THE HYDROLYSIS OF METAL IONS IN AQUEOUS SOLUTION

A DISSERTATION

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OF

MASTER OF SCIENCE

BY

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I certify that the work incorporated in this dissertation is entirely my own and has not been submitted at this or any other University for degree purposes.

D H Cotton

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SUMMARY.

The acidity constant for mercury (I) has been determined by Forsling, Hietanen and Sillen[13] as $10^{-5 \pm 0.3}$ at 25.0°C using the titration method described by Sillen[35]. Their method requires a knowledge of the liquid junction potential of the cell, which they obtained with a precision of four percent.

As the determination is critically influenced by the liquid junction potential of the cell, the present work was undertaken to determine this value with greater precision and hence obtain a better value for the acidity constant of mercury (I).

The liquid junction potential was determined to a precision of about one percent and the acidity constant found to be $10^{-5.12 \pm 0.12}$ at 30.0°C.

Using the titration method an attempt was made to determine the acidity constant for silver ions. This was found to be negligible but an approximate value of the solubility product of silver hydroxide was obtained.

INTRODUCTION.

Hydrolysis is the term applied to any reaction involving the interaction of water with an ion or molecule.

A suitable metal ion when dissolved in water forms a hydrate which can lead to the formation of an acid solution. This phenomenon, known as aquo-acidity, can be explained in terms of the acid-base concepts postulated by Bronsted [8] and Lowry [25]. This theory defines an acid as a molecule or ion containing hydrogen which can be donated as a proton to a suitable acceptor, and a base as a molecule or ion capable of accepting a proton. Thus the relationship between an acid and a base can be represented by the simplified reaction,

$$A \rightleftarrows B + H^+$$

Acid base proton

Although a substance may be inherently an acid it can only function as such if there is a base present which can accept the proton. The following equilibria is thus necessary

$$A_1 + B_1 \rightleftarrows A_2 + B_2$$

B_2 is termed the conjugate base of the acid A_1, while A_2 is the conjugate / .....

conjugate acid of the base B_1.

The hydrated metal ion acts as a Lewis acid in the presence of water by liberating a proton from one or more of the liganded water molecules

$$Me(H_2O)_n^{x+} + H_2O \rightleftarrows [Me(H_2O)_{n-1}(OH)]^{(x-1)+} + H_3O^+$$

or less precisely,

$$Me^{x+} + H_2O \rightleftarrows Me(OH)^{(x-1)+} + H^+$$

The equilibrium constant for this reaction

$$K = \frac{a_{Me(OH)^{(x-1)+}} \cdot a_{H^+}}{a_{Me^{x+}} \cdot a_{H_2O}}$$

is termed the hydrolysis constant, K_h, or better the acidity constant, K_a, for the metal ion Me.

The extent to which the above hydrolysis reaction takes place depends on the proton liberating power of the hydrated metal ion. Thus a metal ion which has a relatively high charge and small ionic radius such as iron (III) will be extensively hydrolysed and consequently very acidic in solution. On the other hand an ion such as iron (II) having a lower charge and higher ionic radius has a much weaker acidic reaction in aqueous solution[28].

This difference / .....

This difference in acidity is due to the strength of the metal-oxygen bond in the hydrate and the resultant weakening of the oxygen-hydrogen bond in the co-ordinated water molecule. A proton can thus be more easily liberated from a hydrated metal ion of large charge and small ionic radius.

This theory gives an over simplification of the mechanism of hydrolysis as it fails to take into account the formation of polynuclear complexes during the hydrolysis of most metals.

Thus it was generally accepted for many years on the basis of the Bronsted-Lowry acid-base concept that during the hydrolysis of iron (III) the uncharged hydroxide was formed.

$$Fe^{3+} + 3H_2O \rightleftarrows Fe(OH)_3 + 3H^+$$

Many workers have attempted to explain their results on the basis of this reaction. However, as pointed out by Sillen[35] this requires either microcrystals or a true solution of the hydroxide, both of which can be ruled out by applying the law of mass action even to crude measurements.

From deviations in both spectrophotometric and magnetic measurements it was evident that other species, possibly polynuclear complexes, formed by the reaction

$$xFe^{3+} + yH_2O \rightleftarrows Fe_x(OH)_y^{(3x-y)+} + 3H^+$$

existed.

Hedström[17] using glass and redox electrodes showed that the dinuclear complex was actually formed as the main product together with two mononuclear complexes. The latter were more evident at lower concentrations of iron (III)

$$Fe^{3+} + H_2O \rightleftarrows Fe(OH)^{2+} + H^+ \quad \log K_1 = -3.05$$

$$Fe\,OH^{2+} + H_2O \rightleftarrows Fe(OH)_2^+ + H^+ \quad \log K_2 = -3.26$$

$$2Fe^{3+} + 2H_2O \rightleftarrows Fe_2(OH)_2^{4+} + 2H^+ \quad \log K_3 = -2.91$$

where K is the respective acidity constant.

Iron (III) is not unique in this respect as most cations eg. Be^{2+}, Al^{3+}, UO_2^{2+}, Cu^{2+}, In^{3+}, form polynuclear complexes in aqueous solutions. For instance the hydrolysis of indium (III) is given by Biedermann[3] as

$$(n+1)\,In^{3+} + 2nH_2O \rightleftarrows In\,[(OH)_2In\,]_n^{n+3} + 2nH^+$$

Although the acid-base concept of Bronsted and Lowry does not take into account the formation of polynuclear complexes it gives an acceptable mechanism for hydrolytic phenomena.

The degree of acidity of a metal ion will be influenced by the extent of complex formation of the metal ion with its associated /.....

its associated anion. Thus hydrolysis is usually carried out on the nitrate or perchlorate which generally do not form complexes with metals.

Methods of Investigation.

There are several methods available for the study of the hydrolysis of metal ions. However many of these methods such as ion exchange, ebullioscopy and cryoscopy are not very accurate and only give an indication of the type of complex formed[5] . Four methods viz: solubility, conductivity, liquid-liquid partition and potentiometry have been used fairly extensively.

The solubility of the metal oxide or hydroxide in solutions of varying acidity has been used to investigate the hydrolysis of metal ions eg. silver[21] and mercury (II)[14]. The hydrolysis of mercury (I) cannot be investigated by this method as the hydroxide on precipitation disproportionates into water, mercury (II) oxide

and mercury / .....

and mercury[34]. The solubility method is limited to studying mononuclear species and is therefore not recommended for systems where polynuclear complex formation is suspected.

Conductivity measurements, also, are of limited application. Measurements cannot be made in solutions of constant ionic strength as the bulk electrolyte would carry most of the current. The ionic mobilities of the ligand and complexed ion are dependant on the composition of the solution, and consequently, in the absence of a constant ionic medium, this leads to difficulties in computing the results. This method can be used for investigating the hydrolysis of metal ions which hydrolyse appreciably in aqueous solution, as the concentration of the highly mobile hydrogen ions can be measured against the background electrolyte.

The solvent extraction, or liquid-liquid partition, method is of particular importance in investigating metal ion hydrolysis at low concentrations of the reacting species. Thus the method is useful for studying the mononuclear hydroxo complexes of metal ion systems in which polynuclear complexes predominate at higher concentrations. The method is not very accurate, but nevertheless,

approximate values of mononuclear hydrolysis constants can be determined.

The potentiometric method is the most accurate and widely applicable technique available for investigating the hydrolysis of metal ions. The hydrogen ion or hydroxyl concentration in the reaction solution is measured potentiometrically with either the glass, hydrogen or quinhydrone electrodes. Other hydrogen indicator electrodes eg. metal oxide electrodes, are seldom used as they are not sufficiently precise for this type of investigation. The glass electrode is generally preferred to the hydrogen or quinhydrone electrodes as the latter two often reduce the metal ion under investigation.

In many instances, the glass electrode is used in conjunction with other methods such as solubility, conductivity and calorimetry. Where possible the glass electrode is used together with the metal ion indicator electrode. Sillen and his school in Stockholm use the glass electrode and a metal electrode in their "titration method" of determining hydrolysis constants [35].

In the titration method both the total metal ion concentration and the ionic strength are maintained constant, whilst the / .....

whilst the hydrogen ion concentration is varied.

The metal ion and hydrogen ion concentrations are determined using the half-cell

$$\text{Me} \;\Big/\; \begin{matrix} aMMe^{x+} \\ hMH^{+} \end{matrix} \quad CMClO_4^- \;\Big/\; CMNaClO_4$$

$$\text{Glass Electrode} \;\Big/\; (C - xa - h)\, MNa^{+} \;\Big/$$

The calomel reference electrode was of the type

$$\text{C.E.} = Hg, \quad Hg_2Cl_2 ; \quad {}^{1}_{4}MNaCl$$

Thus the overall cell is

$$(-)\text{C.E.} \;\Big\|\; CMNaClO_4 \;\Big|\; \begin{matrix} aMMe^{x+} \\ hH^{+} \\ (c - xa - h)M\ Na^{+} \end{matrix} \quad CMClO_4^- \;\Big|\; \begin{matrix} \text{Me} \\ \text{Glass Electrode} \end{matrix} \quad (+)$$

From the above cell we have for the metal electrode

$$E = E_o + \frac{RT}{xF} \ln a_{Me^{x+}} + E_j$$

E_j is the liquid junction potential and E_o is a constant for the cell which can be either evaluated or eliminated.

Liquid Junction Potential.

When two solutions of the same electrolyte are in contact with each other the more concentrated will diffuse into the one of lower concentration. If the cation moves faster than the / .....

the anion, it will tend to diffuse ahead of the anion causing the less concentrated solution to become positive with respect to the more concentrated. A similar type of diffusion occurs at a heterionic boundary. In a concentration cell this separation of charges causes a potential, the liquid junction potential, to be set up across the boundary.

This potential can usually be greatly reduced, or even eliminated, by connecting the two half-cells through a salt bridge containing an electrolyte, such as potassium chloride or ammonium nitrate, in which the cation and anion have approximately the same mobility. The concentration of this electrolyte is generally greater than the concentrations of the cell electrolytes, and will thus be responsible for carrying almost all the current across the boundary or junction [13a,33b].

This type of salt bridge is seldom empolyed in hydrolytic equilibria studies as the liquid junction potential is not reproducible, and often the bridge electrolyte precipitates or complexes one or more of the ions in the test solution. Thus for most investigations, the inert electrolyte used to maintain a constant ionic strength in the test solution (ie: sodium perchlorate)

is also / .....

is also used in the bridge.

Liquid junctions have been classified into four groups by Guggenheim[16] according to the way in which they are formed. There are, however, some indefinite arrangements which are difficult to classify. The four types according to Guggenheim are:

1) Constrained diffusion junction

2) Free diffusion junction

3) Flowing junction

4) Continuous mixture junction.

In the constrained diffusion type junction the two solutions are separated by a porous plug or membrane and diffusion occurs across this constant thickness transition layer. Mixing occurs only in this transition layer.

A free diffusion junction is established by allowing the two solutions to meet at an initially sharp boundary, and then allowing them to diffuse freely. The well defined boundary cannot be maintained. Nevertheless, the liquid junction potential is reproducible and can be used for accurate measurements[27].

The flowing junction was investigated by Lamb and Larson[24]

and subsequently / .....

and subsequently by MacInnes and Yeh [26]. The junction is formed in a T - tube by allowing the two solutions to stream towards each other and flow to waste in parallel streams. The transition layer is therefore very thin. Although the flowing junction has proved to be very reproducible, it is not often used, as it requires fairly large amounts of solution, and also calls for considerable manipulative skill.

The flowing junction may be regarded as a limiting condition for the continuous mixture junction which is defined by Guggenheim as: "the composition at any point of the transition layer is a linear combination of the compositions of the extreme liquids, or in other words, any point of the transition layer may be regarded as a mixture in certain proportions of the two extreme liquids". This junction is unstable and is not practicable[27].

In the cell used by Sillen and coworkers there are two junctions viz: sodium chloride - sodium perchlorate and sodium perchlorate - test solution. The potential of the former junction will be very small and will remain constant throughout the determination. For the second liquid junction, the potential will be

dependant on / .....

dependant on the composition of the test solution.

In the determination of the acidity constants according to Sillen the total metal ion concentration is kept constant while the hydrogen ion concentration is varied. As hydrogen ions have a very high mobility, the liquid junction potential between the test solution and bridge solution will alter appreciably with the changing hydrogen ion concentration.

Using a type of junction which could be classified as a free diffusion junction, Biedermann and Sillen[4] determined the liquid junction potentials of the system

$$(-)\ \text{C.E.} \;\Big|\; 3M\text{NaClO}_4 \;\Big|\; \begin{matrix} aM\text{Me}^{x+} \\ hM\text{H}^{+} \\ (3-ax-h)M\text{Na}^{+} \end{matrix} \qquad 3M\text{ClO}_4^{-} \;\Big|\; \text{Me}\ (+)$$

The concentration of the hydrogen ions was changed while the metal ion concentration, together with the total ionic strength, was kept constant. Hence the only changes in the potential in the above cell were due to the effect of the hydrogen ion concentration on the liquid junction potential.

In computing their results Biedermann and Sillen assumed that a continuous mixture boundary existed at the junction, and used / .....

and used a simplified form of the Henderson equation[18], viz:

$$E_j = - \frac{RT}{F} \ln \left(1 + \frac{dh}{C}\right)$$

where C is the ionic strength

h the hydrogen ion concentration

and d is a variable which can be determined experimentally.

Biedermann and Sillen found a value $d = 1.95 \pm 0.08$. Although d may also be calculated by the Henderson method based on equivalent conductances, viz:

$$d = \frac{\Lambda_{HClO_4} - \Lambda_{NaClO_4}}{\Lambda_{NaClO_4}}$$

this leads to a value $d = 3.3$ for the same system. The difference in these values was attributed by Ekedahl and Sillen[11] to a general leveling of ionic mobilities in electrolyte mixtures.

Present Investigation.

The determination of hydrolysis constants according to Sillen's method is very largely dependant on the accuracy with which the liquid junction potentials can be evaluated.

Using solutions / .....

Using solutions with ionic strengths of 3000 mM Biedermann and Sillen determined d to a precision of about 4 percent. A few experiments carried out on solutions with ionic strengths of 500 mM and 1000 mM gave results "which seemed to show that, within experimental errors, the liquid junction potential can with good approximation be considered as a function of $^{h}/_{I}$ (I being the ionic strength) only", ie. d is independant of the ionic strength. On this assumption Forsling, Hietamen and Sillen [13] determined the acidity constant for mercury (I) in a solution with an ionic strength of 500 mM. The acidity constant was found to be $k = 10^{-5\pm0.3}$

The present investigation was undertaken in an attempt to obtain a more precise value of the acidity constant for mercury (I). This required the determination of the liquid junction potential as precisely as possible for solutions of ionic strength of 500 mM.

In the present work d was determined for three systems involving the metal ion half-cells Ag^{+}/Ag; Hg_2^{2+}/Hg and Hg_2^{2+}, Hg^{2+}/Pt. The values of d for each system were determined to a precision of less than one percent. The hydrolysis constant of

mercury (I)/ .....

mercury (I) was found to be between 1.0×10^{-5} and 1.7×10^{-5} ie. $k_h = 10^{-5 \cdot 12 \pm 0 \cdot 12}$. The best value was found to be 1.6×10^{-5}

No attempts have been made to study the hydrolysis of silver using Sillen's titration. The solubility of the oxide has been studied by Britton[6] and Jellinek and Gordon[20] using silver electrodes. Britton and Wilson[7] used a glass electrode in conjunction with the silver electrode. Faucherre[12] determined the hydrolysis constant for silver using the glass electrode. No other attempts have been made to study the hydrolysis of silver potentiometrically.

The hydrolysis of silver perchlorate was investigated by Sillen's method. The hydrolysis proved negligible. However an approximate value of the solubility product of silver hydroxide was obtained.

EXPERIMENTAL.

A. Liquid Junction Potential.

1. Systems Investigated.

The effect of the hydrogen ion concentration (hmM) on the liquid junction potential was measured by means of the cell

(-) C.E / 500 mM $NaClO_4$ / S / Electrode reversible to $(+)$ metal ion in S.

C.E. is the calomel electrode Hg, Hg_2Cl_2; 4M NaCl. S, the test solution, was composed as follows:

S = a mM Me^{x+}; h mM H^+; 500 mM ClO_4^-; and (500 - ax - h) mM Na^+

where mM is the concentration in millimoles/litre and Me^{x+} is a metal ion of charge x.

The metal ions used were silver, copper (II) and mercury (I). The redox system mercury (I) - mercury (II) was also investigated. In the latter system the composition of the test solution was

S = b mM Hg_2^{2+}; c mM Hg^{2+}; h mM H^+; 500 mM ClO_4^- and

(500-2b-2c-h) mM Na^+

2. Preparation and / .....

2. Preparation and Behaviour of Electrodes.

a. Silver Electrodes.

The behaviour of a silver electrode depends on its previous history and mode of preparation. Several types of electrodes were prepared but most did not give satisfactory results.

Silver wire prepared according to Koltoff and Furman [23] and Clark [10] did not give steady or reversible results when immersed in silver perchlorate solutions.

Platinum wire, sealed into glass tubing and electrolytically coated with silver from a potassium silver cyanide solution, has been used successfully by many workers. Nilsson [30], amongst others, used this type of electrode satisfactorily although equilibrium was not attained rapidly.

When such an electrode was lightly coated with silver chloride by electrolysis in a dilute hydrochloric acid solution, equilibrium was reached almost instantaneously in silver solutions. It was subsequently found that Ekedahl and Sillen [11] had used this type of silver electrode in determining silver ion concentrations.

The electrodes / .....

The electrodes used in this work were prepared according to Brown[9] . As it was found that equilibrium is reached slowly if the silver chloride deposit is too thick, chloridation was carried out for five to ten minutes and not for thirty minutes as described by Brown.

b. Mercury Electrode.

The potential of mercury (I) solutions was measured by a pool of mercury in the reaction vessel. Contact was made with the mercury pool by a piece of platinum wire sealed through the bottom of the vessel into a side arm filled with mercury (Fig. 1).

Equilibrium was reached after a few minutes.

c. Mercury Redox Electrode.

The mercury electrode cannot be used for determining the concentration of mercury (II) as the reaction

$$Hg^{2+} + Hg(l) \rightleftarrows Hg_2^{2+}$$

takes place. This reaction has an equilibrium constant

$$[Hg_2^{2+}]\,[Hg^{2+}]^{-1} = 130$$

Attempts were / .....

Attempts were made to measure the potential of the mercury (I) - mercury (II) couple using a bright platinum foil electrode. The foil was welded to platinum wire sealed into glass tubing. Contact with the lead to the potentiometer was made through mercury in the tubing. The potential of the system was found to drop consistently over a few days. This was attributed to the imperfect seal between the glass and platinum. The solution and mercury come into contact through diffusion and the ensuing reaction between the mercury (II) and mercury causes a drop in the potential.

To overcome this difficulty the foil was welded to a six inch length of platinum wire sealed into glass tubing five inches long. Contact between the platinum wire and potentiometer lead was made using a screw connection.

Before each experiment the platinum foil was cleaned in hot concentrated nitric acid, washed well in distilled water and then heated to redness in an alcohol flame.

This electrode attained equilibrium immediately and did not fluctuate more than a few hundredth of a millivolt on standing for an hour.

d. Copper Amalgam / .....

d. Copper Amalgam Electrode.

As high purity copper wire or foil could not be obtained, copper amalgam was used for measuring the potentials of copper perchlorate solutions.

Generally equilibration between an electrode and solution is greater if the amalgam of the metal is used [33a].

Biedermann and Sillen [4] used the copper amalgam electrode in evaluating liquid junction potentials. Although they found that the electrode was easily polarizable in solutions of high acid strength, the electrode gave steady and reproducible potentials in copper perchlorate solutions where the acidity was less than 0.1M.

Biedermann's and Sillen's work could not be repeated. Although the copper-amalgam was prepared in the same manner, steady potentials could not be obtained. On standing for a few hours red crystals settled out on the amalgam surface.

Berecki-Biedermann [1] also failed to obtain equilibrium with this electrode. She attributed the red crystals which settled out on her amalgam to copper oxide formed by the reaction

$$Cu^{2+} + Cu/Hg(s) + H_2O \rightleftarrows Cu_2O(s) + 2H^+ + Hg(l)$$

3/ .....

3. Preparation and Analysis of Solutions.

All reagents used were of A.R. or equivalent grade. Riedel-de-Haen perchloric acid was preferred on account of its low chloride content.

a. Stock Solutions.

Sodium Perchlorate.

Sodium perchlorate was prepared by the slow addition of sodium carbonate to a mechanically stirred, ice-cold, 60% perchloric acid solution until neutral to narrow range B.D.H. indicator paper. The solution was then boiled to expel carbon dioxide and the warm solution filtered to remove a white insoluble residue, which was most probably potassium perchlorate.

The sodium perchlorate concentration was determined by passing an aliquot through a cation exchange column in its acid form. The liberated hydrogen ions were titrated with standard sodium hydroxide solution using bromo cresol purple as indicator. Two ion exchange columns were used viz: Amberlite I.R. - 120 and Zeo-karb 215. Identical results were obtained using both columns.

The total / .....

The total perchlorate concentration in all solutions used was determined by the above method.

Silver Perchlorate.

Excess of freshly precipitated silver oxide was added to hot (above 70°C) 60% perchloric acid and the solution filtered through a sintered glass crucible. The solution was analysed for the silver ion concentration by Volhand's Method.

The free acid was determined by precipitating the silver with sodium chloride. The silver chloride was filtered off and the filtrate titrated with standard sodium hydroxide solution. It is essential that the silver chloride be well washed as it retains the free acid.

The silver oxide was precipitated from a silver nitrate solution with sodium hydroxide. After filtering and washing with water, it was dissolved in concentrated perchloric acid and reprecipitated with sodium hydroxide. This cycle was repeated until the oxide was free from nitrate.

Mercury (I) / .....

Mercury (I) Perchlorate.

Red mercuric oxide was dissolved in excess perchloric acid and the solution shaken with triply distilled mercury for twenty-four hours[29,32] At this stage only minute traces of mercury (II) could be detected.

The mercury (I) concentration was determined by titrating sodium chloride using bromo phenol blue as an adsorption indicator[32]. If the free acid strength in the solution is greater than 0.04M it must first be neutralised with sodium carbonate.

The free acid concentration was determined as in silver perchlorate above.

Mercuric Perchlorate.

A weighed amount of mercuric oxide was dissolved in a known excess of standard perchloric acid and the solution diluted to the required volume in an "A" - grade standard flask.

Hydrogen sulphide gas was passed through an aliquot of this solution precipitating mercury (II) as the sulphide,

which was / .....

which was filtered off. The filtrate was boiled to expel hydrogen sulphide and, after cooling, titrated with standard sodium hydroxide solution giving the total acid plus mercury (II) concentration in the solution.

These results and those obtained using the ion exchange method agreed to 0.2%.

Copper Perchlorate.

Excess copper oxide was added to hot 60% perchloric acid and the solution filtered through a sintered glass funnel.

The copper concentration was determined iodometrically.

Perchloric Acid.

Concentrated perchloric acid was diluted to approximately 2M, and standardised against a standard sodium hydroxide solution using bromo cresol purple as indicator.

b. Test Solutions / .....

b. Test Solutions.

Two solutions were prepared for each titration by suitable dilution of the above stock solutions. Table 1 gives the concentration of each specie present in the solutions.

The solutions were analysed as above.

4. Apparatus.

Two types of salt bridges were used, both employing 0.5M sodium perchlorate as the bridge electrolyte.

Type I.

Connection between the test solution and the calomel electrode was made via two bridges, through a vessel containing a 0.5M sodium perchlorate pool (Fig. 1).

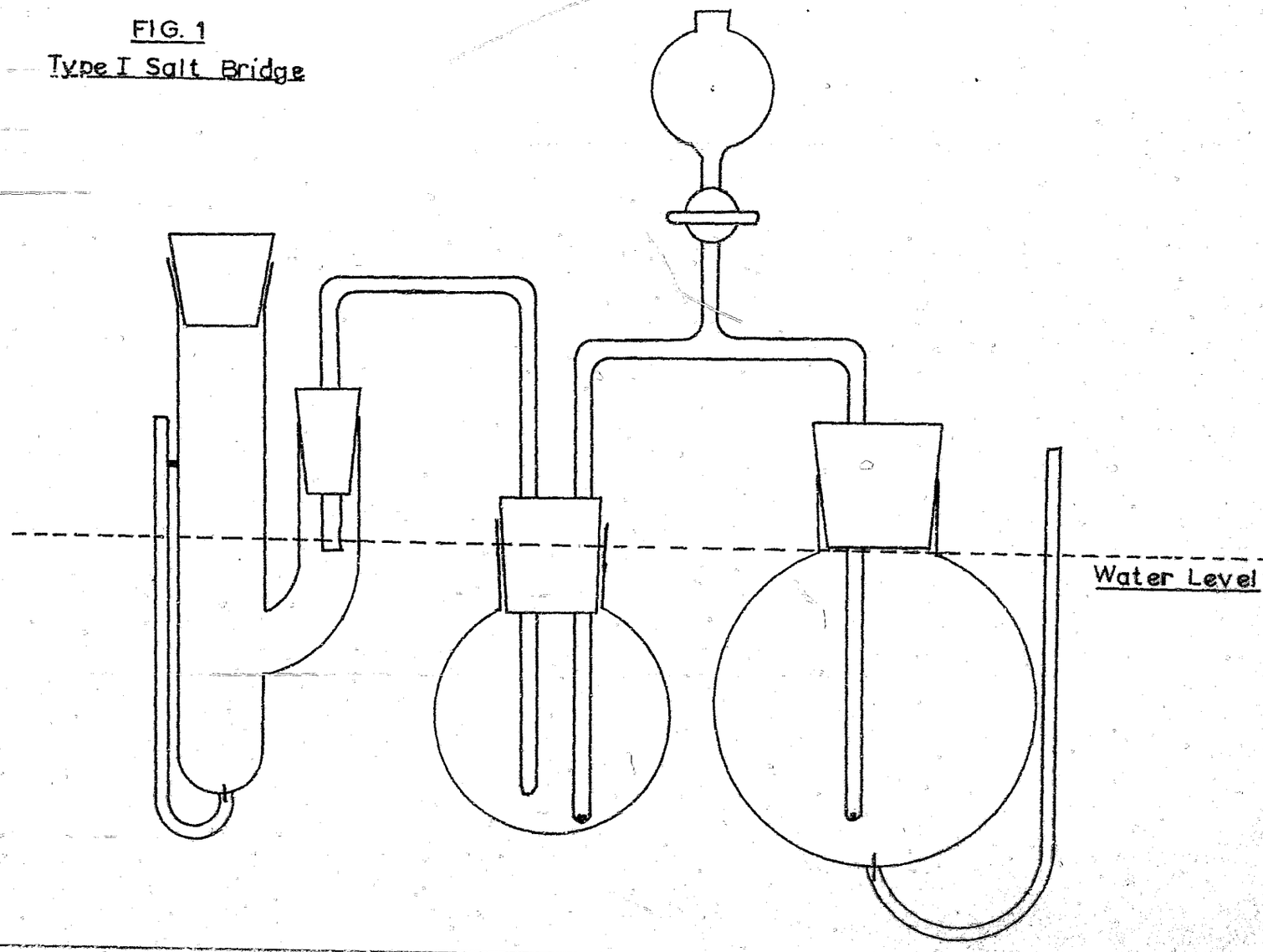
The first bridge, between the test solution and sodium perchlorate pool, was an inverted U-tube sealed at the two extremities with asbestos fibre. The bridge was filled with 0.5M sodium perchlorate through a funnel fitted on the bend. The junction formed by this bridge could be classed, according to Guggenheim's classification, as a constrained diffusion junction.

The sodium / .....

Table 1.

System	S_1	S_2	d
Ag^+/Ag	10.0 mMAg^+ 490.0 mMNa^+	10.0 mMAg^+ 490.0 mMH^+	2.41 2.45 2.43 2.42 2.43
Hg_2^{2+}/Hg	5.0 mMHg_2^{2+} 17.90 mMH^+ 472.0 mMNa^+	5.0 mMHg_2^{2+} 489.3 mMH^+	2.54 2.52 2.53 2.52 2.55
$Hg_2^{2+};Hg^{2+}/Pt$	2.5 mMHg_2^{2+} 2.5 mMHg^{2+} 13.50 mMH^+ 476.0 mMNa^+	2.5 mMHg_2^{2+} 2.5 mMHg^{2+} 489.65 mMH^+	2.52 2.53 2.54

FIG. 1
Type I Salt Bridge



The sodium perchlorate pool and the calomel electrode were connected by an agar gel bridge saturated with sodium chloride.

This bridge had several disadvantages which will be discussed later (page 34). Type II bridge was used in preference to this type.

Type II.

The bridge described by Forsling, Hietanen and Sillen [13] was modified slightly (Figure 2).

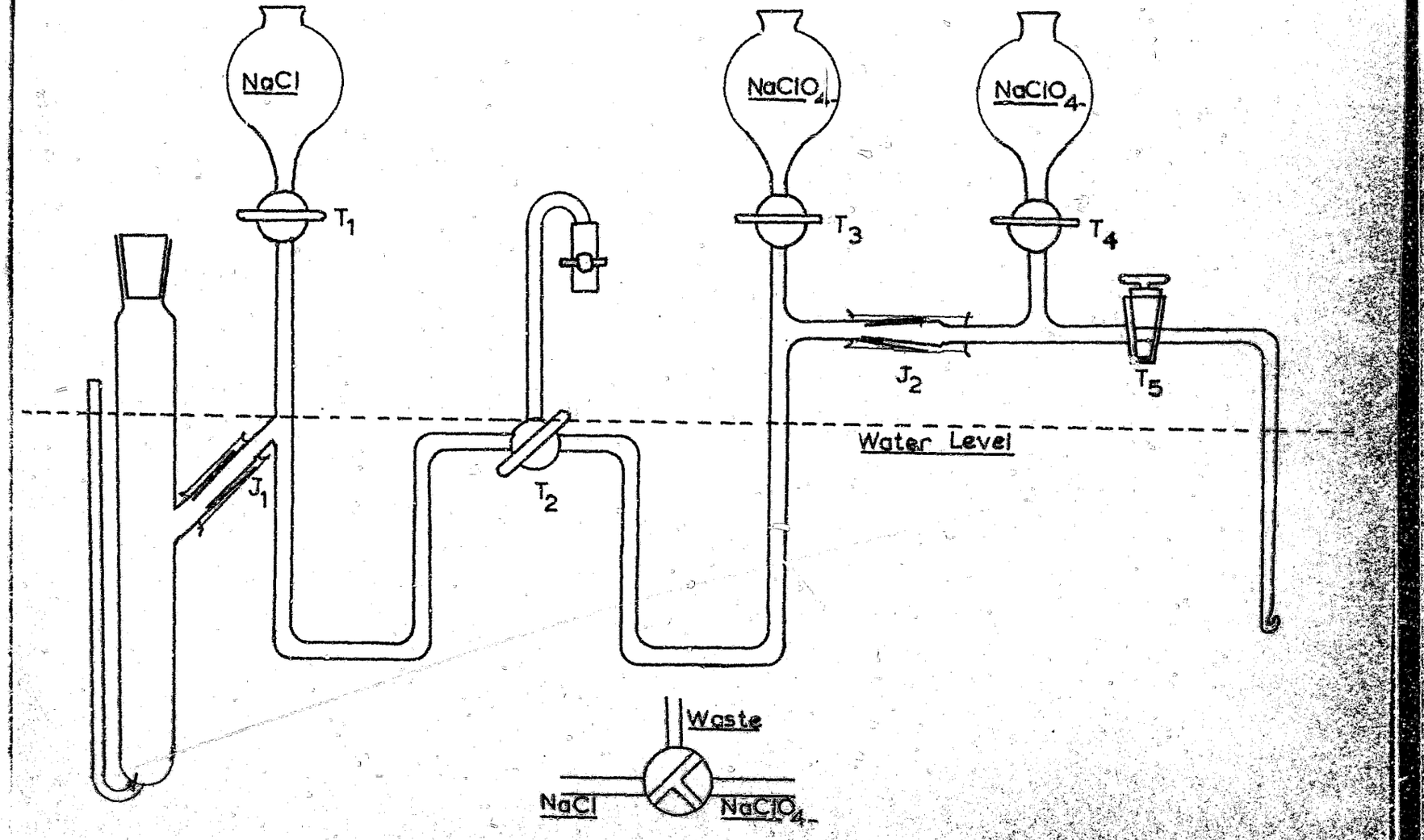
(i) Electrical contact with the mercury pool of the calomel electrode was made through a platinum wire sealed between a side arm and the base of the electrode vessel. The side arm was then filled with mercury. This modification facilitated the preparation of the calomel electrode.

(ii) Contact between the sodium chloride solution of the calomel electrode and the sodium perchlorate solution in the bridge was made around the three-way tap, T_2, which

was greased / .....

FIG. 2

Type II Salt Bridge



was greased on the outer edges only. During a titration T_5 was kept open and T_2 positioned as shown in the inset in Figure 2. Syphoning was found to take place from the waste pipe above T_2 through T_5 into the reaction vessel. This flow was prevented by attaching a short length of rubber tubing, closed with a screw clip, to the waste pipe.

(iii) The quick-fit joints, J_1 and J_2, were held firmly with hooks and rubber bands to prevent leakages.

(iv) To facilitate the filling of the side arm to the right of J_2 with sodium perchlorate solution a funnel was fitted above T_4.

The tap T_2 and quick-fit joint J_2, which were below the level of the water in the thermostat, were coated with water repellant silicone grease.

Before each determination the apparatus to the left of T_2, was flushed with 4M sodium chloride solution and to the right of T_2 with 0.5M sodium perchlorate solution. The side arm to the right of J_2 was filled with 0.5M sodium perchlorate solution, fitted through the stopper in the reaction vessel and then joined

to J_2/.....

to J_2 by the quick-fit joint. T_5 was opened and T_2 positioned as in the inset in Figure 2. The junction was a "J-type" described by Biedermann and Sillen [4].

The apparatus was immersed in an earthed water thermostat controlled at 30.0± 0.05°C with a toluene-mercury regulator. The water in the thermostat was stirred with a Stuart-Turner pump.

The potentials were read on a Pye Vernier Precision Potentiometer in conjunction with a Pye galvanometer.

Nitrogen was bubbled through all solutions to prevent oxidation and to assist in the mixing of the test solutions. The nitrogen was freed of oxygen by passing over heated copper turnings and was then saturated with water vapour by passage through a vessel containing a 0.5M sodium perchlorate solution immersed in the thermostat.

The reaction vessel used for the mercury (I) and copper (II) systems is as shown in Figure 1. A similar vessel without the side arm was used for the other systems. The reaction vessel was fitted with a rubber stopper bored to take the salt bridge

junction, / .....

junction, an electrode and nitrogen inlet.

5. Procedure.

Initially 50.0 mls of S_1 (Table 1) were placed in the reaction vessel in the thermostat and allowed to stand in contact with the respective electrode for approximately thirty minutes for equilibrium to be attained. The hydrogen ion concentration was then altered by small additions of S_2. After each addition of S_2 approximately ten minutes were allowed to elapse before determing the potential of the cell.

Since the metal ion concentration was maintained constant throughout the titration the changes in the potential of the cell are due to the effect of the replacement of sodium ions by the more mobile hydrogen ions on the liquid junction potential.

Details of a typical titration for each system are given in Tables 2, 3 and 4.

6. Calculations / .....

Table 2. (Figs 3a, 3b).

Silver Electrode.

mls S_2	E mV	E_0+E_j' mV	$-E_j'$	$-E_j'/60\cdot15$	$-E_j'/10^{60\cdot15}-1$	h mM	h/500 mM
0	408.40	348.25	0	0	0	0	0
2.0	405.96	345.81	2.44	0.0406	0.098	18.85	0.0377
4.0	403.93	343.78	4.47	0.0743	0.187	36.30	0.0726
6.0	402.21	342.06	6.19	0.1029	0.268	52.50	0.1050
8.0	400.69	340.54	7.71	0.1282	0.344	67.59	0.1352
10.0	399.33	339.18	9.07	0.1508	0.416	81.67	0.1633
12.5	397.85	337.70	10.55	0.1754	0.497	98.00	0.1960
15.0	396.62	336.47	11.78	0.1958	0.570	113.08	0.2262
17.5	395.51	335.36	12.89	0.2143	0.638	127.04	0.2541
20.5	394.34	334.19	14.06	0.2337	0.713	142.48	0.2850
22.5	393.68	333.53	14.72	0.2447	0.757	152.07	0.3041
25.0	392.90	332.75	15.50	0.2577	0.810	163.33	0.3267
27.5	392.22	332.07	16.18	0.2690	0.858	173.87	0.3477
30.0	391.50	331.35	16.90	0.2810	0.910	183.75	0.3675
32.5	390.92	330.77	17.48	0.2906	0.953	193.03	0.3861
35.0	390.37	330.22	18.03	0.2997	0.994	201.76	0.4035
37.5	389.91	329.76	18.49	0.3074	1.030	210.00	0.4200
40.0	389.46	329.31	18.94	0.3149	1.065	217.78	0.4356

Table 3. (Figs. 4a, 4b)

Mercury Electrode.

mls S_2	E mV	E_o+E_j' mV	$-E_j'$ mV	$-E_{j/60\cdot15}'$	$10^{-E_{j/60\cdot15}'-1}$	h mM	$h/500$ mM
0	453.70	432.67	2.23	0.0371	0.089	17.90	0.0358
2.0	451.55	430.52	4.38	0.0728	0.182	36.03	0.0721
4.0	449.67	428.64	6.26	0.1041	0.271	52.82	0.1056
6.0	448.04	427.01	7.89	0.1312	0.353	68.41	0.1368
8.0	446.64	425.61	9.29	0.1544	0.427	82.92	0.1658
10.0	445.40	424.37	10.53	0.1751	0.496	96.47	0.1929
12.5	444.04	423.01	11.89	0.1977	0.577	112.18	0.2244
15.0	442.83	421.80	13.10	0.2178	0.651	126.68	0.2534
17.5	441.69	420.66	14.24	0.2367	0.725	140.11	0.2802
20.0	440.84	419.81	15.09	0.2509	0.782	152.59	0.3052
22.5	440.02	418.99	15.91	0.2645	0.839	164.20	0.3284
25.0	439.22	418.19	16.71	0.2778	0.895	175.03	0.3501
27.5	438.60	417.57	17.33	0.2881	0.941	185.17	0.3703
30.0	437.91	416.88	18.02	0.2996	0.995	194.67	0.3893
32.5	437.27	416.24	18.66	0.3102	1.043	203.60	0.4072
35.0	436.75	415.72	19.18	0.3189	1.084	212.01	0.4240
37.5	436.24	415.21	19.69	0.3273	1.124	219.93	0.4399
40.0	435.76	414.73	20.17	0.3353	1.165	227.41	0.4548

Table 4. (Figs. 5a, 5b).

Mercury Redox Electrode.

mls S_2	$E=E_o+E'_j$ mV	$-E'_j$ mV	$-E'_j/60\cdot15$	$-E'_j/60\cdot15$	h mM	h/500 mM
0	571.95	1.50	0.0249	0.059	13.95	0.0279
1.0	570.98	2.47	0.0411	0.099	23.28	0.0466
2.0	569.93	3.52	0.0585	0.144	32.25	0.0645
3.0	568.95	4.50	0.0748	0.188	40.88	0.0818
4.0	568.00	5.45	0.0906	0.232	49.19	0.0984
5.0	567.15	6.30	0.1047	0.273	57.19	0.1144
6.0	566.32	7.13	0.1185	0.314	64.92	0.1298
7.0	565.60	7.85	0.1305	0.351	72.37	0.1447
8.0	564.89	8.56	0.1423	0.388	79.56	0.1591
9.0	564.19	9.26	0.1539	0.425	86.51	0.1730
10.0	563.52	9.93	0.1651	0.462	93.23	0.1865
11.5	562.71	10.74	0.1785	0.507	102.90	0.2058
13.0	561.90	11.55	0.1920	0.556	112.11	0.2242
14.5	561.12	12.33	0.2050	0.603	120.89	0.2418
16.0	560.46	12.99	0.2160	0.644	129.27	0.2585
17.5	559.87	13.58	0.2258	0.681	137.28	0.2746
20.0	558.92	14.53	0.2416	0.744	149.86	0.2997
22.5	557.99	15.46	0.2570	0.807	161.58	0.3232
25.0	557.30	16.15	0.2685	0.856	172.52	0.3450
27.5	556.64	16.81	0.2795	0.903	182.75	0.3655
30.0	556.00	17.45	0.2901	0.950	192.34	0.3847
32.5	555.36	18.09	0.3007	0.997	201.35	0.4027

6. Calculations and Results.

For the cell

$$(-)\ \text{C.E.} \,\big|\, Me^{x+}\ H^{+} \,\big|\, Me\ (+)$$

where Me^{x+} is Ag^{+} or H_2^{2+}, we have the following equation

$$E = E_o + \frac{RT}{xF} \ln {}^{a}Me^{x+} + E_j$$

$$= E_o + \frac{RT}{xF} \ln [Me^{x+}] + E_j' \quad \ldots\ldots\ldots (1a)$$

$$\text{ie. } E_j' = E_j + \frac{RT}{xF} \ln {}^{f}Me^{x+} \quad \ldots\ldots\ldots (2a)$$

For the redox system Hg_2^{2+}, Hg^{2+}/Pt the equation is

$$E = E_o + \frac{RT}{F} \ln \frac{a_{Hg^{2+}}}{a_{Hg_2^{2+}}} + E_j$$

$$= E_o + \frac{RT}{F} \ln \left[\frac{Hg^{2+}}{Hg_2^{2+}}\right] + E_j' \quad \ldots\ldots\ldots (1b)$$

$$\text{ie. } E_j' = E_j + \frac{RT}{F} \ln \frac{f_{Hg^{2+}}}{f_{Hg_2^{2+}}} \quad \ldots\ldots\ldots (2b)$$

In this / .....

In this investigation $[Hg_2^{2+}] = [Hg^{2+}]$ and thus equation (1b) reduces to

$$E = E_o + E_j'$$

From equation (1a)

$$E \sim \frac{RT}{xF} \ln [Me^{x+}] = E_o + E_j'$$

Thus by subtracting the Nernst term from the measured value of E, $(E_o + E_j')$ is obtained.

Since the liquid junction potential tends to zero as the hydrogen ion concentration tends to zero, E_o can be evaluated by extrapolating the graph of $(E_o + E_j')$ versus the hydrogen ion concentration to zero acidity. Thus the value of the liquid junction potential at any particular hydrogen ion concentration can be obtained by subtracting E_o from the corresponding value of $(E_o + E_j')$.

The extrapolations for the three systems silver, mercury (I) and the mercury (I) - mercury (II) couple are given in Figures 3(a), 4(a) and 5(a) respectively.

The simplified / .....

Fig. 3(a)

Silver Electrode

(Table 2)

$E_o = 348{\cdot}25$

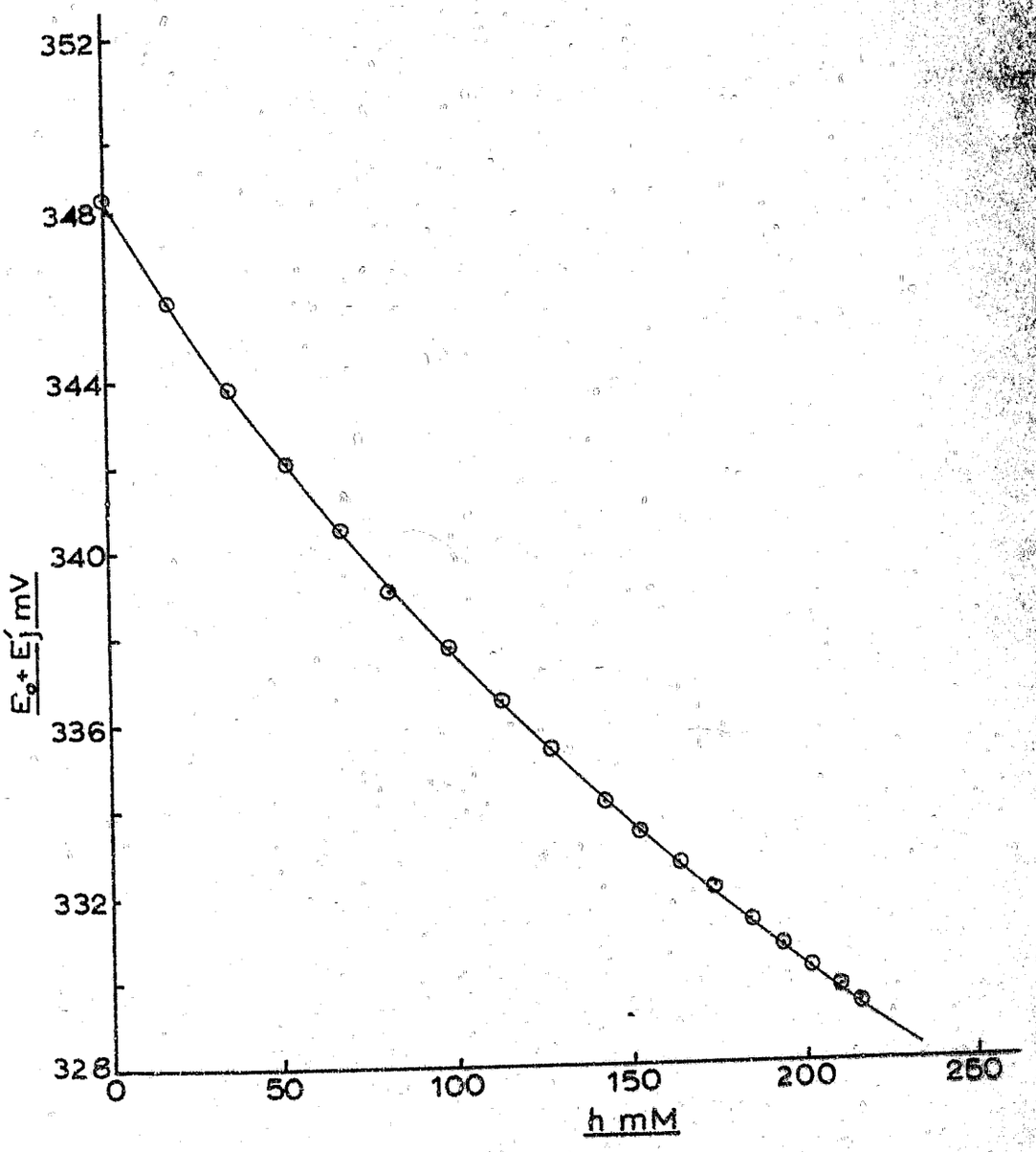


FIG. 4(a)

Mercury (I)/Mercury Electrode (Table 3)

$E_o = 434.90$

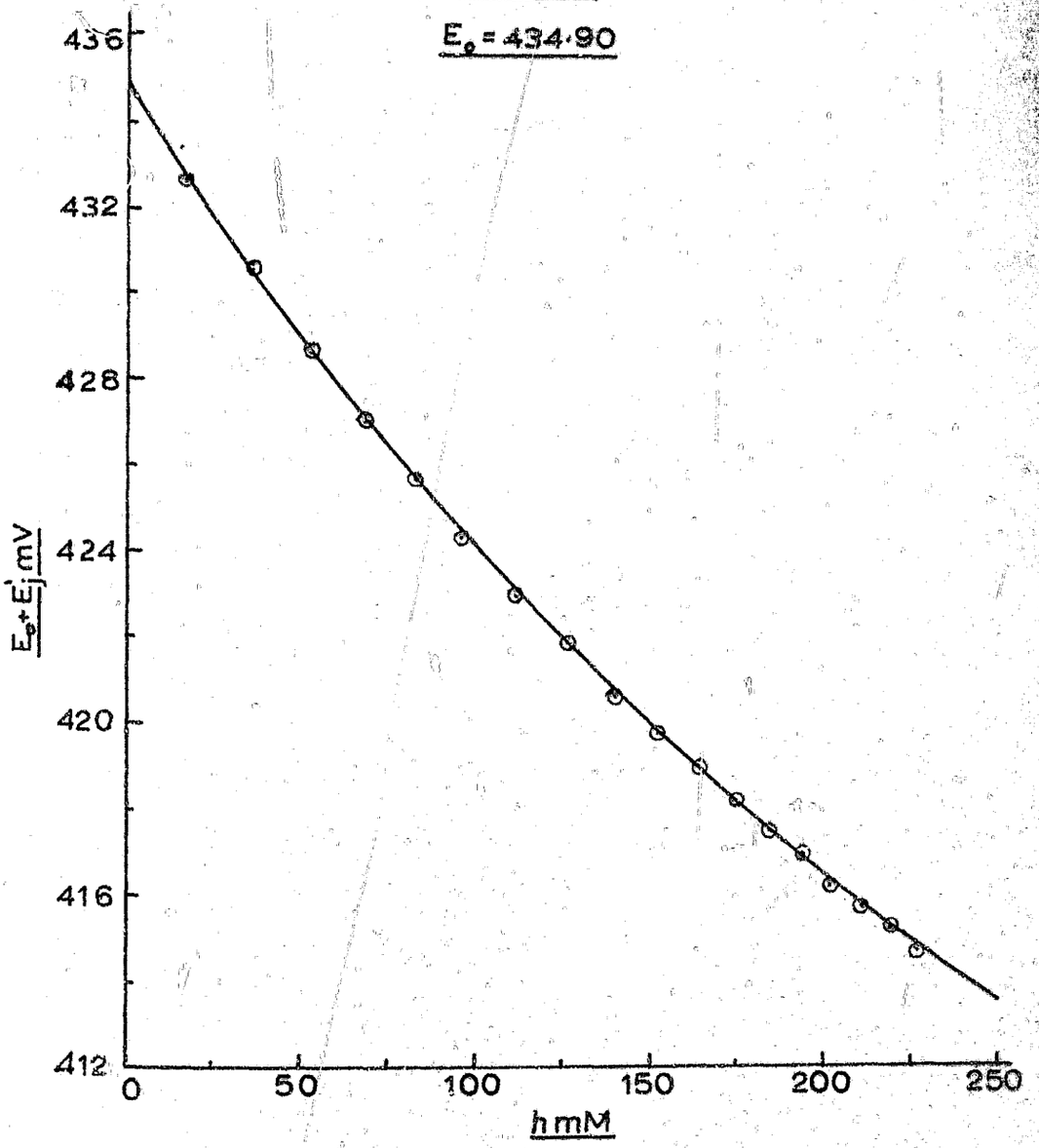
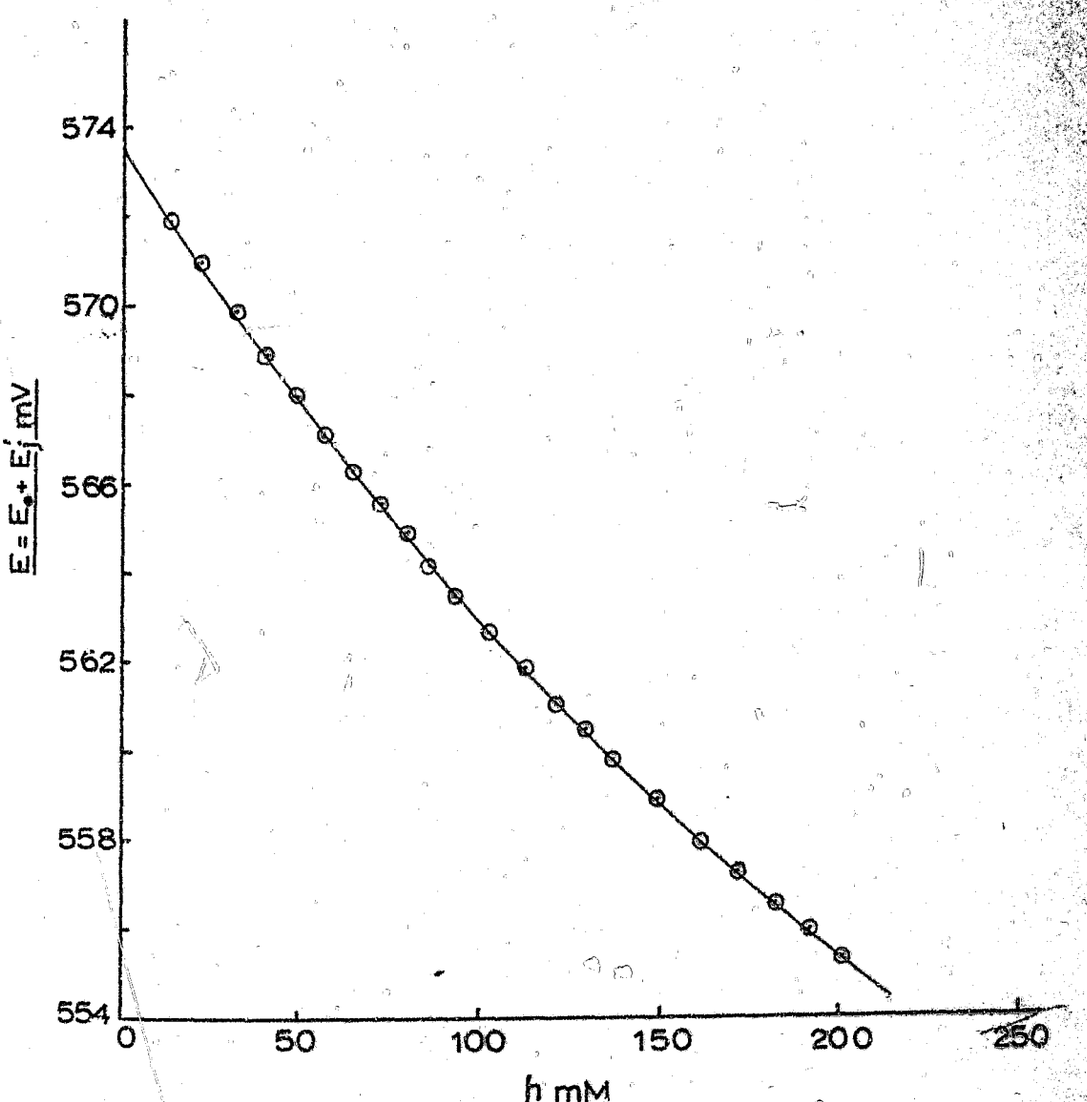


FIG. 5(a)

Mercury Redox Electrode

(Table 4)

E_o=573·45



The simplified Henderson equation (page 14)

$$E_j = \frac{-RT}{F} \ln\left(1 + \frac{dh}{c}\right) \quad \ldots\ldots\ldots\ldots (3)$$

reduces to

$$E_j = -60.15 \log\left(1 + \frac{dh}{500}\right) \quad \ldots\ldots\ldots\ldots (4)$$

at 30.0°C and an ionic strength of 500 mM if the potentials of the above cells are given in millivolts.

Assuming that the activity coefficient terms in equations (2a) and (2b) are negligible ie. the activity coefficients are very close to unity, E_j can be replaced by E_j' and equation (4) rearranged as follows;

$$10^{-E_j'/60.15} - 1 = \frac{dh}{500} \quad \ldots\ldots\ldots\ldots (5)$$

The values of d given in Table 1 were obtained from equation (5) by the method of least squares. d can also be obtained from the slope of the graph $(10^{-E_j'/60.15} - 1)$ versus $h/500$ as shown in Figures 3(b), 4(b) and 5(b) for the three systems studied. The values of d obtained by both methods agreed very closely. The values listed in Table 1 are for the type II salt bridge, as the results obtained for the type I bridge were erratic and non-reproducible.

At low / .....

FIG. 3(b)

Silver Electrode

(Table 2)

d = 2·43

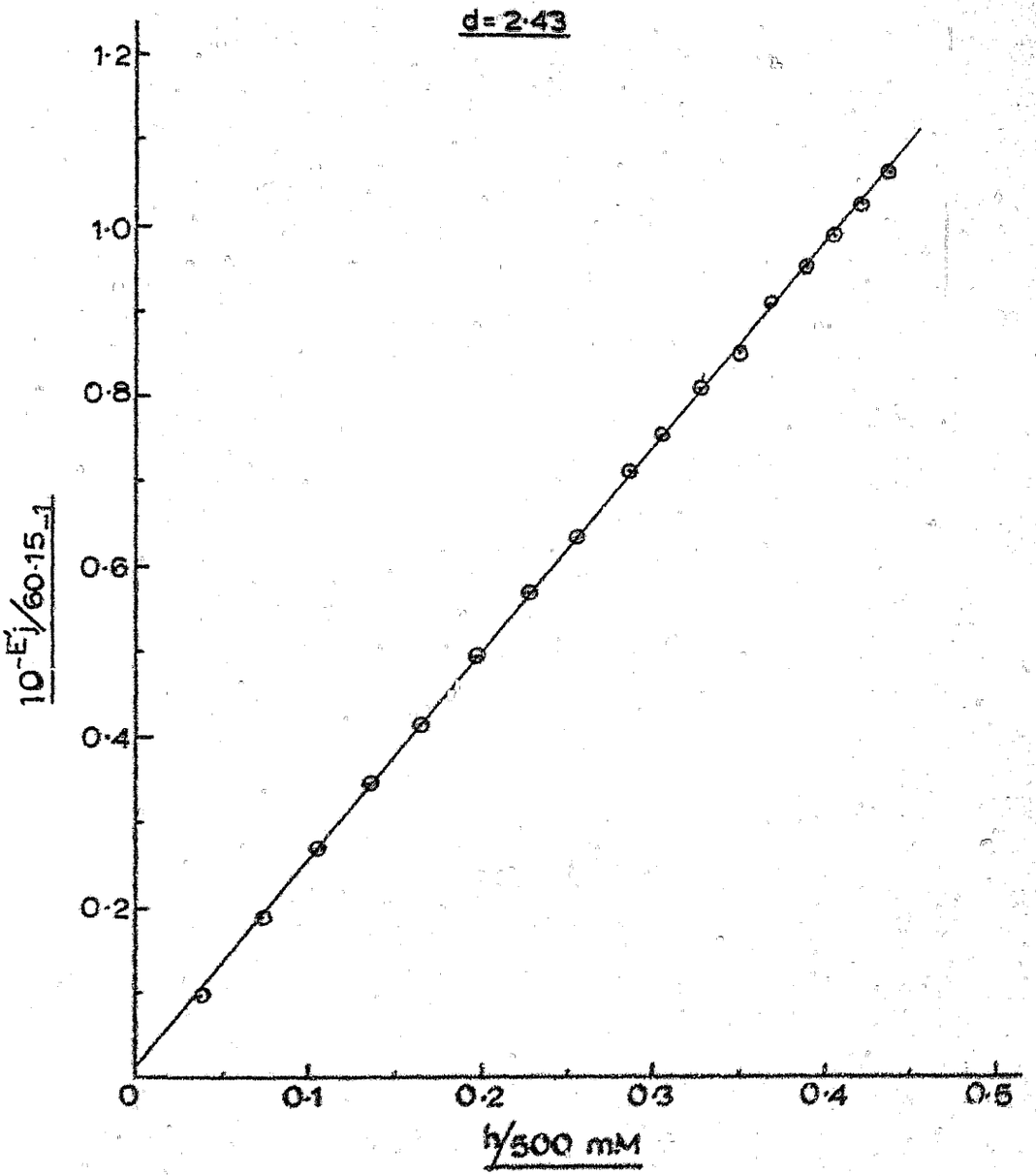


FIG. 4(b)

Mercury(I)/Mercury Electrode

(Table 3)

d = 2·55

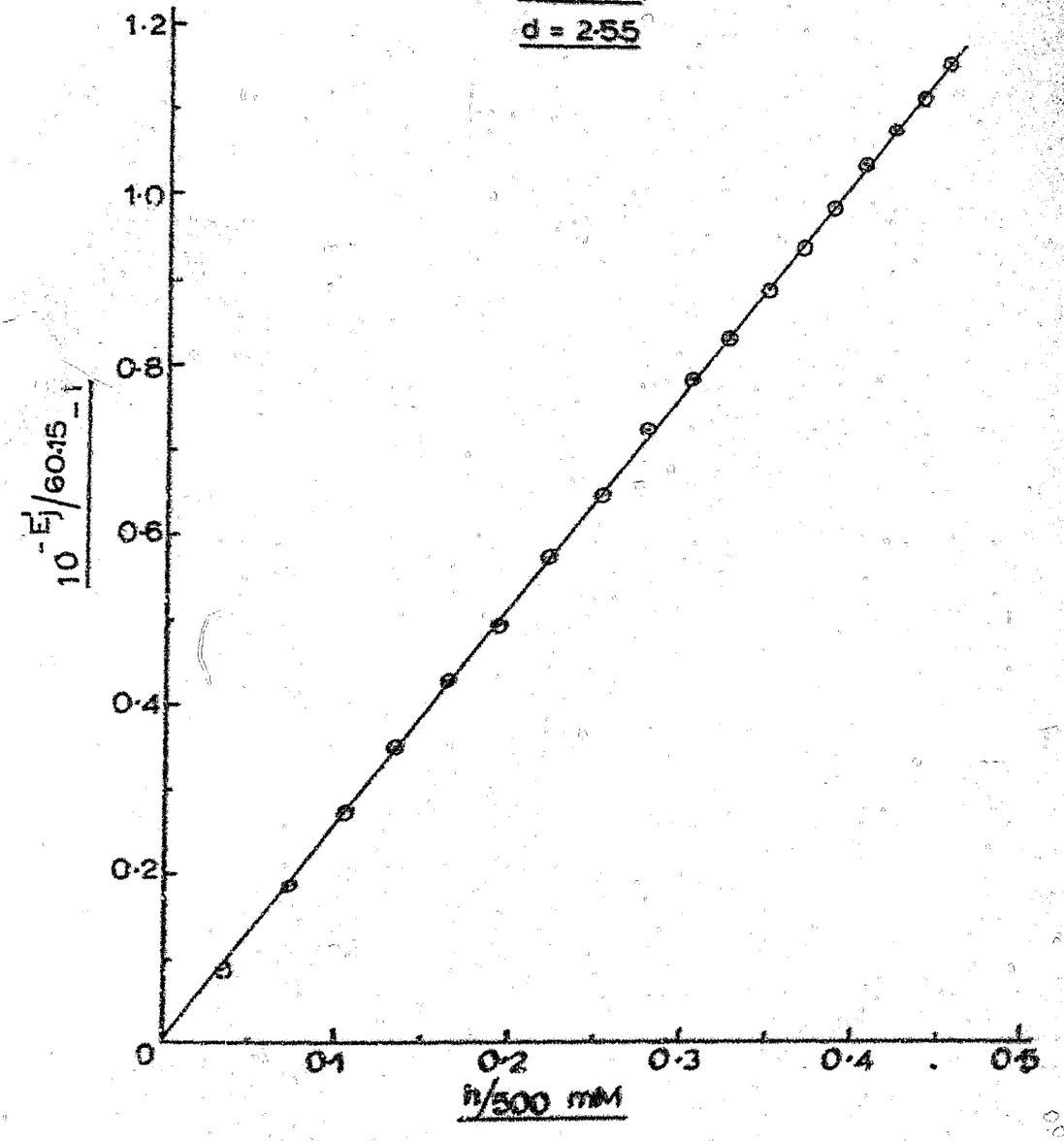


FIG. 5(b)

Mercury Redox Electrode

(Table 4)

d=2·52

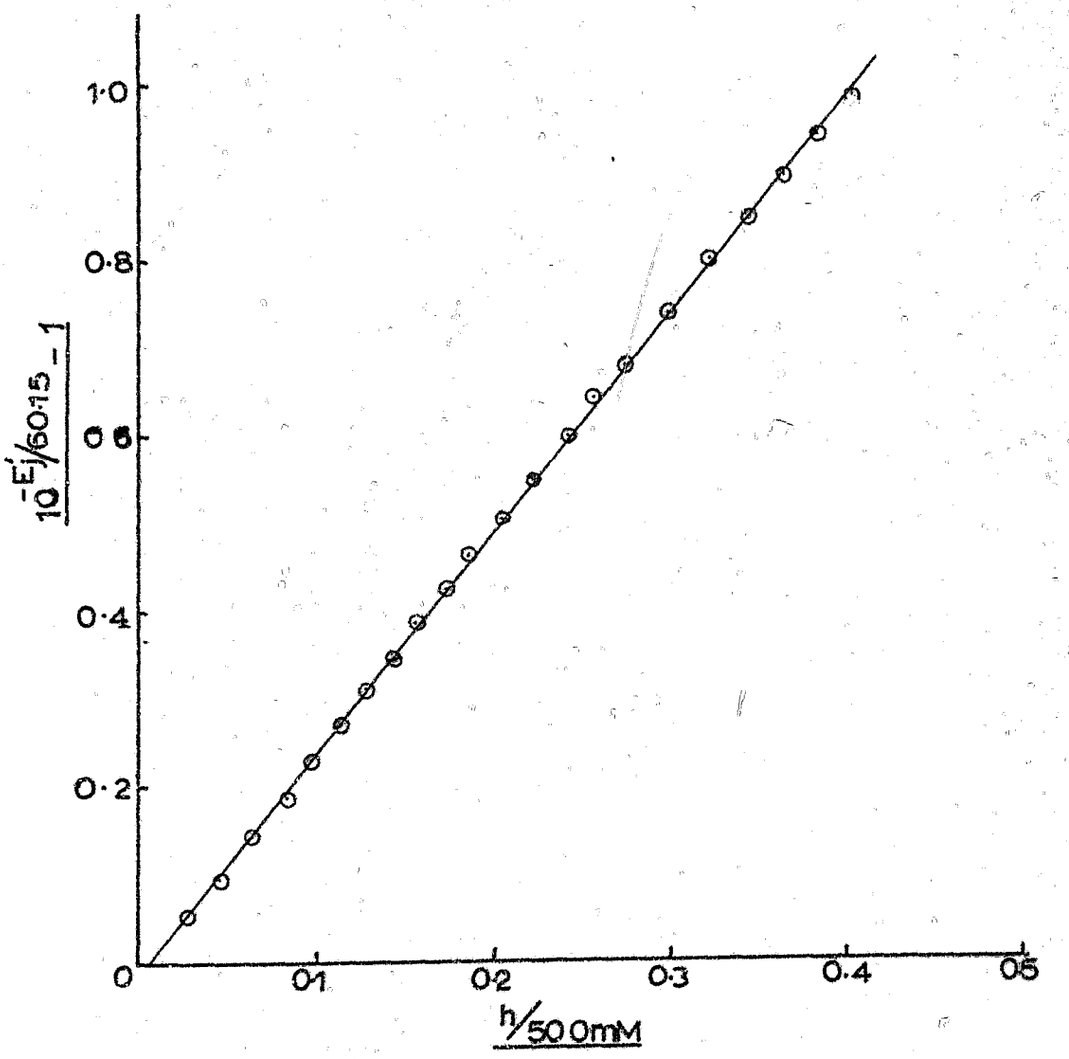
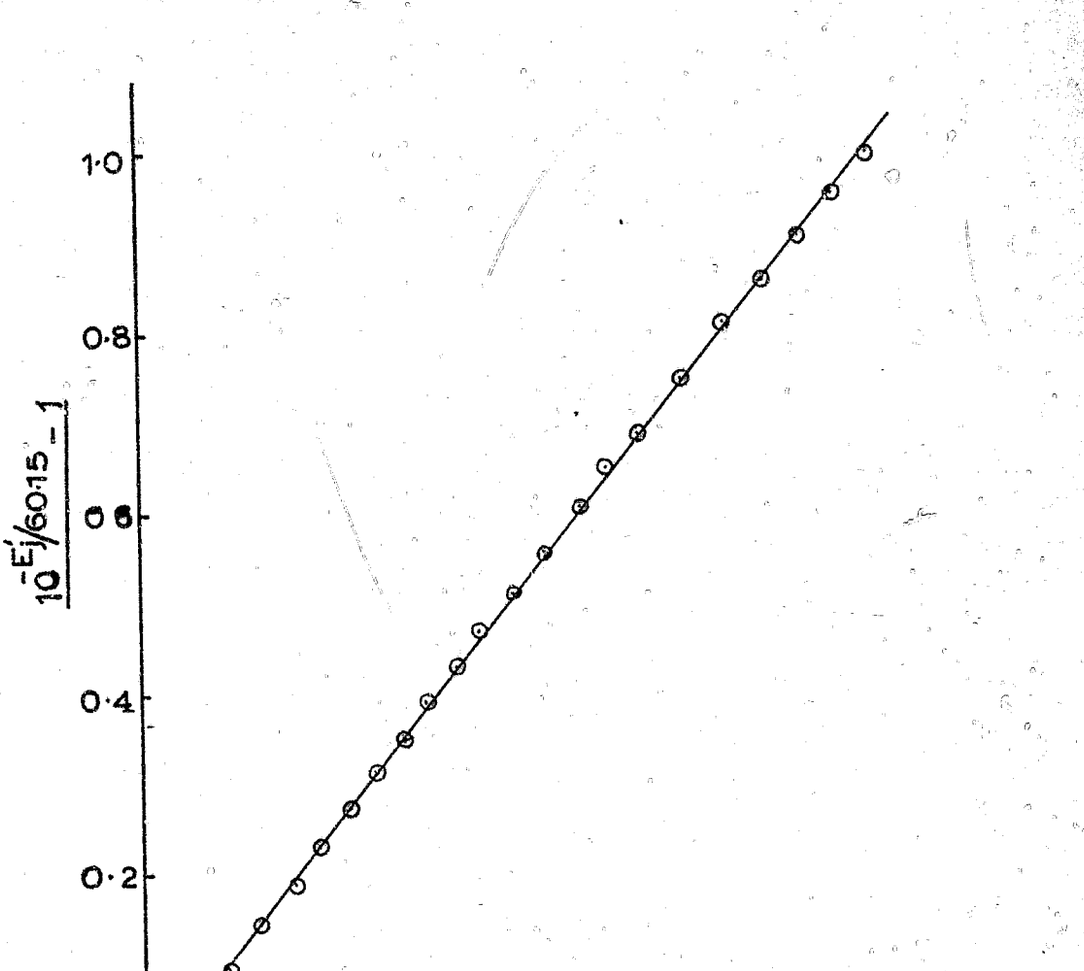


FIG. 5(b)

Mercury Redox Electrode

(Table 4)

d=2·52



At low hydrogen ion concentrations (ie. h 10mM) equation (3) can be rewritten in the form

$$E_j' = - \frac{RT}{2.303F} \frac{dh}{C} \text{ mV}$$

which reduces to

$$E_j' = - \frac{60.15\ d}{2.303 \times 500} h \text{ mV} \qquad \ldots\ldots\ldots\ldots (6)$$

7. Discussion.

The erratic results obtained using the type I salt bridge was attributed to several factors. The level of the test solution was not constant and consequently syphoning took place through the sodium perchlorate bridge. The direction and rate of this flow depended on the relative levels of the test solution and the sodium perchlorate pool.

The sodium chloride in the agar bridge diffused into the sodium perchlorate pool, and was transferred by the syphoning process and by diffusion to the asbestos plugs, where it precipitated the metal ion causing a large increase in the liquid junction potential.

The asbestos plugs also deteriorated with use, and hence the bridge was not suitable for a series of determinations.

Although / .....

Although this bridge would be satisfactory for general work involving liquid junction potentials, it cannot be used for accurate work involving potential changes of the order of a few hundredths of a millivolt. This bridge was therefore not used in the subsequent determinations of the hydrolysis constants.

The type II salt bridge was found to behave very satisfactorily after a few modifications were made (cf. page 27).

The average values of d obtained for the three systems studied (Table 1) were silver 2.43, mercury (I) 2.53 and the mercury (I) - mercury (II) couple 2.53. These values were obtained with a precision of less than one percent. The overall value for d was 2.48 ± 0.07. Biedermann and Sillen[4] found an overall value of $d = 1.95 \pm 0.08$. They made no distinction between the individual systems studied, but do, however, state that the value of d, and thus the liquid junction potential, is independant of the metal ion present.

The values obtained for d in the present work lie within the same experimental range as the values obtained by Biedermann and Sillen, viz. 4 percent.

Although / .....

Although the values of d obtained for the individual systems would indicate that d is dependant on the metal ion employed, the difference obtained between the silver system and mercury systems could possibly be attributed to the differences in the activity coefficients of the ions. Biedermann[2] has found evidence in support of this theory.

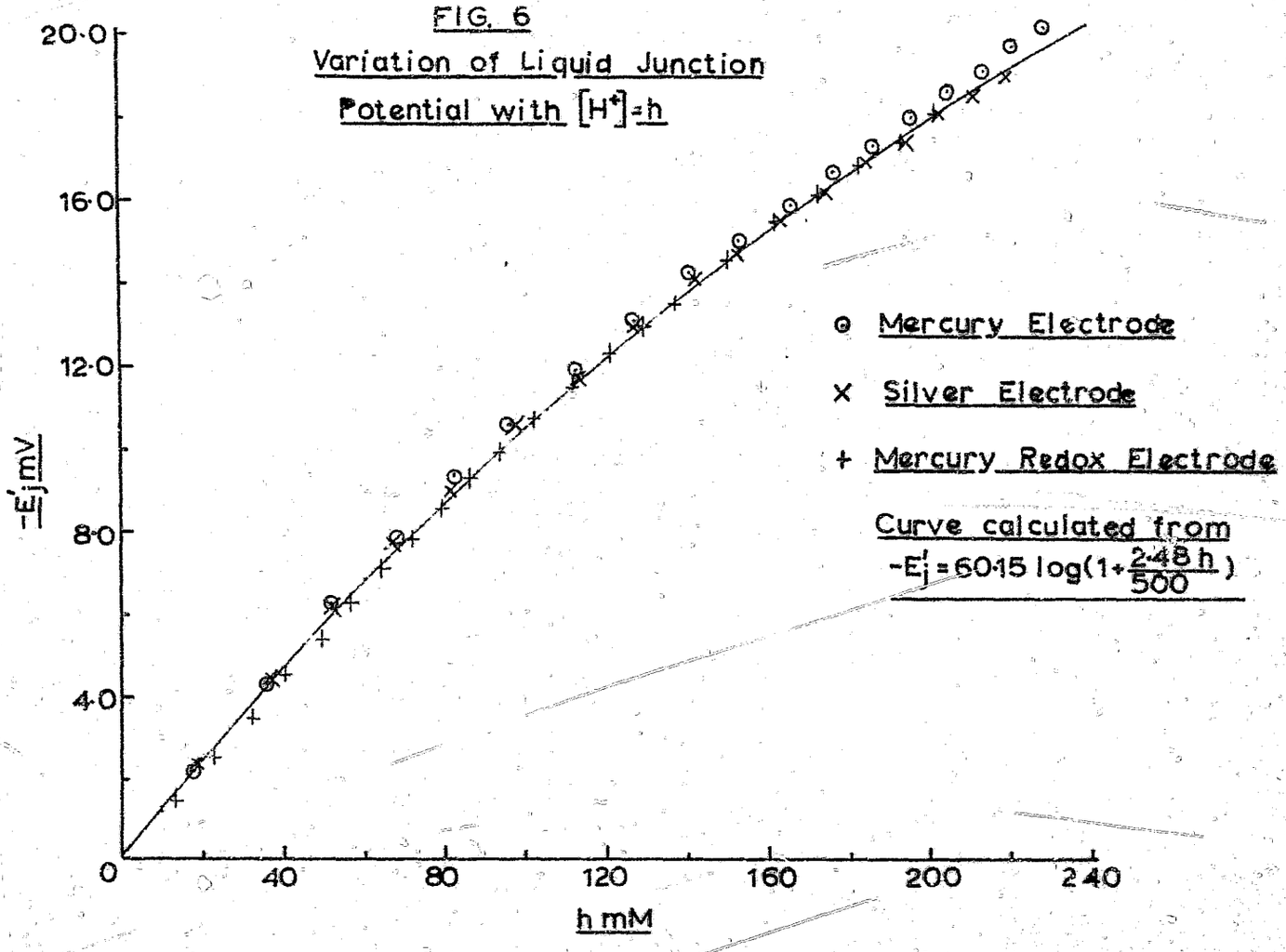
Figure 6 shows the variation of the liquid junction potential with the hydrogen ion concentration. The values for the mercury (I) - mercury (II) couple are lower than for silver and mercury (I). This could be attributed to a slight inaccuracy in the determination of E_o (Figure 5a). Nevertheless these points do follow a pattern similar to those of the mercury (I) system. The points lie very close to each other at the lower acidities but tend to spread at higher acidities. This could be accounted for on the basis of changing activity coefficients.

The inaccuracy in the assumption that $E_j' = E_j$ is also evident from Figures 3b, 4b and 5b. The points plotted fall on a slight curve. However a straight line can be drawn through these points with good approximation. The effect of the activity coefficients is thus very small and equation (5) can be employed with good accuracy.

Biedermann / .....

FIG. 6

Variation of Liquid Junction Potential with $[H^+]=h$



Biedermann and Sillen determined d at 25.0°C using solutions with ionic strengths of 3000 mM. A few determinations were done at 500 mM and 1000 mM. The hydrogen ion concentrations were varied between 0 and 600 mM, 0 and 50 mM and 0 and 100 mM for the above ionic strengths respectively. All these concentrations gave the same value for d viz. 1.95 ± 0.08.

The present work was carried out at 30.0°C with an ionic strength of 500 mM. The hydrogen ion concentration range was 0 to 220 mM. The value obtained for d, viz. 2.48 ± 0.07, was almost 25 percent higher than the value obtained by Biedermann and Sillen.

According to the definition of d viz.

$$d = \frac{\Lambda_{HClO_4} - \Lambda_{NaClO_4}}{\Lambda_{NaClO_4}}$$

it should be dependant only on the conductivities of the electrolytes on either side of the junction. Thus only those factors which influence the conductivity of an electrolyte would be expected to affect d. Two such factors are the temperature and the ionic strength of the solution.

Biedermann and / .....

Biedermann and Sillen found d to be independant of the ionic strength. The value obtained for d ie. 1.95 was considerably lower than the value d = 3.3, calculated from the conductivities of the pure components in a 3000 mM solution. Ekedahl and Sillen[11] attributed this to a general leveling of the ionic mobilities in electrolyte mixtures. If this were so it would be expected that the leveling of the ionic mobilities would not be as pronounced in solutions of lower ionic strength ie. d would be greater in a 500 mM perchlorate solution than in a 3000 mM solution.

Although the ionic conductances of all electrolytes increase with increased temperature, this effect is less noticeable with the more mobile ions[19b], and consequently, at higher temperatures one would expect a decrease in the value of d. For two different temperature conditions the difference in the values d_1 and d_2, viz. Δd, is given by

$$\Delta d = \frac{\Delta\lambda_{H^+} - \Delta\lambda_{ClO_4^-}}{\Delta\lambda_{Na^+} + \Delta\lambda_{ClO_4^-}}$$

where the $\Delta\lambda$ terms represent the increase in each of the ionic conductances. As $\Delta\lambda_{H^+}$ is smaller than $\Delta\lambda_{Na^+}$ and $\Delta\lambda_{ClO_4^-}$, Δd is

consequently / .....

consequently negative. However, the value, d = 1.95, obtained by Biedermann and Sillen at 25.0°C was smaller than the value, d = 2.48, obtained in this work at 30.0°C. To explain the difference between these values, it must be assumed that d is dependant on the physical structure of the junction, and also on the ionic strength of the solution[27a]. Thus d must be a function of the temperature, the physical nature of the junction, and the ionic strength of the medium, in addition to the ionic mobilities of the ions involved.

B. Hydrolysis of Mercury (I).

1. Procedure.

The procedure adopted for the determination of the hydrolysis constant for mercury (I) was the same as that described by Forsling, Hietanen and Sillen[13]. This method, the "titration method", makes use of the cells

$$Hg, Hg_2Cl_2 \; ; \; 4\ M NaCl \;/\; 500\ mM NaClO_4 \;/\; Hg_2^{2+}, H^+ \;/\; \begin{matrix} \text{Glass} \\ \text{Electrode;} \\ Hg(l) \end{matrix}$$

to measure the concentrations of mercury (I) and hydrogen ions.

The results in the present work were based on six titrations. Each titration required three solutions, S_1, S_2 and S_3, which were prepared by the dilution of the stock solutions described previously. The concentrations of these solutions are given in Table 5. Each solution was 500 mM in perchlorate. The total perchlorate in each of the solutions, and the hydrogen ion concentration in solution S_3, were determined as described before. The concentrations of the hydroxyl ions in S_2 and the hydrogen ions in S_3 were determined with potassium hydrogen phthalate and standard sodium hydroxide solution respectively.

As the / .....

As the concentration of mercury (I) in the dilute solutions could not be determined with accuracy, the concentration was assumed to be that obtained by dilution of the stock solution. The concentration of the mercury need not be known accurately.

The titrations were, at first, carried out in two parts. The first part was an acid-base titration involving solutions S_1 and S_2. No mercury was present in the reaction vessel. From this titration a relationship was obtained between the potential of the calomel electrode - glass electrode cell and the logarithm of the hydrogen ion concentration. This relation was used to obtain the hydrogen ion concentration of the test solution in the second part of the titration. In the second part, solution S_3 was added to the solution in the reaction vessel and metallic mercury introduced. The potentials of the calomel electrode - glass electrode and calomel electrode - mercury electrode were determined after equilibrium had been attained.

Additions of S_2 and S_3 were then made in such a manner that the ratio S_3/S_2 was the same as the initial ratio, $S_3/(S_1 + S_2)$. Thus the total mercury concentration was kept

constant / .....

constant throughout the titration.

The glass electrode was found to be insensitive to the small changes in the hydrogen ion concentration experienced in the hydrolysis of mercury (I). It was therefore not used in subsequent titrations. The analytical hydrogen ion concentration was employed together with the rather accurate potentials obtained with the mercury electrode.

The initial acid-base titration was therefore not carried out. At the start of the titration, solutions S_1 and S_2 were placed together with S_3 in the reaction vessel. Metallic mercury was then added and titration carried out as above.

Table 5 gives details of the concentrations and volumes of each solution used. Table 6 gives detailed data for titration 5. The first column in Table 6, viz: x mls, gives the volumes of S_3 added. For each volume of S_3 an equal volume of S_2 was added. The addition was stopped when a permanent precipitate formed.

The titrations were carried out at 30.0° using the reaction vessel shown in Figure 1. Nitrogen, purified

as in / .....

Table 5.

Survey of Titrations.

Titr. No.	S_1	S_2	S_3		mls. added			Symbol Fig. 7
	H^+ mM	OH^- mM	Hg_2^{2+} mM	H^+ mM	S_1	S_2	S_3	
1	40.00	39.70	4.0	9.90	25.0	23.0	48.0	0
2	40.00	39.70	4.0	9.90	25.0	23.0	48.0	Δ
3	40.00	39.70	2.0	9.88	25.0	23.0	48.0	Ø
4	40.00	39.70	2.0	9.88	25.5	24.0	49.5	Ø
5	40.00	39.70	1.0	9.91	25.0	23.0	48.0	x
6	40.00	39.70	1.0	9.91	25.5	24.5	50.0	+

Table 6.

Detailed Data For Titration 5.

x mls	E mV	h mM	log h	δ E mV	$k \times 10^{-5}$ M
0	424.98	5.86	0.7679		
2.00	425.08	5.03	0.7016		
4.00	425.19	4.26	0.6294		
6.00	425.27	3.55	0.5502		
7.03	425.32	3.21	0.5065	0	
8.00	425.36	2.89	0.4609	0	0.20
9.00	425.39	2.58	0.4116	0.01	0.90
10.00	425.41	2.28	0.3579	0.03	1.56
11.00	425.43	1.99	0.2989	0.05	1.61
12.00	425.46	1.71	0.2330	0.06	1.18
12.50	425.45	1.57	0.1959	0.09	1.55
13.00	425.44	1.44	0.1584	0.11	1.77
13.50	425.45	1.30	0.1139	0.12	1.52
14.00	425.44	1.17	0.0682	0.15	1.55
14.50	425.42	1.05	0.0212	0.19	1.63
15.00	425.39	0.918	-0.0372	0.23	1.67
15.50	425.36	0.794	-0.1002	0.28	1.56
16.00	425.29	0.671	-0.1733	0.37	1.61
16.50	425.17	0.551	-0.2588	0.50	1.68
17.00	425.03	0.432	-0.3645	0.66	1.47
17.50	424.69	0.315	-0.5017	1.01	1.38

as in the previous experiments, was passed through the test solutions.

2. Calculations and Results.

The calculations given by Forsling, Hietanen and Sillen were used.

Mercury (I) solutions prepared from the mercury (II) solution by equilibration with metallic mercury always contains slight amounts of the mercury (II) salt.

The equilibrium reaction

$$Hg^{2+} + Hg\ (l) \rightleftarrows Hg_2^{2+}$$

has an equilibrium constant

$$k_o = [Hg_2^{2+}][Hg^{2+}]^{-1} = 132.4 \pm 1 \text{ (ref 13)} \quad (7).$$

Although this equilibrium constant is large ie. the concentration of mercury (II) is small, there will be sufficient mercury (II), which is fairly strongly acidic[17], in the solution to affect the determination of the hydrolysis of the mercury (I).

It is / .....

It is therefore necessary to take into account the acidity due to the mercury (II) present.

The hydrolysis of mercury (II) is given by Hietanen and Sillen [19] as

$$Hg^{2+} + H_2O \rightleftarrows HgOH^+ + H^+ \quad q_1 = [HgOH^+]\, h\, [Hg^{2+}]^{-1} = 0.20 \text{ mM} \quad (8)$$

$$Hg^{2+} + 2H_2O \rightleftarrows Hg(OH)_2 + 2H^+ \quad q_2 = [Hg(OH)_2]\, h^2\, [Hg^{2+}]^{-1} = 0.50 \text{ mM} \quad (9)$$

Since the hydrolysis of mercury (I) is small the only product can be assumed to be Hg_2OH^+ ie.

$$Hg_2^{2+} + H_2O \rightleftarrows Hg_2OH^+ + H^+ \quad k = [Hg_2OH^+]\, h\, [Hg_2^{2+}]^{-1} \quad (10)$$

Assuming that the total mercury concentration is y, then

$$y = [Hg_2^{2+}] + [Hg_2OH^+] + [Hg^{2+}] + [HgOH^+] + [Hg(OH)_2]$$

Substituting equations (8), (9) and (10) in this equation, we get

$$y = [Hg_2^{2+}] + [Hg^{2+}] + kh^{-1}\,[Hg_2^{2+}] + q_1h^{-1}\,[Hg^{2+}] + q_2h^{-2}\,[Hg^{2+}]$$

$$= [Hg_2^{2+}] + kh^{-1}[Hg_2^{2+}] + k_o^{-1}\,[Hg_2^{2+}] + q_1h^{-1}k_o^{-1}[Hg_2^{2+}] + q_2h^{-2}k_o^{-1}[Hg_2^{2+}]$$

$$= [Hg_2^{2+}]\,(1 + kh^{-1} + k_o^{-1}\,(1 + q_1h^{-1} + q_2h^{-2}))$$

$$= [Hg_2^{2+}] \,/\, \ldots\ldots$$

$$= [Hg_2^{2+}] (1 + \psi) \qquad (11)$$

where $\psi = kh^{-1} + k_o^{-1} (1 + q_1 h^{-1} + q_2 h^{-2})$

For the cell

(-) C.E. / $NaClO_4$ / Hg_2^{2+}, H^+ / Hg (+)

we have the equation

$$E = E_o + E_j + \frac{RT}{2F} \ln [Hg_2^{2+}] \qquad (12)$$

From equations (11) and (12) at 30.0°C

$$E = E_o + E_j + 30.08 \log y - 30.08 \log (1+\psi) \qquad (13)$$

By substituting the value d = 2.53 obtained in the previous section we have from equation (6) (page 34)

$$E_j = -0.1321\ h$$

Substituting this value in equation (13)

$$E = E_o - 0.1321h + 30.08 \log y - 30.08 \log (1 + \psi) \qquad (14)$$

An arbitrary value for h is taken (say $h' = 3.21$) where the hydrolysis of mercury (I) is negligible. This value, ie. $h' = 3.21$, and the corresponding values E' and ψ' are then substituted in equation (14) giving

$E' =$ / .....

$$E' = E_o - 0.1321\ h' + 30.08 \log y - 30.08 \log (1 + \psi') \qquad (15)$$

Equation (14) is now subtracted from equation (15)

$$E' - E = 0.1321\ (h - h') + 30.08 \log \frac{1 + \psi}{1 + \psi'} \qquad (16)$$

ie.

$$E' - E + 0.1321\ (h' - h) = 30.08 \log \frac{1 + \psi}{1 + \psi'} = \delta E \qquad (17)$$

$$\delta E = E' - E + 0.1321\ (h' - h) \qquad (17a)$$

$$\delta E = 30.08 \log \frac{1 + \psi}{1 + \psi'} \qquad (17b)$$

δE is obtained from equation (17a) for each value of h and the corresponding potential. E' is the potential obtained for the cell when $h' = 3.21$. Table 6 shows the values of δE for titration 5 (cf. Table 5).

In Figure 7 the values obtained for δE are plotted against log h for each titration. The curves were calculated from equation (17b) using different values for k. The heavy dots are those values quoted by Forsling, Hietanen and Sillen (ref. 13, Table 2b).

The acidity / .....

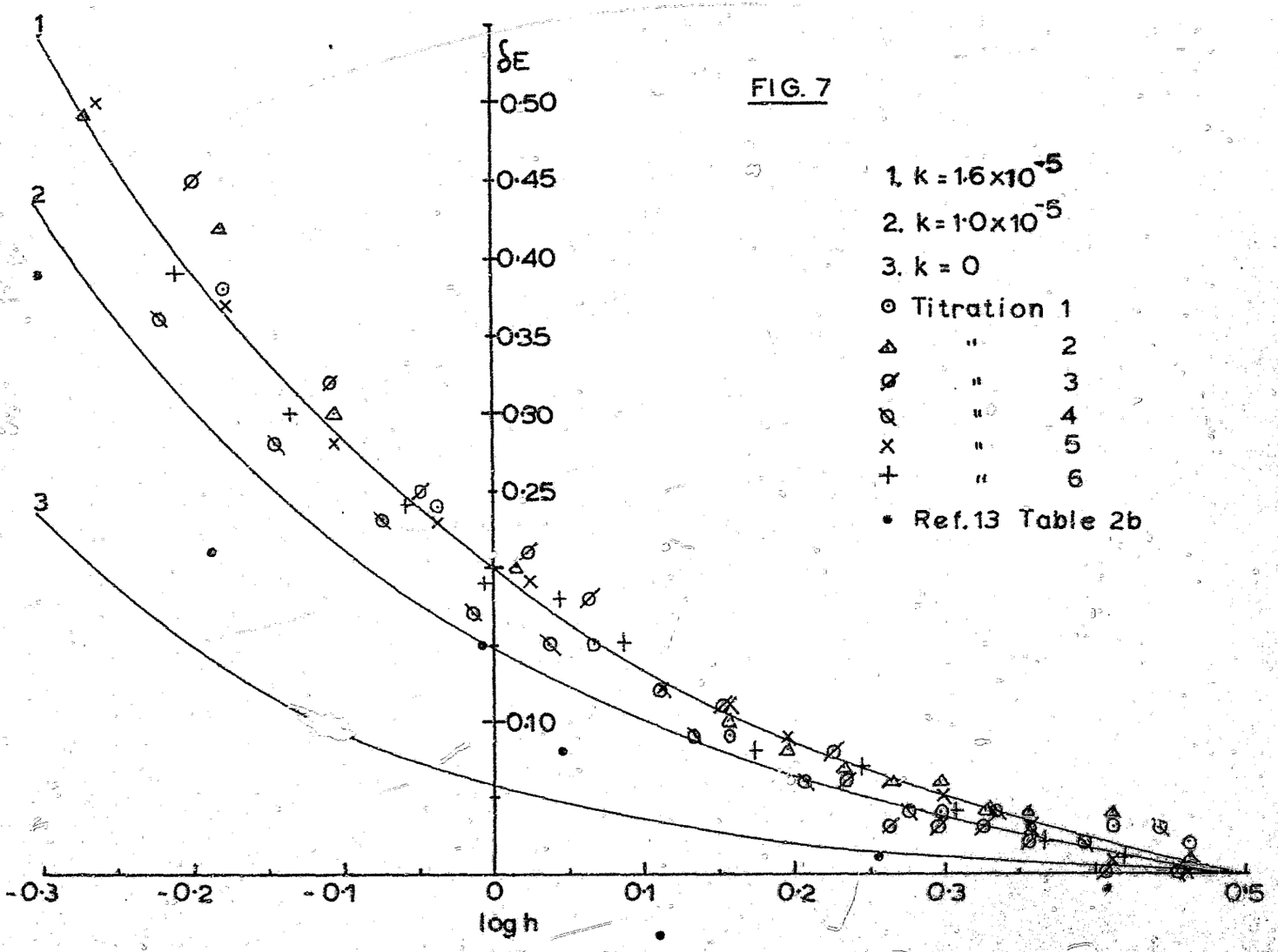

δE
0·50
0·45
0·40
0·35
0·30
0·25
0·10
1
2
3
-0·3
-0·2
-0·1
0
0·1
0·2
0·3
0·5
log h
1. k = 1·6 x 10⁻⁵
2. k = 1·0 x 10⁻⁵
3. k = 0
⊙ Titration 1
△ " 2
ø " 3
⊗ " 4
× " 5
+ " 6
• Ref. 13 Table 2b

FIG. 7

The acidity constant, k, for mercury (I) can be calculated for each individual reading by rearranging equation (15). These values are shown in Table 6 for titration 5.

3. Discussion.

As pointed out by Forsling, Hietanen and Sillen[13] previous investigators failed to take into account the effect of the acidity of mercury (II) when determining the hydrolysis of mercury (I). Thus the values quoted for mercury (I) are often high. In Figure 7 the effect of the hydrolysis of mercury (II) is shown by curve 3 ie. when no hydrolysis of mercury (I) occurs ($k = 0$).

As can be seen from Figure 7 the values of δE, plotted against log h, are grouped around the curve calculated for $k = 1.6 \times 10^{-5}$.

Although good agreement is obtained between the values of k calculated from equation (15) for the individual readings of each titration (cf. Table 6), the correlation between successive titrations is fairly poor.

This lack / .....

This lack of correlation could be attributed to the inaccuracy in attaining the reference hydrogen ion concentration exactly equal to 3.21 mM and the corresponding inaccuracy in the reference potential of the cell. The low values obtained for titration 4 could be attributed to these effects.

The hydrolysis constant cannot be determined with very great precision by this method as the effect of the hydrogen ions, liberated by hydrolysis is not taken into account.

The hydrolysis effect at the higher hydrogen ion concentrations is small and consequently no reliance can be placed on the values for δE when the hydrogen ion concentration is greater than 1.50 mM.

Better agreement is obtained between the individual results of each titration than was obtained by Forsling, Hietanen and Sillen. Figure 7 shows the relation between their results (dark dots) and the present work. A better overall correlation was achieved between the values of k of successive titrations than was indicated by Forsling, Hietanen and Sillen, who obtained $k = 10^{-5 \pm 0.3}$, whereas the value in the present work was $10^{-5.12 \pm 0.12}$. The better correlation in this

work can / .....

work can be attributed to the more precise evaluation of the liquid junction potential.

The higher value for the acidity constant in this work is probably due to the higher temperature used.

C. Hydrolysis of Silver.

1. Procedure.

The titration method of Sillen was used in an attempt to measure the hydrolysis of silver ions.

The concentrations of the solutions used are given in Table 7. These solutions were prepared from stock solutions and analysed as before.

As the changes in the hydrogen ion concentration were found to be less than those experienced with mercury (I), the glass electrode could not be used. The titration was therefore carried out as in the previous section using the cell

(-) C.E. / $NaClO_4$ / Ag^+, H^+ / Ag (+)

The equation for this cell at 30.0°C is

$$E = E_o + E_j + 60.15 \log [Ag^+]$$

The silver electrode was of the same type as those used to determine the liquid junction potential in section A. The electrode proved to be very accurate and reliable.

Approximately / .....

Approximately ten minutes were allowed to lapse between additions of reagents before the potential was determined to allow the test solution to attain equilibrium.

2. Results.

From equation (6) (page 34)

$$E_j = -\frac{60.15}{2.303} dh$$

$$= -0.1269\ h$$

where d = 2.43 obtained previously.

The cell equation

$$E = E_o + E_j + 60.15 \log [Ag^+]$$

can be rearranged to

$$E + 0.1269\ h = E_o + 60.15 \log [Ag^+]$$

Table 7 shows the value of the potential after correcting for the liquid junction potential. The last two figures in the alkaline region, could not be adjusted as the dependance of the liquid junction potential on the hydroxyl ion concentration was not known.

As can / .....

Table 7.

Composition of Solutions.

S_1 500 mMClO^-_4, 40.00 mMH^+ (25.0 mls)

S_2 500 mMClO^-_4 39.32 mMOH^- (23.5 mls)

S_3 500 mMClO^-_4 10.00 mMH^+ , 5.03 mMAg^+

x mls	$[H^+]$= hmM	E mV	$(E-E_j')$mV
0	5.28	370.23	370.90
2.0	4.45	370.34	370.90
4.0	3.68	370.45	370.92
6.0	2.96	370.55	370.93
8.0	2.30	370.62	370.91
10.0	1.69	370.69	370.90
11.0	1.39	370.73	370.91
12.0	1.11	370.76	370.90
13.0	0.84	370.79	370.90
14.0	0.57	370.84	370.91
15.0	0.31	370.89	370.92
15.5	0.19	370.89	370.91
16.0	0.065	370.89	370.90
16.2	0.017	370.89	370.89
16.4	0.032 mMOH^-	370.89	-
16.6	0.129 mMOH^-	370.80	-

As can be seen the adjusted values for the cell potentials remain constant until the alkaline region is reached. Precipitation starts at this point. There thus appears to be no indication of hydrolysis of silver.

Assuming that maximum solubility of the precipitate occurs at 0.032 mM in OH^- ie. just before the potential of the cell changes rapidly, the solubility product can be evaluated. Thus

$$S_o = [Ag^+][OH^-]$$
$$= 0.0025 \times 0.032 \times 10^{-3}$$
$$= 8 \times 10^{-8}$$

ie. $pK_{S_o} = -7.10$

This value agrees closely with those quoted in the literature[5].

pK_{S_o} obtained from other titrations ranged between 6.8 and 7.2.

3. Discussion.

Sillen's method for the determination of hydrolysis constants is not sufficiently sensitive for the determination of / .....

determination of the hydrolysis of silver ions. The effect is very small, and has been investigated by a few workers using rather indirect methods. The values obtained show very poor agreement The present investigation is inconclusive, and no conclusions can be drawn regarding the existence of the Ag_2OH^+ ion as claimed by Johnstone, Cuta and Garrett[21] amongst others.

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