

THERMODYNAMICS AND TRANSPORT PROPERTIES
OF BORNITE

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ABSTRACT

Synthetic Bornite (Cu_5FeS_4) has been produced from its elements and details of its preparation and characterization are given. As this synthetic Bornite had a limited crystal size it was hot-pressed to provide large samples and details of this process are also given.

Thermodynamic measurements were carried out in the composition range Cu_5FeS_4 to Cu_4FeS_4 in both aqueous and solid state cells in which the specimen composition was changed in small steps by coulometric titration. These measurements provided values of copper activity, partial molar entropy and partial molar enthalpy at a series of compositions. In addition, the constituent phases present at different compositions have been investigated by X-ray analysis and scanning electron microscopy. The variation of copper activity with composition was also measured for the hot-pressed material. For this hot-pressed material the ionic conductivity at three different compositions was measured by a four-point technique and the temperature dependence of the electronic conductivity of the starting composition was studied.

In order to carry out the above investigation an organic copper solid electrolyte has been synthesized and characterized. The ionic conductivity of this electrolyte was found by A.C. techniques and its electronic conductivity was measured by the Hebb-Wagner method.

A preliminary investigation of another copper sulphide, chalcocite (Cu_2S), is also presented.

TABLE OF CONTENTS

	Page No.
Abstract	1
Table of Contents	2
List of Figures	5
List of Tables	8
List of Symbols	10
 INTRODUCTION	 12
 1. SOLID-STATE TRANSPORT	
1.1. Introduction	15
1.2. Fast Ion Conductors	15
1.3. Co-ordination Effects	22
1.4. Copper Electrolytes	22
1.5. Solid Solution Electrodes	24
1.6. Cu-Fe-S Ternary	29
 2. THE ELECTROLYTE	
2.1. Introduction	31
2.2. Preparation and Characterization	31
2.3. Electronic Conductivity	40
2.4. A.C. Measurements	
2.4.1. Introduction	44
2.4.2. Experiment	44
2.4.3. Results	45
2.5. Electrocrystallisation of Copper from a Solid Electrolyte	50
2.6. Summary and Conclusions	53

3.	BORNITE	
3.1.	Introduction	56
3.2.	Structure	56
3.3.	Preparation	64
3.4.	Characterization	69
3.5.	Coulometric Titration Cells	
3.5.1.	Introduction	75
3.5.2.	Aqueous Cells	76
3.5.3.	Solid State Cells	79
3.6.	Transport Properties of Hot-Pressed Bornite	
3.6.1.	Electronic Resistivity	100
3.6.2.	Ionic Conductivity and Diffusion Coefficient	104
3.7.	Summary and Conclusions	114
4.	COPPER SULPHIDE	
4.1.	Introduction	119
4.2.	Preparation	119
4.3.	Characterization	120
4.4.	Coulometric Titration Cell	120
4.5.	Summary and Conclusions	131
5.	FINAL CONCLUSIONS	
5.1.	Copper Electrolyte	132
5.2.	Bornite	132
5.3.	Copper Sulphide	133
5.4.	Suggestions for Further Work	133
	TABLES	135

	Page No.
APPENDICES	
A Hebb-Wagner Technique	165
B Programable Data Logger	169
C Van der Pauw Technique for Electronic Conductivity	174
D Ionic Conductivity from Siz-Point Cell	176
E Computing	182
F Diffusion Coefficients and Ionic Conductivity	184
REFERENCES	189
ACKNOWLEDGEMENTS	194

LIST OF FIGURES

Fig. No.	Title	Page No.
1.1	Variation of Conductivity with Temperature.	16
1.2	Structure of β -Alumina.	21
1.3	Cu-Fe-S Ternary.	30
2.1	X-ray Diffraction Pattern for CuBr.	33
2.2	Structure of 1,4-diazabicyclo(2,2,2)octane dibromide.	34
2.3	X-ray Diffraction Pattern for $(\text{CH}_3)_2\text{C}_6\text{H}_4\text{N}_2\text{Br}_2$.	37
2.4	X-ray Diffraction Pattern for the Electrolyte.	39
2.5	Hebb-Wagner Cell.	41
2.6	Hebb-Wagner Plot for Solid Electrolyte.	43
2.7	Admittance Plot for Electrolyte with Non-Blocking Electrodes.	46
2.8	Impedance Plot for Electrolyte with Non-Blocking Electrodes.	46
2.9	Admittance Plot for Electrolyte with Blocking Electrodes.	47
2.10	Impedance Plot for Electrolyte with Blocking Electrodes.	47
2.11	Hot-Pressed Electrolyte from a Coulometric Titration Cell with Copper Electrode.	51
2.12	Copper Fibres on the Surface of the Electrolyte.	52
2.13	An Enlargement of the Surface Area where Copper has been Crystallized out.	54
3.1	Antifluorite Type Structure.	59
3.2	Sphaelerite Type Structure.	60

Fig. No.	Title	Page No.
3.3	Construction of Bornite Unit Cell.	61
3.4	Ordering of Vacant Tetrahedra of Sulphur Atoms in Bornite Structure.	62
3.5	Reaction Tube for Bornite Preparation.	65
3.6	Hot-Pressing of Bornite.	68
3.7	X-ray of Bornite.	70
3.8	X-ray of Hot-Pressed Bornite.	72
3.9	Micrograph of Hot-Pressed Bornite.	74
3.10	Aqueous Cell.	77
3.11	Coulometric Titration Curve for Aqueous Cell.	78
3.12	Layout of Solid State Cell.	80
3.13	Bornite Solid State Cell.	80
3.14	Bornite Coulometric Titration Curve at 85°C.	82
3.15	Bornite Coulometric Titration Curve at 146°C.	84
3.16	Bornite Coulometric Titration Curve at 100°C.	85
3.17	Transient Effect on Reference and Counter Electrodes.	86
3.18	Worst Geometry for Titration Cell.	86
3.19	X-rays of Titration Samples.	89
3.20	Micrograph of Titration Sample 3.	90
3.21	Hot-Pressed Coulometric Titration Cell.	94
3.22	Hot-Pressed Coulometric Titration Curve.	96
3.23	Micrograph of Six-Point Cell Specimen.	99
3.24	X-ray on Six-Point Cell Specimen.	101
3.25	ΔH for Bornite in the Range Cu_5FeS_4 to $\text{Cu}_{4.4}\text{FeS}_4$.	102
3.26	ΔS for Bornite in the Range Cu_5FeS_4 to $\text{Cu}_{4.4}\text{FeS}_4$.	103

Fig. No.	Title	Page No.
3.27	Van der Pauw Cell.	105
3.28	Conductivity of Hot-Pressed Bornite.	106
3.29	Layout of Six-Point Cell.	107
3.30a	Typical Experimental Transients, Six-Point Cell.	110
3.30b	Comparison of Experiment and Theory, Six-Point Cell.	111
3.31	Summary of Experimental Results for Bornite.	115
4.1	X-ray of Cu_2S Preparation.	121
4.2	Cu_2S Solid State Cell.	122
4.3	Coulometric Titration Curve Obtained for Cu-S System.	123
4.4	Cu-S Phase Diagram.	125
4.5	Coulometric Titration Curve of Mathieu and Rickert for the Cu-S System.	126
4.6	Loss of Copper in Electrolyte.	128
4.7	X-ray for Sample from Solid State Cu-S Cell.	129
A	Hebb-Wagner Diagramatic Cell.	166
B	Block Diagram of Data Logger.	171
C	Van der Pauw Specimen Shape.	174
D	Roth's Model for Six-Point Cell.	179

LIST OF TABLES

Table No.	Title	Page No.
0.1*	Theoretical and Practical Energy Densities of Selected Battery Systems.	13
1.1*	Selected Copper and Silver Fast Ion Conductors.	19
2.1	Copper Bromide X-ray Results.	135
2.2*	Analysis of Organic Part of the Electrolyte.	35
2.3	X-ray Diffraction Results for $(\text{CH}_3)_2 \text{C}_6\text{H}_4\text{N}_2\text{Br}_2$.	136
2.4	X-ray Diffraction Results for $94\text{CuBr}/6(\text{CH}_3)_2 \text{C}_6\text{H}_4\text{N}_2\text{Br}_2$.	137
2.5	Admittance Data for Copper Electrolyte with Non-Blocking Electrodes.	140
2.6	Impedance Data for Copper Electrolyte with Non-Blocking Electrodes.	141
2.7	Admittance Data for Copper Electrolyte with Blocking Electrodes.	142
2.8	Impedance Data for Copper Electrolyte with Blocking Electrodes.	143
2.9*	Reported Conductivities for Electrolyte.	49
3.1*	Extent of Bornite Phase at Various Temperatures.	63
3.2	X-ray Diffraction Data for Bornite.	144
3.3	X-ray Diffraction Data for Hot-Pressed Bornite.	145
3.4*	Microprobe Analysis and Density of Hot-Pressed Bornite.	71
3.5*	EDAX Analysis of Hot-Pressed Bornite.	73
3.6	Aqueous Cell Coulometric Titration Data.	146
3.7	85°C Coulometric Titration Cell Data.	147
3.8	146°C Coulometric Titration Cell Data.	149

Table No.	Title	Page No.
3.9	100°C Coulometric Titration Cell Data.	150
3.10*	Preparation of X-ray Titration Samples.	88
3.11*	EDAX Analysis of Titration Sample Number 3.	91
3.12	X-ray Diffraction Results on Coulometric Titration X-ray Samples.	152
3.13*	Lattice Parameters of Coulometric Titration X-ray Samples.	93
3.14	Hot-Pressed Coulometric Titration Cell (150°C).	153
3.15	X-ray Results on Six-Point Cell Specimen.	154
3.16	ΔH and ΔS for Bornite.	155
3.17	Electronic Conductivity by the Van der Pauw Method.	156
3.18*	Ionic Conductivity of Hot-Pressed Bornite.	109
3.19	Transient Results for Six-Point Cell (170°C).	158
3.20*	σ_i and $\tilde{D}$ from Transient at 170°C.	113
3.21*	$\tilde{D}$ Derived from Ionic Conductivity and Transient.	112
4.1	X-ray Diffraction Results for Reacted Cu_2S and Hot-Pressed Cu_2S .	162
4.2	Coulometric Titration Data for Cu-S system.	163
4.3	X-ray Diffraction Results for Cu-S cell.	164
4.4*	ΔS for the Cu-S system at certain compositions.	130

* Signifies table occurs in text.

LIST OF SYMBOLS

A	Area.
a_k	Activity of species k.
B	Absolute mobility.
c_i	Concentration of species i.
D	Diffusion coefficient.
D^*	Self diffusion coefficient.
$\tilde{D}$	Chemical diffusion coefficient
d	Jump distance.
E	Cell equilibrium voltage.
e	Charges on electron or subscript for electron.
F	Faraday's constant.
G	Gibbs free energy.
g	Retarding force.
g_a	Amplification factor.
H	Enthalpy.
i	$\sqrt{-1}$ or subscript for ions.
J_k	Particle flux density for species k.
j	Partial current density.
j	$\sqrt{-1}$ or integer subscript.
k	Species or integer subscript.
L	Thickness or length of specimen.
L_{kk}	General Onsager phenomenological coefficient.
M	Molecular weight.
N_c	Number of carriers.
N	Avogadro's number.
n	Number of electrons involved in the reaction.
n_o	Number of ions available for transport.

R	Universal gas constant.
$R_{AB,CD}$	Voltage between C and D divided by the current between A and B.
S	Entropy.
T	Absolute temperature or subscript for total.
t	Time.
V_k	Voltage due to species k.
x	Distance or variable for composition.
z_k	Charge on species k in electron charge units.
α	Geometric factor.
β	Fraction of mobile species free to move.
σ	Conductivity of species k.
η	Electrochemical potential.
ρ	Resistivity.
ω	Density or angular frequency.
τ	Characteristic time.
ν_a	Attempt frequency.
μ	Chemical potential.
μ_m	Mobility.
$\circ$	Subscript for holes.
$\ominus$	Subscript for electrons.
$'$	Superscript for partial.
$\circ$	Subscript or superscript for standard state.

INTRODUCTION

From reports in the mass media as well as in technical journals, it appears that most of the world's oil resources will be exhausted by the first half of the twenty-first century. This will force man to look for other sources of energy, which are of two main types, the so called "alternative energy sources" (e.g. solar energy), and nuclear energy. Whichever energy source is used in the future, some method must be realized so that the energy is there when and where it is needed. This requires energy storage on a large scale, as nuclear plants are more efficient if run for 24 hours a day at optimum load or if an "alternative power source" is used it will only function when the conditions are favourable (intermittent energy source). This process is known as "load levelling", and can be achieved in different ways.

One method of load levelling used at the present is to pump water up a hillside into a reservoir at night when the load on electrical generation is low. Then during times of peak demand for electricity, this water is used to drive hydro-electric plant, though the number of sites is restricted. Even if energy requirements can be fulfilled by these sources of energy and load levelling, the energy plants tend to be large and therefore not portable. So to answer the problem of powering vehicles small power sources must be created or the energy produced in the large plant must be stored in small light units. If the latter solution is chosen we have two

main aims for our energy storage devices. One type must be capable of storing large quantities of energy at a high efficiency, but its energy density may be low. The other requirement, for vehicles, is a very high specific energy density.

Two main systems have been proposed that could be used for both requirements. One system is based on hydrogen, which can be generated by the electrolysis of water. Then this can be used in pressurized cylinders (or other forms of storage (1)) as a direct replacement for petrol in vehicles, producing no pollution problems. It can also be burnt to provide heating and used also to generate electricity. Another solution would be to use batteries to answer the problem, though present batteries are not economically viable. So there is a large amount of money being invested to produce suitable batteries of which some of the battery systems are given in table 0.1 below.

System	Theoretical Energy Density (W hr/kg)	Expected Realizable Density (W hr/kg)
Lead-Acid	167	40
Fe-Ni	266	60
Ni-Zn	321	90
Na-S	680	150
Li-S	1500	150
Li-TiS ₂	470	130

Table 0.1
Selected Battery Systems

The research work that is detailed in this thesis is directed to looking at the behaviour of a possible type of electrode to be used in high energy density batteries. Actual batteries would use a very electro-negative metal as the mobile species, e.g. Li or Na, but these materials are hard to deal with due to their reactivity. So for a model system copper was chosen, though it will never be used in a high energy density battery, due to its high atomic weight and low electro-negativity. It is however easy to obtain room temperature electrolytes for copper and it is not affected by the atmosphere to the same extent as the more electro-negative materials.

CHAPTER 1

SOLID STATE TRANSPORT

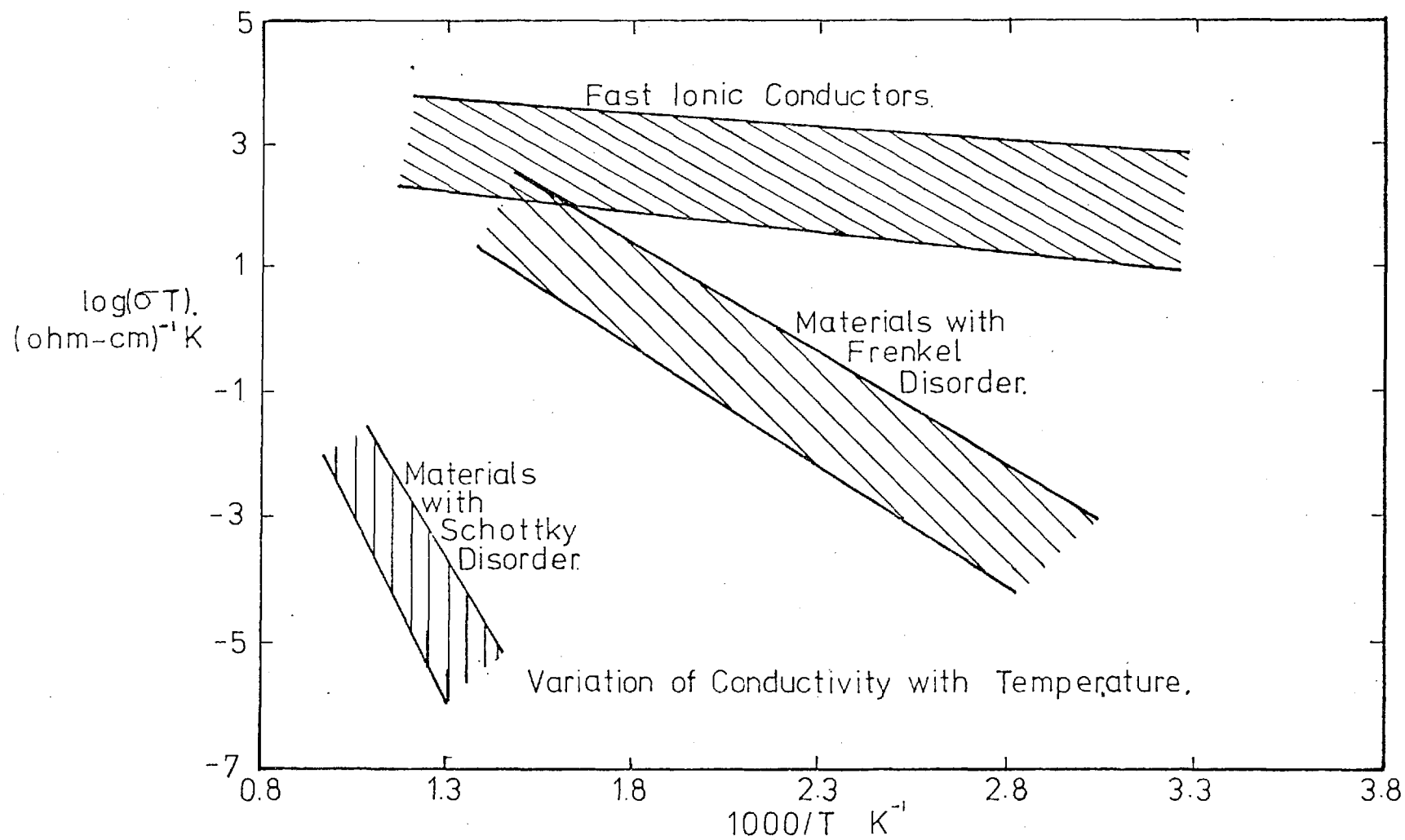
1.1. INTRODUCTION

Solid: Body consisting of particles that maintain their relative positions against some degree of pressure (2).

This is a common authoritative view on what solid means. Having said that it is hoped to show that this is far from true for some solids. In fact it is possible to have ionic motion that is greater in the solid phase than in the liquid phase at a slightly higher temperature (3).

1.2. FAST ION CONDUCTORS

The classical view of transport of ions in a solid is that the above definition is basically true, but there are imperfections in the crystal structure, and it is the point defects that move. Two main types of point defects are interstitial ions (Frenkel disorder) and ion vacancies (Schottky disorder). Materials with Frenkel disorders usually have a higher ionic conductivity than materials with Schottky disorder as can be seen from figure 1.1. These mechanisms did not explain the very high ionic conductivities that were found in some high temperature phases, mainly of copper and silver compounds (4). These highly conducting phases are characterized by a much lower temperature dependence than the normal Frenkel and Schottky disorders (see fig. 1.1).



Bands showing the temperature dependence of the ionic conductivity of three types of material(4)
Figure. 1.1

The ionic conductivity (σ_i) of fast ion conductor, Frenkel, and Schottky materials can usually be represented by the following equation.

$$\sigma_i = \left(\frac{\sigma_o}{T} \right) \exp \left(\frac{-\Delta H}{kT} \right) \quad 1.I$$

Where T is the absolute temperature, σ_o is the conductivity constant, ΔH is the activation enthalpy, and k is Boltzmann's constant. In the fast ion conductors the temperature dependence is low, implying that ΔH is smaller than in classical ionic conductor and, as well, σ_o is considerably smaller than in the normal case. Equation 1.I can be derived from a hopping model (see Appendix F), giving:-

$$\sigma_o = \frac{c_i z_i^2 e^2 \alpha d^2 \beta}{k} \nu_o \exp \left(\frac{\Delta S}{k} \right) \quad 1.II$$

Where α is a geometric factor, c is the concentration of the mobile species (i), and $z_i e$ the charge on them. e is the charge on an electron, d the jump distance, β is the fraction of the mobile species free to move, ν_o is the jump attempt frequency, and ΔS is the entropy of migration. Thus the small σ_o implies either a very low attempt frequency or a very small if not negative entropy of migration, as c_i , d, α , and z_i are all of the same order of magnitude from material to material and β is usually assumed to be close to unity. This, however, may not always be true, as in the case where the number of carriers approaches the number of sites. Each carrier is prevented from occupying any site which is already filled and so it can only move when it is adjacent to a vacant site. Thus, when the total number of available sites is fixed, the value of β will decrease as the concentration of charge

carriers (c_i) is increased towards complete occupancy of sites. This means (from equation 1.II) that the conductivity of an ionic conductor will pass through a maximum as c_i is increased. For many situations however it is appropriate to consider that β is equal to unity, and therefore this value will be assumed in the ensuing discussion.

The ionic conductivity which is required in a fast ionic conductor is of the order of $10^{-1} (\text{ohm cm})^{-1}$. If a term μ , the mobility is defined as the drift velocity per unit electric field, ionic conductivity can be written as

$$\sigma_i = c_i \beta z_i e \mu \quad 1.III$$

Einstein first pointed out that the diffusion coefficient, D^* , is related to the mobility by the following:

$$D^* = \frac{kT}{z_i e} \mu \quad 1.IV$$

Thus it follows that the diffusion coefficient is related to the ionic conductivity by the following (see Appendix F):

$$\sigma_i = \frac{c_i \beta e^2 z_i^2}{kT} D^* \quad 1.V$$

Which implies that at room temperature the self diffusion coefficient (D^*) in a fast ion conductor must be at least $10^{-6} \text{ cm}^2 \text{ sec}^{-1}$, which is only an order of magnitude below that in a liquid ($10^{-5} \text{ cm}^2 \text{ sec}^{-1}$).

To get a better view of the microscopic process taking place in these compounds we must look at what other information there is. In 1935 Ketelaar (5) reported an abnormal rise in the specific heat of Ag_2HgI_4 near its transition from β (low conductivity) phase to the α (high conductivity) phase as well as an unusually small change in

Table 1.1
Selected Copper and Silver Fast Ion Conductors

Material	Temp. Stability Range °K	References
α -AgI	419-828	Strock (7)
α -Ag ₂ S	452-1098	Rahlfis (9)
α -Ag ₂ Be	406-1153	"
α -CuBr	745-763	Hoshino (10) and Krug & Sieg (10)
α -CuS	> 364	Armstrong (15)
α -Cu ₂ HgI ₄	>1040	"
AgAl ₁₁ O ₇	Stable	McGeekin & Hooper (14)
(C ₅ H ₅ NH) ₅ Ag ₄ I ₁₃	<293->373	" "
Ag ₇ I ₄ AsO ₆	<293->373	" "
(CH ₃) ₄ NAg ₄ I ₇	273-393	" "
Ag ₁₇ I ₁₈ P ₂ O ₇	<300-420	" "
Ag ₁₃ (Me ₄ N) ₂ I ₅	> 323	" "
Ag ₇ I ₄ PQ ₄	<300-352	" "
KCN.4AgI	<293->423	" "
RbAg ₄ I ₅	120-~475	" "
KAg ₄ I ₅	137-526	" "
Ag ₈ HgS ₂ I	<293->373	" "

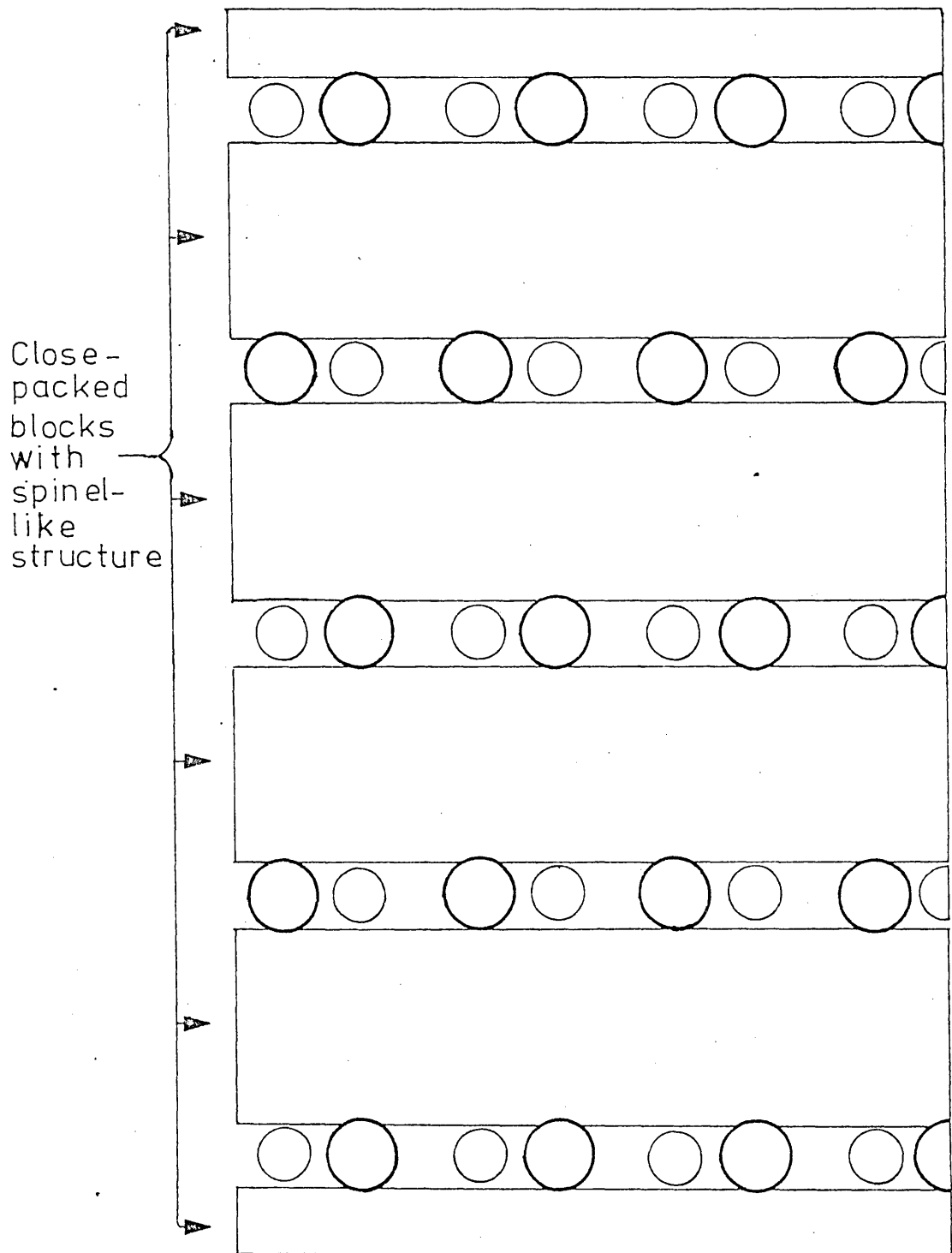
the entropy at the melting point. With the support of X-ray information (6) which shows an average distribution of the cations on their lattice sites, Strock (7) describes a rigid anion lattice with a molten cation lattice. More support is given to the "liquid-like sub-lattice" theory by O'Keefe (8), and others, who found that the entropy change during the melting of some other fast ion conductors is also small.

Since the original realization of fast ion conductors many more have been added and just a few Ag and Cu ones are shown in table 1.1. As is seen from this table some fast

ion conductors are stable at room temperature and just above.

In order for ions to move in a rigid framework they must be small enough to go through this framework. Also their potential energy must not change too much as the ion travels through the structure. So in order to be a good fast ion conductor the material would require a very open structure e.g. β -Alumina. In β -Alumina the structure is made up of layers of close packed spinel-like structures, which are held apart by oxygen atoms, and it is in these layers that ions can move between a large number of equivalent sites (fig. 1.2). As β -Alumina is a layer structure it has the disadvantage that its conduction is only in 2-dimensions. In order to improve on this a 3-dimensional conductor, an interconnected tunnel structure, or skeleton structure is required. It is with this concept that Goodenough et al (12), as well as other workers (13), have worked to produce an ionic conductor which has an open structure allowing motion in all three dimensions.

In order to find materials possessing fast ion conductivity many new techniques have been developed, besides the traditional D.C., A.C., and radio tracer experiments for detecting ionic and electronic conductivity. Probably the most notable of these is Nuclear Magnetic Resonance (N.M.R.) spectroscopy which shows whether the ions are mobile, but does not easily differentiate between movement about a localized site and long range movement between sites. Other techniques that have been applied are given in a recent review on "fast ion conductors" by Huggins (4).



Schematic representation of the structure of beta alumina showing close-packed blocks, separated by bridging layers sparsely populated by M^+ (mobile ions [○]) and oxide ions [●] (4).

Structure of β -Alumina,
Figure 1.2.

1.3. CO-ORDINATION EFFECTS

According to a recent review by McGeehin & Hooper (14) copper and silver are the most common mobile ions in fast ion conductors. To see why they are so, we must see what it is they have in common. Along with gold they are members of group 1B of the periodic table, and these are all capable of being monovalent. Among monovalent metals Cu^{I} and Ag^{I} are unusual because they can occupy 4 co-ordinated sites with anions whereas others usually have 6 or 8 co-ordination. In fact Cu^{I} and Ag^{I} have in some cases been found with 2 or 3 co-ordination, e.g. oxides and nitrides (15). It is this ability to take up low co-ordination positions which allows Ag^{I} and Cu^{I} to pass over saddle points in the lattice potential energy, so they diffuse more easily than other metals. Co-ordination numbers of 4 or less which is usually characteristic of covalent compounds, only occurs if the anion possesses some $\text{d}\pi$ -bonding ability (15).

Looking at it from another point of view, Ag^{I} and Cu^{I} both have their outer d energy levels close to that of their outer S energy levels. Thus they have high polarizabilities, which allow them to take up low co-ordination sites easily compared with other monovalent ions (15).

1.4. COPPER ELECTROLYTES

An electrolyte is a material in which all the electrical conductivity is due to mobile ions. This usually cannot be realized, and thus cells will discharge given long enough. For a commercially produced battery the time of self discharge must be large to give it a long shelf life. In the case of the original copper solid electrolyte used,

(copper (I) halides) the electronic conductivity was only a few orders of magnitude below that of the ionic (e.g. 5 orders of magnitude for CuBr at 673°K (17)). Originally all solid electrolytes known were high temperature ones.

The approach to lowering the high operating temperatures has been to try to stabilize the high temperature fast ionic conductors at lower temperatures by putting other components in the system. This was first done for copper by Takahashi et al (18) in 1973 by using an organic salt in the structure along with a copper (I) halide. These compounds and later ones (19) have attained ionic conductivities up to 3.5×10^{-2} (ohm cm)⁻¹ at 300°K along with electronic conductivities of 10^{-13} (ohm cm)⁻¹ at 300°K. This gives eleven orders of magnitude difference in the conductivities, or a discharge time of a million times longer than with copper bromide.

Some of these organic salts are unstable in galvanic cells (20). So Matsui and Wagner (21) have approached the problem by using a mixture of copper (I) halide with a metal halide. One material made by this method used CuI plus KI to produce KCu_4I_5 . This is related to the solid electrolyte with the highest room temperature conductivity known, RbAg_4I_5 for silver ions, as it has already been stated that copper and silver are very similar (section 1.3.). The result of copying this for copper does not give such good results as the organic salt electrolytes. Though the best one which Matsui and Wagner found, RbCu_4Cl_5 has a conductivity of 8.25×10^{-4} (ohm cm)⁻¹ at 300°K and 1.14×10^{-2} (ohm cm)⁻¹ at 415°K with an electronic conductivity of 10^{-15} (ohm cm)⁻¹ at 300°K (22).

Another copper electrolyte which is not related to the copper (I) halides is based on the sodium electrolyte, β -Alumina with the sodium replaced by copper (23). Though this is a poorer conductor than the two types already mentioned, it has a much larger temperature range.

All copper electrolytes suffer from the problem that copper (I) can be oxidized to copper (II) with a fairly low overpotential (700 mV for Takahashi's organic electrolytes (18)) and this causes electronic conduction in the electrolyte. So any commercial cell would be restricted to a low voltage giving it a low energy density. In a recent communication to the Electro-Chemical Society (24) Raleigh has suggested a possible mechanism for the deterioration of copper electrolytes. This model predicts a front moving through the electrolyte where Cu (I) is oxidized to Cu (II) as long as the cell emf is greater than ≈ 350 mV. Kinetically at least this does not appear to happen as it is stable for voltages up to 700 mV (18).

The main measurements that are carried out on electrolytes are A.C. to achieve the total conductivity, and a Hebb-Wagner type measurement to obtain the electronic conductivity (25). Both of these were used in this work and will be detailed in section 2. Ionic conductivity can also be obtained by a four contact type system as will be given later for the ionic conductivity of Bornite.

1.5. SOLID SOLUTION ELECTRODES

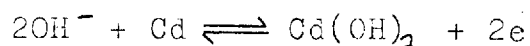
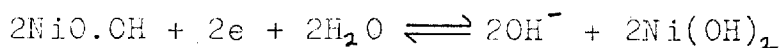
The cell E.M.F. (Electromotive Force) is proportional to the energy released by the chemical reaction that takes place in the cell. By definition,

$$\Delta G = -nFE$$

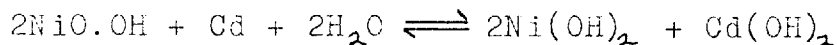
1.VI

where E is the cell equilibrium voltage, ΔG is the Gibbs free energy change, and n is the number of electrons involved in the process, with F being Faraday's constant.

The conventional electrochemical cell is made up in such a way that a chemical reaction takes place at one of the electrodes producing one or more reaction products. For example the nickel-cadmium alkaline cell which has NiO.OH as the positive electrode and Cd as the negative electrode. Reactions occurring at the positive and negative electrodes may be represented by the following equations.



Thus the total cell reaction is



If the second phase cannot be removed from the electrode interface or the mobile species cannot get through the second phase the electrode will rapidly become blocked. This blocking of the electrode is called polarization of the electrode. Also during charging and discharging the electrode undergoes a morphological change. This can cause internal shorts, electrode breakdown, and also loss of reactive area.

If a cell could be discharged and maintain its equilibrium voltage it would have changed the chemical energy into electrical energy with 100% efficiency. If the same amount of energy had been converted into electricity by a 100% efficient dynamo driven by a heat engine, the efficiency would be limited by the Carnot limit (about 20% efficiency for a heat engine working with one reservoir at

373°K and the other at room temperature). Therefore an electrochemical cell is theoretically more efficient than a heat engine in the ideal case.

If the electrode is made up of two phases in equilibrium the activities of the mobile species are defined at the electrode. This means that the voltage is defined by the free energy change.

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad 1.VII$$

where the cell reaction is $aA + bB \rightleftharpoons cC + dD$, and a is the respective activity and ΔG° is the standard free energy and is the free energy change associated with the reaction when the reactants and products are at unit activity.

A constant voltage is a desirable quality in a battery but in a two phase system it is difficult to obtain due to polarization of the interface by the products (concentration polarization). This is one of the main problems with conventional electrodes. It can be overcome by various ways, one example is the Na-S cell where both the electrodes are molten so Na_xS can mix freely in the sulphur. It would of course be better if only one phase were present.

This would require a non-stoichiometric compound which could accommodate the mobile species. In order for a non-stoichiometric solid compound to be formed the mobile species must have a high diffusion rate in the electrode. To be an electrode it must also have a high electronic conductivity. This has therefore defined the basic concept of a Solid Solution Electrode (S.S.E.).

If the diffusion coefficient is high enough there will now be no polarization problem, but the activity at this

electrode is no longer fixed. This means that the cell E.M.F. will change as the activity changes. For a working cell it is desirable for the E.M.F. to be constant over the range of composition for which the cell is going to be used. This range must be large in a practical cell, e.g. Li_xTiS_2 where $x = 0$ to 1.

It would be even better if the voltage were actually constant over composition range. This cannot be so as the chemical diffusion ($\tilde{D}$) depends on the variation of ΔG with composition. If this is equal to zero $\tilde{D} = 0$ according to equation 1.VIII where $\tilde{D}^*$ is the self diffusion coefficient

$$\tilde{D} = \frac{\tilde{D}^* d \ln a}{d \ln x} \quad 1.VIII$$

The solid solution electrode so far requires a high diffusion rate in it, but the diffusion of the mobile species across the electrolyte-electrode interface has not been mentioned. This of course must be rapid, i.e. a large exchange current (low activation polarization), so there must be a good interface. In the case of a solid-liquid interface, assuming that the liquid wets the solid, there will be a good interface, e.g. molten sodium, β -Alumina interface in the Na-S battery. This also has the advantage that changes in the lattice parameters of the electrodes can easily be accommodated, e.g. Li_xTiS_2 in the Li-TiS battery where the c lattice parameter of the TiS_2 can change by about 9% (20) (Li_xTiS_2 is a S.S.E.).

In the solid state cell the choice of electrodes will be restricted by the requirement to find a compound which can form a good contact with the electrolyte. If both the electrode and the electrolyte are solid there is an interface

problem, so it would be best if the interface is coherent. There are problems with this, as the two components will usually have different expansion coefficients.

A solid state cell would have the advantage over others that it would be more rugged, and would have fewer problems in containing the elements of the cell. Also a layer technique can be used, thus giving a large surface area to volume ratio, so increasing the maximum current that can be drawn from the cell. Another advantage of using a solid electrolyte is that they usually have a larger breakdown voltage, as well as fewer problems with side reactions than those using liquid electrolytes.

The only other requirement for an S.S.E. is for the material to be cheap and easily fabricated, to make batteries.

So to summarize, the conditions required for an S.S.E. which were originally set out by Steele (27) in 1973 are as follows:-

1. Good electronic conductor.
2. Large range of composition.
3. A nearly constant E.M.F. for various compositions.
4. Rapid diffusion of the mobile species.
5. Good electrolyte-electrode interface, with a large exchange current.
6. Stable electrolyte-electrode interface.
7. The electrode is cheap to manufacture.

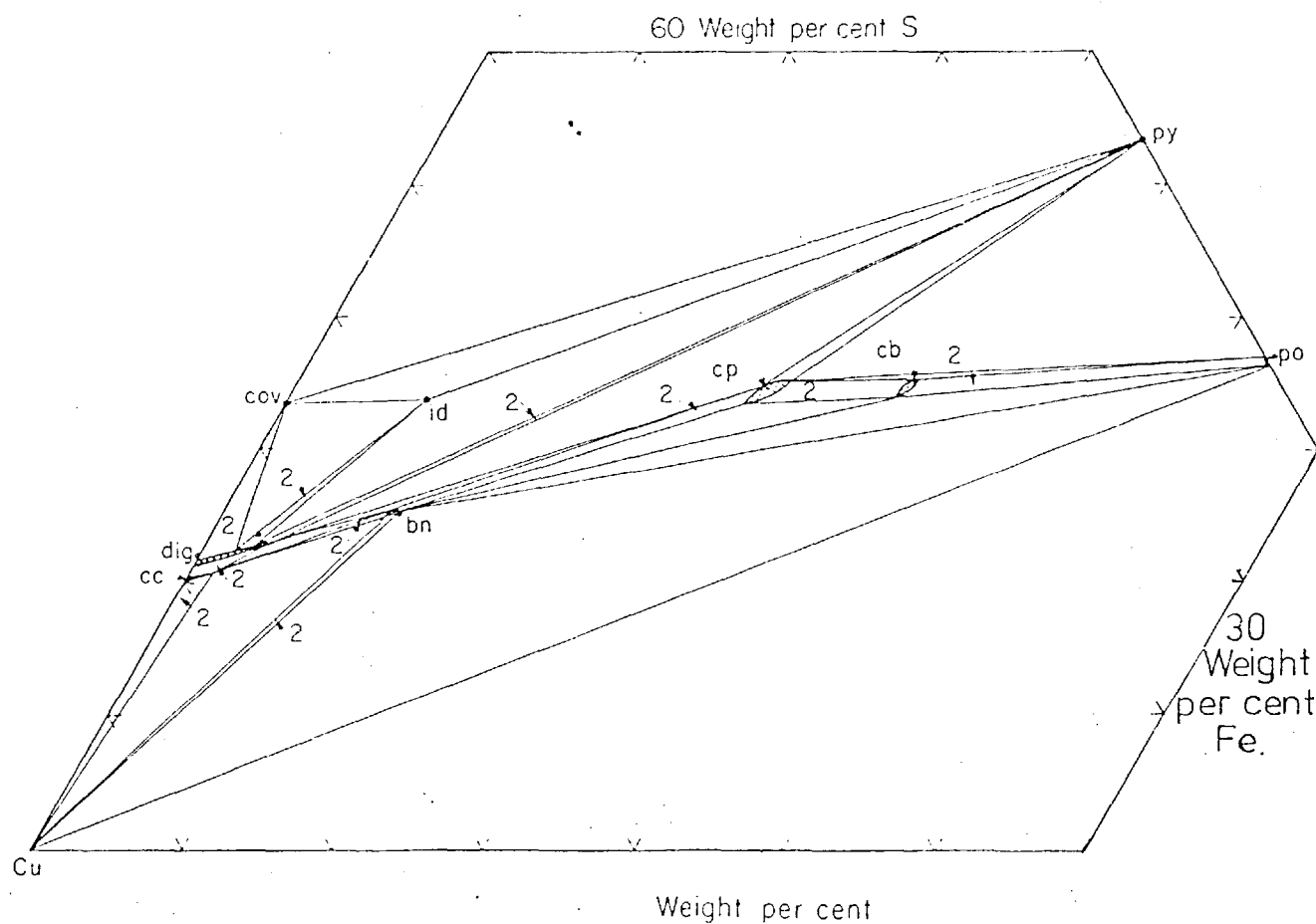
The field of S.S.E.s is a new one and as yet there are few known, but for a review of the field a recent paper by Steele should be consulted (28). As this field is a new one it was felt that the best way to investigate the properties of these electrodes would be to work with copper

as a model system.

1.6. Cu-Fe-S TERNARY

There are a large number of phases in the Cu-Fe-S ternary (see fig. 1.3), which are based on the face centred close packed sulphur lattice, with the metal atoms being ordered in different ways. This system has been of great interest as it contains a number of copper ores which are of economic interest. Thus a lot of work has been done on them, and for different phases in the ternary Yund and Kullerud (29) should be consulted. It was work on the leaching (30) of one of these materials that suggested that it might be suitable for a solid solution electrode as copper appeared to have a high diffusion rate.

The leaching work showed that two copper ions could be readily removed from a copper ore called Bornite (Cu_5FeS_4). Also it appeared that the crystals did not break up on the removal of copper from it. Thus it was a relatively obvious choice as a model system to be worked on. Not only is a high diffusion coefficient required for an S.S.E., but also electronic conductivity, and the copper iron sulphides are all semiconductors (31).



abbrev- iation.	phase	stoichiometric composition
cc.	Hexagonal Chalcocite	Cu_2S
dig.	Digenite	$\text{Cu}_{1.8}\text{S}$
cov.	Covellite	CuS
pa	Hexagonal Pyrrhotite	FeS
py.	Pyrite	FeS_2
bn.	Orthorhombic Bornite	Cu_5FeS_4
id	Idaite	$\text{Cu}_{5.5}\text{FeS}_{6.5}$
cp.	Tetragonal Chalcopyrite	CuFeS_2
cb	Tetragonal Cubanite	CuFe_2S

200°C isothermal section. Assemblages consisting of two condensed phases are indicated by numeral 2.(29).

Figure 1.3
Cu-Fe-S Ternary.

CHAPTER 2

THE ELECTROLYTE

2.1. INTRODUCTION

As has already been mentioned, in recent years there has been a large increase in the number of solid electrolytes (32). For this work it was required to choose an electrolyte that had a high ionic conductivity at room temperature and just above. Also an electrolyte that is easy to produce, as it was only required as a means to an end. In 1975, Takahashi and Yamamoto (19) reported a group of double salt electrolytes based on a copper (I) halide and an organic halide, these having a higher ionic conductivity and lower electronic conductivity than an earlier group (18). The one chosen for production out of these electrolytes was 1,4 Dimethyl 1,4-diazabicyclo (2,2,2) octane dibromide (sometimes referred to as N,N-dimethyl-triethylene diamine) with copper (I) bromide, due to its high conductivity and large range of thermal stability (up to 510°K).

2.2. PREPARATION AND CHARACTERIZATION

The preparation of the electrolyte generally followed the method set out by Armstrong et al (33) in 1974. Copper (I) bromide (Koch-Light Puriss Grade $\geq 99\%$) was purified by twice recrystallizing it from 10% hydrobromic acid under a nitrogen atmosphere. It was then washed with

glacial acetic acid, distilled water, and finally ethanol, after which it was dried under vacuum. The product was very small crystals with a very pale yellow colour. A sample of this product was ground to a fine powder and then pressed in an 8mm stainless steel die to produce a pellet, whose conductivity with platinum electrodes pressed on it was so low that it could not be measured on a radio frequency bridge (Wayne Kerr SR268). When copper electrodes were used the conductivity at 154khz at room temperature was found to be $8 \times 10^{-5} (\Omega \text{cm})^{-1}$. The purified copper (I) bromide was also x-rayed on a diffractometer and the results are shown graphically in figure 2.1 and the numerical values in table 2.1.

The organic part of the electrolyte (fig. 2.2) was produced from 1,4-diazabicyclo (2,2,2) octane dissolved in methanol, with methyl bromide bubbled through it (both supplied by Koch-Light), while the solution was maintained at 0°C, for half an hour. The rate of production of the crystals was high, and the clear liquid became white with crystals precipitating out of solution. The precipitate was filtered off, and then washed with methanol at 0°C, after which it was dried under vacuum for 4 hours before being stored in a desiccator.

The composition of the organic was checked by analysis at Imperial College Analytical Services and by University College Chemistry Department. The results were as follows:-

X-ray Diffraction Intensities.

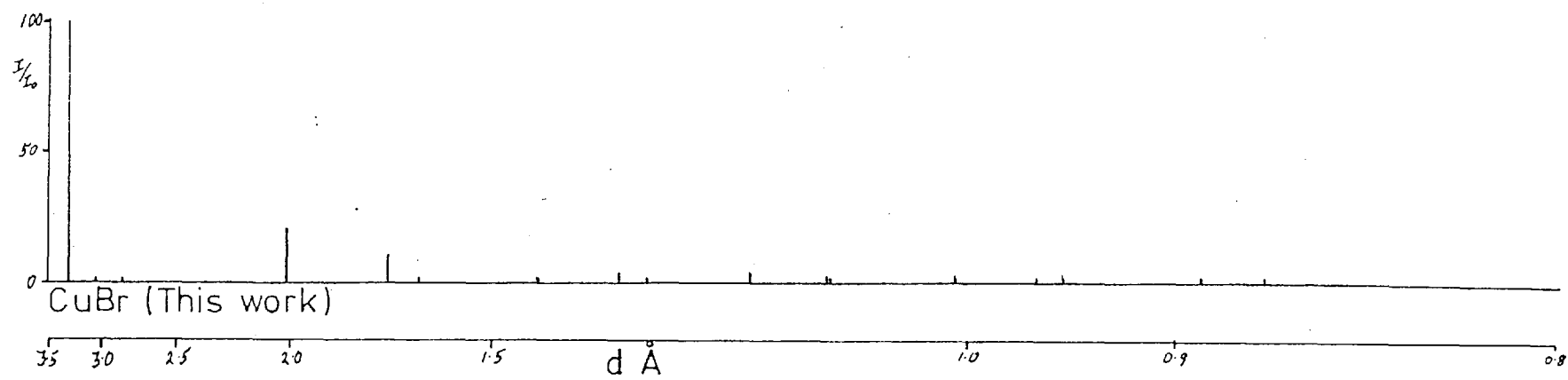
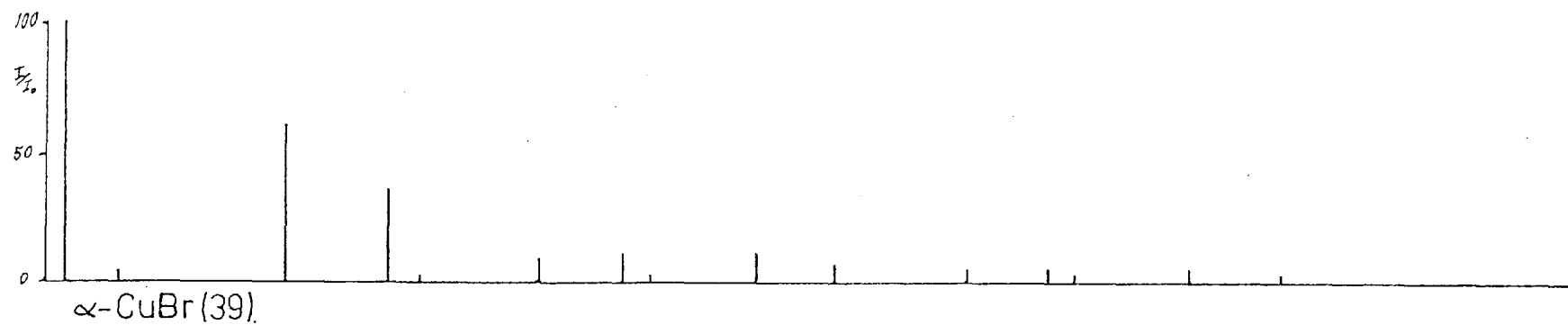
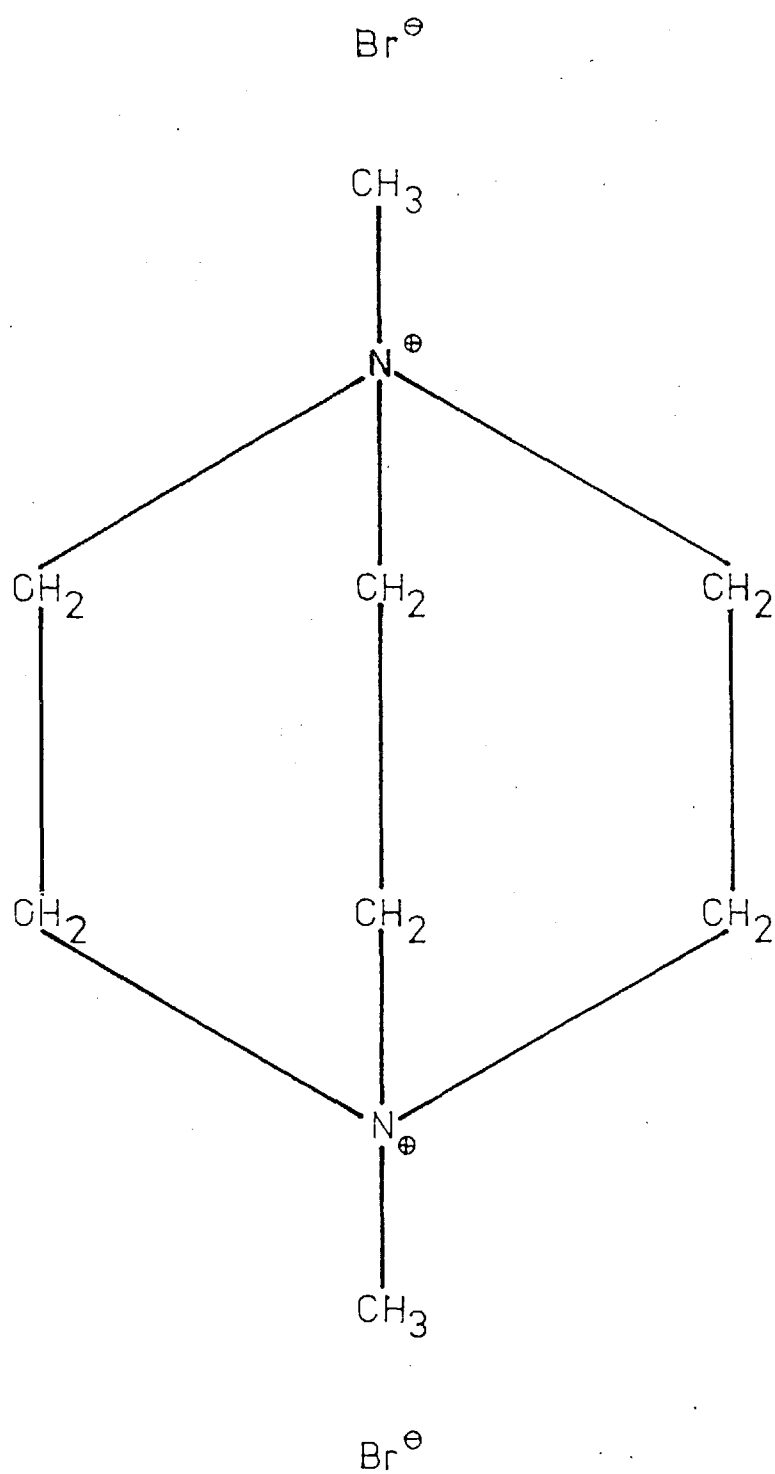


Figure 2.1



Structure of 1,4-diazabicyclo[2,2,2]octane
dibromide.
Figure 2.2

Element	Wt.% found at U.C.	Wt.% found at I.C.	Wt.% Theoretical
C	31.31	--	31.81
H	5.99	--	5.96
N	9.09	9.26 ± 0.01	9.28
Br	52.07	51.0 ± 0.5	52.95

Table 2.2

Analysis of Organic Part of the Electrolyte

As the above results were not as close as was expected it was decided to check the organic component by N.M.R. and I.R. spectrum. The N.M.R. was carried out at University College and gave a $-\text{CH}_2-$ peak which was approximately three times the integrated area as the $-\text{CH}_3-$ peak, plus a peak for water. The I.R. spectra was produced on a double beam grating spectrophotometer, and compared with tri-ethylene diamine as no spectra appears to exist in the literature for 1-4 dimethyl, 1,4 diazabicyclo (2,2,2) octane dibromide. Therefore certain identification is not possible, see Bellamy (34). The $\nu(\text{CH})$ (stretching of CH bonds) vibrations of $-\text{CH}_3$ and $-\text{CH}_2-$ groups showed frequency shifting and splitting with increased peaks at higher frequencies (3000-2900 cm^{-1}) and a decrease in intensity at lower frequencies (2900-2800 cm^{-1}) as expected. The $\delta(\text{CH})$ (bending) of both $-\text{CH}_2-$ and $-\text{CH}_3$ occur in approximately the same region (1500-1400 cm^{-1}) with probably no splitting of $\delta(\text{CH})$ of $-\text{CH}_2-$ from an intensity consideration. The two expected peaks for N^+CH_3 occur at 1212 cm^{-1} and 1147 cm^{-1} which is somewhat lower than the expected region of 1300 cm^{-1} . This shift also occurs in the $\nu(\text{CC})$ and skeletal vibrations

which have large shifts ($>100\text{ cm}^{-1}$). Thus from the I.R. spectra it cannot be definitely established whether this is the correct organic compound but it is compatible with a N-methyl quaternary ammonium salt with the positive charge on the nitrogen diffused. Whereas the N.M.R. spectra seems to leave very little doubt about it being the required organic.

X-rays of the organic were done to provide a method to check the organic when it was produced in the future, but it was found that these varied greatly in the same sample. It was however established that this was due to water being picked up from the atmosphere during X-raying. So in order to obtain an X-ray of the dry material a sample was dried overnight in vacuum. It was then mounted on a diffractometer sample holder in the dry box, with double sided sellotape which had been dried in the same way. After which a layer of polythene was attached over the sample. The results obtained are shown in figure 2.3 and table 2.3 along with the results for the same sample after a week exposed to the air. No mention is made in the literature of the organic picking up water, though the effects of water on CuBr are pointed out.

The required composition for the electrolyte was $94\text{CuBr} \cdot 6(\text{CH}_3)_2\text{C}_6\text{H}_{12}\text{N}_2\text{Br}_2$, which according to Takahashi and Yamamoto (18) is the composition with the highest ionic conductivity ($3 \times 10^{-2} (\text{ohm cm})^{-1}$ at 20°C). The two constituents in the correct ratio were ground together in an agate mortar and pestle with sufficient methanol to form a slurry. After about 15 minutes of grinding in the dry box it was left for the methanol to evaporate off, after

X-ray Diffraction Intensities.

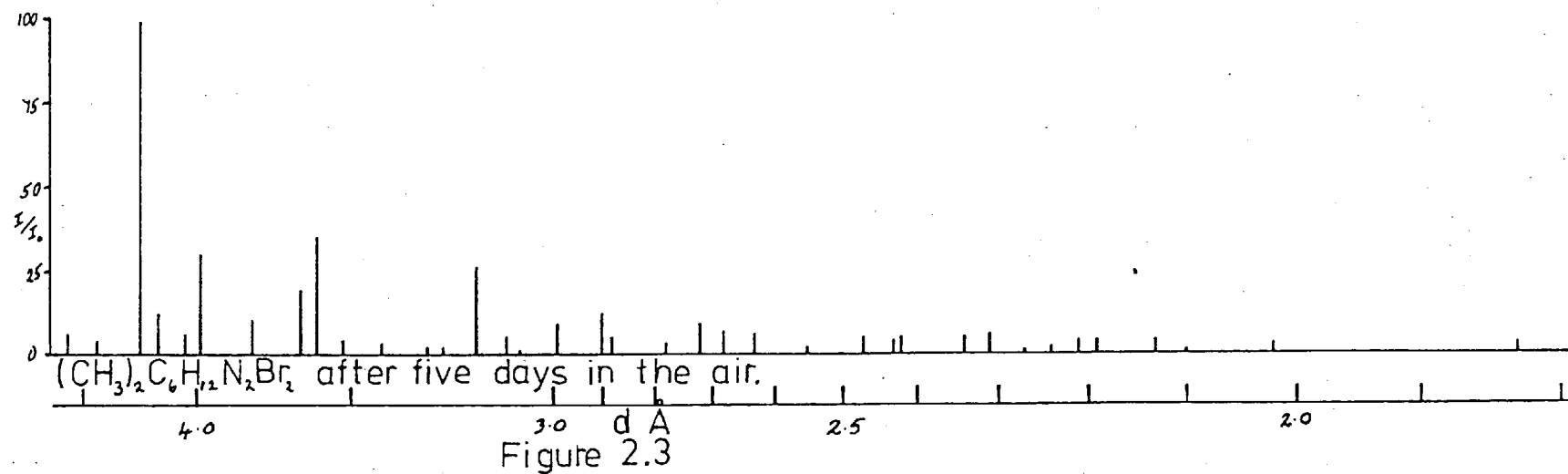
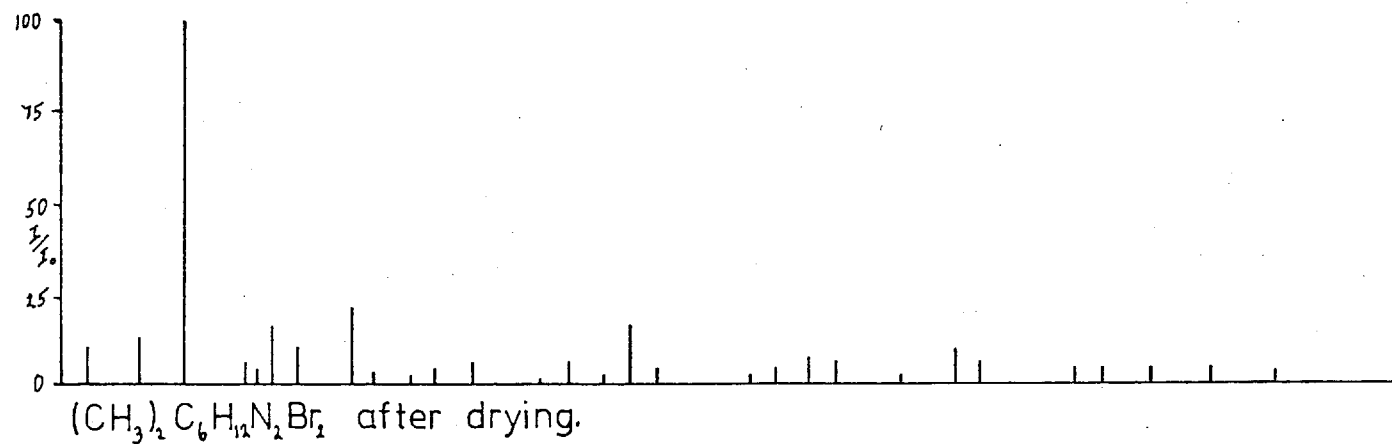


Figure 2.3

which time all last traces were removed by evacuation for an hour. The mixture was then ground again to produce a fine powder. This powder was then pressed in an 8 mm stainless steel split die, using a G-clamp to provide the pressure so it could be carried out in the dry box. A stainless steel die was used after it was found that this mixture caused mild steel dies to corrode rapidly. Pellets produced varied in their thickness from 2 mm to 5 mm.

Next the pellets were hot pressed in an 8 mm graphite die, 3 or 4 at a time with graphite spacers to separate them. Conditions for pressing were a dynamic vacuum (better than 10^{-1} microns) at a temperature of 170°C and a pressure of $6 \times 10^7 \text{ Nm}^{-2}$ for 20 hours. Pellets produced by this method had a density of $3.5 \pm 0.2 \text{ gm.cm}^{-3}$ compared with $3.4\text{--}3.5 \text{ gm.cm}^{-3}$ obtained by Mari (35), and 4.10 gm.cm^{-3} reported by Lazzari et al (36), and a grain size of 1 micron.

Lazzari et al (36) report their electrolyte turns green on exposure to moist air though in this work there has not been any evidence for this when pellets were left out in the air after days. Though the pellets did go dark yellow from the whitish-yellow colour they started, on prolonged exposure to light (of the order of days) as reported by Lazzari.

The X-ray results, which are shown in figure 2.4 and table 2.4, did not seem to be affected by whether the sample was protected from the atmosphere or not over a ten hour period. The X-ray lines are shown along with the results obtained by Taylor (37) as these were the only results available for comparison. As will be seen from the results they do not agree at all, with the ones from this work, being

X-ray Diffraction Intensities.

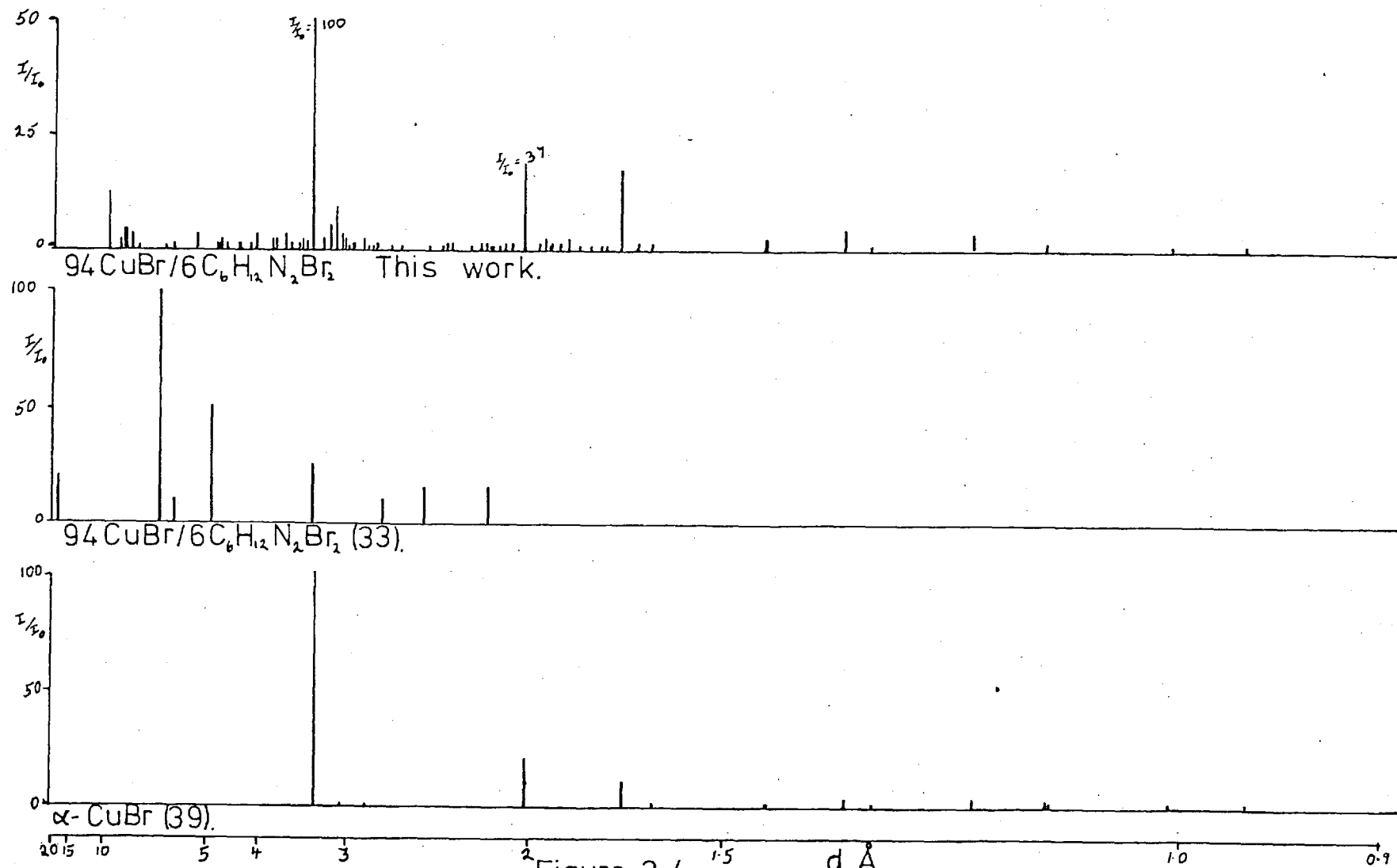


Figure 2.4

more numerous, and containing all the copper (1) bromide lines. Other workers reports of X-rays on this composition of electrolyte state that copper (1) bromide lines are always present (18, 19, 38). From the new lines it is obvious that a new phase has been created but this is not the same as achieved by Taylor. The reliability of X-ray data achieved by Taylor is unsatisfactory as his data for the CuBr bears no resemblance to that shown on the ASTM card for CuBr (39).

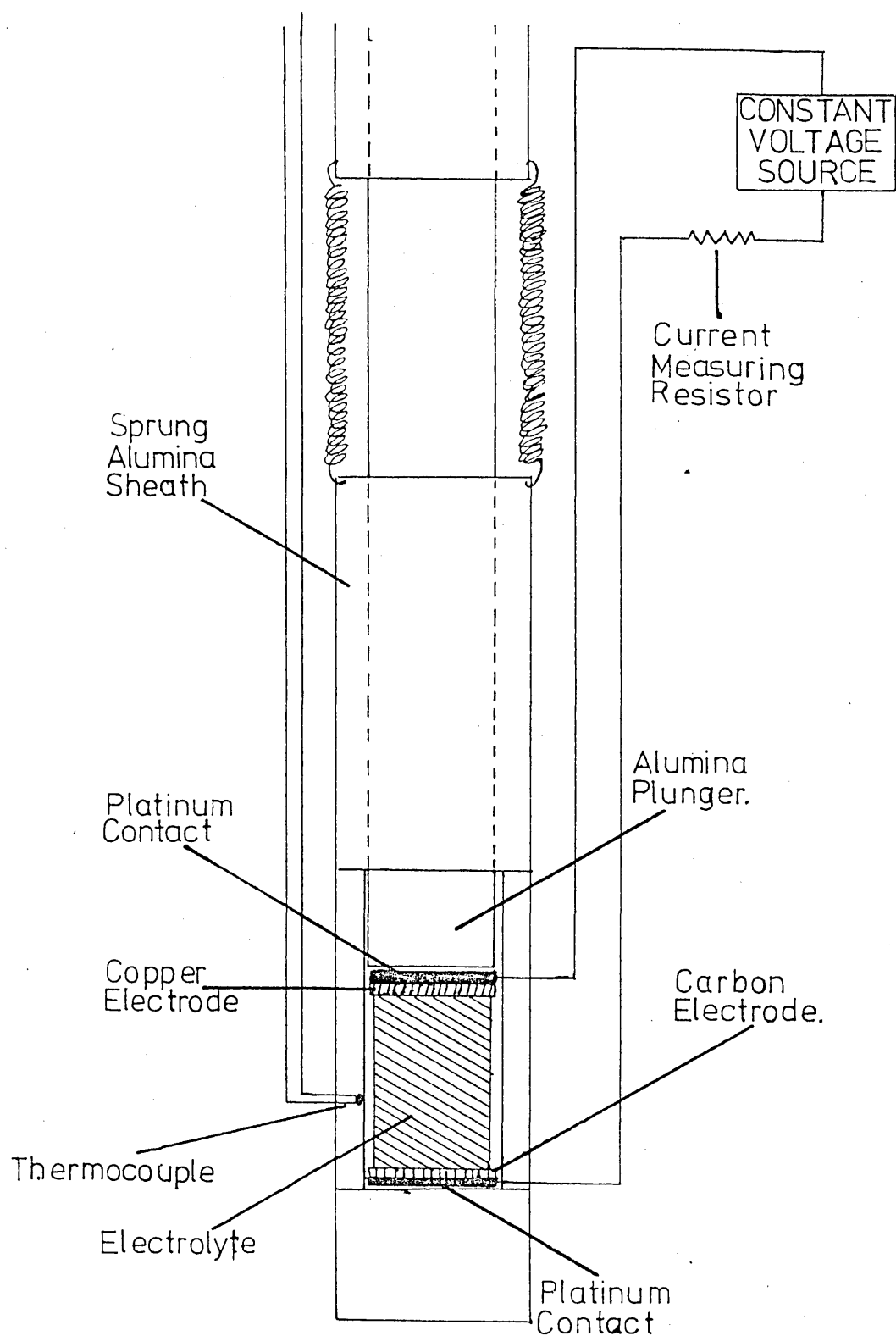
2.3. ELECTRONIC CONDUCTIVITY

The Hebb-Wagner method (25) is used to measure the electronic conduction in an ionic conductor with the activity of the ionic species fixed. The cell consists of a metal electrode, reversible to the ionic species and another electrode which is blocking to the ions, with the sample in between (see fig. 2.5). From the theory (see Appendix A) the current density (J) as a function of applied voltage (E) is

$$J = \frac{I}{A} = \left\{ \sigma_{\ominus}^{\circ} \left[1 - \exp \left(\frac{-EF}{RT} \right) \right] + \sigma_{\oplus}^{\circ} \left[\exp \left(\frac{EF}{RT} \right) - 1 \right] \right\} \frac{RT}{FL} \quad 2.I$$

where I is the current, A is the cross-sectional area, L is the thickness of the sample, F is Faraday's constant, $\sigma_{\ominus}^{\circ}$ and $\sigma_{\oplus}^{\circ}$ are the electronic conductivities in the electrolyte coexisting with metallic copper due to excess electrons ($\ominus$), and electron holes ($\oplus$), R the gas constant, and T the absolute temperature.

In the derivation of equation (2.I) (see Appendix A) it is assumed that the excess electrons and electron holes follow the laws of ideal dilute solutions, their mobilities are independent of concentration, also the change in the



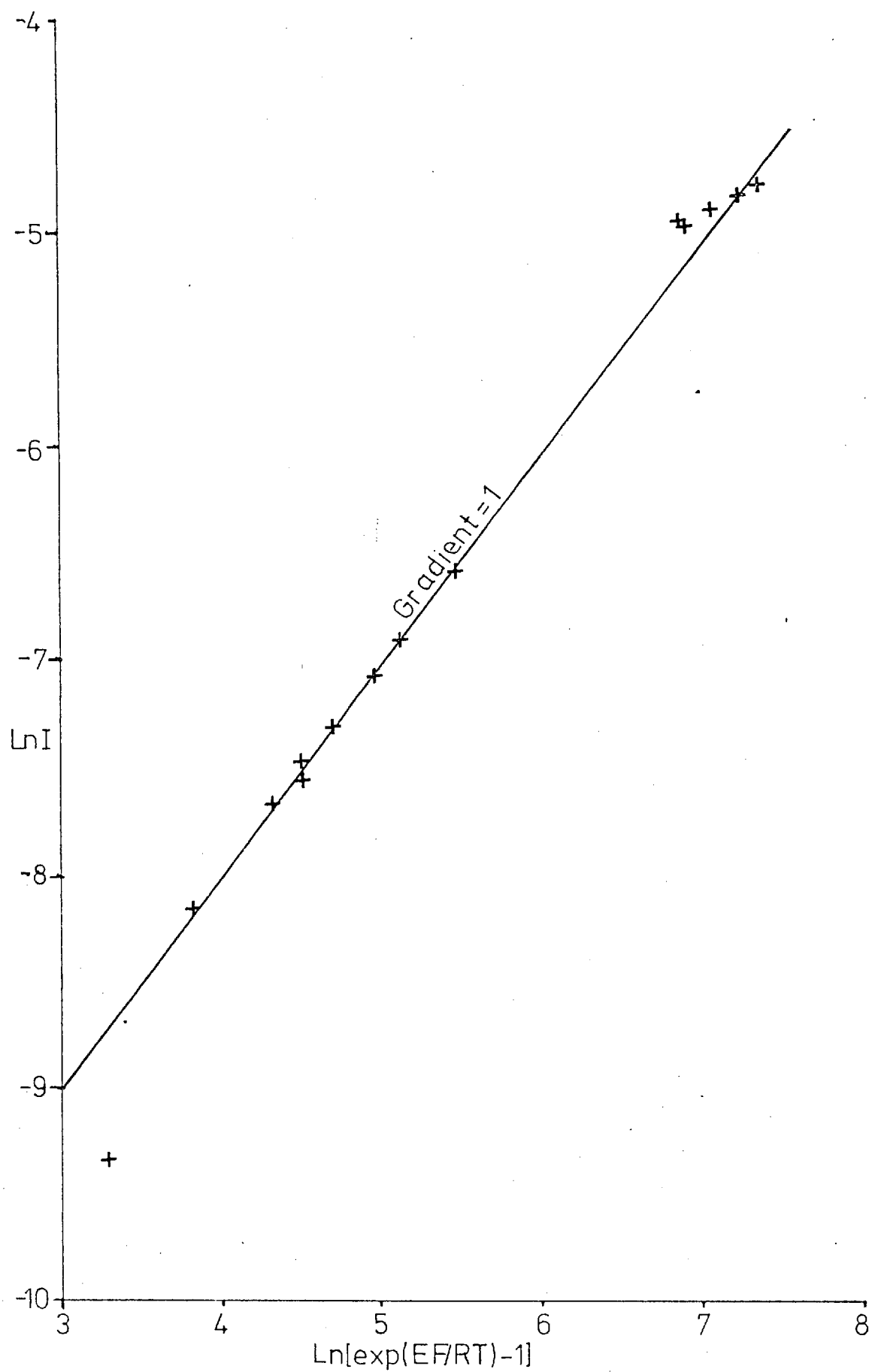
Hebb-Wagner Cell.
Figure 2.5

concentration of the copper ion vacancies with decreasing copper to halogen ratio is small, and decomposition is negligible. Under the above conditions the potential gradient in the electrolyte is almost equal to zero, with most of the potential difference occurring across the graphite/electrolyte interface. As copper (I) bromide is a p-type conductor (17) it would seem reasonable that the electrolyte used here would be predominantly p-type, and it will be seen later on that from the results it is a p-type conductor. Therefore if the electrolyte is predominantly a p-type conductor equation (2.I) reduces to

$$J = \frac{I}{A} \approx \sigma_{\oplus}^{\circ} \left[\exp \left(\frac{EF}{RT} \right) - 1 \right] \frac{RT}{FL} \quad 2.II$$

The concentration of electron holes at the graphite interface is greater than that at the metal interface by a factor $\exp (EF/RT)$, so the holes diffuse down this concentration gradient with little migration as the field is almost zero. It should be noted that the above only holds as long as the applied field is smaller than the decomposition potential for the electrolyte.

As is seen from the results (fig. 2.6) a plot of $\log (I)$ versus $\log \left(\exp \left(\frac{EF}{RT} \right) - 1 \right)$ gives a straight line of slope unity with an error in the gradient of up to 10%, which is within experimental error. Thus from theory $94CuBr \cdot 6(CH_3)_2C_6H_4N_2Br_2$ is a p-type electronic conductor predominantly. Extrapolating the graph to $\log \left(\exp \left(\frac{EF}{RT} \right) - 1 \right) = 0$, $\log I = -11$ which gives a hole electron conductivity of $\approx 10^{-11} \Omega^{-1} cm^{-1}$ at $414^{\circ}K \pm 1^{\circ}$ compared with $2 \times 10^{-11} \Omega^{-1} cm^{-1}$ reported by Takahashi et al (19) at $414^{\circ}K$. Though the Hebb-Wagner is a standard technique used on electrolytes,



Hebb-Wagner plot for solid electrolyte.

Figure 2.6

there is not apparently in the literature any experimental data to show the reliability and error for this electrolyte, just reported values.

2.4. A.C. MEASUREMENTS

2.4.1. INTRODUCTION

To establish the ionic conductivity of the solid electrolyte produced requires a method of electrical measurements in which contact impedance of the sample to the electrodes can either be taken into account or ignored. The most common way of obtaining the conductivity of solid electrolytes is the use of A.C. measurements. In the simplest model it is assumed that the cell is equivalent to a capacitor (the interface) and a resistor (bulk of material) in series. If the frequency applied under these conditions is high enough the conductivity measured will be that of the bulk. This simple model does not fit with experiment very well over the frequency range used. To obtain a better fit the model requires more ideal components, such as a capacitor across the bulk to represent the geometric capacitance (40). When more terms are added to the model the solution from A.C. theory becomes very much more complex than the original model. To help with interpretation of the results therefore, they are plotted in the complex plane in the form of susceptibility, impedance or admittance plots (41).

2.4.2. EXPERIMENT

The measurements were carried out over two frequency ranges with the following equipment. In the audio range (100 Hz to 10 kHz) a Wayne Kerr B221A transformer arm bridge

was used, with a Wayne Kerr S121 signal generator as the source, and a Dynamco Series 71 oscilloscope as a null detector. In the radio frequency range (100 kHz to 10 MHz) a Wayne Kerr B602 bridge was used, with a Wayne Kerr SR268 source and detector.

All samples were hot pressed electrolyte which were ground clean and flat on 600 grade dry silicon carbide paper (except when graphite electrodes were used as these were left on from hot pressing). After which they were coated with copper (non-blocking) or chromium (blocking) to form electrodes in an Edwards model 6E coating unit.

All measurements were carried out under vacuum in the same rig at room temperature ($23^{\circ}\text{C} \pm 2$).

2.4.3. RESULTS AND DISCUSSION

The results can be seen graphically in figures 2.7 to 2.10 and the numerical results in tables 2.5 to 2.8.

The admittance plot with copper electrodes (fig. 2.6) shows a large semicircle with its centre depressed below the x-axis, whereas if the semicircle could be explained in terms of ideal capacitors and resistors it would have its centre on the line. In order to explain why the semicircle has been depressed below the x-axis, a Warburg impedance (42) (arises due to diffusion processes when there are two mobile changed species, and is effectively a transmission line) is often used. This predicts that the centre of the semicircle can only be depressed by $\pi/4$ below the x-axis when two mobile species are present.

Another mechanism to account for the depression of the semicircle was proposed by Jonscher (43) relying on a

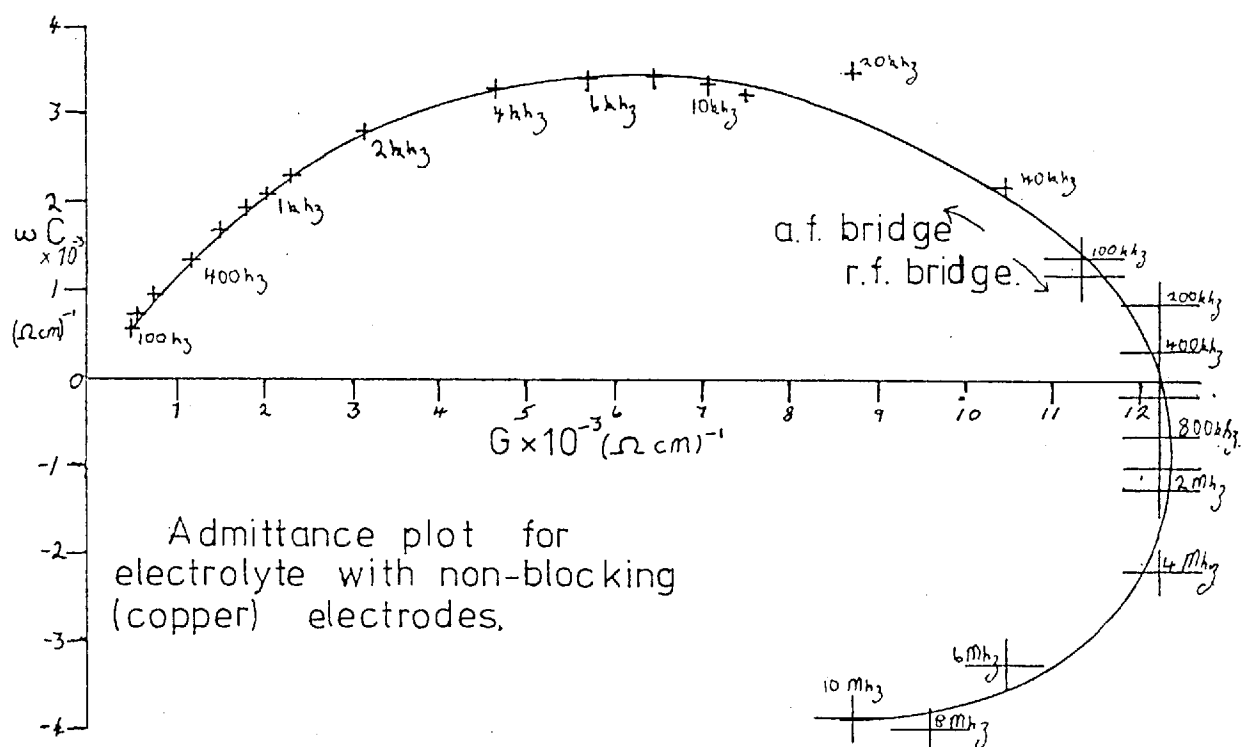


Figure 2.7

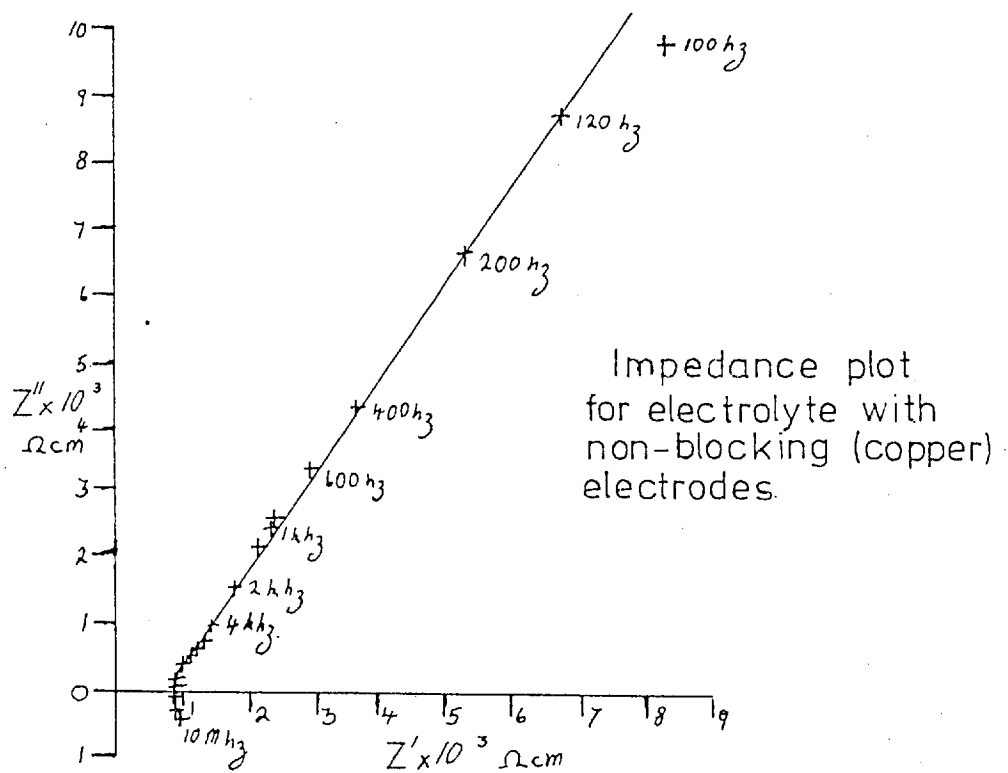
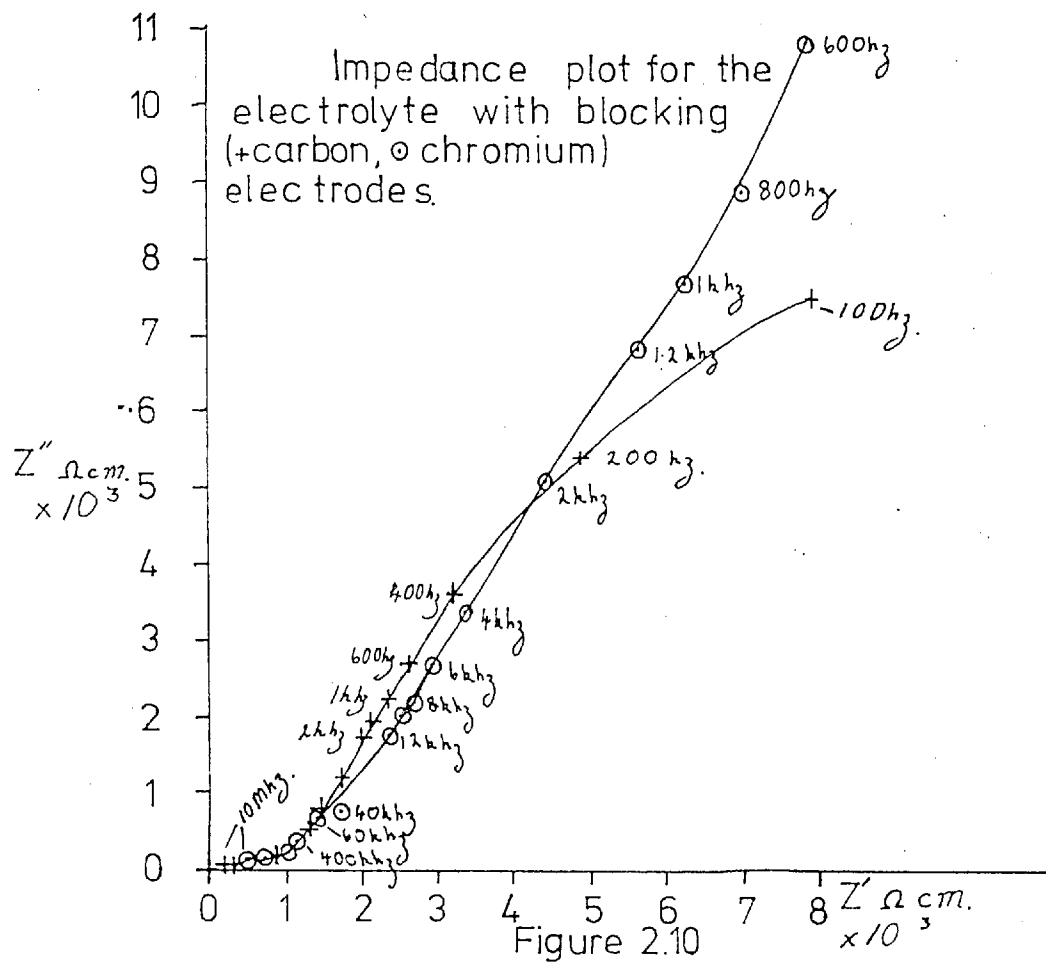
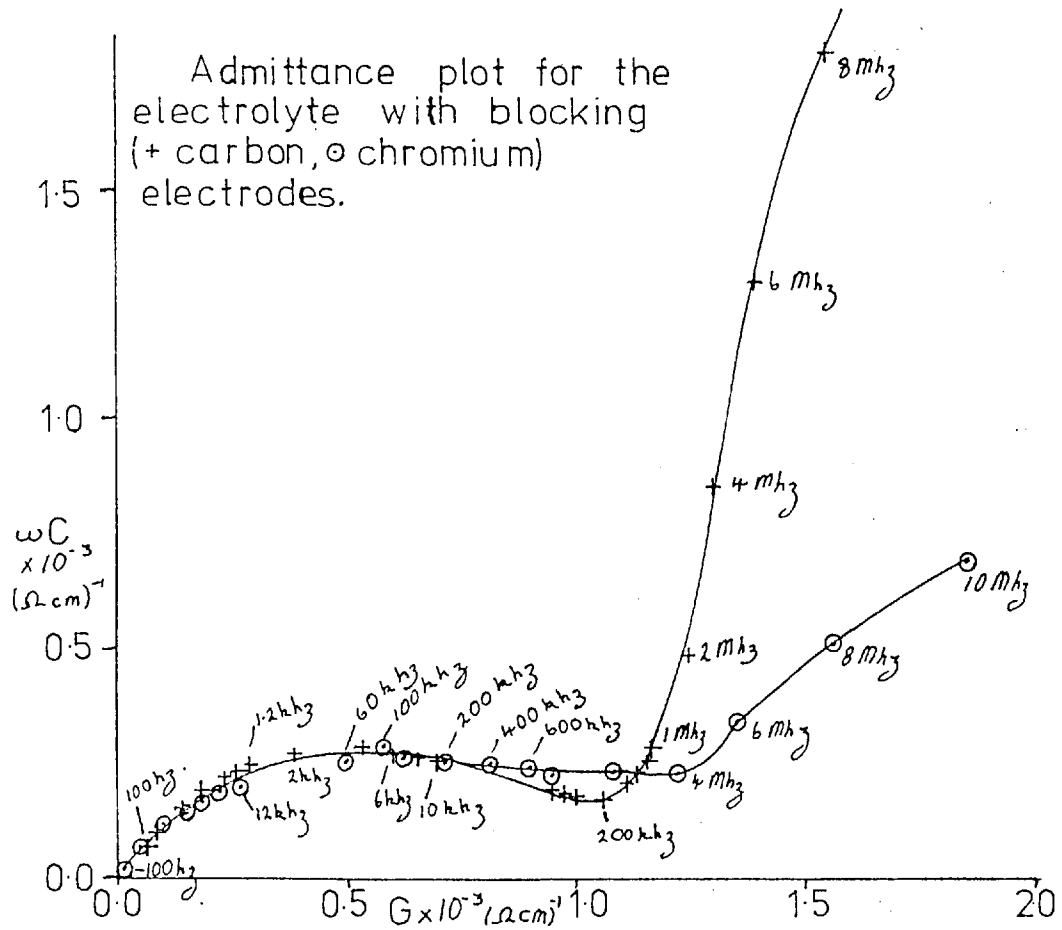


Figure 2.8



non-Debye dielectric (lossy capacitors), but it has been dismissed by Macdonald (44) as a physically non-realizable system. So there seems to be no theory at present to explain the depression of the semicircle in terms of a physical process.

At high frequencies the imaginary part of the admittance plot goes negative as in the impedance plot for copper electrodes. This impedance plot is very similar to that given by Armstrong and Taylor (45) for Ag_4RbI_3 and their explanation for the negative part of the impedance is that suggested by Rice and Roth (46) for ions moving in a sinusoidal field, with a retarding force proportional to their velocity and using Newton's 2nd law. According to this model the conductivity (σ) is given by

$$\sigma = \sigma_0 / (1 + j\omega\tau) \quad 2.III$$

where $\sigma_0 = n_0 z^2 e^2 / g$ and $\tau = m/g$ with g as the retarding force proportional to the ions velocity, n_0 is the number of ions available for motion, ze the charge on the ions, m is the mass of the ions, $j = \sqrt{-1}$, and ω is the angular frequency. As this effect predominates at high frequencies, and the equipment sensitivity and area of operation is limited at these frequencies it proved impossible to say if the above formula was obeyed.

Grant et al, in their work on β -Alumina (47), have recently cast some doubt on the results of Taylor and Armstrong by using lead inductance effects to account for the negative imaginary parts of an impedance plot. The result that is important for this work though is the D.C. conductivity of the electrolyte, and for this purpose it was taken as being the maximum A.C. conductivity which was $1.2 \times 10^{-2} (\Omega\text{cm})^{-1}$

@ $23^{\circ}\text{C} \pm 2^{\circ}$ (see table 2.9 for comparison with other results). Since this work was completed the D.C. conductivity has been measured by a four point technique in this Lab (48) and this gave a result of $1.3 \times 10^{-2} (\Omega\text{cm})^{-1}$.

Conductivity (Ωcm) ⁻¹	Frequency Hz	Temperature °C	Reference
6.5×10^{-3}	1000	25	Sammells et al (20)
1.4×10^{-2}	∞	25	Sammells et al (20)
2×10^{-2}	1000	25	Lazzari et al (36)
3×10^{-2}	1000	20	Takahashi & Yomamoto(19)
3.1×10^{-2}	150000	Room temp.	Armstrong et al (33)
1.2×10^{-2}	200000	23	This work
1.3×10^{-2}	0	25°C extra- polated	Mitchell & Shemilt (48)

Table 2.9
Reported Conductivities for Electrolyte

Figures 2.9 and 2.10 were obtained with blocking electrodes on the same sample, and are the admittance and impedance plots. The admittance of both types of blocking electrodes shows semi-circles at $\sigma' = 0.4 \times 10^{-3} (\Omega\text{cm})^{-1}$ though the depths of the centres below the real axis are different. At the high frequency end of the admittance plots there appears to be the start of two semi-circles, again with their centres depressed below the x axis by different amounts. As the electronic conductivity is dependent on the copper activity (see Hebb-Wagner technique) and this was not fixed for these results, the electronic conductivity was not fixed. Thus it was felt that interpretation of these results was beyond the scope of

this work, although the admittance plots give the impression of at least two R.C. parallel circuits in series. This suggests that the electrodes are not completely blocking as at all times the voltage was kept below the decomposition potential for the electrolyte.

2.5. ELECTROCRYSTALLISATION OF COPPER FROM A SOLID ELECTROLYTE

The work on solid state cells (as will be seen later) used a Cu/electrolyte interface, at which point copper was deposited and removed, during the cycling of the cell. One such interface has been examined on a scanning electron microscope and three of the pictures obtained are presented here.

Figure 2.11 shows a hot-pressed pellet of the electrolyte, with a sheet of copper on top of it (white area), which had been used as the counter electrode. In this picture the copper sheet has been moved from its position on the electrolyte as in the cell to reveal the interface where the copper has been deposited from the electrolyte. The fibres in between the electrolyte and foil are the copper which has been precipitated out of the electrolyte.

An area where these copper fibres are coming out of the electrolyte can be seen in greater detail in figure 2.12. It appears that the copper only crystallizes out of the surface in certain areas, due probably to two effects, the first being the energy required for the nucleation of the copper crystals compared with the energy for the growth of an existing one (49). The second is the tendency of the copper dendrites to push the copper electrode away from the

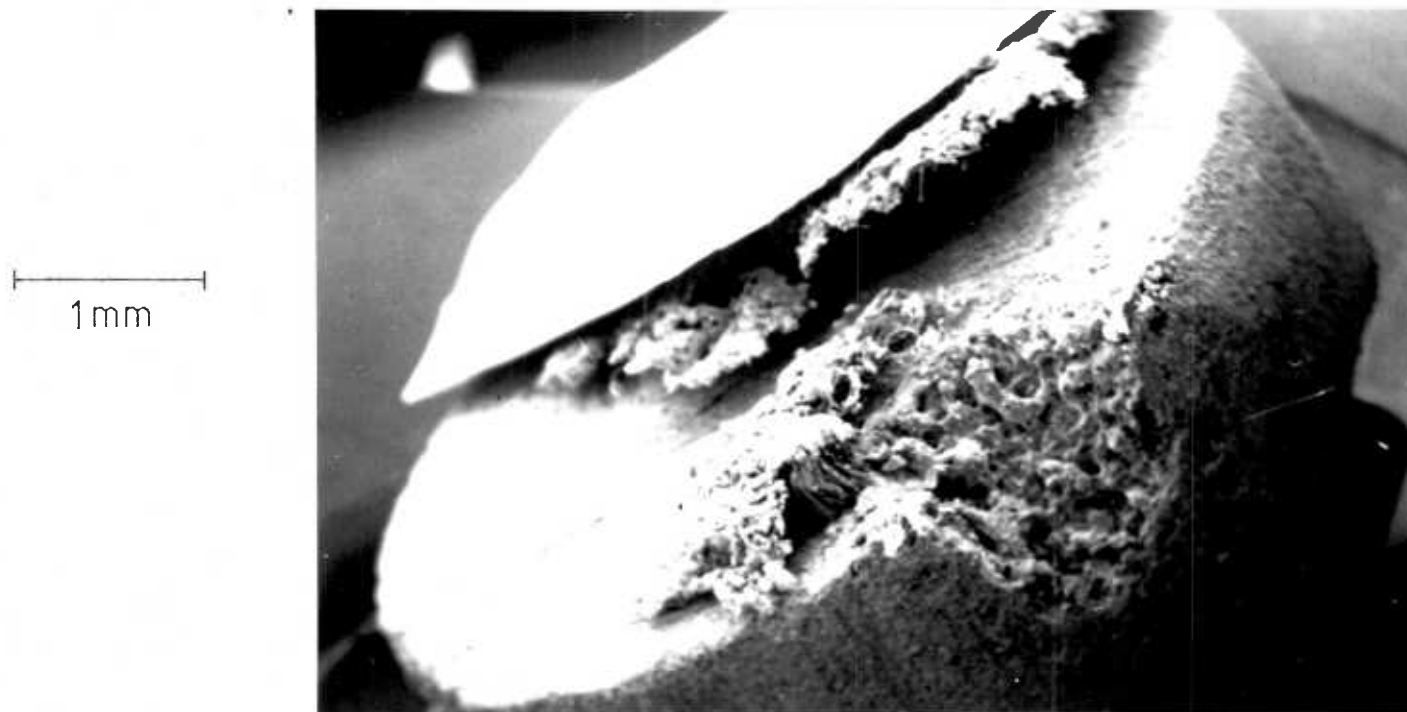


Figure 2.11

Hot-Pressed Electrolyte from a Coulometric Titration Cell with Copper Electrode.

The white area is the copper foil which forms the copper electrode and which has been displaced to reveal the surface of the electrolyte.



Figure 2.12

Copper Fibres on the Surface of the Electrolyte.

Left-hand white area is probably copper oxide, with the copper hairs visible at the top centre of the micrograph. The granular area is the electrolyte (lower right diagonal area of micrograph).

electrolyte. The electrocrystallisation of copper from the electrolyte at the interface is thought to be a rate-determining step from the work of Armstrong et al (33).

The last picture of this interface (fig. 2.13) shows a larger magnification. The crystals (lower right hand portion) of about 1 micron are clustered together in lumps, which appear to have been broken from the surface by the copper hairs growing out of the surface. The exact point where the hairs of copper start to grow is not obvious (i.e. whether the hair starts below the surface or on it). It does however appear from this picture and others that copper most likely grows from the surface. The size of the copper hairs with their $5 \times 10^{-14} \text{ m}^2$ area, seems remarkable as the crystallization of the copper must be uniform over this area. The process which controls this solid state reaction is of great interest for battery applications, as dendritic growth on electrodes is proving a problem in batteries, e.g. Ni dendrites in Ni-Cd batteries. Thus the interface reaction does warrant further investigation, though the problem of dendrite growth is overcome with solid solution electrodes.

2.6. SUMMARY AND CONCLUSIONS

An electrolyte based on copper (I) bromide and 1,4 dimethyl 1,4 diazabicyclo (2,2,2) octane dibromide has been produced. Attempts have been made to characterize this so that a constant quality electrolyte could be produced for the work that was carried out. The properties of the electrolyte produced are summarized below.

Total conductivity $1 \times 10^{-2} (\text{ohm cm})^{-1}$ @ 23°C



Figure 2.13

An Enlargement of the Surface Area where Copper has been Crystallised Out.

The top half of the micrograph shows the copper fibres which have come out of the electrolyte (shown at the bottom of the micrograph). The electrolyte appears crystalline with a grain size around one micron, with the surface broken up.

Electronic conductivity 10^{-11} (ohm cm)⁻¹ @ 141°C

Density 3.5 gcm^{-3}

X-ray always has CuBr lines in it.

Therefore it is possible to produce an electrolyte with a suitably low electronic conductivity to be used in solid state cells. It is also believed that the experimental data presented here is more extensive and complete than that found in the literature.

CHAPTER 3

BORNITE

3.1. INTRODUCTION

This chapter deals with the preparation of Bornite and the results that have been obtained for Bornite from electrochemical cells. First a review of the structure of Bornite and its related phase chalcopyrite is presented. Before this work was carried out there was no information on the activity of copper in Bornite and this is given after the section on the preparation of Bornite. Finally the diffusion coefficient of copper in Bornite was measured in this work.

3.2. STRUCTURE

The structure of Bornite has for many years presented problems, and to this day it has not been universally agreed on. The first attempts to determine the structure were made in 1928 by De Jong (50). He reported a cubic structure for natural Bornite with a unit cell dimension of $10.93 \pm 0.01 \text{ \AA}$.

In 1936 Lundquist and Westgren (51) gave a cubic cell structure with $a = 10.96 \text{ \AA}$ made up of cubic close-packed sulphur atoms, with metal atoms in the interstices; this structure did not account for all the lines on the X-ray diffraction pattern. Later Tunnell and Adams (52) proposed a cubic unit cell of $32.8 \text{ \AA}$, but this was found to be due

to three phases being present when Morimoto et al (53) investigated the same sample in 1960.

The investigations continued, and a second high temperature phase was found by Morimoto and Kullerud (54) in 1961. Besides finding a high temperature phase they also confirmed the existence of a metastable transitional phase. The high temperature phase is stable above 228°C, (it cannot be quenched below this temperature) with a cubic structure where $a = 5.50 \text{ \AA}$. This form has copper and iron on the tetrahedral sites in a face-centred cubic sulphur lattice. There is no ordering of the metal ions and the sites are only partially occupied.

The metastable form is also a cubic structure, but with $a = 10.94 \text{ \AA}$. This metastable state reverts to the low temperature form taking about a week at room temperature.

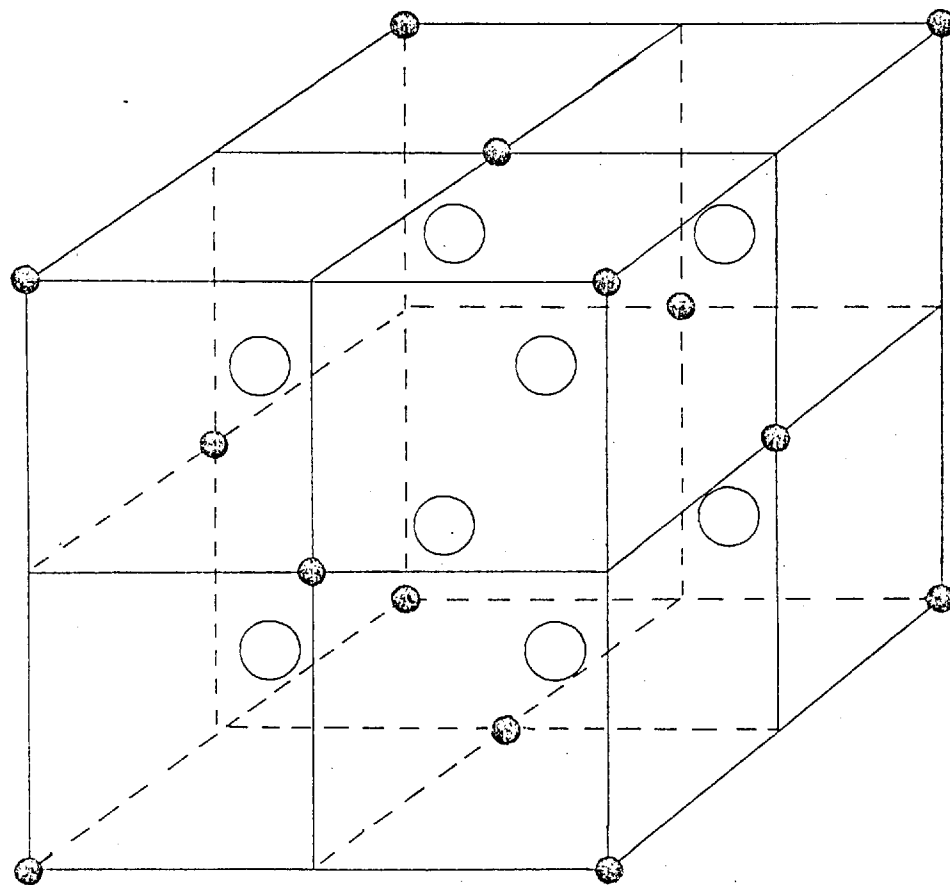
The low temperature form was given a tetragonal structure by Morimoto (55) in 1964 with $a = 10.94 \text{ \AA}$ and $c = 21.88 \text{ \AA}$. The ordering of the copper and iron ions is the reason for the change from the high temperature form.

The discussions on the structure of low temperature Bornite carried on, in an attempt to explain the unaccountable weak lines from the X-ray diffraction patterns. In 1975 Koto and Morimoto (56) decided on an orthorhombic structure for Bornite by the use of Modified Partial Patterson Functions. The cell dimensions obtained were $a = 10.95 \text{ \AA}$, $b = 21.862 \text{ \AA}$, and $c = 10.950 \text{ \AA}$, with a unit cell content of $16 \text{ Cu}_5\text{FeS}_4$. The unit cell is made up of $2 \times 4 \times 2$ face centred cubic cells of sulphur each with $a = 5.5 \text{ \AA}$. These cubes are of two forms, one where all eight tetrahedral sites are occupied, as in the anti-fluorite

structure, by metal atoms (fig. 3.1). The other type of cell has only four metal atoms, thus leaving four tetrahedral vacancies as in the sphalerite structure (fig. 3.2). These cells are then built up as is shown in figure 3.3, which gives a distribution of vacancies as shown in figure 3.4. This then gives routes along which the site occupation is only 50%. These would seem to be the channels along which the copper would most likely migrate, especially as the iron is in the anti-fluorite cells only, and this tends to reduce the mobility of the copper in the anti-fluorite cells (56).

This then deals with the stoichiometric composition of Bornite, the following deals with the non-stoichiometric compound.

In a recent review by Shuey (57), he suggests that the range of stoichiometry is less than 1% for Cu_5FeS_4 at room temperature from all the literature. The exception is a report by Ramdohr (58), who presents evidence for Bornite under certain conditions being made up of chalcopyrite (CuFeS_2) and chalcocite (Cu_2S), as well as giving a larger range for Bornite when it exists. As can be seen from the work of Yund and Kullerud (29) in figure 1.3 they give the range of solid solution as very limited at 200°C . At higher temperatures the range of solid solution increases and the values are given in table 3.1 (29).

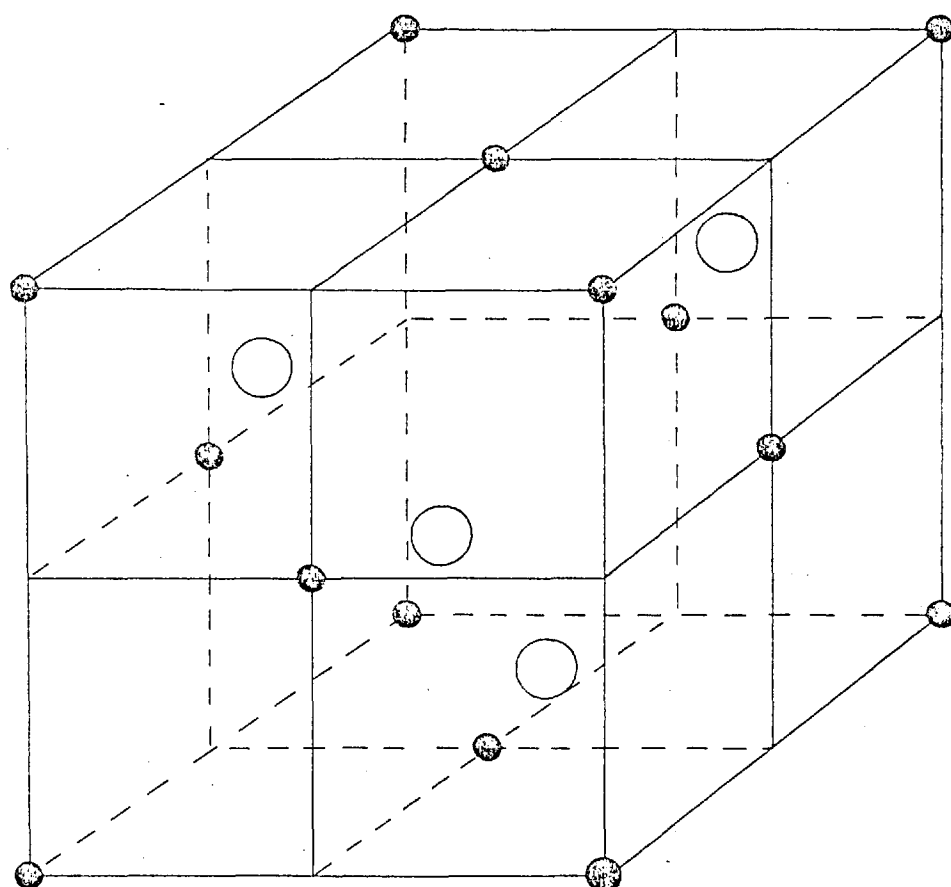


● SULPHUR ATOM

○ METAL ATOM

Antifluorite-Type Structure.

Figure 3.1

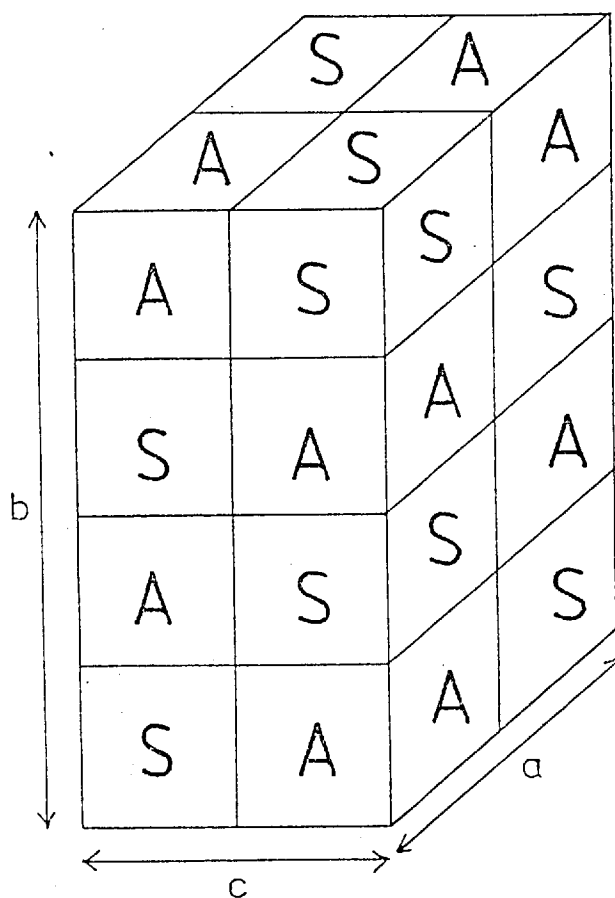


● SULPHUR ATOM

○ METAL ATOM

Sphaelerite-Type Structure.

Figure 3.2

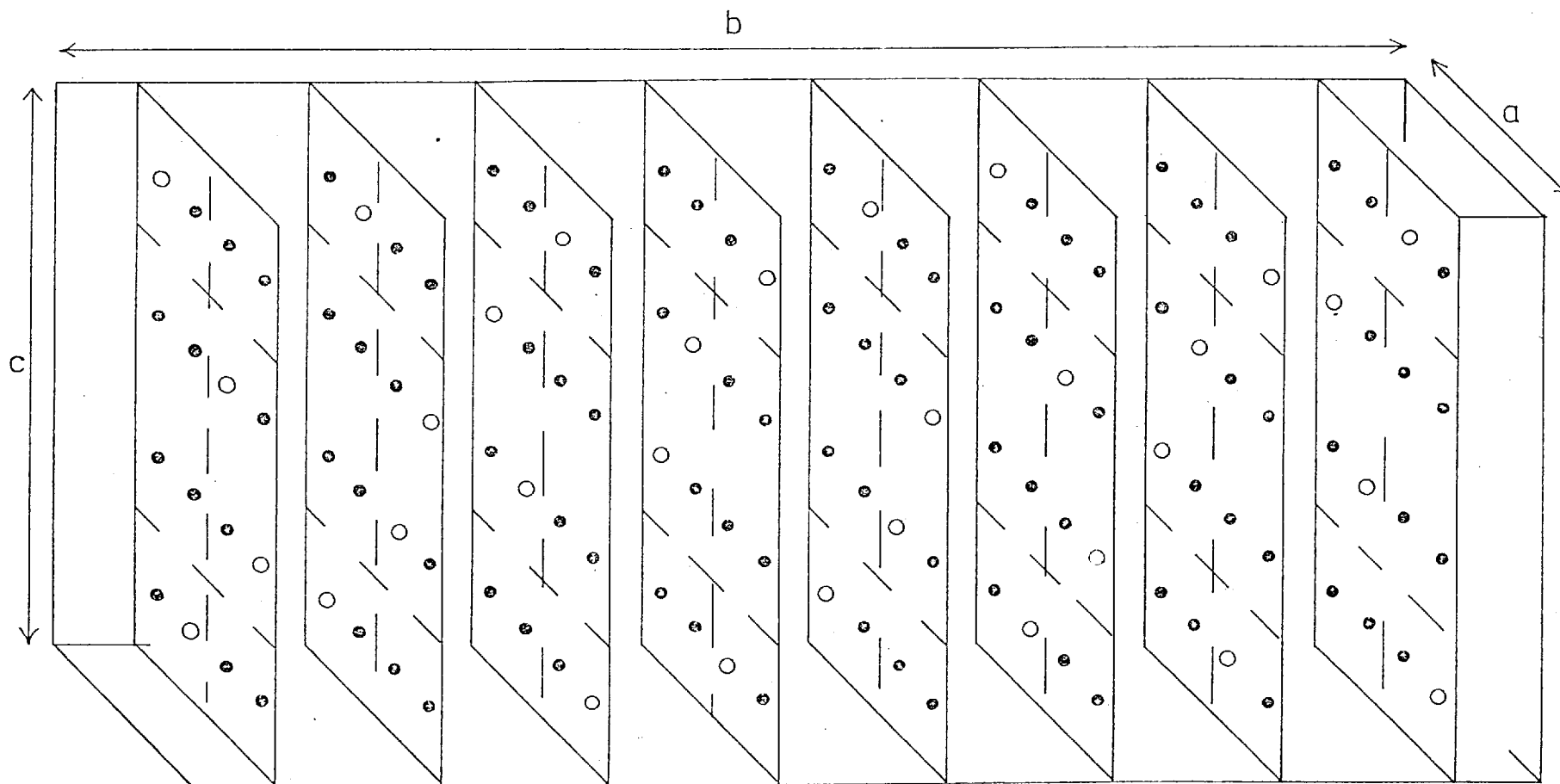


A = Unit cell of Antifluorite-type Structure.

S = Unit cell of Sphaelerite-type Structure.

Construction of Bornite Unit Cell.

Figure 3.3



Ordering of Vacant Tetrahedra of Sulphur Atoms in Bornite Structure. (56.)

○ Vacant Tetrahedral Site

● Tetrahedral Site Containing a Metal Atom

Figure 3.4

Extent of Solid Solution of Bornite	Highest Copper Content of Chalcopyrite Solid Solution	Temp. °C
$\text{Cu}_2\text{S}, \text{Cu}_{1.8}\text{S}, \text{Cu}_{0.99}\text{Fe}_{0.35}\text{S}$	$\text{Cu}_{0.70}\text{Fe}_{0.51}\text{S}$	700
$\text{Cu}_2\text{S}, \text{Cu}_{1.8}\text{S}, \text{Cu}_{1.2}\text{Fe}_{0.34}\text{S}$	$\text{Cu}_{0.74}\text{Fe}_{0.69}\text{S}$	500
$\text{Cu}_{1.8}\text{S}, \text{Cu}_{1.2}\text{Fe}_{0.39}\text{S}$	$\text{Cu}_{0.67}\text{Fe}_{0.51}\text{S}$	400
$\text{Cu}_{1.8}\text{S}, \text{Cu}_{1.25}\text{Fe}_{0.25}\text{S}$	--	300
$\text{Cu}_{1.25}\text{Fe}_{0.25}\text{S}$	--	200

Table 3.1

Extent of Bornite Phase at Various Temperatures

The removal of copper from Bornite as will be detailed later will show that copper has been removed to give an effective formula $\text{Cu}_{3.75}\text{FeS}_4$. This composition as given on Yund and Kullerud's phase diagram is made up of elemental sulphur, chalcopyrite and Bornite. However Sillitoe and Clark (59) give a phase due to the removal of copper from Bornite of Cu_3FeS_4 , which they gave the name idaite. This name has unfortunately been used to describe a large range of composition due to its use in mineralogy (30). Cu_3FeS_4 is said to be probably tetragonal (59) but there is no data presented to support this. Yund (60) calls a phase with a composition $\text{Cu}_{3.38}\text{Fe}_{0.62}\text{S}_4$ idaite, but this is given as a hexagonal system with $a = 3.78 \text{ \AA}$ and $c = 11.18 \text{ \AA}$. The X-ray diffraction pattern (61) for this phase does not however appear in any of the samples that have been X-rayed so it will not be described here.

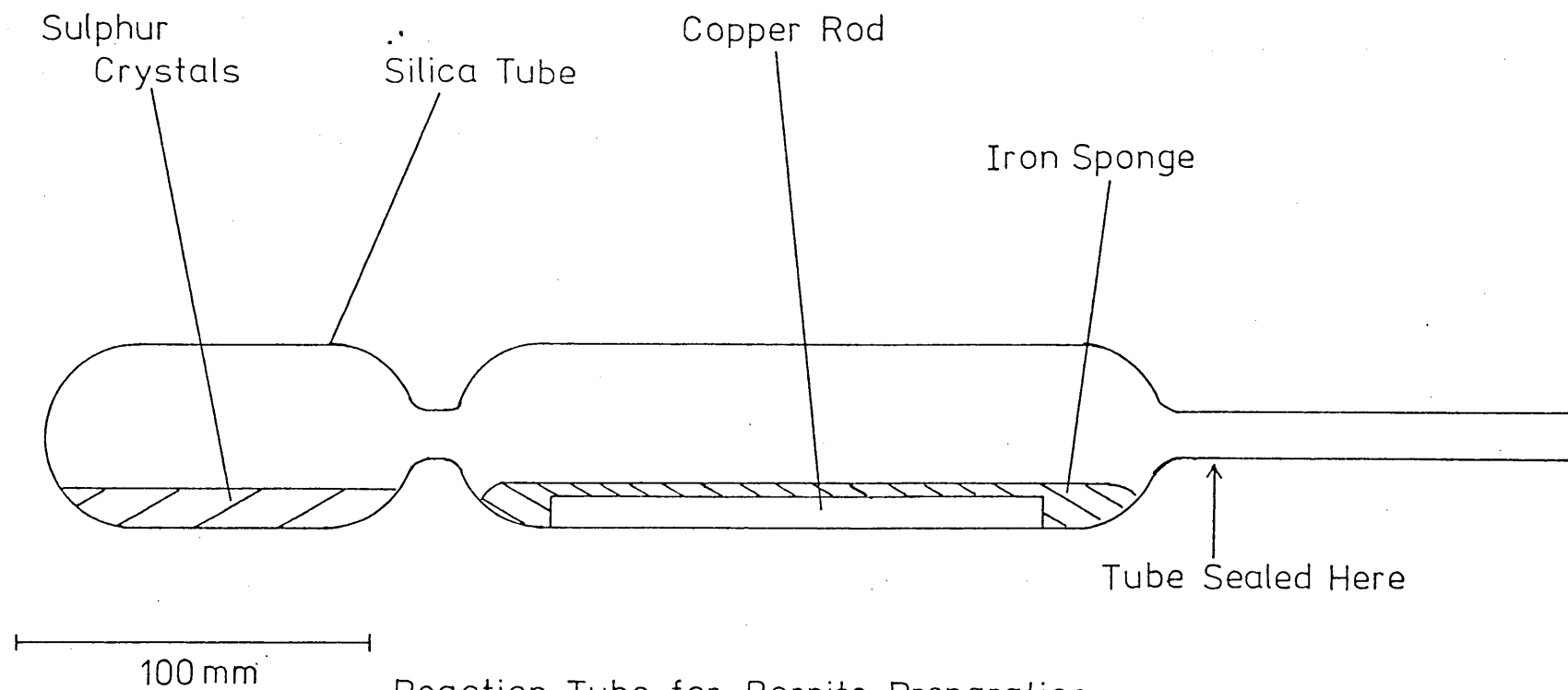
The other phase that should exist from the work of Yund and Kullerud (29) is Chalcopyrite (CuFeS_2). Essentially this is a super-lattice based on the zinc blende structure (see Bornite earlier). Its unit cell is an elongated

tetragonal prism containing four molecules with its c axis double the a axis ($a = 5.24 \text{ \AA}$, $c = 10.30 \text{ \AA}$ (62)). Metallic atoms are surrounded here, as in ZnS, by tetrahedra of sulphur atoms, while each sulphur in turn has a tetrahedron of metallic atoms as closest neighbours, two of which are copper and two iron. In work on leaching (30) it was observed that Cu_5FeS_4 had a chalcopyrite-like structure and it will be this structure that is used to analyse X-ray data later on. The leaching work also gave the interesting result that two copper atoms per formula ($\text{Cu}_2^+\text{Cu}_3\text{FeS}_4$) could be removed before the crystals disintegrated. It was believed in the leaching work that these two easily leachable copper atoms were ionically bound to the structure whereas the others were covalently bound to the sulphur atoms.

3.3. PREPARATION OF BORNITE

The Bornite was prepared by using the stoichiometric amounts of Specpure (Johnson and Matthey Ltd.) copper rod, iron sponge, and recrystallized sulphur. The copper was cleaned with dilute nitric acid, the iron had any oxide removed by passing hydrogen over the iron sponge at 450°C for two hours, and the sulphur was dried in an oven at 100°C for two hours. The weighed elements (in stoichiometric proportions) were placed in a silica tube as shown in figure 3.5. This tube was evacuated to a pressure of less than 0.1 mm of Hg and was then sealed.

After sealing the tube was placed in a furnace and heated up to 500°C over a day. This temperature was maintained until all the sulphur had reacted (no longer



Reaction Tube for Bornite Preparation

Figure 3.5

visible) and then the tube was heated to 900°C for between 10 days and 60 days depending on the size of the crystals required.

After this time it was cooled down very slowly over four days. When 200°C was reached the tube was kept there for a day to allow the phase change to take place so that the low temperature form was produced, after which it was cooled to room temperature. The slow cooling is necessary to prevent the silica tube from breaking as the Bornite sticks to it. This tube was then opened in the dry box and the crystals stored there.

The crystal size produced by the above method was limited to a few millimetres, and aggregates tended to have voids in them. A method of producing a sample for the six point cell was required. A polycrystalline sample of high density was seen to fulfil this requirement. A standard technique which is used in the solid state ionics group is the hot-pressing of specimens. This allows pellets of up to 12.5 mm diameter to be produced with near theoretical density.

Crystals from the above preparation were ground in an agate mortar and pestle to produce a very fine powder under an argon atmosphere, to prevent oxidation. The powder was pressed in an 8 mm hardened steel split die at a pressure of $2 \times 10^8 \text{ Nm}^{-2}$, to produce dark blue to black pellets, which were treated with care as they were fragile.

The choice of dies in which to hot-press the pellets was either an alumina die or a graphite die. As the pressure which could be used was much greater with an alumina die, this was used. In order to press a pellet in an alumina

die the pellet is usually wrapped in metal foil and then alumina powder packed round the pellet in the die as is shown in figure 3.6.

Choice of the wrapping material is limited to a metal which is inert or in equilibrium with the material to be hot-pressed. Therefore platinum and copper foils were used to wrap Bornite, as well as hot-pressing without wrapping to investigate the effect it had. The reason for wrapping the pellet is to prevent it mixing with the alumina powder and to try to cut down loss of any volatile constituents (in this case sulphur loss).

The conditions used for hot-pressing were as follows. The sample was evacuated to a pressure of less than 0.1 mm of Hg, and then heated to 500°C over a three hour period. Argon (high purity) was then admitted and allowed to flow through the furnace slowly (about 1 cc per second) during the rest of the pressing. The sample was heated to the pressing temperature of 950°C, and when this was reached the pressure was applied to the plungers. The force applied to the plungers gave a pressure in the die of $3 \times 10^7 \text{ Nm}^{-2}$. This pressure was maintained until the plungers no longer moved (this proved to be about an hour). At this point power was removed from the furnace and the sample would cool slowly over the next few hours.

As the pressing temperature was only 950°C the alumina powder was not sintered and proved easy to remove. The pellet which was then removed was machined on a high speed diamond saw under oil, with the metal foil being removed before this. Storage of these samples was under argon in the dry box until they were required.

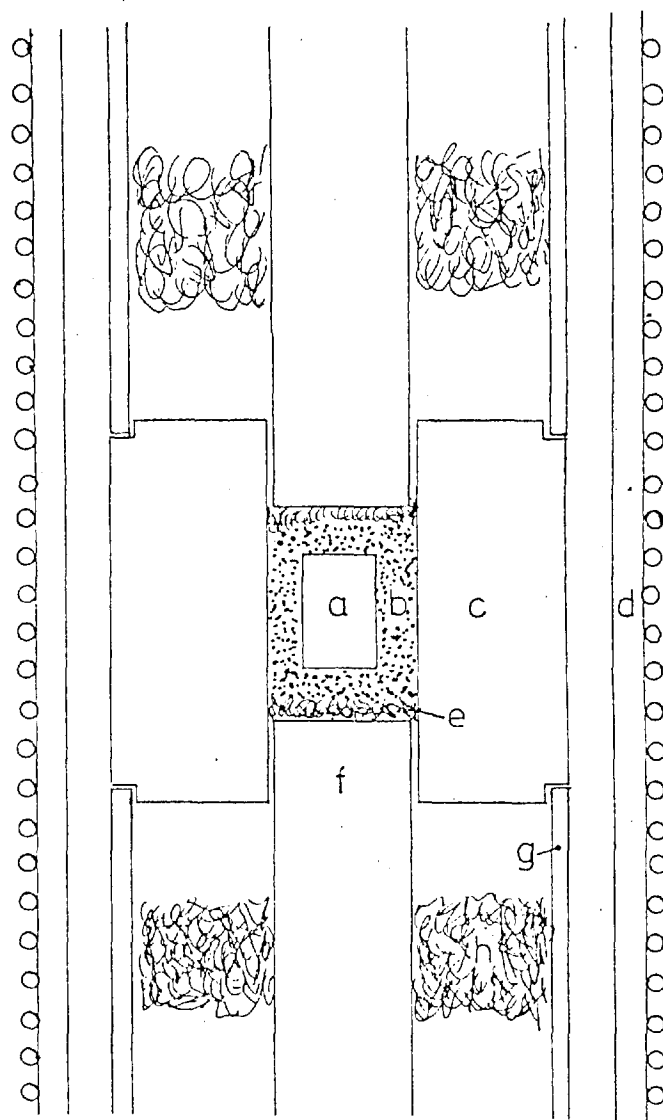


Figure 3.6
Hot-pressing of Bornite.

- a, cold-pressed sample of Bornite,
wrapped in suitable material.
- b, alumina powder.
- c, alumina die.
- d, gas tight furnace tube.
- e, fibre to prevent loss of alumina powder.
- f, alumina plunger.
- g, alumina die support.
- h, fibre to act as heat shield.

3.4. CHARACTERIZATION

Materials produced from their elements were first analysed by X-ray diffraction to make sure the desired phase was present. As will be seen from table 3.2 and X-ray figure 3.7 for a batch of Bornite the X-ray diffraction pattern is in good agreement with the ASTM (63) X-ray data, if only the Berry and Thompson (64) data is used.

Another method of checking that the right phase is present is to check that the phase change from low to high Bornite takes place. This was checked by differential calorimetry but the results showed a phase change on heating between 189°C and 195°C whereas the literature (54) gives the phase change to high Bornite at 227°C, although Townsend et al (65) say that on cooling the metastable phase of Bornite below 150°C, it transforms to the low form. So this phase change detected above could be due to the formation of the metastable form. It therefore did not prove the presence of the correct phase.

Atomic Absorption Analysis was carried out on a number of specimens including this material. It was however found that the results obtained were not consistent. As the time was limited, and the amount of technical assistance was low it served to show that the composition was within 15% of that required. It did however prove possible to send a sample to C.S.I.R.O. in Melbourne for analysis and this gave the composition of $\text{Cu}_{4.96} \text{Fe}_{0.92} \text{S}_4$. Also a sample was analysed on a microprobe by the Geology Department, Imperial College, and this gave a composition of $\text{Cu}_{5.36} \text{Fe}_{1.06} \text{S}_4$. The value obtained from the microprobe of $\text{Cu}_{5.36} \text{Fe}_{1.06} \text{S}_4$ has a high degree of unreliability however due to transport

X-ray Diffraction Intensities.

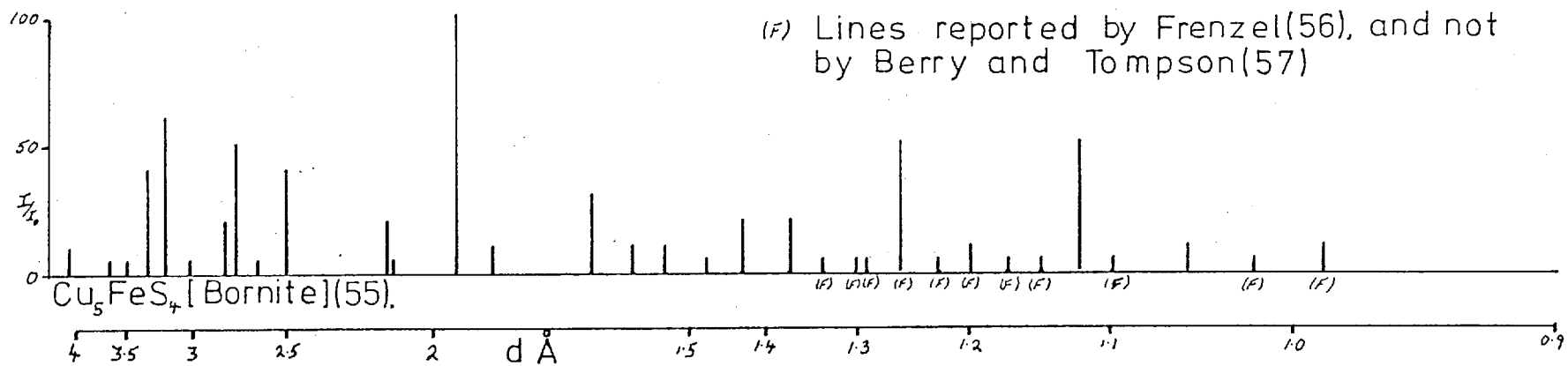
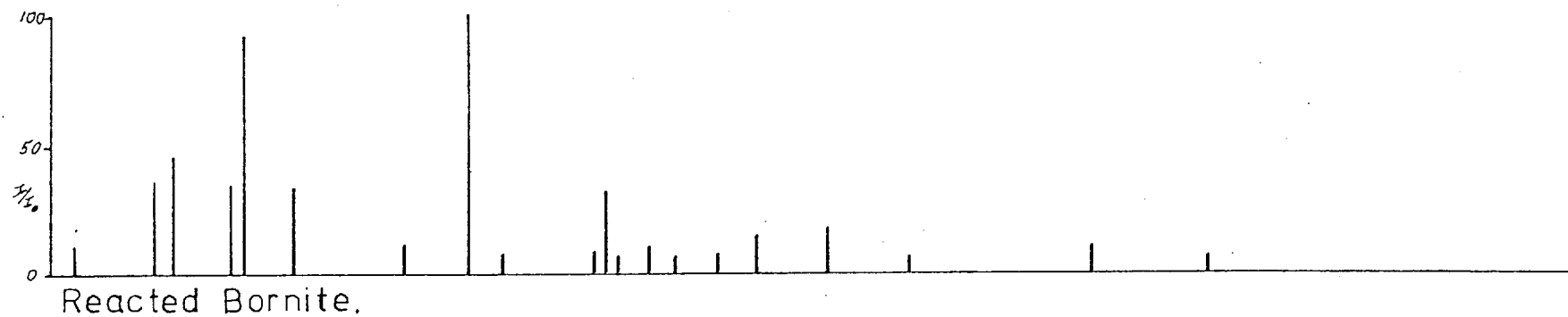


Figure 3.7

of copper during preparation of the sample, and under the electron beam. It was therefore decided from this point on to assume in all future calculations that the starting material was stoichiometric.

As it was necessary to produce a polycrystalline sample of Bornite for the six point cell it was also necessary to characterize it in some way. As is seen from the X-ray diffraction data (fig. 3.8 and table 3.3) the three different types of wrapping produced specimens with very similar X-ray diffraction patterns. Though they all show some Bornite lines, the intensities, positions, and their sharpness have all been affected. Again A.A. Analysis did not prove successful but it showed them all to be copper rich. These three specimens were analysed on the microprobe and the results are shown in table 3.4, however a paper (66) by Monhemius states that the copper in Bornite is mobile under the electron beam, and also surface oxidation occurs changing the composition.

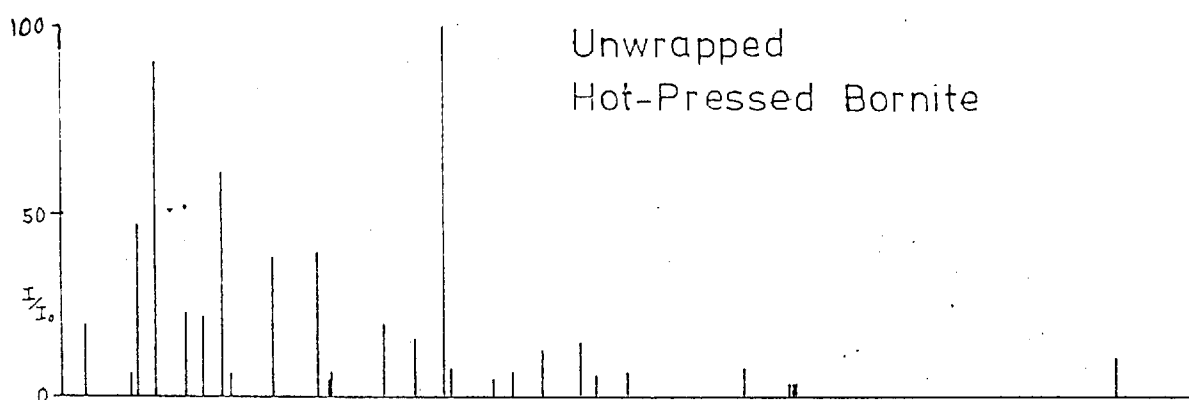
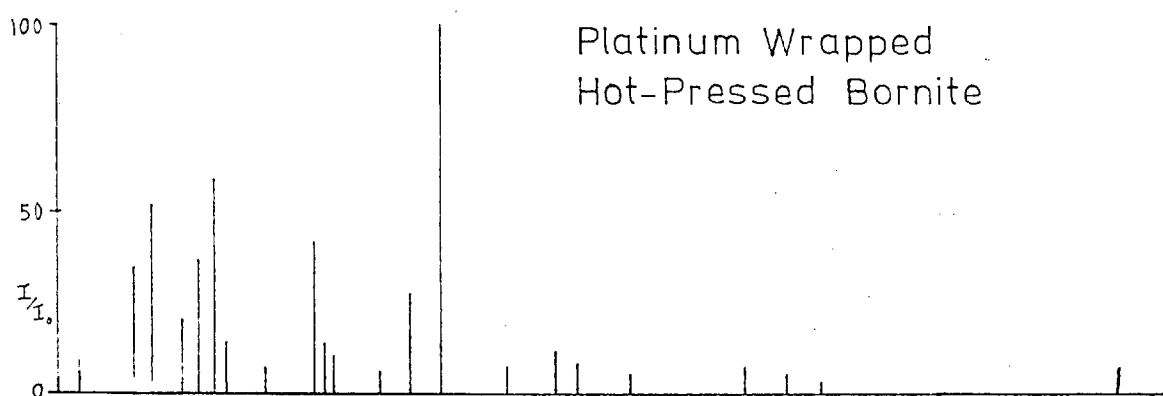
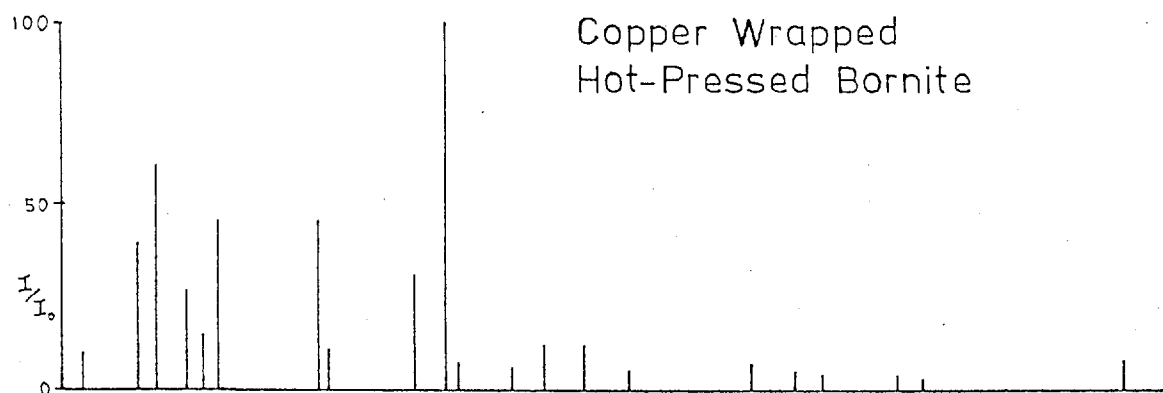
Wrapping Material	Microprobe Analysis	Density Assuming Cu_5FeS_4
Copper	$\text{Cu}_{5.99} \text{Fe}_{1.03} \text{S}_4$	$95\% \pm 3$
Platinum	$\text{Cu}_{5.45} \text{Fe}_{1.00} \text{S}_4$	$99\% \pm 1$
Unwrapped	$\text{Cu}_{6.13} \text{Fe}_{0.90} \text{S}_4$	$98\% \pm 1$

Table 3.4

Microprobe Analysis and Density of Hot-Pressed Bornite

As the structure appears similar for all three materials from the X-ray data, and it is known that the copper wrapped sample absorbed its wrapping giving an effective formula of $\text{Cu}_{5.39} \text{FeS}_4$ it was assumed before analysis that sulphur had

X-ray Diffraction Intensities.



4.0 3.5 3.0 2.5 2.0 d Å 1.5 1.1

Figure 3.8

been lost. The densities of all three were measured and are presented in table 3.4.

The densities appear close to theoretical, and no voids were seen on machining or microscopic work.

From the above results it was decided to work with unwrapped hot-pressed Bornite as it was so similar to the platinum wrapped material, and platinum is expensive.

Figure 3.9 shows a sample of unwrapped Bornite that was polished for measurements on a scanning electron microscope fitted with EDAX (Energy Dispersive Analysis by X-rays) to give an approximate analysis.

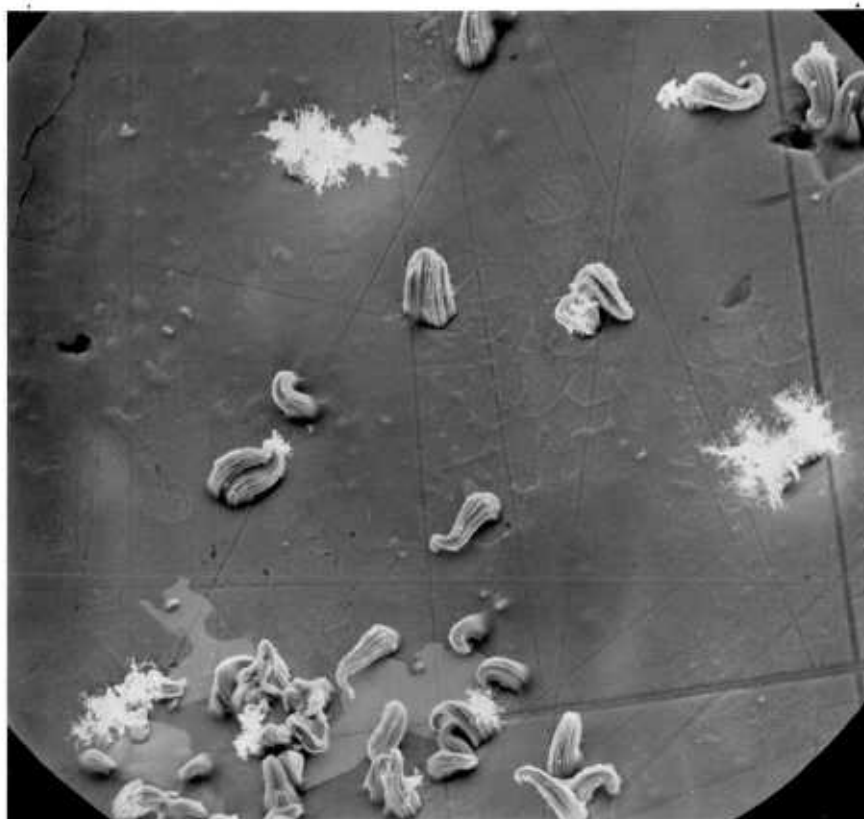
Two types of growth were visible on the polished surfaces, i.e. "solid" and "fibrous" growths. The solid growths appeared to be made up of bundles of fibres. It is probable that these growths were formed due to contact with the atmosphere after the specimen surface had been polished. A second, lighter phase was also visible in addition to the background phase and this second phase appeared to be associated with regions containing a high density of solid and fibrous growths.

Owing to the fluorescence of iron due to the copper radiation the iron analysis is unreliable. The results obtained have therefore been normalized to four sulphur atoms per molecule and are given below in table 3.5.

Phase	EDAX Analysis
Solid Growths	$\text{Cu}_{7.4} \text{Fe}_{4.18} \text{S}_4$
Fibrous Growths	$\text{Cu}_{7.7} \text{Fe}_{1.3} \text{S}_4$
Main Phase	$\text{Cu}_{5.25} \text{Fe}_{0.91} \text{S}_4$

Table 3.5

EDAX Analysis of Hot-Pressed Bornite



50 μ m.

Figure 3.9

Micrograph of Hot-pressed Bornite.

As is seen the solid and fibrous growths seem to have very similar iron to copper ratios, and they both show a large quantity of copper present. It would therefore seem reasonable that these growths are mainly copper oxide, though the analysis cannot determine if oxygen is present. The main phase shows copper excess which is what would be expected from sulphur loss, but it cannot be said how much copper has gone into the growths, or has been removed during polishing. This comment also applies to the microprobe analysis. The minor phase was not analysed but it is there in such low amounts that it could not affect the composition by any large amount. The presence of the copper growths on the surface suggests that the copper in this material has a very high diffusion coefficient.

3.5. COULOMETRIC TITRATION CELLS

3.5.1. INTRODUCTION

The principle of a coulometric titration is to change the composition of the sample by passing a constant current of ions for a known time into or out of the sample. This is a very precise way of altering the composition of the sample. By this method the variation of the free energy with composition can be obtained. Also if the temperature is cycled at each composition the entropy (ΔS) can be obtained from equation 3.I.

$$\Delta S = nF \left[\frac{dE}{dT} \right]_p \quad 3.I$$

and thus the enthalpy (ΔH) from equation 3.II.

$$\Delta G = \Delta H - T\Delta S \quad 3.II$$

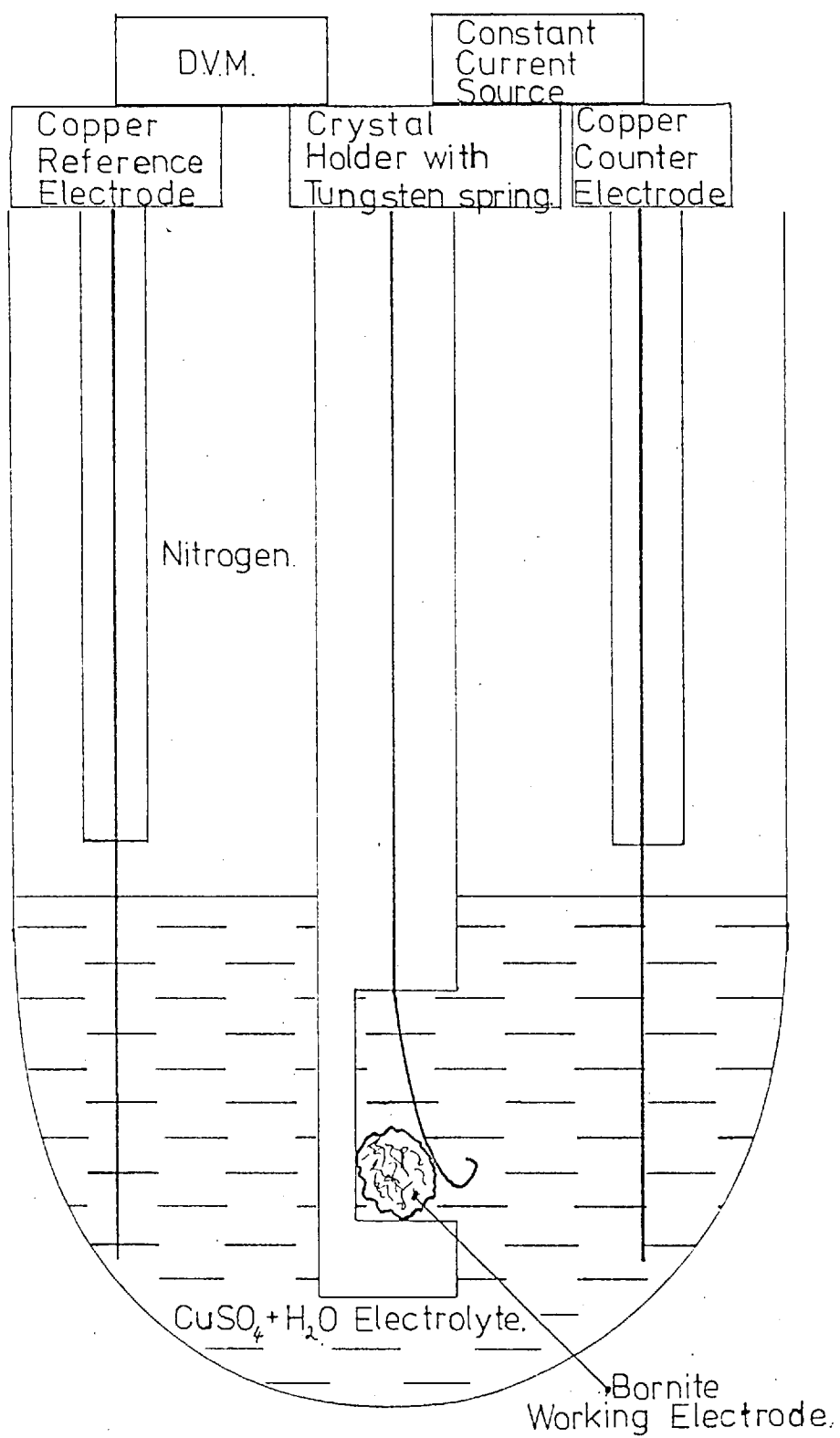
Previous to this work there was no available data on the activity of copper in Bornite.

3.5.2. AQUEOUS CELLS

Cells of the type shown in figure 3.10 were prepared, with an electrolyte of saturated CuSO_4 solution which had been boiled, with oxygen free nitrogen bubbling through it to remove any oxygen in it. The cells were set up in an oxygen free atmosphere, with the crystal faces being ground to remove any oxide on them. Oxygen reacts with Bornite to form an oxide film, thus removing metal from the crystal. Thus the crystals were kept away from the air as much as possible to prevent metal loss. Just before being placed in the cell the crystals were weighed and this weight noted.

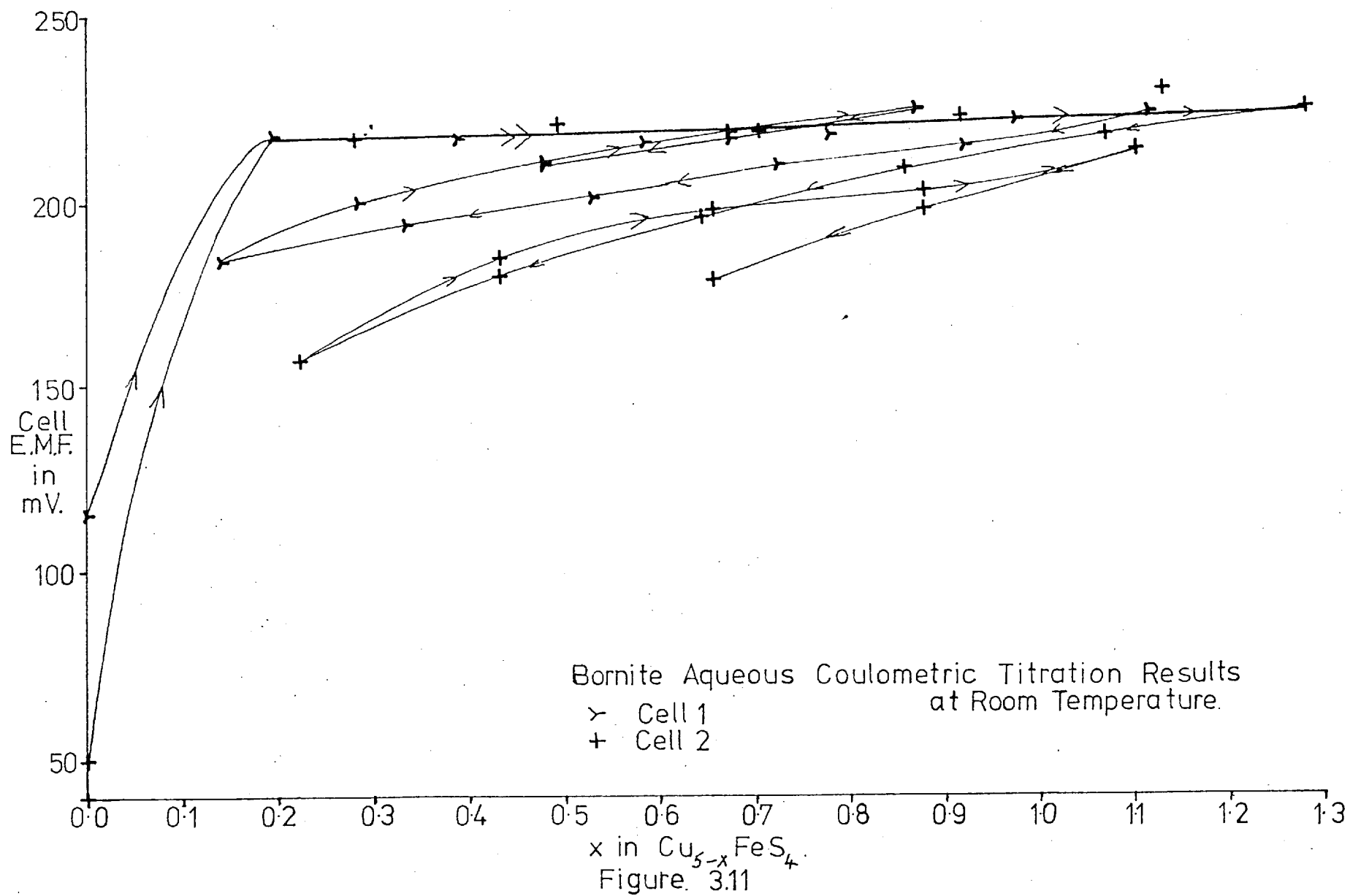
The cells were left for a day or two until a steady voltage was established and then this was noted. A constant current was then passed to remove copper to a composition of $\text{Cu}_{4.8} \text{FeS}_4$. After which the cell was allowed to regain a steady voltage, which was noted, and so on until a composition of $\text{Cu}_{3.7} \text{FeS}_4$ was reached. The process was then reversed and repeated to find the reproducibility of the results. The titration was reversed at $\text{Cu}_{3.8} \text{FeS}_4$ because from earlier experiments it was found that the crystal broke up when the composition reached $\text{Cu}_{3.66} \text{FeS}_4$.

The above measurements were carried out by the programmable data logger detailed in appendix C, and the results produced are shown in figure 3.11 and table 3.6. It is seen from the graph that the Bornite initially has a high copper activity which is not very well defined. After passing the initial current both samples came to the same voltage which was maintained until a composition of $\text{Cu}_{4.2} \text{FeS}_4$ was reached. At this point the voltage becomes somewhat unstable, but the general tendency seems to be for it to



Aqueous Cell.

Figure 3.10



rise. When the current was reversed the activity of the copper again increases, but it does not follow the same path as before. The reason for this is far from clear, but it could be due to some surface reaction between the electrolyte and the crystal.

This path however was followed again when copper was removed from the crystal. The composition was not taken past $\text{Cu}_{3.7}\text{FeS}_4$ as at this point several crystals had already broken up in earlier experiments, which tends to indicate a major phase change. The rate at which an equilibrium voltage was reached (about 3 hours) shows Bornite has an apparently high diffusion coefficient. The time to equilibrium voltage did in fact change with composition to a small degree, but there was not enough data to be able to determine if the different equilibrium voltages obtained at each composition affected the diffusion coefficient.

It appeared from this work that Bornite may be of use as an S.S.E. to carry out measurements on, but its range of composition is only down to $\text{Cu}_{3.7}\text{FeS}_4$, and it seemed reasonable at this time to assume it cannot go above Cu_5FeS_4 . Also its voltage with respect to copper is far too low to ever make a commercial battery. So it was decided to try to carry out future measurements in the solid state, and the aqueous cell work was discontinued.

3.5.3. SOLID STATE CELLS

All the solid state coulometric titration cells were of the form shown in figure 3.12 although two physical realizations were used depending on available equipment and time. The better apparatus is that shown in figure 3.13

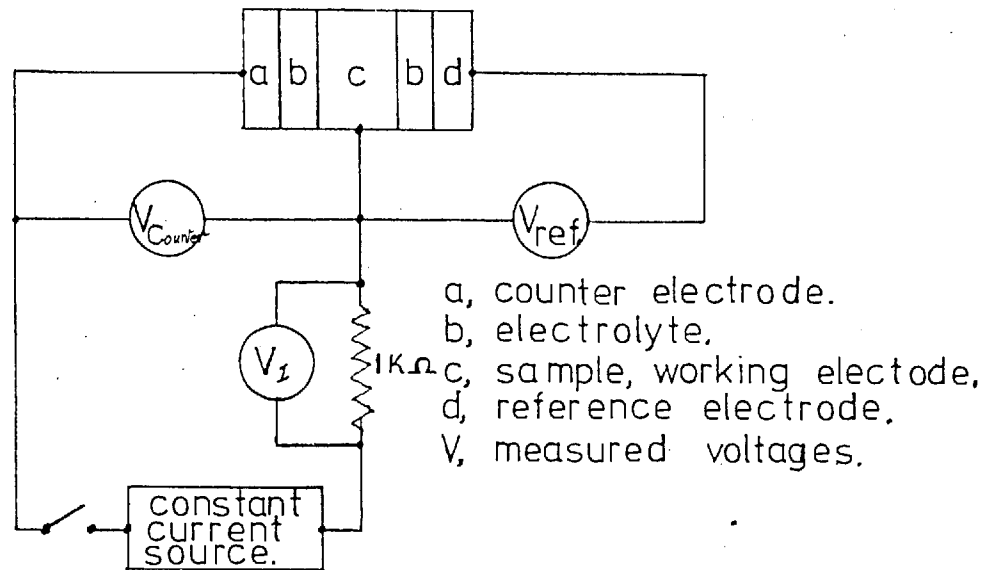


Figure 3.12
Layout of solid state cell.

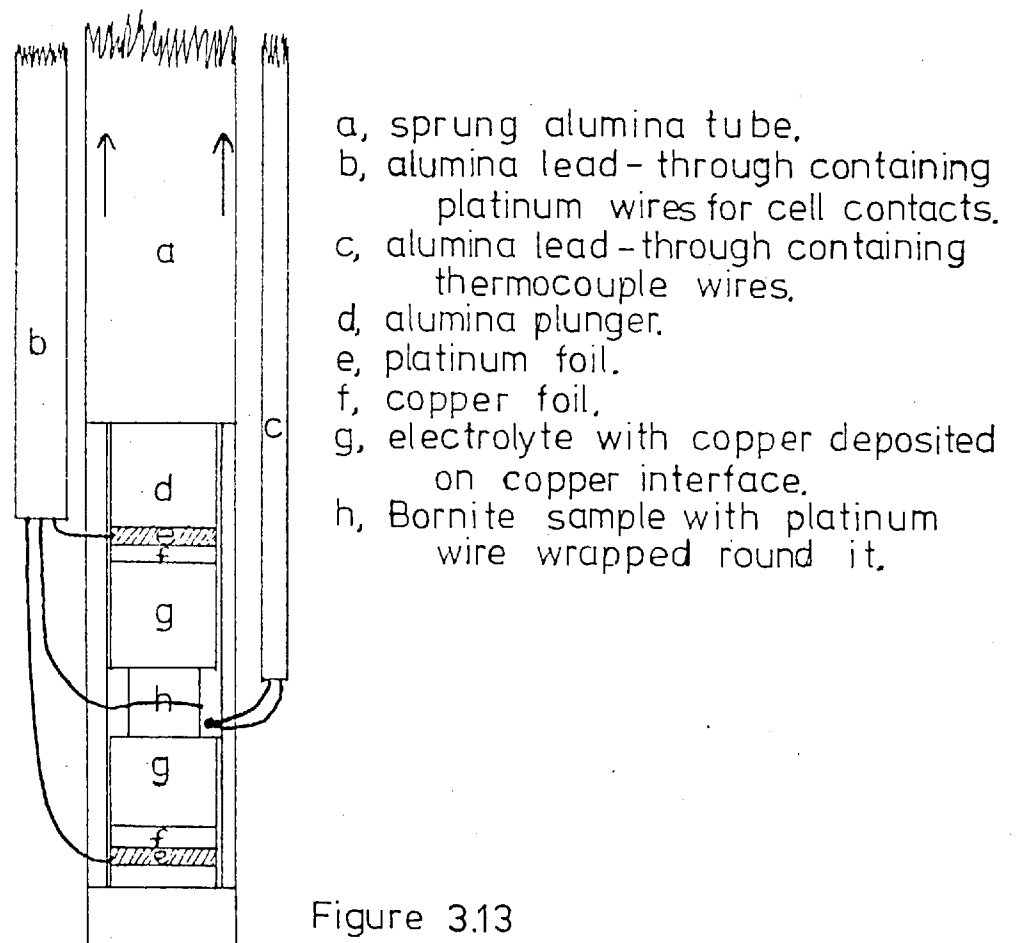


Figure 3.13
Bornite solid state cell.

as it keeps the cell under a constant pressure as well as allowing higher temperatures than the apparatus shown later in connection with the copper sulphide work.

The solid state cell assemblies were maintained at temperature by Kanthal furnaces which were controlled by proportional-band type solid-state controllers. This allows control of a furnace to $\pm 1^\circ\text{C}$ over the life time of an experiment. All cells were also purged with gas, either high purity argon after passing through a titanium furnace, or "white-spot" nitrogen after passing through sodium hydroxide, to remove CO_2 , silica gel followed by magnesium perchlorate to remove water, and a copper furnace at 500°C to remove oxygen. Control of the experiment was left to the data logger after a few initial measurements had been carried out to establish the behaviour of the cell. The actual program was similar to that used for the aqueous cells, though the current passed during a titration varied from 4 microamps to 200 microamps for the normal cells, and reached milliamps for a hot-pressed cell. The over-potential applied to a cell was never allowed to cause the cell voltage to exceed 600 mV as, from the work of Lazzari et al (36), the electrolyte would have broken down. For negative currents the cell voltage was always maintained above zero millivolts for Bornite though for the work on copper sulphide this is not true. After equilibrium had been attained for the cell the equilibrium voltage was recorded as well as the temperature of the cell. Cell temperatures were monitored with a chromel-alumel thermocouple with the junction resting on the sample.

Figure 3.14 shows the results obtained over a four

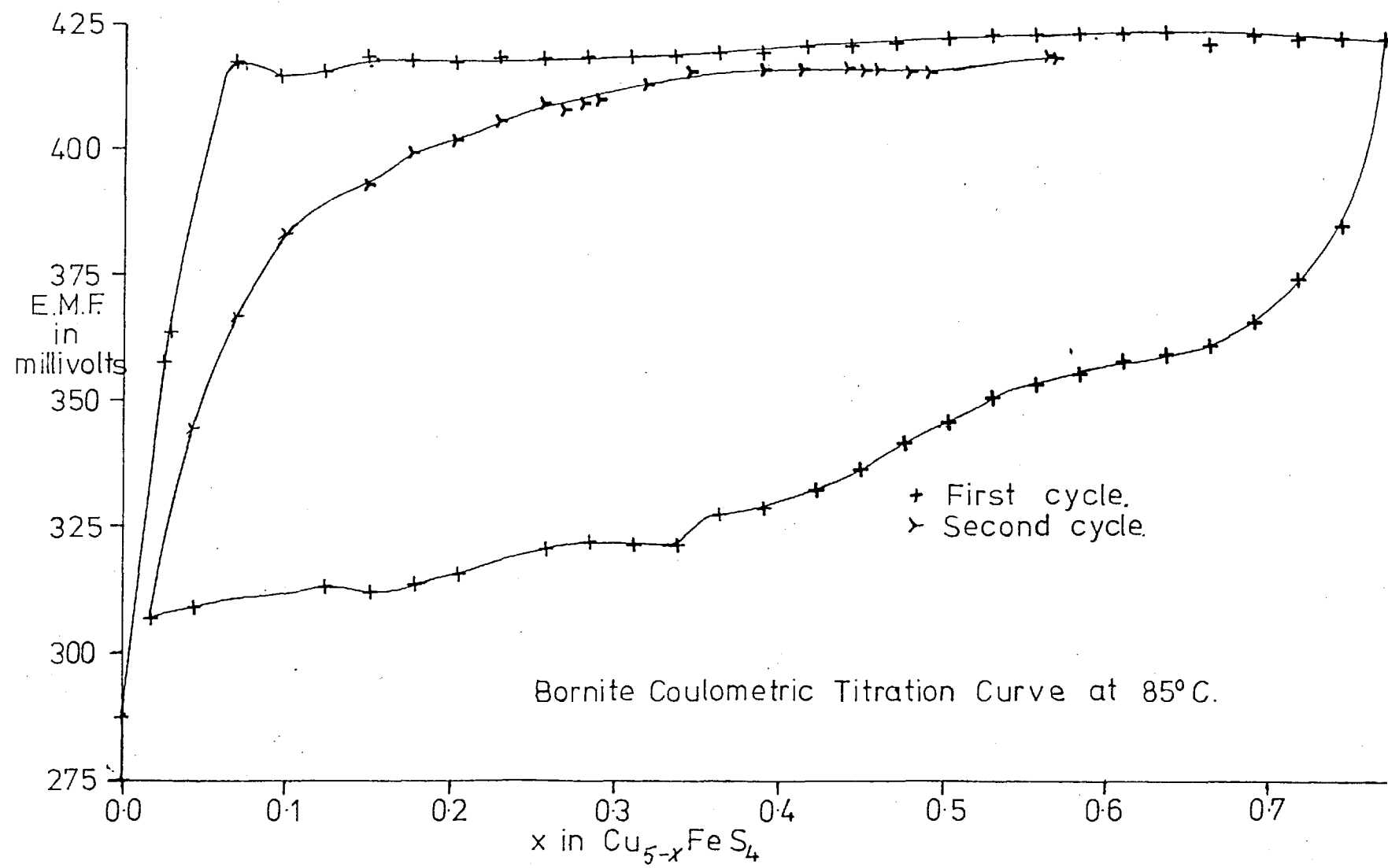


Figure 3.14

month period on a sample of crystalline Bornite at a temperature of $85^{\circ}\text{C} \pm 5^{\circ}\text{C}$. It will be seen from this graph that the initial removal of copper causes the voltage to rise rapidly to a composition of about $\text{Cu}_{4.95}\text{FeS}_4$. The removal of another 0.75 of a copper atom per formula then only causes the voltage to rise by 10 mV, giving a small change in ΔG . On replacement of the copper the voltage returns on a less well defined path which has a greater gradient. Removal of copper for the second time does not show the sharp rise of the initial curve, and it behaves as though it is now easier to remove copper. When the composition reaches $\text{Cu}_{4.7}\text{FeS}_4$ the voltage curve rejoins its initial path. Unfortunately this cell failed at $\text{Cu}_{4.42}\text{FeS}_4$ when it became impossible to pass a current. The sample was removed from this cell and placed in a new cell at 146°C where it was cycled. Results obtained at this higher temperature are shown in figure 3.15. It is again seen that a hysteresis is present, the size of which is apparently dependent on composition where the current was reversed.

Returning to the initial removal of copper, another cell operated at 100°C shows a similar starting effect to that of the initial curve of the former cell (fig. 3.16). At a composition of about $\text{Cu}_{4.96}\text{FeS}_4$ the cell voltage has a small maximum. This would however be impossible if the cell is under true equilibrium. Thus this effect must be due to a kinetically slow step, possibly the formation of a new phase. In order to check that equilibrium had been reached graphs of voltage versus time were plotted for most titrations, and one such graph is shown in figure 3.17.

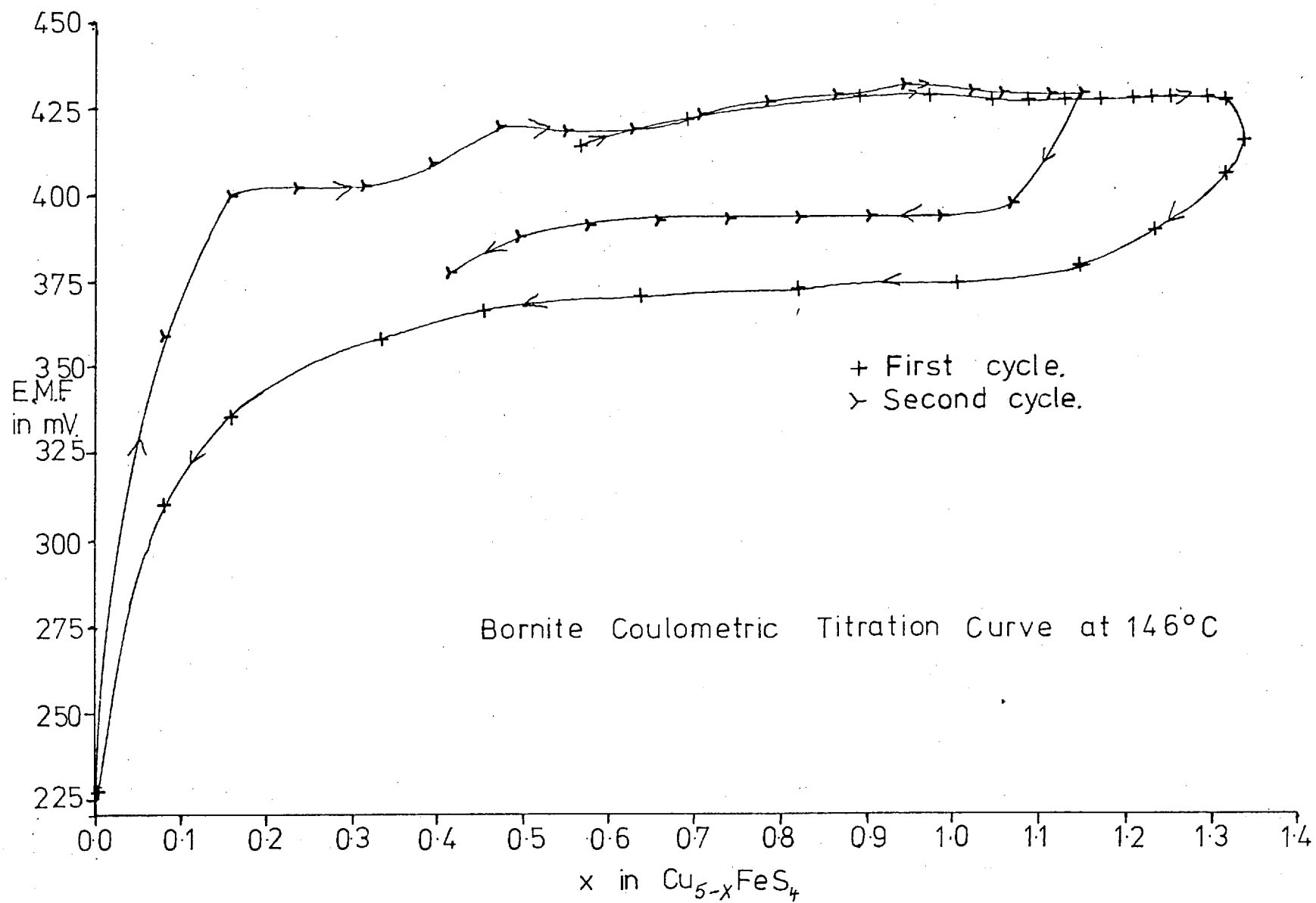


Figure 3.15

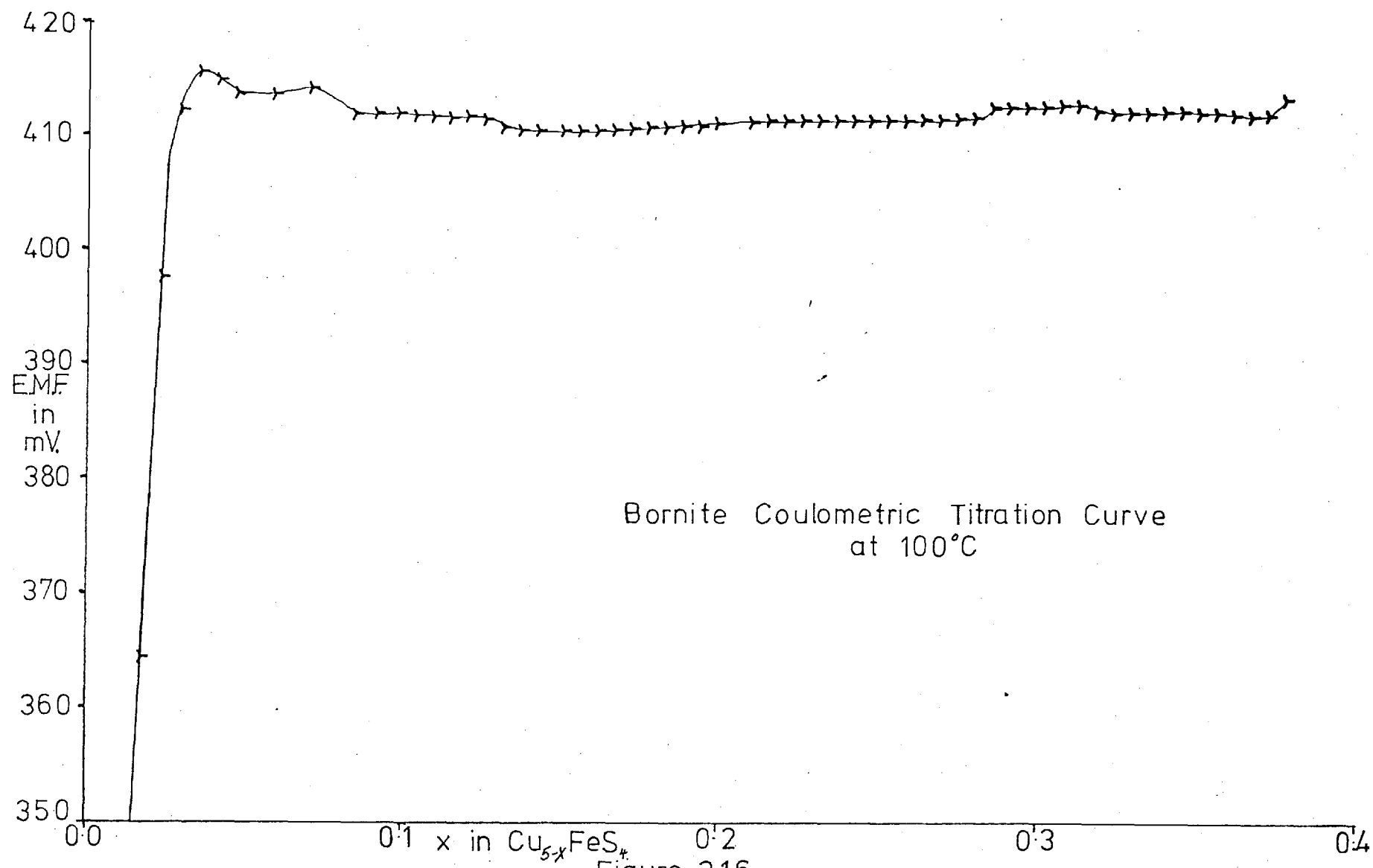


Figure 3.16

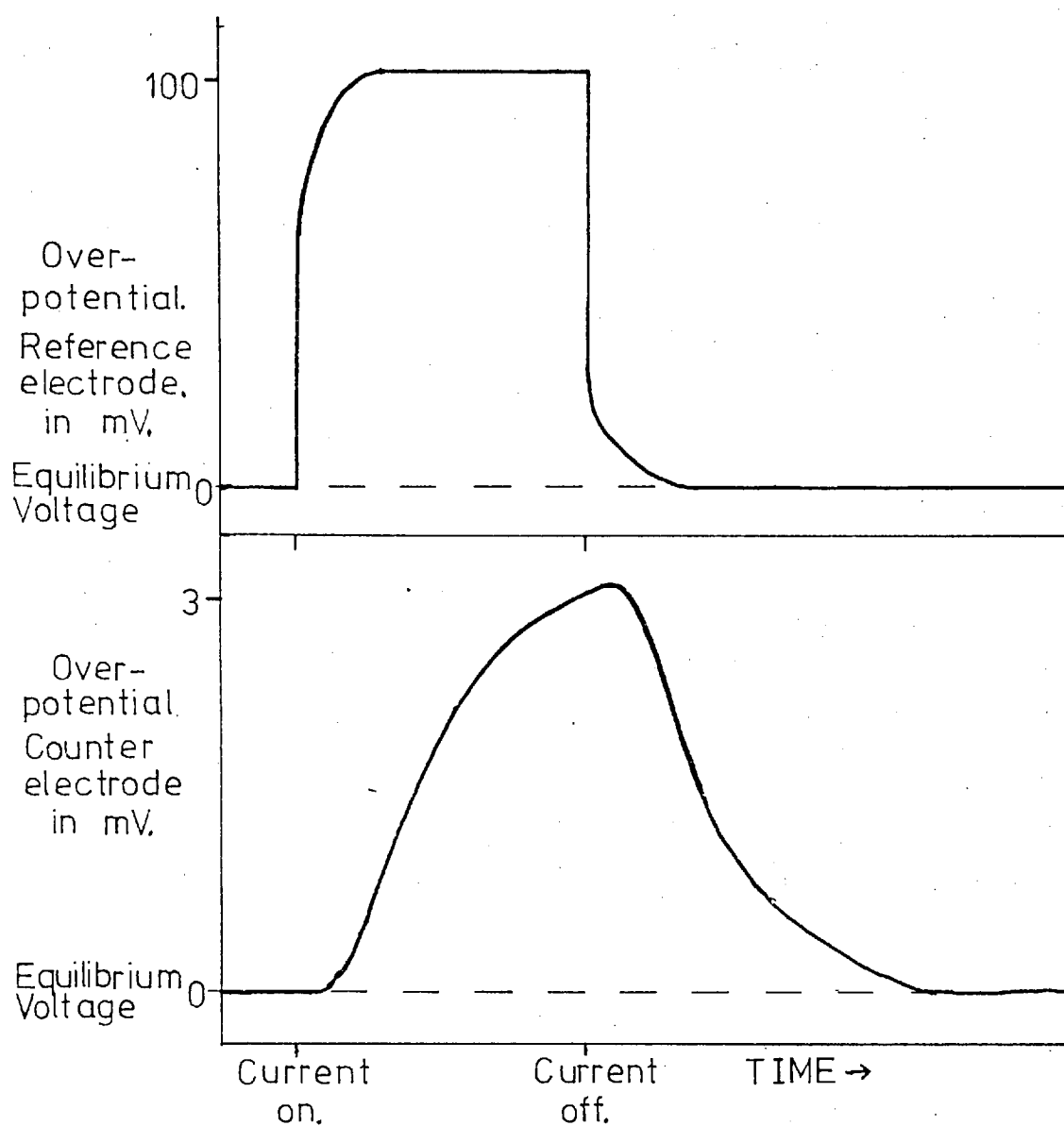


Figure 3.17
Transient effect on reference and counter electrodes.

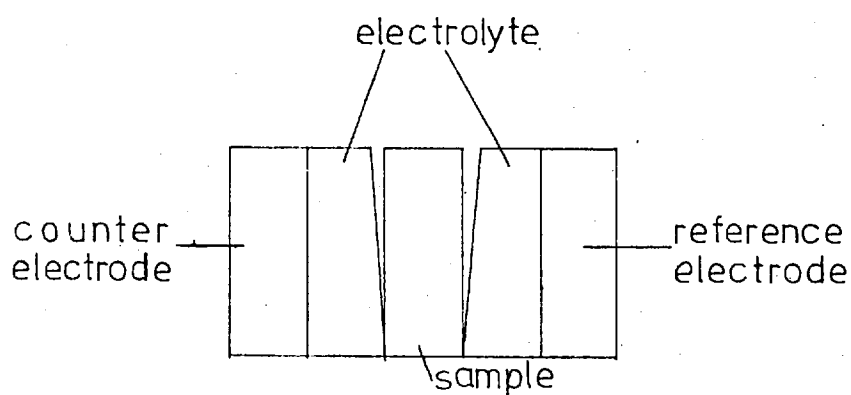


Figure 3.18
Worst geometry for titration cell.

All these plots showed that the reference electrode was affected by the passage of current within 2000 seconds on average and a maximum of 4000 seconds. As the information that the current has been switched on must travel by diffusion across the thickness of the sample (about 1 mm), this indicates a high diffusion coefficient. To relate D (the diffusion coefficient) to the time (t) until the effect of diffusion is noticed across a sample d , a standard formula is

$$d = \sqrt{Dt} \quad 3.III$$

Putting values into equation 3.III, D is found to be approximately $10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ for Bornite at a temperature of 100°C .

Another interesting point is that the reference electrode overshoots the new equilibrium value. It was first thought that this effect must be due to the cell geometry. The worst possible cell geometry, to cause this effect, is shown in figure 3.18. When this was simulated on the computer (appendix E) by using a simple finite difference method it was found that it was impossible to create the excess voltages seen at the reference electrode.

It was decided to carry out an investigation to find out whether the hysteresis could be accounted for on a structural basis. The method decided on was to prepare four samples at 130°C , two of which just had copper coulometrically removed, and two that had had the copper removed and then some replaced (see table 3.10).

Sample No.	Fraction of one Cu removed	Replace Cu	Final Composition
1	0.3241	0	$\text{Cu}_{4.68}\text{FeS}_4$
2	0.7649	0.3803	$\text{Cu}_{4.62}\text{FeS}_4$
3	0.7636	0.5549	$\text{Cu}_{4.79}\text{FeS}_4$
4	0.2341	0	$\text{Cu}_{4.77}\text{FeS}_4$

Table 3.10
Preparation of X-ray Titration Samples

The cell configuration used for the removal and replacement of copper was similar to figure 3.13. Unlike the coulometric cells the current was passed continually in this case in order to speed up the preparation of samples. As the samples reached the required compositions they were dropped out of circuit, the charge required to reach the required compositions having been previously calculated from their weights.

These samples, when they had reached their equilibrium voltages, were consistent with the coulometric titration curve (fig. 3.14). Investigation of the samples on the scanning electron microscope did not prove very successful as two of the samples charged up (nos. 2 and 4). Number 1 proved to be homogeneous, and the cycled specimen number 3 (which is shown in figure 3.20) showed two phases. Analysis of the phases, and the white areas which appear to be a surface deposit, resulted in table 3.11.

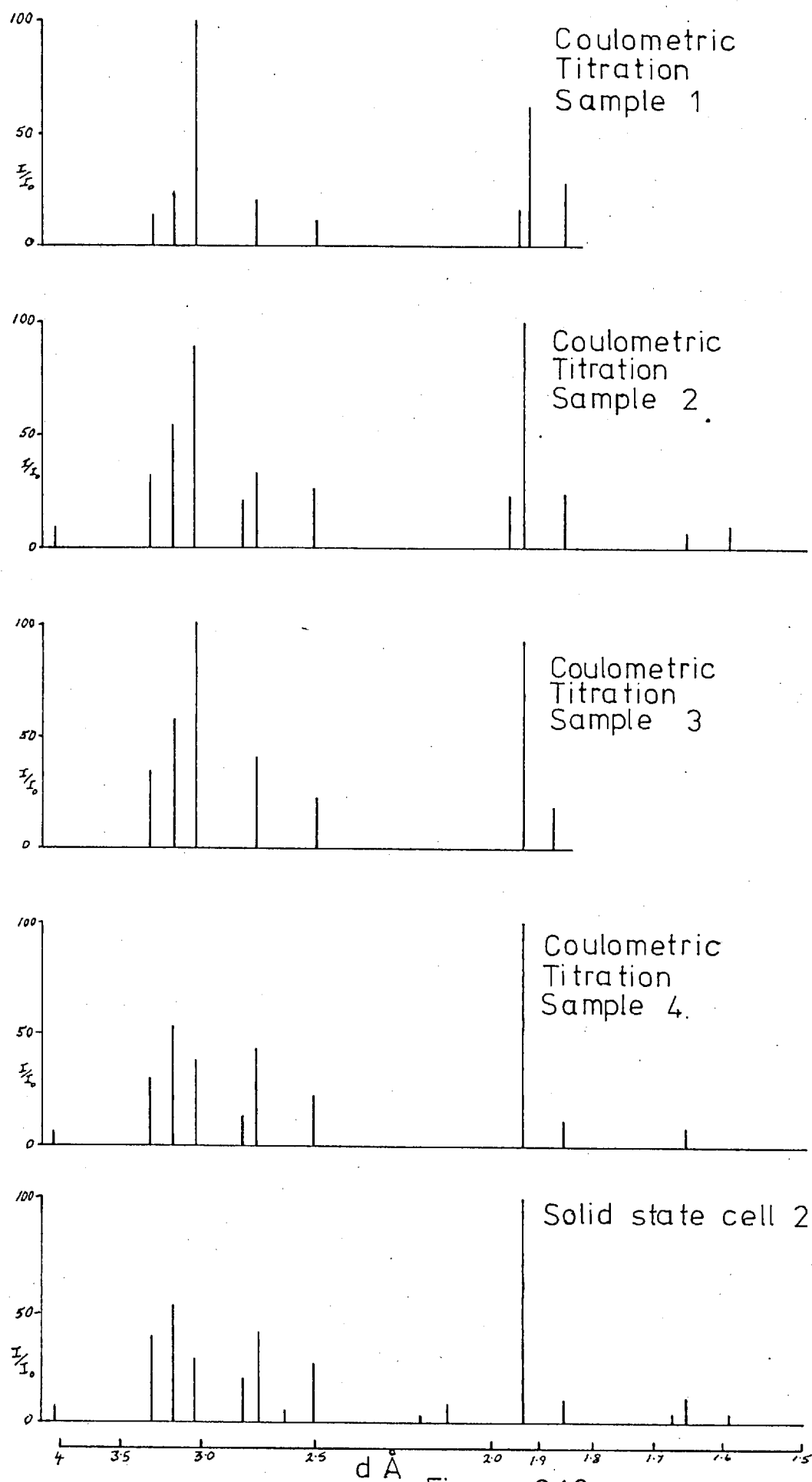
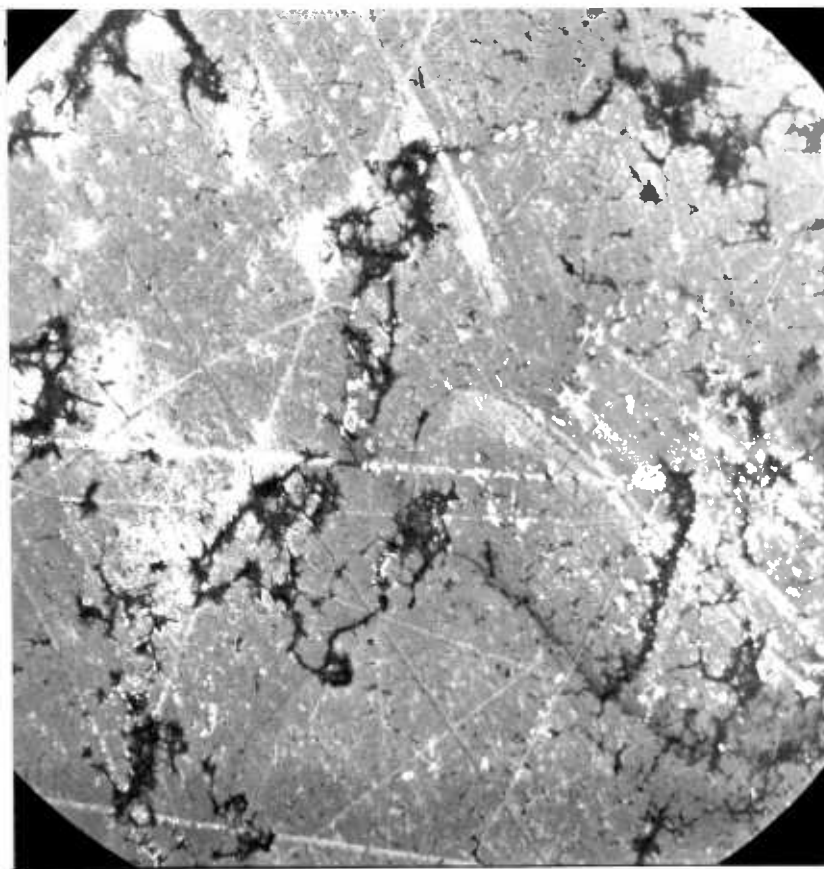


Figure 3.19



50 μm

Micrograph of Titration Sample 3.

Figure 3.20.

Phase	Composition by EDAX
White area	$\text{Cu}_{5.24}\text{Fe}_{0.94}\text{S}_4$
Dark phase	$\text{Cu}_{4.80}\text{Fe}_{0.84}\text{S}_4$
Main phase	$\text{Cu}_{4.77}\text{Fe}_{1.08}\text{S}_4$

Table 3.11

EDAX Analysis of Titration Sample Number 3

It thus appears that the difference between the dark area and the main phase is due to a difference in iron content and not the expected difference in copper content. It should be pointed out at this stage that the electron microscope is capable of performing EDAX on particles down to 2 microns diameter, visual signals should go down even further than that. So if the particle sizes of two phases are much less than 0.1 microns they will not be detected.

X-ray diffraction was also carried out on these specimens and the sample from the 100°C cell. Analysis of the results, which are given in table 3.12, was by interpreting them as a mixture of Bornite lines and chalcopyrite lines. This method was adopted by Ugarte-Alvarez (30) for work on partially leached specimens of Bornite. In this work however he indexed the Bornite lines when the composition was near that of Bornite and the chalcopyrite lines for lower copper content, using the 440 and 44.16 reflections for the Bornite and the 220 and 228 for the chalcopyrite. This method would be quite satisfactory if the 220 and 228 lines of the chalcopyrite had been indexed but these lines are obscured on the X-ray diffraction pattern by the stronger 204 and 424 lines. Thus for the present work the 112 and

204 lines of chalcopyrite were used. In the thesis on leaching a large lattice contraction is shown on changing from Bornite to chalcopyrite by indexing lines from only a single phase. But the results in table 3.13 from this work appear to show the coexistence of both Bornite and chalcopyrite, even though only one phase appears to be present by the scanning electron microscopy.

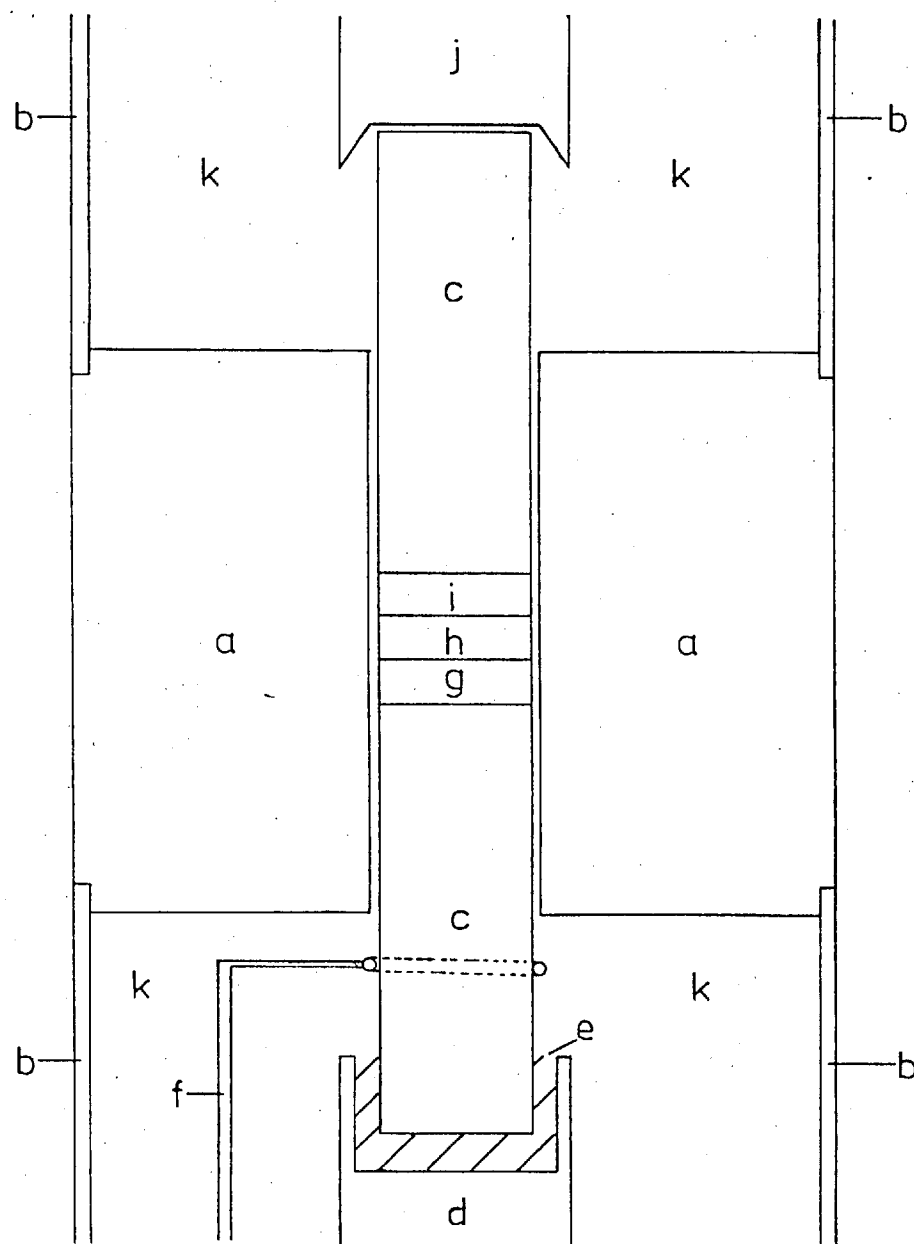
Thus the evidence is conflicting and more work is required to show the interrelationship between Bornite and chalcopyrite and also to reveal what is causing the hysteresis in the coulometric titration graphs.

The final coulometric titration cell was constructed in the hot-press, with the configuration shown in figure 3.21. This arrangement was used in order to provide a cell in which a larger current could be passed, as the cells where the electrolyte was only a pressed contact tended to be restricted due to interface resistance. A larger current was required in order to change the composition quickly as time for this cell was restricted. In this cell the approach was to hot-press the electrolyte directly on to the electrode sample along with the copper counter electrode. The cell was then used in the normal way except that the counter electrode was also used as the reference electrode. Pressing and running conditions were a temperature of 150°C, a pressure of $6 \times 10^7 \text{ Nm}^{-2}$ on the plungers, in a vacuum during pressing and under high purity argon while being run.

Construction of this cell was required for three reasons, the main one of which was to establish the coulometric titration curve for the hot-pressed Bornite. Hot-pressed Bornite was to be used in the six-point cell, and

Table 3.13
Lattice Parameters of Coulometric Titration X-Ray Samples

Sample	Phase Present	System	Lattice Parameter			Standard Deviations		
			a Å	b Å	c Å	a Å	b Å	c Å
Synthetic Bornite	Bornite	Orthorhombic	10.90	10.88	21.80	0.01	0.02	0.02
1	Bornite	Orthorhombic	10.92	10.85	21.79	0.03	0.05	0.06
	Chalcopyrite	Tetragonal	5.21	5.21	10.94	-	-	-
2	Bornite	Orthorhombic	10.92	10.89	21.90	0.02	0.06	0.04
	Chalcopyrite	Tetragonal	5.29	5.29	10.38	-	-	-
3	Bornite	Orthorhombic	10.93	10.92	21.84	0.02	0.03	0.04
	Chalcopyrite	Tetragonal	5.21	5.21	10.59	-	-	-
4	Bornite	Orthorhombic	10.92	10.94	21.84	0.01	0.02	0.01
	Chalcopyrite	Tetragonal	5.25	5.25	10.42	-	-	-
100° Cell	Bornite	Orthorhombic	10.90	10.94	21.81	0.01	0.03	0.04
	Chalcopyrite	Tetragonal	5.27	5.27	10.35	-	-	-



- | | |
|---|-----------------------------------|
| a, 8mm alumina die. | g, Copper foil counter electrode. |
| b, Die supports. | h, Electrolyte. |
| c, 8mm graphite plungers. | i, Bornite. |
| d, Bottom support. | j, Pressure plunger. |
| e, Alumina insulator. | k, High purity argon. |
| f, Thermcouple and counter electrode contact. | |

Hot-pressed Coulometric Titration Cell.

Figure 3.21.

the slope of the coulometric titration curve was required for interpretation of the results. A second reason was to establish the stoichiometry of the starting material as analysis did not prove very successful. Thirdly it would show whether the interface could be improved by hot-pressing or if the polarization was due to some reaction which occurred as the copper ions crossed the interface.

Results obtained from this cell are given in table 3.14 and graphically in figure 3.22. The points on the graph are derived from one and a half cycles of the cell and show a reasonable degree of reproducibility. The graph is fixed by only a few points but these appear to be enough to fix the gradient of the first and last sections, for the six-point cell work. Interface polarization in this cell was greatly reduced on that of the other cells; pumping currents of 5 amps m^{-2} were regularly used with an interface voltage drop of 10 mV and it was possible to use 20 amps m^{-2} for restricted times. This cell proved that the interface potential drop in the other type of cell is due to mechanical defects at the interface.

From the coulometric titration curve for the hot-pressed material it should be possible to establish the composition of this material. Three assumptions are necessary in order to do this, and they are as follows:-

1. Only sulphur has been lost in hot-pressing.
2. The change in iron to copper ratio is sufficiently small so as not to affect the phase present, so that the total number of metal atoms per formula is six at the stoichiometric composition.
3. The starting material is stoichiometric.

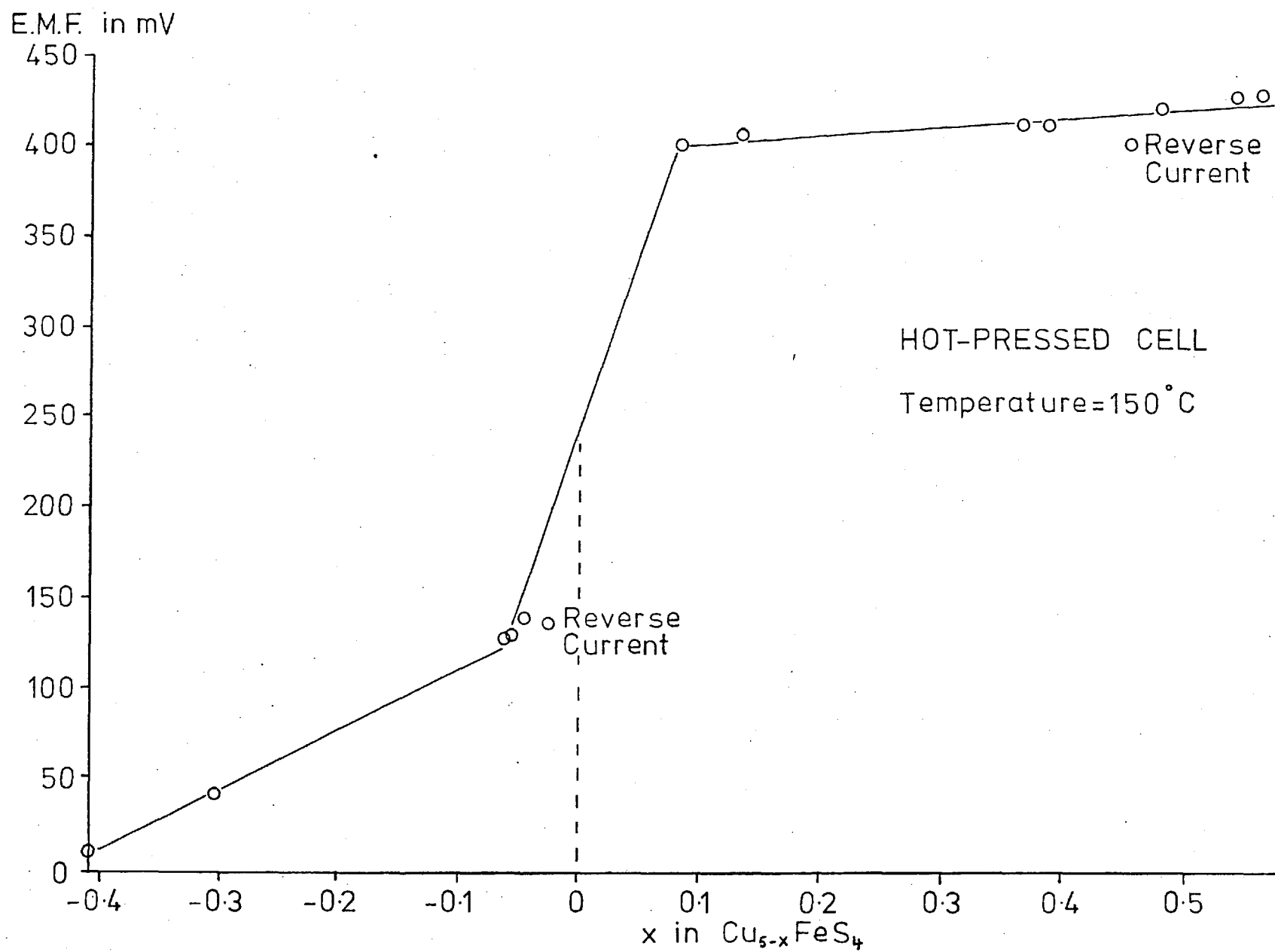


Figure 3.22

Thus the composition of the hot-pressed material is $\text{Cu}_{5p}\text{Fe}_p\text{S}_4$ where p is a constant, and stoichiometric hot-pressed Bornite will have the composition $\text{Cu}_{6-p}\text{Fe}_p\text{S}_4$. By inspection of the coulometric titration curve it will be seen that there is one section with a large gradient which is approximately 1 mV for a change in composition in x of 2.5×10^{-4} (for $\text{Cu}_{6-p-x}\text{Fe}_p\text{S}_4$) and which is very close to the gradient for the stoichiometric material in the other cells (1 mV for a change in composition in $x = 2 \times 10^{-4}$ for the 100°C cell where x is in $\text{Cu}_{5-x}\text{FeS}_4$). It may therefore be assumed that this steep area corresponds to Bornite. The actual stoichiometric composition will therefore exist in this region, but its exact composition can not be ascertained. Therefore it must be assumed that it either occurs at the centre of the steep region or that the coulometric titration curves for the other samples started with stoichiometric material and thus the voltage they started at is the voltage for stoichiometric Bornite. This latter premise was dismissed as all the cells did not start at the same voltages. Also in this case it had been decided to take stoichiometric Bornite as $\text{Cu}_{6-p}\text{Fe}_p\text{S}_4$ and not Cu_5FeS_4 .

Calculation of the value of p is carried out as follows. Firstly a graph of the "number of coulombs passed versus the cell E.M.F. is plotted. From this the mid-point of the steep section can be ascertained and thus the number of coulombs of electricity removed to reach this point found (q). Now the molecular weight of the hot-pressed material is calculated from the formula $\text{Cu}_{5p}\text{Fe}_p\text{S}_4$ which is $374P + 128$. Thus the number of formulae in the sample equals the mass of the sample (m) divided by the molecular weight.

As the formula of the stoichiometric material is $\text{Cu}_{6-p}\text{Fe}_p\text{S}_4$ the amount of copper removed from the hot-pressed Bornite is:

$$5p - 6 + p = 6(p - 1) \quad 3.\text{IV}$$

Therefore the total charge passed to remove this amount of copper is:

$$\frac{6F(p - 1)m}{374p + 128} \quad 3.\text{V}$$

where F is Faraday's constant. This amount of charge has been measured from the coulometric titration graph (q), thus the following formula is derived for p:

$$p = \frac{6Fm + 128q}{6Fm + 374q} \quad 3.\text{VI}$$

In this case p was calculated as 1.08 which gives an effective composition for the hot-pressed material of $\text{Cu}_{5.41}\text{Fe}_{1.08}\text{S}_4$.

This composition disagrees with the analysis that was obtained from the microprobe of $\text{Cu}_{6.13}\text{Fe}_{0.90}\text{S}_4$, but this could easily be due to sample deterioration during preparation.

EDAX of the sample when it was removed from the cell gave a composition of $\text{Cu}_{4.54}\text{Fe}_{0.91}\text{S}_4$ for the main phase, compared to a calculated value, found assuming a starting composition of $\text{Cu}_{5.41}\text{Fe}_{1.08}\text{S}_4$, of $\text{Cu}_{4.46}\text{Fe}_{1.08}\text{S}_4$. This sample appeared under the scanning electron microscope to be a single phase material although there was a precipitate along the grain boundaries of composition $\text{Cu}_{6.07}\text{Fe}_{1.12}\text{S}_4$ from EDAX.

The sample which was used in the six-point cell was also examined in the scanning electron microscope and the result is shown in figure 3.23. This picture shows two phases with a distinct orientation to one another. Analysis by EDAX gave the composition of the phases as $\text{Cu}_{5.7}\text{Fe}_{0.83}\text{S}_4$ (minor phase) and a major phase of $\text{Cu}_{3.6}\text{Fe}_{1.7}\text{S}_4$. These



20 μ m

Figure 3.23
Micrograph of Six-Point Cell Specimen.

analyses are approximate and it seems possible that the two phases are Bornite and chalcopyrite. The overall composition of the sample is $\text{Cu}_{4.54}\text{Fe}_{1.08}\text{S}_4$ using the coulometric titration to fix the composition. If this is a true two phase region the coulometric titration curve should have been flat which it is not, and also the chemical diffusion coefficient should have been very low if not zero which it is not (see later). X-ray results from this sample gave the results shown in table 3.15 and figure 3.24. These results show the main lines of both Bornite and chalcopyrite, which adds support to the theory that the two phases seen are closely related to these phases.

By varying the temperature of the cell whose coulometric titration curve at 85°C is given above, it was possible to obtain values for the entropy change (ΔS) and the enthalpy change (ΔH). This procedure was carried out on the second cycle of this cell at various compositions arrived at after the removal of copper. The results are presented graphically in figures 3.25, 3.26 and numerically in table 3.16. It is seen that both entropy changes and partial enthalpy show a steep gradient between $x = 0$ and 0.1 (x in $\text{Cu}_{5-x}\text{FeS}_4$). At $x = 0.1$ the change in the gradient of the ΔH curve and the minimum in the ΔS curve would suggest that some ordering process is taking place. The rest of the variations are unfortunately small in comparison to the errors in the results, but there are no major changes occurring at other compositions.

3.6. TRANSPORT PROPERTIES OF HOT-PRESSED BORNITE

3.6.1. ELECTRONIC RESISTIVITY

The electronic conductivity of the sample is required to analyse the transient behaviour of the six-point cell.

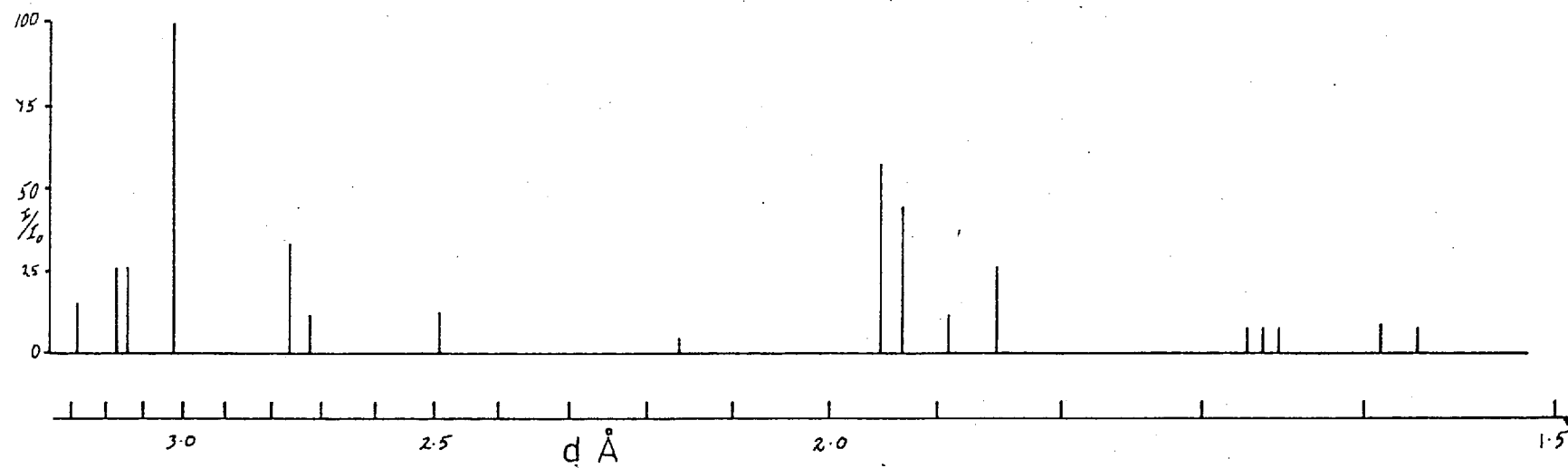
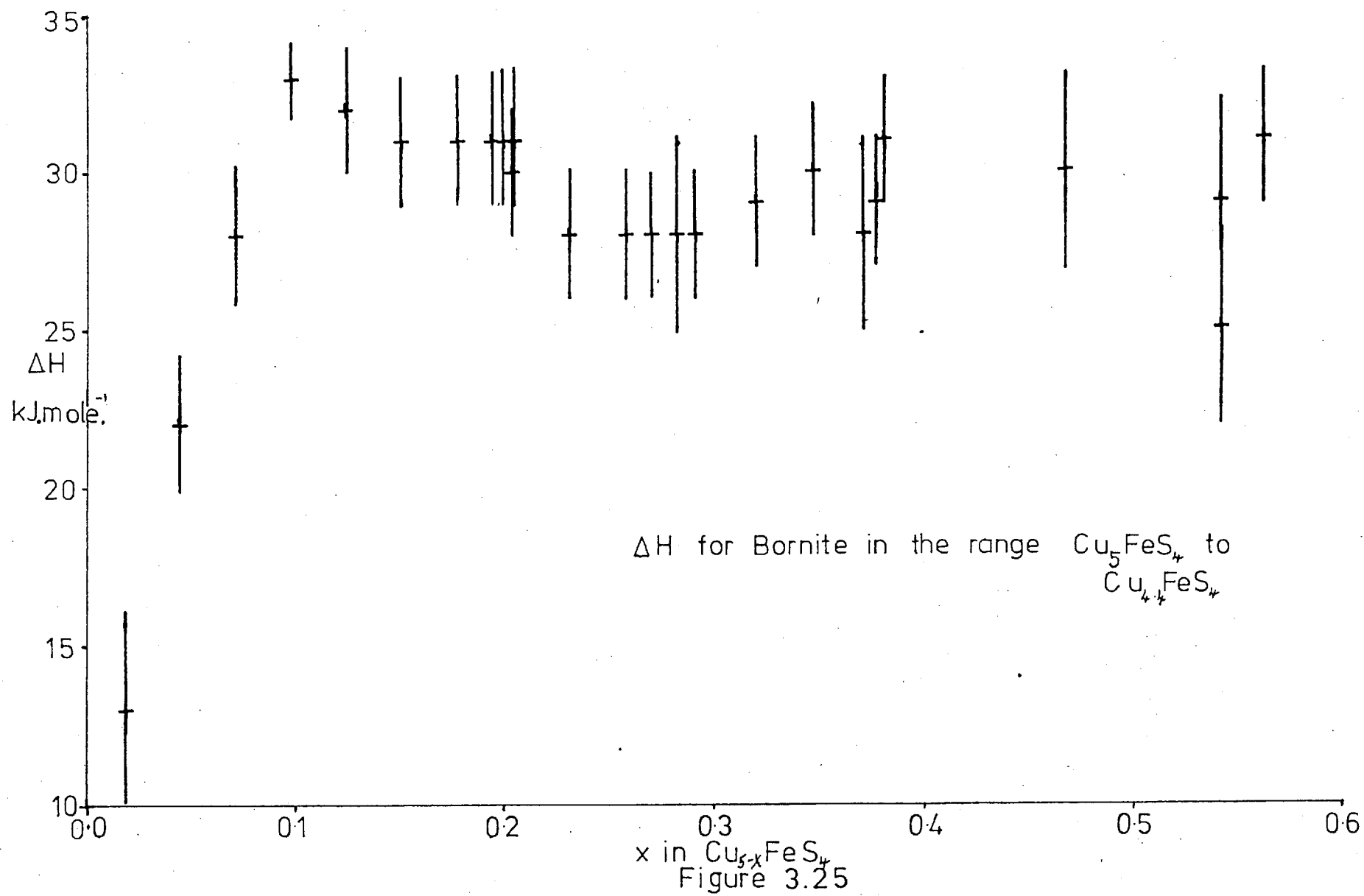
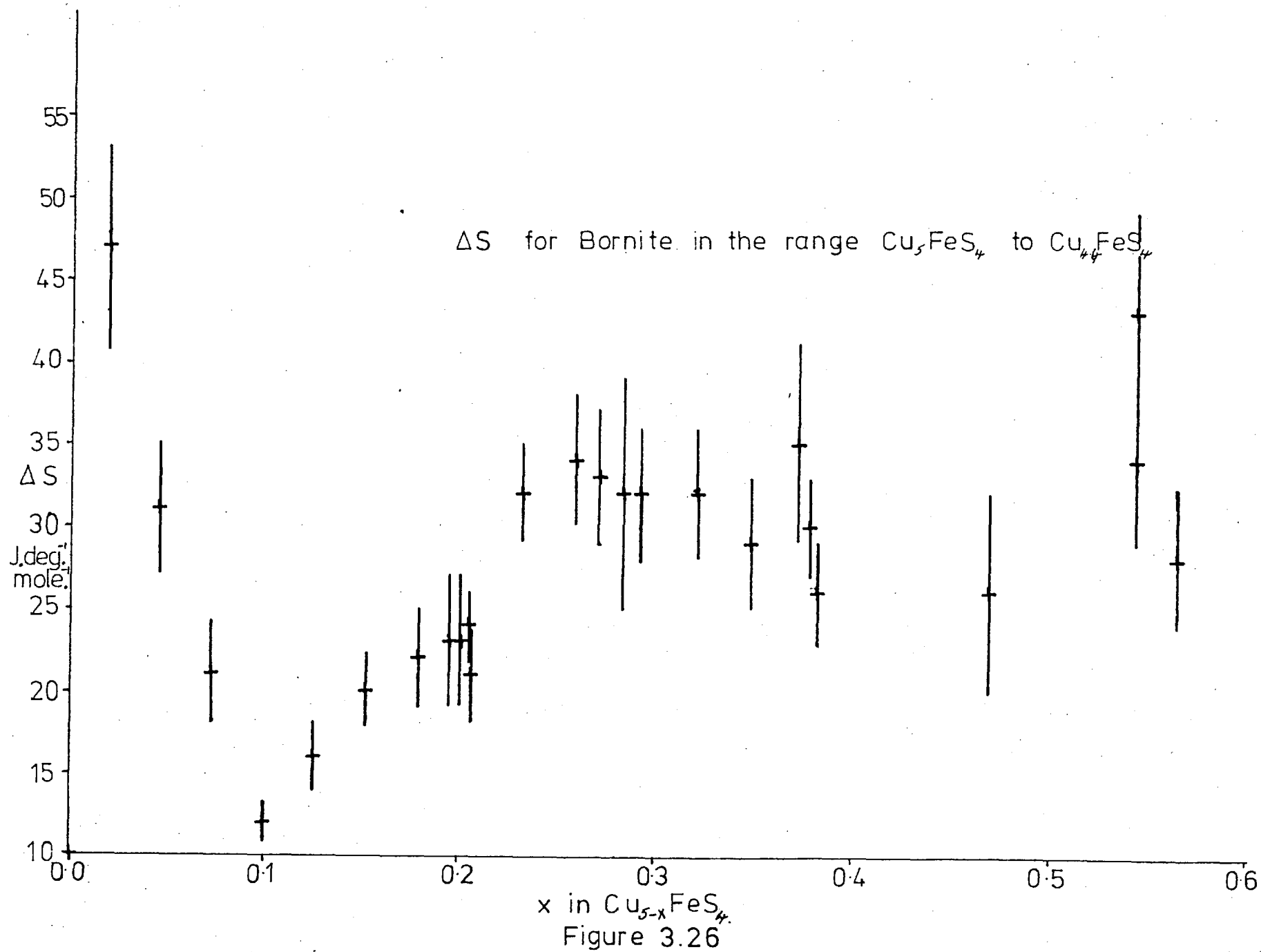


Figure 3.24
X-ray diagram of sample from six point cell.





In order to obtain this the Van der Pauw method (67) was used as detailed in appendix C. Hot-pressed Bornite was machined into a square plate 5 x 5 x 1 mm. The plate was placed in a rig with sprung tungsten contacts on the centres of the sides. This rig was then used in a high purity argon atmosphere and kept at temperature by a Kanthel furnace. The current was passed through two contacts and the voltage across the other two contacts was monitored. Then a current was passed through one of the current contacts from above and one of the voltage contacts as detailed in figure 3.27. The process was then repeated but with the current in the opposite sense. This procedure removes any rectifying effects of the contacts and anisotropy of the sample.

The temperatures at which this experiment was conducted and the electronic conductivities are given in table 3.17 and shown graphically in figure 3.28. From the shape of the curve it is possible to obtain an activation energy for electronic conductivity, which in this case is 2.6×10^{-10} joule per particle above 350°K and 3.7×10^{-10} joule per particle below 350°K. Such a change in the activation energy is characteristic of a change in the mechanism of transport.

3.6.2. IONIC CONDUCTIVITY AND DIFFUSION COEFFICIENT

A six-point cell was constructed, of the type described by Dudley and Steele (68), and shown in figure 3.29, for the purpose of obtaining the ionic conductivity of Bornite. As has been explained earlier the specimen on which these measurements were carried out was a hot-pressed bar of Bornite. This was machined on a diamond saw to a size of 2 mm square

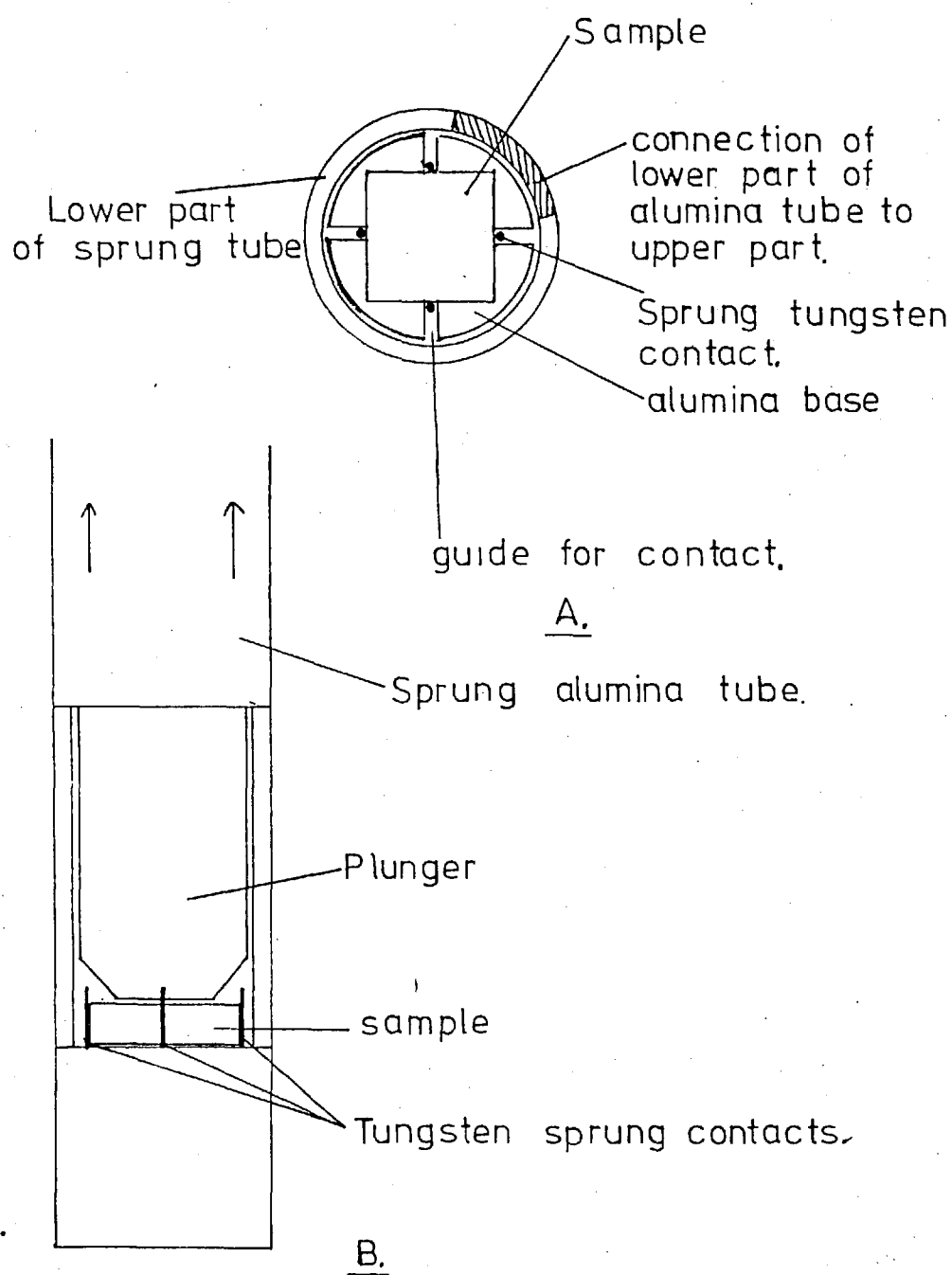
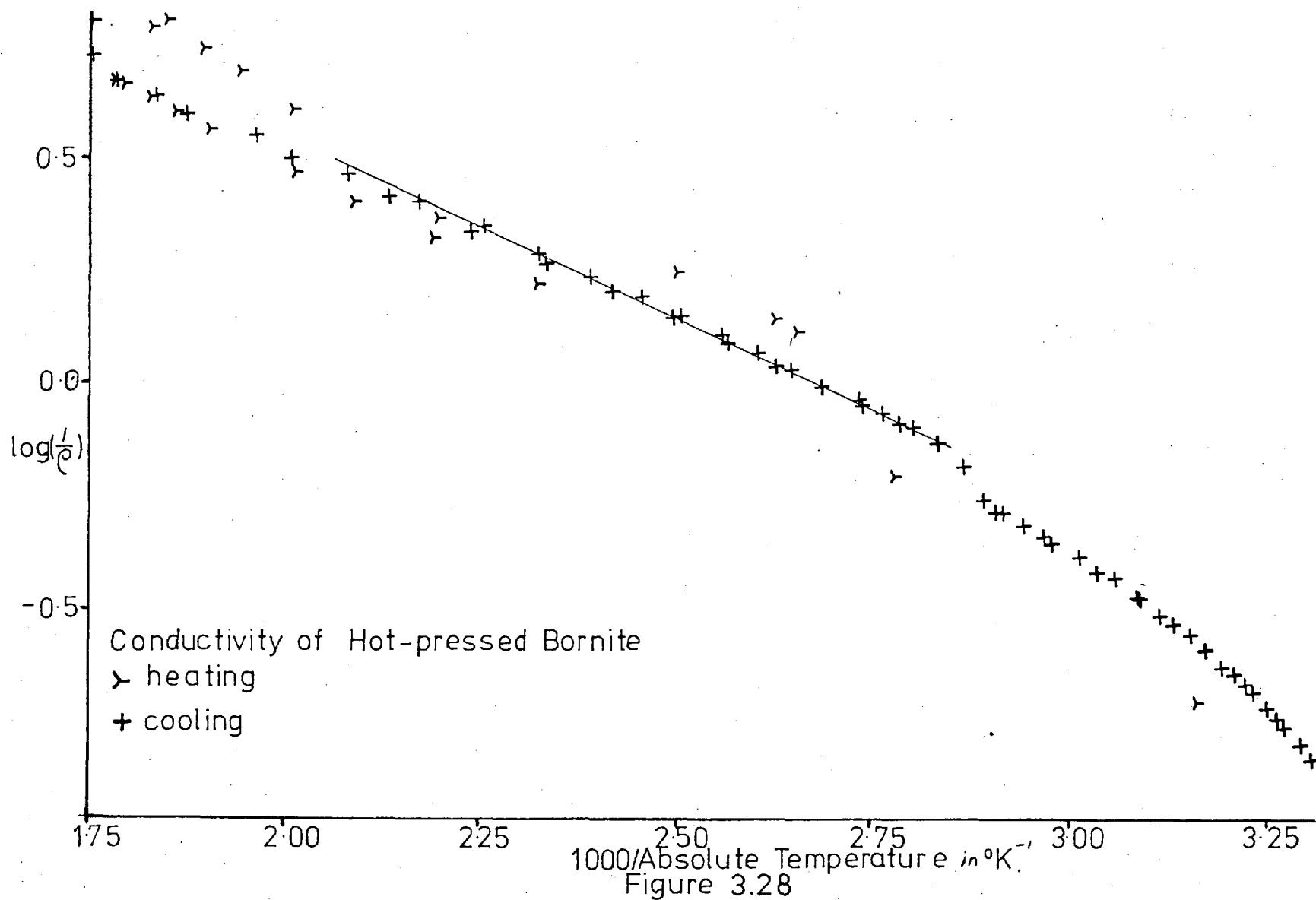


Figure 3.27
 Van der Pauw Cell.
 A, View from the end of the plunger.
 B, Side view of cell.



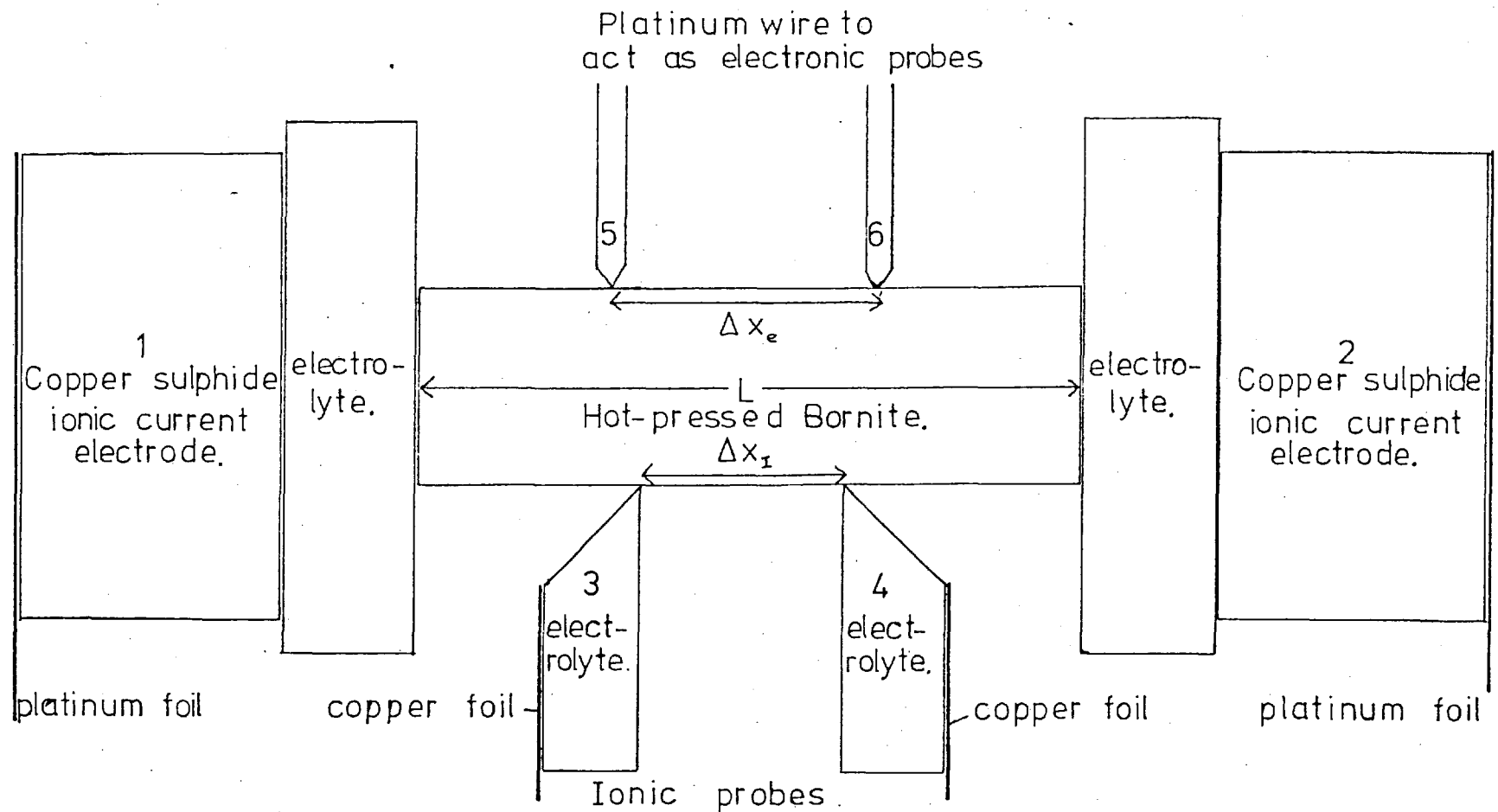


Figure 3.29
Layout of six point cell.

and 6 mm long. The copper working electrodes were constructed from copper sulphide (Cu_2S) which had also been hot-pressed and machined. Hot-pressed electrolyte was used which had been prepared in the way detailed earlier and ground clean on silicon carbide paper. In order to make the ionic reference electrodes a hot-pressed pellet of electrolyte was broken in two and then was ground to form a point at one corner of each piece. These points were very delicate and had to be treated with great care. To complete the reference electrodes, copper was evaporated on to one of the flat faces of the electrolyte, being careful to avoid depositing it on the pointed part.

The relevant theory behind the measurements is detailed in appendix D.

The experiment consists of passing an ionic current between the current electrodes (1 and 2) and monitoring the effect on reference electrodes ((3 and 4) ionic, and (5 and 6) electronic) until equilibrium is attained. The composition of the bar is then changed by passing a current between the ionic current electrodes (1 and 2), and the electronic probes (5 and 6). After equilibrium has been attained in the bar again the experiment is repeated at this new composition, and so on.

The ionic conductivity (for suppressed electronic current) σ'_i is given by

$$\sigma'_i = \frac{J_i \times (\text{Distance Between Ionic Probes})}{\Delta V_i^\infty} \quad 3.VII$$

where J_i is the current density and ΔV_i^∞ is the equilibrium voltage across the ionic probes when a current J_i is passing. As it was impossible to obtain any values for cross-terms between the ionic current and the electronic current it will

be assumed that they are small (see fig. 3.30a). Therefore σ'_i is equal to σ_i , the ionic conductivity. The results that were obtained from this formula are shown in table 3.18.

σ_i ohm ⁻¹ cm ⁻¹	Composition	Temperature °C
1.1×10^{-1}	Cu _{5.41} Fe _{1.08} S ₄	170
2.7×10^{-2}	Cu _{5.17} Fe _{1.08} S ₄	170
1.4×10^{-2}	Cu _{4.67} Fe _{1.08} S ₄	170

Table 3.18
Ionic Conductivity of Hot-Pressed Bornite

It should also be possible to obtain the total conductivity from the instantaneous reference voltages on switching on the current. This however proved impossible, as the probes responded immediately and not as theory predicted, see figure 3.30b and appendix D. The transient behaviour of the ionic probes in fact obeyed an exponential curve so well that the resolution of the D.V.M. was the limiting factor (see table 3.19). A model that predicts the exponential transient behaviour is the simple resistor in parallel with a resistor and capacitor in series. The thermodynamic model reduces to an exponential curve however for long times and it was this that was used to interpret the results at long times.

A characteristic time, τ for the transient can be established by use of the equation (69)

$$\delta V_i = A e^{-t/\tau} \quad 3.VIII$$

where t is the time from switching the current on or off, A is a constant, and $\delta \Delta V_i$ is defined by equation 3.IX.

$$\delta \Delta V_i = \Delta V_i^0 - \Delta V_i^\infty \quad 3.IX$$

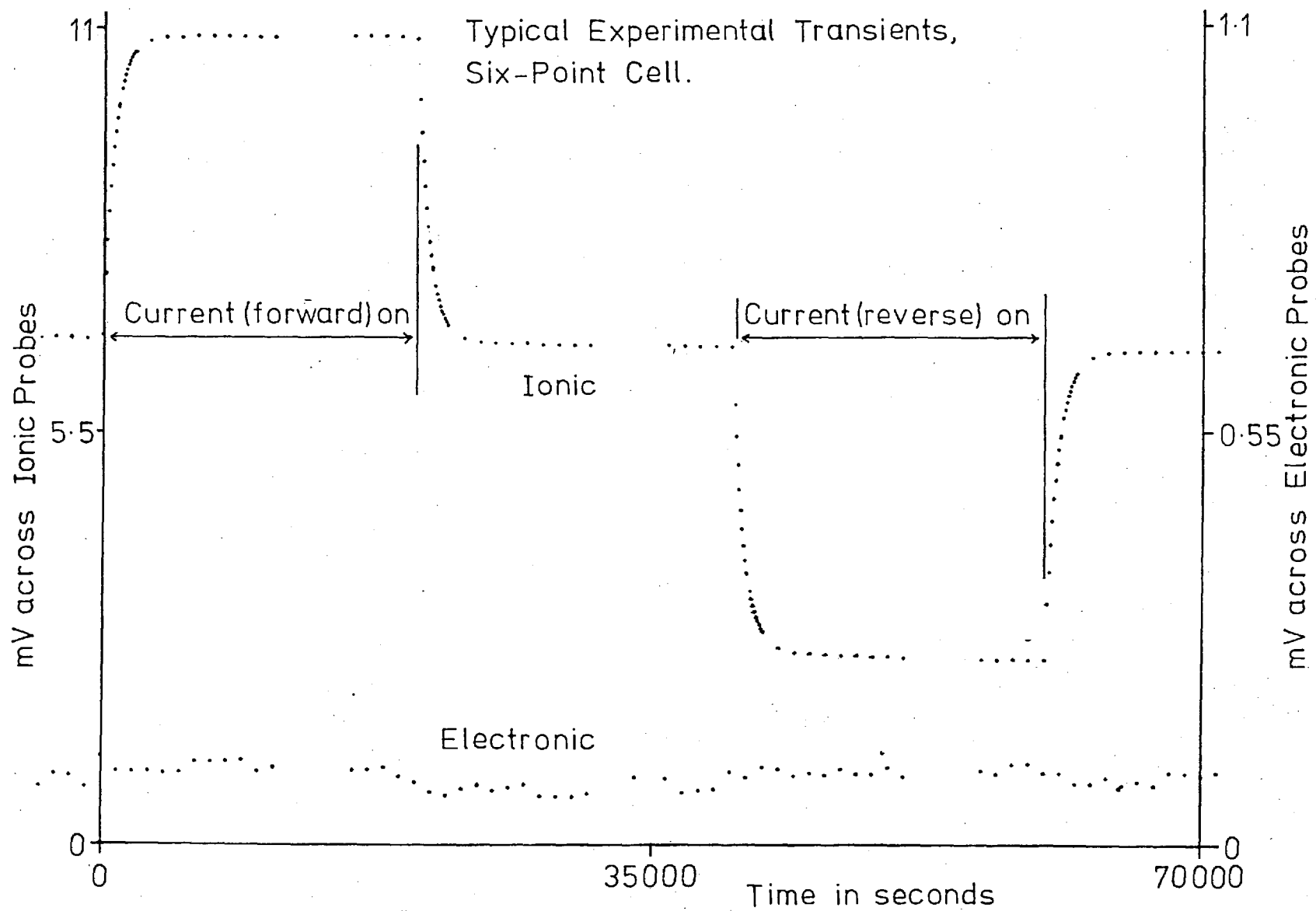


Figure 3.30a

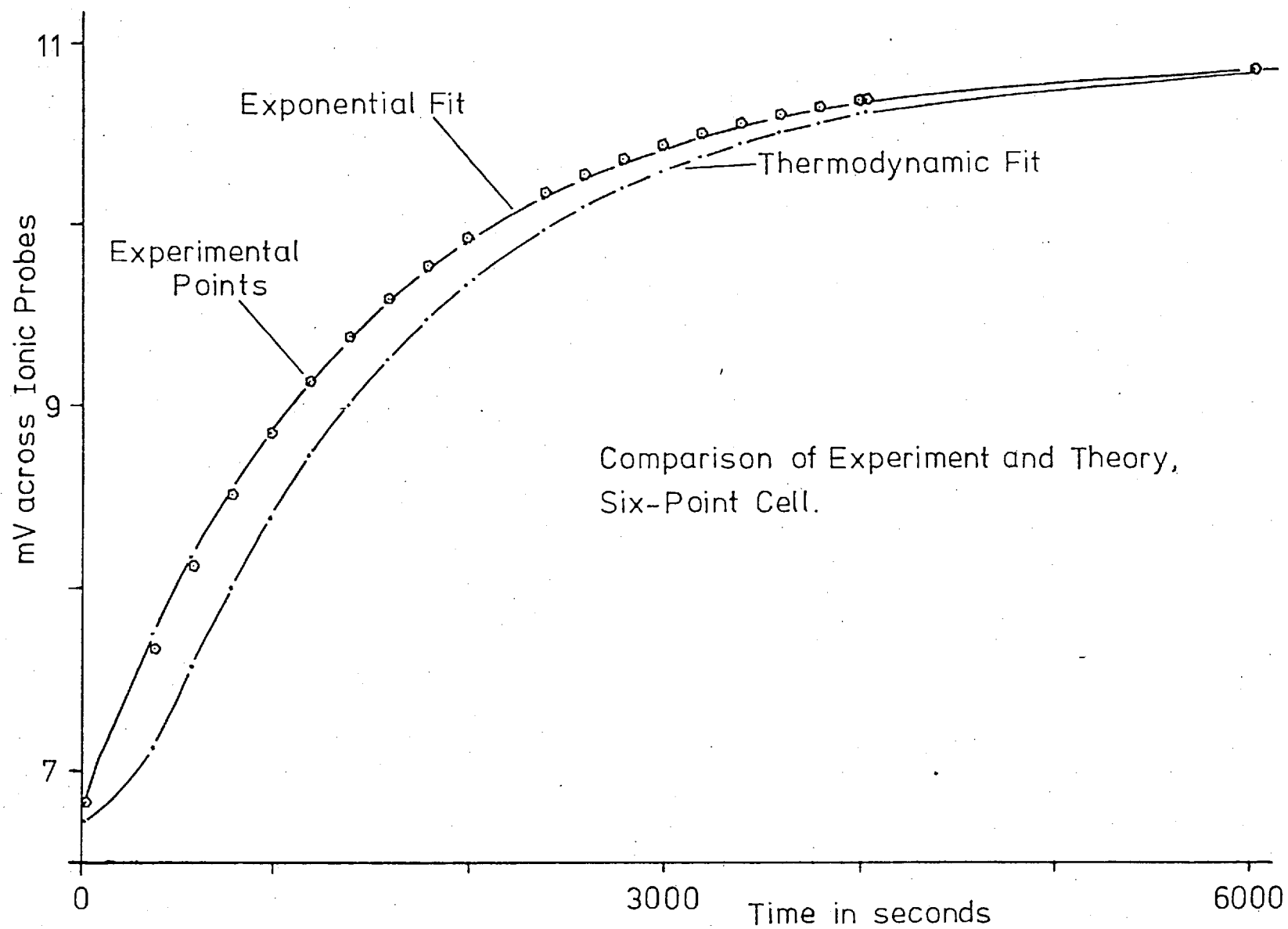


Figure 3.30b

In equation 3.IX ΔV_i^0 is the ionic current probe voltage at time $t = 0$. γ is related to the chemical diffusion coefficient ($\tilde{D}$) by equation D19 of appendix D in which L is the length of the bar specimen (for other symbols see appendix D).

$$\frac{1}{\gamma} = \frac{\tilde{D} \pi^2}{L} = \frac{\pi^2 \sigma_i \sigma_e}{L \sigma_r e^2} \left(\frac{d\mu}{dN} \right) \quad \text{D19 3.X}$$

The values of $\tilde{D}$ obtained from transients (table 3.20) can be compared with the values obtained from the steady state ionic conductivity assuming that the electronic conductivity is very much greater than the ionic (equation D19). This comparison is shown in table 3.21, which shows a good agreement for the second and third pairs of values, although there is over an order of magnitude difference between the first pair. However the slope of the coulometric titration curve is not very well defined for the starting composition and this could easily account for the discrepancy in the first result.

Composition	$\tilde{D}$ average from γ $\text{cm}^2 \text{sec}^{-1}$	$\tilde{D}$ from ionic conductivity $\text{cm}^2 \text{sec}^{-1}$	Temperature $^{\circ}\text{C}$
$\text{Cu}_{5.41} \text{Fe}_{1.08} \text{S}_4$	7.7×10^{-5}	3.4×10^{-4}	170
$\text{Cu}_{5.17} \text{Fe}_{1.08} \text{S}_4$	4.5×10^{-5}	8.3×10^{-5}	170
$\text{Cu}_{1.08} \text{Fe}_{1.08} \text{S}_4$	8.8×10^{-6}	5.6×10^{-6}	170

Table 3.21

$\tilde{D}$ Derived from Ionic Conductivity and Transient

The electronic probes proved unsatisfactory due to the fluctuation in the voltage across them, which was probably due to thermal effects. From theory the instantaneous electronic probe voltage (44 microvolts) was much smaller

Table 3.20
 χ and $\tilde{D}$ from Transients at 170°C

Composition	Current Status	χ sec.	$\tilde{D}$ cm, sec.
$\text{Cu}_{5.41}\text{Fe}_{1.08}\text{S}_4$	Forward on	488	7.0×10^{-5}
	Forward off	416	8.2×10^{-5}
	Reverse on	429	7.9×10^{-5}
	Reverse off	444	7.7×10^{-5}
	Average	444	7.7×10^{-5}
$\text{Cu}_{5.17}\text{Fe}_{1.08}\text{S}_4$	Forward on	699	4.9×10^{-5}
	Forward off	795	4.3×10^{-5}
	Reverse on	778	4.4×10^{-5}
	Reverse off	752	4.6×10^{-5}
	Average	756	4.5×10^{-5}
$\text{Cu}_{4.67}\text{Fe}_{1.08}\text{S}_4$	Forward on	3733	9.16×10^{-6}
	Forward off	3649	9.37×10^{-6}
	Reverse on	4780	7.1×10^{-6}
	Reverse off	3649	9.4×10^{-6}
	Average	3953	8.8×10^{-6}

than the random E.M.F.s observed. It was not possible therefore to determine the magnitude of the cross-coefficients linking electronic and ionic transport as shown in equation D6. However, as the electronic probe voltages are always much smaller than the corresponding ionic probe voltages, these cross-coefficients must also be small or negligible.

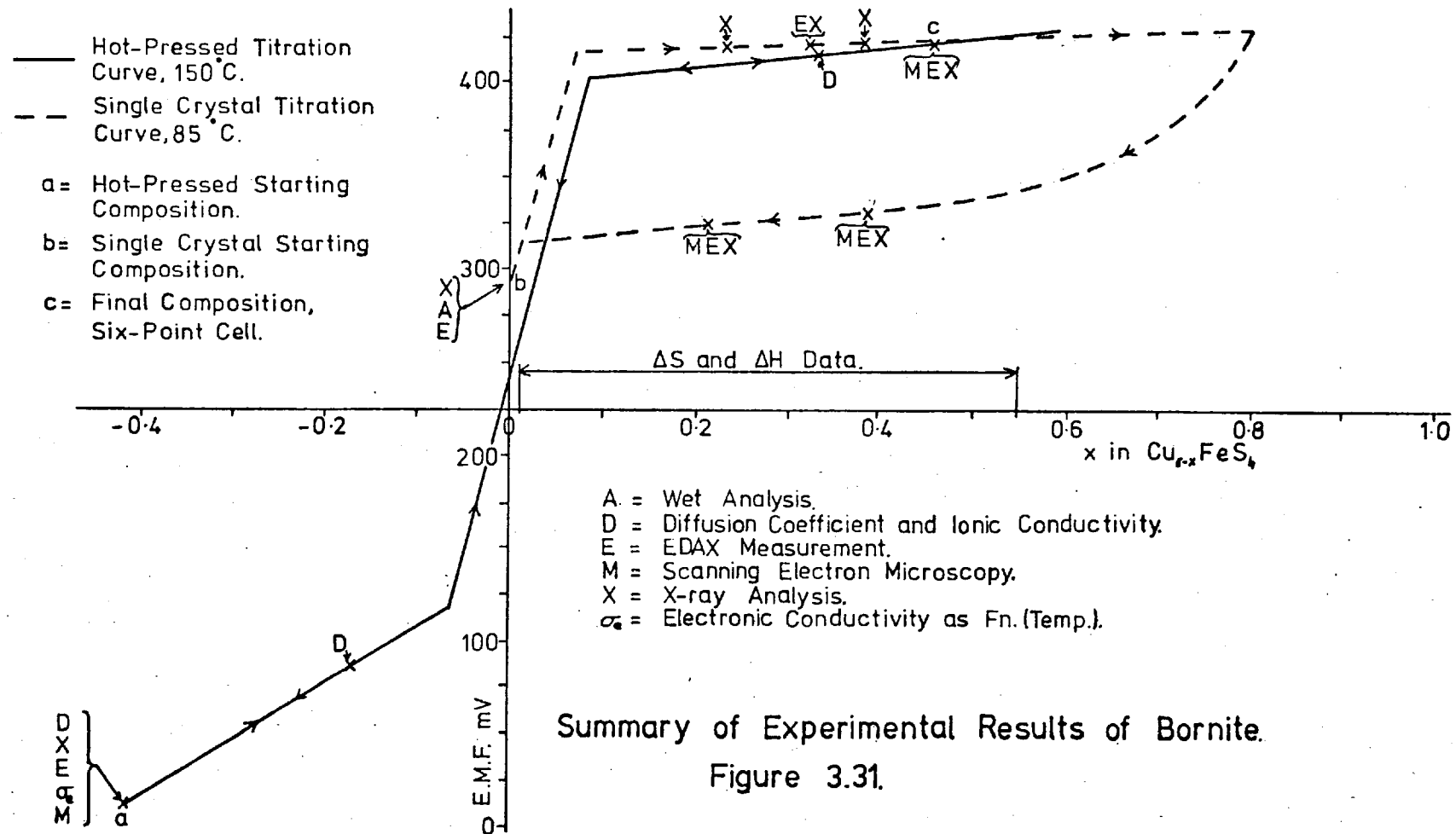
3.7. SUMMARY AND CONCLUSIONS

The preparation of single crystal Bornite from its elements was successful and the product obtained was similar to those prepared by other workers. Although the polycrystalline specimens produced by hot-pressing Bornite powder were all sulphur-poor it was still possible to use them to obtain useful data.

The results from the aqueous electrolyte coulometric titration experiments indicate that there are one or more side reactions occurring during the insertion or removal of copper. These side reactions prevent the cells being reversibly cycled and may be a contributory factor to the disintegration of the single crystal Bornite electrode which occurred if it was attempted to remove copper to give a composition below $\text{Cu}_{3.7}\text{FeS}_4$.

The results obtained using solid-state coulometric titration and six-point cells are summarized in figure 3.31. This figure also indicates the compositions at which microstructural investigations, analyses and diffusion and conductivity measurements were carried out.

Although it was possible to cycle the solid-state coulometric titration cells containing single crystal Bornite the cell E.M.F.s show a hysteresis of approximately 60 mV.



On removing copper from Cu_5FeS_4 , initially the cell E.M.F. increases sharply to approximately 400 mV but subsequent copper removal produces only small changes in the cell E.M.F. At no composition does the slope of the titration curve fall to zero, which would indicate a two-phase region. The microstructural evidence is conflicting with indications of phase separation for some specimens in this composition range although other samples in this range appear to be homogeneous. However, X-ray analysis indicates that Bornite and chalcopyrite are present in all samples in this composition range.

Thus it seems probable that there is long-range ordering of the copper and iron ions among the available sites which produces regions in the material with the Bornite and chalcopyrite structures. The apparently homogeneous microstructure of some samples may be due to the small size of these regions which may be below the resolution of the scanning electron microscope.

The hot-pressed Bornite behaved in a similar manner to the single crystal material if the initial excess of copper due to sulphur loss was taken into account. However for cells with hot-pressed Bornite electrodes the hysteresis in the cell E.M.F. is only approximately 20 mV.

The six-point experiment carried out on a sample of hot-pressed Bornite gave a value for the chemical diffusion coefficient of copper of approximately $10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ at 170°C . However the transients produced by this cell did not follow the theoretical curve predicted by the thermodynamic model. In particular there was no threshold time between the current being switched on or off and the change in the voltage across the probes. Thus it appears that information reaches the

probes faster than is possible by the diffusion of ions and this cannot be predicted using the present thermodynamic model.

The properties of Bornite can now be discussed in the light of the requirements for an S.S.E. (see section 1.5.).

1. Bornite is a good electronic conductor with a conductivity typically $10^{-1} \Omega^{-1} \text{cm}^{-1}$ (57).

2. Bornite has only a limited range of composition as only two out of the five copper ions per formula unit can be removed.

3. There is a relatively large composition range over which the cell E.M.F. is almost constant.

4. The chemical diffusion coefficient of copper for compositions in the region of almost constant cell E.M.F. is high, i.e. approximately $10^{-5} \text{cm}^2 \text{sec}^{-1}$ at 170°C .

5. Using in-situ hot-pressed electrolyte-electrode interface it is possible to obtain interfacial current densities up to 2mA cm^{-2} , although simple pressed contact interfaces only allow current densities in the region of $200 \mu\text{A cm}^{-2}$.

6. There is no information at present on the stability of the electrolyte-electrode interface.

7. Single crystal and hot-pressed Bornite are fairly cheap and easy to fabricate in comparison with some other possible S.S.E. materials.

Although the above summary is promising there are two main disadvantages to the use of Bornite as an S.S.E.

1. Cells constructed using Bornite electrodes would have low theoretical energy densities as for Bornite alone the value is only about $10 \text{ watt hr kg}^{-1}$.

2. Bornite S.S.E.s would have a low efficiency due to the cell E.M.F. hysteresis shown on cycling.

Thus it seems that Bornite is an unlikely candidate for a commercial S.S.E. but it does have an interesting property in that the chemical diffusion coefficient for copper is high in a region of almost constant voltage on change of composition. According to the relationship between the self and chemical diffusion coefficients:

$$\tilde{D}_i = D_i^* \frac{d \ln a_i}{d \ln c_i}$$

this suggests that the self diffusion coefficient for copper is extremely high in this composition range.

CHAPTER 4

COPPER SULPHIDE

4.1. INTRODUCTION

Whilst carrying out the work on Bornite, a system for which there is no coulometric titration or diffusion data, it was decided to work on a system for which there was such data. The chosen substance was copper sulphide as this is related to Bornite. At sufficiently high temperatures ($> 330^{\circ}\text{C}$ (57)) it actually forms a solid solution with Bornite. It is similar to Bornite also in the fact that its structure is based on an f.c.c. sulphur sublattice.

4.2. PREPARATION

The required starting material was chalcocite (Cu_2S) and this was prepared from its elements in a similar silica tube to that used for Bornite (see fig. 3.5). The heating schedule was also similar to that detailed for Bornite in section 3.3., although the tube was only kept at temperature for a week.

On removal from the furnace the tube was found to contain a rod-shaped mass made up of very small crystals, none larger than 1 mm in any direction, and which were dark blue in colour. This mass was removed from the tube and ground to form a fine powder for hot-pressing and X-ray diffraction. Before hot-pressing the Cu_2S was cold-pressed in an 8 mm hardened steel split die at $7 \times 10^8 \text{ Nm}^{-2}$. Pellets

produced by this method had a black shiny appearance and held together well.

Hot-pressing was carried out under vacuum in an 8 mm graphite die, at 950°C for 2 hours, with an applied pressure of $3 \times 10^7 \text{ Nm}^{-2}$. After pressing, the pellets were machined on a high speed diamond saw under oil. The surfaces thus produced were used unpolished in the solid state cell.

4.3. CHARACTERIZATION

This was mainly carried out by X-ray diffraction. The reacted material and hot-pressed materials were analysed and the results (fig. 4.1, table 4.1) were compared with the ASTM index (71). They were found to be in excellent agreement with that for ortho-chalcocite (Cu_2S). Sample density was only 96% of theoretical, so this would have possibly meant an ill-defined surface if any aqueous work had been carried out. The hot-pressed material was also analysed by CSIRO and they gave the analysis as $\text{Cu}_{1.99}\text{S}$. The hot-pressed material was also found to be homogeneous to the resolution of the scanning electron microscope.

4.4. COULOMETRIC TITRATION CELL

A solid-state cell was set up as shown in figure 4.2. The electrolyte was that detailed in chapter 2. The method of carrying out the coulometric titration is detailed in chapter 3.

Results obtained at $106^\circ\text{C} \pm 3$ are presented in figure 4.3 and table 4.2. From the initial curve for E.M.F. v composition it appears that hexagonal chalcocite is a single phase from Cu_2S to $\text{Cu}_{1.994}\text{S}$. After this point the

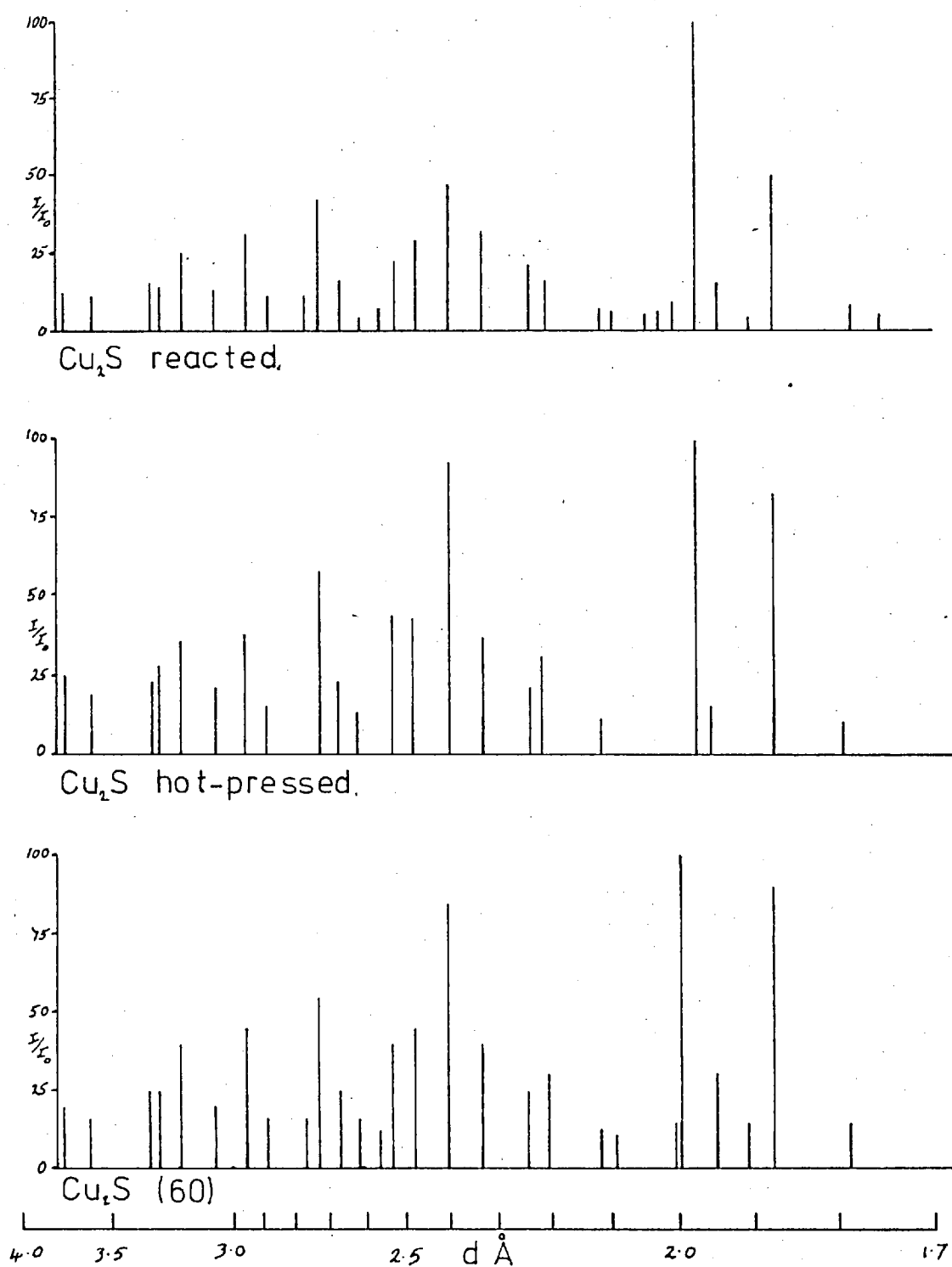
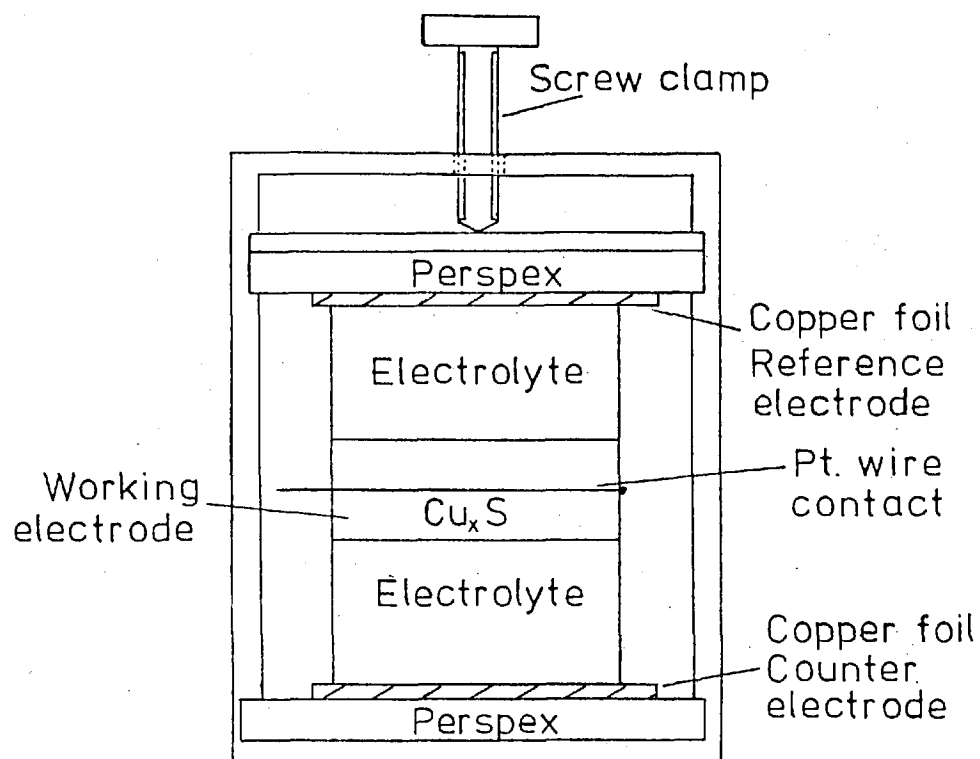


Figure 4.1
X-ray Diffraction Intensities.



Cu_2S Solid State Cell.

Figure 4.2

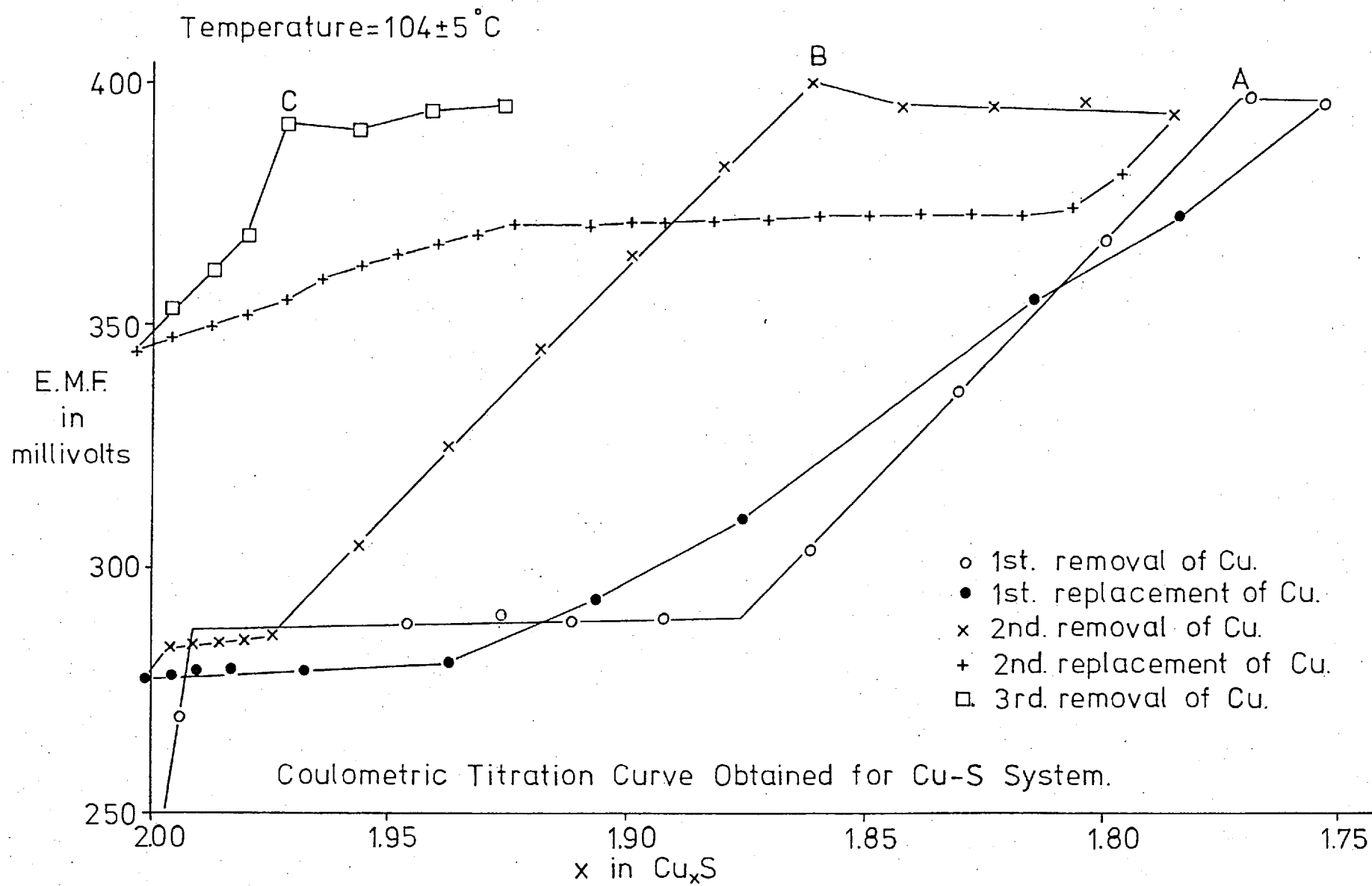


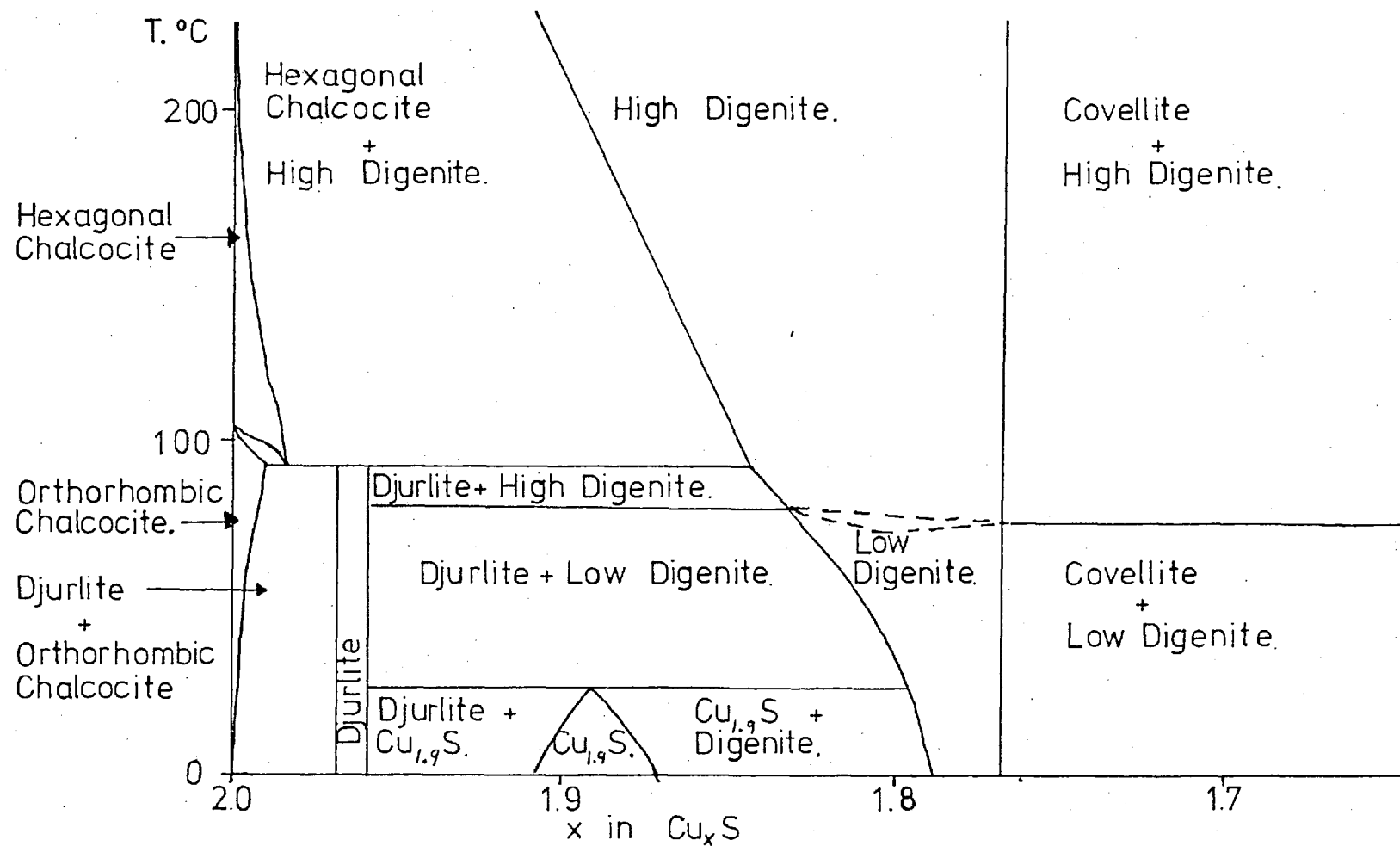
Figure 4.3

curve is flat, characteristic of a two phase region. Roseboom's (72) phase diagram (fig. 4.4) shows that high digenite and hexagonal chalcocite at 104°C are in equilibrium. This flat region extends to $\text{Cu}_{1.874}\text{S}$ from which point the voltage increases again as for a single phase. This region is presumably that of high digenite, and extends to $\text{Cu}_{1.770}\text{S}$. Here again the curve becomes flat for the two phase region of covellite and high digenite. This section of the curve should be compared with figure 4.5 which is the titration curve of Mathieu and Rickert (73). It should be noted that the electrolyte Mathieu and Rickert used was aqueous copper sulphate so all their voltages should be doubled for comparison. This effect is due to the relationship between the cell E.M.F. and the free energy for the cell reaction, i.e.

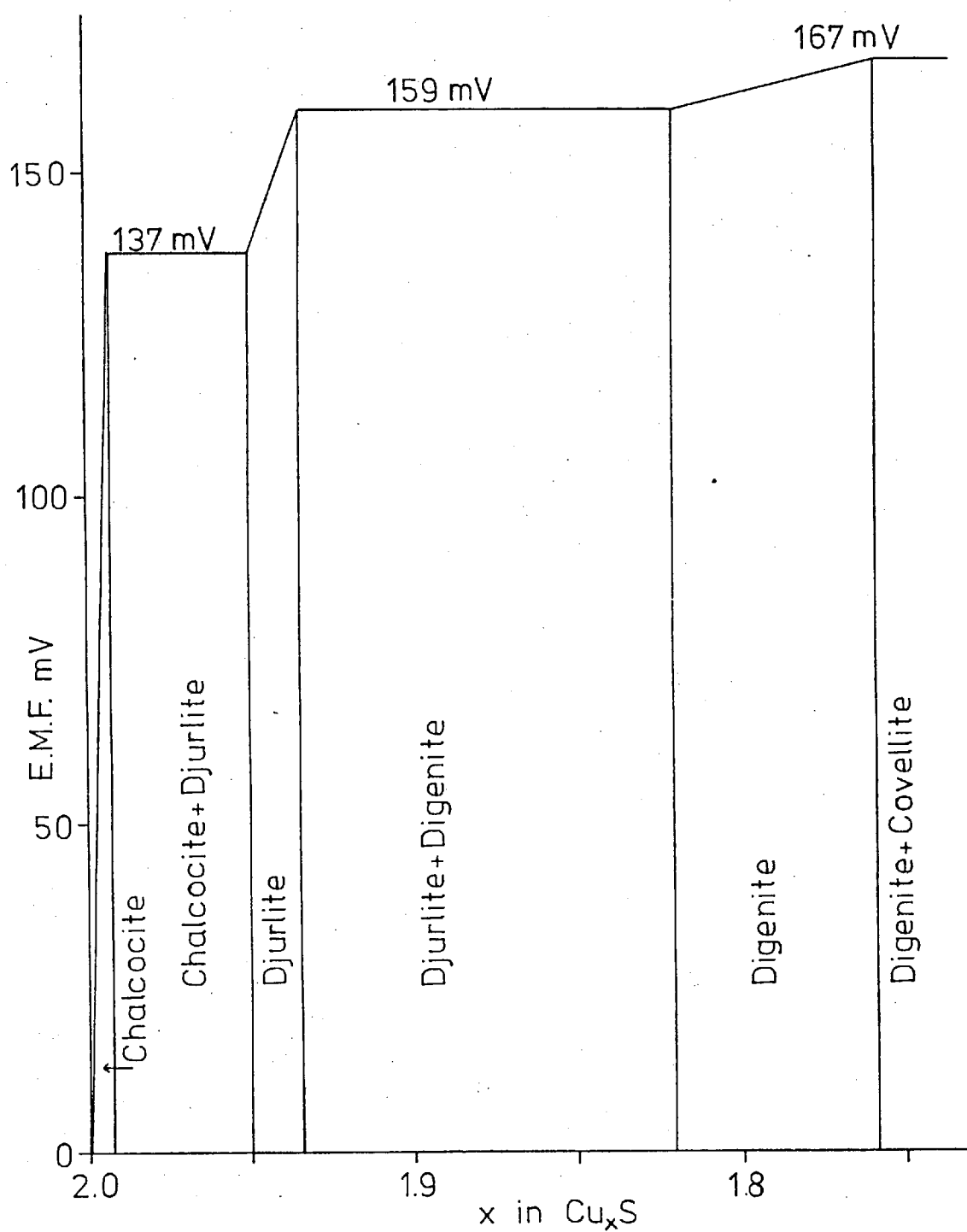
$$\Delta G = -nFE$$

The solid state electrolyte used in this investigation transports copper as Cu^+ so that $n = 1$ for this case. But aqueous copper sulphate transports Cu^{2+} ions so that $n = 2$. Thus, for the same cell reaction, the cell E.M.F. obtained using the solid state electrolyte is twice that found using aqueous copper sulphate as the electrolyte.

Replacing the copper in the structure caused the cell E.M.F. to fall as for a single phase region to a composition of $\text{Cu}_{1.938}\text{S}$. At this point the E.M.F. became constant and had a value close to that obtained for a mixture of high digenite and hexagonal chalcocite. This constant E.M.F. extended to $\text{Cu}_{1.00}\text{S}$, so that the single phase region of hexagonal chalcocite was never entered. On reversing the current the E.M.F. was constant to $\text{Cu}_{1.975}\text{S}$, and then again



Cu-S Phase Diagram, after (72),
Figure 4.4.



Coulometric Titration Curve for Cu-S System, 90°C ;
According to Mathieu and Rickert, (73).

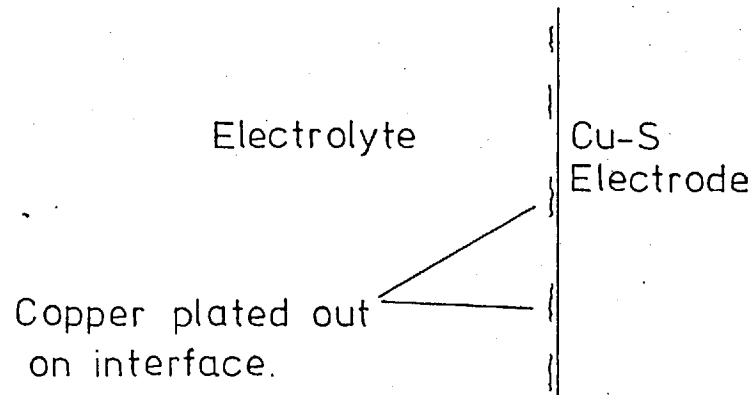
Figure 4.5

it showed single phase behaviour, with the same gradient as the high digenite region. The end of this gradient was at $\text{Cu}_{1.86}\text{S}$, from where the voltage was constant and the same as for the high digenite-covellite region. On replacing the copper again the voltage did not return to the original curve.

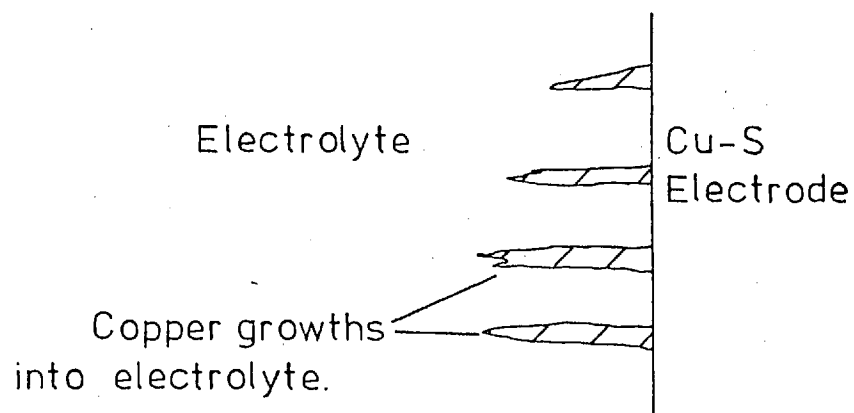
In order to investigate what had been happening in the cell the electrode was removed and then examined in the scanning electron microscope and by X-ray analysis. The microscope revealed the presence of two phases which is what would be expected from the calculated composition of the sample. However the EDAX attachment showed a copper ratio between the major and minor phases of 1.63:1 which is not what is expected. X-ray diffraction also indicated two phases but not Cu_2S and $\text{Cu}_{1.8}\text{S}$ as was expected. In fact X-ray analysis gave the phases as $\text{Cu}_{1.8}\text{S}$ and CuS (table 4.3).

It appears that the replacement of copper in the sulphide is a very slow step. Therefore, if too large a current is applied, copper is plated out on the working electrode (fig. 46a). This probably occurred here as the cell voltage during the replacement of copper became negative with respect to pure copper.

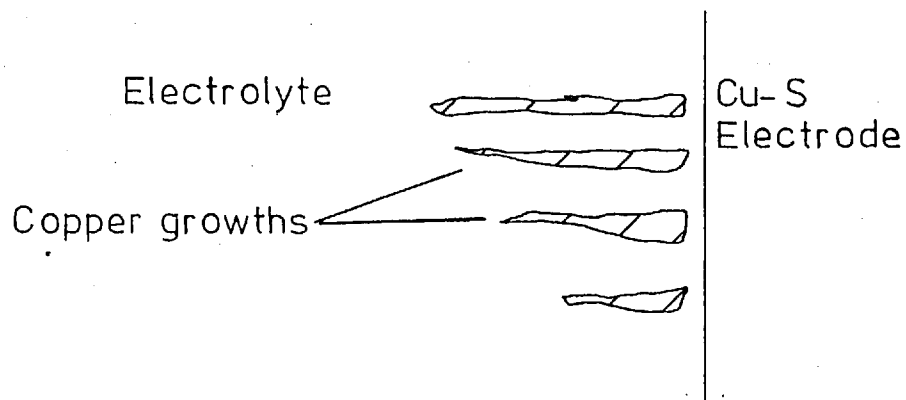
The copper is in fact probably plated out in the form of fibrous growths (fig. 46b), as are seen in chapter 2. As there is no room for expansion in this cell the growths of copper will probably go into the electrolyte. When subsequently the copper diffuses away from the electrode-electrolyte interface, the copper growths will be left isolated in the electrolyte (fig. 46c). Thus the composition change of the electrode is not as great as was calculated.



a) Plating out of Copper from Electrolyte.



b) Fibrous Growths into Electrolyte.



c) Copper Diffused from Interface leaving Copper in the Bulk of the Electrolyte.

Loss of Copper in Electrolyte.

Figure 4.6

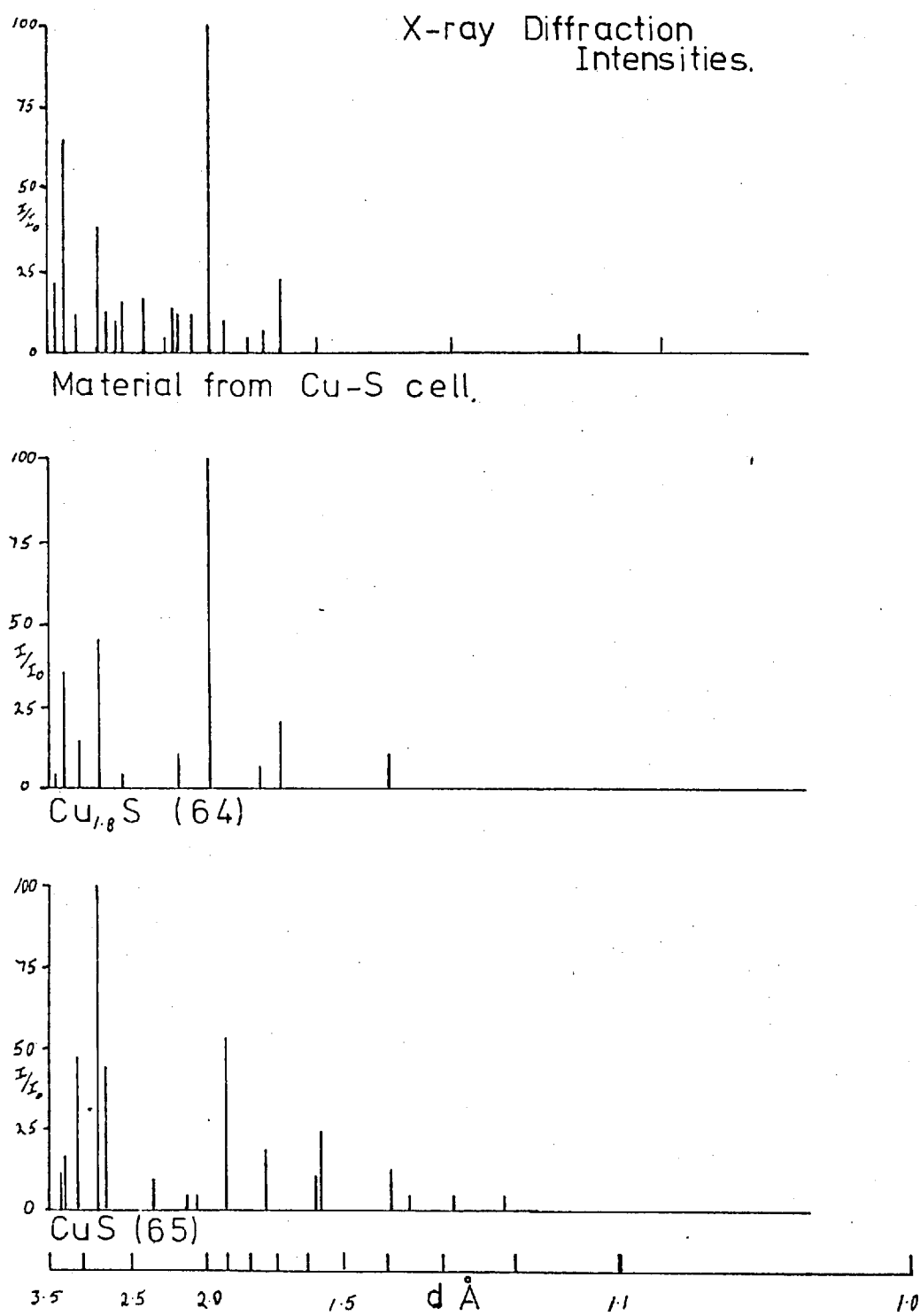


Figure 4.7

When the copper is removed again from the electrode these copper growths will probably have no effect. Unfortunately the electrolyte from this cell was not analysed so that this theory cannot be proved definitely. However this experiment has been repeated using low pumping currents and the results show only a small hysteresis in the cell E.M.F., approximately 20 mV. Therefore figure 4.3 should probably show the three points a, b and c superimposed on one another, thus giving a final composition of $\text{Cu}_{1.74}\text{S}$. This then means that there is a hysteresis of about 20 mV for the upper plateau and 10 mV for the lower plateau. Thus if the above is true it appears that the copper sulphide exhibits less hysteresis than Bornite.

ΔS values were obtained for certain compositions of copper sulphide and these are shown in table 4.4. These values are about twice the value that Etienne and Peters (74) obtained of $21 \pm 10 \text{ J mole}^{-1} \text{ }^\circ\text{K}^{-1}$ (see also ref. 73) for $\text{Cu}_{1.765}\text{S}$. It should of course be noted that ΔS obtained here is for a two phase region.

Composition	$\Delta S \text{ J }^\circ\text{K}^{-1} \text{ Mole}^{-1}$	Temp. Range
$\text{Cu}_{1.73}\text{S}$	47 ± 10	104°C to 50°C
$\text{Cu}_{1.72}\text{S}$	39 ± 10	104°C to 28°C
$\text{Cu}_{1.71}\text{S}$	47 ± 10	109°C to 48°C
$\text{Cu}_{1.69}\text{S}$	40 ± 10	101°C to 36°C

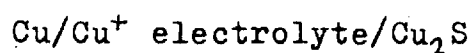
Table 4.4

ΔS for the Cu-S System at Certain Compositions

4.5. SUMMARY AND CONCLUSIONS

Chalcocite has been produced from its elements by direct reaction. Production of samples from this for a coulometric titration cell was by hot-pressing.

It appears that the replacement of copper in depleted copper sulphide is kinetically very slow so that there is a strong tendency for copper to be plated out at the electrode-electrolyte interface. This effect causes a cell of the type:



to behave irreversibly unless very low current densities are applied during the injection of copper into the copper sulphide.

Although it appears that the true coulometric titration curve for copper sulphide exhibits a maximum hysteresis of approximately 20 mV, copper sulphide is not a candidate for an S.S.E. This is due to the slow kinetics, the limited composition ranges of the single phase regions and the very low energy density of this material, i.e. approximately $5 \times 10^{-2} \text{ kW.hrs.kg}^{-1}$.

CHAPTER 5

FINAL CONCLUSIONS

5.1. COPPER ELECTROLYTE

1. A double salt prepared from copper (1) bromide and dimethyl 1,4-diazabicyclo (2,2,2) octane dibromide will act as a satisfactory solid electrolyte for Cu^+ ions. At 141°C the electronic conductivity is typically only 10^{-11} (ohm cm^{-1}) while the ionic conductivity is $>10^{-2}$ (ohm cm^{-1}).

2. The double salt prepared in this investigation does not have the same structure as that produced by the same method by Taylor (37). Although the reasons for this are unclear at present, the product produced here has proved to behave satisfactorily in practice.

5.2. BORNITE

1. Single crystal Bornite can easily be prepared from its elements and polycrystalline hot-pressed Bornite can also be obtained although there is sulphur-loss during hot-pressing.

2. Bornite electrodes in aqueous electrolytes appear to undergo one or more side reactions which cause such cells to be irreversible on cycling and which may contribute to the disintegration of single crystal electrodes at copper contents of less than $\text{Cu}_{3.7}\text{FeS}$.

3. There appears to be micro-phase separation in materials with copper contents less than approximately

$\text{Cu}_{4.25}\text{FeS}_4$ (at 85°C). This phase separation is possibly due to the long-range ordering of copper and iron ions among the available sites in the f.c.c. sulphur sublattice.

4. The chemical diffusion coefficient of copper in Bornite is approximately $10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ at 170°C . As this value of the diffusion coefficient is obtained from Bornite compositions within the micro-phase separation region this relatively high value suggests that the self diffusion coefficient of copper in Bornite is extremely high.

5.3. COPPER SULPHIDE

1. Although the removal of copper from a copper sulphide electrode in a solid-state cell is rapid (at approximately 100°C), the replacement of copper in depleted copper sulphide is kinetically very slow.

5.4. SUGGESTIONS FOR FURTHER WORK

Although the results obtained in this project indicate that Bornite would not be a candidate for a commercial S.S.E. material, they do show some interesting features.

More work is required to investigate the nature of the micro-scale phase separation region found here in samples of copper-deficient Bornite. Such an investigation may also reveal the reason for the high value of the chemical diffusion coefficient of copper found for compositions within this region. The use of an electron microscope fitted with a TEMSCAN facility may be of use in this work as such an instrument has a much improved resolution over the S.E.M. used in the present study.

The electrode-electrolyte interface is also an area requiring extensive research. The importance of the structure

of this interface and its influence upon the kinetics of the interfacial reactions has been demonstrated in this study by the results presented on the copper sulphide electrode cells.

In general, the further study of three-dimensional network materials for use as S.S.E.'s is essential if a commercial fully solid-state battery system is to be developed. If a relatively simple system, such as Bornite, could be more fully understood, this could lead to a better understanding of the factors controlling the properties of these materials. This in turn may aid the design of new materials for S.S.E.'s and so lead to a new solid-state battery system.

Table 2.1
CuBr X-Ray Results

This Work		Swanson et al (39)		
d Å	I/I ₀	d Å	I/I ₀	h k l
3.290	100	3.29	100	111
3.048	<1	-	-	-
2.844	<1	2.846	4	200
2.012	20	2.012	60	220
1.716	10	1.716	35	311
1.643	1	1.643	2	222
1.423	1	1.423	8	400
1.421	1	-	-	-
1.307	3	1.306	10	331
1.272	<1	1.272	2	420
1.162	3	1.161	10	422
1.096	2	1.095	6	511
1.093	1	-	-	-
1.007	<1	1.005	4	440
0.962	<1	0.961	4	531
0.949	<1	0.948	2	600
0.891	<1	0.899	4	620
0.868	<1	0.867	2	533

Table 2.3
X-Ray Diffraction Results $(\text{CH}_3)_2\text{C}_6\text{H}_3\text{N}_2\text{Br}_2$

Protected from Atmosphere		5 Days in Air	
d Å	I/I ₀	d Å	I/I ₀
4.57	10	4.60	6
4.34	13	4.45	4
4.16	100	4.25	100
		4.17	12
3.94	6	4.06	6
3.90	4	4.00	30
3.85	16	3.81	10
3.77	10	3.65	19
3.61	21	3.60	35
3.55	3	3.52	4
3.45	2	3.41	3
3.39	4		
3.30	6	3.29	2
		3.25	2
3.15	1	3.17	26
3.09	6	3.10	5
3.02	2	3.07	1
2.97	16	2.99	9
2.92	4	2.90	12
2.76	2	2.88	5
		2.78	3
2.72	4	2.72	9
2.67	7	2.68	7
2.63	6	2.63	6
2.54	2	2.55	2
2.47	9	2.47	5
2.44	6	2.43	4
		2.42	5
2.33	4	2.34	5
2.30	4	2.31	6
		2.27	1
2.25	4	2.24	2
		2.21	4
2.19	4	2.19	4
2.13	3	2.13	4
		2.10	1
		2.02	3
		1.83	3

Table 2.4
X-Ray Diffraction Results $94\text{CuBr}/6(\text{CH}_3)_2\text{C}_6\text{H}_4\text{N}_2\text{Br}_2$

This Work		K.Taylor's Work (37)		CuBr (39)	
d Å	I/I ₀	d Å	I/I ₀	d Å	I/I ₀
-	-	17.8	20	-	-
9.176	12	-	-	-	-
8.355	2	-	-	-	-
8.088	4	-	-	-	-
7.979	4	-	-	-	-
7.635	3	-	-	-	-
7.260	<1	-	-	-	-
-	-	6.47	100	-	-
6.112	<1	-	-	-	-
-	-	5.94	10	-	-
5.832	1	-	-	-	-
5.157	3	-	-	-	-
-	-	4.89	50	-	-
4.696	1	-	-	-	-
4.648	1	-	-	-	-
4.600	2	-	-	-	-
4.496	1	-	-	-	-
4.275	1	-	-	-	-
4.247	1	-	-	-	-
4.077	1	-	-	-	-
3.983	3	-	-	-	-
3.754	2	-	-	-	-
3.708	2	-	-	-	-
3.590	3	-	-	-	-
3.524	1	-	-	-	-
3.434	1	-	-	-	-
3.395	2	-	-	-	-
3.348	1.5	-	-	-	-
-	-	3.32	25	-	-
3.288	100	-	-	3.290	100
3.184	2	-	-	-	-
3.118	5	-	-	-	-
3.063	9	-	-	-	-

This Work		K.Taylor's Work (37)		CuBr (39)	
d Å	I/I ₀	d Å	I/I ₀	d Å	I/I ₀
-	-	-	-	3.048	< 1
3.015	3	-	-	-	-
2.991	2	-	-	-	-
2.962	< 1	-	-	-	-
2.928	1	-	-	-	-
2.919	1	-	-	-	-
2.846	2	-	-	2.844	< 1
2.812	< 1	-	-	-	-
2.778	< 1	-	-	-	-
2.748	1	-	-	-	-
-	-	2.73	10	-	-
2.590	< 1	-	-	-	-
2.657	< 1	-	-	-	-
-	-	2.47	15	-	-
2.431	< 1	-	-	-	-
2.360	< 1	-	-	-	-
2.339	1	-	-	-	-
2.313	1	-	-	-	-
2.225	< 1	-	-	-	-
2.182	1	-	-	-	-
2.159	1	2.16	15	-	-
2.140	< 1	-	-	-	-
2.133	< 1	-	-	-	-
2.104	< 1	-	-	-	-
2.083	1	-	-	-	-
2.056	1	-	-	-	-
2.011	37	-	-	2.012	20
1.959	1	-	-	-	-
1.939	2	-	-	-	-
1.924	< 1	-	-	-	-
1.918	1	-	-	-	-
1.892	1	-	-	-	-
1.865	2	-	-	-	-
1.833	< 1	-	-	-	-
1.799	< 1	-	-	-	-

This Work		K.Taylor's Work (37)		CuBr (39)	
d Å	I/I ₀	d Å	I/I ₀	d Å	I/I ₀
1.770	<1	-	-	-	-
1.756	<1	-	-	-	-
1.717	17	-	-	1.716	10
1.675	1	-	-	-	-
1.643	1	-	-	1.643	1
1.423	2	-	-	1.423	1
1.421	2	-	-	1.421	1
1.306	4	-	-	1.307	3
1.273	<1	-	-	1.272	<1
1.162	3	-	-	1.162	3
1.096	1	-	-	1.096	2
-	-	-	-	1.093	1
1.006	<1	-	-	1.007	<1
0.963	<1	-	-	0.962	<1

Table 2.5
Admittance Data for Copper Electrolyte
with Non-Blocking Electrodes

Frequency in Hertz	$G \times 10^{-3}$ ($\Omega \text{ cm}$) ⁻¹	$\omega C \times 10^{-3}$ ($\Omega \text{ cm}$) ⁻¹
1×10^7	8.6	-3.84
8×10^6	8.7	-3.51
6×10^6	9.6	-3.94
4×10^6	10.5	-3.29
2×10^6	12.2	-2.18
1.3×10^6	12.2	-1.28
1×10^6	12.2	-0.99
8×10^5	12.2	-0.65
6×10^5	12.2	-0.17
4×10^5	12.2	0.33
2×10^5	12.2	0.88
1.3×10^5	11.3	1.25
1×10^5	11.3	1.43
4×10^4	10.5	2.19
2×10^4	8.7	3.55
1.2×10^4	7.5	3.36
1×10^4	7.1	3.43
8×10^3	6.5	3.44
6×10^3	5.7	3.44
4×10^3	4.65	3.31
2×10^3	3.15	2.80
1.2×10^3	2.29	2.31
1×10^3	2.05	2.15
8×10^2	1.78	1.94
6×10^2	1.48	1.67
4×10^2	1.15	1.36
2×10^2	0.74	0.92
1.2×10^2	0.56	0.72

Table 2.6
Impedance Data for Copper Electrolyte
with Non-Blocking Electrodes

Frequency in Hertz	$Z' \times 10^{-3}$ $\Omega \text{ cm}$	$Z'' \times 10^{-3}$ $\Omega \text{ cm}$
1×10^7	0.0974	-0.0437
8×10^6	0.0987	-0.0397
6×10^6	0.0892	-0.0367
4×10^6	0.0869	-0.0273
2×10^6	0.0794	-0.0142
1.3×10^6	0.0810	-0.0085
1×10^6	0.0814	-0.0065
8×10^5	0.0817	-0.0040
6×10^5	0.0817	-0.0011
4×10^5	0.0819	0.0022
2×10^5	0.0815	0.0058
1.3×10^5	0.0872	0.0096
1×10^5	0.0868	0.0110
4×10^4	0.0915	0.0192
2×10^4	0.0984	0.0400
1.2×10^4	0.1111	0.0498
1×10^4	0.1146	0.0556
8×10^3	0.1206	0.0643
6×10^3	0.1288	0.0776
4×10^3	0.1427	0.1017
2×10^3	0.1774	0.1578
1.2×10^3	0.2164	0.2180
1×10^3	0.2328	0.2437
8×10^2	0.2364	0.2571
6×10^2	0.2964	0.3349
4×10^2	0.3625	0.4284
2×10^2	0.5280	0.6585
1.2×10^2	0.6692	0.8667

Table 2.7
Admittance Data for Copper Electrolyte
with Blocking Electrodes

Frequency in Hertz	Chromium Electrodes		Carbon Electrodes	
	$G \times 10^{-3}$ $(\Omega \text{ cm})^{-1}$	$\omega C \times 10^{-3}$ $(\Omega \text{ cm})^{-1}$	$G \times 10^{-3}$ $(\Omega \text{ cm})^{-1}$	$\omega C \times 10^{-3}$ $(\Omega \text{ cm})^{-1}$
10×10^6	1.85	0.691	1.76	2.45
8×10^6	1.56	0.503	1.55	1.82
6×10^6	1.35	0.339	1.40	1.30
4×10^6	1.22	0.226	1.31	0.85
2×10^6	1.08	0.233	1.25	0.49
1×10^6	0.95	0.226	1.12	0.289
8×10^5	0.94	0.226	1.15	0.256
4×10^5	0.82	0.246	1.11	0.200
2×10^5	0.72	0.250	1.06	0.169
1.3×10^5	0.63	0.253	-	-
1×10^5	0.58	0.292	0.98	0.179
6×10^4	0.50	0.249	1.00	0.188
4×10^4	0.49	0.219	0.945	0.174
1.2×10^4	0.264	0.200	-	-
1×10^4	0.243	0.193	0.702	0.243
8×10^3	0.220	0.182	0.663	0.255
6×10^3	0.186	0.168	0.607	0.264
4×10^3	0.149	0.149	0.533	0.280
2×10^3	0.097	0.112	0.390	0.270
1.2×10^3	0.072	0.087	0.292	0.245
1×10^3	0.064	0.079	0.260	0.233
8×10^2	0.055	0.069	0.223	0.215
6×10^2	0.044	0.061	0.183	0.189
4×10^2	0.033	0.046	0.139	0.154
2×10^2	0.022	0.027	0.092	0.101
1×10^2	0.016	0.015	0.067	0.063

Table 2.8
Impedance Data for Copper Electrolyte
with Blocking Electrodes

Frequency in Hertz	Chromium Electrodes		Carbon Electrodes	
	$Z' \times 10^{-3}$ $\Omega \text{ cm}$	$Z'' \times 10^{-3}$ $\Omega \text{ cm}$	$Z' \times 10^{-3}$ $\Omega \text{ cm}$	$Z'' \times 10^{-3}$ $\Omega \text{ cm}$
10×10^6	0.472	0.176	0.194	0.268
8×10^6	0.580	0.188	0.274	0.318
6×10^6	0.696	0.176	0.384	0.358
4×10^6	0.793	0.148	0.536	0.352
2×10^6	0.884	0.190	0.696	0.274
1×10^6	0.996	0.238	0.802	0.2006
8×10^5	1.006	0.242	0.826	0.1832
4×10^5	1.124	0.340	0.872	0.1572
2×10^5	1.246	0.436	0.920	0.1466
1.3×10^5	1.374	0.556	-	-
1×10^5	1.370	0.682	0.992	0.1826
6×10^4	1.602	0.798	0.966	0.1816
4×10^4	1.702	0.760	1.024	0.1880
1.2×10^4	2.396	1.782	-	-
1×10^4	2.528	2.004	1.266	0.448
8×10^3	2.698	2.232	1.314	0.506
6×10^3	2.960	2.674	1.386	0.602
4×10^3	3.368	3.368	1.470	0.772
2×10^3	4.420	5.102	1.734	1.200
1.2×10^3	5.646	6.824	2.010	1.686
1×10^3	6.240	7.652	2.138	1.910
8×10^2	7.002	8.848	2.324	2.240
6×10^2	7.860	10.808	2.636	2.730
4×10^2	10.146	14.296	3.242	3.580
2×10^2	17.742	22.178	4.926	5.408
1×10^2	32.160	31.156	7.928	7.456

Table 3.2
X-Ray Diffraction Data for Bornite

This Work		ASTMS Data (63)		
dÅ	I/I ₀	hkl	dÅ	I/I ₀
4.02	11	105,213	4.08	10
		214,006	3.64	5
		310,106	3.48	5
3.27	36	116,312	3.31	40
3.13	45	224	3.18	60
		107,321	3.01	5
2.78	34	305,323	2.80	20
2.71	92	008,400	2.74	50
		217,411	2.63	5
2.48	33	413,325	2.50	40
2.09	11	425,511	2.13	20
		336,11.10	2.11	5
1.92	100	440,408	1.937	100
1.84	7	21.11	1.850	10
1.66	8			
1.64	31	624,22.12	1.652	30
1.62	6			
1.57	10	448	1.584	10
1.53	6	712,11.14	1.534	10
1.47	7	705,723	1.474	5
1.42	14	31.14,53.10	1.427	20
1.34	17	800,00.16	1.370	20
		44.12,804	1.335(F)	5
			1.300(F)	5
		660,22.16	1.290(F)	5
1.26	6	62.12	1.258(F)	50
		40.18	1.225(F)	5
		884	1.198(F)	10
		64.12	1.169(F)	5
			1.145(F)	5
1.12	10	44.16,848	1.119	50
		80.12	1.097(F)	5
1.05	6	22.20,66.12	1.053	10
		64.16	1.018(F)	5
			0.9853(F)	10

(F) Lines reported by Frenzel (56) and not by Berry and Thompson (57).

Table 3.3
X-Ray Diffraction Data for Hot-Pressed Bornite

Copper Wrapped		Platinum Wrapped		Unwrapped	
dÅ	I/I ₀	dÅ	I/I ₀	dÅ	I/I ₀
3.751	10	-	-	-	-
-	-	3.743	9	-	-
-	-	-	-	3.720	19
-	-	-	-	3.300	6
3.258	40	3.252	34	3.252	46
3.118	61	3.118	51	3.118	90
2.919	27	2.919	20	2.919	22
2.820	15	2.820	36	2.816	21
2.736	46	2.732	58	-	-
-	-	-	-	2.712	60
-	-	2.669	14	2.665	6
-	-	2.486	7	-	-
-	-	-	-	2.466	37
2.293	46	2.291	41	2.291	39
2.257	11	2.255	14	2.252	4
-	-	-	-	2.244	6
-	-	2.223	10	-	-
-	-	2.079	6	2.076	19
1.992	31	1.992	27	1.988	15
1.913	100	1.913	100	1.913	100
1.883	7	-	-	1.879	7
-	-	-	-	1.799	4
1.763	6	1.763	7	1.759	6
1.701	12	-	-	1.700	12
-	-	1.671	11	-	-
1.630	12	1.633	8	1.633	14
-	-	-	-	1.607	5
1.559	5	1.550	5	1.558	6
1.399	7	1.401	7	1.405	7
-	-	1.356	5	1.356	3
1.352	5	-	-	1.352	3
-	-	-	-	1.349	3
-	-	1.322	3	-	-
1.325	4	-	-	-	-
1.258	4	-	-	-	-
1.237	3	-	-	-	-
1.105	8	1.105	7	1.108	10

Table 3.6
Aqueous Cells Coulometric Titration Data

X in $\text{Cu}_{5-x}\text{FeS}_4$	V cell 1 in mV	X in $\text{Cu}_{5-x}\text{FeS}_4$	V cell 2 in mV
0	116	0	50
0.194	218	0.280	217
0.388	217	0.492	221
0.582	216	0.702	219
0.776	218	0.912	223
0.970	222	1.124	230
1.110	224	1.274	225
0.916	215	1.064	218
0.722	210	0.854	209
0.528	201	0.642	196
0.334	194	0.432	180
0.140	184	0.222	157
0.284	200	0.432	185
0.478	211	0.654	198
0.672	219	0.874	203
0.866	225	1.096	214
0.672	217	0.874	198
0.478	210	0.654	179

Table 3.7
85°C Coulometric Titration Cell Data

X in $\text{Cu}_{5-x}\text{FeS}_4$	Cell EMF in mV	X in $\text{Cu}_{5-x}\text{FeS}_4$	Cell EMF in mV
0	287.6	0.684	422.3
0.027	358.8	0.711	421.4
0.031	364.9	0.738	421.4
0.072	419.4	0.764	421.3
0.098	416.5	0.738	383.9
0.125	417.3	0.711	373.2
0.152	420.2	0.684	364.7
0.178	419.3	0.658	359.9
0.205	418.7	0.631	358.2
0.232	419.9	0.605	357.0
0.258	419.7	0.578	354.5
0.285	219.9	0.551	352.4
0.311	419.8	0.525	349.9
0.338	419.9	0.498	345.0
0.365	420.6	0.471	341.0
0.391	420.8	0.445	335.7
0.418	421.6	0.418	331.6
0.445	421.7	0.391	328.8
0.471	422.2	0.365	327.6
0.498	422.1	0.339	321.5
0.525	422.7	0.312	321.6
0.551	422.7	0.286	322.2
0.578	422.9	0.259	320.9
0.605	422.8	0.206	315.9
0.631	423.1	0.179	314.0
0.658	420.6	0.153	312.4

X in $\text{Cu}_{5-x}\text{FeS}_4$	Cell EMF in mV	X in $\text{Cu}_{5-x}\text{FeS}_4$	Cell EMF in mV
0.126	313.6	0.321	414.3
0.045	309.6	0.348	416.8
0.019	307.5	0.372	418.9
0.045	345.9	0.393	417.1
0.072	368.1	0.416	417.1
0.099	383.2	0.443	417.4
0.125	390.9	0.453	416.9
0.152	394.5	0.457	415.6
0.179	400.9	0.461	417.3
0.205	403.3	0.467	413.0
0.232	407.2	0.468	406.9
0.258	410.7	0.474	413.9
0.271	409.3	0.480	416.4
0.283	410.6	0.486	416.2
0.292	411.3	0.492	416.4

Table 3.8
146°C Coulometric Titration Cell Data

X in $\text{Cu}_{5-x}\text{FeS}_4$	Cell EMF in mV	X in $\text{Cu}_{5-x}\text{FeS}_4$	Cell EMF in mV
0.570	412.5	0.003	226.8
0.694	420.2	0.082	358.0
0.894	426.7	0.160	398.5
0.975	426.9	0.239	400.8
1.002	422.2	0.318	401.4
1.047	425.6	0.396	407.9
1.089	425.6	0.475	418.5
1.131	425.8	0.554	417.0
1.172	425.8	0.632	417.6
1.210	426.2	0.711	421.8
1.232	426.3	0.789	425.5
1.253	426.4	0.868	427.3
1.295	426.3	0.946	430.3
1.316	425.5	1.024	428.5
1.338	413.7	1.060	427.8
1.316	404.1	1.115	427.4
1.235	388.1	1.152	427.6
1.148	378.0	1.070	396.0
1.006	373.0	0.988	392.2
0.823	371.5	0.907	392.3
0.640	369.6	0.825	392.0
0.457	365.3	0.743	391.8
0.337	357.0	0.662	391.3
0.264	367.8	0.580	389.9
0.161	334.4	0.498	386.7
0.082	309.2	0.417	376.3

Table 3.9
100°C Coulometric Titration Cell Data

X in $\text{Cu}_{5-x}\text{FeS}_4$	Cell EMF in mV	X in $\text{Cu}_{5-x}\text{FeS}_4$	Cell EMF in mV
0.018	364.3	0.188	411.2
0.023	397.7	0.194	411.3
0.029	412.4	0.199	411.5
0.035	415.8	0.210	411.6
0.041	415.1	0.215	411.8
0.047	413.9	0.221	411.8
0.059	413.8	0.226	411.8
0.070	414.4	0.232	411.8
0.084	412.1	0.237	411.8
0.091	412.2	0.242	411.8
0.098	412.2	0.248	411.8
0.104	412.0	0.253	411.8
0.109	411.9	0.259	411.8
0.115	411.8	0.264	411.9
0.121	412.0	0.269	411.9
0.126	411.7	0.275	412.0
0.132	411.0	0.280	412.1
0.137	410.8	0.286	413.0
0.142	410.8	0.291	413.0
0.151	410.8	0.296	413.0
0.156	410.8	0.302	413.1
0.161	410.8	0.307	413.2
0.167	410.9	0.313	413.2
0.172	411.0	0.318	412.7
0.178	411.1	0.323	412.5
0.183	411.1	0.329	412.6

X in $\text{Cu}_{5-x}\text{FeS}_4$	Cell EMF in mV	X in $\text{Cu}_{5-x}\text{FeS}_4$	Cell EMF in mV
0.334	412.6	0.361	412.4
0.340	412.7	0.367	412.3
0.345	412.7	0.372	412.4
0.350	412.6	0.378	413.8
0.356	412.6		

Table 3.12
Coulometric Titration X-Ray Samples

Bornite (63)		Chalcopyrite (70)		1		2		3		4		100°C Cell	
hkl	I/I _o	hkl	I/I _o	dÅ	I/I _o	dÅ	I/I _o	dÅ	I/I _o	dÅ	I/I _o	dÅ	I/I _o
105,213	10	-		-		4.04	9	-		4.06	6	4.05	7
116,312	40	-		3.27	14	3.29	32	3.29	34	3.29	30	3.28	38
224	60	-		3.14	23	3.15	54	3.14	57	3.15	53	3.15	52
-		112	100	3.02	100	3.03	89	3.02	100	3.02	38	3.03	28
305,323	20	-		-		2.79	21	-		2.79	13	2.79	19
008,400	50	-		2.73	20	2.73	33	2.73	40	2.73	43	2.72	40
217,411	5	200	7	-		-		-		-		2.61	5
413,325	40	-		2.49	11	2.50	26	2.49	22	2.50	22	2.50	26
-		-		-		-		-		-		2.17	3
336,11.10	5	-		-		-		-		-		2.10	8
-		-		1.94	16	1.96	23	-		-		-	
440,408	100	-		1.92	62	1.93	100	1.93	92	1.93	100	1.93	100
-		204	32	1.85	28	1.85	24	1.87	18	1.85	11	1.85	10
-		-		-		-		-		-		1.67	4
624,22.12	30	-		-		1.65	7	-		1.65	8	1.65	11
-		312	20	-		1.59	10	-		-		1.59	4

Table 3.14Hot-Pressed Coulometric Titration Cell (150°C)

No. of Coulombs of Copper Removed	Cell EMF in mV	X in $\text{Cu}_{1-x}\text{FeS}_2$
0	11.10	-0.412
8.36	43.80	-0.309
29.18	141.4	-0.051
43.13	408.0	0.122
61.49	414.5	0.349
70.58	423.8	0.461
75.56	429.4	0.523
68.59	404.1	0.437
30.49	138.9	-0.035
28.18	132.3	-0.063
27.68	130.0	-0.069
39.08	404.3	0.071
63.17	414.6	0.370
77.27	430.8	0.544

Mass of sample 0.372 gm

Table 3.15
X-Ray Results on Six-Point Cell Specimen

Six-Point Cell Sample		Bornite (63)		Chalcopyrite (70)	
d Å	I/I ₀	hkl	I/I ₀	hkl	I/I ₀
3.28	15	116,312	40		
3.17	26				
3.14	26	224	60		
3.02	100			112	100
2.76	33	008,400	50		
2.72	11				
2.49	12	413,325	40		
2.16	4				
2.16	4	425,511	20		
1.95	57	440,408	100		
1.93	44				
1.89	11			220	16
1.85	26			204	32
1.67	7	{ 22.12 264 624 }			
1.66	7		30		
1.65	7				
1.59	8	448	10	312	20
1.57	7				

Table 3.16
 ΔH and ΔS for Bornite

X in $\text{Cu}_{5-x}\text{FeS}_4$	$-\Delta H$ kcal mole^{-1}	$\pm$ Error kcal mole^{-1}	ΔS $\text{cal deg}^{-1} \text{mole}^{-1}$	$\pm$ Error $\text{cal deg}^{-1} \text{mole}^{-1}$
0.019	13	± 3	47	± 6
0.045	22	± 2	31	± 4
0.072	28	± 2	21	± 3
0.099	33	± 1	12	± 1
0.125	32	± 2	16	± 2
0.152	31	± 2	20	± 2
0.179	31	± 2	22	± 3
0.195	31	± 2	23	± 4
0.201	31	± 2	23	± 4
0.205	30	± 2	24	± 2
0.206	31	± 2	21	± 3
0.232	28	± 2	32	± 3
0.259	28	± 2	34	± 4
0.271	28	± 2	33	± 4
0.283	28	± 3	32	± 7
0.292	28	± 2	32	± 4
0.321	29	± 2	32	± 4
0.348	30	± 2	29	± 4
0.372	28	± 3	35	± 6
0.378	29	± 2	30	± 3
0.382	31	± 2	26	± 3
0.468	30	± 3	26	± 6
0.543	29	± 3	34	± 5
0.543	25	± 3	43	± 6
0.564	31	± 2	28	± 4

Table 3.17
Electronic Conductivity by the Van der Pauw Method

$\text{Log}_{10} \left(\frac{1}{\rho} \right) ((\Omega \text{m})^{-1})$	$\frac{1000}{\text{Absolute Temp.}} ^\circ\text{K}^{-1}$	$\text{Log}_{10} \left(\frac{1}{\rho} \right) ((\Omega \text{m})^{-1})$	$\frac{1000}{\text{Absolute Temp.}} ^\circ\text{K}^{-1}$
0.1172	2.653	-0.0627	2.762
0.1456	2.625	-0.0931	2.801
0.2491	2.500	-0.1273	2.833
0.3706	2.198	-0.1794	2.865
0.6123	2.012	-0.2539	2.890
0.6989	1.945	-0.2827	2.915
0.7488	1.898	-0.3091	2.941
0.8122	1.852	-0.3336	2.967
0.7992	1.838	-0.3573	2.985
0.7966	1.832	-0.3807	3.012
0.7951	1.821	-0.4034	3.030
0.8083	1.789	-0.4255	3.058
0.7958	1.757	-0.4684	3.086
0.7814	1.757	-0.4895	3.106
0.7355	1.757	-0.5099	3.115
0.6463	1.838	-0.5306	3.145
0.5564	1.965	-0.5504	3.155
0.4707	2.083	-0.5674	3.165
0.4078	2.174	-0.5855	3.175
0.3536	2.257	-0.6043	3.185
0.2911	2.326	-0.6232	3.195
0.2395	2.392	-0.6416	3.215
0.1953	2.457	-0.6596	3.226
0.1533	2.506	-0.6775	3.236
0.1114	2.558	-0.9406	3.364
0.0715	2.604	-0.6974	3.163
0.0347	2.646	-0.1997	2.777
-0.0326	2.732	-0.8841	2.512

$\text{Log}_{10}\left(\frac{1}{\rho}\right)((nm)^{-1})$	$\frac{1000}{\text{Absolute Temp.}}^{\circ K^{-1}}$	$\text{Log}_{10}\left(\frac{1}{\rho}\right)((nm)^{-1})$	$\frac{1000}{\text{Absolute Temp.}}^{\circ K^{-1}}$
0.2264	2.325	-0.2779	2.906
0.3302	2.192	-0.3149	2.942
0.4090	2.091	-0.3488	2.977
0.4765	2.016	-0.3811	3.007
0.5733	1.906	-0.4121	3.025
0.6127	1.863	-0.4422	3.064
0.6450	1.831	-0.4713	3.090
0.6749	1.798	-0.4998	3.110
0.6822	1.785	-0.5278	3.133
0.6906	1.787	-0.5555	3.156
0.6822	1.788	-0.5830	3.175
0.6746	1.786	-0.6103	3.195
0.6064	1.877	-0.6371	3.212
0.5077	2.011	-0.6642	3.225
0.4214	2.136	-0.5540	3.241
0.3423	2.241	-0.712	3.254
0.2712	2.336	-0.7346	3.267
0.2090	2.420	-0.7537	3.276
0.1507	2.496	-0.7770	3.286
0.0950	2.566	-0.7912	3.297
0.0434	2.627	-0.8086	3.303
-0.0029	2.685	-0.8248	3.311
-0.0447	2.737	-0.1260	2.832
-0.0840	2.784	-0.1889	2.871

Table 3.19
Transient Results for Six-Point Cell (170°C)

Time in Sec.	Current in μ A	Ionic Probes in mV	Electronic Probes in mV	Thermodynamic Fit For Ionic Probes in mV	Exponential Fit For Ionic Probes in mV
-3990	0	6.779	0.075	-	-
-2990	0	6.794	0.091	-	-
-1990	0	6.791	0.089	-	-
-990	0	6.774	0.075	-	-
10	16.2	6.829	0.116	6.73	6.832
190	16.2	7.666	-	7.13	7.752
290	16.2	8.120	-	7.57	8.170
390	16.2	8.508	-	8.00	8.531
490	16.2	8.842	-	8.38	8.845
590	16.2	9.128	-	8.72	9.117
690	16.2	9.373	-	9.00	9.352
790	16.2	9.583	-	9.25	9.563
890	16.2	9.764	-	9.47	9.734
990	16.2	9.919	-	9.66	9.887
1010	16.2	9.945	0.095	9.69	9.915
1190	16.2	10.165	-	9.96	10.135
1290	16.2	10.264	-	10.09	10.235
1390	16.2	10.348	-	10.19	10.321
1490	16.2	10.423	-	10.28	10.396
1590	16.2	10.485	-	10.36	10.461
1690	16.2	10.539	-	10.43	10.518
1790	16.2	10.586	-	10.49	10.567
1890	16.2	10.626	-	10.54	10.609
1990	16.2	10.661	-	10.59	10.646
2010	16.2	10.666	0.095	10.60	10.652
3010	16.2	10.823	0.095	10.81	10.829
4010	16.2	10.861	0.093	10.86	10.871
5010	16.2	10.867	0.094	10.88	10.881
6010	16.2	10.884	0.108	10.88	10.883
7010	16.2	10.884	0.108	-	-
8010	16.2	10.882	0.109	-	-
9010	16.2	10.885	0.111	-	-

Time in Sec.	Current in μ A	Ionic Probes in mV	Electronic Probes in mV	Thermodynamic Fit For Ionic Probes in mV	Exponential Fit For Ionic Probes in mV
10010	16.2	10.869	0.095	-	-
11010	16.2	10.869	0.101	-	-
16010	16.2	10.886	0.097	-	-
17010	16.2	10.891	0.098	-	-
18010	16.2	10.883	0.100	-	-
19010	16.2	10.869	0.088	-	-
20010	current off at 20000	10.848	0.081	10.84	10.832
20190	0	10.023	-	10.54	9.994
20290	0	9.577	-	10.16	9.604
20390	0	9.189	-	9.77	9.260
20490	0	8.855	-	9.41	8.957
20590	0	8.557	-	9.09	8.689
20690	0	8.308	-	8.81	8.454
20790	0	8.096	-	8.56	8.246
20890	0	7.910	-	8.34	8.062
20990	0	7.751	-	8.14	7.901
21010	0	7.717	0.068	8.11	7.871
21190	0	7.499	-	7.82	7.633
21290	0	7.395	-	7.69	7.522
21390	0	7.308	-	7.57	7.424
21490	0	7.228	-	7.46	7.338
21590	0	7.159	-	7.37	7.262
21690	0	7.118	-	7.29	7.195
21790	0	7.054	-	7.22	7.136
21890	0	7.014	-	7.16	7.084
21990	0	6.970	-	7.10	7.038
22010	0	6.957	0.063	7.09	7.029
23010	0	6.783	0.073	6.80	6.790
24010	0	6.743	0.078	6.72	6.722
25010	0	6.726	0.070	6.70	6.703
26010	0	6.721	0.075	-	-
27010	0	6.725	0.078	-	-
28010	0	6.706	0.063	-	-
29010	0	6.703	0.062	-	-

Time in Sec.	Current in μ A	Ionic Probes in mV	Electronic Probes in mV	Thermodynamic Fit For Ionic Probes in mV	Exponential Fit For Ionic Probes in mV
30010	0	6.699	0.062	-	-
31010	0	6.700	0.066	-	-
36010	0	6.708	0.087	-	-
37010	0	6.693	0.068	-	-
38010	0	6.691	0.072	-	-
39010	0	6.692	0.073	-	-
40010	current on 40000 16.8	6.690	0.096	6.63	6.638
40190	-16.8	5.905	-	6.31	5.784
40290	-16.8	5.472	-	5.91	5.388
40390	-16.8	5.093	-	5.53	5.039
40490	-16.8	4.765	-	5.17	4.733
40590	-16.8	4.481	-	4.84	4.464
40690	-16.8	4.234	-	4.56	4.227
40790	-16.8	4.012	-	4.31	4.019
40890	-16.8	3.816	-	4.09	3.835
40990	-16.8	3.654	-	3.99	3.674
41010	-16.8	3.624	0.088	3.89	3.645
41190	-16.8	3.394	-	3.86	3.408
41290	-16.8	3.289	-	3.57	3.299
41390	-16.8	3.197	-	3.44	3.202
41490	-16.8	3.114	-	3.33	3.118
41590	-16.8	3.043	-	3.22	3.043
41690	-16.8	2.992	-	3.13	2.978
41790	-16.8	2.940	-	3.06	2.920
41890	-16.8	2.888	-	2.99	2.869
41990	-16.8	2.849	-	2.92	2.825
42010	-16.8	2.838	0.103	2.87	2.817
43010	-16.8	2.631	0.100	2.59	2.588
44010	-16.8	2.570	0.091	2.51	2.524
45010	-16.8	2.556	0.094	2.49	2.507
46010	-16.8	2.541	0.092	2.48	2.502
47010	-16.8	2.537	0.100	-	-
48010	-16.8	2.530	0.093	-	-
49010	-16.8	2.522	0.093	-	-

Time in Sec.	Current in μ A	Ionic Probes in mV	Electronic Probes in mV	Thermodynamic Fit For Ionic Probes in mV	Exponential Fit For Ionic Probes in mV
50010	-16.8	2.522	0.102	-	-
51010	-16.8	2.507	0.090	-	-
56010	-16.8	2.482	0.098	-	-
57010	-16.8	2.481	0.094	-	-
58010	-16.8	2.482	0.107	-	-
59101	-16.8	2.477	0.108	-	-
60010	off at 60000	2.474	0.095	2.48	2.532
60190	0	3.240	-	2.82	3.402
60290	0	3.664	-	3.24	3.803
60390	0	4.036	-	3.63	4.153
60490	0	4.363	-	4.01	4.461
60590	0	4.648	-	4.33	4.729
60690	0	4.896	-	4.62	4.965
60790	0	5.112	-	4.86	5.171
60890	0	5.306	-	5.08	5.351
60990	0	5.472	-	5.27	5.509
61010	0	5.500	0.095	5.31	5.539
61190	0	5.731	-	5.59	5.769
61290	0	5.847	-	5.72	5.875
61390	0	5.947	-	5.84	5.968
61490	0	6.032	-	5.93	6.049
61590	0	6.108	-	6.02	6.120
61690	0	6.174	-	6.10	6.182
61790	0	6.234	-	6.17	6.237
61890	0	6.281	-	6.22	6.284
61990	0	6.326	-	6.27	6.326
62010	0	6.330	0.081	-	-
63010	0	6.550	0.081	-	-
64010	0	6.615	0.089	-	-
65010	0	6.620	0.079	-	-
66010	0	6.631	0.084	-	-
67010	0	6.626	0.078	-	-
68010	0	6.637	0.096	-	-
69010	0	6.634	0.094	-	-
70010	0	6.631	0.091	-	-
71010	0	6.633	0.095	-	-

Table 4.1
X-Ray Diffraction Results for
Reacted Cu₂S and Hot-Pressed Cu₂S

Reacted Cu ₂ S		Hot-Pressed Cu ₂ S		ASTMS Card (71) Cu ₂ S		
d Å	I/I ₀	d Å	I/I ₀	d Å	I/I ₀	hkl
3.71	12	3.71	25	3.73	20	242
3.56	11	3.57	19	3.59	16	162,203
3.29	15	3.29	23	3.31	25	322
3.25	14	3.26	28	3.27	25	024,104 +
3.16	25	3.17	36	3.18	40	262,124
3.04	13	3.04	21	3.05	20	342
2.93	31	2.94	38	2.942	45	182, +
2.86	11	2.87	15	2.873	16	411,191
2.75	11	-	-	2.755	16	431,362
2.71	42	2.71	58	2.718	55	440,371
2.65	16	2.66	23	2.659	25	422
2.60	4	2.61	13	2.609	16	115,353, +
2.55	7	-	-	2.555	12	451,314
2.51	22	2.52	44	2.524	40	0102, +
2.46	29	2.47	43	2.469	45	1102, +
2.39	47	2.39	93	2.396	85	344,084
2.32	32	2.32	37	2.325	40	2102,471, +
2.23	21	2.23	21	2.237	25	502,480, +
2.20	16	2.21	31	2.207	30	106,522, +
2.11	7	2.11	11	2.117	12	444,085 +
2.09	6	-	-	2.093	10	513,473, +
2.04	5	-	-	-	-	-
2.02	6	-	-	-	-	-
2.00	9	-	-	2.005	14	562, +
1.97	100	1.97	100	1.977	100	-
1.94	15	1.95	15	1.949	30	-
1.90	4	-	-	1.908	14	-
1.87	50	1.87	83	1.876	90	-
1.78	8	1.79	10	1.787	14	-
1.75	5	-	-	-	-	-

Table 4.2
Coulometric Titration Data for Cu-S System

X in Cu _x S	Cell EMF in mV	X in Cu _x S	Cell EMF in mV
1.994	269.5	1.823	394.9
1.973	286.2	1.804	395.9
1.946	288.5	1.785	393.1
1.933	288.8	1.796	381.1
1.926	290.0	1.807	374.2
1.912	289.2	1.817	372.4
1.892	289.6	1.828	372.6
1.862	303.8	1.839	372.7
1.831	336.3	1.849	372.6
1.800	367.3	1.860	372.3
1.769	396.8	1.871	371.9
1.753	395.3	1.882	371.4
1.784	372.3	1.892	371.1
1.815	355.1	1.899	371.0
1.876	309.8	1.908	370.5
1.907	293.4	1.915	370.5
1.937	280.6	1.931	368.9
1.968	278.9	1.924	370.8
1.983	279.1	1.940	366.9
1.991	279.1	1.948	364.8
1.996	278.1	1.955	362.4
2.001	277.4	1.964	359.6
1.996	283.9	1.971	355.2
1.991	284.8	1.980	352.3
1.985	285.2	1.987	350.1
1.980	285.4	1.996	347.6
1.975	286.3	2.003	344.9
1.956	304.8	1.996	353.7
1.937	325.2	1.987	361.4
1.918	345.3	1.980	368.6
1.899	364.4	1.971	391.7
1.880	382.7	1.956	390.4
1.861	400.0	1.940	394.4
1.842	395.1	1.926	395.4

Table 4.3
X-Ray Diffraction Results for Cu-S Cell

Material From Cell		Cu _{1.8} S (75)			CuS (76)		
d Å	I/I ₀	d Å	I/I ₀	hkl	d Å	I/I ₀	hkl
3.32	21	3.35	4	337	3.287	11	100
3.18	65	3.21	35	555	3.223	16	101
3.02	11	3.01	14	119	3.050	47	102
2.77	38	2.779	45	00 <u>10</u>	2.815	100	103
2.68	12				2.727	44	006
2.59	9						
2.53	15	2.553	4	<u>1111</u>			
2.36	16				2.319	9	105
2.21	4						
2.16	13						
2.13	11	2.141	10	<u>1082</u>	2.099	4	106
2.05	11				2.045	4	008
1.96	100	1.967	100	<u>10100</u>			
1.89	9				1.8980	53	110,107
1.79	4						
1.73	6	1.752	6	<u>11113</u>	1.7364	18	108
1.67	22	1.678	20	<u>5515</u>			
1.56	4				1.5738	10	203
					1.5578	24	116
1.28	44	1.392	10	<u>0020</u>	1.3912	12	118
					1.3550	4	<u>1011</u>
1.13	5				1.2812	4	208
					1.2115	4	213
1.07	4						

APPENDIX A

DERIVATION OF THE HEBB-WAGNER EQUATION (25)

The particle flux density (J_k) (for mobile ions $k = i$ and for electrons $k = e$) equation is

$$J_k = - \underbrace{(c_k B_k / N) (\partial \mu_k / \partial x)}_{\text{Diffusion Term}} - \underbrace{c_k B_k z_k e / \partial \phi / \partial x}_{\text{Migration Term}} \quad A1$$

Where the flux density is in direction x , with μ_k equal to the chemical potential of species k , B_k the absolute mobility, z the charge on the mobile species and with e and N being the charge on the electron and Avogadro's number respectively. The local field is ϕ . This assumes that particles of one type migrate independently of other types, see appendix D.

If there is no concentration gradient in the specimen equation A1 reduces to

$$J_k = -B_k c_k z_k e (\partial \phi / \partial x) \quad A2$$

and the partial current density (j_k) to

$$j_k = -\sigma_k (\partial \phi / \partial x) \text{ if } \frac{\partial \mu_k}{\partial x} = 0 \quad A3$$

Thus σ_k , the partial electronic conductivity of species k , is given by

$$\sigma_k = z_k^2 e F B_k c_k \quad A4$$

from equations A2 and A3 where $j_k = z_k F J_k$ and F is the Faraday constant. The electrochemical potential (η_k) is defined by

$$\eta_k = \mu_k + z_k F \phi \quad A5$$

Thus from equations A1, A4 and A5 we obtain

$$j_h = -(\sigma_h / z_h F) (\partial \eta_h / \partial x) \quad A6$$

The chemical potential of the metal is defined by

$$\mu_{\text{metal}} = \eta_i + z_i \eta_e \quad A7$$

where the ion is a metal ion. Thus by differentiating A7 with respect to x

$$\frac{\partial \eta_i}{\partial x} = \frac{\partial \mu_{\text{metal}}}{\partial x} - z_i \left(\frac{\partial \eta_e}{\partial x} \right) \quad A8$$

Putting A8 into A6

$$j_i = -(\sigma_i / z_i F) \left[\partial \mu_{\text{metal}} / \partial x - z_i (\partial \eta_e / \partial x) \right] \quad A9$$

and the electronic current from A6 is

$$j_e = (\sigma_e / F) (\partial \eta_e / \partial x) \quad A10$$

For an electronic conductor in contact with a mixed conductor, assuming no contact resistance, the chemical potential of the electrons is constant. Also their electrochemical potential in the electronic conductor is equal to that in the adjacent part of the mixed conductor. If the sample is of constant cross-section and of thickness L, from equation A5 for electrons the potential difference for electronic conducting contacts at the ends of the sample is

$$E = -[\eta_e(L) - \eta_e(0)] / F \quad A11$$

Where E is the potential across the specimen and x = 0 is the interface between the pure metal and the mixed conductor, see figure A.

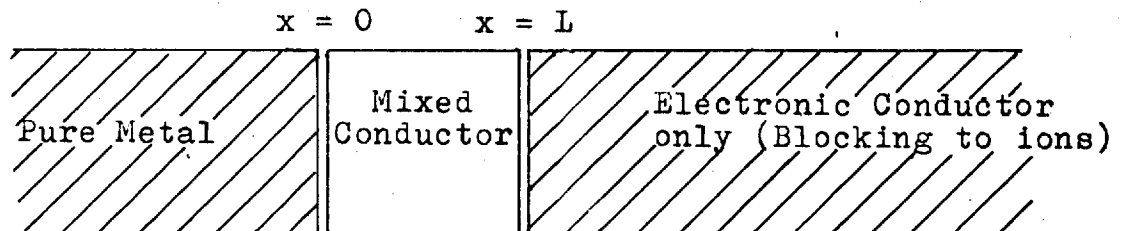


Figure A

Since $f_i = 0$ equation A9 gives

$$\frac{\partial \mu_{\text{metal}}}{\partial x} = z_i \left(\frac{\partial \eta_e}{\partial x} \right) \quad \text{A12}$$

Thus substituting equation A11 into equation A12

$$\mu_{\text{metal}}(L) = \mu_{\text{metal}}(0) - zFE \quad \text{A13}$$

Substituting A11 into A10 with $f_e = f$

$$\sigma_e(x) = \frac{|f|}{\left(\frac{\partial \Delta E}{\partial x} \right)} \quad \text{A14}$$

Putting A12 into A10 and integrating with respect to x we obtain

$$L f = \frac{1}{z_i F} \int_{\mu_{\text{metal}}(0)}^{\mu_{\text{metal}}(L)} \sigma_e d\mu_{\text{metal}} \quad \text{A15}$$

Thus by using equation A14, and differentiating equation A15 and regrouping

$$\sigma_e(\mu_{\text{metal}}) = L (d|f|/dE) \quad \text{A16}$$

As the cation conduction is mainly due to interstitials and vacancies the small changes in the metal to non-metal ratio do not affect the chemical potential of the cations, but do that of the electrons.

Therefore in view of equation A7

$$d\mu_e = d\mu_{\text{metal}}/z_i \quad \text{A17}$$

A change in the concentration of excess electrons ($C_\ominus$) and electron holes ($C_\oplus$) is related to that in the chemical potential of the electrons

$$d\mu_e = RT d \ln C_\ominus = -RT d \ln C_\oplus \quad \text{A18}$$

for sufficiently low concentrations so that the law of ideal solution applies. Thus from equations A17 and A18 it follows that

$$\left. \begin{aligned} C_\ominus &= C_\ominus^\circ \exp \left[(\mu_{\text{metal}} - \mu_{\text{metal}}^\circ) / z_i RT \right] \\ C_\oplus &= C_\oplus^\circ \exp \left[-(\mu_{\text{metal}} - \mu_{\text{metal}}^\circ) / z_i RT \right] \end{aligned} \right\} \quad \text{A19}$$

where the superscript stands for the value in equilibrium with the pure metal. In low concentrations one may assume that mobilities of excess electrons and holes are constant. Therefore

$$\sigma = \sigma_{\ominus}^{\circ} \exp \left[(\mu_{metal} - \mu_{metal}^{\circ}) / z_i RT \right] + \sigma_{\oplus}^{\circ} \exp \left[-(\mu_{metal} - \mu_{metal}^{\circ}) / z_i RT \right] \quad A20$$

Using equation A20 with A16 and A13, and integrating with the boundary conditions $E = 0$ when $\phi = 0$

$$|\phi| = \left\{ \sigma_{\ominus}^{\circ} [1 - \exp(-EF/RT)] + \sigma_{\oplus}^{\circ} [\exp(EF/RT) - 1] \right\} \frac{RT}{FL} \quad A21$$

APPENDIX B

PROGRAMABLE DATA LOGGER

A lot of measurements involved in experimental work are repetitive, and are required twenty-four hours a day. In some of the work published here a very basic controller unit was used to carry out readings and control the experiments. The method of carrying out predetermined actions would be by either mechanical (time switches, cams, etc.) or electrical means and it was the second type that was used here.

Having decided on an electrical method there were two possible routes, one was to use analog methods and the other was to use digital techniques, which are well suited to logical operations. In digital electronics logic operations are carried out either by hard wired logic circuits or by a processor which has a predetermined set of controls (e.g. micro-processor, computer, etc.). As at the time of constructing this controller it was very expensive to use micro-processors, a system using hard wired logic was used. (At the time of writing a micro-processor system is being designed by the author.) The cheapest and most reliable way of obtaining hard wired logic at the time of construction was to use transistor transistor logic (TTL) using bipolar technology in integrated circuits. The most well known and easily available circuits of this type are Texas Instruments series 7400.

The method of construction having been selected it was then necessary to work out the specific requirements of the system and those decided on are laid out below.

1. Measure a series of voltages at certain times.
2. Switch on and off constant current sources.
3. Take action on measured voltages.

These design requirements were satisfied by the circuit which is shown in block diagram form in figure B. The timing of all operations inside the basic time step of the clock (which could be 10 sec or 1 sec) are controlled by the synchronisation unit, which prevents nonallowed operations occurring together, e.g. reading a voltage at the same time as changing the voltage that the analogue to digital converter (A to D) is looking at. The main technical specifications are given below although the circuit diagram for the system will not be given due to its excessive size.

Multiplexer

Incoming voltage switched to A to D converter by Astralux series 110 reed relays of following specification

Contact-Contact resistance $10^{10} \Omega$ when open

" " " 100 Ω when closed

Contact-Coil resistance $10^2 \Omega$

Time between breaking contact and forming a new one 30 mS.

A to D Converter

Data Precision D.V.M.

Input resistance $10^{10} \Omega$.

2 Conversions per second.

Scale both $4\frac{1}{2}$ and $5\frac{1}{2}$ digits models compatible.

Ranges 10 v, 1 v, .1 v controlled electronically.

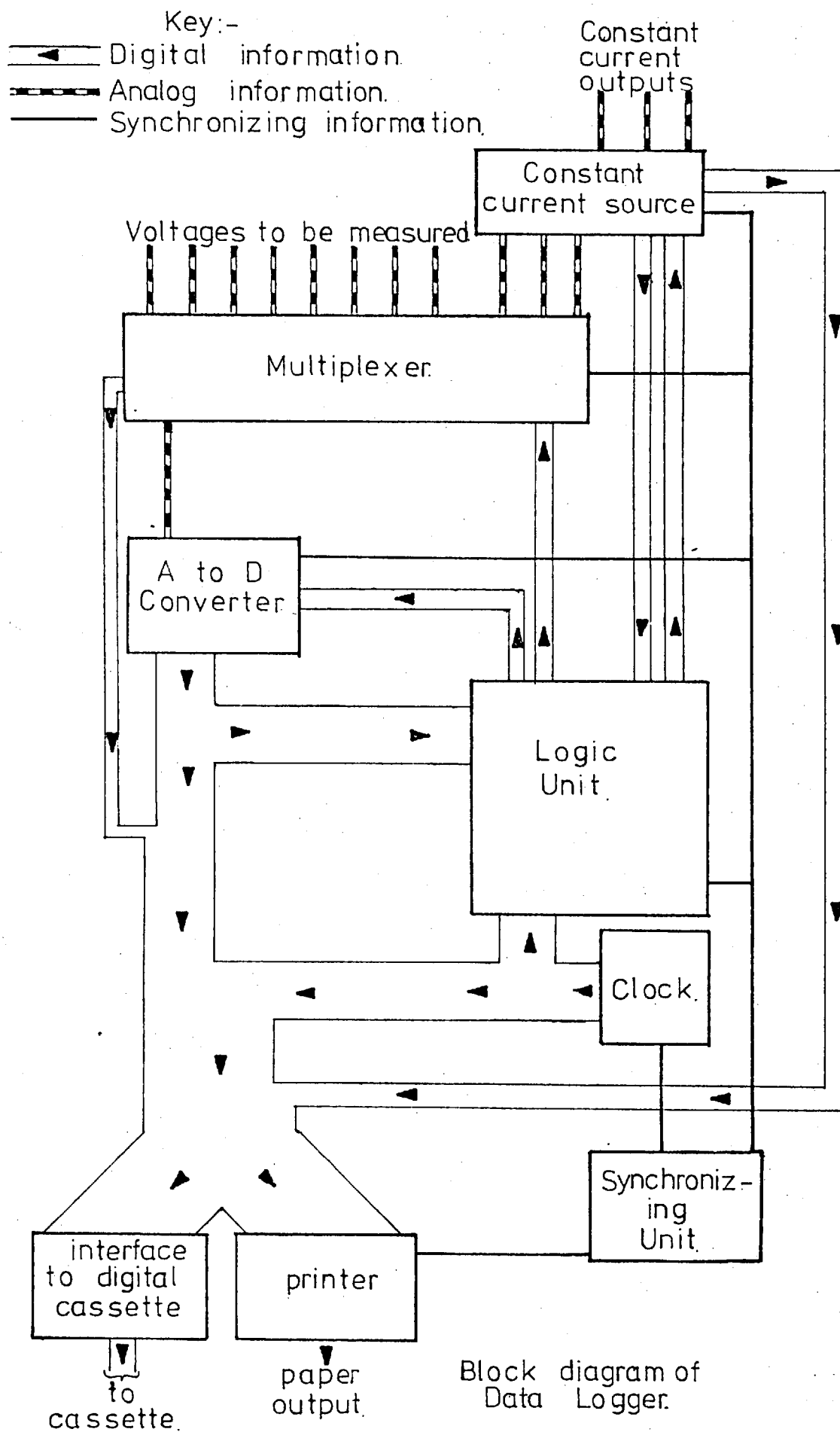


Figure B

Printer

Anadex 18 column ink printer (red and black).

Output format

columns 1-6 the time in seconds.

columns 8 and 9 current sources states.

column 10 voltage source being measured.

columns 12 to 18 the A to D reading.

Clock

Mains cycle counting type.

Accuracy better than 2% short term and better than 0.1% long term.

Current sources

Ranges 10 mA, 1 mA, 100 μ A, 10 μ A.

Adjustment by ten turn pot.

Stability better than 0.1%.

Time between switching from forward to reverse 30 mS.

Switches are Astralux reed relays (see multiplexer).

Digital cassette interface

Allows data to be recorded on a digital cassette recorder in a computer compatible form. This unit was designed by two other members of the group and the author and is based on a Philips digital cassette drive. It is capable of receiving data from 16 such control units.

Logic unit

Hand wired on a 64 strip Vero board which is plugged in so that various plug-in program boards can be put in.

This is a summary of the requirements, and the technical specification of the unit finally built to fulfil them. At the time of writing the unit has worked for 20 months with only two failures in operation and has been out of

service for modifications for about a month. The unit took many months to design and about 2 months to construct, so its actual profit to this project in terms of results was low, but it is now still giving results.

APPENDIX C

VAN DER PAUW TECHNIQUE (67)

According to the work of Van der Pauw the specific resistivity (ρ) of a lamina obeys the following equation

$$\exp(-\pi R_{AB,CD} L / \rho) + \exp(-\pi R_{BC,DA} L / \rho) = 1 \quad C1$$

where $R_{AB,CD}$ and $R_{BC,DA}$ are the resistances defined by the voltage difference between the latter two suffixes over the current for the two former suffixes, see figure C. L is the thickness of the sample. It is proved by Van der Pauw that this equation C1 holds as long as the lamina has a continuous surface.

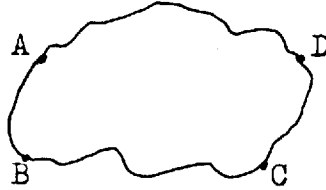


Figure C

In order to facilitate the calculation of ρ , equation C1 can be written as:

$$\rho = \frac{L}{\ln 2} \frac{(R_{AB,CD} + R_{BC,DA})}{2} f\left(\frac{R_{AB,CD}}{R_{BC,DA}}\right) \quad C2$$

where f is a function of $R_{AB,CD} / R_{BC,DA}$ only and satisfies the following equation:

$$\frac{R_{AB,CD} - R_{BC,DA}}{R_{AB,CD} + R_{BC,DA}} = f \operatorname{arc} \cosh \left(\frac{\exp(\frac{\ln 2}{f})}{2} \right) \quad C3$$

If $R_{AB,CD}$ and $R_{BC,DA}$ are almost equal, (i.e. for the case of an almost symmetrical sample with symmetrical contacts) equation C3 can be approximated by:

$$f \approx 1 - \left(\frac{R_{AB,CD} - R_{BC,DA}}{R_{AB,CD} + R_{BC,DA}} \right)^2 \frac{\ln 2}{2} - \left(\frac{R_{AB,CD} - R_{BC,DA}}{R_{AB,CD} + R_{BC,DA}} \right)^4 \left(\frac{(\ln 2)^2}{4} - \frac{(\ln 2)^3}{12} \right)$$

C4

It should be noted that equation C1 only holds for true line contacts, and the expression is more complicated if this is not assumed.

APPENDIX D

ELECTRONIC AND IONIC CONDUCTIVITIES (68, 69)

The transport of the mobile species, for a single system where there are only two mobile species, is governed by the general flux equations.

$$\frac{J_1}{e} = L_{11} \frac{\partial \eta}{\partial x} + L_{12} \frac{\partial \eta_2}{\partial x} \quad D1$$

and

$$\frac{J_2}{e} = L_{21} \frac{\partial \eta}{\partial x} + L_{22} \frac{\partial \eta_2}{\partial x} \quad D2$$

where subscripts 1 and 2 refer to the two species, which are in this case, the electrons (2) and the copper ions (1). J_n is the current density of species n, η_n is the electrochemical potential, and L is the general Onsager phenomenological coefficient.

It follows from equations D1 and D2 that, if only a current of species 1 is passed, then

$$\frac{J_1}{e} = \left(L_{11} - \frac{L_{12}^2}{L_{22}} \right) \frac{\partial \eta}{\partial x} \quad D3$$

using the Onsager relation that $L_{12} = L_{21}$. In a six-point experiment the measured value for the above equation (D3) would be the voltage difference between the two species 1 probes (ΔV_1). This is proportional to the electrochemical potential gradient of species 1, if no current is drawn.

$$\Delta V_1 = \Delta \eta / e \quad D4$$

which gives a conductivity for a sample of unit cross-section of

$$\sigma'_1 = J_1 \frac{\Delta X_1}{\Delta V_1} \quad D5$$

where σ'_1 is the conductivity of species 1 for suppressed conduction of species 2, and ΔX_1 is the spacing of the species 1 probes. As was pointed out by Wagner (78) the addition of the two conductivities for the other species being suppressed, does not add up to the total conductivity. This is due to the cross terms in the transport equations. If however the cross term (L_{12}) is equal to zero the partial conductivities do add up to the total. To establish if the cross terms are equal to zero the following equations derived from D2 and D4 should be used.

$$\left(\frac{\Delta V_2 / \Delta V_1}{\Delta X_2 / \Delta X_1} \right)_{J_2=0} = \frac{-L_{12}}{L_{22}}; \quad \left(\frac{\Delta V_1 / \Delta V_2}{\Delta X_1 / \Delta X_2} \right)_{J_1=0} = \frac{-L_{12}}{L_{11}} \quad D6$$

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As the electronic probes showed no effect during the experiments of the type described by the above equations (D6) it will be assumed that the cross coefficients are small enough to be ignored. Thus equations D1 and D2 become independent giving

$$J_1 = \frac{\sigma_1}{e} \frac{\partial \eta}{\partial x}; \quad J_2 = \frac{\sigma_2}{e} \frac{\partial \eta_2}{\partial x} \quad D7$$

If the assumption of local equilibrium is made, $\text{Cu} \rightleftharpoons \text{Cu}^+ + e^-$ demands that $\eta_i + \eta_e = \mu_{\text{metal}}$, where μ_{metal} is the chemical potential of the metallic copper. Thus for an ionic current equation D7 becomes

$$-J_i = \frac{\sigma_i}{e} \frac{\partial \eta_i}{\partial x} = \frac{\sigma_i}{e} \frac{\partial \mu_{\text{metal}}}{\partial x} \quad D8$$

It follows that the ionic electrochemical potential gradient is identical with the chemical potential gradient of copper. Thus as this varies with composition the value of σ measured is an average, so that currents and hence

composition differences must be kept small.

If the specimen is at equilibrium prior to switching on the current, the chemical potential gradient of copper is zero at the instant of switching on. Equations D7 slightly rewritten in terms of chemical potential gradients $(\frac{\partial \mu}{\partial x})$ and electrical field gradients $(\frac{\partial \phi}{\partial x})$ become

$$-J_i = \sigma_i \left(\frac{\partial \mu_i}{e \partial x} + \frac{\partial \phi}{\partial x} \right) \quad D9$$

$$J_e = \sigma_e \left(-\frac{\partial \mu_e}{e \partial x} + \frac{\partial \phi}{\partial x} \right) \quad D10$$

As $\frac{\Delta \phi}{\Delta x} = \frac{\Delta V}{\Delta x}$ and using Ohms law, the potential across both sets of probes at the instant of switching on is:

$$\frac{\Delta V_i}{\Delta x_i} = \frac{\partial \phi}{\partial x} \quad ; \quad \frac{\Delta V_e}{\Delta x_e} = \frac{\partial \phi}{\partial x} \quad D11$$

The total conductivity is equal to the total current J_T divided by the potential field, at the instant of switching on, i.e.

$$\sigma_{total} = \sigma_i + \sigma_e = J_T \frac{\Delta x_i}{\Delta V_i} = J_T \frac{\Delta x_e}{\Delta V_e} \quad D12$$

Equation D12 thus predicts that the total conductivity can be obtained from the instantaneous voltage on the probes. This effect could not be used in this work as the probe voltage could not be measured quickly enough. It is therefore known what the probe voltage should be at the instant of switching on and at the steady state. However, so far it has not been shown what we would expect on the probes as they change, and it is that which will now be dealt with.

One of the simplest models is that used by Roth (4), and this is shown in figure D.

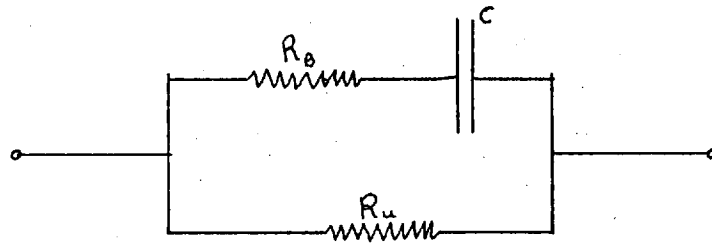


Figure D

where R_b is the resistance to the blocked species, and R_u is the resistance for the unblocked species. This gives an exponential behaviour for the probe E.M.F.s, with a characteristic time (τ) given by

$$\tau = (R_b + R_u)C \quad D13$$

Yokota (69) has however proposed a more sophisticated model from his work with silver tellurides, assuming zero cross coefficients. Equations D9 and D10 can be rewritten in the following form with $J = J_e + J_i$

$$J_e = \frac{\sigma_e}{\sigma_r} J + \frac{\sigma_e \sigma_i}{\sigma_r} \frac{\partial(\mu_e)}{\partial x} \quad D14$$

$$J_i = \frac{\sigma_i}{\sigma_r} J - \frac{\sigma_e \sigma_i}{\sigma_r} \frac{\partial(\mu_e)}{\partial x} \quad D15$$

If it is now assumed that all the metal is ionized, then the rate of change of the carrier concentration is given by:

$$\frac{\partial N_c}{\partial t} = \frac{1}{e} \frac{\partial J}{\partial x} \quad D16$$

if μ is a function of N_c (carrier number) only.

Differentiating D14 and using D16

$$\frac{\partial N_c}{\partial t} = \frac{1}{e} \frac{\partial}{\partial x} \left\{ \frac{\sigma_e}{\sigma_r} J + \frac{\sigma_e \sigma_i}{\sigma_r} \frac{d(\mu_e)}{dN_c} \frac{\partial N_c}{\partial x} \right\} \quad D17$$

If the current density is small so that $\frac{d\mu}{dN_c}$, σ_e , and σ_i are not functions of position, then

$$\frac{\partial N_c}{\partial t} = D \frac{\partial^2 N_c}{\partial x^2} \quad D18$$

the diffusion equation, where

$$\frac{1}{\gamma} = \frac{D\pi^2}{L} = \frac{\pi^2}{L} \cdot \frac{\sigma_i \sigma_e}{\sigma_i e} \left(\frac{d\mu}{dN_c} \right) \quad D19$$

in which γ = the characteristic time, and L is the length of the bar specimen. It turns out that D is in fact $\tilde{D}$, the chemical diffusion coefficient. The value of $\frac{d\mu}{dN_c}$ can be obtained for Bornite if it is assumed that there are two mobile copper ions per formula, and thus the number of carriers is equal to $2 - \zeta$, where the composition is given by $\text{Cu}_{5-3}\text{FeS}_4$. Thus $\frac{d\mu}{dN_c}$ is given by the following

$$\frac{d\mu}{dN_c} = \frac{d\zeta}{dN_c} \cdot \frac{\partial \mu}{\partial \zeta} = \frac{M}{\omega(N)^2} \cdot F \cdot \frac{\partial E}{\partial \zeta} \quad D20$$

where E is the E.M.F. of the sample with respect to copper, M the molecular weight, ω the density, N Avogadro's Number, and F Faraday's constant.

Thus from equations D19 and D20

$$\frac{1}{\gamma} = \frac{\tilde{D}\pi^2}{L^2} = \frac{\pi^2}{L^2} \frac{\sigma_i \sigma_e}{(\sigma_i + \sigma_e)} \frac{M}{F\omega} \frac{\partial E}{\partial x} \quad D21$$

For the actual transient behaviour on passing an ionic current equation D18 must be solved, with the boundary conditions that $J_e = 0$ at $x = 0, L$, and that from equation D14

$$\frac{\partial N_c}{\partial x} = \frac{eJ}{\sigma_e (d\mu/dN_c)} \quad \text{at } x = 0, L \quad D22$$

A solution of equation D18 can take the form of a Fourier series $\phi\left(\frac{x}{L}, \frac{t}{\gamma}\right)$ which is

$$\phi\left(\frac{x}{L}, \frac{t}{\gamma}\right) = \frac{4}{\pi} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp\left[-(2m+1)^2 \frac{t}{\gamma}\right] \cos\left[(2m+1)\frac{\pi x}{L}\right] \quad D23$$

If it is assumed that the zero voltage position is at the centre of the bar, the ionic probes give for an ionic current

$$V_i = \frac{-JL}{\sigma_i} \left(\frac{\Delta X_i}{L} - \frac{1}{2} \right) + \frac{\sigma_e}{\sigma_i} \phi\left(\frac{L-\Delta X_i}{L}, \frac{t}{\gamma}\right) \quad D24$$

and the electronic probes give

$$V_e = \frac{JL}{\sigma_r} \phi\left(\frac{L - X_e}{L}, \frac{t}{\tau}\right) \quad D25$$

for switching on and

$$V_i = \frac{JL}{\sigma_r} \frac{\sigma_e}{\sigma_i} \phi\left(\frac{L - X_i}{L}, \frac{t}{\tau}\right) \quad D26$$

and

$$V_e = \frac{-JL}{(\sigma_i + \sigma_e)} \phi\left(\frac{L - X}{L}, \frac{t}{\tau}\right) \quad D27$$

for switching off.

Equations D24 through D27 are used to predict the transient behaviour of the probes for ionic currents which are small perturbations to the equilibrium condition. For a more detailed account of the behaviour under ionic and electronic currents Yokota (69) should be consulted.

APPENDIX E

COMPUTING (79)

In the work carried out for this thesis the computer was used to plot out graphs, calculate lattice parameters, and also to model diffusion. The method of programing is not important so none of the programs are presented here. However the basis of the simple model that was used for the coulometric cells will be presented here, along with sufficient information to formulate a program to model it.

The model is based on Ficks 2nd Law which is

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad E1$$

where c is the concentration, and D is the diffusion coefficient. It is required to integrate equation E1 in order to see how the system behaves. An easy method of integration is to use a numerical method to give an approximate answer, and the simplest of these methods is the finite difference method. In this method the continuums of time and distance are replaced by discrete steps, Δt for time and Δ for distance. Thus

$$\frac{\partial c}{\partial t} \approx \frac{c_i^{n+1} - c_i^n}{\Delta t} \quad \text{and} \quad \frac{\partial^2 c}{\partial x^2} = \frac{\partial}{\partial x} \left(\frac{\partial c}{\partial x} \right) = \left(\frac{\frac{c_{i+1}^n - c_i^n}{\Delta} - \frac{c_i^n - c_{i-1}^n}{\Delta}}{\Delta} \right) \quad E2$$

where superscripts refer to time and subscripts to position. As this method quantises time and distance there are obviously associated errors, and also the possibility of instability, i.e. the function self oscillating. The self oscillating can be overcome by making sure that the motion is always

damped. In order to establish this condition a Fourier mode is applied in space.

$$c = \hat{c}(t) e^{ikx} \quad E3$$

Using E3 in E2 gives

$$\hat{c}^{n+1} e^{ikx_j} = \hat{c}^n e^{ikx_j} + \frac{D\Delta t}{\Delta^2} \hat{c}^n (e^{ikx_{j+1}} - 2e^{ikx_j} + e^{ikx_{j-1}}) \quad E4$$

which simplifies to

$$\hat{c}^{n+1} = \hat{c}^n \left\{ 1 + \frac{2D\Delta t}{\Delta^2} \left(\frac{1}{2} e^{ik\Delta} + \frac{1}{2} e^{-ik\Delta} - 1 \right) \right\} \quad E5$$

and as $\cos(k\Delta) = \frac{1}{2} e^{ik\Delta} + \frac{1}{2} e^{-ik\Delta}$, we have obtained a simple equation relating the amplitude over consecutive time intervals, the amplification factor (g_a).

$$g_a(\Delta t, \Delta, k) = 1 + \frac{2D\Delta t}{\Delta^2} \left\{ \cos(k\Delta) - 1 \right\} = 1 - \frac{4D\Delta t}{\Delta^2} \sin^2\left(\frac{k\Delta}{2}\right) \quad E6$$

For stability $g_a \leq 1$, therefore

$$1 \geq \left| 1 - \frac{4D\Delta t}{\Delta^2} \sin^2\left(\frac{k\Delta}{2}\right) \right| \quad E7$$

As this is required over all Fourier modes ($k = 0$ to ∞) the sine must be given its maximum value, 1. Therefore E7 becomes

$$\Delta t \leq 0.5 \frac{\Delta^2}{D} \quad E8$$

Thus for a stable numerical solution the time step must be smaller than a maximum time step defined by equation E8. The physical reality of this maximum time step is that it is the time required for information to travel one space step.

Using equation E2 as the model with the appropriate boundary conditions, and equation E8 to prevent instability, the resulting program was used to find the effects of different positions of reference electrodes and counter electrodes on the working electrodes. This gave information on the time dependence of cell voltages.

APPENDIX F

DIFFUSION COEFFICIENTS AND IONIC CONDUCTIVITY

In this appendix we want to define Fick's first law as well as defining diffusion coefficients. If we have a system with a flux of particles, (J_A) passing through an area (A), and the number of particles is (n_A), then the flux is

$$J_A = \frac{n_A}{A} \quad \text{F1}$$

This flux is due to a concentration of moving particles (c_i) which have an average velocity, the drift velocity (v_x), which we shall define perpendicular to the plane across which J_A is measured. It is possible to generalize this and the following to a 3-dimensional case. Thus

$$J_i = c_i v_x \quad \text{F2}$$

The drift velocity may be expressed as a force (f) and a mobility (β_i) so that equation F2 becomes

$$J_i = c_i \beta_i f \quad \text{F3}$$

This force, f is due to a gradient in the potential energy, in fact the total chemical potential energy μ_T . Thus equation F3 becomes

$$J_i = -c_i \beta_i \frac{d\mu_T}{dx} \quad \text{F4}$$

Now μ_T may be split into two components one due to a composition gradient (μ_c), and the other due to imposed forces (μ_e). If the imposed force is due to an electrical

field only then may be written as

$$\frac{d\mu_e}{dx} = z_i e \frac{d\phi}{dx} \quad F5$$

where $z_i e$ is the charge on the mobile species and ϕ is the electric potential applied. Thus equation F4 becomes

$$J_i = -c_i \beta \frac{d\mu}{dx} - c_i \beta z_i e \frac{d\phi}{dx} \quad F6$$

It is the first term on the right-hand side of equation F6 that describes the diffusion and the second term that describes the migration, which in turn is responsible for the ionic conductivity.

If we now consider the special case of tracer diffusion where the diffusing species is chemically the same as the host, we have

$$\mu = \mu_o + kT \ln a \quad F7$$

where μ is the chemical potential, μ_o being the value when $a = 1$, a being the activity coefficient. If the above equation is differentiated with respect to x , we get

$$\frac{d\mu}{dx} = kT \frac{d \ln a}{dx} \quad F8$$

From Henry's law for dilute solutions $a = \gamma c$, where γ is a constant, and the derivative of this is

$$da = \gamma dc \quad F9$$

and if the above is divided by $a = \gamma c$ we get

$$d \ln a = d \ln c \quad F10$$

substituting for $d \ln a$ in equation F8 gives

$$\frac{d\mu}{dx} = kT \frac{d \ln c}{dx} \quad F11$$

Equation F11 can then be used with equation F4 to give

$$J_i = -c_i \beta kT \frac{d \ln c_i}{dx} \quad F12$$

By defining

$$\beta_i kT = D_i^* \quad \text{F13}$$

where D_i^* is defined as the self-diffusion coefficient in the above conditions, equation F12 becomes

$$J_i = -D_i^* \frac{dc_i}{dx} \quad \text{F14}$$

which is Fick's first law.

In the above case of tracer diffusion it was assumed that the system was ideal. In the case when the mobile species is not ideal equation F4 becomes

$$J_i = -c_i \beta_i kT \frac{d \ln a_i}{dx} \quad \text{F15}$$

in a similar way to equation F12. By substituting for β_i from equation F13 and using the following equation

$$c_i = \frac{dc_i}{d \ln c_i} \quad \text{F16}$$

equation F15 becomes

$$J = - \frac{dc_i}{d \ln c_i} \cdot \frac{D_i^* kT}{kT} \cdot \frac{d \ln a_i}{dx} \quad \text{F17}$$

which reduces to the following

$$J = -D_i^* \frac{d \ln a_i}{d \ln c_i} \frac{dc_i}{dx} \quad \text{F18}$$

It can be seen that if in the above equation $D_i^* \frac{d \ln a_i}{d \ln c_i}$ were replaced by $\tilde{D}_i$ we would have the following equation

$$J_i = -\tilde{D}_i \frac{dc_i}{dx} \quad \text{F19}$$

This is the same form as equation F14 and is Fick's first law, but $\tilde{D}_i$ is the chemical diffusion coefficient. Thus the following relation between $\tilde{D}_i$ and D_i^* is given by

$$D_i = D_i^* \frac{d \ln a_i}{d \ln c_i} \quad \text{F20}$$

The relation between the mobility and the ionic conductivity is of great importance and this can be derived from equation F6. In this equation $\frac{d\mu}{dx}$ is very small in comparison to the electric field so equation F6, becomes

$$J_i \approx - c_i \beta_i z_i e \frac{d\phi}{dx} \quad \text{F21}$$

J_i is the flux and to convert this into the ionic conductivity we must use Ohm's law where the current is $J_i z_i e$, the electric field is $\frac{d\phi}{dx}$, and finally the ionic resistivity is σ_i^{-1} . Thus we get the following equation

$$\sigma_i = J_i z_i e \frac{dx}{d\phi} \quad \text{F22}$$

If equation F21 is substituted into equation F22 we arrive at the following equation

$$\sigma_i = c_i z_i^2 e^2 \beta_i \quad \text{F23}$$

From equation F13

$$\sigma_i = \frac{c_i z_i^2 e^2}{kT} D_i^* \quad \text{F24}$$

which is the Nernst-Einstein relation and obeyed as long as Ohm's law is obeyed.

D^* is related to both the jump frequency (ν) and the distance jumped (d) as well as a geometric factor (α) in the simple random-walk equation

$$D^* = \alpha d^2 \nu \quad \text{F25}$$

The average jump frequency is due to a combination of the attempt frequency (ν_0), the energy ΔG (free energy of migration), and also the fraction of the species free to move (β). This gives the equation

$$\nu = \beta \nu_0 \exp.(-\Delta G/RT) \quad \text{F26}$$

ΔG being made up of the entropy, ΔS , and the enthalpy (ΔH), therefore,

$$D^* = \alpha d^2 \beta \nu_0 \exp.(\Delta S/R) \exp.(-\Delta H/RT) \quad F27$$

where d is the jump distance. If it is assumed that only ionic conductivity is taking place the Nernst-Einstein relation gives

$$\sigma_i = D_i^* c_i z_i^2 F^2 / RT \quad F28$$

where c_i is the concentration of the mobile species and $z_i e$ their charge, F being Faraday's constant. Substituting for ν in F28 using equation F27 gives

$$\sigma_i = \frac{D_i^* c_i z_i^2 F^2}{RT} \alpha d \beta \nu_0 \exp.(\frac{\Delta S}{R}) \exp.(\frac{-\Delta H}{RT}) \quad F29$$

$$\sigma_i = \frac{\sigma_0}{T} \exp.(\frac{-\Delta H}{RT}) \quad F30$$

$$\text{when } \sigma_0 = \frac{D_i^* c_i z_i^2 F^2 \beta d \nu_0}{R} \exp.(\frac{\Delta S}{R}) \quad F31$$

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