THERMODYNAMICS AND ELECTROCHEMISTRY
OF THE CHALCOCITE - POTASSIUM ETHYL XANTHATE SYSTEM

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ABSTRACT

Comprehensive thermodynamic calculations have been carried out on
the chalcocite-KEX-water system based on complete mass balance equations
which include both soluble and insoluble species. The calculations have
yielded i) $E_h$-pH stability diagrams for different KEX additions,
ii) equilibrium concentrations and amounts of all the dissolved and
insoluble species including those of CuX and CuX$_2$, iii) two- and three-
dimensional plots showing the effect of $E_h$ and pH on the formation of
selected species, and iv) minimum xanthate additions required to form
CuX and CuX$_2$. These information can be used as a guide in predicting
the optimum conditions for flotation and leaching of chalcocite.

The upper limiting potentials predicted from the thermodynamic
calculations are in excellent agreement with those determined from the
microflotation tests. The lower flotation edges, on the other hand, are
found to be dependent on the sequence of reagent additions. When
xanthate is added after the addition of a reducing or oxidizing agent to
control the potential, they are in reasonable agreement with predicted
values. When the collector is added prior to the potential control,
however, the lower flotation edges are significantly higher than the predictions. The flotation experiments carried out at several different concentrations show that the minimum amount of the collector is required between 0 to 200 mv, as predicted by the thermodynamic calculations.

Voltammetry experiments carried out in the absence of a collector at pH 9.2 and 6.8 suggest that the anodic oxidation of chalcocite results in the formation of Cu₂O, Cu(OH)₂ and S⁰. At potentials below -400 mv, Cu₂S is reduced to Cu⁰ and HS⁻. When xanthate is added, several adsorption peaks are observed. There are indications that the peaks appearing between -200 and -100 mv may involve the reaction between xanthate and Cu⁰. However, at potentials above -40 mv, xanthate may adsorb directly on chalcocite without involving Cu⁰.
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TABLE OF CONTENTS

ABSTRACT .............................................. ii
ACKNOWLEDGEMENT........................................ iv
TABLE OF CONTENTS ...................................... v
LIST OF FIGURES........................................ viii
LIST OF TABLES .......................................... xiv

I. INTRODUCTION ........................................... 1

1.1 General ........................................... 1
1.2 Literature Review .................................... 3
1.3 Objective ........................................... 14

II. EXPERIMENTAL .......................................... 16

2.1 Materials ........................................... 16
2.2 Equipment ........................................... 17
2.3 Procedure ........................................... 18
   2.3.1 Microflotation .................................. 18
   2.3.2 Preparation of Chalcocite Electrode ............. 21
   2.3.3 Voltammetry Experiments ......................... 21

III. THERMODYNAMIC CALCULATIONS ...................... 24

3.1 Outline of the Calculations ......................... 24
3.2 Results of the Calculations . . . . . . . 31

3.2.1 $E_h$-pH Diagrams in the Absence of KEX . . . 31

3.2.2 $E_h$-pH Diagrams in the Presence of KEX . . . 33

a. $10^{-7}$ M KEX . . . . . . . . . . . 33

b. $10^{-6}$ M KEX . . . . . . . . . . . 33

c. $10^{-5}$ M KEX . . . . . . . . . . . 36

d. $10^{-4}$ M KEX . . . . . . . . . . . 36

3.3 Discussion . . . . . . . . . . . . . . . 39

3.3.1 Effect of $E_h$, pH and KEX Concentration on the Formation of CuX and CuX$_2$ . . . . . . 39

a. Effect of $E_h$ . . . . . . . . . . . 39

b. Effect of pH . . . . . . . . . . . 44

3.3.2 Minimum KEX Addition Required for CuX and CuX$_2$ Formation . . . . . . . . . . . . 53

3.3.3 Contour Plots and Three-Dimensional Block Diagrams. . . . . . . . . . . . . . . 58

IV. MICROFLOTA'TION AND ELECTROCHEMICAL STUDIES. . . . . . . 69

4.1 Microflotation . . . . . . . . . . . . . . 69

4.1.1 Effect of Potential and pH. . . . . . . 69

4.1.2 Effect of KEX Concentration . . . . . . 77

4.1.3 Flotation of Copper Powder. . . . . . . 77

4.2 Electrochemical Experiments . . . . . . . . . . . 79

4.2.1 In the Absence of KEX . . . . . . . . . . . 81

a. pH 9.2 . . . . . . . . . . . 81

b. pH 6.8 . . . . . . . . . . . 90
LIST OF FIGURES

Figure 1.1 Linear sweep voltammograms for a natural copper sulfide electrode in 0.1M NaF solution containing 0 M KEX (---) and 2.57 x 10^{-4}M KEX (----). (from Kowal and Pomianowski, 1973).

Figure 1.2 Linear sweep voltammograms for a synthetic copper sulfide electrode in 0.025M Sodium borate (pH 9.3) containing various concentrations of KDTP. (from Chander and Fuerstenau, 1974).

Figure 1.3 Schematic diagram of the microflotation - electrochemical cell used by Richardson and co-workers (O'Dell et al., 1984; Richardson et al., 1984; Walker et al., 1984).

Figure 2.1 Schematic diagram of the microflotation set-up. 19

Figure 2.2 Schematic diagram showing apparatus used for linear sweep voltammetry. 20

Figure 2.3 Working electrode used for the electrochemical studies of chalcocite. 22

Figure 3.1 $E_h$ - pH diagram of the Cu$_2$S - KEX - H$_2$O system in the absence of KEX at $T = 298\,^\circ$K and $P = 1$ atm. 32

Figure 3.2 $E_h$ - pH diagram of the Cu$_2$S - KEX - H$_2$O system for a collector addition of 10^{-7}M at $T = 298\,^\circ$K and $P = 1$ atm. 34

Figure 3.3 $E_h$ - pH diagram of the Cu$_2$S - KEX - H$_2$O system for a collector addition of 10^{-6}M at $T = 298\,^\circ$K and $P = 1$ atm. 35

Figure 3.4 $E_h$ - pH diagram of the Cu$_2$S - KEX - H$_2$O system for a collector addition of 10^{-5}M at $T = 298\,^\circ$K and $P = 1$ atm. 37

Figure 3.5 $E_h$ - pH diagram of the Cu$_2$S - KEX - H$_2$O system for a collector addition of 10^{-4}M at $T = 298\,^\circ$K and $P = 1$ atm. 38
Figure 3.6  Effect of $E_h$ on % CuX for a collector addition of $10^{-7}$ M KEX. The number next to each curve denotes the pH.

Figure 3.7  Effect of $E_h$ on % CuX for a collector addition of $10^{-6}$ M KEX. The number next to each curve denotes the pH.

Figure 3.8  Effect of $E_h$ on % CuX for a collector addition of $10^{-5}$ M KEX. The number next to each curve denotes the pH.

Figure 3.9  Effect of $E_h$ on % CuX for a collector addition of $10^{-4}$ M KEX. The number next to each curve denotes the pH.

Figure 3.10  Effect of $E_h$ on % CuX$_2$ for a collector addition of $10^{-7}$ M KEX. The number next to each curve denotes the pH.

Figure 3.11  Effect of $E_h$ on % CuX$_2$ for a collector addition of $10^{-6}$ M KEX. The number next to each curve denotes the pH.

Figure 3.12  Effect of $E_h$ on % CuX$_2$ for a collector addition of $10^{-5}$ M KEX. The number next to each curve denotes the pH.

Figure 3.13  Effect of $E_h$ on % CuX$_2$ for a collector addition of $10^{-4}$ M KEX. The number next to each curve denotes the pH.

Figure 3.14  Effect of pH on % CuX for a collector addition of $10^{-7}$ M KEX. The number next to each curve denotes the $E_h$ (mv).

Figure 3.15  Effect of pH on % CuX for a collector addition of $10^{-6}$ M KEX. The number next to each curve denotes the $E_h$ (mv).

Figure 3.16  Effect of pH on % CuX for a collector addition of $10^{-5}$ M KEX. The number next to each curve denotes the $E_h$ (mv).

Figure 3.17  Effect of pH on % CuX for a collector addition of $10^{-4}$ M KEX. The number next to each curve denotes the $E_h$ (mv).
Figure 3.18 Effect of pH on % CuX$_2$ for a collector addition of $10^{-7}$ M KEX. The number next to each curve denotes the $E_h$ (mv).

Figure 3.19 Effect of pH on % CuX$_2$ for a collector addition of $10^{-8}$ M KEX. The number next to each curve denotes the $E_h$ (mv).

Figure 3.20 Effect of pH on % CuX$_2$ for a collector addition of $10^{-9}$ M KEX. The number next to each curve denotes the $E_h$ (mv).

Figure 3.21 Effect of pH on % CuX$_2$ for a collector addition of $10^{-10}$ M KEX. The number next to each curve denotes the $E_h$ (mv).

Figure 3.22 Calculated minimum KEX addition required for CuX formation at pH 5, 8 and 11.

Figure 3.23 Contour plot showing the effect of $E_h$ and pH on log $[Cu^{2+}]$ for the Cu$_2$S - H$_2$O system.

Figure 3.24 Three-dimensional block diagram showing the effect of $E_h$ and pH on log $[Cu^{2+}]$ for the Cu$_2$S - H$_2$O system.

Figure 3.25 Contour plot showing the effect of $E_h$ and pH on % CuX for a collector addition of $10^{-7}$ M KEX.

Figure 3.26 Three-dimensional block diagram showing the effect of $E_h$ and pH on % CuX for a collector addition of $10^{-8}$ M KEX.

Figure 3.27 Three-dimensional block diagram showing the effect of $E_h$ and pH on % CuX for a collector addition of $10^{-9}$ M KEX.

Figure 3.28 Three-dimensional block diagram showing the effect of $E_h$ and pH on % CuX for a collector addition of $10^{-10}$ M KEX.

Figure 3.29 Three-dimensional block diagram showing the effect of $E_h$ and pH on % CuX for a collector addition of $10^{-11}$ M KEX.
Figure 4.1 Effect of $E_h$ on flotation recovery of chalcocite at pH 8 and in the absence of a collector.

Figure 4.2 Comparison between chalcocite flotation data and the thermodynamic calculations of this study at (a) pH 8 and (b) pH 11: (i) flotation with $4.7 \times 10^{-5}$ KEX and potential controlled with redox reagents, $\Theta$ (Heyes and Trahar, 1979); (ii) flotation with $1.44 \times 10^{-5}$ M KEX and potential controlled electrochemically, $\Theta$ (Richardson et al., 1984); (iii) calculated % CuX for $10^{-5}$M KEX addition, $\Theta$.

Figure 4.3 Correlation between flotation recovery of chalcocite and calculated % CuX (and % CuX$_2$) for $10^{-5}$M KEX addition at pH 5 with collector added before potential control, $\bullet$; and collector added after potential control, $\Theta$.

Figure 4.4 Correlation between flotation recovery of chalcocite and calculated % CuX (and % CuX$_2$) for $10^{-5}$M KEX addition at pH 8 with collector added before potential control, $\bullet$; and collector added after potential control, $\Theta$.

Figure 4.5 Correlation between flotation recovery of chalcocite and calculated % CuX (and % CuX$_2$) for $10^{-5}$M KEX addition at pH 11 with collector added before potential control, $\bullet$; and collector added after potential control, $\Theta$.

Figure 4.6 Effect of concentration of KEX addition on flotation recovery of chalcocite at pH 8 and different $E_h$ values.

Figure 4.7 Effect of $E_h$ on flotation recovery of copper powder at pH 8 and KEX addition of $10^{-5}$M and $10^{-4}$M.

Figure 4.8 Voltammograms of a chalcocite electrode in a 0.05M Na$_2$B$_4$O$_7$ solution (pH 9.2) for different anodic limits. No stirring. Scan rate = 10 mv/sec.

Figure 4.9 Effect of stirring on the voltammograms for a chalcocite electrode in a 0.05M Na$_2$B$_4$O$_7$ solution (pH 9.2). Scan rate = 10 mv/sec.

Figure 4.10 Cyclic voltammograms of a chalcocite electrode in a 0.05M Na$_2$B$_4$O$_7$ solution (pH 9.2) for potential sweeps between -555 mv and 345 mv. No stirring. Scan rate = 10 mv/sec.
Figure 4.11 Voltammograms of a chalcocite electrode in an unstirred 0.05M KH$_2$PO$_4$/0.05M Na$_2$HPO$_4$ solution (pH 6.8) for different anodic limits. No stirring. Scan rate = 20 mv/sec.

Figure 4.12 Effect of stirring on the voltammograms for a chalcocite electrode in a 0.05M KH$_2$PO$_4$/0.05M Na$_2$HPO$_4$ solution (pH 6.8). Scan rate = 20 mv/sec.

Figure 4.13 Cyclic voltammograms of a chalcocite electrode in an unstirred 0.05M KH$_2$PO$_4$/0.05M Na$_2$HPO$_4$ solution (pH 6.8) for potential sweeps between -355 and 445 mv. Scan rate = 20 mv/sec.

Figure 4.14 Voltammograms of a chalcocite electrode in the absence (---) and presence (-----) of 10$^{-5}$M KEX at pH 9.2. No stirring. Scan rate = 10 mv/sec.

Figure 4.15 Voltammograms of a chalcocite electrode in the absence (---) and presence (-----) of 2.5 x 10$^{-5}$M KEX at pH 9.2. No stirring. Scan rate = 20 mv/sec.

Figure 4.16 Effect of the starting potential on the voltammograms for a chalcocite electrode in an unstirred 0.05M Na$_2$BO$_7$ solution (pH 9.2) containing 2.5 x 10$^{-5}$M KEX. Scan rate = 20 mv/sec.

Figure 4.17 Voltammograms of a chalcocite electrode in the absence (---) and presence (-----) of 2.5 x 10$^{-5}$M KEX at pH 6.8. No stirring. Scan rate = 10 mv/sec.

Figure 4.18 Voltammograms of a chalcocite electrode in an unstirred 0.05M KH$_2$PO$_4$/0.05M Na$_2$HPO$_4$ solution (pH 6.8) containing 0 (---) and 2.5 x 10$^{-5}$ (-----)M KEX. Scan rate = 20 mv/sec.

Figure 4.19 Voltammograms of a chalcocite electrode in an unstirred 0.05M Na$_2$HPO$_4$/0.1M NaOH solution (pH 11) containing 0 (---) and 2.5 x 10$^{-5}$ (-----)M KEX. Scan rate = 20 mv/sec.

Figure 4.20 $E_h$-pH diagram of the Cu$_2$S-H$_2$O system and the anodic and cathodic peak potentials observed from the voltammetry experiments.

Figure 4.21 $E_h$-pH diagram of the Cu$_2$S-KEX-H$_2$O system for a collector addition of 10$^{-5}$M and the anodic and cathodic peak potentials observed from the voltammetry experiments.
Figure 4.22 $E_h$-pH diagram of the Cu$_2$S-KEX-H$_2$O system for a collector addition of $10^{-7}$M and the anodic and cathodic peak potentials observed from the voltammetry experiments.
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table 3.1</th>
<th>Standard Free Energy of Cu-S-H$_2$O compounds at 25°C.</th>
<th>26</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 3.2</td>
<td>Equilibrium Constants and Standard Electrode Potentials at 25°C.</td>
<td>27</td>
</tr>
<tr>
<td>Table 4.1</td>
<td>Possible Reaction Sequences for $A_1$, $C_1$ and $C_3$</td>
<td>88</td>
</tr>
</tbody>
</table>
CHAPTER I

INTRODUCTION

1.1 General

The major source of nonferrous metals such as copper, zinc, nickel, lead and molybdenum are sulfide ores. In the early stages of the extraction of these metals from their ores, froth flotation plays a very important role. From the mine, the ore undergoes mineral processing which starts with crushing and grinding to liberate the valuable minerals from the gangue minerals. After the liberation of valuable minerals, the ground particles are subjected to a concentration process in order to separate the values from the gangue. Froth flotation is the most commonly employed process in the physical separation of the sulfide minerals from the nonsulfide gangue minerals.

Froth flotation uses the differences in the physico-chemical surface properties of various minerals so that certain minerals will attach to air bubbles while others will not. The rising air
bubbles with the hydrophobic minerals collect in a froth layer at the top leaving the gangue in the pulp. However, the majority of naturally occurring minerals are naturally hydrophobic or only slightly hydrophobic. In order to overcome this problem, surface-active reagents called collectors are added to make the surface of selected minerals hydrophobic in character.

Collectors are organic compounds that selectively adhere onto the mineral surface thereby reducing the stability of the hydrated layer on the mineral to a level that allows attachment of the mineral particle to the bubble. Of all the different types of collectors available, the thiol compounds, particularly xanthate, are the most widely used in the flotation of sulfide minerals. The use of xanthates as collectors in flotation was first introduced by Keller (1925). Since then, xanthates of alkali metals, sodium and potassium in particular, have been widely employed and are found to be particularly effective for galena, pyrite, chalcopyrite, covellite, bornite and chalcocite. In the presence of certain modifying agents, they can also be used in the flotation of some of the nonsulfide minerals, such as carbonates and sulfates.

While there was good agreement concerning its effectiveness and use in sulfide flotation, there was a considerable amount of confusion regarding the mechanism of xanthate reactions on sulfur minerals. Numerous theories have been put forward to explain the mechanism of the collector action of thiol-type surfactants on sulfide minerals. Many of the proposed theories have been proved or disproven over the years by various experimental techniques. There has been a wide range of
disciplines involved in the experimental studies but lately, the focus has been on electrochemistry.

Although electrochemical kinetics has been given the major emphasis in the study of the collector mechanism, thermodynamics is still important in understanding some of the underlying mechanisms of flotation. Only thermodynamics can predict whether or not a reaction can take place. It may not be able to tell the rate of the reaction but it can determine the conditions necessary for flotation to occur. Thermodynamics can be applied in predicting flotation response to changes in parameters such as type of collector, types of mineral, temperature, and potential. This would be very helpful in the design and operation of a flotation process. In this regard, it would be advantageous for a mineral engineer to utilize both thermodynamics and kinetics as they both play important roles in flotation practice.

1.2 Literature Review

There has been a considerable amount of research directed towards understanding the mechanism for the interaction of xanthates with sulfide minerals. Early work in this field proposed the "ion adsorption theory" (Gaudin, 1927; Wark and Cox, 1934) where the mechanism of collection is simply the adsorption of collector ions on the mineral surface without further reaction. When xanthate is added, xanthate ions are adsorbed in place of the ions already present on the surface of the mineral. Taggart and his co-workers (1934) disagreed, however, with this concept and postulated that the collector film on the mineral
surface is formed by a chemical reaction, although the surface solubility products of the surface species were found to be less than those for the bulk. Wark and Cox (1934) countered, on the other hand, that if the chemical reaction (or solubility) theory were valid, then both pyrite and marcasite, which have the same chemical composition but different crystalline structures, should form the same kind of chemical compound with xanthate and float under similar conditions. This is not true in actual flotation. They stated further that the adsorption of xanthate by the noble metals can hardly be explained by a chemical reaction. Cook and Nixon (1950) were the others who opposed the "chemical theory" noting that it cannot explain the selective flotation of minerals by xanthate. They also pointed out that if only the collector ions are adsorbed, a large amount of charge will build up on the surface of the mineral. Accordingly, they postulated that xanthic acid rather than xanthate ion is adsorbed at the mineral surface which is known as the "neutral molecule adsorption theory." However, there has been a general tendency by other researchers to discount this theory because most studies support the ion-exchange mechanism rather than the neutral molecule theory. Infra-red spectroscopic (Leja et al., 1963) and microcalorimetric (Mellgren, 1960) data provided further evidence for the chemical theory. Other investigators, (Plaksin and Bessonov, 1957; Plaksin, 1959; Tolun and Kitchener, 1964; Gaudin and Finkelstein, 1965; Finkelstein, 1970) showed, however, that the chemical theory is inadequate and that molecular oxygen is required for the flotation of sulfides with xanthate particularly when the mineral is unoxidized.
This finding was responsible for the development of the electrochemical theory which delineates the role of oxygen on the mineral surface.

Salamy and Nixon (1953) suggested that the interaction between xanthate and oxygen at the mineral surface takes place by separate electrochemical reactions which proceed simultaneously. This developed into the "mixed potential theory" which states that an anodic oxidation of the collector and the cathodic reduction of oxygen, i.e.,

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e \rightarrow 4\text{OH}^- \]  

[1.1]

take place simultaneously at the surface of the mineral. At equilibrium, these would proceed at equal rates, and the potential at which this occurs is referred to as the mixed potential. Several reactions have been proposed by Woods (1984) for the oxidation of the collector. Conforming to the ion adsorption theory, xanthate can chemisorb by,

\[ \text{X}^- \rightarrow \text{X}_{ads} + e \]  

[1.2]

where \( \text{X}^- \) represents the xanthate ion. The mineral itself can be involved in the oxidation reaction and form a metal xanthate compound as follows:

\[ \text{M}_2\text{S} + 2\text{X}^- + 4\text{H}_2\text{O} \rightarrow 2\text{MX} + \text{SO}_4^{2-} + 8\text{H}^+ + 8e \]  

[1.3]

where \( \text{M} \) represents the metal ion of the sulfide mineral. Equation [1.3] is similar to the chemical theory proposed by Taggart. Oxidation of the sulfur in reaction [1.3] may proceed only as far as the formation of elemental sulfur or thiosulfate depending on the conditions of the reaction and the reaction time involved.

Lastly, xanthate can be oxidized to dixanthogen \( \text{X}_2 \), as given by the
following reaction,

$$2X^- \rightarrow X_2 + 2e \quad [1.4]$$

This reaction may occur on the unoxidized mineral surface or even after the mineral has reacted to form MX.

Plaksin and his co-workers (1957) proposed the so-called "semiconductor-adsorption theory," which suggests that oxygen takes up the free electrons present in the conduction band of the sulfide, thereby changing the electron energy level to a state where the adsorption of xanthate is facilitated. However, this theory can be regarded as an extension of the electrochemical theory.

Electrochemical studies on sulfides have become increasingly popular over the years. Various techniques ranging from rest potential measurements to voltammetry have been used for their study. Almost all of the early work concentrated on the galena-xanthate system, however. Rest potential measurements of a galena electrode in xanthate solutions have been reported as early as 1931 (Kamienski, 1931). Majima and Peters (1968) used the rest potentials to determine the degree of oxidation of sulfide minerals, while Allison et al. (1972) utilized it to acquire information to identify reactions occurring at the electrode/solution interface. From the measurements, they were able to correlate the collector oxidation products with the rest potentials.

Steady-state polarization studies on platinum, lead and galena electrodes in xanthate solutions in the presence and absence of oxygen were first reported by Tolun and Kitchener (1964). They found that a mixed potential did exist at which the oxidation of xanthate and the
reduction of oxygen occurred simultaneously on a galena electrode. These authors further stated that a film of lead xanthate and dixanthogen is most probably responsible for the formation of the hydrophobic surface.

Toperi and Tolun (1969) related the rest potentials of a galena electrode measured at different pH values in oxygenated solutions to the thermodynamic potentials for reactions in the PbS-O₂-X system. They showed that the potential range for the flotation of galena falls within the $E_h$-pH region where lead xanthate co-exists with xanthate ion and dixanthogen. Other investigators (Majima and Takeda, 1968; Fuerstenau et al., 1968; Majima, 1969) also utilized the $E_h$-pH diagrams in identifying the reaction products involving the collector and the sulfide mineral.

The most detailed electrochemical study of the chemisorption of xanthate using linear sweep voltammetry was first carried out by Woods (1971). He showed that the anodic oxidation of xanthate on platinum, gold, copper and galena electrodes resulted in the formation of dixanthogen ($X_2$), and that the collector is not chemisorbed but instead forms multilayers on the electrode surface.

Early work on chalcocite-xanthate systems was limited to the identification of the reaction product. The first set of tests showing the reaction between xanthate and chalcocite were conducted by Gaudin et al. (1934). The product formed on the surface of chalcocite after the addition of xanthate was identified as cuprous xanthate which forms a film unleachable by common solvents such as benzene or ether. Gaudin
and Schuhmann (1936) confirmed this in their own work and suggested that the formation of the absorbed film is accompanied by reaction of a portion of the xanthate to form cuprous xanthate. Further adsorption studies by Paterson and Salman (1968) concluded that xanthate reacts chemically with cupric ions to form cuprous xanthate and dixanthogen at the chalcocite surface.

Cyclic voltammetry on a natural copper sulfide electrode, containing 85% chalcocite and 13% bornite, in the presence of xanthate was first reported by Kowal and Pomianowski (1973). The voltammograms for the electrode in a 0.1M NaF solution with a xanthate concentration of $2.57 \times 10^{-4}$M is shown in Figure 1.1. They identified the anodic peaks, $A_1$ and $A_2$, as adsorption prepeaks due to a two-step process similar to that postulated by Woods (1971). Anodic peak $A_3$ was suggested to be a mass-transport controlled current resulting from the formation of copper xanthate on the electrode surface.

Chander and Fuerstenau (1974) investigated the interactions of dithiophosphate (DTP) with platinum, copper and synthetic Cu$_2$S electrodes using linear sweep voltammetry. Figure 1.2 shows the voltammograms for the synthetic copper sulfide electrode in 0.025M borate solution and different amounts of KDTP. The results are similar to the ones obtained by Kowal and Pomianowski. The oxidation products of DTP ions on the copper sulfide electrode were determined to be CuDTP and Cu(DTP)$_2$.

The work on chalcocite was continued by Richardson and his co-workers (Richardson et al., 1984; Walker et al., 1984; O'Dell et al.,
Figure 1.1  Linear sweep voltammograms for a natural copper sulfide electrode in 0.1M NaF solution containing 0 M KEX (---) and 2.57 x 10^{-4} M KEX (----).  
(from Kowal and Pomianowski, 1973).
COPPER SULFIDE (Cu₂S)

0.025 M Sodium Borate (pH 9.3)

50 mV/s

Unstirred

Figure 1.2 Linear sweep voltammograms for a synthetic copper sulfide electrode in 0.025M Sodium borate (pH 9.3) containing various concentrations of KDTP. (from Chander and Fuerstenau, 1974).
1984), who carried out electrochemical experiments using packed-bed electrodes. Figure 1.3 shows the apparatus in which the particulate bed electrodes are compacted for voltammetry experiments. This set-up also included a spectrometric analysis of the solution during the test. Cyclic voltammetry on chalcocite in the presence of xanthate showed the formation of a chemisorbed product near the potential observed by Kowal and Pomianowski where xanthate adsorption occurs. They concluded that the chemisorption of xanthate produces a hydrophobic layer that is responsible for flotation of chalcocite.

With the recognition of electrochemical mechanisms, studies on the significance of potentials in sulfide flotation (Heyes and Trahar, 1977, 1979; Gardner and Woods, 1979; Luttrell and Yoon, 1984; Walker et al., 1984; Trahar, 1983) have been carried out. The potential of the mineral has been controlled electrochemically or by the addition of oxidizing or reducing agents. Heyes and Trahar monitored the redox state of the system by measuring the potential of a platinum electrode in the pulp relative to a reference electrode. The potential of the sulfide mineral was found to be similar to the redox potential of the solution environment. They concluded that the flotation of chalcocite with KEX is strongly dependent on potential.

Gardner and Woods controlled the potential electrochemically at the mineral-solution interface and found that the natural floatability of chalcopyrite is dependent on the potential. Electrochemical flotation of chalcocite was done by Walker et al., and the same dependence on potential was observed.
Figure 1.3 Schematic diagram of the microflotation - electrochemical cell used by Richardson and co-workers (O'Dell et al., 1984; Richardson et al., 1984; Walker et al., 1984).
The possibility of the use of potential measurements in industrial flotation circuits have been discussed by Woodcock and Jones (1970), Natarajan and Iwasaki (1973), Castro and Larrondo (1981), and Rand and Woods (1984). It was suggested that pulp potential may be used to monitor or control flotation. Woods (1983) pointed out, however, that more work is needed to show the dependence of flotation on potential in various recycle streams.

The behavior of copper sulfide flotation systems have also been related to thermodynamic predictions. Chander and Fuerstenau (1975) constructed $E_h$-pH diagrams for the Cu-S-DTP-H$_2$O system and used them to interpret the results of their contact angle experiments. They found that for a finite contact angle, the system has to be in the thermodynamic stability domain of CuDTP or Cu(DTP)$_2$ since these are the metal-reagent species responsible for hydrophobicity of the copper sulfide. However, their thermodynamic calculations for the construction of the stability diagrams are relatively simple.

Few attempts have been made to carry out a comprehensive series of calculations in which many different dissolved and solid species are considered simultaneously. Hepel and Pomianowski (1977) carried out extensive manual thermodynamic calculations for the copper-xanthate-water system. On the basis of these calculations, stability diagrams have been constructed at different xanthate concentrations. This system, instead of one involving sulfides, was considered by the authors due to the complicated behavior of sulfide minerals in flotation.
1.3 Objectives

In order to have a full understanding of the flotation chemistry involved in the flotation of chalcocite, both thermodynamics and kinetics of the system have been studied.

The first part of the work has dealt with the thermodynamic calculations for the chalcocite-water system in the absence and presence of potassium ethyl xanthate. The calculations have been carried out with particular emphasis on constructing \( E_h \)-pH diagrams and determining the regions where copper xanthate and dixanthogen are stable. The approach differs significantly from previous work as it includes all the soluble and insoluble species in the mass balance calculations. Aside from the stability diagrams, the calculations allow the determination of the concentration of any dissolved specie and the amount of xanthate taken up by chalcocite. From these results, the effect of \( E_h \) or pH on the amount of copper xanthate formed can be predicted and compared with actual flotation data.

Another objective of the calculations is to determine the minimum xanthate addition required to form copper xanthate within an \( E_h \)-pH region where its formation is favored. This would be useful in predicting the optimum conditions for chalcocite flotation.

In the second part of the study, microflotation and electrochemical experiments have been conducted on chalcocite as functions of pH, \( E_h \) and xanthate additions using a small Partridge and Smith-type flotation cell. The results of the flotation tests are then compared with those of the thermodynamic calculations.
The kinetics of chalcocite oxidation and that of xanthate adsorption on the mineral have been studied by voltammetry. Voltammograms of a chalcocite electrode have been obtained at pH 6.8, 9.2 and 11 to identify the reaction products.
2.1 Materials

The chalcocite samples used for microflotation experiments were obtained from the Department of Geological Sciences, Virginia Polytechnic Institute and State University. It originated from Butte, Montana and contained some bornite inclusions. For voltammetry experiments, a bornite-free chalcocite specimen was obtained through the courtesy of the Smithsonian Institute. This specimen also originated from Butte, Montana.

The collector reagent used was commercial grade potassium ethyl xanthate (K\textsubscript{2}C\textsubscript{2}H\textsubscript{5}OCS\textsubscript{2}) purified by dissolution in acetone and recrystallized with petroleum ether. This was repeated three times and then stored in ether. Prior to each experiment, a small portion of the reagent was removed and dried in a vacuum dessicator.

Microflotation experiments were done at pH 5 (0.1M KH Phthalate/0.1M NaOH solutions), pH 8 and pH 11 (0.05M Na\textsubscript{2}HPO\textsubscript{4}/0.1M NaOH solutions). Hydrazine hydrate (N\textsubscript{2}H\textsubscript{4}.H\textsubscript{2}O) was used as the reducing agent while the oxidizing agent was hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}). An attempt was made to use a buffer (0.1M KH\textsubscript{2}PO\textsubscript{4}/0.1M NaOH solution) for pH 8, but the addition of the reducing agent changed the pH drastically. Therefore, this pH was controlled by adding sodium hydroxide or hydrochloric acid.
solutions. No frother was used in any of the microflotation experiments.

The electrochemical experiments were conducted at pH 9.2 (0.05M Na$_2$B$_4$O$_7$ solutions), pH 6.8 (0.1M KH$_2$PO$_4$/0.1M NaOH solutions) and pH 11 (0.05M Na$_2$HPO$_4$/0.1M NaOH solutions). All the solutions used were of A.C.S. reagent grade and all the solutions were prepared with double-distilled water. Before each series of experiments, the buffered solution was deoxygenated by purging with low-oxygen nitrogen gas (< 0.5 ppm O$_2$) for at least one hour.

2.2 Equipment

The potential of the pulp in the microflotation tests was measured by placing a platinum-saturated calomel electrode pair into the stirred suspension. The platinum electrode was of the disc-type, and a Fisher Accumet Model 610A potentiometer was used to monitor the potential. Performance of the electrode pair was checked prior to each test by calibration in ZoBell solution (Garrels and Christ, 1965). The ZoBell solution consists of 1/300 M potassium ferrocyanide, 1/300 M potassium ferricyanide and 0.1 M potassium chloride which yields a measured potential of 430 mv (vs SHE) at 25°C. The reference electrode was refilled regularly with saturated KCl solution while the platinum electrode surface was mechanically cleaned before each test with 600-grit silicon carbide paper.

A Partridge and Smith-type flotation cell (Partridge and Smith, 1971) made of Pyrex glass was used for the flotation tests. The
apparatus is shown schematically in Figure 2.1. Bubbles were generated by passing low-oxygen nitrogen gas through a medium porosity glass frit at the bottom of the cell. The gas flow rate was monitored using a Gilmont Micrometer Capillary Flowmeter. Agitation of the pulp was supplied by means of a Teflon coated magnetic stirring bar and a magnetic stirrer.

For the voltammetry experiments, a conventional three electrode system was used. The electrode potential was controlled with a PAR Model 371 Potentiostat/Galvanostat and a PAR Model 175 Universal Programmer. The voltammograms were recorded on a Hewlett Packard 7004B X-Y recorder. Figure 2.2 shows the schematic diagram for this set-up. A saturated calomel electrode was used as the reference electrode, although all potentials reported here are expressed on the standard hydrogen scale. For the analysis of the voltammograms, a Numonics Model 1224 electronic graphics calculator was used to determine the areas under the current-potential curves.

2.3 Procedure

2.3.1 Microflotation:

Samples were checked microscopically for purity and those pieces contaminated with quartz were discarded. They were then crushed, just before each flotation test so as to minimize oxidation, using a porcelain mortar-and-pestle, and hand-screened to obtain a -100+150 mesh size fraction. In each test, a 1-gm freshly ground sample was placed in a beaker containing 100 ml of deoxygenated buffer solution. The pulp
Figure 2.1  Schematic diagram of the microflotation set-up.
Figure 2.2  Schematic diagram showing apparatus used for linear sweep voltammetry.
potential was controlled by adding the reducing or oxidizing agent while monitoring the potential. Two series of experiments were carried out depending on the sequence of reagent addition. In one series, KEX was added first and then the potential was adjusted to a desired value. In the other, the potential was controlled prior to the collector addition. After the reagent addition, the mineral suspension was then conditioned for 5 minutes in a beaker while being agitated gently.

After conditioning, the suspension was transferred to the flotation cell where a one-minute flotation time was employed with a gas flow rate of 40 ml/minute. The particles that floated and those that did not were then collected separately, filtered, air-dried and then weighed to get the flotation recovery.

2.3.2 Preparation of Chalcocite Electrode

A chalcocite electrode was prepared from a mineral specimen with a rectangular cross-section cut from a larger piece with an Isomet diamond saw. This was then permanently attached to a copper lead with Electrodag 199, a carbon-based conducting cement. This assembly was then sealed in a glass holder with Buehler epoxy resin (Figure 2.3). The geometric area exposed to the solution was 0.81 cm². Before each test run, the electrode surface was polished with 400- and 600-grit silicon carbide paper and then rinsed with double-distilled water.

2.3.3 Voltammetry Experiments

Prior to each series of experiments, the 350-ml buffer solution was poured into the cell and deoxygenated with nitrogen gas for one hour.
Figure 2.3 Working electrode used for the electrochemical studies of chalcocite.
Once a test was begun, the gas sparger was raised above the solution with nitrogen continuously introduced to maintain a positive pressure. The potential sweeps were conducted in the absence of xanthate and at xanthate concentrations of $10^{-3}$ and $2.5 \times 10^{-5}$ M.

A conventional three-electrode circuit was used for the experiments. This consisted of the chalcocite mineral electrode (working electrode), a saturated calomel electrode (reference electrode) and an isolated platinum wire electrode (counter electrode) immersed in the buffered solution and connected to the potentiostat. The starting potential, upper and lower potential limits and the scan rate are controlled through the Universal programmer. In the potentiostatic experiments, the potential is applied across the working and reference electrodes. At appropriate potentials, faradaic reactions will occur at the mineral surface and result in the flow of current. This current flows to the counter electrode and the signals are sent to the X-Y recorder.
CHAPTER III.

THERMODYNAMIC CALCULATIONS

3.1 Outline of the Calculations

In the construction of the $E_h$-$pH$ diagrams, the approach is similar to the one used by Pritzker (1985) in his thermodynamic calculations. The difference of his approach to previous ones is that the mass balance includes not only the dissolved species, but all solid species as well. From the mass balance equations, the concentrations of all dissolved species and the weights of the solids can be determined under any $E_h$-$pH$ conditions. This has not been done in previous work of this kind.

The calculations were done with the assumption that only chalcocite is present and that the activity coefficients of all species are taken to be unity. Furthermore, all the reactions are assumed to be reversible and that the potential of the entire system is uniform, so that the calculations can be handled on a thermodynamic basis.

The total amount of copper- ($M_{Cu}$), sulfur- ($M_S$) and xanthate- ($M_X$) bearing species are specified by considering a given amount of chalcocite and potassium ethyl xanthate. The working equations are derived from the mass balance equations for copper-bearing, sulfur-bearing and xanthate-bearing species, which are expressed in terms of the appropriate equilibrium constants. In this system, the possible

24
solids considered are Cu\(^0\), Cu\(_2\)O, Cu(OH)\(_2\), S\(^0\), Cu\(_2\)SO\(_4\), CuSO\(_4\), Cu\(_2\)S, CuS, CuX, CuX\(_2\) and X\(_2\). Mass balance equations can be written for each of the cases where one, two or more, or no solid is stable. For each of the considered cases, these become polynomial equations in one unknown when the E\(_h\) and pH values are substituted. These are solved numerically by a computer program using the secant method. The calculation procedure used here is given in more detail in the work done by Pritzker for the galena-ethyl xanthate system.

The thermodynamic data and ionic equilibria that have been considered in this system are given in Tables 3.1 and 3.2. The calculations have been performed for the case where the oxidation of sulfide proceeds as far as the formation of sulfate at a temperature of 298.15\(^\circ\)K and a pressure of 1 atm.

To understand the calculations clearly, a detailed derivation of one of the working equations is given below. For the case when Cu\(_2\)S (s) and CuX (s) are stable together, the prevailing equilibrium conditions are:

\[ \text{Cu}_2\text{S(s)} = 2\text{Cu}^+(aq) + \text{S}^{2-}(aq), \quad K_{SO} = [\text{Cu}^+]^2[\text{S}^{2-}] = 10^{-48.67} \quad [3.1] \]

\[ \text{CuX(s)} = \text{Cu}^+(aq) + \text{X}^-(aq), \quad K_{SO} = [\text{Cu}^+][\text{X}^-] = 10^{-19.28} \quad [3.2] \]

Mass balances for copper-, sulfur- and xanthate-bearing species yield:

\[ \text{Cu} : \quad 2m_{\text{Cu}_2\text{S}} + m_{\text{CuX}} + \Sigma(\text{Cu}) = M_{\text{Cu}} \quad [3.3] \]

\[ S : \quad m_{\text{Cu}_2\text{S}} + \Sigma(S) = M_S \quad [3.4] \]
<table>
<thead>
<tr>
<th>Dissolved Species</th>
<th>$\Delta G_f^\circ$ (kcal/mole)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^+$ (aq)</td>
<td>-12.10</td>
<td>Hogfeldt (1982)</td>
</tr>
<tr>
<td>Cu$^{2+}$ (aq)</td>
<td>-15.53</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>Cu(OH)$^+$ (aq)</td>
<td>-13.00</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>Cu(OH)$^{2-}$ (aq)</td>
<td>-85.80</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>Cu(OH)$_3^{2-}$ (aq)</td>
<td>-118.50</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>Cu(OH)$_4^{2+}$ (aq)</td>
<td>-157.30</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>Cu$^{2+}$(OH)$_2$ (aq)</td>
<td>-67.00</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>Cu$^{2+}$ (aq)</td>
<td>-43.90</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>CuSO$_4$ (aq)</td>
<td>-165.50</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>S$^{2-}$ (aq)</td>
<td>21.80</td>
<td>Hogfeldt (1982)</td>
</tr>
<tr>
<td>HS$^-$ (aq)</td>
<td>3.01</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>H$_2$S (aq)</td>
<td>-6.54</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>SO$_4^{2-}$ (aq)</td>
<td>-177.34</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>HSO$_4^-$ (aq)</td>
<td>-179.94</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>H$_2$SO$_4$ (1)</td>
<td>-177.34</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>H$_2$O (1)</td>
<td>-56.69</td>
<td>&quot; &quot;</td>
</tr>
<tr>
<td>OH$^-$ (aq)</td>
<td>-37.59</td>
<td>&quot; &quot;</td>
</tr>
</tbody>
</table>

**Gaseous Species**

| H$_2$S (g)       | -7.89                         | Hogfeldt (1982) |

**Solid Species**

| Cu$_2$O (s)      | -34.98                        | Hogfeldt (1982) |
| Cu(OH)$_2$ (s)   | -30.40                        | " " |
| CuS (s)          | -10.23                        | " " |
| Cu$_2$S (s)      | -20.40                        | " " |
| Cu$_4$S$_4$ (s)  | -158.20                       | " " |
| Cu$_2$SO$_4$ (s) | -156.00                       | " " |
### Table 3.2
Equilibrium Constants and Standard Electrode Potentials at 25°C

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium Constant</th>
<th>$E^\circ_{\text{H}}$ (mv)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X^- + H^+ = HX$</td>
<td>$K_1 = 10^{1.64}$</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>$X_2 (1) = X_2 (aq)$</td>
<td>$K_{SO} = 10^{-4.90}$</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>$X_2 (1) + 2e = 2X^-$</td>
<td></td>
<td>$-60$</td>
<td>3</td>
</tr>
<tr>
<td>$CuX (s) = Cu^+ + X^-$</td>
<td>$K_{SO} = 10^{-19.28}$</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>$CuX_2 (s) = Cu^{2+} + 2X^-$</td>
<td>$K_{SO} = 10^{-24.2}$</td>
<td></td>
<td>5</td>
</tr>
</tbody>
</table>

References:

1. Iwasaki and Cooke (1958); Majima (1961); Tornell (1966); Hopstock (1968)
2. Tipman and Leja (1975)
3. Average value of Kakovskii and Arashkevich (1969); Majima and Takeda (1968); Goldstick (1959); DuRietz (1957); Tolun and Kitchener (1964)
4. Kakovskii (1957)
5. DuRietz (1976)
\[ X : \quad m_{\text{CuX}} + \Sigma(X) = M_X \quad [3.5] \]

where \( m_{\text{Cu}_2\text{S}} \) = number of moles of \( \text{Cu}_2\text{S} \) per liter of solution

\( m_{\text{CuX}} \) = number of moles of \( \text{CuX} \) per liter of solution

\( \Sigma(\text{Cu}), \Sigma(S), \Sigma(X) \) = total number of moles of dissolved copper-, sulfur- and xanthate-bearing species, respectively, per liter of solution

\( M_{\text{Cu}}, M_S, M_X \) = total number of moles of copper-, sulfur- and xanthate-bearing species, respectively, per liter of solution

The concentration of each of the copper-bearing species can be expressed in terms of any one of these species since they are all in equilibrium with each other. Using free energy data in Table 3.1, equilibrium constants for the different reactions can be determined and concentrations of each copper-bearing species are expressed in terms of \([\text{Cu}^{2+}]\). This is also done for the sulfur-bearing (expressed in terms of \([\text{S}^{2-}]\), pH, \( E_h \)) and xanthate-bearing ([\( X^- \)], pH, \( E_h \)) species. The total concentration of all the dissolved species in the mass balance become:

\[
\Sigma(\text{Cu}) = \frac{2^x B_{22}}{[\text{H}^+]^2} [\text{Cu}^{2+}]^2 + B_1 [\text{Cu}^{2+}] + \frac{B_2}{[\text{Cu}^{2+}]} \quad [3.6]
\]

\[
\Sigma(S) = B_3 [\text{S}^{2-}] + B_4 [\text{S}^{2-}] \quad [3.7]
\]

\[
\Sigma(X) = 2 \cdot 10^{\frac{2F(E_h-E_{X_2(aq)/X^-})}{2.303 RT}} [\text{X}^-]^2 + (1 + K_1^{H[X^{+}][\text{H}^+]})[\text{X}^-] \quad [3.8]
\]
where

\[
B_1 = 1 + \frac{\beta_{11}}{[H^+]} + \frac{\beta_{21}}{[H^+]^2} + \frac{\beta_{31}}{[H^+]^3} + \frac{\beta_{41}}{[H^+]^4} - \frac{-F(E_h-E_0^{\circ}Cu^{2+/Cu^+})}{2.303 \, RT} \tag{3.9}
\]

\[
B_2 = K_{1CuSO_4} \cdot K_{SO_4Cu_2S} \cdot 10^{2.303 \, RT} \cdot 10 \tag{3.10}
\]

\[
B_3 = 1 + \frac{\beta_{11}[H^+]}{[H^+]^2} + (K_{1H_2S_{aq}} + K_{1H_2S_{g}}) \cdot [H^+]^2 - \frac{8F(E_h-E_0^{\circ}SO_4^{2-}/S^{2-})}{2.303 \, RT} \tag{3.11}
\]

\[
B_4 = K_{SO_4Cu_2S} \cdot (K_{SO_4Cu_2S})^{\frac{1}{2}} \cdot 10^{2.303 \, RT} \cdot 10 \tag{3.12}
\]

Rearranging equations [3.4] and [3.5]:

\[
m_{Cu_2S} = M_S - \Sigma(S)
\]

\[
m_{CuX} = M_X - \Sigma(X)
\]

Substituting these into the mass balance equation for copper-bearing species [3.3] and rearranging yields:

\[
\Sigma(Cu) - 2 \Sigma(S) - \Sigma(X) - M_{Cu} + 2M_S + M_X = 0 \tag{3.13}
\]

When equation [3.13] is expanded by substituting equations [3.6], [3.7] and [3.8], this results in:
From the relationship for the equilibrium between [Cu+] and [Cu2+]:

\[
\frac{2F(E_h - E^o_{\text{Cu}^{2+}/\text{Cu}^+})}{2.303 \text{ RT}} - 2.10 \cdot [X^-]^2 - (1 + K_1 \text{HX} [H^+]) [X^-] - (M_{\text{Cu}} - 2M_S - M_X) = 0
\]  

[3.14]

Equations [3.1] and [3.2] can be used to reduce equation [3.14] into a polynomial equation in one unknown, [Cu2+]. After substituting these and multiplying through by [Cu2+], the final equation obtained is:

\[
\frac{2F(E_h - E^o_{\text{Cu}^{2+}/\text{Cu}^+})}{2.303 \text{ RT}} + [\text{Cu}^{2+}] \left( B_2 - B_4 \right) \cdot (K_{\text{So}} \text{Cu}_2 \text{S})^{1/2} \cdot 10^{-2(2.303 \text{ RT})} - (1 + K_1 \text{HX} [H^+]) (K_{\text{So}} \text{CuX})^{10^{-2}} - B_3 \cdot K_{\text{So}} \text{Cu}_2 \text{S} \cdot 10^{-2F(E_h - E^o_{\text{Cu}^{2+}/\text{Cu}^+})/2.303 \text{ RT}} - (2) \cdot 10^{-2F(E_h - E^o_{\text{Cu}^{2+}/\text{Cu}^+})/2.303 \text{ RT}} = 0
\]  

[3.16]

This can be solved numerically for different $E_h$ and pH values. From the equilibrium relationships, the concentration of all the other species can be calculated once [Cu2+] is known.
The FORTRAN computer program used to do the calculations in this study is listed in Appendix I.

3.2 Results of the Calculations

The amount of chalcocite considered in our calculations is equivalent to an ore assaying 1.8% Cu that is being treated in a flotation circuit operating at 30% solids by weight. A series of computations over the entire $E_h$-pH range was carried out for collector additions of $0$, $10^{-7}$, $10^{-6}$, $10^{-5}$ and $10^{-4}$ M KEX.

3.2.1 $E_h$-pH diagrams in the absence of KEX

Figure 3.1 shows the $E_h$-pH diagram when oxidation of sulfide is allowed to proceed as far as sulfate and when no xanthate is added. In this diagram, as well as in those where xanthate is added, the limits of the domain of relative predominance of the soluble sulfur-bearing species are shown by the dotted lines. The regions where the solids are relatively stable on the other hand, are indicated by solid lines.

As can be seen from the figure, chalcocite is converted to $Cu_2O$ and then to $Cu(OH)_2$ under highly oxidizing conditions, while at low potentials, it is reduced to Cu metal. At acidic pH and high $E_h$, $Cu_2S$ dissolves completely, which is the basis for oxidative leaching processes. This shows how these calculations can be applied not only to flotation systems, but to hydrometallurgical ones as well.
Figure 3.1  $E_h - pH$ diagram of the $\text{Cu}_2S - \text{KEX} - H_2O$ system in the absence of KEX at $T = 298^\circ K$ and $P = 1$ atm.
3.2.2 $E_h$-pH diagrams in the presence of KEX

a. $10^{-7}$M KEX: A similar phase diagram for Cu$_2$S contacted with $10^{-7}$M KEX is given in Figure 3.2. It shows the $E_h$-pH regions in which CuX and CuX$_2$ can be formed along with other co-existing solid phases. One can anticipate that Cu$_2$S flotation will be possible in these regions. CuX is found to co-exist with Cu$_2$S, Cu, Cu$_2$O, Cu(OH)$_2$ in a large region starting at $E_h = -200$ mv to $E_h = 400$ mv and pH 11.5. At moderately oxidizing conditions (up to $E_h = 560$ mv), CuX$_2$ is the only stable solid at acidic pH. However, at pH 4.4, CuX$_2$ co-exists with Cu(OH)$_2$ up to pH 9.0. This agrees with a recent report by Richardson and his co-workers (1984) that the floatability of chalcocite increases significantly at high potentials where formation of CuX$_2$ is possible.

b. $10^{-6}$M KEX: When the KEX addition is increased to $10^{-6}$M, the regions for CuX and CuX$_2$ formation is larger, suggesting that chalcocite can be floated under more reducing and alkaline conditions at a higher reagent dosage. In Figure 3.3, CuX co-exists with other solid species up to pH 12.45. At alkaline conditions, CuX starts to form at $E_h = -250$ mv and is stable up to $E_h = 400$ mv. CuX$_2$ is stable above this $E_h$ value up to a potential of 560 mv. The region where Cu(OH)$_2$ and CuX$_2$ co-exist also increases and is stable up to pH 10. Note that the Cu$_2$O stability region decreased with the increased KEX addition. This might suggest the competition between the reactions for the CuX formation and the oxidation of chalcocite.
Figure 3.2  $E_h$ - pH diagram of the Cu$_2$S - KEX - H$_2$O system for a collector addition of $10^{-7}$M at $T = 298$°K and $P = 1$ atm.
$10^{-6}$ M KEX

Figure 3.3  $E_h$ - pH diagram of the Cu$_2$S - KEX - H$_2$O system for a collector addition of $10^{-6}$M at $T = 298^\circ$K and $P = 1$ atm.
c. $10^{-5}$M KEX: At $10^{-5}$M KEX, the region where CuX and CuX$_2$ is stable has grown considerably (Figure 3.4). CuX is more stable with other copper species up to pH = 13.45 and a lower limit of $E_h = -300$mv. However, at acidic conditions, it is still stable only up to $E_h = 400$ mv. This is due to cupric ions being more stable than cuprous ions at oxidizing conditions. The region where CuX$_2$ is stable by itself remains the same since this is dependent on Cu$^{2+}$ concentration. However, Cu(OH)$_2$ and CuX$_2$ co-exist in a larger region and extends up to pH 11.2. Cu$_2$O is now stable only at pH's greater than 12.45 as the KEX is increased.

d. $10^{-4}$M KEX: The same trend is seen as the collector addition is increased ten-fold (Figure 3.5). The $E_h$-pH regions where CuX and CuX$_2$ are stable have grown further. The lower limit for the formation of CuX has gone down to $E_h = -400$ mv. CuX is also now stable over the entire pH range at slightly reducing conditions. However, the upper limit for the CuX stability region is still at $E_h = 400$ mv. On the other hand, CuX$_2$ is stable even at more oxidizing conditions ($E_h = 640$ mv). The Cu(OH)$_2$ and CuX$_2$ region has a higher pH limit of 12.0. It should also be noted that the entire region where Cu$_2$O alone is stable has completely disappeared. This is due to the high collector concentration where formation of CuX is much more favored over the oxidation of the mineral even at very alkaline conditions. The $E_h$-pH region for Cu$_2$S has also decreased as there is more collector to react with the copper. However, the Cu/Cu$_2$S line does not get affected by the collector as this is at very reducing conditions.
Figure 3.4  \( E_h \) - pH diagram of the \( \text{Cu}_2\text{S} \)-KEX-\( \text{H}_2\text{O} \) system for a collector addition of \( 10^{-5} \) M at \( T = 298^\circ \text{K} \) and \( P = 1 \) atm.
Figure 3.5  $E_h - \text{pH}$ diagram of the Cu$_2$S - KEX - H$_2$O system for a collector addition of $10^{-4}$M at $T = 298^\circ$K and $P = 1$ atm.
3.3 Discussion

3.3.1 Effect of $E_h$, pH and KEX concentration on the formation of CuX and CuX$_2$

In the calculations, the solid phases are also included in the mass balances, so that the quantity of a solid stable in a given region can also be determined. From these values, the effect of $E_h$, pH and xanthate concentration on the amount of CuX or CuX$_2$ that is produced can be studied. This can be used to compare the results of the calculations to the experimental flotation data.

The amount of CuX or CuX$_2$ formed is given by the calculations as the percentage of the number of moles of xanthate initially added that ends up as CuX or CuX$_2$. This quantity is hereupon referred to as $\%$ CuX or $\%$ CuX$_2$ and used to correlate with flotation results.

a. Effect of $E_h$: Figures 3.6 - 3.9 show the effect of $E_h$ on $\%$ CuX at various pH values for KEX additions of $10^{-7}$, $10^{-6}$, $10^{-5}$ and $10^{-4}$ M. $\%$ CuX increases abruptly as the potential is increased and reaches a maximum at a critical potential. This is true for any pH value and KEX addition. All the curves leveled out to the maximum for a certain interval before dropping sharply to zero at another well-defined critical potential. These critical potentials would correspond to the lower and upper limiting potentials for flotation, respectively.

As the KEX addition increases, the curve gets wider indicating that the stability of CuX extends over a larger potential range at a given pH. However, with increasing pH at a given amount of collector, the CuX
Figure 3.6 Effect of $E_h$ on % CuX for a collector addition of $10^{-7}$/M KEX. The number next to each curve denotes the pH.
Figure 3.7 Effect of \( E_h \) on % CuX for a collector addition of 10\(^{-6}\) M KEX. The number next to each curve denotes the pH.
Figure 3.8 Effect of $E_h$ on % CuX for a collector addition of $10^{-5}$M KEX. The number next to each curve denotes the pH.
Figure 3.9  Effect of $E_h$ on % CuX for a collector addition of $10^{-4}$ M KEX. The number next to each curve denotes the pH.
stability range decreases. It should be noted that there is complete conversion of xanthate to CuX at some potential range even at low KEX concentration. This would indicate the good floatability of this mineral relative to other sulfides such as PbS.

\% CuX\textsubscript{2} has been plotted against \textit{E}_h at various pH values in Figures 3.10 - 3.13. It is shown that as compared to \% CuX, CuX\textsubscript{2} is stable only over narrow pH and \textit{E}_h ranges and more oxidizing conditions.

At acidic conditions, the lower limiting potential for CuX\textsubscript{2} formation is constant but varies with \textit{E}_h at more basic pH's. Even at different KEX additions, the lower limiting potential is around 400 mv for pH values less than 7. Decreasing the pH results in an increase in the upper potential limit, which is similar to the response of CuX. On the other hand, increasing the KEX addition widens the CuX\textsubscript{2} stability range only for alkaline pH values. The amount of CuX\textsubscript{2} formed is not affected too much by the ethyl xanthate concentration at low pH.

b. Effect of pH: The effect of pH on \% CuX for different \textit{E}_h values is shown in Figure 3.14 - 3.17. At oxidizing potentials, \% CuX starts and stays at a maximum value before decreasing sharply when an upper pH limit is reached. For reducing conditions, the curves have the same shape as that for the previous plots where it starts at zero and increases abruptly at a critical pH. The curves are much wider compared to those plotted as a function of \textit{E}_h, which indicates that CuX formation is more dependent on \textit{E}_h than pH.

At oxidizing potentials, CuX is stable at very low pH's, even though xanthic acid, HX, is more stable than free xanthate ions. The
Figure 3.10 Effect of $E_h$ on % CuX$_2$ for a collector addition of $10^{-7}$ M KEX. The number next to each curve denotes the pH.
Figure 3.11 Effect of $E_h$ on $\% \text{CuX}_2$ for a collector addition of $10^{-6}\text{ M KEX}$. The number next to each curve denotes the pH.
Figure 3.12  Effect of $E_h$ on % CuX$_2$ for a collector addition of $10^{-5}$M KEX. The number next to each curve denotes the pH.
Figure 3.13  Effect of $E_h$ on % CuX$_2$ for a collector addition of $10^{-4}$M KEX. The number next to each curve denotes the pH.
Figure 3.14  Effect of pH on % CuX for a collector addition of 10^{-7} \text{M} \text{KEX}. The number next to each curve denotes the $E_h$ (mv).
Figure 3.15  Effect of pH on % CuX for a collector addition of 10^{-6} M KEX. The number next to each curve denotes the \( E_h \) (mv).
Figure 3.16 Effect of pH on % CuX for a collector addition of $10^{-5}$ M KEX. The number next to each curve denotes the $E_h$ (mv).
Figure 3.17 Effect of pH on % CuX for a collector addition of $10^{-4}$ M KEX. The number next to each curve denotes the $E_h$ (mv).
formation of xanthic acid may be given by the following reaction,

\[ \text{H}^+ + \text{X}^- \rightarrow \text{HX}. \]  

However, at reducing conditions where the amount of free cuprous ions is less, the above reaction affects CuX formation so that the lower flotation edges occur at higher pH's. The upper edge is determined by the competition between xanthate ions and hydroxyl ions for copper.

At a low KEX addition, the upper pH limit for CuX stability is lower compared to that for higher collector concentrations. This is due to smaller amounts of free xanthate ions available to compete with the hydroxyl ions for copper. However, increasing the KEX addition at very oxidizing conditions does not have a very significant effect on the upper critical pH.

In Figures 3.18 - 3.21, % CuX2 is plotted against pH at various \( E_h \) values and KEX addition. It shows the same trend as that seen for the effect of \( E_h \) on CuX2 formation. The stability range is narrow and at some potentials, complete conversion of xanthate to CuX2 is never attained. The curves are all for high \( E_h \) values since CuX2 is stable only at very oxidizing conditions.

Increasing the xanthate concentration results in a wider stability range. However, the increase is only for the upper pH limit, as the lower limit is unaffected. Also, at higher collector addition, CuX2 becomes stable at more oxidizing potentials.

3.3.2 Minimum KEX Addition required for CuX and CuX2 Formation

Although thermodynamic calculations can determine the maximum ranges of \( E_h \) and pH for metal xanthate formation, as shown in the
Figure 3.18  Effect of pH on % CuX₂ for a collector addition of 10⁻⁷ M KEX. The number next to each curve denotes the $E_h$ (mv).
Figure 3.19 Effect of pH on % CuX₂ for a collector addition of $10^{-6}$ M KEX. The number next to each curve denotes the $E_h$ (mv).
Figure 3.20  Effect of pH on % CuX$_2$ for a collector addition of 10$^{-5}$ M KEX. The number next to each curve denotes the $E_h$ (mv).
Figure 3.21  Effect of pH on % CuX₂ for a collector addition of $10^{-4}$ M KEX. The number next to each curve denotes the $E_h$ (mv).
previous figures, the free energy of formation varies significantly within a given $E_h$-pH region where metal xanthate formation is possible. In order to investigate this further, the minimum xanthate addition required for CuX formation in the Cu$_2$S-KEX-H$_2$O system has been calculated at pH 5, 8 and 11. The results are given in Figure 3.22 and show different minimum KEX requirements at various pH values. Although CuX formation is possible between -400 and 400 mv, it is most favored between -180 and 360 mv, depending on the pH. This is the range where the minimum amount of KEX is required at different pH values. Maximum flotation would be expected in these narrower potential ranges.

As the pH increases, the KEX requirement increases and the optimum potential range shifts towards more reducing potentials. This would indicate that flotation is more favorable at acidic and oxidizing conditions. At pH 5, the KEX requirement is reduced to as low as $10^{-13.3}$ M. This value would seem to be unrealistically low for actual flotation. However, a larger amount of collector may have to be added to achieve a minimum collector coating for flotation.

3.3.3 Contour Plots and Three-Dimensional Diagrams

The results of the thermodynamic calculations have also been used to construct contour diagrams and three-dimensional plots using Surface II (Sampson, 1978), a graphics software system developed by the Kansas Geological Survey. Through this plot, the combined effect of $E_h$ and pH on the stability of copper and xanthate uptake can be more clearly seen.

A contour plot showing the effect of $E_h$ and pH on the amount of Cu$^{2+}$ ions is given in Figure 3.23. The pattern of the contour lines
Figure 3.22 Calculated minimum KEX addition required for CuX formation at pH 5, 8 and 11.
Figure 3.23 Contour plot showing the effect of $E_h$ and pH on $\log [\text{Cu}^{2+}]$ for the Cu$_2$S - H$_2$O system.
show some similarities to the stability domains of the different solids in the \(E_h\)-pH diagram for the Cu\(_2\)S-H\(_2\)O system (Figure 3.1). This is a result of the equilibrium cupric ion concentration being directly related to the solid species present. At reducing conditions, the [Cu\(^{2+}\)] lines are independent of pH as this is in the Cu\(^{2+}\)/Cu\(^0\) region. As the potential is increased, the amount of cupric ions becomes more dependent on pH and less with potential. The lines are totally pH dependent at high pH and \(E_h\) where Cu(OH)\(_2\) is stable.

Figure 3.24 shows the three-dimensional plot in which the changing concentration of cupric ions is shown as a function of both \(E_h\) and pH. This block diagram, even though it shows the data in a rather qualitative manner, presents the general effects of \(E_h\) and pH more clearly. The maximum amount of Cu\(^{2+}\) is shown by the plateau at low pH and very oxidizing potentials.

When 10\(^{-5}\) M KEX is added to the Cu\(_2\)S-H\(_2\)O system, the resulting contour plot shows that % CuX is maximum at neutral conditions (Figure 3.25). The boundary of this region is clearly indicated by the sudden change in slope. The lower boundary corresponds to the CuX/Cu\(_2\)S line while the upper boundary represents the CuX/Cu(OH)\(_2\) phase boundary at alkaline pH, and the CuX/CuX\(_2\) phase boundary at acidic pH. Increasing the collector addition would show the same trend seen for the \(E_h\)-pH diagrams.

Figures 3.26 - 3.29 show the effect of \(E_h\) and pH on % CuX at different KEX additions. The maximum amount of CuX formed for all diagrams is 100% and this plateau increases in size with increasing
Figure 3.24  Three-dimensional block diagram showing the effect of \(E_h\) and pH on \(\log [\text{Cu}^{2+}]\) for the \(\text{Cu}_2\text{S} - \text{H}_2\text{O}\) system.
Figure 3.25  Contour plot showing the effect of $E_h$ and pH on % CuX for a collector addition of $10^{-5}$ M KEX.
Figure 3.26  Three-dimensional block diagram showing the effect of $E_h$ and pH on $\% \text{CuX}$ for a collector addition of $10^{-7} \text{M KEX}$.
Figure 3.27  Three-dimensional block diagram showing the effect of $E_h$ and pH on % CuX for a collector addition of $10^{-6}$ M KEX.
Figure 3.28  Three-dimensional block diagram showing the effect of $E_{h}$ and pH on % CuX for a collector addition of $10^{-5}$ M KEX.
Figure 3.29 Three-dimensional block diagram showing the effect of E_h and pH on % CuX for a collector addition of 10^-4 M KEX.
KEX added. This shows more dramatically the possibility of flotation at more alkaline and reducing conditions as the collector addition is increased. Rotating the viewing angle of the block diagram by 45° would give the % CuX vs. $E_h$ curves at different pH and the effect of pH on % CuX, if rotated to the other side.
4.1 Microflotation

In the thermodynamic calculations, the quantity of an insoluble specie stable in a given region can be determined directly from the computations. This can be used to see the effect of $E_h$ and pH on $\% \text{CuX}$ (or $\% \text{CuX}_2$), which was shown previously. Since both CuX and CuX$_2$ are considered as the reaction products that render chalcocite hydrophobic, their quantities (i.e. $\% \text{CuX}$ or CuX$_2$) may be directly correlated with flotation results. In this chapter, the calculated data from Chapter III is compared with actual flotation results reported in the literature and with those obtained from the experiments.

4.1.1 Effect of Potential and pH:

The effect of redox potential on the flotation of chalcocite in the absence of a collector and frother is shown in Figure 4.1. The test was done at pH 8 and the potential controlled by the addition of hydrazine or hydrogen peroxide. Results show that chalcocite has a slight natural floatability at this pH. The best recovery is only about 30% at a potential of 180 mv. Chalcocite is known to float slightly by collectorless flotation and it is apparently dependent upon the amount of frother (Heyes and Trahar, 1979). The natural floatability seemed to increase with decreasing pH; Fuerstenau and Sabacky (1981) showed good
Figure 4.1  Effect of $E_h$ on flotation recovery of chalcocite at pH 8 and in the absence of a collector.
flotation of chalcocite at pH 6.8, while Heyes and Trahar obtained a recovery of only about 13% over 8 minutes of flotation at pH 11.

In Figure 4.2, the results of the thermodynamic calculations for a KEX addition of $10^{-5}$ M are compared with the experimental data reported by Heyes and Trahar (1977) for the batch flotation of chalcocite at pH 8 and $4.7 \times 10^{-5}$ M KEX addition. The flotation experiments were conducted in a 3-liter modified Denver D1 cell. For each test, the potential of the pulp was adjusted from an initial value of 400 mv to the final value by the addition of either sodium dithionite or sodium hypochlorite. The flotation results of Richardson et al. (1984) for a collector addition of $1.44 \times 10^{-5}$ M KEX are also shown in Figure 4.2. Richardson et al. used a microflotation-electrochemical cell (Figure 1.3) in their experiments where the potential is controlled electrochemically.

Although the collector concentrations used for the three sets of data are different, there is a reasonable agreement between the thermodynamic predictions and their results, particularly with respect to the effect of the pH. The lower flotation edge is independent of pH, based on the thermodynamic calculations and the actual data. However, the onset of flotation occurs at potentials higher than the thermodynamic predictions by approximately 150 mv.

Microflotation experiments on pure chalcocite samples were conducted at pH 5, 8 and 11 with $10^{-5}$ M KEX addition. The results are compared with those of the thermodynamic calculations in Figures 4.3 - 4.5. At each pH, two sets of flotation experiments were carried out. In one, the collector was added after the potential of the pulp had been
Figure 4.2  Comparison between chalcocite flotation data and the thermodynamic calculations of this study at (a) pH 8 and (b) pH 11: i) flotation with $4.7 \times 10^{-5}$ M KEX and potential controlled with redox reagents, $\Theta$ (Heyes and Trahar, 1979); ii) flotation with $1.44 \times 10^{-5}$ M KEX and potential controlled electrochemically, $\oplus$ (Richardson et al., 1984); iii) calculated % CuX for $10^{-5}$ M KEX addition.
Figure 4.3 Correlation between flotation recovery of chalcocite and calculated % CuX (and % CuX₂) for 10⁻⁵M KEX addition at pH 5 with collector added before potential control, -○--; and collector added after potential control, -θ-. 
Figure 4.4 Correlation between flotation recovery of chalcopyrite and calculated % CuX (and % CuX₂) for 10⁻⁵M KEX addition at pH 8 with collector added before potential control, -•--; and collector added after potential control, -œœ.
Figure 4.5  Correlation between flotation recovery of chalcocite and calculated % CuX (and % CuX₂) for 10⁻⁵M KEX addition at pH 11 with collector added before potential control, - ; and collector added after potential control, - .
adjusted by adding either hydrazine or $\text{H}_2\text{O}_2$. In the other, the collector was added prior to the potential control. In both cases, the upper flotation edges agree with the calculated $\% \text{CuX}$ and $\text{CuX}_2$ line. The lower flotation edges, on the other hand, vary significantly depending on the sequence of reagent addition. When KEX was added to the pulp after the potential had been adjusted, the observed lower flotation edge is lower than the calculated value only by about 50 mv. However, when the collector was added before the potential control, the lower flotation edge is shifted upward by about 200 mv. The results obtained in this manner correspond to the those reported by Heyes and Trahar and by Richardson et al., who also carried out their experiments similarly. It appears that there is a basic flaw in adding the collector prior to the potential control. When xanthate is added before the potential control, it will immediately react with the mineral at the open-circuit potential (usually 150-200 mv). Then, when hydrazine is added in sufficient amounts to lower the potential to below -200 mv, the collector coating will desorb, and no flotation will occur. Thus, the flotation results obtained in the first set of experiments, i.e., KEX was added after the potential control, may be regarded to represent the effect of potential on the xanthate adsorption. The second set of experiments merely shows that xanthate desorbs at approximately -200 mv, irrespective of pH.

Although the thermodynamic calculations have been shown to correlate well with the flotation experiments, it should be noted here that the following xanthate chemisorption reaction,
has not been included in the thermodynamic calculations due to the lack of thermodynamic data. This reaction has been proposed by Woods to explain the prewave observed in voltammetry experiments conducted on galena at the very high xanthate concentrations. It is not certain however, whether a prewave exists in the \( \text{Cu}_2\text{S}-\text{H}_2\text{O}-\text{KEX} \) system.

4.1.2 Effect of KEX Concentration

Figure 4.6 shows the result of flotation tests in which the chalcocite sample was floated as a function of xanthate concentration at potentials of -300, 0, 200 and 300 mv. The flotation recovery increases abruptly at a critical KEX concentration and there is complete recovery after that. This critical KEX concentration would correspond to the minimum xanthate addition required for flotation. Although CuX formation is thermodynamically possible at all the potentials tested above, the least amount of xanthate is required at 0 and 200 mv. This is the same potential range that the calculations predicted at pH 8 (Figure 3.22).

Note, here, that minimum KEX addition required is much larger than the calculated minimum. This discrepancy may be explained by the fact that flotation requires a certain minimum surface coverage depending on the surface area and the particle size of the mineral to be floated.

4.1.3 Flotation of Copper Powder

Freshly ground copper powder was floated at pH 8 and at different KEX concentrations to study the effect of potential and to relate it to
Figure 4.6  Effect of concentration of KEX addition on flotation recovery of chalcocite at pH 8 and different $E_h$ values.
chalcoite flotation. The results show that copper flotation is also
dependent on potential like chalcocite (Figure 4.7). Recovery is
maximum at the $E_h$ range from 0 to 300 mv. The upper flotation edge
corresponds to the same potential for chalcocite flotation
(Figure 4.4). There is a difference, though, in the lower flotation
edge. Chalcocite starts to float at much lower potentials than copper
at KEX additions of $10^{-5}$ M. Also, recovery of copper is very low at
this collector level. Increasing the KEX addition ten-fold results in
maximum recovery comparable to that for chalcocite. It is possible that
metallic copper is more easily oxidized than chalcocite and, hence,
requires more xanthate to form CuX. The lower flotation edge is shifted
towards more negative potentials at higher KEX addition. This lower
edge would correspond to the reaction:

$$\text{Cu}^0 + X^- \rightarrow \text{CuX} + e \quad [4.2]$$

On the other hand, the upper flotation edge is unaffected by the amount
of collector added.

4.2 Electrochemical Experiments

Most of the metal sulfides of metallurgical interest are
semiconductors with low band gaps and possess a very high surface
concentration of conducting electrons and positive holes. Hence, these
sulfides can be efficient electrocatalysts for both anodic and cathodic
reactions. Metal sulfides, except sphalerite, behave and can be used
like metals in most electrochemical work.

Linear sweep voltammetry is used here to study chalcocite and other
Figure 4.7 Effect of $E_h$ on flotation recovery of copper powder at pH 8 and KEX addition of $10^{-5}$M and $10^{-4}$M.
possible reaction mechanisms of its oxidation and flotation by xanthate. In this technique, the potential is varied linearly with time and the resulting current recorded as a function of potential. When the potential is swept to a particular potential, \( E_f \), and returned to the starting value or some other potential, \( E_r \), linearly with time, this is called cyclic voltammetry. This is a reversal technique used to characterize unknown systems as well as fairly complicated electrode reactions.

4.2.1 In the absence of KEX

a. pH 9.2: Voltammetry experiments were conducted on a chalcocite electrode in a 0.05 M \( \text{Na}_2\text{B}_4\text{O}_7 \) solution. The scans were begun from a potential of -155 mv and proceeded in the anodic direction at a sweep rate of 10 mv/sec. The starting potential was chosen at a value where it was below the open-circuit potential. This allowed the removal of oxidation products generated while the electrode surface was being polished and transferred to the cell.

The effect of the anodic limit was studied in a series of experiments and the resulting voltammograms are shown in Figure 4.8. They were all scanned, initially, to the switching potential, \( E_s \), then reversed to a potential of -455 mv and returned back in a positive direction to -200 mv. At a potential of about 200 mv, anodic current (\( A_1 \)) starts to flow. This corresponds to the oxidation of chalcocite to copper oxide. Chander and Fuerstenau (1974) observed the same in their experiments.

A cathodic peak (\( C_1 \)) appears at around 200 mv on the return sweep.
Figure 4.8 Voltammograms of a chalcocite electrode in a 0.05M Na$_2$B$_4$O$_7$ solution (pH 9.2) for different anodic limits. No stirring. Scan rate = 10 mv/sec.
This is brought about by the reduction of the oxidation product to Cu$_2$S. Upon reaching the lower switching potential, there is a sharp drop in current and the appearance of another cathodic peak (C$_2$), which indicates the reduction of Cu$_2$S to metallic Cu. On the return sweep, another anodic peak (A$_2$) can be seen. This has been identified as the oxidation of Cu$^0$ back to Cu$_2$S.

Increasing the sweep to higher potential limits shows more distinct anodic and cathodic peaks (A$_1$ and C$_1$), as well as the appearance of another reduction peak, C$_3$. This indicates that more than one oxidation reaction has occurred in the positive scan since C$_3$ appeared only after sweeping to higher potentials. Peaks C$_2$ and A$_2$, on the other hand, are identical for all cases. This would indicate that all the oxidation products have already been reduced to Cu$_2$S by the time the potential has reached -200 mv. The reaction for C$_2$ should, therefore, be:

\[
\text{Cu}_2\text{S} + \text{H}^+ + 2\text{e}^- \rightarrow 2\text{Cu}^0 + \text{HS}^-
\]  

[4.3]

This has a reversible potential of -605 mv at pH 9.2 and assuming [HS$^-$] = 10$^{-6}$M. Walker, Stout and Richardson (1984) suggested the same reaction for C$_2$. At potentials between -305 and -455 mv, they observed a substantial cathodic current which introduces a soluble HS$^-$ specie into solution as detected by a fast-scan UV spectrometer. As for peak A$_2$, this is just the reverse of reaction [4.2].

In Figure 4.9, the effect of stirring on a voltammogram is studied so as to help identify reactions. This experiment will indicate whether there are soluble reaction products involved. If a soluble specie is produced in the forward reaction, then the reverse reaction
Figure 4.9 Effect of stirring on the voltammograms for a chalcocite electrode in a 0.05M Na₂B₄O₇ solution (pH 9.2). Scan rate = 10 mv/sec.
would not occur since the dissolved specie has been dispersed away from
the electrode surface by stirring action.

Both voltammograms show peaks $A_1$, $C_1$, $C_2$ and $C_3$ to be present,
although there is some difference in their relative size. However,
stirring the solution results in the disappearance of the anodic peak,
$A_2$. The cathodic reaction for $C_2$ would, therefore, involve the
formation of a soluble product, such as HS$^-$. This would give additional
support to the suggestion that reaction [4.3] is responsible for $C_2$ and
the reverse of the reaction for $A_2$. As for $A_1$, $C_1$, and $C_3$, all the
reactions seem to involve insoluble species.

Repeated cycling of the potential between -555 and 345 mv showed no
effect on the voltammograms as seen in Figure 4.10. There were no
shifts in the anodic and cathodic peaks brought about by the repeated
cycling. An increase in the number of cycles showed almost no change in
the relative size of the peaks and, therefore, the ratio of the anodic
charge, $Q_A$, to the cathodic charge, $Q_C$, therefore remains constant.
This means that the amounts of the oxidation or reduction products are
not affected by the continuous sweeping and that the reactions are
fairly reproducible.

Analysis of the charge corresponding to each voltammetry peak can
be used to help identify the sequence of reactions. The area under a
peak can be measured to roughly determine the charge involved for that
particular reaction. Knowing this, a relationship between the charges
associated for a particular sequence of reactions can be derived. This
can then be compared to the theoretical charge ratio from different
Figure 4.10 Cyclic voltammograms of a chalcocite electrode in a 0.05M Na₂B₄O₇ solution (pH 9.2) for potential sweeps between -555 mV and 345 mV. No stirring. Scan rate = 10 mV/sec.
proposed reactions. This was used by Pritzker (1985) to analyze the voltammograms for galena.

An attempt has been made to apply this method for the voltammograms here but the separation of cathodic peaks C₁ and C₃ are not distinct enough to be measured separately. However, the total charge for C₁ and C₃ can be roughly approximated and a charge ratio, \( \frac{Q_{C1} + Q_{C3}}{Q_{A1}} \), was found to have an average value of 0.98. The theoretical charge ratio of various possible reaction sequences were solved for and those that are near the average experimental value are given in Table 4.1.

For the anodic reactions given in Table 4.1, the reversible potential for the oxidation to Cu(OH)₂ is 275 mv, while that for Cu₂O is 369 mv. These values are near the potential where A₁ appears in the voltammograms. It is interesting to note that the reactions give elemental sulfur as the oxidation product, instead of SO₄²⁻ or S₂O₅²⁻. Work done on other sulfides, particularly on galena (Gardner and Woods, 1979; Lamache et al., 1984; Pritzker, 1985) concluded that its oxidation reactions involve the formation of metal oxides and oxygenated sulfur species. There is also the controversy concerning the stability of elemental sulfur in alkaline solutions where SO₄²⁻ is thermodynamically more stable. The stability of SO in basic conditions, however, has been proven by Gardner and Woods (1979), especially within the time frame associated with cyclic voltammetry.

Walker, Stout and Richardson also proposed that elemental sulfur is the likely oxidation product, since UV analysis of the solution in their study did not support the presence of thiosulfate. Formation of
Table 4.1
Possible Reaction Sequences For A_1, C_1 and C_3

<table>
<thead>
<tr>
<th></th>
<th>Reaction Steps</th>
<th>Charge Relationship</th>
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| 1. | A_1: Cu_2S + 4H_2O → 2Cu(OH)_2 + S^0 + 4H^+ + 4e  
     C_1: 2Cu(OH)_2 + S^0 + 4H^+ + 4e → Cu_2S + 4H_2O  
     C_3: Cu_2O + 2H^+ + 2e → 2Cu^0 + H_2O | Q_{A1} = Q_{C1} + Q_{C3} |
| 2. | A_1: Cu_2S + 4H_2O → 2Cu(OH)_2 + S^0 + 4H^+ + 4e  
     C_1: Cu_2O + S^0 + 2H^+ + 2e → Cu_2S + H_2O  
     C_3: Cu(OH)_2 + 2H^+ + 2e → 2Cu^0^2+ + 2H_2O | Q_{A1} = Q_{C1} + Q_{C3} |
| 3. | A_1: Cu_2S + 4H_2O → 2Cu(OH)_2 + S^0 + 4H^+ + 4e  
     C_1: 2Cu(OH)_2 + S^0 + 4H^+ + 4e → Cu_2S + 4H_2O  
     C_3: S^0 + H^+ + 2e → HS^- | Q_{A1} = Q_{C1} + Q_{C3} |
| 4. | A_1: Cu_2S + 4H_2O → 2Cu(OH)_2 + S^0 + 4H^+ + 4e  
     C_1: Cu_2O + S^0 + 2H^+ + 2e → Cu_2S + H_2O  
     C_3: 2Cu(OH)_2 + 2H^+ + 2e → Cu_2^0 + 3H_2O | Q_{A1} = Q_{C1} + Q_{C3} |
| 5. | A_1: 2Cu_2S + 11H_2O → 4Cu(OH)_2 + S_2O_3^{2-} + 14H^+ + 12e  
     C_1: 2Cu(OH)_2 + 2H^+ + 2e → Cu_2O + 3H_2O  
     C_3: Cu_2O + S^0 + 2H^+ + 2e → Cu_2S + H_2O | Q_{A1} = 0.75 Q_{C1} + Q_{C3} |
oxygenated sulfur ions involve irreversible reactions so that \(Q_{A1}\) will always be greater than the sum of \(Q_{C1}\) and \(Q_{C3}\). The analysis of the charge however, showed them to be equal, suggesting that no oxy-sulfur ions are being generated in the oxidation reaction. It should also be pointed out here that stirring and repeated cycling has no effect on \(A_1, C_1\) and \(C_3\). This would indicate reversible reactions involving insoluble species, such as elemental sulfur.

The cathodic reactions given in Table 4.1 for \(C_1\) and \(C_3\) show the reduction of the copper oxides back to \(Cu_2S, Cu_2O\) or \(Cu^0\). At pH 9.2, reversible potentials for the \(Cu(OH)_2/Cu_2O\) and \(Cu_2O/Cu^0\) couple are 183 mv and 73 mv, respectively. These values are close to where \(C_1\) and \(C_3\) appear and also involve the formation of insoluble products. The reverse of the two oxidation reactions should also be considered since it is known that the anodic and its corresponding cathodic charge are equal. Sequence 3 gives a different reaction for \(C_3\) and suggests the formation of \(HS^-\) from elemental sulfur.

As for peaks \(C_2\) and \(A_2\), the charge analysis shows the \(Q_{C2}/Q_{A2}\) ratio to be 2.81. This would indicate that not all the reduced species are oxidized back in \(A_2\), suggesting a soluble specie such as \(HS^-\) that is not fully available to the electrode surface during the return scan. There is also the possibility that some of the remaining copper oxide left from the other reactions (such as in sequence 3) is getting reduced to \(Cu^0\). Another possibility is that the previous oxidation and reduction reactions (\(A_1\) and \(C_1\)) may have roughened up the mineral electrode surface, thus increasing its surface area. This would contribute to the
larger cathodic current.

b. pH 6.8: The next series of experiments were done at pH 6.8 (0.05 M \(K_2HPO_4/0.05\ M Na_2HPO_4\) solution) with a starting potential of -155 mv and a scan rate of 20 mv/sec, unless otherwise indicated. Voltammograms were obtained for anodic limits of 245, 345, and 445 mv, as shown in Figure 4.11. The lower switching potential was set at -355 mv for all cases.

When the potential is scanned to 245 mv, the anodic peak (A₁) observed in the voltammogram at pH 9.2 is not present. Therefore, there is also no cathodic peak appearing in the return scan. The cathodic current near the lower switching potential, however, still appears although it is of lower magnitude. C₂ would correspond to reduction of chalcocite as given by reaction [4.3].

Increasing the upper potential limit to 345 mv shows that oxidation of \(Cu_2S\) starts to occur. The current-potential curve here is similar to the one obtained when the potential was scanned to 245 mv at pH 9.2. The scan in the negative direction shows a cathodic peak (C₁) at about 260 mv and C₂ at the lower switching potential. Scanning up to 445 mv results in the appearance of an anodic peak (A₁) at about 405 mv. This indicates the oxidation of chalcocite to copper oxide. C₁ appears at a potential of 200 mv as the scan is reversed in the negative direction. There is no other cathodic peak formed until about -255 where cathodic current (C₂) starts to flow. The absence of C₃ suggests that there is only one oxidation product. A higher switching potential is required for further oxidation of chalcocite to Cu₂O or Cu(OH)₂.
Figure 4.11 Voltammograms of a chalcocite electrode in an unstirred 0.05M KH₂PO₄/0.05M Na₂HPO₄ solution (pH 6.8) for different anodic limits. No stirring. Scan rate = 20 mv/sec.
Figure 4.12 shows the effect of stirring on the voltammograms at pH 6.8. The potential was scanned between -355 and 445 mv with a starting potential of -155 mv. The voltammograms are almost identical except with the disappearance of A2 when the solution is stirred. This is the same as that observed at pH 9.2 (Figure 4.9). The reduction of Cu2S would therefore involve the formation of Cu0 and a soluble sulfur specie such as HS− (reaction [4.3]) or H2S(aq) as given by the reaction,

\[ \text{Cu}_2\text{S} + 2\text{H}^+ + 2\text{e} \rightarrow 2\text{Cu}^0 + \text{H}_2\text{S(aq)} \]  

As for A1 and C1 being unaffected by stirring, this would suggest that the redox reactions are reversible and involves solid species. Determination of the peak currents show them to be about equal \(i_{pa} = i_{pc}\) which further supports the suggestion that the reactions are reversible.

Continuous cycling of the potential between -355 and 445 mv resulted in the voltammograms shown in Figure 4.13. Anodic currents started to flow at around 300 mv and the corresponding cathodic current appears in the return scan. There are no significant shifts in the peak potentials \(E_p\) during the repeated cycling. The peak currents on the other hand, are affected very slightly by the number of cycles. There is a slight increase in the peak current with continuous cycling, particularly from the first to the second cycle. This may have been brought about by the further reduction of the mineral at the lower potential limit. It is also possible that the repeated formation and removal of oxidation products may have roughened up, and thereby increased the surface area of the electrode. A look at the charges,
Figure 4.12 Effect of stirring on the voltammograms for a chalcocite electrode in a 0.05M KH$_2$PO$_4$/0.05M Na$_2$HPO$_4$ solution (pH 6.8). Scan rate = 20 mv/sec.
Figure 4.13  Cyclic voltammograms of a chalcocite electrode in an unstirred 0.05M KH$_2$PO$_4$/0.05M Na$_2$HPO$_4$ solution (pH 6.8) for potential sweeps between -355 and 445 mV. Scan rate = 20 mv/sec.
however, shows that $Q_{A1}$ and $Q_{C1}$ are always equal. The peak currents $i_{pa}$ and $i_{pc}$ are also observed to be almost equal in every sweep. This would suggest that the reactions involved are indeed, reversible.

Analysis of the charge passed for each of the voltammograms in Figure 4.11 was also done. The average charge ratio, $Q_{C1}/Q_{A1}$, was determined to be 0.97. The possible reaction sequences given in Table 4.1, however, cannot be considered here since there is only one oxidation reaction occurring near the upper potential limit. Knowing that the reaction is reversible and that it involves insoluble species, $A_1$ and $C_1$ correspond to the following reactions,

$$Cu_2S + H_2O = Cu_2O + SO + 2H^+ + 2e$$ \[4.5\]

or

$$Cu_2S + 4H_2O = 2Cu(OH)_2 + SO + 4H^+ + 2e$$ \[4.6\]

At pH 6.8, reversible potentials for reactions [4.5] and [4.6] are 511 and 417 mv, respectively. These are near the peak potentials observed from the experiments.

The values of $Q_{A2}$ and $Q_{C2}$ could not be determined since the current peaks for $A_2$ and $C_2$ are not distinct enough to be measured accurately. However, it can be seen that $Q_{C2}$ is definitely larger than $Q_{A2}$.

It should be noted at this point that discussions on the oxidation reactions have not considered the possibility that the electrolyte may be reacting with the electrode surface. Studies on the oxidation of lead metal by Abdul Azim and Anwar (1969) suggested the formation of $Pb(BO_2)_2$ in a 0.1M $Na_2B_4O_7$ solution and $PbHPO_4$ in a phosphate buffer. The experimental results for the chalcocite electrode, however, do not
Figure 4.14 Voltammograms of a chalcocite electrode in the absence (---) and presence (——) of $10^{-3}$M KEX at pH 9.2. No stirring. Scan rate = 10 mv/sec.
show any clear indication that such reactions are occurring.

4.2.2 In the presence of KEX

a. pH 9.2: Voltammograms of a chalcocite electrode obtained at pH 9.2, both in the presence and absence of $10^{-3}$ M KEX, are compared in Figure 4.14. In both cases, the scan begins at a potential of -155 mv and proceeds in the anodic direction at a sweep rate of 10 mv/sec before being reversed. The positive and negative potential limits are 345 and -555 mv, respectively. In the presence of KEX, the anodic current rise starting at 200 mv is reduced significantly as compared to the case when no collector is present. This may be due to the formation of a collector coating which inhibits further oxidation of the mineral. On the return sweep, cathodic peaks $C_1$ and $C_2$ appear, both in the presence and absence of KEX, but the size of the peaks are smaller when xanthate is added. $C_1$ involves the reduction of the oxidation products produced during the anodic sweep while $C_2$ corresponds to the cathodic decomposition of Cu$_2$S to Cu$^0$ (reaction [4.3]).

In the second anodic-going scan, anodic peak $A_2$ appears at around -400 mv for both cases. This would be the current flowing from the oxidation of the C$_2$ products. When xanthate is present, two additional anodic peaks ($A_3$ and $A_4$) are observed near -200 and -50 mv. The fact that the currents rise only after the reduction of Cu$_2$S to Cu$^0$ has occurred suggests that they may involve a reaction between Cu$^0$ and $X^-$. It is also possible, however, that these peaks may be related to the xanthate adsorption reaction not involving Cu$^0$,

$$X^- \rightarrow X_{ads} + e$$  \[4.7\]
The reason for the absence of xanthate adsorption peaks on the first anodic-going scan would probably be that the starting potential of -150 mv was too high and xanthate adsorption had already taken place.

In order to examine the effect of xanthate more closely, experiments in the absence and presence of KEX have been conducted in which the positive and negative potential limits are only 105 and -405 mv, respectively. The starting potential has also been lowered to -295 mv. As can be seen in Figure 4.15, the effect of KEX is more distinct than in previous experiments, particularly when it is considered that collector concentration is only $2.5 \times 10^{-5}$ M.

There is already a considerable difference in the anodic current in the absence and presence of KEX at a potential as low as -245 mv, whereas in the the former case, the currents only diverge above 200 mv. This is most likely due to the fact that the starting potentials in the two experiments are different. This can also explain the behavior observed in Figure 4.14 that the collector seems to inhibit the oxidation of the mineral itself. It is also possible however, that although the chalcocite electrode has been freshly polished prior to each voltammetry experiment, the surface may still be coated with some oxidation products which are readily removed by cathodic polarization. The presence of oxidation products on the mineral surface prior to contact with the KEX solution may inhibit the adsorption of the collector.

The voltammograms for 0 and $2 \times 10^{-5}$ M KEX in Figure 4.15 are similar in the region of the lower potential limit. The cathodic
Figure 4.15 Voltammograms of a chalcocite electrode in the absence (---) and presence (—) of $2.5 \times 10^{-5}$ M KEX at pH 9.2. No stirring. Scan rate = 20 mv/sec.
current rise \( (C'_2) \) can again be attributed to the decomposition of \( \text{Cu}_2\text{S} \) (reaction \([4.3]\)), and the anodic peak \( (A'_4) \) just after the potential reversal is likely due to the oxidation of products from that reaction. However, over the remainder of the scan, the chalcocite electrode is considerably more electroactive when xanthate is present. Additional oxidation peaks at approximately \(-190\) and \(-105\) mv \( (A'_1 \text{ and } A'_2', \text{ respectively}) \) and an anodic rise \( (A'_3') \) beginning at about \(-40\) mv appear during both the first and second anodic-going scans for the \( 2 \times 10^{-5} \text{ M KEX} \) solution.

In Figure 4.16, the potential scans were conducted at different starting potentials to see its effect on the initial current rise. As can be seen, it is very sensitive to the starting potential chosen. When the scan begins at \(-300\) mv, the resulting anodic current in the first cycle is almost identical to that in the second cycle. However, when the starting potential is increased to \(-275\) mv, the initial current rise is not as large and does not show distinct peaks at \(-190\) and \(-105\) mv. A possible explanation for this behavior is that when the initial potential is as low as \(-300\) mv, \( \text{Cu}_2\text{S} \) is reduced to \( \text{Cu}^0 \) to some extent during the first few seconds of the sweep. This is supported by the fact that cathodic current flows at the beginning of the scan. Consequently, the reactions corresponding to anodic peaks \( A'_1 \text{ and } A'_2 \) may involve \( \text{Cu}^0 \) and \( X^- \), such as,

\[
\text{Cu}^0 + X^- \rightarrow \text{CuX} + e \quad (E_h = -195 \text{ mv}) \quad [4.8]
\]

\[
3\text{Cu}^0 + X^- + \text{H}_2\text{O} \rightarrow \text{CuX} + \text{Cu}_2\text{O} + 2\text{H}^+ + 3e \quad (E_h = -114 \text{ mv}) \quad [4.9]
\]
Figure 4.16 Effect of the starting potential on the voltammograms for a chalcocite electrode in an unstirred 0.05M Na₂B₄O₇ solution (pH 9.2) containing 2.5 x 10⁻⁵ M KEX. Scan rate = 20 mv/sec.
The reversible potentials are calculated at pH 9.2 and surface concentrations of X^- and SO_4^{2-} assumed to be 2.5 \times 10^{-5} and 10^{-6} M, respectively. The involvement of CuO in the reaction is further supported by the fact that Woods (1971) also observed an oxidation peak at around -200 mv in his voltammetry experiments on copper metal in the presence of 5 \times 10^{-4} M KEX. Woods concluded that the anodic peak involved a one-electron xanthate adsorption reaction. It should also be pointed out that the copper powder flotation results (Figure 4.7), showed a lower flotation edge at around the same potential. In addition, reaction [4.8] is the same reaction attributed to the lower limiting potential for flotation.

It is not likely that reaction [4.10] is responsible for the onset of flotation since it has been observed in many sulfate systems (Gardner and Woods, 1979; Hamilton and Woods, 1981; Lamache et al., 1984; Peters, 1984; Woods, 1984; Pritzker, 1985) that reactions which generate SO_4^{2-} ions often have large overpotentials. Peters further stated that sulfate ions are virtually inert, kinetically. It should also be recalled that the lower potential limit for chalcocite flotation is essentially independent of pH (Figures 4.3 - 4.5). This suggests that A_1' may be associated with reaction [4.8] since it does not involve H^+ ions. The second xanthate adsorption, A_2', may be due to reaction [4.9].

It is important to point out that the above discussion does not exclude the possibility that xanthate chemisorbs via reaction [4.7]
since it is also pH independent. In fact, it is possible that xanthate absorbs initially through reaction [4.7] and then forms a chemical bond with surface CuO via a reaction similar to reaction [4.8].

A_3 may be attributed to one or both of the following reactions involving chalcocite,

\[
\text{Cu}_2S + 2X^- \rightarrow 2\text{CuX} + S^0 + 2e \quad [4.11]
\]

\[
2\text{Cu}_2S + 4X^- + 3H_2O \rightarrow 4\text{CuX} + S_2O_3^{2-} + 6H^+ + 8e \quad [4.12]
\]

The \(E_h\) value for these two reactions at \([X^-] = 2.5 \times 10^{-5} \text{ M}, \text{pH } 9.2\) and \([S_2O_3^{2-}] = 10^{-6} \text{ M}\) are 66 mv and -95 mv, respectively, and coincide quite closely with the potential (-40 mv) where the current rises.

The cathodic peak (C_{1}') at -220 mv was also observed around the same potential by Kowal and Pomianowski (1973). This may be due to the desorption of xanthate. It is interesting to note that C_{1}' in Figure 4.15 is absent in Figure 4.14. A possible reason for this is that in Figure 4.14, the electrode potential was scanned up to a limit of 350 mv. Referring back to the \(E_h - \text{pH}\) diagram for a \(10^{-5} \text{ M KEX}\) addition (Figure 3.4), it can be seen that at this potential and pH 9.2, CuX and CuX_2 should no longer be stable. Thus, it is likely that any xanthate that has absorbed will have been removed by the time the potential is reversed in the cathodic direction.

b. \textbf{pH 6.8}: Current-potential curves obtained at pH 6.8 in unstirred 0 and \(2.5 \times 10^{-5} \text{ M KEX}\) solutions are shown in Figure 4.17. The potential limits for the scan are -555 and 455 mv with a sweep rate of 10 mv/s. When xanthate is added, the anodic current rise (A_{1}') starts at a slightly higher potential (245 mv) as compared to the one without
Figure 4.17 Voltammograms of a chalcocite electrode in the absence (---) and presence (——) of $2.5 \times 10^{-5}$ M KEX at pH 6.8. No stirring. Scan rate = 10 mV/sec.
collector indicating that the corrosion of Cu$_2$S is inhibited by xanthate adsorption. The peak current is also lower due to the formation of a collector coating on the surface of the electrode. The same has been observed at pH 9.2 (Figure 4.14.). On the return scan, two cathodic peaks (C'_1 and C'_2) appear at around 190 and -430 mv for both cases. The relative size of the peak currents are, however, smaller for the scans in the presence of KEX. Reduction of the anodic oxidation products such as copper oxide and copper xanthate (when KEX is added) to Cu$_2$S is probably responsible for C'_1, while C'_2 involves the reduction of Cu$_2$S to Cu$^0$.

Reversing the scan in the positive direction show the appearance of anodic peak A'_2 in both scans. There are however, two additional peaks, A'_3 and A'_4, brought about by the addition of xanthate. A'_3 and A'_4 were referred to previously as xanthate adsorption peaks. The voltammograms are essentially the same as those obtained at pH 9.2 which might suggest that the reactions are pH independent.

By narrowing the scan to a potential range of -355 to 205 mv, the effect of pH to the xanthate adsorption peaks can be more clearly seen (Figure 4.18). The scan rate was adjusted to 20 mv/sec and the starting potential was higher at -225 mv. The initial current rise is not as large as the one at pH 9.2 and does not show distinct xanthate adsorption peaks. However, the currents are greater than that observed for the voltammograms in the absence of xanthate. The cathodic peak C'_1, responsible for the reaction of CuX and/or S$^0$, is also present here but it is not as distinct. C'_2 and A'_4 are present for both cases and
Figure 4.18 Voltammograms of a chalcocite electrode in an unstirred 0.05M KH$_2$PO$_4$/0.05M Na$_2$HPO$_4$ solution (pH 6.8) containing 0 (---) and 2.5 $\times$ 10$^{-5}$ (-----)M KEX. Scan rate = 20 mv/sec.
are attributed to the decomposition and reconstitution Cu$_2$S, respectively.

Anodic peak $A'_1$ appears near -180 mv while $A'_2$ is observed at around 20 mv. Comparison with the voltammogram at pH 9.2 shows $A'_1$ appears at about the same potential for both cases but $A'_2$ is shifted to a higher potential at pH 6.8. This would indicate that the reaction attributed to $A'_1$ is indeed pH independent and therefore, supports the suggestion that reaction [4.8] is responsible for $A'_1$. The second xanthate adsorption peak is pH dependent and may be represented by reaction [4.9]. The $E_h$ value for this reaction at pH 6.8 and $[X^-] = 2.5 \times 10^{-5}$ M is -19 mv.

The third anodic current rising near 65 mv at pH 6.8 occurs at a lower potential (-40 mv) in the voltammogram obtained in the borate (pH 9.2) solution. Examining the suggested reactions corresponding to $A'_3$ shows that reaction [4.12] is the most likely candidate since it is pH dependent. Its reversible potential is 12 mv at pH 6.8 with $[KEX] = 2.5 \times 10^{-5}$ M and $[S_2O_3^{2-}] = 10^{-6}$ M. Reaction [4.11] has an $E_h$ value of 66 mv at $[KEX] = 2.5 \times 10^{-5}$ M and is also close to the potential where $A'_3$ starts to rise. Therefore, this reaction cannot be excluded as another possible reaction.

c. pH 11: Voltammetry experiments were conducted at pH 11 to further study the effect of pH. Figure 4.19 shows the voltammograms in the presence and absence of KEX. The potential limits are -355 and 545 mv while the starting potential is -295 mv. In the absence of xanthate, current starts to rise near 295 mv as the scan is going in the positive
Figure 4.19 Voltammograms of a chalcocite electrode in an unstirred 0.05M Na$_2$HPO$_4$/0.1M NaOH solution (pH 11) containing 0 (---) and 2.5 x 10$^{-5}$ (----) M KEX. Scan rate = 20 mv/sec.
direction at a rate of 20 mv/sec. The reverse scan shows a reduction peak at 265 mv, while the peaks at the negative potential limits are the same as those observed at different pH values. Addition of collector to the solution results in a significantly reduced anodic current on the initial scan. The cathodic peak on the return sweep is also smaller but there is an additional peak appearing near -55 mv. At the negative potential limit, the cathodic and anodic peaks are similar to those observed in the absence of xanthate. The second anodic-going scan shows no xanthate adsorption peaks. This might be due to the faster oxidation of the sulfide mineral at higher pH values. Voltammetry experiments on pyrite electrodes by Janetski, Woodburn and Woods (1977) showed that the oxidation of the mineral at pH 11 is faster than xanthate oxidation. Another reason is that the xanthate might be bound by a chemical reaction, rather than an electrochemical reaction, with the oxidation product layer. Pomianowski and his co-workers (Czarnecki et al., 1973; Kowal et al., 1973, 1976; Pomianowski and Czarnecki, 1974; Kowal, 1978; Barzyk et al., 1981) found that the binding of xanthate can occur by an electrochemical mechanism on unoxidized (i.e. electrochemically reduced) surface of chalcocite. However, when the electrode surface is partially covered with oxidation products, the amount of bound xanthate exceeded the amount that can be accounted for by electrochemical reactions. The unaccounted xanthate adsorption was attributed to the chemically or non-electrochemically bound xanthate. The chemically-bound xanthate can still inhibit the oxidation of the mineral, thus decreasing the anodic current. Also, there is still the possibility that the scan rate might
not be fast enough to show the xanthate adsorption peaks.

4.3 Correlation of the Experimental Results with the Thermodynamic Calculations

Comparison of the results of the thermodynamic calculations with the flotation data show good agreement at pH 5, 8 and 11. Both show that the flotation of chalcocite is dependent on potential. The upper flotation edge has been attributed in the calculations to the following reaction,

\[
\text{CuX} + 2\text{H}_2\text{O} \rightarrow \text{Cu(OH)}_2 + 2\text{H}^+ + X^- + 2e. \tag{4.13}
\]

The desorption of xanthate observed at the upper potential limit may be attributed to the above reaction.

In the calculations, the lower flotation edge corresponds to the \((\text{Cu}_2\text{S} + \text{Cu}^0)/\text{CuX}\) couple at pH 5 and 8, and to the \(\text{Cu}^0/\text{CuX}\) couple at pH 11. The reactions involved in these couples may be responsible for the onset of flotation. It should be noted that these reactions all involve metallic copper for the formation of CuX.

For the electrochemical experiments conducted in the absence of a collector, the oxidation products were suggested to be \(\text{Cu}_2\text{O}, \text{Cu(OH)}_2\) and \(\text{S}^0\). Comparison with the thermodynamic calculations shows that observed anodic potentials \((A_1)\) are higher than the reversible potentials for the \(\text{Cu}_2\text{O}/\text{Cu(OH)}_2\) couple. The cathodic peaks \(C_1\) and \(C_3\) are in the region where either \(\text{Cu}_2\text{O}\) or \(\text{Cu(OH)}_2\) is stable (Figure 4.20). The calculations have been carried out where the oxidation of sulfur is allowed to proceed to \(\text{SO}_4^{2-}\) so that elemental sulfur is not thermodynamically
Figure 4.20  $E_h$–pH diagram of the Cu$_2$S–H$_2$O system and the anodic and cathodic peak potentials observed from the voltammetry experiments.
stable. The other set of observed anodic potentials ($A_2$) involving the oxidation of $Cu^0$ to $Cu_2S$ are in the region where $Cu^0$ and $Cu_2S$ are stable and are more positive than the predicted potentials for the $Cu^0/Cu_2S$ couple. This difference may be due to kinetic effects which are not included in the calculations. This can be included, to some extent, in the thermodynamic calculations by placing restrictions on the species considered in the system.

The voltammetry experiments conducted in the presence of $2.5 \times 10^{-5} M$ KEX showed xanthate adsorption peaks ($A_1$) observed at potentials near the $(Cu_2S + Cu^0 + CuX)/(Cu^0 + CuX)$ line (Figure 4.21). This first xanthate adsorption peak has been suggested to involve metallic copper, which is also suggested by the calculations. However, the observed peak potentials are higher than the $(Cu_2S + Cu^0)/CuX$ couple. The second xanthate peaks ($A_2$) are in the region where $Cu^0$ and $CuX$ are stable together. It was also suggested that this second adsorption peak involves metallic copper which agrees well with the predicted behavior.

The cathodic peaks $C'_1$ corresponding to the reduction of the xanthate products are observed near the same potential where their respective $A'_1$ are observed. On the other hand, definite comparisons cannot be made for the third anodic peaks involving xanthate since the peak potentials were not observed within the potential scan range for this collector addition. It should also be noted here that there is a difference in the collector concentration used for the calculations and the experiments.

Comparing the electrochemical results with the results of the
Figure 4.21  $E_h$–pH diagram of the Cu$_2$S–KEX–H$_2$O system for a collector addition of $10^{-5}$ M and the anodic and cathodic peak potentials observed from the voltammetry experiments.
calculations for a KEX addition of $10^{-7}$M shows the first adsorption peak potential to be nearer to the reversible potential of the $(\text{Cu}_2\text{S} + \text{Cu}^0)/\text{CuX}$ couple (Figure 4.22). This might suggest that there may be a collector concentration gradient between the electrode surface and the bulk solution where larger amounts of xanthate are used. The second peak potentials are also near the boundary where Cu$_2$O and CuX start to form together. This would be in agreement with the suggestions from the electrochemical experiments that CuX and Cu$_2$O are formed (reaction [4.9]) in the second xanthate adsorption reaction.

Comparison of the flotation results with the electrochemical data shows a difference between the potentials for the lower flotation edge and the first xanthate adsorption peak. The lower flotation edge occurs at a potential of about 200 mv lower than the adsorption peak potential. This might be due to the difference in time involved in the experiment. For the flotation tests, there is a conditioning time of 5 minutes while the electrochemical experiments involve only a few seconds for the oxidation reactions to occur. There is also the possibility that the surface concentration of xanthate might be lower than the bulk concentration. It should be remembered that there was a closer correlation when the KEX concentration was lower (Figure 4.22).

Lastly, it should be noted here that the chemisorption of xanthate via reaction [4.7] has not been included in the thermodynamic calculations due to lack of thermodynamic data for this reaction. The experimental results do not discard the possibility of this reaction being responsible for the adsorption of xanthate. This might be the
Figure 4.22  $E_h$-pH diagram of the Cu$_2$S-KEX-H$_2$O system for a collector addition of $10^{-7}$M and the anodic and cathodic peak potentials observed from the voltammetry experiments.
reason for some of the differences observed between the thermodynamic calculations and the experimental results.
5.1 Thermodynamic Calculations

The results of the thermodynamic calculations for chalcocite both in the absence and presence of potassium ethyl xanthate may be summarized as follows:

1. Comprehensive thermodynamic calculations have been carried out for the Cu$_2$S-KEX-H$_2$O system over the Eh range from -1000 to 1000 mv and the entire pH range. Collector additions considered for the computations are 0, 10$^{-7}$, 10$^{-6}$, 10$^{-5}$, and 10$^{-4}$ M with the oxidation of sulfide allowed to proceed to the formation of sulfate. The results of the calculations have been used to generate Eh-pH stability diagrams for each xanthate addition.

2. The calculations differ significantly from previous work of this kind in that insoluble species present in the system have also been included in the rigorous mass balance equations. Earlier work considered soluble species only and set their total concentration constant over the entire Eh-pH range. In this study, only the total amounts of mineral and collector in the system are fixed so that equilibrium concentrations of all soluble species and the amount of all solid phases will vary according to the Eh and pH.
3. The amounts of CuX and CuX$_2$, as well as all the other species present in the system, for any given $E_h$ and pH have been determined from the calculations. These have been used to construct two-dimensional plots showing the effect of $E_h$ or pH on CuX or CuX$_2$ formation. In addition, contour plots and three-dimensional block diagrams have also been constructed to simultaneously show the effect of $E_h$ and pH on the concentration of Cu$^{2+}$ ions and the amount of CuX formed.

4. The plots showing the effect of $E_h$ or pH on % CuX and % CuX$_2$ are characterized by upper and lower $E_h$ or pH limits defining the range where formation of copper xanthate is maximum. The lower potential limit has been found to be independent of pH but decreases with increasing xanthate addition. The upper limiting potential for CuX and CuX$_2$ formation, on the other hand, is dependent on pH.

5. The minimum xanthate addition required for CuX formation has been calculated to determine the $E_h$-pH region where its formation is most favored. The results show that the KEX requirement is minimum in the potential range from -180 to 360 mv, depending on the pH. Maximum flotation would be expected in this potential range.

6. These thermodynamic calculations can be applied not only to flotation systems, but to hydrometallurgical and geochemical ones as well. The calculations can give information concerning the stability of chalcocite as a function of $E_h$ and pH, which would be very useful for hydrometallurgists involved in the leaching of
copper ores.

5.2 Microflotation

Flotation experiments conducted on chalcocite and copper powder samples show the following results:

1. Microflotation tests of chalcocite in the absence of a collector and frother show that chalcocite has a slight natural floatability at pH 8 and neutral conditions. It is at this potential where chalcocite is known to oxidize to non-stoichiometric, sulfur-rich copper sulfides.

2. Comparisons of experimental data with those predicted thermodynamically show excellent agreement with respect to the upper limiting potentials for flotation at pH 5, 8 and 11. The upper flotation edge are clearly shown to be dependent on pH. The lower flotation edge is observed to occur at a potential about 50 mv lower than that obtained from the calculations, if the potential is adjusted before the collector is added. If the order of reagent addition is reversed, the lower flotation edge is observed to be 150 mv higher than calculated values. This discrepancy is due to the hysteresis between xanthate adsorption and desorption. However, both thermodynamic and flotation data show the lower flotation edge to be independent of pH.
3. Microflotation tests of chalcocite at pH 8 show flotation recovery is highest in the potential range from 0 to 200 mv. This potential range corresponds to the region where, according to the thermodynamic calculations, the KEX requirement for CuX formation is minimal.

4. Flotation of copper powder (-100 + 150 mesh) at pH 8 and xanthate addition of $10^{-4}$M showed good flotation in the potential range from -200 to 450 mv. The lower flotation edge near -200 mv was found to correspond to the reaction:

$$\text{Cu}^0 + X^- \rightarrow \text{CuX} + e.$$  \[5.1\]

5.3 Electrochemical Experiments

The findings of the voltammetry experiments on the chalcocite electrode in the absence and presence of xanthate are:

1. Scanning the potential above about 300 mv at pH 9.2 resulted in more than one oxidation reaction. Repeated cycling and stirring suggested that the anodic reactions were reversible and that these may involve solid products. The possible oxidation products include Cu$_2$O, Cu(OH)$_2$ and S$^0$.

2. Increasing the upper potential limit does not affect the cathodic and anodic reactions observed at potentials below -400 mv and at pH 9.2. However, when the solution is stirred, this results in the disappearance of the anodic peak. Analysis of the charge showed
that not all the reduced species are re-oxidized, suggesting that a soluble specie is involved in the reduction reaction. The reaction attributed to this cathodic current is,

\[ \text{Cu}_2\text{S} + \text{H}^+ + 2e \rightarrow 2\text{Cu}^0 + \text{HS}^- \]  [5.2]

3. At pH 6.8, the oxidation of chalcocite starts at a higher potential (300 mv) as shown by the thermodynamic calculations. The return scan shows only one cathodic peak, indicating that there is only one oxidation product. Continuous cycling and stirring showed no shifts in the peak potential, suggesting reversible reactions involving only solid products. The most probable oxidation products are Cu$_2$O or Cu(OH)$_2$ and S°.

4. The peak currents appearing near the lower potential limits at pH 6.8 correspond to the reduction of Cu$_2$S to Cu$^0$. Stirring the solution had the same effect observed at pH 9.2, suggesting that the reaction involved here is similar to the one at pH 9.2 (reaction [5.2]). There is, however, the possibility that H$_2$S(aq) is produced instead of HS$^-$ since it is thermodynamically more favorable at this pH.

5. In the presence of xanthate, the oxidation of the mineral is reduced significantly. This may be due to the formation of a collector coating which inhibits further oxidation of the mineral.

6. Several oxidation peaks related to the adsorption of xanthate have been observed in the voltammograms at pH 9.2. The two peaks
appearing between -200 and -100 mv are observed only when the starting potential is low. At higher starting potentials (i.e., -155 mv), the peaks appear only on the return scan after the mineral has been reduced to Cu⁰. These, plus the copper powder flotation results, indicate that the anodic peak may involve the reaction of xanthate with Cu⁰. The third oxidation peak appearing above -40 mv most likely involves Cu₂S and xanthate.

7. The first oxidation peak appearing above -200 mv is also observed at pH 6.8. This would suggest that the reaction involved is pH independent and may be given as,

\[ \text{Cu}^0 + \text{X}^- \rightarrow \text{CuX} + e \]  \[5.3\]

There is also the possibility that it may be due to the chemisorption of xanthate involving one electron (reaction [4.7]). The other oxidation peaks are shifted to higher potentials at this pH, suggesting that \( H^+ \) ions are involved in these reactions.

5.4 Recommendations for Future Work

From the information obtained in this study, further work in the following areas are suggested:

1. Thermodynamic calculations should be carried out for cases where the oxidation of sulfide proceeds only as far as the formation of:
   i) thiosulfate, and ii) elemental sulfur. This would account for the sluggishness of sulfide oxidation where elemental sulfur and
thiosulfate can exist although they are not thermodynamically favored. According to Peters (1984) sulfur is not oxidized electrochemically, except at substantial overvoltage. In order to express this overvoltage, the calculations should consider raising the standard free energy values of $\text{SO}_4^{2-}$ and $\text{HSO}_4^-$, as suggested by Peters.

2. The approach used in the thermodynamic calculations done in this study should be carried out for other types of reagents such as dithiophosphates, dithiocarbamates or thionocarbamates. There have been no extensive thermodynamic calculations of any kind done concerning these reagents, except for the relatively limited calculations carried out for dithiophosphates.

3. Microflotation experiments should be carried out using different reducing and oxidizing agents, such as sodium dithionite and sodium hypochlorite, as well as controlling potential electrochemically. This might help explain difference in flotation results obtained by other investigators. The tests should also include the determination of the amount of collector absorbed and the oxidation products of the sulfide in order to facilitate identification of reactions responsible for flotation.

4. Further investigations should be undertaken to identify the surface oxidation products so as to verify the proposed reactions. This may be carried out by examining the electrode surface immediately after each voltammetry experiment using x-ray photoelectron
spectroscopy, Auger spectroscopy, mass spectroscopy, infrared spectroscopy or scanning electron microscopy. There have been some questions however, with these types of techniques since the sample has to be prepared (i.e. drying) before the measurement. An alternative to this would be to do in situ electrochemical modulation spectroscopy (ECMS). This would permit in situ identification of surface products while the electrochemical experiments are in progress.

5. Electrochemical experiments should be conducted using rotating disk electrodes (RDE) to complement cyclic voltammetry studies. In cyclic voltammetry, current peaks often arise from the back reduction or oxidation of the soluble species or the film formed on the electrode surface in the previous sweeps. With the RDE, the soluble species can be spun away from the electrode surface so that the film formation can be distinguished and studied separately. This has been used by Biegler (1976) to study oxygen reduction on sulfide minerals.

6. Intermittent galvanostatic polarization (IGP) experiments have been used by Horvath and Hackl (1965) to check validity of calculated \( E_h - pH \) equilibrium diagrams. More recently, Pritzker (1985) used the method for the galena-water system. This method would be very useful in investigating the equilibrium potentials of electrode processes taking place in the \( Cu_2S-H_2O \) system.
7. The role of oxygen in the flotation of sulfide minerals with thiol collectors has always been a controversy. In this study, experiments were conducted in the absence of oxygen so as not to complicate the analysis of the results. Future work should include the addition of oxygen in the system so as to better approximate the conditions in actual flotation.
REFERENCES


Appendix I

Sample FORTRAN Program Used In Thermodynamic Calculations
COMPUTER PROGRAM FOR THE THERMODYNAMIC-MASS BALANCE CALCULATION OF THE CU2S-H2O-KEX SYSTEM

This program determines the following:
1) equilibrium concentrations of all soluble species
   for pH values between 0 and 14 at a given electrode
   potential
2) pH values at which phase changes occur
3) percentage of xanthate initially added that forms
   CuX (%CuX), CuX2 (%CuX2), or X2 (%X2).

IMPLICIT REAL*8(A-H, O-Z)
DIMENSION D(1500), AHC(1500), AOH(1500)
DIMENSION DCU1(1500), DCU2(1500), DS(1500), DS04(1500), DCUT(1500),
*DXT(1500), DST(1500)
DIMENSION H(150), EE(150), CU2(150), CU1(150), CUOH(150), CUOH2(150),
*CUCUOH3(150), CUOH4(150), CU2OH2(150), CUSULF(150), SS(150),
*SSO4(150), H2SO4(150), HS04(150), HS(150), H2S(150), PH2S(150)
DIMENSION XAN(150), RXAN(150), XAN2(150), PERX1(150), PERX2(150),
*PERX3(150)
DIMENSION CUT(150), ST(150), XT(150)
DIMENSION CAP(20)
DIMENSION DISK(30,150)

Input variables are entered at this part of the program. The required input data are:
1) pH - initial pH value
2) E - electrode potential (vs SHE)
3) AW - atomic weight of metal cation
4) WTSOL - %solids by weight
5) XINIT - total amount of xanthate in system (moles/1).

The amount of copper and sulfur are given by XM and XS, respectively, with a 2 : 1 stoichiometric ratio.

READ(31,1) (CAP(I),I=1,18)
FORMAT(18A4)
WRITE(6,2) (CAP(I),I=1,18)
FORMAT(/**/X.18A4)
READ(31,3) PH, E, AW, WM, RHO, WTSOL, XINIT
FORMAT(7D10.2)
X!:=10. DO=WM/AW/(1.DO/RHO+100.DO/WTSOL-1.DO)
DXM=DLOG10(XM)
XS=0.5D0=XM
DXS=DLOG10(XS)
DXINIT=DLOG10(XINIT)
DXCRIT=-(E+0.06D0)/0.0591D0

Initialization of the various counters

K= 0
N= 0
NN=0
L0=0
L4=0
L5=0
L63 = 0

This calls the subroutine which updates the pH.

CALL UPDATE(K, PH, D, AH, E, N, POW)
IF(N.EQ.1) GO TO 100

The program is made up of different sections, where each section corresponds to the case at which a phase or phases is(are) stable. The appropriate mass balance equation is then solved and then checked if there is another phase(s) more stable. If there is, then the program goes to that particular section and the whole process repeated until the most stable phase is found.

The first section considers the case when elemental sulfur is stable. The subroutines called in the following sections are defined in the last part of the program.

DS(K) = -E/0.0296 -16.08446
DS04(K) = DS(K) + POW
IF(DS04(K) .GT. DXS) GO TO 5
CALL XANTH(K, PH, E, XINIT, DX)
DXT(K) = DXTOTAL(AH, E, K, DX, PH)
CALL CUBAL(AH, E, K, XM, DCU1, DCU2, DS04, DCUT)
DST(K) = SSOL(K, EH, PH, DS, DS04, POW, DCU2)
CALL CCHECK(K, AH, E, DCU2, DCUT, DS04)
IF(DCUT(K) .GT. DXM) GO TO 5
DCUS04 = DCU2(K) + DS04(K)
IF(DCUS04 .GT. 3.1098D0) GO TO 6
CU2S04 = 2. DO*DCU1(K) + DS04(K)
IF(CU2S04 .GT. -1.4929D0) GO TO 7
COP = 1.029567964D0 - 11.387324D0
IF(DCU2(K) .GT. COP) GO TO 8
DCUS = DCU2(K) + DS(K)
IF(DCUS .GT. -35.0009D0) GO TO 9
DCU2S = 2. DO*DCU1(K) + DS(K)
IF(DCU2S .GT. -48.6702D0) GO TO 10
CUX = DCU1(K) + DX(K)
IF(CUX .GT. -19.28D0) GO TO 55
CU2X = 2. DO*DX(K)
IF(CUX .GT. -24.2D0) GO TO 56
CU2HYD = 7.8919D0 - 2. DO*PH
IF(DCU2(K) .GT. CU2HYD) GO TO 11
CUHYD = -8.393D0 - PH
IF(DCU1(K) .GT. CUHYD) GO TO 12

The amount of free xanthate ion (DX) is checked to determine whether it is greater than that required for liquid dixanthogen (DXCRIT) to be stable. If it is, then X2 is also stable together with elemental sulfur.

IF(DX(K) .GT. DXCRIT AND L25 .NE. 0) GO TO 41
IF(DX(K) .GT. DXCRIT) L25 = L25 + 1
IF(DX(K) .GT. DXCRIT) P25 = PH
IF(DX(K) .GT. DXCRIT) DX(K) = DXCRIT
If it is not, then only elemental sulfur is stable.

IF(L4.NE.0) GO TO 4
L4=L4+1
P4=PH
GO TO 4

This section considers the case when no solids are present.

X2=C2GUESS(AH,E,K,POW,XM,XS)
5  IF(L5.NE.0) GO TO 43
L5=L5+1
P5=PH
43  L=3
CALL CUSBAL(AH,E,K,XM,DS,DSO4,DCU1,DCU2,DCUT,POW,X2,XS,LL)
CALL XANTH(K,PH,E,XINIT,DX)
DST(K)=SSOL(K,E,PH,XM,DS,DSO4,POW,DCU2)
DXT(K)=XTOTAL(AH,E,K,DX,PH)
DCUSO4=DCU2(K)+DSO4(K)
IF(DCUSO4.GT.3.1098D0) GO TO 6
CU2SO4=2.DO*DCU1(K)+DSO4(K)
IF(CU2SO4.GT.-1.4929D0) GO TO 7
CU2SO4=2.DO*DCU1(K)+DSO4(K)
IF(DCUSO4.GT.-35.0099D0) GO TO 9
DCU2SO4=2.DO*DCU1(K)+DSO4(K)
IF(DCU2SO4.GT.-48.6702D0) GO TO 10
DUST(K)=SSOL(K,E,PH,XM,DS,DSO4,POW,DCU2)
DXT(K)=XTOTAL(AH,E,K,DX,PH)
CU2HYD=7.8919D0-2.00*PH
IF(DCU2(K).GT.CU2HYD) GO TO 11
CU2HYD=7.8919D0-2.00*PH
IF(DCU2(K).GT.CU2HYD) GO TO 12

The X concentration is checked to see if X2 is stable.

IF(DX(K).GT.DXCRIT. AND. L26.NE.0) GO TO 45
IF(DX(K).GT.DXCRIT) L26=L26+1
IF(DX(K).GT.DXCRIT) P26=PH
45  IF(DX(K).GT.DXCRIT) DX(K) = DXCRIT
CALL UPDATE(K,PH,D,AH,E,N,POW)
IF(N.EQ.1) GO TO 100
GO TO 500

The case when CuSO4 is stable is considered in this section.

X2=C1GUESS(AH,E,K,POW,XS)
6  IF(L6.NE.0) GO TO 601
L6=L6+1
P6=PH
601  CALL CUSO4(AH,E,K,DS,DSO4,DCU1,DCU2,DCUT,POW,X2,XS)
CALL XANTH(K,PH,E,XINIT,DX)
DST(K)=SSOL(K,E,PH,XM,DS,DSO4,POW,DCU2)
DXT(K)=XTOTAL(AH,E,K,DX,PH)
CU2SO4=2.DO*DCU1(K)+DSO4(K)
IF(CU2SO4.GT.-1.4929D0) GO TO 7
COP=E/.029567964D0-11.735D0
IF(DCU2(K).GT.COP) GO TO 8
DCUS=DCU2(K)+DS(K)
IF(DCUS.GT.-35.0009D0) GO TO 9
DCU2S=2.D0*DCU1(K)+DS(K)
IF(DCU2S.GT.-48.6702D0) GO TO 10
CUX=DCU1(K)+DX(K)
IF(CUX.GT.-19.28D0) GO TO 55
CUX2=DCU2(K)+2.D0*DX(K)
IF(CUX2.GT.-24.2D0) GO TO 56
CU2HYD=7.8919D0-2.D0*PH
IF(DCU2(K).GT.CU2HYD) GO TO 11
CUIHYD=-8.398D0-PH
IF(DCU1(K).GT.CUIHYD) GO TO 12
IF(DX(K).GT.DXCRIT.AND.L27.NE.0) GO TO 602
IF(DX(K).GT.DXCRIT) L27 = L27 + 1
IF(DX(K).GT.DXCRIT) P27=PH
CALL UPDATE(K,PH,D,AH,E,N,POW)
IF(N.EQ.1) GO TO 100
GO TO 600

This section considers the situation when Cu2SO4 is present.

7  X2=10.D0**DCU2(K)
700  IF(L7.NE.0) GO TO 603
   L7=L7+1
   P7=PH
603  CALL CU2SUL(AH,E,K,DS,DS04,DCU1,DCU2,DCUT,POW,X2,LL)
    CALL XANTH(K,PH,E,XINIT,DX)
    DST(K)=SSOL(K,E,AH,PH,DS,DS04,POW,DCU2)
    DXT(K)=XTOTAL(AH,E,K,DX,PH)
    COP=E/.029567964D0-11.387324D0
    IF(DCU2(K).GT.COP) GO TO 8
    DCUS=DCU2(K)+DS(K)
    IF(DCUS.GT.-35.0009D0) GO TO 9
    DCU2S=2.D0*DCU1(K)+DS(K)
    IF(DCU2S.GT.-48.6702D0) GO TO 10
    CUX=DCU1(K)+DX(K)
    IF(CUX.GT.-19.28D0) GO TO 55
    CUX2=DCU2(K)+2.D0*DX(K)
    IF(CUX2.GT.-24.2D0) GO TO 56
    CU2HYD=7.8919D0-2.D0*PH
    IF(DCU2(K).GT.CU2HYD) GO TO 11
    CUIHYD=-8.398D0-PH
    IF(DCU1(K).GT.CUIHYD) GO TO 12
    IF(DCUT(K).GT.DXM) GO TO 21
    IF(DCUT(K).GT.DXCRIT.AND.L28.NE.0) GO TO 604
    IF(DX(K).GT.DXCRIT) L28 = L28 + 1
    IF(DX(K).GT.DXCRIT) P28=PH
604  IF(DX(K).GT.DXCRIT) DX(K) = DXCRIT
    CALL UPDATE(K,PH,D,AH,E,N,POW)
    IF(N.EQ.1) GO TO 100
    GO TO 700

The case when Cu metal is stable is handled in this section.
8 IF(L8.NE.0) GO TO 605
   L8=L8+1  
   P8=PH
605 IF(L22.NE.0.OR.L23.NE.0) GO TO 850  
   GO TO 851
850 IF(L24.NE.0) GO TO 851  
   L24=L24+1  
   P24=PH
851 DCU2(K)=E/.029567964DO-11.387324DO  
   DCU1(K)=DCU2(K)-E/.0591D0+2.5890DO
   CALL SULF(AH,E,K,XS,DS,DS04,DCU2,POW)  
   CALL XANTH(K,PH,E,XINIT,DX)  
   DST(K)=SSOL(K,E,AH,PH,DS,DS04,POW,DCU2)  
   DXT(K)=XTOTAL(AH,E,K,DX,PH)  
   DCUS=DCU2(K)+DS(K)
   IF(DCUS.GT.35.0009DO) GO TO 9  
   DCU2S=2.DO+DCU1(K)+DS(K)
   IF(DCU2S.GT.48.6702DO) GO TO 10  
   IF(L52.NE.0) GO TO 36  
   CUX=DCU1(K)+DX(K)  
   IF(CUX.GT.19.28DO) GO TO 55  
   CUX2=DCU2(K)+2.DO+DX(K)  
   IF(CUX2.GT.24.2DO) GO TO 56  
   CU2HYD=7.8919D0-2.DO+PH  
   IF(DCU2(K).GT.CU2HYD) GO TO 11  
   CUIHYD=-.8398D0-PH  
   IF(DCU1(K).GT.CUIHYD) GO TO 12  
   CALL CCHECK(K,AH,E,DCU2,DCUT,DS04)  
   IF(DCUT(K).GE.DXM) GO TO 21
36 If the amount of X exceeds DXCRIT, then both Cu and X2 are stable.
   IF(DX(K).GT.DXINIT.AND.L29.NE.0) GO TO 606  
   IF(DX(K).GT.DXCRIT) L29 = L29 + 1  
   IF(DX(K).GT.DXCRIT) P29=PH
606 IF(DX(K).GT.DXCRIT) DX(K) = DXCRIT  
   CALL UPDATE(K,PH,D,AH,E,N,POW)  
   IF(N.EQ.1) GO TO 100  
   GO TO 8
9 If the amount of X exceeds DXCRIT, then both Cu and X2 are stable.
   X2=C2GUES(AH,E,K,POW,XS)  
900 IF(L29.NE.0) GO TO 607  
   L9=L9+1  
   P9=PH
607 LL=3  
   CALL CUS(AH,E,K,DS,DS04,DCU1,DCU2,DCUT,POW,X2,XS,LL)  
   CALL XANTH(K,PH,E,XINIT,DX)  
   DST(K)=SSOL(K,E,AH,PH,DS,DS04,POW,DCU2)  
   DXT(K)=XTOTAL(AH,E,K,DX,PH)  
   DCUS=2.DO+DCU1(K)+DS(K)  
   IF(DCU2S.GT.48.6702DO) GO TO 10  
   COP=E/.029567964DO-11.378324DO  
   IF(DCU2(K).GT.COP) GO TO 309  
   CUX=DCU1(K)+DX(K)
The program now considers the case when Cu$_2$S is stable.

It is also checked in this section whether X$_2$ may co-exist with Cu$_2$S.

This section considers the situation when Cu(OH)$_2$ is stable, as well as the co-existence of X$_2$ with it.
CALL SULF(AH,E,K,XS,DS,DSO4,DCU2,POW)
CALL XANTH(K,PH,E,XINIT,DX)
DST(K)=SSOL(K,E,PH,DS,DSO4,POW,DCU2)
DXI(K)=XTOTAL(AH,E,K,DX,PH)
IF(L55.NE.O) GO TO 35
CUX=DCU1(K)+DX(K)
IF(CUX.GT.19.28DO) GO TO 55
CUX2=DCU2(K)+2.DO*DX(K)
IF(L57.NE.O) GO TO 357
IF(CUX2.GT.-24.2DO) GO TO 46
CUIHYD=-8398DO-PH
IF(DCU1(K).GT.CU1HYD) GO TO 12
DCUSO4=DCU2(K)+DSO4(K)
IF(DCUSO4.GT.3.1098DO) GO TO 13
CU2SO4=2.DO*DCU1(K)+DSO4(K)
IF(CU2SO4.GT.-1.4929DO) GO TO 15
DCUS=DCU2(K)+DS(K)
IF(DCUS.GT.-35.0009DO) GO TO 17
DCUS1=2.DO*DCU1(K)+DS(K)
IF(DCUS1.GT.-48.6702DO) GO TO 19
CALL CCHECK(K,AH,E,DCU2,DCUT,DSO4)
IF(DCUT(K).GE.XM) GO TO 21
IF(L11.NE.O) GO TO 611
L11=L11+1
P11=PH
611 IF(DX(K).GT.DXINIT.AND.L32.NE.O) GO TO 612
IF(DX(K).GT.DXCRIT) L32=L32+1
IF(DX(K).GT.DXCRIT) P32=PH
612 IF(DX(K).GT.DXCRIT) DX(K)=DXCRIT
CALL UPDATE(K,PH,D,AH,E,N,POW)
IF(N.EQ.1) GO TO 10
GO TO 11

The case when Cu20 is stable is considered in this section.

12 DCU1(K)=-.8398DO-PH
DCU2(K)=DCU1(K)+E/.0591D0-2.5890DO
CU2HYD=7.8919DO-2.DO*PH
IF(DCU2(K).GT.CU2HYD) GO TO 11
CALL SULF(AH,E,K,XS,DS,DSO4,DCU2,POW)
CALL XANTH(K,PH,E,XINIT,DX)
DST(K)=SSOL(K,E,PH,DS,DSO4,POW,DCU2)
DXI(K)=XTOTAL(AH,E,K,DX,PH)
IF(L55.NE.O) GO TO 38
CUX=DCU1(K)+DX(K)
IF(CUX.GT.-19.28DO) GO TO 55
CUX2=DCU2(K)+2.DO*DX(K)
IF(L57.NE.O) GO TO 357
IF(CUX2.GT.-24.2DO) GO TO 46
CUIHYD=-8398DO-PH
IF(DCU1(K).GT.CU1HYD) GO TO 12
DCUSO4=DCU2(K)+DSO4(K)
IF(DCUSO4.GT.3.1098DO) GO TO 13
CU2SO4=2.DO*DCU1(K)+DSO4(K)
IF(CU2SO4.GT.-1.4929DO) GO TO 15
DCUS=DCU2(K)+DS(K)
IF(DCUS.GT.-35.0009DO) GO TO 17
DCUS1=2.DO*DCU1(K)+DS(K)
IF(DCUS1.GT.-48.6702DO) GO TO 19
CALL CCHECK(K,AH,E,DCU2,DCUT,DSO4)
IF(DCUT(K).GE.XM) GO TO 21
The amount of X is checked to see if it is forming together with Cu20.

IF(112.NE.0) GO TO 613
L12=L12+1
P12=PH

613 IF(DX(K).GT.DXCRIT.AND.L33.NE.0) GO TO 614
IF(DX(K).GT.DXCRIT) L33 = L33 + 1
IF(DX(K).GT.DXCRIT) P33=PH

614 IF(DX(K).GT.DXCRIT) DX(K) = DXCRIT
CALL UPDATE(K,PH,D,AH,E,N,POW)
IF(N.EQ.1) GO TO 100
GO TO 12

At this part of the program, the co-existence of two or more solid copper species together will be considered. The next section handles the combination of CuSO4 and Cu(OH)2.

13 IF(L13.NE.0) GO TO 615
L13=L13+1
P13=PH

615 DCU2(K)=7.8919D0-2.DO*PH
DCU1(K)=DCU2(K)-E/7.0591D0+2.5890D0
DDS04=3.1098D0-DCU2(K)
CALL SULF(AH,E,K,XS,DS,DSO4,DCU2,POW)
CALL XANTH(K,PH,E,XINIT,DX)
DXT(K)=XTOTAl(AH,E,K,DX,PH)

IF(DUX.GT.-19.28DO) GO TO 55
CUX2=DCU2(K)+E/2.DO*DX(K)
IF(CUX2.GT.-24.2DO) GO TO 56
IF(DS04.LT.DS04(K)) GO TO 22
GO TO 11

22 DDS04=DDS04
DS(K)=DS04(K)-POW
DST(K)=SS01(K,E,AH,PH,DS,DSO4,POW,DCU2)
CALL CCHECK(K,AH,E,DCU2,DCUT,DS04)
IF(DX(K).GT.DXCRIT.AND.L34.NE.0) GO TO 616
IF(DX(K).GT.DXCRIT) L34 = L34 + 1
IF(DX(K).GT.DXCRIT) P34=PH

616 IF(DX(K).GT.DXCRIT) DX(K) = DXCRIT
CALL UPDATE(K,PH,D,AH,E,N,POW)
IF(N.EQ.1) GO TO 100
GO TO 13

This section handles this time, the case when CuSO4 and Cu20 co-exists.

14 IF(L14.NE.0) GO TO 617
L14=L14+1
P14=PH

617 DCU1(K)=-.8398D0-PH
DCU2(K)=DCU1(K)+E/7.059135928D0-2.588950663D0
DDS04=3.1098D0-DCU2(K)
CALL SULF(AH,E,K,XS,DS,DSO4,DCU2,POW)
CALL XANTH(K,PH,E,XINIT,DX)
DXT(K)=XTOTAl(AH,E,K,DX,PH)
CUX=DCU1(K)+DX(K)
IF(CUX.GT. -19.2800) GO TO 55
CUX2=DCU2(K)+2. DO*DX(K)
IF(CUX2.GT. -24.200) GO TO 56
IF(DDS04.LT.DS04(K)) GO TO 23
GO TO 12
23
DS04(K)=DDS04
DS(K)=DS04(K)-POW
DST(K)=SSOL(K,E,AH,PH,DS,DS04,POW,DCU2)
CALL CCHECK(K,AH,E,DCU2,DCUT,DS04)
IF(DX(K).GT.DXCRIT. AND.L35.NE.0) GO TO 618
IF(DX(K).GT.DXCRIT) L35 = L35 + 1
IF(DX(K).GT.DXCRIT) P35=PH
618
IF(DX(K).GT.DXCRIT) DX(K) = DXCRIT
CALL UPDATE(K,PH,D,AH,E,N,POW)
IF(N.EQ.1) GO TO 100
GO TO 14

The next two sections consider the co-existence of Cu2S04, first with Cu(OH)2, and then with Cu20.

15
IF(L15.NE.0) GO TO 619
L15=L15+1
P15=PH
619
DCU2(K)=7.8919D0-2.DO*PH
DCU1(K)=DCU2(K)-E/.59135928D0+2. 588950663D0
DDS04=1. 4929D0-2.DO*DCU1(K)
CALL SULF(AH,E,K,XS,DS,DS04,POW)
CALL XANTH(K,PH,E,XINIT,DX)
DXT(K)=XTOTAI(AH,E,K,DX,PH)
CUX=DCU1(K)+DX(K)
IF(CUX.GT. -19.2800) GO TO 55
CUX2=DCU2(K)+2. DO*DX(K)
IF(CUX2.GT. -24.200) GO TO 56
IF(DDS04.LT.DS04(K)) GO TO 24
GO TO 11
24
DS04(K)=DDS04
DS(K)=DS04(K)-POW
DST(K)=SSOL(K,E,AH,PH,DS,DS04,POW,DCU2)
CALL CCHECK(K,AH,E,DCU2,DCUT,DS04)
IF(DX(K).GT.DXCRIT. AND.L36.NE.0) GO TO 620
IF(DX(K).GT.DXCRIT) L36 = L36 + 1
IF(DX(K).GT.DXCRIT) P36=PH
620
IF(DX(K).GT.DXCRIT) DX(K) = DXCRIT
CALL UPDATE(K,PH,D,AH,E,N,POW)
IF(N.EQ.1) GO TO 100
GO TO 15

16
IF(L16.NE.0) GO TO 621
L16=L16+1
P16=PH
621
DCU1(K)=-.8398D0-PH
DCU2(K)=DCU1(K)+E/.59135928D0-2. 588950663D0
DDS04=1. 4929D0-2.DO*DCU1(K)
CALL SULF(AH,E,K,XS,DS,DS04,DCU2,POW)
CALL XANTH(K,PH,E,XINIT,DX)
DXT(K)=XTOTAL(AH,E,K,DX,PH)
CUX=DCU1(K)+DX(K)
This portion of the program now handles the case when CuS and Cu(OH)₂ are stable together. The next section after it, considers the situation when CuS co-exists with Cu₂O.

17 IF(L17.NE.0) GO TO 623
L17=L17+1
P17=PH

623 DCU2(K)=-7.8919D0-2.DO*PH
DCU1(K)=DCU2(K)-E/0.059135928D0+2.588950663D0
DDS=-36.935D0-DCU2(K)
CALL SULF(AH,E,K,XS,DS,DSO4,DCU2,POW)
CALL XANTH(K,PH,E,XINIT,DX)
DXT(K)=XTOTAL(AH,E,K,DX,PH)
CUX=DCU1(K)+DX(K)
IF(CUX.GT.-19.28D0) GO TO 55
CUX2=DCU2(K)+2.DO*DX(K)
IF(CUX2.GT.-24.2D0) GO TO 56
IF(DDS.LT.DS(K)) GO TO 26
GO TO 11

26 DS(K)=DDS
DSO4(K)=DS(K)+POW
DST(K)=SSOL(K,E,PH,DS,DSO4,DCU2,POW,DCU2)
CALL CCHECK(K,E,PH,DCU2,DCUT,DSO4)
IF(DX(K).GT.DXCRT.I.AND.L38.NE.0) GO TO 624
IF(DX(K).GT.DXCRT.I) L38 = L38 + 1
IF(DX(K).GT.DXCRT) P38=PH

624 IF(DX(K).GT.DXCRT) DX(K) = DXCRT
CALL UPDATE(K,PH,D,AH,E,N,POW)
IF(N.EQ.1) GO TO 100
GO TO 17

18 IF(L18.NE.0) GO TO 625
L18=L18+1
P18=PH

625 DCU1(K)=-.8398D0-PH
DCU2(K)=DCU1(K)+E/0.059135928D0-2.588950663D0
DDS=-36.935D0-DCU2(K)
CALL SULF(AH,E,K,XS,DS,DSO4,DCU2,POW)
CALL XANTH(K,PH,E,XINIT,DX)
DXT(K)=XTOTAL(AH,E,K,DX,PH)
CUX=DCU1(K)+DX(K)
The following two sections considers the co-existence of Cu$_2$S with Cu(OH)$_2$ first, and then with Cu$_2$O, respectively.

```plaintext
19 IF(L19.NE.0) GO TO 627  
   L19=L19+1  
P19=PH

627 DCU2(K) = 7.8919D0 - 2.0*D0*PH  
   DCU1(K) = DCU2(K) - 0.59135928D0 + 2.588950663D0  
   DDS = -48.8169D0 - 2.0*DCU1(K)  
   CALL SULF(AH,E,K,XS,DS,DSO4,DCU2,POW)  
   CALL XANTH(K,Pt,PA,NI,DX)  
   DXT(K) = XTOTAL(AH6,E,K,DX,POW)  
   CUX = DCU1(K) + DX(K)  
   IF(CUX.GT. -19.28D0) GO TO 55  
   CUX2 = DCU2(K) + 2.0*DX(K)  
   IF(CUX2.GT. -24.2D0) GO TO 56  
   IF(DDS.LT.DS(K)) GO TO 28  
   GO TO 11

28 DS(K) = DDS  
   DSO4(K) = DS(K) + POW  
   DST(K) = SSOL(K,E,PH,DS,DSO4,POW,DCU2)  
   CALL CCHECK(K,AH,E,DCU2,DCUT,DSO4)  
   IF(DX(K).GT.DXCRIT.AND.L39.NE.0) GO TO 626  
   IF(DX(K).GT.DXCRIT) L39 = L39 + 1  
   IF(DX(K).GT.DXCRIT) P39 = PH  
   CALL UPDATE(K,PH,D,AH,E,N,POW)  
   IF(N.EQ.1) GO TO 100  
   GO TO 19

20 IF(L20.NE.0) GO TO 629  
   L20=L20+1  
P20=PH

629 DCU1(K) = -8.3989D0 - PH  
   DCU2(K) = DCU1(K) + 0.59135928D0 - 2.588950663D0  
   DDS = -48.8169D0 - 2.0*DCU1(K)  
   CALL SULF(AH,E,K,XS,DS,DSO4,DCU2,POW)  
   CALL XANTH(K,Pt,PA,NI,DX)  
   DXT(K) = XTOTAL(AH6,E,K,DX,POW)  
   CUX = DCU1(K) + DX(K)  
   IF(CUX.GT. -19.28D0) GO TO 55
```

CUX2 = DCU2(K) + 2. DO*DX(K)
IF(CUX2.GT.-24.2D0) GO TO 56
IF(DS(K).LT.DS(K)) GO TO 29
GO TO 12

29
DS(K) = DDS
DS04(K) = DS(K) + POW
DST(K) = SSOL(K,E,PH,DS,DS04,POW,DCU2)
CALL CCHECK(K,AH,E,DCU2,DCUT,DS04)
IF(DX(K).GT.DXCRIT.AND.L41.NE.0) GO TO 630
IF(DX(K).GT.DXCRIT) L41 = L41 + 1
IF(DX(K).GT.DXCRIT) P41 = PH

630
IF(DX(K).GT.DXCRIT) DX(K) = DXCRIT
CALL UPDATE(K,PH,D,AH,E,N,POW)
IF(N.EQ.1) GO TO 100
GO TO 20

21
X2 = CGUESS(AH,E,K,POW,XM,XS)

201
IF(L21.NE.0) GO TO 631
L21 = L21 + 1
P21 = PH

631
CALL CU2S(AH,E,K,XM,DS,DS04,DCU1,DCU2,DCUT,POW,X2,XS,LL)
CALL XANTH(K,PH,E,XINIT,DX)
DST(K) = SSOL(K,E,PH,DS,DS04,POW,DCU2)
DXT(K) = XTOTAL(AH,E,K,DX,PH)
DCU2S = 2. DO*DCU1(K) + DS(K)
IF(DCU2S.GT.-48.6702D0) GO TO 204
CUX = DCU1(K) + DX(K)
IF(CUX.GT.-19.28D0) GO TO 55
CUX2 = DCU2(K) + 2. DO*DX(K)
IF(CUX2.GT.-24.2D0) GO TO 56
CU1HYD = -0.8398D0 - PH
IF(DCU1(K).GT.CU1HYD) GO TO 12
IF(DX(K).GT.DXCRIT.AND.L42.NE.0) GO TO 632
IF(DX(K).GT.DXCRIT) L42 = L42 + 1
IF(DX(K).GT.DXCRIT) P42 = PH

632
IF(DX(K).GT.DXCRIT) DX(K) = DXCRIT
CALL UPDATE(K,PH,D,AH,E,N,POW)
IF(N.EQ.1) GO TO 100
GO TO 201

204
IF(L0.NE.0) GO TO 633
L0 = L0 + 1
P0 = PH

633
CALL CU2S(AH,E,K,DS,DS04,DCU1,DCU2,DCUT,POW)
CALL XANTH(K,PH,E,XINIT,DX)
DST(K) = SSOL(K,E,PH,DS,DS04,POW,DCU2)
DXT(K) = XTOTAL(AH,E,K,DX,PH)
CUX = DCU1(K) + DX(K)
IF(CUX.GT.-19.28D0) GO TO 55
CUX2 = DCU2(K) + 2. DO*DX(K)
IF(CUX2.GT.-24.2D0) GO TO 56
CU2HYD = 7.8919D0 - 2. DO*PH
IF(DCU2(K).GT.CU2HYD) GO TO 11
CU1HYD = -8398D0 - PH
IF(DCU1(K).GT.CU1HYD) GO TO 12
IF(DX(K).GT.DXCRIT.AND.L43.NE.0) GO TO 634
IF(DX(K).GT.DXCRIT) L43 = L43 + 1
IF(DX(K).GT.DXCRIT) P43 = PH

634
IF(DX(K).GT.DXCRIT) DX(K) = DXCRIT
CALL UPDATE(K,PH,D,AH,E,N,POW)
IF(N.EQ. 1) GO TO 100
GO TO 204
309 IF(L22.NE.0) GO TO 635
L22=L22+1
P22=PH
635 DCU2(K)=E/. 029567964D0-11.387324D0
DCU1(K)=DCU2(K)-E/. 059135928D0+2.588951D0
CALL SULP(AH,E,K,XS,DS,DSO4,DCU2,POW)
CALL XANTH(K,PH,E,XINIT,DX)
DXT(K)=XTOTAL(AH,E,K,DX,PH)
CUX=DCU1(K)+DX(K)
IF(CUX.GT. -19.28D0) GO TO 55
CUX2=DCU2(K)+2.D0*DX(K)
IF(CUX2.GT. -24.2D0) GO TO 56
DDS=-35.0099D0-DCU2(K)
IF(DDS.LT.DS(K)) GO TO 311
GO TO 8
311 DS(K)=DDS
DS04(K)=DS(K)+POW
DST(K)=SSOL(K,E,AH,PH,DS,DSO4,POW,DCU2)
CALL CHECK(K,AH,E,DCU2,DCUT,DS04)
IF(DX(K).GT.DXCRIT AND L44.NE.0) GO TO 636
IF(DX(K).GT.DXCRIT) L44 = L44 + 1
IF(DX(K).GT.DXCRIT) P44=PH
636 CALL UPDATE(K,PH,D,AH,E,N,POW)
IF(N.EQ. 1) GO TO 100
GO TO 309
The program now checks the co-existence of CuS, Cu and X2.

The combination of Cu2S and Cu is now considered. The amount of X is checked to determine if X2 also co-exists with the two other solid species.

310 IF(L23.NE.0) GO TO 637
L23=L23+1
P23=PH
637 DCU2(K)=E/. 029567964D0-11.387324D0
DCU1(K)=DCU2(K)-E/. 059135928D0+2.588951D0
CALL SULP(AH,E,K,XS,DS,DSO4,DCU2,POW)
CALL XANTH(K,PH,E,XINIT,DX)
DXT(K)=XTOTAL(AH,E,K,DX,PH)
IF(L50.NE.0) GO TO 34
CUX=DCU1(K)+DX(K)
IF(CUX.GT. -19.28D0) GO TO 55
CUX2=DCU2(K)+2.D0*DX(K)
IF(CUX2.GT. -24.2D0) GO TO 56
DDS=-48.6702D0-2.D0*DCU1(K)
IF(DX(K).GT.DXCRIT AND L45.NE.0) GO TO 638
34 IF(DX(K).GT. -24.D0) GO TO 56
DST(K)=SSOL(K,E,AH,PH,DS,DSO4,POW,DCU2)
CALL CHECK(K,AH,E,DCU2,DCUT,DS04)
IF(DX(K).GT.DXCRIT AND L45.NE.0) GO TO 638
312 DS(K)=DDS
DS04(K)=DS(K)+POW
DST(K)=SSOL(K,E,AH,PH,DS,DSO4,POW,DCU2)
CALL CHECK(K,AH,E,DCU2,DCUT,DS04)
IF(DX(K).GT.DXCRIT AND L45.NE.0) GO TO 638
The succeeding sections will now consider the cases where the formation of copper xanthates are possible. The first one considered in the next section is CuX.

The stability of CuX2 is now considered in this section.


The combination of Cu, Cu₂S and CuX is considered in this part. The amount of sulfur and xanthate ions are also checked to see whether Cu₂S or CuX no longer co-exists with Cu.

This section considers the co-existence of Cu₂S and CuX, as well as determine when Cu₂S or CuX is no longer stable.

570 IF(L48.NE.0) GO TO 641
L48=L48+1
P48=PH

641 IF(L48.NE.0) GO TO 641
L48=L48+1
P48=PH

550 IF(L58.NE.0) GO TO 549
L58=L58+1
P58=PH

549 IF(K.EQ.1) X2=XM
IF(K.EQ.1) GO TO 551
X2=10. D0*DCU2(K-1)

551 LL=3
CALL CUXCS(X2, AH,E,K,XINIT,LL,DCU2,DCU1,DX,PH,POW,L)
DS(K)=-48.6702D0-2.DO*DCU1(K)
DS04(K)=DS(K)+POW
DX(K)=-19.2800-DCU1(K)
CALL CCHECK(K,AH,E,DCU2,DCUT,DS04)
DXT(K)=XTOTAL(AH,E,K,DX,PH)
DST(K)=SSOL(K,E,AH,PH,DS,DS04,POW,DCU2)
IF(DST(K).GT.DX. AND. L59.NE.0) GO TO 552
IF(DST(K).GT.DXS) L59=L59+1
IF(DST(K).GT.DXS) P59=PH
552 IF(DST(K).GT.DXS) GO TO 40
IF(DTX(K).GT.DXINIT. AND. L60.NE.0) GO TO 553
IF(DTX(K).GT.DXINIT) L60=L60+1
IF(DTX(K).GT.DXINIT) P60=PH
553 IF(DTX(K).GT.DXINIT) GO TO 10
CALL UPDATE(K,PH,D,AH,E,N,POW)
IF(N.EQ.1) GO TO 10
GO TO 550

This time, the presence of Cu2S and CuX2 together is considered.

560 IF (L61.NE.0) GO TO 561
L61=L61+1
P61=PH
561 DCU2(K)=E/0.0296D0-11.3873D0
DCU1(K)=DCU2(K)-E/0.0591D0+2.5890D0
DS(K)=-48.6702D0-2.DO*DCU1(K)
DS04(K)=DS(K)+POW
DX(K)=-19.2800-DCU1(K)
CALL CCHECK(K,AH,E,DCU2,DCUT,DS04)
DXT(K)=XTOTAL(AH,E,K,DX,PH)
DST(K)=SSOL(K,E,AH,PH,DS,DS04,POW,DCU2)
IF(DST(K).GT.DX. AND. L62.NE.0) GO TO 562
IF(DST(K).GT.DXS) L62=L62+1
IF(DST(K).GT.DXS) P62=PH
562 IF(DST(K).GT.DXS) GO TO 56
IF(DTX(K).GT.DXINIT. AND. L63.NE.0) GO TO 563
IF(DTX(K).GT.DXINIT) L63=L63+1
IF(DTX(K).GT.DXINIT) P63=PH
563 IF(DTX(K).GT.DXINIT) GO TO 10
CALL UPDATE(K,PH,D,AH,E,N,POW)
IF(N.EQ.1) GO TO 10
GO TO 560

The case when Cu2O and CuX are both stable is handled in this section.

40 DCU2(K)=E/0.0296D0-11.3873D0
DCU1(K)=DCU2(K)-E/0.0591D0+2.5890D0
DX(K)=-19.2800-DCU1(K)
CALL SULF(AH,E,K,XS,DS,DS04,DCU2,POW)
DXT(K)=XTOTAL(AH,E,K,DX,PH)
DST(K)=SSOL(K,E,AH,PH,DS,DS04,POW,DCU2)
CALL CCHECK(K,AH,E,DCU2,DCUT,DS04)
CU1HYD=-0.8396D0-PH
IF(DCU1(K).GT.CU1HYD. AND. L51.NE.0) GO TO 644
IF(DCU1(K).GT.CU1HYD) L51=L51+1
IF(DCU1(K).GT.CU1HYD) P51=PH
The program now checks the combination of Cu(OH)$_2$ and CuX.

42 IF(DCU1(K).GT.CU1HYD) GO TO 42
DCU2(K)=DCU1(K)+E/0.0591D0-2.5890D0
DX(K)=-19.28D0-DCU1(K)
CALL SULF(AH,E,K,XS,DS,DS04,DCU2,POW)
DXT(K)=XTOTAL(AH,E,K,DX,PH)
DST(K)=SSOL(K,E,AH,PH,DS,DS04,POW,DCU2)
CALL CHECK(K,AH,E,DCU2,DCUT,DS04)
IF(DXT(K).GT.DXINIT.AND.L52.NE.0) GO TO 645
IF(DXT(K).GT.DXINIT) L52=L52+1
IF(DXT(K).GT.DXINIT) PS2=PH
CALL UPDATE(K,PH,D,AH,E,N,POW)
IF(N.EQ.1) GO TO 100
GO TO 40

644 IF(DCU1(K).GT.CU1HYD) GO TO 42
IF(DXT(K).GT.DXINIT.AND.L52.NE.0) GO TO 645
IF(DXT(K).GT.DXINIT) L52=L52+1
IF(DXT(K).GT.DXINIT) PS2=PH
645 IF(DXT(K).GT.DXINIT) GO TO 8
CALL UPDATE(K,PH,D,AH,E,N,POW)
IF(N.EQ.1) GO TO 100
GO TO 40

This section now considers the case when CuX no longer co-exist with Cu(OH)$_2$.

44 DCU1(K)=-0.8398D0-PH
DCU2(K)=DCU1(K)+E/0.0591D0-2.5890D0
DX(K)=-19.28D0-DCU1(K)
CALL SULF(AH,E,K,XS,DS,DS04,DCU2,POW)
DXT(K)=XTOTAL(AH,E,K,DX,PH)
DST(K)=SSOL(K,E,AH,PH,DS,DS04,POW,DCU2)
CALL CHECK(K,AH,E,DCU2,DCUT,DS04)
IF(DXT(K).GT.DXINIT.AND.L53.NE.0) GO TO 646
IF(DXT(K).GT.DXINIT) L53=L53+1
IF(DXT(K).GT.DXINIT) PS3=PH
IF(DXT(K).GT.DXINIT) GO TO 12
CU2HYD=7.8919D0-2.D0*PH
IF(DCU2(K).GT.CU2HYD.AND.L54.NE.0) GO TO 647
IF(DCU2(K).GT.CU2HYD) L54=L54+1
IF(DCU2(K).GT.CU2HYD) PS4=PH
646 IF(DCU2(K).GT.CU2HYD) GO TO 44
CALL UPDATE(K,PH,D,AH,E,N,POW)
IF(N.EQ.1) GO TO 100
GO TO 42

This section now considers the case when CuX2 starts to disappear.

46 IF(L56.NE.0) GO TO 47
L56=L56+1
P56=PH
47 DCU2(K)=7.8919D0-2.D0*PH
DCU1(K)=DCU2(K)-E/0.0591D0+2.5890D0
DX(K)=-12.1D0-0.5D0*DCU2(K)
CALL SULF(AH,E,K,XS,DS,DSO4,DCU2,POW)
DXT(K)=XTOTAL(AH,E,K,DX,PH)
DST(K)=SSOL(K,E,AH,PH,DS,DSO4,POW,DCU2)
CALL CCHECK(K,AH,E,DCU2,DCUT,DSO4)
IF(DXT(K).GT.DXINIT) L57=L57+1
IF(DXI(K).GT.DXINIT) P57=PH
IF(DXI(K).GT.DXINIT) GO TO 11
CALL UPDATE(K,PH,D,AH,E,N,POW)
IF(N.EQ.1) GO TO 100
GO TO 46

This is now the part of the program where the output is handled. The concentration of each species are placed in arrays at pH intervals of 0.1. The amount of xanthate that ended up as CuX (%CuX), CuX2 (%CuX2), or X2 (%X2) are also stored. These are then printed out afterwards.

100 I=0
DO 30 M=1,K,10
I=I+1
H(I)=D(M)
CU2(I)=DCU2(M)
CUOH(I)=-8.8D0+CU2(I)+H(I)
CUOH2(I)=-14.82D0+CU2(I)+2.6D0*H(I)
CUOH3(I)=-26.80D0+CU2(I)+3.6D0*H(I)
CUOH4(I)=-39.96D0+CU2(I)+4.6D0*H(I)
CUO2H2(I)=-10.7D0+2.D0*CU2(I)+2.6D0*H(I)
CU1(I)=DCU1(M)
SS(I)=DS(M)
SSO4(I)=DSO4(M)
CUSULF(I)=2.35D0+CU2(I)+SS04(I)
H2SO4(I)=-1.8D0*H(I)+SSO4(I)
HSO4(I)=1.995D0-H(I)+SSO4(I)
HS(I)=13.897D0-H(I)+SS(I)
H2S(I)=20.9018D0-2.D0*H(I)+SS(I)
PH2S(I)=20.5052D0-2.6D0*H(I)+SS(I)
CU(I)=DCU1(M)
XANT(I)=D(XM)
HXAN(I)=1.52D0-H(I)+XAN(I)
XAN2(I)=2.6D0*XAN(I)+(E-0.08495D0)/0.029567964D0
XT(I)=DXT(M)
XANT=10.0D0*XT(I)
DIFF=XINIT-XANT
IF(DIFF.LE.0.0) PERX1(I)=0.0
IF(DIFF.GT.0.0) PERX2(I)=0.0
IF(DIFF.LE.0.0) PERX3(I)=0.0
CUX=DCU1(M)+DX(M)
IF(CUX.LT.-19.28D0) GO TO 1046
IF(DIFF.GT.0.0.AND.XAN(I).LE.DXCRIT) PERX1(I)=(XINIT-XANT)
*/XINIT=100.0
IF(DIFF.GT.0.0.AND.XAN(I).LE.DXCRIT) PERX2(I)=0.0
IF(DIFF.GT.0.0.AND.XAN(I).LE.DXCRIT) PERX3(I)=0.0
GO TO 1047
1046 IF(DIFF.GT.0.0.AND.XAN(I).LE.DXCRIT) PERX1(I)=0.0
IF(DIFF.GT.0.0.AND.XAN(I).LE.DXCRIT) PERX2(I)=(XINIT-XANT)
*/XINIT=100.0
This part involves the storage of the two-dimensional arrays into disks for use with the SURFACE II programs.

DO 1010 JJ=1, I
DISK(1, JJ)=H(JJ)
DISK(2, JJ)=CU2(JJ)
DISK(3, JJ)=CU1(JJ)
DISK(4, JJ)=CUOH(JJ)
DISK(5, JJ)=CUOH2(JJ)
DISK(6, JJ)=CUOH3(JJ)
DISK(7, JJ)=CUOH4(JJ)
DISK(8, JJ)=CU2OH2(JJ)
DISK(9, JJ)=CUSULF(JJ)
DISK(10, JJ)=SS04(JJ)
DISK(11, JJ)=SS(JJ)
DISK(12, JJ)=HS(JJ)
DISK(13, JJ)=H2S(JJ)
DISK(14, JJ)=PH2S(JJ)
DISK(15, JJ)=H2SO4(JJ)
DISK(16, JJ)=HSO4(JJ)
DISK(17, JJ)=CU(JJ)
DISK(18, JJ)=ST(JJ)
DISK(19, JJ)=XAN(JJ)
DISK(20, JJ)=HXAN(JJ)
DISK(21, JJ)=XAN2(JJ)
DISK(22, JJ)=XT(JJ)
DISK(23, JJ)=PERX1(JJ)
DISK(24, JJ)=PERX2(JJ)
DISK(25, JJ)=PERX3(JJ)
DO 1012 KK=1, 25
1012 WRITE(9,1014) (DISK(KK,JJ),JJ=1,I)
1014 FORMAT(14(1D14.5))
IF(L4.NE.0) GO TO 60
GO TO 61

The phase changes are printed out at this part of the program.

60 WRITE(6,62) P4
62 FORMAT(12X,'S PRECIPITATES OUT AT PH',F7.2)
61 IF(L5.NE.0) GO TO 63
GO TO 64
WRITE(6,65) P5
65 FORMAT(12X,'NO SOLID IS STABLE AT PH',F7.2)
64 IF(L6.NE.0) GO TO 66
GO TO 67
66 WRITE(6,68) P6
68 FORMAT(12X,'CUSO4 PRECIPITATES OUT AT PH',F7.2)
67 IF(L13.NE.0) GO TO 69
GO TO 710
WRITE(6,711) P13
711 FORMAT(12X,'CUSO4 AND CU(OH)2 PRECIPITATE OUT AT PH',
*F7.2)
710 IF(L14.NE.0) GO TO 72
GO TO 73
72 WRITE(6,74) P14
74 FORMAT(12X,'CUSO4 AND CU2O PRECIPITATE OUT AT PH',
*F7.2)
73 IF(L7.NE.0) GO TO 75
GO TO 76
75 WRITE(6,77) P7
77 FORMAT(12X,'CU2SO4 PRECIPITATES OUT AT PH',F7.2)
76 IF(L15.NE.0) GO TO 78
GO TO 79
78 WRITE(6,80) P15
80 FORMAT(12X,'CU2SO4 AND CU(OH)2 PRECIPITATE OUT AT PH',
*F7.2)
79 IF(L16.NE.0) GO TO 81
GO TO 82
81 WRITE(6,83) P16
83 FORMAT(12X,'CU2SO4 AND CU2O PRECIPITATE OUT AT PH',
*F7.2)
82 IF(L8.NE.0) GO TO 84
GO TO 85
84 WRITE(6,86) P8
86 FORMAT(12X,'CU PRECIPITATES OUT AT PH',F7.2)
85 IF(L9.NE.0) GO TO 87
GO TO 88
87 WRITE(6,89) P9
89 FORMAT(12X,'CUS PRECIPITATES OUT AT PH',F7.2)
88 IF(L17.NE.0) GO TO 90
GO TO 910
90 WRITE(6,92) P17
92 FORMAT(12X,'CUS AND CU(OH)2 PRECIPITATE OUT AT PH',
*F7.2)
910 IF(L18.NE.0) GO TO 93
GO TO 320
93 WRITE(6,95) P18
95 FORMAT(12X,'CUS AND CU2O PRECIPITATE OUT AT PH',F7.2)
320 IF(L22.NE.0) GO TO 321
GO TO 94
321 WRITE(6,322) P22
322 FORMAT(///12X,'CUS AND CU PRECIPITATE OUT AT PH',F7.2)
94 IF(L10.NE.0) GO TO 96
GO TO 97
96 WRITE(6,98) P10
98 FORMAT(///12X,'CU2S PRECIPITATES OUT AT PH',F7.2)
97 IF(L19.NE.0) GO TO 99
GO TO 101
99 WRITE(6,102) P19
102 FORMAT(///12X,'CU2S AND CU(OH)2 PRECIPITATE OUT AT PH',
*F7.2)
101 IF(L20.NE.0) GO TO 103
GO TO 323
103 WRITE(6,105) P20
105 FORMAT(///12X,'CU2S AND CU2O PRECIPITATE OUT AT PH',
*F7.2)
322 IF(L23.NE.0) GO TO 324
GO TO 326
324 WRITE(6,325) P23
325 FORMAT(///12X,'CU2S AND CU PRECIPITATE OUT AT PH',F7.2)
326 IF(L24.NE.0) GO TO 327
GO TO 104
327 WRITE(6,328) P24
328 FORMAT(///12X,'ONLY CU IS STABLE ABOVE PH',F7.2)
104 IF(L11.NE.0) GO TO 106
GO TO 107
106 WRITE(6,108) P11
108 FORMAT(///12X,'CU(OH)2 PRECIPITATE OUT AT PH',F7.2)
107 IF(L12.NE.0) GO TO 109
GO TO 110
109 WRITE(6,111) P12
111 FORMAT(///12X,'CU2O PRECIPITATES OUT AT PH',F7.2)
110 IF(L21.NE.0) GO TO 112
GO TO 113
112 WRITE(6,114) P21
114 FORMAT(///12X,'NO PRECIPITATE APPEARS ABOVE PH',F7.2)
113 IF(L0.NE.0) GO TO 115
GO TO 116
115 WRITE(6,117) P0
117 FORMAT(///12X,'CU2S PRECIPITATES OUT AT PH',F7.2)
116 IF(L25.NE.0) GO TO 118
GO TO 119
118 WRITE(6,120) P25
120 FORMAT(///12X,'S AND X2 ARE STABLE AT PH',F7.2)
119 IF(L26.NE.0) GO TO 121
GO TO 122
121 WRITE(6,123) P26
123 FORMAT(///12X,'X2 ALONE IS STABLE AT PH',F7.2)
122 IF(L29.NE.0) GO TO 124
GO TO 125
124 WRITE(6,126) P29
126 FORMAT(///12X,'CU AND X2 ARE STABLE AT PH',F7.2)
125 IF(L30.NE.0) GO TO 127
GO TO 128
127 WRITE(6,129) P30
129 FORMAT(///12X,'CUS AND X2 ARE STABLE AT PH',F7.2)
128 IF(L31.NE.0) GO TO 130
   GO TO 131
130 WRITE(6,132) P31
   132 FORMAT(12X,'CU2S AND X2 ARE STABLE AT PH',F7.2)
131 IF(L32.NE.0) GO TO 133
   GO TO 134
133 WRITE(6,135) P32
   135 FORMAT(12X,'CU(OH)2 AND X2 ARE STABLE AT PH',F7.2)
134 IF(L33.NE.0) GO TO 136
   GO TO 137
136 WRITE(6,138) P33
   138 FORMAT(12X,'CU2O AND X2 ARE STABLE AT PH',F7.2)
137 IF(L40.NE.0) GO TO 139
   GO TO 140
139 WRITE(6,141) P40
   141 FORMAT(12X,'CU2S, CU(OH)2 AND X2 ARE STABLE AT PH',F7.2)
140 IF(L41.NE.0) GO TO 142
   GO TO 143
142 WRITE(6,144) P41
   144 FORMAT(12X,'CU2S, CU2O AND X2 ARE STABLE AT PH',F7.2)
143 IF(L43.NE.0) GO TO 145
   GO TO 146
145 WRITE(6,147) P43
   147 FORMAT(12X,'CU2S AND X2 ARE STABLE PH',F7.2)
146 IF(L44.NE.0) GO TO 148
   GO TO 149
148 WRITE(6,150) P44
   150 FORMAT(12X,'CUS, CU AND X2 ARE STABLE AT PH',F7.2)
149 IF(L45.NE.0) GO TO 151
   GO TO 152
151 WRITE(6,153) P45
   153 FORMAT(12X,'CU2S, CU AND X2 ARE STABLE AT PH',F7.2)
152 IF(L46.NE.0) GO TO 154
   GO TO 155
154 WRITE(6,156) P46
   156 FORMAT(12X,'CU2S, CU2O AND X2 ARE BOTH STABLE AT PH',F7.2)
155 IF(L47.NE.0) GO TO 157
   GO TO 158
157 WRITE(6,159) P47
   159 FORMAT(12X,'CU2S AND CU2O ARE BOTH STABLE AT PH',F7.2)
158 IF(L58.NE.0) GO TO 160
   GO TO 161
160 WRITE(6,162) P58
   162 FORMAT(12X,'CU2S AND CUX ARE BOTH STABLE AT PH',F7.2)
161 IF(L59.NE.0) GO TO 163
   GO TO 164
163 WRITE(6,165) P59
165 FORMAT(12X,'CU2S IS NO LONGER STABLE, BUT CUX STILL IS AT PH',F7.2)
164 IF(L60.NE.0) GO TO 166
   GO TO 167
166 WRITE(6,168) P60
   168 FORMAT(12X,'CUX IS NO LONGER STABLE, BUT CU2S STILL IS AT PH',F7.2)
167 IF(L61.NE.0) GO TO 1260
   GO TO 1261
1260 WRITE(6,1262) P61
1262 FORMAT(//////12X,'CU2S AND CUX2 ARE BOTH STABLE AT PH',F7.2)
1263 IF(L62.NE.O) GO TO 1263
1264 GO TO 1265
1265 WRITE(6,1265) P62
1266 FORMAT(//////12X,'CU2S IS NO LONGER STABLE,BUT CUX2 STILL
*IS AT PH',F7.2)
1267 IF(L63.NE.O) GO TO 1266
1268 WRITE(6,1268) P63
1269 FORMAT(//////12X,'CUX2 IS NO LONGER STABLE,BUT CUX2 STILL
*IS AT PH',F7.2)
1270 IF(L48.NE.O) GO TO 160
1271 GO TO 161
1272 WRITE(6,162) P48
1273 FORMAT(//////12X,'CU,CU2S AND CUX ARE ALL STABLE AT PH',
*F7.2)
1274 IF(L49.NE.O) GO TO 163
1275 GO TO 164
1276 WRITE(6,165) P49
1277 FORMAT(//////12X,'CU2S IS NO LONGER STABLE,BUT CU AND CUX
*STILL ARE AT PH',F7.2)
1278 IF(L50.NE.O) GO TO 166
1279 WRITE(6,168) P50
1280 FORMAT(//////12X,'CUX IS NO LONGER PRESENT,WHEREAS CU AND
*CU2S STILL ARE AT PH',F7.2)
1281 IF(L51.NE.O) GO TO 169
1282 GO TO 170
1283 WRITE(6,171) P51
1284 FORMAT(//////12X,'CU2O AND CUX ARE BOTH STABLE AT PH',F7.2)
1285 IF(L52.NE.O) GO TO 172
1286 WRITE(6,174) P52
1287 FORMAT(//////12X,'CUX DISAPPEARS,BUT CU STILL EXISTS AT PH',
*F7.2)
1288 IF(L53.NE.O) GO TO 175
1289 GO TO 176
1290 WRITE(6,177) P53
1291 FORMAT(//////12X,'CUX HAS JUST DISAPPEARED,BUT CU2O IS STILL
*STABLE AT PH',F7.2)
1292 IF(L54.NE.O) GO TO 178
1293 GO TO 179
1294 WRITE(6,180) P54
1295 FORMAT(//////12X,'CU(OH)2 AND CUX ARE NOW STABLE AT PH',
*F7.2)
1296 IF(L55.NE.O) GO TO 181
1297 GO TO 182
1298 WRITE(6,183) P55
1299 FORMAT(//////12X,'CUX IS NO LONGER STABLE,BUT CU(OH)2 STILL
*IS AT PH',F7.2)
1300 IF(L56.NE.O) GO TO 184
1301 GO TO 185
1302 WRITE(6,186) P56
1303 FORMAT(//////12X,'CU(OH)2 AND CUX2 ARE NOW STABLE AT PH',
*F7.2)
1304 IF(L57.NE.O) GO TO 187
1305 GO TO 188
1306 WRITE(6,189) P57
This is the end of the main program and the next part contains all the subprograms that have been used here.

Subroutine UPDATE is the subprogram called in the main program to update the pH by increments of 0.01.

SUBROUTINE UPDATE(K, PH, D, AH, E, N, POW)
   IMPLICIT REAL*8(A-H, O-2)
   DIMENSION D(1500), AH(1500)
   PH = PH + 0.0100
   IF (PH.GT.14.00) GO TO 10
   K = K + 1
   D(K) = PH
   AH(K) = 10.00**(-PH)
   POW = E / 00739199D0 - 20.1433983D0 + 8.00*PH
   GO TO 20
10   N = 1
20   RETURN
END

Subroutine SULF solves the mass balance equation for the sulfur-bearing species when they are all soluble.

SUBROUTINE SULF(AH, E, K, XS, DS, DS04, DCU2, POW)
   IMPLICIT REAL*8(A-H, O-2)
   DIMENSION AH(1500), XS(1500), DS04(1500), DCU2(1500)
   TOT = STOTAL(AH, K, POW, L)
   IF (L.EQ.1) GO TO 10
   T = TOT + 223.87D0*10.00**DCU2(K)
   S04 = XS / T
   DS04(K) = DLOG10(S04)
   DS(K) = DS04(K) - POW
   GO TO 20
10   Y = DCU2(K) + POW
   IF (Y.GT.70.00) GO TO 30
   TT = DCU2(K) + POW
   IF (TT.LT.-74.00) GO TO 50
   T = TOT + 223.87D0*10.00**DCU2(K)*10.00**POW
   GO TO 60
30   TT = TOT
60   S = XS / T
   DS(K) = DLOG10(S)
   DS04(K) = DS(K) + POW
   GO TO 20
30   DS(K) = DLOG10(XS) - 2.35D0 - Y
   DS04(K) = DS(K) + POW
20   RETURN
END

Subroutine XANTH solves the quadratic equation for the xanthate mass balance when all the xanthate species are soluble.
SUBROUTINE XANTH(K, PH, E, XINIT, DX)
IMPLICIT REAL*8(A-H, O-Z)
DIMENSION AH(1500), DX(1500)
A=2. DO**10. DO**(E-0. 08495D0)/0. 029567964D0
B=1. DO+10. DO**(1. 52DO-PH)
C=-XINIT
RATIO=4. DO*A*C/B/B
IF(DABS(RATIO). LT. 1. D-06) GO TO 10
ROOT=(-B+DSQRT(B*B-4. DO*A*C))/2. DO/
GO TO 20
10 ROOT=-C/B
20 DX(K)=DLOG10(ROOT)
RETURN
END

Subroutine CUXAN sets up the mass balance equation for the case when CuX is stable. The solution of the resulting polynomial equation is determined by calling subroutine SOLVE.

SUBROUTINE CUXAN(X2, AH, E, K, XM, XINIT, LL, DCU2, DCU1, DX, PH, POW)
IMPLICIT REAL*8(A-H, O-Z)
DIMENSION AH(1500), DCU2(1500), DCU1(1500), DX(1500)
T=TOTAL(AH,K)
S=TOTAL(AH,K,POW,L)
IF(POW.LT.-35.DO) GO TO 70
IF(POW.GT.35.DO) GO TO 10
DA=-8. 04903D0-2.
DO: *DA
IF(DA.LT. -74.DO) GO TO 30
A=10. DO**DA
GO TO 40
30 A=O.DO
40 DB1=2.35DO+POW+DLOG10(T)
IF(DB1.LT. -74.DO) GO TO 50
Bl=lO.DO**DB1
GO TO 60
50 Bl=O.DO
60 B2=2. DO*1. 9953D-11/AH(K)**2. DO*S
B=Bl+B2
C=T+S+223. 87DO*10. DO**POW*(XINIT-0. 5DO*XM)
D1=-(XM-XINIT)*S
D2= -223. 87DO*10. DO**(-19. 28DO)*10. DO**POW*(1. DO+10. DO**(1. 52DO- *PH))/10. DO**(E- 0. 1531D0)/0. 0591DO)
D=31+D2
G1=10. DO**((-19. 28DO)*10. DO**((E-0. 1531DO)/0. 0591DO)*1. DO+ *10. DO**(1. 52DO-PH))*S
G2=-2. DO*223. 87DO*10. DO**((-38. 56DO)*10. DO**((E-0. 08495DO)/0. 02956D *O)*10. DO**POW*10. DO**((E-0. 1531DO)/0. 02956DO)
G=G1+G2
GO TO 20
10 A=2. DO*1. 9953D-11/AH(K)**2. DO*223. 87DO
B=223. 87DO*T+2. DO*1. 9953D-11/AH(K)**2. DO*S
C=T+S+223. 87DO*(XINIT-0. 5DO*XM)
D=-(XM-XINIT)*S-223. 87DO*10. DO**((-19. 28DO)*10. DO**((E-0. 1531DO)/0. 0591DO)
G=-10. DO**((-19. 28DO)*10. DO**((E-0. 1531DO)/0. 0591DO)*1. DO+ *10. DO**(1. 52DO-PH))*S-2. DO*223. 87DO*10. DO**((-38. 56DO)*10. DO**((E- *0. 08495DO)/0. 02956DO)*10. DO**((E-0. 1531DO)/0. 02956DO)
GO TO 20
A=0.DO
B=2.DO*1.9953D-11/AH(K)**2.DO*S
C=T**S
D=-(XM-XINIT)**S
G=-10.DO***(-19.28.DO)*10.DO**((E-0.1531.DO)/0.0591.D0)*(1.DO+10.DO***(1.52.DO-PH))**S
H=-2.DO*10.DO**((E-0.08495.DO)/0.02956.DO)*10.DO***(-38.56.DO)*10.DO***(E-0.1531.DO)/0.02956.DO)*S
R=0.DO
CALL SOLVE(X2,A,B,C,D,G,H,R,XN,K,XINIT,LL)

DCU2(K)=DLOG10(DCU1(K))
DCU1(K)=DCU2(K)+E/0.0591.DO+2.5890.DO
DX(K)=-19.28.DO*DCU1(K)
RETURN
END

Subroutine CUXAN2 sets up and solves the mass balance equation
for the case when CuX2 is stable by using SOLVE.

SUBROUTINE CUXAN2(X2,AH,E,K,XM,XINIT,LL,DCU2,DCU1,DX,PH,POW)
IMPLICIT REAL*8(A-H,O-Z)
DIMENSION AH(1500),DCU2(1500),DCU1(1500),DX(1500)
T=CTOTAL(AH,E,K)
S=STOTAL(AH,E,K)
IF(POW.LT.-35.DO) GO TO 70
IF(POW.GT.35.DO) GO TO 10
DA=-7.74794.DO-2.D0*DLOG10(AH(K))+POW
IF(DA.LT.-74.DO) GO TO 30
A=10.DO**DA
GO TO 40
A=0.DO
DB1=2.65102.DO+POW+DLOG10(T)
IF(DB1.LT.-74.DO) GO TO 50
B1=10.DO**DB1
GO TO 60
B1=0.DO
B2=6.DO*1.9953D-11/AH(K)**2.DO*S
B=B1+B2
C=223.87.DO*10.DO**POW*(XINIT-XM)+2.DO*T**S
D1=-10.DO***(E-12.DO)*223.87.DO*10.DO**POW*(1.DO+10.DO***(1.52.DO-PH))
D2=-2.DO*10.DO**((E-0.08495.DO)/0.02956.DO)*10.DO**(-24.2.DO)**S
*223.87.DO*10.DO**POW+2.DO*XM-XINIT)**S
D=D1+D2
GO TO 20
A=4.DO*1.9953D-11/AH(K)**2.DO*223.87.DO
B=2.DO*223.87.DO*T**4.DO*1.9953D-11/AH(K)**2.DO*S
C=2.DO*T**S+223.87.DO*(XINIT-XM)
D1=-10.DO**(E-12.DO)*223.87.DO*(1.DO+10.DO***(1.52.DO-PH))
D2=-(2.DO*XM-XINIT)**S+2.DO*10.DO**((E-0.08495.DO)/0.02956.DO)**S
**10.DO**(-24.2.DO)*223.87.DO
D=D1+D2
GO TO 20
A=0.DO
B=4.DO*1.9953D-11/AH(K)**2.DO*S
C=2.DO*T**S
D=-(2.DO*XM-XINIT)**S
G=-10.DO**(-12.DO)*(1.DO+10.DO***(1.52.DO-PH))**S
H=-2.0D0*10.0D0**(-24.2D0)*10.0D0**((E-0.08495D0)/0.02956D0)*S
R=0.0D0
CALL SOLVE(X2,A,B,C,D,G,H,R,XN,K,XINIT,LL)
DCU2(K)=DLOG10(XN)
DCU1(K)=DCU2(K)-E/0.0591D0+2.5890D0
DX(K)=-12.10D0-0.5D0*DCU2(K)
RETURN
END

XTOTAL is a function subprogram that calculates the total dissolved xanthate bearing species concentration.

FUNCTION XTOTAL(AH,E,K,DX,PH)
IMPLICIT REAL*8(A-H,0-Z)
DIMENSION AH(1500),DX(1500)
A=(1.0D0+10.0D0**(1.52D0-PH))*10.0D0**DX(K)+2.0D0*10.0D0**
*(E-0.08495D0)/(0.02956D0)*10.0D0**((E-0.08495D0)/0.02956D0)*10.0D0**((E-0.08495D0)/0.02956D0)
XTOTAL=DLOG10(A)
RETURN
END

Subroutine CUXCS sets up and solves the mass balance equation for the situation when Cu2S and CuX are stable together.

SUBROUTINE CUXCS(X2,AH,E,K,XINIT,LL,DCU2,DCU1,DX,PH,POW,L)
IMPLICIT REAL*8(A-H,0-Z)
DIMENSION AH(1500),DCU2(1500),DCU1(1500),DX(1500)
T=XTOTAL(AH,E,K)
S=STOTAL(AH,E,K,POW,L)
R=2.0D0*1.9953D-11/AH(K)**2.0D0
A=T
B=XINIT
C1=-10.0D0**((-19.28D0)*10.0D0**((E-0.1531D0)/0.02956D0)**(1.0D0+10.0D0**
*(1.52D0-PH)))*10.0D0**((E-0.1531D0)/0.02956D0)**10.0D0**(-38.56D0)*10.0D0**((-19.28D0)/0.02956D0)
D1=-2.0D0*10.0D0**((-19.28D0)/0.02956D0)*S
D2=-2.0D0*10.0D0**((-19.28D0)/0.02956D0)*S
D=D1+D2
G=0.0D0
H=0.0D0
IF(POW.LT.-35.0D0) GO TO 30
IF(POW.GT.35.0D0) GO TO 10
C2=-223.87D0*2.1368D-49*10.0D0**((-19.28D0)/0.02956D0)**POW
GO TO 20
30  C2=0.0D0
GO TO 20
10  C2=-223.87D0*2.1368D-49*10.0D0**((-19.28D0)/0.02956D0)
20  C=C1+C2
CALL SOLVE(X2,A,B,C,D,G,H,R,XN,K,XINIT,LL)
DCU2(K)=DLOG10(XN)
DCU1(K)=DCU2(K)-E/0.0591D0+2.5890D0
DX(K)=-19.28D0*DCU1(K)
RETURN
END

STOTAL is a function subprogram that calculates a factor used
in solving for the total dissolved sulfur species concentrations.

```fortran
FUNCTION STOTAL(AH,K,POW,L)
IMPLICIT REAL*8(A-H,0-Z)
DIMENSION AH(1500)
IF(POW.GT.35.DO) GO TO 10
L=1
A=1.D0
B=7.8959D+13*AH(K)
C=7.977D+20*AH(K)**2.D0
D=3.2002D+20*AH(K)**2.D0
IF(POW.LT.-35.DO) GO TO 30
F=10.DO**POW
G=98.85D0*AH(K)*F
H=AH(K)**2.D0*F
GO TO 40
30 F=0.DO
G=0.DO
H=0.DO
40 STOTAL=A+B+C+D+F+G+H
GO TO 20
10 L=2
A=1.D0
B=98.85D0*AH(K)
C=AH(K)**2.D0
STOTAL=A+B+C
20 RETURN
END
```

Function SSOL determines the total concentration of soluble sulfur species once the sulfide ion concentration is known.

```fortran
FUNCTION SSOL(K,E,AH,PH,DS,DS04,POW,DCU2)
IMPLICIT REAL*8(A-H,0-Z)
DIMENSION AH(1500),DS(1500),DS04(1500),DCU2(1500)
A=STOTAL(AH,K,POW,L)
CRIT=DS04(K)+DCU2(K)+2.35D0
IF(L.EQ.1.AND.CRIT.LT.-74.DO) B=10.DO**DS(K)*A
IF(L.EQ.1.AND.CRIT.LT.-74.DO) GO TO 10
IF(L.EQ.1) B=10.DO**DS(K)*A+223.87D0*10.DO**DS04(K)*10.DO**DCU2(K)
IF(L.EQ.2) B=10.DO**DS04(K)*A+223.87D0*10.DO**DS04(K)*10.DO**DCU2(K)
10 SSOL=DLOG10(B)
RETURN
END
```

Subroutine CCHECK determines whether the calculated total amount of copper exceeds the given amount.

```fortran
SUBROUTINE CCHECK(K,AH,E,DCU2,DCUT,DS04)
IMPLICIT REAL*8(A-H,0-Z)
DIMENSION AH(1500),DCU2(1500),DCUT(1500),DS04(1500)
T=STOTAL(AH,E,K)
IF(DS04(K).LT.-74.DO) GO TO 50
O=223.87D0*10.DO**DS04(K)
GO TO 60
50 O=0.DO
```
Function CTOTAL calculates the total concentration of soluble copper species.

Function CTOTAL calculates the total concentration of soluble copper species.

**FUNCTION CTOTAL(AH,E,K)**

**IMPLICIT REAL*8(A-H,O-Z)**

**DIMENSION AH(1500)**

A=1. DO
R=1. D=0/8/AH(K)
B=1.5136D-15/AH(K)**2.D0
C=1.5849D-27/AH(K)**3.D0
F=1.2589D-40/AH(K)**4.D0
H=10. D=**(-E-.1531D0)/.059135928D0
CTOTAL=A+B+C+F+H+R
RETURN
END

**SUBROUTINE CUBAL(AH,E,K,XM,DCU1,DCU2,DS04,DCUT)**

**IMPLICIT REAL*8(A-H,O-Z)**

**DIMENSION AH(1500),DCU1(1500),DCU2(1500),DS04(1500),**
*DCUT(1500)**

T=CTOTAL(AH,E,K)
IF(DS04(K).LT.-74.DO) B=T
IF(DS04(K).LT.-74.DO) GO TO 23
B=T+223.87DO+10.DO**DS04(K)
A=2. DO**1.9953D-11/AH(K)**2.D0
C=-XM
DNUM=DSQRT(B**2.D0-4.DO*A*C)
Y=(-B-DNUM)/B
IF(DABS(Y).LT.1.D-08) GO TO 10
DCU2(K)=DLOG10(DCU2)
DCU1(K)=DCU2(K)-E/.059135928D0+2.588950663D0
GO TO 20
CU2=XM/B
DCU2(K)=DLOG10(CU2)
DCU1(K)=DCU2(K)-E/.059135928D0+2.588950663D0
GO TO 20
CALL CCHECK(K,AH,E,DCU2,DS04)
RETURN
END

**SUBROUTINE CUSBAL(AH,E,K,XM,DS,DS04,DCU1,DCU2,DCUT,POW,X2,XS,LL)**

**IMPLICIT REAL*8(A-H,O-Z)**

**DIMENSION AH(1500),DS(1500),DS04(1500),DCU1(1500)**
*DCU2(K),DCUT(1500)**

T=CTOTAL(AH,E,K)
S=STOTAL(AH,K,POW,L)
G=0.DO

TOT=T+O
IF(DCU2(K).GT.36.DO) GO TO 10
IF(DCU2(K).LT.-30.DO) GO TO 30
CUT=10.DO**DCU2(K)*TOT+2.DO*1.9953D-11/AH(K)**2.DO*10.DO**2.DO*DCU2(K)
GO TO 40
CUT=10.DO**DCU2(K)*TOT
GO TO 20
DCUT(K)=DLOG10(CUT)
GO TO 20
RETURN
END
H=0.DO
IF(POW.LT.-35.DO) GO TO 70
IF(POW.GT.35.DO) GO TO 10
DA=-8.04903D0-2.DO*DLOG10(AH(K))+POW
IF(DA.LT.-74.DO) GO TO 30
A=10.DO**DA
GO TO 40
A=0.DO
40
DB1=2.35D0+POW+DLOG10(T)
IF(DB1.LT.-74.DO) GO TO 50
B1=10.DO**DB1
GO TO 60
B1=0.DO
50
B2=2.DO*1.9953D-11/AH(K)**2.DO*S
B=B1+B2
C=T**S+223.87D0*10.DO**POW*(XS-XM)
D=XM*S
R=0.DO
GO TO 20
10
A=2.DO**223.87D0**1.9953D-11/AH(K)**2.DO*S
B=223.87D0*T+2.DO*1.9953D-11/AH(K)**2.DO*S
C=T**S+223.87D0*(XS-XM)
D=XM*S
R=0.DO
GO TO 20
20
CALL SOLVE(X2,A,B,C,D,G,H,R,XN,K,XINIT,LL)
CU=XN
GO TO 80
70
CU=XM/T
80
DCU2(K)=DLOG10(CU)
DCU1(K)=DCU2(K)-E/0.059135928D0+2.588950663D0
CALL SULF(AH,E,K,XS,DS,DSO4,DCU2,POW)
CALL CCHECK(K,AH,E,DCU2,DCU2,DSO4)
RETURN
END

C Subroutine SOLVE is the subprogram used to find the solution of the polynomial mass balance equation by applying the secant method.
C
SUBROUTINE SOLVE(X2,A,B,C,D,G,H,R,XN,K,XINIT,LL)
IMPLICIT REAL*8(A-H,O-Z)
X1=0.80D0*X2
F1=CUCAL(X1,A,B,C,D,G,H,R,LL)
F2=CUCAL(X2,A,B,C,D,G,H,R,LL)
2
XN=(X1*F2-X2*F1)/(F2-F1)
FN=CUCAL(XN,A,B,C,D,G,H,R,LL)
PERDIF=(XN-X2)/X2
IF(DABS(PERDIF).LT.1.D-05) GO TO 1
X1=X2
X2=XN
F1=F2
F2=FN
GO TO 2
1
RETURN
END
C Function CUCAL is called by the subroutine SOLVE to calculate
the polynomials of the function being solved.

```fortran
FUNCTION CUCAL(X,A,B,C,D,G,H,R,LL)
IMPLICIT REAL*8(A-H,O-Z)
GO TO (30,40,50),LL
30 IF(X.LT.1.D-13) GO TO 10
   CUCAL=A*X**2. D0*X**2. D0*X**2. D0+C*X*X*X+D*X*X+G*X+H
   GO TO 20
40 IF(X.LT.1.D-18) GO TO 11
   CUCAL=A*X**2. D0*X**2. D0+B*X*X*X+C*X*X+D*X+G*DSQRT(X)+H
   GO TO 20
50 IF(X.LT.1.D-18) GO TO 12
   CUCAL=R*X**2. D0*X**2. D0+A*X**3. D0+B*X**2. D0+C*X+D
   GO TO 20
10 CUCAL=B*X**2. D0*X**2. D0+C*X*X*X+D*X*G*X+H
   GO TO 20
11 CUCAL=B*X*X*X+G*X*X+D*X*G*DSQRT(X)+H
   GO TO 20
12 CUCAL=A*X**3. D0+B*X**2. D0+C*X+D
   RETURN
END
```

Function CGUESS approximates the solution of a polynomial equation, which is to be used as an initial guess in the secant method.

```fortran
FUNCTION CGUESS(AH,E,K,POW,XM,XS)
IMPLICIT REAL*B(A-11,u-l.)
DIMENSION AH(lSOO) T=CTOTAL(AH,E,K) S=STOTAL(AH,K,POW,L)
IF(POW.GT.35.DO) GO TO 10
   A=223.87DO*10.DO**Pow,T+2.DO**POW*(XS-XM)
   C=-XM*S
   DNUM=DSQRT(B**4.DO*A*C)
   IF(DNUM.EQ.B) GO TO 40
   CGUESS=(-B+DNUM)/2.DO/A
   GO TO 30
20 CGUESS=XM/T
   GO TO 30
10 A=223.87DO*T+2.DO*1.9953D-11/AH(K)**2.DO*S
   B=T**S+223.87DO*(XS-XM)
   C=-XM*S
   DNUM=DSQRT(B**4.DO*A*C)
   IF(DNUM.EQ.B) GO TO 40
   CGUESS=(-B+DNUM)/2.DO/A
   GO TO 30
40 CGUESS=XM/T
   GO TO 30
50 CGUESS=XM/T
30 RETURN
END
```

Subroutine CuS04 sets up the mass balance equation for the case when CuS04 is stable and then finds its solution.
SUBROUTINE CUS04(AH,E,K,DS,DS04,DCU1,DCU2,DCUT,POW,X2,XS)
IMPLICIT REAL*8(A-H,0-Z)
DIMENSION AH(1500),DS(1500),DS04(1500),DCU1(1500),
*DCU2(1500),DCUT(1500)
B=CTOTAL(AH,E,K)
S=STOTAL(AH,K,POW,L)
IF(L.EQ.1) GO TO 10
GO TO 20
10 A=2.D0*1.9953D-11/AH(K)**2.DO
C=-XS
D=-1287.73D0*10.DO**(-POW)*S
R=0.DO
GO TO 30
20 A=2.D0*1.9953D-11/AH(K)**2.DO
C=-XS
D=-1287.73D0*S
R=0.DO
G=0.DO
H=0.DO
30 CALL SOLVE(X2,A,B,C,D,G,H,R,XN,K,XINIT)
CU=XN
DCU2[K]=DLOG10(CU)
DCU1[K]=DCU2(K)-E/.059135928DO+2.588950663DO
DS04[K]=3.109800-bCUZ(K)
DS(K)=S04(K)-POW
CALL CCHECK(K,AH,E,DCU2,DCUT,DS04)
RETURN
END

FUNCTION C1GUES(AH,E,K,POW,XS)
IMPLICIT REAL*8(A-H,0-Z)
DIMENSION AH(1500)
A=CTOTAL(AH,E,K)
B=-XS
IF(L.EQ.1) C=-1287.73D0*10.DO**(-POW)*B
IF(L.NE.1) C=-1287.73D0*B
C1GUES=(-B+DSQRT(B*B-4.DO*A*C))/2.DO/A
RETURN
END

SUBROUTINE CU2SUL(AH,E,K,DS,DS04,DCU1,DCU2,DCUT,POW,X2,LL)
IMPLICIT REAL*8(A-H,0-Z)
DIMENSION AH(1500),DS(1500),DS04(1500),DCU1(1500),
*DCU2(1500),DCUT(1500)
R=2.DO*1.9953D-11/AH(K)**2.DO
X=TOTAL(AH,E,K)
A=10.DO**(E/.059135928DO+2.588950663DO)*X
B=0.DO
C=-223.87D0*3.2441D-02*10.DO**(E/.029567964DO-5.17790133DO)
Y=STOTAL(AH,K,POW,L)
IF(L.EQ.1) GO TO 10
GO TO 20
D=-2.D0*3.2441D-02*10.DO**(-POW)*Y
10 D=-2.D0*3.2441D-02*10.DO**(-POW)*Y
20 GO TO 30
30 D=-2.D0*3.2441D-02*Y
D=-2.D0*3.2441D-02*Y
10 GO TO 30
30 G=O.DO
H=O.DO
CALL SOLVE(X2,A,B,C,D,G,H,R,XN,K,XINIT,LL)
10 CU=XN
20 DCU2~Ki=DLOG10(CU)
30 DCU1(K)=DCU2(K)-E/.059135928D0+2.588950663D0
30 DS04(K)=1.4929D0-2.DO**DCU1(K)
30 DS(K)=DS04(K)-POW
30 CALL CCHECK(K,AH,E,DCU2,DCUT,DS04)
RETURN
END

FUNCTION C2GUES(AH,E,K,POW,XS)
IMPLICIT REAL*8(A-H,0-Z)
DIMENSION AH(1500)
A=CTOTAL(AH,E,K)
B=-XS
D=STOTAL(AH,K,POW,L)
IF(L.EQ.1) C=-9.9784D-36*D
IF(L.NE.1) C=-9.9784D-36*10.DO**POW*D
C2GUES=(-B+DSQRT(B**2-4.DO*A*C))/2.DO/A
RETURN
END

SUBROUTINE CUS(AH,E,K,DS,DS04,DCU1,DCU2,DCUT,POW,X2,XS,LL)
IMPLICIT REAL*8(A-H,0-Z)
DIMENSION AH(1500),DS04(1500),DCU1(1500),DCU2(1500),DCUT(1500)
R=O.DO
G=O.DO
H=O.DO
A=2.DO*1.9953D-11/AH(K)**2.DO
B=CTOTAL(AH,E,K)
C=-XS
S=STOTAL(AH,K,POW,L)
IF(L.EQ.1) GO TO 10
GO TO 20
10 D=-9.9784D-36*S
10 GO TO 30
20 D=-9.9784D-36*10.DO**POW*S
20 GO TO 30
30 CALL SOLVE(X2,A,B,C,D,G,H,R,XN,K,XINIT,LL)
30 CU=XN
30 DCU2(K)=DLOG10(CU)
30 DCU1(K)=DCU2(K)-E/.059135928D0+2.588950663D0
30 DS04(K)=35.000900-DCU2(K)
30 DS(K)=DS04(K)-POW
30 CALL CCHECK(K,AH,E,DCU2,DCUT,DS04)
RETURN
Subroutine CU2S sets up and solves the mass balance equation for the case when Cu2S is stable.

```fortran
SUBROUTINE CU2S(AH, E, K, DS, DS04, DCU1, DCU2, DCUT, POW, LL)
IMPLICIT REAL*8(A-H, O-Z)
DIMENSION AH(1500), DS(1500), DS04(1500), DCU1(1500),
* DCU2(1500), DCUT(1500)
A=CTOTAL(AH, E, K)
B=0.0D0
DC=-46.3202D0+POW/E.029567964D0-5.177901326D0
IF(DC.LT.-74.D0) GO TO 400
C=-10.D0**DC
GO TO 500
400 C=0.0D0
500 ST=STOTAL(AH, E, POW, L)
IF(L.EQ.1) GO TO 100
GO TO 200
100 D=-48.3692D0+E/.029567964D0-5.177901326D0+DLOG10(ST)
IF(DD.LT.-74.D0) GO TO 350
D=-10.D0**DD
GO TO 300
*6D0)*ST
300 A1=B/A
DA3=DLOG10(-D)-DLOG10(A)
IF(DA3.LT.-8.0D0) GO TO 31
A2=C/A
A3=D/A
P=-A1**2.D0/3.D0+A2
IF(P.LT.0.D0) R=-DABS(P/3.D0)**3.D0+(DABS(Q/2.D0))**2.D0
IF(P.GT.0.D0) R=(P/3.D0)**3.D0+(DABS(Q/2.D0))**2.D0
IF(R.LT.0.D0) GO TO 10
SS=-Q/2.D0+DSQRT(R)
IF(SS.LT.0.D0) S=-DABS(SS)**(1.D0/3.D0)
IF(SS.GT.0.D0) S=SS**(1.D0/3.D0)
TT=-Q/2.D0-DSQRT(R)
IF(TT.LT.0.D0) T=-DABS(TT)**(1.D0/3.D0)
IF(TT.GT.0.D0) T=TT**(1.D0/3.D0)
CU=S+T-A1/3.D0
IF(CU.LT.0.D0) GO TO 30
GO TO 20
10 THEDA=DARCOS(-Q/2.D0/DSQRT((-P/3.D0)**3.D0))
CU=2.D0*DSQRT(-P/3.D0)**DCOS(THEDA/3.D0)-A1/3.D0
IF(CU.LT.0.D0) GO TO 30
GO TO 20
30 CU=(-D/A)**(1.D0/3.D0)
GO TO 20
31 DCU2(K)=(1.D0/3.D0)*DA3
GO TO 21
350 DCU2(K)=(DD-DLOG10(A))/3.D0
GO TO 21
20 DCU2(K)=DLOG10(CU)
21 DCU1(K)=DCU2(K)-E/.059135928D0+2.588950663D0
DS(K)=-48.6702D0-2.D0*DCU1(K)
DS04(K)=DS(K)+POW
```

CALL CCHECK(K,AH,E,DCU2,DCUT,DS04)
RETURN
END

C This terminates the program and what follows is an example
C of the input data required to run the program.

C INPUT DATA E=-0.24V AW=63.54 WM=2.0 RHO=3.0 WTSOL=30.0 XINIT=1.D-05
  -0.01D0  -0.24D0  63.54D0  2.0D0  3.00D0  30.0D0  1.0D-05
C
C
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