THE SOLUBILITY OF MERCUROUS CHLORIDE IN WATER AT 25°C

A Thesis Submitted in Part-Fulfilment of the
Requirements for the Degree of Master of Science
of Rhodes University, Grahamstown, South Africa.

BY

DENNIS ALWIN CLUR

January, 1958.

ACKNOWLEDGEMENTS

The author wishes to acknowledge his indebtedness to:

Professor W.F. Barker, B.Sc., Ph.D., F.R.I.C., F.R.S.S. Af., whose interest and guidance throughout the author's career have been deeply appreciated.

Dr E.T. Verdier, M.Sc., (S.A.); Docteur es Sciences Physiques (France), whose assistance, encouragement, and interest throughout this work have been quite invaluable.

Professor J.A. Gledhill, Ph.D., (S.A.), Ph.D., (Yale), for advice and discussion.

Mr F. van der Water, for his skilful assistance with the technical aspects of the work.

Mr D.R. Rosseinsky, M.Sc., and Mr N.P. Finkelstein, M.Sc., for our harmonious collaboration.

The South African Council for Scientific and Industrial Research, for a grant held during this research.

Messrs African Explosives and Chemical Industries Limited, for an A.E. & C.I. Physical Science Scholarship held during the author's undergraduate years.

CONTENTS.

---

1. GLOSSARY OF ABBREVIATIONS AND SYMBOLS.

Below are listed the abbreviations used throughout the text.

A, B	constants in the Debye-Huckel formula.
a_i	activity of ionic species i.
c	molar concentration.
d	density of water.
E	total electromotive force of a cell in absolute volts.
E^o	standard electromotive force.
E_j	liquid junction potential.
F	Faraday.
K	thermodynamic equilibrium constant.
K_w	ionic product of water.
M	molar
m	molal concentration.
mV	millivolts.
N	normal.
nm/cm	nanomho per centimeter. 10^{-9} ohm^{-1} cm^{-1}.
°C	degrees centigrade.
ppm	parts per million.
Q	cell constant.
R	ideal gas constant per mole.
	resistance in ohms.
R_e	extrapolated resistance from resistance-time curve.
rpm	revolutions per minute.
T	absolute temperature.
γ	molal ionic activity coefficient.
κ_{cal}	specific conductance of a saturated mercurous chloride solution.
κ_{H_2O}	specific conductance of water.
Λ_c	equivalent conductance at molar concentration c.
Λ_o	equivalent conductance at infinite dilution.
λ	equivalent ion conductance at infinite dilution.

2

INTRODUCTION

In 1955, Dry and Gledhill, both formerly of this Department, published their paper on the Solubility of Mercurous Chloride in Water at 25°C, (1), and it was originally intended that this thesis should be an extension of the study to cover the temperature range from 5 to 55°C.

A preliminary investigation at 25°C, however, failed to yield results which were consistent with their findings, even though their apparatus and experimental technique were used. In an effort to resolve these difficulties their method of saturating the calomel in the conductance cell was thoroughly investigated, and as this procedure was found to be responsible, it was necessary to evolve an entirely new approach.

The technique finally adopted was to saturate the mercurous chloride solutions by mechanical stirring in siliconed vessels and to carry out the conductance, pH, and total mercury concentration measurements on the filtered solution. This method gave good results, and was free from the many extrapolations prevalent in the original procedure.

As Dry and Gledhill (1) pointed out, the following equilibria are established when mercurous chloride dissolves, as a result of dissociation, hydrolysis, and complex-ion formation:

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

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

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

(4) $Hg^{2+} + 2\,Cl^- \rightleftharpoons HgCl_2$

(5) $Hg^{2+} + 3\,Cl^- \rightleftharpoons HgCl_3^-$

(6) $Hg^{2+} + 4\,Cl^- \rightleftharpoons HgCl_4^{2-}$

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

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

(9) $Hg^{2+} + 2\,H_2O \rightleftharpoons Hg(OH)_2 + 2\,H^+$

The hydrolysis of the mercurous ion is a small effect and it is assumed that only Hg_2OH^+ is formed (2).

A saturated mercurous chloride solution, therefore, contains nine different ionic species, two undissociated compounds, and possibly mercury as well.

Apart from the modified experimental procedure found necessary in the present work, it had to be borne in mind that the equilibrium constants for equilibria (1) to (9) were available only for 25°C (2,3,4). Hence, while Dry and Gledhill's pH measurements were necessary only as a check on the HCl concentration in the saturated solution from conductimetry (1), at other temperatures the pH would have to be independently obtained. Thus a detailed investigation of the factors influencing the accuracy of the pH measurements (notably the liquid junction potential) was undertaken. Similarly, the reliability of the determination of total mercury in solution was checked and improved.

The ultimate object of this research was to determine the concentrations of the various ionic and molecular species present in a mercurous chloride solution saturated at 25°C, using the theoretical approach of Dry and Gledhill (1), and the practical modifications outlined above.

3 SURVEY OF PREVIOUS WORK ON THE SOLUBILITY AND SOLUBILITY PRODUCT OF MERCUROUS CHLORIDE

The solubility of mercurous chloride in water cannot be measured by the conventional methods of analytical chemistry as it is too sparingly soluble. However, electrical, and to a lesser degree optical methods, are ideally suited by virtue of their greater sensitivity, and have been both directly and indirectly used for the elucidation of the problem in the past.

The values emerging from these researches differ considerably; those for the solubility and for the solubility product being equally discordant.

In 1893, Behrend (5) measured the e.m.f. of the chain

$$\mathrm{Hg\text{-}Hg_2Cl_2} \mid \mathrm{KCl_{(0.1N)}} \mid \mathrm{Hg_2(NO_3)_2}\ \ (0.1N)\ ,\ \mathrm{HNO_3} \mid \mathrm{Hg}$$

at 18°C, and calculated the solubility of calomel in pure water to be 7.5×10^{-4} gm/litre. While Ogg (6), in 1898, obtained the value 4.7×10^{-4} gm/litre from the potential of the cell

$$\mathrm{Hg\text{-}Hg_2Cl_2} \mid \mathrm{KCl_{(0.1N)}} \mid \mathrm{Hg_2(NO_3)_2}\ \ (0.1N)\ ,\ \mathrm{HNO_3}\ (0.1N) \mid \mathrm{Hg}$$

Five years later, Sherrill (7) deduced the solubility to be 4.5×10^{-4} gm/litre from his work on the complex formation of mercury halides, and gives the solubility product as 3.5×10^{-18}.

In 1904, Ley and Heimbucher (8), reviewing previous potentiometric work, contended that inconsistent results arose since, due to hydrolysis, the mercurous ion concentration was not accurately defined, and the diffusion potential of the free acid underestimated. In order to overcome these difficulties they used the strongly dissociated perchlorate salt, and having determined its degree of hydrolysis, measured the e.m.f. of the chains

$$\left.\begin{array}{ll}(i) & \mathrm{Hg\text{-}Hg_2Cl_2} \mid \mathrm{KCl_{(0.1N)}} \vdots\ \mathrm{KNO_3}\ (0.1N) \vdots\ \mathrm{Hg_2(ClO_4)_2}\ (0.1N) \mid \mathrm{Hg} \\ (ii) & \mathrm{Hg\text{-}Hg_2Cl_2} \mid \mathrm{KCl_{(1.0N)}} \vdots\ \mathrm{KNO_3}\ (0.1N) \vdots\ \mathrm{Hg_2(ClO_4)_2}\ (0.1N) \mid \mathrm{Hg}\end{array}\right\}$$

at 20°C. They then showed the diffusion potential of the free acid to be negligible, and assuming the saturated solution to be completely dissociated, obtained the somewhat lower value of 3.8×10^{-4} gm/litre for the solubility, and, at ionic strengths of 0.1N and 1.0N respectively, 2.0 and 3.5×10^{-18} for the solubility product.

Brodsky and Scherschewer (9) in their paper, The Solubility Products of Mercurous Halides in Water, also point out that hydrolysis, and oxidation of the mercurous ion, may well be responsible for the inconsistency of the published data.

They measured the e.m.f. of the cell

$$\mathrm{Hg} \;\Big|\; \mathrm{Hg_2\,(NO_3)_2}\ c_o \;\vdots\; \mathrm{KNO_3}\ (\mathrm{satd.}) \;\vdots\; \mathrm{KCl}\ \ c \;\Big|\; \mathrm{Hg_2Cl_2\text{-}Hg}\ ,$$

and having corrected for hydrolysis and diffusion effects, calculated the solubility product of calomel to be 12.2 x 10^{-19} at 26.5°C.

Later, in 1929, Brodsky (10) determined the activity of the mercurous ion in potassium chloride solutions saturated with calomel, from the e.m.f. of the chains

$$\left.\begin{array}{ll} \text{(i)} & \mathrm{Hg} \;\Big|\; \mathrm{Hg_2(NO_3)_2}\ c_n \;\vdots\; \mathrm{KNO_3}\ (\mathrm{satd.}) \;\vdots\; \mathrm{Hg_2(NO_3)_2}\ c' \;\Big|\; \mathrm{Hg} \\ \text{(ii)} & \mathrm{Hg} \;\Big|\; \mathrm{Hg_2(NO_3)_2}\ c_n \;\Big|\; \mathrm{KNO_3}\ (\mathrm{satd.}) \;\vdots\; \mathrm{KCl}\ \ c' \;\Big|\; \mathrm{Hg_2Cl_2\text{-}Hg} \end{array}\right\}$$

On combining this with Harned's value for the activity of the mercurous ion in potassium chloride solutions (11), he was able to correct his above figure to 15.1 x 10^{-19}, and estimated the solubility product of calomel at 25°C to be 11.5 x 10^{-19} by interpolation.

More recently, Christensen (12) determined the solubility product of mercurous chloride in water by the Owen cell method (13), and found it to be 5.3 x 10^{-18} at 25°C. In 1947, Jonsson, Qvarfort, and Sillen (14) calculated the solubility product to be (1.32 ± 0.03) x 10^{-17}, from potentiometric titrations of the mercurous ion with chloride, under the strict experimental conditions of 25°C, a 0.01 molar hydrogen ion concentration, and a total ionic strength of 0.5 molar.

The specific conductance of a saturated calomel solution was first measured in 1890 by Kohlrausch and Rose (15). The salt was precipitated from a mercurous nitrate solution with an excess of hydrochloric acid, and, after several washings a suitable amount was transferred to a small, cylindrical 25 ml flask containing a thermometer between two horizontally opposed platinum electrodes. The cell was then rotated in the thermostat to keep the calomel well stirred, and saturation was reached in half an hour. The resistance of the cell was measured with an alternating current bridge, and the investigation carried out in the dark to prevent the conductance increasing with time.

From their measurements they calculated the specific conductance of a calomel solution saturated at 24.6°C to be 2,130nm/cm. In a later paper, Kohlrausch (16) used this figure to calculate the solubility of calomel in water at 24.6°C as 2.8 mg/litre. However, his results are merely estimates of the general order of the solubility and its temperature dependence. Further, as nothing was known of the conditions pertaining in the solution, he stated that there was a possible uncertainty of 50 per cent in his values.

In 1955, Dry and Gledhill (1) showed that, due to hydrolysis and complex-ion formation, precision conductivity work could not resolve the problem alone, but that it gave an accurate measure of the total ionic concentration in the saturated solution. This, supplemented by hydrogen ion concentration and total mercury measurements, and the use of equilibrium constants determined by Sillen and his co-workers (2,3,4), then yielded the concentrations of the ionic and molecular species existing in the saturated solution, and gave an insight into the process which takes place when mercurous chloride dissolves.

4 THE SPECIFIC CONDUCTANCE OF A SATURATED MERCUROUS CHLORIDE SOLUTION IN WATER AT 25°C

4.1 OUTLINE AND THEORY OF METHOD

Although the classical equation relating the specific conductance of a sparingly soluble salt to its solubility in ultra pure water cannot be used to yield the solubility of mercurous chloride directly, due to hydrolysis and complex-ion formation, the specific conductance is, nevertheless, an excellent measure of the total ionic concentration existing in the saturated solution.

The specific conductance of a saturated calomel solution, κ cal, is given by the following equation.

$$\kappa\ \mathrm{cal} = \frac{1}{1000}\Big\{ (c_{H^+}\lambda_{H^+}) + (c_{Cl^-}\lambda_{Cl^-}) + (c_{Hg_2^{2+}}\lambda_{Hg_2^{2+}}) + (c_{Hg^{2+}}\lambda_{Hg^{2+}}) + (c_{HgCl^+}\lambda_{HgCl^+}) + (c_{HgOH^+}\lambda_{HgOH^+}) + (c_{HgCl_3^-}\lambda_{HgCl_3^-}) + (c_{HgCl_4^{2-}}\lambda_{HgCl_4^{2-}}) \Big\} \quad ....(1)$$

where c denotes the concentration in gram equivalents per litre, and λ the ion conductance at infinite dilution.

κ cal is calculated from the electrical resistance of the saturated solution by means of the following equation:

$$\kappa \text{ cal} = \frac{Q}{R} \qquad \ldots\ldots\ldots(2)$$

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

As the conductance of the electrolyte alone is required, the conductivity of the solvent must be subtracted from the value of κ cal above. Therefore, both the specific conductance of the saturated solution, and that of the conductivity water used as solvent, must be determined in work of this nature.

The Solvent Correction

Theoretically, the only ions present in conductivity water are hydrogen and hydroxyl ions resulting from the ionisation of the water molecule according to the equation:

$$H_2O \rightleftharpoons H^+ + OH^- \qquad \ldots\ldots\ldots(3)$$

For which it is true that

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

where K_w denotes the ionic product of water, and <u>a</u> the activity of the respective ions. Assuming the activity coefficients of the ions to be unity at these low concentrations, the above may be written as

$$K_w = c_{H^+} \cdot c_{OH^-}$$

Therefore,

$$c_{H^+} = c_{OH^-} = 1.004 \times 10^{-7} \text{ molal} = c.$$

Also,

$$\Lambda^\circ_{H_2O} = \lambda_{H^+} + \lambda_{OH^-}$$

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

$\Lambda^{\circ}_{H_2O}$ is the equivalent conductance of water at infinite dilution.

With these values, κ_{H_2O} can be calculated from the equation below:

$$\kappa_{H_2O} = \frac{\Lambda^{\circ}_{H_2O} \cdot c \cdot d}{1000} \qquad \ldots\ldots\ldots(4)$$

where d is the density of water at 25°C. On substituting the values of $\Lambda^{\circ}_{H_2O}$, c , and d in equation (4) the specific conductance of water is given as 55 nm/cm, where 1 nm/cm is equivalent to 1×10^{-9}/ ohm cm.

In practice, however, this value for the conductivity of water has never been obtained : the conductivity of the water used in this research varied between 60 and 90 nm/cm. Hence, 5 to 35 nm/cm of the conductivity was attributed to ions other than H^+ or OH^- present as impurities (17).

It is normal practice to subtract the entire conductivity of the solvent from that of the electrolytic solution. If this were done in the present case, however, over-correction would result. Consider a saturated calomel solution at 25°C which, by virtue of hydrolysis, is of pH 5.125 (1). At this pH only 1.3×10^{-9} gram equivalents per litre ionise, and

$$\kappa_{H_2O} = 0.7 \text{ nm/cm} = 1 \text{ nm/cm approx.}$$

That is, the specific conductance of the water has decreased by 54 nm/cm. Therefore, when using water of say 75 nm/cm in the determination of the conductivity of a saturated calomel solution the solvent correction is not 75, but 75 less 54 i.e. 21 nm/cm. It was assumed that the remaining impurities in the water were unaffected by the calomel.

4.2. DESCRIPTION, STANDARDISATION AND CALIBRATION OF APPARATUS.

4.2.1. Temperature Control Apparatus.

The Constant Temperature Room.

All the apparatus was housed in a constant temperature room run at 24.0 ± 0.1°C. The incoming air was cooled by continuous refrigeration, and the temperature controlled by intermittent heating operated by a thyratron relay (16). The heat was evenly distributed by the wall and room fans.

The Thermostat.

The lagged copper thermostat used was that described by Malan (17), designed for operation at any temperature from 5 to 55°C. The inner bath, in which the conductance cell was suspended, was filled with paraffin. This ensured the complete elimination of the capacitive shunt errors when water is used. A perspex lid was used, as wood showed a tendency to absorb moisture and warp: transparency was an additional advantage.

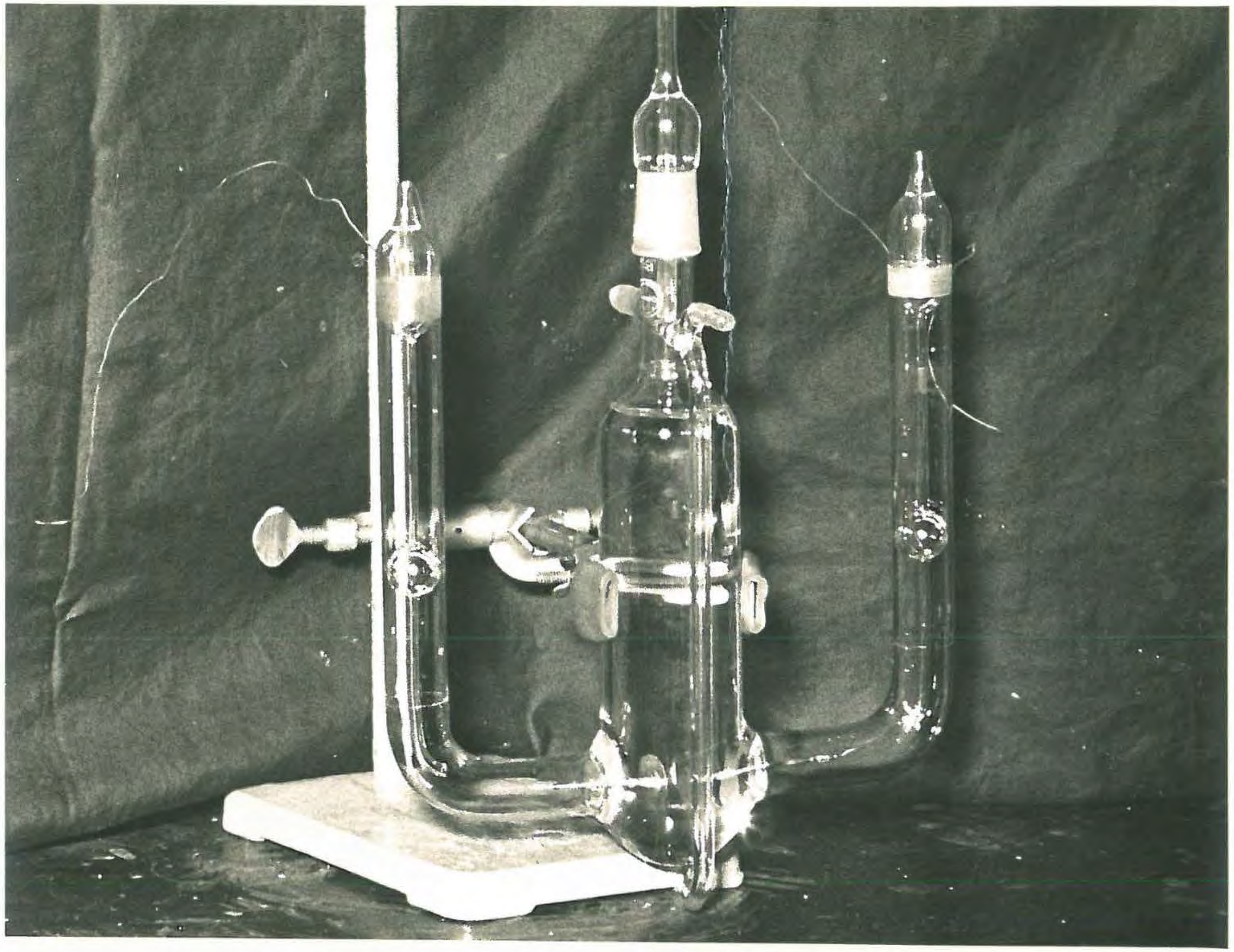
The thermostat temperature was accurately set at 25 ± 0.01°C with the aid of a standard thermometer calibrated by the National Physical Laboratories, England (1955). The corresponding value on a Beckmann differential thermometer was then maintained to ± 0.002°C by an electronic relay circuit controlled by a toluene-mercury thermoregulator, a detailed account of which can be found elsewhere (18).

Efficient stirring of the water thermostat was effected by a paddle stirrer driven at about 150 r.p.m. by a converted gramophone motor. The paraffin in the inner thermostat was kept in circulation by stirring with air equilibrated to the thermostat temperature. The inner thermostat was provided with a wooden lid.

4.4.4. The Conductance Bridge.

The precision conductance bridge used in this work was built in this Department, and described in full elsewhere (18).

PLATE I



THE GLEDHILL
CONDUCTANCE CELL

Briefly, it was constructed on the lines suggested by Luder (19), but with the components so mounted that all controls could be panel operated. The bridge current was generated by a high frequency oscillator, providing any one of five frequencies. An accurate determination of the balance point was made possible by the use of a high gain amplifier, and the aid of an oscilloscope as a null point detector.

The bridge was completely overhauled at the outset of this research to ensure that 10,000 ohms could be measured accurately to 0.1 ohm. The replacement of shielded leads by coaxial cable increased the discrimination to better than 0.5 ohm in 10^4. The oscillator was restandardised, but as the accuracy of the specific conductance of a saturated calomel solution is approximately 0.2 percent, it was deemed unnecessary to recalibrate the bridge resistances which were guaranteed to an accuracy of 0.1 per cent by the manufacturers.

When the bridge was balanced the following relation held (20)

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

where R_4 is the unknown resistance, R_3 the variable arm resistance and $p^2C^2R_3^3$ a capacitance term. However, as the correction $p^2C^2R_3^3$ was found to be negligible in practice, it was ignored, and the bridge, therefore, was direct reading.

Measurements were taken by balancing the bridge with the ratio arms direct and then with them reversed. The oscillator input to the bridge was then reversed and the procedure repeated. The arithmetic mean of the four readings was accepted as the correct resistance.

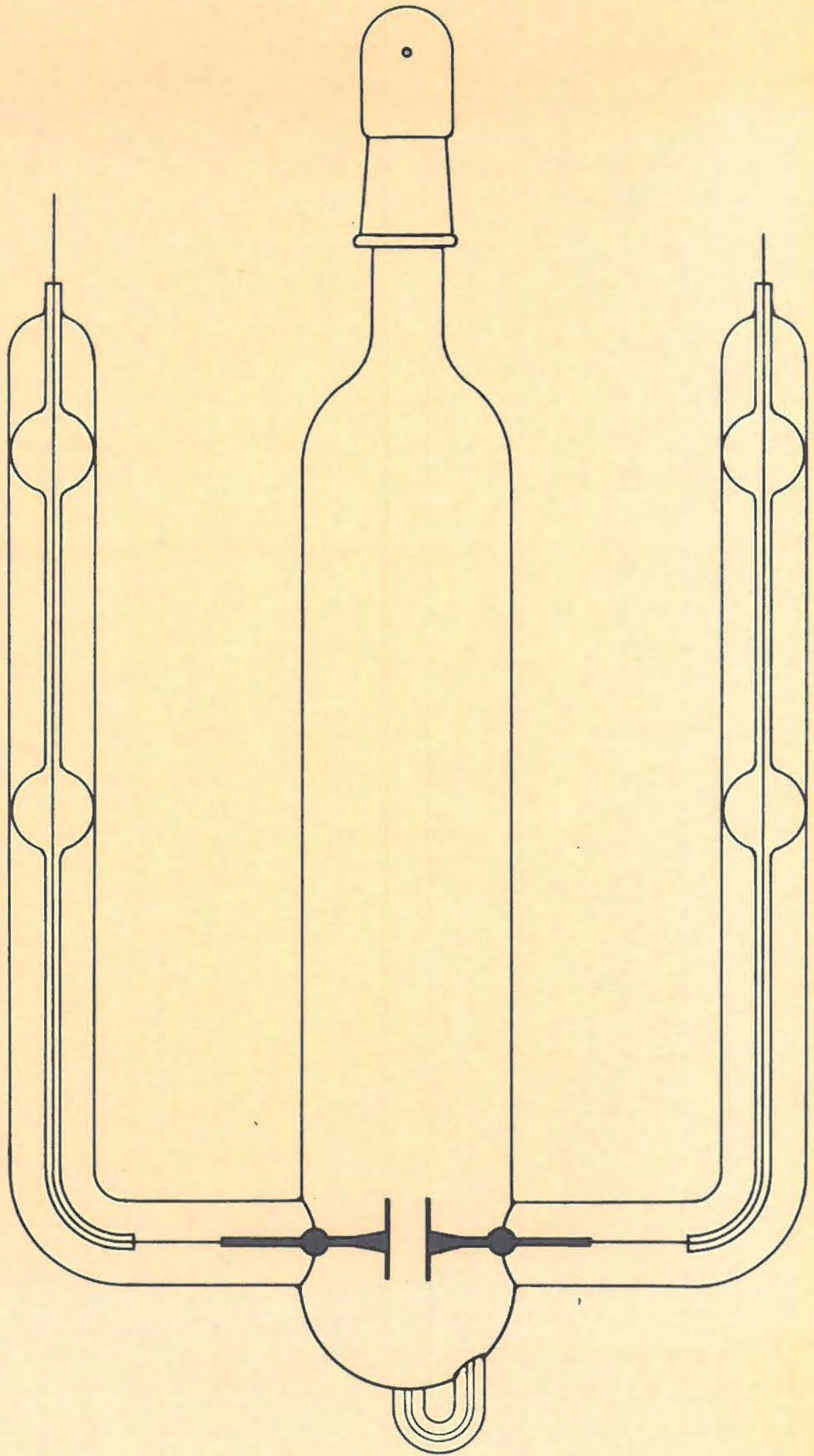
As the solutions used in this research had high resistances, 3.2×10^4 to 1.4×10^6 ohms, the polarisation correction was negligible, and readings were taken at a frequency of 2 kilocycles per second only.

4.2.3. <u>Conductance Cells</u>.

<u>The Gledhill Cell</u>.

The Gledhill Cell, shown in Fig.1, was specially designed in this Department to overcome the Parker Effect (21). By widely separating the electrode leads the capacitive shunt effects responsible are eliminated.

FIG. 1. THE CONDUCTANCE CELL.



The cell was made of pyrex glass to minimise ion exchange between the cell solution and the glass walls, and allowed a stream of nitrogen to be passed through or over the cell contents when suspended in the paraffin thermostat. A closely fitting cap prevented any back diffusion of carbon dioxide into the cell solution.

As a long time was required to leach out a cell after it had contained an electrolytic solution, two cells were in general use, one, with platinised electrodes, for measuring the specific conductance of the saturated calomel solution and the other, with bright platinum electrodes, for the conductance water used.

A detailed description of the cell is given in Gledhill's M.Sc thesis (22).

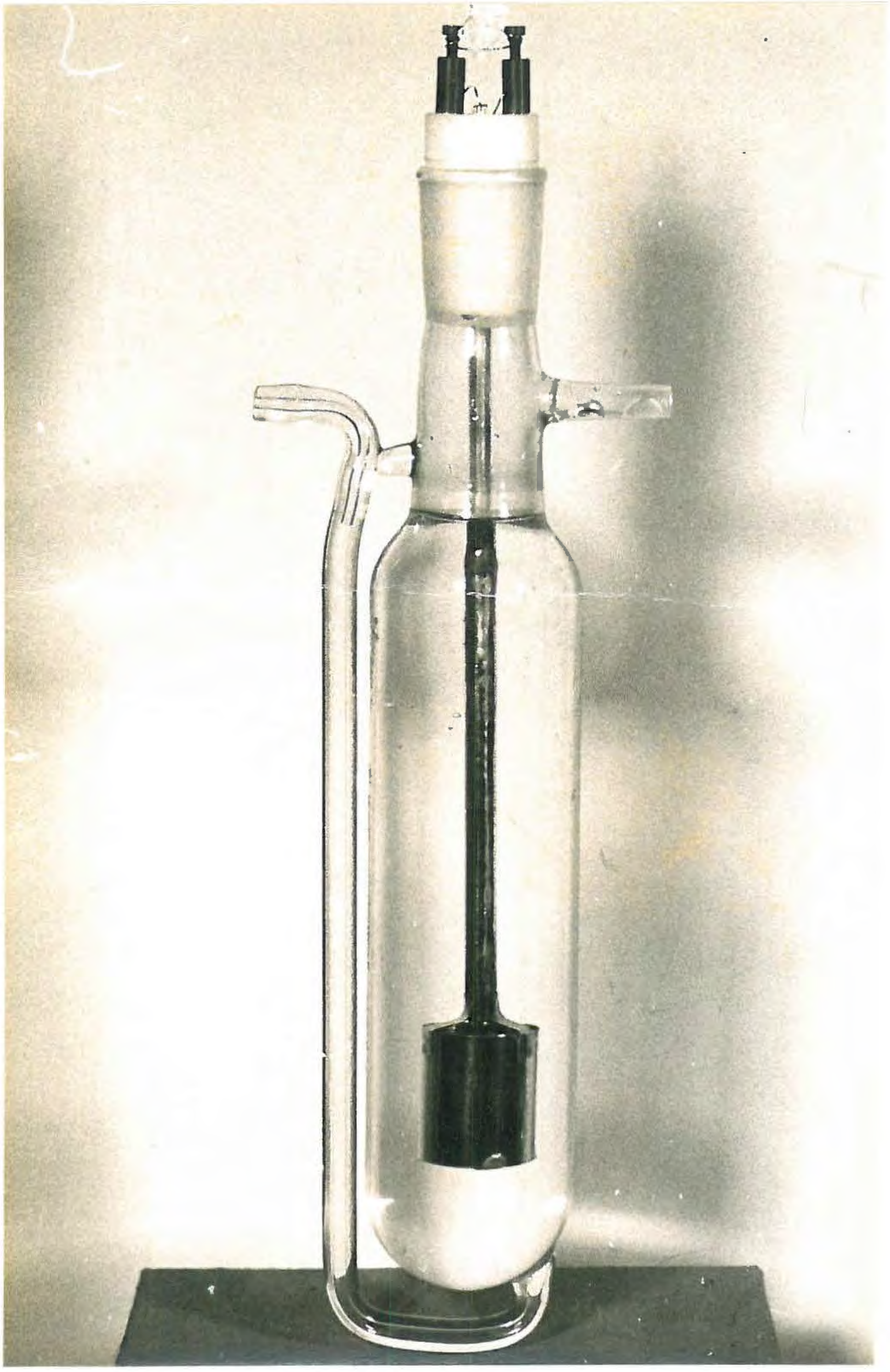
The Dipping Electrodes Cell.

As it was important to investigate the effect of siliconing the cell walls in reducing the solubility of glass and ion exchange with the electrolyte, a conductance cell with dipping electrodes was required. In a cell of this type the leads necessarily pass into the solution, and as Shedlovsky (23) points out, there is then a capacity-resistance shunt across the unknown resistance.

Consequently, the dipping electrodes cell used in this work was designed to overcome this limitation, and was constructed along the lines recommended by Nichol and Fuoss (24).

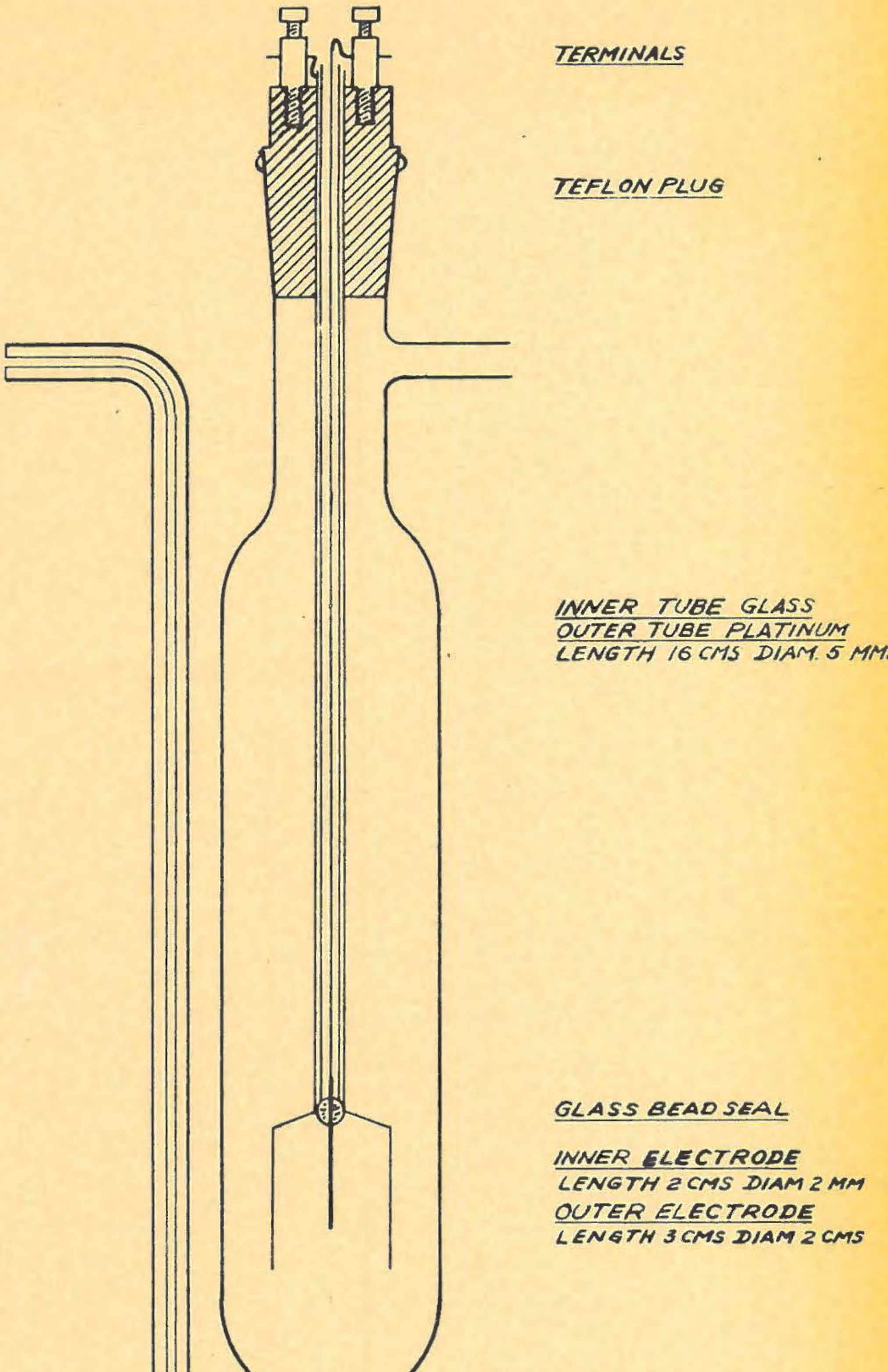
The electrodes, of bright platinum, consisted of a stout rod and a concentric cylinder insulated from one another by a soft glass-platinum seal. The lead to the cylindrical electrode was a platinum tube, which acted as a shield for the rod electrode lead, and was insulated from it by a glass tube. Strips of platinum were gold-soldered across the bottom of the cylindrical electrode, to provide the further electrical shielding necessary to ensure that the resistance was independent of the vertical position of the electrodes with respect to the bottom of the cell.

PLATE II



THE DIPPING ELECTRODES CONDUCTANCE CELL

FIG.2. THE DIPPING ELECTRODES CELL.



The electrode dimensions were calculated to give a cell constant of about 0.12 by means of the approximate equation

$$Q = \frac{1}{2\pi l} \ln \frac{b}{a} \qquad \text{.............. (6)}$$

where Q is the cell constant, l the length of the cylinder, and, a and b, the radii of the inner and outer electrodes.

The electrode assembly was mounted on a teflon plug which was machined to a standard taper so that the electrodes were interchangeable.

The cell vessels were of about 300 ml. capacity, with a standard conical neck to accommodate the electrode assembly. They were designed to allow a stream of nitrogen flow through or over the cell as desired when suspended in the paraffin thermostat. The cell is illustrated in Fig.2.

Cell Constants.

As the Gledhill cells used in this research had been employed by a number of previous workers in this department, their cell constants had been frequently checked and were accurately known to 4 parts in 1.2×10^5.

The accepted cell constants were as follows:

(i) The Electrolyte Cell : 0.11823
(ii) The Conductance Water Cell : 0.10950

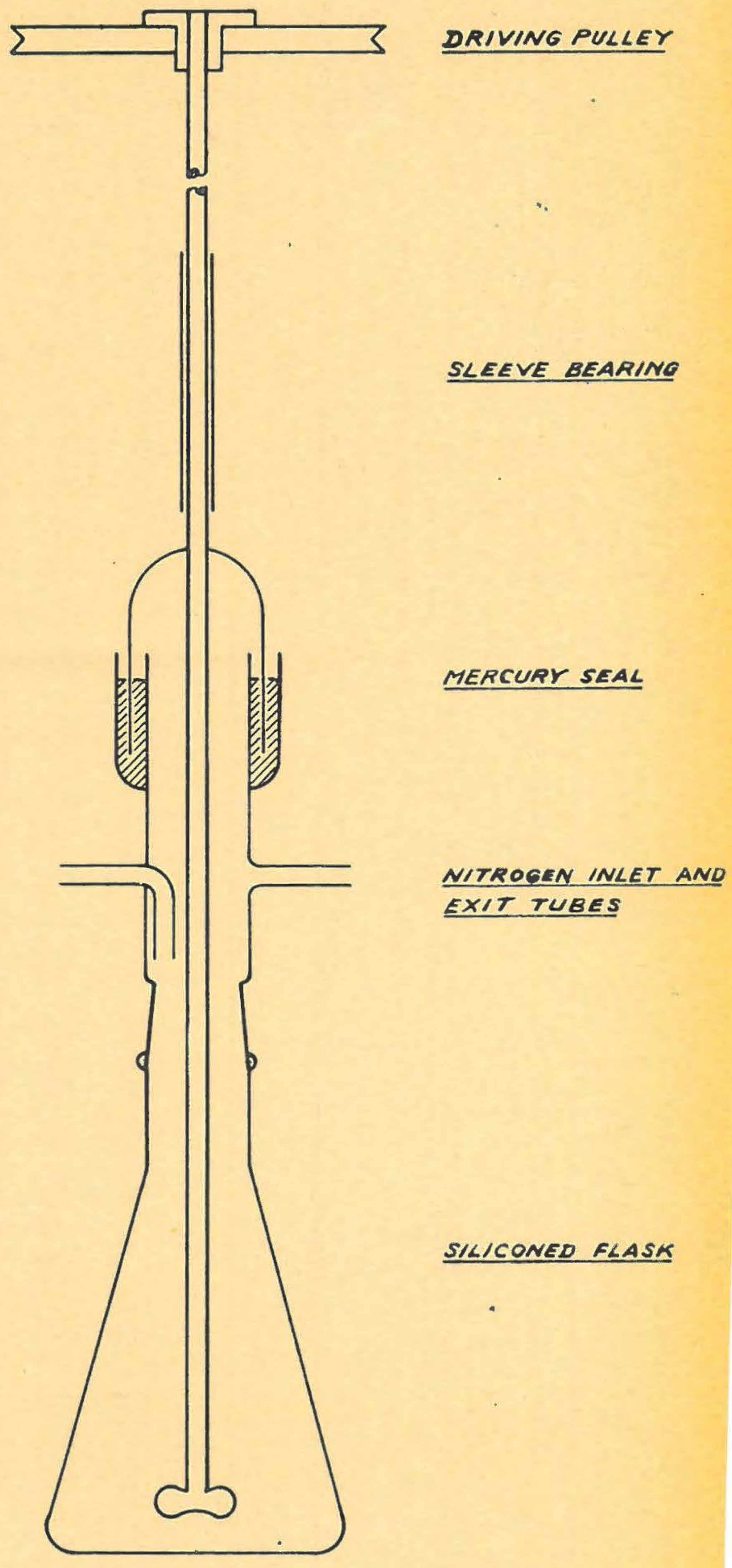
The cell constant of the Dipping Electrodes Cell was not required, but was determined approximately as 0.122.

4.2.4. The Sealed Stirrer.

In order to investigate the effect of saturating calomel solutions by mechanical stirring, a special assembly was designed to operate in an atmosphere of nitrogen.

The apparatus was constructed entirely of pyrex glass, and, as can be seen in the diagram (Fig.3), consisted essentially of an electrically driven paddle stirrer dipping into a conical flask via a mercury seal.

FIG.3. THE SEALED STIRRER



The mercury seal, a novel one, was effected by an inverted cup attached to the stirrer rod revolving in a cylindrical trough of mercury. The construction differed from conventional design in this respect: the stirrer rod bearing, a stout walled glass tube well lubricated with silicone grease, was situated above the mercury seal and not below it. This was done in order to prevent grease, impurities and ground glass from contaminating the solution in the flask below.

The shoulder supporting the trough was attached to the flask by a ground glass joint, and contained glass tubes for flushing out the system with nitrogen before use.

The flask and paddle stirrer were siliconed to counter ion exchange effects during saturation, and the apparatus was put into use after numerous tests had shown that the specific conductance of water was not altered by 24 hours stirring.

The apparatus was designed to stir at 200 r.p.m. when firmly clamped in a water thermostat.

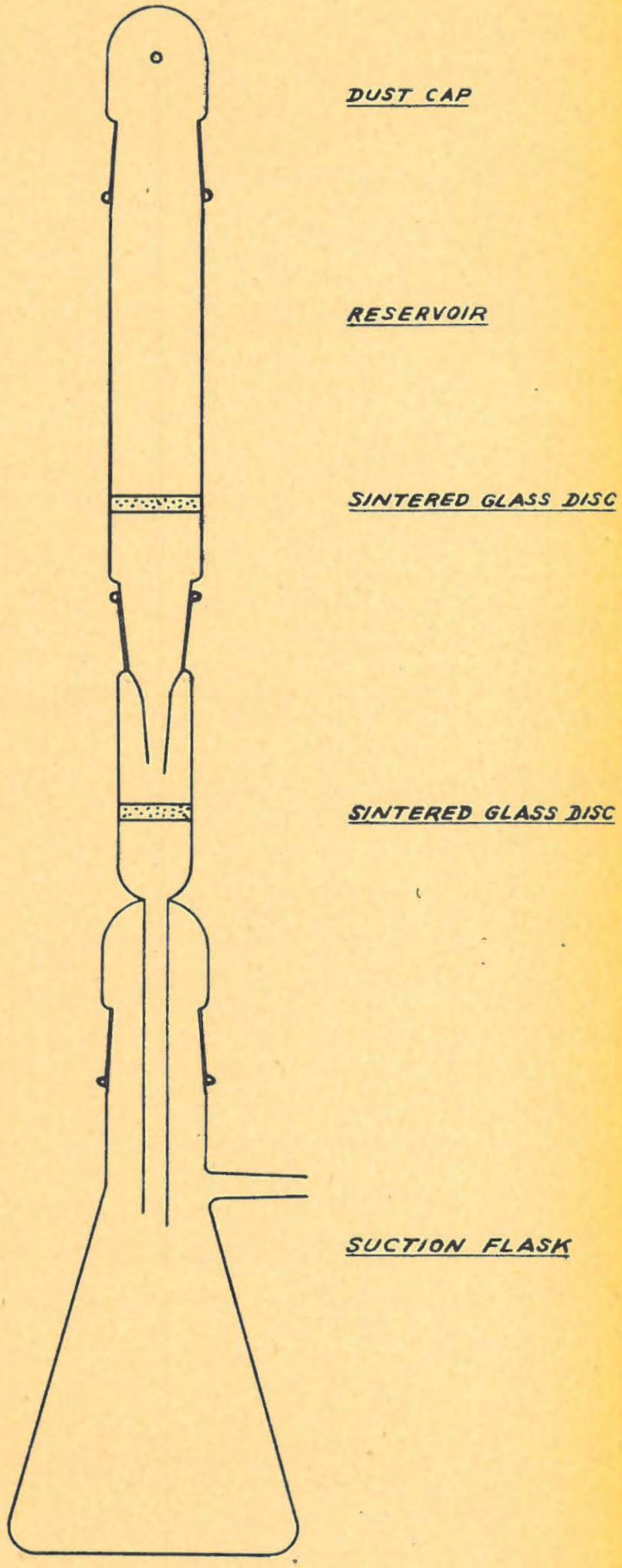
4.2.5. The Double Filter.

The apparatus used to separate the solid calomel from its saturated solution is shown in Fig.4.

It comprised of two filtration units (each embodying a Grade 0 sintered glass disc), and a suction flask fitted together by standard ground glass joints. The upper unit was covered with a glass cap to prevent impurities from entering the system.

After ten days washing with conductance water filtration caused no change in the conductance of the water used, and the filter was then ready for use. The filter was extremely efficient and in no circumstance was solid calomel ever detected in the filtrate.

FIG. 4. THE DOUBLE FILTER



4.3. PREPARATION AND STANDARDISATION OF MATERIALS.

4.3.1. Conductance Water.

It is imperative that the water used for conductivity work be of the highest possible purity to ensure a very small solvent correction.

The conductivity water used throughout this research was obtained from an automatic, recycling conductance water still developed in this laboratory (25). Distilled tap water was distilled in two stages. The first distillation was from alkaline permanganate to remove any organic matter and non-volatile acid impurities. The second was from phosphoric acid to ensure the complete removal of all non-volatile alkaline impurities as well as ammonia.

The "ultra-pure" water prepared in this way had a specific conductance between 60 and 90 nm cm^{-1}.

It was collected and stored in well leached pyrex flasks with ground glass caps, little or no increase in the conductance being observed when the water was kept for several days in this manner. Well steamed out polythene containers were also tried but the water kept in this way deteriorated very rapidly indeed.

The design and construction of the stainless steel kettle used in the first stage of the still presented several difficulties. Originally, a conical boiler was used, but this tended to bump disastrously and was therefore replaced by a squat cylindrical type which ended the trouble. Unless extreme care is taken to prevent overheating while welding the vessel, carbon is vaporised and the composition of the stainless steel changes. This apparently was the case in the construction of the present kettle, as the caustic solution was found to attack the steel with the formation of a black, flakey compound.

It is important, too, that the bottom of the boiler be perfectly flat, as surface irregularities prevent the heater element from being firmly and evenly held, with the result that the heating element frequently burnt out. A lead disc fitted between the base of the kettle and the element seems to have solved the problem.

Violent bumping was encountered in the phosphoric acid boiler, generally after the still had been in operation several days. Various techniques were tried to prevent this; the most successful being the introduction of a glass tube sealed at the upper end.

It was observed that the phosphoric acid became pink in colour when the best water was being produced. The most reasonable theory is that Mn_2O_7 is carried over in the steam from the alkaline permanganate solution, and that the phosphoric acid turns pink only when the organic impurities have been completely oxidised.

4.3.2. The Purification of Nitrogen.

The cells used in this research required a current of nitrogen both to keep the contents well stirred, and to remove all volatile impurities remaining in the water after distillation. It is essential, therefore, that the nitrogen be very carefully purified to ensure that no impurities are introduced from this source.

Cylinder dry nitrogen was passed through concentrated sulphuric acid to dry it and remove ammonia, then through a tube containing metaphosphoric acid and one of soda-lime to free it from ammonia and carbon dioxide respectively. The nitrogen was then thoroughly deoxygenated by passing over reduced copper in an electrically heated silica tube. (The copper turnings were found to be contaminated with traces of oil, and were, therefore, cleaned with repeated washings of redistilled petrol ether.)

The above was carried out well away from the constant temperature room to avoid raising the temperature of the surrounding air.

In the constant temperature room the gas was led into a large pyrex conical flask which acted as a buffer and had a mercury pressure regulator attached. The nitrogen then bubbled through concentrated sulphuric acid to ensure it was dry before passing through the final train of soda-lime tubes, where the last traces of carbon dioxide were removed. Originally, these were followed by a U-tube of meta-phosphoric acid to absorb the remaining traces of ammonia, and a concentrated sulphuric acid bubbler to finally dry the gas and act as a trap for any solid particles. However, the non-deliquescent soda-lime was found to saturate the dry gas passing over it; this water being subsequently absorbed by the meta-phosphoric acid. This difficulty was overcome by dehydrating the soda-lime over silica gel and placing the concentrated sulphuric acid bubbler between the soda-lime tubes and the meta-phosphoric acid. Later in the work the sulphuric acid bubbler was replaced by a U-tube of silica gel to eliminate the possibility of any sulphuric acid vapours passing to the cell. A U-tube of solid cupric chloride was included in the original train, but was found redundant and removed.

The gas then passed through a flow meter and via temperature equilibrating copper coils in the thermostat to the cell. The flow meter was a differential pressure type designed to use conductance water. It was used in setting the gas bubbling rate in the cell, and gave a visual indication of any undesirable variations in the cell bubbling rate. (Note. Small quantities of self indicating soda-lime were introduced at the far ends of the soda-lime tubes to show when renewal was necessary).

4.3.3. Mercury.

Commercial mercury was washed several times by swirling with carbon tetrachloride, and then subjected to aspiration of air under dilute nitric acid for three days, and under several changes of conductance water for short periods. After drying it was distilled in an all-glass still under reduced pressure of air (delivered under the surface by means of a capillary); large head and tail fractions being rejected. Immediately before use in the preparation of calomel electrodes, batches were redistilled in a vacuum still swept out with pure, dry nitrogen before evacuation (26).

4.3.4. Potassium Chloride.

The potassium chloride used to make up the 0.01M solutions required for the preparation of mercurous chloride, was Merk G.R. three times recrystallised from conductance water. During the first of these the hot solution was filtered through sintered glass to eliminate solid impurities. The subsequent recrystalisations were carried out entirely in platinum ware, and the mother liquor removed by decantation. The product was dried at 115°C for 24 hours, at 250°C for three days, and stored over silica gel.

4.3.5. Mercurous Nitrate - $Hg_2(NO_3)_2.2H_2O$.

Difficulty was experienced in finding in the literature an adequate method for the preparation of mercurous nitrate in a pure form. It was felt to be essential that strict precautions be taken to ensure that the product was quite free from the many basic forms and other hydrates which can be produced by the action of nitric acid on mercury. A satisfactory method was finally evolved on the basis of the phase diagram for the system $Hg_2O - H_2O - N_2O_5$ drawn up by Denham and Fife (27).

The preparation was carried out in the dark to prevent the formation of mercuric salts. 205 ml of 5N reagent grade nitric acid was allowed to react in the cold with 106 gm purified mercury. After stirring for 22 hours the first crystals appeared. These were allowed to age for 24 hours, filtered off through sintered glass, and recrystalised by slow evaporation from a minimum of 0.6N nitric acid. The product was filtered off, dried in vacuo over silica gel and stored in the dark. The crystals were pure white in colour and showed no sign of the orange basic salt.

This was then used to prepare the 0.01M mercurous nitrate solutions required for the precipitation of mercurous chloride.

4.3.6. The Preparation and Standardisation of 0.01M Mercurous Nitrate Solutions.

The accurate determination of the concentration of the 0.01M mercurous nitrate solutions was necessary as an exactly equivalent quantity was required to react with the 0.01M potassium chloride solution in the preparation of mercurous chloride.

As solid mercurous nitrate is deliquescent, and cannot, therefore, be obtained in a state of appropriate purity for accurate weighing, approximate 0.01M solutions were prepared and standardised. The mercurous nitrate solutions were made up assuming the crystals contained 5 per cent moisture, and adding just sufficient nitric acid to prevent the precipitation of the yellow basic nitrate. A little pure mercury was added as a preservative (28), and the solutions were found to be quite stable.

The following methods for the standardisation of mercury solutions were investigated.

(i) Electrodeposition.

Dry (29) standardised his mercurous nitrate solution according to the method given by Scott (30), except that copper plated platinum cathodes were used to 'facilitate both the deposition of the mercury and its removal afterwards'. This procedure was, therefore, the first investigated in the present work; and was found to yield inconsistent results. The method was then varied by carrying out the deposition in dilute hydrochloric acid using hydroxylamine hydrochloride as an anode depolariser; bright platinum cathodes being used. However, the results obtained were not an improvement on those yielded by Scott's Procedure.

On returning two plated cathodes to the plating solution for a further two hours electrolysis a loss in weight was observed. Apparently, therefore, the low results were caused by the mercury not adhering very well.

Due to the large discrepancy between the observed values the method proved unsatisfactory as an accurate means of standardisation, and was therefore discarded.

(ii) By Titration using an Adsorption Indicator.

Kolthoff and Larson (28) showed that mercurous nitrate solutions could be accurately standardised by titration with halide solutions, using bromo-phenol blue as an adsorption indicator. The method was tried using 0.01M solutions, but an accuracy of only 0.5 to 0.9 per cent could be obtained, depending upon whether bromide or chloride solutions were used.

TABLE I.

Summary of Electrodeposition Results.

Method	True Value. gm Hg per 50 ml.	Observed value. gm Hg per 50 ml.	
Depositing on copper plated platinum cathodes in dil. nitric acid solution.	0.1945	0.1938	0.1933
		0.1953	0.1936
		0.1929	0.1930
		0.1950	0.1860
Depositing on bright platinum cathodes in hydrochloric acid soln.	0.1945	0.1893	0.1920
Depositing on bright platinum cathodes in nitric acid soln.	0.1945	0.1942	0.1864
		0.1804	0.1898

The method was, therefore, unsuitable for the accurate calibration of mercurous nitrate solutions of this dilution.

(iii) By Potentiometric Titration.

As mercurous halides are very sparingly soluble in water, it was considered that mercurous salt solutions might lend themselves to accurate analysis by potentiometric titration with halide solutions. A survey of the literature revealed that Behrend (5) first applied the mercury electrode to the titration of halides in 1893, and in agreement with his statements, Treadwell and Weiss (31) and Kolthoff and Verzijl (32) found that chloride and bromide could be accurately titrated with mercurous nitrate as reagent. The latter showed, too, that even very dilute halide solutions (e.g. 25 p.p.m. I^-) can be rapidly and accurately analysed by potentiometric titration. The method appeared, therefore, most suitable for the standardisation of the dilute solutions used in this work.

Initially, the mercurous ion was titrated with bromide. A sharp break in potential was observed at the equivalence point, and the procedure proved a precise and accurate means of standardisation.

It was then decided to investigate the possibility of replacing the bromide with chloride, for, if a comparable degree of accuracy was attainable, the two solutions required for the preparation of calomel could be standardised against each other. This, besides giving the exact volumes needed for equivalence directly, would obviate the accurate preparation of the potassium chloride solution.

As was anticipated from a consideration of the solubility products of mercurous bromide and mercurous chloride, about 10^{-21} and 10^{-18} respectively, the jump in potential was less when chloride was used. The change in potential per drop of titrant at the equivalence point was 20 mV, one fifth of that obtained with bromide. The end point, nevertheless, was sharp and well defined and the accuracy in no way impaired.

The titration was also carried out with the reagents reversed, and as no difference was observed either in the equivalence point, or in the change of potential per drop of titrant at this instant, it was concluded that any preferential ion adsorption was small.

Since, in the preparation of calomel, the mercurous nitrate solution was to be added to the potassium chloride dropwise over a period of 45 minutes, a titration was carried out under identical conditions to check whether the equivalence point might differ from that obtained in the normal manner. The results were coincident, once again showing that little adsorption took place, and the normal procedure could be reliably used.

In view of the advantages, therefore, it was resolved to use the potassium chloride solutions prepared for the calomel precipitation, in the titration, and so standardise the two solutions with respect to each other.

The following cell was set up:

$$\mathrm{Hg}\;\Big|\;\mathrm{Hg_2}^{2+}\;\vdots\;\mathrm{NH_4NO_3}\ (\mathrm{satd.})\;\vdots\;\mathrm{KCl}\ (0.1\mathrm{N})\;\Big|\;\mathrm{Hg_2Cl_2 - Hg}\ ,$$

and the variation of the potential of the mercury electrode with change in mercurous ion concentration, measured against a decinormal calomel electrode.

(i) <u>The Mercury Electrode.</u>

The electrode was prepared from a small platinum foil, cleaned in hot nitric acid, washed well with distilled water, and annealed by heating to redness in an oxidising flame. It was then electrolytically coated with mercury from a mercurous nitrate solution containing a little nitric acid. After washing with conductance water the electrode was ready for use.

A platinum wire dipping into a mercury pool was also found satisfactory, but much less convenient.

(ii) The Calomel Electrode.

The calomel reference electrode, with its characteristic adherent skin of calomel on the mercury surface, was prepared in a siliconed vessel as recommended by Hills and Ives (25). It was unnecessary to deoxygenate the potassium chloride solution as the potentials were only required to the nearest millivolt.

Procedure.

The apparatus was set up in a constant temperature room at 24°C. The titration half cell, into which the mercury electrode and an electrically driven stirrer dipped, was connected to the calomel electrode by means of a saturated ammonium nitrate salt bridge with porous plug junctions. The whole was rigidly mounted to prevent exposing the calomel electrode to unnecessary vibration.

A known volume of the 0.01M potassium chloride solution in the titration half cell was then titrated with the 0.01M mercurous nitrate solution, and the corresponding changes in cell potential measured on a Tinsley potentiometer to the nearest millivolt. The end point of the titre was obtained graphically from the peak of a plot of voltage change per unit volume of titrant versus volume of titrant, according to the method proposed by Hostetter and Roberts (33).

This gave the exactly equivalent quantity of mercurous ion required to react with the known volume of chloride in the accurate preparation of mercurous chloride.

4.3.7. Mercurous Chloride.

The mercurous chloride was prepared using the method described by Dry (29). Accordingly, to 50 ml of the 0.01M potassium chloride solution. accurately measured into a conical flask containing about 100 ml of conductance water, an exactly equivalent quantity of the 0.01M mercurous nitrate solution was added dropwise over a period of 45 minutes. The flask was constantly shaken, and the precipitation carried out in the cold.

The suspension was then digested at 50 to 60°C in a water bath, to favour the growth of the larger particles at the expense of the smaller ones. In this way adsorption was reduced to a minimum, and the precipitate rendered easily washable. To ensure the complete removal of foreign ions the mercurous chloride was washed 50 times with conductance water before use.

The calomel prepared in this way did not darken on exposure to light, and could be kept indefinitely. It is probable that the blackening observed by Vogel (34) was due to presence of impurities. Hada (35) noticed that the darkening was accelerated by the presence of either potassium chloride or hydrochloric acid. However, the presence of potassium chloride was found to have no influence on the calomel used in this work, even when exposed to electric light for several weeks.

Microscopic Examination.

As the solubility of a substance is dependent on particle size, it is important in solubility work that a precipitate of uniform crystal size be employed. In order to investigate the effect of digestion on crystal form, three calomel precipitates were examined microscopically.

The crystals were found to be needle-like in structure, tending to form twigs and open clusters. The precipitates digested at 45° and 60°C yielded crystals which averaged 8 by 0.5 microns in size, while the suspensions digested at 25°C showed a variation of crystal sizes from 3 to 26 microns in length.

It was evident, therefore, that a high digestion temperature should be used if a uniform crop is desired, and a value of 50 to 60°C was decided upon and subsequently used in this work.

4.3.8. Cleaning of Glassware.

Before use all glassware was thoroughly cleaned by treatment successively with alcohol-nitric acid mixture, and aqua regia, followed by steaming and rinsing with conductance water.

4.3.9. Cleaning of Rubber.

All rubber bungs and tubes used were boiled in 6N sodium hydroxide solution for half an hour, and in successive washes of tap water. They were finally washed with distilled water until a neutral solution resulted.

4.3.10. Siliconing of Glassware.

At a temperature of 60°C the vessels to be siliconed were filled with a two per cent solution of Dow-Corning No. 200 Fluid in redistilled carbon tetrachloride. They were then emptied, dried in air, and cured at 300°C for 45 minutes. This differs from the Hills and Ives' procedure of baking at 165°C for two hours but is in accord with the recommendations of the makers of the fluid (36), and was found to produce better siliconing. After cooling the vessels were rinsed ten times with carbon tetrachloride, dried, and then swirled five times with conductance water, and dried again.

4.4 MEASUREMENT OF THE SPECIFIC CONDUCTANCE OF CONDUCTIVITY WATER AT 25°C.

At the beginning of the work the cell was steamed and well leached out with conductance water to clean it thoroughly. However, once in routine use, three washings with the water to be measured were sufficient before each run.

Approximately 300 ml of conductance water was added to the cell, the cap replaced, and the cell suspended in the paraffin thermostat. The time was noted, and a stream of nitrogen bubbled through the cell contents at a constant rate. This was adjusted with the aid of a differential pressure flow meter, and determined by counting the bubbles passing through the solution.

As the cell resistance was far too high to measure directly on the bridge, a standardised 10,000 ohm General Radio resistance was connected in parallel with the cell, and the resistance of the combination measured at frequent intervals over a period of 24 hours.

The resistance rose rapidly with time as the nitrogen swept the volatile impurities, such as carbon dioxide and ammonia, from the water in the cell. Then, after reaching a maximum it fell at the gradual but constant slope of 0.1 to 0.5 ohms per hour. This was ascribed to the continual solution of glass from the cell walls by ion exchange between hydrogen ions in solution and ions from the glass surface (37).

A typical plot of resistance against time obtained in this work is given in Fig.5. Since the solution of glass took place at a constant rate, the effect was nullified by extrapolating the constant portion BC of the curve to zero time, and the value so obtained was accepted as the true resistance of the water in parallel with the 10,000 ohm standard.

The specific conductance of the water was calculated from the following equation

$$H_2O = \frac{Q\ (\ R_s - R_e\ )}{R_sR_e} \quad \text{..............} \quad (7)$$

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

The specific conductance of the water used in this work was between 60 and 90 nanomhos per centimetre.

4.4.1. The Use of a Silicone Coating to prevent the Solution of Glass in Water.

As can be seen in Section 4.4 even the very slight solubility of Pyrex glass is significant in conductivity work involving dilute solutions, and in order to increase the accuracy of conductance measurements, especially when more complex solutions are concerned, it was decided to investigate the possibility of preparing glass-free solutions.

At first the use of polythene vessels was considered in place of glass, but experiments showed that, in spite of careful steaming and excessive washing, they rapidly contaminated conductance water, due probably to the plasticiser present, and were therefore unsuitable for use.

The possibility of insulating the solution from the glass surface by some inert film was then investigated, and a siloxane silicone film was considered the most promising. Not only is it an extremely effective water repellant, but it can also be tightly bonded to a glass surface. Further, its matrix is a simple one, $[R_2SiO]_n$, containing no ionic species which might dissolve and alter the conductance of the solution (36).

The silicone was carefully applied to a pyrex flask as described in Section 4.3.10, and after a number of washings with conductance water, water of known conductivity was added to the flask and the ground glass stopper replaced. After gently swirling for 15 minutes the conductance of the contents was determined, and as can be seen in Table II the first two runs showed that the specific conductance of the water had been increased by the last traces of impurity, while the result of the third run reproduced the known conductivity of the water identically. The experiment was then repeated with water of a lower conductivity, and the result agreed exactly with the conductance of the water used.

TABLE II.

Conductance of Water from Siliconed Flask

Sample	Experiment 1. Specific Conductance	Experiment 2. Specific Conductance
Water used for Experiment	71 nm cm^{-1}	61 nm cm^{-1}
Water from Siliconed Flask:		
Run 1.	184	61
Run 2.	124	-
Run 3.	71	-

These experiments showed conclusively that a silicone film can be successfully applied to a glass surface in the extremely pure state required by conductivity work, and that the silicone used did not contain soluble species which would increase the conductance of very dilute solutions brought into contact with it. Further, since the results before and after swirling in the siliconed flask were in excellent agreement, the experiments indicated that the solution of glass had been negligible.

The next experiment was to investigate this reduction in the solution of glass more closely by examining the slope of the resistance time curve obtained when a siliconed conductivity cell was used. For if the gradual drop of resistance with time observed above (see 4.4), was due to the solubility of glass as postulated by Gledhill and Malan (37), the curve would remain constant at its maximum, and be independent of bubbling rate, if the solution of glass had been completely prevented.

However, it was not possible to silicone a Gledhill cell since, firstly, the platinum electrodes might also become siliconed and their electrical properties altered, and, secondly, it was doubtful if the pyrex glass-platinum seals would survive baking at 250°C without cracking. Therefore, a special dipping electrodes cell was constructed with cell vessels which could be treated independently of the electrodes (see 4.2.3.).

The cell vessel and electrode assembly were washed with the water to be used, and the resistance-time curve determined as previously described (see 4.4.). Two cell vessels were used, one untreated and the other carefully siliconed, in order to obtain a direct comparison using the same water sample. Various nitrogen bubbling rates were used, and the constant slopes of the resistance-time curves recorded. The results are summarised in Table III.

TABLE III.

Effect of Siliconing on Resistance-time Curve.

Nitrogen Bubbling Rate	Slope of Resistance-time Curve	
	Unsiliconed Cell	Siliconed Cell
bubbles/second.	ohms/hour.	ohms/hour.
1.1	0.14	< 0.05
1.5	0.20	< 0.05
3.6	0.45	0.05
6.0	0.50	0.10

As can be seen in the Table, a considerable decrease in the gradient of the resistance-time curve resulted when the siliconed cell was used which showed that the reaction responsible for the fall in resistance usually observed was slowed down a great deal by the presence of the silicone film. It followed, too, that this reaction took place at the liquid-glass interface, and was almost certainly the solution of glass. The fact that small slopes, which increased with bubbling rate, were observed in spite of the silicone coating indicated that although the solution of glass had been largely overcome by the treatment, it had not been completely prevented.

General Conclusions.

The results of this work have led to the following general conclusions, the importance of which applies not only to conductivity work but to the field of dilute solutions as a whole.

(1) That polythene ware is unsuitable for use with very dilute solutions.

(2) That a silicone film can be applied to a pyrex glass surface in the state of purity demanded by conductivity work.

(3) That the reaction responsible for the fall in the resistance of conductance water observed with time is due to the solution of glass from the walls of the conductance cell.

(4) That the solution of glass in water can be considerably restricted by siliconing the glass surface.

4.5 THE MEASUREMENT OF THE SPECIFIC CONDUCTANCE OF A SATURATED MERCUROUS CHLORIDE SOLUTION AT 25°C BY DRY AND GLEDHILL'S METHOD.

4.5.1. Experimental.

Since the standard method developed in this Department for the determination of the specific conductance of saturated sparingly soluble salt solutions, was to saturate the solution in the cell and determine its resistance graphically, and especially as this technique was employed by Dry and Gledhill (1) in their work on the solubility of mercurous chloride, it was the obvious approach to be used in this research.

Accordingly, the mercurous chloride precipitate was washed three times and added to the conductance cell as a finely divided suspension in about 300 ml. of conductivity water. To avoid the possibility of supersaturation,. sufficient precipitate was added to ensure that an excess of calomel would be present when equilibrium was attained. The cell was then suspended in the paraffin thermostat, and purified nitrogen bubbled through the cell contents at a constant rate. This was set with the aid of a flow meter, and measured by counting the bubbles passing through the cell solution - a rubber tube 'stethoscope' was found invaluable for this operation. The cell resistance was measured at regular intervals over 24 hours and the resistance-time curve drawn in the usual way.

As the resistance of the saturated solution was of the order of 3.3×10^4 ohms, it could be measured directly on the bridge, and the 10,000 ohm shunt resistance was not required.

The specific conductance was calculated from the resistance of the saturated solution, obtained by graphical extrapolation from the resistance-time curve (see below), and corrected for the effective conductivity of the solvent water used (see 4.1.).

4.5.2. Discussion of Results.

It is felt that before the results obtained in this section of the work are discussed, one or two examples should be given in order to illustrate how the resistance-time curve obtained is related to the various processes taking place in the cell solution.

Consider the case of any pure, sparingly soluble salt dissolving in theoretically pure conductivity water to form a saturated solution in the conductivity cell. Theoretically the resistance of the cell will change with time in the following way. At first the cell resistance will be high and almost equivalent to that of the solvent alone, but as the salt dissolves more and more ions become available to carry the current, and the resistance falls accordingly. The drop in resistance will be rapid initially, but as the solution becomes saturated with the salt the rate of solution declines, and ions are provided at an ever decreasing rate.

The resistance, therefore, will also fall at an ever decreasing rate until, when the solution is saturated, it will remain constant with time. The resistance- time curve traced out by the above is shown in Fig.6.

In practice there is not only the solution of salt to contend with but the removal of volatile impurities, e.g. carbon dioxide and ammonia, and the continual solution of glass from the cell walls as well. The influence of the former on the resistance-time curve will be noticed early on. Consider, for example, the initial rise AB in the resistance-time curve obtained by Gledhill and Malan (37) in their work on the solubility of silver chloride (see Fig.7.). This was due to the rapid increase in cell resistance as the volatile impurities were swept off, completely offsetting the fall in resistance caused by the solution of the salt. At B the effects were balanced, while along curve BC the last traces of carbon dioxide were removed, and the effect of the salt dissolving was predominant. The influence of the continual solution of glass, although taking place at a constant rate throughout the run, only becomes apparent when the solution has been saturated with the salt. In the ideal case above, the resistance then remained constant as no further ions were available to transport current, however, in the practical case ions are continually being added as the glass dissolves, and after saturation the resistance continues to drop but at a very small though constant rate. In the silver chloride example, this corresponds to portion CD of the curve the gradient of which, 0.3 ohm per hour, was identical to that obtained with water alone. Gledhill and Malan (37) then found the resistance of the saturated solution by extrapolating CD to zero time in order to nullify the effect of the dissolved glass, and as the results obtained in this way agreed excellently with their potentiometric values and those of Guggenheim (38), this became the standard method adopted in this Department.

RESISTANCE - TIME CURVES FOR SPARINGLY SOLUBLE SALTS

(TIME SCALES VERY APPROXIMATE)

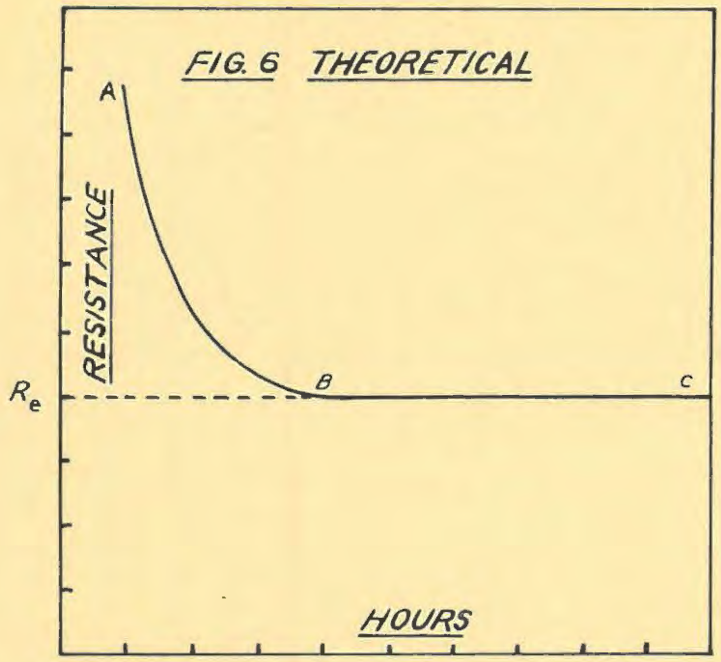


FIG. 6 THEORETICAL

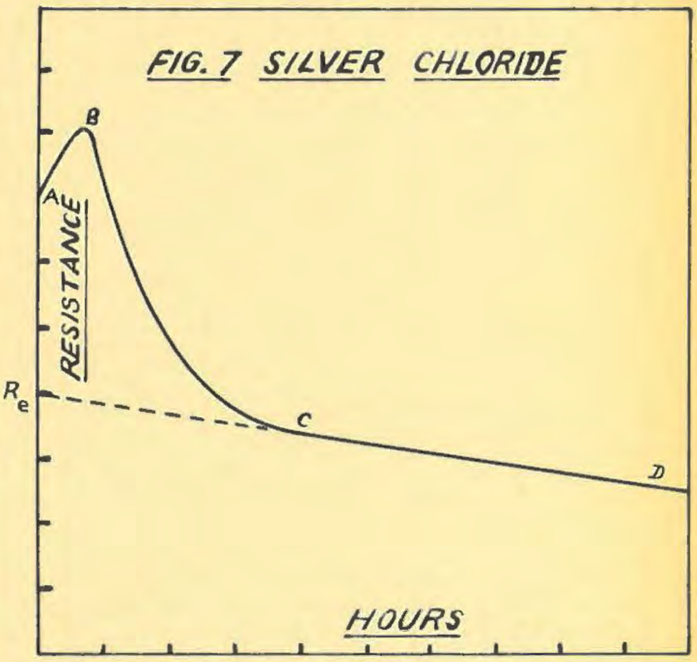


FIG. 7 SILVER CHLORIDE

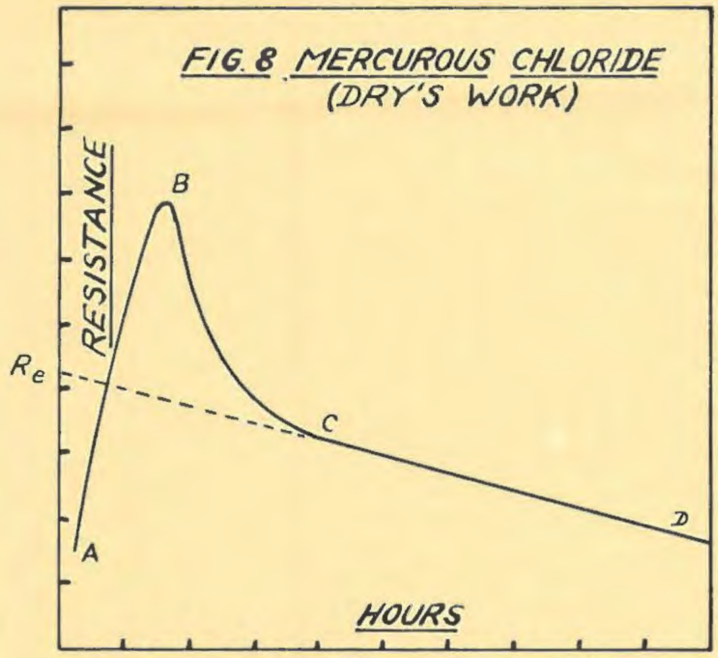


FIG. 8 MERCUROUS CHLORIDE (DRY'S WORK)

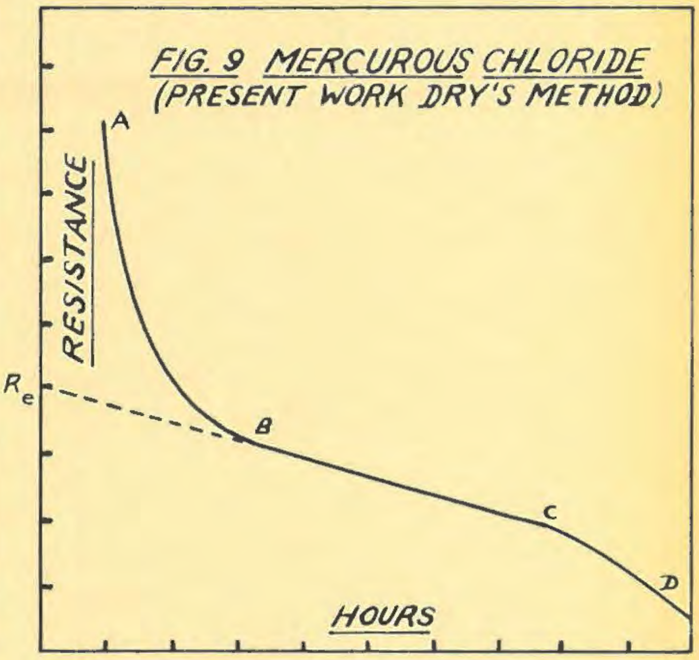


FIG. 9 MERCUROUS CHLORIDE (PRESENT WORK DRY'S METHOD)

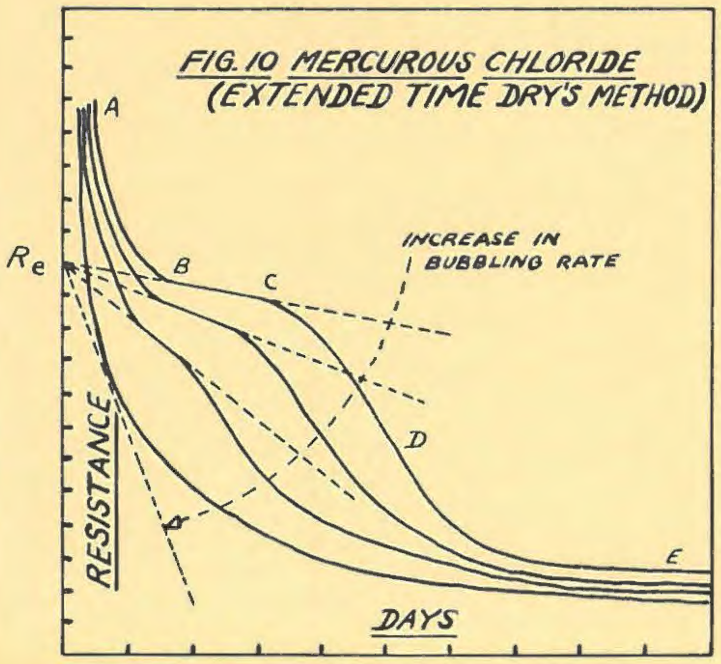


FIG. 10 MERCUROUS CHLORIDE (EXTENDED TIME DRY'S METHOD)

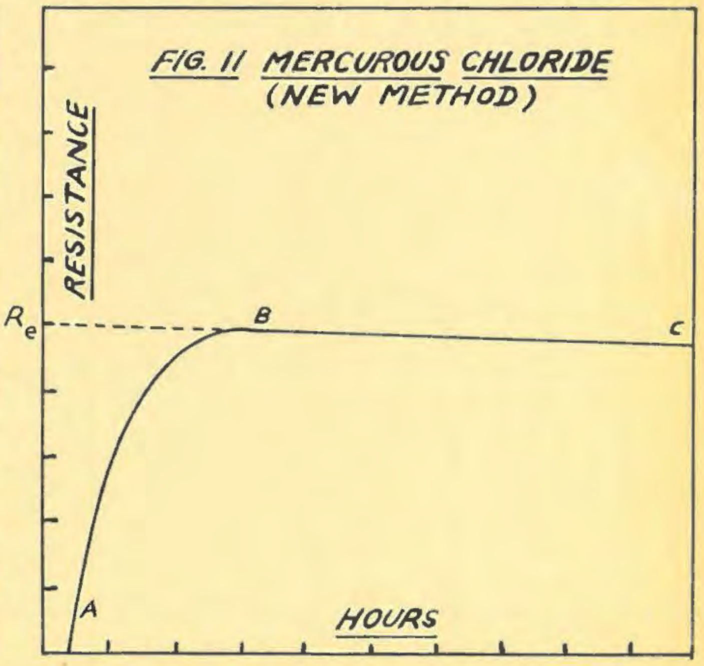


FIG. 11 MERCUROUS CHLORIDE (NEW METHOD)

Further work on silver bromide by Gledhill and Malan (39) gave similar resistance-time curves but with greater slopes than those expected from the solution of glass alone. This increase in gradient was attributed to ion exchange phenomena on the cell walls, which are more serious in the case of the much more dilute silver bromide solution. Nevertheless, the solubility values calculated using the extrapolation technique outlined above, were in complete agreement with those determined potentiometrically. Thus the extrapolation was justified even when the constant slope of the resistance-time curve was greater than that observed with water.

Dry and Gledhill (1) studying the solubility of calomel by this method, found that the constant portion of their curves had an even greater slope than the silver bromide traces, and, indeed, depended on the rate at which the nitrogen was bubbled through the cell solution and how thoroughly the cell had been washed out before use. A copy of their curve is given in Fig.8., and is somewhat similar to that obtained with silver chloride (see Fig.7). Again ion exchange effects were put forward as an explanation, and it was stated that as a saturated calomel solution had a pH of 5.125 units the effect would be much greater than in a neutral solution e.g. silver chloride.

In this research, however, it was impossible to reproduce this curve in spite of the fact that their techniques were rigidly adhered to, and exactly the same apparatus used. The resistance-time curve obtained by the present author for a saturated mercurous chloride solution is illustrated in Fig.9., and the differences are immediately apparent. Firstly, the resistance does not rise as the carbon dioxide is swept off, but falls along AB in much the same way as shown in the theoretical curve (see Fig.6.). This shows that the rate of solution had a much greater influence on the resistance than the removal of volatile impurities. Secondly, and the most serious difference, the gradient of straight line BC did not remain constant indefinitely but gradually increased along CD.

However, by extrapolating the constant portion BC of the curve to zero time a series of values for the specific conductance of the saturated solution were obtained (see Table IV), and gave a final figure of 3516 ± 30 nm cm^{-1} at 25°C. A value which is concordant with that claimed by Dry (1), 3508 ± 10 nm cm^{-1}, but the degree of reproducibility is much less in spite of the fact that probably as many determinations were carried out as in his work.

The reason for this being that beyond a certain time there is a disconcerting drop in the resistance of the saturated solution which Dry seems to have ignored or not noticed, with the result that it is impossible to say whether the solution had really become saturated at the point B on the resistance-time curve as postulated. Since, therefore, it appeared that no reliance could be placed on the extrapolation it was imperative to study this subsequent drop in resistance before any real accuracy could be claimed for the conductivity values obtained.

It was hence decided to take resistance measurements over prolonged periods of time, and not restrict the readings to 24 hours. As can be seen from Fig.10 a very striking family of curves resulted.

As before, the resistance fell rapidly at first, and after six hours dropped at a constant rate, between 18 and 150 ohms per hour, which was very much greater than that expected from the solution of glass alone. (Dry, too, recorded slopes of this magnitude). After a constant period of about 5 hours, the resistance fell almost logarithmically with time (along CD), passing through a maximum gradient of 200 to 400 ohms per hour, and finally approached a second constant region after eight days. The solution then appeared very close to a secondary saturation, although the equilibrium state was never reached.

The influence of bubbling rate was very significant. An increase both increased the slope of the constant portion BC, and caused the constant period to diminish, until, at higher bubbling rates, it could only be represented by a tangent to the curve.

TABLE IV.

Specific Conductances of Saturated Calomel Solutions at 25°C Calculated from Zero Time Resistances Extrapolated from Constant Portion BC of the Resistance-Time Curve.

Run	Specific Conductance nm cm^{-1}.	Slope of BC. ohms/hour.	Bubbling Rate Bubbles per sec.
B1	3483	225	1.5
B2	3460	300	1.5
D1	3532	102	1.5
D3	3536	75	1.5
E1	3430	239	1.5
F1	3481	360	1.5
F2	3525	122	1.0
F3	3443	164	0.8
F4	3522	57	0.8
F5	3563	78	0.8
F6	3562	54	0.8
F7	3541	53	0.8
G1	3530	40	0.7
H1	3555	35	0.7
H2	3544	50	0.8
I1	3519	19	0.8
I2	3540	30	0.9
I3	3502	71	0.6
I6	3469	38	0.7
I7	3552	38	0.6
I8	3543	26	0.6

In trying to find an explanation for this anamalous behaviour the equilibria existing in a saturated mercurous chloride solution at 25°C must be considered. In saturated solutions of silver chloride and silver bromide only one equilibrium is present, but saturated calomel solutions are far more complex and nine equilibria exist. (See 2.).

It will at once be realised that any process which could upset these equilibria might be responsible for the behaviour observed above, and the following possibilities have been considered.

(i) Impurities in the Nitrogen.

In view of the significant dependence on bubbling rate this effect is probably the most obvious. However, extreme care was taken in purifying the gas (see 4.3.2.), and as the nitrogen supply had no adverse effect on the conductance water measurements, it was very unlikely that ionic impurities had been introduced from this source. The chance that small quantities of oxygen might be present which could be catalysed by the platinum electrodes to oxidise the ions in solution, was also considered remote as every precaution was taken to ensure that the nitrogen was oxygen free.

(ii) Ion Exchange.

Ion exchange phenomena on the glass walls of the cell were more likely to have been responsible: the most probable exchange being between hydrogen ions, which are readily adsorbed on the glass surface, and ions from the soluble constituents of the pyrex glas. A consideration of the equilibria existing in the saturated solution immediately shows that a loss of hydrogen ions will cause an upset of the solution balance, and more calomel will dissolve. This effect will clearly depend upon the rate at which the solution flows past the glass walls and, therefore, upon the bubbling rate of the stirring gas. Since the bubbling rate is kept constant throughout a run this effect will be constant i.e. both calomel and glass are dissolving at a constant rate, and it explains why the gradient of the resistance-time curve is greater than that obtained with water alone.

Extrapolation of this line to zero time should completely nullify the effect of these processes, and the resistance of the saturated solution so obtained should be the true one. The dependence of the constant slopes upon the bubbling rate is also explained by this mechanism, as an increase in bubbling rate will cause the rate of solution of calomel to increase accordingly.

What this mechanism does not explain is why the gradient should increase with time after remaining constant for some hours, since according to the above the slope should remain constant indefinitely provided the bubbling rate does not vary. However, on closer inspection the equilibria revealed that the chloride ion concentration increases considerably with the removal of hydrogen ions, and threw more light on the problem. It is well known that calomel is soluble in solutions of chloride ion (40) and it is on this fact that the following theory is based.

It is thought that after the curve had fallen at a constant rate for several hours due to the mechanism described above, the chloride ion concentration increased beyond a certain limit, and slowly caused more calomel to dissolve by forming the complex $HgCl_4^{2-}$ ion. The resistance would then drop, increasing the gradient of the curve, and, as the solution became saturated with this species would fall at a gentler rate.

This idea not only explains the increase in the gradient of the resistance-time curve after the rate of fall had been constant for several hours, but also points out why the constant period diminishes with increase in bubbling rate. As the stirring is increased the rate of ion exchange and the rate of chloride ion formation is increased, so that the chloride ion concentration exceeds its 'limit' sooner and the effect of solution of calomel by $HgCl_4^{2-}$ ion formation is noticed earlier.

The extremely large equilibrium constant for the reaction. $Hg^{2+} + 4Cl^- \rightleftharpoons HgCl_4^{2-}$, approximately 10^{15}, would explain why the solution approached but never reached saturation during the time of the experiment. Unfortunately, it was not possible to verify this as the $HgCl_4^{2-}$ concentration present could not be measured by apparatus and techniques available in this Department.

It was thought that by using a cell with siliconed walls this effect might be overcome, and a special dipping electrodes cell was designed for the purpose (see 4.2.3.). The resistance-time curves obtained were similar to the high bubbling rate curves obtained above, but logarithmic in shape, which meant that the solution could only be completely saturated after infinite time. This would be expected if the $HgCl_4^{2-}$ complex-ion was being formed by the continual solution of calomel by the chloride ion as postulated.

(iii) Adsorption Effects.

Cox, Kraus, and Fuoss (41) stated that bright platinum electrodes should be used when measuring the resistance of solutions above 10,000 ohms to reduce adsorption errors, and as the resistance of the calomel solutions measured in this work was over three times this value, several runs were carried out using a cell with bright platinum electrodes to investigate this effect.

The resistance-time curves observed were similar to those obtained above when platinised electrodes had been used, with the marked exception that the constant period was almost three times as long for a given bubbling rate. The slope too, was gentler and the fall away from the constant gradient more gradual.

It appeared, therefore, that the process responsible for the observed effects was slowed down quite considerably by the use of bright platinum electrodes, and suggested that the process which was upsetting the equilibria in the saturated solution, was influenced by the platinum surface. Both adsorption and catalysis were therefore considered.

If adsorption effects were responsible it was thought that the metallic mercury formed by the reaction $Hg_2^{2+} \rightleftharpoons Hg_s + Hg^{2+}$ might be preferentially adsorbed, since no sign of greyness due to the formation of mercury was found on the precipitate in the cell. It will be realised that this effect will also upset the equilibria existing and cause more calomel to dissolve. It is possible, therefore, to explain in part the observed results by similar arguments to those used above.

This effect, it was considered, might give rise to some type of calomel electrode, and that it should be possible to measure some potential difference across the cell leads. A Tinsley potentiometer was used for the experiment and yielded some interesting results. A potential difference of 0.8 mV was found across the platinised electrode cell, and 0.3 mV across the cell with bright platinum electrodes.

Once more the effect with bright electrodes was much less marked, and it seemed that adsorption was definitely taking place. A run was then performed taking potentiometric and resistance measurements concurrently. However, no correlation between the two could be found.

It might be felt the above potentials were too small for alarm, but it must be emphasised that, firstly, no potential should be found across a conductance cell under any circumstance, and, secondly, that the effect could be much larger than the potentials might indicate, since the voltage measured was the potential difference between two very similar 'calomel electrodes' in the same very dilute solution, and is really only an indication of the difference in state of the electrodes.

Adsorption effects, then, might quite feasibly have been responsible for upsetting the equilibria in the saturated solution.

(iv) Catalysis.

The possibility of the platinum electrodes catalising some reaction in the saturated solution cannot be overlooked, and one aspect has already been mentioned (see (i) above). It has been suggested that the reaction $Hg^{2+} + Hg_{(s)} \rightleftharpoons Hg_2{}^{2+}$ might be heterogeneous (42); if so the reaction rate would be accelerated by the greater surface area of the platinised electrodes, and would explain why the upset in equilibria takes place sooner when the cell with platinised electrodes was used.

4.5.3. Conclusions.

(i) The solubility of calomel is obviously influenced by various effects inherent in the method of saturation used, namely saturation in the conductivity cell, and, therefore, it is impossible to attempt to prepare a saturated solution of calomel using Dry's procedure, measure its specific conductance, and eventually use it for subsequent analysis.

(ii) One or all of the above mentioned possibilities might have been responsible for the behaviour observed, and in order to overcome these difficulties a new approach should be investigated in which these disturbing factors, if not entirely eliminated, are reduced considerably so that reasonable corrections can be applied.

4.6. MEASUREMENT OF THE SPECIFIC CONDUCTANCE OF A SATURATED MERCUROUS CHLORIDE SOLUTION IN WATER BY A NEW METHOD

4.6.1. Introduction.

A method was required which would prevent ion exchange, adsorption and catalytic effects from taking place, and it was felt that these factors could be overcome by saturating the calomel solution in a siliconed vessel in the absence of platinum. It was considered, too, that mechanical stirring would be an advantage, so that any possibility of poisoning by impurities in the nitrogen could be avoided. The preparation of the saturated solution in this way seemed straight forward enough, but the measurement of its specific conductance presented a difficult problem.

As the existing cells had to be used, the effects responsible for the anomalous solubility of calomel observed above would recur immediately the saturated solution was added, and the end of the proposed method of saturation would be defeated. However, an answer to the problem suggested itself.

The work done above indicated that the observed results were due to these various effects causing an increase in the solubility of calomel, and it was thought that if a filtered saturated solution was added to the cell no solid salt would be available for further solution, and these processes could no longer be effective. It was realised that adsorption, ion exchange and catalysis would still occur, but it was considered that their effect on the solid free solution would be insignificant in comparison, and could be corrected for by extrapolating the resistance-time curve to zero time.

This technique proved most successful, and was the one finally adopted in this research.

4.6.2. Procedure.

The precipitate was washed three times with the conductance water to be used as a solvent, and a portion transfered to the siliconed flask of the stirrer assembly (see 4.2.4) as a fine suspension in 300 ml conductance water. After washing the siliconed paddle stirrer, the flask was carefully fitted to the apparatus so that the stirrer dipped into the suspension to a convenient depth. When the assembly had been lowered into the water thermostat (25°C), and rigidly clamped to prevent vibration, an atmosphere of nitrogen was introduced, and the suspension stirred for 24 hours.

The saturated solution was then carefully filtered, through a 'double filter' maintained at 25°C (see 4.3.4) which embodied two very fine sintered glass discs, and after about 50 ml had passed through as washings the filtrate was collected. After washing the conductance cell three times with this solution the cell was filled with it, and suspended in the paraffin thermostat Nitrogen was bubbled through the cell at a constant rate of 2 bubbles per second, and the resistance measured at regular intervals for 24 hours. The specific conductance of the saturated calomel solution was finally calculated from the extrapolated resistance of the resistance-time curve as detailed in the following section.

4.6.3. Discussion of Results.

The resistance-time curve obtained is shown in Fig.11. The resistance rose rapidly at first due to the removal of volatile impurities, such as carbon dioxide and ammonia, (portion AB). After two hours it reached a maximum, and then fell off slowly and regularly at a rate of 12 ohms per hour (along straight line BC) a rate only 8 ohms per hour greater than that obtained for water alone, and when compared with the slopes obtained previously, 26-360 ohms per hour (see 4.5.2. Table IV), shows the vast improvement achieved by this new technique. In order to correct for this small effect, arising from the solution of glass, adsorption, and ion exchange at the cell walls as mentioned above, the straight line BC was extrapolated back to zero time, and the resistance (R_e) so obtained regarded as the true resistance of the saturated calomel solution.

To justify the extrapolation procedure employed readings in several cases were taken for five days. No change in the slope was observed, and the technique, therefore, was adopted with confidence.

Further, to ensure that the anomalous behaviour found earlier (see 4.5.2.) had been prevented by saturating the solution in a siliconed vessel, the saturated solutions were prepared using various stirring times of up to 120 hours in duration, and their specific conductances compared. On the basis of the resistance-time curves obtained using Dry's technique (see 4.5.2.), it was apparent that the conductance of the saturated solutions would increase with stirring time if the factors causing the odd solubility of calomel were still active. However, as can be seen in Table V., the results were constant, within the experimental error of the work, and showed conclusively that the effects responsible for the anomalous solubility had been successfully overcome in the new procedure.

Experiments were carried out, too, in which the suspensions were stirred in the presence of a strip of bright platinum. The platinum was found to have no effect on the specific conductance of the saturated solution, and indicated that the reaction $Hg_2^{2+} \rightleftharpoons Hg(s) + Hg^{2+}$ is not heterogeneously catalysed as suggested (42).

Assuming that the extrapolated resistance R_e was the correct resistance of a mercurous chloride solution saturated at 25°C, the specific conductance of the solution was calculated from Equation 2. The conductance of the solution as determined above is the sum of the specific conductances due to all the ions which result when the calomel goes into solution, plus that of the solvent water. Therefore, to obtain the conductivity of the solute alone, the specific conductance of the water, which had been corrected for depression of ionisation as shown in section 4.1.1., was subtracted from the observed specific conductance of the solution.

The results obtained are given in Table V and from them the figure 3492 ± 12 nm cm^{-1} emerges as the accepted value of the specific conductance of a mercurous chloride solution in water at 25°C. A figure which completely supercedes the accuracy, reproducibility, and reliability of that obtained earlier in this work using Dry's technique, namely 3516 ± 30 nm cm^{-1}, since the uncertainties arising from the anomalous solubility previously observed have been successfully eliminated in the new procedure.

Dry and Gledhill's (1) value, 3508 ± 10 nm cm^{-1}, is concordant with that obtained in the present work, but it must be pointed out that they found the specific conductance of their saturated mercurous chloride solutions depended on the bubbling rate of the stirring gas through the cell, and that their value was obtained by extrapolating a specific conductance vs. bubbling rate curve to zero bubbling rate. No satisfactory reason for this dependence was given, but it was suggested that it seemed to be connected with ion exchange at the cell walls, an effect which was found responsible for the anomalous solubility observed in the present work when Dry's technique was used and which ultimately invalidated the method.

TABLE V.

THE SPECIFIC CONDUCTANCE OF A SATURATED MERCUROUS CHLORIDE SOLUTION IN WATER AT 25°C.

Stirring^{+} Time	Specific Conductance		
	Saturated Solution.	Water	Mercurous Chloride.
hours	nm/cm.	nm/cm.	nm/cm.
24	3505	79	3480
24	3533	79	3508*
25	3537	98	3493
36	3492	69	3477
38	3496	67	3483
43	3493	69	3478
48	3552	98	3508*
72	3517	66	3505
113	3516	86	3484
120	3519	67	3506

$^{+}$At least 18 hrs. stirring was required for saturation.

*Platinum present when saturating.

5. THE TOTAL MERCURY CONTENT OF A SATURATED MERCUROUS CHLORIDE SOLUTION IN WATER AT 25°C.

5.1. OUTLINE OF METHOD.

As the total mercury concentration in a calomel solution saturated at 25°C is of the order of 10^{-5} moles per litre, the usual volumetric and gravimetric methods for the determination of mercury were impracticable, and an accurate colorimetric technique was used.

The method was first suggested by Fischer and Leopoldi (43), and depends on the reaction between mercury and excess dithizone reagent. In fairly acid medium this yields the orange coloured keto complex, which is soluble in carbon tetrachloride, and, in the presence of the green excess dithizone, gives a solution with a mixed colour. The hue is directly related to the amount of mercury present, and in visual work is compared with a series of standards all prepared with the same quantity of dithizone as the unknown solution.

A spectrophotometer was used in this research, and it was therefore possible to measure the mixed colour solution at two different wavelengths: 500 mμ (adsorption by mercuric dithizonate) or 626 mμ (adsorption by the excess dithizone). The former was decided upon, and the mercury concentration in the saturated solution determined by the Transmittance-Ratio method in which the instrument is set to read zero with the photo cell in darkness, and to read 100 per cent transmittance when exposed to light that had passed through the least concentrated reference solution.

5.2. DESCRIPTION AND STANDARDISATION OF APPARATUS AND MATERIALS

5.2.1. The Spetrophotometer.

A Beckmann Model DU quartz spectrophotometer was employed in this section of the work, and gave little trouble once its initial instability had been overcome. A detailed description of the instrument is given by the makers, and no attempt will, therefore, be made to give a working account of it here.

5.2.2. The Cleaning of Cuvettes.

At the outset of the work the cuvettes were cleaned with chromic acid; then only occasionally. Once in routine use the cuvettes were rinsed in 95 per cent alcohol, and soaked for 30 minutes in a synthetic detergent, Teepol. They were then washed well with ion exchange water, and air dried after swirling in redistilled absolute alcohol. A special chamois leather tipped tongs was used for handling the cuvettes.

5.2.3. Preparation of Standard Solutions.

In the preparation of the standard mercury solutions special care was taken to prevent adsorption errors. Pyrex-ware was used throughout, and as mercury is most strongly adsorbed from neutral solutions, the standards were made up in normal A.R.Q. sulphuric acid. The standard flasks were provided with well fitting ground glass stoppers, as rubber, besides containing small amounts of mercury, reacted with the dilute solutions used to form mercuric sulphide. The flasks were standardised at 24°C the temperature at which the standard solutions were prepared.

Since under the experimental conditions of this work the mercury to be determined was present as mercuric chloride, this salt was chosen for the preparation of the standard solutions so that conditions could be as similar as possible. It was found necessary to handle the dry salt, Merck G.R. mercuric chloride, with a platinum spatula as nickel reacted with the salt to give a grey deposit of mercury.

A stock solution was made up containing 10^{-2} moles mercury per litre, and from this the working standard, 10^{-5} molar, was prepared by two intermediate stages of dilution, using calibrated standard flasks and a Grade A burette.

As even acidified mercury solutions may undergo an appreciable change in concentration on standing, especially when they are very dilute, the working standard was freshly prepared before use and exposed only to subdued light.

5.2.4. Preparation of Dithizone Reagent.

Since dithizone as supplied generally contains a yellow oxidation product, it was purified as instructed by Snell (44). Accordingly, 0.025 gm of dithizone was shaken for about half an hour with 25 ml redistilled carbon tetrachloride, to dissolve it, and then with 200 ml conductance water to which 10 ml 6N A.R. NH_4OH had been added to dissolve the pure dithizone. The carbon tetrachloride layer containing the oxidation product was discarded, and the aqueous layer shaken with 20 ml portions of carbon tetrachloride until no trace of pink was present in the extract.

The aqueous solution was then free from oxidation product, and on precipitating with 1:1 hydrochloric acid, the pure dithizone was extracted with 30 ml quantities of carbon tetrachloride. The extracts were combined and made up to 250 ml.

To increase the stability of the solution it was kept in a dark coloured bottle, and stored in a refrigerator. In this way dithizone solutions were found to remain stable for several months.

5.3 EXPERIMENTAL TECHNIQUE, RESULTS, AND DISCUSSION

5.3.1 Setting the Spectrophotometer.

The Beckmann spectrophotometer was switched on and allowed to warm up for about half an hour before use. The sensitivity control was turned fully clockwise, to maximum, and the dark current adjusted to give zero deflection on the meter. A gradual drift was noticeable until the instrument had completely warmed up. The wavelength dial was set to 500 mu, and with the correct photo tube in position, the apparatus was ready for use.

5.3.2 Preparation of the Calibration Curve

A calibration curve was traced from the absorbances of dithizone extracts of four different standard mercuric chloride solutions, whose concentrations embraced the figure expected in a saturated calomel solution at 25°C.

The required volume of freshly prepared standard solution was accurately added to a separating funnel with a micro burette.

The tap and stopper of which had been carefully ground in to prevent leaks, and the tap lubricated with carbon tetrachloride. 5 ml dithizone reagent was added from a burette, and the solution shaken for a minute to develope the mixed colour. The funnel was then clamped vertically, and left for a while so that complete separation might take place. After drying the stem of the funnel with a roll of filter paper if necessary, and rinsing the stem and cuvette with a little of the extract, the extract was run into the cuvette and the cover glass placed in position.

With the least absorbant extract in the light beam, the instrument was set to read 100 per cent transmittancy by flicking the selector switch to 'Check' and adjusting the slit width to give zero deflection on the meter. The absorbances of the other extracts were measured relative to this by flicking the selector switch to position 1, and adjusting the absorbance dial to return the meter needle to its null position. On plotting absorbance against concentration a straight line calibration curve was obtained.

5.3.3. Analysis of the Saturated Calomel Solution.

10 ml. of the filtered saturated calomel solution was pipetted into a separating funnel, two drops of 6N hydrochloric acid added, and 5 ml of dithizone reagent carefully run in from a burette. The preparation of the extract, and the measurement of its absorbance was carried out as described above (see 5.3.2), and the mercury concentration read off from the calibration curve in the normal way.

5.3.4. Discussion of Results.

TABLE VI

TOTAL MERCURY CONCENTRATION IN A SATURATED MERCUROUS CHLORIDE SOLUTION IN WATER AT 25°C.

Stirring Time	Total Mercury
Hours	moles/litre
48	7.21×10^{-6}
56	7.16×10^{-6}
58	7.20×10^{-6}
72	7.12×10^{-6}
100	7.24×10^{-6}
120	7.24×10^{-6}

Table VI summarises the results obtained, and gives the total mercury concentration existing in a saturated mercurous chloride solution in water at 25°C as (7.20 ± 0.04) x 10^{-6} moles per litre.

Though concordant with Dry's (1) value, namely (7.5 ± 0.3) x 10^{-6} moles per litre, it can be seen from the figures that a greater precision has been attained in the present work, and this increase in precision is thought due to two reasons:

(i) A quartz spectrophotometer was used in this research, an instrument much superior to the photolometer employed by Dry.

(ii) In Dry's research the calomel solutions were saturated in the conductance cell, from which filtered aliquots were drawn for analysis, and it was found that the mercury concentration of the saturated solution depended on the conductivity of the solution of calomel brought about by the factors discussed earlier (see 4.5). It was therefore necessary to use an extrapolation technique to determine the 'true' mercury concentration present - a method in which uncertainties can well be expected, especially in Dry's case where the values to be extrapolated lay on a curved line.

In the present investigation the results obtained were independent of stirring time once saturation had been reached, and no extrapolation was required to arrive at the final result.

6. THE HYDROGEN ION CONCENTRATION IN A SATURATED MERCUROUS CHLORIDE SOLUTION AT 25°C.

6.1 INTRODUCTION.

In the study of the solubility of mercurous chloride in water, an accurate knowledge of the hydrogen ion concentration is necessary to determine the extent of hydrolysis of the mercurous ion in solution, and to supplement the conductivity measurements by defining the hydrochloric acid concentration as precisely as possible.

The pH cannot be determined directly by using a hydrogen electrode, since, firstly, the hydrogen gas would reduce the mercury salts to metallic mercury in the presence of platinum, and, secondly, it is well known that the potential of the electrode is not stable in weakly buffered solutions.

A glass electrode is ideally suited, and Dry and Gledhill (1) used a carefully standardised technique employing a glass electrode pH meter for their pH measurements.

However, in the light of precision liquid junction potential work (45) being carried out in this Department at the time, it appeared that due to the liquid junction potential errors involved, too great an accuracy might have been claimed in their final result, 5.085 ± 0.01 units, and it was decided to investigate the degree of this error practically before proceeding with the pH measurements envisaged in this work.

6.2 A PRACTICAL INVESTIGATION OF THE LIQUID JUNCTION POTENTIAL ERROR IN pH MEASUREMENTS WITH A GLASS ELECTRODE.

6.2.1. Introduction.

In order to supplement the conductivity and total mercury measurements in calculating the solubility of calomel in water the pH of the saturated solution must be known accurately to at least 0.01 pH unit.

Although pH's are generally quoted and regarded accurate to 0.01 - 0.02 pH units, theoretical considerations indicate that residual liquid junction potentials involved must give rise to errors far in excess of this limit. Dole (46) mentions that these may be as great as 0.1 pH unit, but does not appear to have adequate experimental support for this statement. It was, hence, essential that these conflicting views should be resolved before the accurate determinations envisaged could be carried out. The purpose of this investigation is, therefore, to demonstrate the order of magnitude of the error due to the liquid junction potentials under the conditions pertaining during pH measurements, and in addition show the significance of the common neglect of certain fundamental properties of liquid junctions.

It has been shown (47) that the magnitude, stability, and reproducibility of liquid junction potentials depend, among other things, on the way in which the liquid junction is made. A satisfactory junction should give a stable, reproducible potential, and, in addition, when used with pH meters, should be simple to set up. The junctions usually embodied in the electrodes of commercial meters are chosen primarily to satisfy the requirements of convenience, for they are what Guggenheim (47) called "indefinite type" junctions. These he found to be extremely irreproducible and unstable. He also showed that, in order to satisfy the requirements of stability, a junction must be made so as to have "cylindrical symmetry", i.e. all concentration and potential gradients must be parallel to the axis of the tube. This is achieved in practice by forming the junction in a tube of regular bore, at a point some distance from its ends. Normally this type of junction is not used with pH meters, in spite of its advantages and the fact, as will be shown, that it can be very simply set up.

6.2.2. Experimental.

The cell studied was a conventional pH cell

$$\text{Ag-AgCl} \;\Big|\; \text{HCl} \;\Big|\; \text{glass} \;\Big|\; \begin{matrix}\text{Potassium hydrogen}\\ \text{phthalate pH} = 4.00\end{matrix} \;\vdots\; \text{KCl}_{(\text{satd.})} \;\Big|\; \text{Hg}_2\text{Cl}_2\text{-Hg}$$

The liquid junction between the buffer and saturated potassium chloride solution was prepared in different ways, and the variation of pH with time observed for each type of junction. Any change in the measured pH can only be caused by variations in the boundary layer, and hence in the junction potential. Care was taken to follow, as far as possible, the procedures usually used in pH work. Thus, the meter was set on the standard value of 4.00 pH units immediately after the junction had been made.

The pH meter used was a Marconi Type TF 717A, which embodies a potentiometric measuring circuit. A Sorensen Model 1001 voltage regulator and a constant voltage transformer were used to eliminate the effects of mains fluctuations. In addition, to ensure that any pH fluctuation was due to unsteady junction potentials, the stability and reproducibility of the meter were checked by balancing it against a standard potential. No change in meter reading was observed over 16 hours. The room temperature did not vary during any one run by more than 1°C, and, as the meter used has automatic temperature compensation, temperature effects could be neglected.

Four types of liquid junctions were considered:

(a) Wick junction (As in the Beckmann electrode).

(b) Porous plus junction (As in the Marconi electrode).

(c) Simple dipping junction. This junction is one widely used with common laboratory calomel electrodes. The two solutions make contact at

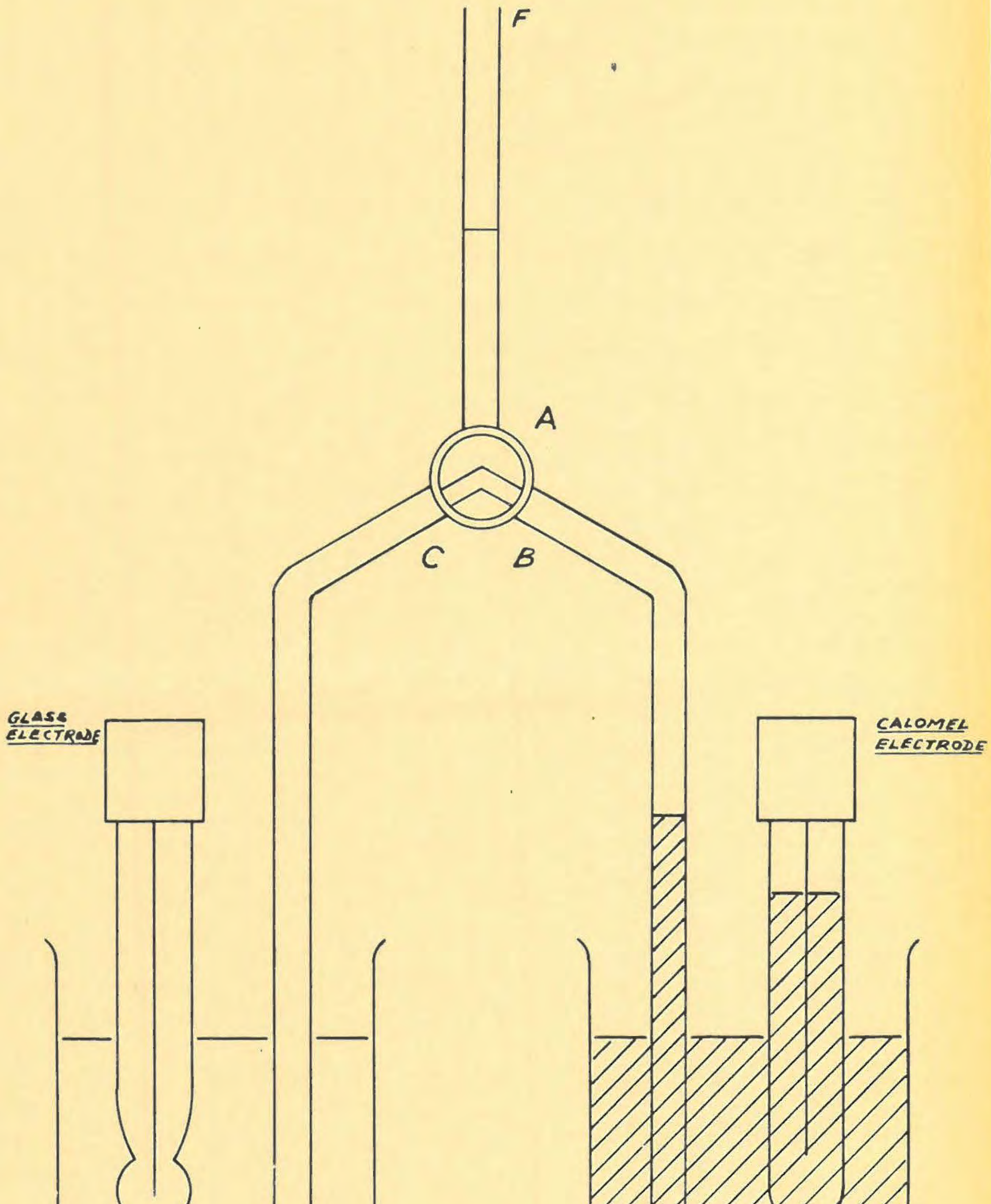


FIG. 13. CYLINDRICALLY SYMMETRICAL JUNCTION

the end of a tube, filled with the first and dipping into the second. In Type A the saturated potassium chloride solution was the upper, and in Type B the lower of the two solutions.

(d) Cylindrically symmetrical junction. This was made as follows. The path DBCE (see Fig.13) of a 120° three-way tap was completely filled with buffer solution, and any solution projecting beyond D and E removed with a piece of filter paper. With the tap turned so as to seal all three limbs, this bridge was carefully lowered, until D and E dipped into the buffer and saturated potassium chloride solution containers respectively. A and B were connected, and potassium chloride solution slowly drawn about 2 cms up DB. Again all the limbs were sealed, and a tight fitting rubber bung inserted in F. The tap was now turned to connect A and C, momentarily, and then B and C. By this means it was ensured that the sharp boundary in DB was not disturbed when B and C were connected. The saturated potassium chloride and buffer solutions were now in contact at a point in DB. This junction may be used in conjunction with commercial electrodes, as shown in Fig.13. No junction potential arises at the plug or wick of the commercial electrode, as it is dipping into a saturated potassium chloride solution.

6.2.3. Discussion of Results.

In Table VII an analysis of the readings taken with the various types of junction is given. These are considered under three headings, viz. the readings taken during the first two hours after the junction had been set up, the readings taken after this period, and the readings taken over the whole period of the run. An indication of the stability of the readings in each of the cases treated is given by the mean deviation from the mean of the readings during each of the three periods, while the mean pH during any period from the pH at which the meter was originally set indicates the reproducibility of the liquid junction potential. The data of Table VII are summarised in Table VIII to facilitate comparison, and, in addition two other important stability characteristics are indicated: the time which elapsed between the establishment of the junction and the attainment of a period of stability, and the duration of the period of stability.

Before considering the implications of these data the meaning of the term "period of stability" should be clarified. It was found that, in all cases except that of the simple dipping junction, Type A, the making of the junction was followed by wide fluctuations of potential which gradually decreased in magnitude until a steady state was reached. In this steady state variations in potential still occurred, but their magnitude remained constant. It is the period during which this steady state persisted which is known as the "stable period". Both the time taken for the stable period to be arrived at, and its duration, varied from run to run, but the limits within which the steady state pH varied were less random, and clearly dependent on the type of junction concerned. The figures in the Tables show that the porous plug, and the simple dipping Type A junctions were the least stable. The potentials at the latter, indeed, varied randomly throughout the whole period of a run, and no steady state could ever be detected. While the overall stability of the simple dipping Type B, (± 0.017 pH), wick, (± 0.013 pH), and cylindrically symmetrical junctions, (±-0.016 pH), were very similar, it is evident that the stability of the last was considerably greater than that of any other type (± 0.002 pH) once the steady state was reached.

Two other marked differences in the behaviour of cylindrically symmetrical and conventional junctions are noteworthy. The first of these is the fact that the increase in stability as the junctions approach the steady state was much greater for cylindrically symmetrical junctions; the second is that the steady state did not deteriorate in the cylindrically symmetrical case. Readings were taken for as long as 24 hours without any decrease in stability becoming manifest. In the other cases, however, it was found that the magnitude of the variations in pH increased after the steady state had been in existence for some hours.

A striking feature of the results is the degree of irreproducibility of the potentials at all the types of junction treated above. They indicate that reproducible potentials are those at wick type junctions, and that these are considerably more satisfactory than the potentials at cylindrically symmetrical junctions. Even with wick junctions, however, it must be expected that irreproducibility at the liquid junction will introduce an uncertainty of 0.040 pH units in any complete determination. If, in addition, the instability of the junction is considered, the resultant uncertainty is seen to be of the order of 0.060 pH units. The significance of this figure is apparent if it is considered in the light of the statement made at the beginning of this section - that pH's measured by the techniques described above are commonly regarded as being accurate to within 0.01 to 0.02 pH units.

6.2.4. Further Considerations of Cylindrically Symmetrical Junctions.

It was considered that the irreproducibility shown above by cylindrically symmetrical junctions was not inherent in the junctions themselves, but was caused by a fundamental error in the conventional pH determination procedure which was used here, which involves setting the meter, or reading the pH, immediately after the junction is made. The above results, however, as well as theory (48), and accurate experimental work (45, 49) show that junction potentials, and in particular those at cylindrically symmetrical junctions are unstable directly after their formation but gradually steady with time. Thus the conventional procedure leads to readings being taken, and the meter being standardised at the most unfavourable time. It would surely be more satisfactory if the initial instabilities were allowed to die away and the steady state were reached, before reading or setting the meter.

To prove this theory, another set of readings was made with cylindrically symmetrical junctions, using the following procedure. A cylindrically symmetrical junction was set up as described above, and, after a lapse of two hours, the meter set at the pH of the buffer. A new junction was then made and its pH followed until the steady state was reached. The results are shown in Table IXA. They show that the modification indeed produces a marked improvement, and reduces the uncertainty in a complete pH determination to within 0.01 pH units.

The very real drawback of this method is that 2 to 3 hours are necessary for each pH reading. It was, however, also found possible to reduce considerably the time taken to set up the steady state by taking special precautions to minimise mixing of the two solutions as the junction is made.

These consisted in siliconing the walls of the tube, and carefully grinding flat its end. The marked improvement resulting is shown in Table IXB. Initial fluctuations were much smaller and the period of stability was reached in less than 30 minutes. Thus it is possible to reduce the time necessary for a reading to under half an hour without sacrificing in any degree the accuracy of the method.

It must be emphasised, however, that, although stable reproducible junction potentials can be obtained by this careful technique, the actual junction potential error is not thereby eliminated. To minimise it, it is necessary, in addition, to ensure that the pH of the buffer used for standardising the meter be as near as possible to that of the unknown solution, in which case the two junction potentials will tend to cancel.

6.2.5. Conclusions.

It has been shown that with the equipment generally used in pH determinations, an uncertainty of at least 0.1 pH unit must be expected in any measurement, but that this can be reduced to 0.01 pH units by using a free diffusion junction with "cylindrical symmetry".

The results of this purely practical investigation substantiate the statement by Dole (46) that the potentials at indefinite type junctions "may be in error by as much as 3-5 mV or 0.1 pH unit", although, where the junction is cylindrically symmetrical, "fluctuations in its potential would be less than 0.01 pH unit".

Note added in typing.

A paper on this section of the work has been accepted for publication by the Journal of the South African Chemical Institute.

TABLE VII - BEHAVIOUR OF VARIOUS JUNCTION TYPES STUDIED

	POROUS PLUG JUNCTION								SIMPLE DIPPING JUNCTION (TYPE B)			
Experiment number	1	2	3	4	5	6	7	Mean	1	2	3	Mean
Mean deviation from mean for results taken:												
(1) during the first two hours.	0.031	0.007	0.007	0.041	0.033	0.014	0.051	0.026	0.018	0.015	0.017	0.017
(2) after the first two hours.	0.018	0.011	0.099	0.010	0.055	-	0.019	0.020	0.012	0.017	0.007	0.012
(3) for the complete run.	0.093	0.008	0.009	0.067	0.056	0.015	0.036	0.040	0.016	0.018	0.016	0.017
Difference between pH meter setting and mean value obtained:												
(1) during the first two hours.	-0.012	+0.013	+0.011	-0.039	+0.026	-0.028	+0.017	0.010	-0.022	-0.025	-0.043	0.030
(2) after the first two hours.	-0.110	+0.011	+0.013	-0.167	+0.138	-	+0.051	0.070	-0.022	-0.052	-0.059	0.044
(3) for the complete run.	-0.052	+0.006	+0.013	-0.109	+0.067	-0.031	+0.041	0.046	-0.021	-0.047	-0.053	0.040
Number of readings:												
(1) during the first two hours.	14	10	7	5	7	9	8		5	4	7	
(2) after the first two hours.	9	7	13	6	4	1	16		9	20	7	
(3) for the complete run.	23	17	20	11	11	10	24		14	24	14	

TABLE VII (cont'd) - BEHAVIOUR OF VARIOUS JUNCTION TYPES STUDIED

	WICK JUNCTION										
Experiment number	1	2	3	4	5	6	7	8	9	10	Mean
Mean deviation from mean for results taken:											
(1) during the first two hours.	0.004	0.014	0.012	0.010	0.013	0.008	0.014	0.010	0.010	0.006	0.010
(2) after the first two hours.	0.009	0.006	0.024	0.007	0.007	0.009	0.006	0.008	0.008	0.021	0.010
(3) for the complete run.	0.014	0.011	0.021	0.009	0.013	0.009	0.013	0.015	0.009	0.018	0.013
Difference between pH meter setting and mean value obtained:											
(1) during the first two hours.	-0.007	-0.016	+0.010	-0.008	-0.010	+0.015	-0.022	+0.031	+0.005	+0.047	0.017
(2) after the first two hours.	-0.049	0.000	+0.034	-0.016	-0.027	+0.005	-0.032	+0.063	+0.003	+0.021	0.025
(3) for the complete run.	-0.033	-0.006	+0.023	-0.010	-0.019	+0.007	-0.027	+0.041	+0.004	+0.032	0.020
Number of readings:											
(1) during the first two hours.	4	7	5	5	7	4	13	15	2	3	
(2) after the first two hours.	14	10	6	8	7	14	5	7	5	4	
(3) for the complete run.	18	17	11	13	14	18	18	22	7	7	

TABLE VII (cont'd) - BEHAVIOUR OF VARIOUS JUNCTION TYPES STUDIED

	CYLINDRICALLY SYMMETRICAL JUNCTION										
Experiment number	1	2	3	4	5	6	7	8	9	10	Mean
Mean deviation from mean results taken:											
(1) during the first two hours.	0.005	0.041	0.003	0.025	0.028	0.013	0.009	0.006	0.013	0.032	0.017
(2) after the first two hours.	0.002	0.003	0.003	0.002	0.002	0.002	0.002	0.002	0.004	0.002	0.002
(3) for the complete run.	0.004	0.053	0.013	0.020	0.012	0.011	0.007	0.011	0.012	0.027	0.016
Difference between pH meter setting and mean value obtained:											
(1) during the first two hours.	+0.013	-0.046	-0.006	-0.044	+0.032	-0.048	-0.013	-0.029	+0.016	+0.015	0.026
(2) after the first two hours.	+0.012	-0.111	-0.028	-0.089	+0.046	-0.029	-0.007	-0.006	-0.007	-0.036	0.037
(3) for the complete run.	+0.013	-0.088	-0.019	-0.059	+0.039	-0.036	-0.011	-0.018	+0.009	-0.014	0.031
Number of readings:											
(1) during the first two hours.	13	6	5	11	3	3	11	10	12	6	
(2) after the first two hours.	7	5	7	5	9	4	6	11	6	8	
(3) for the complete run.	20	11	12	16	12	7	17	21	18	14	

TABLE VIII - SUMMARY OF THE BEHAVIOUR OF JUNCTION TYPES STUDIED

Junction Type	Simple Dipping		Wick	Porous Plug	Cylindrically Symmetrical	
	Type A.	Type B.			Unsiliconed	Siliconed
Mean deviation from mean for readings taken:	Unstable					
(1) during the first two hours of run		0.017	0.010	0.026	0.017	0.004
(2) after first two hours of run		0.012	0.010	0.020	0.002	0.001
(3) during the complete run		0.017	0.013	0.040	0.016	0.004
Difference between original meter setting and mean pH	Completely					
(1) during the first two hours of run		0.030	0.017	0.019	0.026	0.005
(2) after first two hours of run		0.044	0.025	0.070	0.037	0.011
(3) during the complete run		0.040	0.020	0.046	0.031	0.008
Time taken to reach stability (hours)		0 - 3	0 - 2	0 - 3	1 - 2.5	0 - 0.5
Period of stability in hours		2 - 7	3 - 5	4	5	5

TABLE IX - RESULTS WITH METER SET AT BUFFER pH DURING 'STEADY STATE'

Experiment Number	A. Unsiliconed				B. Siliconed			
	1	2	3	Mean	1	2	3	Mean
Mean deviation from the mean of readings taken:								
(1) during 1st two hours	0.041	0.066	0.012	0.020	0.002	0.004	0.002	0.003
(2) after 1st two hours	0.003	0.002	0.002	0.002	0.002	0.003	0.000	0.002
(3) during the complete run	0.033	0.011	0.011	0.018	0.006	0.003	0.003	0.004
Difference between original meter setting and mean pH								
(1) during the first two hours	+0.064	-0.022	-0.018	0.035	-0.012	+0.011	-0.002	0.008
(2) after the first two hours	-0.003	+0.002	+0.003	0.003	-0.001	+0.012	+0.005	0.006
(3) during the complete run	+0.022	-0.011	-0.006	0.013	-0.007	+0.011	+0.003	0.007
Number of readings:								
(1) during the first two hours	6	10	5		12	8	7	
(2) after the first two hours	5	11	7		9	11	11	
(3) for the complete run	11	21	12		21	19	18	

6.3 POSSIBLE UNCERTAINTIES IN DRY'S pH METHOD

The results of the investigation above brought into sharp relief the magnitude of the residual junction potential error which can be expected in normal pH work. In view of these findings, it was decided to analyse Dry's pH method, and obtain some estimate of the uncertainties possible due to errors of this kind.

Dry measured the pH of his saturated calomel solution with a glass electrode pH meter, using a specially designed cell to prevent chloride ions from the saturated calomel reference electrode upsetting the equilibria in the bulk solution. The pH meter error was determined by measuring the potential of a hydrogen electrode in a buffer yielding the same pH reading on the meter as a typical saturated calomel solution. That is, in evaluating his figure, the e.m.f!s of the following cells were measured:

(a) $\text{Glass} \mid Hg_2Cl_2\ (\text{satd.}) \ \vdots\ Ej(1)\ \ KCl\ (\text{satd.}) \mid Hg_2Cl_2 - Hg$

$$E_1 = E_g^{\circ} - \frac{RT_1}{F} \ln a_{(1)\,H^+} + Ej(1) \qquad \ldots\ldots (1)$$

(b) $\text{Glass} \mid \text{Buffer A} \ \vdots\ Ej(2)\ \ KCl_{(\text{satd.})} \mid Hg_2Cl_2\text{-}Hg$

$$E_2 = E_g^{\circ} - \frac{RT_2}{F} \ln a_{(2)\,H+} + Ej(2) \qquad \ldots\ldots (2)$$

(c) $H_2 \mid \text{Buffer A} \ \vdots\ Ej(3)\ \ KCl_{(\text{satd.})} \ \vdots\ Ej(a)\ \ KCl_{(0.1N)} \mid Hg_2Cl_2\text{-}Hg$

$$E_3 = E^{\circ}_{Hg,Hg_2^{2+}} - \frac{RT_3}{F} \ln a_{(3)H^+} \cdot a_{Cl^-} + Ej(3) + Ej(a) \qquad \ldots\ldots (3)$$

(d) $H_2 \mid \begin{array}{l}\text{Buffer B}\\ pH=4.00\end{array} \ \vdots\ Ej(4)\ \ KCl_{(\text{satd.})} \ \vdots\ Ej(b)\ \ KCl_{(0.1N)} \mid Hg_2Cl_2\text{-}Hg$

$$E_4 = E_{Hg,Hg_2^{2+}} - \frac{RT_4}{F} \ln a_{(4)H^+} \cdot a_{Cl^-} + Ej(4) + Ej(b) \qquad \ldots\ldots (4)$$

Assuming $T_2 = T_3$, $a_{(2)H^+} = a_{(3)H^+}$, $Ej(a) = Ej(b)$, and $Ej(2) = Ej(3)$, he derived his final equation from a combination of the above, namely:

$$-\log a_{(1)H^+} = \frac{(Ej(4) - Ej(1)) - (E_4 - E_3) - 2.303\,\frac{RT_4}{F}\log a_{(4)H^+}}{2.303\,\frac{RT_1}{F}}$$

E_4 and E_3 were the measured potentials, while the junction potentials $Ej(1)$ and $Ej(4)$ were computed from the Henderson Equation (50).

The saturated calomel reference electrode used in cells (a) and (b), was a commercial model with a porous plug junction. In cells (c) and (d), the hydrogen and calomel half cells were connected by a salt bridge of saturated potassium chloride solution, and the liquid junctions, made at the tip of a somewhat drawn out narrow tube, were of the simple dipping type.

The results of the work above (see 6.2) show that with these junctions uncertainties of ± 0.026 and ± 0.017 pH units can be expected respectively, and must limit any attempts to equate the potentials arising at junctions of this type, such as $Ej_{(2)}$ and $Ej_{(3)}$, or $Ej_{(a)}$ and $Ej_{(b)}$.

Further, as a porous plug junction was used in the glass electrode work, an uncertainty of ± 0.026 pH units is predicted in the measured potential E_1 due to fluctuations in $Ej_{(1)}$. In point of fact Dry's measurements showed a maximum fluctuation of ± 0.03 pH units, which it is felt arose from this source. However, Dry correlated the variation in his readings with the specific conductance of the saturated solution at its time of transfer from the conductivity cell to the pH vessel, and obtained his final figure of 5.18 ± 0.01 units for the pH of a saturated calomel solution at 25°C by extrapolation.

The precision of the e.m.f. measurements (E_3 and E_4) must also be limited by the uncertainty of the liquid junction potentials involved, and a variation of ± 0.5 mV is probable in $Ej_{(4)}$ alone. It is very likely, therefore, that the overall precision will be less than ± 0.3 mV as claimed by Dry.

The above shows clearly the limitations not only of Dry's pH method but also of any pH method in which liquid junctions are necessary. Fortunately, as the equilibrium constants of the equilibria (1) to (9) (see 1) are known at 25°C, a high degree of accuracy was not imperative, and Dry's pH value was necessary only as a check on the hydrochloric acid concentration obtained conductimetrically. However, in the work at the other temperatures considered (5-55°C) the equilibrium constants are not known, and precision pH measurement is essential. Dry's method, therefore, would not be suitable, and it was decided to find a more accurate procedure which would obviate the use of liquid junctions as far as possible.

6.4 A NEW METHOD FOR THE DETERMINATION OF THE HYDROGEN ION CONCENTRATION IN A SATURATED CALOMEL SOLUTION AT 25°C

6.4.1 Outline and Theory

In view of the large uncertainties in residual liquid junction potentials, a method was required which would eliminate, as far as possible, the need for liquid junctions, and the following type of cell suggested itself.

$$\text{Glass} \mid \text{Saturated Calomel Solution} \mid Hg_2Cl_2\text{-}Hg$$

Since Dry (29) showed that 97.5 per cent of the ionised material in a saturated calomel solution at 25°C is hydrochloric acid, this cell is equivalent to:-

$$\text{Glass} \mid HCl\ (m) \mid Hg_2Cl_2 - Hg$$

The use of this type of cell was considered (on paper) the most accurate and precise means of measuring the pH of saturated calomel solutions, since (a) the necessity of liquid junctions is obviated, (b) special low resistance soft-glass glass electrodes, capable of giving results of precision comparable to that of the best results obtained with the hydrogen electrode, are now available, and (c) extremely stable and reproducible calomel electrodes can now be prepared. (The stability of calomel electrodes using such extremely dilute chloride solutions was not known, however, and remained to be investigated).

Of fundamental importance it must be remembered that two distinct potentials must be recognised when a glass electrode is placed in solution, namely:

(i) A potential set up instantaneously which varies with the hydrogen ion concentration of the solution (the hydrogen electrode function of the glass electrode); and

(ii) The asymmetry potential which is due to differences in the two surfaces of the glass membrane.

In order to overcome the latter, it is general practice to measure the asymmetry potential at the outset, and use this value to correct the final series of measurements. Covington and Prue (51), however, in their paper on precise measurements with glass electrodes, found that this potential is not constant and recommend a simple extrapolation procedure to overcome this difficulty.

To eliminate asymmetry potential errors in this research, then, it was decided to emulate their method and obtain the extrapolated values of the e.m.f. E_a and E_b that the cells (a) and (b)

$$\boxed{\text{Ag-AgCl} \,\vdots\, \text{HCl}_{(m')}}\ \ \text{glass}\ \Big|\ \ \text{HCl}_{(m_1)}\ \Big|\ \text{Hg}_2\text{Cl}_2\text{-Hg} \qquad (a)$$

$$\boxed{\text{Ag-AgCl}\ \big|\ \text{HCl}_{(m')}}\ \ \text{glass}\ \Big|\ \begin{matrix}\text{Satd. calomel soln.}\\ \text{i.e. HCl}_{(m_2)}\end{matrix}\ \Big|\ \text{Hg}_2\text{Cl}_2\text{-Hg}\ (b)$$

would have at the moment of transfer of the glass electrode from one cell to the other; in this way the asymmetry potential is the same for the two cells. The enclosed part on the left of (a) and (b) above represents the glass electrode filled with hydrochloric acid, and containing an internal silver - silver chloride reference electrode.

Assuming the glass membrane is permeable to hydrogen ions only, cells (a) and (b) can be combined to give the thermodynamically equivalent cell

$$\text{Hg-Hg}_2\text{Cl}_2\ \Big|\ \text{HCl}\ _{(m_1)}\Big|\ \text{H}_2\ \Big|\ \text{HCl}\ _{(m_2)}\ \Big|\ \text{Hg}_2\text{Cl}_2\text{-Hg},$$

whose e.m.f. E is given by

$$E = E_b - E_a = -2k\ \log\ (m_2\,\gamma_2) + 2k\ \log\ (m_1\,\gamma_1)$$

where $k = \frac{RT}{F}$ ln 10, and m_1, m_2 and γ_1, γ_2 are the respective molalities and mean ionic activity coefficients of the hydrochloric acid. Since the asymmetry potential makes the same contribution to both cells its effect is eliminated.

Since the hydrochloric acid solutions are very dilute (the hydrochloric acid in cell (a) must essentially be of the same order of concentration as that resulting from the solution of calomel in cell (b);

$$\gamma_1 = \gamma_2 = 1.$$

Therefore,

$$E = -2k \log m_2 + 2k \log m_1.$$

As cell (a) is the same for the series of measurements, the electrode assembly as a whole can be regarded as having a kind of "standard" potential E^{o}, then

$$E = E^{o} - 2k \log m_2,$$

where $E^{o} = 2k \log m_1$.

Now since m_1 is known (the solution is accurately prepared), the hydrogen ion concentration in the saturated calomel solution - m_2 - can be calculated from the measured potential E.

6.4.2 The Stability of Very Dilute Calomel Electrodes

The success of the cell above depends on the stability of the calomel electrodes. Hills and Ives (26) in their paper on the calomel electrode, showed that by taking special precautions the calomel electrode is stable and reproducible to ± 10 μV, reaches its constant potential in 2 to 4 hours, and shows no concentration polarisation effects such as those associated with the silver-silver chloride electrode (52). They showed, too, that the electrode is highly satisfactory even in the most dilute hydrochloric acid solutions, with no loss in reproducibility with decreasing concentration. The most dilute hydrochloric acid solution studied, however, was 10^{-3}N, and, as the solutions to be measured in this research were of the order of 10^{-5} moles/litre, it was necessary to investigate the stability of such very dilute electrodes before proceeding with the final design of the cell.

Experimental

The behaviour of the very dilute calomel electrodes was observed by measuring the resultant potentials when two identical half cells were opposed.

The Cell Vessel. The cell vessel used is illustrated in fig. 14 and was of 300 ml capacity. The calomel electrodes were prepared in the 5mm glass tubes A, and contact with the mercury pool of the electrodes made by means of a long platinum wire B. The end of the nitrogen bubbling tube C was turned upwards to eliminate the effects of bubbling pressure disturbance on the calomel layer.

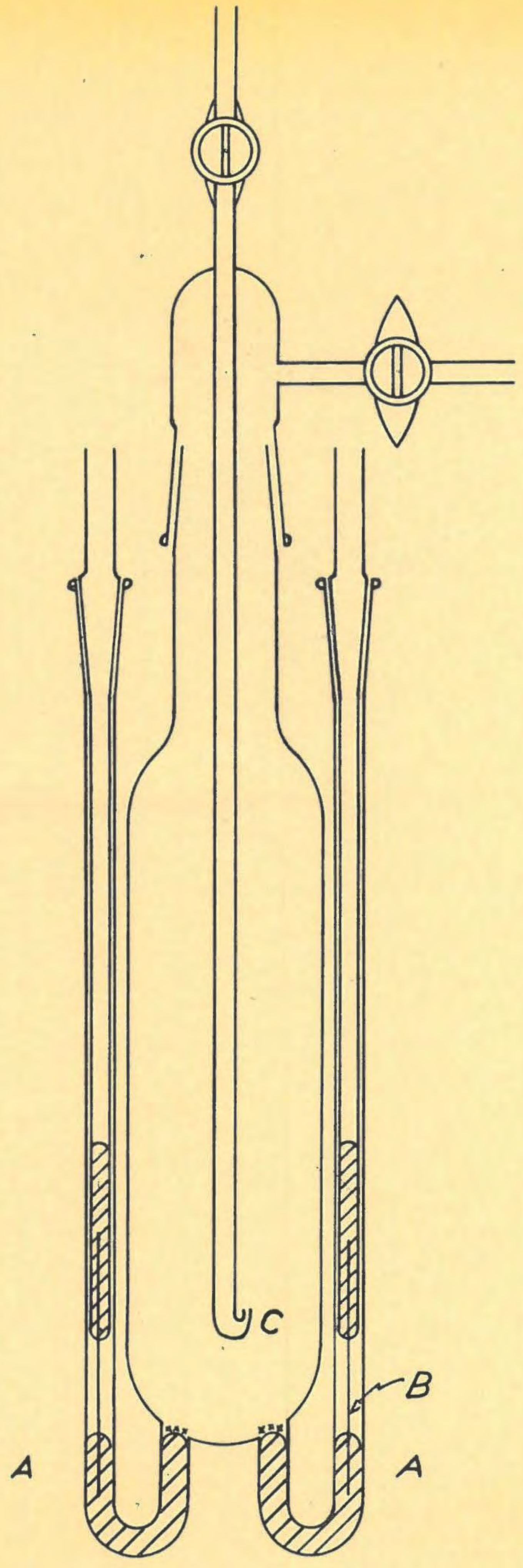


FIG. 14 THE CALOMEL CELL

The Calomel Electrodes. The calomel electrodes were made by the general method of Hills and Ives (26). The cell vessel was cleaned, steamed for three hours, dried and siliconed as described elsewhere (see 4.3.10). It was then swept out with pure, dry nitrogen, and a small amount of anaerobic mercury added carefully to just fill the U's of the A tubes as shown in the figure. In a ground glass stoppered test tube a few ml of the mercury were shaken vigorously with a little pure dry calomel. Small amounts of the resulting grey skin were added to the pools of mercury in the tubes, until the entire exposed surface was covered with the spreading film. It was noticed that when only enough skin was added to form a surface of islands separated by clear mercury, the electrode gave unstable potentials. The electrolyte was only added when the vessel had been rigidly clamped in the thermostat.

Potentiometric Apparatus. A Tinsley vernier potentiometer which a contempory worker had accurately standardised, was used to measure the cell potentials. A Kipp A75 light spot galvanometer was used as a null point detector. To prevent electrostatic leakage all components of the circuit were mounted on an equipotential surface (53), while shielded leads were used to eliminate A.C. pick-up. Reversing switches were employed to investigate the presence of thermal e.m.f.'s, but at no time were such potentials found to exceed 1 μ V.

Temperature Control. The experiment was carried out at 25 ± 0.01 °C. The thermostat used was one similar to that previously described (see 4.2.1), however, mechanical stirring was dispensed with, as the attendant agitation upset the cell potentials, and a circulating pump was used instead.

Procedure

The cell was firmly clamped in the thermostat to prevent any unnecessary vibration, and the filtered saturated calomel solution carefully added so as not to disturb the 'skin' of the electrodes. The bubbling assembly was then fitted into the neck of the cell, and purified nitrogen bubbled through the solution at a steady rate for 8 to 12 hours to bring it to equilibrium. The nitrogen was purified as described elsewhere (see 4.3.2), and presaturated by bubbling through conductance water at the thermostat temperature. The e.m.f. was measured at regular intervals over 24 hours to the nearest μ V.

Results

The results of seven replicate runs showed that from 4 to 12 hours were required for the cell to reach equilibrium. The final stable potentials were constant to within 10 μ V. Usually the potential was read at regular intervals until it had been constant for 12 hours, but even when this was extended to 5 days in the final run, no deterioration of stability was noticeable. It was found that the slightest mechanical disturbance destroyed the stability of the potentials, but that after about two to three hours the stability was restored to its original value. The replicate runs were reproducible to within 25 μ V.

The effect of small pressures on the cell potential was also investigated, as it was possible that some of the electrolyte might have to be raised to a higher level than that in the cell vessel, by nitrogen pressure, in the final pH cell. The pressures investigated were 0 to 15 cms of water, and the variation in potential recorded over the 16 readings was ± 10 μV.

In several further tests experiments were carried out using an unfiltered saturated calomel solution with excess solid calomel in suspension, and dispensing with the calomel skin on the mercury pools of the electrodes. It was of interest to note whether the solid calomel settling out on the mercury would result in the formation of stable calomel electrodes. Unfortunately, the electrodes made in this way were not reproducible, and stable only to ± 50 μV after bubbling for 21 hours.

Conclusions

The results obtained show

(i) That even when the chloride ion concentration in the electrolyte is extremely small, of the order of 10^{-5} gm ions/litre, calomel electrodes providing stable and reproducible potentials can be prepared; and

PLATE III

THE pH CELL

(ii) That the cell potential is virtually independent of small excess pressures.

6.4.3 The pH Cell

The pH cell designed and constructed on the basis of the above, is shown diagrammatically in fig. 15. Essentially the cell embodies two independent cells using a glass electrode which is common to both. The cell was constructed entirely of pyrex glass, and the two side vessels A and B, containing the calomel electrodes, can independently be connected to the central cup C, which houses the glass electrode, by means of the Y-taps D and E. In such a way the potentials of two cells can be measured in which the glass electrode is common.

The Side Vessels. These were identical to those described in the investigation above; one in fact being the vessel used for those experiments. They were provided with two calomel electrodes for the sake of comparison.

The Central Cup. (Originally, the glass electrode was to have been inserted into the neck of the side vessels, but in view of the possible washing difficulties, when transferring the electrode from one vessel to another, this idea was discarded.) The central cup was designed just large,enough to embrace the bulb of the glass electrode, so that aliquots of electrolyte pumped into it for washing would be kept to an absolute minimum. To prevent accidentally breaking the electrode when removing it from the cup the glass electrode was specially mounted in a ground glass collar which accurately fitted the ground glass rim of the cup. The cup was provided with a tube, F, for bubbling nitrogen through the solution and keeping it well stirred. Tap G controlled the bubbling rate. The gas escaped via exit capillary H.

The Y-Taps. These connected the side vessels to the central cup, and by suitable manipulation the glass electrode could be washed by, and brought in contact with, either of the side vessel solutions.

Electrodes. The cell was designed to use carefully prepared calomel electrodes (see 6.4.2) and a special soft-glass low resistance glass electrode, so that potentials could be directly measured by a vernier

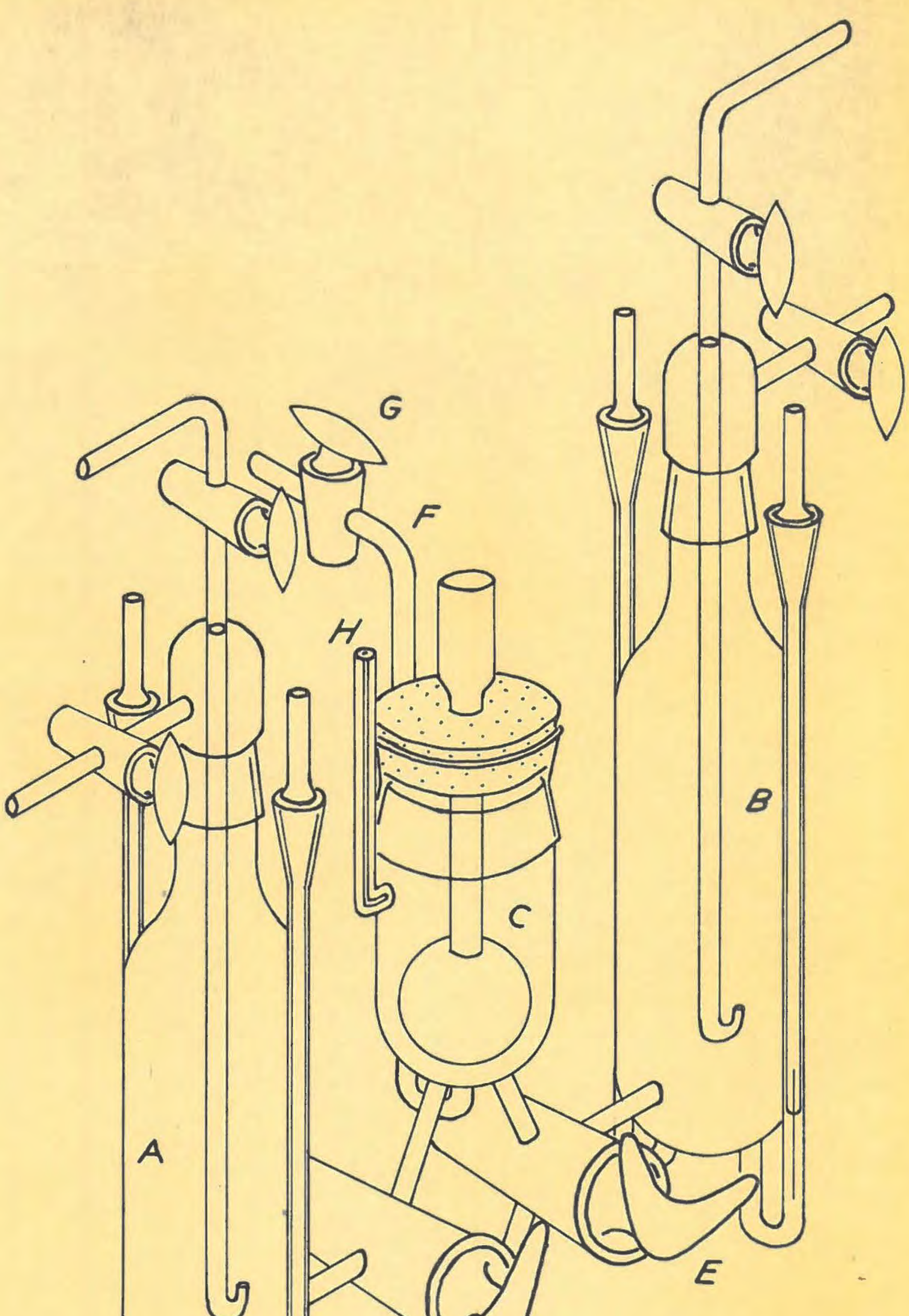


FIG. 15 - THE pH CELL

potentiometer. The glass electrode was a Type 9000 (Blue Trade Mark) made by the Jaener Glaswerk, Bavaria, ready for filling with 0.1 M hydrochloric acid, and use with an internal silver-silver chloride electrode of the thermal electrolytic type e.g. as prepared by Malan (17).

6.4.4 Readings and Results.

Unfortunately, owing to extremely long delays in the delivery of the special glass electrodes and of a galvonometer with required characteristics it was not possible for the author to take any readings. For the sake of completing this thesis, however, it has been necessary to calculate the solubility of calomel on the assumption that Dry's value of the pH of a saturated calomel solution at 25°C is the correct one. That is 5.085 ± 0.01 pH units.

7. THE NATURE OF A MERCUROUS CHLORIDE SOLUTION IN WATER AT 25°C

7.1. GENERAL SURVEY

The most accurate value for the pH of a saturated calomel solution at 25°C available, is 5.085 ± 0.01 pH units determined by Dry (1) in 1955. This corresponds to a hydrogen ion concentration of $(8.2 \pm 0.2) \times 10^{-6}$ g. ion/litre, and showed that hydrolysis of the cations in solution occurred to a large extent. As calculation indicated that the concentrations of the two complex mercuric anions are negligible, and since the hydroxyl ion concentration at this pH is only 10^{-9} g. ion/l, the only anion present in any significant amount is the chloride ion. Hence, hydrochloric acid may be considered one of the major constituents of the saturated solution.

The contribution of this hydrochloric acid to the conductivity of the solution was subsequently calculated. Substitution in the Onsager Equation, namely

$$\Lambda_o = \Lambda_c - (A + B\Lambda_o)\sqrt{c} \qquad \text{..... (8)}$$

(where Λ_o is the equivalent conductance at infinite dilution, Λ_c the equivalent conductance at the concentration $\underline{c}$, and A and B are constants), gave the equivalent conductance of the hydrochloric acid at the approximate ionic concentration present in a saturated calomel solution (8.4×10^{-6} mole/l) as 425.6, and with the hydrogen ion concentration quoted above, this yielded the specific conductance required: 3490 ± 90 nm/cm. Thus the mercury containing ions were only responsible for a small proportion (2 to 104 nm/cm) of the observed conductivity of 3492 ± 12 nm/cm.

As the equivalent conductances of the mercury containing cations are unknown, a reasonable assumption of their values was necessary in order to calculate the concentration of these species from the conductivity figures above. Kohlrausch (16) estimated the equivalent conductance of the mercurous ion to be 60, and it was therefore considered that those of the other mercury containing cations would lie close to this value, and certainly between 30 and 80. Hence the equivalent conductivity of any of their chlorides was assumed to be 130 ± 25, and their total concentration found to lie between 0.2×10^{-7} and 8×10^{-7} equiv./l. Since the experimental figure for the total mercury content was 7.2×10^{-6} mole/litre, it was evident that practically all the mercury must be present in the form of unionised species, namely $HgCl_2$ and $Hg(OH)_2$.

It can be concluded from the above, therefore, that the greatest part of the dissolved material in a calomel solution saturated at 25°C, is in the form of HCl, $HgCl_2$, and $Hg(OH)_2$, NOT Hg_2Cl_2 !

7.2. AN ESTIMATION OF THE CONCENTRATION OF THE VARIOUS SPECIES EXISTING IN A SATURATED MERCUROUS CHLORIDE SOLUTION AT 25°C.

A saturated mercurous chloride solution contains no less than six cations (Hg_2^{2+}, Hg^{2+}, $HgOH^+$, $HgOH^+$, Hg_2OH^+, $HgCl^+$, and H^+), four anions (Cl^-, $HgCl_3^-$, $HgCl_4^{2-}$, and OH^-) and two unionised species ($Hg(OH)_2$ and $HgCl_2$), produced by the establishment of the equilibria set out in Table X below. The equilibrium constants shown are the thermodynamic values carefully estimated by Dry and Gledhill (1), mainly from those determined by Sillén and his co-workers (2,3,4) referring only to the special conditions of their experiments.

TABLE X - EQUILIBRIA AND EQUILIBRIUM CONSTANTS.

	Equilibrium	$\log K_i$
(1)	$Hg_2Cl_{2(s)} \rightleftharpoons Hg_2^{2+} + 2\,Cl^-$	18.123 ± 0.003
(2)	$Hg^{2+} + Hg_{(liq)} \rightleftharpoons Hg_2^{2+}$	2.114 ± 0.032
(3)	$Hg^{2+} + H_2O \rightleftharpoons HgOH^+ + H^+$	4.91 ± 0.20
(4)	$Hg^{2+} + 2H_2O \rightleftharpoons Hg(OH)_2 + 2H^+$	6.35 ± 0.12
(5)	$Hg_2^{2+} + H_2O \rightleftharpoons Hg_2OH^+ + H^+$	5.6 ± 0.4
(6)	$Hg^{2+} + Cl^- \rightleftharpoons HgCl^+$	7.34 ± 0.27
(7)	$Hg^{2+} + 2Cl^- \rightleftharpoons HgCl_2$	14.26 ± 0.09
(8)	$Hg^{2+} + 3Cl^- \rightleftharpoons HgCl_3^-$	-
(9)	$Hg^{2+} + 4Cl^- \rightleftharpoons HgCl_4^{2-}$	-

These K values were used in the calculations below: K_8 and K_9 were not required since preliminary calculation showed that the concentrations of $HgCl_3^-$ and $HgCl_4^{2-}$ would be of the order of 10^{-10} and 10^{-14} mole/litre respectively, and therefore negligible.

The concentrations of the various species existing in a saturated calomel solution at 25°C were computed by the method of successive approximations used by Dry and Gledhill (1).

(a) Reasonable values of the hydrogen ion and chloride ion concentrations were assumed on the above basis (see 7.1), namely 8.2×10^{-6} and 8.6×10^{-6} g.ion/litre respectively.

(b) The concentrations of Hg_2^{2+}, Hg^{2+}, $HgCl^+$, $HgOH^+$, and Hg_2OH^+ were calculated from their equilibrium equations given below.

(1) $$m_{Hg_2^{2+}} = \frac{K_1}{m_{Cl^-}^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

(2) $$m_{Hg^{2+}} = \frac{m_{Hg_2^{2+}}}{K_2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

(3) $$m_{HgOH^+} = \frac{K_3\, Hg^{2+}}{m_{H^+}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

(4) $$m_{Hg_2OH^+} = \frac{K_5 \ Hg_2^{2+}}{m_{H^+}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (12)$$

(5) $$m_{HgCl^+} = K_6 . m_{Hg}{}^{2+} . m_{Cl^-} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (13)$$

(c) The total number of equivalents per litre of all positive ions other than hydrogen ion, C, was then evaluated.

$$C = 2m_{Hg_2^{2+}} + 2m_{Hg^{2+}} + m_{HgCl^+} + m_{HgOH^+} + m_{Hg_2OH^+} \quad \ldots\ldots \quad (14)$$

Since chloride ion is the only significant anion present in solution, C corresponds to the concentration of chloride ion equivalent to all the cations except hydrogen ion, and the ionic components of the solution can be regarded as a mixture of hydrochloric acid at the concentration of hydrogen ion, and the chlorides of the mercury-containing cations at the concentration C equiv./litre, the specific conductance of which must equal the value observed (3492 nm/cm.) i.e.

$$\frac{m_{HCl} \Lambda_{HCl}}{1000} + \frac{C \lambda_{Cl^-}}{1000} + \frac{C \lambda_{Hg\ cation}}{1000} = \varkappa_{cal} \quad \ldots\ldots \quad (15)$$

Hence, since the equivalent conductance of hydrochloric acid at the concentration concerned, (8.4×10^{-6} mole/l), is 425.6, and assuming the equivalent conductance of the chlorides of the mercury-containing cations to be 130 ± 25 (see 7.1), it follows that

$$0.4256 \ m_{H^+} + 0.130 \ C = 3492 \times 10^{-9}. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (16)$$

(d) From this equation, then, a new value for the hydrogen ion concentration was obtained, which was a better approximation to m_{H^+} than the one originally assumed in (a) above.

(e) A better value of m_{Cl^-} was subsequently obtained by using the condition of electrical neutrality, which requires the new value for m_{Cl^-} to be equal to $m_{H^+} + C$.

(f) With these second approximations the whole process from (a) to (e) was repeated until the figures for m_{H^+} and m_{Cl^-} were self-consistent. The limits of error of the various quantities involved were taken into account in order to set limits of error to the concentrations so deduced.

The concentrations of the two unionised mercuric compounds were also calculated. Consideration of the equilibria existing in the saturated solution showed that one hydrogen ion is present in solution for every OH group in a molecule or ion of $Hg(OH)_2$, $HgOH^+$, and Hg_2OH^+. Hence,

$$m_{Hg(OH)_2} = m_{H^+} - m_{HgOH^+} - m_{Hg_2OH^+} \text{ .... } (17)$$

from which $m_{Hg(OH)_2}$ was calculated since the three right-hand quantities were known. The concentration of the mercuric chloride was obtained by summing up the concentrations of all the mercury-containing species and subtracting this from the experimental figure for the total mercury concentration.

The concentrations of the various species obtained in this way are summarised in Table XI, with which the values obtained by Dry and Gledhill (1) are compared.

TABLE XI - CONSTITUENTS OF A SATURATED MERCUROUS CHLORIDE SOLUTION IN WATER AT 25°C.

Species	Concentration (mole or g.ion/litre)	
	Present Work	Dry and Gledhill
H^+	$(8.14 \pm 0.01) \times 10^{-6}$	$(8.17 \pm 0.08) \times 10^{-6}$
Cl^-	$(8.36 \pm 0.11) \times 10^{-6}$	$(8.40 \pm 0.14) \times 10^{-6}$
$Hg(OH)_2$	$(4.00 \pm 0.05) \times 10^{-6}$	$(4.03 \pm 0.10) \times 10^{-6}$
$HgCl_2$	$(3.01 \pm 0.03) \times 10^{-6}$	$(3.3 \pm 0.4) \times 10^{-6}$
Hg_2OH^+	14×10^{-8} (limits 4-23)	10×10^{-8} (limits 4-25)
$HgCl^+$	3×10^{-8} (limits 1.6-4.6)	2.7×10^{-8} (limits 1.33-5.5)
Hg^{2+}	$(1.90 \pm 0.04) \times 10^{-8}$	$(1.90 \pm 0.01) \times 10^{-8}$
$HgOH^+$	$(1.56 \pm 0.55) \times 10^{-8}$	1.4×10^{-8} (limits 0.8 - 2.5)
Hg^{2+}	$(1.46 \pm 0.14) \times 10^{-10}$	$(1.46 \pm 0.11) \times 10^{-10}$

7.3 DISCUSSION

The results obtained in the present work are in good agreement with Dry and Gledhill's values, and consolidate the existing understanding of saturated mercurous chloride solutions. However, in view of the limitations found in their experimental technique their figures cannot be considered as accurate or reliable as those determined in this research.

The figures in Table XI (see 7.2) show clearly the state of affairs existing in a saturated mercurous chloride solution at 25°C, and give a lucid exposition of the process by which the solid goes into solution.

Mercurous chloride dissolves with the formation of mercurous and chloride ions, and 95.6% of the mercurous ions formed undergo disproportionation to mercuric ions and mercury. 89% of the remaining mercurous ions are hydrolysed to Hg_2OH^+. 56.8% of the mercuric ions hydrolyse to form $Hg(OH)_2$, and 42.7% react with chloride ions to form $HgCl_2$. Only 0.26% of the mercury remains in the form of mercurous ions, and only 0.002% of the mercuric ions remain unchanged.

Of the ionised species in solution only 0.23% is present as mercurous chloride, while 97.6% is hydrochloric acid responsible for 99.2% of the observed conductivity. The remaining 0.8% is due mainly to $HgOH^+$ and chloride ions.

8. CONCLUSION.

THE SOLUBILITY OF MERCUROUS CHLORIDE IN WATER AT 25°C.

In view of the complex nature of a saturated mercurous chloride solution in water at 25°C, its solubility is difficult to define exactly.

(i) If it is defined as the concentration of mercurous chloride in solution, then Table XI above (see 7.2) gives its solubility as $(1.90 \pm 0.04) \times 10^{-8}$ mole/litre.

(ii) If it is defined as the number of moles of solid obtained on evaporating a litre of saturated solution to dryness after filtering it, then the solubility is equivalent to the total mercury concentration, i.e. $(7.20 \pm 0.04) \times 10^{-6}$ mole/litre.

(iii) If it is defined as the loss in weight of a known quantity of mercurous chloride after equilibration with a litre of water, the result would be complicated by the precipitation of metallic mercury from the disproportionation of the mercurous ion.

None of these definitions provide an accurate answer to the problem, and indeed no solubility definition can. It must therefore be concluded that mercurous chloride does not have a solubility in any strict sense, but dissolves in water at 25°C very sparingly, with reaction, to provide an equilibrium concentration of products.

9. BIBLIOGRAPHY.

Abbreviations of the titles of journals conform with the system used in "Chemical Abstracts".

(1) Dry and Gledhill, Trans. Faraday Soc., 51, 119, (1955).

(2) Forsling, Hietanen, and Sillén, Acta Chem. Scand., 6, 906, (1952).

(3) Sillén, Acta Chem. Scand., 3, 539, (1949).

(4) Hietanen and Sillén, Acta Chem. Scand., 6, 747, (1952).

(5) Behrend, Z. physik. Chem., 11, 466, (1893).

(6) Ogg, Z. physik. Chem., 27, 285, (1898).

(7) Sherrill, Z. physik. Chem., 43, 705, (1903).

(8) Ley and Heimbucher, Z. Elektrochem., 10, 303, (1904).

(9) Brodsky and Scherschewer, Z. Elektrochem., 32, 1, (1926).

(10) Brodsky, Z. Elektrochem., 35, 836, (1929).

(11) Harned, J.Am.Chem. Soc., 51, 416, (1929).

(12) Christensen, Thesis, Christchurch College, N.Z. (Parton, Private Communication).

(13) Owen, J. Am. Chem. Soc., 60, 2229, (1938).

(14) Jonsson, Quarfort, and Sillen, Acta Chem. Scand., 1, 461, (1947).

(15) Kohlrausch and Rose, Z. physik. Chem., 12, 234, (1893).

(16) Kohlrausch, Z. physik. Chem., 64, 129, (1908).

(17) Malan, Ph.D Thesis, Rhodes Univ., S.A., (1953).

(18) Faure, Ph.D Thesis, Rhodes Univ., S.A., (1953).

(19) Luder, J. Am. Chem. Soc., 62, (1940).

(20) Jones and Josephs, J. Am. Chem. Soc., 50, 1049, (1928).

(21) Jones and Bollinger, J. Am. Chem. Soc., 53, 411, (1931).

(22) Gledhill, M.Sc Thesis, Univ. of S.A., (1943).

(23) Shedlovsky, J. Am. Chem. Soc., 54, 1411, (1932).

(24) Nichol and Fuoss, J. Phys. Chem., 58, 696, (1954).

(25) Faure, Faure, and Gledhill, J. S.African Chem. Inst., 4, 19, (1951).

(26) Hills and Ives, J. Chem. Soc., 305, (1951).

(27) Denham and Fife, J. Chem. Soc., 1416, (1933).

(28) Kolthoff and Larson, J. Am. Chem. Soc., 56, 1881, (1934).

(29) Dry, M.Sc Thesis, Rhodes Univ., S.A., (1954).

(30) Scott, "Standard Methods of Chemical Analysis", Vol. 1, D. van Nostrand, New York, (1927).

(31) Treadwell and Weiss, Helv. Chim. Acta, 2, 691, (1919).

(32) Kolthoff and Verzijl, Rec. trav. chim., 42, 1056, (1923).

(33) Hottstetter and Roberts, J. Am. Chem. Soc., 41, 1337, (1919).

(34) Vogel, J. Pharm. Chem., 1, 194, (1815).

(35) Hada, J. Chem. Soc., 69, 1667, (1896).

(36) "The Dow-Corning Silicone Notebook," Ref. No. 2003.

(37) Gledhill and Malan, Trans. Faraday Soc., 48, 258, (1952).

(38) Guggenheim, Trans. Faraday Soc., 50, 231, (1954).

(39) Gledhill and Malan, Trans. Faraday Soc., 49, 166, (1953).

(40) Rummel, Dissertation Abstr., 12, 816, (1952).

(41) Cox, Kraus, and Fuoss, Trans. Faraday Soc., 31, 749, (1935).

(42) Ives, Private communication.

(43) Fischer and Leopoldi, Z. anal. Chem., 103, 241, (1935).

(44) Snell, "Colorimetric Methods of Analysis", Chapman and Hall, (1936).

(45) Finkelstein, Trans. Faraday Soc., 53, 1618, (1957).

(46) Dole, "The Glass Electrode", John Wilely and Sons, Inc., New York, 111, (1941).

(47) Guggenheim, J. Am. Chem. Soc., 52, 1315, (1930).

(48) Taylor, J. Phys. Chem., 31, 1478, (1927).

(49) Ferguson, van Lente, and Hitchins, J. Am. Chem. Soc., 54, 1279, (1932).

(50) Henderson, Z. physik. Chem., 59, 118, (1907).

(51) Covington and Prue, J. Chem. Soc., 3696, (1955).

(52) Smith and Taylor, J. Am. Chem. Soc., 64, 3053, (1942).

(53) White, J. Am. Chem. Soc., 36, 2011, (1914).
