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The determination of the stability constants of metal chloro complexes

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"THE DETERMINATION OF THE STABILITY CONSTANTS OF

METAL CHLORO COMPLEXES"

A Thesis submitted in partial fulfilment of the

requirements for the degree of

BACHELOR OF SCIENCE (HONOURS)

By

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November, 1968.

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SUMMARY

The chloro complexes of Copper (II), Zinc (II), Cadmium (II) and the Mercury (II) ions have been investigated using potentiometric methods, and the recently available chloride ion activity electrode. The cumulative stability constants at $25^{\circ}C$ for the system of complexes has been evaluated at Zinc $B_1 = 6.68$, Cadmium $B_1 = 4.7 \times 10^1$, Copper $B_1 = 0.61 \times 10^2$, $B_2 = 1.6 \times 10^4$ and Mercury $B_1 = 3.2 \times 10^6$, $B_2 = 1.4 \times 10^{10}$, $B_3 = 5.5 \times 10^{12}$ and $B_4 = 4.3 \times 10^{14}$. By determining the stability constants over the temperature range $(25-50^{\circ}C)$, the values $\triangle H = 0.83$ KCals/mole, $\triangle S = 11.2$ cals/deg. and $\triangle G = -2.5$ KCals/mole have been calculated for the highest complex of mercury from the V'ant Hoff Isochore using standard computer programs.

The observed trend in stability is found to be $Zn^{2+} < Cd^{2+} < Cu^{2+} < Hg^{2+}$; and this is discussed in relation to a combination of electrostatic and covalent interactions, together with addition stabilisation due to different available bonding orbitals of the cations.

CHAPTER I

INTRODUCTION

SECTION 1

AIMS

The Aims of this project are to study potentiometrically the stability constants of several metal chloro complexes. Specifically the four main aims are:

(i)   To determine the stability constants for the chloro complexes of Copper (II), Zinc (II), Cadmium (II) and Mercury (II).

(ii)   To determine the stability constants over a range of temperature ($25-50^{\circ}$C) in order to evaluate the thermodynamic quantities $\triangle G$, $\triangle H$ and $\triangle S$ for the complexing reaction.

(iii)   To evaluate the worthwhileness of the Chloride Ion Activity Electrode.

(iv)   To arrange the metal ions in an order of increasing stability and to explain the trend found.

SECTION 2

REVIEW OF THE CHEMISTRY OF THE METAL IONS AND METAL CHLORO COMPLEXES

The metals investigated were those of Groups IB and IIB of the periodic table.

The Group IIB metals have S^2 electrons outside filled d shells, whereas the Group IB metals can lose one S electron, and one or two d electrons to give complexes or ions in the I, II and III oxidation states [1]. This is no longer possible for the Group IIB metals and there is no evidence for oxidation states higher than II.

The third ionisation potentials are extremely high for Zn, Cd and Hg and energies of salvation or lattice energies cannot suffice to render the III oxidation state chemically stable. See Table I.

Table I

Ionization Potential	Zinc	Cadmium	Mercury
1st	9.39 e.v.	8.99 e.v.	10.43 e.v.
2nd	17.89 "	16.84 "	18.65 "
3rd	40.00 "	38.00 "	34.30 "

The ions Zn^{2+}, Cd^{2+} and Hg^{2+} all have filled d orbitals, because of this, these metal ions are regarded as non-transitional. As the maximum co-ordination number for these ions with the chloride ligand is four [2], [3], [4], the maximum formed complex is $[MX_4]^{2-}$.

The orbitals used in the complex are the 4S, $4P^3$ orbitals, and the shape of the complex is tetrahedral. Fig. I.

The stability of these complexes is attributed partly to the covalence in the bonds, achieved by the use of metal SP^3 hybrid orbitals, and partly to the fact that the tetrahedral configuration is the most stable one for four co-ordination from an electrostatic point of view.

Raman Spectra studies [5] have shown the steriochemistry of the complex $[MCl_2]$ to be linear, $[MCl_3]^-$ to be planar, and $[MCl_4]^=$ to be tetrahedral, and no evidence has been found for square planar four co-ordination complexes of these ions.

The Cu^{2+} has a d^9 configuration, and there is a possibility of two structures of the $[CuCl_4]^=$ complex. One is the SP^2d square planar complex and the other is an SP^3 tetrahedral. The tetrahedral would suffer the Jahn-Teller distortions to give a distorted tetrahedral complex.

Spectral investigations have been carried out on $[CuCl_4]^=$ [6], and the structure of the ion identified as a distorted tetragonal, formed by pushing the atoms at the ends of diagonal up from the plane and those at the other end of the diagonal down from the plane. The tetragonal structure is shown in Fig. II.
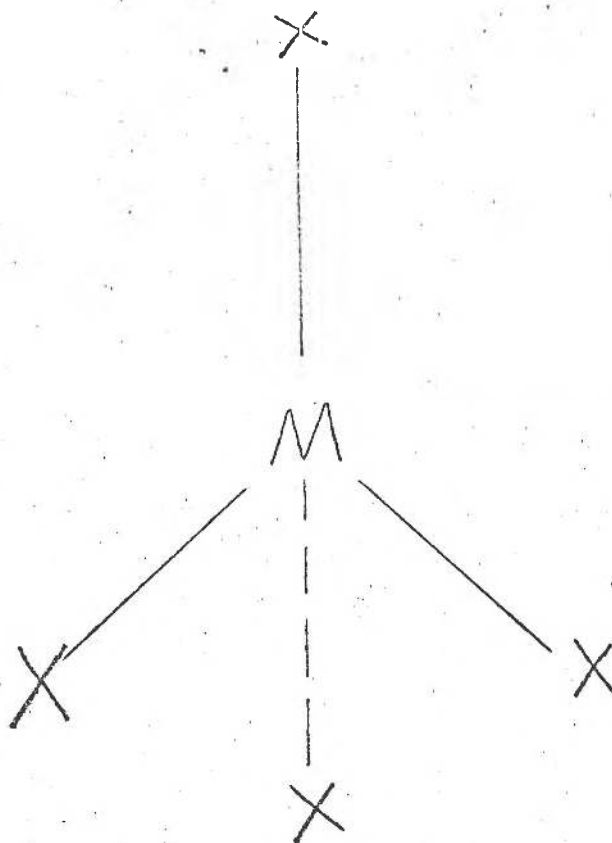
FIG. I   The Tetrahedral structure of the chloro complex of the Group IIB metals.
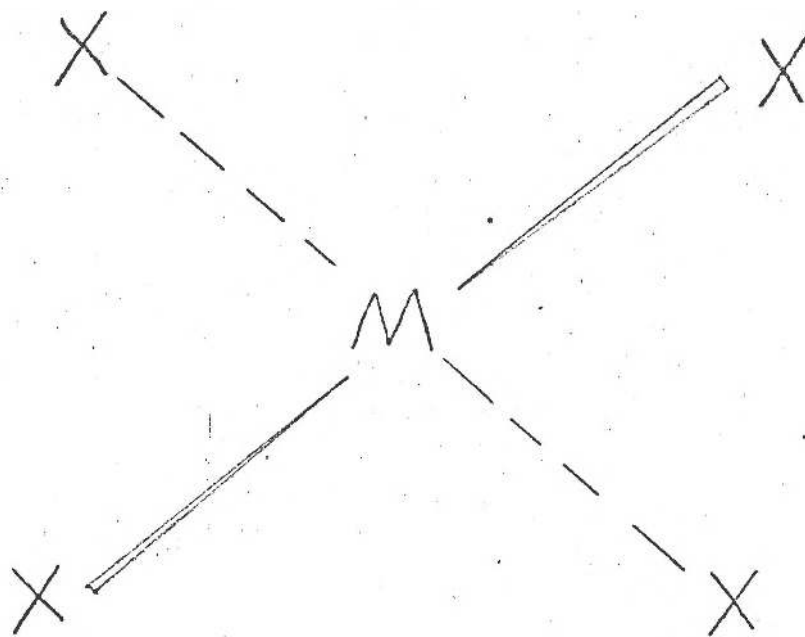
FIG. II   The distorted square planar structure of the chloro complex of copper (11).

Previous Work on Metal Chloro Complexes

Previous workers who have determined the stability constants of the chloro complexes of the metals investigated have used several techniques. The most important of these and the most relevant to the present work is the potentiometric [7] [11] [12] [18] [19] [20] [21] [22] investigation using metal electrodes for the determination of the free metal ion concentration, and estimating the free chloride ion concentration.

Other methods that have been employed include; conductivity [23], spectrophotometry [14], cation exchange [13] [15], solubility [9] [10], freezing paint determinations [16] [17] and distribution between two phases [8]. Details of the stability constants obtained by these methods and applicable to the metals under study in this present work appear in table. 2 5.

SECTION 3

PRINCIPLES OF DETERMINATION OF STABILITY CONSTANTS

In studying the formation of co-ordination complexes in solution, two kinds of stability are important, namely, thermodynamic stability and kinetic stability. The thermodynamic stability of a species is a measure of the extent to which this species will form from or be transformed into other species when the system has reached equilibrium, whereas the kinetic stability refers to the speed with which transformations leading to the attainment of equilibrium will occur.

The scope of the present work only involves the thermodynamic stability of the complex.

When a monodentate ligand X is added to the metal ion M, the following equilibrium expressions are set up.

$$M + X \rightleftharpoons MX \qquad K_1 = \frac{[MX]}{[M][X]} \qquad (1)$$

$$MX + X \rightleftharpoons MX_2 \qquad K_2 = \frac{[MX_2]}{[MX][X]} \qquad (2)$$

$$MX_2 + X \rightleftharpoons MX_3 \qquad K_3 = \frac{[MX_3]}{[MX_2][X]} \qquad (3)$$

$$MXn-1 + X \rightleftharpoons MXn \qquad Kn = \frac{[MXn]}{[MXn-1][X]} \qquad (4)$$
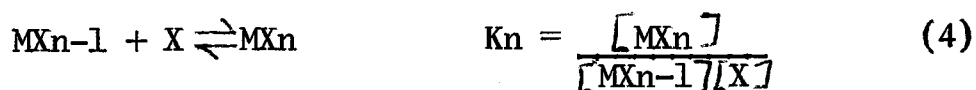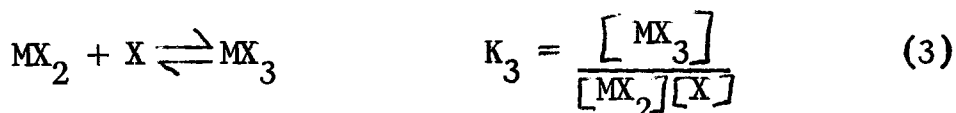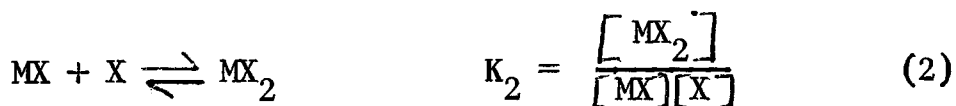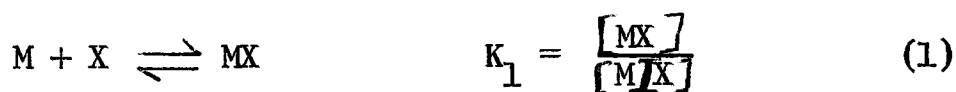
There are n such equilibria set up, where n represents the maximum co-ordination number of the metal ion for that particular ligand.

Another set of equilibrium expressions can also be set up.

$$M + X \rightleftharpoons MX \qquad B_1 = \frac{[MX]}{[M][X]} \qquad (5)$$

$$M + 2X \rightleftharpoons MX_2 \qquad B_2 = \frac{[MX_2]}{[M][X^2]} \qquad (6)$$

$$M + 3X \rightleftharpoons MX_3 \qquad B_3 = \frac{[MX_3]}{[M][X]^3} \qquad (7)$$

$$M + nX \rightleftharpoons MXn \qquad B_n = \frac{[MXn]}{[M][X]^n} \qquad (8)$$
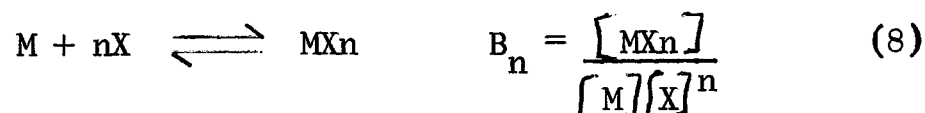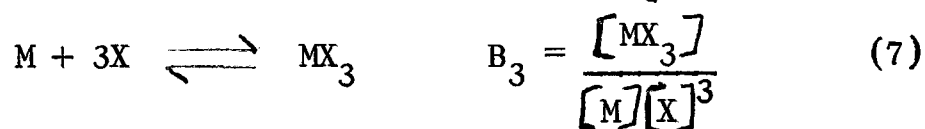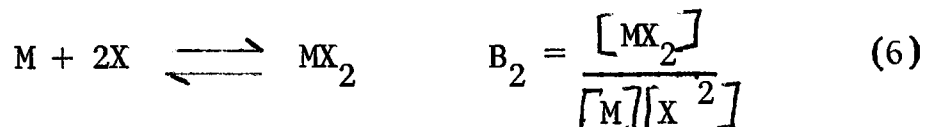
The relationship between the two sets of equilibrium expressions is

$$B_t = K_1, K_2, K_3 \ldots\ldots\ldots K_t = \sum_{i=1}^{i=t} K_i \qquad (9)$$

Where the K_i values denote the stepwise formation constants (or stability constants) and the B_i values denote the overall formation or stability constants.

The total concentrations M and X of the metal and Ligand respectively are given by

$$M = m + [MX^+] + [MX_2] + [MX_3^-] + \ldots + [MXn] \qquad (10)$$

$$X = x + [MX^+] + 2[MX_2] + 3[MX_3^-] + \ldots + N[MXn] \qquad (11)$$

where m = concentration of free metal ion

x = concentration of free ligand

Equations (10) and (11) can be written in terms of the overall stability constants as

$$M = m \sum_{o}^{n} B_n X^n \qquad (12)$$

$$X = x + m \sum_{1}^{n} n\, B_n X^n \qquad (13)$$

In order to calculate the overall stability constants, the quantities M, X, m and x should be known, and in principal if three of these quantities are known it is possible to calculate the B_n values.

Previous workers studying metal chloro complexes have used potentiometric measurements to evaluate the free metal concentration. For each metal concentration they also knew both the total metal concentration and total chloride concentration.

This was sufficient information to allow the calculation of the stability constants using one of the methods surveyed by Rossotti and Rossotti.[24]

However, if the other variable of the system i.e. the free chloride concentration, x, could be monitored the evaluation of the stability constants would be greatly simplified.

In this present work, the free chloride concentration has been monitored using the Chloride Ion Activity Electrode. This electrode[*] is a recent development and has been used here for the first time to assist in the evaluation of the stability constants.

Consequently, as each of the four quantities, M, X, m, and x are known, either of equations can be solved simultaneously over a set of data points to yield the only unknown in the equations, viz. the B_n values.

This method is possible provided n is known in equarions (10) and (11), and that dynamic equilibrium has been established.

Types of Stability Constants

Stability constants at a given temperature are usually reported either as activity quotients, which are thermodynamic stability constants, or as concentration quotients, which are stoichiometric stability constants. Activity quotients should be independent of the ionic medium, while concentration quotients are valid only for solutions of a particular composition.

In this work concentration coefficients are determined in the presence of a large excess of background Electrolyte.

[*] Athom News, October 1967, Vol.6 No.2.
A periodic review of developments in the design, construction and application of scientific apparatus and instruments.

It is thus assumed that the activity coefficients are independent of the concentrations of the reacting species and depend only on the nature and concentration of the background electrolyte.

Computation of thermodynamic constants from measurements of M and X requires a knowledge of the activity coefficients of each of the $n + 2$ species in solution, and this is extremely difficult to obtain. Thermodynamic constants are, therefore better obtained by extrapolating to infinite dilution stoichiometric values which have been determined using solutions of known ionic strength.

For the first step of complex formation between M^{2+} and X^-
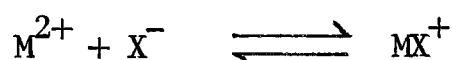
$$M^{2+} + X^- \rightleftharpoons MX^+$$

The thermodynamic stepwise stability constant is given by

$$K_i^T = \frac{[MX^+]}{[M^{2+}][X^-]} \times \frac{\gamma_{MX^+}}{\gamma_{M^{2+}}\gamma_{X^-}} \tag{14}$$

The stoichiometric stepwise constant is given

$$K_1^S = \frac{[MX^+]}{[M^{2+}][X^-]} \tag{15}$$

Thermodynamic stability constants are necessary as a basis for discussing the factors involved in the stability of a complex. They are related to the standard enthalpies and entropies of complex formation in the pure solvent. However it is often difficult to obtain accurate values of thermodynamic stability constants. This is

especially so if the values of the activity coefficient terms given by equation (14), can not be obtained. In such cases it is preferable to obtain reliable values of the stoichiometric constants (quasithermodynamic values), where these describe the stability of a species relative to the experimental system used.

SECTION 4

THE CHLORIDE ION ACTIVITY ELECTRODE

The Model 92-17 Liquid Ion Exchange Chloride Ion Activity Electrode directly measures chloride ion activity. Once calibrated against solutions of known chloride ion activity this electrode, without regard to sample ionic composition or total ionic strength, measures chloride ion activity in the unknown.

The chloride electrode develops a potential which is proportional to the logarithm of the activity of the chloride ion in solution. The potentials may be read directly in millivolts on a sensitive value voltmeter or precision potentiometer.

The principle of the chloride electrode is identical with that of a glass electrode, but instead of developing an electrical potential across a glass membrane, it develops the potential across a thin layer of water immicible liquid ion exchanger, this liquid being held in place by a thin porous inert membrane disc. See Fig. III.

The liquid ion exchanger exhibits a very high specificity for chloride ion. A chloride containing internal filling solution contacts the inside surface of the membrane disc, and the chloride ion in this solution provides a stable potential between the inside of the membrane and the internal solution, as well as for the reference electrode. Thus changes in potential

The Chloride Ion Activity Electrode.

Passages for charging the electrode.

Internal Aqueous filling solution

Ion exchanger reservoir

Porous membrane

Ag-AgCl reference electrode
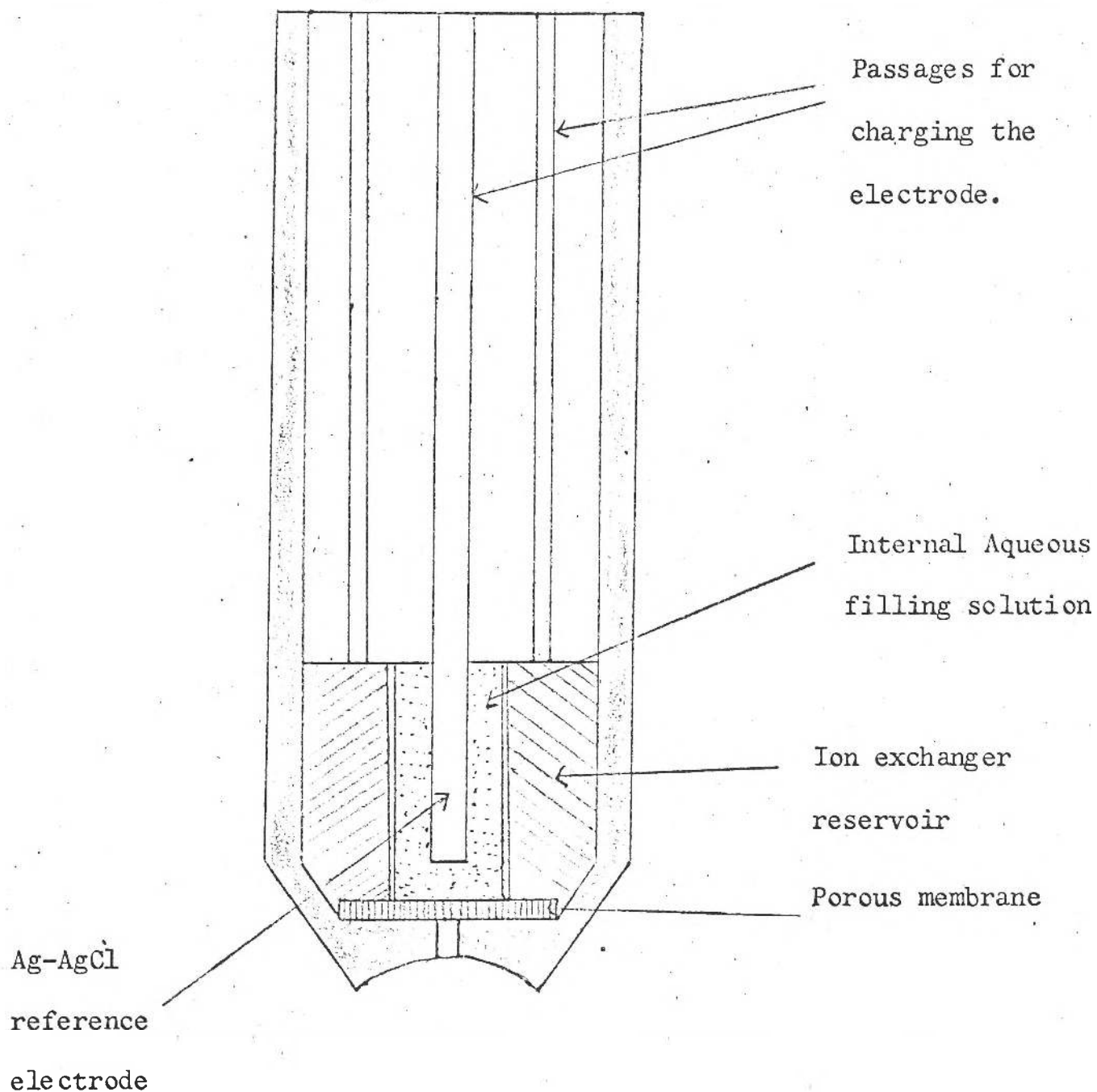
FIG. III   Cross section showing liquid ion exchange chloride ion activity electrode

are only due to changes in the sample chloride ion activity.

The electrode exhibits nernst behaviour in pure chloride solutions down to 2×10^{-4} molar chloride ion in accordance with the following equation.

$$E = Constant - \frac{2.303RT}{F} \log A_{cl^-}$$

where

E = measured total potential of the system.

$Constant$ = the portion of the total potential due to choice of reference electrode and internal solution.

$\frac{2.3RT}{F}$ = Nernst factor (59.15 Mv at $15^{\circ}C$)

R & F are Constants.

A_{cl^-} = the chloride ion activity in the sample.

Unfortunately the chloride electrode responds to some extent to anions other than chloride, although not to cations.

Table 2 shows the extent of response to a variety of anions relative to chloride and points to the choice of anions which may be present in the cell system.

Table 2

Table of Selectivity Constants for Interfering Anions

Interfering Ion	Ki
ClO_4^-	32.0
I^-	17.0
NO_3^-	4.2
Br^-	1.6
OH^-	1.0
OAC^-	0.32
HCO_3^-	0.19
$SO_4^=$	0.14
F^-	0.10

where Ki is the selectivity constant and the activity of chloride ions in mixed anion solutions is given by

$$E = Constant - \frac{2.3RT}{F} \log (^A cl^- + Ki\ Ci)$$

e.g. In a solution containing a five fold excess of flouride over chloride, the flouride present would make the level of chloride appear to be one half again as large as the actual level of chloride present.

The electrode responds linearly to chloride activities in the range (10^{-1} to 10^{-5}) molar. The limit of detection is determined by the small but finite solubility of the liquid ion exchanger.

In solutions more concentrated than 10^{-1} M the liquid ion

exchanger behaves in a non-theoretical way.

The electrode was able to be used in the PH range

(2 - 10.5). The upper limit depends on both the chloride ion

concentration and the hydroxyl ion concentration. See Fig. IV.

FIG. IV Electrode potential behavior versus solution pH in pure NaCl solutions
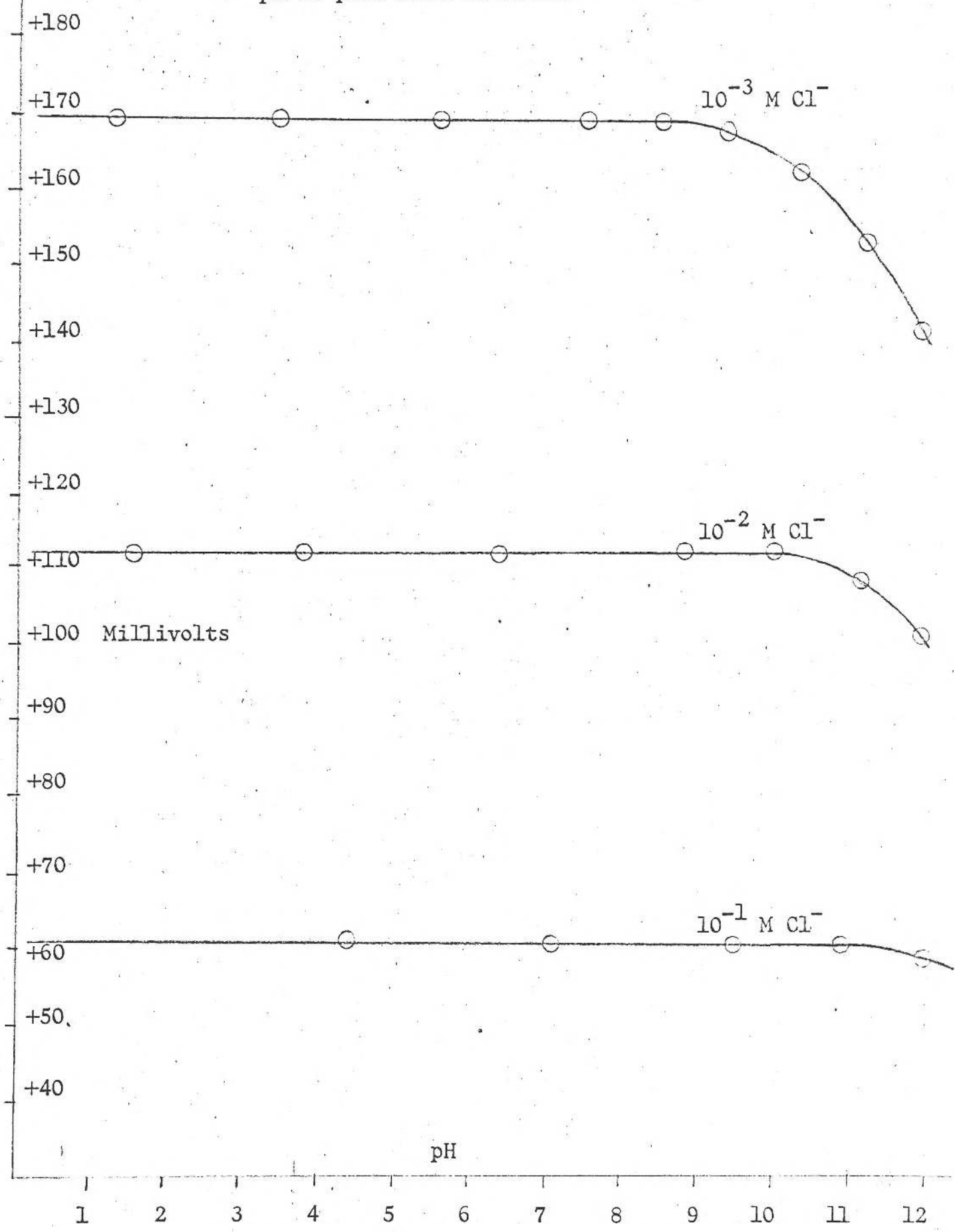
SECTION 5

THE POTENTIAL OF A METAL ELECTRODE

According to modern views,[25] [25a] a metal is considered

to consist mainly of metal ions and free electrons of high

mobility. When a metal is placed in water there is a tendency for

metal ions to leave the metal and enter the liquid phase in which

they are freely soluble.

If the metal is placed in a solution already containing

some of the particular metal ions; these ions will oppose the

tendency for metal ions from the metal to enter the solution.

We may say that the metal ions are soluble in both the metal and

the liquid phase and hence they tend to distribute themselves

between the two phases. This leads then to the establishment of an

electrical double layer. When copper ions are placed in pure, air-

free water, some copper ions leave the metal and enter the metal

solution interface, leaving the metal negatively changed. If the

solution contains copper chloride, copper ions from the solution

enter the metal. In order to maintain electroneutrality of the

solution, an equivalent amount of chloride ions are dragged to the

interface, forming the negative side of the double layer, while the

metal becomes positively charged.

The fact that there is an electrical double layer at the

interface between a metal and a solution means that there is a

difference in potential between the two phases. The phase containing the excess of positive electricity is at a more positive potential than the phase with the excess of negative electricity.

Thus for the copper system, the potential of the copper is positive with respect to the solution. It is in the relative change of this potential between the copper and the solution as a function of the copper ion concentration that is of interest.

Therefore changes in the composition of the solution will cause changes in the potential. The difference in potential between the two phases can be accurately determined by measuring the Electromotive Force (E.M.F.) of a cell containing these two phases, against a reference electrode have a constant potential.

The reference electrode used in all investigations was the calomel electrode saturated with respect to potassium chloride.

The normal types of metal electrodes used are the pure metal electrode, as has been discussed for copper, and the amalgam electrode. The amalgam electrode has a pure metal dissolved in mercury and is of the same principle as the pure metal electrode but that the surface area is very much greater. As polarisation problems are associated with small surface area electrodes, the amalgam electrode is commonly used.

The metals investigated undergo the reversible reaction.

$$M^{2+} + 2e^- \rightleftharpoons M \text{ (S)}$$
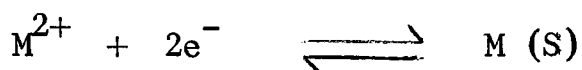
when placed in a solution of the ion M^{2+}.

The potential acquired by the metal is given by the Nernst equation.

$$E = Eo^1 + Ej + \frac{RT}{nF} \times \ln\left[M^{2+}\right]$$

where

Eo^1 = a constant for any particular cell

Ej = the liquid junction potential.

The following assumptions are made:

(i)   The activity coefficients can be held constant so that m depends only on the concentration of one or more species.

(ii)   The temperature of the cell can be controlled to $\pm 0.1^\circ C$.

(iii)   The liquid junction potential, Ej, is assumed to be constant throughout the measurements.

(iv)   The value of Eo^1 can be determined using solutions in which m is known.

The purpose of the E.M.F. measurements was to measure the ratio of the total metal concentration to the free metal concentration at each ligand concentration. The ratio is defined by

$$\propto = \frac{M}{m} = \frac{\text{Total Metal}}{\text{Free Metal}}$$

CHAPTER II

EXPERIMENTAL

SECTION 1

USE OF THE CHLORIDE ION ACTIVITY ELECTRODE

Electrode potentials developed in four standards of known chloride ion activity were measured using a Metrohm expanded scale millivolt meter; and plotted against the corresponding activity values to produce an activity calibration curve. See Fig. V. The electrode potential developed in the cell by the free chloride ions is converted directly to chloride ion activity by means of the calibration curve.

The activity of the chloride ion is determined because it is the activity which determines the extent to which chloride ion reacts with other species in the solution.

Normal salt bridges which are used in the calomel electrode e.g. conc KCl or KNO_3 obviously could not be used because of diffusion into the cell and/or anion interference. A 10^{-3} M $K_2 SO_4$ bridge was found to be satisfactory.

FIG. V   Chloride Ion activity calibration curve.
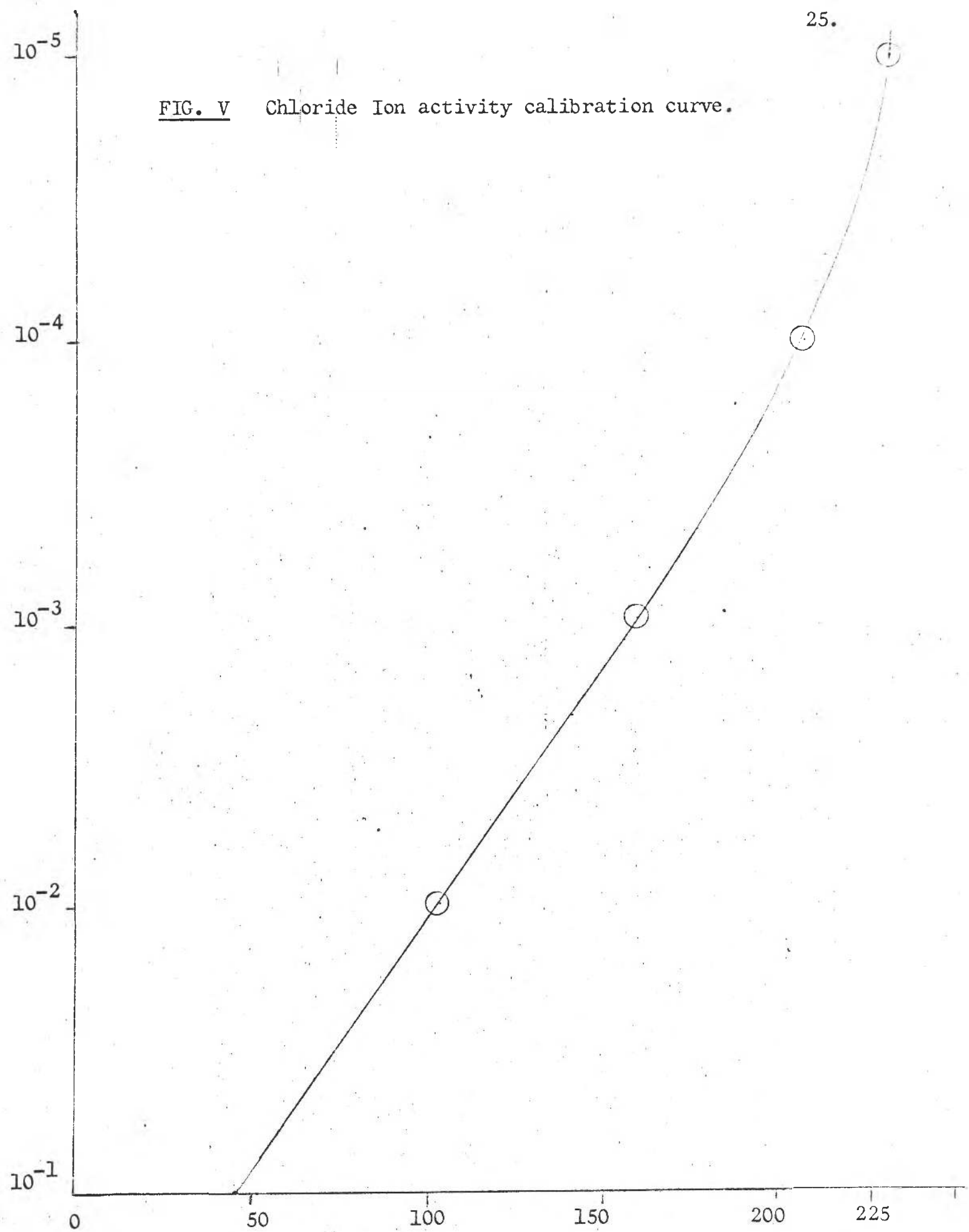
SECTION 2

THE METAL ELECTRODE SYSTEM

Using a pure cadmium metal electrode to measure the potential of the free cadmium ions in solution a drift in the potential occurred due to polarisation effects. The potential could not be stabilized even when the size of the metal electrode was increased and when a cadmium coated, platinum gause electrode was used.

Equilibration between the electrode and the solution is extremely fast however, when an amalgam electrode M - Hg is used. A cadmium amalgam electrode was made by dissolving 3 grams of pure cadmium into triply distilled mercury, 100 gms. The amalgam was stored and used under nitrogen, because in an oxidising atmosphere cadmium hydronide and finely divided cadmium metal were displaced from the amalgam and interferred with the potential developed by the free cadmium ions. Therefore the couple Cd^{2+}/Cd - Hg forms a half cell and the potential of the galvanic cell is measured against a calomel electrode.

The zinc system was similar to that of cadmium, as large surface area pure zinc electrodes gave unstable potentials in solutions of zinc ions. A 3% Zn amalgam electrode was prepared by dissolving zinc in mercury. When used in an atmosphere of nitrogen (26) the electrode developed a stable potential, and reproducible results were obtained.

The mercury system employed the use of a pure mercury electrode. A problem associated with this was that mercury metal reduces mercury Hg^{2+} to Hg^{+} very rapidly when Hg^{o} and Hg^{2+} are in contact with each other, so separated cells were used, connected up by a platinum bridge, Fig. VI.

The response is rapid and excellent reproducibility was obtained.

The copper system was the most complex. The pure copper electrode gave irreproducible results, even when large surface area electrodes were used. A 3% copper amalgam electrode was prepared by an electrodeposition process using a mercury cathode. The amalgam was found to be unstable and contamination of the cell occurred even when kept under nitrogen. After this copper amalgams were prepared in much smaller concentrations, but even then they were unstable and broke down.

Bjerrum and Nielsen [27] had prepared and used a 5% Cu-Hg amalgam electrode for measurement of the copper ion potential, but had made no reference to the instability of the electrode as found in the present work.

A possible explanation which could suggest the behaviour of the amalgam in the present work was that some other metal, e.g. iron, was already dissolved in the mercury forming an amalgam, and
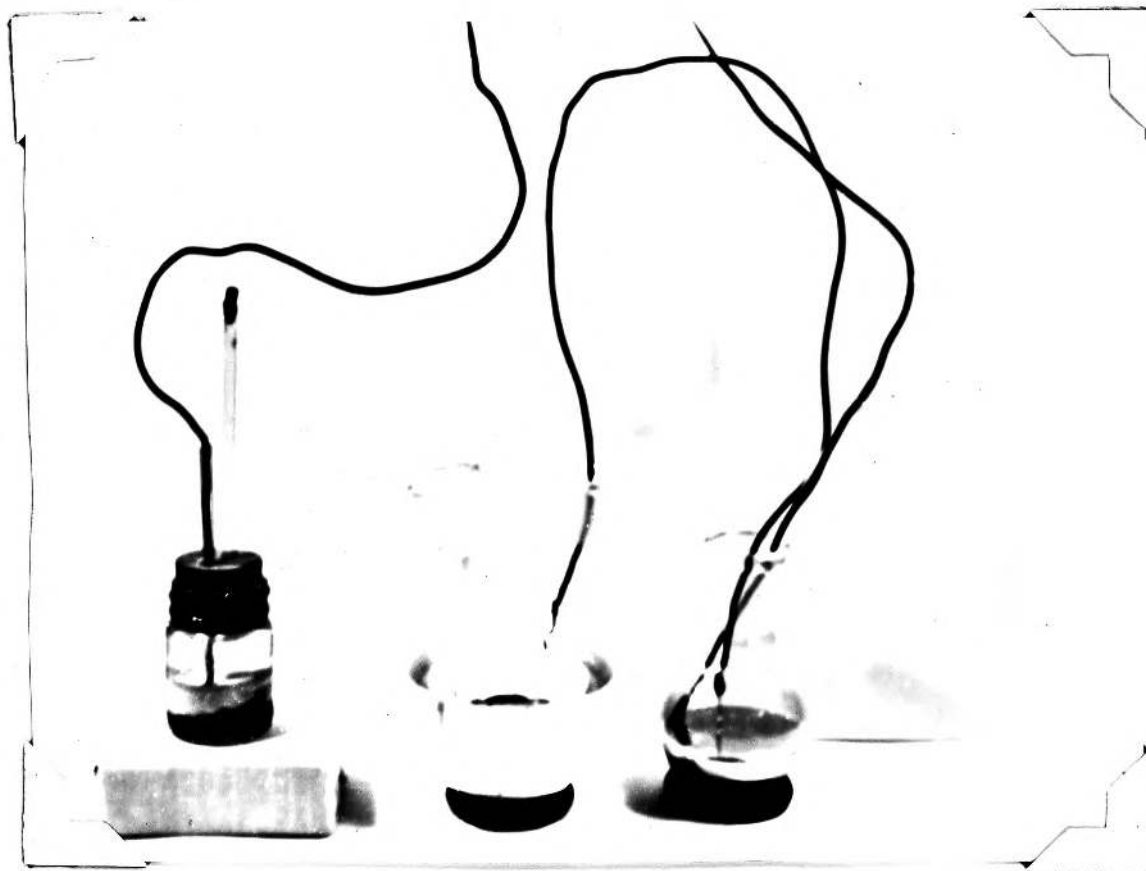
FIG. VI   The Hg^{2+}/Hg^{o} Cell System.

Left to Right

(a)   Calomel electrode

(b)   Cell containing Hg^{2+} solution

(c)   Platinum bridge

(d)   Cell containing Hg^{o}

(e)   Platinum electrode

when the copper amalgam was formed the iron was displacing the copper from the amalgam.

To test this theory, pure mercury was obtained and then triply distilled, so that it should be clean, but on forming the copper amalgam it was again found to be unstable.

A modified form of the copper electrode was eventually used and gave reproducible results. It involved the use of pure copper metal coated with a thin layer of mercury. The electrode was easy to use and it was not necessary to keep the cell under nitrogen, as the surface of the electrode was unaffected by the solution.

SECTION 3

POTENTIOMETRIC MEASUREMENTS

To obtain a set of measurements the following procedure was used. 200 mls of 10^{-3} molar M Cl_2 stock solution was placed in the cell and thermostated to the working temperature. The metal electrode, chloride electrode and the saturated calomel electrode were placed in the cell, and the system allowed to come to equilibrium, Fig. VII. The potentials of both the chloride electrode and metal electrode were measured, and 5×10^{-2} molar NaCl was added in 5 ml increment, and the whole procedure repeated until 100 mls of the sodium chloride solution had been added. The total metal ion concentration and ligand ion concentration were known by calculation, due to the amount of dilution.

The free chloride activity was obtained by checking the potentials against the chloride electrode calibration curve already obtained at the working temperature.

The free metal concentration was obtained by use of the Nernst equation and by the use of calibrating known metal concentrations against the potential developed, and referring the potentials obtained from cell measurements to this calibration curve.

The results obtained from the measurements are shown in Table 3 - 12.
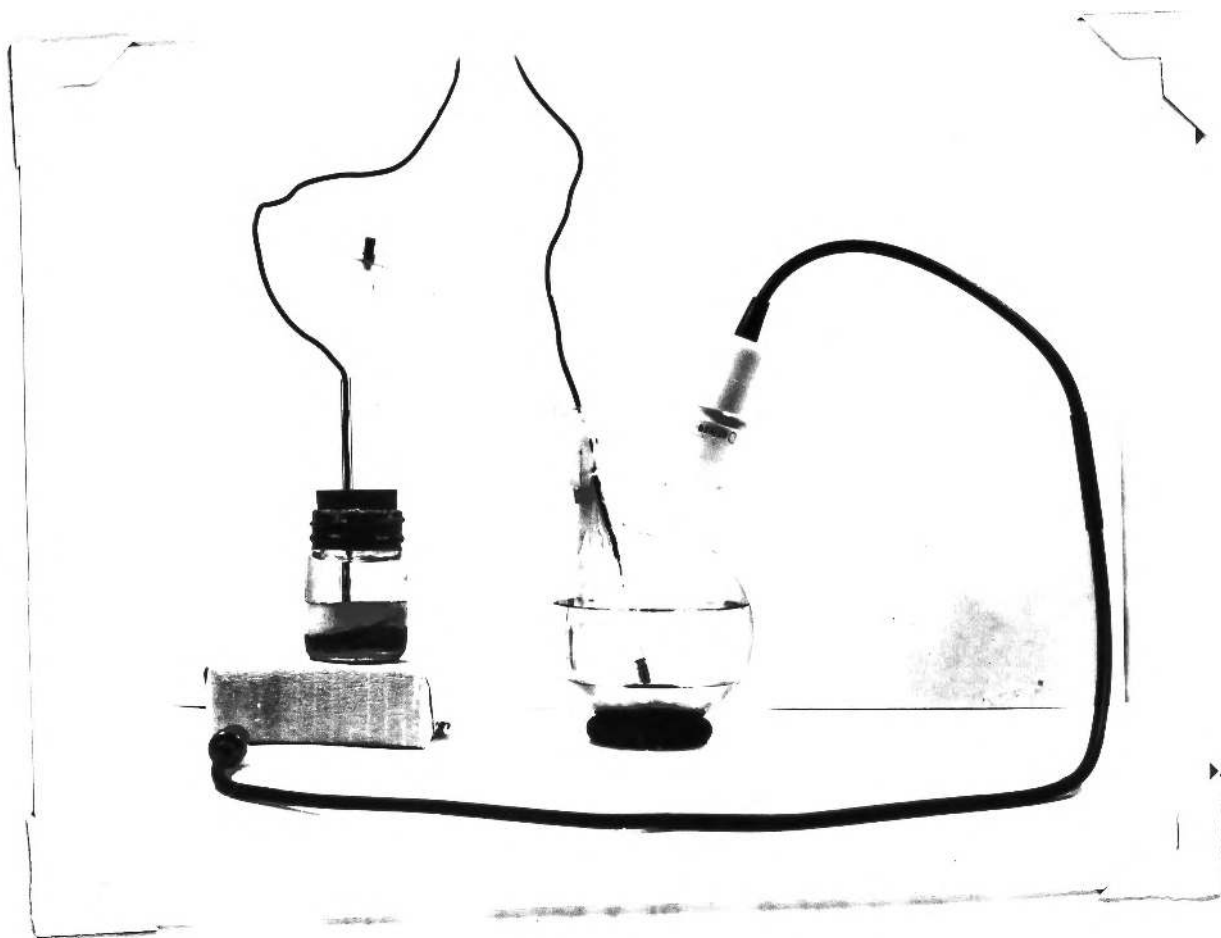
FIG. VII   The Cell System.

Left to Right

(a)   Calomel electrode

(b) N_2 gas inlet tube

(c)   Platinum electrode

(d)   C.I.A.E.

and the amalgam pool is shown in the cell.

Table 3

Copper System at 25°C

Addition	Cu^{2+} Pot.	Cl Pot	Free $[Cu^{2+}]$	Free $[Cl^-]$	Total $[Cu^{2+}]$
0.00 mls.	10.0 Mv	137.5 Mv	9.600×10^{-4}	1.462×10^{-3}	1.000×10^{-3}
3.0	11.7	128.9	8.913×10^{-4}	2.879×10^{-3}	9.804×10^{-4}
6.0	13.6	122.4	7.852×10^{-4}	3.462×10^{-3}	9.615×10^{-4}
9.0	14.7	118.3	7.178×10^{-4}	3.892×10^{-3}	9.434×10^{-4}
12.0	15.7	115.3	6.683×10^{-4}	4.292×10^{-3}	9.259×10^{-4}
15.0	16.5	111.2	6.397×10^{-4}	4.462×10^{-3}	9.091×10^{-4}
18.0	17.7	107.1	5.957×10^{-4}	4.842×10^{-3}	8.929×10^{-4}
21.0	18.5	104.5	5.623×10^{-4}	5.395×10^{-3}	8.772×10^{-4}
30.0	22.1	99.8	4.365×10^{-4}	7.498×10^{-3}	8.333×10^{-4}
40.0	25.5	93.5	3.428×10^{-4}	8.318×10^{-3}	7.895×10^{-4}
50.0	28.8	90.8	2.754×10^{-4}	9.162×10^{-3}	7.500×10^{-4}
60.0	30.5	87.0	2.455×10^{-4}	1.059×10^{-2}	7.143×10^{-4}
80.0	35.4	82.0	1.758×10^{-4}	1.228×10^{-2}	6.522×10^{-4}
100.0	41.8	79.2	1.122×10^{-4}	1.429×10^{-2}	6.000×10^{-4}
120.0	46.2	77.0	8.318×10^{-5}	1.585×10^{-2}	5.555×10^{-4}
140.0	49.7	74.4	6.331×10^{-5}	1.721×10^{-2}	5.172×10^{-4}

Table 4

Copper System at 40°C

Addition	Cu^{2+}Pot	Cl Pot	Free $[Cu^{2+}]$	Free $[Cl^-]$	Total $[Cu^{2+}]$
0.00 mls.	8.7 Mv	141.7 Mv	9.50×10^{-4}	1.811×10^{-3}	1.00×10^{-3}
3.0	10.0	129.6	8.511×10^{-4}	3.120×10^{-3}	9.804×10^{-4}
6.0	11.0	122.5	7.943×10^{-4}	4.260×10^{-3}	9.615×10^{-4}
9.0	12.2	116.5	7.244×10^{-4}	4.420×10^{-3}	9.434×10^{-4}
12.0	13.5	113.5	6.683×10^{-4}	4.830×10^{-3}	9.259×10^{-4}
15.0	15.2	110.2	5.929×10^{-4}	5.120×10^{-3}	9.091×10^{-4}
18.0	16.5	107.4	5.458×10^{-4}	5.820×10^{-3}	8.929×10^{-4}
21.0	17.7	104.4	5.035×10^{-4}	7.128×10^{-3}	8.772×10^{-4}
30.0	23.0	99.8	3.548×10^{-4}	8.830×10^{-3}	8.333×10^{-4}
40.0	27.0	95.1	2.661×10^{-4}	1.030×10^{-2}	7.895×10^{-4}
50.0	29.5	92.3	2.239×10^{-4}	1.122×10^{-2}	7.500×10^{-4}
60.0	32.5	88.3	1.837×10^{-4}	1.259×10^{-2}	7.143×10^{-4}
80.0	37.4	84.0	1.318×10^{-4}	1.413×10^{-2}	6.522×10^{-4}
100.0	44.0	81.1	8.414×10^{-5}	1.560×10^{-2}	6.000×10^{-4}
120.0	48.4	78.4	6.166×10^{-5}	1.718×10^{-2}	5.555×10^{-4}
140.0	54.0	75.2	4.217×10^{-5}	1.914×10^{-2}	5.172×10^{-4}

Table 5

Copper System at 50°C

Addition	Cu^{2+} Pot	Cl Pot	Free $[Cu^{2+}]$	Free $[Cl^-]$	Total $[Cu^{2+}]$
0.0 mls.	10.2 Mv	149.0 Mv	9.441×10^{-4}	1.778×10^{-3}	1.00×10^{-3}
3.0	12.1	138.6	8.710×10^{-4}	3.020×10^{-3}	9.804×10^{-4}
6.0	13.8	132.4	8.128×10^{-4}	4.026×10^{-3}	9.615×10^{-4}
9.0	14.9	126.0	7.499×10^{-4}	4.222×10^{-3}	9.434×10^{-4}
12.0	16.1	121.6	7.079×10^{-4}	4.582×10^{-3}	9.259×10^{-4}
15.0	18.2	118.9	5.957×10^{-4}	5.000×10^{-3}	9.091×10^{-4}
18.0	19.1	115.4	5.070×10^{-4}	5.720×10^{-3}	8.929×10^{-4}
21.0	22.6	113.5	4.624×10^{-4}	6.839×10^{-3}	8.772×10^{-4}
30.0	26.2	109.6	3.548×10^{-4}	7.980×10^{-3}	8.333×10^{-4}
40.0	29.7	102.7	2.410×10^{-4}	1.012×10^{-2}	7.895×10^{-4}
50.0	31.4	99.8	1.862×10^{-4}	1.122×10^{-2}	7.500×10^{-4}
60.0	37.2	96.2	1.429×10^{-4}	1.273×10^{-2}	7.143×10^{-4}
80.0	43.1	92.3	8.414×10^{-5}	1.436×10^{-2}	6.522×10^{-4}
100.0	48.9	89.0	5.957×10^{-5}	1.585×10^{-2}	6.000×10^{-4}
120.0	56.2	87.0	4.169×10^{-5}	1.699×10^{-2}	5.555×10^{-4}
140.0	60.6	84.7	3.162×10^{-5}	1.862×10^{-2}	5.172×10^{-4}

Table 6

Zinc System at 25°C

Addition	Zn^{2+}	Cl^-	Total $[Zn^{2+}]$	Free $[Zn^{2+}]$	Free $[Cl^-]$
0.00 mls	1104.0 Mv	137.0 Mv	1.00×10^{-3}	9.960×10^{-4}	1.899×10^{-3}
2.0	1104.4	130.1	9.868×10^{-4}	9.376×10^{-4}	2.519×10^{-3}
4.0	1105.2	126.2	9.740×10^{-4}	8.511×10^{-4}	3.049×10^{-3}
6.0	1105.9	123.5	9.615×10^{-4}	8.241×10^{-4}	3.439×10^{-3}
8.0	1106.4	120.5	9.493×10^{-4}	7.674×10^{-4}	3.699×10^{-3}
10.0	1107.0	117.5	9.375×10^{-4}	7.328×10^{-4}	3.890×10^{-3}
15.0	1108.5	112.2	9.090×10^{-4}	6.427×10^{-4}	4.890×10^{-3}
20.0	1109.7	107.6	8.823×10^{-4}	5.834×10^{-4}	5.754×10^{-3}
30.0	1110.5	102.5	8.333×10^{-4}	5.395×10^{-4}	6.918×10^{-3}
40.0	1111.2	98.3	7.894×10^{-4}	5.129×10^{-4}	8.260×10^{-3}
50.0	1111.5	92.0	7.500×10^{-4}	5.012×10^{-4}	1.052×10^{-2}
60.0	1112.0	88.5	7.143×10^{-4}	4.753×10^{-4}	1.197×10^{-2}
80.0	1113.1	85.5	6.522×10^{-4}	4.416×10^{-4}	1.334×10^{-2}
100.0	1113.6	83.5	6.000×10^{-4}	4.217×10^{-4}	1.445×10^{-2}
120.0	1114.6	82.0	5.556×10^{-4}	3.855×10^{-4}	1.556×10^{-2}

Table 7

Zinc System at 40°C

Addition	Zn^{2+}	Cl^-	Total $[Zn^{2+}]$	Free $[Zn^{2+}]$	Free $[Cl^-]$
0.00 mls	1101.1 mv.	140.0 m.v.	1.000×10^{-3}	9.900×10^{-4}	1.690×10^{-3}
2.0	1101.6	131.2	9.868×10^{-4}	9.333×10^{-4}	2.494×10^{-3}
4.0	1102.3	127.1	9.740×10^{-4}	8.810×10^{-4}	3.025×10^{-3}
6.0	1102.9	124.1	9.615×10^{-4}	8.414×10^{-4}	3.442×10^{-3}
8.0	1103.5	121.2	9.493×10^{-4}	7.943×10^{-4}	3.710×10^{-3}
10.0	1104.0	118.0	9.375×10^{-4}	7.586×10^{-4}	3.926×10^{-3}
15.0	1104.8	112.9	9.090×10^{-4}	7.079×10^{-4}	4.860×10^{-3}
20.0	1105.5	108.1	8.823×10^{-4}	6.683×10^{-4}	5.728×10^{-3}
30.0	1107.0	102.1	8.333×10^{-4}	5.984×10^{-4}	6.982×10^{-3}
40.0	1109.1	97.7	7.894×10^{-4}	5.012×10^{-4}	9.078×10^{-3}
50.0	1111.4	94.1	7.500×10^{-4}	4.169×10^{-4}	1.143×10^{-2}
60.0	1112.5	91.5	7.143×10^{-4}	3.784×10^{-4}	1.429×10^{-2}
80.0	1113.5	89.3	6.522×10^{-4}	3.467×10^{-4}	1.578×10^{-2}
100.0	1114.1	86.5	6.000×10^{-4}	3.327×10^{-4}	1.637×10^{-2}
120.0	1114.6	84.5	5.556×10^{-4}	3.177×10^{-4}	1.786×10^{-2}

Table 8

Zinc System at 50°C

Addition	Zn^{2+}	Cl^-	Total $[Zn^{2+}]$	Free $[Zn^{2+}]$	Free $[Cl^-]$
0.00 mls	1098.3 mv	154.5 mv	1.000×10^{-3}	9.780×10^{-4}	1.622×10^{-3}
2.0	1099.3	142.4	9.868×10^{-4}	9.078×10^{-4}	2.489×10^{-3}
4.0	1099.7	138.4	9.740×10^{-4}	8.630×10^{-4}	3.032×10^{-3}
6.0	1100.4	134.6	9.615×10^{-4}	8.166×10^{-4}	3.448×10^{-3}
8.0	1100.9	131.4	9.493×10^{-4}	7.762×10^{-4}	3.742×10^{-3}
10.0	1101.6	128.5	9.375×10^{-4}	7.345×10^{-4}	3.981×10^{-3}
15.0	1101.9	122.7	9.090×10^{-4}	7.079×10^{-4}	4.910×10^{-3}
20.0	1102.3	117.5	8.823×10^{-4}	6.761×10^{-4}	5.821×10^{-3}
30.0	1103.1	112.1	8.333×10^{-4}	6.310×10^{-4}	7.079×10^{-3}
40.0	1104.3	102.5	7.894×10^{-4}	5.728×10^{-4}	9.661×10^{-3}
50.0	1105.7	94.5	7.143×10^{-4}	5.129×10^{-4}	1.251×10^{-2}
60.0	1107.0	89.0	6.522×10^{-4}	4.571×10^{-4}	1.542×10^{-2}
80.0	1108.2	86.0	6.000×10^{-4}	4.093×10^{-4}	1.698×10^{-2}
100.0	1109.8	84.5	5.556×10^{-4}	3.548×10^{-4}	1.778×10^{-2}
120.0	1110.9	83.0	5.172×10^{-4}	3.177×10^{-4}	1.884×10^{-2}

Table 9

Cadmium System at 25°C

Addition	Cd^{2+}	Cl^-	Free $[Cd^{2+}]$	Free $[Cl^-]$	Total $[Cd^{2+}]$
0.00 mls	681.6 mv	143.0 mv	9.226×10^{-4}	1.778×10^{-3}	10.00×10^{-4}
2.0	682.8	137.8	8.395×10^{-4}	2.213×10^{-3}	9.90×10^{-4}
4.0	684.5	134.2	7.345×10^{-4}	2.512×10^{-3}	9.804×10^{-4}
6.0	685.0	129.8	7.063×10^{-4}	3.020×10^{-3}	9.709×10^{-4}
8.0	685.5	126.5	6.792×10^{-4}	3.428×10^{-3}	9.615×10^{-4}
10.0	686.0	122.2	6.546×10^{-4}	4.027×10^{-3}	9.524×10^{-4}
12.0	686.8	120.6	6.145×10^{-4}	4.315×10^{-3}	9.434×10^{-4}
14.0	687.4	118.5	5.864×10^{-4}	4.667×10^{-3}	9.346×10^{-4}
20.0	688.4	114.0	5.420×10^{-4}	5.559×10^{-3}	9.091×10^{-4}
30.0	689.3	108.8	5.058×10^{-4}	6.761×10^{-3}	8.696×10^{-4}
40.0	690.3	104.3	4.667×10^{-4}	8.035×10^{-3}	8.333×10^{-4}
50.0	692.1	101.7	4.064×10^{-4}	9.120×10^{-3}	8.000×10^{-4}
60.0	693.7	98.2	3.589×10^{-4}	1.012×10^{-2}	7.692×10^{-4}
70.0	695.1	96.0	3.218×10^{-4}	1.122×10^{-2}	7.407×10^{-4}
80.0	696.5	93.5	2.897×10^{-4}	1.230×10^{-2}	7.143×10^{-4}
100.0	698.2	89.5	2.530×10^{-4}	1.429×10^{-2}	6.667×10^{-4}
120.0	700.1	86.4	2.180×10^{-4}	1.641×10^{-2}	6.250×10^{-4}
140.0	701.6	82.2	1.939×10^{-4}	1.884×10^{-2}	5.882×10^{-4}

Table 10

Mercury System at 25°C

Additions	Hg^{2+}	Cl^-	Total $[Hg^{2+}]$	Free $[Hg^{2+}]$	Free $[Cl^-]$
0.00 mℓs	457.3 Mv.	196.5 Mv.	5.00×10^{-3}	6.46×10^{-6}	2.426×10^{-4}
4.0	397.4	160.1	4.902×10^{-3}	3.520×10^{-8}	2.610×10^{-3}
8.0	386.2	146.2	4.808×10^{-3}	2.050×10^{-8}	3.210×10^{-3}
10.0	378.4	138.0	4.762×10^{-3}	1.514×10^{-8}	3.630×10^{-3}
12.0	370.2	133.1	4.717×10^{-3}	8.412×10^{-9}	4.120×10^{-3}
16.0	362.4	127.9	4.630×10^{-3}	5.210×10^{-9}	5.318×10^{-3}
20.0	353.7	124.3	4.545×10^{-3}	2.269×10^{-9}	6.712×10^{-3}
24.0	350.8	121.2	4.464×10^{-3}	1.862×10^{-9}	7.341×10^{-3}
28.0	347.3	117.6	4.386×10^{-3}	1.425×10^{-9}	7.921×10^{-3}
30.0	343.7	116.2	4.348×10^{-3}	1.055×10^{-9}	8.520×10^{-3}
32.0	340.4	113.9	4.310×10^{-3}	8.425×10^{-10}	9.081×10^{-3}
36.0	338.2	110.5	4.237×10^{-3}	6.720×10^{-10}	9.630×10^{-3}
40.0	334.0	109.6	4.167×10^{-3}	5.012×10^{-10}	1.145×10^{-2}
50.0	329.9	105.9	4.000×10^{-3}	3.659×10^{-10}	1.181×10^{-2}
60.0	321.8	101.2	3.846×10^{-3}	1.965×10^{-10}	1.222×10^{-2}
80.0	320.0	98.6	3.571×10^{-3}	1.712×10^{-10}	1.389×10^{-2}
100.0	316.1	97.3	3.333×10^{-3}	1.259×10^{-10}	1.531×10^{-2}
120.0	312.2	95.7	3.125×10^{-3}	9.406×10^{-11}	1.672×10^{-2}
140.0	307.2	94.7	2.941×10^{-3}	6.407×10^{-11}	1.762×10^{-2}

Table 11

Mercury System at 40°C

Additions	Hg^{2+}	Cl^-	Total $[Hg^{2+}]$	Free $[Hg^{2+}]$	Free $[Cl^-]$
0.00 mls.	460.1 Mv.	196.0 Mv.	5.00×10^{-3}	5.442×10^{-6}	2.344×10^{-4}
4.00	398.2	159.6	4.902×10^{-3}	4.962×10^{-8}	2.512×10^{-3}
8.00	389.6	145.8	4.808×10^{-3}	4.102×10^{-8}	3.106×10^{-3}
10.00	383.0	137.6	4.762×10^{-3}	3.200×10^{-8}	3.532×10^{-3}
12.00	375.6	132.8	4.717×10^{-3}	1.235×10^{-8}	4.025×10^{-3}
16.00	369.8	127.4	4.630×10^{-3}	8.884×10^{-9}	5.212×10^{-3}
20.00	365.5	123.8	4.545×10^{-3}	7.773×10^{-9}	6.607×10^{-3}
24.00	361.4	120.7	4.464×10^{-3}	6.016×10^{-9}	7.242×10^{-3}
28.00	358.7	117.2	4.386×10^{-3}	4.325×10^{-9}	7.816×10^{-3}
30.00	356.0	115.9	4.348×10^{-3}	3.189×10^{-9}	8.414×10^{-3}
32.00	352.7	113.4	4.310×10^{-3}	2.524×10^{-9}	8.984×10^{-3}
36.00	349.4	110.2	4.237×10^{-3}	1.983×10^{-9}	9.524×10^{-3}
40.00	346.2	108.9	4.167×10^{-3}	1.566×10^{-9}	1.047×10^{-2}
50.00	340.4	105.2	4.000×10^{-3}	1.070×10^{-9}	1.084×10^{-2}
60.00	333.7	100.7	3.846×10^{-3}	6.759×10^{-10}	1.122×10^{-2}
80.00	325.0	98.0	3.571×10^{-3}	3.367×10^{-10}	1.288×10^{-2}
100.00	319.4	96.7	3.333×10^{-3}	2.236×10^{-10}	1.429×10^{-2}
120.00	315.7	95.2	3.125×10^{-3}	1.517×10^{-10}	1.567×10^{-2}
140.00	310.8	94.0	2.941×10^{-3}	1.122×10^{-10}	1.660×10^{-2}

Table 12

Mercury System at 50°C

Addition	Hg^{2+}	Cl^-	Total $[Hg^{2+}]$	Free $[Hg^{2+}]$	Free $[Cl^-]$
0.00 mls.	461.5 mv	195.3 mv	5.00×10^{-3}	5.387×10^{-6}	2.239×10^{-4}
4.00	402.0	160.0	4.902×10^{-3}	3.621×10^{-8}	2.334×10^{-3}
8.00	394.7	146.2	4.808×10^{-3}	2.254×10^{-8}	2.854×10^{-3}
10.00	390.0	138.3	4.762×10^{-3}	1.858×10^{-8}	2.985×10^{-3}
12.00	379.4	132.4	4.717×10^{-3}	9.213×10^{-9}	3.582×10^{-3}
16.00	374.2	126.8	4.630×10^{-3}	8.416×10^{-9}	4.812×10^{-3}
20.00	370.3	120.5	4.545×10^{-3}	5.232×10^{-9}	5.370×10^{-3}
24.00	362.0	119.8	4.464×10^{-3}	3.721×10^{-9}	6.035×10^{-3}
28.00	359.8	116.4	4.386×10^{-3}	2.964×10^{-9}	6.649×10^{-3}
30.00	357.9	112.5	4.348×10^{-3}	2.439×10^{-9}	7.329×10^{-3}
32.00	353.9	111.2	4.310×10^{-3}	2.013×10^{-9}	8.065×10^{-3}
36.00	350.2	109.6	4.237×10^{-3}	1.624×10^{-9}	8.792×10^{-3}
40.00	348.0	105.6	4.167×10^{-3}	1.225×10^{-9}	9.550×10^{-3}
50.00	342.7	104.9	4.000×10^{-3}	7.966×10^{-10}	1.059×10^{-2}
60.00	336.3	103.5	3.846×10^{-3}	4.742×10^{-10}	1.202×10^{-2}
80.00	326.6	99.1	3.571×10^{-3}	2.525×10^{-10}	1.333×10^{-2}
100.00	320.9	96.0	3.333×10^{-3}	1.680×10^{-10}	1.380×10^{-2}
120.00	315.5	93.4	3.125×10^{-3}	1.268×10^{-10}	1.462×10^{-2}
140.00	311.3	90.8	2.941×10^{-3}	8.752×10^{-11}	1.514×10^{-2}

Significance of Changes in potential of M^{2+}/M upon addition of Cl^-

Table 13 shows that the order of stability of the complexes is as

$$Zn^{2+} < Cd^{2+} < Cu^{2+} \ll Hg^{2+}$$

This is a reasonable assumption, as the change in $\triangle E$, determines the amount of metal ion taken up in the complex and hence the stability, and as a greater change occurs with Hg^{2+} than with Cu^{2+} upon addition of ligand, the Hg^{2+} complex is the most stable. As only small changes occur with Cd^{2+}, Zn^{2+} and Cu^{2+} their chloro complexes are weak. This same trend was also found by Riley.[28]

Table 13

Changes in potential of M^{2+}/M at $25^{\circ}C$.

Addition of NaCl	Cu^{2+}	Hg^{2+}	Zn^{2+}	Cd^{2+}
5.0 mls	6.6 *mv*	74.0 *mv*	3.0 *mv*	5.4 *mv*
10.0	10.0	96.0	5.7	8.4
15.0	12.8	114.0	6.5	10.3
20.0	15.5	123.0	7.2	11.4
25.0	18.8	128.9	7.5	13.5
30.0	20.5	134.6	8.0	14.7
40.0	24.2	139.2	9.0	15.5
50.0	27.6	141.2	9.5	16.6

Polarography Analysis

By way of confirmation of the weak stability of the metal chloro complexes, polarographic studies were carried out using a Cambridge Model Recording Polarograph, Table 14 shows characteristics of procedure and apparatus used.

Table 14

Reference electrode	= Satd. calomel electrode with a 10^{-3}M Na_2SO_4 salt bridge.
Column height	= 40 cms.
Mass of drop of Hg	= 1.6 mgs/sec.
Time for drop	= 4.4 secs.

The studies were made on Zinc and Cadmium systems using a 1.0M $NaNO_3$ background electrolyte, by running a polarogram of uncomplexed metal ions, and then adding ligand and running further polarograms.

The recording apparatus was unable to pick up the small changes in the $E_{\frac{1}{2}}$ value associated with complexing, and this confirmed that the Zinc and Cadmium chloro complexes were weak.

CHAPTER III

RESULTS AND DISCUSSIONS

METHOD OF CALCULATION OF STABILITY CONSTANTS

Two methods were employed for the calculation of stability constants.

Method I

The total metal ion concentration is expressed as

$$M = m + \left[MX^{+}\right] + \left[MX_{2}\right] + \left[MX_{3}^{-}\right] + \left[MX_{4}^{=}\right]$$

which reduces to

$$\frac{M}{m} = 1 + B_{1}X + B_{2}X^{2} + B_{3}X^{3} + B_{4}X^{4}$$

where   M = Total metal ion concentration

m = Free metal ion concentration

x = Free ligand ion concentration

This is a quartic equation in the free ligand concentration x, and is of the form

$$y = Ax^{4} + Bx^{3} + Cx^{2} + Dx + E,$$

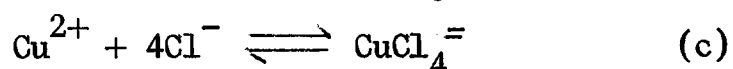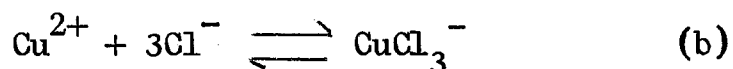where y is obtained from metal electrode measurements and x is obtained from C.I.A.E. measurements.

Sets of values of y and x were fed into a 60K, I.B.M. - 1620 computer system.

The coefficients A, B, C and D of the equation were printed out and these coefficients correspond to the cumulative stability constants B_{4}, B_{3}, B_{2} and B_{1} respectively.

This method* was found to be restictive for the weak chloro complexes of Cu, Zn and Cd. The reason for this was that for the complexes with co-ordination numbers 2, 3 and 4, dynamic equilibrium had not been established as they are weak complexes.

The equilibria

$$Cu^{2+} + 2Cl^- \rightleftharpoons CuCl_2 \qquad (a)$$

$$Cu^{2+} + 3Cl^- \rightleftharpoons CuCl_3^- \qquad (b)$$

$$Cu^{2+} + 4Cl^- \rightleftharpoons CuCl_4^= \qquad (c)$$
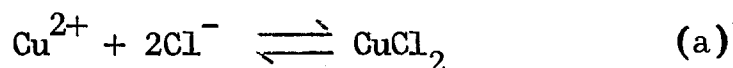
have to be forced in the appropriate direction by the addition of large concentrations of ligand. This was not possible in this present work, because of the limitations of the chloride electrode.

For the strong chloro complex of mercury, the values of B_4, B_3, B_2 and B_1 were acceptable because for these, the equilibriums had been established.

Method II

This method overcame the difficulties associated with method I above.

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* Non Linear Least-Square Curve Fitting Program

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Published by I.B.M. Australia for 1620 Computers

The expression [29] is given by

$$Bn = \frac{(M - m)}{m \left\{ X - n (M - m) \right\}^n} \tag{16}$$

where

M = total metal ion concentration

m = free metal ion concentration

X = total ligand ion concentration

n = co-ordination number

but

$$X - n (M - m) = x, \tag{17}$$

the free ligand concentration.

Equation 17 is readily verified by using the expressions given in equations (10) and (11) for the total metal ion and ligand concentrations.

This x is measured by using the chloride ion activity electrode.

Expression (16) then reduces to

$$Bn = \frac{(M - m)}{m (x)^n}$$

and was evaluated by using a Forgo computer program and feeding in the values M, m and x. A listing of the program is found in the Appendix.

From t sets of data points t values of B_1, B_2, B_3 and B_4 were obtained, and these values were plotted against the total

chloride concentration. If a minimum occurred in the plot it meant that dynamic equilibrium for the expressions (a), (b) and (c) above had been established, and the value of the cumulative stability constants at this minimum was recorded. If no minimum occurred the B value could not be obtained.

The reasoning for this method of approach is as follows:

Suppose n = 1, the first complex formed is MX^+

M – m = concentration of metal ions bound in the form of a complex to ligand.

Therefore M – m = $\left[MX^+ \right]$

As the concentration of halide increases by addition, the concentrations of $\left[MX_2 \right]$, $\left[MX_3^- \right]$ and $\left[MX_4^= \right]$ also increases, so the value of M – m becomes progressively larger than $\left[MX^+ \right]$, consequently, the value of B_1, will show a continuous increase, when B_1 is plotted against the total halide concentration.

The same reasoning is applied for the evaluation of the B_2, B_3 and B_4 values.

From this method, if a minimum value of the stability constant for the t sets of data points is found, then this value is recorded. Tables 15-24 show the entire sets of B values obtained by this method and Figs. VIII, IX and X are plots of the logs of the B values for copper, versus the addition of NaCl and shows the minimum values obtained.

Table 15

Copper System at 25°C

B_1	B_2	B_3	B_4
$0.61 \times 10^{+2}$	$0.19 \times 10^{+5}$	$0.13 \times 10^{+8}$	$0.91 \times 10^{+10}$
$0.64 \times 10^{+2}$	$0.12 \times 10^{+5}$	$0.42 \times 10^{+7}$	$0.15 \times 10^{+10}$
$0.65 \times 10^{+2}$	$0.19 \times 10^{+5}$	$0.54 \times 10^{+7}$	$0.16 \times 10^{+10}$
$0.81 \times 10^{+2}$	$0.21 \times 10^{+5}$	$0.53 \times 10^{+7}$	$0.14 \times 10^{+10}$
$0.90 \times 10^{+2}$	$0.21 \times 10^{+5}$	$0.49 \times 10^{+7}$	$0.11 \times 10^{+10}$
$0.94 \times 10^{+2}$	$0.21 \times 10^{+5}$	$0.47 \times 10^{+7}$	$0.11 \times 10^{+10}$
$0.10 \times 10^{+3}$	$0.21 \times 10^{+5}$	$0.44 \times 10^{+7}$	$0.91 \times 10^{+9}$
$0.10 \times 10^{+3}$	$0.19 \times 10^{+5}$	$0.36 \times 10^{+7}$	$0.66 \times 10^{+9}$
$0.12 \times 10^{+3}$	$0.16 \times 10^{+5}$	$0.22 \times 10^{+7}$	$0.29 \times 10^{+9}$
$0.16 \times 10^{+3}$	$0.19 \times 10^{+5}$	$0.23 \times 10^{+7}$	$0.27 \times 10^{+9}$
$0.19 \times 10^{+3}$	$0.21 \times 10^{+5}$	$0.22 \times 10^{+7}$	$0.24 \times 10^{+9}$
$0.18 \times 10^{+3}$	$0.17 \times 10^{+5}$	$0.16 \times 10^{+7}$	$0.15 \times 10^{+9}$
$0.22 \times 10^{+3}$	$0.18 \times 10^{+5}$	$0.15 \times 10^{+7}$	$0.12 \times 10^{+9}$
$0.30 \times 10^{+3}$	$0.21 \times 10^{+5}$	$0.15 \times 10^{+7}$	$0.10 \times 10^{+9}$
$0.36 \times 10^{+3}$	$0.23 \times 10^{+5}$	$0.14 \times 10^{+7}$	$0.90 \times 10^{+8}$
$0.40 \times 10^{+3}$	$0.23 \times 10^{+5}$	$0.14 \times 10^{+7}$	$0.79 \times 10^{+8}$

Table 16

Copper System at 40°C

B_1	B_2	B_3	B_4
$0.66 \times 10^{+2}$	$0.16 \times 10^{+5}$	$0.89 \times 10^{+7}$	$0.49 \times 10^{+10}$
$0.64 \times 10^{+2}$	$0.16 \times 10^{+5}$	$0.50 \times 10^{+7}$	$0.16 \times 10^{+10}$
$0.67 \times 10^{+2}$	$0.12 \times 10^{+5}$	$0.27 \times 10^{+7}$	$0.64 \times 10^{+9}$
$0.68 \times 10^{+2}$	$0.15 \times 10^{+5}$	$0.35 \times 10^{+7}$	$0.79 \times 10^{+9}$
$0.80 \times 10^{+2}$	$0.17 \times 10^{+5}$	$0.34 \times 10^{+7}$	$0.71 \times 10^{+9}$
$0.10 \times 10^{+3}$	$0.20 \times 10^{+5}$	$0.40 \times 10^{+7}$	$0.78 \times 10^{+9}$
$0.11 \times 10^{+3}$	$0.19 \times 10^{+5}$	$0.32 \times 10^{+7}$	$0.55 \times 10^{+9}$
$0.10 \times 10^{+3}$	$0.15 \times 10^{+5}$	$0.20 \times 10^{+7}$	$0.29 \times 10^{+9}$
$0.15 \times 10^{+3}$	$0.17 \times 10^{+5}$	$0.20 \times 10^{+7}$	$0.22 \times 10^{+9}$
$0.19 \times 10^{+3}$	$0.19 \times 10^{+5}$	$0.18 \times 10^{+7}$	$0.17 \times 10^{+9}$
$0.21 \times 10^{+3}$	$0.19 \times 10^{+5}$	$0.17 \times 10^{+7}$	$0.15 \times 10^{+9}$
$0.23 \times 10^{+3}$	$0.18 \times 10^{+5}$	$0.14 \times 10^{+7}$	$0.11 \times 10^{+9}$
$0.28 \times 10^{+3}$	$0.20 \times 10^{+5}$	$0.14 \times 10^{+7}$	$0.99 \times 10^{+8}$
$0.39 \times 10^{+3}$	$0.25 \times 10^{+5}$	$0.16 \times 10^{+7}$	$0.10 \times 10^{+9}$
$0.47 \times 10^{+3}$	$0.27 \times 10^{+5}$	$0.16 \times 10^{+7}$	$0.92 \times 10^{+8}$
$0.59 \times 10^{+3}$	$0.31 \times 10^{+5}$	$0.16 \times 10^{+7}$	$0.84 \times 10^{+8}$

Table 17

Copper System at 50°C

B_1	B_2	B_3	B_4
$0.78 \times 10^{+3}$	$0.19 \times 10^{+5}$	$0.11 \times 10^{+8}$	$0.59 \times 10^{+10}$
$0.69 \times 10^{+3}$	$0.14 \times 10^{+5}$	$0.46 \times 10^{+7}$	$0.15 \times 10^{+10}$
$0.68 \times 10^{+3}$	$0.11 \times 10^{+5}$	$0.28 \times 10^{+7}$	$0.70 \times 10^{+9}$
$0.68 \times 10^{+3}$	$0.14 \times 10^{+5}$	$0.34 \times 10^{+7}$	$0.81 \times 10^{+9}$
$0.67 \times 10^{+3}$	$0.15 \times 10^{+5}$	$0.32 \times 10^{+7}$	$0.70 \times 10^{+9}$
$0.11 \times 10^{+3}$	$0.21 \times 10^{+5}$	$0.42 \times 10^{+7}$	$0.84 \times 10^{+9}$
$0.13 \times 10^{+3}$	$0.23 \times 10^{+5}$	$0.41 \times 10^{+7}$	$0.71 \times 10^{+9}$
$0.13 \times 10^{+3}$	$0.19 \times 10^{+5}$	$0.28 \times 10^{+7}$	$0.41 \times 10^{+9}$
$0.17 \times 10^{+3}$	$0.21 \times 10^{+5}$	$0.27 \times 10^{+7}$	$0.33 \times 10^{+9}$
$0.22 \times 10^{+3}$	$0.22 \times 10^{+5}$	$0.22 \times 10^{+7}$	$0.22 \times 10^{+9}$
$0.27 \times 10^{+3}$	$0.24 \times 10^{+5}$	$0.21 \times 10^{+7}$	$0.19 \times 10^{+9}$
$0.31 \times 10^{+3}$	$0.25 \times 10^{+5}$	$0.19 \times 10^{+7}$	$0.15 \times 10^{+9}$
$0.47 \times 10^{+3}$	$0.33 \times 10^{+5}$	$0.23 \times 10^{+7}$	$0.16 \times 10^{+9}$
$0.57 \times 10^{+3}$	$0.36 \times 10^{+5}$	$0.23 \times 10^{+7}$	$0.14 \times 10^{+9}$
$0.73 \times 10^{+3}$	$0.43 \times 10^{+5}$	$0.25 \times 10^{+7}$	$0.15 \times 10^{+9}$
$0.82 \times 10^{+3}$	$0.44 \times 10^{+5}$	$0.24 \times 10^{+7}$	$0.13 \times 10^{+9}$

Table 18

<u>Zinc System at $25^{\circ}C$</u>

B_1	B_2	B_3	B_4
$0.66 \times 10^{+1}$	$0.25 \times 10^{+4}$	$0.14 \times 10^{+7}$	$0.77 \times 10^{+9}$
$0.21 \times 10^{+2}$	$0.83 \times 10^{+4}$	$0.33 \times 10^{+7}$	$0.13 \times 10^{+10}$
$0.47 \times 10^{+2}$	$0.16 \times 10^{+5}$	$0.51 \times 10^{+7}$	$0.17 \times 10^{+10}$
$0.48 \times 10^{+2}$	$0.14 \times 10^{+5}$	$0.41 \times 10^{+7}$	$0.12 \times 10^{+10}$
$0.64 \times 10^{+2}$	$0.17 \times 10^{+5}$	$0.47 \times 10^{+7}$	$0.13 \times 10^{+10}$
$0.72 \times 10^{+2}$	$0.18 \times 10^{+5}$	$0.47 \times 10^{+7}$	$0.12 \times 10^{+10}$
$0.85 \times 10^{+2}$	$0.17 \times 10^{+5}$	$0.35 \times 10^{+7}$	$0.72 \times 10^{+9}$
$0.89 \times 10^{+2}$	$0.15 \times 10^{+5}$	$0.27 \times 10^{+7}$	$0.47 \times 10^{+9}$
$0.79 \times 10^{+2}$	$0.11 \times 10^{+5}$	$0.16 \times 10^{+7}$	$0.24 \times 10^{+9}$
$0.65 \times 10^{+2}$	$0.79 \times 10^{+4}$	$0.96 \times 10^{+6}$	$0.12 \times 10^{+9}$
$0.47 \times 10^{+2}$	$0.45 \times 10^{+4}$	$0.43 \times 10^{+6}$	$0.41 \times 10^{+8}$
$0.42 \times 10^{+2}$	$0.35 \times 10^{+4}$	$0.29 \times 10^{+6}$	$0.24 \times 10^{+8}$
$0.36 \times 10^{+2}$	$0.27 \times 10^{+4}$	$0.20 \times 10^{+6}$	$0.15 \times 10^{+8}$
$0.29 \times 10^{+2}$	$0.20 \times 10^{+4}$	$0.14 \times 10^{+6}$	$0.97 \times 10^{+7}$
$0.28 \times 10^{+2}$	$0.18 \times 10^{+4}$	$0.12 \times 10^{+6}$	$0.75 \times 10^{+7}$

Table 19

Zinc System at 40°C

B_1	B_2	B_3	B_4
$0.69 \times 10^{+1}$	$0.35 \times 10^{+4}$	$0.21 \times 10^{+7}$	$0.12 \times 10^{+10}$
$0.23 \times 10^{+2}$	$0.92 \times 10^{+4}$	$0.37 \times 10^{+7}$	$0.15 \times 10^{+10}$
$0.35 \times 10^{+2}$	$0.12 \times 10^{+5}$	$0.38 \times 10^{+7}$	$0.13 \times 10^{+10}$
$0.41 \times 10^{+2}$	$0.12 \times 10^{+5}$	$0.35 \times 10^{+7}$	$0.10 \times 10^{+10}$
$0.53 \times 10^{+2}$	$0.14 \times 10^{+5}$	$0.38 \times 10^{+7}$	$0.10 \times 10^{+10}$
$0.60 \times 10^{+2}$	$0.15 \times 10^{+5}$	$0.39 \times 10^{+7}$	$0.99 \times 10^{+9}$
$0.58 \times 10^{+2}$	$0.12 \times 10^{+5}$	$0.25 \times 10^{+7}$	$0.51 \times 10^{+9}$
$0.56 \times 10^{+2}$	$0.98 \times 10^{+4}$	$0.17 \times 10^{+7}$	$0.30 \times 10^{+9}$
$0.56 \times 10^{+2}$	$0.81 \times 10^{+4}$	$0.12 \times 10^{+7}$	$0.17 \times 10^{+9}$
$0.63 \times 10^{+2}$	$0.70 \times 10^{+4}$	$0.77 \times 10^{+6}$	$0.85 \times 10^{+8}$
$0.70 \times 10^{+2}$	$0.61 \times 10^{+4}$	$0.54 \times 10^{+6}$	$0.47 \times 10^{+8}$
$0.62 \times 10^{+2}$	$0.43 \times 10^{+4}$	$0.30 \times 10^{+6}$	$0.21 \times 10^{+8}$
$0.56 \times 10^{+2}$	$0.35 \times 10^{+4}$	$0.22 \times 10^{+6}$	$0.14 \times 10^{+8}$
$0.49 \times 10^{+2}$	$0.30 \times 10^{+4}$	$0.18 \times 10^{+6}$	$0.11 \times 10^{+8}$
$0.42 \times 10^{+2}$	$0.23 \times 10^{+4}$	$0.13 \times 10^{+6}$	$0.74 \times 10^{+7}$

Table 20

Zinc System at 50°C

B_1	B_2	B_3	B_4
$0.70 \times 10^{+1}$	$0.46 \times 10^{+4}$	$0.28 \times 10^{+7}$	$0.18 \times 10^{+10}$
$0.35 \times 10^{+2}$	$0.14 \times 10^{+5}$	$0.56 \times 10^{+7}$	$0.23 \times 10^{+10}$
$0.42 \times 10^{+2}$	$0.14 \times 10^{+5}$	$0.46 \times 10^{+7}$	$0.15 \times 10^{+10}$
$0.51 \times 10^{+2}$	$0.15 \times 10^{+5}$	$0.43 \times 10^{+7}$	$0.13 \times 10^{+10}$
$0.60 \times 10^{+2}$	$0.16 \times 10^{+5}$	$0.43 \times 10^{+7}$	$0.11 \times 10^{+10}$
$0.69 \times 10^{+2}$	$0.17 \times 10^{+5}$	$0.44 \times 10^{+7}$	$0.11 \times 10^{+10}$
$0.58 \times 10^{+2}$	$0.12 \times 10^{+5}$	$0.24 \times 10^{+7}$	$0.49 \times 10^{+9}$
$0.52 \times 10^{+2}$	$0.90 \times 10^{+4}$	$0.15 \times 10^{+7}$	$0.27 \times 10^{+9}$
$0.45 \times 10^{+2}$	$0.64 \times 10^{+4}$	$0.90 \times 10^{+6}$	$0.13 \times 10^{+9}$
$0.39 \times 10^{+2}$	$0.41 \times 10^{+4}$	$0.42 \times 10^{+6}$	$0.43 \times 10^{+8}$
$0.31 \times 10^{+2}$	$0.25 \times 10^{+4}$	$0.20 \times 10^{+6}$	$0.16 \times 10^{+8}$
$0.28 \times 10^{+2}$	$0.18 \times 10^{+4}$	$0.12 \times 10^{+6}$	$0.75 \times 10^{+7}$
$0.27 \times 10^{+2}$	$0.16 \times 10^{+4}$	$0.95 \times 10^{+5}$	$0.56 \times 10^{+7}$
$0.32 \times 10^{+2}$	$0.18 \times 10^{+4}$	$0.10 \times 10^{+6}$	$0.57 \times 10^{+7}$
$0.33 \times 10^{+2}$	$0.18 \times 10^{+4}$	$0.94 \times 10^{+5}$	$0.50 \times 10^{+7}$

Table 21

Cadmium System at 25°C

B_1	B_2	B_3	B_4
$0.47 \times 10^{+2}$	$0.27 \times 10^{+5}$	$0.15 \times 10^{+8}$	$0.84 \times 10^{+10}$
$0.81 \times 10^{+2}$	$0.37 \times 10^{+5}$	$0.17 \times 10^{+8}$	$0.75 \times 10^{+10}$
$0.13 \times 10^{+3}$	$0.53 \times 10^{+5}$	$0.21 \times 10^{+8}$	$0.84 \times 10^{+10}$
$0.12 \times 10^{+3}$	$0.41 \times 10^{+5}$	$0.14 \times 10^{+8}$	$0.45 \times 10^{+10}$
$0.12 \times 10^{+3}$	$0.35 \times 10^{+5}$	$0.10 \times 10^{+8}$	$0.30 \times 10^{+10}$
$0.11 \times 10^{+3}$	$0.28 \times 10^{+5}$	$0.70 \times 10^{+7}$	$0.17 \times 10^{+10}$
$0.12 \times 10^{+3}$	$0.29 \times 10^{+5}$	$0.67 \times 10^{+7}$	$0.15 \times 10^{+10}$
$0.13 \times 10^{+3}$	$0.27 \times 10^{+5}$	$0.58 \times 10^{+7}$	$0.12 \times 10^{+10}$
$0.12 \times 10^{+3}$	$0.22 \times 10^{+5}$	$0.39 \times 10^{+7}$	$0.71 \times 10^{+9}$
$0.11 \times 10^{+3}$	$0.16 \times 10^{+5}$	$0.23 \times 10^{+7}$	$0.34 \times 10^{+9}$
$0.98 \times 10^{+2}$	$0.12 \times 10^{+5}$	$0.15 \times 10^{+7}$	$0.19 \times 10^{+9}$
$0.11 \times 10^{+3}$	$0.12 \times 10^{+5}$	$0.13 \times 10^{+7}$	$0.14 \times 10^{+9}$
$0.11 \times 10^{+3}$	$0.11 \times 10^{+5}$	$0.11 \times 10^{+7}$	$0.11 \times 10^{+9}$
$0.12 \times 10^{+3}$	$0.10 \times 10^{+5}$	$0.92 \times 10^{+6}$	$0.82 \times 10^{+8}$
$0.12 \times 10^{+3}$	$0.97 \times 10^{+4}$	$0.79 \times 10^{+6}$	$0.64 \times 10^{+8}$
$0.11 \times 10^{+3}$	$0.80 \times 10^{+4}$	$0.56 \times 10^{+6}$	$0.39 \times 10^{+8}$
$0.11 \times 10^{+3}$	$0.69 \times 10^{+4}$	$0.42 \times 10^{+6}$	$0.26 \times 10^{+8}$
$0.11 \times 10^{+3}$	$0.57 \times 10^{+4}$	$0.30 \times 10^{+6}$	$0.16 \times 10^{+8}$

Table 22

Mercury System at $25^{\circ}C$

B_1	B_2	B_3	B_4
$3.18 \times 10^{+6}$	$0.14 \times 10^{+11}$	$0.61 \times 10^{+14}$	$0.32 \times 10^{+18}$
$0.53 \times 10^{+8}$	$0.20 \times 10^{+11}$	$0.78 \times 10^{+13}$	$0.30 \times 10^{+16}$
$0.73 \times 10^{+8}$	$0.23 \times 10^{+11}$	$0.71 \times 10^{+13}$	$0.22 \times 10^{+16}$
$0.87 \times 10^{+8}$	$0.24 \times 10^{+11}$	$0.66 \times 10^{+13}$	$0.18 \times 10^{+16}$
$0.14 \times 10^{+9}$	$0.33 \times 10^{+11}$	$0.80 \times 10^{+13}$	$0.19 \times 10^{+16}$
$0.17 \times 10^{+9}$	$0.31 \times 10^{+11}$	$0.59 \times 10^{+13}$	$0.11 \times 10^{+16}$
$0.30 \times 10^{+9}$	$0.44 \times 10^{+11}$	$0.66 \times 10^{+13}$	$0.99 \times 10^{+15}$
$0.33 \times 10^{+9}$	$0.44 \times 10^{+11}$	$0.61 \times 10^{+13}$	$0.83 \times 10^{+15}$
$0.39 \times 10^{+9}$	$0.49 \times 10^{+11}$	$0.62 \times 10^{+13}$	$0.78 \times 10^{+15}$
$0.48 \times 10^{+9}$	$0.57 \times 10^{+11}$	$0.67 \times 10^{+13}$	$0.78 \times 10^{+15}$
$0.56 \times 10^{+9}$	$0.62 \times 10^{+11}$	$0.68 \times 10^{+13}$	$0.75 \times 10^{+15}$
$0.65 \times 10^{+9}$	$0.68 \times 10^{+11}$	$0.71 \times 10^{+13}$	$0.73 \times 10^{+15}$
$0.73 \times 10^{+9}$	$0.63 \times 10^{+11}$	$0.55 \times 10^{+13}$	$0.48 \times 10^{+15}$
$0.93 \times 10^{+9}$	$0.78 \times 10^{+11}$	$0.66 \times 10^{+13}$	$0.56 \times 10^{+15}$
$0.16 \times 10^{+10}$	$0.13 \times 10^{+12}$	$0.11 \times 10^{+14}$	$0.88 \times 10^{+15}$
$0.15 \times 10^{+10}$	$0.11 \times 10^{+12}$	$0.78 \times 10^{+13}$	$0.56 \times 10^{+15}$
$0.17 \times 10^{+10}$	$0.11 \times 10^{+12}$	$0.74 \times 10^{+13}$	$0.48 \times 10^{+15}$
$0.20 \times 10^{+10}$	$0.12 \times 10^{+12}$	$0.71 \times 10^{+13}$	$0.43 \times 10^{+15}$
$0.26 \times 10^{+10}$	$0.15 \times 10^{+12}$	$0.84 \times 10^{+13}$	$0.48 \times 10^{+15}$

Table 23

Mercury System at 40°C

B_1	B_2	B_3	B_4
$0.39 \times 10^{+7}$	$0.17 \times 10^{+11}$	$0.71 \times 10^{+14}$	$0.30 \times 10^{+18}$
$0.39 \times 10^{+8}$	$0.16 \times 10^{+11}$	$0.62 \times 10^{+13}$	$0.25 \times 10^{+16}$
$0.38 \times 10^{+8}$	$0.12 \times 10^{+11}$	$0.39 \times 10^{+13}$	$0.13 \times 10^{+16}$
$0.42 \times 10^{+8}$	$0.12 \times 10^{+11}$	$0.34 \times 10^{+13}$	$0.96 \times 10^{+15}$
$0.95 \times 10^{+8}$	$0.24 \times 10^{+11}$	$0.59 \times 10^{+13}$	$0.15 \times 10^{+16}$
$0.10 \times 10^{+9}$	$0.19 \times 10^{+11}$	$0.37 \times 10^{+13}$	$0.71 \times 10^{+15}$
$0.88 \times 10^{+8}$	$0.13 \times 10^{+11}$	$0.20 \times 10^{+13}$	$0.68 \times 10^{+15}$
$0.10 \times 10^{+9}$	$0.14 \times 10^{+11}$	$0.20 \times 10^{+13}$	$0.64 \times 10^{+15}$
$0.13 \times 10^{+9}$	$0.17 \times 10^{+11}$	$0.21 \times 10^{+13}$	$0.56 \times 10^{+15}$
$0.16 \times 10^{+9}$	$0.19 \times 10^{+11}$	$0.23 \times 10^{+13}$	$0.51 \times 10^{+15}$
$0.19 \times 10^{+9}$	$0.21 \times 10^{+11}$	$0.24 \times 10^{+13}$	$0.49 \times 10^{+15}$
$0.22 \times 10^{+9}$	$0.24 \times 10^{+11}$	$0.25 \times 10^{+13}$	$0.49 \times 10^{+15}$
$0.25 \times 10^{+9}$	$0.24 \times 10^{+11}$	$0.23 \times 10^{+13}$	$0.48 \times 10^{+15}$
$0.34 \times 10^{+9}$	$0.32 \times 10^{+11}$	$0.29 \times 10^{+13}$	$0.51 \times 10^{+15}$
$0.51 \times 10^{+9}$	$0.45 \times 10^{+11}$	$0.40 \times 10^{+13}$	$0.53 \times 10^{+15}$
$0.82 \times 10^{+9}$	$0.64 \times 10^{+11}$	$0.50 \times 10^{+13}$	$0.56 \times 10^{+15}$
$0.10 \times 10^{+10}$	$0.73 \times 10^{+11}$	$0.51 \times 10^{+13}$	$0.54 \times 10^{+15}$
$0.13 \times 10^{+10}$	$0.84 \times 10^{+11}$	$0.54 \times 10^{+13}$	$0.54 \times 10^{+15}$
$0.16 \times 10^{+10}$	$0.95 \times 10^{+11}$	$0.57 \times 10^{+13}$	$0.56 \times 10^{+15}$

Table 24

Mercury System at 50°C

B_1	B_2	B_3	B_4
$0.41 \times 10^{+7}$	$0.18 \times 10^{+11}$	$0.83 \times 10^{+14}$	$0.37 \times 10^{+18}$
$0.58 \times 10^{+8}$	$0.25 \times 10^{+11}$	$0.11 \times 10^{+14}$	$0.46 \times 10^{+16}$
$0.75 \times 10^{+8}$	$0.26 \times 10^{+11}$	$0.92 \times 10^{+13}$	$0.32 \times 10^{+16}$
$0.86 \times 10^{+8}$	$0.29 \times 10^{+11}$	$0.96 \times 10^{+13}$	$0.32 \times 10^{+16}$
$0.14 \times 10^{+9}$	$0.40 \times 10^{+11}$	$0.11 \times 10^{+14}$	$0.31 \times 10^{+16}$
$0.11 \times 10^{+9}$	$0.24 \times 10^{+11}$	$0.49 \times 10^{+13}$	$0.10 \times 10^{+16}$
$0.16 \times 10^{+9}$	$0.30 \times 10^{+11}$	$0.56 \times 10^{+13}$	$0.10 \times 10^{+16}$
$0.20 \times 10^{+9}$	$0.33 \times 10^{+11}$	$0.55 \times 10^{+13}$	$0.90 \times 10^{+15}$
$0.22 \times 10^{+9}$	$0.33 \times 10^{+11}$	$0.50 \times 10^{+13}$	$0.76 \times 10^{+15}$
$0.24 \times 10^{+9}$	$0.33 \times 10^{+11}$	$0.45 \times 10^{+13}$	$0.62 \times 10^{+15}$
$0.27 \times 10^{+9}$	$0.33 \times 10^{+11}$	$0.41 \times 10^{+13}$	$0.54 \times 10^{+15}$
$0.30 \times 10^{+9}$	$0.34 \times 10^{+11}$	$0.38 \times 10^{+13}$	$0.53 \times 10^{+15}$
$0.36 \times 10^{+9}$	$0.37 \times 10^{+11}$	$0.39 \times 10^{+13}$	$0.53 \times 10^{+15}$
$0.47 \times 10^{+9}$	$0.45 \times 10^{+11}$	$0.42 \times 10^{+13}$	$0.52 \times 10^{+15}$
$0.67 \times 10^{+9}$	$0.56 \times 10^{+11}$	$0.47 \times 10^{+13}$	$0.52 \times 10^{+15}$
$0.11 \times 10^{+10}$	$0.80 \times 10^{+11}$	$0.60 \times 10^{+13}$	$0.54 \times 10^{+15}$
$0.14 \times 10^{+10}$	$0.10 \times 10^{+12}$	$0.75 \times 10^{+13}$	$0.55 \times 10^{+15}$
$0.17 \times 10^{+10}$	$0.12 \times 10^{+12}$	$0.79 \times 10^{+13}$	$0.54 \times 10^{+15}$
$0.22 \times 10^{+10}$	$0.15 \times 10^{+12}$	$0.97 \times 10^{+13}$	$0.64 \times 10^{+15}$

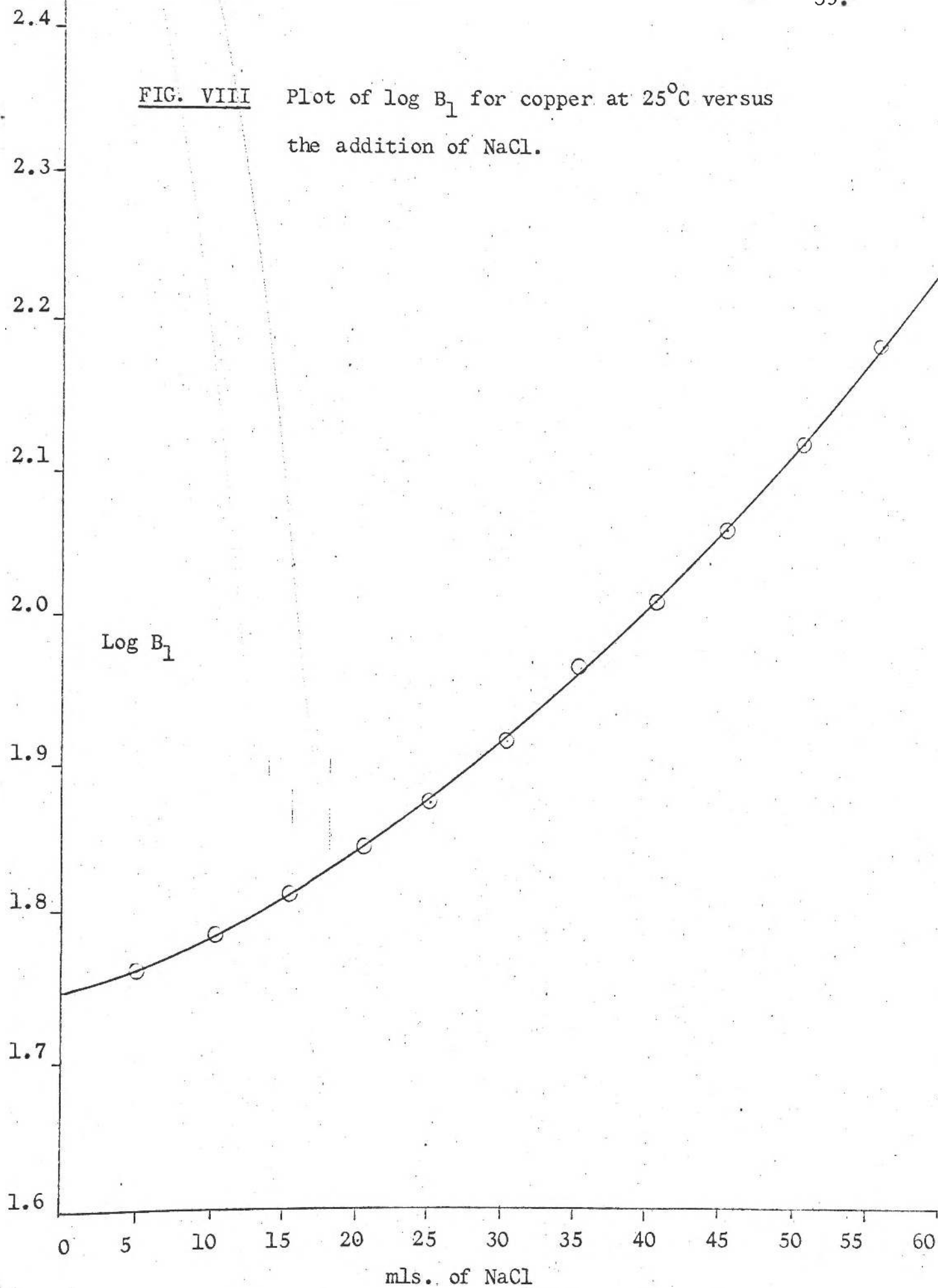FIG. VIII   Plot of log B_1 for copper at 25°C versus the addition of NaCl.

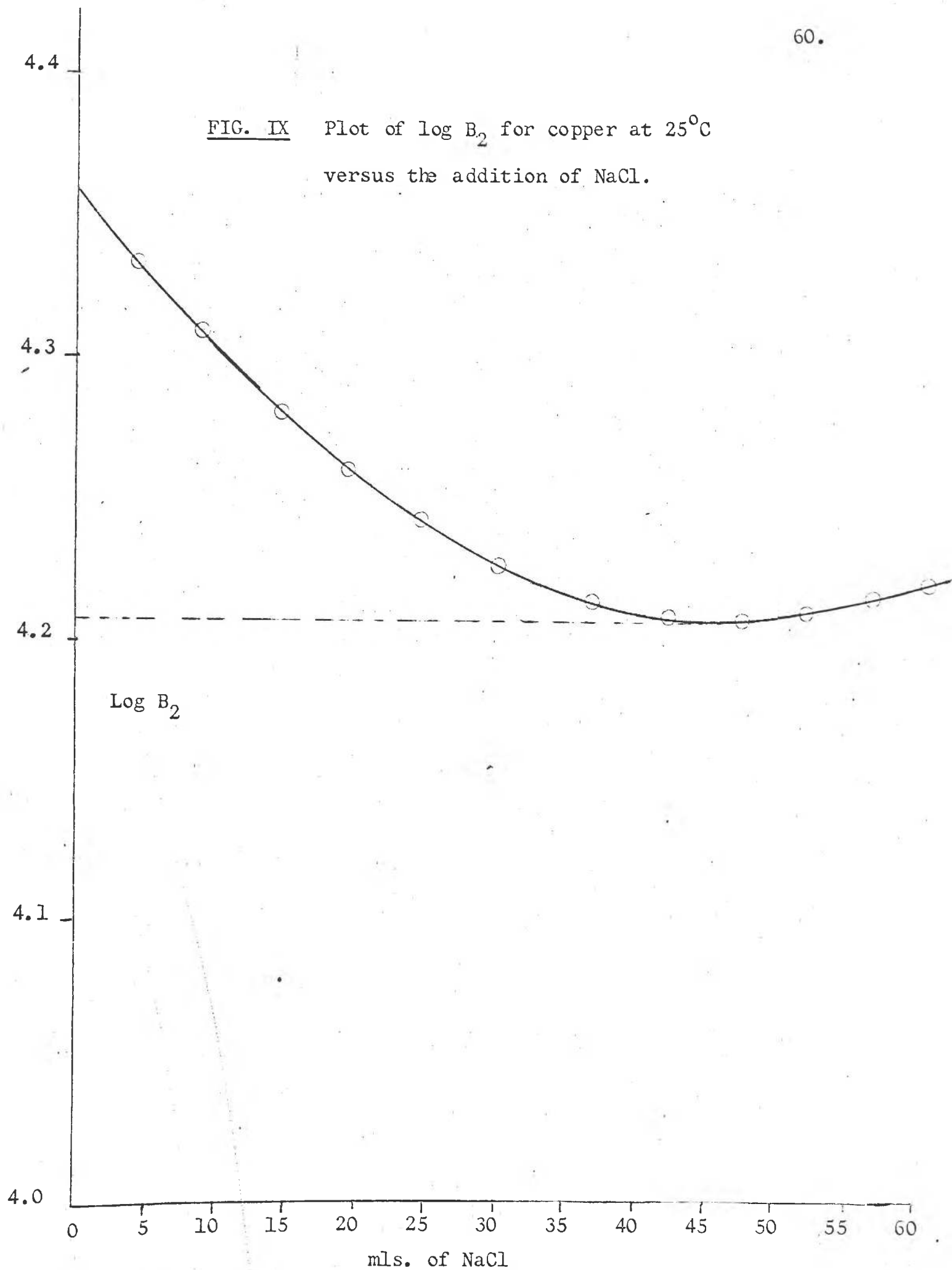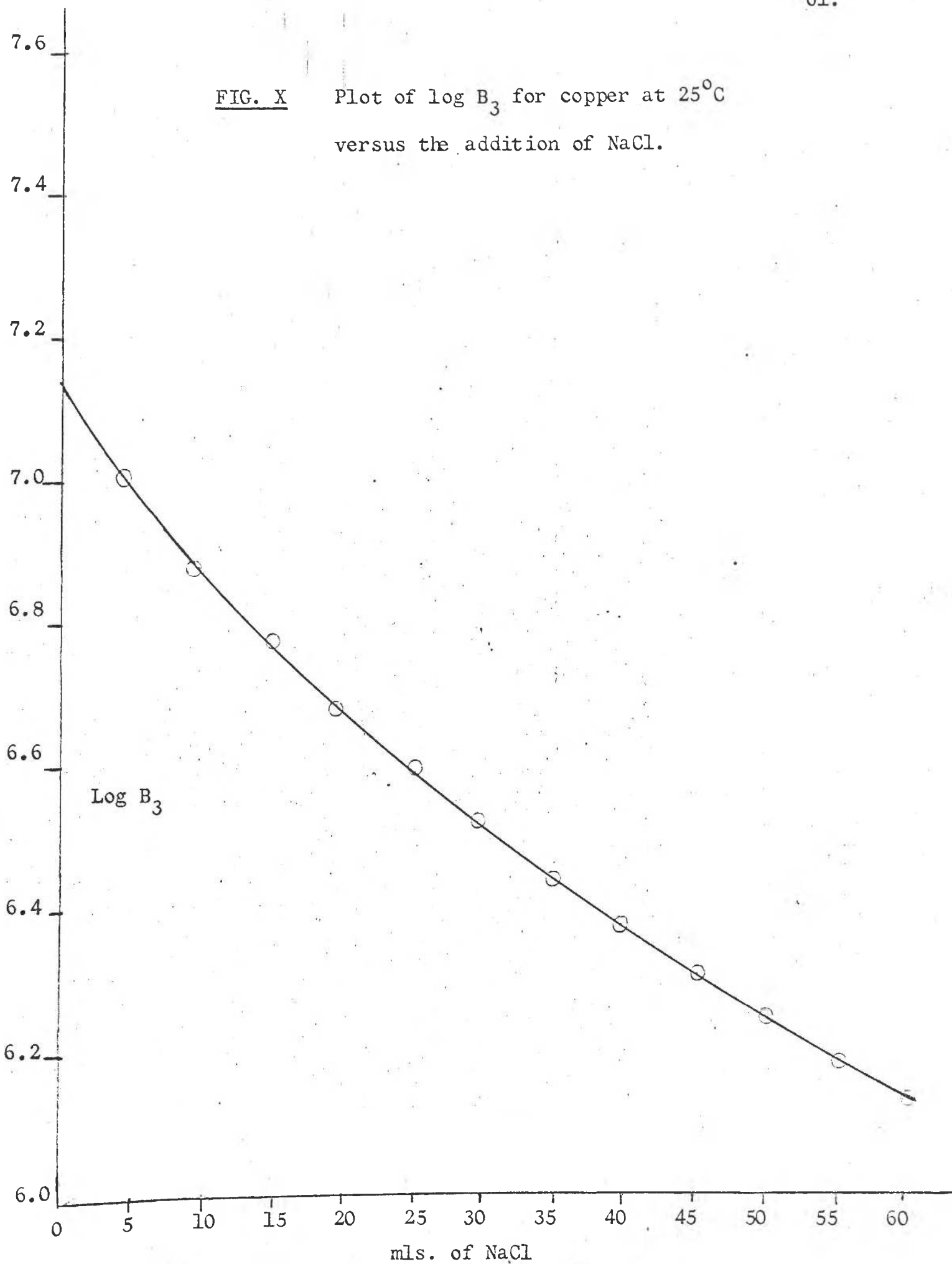FIG. IX   Plot of log B_2 for copper at $25^{\circ}C$ versus the addition of NaCl.

FIG. X   Plot of log B_3 for copper at $25^{\circ}C$ versus the addition of NaCl.

SECTION 2

STABILITY CONSTANTS OF METAL CHLORO COMPLEXES

Table 25

The Mercury System

Temp.	B_1	B_2	B_3	B_4	Reference
25°C	3.2×10^6	0.14×10^{11}	0.55×10^{13}	0.43×10^{15}	Present Work
25°C	5.49×10^6	1.66×10^{13}	1.17×10^{14}	1.17×10^{15}	7
25°C	5.49×10^6	1.66×10^{13}	1.48×10^{14}	1.66×10^{15}	8
25°C	1.90×10^7				9
25°C	2.88×10^7				10
40°C	3.9×10^6	0.12×10^{11}	0.20×10^{13}	0.48×10^{15}	Present Work
50°C	4.1×10^6	0.18×10^{11}	0.38×10^{13}	0.52×10^{15}	Present Work

Varying Ionic Strength

Table 26

The Copper System

Temp.	B_1	B_2	Reference
25°C	0.61×10^2	1.6×10^4	Present Work
25°C	0.41×10^2	1.0×10^3	11
25°C	6.30×10^2	2.51×10^4	12
25°C	9.55		13
25°C	5.62		14
40°C	0.64×10^2	1.50×10^4	Present Work
50°C	0.69×10^2	1.90×10^4	Present Work

Ionic Strength = 0.1M

63.

Table 27

Zinc System

Temp.	B_1	Reference
$25^{\circ}C$	6.68	Present Work
$25^{\circ}C$	5.25	15
$25^{\circ}C$	9.12	16
$25^{\circ}C$	4.79	17
$25^{\circ}C$	3.98	18
$25^{\circ}C$	$1.58 \times 10^2 - 7.94$	19
$40^{\circ}C$	9.60	Present Work
$50^{\circ}C$	7.07	Present Work

Ionic Strength = 0.1M

Table 28

Cadmium System

Temp.	B_1	Reference
$25^{\circ}C$	0.47×10^2	Present Work
$25^{\circ}C$	0.39×10^2	20
$25^{\circ}C$	0.35×10^2	21
$25^{\circ}C$	0.89×10^2	22
$25^{\circ}C$	1.0×10^2	23

Ionic Strength = 0.1M

SECTION 3

DISCUSSION

Tables (25-28) show the good agreement between other workers and this present study. This emphasises the fact that the chloride ion activity electrode is an extremely useful tool for the determination of stability constants. Previous workers who have used potentiometric methods, have had to use a series of approximations in order to estimate the free chloride ion concentration and these were dependent upon the free metal ion concentration. The present work removed the need to approximate because the chloride ion concentration is independent of the free metal ion concentration.

Factors Controlling the Stability of Metal Complexes

The metal ions are placed in the following order of increasing stability of their chloro complexes.

$$Zn^{2+} < Cd^{2+} < Cu^{2+} << Hg^{2+}$$

No simple picture of interaction between ligand and metal ion in terms of purely coulombic forces will explain why, e.g. no ammines of Na^+ exist while those of Cu^{2+} and Ag^+ are stable in aqueous solution, for the dipole moment of water is larger than that of ammonia. However, ammonia $(\alpha = 2.4 \times 10^{-24})$ is more polarizable than water $(\alpha = 1.5 \times 10^{-24})$, and by considering ion-dipole and induced dipole interactions, Van Arkel and Baer [30] were able to show that the tendency towards ammine formation should increase with

lie on a smooth curve when plotted against the recipocal of their ionic radii, those of the transition metals deviate in the direction of higher stability and to an extent which follows that already shown.

This disposes of the idea that complex stability in this series is governed by purely electrostatic forces.

A similar effect can be observed among chloro complexes. If complex between cations and anions were purely electrostatic in character, a simple relationship would exist between their dissociation constants, K, and the radius, r, of the unhydrated ion and its valency, Z. But Irving and Williams [31] showed that the chloro complexes of transition metals (and of bivalent ions such as Pb^{2+} and Hg^{2+}) are much more stable than can be accounted for by purely electrostatic forces of attraction.

The stabilities are measured relative to those of aqueous complexes. As the stability increases regularly along the series manganese to copper, it follows that there is a similar monotonic rise in absolute stability from Mn to Cu. in the case of ammine complexes, since the increments in relative stability on replacing water by ammonia molecules increases in the same order.

That replacement of water by a more polarizable ligand should lead to an enhanced stability is not surprising. That the increments in stability should increase monotonically along the series can only

mean that some additional stabilising factor is in operation which increases in extent as we move along the series, this must be the tendency towards the formation of a covalent bond between metal and ligand. This point was emphasised by Irving [31] who investigated the series using different types of ligands and found the stability increment from metal to metal is greatest for nitrogen-type ligands (e.g. ethylenediamine) less for nitrogen-oxygen type ligands (e.g. glycine) and still less for oxygen-oxygen type ligands (e.g. oxalic acid). Therefore, the more electropositive the co-ordinating atom of the ligand, the greater the stability increment from metal to metal; this emphasises the significance of covalent bonding in determining the stability of complexes.

Any more elaborate picture of co-ordination must take into account the available electronic levels of the (acceptor) metal ion and the electron availability of the (donor) ligand. As a measure of the electron affinity of the acceptor cation, the second ioxisation potential corresponding to the process

$$M \ (\text{gas}) \rightleftharpoons M^{2+} \ (\text{gas}) \ + \ 2e^-$$
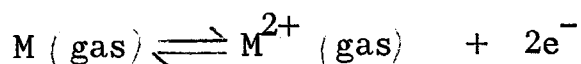
is adopted. This refers to the free atom and reflects the ground-state energy levels of the electrons. The strength of the co-ordination link may thus be related to the loss of potential energy when electrons are donated from the high energy levels of the ligand to the lower energy levels of the metal ion. The clear correlation

between ionisation potential and complex stability must not be underestimated, and it is of the greatest significance that, as Table 29 shows, the second ionisation potential rises along the transition series to a maximum at copper and falls again at zinc. The results obtained from present work show that copper forms a much stronger complex than zinc. In other words the second ionisation potential is a measure of the driving force towards complex formation.

The order suggested, show that two parameters respectively, serve as a guide to the magnitude of the electrostatic and covalent interactions, viz. the reciprocal of the ionic radius and the second ionisation potential, both increase monotonically throughout the series from manganese to copper. Therefore, provided there is an increase in interaction energy on replacement of water by some other ligand, there is bound to be a monotonic gain in stability in passing along the series from Mn to Cu, and fall to Zn, irrespective of the extent to which either or both of these factors operate.

When considering cadmium, it is noted from Table 29 that the ionic radius is greater than that of nickel, although the ionisation potentials are almost identical. Therefore, it is clear that the relative stabilities of Cd and Ni complexes depend on the nature of the ligand.

Consider the aquo complexes. When the water is replaced by the iodide ion, however, there is a slight increase in electron-

donating power, but since the iodide ion is so much larger than the water molecule the decrease in electrostatic interaction due to the greater charge separation will be more significant with the smaller Ni^{2+} ion, and since the gain in covalent interaction energy is much the same (I.P. Ni $\simeq$ Cd) the stability order is Cd $>$ Ni.

An extension of this is that all bivalent ions of large radius and high ionisation potential, i.e. Mercury^{2+} will form strong complexes with Cl^-, I^- and Br^- whereas those of large radius and low ionisation potential e.g. Barium^{2+} will not.

With ions of moderately small radius and moderately high ionisation potential, the stability is dependent upon the two factors; the electrostatic and covalent interactions and is given by the order of bivalent ions of the first transition series

$$Co < Ni < Cu > Zn$$

and the overall order of the metal ions investigated has now been explained and is given by

$$Zn^{2+} < Cd^{2+} < Cu^{2+} << Hg^{2+}$$

The chloride compounds of Zn, Cd and Cu are ionic and crystallise in layer lattices but the mercuric halides are covalent and so would point to their complexes being stable.

The copper complexes are usually more stable than the above argument predicts as a result of the ligand field stabilisations due

to the Jahn Teller Effect, but this does not affect the overall stability order.

## Discussion on Thermodynamic Data obtained from Stability Constants

The measurements were made over a range of temperatures so that thermodynamic data could be calculated from the stability constants obtained, using the V'ant Hoff Isochore. As the B_4 values were only calculated for the mercury complexes, the evaluation of thermodynamic data was limited to this metal chloro complex. Table 30.

Table 30

Hg^{2+}	$H25^{\circ}C$	$S25^{\circ}C$	$G25^{\circ}C$	Correlation
	0.83 KCals/mole	11.2 cals/deg	-2.5 KCals/mole	Coefficient = 0.996

where a correlation coefficient $>$ 0.95 is acceptable.

The stability of a complex in solution is measured by the equilibrium constant, K, for the reaction

$$M(H2O)_a + X(H2O)_b \underset{\longleftarrow}{\overset{K}{\longrightarrow}} MX(H2O)_c + (a + b - c) H2O$$
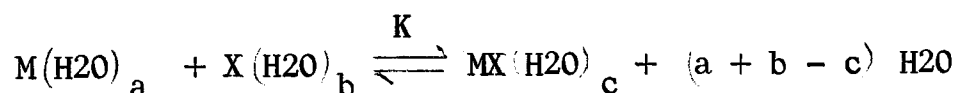
where M is the metal ion, and X is the ligand. The equilibrium constant, K, can be expressed in the form

$$-2.303 \ RT \ \log K = \triangle G = \triangle H - T \triangle S$$

where $\triangle G$, $\triangle H$ and $\triangle S$ are the standard molar free energy, heat and entropy of formation of a complex from its components in aqueous solution at $25^{\circ}C$.

Where a metal ion is in an aqueous solution, it is surrounded by a sphere of water molecules forming an aquo complex. When ligand is added to this solution the hydration sphere has to be broken and ligand molecules replace the water molecules in the complex to form the chloro complex. $Thus$.

(i) The positive $\triangle H$ would be due to the energy required to break up the hydration spheres of both the metal and the ligand in solution before the complex is formed. This would account for the particularly large value of $\triangle H$ for the chloride complex. The chloride ion could form hydrogen bonds with the water molecules and would also tend to form associated species with H^+ ions in the aqueous medium. Significantly greater amounts of energy would be necessary to break this "hydration" sphere to enable the chloride to become part of the inner co-ordination sphere.

(ii) In the complexes studied there were reactions between cations and anions with a resulting reduction in the total number of ions in solution and a concomitant neutralisation of charge.

Frank and Evans [32] have suggested that ions in aqueous solution order the water molecules around them so as to form an "iceberg", the process being similar to a partial freezing of the liquid. On this picture the removal of ions from solution, as in the

process of complex formation between oppositely charged ions will lead to a breakdown of the "icebergs" and a resulting entropy charge favouring complex formation. The entropy value obtained from this present work is in agreement with this picture and favours complex formation.

The V'ant Hoff Isochore is limited to a linear relationship only between Ka and $\frac{1}{T}$. The B_1, B_2 and B_3 values are not linear with temperature and can only be evaluated using the non-emperical Clarke and Glew equation or the emperical Harned-Robinson or Everett and Wynne-Jones equation. However the overall stability constant, B_4, gives a picture of the overall complex and calculations have been restricted to the B_4 values for the mercury chloro complex.

APPENDIX

```
C  C  CALCULATION OF STABILITY CONSTANTS

   3 READ 32

     PRINT 32

  32 FORMAT (40H)

   1 READ,AMS,AMD,X

     IF(AMS)3,2,2

   2 BA=(AMS-AMD)/(AMD*X)

     BB=BA/X

     BC=BB/X

     BD=BC/X

     PUNCH 11,BA,BB,BC,BD

  11 FORMAT(E10.2,4X,E10.2,4X,E10.2,4X,E10.2)

     GO TO 1

     END
```

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ACKNOWLEDGMENTS

The Author wishes to thank Mr. F.M. Hall for suggesting the outline of the project and for his guidance and discussion throughout. He would also like to express his appreciation to other members of the academic staff and research students of the Wollongong University College Chemistry Department for their help and advice, especially Mr. G.L. Jackson. Appreciation is also expressed to the technical staff of the college.

The author is indebted to the Electrolytic Refining and Smelting Company Pty. Ltd. for their assistance in financing the work. Special thanks are due to the author's family and fiancee for their encouragement and interest throughout the project.