

AN ELECTROCHEMICAL STUDY OF THE CARROLLITE - CHALCOPYRITE SYSTEM
IN XANTHATE AND CYANIDE CONTAINING SOLUTIONS.

BY

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DECLARATION

I declare that this dissertation was written in accordance with the rules and regulation governing the award of the Degree of Master of Mineral Sciences of the university of Zambia. I further declare that the dissertation has neither in part nor in whole been presented as substance for award of any degree, either to this or any other University.

Where other people's work has been drawn upon acknowledgement has been made.

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DEDICATIONS

To the entire family for love and understanding.

ABSTRACT

A study has been made of the electrochemical behaviour of carrollite and chalcopyrite in the presence of xanthate and cyanide in aqueous solution. The investigations involved measurements of rest potentials and cyclic voltammetry of the sulphide minerals under study.

The results showed that the measured rest potential depends on among other things, the subsequent stable species on the mineral surfaces. In acid media Co^{2+} and Cu^{2+} ions determined the measured rest potentials on the carrollite electrode whilst $\text{Co}(\text{OH})_2$ and Cu_2O were responsible for the potential in alkaline media. Cu^{2+} and Fe^{2+} ions determined the measured potential on the chalcopyrite electrode in acidic media whilst $\text{Fe}(\text{OH})_3$ and Cu_2O were the potential determining species in alkaline media.

The major xanthate oxidation product, dixanthogen was present on the carrollite in sufficient quantities at pH 9.2 but not at pH 7.0 and 11.0. At this pH value the carrollite was rendered hydrophobic. In the presence of cyanide, carrollite was hydrophilic particularly at high values as predicted by the magnitudes of the potentials. In case of chalcopyrite dixanthogen formed only at pH value of 7.0 and 9.2. At pH 11.0 metal xanthate was the major product and was responsible for hydrophobicity even in the presence of cyanide. Thus the role of cyanide as a depressant was to introduce an anodic oxidation reaction which proceeded faster than the xanthate oxidation reaction on both minerals.

On the basis of the above electrochemical behaviour an effecient separation between the two minerals appears possible only by precise control of both xanthate and cyanide concentration under carefully optimised conditions.

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LIST OF ABBREVIATIONS

The list of abbreviations or symbols used in electrochemical literature remain far from uniform. Hence the symbols used in this thesis are listed below as an aid to the reader and are in conformity to the IUPAC convention.

<u>SYMBOLS</u>	<u>UNITS.</u>
e = electronic charge.	(V)
E^0_e = standard potential.	(V)
E^c_e = cathodic potential.	(V)
E^A_e = anodic potential.	(V)
ζ = zeta potential.	(V)
E = potential vs a reference electrode.	(V)
i = current.	(A)
I = current density.	(A m ⁻²)
i_0 = exchange current.	(A)
I_0 = exchange current density.	(A)
I = peak current density, superscripts A and B denotes the anodic and cathodic currents respectively.	(A m ⁻²)
α = transfer coefficient; subscripts A and C indicate the anodic and cathodic processes respectively.	(dimensionless)
A = geometric area of the electrode.	(m ²)
R = gas constant.	(J K ⁻¹ mol ⁻¹)
or = resistance.	(Ω)
C_i = concentration of species i at the electrode surface, subscripts A and B indicate	

	species A and B.	(mol m ⁻³)
μm	= micrometers	
ppm	= parts per million.	
KEX	= potassium ethyl xanthate	
CN ⁻¹	= cyanide ions	
X ⁻¹	= xanthate ion	
mA	= milliamperes	
C ⁰ _i	= concentration of species i at the surface of the electrode.	(mol m ⁻³)
F	= Faraday's constant.	(Coul.mol ⁻¹)
q	= charge .	(coulomb)
M	= moles of electroactive species in electrolysis cell.	(mol.)
n	= number of electrons involved in an overall electrode reaction.	(dimensionless)
p	= type of semi-conductor.	
η	= overpotential; E-E ₀ subscript A and C indicate anodic and cathodic overpotentials respectively.	(V)
k	= rate constant for a chemical reaction, various subscripts depend on the type of reaction.	(s ⁻¹)
\overleftarrow{k}	= rate constant for cathodic process.	(s ⁻¹)
\overrightarrow{k}	= rate constant for anodic process.	(s ⁻¹)
\overleftarrow{k}_0	= rate constant for cathodic process at 0V vs reference electrode.	(s ⁻¹)
\overrightarrow{k}_0	= rate constant for anodic process at 0V vs reference electrode.	(s ⁻¹)
IUPAC	= International Union of Pure and Applied Chemistry.	

XPS	=	X-ray photo electronspectroscopy.	
t_e	=	electronic transference number.	(dimensionless)
\dot{Q}	=	sweep rate.	(mVs^{-1})
p	=	semi-conductor type: +ve.	(accept e^{-1})
n	=	semi-conductor type: -ve.	(donor e^{-1})
M^{n+}	=	metal ions.	(mol m^{-3})
M	=	stable metal.	

1.0 INTRODUCTION

Sulphide minerals are recognised as a major source of base minerals among which copper, lead, zinc, nickel and cobalt are the most important. These sulphides usually occur in complex aggregates and separation of these minerals is predominantly effected by the use of surface properties.¹

In Zambia, cobalt occurs in economical quantities at several of its mines as either carrollite (CuCo_2S_4) or as cobaltiferous pyrite in association with other copper sulphides among which chalcopyrite and bornite are the most important.^{1,2} However, the cobalt content of the ore is much lower than that of the copper with which it is associated. Typical grades are 1.5% - 2.5% Cu and 0.09% - 0.12% Co. Consequently, it is necessary to produce separate concentrates of copper and cobalt in order to provide a feed which is acceptable to the cobalt plants

Cobalt is used as an alloying element in a number of industries. Some of these uses are:

- a) For permanent and soft magnetic materials.
- b) In super alloys such high temperature creep resistant alloys.
- c) Hard facing and resistant alloys.
- d) Sintered carbide cutting tools.
- e) Electrical resistant alloys and
- f) High temperature spring and bearing alloys.

Due to an increasing demand for cobalt and the large number of industries which use the metal, there is need for increased production of the metal to match the requirements of these industries. ³ This can be achieved by efficient separation of cobalt bearing minerals from those of copper. The separation of cobalt bearing minerals from copper minerals is done by the process of differential or segregation flotation.

Froth flotation is a principal separation used in the mineral industry. The mined mineral ores are usually heterogeneous mixtures. For sulphide minerals, flotation provide the means of separation and concentration of the valuable components of these ores. This provide a grade of mineral concentrates suitable as feed for efficient hydrometallurgical and pyrometallurgical operation which are used to produce a metal of required specifications acceptable at the metal market.

Zambia Consolidated Copper Mines (ZCCM) limited, has a number of operating concentrators which produce cobalt concentrates. Nkana, Baluba and Chibuluma produce the bulk of the concentrates which are treated at Nkana and Chambishi Roast Leach Electrowin cobalt plants. Recently, Nchanga and Konkola concentrators began producing cobalt concentrates. Though there are variations in the mineralogy of the feed materials to these concentrators, the beneficiation techniques of the ores are similar.

Cobalt bearing minerals are depressed by the addition of sodium cyanide solution and by a high pulp pH(either 11.0 or 12.0). The copper minerals are floated off using a relatively weak flotation collector such as sodium ethyl xanthate. The cobalt minerals are then activated by reducing the pH to about 8.0 and floated with a strong and less specific collector such as amyl xanthate to obtain cobalt concentrates.

For all operating concentrators, there are losses of both cobalt and copper to the other concentrates. In practice, it is not absolutely essential to remove all the copper from the cobalt concentrates, since provisions are made to recover this copper in the copper electrowinning section of the cobalt plants. Typically a 5:1 ratio of copper to cobalt is acceptable. However, for economical reasons it is preferable to route as much copper to the smelter as possible rather than to the cobalt plants.

On the other hand, any cobalt which reports to the copper concentrates is ultimately lost to the smelter slags. It is this cobalt which should be saved and with cobalt metal currently priced at K42 000 per tonne(about £2 100 per tonne)⁴ there is clearly an incentive in improving the separation efficiency of cobalt from copper mineral during flotation.

The mechanism of separation of these two minerals by the use of cyanide and lime addition is obscure. Often, the cobalt minerals are not prevented from floating, but rather merely retarded. Furthermore, the cyanide does sometimes also depress the chalcopryrite.⁵ The problem, of separation has been under investigation by ZCCM with a view of understanding the mechanism of depression.

Preliminary investigations into the possibilities of improving the separation efficiency between copper and cobalt minerals have been carried out by the Research and Development (R&D) department of Technical Services, ZCCM.^{6, 7, 8} In all their previous studies, a reasonable good separation were achieved. Nevertheless, these studies failed to resolve the problem completely. It is possible that improved separation could probably have been attained if flotation conditions were determined from electrochemical studies. These studies would have provided a more fundamental approach to these problems of separation between copper and cobalt minerals. In many such systems, electrochemical studies form a logical basis for the understanding of the flotation characteristics of the sulphide minerals. This is because, the interaction between sulphide minerals and other components of the flotation pulp takes place by electrochemical mechanisms.⁹ The collector -mineral interaction probably takes place in the double layer. Furthermore, for sulphide minerals, the solid phase can act

as a conductor or semi - conductor and can gain or lose electrons from their conducting bands.⁹

The implication of this is that reactions where electrons are transferred between the dissolved species and the mineral do take place across the double layer and may result in chemical changes in the interacting species. These changes will generally involve anodic oxidation at the mineral surface coupled with cathodic reduction of oxygen. It is implicit from the nature of this "mixed potential" model that electrochemical techniques are indispensable to the study of the reactions at sulphide mineral surfaces. Previous studies on these minerals at ZCCM's Research and Development department had ignored these considerations. In view of these shortcomings, electrochemical techniques were employed in this study in an attempt to understand the electrochemical behaviour of carrollite and chalcopyrite. An attempt was made to elucidate the mechanism of interaction between copper and cobalt sulphides in the presence and absence of xanthate and cyanide solutions. These reagents were employed as they are the principal reagents used in actual plant practice although the basis of the separation is not completely understood. Specifically, an attempt was made to understand the mechanism of cyanide depression of carrollite and how its presence affected chalcopyrite during the process of acquiring a hydrophobic surface. The general assumption was made that flotation reagents such as xanthate and cyanide interact with sulphide minerals by electrochemical mechanisms.

Electrochemical studies involved the measurements of open circuit or rest potentials of carrollite and chalcopyrite in the presence and absence of xanthate and cyanide solutions. Open circuit potentials were then correlated to extracts from the mineral surfaces. Cyclic voltammograms of both carrollite and chalcopyrite were recorded over the pH range 4.6 to 11.0 to study the anodic oxidation of xanthate and the influence of cyanide on the oxidation process. Although chalcopyrite has been extensively studied by a number of other researchers, it was included in this work because it is usually the most common copper mineral which occurs with carrollite. Furthermore, voltammetric behaviour of many sulphide minerals can vary depending on what other components are present. The electrochemical behaviour of chalcopyrite may not therefore be necessarily the same as that reported in the literature even if the same conditions were used. Nevertheless, the results of these studies were compared to the reported behaviour of chalcopyrite in similar systems.

Although cyclic voltammetry is a useful technique in assessing the behaviour of most electrochemical systems, it requires other additional in-situ or ex-situ techniques to supplement the characterisation and the complete understanding of the mechanisms involved in these rather complex systems.¹⁰ Surface techniques are perhaps by far the most widely used to identify species formed on the mineral surfaces due to oxidation and interactions with various reagents in the system. None of these techniques were used in this work due to their unavailability.

Instead, infrared and ultraviolet spectroscopy were used to identify xanthate products on the surfaces of minerals.

In addition, bubble attachment was observed visually where possible to determine the degree of hydrophobicity. It was not possible to measure actual contact angles due to lack of equipment.

In carrying out this work, there were a number of limitations as to what could be done experimentally and how accurately the information obtained could be interpreted. The major technical drawback was the non availability of thermodynamic data on carrollite. This meant that a comparison or prediction of expected reaction products was not possible. Hence some of the interpretation of the voltammetric behaviour were based on speculative information supported by empirical observations. Until such a time that sufficient reliable thermodynamic data are established on carrollite, the results of electrochemical experiments in this area will raise doubts with regard to their validity.

2.0 ELECTROCHEMICAL SYSTEMS

2.1.0 GENERAL CONSIDERATIONS.

Electrochemistry is defined as the physical chemistry of ions in solutions and the phenomena which occur at the solid-liquid interface. Bockris and Reddy¹¹ refer to electrochemistry as being divided into two fundamental domains, ionics and electrodictics. Ionics is restricted to the behaviour of ions in solutions and examples include many familiar redox processes. Electrodictics represent the main part of electrochemistry and involves the study of charged interfaces and conditions governing the charge transfer reactions across them. Considering hydrometallurgical and mineral processing applications, electrodictics suggest the following simple relationship for a conducting solid (bulk or surface).

Electrodictics : Solid = ions in solution + electrons in the solid

An excellent example of the field of electrodictics is the study of metal corrosion in aqueous solutions.

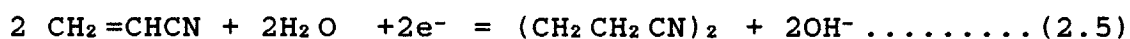
2.1.1 ELECTRODE REACTIONS AND CELL CHEMISTRY

An electrode reactions is a heterogeneous chemical process involving the transfer of electrons to or from a surface, generally a metal or a semi-conductor. The electrode reaction may be an anodic process where by a species is oxidised by the loss of electrons to the electrode. e.g





By convention¹², the current density, I for an anodic process is a positive quantity. Conversely, the charge transfer may be a cathodic reaction in which case the species is reduced by the gain of electrons from the electrode. e.g



and the current density for a cathodic process is a negative quantity.

Electrode reactions may occur in many forms. The electro-active species may be organic, inorganic, neutral or charged, a species dissolved in solution, the solvent itself, a film on the electrode surface or indeed, the electrode material itself. Moreover, the product may be dissolved in solution, a gas or a new phase on the electrode surface.

In general, an electrochemical cell will have an anode and a cathode upon which oxidation and reduction occur respectively when connected through an electrolyte and an external circuit.

The overall charge balance is controlled by the amount of these individual processes which also give the total chemical change when their effects are added.

Since electron transfer at the anodic and cathodic surfaces results in ions passing through the electrolyte and electrons through wires externally connected to the two electrodes, a convenient measure of the rate of cell reaction is by using the following equation:

$$i = AI \dots \dots \dots (2.7)$$

where

i = the external circuit current (A)

A = the electrode cross sectional area (m^2)

I = the current density (Am^{-2})

The total charge, q , passes during a time t , gives an indication of the amount of chemical change which is likely to have occurred in the cell.

Using the Faraday's law of electrolysis:

$$q = \int_0^t i dt = mnF \dots \dots \dots (2.8)$$

where q is the amount of charge required to convert m moles of a starting material to products in an electrode reaction involving n electrons per molecule of substance.

The thermodynamic requirement for a cell reaction to proceed when two electrodes are connected by an external circuit is that, the free energy change associated with the net cell reaction must be negative. However, this is not always the case and hence the need to supply energy to the system by applying a potential between the electrodes. The applied potential should be greater than the difference between the reversible potential of the cathode anode of the cell ($E^c_e - E^a_e$) which is calculated from

$$\Delta G = -nF (E^c_e - E^a_e) \dots \dots \dots (2.9)$$

where ΔG is the free energy change associated with the overall reaction. Though thermodynamically the net reaction may be favourable, the rate of the reaction will greatly be affected by the kinetics of the two electrode reactions. This requires applying an overpotential - to increase the rate of the electrode reactions. The movement of ions in solution requires extra energy. Hence the overall cell voltage required to bring about a change by electrolysis is given by

$$V = E^c_e - E^a_e - \eta_A - \eta_c - iR \dots \dots \dots (2.10)$$

where R is the resistance of the electrolyte solution between the electrodes. Equation 2.10, is very important in applied electrochemistry as in nearly all cells the overpotentials and iR terms represent energy inefficiencies which must be kept as low as possible.

To avoid the interferences on the current-potential response during an electrochemical experiment due to overpotentials and iR contributions, a cell is designed to include a third electrode, the reference electrode. This electrode is placed in luggin probe, the tip of which is positioned as close as possible to the working electrode surface. The working electrode potential is then controlled with respect to the reference electrode using a feedback circuit or a potentiostat. The principle on which a potentiostat works is shown in Figure 2.1. The important component is the operational amplifier of the potentiostat and the feedback circuit which drives the current between the working and secondary/counter electrodes while ensuring that no current passes through the reference electrode circuit. This greatly reduces the iR contribution to a small negligible value. To reduce serious polarisation of the counter electrode, it is made larger than the working electrode.

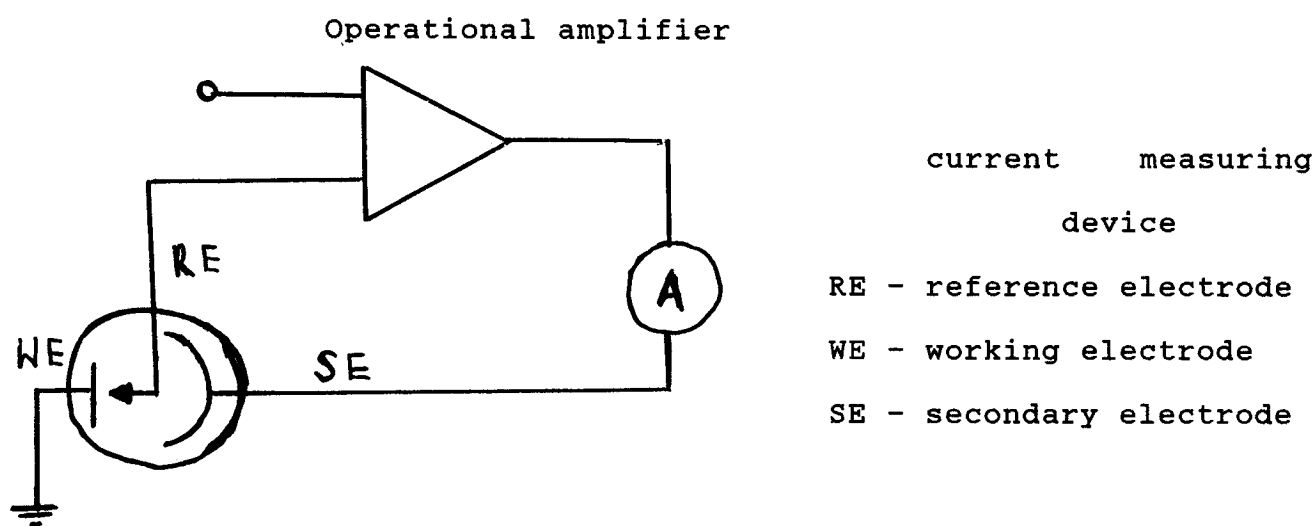


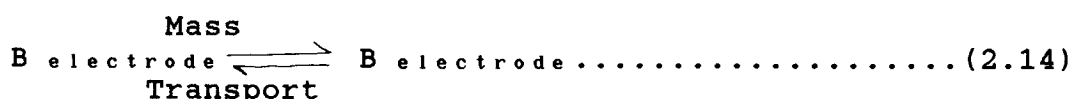
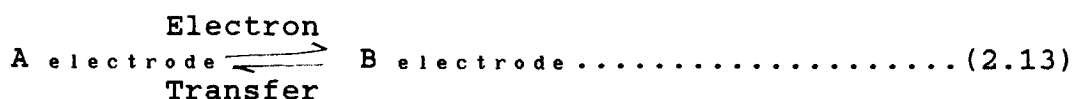
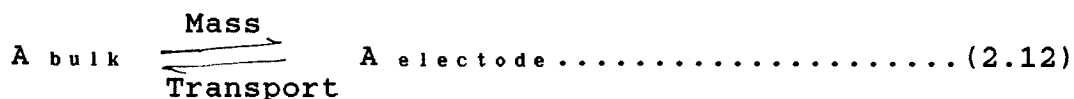
FIGURE 2.1 The principle of a potentiostat.

2.2.0 THE NATURE OF ELECTRODE REACTIONS.

The nature of electrode reactions may be so complex that they may involve many additional steps before yielding the final products. In a simple example involving initially A in solution which can be reduced to B on an inert electrode in an electro-active electrolyte as follows:



The reaction path may proceed as follows:



The reduction rate of A, which is measured by the cathodic current density, will be determined by the rate of the slowest process. This means that, in understanding of the characteristics of electrode reactions of this nature, mass transport and electron transfer processes (or other steps which may be involved) need to be understood too. Three basic steps which require consideration under these additional processes are: coupled chemical reactions, adsorption and phase formation.

2.2.1 COUPLED CHEMICAL REACTIONS

These include reactions involving electron transfer resulting in a species which may not be stable in the electrolysis medium. This may only be an intermediate product which undergoes a chemical change to form the final product. This kind of reactions are common for organic compounds. The response recorded in many electrochemical experiments is extensively changed by the chemical reactivity of the product of electron transfer. Indeed, the study of chemical reactions of intermediate either adsorbed on the electrode surface or free in the solution close to the electrode surface has become a major application of several techniques. e.g cyclic voltammetry, rotating ring disc electrode, spectro-electrochemistry and double potential step. The double potential step technique is one in which the potential E_1 is chosen so that no reaction occurs, then at time $t = 0$ a pulse is made to a potential E_2 , where the reaction of A is diffusional controlled. After a time at this potential it is stepped back to a potential E , where B is reoxidised usually to A again at a diffusional controlled rate. This is shown in Figure 2.2 below.

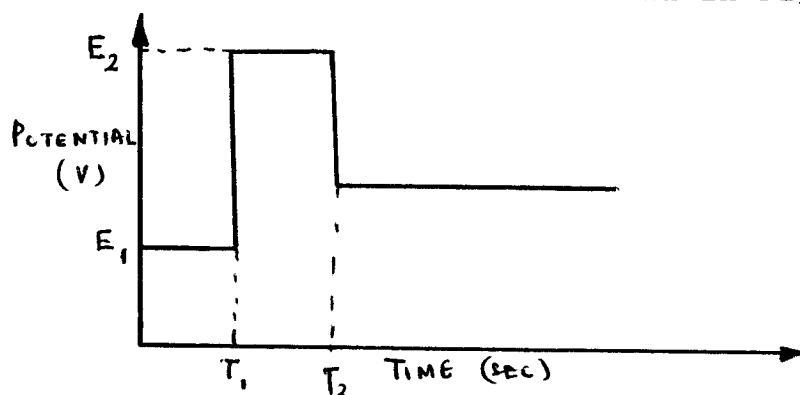


FIGURE 2.2 Potential - time profile for double potential step studies

2.2.2 ADSORPTION

In this group, steps such as those shown in sequence (2.12) to (2.14) for reactants, intermediates and /or products adsorbed on the electrode surface are the most common. These adsorbed species are very useful in electro-catalysis as they serve as lower sites. Other important applications of adsorbed species are in surface modifications of products. e.g in metal deposition and to slow down transfer reactions as in corrosion inhibition.

Adsorption usually involves the formation of some kind of bond between the adsorbate and the electrode surface. The nature of this bonding can vary from electrostatic, involving charged dipoles (e.g adsorption of amines), to that due to covalent bonding. The nature by which the adsorbate is bonded to the electrode surface will alter subsequently the electrode behaviour and, indeed the final product.

There are many examples of either neutral or charged species being adsorbed essentially unchanged or reversibly on the electrode. The extent of adsorption is usually expressed as a surface coverage. i.e the fraction of the surface covered by the adsorbate. Such adsorption must be considered as a competition both between the solution medium and the electrode for the species and hence will depend on the solvent, electrolyte,

adsorbate structure and concentration of any other species in the system as well as the nature of the electrode. If the electrode is positively charged, it will promote adsorption of anions, while a negatively charged surface will enhance cation adsorption. In addition to this, the charge on the electrode can interact with dipoles in the solution leading to their adsorption and orientation at the surface. Neutral molecule adsorption occurs most strongly where competition from charged species is minimum and this is when the electrode is at the potential of zero charge.

The adsorption of an electro-active species can affect the kinetics of a redox couple in solution most commonly by reducing it's rate. The mode for this inhibition can be envisaged as that:

- a) there is a reduction in electrode area active for electron transfer or
- b) the electron transfer must occur over a greater distance.

However, cases are also known where adsorption does catalyse electron transfer.

2.2.3 PHASE FORMATION

The electrode reaction may involve the formation of a new phase. (e.g the electro-deposition of metals in plating, refining and

winning or bubble formation when a gas is produced.) or the transformation of one solid to another. The formation of a new phase is in itself a multistep process requiring both nucleation and subsequent growth. The latter may involve the diffusion of metal adatoms across the lattice at an appropriate site. However, since reactions may involve several transfer processes, the above mechanisms may occur together or sandwiched between one another.

2.3 ELECTRON TRANSFER

Consider a system in which an electrode reaction



can occur in a cell as shown below in Figure 2.3, in which a small and inert working electrode(WE) and a large platinum electrode act as both the counter/secondary and reference electrode and both are placed in aqueous solution but separated by a glass frit. By bubbling hydrogen over the platinum electrode surface, it behaves as a normal hydrogen electrode whose potential by convention is taken as zero. The solution in the working compartment is deoxygenated and contains low concentrations C_A and C_B of the electro-active species A and B respectively. The area of the counter electrode is much larger than the working electrode to minimise polarisation of the former and iR is reduced significantly between the electrodes and solution by the use of low concentrations of the electro-active species.

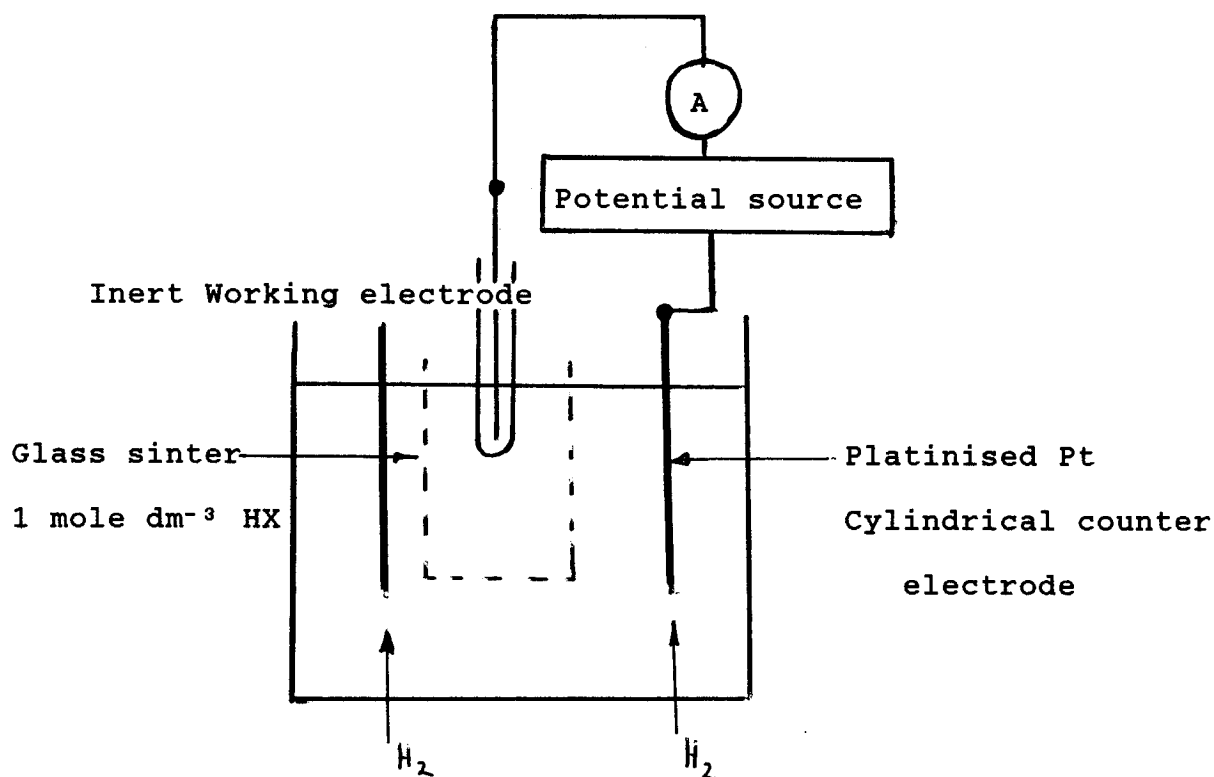


FIGURE 2.3 Schematic cell used in the development of the equations describing the thermodynamics and kinetic of electron transfer process.

For any chemical process, it is necessary to consider the thermodynamics and kinetics of the electron transfer process. If the cell potential is monitored while no current flows through the cell, the potential of the working electrode will eventually reach a steady state value indicating that the cell has attained equilibrium. The potential of the working electrode (WE) is then given by the Nerst equation:

$$E_e = E^0_e + (RT/nF) \ln C_A/C_B \dots \dots \dots (2.16)$$

where the equilibrium (reversible) potential E_e ,is related to the standard potential of the redox couple A/B , E^0_e and to the surface concentrations of A and B, C_A and C_B (assuming that the activity coefficients of A and B are unity so that concentrations rather than activities may be used in the Nerst equation). The standard potential is a particular potential when the surface concentrations of A and B are equal. As no current has passed through the cell, no chemical changes have occurred, and the surface concentration must therefore be equal to the bulk concentration C^0_A and C^0_B we may write

$$E_{cell} = E_{WE} - E_{SHE} = E_{WE} - 0$$

or

$$E_{cell} = E^0_{WE} + (RT/nF) \ln C^0_A / C^0_B$$

While no current is flowing and there is no overall chemical change in the cell, there must be a dynamic equilibrium at the surface of the WE i.e the reduction of A and the oxidation of B are both occurring , but the processes are of equal rates:

$$-I = I = I_0 \dots\dots\dots (2.18)$$

where I_0 is an important kinetic parameter characteristic of an electron transfer process known as the exchange current density and I and I are the partial current densities for the forward and reverse reactions. The negative sign refers to the sign convention that the cathodic current is negative.

If the potential of the WE is made more negative than the equilibrium of A and B, equilibrium can only be re-established when the surface concentrations of A and B have taken up the new values demanded by the Nerst equation (2.16) at the applied potential. This will require current to flow through the electrode/solution interface. In fact, a decrease in the ratio, C_A/C_B , is necessary and this can only be brought about by a cathodic current. Conversely, if the potential of the working electrode is made more positive than E_e , an anodic current should be observed. So far, all predications of $I - E$ behaviour are based on thermodynamics only. However, the current flowing at any given potential depends also on the kinetics of the charge transfer process. At any potential the measured current density is given by:

$$I = \bar{I} + \overset{\leftarrow}{I} \dots \dots \dots (2.18)$$

where \bar{I} is negative and these partial current densities are only dependent on the applied potential and the concentration of the electro-active species at the site of electron transfer:

$$\text{i.e. } \bar{I} = - n F \bar{k} C \quad \text{and} \quad \overset{\leftarrow}{I} = n F \overset{\leftarrow}{k} C \dots \dots \dots (2.20)$$

The rate constants, \bar{k} and $\overset{\leftarrow}{k}$, vary with the applied potential and from experiments, these are found to vary with potential according to the equations of the form:

$$\bar{k} = \bar{k} \exp (- \bar{n} F / RT * E) \quad \text{and} \quad \overset{\leftarrow}{k} = \overset{\leftarrow}{k} \exp (\overset{\leftarrow}{n} F / RT * E) \dots (2.21)$$

where α and β are constants which vary between 0 and 1.0 and are generally approximately equal to 0.5. These are known as the transfer coefficients for the anodic and cathodic processes respectively. For a simple electron transfer process, $\alpha + \beta = 1.0$, so that one transfer coefficient may be eliminated from any equation. Defining the overpotential η as the deviation of the potential from the equilibrium value

$$\eta = E - E_e \dots \dots \dots (2.22)$$

and noting that the exchange current density,

$$I_0 = -I_{\leftarrow} = I_{\rightarrow} \quad \text{at } \eta = 0,$$

this leads to the Butler-Volmer equation:

$$I = I_0 \left[\exp(\alpha nF/RT \eta) - \exp(-\beta nF/RT \eta) \right] \dots \dots \dots (2.23)$$

This is the fundamental equation of electrode kinetics and it shows how the current density varies with the exchange current density, overpotential and the transfer coefficients. Three limiting cases occur:

a) At high positive overpotentials $I_{\leftarrow} \gg I_{\rightarrow}$

equation 2.22 gives the anodic current density as

$$\log |I_{\leftarrow}| = \log I_0 - \alpha nF/2.303RT \eta \dots \dots \dots (2.24)$$

b) At high negative potential $I_{\leftarrow} \ll I_{\rightarrow}$

and equation 2.22 gives the cathodic current density as

$$\log |I_{\rightarrow}| = \log I_0 - \beta nF/2.303RT \eta \dots \dots \dots (2.25)$$

c) The third limiting case is applied at low values of overpotentials such as :

$$\frac{RT}{nF} \ll \left(\frac{RT}{nF} \right) \text{ and } \frac{RT}{nF} \ll \left(\frac{RT}{nF} \right)$$

the expansion of the exponential term of equation 2.22 gives:

$$I = I_0 nF/RT \exp \left(\frac{nF}{RT} \left(E - E^0 \right) \right) \dots \dots \dots (2.26)$$

Equations 2.24 and 2.25 are known as the tafel equations and are the basis of determining the exchange current density and the transfer coefficients. While these two parameters characterise completely the kinetics of an electrode reaction, the exchange current density varies with concentration of both A and B.

2.2 ELECTROCHEMICAL TECHNIQUES.

A fairly wide range of electrochemical techniques is available for electrochemists to enable the determination of kinetic and thermodynamic data related to electrode reactions/processes. The technique used varies according to the sort of information needed and the nature of the electrode process. In general, steady state techniques and potential sweep techniques are widely used. In mechanistic investigations, cyclic voltammetry is probably the most useful technique of all.

An electrochemical spectrum indicating the potential at which processes occur can be rapidly obtained, while from sweep rate dependence the involvement of coupled homogeneous reactions is easily identified. Other complications such as adsorption can also be recognised. In view of these capabilities, cyclic voltammetry is nearly always the preferred technique when studying a system for the first time, though better techniques probably exist from which more precise kinetic data can be obtained

The potential - time wave form used for potential sweep is shown in Figure 2.4 below:

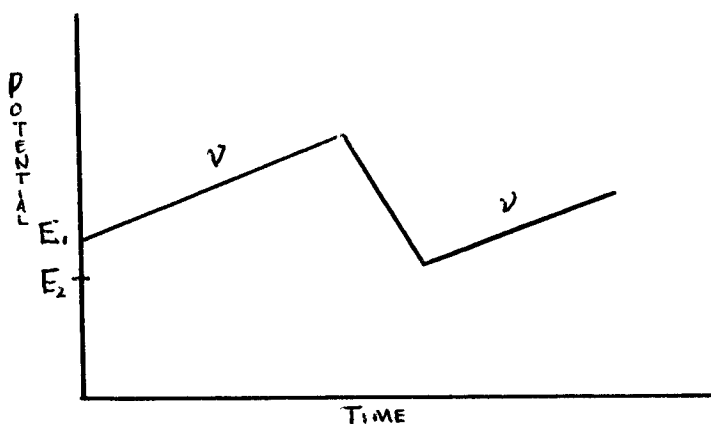


FIGURE 2.4 Potential - time profile for sweep voltammetry.

In linear potential sweep voltammetry (LPSV) the potential of an electrode is terminally varied between two potential limits E_1 and E_2 at a known sweep rate. Cyclic voltammetry (CV) is done in a similar way as linear potential sweep voltammetry, but the potential is reversed on reaching the limit E_1 back to E_2 . The sweep rate may vary from a few mVs^{-1} to a few hundred Vs^{-1} . Fast

scan rates are usually achieved by use of computers. If a system is being studied for the first time by cyclic voltammetry, usually one starts with a series of qualitative experiments in order to have a feel of the system, before proceeding to semi-quantitative and finally to quantitative studies from which kinetic parameters may be calculated. Voltammograms are usually recorded over a wide range of sweep rates for various values of E_1 and E_2 . In general, there will be several peaks and by observing how these peaks appear and disappear as the potential limits and sweep rates are varied and noting the differences between the first and subsequent cycles, it is possible to determine how the processes represented by the peaks are related. Sweep rate dependence of peak amplitudes, the role of adsorption, diffusion and coupled homogeneous chemical reactions may be identified. However, kinetic data can only be accurately obtained from the first sweep, though subsequent cyclic voltammograms frequently provide useful mechanistic information.

Other potential step techniques of immediate use include chronopotentiometry and chronoamperometry/chronocoulometry. In the former, the working electrode is subject to a constant flow of current and the potential-time response is recorded, while in the latter the electrode potential is instantaneously changed to some value and either the current-time or charge-time responses are recorded.

2.6 DESIGN OF ELECTROCHEMICAL EXPERIMENTS.

The design of electrochemical experiments varies depending on the electrode reactions to be studied and the technique to be used. The three important categories of electrochemical experimental techniques are

- a) **Equilibrium techniques** - these involve measurements done at equilibrium or perturbation from equilibrium by small amplitudes. Among these are potentiometry, amperometry, differential capacitance, measurements of surface tensions and impedance. These enable the evaluation of solubility coefficients, activity coefficients and equilibrium potentials.
- b) **Steady state techniques** - typical techniques in this category are voltammetry, polarography, coulometry and the rotating electrode method. Measurements are made when steady state is attained and the cells are specially designed to suit this purpose.
- c) **Transient techniques** - in which the system is perturbed from equilibrium or steady state conditions. The electrochemical information is obtained from the time relaxation as the system adjusts to new steady state conditions. Typical examples include double potential step, chronoamperometry, chronocoulometry and chronopotentiometry.

In all electrochemical experiments, precise control and accurate measurement of potential, charge and/or current are essential requirements of the experiments. In addition modern electrochemical investigations are supplemented with in-situ spectroscopic techniques to improve the quality of the data generated.

2.6.1.0 DESIGN OF ELECTROCHEMICAL CELLS

An electrochemical cell consists of primarily electrodes, electrolyte and the container. Commonly glass frits, separators and membranes may be incorporated to isolate the anolyte from the cathlyte. Three electrode are commonly used: the Working electrode (WE) which defines the interface understudy, the Reference electrode (RE) which maintains a constant reference potential and the Counter electrode (CE) which supplies the current. The cell and electrode design should be such that the experimental data generated are characterisitic only of the reactions at the working electrode.

2.6.1.1 WORKING ELECTRODES

Design of working electrodes vary with the problem to be studied. They could vary from small sheres and discs to metal foils or single crystals of semi-conductors or even powdered bed electrodes. In principle, they must not react chemically with the solution component.

In experiments involving species in solution usually an inert working electrode such as platinum or graphite is used. However, working electrodes can be made out of the material to be studied as long as electrical contact is possible with the material.

In both cases, whether an inert or an active electrode is used as a working electrode, it is important to establish a satisfactory pre-treatment of the electrode surface. This should give a reproducible state of oxidation, surface morphology and freedom from adsorbed impurities.

The most common pre-treatment procedure for solid electrodes is by polishing on emery paper when a coarse surface is required. To obtain a fine smooth surface a cloth impregnated with diamond particles of size down to $1.0\text{ }\mu\text{m}$ is used, followed by alumina of fixed grain size down to $0.05\text{ }\mu\text{m}$. In all cases, care should be exercised during polishing. Furthermore, measures should be instituted to ensure that polishing does not affect the kinetics of the electrode process. Usually electrodes are also chemically etched to produce a smooth surface.

A convenient way of mounting solid electrodes that readily permit polishing and other pre-treatment procedures is to seal a rod of material in an inert tube such as that only the circular cross section is exposed. Some materials can be sealed in a glass tube simply by heating under a vacuum. The seal on the glass can be achieved using epoxy resin. Plastics such as Teflon and Kel-F can also be used.

2.6.1.2 COUNTER ELECTRODE

The purpose of a counter electrode is to supply the current required by the working electrode without interference in the measured response of the cell. When this electrode involves gas evolution, it is isolated from the working compartment. The surface area must be larger than that of the working electrode and for all practical purposes the counter electrode must be inert and remain clean and free from surface poisoning.

2.6.1.3 REFERENCE ELECTRODE

The role of reference electrode is to provide a fixed potential which is constant during an experiment. The potential of the working electrode is controlled through the potentiostat and takes up a potential relative to the reference electrode.

The criterion for a half cell to be used as reference electrode is that, it should maintain a constant potential even if a few microamperes are passed through it. In theory, no current should pass through the reference electrode.

Various half electrodes can be employed as reference electrodes as long as reactants, products and the electrolytes used do not interfere with the electrodes' behaviour resulting in false potentials.

Among the widely used reference electrodes in aqueous solutions are those classified in two major groups:

- a) the fixed potential types (e.g the calomel electrode and the silver-silver halide and
- b) the indicator type (e.g the metal/metal ions electrode and the ion selective electrodes)

The reference electrode is often designed to be as compatible as possible to the system under study. In some cases, it is only possible to measure the potential of the working electrode through a salt bridge connecting the working compartment to the

reference electrode and their potentials compared to the standard hydrogen electrode (SHE)

Table 2.1 below show some of the most commonly used reference electrodes with their potentials compared to the standard hydrogen electrode.

COMMON	CHEMICAL NAME	ELECTRODE	POTENTIAL Vs.SHE
Standard calomel electrode-SCE		Hg/Hg ₂ Cl ₂ , Sat. KCl	+0.241
Calomel		Hg/Hg ₂ Cl ₂ , 1.0 M KCl	+0.280
Mercurous sulphate		Hg/Hg ₂ SO ₄ , Sat. K ₂ SO ₄	+0.640
Mercurous oxide		Hg/HgO, 1.0 M NaOH	+0.098
Silver chloride		Ag/AgCl, Sat. KCl	+0.197

TABLE 2.1 Some common reference electrodes and their potentials compared to the standard hydrogen electrode.

3.0 ELECTROCHEMISTRY OF SULPHIDE MINERALS

The electronic properties of most sulphide minerals are such that corrosion and galvanic couples are readily established in aqueous systems. This is true mainly to the p-type, n-type or metallic compounds for which the electronic transport number, $t_e = 1$. As a result of their electronic conductivity, certain minerals can participate in coupled charge transfer processes analogous to a metal corroding in aqueous solution. From a thermodynamic view point, most hydrometallurgical dissolution reactions are strongly favoured such that the reverse reaction kinetics are usually unimportant. The build up of ions in solution, however, may significantly affect the kinetics by influencing the potential at the mineral (electrode) / solution interface.

3.1.0 PROPERTIES OF SULPHIDE MINERALS.

Several investigators have presented information on the electrochemical behaviour of sulphide and oxide minerals. Sulphide minerals have received the most attention as they are recognised as the valuable source of most of non-ferrous metals. Koch¹³ has reviewed the electrochemistry of sulphide minerals. Sheuy¹⁴ has reviewed the electronic properties of both sulphide and oxide minerals. Jellinek¹⁵ has pointed out that all sulphides of the main group (i.e. non-transition) elements including

zinc, mercury and cadmium are diamagnetic insulators or semiconductors. This is because, in terms of the simple band structure model, the valence and conduction bands are respectively filled and emptied and do not overlap. In the transition metal sulphides, the electronic structure and hence electrical and magnetic properties are complicated by the presence of the d electrons.¹⁶

Table 3.1 below shows resistivity, electronic and structural information for selected sulphide minerals. The covalent character of most sulphide minerals provides non-localisation of charge resulting in appreciable intrinsic electronic conductivity. The ability of many sulphide minerals to form non-stoichiometric compounds results in increased conduction via electron holes or excess electrons. Oxide minerals, however, are more ionic in nature and usually have higher resistivities as compared to sulphate.

NAME	FORMULA	RESISTIVITY OHM-M	USUAL CONDUCTOR TYPE	CRYSTAL STRUCTURE	IONIC STRUCTURE
Bornite	Cu_5FeS_5	$10^{-3} - 10^{-6}$	p	Tetragonal	$(\text{Cu}^+)_5\text{Fe}^{3+}(\text{S}^{2-})_4$
Chalcocite	Cu_2S	$10^{-2} - 10^{-5}$	p	Orthorhombic	$(\text{Cu}^+)_2\text{S}^{2-}$
Chalcopyrite	CuFeS_2	$10^{-3} - 10^{-4}$	p	Tetragonal	$(\text{Cu}^+)\text{Fe}^{3+}(\text{S}^{2-})_4$
Carrollite	CuCo_2S_4	10^{-4}	metallic	Cubic	$\text{Cu}^{2+}(\text{Co}^{3+})_2(\text{S}^{2-})_4$
Pyrite	FeS_2	$10^{-2} - 10^{-3}$	n & p	Cubic	$\text{Fe}^{2+}(\text{S}^{2-})_4$

Table 3.1 Electronic and structural properties of selected sulphide minerals.

A fundamental property of semi-conducting minerals is the characteristics "rest potential" corresponds to equilibrium (no net anodic or cathodic currents) electrode potential of the minerals of interest.

Table 3.2 below show values of rest potentials for the indicated sulphide minerals.

MINERAL	REST POTENTIAL VOLTS V.s	CONDITION SOLUTION	TEMPERATURE °C	REFERENCES
FeS_2	0.63	1.0 M H_2SO_4	25	17,18
Cu_2S	0.44	1.0 M H_2SO_4	20	19
PbS	0.28	1.0 M H_2SO_4	20	19
ZnS	-0.24	1.0 M H_2SO_4	20	19
CuFeS_2	0.54	1.0 M H_2SO_4	20	20

TABLE 3.2 Rest potential of sulphide minerals.

It is important to remember that any mineral electrode system will establish and maintain a certain equilibrium potential that depends not only on the solution composition, but also on the composition of the solid phase. This was found to be the case by Koch and co-worker²¹ for the electrochemical oxidation of Cu_2S to CuS in an aqueous acid solution. The change in the measured rest potential was explained on the basis of the sequential formation of a series of CuS compounds each with its corresponding potential.

Wells^{22, 23} carried out an electrochemical study of study minerals. His results²³ confirmed that these minerals have different rest potentials when they are present in different concentrations. Sato²⁴ suggested that the electrode potential of sulphide minerals was controlled by the first -step reaction of the oxidation mechanism for the sulphide mineral in oxidising solution and by the reduction mechanism in a reducing solution. More detailed discussions on rest potentials and mixed potentials are presented in subsequent sections.

3.2 OXIDATION OF SULPHIDE MINERALS

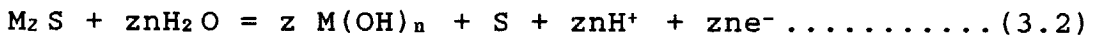
Interaction between the constituents of sulphide minerals in flotation systems depends on the prior or simultaneous oxidation of the minerals. The potential difference at the mineral-solution interface is the most important parameter because it determines the reactions that may occur and the rates at which they occur. Thus the floatability of sulphide minerals, excluding those which are naturally hydrophobic, is greatly influenced by the degree of oxidation of the mineral surface. Recently, attention has focused on the electrochemical behaviour of sulphide minerals in neutral and alkaline solutions, which generally the most relevant conditions in practical flotation.

Various investigators have used different electrochemical techniques to further their understanding of the electrochemical behaviour of different sulphide mineral electrodes in solutions of different compositions. Linear Potential Sweep Voltammetry (LPSV) which is perhaps the most widely used technique has successfully been applied to pyrite^{25, 26}, galena^{27, 28}, chalcopyrite²⁹, chalcocite³⁰ and pyrrhotite²⁶ in detailed studies.

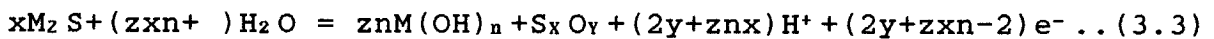
It has generally been postulated that the initial oxidation of simple sulphide minerals in acid solutions correspond to a reaction of the type³¹:



with its equivalent in neutral or alkaline solutions as :



Further oxidation may lead to the production of oxy-sulphur species as follows:



Some form of equation (3.3) is generally the thermodynamically favoured oxidation reaction but for many sulphide minerals it

does not proceed rapidly beyond the production of sulphur (i.e reaction 3.2). This sulphur remains on the surface for periods longer than those associated with normal flotation separation. For other sulphide minerals, the production of thiosulphates and sulphates by reaction (3.3) does proceed at a reasonable rate but usually only at overpotentials of varying magnitudes.³²

Oxidation leading to sulphur-like products is usually considered to be critical in rendering some sulphide minerals such as chalcopyrite^{29,33} and galena^{28,34} naturally floatable (self induced floatability). However, oxidation leading to further oxidation products such as sulphates deteriorates this self induced floatability property. The nature of the oxidation products is important especially where they are soluble. Under such conditions they will be expected to dissolve in the bulk of the solution under well stirred conditions as those in flotation cells and will not be available for reverse reaction when the system is subjected to a reducing environment. This would be expected of oxy-sulphur species like those expected in reaction (3.3).

The insoluble ones such as those expected in reaction (3.2) will be readily available for reduction to reverse the forward reaction. The appearance of metal species during reduction in the

former case will adversely affect the subsequent mineral-collector interaction. Electrochemical methods alone can not be used to identify which kinds of products are formed and let alone whether they are insoluble (in which case remain on the mineral surface) or are soluble (diffuse in the solution). This requires the use of other more specific techniques of surface analysis.

Surface oxidation studies of sulphide minerals are very important as nearly all sulphide minerals undergo oxidation on slight exposure to air. Infact, case have been cited where fine grained iron sulphide minerals oxidises rapidly in air, e.g dust explosions³⁵ and hot underground problem³⁶⁻³⁸ due to spontaneous combustion that have occurred during mining. Bornite tarnishes rapidly in air to give variegated blue and purple colours. Other sulphides are similarly reactive but passivate as oxidation products develop on the surface of the minerals.

3.2.1 REST POTENTIALS

Rest potentials or " open circuit " potentials are they are vaguely referred to, provide valuable information on the identity of the reactions occurring at the electrode/solution interface when interpreted properly. One approach is to compare the

measured rest potentials with the equilibrium potentials for various processes derived from thermodynamic data.

It is usual to express the various equilibrium potentials for a system in the form of an E_h -pH diagram as derived by Pourbaix³⁹ for metal systems and adapted for minerals by Garrels and Christ⁴⁰. E_h is the potential, E referred to the standard hydrogen electrode. Figures 3.1, 3.2 and 3.3 show such diagrams for simplified cobalt - sulphur - water, copper - sulphur - water and copper - iron - water systems respectively. The equilibrium lines represent processes involving dissolved species corresponding to concentrations of $10^{-6}M$ the minimum concentrations at which the reactions need to be considered. These diagrams are electrochemical phase diagrams and gives the conditions of potential and solution composition within which a phase is thermodynamically stable.

The use of equilibrium potentials to determine electrochemical reactions or the composition of solid surfaces assumes that for an anodic reaction to take place, the measured rest potential of the electrode with respect to a reference electrode must be above the equilibrium potential for that process. The reverse situation is true for the cathodic reaction to occur. Since different reactions have different equilibrium potential it is, in principle, possible to distinguish between these reactions from the knowledge of measurements of rest potentials of

sulphide mineral electrodes.

This approach was used by Allison et al ⁴¹ and by Goold and Finkelstein⁴² to survey a range of sulphide minerals in solutions of various thiol collectors. Rest potentials were correlated with of reactions products extracted from the mineral surface. Though useful information can be obtained from comparison of rest potentials to equilibrium potentials calculated from thermodynamic data, care must be exercised in identifying surface reaction in this way. Two limitations need to be borne in mind. Firstly, calculated equilibrium potentials are derived from thermodynamic properties of bulk phases under conditions where multilayers are possible. Flotation, however, generally occurs after the formation of sub monolayers and the thermodynamic properties of such surface species can differ significantly from those of the bulk phases. The second problem with the application of thermodynamic data arise from the irreversibility of many reactions involving sulphide minerals. For instance, reactions in which sulphate is formed usually require considerable overpotentials and other products such as sulphur and thiosulphates appear under conditions in which sulphate is a stable species. Thus, the process may occur because it has a greater rate rather than that it has the most favourable

equilibrium potential. This particularly true for complex reactions for which the potential has not been determined experimentally. It is, therefore, not necessary true to conclude that a reaction will proceed simply because the measured rest potential is different from the equilibrium potential. This prompted Wark⁴³ to emphasise the importance of supporting thermodynamics with kinetic evidence as the former provides only half the story.

3.2.2 MIXED POTENTIAL MODELS OF COLLECTOR ADSORPTION

Sulphide minerals can be floated in a similar manner as oxide minerals with long chain collector ions which adsorb in the double layer. However, short chain xanthates (dithiocarbonates), which were introduced as collectors for sulphide minerals in 1925⁴⁴, are much more selective and are reasonably inert for most common gangue minerals. However, the mechanism of flotation with thiol collectors differs from that of ion adsorption as for oxide minerals, but may involve oxidative adsorption processes at the mineral surface.

Sulphide minerals in general display good electronic conductivity and can hence sustain coupled anodic and cathodic processes on their surfaces. It was recognised as early 1830⁴⁵ that corrosion type of reactions could play an important role in determining the behaviour of sulphide mineral ores in nature. However, it was not until the middle of this century that the first electrochemical mechanism of sulphide mineral - collector interaction was postulated.

A number of theories have since been advanced to account for the hydrophobic surface generated during the interactions between the sulphide mineral and the collector. Taggart and co-workers⁴⁶ developed a theory based on chemical reactions. Wark⁴⁷ and Sutherland and Wark⁴⁸ drew attention to the fact that, that model was inconsistent with the established values of the solubility product of the species involved. They believed that the interaction of thiol collectors with sulphide minerals should be considered as an adsorption process. To support this concept, it was shown that competitive adsorption between xanthate and hydroxide ions could be explained in terms of the Barsky relationship between the upper pH limit of flotation and the collector concentration.

Cook and co-workers⁴⁹ pointed out that adsorption of collector ions would lead to the surface of the mineral being highly charged which is not the expected condition for flotation to take place (hydrophobicity). This led them to propose a model by which the undissociated acid form of the collector is adsorbed rather than the ion. This possibility was observed as early as 1934 by Wark and Cox⁵⁰. However, Sutherlands and Wark⁴⁸ suggested that co-adsorption of ions of opposite sign was probably a better model.

Salamy and Nixon⁵¹ suggested a third model by which a neutral surface could be generated if a solid is an electronic conductor such as sulphide minerals. Due to the presence of electrons or holes in the lattice surface, reactions involving oxygen could easily occur. This model was supported by investigations of Plaskin and Bessonov⁵² who showed that oxygen was essential for sulphide mineral flotation with xanthate collectors.

The interaction between collector and oxygen at the mineral surface takes place by separate electrochemical reactions which proceed simultaneously. The anodic oxidation reaction involves the collector transferring electrons to the mineral surface and these electrons are transferred back to the solution phase by the cathodic reduction of oxygen.

Wark's adsorption model would be given by the anodic process:



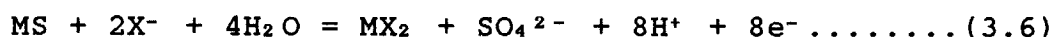
and that of oxygen reduction as:



where X^- represent xanthate ion.

A schematic representation of the possible electrochemical reactions in which some form of reaction 3.4 is the anodic process is shown in Figure 3.4.

Taggart's chemical mechanism involved an anodic process of the type:



where MS represent a sulphide mineral. This reaction can proceed either in a single step (Figure 3.4(b)) or via separate processes occurring at different times (Figures 3.4 (c) and 3.4 (d)). This may involve one reaction in which the sulphide mineral surface oxidises to sulphate due to exposure to air and this species could exchange with a xanthate ion when added. Thiol collectors could also oxidise to dithiolate as was recognised by Salamy and Nixon ⁵¹ as follows:

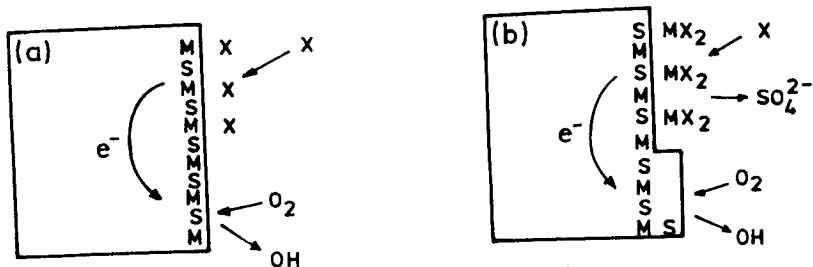
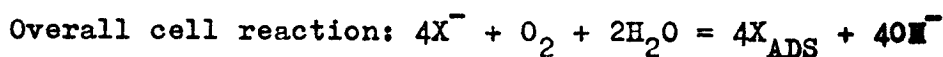
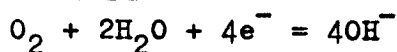


An anodic reaction such as (3.5) or (3.6) could take place on the surface of the mineral particle if the potential is such that both the anodic process and the cathodic reduction of oxygen proceed at finite rates. Such a potential is called the " Mixed potential".

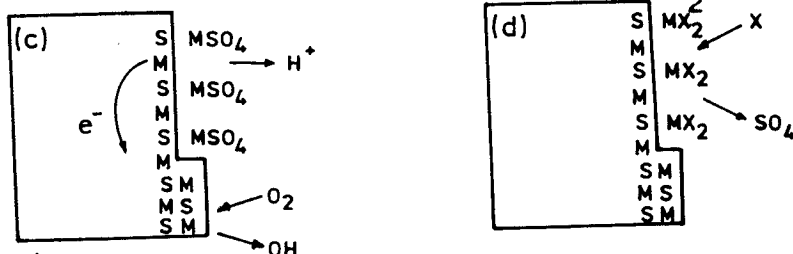
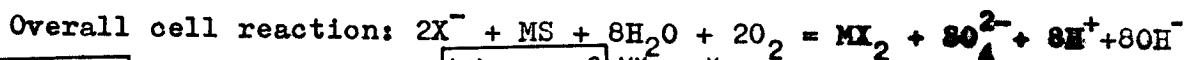
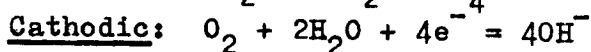
a) Anodic



Cathodic



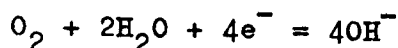
b) Anodic



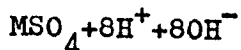
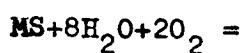
c) Anodic



Cathodic



Overall cell reaction:



d) Ion exchange

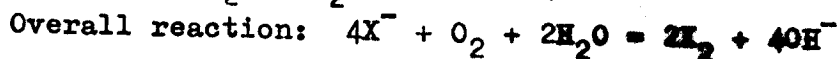
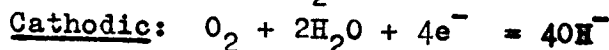
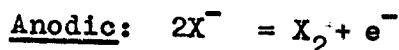
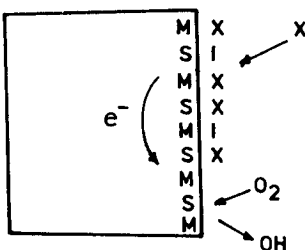


Figure 3.4: Schematic representation of the mixed potential mechanism for the interaction of thiol collectors with sulphide minerals in which the anodic process is (a) chemisorption, reaction (3.4), (b) reaction to form a metal collector compound, reaction (3.6), (c & d) reaction occurring in two stages. (c) oxidation of the mineral and (d) ion exchange with the collector and (e) formation of dio-thiolate reaction (3.7).

In considering the mixed potential model, it is important to realise that the most likely situation is that, this potential will be determined by a number of reactions. The requirement for this is that the sum of the rates of cathodic and anodic reactions be equal to each other.

The mixed potential model introduced a new significance to electrode potentials in flotation systems. This potential determines the identity of the reactions that take place at the mineral surfaces and the rate of these processes. Previous considerations of the importance of the potential across the mineral-solution interface⁵³ has emphasised its effect on the electrocapillarity phenomena associated with the electrical double layer and ion adsorption.

Poling⁵⁴ pointed out that the xanthate ion appears to be specifically adsorbed in the double layer at the sulphide mineral since the zeta potentials of sulphide minerals displayed a negative shift when xanthate ions are present in solution. This raised doubts to the validity of the model based on neutral species adsorption. However, xanthate ions can be present in the

dounele layer without contributing to the hydrophobicity. This was found to be the case for platinum by Woods⁵⁵. The strong attraction for water of charged polar head groups of amphillic collectors is known to influence the neighbouring CH₂ groups such that their contribution to the hydrophobic effect is substaintially diminished.⁵⁶ Thus only when the charge on the short chain xanthate is removed by chemisorption, by bonding to the surface of the metal atom, or by dimerisation to dixanthogen, will hydrophobic interaction between the hydrocarbon chain and water be significant. This view point is supported by the fact that alkali xanthates are readily soluble, while dixanthogen are only slightly soluble in aqueous solutions and behave as typical hydrophobic species.⁵⁷

Other experimental evidence available in the literature by Tolun and Kitchner⁵⁸, Ahmed⁵⁹, Gardener and Woods⁶⁰ support the mixed potential model. The most remarkable breakthrough in this area was when it was demonstrated that flotation in the presence of xanthate occurs at about the same potential when air is used as that obtained in a nitrogen atmosphere when the potential is controlled by an external source.^{60, 61}

3.2.3 CATHODIC REDUCTION OF OXYGEN AT SULPHIDE MINERAL SURFACES

The reduction of oxygen is the most important reaction in a number of metallurgical processes of interest involving sulphide minerals. In addition to mineral flotation, it plays a role in the weathering of sulphide minerals in nature^{24, 62} in oxidation during mining, storage and transportation⁶³ and in a variety of leaching techniques.⁶⁴

Sulphide minerals have been shown by a number of workers^{58, 65, 66, 67, 68, 69, 70, 71, 72, 73} to exhibit electrocatalytic activity for the oxygen reduction. Beigler et al⁷⁰ and Rand⁷¹ carried out comparative studies on sulphide mineral activity and noted that the activity for oxygen reduction varies quite remarkably between various sulphide minerals studied in alkaline solutions, the media most relevant to sulphide mineral flotation. Pyrite was found to be most active although only slightly less than gold or noble metals. The thiospinel, linneaite (Co_3S_4) has been found by Ahmed⁷² to be the most active than pyrite.

Detailed studies of oxygen reduction on pyrite⁵⁷ have shown that the reaction proceeds through the intermediate formation of hydrogen peroxide:



The presence of hydrogen peroxide and its influence have not been well established in detail. However, there are two mechanisms by which peroxide could influence flotation response. First, it reacts with xanthate to form other compounds with different collector properties⁷³ such as perxanthates. Secondly, it could catalyse oxidation of the mineral. This leads to the notion that oxygen may not be essential for the flotation of sulphide minerals with thiol collectors. It is the species which can undergo reduction at potentials of xanthate oxidation that are required. Oxygen may play the role of keeping those oxidants in their oxidised form.

3.2.4 DEPRESSION OF FLOTATION.

The separation of one sulphide mineral from another in a complex ore depends on the ability to selectively depress chosen components. The mode of depression may be complex. Electrochemical studies have provided useful information which has extended the knowledge of the mode of action of depressants. Furthermore, the mixed potential approach for sulphide mineral flotation has provided an eye opener to various ways in which

depression of flotation could occur.

Adsorption of a collector can be prevented as a result of one or more of the following mechanisms:

- a) Enhancement of the anodic oxidation of the mineral so that it occurs more rapidly than the collector oxidation.
- b) The introduction of another anodic reaction which is more favourable than the collector oxidation.
- c) Inhibition of the anodic oxidation of the collector.
- d) Formation of surface species which prevent collector adsorption on the mineral surface.
- e) Reduction of oxygen activity in the system, and
- f) Prevention of cathodic reduction of oxygen.

Janetske et al²⁵ showed that the depression of pyrite by alkali was by the first mechanism. In their findings they were able to relate the critical pH and the collector concentration which will result in the formation of a hydrophobic surface. At low pH, the oxidation of the collector occurs at lower potentials than that of pyrite. The mixed potential of the system is then that of oxidation of xanthate to dixanthogen and oxygen reduction while the oxidation of the mineral occurs at higher pH values. From

various experiments, they came up with an expression similar to the Barsky relation which was first used by Gaudin⁷⁴ for the critical pH for flotation with concentration of collector for various sulphide minerals.

Cyanide was found to change the potential of the mercury surface so that adsorption of xanthate was not possible. The depression of chalcopyrite by cyanide was observed to be due to changes in its potential in a similar way to that of mercury so that xanthate adsorption could not occur.⁷⁵ A similar observation was noted by Heyes and Trahar⁷⁶ that the presence of cyanide ions decreased the potential of the pulp to values below the flotation threshold. Their conclusion was that strong complexing with copper was not the reason for depression since the presence of a strong complexing agent as such EDTA was not effective. Reduction of Cu(II) to Cu(I) was considered as an important factor in the depressant action of cyanide.

The depression of chalcocite by cyanide was no exception. The presence of cyanide ions decreased the potential of the chalcocite electrode and copper ions in solution.⁷⁷ Thus, cyanide enhances the anodic dissolution of the mineral, but its depressing capability decreases as more of it is complexed with increasing amounts of dissolved copper. Hence, conditioning with cyanide could significantly change the surface stoichiometry of

the mineral through the promotion of copper dissolution in the case of chalcocite and chalcocite.

However, Agar et al⁷⁸, found that the depression of other sulphide minerals like in the pentlandite/pyrrhotite/chalcopyrite system was rather different from the mechanism of the copper minerals. Whilst floatability of chalcopyrite in the presence of cyanide recovered with time, this was not the case with pentlandite or pyrrhotite.

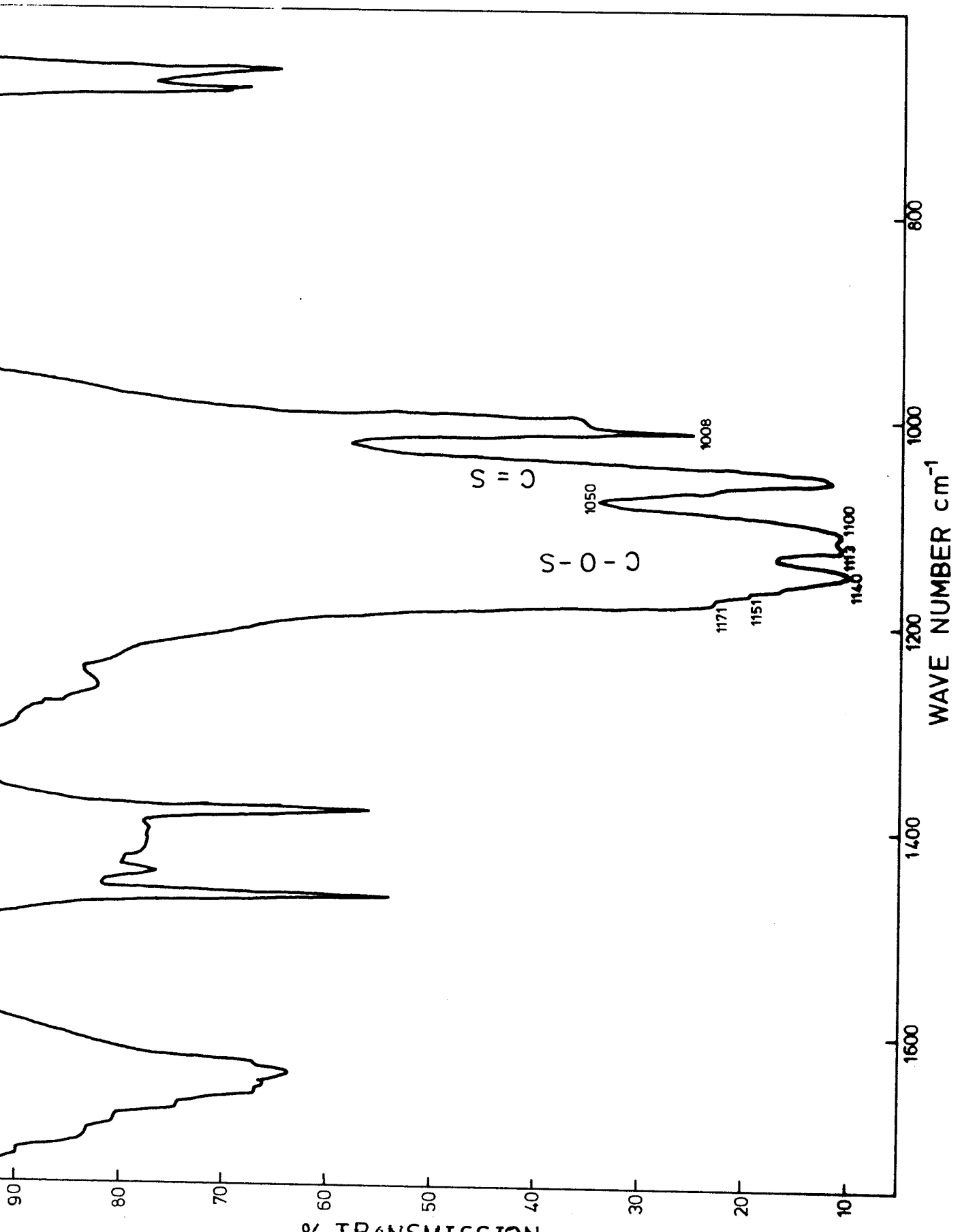
4.0 EXPERIMENTAL PROCEDURE AND EQUIPMENT

4.1 REAGENTS AND SOLUTION PREPARATION.

All reagents used in the experiments were analytical grade reagents, except for potassium ethyl xanthate and amyl xanthate which were of commercial grade. These were purified by dissolving in a minimum amount of acetone and crystallised twice from acetone with the addition of di-ethyl ether. The resulting material was filtered and washed with ether, vacuum dried and stored in a refrigerator.

Di-ethyl dixanthogen was prepared by reacting purified potassium ethyl xanthate with stoichiometric amounts of potassium iodide solution. The dixanthogen was extracted into iso-hexane and subsequently recovered by evaporating the iso-hexane at 60°C. Infrared spectra for the purified ethyl xanthate and dixanthogen obtained using a potassium bromide (KBr) pellet are shown in Figures 4.1 (a) and 4.1 (b) respectively. Their structures are shown below in Figures 4.2 (a) and 4.2 (b). The spectra of ethyl xanthate and dixanthogen compared well with the reported spectra in the literature.^{41, 42} This was assumed to indicate that the obtained reagents were reasonably pure.

Figure 4.1 (a) Infrared spectrum of potassium ethyl xanthate ($\text{C}_2\text{H}_5\text{COS}_2\text{K}$)



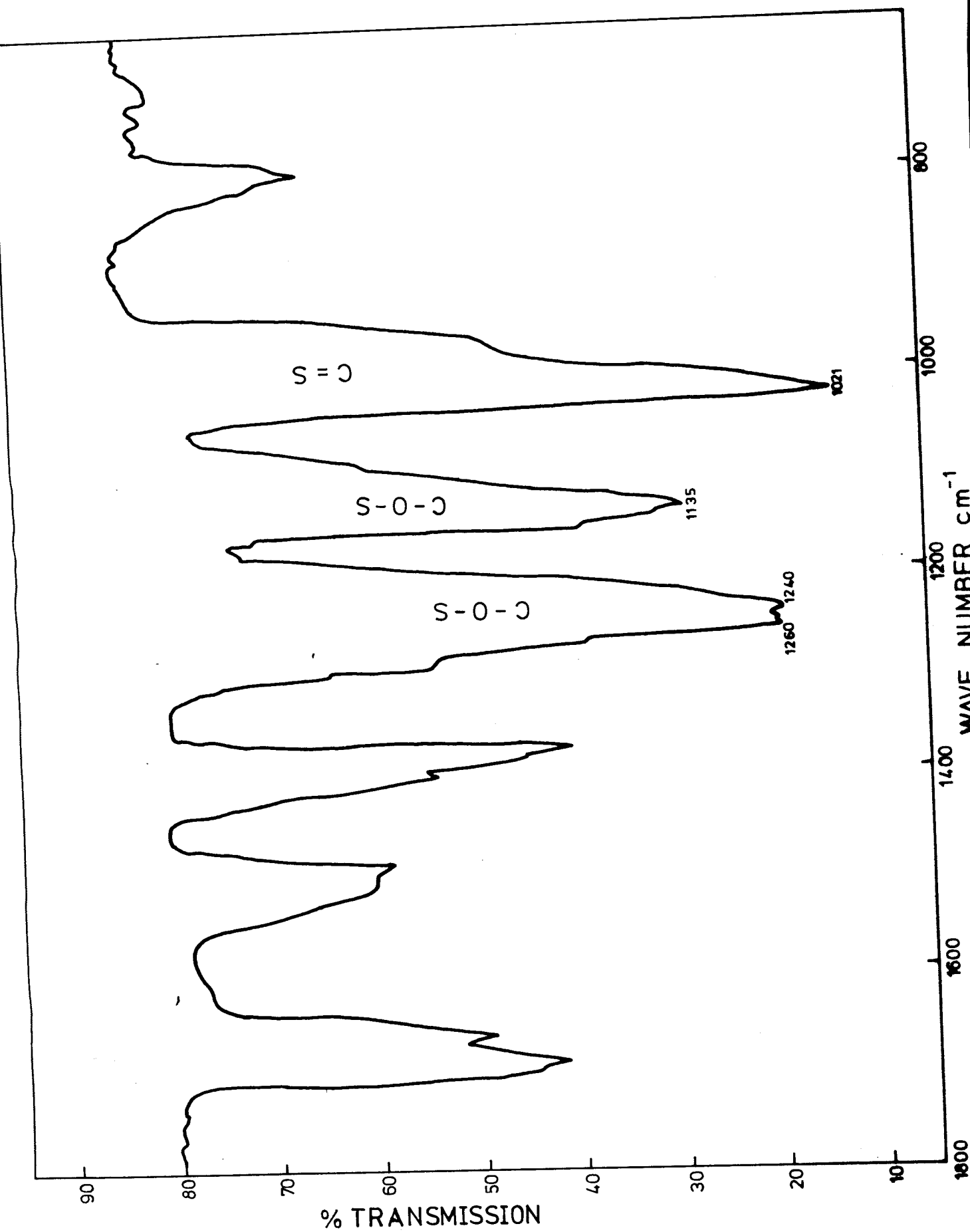
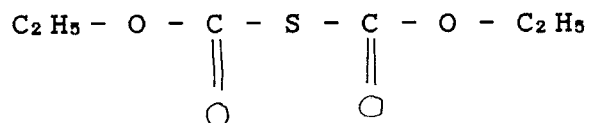


Figure 4.1 (b): Infrared spectrum of di-ethyl dioxanthogen.

The composition of the electrolyte of different pH solutions employed in this work are similar to those used by Gardner et al^{7,9} as shown in the Table 4.1

pH	Electrolyte composition
1.0	0.1 M HClO ₄
4.6	0.05 M CH ₃ COOH + 0.05 M CH ₃ COONa
7.0	0.025 M KH ₂ PO ₄ + 0.025 M Na ₂ HPO ₄
9.2	0.05 M Na ₂ HPO ₄
11.0	0.025 M NaHCO ₃ + 0.023 M NaOH
13.0	0.1 M NaOH

Table 4.1 Composition of the cell electrolytes used in all experiments.



It should be noted that when xanthate was used in the experiments, the solution for pH 11.0 was obtained by adding a few drops of 0.1M NaOH to the borate buffer (pH 9.2).

Doubly distilled water with a conductivity of 1×10^{-6} mho was used in making the buffer solutions. When xanthate and cyanide were needed, thoroughly degassed buffer solutions with high purity 'oxygen free' nitrogen were used to make stock solutions which were kept air tight before use. Fresh stock solutions were made immediately before use.

Chromic acid was used to clean all glassware. The glassware was washed 5 to 6 times with tap water and then 3 to 4 times with doubly distilled water and left to dry in an oven.

4.2.1 ELECTRODES.

Carrollite and chalcopyrite electrodes were prepared from massive specimen of the minerals obtained from the Technical Services (TS), a research unit of Zambia Consolidated Copper Mines Limited (ZCCM). in Zambia.

The mineral phase quantification of a carefully prepared mounted polished section of carrollite done by point counting on a modified microscope stage with a swift Automatic Point Counter Model F415C showed that its composition was 89.6% CuCo_2S_4 , 8.2% CuFeS_2 and 2.2% gangue minerals mainly silicates. The mineral consisted of coarse grained carrollite crystals with intergrowths of siliceous gangue. Chalcopyrite was distributed in the matrix at assorted spots. Electron microprobe analysis using a Jeol JXA-50A Electron probe micro Analyser and X-ray diffraction by a phillips Diffractometer revealed that there was also traces of linnaeite (Co_3S_4) and that chalcopyrite occurred in association with pyrite. Solid substitution of copper for cobalt was also readily identified. This is expected since there is complete solid solution between linnaeite and carrollite.⁸⁰ This could suggest that carrollite may be represented by a chemical formula of the form:



where x can vary from 0 to 1.0.

Using the point counting technique, chalcopyrite was found to comprise of 75.1% CuFeS_2 , 19.5% FeS_2 , 1.7% Cu_2S and 3.7%

gangue. Electron micro probe analysis revealed the presence of bismuth sulphide and a bismuth-silver sulphide disseminated in isolated spots in the main chalcopyrite matrix. Minor amounts of galena were also detected by this method. X-ray diffraction showed only the presence of pyrite.

4.3 ELECTRODE FABRICATION

The preparation of the electrode for carrollite from a massive specimen of the mineral involved boring a 5mm diameter, by 8mm in length core of the mineral at a carefully selected portion avoiding as much as possible inclusions cracks or voids. Because of the coarse crystal structure of the specimen, conventional methods of cutting a core failed due to the specimen cracking. Spark erosion was adapted for this mineral to get a strong compact core. The procedure was as follows:

A carrollite block specimen was sliced in 8mm plates using a diamond saw. One of these plates was carefully clamped on a V block and the entire assembly was put in a bath of kerosene. A 6mm internal diameter copper borer was then fitted in the chuck of the spark eroding machine. When the power was switched on, the borer lower automatically until it was almost touching the block at a selected portion. A spark developed on the tip of the borer and the mineral resulting in slow erosion of the mineral to eventually give a mineral core of diameter just slightly smaller

than the internal diameter of the copper borer. The kerosene bath cooled the specimen as heat was generated during this operation. The resulting cores were then washed in petroleum ether and left to air dry for a day. The cores were washed thoroughly with distilled water on the following day and then left to dry in an oven for about two hours. The mineral cores were then cleaned by gentle grinding/polishing on a P1200 sand paper before attaching to the copper conductor. The copper conductors were made as 5mm diameter cores from a 10mm thick copper plate. On the flat surface end, 6mm deep holes were drilled using a 3mm diameter drill bit , followed by internal threading. The copper cores were then attached to mineral cores on the end without threads using silver-loaded epoxy resin for electrical conduction. The assembly gave a strong bond after two days. After smooth polishing of the surface the assembly was encapsulated in araldite epoxy resin in 30mm diameter mounts and left to harden for two days.

After two days, the mounted samples were then machined down to fit in a teflon holder specially designed to expose only one flat ground surface of the electrode to the test solution. A stainless steel rod was then passed through the teflon and screwed onto the copper as shown in Figure 4.1 (a complete assembly of the electrode.) The teflon on the top was designed to fit securely in the tapped ground fits of the cell cap. The bottom teflon holder could easily slide up and down to facilitated any adjustments.

The exposed mineral surface area was 0.196cm^2 . In using spark erosion, the possibility of overheating the is quite high and this could probably result in effects that could change the subsequent behaviour of the mineral electrode. However, it was assumed that the kerosene provided a sufficient cooling effect to avoid overheating the mineral. Under the circumstances, this method was the most appropriate which gave an intact solid (compact) electrode.

In the case of chalcopyrite, it was easy to drill out a core from the mineral specimen using conventional means. A hand drilling machine fitted with a water jacketed 6mm diameter borer was used. Resulting cores were cleaned after drying in an oven. Cleaning and mounting were done in a similar way as was in the case of carrollite using silver loaded epoxy resin and subsequently in araldite resin. After hardening, the resulting mounted specimens were machined similarly to carrollite samples so as to fit in the same steel rods and teflon holders. This facilitated easy removal of a specimen/mineral after experiment in order to fit the other mineral to be studied.

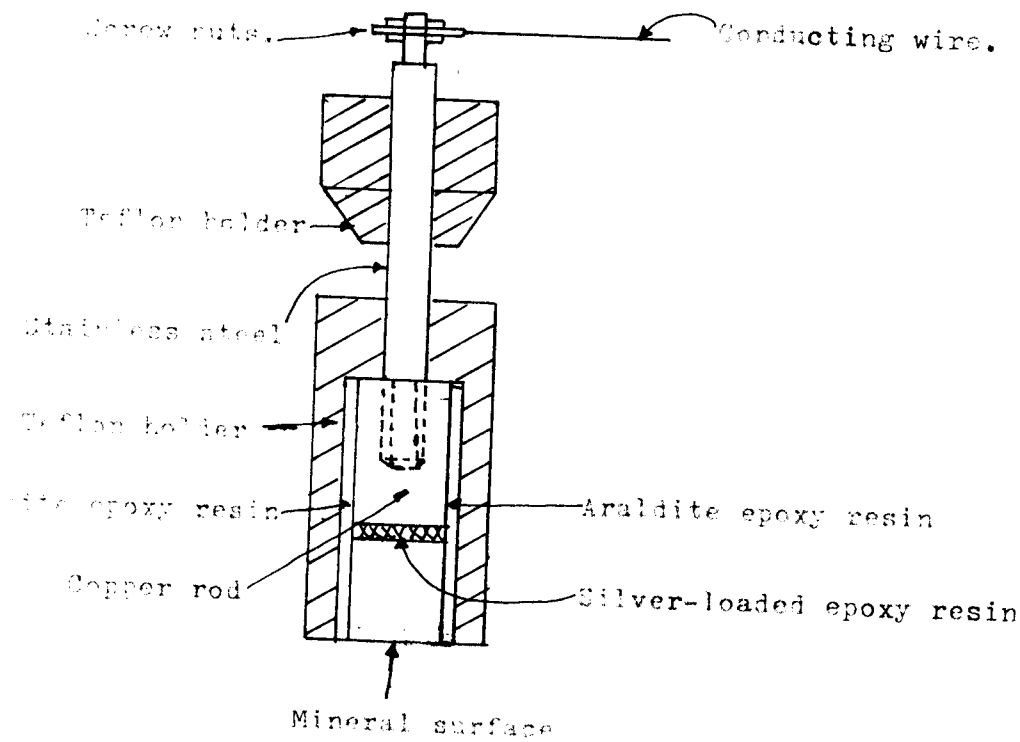


FIGURE 4.1 Electrode assembly.

Nuts

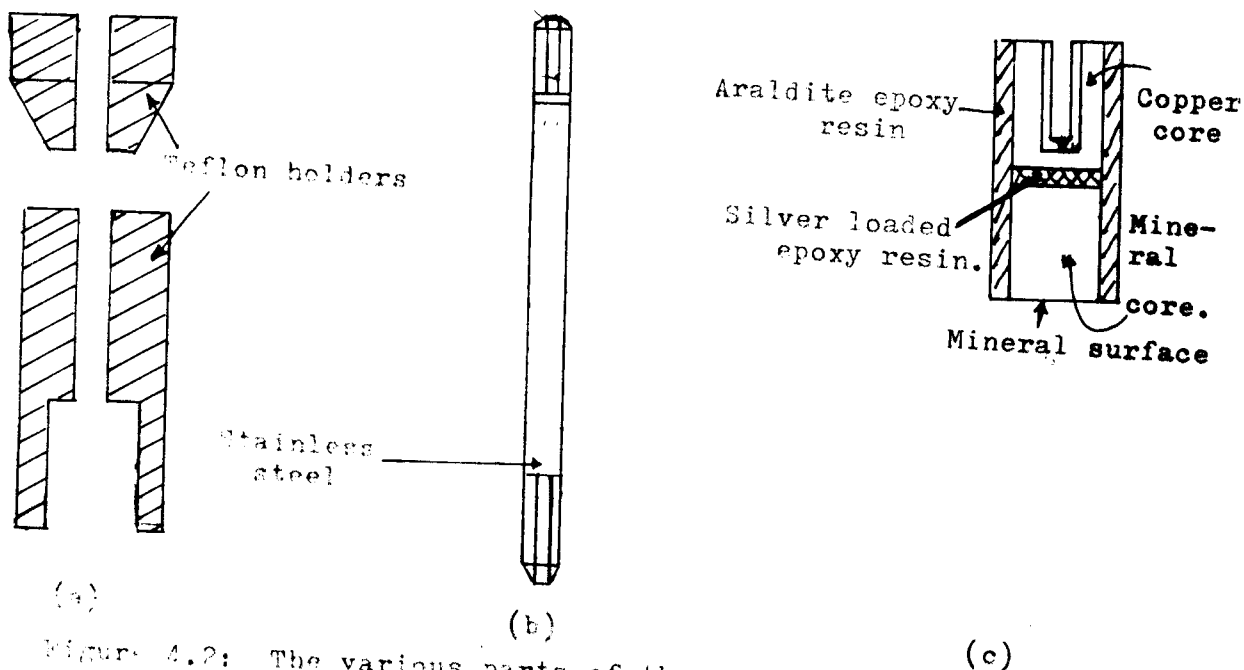


Figure 4.2: The various parts of the electrode assembly.

4.4 ELECTROCHEMICAL APPARATUS AND METHOD.

A 150 millilitre glass cell was used in all experiments. It had five holes on top through which a working electrode (mineral electrode), a counter electrode (1.0 cm² platinum sheet), a reference electrode, a gas inlet and outlet and a thermometer could be fitted through ground joints to give an airtight atmosphere in the cell.

Initially a silver wire dipped in silver chloride saturated with potassium chloride was used as a reference electrode. This was found to give inconsistent values of potentials when xanthate was added. The membrane (made of vycol frit) was found to be blocked with possibly xanthate precipitates. Subsequently, the saturated calomel electrode was used as a reference electrode. To avoid any possible xanthate precipitates blocking the pores of the membrane, it was kept in a separate compartment connected to the cell through a salt bridge of saturated potassium chloride.

All potentials measured against the calomel electrode were converted to the standard hydrogen electrode assuming this to be 0.245 volts.⁸¹

A EG & G Princeton Applied Research Model 362 Scanning Potentiostat which had a built-in sweep generator was used to control the potential of the working electrode against the reference electrode. Electrochemical studies were carried out in a nitrogen atmosphere and the voltammograms (current-potential curves) were recorded on a Brynas 26000 A4 X-Y recorder. The currents and potentials were monitored on a 171 and another 174 Keithley digital multimeters connected to a 1723 ISB interface respectively.

In separate experiments. open circuit potentials (' rest potentials / mixed potentials') as function of pH, against the calomel electrode in the electrochemical cell saturated with high purity ' oxygen free ' nitrogen or oxygen, were measured for each mineral. The study with oxygen was done to assess the manner in which the measured potentials varied with the gas used. In any case air used in actual flotation systems always has oxygen and this would be expected to play a role in an electrochemical reactions especially when xanthate is present.

Open circuit potentials were also measured in solutions containing varying concentrations of xanthate and cyanide. In order to assess the time taken for a mineral electrode to attain a steady potential value, a digital meter was connected to a Servogor 460 Y-t recorder

The open circuit potentials of the mineral of interest was measured through the potentiostat which acted as 'buffer'. Figures 4.3 (a) and 4.3 (b) show the cell assemblies used in the experiments involving solutions without and with reagents.

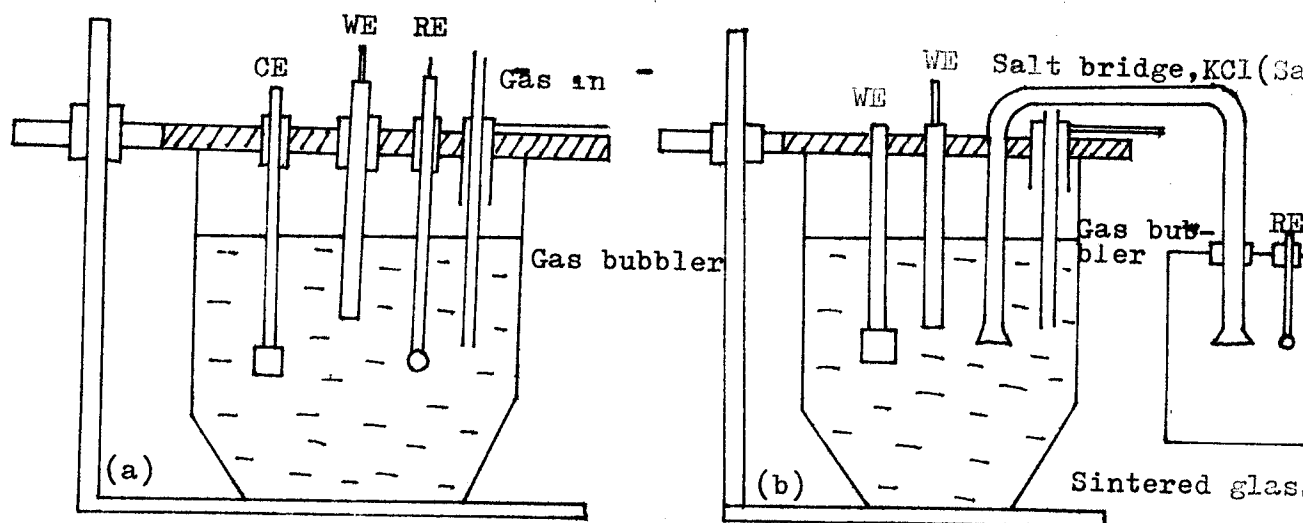


Figure 4.3 Cell assembly for open circuit potential measurements and subsequent cyclic voltammetric studies.

(a) cell assembly used without any reagent addition.

(b) cell assembly used with reagent addition.

In both Figures CE, WE and RE represent the counter, working and reference electrodes respectively.

The procedure followed in open circuit potential measurements is outlined below:

The cell was filled with the buffer solution of interest for twenty to thirty minutes. The mineral specimen was then transferred immediately into the cell after it had been gently ground on a P1200 sand paper, washed with the buffer solution and dried with a soft tissue. The gas bubbler was allowed to bubble the gas in the solution and hence agitated the solution for as long as the steady potential took to be established. The bubbler was then lifted to the surface of the solution. The cell assembly in Figure 4.3 (a) was used when no additives were present and that in Figure 4.3 (b) was used when reagents were present. For subsequent experiments of cyclic voltammetric behaviour with and without additives cell assembly in Figure 4.3 (b) was used and only 'oxygen free' nitrogen gas was used in all the experiments. The position of the counter electrode was kept in the same place during the cyclic voltammetric studies as much as possible.

The potential range covered for cyclic voltammetric studied varied with the solution pH for both carrollite and chalcopyrite electrodes. However, the sweep rates for all voltammograms was kept constant at 5mVs^{-1} . Slow scan rates are preferred when dealing with solid working electrodes as they give sufficient time for the application of the potential for a reaction to proceed to completion. The following potential ranges were used for a carrollite electrode to record all the voltammograms.

<u>SOLUTION pH</u>	<u>POTENTIAL RANGE</u> <u>VOLTS VS SHE</u>
4.6	- 0.30 to 1.10
7.0	- 0.28 to 0.80
9.2	- 0.25 to 0.80
11.0	- 0.30 to 0.60
13.0	- 0.70 to 0.60

These potentials were arrived at purely by empirical observations and were confined to the potential range in which only one anodic peak and presumably its corresponding cathodic peak appeared. This was assumed to correspond to the initial oxidation of the mineral which gave an atomic layer of products. The potential ranges used for recording cyclic voltammograms for the chalcopyrite electrode were similar to those reported before.^{29, 32}

<u>SOLUTION pH</u>	<u>POTENTIAL RANGE</u> <u>VOLTS VS SHE</u>
4.6	- 0.40 to 0.40
7.0	- 0.40 to 0.50
9.2	- 0.40 to 0.50
11.0	- 0.55 to 0.33

The cell was washed with chromic acid after every experiment and then thoroughly rinsed with tap water and then doubly distilled water before doing the next experiment. The electrode was also given a gentle polish before doing the next run. This was done so that the cell was free from the contamination of the previous solution and also to expose a clean new electrode surface for each experiments.

5.0 EXPERIMENTAL RESULTS AND DISCUSSIONS

5.1.0 OPEN CIRCUIT POTENTIALS.

The open circuit potentials of carrollite and chalcopyrite mineral electrode in solutions of different pH compositions saturated with nitrogen or oxygen are shown in Figure 5.1 (a) and 5.1 (b) respectively. The corresponding values are tabulated in Table 5.1 (a) and (b) respectively as shown in the appendix.

For both minerals ' rest ' or open circuit potentials tends to decrease with increase in the solution pH. When the test solution was saturated with nitrogen and the electrode immediately transferred to the cell after a gentle polish on a P1200 abrasion paper, the potential drifted at first quite rapidly and then slowly towards a steady value. In both cases the drift was from a higher potential value to a lower one. The period taken to attain these steady potentials varied from thirty minutes to one and half hours on the average. The potentials reported here are those obtained when the gas bubbler was positioned on the surface of the solution and were taken as averages between three measured values for each experiments. These potentials in most cases turned out to be quite reproducible. When the gas used was oxygen, the potentials increased for both minerals as can be seen from Figures 5.1 (a) and 5.1 (b).

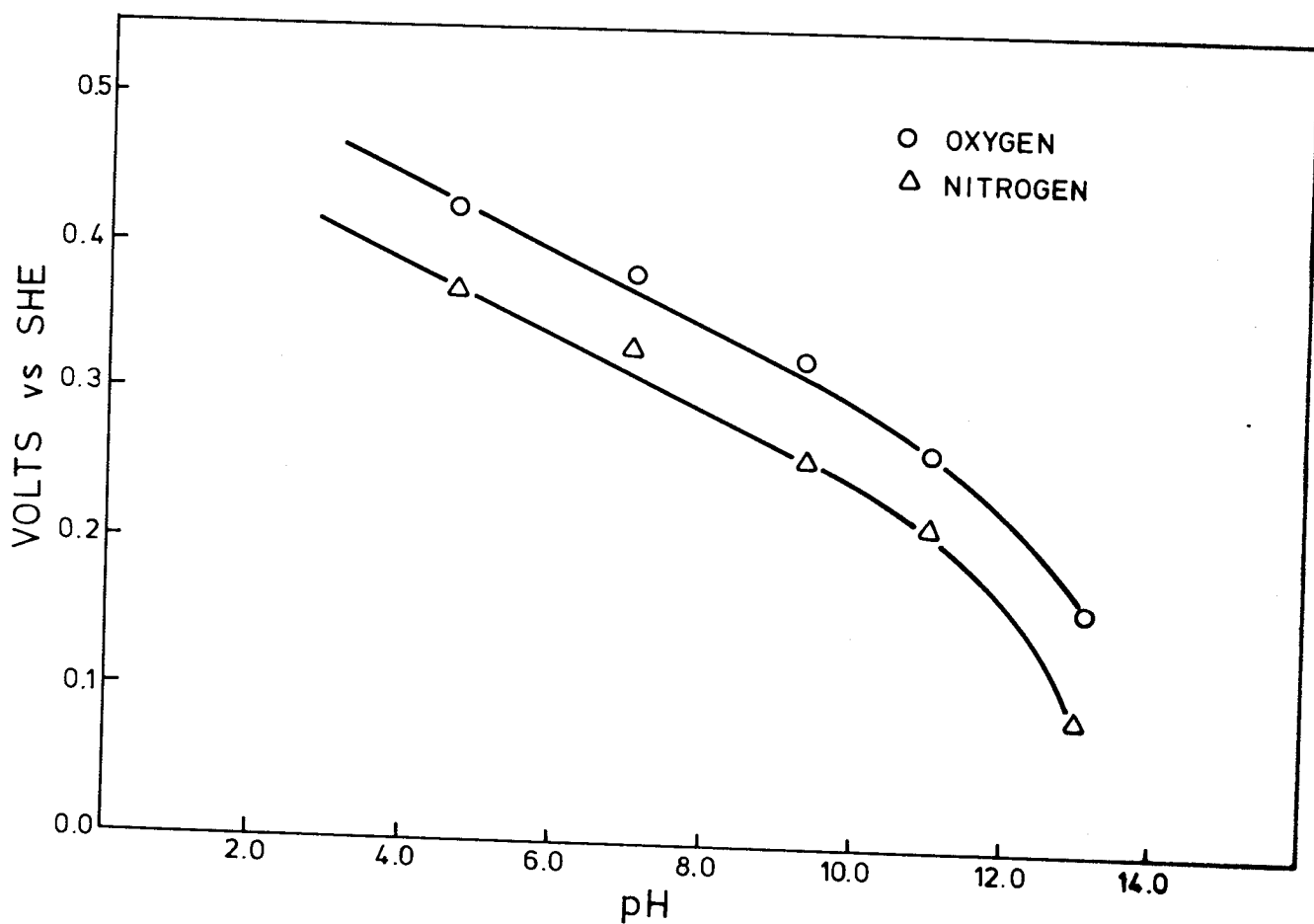


Figure 5.1(a) Open circuit potentials of carrollite as a function of pH in solution saturated with nitrogen and oxygen.

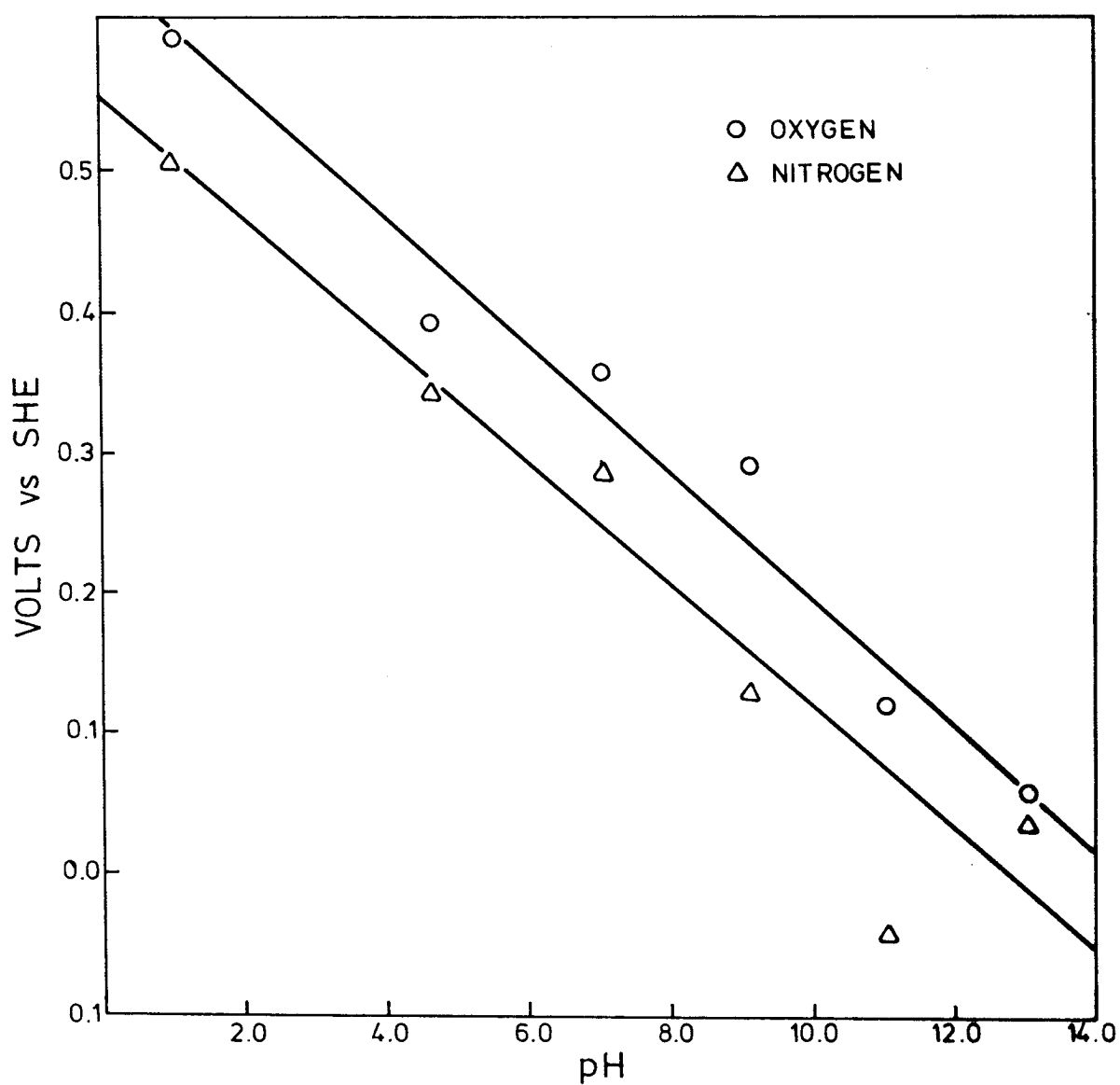


Figure 5.1(b) Open circuit potentials of chalcopyrite as a function of pH solution saturated with nitrogen or oxygen.

In attempt to correlate the measured rest potential with the likely species which could be responsible for the measured rest potentials under the conditions of measurements, a comparison with E_h - pH diagrams was done. In the case of carrollite, no E_h - pH diagrams could be found in the literature. Furthermore, there is no thermodynamic data for this mineral at room temperature except at elevated temperatures from which construction of E_h - pH diagrams for use at room temperature is not justifiable.

In light of this it was decided to use separate cobalt - sulphur - water and copper - sulphur - water systems as shown in Figures 3.1 and 3.2 respectively. The assumption was that for a carrollite - water system, the resulting E_h - pH diagram will be a super imposition of the two systems. From the two figures, it is clear that in acid and near neutral solution conditions, the measured rest potentials fell in the region where Co^{2+} and Cu^{2+} were the stable species, in both nitrogen and oxygen aeration. In alkaline solutions the potentials fell in the region where $Co(OH)_2$ and Cu_2O were the stable species. Of course, other species could have been present but the above were deemed to be the most important ones responsible for the acquired potential. The equilibrium values of the rest potentials measured will depend on the subsequent stable species produced on the surface of the sulphide

mineral. Hence the most likely mechanism responsible for the rest potentials in acidic media will be the dissolution of the sulphide mineral to give ionic species in solution. The degree of dissolution will depend on many factors, but as long as the dissolution process is taking place, the potential will continuously drift. The potential in all cases drifted towards lower values. This could be due to the changes in the concentration of the potential determining ions in solution with time. It is apparent from this that the measured potentials could be expressed in a Nernst - type of equation in analogy to that used to express potentials for metals in equilibrium with their metal ions in solutions. i.e

For a reaction involving a metal M,



for which the potential is given as:

$$E = E^0 + (RT/nF) \ln a_{M^{n+}} \dots \dots \dots (5.2)$$

where $a_{M^{n+}}$ is the activity of the metal ions.

However, in the case of metal sulphides an extra term is needed to take into account the chemical potential of the metal in the form of a sulphide. i.e

For a reaction involving a metal sulphide $M^0(MS)$



for which potential is given as

$$E = E^0 - (RT/nF) \ln a_{M^0}(MS) + (RT/nF) a_{M^{n+}} \dots (5.5)$$

where $a_{M^0}(MS)$ represents the activity of the metal in the form of a sulphide mineral.

The sulphide mineral can be expected to have a stoichiometry which is related to the chemical potential of the metal sulphide. Thus, there could be an upper and lower limit to the measured chemical potential which would be defined by the limits of the composition the mineral can have. This means that the upper limit may be due to metal ions (Co^{2+} , Cu^{2+}) / sulphur equilibrium while the lower limit is defined by the mineral / metal ions equilibrium. Under these conditions the potential measured would be expected to be a compromise between the two limits and will largely depend on the amount of metal ions in solution in this case Co^{2+} and Cu^{2+} . The fact that oxygen aeration results in higher values of measured potentials was a clear indication that it influences the mechanism of rest potential attainment. From the E_h - pH diagrams, the lower limit of the potential will correspond to a situation where no Co^{2+} or Cu^{2+} ions are present in solution. Hence, from these observations, it is logical to conclude that the reason why oxygen affected the measured rest potential in the way it did was because it probably increased the amounts of ions passing into solution in acid media, thereby increasing the rate of dissolution of the mineral.

The situation is rather complex in alkaline media. The species which appeared to be responsible for the attained potential are $\text{Co}(\text{OH})_2$ and Cu_2O . For all practical purposes, these would form a passivation layer on the mineral surface so that once formed there would not be further change in the measured rest potentials. If this were true, the rest potentials would be expected to be similar in the presence of nitrogen and oxygen. In view of the observed differences, it is not clear whether the role of oxygen is to further oxidise the above species to higher oxides or hydroxides resulting in a higher measured rest potential or simply increasing the thickness of the initial products.

The E_h - pH diagram for chalcopyrite is shown in Figure 3.3. The diagram shows that the measured rest potentials fall again in the region where metal ions are the stable species in acidic media and oxides as the most stable species in alkaline media. In the case of chalcopyrite in alkaline range the existence of other sulphides and / or metallic copper could be considered. The oxides of iron could also be considered as possible species which can play a role in establishing the value of the rest potential measured. For clarity and simplification these are left out in the E_h - pH diagram. In practice, however, the oxides of iron form more readily than those of copper and may be regarded as critical in the electrochemical behaviour of this mineral.

The measured rest potentials of the chalcopyrite electrode in general behaved in a very similar manner to that of the carrollite electrode. It showed a similar decrease with increase in solution pH and potential in oxygen saturated solution. In oxygen saturated solutions the recorded potentials were higher than in nitrogen.

An explained observation was the large fall in the rest potential for both mineral electrodes at pH 11.0 especially when the solution was saturated with nitrogen. The potential would be expected to fall less if the mechanism were that of hydroxide formation. This is because at such solution pH, the mineral would be expected to form oxides or hydroxides readily. The potentials of the minerals were temporarily held at either a higher or lower potential in relation to the attained rest potential for both minerals. However, after the short polarisation periods the potentials rapidly drifted back towards their original values. This lead to the suggestion that the processes for attaining these rest potentials were reasonably reversible. This was further supported by the speed at which these potentials were retained when the electrodes were subjected to perturbations of + or - 50mV about the rest potential. As soon as the perturbation was stopped, no matter for how long it had been persisted, the potentials almost instantaneously attained their original values. However, the potentials drifted sluggishly or slowly towards their rest potentials when the electrodes were held for

more than ten minutes below or above their rest potential values. In each case, the new rest potentials were either just slightly less or a bit more than the original rest potentials depending on the pre treatment.

It is important to appreciate that the rest potentials reported would have probably kept on drifting if left for days. However, the drift would have not be expected to be significant. For subsequent cyclic voltammetric studies, these rest potentials provided a very convenient point from which to begin the sweep cycle. Polishing the electrode when measuring the rest potentials for the same mineral in the same solution gave potentials which were not exactly the same. One reason for that could have been due to the new surfaces produced by this pretreatment which may not necessarily be the same as the first one. Indeed, Mehta et al⁸³ found that when two sulphide minerals are in contact, there could be a galvanic interaction which could influence the measured rest potentials. Polishing could have resulted in new sulphide mineral phases which could either galvanically accelerate or retard the process of rest potential attainment.

From Figures 5.1 (a) and (b), the decrease in the rest potentials could be expressed by linear relationships in which the negative slopes indicate the rates of change of the potentials with solution pH. These approximate linear

relationships gave the slopes as 0.024 V/pH units and 0.045 V/pH units for carrollite and chalcopyrite respectively. However, this linear relationships are not satisfied at higher pH values for both minerals. From this, it is clear that the decrease in the measure rest potentials is higher for chalcopyrite for every increase in pH units. The linear decrease in the rest potentials for both minerals in either oxygenated or nitrogenated solutions as the solution pH is increased could suggest that the potential values are probably due to new phases on both mineral surfaces which fall linearly in the domains represented by the E_h - pH.

The establishment of a rest potential by a mineral when put in an aqueous solution is a common phenomenon in almost all metals and minerals. This potential when measured may not necessarily be equal to the calculated potentials based on thermodynamic data. In general various factors such as the purity of the solution, the type of electrode, electrode preparation and type of atmosphere (oxidising, reducing or inert) have pronounced effects on the measured rest potentials.

The nature of the measured rest potentials and how they are established is therefore a very complex mechanism to explain. It is also certain not certain whether the potential depend on the thermodynamic properties or on kinetic factors alone. However, what appears to be true is that when the mineral is put in an

aqueous solution , the thermal energy will cause ions to collide continuously with the mineral surface. Any ion with sufficient energy will surmount the energy barrier (Activation energy) and succeed in releasing or acquiring electrons at the mineral surface.⁸⁴ Either way, the mineral surface will change from its original form to a new phase which will be responsible for this potential.

Visual and microscopic examination of the mineral electrode surface after rest potential measurements showed shiny surfaces for both minerals with no visible signs of any oxidation products. When left overnight in a solution of about neutral pH, the surface of chalcopyrite was no longer shiny, it turned pale yellow whilst the carrollite electrode surface was still shiny and showed no changes at all.

Measurements of rest potentials in flotation practice and experiments become of significance when various reagents are added to flotation electrolytes among which xanthate is perhaps the most widely used for sulphide minerals. In the separation of one sulphide mineral from another in a complex ore, liberated mineral sulphides are separated by depressing chosen sulphide particle and floating off others. The control of solution pH is maybe one of the most widely applied methods for the modulation

of sulphide mineral flotation. However, cyanide addition is used in practice to suppress minerals such as pyrite and other similar sulphides.

Due to the importance of these reagents in sulphide flotation, rest potentials of carrollite and chalcopyrite mineral electrodes were measured in solutions containing various concentrations of potassium ethyl xanthate and sodium cyanide. These measurements and subsequent cyclic voltammetric studies were done in the pH range of 7.0 to 11.0 as this is the region of relevance to flotation.

In order to interpret the measured rest/mixed potentials in solutions containing xanthate, the redox potential for the oxidation of xanthate to dixanthogen must be used as a standard comparison value. From IUPAC and as determined by Tekeda and Majima^{8,2} this has a value of 0.13 volts in a solution of pH 7.0 and with $6.25 \times 10^{-4} \text{ M}$ ethyl xanthate. A value for the xanthate oxidation can be calculated at any pH and xanthate concentration as the xanthate / dixanthogen reaction is pH independent:



$$E^0 = -0.06 \text{ V}$$

$$E = E^0 - (RT/nF) \ln [\text{X}^-]^2 / [\text{X}_2] \dots \dots \dots (5.3)$$

where

[X_2] represent dioxanthogen concentration

[X^-] represent xanthate concentration

T absolute temperature

R Gas constant

F Faraday's constant

n number of electrons involved in a reaction.

Since X_2 is a pure liquid, its activity is unit and at 298 K, equation 5.3 becomes

$$E = E^0 - 0.059 \log [X^-]$$

$$E = - 0.06 - \log [X^-] \dots \dots \dots (5.4)$$

This equation enables a comparison of measured rest potentials of the minerals in solutions containing any concentration of xanthate. The same expression is valid when depressants are present in solution. When the measured rest potential is larger than the reversible xanthate / dioxanthogen potential then dioxanthogen is likely to have formed and when it is cathodic or less than the xanthate / dioxanthogen potential, then dioxanthogen is not likely to have formed but it could be possible that a metal xanthate may have formed. However, in order to use this empirical equation, it is usual to assess whether the products

extracted from the electrode are compatible with the electrode potentials obtained from the experimental measurements.

Infrared and ultraviolet spectroscopy were used for the identification of the reaction products. As the direct application of these techniques to the surface was impossible, it was necessary for the products to be extracted into suitable solvents for examination. It was recognised that such a procedure has important disadvantages; the extraction may discriminate against products that are particularly strong bonded⁸⁵ and the extracted products may undergo changes on drying⁸⁶ in the extractant or in the preparation of samples for spectrophotometry.⁸⁷ Hence it should be understood that the conclusions of this work must be confined to surface products that are amenable to extraction. This limitation is shared by many investigators who have used similar method.^{41, 42}

Tables 5.2 (a) and (b) in the appendix show the measured value in solution with varying xanthate concentrations in oxygen and nitrogen atmosphere respectively. Table 5.2 (c) shows the effect of sodium cyanide concentration and Table 5.2 (d) shows this at a constant xanthate dosage respectively. the change in measured rest potentials for these conditions are shown diagrammatically in Figure 5.2 (a), (b), (c) and (d) respectively.

The most noticeable effect of potassium ethyl xanthate addition to the system when saturated with both nitrogen and oxygen is the rapid decrease in the rest potential of the mineral with increasing concentration of xanthate. The fall in oxygen saturated solutions was much more pronounced than in nitrogen saturated solutions for the same xanthate concentration. Figure 5.2 (b) show that the decrease in the potential tends^{to} be high at near neutral and high pH solution for the same xanthate concentration. the measured rest potentials tend to decrease with increasing cyanide addition and with pH of the solution. This is shown in Figure 5.2 (c).

In Figure 5.2 (d), at constant xanthate addition, the potential of the carrollite electrode electrode in the presence of low cyanide concentration fell quite rapidly at pH 9.2. At higher cyanide concentration the measured potential was more or less constant and similar to that recorded at pH 9.2. However at pH values of 7.0 and 11.0 the recorded potentials decreased at higher cyanide concentrations.

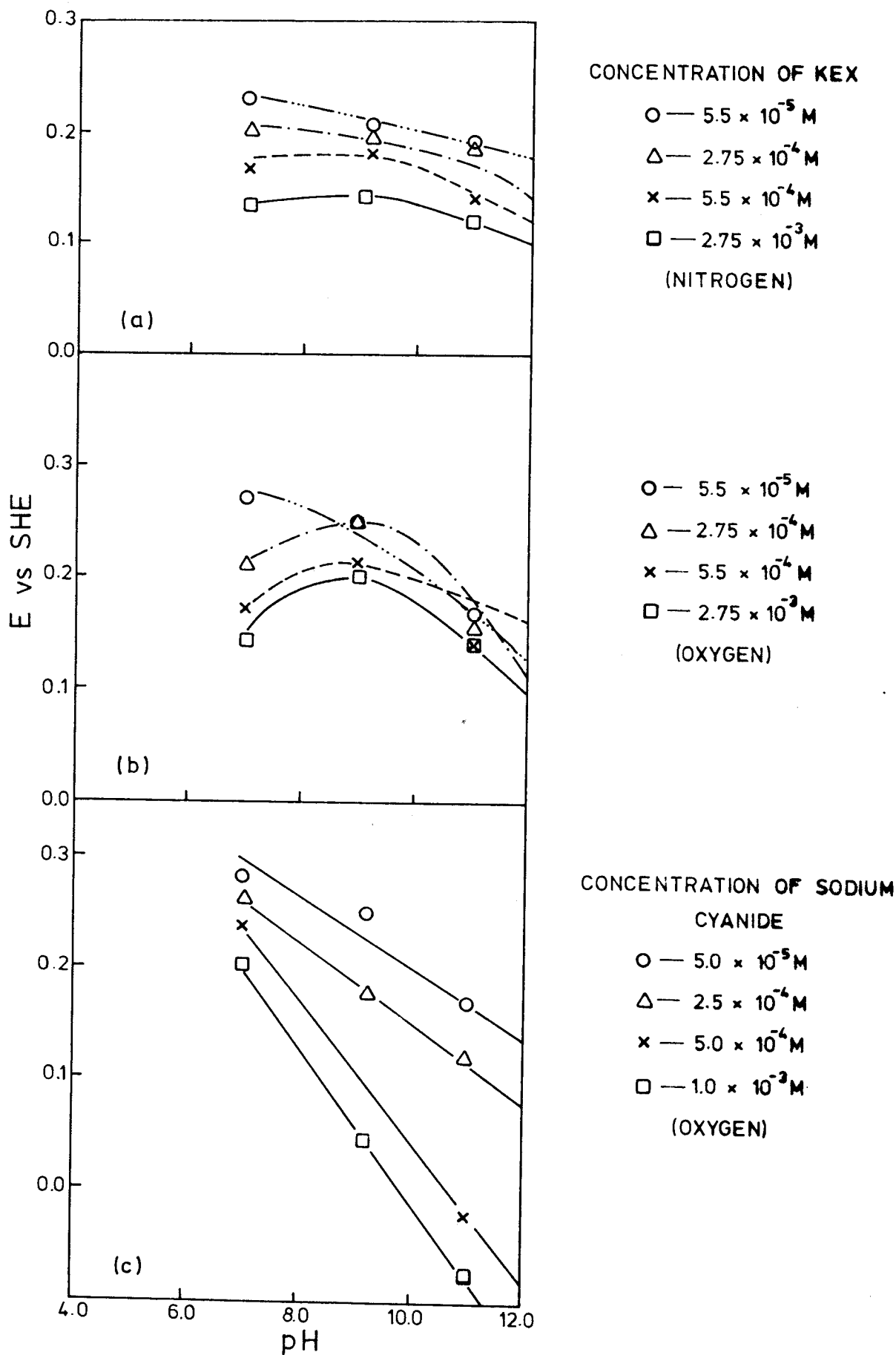


Figure 5.2 Open circuit potentials of carrollite as a function of pH
 (a) and (b) containing different concentrations of xanthate saturated with nitrogen and oxygen respectively
 (c) Different concentrations of sodium cyanide.

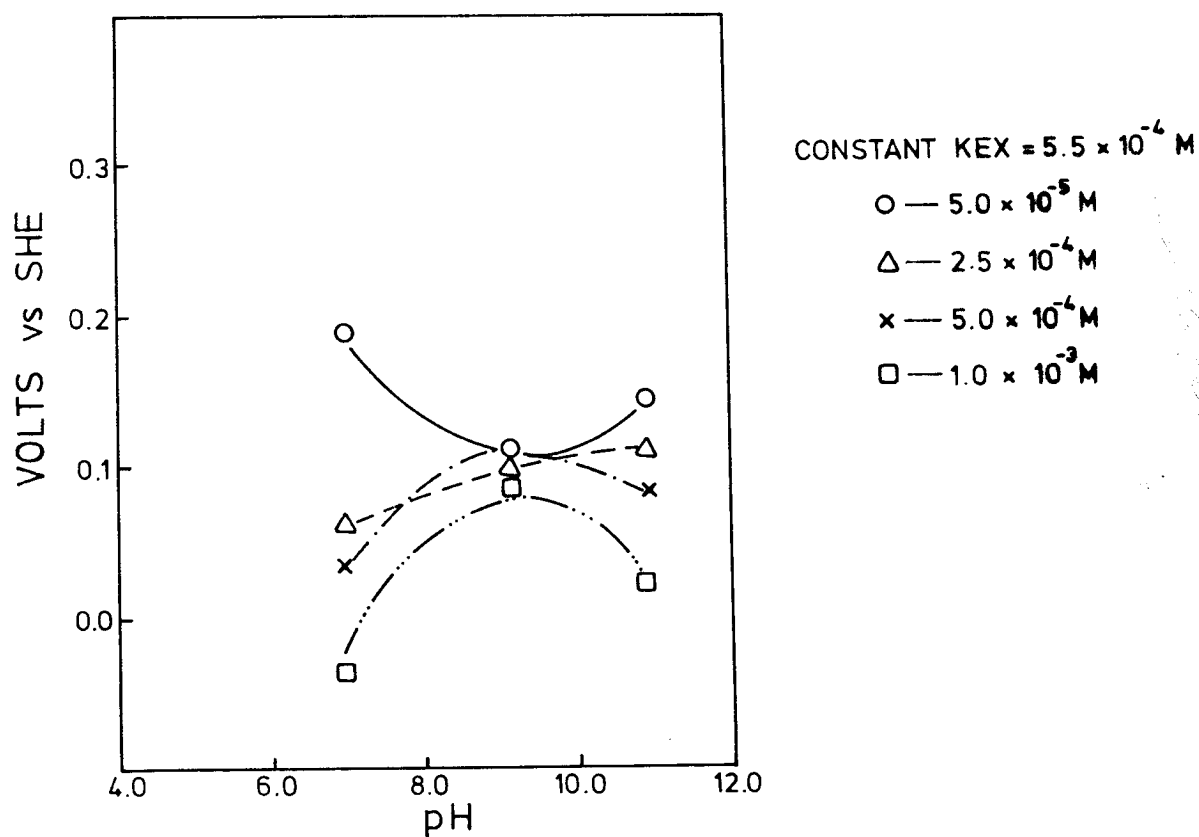


Figure 5.2 Open circuit potentials of carrollite as a function of pH in solutions containing potassium ethyl xanthate and sodium cyanide.

In comparison with the standard redox potential for the xanthate / dixanthogen couple, value at pH 7.0 and 9.2. This suggests that dixanthogen will readily be formed on the carrollite mineral electrode at these pH values for nearly all the xanthate concentration used. From Infrared spectra in Figure 5.7 and 5.8, it appears that more dixanthogen is formed at pH 9.2 than at pH 7.0.

The probable mechanism responsible for the decrease in the rest potential after xanthate addition could be due to the physical adsorption of the xanthate ions on the mineral surface. The specific adsorption of negatively charged species will lead to a rapid fall in the surface charge (potential).⁵³

After sometimes, the potential reaches a point of arrest which may be due to chemisorption of the xanthate forming a strong bond on the mineral surface with loss of an electron to give dixanthogen. This was thought to be the case as there was generally weak or no bubble attachment to the mineral surface upon inserting the electrode in the cell. However, after 1- 2 minutes strong bubble attachment was observed. Bubbles were produced by rapidly passing nitrogen or oxygen in the cell solution.

In nitrogen atmosphere, no matter how long the experiment was run, the bubbles only weakly adhered to the mineral at pH 7.0 and 9.2. This did not seem to change with the concentration of xanthate. In oxygenated solutions the number of bubbles and strength of adherence significantly increased with both the solution pH (at least up to 9.2) and the xanthate concentration.

Although the measure of hydrophobicity was based on these observations, there was no direct way of extracting the oxidation products from the surface of the mineral. An indirect method was used in this respect:

About one gram of the mineral of average size $75\mu\text{m}$ - $106\mu\text{m}$ was stirred with a buffer solution with an appropriate amount of xanthate in a flask with nitrogen or oxygen for about one hour. It was assumed that the individual particles would behave in a similar manner to the electrode. Thus the particles were expected to establish similar potentials to those of the electrodes so that the oxidation products on their surface could be assumed to be similar in nature to those on the electrode.

The mineral particles were then washed with distilled water, transferred to a separating funnel and then shaken with 50 millilitres of ether and then with carbon disulphide. In the case of ether extracts, they were evaporated on a KBr disc for infrared spectrographic measurements.

The infrared spectra shown in Figure 5.7 and 5.8 were obtained from extracts of carrollite mineral particles. In the figure (a) and (b) show the spectra obtained for the ether and carbon disulphide extracts respectively. Figure 5.7 was obtained at pH 7.0 in the presence of $5.5 \times 10^{-4} \text{M}$ potassium ethyl xanthate while Figure 5.8 was obtained at pH 9.2 with the same xanthate concentration.

The two diagrams show that the oxidation products are certainly present at these pH values and that relatively more dixanthogen is formed at pH 9.2. At both pH values the predominant oxidation product appear to be same and similar to the dixanthogen. The identification of dixanthogen is based on the C=S stretching vibrations being retained at 1200 to 1070 cm^{-1} , while the C-O-C stretching was shifted to 1250 cm^{-1} .

Table 5.2 (c) in the appendix shows the change in the potential of the carrollite electrode with pH in different concentrations of sodium cyanide. Table 5.2 (d) shows similar conditions to 5.2 (c) except that a xanthate concentration of $5.5 \times 10^{-4} \text{M}$ was added at all pH values and concentrations of cyanide. These variations are shown diagrammatically in Figures 5.2 (c) and 5.2 (d) respectively. The measured rest potential fell more or less linearly with pH for all cyanide concentrations. In Figure 5.2 (d) the fall in the mineral potential at near neutral and high pH values could be interpreted in terms of depression. Since the lower the rest potential value obtained, the less likely will oxidation of xanthate occur and an hydrophilic surface can be expected. Weak bubble attachment was observed for the entire pH range at a cyanide concentration of $5.5 \times 10^{-4} \text{M}$ and diminished with a higher cyanide concentration. However, the measured potentials show that there is a possibility of dixanthogen formation at pH 9.2 as the potential at this pH does not fall well below the xanthate / dixanthogen redox couple. However, this could not be detected by bubble attachment tests.

Figure 5.7: Infrared spectra of extracts from carrollite mineral contacted with 5.5×10^{-4} M KEX in oxygen saturated solutions at pH 7.0..

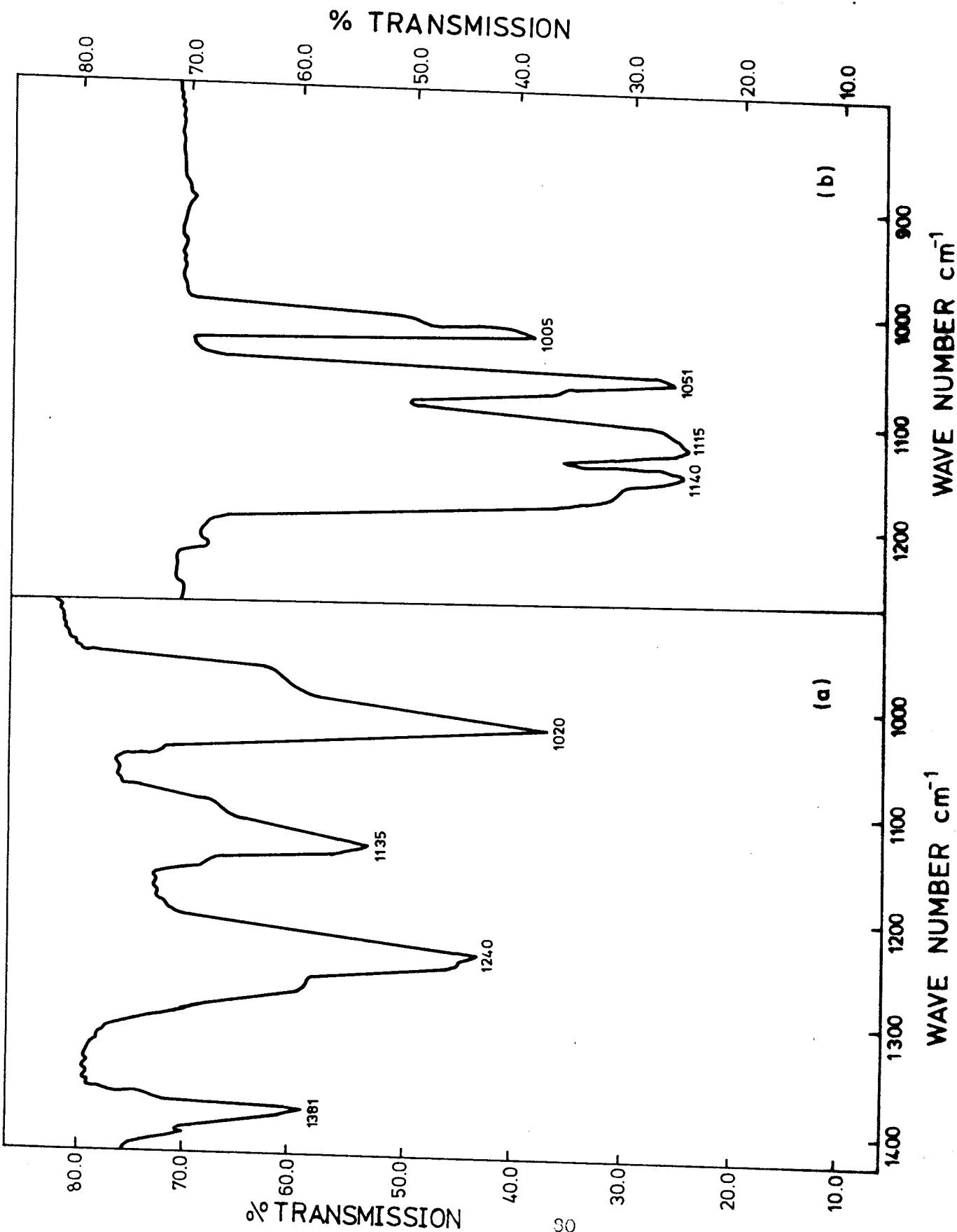
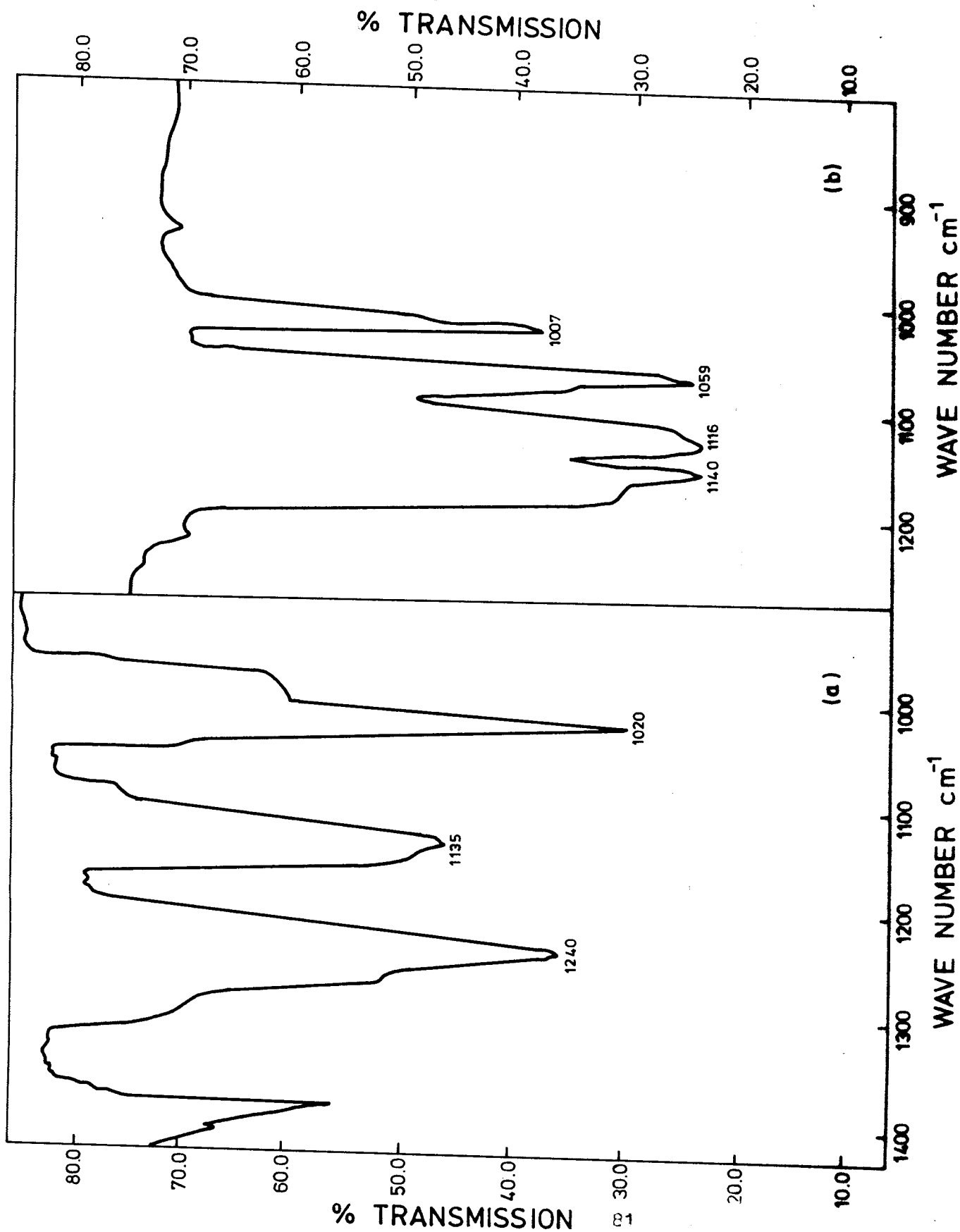


Figure 5.8: Infrared spectra of extracts from carrollite mineral contacted with 5.5×10^{-4} M KEX in oxygen saturated solutions at pH 9.2.



This showed that if dixanthogen formed, then it should have been in very small quantities.

Tables 5.3 (a) and 5.3 (b) in the appendix give the measured potential values for a chalcopyrite electrode in solutions containing various concentrations of xanthate for nitrogen and oxygen saturated solutions respectively. Tables 5.3 (c) and 5.3 (d) in the same appendix show the measured potential values in solutions containing varying concentrations of sodium cyanide with a constant concentrations of potassium ethyl xanthate. Diagrammatical representations of the above data are shown in Figures 5.3 (a) , 5.3 (b) , 5.3 (c) and 5.3 (d) respectively.

Chalcopyrite showed similar behaviour to that of carrollite. The measured rest potentials in oxygenated solutions with xanthate showed that dixanthogen was formed more readily at pH 9.2. Indeed, spectroscopic studies/ measurements revealed that dixanthogen formed in appreciable amounts as the spectrum in Figure 5.9 (a). The spectrum in Figure 5.3 (b) shows that there could be some soluble xanthate compound in the carbon disulphide. This is because the spectrum differed from that of pure xanthate though it bore some resemblance to the of metal xanthates.

Significant differences in the behaviour of chalcopyrite from carrollite was apparent when sodium cyanide was added to the solutions. A much smaller decrease in the measured rest potentials was observed at pH 7.0 and 9.2, than at pH 11.0 where the fall in potential was drastic. A similar trend in the large fall of the rest potentials at pH 11.0 was noticeable in the presence of a constant concentration of potassium ethyl xanthate as shown in Figure 5.3 (d). From the magnitudes of the measured rest potentials presented and on the basis of equation 5.4, dixanthogen is not expected to form on chalcopyrite at this pH value. This rather surprising as chalcopyrite would be expected to be hydrophobic at this pH value even in the presence of cyanide ions. Bubble attachment tests were performed on the mineral surface. The results indicated that there was little or no bubble attachment at this pH. This meant that little or no dixanthogen was formed at the above cyanide concentrations. The test assumed that hydrophobicity results from the presence of dixanthogen on the mineral surface.

Figure 5.9 : Infrared spectra of extracts from chalcopyrite mineral contacted with 5.5×10^{-4} M KEX in oxygen saturated solutions at pH 9.2.

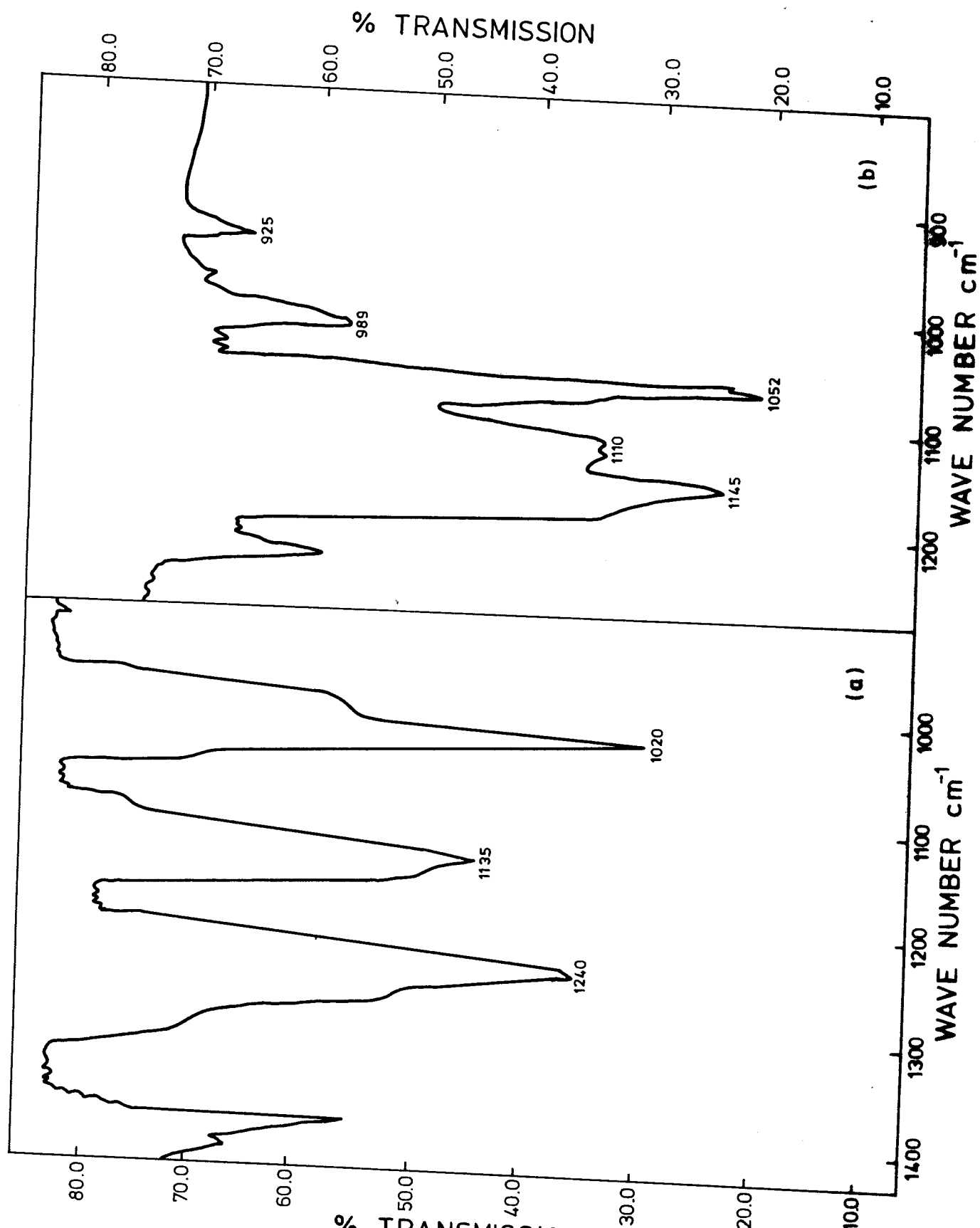
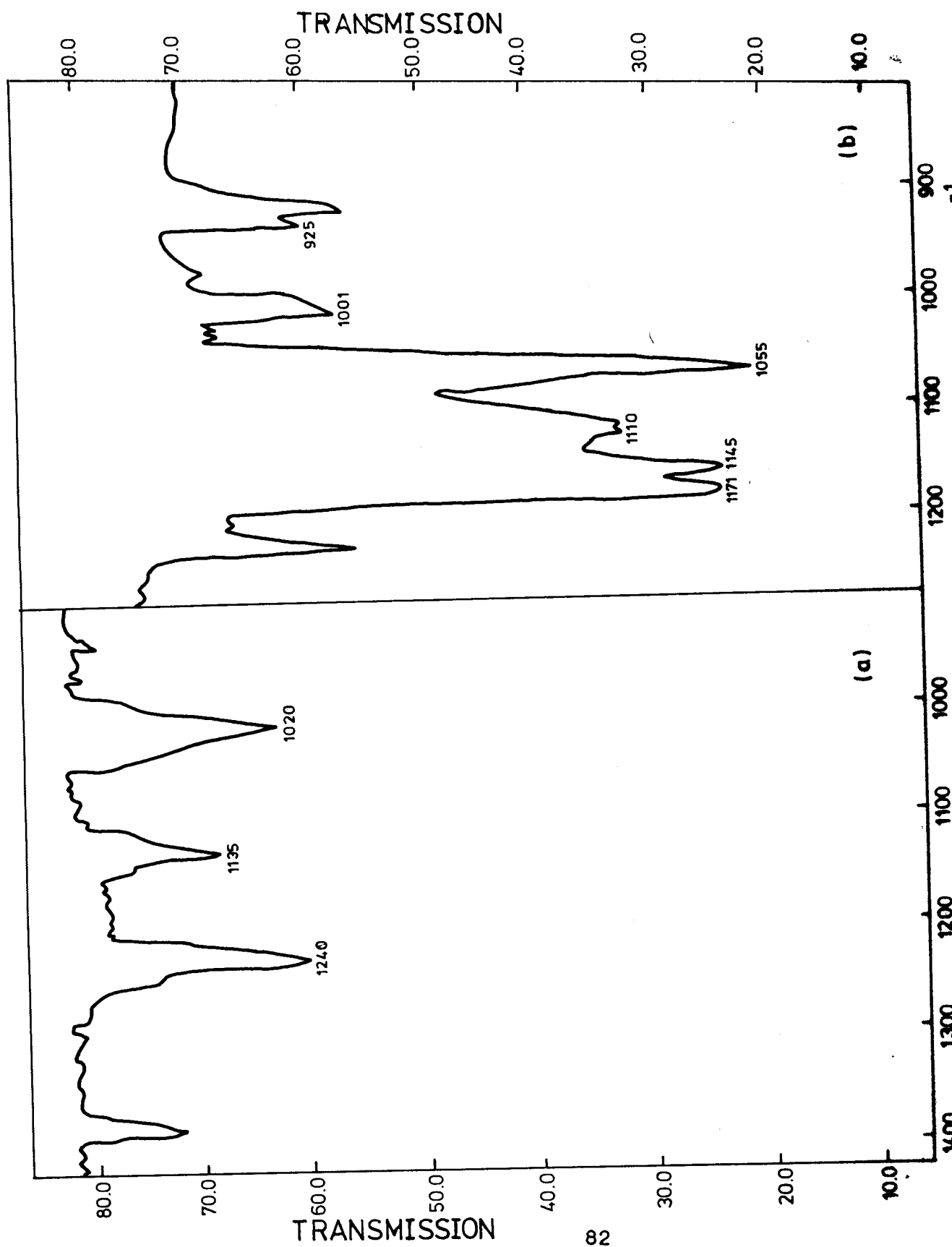


Figure 5.10 show infrared obtained for chalcopyrite contacted with a solution containing 5.5×10^{-4} M ethyl xanthate and 5.0×10^{-4} M cyanide at pH 11.0. A little amount of dixanthogen is certainly present but it appears that most of the xanthate simply remain in its original form. This can be deduced from the spectrum shown in in Figure 5.10 (b) for carbon disulphide extracts from the chalcopyrite particles.

The results for chalcopyrite were repeated to ascertain these results but were consistently the same. The conclusion was therefore made that for chalcopryrite there was little or no dixanthogen formation. This conclusion agreed with the observed rest potentials, bubble attachment and infrared results.

A possible explanation for the unexpected behaviour of the chalcopyrite electrode could have been due to the appreciable amounts of pyrite in the mineral (20.0%). Pyrite is known to affect the potential of various minerals when in contact with it.⁸³ Furthermore, pyrite is well known to be easily depressed even by small amounts of cyanide.²⁵

Figure 5.10 Infrared spectra of extracts from chalcopyrite mineral contacted with 5.5×10^{-4} M KEX and 5.5×10^{-4} M cyanide in oxygen saturated solutions at pH 11.0.



Tables 5.4 (a) and 5.4 (b) in the appendix show the measured rest potentials for a carrollite electrode in nitrogen and oxygen saturated solutions containing varying concentrations of potassium amyl xanthate. The potential variations are shown in Figures 5.4 (a) and 5.4 (b) respectively.

A similar decrease in potential was readily seen in both cases. However, in these cases, it appeared like that there was a greater decrease in the potentials at pH 9.2 for low concentrations of amyl xanthate. This decrease in the rest potential of the mineral at this pH value could be due to the readiness with which amyl xanthate reacted with the mineral surface. All the rest potentials measured for the mineral were well above the theoretical amyl xanthate / di amyl dixanthogen redox couple. This implies that the latter was likely to have formed on the surface of the mineral. No extracts were obtained for infrared spectroscopy as it was felt that the identification of xanthate products for the ethyl xanthate system was sufficient. In any case amyl xanthate was used only to compare the behaviour of the rest potentials of the mineral electrode in the presence of a thiol collector with a longer carbon chain length. Furthermore, amyl xanthate is not commonly used in the flotation of sulphide minerals. This is because, it is less

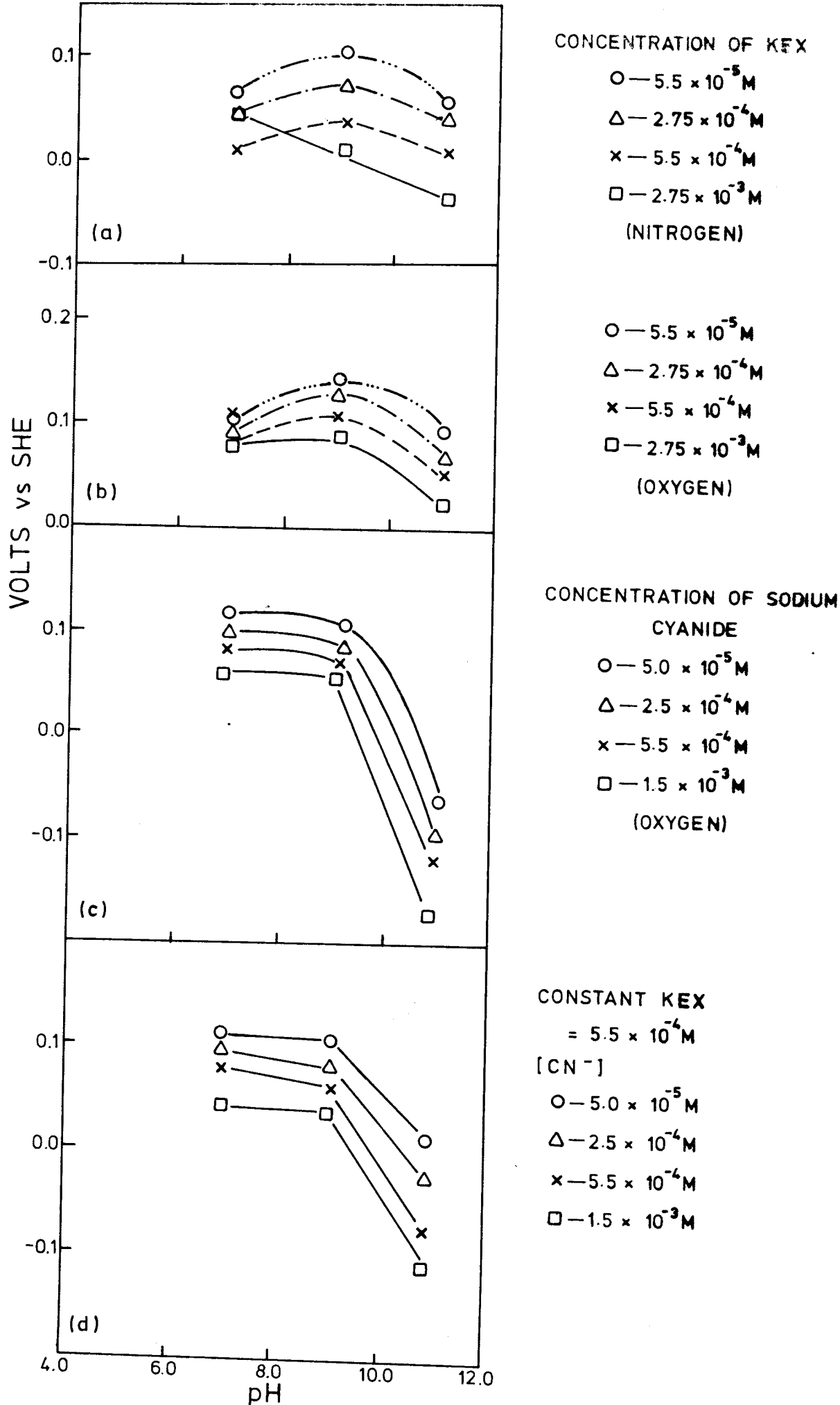


Figure 5.3 Open circuit potentials of chalcopyrite as a function of pH. condition as shown above.

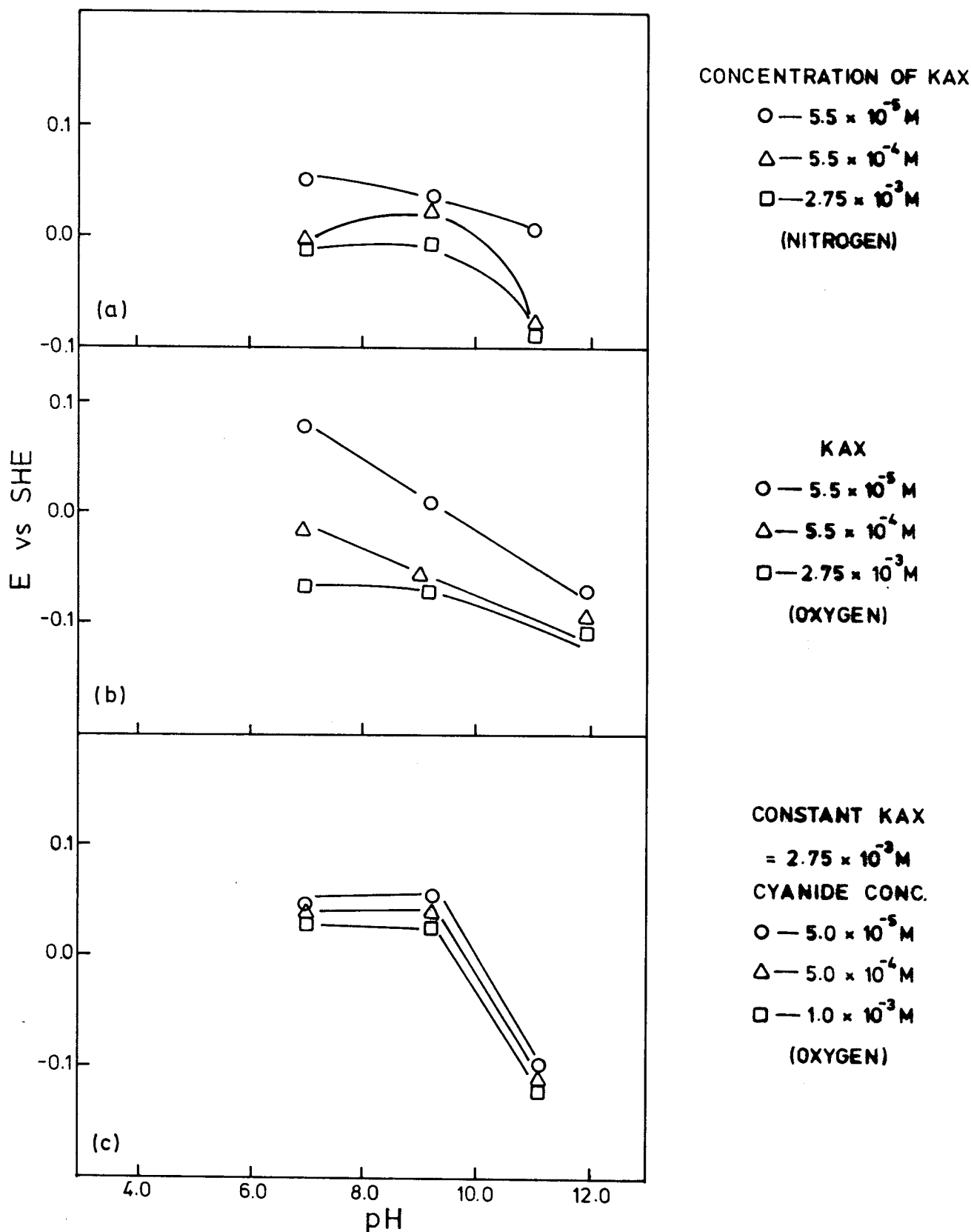


Figure 5.4 Open circuit potentials of carrollite as a function of pH. Conditions as shown above.

specific and could even float many other components in the mineral pulp. In practice amyl xanthate is used in actual flotation only as a booster collector and not as the main collecting reagent.

Table 5.4 (c) shows the measured rest potentials for a carrollite mineral electrode in solutions with different concentrations of sodium cyanide at a constant concentration of amyl xanthate in oxygenated solutions. The presence of cyanide resulted in a large decrease of the measured rest potential of the mineral to lower potentials particularly at pH 7.0. This in principle, implies that as the concentration of cyanide increases there will be a greater possibility that carrollite will not respond to flotation by amyl xanthate. Di amyl dixanthogen will not form to induce hydrophobicity on the mineral surface due to low potentials in the presence of cyanide ions.

Tables 5.5 (a) and 5.5 (b) gives rest potentials of the chalcopyrite electrode in solutions containing various concentrations of amyl xanthate in nitrogen and oxygen saturated solutions. These potentials are shown in Figures 5.5 (a) and 5.5 (b) respectively. The measured rest potentials show that di

amyl dixanthogen will readily form in oxygenated solutions at pH values 7.0 and 9.2 , but not so readily at pH 11.0.

Table 5.5 (c) shows the measured rest potentials in solutions containing a constant amyl xanthate concentration with different concentrations of sodium cyanide. There is a large decrease in the rest potential at pH 11.0. This shows that cyanide readily prevents amyl xanthate oxidation at this pH value on the chalcopyrite electrode. The ability of cyanide to prevent xanthate oxidation as the pH of the solution is increased, led Sutherland and Wark ⁴⁸ to conclude that the cyanide ions is the active depressant and not the un dissociated acid for this mineral. It is possible that some form of xanthate compound could have formed of the surface of the mineral at lower pH than 11.0, but since no infrared spectra were obtained, this could not be proved.

One would have expected that if the mode of depression by cyanide ions was its competitive adsorption with xanthate ions for the mineral surface, at high xanthate concentrations(2.75×10^{-3}), the xanthate ions will certainly be in excess of the cyanide ions. With such a mechanism, the cyanide ions would not be expected to act effectively. These speculations certainly show how obscure and difficult it is to explain the depressant action of cyanide purely on the basis of measured rest potentials only.

