THE DETERMINATION OF THE SOLUBILITY OF MERCUROUS CHLORIDE AT 25°C.

A Thesis Submitted In Part-Fulfilment Of The Requirements Of Rhodes University For The Degree of Master of Science.

By

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CONTENTS.

1. ABBREVIATIONS, SYMBOLS AND UNITS.

The following are used throughout the text.

nm/cm.	-	nanamho per centimeter = 10^{-9} /ohm cm
a	-	activity
c	-	molar concentration
m	-	molal concentration
D	-	demal concentration
do	-	density of water
E	-	electromotive force of cell in absolute volts
E^o	-	Standard electromotive force
Ej	-	liquid junction potential
F	-	Fareday
f	-	frequency
K	-	thermodynamic equilibrium constant
Kw	-	Ionic Product of water
R	-	Gas Constant
	-	or, Resistance in ohms
S	-	solubility
T	-	absolute temperature
^oC	-	degrees centigrade
Q	-	cell constant
Zi	-	valence of ionic species i
γi	-	molal ionic activity coefficient of ionic species i
$\gamma_\pm$	-	molal mean activity coefficient
$\kappa_{cal.}$	-	specific conductance of a saturated calomel solution
κ_{H_2O}	-	specific conductance of water
Λ	-	equivalent conductance of electrolyte
λ	-	equivalent ionic conductance
μ	-	ionic strength

2. INTRODUCTION.

After the publication of the paper by Gledhill and Malan (1) in which precision conductance techniques were used for the first time in the determination of the solubility of silver chloride, Dr. N.H. Parton of Christchurch College, New Zealand, wrote to Gledhill and suggested that the same methods might be rewarding if applied to the determination of the solubility of mercurous chloride.

A review of the Chemical literature showed that the values for the solubility of mercurous chloride were not at all consistent.

From the electrometric titration of potassium chloride solution with a mercurous nitrate solution Behrend (2) in 1893 calculated the solubility of calomel to be 2.1×10^{-4} gm/litre at 18°C. In 1903 Sherril (3) gave the solubility of calomel as 4.7×10^{-4} gm/litre at 25°C. Ley and Heimbucher (4) measured the e.m.f.'s of two cells which consisted of the combination of 0.1N mercurous perchlorate solutions with a 0.1 N and a 1.0 N calomel electrode respectively. From their results they calculated the solubility of mercurous chloride to be 3.8×10^{-4} gm/litre at 20°C. In 1904 Sauer (5), as a result of his work on the e.m.f.'s. of calomel electrodes, found that mercurous chloride was 10% more soluble when finely divided than when coarsely crystalline. Kohlraush (6) found the specific conductance of an aqueous solution of mercurous chloride to be 2,130 nm/cm. at 24.6°C. (1 nm/cm. = 1×10^{-9} /ohm.

cm.) From this he calculated the solubility of the salt to be 2.8×10^{-3} gm/litre at the above temperature.

The values found in the literature for the Solubility Product (Ks) of mercurous chloride are just as discordant. From figures given by Ley and Heimbucher (4) for the concentrations of Hg_2^{2+} ions in KCl solutions at 20°C, Ks is found to be equal to 2×10^{-18} and 3.5×10^{-18} at ionic strengths (μ) 0.1 and 1.0 respectively. According to Kohlrausch (6) the solubility product is 8.4×10^{-16} at 24.6°C, as deduced from his conductometric measurements. Brodsky (7), from e.m.f. measurements on mercurous nitrate solutions calculated Ks to be 1.15×10^{-18} at 25°C. Determined by the Owen Cell (8) method Christensen (9) found Ks to be 5.3×10^{-18} at 25°C. Under the experimental conditions of 25°C, H^+ ion concentration (c_{H^+}) = 0.01 molar and ionic strength 0.5, Sillén, Jonsson and Qvarfort (10) determined Ks to be 1.32×10^{-17}.

When mercurous chloride goes into solution we have, as a result of dissociation, hydrolysis and complex-ion formation, the following equilibria existing:-

(1) $Hg_2Cl_{2\,(s)} = Hg_2^{2+} + 2Cl^-$

(2) $Hg^{2+} + Hg_{(s)} = Hg_2^{2+}$

(3) $Hg^{2+} + Cl^- = HgCl^+$

(4) $Hg^{2+} + 2Cl^- = HgCl_2$

(5) $Hg^{2+} + 3Cl^{-} = HgCl_3^{-}$

(6) $Hg^{2+} + 4Cl^{-} = HgCl_4^{=}$

(7) $Hg_2^{2+} + H_2O = Hg_2OH^{+} + H^{+}$

(8) $Hg^{2+} + H_2O = HgOH^{+} + H^{+}$

(9) $Hg^{2+} + 2H_2O = Hg(OH)_2 + 2H^{+}$

Since the hydrolysis of the Hg_2^{2+} ion is a small effect it is assumed that the only product is Hg_2OH^{+} . (11). A saturated calomel solution hence contains nine different ionic species, two undissociated mercuric compounds and possibly mercury as well.

From electrometric measurements Sillén and his co-workers (12) determined the equilibrium constants of the nine above mentioned equilibria. These constants were, however, only valid under the special conditions of their experiments, namely, 25°C and ionic strength 0.5.

The object of the present work was to endeavour to determine the various ionic and molecular concentrations present in a saturated calomel solution at 25°C and so determine the solubility of calomel in conductance water. The analysis of the saturated calomel solution at 25°C was carried out in three independent stages; (a) determination of the specific conductance, which was a measure of the ionic concentration of the solution; (b) measurement of the pH which gave an indica-

tion of the extent of hydrolysis; and finally, (c) the determination of the total concentration of mercury salts in solution. It was thought that the combination of the above three experimental results with Sillén's equilibrium constants, corrected to infinite dilution, would lead to the solution of the problem.

3. SPECIFIC CONDUCTANCE OF A SATURATED SOLUTION OF MERCUROUS CHLORIDE AT 25°C.

3.1 OUTLINE AND THEORY OF METHOD.

The classical method of determining the solubility (S) of sparingly soluble salts by conductometric methods is by using the equation

$$S = \frac{1000 \times \kappa}{\Lambda_s} \quad \ldots\ldots\ldots (1)$$

where κ is the specific conductance of the saturated solution and Λ_s is the equivalent conductance of the salt at concentration S. Due to the presence of ions other than Hg_2^{2+} and Cl^- ions in the solution as the result of hydrolysis and complex ion formation the above equation (1) is, however, not applicable in the case of mercurous chloride.

The accurate determination of the specific conductance of a saturated calomel solution was nevertheless an excellent measure of the total number of ions present in the solution. We have:

$$\kappa_{cal.} = \frac{1}{1000}\left(C_{H^+}\lambda_{H^+} + C_{Cl^-}\lambda_{Cl^-} + C_{Hg_2^{2+}}\lambda_{Hg_2^{2+}} + C_{Hg^{2+}}\lambda_{Hg^{2+}} + C_{HgCl^+}\lambda_{HgCl^+} + C_{HgOH^+}\lambda_{HgOH^+} + C_{Hg_2OH^+}\lambda_{Hg_2OH^+} + C_{HgCl_3^-}\lambda_{HgCl_3^-} + C_{HgCl_4^=}\lambda_{HgCl_4^=}\right) \quad \ldots\ldots\ldots (2)$$

where c denotes molarity and λ equivalent ionic conductance.

The specific conductance of an electrolytic solution is calculated from the equation

$$\kappa = \frac{Q}{R} \qquad \ldots\ldots\ldots\ldots (3)$$

where Q is the cell constant and R is the resistance of the solution.

To obtain the conductance due to the electrolyte alone we must subtract from the above value of κ the specific conductance due to the solvent itself. Hence to be able to apply the solvent (water) correction, it was necessary to make a separate determination of the conductance of the water which was used to prepare the electrolytic solution. Theoretically the only ions present in pure conductance water are hydrogen and hydroxyl ions which result from the ionisation of water molecules

$$H_2O \quad = \quad H^+ \quad + \quad OH^-$$

$$Kw \quad = \quad a_{H^+} \cdot a_{OH^-} \quad = \quad 1.008 \times 10^{-14}$$

where Kw is the Ionic Product of water and a denotes activity. Assuming the activity coefficients of the H^+ and OH^- ions to be unity at these low concentrations

$$Kw \approx c_{H^+} \times c_{OH^-}$$

$$\therefore \quad c_{H^+} = c_{OH^-} = 1.004 \times 10^{-7} = c$$

also

$$\Lambda^{\circ}_{H_2O} = \lambda^{\circ}_{H^+} + \lambda^{\circ}_{OH}$$

$$= 548.2 \quad \text{at } 25^{\circ}C$$

where $\Lambda^{\circ}_{H_2O}$ is the limiting equivalent conductance of water. With these values μ can be calculated from

$$\mu = \frac{\Lambda^{\circ}_{H_2O} \times c \times d_o}{1000} \quad \ldots\ldots\ldots (4)$$

where d_o is the density of water at 25°C. On substituting the values of Λ_{H_2O}, c and d_o we obtain

$$\mu_{H_2O} = 55 \text{ nm/cm.}$$

where 1 nm/cm.= 1×10^{-9} /ohm.cm. In practice, however, the above value for μ_{H_2O} is as yet unattainable. μ_{H_2O} for the conductance water used in this work varied from 65 to 85 nm/cm. Hence 10 to 30 nm/cm. of the conductance was attribu-

ted to impurities other than H^+ and OH^- ions. (13).

Consider now a saturated calomel solution at 25°C which is of pH 5.125 (Sec Section 4.41). At this hydrogen ion concentration the ionisation of water is depressed and hence κ_{H_2O} is diminished.

$$pH = 5.125 \qquad C_{H^+} = 7.5 \times 10^{-6} \text{ mole/litre.}$$

$$C_{OH^-} = \frac{KW}{C_{H^+}}$$

$$= 1.3 \times 10^{-9} \text{ mole/litre.}$$

i.e. 1.3×10^{-9} gram equivalents of water per litre ionise.

$$\kappa_{H_2O} = \frac{\Lambda^0_{H_2O} \times c \times d_o}{1000} \qquad \ldots\ldots\ldots (4)$$

$$= 0.7 \text{ nm/cm.}$$

$$\approx 1 \text{ nm/cm.}$$

i.e. κ_{H_2O} has decreased by 54 nm/cm. Therefore when using water of say κ = 75 nm/cm. in the determination of the conductance of a saturated calomel solution, the solvent correction is not 75 but 75 - 54, i.e. 21 nm/cm. It was

assumed that the remaining impurities in the water were unaffected by the calomel.

3.2. DESCRIPTION STANDARDISATION AND CALIBRATION OF APPARATUS.

3.21 TEMPERATURE CONTROL APPARATUS

All apparatus used in the conductance determinations was housed in a constant temperature room which was maintained at 24 ± 0.1°C. A relay controlled the room heaters and when the external temperature exceeded 24°C (i.e. during the summer months) refigeration was used to keep the temperature down.

The paraffin oil thermostat in which the conductance cells were suspended, was surrounded by a water thermostat which was maintained at 25 ± 0.01°C. A thermometer, calibrated by the National Physical Laboratory, Pretoria, was used to measure the thermostat temperature.

3.22 BRIDGE.

The conductance bridge used in this work was built on the lines suggested by Luder (14) but the components were mounted so that all the controls were brought out on one front panel. As the accuracy of the determination of the specific conductance of a saturated calomel solution was found to be approximately 0.2% it was not necessary to recalibrate the

bridge resistances, as they were General Radio decade resistances, which are guaranteed to an accuracy of 0.1%.

When the bridge is balanced we have

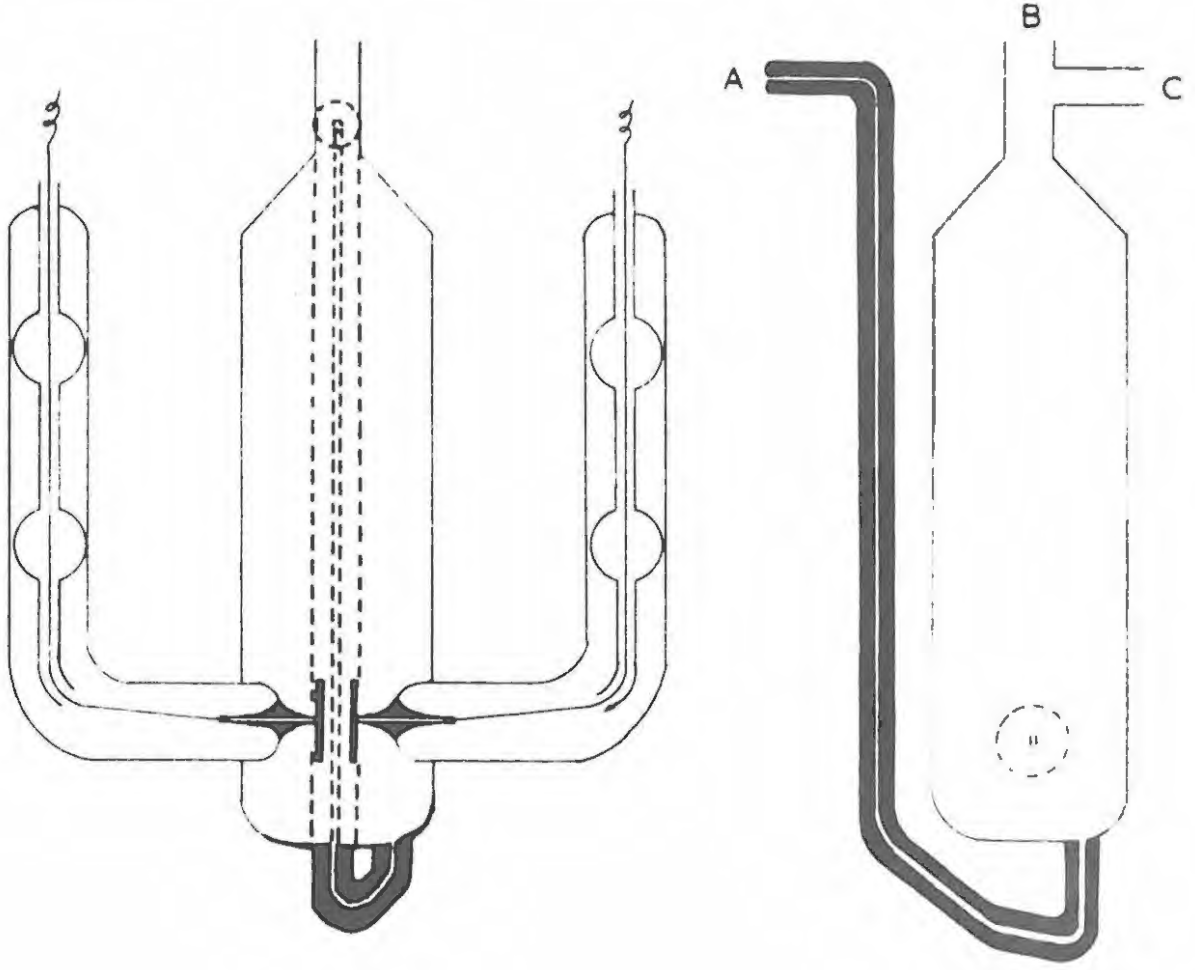
$$R_4 = R_3 - p^2C^2R_3^3 \quad \ldots\ldots\ldots\ldots\ldots (5)$$

where R_4 is the resistance to be determined, R_3 the resistance as read off from the variable arm of the bridge and the term $p^2C^2R_3^3$ the capacitance, where $p = 2\pi f$, f being the frequency. The above equation is derived elsewhere (15). It was found in practice, however, that the correction $p^2C^2R_3^3$ was insignificant and it was hence ignored. The bridge was therefore direct reading, the unknown resistance being equal to the resistance of the variable arm.

The bridge was balanced with the ratio arms direct and then again with them reversed - the oscillator leads were then reversed and the procedure repeated. The arithmetic mean of the above four readings was taken as the correct resistance. (R_4).

As the solutions used in this work had high resistances, 3.2×10^4 to 1.4×10^6 ohms, the polarisation correction (16) was negligible and readings were therefore taken at one frequency only (1,000 cycles/sec). The resistances of the bridge and cell leads, being of the order 0.2 ohm, were also ignored.

FIG. 1. THE CONDUCTANCE CELL



3.23 CONDUCTANCE CELLS.

The Pyrex conductance cells used are of a type designed to minimise the Parker effect (17) and also to allow a stream of gas to be passed through, or over, the contents of the cell when it was suspended in the thermostat. A diagram of a cell is given in fig. 1. The gas enters the cell via the capillary A, bubbles through the solution contained in the body of the cell and escapes into the atmosphere through the neck B. If, at any stage of the experiment it is not desired to have gas bubbling through the cell contents, back diffusion of atmospheric carbon dioxide into the solution is prevented by passing the gas through C instead.

As a long time was required to leach out a cell after it had contained an electrolytic solution, two cells were employed in practice: one to measure the conductance of the water used in the experiments and the other for the determination of the conductance of saturated calomel solutions.

A fully detailed description of all the above apparatus is given by Gledhill (18) in his M.Sc. thesis.

3.24 CELL CONSTANT OF THE CALOMEL CONDUCTANCE CELL.

A solution which contained 0.74563 gram KCl (purified as described in section 3.32) per 1000 gram solution in

vacuo was prepared by weighing. The specific conductance of the KCl in such a solution is 0.00140877 /ohm.cm at 25°C, according to Jones and Bradshaw (19).

The resistance of the conductance cell filled with this solution was accurately measured at 25°C on the Faure-Goddard bridge (20), at five different frequencies, namely, 1950, 1300, 900, 650 and 500 cycles/sec. A steady stream of purified air was passed through the cell to remove all dissolved gases. The resistances of the bridge and cell leads were taken to be 0.274 ohm as determined by A. Faure (20) and 0.227 ohm as determined by Malan (13) respectively. The cell resistances measured with the bridge were hence corrected by these amounts.

To determine the polarisation correction the method of Jones and Christian (16) was followed. The resistances (R) were plotted against $p^{-\frac{1}{2}}$ where $p = \pi f$ and f is the frequency in cycles/sec. The resistance obtained on extrapolation to infinite frequency, which came to 83.92 ± 0.02 ohm, was taken as the true resistance of the KCl solution at 25°C.

As the specific conductance of the water used was 90 mm/cm. the conductance of the 0.01 demal KCl solution was (0.00140877 + 0.00000009) /ohms. cm, which to the nearest whole fifth significant figure came to 0.0014089 /ohm.cm. The cell constant Q was calculated from the relation

$$Q = \varkappa R \qquad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

$$= 0.11823 \pm 0.00002$$

This was in good agreement with the value 0.11820 ± 0.00004 as determined by Malan (13) for the same cell.

3.3. PREPARATION AND STANDARDISATION OF MATERIALS.

3.31 CONDUCTANCE WATER.

All conductance water used in this work was obtained from the automatic recycling still developed in this laboratory. The water is distilled in two stages: the first from alkaline permanganate which removes acid and destroys any organic impurities present in the water; the second from a phosphoric acid solution which removes the alkaline impurities - mainly ammonia.

The water was collected and stored in well-leached Pyrex flasks. It was found that there was little or no increase in the conductance of the water when kept in these flasks over a period of several days.

A detailed description of the still appears elsewhere. (21)

3.32. 0.01M POTASSIUM CHLORIDE SOLUTIONS

In making up the 0.01 molar KCl solutions used in the preparation of the Hg_2Cl_2 (See section 3.38) Kahlbaum A.R. KCl was used. For the determination of the cell constant, however, the A.R. KCl was twice recrystallised and then heated in a platinum boat for 45 minutes at 550°C in an atmosphere of de-oxygenated and dried nitrogen, to remove all traces of moisture from the salt. The KCl solutions were prepared by weighing, all weights having been corrected to vacuum.

3.33. MERCURY.

Mercury, under dilute nitric acid, was subjected to aspiration of air for two days. It was then washed with conductance water, dried and twice distilled under reduced pressure - the head and tail fractions of each distillation being rejected.

When the pure mercury was to be introduced into the conductance cell it was in addition washed 50 times by decantation with conductance water.

3.34. MERCUROUS NITRATE. $(Hg_2(NO_3)_2 2H_2O)$

Crystals of mercurous nitrate were obtained by the action in the cold of 5N A.R. nitric acid on mercury.

(It was found that when the acid was much below 5N, e.g. 2N, the reation was slow with the simultaneous formation of the yellow basic nitrate.) The salt was recrystallised from 0.6N nitric acid by slow evaporation, dried and stored in the dark over silica gel.

Approximately 0.01 molar solutions were prepared by weighing and adding just sufficient nitric acid to prevent the precipitation of the yellow basic nitrate. The solutions were kept in the dark and found to be quite stable.

3.35. MERCURIC OXIDE (HgO)

Following the instructions of Schoch (22) 100 ml. of a hot solution of 1 part of mercuric chloride in 2 parts by weight of water was gradually added to 500 ml. of a hot solution of 1 part of potassium hydroxide in 2 parts of water, and the mixture was then boiled under reflux for five hours. The orange mercuric oxide precipitate was washed by decantation with conductance water 40 times.

3.36. MERCUROUS PERCHLORATE ($Hg_2(ClO_4)_2 4H_2O$)

The mercurous perchlorate was prepared according to Chikashige (23). Mercuric oxide was triturated in a glass mortar with 20% redistilled perchloric acid till the solution became turbid. The solution was filtered through a sintered glass filter funnel, a few drops of perchloric acid added

(to prevent the formation of the basic perchlorate) and then shaken vigorously with excess mercury for fifteen minutes. Crystallisation was induced by evaporating off the water in a vacuum. The crystals were stored in the dark over silica gel.

The 0.01 molar mercurous perchlorate solutions were prepared by weighing. Approximately 1 ml. 20% perchloric acid and 0.5 ml. of pure mercury were added to the solutions, which were kept in the dark. Under these conditions no decomposition of the mercurous perchlorate was observed.

3.37. STANDARDISATION OF THE MERCUROUS SALT SOLUTIONS.

As mercurous nitrate and mercurous perchlorate are deliquescent the 0.01 M solutions could not be accurately prepared by weighing in the normal way and hence it was necessary to analyse the solutions after they had been made up.

At first the Hg was determined by precipitating it as Hg_2Cl_2 according to Hillebrand (24) but, possibly due to the slight solubility of Hg_2Cl_2, this method gave low results. The determination of Hg by electrodeposition was found to be more reliable. The method given by Scott (25) was used, except that a thin layer of copper was first deposited on the cathode to facilitate both the deposition of the mercury and its removal afterwards.

3.38 MERCUROUS CHLORIDE. (Hg_2Cl_2)

The method followed for the preparation of mercurous chloride was similar to that used by Malan (13) in his preparation of silver chloride.

The 0.01 M $Hg_2(NO_3)_2$ (or $Hg_2(ClO_4)_2$) solution was added dropwise from a burette to 50. ml. exactly 0.01 M KCl solution with constant shaking until equivalent amounts were present. The mercurous salt solution was added slowly over a period of 45 minutes. Precipitation was carried out in the cold.

The precipitate was then digested for two hours on an electric heating mantle at 45°C. (According to Berthe (26) the conversion of Hg_2Cl_2 to $HgCl_2$ by water occurs above 50°C.) The digestion favours the growth of larger particles at the expense of the smaller ones and in this way adsorption is reduced to a minimum and the precipitate is also easily washable. To ensure the complete removal of ions foreign to the Hg_2Cl_2 lattice the precipitate was washed at least 50 times with conductance water.

Vogel (27) found that calomel kept under water blackened when exposed to light. It was found in this work, however, that no such change occured when the calomel, prepared as described above, was kept under water and exposed to light for several weeks. According to Hada (28) the darkening of the precipitate was more rapid if KCl or HCl were present.

It therefore seems that the calomel used by these workers was not entirely free of foreign ions.

3.39. NITROGEN FOR STIRRING CELL CONTENTS.

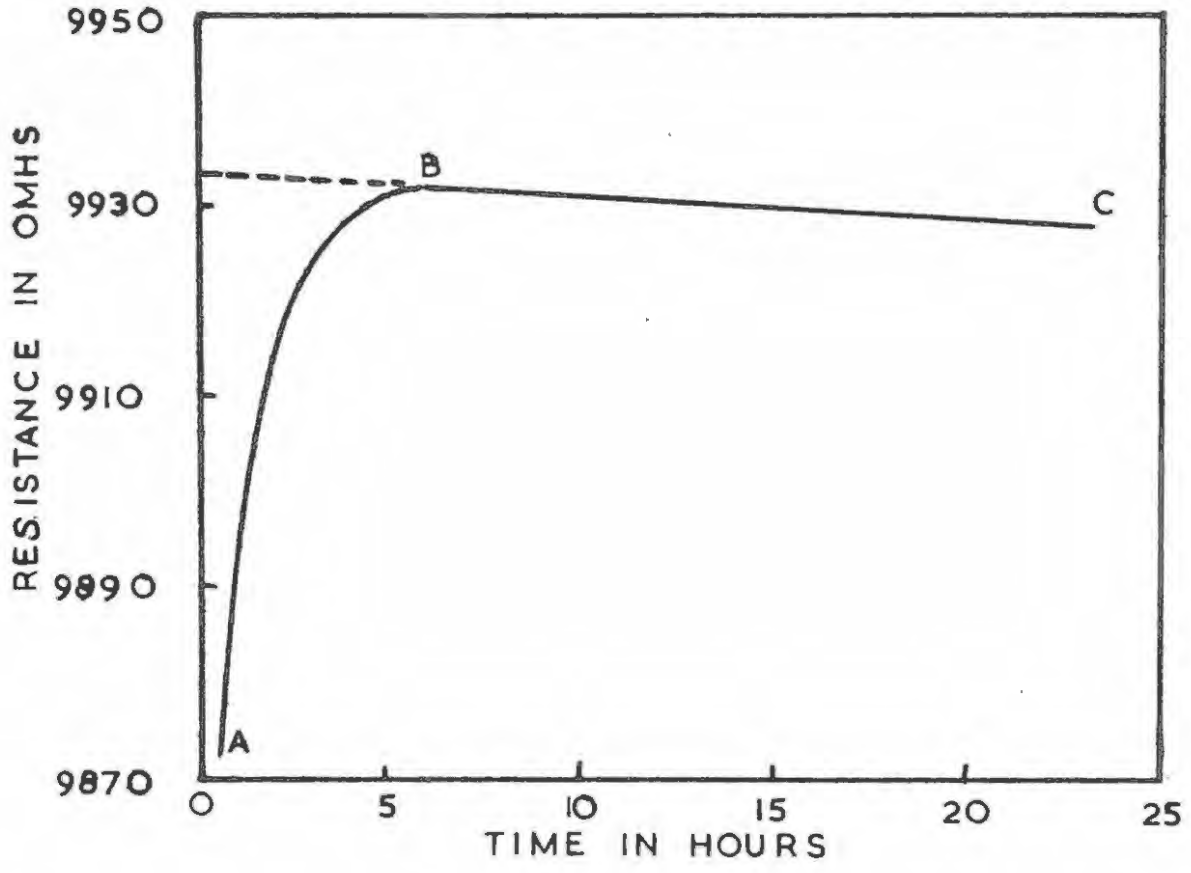
Commercial dry nitrogen was purified by passing it through a train consisting of red hot copper filings in a silica tube to remove traces of oxygen; concentrated sulphuric acid bubblers to dry the gas; several U-tubes containing soda lime to remove carbon dioxide and acid impurities; a U-tube filled with solid meta phosphoric acid to remove traces of ammonia and alkaline impurities and finally bubblers containing conductance water to saturate the nitrogen with water vapour at 25°C before it entered the conductance cell.

3.4. EXPERIMENTAL TECHNIQUE, RESULTS AND DISCUSSION

3.41. MEASUREMENT OF THE SPECIFIC CONDUCTANCE OF THE CONDUCTANCE WATER (λ_{H_2O})

Approximately 300 ml. of conductance water was placed in the conductance cell which was then immersed to a suitable depth in the thermostat. Volatile impurities, mainly CO_2, were removed from the conductance water in the cell by bubbling through it a steady stream of purified nitrogen. The cell resistance, which was measured at regular intervals, was found to rise rapidly to a maximum, after which it

FIG. 2. GRAPH OF RESISTANCE AGAINST TIME FOR CONDUCTANCE WATER AT 25°C.



dropped at a slow and regular rate due presumably to the continual solution of glass from the cell walls (13). The rate at which the conductance rose due to the solution of glass varied from 0.3 to less than 0.05 nm/cm/hour depending on the bubbling rate and on how well the cell was leached out.

A typical plot of resistance (R) against time (t) is given in fig. 2. The resistance R_4' obtained on extrapolating the linear slope CB to time $t=0$ is assumed to correspond to the resistance which the cell would have if all the dissolved gases were removed from the water and no glass from the cell walls had entered into solution.

As the resistance of the water was too high for direct measurement on the bridge a 10,000 ohm resistance was connected in parallel with the conductance cell and the resultant resistance measured (R_4). The specific conductance (κ_{H_2O}) was calculated from the equation

$$\kappa_{H_2O} = \frac{Q(R_s - R_4')}{R_s R_4'} \qquad \ldots\ldots\ldots\ldots (7)$$

where Q is the cell constant, R_s the shunt resistance and R_4' the extrapolated value of the resistance of the shunt and cell in parallel.

FIG. 3. GRAPH OF RESISTANCE AGAINST TIME FOR SATURATED CALOMEL SOLUTION AT 25° C.

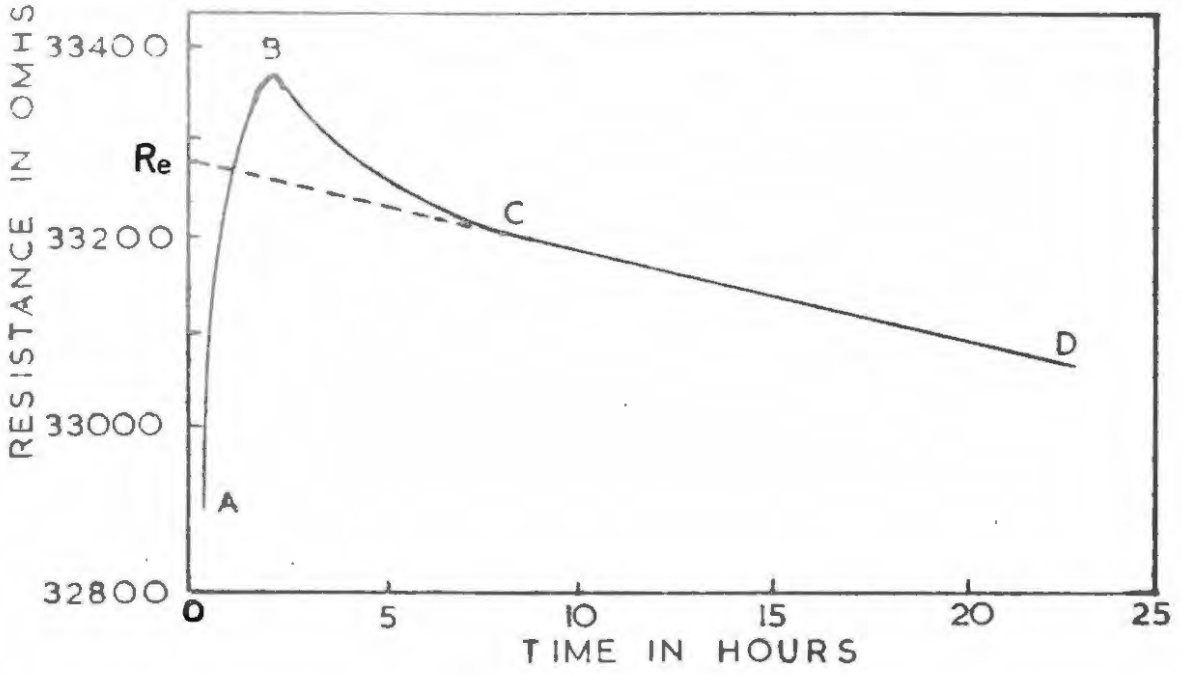
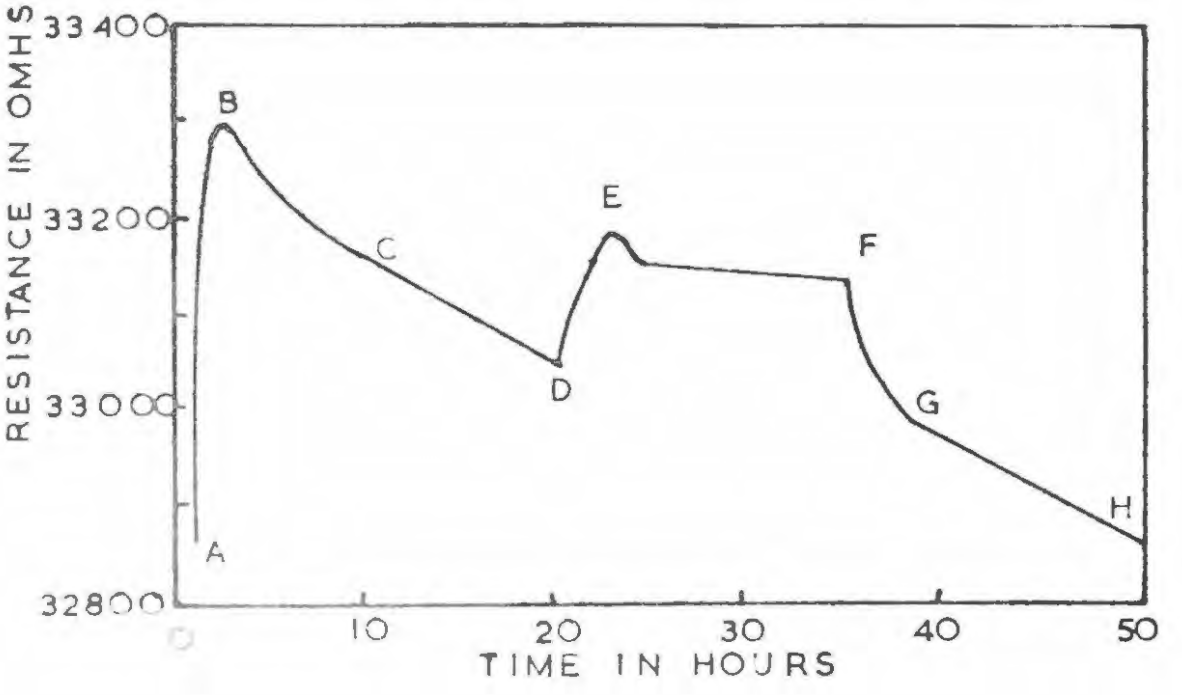


FIG. 4. GRAPH OF RESISTANCE AGAINST TIME FOR SATURATED CALOMEL SOLUTION AT 25° C.



It was found that the addition of approximately 0.2 ml. of pure mercury to the water in the conductance cell did not alter the conductance of the water. Hence no ions are formed in any appreciable amount when mercury is added to pure water.

3.42. MEASUREMENT OF THE SPECIFIC CONDUCTANCE OF A SATURATED CALOMEL SOLUTION AT 25°C (κ_{cal})

The technique employed was similar to that developed by Malan (13) in his work on silver chloride. For each determination of κ_{cal} the conductance cell, containing approximately 250 ml. of conductance water with Hg_2Cl_2 in suspension was placed in the thermostat and purified nitrogen was bubbled through the cell contents. Sufficient Hg_2Cl_2 was taken to ensure that a perceptible excess of solid calomel was present when equilibrium was attained. Thus the possibility of supersaturation was avoided. The specific conductance of the water used in each of these experiments was separately determined so that the solvent correction was known.

The cell resistance was measured at regular intervals over a period of approximately 24 hours. A typical graph of resistance against time is given in fig. 3. The portion AB of the graph corresponds to the removal of dissolved gases resulting in the rapid rise in the cell resistance. The curved drop BC is due to the continual solution of Hg_2Cl_2 and glass from the cell walls while the straight line CD corresponds presumably to the solution of glass and ion exchange

between the ions in the solution and those from the Pyrex glass. At the point C therefore the solution is completely saturated with Hg_2Cl_2.

It was found that the gradient of the line CD (fig. 3) depended on the bubbling rate and on how well the cell had been washed out since the previous experiment. The gradual increase of conductance of the solution in the cell after saturation with calomel was reached was probably due to ion exchange (13), the most likely exchange being between the fast moving H^+ions which are readily adsorbed on the glass walls, and the slower moving ions from the soluble constituents of the Pyrex glass. On comparing the work done on neutral salts by other investigators in this laboratory with the present work on Hg_2Cl_2 it was found that the gradient of the line CD was much greater in the case of Hg_2Cl_2 than it was for neutral salts such as KCl and AgCl under similar conditions. The slopes for Hg_2Cl_2 solutions varied from 1 to 12 nm/cm/hour as against 0.3 nm/cm/hour for AgCl. (13). As the pH of a saturated calomel solution at 25°C was found to be 5.125 (See section 4.41) it would be expected that, due to the higher H^+ion concentration, any ion exchange involving H^+ions would take place at a much greater rate than in the case of a neutral solution. This was thought to be the reason for the greater slopes observed in the case of Hg_2Cl_2.

When repeating a determination of $\mathcal{H}_{cal.}$, using the same Hg_2Cl_2 as used in the previous determination, by pouring out of the cell as much as possible of the saturated solution and then refilling the cell with conductance water, it was found that the gradient of the line CD was always considerably greater during the second than during the first determination, in spite of the fact that the bubbling rates were the same for both experiments. On doing a third run on the same Hg_2Cl_2 the slope was even greater. The final resistance of the calomel solution obtained on extrapolating DC to time $t = 0$ was always found to be approximately 0.3% lower than the value for the previous determination. When, however, instead of just pouring out the saturated calomel solution from the cell the solid undissolved calomel was also removed and both the cell and the calomel rewashed several times with conductance water no appreciable change in the extrapolated value of the resistance was found when the determination was repeated, with this same calomel sample. The previous differences observed were hence presumably due to the fact that when the second determination was started on the same calomel there was approximately 10 ml. of saturated solution from the previous run in the cell - it had not been possible to remove these last few ml. without losing most of the solid calomel as well.

Work done later on the determination of the total

concentration of mercury present in a saturated calomel solution at 25°C revealed that there was some definite correlation between the gradient of the line CD and the concentration of mercury in the solution. It was shown that when a quantity of calomel solution was removed from the conductance cell the gradient of CD as well as the concentration of mercury in solution increased. The more aliquots of solution extracted, the steeper the slope of CD became. When, after some calomel solution had been removed, the cell was refilled with conductance water and allowed to come to equilibrium again it was also found that both the slope of CD and the mercury concentration had increased.

No satisfactory explanation for the above effects could be found. An attempt to verify the ion exchange postulation was made by testing the saturated calomel solution for the presence of Na^+ and K^+ ions, which were the most likely to come from the glass, with the aid of a flame photometer. It was found, however, that the concentrations of the Na^+ and K^+ ions, if there were any there at all, were too low for detection.

According to the literature (27) calomel was photosensitive and so the preparation of the Hg_2Cl_2 by precipitation, and all subsequent work, was carried out in red light. It was found, however, that the calomel prepared in this work underwent no visual change when it

was kept under water and exposed to daylight for several weeks. A number of experiments were consequently carried out in ordinary electric light. The constant temperature room in which all work was done, was, however, only illuminated when it was occupied and hence the calomel was never excessively exposed to white light. Under these conditions the results did not differ appreciably from those obtained in red light.

We have in the conductance cell as a result of the equilibrium

$$Hg_2^{2+} = Hg_{(s)} + Hg^{2+}$$

metallic mercury present. It was thought that the activity of this mercury might not have been unity due to either, some of it dissolving, or it being very finely divided (of colloidal size) which results in a large increase of the surface area of the mercury. The effect of adding purified mercury to the calomel solution was therefore studied. It was shown that the effect was negligible irrespective of the stage (i.e. the preparation of the Hg_2Cl_2 or later) at which the mercury was added to the system. From this it was deduced that the activity of the metallic mercury, which was present in the conductance cell due to the above mentioned equilibrium, was unity. If this

were not the case the addition of excess mercury to the system, which would then definitely make the activity of mercury unity, would have disturbed the existing equilibria and hence caused a change in the conductance of the solution.

The resistance obtained on extrapolating DC to time t=0 (point R_e on graph - see fig. 3) was assumed to represent the resistance of the saturated calomel solution free of all volatile impurities and corrected for the secondary effects such as the solution of glass and ion exchange over the duration of the experiment. Assuming that the extrapolated resistance R_e was the correct resistance of a saturated calomel solution at 25°C the specific conductance of the solution was calculated from equation 3 (section 3.1.) The conductance of the solution as determined above is the sum of $\kappa_{cal.}$ - the specific conductance due to all the ions which result when the calomel goes into solution (see section 2) - and the conductance due to the solvent, κ_{H_2O} . Therefore to obtain $\kappa_{cal.}$ alone, κ_{H_2O} , which has been corrected for the depression of the ionisation of the water as shown in section 3.1, is subtracted from the observed specific conductance of the solution.

Initial disagreement between the results of successive experiments led to the surprising discovery that the extrapolated value of the resistance of the saturated calomel solution depended on the rate at which the nitrogen bubbled

through the cell. When the bubbling rate is changed during an experiment the cell resistance changes too. Consider fig. 4. The portion ABCD of the graph represents the normal behaviour when nitrogen is bubbled through the Hg_2Cl_2 suspension. At the point D the stream of nitrogen was suddenly passed over, instead of through, the solution. This is equivalent to decreasing the bubbling rate suddenly to zero. The cell resistance now rose rapidly to E and remained practically constant at that value. At F the nitrogen was once again bubbled through the solution and the resistance dropped sharply to G after which it continued to decrease normally along GH as before. This behaviour clearly demonstrates the dependence of $\mu_{cal.}$ on the bubbling rate. The specific conductance was hence determined at various bubbling rates. The results obtained are given below in Table 1.

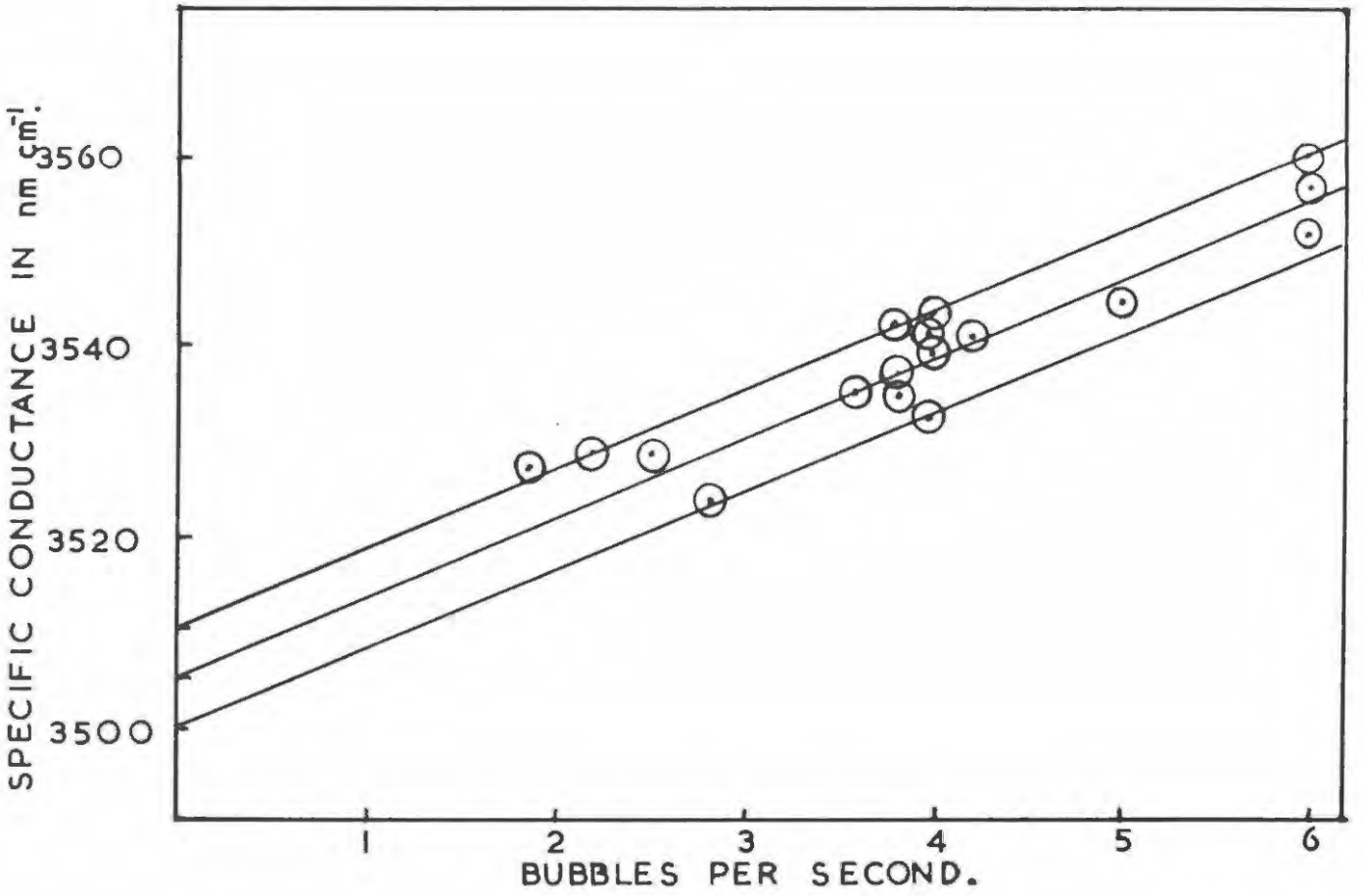
TABLE I. SPECIFIC CONDUCTANCE OF Hg_2Cl_2 AT 25°C.

Age of ppt. days.	Bubbling rate Bubbles/sec	μ_{H_2O} nm/cm.	μ_{H_2O} at pH = 5.125 nm/cm.	$\mu_{cal.}$ corrected nm/cm.
11	6 .0	69	15	3557
10	6 .0	78	24	3560
6	6 .0	84	30	3552
7	6 .0	84	30	3560
8	6 .0	82	28	3557

Age of ppt. days.	Bubbling rate Bubbles/sec	γ_{H_2O} nm/cm.	γ_{H_2O} at pH = 5.125 nm/cm.	$\gamma_{cal.}$ corrected nm/cm.
9	5.0	76	22	3545
9	4.2	84	30	3541
12	4.0	65	11	3534
13	4.0	65	11	3539
13	4.0	65	11	3534
14	4.0	65	11	3544
7	4.0	78	24	3544
9	4.0	71	17	3542
8	3.8	73	19	3536
10	3.8	73	19	3539
12	3.8	69	15	3543
6	3.6	73	19	3535
22	2.8	71	17	3524
9	2.5	73	19	3529
7	2.2	70	16	3529
7	1.9	70	16	3528

No difference was observed between the values of $\gamma_{cal.}$ for calomel obtained from the precipitation by the slow addition of KCl to $Hg_2(NO_3)_2$ or $Hg_2(ClO_4)_2$ solutions. The age of the precipitate too was found to have no marked effect on the results, as may be seen from Table 1.

FIG. 5. GRAPH OF SPECIFIC CONDUCTANCE AGAINST BUBBLING RATE FOR SATURATED CALOMEL SOLUTION AT 25°C.



A graph of $\lambda_{cal.}$ against bubbling rate was plotted. (fig. 5). The relation appeared to be a linear one and the best straight line through the points was therefore calculated by the method of simultaneous equations. (29). The value of $\lambda_{cal.}$ at zero bubbling rate, obtained by extrapolation came to 3505 ± 5 nm/cm. It was assumed that at zero bubbling rate all the previously mentioned effects of ion exchange and mercury content, which were obviously connected with the rate of stirring of the cell contents by the nitrogen bubbles, would no longer be felt, and hence the value of $\lambda_{cal.}$ at this point was taken as being the true one.

4. pH OF THE SATURATED CALOMEL SOLUTION AT 25°C.

4.1. OUTLINE AND THEORY OF METHOD.

The hydrogen ion concentration of a saturated calomel solution could not be determined directly by the ordinary hydrogen electrode method as the hydrogen gas would reduce the mercury salts to metallic mercury in the presence of platinum. Furthermore, it is a well known fact that the potential of a hydrogen electrode is not steady in weakly buffered solutions.

The two above objections were overcome by measuring the pH of the calomel solution with a glass electrode pH-meter, which is well suited for weakly buffered solutions. To eliminate any possible error due to the pH-meter itself a borax-succinic acid buffer was prepared which gave the same pH reading on the meter as did a typical calomel solution. The potential of a hydrogen electrode in the above mentioned buffer was then measured. The hydrogen ion concentration of the calomel solution was calculated as outlined below.

Consider the following cells:-

Cell (i)

Glass Electrode	sat. Hg_2Cl_2 solution	sat. KCl	Hg_2Cl_2-Hg

E_{y_1}

e.m.f. = E_1

Cell (ii)

Glass Electrode	Borax-Succinic acid buffer	sat. KCl	Hg_2Cl_2-Hg

E_{γ_2}

e.m.f. = E_2

Cell (iii)

H_2	Borax-Succinic acid buffer	sat. KCl	N/10 KCl	Hg_2Cl_2-Hg

E_{γ_3} $E_{\gamma a}$

e.m.f. = E_3

Cell (iv)

H_2	0.05M $KHC_8H_4O_4$	sat. KCl	N/10 KCl	Hg_2Cl_2-Hg

E_{γ_4} $E_{\gamma b}$

e.m.f. = E_4

E_γ denotes liquid junction potential. The 0.05 molar solution of potassium hydrogen phthalate contained in the left hand side of cell (iv) above is the primary British standard which by definition is of pH 4.005 at 25°C. (30).

We have:

$$E_1 = E_g^o - \frac{RT_1}{F} \ln a_{1H^+} + E_{\gamma_1} \quad \ldots\ldots (8)$$

$$E_2 = E_g^o - \frac{RT_2}{F} \ln a_{2H^+} + E_{\gamma_2} \quad \ldots\ldots (9)$$

where a denotes ionic activity, E_g^o is a constant for the Glass Electrode - Calomel reference electrode cell, R is the universal Gas Constant, F the Faraday and T the absolute temperature.

As E_1 was made equal to E_2 we get on equating (8) and (9)

$$- \ln a_{1_{H^+}} = \frac{(E_{\gamma_2} - E_{\gamma_1}) - \frac{RT_2}{F} \ln a_{2H^+}}{\frac{RT_1}{F}} \quad \ldots\ldots (10)$$

also

$$E_3 = E^o_{Hg\,Hg_2^{2+}} - \frac{RT_3}{F} \ln\left(a_{3H^+}^{x}\, a_{Ce^-}\right) + E_{\gamma_3} + E_{\gamma_a} \quad \ldots\ldots (11)$$

and

$$E_4 = E^o_{Hg\,Hg_2^{2+}} - \frac{RT_4}{F} \ln\left(a_{4H^+} \times a_{Ce^-}\right) + E_{\gamma_4} + E_{\gamma_b} \quad \ldots\ldots (12)$$

If $T_4 = T_3$ we obtain on subtracting equation (11) from (12) and rearranging, that

$$\frac{RT_3}{F} \ln a_{3H^+} = (E_4 - E_3) - (E_{\gamma_4} - E_{\gamma_3}) + \frac{RT_4}{F} \ln a_{4H^+} \quad \ldots\ldots\ldots (13)$$

$$(E_{\gamma_a} = E_{\gamma_b})$$

Substituting this value of $\frac{RT_3}{F} \ln a_{3H^+}$ in equation (10) and converting the Naperian logarithms to natural logarithms we obtain

$$-\log a_{1H^+} = \frac{(E_{\gamma_4} - E_{\gamma_1}) - (E_4 - E_3) - \frac{2.303RT_4}{F} \log a_{4H^+}}{\frac{2.303RT_1}{F}} \quad \ldots\ldots\ldots\ldots (14)$$

$$(T_1 = T_3 \ , a_{2H^+} = a_{3H^+} \ , \quad E_{\gamma_2} = E_{\gamma_3})$$

The liquid junction potentials were estimated by employing Henderson's (31) "continuous mixture" boundary equation:

$$E_\gamma = \frac{RT}{F} \frac{(U_1 - V_1) - (U_2 - V_2)}{(U_1' + V_1') - (U_2' + V_2')} \ln \frac{(U_1' + V_1')}{(U_2' + V_2')} \quad \ldots\ldots (15)$$

where

$$U = \sum c_+ u_+$$

$$V = \sum c_- u_-$$

$$U' = \sum c_+ z_+ u_+$$

$$V' = \sum c_- z_- u_-$$

c = concentration in mole/litre.

u = ionic mobilities

z = valency

Subscripts 1 and 2 denote the two solutions which go to

make up the liquid junction.

In calculating the conductance due to hydrogen ions in the saturated calomel solution we must know the molarity of this ion. We have that

$$c_{H^+} = \frac{a_{H^+}}{\gamma_{H^+}} \qquad \ldots\ldots\ldots (16)$$

where c = molarity

γ = molar activity coefficient.

The activity coefficient may be estimated from the Debye-Hückel Limiting Law,

$$-\log \gamma_i = A Z_i^2 \sqrt{\mu} \qquad \ldots\ldots\ldots (17)$$

where A = a constant (0.509 for water at 25°C)

Z = valency

μ = ionic strength

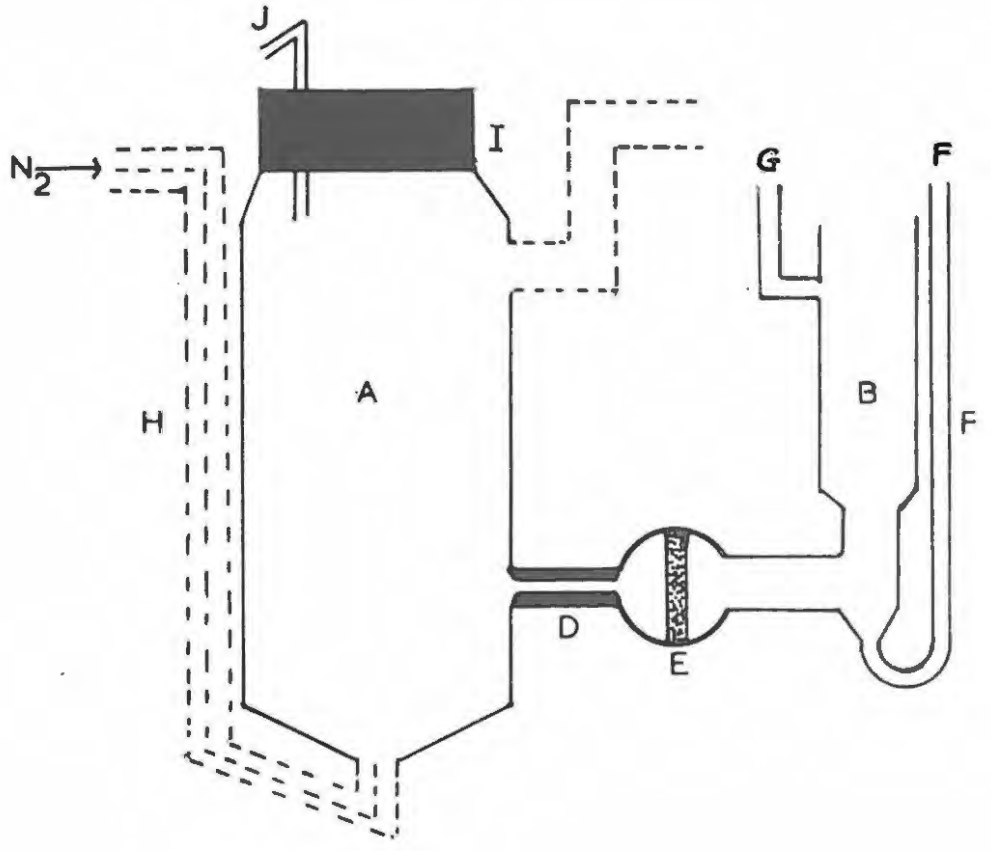
$$\mu = \tfrac{1}{2} \sum c_i z_i^2 \qquad \ldots\ldots\ldots (18)$$

4.2. DESCRIPTION AND STANDARDISATION OF APPARATUS.

4. 21. pH METER.

The pH-meter used in this work was a Marconi pH-meter Type TF 717A. Irregular drifting of the pH reading during determinations was found to correspond to sudden changes in the mains voltage. This source of error was eliminated by installing a constant voltage transformer in the input circuit.

FIG. 6. THE pH CELL.



Special attention was paid to the electrode assembly of the meter. The electrodes were well washed and dried before and after each pH determination. The salt bridge junction of the calomel reference electrode too was carefully renewed after each experiment and the saturated KCl regularly replaced with fresh solution.

The meter was operated according to the set of instructions supplied with it and standardised with a 0.05M potassium hydrogen phthalate solution.

4.22. pH - CELL.

If any seepage of saturated KCl from the calomel reference electrode into the saturated calomel solution occurred, this would disturb the equilibria existing between the various ions and molecules present and hence the pH of the solution would be altered. To avoid this a special Pyrex cell was constructed to contain the calomel solution.

A diagram of the cell is given in fig. 6. The compartments A and B had capacities of 200 ml. and 20 ml. respectively. The function of the sintered-glass filter E and the capillary D was to minimise any back diffusion of liquid from B into A. Like the conductance cells, this cell could be suspended in the oil thermostat, and allowed a stream of gas (nitrogen) to be passed through, or over, the contents of compartment A.

Calomel solution from compartment A was forced over into compartment B by closing F and B (with a ground glass cap and rubber stopper respectively) and applying suction to G. The solution in B was removed by opening G and applying suction at F. In this way several pH determinations could be done on one sample of calomel solution without the danger of contaminating the bulk of the solution contained in compartment A by the possible seepage of KCl from the reference electrode which was dipped into the solution contained in compartment B.

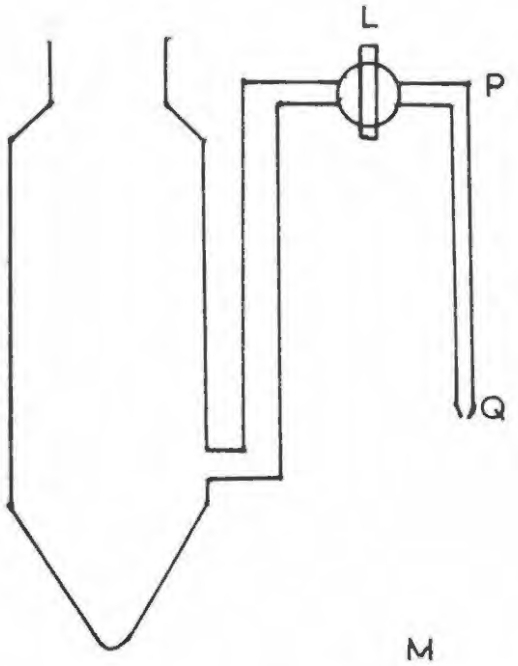
The glass and calomel reference electrodes of the Marconi pH-meter were fitted with suitable rubber stoppers so that they could be held firmly in position to the required depth in the calomel solution in compartments A and B respectively. When the reference electrode was in position and both G and F were closed with their ground glass caps the compartment B, which was completely filled with calomel solution from A, was sealed off from the atmosphere. The rubber stopper I was fitted with a thin glass tube J through which the nitrogen could escape from the compartment A when the glass electrode was in position.

4.23. HYDROGEN AND CALOMEL HALF-CELLS

The hydrogen-calomel cell consisted of two separate half-cells which could be connected by a salt bridge of

FIG. 7. THE HYDROGEN AND CALOMEL HALF-CELLS.

FIG. 7A.



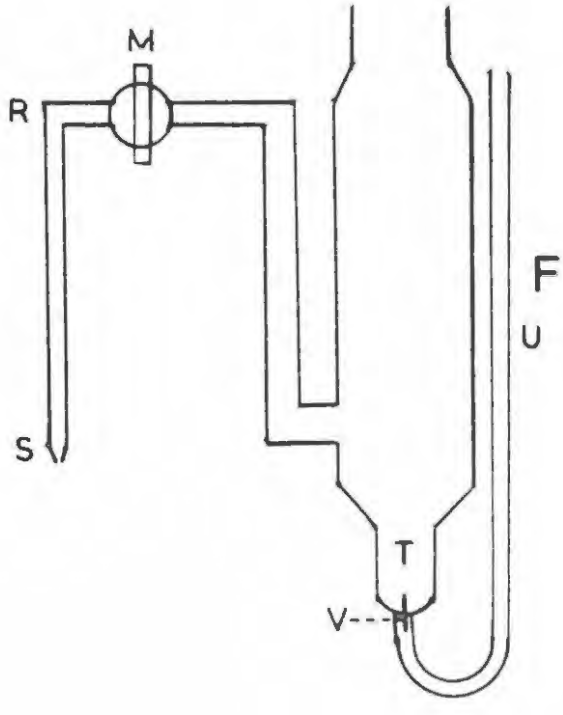


FIG. 7B.

saturated KCl. A diagram of the two half-cells is given in fig. 7. - fig. 7(a) shows the hydrogen and fig. 7(b) the calomel half-cell. The two cells have capacities of 150 and 60 ml. respectively.

To prevent diffusion of the saturated KCl of the salt bridge into the two cells, sections PQ and RS of the side arms were made of narrow glass tubing with the ends Q and S drawn out somewhat. As an additional precaution the glass taps L and M were always closed when e.m.f. readings were not being taken. Both cells were equipped with rubber stoppers which excluded the atmosphere from the cell contents and held in position the gas inlet and outlet tubes, as well as the hydrogen electrode in the case of the hydrogen half-cell. The mercury of the calomel electrode is placed in the compartment T at the bottom of the calomel half-cell. Contact with this mercury is made by the platinum seal V and a column of mercury in tube U. The calomel electrode vessel was treated with a 1% solution of Dow-Corning Silicone Fluid No. 200 in carbon tetrachloride as described by Hills and Ives (32).

The salt bridge consisted of a 50 ml. beaker filled with saturated KCl solution into which the portions PQ and RS of the side arms of the half-cells were lowered to a suitable depth. For convenience two hydrogen

half-cells were utilised, one to contain the standard buffer and the other to contain the buffer of unknown pH.

Following the instructions given by Hills and Ives (32) three normal hydrogen electrodes and a deci-normal calomel electrode with its characteristic adherent skin of calomel on the exposed mercury surface, were prepared. The potential of the calomel electrode was found to be unaffected by rocking the vessel and was quite steady over a period of several days, if oxygen was absent from the potassium chloride solution. The hydrogen electrodes were kept under distilled water when not in use.

The e.m.f. of the hydrogen-calomel cell was measured on a Tinsley Vernier potentiometer, a critically damped Leeds Northrup galvanometer of sensitivity 1.19 μ volt/m.m. and internal resistance 39.4 ohm being used to determine the point of balance. The standard cell used to standardise the potentiometer was calibrated against another standard cell which had been standardised by the National Physical Laboratory, Pretoria. Both the above standard cells, supplied by the Eppley Laboratory Inc., had N.B.S. certificates.

4.3. PREPARATION AND STANDARDISATION OF MATERIALS.

4.31. SATURATED CALOMEL SOLUTION

The samples of calomel solutions used in the pH determinations were calomel solutions remaining in the conductance cell after a determination of Λ_{cal} had been made. The advantages of using these solutions were that the quality of the calomel was known (from the value of Λ_{cal}) and that the solution was known to have been saturated at 25°C.

4.32. BUFFER SOLUTIONS.

(a) REFERENCE BUFFER.

A 0.05 molar potassium hydrogen phthalate solution, prepared from pure potassium hydrogen phthalate, (National Bureau of Standards Sample 84c) was used as the standard reference buffer. The pH of this buffer is given as 4.005 at 25°C. (30).

(b) BORAX-SUCCINIC ACID BUFFER.

This buffer was prepared by adding from a burette a 0.05 molal borax solution to 50 ml. 0.05 molal succinic acid solution until the desired pH was reached. Borax which had been recrystallised twice and then dried with alcohol and ether, and A.R. succinic acid were used respectively in the preparation of the above

mentioned solutions.

4.33. POTASSIUM CHLORIDE SOLUTIONS.

The saturated and deci-normal potassium chloride solutions which were used as the salt bridge and in the calomel reference electrode respectively, were prepared from twice recrystallised A.R.KCl.

4.34. ELECTROLYTIC CALOMEL.

Using the method given by Hills and Ives (32) electrolytic calomel was prepared by the electrolysis of 2N HCl (prepared by dilution of redistilled A.R. HCl) with a pool of pure mercury as the anode. Electrolysis was carried out with an applied potential difference of 2 volts and a current of 0.3 to 0.5 amperes was maintained by rapid stirring of the electrolyte directly above the pool of mercury. After two hours the electrolysis was stopped and the suspension stirred for 10 to 12 hours. The electrolyte was then decanted off and replaced by fresh 2N HCl and stirred again for a further 6 hours. The calomel was then washed by decantation 40 times with conductance water, drained and dried in a vacuum. It was stored in the dark over P_2O_5.

4.35. HYDROGEN.

Hydrogen from a cylinder was purified by passing it over cupric chloride to remove any hydrogen sulphide and then over platinised asbestos and reduced copper filings heated to 700°C in silica tubes to remove all traces of oxygen. The purified gas was then passed through two bubblers (inside the constant temperature room) containing conductance water so that the hydrogen would be saturated with water vapour at 24°C before it entered the hydrogen half-cell.

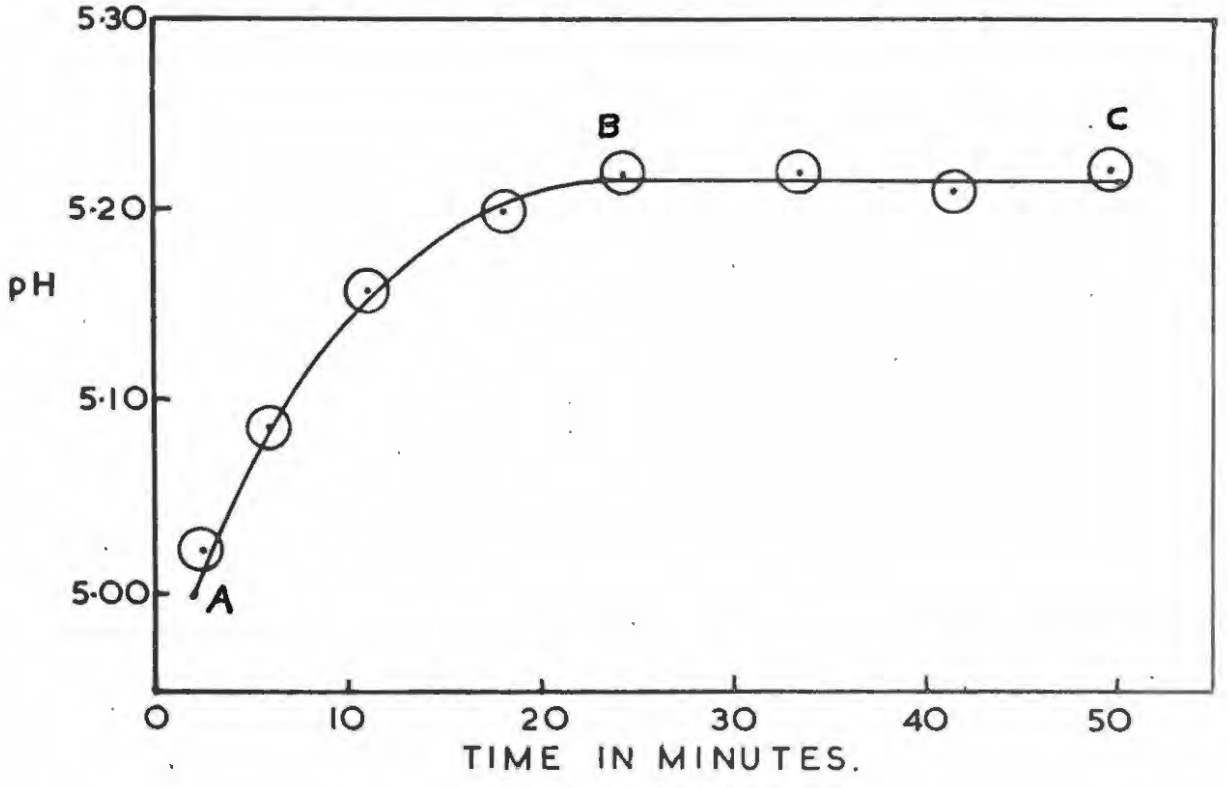
All connections in the purification train were made with polyvinyl chloride tubing, rubber being excluded.

4.4. EXPERIMENTAL TECHNIQUE, RESULTS AND DISCUSSION.

4.41. DETERMINATION OF THE pH OF THE SATURATED CALOMEL SOLUTION USING THE MARCONI pH-METER.

Immediately after a determination of κ_{sol} the saturated calomel solution was decanted from the conductance cell into compartment A of the pH cell. The pH cell was then placed in the thermostat and a steady stream of nitrogen passed through the solution for about two hours. Compartment B was then completely filled with calomel solution from compartment A (see fig. 6.) by applying suction as previously described and the calomel reference electrode immediately placed firmly in position so that approximately

FIG. 8. GRAPH OF pH AGAINST TIME FOR SATURATED CALOMEL SOLUTION AT 25° C.



four centimeters of the electrode were immersed. The glass electrode was then installed in compartment A so that the bulb was well covered with the calomel solution, while the "Temperature Compensator" was immersed to a depth of at least three centimeters in the thermostat.

It was found that the pH of the calomel solution rose with time and then came to a steady value. A typical plot of pH against time is given in fig. 8.

A similar phenomenon was shown to occur in trial determinations of the pH of conductance water which was exposed to the atmosphere and through which a steady stream of nitrogen was being passed. From this it was deduced that back diffusion of CO_2 from the atmosphere into the water took place to a large extent. When, however, the electrode system of the pH meter was dipped into the water in an attempt to determine the pH the surface of the water exposed to the atmosphere was automatically diminished and hence back diffusion of CO_2 could not occur to the same extent as it had before. The result was that some CO_2 was removed from the water by the nitrogen and hence the pH of the water rose.

The rise AB (fig. 8.) was hence put down mainly to the removal of CO_2 which was present in the calomel solution due to back diffusion from the atmosphere through the relatively large opening of compartment A when the glass electrode was not in position. With the glass

electrode in position, however, the only opening to the cell contents was through the glass tube **J** (See fig. 6.) and hence with the fairly rapid bubbling rate used (4 to 6 bubbles per second) back diffusion through **J** was negligible. When all the CO_2 was removed the pH of the calomel no longer changed with time - portion BC of the graph.

Another effect which caused a rise in the pH reading was the increase of the temperature of the electrode contents from 24°C (room temperature) to 25°C (thermostat temperature). The e.m.f. of the cell is given by

$$E = E_g^o + \frac{2.303\ RT}{F} \times pH \qquad \ldots\ldots\ldots\ldots (19)$$

As E increases with a rise of temperature (T) the pH reading as given by the meter would also rise. The above effect was, however, relatively small and only accounted for approximately 10% of the observed rise in pH.

Due to the limited sensitivity of the pH-meter no change in the pH reading was observed when the bubbling rate was altered.

Immediately after each pH determination the standardisation of the instrument was checked with the potassium hydrogen phthalate buffer.

It was assumed that the final steady pH reading (portion BC - fig. 8.) represented the pH of the saturated calomel solution when all the CO_2 was removed. The results obtained for the pH are given below in table 2. Column A gives the value of H_{cal} at the time when the calomel solution was transferred to the pH cell and column B gives the pH's of these solutions as read off the Marconi pH-meter.

Table 2. pH of the Saturated Calomel Solution at 25°C.

A	B
3540	5.215
3540	5.215
3550	5.205
3550	5.215
3560	5.210
3575	5.200
3575	5.205
3595	5.195
3595	5.200
3600	5.225
3600	5.220
3600	5.245
3610	5.225
3610	5.225
3650	5.235
3650	5.250

The mean pH reading was 5.220.

4.42 PREPARATION OF BUFFERS OF pH 5.215.

A borax-succinic acid buffer (made from 0.05 molal solutions as described in section 4.32 (b)) was prepared so that the pH reading registered on the Marconi pH-meter for the buffer was identical with that obtained for a typical saturated calomel solution at 25°C, 5.215. The buffer solutions were contained in a 100 ml. beaker which was placed so that the electrode system, supported by the stand supplied with the pH-meter, could be lowered directly into the beaker.

For easier manipulation of the components of the system, the beaker containing the buffer was not placed in the oil thermostat, as was the calomel pH-cell. Hence the temperature of the system was that of the constant temperature room - i.e. 24°C.

The effect of atmospheric carbon dioxide on the pH of the buffer was shown to be negligible by the fact that there was no detectable difference between the pH reading of the buffer in the beaker and that of the same buffer in a cell through which a steady stream of nitrogen was being passed.

As a check a second buffer, prepared from 0.025 molal succinic acid and borax solutions, was also made up to

give the same pH reading on the meter as did the calomel solution. In both the above cases the calibration of the pH meter was checked with the standard postassium hydrogen phthalate buffer after each determination.

NOTE.

In this work the buffers were prepared to give a pH reading of 5.215 instead of 5.220, the mean value of pH as obtained from table 2. This was due to the fact that at the time the pH readings 5.245 and 5.250 of table 2 were considered incorrect and hence the mean value, as obtained from the remaining figures, was taken to be 5.215. In view of later developments, however, the high pH readings mentioned above appeared to be relevant and were therefore again included in table 2, with the result that the mean pH reading now came to 5.220. Hence the actual pH of the buffers as obtained from the potentials of a hydrogen electrode dipped into the buffers, was not taken to be equal to the pH of the saturated calomel solution but instead as a determination of the error of the pH-meter in the pH range 5.1 to 5.3 i.e. the correction to be applied to the pH readings.

$$= (5.215 - \text{true pH of buffer})$$

and hence the true pH of the calomel solution

$$= (5.220 - \text{Correction}).$$

4.43. DETERMINATION OF THE TRUE pH OF THE SATURATED CALOMEL SOLUTION.

To evaluate the true hydrogen ion concentration of the calomel solution it was necessary to determine the potentials of the two cells

$$H_2 \;|\; \text{borax-succinic acid buffer} \;\vdots\; \text{sat. KCl} \;\vdots\; \text{N/10 KCl} \;|\; Hg_2Cl_2\text{-}Hg \quad \ldots\ldots \text{ cell (iii)}$$

$$\text{e.m.f.} = E_3$$

and

$$H_2 \;|\; 0.05M\ KHC_8H_4O_4 \;\vdots\; \text{sat. KCl} \;\vdots\; \text{N/10 KCl} \;|\; Hg_2Cl_2\text{-}Hg \quad \ldots\ldots \text{ cell (iv)}$$

$$\text{e.m.f.} = E_4$$

The same reference electrode was used for both the above cells. From the e.m.f.'s of the cells the true hydrogen ion concentration of the calomel solution could be calculated as outlined in section 4.1.

As the determinations with the pH-meter of the pH of the borax-succinic acid buffers were carried out at 24°C the determinations of the potentials of the cells (iii) and (iv) above were carried out at the same temperature.

On introducing the buffers and the deci-normal potassium chloride solutions into the hydrogen and calomel half-cells respectively, the taps L and M (See Fig. 7) were closed so that no liquid entered the side arms. Hence when purified hydrogen and nitrogen was bubbled through the respective half-cells there were no stagnant regions of solution not swept out by the gas. The result was that all the buffer could be saturated with hydrogen and all the dissolved oxygen could be removed from the KCl solution. After two hours' bubbling the taps L and M were opened, the side arms filled with solution by suction and the taps closed again. The sections PQ and RS of the side arms were then lowered into the salt bridge solution to such a depth that with the taps L and M open no siphoning of the saturated KCl into the half-cells, and vice versa, would occur due to a difference in level between the solutions.

To determine the e.m.f. of the cell the stream of nitrogen bubbles through the calomel half-cell was temporarily ceased, taps L and M opened and the balancing potential read from the Tinsley potentiometer in the usual way. After each determination the standardisation of the potentiometer was checked against the standard cell.

It was found that to obtain reproducible results when determining the potential of a specified hydrogen electrode in the two different types of buffer, it was necessary to soak the electrode in distilled water for several hours after having used it in one buffer before it could be reliably used in the next. The three hydrogen electrodes were found not to be identical in practice - their potentials in the same buffer differed up to ± 0.3 milli volts from the mean value. Due to the fact that the depth of the hydrogen bubbler in the hydrogen half-cell only affected the value of the e.m.f. in the fifth decimal place (32), the depth of the bubbler in the present work, in which only four significant figures were attainable, was of no consequence.

The results obtained for the e.m.f.'s. of the two cells are given below in table 3.

Table 3. E.M.F.'s of Cells (iii) and (iv)

	Hydrogen Electrode	E_4 Volts	E_3 Volts	(E_4-E_3)	Mean Volts
For Buffer	A	0.5690	0.6384	-0.0694	
prepared from	A	0.5690	0.6394	-0.0704	
0.05 Molal	A	0.5692	0.6394	-0.0702	
borax & succinic	B	0.5697	0.6394	-0.0697	
acid solutions	B	0.5693	0.6392	-0.0699	-0.0700

	Hydrogen Electrode	E_4 Volts	E_3 Volts	(E_4-E_3)	Mean Volts
	B	0.5697	0.6399	-0.0702	
	C	0.5696	0.6395	-0.0699	
	C	0.5694	0.6397	-0.0703	
	C	0.5695	0.6397	-0.0702	
	A	0.5690	0.6388	-0.0698	
For buffer	A	0.5692	0.6389	-0.0697	
prepared	B	0.5693	0.6389	-0.0696	-0.0698
from 0.025M	C	0.5695	0.6391	-0.0696	
solutions	C	0.5693	0.6391	-0.0698	

The mean value of (E_4-E_3) for the two borax-succinic acid buffers was -0.0699 volts.

We have from section 4.1

$$-\log a_{1H^+} = \frac{(E_{\gamma_4} - E_{\gamma_1}) - (E_4-E_3) - \frac{2.303\ RT_4}{F} \log a_{4H^+}}{\frac{2.303RT_1}{F}} \quad \ldots\ldots\ldots\ldots (14).$$

The liquid junction potentials E_{γ_4} and E_{γ_1}, were calculated using equation (15) and they were found to be 0.0028 volt and 0.0058 volt respectively. Therefore $(E_{\gamma_4} - E_{\gamma_1})$ came to -0.0030 volt.

Hence from equation (14) above

$$-\log a_{H^+} = \frac{(-0.0030)-(-0.0699)-(-2.303 \times 2.56 \times 10^{-2} \times 4.005)}{2.303 \times 2.569 \times 10^{-2}}$$

$$= 5.122 = \text{pH}$$

as $-\ln a_{H^+} = \text{pH}$ by definition. (30).

The correction therefore to be applied to the readings of the pH-meter at pH's round about 5.0 to 5.2 was

$$= -(5.215 - 5.122)$$

$$= -\ 0.093$$

$$\approx -\ 0.095 \text{ pH units.}$$

The corrected pH of a saturated calomel solution was hence

$$5.220 - 0.095$$

$$= 5.125$$

5. THE MERCURY CONTENT OF A SATURATED CALOMEL SOLUTION AT 25°C.

5.1. OUTLINE AND THEORY OF METHOD

The total concentration of mercury present in a saturated calomel solution is of the order of 1×10^{-5} mole/litre. This makes the determination of mercury by the normal volumetric and gravimetric methods impracticable. It was hence decided to employ a colorimetric method of analysis, the differential technique (33) being used. Dithizone was used as the reagent for the detection of mercury as suggested by Fischer and Leopoldi (34).

When a mercury solution is shaken up with some dithizone reagent the mercury forms a coloured precipitate with the dithizone. This precipitate is soluble in CCl_4 and imparts to the solution an orange colour. The shade of the CCl_4 layer depends on the amount of mercury originally present in the aqueous solution and hence a series of colours, ranging from the original dithizone green to a clear orange, may be obtained by treating a fixed volume of the dithizone solution with aqueous solutions containing different amounts of mercury salts. Therefore by comparing the colour of the dithizone extract obtained from a solution of unknown mercury content with that obtained from a solution of known mercury content it was possible to estimate the amount of mercury contained in the unknown solution.

5.2. DESCRIPTION AND STANDARDISATION OF APPARATUS.

5.21. PHOTELOMETER.

The instrument used in this work for the colorimetric measurements was a Cenco-Sheard spectrophotelometer, a detailed description of which appears elsewhere. (35). It was found in practice that in spite of the constant voltage transformer supplied with the instrument, the fluctuations in the A.C. mains caused simultaneous fluctuations in the galvanometer reading. The 6 volt, 18 ampere ribbon filament bulb was therefore replaced by a 12 volt 36 watt lamp which was connected to a steady 12 volt D.C. supply obtained from lead accumulators.

To determine the wavelength at which the given photelometer was at its maximum sensitivity (i.e. the wavelength at which the dithizone-mercury extract absorbed the maximum amount of incident light) the transmission (T) of a typical extract was measured over the wavelength range 280 to 740 millimicrons ($m\mu$). We have that

$$T = \frac{I}{I_o} \qquad \ldots\ldots\ldots\ldots (19)$$

where I and I_o are the galvanometer deflections when the extract and the solvent (CCl_4) are placed respectively in the light path. The plot of transmission-per cent

FIG.9. GRAPH OF TRANSMISSION-PER CENT AGAINST WAVELENGTH FOR DITHIZONE-MERCURY EXTRACT.

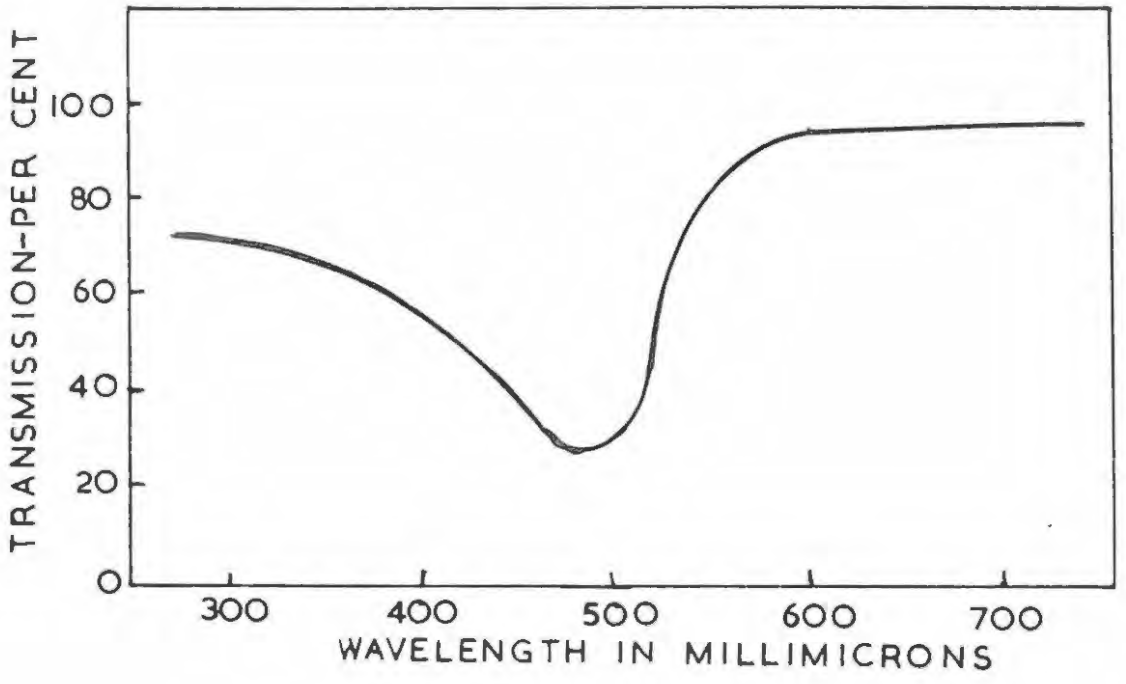
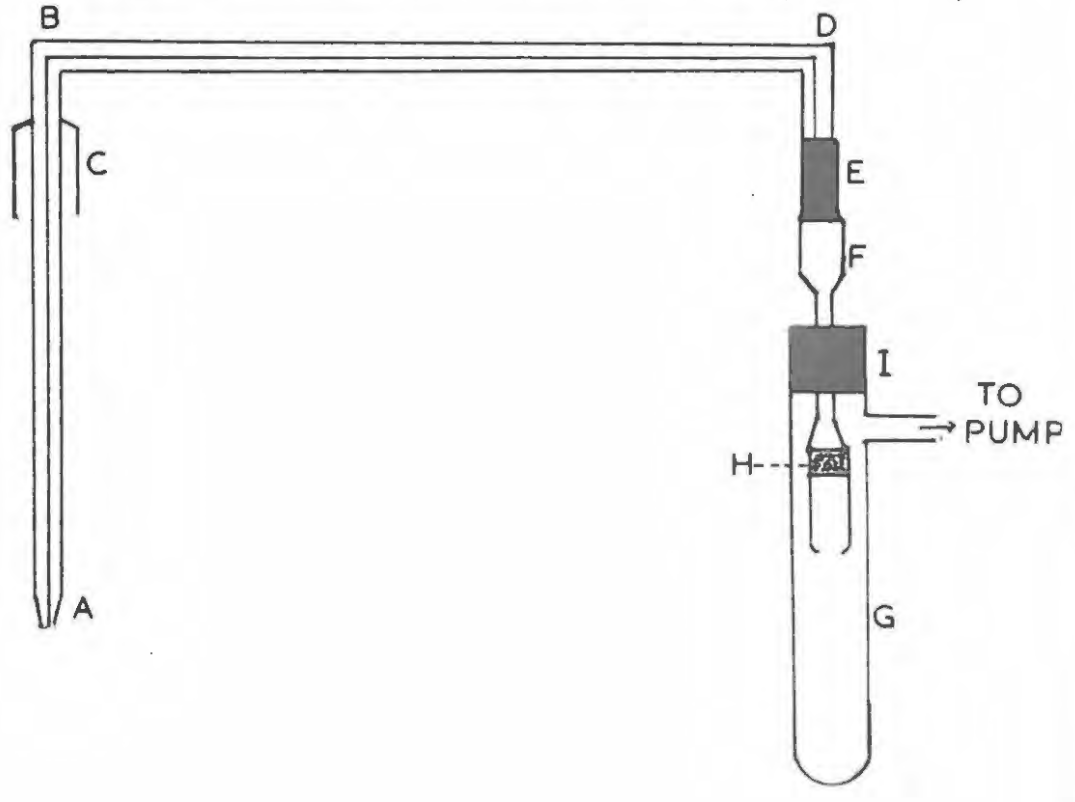


FIG.10. THE CALOMEL FILTER.



against wavelength is given in fig. 9. As may be clearly seen from this graph the instrument was at its maximum sensitivity in the wavelength band 480 to 500 mμ. All absorption measurements were hence made in this wavelength range.

5.22. THE FILTER FOR THE FILTRATION OF THE CALOMEL SOLUTION

The saturated calomel solution, as prepared in the conductance cell, had in suspension an excess of solid calomel particles and hence it was essential to filter the solution prior to the determination of the total mercury concentration. To forestall any disturbance of the equilibrium conditions by atmospheric carbon dioxide a simple device whereby a quantity of calomel solution could be extracted from the conductance cell and filtered before it came into contact with the atmosphere was used. A sketch of the apparatus appears in fig. 10. ABD is a 1 mm. diameter capillary tube which is attached to the filter F by means of a rubber collar E. The filter F is provided with a rubber stopper I so that it can be enclosed by the filter tube G. The section AB of the

capillary is placed inside the conductance cell and is kept in position by the glass cap C. On applying suction to the filter tube calomel solution from the cell is drawn up the capillary, filtered through the No. 4 sintered-glass disc H and finally collected at the bottom of G.

5.3. PREPARATION AND STANDARDISATION OF MATERIALS.

5.31. DITHIZONE REAGENT.

The dithizone (diphenylthiocarbazone) as supplied contained some of the yellow oxidation product and it was therefore purified as instructed by Snell. (36). 0.025 gram of dithizone was dissolved in CCl_4 and the solution shaken up with 200 ml. of water and 10 ml. 6N NH_4OH. The CCl_4 layer was discarded and the aqueous layer, which contained the pure dithizone, shaken with 20 ml. portions of CCl_4 until no trace of pink was shown in the extract (the solution was then free of all the oxidation product.) The aqueous solution was acidified with HCl and the dithizone extracted with 30 ml. portions of CCl_4. The extracts were combined and made up to 250 ml. and stored in the dark. As the dithizone slowly deteriorated on standing (especially when exposed to daylight) a fresh solution was prepared every two weeks.

5.32. STANDARD MERCURY SOLUTIONS.

Under the experimental conditions of this work the mercury to be determined was present as mercuric chloride. (See section 5.4.) The standard solutions were therefore prepared from mercuric chloride so that the conditions could be as similar as possible. Solutions of the desired concentration were obtained by careful dilution of a stock solution which was prepared from dried A.R. mercuric chloride by weighing.

5.4. EXPERIMENTAL TECHNIQUE, RESULTS AND DISCUSSION.

The procedure in the preparation of the dithizone-mercury extract was as follows: to 10 ml. of the mercury solution contained in a separating funnel add 5 ml. of 0.1N HCl and then 10 ml. of dithizone reagent (prepared from the stock solution by suitable dilution with CCl_4); stopper the separating funnel and shake the contents vigorously for 15 to 20 seconds; rinse the absorption cell twice with some of the CCl_4 extract, then fill the cell and slide on the cover glass.

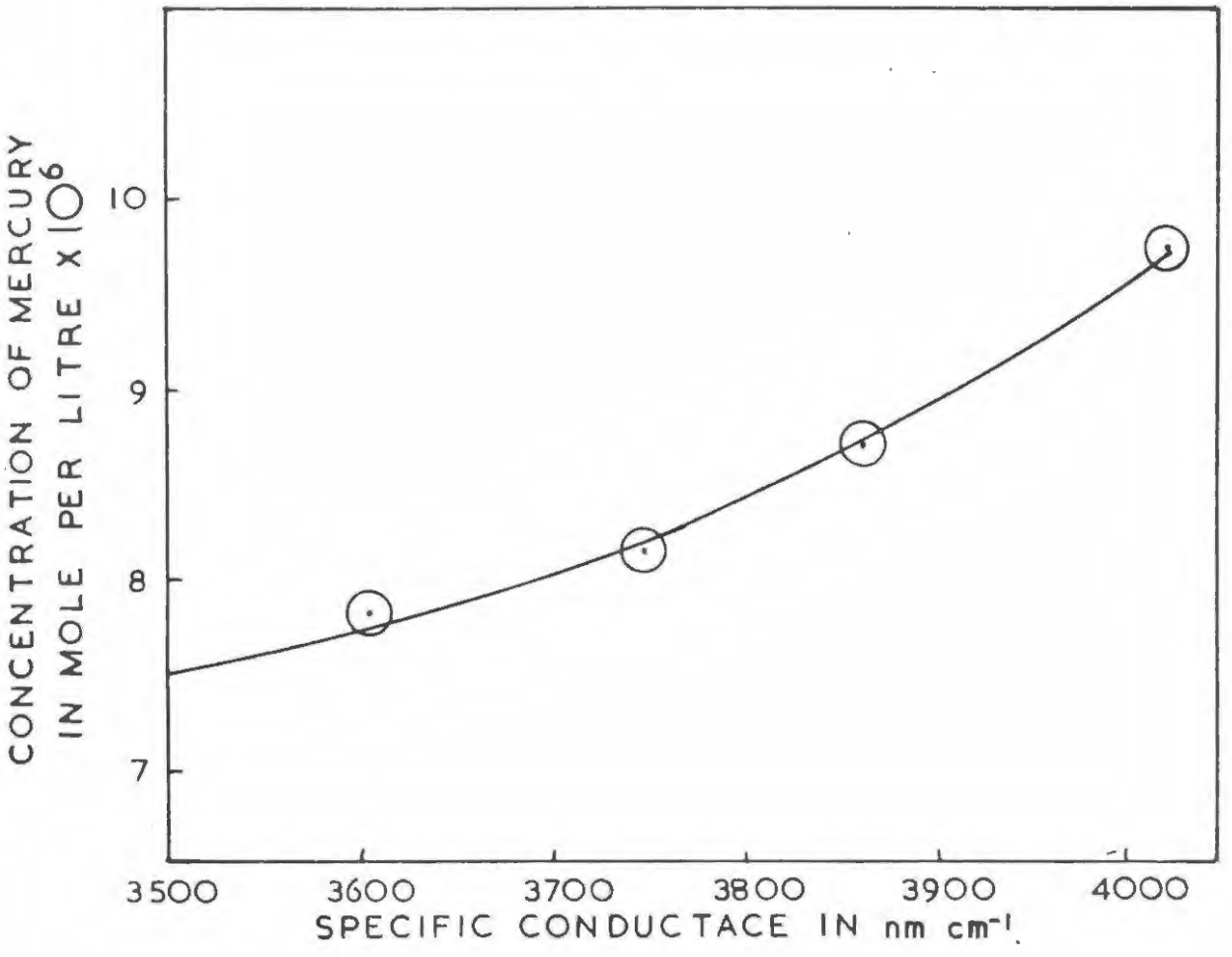
A calibration curve was obtained from the dithizone extracts of four standard mercuric chloride solutions of different known concentrations. The entrance and exit slits of the spectrophotelometer were set so that

a maximum scale deflection was obtained on the galvanometer when the extract of the lowest mercury concentration was in the light beam. The differences in the galvanometer readings between this extract and the others (the more concentrated ones) were determined and a graph of these differences against the mercury concentration was plotted. Hence if the difference in the galvanometer readings of the low known standard and any solution of unknown mercury content were determined, the mercury concentration of that solution could be read off from the calibration curve.

After a number of preliminary determinations of the concentration of mercury in a saturated calomel solution (filtered as described in section 5.22) it became apparent that the results depended on the conductance of the solution at the time when the calomel sample was withdrawn from the conductance cell. Extracts of saturated calomel solution were hence taken from the cell at suitable time intervals and the specific conductance of the solution at the time noted.

It was observed that after each extract was made from the conductance cell the rate at which the conductance of the remaining solution in the cell rose with time increased. On determining the mercury contents of the different extracts it was found that the mercury

FIG. 11. GRAPH OF MERCURY CONCENTRATION AGAINST SPECIFIC CONDUCTANCE FOR SATURATED CALOMEL SOLUTION AT 25° C.



concentration increased as the conductance of the solution did. A typical plot of specific conductance against mercury concentration is given in fig. 11. The graph was found to be curved, which was put down to the observed fact that the rate at which the conductance of the solution, and hence the rate at which the concentration of the mercury rose, increased with each extraction. From the graph the concentration of mercury at the specific conductance 3505 nm/cm. (the corrected value of K_{cal} at 25°C) was estimated by extrapolation.

It was found that the calomel solution extracts deteriorated, the mercury concentration decreasing, slowly on standing. When, however, the solutions were acidified with a few drops of 6N HCl no appreciable change in the mercury concentration was observed even after standing for a week. All calomel solutions were hence acidified immediately after extraction from the conductance cell and kept in stoppered Pyrex test tubes. The effect of the type and concentration of the acid added to the calomel solution was studied by adding to samples of filtered calomel solution different amounts of hydrochloric and nitric acid and then determining the concentration of mercury present. It was found that the addition of excess acid above 2 drops of 6N HCl had no effect on the results. Using the corrected

values for Sillén's equilibrium constants (see section 7.1) it was shown by calculation that when 12 ml. of calomel solution was acidified with 2 drops of 6N HCl (these quantities being the ones used in this work) virtually all the mercury in solution was present as $HgCl_2$, the concentrations of $Hg(OH)_2$ and Hg_2OH^+ being of the order 6×10^{-18} and 1×10^{-15} mole/litre respectively. As a check on this some calomel solution was treated with chlorine water, which would oxidise all mercurous mercury present to the mercuric state. (excess chlorine was driven off by boiling). No observable change in the mercury concentration as a result of this treatment was found. As the mercury in the acidified calomel extracts was present as $HgCl_2$ the standard solutions were therefore prepared from A.R. $HgCl_2$. (Section 5.32).

Since it was possible that very fine or colloidal particles of solid Hg_2Cl_2 might have passed through the sintered-glass filter several experiments were carried out in which the calomel solution was filtered through a film of nitrated cellulose. The sintered-glass pad H of the filter F (see fig. 10.) was covered with a dilute collodion solution. (nitrated cellulose dissolved in an ether-alcohol mixture). On the evaporation of the solvent a thin film of cellulose was deposited on the pad H.

Such a film acts as an excellent filter and should hold back all fine solid particles. It was found in practice that a freshly deposited cellulose pad absorbed mercury from the calomel solution when it was drawn through the pad. After drawing through approximately 10 ml. of solution, however, the pad appeared to become saturated and no longer absorbed mercury. This effect was shown by drawing through the filter successive aliquots of known standard $HgCl_2$ solution and determining the mercury concentrations after the filtration. The results obtained by filtering the calomel solution through a "saturated" cellulose film were no different from those previously determined by filtration directly through the sintered-glass disc.

As stated in section 3.41, the addition of pure mercury to conductance water did notalter the conductance of that water. On testing this water, after it had been well boiled with nitric acid to convert any mercury present to the soluble nitrate, with the dithizone reagent no appreciable change in colour of the reagent could be detected. The solubility of metallic mercury in conductance water was hence estimated to be less than 1×10^{-7} mole/litre. It was therefore assumed that the value obtained for the concentration of mercury in solution in the saturated calomel

solution did not include any metallic mercury which was present in the conductance cell due to the equilibrium

$$Hg^{2+} + Hg = Hg_2^{2+}.$$

The colours of the mercury-dithizone extracts were found to deteriorate slowly. After standing for two hours the results obtained on repeating the determinations with the same dithizone extracts were observed to be about 1 to 2% lower than before. Since, however, the work (dithizone extraction and absorption measurements) on a set of calomel and standard mercuric chloride solutions was normally completed in approximately 30 minutes the deterioration of the colour of the extracts was ignored; the accuracy of the determination itself was approximately 1%.

The results obtained for the concentration of mercury are given below in table 4.

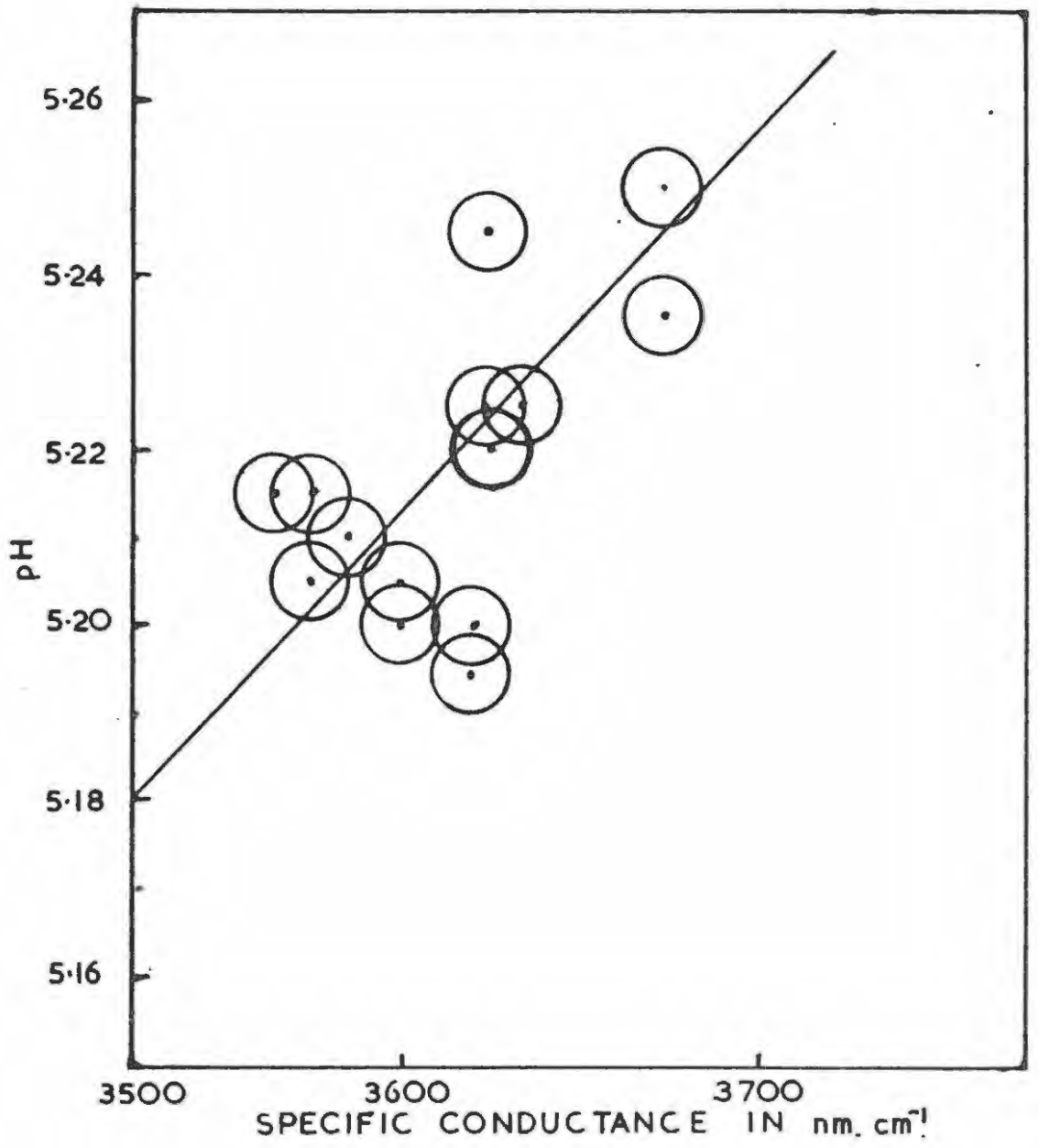
Table 4. Concentration of Mercury in a Saturated Calomel Solution at 25°C.

Determination No.	Hcal at time of extraction.	$m_{Hg} \times 10^6$	$m_{Hg} \times 10^6$ corrected for acid added.	$m_{Hg} \times 10^6$ at Hcal =3505 nm/cm.
1	3605	7.7	7.8	7.6
	3750	8.1	8.2	
	3865	8.7	8.8	
	4025	9.7	9.8	

Determination No.	Hal at time of extraction.	$m_{Hg} \times 10^6$	$m_{Hg} \times 10^6$ corrected for acid added.	$m_{Hg} \times 10^6$ at Hal. = 3505 nm/cm.
	3640	7.7	7.8	
	3675	8.0	8.1	
	3725	8.0	8.1	
2	3885	8.55	8.65	7.4
	3965	9.3	9.4	
	4020	9.3	9.4	
	3635	7.4	7.5	
	3700	7.45	7.55	
3	3840	8.0	8.1	7.2
	3930	8.65	8.75	
	4010	9.0	9.1	
	3590	7.4	7.5	
	3705	7.7	7.8	
4	3820	7.95	8.05	7.3
	3925	8.6	8.7	
	3590	7.5	7.6	
	3630	7.7	7.8	
5	3700	8.05	8.15	7.4
	3840	8.35	8.45	
	4010	9.0	9.1	

The concentration of mercury in a saturated calomel solution at 25°C was hence taken to be $(7.4 \pm 0.2) \times 10^{-6}$ mole/litre.

FIG. 12. GRAPH OF pH AGAINST SPECIFIC CONDUCTANCE FOR SATURATED CALOMEL SOLUTION AT 25° C.



6. FURTHER CONSIDERATIONS OF THE pH OF THE SATURATED CALOMEL SOLUTION.

The work on the concentration of mercury present in the calomel solution was done after the pH determinations, and when the former had revealed that the concentration of mercury in solution depended on the conductance of the solution it was very probable that the hydrogen ion concentration too was dependent on $\mathcal{H}_{cal.}$. A plot of the available pH readings against the value of $\mathcal{H}_{cal.}$ at the time when the calomel solution was transferred over into the pH cell is given in fig. 12. From the plot it seems apparent that the pH rises (i.e. H^+ ion concentration decreases) with increasing conductance.

Using the estimated values of the equilibrium constants (see section 7.1) for the equilibria existing in a calomel solution, together with an approximate value of the hydrogen ion concentration, it was shown by calculation that

$$\frac{d\, m_{Hg_T}}{d\, m_{H^+}} < 0 \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (20)$$

$$\frac{d\, \mathcal{H}_{cal.}}{d\, m_{H^+}} < 0 \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (21)$$

$$\frac{d\, \mathcal{H}_{cal.}}{d\, m_{Hg_T}} > 0 \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (22)$$

where m_{Hg_T} is the total concentration of mercury in solution. The fact that the differential coefficient (21)

was negative verified the deduction obtained from fig. 12 that the H^+ion concentration decreased with increasing conductance of the calomel solution. A straight line was therefore drawn through the available points and the value of the pH at κ_{cal} = 3,505 nm/cm. was estimated by extrapolation. The extrapolated value of the pH was found to be 5.18 ± 0.01 which corrected (see section 4.43) came to 5.085±0.01. Therefore the H^+ion concentration was 8.2 ± 0.1 x 10^{-6} mole/litre.

The accuracy of the extrapolation was, however, limited as no pH determinations were carried out for calomel solutions which had specific conductances higher than 3600 nm/cm. and hence there was not sufficient spreading of points to enable a more accurate extrapolation to be made.

7.0 DISCUSSION AND CONCLUSIONS.

The interpretation of the experimental results lead to some surprising conclusions. The low value of 5.085 for the pH of a saturated calomel solution, corresponding to a hydrogen ion concentration of 8.2×10^{-6} mole/litre, indicated that hydrolysis of the cations occurred to a large extent. Also, since the OH^- ion concentration must be of the order 10^{-9} mole/litre and those of $HgCl_3^-$ and $HgCl_4^=$ were shown to be even smaller than this (section 7.1), the only anion present in any appreciable quantity was Cl^-.

The equivalent conductance of HCl at the concentration 8.4×10^{-6} mole/litre (the approximate concentration of ions in a saturated calomel solution) was calculated from the Onsager Equation

$$\Lambda = \Lambda_o - (A + B\Lambda_o)\sqrt{c} \qquad \ldots\ldots\ldots (23)$$

where Λ_o = Equivalent conductance at infinite dilution

Λ = Equivalent conductance at concentration c

and A and B are constants.

Λ_{HCl} at $c = 8.4 \times 10^{-6}$ mole/litre was found to be 425.6. The conductance due to the HCl in the saturated calomel solution was hence

$$\gamma_{HCl} = \frac{8.2 \times 10^{-6} \times 425.6}{1000}$$

$$= 3490 \text{ nm/cm.}$$

Thus the mercury-containing ions were only responsible for about 15 nm/cm. of the observed specific conductance of 3,505 nm/cm!

It was instructive to calculate the expected concentrations of the various ions present from the equilibrium constants and the conductivity. It was, however, first necessary to estimate the values of these constants at infinite dilution from Sillén's figures for ionic strength 0.5.

7.1. ESTIMATION OF THE THERMODYNAMIC EQUILIBRIUM CONSTANTS OF THE EQUILIBRIA EXISTING IN AN AQUEOUS CALOMEL SOLUTION AT 25°C.

The equilibria existing in a saturated calomel solution are

(1) $Hg_2Cl_{2(s)} = Hg_2^{2+} + 2Cl^-$

(2) $Hg^{2+} + Hg_{(s)} = Hg_2^{2+}$

(3) $Hg^{2+} + Cl^- = HgCl^+$

(4) $Hg^{2+} + 2Cl^- = HgCl_2$

(5) $Hg^{2+} + 3Cl^{-} = HgCl_3^{-}$

(6) $Hg^{2+} + 4Cl^{-} = HgCl_4^{=}$

(7) $Hg_2^{2+} + H_2O = Hg_2OH^{+} + H^{+}$

(8) $Hg^{2+} + H_2O = HgOH^{+} + H^{+}$

(9) $Hg^{2+} + 2H_2O = Hg(OH)_2 + 2H^{+}$

Using the electrometric methods Sillén and his co-workers (12) studied all the above equilibria and evaluated the equilibrium constant of each. Their values, given below in table 5 were, however, only valid under the conditions of their experiments, namely, 25°C and total ionic strength 0.5.

Table 5.

Equilibrium No.	Equilibrium constant (k_i)
(1)	$(1.32 \pm 0.03) \times 10^{-17}$
(2)	129.2 ± 1.0
(3)	$(5.45 \pm 0.23) \times 10^{6}$
(4)	$(1.65 \pm 0.10) \times 10^{13}$
(5)	$(1.2 \pm 0.5) \times 10^{14}$
(6)	$(1.2 \pm 0.2) \times 10^{15}$
(7)	$(1.25 \pm 0.75) \times 10^{-5}$
(8)	$(2.0 \pm 0.3) \times 10^{-4}$
(9)	$(5.0 \pm 0.6) \times 10^{-7}$

Approximate calculations using the above constants showed that the concentrations of the $HgCl_3^-$ and $HgCl_4^=$ ions were of the order 1×10^{-10} and 5×10^{-15} mole/litre respectively. The equilibria (5) and (6) were therefore ignored in this work.

The thermodynamic equilibrium constants (K_i) could be obtained from Sillén's equilibrium constants (k_i) if the values of the activity coefficients (γ_i) of all the ions and molecules present in a calomel solution were known at ionic strength $\mu = 0.5$. The determination of single ionic activity coefficients is, however, impossible and so to overcome this difficulty the thermodynamic constants were estimated as follows:

Consider equilibrium no. (2).

$$K_2 = \frac{a_{Hg_2^{2+}}}{a_{Hg^{2+}}}$$

$$= \frac{m_{Hg_2^{2+}} \times \gamma_{Hg_2^{2+}}}{m_{Hg^{2+}} \times \gamma_{Hg^{2+}}}$$

where a and m denote activity and molality respectively. Hence at $\mu = 0.5$.

$$K_2 = k_2 \frac{\gamma_{Hg_2^{2+}}}{\gamma_{Hg^{2+}}} \qquad \ldots\ldots\ldots\ldots\ldots (24)$$

Taking $\gamma_{Hg_2^{2+}} = \gamma_{Hg^{2+}}$, which appears to be a reasonable assumption, the ratio $\gamma_{Hg_2^{2+}} / \gamma_{Hg^{2+}}$ becomes unity and hence

$$K_2 = k_2$$

The above deduction is borne out by the fact that Sillén evaluated k_2 to be 129.2 ± 1.0 and that Forsling, Hietanen and Sillén later estimated K_2 to be 130 ± 10. The value used for K_2 in this work was hence 130 ± 10 as found by Sillén.

Combining the equilibria (2) and (9) we obtain

$$\frac{K_9}{K_2} = \frac{m_{Hg(OH)_2}\, m^2_{H^+}}{m_{Hg_2^{2+}}} \times \frac{\gamma_{Hg(OH)_2}\, \gamma^2_{H^+}}{\gamma_{Hg_2^{2+}}}$$

$$= \frac{k_9}{k_2} \times \frac{\gamma_{Hg(OH)_2}\, \gamma^2_{H^+}}{\gamma_{Hg_2^{2+}}} \quad \text{at } \mu = 0.5\text{m.}$$

$$K_9 = \gamma_{Hg(OH)_2} \frac{k_9 K_2}{k_2} \left(\frac{\gamma^2_{H^+}}{\gamma_{Hg_2^{2+}}}\right) \qquad \ldots\ldots\ldots\ldots (25)$$

From the values of the activity coefficients of neutral molecules such as nitrous oxide, ethane, diactone alcohol and ethyl acetate at $\mu = 0.5$ (37) the value of $\gamma_{Hg(OH)_2}$ was estimated to be 1.10 ± 0.05. The ratio $\gamma^2_{H^+} / \gamma_{Hg_2^{2+}}$ at $\mu = 0.5$ was estimated by extrapolation using the values of this ratio at

different ionic strengths as determined by Bonner and Unietis (38). The ratio was found to be 4.1 ± 0.1. Hence substituting in equation (25)

$$K_9 = \frac{(1.1 \pm 0.05) \times ((5.0 \pm 0.6) \times 10^{-7}) \times (130 \pm 10) \times (4.1 \pm 0.1)}{129 \pm 1}$$

Using the upper limits

$$K_9 = \frac{1.15 \times 5.6 \times 10^{-7} \times 140 \times 4.2}{130}$$

$$= 2.91 \times 10^{-6}$$

and the lower limits

$$K_9 = \frac{1.05 \times 4.4 \times 10^{-7} \times 120 \times 4.0}{128}$$

$$= 1.73 \times 10^{-6}$$

K_9 was hence taken as

$$(2.3 \pm 0.6) \times 10^{-6}$$

Similarly from the equilibria (1) and (9) we obtain

$$K_1 = \frac{k_1 k_9}{K_9} \times \frac{\gamma_{Hg_2^{2+}} \gamma_{Cl^-}^2 \gamma_{Hg(OH)_2} \gamma_{H^+}^2}{\gamma_{Hg^{2+}}}$$

$$= \gamma_{Hg(OH)_2} \frac{k_1 k_9}{K_9} \times \gamma_{\pm HCl}^4 \qquad \ldots\ldots\ldots\ldots (26)$$

assuming $\gamma_{Hg_2^{2+}} = \gamma_{Hg^{2+}}$. $\gamma_{\pm HCl}$ at $\mu = 0.5$ was taken to be 0.76. (37)

Substituting

$$K_1 = \frac{(1.1\pm0.05)\times((1.32\pm0.03)\times10^{-17})\times((5.0\pm0.6)\times10^{-7})\times(0.76)^4}{((2.32\pm0.59)\times10^{-6})}$$

which on evaluation gives 9.08×10^{-19} and 1.26×10^{-18} as the lower and upper limits respectively. K_1 was hence taken as

$$1.08 \pm 0.18 \times 10^{-18}$$

NOTE. If, when calculating the upper and lower limits of an equilibrium constant, the equation includes a quotient of the type k_9/K_9 the values for k_9 and K_9 must both be either the largest or smallest values allowable for these two constants. As can be seen from the evaluation of K_9, for example, the upper limit of K_9 is obtained only by using the upper limit of k_9 in equation (25) and hence it is meaningless to couple with the largest value of K_9 any value of k_9 but the largest one.

From equilibria (4) and (9)

$$K_4 = \frac{K_9 k_4}{k_9} \times \frac{\gamma_{HgCl_2}}{\gamma_{Hg(OH)_2}\,\gamma^2_{H^+}\,\gamma^2_{Cl^-}}$$

$$= \frac{K_9 k_4}{k_9\,\gamma^4_{\pm HCl}} \qquad \ldots\ldots\ldots\ldots (27)$$

assuming $\gamma_{Hg(OH)_2} = \gamma_{HgCl_2}$

Hence

$$K_4 = \frac{((2.32\pm0.59)\times10^{-6}) \times ((1.65\pm0.10)\times10^{13})}{((5.0\pm0.6)\times10^{-7})\times(0.76)^4}$$

$$= (2.28\pm0.45)\times10^{14}$$

The combination of equilibria (9) and (7) yields

$$K_7 = \frac{K_9 k_7}{k_9} \times \frac{\gamma_{Hg_2OH^+}\ \gamma_{Hg^{2+}}}{\gamma_{Hg_2^{2+}}\ \gamma_{Hg(OH)_2}\ \gamma_{H^+}}$$

$$= \frac{K_9 k_7}{k_9\ \gamma_{Hg(OH)_2}} \qquad \ldots\ldots\ldots\ldots (28)$$

assuming $\gamma_{Hg_2^{2+}} = \gamma_{Hg^{2+}}$ and $\gamma_{Hg_2OH^+} = \gamma_{H^+}$

Hence

$$K_7 = \frac{((2.32\pm0.59)\times10^{-6}) \times((1.25\pm0.75)\times10^{-5})}{(1.1\pm0.05) \times ((5.0\pm0.6)\times10^{-7})}$$

$$= (5.8\pm4.1)\times10^{-5}$$

Similarly from (3) and (7)

$$K_3 = \frac{K_7 k_3}{k_7\ \gamma_{\pm HCl}^2} \qquad \ldots\ldots\ldots\ldots (29)$$

assuming $\gamma_{Hg_2^{2+}} = \gamma_{Hg^{2+}}$ and $\gamma_{HgOH^+} = \gamma_{HgCl^+}$

$$K_3 = \frac{((5.81\pm4.1)\times10^{-5}) \times ((5.45\pm0.23)\times10^{6})}{((1.25\pm0.75)\times10^{-5}) \times (0.76)^2}$$

$$= (3.98\pm0.88)\times10^{7}$$

Finally, from (8) and (3)

$$K_8 = \frac{K_3 k_8 \gamma^2_{\pm HCl}}{k_3} \qquad \ldots\ldots\ldots (30)$$

assuming $\gamma_{HgOH^+} = \gamma_{HgCl^+}$

$$K_8 = \frac{((3.98\pm0.88)\times10^{7}) \times ((2.0\pm0.3) \times 10^{-4}) \times (0.76)^2}{((5.45\pm 0.23) \times 10^{6})}$$

$$= (8.6 \pm 2.8) \times 10^{-4}$$

The above results are tabulated below in table 6.

Table 6.

Equilibrium No.	k_i (at $\mu = 0.5$)	K_i (corrected to $\mu = 0$)
(1)	$(1.32\pm0.03)\times10^{-17}$	$(1.08\pm0.18)\times10^{-18}$
(2)	129.2 ± 1.0	130 ± 10
(3)	$(5.45\pm0.23)\times10^{6}$	$(3.98\pm0.88)\times10^{7}$
(4)	$(1.65\pm0.1)\times10^{13}$	$(2.28\pm0.45)\times10^{14}$
(5)	$(1.2\pm0.5)\times10^{14}$	-
(6)	$(1.2\pm0.2)\times10^{15}$	-
(7)	$(1.25\pm0.75)\times10^{-5}$	$(5.8\pm4.1)\times10^{-5}$
(8)	$(2.0\pm0.3)\times10^{-4}$	$(8.6\pm2.8)\times10^{-4}$
(9)	$(5.0\pm0.6)\times10^{-7}$	$(2.3\pm0.6)\times10^{-6}$

The value of K_1 as estimated from Sillén's constants was thus found to be $1.08 \pm 0.18 \times 10^{-18}$. This

figure agrees reasonably well with Brodsky's value, 1.15×10^{-18}.

Now, in addition, K_1 may be calculated from the relation

$$-E^{o}_{Hg_2Cl_2} = -E^{o}_{HgHg_2^{2+}} + \frac{RT}{2F} \ln Ks \qquad \ldots\ldots\ldots\ldots (30)$$

where E^o denotes Standard Electrode potential and Ks = Solubility Product = K_1. The values of $E^{o}_{Hg_2Cl_2}$ and $E^{o}_{Hg\,Hg_2^{2+}}$ have been accurately determined by electrometric measurements. Hills and Ives (32) found $E^{o}_{Hg_2Cl_2}$ to be -0.26796 ± 0.00001 volt, while Bonner and Unietis (38) recently evaluated $E^{o}_{HgHg_2^{2+}}$ to be -0.7969 ± 0.0001 volt. Substituting these values in equation (30) and using the most recent figures for the Faraday F and the Gas constant R (39) we obtain

$$\log Ks = \frac{-2 \times 96{,}495 \times (0.5289 \pm 0.0001)}{2.3026 \times 8.3166 \times 298.16}$$

$$= -17.877 \pm 0.003$$

whence

$$Ks = K_1 = 1.32 \pm 0.01 \times 10^{-18}$$

Now, as the above value of K_1 was derived from accurately determined data whereas the figure

$1.08 \pm 0.18 \times 10^{-18}$ was obtained by a method of approximation, it was assumed that the value $1.32 \pm 0.01 \times 10^{-18}$ was the correct one. In the calculations to follow hence, $K_1 = (1.32 \pm 0.01) \times 10^{-18}$ was used. The values of K_2 to K_9 used were as given in table 6.

7.2. ESTIMATION OF THE CONCENTRATIONS OF THE IONIC AND MOLECULAR SPECIES PRESENT IN A SATURATED SOLUTION OF CALOMEL AT 25°C.

This complex problem was tackled by following the method of successive approximation. The procedure was:-

(a) Reasonable values of the concentrations of the H^+ and Cl^- ions were assumed - in the neighbourhood of 8.2×10^{-6} mole/litre.

(b) The concentration of Hg_2^{2+} ions was calculated.

$$c_{Hg_2^{2+}} = \frac{K_1}{c^2_{cl^-}}$$

$$\text{or } m_{Hg_2^{2+}} = \frac{K_1}{m^2_{cl^-}} \qquad \ldots\ldots\ldots (31)$$

(In all these calculations the solutions are sufficiently dilute to allow molarities (c_{cl^-}) and molalities (m_{cl^-}) to be used interchangeably and activity coefficients to be taken as unity).

Similarly the following were calculated

(c) $$m_{Hg^{2+}} = \frac{m_{Hg_2^{2+}}}{K_2} \quad \ldots\ldots\ldots (32)$$

(d) $$m_{HgCl^+} = K_3 m_{Hg^{2+}} \cdot m_{Cl^-} \quad \ldots\ldots\ldots (33)$$

(e) $$m_{Hg_2OH^+} = \frac{K_7 m_{Hg_2^{2+}}}{m_{H^+}} \quad \ldots\ldots\ldots (34)$$

(f) $$m_{HgOH^+} = \frac{K_8 m_{Hg^{2+}}}{m_{H^+}} \quad \ldots\ldots\ldots (35)$$

(g) The total positive charge ($c\sigma$) present in a saturated calomel solution was then evaluated

$$c\sigma = 2m_{Hg_2^{2+}} + 2m_{Hg^{2+}} + m_{HgCl^+} + m_{Hg_2OH^+} + m_{HgOH^+} \quad \ldots\ldots (36)$$

Since Cl^- is the only significant anion $c\sigma$ was the concentration of Cl^- ions equivalent to all the cations except H^+ ions. The ionic components of the solution could hence be regarded as a mixture of HCl at concentration m_{H^+} and the chlorides of the mercury-containing ions at total concentration $c\sigma$ equivalents/litre.

We now require the conductivity of this mixture to be equal to the observed value 3,505 nm/cm. The equivalent conductance of HCl at the concentration 8.4×10^{-6} mole/litre was found to be 425.6 (see section 7.0), λ_{H^+} and λ_{Cl^-} being 349.5 and 76.1 respectively. Kohlrausch estimated the equivalent

conductance of the Hg_2^{2+} ion to be 60 and as no values were available it was assumed that the ionic conductances of the Hg_2^{2+} as well as the Hg^{2+}, $HgCl^+$, $HgOH^+$ and Hg_2OH^+ ions were approximately 60. Since, however, these ions are responsible for less than 0.5% of the total conductance, the lack of accurate knowledge of the equivalent conductances is not serious. We have hence for the calomel solution that

$$\frac{m_{HCl}\,\Lambda_{HCl}}{1000} + \frac{c\sqrt{}\,\lambda_{Cl^-}}{1000} + \frac{c\sqrt{}\,60}{1000} = \kappa_{cal.} \quad \ldots.(37)$$

where κ_{cal} = specific conductance of the solution = 3,505 nm/cm. Substituting numerical values and remembering that $m_{HCl} = m_{H^+}$

$$0.4256\, m_{H^+} + 0.136 c\sqrt{} = 3{,}505 \times 10^{-6}$$

or

$$m_{H^+} = \frac{3505 \times 10^{-6} - 0.136\, c\sqrt{}}{0.4256} \quad \ldots\ldots. (38)$$

Hence the next steps were:

(h) A better approximation of m_{H^+} was calculated by means of equation(38).

(i) A better value of m_{Cl^-} was then obtained by using the condition of electrical neutrality,

$$m_{H^+} + c\sqrt{} = m_{Cl^-} \quad \ldots\ldots\ldots (39)$$

(j) With these new values the whole procedure (b) to (i) was repeated until the figures for m_{H^+} and m_{Cl^-} were self consistent.

By the above procedure self consistent values of the concentrations were found using both the maximum and the minimum figures for the equilibrium constants from table 6. The values obtained are given below in table 7.

Table 7.

m	$10^6 m_{H^+}$	$10^6 m_{Cl^-}$	$10^8 m_{Hg_2^{2+}}$	$10^{10} m_{Hg^{2+}}$	$10^8 m_{HgCl^+}$
max.	8.21	8.46	1.92	1.7	5.57
min.	8.13	8.30	1.82	1.2	3.33

m	$10^8 m_{Hg_2OH^+}$	$10^8 m_{HgOH^+}$	$10^6 c\sigma$	$\Lambda\sigma$ nm/cm.
max.	23.6	1.2	0.34	21
min.	3.6	0.9	0.11	6

The last column gives the total conductance of the mercury-containing ions.

The values found in this way for m_{H^+} corresponded to a pH of 5.088 ± 0.002. This was in excellent agreement with the extrapolated value of 5.085 ± 0.01 which was obtained from the experimental results. (See section 6).

The total mercury content of a saturated calomel solution could also be evaluated if the concentrations of the two unionised species, $HgCl_2$ and $Hg(OH)_2$, were calculated from the relative equilibrium constants.

$$m_{HgCl_2} = K_4 \cdot m_{Hg^{2+}} \cdot m^2_{Cl^-} \quad \ldots\ldots (40)$$

$$m_{Hg(OH)_2} = K_9 \frac{m_{Hg^{2+}}}{m^2_{H^+}} \quad \ldots\ldots (41)$$

Using the maximum and minimum values from table 6 we found that $m_{HgCl_2} = (2.38 \pm 0.75) \times 10^{-6}$ and $m_{Hg(OH)_2} = (5.2 \pm 1.75) \times 10^{-6}$. The total concentration of mercury in solution is given by the sum

$$m_{Hg_2^{2+}} + m_{Hg^{2+}} + m_{HgCl^+} + m_{HgOH^+} + m_{Hg_2OH^+} + m_{HgCl_2} + m_{Hg(OH)_2}$$

$$= (7.79 \pm 2.63) \times 10^{-6} \text{ mole/litre.}$$

This agrees well with the experimental value $(7.4 \pm 0.2) \times 10^{-6}$.

It has hence been shown that the experimentally determined values of the specific conductance, the pH and the mercury concentration, while they lead to the rather surprising conclusion that the predominant constituent of a saturated calomel solution is HCl, were in complete agreement with the work of Sillen and his co-workers at much higher concentrations of

mercury salts.

The above calculations clearly showed that the conductance of a saturated calomel solution was largely due to the HCl present and hence the concentration of HCl was determined within narrow limits by the experimental conductance value, which was thought to be accurate to within 0.15%. The experimental pH value, although it was in good agreement with the value obtained from the conductance, was because of its wider limits, not so restrictive and hence served only as a check on the correctness of the interpretation of the conductance work. The experimentally determined value for the total mercury concentration was on the other hand much more precise than the value $(7.79 \pm 2.63) \times 10^{-6}$ mole/litre estimated from the corrected equilibrium constants. From the experimental figure and the value $m\Gamma = (0.22 \pm 0.12) \times 10^{-6}$, where $m\Gamma = m_{Hg_2^{2+}} + m_{Hg^{2+}} + m_{HgCl^+} + m_{HgOH^+} + m_{Hg_2OH^+}$, it was deduced that the concentration of mercury in solution present as unionised salts ($HgCl_2$ and $Hg(OH)_2$) was

$$(7.4 \pm 0.2) \times 10^{-6} - (0.22 \pm 0.12) \times 10^{-6}$$

$$= (7.2 \pm 0.3) \times 10^{-6} \text{ mole/litre.}$$

Now from the equilibria (7), (8) and (9) (see section 7.1) it is evident that for every OH group in a hydrolised mercury ion there is a hydrogen ion in solution i.e.

$$m_{H^+} = m_{Hg_2OH^+} + m_{HgOH^+} + 2m_{Hg(OH)_2} \quad \ldots\ldots\ldots (42)$$

Substituting the values of m_{H^+}, m_{HgOH^+} and $m_{Hg_2OH^+}$ as obtained from table 7 into the equation above it was found that

$$m_{Hg(OH)_2} = (4.01 \pm 0.07) \times 10^{-6} \text{ mole/litre}$$

It followed at once that

$$m_{HgCl_2} = (7.2 \pm 0.3) \times 10^{-6} - (4.01 \pm 0.07) \times 10^{-6}$$

$$= (3.2 \pm 0.4) \times 10^{-6} \text{ mole/litre.}$$

The above values are well within the range as obtained from equations (40)and (41). The probable values of the concentrations of the ionic and molecular species present in a saturated calomel solution at 25°C are given below in table 8.

Table 8.

Species	Concentration mole/litre
H^+	$(8.17 \pm 0.04) \times 10^{-6}$
Cl^-	$(8.38 \pm 0.08) \times 10^{-6}$

Species	Concentration mole/litre
Hg_2^{2+}	$(1.87 \pm 0.05) \times 10^{-8}$
Hg^{2+}	$(1.45 \pm 0.25) \times 10^{-10}$
$HgCl^+$	$(4.95 \pm 1.62) \times 10^{-8}$
Hg_2OH^+	$(1.36 \pm 1.0) \times 10^{-7}$
$HgOH^+$	$(1.58 \pm 0.66) \times 10^{-8}$
$HgCl_2$	$(3.2 \pm 0.4) \times 10^{-6}$
$Hg(OH)_2$	$(4.01 \pm 0.07) \times 10^{-6}$

7.3. DISCUSSION.

It is of interest to consider in detail the meaning of the figures in table 8. In a saturated calomel solution at 25°C we find that 97.5% of the ionised material is HCl and that only 0.23% of it is mercurous chloride. The HCl is responsible for 99.4% of the conductance of the solution, the remaining 0.6% being due mainly to the Hg_2OH^+ and Cl^- ions. Of the total mercury in solution 97.3% is in the form of un-ionised mercuric salts, 54% of this being $Hg(OH)_2$ and 43% $HgCl_2$. The metallic mercury produced by the reduction

$$Hg_2^{2+} \longrightarrow Hg_{(s)} + Hg^{2+}$$

is precipitated out of the solution.

If hydrolysis did not occur the solubility S and the solubility product K_1 would be related by the simple equation

$$K_1 = m_{Hg_2^{2+}} \cdot m^2_{Cl^-} = S(2S)^2 = 4S^3$$

so that the solubility would have been

$$So = \left(\frac{K_1}{4}\right)^{\frac{1}{3}} \qquad \ldots\ldots\ldots (43)$$

$$= 7.0 \times 10^{-7} \text{ mole/litre.}$$

Due to the actual complicated situation, however, the answer obtained for the solubility depends on how this quantity is defined. If it is defined as the concentration of the mercurous chloride itself in solution, then from table 8, $S_1 = (1.87 \pm 0.05) \times 10^{-8}$ mole/litre. If, on the other hand, it is defined as the number of moles of solid obtained on evaporating down a litre of saturated solution after filtering it, we find, remembering that HCl is volatile,

$$S_2 = m_{Hg_2^{2+}} + m_{Hg^{2+}} + m_{HgCl^+} + m_{AgOH^+} + m_{Hg_2OH^+} + m_{Hg(OH)_2} + m_{HgCl_2}$$

$$= (7.4 \pm 0.2) \times 10^{-6} \text{ mole/litre.}$$

Alternately the solubility y may be determined by taking say xmoles of calomel, equilibrating it with a

litre of water and then determining the number of moles, z, remaining undissolved. y is then defined as equal to x - z. But in the case of calomel it should be noted that for every mercuric atom in the solution one atom of metallic mercury has been precipitated, i.e. $(7.27 \pm 0.5) \times 10^{-6}$ mole of Hg. Thus if the solubility were determined by filtering off the residue and determining the loss of weight the answer would be incorrect.

Expressed in grams per litre the above figures are

$S_o = 3.3 \times 10^{-4}$ g/litre; $S_1 = (8.8 \pm 0.1) \times 10^{-5}$ g/litre

$S_2 = (3.5 \pm 0.1) \times 10^{-3}$ g/litre.

7.4. CRITICISM OF PREVIOUS WORK.

The different values of the solubility (S) found in the literature are given below in table 9.

Table 9. Solubility of Calomel.

Temperature °C	Solubility $\times 10^4$ g/l	Authors.	Date.	Reference No.
18	2.1	Behrend	1893	2
25	4.7	Sherrill	1903	3
20	3.8	Ley and Heimbucher	1904	4

Temperature °C	Solubility x10^4 g/l	Authors	Date	Reference No.
18	21	Kohlrausch	1908	6
24.6	28	Kohlrausch	1908	6

Behrend, Sherrill and Ley and Heimbucher deduced their values of solubility from e.m.f. measurements and these values were therefore really estimates of So made according to equation (43). These figures, therefore, bear no relation to the actual amount of calomel dissolving in a litre of solution.

The work of Kohlrausch calls for some comment. He found the specific conductance of a saturated calomel solution at 24.6°C to be 2,130 nm/cm. as compared with 3,505 nm/cm. at 25°C as determined in the present work.

Kohlrausch obtained his figure by subtracting the conductance of the water, determined separately as 2,200 nm/cm, from the total conductance of the solution, 4,330 nm/cm. He, however, completely underestimated the amount of hydrolysis, estimating only that his result may be in error by as much as 50% due to this cause. The large H^+ ion concentration would repress, not only the ionisation of the water, but also most of the ionisation of the CO_2 with which Kohlrausch's water was saturated at atmospheric

pressure. Hence, by simply subtracting the conductance of the water, Kohlrausch was in effect overcorrecting considerably for the solvent conductance. It is reasonable to estimate that in actual fact the solvent correction for Kohlrausch's calomel solution was only about 830 nm/cm., so that his figures are not necessarily inconsistent with the present ones. The great advantage of using ultra-pure water in conductance work is therefore evident.

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