

C O P P E R (I) I N S O L U T I O N

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A thesis submitted for

the degree of

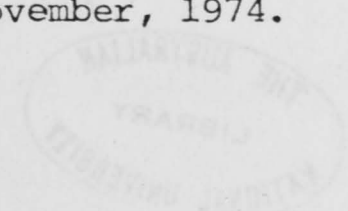
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The work described in this thesis is my own, except where otherwise stated, and has not been submitted in support of an application for any other degree. It was carried out in The Research School of Chemistry, The Australian National University (1971-1974) during the tenure of an Australian National University Postgraduate Scholarship.

J. Tilley

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UNITS AND ABBREVIATIONS

SI units have been used in this thesis. The symbol M has been used to represent mol dm^{-3} and square brackets to represent concentration. The term "ion" is not intended to mean the free ion (only found in the gaseous state). In this thesis, "ion" is to be taken as the solvated or complexed species of the free ion in solution. Unless otherwise stated, all solubility and equilibrium constants are based on the molar concentration scale.

The following abbreviations appear in this thesis:

AN	acetonitrile
tu	thiourea
SDMF	dimethylthioformamide
PY	pyridine
AA	allyl alcohol
SCE	saturated calomel electrode
DMF	dimethylformamide
DMSO	dimethylsulphoxide
TATB	tetraphenylarsonium-tetraphenylboride
E_{LJ}	liquid junction potential
KSO	solubility product

SUMMARY

This thesis has been divided into four chapters. The first deals with the chemistry of Cu(I) species in solution. The stabilisation of Cu^+ in water by a variety of ligands has been examined in detail. Changes in the free energy of Cu^+ on transfer from water to aqueous solutions of the ligands have been determined potentiometrically. Some free energy changes of Cu(II) species have been likewise determined. Stability constants of some Cu(I) complexes have been measured and three complexes synthesised. The effect of pH on the stability of Cu(I) complexes in solution has also been studied.

The second chapter deals with the solubilities of Cu(I) salts, and with equilibria involving Cu(I) species, in non-aqueous solvents and in mixtures of acetonitrile and water in particular. Solvent transfer activity coefficients have been evaluated and used to predict solubilities, and equilibrium constants, in the solvents mentioned above. The predicted values have been compared with those determined experimentally and good agreement has been found.

Chapter 3 discusses practical applications of some of the work described in the preceding two chapters. Particular attention has been paid to the use of hydrometallurgical techniques for the recovery and processing of copper. The relevance of some of the work in the thesis to copper-catalysed organic chemical reactions, and to biological chemistry, is also briefly mentioned.

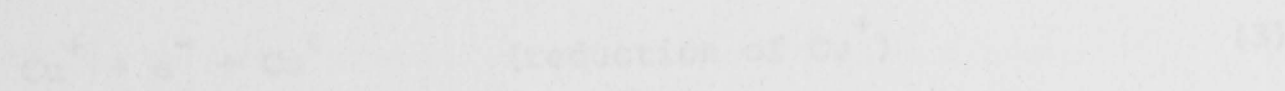
Chapter 4 describes the reagents and techniques used in chapters 1 to 3. An Appendix which gives stability constants of Cu(I) and Cu(II) complexes has been included.

The reaction is not a simple one as it involves the following
intermediate reaction:



The equilibrium constant for reaction 1 is $10^6 \text{ mol}^{-1} \text{ dm}^3$.

Reaction 1 can be represented as an oxidation and a reduction as follows:



When these electrode reactions are prevented or completely
inhibited aqueous solutions of Cu^+ are obtained. This has been achieved by

CHAPTER 1

STABILISATION OF Cu(I) IN SOLUTION

It is well known that Cu^+ is not stable in aqueous solution and
readily undergoes disproportionation to Cu^{2+} and Cu^0 .

Largely as a result of the facility of the disproportionation reaction,
 $Cu(I)$ complexes are not as stable as those of $Cu(II)$. However,
stability constants for a number of $Cu(I)$ complexes have been tabulated by
Bjerrum and Nielsen (1957) and are given in a review by Bjerrum
(1961). The stability constants of $Cu(I)$ complexes found in the literature are
summarised in the Appendix.

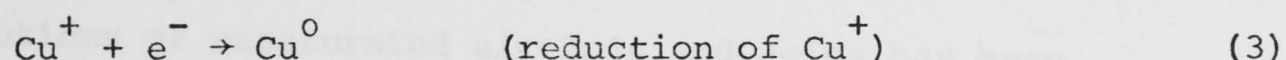
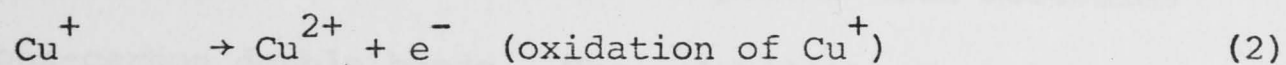
One of the reasons why $Cu(I)$ complexes are not as stable as those of
 $Cu(II)$ is that the d_{10} configuration of $Cu(I)$ is not as stable as the
 d_9 configuration of $Cu(II)$. The d_{10} configuration is more stable than
the d_9 configuration because of the larger crystal field stabilization energy
of the d_{10} configuration. The d_{10} configuration is more stable than
the d_9 configuration because of the larger crystal field stabilization energy
of the d_{10} configuration. The d_{10} configuration is more stable than
the d_9 configuration because of the larger crystal field stabilization energy
of the d_{10} configuration.

1.1. Introduction

The Cu(I) ion is not a stable species in water, the following disproportionation reaction occurring:



The equilibrium constant for reaction 1 is $10^6 \text{ mol}^{-1} \text{ dm}^3 \text{ l}^{-1}$. The reaction can be represented by an oxidation and a reduction step as follows:



When these electron transfer reactions are prevented or considerably inhibited, aqueous solutions of Cu^+ are obtained. This has been achieved by Altermatt and Manahan² who were able to keep solutions of Cu(I) perchlorate in aqueous perchloric acid (0.1M) at 0° for 10 hours before disproportionation was detected. This entailed the use of scrupulously clean glassware and the exclusion of oxygen and metal surfaces. The extreme instability of these solutions makes their use impractical for studying Cu(I) species in solution. However, as will be shown later, stable Cu(I) salt solutions are easily obtainable in aqueous media by complexing the ion with ligands which stabilise the Cu(I) state.

Largely as a result of the facility of the disproportionation reaction (1), the chemistry of Cu(I) is not as extensive as that of Cu(II). However, stability constants for a variety of Cu(I) complexes have been tabulated by Sillén¹, and olefinic Cu(I) complexes are discussed in a review by Hartley³. Stability constants of Cu(I) complexes found in the literature are tabulated in the Appendix.

One of the earliest reported studies on nitrile complexes of Cu(I) is that of Morgan⁴, who in 1923 described the preparation and some properties of $\text{Cu}(\text{AN})_4\text{NO}_3$, $\text{Cu}(\text{NCCH}_2\text{CH}_2\text{CN})_2\text{NO}_3$, $\text{Cu}.\text{AN}.\text{Cl}$, and $\text{Cu}.\text{AN}.\text{Br}$ (AN = acetonitrile). Further work involving nitriles as Cu(I) ligands has been reported by Hathaway and co-workers⁵, Hemmerich and Sigwart⁶, Farha and Iwamoto⁷, Manahan and Iwamoto⁸, Kubota and Johnston⁹, and Günter and Zuberbühler¹⁰.

Studies concerned with the redox potentials of copper complexes have been carried out by a number of workers. James and Williams¹¹ studied copper complexes of 1,10-phenanthrolines, bipyridyls and other nitrogenous bases; Hawkins and Perrin¹² used pyridine, 4-methylpyridine, imidazole, benzimidazole, and 2-methylthioethylamine as ligands while Vallon and Badinand¹³ studied copper complexes of penicillamine and N-acetylpenicillamine.

A number of papers have described Cu(I) complexes with molecules containing carbon-carbon double bonds. The solubility of Cu(I) chloride in aqueous solutions of unsaturated alcohols and acids has been determined^{14,15} and studies involving allyl alcohol^{16,17}, propene and 2-methylpropene¹⁸, and cycloolefins^{19,20,21} have also been made.

Other ligands studied include diphenylphosphinobenzene-m-sulphonate²², ammonia²³, benzene^{21,24}, dipyridyl, orthophenanthroline and thiourea²⁵, triphenylphosphine, triphenylarsine, and triphenylstibine²⁶, the chloride ion^{10,27}, cysteine²⁸, the cyanide ion²⁹, and amines³⁰. This list is not exhaustive but indicates the wide variety of ligands able to stabilise Cu(I).

Recent work by Parker and his group³¹ has demonstrated the use of aqueous acetonitrile solutions of Cu(I) salts to facilitate the extraction and refining of copper metal. The technique relies on the fact that AN can be added to acidic solutions of Cu²⁺ and Cu⁰ to dissolve copper metal, and subsequently removed from the resultant Cu(I) salt solutions (e.g. by steam distillation) to precipitate pure copper and regenerate Cu²⁺. These reactions will be discussed in greater detail in Chapter 3.

As will be shown in this work, other ligands are amenable to these operations, particularly low-boiling liquids or gases, where addition and removal are facile processes. A variety of ligands which stabilise Cu(I) in aqueous solutions have been examined, i.e. CN⁻, S₂O₃²⁻, SCN⁻, Cl⁻, Br⁻, I⁻, thiourea(tu), dimethylthioformamide (SDMF), pyridine (py), ammonia, allyl alcohol (AA), acetonitrile, ethylene, propylene, and carbon monoxide together with mixtures of ligands (e.g. AN and Cl⁻, AN and CO).

Potentials of the Cu^+/Cu^0 and $\text{Cu}^{2+}/\text{Cu}^+$ couples have been measured over a range of ligand concentrations enabling the free energy of transfer of Cu^+ and Cu^{2+} from water to aqueous solutions of the ligands to be determined. Differences between the standard free energy of an ion (or other chemical species) in water, \bar{G}_i^W , and in aqueous complexing media, \bar{G}_i^S , can be viewed loosely as the free energy required to transfer the ion from water to the given medium. ${}^W\Delta\bar{G}_i^S$ is defined by:

$${}^W\Delta\bar{G}_i^S \equiv \bar{G}_i^W - \bar{G}_i^S = 2.303RT \log \gamma_i^S, \quad (4)$$

where γ_i^S is the transfer activity coefficient. 32

A negative value of ${}^W\Delta\bar{G}_i^S$ indicates that the ion is more stable in medium S than in water. Thus, measurements have been made which have enabled values of ${}^W\Delta\bar{G}_{\text{Cu}^+}^S$ to be determined in a variety of aqueous media. In this way, a measure of the relative stability of the copper (I) species in various media has been obtained.

In Chapter 2 use is made of transfer activity coefficients to calculate solubility and equilibrium constants in new media. The use of γ_i^S values rather than free energies for these calculations was found to be more convenient as much solubility and equilibrium data in the literature are given in terms of solubility products and equilibrium constants rather than free energy changes. However, it should be noted that the two quantities, ΔG and γ , are forms of the same thermodynamic quantity (see equation 4). Further discussion on the use of γ_i^S values follows in Chapter 2.

Potentiometry has been employed to detect the highest Cu(I) complex (i.e. the complex containing the most ligands) formed in solution and to measure its stability constant. The effect of pH on the stability of the Cu(I) complexes in solution has been studied and three solid Cu(I) complexes prepared and, in the case of $\text{Cu}(\text{AN})_4\text{HSO}_4$, characterized.

1.2. Results and Discussion

1.2.1. Potentials of Cu^+/Cu^0 and $\text{Cu}^{2+}/\text{Cu}^+$ Couples

The potentials of the Cu^+/Cu^0 and $\text{Cu}^{2+}/\text{Cu}^+$ couples in water and aqueous solutions of ligands are given in Tables 1.1, 1.2 and 1.3. The free energy of transfer of the Cu(I) ion from water to solutions of the various ligands, ${}^W\Delta G_{\text{Cu}^+}^{\text{S}} \text{ (kJ mol}^{-1}\text{)}$ was calculated as follows:

$${}^W\Delta G_{\text{Cu}^+}^{\text{S}} = (E_{\text{Cu}^+/\text{Cu}^0}^{\text{S}} - E_{\text{Cu}^+/\text{Cu}^0}^{\text{W}}) \cdot 0.096 \quad (5)$$

where $E_{\text{Cu}^+/\text{Cu}^0}^{\text{S}}$ and $E_{\text{Cu}^+/\text{Cu}^0}^{\text{W}}$ are the potentials in mV of the Cu^+/Cu^0 couple in the ligand solutions and in water.

${}^W\Delta G_{\text{Cu}^{2+}}^{\text{S}} \text{ (kJ mol}^{-1}\text{)}$ was calculated as follows:

$${}^W\Delta G_{\text{Cu}^{2+}}^{\text{S}} = (E_{\text{Cu}^{2+}/\text{Cu}^+}^{\text{S}} - E_{\text{Cu}^{2+}/\text{Cu}^+}^{\text{W}}) \cdot 0.096 + {}^W\Delta G_{\text{Cu}^+}^{\text{S}} \quad (6)$$

Values of ${}^W\Delta G_{\text{Cu}^+}^{\text{S}}$ calculated using equation 5 are given in Figures 1.1 and 1.2.

Cu(I) salt solutions used to obtain the potentials given in Table 1.1 were prepared by dissolving $\text{Cu}(\text{AN})_4\text{ClO}_4$ (0.01M) in the presence of each ligand. Thus, each solution contained 0.04 moles per litre of AN. This will have a small effect on the measured potential when ligand concentrations are low (i.e. 0.1M), but at higher concentrations this effect will be minimal. For example, a solution of AN (0.4M) and SDMF (2M) gave a potential reading of 682mV for the Cu^+/Cu^0 couple versus the SCE. Upon increasing the AN content to 1.2M the reading only changed to 678mV. It is therefore expected that AN(0.04M) in solutions containing much greater amounts of a stronger ligand will have a negligible effect on measured Cu^+/Cu^0 potentials.

TABLE 1.1.

Potentials^a of Cu^+/Cu^0 and $\text{Cu}^{2+}/\text{Cu}^+$ Couples at 25° in Aqueous Solutions of Ligands.

Ligand(s)	Potentials (mV) in solutions containing $x \text{ mol dm}^{-3}$ of ligand(s)				
	Cu^+/Cu^0			$\text{Cu}^{2+}/\text{Cu}^+$	
	x=0.1	x=0.5	x = 2	x=0.1	x=0.5
Water ^b	160	160	160	-89	-89
CN^-	-1300(11.2)	-1420(11.5)	-1550(11.8)	c	c
tu	- 500	- 670	d	c	c
$\text{S}_2\text{O}_3^{2-}$	- 470(11.4)	- 630(11.5)	- 750(11.6)	c	c
SDMF ^e	- 360	- 550	- 680	c	c
SCN^-	f	f	- 550(11.0)	c	c
Cl^-	f	- 100	- 200	f	160
Br^-	f	- 170	- 270	f	220
I^-	f	f	- 450	c	c
AA	- 20	- 70	- 90	120	170
AN	20	- 50	- 130	40	120
PY ^g	- 180(6.8)	- 270(7.6)	- 360(7.8)	140(6.8)	100(7.6)
NH_3	h	- 400(12.2)	- 440(12.1)	h	f
AA, Cl^-	- 90	- 190	- 290	-	-
AN, Cl^-	f	- 130	- 230	-	-

Solution pH = 2-3 except where parenthesised values indicate otherwise.

All ionic ligands are potassium salts except $\text{S}_2\text{O}_3^{2-}$ which is the sodium salt.

Abbreviations used are as follows: tu, thiourea; SDMF, dimethylthioformamide; AA, allyl alcohol; AN, acetonitrile; py, pyridine.

a Saturated calomel electrode (SCE) reference, estimated error in potentials ± 10 mV. Cu(I) and Cu(II) concentration 0.01 M.

b Reference 33.

c Cu^{2+} reduced to Cu^+ by the ligand.

d 2M solution precluded by insolubility of tu.

e 0.4M AN present.

f Precipitation occurred.

g 1.9M AN present.

h Stable solution of Cu^+ could not be prepared (see text).

TABLE 1.2.

Potentials^a of Cu^+/Cu^0 and $\text{Cu}^{2+}/\text{Cu}^+$ Couples at 25° in Aqueous Solutions^b of Propylene, Ethylene and Carbon Monoxide.

Ligand	Potentials (mV) in solutions under a ligand pressure of $10^5 x$ pascals			
	Cu^+/Cu^0		$\text{Cu}^{2+}/\text{Cu}^+$	
	$x = 0.95$	$x = 4.75$	$x = 0.95$	$x = 4.75$
Water ^c	160	160	-89	-89
Propylene	10	-30	50	90
Ethylene	-30	-80	110	160
CO	-70	-110	120	160

a SCE reference, estimated error in potentials ± 10 mV. Cu(I) and Cu(II) concentration 0.01M.

b Solution pH 2-3.

c Reference 33.

TABLE 1.3.

Potentials^a of Cu^+/Cu^0 and $\text{Cu}^{2+}/\text{Cu}^+$ Couples at 25° in Aqueous Solutions^b of two Ligands.

Ligands	Potentials (mV) in solutions under a ligand pressure of $10^5 \times \text{Pa}$			
	Cu^+/Cu^0		$\text{Cu}^{2+}/\text{Cu}^+$	
	$x = 0.95$	$x = 4.75$	$x = 0.95$	$x = 4.75$
Water ^c	160	160	-89	-89
Ethylene, 0.1M Cl^-	-70	-100	150	170
Ethylene, 0.1M AN	-40	-90	-	-
Ethylene, 0.5M AN	-80	-110	-	-
Ethylene, 2M AN	-160	-170	-	-
CO, 0.1M Cl^-	-110	-150	170	210
CO, 0.1M Br^-	-120 ^{d,e}	-160	d	210
CO, 0.1M AN	-70	-120	-	-
CO, 0.5M AN	-100	-140	-	-
CO, 2M AN	-160	-190	-	-
CO, 0.1M pyridine ^f	d	-230	d	160

a SCE reference, estimated error ± 10 mV. Cu(I) and Cu(II) concentration 0.01M.

b Solution pH 2-3 unless otherwise stated.

c Reference 33.

d Precipitation occurred.

e Extrapolated value.

f pH = 7.

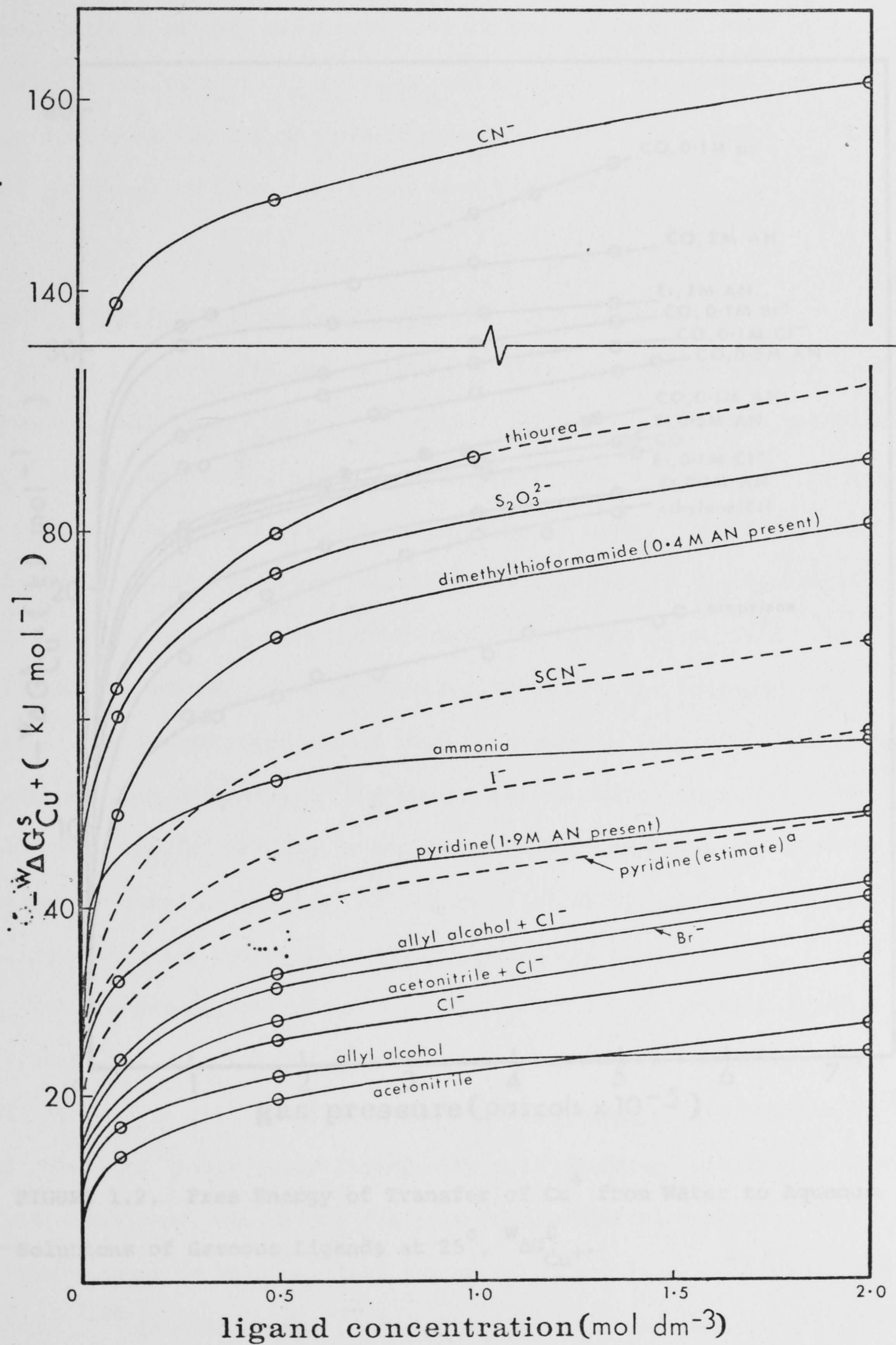


FIGURE 1.1. Free Energy of Transfer of Cu^+ from Water to Aqueous Solutions of Ligands at 25° , ${}^W\Delta G_{\text{Cu}^+}^S$.

a See text.

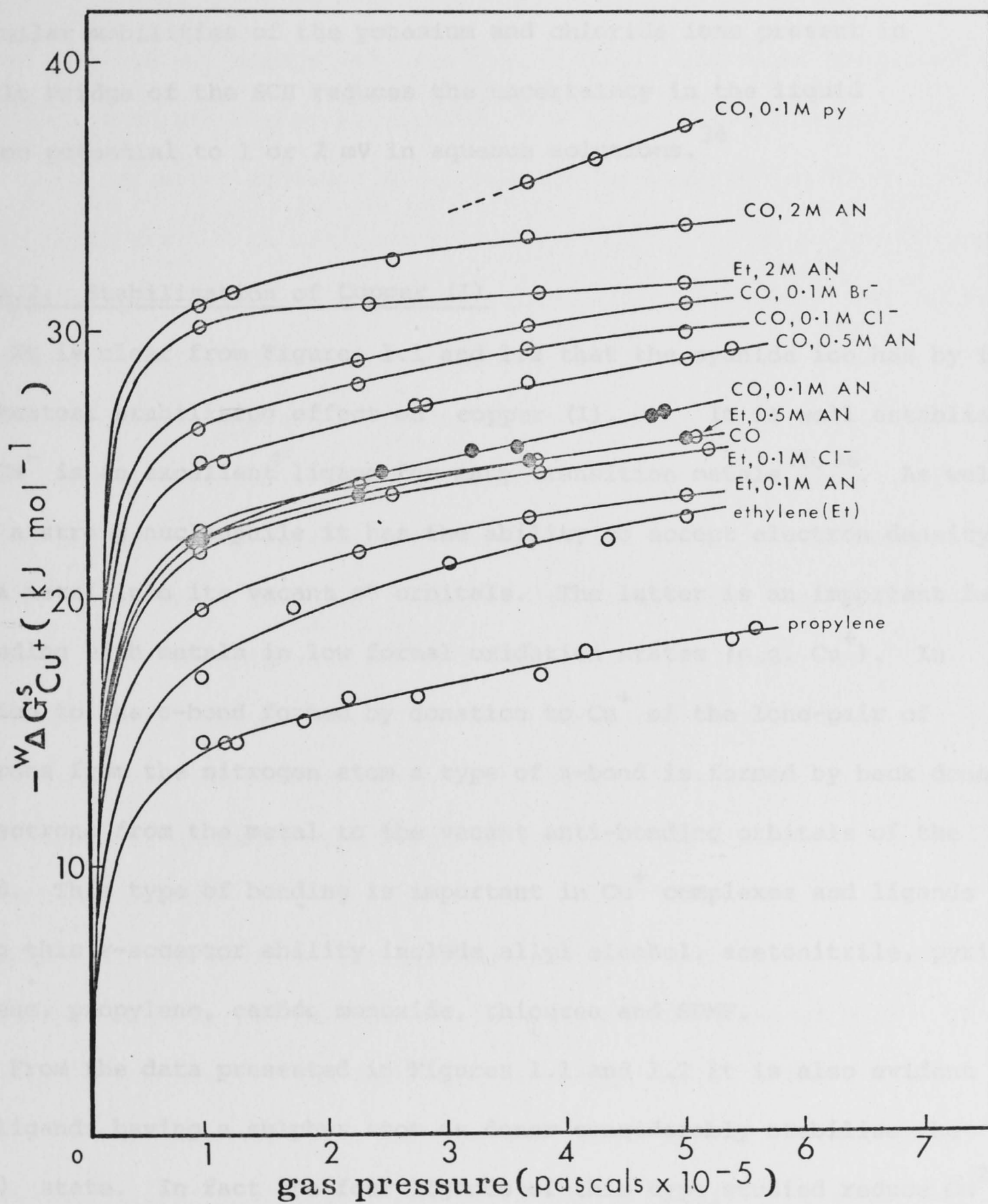


FIGURE 1.2. Free Energy of Transfer of Cu^+ from Water to Aqueous Solutions of Gaseous Ligands at 25° , $W\Delta G^S_{Cu^+}$.

The potentiometric measurements made involved the use of a saturated aqueous calomel electrode in a variety of aqueous solutions. The similar mobilities of the potassium and chloride ions present in the salt bridge of the SCE reduces the uncertainty in the liquid junction potential to 1 or 2 mV in aqueous solutions.³⁴

1.2.2. Stabilisation of Copper (I)

It is clear from Figures 1.1 and 1.2 that the cyanide ion has by far the greatest stabilising effect on copper (I). It is well established that CN^- is an excellent ligand for many transition metals^{35, 36}. As well as being a strong nucleophile it has the ability to accept electron density from a metal into its vacant π^* orbitals. The latter is an important factor in bonding with metals in low formal oxidation states (e.g. Cu^+). In addition to the σ -bond formed by donation to Cu^+ of the lone-pair of electrons from the nitrogen atom a type of π -bond is formed by back donation of electrons from the metal to the vacant anti-bonding orbitals of the ligand. This type of bonding is important in Cu^+ complexes and ligands having this π -acceptor ability include allyl alcohol, acetonitrile, pyridine, ethylene, propylene, carbon monoxide, thiourea and SDMF.

From the data presented in Figures 1.1 and 1.2 it is also evident that ligands having a sulphur atom as donor considerably stabilise the Cu (I) state. In fact the four ligands of this type studied reduce Cu^{2+} to Cu^+ in solution. Again these ligands are able to accept electron density from the metal atom into vacant orbitals forming dative π -bonds.

The concept of hard or class (a) and soft or class (b) ligands and acceptors^{37, 38} is also useful in describing results obtained. Ahrland, Chatt, and Davies³⁸ state that class (b) character appears to depend on the availability of electrons from the lower d-orbitals of the metal for dative π -bonding. Ahrland has described in detail the nature of class (a) and

class (b) acceptors and donors³⁹ and factors contributing to class (b) behaviour in acceptors⁴⁰. The Cu(I) ion is classified as a class (b) or soft cation. Thus, the high stability shown with ligands having a sulphur atom as donor is not unexpected (see Figure 1.1). The outer electrons of the sulphur atom are highly polarizable this being a characteristic property of class (b) donors. Also, the order of stabilities shown by the halides in Figure 1.1 is consistent with the class (a), class (b) concept with iodide being softer than bromide which in turn is softer than chloride.

Figure 1.1 illustrates the difference in curve shapes between allyl alcohol and ammonia and the remainder of the ligands. The stabilisation of Cu^+ by allyl alcohol and ammonia levels off after a ligand concentration of 0.5M has been reached, whereas the stabilisation due to AN, Cl^- and Br^- , for example, continues to increase. This is due to the fact that allyl alcohol only forms a 1:1 complex with Cu^+ and ammonia a 2:1 complex; the other ligands may form complexes with ligand to metal ratios of 3:1 and 4:1, as will be discussed later in this chapter. The broken lines shown in Figure 1.1 were obtained by assuming similar curve forms to those exhibited by neighbouring ligands.

The full curves drawn for pyridine and SDMF were obtained from measurements made in the presence of 1.9M and 0.4M AN respectively. The AN was necessary to prevent the formation of precipitates in the solutions under study. For SDMF a small error is expected due to the AN present; however, for pyridine significant errors due to the added AN are expected. The broken line in Figure 1.1 will give a more accurate representation of the stabilisation of Cu^+ due to pyridine. The precipitate formed when no AN was added was the tetrakis(pyridine)copper(I) complex and further details will be given later. The insolubility of this complex in aqueous solutions explained the observed fact that Cu(I) salt solutions could not be formed in the presence of pyridine by the reaction of Cu^{2+} and Cu^0 in water.

In Figure 1.2 similar curves to that exhibited by allyl alcohol are found for propylene, ethylene, and carbon monoxide. These gaseous ligands in order of decreasing Cu^+ stabilisation are $\text{CO} > \text{ethylene} > \text{propylene}$. The reason for this order is thought to be a steric one as indicated by Hartley in his review of olefin and acetylene complexes of transition metals³. The optimum approach of the metal to the olefin may be hindered by groups attached to the α and β carbon atoms. CO has no attached groups, ethylene has four hydrogen atoms, and propylene has three hydrogen atoms and a methyl group attached to the doubly-bonded carbon atoms.

Figures 1.1 and 1.2 show the stabilisation of Cu^+ by various combinations of ligands. In all cases the degree of stabilisation afforded Cu^+ by the mixtures of ligands is equal to or greater than that afforded by each individual ligand. The results are consistent with the following orders of Cu^+ stabilisation strengths, i.e. $\text{CO} > \text{ethylene}$, $\text{Br}^- > \text{Cl}^- > \text{AN}$, and with competition between ligands for sites around copper (I). For example, the results in Figure 1.2 for mixtures of ethylene and AN, and CO and AN show that, at low concentrations of AN, the value of the free energy of transfer (ΔG_{tr}) from water to the mixture is approximately the same as ΔG_{tr} from water to the solution containing the gas alone. However, as the concentration of AN increases, ΔG_{tr} from water to the mixture approaches ΔG_{tr} from water to a solution of AN alone. That is, at low concentrations of AN the gaseous ligand is the stronger competitor for the ligand sites around Cu^+ , whereas at higher concentrations of AN the latter competes more effectively.

Mixtures of allyl alcohol and chloride ion, and AN and Cl^- were studied as mixed complexes of each pair of ligands with Cu^+ are known^{4,14}. The results found are given in Figure 1.1 and show an interesting difference between the two combinations. The AN, Cl^- results show that the stabilisation of Cu^+ obtained with these ligands is only slightly greater than that found for Cl^- alone. In contrast the AA, Cl^- mixtures markedly

increase the stabilisation over that found for Cl^- . The increased stabilisation provided by the combination of allyl alcohol and the chloride ion suggests that a synergistic effect may be operating.

1.2.3. Stabilisation of Cu(I) and Cu(II)

The only two ligands which appreciably stabilise Cu^{2+} as well as Cu^+ are ammonia and pyridine. Free energies of transfer of Cu^{2+} from water to aqueous solutions of NH_3 and pyridine have been calculated from the potentials given in Table 1.1 and are given in Table 1.4. Cu(I) salt solutions could not be prepared in 0.1M solutions of ammonia for the following reasons. At a pH of 5 Cu_2O precipitated, and at pH 4.8 disproportionation of Cu^+ occurred. The difficulty experienced highlights the competition for ammonia by the proton, Cu^+ , and Cu^{2+} which will be discussed further in a following section.

TABLE 1.4.

Free Energy of Transfer of Cu^{2+} from Water to Aqueous Solutions of Ammonia and Pyridine at 25° , ${}^W\Delta G_{\text{Cu}^{2+}}^S$.

Ligand	${}^W\Delta G_{\text{Cu}^{2+}}^S$ at ligand concentrations of $x \text{ mol dm}^{-3}$ (kJ mol^{-1})			
	$x = 0.1$	$x = 0.5$	$x = 1$	$x = 2$
Ammonia	a	b	-79.9	-80.7
Pyridine	-5.9	-21.3	-	-

a Cu^+/Cu^0 couple could not be measured at this concentration of NH_3 (see text).

b Cu(OH)_2 precipitated.

The ability of NH_3 and pyridine to stabilise Cu^+ and Cu^{2+} has important implications when equilibria such as $\text{Cu}^{2+} + \text{Cu}^0 \rightleftharpoons 2\text{Cu}^+$ are considered. Ligands which stabilise Cu^+ only may shift the reaction to the right while those which stabilise Cu^+ and Cu^{2+} may or may not shift the equilibrium depending on the relative degrees of stabilisation. It should be noted that stabilisation of Cu^{2+} would need to be twice that of Cu^+ to prevent any shift of the equilibrium to the right.

1.2.4. Effect of pH on the Stability of Copper (I)

It can be seen from Tables 1.1, 1.2, and 1.3 that potential measurements have been made at various pH values. This was necessary because the ability of each ligand to stabilise Cu^+ was affected by pH. Figure 1.3 shows the effect of pH on the potential of the Cu^+/Cu^0 couple in the presence of various ligands. It is evident that within a pH range of 2 to 6 the ability of acetonitrile, allyl alcohol, Cl^- , SCN^- , SDMF and thiourea to stabilise Cu^+ is little affected. Thus, potential measurements involving these ligands were made at pH values between 2 and 3. However, CN^- , $\text{S}_2\text{O}_3^{2-}$, pyridine and ammonia show marked effects over this pH range. Potential measurements in solutions containing the first three ligands were made at the pH which resulted from their dissolution in water. These pH values are contained in parentheses after the potentials given in Table 1.1. Sodium hydroxide was added to ammoniacal solutions to give the pH indicated in Table 1.1.

A number of factors need to be considered to explain the data presented in Figure 1.3. Firstly, at low pH values the proton will compete with Cu^+ for the more basic ligands, i.e. CN^- , $\text{S}_2\text{O}_3^{2-}$, pyridine, NH_3 . In the case of $\text{S}_2\text{O}_3^{2-}$ the ligand was decomposed by acid and SO_2 eventually liberated. Also, as the pH was lowered cyanide ions associated with protons to form HCN in solution and pyridine and NH_3 were protonated. In the preceding cases the potential of the Cu^+/Cu^0 couple became more positive as the effective ligand became unavailable to the Cu(I) ion and, as illustrated in Figure 1.3, a sharp downturn in the plot of the Cu^+/Cu^0

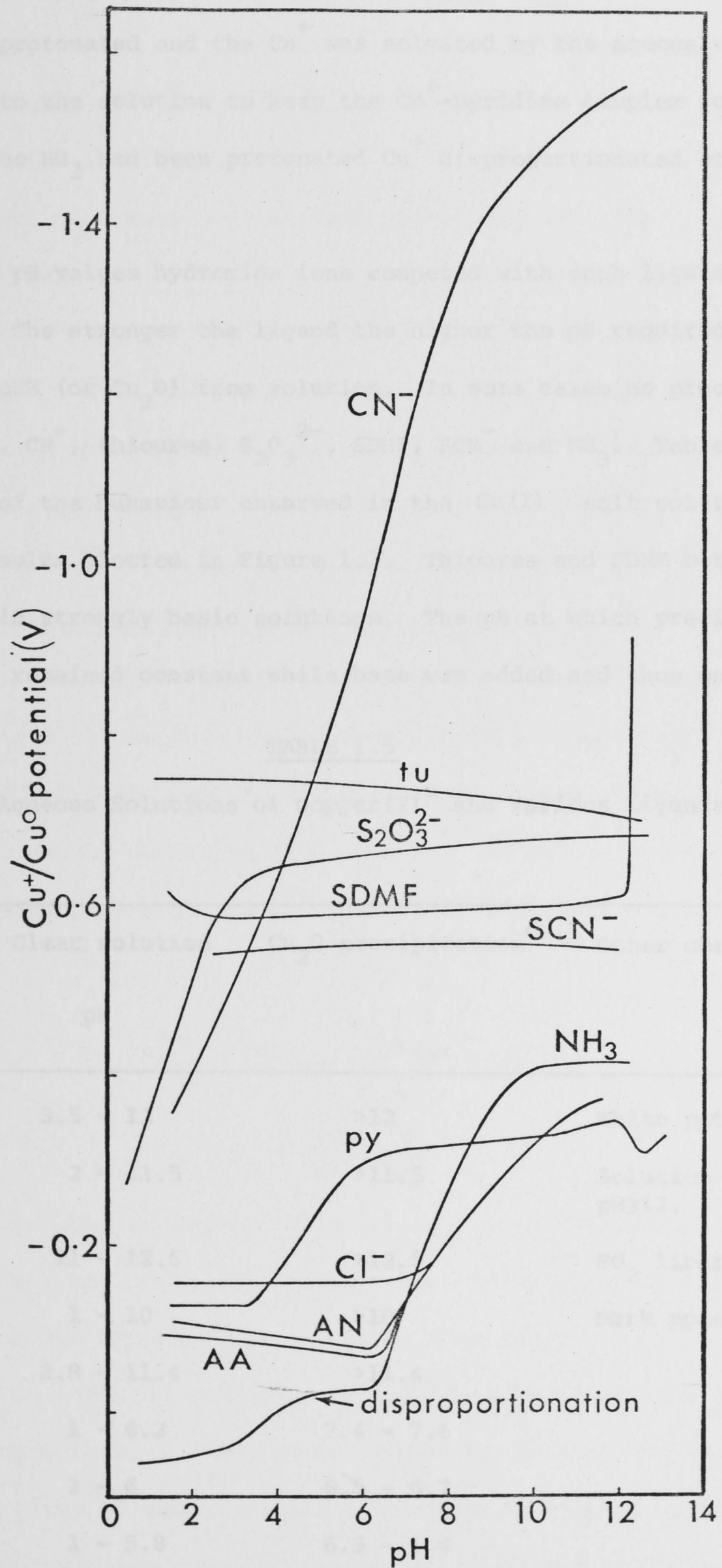


FIGURE 1.3. Effect of pH on the Potential of the Cu^+/Cu^0 Couple^a in Aqueous Solutions of Ligands.

a SCE reference.

potential versus pH occurred. The plot for pyridine fell until all of the pyridine was protonated and the Cu^+ was solvated by the acetonitrile introduced into the solution to keep the Cu^+ -pyridine complex soluble. When all of the NH_3 had been protonated Cu^+ disproportionated at a pH of 4.5 to 5.

At high pH values hydroxide ions competed with each ligand for the Cu (I) ion. The stronger the ligand the higher the pH required to precipitate CuOH (or Cu_2O) from solution. In some cases no precipitate was obtained, i.e. CN^- , thiourea, $\text{S}_2\text{O}_3^{2-}$, SDMF, SCN^- and NH_3 . Table 1.5 contains descriptions of the behaviour observed in the Cu(I) salt solutions used to obtain the results plotted in Figure 1.3. Thiourea and SDMF both appeared to decompose in strongly basic solutions. The pH at which precipitation of Cu_2O occurred remained constant while base was added and thus could be

TABLE 1.5

Behaviour of Aqueous Solutions of Copper(I)^a and Various Ligands^b at Varying pH Values.

Ligand ^c	Clear solution pH	Cu_2O precipitation ^d	Other observations
CN^-	3.5 - 12	>12	White ppte at pH 3-4
tu	2 - 11.5	>11.5	Solution brown at pH>12.
$\text{S}_2\text{O}_3^{2-}$	11 - 12.5	>12.5	SO_2 liberated at pH 1
SDMF	1 - 10	>10	Dark ppte at pH>10.
SCN^-	2.8 - 11.4	>11.4	
Cl^-	1 - 6.2	7.4 - 7.6	
AA	1 - 6	6.5 - 6.7	
AN	1 - 5.8	6.3 - 6.4	
PY^e	2 - 11.8	12.3 - 12.6	
NH_3	1 - 11.9	>11.9	

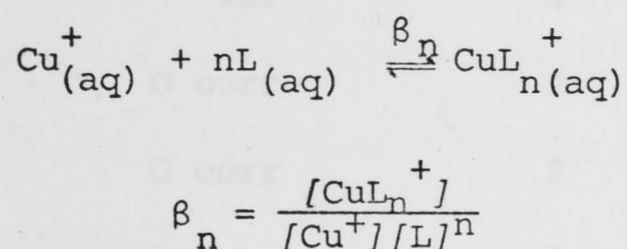
(Table 1.5 continued)

- a 0.01M CuClO_4 .
 - b Ligand concentration = 1M, except $\text{SCN}^- = 2\text{M}$.
 - c Abbreviations as in Table 1.1.
 - d Point at which pH remained constant while base was added.
 - e 1.9M AN present.
-

readily detected. Also, the point at which the slope of the plots in Figure 1.3 change abruptly indicates the pH at which precipitation occurred in the case of allyl alcohol, AN and Cl^- . The practical significance of these results will be discussed in a later chapter.

1.2.5. Stability Constants of Cu(I) Complexes

Table 1.6 contains stability constants for some Cu(I) complexes in aqueous solution. Literature values found for the ligands studied in this work have been included together with constants determined by the potentiometric method described in Chapter 4. No literature values could be found for SDMF, ethylene and CO. The following equilibrium has been measured:



Results are expressed as concentration, rather than thermodynamic, constants as no corrections for ionic effects have been made. Many of the literature values in Table 1.6 are also concentration constants.

As well as enabling stability constants to be determined, the method used in this work enables the highest complex in solution to be found. This number (n) is given in Table 1.6 and applies to Cu^+ -ligand ratios of 1:10 to 1:200. The potentiometric method is simple, rapid and accurate its main disadvantage being that stability constants for lower complexes can only be obtained with difficulty. It can be seen in Table 1.6 that the order of the

TABLE 1.6.

Stability Constants of Cu(I) Complexes in Aqueous Solutions

$$\text{Cu}^+_{(\text{aq})} + n\text{L}_{(\text{aq})} \xrightleftharpoons{\beta_n} \text{CuL}_n^+_{(\text{aq})}$$

Ligand ^a	T ^o C	Conditions ^b	n	Log β_n	Reference
CN ⁻	25	0 corr	4	30.3	1
	25	0 corr	4	27.56	1
	~18	var	4	28.0	1
	~18	var	4	27.3	1
tu	25	0.1 KNO ₃	4	15.39	25
	25	$\mu \sim 0.02$	4	14.8	c
S ₂ O ₃ ²⁻	25	1 Na ₂ SO ₄	3	13.64	1
	25	1.2 KNO ₃	3	14.3	1
	25	$\mu \sim 0.02$	3	14.1	c
SDMF	25	$\mu \sim 0.02$	4	13.6	c
SCN ⁻	25	var	4	9.15	1
	20	var	4	10.09	1
Cl ⁻	25	0 corr	2	5.54	1
	25	0 corr	2	4.73	1
	23	0 corr	3	5.84	1
	20	0 corr	3	5.7	1
	25	5 NaClO ₄	3	5.99	27
Br ⁻	25	0 corr	2	5.92	1
	~19	KBr var	2	5.04	1
	25	var	3	6.1	c
I ⁻	~19	var	2	8.19	1
	25	0 corr	2	8.85	1
	20	0.6 NaNO ₃	2	9.03	1

(Table 1.6. continued)

AA	25	0.1 HClO ₄	1	4.72	14
	25	0.1 NaClO ₄	1	4.7	17
AN	25	0.1 LiClO ₄	3	4.1	41
	25	$\mu \sim 0.02$	3	4.6	c
py	25	$\mu \sim 0.02$	3	8.4	c
NH ₃	25	0.15 K ₂ SO ₄	2	10.55	41
	18	1 NH ₄ NO ₃	2	10.86	1
Propylene	25	0 corr	1	5.02	18

a Abbreviations as in Table 1.1.

b 0 corr = corrected to zero ionic strength.

var = varying ionic strength

0.1 MX = 0.1 molar MX.

μ = ionic strength.

c This work.

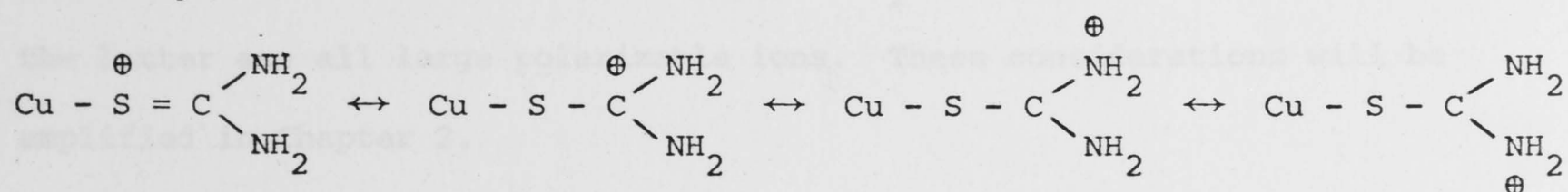
stability constants is the same as that of the free energies of transfer found in Figures 1.1 and 1.2 which is expected. The detection of tetracoordinated Cu⁺ in the presence of thiourea confirms the polarographic result of Onstott and Laitinen²⁵.

In the case of AN, the highest complex found in this study (i.e. 3) is at variance with a value of 2 found by Hemmerich and Sigwart⁶ for solutions containing similar metal-ligand ratios. The explanation can be found in the two different methods of measurement. DC polarography (as used by Hemmerich and Sigwart) can detect electrochemical charge transfer processes having rates of 10^{-2} cm sec⁻¹ or lower. Potentiometry detects the highest equilibrium complex formed under specific experimental conditions. It is conceivable that the reaction $\text{Cu}(\text{AN})_3^+ + e^- \rightarrow \text{Cu}(\text{Hg})$ is too fast to enable

its detection by DC polarography. Voltammetry, a technique capable of detecting faster processes, has been used to study the AN complexes of Cu^+ in water⁸ and $\text{Cu}(\text{AN})_3^+$ was detected.

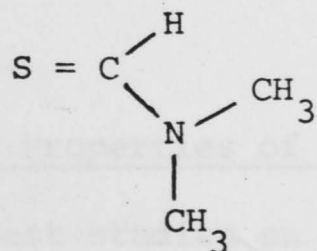
The highest pyridine complex found was $\text{Cu}(\text{py})_3^+$ which disagrees with the 1:2 complex found by Gupta and Chatterjee²³ for solutions containing 0.1 - 0.55M pyridine. Chen and Iwamoto⁴² also state that the highest complex that Cu(I) is known to form with pyridine in water is $\text{Cu}(\text{py})_2^+$. Again polarographic techniques were employed in these reports so that a similar argument to that proposed above may apply. However, work by Chen and Iwamoto in propylene carbonate^{30,42} has demonstrated the existence of a quadricovalent Cu(I)-pyridine complex. No previously measured value of the stability constant of $\text{Cu}(\text{py})_3^+$ could be found in the literature although James and Williams¹¹ have calculated a value of $10^{8.29}$ which is close to that determined in this work, i.e. $10^{8.4}$ (see Table 1.6).

Stability constants of the Cu(I) complexes of thiourea and SDMF might be expected to be very similar because of the identical nature of the donor atom (C=S). The fact that the value for SDMF is lower may be explained by the greater ability of thiourea to disperse charge. The following tautomeric forms can be drawn:



Thus the positive charge can be delocalised over the whole thiourea molecule.

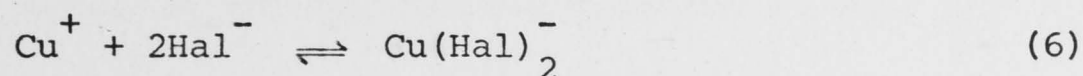
This cannot be achieved in SDMF which has the following structure:



Charge may still be delocalised onto the tertiary amino nitrogen atom but not onto the hydrogen atom. Another factor which may help to explain the stability difference between the thiourea and SDMF complexes of Cu^+ is ligand

solvation. It should be remembered when comparing the stability constants listed in Table 1.6 that they refer to water-solvated species and differences in ligand solvation may be important. Attention has been drawn to this factor in a recent communication by Hinz and Margerum⁴³.

It is interesting to compare the stability constants of some Cu(I) complexes in water and in anhydrous acetonitrile. Heerman and Rechnitz⁴⁴ have determined values for the halides by potentiometry. These are given in Table 1.7 together with values for thiourea, SDMF and pyridine measured in this work. It can be seen that the order of stability of the halide complexes is reversed on transfer from water to AN. This is primarily a result of the different solvation of the halides in the two solvents. The free energies of transfer from water to AN of Cl^- , Br^- and I^- have been reported by Cox et. al.⁴⁵ to be 42.2, 31.6 and 18.8 kJ mol⁻¹ respectively. The higher activity of Cl^- in AN displaces equilibrium 6 (Hal = Cl) further to the right than the relatively smaller increase in Br^- and I^- activity (Hal = Br or I). The activity of Cu^+ is constant in all three equilibria



and free energies of transfer of the $\text{Cu}(\text{Hal})_2^-$ complexes will be similar as the latter are all large polarizable ions. These considerations will be amplified in Chapter 2.

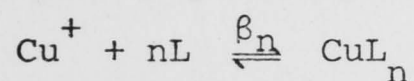
The differences in stabilities of the thiourea, SDMF and pyridine complexes in water and AN are largely due to the decreased activity of Cu^+ in AN. Solvation of the ligands and Cu(I) complexes will also be changed but not to the same extent.

1.2.6. Preparation and Properties of Some Cu(I) Complexes

In some of the earliest studies on nitrile complexes of Cu(I)⁴ Morgan proposed a tetrahedral disposition of ligands about quadricovalent Cu(I). Further reports^{5,8,9,29} supported this proposal and helped lead to the current view that the preferred configuration of ligands about quadricovalent

TABLE 1.7.

Stability Constants of Complexes of Cu(I) with Cl^- , Br^- , I^- , Thiourea, SDMF and Pyridine in Water and Acetonitrile at 25° .



Ligand ^a	n	log β_n	
		Water	Acetonitrile
Cl^-	2	5.54 ^b , 4.73 ^b	10.7 ^c
Br^-	2	5.92 ^b	7.8 ^c
I^-	2	8.85 ^b	6.4 ^c
tu ^d	4	14.8	9.41
SDMF ^d	4	13.6	-
	1	-	2.32
py	3	8.4	-
	1	-	1.72

a Abbreviations as in Table 1.1.

b Reference 1.

c Reference 42.

d This work.

Cu(I) is tetrahedral^{36,46,47} although linear two-coordinate and planar three-coordinate Cu(I) complexes are known^{36,47}. The importance of dative π -bonding in Cu(I) complexes has been discussed earlier in this chapter.

Further discussions on the coordination number of the Cu(I) ion and the type of bonding exhibited may be found in papers by James and Williams¹¹ and Hawkins and Perrin¹². Bonding in linear two-coordinate Cu(I) complexes (e.g. $\text{Cu}(\text{NH}_3)_2^+$) has been considered to involve sp-hybridisation¹¹ although an alternative explanation invoking mixing of the s- and d- states has been proposed⁴⁸.

Recent studies by Parker and co-workers³¹ have involved the use of Cu(I) salt solutions for the extraction and refining of copper metal. The Cu(I) state has been stabilised by organic nitriles in an aqueous sulphuric acid medium where the bisulphate ion predominates. No previous relevant work involving this anion has been reported and so tetrakis(acetonitrile) copper(I) bisulphate was prepared by the reaction of CuSO_4 , sulphuric acid and copper powder in AN as detailed in Chapter 4. The equivalent conductance of a 0.0093M solution of the complex in AN was found to be $118 \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25° , which is indicative of a 1:1 electrolyte⁵. The pK_a of the bisulphate moiety was determined in a solution containing 80% by volume of AN and 20% water and found to be 4.8 which is similar to that measured in work described in Chapter 2.

In air the colourless transparent crystals of the complex begin to disproportionate immediately, a behaviour which contrasts to that of $\text{Cu}(\text{AN})_4\text{ClO}_4$ whose crystals are stable in air for about 15 minutes. Hathaway et. al.⁵, explaining the instability of the $\text{Cu}(\text{AN})_4\text{NO}_3$ complex compared to the analogous ClO_4^- and BF_4^- complexes, invoked the concept of weak coordination of the nitrate ion to the metal with a resultant distortion of the tetrahedron of AN molecules and a lowering of stability. The similar instability of the HSO_4^- complex may be due to a similar weak coordination of the bisulphate anion. Infra-red absorption peaks found for ionic NaHSO_4 are shifted in the spectrum of $\text{Cu}(\text{AN})_4\text{HSO}_4$ (see Table 1.8). In particular, the absorption peak at 872 cm^{-1} in the spectrum of NaHSO_4 has shifted to 839 cm^{-1} for $\text{Cu}(\text{AN})_4\text{HSO}_4$.

TABLE 1.8.

Infra-red Absorption Frequencies (cm^{-1})

$\text{Cu}(\text{AN})_4\text{HSO}_4^{\text{a}}$	$\text{NaHSO}_4^{\text{b}}$
394 m	
432 m	453 w
	519 w
587 s	591 s
735 w	734 w
775 m	819 m
839 s	872 s
919 vw, sh ^c	
934 w, sh ^c	
1048 s	1068 s
1158 vs	1173 vs
1238 vs	1218 vs
2273	
split ^c	
2304	

Abbreviations: vw, very weak; w, weak; m, medium; s, strong;
vs, very strong; sh, shoulder.

a Nujol mull.

b KBr disc.

c Absorptions due to $\text{AN}^{5,49}$.

Further evidence supporting the abovementioned hypothesis was obtained by measurement of the Cu^+/Cu^0 couple in solutions containing Cu^+ (0.01M), sulphuric acid (1M) or perchloric acid (1.1M), and carbon monoxide at pressures of 0.95×10^5 and 4.75×10^5 pascals. Table 1.9 gives the results of these measurements and it can be seen that the solution containing H_2SO_4 gives a more negative value for the Cu^+/Cu^0 couple. It seems therefore that a

favourable interaction occurs between Cu^+ and HSO_4^- , although the exact nature of the interaction cannot be gauged from this single experiment. HSO_4^- may ion-pair more strongly than ClO_4^- with Cu(I) species, or there may be weak coordination between Cu^+ and HSO_4^- . However, together with the IR spectral and stability properties of $\text{Cu}(\text{AN})_4\text{HSO}_4$ weak coordination of HSO_4^- is indicated.

TABLE 1.9.

Potentials^a of the Cu^+/Cu^0 Couple in Acidified Aqueous Solutions under Carbon Monoxide at 25^o.

Solution composition	Cu^+/Cu^0 potential (mV) at CO pressure of 10^5 x pascals	
	x = 0.95	x = 4.75
0.01M Cu^+ , 1M H^+ , 1M HSO_4^- , 0.005M SO_4^{2-} b	-81	-126
0.01M Cu^+ , 1.1M H^+ , 1.1M ClO_4^-	-62	-101

a SCE reference.

b Calculated from pK_a 's of H_2SO_4 in water.

Chen and Iwamoto⁴² have prepared tetrakis(pyridine)copper(I) perchlorate in propylene carbonate by displacement of AN from $\text{Cu}(\text{AN})_4\text{ClO}_4$ by pyridine. They state that the 2:1 complex of pyridine and Cu^+ is the

highest known in aqueous solution. However, as discussed previously, the addition of a little acetonitrile enables the 3:1 complex to be detected and in fact, $\text{Cu}(\text{py})_4\text{ClO}_4$ was prepared by the reaction of $\text{Cu}(\text{AN})_4\text{ClO}_4$ and pyridine in a mixture of AN and water (see Chapter 4 for details). The product obtained was light yellow with no greenish tinge (that prepared in propylene carbonate by Chen and Iwamoto had a greenish tinge) indicating complete absence of any Cu(II). An infra-red spectrum of the complex in a Nujol mull gave no evidence of the presence of water or AN.

Tetrakis(acetonitrile)copper(I) perchlorate was prepared and recrystallized by a previously reported method⁵. Its use as a reagent for the introduction of $\text{Cu}(\text{AN})_n^+$ species into aqueous solution has been described by Hemmerich and Sigwart⁶. In the work carried out in this thesis $\text{Cu}(\text{AN})_4\text{ClO}_4$ was found to be very useful for the preparation of Cu(I) salt solutions.

Its advantages can be summarised as follows:

- A. Easy to prepare and purify.
- B. Indefinitely stable when stored under dry nitrogen. Stable for 15 minutes in the air allowing laboratory manipulations (e.g. weighing) to be performed with little risk of decomposition.
- C. Because of the relatively weak interaction between Cu^+ and AN in solution (see Figure 1.1) many ligands will displace AN, thus providing a method of obtaining Cu(I) salt solutions suitable for investigation.

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... interest has been shown in the measurement of solvent transfer
 activity coefficients for single ions and for molecular species. The solvent
 activity coefficient (γ_i^s) of a chemical species i in a transfer
 from a reference solvent a to another solvent b at temperature T can
 be represented by:

$$\ln \gamma_i^s = \frac{1}{RT} (\mu_i^s - \mu_i^a) \quad (1)$$

where μ_i^a and μ_i^b are the standard chemical potentials of i in solvents a
 and b respectively. Thus γ_i^s gives a measure of the difference in free
 energy or "activity" of i in the two solvents.

CHAPTER 2

It has been found that the activity of many chemical species can
 be significantly altered by changing the solvent. Chloride ion, for example,
 is much more active in N,N' -dimethylformamide (DMF) than in water.
 Consequently, reactions in water involving the chloride ion as a catalyst
 may be accelerated by transferring the reaction to DMF.

SOLUBILITIES AND EQUILIBRIA INVOLVING COPPER (I)

both solvents; this is not always the case.
 Other examples of this effect is the greater solubility of the
 $Cu(I)$ ion by acetone... In water the stable
 soluble species of copper is the $Cu(II)$ ion. Addition of small amounts of
 ammonia to the $Cu(II)$ ion forms the stable species, and this occurs
 to such an extent that copper metal is dissolved as Cu^{2+} in the form of
 $Cu(NH_3)_2^+$.



In water the equilibrium constant for reaction 2 is $10^{-6} \text{ mol dm}^{-3}$. The
 equilibrium constant is approximately $10^{-10} \text{ mol dm}^{-3}$ because of the
 preferential solvation of Cu^+ by NH_3 and the relative instability of Cu^{2+} in
 NH_3 . In an aqueous solution of NH_3 (0.1 mole fraction) the equilibrium
 constant is $10^{-3} \text{ mol dm}^{-3}$. In this case Cu^{2+} is solvated by water and Cu^+ by

2.1. Introduction

Recent interest has been shown in the measurement of solvent transfer activity coefficients for single ions and for molecules^{1,2,3}. The solvent transfer activity coefficient (${}^o\gamma_i^s$) of a chemical species i on transfer from a reference solvent o to another solvent s at temperature T can be represented by:

$$\ln {}^o\gamma_i^s = \frac{1}{RT} (\mu_i^s - \mu_i^o) \quad , \quad (1)$$

where μ_i^s and μ_i^o are the standard chemical potentials of i in solvents s and o respectively. Thus, ${}^o\gamma_i^s$ gives a measure of the difference in free energy or "activity" of i in the two solvents.

It has been found^{1,2,3} that the activity of many chemical species can be significantly altered by changing the solvent. Chloride ion, for example, is much more energetic in *N,N'*-dimethylformamide (DMF) than in water^{1,2,3}. Consequently, reactions in water involving the chloride ion as a reactant may be accelerated by transferring the reaction to DMF. Implicit in the statement is the assumption that the same reaction mechanism applies in both solvents; this is not always the case.

Another example of this effect is the greater stabilisation of the Cu (I) ion by acetonitrile (AN) compared to water⁴. In water the stable soluble species of copper is the Cu(II) ion. Addition of small amounts of AN results in the Cu (I) ion becoming the stable species, and this occurs to such an extent that copper metal is dissolved by Cu^{2+} in AN to form Cu^+ , i.e.,



In water the equilibrium constant for reaction 2 is $10^{-6} \text{ mol dm}^{-3}$ ⁵. The equilibrium constant is approximately $10^{20} \text{ mol dm}^{-3}$ in AN⁴ because of the preferential solvation of Cu^+ by AN and the relative instability of Cu^{2+} in AN. In an aqueous solution of AN (0.1 mole fraction) the equilibrium constant is 10^8 mol dm^{-3} ⁴. In this case Cu^{2+} is solvated by water and Cu^+ by AN.

This chapter deals with solubility and equilibrium changes involving the Cu(I) ion on transfer from water to some aprotic solvents and solvent mixtures, particularly those of AN and water. Solubilities and equilibria in AN-water mixtures have been measured, and compared with results predicted from solubility products and equilibrium constants in water, and the appropriate solvent transfer activity coefficients. Measurements involving Ag^+ are also given. Ag^+ is preferentially solvated by AN compared to water, but not to the same extent as Cu^{+2} . However, its behaviour on transfer from water to AN parallels that of Cu^+ and measurements have been made in the solvent systems studied.

Solubilities of the following Cu(I) salts in AN-water mixtures have been measured: sulphide, hydroxide, cyanide, chloride, bromide, iodide and thiocyanate. Calculation of some solubilities has required a knowledge of the dissociation constants of sulphuric acid in AN-water mixtures. These have been measured together with the solubility of sulphur and hydrogen sulphide in the same solutions. It has been shown that reliable predictions of the behaviour of chemical species in new environments can be made using solvent transfer activity coefficients.

The equilibrium, $\text{Cu}_2\text{S} + 4\text{Cl}^- + 2\text{H}^+ \rightleftharpoons 2\text{CuCl}_2^- + \text{H}_2\text{S}$, has been examined in water, acetone, DMF and dimethyl sulphoxide (DMSO), and it provides an excellent example of the use of solvent transfer activity coefficients to predict hitherto unknown chemical behaviour.

2.2. Results and Discussion

2.2.1. The Behaviour of Solutes in Mixtures of Acetonitrile and Water

2.2.1.1. General Considerations

Before discussing the solubilities and equilibria studied in this work, a brief look at the behaviour of various ions and molecules in AN-water mixtures is appropriate. Figure 2.1. gives the solvent activity coefficients of Cu^+ , Cu^{2+} , Ag^+ , H^+ , Cl^- , Br^- , I^- , H_2O , H_2S and sulphur for

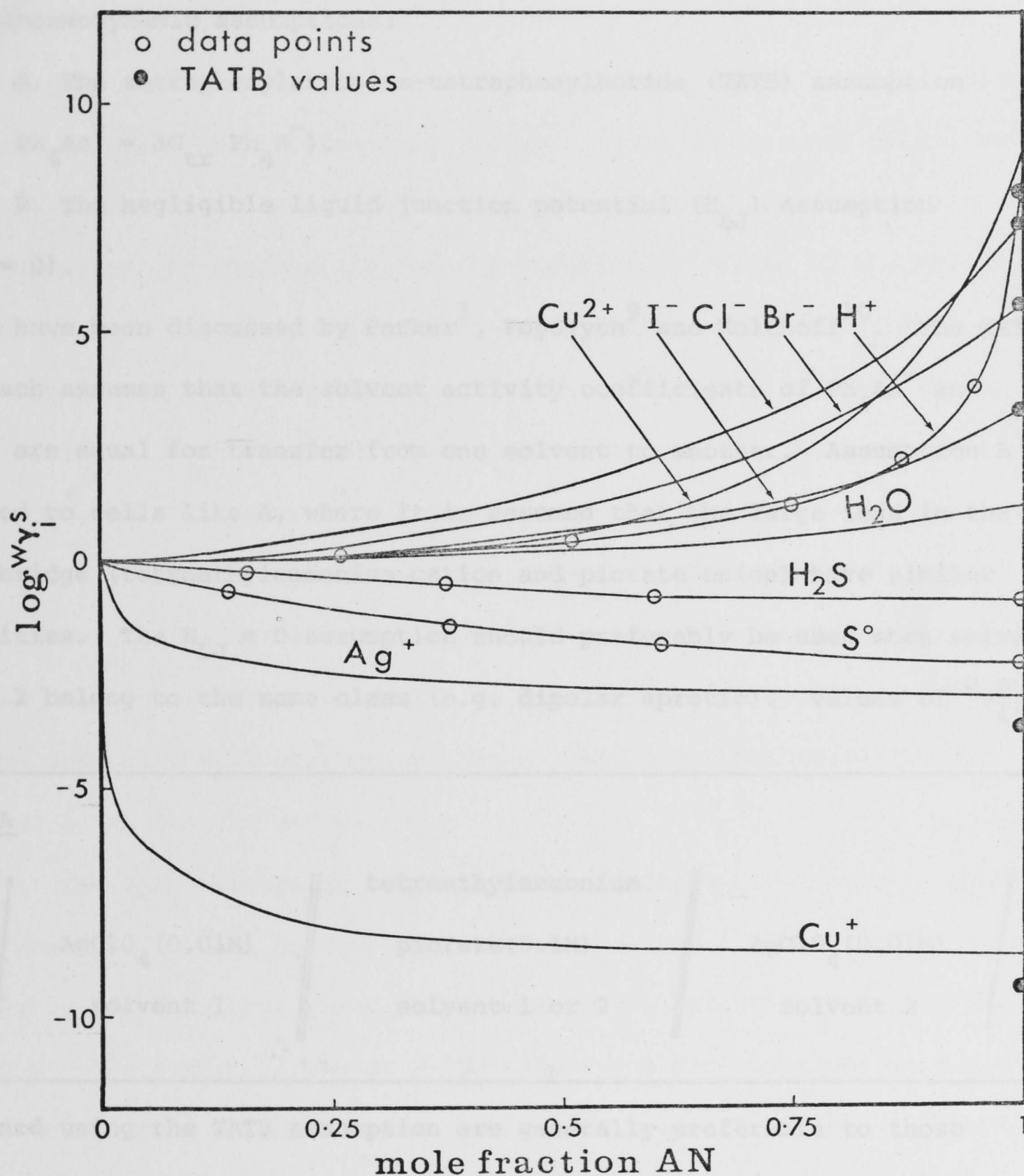


FIGURE 2.1. Solvent Activity Coefficients for Transfer from Water to AN-Water Mixtures, $\log W_S^i$, of Cu^{2+} ^a, H^+ ^b, Cl^- ^c, Br^- ^c, I^- ^c, H_2O ^d, H_2S ^e, S^0 ^e, Ag^+ ^a and Cu^+ ^a at 25° .

a $E_{\text{LJ}} = 0^4$.

b $E_{\text{LJ}} = 0$, this work.

c Based on TATB value in AN⁶, and curve shape for $\log W_S^{\text{Cl}^-}$ ($E_{\text{LJ}} = 0$)⁴.

d From vapour pressure measurements⁸.

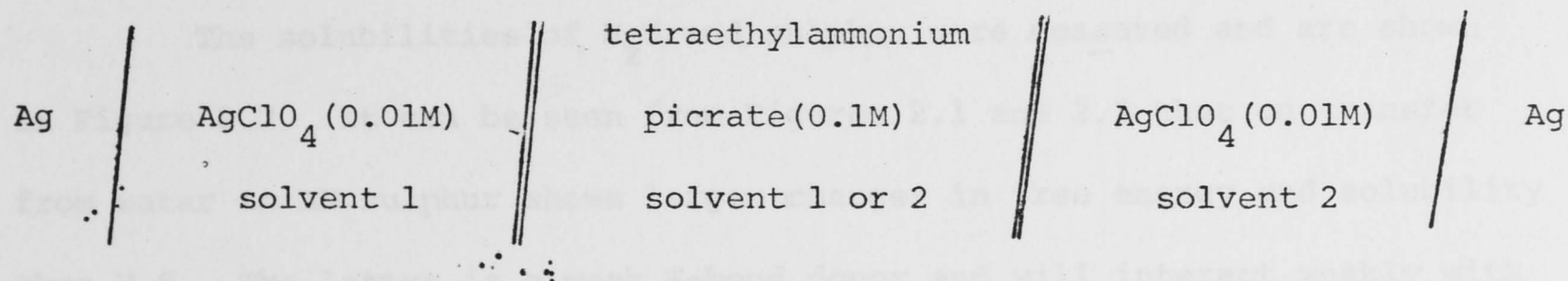
e This work (see Figure 2.2).

transfer from water to AN-water mixtures at 25° (expressed as $\log \frac{W}{\gamma_i^{AN/W}}$). Values for single ions were obtained by invoking one of the following two extrathermodynamic assumptions:

- A. The tetraphenylarsonium-tetraphenylboride (TATB) assumption ($\Delta G_{tr} \text{ Ph}_4\text{As}^+ = \Delta G_{tr} \text{ Ph}_4\text{B}^-$).
- B. The negligible liquid junction potential (E_{LJ}) assumption ($E_{LJ} = 0$).

These have been discussed by Parker¹, Popovych⁹ and Kolthoff¹⁰. The TATB approach assumes that the solvent activity coefficients of Ph_4As^+ and Ph_4B^- are equal for transfer from one solvent to another. Assumption B is applied to cells like A, where it is assumed that the large ions in the salt bridge (tetraethylammonium cation and picrate anion) have similar mobilities. The $E_{LJ} = 0$ assumption should preferably be used when solvents 1 and 2 belong to the same class (e.g. dipolar aprotic). Values of γ_i^S

CELL A



obtained using the TATB assumption are generally preferable to those obtained from the $E_{LJ} = 0$ assumption because the latter is justified only on the grounds of (a) similar mobilities of the bridge ions and (b) agreement with other assumptions.

Diggle and Parker⁷ have investigated liquid junction potentials at a number of dissimilar solvent junctions within the framework of the TATB assumption. For junctions between AN and water, E_{LJ} was 40 mV with a silver metal electrode in an aqueous solution of AgClO_4 (0.01M) as the reference, and 93 mV with a saturated calomel electrode in aqueous solution as the reference. The TATB assumption is considered valid because of the similar

chemical and electrical properties of the two tetraphenyl-substituted ions. Their interaction with a variety of solvents is likely to be similar.

Three kinds of solute-solvent interaction have been distinguished to help explain the behaviour of the solutes in water, in AN, and in their mixtures (Figure 2.1.). The first group of ions, consisting of H^+ , Cu^{2+} , Cl^- , Br^- and I^- , are better solvated by water than by AN. Hydrogen bonding in water is mainly responsible for the superior solvation of the halide ions. Interaction with the basic oxygen atom of the water molecule is the most important factor governing the solvation of Cu^{2+} and H^+ . The nitrogen atom of AN is a very weak base and dipole-dipole interactions should be mainly responsible for the solvation of ions and neutral molecules. Exceptions are ions of the second group, Cu^+ and Ag^+ , where the π -acceptor ability of AN is operative. The nature of the specific interaction between AN and Cu^+ and Ag^+ has been described in Chapter 1. The third group consists of the neutral molecules H_2S , sulphur and water, the former two being better solvated by AN than by water.

The solubilities of H_2S and sulphur were measured and are shown in Figure 2.2. It can be seen from Figures 2.1 and 2.2 that on transfer from water to AN sulphur shows larger changes in free energy and solubility than H_2S . The latter is a weak H-bond donor and will interact weakly with water; the sulphur molecule, having no dipole moment, will not interact. Both species are less solvated in water because water structure is disrupted by the neutral molecules. As the amount of AN in solution increases the structure of the solvent diminishes resulting in increased solubility of H_2S and sulphur.

Figure 2.1 demonstrates that only a small amount of the active solvent is needed to cause significant stabilisation of an ion interacting specifically with that solvent. For example, changing the solvent from water to one containing AN (mole fraction 0.1) changes the free energy of Cu^+ by 29.3 kJ mol^{-1} . On the other hand the free energy of the proton

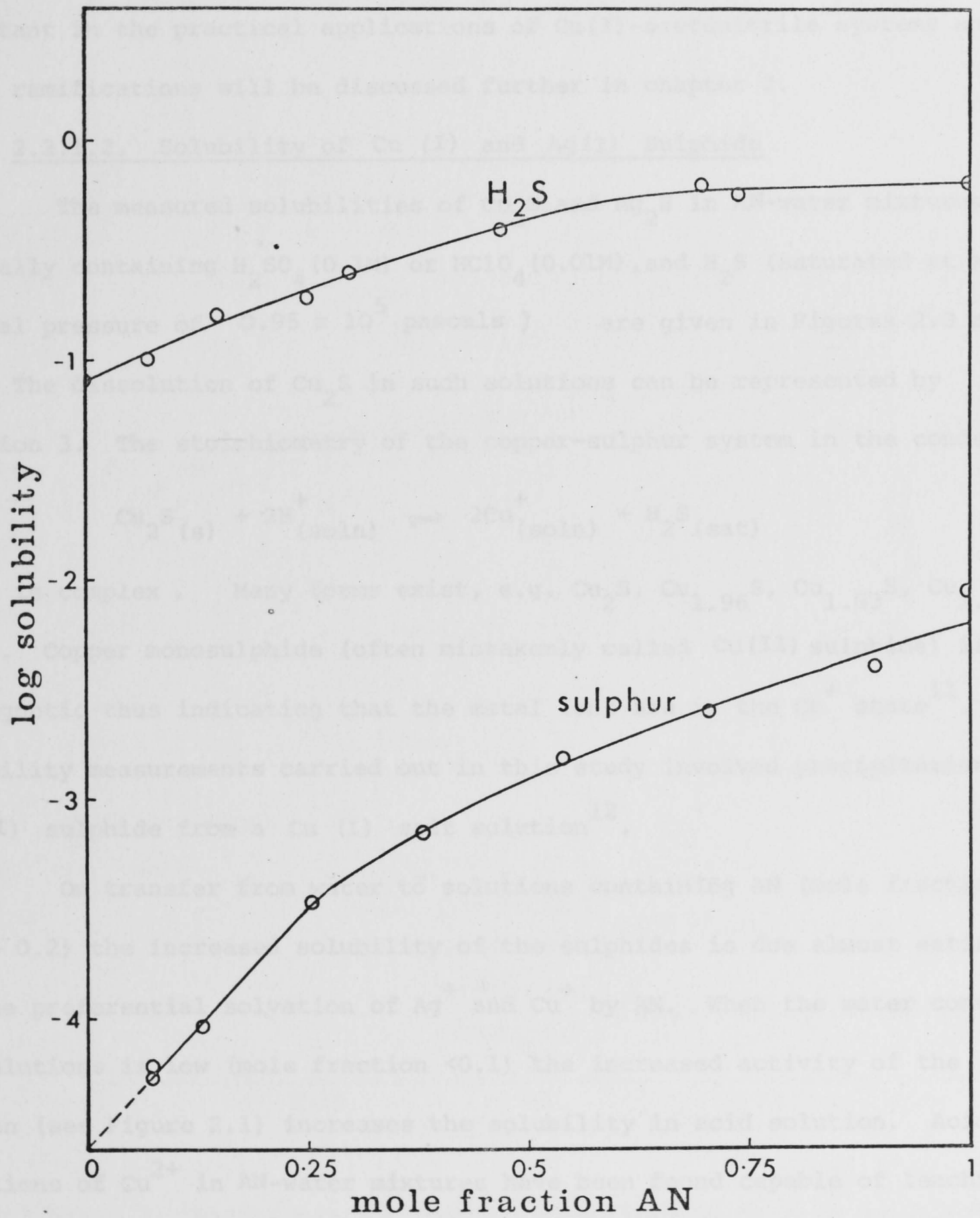


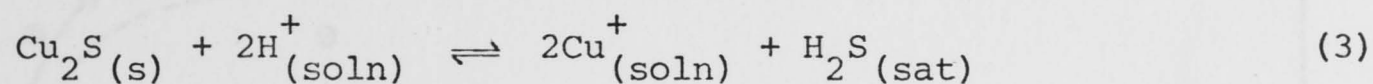
FIGURE 2.2. The Solubility of H₂S and Sulphur in Mixtures of Acetonitrile (AN) and Water at 25°.

Units of concentration mol dm⁻³.

changes by 21 to 25 kJ mol⁻¹ on transfer from a solution containing AN (mole fraction 0.9) to anhydrous AN (see Figure 2.1). These effects are important in the practical applications of Cu(I)-acetonitrile systems and their ramifications will be discussed further in chapter 3.

2.2.1.2. Solubility of Cu (I) and Ag(I) Sulphide

The measured solubilities of Cu₂S and Ag₂S in AN-water mixtures initially containing H₂SO₄ (0.1M) or HClO₄ (0.01M), and H₂S (saturated at a partial pressure of 0.95 x 10⁵ pascals) are given in Figures 2.3 and 2.4. The dissolution of Cu₂S in such solutions can be represented by reaction 3. The stoichiometry of the copper-sulphur system in the condensed



phase is complex. Many forms exist, e.g. Cu₂S, Cu_{1.96}S, Cu_{1.83}S, Cu_{1.78}S, Cu₉S₅. Copper monosulphide (often mistakenly called Cu(II) sulphide) is diamagnetic thus indicating that the metal ions are in the Cu⁺ state¹¹. The solubility measurements carried out in this study involved precipitation of Cu (I) sulphide from a Cu (I) salt solution¹².

On transfer from water to solutions containing AN (mole fraction 0.1 - 0.2) the increased solubility of the sulphides is due almost entirely to the preferential solvation of Ag⁺ and Cu⁺ by AN. When the water content of solutions is low (mole fraction <0.1) the increased activity of the proton (see Figure 2.1) increases the solubility in acid solution. Acidic solutions of Cu²⁺ in AN-water mixtures have been found capable of leaching copper from Cu₂S. This process will be discussed further in chapter 3.

2.2.1.3. Dissociation of Sulphuric Acid and Hydrogen Sulphide

The dissociation constants of sulphuric acid and H₂S in AN-water mixtures at 25^o are shown in Figure 2.5. The first dissociation constant of H₂SO₄ in anhydrous AN has been determined by Kolthoff and co-workers¹³, while the second was measured by Kolthoff and Chantooni¹⁴. The titration curves obtained for H₂SO₄ in AN-water mixtures (Figure 2.6) show that in

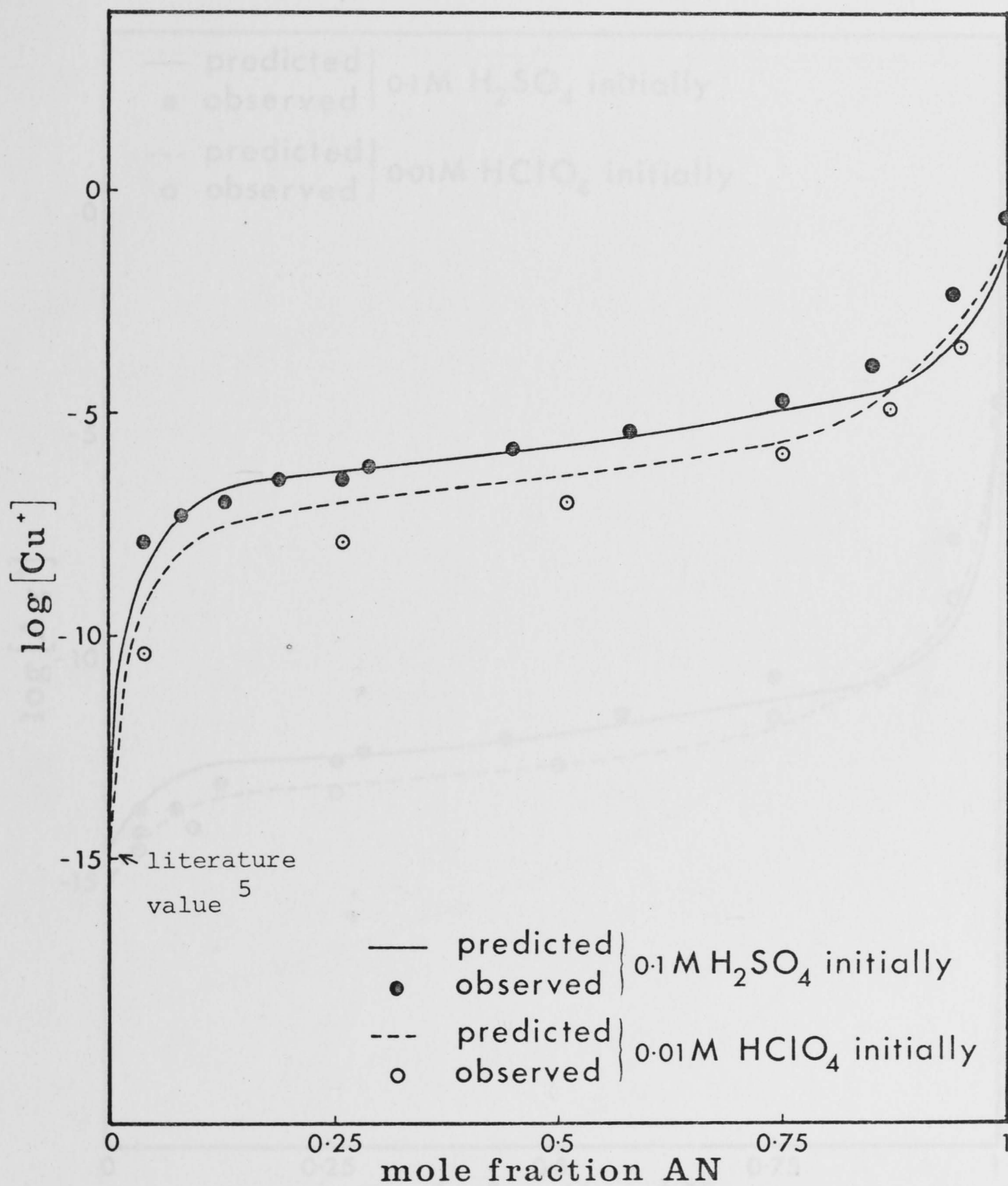


FIGURE 2.3. Measured and Predicted Solubility of Cu_2S in Acidified Mixtures of Acetonitrile (AN) and Water at 25° .

Units of concentration mol dm^{-3} .

Measurement error ± 0.2 log unit.

Error in predicted values ± 0.5 log unit.

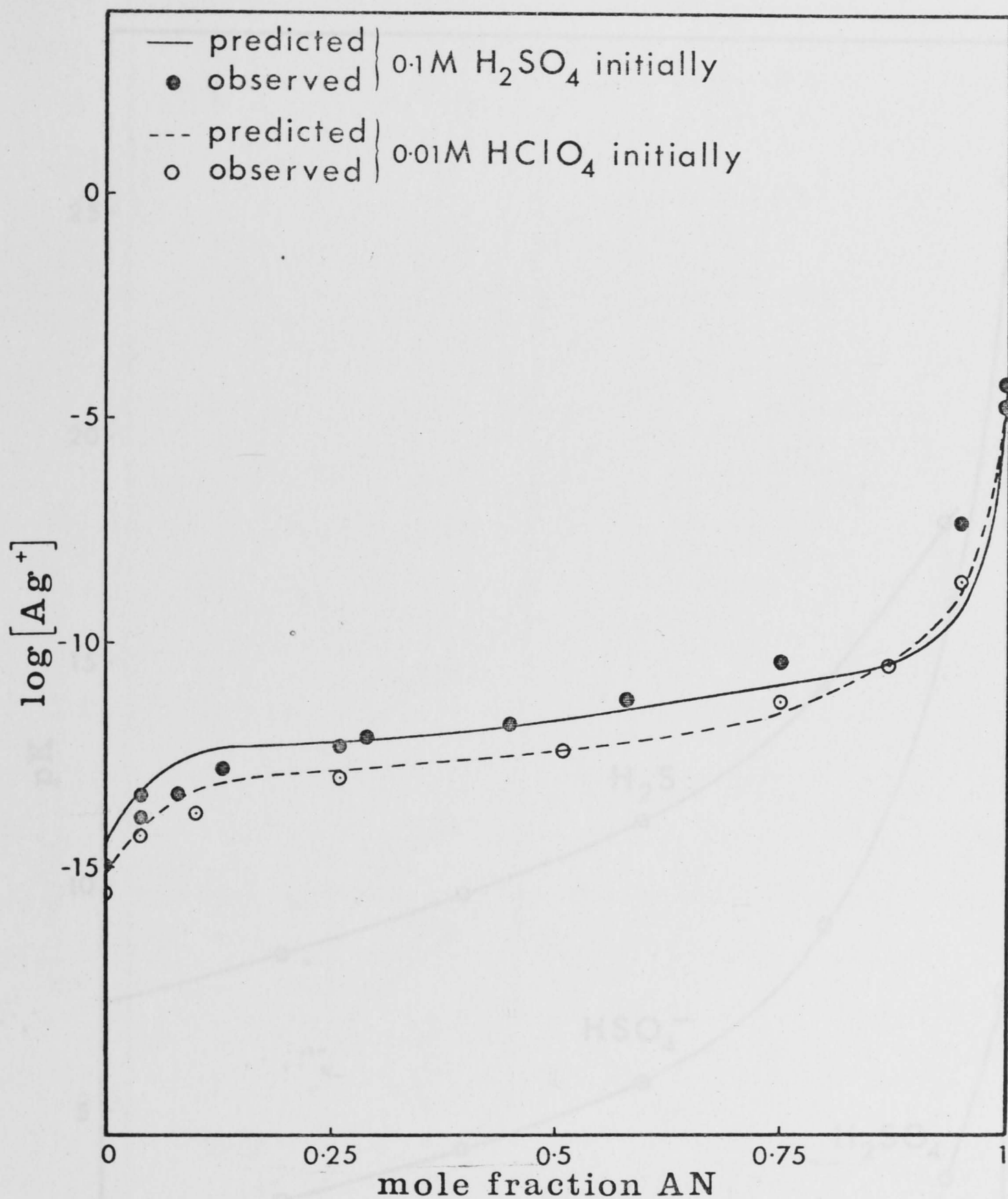


FIGURE 2.4. Measured and Predicted Solubility of Ag_2S in Acidified Mixtures of Acetonitrile (AN) and Water at 25° .

Units of concentration mol dm^{-3} .

Measurement error ± 0.2 log unit.

Error in predicted values ± 0.5 log unit.

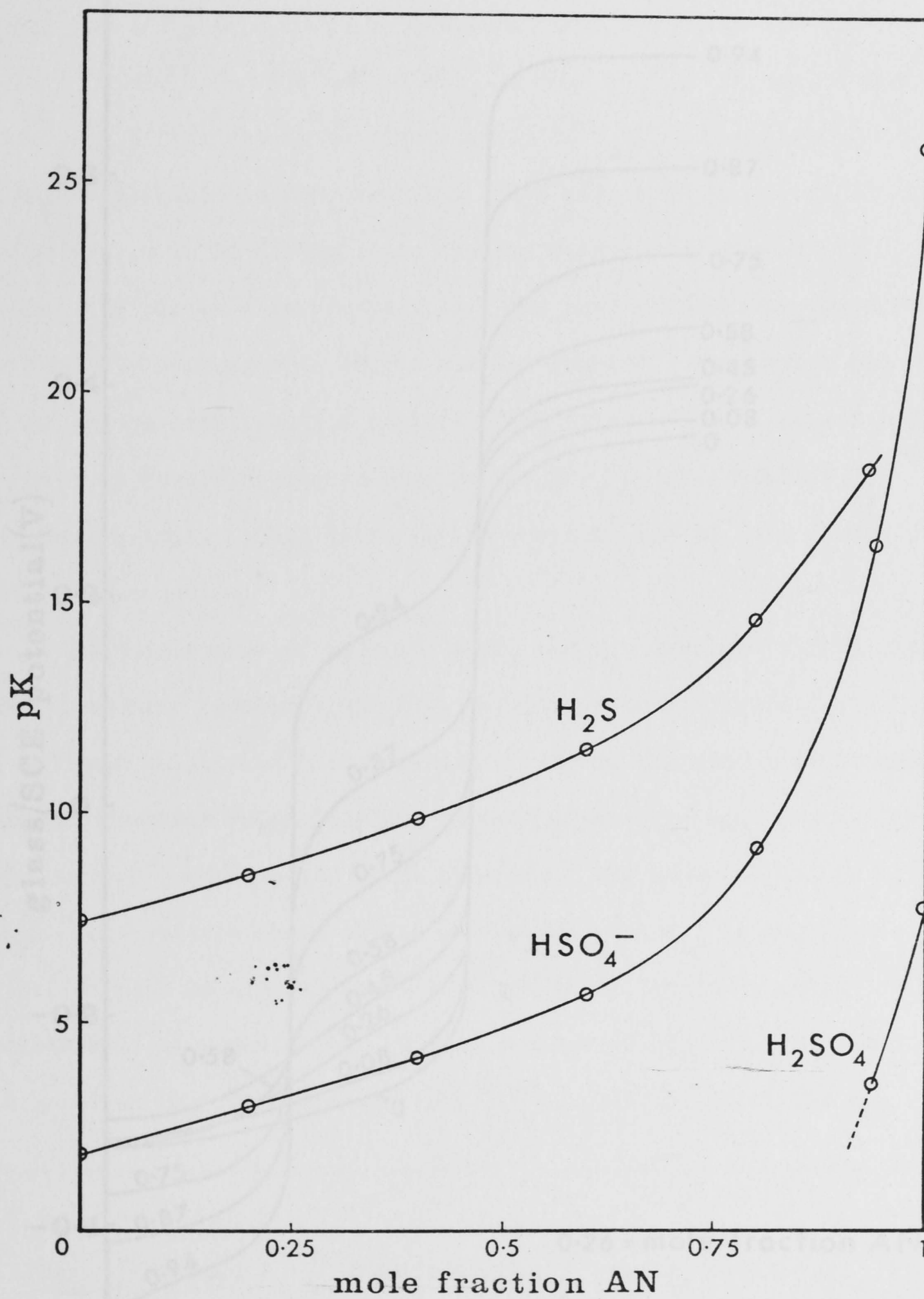


FIGURE 2.5. Dissociation Constants of H_2SO_4 and H_2S in Mixtures of Acetonitrile (AN) and Water at 25° .

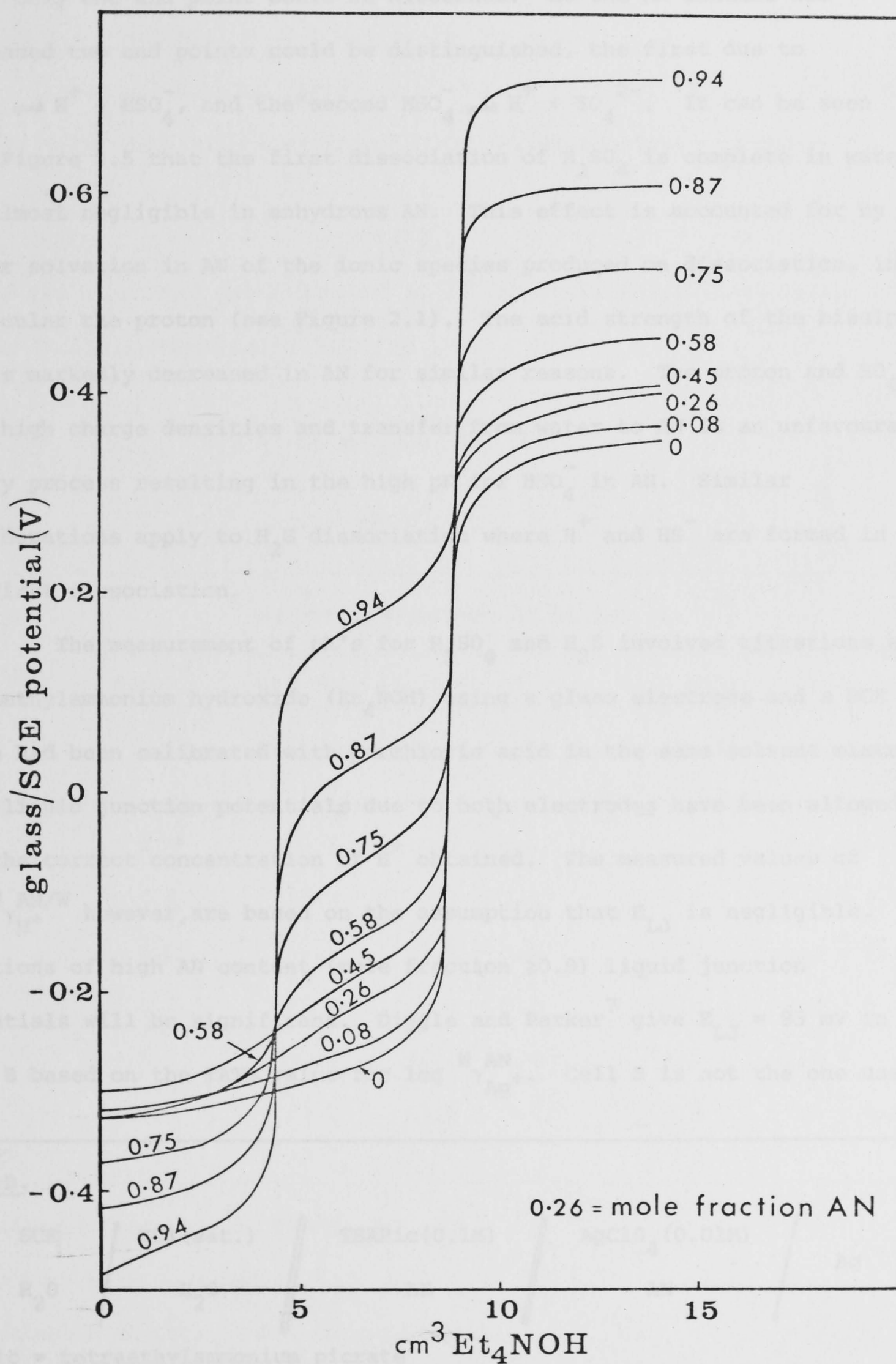


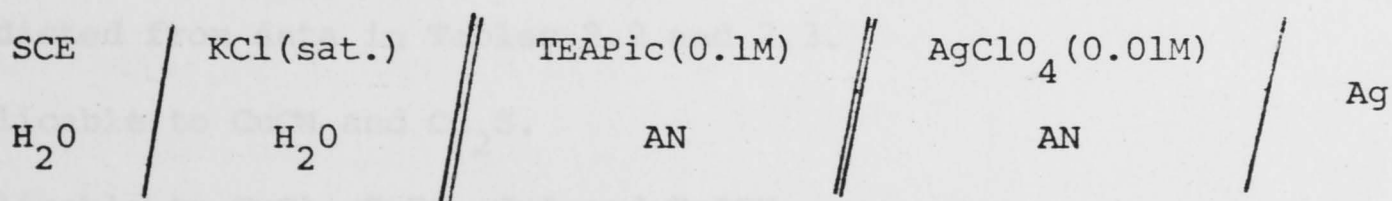
FIGURE 2.6. Titration^a Curves in Mixtures of Acetonitrile (AN) and Water at 25^o.

a $15 \text{ cm}^3 \text{ H}_2\text{SO}_4$ (0.01 M) v. tetraethylammonium hydroxide (0.035 M).

water and solutions containing smaller quantities of AN (mole fraction <0.5) only one end point could be discerned. As the AN content was increased two end points could be distinguished, the first due to $\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4^-$, and the second $\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$. It can be seen from Figure 2.5 that the first dissociation of H_2SO_4 is complete in water and almost negligible in anhydrous AN. This effect is accounted for by the poorer solvation in AN of the ionic species produced on dissociation, in particular the proton (see Figure 2.1). The acid strength of the bisulphate ion is markedly decreased in AN for similar reasons. The proton and SO_4^{2-} have high charge densities and transfer from water to AN is an unfavourable energy process resulting in the high pK for HSO_4^- in AN. Similar considerations apply to H_2S dissociation where H^+ and HS^- are formed in the first dissociation.

The measurement of pK's for H_2SO_4 and H_2S involved titrations with tetraethylammonium hydroxide (Et_4NOH) using a glass electrode and a SCE which had been calibrated with perchloric acid in the same solvent mixtures. Thus, liquid junction potentials due to both electrodes have been allowed for and the correct concentration of H^+ obtained. The measured values of $\log \frac{W_{\text{AN}}}{W_{\text{H}^+}}$ however, are based on the assumption that E_{LJ} is negligible. In solutions of high AN content (mole fraction ≥ 0.9) liquid junction potentials will be significant. Diggle and Parker⁷ give $E_{\text{LJ}} = 93 \text{ mV}$ in cell B based on the TATB value for $\log \frac{W_{\text{AN}}}{\gamma_{\text{Ag}^+}}$. Cell B is not the one used in

CELL B.



TEAPic = tetraethylammonium picrate

the present work, but it serves to illustrate that some uncertainties in the values of $\log \frac{W_{\text{AN}}}{\gamma_{\text{H}^+}}$ at high concentrations of AN are to be expected.

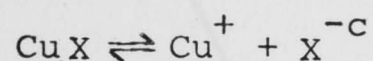
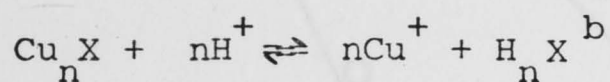
However, as will be explained in a following section, these uncertainties do not invalidate calculations made using the values of $\log \frac{W_{AN/W}}{\gamma_H^+}$ obtained.

2.2.1.4. Solubility of Cu(I) Salts

The measured solubilities of a variety of Cu(I) salts in solutions of AN and water initially containing HClO_4 (0.1M) are given in Table 2.1.

TABLE 2.1.

Measured and Predicted Solubilities^a at 25° of Cu(I) Salts in AN-Water Mixtures Initially Containing HClO_4 (0.1M).



Salt	Solubility (expressed as $\log [\text{Cu}^+]^d$)				
	Water ^e	0.1 mole fraction AN		0.26 mole fraction AN	
		Observed	Predicted	Observed	Predicted
CuCl	- 3.4	-0.5	0.3 ± 0.4	-0.7	0.4 ± 0.4
CuBr	- 4.2	-1.2	-0.7 ± 0.4	-0.6	-0.3 ± 0.4
CuI	- 6.0	-2.1	-2.5 ± 0.4	-1.6	-2.0 ± 0.4
CuSCN	- 6.5	-3.0	-3.0 ± 0.4	-2.5	-2.4 ± 0.4
CuCN	- 5.7	-2.2	-2.1 ± 0.4	-1.8	-1.4 ± 0.4
Cu_2S^f	-14.9	-8.7	-7.8 ± 0.4	-7.9	-7.0 ± 0.4

a Predicted from data in Tables 2.2 and 2.3.

b Applicable to CuCN and Cu_2S .

c Applicable to CuCl, CuBr, CuI and CuSCN.

d Units of concentration mol dm^{-3} .

e Calculated from data in Table 2.2.

f HClO_4 (0.01M) initially present; solution saturated with H_2S at a partial pressure of 0.95×10^5 pascals.

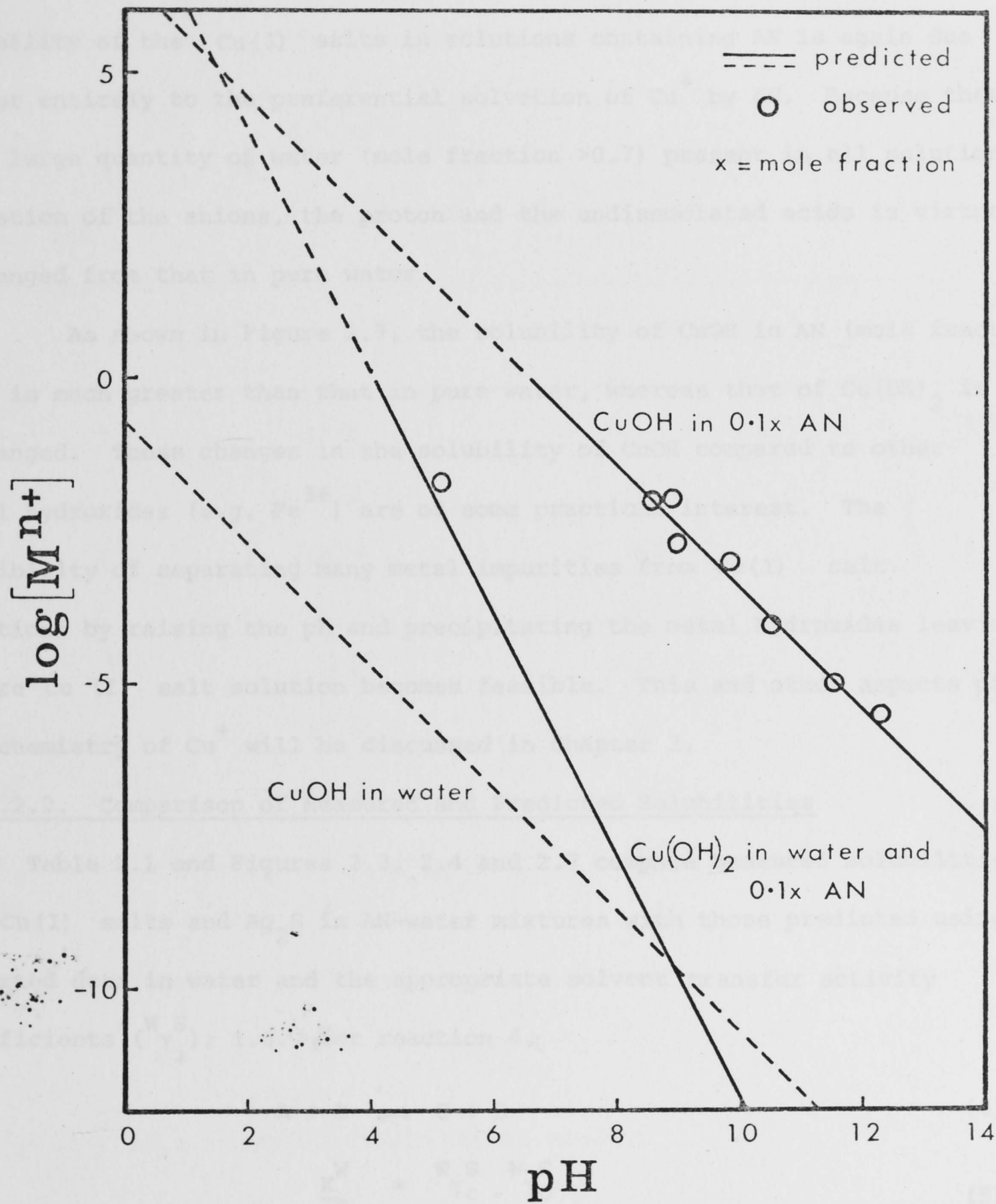


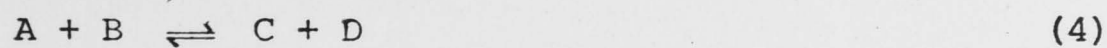
FIGURE 2.7. pH Dependence of Copper Hydroxide Solubilities in Water and Acetonitrile (mole fraction 0.1). Units of concentration mol dm^{-3} .

Figure 2.7 shows the solubilities of $\text{Cu}(\text{OH})_2$ and CuOH in water and aqueous solutions of AN (mole fraction 0.1) at various pH values. The increased solubility of the $\text{Cu}(\text{I})$ salts in solutions containing AN is again due almost entirely to the preferential solvation of Cu^+ by AN. Because there is a large quantity of water (mole fraction >0.7) present in all solutions, solvation of the anions, the proton and the undissociated acids is virtually unchanged from that in pure water.

As shown in Figure 2.7, the solubility of CuOH in AN (mole fraction 0.1) is much greater than that in pure water, whereas that of $\text{Cu}(\text{OH})_2$ is unchanged. These changes in the solubility of CuOH compared to other metal hydroxides (e.g. Fe^{3+}) are of some practical interest. The possibility of separating many metal impurities from $\text{Cu}(\text{I})$ salt solutions by raising the pH and precipitating the metal hydroxides leaving a pure $\text{Cu}(\text{I})$ salt solution becomes feasible. This and other aspects of the chemistry of Cu^+ will be discussed in chapter 3.

2.2.2. Comparison of Measured and Predicted Solubilities

Table 2.1 and Figures 2.3, 2.4 and 2.7 compare measured solubilities of $\text{Cu}(\text{I})$ salts and Ag_2S in AN-water mixtures with those predicted using reported data in water and the appropriate solvent transfer activity coefficients ($\gamma_i^{\text{W S}}$); i.e., for reaction 4,



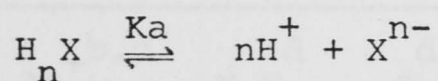
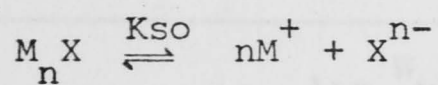
$$\frac{K^{\text{W}}}{K^{\text{S}}} = \frac{\gamma_{\text{C}}^{\text{W S}} \cdot \gamma_{\text{D}}^{\text{W S}}}{\gamma_{\text{A}}^{\text{W S}} \cdot \gamma_{\text{B}}^{\text{W S}}}, \quad (5)$$

where K^{W} and K^{S} are the equilibrium constants of reaction 4 in water and solvent S respectively. Calculations have been based on the data in water given in Table 2.2 and the solvent transfer activity coefficients listed in Table 2.3.

The solubility of a binary $\text{Cu}(\text{I})$ salt in a solution of a weak acid can be represented by equation 6. For strong acids equation 7 applies.

TABLE 2.2.

Reported⁵ Solubility Products of Cu(I), Cu(II) and Ag(I) Salts and
Dissociation Constants of Acids in Water at 25⁰.



Salt	Log K _{so}	Acid	pK _a
Cu ₂ S	-48.6	H ₂ S	7.0
Ag ₂ S	-49.2	HS ⁻	14.0
CuCN	-19.5	HCN	9.2
CuCl	-6.7	HCl	a
CuBr	-8.3	HBr	a
CuI	-12.0	HI	a
CuSCN	-13.0	HSCN	-0.85
CuOH	-14.7	H ₂ O	14.0
Cu(OH) ₂	-19.9		

a Strong acid; complete dissociation assumed.

TABLE 2.3.

Solvent Activity Coefficients^a for Transfer from Water to AN-Water Mixtures,
 $\gamma_i^{W_{AN/W}}$, of H^+ , Cu^+ , Ag^+ , H_2S , S , Cl^- , Br^- , I^- , SCN^- and HCN at 25° .

[AN] (mole fraction)	$\log \gamma_i^{W_{AN/W}}$									
	H^+ ^b	$Cu^{+b,c}$	$Ag^{+b,c}$	H_2S ^d	S ^d	Cl^- ^e	Br^- ^f	I^- ^g	SCN^- ^h	HCN ⁱ
0	0	0	0	0	0	0	0	0	0	0
0.04	0	-5.6	-1.2	-0.1	-0.2					
0.10	0	-7.0	-2.0	-0.2	-0.5	0.1	0	0	0	-0.2
0.26	0.1	-8.1	-2.5	-0.4	-1.1	0.6	0.3	0.1	0.1	-0.4
0.51	0.4	-8.5	-2.8	-0.7	-1.7					
0.75	1.2	-8.6	-2.9	-0.9	-2.1					
0.87	2.2	-8.7	-3.0	-0.9	-2.2					
0.95	3.8	-8.7	-3.0	-0.9	-2.3					
1	8.1 ^j	-9.4 ^k	-3.7 ^k	-0.9	-2.3					

a Units of concentration mol dm^{-3} .

b Based on $E_{LJ} = 0$ assumption.

c Reference 4.

d From solubility measurements, this work.

e Based on $\log \gamma_{Cl^-}^{W_{AN/W}} = 7.4$ (TATB)⁶; assuming same curve shape as $E_{LJ} = 0$ values⁴.

f Based on $\log \gamma_{Br^-}^{W_{AN/W}} = 5.6$ (TATB)⁶; as for footnote e.

g Based on $\log \gamma_{I^-}^{W_{AN/W}} = 3.3$ (TATB)⁶; as for footnote e.

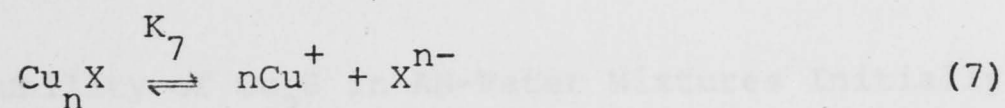
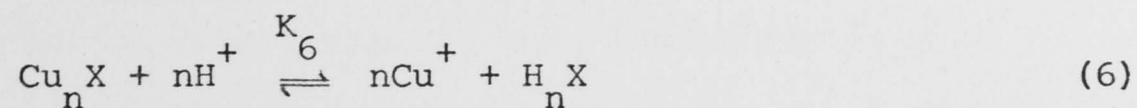
h Assumed that $\log \gamma_{SCN^-}^{W_{AN/W}} = \log \gamma_{I^-}^{W_{AN/W}}$.

i Assumed that $\log \gamma_{HCN}^{W_{AN/W}} = \log \gamma_{H_2S}^{W_{AN/W}}$.

j Reference 2 (TATB).

k $E_{LJ} = 0$ value⁴ corrected for E_{LJ} ⁷ to give TATB value.

Consider the equilibrium represented by equation 6 when $H_n X$ is saturated at



a partial pressure of 1 atmosphere:

$$\log K_6^{AN/W} = \log K_6^W + n \log \gamma_{H^+}^{AN/W} - n \log \gamma_{Cu^+}^{AN/W} \quad (8)$$

A $\log \gamma$ term for $H_n X$ is not required because solutions were saturated with $H_n X$ and therefore the latter's activity remained constant. It can be seen from equation 8 that systematic errors in values of $\log \gamma_{H^+}$ and $\log \gamma_{Cu^+}$ due to extrathermodynamic assumptions will cancel if the same assumption and experimental technique were used in their measurement. This cancellation has been facilitated where possible. Following on from equations 6 and 8,

$$\log [Cu^+] = \frac{1}{2} \log K_6^{AN/W} + \log [H^+] - \frac{1}{2} \log [H_n X]. \quad (9)$$

Data calculated using equation 9 are summarised in Table 2.4 for the solubility of Cu_2S in solutions of AN and water initially containing H_2SO_4 (0.1M) and H_2S (saturated at a partial pressure of 0.95×10^5 Pa.) Equations 6 to 9 were similarly used to calculate all of the solubilities shown in Tables 2.1 and 2.4 and Figures 2.3, 2.4 and 2.7.

It is evident from the results shown in these tables and figures that useful predictions of chemical behaviour in new environments can be made if the requisite data are available. Differences between observed and predicted solubilities may be caused in some instances by uncertainties in solubility products and dissociation constants reported for the relevant salts and acids in water. For example, reported values⁵ for the solubility product of Cu_2S in water at 25⁰, corrected to zero ionic strength, vary from $10^{-47.60}$ to $10^{-49.44}$. Similar values⁵ for Ag_2S vary from $10^{-48.07}$ to $10^{-53.98}$, while pKa's for H_2S range from 6.79 to 7.06; those for HS^- lie between 12.2 and 15.0⁵. In Table 2.1 differences between measured and

TABLE 2.4.

Calculated Data^a for the Solubility of Cu_2S in AN-Water Mixtures Initially Containing H_2SO_4 (0.1M) and H_2S (saturated at a partial pressure of 0.95×10^5 Pa.).

[AN] (mole fraction)	$\log K_6^b$	$\log [\text{H}^+]^c$	$\log [\text{H}_2\text{S}]^d$	$\log [\text{Cu}^+]^e$
0	-27.6 ^f	-0.9	-1.1	-14.1
0.04	-16.4	-0.9	-1.0	- 8.6(-7.9) ^g
0.10	-13.6	-0.9	-0.9	- 7.2(-7.1)
0.26	-11.2	-1.0	-0.7	- 6.3(-6.5)
0.51	- 9.8	-1.0	-0.3	- 5.7(-5.6)
0.75	- 8.0	-1.0	-0.2	- 4.9(-4.7)
0.87	- 5.8	-1.7	-0.2	- 4.5(-3.8)
0.95	-2.6	-2.0	-0.2	-3.2(-2.1)
1	6.0	-5.1	-0.2	-2.0(-0.6)

a Temperature 25° ; units of concentration mol dm^{-3} .

b Calculated using equation 8 and data from Table 2.3.

c Calculated from the pKa's of sulphuric acid (see Figure 2.5) and $\log K_6$.

d See Figure 2.2.

e Calculated using equation 9, estimated error ± 0.4 log units.

f Calculated from data in Table 2.2.

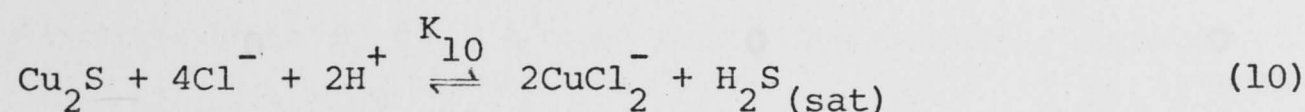
g Measured solubilities.

predicted solubilities of the Cu(I) halides may be due to formation of molecular species in solution rather than Cu (I) and halide ions. Solubility products refer to the equilibrium $\text{CuX} \rightleftharpoons \text{Cu}^+ + \text{X}^-$, so that formation of molecular species will complicate comparisons between measured and predicted solubilities.

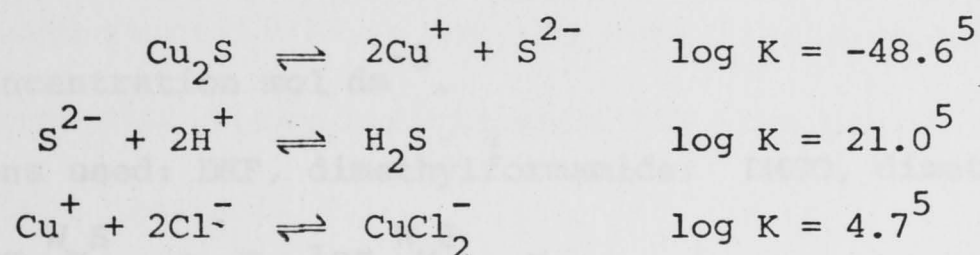
2.2.3. Equilibria Involving Copper (I).

2.2.3.1. Studies in Dipolar Aprotic Solvents

Reaction 10 has an equilibrium constant in water, K_{10}^W , of $10^{-18.2} \text{ mol}^{-3} \text{ dm}^9$.



(see calculation below). In dipolar aprotic solvents (e.g. acetone, dimethylformamide (DMF) and dimethyl sulphoxide (DMSO)) it may proceed to the right because of the increased activity of the chloride ion in these solvents (see Table 2.5). K_{10}^W was calculated from the equilibrium constants of the following reactions in water at 25° :



The following experiments were conducted in acetone, DMF and DMSO to ascertain whether Cu_2S would dissolve in solutions of H^+ and Cl^- (reaction 10). Cu_2S (0.8g), tetraethylammonium chloride (Et_4NCl) (0.1M) and H_2SO_4 (0.05M) were stirred for 2 hours in each solvent. In acetone and DMF Cu_2S was completely dissolved, albeit slowly, at room temperature (24°) under a hydrogen sulphide pressure of 0.95×10^5 Pa. Upon heating, the reaction in DMF quickly proceeded to completion, while that in acetone was still slow. This was partly due to the limited solubility of Et_4NCl in acetone. Cu_2S did not dissolve completely in DMSO and, from the measured concentration of copper in solution, an equilibrium constant for reaction 10 in DMSO, K_{10}^{DMSO} , of $10^{-1.1} \text{ mol}^{-3} \text{ dm}^9$ was deduced.

TABLE 2.5.

Solvent Activity Coefficients^a of Cl^- , H^+ and CuCl_2^- at 25° for Transfer from Water to Acetone, DMF and DMSO, $\frac{W^S}{\gamma}$.

Solvent ^b	Log $\frac{W^S}{\gamma_i}$		
	Cl^-	H^+	CuCl_2^- ^c
Water	0	0	0
Acetone	9.0 ^d	5.0 ^e	2.3 ^f
DMF	7.3 ^g	-2.5 ^h	2.6 ⁱ
DMSO	6.4	-3.3 ^h	1.0 ⁱ

a Units of concentration mol dm^{-3} .

b Abbreviations used: DMF, dimethylformamide; DMSO, dimethyl sulphoxide.

c Assuming $\log \frac{W^S}{\gamma_{\text{CuCl}_2^-}} = \log \frac{W^S}{\gamma_{\text{AgCl}_2^-}}$.

d Reference 15.

e Calculated from the pK of HCl in water and acetone⁵, $\log \frac{W^{\text{acetone}}}{\gamma_{\text{Cl}^-}}$ and $\log \frac{W^{\text{acetone}}}{\gamma_{\text{HCl}}}$ (assuming $\log \frac{W^{\text{acetone}}}{\gamma_{\text{H}_2\text{S}}} = \log \frac{W^{\text{acetone}}}{\gamma_{\text{HCl}}}$). $\log \frac{W^{\text{acetone}}}{\gamma_{\text{H}_2\text{S}}}$ was found from solubility measurements.

f $\log \frac{W^{\text{acetone}}}{\gamma_{\text{AgCl}_2^-}}$ calculated from the stability constant of AgCl_2^- in water¹⁶ and acetone¹⁷, $\log \frac{W^{\text{acetone}}}{\gamma_{\text{Cl}^-}}$ and $\log \frac{W^{\text{acetone}}}{\gamma_{\text{Ag}^+}}$ 15.

g Reference 6.

h Reference 2.

i Reference 18.

Solutions of Et_4NCl (0.1M) and Cu^+ (0.1M) in the three solvents were saturated with H_2S . No precipitate formed in acetone and DMF but a black precipitate was produced in DMSO. Analysis of the remaining copper in solution confirmed the value of $10^{-1.1} \text{ mol}^{-3} \text{ dm}^9$ found for K_{10}^{DMSO} in the previous experiment. Thus in acetone and DMF, Cu(I) sulphide can be dissolved by the action of chloride ion in acidic media, whereas in DMSO only partial dissolution is effected.

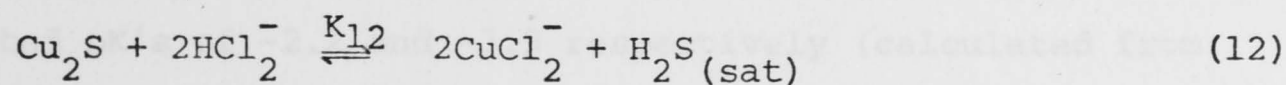
Estimates of $\log K_{10}^{\text{S}}$ in the three solvents can be made using solvent activity coefficients of Cl^- , H^+ and CuCl_2^- for transfer from water to each solvent (values are listed in Table 2.5). Equation 11 was used to gain estimates of $\log K_{10}^{\text{S}}$ which, together with experimental observations

$$\log K_{10}^{\text{S}} = \log K_{10}^{\text{W}} + 4 \log \gamma_{\text{Cl}^-}^{\text{WS}} + 2 \log \gamma_{\text{H}^+}^{\text{WS}} - 2 \log \gamma_{\text{CuCl}_2^-}^{\text{WS}} \quad (11)$$

of reaction 10, are shown in Table 2.6. It can be seen that experimental observations are consistent with the predicted equilibrium constants.

However, in acetone reaction 10 is not the most likely to occur where the high activities of the proton and chloride ion (see Table 2.5) make HCl_2^- a more appropriate reactant.

Reaction 12 is more likely to be relevant in acetone. The pK of HCl in acetone measured by Everett and Rasmussen¹⁹ is approximately 8.5 and



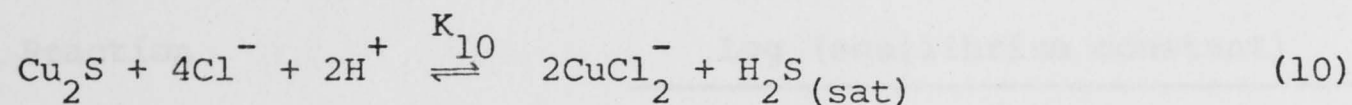
the formation constant of HCl_2^- in acetone has been assumed to equal that in AN, i.e. $10^{2.23} \text{ mol}^{-2} \text{ dm}^6$ ¹³. The pK of HCl in AN (8.94)¹³ is similar to that in acetone (8.5) and the activity of Cl^- in both solvents is similar ($\log \gamma_{\text{Cl}^-}^{\text{AN}} = 7.4$ ⁶ and $\log \gamma_{\text{Cl}^-}^{\text{acetone}} = 9.0$ ¹); therefore a similar constant for the formation of HCl_2^- in both solvents is expected. These values enable the equilibrium constant of reaction 13 in acetone to be evaluated as



$10^{21.46} \text{ mol}^4 \text{ dm}^{-12}$, and combining this with K_{10} gives a value for K_{12} of $10^{-0.36} \text{ mol} \text{ dm}^{-3}$. In DMF and DMSO HCl is still a relatively strong

TABLE 2.6.

Estimated^a Values of Log K_{10} in Acetone, DMF^b and DMSO^b at 25° and Experimental Observations on Reaction 10.



Solvent	Log K_{10} (estimated) (mol ⁻³ dm ⁹)	Experimental observations
Acetone	21.1	Slow dissolution of Cu_2S .
DMF	1.9	Complete dissolution of Cu_2S .
DMSO	- 1.7	Incomplete dissolution of Cu_2S ; $\log K_{10} = -1.1$ (experimental).

a See text

b Abbreviations as in Table 2.5.

acid with estimated pK's of -2.2 and -3.9 respectively (calculated from the pK of HCl in water, i.e. -7⁵, $\log \gamma_i^{\text{W S}}$ values for Cl^- and H^+ given in Table 2.5, and $\log \gamma_{\text{HCl}}^{\text{W S}} = -1$). Thus, in DMF and DMSO reaction 10 is still appropriate.

2.2.3.2. Equilibria in Mixtures of Acetonitrile and Water

Having demonstrated the reliability of predictions made for a variety of equilibria using solvent transfer activity coefficients, equilibrium constants for many reactions can be confidently predicted. Table 2.7 contains a number of reactions and their equilibrium constants in water and in solutions containing AN (mole fraction 0.1 and 0.26). Constants for

TABLE 2.7.

Equilibrium Constants^a of Reactions in Water and AN-Water Mixtures at 25°.

Reaction	Log (equilibrium constant)		
	Water	AN(0.1x) ^a	AN(0.26x)
$\text{Cu}_2\text{S}_{(s)} + 2\text{H}^+ \rightleftharpoons 2\text{Cu}^+ + \text{H}_2\text{S}_{(sat)}$	-27.6	-13.6	- 9.8
$\text{Cu}_2\text{S}_{(s)} + \text{Cu}^{2+} \rightleftharpoons \text{CuS}_{(s)} + 2\text{Cu}^+$	-13.4	0.6	2.8
$\text{CuCN}_{(s)} + \text{H}^+ \rightleftharpoons \text{Cu}^+ + \text{HCN}_{(sat)}$	-10.3	- 3.3	- 2.1
$\text{CuN}_3_{(s)} + \text{H}^+ \rightleftharpoons \text{Cu}^+ + \text{HN}_3_{(sat)}$	- 3.6	3.4	4.2
$\text{CuOH}_{(s)} + \text{H}^+ \rightleftharpoons \text{Cu}^+ + \text{H}_2\text{O}$	- 0.7	6.6	7.7
$2\text{CuOH}_{(s)} + \text{Cu}^{2+} \rightleftharpoons \text{Cu}(\text{OH})_2_{(s)} + 2\text{Cu}^+$	- 9.5	4.5	6.7
$\text{Ag}_2\text{S}_{(s)} + 2\text{H}^+ \rightleftharpoons 2\text{Ag}^+ + \text{H}_2\text{S}_{(sat)}$	-28.2	-24.2	-23.0
$\text{Cu}(\text{OH})_2_{(s)} + 2\text{H}^+ \rightleftharpoons \text{Cu}^{2+} + 2\text{H}_2\text{O}$	8.1	8.2	8.6

a x = mole fraction.

reactions in water were calculated from recorded data^{5,20}, while those in AN-water mixtures were calculated from the equilibrium constants in water and values of $\log \frac{W_{AN/W}}{\gamma_i}$ described previously. Equilibria involving the Cu (I) ion show marked changes upon addition of small quantities of AN, while those involving only ions preferentially solvated by water (e.g. H^+ , Cu^{2+}) are slightly affected.

2.3. References

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CHAPTER 3

COPPER (I) IN MINERAL CHEMISTRY, ORGANIC
CHEMISTRY, AND BIOLOGICAL CHEMISTRY

The area of mineral chemistry is the field of most relevance to results of the work previously described. Chemical reactions useful for the recovery and refining of copper have been described and these could have industrial applications. Chemical engineering aspects of the development of these processes, such as optimization of conditions and process costing, have not been dealt with as they are outside the scope of this thesis. The chemistry described is not an exhaustive account of all possible useful reactions but merely exemplifies its applicability.

The role of the $Cu(I)$ ion and its complexes in organic chemical catalysis and in biochemistry is briefly outlined here to demonstrate further useful applications of the inorganic chemistry described in this work. The ability of a scientist to see applications for his results

3.1. Introduction

Acquisition of new knowledge has been a popular and well supported aspect of Man's endeavours for centuries. Until recently there has been no undue pressure on university research workers to produce results which are seen to be "useful" by the organizations which support "academic" research. Even the "man in the street" appears to have been unconcerned about the "usefulness" or otherwise of research carried out in universities and similar institutions. This situation is rapidly changing due to a number of factors. The size of the Earth's human population has finally reached the point where thinking people can see the finiteness of many of our important resources (e.g. crude oil, arable land). Industrialised nations are finding that they have less resources (expressed in terms of money) at their disposal. Consequently any activity requiring a significant sum of money for its operation is being more closely scrutinised in terms of its benefits to a community. So-called "academic" research is such an activity. Thus this chapter suggests possible applications of some of the academic research described in the previous chapters.

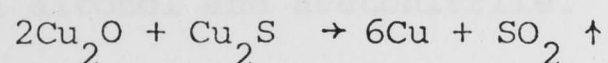
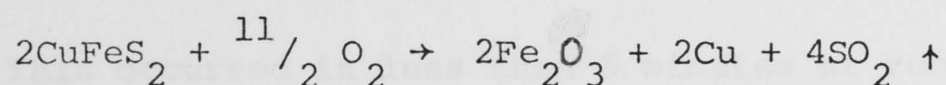
The area of mineral chemistry is the field of most relevance to results of the work previously described. Chemical reactions useful for the recovery and refining of copper have been described and these could have industrial applications. Chemical engineering aspects of the development of these processes, such as optimisation of conditions and process costing, have not been dealt with as they are outside the scope of this thesis. The chemistry described is not an exhaustive account of all possible useful reactions but merely exemplifies its applicability.

The role of the Cu(I) ion and its complexes in organic chemical catalysis and in biochemistry is briefly examined here to demonstrate further useful applications of the inorganic chemistry described in this work. The ability of a scientist to see applications for his results

outside his own specialised branch of science is increasing in importance as the popularity of interdisciplinary research grows.

3.2. Cu⁺ in Mineral Chemistry

In recent years the opinion has been expressed^{1,2} that the recovery of metals by pyrometallurgical techniques (e.g. smelting) is becoming less acceptable in terms of atmospheric pollution and, to a lesser extent, in terms of consumption of large quantities of crude-oil products used in the firing of some smelters and furnaces. The major pollution problem involves the production of large amounts of sulphur dioxide during blast furnace operations, e.g.

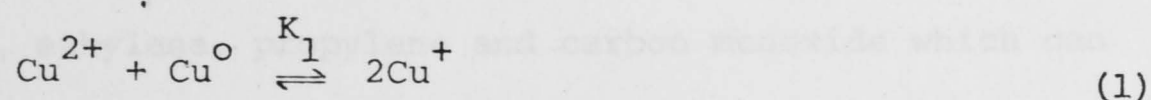


Alternative methods for the recovery and processing of metals such as copper have been investigated and, in some cases, applied. For example, a commercial plant for the recovery and refining of copper using a liquid ion exchange process has been in successful operation since 1968³. Also, an ammine carbonate system has been used to obtain copper from a variety of scrap materials in a small plant which began operating in 1959⁴. Leaching using an ammoniacal ammonium carbonate solution at 49 - 60°C has been employed. Here two-thirds of the copper in solution is in the Cu(I) form.

3.2.1. Copper Recovery using Cu(I) Salt Solutions

3.2.1.1. Production of Cu(I) Salt Solutions

The stabilisation of Cu⁺ relative to Cu²⁺ afforded by many of the ligands studied in chapter 1 increases the oxidising power of the aquated Cu(II) ion in solutions containing these ligands. Table 3.1 shows the effect of added ligands on reaction 1. Log K, in each aqueous ligand



solution, S, was calculated from that in water, $\log K_1^W$, and the solvent activity coefficient, γ , of Cu^+ and Cu^{2+} for transfer from water to the new medium, as shown in equation 2. Log γ values were calculated from data

$$\log K_1^S = \log K_1^W + \log \gamma_{\text{Cu}^{2+}}^{WS} - 2 \log \gamma_{\text{Cu}^+}^{WS} \quad (2)$$

contained in Tables 1.1 and 1.2 of chapter 1. It can be seen from Table 3.1 that all of the ligands cause reaction 1 to be reversed enabling copper metal to be dissolved at diffusion controlled rates⁶ by Cu^{2+} .

Solutions containing CuSO_4 (0.1M), enough H_2SO_4 to give a pH of 2 to 3, and the appropriate ligand (see Table 3.1) were stirred with copper powder (-100 mesh, in excess) until the blue colour of the Cu(II) ion disappeared. This occurred in less than 5 minutes at room temperature with Cl^- , Br^- , allyl alcohol and acetonitrile. Solutions containing the gaseous ligands at atmospheric pressure decolourised more slowly due mainly to their low solubility in water. The solubility of propylene in water at 21.1° and 149.6×10^3 Pa is $9.2 \times 10^{-3} \text{ mol dm}^{-3}$ ⁷, and the solubility of ethylene in 5% aqueous H_2SO_4 at room temperature and a pressure of 0.95×10^5 Pa was measured and found to be $3.7 \times 10^{-3} \text{ mol dm}^{-3}$.

The production of copper from waste materials (e.g. copper wire, radiator scrap) using solutions of Cu^{2+} and the ligands contained in Table 3.1 is an application of the chemistry described in this thesis. This process is important in terms of the increasing need to recycle copper rather than rapidly deplete the world's reserves of copper ores. Pure copper can be obtained from resulting Cu(I) salt solutions by (a) removal of the ligand to produce Cu^0 and Cu^{2+} (b) hydrogen reduction and (c) electrodeposition at a cathode.

3.2.1.2. Disproportionation of Cu (I) Salt Solutions

The disproportionation process is amenable to ligands like allyl alcohol, acetonitrile, ethylene, propylene and carbon monoxide which can be distilled from Cu(I) salt solutions by heating or by pressure

TABLE 3.1

Equilibrium Constant ($\log K_1$ mol dm⁻³) of the Reaction $\text{Cu}^{2+} + \text{Cu}^0 \rightleftharpoons 2\text{Cu}^+$ in Aqueous Solutions of Various Ligands at 25°.

Ligand ^a	$\log \frac{W_S}{\gamma_{\text{Cu}^{2+}}}$ ^b	$\log \frac{W_S}{\gamma_{\text{Cu}^+}}$ ^b	$\log K_1$
Water	0	0	-6.0 ^d
Cl ^{-d}	0	-6.0	6.0
Br ^{-d}	0	-7.2	8.4
AA ^d	0	-4.3	2.6
AN ^d	0	-4.8	3.6
Propylene ^e	0	-3.2	0.4
Ethylene ^e	0	-4.0	2.0
CO ^e	0	-4.5	3.0

a Abbreviations as in Table 1.1, chapter 1.

b From Tables 1.1 and 1.2, chapter 1.

c Reference 5.

d Concentration, 2 mol dm⁻³.

e Pressure, 4.75×10^5 Pa.

reduction. Cl^- and Br^- are unsuitable for distillation of course. Allyl alcohol and acetonitrile both form constant boiling mixtures with water; an azeotrope containing allyl alcohol (72.3%) boils at 87.5° ⁸ while one containing acetonitrile (83% W/W) boils at 76.5° ⁹. To obtain copper powder and not Cu_2O by disproportionation of the Cu(I) ion, ($[\text{Cu}^+] > 0.1\text{M}$), distillations must be carried out at $\text{pH} < 2.5$. However, Cu(I) salt solutions containing allyl alcohol consumed acid. An aqueous solution of CuSO_4 (0.1M), allyl alcohol (2M) and enough HClO_4 to give a pH of 2 to 3 was stirred with excess copper powder. A clear solution was initially obtained which became opaque and orange in colour at a pH of 5; lowering the pH below 4 restored a clear colourless solution. Consumption of acid had caused the precipitation of Cu_2O (orange colour). It appeared that allyl alcohol or, more likely, its complex with Cu^+ had reacted to consume acid. (It is known that H_2SO_4 can add across double bonds). If allyl alcohol were reacting, it would be unsuitable as a competitive ligand for Cu^+ in industrial processes as losses would prove uneconomic. Acetonitrile is more suitable because its only chemical loss is due to hydrolysis in acid solution at a rate which would cause a 16% loss in two years at 50° ⁹.

Ethylene, propylene and carbon monoxide are most amenable to the disproportionation reaction. In 1939 a patent was taken out covering their use for the processing of copper¹⁰ but detailed studies were not reported until kinetic measurements were recently taken on a coppery-recovery process using carbon monoxide¹¹. The removal of the three gases from solution by distillation is a facile process. However, in view of their limited solubility in water, the concentrations of Cu^+ which could be obtained in aqueous solutions were of some interest. Thus, acidified solutions of CuSO_4 were saturated with ethylene at atmospheric pressure and stirred with an excess of copper powder (-100 mesh) for 1 hour. The concentrations of Cu^+ and Cu^{2+} in the resulting solutions are given in Table 3.2. A

TABLE 3.2.

Cu(I) and Cu(II) Ion Concentrations in Aqueous Acidic Solutions^a
Saturated with Ethylene at Atmospheric Pressure^b.

$[\text{Cu}^{2+}]$ (mol dm ⁻³)	$[\text{Cu}^+]$ (mol dm ⁻³)
0.21	0.14
0.37	0.17
0.41	0.19

a. Initial $[\text{H}_2\text{SO}_4] = 0.3 \text{ mol dm}^{-3}$; temperature 25° .

b $0.95 \times 10^5 \text{ Pa}$.

solution containing Cu^+ (1.25 mol dm^{-3}) and Cu^{2+} (1.37 mol dm^{-3}) was obtained by agitating an aqueous solution (100cm^3) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (50g) and H_2SO_4 (10g) with acid-washed copper powder (-300 mesh, 10g) in a PAAR pressure reaction apparatus for 1 hour in the presence of ethylene ($4.75 \times 10^5 \text{ Pa}$). Steam distillation of the Cu(I) salt solutions yielded 3.9g of copper powder. Thus, industrially acceptable Cu(I) salt solutions can be obtained at moderate ethylene pressures. Analysis of Cu(I) sulphate solutions containing ethylene ($0.95 \times 10^5 \text{ Pa}$) showed that an ethylene to Cu^+ molar ratio of 1.5 to 1 is sufficient to stabilise a 0.1 molar solution of Cu_2SO_4 (see Figure 3.1). Figure 3.2 shows a simplified flow diagram for a process utilising the materials and principles described above. It is informative to note that in theory the

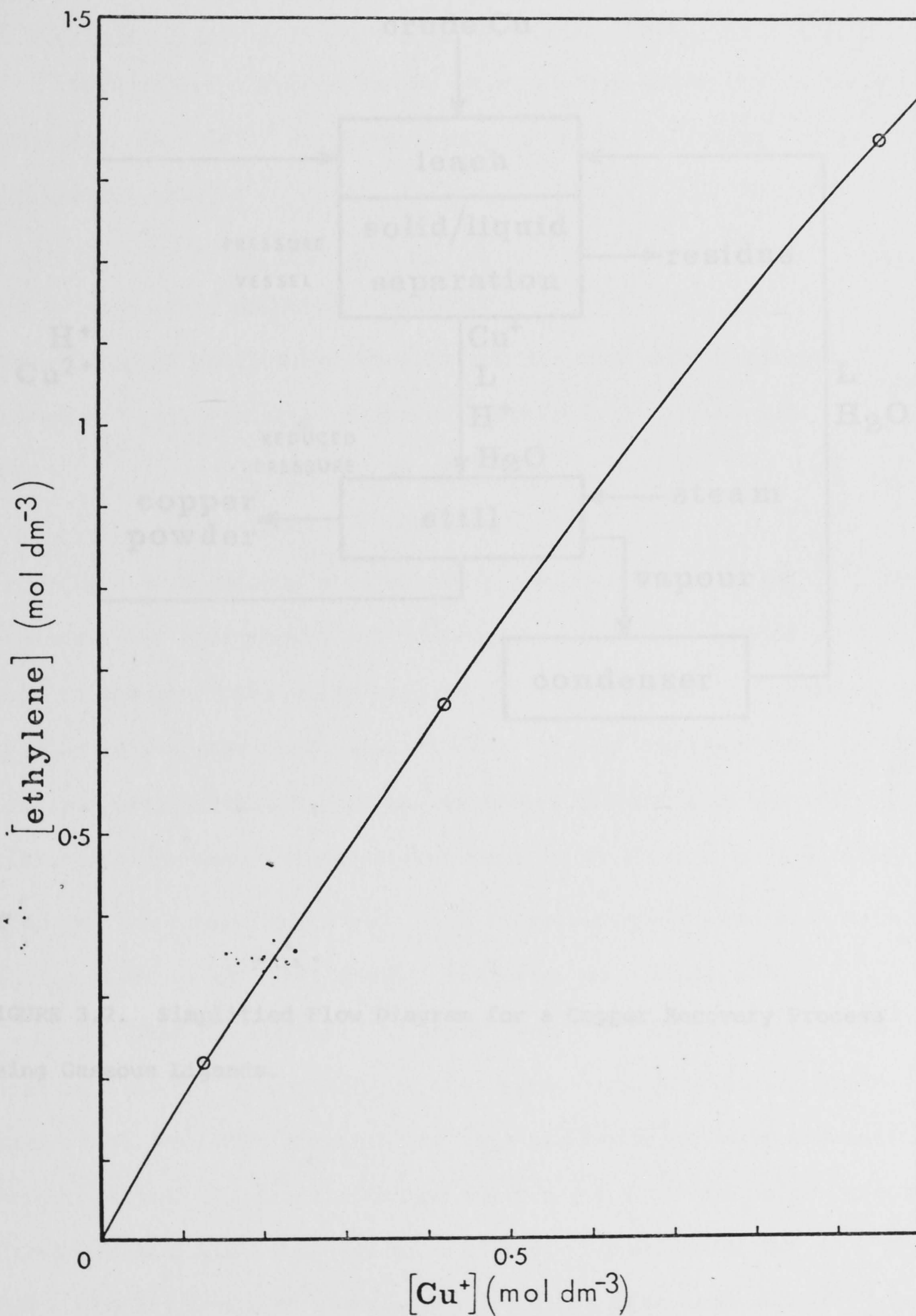


FIGURE 3.1. Solubility of Ethylene^a in Acidified^b Cu(I) Sulphate Solutions at 25°.

a Pressure 0.95×10^5 Pa.

b Initial $[H_2SO_4] = 0.3 \text{ mol dm}^{-3}$.

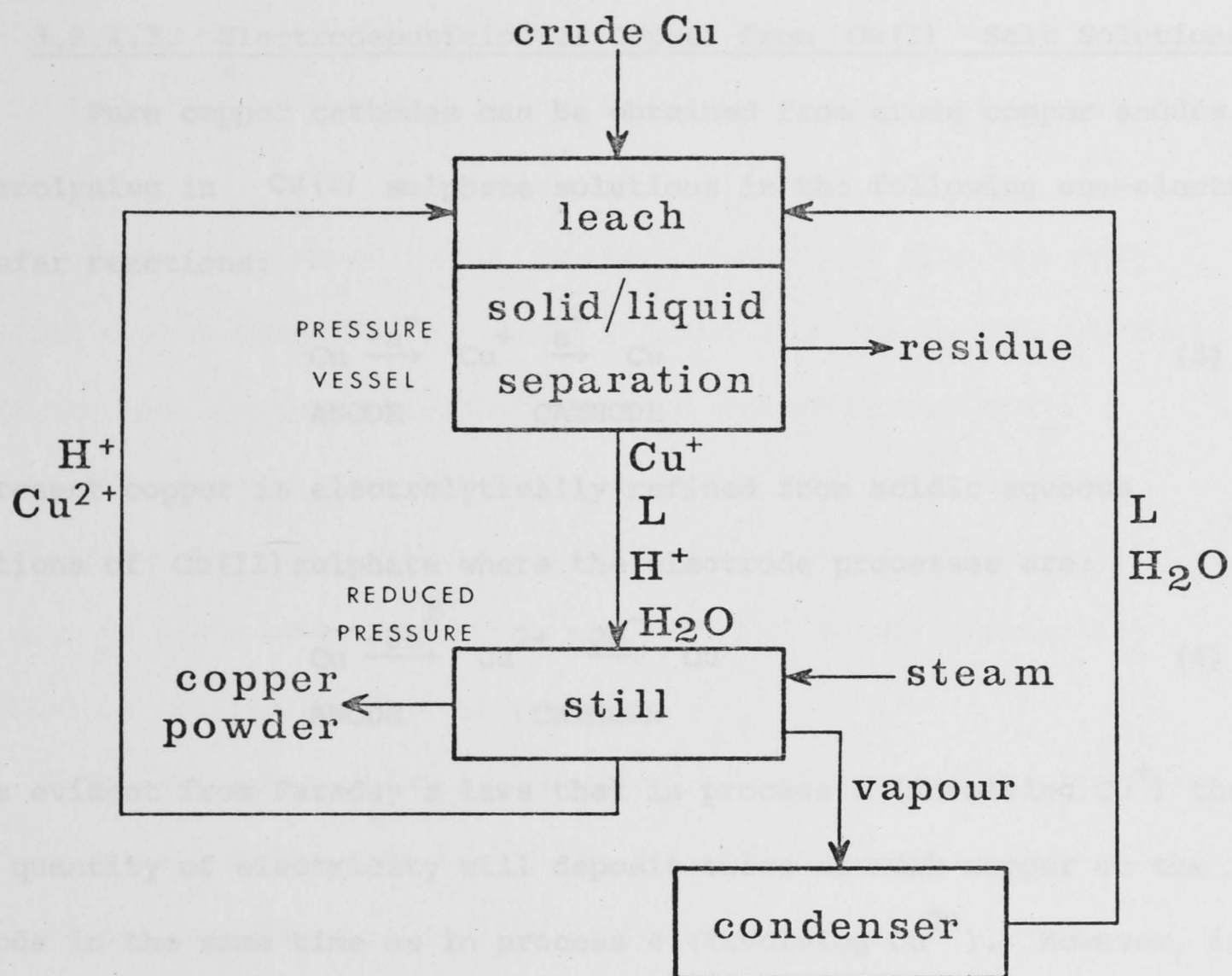
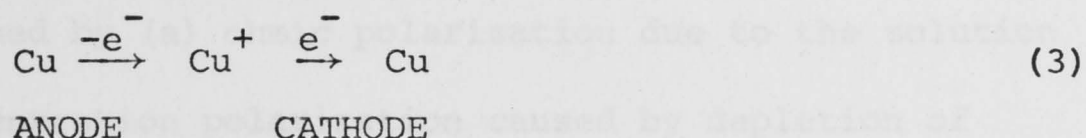


FIGURE 3.2. Simplified Flow Diagram for a Copper Recovery Process using Gaseous Ligands.

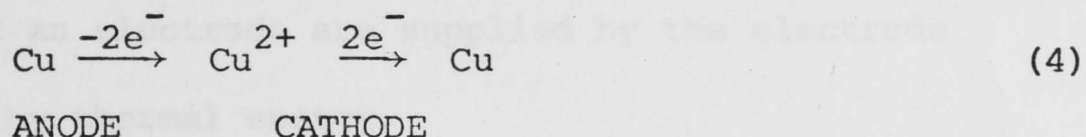
only materials consumed are steam and crude copper; leaching materials would be recycled.

3.2.1.3. Electrodeposition of Copper from Cu(I) Salt Solutions

Pure copper cathodes can be obtained from crude copper anodes by electrolysing in Cu(I) sulphate solutions in the following one-electron transfer reactions:



At present copper is electrolytically refined from acidic aqueous solutions of Cu(II) sulphate where the electrode processes are:



It is evident from Faraday's laws that in process 3 (involving Cu^+) the same quantity of electricity will deposit twice as much copper on the cathode in the same time as in process 4 (involving Cu^{2+}). However, in still electrolyte solutions, significantly higher voltages were encountered with process 3. Thus, measurements of electrode potentials in acidified nitrile-water mixtures were made in an attempt to understand the reasons for the higher voltages. Similar measurements were also made in acidified mixtures of allyl alcohol and water as a comparison.

Two planar electrodes of copper (purity > 99.9%, area 25 cm^2 , separation 2.54 cm) were placed in the appropriate solutions contained in a beaker (400 cm^3). The potential of each electrode was measured against a saturated calomel electrode situated equidistant from the copper electrodes. Constant currents were supplied by a Hewlett-Packard Model No. 6226 B power supply. Freshly prepared electrolyte solutions were used and were protected from the atmosphere by a film of paraffin oil or a plastic film covering the top of the beaker, thus minimising evaporative losses and oxidation of Cu^+ to Cu^{2+} . Readings were taken when steady potentials had been obtained.

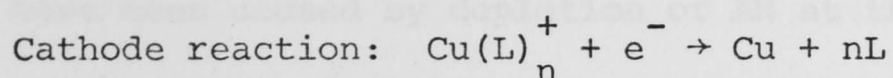
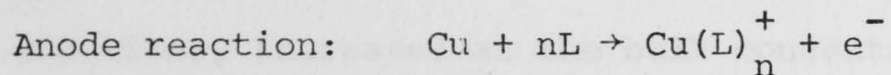
Table 3.3 summarises the data obtained. Electrode polarisations given were found by subtracting the rest potential of each electrode (the potential obtained with no applied external emf) from the potentials exhibited when a current of 0.5A was impressed on the cell (working potential).

In an electrolysis cell, voltage deviations from the rest potential may be caused by (a) ohmic polarization due to the solution resistance, (b) concentration polarization caused by depletion of electroactive species near electrode surfaces, and (c) activation polarization. The activation energies required for electrochemical processes to occur at an electrode are supplied by the electrode potential as well as by thermal energy.

The resistance of all solutions between the copper electrodes at the rest potential was less than 0.01 ohm. Thus, contributions to polarisation from this source will be insignificant. In stirred electrolyte solutions concentration polarization is minimised although thin diffusion layers still exist near electrode surfaces¹². Thus, the polarisation of both electrodes in stirred solutions is probably due to activation polarisation. As the concentrations of acetonitrile and allyl alcohol increased (Table 3.3), the anode polarisations increased in a positive direction, the cathode polarisations in a negative direction. Potentials characterising reactions at polarised metal electrodes often include contributions from (a) electron transfer, (b) surface diffusion of ions or atoms, (c) atomic or electronic rearrangement, (d) adsorption or desorption, and (e) reaction of ions with the solvent (e.g. solvation) or with chemical species in solution. Thus, it is difficult to pinpoint the particular process, or processes, causing the electrode polarisations in stirred solutions shown in Table 3.3. However, the stripping of solvent molecules from Cu(I) ions at the cathode is one process likely to contribute to activation polarisation in the electrolytes studied.

TABLE 3.3.

Polarization of Copper Electrodes during Electrolysis^a in Electrolytes^b
Containing Acetonitrile and Allyl Alcohol.



L = acetonitrile (AN) or allyl alcohol (AA)

Electrolyte ^b		Anode polarisation (mV) ^c		Cathode polarisation (mV) ^c	
[AN] mole fraction	[AA] mole fraction	Stirred solution	Still solution	Stirred solution	Still solution
		60	65	-105	-133
0.13		87	140	- 86	-161
0.22		117	158	-117	-181
0.34		194	211	-189	-262
	0.04	66	84	- 61	-102
	0.10	88	106	- 74	-113
	0.18	114	133	- 87	-135
	0.28	205	232	-153	-185

a Temperature 26^o, current 0.5A (current density 200 A m⁻²).

b All electrolytes contained H₂SO₄ (1.9M) and Cu⁺ (0.31M) except where otherwise stated.

c Change from the rest potential.

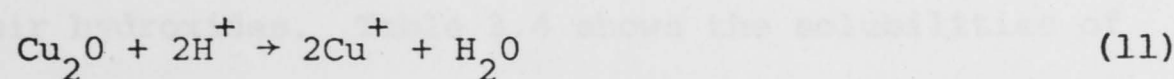
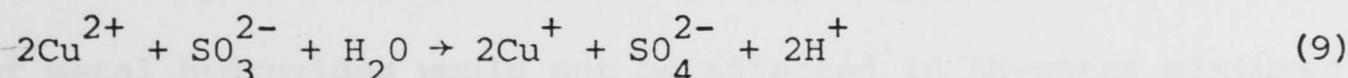
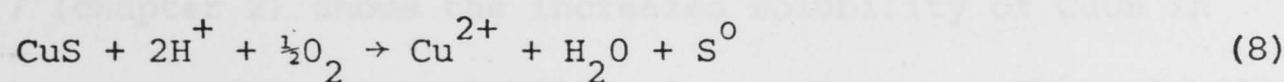
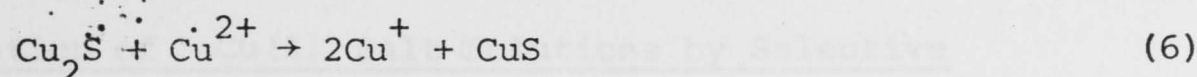
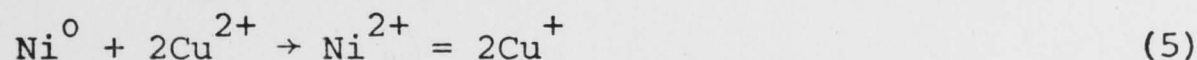
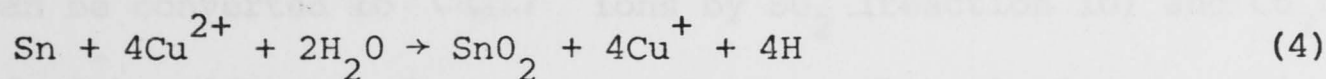
d Aqueous CuSO₄ solution ([Cu²⁺] = 0.63M).

Increased polarisation of both electrodes was found in still solutions containing acetonitrile and allyl alcohol and was probably caused by concentration polarization. The greater anode polarisation in still solutions containing acetonitrile, compared with that in stirred solutions, increased as the bulk concentration of AN decreased. This may have been caused by depletion of AN at the anode. In an aqueous solution containing AN (mole fraction 0.13) only 1 molecule in 6 is AN. In the aqueous Cu(II) sulphate solution, a large increase in anode potential in a still solution was not observed, as an abundance of water molecules was always present. Thus, to achieve potentials comparable to those in the aqueous system, stirring of electrolytes containing acetonitrile would be necessary.

3.2.2. The Use of Organic Nitriles in Copper Processing

Parker and co-workers have carried out extensive studies in this field^{9,13} and some work has been the subject of patent applications^{14,15}.

Reactions 4 to 11 represent some of the processes studied. In all



reactions, acidified solutions of water and an organic nitrile are used at 25 to 50° to produce a Cu(I) salt solution (reaction 8 is exceptional in that a Cu(II) salt solution is obtained).

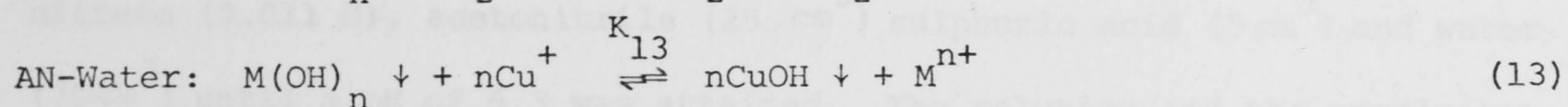
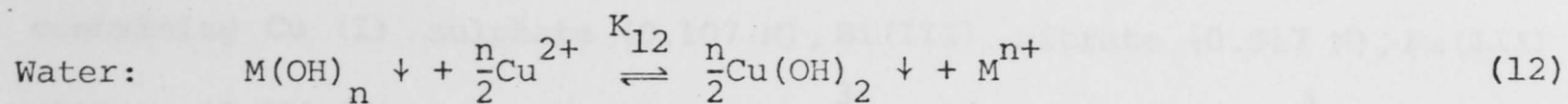
Reaction 4 could be used for removal of tin from tinned copper scrap leaving pure copper, and producing a Cu(I) salt solution from which copper could be recovered. Reaction 5 would facilitate the separation of copper from nickel-copper mattes producing a NiSO_4 solution suitable for further processing to nickel metal. Reaction 5 was also shown to proceed in a solution containing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (12.5 g), sulphuric acid (2.5 cm^3), allyl alcohol (10 cm^3) and water (37.5 cm^3). Nickel powder (-100 mesh, 1 g) was dissolved by the above solution after 30 minutes' stirring at 24° . The leaching of Cu_2S (chalcocite) and CuS (covellite) is represented by equations 6, 7 and 8, the latter representing a process in which Cu^{2+} catalyses the reaction of sulphuric acid and oxygen with covellite. As Cu^+ is formed it is oxidised by oxygen to Cu^{2+} with the consumption of acid, thus avoiding the reaction of Cu^+ with sulphur which complicates reaction 4⁹. Cu(II) salt solutions from a variety of sources can be converted to pure copper powder via Cu(I) salt solutions if salts of sulphurous acid are used as reductants in equations 9 and 10. Oxidised copper ores can be converted to Cu(I) ions by SO_2 (reaction 10) and Cu_2O can be leached with acid to produce a pure Cu(I) salt solution (reaction 11).

3.2.3. Purification of Cu(I) Salt Solutions by Selective Precipitation of Hydroxides.

Figure 2.7 (chapter 2) shows the increased solubility of CuOH in AN-water mixtures compared to its solubility in pure water. The solubility of many other metal hydroxides would not be affected in AN-water mixtures, so that metal impurities might be removed from Cu(I) salt solutions by precipitation of their hydroxides. Table 3.4 shows the solubilities of some metal hydroxides in water and in solutions containing acetonitrile (mole fraction 0.1 and 0.26). Experiments were carried out in AN-water mixtures to determine whether reasonable separations could be achieved in practice where problems, such as co-precipitation and mixed salts, could be expected.

TABLE 3.4.

Solubilities of Metal Hydroxides in Water and AN-Water Mixtures at 25°.



Metal M^{n+}	Log K_{so}^a of	Log K_{12} (Water)	Log K_{13}	
	M(OH)_n in Water		AN(0.1x) ^{b,c}	AN(0.26x) ^{c,d}
Cu^{2+}	-19.32	0	- 3.92	- 6.12
Cu^+	-14.7	- 5.04 ^e	0	0
Fe^{2+}	-15.82	3.5	- 0.42	- 2.62
Fe^{3+}	-36.85	- 7.87	-13.75	-17.05
Sn^{2+}	-28.1	- 8.78	-12.7	-14.9
Ni^{2+}	-15.5	3.82	- 0.1	- 2.3
Sb^{3+}	-41.4	-12.42	-18.3	-21.6
Bi^{3+}	-30.37	- 1.39	- 7.27	-10.57
Zn^{2+}	-16.5	2.82	0.9	- 1.3

a K_{so} = solubility product⁵.

b x = mole fraction ; $\log \gamma_{\text{Cu}^+} = -7.0$ (see Figure 2.1, chapter 2).

c $\log \gamma_{\text{M}^{n+}} \sim 0$.

d $\log \gamma_{\text{Cu}^+} = -8.1$ (see Figure 2.1, chapter 2).

e Hypothetical, Cu^+ disproportionates in water.

Experiment 1.

Sodium hydroxide pellets were added to a solution initially containing Cu (I) sulphate (0.107 M), Bi(III) nitrate (0.017 M), Fe(III) nitrate (0.011 M), acetonitrile (25 cm³) sulphuric acid (5 cm³) and water (70 cm³) until a pH of 6.3 was attained. The solution and the precipitate which had formed were analysed for Cu, Bi and Fe to give the following results:

Solution: [Cu]	0.098 M	Precipitate: Cu	0.057 g
[Bi]	0*	Bi	0.355 g
[Fe]	0*	Fe	0.061 g

* Not detected, i.e. $< 10^{-5}$ M.

Experiment 2.

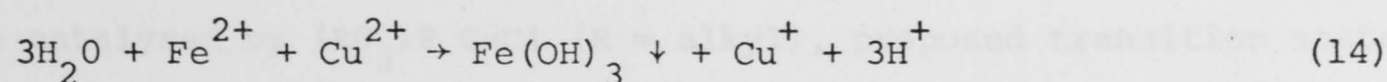
This was the same as experiment 1 except that the initial solution contained Cu⁺ (0.017 M), Bi³⁺ (0.015 M), Fe³⁺ (0.011 M), H₂SO₄ (5 cm³), AN (25 cm³) and water (70 cm³). Analysis of the precipitate and the solution at pH 6.3 gave the following results:

Solution: [Cu]	0.0154 M	Precipitate: Cu	0.01 g
[Bi]	0*	Bi	0.314 g
[Fe]	0*	Fe	0.061 g

* Not detected, $< 10^{-5}$ M.

8.4 and 9.4% of the copper was precipitated in experiments 1 and 2 respectively. Studies on the optimisation of this process are beyond the scope of this thesis; however, by redissolving the copper contained in the precipitate, and again raising the pH to 6.3, a total of 99% of the original copper present would be obtained in a pure Cu(I) salt solution. Also, increasing the amount of acetonitrile in the initial impure solution would help to retain Cu⁺ in solution.

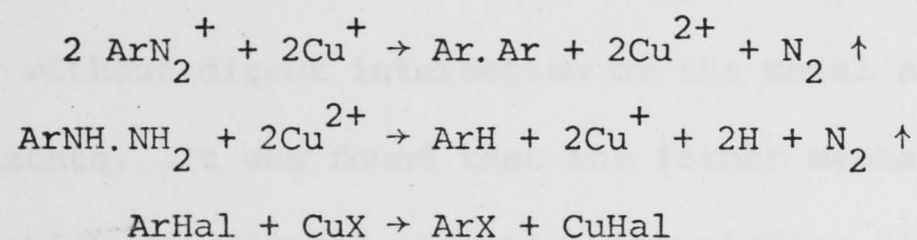
Reaction 14 was found to proceed in a solution of AN and water whose



pH was between 3 and 6. Cu(II) oxide (0.8 g) and $\text{FeSO}_4 \cdot 2\text{H}_2\text{O}$ (1.9 g) were added to a mixture of AN (25 cm^3) and water (75 cm^3). The resulting mixture was stirred in a closed vessel at 40° for 110 minutes at which time the solution contained copper (0.06 M) and iron (0.05 M) at a pH of 3.2. CaCO_3 was added raising the pH to 6.2. After a further 10 minutes the solution contained copper (0.1 M) and an undetectable quantity of iron ($< 10^{-5} \text{ M}$). In this experiment, separation of iron was achieved with no loss of copper through precipitation.

3.3. Compounds of Cu(I) in Organic Chemical Reactions

Copper and a variety of copper salts have been used to promote or assist many organic chemical reactions^{16,17,18}, e.g.,

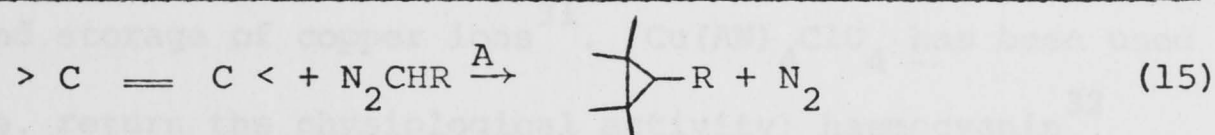


The following compounds of Cu(I) have been successfully used in organic chemical reactions: Cu(I) oxide^{19,20}, Cu(I) halides^{16,19,21}, Cu(I) acetate²², trialkylphosphite Cu(I) Cl²³, Cu(I) trifluoromethanesulphonate²⁴, $(n\text{-Bu}_2\text{S})_2 \text{Cu} \text{I}$ ²⁵, and (heterocyclic amine)Cu(I) perchlorates²⁶. Some reactions apparently promoted by copper metal or Cu(II) salts are now thought to involve Cu^+ as the actual catalyst^{19,24,27}. Bacon and Hill¹⁸, in a review of copper-promoted reactions of aromatic molecules (published in 1965), stated that "the relative energies of the oxidation states of the metal, and the type and stability of the complexes which it forms in its different oxidation states are highly relevant to copper-promoted aromatic reactions", and "the stability of Cu(I) complexes has been little studied, either in aqueous or non-aqueous solution and would repay investigation".

Moser²³, in a study of the reaction of ethyl diazoacetate and cyclohexene catalysed by $(\text{RO}_3)\text{P} \text{CuCl}$ (R = alkyl), proposed transition states

in which the Cu atom was simultaneously attached to the olefin and the carbene (carboxy-methylene). Both would be coordinated via the donation/back-donation bonding picture described for olefins and other π -acceptors in chapter 1.

A second study by Salomon and Kochi (1973)²⁴ describes cyclopropanation reactions with diazo compounds shown in equation 15. One suggested mechanism for this reaction involves the diazo compound reacting



A = benzene adduct of Cu(I) trifluoromethanesulphonate²⁸

directly with a copper-olefin complex. A second possibility involves bimolecular transfer of the carbene from a copper complex to a free olefin, with or without direct interaction of the metal and the olefin in the transition state. It was found that the former mechanism was followed by Cu(I) salts which coordinated strongly with olefins (i.e. salts with a weakly coordinating anion such as ClO_4^- and BF_4^-). Here, the relative stabilities of the copper-olefin complexes determined the olefin selectivity of these catalysts. The second mechanistic pathway was followed when Cu(I) catalysts which did not coordinate strongly to olefins (i.e. salts with a strongly coordinating anion such as Cl^- and Br^-) were used. Thus, in a mixture of olefins, Cu(I) catalysts of the first kind preferentially cyclopropanated the least substituted olefin (i.e. the one forming the strongest complex with Cu^+), while those of the second kind favoured reaction with the most highly substituted olefin.

Thus, knowledge of the stabilities of Cu(I) complexes, and the nature and number of ligands coordinated to Cu^+ , can be useful in choosing the most suitable Cu(I) compound to catalyse a particular reaction. Work described in chapter 1 of this thesis is therefore relevant. Also, as non-aqueous solvents are commonly used for the above reactions, data in such solvents can be obtained from aqueous data and the appropriate solvent transfer activity coefficients as demonstrated in chapter 2.

3.4 Cu(I) in Biological Chemistry

It is well known that trace amounts of many metals are essential for life^{29,30}. Metals such as copper are necessary for the proper functioning of many enzymes, the natural catalysts whose activity is linked to all physiological functions²⁹. Copper enzymes are involved in functions such as electron transfer reactions (e.g. ascorbic acid oxidase, cytochrome c oxidase, tyrosinase), the transport of oxygen molecules (e.g. haemocyanin) and the transport and storage of copper ions³¹. $\text{Cu}(\text{AN})_4\text{ClO}_4$ has been used to reconstitute (i.e. return the physiological activity) haemocyanin³² indicating that the Cu (I) state of copper is probably involved in this oxygen-binding protein³³.

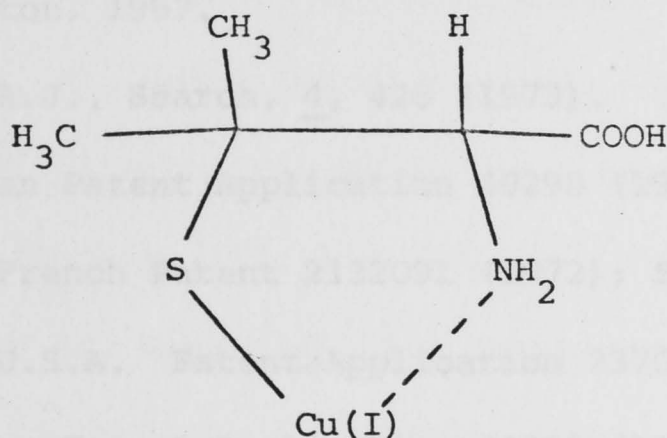
For a clearer picture of the mechanisms involved in enzyme-catalysed reactions, knowledge of the factors that determine the coordination, and coordination tendency, of metal ions in enzyme-metal ion-substrate complexes is invaluable. Data presented in chapter 1 showed that Cu^+ formed its strongest complexes with the cyanide ion and ligands containing a sulphur donor atom. The ability of CN^- to act as a poison is due to its complete inhibition of all copper and iron oxidases (presumably caused by complexation of the metal). Binding sites for Cu(I) in proteins will presumably have a hydrophobic environment³¹ to prevent disproportionation of Cu^+ or its oxidation to Cu^{2+} , an ion which is strongly solvated in aqueous environments. The Cu(I) ion may be bound to groups such as $> \text{C} = \text{S}$, $> \text{C} = \text{C} <$, $-\text{N} = \text{N} -$ and $-\text{N} = \text{C} <$ which are able to participate in dative π -bonding as described in chapter 1. Also, complexes of Cu^+ with SDMF, thiourea, pyridine and allyl alcohol may be useful as models for Cu(I) binding sites in the hydrophobic environments previously mentioned.

The ability of ammonia and pyridine to form strong complexes with Cu^+ and Cu^{2+} suggests that amino sites on proteins may be involved in electron-transfer reactions; the latter are favoured by the low oxidation potential of Cu^+ . The ease of air-oxidation of Cu^+ in ammoniacal solutions studied in chapter 1 required the complete exclusion of oxygen to preserve copper

in its monovalent state. It is not surprising, therefore, that the last step in mitochondrial respiration, where oxygen is reduced to water, is catalysed by the copper protein cytochrome oxidase³¹.

The redox behaviour of Cu^+ and Cu^{2+} and the ability of ligands to coordinate to these ions are influenced by pH, ionic strength and solvent polarity. The effect of pH on the stability of some Cu(I) complexes (chapter 1) and studies on the behaviour of Cu^+ in non-aqueous environments (chapter 2) are therefore relevant.

Wilson's disease, which involves a build-up of copper in human tissues, particularly the brain and the liver, can be treated by administering a drug such as penicillamine which leaches copper out of the tissues³⁴ in a Cu(I) chelate form³⁵ illustrated below.



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Diethylamine (AR) was purified using the method of Cameron et. al. (1957). The material was allowed to stand over calcium hydride for 48 hours. After decanting it was fractionally distilled from phosphorus pentoxide (5 g per 100 ml) and refluxed over calcium hydride (1 g per 100 ml) for 5 hours. Finally it was fractionally distilled from calcium hydride at a very slow rate.

Water from an all-glass still was degassed by boiling in and allowing it to cool with a stream of oxygen-free nitrogen bubbling through it.

CHAPTER 4

Diethylamine (AR, Mallinckrodt), Diethylamine (AR, Mallinckrodt), and Diethylamine (AR, Ajax Chemicals Ltd.) were used without further purification.

4.1.2. Acids

Hydrogen sulphide (AR) was prepared by passing a saturated solution of barium hydroxide (500 mg) through the distilled water (300 ml) before being passed into the solution.

Phosphoric acid (AR, 85% W/W, Ajax Chemicals Ltd.) and perchloric acid (AR, 70-72% W/W, Ajax Chemicals Ltd.) were used without further purification.

EXPERIMENTAL

4.1.3. Copper Compounds

4.1.3.1. Simple Salts

Cu(II) perchlorate (Research Organic/Inorganic Chemical Corporation) was vacuum-dried at 50° for 48 hours to yield the pentahydrate.

Cu(II) sulphate was prepared using a procedure similar to that described by Cleaver and Sauer. Finely ground copper powder (AR, Ajax) was covered with water; sulphuric acid was added. Slightly more than the theoretical amount of sulphur was dissolved in a large quantity of

4.1. Reagents

4.1.1. Solvents

Acetonitrile (AN) was purified using the method of Coetzee et. al.¹. Acetonitrile (LR, Ajax Chemicals Ltd.) was allowed to stand over calcium hydride for 48 hours. After decanting it was fractionally distilled from phosphorus pentoxide (5 g per dm^3) and refluxed over calcium hydride (5 g per dm^3) for 5 hours. Finally it was fractionally distilled from the calcium hydride at a very slow rate.

Water from an all-glass still was deoxygenated by boiling it and allowing it to cool with a stream of oxygen-free nitrogen bubbling through it.

Dimethylformamide (AR, Mallinckrodt), dimethylsulphoxide (AR, Mallinckrodt), and acetone (AR, Ajax Chemicals Ltd.) were used without further purification.

4.1.2. Acids

Hydrogen sulphide (Tech. grade, Matheson Co. Inc.) was bubbled through a saturated solution of barium hydroxide (300 cm^3) and through two quantities of distilled water (300 cm^3) before being passed into test solutions.

Sulphuric acid (AR, 95-98% W/W, Ajax Chemicals Ltd.) and perchloric acid (AR, 70-72% W/W, Ajax Chemicals Ltd.) were used without further purification.

4.1.3. Copper Compounds

4.1.3.1. Simple Salts

Cu(II) perchlorate (Research Organic/Inorganic Chemical Corporation) was vacuum-dried at 60° for 48 hours to yield the pentahydrate.

Cu (I) sulphide was prepared using a procedure similar to that described by Glemser and Sauer². Finely ground copper powder (LR, May and Baker) was covered with carbon disulphide in a beaker. Slightly more than the theoretical amount of sulphur was dissolved in a large quantity of

carbon disulphide and added to the beaker's contents. After standing overnight the resultant Cu(I) sulphide was filtered, washed with fresh carbon disulphide and allowed to dry. Analysis for copper indicated a purity of greater than 99%.

4.1.3.2. Tetrakis(Acetonitrile)Copper(I) Bisulphate

Enough $\text{CuSO}_4 \cdot \frac{5}{2} \text{H}_2\text{O}$ to produce a 0.25 M solution was added to acetonitrile in a flask. Excess copper powder and enough sulphuric acid to give a pH of 2 was added. The mixture was refluxed for 2 hours and the flask and its contents transferred to a glove-box which was continually flushed with dry oxygen-free nitrogen. The hot colourless solution was filtered and the filtrate allowed to cool. The transparent colourless crystals which formed were filtered off and allowed to dry in the glove box. Analysis gave the following results: Cu, 19.65; S, 10.0; C, 29.1; H, 3.9% ($\text{Cu}[\text{CH}_3\text{CN}]_4\text{H}_2\text{SO}_4$ requires Cu, 19.55; S, 9.9; C, 29.6; H, 4.0%).

4.1.3.3. Tetrakis(pyridine)Copper(I) Perchlorate

Acetonitrile (40 cm^3) pyridine (40 cm^3) and water (120 cm^3) were added to a flask and the mixture deoxygenated by bubbling nitrogen through it for 5 minutes. White crystals of $\text{Cu}[\text{CH}_3\text{CN}]_4\text{ClO}_4$ (1.31 g) were dissolved in the mixture producing a yellow solution which deposited a yellow solid after evacuation on a vacuum pump. The precipitate was filtered and dried at room temperature under reduced pressure (13 - 65 pascals). Analysis gave the following results: C, 50.69; H, 4.35; N, 11.83; Cu, 12.8% ($\text{Cu}[\text{C}_5\text{H}_5\text{N}]\text{ClO}_4$ requires C, 50.11; H, 4.21; N, 11.69; Cu, 13.25%).

4.1.3.4. Tetrakis(Acetonitrile)Copper(I) Perchlorate

The method described by Hathaway et. al.³ was used to prepare this complex. A solution of Cu(II) perchlorate pentahydrate and copper powder in acetonitrile was refluxed until colourless. The hot solution was filtered and the white crystals which separated on cooling were recrystallized from hot acetonitrile and dried under reduced pressure. Analysis gave the following results: C, 29.56; H, 3.70; N, 17.29; Cu, 19.27% ($\text{Cu}[\text{CH}_3\text{CN}]_4\text{ClO}_4$ requires C, 29.37; H, 3.70; N, 17.12; Cu, 19.41%).

4.1.4. Ligands

4.1.4.1. Non-Gaseous

Potassium chloride (AR, Ajax Chemicals Ltd., purity > 99.8%), potassium bromide (AR, Ajax Chemicals Ltd., purity > 98.5%), and potassium iodide (AR, BDH, purity > 99.8%) were dried in air at 120⁰ for 48 hours. Sodium thiosulphate (AR, Ajax Chemicals Ltd., purity > 99%), potassium thiocyanate (AR, Ajax Chemicals Ltd., purity > 98%), and potassium cyanide (AR, BDH, purity > 97%) were obtained from previously unopened containers and used without further purification. Aqueous ammonia (AR, 28-30% W/W NH₃, Ajax Chemicals Ltd.) was used without further purification.

Thiourea (LR, Ajax Chemicals Ltd., purity > 99%) was twice recrystallized from hot water and vacuum dried for 48 hours.

Allyl alcohol was purified using the method described by Vogel⁴. 200 cm³ of allyl alcohol (LR, Ajax Chemicals Ltd., purity > 97.5%) was mixed with carbon tetrachloride (50 cm³) and slowly distilled through a fractionating column. The fraction boiling at 93-97⁰ was collected.

Dimethylthioformamide (SDMF) was prepared from dimethylformamide and phosphorus pentasulphide by the method of Pettit and Garson⁵ and fractionally distilled twice under reduced pressure. It was stored in the dark.

Pyridine (AR, Ajax Chemicals Ltd., purity > 99%) was distilled twice through a fractionating column.

4.1.4.2. Gaseous

Carbon monoxide was obtained in cylinders at 1.14×10^7 Pa supplied by the Matheson Co. Ethylene and propylene under high pressure were obtained from Commonwealth Industrial Gases.

4.1.5. Miscellaneous

Ag (I) perchlorate (LR, BDH) was dried to the anhydrous salt at 60⁰ under vacuum and stored in a desiccator in the dark. Tetraethylammonium perchlorate was prepared by neutralizing tetraethylammonium hydroxide (Eastman, 10% aqueous solution) with perchloric acid. The precipitated salt was recrystallized three times from hot water. Tetraethylammonium chloride

(Eastman) was recrystallized twice from dimethylacetamide and washed with ether.

4.2. Preparation of Cu(I) Salt Solutions

A. Cu(II) sulphate pentahydrate (AR, Ajax, purity > 99%) or Cu(II) perchlorate pentahydrate solutions were stirred under a nitrogen atmosphere with copper powder (LR, May and Baker), a little acid and the appropriate Cu(I) ligand until a colourless solution was obtained.

B. Tetrakis(acetonitrile)copper(I) perchlorate was dissolved in deoxygenated aqueous solutions containing the appropriate Cu(I) ligand.

C. Solutions containing Cu^{2+} (0.01 M) were reduced to Cu(I) salt solutions (0.01 M) by some ligands (e.g. thiourea, $\text{S}_2\text{O}_3^{2-}$). This method was only used in solutions having a high ligand to metal ratio where a relatively small and insignificant amount of oxidised ligand was produced.

4.3. General Techniques

4.3.1. Potentiometry

The individual electrochemical cells used for potentiometric measurements are described under following appropriate headings in this chapter. All potential readings were obtained with a Radiometer pH Meter Type PHM 26 using the expanded millivolt scale. The saturated calomel electrode (SCE) used as a reference in aqueous solutions was a Radiometer K 401 type and was stored in a saturated aqueous solution of potassium chloride when not in use. Copper, silver, and platinum wire electrodes were cleaned before use by immersing them in concentrated nitric acid for 3 seconds, rinsing with acetone, and wiping dry with soft tissues. All pH measurements were made with a Radiometer G 202C glass electrode and the SCE and meter described above.

4.3.2. Conductance

Measurements were made using a Type B221 Wayne Kerr bridge and conductivity cell (10 cm^3) of cell constant 1.93 cm^{-1} . The cell was immersed in an oil bath maintained at $25 \pm 0.1^\circ$.

4.3.3. Infra-Red Spectroscopy

Spectra were recorded on a Perkin-Elmer 457 grating IR spectrophotometer. The wavelength standard was polystyrene.

4.4. Chemical Analyses

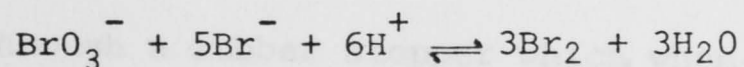
4.4.1. Cu(I)/Cu(II) Mixtures

A solution containing Cu^{2+} (~ 2 mmol) was cooled in ice. KI (1 g) was added and the solution made basic with Na_2CO_3 . It was then re-acidified with a slight excess of acetic acid and the liberated iodine titrated with standard 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ in the usual manner.

The total copper in solution was determined in a similar manner after oxidising any Cu^+ present with a small quantity of nitric acid which was subsequently removed by careful evaporation to dryness. The concentration of Cu^+ was found by difference.

4.4.2. Ethylene

Analysis was accomplished by bromination of the ethylene with a mixture of KBr and KBrO_3 (KBr(25.5g) and KBrO_3 (6.96g) in water (500cm^3)) in acid solution and iodometric determination of the excess BrO_3^- with KI and $\text{Na}_2\text{S}_2\text{O}_3$. The KBr/ KBrO_3 was standardised by adding 5cm^3 to glacial acetic acid (25cm^3) and HCl (0.5cm^3) which had previously been cooled in an ice bath. 15% aqueous KI (5cm^3) was slowly added and, after a further addition of water (50cm^3), the liberated iodine was titrated with standard 0.1N $\text{Na}_2\text{S}_2\text{O}_3$. Each mole of BrO_3^- produced 3 moles of Br_2 as follows:



Thus 1 mole of BrO_3^- brominated 3 moles of olefin.

4.4.3. Miscellaneous

Determinations of copper and iron concentrations in some solutions were made by atomic absorption spectroscopy using an EEL 240 spectrometer.

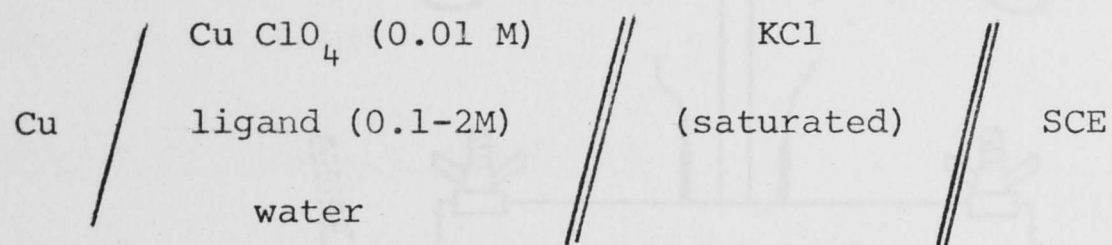
Elemental analyses were carried out in the Micro-Analytical Section of the Australian National University, Canberra, A.C.T.

4.5. Measurement of Cu^+/Cu^0 and $\text{Cu}^{2+}/\text{Cu}^+$ Potentials

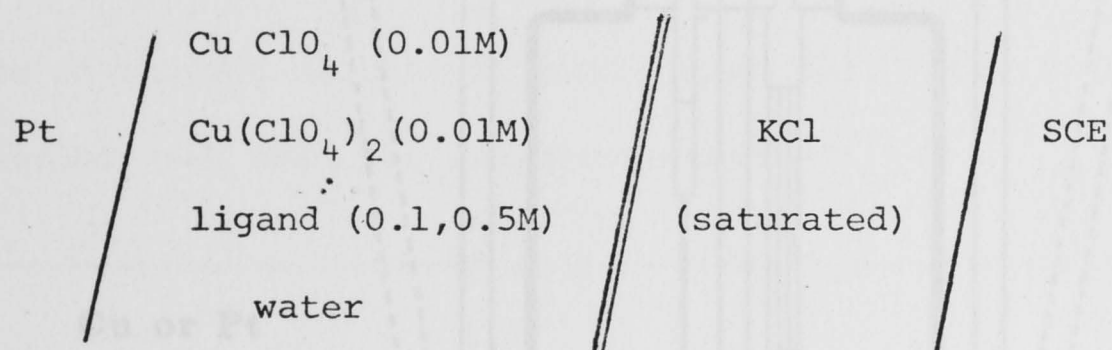
4.5.1. Non-Gaseous Ligands

Cells A and B were used to measure the potentials of the Cu^+/Cu^0 and $\text{Cu}^{2+}/\text{Cu}^+$ couples respectively in the presence of various ligands.

CELL A, Cu^+/Cu^0 Couple.



CELL B, $\text{Cu}^{2+}/\text{Cu}^+$ Couple.



Cu (I) salt solutions were initially deoxygenated by bubbling nitrogen and subsequently blanketed with nitrogen while measurements were made.

4.5.2. Gaseous Ligands

Potential measurements in cells A and B were made using the apparatus illustrated in Figure 4.1 which consisted of a 500cm^3 glass pressure reaction vessel (manufactured by the PAAR Instrument Co., Inc., Moline, Illinois, U.S.A.) held in a metal clamping device which enabled pressures of 5.1×10^5 pascals to be maintained. The two electrodes and the gas inlet/outlet tubing passed through a rubber stopper which, when compressed by the clamping device, produced a gas-tight seal. The solution under study was stirred magnetically and gas pressures were read on a Floyd pressure gauge. Copper and platinum wire electrodes were screwed into a holder held in the rubber stopper.

Prior to each measurement the glass vessel was evacuated using a water pump. Gas was then allowed to enter until a pressure of 2.3×10^5 pascals

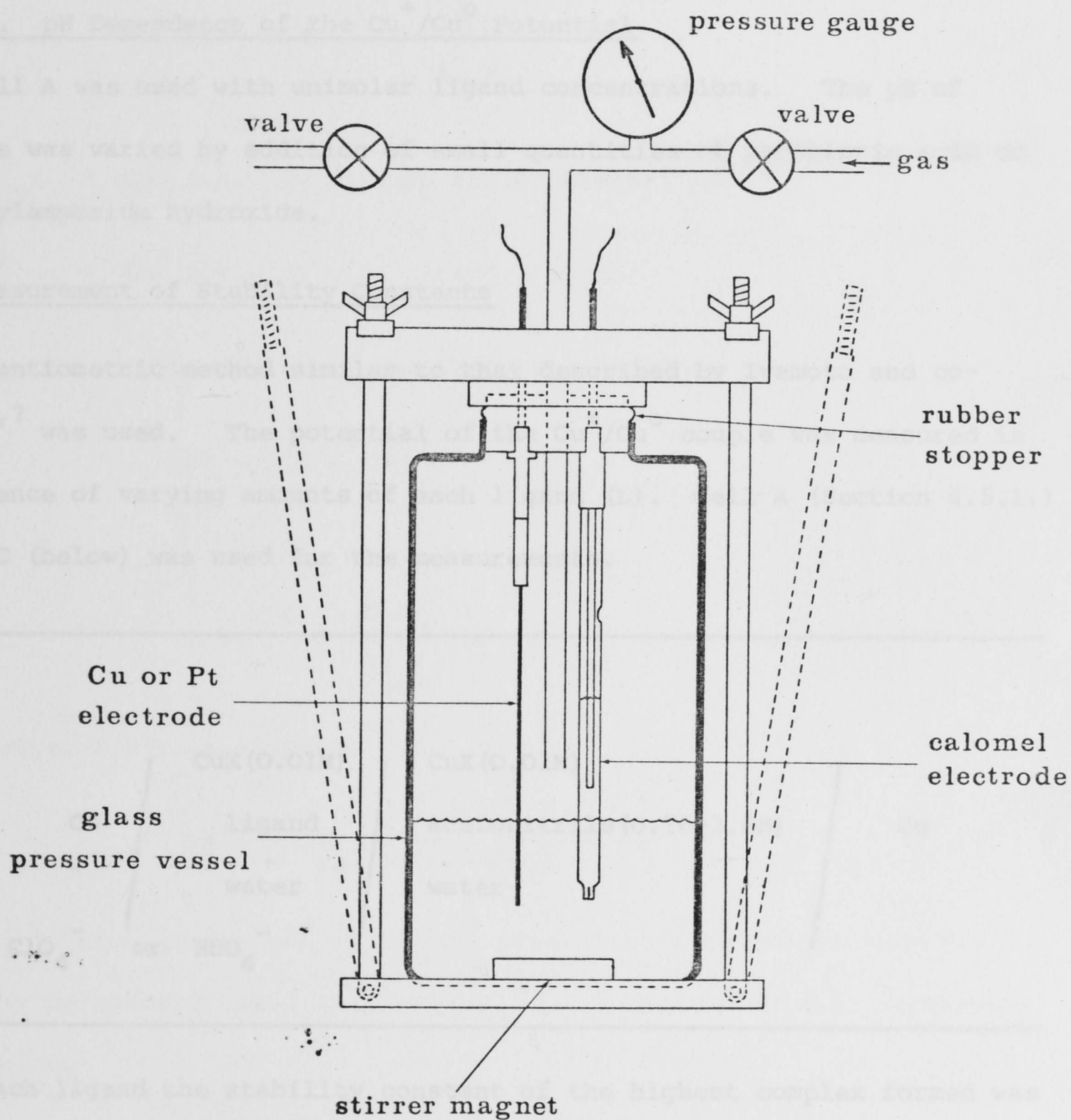


FIGURE 4.1. Apparatus used for the Measurement of Cu^+/Cu^0 and $\text{Cu}^{2+}/\text{Cu}^0$ Potentials in Solutions of Gaseous Ligands.

was attained. The vessel was evacuated again and gas allowed to enter until a pressure of 5.1×10^5 pascals was reached. Solutions were stirred until a constant potential reading was obtained (usually after 30 min.). Readings at successively lower pressures were then made.

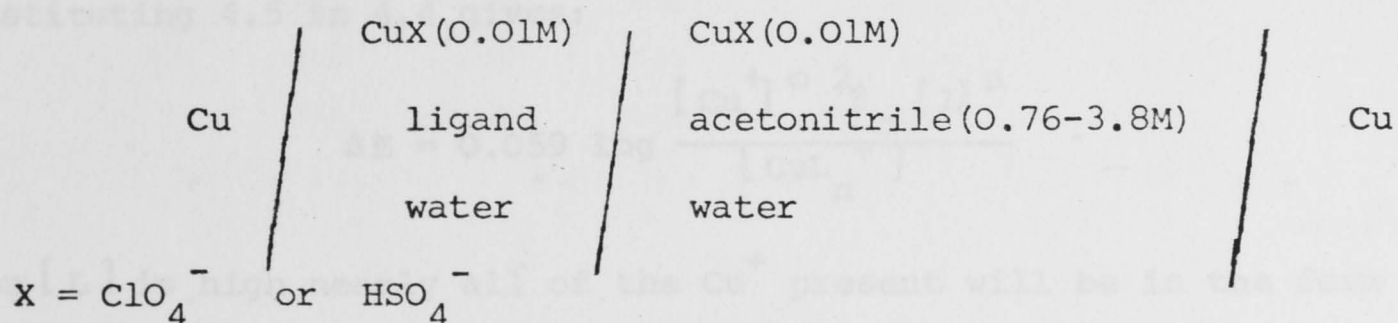
4.5.3. pH Dependence of the Cu^+/Cu^0 Potential

Cell A was used with unimolar ligand concentrations. The pH of solutions was varied by addition of small quantities of perchloric acid or tetraethylammonium hydroxide.

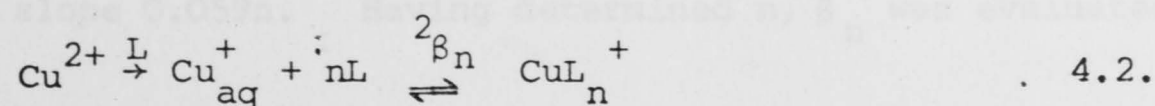
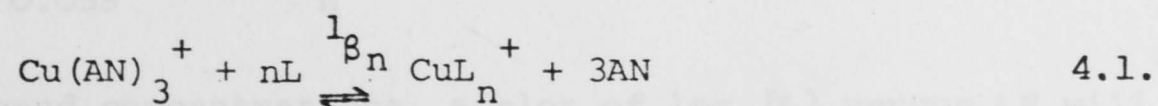
4.6. Measurement of Stability Constants

A potentiometric method similar to that described by Iwamoto and co-workers^{6,7} was used. The potential of the Cu^+/Cu^0 couple was measured in the presence of varying amounts of each ligand (L). Cell A (Section 4.5.1.) or cell C (below) was used for the measurements.

CELL C.



For each ligand the stability constant of the highest complex formed was determined. Two slightly different types of measurement were made. The first involved solutions of Cu^+ stabilised by acetonitrile (pyridine, SDMF, AN) and the second concerned Cu(I) salt solutions produced by the reduction of Cu^{2+} with the ligand being studied (thiourea and $\text{S}_2\text{O}_3^{2-}$). Equations 4.1 and 4.2 represent the formation of complexes in each case.



To determine the number of ligand molecules present in the highest complex formed, a plot of the change in potential of the Cu^+/Cu^0 couple (ΔE) versus the logarithm of the total ligand concentration ($\log [L]$) was made. From the Nernst equation at 25° ,

$$\Delta E = 0.059 \log \frac{a_{\text{Cu}^+}^0}{a_{\text{Cu}^+}^L}, \quad 4.3$$

where $a_{\text{Cu}^+}^0 = \text{Cu}^+$ activity with no ligand present and,

$a_{\text{Cu}^+}^L = \text{Cu}^+$ activity with ligand present.

Assuming activity coefficients are unity 4.3 becomes:

$$\Delta E = 0.059 \log \frac{[\text{Cu}^+]^0}{[\text{Cu}^+]^L}, \quad 4.4$$

and from 4.2,

$$[\text{Cu}^+]^L = \frac{[\text{CuL}_n^+]}{\beta_n [L]^n}. \quad 4.5.$$

Substituting 4.5 in 4.4 gives:

$$\Delta E = 0.059 \log \frac{[\text{Cu}^+]^0 \beta_n [L]^n}{[\text{CuL}_n^+]}. \quad 4.6$$

When $[L]$ is high nearly all of the Cu^+ present will be in the form CuL_n^+ , so it may be assumed that $[\text{Cu}^+]^0 = [\text{CuL}_n^+]$. Substituting this expression in 4.6 gives:

$$\Delta E = 0.059 \log \beta_n [L]^n,$$

$$\text{i.e. } \frac{\Delta E}{0.059} = \log \beta_n + n \log [L]. \quad 4.7$$

For equilibrium 4.1 equation 4.7 becomes:

$$\frac{\Delta E}{0.059} = \log \beta_n + n \log [L] - 3 \log [AN].$$

Thus, at high ligand concentrations, a plot of $\log [L]$ versus ΔE will give a straight line of slope $0.059n$. Having determined n , β_n was evaluated at

various ligand concentrations. Example 1 below shows the data recorded and the calculations performed.

Example 1. Calculation of the stability constant of the complex formed between Cu^+ and SDMF.

Cell A, 25° .

Initial solution composition: acetonitrile, 3.8M; Cu^+ , 0.01M; pH, 2-3; HSO_4^- anion.

SDMF added (ml)	ΔE (mV)	[SDMF] Mol l^{-1}	$-\log[\text{Cu}(\text{AN})_3^+]^a$	$\log[\text{Cu}(\text{SDMF})_4^+]^b$	$-4 \log[\text{SDMF}]$	$3 \log[\text{AN}]$	$\log \beta_4^c$
0	0	0	2.00	-	-	-	-
0.1	173	0.111	4.93	-2.00	3.80	1.73	8.46
0.2	260	0.220	6.40	-2.01	2.64	1.72	8.75
0.3	302	0.327	7.12	-2.01	1.96	1.71	8.78
0.4	333	0.432	7.65	-2.02	1.44	1.69	8.76
0.5	359	0.535	8.08	-2.02	1.08	1.68	8.82
0.6	376	0.636	8.37	-2.03	0.80	1.66	8.80
0.7	391	0.735	8.63	-2.03	0.52	1.65	8.77
0.8	403	0.832	8.83	-2.03	0.32	1.64	8.76
0.9	412	0.928	8.99	-2.04	0.12	1.63	8.70
1	421	1.020	9.14	-2.04	-0.04	1.61	8.67
						average ^d	8.76

a from ΔE using the Nernst equation

b assuming all copper is in this form

c $\log \beta_4 = \log[\text{Cu}(\text{SDMF})_4^+] + 3 \log[\text{AN}] - 4 \log[\text{SDMF}] - \log[\text{Cu}(\text{AN})_3^+]$

d excluding $\beta_4 = 8.46$

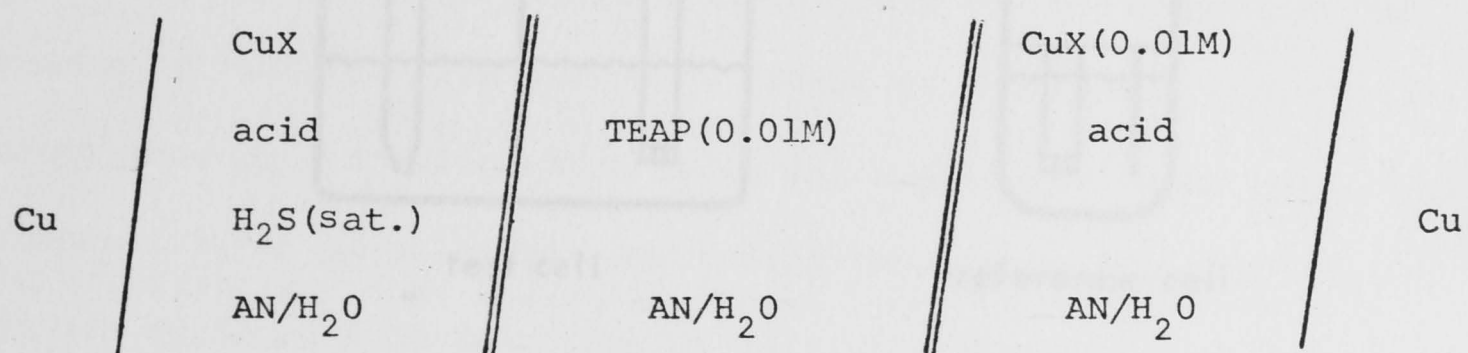
Stability constants measured in the presence of $\text{AN}(2\beta_n)$ were converted into equivalent $1\beta_n$ values using the stability constant of $\text{Cu}(\text{AN})_3$ measured by the method described above. Values of ΔE were calculated from the literature value of the potential of the Cu^+/Cu^0 couple (SCE reference) in water⁸, and the potentials measured in solutions containing various amounts of AN.

4.7. Measurement of Solubilities

4.7.1. Cu(I) Sulphide

Solutions of Cu(I) perchlorate (0.01M) in varying mixtures of AN and water containing either sulphuric acid (0.1M) or perchloric acid (0.01M) were saturated with hydrogen sulphide at a partial pressure of 0.95×10^5 Pa. Cu (I) salt solutions were obtained by the reaction of $\text{Cu}(\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$ and copper powder in the appropriate solvent mixture. The activity of Cu^+ was measured potentiometrically using cell D. Liquid junction potentials due to solvent-solvent interactions were eliminated. The test solution was magnetically stirred under a blanket of nitrogen. An H-type salt bridge was used with porosity 4 glass frits at the ends of each arm

CELL D.



TEAP = tetraethylammonium perchlorate

X = HSO_4^- and/or ClO_4^-

to permit electrical contact without undue leakage of the bridge electrolyte into the two halves of the cell. The apparatus used is illustrated in Figure 4.2. H_2S was bubbled through the solution until a constant potential reading was obtained (bubbling for 5 minutes was usually sufficient). It was assumed that the solution was saturated with H_2S at this point. No measurements were made with perchloric acid in anhydrous AN because of the potentially explosive nature of this solution.

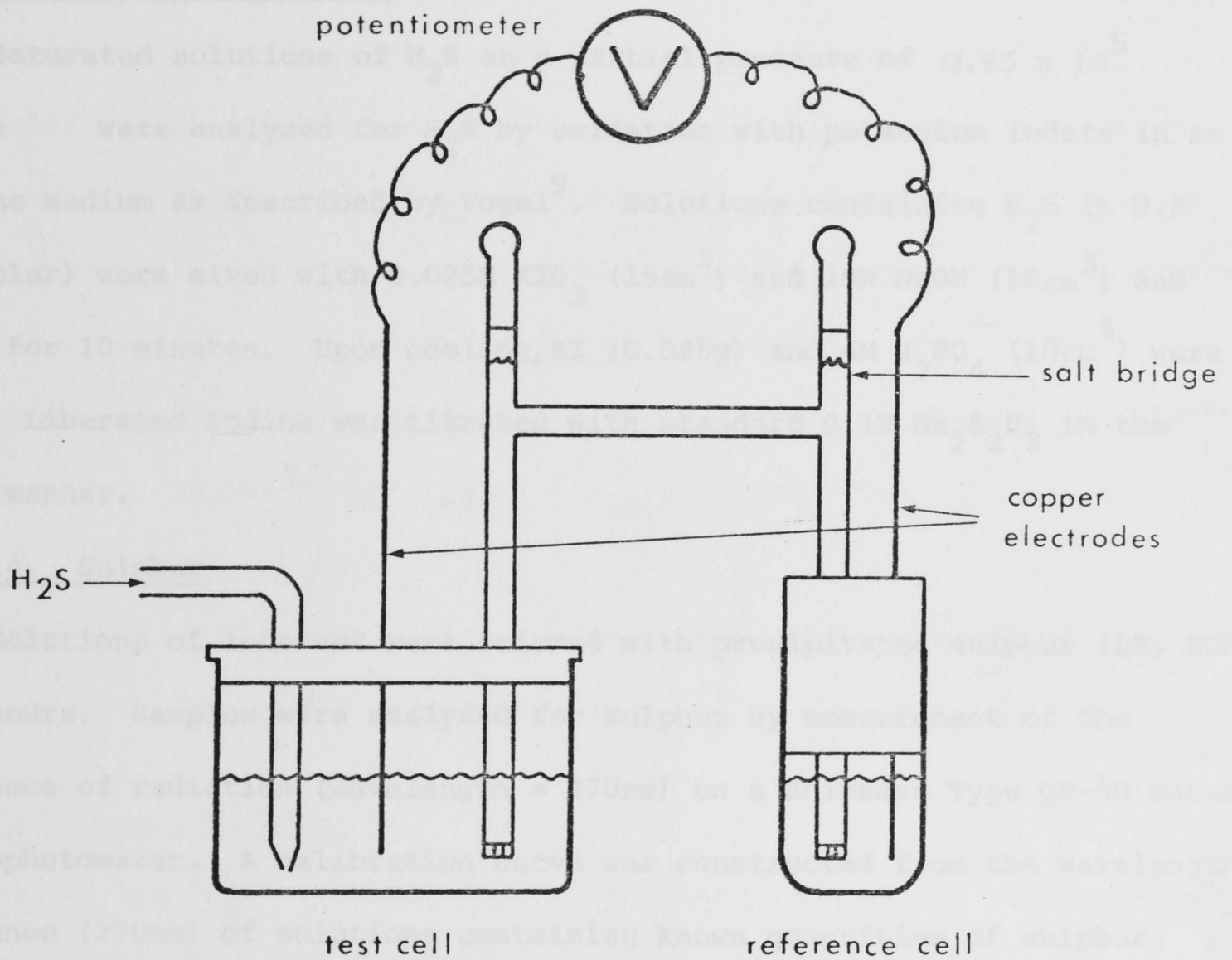


FIGURE 4.2. Apparatus used to Measure the Solubilities of Cu_2S and Ag_2S in Acidified Mixtures of Acetonitrile and Water.

4.7.2. Silver Sulphide

The same apparatus and procedure as that for Cu_2S was used except that AgClO_4 replaced CuClO_4 and silver wire electrodes were employed.

4.7.3. Hydrogen Sulphide

Saturated solutions of H_2S at a partial pressure of 0.95×10^5 pascals were analysed for H_2S by oxidation with potassium iodate in an alkaline medium as described by Vogel⁹. Solutions containing H_2S (~ 0.2 millimolar) were mixed with 0.025M KIO_3 (15cm^3) and 10M NaOH (10cm^3) and boiled for 10 minutes. Upon cooling, KI (0.025g) and 4M H_2SO_4 (10cm^3) were added. Liberated iodine was titrated with standard 0.1N $\text{Na}_2\text{S}_2\text{O}_3$ in the normal manner.

4.7.4. Sulphur

Solutions of interest were stirred with precipitated sulphur (LR, BDH) for 8 hours. Samples were analysed for sulphur by measurement of the absorbance of radiation (wavelength = 270nm) on a Shimadzu Type QR-50 manual spectrophotometer. A calibration curve was constructed from the wavelength absorbance (270nm) of solutions containing known quantities of sulphur. Oxygen was excluded from solutions by initially flushing with nitrogen and then maintaining an atmosphere of nitrogen over the surface.

4.7.5. Cu(I) Salts

Salts were stirred with successive fresh volumes of the appropriate solvent mixture in stoppered flasks under nitrogen until the concentration of Cu^+ remained constant. $[\text{Cu}^+]$ was determined by atomic absorption spectroscopy. Solutions for analysis contained a small amount of nitric acid to oxidise Cu^+ to Cu^{2+} and thus prevent the disproportionation of Cu^+ into Cu^{2+} and copper metal.

4.8. Dissociation Constants of Acids

4.8.1. Sulphuric Acid

Aliquots of 0.01M H_2SO_4 (15cm^3) in varying AN-water mixtures were titrated with 0.035M tetraethylammonium hydroxide (Et_4NOH) in the same

solvent. The glass/SCE system used to measure pH was calibrated using 0.1M to 0.0002M perchloric acid in the different solvent compositions. Plots of the negative logarithm of the activity of the proton versus the millivolt reading obtained from the glass/SCE system gave straight lines for each solvent mixture. It was assumed that perchloric acid was completely dissociated in all cases¹⁰ and that the Debye-Hückel activity coefficients were unity. pK values for H_2SO_4 were found by assuming that the negative logarithm of the activity of the proton at the half-neutralization point was equal to the pK; i.e., for the reaction $\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$ the equilibrium constant, K, is equal to $(a_{\text{H}^+} \cdot a_{\text{SO}_4^{2-}}) / a_{\text{HSO}_4^-}$, where a_x is the activity of x. Assuming that $a_{\text{HSO}_4^-} = a_{\text{SO}_4^{2-}}$, $\log K = \log a_{\text{H}^+}$, or $\text{pK} = \text{pH}$.

4.8.2. Hydrogen sulphide

Solutions of H_2S were titrated with Et_4NOH and the results treated in a similar way to those for sulphuric acid.

4.9. Measurement of $\log \gamma_{\text{H}^+}^{\text{W S}}$

Values of $\log \gamma_{\text{H}^+}^{\text{W S}}$ were obtained as a consequence of the calibration of the glass/SCE system used in the determination of acid dissociation constants. For each AN-water mixture a plot of $-\log a_{\text{H}^+}$ versus the glass/SCE potential was made. Extrapolation of the resultant straight line to $-\log a_{\text{H}^+} = 0$ gave a millivolt reading, E_s , for each solvent mixture, S. Thus at 25° , $\log \gamma_{\text{H}^+}^{\text{W S}} = (E_s - E_w) / 59.15$, where E_w mV is the glass/SCE potential in water. $\log \gamma_{\text{H}^+}^{\text{W AN}}$ had been determined previously by Kolthoff and Chantooni¹¹.

4.10. References

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Stability Constants of Copper(I) and Copper(II) Complexes in Aqueous

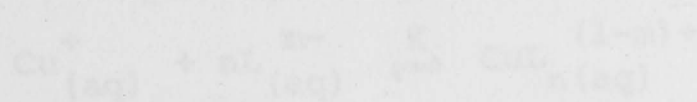
Solution.

The following tables have been compiled from data in the literature up to July, 1974. Complexes between Cu(I) and one ligand only (i.e., no mixed ligand complexes) in aqueous solution and between temperatures of 15° and 30° have been included. The corresponding Cu(II) complexes have been included where available and were taken from references 1 and 2 only. For complexes of Cu(I) all reasonable effort was made to ensure an extensive and accurate survey but some data may have been missed. The tables have been divided into four groups as follows:

1. Ionic ligands.
2. Nitrogen-donor ligands.
3. Sulphur-donor and miscellaneous ligands.
4. Olefinic ligands.

A P P E N D I X

Values have been expressed as K_1 , β_2 , β_3 and β_4 and these refer to the equilibria represented by equation 1.



The equilibrium constant, K , for reaction 1 is:

$$K = \frac{[\text{CuL}_n]}{[\text{Cu}^+][\text{L}]^n}$$

$$\text{and } \log K = \log[\text{CuL}_n] - \log[\text{Cu}^+] - n \log[\text{L}]$$

The terms K_1 , β_2 , β_3 and β_4 used in the tables are as follows:

$$K_1 = \log K \text{ when } n = 1,$$

$$\beta_2 = \log K \text{ when } n = 2,$$

$$\beta_3 = \log K \text{ when } n = 3,$$

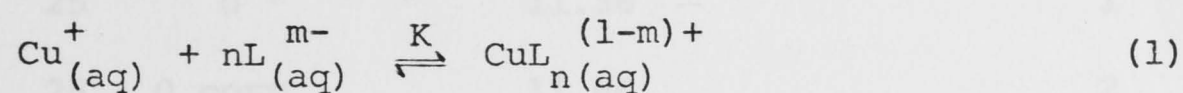
$$\beta_4 = \log K \text{ when } n = 4.$$

Stability Constants of Copper(I) and Copper(II) Complexes in Aqueous Solution.

The following tables have been compiled from data in the literature up to July, 1974. Complexes between Cu(I) and one ligand only (i.e. no mixed ligand complexes) in aqueous solution and between temperatures of 15° and 30° have been included. The corresponding Cu(II) complexes have been included where available and were taken from references 1 and 2 only. For complexes of Cu(I) all reasonable effort was made to ensure an extensive and accurate survey but some data may have been missed. The tables have been divided into four groups as follows:

1. Ionic ligands.
2. Nitrogen-donor ligands.
3. Sulphur-donor and miscellaneous ligands.
4. Olefinic ligands.

Values have been expressed as K_1 , β_2 , β_3 and β_4 and these refer to the equilibria represented by equation 1.



The equilibrium constant, K , for reaction 1 is:

$$K = \frac{[\text{CuL}_n^{(1-m)+}]}{[\text{Cu}^+] [\text{L}^{m-}]^n}$$

$$\text{and } \log K = \log[\text{CuL}_n^{(1-m)+}] - \log[\text{Cu}^+] - n \log[\text{L}^{m-}]$$

The terms K_1 , β_2 , β_3 and β_4 used in the tables are as follows:

$$\begin{aligned} K_1 &= \log K \quad \text{when } n = 1, \\ \beta_2 &= \log K \quad \text{when } n = 2, \\ \beta_3 &= \log K \quad \text{when } n = 3, \\ &\vdots \\ \beta_4 &= \log K \quad \text{when } n = 4. \end{aligned}$$

The symbols and abbreviations used in the tables have the following meanings:

T	temperature
rt	room temperature
μ	ionic strength
$\rightarrow 0$	extrapolated to zero ionic strength
0 corr	corrected to zero ionic strength by means other than extrapolation
var	varying ionic strength

TABLE 1. Ionic Ligands

Metal/Ligand	T ^o C	μ	K ₁	β_2	β_3	β_4	Reference
Cu ⁺ , e ⁻	25	0 corr	8.80				1
	25	0	8.76				1
Cu ²⁺ , e ⁻	25	0 corr	2.68	11.44			1
	25	0		11.38			1
	25	0 corr		11.66			2
Cu ⁺ , CN ⁻	~18	var				27.3	1
	~18	var				28	1
	25	0 corr		23.8			1
	18	var			20.78		1
	25	0 corr		16			1
	25	0 corr				27.56	1
	25	0 corr		24.0		30.3	1
	20	var		21.7			1
Cu ⁺ , SCN ⁻	25	var				9.15	1
	18	var		12.11			1

Metal/Ligand	T °C	μ	K ₁	β_2	β_3	β_4	Reference
	20	var			9.90	10.09	1
	rt	var				10.64	1
	20	var				10.88	1
	25	5		11.00			1
Cu ²⁺ , SCN ⁻	18	1.05	1.92		5.19	6.52	1
	18	0 corr	2.56				1
	25	0.5	1.74				1
	25	0.1	1.90				1
	25	0.05	1.99				1
	25	0 corr	2.30				1
	25	0 corr	2.33				1
	30	0 corr	2.39				2
	25	0 corr	0.08				1
Cu ⁺ , S ₂ O ₃ ²⁻	25	2.7			14.1		this work
	25	var			13-14		1
	18	var		11.69			1
	25	3			13.64		1
	25	1.2			14.30		1
	25	2.4	10.35				1
Cu ²⁺ , S ₂ O ₃ ²⁻	25	var		12.29			1
	25	var					1
Cu ⁺ , SO ₃ ²⁻	25	2.4		8.5			1
	25	3	7.85				1
	25	var					1
Cu ⁺ , Cl ⁻	~18	var		4.60			1
	~18	var		5.5	5.7		1
	25	0 corr		5.54			1
	23	0 corr			5.84		1

Metal/Ligand	T ^o C	μ	K ₁	β_2	β_3	β_4	Reference
	25	0 corr		4.73	4.23		1
	25	0 corr		4.94			1
	18	var			5.30		1
	20	0 corr		5.5	5.7		1
	25	6.5		6.04	5.98	5.60	2
	20	0.2	3.63				3
	25	5	2.70	6.00	5.99		4
Cu ²⁺ , Cl ⁻	~18	var	2.80				1
	rt	var	2.15				1
	25.2	1	0.11				1
	25	0 corr	0.05				1
	25	0 corr	0.40				1
	25	0 corr	0.08				1
	20	1.5	-0.40				1
	25	2.15	0.74				1
	20	0.69	0.98				1
	30	1	1.18	0.87	0.79	0.88	2
	25	0 corr	0.3				2
		var	-0.11				2
		var					1
Cu ⁺ , Br ⁻	~19	var		5.04			1
	25	0 corr		5.92			1
	25	var			6.1		this work
Cu ²⁺ , Br ⁻	~18	var	5.68				1
	18	var	-1.20				1
	25	0 corr	-0.03				1
	~22	1	0.32				1
	25	2.15	0.55				1

Metal/Ligand	T °C	μ	K ₁	β_2	β_3	β_4	Reference
		0.6	0.70				1
	25	2	-0.55				1
	25	1	-0.64				1
		0.6	0.68				1
		0 corr	2				1
	25	3	-0.55				2
Cu ⁺ , I ⁻	~19	var		8.19			1
	25	0 corr		8.85			1
	25	5			9.38		1
	20	0.6		9.03			1
	20	4				9.85	1
	20	var			9.74		1
	20	3.9		8.68		8.44	2
Cu ⁺ , P ₂ O ₇ ⁴⁻	25	1		26.72			1
Cu ²⁺ , P ₂ O ₇ ⁴⁻	20	0.8	13.2				1
	25	var	6.4				1
	18	var		9.51			1
	25	var		11.87			1
	25	1	8.7	12.65			1
	25	var	5.2	10.1			1
	25	var	8.17	8.99			1
	25	1	9.07				1
	25	0.1	7.3				2
	25	1	7.6	12.45			2

TABLE 2. Nitrogen-donor^a Ligands

Metal/Ligand	T ^o C	μ	K ₁	β_2	β_3	β_4	Reference
Cu ⁺ , NH ₃	18-21	var		8.74			1
	18	2	5.93	10.86			1
	rt	2		11.2			1
	30	0.5		10.4			2
	25	0.3		10.55			2
	30	2		11.66			5
	30	2		10.13			6
Cu ²⁺ , NH ₃	30	2		10.31			6
	16	var				9.3	1
		var				15.74	1
	18	2	4.31				1
	18	0 corr	4.25				1
	18	2				13.34	1
	rt	2				13.5	1
	30	2	4.15			12.67	1
	30	0 corr	3.99			12.03	1
	25	1				12.63	1
	25	→0	4.01				1
	18	var				14.31	1
	25	var				14.14	1
	25	2	4.27			13.05	1
	25	2.1			7.865	13.05	1
25	1	4.27				1	
30	var				8.5	1	
30	2	4.13		7.16		2	
25	1	4.16				13.05	2

Metal/Ligand	T °C	μ	K ₁	β_2	β_3	β_4	Reference
	20	1	4.15	7.65	10.54	12.67	2
	30	2		11.66		14.38	2
	30	0.5				12.3	2
	22	2	4.09	7.54	10.55	12.63	2
Cu ⁺ , methylamine	30	2		9.21			6
	30	2		9.62			6
Cu ⁺ , ethylamine	30	0.5		10.1			2
Cu ²⁺ , ethylamine	30	0.5				11.5	2
Cu ⁺ , ethylenediamine	25			10.8			1
	25	0.3		11.4			2
	30	2		10.63			6
Cu ²⁺ , ethylenediamine	25	1	10.72				1
	25	1	10.75				1
	30	0.5	10.55	19.60			1
	25	0.5	10.76				1
	25	0.1		19.72			1
	25	2.15	11.02	20.61			1
	30	→0	10.36				1
	25	1.4	10.72				1
	25	0.1	10.5				1
	30	0.1	11.12				1
	20	→0	10.67				1
	25	0.1	10.6				1
	25	0.17		8.48			2
	20	→0	10.66				2

Metal/Ligand	T °C	μ	K ₁	β_2	β_3	β_4	Reference
	25	→0	8.29				1
	25	0.01	6.51				1
	25	0.54		15.1			1
	25	0.45		15.1			1
	25	0.1	8.38				1
	20	0.1	8.12				1
Cu ²⁺ , sarcosine	20	0.01	8.5	15.4			1
Cu ²⁺ , sarcosine	20	~0.01	8.34				1
	22		8.1	15.0			1
	30	0.09	8.04	14.43			1
	25	0.1	8.0				1
	25	0.15		13.10			1
Cu ²⁺ , pyridine	20	0.001	8.60	15.20			1
	25	0.3		15.2			2
	25	0.25		14.6			2
	25	0.15	8.18	15.02			2
	20	→0	8.59				2
Cu ²⁺ , pyridine	20	0.1	8.6				2
	25	1	8.29	15.30			2
	25	1	8.33	15.20			2
	25	0.2	8.46				2
	25	0 corr	8.58				2
	25	0.5	8.11	14.43			2
	25	0.1	8.23	15.19			2
	25	0.1	8.27				2
	25	0.5	8.12	14.87	15.3		2
		:					
	25	→0	8.50	14.30	15.10	16.04	2

Metal/Ligand	T ^o C	μ	K ₁	β_2	β_3	β_4	Reference
Cu ²⁺ , ethylenediamine	25	→0	8.54	3.40			2
	20	0.1	8.22	8.51			2
Cu ²⁺ , ethylenediamine	25	0.5	8.21	15.00			2
	25	0.1	7.59	14.76		16.49	2
	25	0.1				15.44	2
Cu ⁺ , sarcosine ^b	25	0.3	5.7	~9.2			2
Cu ²⁺ , sarcosine ^b	25	0.01	7.83	7.83			1
	25	0.1	7.94				1
Cu ²⁺ , diethylenetriamine	25	1	7.84	7.51			2
	20	→0	8.16	7.99			2
Cu ²⁺ , diethylenetriamine	25	0.5				16.00	1
Cu ⁺ , pyridine	25	→0.1	3.3				1
	25	0.3	3.9		8.29		2
	20	0.15	3.17	6.64			2
Cu ²⁺ , triethylenetriamine	30	2		8.14			2
Cu ²⁺ , triethylenetriamine	25	~0.02	4.7		8.4		this work
Cu ²⁺ , pyridine	25	0.5	2.41				1
	25	0.5	2.52				1
	25	1	2.59	4.33	5.93	6.54	1
	25	→0.1	2.36				2
	20	0.15	2.65	4.86	6.90	8.45	2
	25	1	2.46				2
Cu ²⁺ , glycine ^b	25	0.5	2.408	~10.0			2
Cu ²⁺ , glycine ^b	25	0.1	2.54				2
	20	1	2.4	4.3	5.68	6.58	2
	25	0.61	2.60	4.54	5.8	6.7	2
	25	~0	2.50	4.30	5.16	6.04	2
	25	1		15.22	15.23		

Metal/Ligand	T ^o C	μ	K ₁	β_2	β_3	β_4	Reference
Cu ⁺ , ethanolamine	30	2		9.40			6
	30	2		9.51			6
Cu ²⁺ , ethanolamine	30	→0	5.78	6.68			1
	25	0.5	6.83	10.73		16.48	1
Cu ²⁺ , imidazole	25	0.1	4.33			15.44	2
	25	~0.1	5.7				2
	25	0.43	4.73			12.3	2
	25	0.15	4.36				1
Cu ⁺ , diethanolamine	30	2	8.20	7.51			6
	30	2	4.33	7.98			6
Cu ²⁺ , diethanolamine	25	0.5	4.26	7.87	10.73	16.00	1
	25	~0.1	5.4				2
	25	0.43	4.75				2
Cu ⁺ , triethanolamine	30	2		4.39			6
Cu ²⁺ , triethanolamine		var	4.7				1
	25	0.5	4.23				1
	25	~0.03	4.30	15.10			1
	25	2	4.79	15.02			2
	25	~0.1	3.9				2
	25	0.43	4.44	15.1			2
	25	0		15.34			1
Cu ⁺ , glycine ^b	25	0.3		~10.0			2
Cu ²⁺ , glycine ^b	25	→0	8.62				1
	20	0.5	8.22	15.0			1
	20	0.03	8.15		16.4		1
	25	0.1	8.07	15.13			1
	25	1	8.20	15.28	16.25		1

Metal/Ligand	T ^o C	μ	K ₁	β_2	β_3	β_4	Reference
Cu ⁺ , imidazole	25	0.15		10.8			1
	25	0.3		10.44			2
	20	0.15	5.78	10.98			2
	25	0.1 ^c	6.83	10.73			7
Cu ²⁺ , imidazole	25	0.16	4.33				1
	25	0.16	4.20				1
	25	0.15				12.6	1
Cu ⁺ , L-carnosine ^b	22.5	0.16	4.36				1
Cu ²⁺ , L-carnosine ^b	25	0.135	4.20				1
	25	0.3	4.33				2
Cu ⁺ , 2,2'-bipyridyl	20	0.15	4.26	7.87	10.73	12.98	2
	25	0.2	4.15				2
Cu ²⁺ , 2,2'-bipyridyl	25	0.16	4.31				2
	25	0.1	4.46				1
Cu ⁺ , α -alanine ^b	25	0.3		\sim 9.6			2
Cu ²⁺ , α -alanine ^b	25	0.01	8.18				1
	25	\rightarrow 0	8.51				1
	25	0.01		15.10			1
	25	0.1		15.01			1
	25	\rightarrow 0	8.40				1
	25	0.01		15.1			1
	25	0		15.54			1
	25	\sim 0.1		14.82			1
	20	0 corr	8.66				2
	25	0.3		15.0			2
Cu ⁺ , histidyl-histidine	20	0.1	8.15				2
	20	0.1	8.5				2
	25	0.2	8.29				2

Metal/Ligand	T ^o C	μ	K ₁	β_2	β_3	β_4	Reference
Cu ⁺ , L-picoline	20	0 corr	9.82	7.65	8.5		1
Cu ²⁺ , L-picoline	25	0.2	9.43				1
	25	0.1	9.48				1
	25	0.015	9.55	16.04			2
	20	~0	9.76	2.8			2
	22	1.5	9.83				2
Cu ⁺ , D-picoline	25	0.2	8.99	7.78	8.6	9.0	2
Cu ⁺ , L-carnosine ^b	25	0.1 ^c	7.24	11.42			7
Cu ²⁺ , L-carnosine ^b	25	0.16	4.2				1
	25	1.3	2.76				2
Cu ⁺ , 2,2'-bipyridyl	25	0.1	7.70	14.2	6.12	6.9	1
	25	0.3		13.18			2
Cu ²⁺ , 2,2'-bipyridyl	25	0.1	6.33	16.28	17.85		1
	25	1	6.44	8.20	8.8	9.2	1
Cu ²⁺ , L-picoline	20	0.1	8.0				1
	25	0.3	8.15				2
	25	0.1	8.15	5.39	7.56	9.26	2
	30	1	8.39				2
	25	1.3	2.99				2
Cu ⁺ , glycyl-L-histidine ^b	25	0.1 ^c	6.72	11.58	5.16	6.77	7
Cu ⁺ , histidyl-histidine ^b	25	0.1 ^c	7.95	12.47	8.00	10.97	7
Cu ²⁺ , histidyl-histidine ^b	25	0.135		12.92			1
Cu ⁺ , histamine	25	0.1	6.71	10.33			1
	25	0.1	12.0				1
Cu ²⁺ , histamine	25	0.135	9.55				1
	30	1	9.60				1
	20	0.015		16.2			1

Metal/Ligand	T °C	μ	K ₁	β_2	β_3	β_4	Reference
Cu ⁺ , α -picoline	25	0.1	5.40	7.65	8.5		2
Cu ²⁺ , α -picoline	20	0.2	14.6				1
Cu ²⁺ , 1,10-phenanthroline	25	0.1	1.3				2
	25	1.3	1.75				2
	25	0.61	1.69	2.8			2
Cu ⁺ , β -picoline	25	0.1	5.60	7.78	8.6	9.0	2
Cu ²⁺ , β -picoline	20	0.1	9.0				1
	25	0.1	2.77				2
	25	1.3	2.76				2
	25	0.61	2.70	4.72	6.12	6.9	2
Cu ⁺ , γ -picoline	20	0.15	4.30	7.65			2
	25	0.1	5.65	8.20	8.8	9.2	2
Cu ²⁺ , γ -picoline	20	0.1	16.0				1
	25	0.5	2.82				1
	20	0.15	2.56	5.39	7.66	9.54	2
	25	0.1	2.88				2
	25	1.3	2.99				2
	25	0.61	2.93	5.16	6.77	8.08	2
Cu ⁺ , benzimidazole	20	0.15	4.47	9.73			2
Cu ²⁺ , benzimidazole	20	0.15	3.56	6.34	9.00	10.97	2
Cu ⁺ , histamine	25	0.1 ^c	6.71	10.32			7
Cu ²⁺ , histamine	25	0.135	9.55				1
	30	1	9.60				1
	20	0.015		16.2			1

Metal/Ligand	T ^o C	μ	K ₁	β_2	β_3	β_4	Reference
Cu ⁺ , 1,10-phenanthroline	25	0.3		15.82			2
Cu ²⁺ , 1,10-phenanthroline	20	0.1	9.30				1
(phen)	25	0.4	6.30				1
	25	0.01	9.08		20.94		1
	25	0.1	7.4		17.00		1
	25	0.3	8.82				2
	25	0.1	8.82				2
	25	0.5	9.16				2
Cu ⁺ , 2-chloro-phen	25	0.3		14.6			2
Cu ²⁺ , 2-chloro-phen	25	0.3	5.60				2
Cu ⁺ , 2-methyl-phen	25	0.3		16.95			2
Cu ²⁺ , 2-methyl-phen	25	0.3	7.4				2
	25	0.1	7.40				2
Cu ⁺ , 2,9-dimethyl phen	25	0.3		19.1			2
Cu ²⁺ , 2,9-dimethyl phen	25	0.3	~6.1				2
	25	0.1	5.2				2
Cu ⁺ , 2,2':6,2"-terpyridine	25	0.3	~9.3				2
Cu ²⁺ , 2,2':6,2"-terpyridine	25	0.3	~13.0				2
Cu ⁺ , 2,2'-biquinolyl	25	0.3		~16.5			2
Cu ²⁺ , 2,2'-biquinolyl	25	0.3	4.27				2

Metal/Ligand	T ^o C	μ	K ₁	β_2	β_3	β_4	Reference
Cu ⁺ , acetonitrile	25	0.1		4.35			2
Cu ⁺ , cysteine ^a	25	0.1		3.9	4.1		2
Cu ²⁺ , cysteine ^b	20	0.2	3.28				3
Cu ²⁺ , cysteine ^c	25	~0.02			4.6		this work

- a Cu⁺ ligand donor atom
- b Anionic form of ligand
- c 0.19M acetonitrile present

TABLE 3. Sulphur-donor^a and Miscellaneous Ligands

Metal/Ligand	T ^o C	μ	K ₁	β_2	β_3	β_4	Reference
Cu ⁺ , cysteine ^b	25	1	19.2				1
Cu ²⁺ , cysteine ^b	25	0.17		16.0			2
Cu ⁺ , penicillamine ^b	25	1	19.53				2
Cu ²⁺ , penicillamine ^b	25	0.15	16.5				2
	25	0.17		15.13			2
Cu ⁺ , thiourea	25	0.1				15.39	8
	25	~0.02				14.8	this work
Cu ⁺ , 2-(methylthio)-ethylamine	20	0.15	5.65	10.98			2
Cu ²⁺ , 2-(methylthio)-ethylamine	30	1	5.58				1
	30	0 corr	5.42				1
	20	0 corr	5.61				1
	20	0.15	5.30	9.68			2
Cu ⁺ , 3-(diphenylphosphino)-benzenesulphonic acid ^c	25	1	5.76				2
Cu ⁺ , dimethylthioformamide	25	~0.02				13.6	this work

a Cu⁺ ligand donor atom

b Dianionic form of ligand

c Anionic form of ligand

TABLE 4. Olefinic Ligands^a

Ligand	Structure	T ^o C	μ	K ₁	Reference
propene	$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{CH}_3 \end{array}$	25	→0	5.02	9
2-methyl propene	$\begin{array}{c} \text{H} & & \text{CH}_3 \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{CH}_3 \end{array}$	25	→0	4.49	9
allyl alcohol (AA)	$\begin{array}{c} \text{H} & & \text{CH}_2\text{OH} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	25	0.1	4.72	1
	$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	25	0.1	4.7	2
2-chloro-AA	$\begin{array}{c} \text{H} & & \text{CH}_2\text{OH} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{Cl} \end{array}$	25	0.1	2.66	1
	$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	25	0.1	2.34	10
1-methyl-AA	$\begin{array}{c} \text{H} & & \text{CH(OH)CH}_3 \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	25	0.1	4.52	1
2-methyl-AA	$\begin{array}{c} \text{H} & & \text{CH}_2\text{OH} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{CH}_3 \end{array}$	25	0.1	3.96	1
α,α -dimethyl AA	$\begin{array}{c} \text{H} & & \text{C(CH}_3)_2\text{OH} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	25	0.1	4.40	10
γ,γ -dimethyl AA	$\begin{array}{c} \text{CH}_3 & & \text{CH}_2\text{OH} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{CH}_3 & & \text{H} \end{array}$	25	0.1	4.04	10
maleic acid	$\begin{array}{c} \text{HOOC} & & \text{COOH} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	25	0.1	3.05	1
fumaric acid	$\begin{array}{c} \text{HOOC} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{COOH} \end{array}$	25	0.1	3.96	1

Ligand	Structure	T ^o C	μ	K ₁	Reference
vinylacetic acid		25	0.1	4.53	1
crotonic acid		25	0.1	3.20	1
itaconic acid		25	0.1	3.34	11
tiglic acid		25	0.1	2.32	11
β,β-dimethylacrylic acid		25	0.1	2.04	11
mesaconic acid		25	0.1	2.61	11
citraconic acid		25	0.1	1.34	11
crotyl alcohol		25	0.1	4.00	1
2-methylbut-2-en-1-ol		25	0.1	3.55	1
3-methylbut-3-en-2-ol		25	0.1	3.60	10
methylvinylcarbinol		25	0.1	4.52	10

Ligand	Structure	T ^o C	μ	K ₁	Reference
ethylvinylcarbinol	$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{H} & & \text{C}(\text{C}_2\text{H}_5)\text{HOH} \end{array}$	25	0.1	4.59	10
4-methylpent-4-en-2-ol	$\begin{array}{c} \text{H} & & \text{CH}_3 \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{H} & & \text{CH}_2\text{CH}(\text{OH})\text{CH}_3 \end{array}$	25	0.1	4.20	1

a Cu(II) does not form complexes with carbon-carbon double bonds

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