose (391). However, other authors have extended this temperature range. Information of West (388) extended from -76.4°F (-60.2°C) to 1300°F (704.5°C), using fundamental data and basic thermodynamic equations. Lewis and Fredericks (390) made measurements which extended the experimental data to 220°C and 1700 atm. This data was previously reported in the thesis of Lewis (157).

Earlier experimental data (392, 393) is largely superseded by these publications. More recently, the vapour pressures of H_2S and D_2S were measured over the range -78° to 30°C (394). A compilation of the physical constants of liquid hydrogen sulphide is presented in Table 5.1. Further details are included by Feher (387).

The value of the dissociation constant included in this table is due to Jander (395, 396), and represents the equilibrium constant of the reaction:-



Melting Point (1 atm.)	-85.5°C	} see text
Boiling Point (1 atm.)	-60.3°C	
Critical Temperature	100.4°C	
Critical Pressure	88.9 atm.	
Critical Density	0.3103 g cm ⁻³	}
Dissociation Constant (-78°C)	25.10 ⁻³⁴	
Dielectric Constant (194.6°K)	8.99	} (397)
" " (212.0°K)	8.04	
Dipole Moment (194.6°K)	0.88 D	
" " (212.0°K)	0.78 D	} (398)
Conductivity (DC, -78.5°C)	3.7.10 ⁻¹¹ Ω ⁻¹ cm ⁻¹	
Polarizability	3.78 cm ³	(418)
Density at Melting Point	~1 g cm ⁻³	} (400,401)
" " Boiling Point	0.950 g cm ⁻³	
Viscosity at 191°K	0.547 (η _{H₂S} /η _{H₂O})	} (402)
" " 212.9°K	0.45 (η _{H₂S} /η _{H₂O})	
Expansion Coefficient (average) (-84 to -62°C)	0.00174 deg ⁻¹	(403)
Surface Tension (189°K)	33.418 dyne cm ⁻¹	} (404)
" " (210.8°K)	28.783 dyne cm ⁻¹	
Parachor	82.0	(403,405,406)
Molar Heat Capacity (200°K)	16.26 cal. mole ⁻¹ deg ⁻¹	(408,409)
Enthalpy of melting	568.1 ± 0.4 cal mole ⁻¹	(408,412)
Entropy of melting, ΔS _m	3.03 eu	(411)
Enthalpy of vapourisation (mp)	4676 ± 5 cal mole ⁻¹	} (408,412,
" " " (bp)	4451 cal mole ⁻¹	
Entropy of vapourisation	21.3 eu	(411)
Molar Cyroscopic Constant	3.83°C	} (416,417)
Molar Ebullioscopic Constant	0.63°C	

Table 5.1 Physical Data of Hydrogen Sulphide, together with sources of reference.

Jander regarded liquid hydrogen sulphide as a water-like solvent, a view now held to be largely misguided. His work is discussed in more detail below.

The value of specific conductivity quoted is that of Satwalekar et al (398). Large discrepancies occur in the literature regarding the electrical conductivity of H_2S , almost certainly due to the presence of impurities. The presence of even a small amount of water causes large variations. The formation of a compound $\text{H}_2\text{S} \cdot 5.7\text{H}_2\text{O}$ has been reported (399, 400).

A large number of correlations of the solvent properties of liquid hydrogen sulphide have been published, mostly in the first half of this century. Fehér (387) has discussed the solvent properties in terms of the factors governing the solvation forces - the dipole moment, molar volume, polarizability and dielectric constant. The solubility of polar gases (eg HCl , HBr) or polar liquids (eg acetone, ethyl ether, ethanol, carbon disulphide, alkyl halides) is readily explained by this approach. In the case of solids, the heat of sublimation was taken as a measure of the intermolecular forces that must be overcome to produce a molecular dispersion in solution. The value 15 kcal/mole was cited as the maximum heat of sublimation permissible for a material to be readily soluble in liquid hydrogen sulphide. Among the compounds that should be soluble are covalent materials crystallizing in molecular form, such as ZnCl_2 , HgF_2 , HgCl_2 , HgBr_2 , HgI_2 , CCl_4 , CBr_4 , SiCl_4 , SnCl_2 , PCl_3 , PBr_3 , BiCl_3 , ICl_3 , I_2 , AlCl_3 , AlBr_3 , AlI_3 .

Ionic compounds have much higher heats of sublimation, typically 60 kcal/mole, and to form an ionic (rather than a molecular) dispersion would need three or four times this energy. Solubility of ionic compounds is not therefore expected to occur in liquid hydrogen sulphide. To reduce the solvation forces necessary to promote solution of ionic species, larger cations may be used (eg alkyl ammonium ions), which has the effect of reducing electrostatic interaction in the molecule. This should increase the solubility of these compounds in liquid hydrogen sulphide. The low dielectric constant of this solvent will, however, result in only a low degree of ionization in solution.

By and large, experimental results agree well with these predictions. Early work on the solvent properties of liquid hydrogen sulphide was reviewed by Wilkinson (419) and Jander (395, 396, 420). Wilkinson considered liquid H_2S as similar to a hydrocarbon rather than water-like, very few inorganic substances being soluble in it. Salts of metals with strong acids were insoluble, and only AlCl_3 , HCl , HBr , ZrCl_2 and a few sulphides were reported to dissolve. With the exception of COCl_2 , which is insoluble in water and soluble in liquid H_2S , Group IV halides are hydrolysed by water but dissolved liquid H_2S without reaction. At elevated temperature, the halides of phosphorous and arsenic reacted with liquid H_2S to form sulphides, but hydrolyse in water to form soluble acids. This, and much other similar evidence, was cited by Wilkinson to support his concept of liquid H_2S as a non-polar, hydrocarbon-like solvent.

Jander, however, adopted the opposite view, suggesting that hydrogen sulphide was water-like in its properties, and proposing the autoionization (with formation of H_3S^+) described above. This view was based on a number of factors, including: (1) Conductivity measurements which indicated enhanced conduction by solutes; (2) Neutralization of NaSH by HCl to form NaCl ; (3) Conductimetric titration of $(\text{Et}_3\text{NH})^+\text{SH}^-$ with acids; (4) Colour changes of indicators similar to those found in water; (5) The existence of a metal activity series ($\text{Na} > \text{K} > \text{Cu} > \text{Ag} > \text{Hg}$) for the formation of hydrogen and the metal sulphide with liquid H_2S ; (6) Amphoteric behaviour - ie As_2S_3 soluble in solutions of both HCl and $(\text{Et}_3\text{NH})^+\text{SH}^-$ in liquid H_2S .

Jander called hydrogen sulphide and similar materials 'quasi aqueous' solvents - eg HF , NH_3 , SO_2 , HCN . The view of Wilkinson is generally regarded as correct nowadays, Jander's opinion apparently being based on misinterpretation of data as well as incorrect information. Hydrogen sulphide may be considered a non polar, hydrocarbon-like solvent, with only limited ionization resulting when solubility does occur.

As early as 1901 it had been recorded (421) that while a small amount of KCl could be dissolved in liquid H_2S , the solution was non-conducting. Following this, there were many tabulations of the solubilities and reactivities of materials, both inorganic (399, 422 - 424, 434) and organic (425-429) published during the first half of the present century. Often measurement of the conductance of such solutions

was reported (395, 398, 402, 419, 420, 424, 425, 429 - 433, 450, 451).

In general, ionic materials with low lattice energies (eg ammonium halides) were the only salts found to be soluble. Mostly inorganic materials were insoluble and organic materials soluble. Inorganic materials that were soluble either dissolved without reaction (eg SiO_2 , PCl_3 , CS_2), formed materials of the type $\text{MX}_n \cdot m\text{H}_2\text{S}$ (eg Al, Be, Ti, Sn halides), or thiohydrolysed (eg Hg(II), Cu(I), Ag, P, S halides). Metals and their salts were generally without reaction in liquid H_2S , although the alkali metals slowly hydrolysed (435). Na_2CS_3 was formed from CS_2 and hydrated Na_2S in liquid H_2S (423). The report by Lineken (436) covered this period of publications. A great many correlations of the solubility and interaction of inorganic materials with liquid H_2S were made, frequently contradictory. If any one factor can be singled out, it is the very slow rate of any reaction that occurs, measured in weeks or months. This was attributed to the very low ionization present. In general, such data referred to experiments in sealed tubes at room temperature, and variations in conditions, purity and time may well explain some of the discrepancies noted.

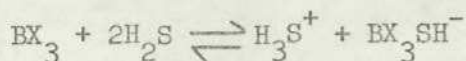
The data referring to organic materials is rather more satisfactory. The presence of a double bond was usually shown by the development of a thiol smell with liquid H_2S . Amines reacted to give instable addition compounds, while aldehydes substituted a sulphur atom for the oxygen of the aldehyde group to form a thioaldehyde. Acyl halides substituted an SH group for the halide and sulphur for oxygen

to form dithio acids. Acetyl chloride and bromide were converted to the dithioacetic acid, which then lost H_2S to form a thioanhydride.

Most organic materials (with the exception of those that react) give non-conductivity solutions in liquid H_2S . The conductivity increase when organic bases are dissolved in liquid H_2S was first reported in 1904 (425), when the formation of a sulphide with bases such as piperidine, quinoline and di-isobutylamine was postulated. Since then, the high solubility and conductivity of amines and alkyl ammonium salts in liquid H_2S has been the subject of several papers. The earlier work is included in the conductivity references above. The autoionization proposed by Jander (395, 396, 420) was based on the titration of such a solution with HCl . However, later work of Cotton and Waddington (384) and McDaniel and Evans (437) disagreed with Jander's results; the formation was shown of tetra-alkylammonium sulphides, R_4NSH , coordinating H_2S loosely at low temperatures with hydrogen bond energies of 5-14 kcal/mole. While it is believed that these salts are dissociated into ions in solution, liquid H_2S has a poor ionizing power for the hydrogen halides, which are largely undissociated in solution. Neutralization, it was suggested, involved a direct proton transfer from HCl to the base.

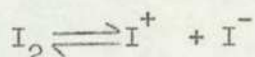
Cotton and Waddington have also examined (438) the neutralization of these bases in liquid H_2S with Lewis acids of boron, with the formation of salts of the type

$R_4N^+BX_3^-$. No conductivity increase was observed when BX_3 was added to the pure solvent, and so the reaction



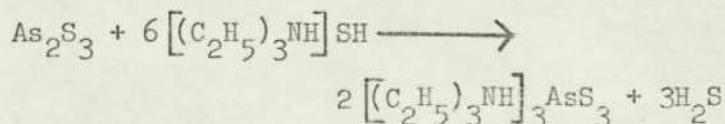
is unlikely. The reactions of tetra alkylammonium hydrogen sulphides with diborane indicated an anion $B_2H_6SH^-$ is initially formed, and this gradually loses hydrogen. This was later confirmed by ^{11}B NMR (448). The chemical behaviour of a number of Group IV, V and VI compounds in liquid H_2S was studied (439), and tetra alkylammonium salts containing anions such as $SiCl_4S^{2-}$, $(SiF_4)_2S^{2-}$ and $SiCl_4(SH)_2^{2-}$ isolated after neutralization. Condensation of silicon difluoride with liquid H_2S at liquid nitrogen temperature led to polymers such as SiF_2HS (449).

Iodine functions as a true electrolyte in liquid H_2S , increasing its conductivity by 10^4 (433, 450):-



$SbCl_3$ also greatly increases the conductivity of liquid H_2S (by 10^7), and this has been attributed (396) to formation of a complex acid, $H_3SbCl_3(SH)_3$, which dissociates stepwise.

^{35}S exchange has been examined (440, 441) in neutral and basic solutions of materials in liquid H_2S . Very slow exchange was observed in neutral solutions of CS_2 , CH_3SCH_3 or C_2H_5SH . In basic solutions, arsenic and antimony sulphides, CS_2 and S showed rapid exchange, attributed to the presence of thioanionic species, eg:

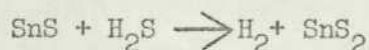


Triethylamine was postulated as opening the S_8 rings of elemental sulphur, with the formation of polysulphides.

Solubility of sulphur in liquid H_2S has been recently studied (442, 443). The solubility reported was 5.10^{-6} mole $S_8/g H_2S$ at $-80^\circ C$ and 5.10^{-5} mole $S_8/g H_2S$ at $80^\circ C$. A further review, on the $S-H_2S-H_2S_x$ system, was published by Wiewiorowski (444). The interest in this type of system stems from the occurrence of H_2S in sulphur deposits. The proposed use of liquid H_2S to recover oil deposits (445-447) also requires such information.

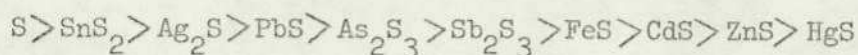
The reaction of S_nCl_2 ($n = 1, 2, 3, \dots$) with liquid H_2S led to sulfane, H_2S_x ($x = n + 2$) (452). The reaction of B_2O_4 and SO_3HCl led to B_2Cl_4 , H_2S and $H_2S_2O_3$, respectively (453, 454).

Finally, reference must be made to the work on the solvent properties of liquid H_2S conducted by Lewis (157). It formed an evaluation of the possibility of crystal growth of the sparingly soluble heavy metal sulphides in high density, supercritical H_2S . The background was the ability of supercritical gases to dissolve and transport solids, and the success met with in analogous aqueous systems (ie growth of quartz). Solubility tests were conducted for a number of sulphides at room temperature, in sealed tubes. CdS , AgS , Sb_2S_3 , PbS , ZnS and SnS were apparently insoluble, although SnS reacted to form SnS_2 (identified by X-ray powder diffraction):-

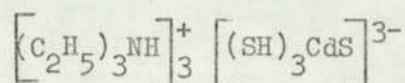


Using an isopiestic method, an order of solubility was found which agreed with that calculated from Raoult's law.

This suggested that H_2S behaved as in ideal solvent:-



It was found that CdS , Ag_2S , SnS , ZnS and possibly PbS dissolved in basic solutions of triethylamine in liquid H_2S . In the case of cadmium, the ionic species was purported to be:-



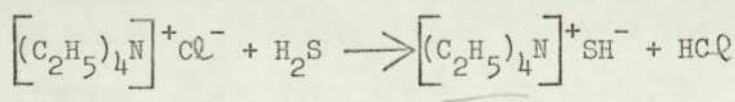
Conductivity measurements were made on supercritical H_2S . The results suggested that there was only slight dissociation above the critical temperature, and that metal sulphides interacted only weakly. Only in the presence of an organic base (ie triethylamine) did appreciable ionization occur.

Attempts at crystal growth of the heavy metal sulphides in supercritical H_2S were not particularly successful. A limited amount of recrystallization of SnS_2 and PbS occurred, and the use of triethylamine promoted a little recrystallization of cadmium sulphide. The conclusion reached by Lewis was that in pure H_2S , solutions of metal sulphides were unionized, and that the use of a mineralizer would be essential for successful results. Water, triethylamine, hydrogen chloride and organo-substituted ammonium halides were suggested, but this approach was not followed up.

There was thus a good basis from which to develop the present work. The use of liquid hydrogen sulphide as a solvent for hydrothermal synthesis would require a base to promote solubility as well as finely divided sulphides as starting materials. Attempts by Lewis to use supercritical conditions had not shown any distinct advantages over sub-critical conditions, ionization and solubility not being appreciably increased. Increase in solubility would be the only incentive for using supercritical conditions, and there was evidence to suggest that this could be more readily achieved through the use of (soluble) organic bases. Further, a possibility existed of decomposing such bases with excessive temperature.

Therefore, two approaches were adopted. A series of experiments was conducted using an inorganic base (NaSH) in direct analogy with the preparation of conventional zeolites. Both sub-critical and super-critical conditions were used.

Secondly, a series of sub-critical experiments using the organic base $(C_2H_5)_4N^+SH^-$ were carried out. The reported solubility of certain metal sulphides in H_2S solutions of such bases gave incentive to this approach. The organic base used (abbreviated to $Et_4N^+SH^-$) possessed the advantage over the chloride of not liberating HCl in solution:-



Triethylamine, $(C_2H_5)_3N$, and triethylamine chloride, $[(C_2H_5)_3NH]^+Cl^-$ have also been used as bases in liquid H_2S , but the larger tetra alkyl ammonium ion of $(C_2H_5)_4N^+SH^-$ possesses stronger basic properties in liquid H_2S (384), and has been incorporated into conventional zeolites in place of the alkali metal ion (455).

In view of the slowness of reaction which seemed universal among the investigations of the solvent properties of liquid H_2S , the experiments were conducted for 1-4 weeks. The metal sulphides used were Al_2S_3 , In_2S_3 , SiS_2 , GeS_2 and SnS_2 , all of which were potentially capable of forming a thiozeolite structure (see Chapter 2). The preparation of these sulphides (together with the bases) has been described in Chapter 3. While SnS_2 , GeS_2 and In_2S_3 were readily prepared in a finely divided form suitable for the hydrothermal synthesis, the preparation of pure Al_2S_3 and SiS_2 presented greater problems and frequently led to crystalline material that would not be expected to be so reactive. For this reason, aluminium and silicon were used as their mercaptides, $Si(SET)_4$ and $Et_2Al(SET)$, although some commercial Al_2S_3 and SiS_2 (of unknown purity) was obtained - see Chapter 3, and used in a few experiments. Decomposition of the mercaptides to form the finely divided sulphides was likely to occur under reaction conditions (see Chapter 3).

The range of experiments undertaken is listed in Table 5.2. The organic base was not used in conjunction with aluminium and silicon as a possibility existed of side

Experiment 5.1	$\text{Et}_2\text{AlSEt} / \text{Si}(\text{SEt})_4 / \text{Na}^+$	1 week @ 50°C
5.2	"	1 week @ 85°C
5.3	"	1 week @ 85°C
5.4	"	1 week @ 150°C
5.5	"	1 week @ 200°C
5.6	"	24 hr @ 350°C & 2 weeks @ 85°C
5.7	$\text{Al}^{3+} / \text{Si}^{4+} / \text{Na}^+$	3 weeks @ 85°C
5.8	"	1 week @ 350°C
5.9	$\text{In}^{3+} / \text{Sn}^{4+} / \text{Na}^+$	1 week @ 85°C
5.10	"	3 weeks @ 85°C
5.11	$\text{In}^{3+} / \text{Ge}^{4+} / \text{Na}^+$	2 weeks @ 85°C
5.12	$\text{In}^{3+} / \text{Sn}^{4+} / \text{Et}_4\text{N}^+$	2 weeks @ 85°C
5.13	$\text{In}^{3+} / \text{Ge}^{4+} / \text{Et}_4\text{N}^+$	2 weeks @ 85°C
5.14	$\text{In}^{3+} / \text{Sn}^{4+} / \text{Et}_4\text{N}^+$	1 week @ 60°C
5.15	$\text{In}^{3+} / \text{Ge}^{4+} / \text{Et}_4\text{N}^+$	1 week @ 60°C
5.16	$\text{In}^{3+} / \text{Ge}^{4+} / \text{Et}_4\text{N}^+ / 5\% \text{ 13X zeolite}$	1 week @ 85°C
5.17	$\text{In}^{3+} / \text{Ge}^{4+} / \text{Et}_4\text{N}^+ / \text{Na}^+ /$ 5% 13X zeolite	4 weeks @ 85°C

Table 5.2 Hydrothermal Reactions Conducted in Hydrogen Sulphide.

reactions with the mercaptide feedstock. The methods of examination employed for characterizing the reaction products included X-ray powder patterns, infra-red spectroscopy, surface area by nitrogen adsorption and chemical examination. Once recrystallization of the feedstock had been established and the chemical composition, reactivity, etc, determined, the intention was to use tests for zeolitic properties. These would be selective adsorption based on the size of the adsorbate molecule, ion exchange, etc.

5.2 EXPERIMENTAL

5.2.1 Manipulation and Equipment

In view of the highly dangerous nature of hydrogen sulphide, special precautions were taken in operations involving this material. Hydrogen sulphide is more toxic than hydrogen cyanide, 30 minutes exposure to 500 ppm being sufficient to cause death. Above 1000 ppm, loss of consciousness and death is almost immediate. The high toxicity of H_2S is to some extent offset by the extremely strong smell it possesses, which is intolerable at concentrations well below the maximum safe concentration. The minimum perceptible smell is 0.13 ppm, and at 5 ppm is readily noticed. 20 ppm is generally considered to maximum safe level for continuous exposure. Higher concentrations are increasingly unpleasant, but prolonged exposure to even small concentrations of the gas causes loss of the sense of smell due to paralysis of the olfactory nerve endings. It is therefore dangerous to rely on the sense of smell as a means of detecting the

gas, although if evasive action is taken as soon as the gas is smelt, and care is taken not to inhale until clear of the danger area, it is unlikely that accidents will occur unless in a confined space.

A useful safety report on hydrogen sulphide has been prepared by the API (456), and it is from this that the figures quoted in the last paragraph were obtained. In view of the large quantities of hydrogen sulphide used in the autoclaves (100 g), extreme precautions were taken in handling the material. If it is accepted that 100 ppm is the maximum concentration that could be tolerated for an extended period of time, then 100 g would require diluting to rather more than 500 cubic metres to render it safe. It was therefore necessary to site the high pressure equipment in a well ventilated position to ensure that dangerous concentrations of the gas could not build up in the event of an accident during transfer or a leak developing.

The site chosen was a small hut on the roof of the Chemistry Department, and all handling operations were carried out in the open air. The hut, which was about 12 foot by 12 foot by 12 foot, was fitted with a large chimney incorporating a powerful extractor fan which was switched on whenever an operator entered the enclosure. The building was effectively a large fume cupboard situated in the open air, and was thus ideal for the purposes required.

Some consideration was given to the design and materials used for the high pressure equipment. Various reports on the handling and corrosion problems experienced with hydrogen sulphide have appeared in the literature. Bice, Prange and Weis (457) described the performance of a large plant used for the manufacture of tertiary alkyl mercaptans from liquid hydrogen sulphide and olefins. Corrosion problems were not severe as long as the hydrogen sulphide was kept free of moisture. The corrosion rate of carbon steel was almost 0.001 inch/year with anhydrous H_2S , but as much as 0.1 inch/year in the presence of water. Pure copper was rapidly attacked, even when dry, but copper alloys (eg brass), aluminium, Stellite, Inconel, Ni-Resist, and 304 and 316 stainless steels all showed good resistance to corrosion. Hard magnetic steels were found to be subject to hydrogen embrittlement if stressed, and the use of ductile materials was recommended. This was especially prevalent in springs and Bourdon tubes made of plain steel or 304 stainless steel. Type 316 stainless steel was more satisfactory from this point of view.

A review of sulphide corrosion problems in the petroleum industry was published by Hudgins (458). Sulphide stress cracking through hydrogen embrittlement of high strength steels was one of the major problems outlined, but was most prevalent in aqueous environments. The use of steels of less than 100 000 psi yield strength (Rockwell C-20-20 hardness) was recommended to overcome this.

Aluminium coating of steel has been found to give excellent protection against corrosion by hydrogen sulphide (459), believed due to the formation of an aluminium sulphide film on the metal surface (460). An early report (461) suggested that iron, copper, and zinc did not corrode in contact with liquid hydrogen sulphide. In view of conflicting reports (457) of the rapid corrosion of copper under these conditions, it seems likely that traces of moisture greatly accelerate the corrosion rate.

It was decided that two 300 ml autoclaves would be purchased. This size allowed for sufficient product for the various tests it was required to make. In view of the exacting specification required, the autoclaves were made to special order by the Mechanical Engineering Branch at the British Petroleum Research Centre at Sunbury-on-Thames. Type 316 stainless steel was used, and $\frac{1}{16}$ inch corrosion penetration was allowed for. The rating of the autoclaves was 400°C and 4000 psig, with a hydraulic test to 9750 psig. The design of the equipment is shown in Figure 5.1. The body was machined out of solid metal bar, and the sealing to the cap was by means of an aluminium gasket. The cap was located with a separate cap nut, which contained the six screws used to tighten the cap to the body. A thrust ring of heat treated Caxton steel was fitted between the tightening screws and the cap. The cap carried an adaptor, which screwed onto an aluminium sealing washer. This adaptor carried

- (1) A central thermocouple tube;
- (2) A nickel bursting

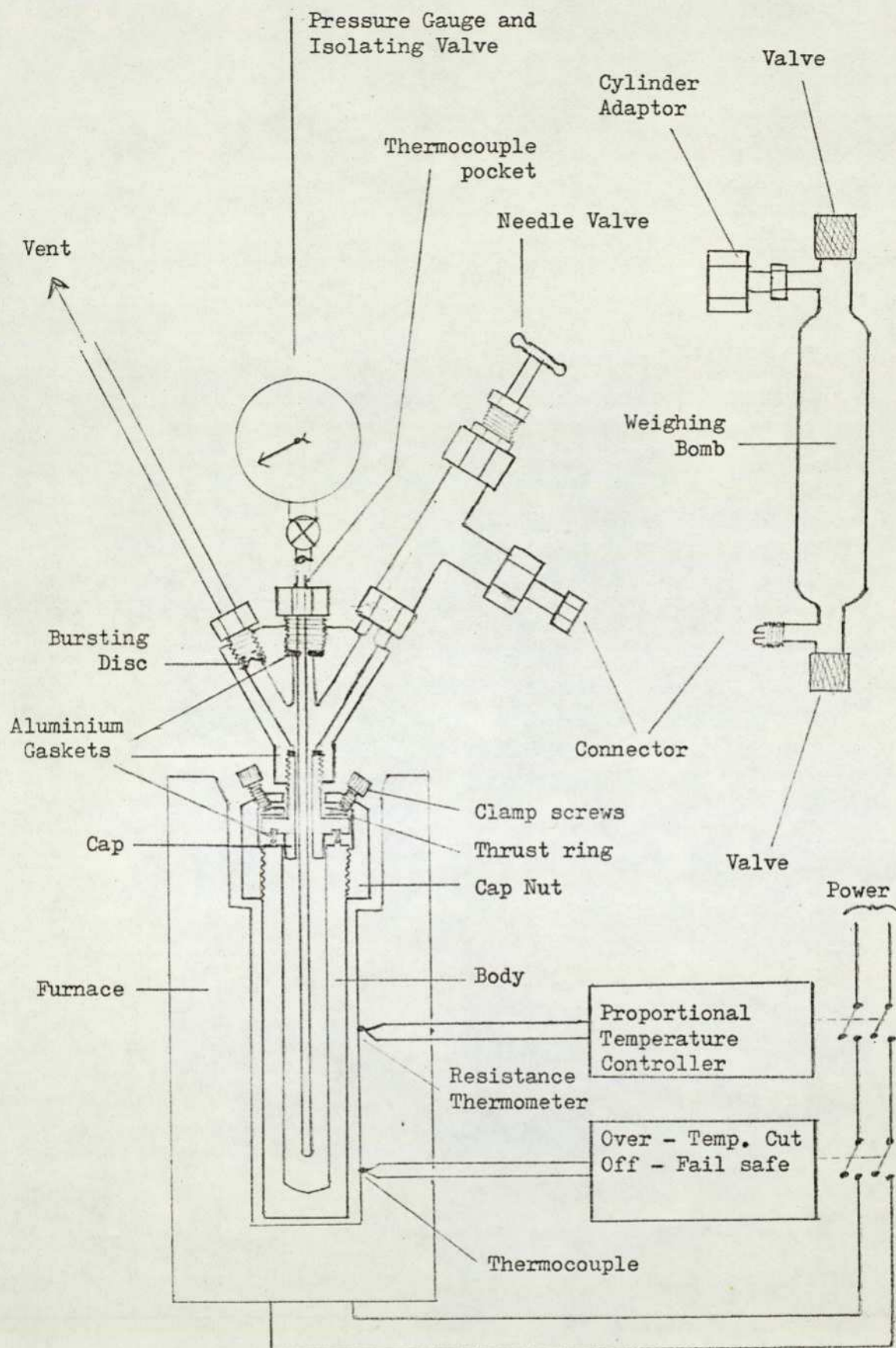


Fig. 5.1 Autoclave and associated equipment.

disc and vent; (3) A Bourdon pressure gauge rated to 6000 psig with a Clockhouse isolating valve; (4) A stainless steel needle valve, rated to 400 atm at 400°C. The valves has graphitized asbestos packing, and were arranged with the needle sealing to the autoclave.

The autoclaves were heated in specially made electric furnaces. They consisted of welded mild steel tube, wound with high temperature Pyrotenax cable (1500 watts) and lagged with Newtherm calcium silicate lagging. Temperature control was by means of a proportional control module (assembled at Sunbury), operating through a resistance thermometer mounted on the furnace wall. The proportional band was adjustable to give maximum heating rate without instability of the control circuits, and a reset control allowed deviation of the ultimate temperature from the set point to be corrected. An additional controller (Ether, type 17-90B) was operated by a separate thermocouple mounted on the furnace wall, and was used to shut the whole unit down in the event of a temperature runaway. The bursting disc lines were attached to extension tubes running through the roof of the autoclave building when the equipment was in use.

A small weighing bomb (rated to 10 000 psig at 25°C) was used to transfer the hydrogen sulphide to the autoclaves. It was also constructed from 316 stainless steel, and carried a needle valve at each end. An adaptor

on one needle valve mated with the valve on the hydrogen sulphide cylinder (a 90 lb cylinder of Mattheson CP grade, 99.9 per cent, obtained from Cambrian Gases). An adaptor on the other needle valve of the weighing bomb mated with the needle valves on the autoclaves.

The method of loading the autoclaves was as follows. In view of the instability of some of the reagents towards moisture, precautions were taken to avoid their unnecessary contact with the atmosphere. The solid reagents were weighed in the dry box into a small screw capped jar. The autoclave cap was removed, the aluminium gasket inspected and replaced if necessary, and the clamping screws and cap thread lubricated with anti-seizure compound. The body of the autoclave was covered with a large polythene bag and purged out with dry nitrogen for several minutes. The solid feedstock was then quickly added, still under a nitrogen purge, and the autoclave reassembled. It was then evacuated through the needle valve by means of a rotary pump, and the needle valve closed.

The required amount of hydrogen sulphide was transferred to the weighing bomb in the following manner. It was attached to the gas cylinder, and evacuated by means of a rotary pump attached to the other needle valve. It was then chilled in liquid nitrogen, the cylinder inverted, and the valves operated to allow liquid to flow into the bomb. It was necessary to remove the bomb periodically to weight it and so determine the amount of material transferred.

With practice, it was possible to fill the bomb to slightly more than the required level at the first attempt, and then to vent off excess gas into sodium hydroxide solution.

The bomb was allowed to warm to room temperature and attached to the autoclave. The assembly was tilted, and the valves operated to allow the liquid to flow into the autoclave. The bomb was finally warmed to ensure complete transfer of the hydrogen sulphide. Finally, the bomb was removed and weighed to obtain the weight of gas transferred.

A compressed air breathing apparatus was purchased from Siebe Gorman Limited, and was always kept available, near the autoclaves in case of accident. However, no accident was experienced during handling, and the autoclaves and associated equipment were found to be very reliable in use. Very little evidence of corrosion was found on the stainless steel components or aluminium gaskets. Very slight corrosion of the nickel bursting discs was encountered, but insufficient to cause failure. No problems were encountered with the pressure gauges or needle valves, although the original valves quickly siezed as they had hardened steel needles. These were replaced with valves employing stainless steel needles.

In spite of the highly dangerous and unpleasant nature of hydrogen sulphide, the handling techniques outlined ensured that no accident or inconvenience occurred. The autoclaves were always vented into concentrated sodium hydroxide solution to prevent an escape of gas to the atmosphere.

5.2.2 Safety Calculations

Calculations were performed to ensure that the pressure that could develop during the course of an experiment should not exceed the maximum pressure rating of the autoclaves (4000 psi). In addition, it was highly undesirable that a bursting disc should fail during use. These were rated at 3500 psi, and to allow an adequate safety margin, the maximum pressure for continuous operation was fixed at 2500 psi. This is considerably above the critical pressure of hydrogen sulphide (1306 psi, 88.9 atm), and it was therefore necessary to calculate the maximum weight of gas that could be used in the 300 ml autoclave without exceeding 2500 psi (170.1 atm) at 400°C, the maximum operating conditions. Unfortunately, the thermodynamic data available did not extend to the required temperature and pressure. The maximum pressure calculated by West (388) at 760°F (390°C) was 70 atm, (1029 psi), when the density of the supercritical gas was 13.6 g/300 ml. The nearest data of Lewis (390) is a density of 8 mole/litre (82 g / 300 ml) at 453°K (180°C) and 178 atm, (2660 psi). These figures gave an indication of the maximum autoclave loadings that could be used with the maximum temperature and pressure ratings, although in practice these extreme conditions were not employed. The maximum autoclave loading commonly employed was 100 g H₂S. Reference to the data of Lewis (390) indicated that a density of 100 g/300 ml (10 mole/litre, approximately) would produce 176 atm at 433°K (2584 psi at 160°C) or 240 atm at 493°K (3700 psi at 200°C).

The other source of pressure that had to be considered was gas produced by decomposition of the mercaptide salts. The worst conditions that might be encountered were decomposition of all the

ethyl residues to ethane. The pressure that would result was calculated for typical quantities used (5 g $\text{Si}(\text{SEt})_4$; 5 g Et_2AlSEt):-

$$5 \text{ g } \text{Et}_2\text{AlSEt} \text{ would lead to } \frac{5 \times 90}{140} = 3.6 \text{ g ethane}$$

and $5 \text{ g } \text{Si}(\text{SEt})_4 \text{ would lead to } \frac{5 \times 120}{272} = 2.2 \text{ g ethane}$

$$5.8 \text{ g ethane will occupy } \frac{5.8 \times 22.4}{30} = 4.33 \text{ litre at NTP}$$

At 100°C , the pressure (assuming $\frac{PV}{T} = \text{constant}$) will be:-

$$\frac{14.7 \times 4.33}{273} = \frac{P \times 0.3}{373}$$

whence $P = 290 \text{ psi}$

Similarly, at 200°C , $P = 367 \text{ psi}$

In practice, decomposition of the mercaptide group to thiol was a more likely reaction. This would lead to a lower pressure, (ie vapour pressure of EtSH at $121.9^\circ\text{C} = 147 \text{ psi}$).

Calculations of this nature were performed for the individual experiments, and the results are detailed in the following sections. Decomposition of all organic residues from Et_2AlSEt and $\text{Si}(\text{SEt})_4$ to ethane was taken as representing the worst conditions that could be encountered, although not likely in practice.

5.2.3 Reactions of Mercaptides of Aluminium and

Silicon with Sodium Hydrosulphide in Liquid

Hydrogen Sulphide

Experiment 5.1 (Al^{3+} , Si^{4+} , Na^+ , 1 week at 50°C)

The proportions of reagents used in this and subsequent experiments duplicated in the sulphur system typical zeolite preparations. An initial mixture for the formation of zeolite A with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 1.0$ was (60, p 62):-

SiO_2	:	Al_2O_3	:	Na_2O
0.51		0.51		1.50 mole/litre

with 85 per cent solvent. Converting this to the sulphur system with a constant cation ratio, it becomes

Al_2S_3	SiS_2	Na_2S
0.51	0.51	1.50 mol/litre
or 77	63	117 g/litre

With 85 per cent solvent, the total weight = $\frac{(77 + 63 + 117)}{15} 100$

$$= 1712 \text{ g}$$

$$\therefore \text{wt } \text{H}_2\text{S} = 1712 - 257 = 1455 \text{ g}$$

In fact this experiment used as starting materials $\text{Si}(\text{SEt})_4$

Et_2AlSEt and NaSH . The ratio then becomes:-

Et_2AlSEt	$\text{Si}(\text{SEt})_4$	NaSH
1.02	0.51	3.00 mole/1455 g H_2S
or 5.12	4.78	5.77 g/50 g H_2S

The experiment was conducted at 50°C . From the thermodynamic data of Sage and Lacey (389) and West (388), the vapour pressure of H_2S at 50°C , with a specific volume of 0.3 litre/50 g (3.26 cu ft/lb mole) is 560 psi and 520 psi respectively. The pressure due to ethane (assuming total decomposition of the mercaptides) is 229 psi at 50°C (calculated as in Section 5.2.2). The maximum autoclave pressure would then be about 790 psi.

The autoclave was loaded as described in Section 5.2.1. 54.50 g of H_2S were used. The experiment was conducted for 1 week, the probe temperature being 48°C , the oven temperature 60°C , and the pressure 510 psi. This pressure was considerably less than the calculated value, being in the order of the H_2S vapour pressure.

The product was obtained as a pale coloured, hard solid, and it could not be completely removed from the autoclave without risk of excessive contact with the atmosphere. A representative sample was obtained, but a yield cannot therefore be given. It was stored in the dry box. From the solid appearance of the material, it appeared that decomposition of the mercaptides had occurred. The material hydrolysed when moistened with water, liberating hydrogen sulphide and leaving an insoluble residue. Both SiS_2 and As_2S_3 react in this way. The aqueous solution remaining liberated more hydrogen sulphide when treated with dilute hydrochloric acid, and a slight precipitate of sulphur formed (soluble in xylene to form a golden solution). This implied that a soluble polysulphide was present as well as excess sodium hydrosulphide.

A sample of the material was washed with toluene, dried under vacuum, ground and sealed in a glass capillary for x-ray powder diffraction (see Section 3.2). The powder pattern is illustrated in Figure 5.2, and the tabulation is included in Appendix A2. Only one diffraction line was observed, and this corresponded to the strongest line of NaSH (Appendix A6). The material was therefore essentially non-crystalline, and it was apparent that no recrystallization had occurred and no new (crystalline) phases had been formed. The absence of any of the other diffraction lines of NaSH was surprising in view of the crystalline nature of this material (Appendix A4). The conversion of a large part of the NaSH to non-crystalline sodium polysulphide was one possibility in view of the detection of a

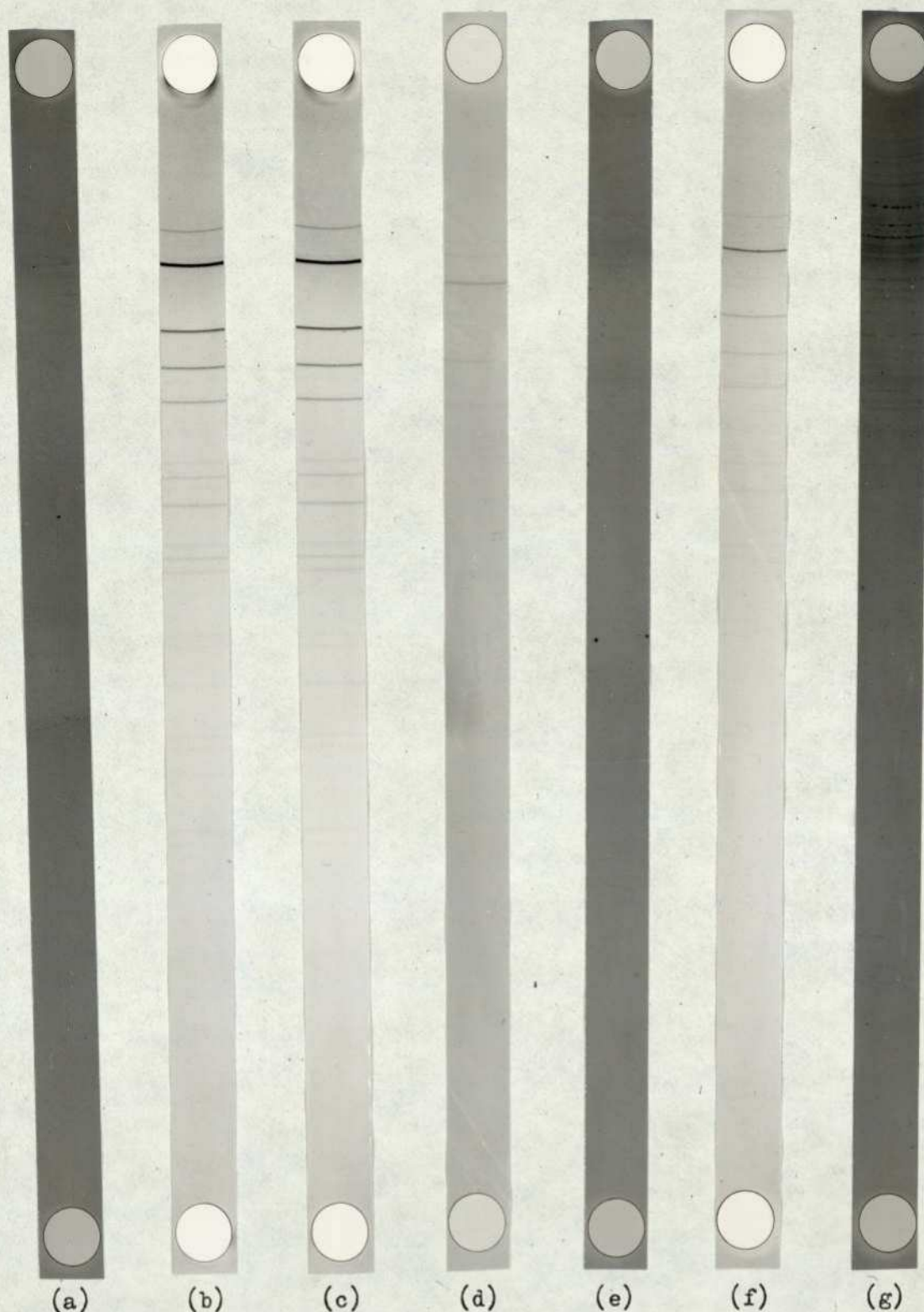
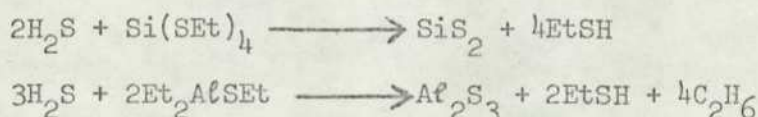


Fig. 5.2 X-Ray Powder Patterns of the Products from the Hydrothermal Reaction of Silicon and Aluminium Mercaptides with Sodium Hydrosulphide in Liquid Hydrogen Sulphide.

- | | |
|---------------------------------------|----------------------------|
| (a) Experiment 5.1. | Copper $K\alpha$ Radiation |
| (b) Experiment 5.2. | Copper $K\alpha$ Radiation |
| (c) Experiment 5.3. | Copper $K\alpha$ Radiation |
| (d) Experiment 5.4. | Cobalt $K\alpha$ Radiation |
| (e) Experiment 5.5; Dark aggregate. | Copper $K\alpha$ Radiation |
| (f) Experiment 5.5; Bulk of material. | Copper $K\alpha$ Radiation |
| (g) Experiment 5.6. | Copper $K\alpha$ Radiation |

soluble polysulphide in the product. An oxidation was thus implied. It seemed that any Al_2S_3 and SiS_2 formed were also in a non-crystalline form. In view of the solid nature of the product, decomposition of the gelatinous mercaptides had apparently occurred, probably with the formation of ethane and thiol:-



The general conclusion was therefore that at the reaction temperature used, no crystallization of the non-crystalline Al_2S_3 and SiS_2 was found, a conversion of NaSH to (non-crystalline) polysulphide being the only reaction noted.

Experiment 5.2 (Al^{3+} , Si^{4+} , Na^+ , one week at 85°C)

Experiments 5.2 and 5.3 represent repeats at 85°C of the first experiment, in an attempt to promote crystallization of the products. 85°C is still in the sub-critical region, and the autoclave loading was the same as in the first experiment except for varying the amounts of hydrogen sulphide. In Experiment 5.2, 30 g were used, the specific volume being 0.3 litre/30 g (5.46 cu ft/lb mole). The vapour pressure according to Sage and Lacey (389) and West (388) was estimated as 900-1000 psi. The pressure due to ethane (assuming decomposition of the mercaptides to form ethane) was estimated as 254 psi (see Section 5.2.2), and therefore the maximum pressure expected was about 1200 psi.

The autoclave was loaded as in the previous experiment, 36.30 g of H_2S being employed. It was heated to 85°C probe temperature (90°C oven temperature) for one week, the pressure

being 720 psi. As in Experiment 5.1, this was considerably less than the calculated pressure. The product was again obtained as a hard solid, and it was impossible to remove it completely without risk of excessive contact with the atmosphere. It hydrolysed on contact with water to liberate H_2S , and the aqueous solution obtained precipitated sulphur on treatment with dilute acid, although less than in the previous experiment. Therefore it seemed less polysulphide had been formed.

It again appeared that decomposition of the mercaptides had occurred to form Al_2S_3 and SiS_2 . An infra-red spectrum (KBr disc) of the solid product showed no organic features characteristic of the parent mercaptides. An X-ray powder pattern (Figure 5.2, Appendix A2) revealed the presence of crystalline NaSH (cf Appendix A6). There was only a single line ($d = 1.52$) that could be attributed to SiS_2 , and no evidence for crystallization of Al_2S_3 . There were no lines at the wider spacings associated with the formation of complex phases with larger unit cells (d greater than about $5\text{\AA}$). It therefore seemed that the only reaction that had occurred was the decomposition of the mercaptides to form Al_2S_3 and SiS_2 in a finely divided, non-crystalline form. It appeared that less conversion of NaSH to non-crystalline polysulphide had occurred than in the first experiment.

Experiment 5.3 (Al^{3+} , Si^{4+} , Na^+ , one week at 85°C)

This experiment was identical to experiment 5.2, except for the use of a larger quantity of hydrogen sulphide (60 g) to assess the effect of concentration on the reaction

pattern. The specific volume was 300 ml/60 g (2.73 cu ft/lb mole). At 85°C, the pressure expected was 1050 psi and 1000 psi according to Sage and Lacey (389) and West (388) respectively. The maximum system pressure (including ethane) would then be about 1300 psi.

62.38 g of H_2S were used, and the autoclave was heated to 85°C (probe), 95°C (oven) for one week. The pressure was 920 psi. The appearance, chemical properties and X-ray powder pattern (Figure 5.2) of the product were identical to those from the previous experiment. The additional volume of hydrogen sulphide had apparently had little effect on the overall course of the reaction, decomposition of the mercaptides still being the only effect noted. No evidence for crystallization of the amorphous sulphides was obtained, the only crystalline phase present being NaSH.

Experiment 5.4 (Al^{3+} , Si^{4+} , Na^+ , one week at 150°C)

This experiment represented the first use made of supercritical conditions. The autoclave loading was identical to Experiment 5.1. The specific volume of the H_2S was 0.3 litre/50 g (3.26 cu ft/lb mole), and at the reaction temperature of 150°C the pressure expected (388, 389) was about 1100 psi. The pressure expected from ethane if this was formed was 300 psi, the maximum total pressure therefore being about 1400 psi.

54.89 g of H_2S were used, and the autoclave was heated to 150°C (probe), with an oven temperature of 155°C and a pressure of 1330 psi. This pressure was much closer to the calculated value than in the previous experiments, and the

product was removed from the reactor more readily, as a fine powder. This suggested that the mercaptides had decomposed more completely to sulphides. The product again hydrolysed with water, but comparatively little polysulphide was detected. The X-ray powder data (Figure 5.2; Appendix A2) showed the presence of NaSH together with some additional weak lines. Many of these may be accounted for by SiS_2 and Al_2S_3 (Appendix A6), but the lines were very weak and crystallization was far from complete. Again, there were no lines at wider spacing that would suggest the formation of complex phases of larger unit cell.

The conclusions were therefore similar to those from the previous experiments - the mercaptides had decomposed to form sulphides, but no complex crystalline phases had been formed. Slight crystallization of Al_2S_3 and SiS_2 was apparent, however, at 150°C .

Experiment 5.5 (Al^{3+} , Si^{4+} , Na^+ , one week at 200°C)

This was a similar experiment to 5.4, but conducted at 200°C . The same autoclave loading was employed. The pressure estimated for the H_2S from thermodynamic data (388, 389) was about 2000 psi, and the ethane pressure (assuming complete decomposition of the mercaptides) was calculated to be 334 psi. The maximum total pressure was therefore estimated at 2350 psi.

53.60 g of H_2S were employed. The oven temperature was 200°C , and the probe temperature 190°C . The pressure was initially 1530 psi, but this rose to 1590 psi over the following 48 hours. As the temperature only increased by

2°C in this time, a reaction within the autoclave was suggested.

The experiment was continued for one week.

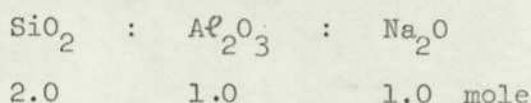
The product was similar to that from the previous reaction although rather darker in colour and not completely uniform. Some hard, dark aggregates were present. The chemical reactions were similar to those of the product from the previous experiment, and the material did not reveal any new phases with x-ray powder diffraction. Two samples were used, one of the bulk of the material and one of the dark material. The results (Figure 5.2, Appendix A2) again indicated that the only crystalline product present to any extent was NaSH (Appendix A6). The lighter material appeared to be predominantly NaSH, while the darker material was essentially non-crystalline, only very weak lines characteristic of NaSH being present. This suggested that the dark aggregates were the decomposed mercaptides, which were separated due to poor mixing of the feedstocks in the supercritical hydrogen sulphide.

Experiment 5.6 (Al^{3+} ; Si^{4+} ; Na^+ , 1 week at 85°C
+ preheat to 350°C)

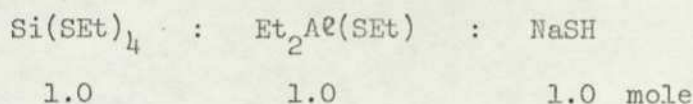
It was apparent from the first five experiments that whilst some decomposition of the mercaptides to form Al_2S_3 and SiS_2 was occurring under all the conditions used, complete decomposition appeared to occur only at the higher temperatures. For this reason, a pre-heating to 350°C with a small amount of hydrogen sulphide was used in Experiment 5.6 to assist the complete decomposition of these materials. It was also evident that no complex phases were being formed, and one of the main reasons was felt to be the low solubility of NaSH in liquid H_2S . As no benefit had been found to result from the use of higher (supercritical) temperatures, 85°C was used in this experiment.

Less NaSH was employed, as the excess used in the first five experiments was apparently serving no useful purpose in view of its low solubility, and in fact hindered x-ray tabulation of any new lines. A larger volume of hydrogen sulphide was employed to assist the solubility of the starting materials.

Instead of using the starting mixture of a typical zeolite preparation, the proportions of Si, Al and Na found in a typical zeolite (Zeolite A) were employed (60, p 62):-



Using mercaptides as starting materials, this becomes:-



100 g of H_2S were used for the main reaction; this had a specific volume of 0.3 litre/100 g (1.64 cu ft/lb mole). From the data of Sage and Lacey (389), the pressure expected was 1000 psi at 85°C . 20 g of H_2S were used for the preheating. The expected pressure (0.236 cu ft/lb, 350°C) was estimated as 1325 psi from data of West (388). Assuming complete decomposition of the mercaptides to ethane, the pressure due to the ethane at 350°C was calculated as 600 psig by the method outlined in Section 5.2.2. Therefore, the maximum total pressure expected during the preheating was 1925 psi.

The quantity of H_2S used in this experiment (100 g) was arrived at from a consideration of the volume of liquid that would be present under the reaction conditions. From the thermodynamic

data of Sage and Lacey (389) the specific volume of liquid H_2S and its saturated vapour at 85°C is:-

Specific volume of gas = 3.66 cu ft/lb mole = 0.149 g/ml

and Specific volume of liquid = 0.9599 cu ft/lb mole = 0.569 g/ml

If the volume of liquid in the 300 ml autoclave is V ml, the volume of gas is $(300 - V)$ ml.

$\therefore$ wt of liquid = 0.569 V g

and wt of gas = 0.149 $(300 - V)$ g

As 100 g of H_2S were used, $0.569 V + 0.149 (300 - V) = 100$

whence $V = \underline{127 \text{ ml}}$

This represented a convenient volume of liquid.

A similar calculation showed that the 60 g of H_2S used in Experiment 3.6 had a volume of 36 ml under the experimental conditions used.

The autoclave was loaded, and 20.05 g of H_2S added. It was heated to 350°C (oven temperature), the probe temperature being 320°C and the pressure 1920 psi. The autoclave was vented hot to assist in the removal of any organic sulphides or thiols formed. It was refilled with 100.10 g of fresh H_2S , and heated to 85°C (probe), 90.0°C oven temperature for one week. The pressure was 930 psi, close to the calculated value (1000 psi).

The product was obtained as a free-flowing pale brown powder, quite uniform in appearance and texture. A yield of 6.99 g was obtained, representing 91.5 per cent of the total weight of Al_2S_3 , SiS_2 and NaSH expected to be present.

The chemical reactions of the material were identical to those of the products from the previous experiments, indicating the

formation of hydrolysable sulphide and a little soluble polysulphide. The x-ray powder pattern (Figure 5.2, Appendix A2) indicated that considerable crystallization had occurred, a large number of diffraction lines being observed. The presence of NaSH was apparent, although the lines were considerably less intense than those found previously, due presumably to the smaller amount present. The presence of crystalline Al_2S_3 and SiS_2 was indicated by characteristic lines (cf Appendix A6), and the presence of new phases was also indicated by many additional lines, including those of larger 'd' value (up to $9.22 \text{ \AA}$). Thus the formation of material with larger unit cells was indicated, although many of the lines found are near to those observed in commercial silicon disulphide (Appendix A4), and are possibly weak reflections associated with this material. Nevertheless, it was apparent that at least considerable crystallization of aluminium and silicon disulphide had occurred, although the part played by the hydrogen sulphide in this was uncertain, as the NaSH will have been near its melting point (357°C) during the preheating, and may have been involved. Certainly, it appeared that the preheating to 350°C had resulted in a more free-flowing product, and its uniform nature implied better mixing than had been obtained in the experiments conducted wholly under super-critical conditions.

5.2.4 Reaction between $\text{Et}_2\text{Al SET}$ and Si(SET)_4

In order to throw further light on the part played by hydrogen sulphide in the decomposition of the mercaptides observed in Experiments 5.1 - 5.6, the reaction of $\text{Et}_2\text{Al SET}$ and Si(SET)_4 in the absence of solvent was investigated. Two experiments were conducted, one with the two mercaptides only, and the other with sodium hydrosulphide.

(i) Et_2AlSEt (2.0 g) and $\text{Si}(\text{SEt})_4$ (2.0 g) were mixed, no reaction being observed until the mixture was warmed, when it rapidly solidified to a white, opaque gel-like material. The solid was well washed with toluene (in the dry box), and dried under vacuum. The infra-red spectra of nujol and hexachlorobutadiene mulls (Figures 5.3 and 5.4) revealed that the material was essentially inorganic in nature. The alkyl $\nu(\text{C-H})$ bands between 2900 cm^{-1} and 3000 cm^{-1} were very weak, and further very weak bands at 975 cm^{-1} and 1260 cm^{-1} associated with the mercaptides indicated that only a trace of organic residues remained.

An x-ray powder pattern was obtained of the solid material, but showed no lines. The material was therefore non-crystalline. It reacted with water to liberate hydrogen sulphide. A solid residue remained, which was partially soluble in dilute hydrochloric acid to leave a trace of residue assumed to be silica. The solution was shown to contain aluminium with alizarin. It therefore seemed that the mercaptides had decomposed to the sulphides on being warmed together.

(ii) Et_2AlSEt (2.0 g), $\text{Si}(\text{SEt})_4$ (1.9 g) and NaSH (1.2 g) were mixed with the immediate evolution of a gas and the deposition of a pale yellow, finely divided solid. On heating the tube, the reaction went to completion and a clear yellow solution and pale yellow precipitate remained. As in the previous experiment, the residue was shown to be essentially inorganic in nature, and to probably consist of aluminium and silicon sulphides. Crystalline NaSH was also present in the residue from the present experiment, this being the only phase detected by x-ray diffraction (Figure 5.5, Appendix A2; cf Appendix A6).

Therefore, a similar result was obtained in both reactions, the mercaptides interacting to deposit non-crystalline SiS_2 and Al_2S_3 .

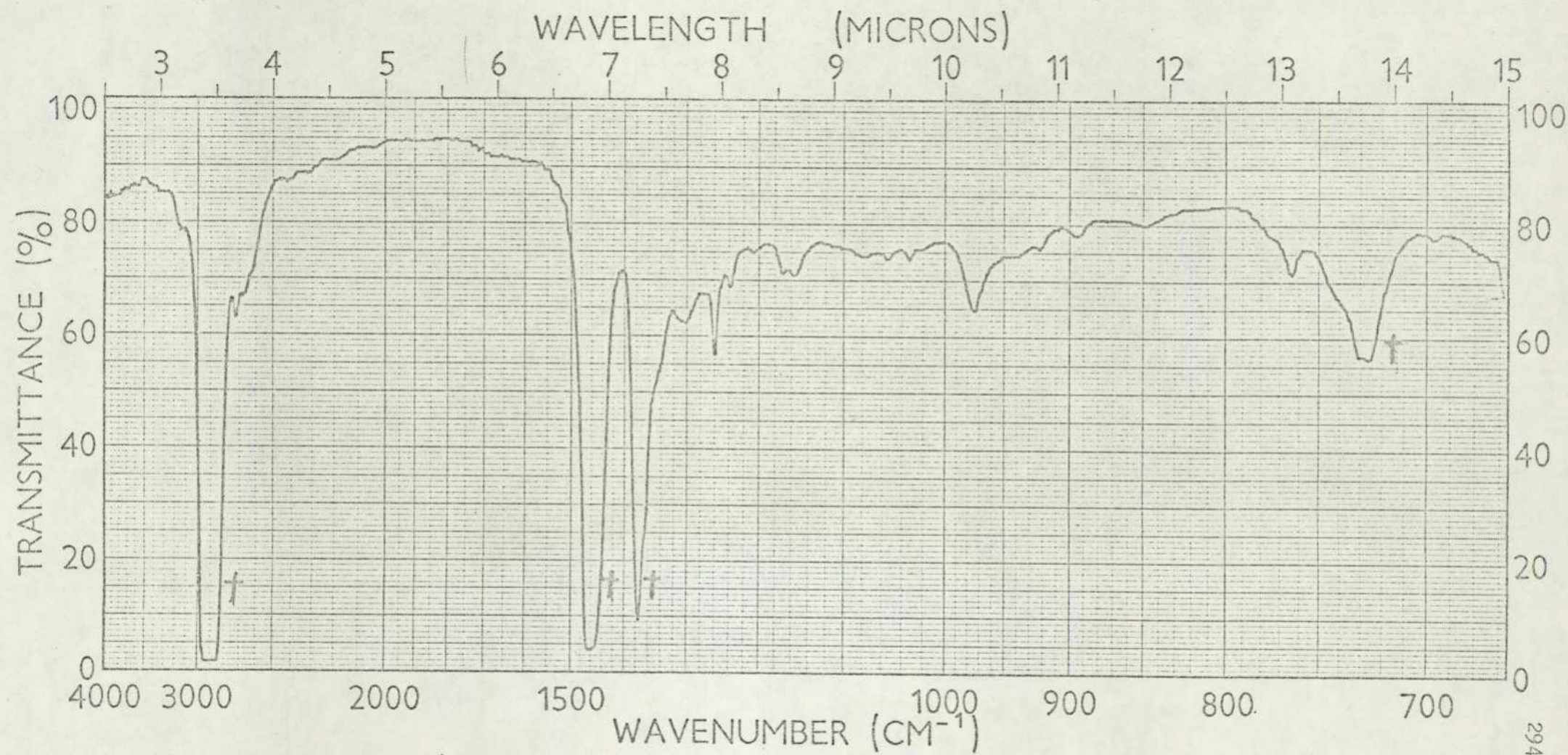


Fig. 5.3 Infrared Spectrum of solid product isolated from the reaction between Et_2AlSEt and $\text{Si}(\text{SEt})_4$. Nujol mull. Peaks marked † due to nujol.

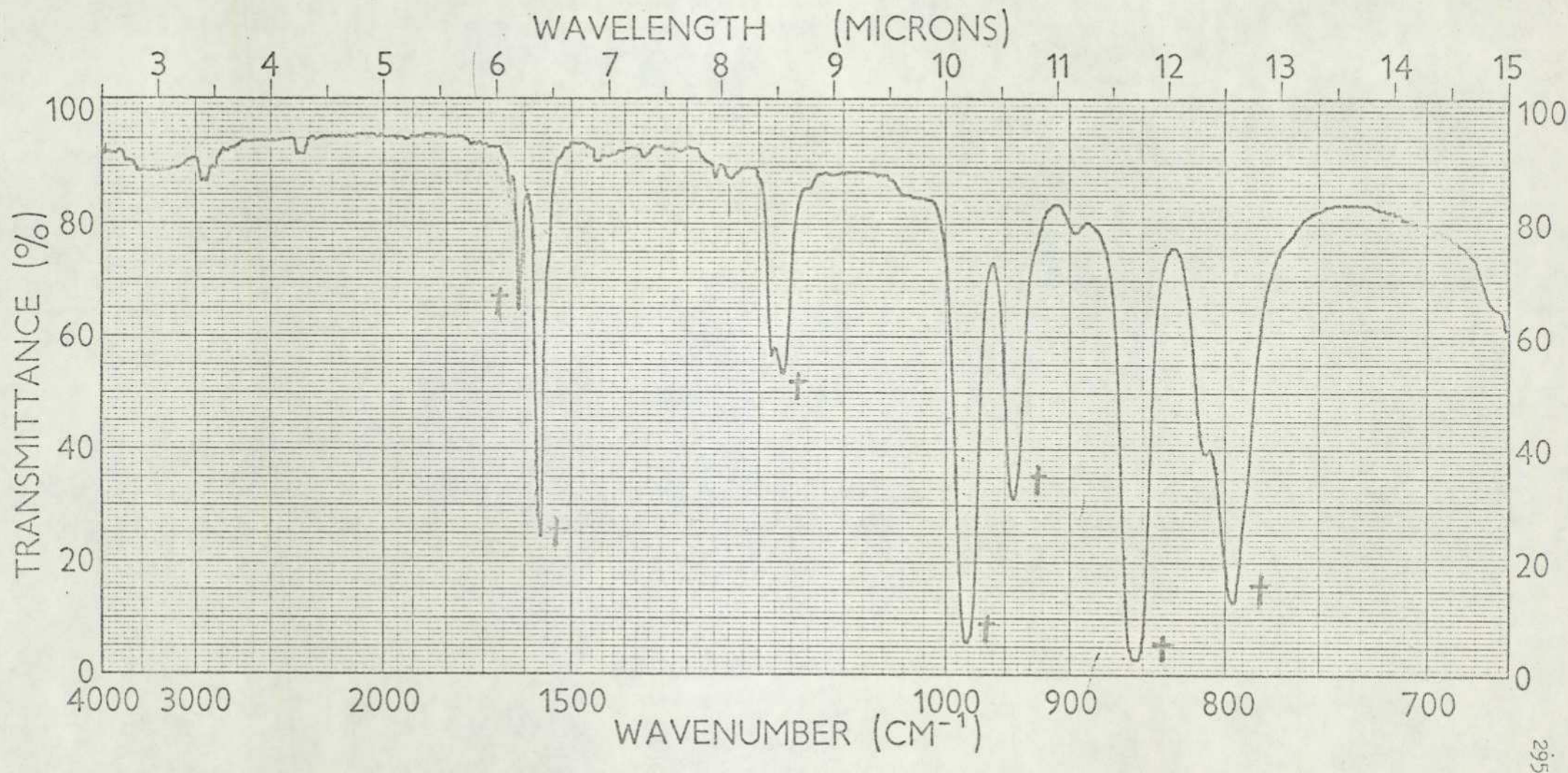


Fig. 5.4 Infrared Spectrum of solid product isolated from the reaction between Et_2AlSEt and $\text{Si}(\text{SEt})_4$. Hexachlorobutadiene mull. Peaks marked † due to hexachlorobutadiene.

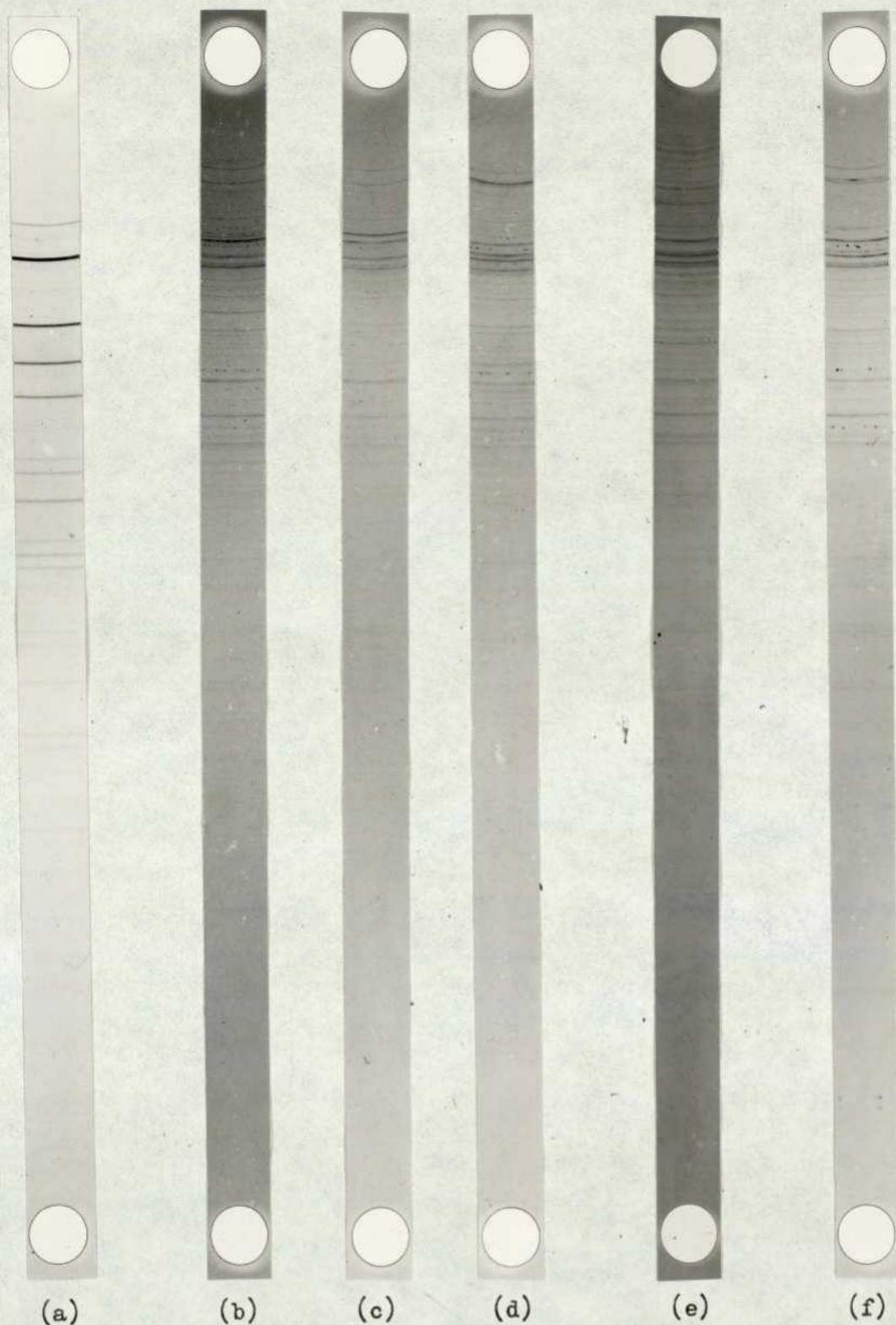


Fig. 5.5 X-Ray Powder Patterns .

(a) Solid Product isolated from the reaction between Et_2AlSEt , $\text{Si}(\text{SEt})_4$ and NaSH .

(b - f) Products from the Hydrothermal Reaction of aluminium and silicon sulphides with sodium hydrosulphide in liquid hydrogen sulphide.

(b) Experiment 5.7; Grey material. (e) Experiment 5.8.

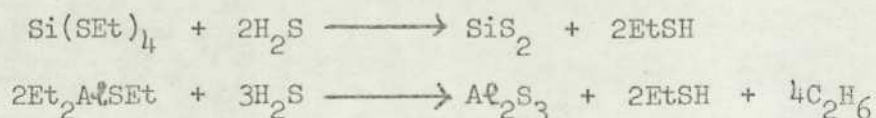
(c) Experiment 5.7; Yellow material. (f) Experiments 5.7& 5.8; Blank.

(d) Experiment 5.7; Control

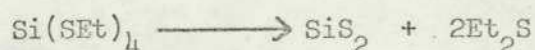
Exposure to Radiation.

When NaSH was present, this apparently did not affect the course of the reaction.

These reactions are very similar to those observed in the experiments employing liquid hydrogen sulphide as solvent, and indicated the suitability of these starting materials for the formation of finely divided Al_2S_3 and SiS_2 . In the presence of liquid H_2S , it might be supposed that decomposition of the mercaptides to thiols would occur (in direct analogy with the hydrolysis of alkoxides by water):-



In the absence of H_2S , such reactions would not be possible. $Si(SET)_4$ could decompose to diethyl sulphide;



but a more complex reaction would be indicated for Et_2Al^iSET .

5.2.5 Carbon and Hydrogen Analyses of Products of Experiments 5.1 - 5.6

To throw further light on the decomposition of the mercaptides in these experiments, representative samples of the vacuum dried products were analysed with an F and M Model 185 carbon, hydrogen and nitrogen analyser. The results are presented in Table 5.3, and show a surprising consistency in view of the differing conditions used. Virtually complete decomposition of the mercaptides was suggested, even at $50^\circ C$, essentially inorganic products being obtained. The atomic ratio of carbon to hydrogen found in these analyses (CH_5 to CH_6) indicate an excess of hydrogen, possibly due to SH^- or water contamination during handling.

5.2.6 Reactions of the Sulphides of Aluminium and Silicon with Sodium Hydrosulphide in Liquid H_2S

In the first group of experiments (5.1 - 5.5), interesting but incomplete crystallization had been found at $85^\circ C$, following a

Experiment	Carbon (%)	Hydrogen (%)	Temp. (°C)
5.1	3.89, 4.30	2.14, 2.19	50
5.5	4.95, 4.13	2.25, 2.30	200
5.6	4.71, 4.71	1.92, 1.92	350 (preheat)

(C:H atomic ratio is about 1:5 to 1:6)

Table 5.3 Carbon and Hydrogen Content by Weight of the products of Experiments 5.1, 5.5 & 5.6 .

Experiment	Et_4N^+ (%)	Na^+ (%)	Et_4N^+ (mole %)	Na^+ (mole %)
5.10	—	4.45	—	0.195
5.11	—	1.74	—	0.075
5.12	27.8	—	0.214	—
5.13	24.3	—	0.187	—
5.14	29.4	—	0.236	—
5.15	28.5	—	0.219	—
5.16	27.1	—	0.208	—
5.17green	6.2	2.22	0.048	0.101
5.17yellow	27.9	3.33	0.214	0.144

Table 5.4 Cation concentrations of the Washed Products from the Hydrothermal Preparations in Hydrogen Sulphide.

Experiment	Residue	Solution
5.10	Trace of yellow In_2S_3	
5.11	Small amount of black material	Colourless
5.12	"	Dark green
5.13	"	Dark green
5.14	"	Yellow-green
5.15	"	Dark orange
5.16	"	Dark orange
5.17	"	Dark orange

Table 5.5 Base Solubility Tests of Materials from the Hydrothermal Preparations in Hydrogen Sulphide.

preheating to 350°C to aid decomposition of the mercaptides. In an attempt to discover whether this crystallization was due to the high preheating temperature or to the reaction period at 85°C , two further experiments were carried out. In the first (Experiment 5.7), an extended reaction period at 85°C was used, and in the second, reaction was conducted wholly at 350°C . In view of the fact that carbonaceous residues were formed when aluminium and silicon mercaptides were used as starting materials, commercial Al_2S_3 and SiS_2 was used in these experiments. The sources and purities of these materials were discussed in Chapter 4.

Experiment 5.7 (Al^{3+} , Si^{4+} , Na^+ , 3 weeks at 85°C)

The proportion of reagents used was the same as in Experiment 5.6 (ie a Si:Al:Na ratio typical of zeolites):-

SiS_2	:	Al_2S_3	:	NaSH
2.0		1.0		2.0 mole
5.00		4.10		3.06 g

As in Experiment 5.6, 100 g of H_2S would be expected to produce 1000 psi pressure under the experimental conditions. The sulphides were finely ground (>44 mesh) in the dry box, and well mixed in the required proportion. To enable any crystallization that occurred to be readily assessed, a control experiment was conducted in which a sample of the reaction mixture was heated in a sealed tube at 85°C for the duration of the main experiment. Thus any crystallization promoted by the H_2S would be immediately apparent. An x-ray powder pattern of the starting mixture was obtained before the sodium hydrosulphide was added (Blank)

The autoclave was loaded by the usual technique and the H_2S (96.40 g) added. The temperature was raised to 85°C (probe) for

three weeks, the pressure being 920 psi. A yield of 10.71 g of a grey granular material was obtained, representing 88 per cent of the weight of sulphides taken. The difference arose from losses in handling. The product was not uniform in appearance, containing some yellow aggregates as well as the grey material. X-ray powder patterns were obtained of the two materials and also of the control experiment (Figure 5.5; Appendix A2). All the diffraction patterns (including the blank) were very similar, the only differences being some intensity variations. This suggested that no crystallization had been promoted by the hydrogen sulphide. The diffraction patterns of the two parts of the reaction product showed that the yellow material was mainly NaSH (Appendix A4, A6) and that the grey material was mainly Al_2S_3 and SiS_2 . It was therefore apparent that no reaction had occurred in either the main experiment or the control experiment, the only effect noticed being a tendency for the NaSH to segregate to form discrete lumps. No new phases were indicated by the x-ray data and the hydrogen sulphide had produced no additional crystallization.

Experiment 5.8 (Al^{3+} , Si^{4+} , Na^+ , 1 week at $350^{\circ}C$)

The same proportion of reagents was used as in the previous experiment, except that 40 g of H_2S were used. The pressure for this specific volume (0.3 litre/40 g; 0.120 cu ft/lb; 4.08 cu ft/lb mole) was estimated from the data of West (388) and Sage and Lacey (389) to be about 3000 psi.

The autoclave was loaded with the sulphide mixture and H_2S (40.50 g) added. The temperature was raised to $350^{\circ}C$ (probe), $360^{\circ}C$ (oven) for one week, the pressure being 3300 psi. A yield of 92 per cent of the sulphide used was obtained, and the product was considerably more uniform than that from the previous experiment. An

x-ray powder pattern (Figure 5.5; Appendix A2) revealed that extensive recrystallization had occurred, although considerable quantities of the starting sulphides remained.

It thus seemed that crystallization of new phases was very slow, even at 350°C , when the NaSH will have been near its melting point (357°C). It therefore seemed that very extended reaction times would be needed to promote the complete recrystallization of the feedstock to complex phases, and this was felt to be largely due to the negligible solubility of the sulphides expected in the hydrogen sulphide.

5.2.7 Reactions of the Sulphides of Indium, Tin and Germanium with Sodium Hydrosulphide in Liquid Hydrogen Sulphide

The preparation of SnS_2 , GeS_2 and In_2S_3 was described in Chapter 4. For the purpose of evaluating the extent to which crystallization of the feedstock was occurring, a 'blank' x-ray powder pattern was obtained of the sulphide mixture before the NaSH was added. In most of the subsequent experiments, a 'control' reaction was set up, in which a sample of the reaction mixture was sealed in an evacuated Pyrex tube, and kept at the reaction temperature for the duration of the main experiment. In this way, the part played by the hydrogen sulphide in any crystallization that occurred was revealed.

Experiment 5.9 (In^{3+} , Sn^{4+} , Na^+ , 1 week at 85°C)

In_2S_3 (1.0 g) and SnS_2 (1.0 g) were reacted with NaSH (5.0 g) in an initial assessment of this system.

The In_2S_3 and SnS_2 were finely ground and mixed together, a blank x-ray diffraction pattern obtained, and then the NaSH added. The mixture was then loaded into the autoclave, H_2S (103.5 g) added, and the autoclave heated to 82° (probe), 85°C (oven) for one week.

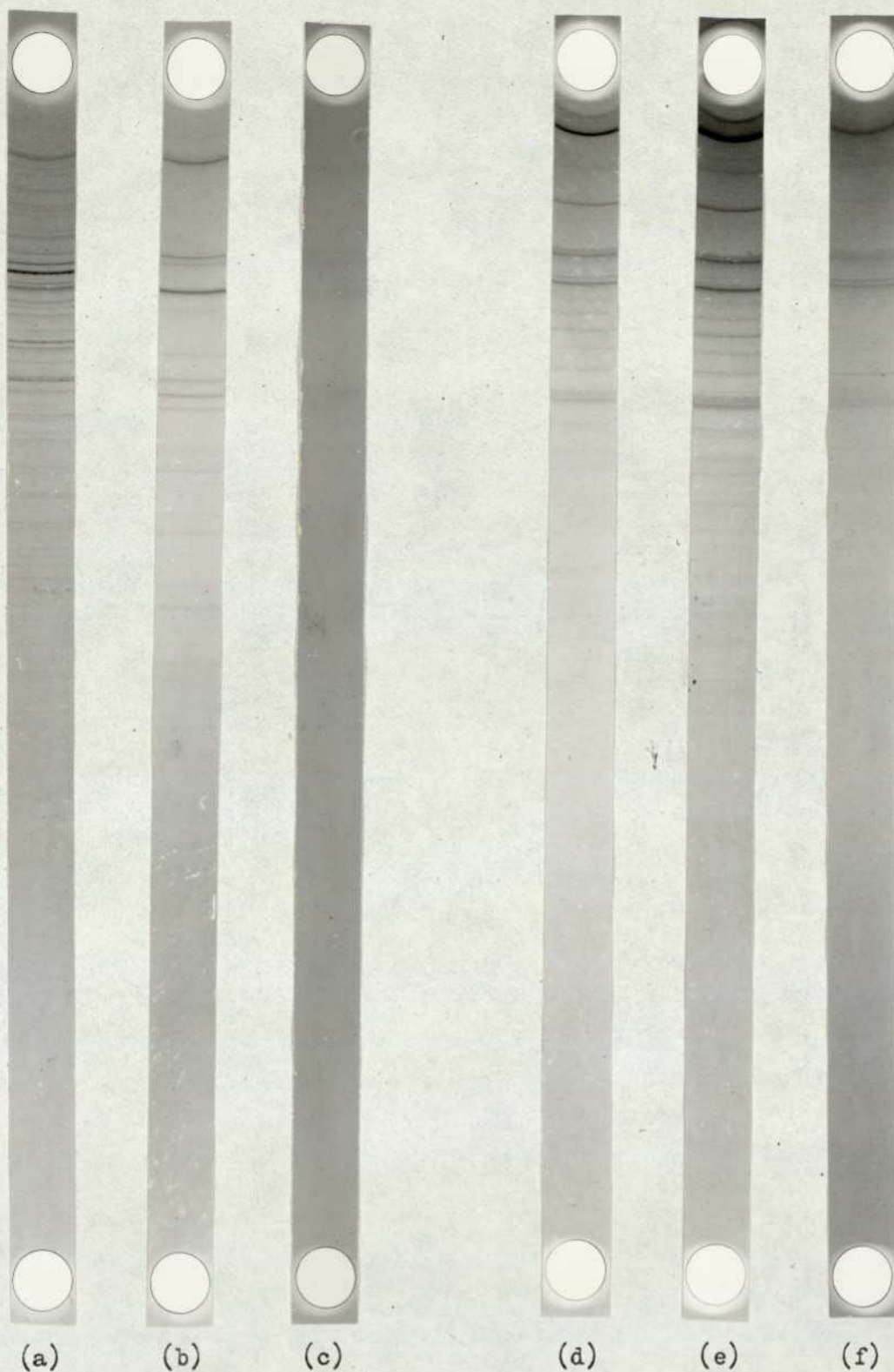


Fig.5.6 X-Ray Powder Patterns of the Products from the Hydrothermal Reaction of Indium (III) Sulphide and Tin (IV) Sulphide with Sodium Hydrosulphide in Liquid Hydrogen Sulphide at 85°C.

- | | |
|-----------------------------------|------------------------------------|
| (a) Experiment 5.9; Ex-Reactor. | (d) Experiment 5.10; Ex-Reactor. |
| (b) Experiment 5.9; Water-Washed. | (e) Experiment 5.10; Water-Washed. |
| (c) Experiment 5.9; Blank. | (f) Experiment 5.10; Control. |

Copper K α Radiation

A control experiment was set up, a sample of the reaction mixture being heated to 85°C in a sealed tube, for the duration of the experiment. The reaction time was increased to three weeks in the hope that the reactions would go to completion.

The autoclave was loaded and H_2S (101.70 g) added. After three weeks at 85°C (probe), 89°C (oven), with a pressure of 820 psi, a deep yellow coloured product was obtained. 8.74 g was obtained, representing 80 per cent of the sulphides used. Difficulty was always experienced in completely extracting the material from the autoclaves, accounting for this deficit.

The product from the control experiment was similar in appearance. The x-ray powder patterns (Figure 5.6; Appendix A2), again revealed considerable crystallization of the non-crystalline feedstock, and much of the crystalline material was retained after washing with water. Much less crystallization was observed in the control experiment, and thus it seemed that extensive promotion of crystallization by the solvent had occurred. In view of the stability of the crystalline material to water washing, it seemed that the reduced amount of base and extended reaction time used in this experiment had resulted in variations in the product compared to that obtained in the previous experiment. Again, a possibility existed of the presence of crystalline SnS_2 (and possibly In_2S_3) in the residue remaining after water washing, although correlation with the ASTM data for these compounds (Appendix A6) was not good. It seemed that as in the previous experiment, crystallization of the feedstock had occurred and that the materials formed were more complex than could be accounted for by crystalline SnS_2 and In_2S_3 . In view of the similarity between the washed and unwashed samples, it seemed

that very little free base remained after the reaction, and the formation of ternary or more complex sulphides was suggested.

Experiment 5.11 (In^{3+} , Ge^{4+} , Na^+ , 2 week at 85°C)

This experiment constituted a repeat of Experiment 5.10, with GeS_2 in place of SnS_2 .

GeS_2	:	In_2S_3	:	NaSH
2.0		1.0		2.0 mole
3.00		3.58		1.28 g

The autoclave was loaded and H_2S (92.00 g) added. It was heated to 85°C (probe), 90°C (oven) for two weeks, the pressure being 825 psi. A control experiment was also conducted. The product from this experiment was pale grey, in comparison to the pale yellow colour of the starting mixture. The x-ray powder patterns (Figure 5.7; Appendix A2) revealed the virtually completely non-crystalline nature of In_2S_3 and GeS_2 used, and showed that a limited amount of crystallization had occurred in the control experiment. Rather more extensive crystallization was observed in the product from the autoclave, but most of this was lost on washing the material with water.

The presence of excess base in the ex-reactor sample was suggested by reference to the ASTM data for NaSH (Appendix A6). Neither In_2S_3 nor GeS_2 are soluble in water, and therefore the non-crystalline nature of the water washed sample indicated that little crystallization of these materials had occurred. The similarity of its diffraction pattern to that of the blank indicated that considerable quantities of non-crystalline In_2S_3 and GeS_2 remained after reaction. The extensive crystallization found in the material removed from the autoclave was apparently due to soluble phases extracted with water.

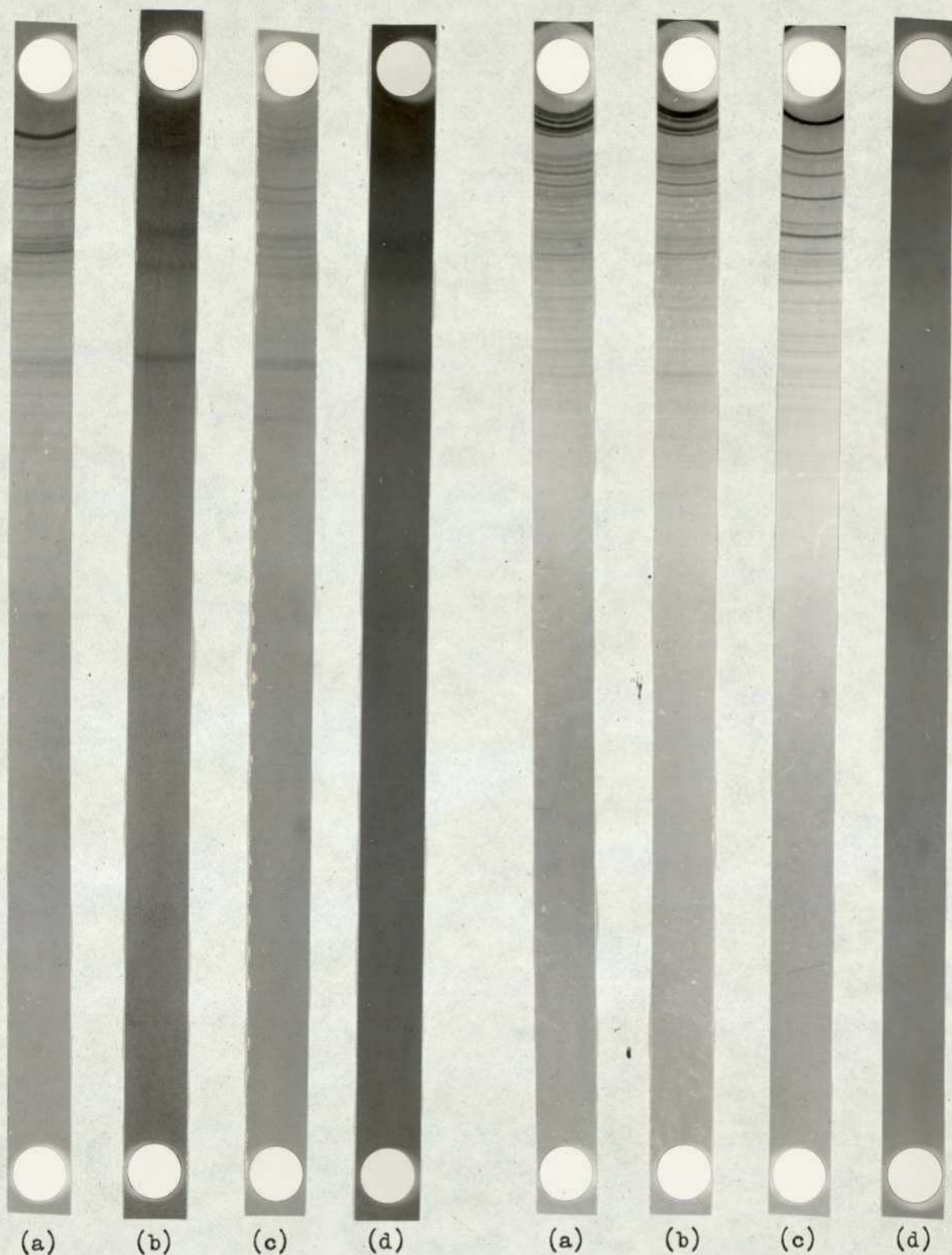


Fig.5.7

Fig.5.8

Fig.5.7 X-Ray Powder Patterns of the Products from the Hydrothermal Reaction of In_2S_3 and GeS_2 with NaSH in Liquid H_2S at 85°C . Experiment 5.11.

(a) Ex-Reactor. (b) Water-Washed. (c) Control. (d) Blank.

Fig.5.8 X-Ray Powder Patterns of the Products from the Hydrothermal Reaction of In_2S_3 and SnS_2 with $\text{Et}_4\text{N}^+\text{SH}^-$ in Liquid H_2S at 85°C . Experiment 5.12.

(a) Ex-Reactor. (b) Water-Washed. (c) Control. (d) Blank.

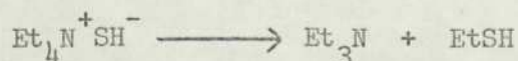
Copper $\text{K}\alpha$ Radiation.

Therefore, as in the reactions employing SnS_2 , considerable crystallization of the feedstock had occurred. However, less evidence for the formation of crystalline GeS_2 was obtained than was found for the formation of crystalline SnS_2 , and the complex phases apparently formed by GeS_2 were considerably more soluble in water than those of SnS_2 . Either ternary sulphides formed with the base, or more complex sulphides, could have been responsible for the diffraction features observed, and it seemed that a definite rôle of liquid hydrogen sulphide in promoting this crystallization had been established.

5.2.8 Reactions of the Sulphides of Indium, Tin and Germanium with Tetra Ethylammonium Hydrosulphide in Liquid Hydrogen Sulphide

In view of the known solubility of certain metal sulphides in hydrogen sulphide solutions of organic bases (Section 5.1), a much greater possibility existed of forming complex sulphides in this type of system than with a sparingly soluble inorganic base.

Literature reports suggested that tetra ethylammonium hydrosulphide, $\text{Et}_4\text{N}^+\text{SH}^-$, would be thermally stable to at least 150°C . Therefore, the optimum temperature for the hydrothermal synthesis appeared to be 85°C , just below critical, where the maximum temperature consistent with an adequate amount of liquid present offered the greatest chance of solubility. The rather unstable nature of the base led to the possibility of decomposition to form amine and thiol:-



However, the amine would itself possess basic properties in liquid H_2S , and the presence of thiol would probably not be a disadvantage. Available data indicated that there would be adequate solubility of the base under sub-critical conditions, which were therefore used throughout this series of experiments.

In view of the ready solubility of the organic base in liquid hydrogen sulphide, reaction mixtures typical of those used in zeolite preparations were employed. Because of the stability of In_2S_3 , SnS_2 and GeS_2 towards water and methanol, excess base was easily removed after the experiment by washing the product. It was hoped that any complex sulphides formed would be insoluble under these conditions.

Experiment 5.12 (In^{3+} , Sn^{4+} , Et_4N^+ , 2 weeks at 85°C)

This experiment was based on a typical zeolite preparation (60, p 62) with a $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of 2:1, and 85 per cent solvent,

ie	SnS_2	:	In_2S_3	:	$\text{Et}_4\text{N}^+\text{SH}^-$
	0.70		0.35		3.16 mole/litre
	128.0		114.6		515.0 g/litre

$$\text{For 85\% solvent, weight of H}_2\text{S} = \frac{(128 + 114 + 515)}{15} 85 = 4283 \text{ g}$$

The starting mixture used was SnS_2 (2.98 g), In_2S_3 (2.66 g), $\text{Et}_4\text{N}^+\text{SH}^-$ (12.02 g), H_2S (100.0 g). The autoclave was loaded, and heated to 85°C (oven), 80°C (probe) for two weeks. The pressure was 830 psi (calculated H_2S pressure = 1000 psi - Experiment 5.6). A blank diffraction pattern (without base) was obtained, and a control experiment was conducted as previously.

The product obtained from the autoclave was a brown solid, in contrast to the pale cream starting mixture. As in previous experiments, was difficult to completely remove it from the autoclave. The mixture in the control experiment also became dark, and developed an oily texture.

Samples of the control and ex-reactor materials were dried under vacuum and x-ray powder patterns obtained (Figure 5.8; Appendix A2).

A sample of the ex-reactor material was washed with methanol and water and an x-ray pattern obtained.

The control experiment had lines in its diffraction pattern characteristic of $\text{Et}_4\text{N}^+\text{SH}^-$ (Appendix A4). The bulk of the crystallinity present appeared to be due to this material, although some changes in the lines of wide spacing indicated that a certain amount of recrystallization may have occurred. Et_3N and EtSH formed by decomposition of the base may have acted as a flux to promote such crystallization. Their presence in the sample vapour were detected by GLC.

The ex-reactor sample revealed many new lines in its diffraction pattern, including those of wide spacing (up to $d = 11.95 \text{ \AA}$). Obviously, extensive recrystallization had occurred, and furthermore the products were not soluble in methanol or water, the diffraction patterns of the ex-reactor and washed samples being nearly identical.

Therefore, it seemed that the H_2S had promoted recrystallization of the sulphide feedstock, and further tests were conducted to investigate the nature of the materials formed. An infra-red spectrum was obtained of the washed product (Figure 5.9), and showed a similarity to the spectrum of $\text{Et}_4\text{N}^+\text{SH}^-$ (Figure 4.31). The chief difference was the absence of $\nu(\text{S-H})$ near 2600 cm^{-1} , implying that the product contained the Et_4N^+ group in an ionic material of some sort. This was confirmed by a carbon, hydrogen and nitrogen analysis of the material.

Found: C, 20.5, 20.9 ; H, 4.37, 4.37 ; N, 2.92, 2.92%

Calculated for 28.0% of $(\text{C}_2\text{H}_5)_4\text{N}^+$: C, 20.65; H, 4.33 ; N, 3.01%

The washings from the methanol and water treatments were yellow, indicating that either excess base or a new (soluble) phase was being removed. It was evident that interesting reactions had been promoted by the liquid hydrogen sulphide, extensive recrystallization occurring to form new, insoluble phases containing the Et_4N^+ ion and a large unit cell.

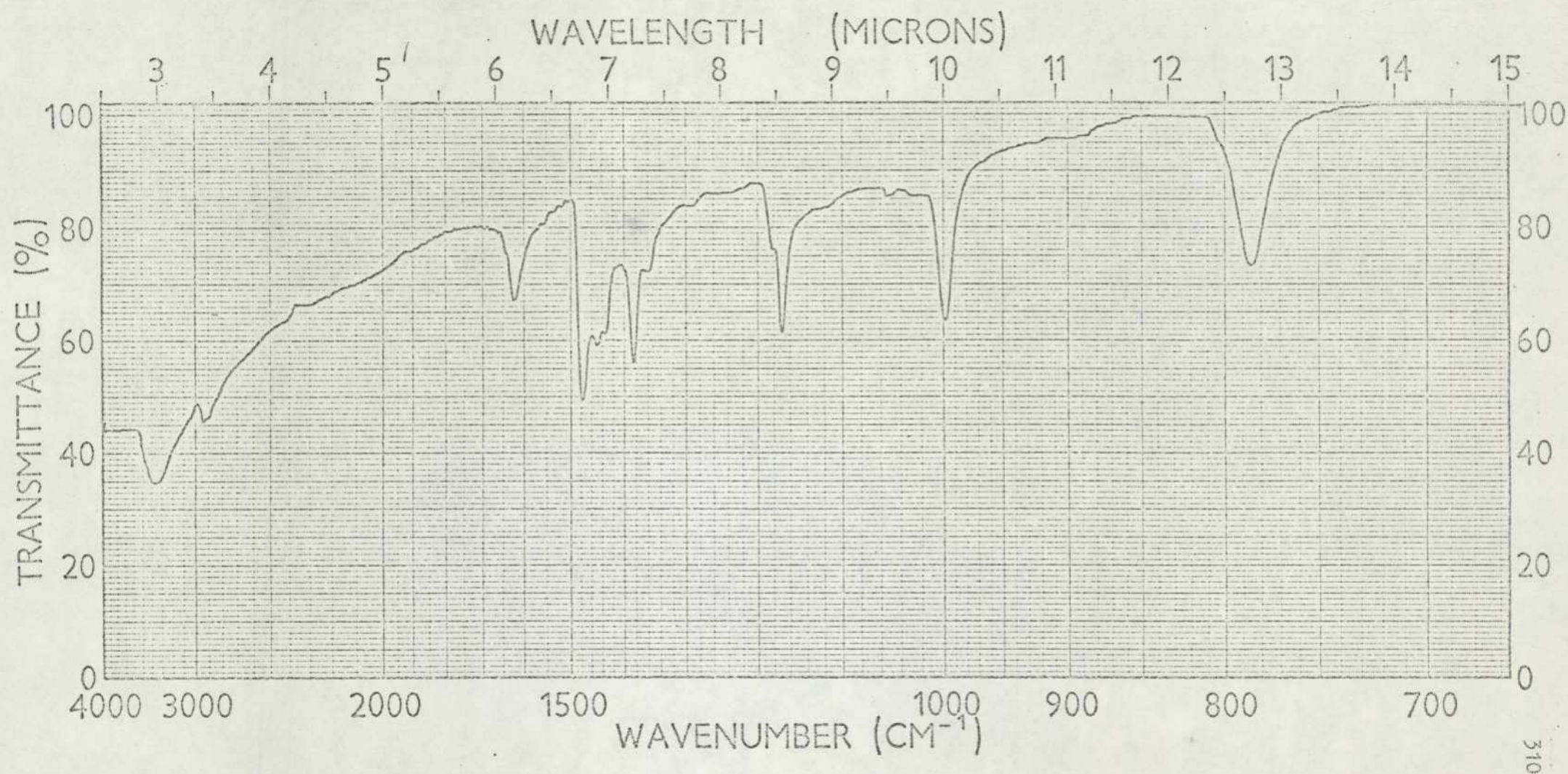


Fig. 5.9 Infrared Spectrum of the product from Experiment 5.12 , after washing with water and methanol. KBr disc.

Experiment 5.13 (In^{3+} , Ge^{4+} , Et_4N^+ , 2 weeks at 85°C)

This experiment constituted a repeat of Experiment 5.12, with germanium in place of tin. The starting mixture became:-

GeS_2	:	In_2S_3	:	$\text{Et}_4\text{N}^+\text{SH}^-$
0.70		0.35		3.16 mole/litre
or: 2.34		2.77		12.52 g/100 g H_2S

A blank diffraction pattern (before the addition of base) was obtained, and a control experiment without H_2S was conducted.

The reactor was loaded, H_2S (126.5 g) added and the autoclave heated to 85°C for two weeks. The probe temperature was 75°C , the oven 85°C , and the pressure 810 psi. The control material became green after a few hours at 85°C , but later faded to white, with a few drops of liquid on the walls of the tube above the sample. This was later identified by GLC as being a mixture of EtSH and Et_3N , attributed to decomposition of the base. The material removed from the autoclave was brown and moist, liberating gas identified as hydrogen sulphide. The material slowly solidified on standing for a few hours in the dry box. It was therefore implied that coordinated H_2S caused the material to remain liquid when the autoclave was vented, solidification occurring as the H_2S was lost.

Samples of the materials from the experiment and control reactions were dried under vacuum and x-ray powder patterns obtained (Figure 5.10; Appendix A2). A sample of the material from the autoclave was washed with methanol and water, leaving a white substance. Its diffraction pattern was also obtained, and an infrared spectrum taken of a KBr disc. The spectrum revealed the presence

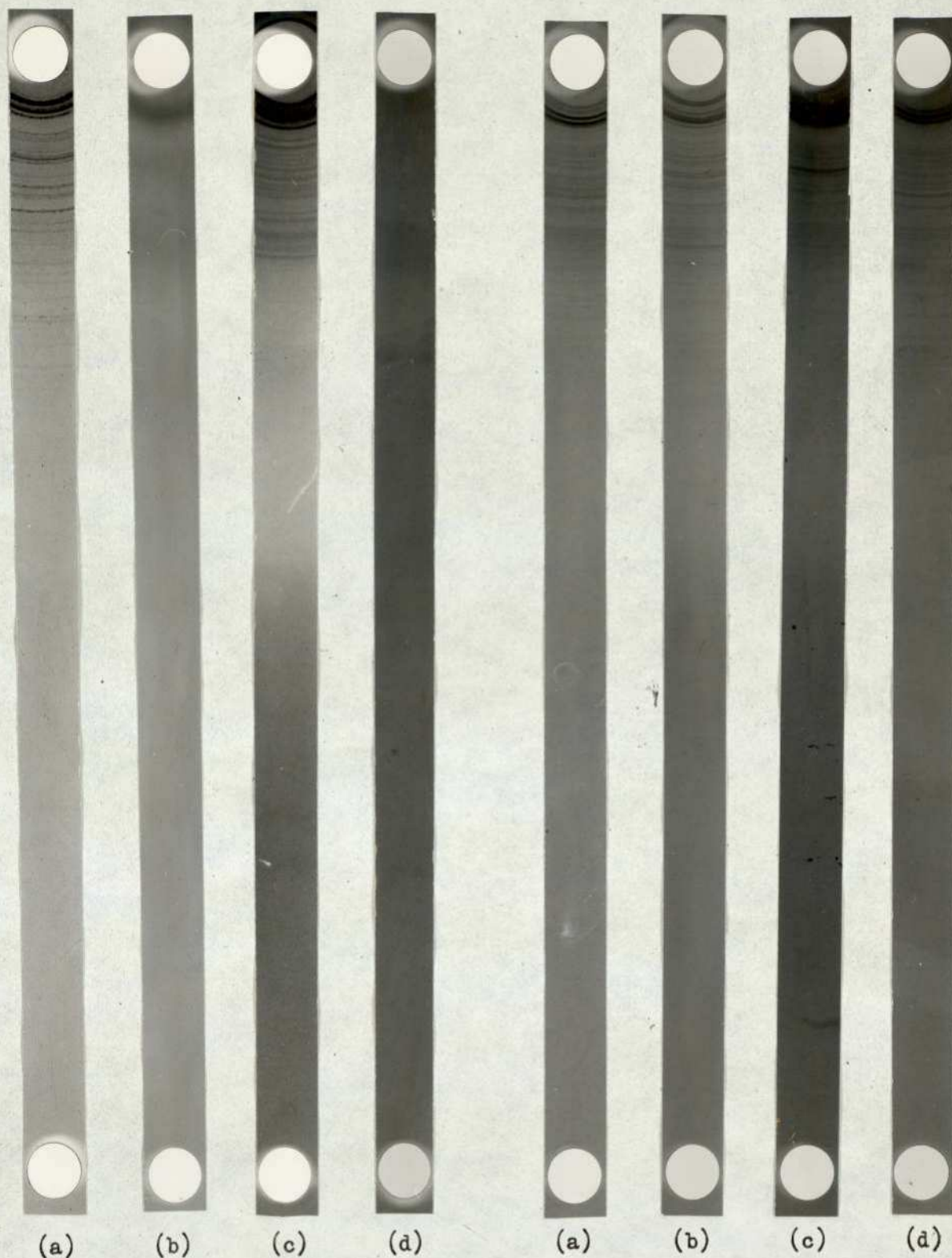


Fig.5.10

Fig.5.11

Fig.5.10 X-Ray Powder Patterns of the Products from the Hydrothermal Reaction of In_2S_3 and GeS_2 with $\text{Et}_4\text{N}^+\text{SH}^-$ in Liquid H_2S at 85°C . Experiment 5.13.

(a) Ex-Reactor. (b) Water-Washed. (c) Control. (d) Blank.

Fig.5.11 X-Ray Powder Patterns of the Products from the Hydrothermal Reaction of In_2S_3 and SnS_2 with $\text{Et}_4\text{N}^+\text{SH}^-$ in Liquid H_2S at 60°C . Experiment 5.14.

(a) Ex-Reactor. (b) Water-Washed. (c) Control. (d) Blank.

Copper $\text{K}\alpha$ Radiation.

of the Et_4N^+ group as in the previous experiment and this was confirmed by carbon, hydrogen and nitrogen analysis.

Found: C, 17.9; H, 4.0; N, 2.4%

Calculated for 24.3% of $(\text{C}_2\text{H}_5)_4\text{N}^+$: C, 17.9; H, 3.74; N, 2.62%

As in the previous experiment, the ex-reactor material gave a diffraction pattern containing many lines, including those of wide spacing. Many of these were also present in the control experiment, but on washing the material most of the crystallinity was lost. Therefore, the organic derivative identified by infrared and elemental analysis was non-crystalline in this experiment. X-ray data indicated the presence of excess base in both the main and control experiments, and this was confirmed by the yellow colour of the washings. Many more lines were observed in the diffraction pattern of the control sample in this experiment, far more than could be accounted for by the base. The Et_3N and EtSH formed probably acted as a flux to promote this crystallization. The sample from the autoclave showed more extensive crystallization than the control sample, however, and many differences were apparent. Therefore, promotion of crystallization by the H_2S was again found, although not to the same extent as in the previous experiment. The main difference noted on replacing tin with germanium was a loss of most of the crystallinity on washing the product, suggesting that most of the crystalline phases formed were soluble.

Experiment 5.14 (In^{3+} , Sn^{4+} , Et_4N^+ , 1 week at 60°C)

The previous two experiments (5.12 and 5.13) were repeated (5.14 and 5.15) with the temperature reduced to 60°C , in an attempt to prevent decomposition of the base with the formation of amine and thiol. The quantity of H_2S was increased to 150 g (about 90 per cent solvent) to encourage the complete dissolution of the soluble

phases formed. The pressure at 60°C was estimated from Sage and Lacey (389), with a specific volume of 0.3 litre/150 g (1.09 cu ft/lb mole), to be about 700 psi.

A control experiment was set up, the autoclave loaded with SnS_2 (2.98 g), In_2S_3 (2.66 g) and $\text{Et}_4\text{N}^+\text{SH}^-$ (12.02 g), and H_2S (155.00 g) added. The temperature was held at 60°C (oven), 55°C (probe), for one week. The pressure was 610 psi.

When the feedstocks were mixed before the experiment, a darkening was noticed. This implied that reaction was occurring before the solvent was added, possibly as a result of traces of Et_3N and EtSH being present. The blank x-ray powder pattern was therefore obtained on a vacuum dried sample of the complete feedstock mixture, rather than just the mixture of Group IIIb and IVb sulphides as previously. It revealed the presence of crystalline phases other than $\text{Et}_4\text{N}^+\text{SH}^-$ (Figure 5.11; Appendix A2; cf Appendix A4).

At the end of the reaction period the control sample had become yellow-green and moist in appearance, decomposition of the base having apparently still occurred. Much of the crystallinity found in the pre-reaction blank was lost, the remaining diffraction lines being rather diffuse (Figure 5.11; Appendix A2). The powder pattern of the dark yellow ex-reactor material showed crystallinity very similar to that found at 85°C (Experiment 5.12), although not so completely developed. The crystallinity was again stable towards methanol and water washing, additional diffraction lines becoming visible as excess base was removed. Strong lines with wide 'd' spacings (up to 12.46 Å) were again found, and it was apparent that the H_2S solvent had promoted crystallization of the feedstock, although not to the extent found at 85°C. The diffraction lines

were rather weaker and fewer in number in the present case.

Decomposition of the base had apparently still occurred at 60°C.

The infra-red spectrum of a KBr disc of the washed product (Figure 5.9) again indicated retention of the Et_4N^+ ion, and this was confirmed by the carbon, hydrogen and nitrogen analysis:

Found: C, 21.4; H, 4.8; N, 3.2%

Calculated for 29.4% of $(\text{C}_2\text{H}_5)_4\text{N}^+$: C, 21.69; H, 4.55; N, 3.16%

The general conclusion was therefore that the crystallization found in this experiment was similar to that found at 85°C, but that the reduction in temperature to 60°C had reduced the extent of the reaction.

Experiment 5.15 (In^{3+} , Ge^{4+} , Et_4N^+ , 1 week at 60°C)

This experiment was similar to Experiment 5.14, with germanium in place of tin. GeS_2 (2.34 g), In_2S_3 (2.77 g) and $\text{Et}_4\text{N}^+\text{SH}^-$ (12.52 g) were loaded into the autoclave, and H_2S (150.00 g) added. A diffraction pattern of the feedstock mixture (including base) was obtained, and a control experiment set up.

The autoclave was heated at 60°C (oven), 55°C (probe) for one week. The pressure was 5.90 psi. At the end of this time, the control experiment had become brown in colour. The material removed from the autoclave was dark and moist in appearance, similar to the product obtained from this system at 85°C (Experiment 5.13).

— X-ray powder patterns were obtained on vacuum dried samples of the control and ex-reactor product, and also of this product after washing with methanol and water. (Figure 5.12; Appendix A2). The powder pattern of the control material showed strong diffraction lines characteristic of $\text{Et}_4\text{N}^+\text{SH}^-$ (Appendix A4), with only two additional lines, both at wider spacing. A certain number of

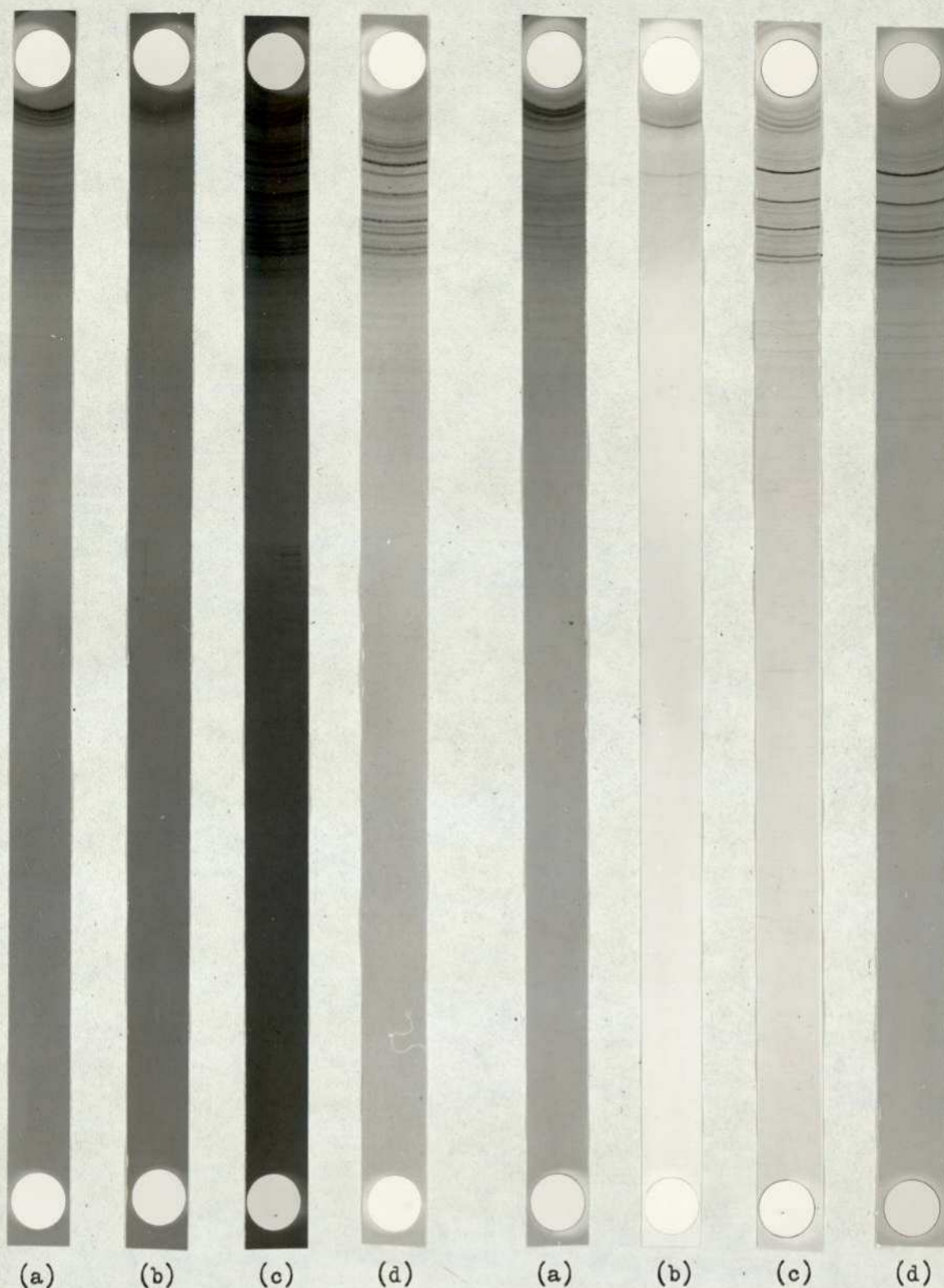


Fig.5.12

Fig.5.13

Fig.5.12 X-Ray Powder Patterns of the Products from the Hydrothermal Reaction of In_2S_3 and GeS_2 with $\text{Et}_4\text{N}^+\text{SH}^-$ in Liquid H_2S at 60°C . Experiment 5.15.

(a) Ex-Reactor. (b) Water-Washed. (c) Control. (d) Blank.

Fig.5.13 X-Ray Powder Patterns of the Products from the Hydrothermal Reaction of In_2S_3 and GeS_2 with $\text{Et}_4\text{N}^+\text{SH}^-$ in Liquid H_2S at 85°C . Seeded with 5% of 13X Zeolite. Experiment 5.16.

(a) Ex-Reactor. (b) Water-Washed. (c) Control. (d) Blank.

Copper $\text{K}\alpha$ Radiation.

additional lines were present in the diffraction pattern of the ex-reactor sample. As in the experiment employing tin (5.14), reaction at 60°C seemed to proceed similarly to reaction at 85°C (Experiment 5.13), but with less extensive crystallization at the lower temperature. There was not an exact correlation between the diffraction patterns obtained at the two temperatures, although the general characteristics were similar. In both cases, the crystallinity was lost on washing.

An infra-red spectrum (similar to Figure 5.9) was obtained of the washed sample, and the presence of a similar quantity of Et_4N^+ was indicated in spite of the non-crystalline nature of the material.

Found: C, 21.4; H, 4.15; N, 2.9%

Calculated for 28.6% of $(\text{C}_2\text{H}_5)_4\text{N}^+$:— C, 20.99; H, 4.40; N, 3.06%

The overall conclusion was therefore that reducing the reaction temperature from 85°C to 60°C had not markedly altered the course of the reaction in either the $\text{Sn}^{4+}\text{-In}^{3+}\text{-Et}_4\text{N}^+$ or the $\text{Ge}^{4+}\text{-In}^{3+}\text{-Et}_4\text{N}^+$ systems, although in both cases the rate of reaction (and hence extent of crystallization) was reduced. No reduction in the tendency for $\text{Et}_4\text{N}^+\text{SH}^-$ to decompose into Et_3N and EtSH was found to result from reducing the temperature, and reaction at 85°C appeared to represent the most suitable conditions.

Experiment 5.16 (In^{3+} , Ge^{4+} , Et_4N^+ , 1 week at 85°C,
seeded with 5 per cent 13X zeolite)

This and the following experiment (5.17) were an optimization of the system employing tetraalkylammonium hydrosulphide as base. They were conducted at 85°C as no advantage had been found to result from the use of a lower temperature. In view of the

extensive crystallization found in the previous experiments, the quantity of solvent present was increased by 100 per cent to ensure the complete dissolution of the soluble phases. GeS_2 was used, and the starting mixture (based on Experiment 5.13) was GeS_2 (1.75 g), In_2S_3 (2.08 g), $\text{Et}_4\text{N}^+\text{SH}^-$ (9.45 g) and H_2S (150 g). In an attempt to promote the required type of crystallization, five per cent w/w of 13X zeolite was added to 'seed' the mixture. The purity and source of this material was described in Chapter 3.

An x-ray 'blank' diffraction pattern was obtained of the complete feedstock mixture, and a control experiment without solvent was set up. The autoclave was heated to 85°C (oven), 75°C (probe) for one week, the pressure being 900 psi. The material was removed from the autoclave as a black, oily liquid that liberated H_2S and slowly solidified. It was similar in appearance to the products from the previous reactions employing GeS_2 with the organic base. The material from the control experiment was a pale orange-pink colour, similar to Experiment 5.13. X-ray powder patterns were obtained of the vacuum dried control and ex-reactor samples, and of product after methanol and water washing (Figure 5.13; Appendix A2). The ex-reactor pattern was very similar to that previously obtained with this system (Experiment 5.13). Again, most of the crystallinity was lost on washing, only a few of the strongest diffraction lines remaining. No lines attributable to the zeolite were detected, its concentration apparently being insufficient. The material from the control experiment gave a diffraction pattern very similar to the control from Experiment 5.13, although some line positions and intensities varied slightly.

An infra-red spectrum (KBr disc) and carbon, hydrogen and nitrogen analysis was obtained of the water washed sample. These were similar to those obtained in previous experiments, indicating the retention of the Et_4N^+ ion.

Found: C, 20.2; H, 4.1; N, 2.8%

Calculated for 27.1% of $(\text{C}_2\text{H}_5)_4\text{N}^+$: C, 19.99; H, 4.20; N, 2.92%

The overall course of this reaction was therefore very similar to Experiment 5.13, and the increased volume of solvent and use of seeding agent had been without effect.

Experiment 5.17 (In^{3+} , Ge^{4+} , Et_4N^+ , Na^+ , 4 weeks at 85°C , seeded with 5 per cent 13X zeolite)

The final experiment of this series employed two innovations. Firstly, a longer reaction period (four weeks) was allowed in an attempt to encourage reaction to proceed to completion, and promote crystallization of the residue isolated by solvent washing. Secondly, half of the tetrethylammonium hydrosulphide was replaced by the equivalent quantity of sodium hydrosulphide. It was felt possible that the tetraethylammonium ion was too large to become incorporated in a complex sulphide analogous to the zeolites. This should not be the case, as conventional zeolites have been prepared using these bases, and it was expected that the larger sulphide ion would facilitate their incorporation into a thioanalogue. Nevertheless, it was felt worthwhile investigating the effects of using a mixed-base system, the organic base providing the solvent medium for the Groups IIIb and IVb sulphides, and the sodium hydrosulphide providing a source of charge balancing cation.

The feedstock was GeS_2 (1.75 g), In_2S_3 (2.08 g), $\text{Et}_4\text{N}^+\text{SH}^-$ (4.73 g), NaSH (1.63 g) and H_2S (175.0 g). Five per cent w/w zeolite

were again added to seed the mixture. After loading, the autoclave was heated to 85°C (oven), 75°C (probe) for four weeks, the pressure being 720 psi. A blank diffraction pattern was obtained on the feedstock mixture, and a control experiment was set up.

The product was removed from the autoclave as a moist, non-uniform solid consisting of black and yellow particles. The control material was pale cream and practically dry. X-ray diffraction patterns were obtained of vacuum dried samples of both materials, and also of the methanol and water washed product from the autoclave (Figure 5.14; Appendix A2). After washing, a mixture of yellow and green particles remained, and these were separated under a microscope (X50) for further study.

A considerable amount of crystallization was indicated in the ex-reactor sample, and most of this was lost on washing, both the yellow and green materials being essentially non-crystalline. Thus it seemed that either decomposition had occurred or that the crystalline materials were soluble. The control experiment developed only limited crystallinity in comparison with the reaction and most of the diffraction lines found with the ex-reactor material corresponded to lines found in either the $\text{Ge}^{4+}\text{-In}^{3+}\text{-Na}^{+}$ or the $\text{Ge}^{4+}\text{-In}^{3+}\text{-Et}_4\text{N}^{+}$ system (Experiments 5.11 and 5.13). There was no indication of the formation of a new phase.

The infra-red spectra of both the constituents of the washed product showed evidence for retention of Et_4N^{+} (similar to Figure 5.9). However, elemental analysis showed that the yellow material contained most of the organic derivative.

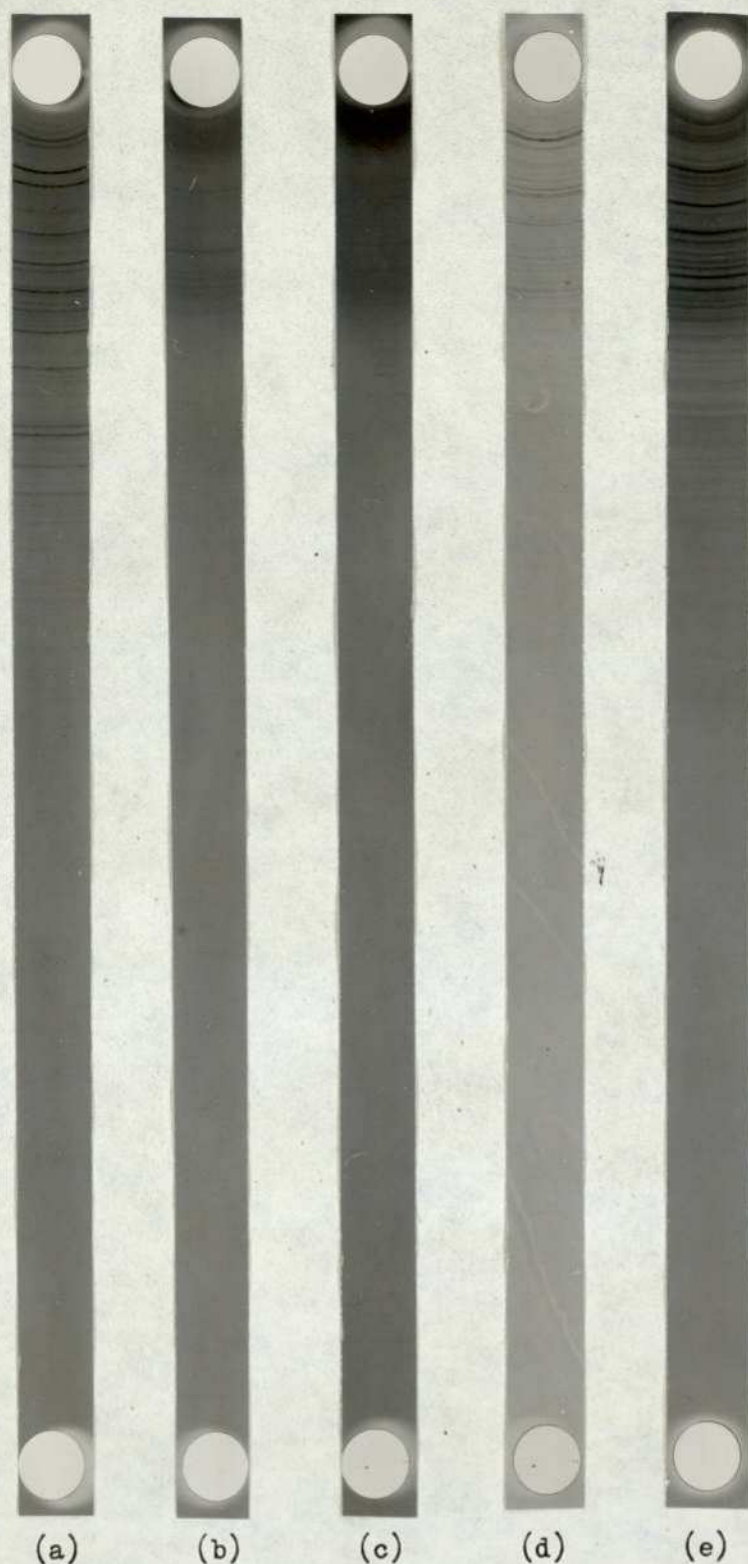


Fig. 5.14 X-Ray Powder Patterns of the Products from the Hydrothermal Reaction of In_2S_3 and GeS_2 with $\text{Et}_4\text{N}^+\text{SH}^-$ and NaSH in Liquid H_2S at 85°C . Seeded with 5% of 13X Zeolite. Experiment 5.17.

- (a) Ex-Reactor.
- (b) Water-Washed; Green Phase.
- (c) Water-Washed; Yellow Phase.
- (d) Control.
- (e) Blank.

Copper $\text{K}\alpha$ Radiation.

Found: (Yellow Material): C, 20.8; N, 4.3; N, 2.8%

(Green Material): C, 6.1; H, 1.58; N, 0.63%

Calculated: (Yellow Material): 27.9% of $(C_2H_5)_4N^+$; C, 20.6; H, 4.29;
N, 3.00%

(Green Material): 6.2% of $(C_2H_5)_4N^+$; C, 4.58, H, 0.95;
N, 0.67%

It seemed therefore that the two bases had produced separate reactions, and that a single homogeneous product had not been formed. A very few weak diffraction lines were observed in the powder pattern of the green material, and these did not correspond to lines found in the $In^{3+}-Ge^{4+}-Na^+$ system (Experiment 5.11). Therefore the formation of a new phase was possible, although the low intensity of these lines precluded the possibility of extensive recrystallization.

5.2.9 Further Characterization of the Products from

Experiments 5.10 - 5.17

5.2.9.1 Sodium Analysis

One of the most significant features of the experiments employing tetraalkylammonium hydrosulphide as base was the very consistent quantity of the basic ion (Et_4N^+) remaining in the products after excess base had been removed by washing with methanol and water. This suggested that an insoluble, complex phase was being formed, either a ternary $(M_x^1 M_y^2 S_n)$, a quarternary $(M_x^1 M_y^2 M_z^3 S_n)$, or a more complex sulphide. To complete this assessment, the quantity of sodium remaining in the solid phase after washing the products from Experiments 5.10, 5.11 and 5.17 was measured. In these experiments, NaSH had been employed as base, and if a new phase was formed similar to those found when an organic base was used, then an equivalent quantity of sodium would be expected to remain in the washed product.

Sodium was determined with an EEL flame photometer, the sample (0.1 g) being dissolved in 50 per cent HCl, the solution nearly neutralized with ammonia, and made up to 250 ml. The instrument was calibrated with solutions of NaCl, and a reagent blank was deducted. AR grade reagents were used throughout. The results of these analyses are collected in Table 5.4. It may be seen that the sodium concentration of these materials varied more than did the organic ion concentration of the corresponding materials. Nevertheless, the values are of the same order of magnitude, and the implication was that reaction in the inorganic flux had been much slower and less complete. There was no appreciable variation detected in the amount of sodium found in the green and yellow phases of Experiment 5.17.

5.2.9.2 Ion Exchange

If the phases formed had possessed zeolitic properties, then the cation would be performing a charge balancing function, and should be readily ion-exchanged with other cations of similar size, or less. Ion exchange with NaCl solution was attempted with several of the products containing Et_4N^+ , but in no case was any retention of sodium observed. After contacting the material with dilute NaCl solution, it was filtered off and well washed with water before being dissolved in dilute acid for the sodium determination. In all cases the values obtained were of the same order as the solvent blank, indicating that no exchange had occurred.

5.2.9.3 Base Solubility Tests

Conventional zeolites are prepared in alkaline media, and precipitate from solutions of the ternary oxides. By analogy, it might be expected that any zeolitic phase formed in sulphide

systems would be insoluble in basic sulphide solution, and therefore a possible means of separating any thiozeolite phases from the reaction mixtures suggested itself.

The extraction of the various reaction mixtures with a 10 per cent w/w aqueous solution of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (AR grade) was therefore investigated. The method was only applicable to systems where the water stable Group IIIb and IVb sulphides had been used. The results are collected in Table 5.5. In Experiments 5.11 - 5.17, very small amounts of black residue were obtained, and these materials were filtered off, washed with distilled water and dried under vacuum. Infra-red spectra (KBr discs) and x-ray powder patterns were obtained of the materials. The infra-red data did not reveal any features attributable to organic residues, and the x-ray data (Figure 5.15; Appendix A2) showed that the materials possessed only weak crystallinity. Lines characteristic of 13X zeolite were found where this material had been used as seeding agent (Experiments 5.16 and 5.17). In Experiment 5.11, the lines found after base washing corresponded with those found in the water washed sample. In Experiments 5.12 and 5.14, most of the lines found after water washing were lost on base washing, and in the other patterns any diffraction lines present were very weak.

It seemed from these tests, therefore, that the new phases formed in the hydrothermal systems investigated did not possess properties characteristic of zeolites. Although water-insoluble materials were isolated, and these shown to contain cations from the basic media in consistent proportions, these cations could not be ion-exchanged, and the materials containing germanium exhibited very little crystallinity. The almost complete solubility of all

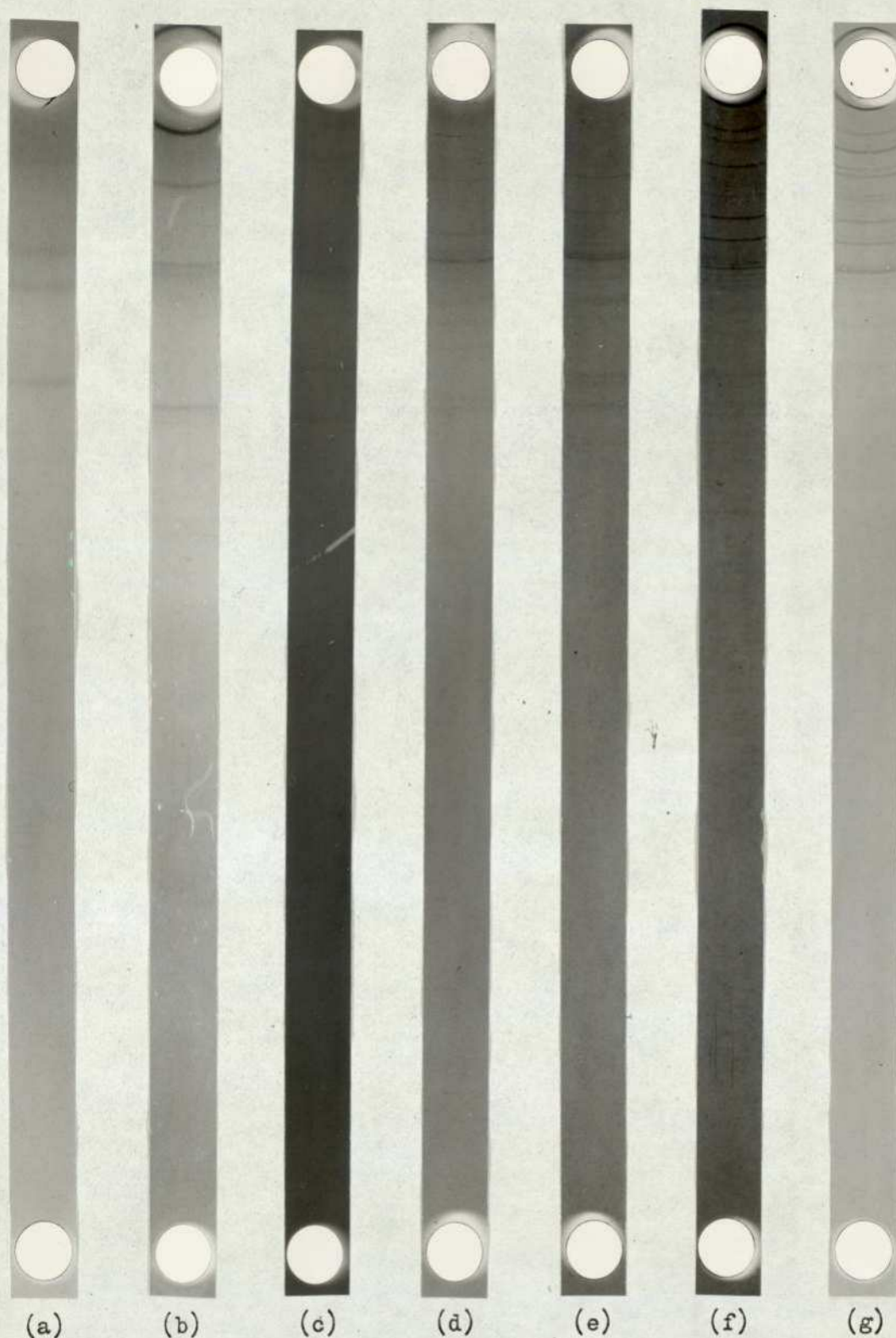


Fig. 5.15 X-Ray Powder Patterns of the Products from the Base Solubility Tests conducted on the Materials obtained from the Hydrothermal Reactions in Liquid Hydrogen Sulphide.

(a) Experiment 5.11.
(b) Experiment 5.12.
(c) Experiment 5.13.
(d) Experiment 5.14.

(e) Experiment 5.15.
(f) Experiment 5.16.
(g) Experiment 5.17.

Copper K α Radiation.

the materials in dilute aqueous solutions of basic sulphides was also not indicative of zeolitic properties. The very small amounts of residue remaining were in all cases only weakly crystalline, and may well have been due to impurities in the starting materials.

On the other hand, it seemed evident that the liquid hydrogen sulphide had promoted reaction to form new phases in many cases, and the organic base had undoubtedly formed a medium in which the metal sulphides had dissolved. The formation of simple ternary sulphides (eg analogous to sodium thiogermanate) was a possibility, besides the formation of more complex phases that were not zeolitic in their properties.

5.2.10 Ternary Reactions in Liquid Hydrogen Sulphide

To enable a better assessment to be made of the reactions that had occurred during the hydrothermal preparations in liquid hydrogen sulphide, the individual reactions of each of the Group III b and IV b sulphides used during the latter stages of the work were investigated in each of the basic media employed. The experimental conditions were similar to those used in the main hydrothermal reactions, and the intention was to see whether any of the new phases that had been identified in the X-ray powder patterns from these experiments could be attributed to ternary sulphides formed between individual Group III b or IV b sulphides and the base. In particular, it was hoped to see whether the diffraction lines of high 'd' value (above about 12 Å) found with many of the products could be attributed to simple ternary sulphides, or whether these indicated the formation of more complex sulphides of correspondingly larger unit cell.

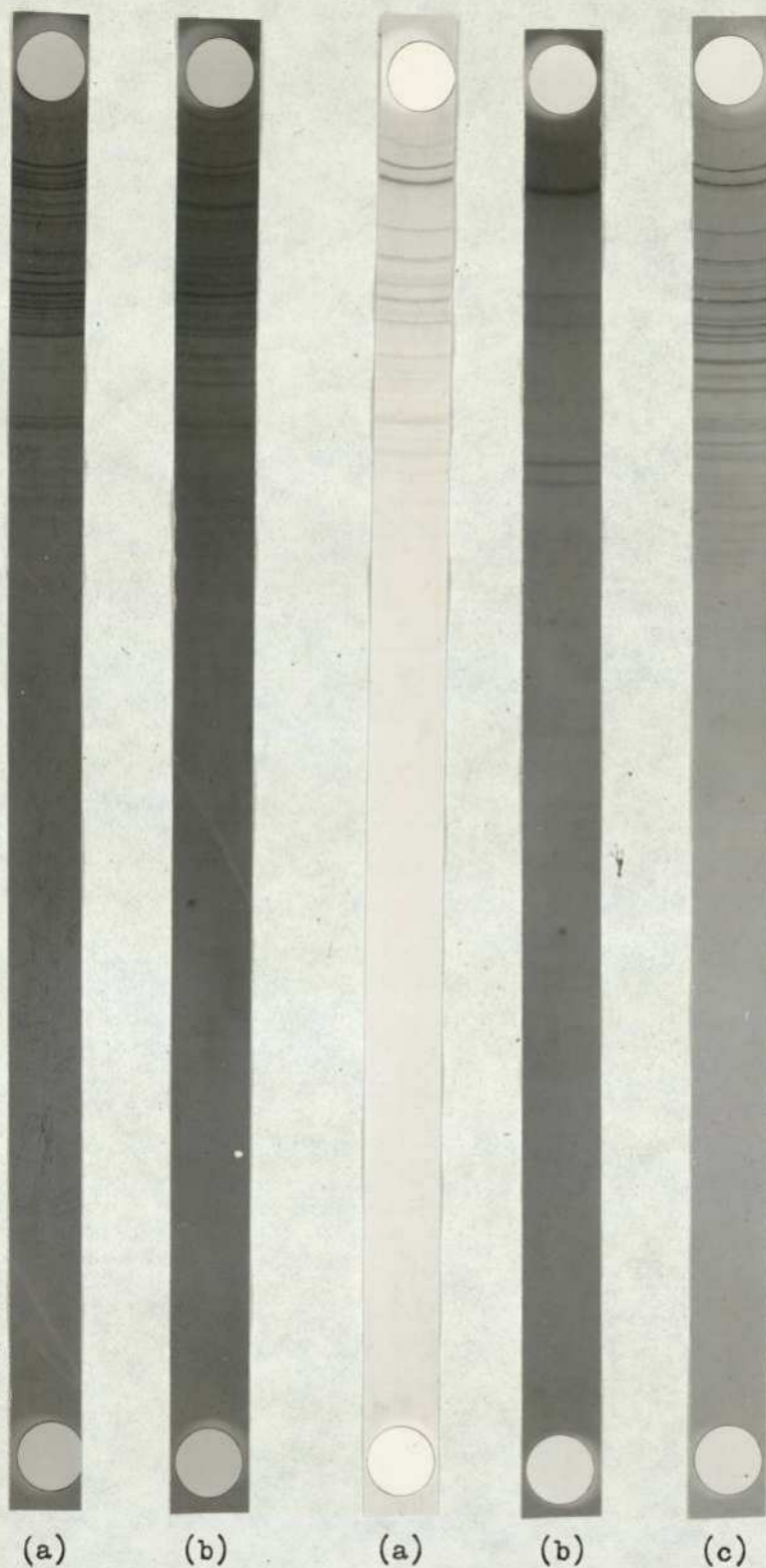


Fig. 5.16

Fig. 5.17

Fig. 5.16 X-Ray Powder Patterns of the Product from the reaction of GeS_2 and NaSH in Liquid H_2S at 85°C . Experiment 5.18.

(a) Ex-Reactor. (b) Methanol Washed.

Fig. 5.17 X-Ray Powder Patterns of the Product from the reaction of SnS_2 and NaSH in Liquid H_2S at 85°C . Experiment 5.19.

(a) Ex-Reactor. (b) Water Washed. (c) Methanol Washed.

Copper K_α Radiation.

suggested that one or more of these materials have been formed. The diffraction pattern of the methanol-washed product corresponded fairly closely with NaGeS_2 , although there were some further lines of weak intensity present.

It therefore seemed that a mixture of Na-Ge ternary sulphides have been formed, and that at least some of these were soluble in water or methanol. The rather weak intensity of the diffraction patterns suggested that crystallization was incomplete. The weak line at $d = 12.50 \text{ \AA}$ probably resulted from a superlattice diffraction rather than a large unit cell.

Experiment 5.19 (Sn^{4+} , Na^+)

The material formed was pale yellow and rather non-uniform in appearance. It was almost completely soluble in methanol or water, only a small amount of residue remaining. X-ray powder patterns were obtained on (1) the ex-reactor material; (2) the material remaining after methanol-washing; (3) the material remaining after water-washing (Figure 5.17; Appendix A3).

The diffraction pattern of the ex-reactor material revealed a large number of lines, including a weak one of wide spacing ($d = 11.79 \text{ \AA}$). The pattern of the methanol washed material was similar, but after water-washing only a few weak lines remained, close to lines associated with SnS_2 (Appendix A6). Thus it appeared that some recrystallization of the essentially non-crystalline SnS_2 has occurred, and that this remained after washing the product with water.

Many other lines were found in the powder pattern of the ex-reactor material besides those associated with SnS_2 and NaSH

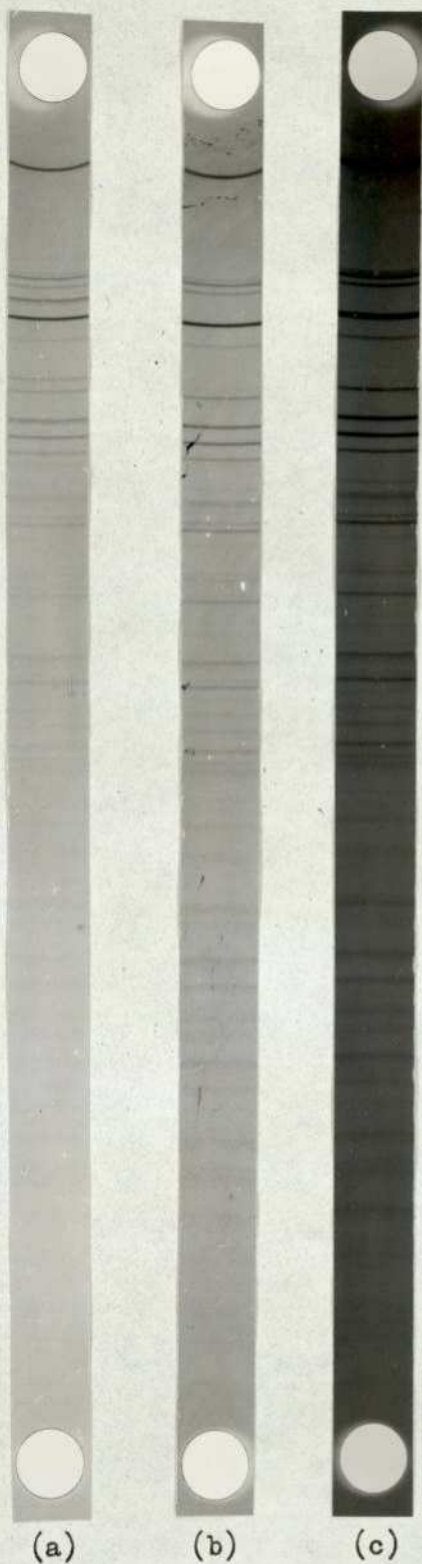


Fig. 5.18

Fig. 5.18 X-Ray Powder Patterns of the Product from the reaction of In_2S_3 and NaSH in Liquid H_2S at 85°C . Experiment 5.20.

(a) Ex-Reactor. (b) Water Washed. (c) Methanol Washed.

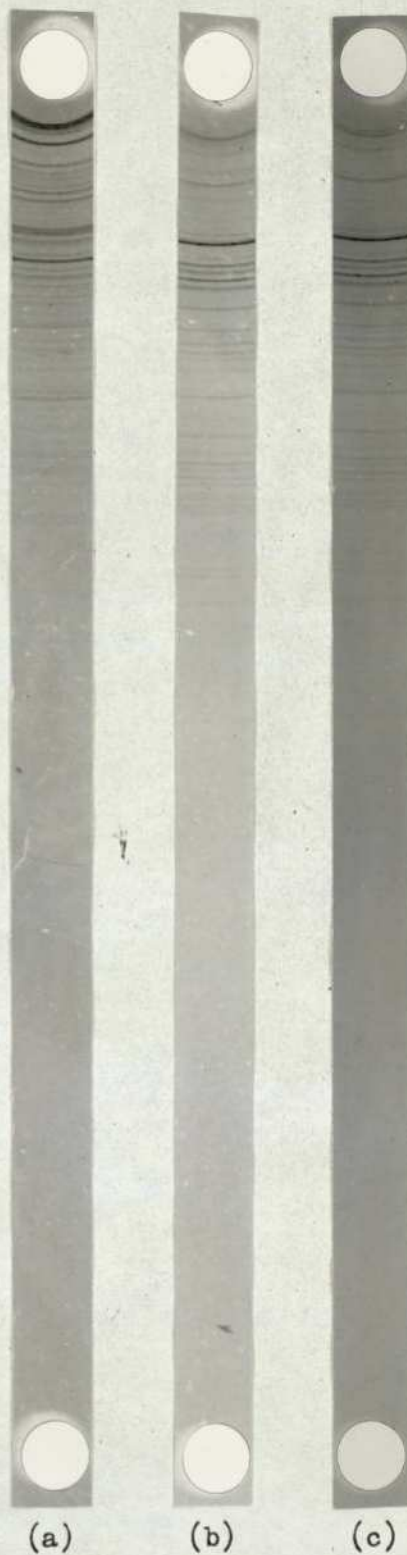


Fig. 5.19

Fig. 5.19 X-Ray Powder Patterns of the Product from the reaction of GeS_2 and $\text{Et}_4\text{N}^+\text{SH}^-$ in Liquid H_2S at 85°C . Experiment 5.21.

(a) Ex- Reactor. (b) Water Washed. (c) Methanol Washed.

Copper $\text{K}\alpha$ Radiation.

matching calculated diffractions for NaInS_2 . As many of the calculated diffractions will only be weak, a certain number of absences in the observed diffraction pattern do not invalidate the assignment.

Therefore, the only product from this reaction was NaInS_2 . Lines attributed to $\alpha\text{-In}_2\text{S}_3$ are also found in NaInS_2 , and therefore there was no evidence for the crystallization of $\alpha\text{-In}_2\text{S}_3$. It is significant that liquid hydrogen sulphide had promoted the formation of NaInS_2 from In_2S_3 and NaSH at 85°C , in direct analogy with the formation of this compound in water. In the absence of a solvent, temperatures above 300°C are required (68).

Experiment 5.21 (Ge^{4+} , Et_4N^+)

The product was obtained as a viscous black liquid which liberated H_2S and slowly solidified. It appeared that the product contained coordinated H_2S which was lost slowly when the autoclave was vented. Samples of the solid material were washed with methanol and water, but with little change in appearance except for the removal of excess base. X-ray powder patterns were obtained of the ex-reactor material (vacuum dried) and of the washed materials. (Figure 5.19 ; Appendix A3). A large amount of recrystallization was indicated, and many lines of high 'd' value (up to $10 \text{ \AA}$) were present. Many of these lines, as well as those attributed to excess base, were lost on washing. Many of the remaining lines were attributed to orthorhombic sulphur (Appendix A6), indicating the formation of elemental sulphur. The presence of soluble complex sulphides was indicated by this data, but less soluble complex phases were indicated by infra-red and elemental analyses of the methanol washed material. The infra-red spectrum was similar to Figure 5.9, indicating

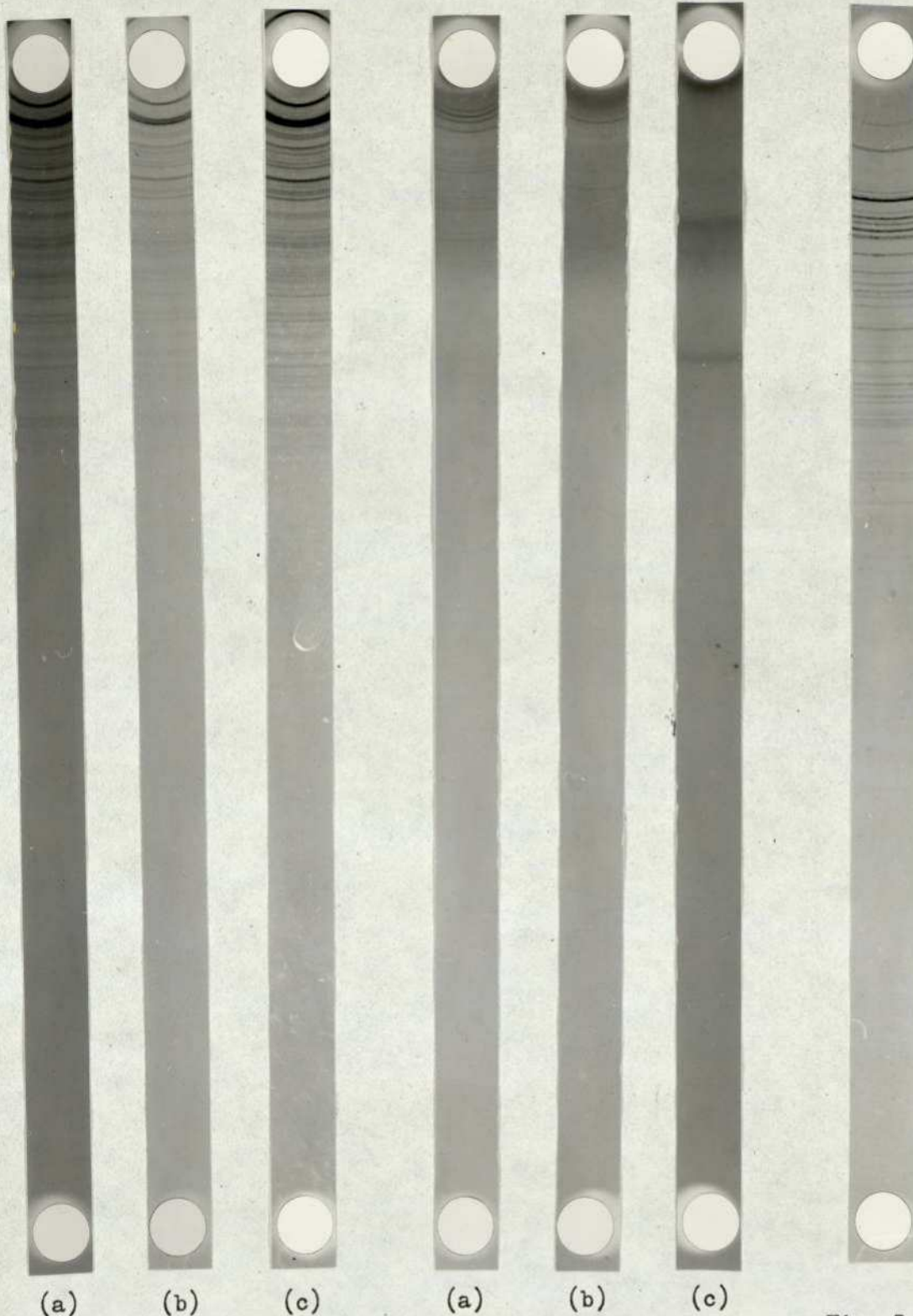


Fig. 5.20

Fig. 5.21

Fig. 5.22

Fig. 5.20 X-Ray Powder Patterns of the Product from the reaction of SnS_2 and $\text{Et}_4\text{N}^+\text{SH}^-$ in Liquid H_2S at 85°C . Experiment 5. 22.

(a) Ex-Reactor. (b) Water Washed. (c) Methanol Washed.

Fig. 5.21 X-Ray Powder Patterns of the Product from the reaction of In_2S_3 and $\text{Et}_4\text{N}^+\text{SH}^-$ in Liquid H_2S at 85°C . Experiment 5.23.

(a) Ex-Reactor. (b) Water Washed. (c) Methanol Washed.

Fig. 5.22 X-Ray Powder Pattern of the Product from the reaction of $\text{Et}_4\text{N}^+\text{SH}^-$ in Liquid H_2S at 85°C . Experiment 5.24.

Copper $\text{K}\alpha$ Radiation.

that slowly solidified. The solid became dark grey after washing with methanol or water. X-ray powder patterns, infra-red and elemental analyses were obtained as in the previous experiments.

The elemental and infra-red data (similar to Figure 5.9) again indicated retention of the $(C_2H_5)_4N^+$ group. Found: C, 16.38; H, 3.01; N, 2.11 per cent; Calculated for 21.5 per cent of $(C_2H_5)_4N^+$: C, 15.86; H, 3.33; N, 2.31 per cent.

The X-ray powder patterns were rather weak (Figure 5.21; Appendix A3), although many new lines (including those of wide spacing) were found. Most of these were lost on washing with methanol or water. There was evidence for excess base in the ex-reactor product, and also the possibility of β - In_2S_3 and elemental sulphur (Appendix A6), but other lines ('d' up to 10.99 Å) indicated the formation of new (soluble) phases.

Experiment 5.24 ($Et_4N^+SH^-$ -decomposition test)

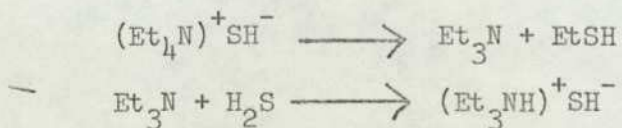
In view of the black, oily texture of the products formed with the organic base, $Et_4N^+SH^-$, and the presence of Et_3N and EtSH in some of the control experiments where this base had been used, its reaction with liquid hydrogen sulphide was investigated. It was required to determine the extent to which it decomposed under the experimental conditions employed.

— A sample of $Et_4N^+SH^-$ (3.5 g) was heated at 85°C (oven), 78°C (probe), in H_2S (50.0 g) for two weeks. The pressure was 720 psi. After the reaction period the product had the black, oily appearance found in previous reactions employing this base. Mixed in with the material were some well formed crystals of a pale yellow colour. They were soluble in xylene and identified

by an x-ray powder pattern (Figure 5.22; Appendix A3) as elemental sulphur in its orthorhombic form (Appendix A6).

It was attempted to vacuum dry a sample of the oily residue for an x-ray powder pattern, but the material did not solidify as did that from the earlier reactions employing this base. An infra-red spectrum was obtained of a small amount of the material pressed between two KBr discs. (Figure 5.23). It was basically similar to the infra-red spectrum of $\text{Et}_4\text{N}^+\text{SH}^-$ (Figure 4.31), but there were differences in the relative intensities of certain peaks. For instance, the shoulder at 1115 cm^{-1} had become a large peak at 1015 cm^{-1} , and the shoulder at 1230 cm^{-1} had become a peak at 1220 cm^{-1} . The (N-H) bending mode (always present as a weak peak near 1600 cm^{-1} in $\text{Et}_4\text{N}^+\text{SH}^-$) had become somewhat broadened. Possibly most significant was the replacement of $\nu(\text{S-H})$ at 2570 cm^{-1} in $\text{Et}_4\text{N}^+\text{SH}^-$ with a band at 2500 cm^{-1} and a group of partially resolved bands around 2650 cm^{-1} . This could be due to $\nu(\text{N-H})$, but is more likely due to coordinated H_2S in view of the shifting of the $\nu(\text{S-H})$ band from 2570 cm^{-1} .

Therefore it was apparent that the base was undergoing substantial modification during the reaction period in liquid H_2S . Coordination with the solvent was likely, but decomposition to form $(\text{Et}_3\text{NH})^+\text{SH}^-$ was also a possibility:-



The presence of elemental sulphur in the product from this reaction (and also the presence of polysulphide in the products from some of the earlier reactions) suggested that oxidation had occurred. Base catalysed oxidation with gaseous oxygen was one possibility, although the source of such oxygen contamination is not clear. The specification

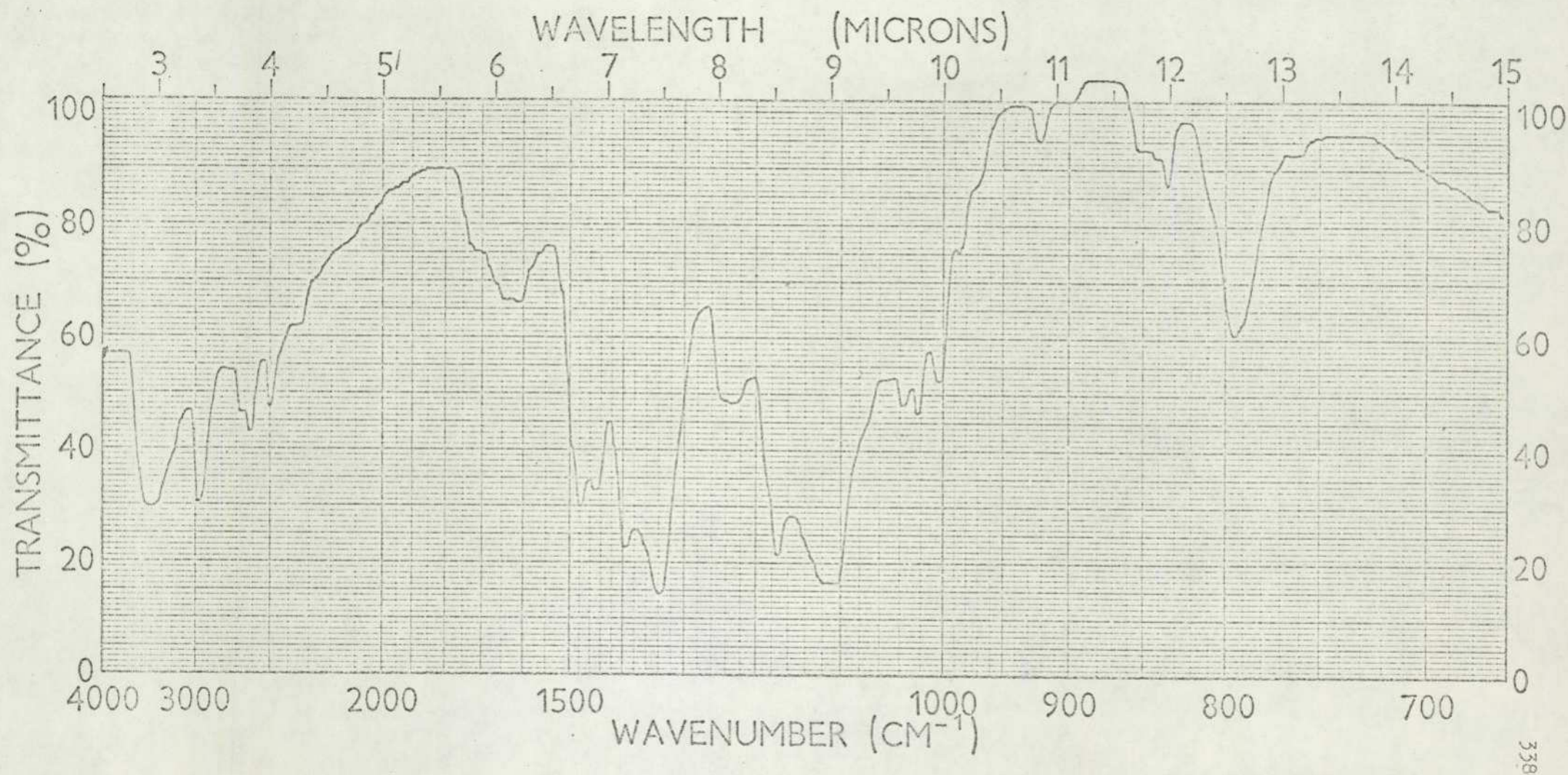


Fig. 5.23 Infrared Spectrum of the product from the reaction between $\text{Et}_4\text{N}^+\text{SH}^-$ and liquid H_2S . KBr disc.

of the H_2S did not suggest that appreciably oxygen could be present as an impurity. Seepage into the evacuated autoclave during filling seemed unlikely as the units were completely pressure-tight during use. The only other possibility would be reduction of one of the reagents present (eg Sn^{4+} to Sn^{2+}), but this explanation would not be applicable in the present experiment. Therefore, some contamination must be conceded as responsible for sulphur formation, at least in the present experiment.

5.4 CONCLUSIONS

The factors that had emerged in the study of the hydrothermal solvent properties of liquid and supercritical hydrogen sulphide may be summarised as follows. Firstly, the rôle of the hydrogen sulphide in promoting reaction and crystallization in the systems examined had been demonstrated. When this component was omitted, reactivity and crystallization was generally very much less, clearly indicating its power as a solvent. Secondly, the greater degree of solubility and reactivity of the Group III b and IV b sulphides in the organic rather than inorganic base was demonstrated, and the formation of complex sulphides in these media was indicated. Thirdly, it seemed that the sulphides of the lower elements of Groups III b and IV b were more reactive in the inorganic base than were the sulphides of aluminium and silicon. Fourthly, the complex sulphides formed in these systems had not been shown to possess properties that would be associated with sulphur analogues of zeolites. In general, it seemed that the reaction products could be considered as mixtures of ternary phases formed between the individual sulphides and the base, many of which had been shown to produce X-ray powder patterns characteristic of large unit cells.

As was predicted, the controlling factor in these experiments was the establishment of suitable basic media in which the Group III b and IV b sulphides could be dissolved. It seemed highly likely that solution of these sulphides as ternary phases occurred. There was no evidence to suggest, however, that these ternary phases were reacting to form more complex, insoluble sulphides, in the way that aluminosilicate gels react under aqueous hydrothermal conditions to form zeolites. It appeared that the ternary sulphides were remaining in solution, and were precipitated unchanged when the hydrogen sulphide was removed. In addition to this, there was also evidence to suggest that some crystallization of the non-crystalline binary sulphide feedstock occurred, indicating a certain amount of ionic or molecular mobility in solution.

The low solubility of ionic materials in liquid H_2S was discussed in the first part of this Chapter. Only where large ions are present are the electrostatic forces reduced to the point where the weak solvation forces of liquid H_2S are able to promote solution. In general, only covalent materials crystallizing in molecular form are soluble, and the three dimensional close-packed anion structures of the Group III b and IV b sulphides do not fall into this category. This is consistent with their observed solubility in basic solutions containing the large tetraethyl-ammonium ion, where complex ionic species may be formed to promote solubility.

The reported formation of complex phases under such conditions ie $\left[(C_2H_5)_3NH \right]_3 AsS_3$, has been discussed in the first part of this chapter. It is not completely established, however, the degree to which such species are ionized in solution in liquid H_2S . Conductivity measurements indicate that in the case of solutions of organic bases, ionization must be considerable.

However, covalent species are probably unionized in solution, consistent with the low dielectric constant of H_2S . For instance, SiCl_4 is readily soluble in both water and liquid H_2S , but whereas hydrolysis to hydrated silicon species is immediate in water, the corresponding thiohydrolysis with H_2S occurs only at high temperature (see Chapter 4).

The proposed solubility of the sulphides of germanium, tin and indium in solutions of $\text{Et}_4\text{N}^+\text{SH}^-$ in liquid H_2S is therefore in agreement with the published properties of such solutions, and the detection of the Et_4N^+ group in the products indicated the formation of complex ions. Far less evidence for similar solubility in $\text{NaSH}/\text{H}_2\text{S}$ mixtures was found, although a certain amount of reactivity was detected.

Reaction of the mercaptides of aluminium and silicon, Et_2AlSET and $\text{Si}(\text{SET})_4$ in $\text{NaSH}/\text{H}_2\text{S}$ mixtures resulted in the formation of Al_2S_3 and SiS_2 in a finely divided, non-crystalline state. Virtually complete decomposition of the mercaptides to form sulphides was indicated under all the conditions used, even at 50°C . However, very little tendency for the non-crystalline Al_2S_3 and SiS_2 to react and form complex species was detected. Only above the critical temperature was slight crystallization of Al_2S_3 and SiS_2 observed, and the formation of new (more complex) phases only occurred (to a very limited degree) at 350°C . The flux of nearly molten NaSH may well have played a part in the crystallization processes at this temperature.

Only with the sulphides of indium, germanium and tin was appreciable reactivity with the inorganic base detected.

Evidence for the formation of ternary Na-In, Na-Sn and Na-Ge sulphides at 85°C was obtained, those of germanium and tin being at least partially soluble in methanol or water. In the case of indium, complete conversion of In_2S_3 to NaInS_2 was found, the product being identified by its X-ray powder pattern after excess base had been removed by washing with methanol. A temperature in excess of 300°C is required for this reaction in the absence of solvent, and therefore direct evidence for the interaction of liquid H_2S as a solvent was obtained. It may be inferred that sufficient solubility of the NaSH occurred to enable reaction with In_2S_3 to proceed in solution during the extended reaction period of two weeks. Thus, the feasibility of the reaction systems employing NaSH as base was demonstrated, although the extent to which ionic reactions were involved in the formation of NaInS_2 is not known.

Similar results were obtained when the organic base $\text{Et}_4\text{N}^+\text{SH}^-$ was used in place of NaSH. Interaction of the base with the solvent was indicated, with the formation of a dark, viscous liquid possibly involving coordination of H_2S . Reaction of the solution with In_2S_3 , GeS_2 or SnS_2 produced evidence for the formation of new phases in each case. The X-ray powder patterns contained lines not accounted for by crystallization of the starting material, and new diffraction lines of high 'd' value suggested the formation of materials with large unit cells. Only the new phases formed with indium appeared to be appreciably soluble in methanol or water, and the residues remaining after methanol washing were shown to contain the Et_4N^+ group, suggesting the formation of ternary sulphides of the type $(\text{Et}_4\text{N})_x\text{M}_y\text{S}_z$.

In all cases, the possibility existed of contamination of these ternary sulphides with unreacted starting material. This, together with uncertainty as to whether only a single ternary sulphide was formed, made their accurate identification impossible within the restrictions of the approaches adopted. No evidence was obtained that suggested the formation of phases more complex than the ternary sulphides in any of the main hydrothermal reactions. It seemed that lines of wide spacing in the powder patterns of the products from these reactions could be satisfactorily explained by the formation of ternary sulphides. In the experiments employing indium and tin or indium and germanium sulphides with NaSH, the majority of diffraction lines in the powder patterns of the products coincided with lines found with the individual ternary sulphides. Only a few diffraction lines could not be explained in this way. Similar results were obtained in the experiments employing $\text{Et}_4\text{N}^+\text{SH}^-$ as base, the diffraction patterns being interpreted as mixtures of ternary sulphides. Crystallization seemed less complete at 60°C than at 85°C , and attempts to seed the mixture with 13X zeolite, or the use of a mixed base system ($\text{NaSH}/\text{Et}_4\text{N}^+\text{SH}^-$) did not significantly alter the course of the reaction.

The chemical nature of the products from these reactions was in general agreement with the conclusions already reached. The solubilities of the products in water, organic solvents and aqueous sulphide solutions all pointed to the formation of ternary rather than complex phases. Although the presence of cations from the base was detected in the washed products from these reactions, the absence of any ion exchange precluded the formation of phases analogous to zeolites.

Therefore, only partial analogy with the type of aqueous hydrothermal system used to prepare zeolites was demonstrated. The crystallization of complex phase did not proceed in the sulphur system in the way it does under aqueous conditions, although this did not appear to be the result of a solubility limitation in view of the ready formation of ternary sulphides under suitable conditions. Rather, the fundamental differences between the chemistry of the sulphides and oxides appeared to prevent the low temperature formation of complex sulphides under conditions analogous to the hydrothermal formation of aluminosilicates. It seems unlikely that sulphur analogues of zeolites or related oxides could be formed in systems other than the hydrothermal type considered here, and for this reason the formation of this type of compound must be considered infeasible in the light of evidence obtained.

CHAPTER 6. AQUEOUS REACTIONS

6.1 INTRODUCTION AND LITERATURE

The previous chapter considered the formation of complex sulphides by the hydrothermal reaction of simple sulphides in liquid hydrogen sulphide as solvent. However, as was pointed out in the Introduction to that chapter, some of the sulphides used (In_2S_3 , GeS_2 and SnS_2) were stable in aqueous media with respect to hydrolysis to oxides or oxide species, and therefore the possibility existed of conducting the hydrothermal preparation of complex sulphides from these starting materials in aqueous solution. This approach is described in the present chapter. To avoid any hydrolysis of the sulphides that might occur under the reaction conditions, the basic media required for the hydrothermal preparation were obtained with sodium sulphide rather than sodium hydroxide, the base conventionally used in the preparation of zeolites in hydrothermal systems.

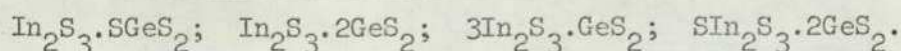
The work described is therefore concerned with the reactions of the sulphides of indium, germanium and tin in aqueous solutions of sodium sulphide. Ideally, this type of reaction should include work conducted in an autoclave, at temperatures above 100°C . This would then be in direct analogy with the formation of zeolites in hydrothermal systems above 100°C and 1 atmosphere pressure. However, zeolites have been formed below 100°C (see Chapter 2), and this type of preparation may then be conducted in open vessels at atmospheric pressure. It may still be described as 'hydrothermal', as the basic experimental concept remains unchanged, only the temperature being reduced.

As it was not wished to interrupt the main experimental programme employing liquid hydrogen sulphide, this phase of the work was conducted wholly at atmospheric pressure, and not in the high pressure equipment. Although it was obviously desirable to extend this approach to higher pressures, it was felt that the use of atmospheric pressure laboratory techniques below 100°C offered the best compromise with the availability of equipment in a preliminary study to characterise the results that may be expected from this type of system.

Only a very limited number of publications relate to this type of system. The three sulphides of interest in the present work (SnS_2 , GeS_2 and In_2S_3) are all reported to dissolve quite readily in aqueous alkaline sulphide solution, with the formation of ternary sulphides, which may be crystallized from solution in various degrees of hydration. This has been discussed in Chapter 2, and the compounds isolated by such techniques detailed. They may be represented (in aqueous solution) as $\text{M}'_x \text{M}''_y \text{S}_z$, where M' = alkali metal, and M'' is Ge, Sn or In. Their preparation presents no difficulty, provided that the alkali metal sulphide is kept in excess, and they may be formed from the halides as well as the sulphides under such conditions. A tendency for NaInS_2 to form polythioindates was observed in polysulphide solution (76). These compounds may be written as $\text{NaIn}(\text{S}_2)_2$, $\text{NaIn}(\text{S}_3)_2$ and $\text{NaIn}(\text{S}_4)_2$. The polysulphides $\text{In}_2(\text{S}_2)_3$, etc were also reported.

The only reports of the formation of complex, insoluble phases from the reaction of the sulphides of a Group III b element with a Group IV b element in aqueous sulphide solution relate to the co-precipitation of gallium sulphide with other sulphides. This process has been described by Sheka, Chaus and Mityureva in their book on the chemistry of gallium (470). Gallium sulphide is precipitated in the pH range of 2 - 3, but may be co-precipitated with the sulphides of certain heavy, non-ferrous metals in more acidic (0.2 N HCl) and alkaline solutions. Also, co-precipitation occurs with the precipitation of aluminium or iron hydroxide. Sulphides with which gallium sulphide was co-precipitated include those of zinc, arsenic and copper. A tendency to form complex phases was also noted. For instance, when gallium was precipitated with iron sulphide, $\text{Ga}(\text{FeS}_2)_3$ was formed. Interaction between gallium ions and sulphide or hydrosulphide ions on the surface of the precipitate, or the formation of solid solutions, were proposed as explanations.

More recently, the co-precipitation of gallium sulphide with the sulphides of indium, bismuth and germanium have been reported (471-473). Co-precipitation in the In_2S_3 - Ga_2S_3 system was attributed to the secondary exchange adsorption leading to the colloidal dispersion of Ga_2S_3 or $\text{Ga}(\text{SH})_3$ throughout the In_2S_3 gell. Co-precipitation was found to be decreased by the presence of Tl^{4+} ions or by increasing H^+ concentration. In the co-precipitation of gallium and germanium sulphides a number of double sulphides were formed:-



The reactivity for the formation of this type of compound increased

in the order $\text{Ga} < \text{In} < \text{Tl}$. A complex phase In_4GeS_6 was formed from InCl_3 and Na_8GeS_6 (475).

Co-precipitation of this type is not confined to sulphides. Analogous co-precipitation of GeO_2 with $\text{In}(\text{OH})_3$ from aqueous solutions of their salts has been reported (474). Formation of indium germanates ($2\text{In}_2\text{O}_3 \cdot \text{GeO}_2 \cdot x\text{H}_2\text{O}$; $\text{In}_2\text{O}_3 \cdot 2\text{GeO}_2 \cdot y\text{H}_2\text{O}$) as the phase precipitated was believed to occur.

The main difference between these precipitations and the type of work described in the present Chapter is the higher pH (ie excess of base) employed in the hydrothermal system. Instead of precipitating sulphides in carefully controlled ratios, in the present work the reaction of the Groups III b and IV c sulphides was examined in an excess of alkaline sulphide solution. The systems employed were chosen to be analogous to those from which zeolites are precipitated. Gallium sulphide was not used in this work in view of its partial hydrolysis in aqueous solution (see Chapter 2).

6.2 EXPERIMENTAL

The germanium, indium and tin sulphides employed, GeS_2 , In_2S_3 and SnS_2 , were prepared by the methods described in Chapter 4. The sodium sulphide used was AR grade $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, supplied by BDH and used without further purification. In view of its deliquescent nature it was weighed out in the dry box, but apart from this all experimental work was conducted on the bench.

6.2.1 Analytical Methods

The precipitates formed from these systems were analysed for their constituent elements. Sulphur was determined by dissolving the material in sodium hydroxide solution, and determining the sodium sulphide formed by reaction with standard iodine. This technique has been described in Chapter 3. Sodium was determined by dissolving the material in dilute hydrochloric acid, and using a flame photometer (see Chapter 5).

Indium, germanium and tin were all determined colourimetrically. The indium determination was derived from data in 'Methods of Quantitative Inorganic Analysis' (476). 25 ml of a solution containing 0.15-1.00 mg indium in dilute HCl were put into a 250 ml separating funnel, and 2.5 ml of pH = 3.5 buffer solution (sodium acetate - acetic acid) added. 5 ml of 0.01 M oxine in chloroform containing 1 per cent ethanol was added, and the mixture was well shaken. The chloroform was run off into a 25 ml volumetric flask, and the aqueous layer extracted with four 5 ml aliquots of chloroform/oxine. The solution was then made up to 25 ml with chloroform, and the optical density measured against a blank determination at 395 mμ, in a 0.5 cm silica cell. The only element of interest interfering with this determination was tin (Sn^{2+}). It was claimed that Sn^{4+} does not interfere.

The germanium determination was obtained from 'Standard Methods of Chemical Analysis' (477). 25 ml of a solution containing 1-5 mg of germanium in dilute acid was neutralised with 5N sodium hydroxide, and AR glacial acetic acid (30 ml) added. It was diluted to 80 ml, and 10 ml of freshly prepared 2.5 per cent ammonium molybdate solution added. The solution was made up to

100 ml with distilled water, and the optical density measured against a blank determination at 440 m μ , in a 4 cm silica cell. None of the other elements of interest in this work was reported to interfere with this determination.

The tin determination employing 'Dithiol' reagent was obtained from Vogel (478, p 800). 10 ml of a solution containing 0.05 - 0.5 mg of tin in dilute acid was added to a 25 ml volumetric flask, and 1 drop of thioglycollic acid, 2.0 ml of concentrated HCl, 0.5 ml of a 1 per cent solution of Teepol in water and 1.0 ml of freshly prepared 'Dithiol' reagent were added. The dithiol reagent was prepared by dissolving 0.1 g of the solid (obtained from BDH) in 2.5 ml of 5 M NaOH solution, adding 0.5 ml of thioglycollic acid and making up to 50 ml with distilled water. When the 'Dithiol' had been added to the tin determination, the mixture was placed in a water bath at 60°C for 10 minutes while the characteristic red colour of the complex developed. The solution was then cooled to room temperature, made up to 25 ml and the optical density measured at 545 m μ against a blank determination in a 1 cm silica cell.

The optical densities in these three determinations were measured in a Unicam SP 600 spectrophotometer. The instrument was calibrated with standard solutions of indium chloride dissolved in dilute HCl, germanium disulphide dissolved in ammonia and AR hydrated stannic chloride, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, dissolved in dilute HCl. Graphs of concentration versus optical density under the standard determination conditions were prepared.

6.2.2 Reactions

Experiment 6.1

This experiment formed an initial assessment of this type of system. The interaction of the thiostannate and thioindate ions in sodium sulphide solution was investigated.

Initially, a solution of each of the metal sulphides in sodium sulphide solution was prepared by dissolving 1 g of SnS_2 and 1 g of In_2S_3 each in 10 g of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in 100 ml of distilled water. The stannic sulphide dissolved readily on warming to give a clear, colourless solution. The indium sulphide dissolved on boiling to give a clear, pale orange solution. The two solutions were mixed cold and brought to the boil. No visible reaction occurred except a slight darkening in colour. The mixture was boiled gently for 6 hours, but without any further change in appearance or formation of a precipitate. The pH of the solution was 14.0, measured with an EIL vibret meter calibrated with 0.05 M potassium hydrogen phthalate ($\text{pH} = 4.005$) and 0.05 M borax ($\text{pH} = 9.180$) at 25°C .

By direct comparison with the formation of zeolites, it might be inferred that this pH is too high due to the large excess of base used, and therefore the experiment was repeated under conditions of lower pH. A 1:1 mole ratio of In_2S_3 : SnS_2 was used with a minimal excess of the sodium sulphide base.

In_2S_3 (1.79 g) and SnS_2 (1.00 g) were placed in about 100 ml of distilled water, and 1.0 g of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ added. The mixture was brought to the boil, and further sodium sulphide

added until the indium and tin sulphides had just dissolved. About 10.0 g were used. In this way a large excess of base was avoided. However, the pH of the resulting solution was still about 14.0, and no precipitation or other reaction was observed on mixing and boiling.

Experiment 6.2

In an attempt to investigate the pH range in which the ternary sulphides of indium and tin remain in solution, and thereby obtain information as to the minimum pH at which this type of reaction may be conducted, a mixture of their solutions was titrated against hydrochloric acid, and the pH at which the various phases precipitated recorded.

A similar starting mixture to that used in the previous experiment was employed, 1.79 g In_2S_3 and 1.00 g SnS_2 being dissolved in the minimum necessary volume of sodium sulphide solution. 1.0 N hydrochloric acid was then added dropwise, and the pH monitored as the various precipitates formed. This data is included in Table 6.1.

Precipitates II and III were taken to be indium and tin sulphides respectively by their characteristic colours. Precipitate I was shown by qualitative analysis to be a ternary sulphide of sodium and tin. It was checked for the characteristic blue flame test for indium, but none was detected. It dissolved in dilute hydrochloric acid with liberation of hydrogen sulphide. The solution was made alkaline with ammonia. A white precipitate was formed which was shown to contain tin by dissolving it in dilute hydrochloric acid and precipitating

pH	Observation
14.0	Starting pH. Pale orange solution.
12.0	Solution becoming chrome yellow.
11.0	Cloudiness developing. Flocculent white precipitate appeared on standing. Filtered- Ppt. I.
10.0	No further precipitation.
9.0	Flocculent yellow precipitate formed. Filtered- Ppt. II.
8.0	Cloudiness developing. Colour becoming orange.
7.0	Flocculent pale brown precipitate formed. Filtered. Ppt. III.
0.0	Solution colourless. No further reaction.

Table 6.1 Reaction of In_2S_3 and SnS_2 in sodium sulphide solution, with dilute hydrochloric acid. (Experiment 6.2).

pH	Observation
12.7	Starting pH.
12.0	White precipitate forming.
11.3	Precipitation complete. Filtered. Ppt. I.
10.1	Solution becoming cloudy. Green Colour.
9.2	White Precipitate. Filtered. Ppt. II.
8.1	Yellow precipitate. Filtered. Ppt. III.
8.0	Solution colourless.
7.7	Solution becoming cloudy.
6.5	Yellow precipitate formed. Filtered. Ppt. IV
0.0	Solution colourless. No further reaction.

Table 6.2 Reaction of In_2S_3 and SnS_2 in sodium sulphide solution, with dilute hydrochloric acid. (Experiment 6.3).

pH	Observation
12.9	Starting pH.
12.8	Becoming pale green in colour.
12.3	White precipitate forming.
12.0	Precipitation complete. Filtered. Ppt. I.
11.0	Solution becoming cloudy. Green in colour.
10.5	White precipitate formed. Ppt. II.
9.0	Precipitate redissolving.
8.2	Clear green solution.
5.9	Solution becoming cloudy.
2.8	White precipitate formed. Filtered. Ppt. III.
0.0	Solution colourless. No further reaction.

Table 6.3 Reaction of In_2S_3 and GeS_2 in sodium sulphide solution, with dilute hydrochloric acid. (Experiment 6.4).

the dark yellow precipitate of stannic sulphide with H_2S , which dissolved in excess acid. The ammonia solution was shown to contain sodium by evaporating it to dryness and heating to remove ammonium salts, dissolving it in water and reacting the solution with zinc uranyl acetate to form the yellow crystalline precipitate characteristic of sodium.

It seemed therefore that the pH that could be used under these conditions was limited by the solubility of the sodium-tin ternary sulphide, which was not stable in solutions more acid than pH 12. No evidence for the precipitation of a more complex phase than the binary and ternary sulphides was obtained.

Experiments 6.3 and 6.4

Having established that reaction of the sulphides of tin and indium in sodium sulphide solution should be possible in a solution no more alkaline than pH 12, the above reaction was repeated in the presence of the minimal quantities of sodium sulphide (Experiment 6.3). A similar reaction was conducted in parallel in which the sulphide of germanium (GeS_2) was used in place of stannic sulphide (Experiment 6.4).

A typical composition for a zeolite starting mixture transcribed to the sulphur system would be (see Chapter 5):-

	$\text{Na}_2\text{S} \cdot \text{H}_2\text{O} : \text{In}_2\text{S}_3 : \text{SnS}_2$		
	1.58	0.35	0.70 mole/l
	379	114	127 g/l
	3.20	0.96	1.06 g/8.5 ml
and	$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O} : \text{In}_2\text{S}_3 : \text{GeS}_2$		
	1.58	0.35	0.70 mole/l
	379	114	136 g/l
	3.20	0.96	1.15 g/8.5 ml

It was attempted to prepare solutions of the GeS_2 , SnS_2 and In_2S_3 in the theoretical amounts of sodium sulphide. Whilst no difficulty was encountered in dissolving the SnS_2 and GeS_2 in 1.0 g of sodium sulphide in 20 ml of water each, it was not found to be possible to dissolve the 1.92 g of In_2S_3 required for the two experiments in the remaining amount of sodium sulphide (4.4 g, dissolved in 25 ml water). It initially dissolved readily if the sodium sulphide solution was boiled and the In_2S_3 (ground to a fine powder) slowly added, but the ternary sulphide apparently became saturated in solution, and precipitated out before the whole of the In_2S_3 was added. This precipitation was only redissolved when further sodium sulphide was added. It was found to be necessary to use 15 g of sodium sulphide to keep the 1.92 g of In_2S_3 in solution in 20 ml of water.

The pH of the three ternary sulphide solutions was measured:-

In/Na	pH = 13.2
Sn/Na	pH = 9.5
Ge/Na	pH = 10.5

The solution of the indium ternary sulphide was divided in two, and mixed with the solutions of tin and germanium sulphides. Both the Sn-In and the Ge-In solutions were green at this stage. They were boiled vigorously for several hours, their volume being maintained at 20 ml with distilled water. The colour of both solutions gradually became yellow, and finally orange-red, but no precipitation occurred. The solutions were

cooled to room temperature and left standing overnight. No further changes were noted, so the two solutions were gradually acidified with $N HCl$, as in the previous experiment. The observations made are included in Tables 6.2 and 6.3.

In the Indium - tin reaction (Experiment (6.3), four separate precipitates were obtained, two of them occurring at very close pH values (9.20 and 8.10 respectively), and not being completely separated. It is apparent that the smaller amount of sodium sulphide used had resulted in different precipitation characteristics in this experiment compared to Experiment 6.2 (see Table 6.1). The white precipitate found in the present experiment at pH 9.20 was not found in the earlier reaction. The present reaction had therefore yielded two yellow precipitates (III and IV), probably attributed to indium and tin sulphides respectively, as in the previous reaction. It also yielded two colourless precipitates (I and II), probably attributed to the ternary sulphides of indium and tin with sodium. Precipitate II could not be separated from the precipitate of indium sulphide (III).

The precipitate I was filtered off, washed with distilled water and dried. It was analysed for indium, tin, sodium and sulphur in case it should contain any more complex phase than the ternary sulphide.

Found: Na, 11.62, 11.47; S, 32.00, 35.79; In, 51.98; Sn, 3.36%

— Calculated for $NaInS_2$; Na, 11.4; S, 31.7; In, 56.9%

Precipitate I therefore appeared to be the ternary sulphide of sodium and indium with a small amount of tin present. Complex phase formation in this reaction was therefore precluded. Precipitate II was probably the ternary sulphide of tin and sodium. It is interesting to note that with the larger excess of sodium sulphide employed in Experiment 6.2, the Na-Sn sulphide precipitated at higher pH than the Na-In sulphide,

which is the reverse order to that found in the present reaction.

In the indium-germanium reaction (Experiment 6.4), only three precipitates were formed, and the second redissolved almost as soon as it was formed. The first precipitate (which appeared at about the same pH as the first precipitate in the In-Sn reaction) was separated and analysed for indium, germanium, sodium and sulphur in case it contained any complex phases.

Found: Na, 10.38, 10.36; S, 58.35; In, 34.04%. Ge, None detected.

Calculated for $\text{Na}_3\text{In}_2\text{S}_{12}$: Na, 10.09; S, 56.30; In, 33.61%

for $\text{NaIn}(\text{S}_3)_2$: Na, 6.96; S, 58.26; In, 34.78%.

The analysis is very different to that of the first precipitate formed in the In-Sn system, which corresponded fairly closely with NaInS_2 . The analysis of the present material corresponds most nearly with $\text{Na}_3\text{In}_2\text{S}_{12}$, but is in approximate agreement with $\text{NaIn}(\text{S}_3)_2$, a polysulphide reported to be formed in this type of system (76). It seemed that considerable supersaturation of the sodium indium ternary sulphide could occur, and the particular phase that precipitated depended on the particular conditions. Considerable variation in composition was indicated by the difficulty experienced in obtaining three separate samples for the sodium, indium and tin analyses which would give a total composition of 100 per cent.

The absence of any germanium in the precipitate ruled out the possibility of complex phase formation. Precipitate I appeared to be a sodium-indium ternary sulphide, precipitate II was probably a sodium-germanium ternary phase, while precipitate III, which existed in acid conditions was probably GeS_2 . Apparently no indium sulphide was obtained under the conditions of this experiment.

Experiments 6.5 and 6.6

These experiments constituted a repetition of Experiments 6.3 and 6.4, with further effort to reduce the excess of sodium sulphide to more nearly the level equivalent to the sodium hydroxide used in typical zeolite preparations. It was felt that the highly basic media employed were probably a contributory factor in the failure to precipitate any complex phases analogous to thiozeolites.

Freshly prepared indium sulphide was used in an attempt to promote its solubility. 1.35 g of indium metal were dissolved in 50 per cent HCl and evaporated to dryness. In_2S_3 was precipitated by dissolving this chloride in buffer solution and saturating with hydrogen sulphide (Section 4.3.5). The In_2S_3 was centrifuged off and washed with distilled water.

1.35 g of indium when converted to its sulphide (1.92 g) require 1.42 g of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ to form NaInS_2 . This represents the minimum quantity of sodium sulphide needed to form the ternary phase. Any further addition will merely increase the basicity of the solution. For the zeolite preparation being attempted a 1.5 times molar excess of base was required (see Experiment 6.3).

Sodium sulphide was added to the indium sulphide suspended in 25 ml of boiling water until the solid dissolved. 4.5 g were required (cf 15 g in previous experiment). A dark green solution was obtained, with a pH of 13.5. There was still an undesirable excess of base present, but this seemed inevitable in view of the difficulties experienced in dissolving the indium sulphide. The neutralization experiments conducted previously had indicated that the ternary sulphide should be stable in solution of pH 12 or above.

To avoid adding any further sodium sulphide to the mixture, the solution of indium sulphide was divided in two, and the SnS_2 (1.06 g) and GeS_2 (1.15 g) were added directly to each portion (Experiment 6.5 and Experiment 6.6 respectively). These sulphides readily dissolved, and on boiling a white precipitate formed in each case. The flasks were stoppered and kept in an oven at 80°C for 1 week, with frequent stirring to promote crystallisation. At the end of this time, the precipitates were filtered off and washed with water. They were then dried under vacuum, and x-ray powder patterns and elemental analyses obtained.

The x-ray powder diffraction pattern (Figure 6.1; Appendix A5) indicated that the materials were practically non-crystalline. The elemental analyses were as follows:-

Product from Experiment 6.5,

Found: Na, 9.80; In, 37.40; Sn, 10.10; S, 42.16 per cent.

Product from Experiment 6.6,

Found: Na, 11.00; In, 47.70; Ge 2.20; S, 31.21 per cent.

In the tin-indium system (Experiment 6.5), the bulk of the material appeared to be the ternary sulphide of sodium and indium, but the analysis did not correspond to NaInS_2 , 10.1 per cent w/w of tin being present. The non-crystalline nature of the materials precluded formation of a complex (zeolitic) phase, and some form of co-precipitation seemed likely. The analysis corresponded most closely to $\text{Na}_5\text{In}_4\text{SnS}_{15}$, and probably represents a mixture of NaInS_2 with ternary sulphides of tin and sodium. The high sulphur content indicated that some oxidation to polysulphide or free sulphur occurred.

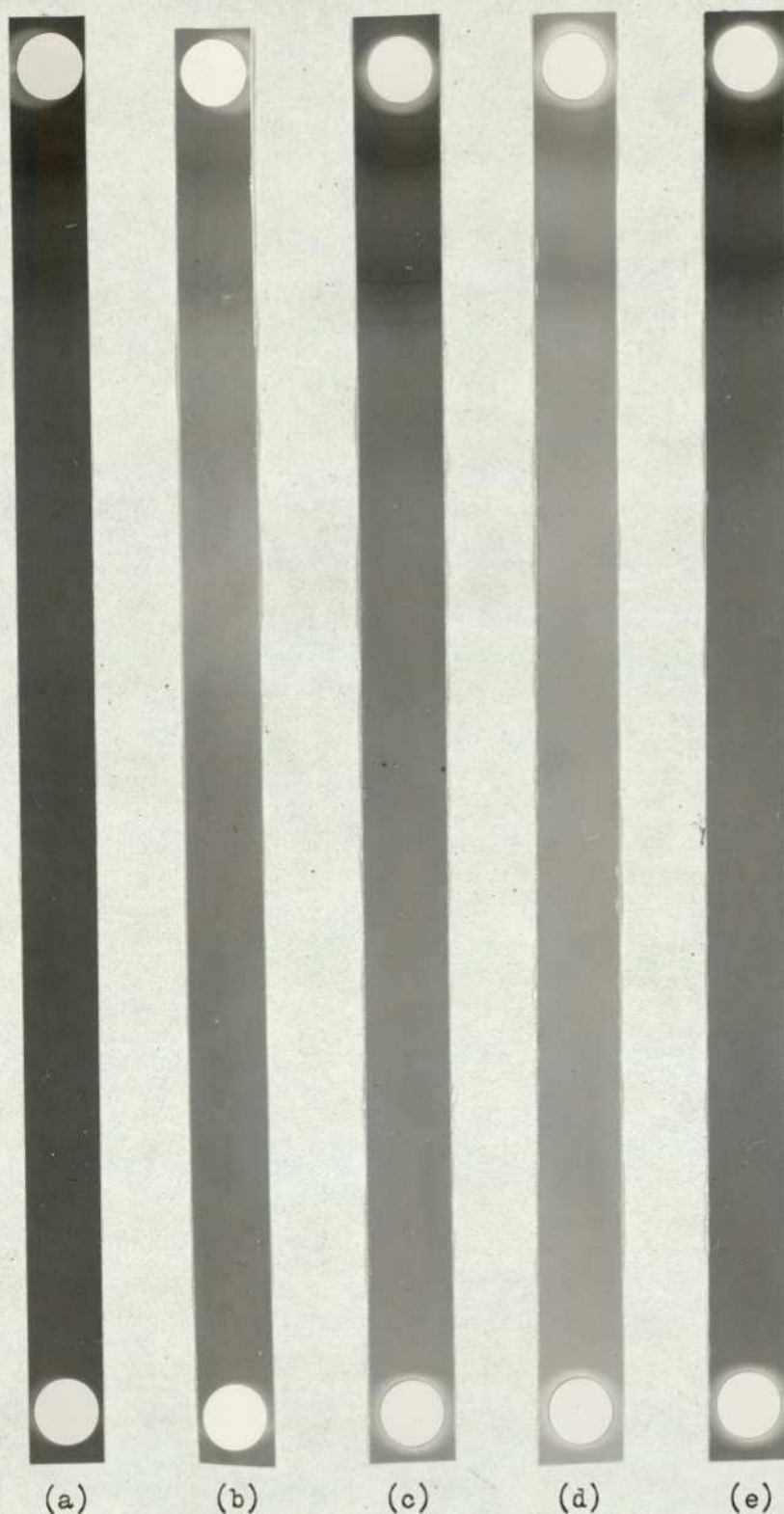


Fig. 6.1 X-Ray Powder Patterns of the Solid Products isolated from the Reactions of In_2S_3 , GeS_2 and SnS_2 in Aqueous Solutions of Na_2S .

- (a) Experiment 6.5.
- (b) Experiment 6.6.
- (c) Experiment 6.7.
- (d) Experiment 6.8; Powder Phase.
- (e) Experiment 6.8; 'Crystalline' Phase.

Copper $\text{K}\alpha$ Radiation.

Only a trace of germanium was detected in the product from the germanium-indium system (Experiment 6.6), the bulk of the material appearing to be the ternary sulphide of sodium and indium. However, the analysis did not correspond completely to NaInS_2 (Reqd, Na, 11.4; In, 56.9; S, 31.7 per cent). The deficit in the analysis showed that partial hydrolysis had occurred with the longer reaction period. The lack of crystallinity precluded the formation of new phases analogous to zeolites, and this was confirmed by the low level of germanium present.

It therefore seemed that in spite of the reduced amount of sodium sulphide used in these experiments, no tendency to form complex phases had been found. Reduction of the pH had merely led to the precipitation of the ternary sulphide of indium, albeit contaminated with a small amount of tin or germanium. No crystallinity had developed in spite of the prolonged reaction time allowed, the products being essentially x-ray amorphous.

Experiments 6.7 and 6.8

These experiments used similar reaction mixtures and conditions to 6.5 and 6.6, with the addition of about 5 per cent 13X zeolite in each case to promote crystallization of the required type. It was hoped that the zeolite would seed the mixture. The reaction mixture was prepared as in the previous experiments, the only variation besides the zeolite addition being an increase in the amount of sodium sulphide used from 4.5 g to 8 g, in an attempt to prevent precipitation of the sodium-indium sulphide. The pH of the solution was similar, being 13.5.

The two reaction mixtures were boiled and placed in an oven at 80°C for 1 week. No precipitation occurred initially in either

case, but after about 24 hours a white precipitate slowly formed from the germanium-indium reaction (Experiment 6.8). The solution was coloured green. The tin-indium reaction (Experiment 6.7) remained clear, being light brown in colour, and free from any precipitate. On removing the flasks from the oven and allowing them to cool to room temperature, a precipitate appeared in the tin-indium system. The remaining solution was green, being similar in appearance to that of the germanium-indium system. The mixtures were kept at room temperature for a further two weeks, with constant stirring, to aid crystallization.

At the end of this time the solids were filtered off, washed with water and dried under vacuum. The tin-indium product was a very pale green powder (Yield = 0.45 g). The germanium-indium product was also pale green in colour, but appeared to be composed of a mixture of a powder and a crystalline material (Yield = 1.11 g).

X-ray powder patterns were obtained of the tin-indium product (Experiment 6.7) and of the two phases of the germanium-indium product (Experiment 6.8) which were separated under a microscope (X50). All the samples were practically non-crystalline, (Figure 6.1, Appendix A5), only the tin-indium product possessing very slight crystallinity. The diffraction lines observed were similar, but not identical, to those found in 13X zeolite. Accurate assignment was not possible in view of the very weak diffractions found, but the possibility of the formation of a new phase did exist. Crystallization can only have been very limited, however. Elemental analyses were performed as in the previous experiments:

Product from Experiment 6.7:

Found: Na, 11.12; In, 50.70; S, 29.42 per cent; Sn not detectable.

Product from Experiment 6.8:

Found: Na, 9.86; In, 33.40; Ge, 1.18; S, 30.22 per cent.

Calculated for NaInS_2 : Na, 11.4; In, 56.9; S, 31.7 per cent. Once again, the predominant phase in each case appeared to be a ternary sulphide of indium and sodium, although the indium content was lower than that required for NaInS_2 . As in the previous experiments (6.5 and 6.6) it is possible that the extended reaction period had led to a certain amount of hydrolysis, as the analysis does not total 100 per cent. In any case, the presence of molecular sieve will cause an inaccuracy in the analysis.

The overall conclusion was that, as in the previous experiments, only very little formation of complex sulphides or crystallization had occurred, the main product obtained being the ternary sulphide of indium and sodium, which had precipitated from solution as a result of its limited solubility under the experimental conditions used. Only a trace of the Group IV element was detected in the product, this probably being due to co-precipitation or formation of insoluble GeO_2 .

6.3 CONCLUSIONS

No formation of complex sulphides was found in an examination of the reaction of indium sulphide with germanium or tin sulphide in aqueous sodium sulphide solution. In spite of the variety of reaction conditions used, the ternary sulphides formed in these systems did not interact to form any insoluble phases that could be described as analogues of zeolites.

One limiting factor was undoubtedly the tendency of the ternary sulphide of indium and sodium to precipitate from solution if a large excess of base were not used. This was in contrast to the sulphides of tin and germanium, which dissolved readily and remained in solution as long as the pH did not fall below about 10.0. The

formation of polysulphides was suggested by some of the analyses obtained for the indium-sodium ternary sulphide, and phases such as $\text{NaIn}(\text{S}_x)_2$ were suggested. This is certainly consistent with the supersaturation and sudden precipitation found in this system. The green colour found in many of the solutions suggested formation of sulphur radicals or ions of the type discussed in Chapter 2, and this system has the appearance of being considerably more complex than the oxide systems from which zeolites are precipitated.

Undoubtedly, the excess of sodium sulphide added played an important part on the nature of the reactions occurring. When the mixtures were neutralised with dilute acid, both the ternary-sulphides and the binary sulphides were formed, suggesting that the complex ion formation in solution was limited by the amount of base initially present. However, reduction in the amount of sodium sulphide added did not encourage the formation of complex sulphides; the only effect noted was the precipitation of the sodium-indium ternary phase. Whether this was a limiting factor in preventing the pH of the solution being reduced to the region where precipitation of complex phases might occur is not known. There is no evidence to suggest that the formation of such phases in this type of system is possible.

The very low concentration of the Group IVb element found in some of the precipitates is probably due to co-precipitation (or in the case of germanium to hydrolysis to form insoluble germanium dioxide). The longer reaction periods latterly employed had apparently resulted in a certain amount of hydrolysis.

Although materials such as In_4GeS_6 have been reported (see the Introduction), no compounds of this type were found in the

present work. They are only reported to be formed under more acidic conditions. No crystalline phases were found, and the use of 13X zeolite as seeding agent did not encourage any appreciable crystallization.

The overall conclusions were therefore the same as those reached from the reactions conducted in liquid hydrogen sulphide (Chapter 5). Solution of the Group IIIb and IVb sulphides in the form of ternary sulphides with the base occurred quite readily, but interaction of these ternary sulphides in solution to produce insoluble complex phases has not been found. A comparatively large range of experimental conditions was investigated below 100°C, and the lack of any complex sulphide formation under any of these conditions therefore seems to reflect a basic difference between the sulphide and oxide system in this context, too large to be overcome within the limitations of the approaches adopted.

CHAPTER 7. FURTHER CHARACTERIZATION OF THE REACTION PRODUCTS

7.1 INTRODUCTION AND LITERATURE

The preparative work described in the earlier chapters was concerned with the formation of sulphides with structures analogous to the aluminosilicates, especially zeolites. The latter materials have unique and valuable properties, most of which are concerned with their large surface areas and catalytic activity. Although the results obtained from the preparative studies conducted in the various sulphide systems had not indicated the formation of any complex, crystalline phases that could be considered as analogues of the crystalline aluminosilicates, it was nevertheless thought worthwhile to obtain a measure of the surface area and catalytic activity of the materials obtained. This enabled a more complete characterization of the reaction products to be obtained and formed a further search for areas of analogy between the oxide and sulphide systems.

7.1.1 Surface Area Measurements

An examination of the properties of zeolites (60) reveals a surface area (measured by nitrogen adsorption) of several hundred metre squared per gram, besides the high (and selective) adsorptive capacity for larger molecules. The weight increase of a zeolite can be as much as 50 per cent when the pores become filled with molecules able to penetrate into the structure. Furthermore, by obtaining a measurement of the relative adsorptive capacity for molecules of graded size, a measure of the cross sectional size of the various channels and voids in the zeolite structure can be obtained.

Therefore, the first requirement was a measurement of the total surface area of the reaction products by nitrogen adsorption. Any materials possessing comparatively high surface areas would then be suitable for further examination by means of the selective adsorption of various molecules of larger size. The techniques of surface area measurement by nitrogen adsorption have been reviewed by Emmett (479), and more recently by Innes (480). A more general discussion of adsorption has been given by deBoer (407). The adsorption is normally conducted at liquid nitrogen temperature, and may be measured by either volumetric or gravimetric techniques. Volumetric techniques rely on monitoring the volume of gas that is adsorbed by the adsorbent, while gravimetric techniques measure the weight change of the adsorbent as adsorption takes place. Gravimetric methods are generally quicker, and lend themselves to automation. However, temperature control of the sample is less reliable as it is suspended in a balance pan, and not in direct contact with the walls of the equipment.

An ideal adsorption isotherm is shown in Figure 7.1 (Brunauer Type II for multilayer adsorption (365)). The initial sharp rise in gas adsorbed with increasing pressure is attributed to the filling of the first monolayer. There then follows a point of inflection (generally termed Point B), above which a long, linear part of the isotherm is regarded as representing the filling of the second layer of adsorbed gas. The Point B therefore offers a measure of the quantity of gas required to form a monolayer,

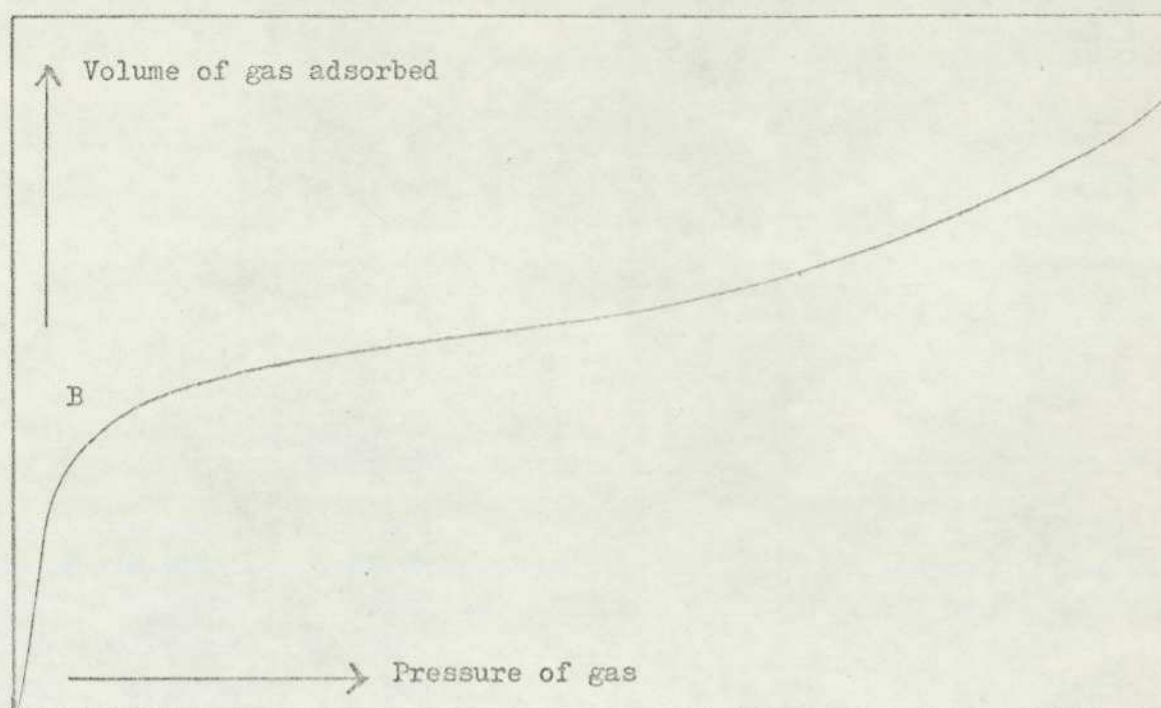


Fig. 7.1 Ideal adsorption isotherm for determination of surface area.

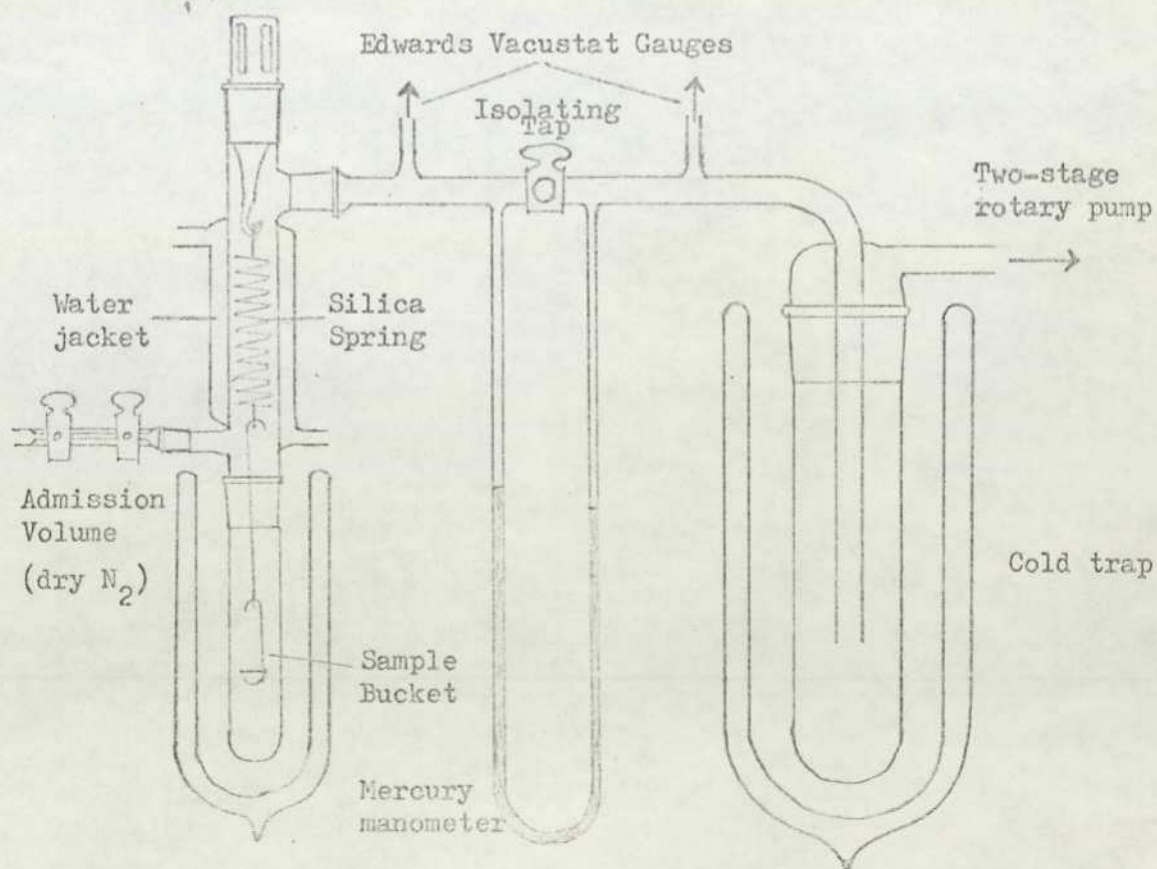


Fig. 7.2 Microbalance for surface area measurements.

but in many real systems the curves obtained are so far removed from the ideal that identification of the Point B becomes impossible.

To overcome this, the Brunauer-Emmett-Teller equation was developed (BET method):-

$$\frac{\rho}{V(\rho_0 - \rho)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \cdot \frac{\rho}{\rho_0}$$

where ρ = volume of gas adsorbed

ρ_0 = vapour pressure of liquid adsorbed

V = volume of gas adsorbed

V_m = volume of gas adsorbed at monolayer

C = constant

This equation was derived from a consideration of multilayer physical adsorption, and a plot of $\frac{\rho}{V(\rho_0 - \rho)}$ versus $\frac{\rho}{\rho_0}$ gives a straight line with slope $\frac{C-1}{V_m C}$ and intercept $\frac{1}{V_m C}$. Thus a measure of V_m , the volume of gas required to form a monolayer, may be obtained, and from this the surface area of the adsorbent can be found from the known molecular diameter of the adsorbate, assuming close packing in the unimolecular layer.

When this technique is employed for the determination of surface area by nitrogen adsorption at liquid nitrogen temperature, the vapour pressure of the liquid adsorbate (ρ_0) becomes equal to atmospheric pressure. The adsorption isotherm (Figure 7.1) is generally plotted as the volume (or weight) of adsorbate per unit mass of adsorbent versus ρ/ρ_0 , the reduced pressure. Similarly, the BET plot may be in terms of the weight rather than the volume of gas adsorbed. The surface area of the adsorbent is generally presented as the specific surface (S), expressed as metre squared per gram.

The surface area measurements made in the present work used both the Point B and BET methods of estimating the quantity of nitrogen required to form a monolayer. A gravimetric technique was employed; the specific surface of the adsorbate was estimated from the following relationship:-

$$S = \frac{x_m}{M} \cdot N \cdot A \text{ m}^2/\text{g}$$

where x_m = weight of N_2 to form a monolayer (g/g)

M = molecular weight of nitrogen

N = Avagadro's number = $6.023 \cdot 10^{23}$

A = area of nitrogen molecule = $16.2 \text{ (\AA)}^2$
 $= 16.2 \cdot 10^{-20} \text{ m}^2$

The BET monolayer capacity is of doubtful validity unless the isotherm exhibits a well-defined Point B. It is generally regarded nowadays that the BET measure of surface area has little meaning for porous adsorbents, where micropore filling and capillary condensation in mesopores can cause gross deviations from the ideal isotherms. Much effort has been applied in recent years to overcome these deficiencies, and one of the most significant approaches has been the t-plot of Lippens and deBoer (481-497). Information about the specific surface area, size and shapes of pores, reversible capillary condensation and pore filling may be obtained by plotting the experimental volumes of adsorbed nitrogen as a function of the statistical (average) thickness of the adsorbed layer, (t). This method was extended into a system of complete pore structure analysis by Braunuer (498-501), and the surface

area of microporous adsorbants has also been considered by Dubinin (502-504), Bering et al (505-506) and Dollimore and Heal (507). This is a widely developing subject, but in view of the nature of the materials obtained in the present work, it was felt that the standard BET approach would yield adequate accuracy for the purpose required.

7.1.2 Catalytic Activity Measurements

The object behind the catalytic tests carried out on the sulphides prepared was an examination for common features with the catalytic properties of aluminosilicates. The catalytic activity observed must therefore be correlated with the known activity of both aluminosilicates and sulphides.

It would be inappropriate to attempt to review here the very extensive field of aluminosilicate catalysis. Such materials are widely used either as catalysts in their own right, or alternatively as supports for metallic catalysts. The acid nature of the surfaces of aluminosilicates gives them activity for the catalysis of reactions such as cracking and isomerization of hydrocarbons. When these properties are combined with the well defined structural geometry of zeolites, then valuable selective catalysts result. The nature of zeolites and their properties are discussed in Chapter 2 (2.1.4.1). Many reviews have appeared on the catalytic properties of these materials, especially useful being those of Turkevich (508-511), Venuto and Landis (512), Riekert (513) and Weisz (514). Reactions catalysed include cracking, hydrogenation, dehydrogenation, isomerization, polymerization, cyclization, etc. Reactions such

as the oxidation of hydrogen sulphide and the sulphurization of carbon monoxide have been discussed in Chapter 3. It is a noteworthy factor that for reactions such as cracking, zeolites possess activities up to 10 000 times greater than high surface area silica-alumina.

A reaction associated with oxide catalysts is that of catalytic reforming. This process aimed at converting low octane hydrocarbons to olefins and aromatic hydrocarbons of high octane number. Although this type of reaction is invariably conducted over supported metal catalysts nowadays, it was initially developed using hydrogenation-dehydrogenation catalysts such as molybdenum and chromium oxides (515). One of the principal reactions in this process is the cyclization and aromatization of hydrocarbons (516), and the high catalytic activity for this reaction (in the conversion of *n*-hexane to benzene) found in tellurium doped zeolites described in Chapter 3. Also described were the general catalytic properties of sulphided zeolites and ultramarines with especial reference to the work of Dudzik. Such materials were found to have high catalytic activity for reactions such as dehydrogenation, cracking and hydrodesulphurization. This activity was attributed to the presence of sulphur radicals in the aluminosilicate lattice. Improvements to catalyst activity and selectivity by means of sulphiding was also briefly discussed in Chapter 3. There have been a great many reports and patents relating to this type of treatment.

Isomerization of hydrocarbons, a reaction generally associated with acid catalysts, has been found to occur not only on alumina, silica and aluminosilicates, but also on many other oxides, and also on certain sulphides. The subject has been

reviewed by Condon (517). Molybdenum sulphide and molybdenum sulphide-cobalt sulphide catalysts have shown activity for the isomerisation of straight chain paraffins, the conversion of cyclohexane to methylcyclopentane, and several other similar reactions.

One of the principal uses of sulphides as catalysts is in the hydrodesulphurization reaction. This has been reviewed by McKinley (518) and by Schuman and Shalit (519). The catalyst used is almost invariably a sulphided mixture of cobalt and molybdenum or nickel and molybdenum, supported on alumina. However, other catalysts have been used, and included are tungsten and nickel sulphides, ferrous sulphide and sulphided platinum or palladium reforming catalysts. The exchange reactions between deuterium and hydrogen, methyl mercaptan, ethyl mercaptan and thiophen on molybdenum and tungsten disulphides (522-525) demonstrated the activity of the sulphide catalysts for the activation of the H-S, H-C and H-H bonds. It is interesting to note that paramagnetic sulphur in the form of chains of atoms with an unpaired electron at either end has been found on sulphided molybdena-alumina catalysts(526), analogous to the species detected by Dudzik in sulphided zeolites (see Chapter 3).

Supported nickel sulphide has received widespread use as a hydrogenation-dehydrogenation catalyst (520), owing to many favourable properties, including low cracking activity and resistance to poisoning by sulphur. The partial sulphiding of supported nickel catalysts has been found to lead to very useful selective hydrogenation catalysts (521).

Many types of reaction have been reported as being catalysed by metal sulphides, and the following should be mentioned. The formation of thiols by the reductive thiolation of aldehydes occurs over the sulphides of cobalt, molybdenum or nickel (527). The sulphides of copper, nickel and cadmium have proved effective for the decomposition of ethyl mercaptan to ethylene and hydrogen sulphide (528). Patents relate to the oxidation of hydrogen sulphide by oxygen, carbon monoxide or carbon dioxide over supported catalysts consisting of an alkali sulphide with a sulphide of nickel, cobalt, manganese, cadmium, tin or aluminium (529). The supported oxide or sulphide of aluminium, cobalt, iron, molybdenum or nickel has been found to catalyse the conversion of dibenzyl to toluene (530). Finally, the acidity and catalytic activity of zinc sulphide for the isomerisation of cis-2-butene was investigated (531). It was found that zinc sulphide showed a loss of surface area due to sintering at 500°C; this could be retarded by doping with Al^{3+} on Ga^{3+} . The concentration of acid sites on pure zinc sulphide was found to be similar to that on the silica aluminas and zeolites.

The reactions examined in the present work were (i) the isomerization of 4 methyl pentene-1, (ii) the dehydrocyclization of n-hexane. The first reaction was intended to show the presence of acid sites on the catalyst surface, a characteristic feature of aluminosilicates, which, as has been indicated above, is also found on some sulphides. The reaction represented by (ii) is commonly associated with mixed oxides, although it is more commonly carried out over supported metals nowadays. It is

of especial relevance to the present work in view of the very high activity and selectivity of tellurium doped zeolites for this reaction.

7.2 EXPERIMENTAL

7.2.1 Surface Area Measurements

7.2.1.1 Description of Apparatus

This was a simple McBain balance constructed in the laboratory (Figure 7.2). A two stage rotary pump was used, which with a liquid nitrogen trap gave a pressure in the system of less than 1.10^{-3} Torr. The backing pressure was measured by means of an Edwards' Vacustat gauge, and the balance pressure was measured with a differential mercury manometer (above 10 Torr) and with a second Vacustat below this pressure. The silica spring was thermostatted at 25°C , and the sample area could be either cooled with a liquid nitrogen bath or heated with a tube furnace for sample outgassing. The sample was contained in a pyrex bucket. Nitrogen (BOC oxygen free grade, passed through a molecular sieve drying tower) was admitted via a two valve system to enable small volumes to be admitted in a controlled manner. A travelling telescope was used to measure the spring extension.

The method of operating the balance was as follows:-
The sample was placed in the bucket and the system pumped down. The sample was then heated if outgassing was required, its temperature being taken as that of the furnace. The sample tube was then cooled in liquid nitrogen, and the isolating tap closed. The sample zero position was recorded with the travelling telescope, and then change in reading with progressive nitrogen admissions noted. The method of admitting nitrogen was to open and close the valve on the supply side so as to fill the

admission volume, and then to open the valve on the balance side to let the gas dose into the system. The system was finally let up to atmospheric pressure with nitrogen and the sample removed. The barometric pressure at the time of the experiment was recorded. The zero position for the spring with the bucket empty was checked before the commencement of each experiment, and in this way the weight of sample used was known. The development of electrostatic charges on the sample during the experiments caused risk of loss through scattering. This was overcome by lightly compressing the more finely divided materials, and the use of a radioactive source to remove this charging effect was not required.

The silica spring was calibrated with analytical weights up to 150 mg. The sensitivity over this range was 21.7837 cm/g, obtained from a graph of extension versus weight. The smallest extension that could be measured was 0.002 cm; this corresponded to 0.1 mg weight change in the sample. The sample size was about 100 mg, and therefore the absolute sensitivity of the balance was about 0.1 per cent w/w.

A test was conducted on active charcoal, which had been previously checked by the manufacturers and found to have a specific surface of $65 \text{ m}^2/\text{g}$. It was activated at 150°C for 15 minutes, after which time no further weight change was recorded. The tabulated results for this and the subsequent determinations are presented in Appendix A7. The weight uptake versus P/P_0 and BET $P/(P_0 - P)_x$ versus P/P_0 graphs are illustrated in Figures 7.3 and 7.4. Good agreement was observed between both the BET and 'Point B' estimation of the quantity of nitrogen required to form a monolayer, and the adsorption isotherm (Figure 7.3) was very similar to the

ideal isotherm illustrated in Figure 7.1. The specific surface area obtained from these results was an average of $82 \text{ m}^2/\text{g}$; this is slightly higher than the manufacturers value, but is in agreement with an independent determination made in the university on a Cahn micro-balance ($80 \text{ m}^2/\text{g}$).

The minimum specific surface area that could be determined with the equipment with any degree of accuracy can be assessed by using the minimum detectable weight change in the specific surface calculation. Assuming a 100 mg sample, this becomes 1.10^{-3} g/g

$$\text{Then } S = \frac{1.0 \times 10^{-3} \times 6.023 \times 16.2 \times 10^{23} \times 10^{-20}}{28} = 3.49 \text{ m}^2/\text{g}$$

Thus, ready discrimination between low surface area sulphides or oxides ($10\text{-}20 \text{ m}^2/\text{g}$) and the higher surface area zeolites and related materials (over $100 \text{ m}^2/\text{g}$) was possible.

7.2.1.2 Measurements made

Surface area determinations were conducted on the water washed products from Experiments 5.10, 5.11, 5.12, 5.13 and 5.17, activated at 100°C in vacuo. The results, calculated by both 'Point B' and BET methods are collected in Table 7.1. The data plots are presented in Figures 7.5 to 7.14, and the tabulations are in Appendix A7. It may be seen that agreement between the two methods was generally within experimental error, and that low surface areas were obtained in all cases, confirming the conclusions reached about the nature of these materials in Chapter 5. The shape of the isotherms obtained (with the possible exception of that from Experiment 5.11) would at one time have been attributed to Langmuir monolayer adsorption (Brunauer Type I isotherm (365)). However, as was pointed out by de Boer (407), a similar isotherm will occur if negligible adsorbent-adsorbate interaction occurs as long as strong inter-molecular forces occur in the adsorbed layer.

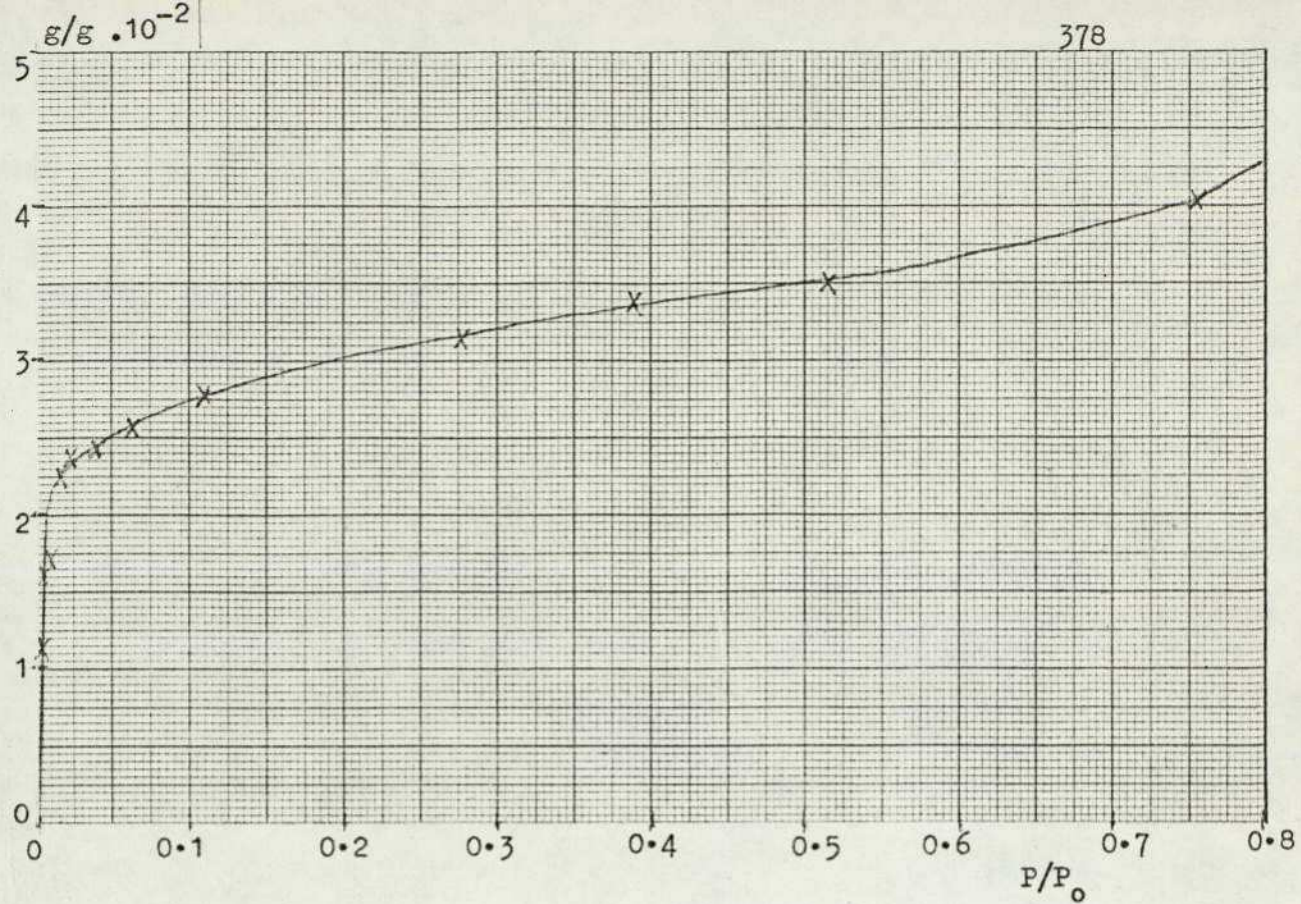


Fig. 7.3 Adsorption isotherm for Active Carbon.

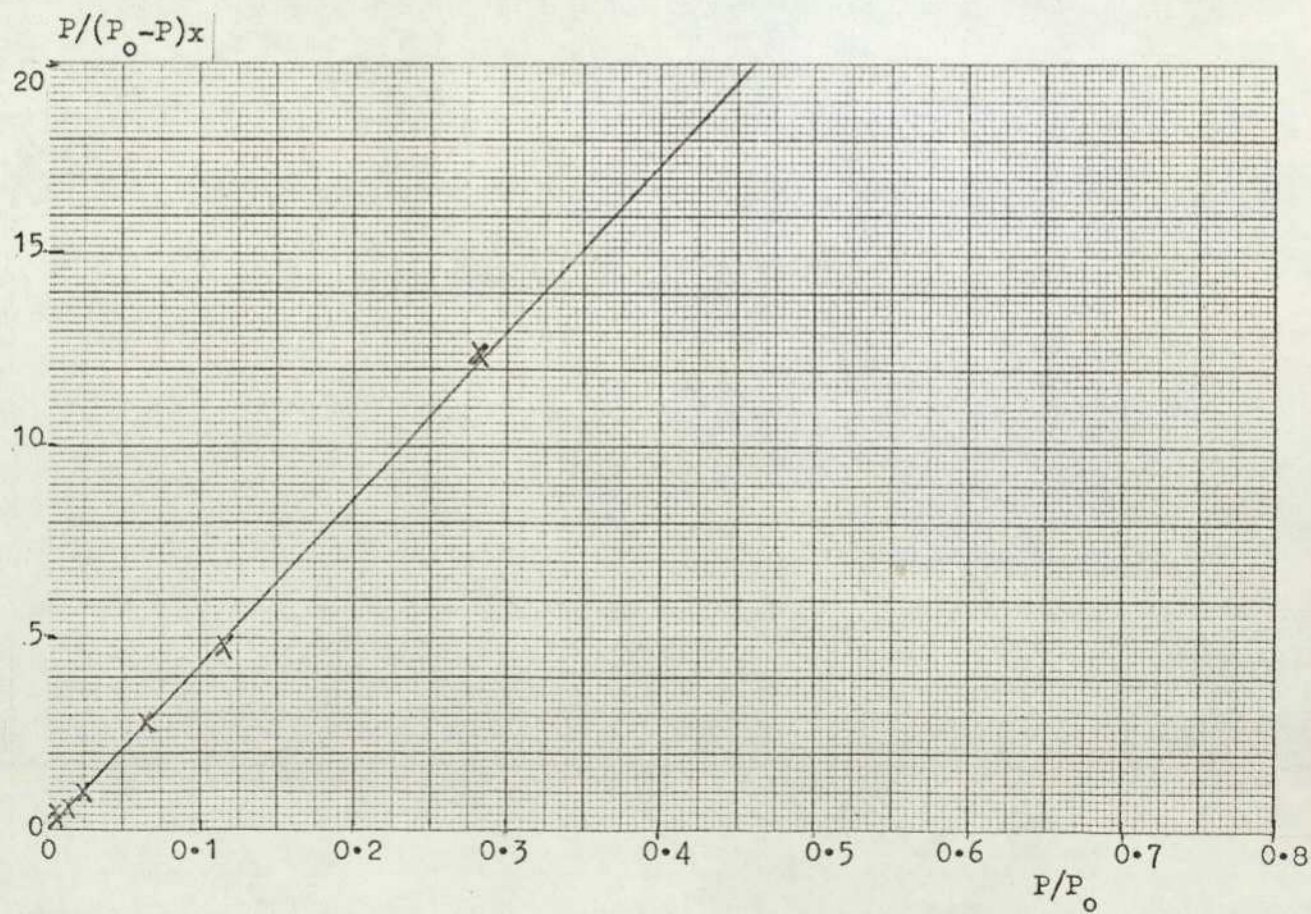


Fig. 7.4 B.E.T. plot for Active Carbon.

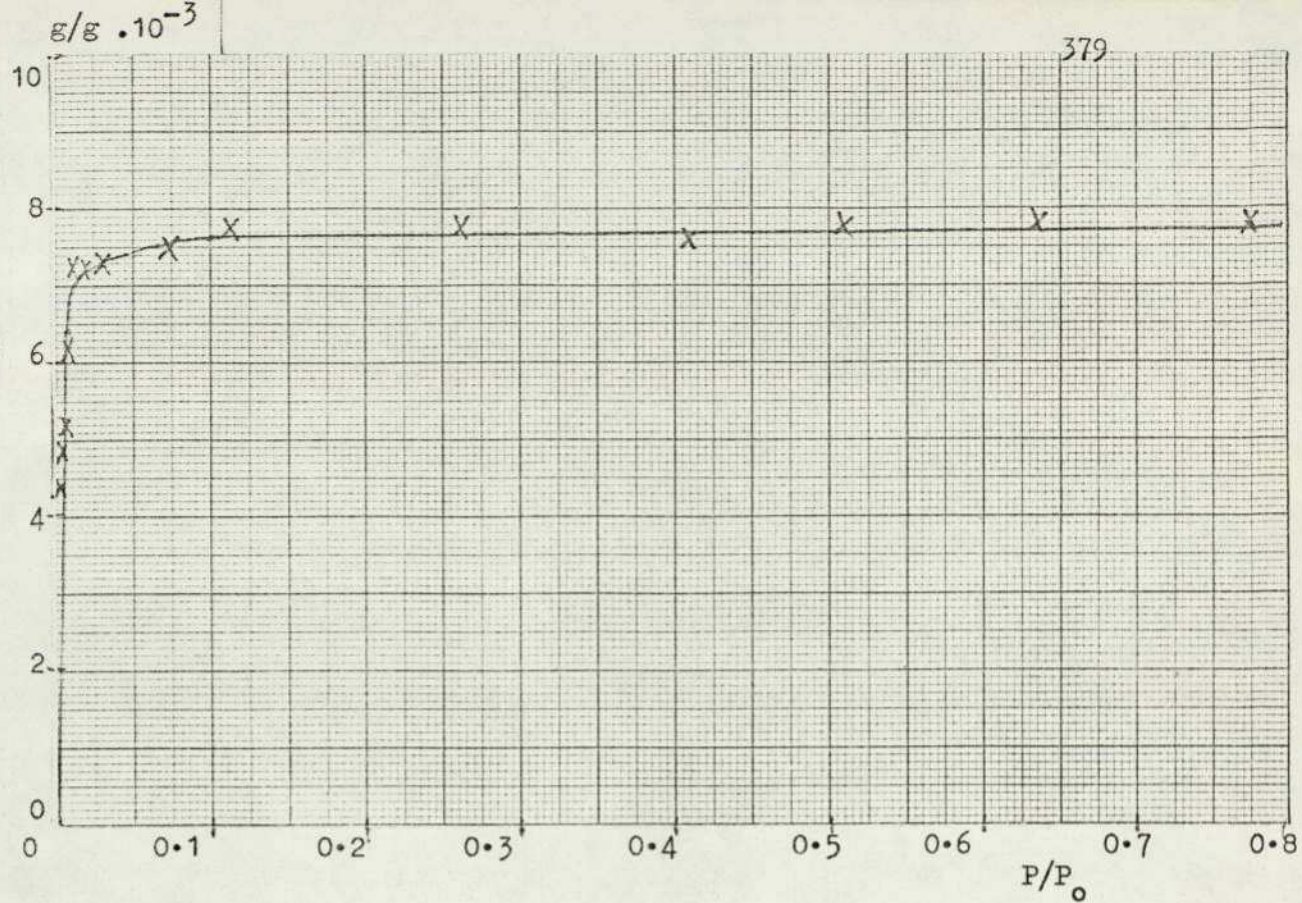


Fig. 7.5 Adsorption isotherm for Experiment 5.10.

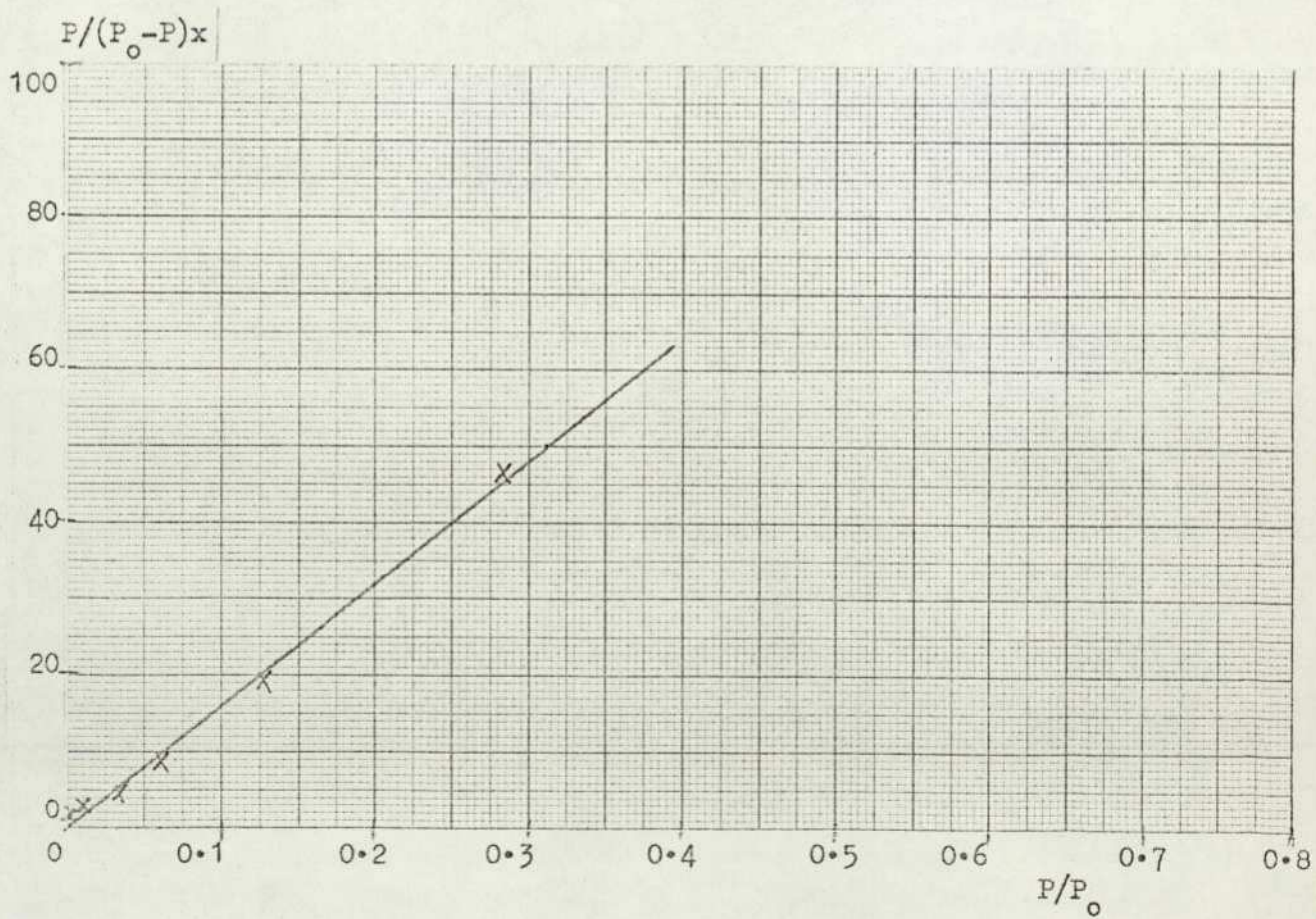


Fig. 7.6 B.E.T. plot for Experiment 5.10.

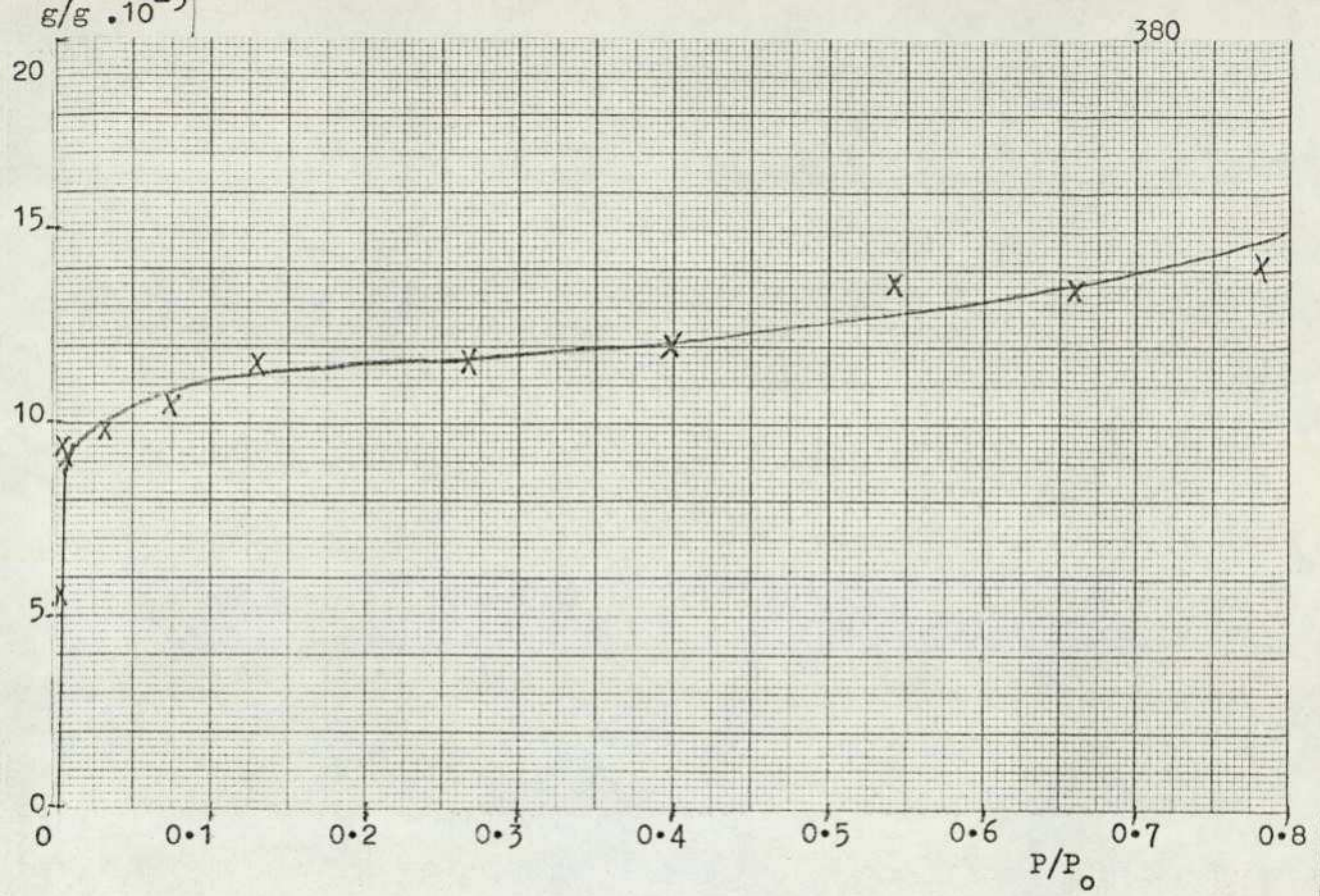


Fig. 7.7 Adsorption isotherm for Experiment 5.11.

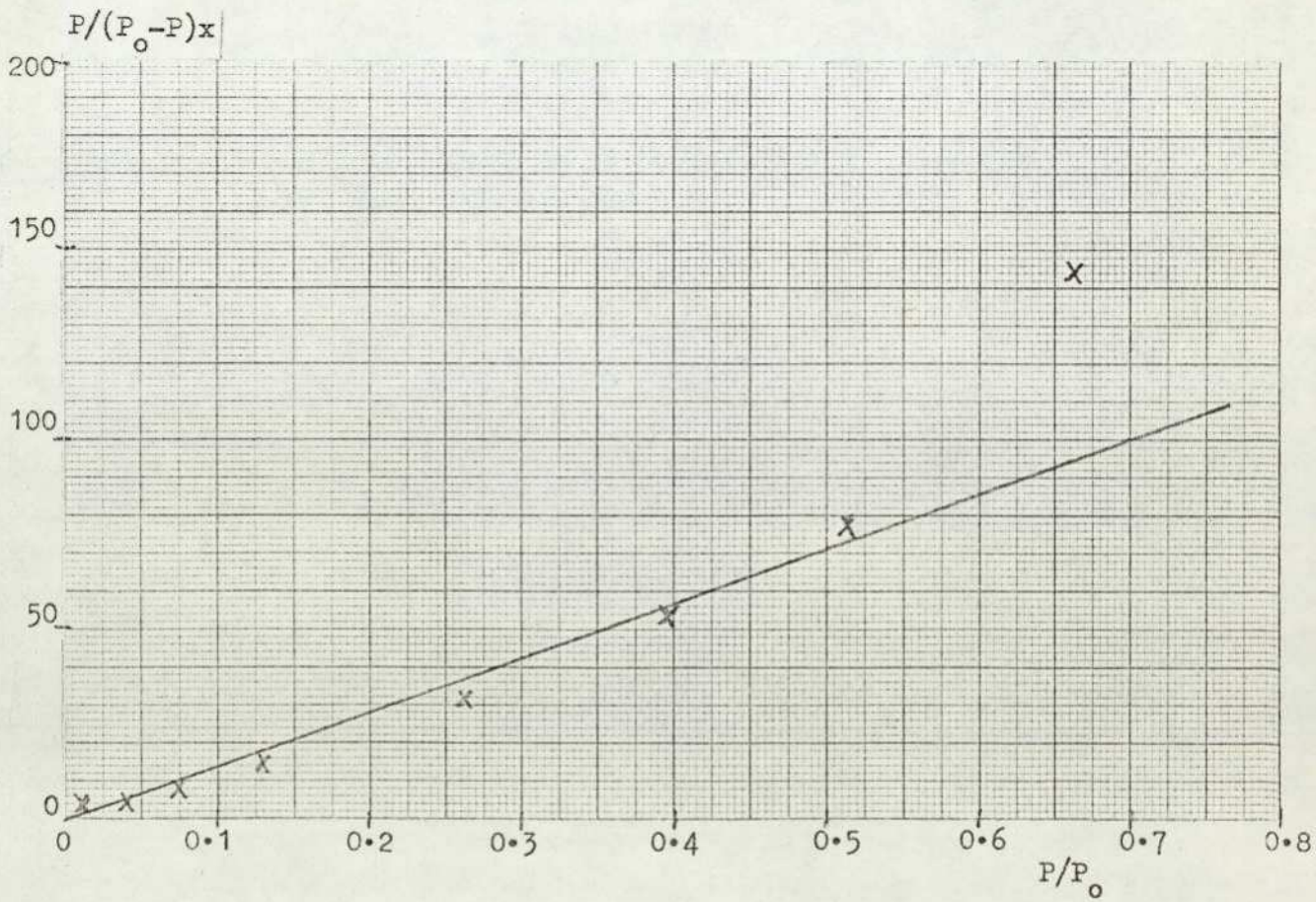


Fig. 7.8 B.E.T. plot for Experiment 5.11.

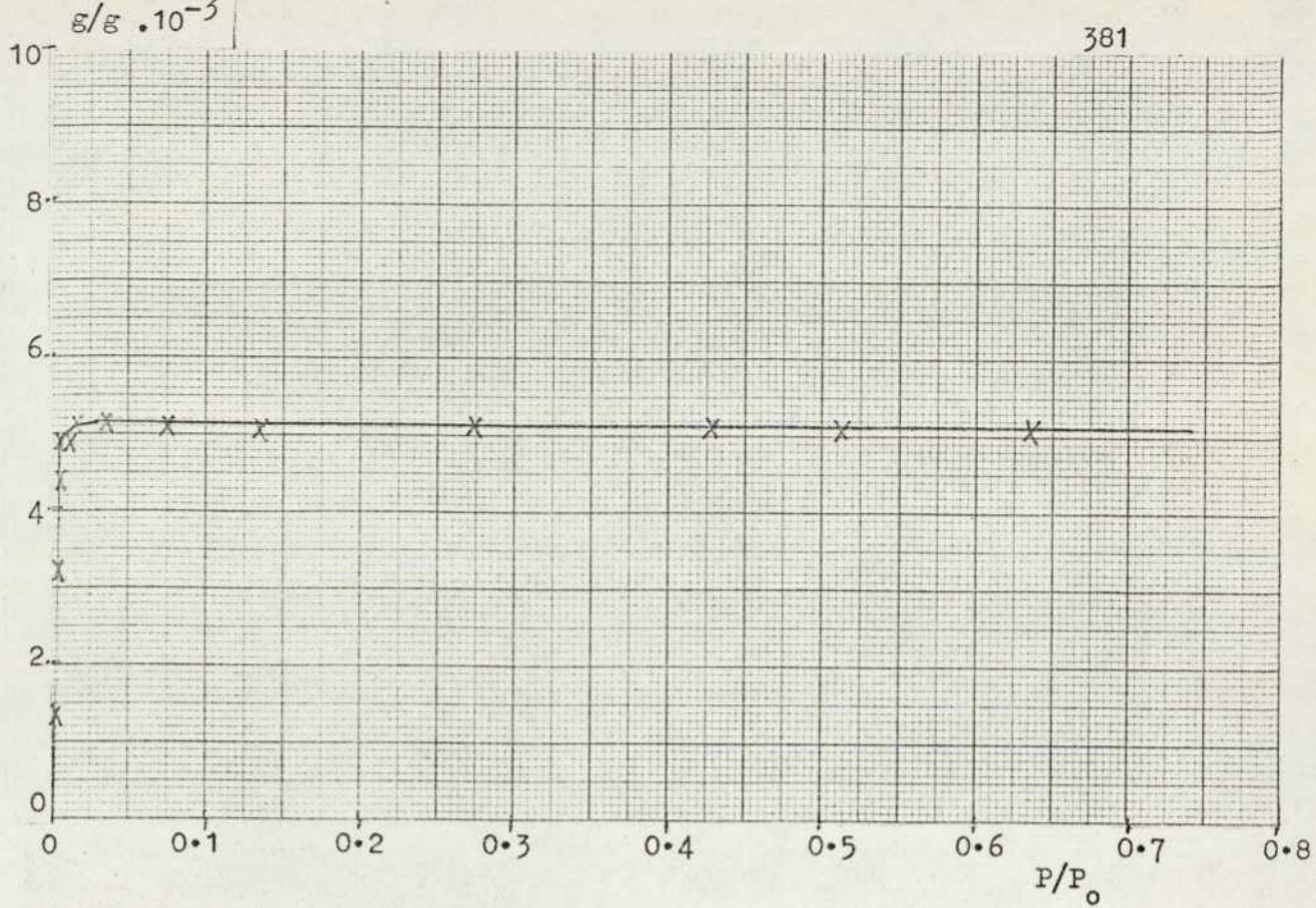


Fig. 7.9 Adsorption isotherm for Experiment 5.12.

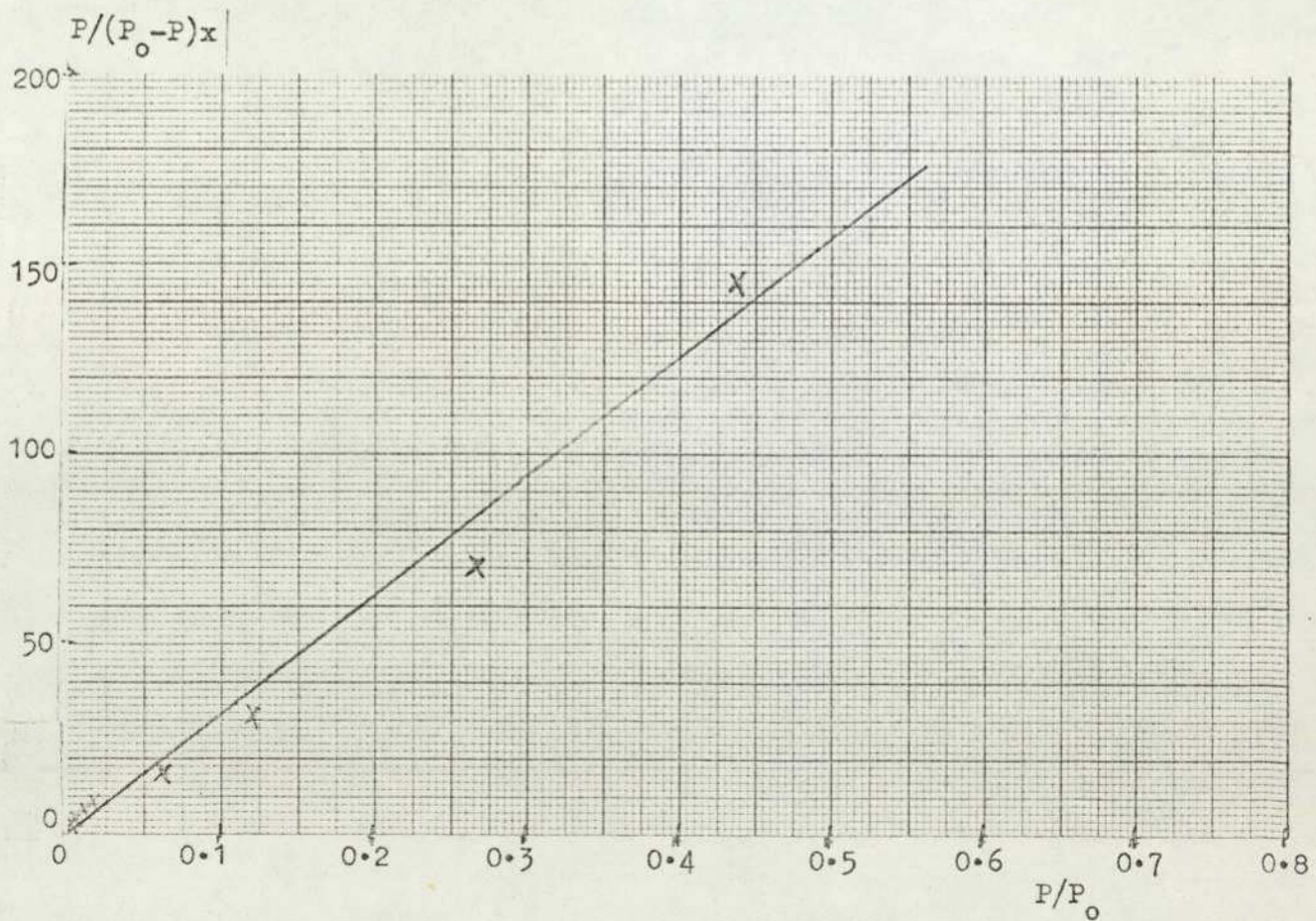


Fig. 7.10 B.E.T. plot for Experiment 5.12.

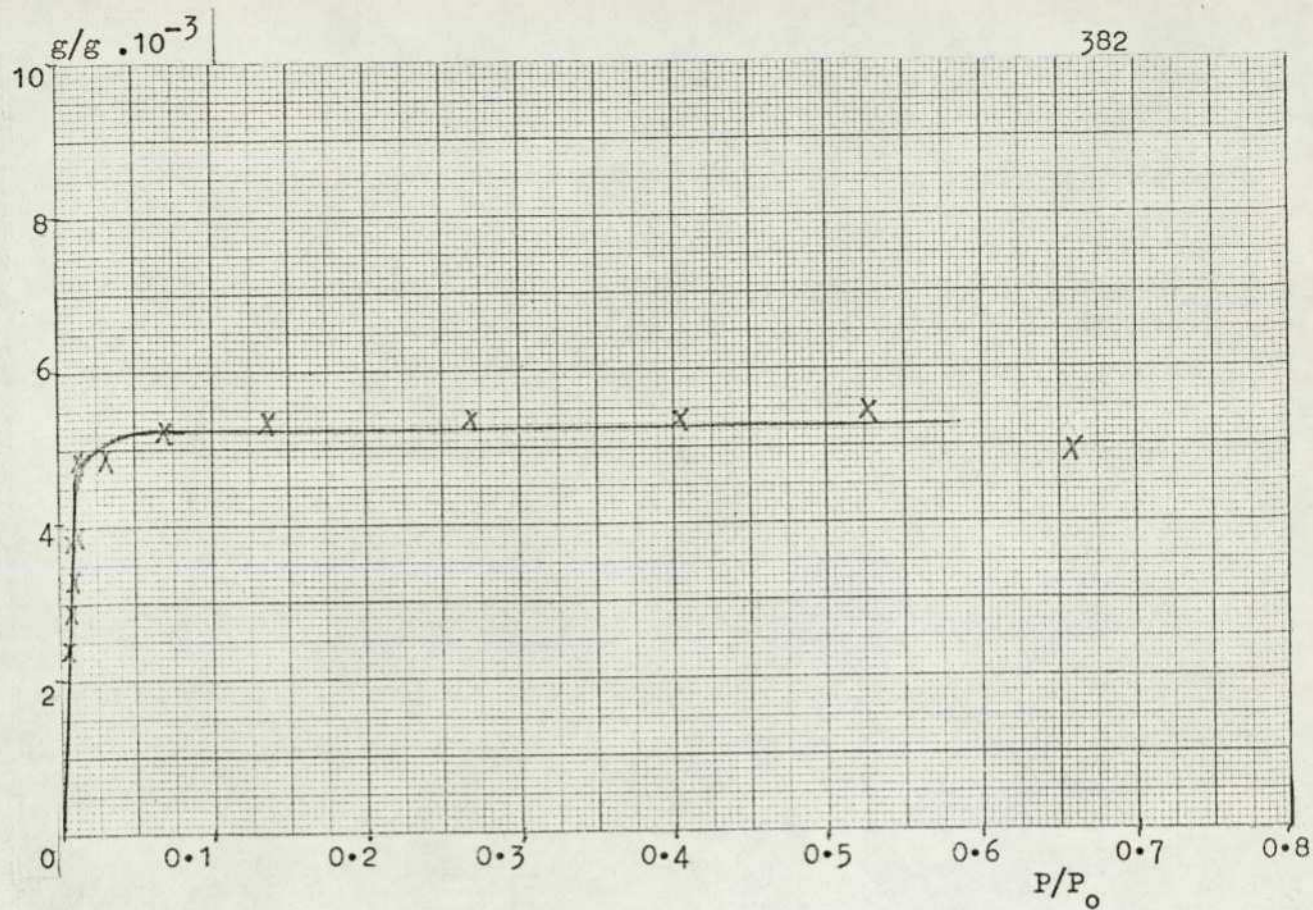


Fig. 7.11 Adsorption isotherm for Experiment 5.13.

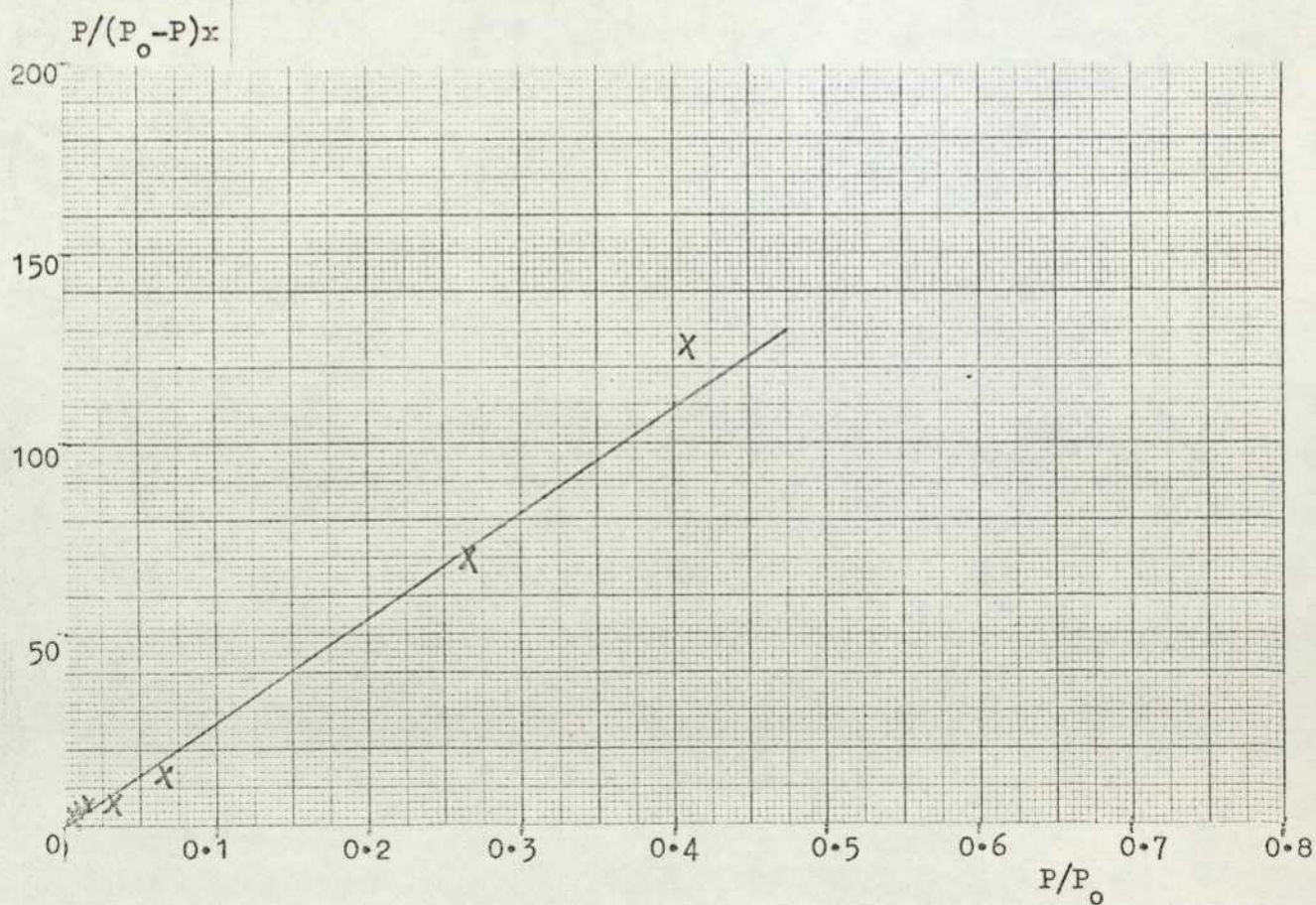


Fig. 7.12 B.E.T. plot for Experiment 5.13.

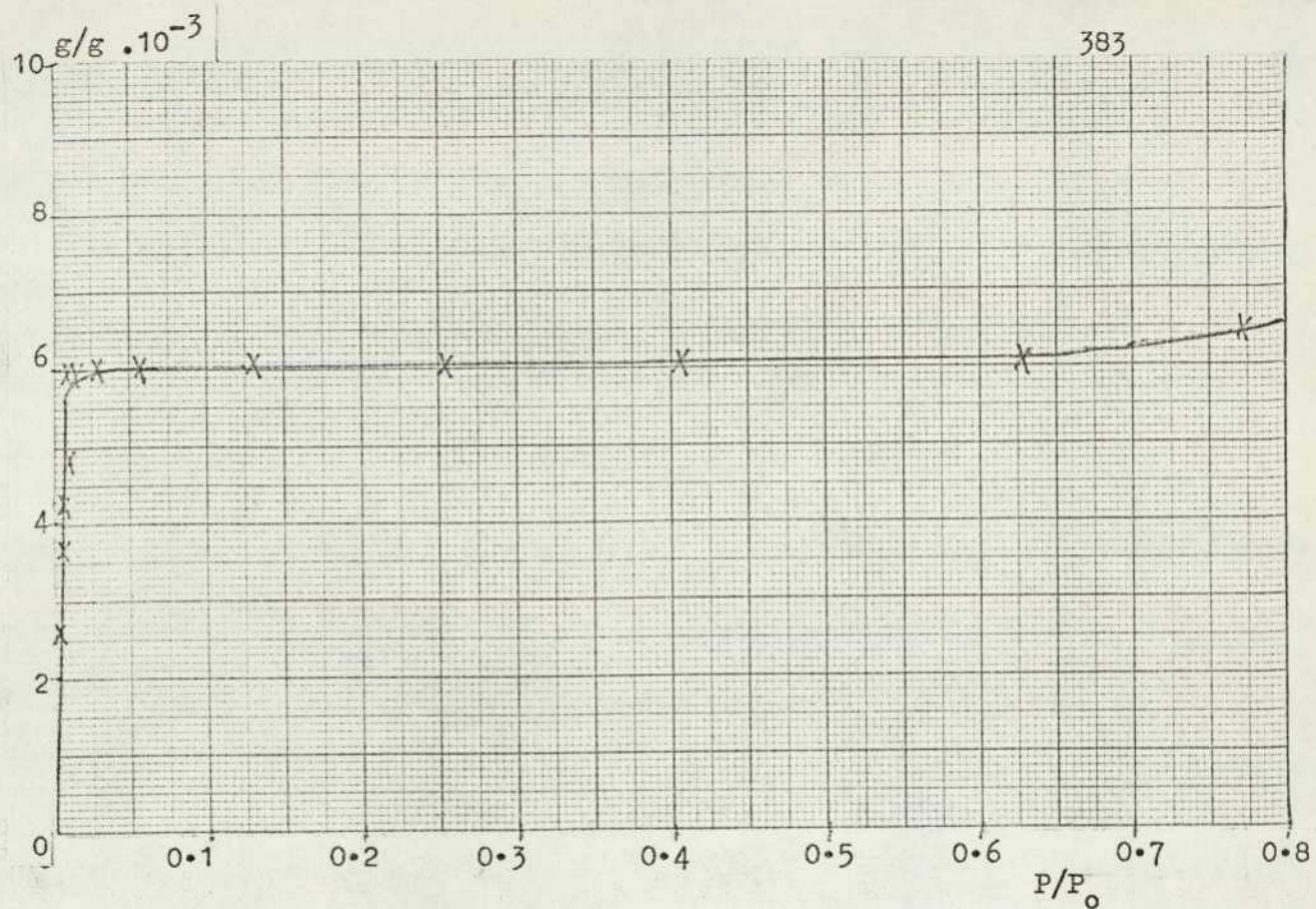


Fig. 7.13 Adsorption isotherm for Experiment 5.17.

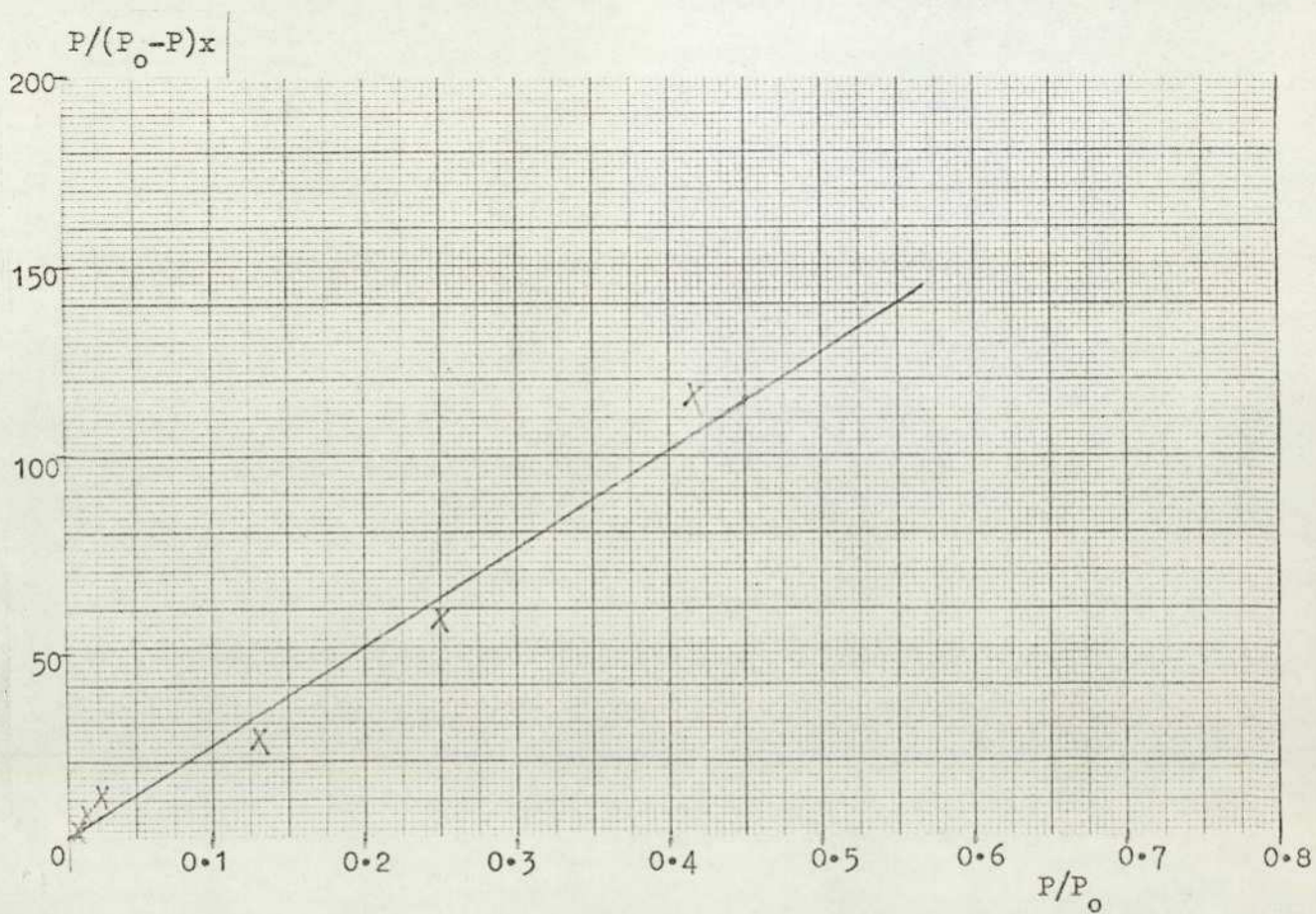


Fig. 7.14 B.E.T. plot for Experiment 5. 17.

Experiment	System	S (m^2/g)	
		Point B	BET
5.10	$\text{In}^{3+}/\text{Sn}^{4+}/\text{Na}^+$	26	22
5.11	$\text{In}^{3+}/\text{Ge}^{4+}/\text{Na}^+$	35	24
5.12	$\text{In}^{3+}/\text{Sn}^{4+}/\text{Et}_4\text{N}^+$	17	11
5.13	$\text{In}^{3+}/\text{Ge}^{4+}/\text{Et}_4\text{N}^+$	17	13
5.17	$\text{In}^{3+}/\text{Ge}^{4+}/\text{Et}_4\text{N}^+/\text{Na}^+$	21	14

Table 7.1 Specific Surface of the water washed products, determined by nitrogen adsorption at liquid nitrogen temperature. Calculated using both Point B and BET estimation of Monolayer.

Experiment	System	Conversion of n-hexane to benzene (mole %)
5.10	$\text{In}^{3+}/\text{Sn}^{4+}/\text{Na}^+$	1.55
5.11	$\text{In}^{3+}/\text{Ge}^{4+}/\text{Na}^+$	None detected
5.12	$\text{In}^{3+}/\text{Sn}^{4+}/\text{Et}_4\text{N}^+$	0.56
5.13	$\text{In}^{3+}/\text{Ge}^{4+}/\text{Et}_4\text{N}^+$	2.08
5.17	$\text{In}^{3+}/\text{Ge}^{4+}/\text{Et}_4\text{N}^+/\text{Na}^+$	0.65

Table 7.2 Activity of the water washed products for the conversion of n-hexane to benzene at 650°C .

Nitrogen : n-hexane ratio = 10 : 1

GHSV = 1000 v/v/hr

It is generally regarded nowadays that this type of isotherm may be attributed to micropore filling as well as to Langmuir type adsorption.

7.2.2 Catalytic Activity Measurements

7.2.2.1 Description of Apparatus

A conventional continuous flow microreactor was used for the catalyst tests, (Figure 7.15). The catalyst was contained in a 2.5 mm ID silica/glass tube between quartz wool plugs. This was heated in a tube furnace, temperature control of which was by means of a thermocouple placed in contact with the reactor tube. A Variac variable transformer connected between the controller and the heater windings prevented temperature overshoot which can occur owing to thermal lag in this type of arrangement. It enabled a controlled heating rate to be obtained. The liquid feedstock was contained in a saturator fitted with a thermostatted water jacket. The feed gas was assumed to be saturated at the thermostat temperature and could be diluted with a separate gas stream if required. A by-pass arrangement allowed the saturator flow to be established and the feed concentration checked on the GLC before it was admitted to the catalyst bed. The separate carrier supply to the catalyst bed enabled the catalyst to be preheated to the required temperature before the feed gas was admitted. Flow control was by means of needle valves in the gas supply, which was regulated by means of Negretti pressure regulators. Two carrier gases were used during the course of this work - nitrogen and hydrogen. BOC oxygen free grade was used in each case, and it was further purified by passing it through manganous oxide and activated molecular sieve columns to remove oxygen and water respectively.

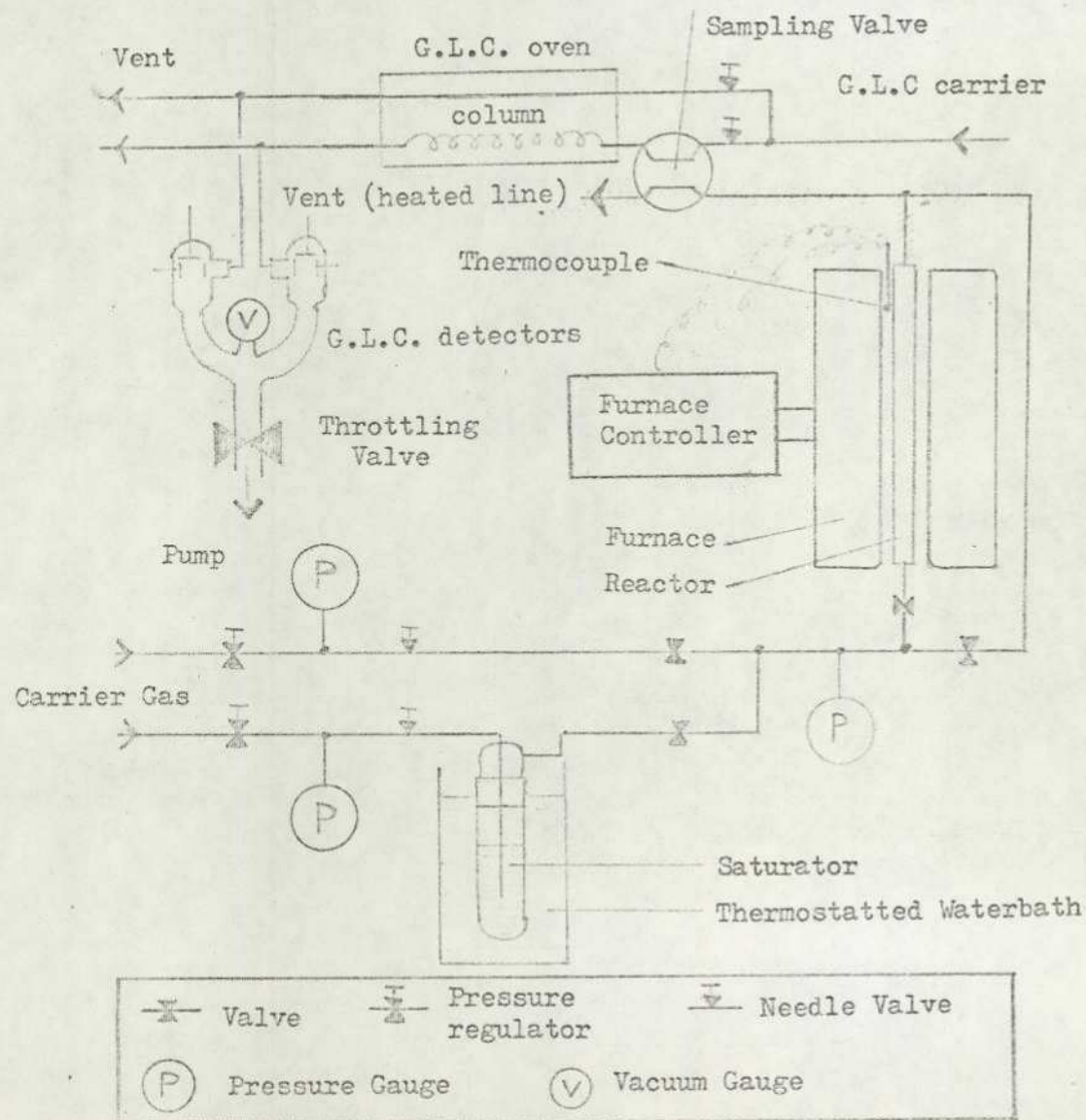


Fig. 7.15 Microreactor used for Catalytic Activity Tests.

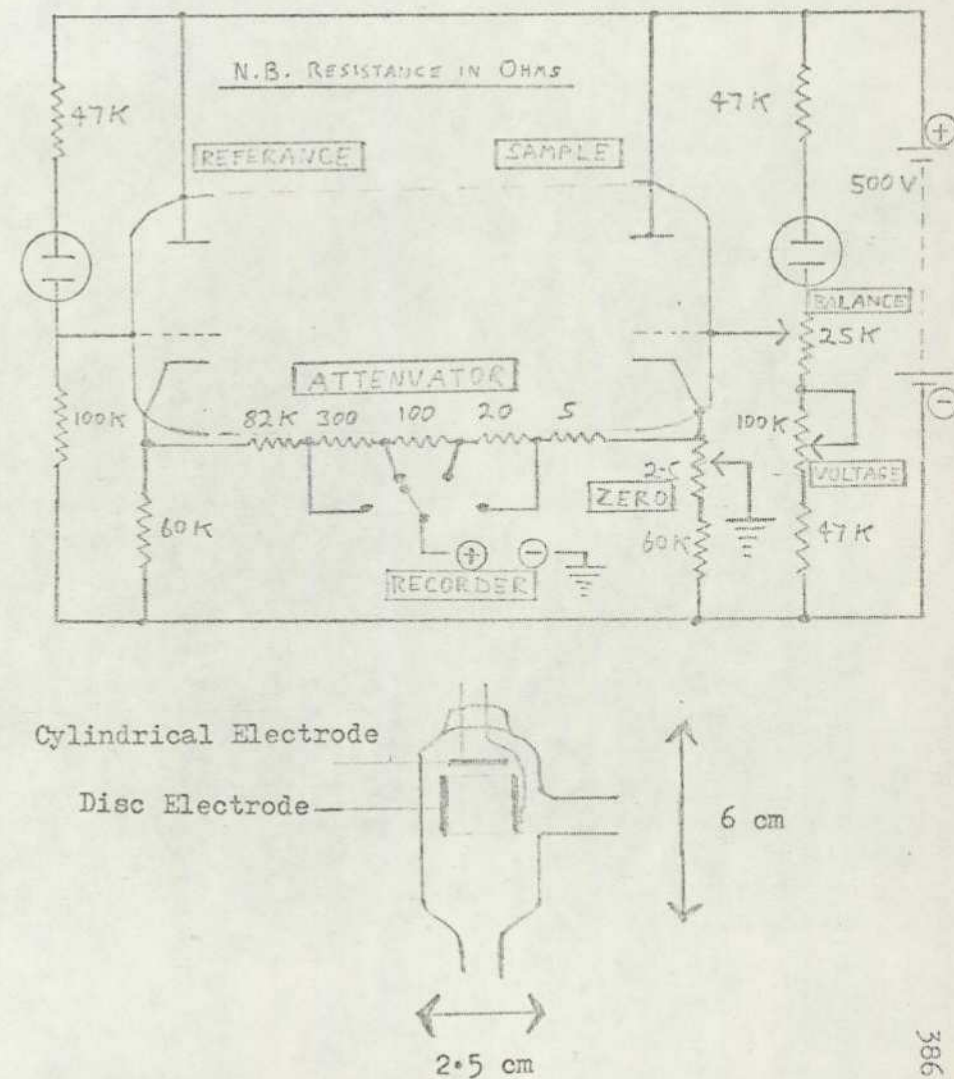


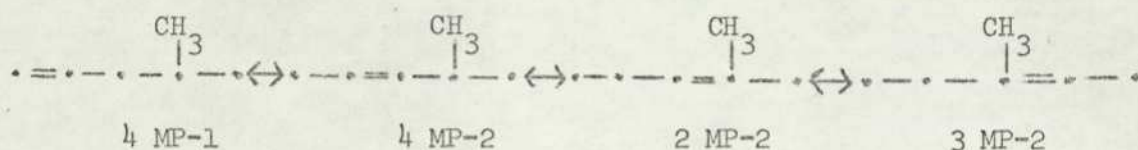
Fig. 7.16 Glow-Discharge Detector and Control Circuit for use with 10 mv. Recorder.

The gas stream leaving the reactor was passed through a six-port valve which was connected as a sampling valve for the chromatograph. The effluent line from the reactor to the sampling valve and vent was wound with heating tape to prevent condensation of the product. The chromatograph column was 6 foot x $\frac{1}{4}$ inch, packed with 28 per cent SE 30 silicone gum on 72 - 100 mesh celite. It was conditioned at 250°C for 10 hours at 85 ml/min nitrogen before use. A reference stream of nitrogen was passed through the chromatograph oven, sample and reference detectors being employed. The detectors used were of the vacuum discharge type, constructed in the laboratory. They consisted (Figure 7.16) of a pair of iron electrodes mounted in a pyrex glass tube, connected at one end to a vacuum pump, and at the other (via a capillary flow restrictor) to the effluent lines from the GLC. A high voltage was applied to the electrodes, a glow-discharge established, and the current flowing in each detector balanced in a bridge arrangement. When no gas was being eluted from the GLC column, pure carrier gas bled into each detector and the bridge was then balanced, the current flowing in each unit being similar. By keeping the resistance ratio in the sample arm the same as on the reference side, noise on the HT line was also balanced out. When a component was eluted from the column, this appeared in the sample detector and the voltage across the discharge changed. This caused the bridge to become unbalanced, and the recorder connected in it registered a peak. The arrangement gave a linear response over at least a hundredfold variation in the concentration of hydrocarbon components up to about 0.1 torr partial pressure. It was only necessary to ensure that the pressure in the detector remained constant, and this was controlled by the throttling valve in the pumping line. The detectors were operated at 500 volts and 3-5 torr pressure. Although not as

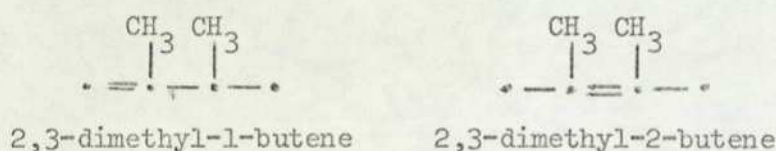
convenient in operation as a commercial katharometer or flame ionization detector, these discharge detectors were very sensitive and had the advantages of being readily constructed and robust, and served a need when no other instruments were available.

7.2.2.2 Isomerization of 4-Methyl-pentene-1

The feedstock was obtained from Koch-Light and was distilled over calcium sulphate before use. The fraction collected between 54.0 and 55.0°C was used; the reported boiling point is 53.6 to 53.9°C. The isomerization sequence expected was:-



The formation of 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene was also possible:-



The chromatograph was operated with an oven temperature of 45°C and a flow rate of 85 ml/min. Calibration samples of the various hydrocarbons expected to be formed were donated by the British Petroleum Company Research Centre at Sunbury-on-Thames. Only partial resolution of the 4-methyl-pentene-1 and 4-methyl-pentene-2 isomers was obtained (bp = 53.7°C and 56.2°C), and similarly the 2-methyl-pentene-2 and 3-methyl-pentene-2 isomers (bp = 67.3°C and 66.9°C) were not resolved, but a clear difference in retention time was observed between the 4-methyl-pentene-1 feedstock and the materials likely to be formed as products.

The 4-methyl-pentene-1 saturator was operated at 25°C, and nitrogen was used as carrier gas, as tests had indicated that

decomposition of the catalyst and formation of hydrogen sulphide occurred if hydrogen was used. The nitrogen:hydrocarbon ratio was 10:1, and the GHSV (gas hourly space velocity) was 1000 ml feedstock/ml catalyst/hour. 0.2 g of catalyst was used in each test, the average density being 1.35 g/ml. It was necessary to pellet the catalyst in a small press, and grind and sieve it to 60 - 80 mesh before use to avoid the reactor becoming blocked.

The water washed reactor products from Experiments 5.10; 5.11; 5.12; 5.13; and 5.17; were tested at temperatures between 150° and 575°C, but in no case was any appreciable isomerization of the feedstock observed. Only over 500°C did traces of dimethyl butenes appear in the effluent gas stream, which was largely unconverted 4-methyl-pentene-1. The only other materials found in the effluent gas stream were some carbon disulphide and hydrogen sulphide from decomposition of the catalyst.

7.2.2.3 Dehydrocyclization of n-Hexane

The conditions used in this set of experiments were similar to those used in the isomerization tests, ie a nitrogen:hydrocarbon ratio of 10:1 and a GHSV of 1000 ml hexane/ml catalyst/hour.

The principal products expected from this reaction were benzene, cyclohexane and possibly methylcyclopentane. The GLC oven was operated at 75°C, and a good separation of these components was obtained. The chromatograph was calibrated quantitatively for n-hexane and benzene. Known quantities were injected from a 50 µl syringe into a 5 litre flask containing a few rolls of metal gauze and fitted with a septum cap. The synthetic gas mixture, after mixing, was pumped through the sampling valve with a 20 ml glass syringe. The response of the GLC for known concentrations of the various components was thereby measured, and calibration graphs prepared.

The n-hexane used was BDH 'Specpure' grade passed through Sinclair Baker alumina activated at 400°C. The materials tested for activity were the water washed products from Experiments 5.10; 5.11; 5.12; 5.13; 5.17. Very slight conversion of hexane to benzene was found in each case except 5.11, and the mole per cent conversion of hexane to benzene is presented in Table 7.2. Reaction was conducted at temperatures between 150° and 700°C. The optimum temperature for benzene formation was 650°C, and this is the temperature at which the reported conversion was obtained. Cracking was found at temperatures of 600°C and above; a test without catalyst showed that this was wholly due to reactor wall cracking.

Carbon disulphide was found in all the reactor off-gases. Tests were conducted in which the catalyst was heated in nitrogen alone; carbon disulphide was initially found in all cases where the tetraethylammonium base had been used in the catalyst preparation. However, a much larger concentration was found when the hexane feed was admitted, and catalyst decomposition during the reaction was therefore indicated. As in the case of the isomerization studies, pretreatment of the catalyst in hydrogen led to the formation of large amounts of hydrogen sulphide. The catalysts were found to be inactive for benzene formation following this treatment.

It therefore seemed that a sulphide species was responsible for the low level of conversion of n-hexane to benzene observed.

Whilst pretreatment to the reaction temperature in nitrogen, and the use of nitrogen as carrier did not affect the catalyst, the use of hydrogen for these functions resulted in complete loss of activity through loss of sulphur as H_2S . It must be stressed that these conversions were very low in comparison with conventional reforming catalysts, which would be expected to give 20 - 30 mole

per cent conversion of n-hexane to benzene at 500 - 600°C and the feed rate used. The low surface areas determined for these materials (Table 7.1) will have a marked bearing on this.

7.3 CONCLUSIONS

As was indicated in the introduction, certain sulphides possess activity for isomerization of olefins, attributable to their acidic properties. The sulphides tested in the present work showed a lack of isomerization activity, and it is therefore concluded that these materials did not possess appreciable surface acidity of the type found in aluminosilicates. It was only in the dehydrocyclization reaction that a small catalytic activity was found, and this was completely selective to benzene formation. This activity is in direct analogy with the dehydrocyclization activity of molybdenum and chromium oxides, which act by preliminary dehydrogenation of the linear paraffin and subsequent cyclization of the highly unsaturated intermediate(532). This is in contrast to the activity of metallic (Pt) catalysts, which in the absence of acid isomerization activity yield cyclopentane derivatives. The very low surface area serves to explain the very low overall activity found. Very little cracking was found with this reaction, and that which was observed was wholly attributable to the walls of the reactor, at the high temperature used. The maximum dehydrocyclization activity was observed at 650°C, which is at least 100° above the temperature at which this reaction is normally conducted. The low cracking activity is again indicative of the low acidity on the surface of these sulphides.

These experiments therefore served to confirm the views already reached concerning the nature of the sulphides prepared in the hydrothermal system. The very low surface area and catalytic activities measured precluded species analogous to aluminosilicates, and supported their characterization as mixtures of simple sulphides. It is interesting, however, that the high selectivity for conversion of n-hexane to benzene is also found in tellurium doped zeolites, as was described in Chapter 3.

CHAPTER 8. CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

It was shown in Chapter 2 that many of the Group IIIb and IVb sulphides should be capable of forming structures analogous to the alumino-silicates. Radius ratio considerations were favourable, and the required tetrahedrally based structure was geometrically feasible. Predictions of the chemical aspects were not as easy to make. Certainly it seemed that the increased co-valency likely to be found in the metal sulphur bonds as compared to metal oxygen bonds would require careful consideration of the stereochemistry, but a consideration of the structures adopted by known Group IIIb and IVb sulphides and complex sulphides showed that many of the structures were very similar to analogous oxides. The tetrahedral coordination found in the SiO_4 building blocks of the silicates occurs in many of the Group IVb sulphides, and given the correct system, there seemed a good chance that complex framework sulphides analogous to the alumino-silicates could be formed.

It was therefore disappointing that no tendency to form these structures was found. Early work attempted the direct sulphiding of 13X zeolite at elevated temperature with CS_2 . This technique was known to work with the more compact oxides, but it was not found to be possible to sulphide the zeolite lattice in this way without a total loss of crystallinity. The replacement of oxygen by sulphur resulted in a complete loss of the structural framework. Below the temperature at which structural sulphiding occurred ($\sim 500^\circ\text{C}$) a tendency for reactive sulphide species to become absorbed within the zeolite lattice was observed. At least a part of the activity appeared to be due to the zeolite catalysed oxidation of absorbed carbon disulphide, which occurred when the materials were exposed to air.

This section of the work was necessarily limited in its scope. It could be usefully extended by the use of other sulphiding agents (eg H_2S , organic sulphides) and also the use of other zeolites which may well react differently. Of especial interest would be the use of germanium-gallium analogues of zeolites. As was indicated in Chapter 2, the lower group elements are more likely to form sulphur analogues of zeolites than are aluminium and silicon.

Even if such thiozeolites should be capable of formation, it is by no means certain that sulphiding of a framework oxide with such an open structure would be possible without destruction of the lattice. For this reason the main emphasis in this research was placed upon the synthesis of sulphur analogues of zeolites in systems analogous to those in which the oxide structures are formed. The results of this approach may be briefly summarised:- although solubility of the elemental sulphides in the hydrothermal flux readily occurred, no tendency was observed for complex sulphides to precipitate from solution in the manner of zeolites and related materials.

The solubility of Group IIIb and IVb sulphides in aqueous solutions of alkali metal sulphides is well established. The failure of the complex sulphide species in solution to react and produce insoluble species analogous to zeolites is probably conclusive evidence against the formation of such materials under the conditions used. The solubility of Group IIIb and IVb sulphides in similar solutions employing hydrogen sulphide as solvent is a less well documented topic, however, and the results obtained are significant in that they illustrate an area of analogy between water and hydrogen sulphide. The solubility of these sulphides in the highly basic

solutions of tetraethyl-ammonium hydrosulphide was undoubtedly the best way to obtain the required solutions. However, it was somewhat surprising that appreciable solubility (especially of the lower sub-group sulphides) occurred in solutions of the sparingly soluble sodium hydrosulphide in liquid hydrogen sulphide. Whether or not ionic processes were involved is not known, but the formation of NaInS_2 from NaSH and In_2S_3 was shown to occur readily at 85°C in liquid hydrogen sulphide, directly in analogy with the formation of this compound in aqueous solution.

The participation of liquid hydrogen sulphide as a solvent in these systems was clearly demonstrated. Two distinct classes of reaction were identified: (1) crystallisation of non-crystalline feedstock: (2) the formation of new (crystalline) phases, which appeared to be restricted to ternary sulphides (ie $\text{M}'\text{M}''\text{S}_z$). As predicted from theoretical considerations, the lower sub-group elements appeared to be more reactive, crystallisation of aluminium and silicon sulphides only occurring at elevated (supercritical) temperatures. In view of the solubility of the metal sulphides in the basic media, insufficient interaction with the solvent (eg hydrogen bonding) is implied by the failure to precipitate complex phases.

An obvious extension of this work would be the use of alternative basic media in an attempt to optimise conditions. The pH of the solution is likely to play an important part. Variation in base type and concentration is necessary to control this. The use of organic bases with larger alkyl constituents (eg lauryl trimethyl) might well affect the crystallization

processes, favouring the formation of more open structures. The use of gallium sulphide would be of interest to complete the examination, whilst other sulphides with suitable ionic size and stoichiometry might be considered. The use of alternative fluxes (ie molten salts) is also worthy of consideration.

In general, the properties of the reaction products were in character with the nature of the materials. Of particular interest, however, was the slight catalytic activity some of the materials were found to have in the conversion of n-hexane to benzene. This would be worthy of further study. Attempts to increase the surface area of the materials (possibly by the use of an inert support) would be necessary to increase the activity, and the initiation of a more comprehensive programme to characterise the catalytic activity of the various simple and complex sulphides involved would be of value.

One other set of original data came out of the work conducted, and this related to the formation of mercaptide derivatives of aluminium, $Al(SR)_3$. It was not found to be possible to prepare this type of material by a method analogous to that used to prepare $Si(SR)_4$ (ie reaction of $SiCl_4$ with $NaSR$). This was in part due to the difficulty of separating the product (insoluble in the case of aluminium, but not of silicon) from the $NaCl$ formed, and the use of a different base (ie ammonia) in conjunction with the mercaptan would be one way of overcoming this. However, attempts to prepare this class of material from ethylaluminium indicated that reaction further than $EtAl(SET)_2$ was not possible, probably due to polymerization of the product.

Literature and patent reports relating to the formation of $Al(SR)_3$ from solutions in coordinating solvents, or from the reaction between aluminium and thiol, were not substantiated.

REFERENCES

N.B. Unless otherwise stated, all boiling points, melting points, etc. quoted in this thesis were taken from the 'Handbook of Chemistry and Physics' Chemical Rubber Publishing Company, 38th Edn., 1956.

1. Mason, B. 'Principles of Geochemistry' 2nd. Edn., New York, (1958).
2. Goldschmidt, V.M.; J. Chem. Soc., 655(1937).
3. Sanderson, R.T. 'Chemical Periodicity' Reinhold, (1960).
4. Durrant & Durrant, 'Introduction to Advanced Inorganic Chemistry' 2nd. Edn., Longmans, (1970). p. 638 et seq.
5. Wells, A.F. 'Structural Inorganic Chemistry' 3rd. Edn., Oxford, (1962).
6. Nickless, G. (Ed.) 'Inorganic Sulphur Chemistry' Elsevier, (1968).
7. Pauling, L. 'The Nature of the Chemical Bond' 2nd. Edn., Cornell University Press, (1948).
8. Pimentel, G.C. & McClellan, A.L. 'The Hydrogen Bond' Freeman, (1960).
9. Mertes, M.P. 'Hydrogen Bonding by Sulphur Functions' in 'Mechanisms of Reactions of Sulphur Compounds, Vol. 2' Quart. Rep. on Sulphur Chemistry, Intrascience (1965). p.27.
10. Bulanin, M.O., Denisov, G.S. & Pushkina, R.A.; Optik. Spekt., 6, 754(1959).
11. Colebrook, L.D. & Tarbell, D.S.; Proc. Nat. Acad. Sci., U.S., 47, 993 (1961).
12. Schmidbaur, H. & Siebert, W.; Ber., 97, 2090(1964).
13. Tursi, A.J. & Nixon, E.R.; J.Chem. Phys., 53, 518(1970).
14. Wagner, W.C., Weinberger, A.J. & Stoughton, R.W.; J.Phys. Chem., 73, 3518(1969).
15. Lowden, J.E., Kennedy, L.A., Sulzmann, K.G.P. & Penner, S.S.; J. Quant. Spect. Rad. Transfer, 10, 17(1970).
16. McDaniel, D.H. & Evans, W.G.; Inorg. Chem., 5, 2180(1966).
17. Bragg, L. & Claringbull, G.F. 'The Crystalline State' Vol.4 - 'Crystal Structures of Minerals' Bell & Sons, (1965). p.45.
18. Wyckoff, R.W.G. 'Crystal Structures' 2nd. Edn., Interscience. Vol. 1 (1963); Vol. 2 (1964); Vol. 3 (1965).
19. Ross, V.; Econ. Geol., 52, 755(1957).
20. Flahaut, J.; Ann. Fac. Sci. Saigon, 121(1960).
21. Hellner, E.; J. Geol., 66, 503(1958).
22. Zachariasen, W.H.; Z. Krist., 67, 226(1928).
23. Laubergayer, A.W. & Morton, D.S.; J. Amer. Chem. Soc., 54, 2303(1932).
24. Smith, G.S. & Isaacs, P.B.; Acta. Cryst., 17, 842(1964).
25. Hägg, G. & Söderholm, G.; Z. Phys. Chem., B29, 88(1935).
26. Roy, R., Hill, V.G. & Osborn, E.F. J.Amer. Chem. Soc., 74, 719(1952).
27. Gibbs, R.E.; Proc. Roy. Soc., A113, 351(1927).
28. Goldschmidt, V.M.; Z. Phys. Chem., B17, 172(1932).
29. Zintl, E. & Loosen.; Z. Phys. Chem., A174, 301(1935).

30. Büssen, W., Fischer, H. & Gruner, E.; *Naturwiss.*, 23, 740 (1935).
31. Prewitt, C.T. & Young, H.S.; *Science*, 149, 535 (1965).
32. Silverman, M.S. & Soulen, J.R.; *Inorg. Chem.*, 4, 129 (1965).
33. Zachariasen, W.H.; *J. Chem. Phys.*; 4, 618 (1936).
34. Zachariasen, W.H.; *Phys. Rev.*, 49, 884 (1936).
35. Ch'un-hua et. al.; *Proc. Acad. Sci. U.S.S.R. (Chem. Sect.)*, 151, 662 (1963).
36. Rubenstein, M. & Roland, G.; *Acta. Cryst.*, B27, 505 (1971).
37. Oftedal, I.; *Norsk. Geol. Tidskr.*, 2, 225 (1926).
38. Oftedal, I.; *Neues. Jahrb. Mineral.*, A1927, 115 (1926).
39. Flahaut, J.; *C.R. Acad. Sci.*, 232, 334 (1951).
40. Flahaut, J.; *C.R. Acad. Sci.*, 232, 2100 (1951).
41. Flahaut, J.; *Ann. Chim. (Paris)*, 7, 632 (1952).
42. Schaefer, H.; Schaefer, G. & Weiss, A., *Z. Anorg. Allgem. Chem.*, 325, 77 (1963).
43. Sheka, I.A.; Chaus, I.S. & Mityurera, T.T. 'The Chemistry of Gallium' Elsevier (1966)
44. Hahn, H. & Klinger, W.; *Z. Anorg. Allgem. Chem.*, 259, 135 (1949).
45. Hahn, H.; *Angew. Chem.*, 64, 203 (1952).
46. Hahn, H. & Frank, G.; *Z. Anorg. Allgem. Chem.*, 278, 333 (1955).
47. Goodyear, J., Duffin, W.J. & Steigmann, G.A.; *Acta. Cryst.*, 14, 1168 (1961).
48. Goodyear, J. & Steigmann, G.A.; *Acta. Cryst.*, 16, 946 (1963).
49. Hahn, H. & Klinger, W.; *Z. anorg. Chem.*, 260, 97 (1949).
50. Huber, M.; *C.R. Acad. Sci.*, 253, 471 (1961).
51. Rooymans, C.J.M.; *J. Inorg. Nucl. Chem.*, 11, 78 (1959).
52. Steigmann, G.A., Sutherland, H.H. & Goodyear, J.; *Acta. Cryst.*, 19, 967 (1965).
53. Chao, E.C.T., Fahey, J.J., Littler, J. & Milton, D.J.; *J. Geophys. Res.*, 67, 419 (1962).
54. Breck, D.W.; *J. Chem. Ed.*, 48, 678 (1964).
55. Barrer, R.M.; *Endeavour*, 23, 122 (1964).
56. Barrer, R.M.; *Brit. Chem. Eng.*, 7, 267 (1959).
57. Hersh, C.K. 'Molecular Sieves' Reinhold, (1961).
58. Sokolov, V.A. et. al. 'Molecular Sieves and their Use' Moscow (1964) trans. pub. by J. Crosfield & Sons. Ltd., Warrington (1965).
59. Barrer, R.M.; *Chem. Ind. (London)*, 1203 (1968).
60. 'Molecular Sieves' Papers read at the Conference held at the School of Pharmacy (Univ. London), 4-6th April 1967. *Pub. Soc. Chem. Ind.*, 14 Belgrave Square, London S.W.1, (1968).
61. Flahaut, J., Domange, L., Guittard, M. & Ourmitchi, M.; *Bull. Soc. Chim. France*, 2382 (1961).
62. Bok, L.D.C. & Boeyens, J.C.A.; *J.S. African Chem. Inst.*, 10, 40 (1957).
63. Hoppe, R.; *Bull. Soc. Chim. France*, 1115 (1965).

64. Hahn, H., Gunter, F., Klinger, W., Störger, A.D. & Störger, G.; Z. Anorg. Allgem. Chem., 279, 241(1955).
65. Hahn, H., Gunter, F., Klinger, W., Meyer, A.D. & Störger, G.; Z. Anorg. Allgem. Chem., 271, 153(1953).
66. Ivanov-Emin, B.N. & Rabovik, Ya.I.; J. Gen. Chem.(U.S.S.R.), 17, 1247(1947).
67. Chaus, I.S. & Sheka, I.A.; Zh. Neorg. Khim., 7, 2162(1962).
68. Hoppe, R., Lidecke, W. & Frorath, F.C.; Z. Anorg. Allgem. Chem., 309, 49(1961).
69. Hoppe, R.; Angew. Chem., 11, 457(1959).
70. Rooymans, C.J.M. 'Reactivity of Solids' G.M.Schwab, Ed. Elsevier (1965). p.100.
71. Meyer, R.E.; Ann. 150, 137(1869).
72. Schneider, R.; J. Prakt. Chem., 2, 209(1874).
73. Vachnadze, E.S. & Nanobashvili, E.M.; Issled. v Obl. Elektrokhim. i Rad. Khim., Akad. Nauk. Gruz S.S.R., Inst. Neorgan. Khim. i Elektrokhim., 86(1965).
74. Vachnadze, E.S. & Nanobashvili, E.M.; Soobsch. Akad. Nauk. Gruz. S.S.R., 21, 531(1958).
75. *ibid.*, 33, 85(1964).
76. *ibid.*, 33, 331(1964).
77. *ibid.*, 45, 85(1967).
78. Mellor, J.W. 'A Comprehensive Treatise on Inorganic and Theoretical Chemistry' Longmans (1946).
79. Weiss, A. & Rocktäschel, G.; Z. Anorg. Allgem. Chem., 307, 1(1960).
80. Rocktaschel, G., Ritter, W. & Weiss, A.; Z. Naturforschg., B19, 958(1964).
81. Hardy, A., Perez, G. & Serment, J.; Bull. Soc. Chim. France, 2638(1965).
82. Michelet, A. & Flahaut, J.; C.R.Acad. Sci., C268, 326(1969).
83. Serment, J., Perez, G. & Hagermuller, P.; Bull. Soc. Chim. France, 561(1968).
84. Maslov, V.I. & Polyvyannyi, I.R.; Tr. Inst. Met. Obogashch. Akad. Nauk. Kaz. S.S.R., 21, 50(1967).
85. Schwarz, R. & Giese, H.; Ber., B63, 778(1930).
86. Willard, H.H. & Zeuhlke, C.W.; J. Amer. Chem. Soc., 65, 1887(1943).
87. Sevrykov, N.N., Salikova, G.E. & Dolganov, V.P.; Z. Neorg. Khim., 14, 26(1969). Trans. of J. Inorg. Chem., 14, 12(1969).
88. Maurin, M. & Ribes, M.; C.R.Acad. Sci., C262, 1876(1966).
89. Oliver-Fourcade, J., Ribes, M., Philippot, E. & Maurin, M.; C.R.Acad. Sci., C272, 1964(1971).
90. Philippot, E., Ribes, M. & Lindquist, O.; Rev. Chim. Miner., 8, 477(1971).
91. Krebs, B., Pohl, S. & Schiwy, W.; Angew. Chem., 2, 897(1970).
92. Putkaradze, N.V. & Nanobashvili, E.M.; Soobshch. Akad. Nauk. Gruz. S.S.R., 42, 79(1966).
93. Sevrykov, N.N. & Salikova, G.E.; Zh. Neorg. Khim., 15, 1634(1970).
94. Jelley, E.; J.Chem. Soc., 1580(1933).

95. Babko, A.K. & Lisetskaya, G.S.; Zh. Neorg. Khim., 1, 969 (1956).
96. Sevryukov, N.N.; Sb. Nauchn. Tr., Inst. Tsvetn. Metal., 34 (1960).
97. Hahn, H. & Gunter, F.; Z. Anorg. Allgem. Chem., 269, 227 (1952).
98. Steigmann, G.A.; Acta. Cryst., 23, 142 (1967).
99. Lappe, F., Niggli, A., Nitsche, R. & White, J.G.; Z. Krist., 117, 146 (1962).
100. Flahaut, J., Domange, L., Patrie, M., Bostsarron, A.M. & Guittard, M., Adv. Chem. Ser., 39, 179 (1963).
101. Ribes, M., Philippot, E. & Maurin, M.; C.R.Acad. Sci., C270, 716 (1970).
102. *ibid.*, C270, 1873 (1970).
103. deSaint-Griniez, D., Lanuelle, P. & Flahaut, J.; C.R.Acad. Sci., C267 1029 (1968). Correction in part to *ibid.* C247, 1866 (1958).
104. Flahaut, J., Domange, L., Guittard, M. & Fährat, M.S.; C.R.Acad. Sci., C253, 1956 (1961).
105. Perez, G. & Duale, M. C.R.Acad. Sci., C269, 984 (1969).
106. Michelet, A., Lanuelle, P. & Flahaut, J., C.R.Acad. Sci., C262, 753 (1960).
107. Michelet, A.; Perez, G., Etienne, J. & Darriet-Duale, M.; C.R.Acad. Sci., C271, 513 (1970).
108. Flahaut, J.; Bull. Soc. Chim. France, 1282 (1960).
109. Boivin, J.C., Thomas, D. & Tridot, G.; C.R.Acad. Sci., C264, 1286 (1967).
110. McEwan, D.M.C.; Trans. Farad. Soc., 44, 349 (1948).
111. Flahaut, J., Domange, L. & Patrie, M.; C.R.Acad. Sci., C247, 1866 (1958).
112. Domange, M., Flahaut, J. & Patrie, M.; Bull. Soc. Chim. France, 2, 229 (1960).
113. Michelet, A. & Flahaut, J.; C.R.Acad. Sci., C269, 1203 (1969).
114. Guittard, M., Julien-Pouzol, M., Laurelle, P. & Flahaut, J.; C.R.Acad. Sci., C267, 767 (1968).
115. Guittard, M. & Julien-Pouzol, M.; Bull. Soc. Chim. France, 2467 (1970).
116. Cabestaing, C. & Galigné, J.; C.R.Acad. Sci., C270, 488 (1970).
117. Gaston, C. & Laurelle, P.; C.R.Acad. Sci., C270, 410 (1970).
118. Palache, C., Berman, H. & Frondel, C. 'Danas System of Mineralogy' 7th. Edn., Wiley (1944). Volume 1.
119. Kohlmeyer, E.J. & Retzlaff, H.W.; Z. Anorg. Chem. 261, 248 (1950).
120. Hempel, W. & von Haasy, H.; Z. Anorg. Chem., 23, 32 (1900).
121. Sarkisov, E.S., Lidin, R.A. & Vengellerskaya, N.S.; Isv. Akad. Nauk. S.S.R., Neorg. Mater., 6, 184 (1970).
122. Hahn, H. & Stuck, G.; Naturwiss., 54, 225 (1967).
123. Parthé, E., Yvon, K. & Deitch, R.H.; Acta. Cryst., B25, 1164 (1969).
124. Darcy, L., Baltzer, P.K. & Lopatin, E.; J. Appl. Phys. 39, 898 (1968).
125. Grund, A. & Pizy, M.M.; Acta. Cryst., 5, 837 (1952).
126. Seemann, H.; Acta. Cryst., 2, 251 (1956).
127. *Idem.* et al.; Z. Anorg. Chem., 269, 141 (1962).

128. Gattow, G.; *Acta, Cryst.*, 10, 549(1957).
129. Roy, R. & White, W.B.; *J. Cryst. Growth*, 3-4, 33(1968).
130. Rabenau, A. & Rau, H.; *Phillips Tech. Rev.*, 30, 89(1969).
131. Laudise, R.A. & Kolb, E.D.; *Endeavour*, 28, 114(1969).
132. Laudise, R.A. & Nielsen, J.W.; *Solid State Phys.*, 12, 149(1961).
133. Brady, E.L.; *J. Phys. Chem.*, 57, 706(1953).
134. White, E.A.D.; *Quart. Rev. (London)*, 15, 1(1961).
135. Van Praagh, G.; *Research*, 1, 458(1948).
136. Barrer, R.M.; *Chem. Britain*, 380(1966).
137. Kennedy, G.C.; *Econ. Geol.*, 45, 639(1950).
138. Olsson, K.; *Ark. Kemi*, 13, 367(1958).
139. Ollson, K. & Gronwall, C.; *Ark. Kemi.*; 17, 529(1961).
140. Smith, F.G.; *Econ. Geol.*; 35, 646(1940).
141. Smith, F.G.; *Trans. Roy. Soc. Canada*, 40, 99(1946).
142. Laudise, R.A. & Ballman, A.A.; *J. Phys. Chem.*, 64, 688(1960).
143. Bryatov, L.V. & Kuz'mina, I.R.; *Rost. Krist. Akad. Nauk. S.S.S.R., Inst. Krist.*, 3, 416(1961).
144. Laudise, R.A., Kolb, E.D. & De Neufirelle; *Amer. Miner.* 50, 382(1965).
145. Kolb, E.D., Caporaso, A.J. & Laudise, R.A.; *J. Cryst. Growth*, 3,4, 422(1968).
146. Dronov, A.V. & Gareev, I.G.; *Geol. Rud. Mestorozhd.*, 10, 87(1968).
147. Popolitov, V.I.; *Kristallografiya*, 14, 545(1969).
148. Cambi, L. & Elli, M.; *Chim. Ind. (Milan)*, 51, 3(1969).
149. *ibid.*, 46, 1275(1964).
150. Rabenau, A. & Rau, H.; *Phillips Tech. Rev.*, 30, 89(1969).
151. Rabenau, A. & Rau, H.; *Solid State Comm.*, 5, 331(1967).
152. Rabenau, A. & Rau, H.; *Mat. Res. Bull.*, 2, 609(1967).
153. Kolb, E.D. & Laudise, R.A.; *J. Cryst. Growth*, 7, 199(1970).
154. Morimoto, Y., Wakino, K., Kanamaru, F. & Koizumi, M.; *J. Amer. Ceram. Soc.*, 54, 71(1971).
155. Popilitov, V.I. & Litvin, B.N.; *Kristallografiya*, 13, 571(1968).
156. Fredericks, W.J., Rosztoczy, F.E. & Hatchett, J.; *U.S. Dept. Com., Office. Tech. Serv.*, AD407,600 (1963). [*Chem. Abs.* 60, 6275f(1964)].
157. Lewis, L.C. 'An Investigation Of the Crystal Growth of the Heavy Metal Sulphides in Supercritical Hydrogen Sulphide' Thesis submitted to Oregon State University, June 1968.
158. Arutyunyan, L.A. & Khurshudyan, K.Kh.; *Geokhimiya*, 650(1966).
159. Koval's'kii, P.M., Vel'nik, V.M. & Shneider, A.D.; *Vkr. Fiz. Zh.*, 11, 921(1966).
160. Addamiano, A. & Manuel, A.; *J. Appl. Phys.*, 31, 36(1960).
161. Ravich, L.E.; *U.S. Patent*, 2,890,939. Jun. 16th., 1959.
162. Grillot, E.; *C.R. Acad. Sci.*, C242, 779(1956).

163. Sysoev, L.A., Konvisar, L.V. & Raiskin, E.K.; German Patent, 1,289,034. Feb. 13th., 1969 & U.S. Patent, 3,414,387, Dec. 3rd. 1968.
164. Paorici, C. & Zuccalli, G.; J. Cryst. Growth., 7, 265 (1970).
165. Samelson, H.; J. Appl. Phys., 33, 1779 (1962).
166. Jona, F. & Mandel, G.; J. Phys. Chem. Solids, 25, 187 (1964).
167. Bouchard, R.J.; J. Crystal Growth, 2, 40 (1968).
168. Krembeller, A. & Levine, A.K.; Sylvania Tech., 10, 67 (1957).
169. Nitsche, R., Sargent, D.F. & Wild, P.; J. Cryst. Growth., 1, 52 (1967).
170. Nitsche, R.; Phys. and Chem. of Solids., 17, 163 (1960); Physica, 26, 647 (1960).
171. Lutz, H.D., Lovasz, Cs., Bertram, K.H., Sreckovic, M. & Brinker, U.; Monatsh. Chem., 101, 519 (1970).
172. Shick, L.K. & Von Neida, A.R.; J. Cryst. Growth, 5, 313 (1969).
173. Von Neida, A.R. & Shick, L.K.; J. Appl. Phys., 40, 1013 (1969).
174. Shand, W.A.; J. Cryst. Growth, 5, 203 (1969).
175. Gashurov, G. & Levine, A.K.; J. Chem. Eng. Data, 5, 517 (1960).
176. Wilke, K.Th.; Schultze, D. & Toepfer, K.; J. Cryst. Growth, 1, 41 (1967).
177. Johnson, R.E. & Parker, S.G.; U.S. Patent, 3,374,067. 19th Mar. 1968.
178. Parker, S.G. & Pinnell, J.E.; J. Cryst. Growth, 3-4, 490 (1968).
179. Linares, R.C.; Trans. Met. Soc. A.I.M.E., 242, 441 (1968).
180. Harsy, M.; Krist. Tech.; 2, 447 (1967).
181. Rubenstein, M.; J. Cryst. Growth, 3-4, 302 (1968).
182. Yoder, H.S.; Amer. J. Sci., (1952), Bowen Volume, Part 2., p. 569.
183. Balascio, J.F., White, W.B. & Roy, R.; Mater. Res. Bull., 2, 913 (1967).
184. Luzhnaya, N.P.; J. Cryst. Growth, 3-4, 97 (1968).
185. Barrer, R.M.; J. Chem. Soc., 195 (1959).
186. Barrer, R.M. & Marshall, D.J.; J. Chem. Soc., 6616 (1965).
187. Barrer, R.M. & Dicks, L.W.R.; J. Chem. Soc., 1379 (1966).
188. Selbin, J. & Mason, R.B.; J. Inorg. Nucl. Chem., 20, 222 (1961).
189. Kuhl, G.H.; J. Inorg. Nucl. Chem., 33, 3261 (1971).
190. Piontkovskaya, M.A. & Shameko, K.; Isv. Akad. Nauk. S.S.S.R., Neorg. Mater., 6, 1151 (1970).
191. *ibid.*, 6, 794 (1970).
192. Park, C. Sung-Uk.; French Patent, 1,563,559. 11th Apr. 1969.
193. Argauer, R.J.; U.S. Patent, 3,431,219. 4th Mar. 1969.
194. Young, D.A.; British Patent, 1,188,188. 15th Apr. 1970.
195. Young, D.A.; U.S. Patent, 3,329,480. 4th July 1967.
196. Robson, H.E.; U.S. Patent, 3,328,119. 27th June 1967.
197. Ermolenko, N.F., Levina, S.A. & Parsevich-Kolyada, L.V.; Dokl. Akad. Nauk. Belorussk. S.S.S.R., 8, 394 (1964).

198. Pansevich-Kolyada, L.V. & Ermolenko, N.F.; Zh. Fiz. Khim., 40, 2383(1966).
199. Grose, R.W. & Flanigen, E.M.; German Patent, 1,959,241. 11th Jun. 1970.
200. Wacks, K.; German Patent, 1,174,749. 30th July 1964.
201. Neimark, I.E., Piotkovskaya, M.A., Rastrenenko, A.I., Shameko, G.S., Il'in, V.G., Eremeuko, A.M. & Antonovskaya, S.N.; Mater. Vses. Soveshch. po Tseolitam, 2nd., Leningrad 1964, 146. (Pub. 1965).
202. Levina, S.A., Malashevich, L.N. & Ermolenko, N.F.; Vesti. Akad. Nauk. Belarusk S.S.R., Ser. Khim. Navuk, 10(1965).
203. Nowotny, H. & Wittmann, A.; Monatsh. Chem., 85, 558(1954).
204. Nowotny, H. & Wittmann, A. Monatsh. Chem.; 84, 701(1953).
205. Nowotny, H. & Szekely, G.; Monatsh. Chem.; 83, 568(1952).
206. Wittmann, A. & Nowotny, H.; Monatsh. Chem., 87, 654(1956).
207. Wittmann, A., Nowotny, H. & Münster, N.; Monatsh. Chem., 90, 7(1959).
208. Zemann, J.; Acta. Cryst., 12252(1959).
209. Papamantellos, P. & Wittmann, A.; Monatsh. Chem., 92, 805(1961).
210. Papamantellos, P. & Wittmann, A.; Monatsh. Chem., 93, 582(1962).
211. Eulenberger, G., Nowotny, H. & Wittmann, A. Monatsh. Chem., 92, 949(1961).
212. Wittmann, A., Voellenkle, H. & Nowotny, H.; Monatsh. Chem., 94, 440(1963).
213. Papamantellos, P. & Wittmann, A.; Monatsh. Chem., 96, 1014(1965).
214. Wittmann, A. & Modern, E.; Monatsh. Chem., 96, 1154(1965).
215. Marksteiner, A., Neckel, A. & Nowotny, H.; Monatsh. Chem., 96, 1427(1965).
216. Bittner, H. & Kerber, W.; Monatsh. Chem., 100, 427(1969).
217. Hauser, E., Nowotny, H. & Seifert, K.J.; Monatsh. Chem., 101, 715(1970).
218. Bittner, H. & Hauser.; Monatsh. Chem.; 101, 1471(1970).
219. Hauser, E., Bittner, H. & Nowotny, H.; Monatsh. Chem., 101, 1864(1970).
220. Walenta, K.; Min. Petrog. Mitt.; 11, 121(1966).
221. Goldsmith, J.R.; J. Geol., 58, 518(1950).
222. Goldsmith, J.R.; Z. Krist., 106, 213(1955).
223. Kolomieto, B.; Soviet Sci. Rev.; 22(July 1970).
224. Greenwood, N. 'Ionic Crystals, Lattice Defects and Non-Stoichiometry' Butterworths, 1958.
225. 'Molecular Sieve Zeolites'. Parts 1 & 2. 2nd. International Conf.,
& 226. Worcestor Polytechnic Inst., Worcestor, Mass.. Sept. 8th - 11th.,
1970. Pub.: Adv. Chem. Ser., 101 & 102. A.C.S., 1971.
227. Frémy, E.; Ann. Chim. Phys., 38, 322(1853).
228. Jannigen, M.M.; German Patent, 80944 (1895).
229. Clearfield, A.; Acta. Cryst., 16, 135(1963).
230. Amer. Perfumer. Cosmet., 77, 42(1962).

231. Kumins, C.A. & Gessler, A.E.; Ind. & Eng. Chem., 45, 567 (1953).
232. Dragulescu, C., Getia, V. & Tribunescu, P.; Bull. Stünt. Tehnic. Inst. Politehnic Timisoara, 6, 33 (1961).
233. Frener, J.S. & Ward, R.; J. Amer. Chem. Soc., 72, 2870 (1950).
234. Winterling, A.; Chemiker-Ztg., 85, 230 (1961).
235. Satava, V.; Silikaty, 6, 16 (1962).
236. Singer, J.; Z. Anorg. Chem., 204, 232 (1932).
237. Kumins, C.A.; U.S. Patents 2,544,693; 2,544,694 & 2,544,695 Mar. 13th. 1951.
238. Yamaguchi, G. & Kubo, Y.; Bull. Chem. Soc. Japan, 41, 2641 (1968).
239. *ibid.*, 41, 2645 (1968).
240. Kubo, Y. & Yamaguchi, G.; Bull. Soc. Chem. Japan, 42, 1897 (1969).
241. Kumins, C.A.; Amer. Ink Maker, 32, 47; 51; & 113 (1954).
242. Leschewski, K. & Möller, H.; Naturwiss., 19, 771 (1931).
243. Leschewski, K. & Möller, H.; Ber., 67, 1684 (1934).
244. Leschewski, K.; Z. Angew. Chem., 48, 533 (1935).
245. Leschewski, K. & Podschus, E.; Ber., 68, 1872 (1935).
246. Blitz, W.; Z. Anorg. Allgem. Chem., 127, 169 (1923).
247. Ostwald, W.; Z. Kolloid, 38, 341 (1925).
248. Jen, T.P.; Tung. Univ. Res. Inst., Ann. Rep. Bur. Chem., 3, 27 (1936).
249. Gorshtein, A.E. & Nikolaeva, N.N.; J. Appl. Chem. (USSR), 44, 613 (1971).
250. Hofmann, U. & Herzentiel, E.; Z. Anorg. Allgem. Chem., 329, 102 (1964).
251. Gardener, D.M. & Fraenkel, G.K.; J. Amer. Chem. Soc., 77, 6399 (1955).
252. Dudzik, Z.; Bull. Acad. Pol. Sci., Ser. Sci. Chim., 15, 401 (1967).
253. Gardener, D.M. & Fraenkel, G.K.; J. Amer. Chem. Soc., 78, 3279 (1956).
254. *ibid.*, 78, 6411 (1956).
255. Boettcher, R., Wartenig, S., Windsh, W. & Zschurke, A.; Z. Naturforsch., A23, 1766 (1968).
256. Hofmann, U., Herzenstiel, E., Schoenemann, E. & Schwarz, K.H.; Z. Anorg. Allgem. Chem., 367, 119 (1969).
257. Morton, J.R.; Proc. Colloq. Ampère, 15 (1968). Pub. North Holland, 1969. p. 299.
258. Pflugmacher, A., Schorning, D. & Schwartz, R.; Z. Anorg. Allgem. Chem., 295, 93 (1958).
259. Matsunaga, Y.; Can. J. Chem., 38, 309 (1960).
260. Kumins, C.A.; U.S. Patent, 2,759,844, Aug. 21st. 1956.
261. Dudzik, Z. & Kinastowski, S. Bull. Acad. Pol. Sci., Ser. Chim., 11, 321 (1963).
262. Kinastowski, S. & Dudzik, Z.; Bull. Soc. Chim. France, 10, 2115 (1963).
263. Dudzik, Z.; Bull. acad. Pol. Sci., Ser. Sci. Chim., 15, 405 (1967).
264. *ibid.*, 15, 409 (1967).
265. *ibid.*, 15, 583 (1967).

266. Dudzik, Z. & Preston, K.F.; J. Coll. Interface Sci., 26, 374(1968).
267. Dudzik, Z. & Cveticarović, R.J. 'Catalytic Properties of Molecular Sieves containing trapped Sulphur Radicals' Paper read at the 4th. Inter. Congress on Catalysis, Moscow, 1968.
268. Kinastowski, S. & Dudzik, Z.; Polish Patent 57,018, 28th. Mar. 1969.
269. Rychly, J. & Lazar, M.; J. Polym. Sci. B7, 843(1969).
270. Martinez, F.B.; Anales Real Soc. Españ. Fíz. y-quóm, B45, 533; 735 (1949).
271. Barrer, R.M. & Whiteman, J.L.; J. Chem. Soc.(A), 13(1967).
272. Kirk, R.D.; J. Electrochemical Soc., 101, 461(1954).
273. Kirk, R.D.; Amer. Miner., 40, 22(1955).
274. Kerr, G.T. & Johnson, G.C.; J. Phys. Chem., 64, 381(1960).
275. Kerr, G.T. & Johnson, G.C.; U.S. Patent 2,971,824, Feb. 14th, 1961.
276. Addison, W.E. & Walton, A.; J. Chem. Soc., 4741(1961).
277. Adlriankina, M.A., Keltsev, N.V. Torocheshnikov, N.S. & Shumyalskii, Y.I.; Tr. Mosk. Khim. Technol. Inst., 123(1969).
278. Deo, A.V. & Dulla-Lava, I.G.; J. Catal., 21, 270(1971).
279. Kerr, G.T.; U.S. Patent 2,983,580 May 9th. 1961.
280. (Thiokol Chemical Corp.). Neth. Appl. 6,503,449. 20th Sept. 1965.
281. Miale, J.N. & Weisz, P.B.; J. Catal., 20, 288(1971).
282. Miale, J.N. & Weisz, P.B.; U.S. Patent, 3,471,412, 7th. Oct. 1969.
283. Lang, W.H., Mikovsky, R.J. & Silvestri, A.J.; J. Catal., 20, 293(1971).
284. Mikovsky, R.J.; Silvestri, A.J., Dempsey, E. & Olson, D.H.; J. Catal., 20, 371(1971).
285. Gilewicz, J. & Malinsky, R.; Poznan. Tow. Przizy, Nauk. Pr. Kom. Mat.-Przyr., 12, 59(1968).
286. Wells, P.B.; J. Catal., 19, 372(1970).
287. Miale, J.N. & Weisz, P.B.; U.S. Patent 3,175,855; Mar. 16th., 1965.
288. *ibid.*, 3,175,967; Mar. 30th., 1965.
289. Young, D.A.; U.S. Patent, 3,239,451; Mar. 8th., 1966.
290. *ibid.*, 3,342,725; Sept. 19th., 1967.
291. Engebreston, G.R. & Mooi, J. U.S. Patent 3,337,446; Aug., 22nd., 1967.
292. Garwood, W.E.; U.S. Patent, 3,247,278; Apr. 19th., 1966.
293. (Gulf Research and Development Co.) British Patent 996,917; Jun. 30th., 1965.
294. Stamicarbon, N.V.; Neth. Appl. 6,516,208; June 14th., 1967).
295. (Mobil Oil Corp.) British Patent 1,064,985; Apr. 12th., 1967.
296. Levina, S.A.; Dokl. Acad. Nauk. Beloruss S.S.R.; 12, 908(1968).
297. Symons, M.C.R.; J. Chem. Soc., 2440(1957).
298. Ingram, D.J.E. & Symons, M.C.R.; J. Chem. Soc., 2437(1957).
299. Stillings, M., Symons, M.C.R. & Wilkinson, J.G.; J. Chem. Soc. (D), 372(1971).

300. Stillings, M., Symons, M.C.R. & Wilkinson, J.G.; J.Chem. Soc. (A), 3201(1971).
301. Gillespi, R.J. & Passmore, J.; J.Chem. Soc. (D), 1333(1969).
302. Giggenbach, W.; J. Inorg. Nucl. Chem., 30, 3189(1968).
303. Gruer, D.M., McBeth, R.L. & Zielen, A.J.; J. Amer. Chem. Soc., 93, 6691(1971).
304. Kerridge, D.H. & Mosely, M.; J.Chem.Soc.(A), 352(1967).
305. Hersch, P.A.; Anal.Chem., 32, 1030(1960).
306. Vogel, A.I. 'A Textbook of Quantitative Inorganic Analysis, including Elementary Instrumental Analysis' 3rd. Edn. Longmans, 1961.
307. Ingram, G. 'Methods of Organic Elemental Microanalysis' Chapman and Hall, 1962.
308. Merritt, M.V. & Sawyer, D.T.; Inorg. Chem., 9, 211(1970).
309. Giggenbach, W.; Inorg. Chem., 10, 1306(1971).
310. *ibid.*, 10, 1308(1971).
311. Olson, D.H., Mikovsky, R.J.; Shipman, G.F. & Dempsey, E.; J. Catal. 24, 161(1972).
312. Saksena, B.D.; Trans. Farad. Soc., 57, 242(1961).
313. Zhdanov, S.P.; Kiselev, A.V., Lygin, V.I. & Titova, T.I.; Zh. Fiz. Khim., 38, 2408(1964).
314. Zhdanov, S.P., Kiselev, A.V., Lygin, V.I. & Titova, T.I.; Dokl. Akad. Nauk. S.S.S.R., 150, 584(1963).
315. Fehér, F. & Goller, H.; Z. Naturforsch., B25, 250(1970).
316. Schumann, H. & Schmidt; Angew. Chem.Int. Edn., 4, 1007(1965).
317. Coates, G.E. & Makherjee, R.N.; J.Chem. Soc., 1295(1964).
318. Adams, D.M. & Cornell, J.B.; J.Chem. Soc. (A), 884(1967) & 1299(1968).
319. Flint, C.D. & Goodgame, M.; J. Chem. Soc. (A), 744(1966).
320. Karr, C. & Kovach, J.J.; Appl. Spec., 23, 219(1969).
321. Bradley, D.C. 'Metal Alkoxides' in: Prog. in Inorg. Chem., 2, 303 (1960). Ed. F.A. Cotton, Pub. Interscience.
322. Mehrotra, R.C. 'Synthesis and Properties of Alkoxy- and Alkylalkoxy silanes' in: 'Organosilicon Chemistry- special lectures presented at the International Symposium on Organosilicon Chemistry' Prague, 6-9th Sept. 1965. Pub. Butterworths, 1966.
323. Barrer, R.M. & Denny, P.J.; J. Chem. Soc., 971(1961).
324. Aiello, R. & Barrer, R.M.; J. Chem. Soc.(A), 1470(1970).
325. Abel, E.W. & Armitage, D.A.; Adv. Organometallic Chem., 5, 2(1967).
326. Backer, H.J. & Stienstra, F.; Rec. Trav. Chim., 51, 1196(1932).
327. *ibid.*, 52, 912(1933).
328. *ibid.*, 54, 38(1935).
329. Backer, H.J. & Klasens, H.A.; Rec. Trav. Chim., 61, 500(1942).
330. *ibid.*, 61, 513(1942).

331. Backer, H.J. & Stienstra, F.; *Rec. Trav. Chim.*, 52, 1033 (1933).
332. *ibid.*, 54, 607 (1935).
333. Backer, H.J. & Kramer, J.; *Rec. Trav. Chim.*, 52, 916 (1933).
334. *ibid.*, 53, 1101 (1934).
335. Backer, H.J. & Stedehouder, P.L.; *Rec. Trav. Chim.*, 52, 437 (1933).
336. *ibid.*, 52, 923 (1933).
337. *ibid.*, 52, 1039 (1933).
338. Backer, H.J. & Dreuth, W.; *Rec. Trav. Chim.*, 70, 559 (1951).
339. Abel, E.W.; *J. Chem. Soc.*, 4460 (1960).
340. Schmidt, M. & Weber, M.; *Inorg. Chem.*, 1, 909 (1962).
341. Bart, J.C. & Daly, J.J.; *Chem. Comm.*, 1207 (1968).
342. Schmeisser, M.; German Patent, 1,008,265, 16th. May, 1957.
343. Schmeisser, M., Müller, H. & Burgemeister, W.; *Angew. Chem.*, 69, 781 (1957).
344. McNicol, B.D., Pott, G.T. & Loos, K.R.; *J. Phys. Chem.*, 76, 3388 (1972).
345. Neuworth, M.B., Laufer, R.L. & Previc, E.P.; U.S. Patent, 3,032,595, 1962, May 1st.
346. Kitasaki, K., Mc.Closkey, A.L. & Woods, W.G.; U.S. Patent, 3,082,234, 1963, Mar. 19th.
347. Davidson, N. & Brown, H.C.; *J. Amer. Chem. Soc.*, 64, 316 (1942).
348. Jenker, H.; German Patent, 1,031,306, Jun. 4th., 1958.
349. Kujoshi, K., Allen, L. et al.; U.S. Patent, 3,082,234, Mar. 19th. 1963.
350. Brauer, D.J. & Stucky, G.D.; *J. Amer. Chem. Soc.*, 91, 5462 (1969).
351. Zakhaskin, L.I. & Cavrilenko, V.V.; *Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk.*, 1391 (1960).
352. Lalancette, J.M., Beauregard, Y & Bhéreur, M.; *Can. J. Chem.*, 48, 1093 (1970).
353. *ibid.*, 49, 2983 (1971).
354. Geiersberger, K. & Galster, H.; *Angew. Chem.*, 64, 81 (1952).
355. Geiersberger, K. & Galster, H.; *Z. Anorg. Allgem. Chem.*, 274, 289 (1953).
356. Tani, H. & Araki, N.; Japanese Patent, 69,27,012, 11th. Nov. 1969.
357. Imaeda, H., Hirabagashi, T., Itoh, K. & Ishii, Y.; *Organometallics in Chem. Synthes.*, 1, 115 (1970 - 1971).
358. Mehrotra, R.C., Gupta, V.D. & Suknani, D.; *Inorg. Chim. Acta. Rev.*, 111 (1968).
359. Allum, K.G., Creighton, J.A., Green, J.H.S., Minkoff, G.J. & Prince, L.J.S.; *Spectrochim. Acta.*, A24, 927 (1968).
360. R. Adams, et al. *Organic Synthes.*, 42, 22 (1962).
361. Bradley, D.C. & Marsh, C.H.; *Chem. & Ind.*, 361 (1967).
362. Adams, D.M. 'Metal Ligand and Related Vibrations' Arnold.
363. Coates, G. 'Organometallic Compounds' Vol. 1 Methuen, 3rd. Edn. 1967.
364. Seidel, A. 'Solubilities of Inorganic and Metal Organic Compounds' 4TH. Edn., Van Nostrand, 1958.

365. Brunauer, S. 'The Adsorption of Gases and Vapours' Volume 1; Physical Adsorption. Oxford, University Press, 1944.
366. Knap, J.E., Leech, R.E., Reid, A.J. & Tamplin, W.S.; Ind. & Eng. Chem., 49, 874 (1957).
367. 'Leaflet on the Handling of Aluminium Alkyl Compounds' Professional Association of the Chemical Industry, 1963.
368. Hay, J.N.; Hooper, P.G. & Robb, J.C.; J. Organometal. Chem., 28, 193 (1971).
369. Latimer, W.M. 'Oxidation Potentials' Prentice Hall, 1952. p.282.
370. Brauer, G. 'Handbook of Preparative Inorganic Chemistry' 2 Vols., English Translation, Academic Press, 1963.
371. Maletsky, L.; Gazz. Chim. Ital., 78, 702 (1948).
372. Haas, A.; Angew. Chem., Int. Edn., 4, 1014 (1965).
373. Hengge, E. & Olbrich, G.; Z. Anorg. Allgem. Chem., 365, 321 (1969).
374. Whittington, J.A.; U.S. Patent 1,549,398. Aug. 11th., 1925.
375. Veller, S.M.; J. Gen. Chem., USSR, 7, 1819 (1937).
376. Schumb, W.C. & Bernard, W.J.; J. Amer. Chem. Soc., 77, 862 (1955).
377. Panckhurst, D.J., Wilkins, C.J. & Craighead, P.W.; J. Chem. Soc., 3395 (1955).
378. Nikitin, B.A. & Ioffe, E.M.; Dokl. Akad. Nauk. SSSR, 60, 595 (1948).
379. Mehrotra, R.C., Gupta, V.D. & Sukhami, D.; J. Inorg. Nucl. Chem., 29, 83 (1967).
380. Johnson, E.B. & Dennis, L.M.; J. Amer. Chem. Soc., 47, 790 (1925).
381. Glockling, F. 'The Chemistry of Germanium' Academic Press, 1969. p. 28 et seq & p. 116 et seq.
382. Pugh, W.; J. Chem. Soc., 2369 (1930).
383. Hahn, H. & Klinger, W.; Z. Anorg. Chem., 260, 97 (1949).
384. Cotton, J.D. & Waddington, T.C.; J. Chem. Soc. (A), 785 (1966).
385. Bastian, E.J. & Martin, R.B.; J. Phys. Chem., 77, 1129 (1973).
386. Charlot, G. & Tremillon, B. 'Chemical Reactions in Solids and Melts' Pergamon Press, 1969. p.237.
387. Fehér, F. 'The Chemistry of Non Aqueous Solvents' Ed. J.J. Lagowski. Academic Press, 1970. Vol. 3, p.219.
388. West, J.R.; Chem. Eng. Progress, 44, 287 (1948).
389. Sage, B.H. & Lacey, W.N. 'Lighter Hydrocarbons, Hydrogen Sulphide and Carbon Dioxide' A.P.I., 1955. p.30.
390. Lewis, L.L. & Fredericks, W.J.; J. Chem. Eng. Data., 13, 482 (1968).
391. Reamer, H.H., Sage, B.H. & Lacey, W.N.; Ind. Eng. Chem., 42, 140 (1950).
392. Gardoso, E.; Gazz. Chim. Ital.; 51, 153 (1921).
393. Giaque, W.F. & Blue, R.W.; J. Amer. Chem. Soc.; 58, 831 (1936).
394. Clarke, E.C.W. & Glew, D.N.; Canad. J. Chem., 48, 764 (1970).
395. Jander, G. & Schmidt, H.; Weiner Chem. Z.; 46, 49 (1943).
396. Jander, G. 'Die Chemie in Wasserähnlichen Lösungsmitteln' Springer-Verlag, Berlin, 1949. Chapter 4.

397. Havriliak, S., Swenson, R.W. & Cole, R.H.; J. Chem. Phys., 23, 134 (1955).
398. Satwalekar, S.D., Butler, L.W. & Wilkinson, J.A.; J. Amer. Chem. Soc., 52, 3045 (1930).
399. Quam, G.N.; J. Amer. Chem. Soc., 47, 103 (1925).
400. Meyer, B. & Smith, J. 'The Chemistry of Liquid Hydrogen Sulphide as a Solvent' 4th. Annual Sulphur Symposium, Calgary, Alberta, 1969.
401. Klemenc, A. & Bankowski, O.; Z. Anorg. Allgem. Chem., 208, 348 (1932).
402. Steel, B.D., McIntosh, D. & Archibald, E.H.; Phil. Trans. Roy. Soc. London (A), 205, 99 (1906). German Trans.: Z. Phys. Chem., 55, 129 (1906).
403. Robinson, P.L. & Scott, W.E.; J. Chem. Soc.; 972 (1932).
404. Landolt-Börnstein, V.; *Ergänzungsband* 1 (1927).
405. West, C.D.; J. Phys. Chem., 39, 493 (1935).
406. Pearson, T.G. & Robinson, P.L.; J. Chem. Soc., 736 (1934).
407. deBoer, J.H. 'The Dynamical Character Of Adsorption' Oxford, 1968, 2nd. Edn.
408. Clusius, K. & Frank, A.; Z. Physik. Chem., B34, 420 (1936).
409. Giaque, W.F. & Blue, R.W.; J. Amer. Chem. Soc., 58, 831 (1936).
410. Kruis, A. & Clusius, K.; Z. Physik. Chem., B38, 156 (1938).
411. Clusius, K. & Frank, A.; Naturwiss., 24, 62 (1936).
412. Clusius, K. & Frank, A.; Z. Physik. Chem., B42, 395 (1939).
413. Gattow, G. & Krebs, B.; Z. Anorg. Allgem. Chem., 325, 15 (1963).
414. Estreicher, T. & Schnerr, A.; Bull. Acad. Cracow, A., 345 (1910).
415. Stavely, L.A.K. & Tupmann, W.I.; J. Chem. Soc., 3597 (1950).
416. Beckmann, E. & Waentig, P.; Z. Anorg. Allgem. Chem., 67, 17 (1910).
417. Beckmann, E. & Weber, W.; Z. Anorg. Allgem. Chem., 74, 297 (1912).
418. Denbigh, K.G.; Trans. Farad. Soc., 36, 936 (1940).
419. Wilkinson, J.A.; Chem. Rev., 8, 237 (1931).
420. Jander, G.; Naturwis., 32, 169 (1945).
421. Skilling, W.T.; Amer. Chem. J., 26, 383 (1901).
422. Blitz, W. & Keunecke, E.; Z. Anorg. Allgem. Chem., 147, 171 (1925).
423. Guest, H.P.; Iowa State Coll. J. Sci., 8, 197 (1933).
424. Ralson, A.W. & Wilkinson, J.A.; J. Amer. Chem. Soc., 50, 258 (1928).
425. Walker, J.W., McIntosh, D. & Archibald, E.; J. Chem. Soc., 85, 1098, (1904).
426. Meints, R.E. & Wilkinson, J.A.; J. Amer. Chem. Soc., 51, 803 (1929).
427. Borgeson, R.W. & Wilkinson, J.A.; J. Amer. Chem. Soc., 51, 1453 (1929).
428. King, W.B. & Wilkinson, J.A.; J. Amer. Chem. Soc., 54, 3070 (1932).
429. Ralston, A.W. & Wilkinson, J.A.; J. Amer. Chem. Soc., 50, 2160 (1928).
430. Chipman, H.R. & McIntosh, D.; Proc. Trans. Novascotian Inst. Sci., 16, 189 (1928).

431. Lineken, E.E. & Wilkinson, J.A.; J. Amer. Chem. Soc., 62, 251(1940).
432. Antony, U. & Magri, G.; Gazz. Chim. Ital., 35, 206(1905).
433. Quam, G.N.; J. Amer. Chem. Soc., 47, 989(1925).
434. Heisig, G.B.; J. Amer. Chem. Soc., 60, 359(1938).
435. West, C.D.; Z. Krist., 88, 97(1934).
436. Lineken, E.E.; Rept. New. Engl. Assoc. Chem. Teachers, 42, 198(1941).
437. McDaniel, D.H. & Evans, W.G.; Inorg. Chem., 5, 2180(1966).
438. Cotton, J.D. & Waddington, T.C.; J. Chem. Soc.(A), 789(1966).
439. *ibid.*, 793(1966).
440. Mickelsen, J.R., Norris, T.H. & Smith, R.C.; Inorg. Chem., 5, 911(1966).
441. Mickelsed, J.R. & Norris, T.H.; Inorg. Chem., 5, 917(1966).
442. Smith, J.J., Jensen, D. & Meyer, B.; J. Chem. Eng. Data, 15, 144(1970).
443. Meyer, B. & Smith, J.J. 'The Chemistry of Liquid Hydrogen Sulphide as a Solvent' 4th. Annual Sulphur Symposium, Calgary, Alberta, 1969.
444. Wiewiorowski, T.K.; Endeavour, 29, 9(1970).
445. Terres, E. & Vollmer, W.; Petroleum Z., 31, 1(1935).
446. Bernard, G.G.; U.S. Patent 3,163,213. Dec. 29th., 1964.
447. Bond, D.C.; U.S. Patent 3,186,482. Jun. 1st., 1965.
448. Keller, P.C.; J. Chem. Soc.(D), 209(1969).
449. Sharp, K. & Margrave, J.L.; Inorg. Chem., 8, 2655(1969).
450. Lineken, E.E.; Amer. Chem. Soc., 68, 1966(1946).
451. *ibid.*, 69, 467(1947).
452. Fehér, F. & Kruse, W.; Z. Anorg. Allgem. Chem., 293, 302(1957).
453. Wartik, T. & Apple, E.F.; J. Amer. Chem. Soc., 80, 6155(1958).
454. Schmidt, M. & Talsky, G.; Chem. Ber., 92, 1526(1959).
455. Barrer, R.M. & Denny, P.J.; J. Chem. Soc., 971(1961).
456. 'Air Toxicological Review No. 8; Hydrogen Sulphide' Amer. Petr. Inst., Dept. of Safety, Mar. 1948.
457. Bice, W.O., Prange, F. & Weis, R.E.; Ind. Eng. Chem., 44, 2497(1952).
458. Hudgins, C.M.; Materials Protection, 8, 41(1969).
459. Tisinai, G.F. & Samans, C.H.; Petrol. Refiner, 38, 153(1959).
460. Mrowec, S., Wallischowa, K. & Werber, T.; Roczniki Chem., 34, 337(1960).
461. Dumail, R., Ribes, M. & Philippot, E.; C.R. Acad. Sci.(B), 271, 1456(1970).
462. Krebs, B. & Pohl, S.; Z. Naturforsch., B26, 853(1971).
463. LeBlanc, A., Danot, M. & Ronxel, J.; Bull. Soc. Chim. France, 87(1969).
464. Ribes, M. & Maurin, M.; Rev. Chim. Miner., 7, 75(1970).
465. Philippot, E., Ribes, M. & Maurin, M.; Rev. Chim. Miner., 8, 99(1971).
466. Dumail, R., Ribes, M. & Philippot, E.; C.R. Acad. Sci., C272, 303(1971).

467. Jumas, J.C., Ribes, M. & Philippot, E.; C.R. Acad. Sci., C273, 1356(1971).
468. Jumas, J.C., Ribes, M., Philippot, E. & Maurin, M.; C.R. Acad. Sci., C272, 1811(1971).
469. Chivers, T. & Drummond, I.; Chem. Soc. Rev., 2, 233(1973).
470. Sheka, I.A.; Chaus, I.S. & Mityureva, T.T. 'The Chemistry of Gallium' Elsevier, 1966. Chapter 10.
471. Malofeeva, G.I., Loginov, A.A. & Rudnev, N.A.; Zh. Anal. Khim., 23, 1291(1968).
472. Chaus, I.S.; Kotova, L.B. & Sheka, I.A.; Isv. Akad. Nauk. SSSR, Neorg. Mater., 5, 2110(1969).
473. Chaus, I.S., Kisilinskaya, G.E. & Sheka, I.A.; Isv. Akad. Nauk. SSSR, Neorg. Mater., 6, 129(1970).
474. Sarkisov, E.S., Lidin, R.A. & Krymskaya, E.B.; Isv. Akad. Nauk. SSSR, Neorg. Mater., 6, 281(1970).
475. Putkaradze, N.V.; Soobsch. Akad. Nauk. Gruz, SSSR, 41, 559(1966).
476. Kodama, K. 'Methods of Quantitative Inorganic Analysis' Interscience 1963.
477. Furman, N.H. (Ed.) 'Standard Methods of Chemical Analysis' 6th. Edn., Van Nostrand,
478. Vogel, A.I. 'A Textbook of Quantitative Inorganic Analysis' 3rd. Edn Longmans, 1961.
479. Emmett, P.H.; Catalysis, 1, 31(1954).
480. Innes, W.B. 'Experimental Methods in Catalytic Research' Academic Press, 1968. Chapter 2.
481. Lippens, B.C., Linsen, B.G. & deBoer, J.H.; J. Catal., 3, 32(1964).
482. deBoer, J.H. & Lippens, B.C.; J. Catal., 3, 38(1964).
483. Lippens, B.C. & deBoer, J.H.; J. Catal., 3, 44(1964).
484. deBoer, J.H., Van der Heuvel, A. & Linsen, B.G.; J. Catal., 3, 268(1964)
485. Lippens, B.C. & deBoer, J.H.; J. Catal., 319(1965).
486. deBoer, J.H., Linsen, B.G. & Osinga, Th.J.; J. Catal., 4, 643(1965).
487. deBoer, J.H., Linsen, B.G., Van der Plas, Th. & Zondervan, G.J.; J. Catal., 4, 649(1965).
488. Broekhoff, J.C.P., Linsen, B.G. & Meijen, A.J.; J. Catal., 7, 135(1965).
489. Broekhoff, J.C.P. & deBoer, J.H.; J. Catal., 2, 8(1967).
490. *ibid.*, 2, 15(1967).
491. *ibid.*, 10, 153(1968).
492. *ibid.*, 10, 368(1968).
493. *ibid.*, 10, 377(1968).
494. *ibid.*, 10, 391(1968).
495. deBoer, J.H., Linsen, B.G., Broekhoff, J.C.P. & Osinga, Th.J.; J. Catal., 11, 46(1968).
496. Radzy, F. & Sellevold, E.J.; J. Colloid Interface Sci., 39, 367(1972).

497. *ibid.*, 39, 379(1972).
498. Mikhail, R.Sh., Brunauer, S. & Bodor, E.E.; *J. Colloid Interface Sci.*, 26, 45(1968).
499. *ibid.*, 26, 54(1968).
500. Brunauer, S.; *J. Colloid Interface Sci.*, 39, 435(1972).
501. *ibid.*, 41, 612(1972).
502. Dubinin, M.M.; *Zh. Fiz. Khim.*, 36, 1806(1962).
503. Dubinin, M.M., Zhukovskaya, E.G. & Murdmaa; *Zh. Fiz. Khim.*, 37, 426(1963).
504. Dubinin, M.M.; *J. Colloid Interface Sci.*, 23, 487(1967).
505. Bering, B.P., Zhukovskaya, E.G., Rakhmukov, B.Kh. & Serpinski, V.V.; *Isv. Akad. Nauk. SSSR, Ser. Khim.*, 1656(1967).
506. *ibid.*, 1662(1967).
507. Dollimore, D. & Heal, G.R.; *Nature*, 208, 1092(1965).
508. Turkevich, J.; *Catal. Rev.*, 1, 1(1967).
509. Turkevich, J., Murakami, Y., Fumio, N. & Cisarowski, S.; in: 'Kinetics and Catalysis' Weisz, P.B. & Hall, W.K. (Eds.); *Chem. Eng. Prog. Symp. Ser.*, 63, 75(1967).
510. Turkevich, J. & Ono, Y.; *Adv. Catal.*, 20, 135(1969).
511. Turkevich, J. & Ono, Y.; *Adv. Chem. Ser.*, 315(1971).
512. Venuto, P.B. & Landis, P.S.; *Adv. Catal.*, 18, 259(1968).
513. Rieckert, L.; *Adv. Catal.*, 21, 281(1970).
514. Weisz, P.B.; *Chemtec.*, 498(1973).
515. Ciapetta, F.G., Dobres, R.M. & Baker, R.W.; *Catalysis*, 6, 495(1958). (Ed. P.H. Emmett).
516. Steiner, H.; *Catalysis*, 4, 529(1956). (Ed. P.H. Emmett).
517. Condon, F.E.; *Catalysis*, 6, 43(1958). (Ed. P.H. Emmett).
518. McKinley, J.B.; *Catalysis*, 5, 405(1957). (Ed. P.H. Emmett).
519. Schuman, S.C. & Shalit, H.; *Catal. Rev.*, 4, 245(1970).
520. Kirkpatrick, W.J.; *Adv. Catal.*, 3, 329(1951).
521. Bourne, K.H., Holmes, P.D. & Pitkethly, R.C. 'The Selectivity of Sulphided Nickel Catalysts' Paper read at the 3rd. Int. Cong. on Catalysis, Amsterdam, 20 - 25th., July 1964.
522. Wilson, R.L., Kemball, C. & Galwey, A.K.; *Trans. Farad. Soc.*, 58, 583(1962).
523. Wilson, R.L. & Kemball, C.; *J. Catal.*, 3, 426(1964).
524. Kieran, P. & Kemball, C.; *J. Catal.*, 4, 380(1965).
525. *ibid.*, 4, 394(1965).
526. Seshadri, K.S.; Massoth, F.E. & Petrakis, L.; *J. Catal.*, 19, 95(1970).
527. Farlow, M.W., Lazier, W.A. & Signaigo, F.K.; *Ind. & Eng. Chem.*, 42, 2547(1950).
528. Boivin, J.L. & McDonald, R.; *Can. J. Chem.*, 33, 1281(1955).

- 529. Spillane, P.X.; British Patent 642,726, Sept. 13th. 1950;
U.S. Patent, 2,559,325, July 3rd. 1951.
- 530. (Inst. of Synthetic Org. Chem. Res.); Japanese Patent
153,805 Nov. 20th. 1942.
- 531. Nematsu, T.; Suzuki, M. & Hashimoto, H.; J. Chem. Soc. Japan;
Chem. & Ind. Chem., 24(1973).
- 532. Kazansky, B.A.; Isagulyants, G.V.; Rozengart, M.I.; Dubinsky, Yu.G. &
Kovalenko, L.I.; Paper 92, 5th. Congress of Catalysis . Vol. 2 ,
1277(1972).

APPENDICES 1 TO 5 ; X RAY POWDER PATTERN TABULATIONS

APPENDIX A1 . Diffraction Data for 13X Zeolite.

$d(\text{\AA}); (I/I_0)$

Found	Reported	(60, p.47)
14.52 (100)	14.46 (100)	
8.85 (50)	8.85 (18)	
7.70 (50)	7.54 (12)	
5.71 (50)	5.73 (18)	
4.85 (30)	4.81 (5)	
4.42 (50)	4.42 (9)	
	4.23 (1)	
3.95 (30)	3.95 (4)	
3.84 (50)	3.81 (21)	
	3.77 (3)	
	3.61 (1)	
	3.50 (1)	
3.32 (50)	3.34 (8)	
	3.25 (1)	
3.03 (20)	3.05 (4)	
3.00 (20)	2.94 (9)	
2.86 (50)	2.88 (19)	
2.78 (30)	2.79 (8)	

APPENDIX A2 Hydrothermal Preparations in Hydrogen Sulphide

Experiment 5.1		Experiments 5.2 & 5.3		Experiment 5.4	
$d(\text{\AA})$	(I/I_0)	$d(\text{\AA})$	(I/I_0)	$d(\text{\AA})$	(I/I_0)
2.93	(vvw)	3.67	(20)	3.58	(20)
		3.31	(5)	3.33	(30)
		3.06	(5)	2.97	(100)
		2.98	(100)	2.61	(20)
		2.30	(70)	2.51	(10)
		1.98	(60)	2.23	(50)
		1.79	(50)	1.97	(10)
		1.52	(10)	1.84	(5)
		1.48	(20)	1.81	(5)
		1.45	(1)	1.78	(5)
		1.40	(30)	1.44	(5)
		1.29	(10)	1.40	(5)
		1.26	(20)		
		1.24	(20)		
		1.12	(5)		
		1.10	(5)		
		1.05	(5)		
Experiment 5.5		Experiment 5.6		Experiment 5.7	
$d(\text{\AA})$	(I/I_0)	$d(\text{\AA})$	(I/I_0)	$d(\text{\AA})$	(I/I_0)
(Dark Phase)		9.22	(10)	5.75	(5)
		7.60	(15)	5.68	(30)
3.19	(vvw)	6.92	(15)	4.86	(30*)
2.96	(vvw)	5.77	(25*)	4.73	(30)
2.79	(vvw)	5.44	(15)	4.43	(5*)
		5.33	(15)	4.28	(5*)
(White Phase)		4.88	(20)	3.46	(20*)
		4.52	(25)	3.33	(20*)
3.56	(40)	4.30	(5)	3.23	(100)
3.30	(10)	4.00	(10)	3.13	(80*)
2.96	(100)	3.91	(5*)	3.06	(30*)
2.60	(10)	3.86	(80*)	2.98	(80)
2.24	(80)	3.60	(20*)	2.88	(60)
1.94	(60)	3.42	(60*)	2.83	(80)
1.78	(60)	3.35	(20*)	2.66	(20)
1.48	(10)	3.23	(100*)	2.56	(10)
1.40	(20)	3.08	(50)	2.49	(10)
		2.98	(50)	2.20	(30)
		2.90	(60)	2.15	(10)
		2.85	(50*)	2.09	(10)
		2.62	(50)	2.06	(5)
		2.51	(15)	2.02	(10)
		2.43	(30)	1.92	(10*)
		2.13	(30*)	1.88	(50)
					(cont.)
					1.82 (20*)
					1.77 (10*)
					1.75 (5)
					1.69 (60)
					1.64 (30*)
					1.61 (10)
					1.58 (30)

* Broken Line

Experiment 5.8

Experiment 5.9

(Blank available from 5.7)

Blank *

Ex-Reactor

Water-Washed

 $d(\text{\AA}) (I/I_0)$ $d(\text{\AA}) (I/I_0)$ $d(\text{\AA}) (I/I_0)$ $d(\text{\AA}) (I/I_0)$

9.36 (5)
 6.80 (10)
 6.22 (30)
 5.76 (20)
 5.33 (10)
 4.70 (10)
 4.49 (30)
 4.29 (5)
 4.03 (30)
 3.50 (10)
 3.34 (5)
 3.22 (100)
 3.17 (5)
 3.06 (10)
 2.98 (80)
 2.89 (80)
 2.83 (50)
 2.72 (50)
 2.50 (50)
 2.39 (20)
 2.34 (10)
 2.25 (10)
 2.19 (20)
 2.12 (5)
 2.10 (40)
 1.92 (10)
 1.86 (40)
 1.77 (5)
 1.74 (5)
 1.69 (60)
 1.61 (40)
 1.58 (40)

5.85 (diff)

3.27 (diff)

3.14 (diff)

2.68 (diff)

1.89 (diff)

7.63 (5)
 6.74 (50)
 6.01 (20)
 5.63 (15)
 4.93 (20)
 4.84 (10)
 4.38 (20)
 4.25 (20)
 4.11 (20)
 3.79 (5)
 3.70 (15)
 3.58 (40)
 3.27 (5)
 3.25 (20)
 3.10 (60)
 2.97 (100)
 2.89 (5)
 2.82 (50)
 2.76 (60)
 2.60 (20)
 2.55 (15)
 2.47 (30)
 2.32 (15)
 2.28 (5)
 2.24 (70)
 2.19 (60)
 2.09 (20)
 2.04 (5)
 2.00 (20)
 1.97 (30)
 1.91 (20)
 1.84 (5)
 1.81 (5)
 1.78 (20)
 1.77 (10)
 1.71 (10)
 1.68 (15)
 1.57 (5)
 1.55 (5)
 1.53 (5)
 1.48 (10)
 1.47 (10)
 1.45 (5)
 1.43 (15)
 1.33 (5)
 1.32 (5)
 1.29 (5)
 1.26 (10)
 1.23 (10)

8.94 (5)
 6.57 (80)
 5.07 (60)
 4.77 (50)
 2.75 (100)
 2.54 (20)
 2.16 (30)
 1.99 (50)
 1.90 (60)
 1.83 (40)
 1.71 (1)
 1.66 (5)
 1.60 (1)
 1.57 (20)
 1.42 (5)
 1.29 (15)
 1.26 (10)
 1.21 (20)

* Before addition of NaSH.

Experiment 5.10

Control*	Ex-Reactor	Water-Washed
$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$
9.02 (100)	8.65 (100)	11.57 (50)
6.63 (5)		8.54 (100)
		6.65 (5)
		5.83 (10)
4.42 (5)	4.27 (50)	4.28 (60)
	4.05 (1)	
	3.90 (1)	
3.24 (5)	3.21 (20)	3.24 (20)
3.13 (5)	3.12 (60)	3.13 (50)
		3.02 (5)
2.84 (60)	2.82 (10)	2.81 (5)
2.74 (60)	2.73 (60)	2.74 (80)
		2.58 (5)
	2.45 (5)	2.44 (20)
	2.31 (10)	
	2.28 (20)	
	2.19 (1)	
	2.14 (10)	
2.00 (50)	2.01 (20)	2.14 (20)
		2.02 (30)
		1.90 (5)
	1.86 (20)	1.87 (5)
		1.85 (5)
	1.82 (30)	1.82 (20)
		1.72 (5)
		1.69 (5)

(Blank available
from 5.9)

* All very diffuse

Experiment 5.11			
Blank *	Control	Ex-Reactor	Water-Washed
$a(\text{\AA}) (I/I_0)$	$a(\text{\AA}) (I/I_0)$	$a(\text{\AA}) (I/I_0)$	$a(\text{\AA}) (I/I_0)$
	9.17 (20)		
	7.63 (30)	7.81 (100)	
	6.90 (30)	6.69 (10)	
	6.46 (10)	5.97 (20)	
	5.51 (10)	4.84 (20)	
	4.53 (100)	4.52 (40)	
		4.31 (10)	
		4.19 (5)	
	4.08 (80)	3.97 (40)	
		3.55 (5)	
		3.43 (5)	
3.20(diff)	3.25 (50)	3.21 (10)	3.23(diff)
		3.13 (10)	
		3.03 (5)	
	3.06 (50)	2.96 (60)	
	2.92 (50)	2.85 (30)	
2.70(diff)		2.71 (5)	
		2.65 (10)	2.69(diff)
		2.50 (5)	
		2.38 (5)	
		2.34 (5)	
		2.25 (10)	
		2.20 (5)	
		2.08 (5)	
		1.98 (5)	
		1.93 (10)	
1.89(diff)		1.91 (10)	1.90(diff)
		1.85 (10)	
		1.82 (10)	

* Before addition of NaSH

Experiment 5.12

Blank*	Control	Ex-Reactor	Water-Washed & Methanol-Washed
$d(\text{\AA})$ (I/I ₀)	$d(\text{\AA})$ (I/I ₀)	$d(\text{\AA})$ (I/I ₀)	$d(\text{\AA})$ (I/I ₀)
	10.70 (100)	11.95 (80)	11.68 (100)
		10.85 (60)	10.79 (100)
		9.89 (100)	9.70 (60)
		9.08 (100)	8.62 (50)
		8.43 (60)	8.35 (80)
		7.89 (50)	7.89 (50)
5.98 (vw)	6.66 (60)	6.22 (10)	6.10 (5)
	6.19 (20)	5.95 (10)	5.78 (5)
		5.54 (30)	5.52 (30)
	5.23 (50)	5.14 (50)	5.11 (20)
		4.85 (10)	4.73 (5)
		4.64 (50)	4.59 (20)
		4.41 (5)	4.38 (5)
	4.30 (80)	4.25 (20)	4.22 (20)
		4.12 (5)	Then as Ex-Reactor Sample.
		3.91 (10)	
		3.81 (5)	
		3.80 (5)	
	3.60 (20)	3.55 (5)	
	3.48 (10)	3.37 (10)	
	3.33 (80)	3.30 (10)	
	3.10 (5)	3.21 (10)	
	3.05 (20)	3.05 (5)	
	2.91 (5)	2.94 (10)	
	2.83 (10)	2.86 (10)	
	2.75 (10)	2.72 (5)	
	2.71 (40)	2.55 (10)	
	2.60 (40)	2.45 (5)	
	2.39 (30)	2.40 (10)	
	2.30 (20)	2.35 (5)	
		2.31 (5)	
	2.22 (10)	2.27 (5)	
		2.20 (5)	
	2.14 (10)	2.14 (5)	
	2.10 (20)		
	2.06 (10)	2.05 (10)	
	2.03 (5)		
	2.00 (20)	1.88 (5)	
	1.87 (10)		
	1.83 (10)	1.82 (10)	
	1.79 (20)	1.78 (5)	
	1.73 (10)		

* Before addition of $\text{Et}_4\text{N}^+\text{SH}^-$.

Experiment 5.13

No Lines present on Blank.

<u>Control</u>	<u>Ex-Reactor</u>	<u>Water-Washed & Methanol-Washed</u>
$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$
13.00 (100)	11.20 (20)	
10.29 (60)	10.09 (100)	
9.62 (60)	9.60 (80)	
	8.93 (30)	
8.31 (80)	8.50 (100)	
7.03 (30)	7.86 (60)	
6.42 (60)	6.32 (20)	6.52(diffuse)
	6.09 (5)	
5.90 (10)	5.87 (10)	
5.61 (10)	5.42 (1)	
5.34 (10)	5.27 (5)	
5.11 (20)	5.04 (10)	
4.67 (20)	4.90 (50)	
4.44 (10)	4.75 (30)	
	4.55 (1)	
4.28 (10)	4.24 (10)	
4.08 (20)	4.08 (1)	
	3.93 (50)	
	3.70 (30)	
3.52 (20)	3.65 (20)	
3.47 (20)	3.36 (50)	
3.22 (10)	3.13 (10)	
3.15 (10)	3.02 (20)	
2.99 (5)		
2.95 (5)	2.88 (1)	
2.83 (30)	2.81 (5)	
	2.57 (10)	
	2.46 (10)	
	2.37 (10)	
	2.08 (10)	
	2.05 (10)	

Experiment 5.14

Blank*	Control	Ex-Reactor	Water-Washed
$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$
		12.33 (50)	12.46 (80)
	11.46 (30)		11.64 (80)
11.09 (60)	11.31 (80)	10.94 (40)	
9.86 (100)		9.86 (100)	9.94 (60)
		9.05 (80)	9.17 (60)
	8.58 (100)	8.57 (60)	8.47 (100)
			7.90 (50)
			7.53 (5)
			7.23 (5)
			6.40 (10)
6.13 (5)			6.07 (5)
5.90 (5)		5.87 (5)	5.77 (1)
5.49 (10)	5.44 (80)	5.50 (20)	5.52 (10)
			5.28 (20)
5.15 (20)		5.17 (20)	5.11 (5)
4.80 (20)	4.87 (20)	4.80 (10)	4.73 (10)
4.50 (20)	4.66 (20)	4.50 (10)	4.59 (20)
		4.49 (5)	4.38 (5)
4.29 (20)	4.31 (5)	4.30 (5)	4.22 (10)
4.08 (50)	4.11 (5)	4.06 (10)	4.07 (5)
			3.94 (1)
3.77 (30)	3.80 (10)	3.79 (5)	3.74 (20)
		3.69 (5)	3.55 (10)
3.41 (20)			3.35 (1)
	3.28 (20)	3.28 (10)	3.21 (5)
3.16 (10)		3.19 (5)	3.12 (5)
3.10 (10)		3.11 (5)	3.07 (5)
3.00 (5)	2.93 (20)		2.92 (20)
2.81 (5)	2.83 (20)		2.86 (5)
2.71 (1)			
2.65 (1)			
2.51 (5)			
2.36 (10)			
2.19 (10)			
2.04 (5)			

*After addition of $\text{Et}_4\text{N}^+\text{SH}^-$.

Experiment 5.15

Blank*	Control	Ex-Reactor	Water-Washed
$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$
	13.19 (5)		
	10.91 (10)	10.67 (100)	
9.72 (10)	9.72 (50)	9.74 (20)	
8.30 (5)	8.88 (30)	8.33 (50)	8.33 (medium)
7.20 (5)	7.31 (5)	7.75 (5)	
6.84 (20)	6.76 (10)	6.63 (10)	
6.54 (50)	6.53 (20)		
6.16 (30)	6.19 (20)	5.97 (10)	
5.42 (100)	Then as blank sample.	5.58 (10)	
		5.24 (10)	
		5.07 (10)	
4.85 (50)		4.81 (20)	
		4.70 (5)	
4.24 (50)		4.39 (10)	
4.12 (20)		4.11 (10)	
3.87 (10)		3.85 (20)	
3.65 (5)		3.70 (5)	
3.53 (80)		3.60 (5)	
3.42 (20)			
3.27 (50)		3.29 (20)	
3.13 (10)			
3.02 (50)			
2.95 (50)			
2.72 (10)			
2.66 (5)			

*After addition of $\text{Et}_4\text{N}^+\text{SH}^-$.

Experiment 5.16

Blank*	Control	Ex-Reactor	Water-Washed
$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$
	13.07 (10)	13.12 (10)	
	10.91 (10)	10.98 (100)	
9.62 (5)	9.71 (20)	10.05 (100)	9.82 (5)
8.94 (5)	8.84 (20)	9.60 (60)	
8.30 (5)	8.34 (5)	8.98 (60)	8.50 (100)
		8.66 (50)	
6.76 (5)	6.76 (5)	7.86 (50)	
6.51 (10)	6.56 (5)	7.04 (5)	
		6.39 (30)	
6.09 (5)	6.09 (10)	6.09 (5)	
5.79 (5)	5.85 (10)	5.86 (10)	
5.41 (100)	5.40 (100)	5.48 (50)	
4.96 (10)	Then as blank sample.	5.24 (15)	4.90 (50)
		4.99 (5)	
		4.76 (10)	
		4.31 (5)	
4.24 (80)		4.12 (10)	4.23 (5)
4.14 (5)		3.90 (5)	
3.90 (5)		3.79 (5)	
3.63 (5)		3.69 (10)	
3.47 (80)		3.45 (5)	
3.28 (20)		3.38 (20)	
3.12 (10)		3.31 (5)	
3.02 (5)		3.17 (10)	
2.94 (60)		3.03 (5)	
2.81 (1)		2.88 (5)	
2.72 (1)		2.83 (5)	
2.64 (1)			
2.45 (1)			
2.40 (1)			
2.27 (20)			
2.16 (20)			
2.11 (10)			
2.03 (20)			
2.00 (10)			
1.93 (5)			
1.86 (1)			
1.76 (10)			

*After addition of $\text{Et}_4\text{N}^+\text{SH}^-$.

Experiment 5.17

Blank*	Control	Ex-Reactor	Water-Washed	
			Green Phase	Yellow Phase
$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$
12.81 (20)	12.32 (5)	12.68 (12)		
11.79 (30)				
10.83 (5)		10.95 (20)		
9.76 (10)	9.71 (50)	9.81 (80)		
	8.97 (100)	8.97 (60)		
8.38 (10)	8.31 (50)			
8.30 (5)				
7.28 (30)		7.85 (1)		
6.81 (10)	6.87 (5)	6.70 (100)	6.95 (1)	
6.56 (100)	6.54 (5)			
6.13 (20)	6.14 (5)			
5.80 (10)	5.82 (20)	5.92 (80)	5.72 (50)	5.75 (vvw)
5.56 (5)	5.54 (5)	5.60 (5)		
5.26 (1)	5.43 (60)			
	5.23 (80)	5.24 (1)		
	5.12 (60)			
4.94 (100)		4.83 (10)		
4.62 (10)	4.55 (5)			
4.51 (5)	4.46 (5)			
4.39 (5)	4.35 (10)			
4.14 (100)	4.25 (10)			
	4.12 (5)	4.19 (60)		
	4.05 (5)	4.10 (5)		
3.92 (80)		4.00 (1)		
	3.85 (5)		3.84 (100)	3.81 (vvw)
3.67 (10)	3.72 (10)	3.76 (1)		
3.66 (60)	3.65 (5)			
3.53 (60)	3.54 (30)	3.56 (80)		
3.41 (80)	3.42 (5)	3.43 (30)	3.47 (20)	
		3.36 (1)		
3.28 (100)	3.31 (5)	3.30 (1)	3.33 (50)	3.33 (vvw)
	3.22 (5)	3.17 (10)	3.22 (50)	
3.10 (80)	3.15 (5)	3.11 (80)		
	3.04 (20)	3.07 (5)		
2.99 (5)	2.95 (5)	2.96 (10)		
2.94 (10)				
2.88 (30)		2.88 (30)	2.88 (10)	2.88 (vvw)
2.80 (1)		2.81 (1)		
2.73 (20)		2.77 (1)		
2.66 (1)		2.71 (20)		
2.57 (10)		2.65 (50)	2.63 (1)	
2.45 (10)				
2.36 (5)		2.34 (30)		
2.32 (1)		2.29 (5)		
2.21 (5)		2.25 (5)		
		2.19 (5)		
2.16 (20)		2.15 (5)		
2.06 (20)		2.08 (1)		
2.00 (20)		2.00 (5)		
		1.97 (10)		
		1.93 (60)		

*After addition of NaSH & $\text{Et}_4\text{N}^+\text{SH}^-$

Base Solubility Tests on Materials from the Hydrothermal Preparations.

Expt. 5.11	Expt. 5.12	Expt. 5.13	Expt. 5.14	Expt. 5.15
$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$
6.2 (w)	10.64 (m) 5.40 (w)		6.11 (w) 5.00 (vw) 3.42 (vw)	4.95 (vw) 3.84 (w) 3.48 (vw) 3.24 (vw) 3.04 (vw)
3.1 (w)	3.14 (vw)		2.97 (vw) 2.73 (vw) 2.49 (vw) 2.29 (vw)	2.96 (m) 2.66 (vw) 2.47 (vw) 2.31 (vw)
2.6 (w)			2.10 (vw) 1.79 (vw) 1.74 (vw)	1.91 (vw) 1.86 (vw) 1.75 (vw)
1.9 (w)	1.81 (w)	2.04 (vvw) 1.76 (vw)		
	Expt. 5.16		Expt. 5.17	
	$d(\text{\AA}) (I/I_0)$		$d(\text{\AA}) (I/I_0)$	
	14.41 (100) 8.76 (50) 7.56 (30) 5.72 (60)		14.41 (100) 8.82 (50) 7.48 (30) 6.95 (60) 5.69 (40) 5.35 (50) 4.80 (10) 4.56 (10) 4.38 (10) 4.20 (5) 3.94 (5) 3.80 (50) 3.75 (2) 3.61 (2) 3.41 (5) 3.34 (40) 3.25 (2)	
	4.41 (20) 3.95 (10) 3.80 (80)			
	3.33 (60) 3.05 (1) 2.94 (5) 2.88 (20) 2.79 (5) 2.73 (5) 2.66 (5)		2.89 (30) 2.78 (5) 2.72 (5) 2.65 (5)	

Reaction between Et_2AlSEt , $\text{Si}(\text{SEt})_4$ and NaSH .

$d(\text{\AA}) (I/I_0)$
3.61 (20)
2.97 (100)
2.24 (50)
1.98 (20)
1.79 (20)

Experiment 5.18		Experiment 5.19	
Ex-Reactor	Methanol-Washed	Ex-Reactor & Methanol-Washed	Water-Washed
$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$
12.50 (10)	12.48 (10)	11.79 (20)	
	10.02 (1)	6.89 (80)	
	7.98 (1)	6.01 (100)	6.01 (100)
	7.30 (1)	5.81 (1)	
6.70 (100)	6.75 (100)	4.22 (50)	
	6.50 (1)	3.77 (1)	
6.25 (60)	6.18 (80)	3.62 (50)	
5.92 (5)	5.95 (60)	3.53 (30)	
5.75 (10)		3.44 (1)	
5.52 (80)		3.27 (10)	
5.24 (10)		3.17 (20)	
4.91 (30)	4.84 (50)	2.99 (80)	2.99 (50)
4.77 (5)		2.78 (30)	
4.53 (60)		2.72 (50)	2.72 (50)
	4.37 (5)	2.67 (20)	
4.27 (30)	4.23 (5)	2.62 (50)	
	4.15 (5)	2.55 (30)	
	4.11 (1)	2.47 (1)	
3.81 (1)		2.41 (50)	
3.65 (10)		2.38 (50)	
3.57 (1)	3.56 (20)	2.28 (10)	
3.42 (1)	3.42 (5)	2.19 (30)	
		2.17 (30)	
3.28 (10)	3.27 (5)	2.05 (1)	
3.14 (60)	3.13 (20)	2.01 (5)	
3.07 (5)		1.99 (5)	
2.99 (60)	3.00 (60)	1.97 (5)	
2.90 (50)	2.90 (30)	1.95 (10)	
2.82 (60)		1.89 (30)	
	2.79 (1)	1.85 (1)	
	2.75 (1)	1.83 (5)	
2.71 (50)	2.71 (10)	1.81 (5)	1.81 (80)
	2.61 (30)	1.75 (1)	
2.56 (50)	2.56 (30)	1.72 (5)	1.72 (60)
	2.46 (1)		
	2.40 (10)		
2.28 (5)	2.26 (5)		
	2.19 (10)		
	2.10 (1)		
	2.05 (1)		
1.99 (10)	1.98 (1)		
1.94 (20)	1.94 (10)		
	1.89 (10)		
1.68 (5)			

Experiment 5.20		Experiment 5.21	
Ex-Reactor	Methanol & Water-Washed	Ex-Reactor	Methanol & Water-Washed
$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$	$d(\text{\AA}) (I/I_0)$
6.65 (80)	9.16 (10*)	10.02 (100)	
3.58 (5)	6.65 (80)	9.47 (100)	9.85 (10)
3.32 (10)	5.32 (1*)	8.87 (50)	9.24 (20)
3.26 (50)	3.32 (20)	7.81 (100)	7.74 (10)
3.13 (30)	3.25 (60)	6.95 (1*)	6.64 (30)
2.96 (60)	3.13 (50)	6.27 (60)	
2.91 (5)		5.84 (30)	
2.75 (100)	2.75 (100)	5.56 (20)	
2.54 (10)	2.54 (30)	5.38 (10)	5.22 (1)
2.24 (30)	2.39 (5)	5.21 (30)	4.96 (1)
2.15 (50)	2.15 (50)	4.99 (50)	4.63 (5)
1.99 (50)	1.99 (60)	4.73 (50)	4.06 (20)
1.98 (5)		3.95 (60)	3.91 (5)
1.90 (50)	1.90 (60)	3.85 (60)	3.86 (100)
1.83 (30)	1.82 (50)	3.69 (30)	
Then as washed	1.71 (10)	3.62 (10)	3.57 (10)
samples.	1.65 (10*)	3.44 (20)	3.50 (50)
	1.63 (5)	3.34 (80)	3.34 (30)
	1.59 (30)	3.21 (20)	3.22 (60)
	1.57 (50)	3.10 (30)	3.10 (30)
	1.52 (5)	2.99 (20)	
	1.44 (5)	2.92 (1)	2.96 (1)
	1.42 (10)	2.86 (10)	2.85 (30)
	1.37 (50)	2.78 (10)	2.80 (1)
	1.33 (1)	2.67 (5)	2.70 (1)
	1.31 (1)	2.60 (5)	2.62 (20)
	1.27 (1)	2.55 (10)	2.57 (5)
	1.25 (50)	2.50 (5)	2.50 (20)
	1.22 (10)	2.44 (5*)	2.42 (20)
	1.21 (60)	2.36 (5*)	2.37 (10)
	1.19 (5)	2.28 (5*)	2.29 (10)
	1.17 (20)	2.24 (1)	2.21 (1)
	1.14 (20)	2.11 (10*)	2.17 (5)
	1.11 (50)	2.08 (20)	2.12 (20)
	1.10 (30)	2.03 (30)	2.05 (1)
	1.09 (20*)	1.99 (10*)	1.99 (5)
	1.06 (1)	1.89 (5*)	1.90 (20)
	1.04 (1)	1.83 (1)	1.82 (20)
	1.03 (5)	1.78 (5)	1.76 (10)
	1.00 (1)	1.76 (10)	1.75 (20)
	0.994 (1)		1.72 (20)
	0.953 (5)		1.70 (10)
	0.943 (1)		
	0.938 (5*)		
	0.916 (10*)		
	0.899 (10*)		
	0.881 (10*)		
	0.874 (1)	0.838 (1*)	
	0.872 (5)	0.826 (5)	
	0.859 (5)	0.824 (1)	
	0.856 (1)	0.817 (5)	
	0.847 (5*)	0.814 (1)	
		0.803 (1)	

*Broken Lines

*Broken Lines

Calculated Values of $\sin^2\theta$ for NaInS_2 and Values of $\sin^2\theta$ for the
Product from Experiment 5.20

NaInS_2 has a hexagonal unit cell, with $a = 3.80 \text{ \AA}$ and $c = 19.8 \text{ \AA}$ (68).
The diffraction of all possible combinations of Miller Indices (hkl)
were calculated by the method outlined by Lipson & Steeple ('Inter-
pretation of X Ray Powder Diffraction Patterns' Macmillan, 1970).

The Formula for $\sin^2\theta$ in a hexagonal system is:

$$\sin^2\theta_{hkl} = \lambda^2/3a^2 (h^2 + hk + k^2) + \lambda^2/4c^2 (l^2) \quad \text{where } \lambda = \text{wavelength}$$

$$\theta = \text{Bragg Angle}$$

Using the permitted values of $(h^2 + hk + k^2)$ listed by Lipson and
Steeple, all possible values of $\sin^2\theta$ were calculated and compared to
the values found with the powder patterns from Experiment 5.20.

hkl	$\sin^2\theta$		$d(\text{found})(\text{\AA})$	hkl	$\sin^2\theta$		$d(\text{found})(\text{\AA})$
	calc.	found			calc.	found	
000	0.0000			00 13	0.2535		
001	.0015			205	.2571	0.2564	1.52
002	.0060	0.0071	9.16	118	.2606		
003	.0135	.0134	6.65	10 12	.2709		
004	.0240	.0209	5.32	206	.2736		
005	.0375			119	.2862	.2857	1.44
006	.0540	.0540	3.32	207	.2931		
100	.0549			00 14	.2940	.2936	1.42
101	.0564	.0563	3.25	10 13	.3084		
102	.0609	.0607	3.13	11 10	.3147	.3149	1.37
103	.0684			208	.3156		
107	.0735			00 15	.3375	.3365	1.33
104	.0789	.0787	2.75	209	.3411		
105	.0924	.0920	2.54	11 11	.3462		
008	.0960			10 14	.3489	.3481	1.31
106	.1089	.1043	2.39	20 10	.3696	.3686	1.27
009	.1215			11 12	.3807	.3795	1.25
107	.1284	.1285	2.15	00 16	.3840		
00 10	.1500			210	.3843		
108	.1509	.1506	1.99	211	.3858		
110	.1647	.1641	1.90	212	.3903		
111	.1662			10 15	.3924		
112	.1707			213	.3978	.3992	1.22
109	.1764			20 11	.4011		
113	.1782	.1786	1.82	214	.4083	.4068	1.21
00 11	.1815			11 13	.4182	.4197	1.19
114	.1887			215	.4218		
115	.2022			00 17	.4335		
10 10	.2049	.2043	1.71	20 12	.4356		
00 12	.2160			216	.4383	.4382	1.17
116	.2187	.2178	1.65	10 16	.4389		
200	.2196			217	.4578	.4560	1.14
201	.2211			114	.4587		
202	.2256	.2253	1.63	2013	.4734		
203	.2331			218	.4803	.4791	1.11
10 11	.2364	.2357	1.59	00 18	.4860		
117	.2382			10 17	.4884		
204	.2436	.2428	1.57	300	.4941	.4921	1.10

hkl	$\sin^2 \theta$		$d(\text{found})(\text{\AA})$	hkl	$\sin^2 \theta$		$d(\text{found})(\text{\AA})$
	calc.	found			calc.	found	
301	0.4956			30 13	0.7476		
302	.5001			315	.7512		
11 15	.5022	0.5025	1.09	228	.7548		
219	.5058			20 19	.7611		
303	.5076			11 20	.7647		
20 14	.5136			316	.7677	0.7663	0.881
304	.5186			21 16	.7683		
305	.5316	.5327	1.06	229	.7803	.7779	0.874
21 10	.5343			10 22	.7809	.7824	0.872
10 18	.5409			30 14	.7881		
00 19	.5415			00 23	.7935		
306	.5481	.5460	1.04	317	.8072	.8057	0.859
11 16	.5487			22 10	.8088		
20 15	.5571			318	.8097		
21 11	.5638	.5639	1.03	21 17	.8178	.8112	0.856
307	.5676			20 20	.8196		
308	.5901	.5896	1.00	11 21	.8262	.8298	0.847
10 19	.5964			30 15	.8316		
11 17	.5982			319	.8352		
00 20	.6000			22 11	.8403		
21 12	.6003	.6015	0.994	10 23	.8484	.8473	0.838
20 16	.6036			31 10	.8637		
309	.6156			00 24	.8640		
21 13	.6378			21 18	.8703	.8708	0.826
30 10	.6441			22 12	.8748		
11 18	.6507			30 16	.8781	.8766	0.824
20 17	.6531			400	.8784		
10 20	.6549	.6554	0.953	401	.8799		
220	.6588			20 21	.8811		
221	.6603			402	.8844		
0021	.6615			11 22	.8907	.8918	0.817
222	.6648	.6685	0.943	31 11	.8952	.8975	0.814
223	.6723			403	.9019		
30 11	.6756	.6751	0.939	22 13	.9123		
21 14	.6783			404	.9124		
224	.6828			405	.9159		
225	.6963			10 24	.9189		
20 18	.7056			21 19	.9258	.9258	0.803
11 19	.7062	.7085	0.916	30 17	.9276		
30 12	.7101			31 12	.9297		
226	.7128			406	.9324		
310	.7137			00 25	.9375		
311	.7152			20 22	.9456		
10 21	.7164			407	.9519		
312	.7197			22 14	.9528		
21 15	.7218			11 23	.9582		
00 22	.7260			31 13	.9672		
313	.7272			408	.9744		
227	.7325	.7355	0.899	30 18	.9801		
314	.7377			21 20	.9843		
				22 15	.9963		
				409	.9999		

Experiment 5.22		Experiment 5.23		
Ex-Reactor, Methanol & Water-Washed.		Ex-Reactor	Water-Washed	Methanol-Washed
$d(\text{\AA})$ (I/I ₀)		$d(\text{\AA})$ (I/I ₀)	$d(\text{\AA})$ (I/I ₀)	$d(\text{\AA})$ (I/I ₀)
12.11 (80)		10.99 (60)		14.33 (v.diffuse)
10.46 (5)		9.94 (100)		
9.73 (5)		9.07 (80)	8.34 (100)	
9.03 (80)		7.77 (80)	6.91 (20)	
8.51 (100)		6.15 (5)		
7.41 (20)		5.87 (5)		
7.11 (20)		5.54 (5)		
6.35 (30)		5.23 (5)	5.20 (1)	
5.96 (20)		5.02 (20)	4.91 (1)	
5.66 (5)		4.82 (1)		
5.39 (10)		4.69 (1)		
5.20 (20)		4.50 (1)		
5.04 (1)		4.35 (5)		
4.67 (60)		4.26 (1)	4.25 (60)	
4.57 (1)		4.10 (10)		
4.45 (5)		3.93 (5)	3.99 (1)	
4.28 (10)		3.80 (10)		
4.20 (10)		3.52 (1)		
4.05 (50)		3.30 (5)		3.38 "
3.87 (1)		3.18 (5)		3.25 "
3.71 (5)		2.78 (5)		2.80 "
3.62 (5)				2.63 "
3.48 (1)				1.90 "
3.42 (5)				
3.33 (10)				
3.23 (5)				
3.19 (5)				
3.11 (10)				
3.05 (10)				
2.89 (5)				
2.80 (5)				
2.74 (5)				
2.70 (10)				
2.66 (10)				
2.61 (1)				
2.60 (1)				
2.51 (5)				
2.45 (1)				
2.44 (30)				
2.39 (5)				
2.34 (1)				
2.27 (30)				
2.21 (30)				
2.17 (5)				
2.11 (5)				
2.07 (1)				
2.03 (1)				
1.99 (20)				
1.97 (10)				
1.91 (30)				
1.89 (1)				
1.85 (5)				
1.82 (5)				
1.80 (10)				

Experiment 5.24

$d(\text{\AA})$	(I/I_0)
7.70	(30)
5.73	(60)
4.81	(1)
4.18	(1)
4.05	(30)
3.93	(5)
3.85	(100)
3.56	(10)
3.45	(80)
3.34	(60)
3.23	(80)
3.10	(60)
2.85	(60)
2.69	(1)
2.64	(50)
2.56	(20)
2.49	(50)
2.37	(50)
2.32	(50)
2.21	(1)
2.14	(10)
2.11	(30)
1.99	(5)
1.96	(5)
1.90	(30)
1.82	(20)
1.78	(30)
1.75	(20)
1.72	(30)
1.70	(30)
1.66	(5)
1.65	(5)
1.62	(20)
1.61	(10)
1.56	(1)
1.54	(1)
1.50	(1)
1.47	(1)
1.44	(10)
1.42	(10)
1.36	(10)

APPENDIX A4 Feedstock Tests for Crystallinity and Purity

SiS_2	Al_2S_3	NaSH	$\text{Et}_4\text{N}^+\text{SH}^-$
$d(\text{\AA})$ (I/I ₀)	$d(\text{\AA})$ (I/I ₀)	$d(\text{\AA})$ (I/I ₀)	$d(\text{\AA})$ (I/I ₀)
8.37 (5)	5.42 (5)	6.63 (5)	6.78 (5)
7.58 (1)	5.29 (50)	3.60 (50)	6.11 (20)
5.67 (10)	4.71 (60)	3.30 (5)	5.87 (20)
4.91 (1)	3.47 (10)	3.17 (1)	5.40 (100)
4.86 (20)	3.23 (100)	3.13 (5)	5.06 (5)
4.41 (80)	2.98 (60)	3.07 (10)	4.23 (80)
4.23 (1)	2.87 (50)	2.98 (100)	3.90 (20)
4.02 (5)	2.82 (80)	2.87 (1)	3.63 (20)
3.96 (1)	2.75 (5)	2.59 (10)	3.52 (60)
3.90 (100)	2.66 (10)	2.54 (5)	3.39 (30)
3.66 (80)	2.56 (1)	2.49 (1)	3.14 (10)
3.55 (5)	2.49 (30)	2.26 (80)	3.03 (50)
3.42 (50)	2.38 (1)	2.21 (5)	2.93 (50)
3.34 (50)	2.33 (1)	1.99 (60)	2.71 (1)
3.21 (60)	2.18 (50)	1.95 (1)	2.63 (1)
3.12 (80)	2.14 (30)	1.91 (5)	2.50 (1)
2.99 (5)	2.08 (20)	1.82 (1)	2.45 (5)
2.83 (20)	2.05 (10)	1.80 (60)	2.40 (5)
2.60 (10)	2.01 (20)	1.43 (20)	2.34 (1)
2.48 (10)	1.91 (5)	1.41 (30)	2.25 (20)
2.46 (10)	1.86 (80)	1.30 (20)	2.19 (1)
2.37 (1)	1.76 (20)	1.27 (30)	2.14 (20)
2.28 (1)	1.74 (5)	1.24 (30)	2.12 (5)
2.21 (10)	1.69 (60)	1.13 (5)	2.03 (10)
2.17 (10)	1.64 (10)	1.11 (5)	1.99 (5)
1.92 (20)	1.60 (20)	1.05 (5)	1.93 (5)
1.83 (1)	1.57 (60)	0.994 (5)	1.76 (20)
1.79 (1)	1.51 (50)	0.981 (1)	1.74 (1)
1.76 (1)		0.908 (5)	1.69 (5)
1.72 (5)		0.906 (5)	1.67 (10)
1.70 (5)			
1.64 (50)			
1.60 (5)			
1.36 (5)			
1.25 (5)			
1.11 (5)			
1.05 (5)			

In_2S_3	SnS_2	GeS_2
Nearly completely non - crystalline		
$d(\text{\AA})$	$d(\text{\AA})$	$d(\text{\AA})$
6.11	10.05	6.43
2.68	6.29	3.42
1.88		2.60
		1.76

(All very diffuse).

APPENDIX A5 Aqueous Reactions

Experiment 6.5 (6.6 similar)

$d(\text{\AA})$

7.50

3.26

1.86

Very diffuse, and of decreasing intensity.

Experiment 6.7 (6.8 similar)

The same very diffuse bands as above, plus the following:

$d(\text{\AA})$ (I/I₀)

14.63 (30)

7.06 (80)

5.01 (10)

4.07 (80)

3.78 (10)

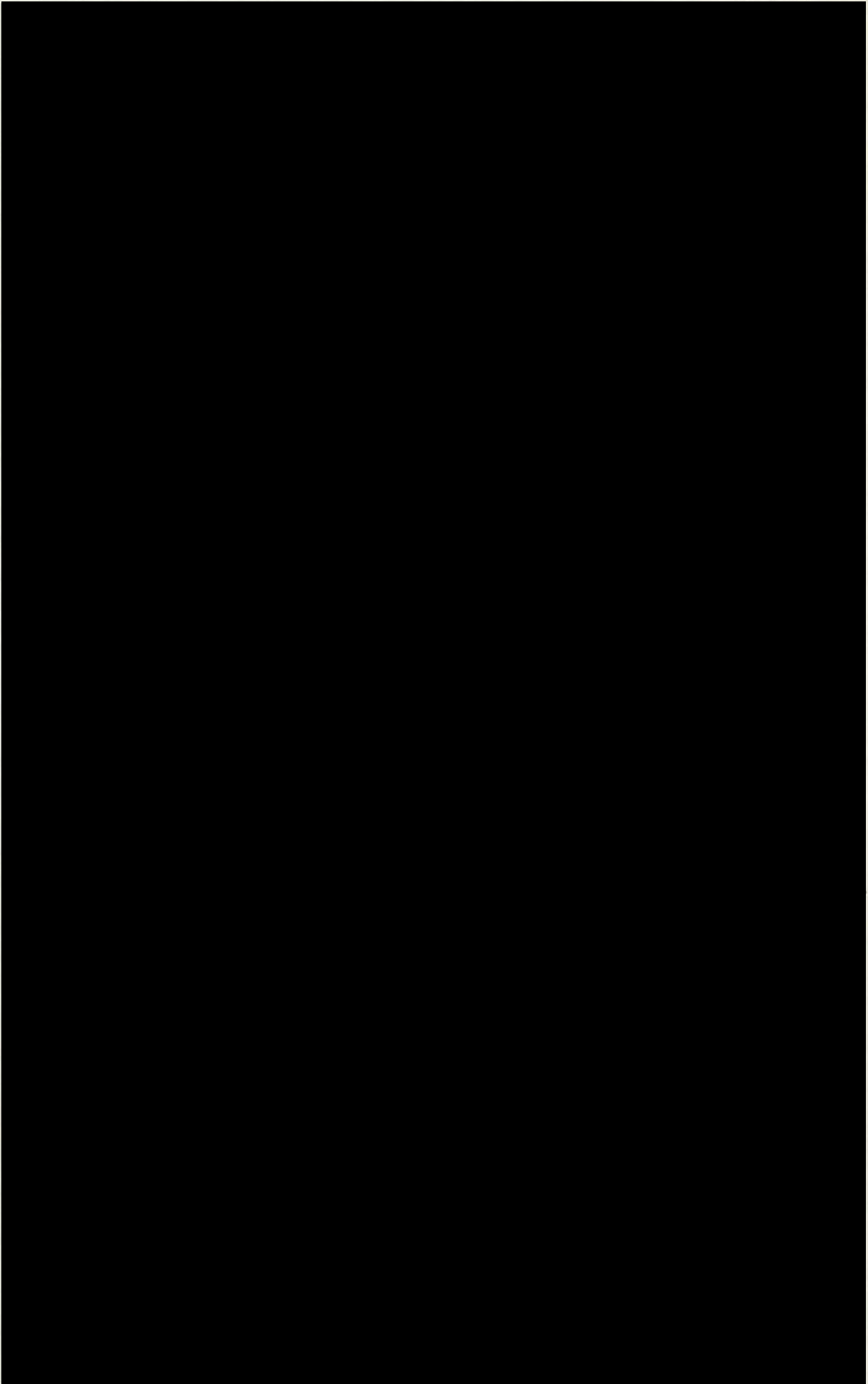
3.16 (100)

2.89 (5)

2.67 (50)

APPENDIX A6 Reference X - Ray Powder Diffraction Data from the ASTM file.

(Compiled by the Joint Committee on Powder Diffraction Studies, 1972)



APPENDIX A7 Surface Area Tabulations

Equipment Test With Active Charcoal

P (torr)	Wt. Uptake (g)	x (g/g)	P/P ₀	P/(P ₀ -P)x
0.25	0.000551	0.01078	0.000325	0.03019
1.6	0.000827	0.01619	0.002082	0.12889
3.0	0.000918	0.01797	0.003904	0.21813
4.1	0.001148	0.02247	0.005336	0.23875
8.0	0.001194	0.02337	0.010412	0.44096
18.0	0.001240	0.02427	0.023427	0.98841
53.0	0.001332	0.02607	0.068979	2.84195
92.0	0.001423	0.02785	0.119737	4.88419
214.0	0.001607	0.03145	0.278519	12.27465
301.0	0.001699	0.03325	0.391749	19.37011
398.0	0.001719	0.03505	0.517993	30.66067
584.0	0.002066	0.04044	0.760070	78.33565

Wt. Sample = 0.051093 g. Atmospheric Pressure = 768.35 torr

1) From plot of $P/(P_0-P)x$ vs. P/P_0 ,

$$\text{Slope} = 18.0/0.4175 = 43.1138 \quad \& \quad \text{Intercept} = 0.0000$$

$$1/(\text{Slope} + \text{Intercept}) = x_m = 0.02319$$

$$\text{Specific Surface} = (x_m/M)N_A = \frac{0.02319 \cdot 6.023 \cdot 16 \cdot 2 \cdot 10^{23} \cdot 10^{-20}}{28} \\ = 80.80 \text{ m}^2/\text{g}$$

2) From plot of g/g vs. P/P_0 ,

$$x_m = 0.024$$

$$\text{Specific Surface} = \frac{0.024 \cdot 6.023 \cdot 16 \cdot 2 \cdot 10^{23} \cdot 10^{-20}}{28} = 83.63 \text{ m}^2/\text{g}$$

Experiment 5.10

P (torr)	Wt. Uptake (g)	x (g/g)	P/P ₀	P/(P ₀ -P)x
0.06	0.000416	0.004374	0.0000783	0.01792
0.72	0.000462	0.004857	0.0009404	0.1938
2.4	0.000485	0.005099	0.0031348	0.6167
4.0	0.000576	0.006056	0.005225	0.8672
7.0	0.000691	0.007265	0.009143	1.2701
10.0	0.000691	0.007265	0.013061	1.8217
25.0	0.000691	0.007265	0.03265	4.6464
52.0	0.000714	0.007507	0.06792	9.7069
100.0	0.000737	0.007748	0.13062	19.3907
204.0	0.000737	0.007748	0.26645	46.8825
323.0	0.000714	0.007507	0.42189	97.2159
397.0	0.000737	0.007748	0.51854	139.0105
490.0	0.000737	0.007748	0.6400	229.4759
600.0	0.000737	0.007748	0.7837	467.6539

Wt. Sample = 0.095114 g. Atmospheric Pressure = 765.60 torr

1) From plot of $P/(P_0 - P)x$ vs. P/P_0 ,

$$\text{Slope} = 50.0/0.310 = 161.29 \quad \& \quad \text{Intercept} = 0.0000$$

$$1/(\text{Slope} + \text{Intercept}) = x_m = 6.2 \cdot 10^{-3}$$

$$\text{Specific Surface} = \frac{6.2 \cdot 10^{-3} \cdot 6.032 \cdot 10^{23} \cdot 16.2 \cdot 10^{-20}}{28}$$

$$= 21.60 \text{ m}^2/\text{g}$$

2) From plot of g/g vs. P/P_0 ,

$$x_m = 7.6 \cdot 10^{-3}$$

$$\text{Specific Surface} = \frac{7.6 \cdot 10^{-3} \cdot 6.023 \cdot 10^{23} \cdot 16.2 \cdot 10^{-20}}{28}$$

$$= 26.48 \text{ m}^2/\text{g}$$

Experiment 5.11

P (torr)	Wt. Uptake (g)	x (g/g)	P/P ₀	P/(P ₀ -P)x
0.001	0.00064	0.00569	0.0000013	0.0002347
1.0	.00108	.00691	.001335	0.2347
2.2	.00108	.00961	.002938	0.3066
3.4	.00105	.00934	.004540	0.4883
5.8	.00105	.00934	.007745	0.8357
24.0	.00110	.00979	.03205	3.3818
57.0	.00117	.01041	.07611	7.9137
98.0	.00131	.01166	.13086	12.912
201.0	.00133	.01183	.26839	31.010
299.0	.00137	.01219	.39925	54.519
388.0	.00156	.01388	.51809	77.456
494.0	.00151	.01344	.65963	144.196
585.0	.00160	.01424	.78115	250.653

Wt. Sample = 0.11238 g. & Atmospheric Pressure = 748.90 torr

1) From plot of $P/(P_0 - P)x$ vs. P/P_0 ,

$$\text{Slope} = 100.0/0.7 = 142.85 \quad \& \quad \text{Intercept} = 0.0000$$

$$1/(\text{Slope} + \text{Intercept}) = x_m = 7.00 \cdot 10^{-3}$$

$$\text{Specific Surface} = \frac{7.0 \cdot 10^{-3} \cdot 6.023 \cdot 10^{23} \cdot 16.2 \cdot 10^{-20}}{28}$$

$$= 24.40 \text{ m}^2/\text{g}$$

2) From plot of g/g vs. P/P_0 ,

$$x_m = 10.0 \cdot 10^{-3}$$

$$\text{Specific Surface} = \frac{10.0 \cdot 10^{-3} \cdot 6.023 \cdot 10^{23} \cdot 16.2 \cdot 10^{-20}}{28}$$

$$= 34.85 \text{ m}^2/\text{g}$$

Experiment 5.12

P (torr)	Wt. Uptake (g)	x (g/g)	P/P ₀	P/(P ₀ - P)x
0.001	0.000138	0.001416	0.0000013	0.000935
0.60	.000321	.003295	.000794	0.2414
2.2	.000413	.004239	.002914	0.6894
3.6	.000482	.004946	.004769	1.0046
6.9	.000482	.004946	.009139	1.8648
11.0	.000505	.005183	.01457	2.8526
25.0	.000505	.005183	.03311	6.60764
55.0	.000505	.005183	.07285	15.1595
101.0	.000482	.004946	.1337	31.224
207.0	.000505	.005183	.2742	72.882
325.0	.000505	.005183	.4305	145.820
395.0	.000505	.005183	.5232	211.728
503.0	.000482	.004946	.6663	403.562
650.0	.000459	.004711	.8609	1314.19

Wt. Sample = 0.097435 g. & Atmospheric Pressure = 755.00 torr

1) From plot of $P/(P_0 - P)x$ vs. P/P_0 ,

$$\text{Slope} = 150.0/0.480 = 312.5 \quad \& \quad \text{Intercept} = -3.00$$

$$1/(\text{Slope} + \text{Intercept}) = x_m = 3.23 \cdot 10^{-3}$$

$$\text{Specific Surface} = \frac{3.23 \cdot 10^{-3} \cdot 6.023 \cdot 10^{23} \cdot 16.2 \cdot 10^{-20}}{28}$$

$$= 11.2 \text{ m}^2/\text{g}$$

2) From plot of g/g vs. P/P_0 ,

$$x_m = 5.0 \cdot 10^{-3}$$

$$\text{Specific Surface} = \frac{5.0 \cdot 10^{-3} \cdot 6.023 \cdot 10^{23} \cdot 16.2 \cdot 10^{-20}}{28}$$

$$= 17.4 \text{ m}^2/\text{g}$$

Experiment 5.13

P (torr)	Wt. Uptake (g)	x (g/g)	P/P ₀	P/(P ₀ - P)x
0.10	0.000275	0.002859	0.0001341	0.0469
0.90	.000229	.002381	.001206	0.5074
2.10	.000321	.003338	.002816	0.8459
3.40	.000367	.003816	.004559	1.2001
5.80	.000367	.003816	.007777	2.0540
9.0	.000459	.004773	.01207	2.5593
22.0	.000459	.004773	.02950	6.3681
50.0	.000505	.005251	.06704	13.6851
104.0	.000505	.005251	.1394	30.8596
202.0	.000505	.005251	.2709	70.7407
300.0	.000505	.005251	.4023	128.1558
398.0	.000505	.005251	.5337	217.9270
502.0	.000459	.004773	.6731	431.3827
632.0	.000459	.004773	.8474	1163.4756

Wt. Sample = 0.096173 g. & Atmospheric Pressure = 745.80 torr

1) From plot of $P/(P_0 - P)x$ vs. P/P_0 ,

$$\text{Slope} = 110.0/0.40 = 275.0 \quad \& \quad \text{Intercept} = 0.0000$$

$$1/(\text{Slope} + \text{Intercept}) = x_m = 3.64 \cdot 10^{-3}$$

$$\text{Specific Surface} = \frac{3.64 \cdot 10^{-3} \cdot 6.023 \cdot 10^{23} \cdot 16 \cdot 2 \cdot 10^{-20}}{28}$$

$$= 12.7 \text{ m}^2/\text{g}$$

2) From plot of g/g vs. P/P_0 ,

$$x_m = 5.0 \cdot 10^{-3}$$

$$\text{Specific Surface} = \frac{5.0 \cdot 10^{-3} \cdot 6.023 \cdot 10^{23} \cdot 16 \cdot 2 \cdot 10^{-20}}{28}$$

$$= 17.4 \text{ m}^2/\text{g}$$

Experiment 5.17

P (torr)	Wt. Uptake (g)	x (g/g)	P/P ₀	P/(P ₀ - P)x
0.01	0.00023	0.002672	0.0001431	0.004868
1.20	0.0032	0.03718	0.001561	0.42047
2.50	0.0037	0.04299	0.003252	0.75888
3.80	0.0042	0.04880	0.004942	1.01617
6.90	0.0051	0.05925	0.008975	1.66413
8.50	0.0051	0.05925	0.01106	1.88687
21.00	0.0051	0.05925	0.02732	4.73966
51.00	0.0051	0.05925	0.06633	11.99165
101.00	0.0051	0.05925	0.1314	25.52632
194.00	0.0051	0.05925	0.2523	56.96332
314.00	0.0051	0.05925	0.4084	116.525
502.00	0.0051	0.05925	0.6530	317.560
613.00	0.0055	0.06390	0.7973	618.911

Wt. Sample = 0.08607 g. & Atmospheric Pressure = 768.80 torr

1) From plot of $P/(P_0 - P)x$ vs. P/P_0 ,

$$\text{Slope} = 120.0/0.465 = 258.66 \quad \& \quad \text{Intercept} = 2.0$$

$$1/(\text{Slope} + \text{Intercept}) = x_m = 3.84 \cdot 10^{-3}$$

$$\text{Specific Surface} = \frac{3.84 \cdot 10^{-3} \cdot 6.023 \cdot 10^{23} \cdot 16 \cdot 2 \cdot 10^{-20}}{28}$$

$$= 13.38 \text{ m}^2/\text{g}$$

2) From plot of g/g vs. P/P_0 ,

$$x_m = 5.9 \cdot 10^{-3}$$

$$\text{Specific Surface} = \frac{5.9 \cdot 10^{-3} \cdot 6.023 \cdot 10^{23} \cdot 16 \cdot 2 \cdot 10^{-20}}{28}$$

$$= 20.56 \text{ m}^2/\text{g}$$