

MEASUREMENTS OF THE SOLUBILITIES
OF SOME SILVER HALIDES IN
WATER BY ELECTRICAL METHODS

by

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NOTES ON ARRANGEMENT

Summary tables of the results
are given in the text. All the
experimental data are grouped
in an appendix.

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1. ABBREVIATIONS, SYMBOLS AND UNITS.

The following are used throughout the text.

| | | |
|--------------------|---|---|
| Cond. | - | conductivity |
| g. equiv./l. | - | gram equivalents per litre |
| nm./cm. | - | nanomho per centimetre = 1×10^{-9} $\text{ohm}^{-1} \cdot \text{cm}^{-1}$. |
| a | - | activity |
| c | - | molar concentration (in gram moles per 1000 millilitres of solution) |
| $^{\circ}\text{C}$ | - | degrees centigrade |
| d_0 | - | density of solvent (water) |
| d | - | density of saturated silver halide solution |
| D | - | demal concentration or dielectric constant of solvent (water) |
| E | - | electromotive force of cell in Absolute Volts |
| E° | - | standard electromotive force of cell |
| $\pm E_j$ | - | unknown liquid junction potential |
| F | - | Faraday |
| f | - | frequency |
| f_i | - | rational activity coefficient or stoichiometric ionic mole fractional activity coefficient of ionic species i |
| f_{\pm} | - | stoichiometric mean ionic mole fractional activity coefficient |
| ΔH° | - | standard heat of reaction |
| K | - | thermodynamic solubility product or dissociation constant |
| K_w | - | ionic product of water |
| M_1 | - | molecular weight of solvent (water) |
| M_2 | - | molecular weight of solute (silver halide) |
| m | - | molal concentration (in gram moles per 1000 grams of solvent) |
| R | - | gas constant per mole or resistance in ohms |
| s | - | solubility in gram equivalents per litre |
| T | - | Absolute temperature |

| | |
|---------------------|--|
| ν | - number of ions produced by one molecule of electrolyte on dissociation |
| X | - represents either Cl or Br |
| x | - fraction of total molality |
| z_i | - valence of ionic species i |
| α | - Debye - Hückel limiting slope or constant in Onsager equation |
| β | - constant in Onsager equation |
| γ_i | - molal ionic activity coefficient of ionic species i |
| γ_{\pm} | - molal mean ionic activity coefficient |
| κ_i | - specific conductance of electrolyte species i |
| κ_{H_2O} | - specific conductance of water |
| Λ_i° | - limiting equivalent conductance of electrolyte species i |
| Λ_i | - equivalent conductance of electrolyte species i |
| Λ_s | - equivalent conductance of electrolyte at concentration s |
| λ_i° | - limiting equivalent ionic conductance of ionic species i |
| v_i | - velocity of ionic species i |
| r | - ional concentration |

PART I.

THE SOLUBILITY OF SILVER CHLORIDE AND SILVER BROMIDE
IN WATER AT 25°C BY CONDUCTOMETRIC
AND POTENTIOMETRIC METHODS.

2. INTRODUCTION.

The solubilities of the silver halides cannot be determined by the conventional methods of analytical chemistry because they are too sparingly soluble (of the order 1×10^{-5} to 1×10^{-6} g. equiv./l. at 25°C.) However, electrical, and to a lesser extent optical methods, are admirably suited because of their greater sensitivity. The conductometric and potentiometric methods are the two most important electrical techniques for the measurement of the solubilities of sparingly soluble salts, and are the ones employed in this research.

There are large discrepancies between the published values for the solubility of silver chloride. Results obtained by the conductometric and potentiometric methods disagree. In addition, figures quoted by independent authors using the same method differ by as much as 15%. Available published data at or near 25°C are shown in tables 1 and 2.

TABLE 1. - SOLUBILITY OF SILVER CHLORIDE FROM
CONDUCTANCE MEASUREMENTS.

| Temp. (°C) | solubility 10^{-5} equiv./l | χ_{H_2O} nm./cm. | solvent corr. % total cond. | authors | date | ref. no. |
|---------------|----------------------------------|--------------------------|--------------------------------------|------------------------|------|-------------|
| 26.5 | 1.82 | - | - | Holleman | 1893 | (1) |
| 26.0 | 1.56 | - | - | Kohlrausch and Rose | 1893 | (2) |
| 25.0 | 1.304 | 1600 | 45 | Kohlrausch | 1908 | (3) |
| 25.0 | 1.55 | 350 | 16 | Davies and Jones | 1949 | (4) |

TABLE 2. - SOLUBILITY OF SILVER CHLORIDE AT 25°C
FROM E.M.F. AND ANALYTICAL MEASUREMENTS.

| solubility 10^{-5} equiv./l | method | authors | date | ref. no. |
|----------------------------------|------------|-----------------------|------|-------------|
| 1.25 | e.m.f. | Goodwin | 1894 | (5) |
| 1.41 | e.m.f. | Thiel | 1900 | (6) |
| 2.16 | analytical | Noyes and Kohr | 1902 | (7) |
| 1.429 | e.m.f. | van Rossem | 1912 | (8) |
| 1.2 | e.m.f. | Rolla | 1913 | (9) |
| 1.20 | e.m.f. | Hahn and Schulze | 1927 | (10) |
| 1.55 | e.m.f. | Hahn and Klockmann | 1930 | (11) |
| 1.314 | e.m.f. | Brown and McInnes | 1935 | (12) |
| 1.334 | e.m.f. | Owen | 1938 | (13) |

5.

There are no published values for the solubility of silver bromide at 25°C by the conductometric method. Furthermore, very few solubility determinations by other methods have recently been made. The available values are shown in table 3.

TABLE 3. - SOLUBILITY OF SILVER BROMIDE AT 25°C.

| solubility 10 ⁻⁷ equiv./l | method | authors | date | ref. no. |
|---|----------------|-------------------------|------|-------------|
| 6.66 | e.m.f. | Goodwin | 1894 | (5) |
| 8.1 | e.m.f. | Thiel | 1900 | (6) |
| 8.0 | e.m.f. | Bodländer and Fittig | 1902 | (14) |
| 7.3 | e.m.f. | Abegg and Cox | 1903 | (15) |
| 8.8 | analytical | Hill | 1908 | (16) |
| 0.5 | e.m.f. | Rolla | 1913 | (9) |
| 1.55 | e.m.f. | Hahn and Schulze | 1927 | (10) |
| 1.8 | tyndallometric | Bedel | 1938 | (17) |
| 7.04 | e.m.f. | Owen and Brinkley | 1938 | (18) |

The above table reveals discrepancies as great as 94% in the published data!

Several authors (13) (19) (20) have attributed the discrepancies to the variability of the physical condition of samples of the silver halides prepared by different methods. This, they maintain, leads to actual differences in the solubilities of the silver halides;

e.g. the silver halides used in the conductometric determinations are prepared by precipitation methods, whereas in the potentiometric determinations they are usually prepared either thermally or by electrolysis.

However, in all the conductometric work previously done the conductance of the water has been a very large fraction of the total conductivity; e.g. in Kohlrausch's (3) work on silver chloride the solvent correction was nearly 50% of the total, and this is undoubtedly the largest single source of error. In the potentiometric method the chief uncertainty lies in the liquid junction potential, which most previous investigators tried to eliminate unsuccessfully with the aid of salt bridges. It is the opinion of the author that these two factors alone could lead to errors of sufficient magnitude to account for the discrepancies in tables 1, 2 and 3.

Precision measuring apparatus has been used in the present work, and elaborate precautions have been taken to reduce all experimental errors to the minimum. In addition, every effort has been made to eliminate uncertain factors such as large solvent corrections and liquid junctions. In this way it is hoped to establish whether silver halides prepared by different methods show real variations in solubility.

3. THE CONDUCTOMETRIC METHOD.

3.1 Theory of the Conductometric Method.

The specific conductance κ of a salt in saturated solution is related to the solubility s by the well-known equation

$$s = \frac{1000\kappa}{\Lambda_s} \quad \dots\dots\dots 1.$$

where Λ_s is the equivalent conductance of the salt at concentration s . The concentration is expressed in g. equiv./l. (normality.)

As a first approximation, if the concentration of the solution is sufficiently small (as in the case of saturated solutions of sparingly soluble salts) the value of Λ_s may be assumed to be equal to the limiting equivalent conductance Λ° . The latter may be found by the relation

$$\Lambda^\circ = \lambda_+^\circ + \lambda_-^\circ \quad \dots\dots\dots 2.$$

the values of λ_+° and λ_-° being the limiting equivalent conductances of the ionic constituents obtained from the conductances of more soluble salts and transport number data.

For accurate work, however, it is preferable to use a value for the actual conductance Λ_s obtained by means of a curve, or equation, connecting Λ with the concentration. Since the concentrations of the saturated solutions studied fall within the range of

applicability of the Debye-Hückel-Onsager Theory for strong electrolytes, the Onsager equation (21)

$$\Lambda_s = \Lambda^\circ - (\beta + \alpha \Lambda^\circ) s^{\frac{1}{2}} \quad \dots\dots\dots 3.$$

may be used to calculate a better value of Λ_s at concentration s . α and β are constants, and using the most recently published values of the fundamental constants (22) have the values at 25°C

$$\alpha = 60.19$$

$$\beta = 0.2289$$

Equation 3 therefore assumes the form

$$\Lambda_s = 138.26 - 91.72 s^{\frac{1}{2}} \quad \dots\dots\dots 4.$$

for silver chloride and

$$\Lambda_s = 140.22 - 92.18 s^{\frac{1}{2}} \quad \dots\dots\dots 5.$$

for silver bromide, since

$$\lambda_{Ag^+}^\circ = 61.92 \quad (23)$$

$$\lambda_{Cl^-}^\circ = 76.34 \quad (23)$$

$$\lambda_{Br^-}^\circ = 78.30 \quad (24)$$

It is now possible to calculate the true thermodynamic solubility product K from the equation

$$K_{AgX} = a_{Ag^+} \times a_{X^-} \quad \dots\dots\dots 6.$$

where X represents either Cl or Br

$$= s_{Ag^+} \times s_{X^-} \times \gamma_{Ag^+} \times \gamma_{X^-}$$

$$= s_{Ag^+} \times s_{X^-} \times \gamma_{\pm}^2$$

where γ_{Ag^+} and γ_{X^-} represent the molal ionic activity coefficients at concentration s of the silver and halide ion respectively.

The solubility s calculated from equation 1 is converted from normality (which is numerically equal to molarity in the case of uni-univalent electrolytes) to molality by the relation

$$m = \frac{1000 C}{1000 d_0 - C M_2} \quad \dots\dots\dots 7.$$

The rational activity coefficient or stoichiometric mean ionic mole fractional activity coefficient of a strong electrolyte, which dissociates into v kinds of ions, is obtained from the Debye-Hückel limiting equation (21)

$$\log f_{\pm} = -\alpha \Gamma^{\frac{1}{2}} \quad \dots\dots\dots 8.$$

where

$$\Gamma = s \sum_i^v \nu_i z_i^2$$

and

$$\alpha = \frac{1}{v} \left(\sum_i^v \nu_i z_i^2 \right)^{\frac{3}{2}} \cdot \frac{1.283 \times 10^6}{(DT)^{\frac{3}{2}}}$$

In the important special case of solutions containing only a single uni-univalent electrolyte, the limiting law may be written

$$\log f_{\pm} = -\alpha s^{\frac{1}{2}} \quad \dots\dots\dots 9.$$

Since the solubilities of the silver halides are here expressed in molalities, the mole fractional mean ionic activity coefficient calculated above has to be converted to the molal mean ionic activity coefficient by the relation

$$f_{\pm} = \gamma_{\pm} (1 + 0.001 m v M_1)$$

At the high dilutions encountered in the present work the last term on the right hand side of the

equation can be neglected, so that

$$f_{\pm} = \gamma_{\pm}$$

3.2 Description, calibration and standardisation of apparatus.

Note: The apparatus described here is used throughout the research. Any additional apparatus or further modifications are described in their appropriate sections.

The apparatus was that used by Gledhill (25) and described in his M.Sc. thesis, with some modifications.

3.21 Temperature Control Apparatus.

3.211 Constant Temperature Room.

The apparatus is housed in a constant temperature room run at 24°C. The room heaters are controlled by a relay, and refrigeration is supplied to the room during the summer months when the outside temperature exceeds 24°C. Thermometers were hung in various parts of the room to observe the distribution of heat by the wall and room fans. A typical set of temperature readings are recorded in the accompanying table. It appeared from observations taken over a period of weeks that temperature control to $\pm 0.2^{\circ}$ is possible throughout the room during both winter and summer.

| Date | Thermometer readings in °C. | | | | |
|----------|-----------------------------|------|------|------|------|
| | A. | B. | C. | D. | E. |
| 10 April | 24.1 | 24.2 | 23.8 | 23.9 | 23.9 |
| 11 April | 24.2 | 24.3 | 23.9 | 24.0 | 24.0 |
| 12 April | 24.1 | 24.2 | 23.9 | 24.0 | 24.0 |
| 13 April | 24.0 | 24.1 | 23.8 | 23.9 | 23.9 |

3.212 Thermostat.

Uncertainty in the solvent correction and in locating the saturation point limited the final accuracy of the solubility determinations. This uncertainty exceeded 0.1%. Consequently it was only necessary to bring the thermostat to within 0.04° of 25°C to ensure an error of less than 0.1% in the conductance values. This assumes a change of 2.5% per degree in the conductance of the solutions.

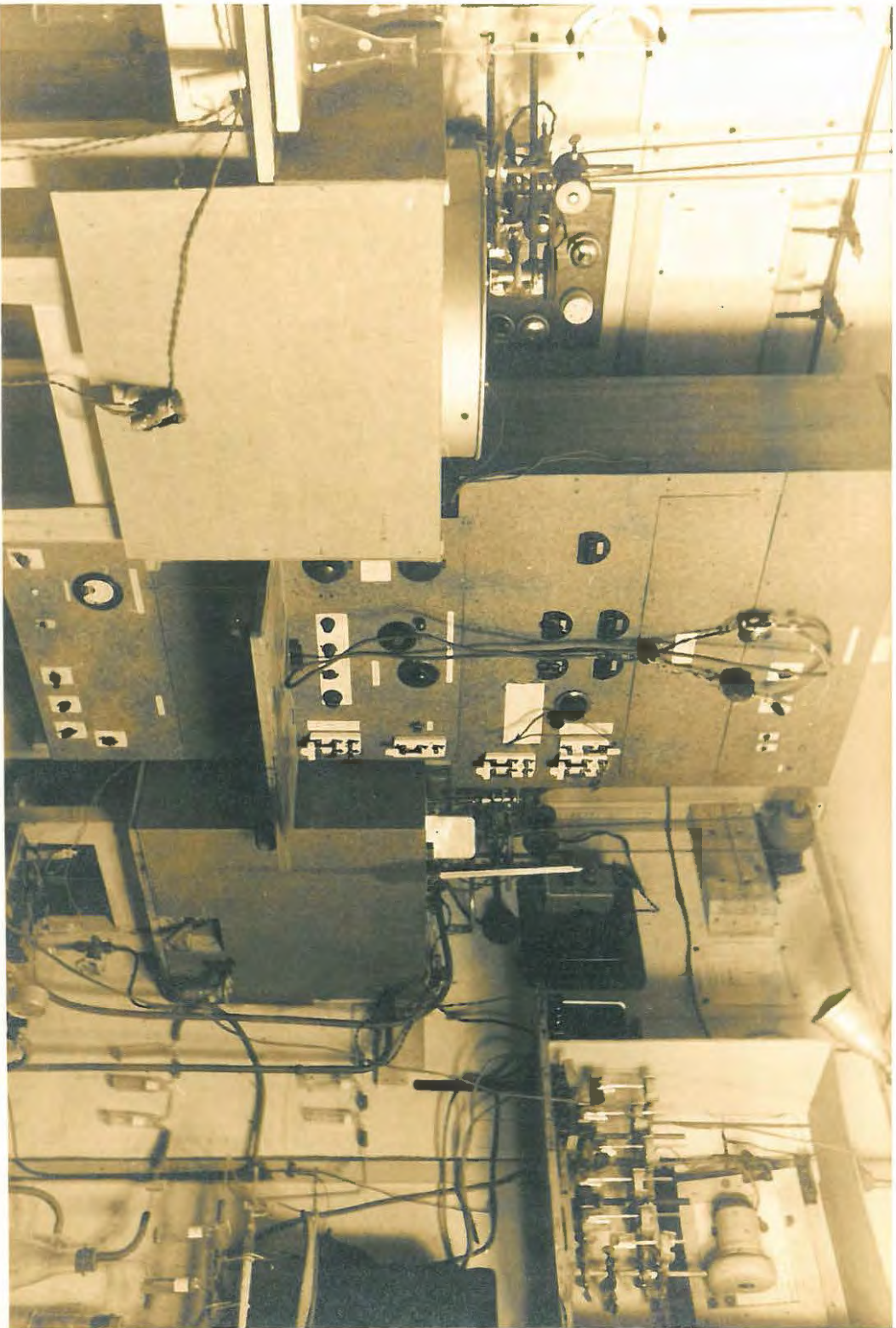
The thermostat was similar to the vessel employed by Gledhill (25), and the outer bath was filled with distilled water. The thermoregulator bulb contained strips of copper foil to make the toluene more sensitive to heat change. Body radiation from an observer near the thermostat affected the thermoregulator and altered the temperature slightly. This difficulty was overcome by screening the thermoregulator with a piece of highly polished aluminium. Work done on the efficiency of

stirring rates by Kambara, Oyamada and Mitsui (26) showed that a high rate of stirring was as important in maintaining a constant temperature as any elaborate relay system. The stirring rate was therefore increased to 250 r.p.m.

The temperature of the outer bath was measured by immersing in it four thermometers. Thermometers no. 244 and 245 are solid stem, mercury-in-glass thermometers graduated from -10° to 105°C to 0.1° . Thermometers no. 2314 and 26,441 are solid stem, mercury-in-glass type graduated from 17° to 35°C to 0.01° . They were calibrated to an accuracy of $\pm 0.02^{\circ}$ by the National Physical Laboratory, Pretoria. The fluctuations of temperature were measured on a 5° Beckmann thermometer, A_3 graduated to 0.01° .

The inner bath of the thermostat was filled with paraffin rather than water, because of the errors which are introduced by capacitative shunts if water is used. The fluctuation in the temperature of the inner bath was also measured on Beckmann thermometer A_3 . A typical set of temperature readings and fluctuations are recorded in the accompanying table. It appeared that the thermostat could be regulated to within 0.02° of 25°C . No temperature fluctuation was observed in the inner bath, and it is most unlikely

PLATE I. THE CONDUCTANCE BRIDGE AND THERMOSTATS.



| Time | Outer | | Bath | | Inner | |
|------------|----------|------------|---------|---------|----------------|------------------------|
| | No. 2314 | No. 26,441 | No. 244 | No. 245 | A ₃ | Bath A ₃ |
| 9.30 a.m. | 24.972 | 24.972 | 25.00 | 24.97 | 4.087 | 4.087 |
| 10.0 a.m. | 24.970 | 24.973 | 24.98 | 24.98 | 4.089 | 4.087 |
| 10.30 a.m. | 24.970 | 24.972 | 24.98 | 24.98 | 4.085 | 4.087 |
| 11.0 a.m. | 24.972 | 24.974 | 25.00 | 24.97 | 4.087 | 4.087 |

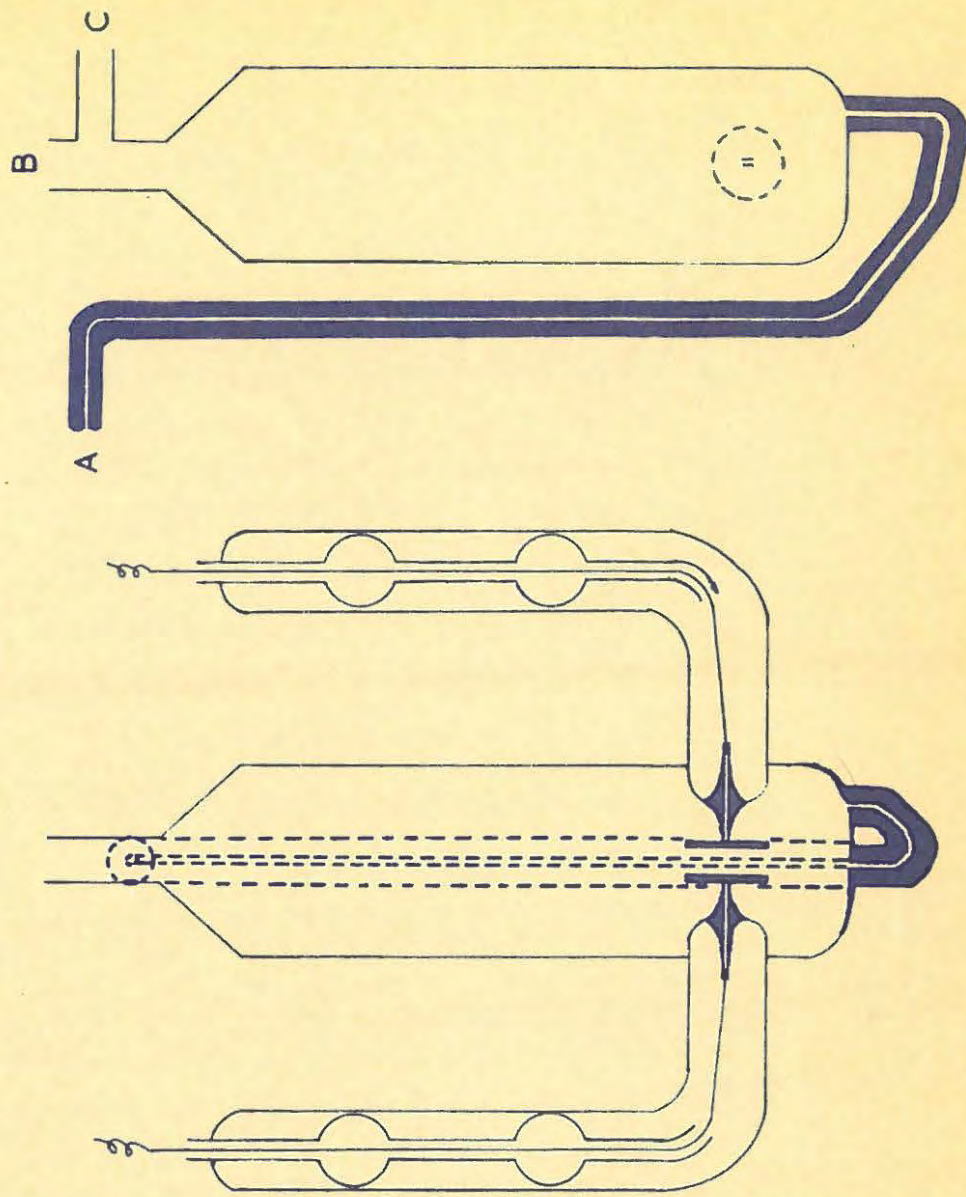
that the variation in the temperature of the cell contents would be any greater.

3.22 Bridge.

The calibration and interchecking of the bridge resistances was abandoned by Gledhill (25) because he was unable to obtain standardised resistance boxes or any accurately known electrical standards. The General Radio decade resistances, however, are guaranteed to an accuracy of 0.1%, and it was not necessary to recalibrate them in the present work.

When measuring low resistances of the order of 80 ohms at the lowest frequency (500 cycles) the sensitivity dropped off considerably, and it was impossible to balance the bridge to better than 0.05 ohm. The oscillator output was therefore connected to the grid of a cathode follower. This prevented variable loading on the oscillator, which caused the oscillation to "fade out" when measuring low resistances. In this

FIG. 1. THE CONDUCTANCE CELL



way the sensitivity was greatly increased, and balance to 0.01 ohm in 10,000 was thereafter possible.

The oscillator frequencies were known to drift slightly over a period of months. This drift was noticed when Festenstein (27) recalibrated the oscillator in 1947. In the present work, however, frequencies of 500 to 2,000 cycles were only used in applying the polarisation correction in the determination of the cell constants. This correction proved to be less than 0.1%, and recalibration of the oscillator was not necessary.

The resistance of the bridge leads to the cell was determined using the D.C. potential drop method, and was found to be 0.036 ohm. All resistances measured directly on the bridge without a shunt were corrected by this amount.

3.23 Conductance Cells.

The cells are shown in fig. 1. They are made of Pyrex and are similar to ones used in this laboratory for accurate conductometric titrations. "Parker Effect" (28) is eliminated by the special design, which also enables a stream of gas to be bubbled through the contents when the cell is in the thermostat. The gas enters the capillary tube at A and passes out through

B. A soda-lime guard tube over B very effectively excludes all back diffusion of carbon dioxide from the atmosphere. Gas can also be passed over the top of the contents through C if it is necessary to stop the stirring while taking readings.

The resistance of the cell leads was determined by the D.C. potential drop method with the electrodes shorted out with pure, dry mercury. The values found were 1.0 ohm for cell I, and 0.227 ohm for cell II, and all resistances have been corrected by this amount.

Because of the long time required to leach out a cell after it has contained electrolyte solution, cell I, with bright, unplatinised electrodes, was reserved solely for measuring the specific conductance of the water used in each determination. Cell II was used for measuring the specific conductance of the silver halide solutions, and its electrodes were lightly platinised using 7 coulombs per electrode according to the directions of Jones and Bollinger (29). This reduced the polarisation correction to a minimum without unduly increasing adsorption errors.

A point which immediately occurs is that the rate of solution of glass (see sections 3.423 and 3.425) in the two cells may be different. This is known to be negligible, because the results obtained with

different cells have been checked by various workers, all of whom have found about the same rate of solution of glass.

3.24 Burettes.

Grade A Normax burettes were used for the preparation of the silver halide precipitates. They were calibrated by a method approved by the National Physical Laboratory and given in Vogel's Quantitative Inorganic Analysis (30).

3.25 Weights.

Two sets of brass weights were employed. One set (maximum weight 50 g.) was used for weighing the required amounts of salts, and a second set (maximum weight 1000 g.) for weighing the solutions. Each set was standardised separately by T.W.Richards's method of intercomparison (30) and found to be comparable within 0.01%. The 20 g. weights from each set were also compared with a 20 g. quartz standard weight, making due allowance for the buoyancy of air. They were found to agree to 0.003%, well within the required limit of accuracy.

3.3 Preparation and standardisation of materials.

Note: For preparation of conductivity water see

section 3.42

3.31 Air.

The air, used to remove the volatile impurities and stir the contents of the cells, was passed from a compressor (at 45 lbs. pressure) through two concentrated sulphuric acid bubblers to remove ammonia and dry it and through a U-tube of solid cupric chloride to remove any traces of hydrogen sulphide. A long train of soda-lime tubes and a U-tube of solid metaphosphoric acid removed all carbon dioxide and the last traces of ammonia. Finally it was passed through a water bubbler to give it preliminary saturation with water vapour at 24°C, and then into the thermostat where it was brought to 25°C and saturated in a potash bulb with water vapour at that temperature.

3.32 Potassium chloride.

(a) Kahlbaum's G.R. potassium chloride was twice recrystallised from conductivity water. The salt was then fused in a platinum crucible, and transferred while still hot to a desiccator (31). It was used to make up the 0.01D potassium chloride solutions employed in the determination of the cell constant.

(b) The potassium chloride used for the preparation

of the silver chloride precipitates was Kahlbaum's G.R. reagent dried at 250°C for 3 weeks in an electric oven. It was stored in a desiccator over silica-gel.

3.33 Potassium bromide.

Merck's G.R. potassium bromide was recrystallised once from conductivity water, and dried at 115°C for 5 days in an electric oven. It was stored in a desiccator over silica-gel.

3.34 Silver nitrate.

Merck's G.R. silver nitrate was recrystallised once from conductivity water, and dried at 95°C for 5 days in an electric oven. It was stored in a black desiccator over silica-gel away from light and reducing fumes.

3.35 Silver chloride.

According to Stas (19) there are four modifications of silver chloride depending on the mode of preparation and the conditions of precipitation; (a) gelatinous, (b) cheesy-flocculent, (c) pulverulent and (d) granular crystalline or fused. The latter, he claimed, is almost insoluble in water, whereas the cheesy-flocculent variety has the greatest solubility on standing or if made pulverulent by shaking with water. He also found

that occlusion of silver nitrate was negligible at concentrations less than decinormal.

T.W. Richards (32) prepared his pure silver chloride in the determinations of atomic weights by precipitation from dilute solutions of recrystallised silver nitrate and redistilled hydrochloric acid. Occlusion of silver nitrate by the precipitated silver chloride was diminished by allowing the latter to stand for a long time in a solution containing excess of neither silver nor chloride ions.

In another paper Richards and Wells (33) reported that freshly precipitated silver chloride is more soluble in water at any particular temperature than that left in contact with the solvent for any length of time. This, they maintained, is due to the fact that the secondary growth of primary particles is a slow process, and the freshly-prepared precipitate is in a more finely divided state.

Johnson and Hulett (34) confirm this. They found that a curdy, freshly-prepared precipitate could be washed in a measure unattainable with crystalline powders, showing that the innermost recesses of the solid are more than usually accessible. They concluded that the structure was very loosely knit and fine.

Experiments by Hahn and Schulze (10) failed to

confirm the observations of Stas (19) that a less soluble form could be obtained under certain conditions.

Lange and Crane (35) carried out the precipitation of silver halides in a known excess of silver or halogen ions in red light with stirring. Special value was ascribed to careful washing of the precipitates. As appeared from the work of Labes (36) the electrokinetic potential of many precipitates depends, even in sign, on the type of ion present in excess during the precipitation. These differences became smaller on intensive washing and finally disappeared; the number of washings amounted to 25, 50 and 80.

Johnson and Hulett (34) determined the solubility of silver chloride at 0°C conductometrically. Their silver chloride, prepared by precipitation and washed by different procedures, yielded solutions in which a varying excess of chloride ions was present presumably due to adsorption of some kind. This, they claimed, places limitations on the interpretation of the results of solubility determinations.

Greene and Frizzel (37) investigated the precipitation of silver chloride by mixing silver nitrate and hydrochloric acid. They found that there were two stages: an initial rapid growth in opalescence followed by a period of slow development to a maximum. They advocated

precipitation from dilute solutions. Excess of either silver nitrate or hydrochloric acid was permissible, but as the concentration of either reagent present in excess was increased, the particle size of the precipitate decreased.

Careful determinations by Pinkus and Hanrez (38) also failed to confirm the observations of Stas (19). They found that the ionic solubility of all the flocculent and crystalline precipitates is the same within the limits of experimental error, whereas the solubility of the colloidal suspension is definitely higher. They concluded that the solubility of silver chloride is a well-defined constant, independent of the mode of preparation or the physical structure, except in the case of the fine, colloidal suspension. The latter gave results 1 - 5% higher than the flocculent or crystalline solids.

Davies and Jones (4) prepared their silver chloride by precipitation from potassium chloride and silver nitrate solutions. The precipitates were washed 6 times by decantation. Portions of the precipitate were then boiled in 2-litre flasks of distilled water, filtered hot, and the solution allowed to cool slowly in the dark. The crystals thus formed were washed with conductivity water, suspensions made up at 25°C, and

aged for 2 weeks in the dark.

There appears to be a distinct divergence of opinion amongst previous investigators as to the most suitable method of preparing silver chloride. The following precautions were taken by the author to ensure a precipitate that was not colloidal in nature, and in which adsorption errors would be reduced to a minimum;

(a) 50 ml. of 0.01 molar silver nitrate was added to 50 ml. of 0.01 molar potassium chloride solution. This was done because silver ions are preferentially adsorbed on the precipitate, and an excess of the latter must be avoided at all times.

(b) The silver nitrate was added very slowly from a burette (50 ml. added over a period of 45 minutes) with constant shaking. As far as possible this avoided excess of silver ions due to high local concentrations at any point.

(c) Precipitation was first carried out in the cold to hold back the process of secondary aggregation for some time. (1 hour.) The suspension was then digested at 90°C for 2 hours on an electric heating mantle to favour the growth of larger particles at the expense of the smaller ones. Under these conditions well-formed macrocrystals of silver chloride resulted. In this way adsorption was reduced to a minimum and the precipitate

could easily be washed. Equivalent quantities of silver nitrate and potassium chloride solutions were employed to ensure excess of neither silver nor chloride ions when precipitation was complete.

(d) In order to eliminate the attendant complications of photochemical decomposition, the precipitation and all subsequent treatment of the silver chloride was carried out in red light.

(e) Each precipitate was washed 30 times with distilled water by decantation, and a further 20 - 30 times with conductivity water. The ratio of water to precipitate was about 50 : 1. These washings were carried out in conical Pyrex flasks with glass covers.

3.36 Silver bromide.

According to Wilsey (39) the crystal structures of silver chloride and silver bromide are both simple cubic when precipitated from the potassium halide and silver nitrate. The same precautions were therefore taken in the preparation of the silver bromide precipitates as in the case of silver chloride.

3.4 Experimental results and discussion.

3.41 Experimental technique.

Conductance cell I, used for measuring the specific

conductance of the water, was shunted with a 10,000 ohm resistor as suggested by Shedlovsky (40). This General Radio Company type 500-J parallel resistor had a negligible change with frequency and was frequently measured alone. At 24°C it had a resistance of 10,000.4 ohms.

Conductance cell II, used for measuring the specific conductance of the saturated silver halide solutions, was cleaned by leaching 10 times with conductivity water and allowing it to stand filled with water for 6 hours each time. This completely removed any impurities adsorbed on the electrodes and glass walls.

After the contents had been added to the cell, it was immersed in the thermostat and purified air was bubbled through the contents at a rate of 4 bubbles per second. Resistance readings were taken at regular intervals until the resistance had passed through a maximum and was dropping at a steady rate, when the final readings were taken. The procedure was to balance the bridge with the ratio arms direct and then again with them reversed. The oscillator leads were then reversed and the procedure repeated. This gave four resistance readings, the arithmetic mean of which was taken as correct.

Since most of the solutions investigated in this

research had extremely high resistances, the polarisation correction was found to be negligible and the readings were taken at one frequency only. (1000 cycles.) For the same reason it was not necessary to correct for the lead resistances of the conductance cells. Unless otherwise stated, all resistance readings of the saturated salt solutions were measured using the 10,000 ohm shunt resistor.

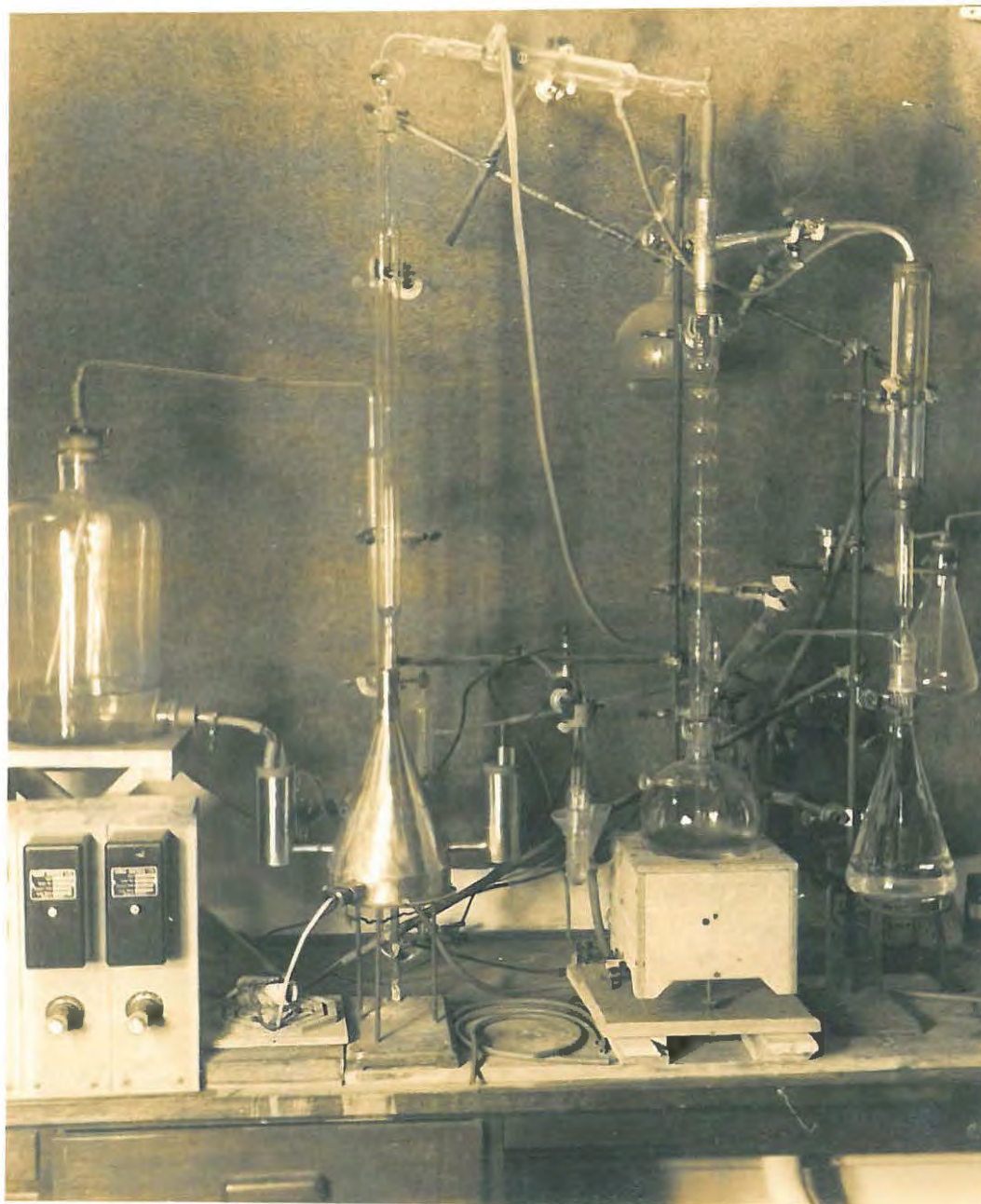
On the other hand, the resistance of the 0.01N potassium chloride solutions used in the determination of the cell constants was only about 84 ohms. In this case the polarisation correction was not negligible. The resistance readings were therefore repeated at each of the other frequencies, and resistance R plotted against $p^{-\frac{1}{2}}$ (where $p = 2 \pi f$) in order to apply the polarisation correction as suggested by Jones and Christian (41). The correction for the resistances of the cell leads was also applied in this case.

3.42 Conductivity water.

3.421 Introduction.

For reliable conductometric determinations at the extremely low concentrations encountered in this work it is essential to keep the specific conductance of the water as low as possible. The correction to be applied

PLATE 2. THE CONDUCTANCE WATER STILL.



for its conductance depends on the nature of the impurities present, and the way they will react with the ions of the salt under investigation.

A large number of papers have been published describing stills for the production of conductivity water. In a number of these the authors claim to have prepared "ultra-pure" water of specific conductance less than 100 nm./cm. Kohlrausch and Heydweiller (42) in their classical experiment, which involved 42 distillations in vacuo, prepared water with a specific conductance of about 62 nm./cm. (recalculated to 25°C.) Kraus and Dexter (43) obtained their best water with a specific conductance of 66 nm./cm. from their still in the middle of the day.

Despite this there have been no published reports of experimental work in which the conductivity of the water was less than 120 nm./cm.

3.422 Preparation.

A considerable amount of thought was given to the construction of a suitable still capable of delivering relatively large quantities of "ultra-pure" conductivity water required in this research.

Previously conductivity water had been prepared in this laboratory by distillation of tap water. The water

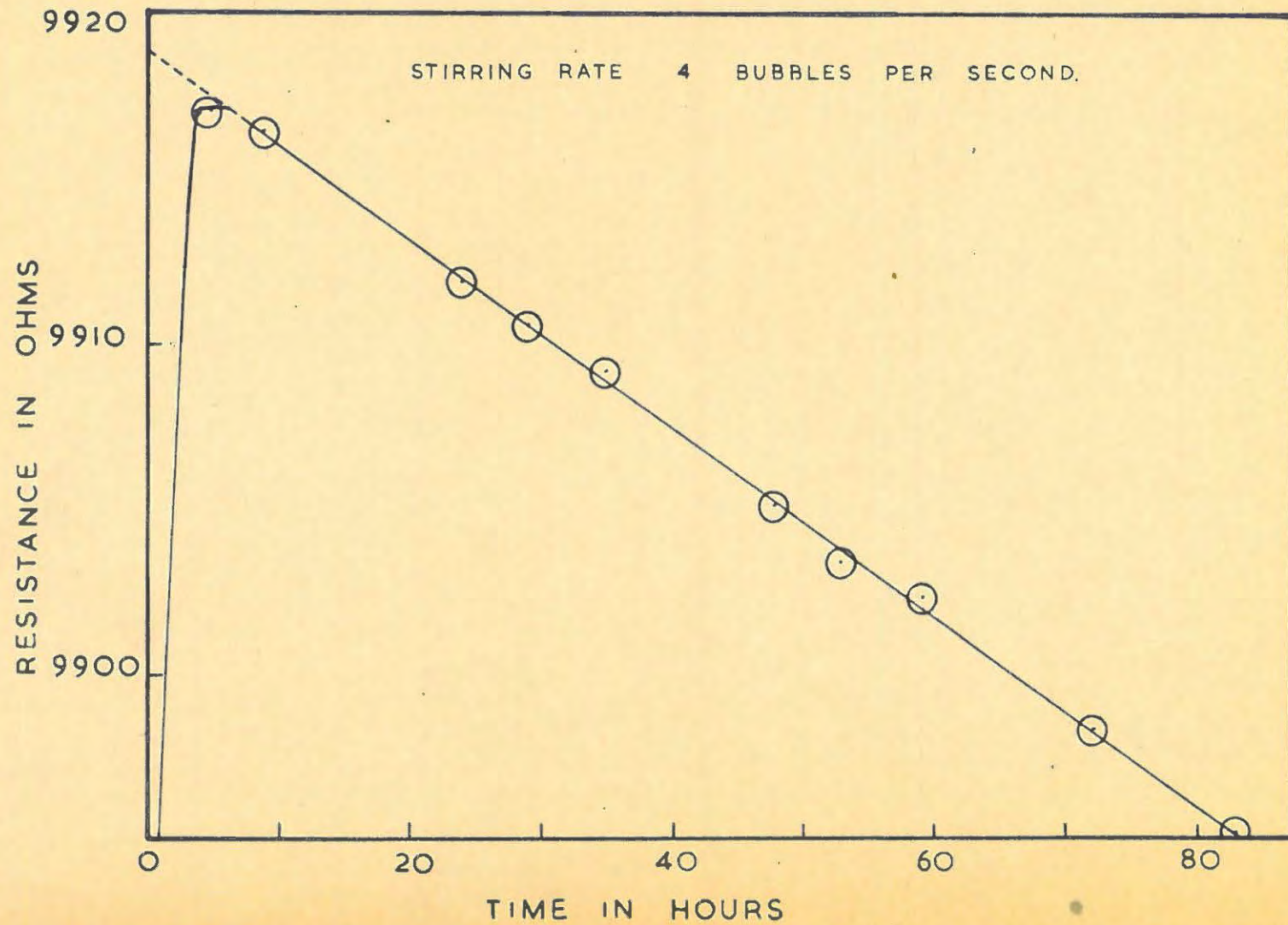
was distilled from a flask containing alkaline permanganate, through an intermediate condenser into a second flask, and then redistilled through another condenser and collected. The best water obtained in this way had a specific conductance of 130 nm./cm., but the average value was much higher. (approximately 300 nm./cm.)

Later the conductivity water was prepared by a new method suggested by P.K.Faure (44). The water was distilled from a phosphoric acid solution, through a fractionating column and a condenser, and collected. Water prepared in this way had a low specific conductance, and the lowest value reached was actually 97 nm./cm., but in general the average conductance was 150 - 200 nm./cm.

The best water was obtained from a still after it had been running for several hours. This is probably due to leaching out of those parts of the still which have not been in contact with water when the still is shut down overnight. Furthermore, it was preferable to remove all the ammonia in the still, followed by subsequent removal of the carbon dioxide in the conductance cell. Better results were obtained in this way than the removal of both gases in the still.

An automatic, recycling, electrically heated still (45)

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



was constructed which incorporates these requirements. It operates continuously and the water is distilled in two stages. The first distillation is from alkaline permanganate to remove all organic impurities and non-volatile acid impurities. The second distillation is from phosphoric acid which removes all non-volatile alkaline impurities as well as ammonia. The still delivers about 16 litres of water daily with a specific conductance between 70 and 90 nm./cm.; the best water obtained reaching 62 nm./cm. The water is received and stored in well-seasoned Pyrex flasks with outside ground glass caps.

3.423 EXPERIMENT I.

Measurement of the specific conductance $\chi_{\text{H}_2\text{O}}$
of conductivity water.

300 ml. of conductivity water were placed in cell I and purified air was bubbled through the contents at a constant rate of 4 bubbles per second. This removed carbon dioxide from the water and stirred the contents of the cell. At the same time resistance readings were taken at regular intervals. The experimental data are recorded in appendix A.

From the plot of resistance against time in fig. 2 it can be seen that the resistance rose rapidly to a

maximum value after 3.5 to 4 hours, and then proceeded to fall at a steady rate of 0.3 ohm/hr. This corresponds to an increase of 0.3 nm./cm.hr. in the specific conductance. The value is in good agreement with that obtained by P.K.Faure (44) when conducting a similar experiment over a period of 3 weeks in this laboratory.

3.424 EXPERIMENT 2.

It was also important to know the rate at which conductivity water deteriorated when kept in the receiving flasks. Earlier workers (25) (27) in this laboratory, using conductivity water of specific conductance between 300 and 800 nm./cm., found that the water deteriorated very rapidly when kept in Pyrex flasks with tinfoil-covered rubber stoppers.

To investigate this effect three 2-litre Pyrex receiving flasks with outside ground glass caps were filled with conductivity water from the still. A sample of water was taken from each of the three flasks and the specific conductance was measured. Another sample from each flask was measured 72 hours later. The values are recorded in the accompanying table.

The mean increase in specific conductance of water stored in these flasks for 72 hours was 2.6 nm./cm. This corresponds to an increase in the specific conductance

| Flask | time in hours | $\kappa_{\text{H}_2\text{O}}$ in nm./cm. |
|-------|---------------|--|
| 1 | 0 | 96.3 |
| 1 | 72 | 99.6 |
| 2 | 0 | 98.5 |
| 2 | 72 | 100.5 |
| 3 | 0 | 97.8 |
| 3 | 72 | 100.1 |

of 0.036 nm./cm.hr. or 0.87 nm./cm.day. This effect can safely be neglected in the present work, because at no time during an experiment was the conductivity water stored in a receiving flask for longer than 72 hours.

3.425 Theoretical considerations in the application of the solvent correction.

It is possible to calculate the specific conductance of water at 25°C due only to its dissociation into H^+ and OH^- ions as follows:

$$\begin{aligned}
 & K(\text{H}_2\text{O}) \longrightarrow [\text{H}^+] \times [\text{OH}^-] \\
 \text{and } & K_w = [\text{H}^+] \times [\text{OH}^-] \dots\dots\dots 10. \\
 & = 1.008 \times 10^{-14}
 \end{aligned}$$

But $[\text{H}^+] = [\text{OH}^-] = 1.004 \times 10^{-7}$ assuming the activity coefficients of the H^+ and OH^- ions to be unity at these high dilutions. Therefore the specific conductance $\kappa_{\text{H}_2\text{O}}$, due to the ionisation into H^+ and OH^- ions only, can be expressed by the equation

$$\kappa_{\text{H}_2\text{O}} = \frac{\overset{31.}{\lambda}_{\text{H}_2\text{O}}^{\circ} \times \overset{m}{c} \times d_0}{1000} \dots\dots 11.$$

where $\lambda_{\text{H}_2\text{O}}^{\circ}$ is the limiting equivalent conductance of water and is $= \lambda_{\text{H}^+}^{\circ} + \lambda_{\text{OH}^-}^{\circ}$ by the law of the independent migration of ions.

$$= 349.8 + 198.4$$

$$= 548.2$$

and $c = [\text{H}^+] = [\text{OH}^-]$

$$\kappa_{\text{H}_2\text{O}} = \frac{548 \times 1.004 \times 10^{-7} \times 0.997}{1000}$$

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

Since the average value of the specific conductance of the water used was between 70 and 90 nm./cm., approximately 15 - 35 nm./cm. of the conductance is contributed by impurities other than H^+ and OH^- ions. This residual conductance may be due to several contributing factors:

(a) Incomplete removal of volatile impurities.

The most persistent impurities are undoubtedly carbon dioxide and ammonia. The success achieved in this laboratory in the preparation of "ultra-pure" water has been largely due to the almost complete removal of ammonia in the still, followed by the removal of carbon dioxide in the cell.

Exhaustive experiments were conducted by P.K.Faure (44) to investigate the extent to which carbon dioxide

and ammonia are actually removed in the cell by bubbling purified air through the contents. He showed that carbon dioxide introduced into the water is completely removed by the current of air in a few hours. Ammonia alone can also be completely removed although much more slowly. Carbon dioxide and ammonia together presumably form ammonium bicarbonate, and experiment shows that this too can be removed almost completely, but at an extremely slow rate. The removal is so slow that traces of ammonium bicarbonate will still be present in the water at the conclusion of an experiment.

(b) Ion exchange.

Inspection of fig. 2 shows that the resistance of the water rises rapidly at first and reaches a maximum value after 3 - 4 hours. It then falls in a slow and regular manner at the rate of 0.3 ohm/hr., corresponding to an increase in the specific conductance of 0.3 nm./cm.hr. The initial rise in resistance is due chiefly to the rapid removal of carbon dioxide from the water. The subsequent regular fall is probably due to ion exchange between the fast-moving H^+ and OH^- ions, which become adsorbed on the glass walls of the cell, and slower-moving ions from the soluble constituents of the Pyrex glass. The most probable soluble constituents are sodium ions and silicate ions. The adsorbed H^+ and

OH^- ions are replaced by further dissociation of water molecules, so that the nett effect is the addition to the solution of soluble ion constituents from the glass. This would explain why the conductance increases in this manner, and also why a more rapid stirring rate, resulting in increased diffusional effects, causes an increase in the rise of the specific conductance with time.

(c) Effect of oxygen.

In the present work the contents of the cells were stirred with purified, compressed air. It was later found that when oxygen-free, purified nitrogen was used, the specific conductance increased more slowly under the same conditions of temperature and stirring rate. Although no satisfactory theoretical explanation is offered for this phenomenon, it is probable that the presence of oxygen increases the rate of solution of glass in some way. Purified, oxygen-free nitrogen was therefore employed as stirring gas in all the subsequent work at the other temperatures.

Thus the most probable impurities contributing to the residual conductance of the water are traces of ammonia and carbon dioxide present as ammonium bicarbonate, and sodium silicate dissolved from the glass walls of the cell.

It is well-known according to the Fuoss-Onsager theory (46) that when more than 2 species of ion are present in a solution complex interactions occur. The greatest effect occurs when there are large differences between the mobilities of the ions. It seemed possible that the conductance due to the fast-moving H^+ and OH^- ions might be affected significantly by the presence of the slower Ag^+ and Cl^- ions.

In order to apply the matrix calculation it is necessary to know the exact concentrations of the different ions. This requires a knowledge of the pH of both the water and the saturated solutions. No actual pH determinations were done on the water used in the present work.

Ellis and Kiehl (47) prepared conductivity water by one distillation from water or sodium hydroxide solution. pH measurements made on successive fractions of the distillate were high at first ($pH > 8.0$), and only became constant after about half the distillation had been completed. This, they maintained, indicates the presence of ammonia in the first fractions. Nessler's reagent added to the boiler also failed to hold the ammonia in the first few fractions. When phosphoric acid was added to the boiler all the fractions had about the same pH, indicating that phosphoric acid

retains all the ammonia. A series of distillations using Pyrex, "No-Solvit" and silver vessels as receivers indicated that the glass contributes a very small alkalinity to the water, but the effect is very slight. The best value for the pH of "ultra-pure" water is given as 7.01 at 27.5°C.

These observations were confirmed by Cranston and Brown (48) who also obtained water of pH = 7.0 by distillation from phosphoric acid in Pyrex apparatus. Kolthoff and Kameda (49) prepared "ultra-pure" water of pH between 7.0 and 7.05 by a first distillation from sulphuric acid and two subsequent distillations from water alone. The final distillate was collected in quartz apparatus, and the carbon dioxide was removed by a stream of carbon dioxide and ammonia-free air. Consequently there is no reason to believe that the pH of the water used in the present work lies outside the range 7.0 ± 0.1

Edwards and Evans (50) performed pH determinations on potassium chloride solutions of diminishing concentrations made up with "ultra-pure" water from an Ellis and Kiehl still. The values they obtained were:

| | | | | | |
|-------------------------------------|------|------|------|------|------|
| Concentration in $m \times 10^5$ | 1011 | 112 | 13.2 | 1.3 | 0 |
| pH | 6.75 | 6.86 | 6.90 | 6.93 | 6.98 |

It appeared that as the concentration of the salt solutions diminishes the pH of the solutions approaches 7.0. Since the concentrations of the silver halides in the saturated solutions are of the order 1×10^{-5} to 1×10^{-6} g. equiv./l., it is unlikely that the pH of the saturated solutions falls outside the range 7.0 ± 0.1

We are now in a position to apply the Fuoss-Onsager theory (46) to the solvent correction. Calculation of the elements of the interaction matrices give:

| Ionic mobilities corrected | Ionic mobilities uncorrected |
|---|---|
| $\lambda_{\text{Ag}^+}^{\circ} = 61.7$ | $\lambda_{\text{Ag}^+}^{\circ} = 61.9$ |
| $\lambda_{\text{Cl}^-}^{\circ} = 76.1$ | $\lambda_{\text{Cl}^-}^{\circ} = 76.3$ |
| $\lambda_{\text{H}^+}^{\circ} = 349.1$ | $\lambda_{\text{H}^+}^{\circ} = 349.8$ |
| $\lambda_{\text{OH}^-}^{\circ} = 198.0$ | $\lambda_{\text{OH}^-}^{\circ} = 198.4$ |

in a saturated solution of silver chloride in water of pH = 7.0 at 25°C. The corresponding ionic mobilities, uncorrected for the mixture effect, are given on the right hand side of the table for comparison. The equivalent conductance of the water in this case is 547.1 compared with 548.2 in the absence of silver chloride. The difference of 1 part in 550 will obviously produce no significant change in a solvent conductivity of less than 100 nm./cm. Similarly the effect of the H^+ and OH^- ions on the conductance of the silver halide

was found to be negligible. The application of the solvent correction by simply subtracting the conductivity due to the water is therefore fully justified. This is also true of the silver bromide solutions since the bromide ion has almost the same mobility as the chloride ion.

3.43 Determination of the cell constants.

Note: The cell constant of cell I had previously been determined by A. Faure (51) and was found to be 0.1095 ± 0.0003 .

EXPERIMENT 3.

A 0.01D potassium chloride solution was prepared according to the directions of Jones and Bradshaw (31). The specific conductance of the potassium chloride is $0.00140877 \text{ ohms}^{-1} \cdot \text{cm}^{-1}$, at 25°C , and to this must be added the specific conductance contributed by the water. Cell II was rinsed out 6 times with the solution before filling so that adsorption would take place during the initial washings.

The resistance of the solution was low. (about 84 ohms.) Previous workers (25) (27) in this laboratory used cells with smooth, unplatinised electrodes. When measuring low resistances they were unable to balance the bridge at the lower frequencies owing to the high

parallel capacitance required. To overcome this difficulty they employed a series resistor of approximately 1000 ohms. The author found that with the light platinisation given to the electrodes (7 coulombs each) the reactance of the cell was sufficiently reduced to enable the resistance of the 0.01N potassium chloride solution to be measured directly. This is a decided advantage, as it eliminates any errors in computing the value of a series resistor. By the use of a variable condenser decade the parallel capacitance required was found to be 0.006 micro-farads, which at this low resistance made the correction term $p^2 c_3^2 r_3^2$ (25) negligible.

The final resistance readings were taken when a constant value had been obtained. This took approximately 3 hours. The total resistance of the bridge and cell leads is 0.263 ohm, and the resistance readings were corrected by this amount. The corrected values of the cell resistance R at the different frequencies f are tabulated below.

| Nominal frequency (in c.p.s.) | Resistance (ohms) | $\frac{R}{f}^{-\frac{1}{2}}$ |
|----------------------------------|----------------------|------------------------------|
| 2000 | 84.047 | 0.02132 |
| 1000 | 84.060 | 0.02992 |
| 500 | 84.137 | 0.04397 |

FIG. 3. ELIMINATION OF POLARISATION BY
EXTRAPOLATION TO INFINITE FREQUENCY

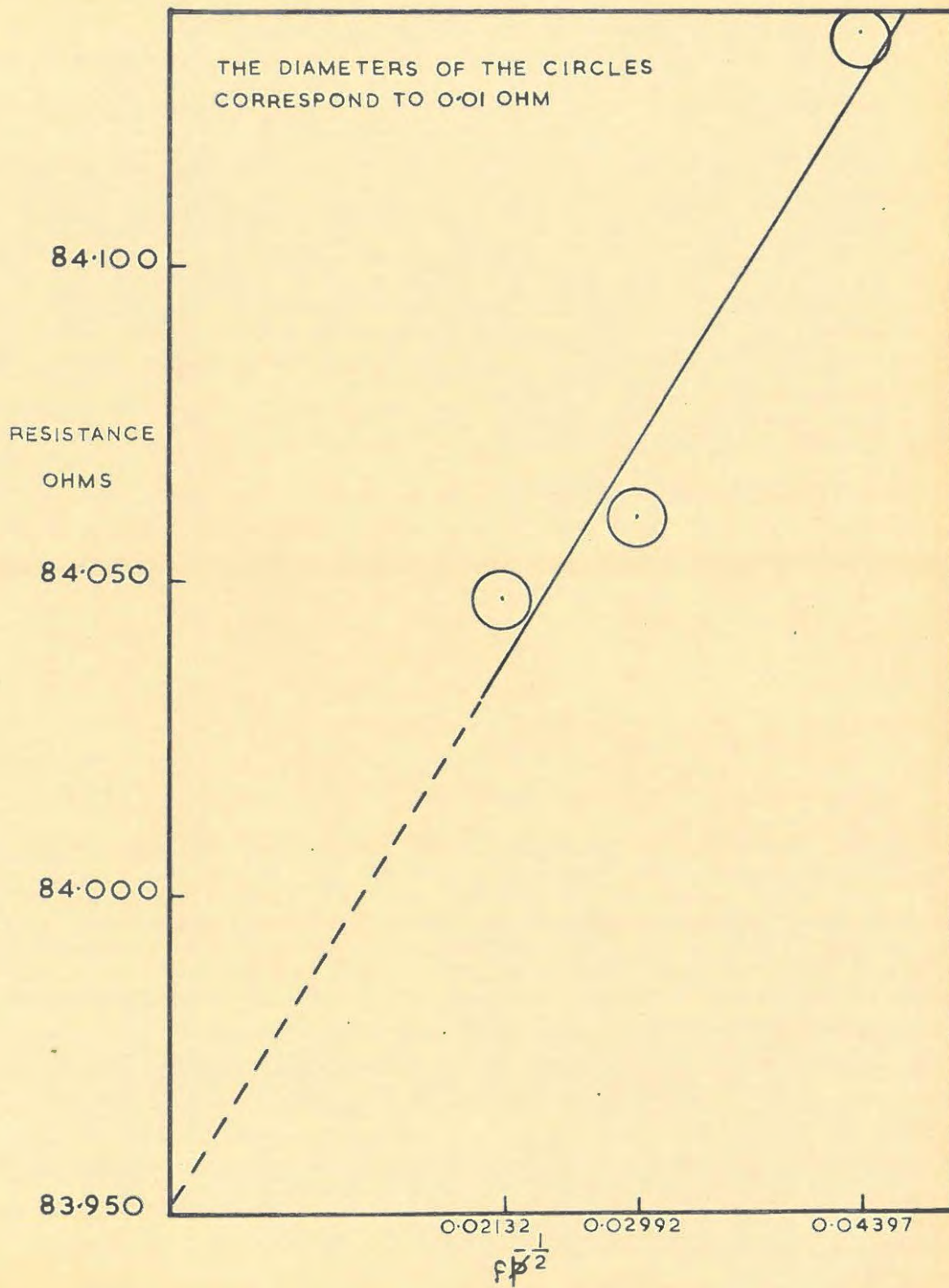
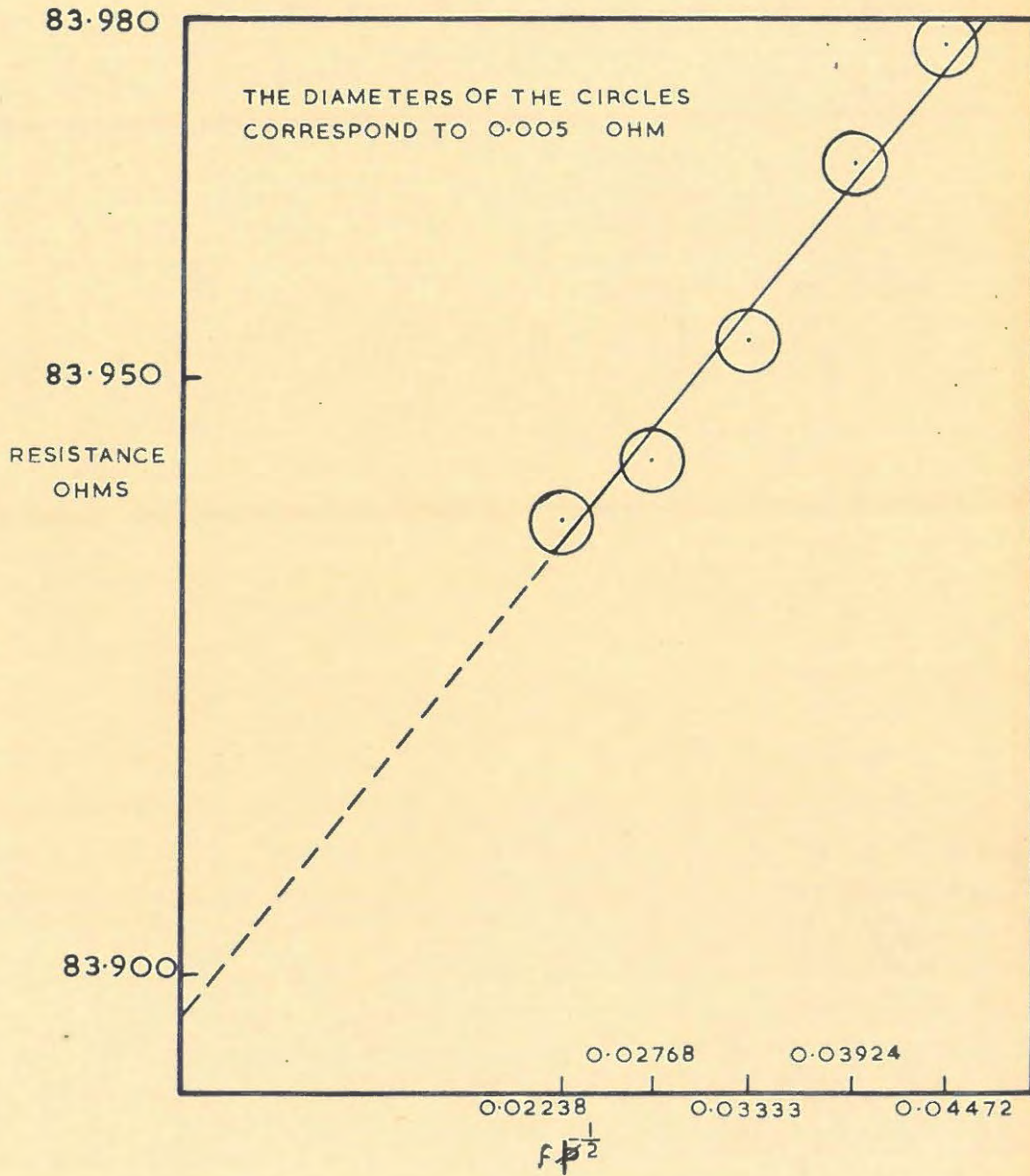


FIG. 4. ELIMINATION OF POLARISATION BY
EXTRAPOLATION TO INFINITE FREQUENCY



To determine the polarisation correction, and hence the true resistance of the solution, R was plotted against $p^{-\frac{1}{2}}$ (where $p = 2\pi f$) according to the method of Jones and Christian (41) and extrapolated to infinite frequency (see fig. 3). The final corrected value for the resistance was 83.955 ohms. The specific conductance of the water used was 115 nm./cm. Thus the specific conductance of the 0.01D potassium chloride solution was 0.0014089 ohm⁻¹.cm⁻¹., leading to a value of 0.11828 for the cell constant of cell II.

As a check another 0.01D potassium chloride solution was prepared, and the resistance of the solution was measured on the Faure-Goddard bridge (52). On this bridge the interference from harmonics at low frequencies is eliminated by the use of a cathode ray oscilloscope as null indicator. The total resistance of the bridge and cell leads is 0.472 ohm, and the resistance readings were corrected by this amount. The corrected values of the cell resistance R at the different frequencies f are shown in the accompanying table.

The final corrected value of the resistance was 83.396 ohms (see fig. 4). The specific conductance of the 0.01D potassium chloride solution was 0.0014089 ohm⁻¹.cm⁻¹., leading to a value of 0.11820 for the cell constant of cell II.

| Nominal frequency (in c.p.s.) | Resistance (ohms) | $p^{-\frac{1}{2}}$ |
|----------------------------------|----------------------|--------------------|
| 2000 | 83.938 | 0.02238 |
| 1300 | 83.943 | 0.02768 |
| 900 | 83.953 | 0.03333 |
| 650 | 83.968 | 0.03924 |
| 500 | 83.978 | 0.04472 |

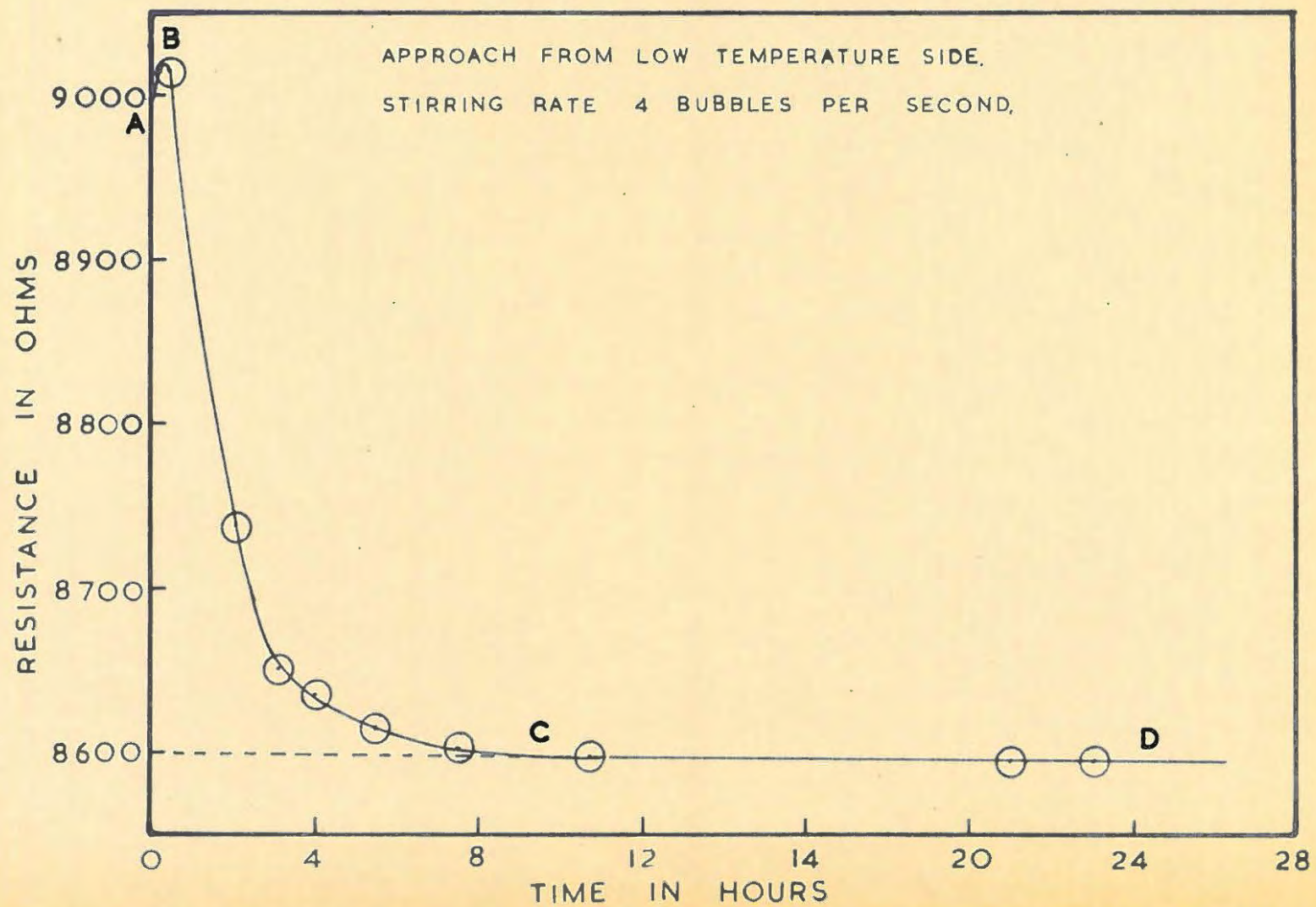
Since only 3 frequencies could be used on the bridge employed by the author, some difficulty was experienced in drawing the best straight line through the points. A best straight line was also fitted to the 3 points by the method of least squares (53). This lead to an extrapolated resistance of 83.896 ohms and a cell constant of 0.11820; in excellent agreement with the value obtained on the Faure-Goddard bridge. A similar extrapolation of the values obtained at 5 frequencies on the latter bridge again lead to a value of 0.11820 for the cell constant. 0.11820 ± 0.00004 was therefore accepted as the best value for the cell constant of cell II at 25°C.

3.44 Silver chloride results.

For experimental data see appendix B.

In each determination a quantity of conductivity water, whose specific conductance had previously been

FIG. 5. GRAPH OF RESISTANCE AGAINST TIME
FOR SATURATED AGCL SOLUTION AT 25°C.



determined, was placed in cell II at 24°C with silver chloride in suspension. Special care was taken to ensure that a definite excess of solid silver chloride was present, because silver chloride solutions tend to become supersaturated in the absence of solid seed (4).

The cell was then put into the thermostat and purified air was bubbled through the contents at 4 bubbles per second. Because 3 processes were going on simultaneously, a graphical method was used to show when saturation was complete. Fig. 5 shows a typical graph of resistance against time when saturation is approached from the low temperature side. (24°C .) The portion AB corresponds to fast removal of dissolved gases (chiefly carbon dioxide and some ammonia) by the stirring air. The rapid fall BC is due to the continuing solution of silver chloride and glass, the effect of which then becomes noticeable. The steady rate of drop over section CD is due to the solution of glass alone. This was found to be about 0.3 ohm/hr., corresponding to an increase in the specific conductance of 0.5 nm./cm.hr. Thus the solution is completely saturated with silver chloride at point C, which can be located to within 4 nm./cm. The solvent correction, consisting of the observed specific conductance of the pure water plus the conductance due to the glass dissolved in the time taken to reach

the point C, is subtracted from the value obtained above. This gives the specific conductance κ_{AgCl} due to the silver chloride alone. The results, given in table 4, are calculated using equations 1 and 4.

TABLE 4. - SOLUBILITY OF SILVER CHLORIDE.

| No. of expt. | age of ppt. days | κ_{AgCl} soln. at C nm./cm. | $\kappa_{\text{H}_2\text{O}}$ nm./cm. | time to C in hrs. | corr. for glass nm./cm. | κ_{AgCl} nm./cm. | sol. equiv./l. $\times 10^{-5}$ |
|--------------|------------------|---|---------------------------------------|-------------------|-------------------------|--------------------------------|---------------------------------|
| 4 | 20 | 1972 | 95 | 120 | 36 | 1841 | 1.336 |
| 5 | 8 | 2135 | 96 | 72 | 21 | 2018 | 1.464 |
| 6 | 10 | 1926 | 82 | 12 | 4 | 1840 | 1.335 |
| 7 | 4 | 1935 | 87 | 19 | 6 | 1842 | 1.336 |
| 8 | 5 | 1942 | 89 | 14 | 4 | 1849 | 1.341 |
| 9 | 7 | 1951 | 96 | 33 | 10 | 1845 | 1.338 |
| 10 | 9 | 2160 | 95 | 72 | 22 | 2043 | 1.483 |

In view of the unexpectedly long time taken to reach saturation from the low temperature side in expt. 4, it was decided to approach saturation from the high temperature side in expt. 5. For this purpose the silver chloride suspension was preheated at 90°C for 1.5 hours in a conical Pyrex flask on an electric heating mantle. It was then allowed to cool down to 30°C with constant shaking, and was placed in the cell.

The resistance rose gradually over a period of 72

hours due to the precipitation of excess of silver chloride initially present in the solution. It then fell steadily at approximately 0.5 ohm/hr. This is equivalent to an increase in the specific conductance of 0.8 nm./cm.hr. No satisfactory explanation is offered for the faster rate of drop observed in this case. The maximum value of the resistance was taken as the point at which saturation is attained. The solubility value was about 9% higher than in the previous experiment.

This phenomenon should not be attributed to a real change in the solubility of the silver chloride under these conditions. In expt. 6, 7 and 8 samples of silver chloride were used which had failed to give reproducible results from the high temperature side, simply by pouring off the solution and adding fresh water at 24°C to the precipitate remaining in the cell. Saturation was then reached much more quickly as may be seen by comparing the times for expt. 6, 7 and 8 with that for expt. 4, where the suspension had not been preheated. Apparently the precipitate in expt. 6, 7 and 8 was in a different physical state from that in expt. 4, probably having a smaller particle size.

Expt. 9 was performed in an exactly similar manner to expt. 4. It is significant that the time taken to reach saturation was only 33 hours as compared with

120 hours in expt. 4. This may be due to the fact that the precipitate used in expt. 9 had been aged for only 7 days as compared with 20 days in expt. 4. Despite this the solubility was not noticeably affected.

Saturation was again approached from the high temperature side in expt. 10. The rate of drop of the resistance was the same as that observed in expt. 5 which was carried out under the same conditions. The solubility value was 10% higher and not in very good agreement with the value obtained in expt. 5.

Having obtained concordant results from the low temperature side, it was decided to investigate the anomalous behaviour when saturation is approached from the high temperature side. Several factors may account for the greater solubility observed.

(a) Supersaturation.

It seemed unlikely that supersaturation could occur at all, as great care was taken to ensure a large excess of solid silver chloride in the solutions. In fact, particles of solid silver chloride were visible in the solutions used for the high temperature runs.

(b) Smaller particle size.

It is well-known that the solubility of a crystalline precipitate increases greatly when the size of the particle is less than 0.01 mm. in diameter. This is

due to the increased role played by surface effects. It is possible that in approaching saturation from the high temperature side crystals of silver chloride in a very finely divided state are formed on cooling. If the size of the particles was less than the approximate limit of 0.01 mm., this would account for the greater solubility observed. However, as previously stated, subsequent runs performed on such samples of silver chloride, by approaching saturation from the low temperature side, indicated that the size of the particles in no way affected the solubility.

(c) Errors in the solvent correction.

Preheating the silver chloride suspensions at 90°C for 1.5 hours will cause a certain amount of deterioration of the conductivity water because of the increased rate of solution of glass at the higher temperature. Although it was anticipated that this deterioration would be slight, a series of experiments was conducted to investigate it.

Samples of conductivity water of known specific conductance were preheated at 90°C for 1.5 hours in conical Pyrex flasks similar to those used for preheating the suspensions. The specific conductance was then measured again. The results are given in tabular form.

| Sample no. | $\kappa_{\text{H}_2\text{O}}$ in nm./cm. before preheating | $\kappa_{\text{H}_2\text{O}}$ in nm./cm. after preheating |
|------------|---|--|
| 1 | 98 | 250 |
| 2 | 85 | 229 |
| 3 | 90 | 237 |

The increase in conductance was phenomenal and much greater than expected. Apparently the rate of solution of glass increases very rapidly with increase in temperature, and does not seem to be reproducible.

When this additional correction for the solution of glass was made in expt. 5 and 10, it yielded 1.354×10^{-5} and 1.373×10^{-5} g. equiv./l. respectively for the solubility. These values are still 1.3% and 2.7% respectively higher than the values obtained when saturation was approached from the low temperature side, but show much closer agreement.

It was evident that the present technique for approaching saturation from the high temperature side was unsatisfactory due to the lack of reproducibility of the solvent correction at such high temperatures. In addition, the solvent correction, which had previously been reduced to 5 - 6% in approaches from the low temperature side, was increased to 12% by the additional solution of glass at these elevated temperatures. It is believed that factor (c) alone is responsible for

the discrepancies observed in table 4.

The mean of the concordant values (excluding the results obtained in expt. 5 and 10) is

$$(1.337 \pm 0.004) \times 10^{-5} \text{ g. equiv./l.}$$

where the limits of error have been estimated from the uncertainties in locating the saturation point and in the water correction. This corresponds to a thermodynamic solubility product

$$K_{\text{AgCl}} = (1.778 \pm 0.008) \times 10^{-10}.$$

5.441 EXPERIMENT 11.

Effect of ultra-violet light.

The sensitivity of silver halides to strong light is well-known. A considerable amount of work has been published on the effect of light on solid, crystalline silver halides and silver halide photographic emulsions. On the other hand there is no published data on the effect of strong light on the conductance of saturated solutions of silver halides in water. Although all the present work on silver halides was done in red light to avoid photochemical decomposition, one experiment was carried out to observe this effect.

The resistance of a saturated silver chloride solution was measured at regular intervals until it was dropping steadily. The solution was then exposed to radiation

for 10 minutes. The source was a Philora black bulb mercury discharge lamp radiating ultra-violet energy almost entirely in the 3650 Å line, although a small amount of visible light is also radiated in the 4047 Å line. Whereas the normal drop in resistance was about 0.3 ohm/hr., the rate of drop increased to 0.8 ohm/hr. while the solution was exposed. After that the rate dropped back to normal again. This corresponds to an increase in the rate of drop of the resistance (or the rate of increase of the conductance) of nearly 300%.

Further investigation of this effect fell outside the scope of the thesis. Nevertheless it was sufficient to emphasise that exposure to strong light has a very marked effect on the conductance of silver chloride solutions, and the precautions taken to exclude it are fully justified.

3.45 Silver bromide results.

For experimental data see appendix C.

The silver bromide suspensions received the same treatment as the silver chloride ones, except that the stirring rate was increased to 6 bubbles per second. It was hoped to attain saturation more rapidly in this way. The stirring rate for the water measurements remained unchanged. The results were obtained by

FIG. 6. GRAPH OF RESISTANCE AGAINST TIME FOR SATURATED AGR SOLUTION AT 25°C.

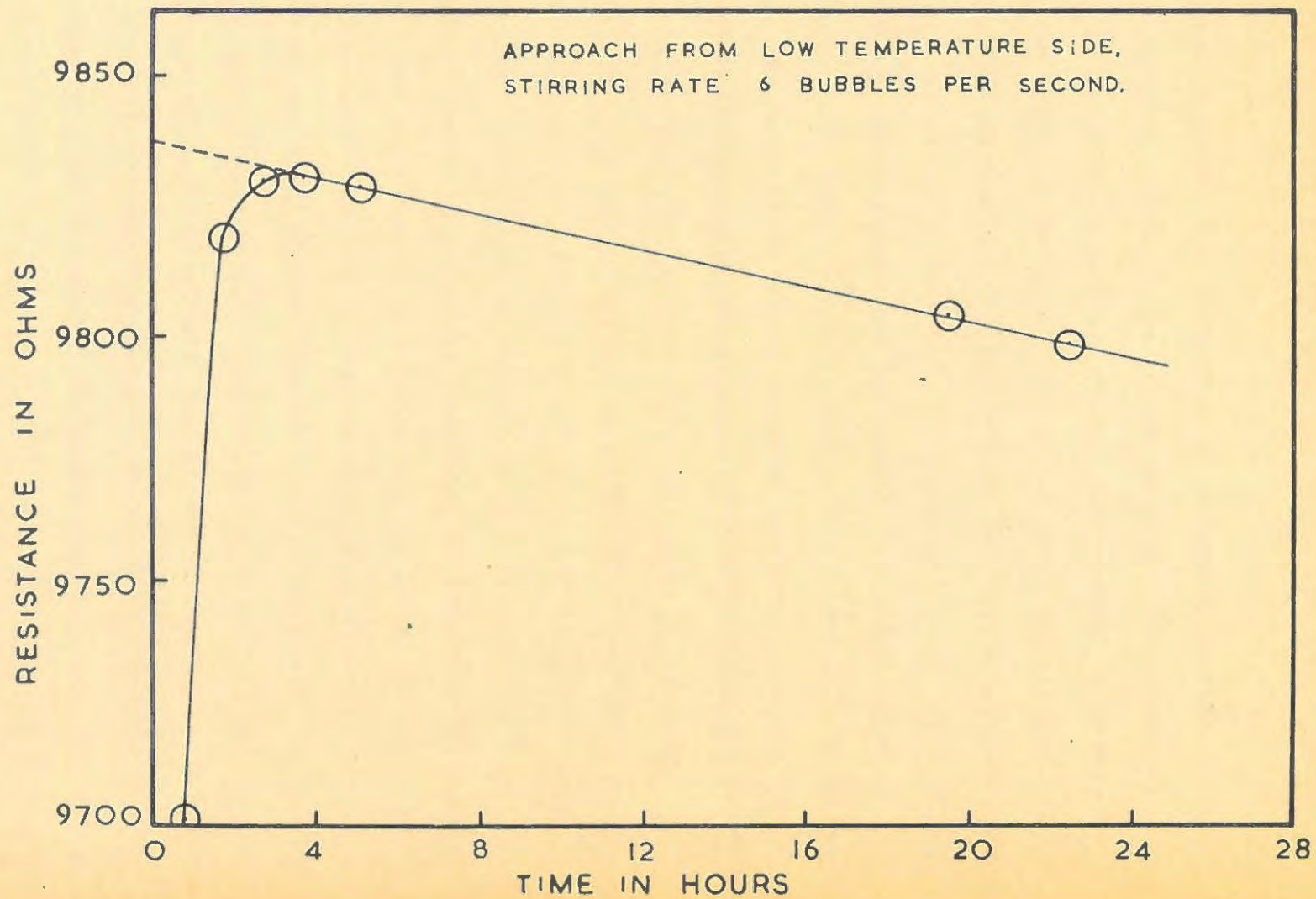


TABLE 5. - SOLUBILITY OF SILVER BROMIDE.

| No. of expt. | age of ppt. days | extrapolated to zero time | | | |
|--------------|------------------|---|--|-----------------------------------|------------------------------------|
| | | $\kappa_{\text{AgBr soln.}}$ nm./cm. | $\kappa_{\text{H}_2\text{O}}$ nm./cm. | κ_{AgBr} nm./cm. | sol. equiv./l. $\times 10^{-7}$ |
| 12 | 4 | 192 | 93 | 99 | 7.06 |
| 13 | 3 | 196 | 96 | 100 | 7.14 |
| 14 | 5 | 191 | 89 | 102 | 7.28 |
| 15 | 4 | 190 | 89 | 101 | 7.21 |
| 16 | 6 | 193 | 94 | 99 | 7.06 |

The mean of the concordant values is

$$(7.15 \pm 0.20) \times 10^{-7} \text{ g. equiv./l.}$$

The limit of error was estimated from the uncertainty in the extrapolations. This corresponds to a thermodynamic solubility product

$$K_{\text{AgBr}} = (5.20 \pm 0.04) \times 10^{-13}.$$

Even with the "ultra-pure" water used the solvent correction amounted to almost 50% of the total conductivity.

3.46 Further theoretical considerations in the interpretation of the results.

Two other factors require investigation since they may possibly affect the interpretation of the conductometric results considerably.

(a) Hydrolytic precipitation.

Both silver halides are the salts of strong acids on the one hand, and a strong, sparingly soluble base on the other. Consequently there is a limiting concentration of the pure salt in water. If it is exceeded precipitation of the base will take place. This concentration is referred to as $c_{\max.}$ - the maximum concentration of pure salt stable in water. If the solubility of the salt is low enough so that $c_{\max.} > s$, then a saturated solution of the salt is possible in pure water without excess of acid, and the salt is said to be congruently soluble in water. If, however, $c_{\max.} < s$, the salt is incongruently soluble in water, and a saturated solution of the salt is possible only in excess of the acid. This is due to precipitation of the base, silver hydroxide, and is usually called "hydrolytic precipitation." In the latter case the conductometric method will give erroneous values for the solubilities of the silver halides.

To prove that $c_{\max.} > s$.

For electrical neutrality

$$[H^+] - [OH^-] = 0 \quad \dots\dots 12.$$

$$\text{and } c_{\max.} = \frac{K_{AgOH}}{f_{\pm} \cdot K_w^{1/2}} \quad \dots\dots 13.$$

$$\text{where } K_{AgOH} = 1.93 \times 10^{-8} \quad (54)$$

and f_{\pm} is the activity coefficient of a univalent ion according to the Debye-Hückel limiting law.

$$c_{\text{max.}} = \frac{1.93 \times 10^{-8}}{f_{\pm} (1 \times 10^{-14})^{\frac{1}{2}}}$$

$$= \frac{1.93 \times 10^{-1}}{f_{\pm}}$$

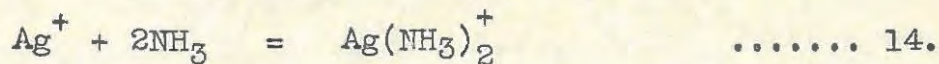
> s

since $s = 1.337 \times 10^{-5}$ g. equiv./l. for silver chloride and 7.15×10^{-7} g. equiv./l. for silver bromide, and $0 < f_{\pm} < 1$.

Hence hydrolytic precipitation cannot take place.

(b) Formation of the silver-ammonia
complex ion.

It is well-known that ammonia in the presence of a solution of a silver salt forms the stable silver-ammonia complex ion according to the equation



This accounts for the fact that sparingly soluble silver halides are soluble in strong ammoniacal solutions.

The instability constant of the complex ion

$$K = \frac{[\text{Ag}^+] \times [\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]} \quad \dots\dots\dots 15.$$

$$= 6.8 \times 10^{-8} \quad (30)$$

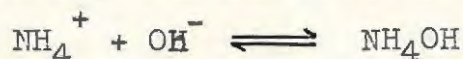
and its magnitude clearly shows that only a very small

silver ion concentration is produced by the dissociation of the complex ion.

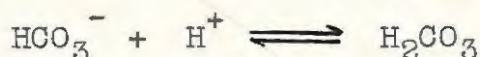
It has previously been suggested (see section 3.425) that the residual conductance of the water is most probably due to incomplete removal of ammonia and carbon dioxide, and to soluble constituents dissolved from the glass walls of the cell. Nothing definite is known about the nature of the ions and the relative contributions they make to the residual conductance. We shall take the extreme case and assume that the conductivity of the water is due to hydrogen, hydroxyl, ammonium and bicarbonate ions only.

Proof that the effect of the formation of $\text{Ag}(\text{NH}_3)_2^+$ in saturated silver halide solutions is negligible. (55)

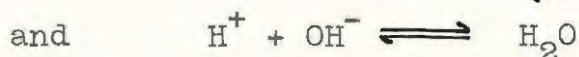
To calculate the degree of hydrolysis of the ions the following equilibria are required:



$$\text{where } K_b = \frac{[\text{NH}_4^+] \times [\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad \dots\dots 16.$$



$$\text{where } K_a = \frac{[\text{HCO}_3^-] \times [\text{H}^+]}{[\text{H}_2\text{CO}_3]} \quad \dots\dots 17.$$

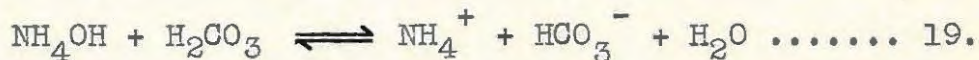


$$\text{where } K_w = [\text{H}^+] \times [\text{OH}^-] \quad \dots\dots 10.$$

The hydrolysis constant K_h is conveniently obtained as

$$K_h = \frac{K_w}{K_a K_b} = \frac{(\text{NH}_4\text{OH}) \times (\text{H}_2\text{CO}_3)}{(\text{NH}_4^+) \times (\text{HCO}_3^-)} \quad \dots\dots 18.$$

which is the equilibrium constant for



Let the stoichiometric concentration of NH_4HCO_3 be c , and let a fraction x of the ammonium ions and a fraction y of the bicarbonate ions be hydrolysed.

Then by the above equations

$$(\text{NH}_4^+) = c(1 - x) \quad \dots\dots 20.$$

$$(\text{HCO}_3^-) = c(1 - y) \quad \dots\dots 21.$$

$$(\text{NH}_4\text{OH}) = cx \quad \dots\dots 22.$$

$$(\text{H}_2\text{CO}_3) = cy \quad \dots\dots 23.$$

$$\begin{aligned} (\text{OH}^-) &= K_b \frac{(\text{NH}_4\text{OH})}{(\text{NH}_4^+)} \\ &= K_b \frac{x}{1-x} \quad \dots\dots 24. \end{aligned}$$

$$\begin{aligned} (\text{H}^+) &= K_a \frac{(\text{H}_2\text{CO}_3)}{(\text{HCO}_3^-)} \\ &= K_a \frac{y}{1-y} \quad \dots\dots 25. \end{aligned}$$

Substituting into eqn. 18 from eqn. 20, 21, 22 and 23

we get
$$K_h = \frac{cx \cdot cy}{c(1-x) \cdot c(1-y)}$$

$$= \frac{x y}{(1-x)(1-y)} \quad \dots\dots\dots 26.$$

For electrical neutrality

$$[H^+] + [NH_4^+] = [OH^-] + [HCO_3^-] \quad \dots\dots\dots 27.$$

$$K_a \frac{y}{1-y} + c(1-x) = K_b \cdot \frac{x}{1-x} + c(1-y) \quad \dots\dots\dots 28.$$

By eqn. 26: $\frac{x}{1-x} = K_h \cdot \frac{y}{1-y}$ $\dots\dots\dots 29.$

$$\therefore x = \frac{K_h \cdot (1-y)}{y + K_h(1-y)} \quad \dots\dots\dots 30.$$

and $1-x = \frac{y}{y + K_h(1-y)}$
 $= \frac{1}{1 + K_h \cdot \frac{1-y}{y}} \quad \dots\dots\dots 31.$

Substitution from eqn. 29 and 31 into eqn. 28 we get

$$K_a \frac{y}{1-y} + c \frac{y}{y + K_h(1-y)} = K_b \cdot K_h \frac{1-y}{y} + c(1-y)$$

This equation is of the fourth order if solved for y , therefore we solve for c :

$$c = \frac{K_b \cdot K_h \cdot \frac{1-y}{y} - K_a \cdot \frac{y}{1-y}}{y - \frac{1}{1 + \frac{y}{K_h(1-y)}}} \quad \dots\dots\dots 32.$$

Values of y may now be chosen and the corresponding value of c calculated from eqn. 32. x can be obtained from eqn. 30, and it is then possible to calculate all the concentrations in eqn. 20, 21, 22, 23, 24 and 25,

and hence calculate the conductivity. From a graph of conductivity against concentration the total concentration c of NH_4HCO_3 corresponding to any particular conductivity can be found.

Using the published values

$$K_a = 4.54 \times 10^{-7} \quad (56)$$

$$K_b = 1.74 \times 10^{-5} \quad (57)$$

$$K_w = 1.008 \times 10^{-14}$$

$$\lambda_{\text{H}^+}^{\circ} = 349.8$$

$$\lambda_{\text{OH}^-}^{\circ} = 198.4$$

$$\lambda_{\text{NH}_4^+}^{\circ} = 73.4 \quad (58)$$

$$\lambda_{\text{HCO}_3^-}^{\circ} = 44.5 \quad (59)$$

it is found that

$$c = 3.8 \times 10^{-7}$$

for water of specific conductance = 95 nm./cm.

Even if all the ammonium bicarbonate were hydrolysed,

$$[\text{NH}_3] \leq 3.8 \times 10^{-7}$$

If all this combines with Ag^+ ions it will only reduce the $[\text{Ag}^+]$ of a saturated silver chloride solution from 1.34×10^{-5} to 1.32×10^{-5} g. ion/l.

Under this extreme condition, which cannot be attained in practice (because no ammonia could be in the complex if $[\text{NH}_3] = 3.8 \times 10^{-7}$) we have from eqn. 15

$$\frac{1.32 \times 10^{-5} (3.8 \times 10^{-7})^2}{[\text{Ag}(\text{NH}_3)_2^+] } \geq 6.8 \times 10^{-8}$$

$$\left[\text{Ag}(\text{NH}_3)_2^+ \right] \leq \frac{1.32 \times 3.8^2 \times 10^{-19}}{6.8 \times 10^{-8}}$$

$$\leq 2.8 \times 10^{-11}$$

in a saturated silver chloride solution

and $\left[\text{Ag}(\text{NH}_3)_2^+ \right] \leq \frac{5.25 \times 10^{-7} \times (3.8 \times 10^{-7})^2}{6.8 \times 10^{-8}}$

$$\leq 1.1 \times 10^{-12}$$

in a saturated silver bromide solution.

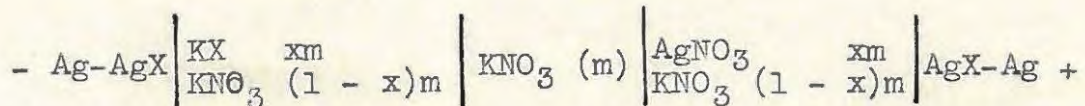
Hence only a negligible fraction of the silver ions can be in the complex, and in practice the effect can be neglected.

4. THE POTENTIOMETRIC METHOD.

4.1 Theory of the Potentiometric Method.

The method employed here is due to Owen and the theory is described in detail elsewhere (13).

In brief it involves measuring the e.m.f.s of the cells:



These cells contain solutions of varying concentrations of the dissimilar ions (Ag^+ and X^-), but are kept at constant ionic strength by the addition of an inert electrolyte (potassium nitrate). The liquid junction potential is eliminated by extrapolating the concentration of the dissimilar ions back to zero.

Extrapolation to zero ionic strength eliminates the effect of the inert electrolyte (potassium nitrate). The e.m.f. of the cell is given by the equation

$$E = k \log \frac{a'_{\text{Ag}^+}}{a_{\text{Ag}^+}} \pm E_j \quad \dots\dots\dots 33.$$

E_j is the sum of the unknown liquid junction potentials,

$$k = \frac{2.303RT}{2F} = 0.0001988T, \text{ and } a'_{\text{Ag}^+} \text{ and } a_{\text{Ag}^+} \text{ represent}$$

the activities of the silver ion in the right hand and left hand solutions respectively.

Substituting the value of the solubility product

$$K_{AgX} = a_{Ag^+} \times a_{X^-} \dots\dots\dots 6.$$

and replacing the activities by concentrations and activity coefficients, extrapolation to $x = 0$ yields an equation of the form

$$\left(E - 2k \log xm \right)_{x=0} = -k \log K + \left(k \log \gamma_{Ag^+} \gamma_{X^-} \right)_{x=0} \dots\dots\dots 34.$$

To facilitate graphical representation, the term $2k \alpha m^{\frac{1}{2}}$ is added to both sides of the equation.

We then get

$$\left(E - 2k \log xm + 2k \alpha m^{\frac{1}{2}} \right)_{x=0} = -k \log K + \left(k \log \gamma_{Ag^+} \gamma_{X^-} + 2k \alpha m^{\frac{1}{2}} \right)_{x=0} \dots\dots\dots 35.$$

The determination of $\left(E - 2k \log xm + 2k \alpha m^{\frac{1}{2}} \right)_{x=0}$

by extrapolation at various values of m is shown in fig. 9 and 11. Evaluation of $-k \log K$ (see also section 4.36) by subsequent extrapolation of these intercepts to $m = 0$ is given in fig. 10 and 12.

To check the graphical extrapolation a best straight line was fitted to the points by the method of least squares (53). The intercepts so obtained were believed to be more accurate, and were used in the final calculation of the solubility products.

4.2 Description, calibration and standardisation of apparatus.

4.21 Thermostat.

Measurements were made with the e.m.f. cell in the thermostat used for the conductance work, but with the inner paraffin thermostat removed.

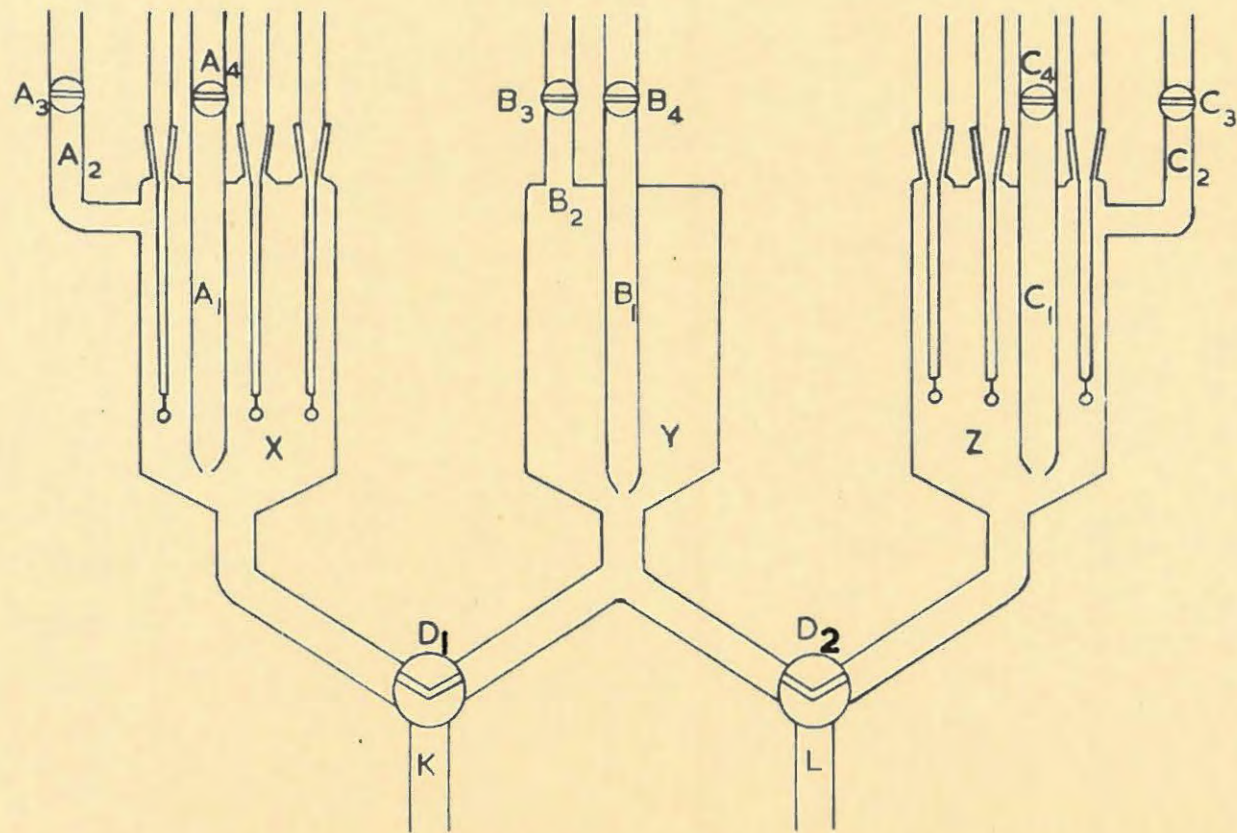
4.22 Measuring apparatus.

A potentiometer of the Tinsley vernier type was used. It was standardised by measuring the potential drop across sections of a calibrated resistance decade box with mercury cup contacts. The nominal values of the small coil, reading the fourth and fifth decimal fractions of a volt, were assumed to be correct. The corrections to be applied to the nominal values on the other two coils are given in appendix D.

The e.m.f.s are expressed in absolute volts with the aid of an Eppley standard cadmium cell. The cell was frequently compared with another Eppley cadmium cell of similar design calibrated to an accuracy of 0.02 millivolts by the National Physical Laboratory, Pretoria.

The null-indicating apparatus consisted of a galvanometer with a universal shunt in circuit. The galvanometer was of the d'Arsonval type, and was placed

FIG. 7. THE E.M.F. CELL ASSEMBLY



on a slate slab sunk into the main wall. The galvanometer lamp and scale were fixed to two metal "parrot perches" also sunk into the main wall. In this way all vibration of the null-indicating apparatus was completely eliminated.

Reversing switches were used to investigate the possible presence of thermal e.m.f.s, but at no time were any such potentials observed to exceed 0.01 millivolt.

4.23 E.m.f. cell.

The cell construction is illustrated in fig. 7. It is similar to the one employed by Owen (13) with certain modifications. A central compartment Y was introduced for the potassium nitrate solution, and provision was made for bubbling purified nitrogen through the solution in each compartment. Smaller quantities of solution could be used since no transfer from external flasks was necessary.

The other two compartments, X and Z, contain 3 electrodes each let in through ground glass joints lightly greased with Silicone grease. Care was taken not to let the solutions come into contact with the greased joints. Nitrogen was bubbled into each compartment through A_1 , B_1 and C_1 , and passed out again through

A₂ B₂ and C₂. Both the inlet and outlet tubes are fitted with stopcocks. Two 120° three-way stopcocks were fitted at D₁ and D₂, and the liquid junctions were formed in these by the shearing method.

Manipulation of the cell and the formation
of sheared liquid junctions.

Each compartment of the cell was filled with the solution to the same level (approximately 1 cm. below the ground glass joints). K and L, carrying waste solutions from the cell were also filled with liquid. These tubes protruded over the edge of the thermostat, and a measuring cylinder was placed beneath each tube. The cell was placed in the thermostat and purified nitrogen was bubbled through the contents of each compartment simultaneously for 1.5 hours. All traces of oxygen and carbon dioxide were thus removed from the solutions.

10 ml. of potassium nitrate solution were then displaced from Y to waste (5 ml. through each three-way stopcock D₁ and D₂) by applying a pressure of nitrogen gas with stopcock B₃ closed. Similarly 10 ml. of solution were displaced from X through D₁ and 10 ml. of solution from Z through D₂. With D₁ and D₂ closed, A₃ B₃ and C₃ were opened for 5 seconds each to allow the nitrogen

pressure above the solutions to equilibrate to atmospheric pressure. All the stopcocks were then closed, and D_1 and D_2 turned to connect the three compartments. Fresh liquid junctions could be formed by repeating this procedure. Preliminary experiments performed with highly coloured potassium permanganate solutions showed that the liquid junctions formed in this way at D_1 and D_2 are not visibly affected by diffusion over a period of 2 hours.

After each set of readings the cell was thoroughly rinsed with conductivity water and dried with a current of air.

4.5 Preparation and standardisation of materials.

4.31 Water.

Conductivity water from the automatic, recycling still (see section 3.422) was used for making up all the solutions in the e.m.f. work. The concentrations of the solutions were based upon the weights of water and dry salts. Vacuum corrections were applied throughout.

4.32 Nitrogen.

The nitrogen was purified as follows: from a cylinder it was passed through the following absorbers:

a solution of silver nitrate to remove traces of hydrogen sulphide; a solution of acid potassium permanganate to remove reducing agents; concentrated sulphuric acid to dry the nitrogen and remove ammonia; heated copper to remove the last traces of oxygen; and a series of U-tubes containing soda-lime to remove carbon dioxide. Finally it was passed through a water bubbler to saturate the nitrogen with water vapour at 24°C , and then into the thermostat where it was brought to 25°C and saturated with water vapour at that temperature.

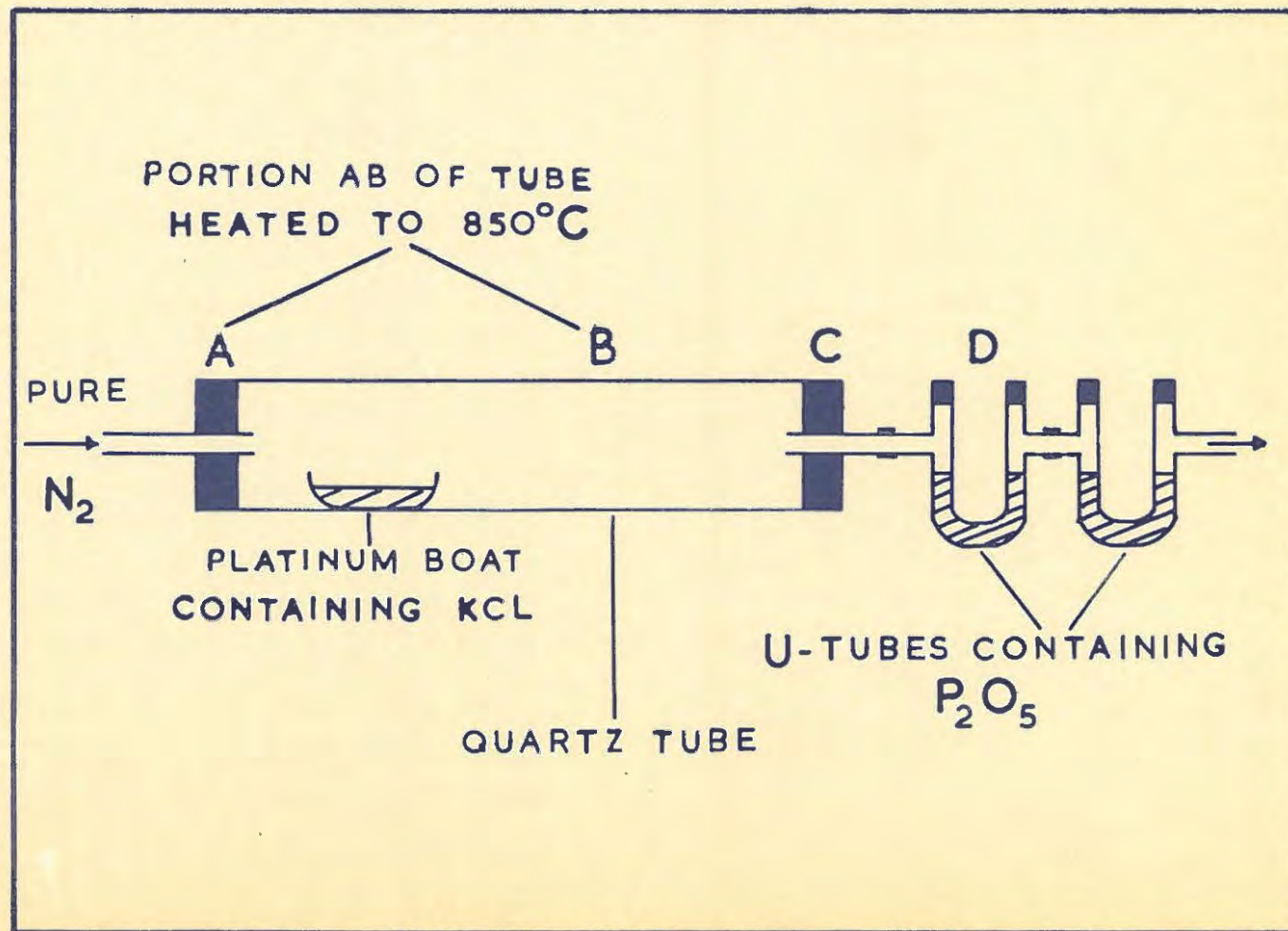
4.33 Potassium chloride.

The potassium chloride was prepared in a similar manner to that described in section 3.32 (b).

During the conductometric work it was noticed that cell constants determined using this potassium chloride gave results which differed from those obtained using fused potassium chloride by 0.25%. It was suspected that this discrepancy was due to the presence of residual moisture occluded in the potassium chloride, and which was not removed by drying in an electric oven.

To confirm this an experiment was carried out to determine the percentage moisture in this potassium chloride by a gravimetric method.

FIG. 8. APPARATUS FOR GRAVIMETRIC DETERMINATION
OF THE MOISTURE CONTENT OF KCL



The apparatus used is illustrated in fig. 8. Nitrogen from a cylinder was passed successively through absorbers of silver nitrate solution to remove all traces of hydrogen sulphide; concentrated sulphuric acid to dry the gas; two U-tubes of soda-lime to remove carbon dioxide; heated copper to remove the last traces of oxygen; and finally through a U-tube containing glass wool dusted with phosphorus pentoxide to remove the last traces of moisture. It was then passed over a weighed sample of the potassium chloride which was placed in a platinum boat in portion AB of a quartz tube. The latter was heated electrically by a combustion furnace to 850°C for 10 minutes. On fusion the potassium chloride partly sublimes, and the sublimate deposited on the cooler portion BC of the quartz tube. The liberated moisture passed out at the far end of the quartz tube, and was absorbed by a previously weighed U-tube D containing glass wool dusted with phosphorus pentoxide.

The moisture content was found to be 0.25%; in exact agreement with the value obtained by the conductometric method. Addink (60) observed that potassium chloride, stored in an evacuated desiccator over phosphorus pentoxide, also contained residual moisture occluded in the interior of the crystals, which could only be

removed by heating in an atmosphere of nitrogen at 550°C. His apparatus (61) was similar to that described on the previous page.

The silver nitrate and potassium bromide were similarly investigated, but were found on fusion to contain no moisture. It was not necessary to determine the percentage moisture, if any, present in the potassium nitrate, as an inspection of the symmetry of the electrode-electrolyte system shows. The presence of moisture in the potassium nitrate would lead to slightly erroneous values of the individual ionic strengths plotted, but the excellent agreement obtained with the e.m.f. values quoted by Owen (13) (assuming that his potassium nitrate was completely free from moisture) indicated that the percentage moisture was very small. In any case this error is completely eliminated on final extrapolation to zero ionic strength.

4.34 Silver - silver chloride electrodes.

The electrodes were prepared by Harned's method (62) with slight modifications. 6 inch lengths of platinum wire were sealed into Pyrex tubing using a graded seal of Uranium glass, and wound into small spirals. Pure silver oxide paste was prepared by adding 0.1N solution of A.R. sodium hydroxide to an excess of 0.1N silver

nitrate solution. The chocolate-brown silver oxide precipitate was washed 25 times by decantation with conductivity water. The paste was then applied to the clean platinum spirals till evenly coated, and fired at 500°C for 7 minutes in an electric furnace.

The six electrodes were then electrolysed in series in 0.5 molal Kahlbaum's G.R. hydrochloric acid solution at 3 milliamps for 3 hours. No distinction was made as to which electrodes were to be used in the silver solutions and which in the chloride solutions. They were shielded from strong light at all times. The electrodes were washed with conductivity water for 2 hours changing the water every 30 minutes, and finally left overnight in some of the solution in which they were to be employed.

Fresh electrodes were prepared for each set of readings by cleaning the silver - silver chloride coating off the platinum spiral with concentrated potassium cyanide followed by concentrated nitric acid. Electrodes prepared in this way were reproducible to 0.05 millivolt.

4.35 Silver - silver bromide electrodes.

Initially the electrodes were prepared by the method suggested by Keston (63). An intimate mixture containing 90% silver oxide and 10% silver bromate was made into

a paste. This was applied to the clean platinum spirals till evenly coated, and fired at 650°C for 7 minutes in an electric furnace. The electrodes were washed with conductivity water for 2 hours and left overnight in the solutions in which they were to be employed. They were carefully shielded from strong light.

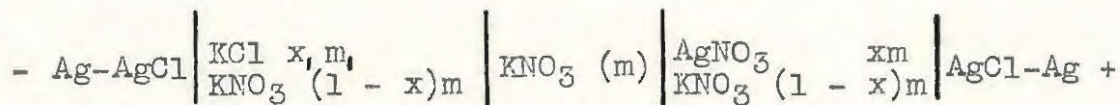
The silver bromate was prepared in a similar manner to the silver oxide using potassium bromate as the precipitating agent. These electrodes were reproducible in the most concentrated 0.05 molal range, but became most erratic in the more dilute solutions. It was also noticed that on cleaning the electrodes with concentrated potassium cyanide followed by concentrated nitric acid a black deposit remained on the platinum spirals. This is probably due to the fact that on firing the electrodes at 650°C the silver alloys with the platinum, and on dissolving the silver with concentrated nitric acid finely divided platinum black remains. This may be one of the reasons for the lack of reproducibility of electrodes prepared in this way.

The thermal method was finally abandoned, and the electrodes were prepared electrolytically in a manner similar to that employed for the preparation of the silver - silver chloride electrodes. When prepared in this way the electrodes were reproducible to 0.05 millivolt

even in the most dilute solutions.

4.36 Correction to the Potentiometric Theory
due to 0.25% moisture in the potassium chloride.

In the cell



the potassium chloride - potassium nitrate solution is made up to be xm moles per 1000 g. of water with respect to potassium chloride. In actual fact it contains x, m_1 moles of potassium chloride.

But $x, m_1 = xm(1 - a)$ where $a = 0.0025$. It also contains $(1 - x)m$ moles of potassium nitrate, so that the total molality is $m(1 - ax)$. On extrapolation to $x = 0$ we shall still get m .

Equation 34 now becomes

$$\left(E - 2k \log xm \right)_{x=0} - k \log(1 - a) = -k \log K + \left(k \log \gamma_{X^-} \gamma_{Ag^+} \right)_{x=0} \dots\dots\dots 36.$$

$$\left(E - 2k \log xm \right)_{x=0} = -k \log K + k \log(1 - a) + \left(k \log \gamma_{X^-} \gamma_{Ag^+} \right)_{x=0} \dots\dots\dots 37.$$

$$= -k \log K + k \left(-a - \frac{a^2}{2} \dots \right) + \left(k \log \gamma_{X^-} \gamma_{Ag^+} \right)_{x=0} \dots\dots\dots 38.$$

writing out $\log(1 - a)$ as a power series. Neglecting terms higher than the first in the series we get

$$\left(E - 2k \log xm \right)_{x=0} = -k \log K - ka + \left(k \log \gamma_{X-} \gamma_{Ag+} \right)_{x=0} \dots \dots \dots 39.$$

Adding $2k \alpha m^{\frac{1}{2}}$ to both sides we get

$$\left(E - 2k \log xm + 2k \alpha m^{\frac{1}{2}} \right)_{x=0} = -k \log K - ka + \left(k \log \gamma_{X-} \gamma_{Ag+} + 2k \alpha m^{\frac{1}{2}} \right)_{x=0} \dots \dots \dots 40.$$

Hence the intercept in the second extrapolation will be $-k \log K - ka$.

4.4 Experimental results and discussion.

4.41 Silver chloride results.

The potentiometric measurements reported by Owen (13) have been repeated here for comparison with the values obtained by the conductometric method. The experimental data are collected in table 6.

The observed potentials were lower than those found by Owen (13), but only by an average of 0.08 millivolt, which is within the estimated limit of error of 0.1 millivolt. At low silver ion concentrations the results were erratic unless extra time was allowed for equilibrium to be established. The recorded e.m.f. values are

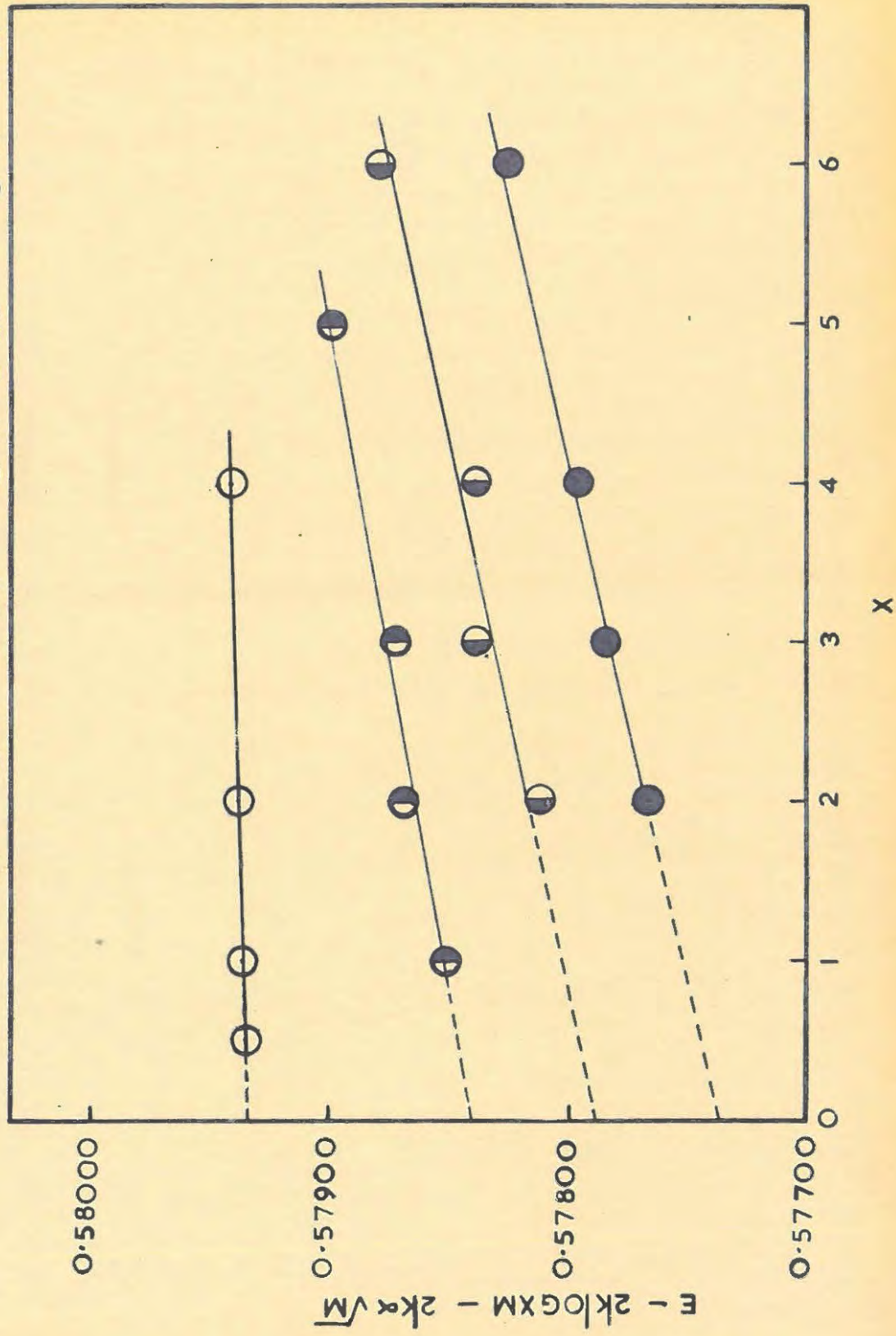
TABLE 6. - OBSERVED ELECTROMOTIVE FORCES AND INTERCEPTS FROM THE FIRST EXTRAPOLATION BY THE GRAPHICAL METHOD AND THE METHOD OF LEAST SQUARES. (see fig. 9)

| m | x | E | Intercepts from first extrapolation | |
|------|------|---------|--|---------------|
| | | | graphical | least squares |
| 0.05 | 0.4 | 0.36491 | | |
| | 0.2 | 0.32926 | 0.57934 | 0.57933 |
| | 0.1 | 0.29362 | | |
| | 0.05 | 0.25798 | | |
| 0.03 | 0.5 | 0.35274 | | |
| | 0.3 | 0.32622 | 0.57841 | 0.57842 |
| | 0.2 | 0.30534 | | |
| | 0.1 | 0.26955 | | |
| 0.02 | 0.6 | 0.34298 | | |
| | 0.4 | 0.32174 | 0.57787 | 0.57782 |
| | 0.3 | 0.30695 | | |
| | 0.2 | 0.28585 | | |
| 0.01 | 0.6 | 0.30931 | | |
| | 0.4 | 0.28819 | 0.57735 | 0.57734 |
| | 0.3 | 0.27330 | | |
| | 0.2 | 0.25227 | | |

expressed in absolute volts, and each value is the mean of the nine pairwise combinations of the six electrodes.

FIG. 9. ELIMINATION OF E_j BY EXTRAPOLATION

○ $M = 0.05$ ◐ $M = 0.03$ ◑ $M = 0.02$ ● $M = 0.01$



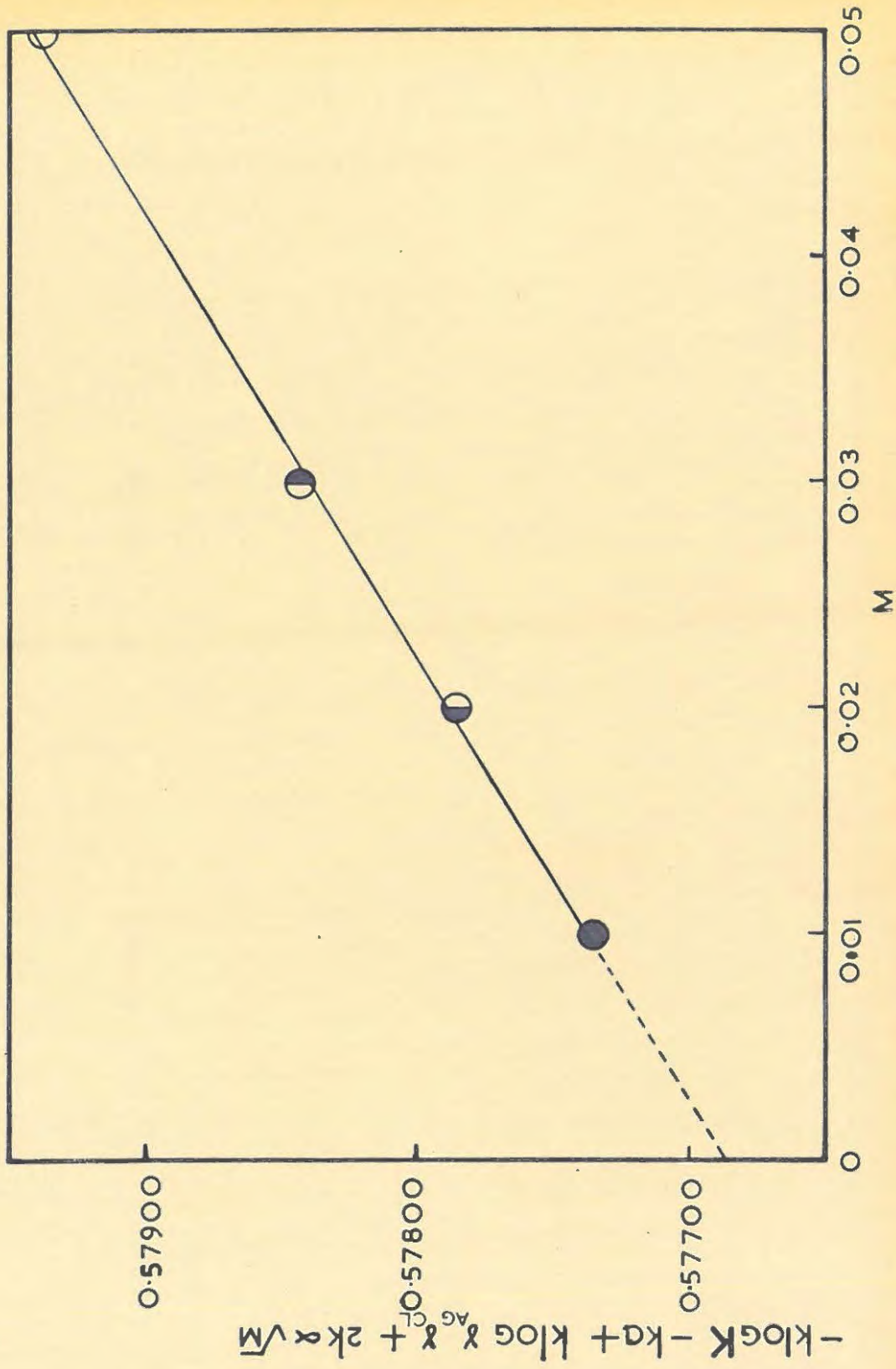
They were generally comparable within 0.1 millivolt. The overall reproducibility of the cell was also of this order. This can be seen in fig. 9, where the radii of the plotted circles are 0.1 millivolt. The points lie fairly well on straight lines, and confirm Owen's observations (13) about the linearity of the extrapolation function. This is also supported by subsequent work done on electromotive force cells by Owen and Brinkley (18) (64) and Owen and King (65).

Fig. 10 shows the plots of the intercepts, obtained from the extrapolations in fig. 9, against m , which according to eqn. 40 permits the evaluation of $-k\log K - k_a$ by extrapolation to $m = 0$. These extrapolations are also linear within the estimated uncertainty of ± 0.1 millivolt for the plotted points, which have radii corresponding to 0.1 millivolt. It is seen that the straight line intersects all the circles, and it appears from the graph that the extrapolative uncertainty in $-k\log K - k_a$ does not exceed 0.2 millivolt.

The intercept $-k\log K - k_a$, from the extrapolation in fig. 10, is recorded in table 7. The first and second extrapolations were also performed by the method of least squares, and these values were preferred in the final calculation of the solubility product.

The solubility of silver chloride in pure water

FIG. 10. EVALUATION OF $-k \log K - k_a$ BY
 EXTRAPOLATION TO INFINITE DILUTION



is calculated by the equation

$$\log m = \frac{1}{2} \log K + \alpha c^{\frac{1}{2}} \dots\dots\dots 41.$$

where α is the Debye-Hückel limiting slope. This assumes the applicability of the Debye-Huckel limiting law at such high dilutions.

TABLE 7. - SOLUBILITY OF SILVER CHLORIDE.

| -klogK - ka graphical | -ka least squares | -logK | K x 10 ¹⁰ | solubility | |
|--------------------------|-------------------------|--------|----------------------|----------------------|----------------------|
| | | | | m x 10 ⁻⁵ | c x 10 ⁻⁵ |
| 0.57695 | 0.57685 | 9.7520 | 1.770 ±0.006 | 1.336 ±0.003 | 1.332 ±0.003 |

4.42 Silver bromide results.

The experimental results are collected in table 8. As in the case of the previous determinations on silver chloride, erratic results were obtained with low silver ion concentrations unless precautions were taken to rinse the electrodes thoroughly with the required solutions and to allow extra time for equilibrium.

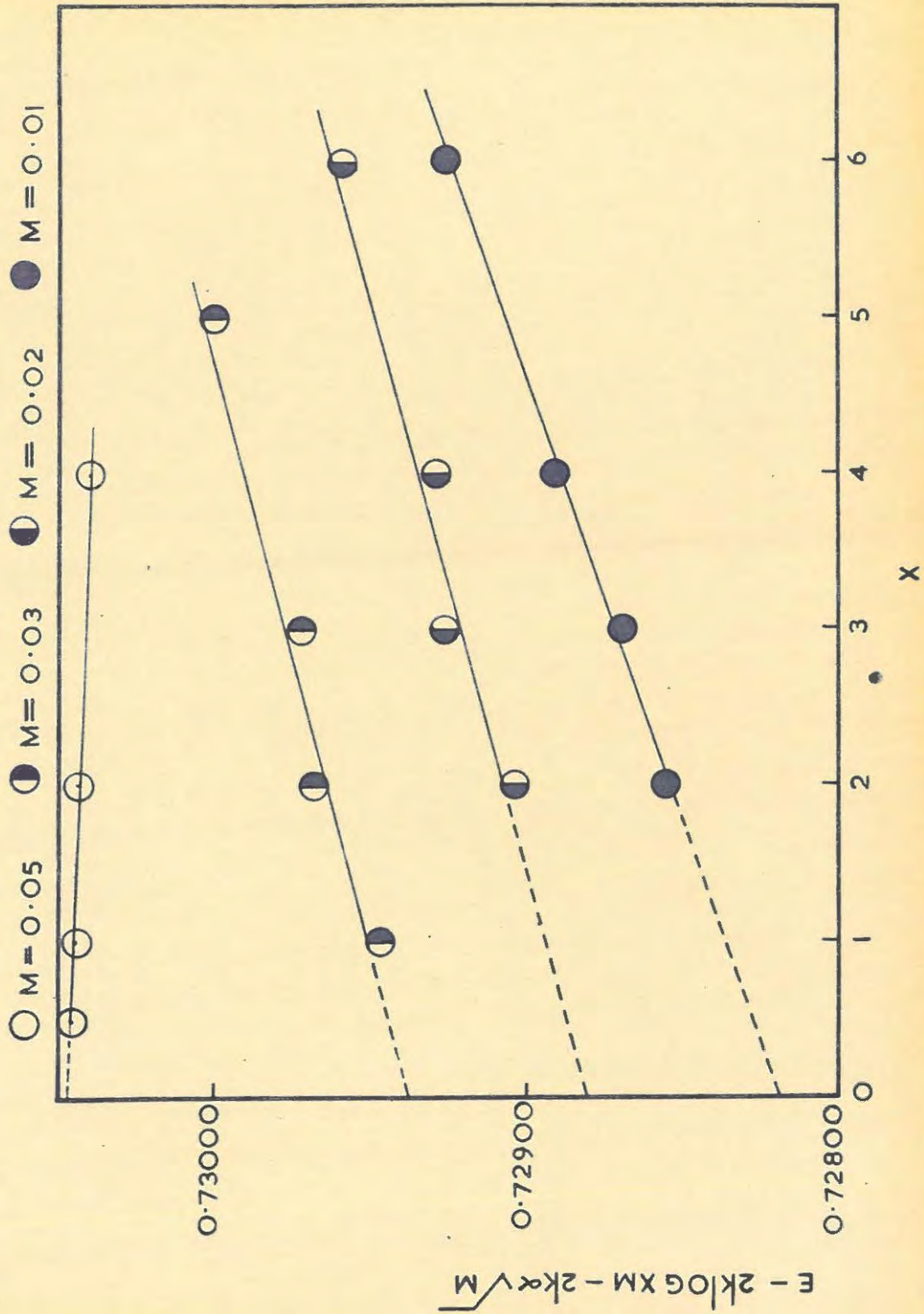
The e.m.f. values quoted in the 0.05 molal range (and indicated by asterisks) were obtained using silver - silver bromide electrodes prepared by Keston's thermal method (63). When this method was finally abandoned due to lack of reproducibility, two of the e.m.f. values were rechecked using silver - silver

TABLE 8. - OBSERVED ELECTROMOTIVE FORCES AND INTERCEPTS FROM THE FIRST EXTRAPOLATION BY THE GRAPHICAL METHOD AND THE METHOD OF LEAST SQUARES. (see fig. 11)

| m | x | E | Intercepts from | |
|------|------|----------|-----------------|---------------|
| | | | graphical | least squares |
| 0.05 | 0.4 | 0.51590* | | |
| | 0.2 | 0.48031* | 0.73052 | 0.73046 |
| | 0.1 | 0.44470* | | |
| | 0.05 | 0.40910* | | |
| 0.03 | 0.5 | 0.50375 | | |
| | 0.3 | 0.47722 | 0.72944 | 0.72938 |
| | 0.2 | 0.45633 | | |
| | 0.1 | 0.42051 | | |
| 0.02 | 0.6 | 0.49378 | | |
| | 0.4 | 0.47264 | 0.72887 | 0.72882 |
| | 0.3 | 0.45783 | | |
| | 0.2 | 0.43673 | | |
| 0.01 | 0.6 | 0.46032 | | |
| | 0.4 | 0.43915 | 0.72827 | 0.72817 |
| | 0.3 | 0.42414 | | |
| | 0.2 | 0.40316 | | |

bromide electrodes prepared electrolytically. The values agreed within the experimental error of 0.05 millivolt,

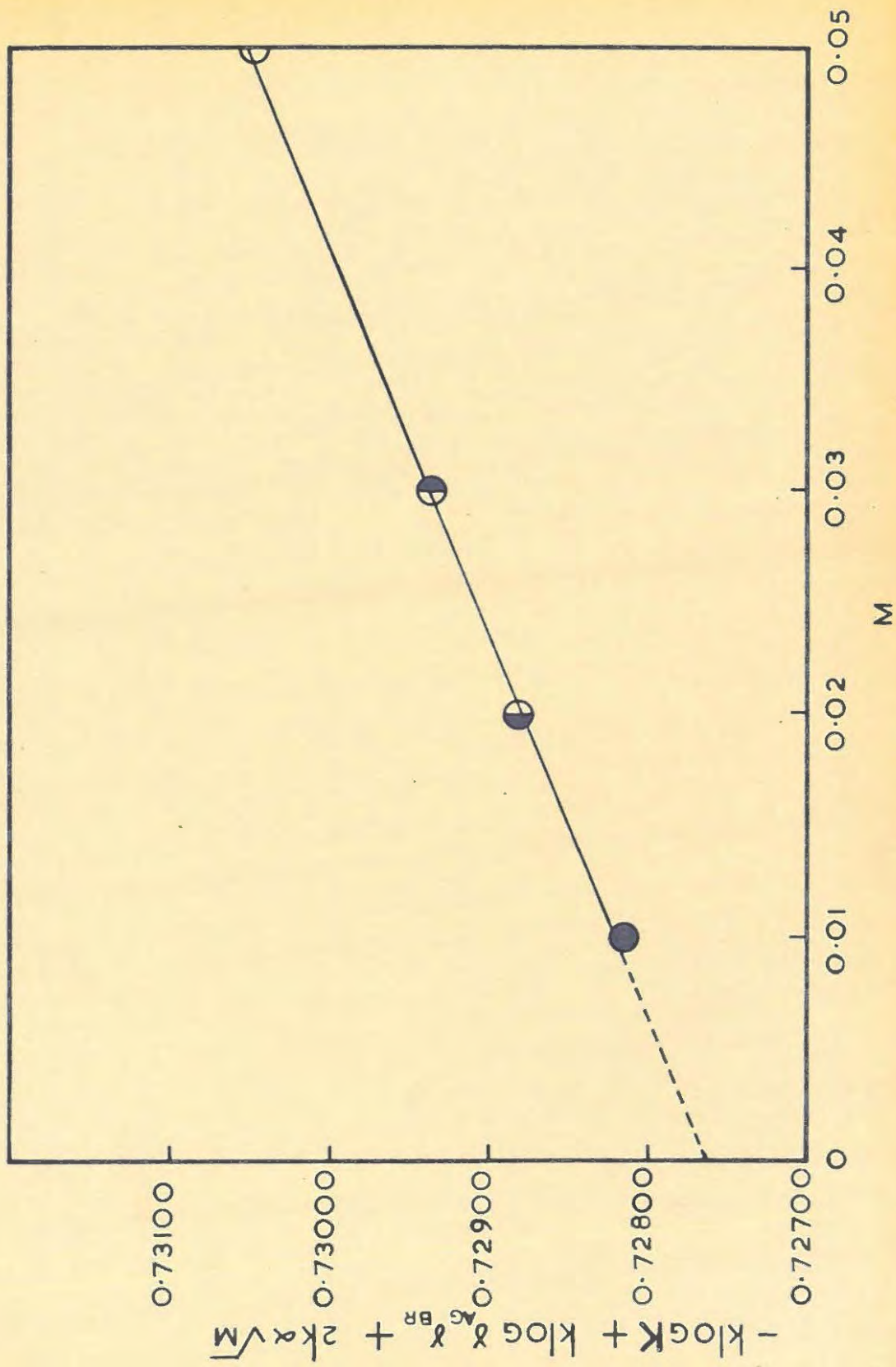
FIG. II. ELIMINATION OF E_j BY EXTRAPOLATION



and indicated that there was nothing inherently wrong with electrodes prepared by the thermal method. It had probably not been sufficiently standardised to give reproducible electrodes in the more dilute solutions. Contrary to the opinion of Stas (19) this agreement also indicated that there is no essential difference in solubility between silver bromide prepared thermally and the electrolytic variety. The reproducibility of the silver - silver bromide electrodes (prepared electrolytically) and the overall reproducibility of the cell was the same as that for the silver chloride determinations.

The intercepts from the first extrapolation were obtained both by the graphical method (see fig. 11) and the method of least squares; the values obtained by the latter method being preferred. Fig. 12 shows the plot of the intercepts, obtained from the first extrapolation, against m , which according to eqn. 35 permits the evaluation of $-k \log K$ by extrapolation to $m = 0$. It is noted from the graphs in fig. 11 and 12 that these extrapolations are once again linear within the estimated uncertainty of ± 0.1 millivolt for the plotted points, which have radii corresponding to 0.1 millivolt. This offers further experimental confirmation of Owen's hypothesis (13).

FIG.12. EVALUATION OF $-k \log K$ BY EXTRAPOLATION
TO INFINITE DILUTION



The intercept $-k \log K$ from the extrapolation in fig. 12 is recorded in table 9. The value obtained by the method of least squares is also recorded, and is the one used in the final evaluation of the solubility product.

The solubility of silver bromide in pure water was calculated using eqn. 41 as in the case of silver chloride.

TABLE 9. - SOLUBILITY OF SILVER BROMIDE.

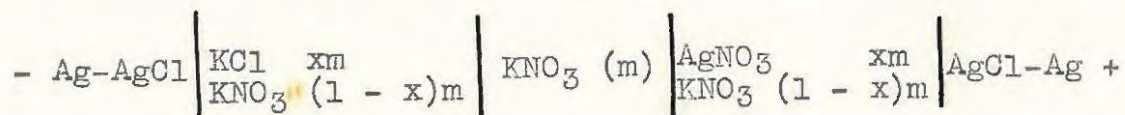
| $-k \log K$ graphical | $-k \log K$ least squares | $-\log K$ | $K \times 10^{13}$ | solubility $m \times 10^{-7}$ | $c \times 10^{-7}$ |
|--------------------------|---------------------------------|-----------|--------------------|----------------------------------|--------------------|
| 0.72775 | 0.72765 | 12.298 | 5.04 ± 0.06 | 7.09 ± 0.3 | 7.07 ± 0.3 |

In both section 4.41 and 4.42 the limits of error have been estimated from the potentiometric error of ± 0.05 millivolt and the possible errors in making up the solutions.

4.43 Comparison with other e.m.f. data.

It is of interest to compare the cells

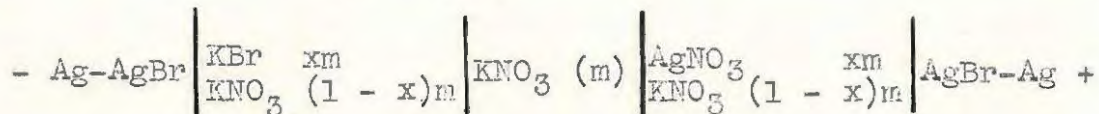
(1)



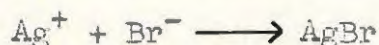
for which the cell reaction is



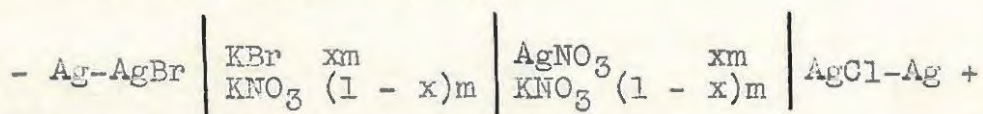
and (II)



having the cell reaction



with the cell (III)



employed by Owen and King (65).

The overall cell reaction for the latter cell is



and the e.m.f. of the cell is given by the equation

$$E = E^0 - k \log \frac{a_{\text{Cl}^-}}{a_{\text{Br}^-}} + E_j \quad \dots\dots\dots 42.$$

An inspection of the electrode - electrolyte systems of these cells indicates that at the same overall ionic strengths and corresponding concentrations of the silver and the halide ions (the e.m.f. of cell (II)) - (the e.m.f. of cell (I)) = (the e.m.f. of cell (III)) (disregarding the unknown liquid junction potentials).

The recorded e.m.f. values given in sections 4.41 and 4.42, together with the corresponding values quoted by Owen and King (65), are grouped in table 10 for the purpose of comparison.

It is observed that the difference between the e.m.f.s

TABLE 10. - COMPARISON WITH OTHER E.M.F. DATA.

| m | x | e.m.f. data | | | |
|------|------|-------------|--------------|---------------|---------------------------|
| | | cell (I) | cell (II) | cell (III) | cell - cell (II) - (I) |
| 0.05 | 0.4 | 0.36491 | 0.51590 | 0.15120 | 0.15099 |
| | 0.2 | 0.32926 | 0.48031 | 0.15125 | 0.15105 |
| | 0.1 | 0.29362 | 0.44470 | 0.15127 | 0.15108 |
| | 0.05 | 0.25798 | 0.40910 | 0.15127 | 0.15112 |
| 0.03 | 0.5 | 0.35274 | 0.50375 | 0.15116 | 0.15101 |
| | 0.3 | 0.32622 | 0.47722 | 0.15110 | 0.15100 |
| | 0.2 | 0.30534 | 0.45633 | 0.15114 | 0.15099 |
| | 0.1 | 0.26955 | 0.42051 | 0.15111 | 0.15096 |

of cells (II) and (I) differed from the corresponding e.m.f.s quoted by Owen and King (65) for cell (III) by 0.2 millivolt or less. This discrepancy is slightly greater than the estimated limit of error of 0.1 millivolt for these cells, but is most probably due to differences between the liquid junction potentials in the three cells and the effect of the inert electrolyte (potassium nitrate).

5. SUMMARY AND CONCLUSIONS.

It is significant that the values obtained for the solubilities of the silver halides by the conductometric and the potentiometric methods agree within the estimated limits of experimental error. The best value for the solubility of silver chloride appears to be

$$s_{\text{AgCl}} = (1.334 \pm 0.005) \times 10^{-5} \text{ g. equiv./l.}$$

It is a weighted mean of the figures obtained by the conductometric and the potentiometric methods, and is derived as follows:

$$\begin{array}{l} \text{Mean weighted inversely} \\ \text{as the limits of error} \end{array} = \frac{1.337 + \frac{1}{0.004} + 1.332 + \frac{1}{0.003}}{\frac{1}{0.004} + \frac{1}{0.003}}$$

This corresponds to a thermodynamic solubility product

$$K_{\text{AgCl}} = (1.774 \pm 0.01) \times 10^{-10}$$

The conductometric value refers to precipitated silver chloride washed and aged for several days or weeks. The potentiometric value, on the other hand, refers to electrolytic silver chloride washed and aged for one day. It therefore seems unlikely that the differences in tables 1 and 2 are caused by the physical condition of the silver chloride. They are most probably due to experimental errors arising from the solvent correction or the liquid junction potentials.

The nephelometric technique is the only other method which has given reasonable values for the solubility

of silver chloride. The published values are given in table 11.

TABLE 11. - SOLUBILITY OF SILVER CHLORIDE AT 25°C
FROM NEPHELOMETRIC MEASUREMENTS.

| solubility 10^{-5} equiv./l | authors | date | ref. no. |
|----------------------------------|--------------------------|------|-------------|
| 1.42 | Pinkus and Berkolaiko | 1930 | (66) |
| 1.278 | Popoff and Neuman | 1930 | (67) |
| 1.273 | Neuman | 1932 | (68) |
| 1.49 - 1.56 | Eversole and McLachan | 1932 | (69) |
| 1.388 | Dave and Krishnaswami | 1933 | (70) |
| 1.277 | Pinkus and Schepmans | 1938 | (71) |

The mean of these results is 1.36×10^{-5} g. equiv./l. It agrees sufficiently well with the value found previously to suggest that the solubility of freshly precipitated silver chloride does not differ significantly from that of the aged precipitate.

The best value for the solubility of silver bromide may be taken as

$$s_{\text{AgBr}} = (7.09 \pm 0.05) \times 10^{-7} \text{ g. equiv./l.}$$

Once again this is the mean, weighted inversely as the limits of error, of the conductometric and the potentiometric figures.

It leads to a thermodynamic solubility product

$$K_{\text{AgBr}} = (5.08 \pm 0.10) \times 10^{-13}$$

This agrees quite well with the value 7.04×10^{-7} g. equiv./l. calculated by Owen and Brinkley (18) from the standard potentials of the silver and the silver - silver bromide electrodes.

There appears to be no significant difference in solubility between samples of silver bromide prepared either thermally, by electrolysis, or by precipitation.

PART II.

THE SOLUBILITY OF SILVER CHLORIDE AND SILVER BROMIDE
IN WATER FROM 5 TO 55°C BY THE CONDUCTOMETRIC METHOD.

1. INTRODUCTION.

There have been no recent conductometric determinations of the solubilities of silver chloride and silver bromide from 0 to 100°C. The available values are given in tables 12 and 13.

TABLE 12. - SOLUBILITY OF SILVER CHLORIDE FROM
CONDUCTANCE MEASUREMENTS.

| Temp. (°C) | solubility 10^{-5} equiv./l | solvent corn. % total cond. | authors | date | ref. no. |
|---------------|----------------------------------|--------------------------------------|------------------------|------|-------------|
| 0.0 | 0.32 | - | Johnson and Hulett | 1933 | (34) |
| 1.55 | 0.39 | 72 | Kohlrausch | 1908 | (3) |
| 2.0 | 0.53 | - | Kohlrausch and Rose | 1893 | (2) |
| 4.68 | 0.46 | 75 | Kohlrausch | 1908 | (3) |
| 9.97 | 0.62 | - | Kohlrausch | 1908 | (3) |
| 10.0 | 0.68 | - | Kohlrausch and Rose | 1893 | (2) |
| 13.8 | 0.97 | - | Holleman | 1893 | (1) |
| 17.51 | 0.91 | 52 | Kohlrausch | 1908 | (3) |
| 18.0 | 1.06 | - | Kohlrausch and Rose | 1893 | (2) |
| 18.0 | 1.12 | - | Kohlrausch | 1904 | (72) |
| 18.0 | 1.05 | 23 | Melcher | 1910 | (73) |

TABLE 12. (continued).

| Temp. (°C) | solubility 10^{-5} equiv./l | solvent corr. % total cond. | authors | date | ref. no. |
|---------------|----------------------------------|--------------------------------------|------------------------|------|-------------|
| 19.95 | 1.06 | 60 | Böttger | 1903 | (54) |
| 25.86 | 1.35 | 39 | Kohlrausch | 1908 | (3) |
| 54.0 | 2.11 | - | Kohlrausch and Rose | 1893 | (2) |
| 34.12 | 1.91 | 28 | Kohlrausch | 1908 | (3) |
| 42.0 | 2.83 | - | Kohlrausch and Rose | 1893 | (2) |
| 50.0 | 3.65 | 5 - 6 | Melcher | 1910 | (73) |
| 100.0 | 14.7 | - | Melcher | 1910 | (73) |
| 100.0 | 15.2 | - | Böttger | 1906 | (74) |

TABLE 13. - SOLUBILITY OF SILVER BROMIDE FROM
CONDUCTANCE MEASUREMENTS.

| Temp. (°C) | solubility 10^{-7} equiv./l | solvent corr. % total cond. | authors | date | ref. no. |
|---------------|----------------------------------|--------------------------------------|-----------------------------|------|-------------|
| 18.0 | 21.1 | - | Kohlrausch and Rose | 1893 | (2) |
| 19.96 | 4.4 | - | Bottger | 1903 | (54) |
| 20.2 | 27.0 | - | Holleman | 1893 | (1) |
| 21.0 | 5.7 | - | Kohlrausch | 1904 | (72) |
| 21.1 | 5.7 | 95 | Kohlrausch and Dodezalek | 1901 | (75) |
| 38.4 | 68.2 | - | Holleman | 1893 | (1) |
| 100.0 | 197.0 | 23 | Böttger | 1906 | (74) |

None of these values appear reliable mainly because of the extremely large solvent corrections. This is particularly noticeable in the case of the silver bromide determinations where the solvent correction sometimes amounted to more than 90% of the total conductivity. Furthermore, the temperature range is very inadequately covered. Published data obtained by e.m.f. and other methods are given in tables 14 and 15 for comparison.

TABLE 14. - SOLUBILITY OF SILVER CHLORIDE BY
OTHER METHODS.

| Temp. (°C) | solubility 10^{-5} equiv./l | method | author | date | ref. no. |
|---------------|----------------------------------|----------------|----------------------|------|-------------|
| 5.0 | 0.505 | e.m.f. | Owen | 1938 | (13) |
| 15.0 | 0.841 | e.m.f. | Owen | 1938 | (13) |
| 20.0 | 1.08 | e.m.f. | Hahn and Klockman | 1930 | (11) |
| 20.0 | 0.31 | tyndallometric | Bedel | 1938 | (17) |
| 21.0 | 1.07 | colorimetric | Whitby | 1910 | (76) |
| 35.0 | 2.048 | e.m.f. | Owen | 1938 | (13) |
| 45.0 | 3.026 | e.m.f. | Owen | 1938 | (13) |
| 100.0 | 15.1 | colorimetric | Whitby | 1910 | (76) |

By using "ultra-pure" conductivity water in the measurements reported in part II it has been possible to reduce the solvent correction considerably,

TABLE 15. - SOLUBILITY OF SILVER BROMIDE BY
OTHER METHODS.

| Temp. (°C) | solubility 10^{-7} equiv./l | method | author | date | ref. no. |
|---------------|----------------------------------|--------|----------|------|-------------|
| 18.0 | 6.4 | e.m.f. | Kolthoff | 1921 | (77) |
| 18.0 | 7.0 | e.m.f. | Masaki | 1930 | (78) |

particularly in the case of the silver bromide determinations.

2. VARIATION WITH TEMPERATURE OF THE THEORETICAL COEFFICIENTS α AND β IN THE ONSAGER EQUATION.

These coefficients were calculated using the most recently published values of the fundamental constants by Bearden and Watts (22), viscosities by Dorsey (79) and the dielectric constants reported by Wyman (80). They are recorded in table 16.

TABLE 16. - VALUES OF α AND β FROM 5 TO 55°C.

| Temperature (°C) | α | β |
|------------------|----------|---------|
| 5.0 | 0.2216 | 35.12 |
| 15.0 | 0.2250 | 46.84 |
| 25.0 | 0.2289 | 60.19 |
| 35.0 | 0.2335 | 75.30 |
| 45.0 | 0.2387 | 91.59 |
| 55.0 | 0.2444 | 108.66 |

3. - CRITICAL SURVEY OF THE LITERATURE FOR VALUES OF
THE LIMITING IONIC MOBILITIES OF THE CHLORIDE,
BROMIDE AND SILVER IONS FROM 5 TO 55°C.

Several papers quote values for the limiting equivalent conductances of potassium chloride, potassium bromide, sodium chloride and hydrochloric acid, as well as the limiting ionic mobilities of their constituent ions at various temperatures. These values are recorded in table 17.

Combining the data of Owen and Sweeton (81) and Owen and Zeldes (82) it is possible to calculate the limiting ionic mobilities of the potassium ion and hence the bromide ion at 5 and 55°C. These values are denoted by asterisks in table 17.

On the other hand, an exhaustive literature search revealed an almost complete lack of published data for the limiting ionic mobilities of the silver ion from 5 to 55°C. Available values are those of Noyes (79) ($\lambda_{Ag^+}^{\circ} = 53.8$ at 18.0°C), Kohlrausch (89) ($\lambda_{Ag^+}^{\circ} = 54.02$ at 18.0°C), and McInnes, Shedlovsky and Longworth (23) ($\lambda_{Ag^+}^{\circ} = 61.92$ at 25.0°C).

In addition, data are given in the Int. Crit. Tables (79) on the variation of the equivalent conductances of potassium nitrate and silver nitrate with concentration at various temperatures. From this data the limiting

TABLE 17. - LIMITING EQUIVALENT CONDUCTANCES AND IONIC MOBILITIES FROM 5 TO 55°C.

| Temp. (°C) | Λ_{KCl}° | Λ_{NaCl}° | Λ_{KBr}° | Λ_{HCl}° | $\lambda_{Cl^-}^{\circ}$ | $\lambda_{Br^-}^{\circ}$ | $\lambda_{K^+}^{\circ}$ | $\lambda_{H^+}^{\circ}$ | $\lambda_{Na^+}^{\circ}$ | author | ref. no. |
|---------------|-------------------------|--------------------------|-------------------------|-------------------------|--------------------------|--------------------------|-------------------------|-------------------------|--------------------------|---|-------------|
| 5.0 | | | | 297.6 | 47.0 | | | 250.6 | | Owen & Sweeton | (81) |
| | 94.26 | | 96.0 | | | | | | | Owen & Zeldes | (82) |
| | | | | | | 48.74* | 47.26* | | | | |
| 15.0 | | | | 362.1 | 61.2 | | | 300.9 | | Owen & Sweeton | (81) |
| | 120.86 | | | | | | | | | Li & Fang | (83) |
| | 120.88 | | | | 61.31 | | 59.57 | | | Li & Brull | (84) |
| | 121.09 | | | | | | | | | Gordon | (85) |
| | 121.07 | 101.18 | 122.81 | | 61.42 | 63.15 | 59.66 | 300.6 | 39.75 | Benson & Gordon | (86) |
| | 121.09 | 101.20 | 122.84 | | 61.43 | 63.17 | | | | Gunning & Gordon | (87) |
| 25.0 | | | | 426.2 | 76.3 | | | 349.9 | | Owen & Sweeton | (81) |
| | | | | | 76.32 | | | | | MacInnes, Shedlovsky & Longsworth | (23) |
| | 149.84 | | | | | | | | | Li & Fang | (83) |
| | 149.84 | | | | 76.34 | | 73.50 | | | Li & Brull | (84) |
| | 149.85 | 126.45 | 151.64 | | 76.35 | 78.14 | 73.50 | 349.82 | 50.10 | Benson & Gordon | (86) |

| Temp. (°C) | λ_{KCl} | λ_{NaCl} | λ_{KBr} | λ_{HCl} | λ_{Cl^-} | λ_{Br^-} | λ_{K^+} | λ_{H^+} | λ_{Na^+} | author | ref. no. |
|---------------|-----------------|------------------|-----------------|-----------------|------------------|------------------|-----------------|-----------------|------------------|---------------------|-------------|
| 25.0 | 149.82 | 126.42 | | | | | | | | Snedlovsky | (40) |
| | | | | | 75.8 | | | | | Moyes & Falk | (88) |
| | 149.88 | | 151.68 | | | | | | | Owen & Zeldes | (82) |
| | 149.88 | 126.48 | 151.67 | | 76.36 | 78.15 | | | | Gunning & Gordon | (87) |
| 30.0 | | | | | 84.00 | | | | | Li & Fang | (83) |
| | | | | | 84.22 | | | | | Gordon | (85) |
| 35.0 | | | | 489.2 | 92.5 | | | 396.7 | | Owen & Sweeton | (81) |
| | 179.40 | | | | 91.68 | | 87.71 | | | Li & Brull | (84) |
| | 180.42 | 153.75 | 182.24 | | 92.22 | 94.03 | 88.21 | 397.0 | 61.53 | Benson & Gordon | (86) |
| | 180.50 | 153.85 | 182.32 | | 92.26 | 94.07 | | | | Gunning & Gordon | (87) |
| 40.0 | | | | | 99.42 | | | | | Li & Fang | (83) |
| | | | | | 100.52 | | | | | Gordon | (85) |
| 45.0 | | | | 550.3 | 109.5 | | | 440.8 | | Owen & Sweeton | (81) |
| | 208.96 | | | | 107.15 | | 101.81 | | | Li & Brull | (84) |
| | 212.42 | 182.65 | 214.17 | | 108.90 | 110.68 | 103.49 | 441.4 | 73.77 | Benson & Gordon | (86) |
| | 212.49 | 182.73 | 214.18 | | 108.95 | 110.65 | | | | Gunning & Gordon | (87) |
| 55.0 | | | | 609.5 | 127.4 | | | 482.1 | | Owen & Sweeton | (81) |
| | 245.69 | | 247.15 | | | | | | | Owen & Zeldes | (82) |
| | | | | | 128.86* | 118.29* | | | | | |

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FIG. 13. EVALUATION OF Λ_0 FOR AgNO_3 AT 0°C
 BY EXTRAPOLATION TO ZERO CONCENTRATION.

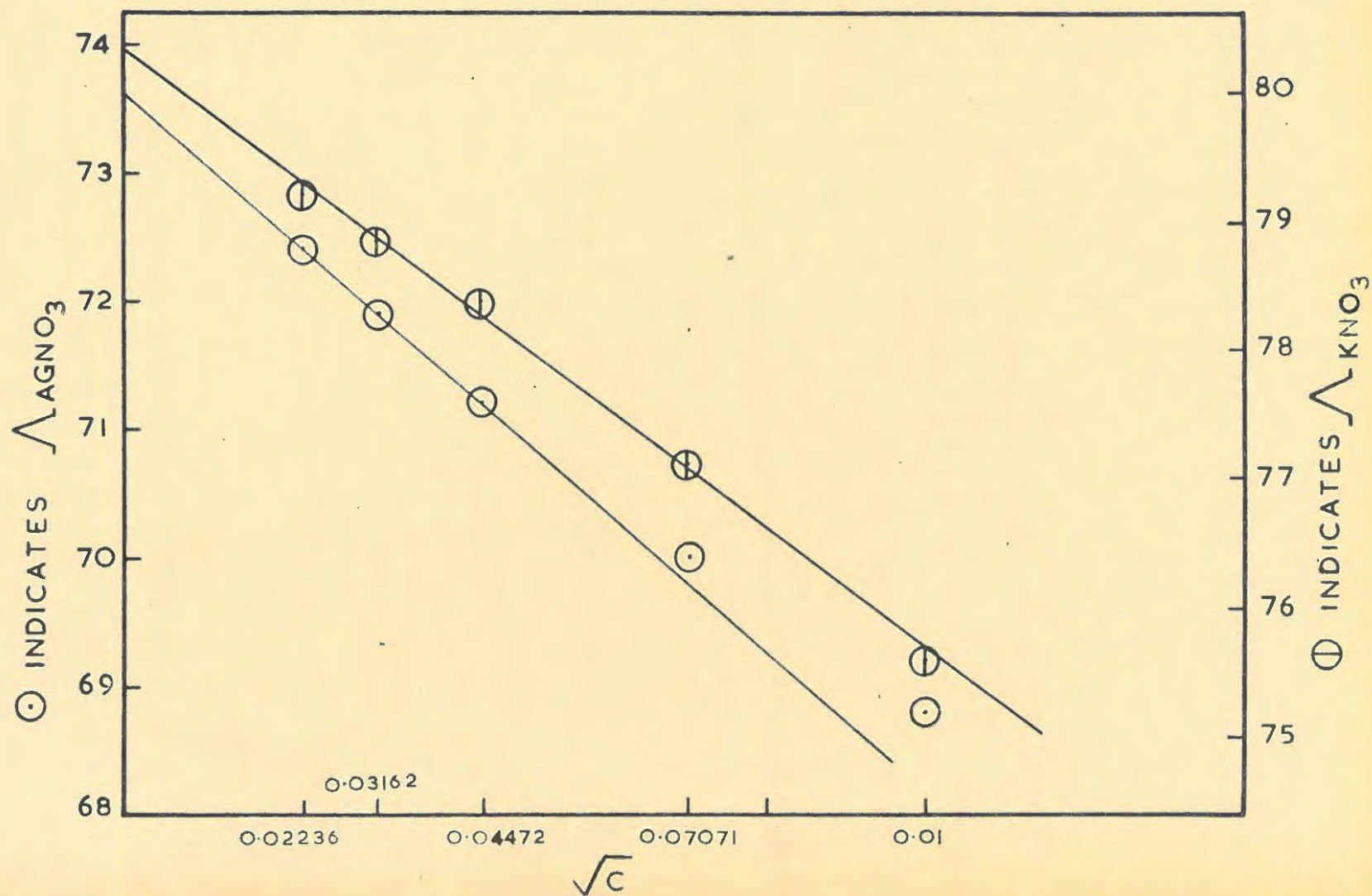


FIG. 14. EVALUATION OF Λ_0 FOR AgNO_3 AND KNO_3 AT 18°C BY EXTRAPOLATION TO ZERO CONCENTRATION.

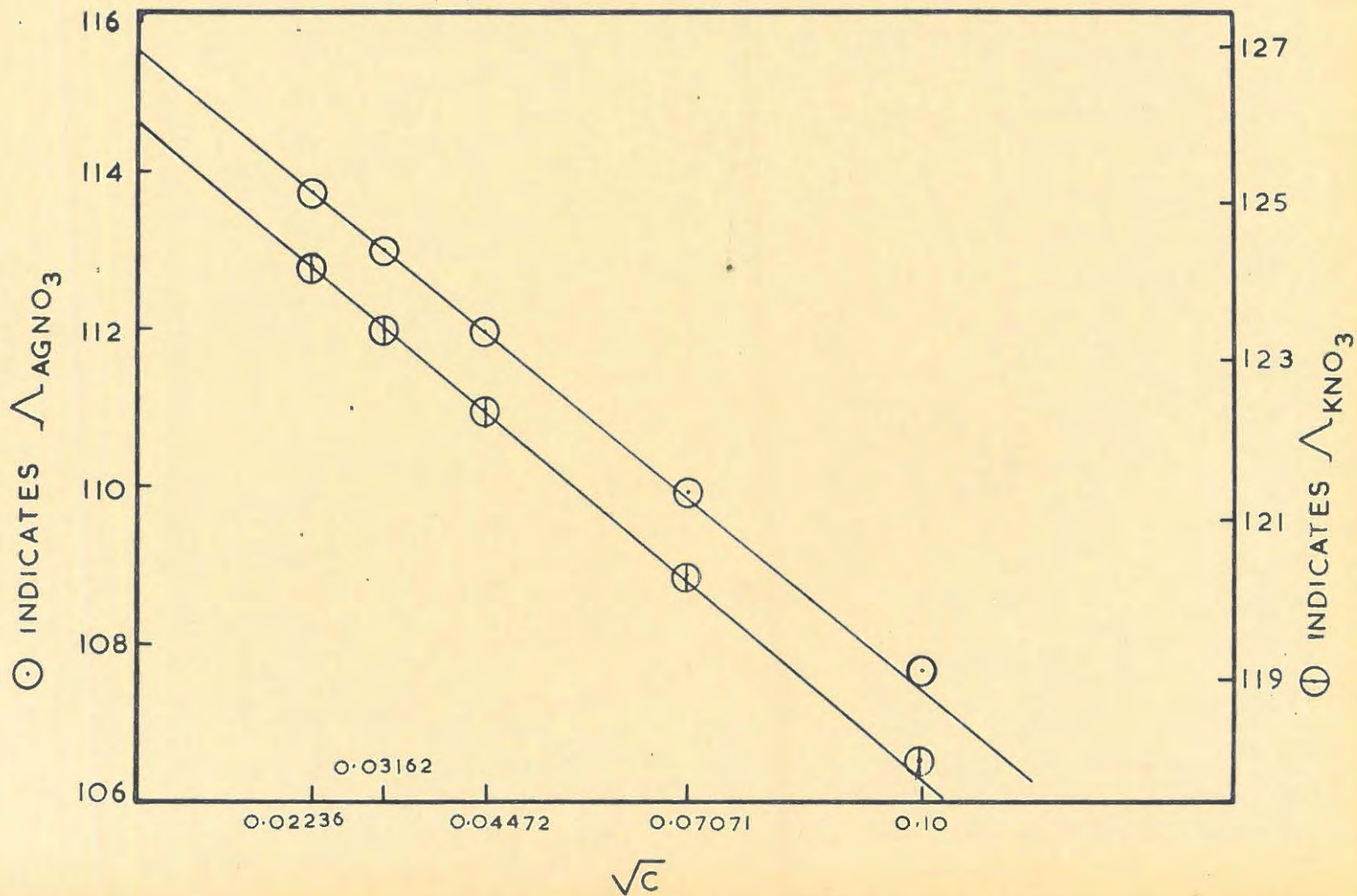


FIG. 16. EVALUATION OF Λ_0 FOR AgNO_3 AND KNO_3 AT 50°C BY EXTRAPOLATION TO ZERO CONCENTRATION.

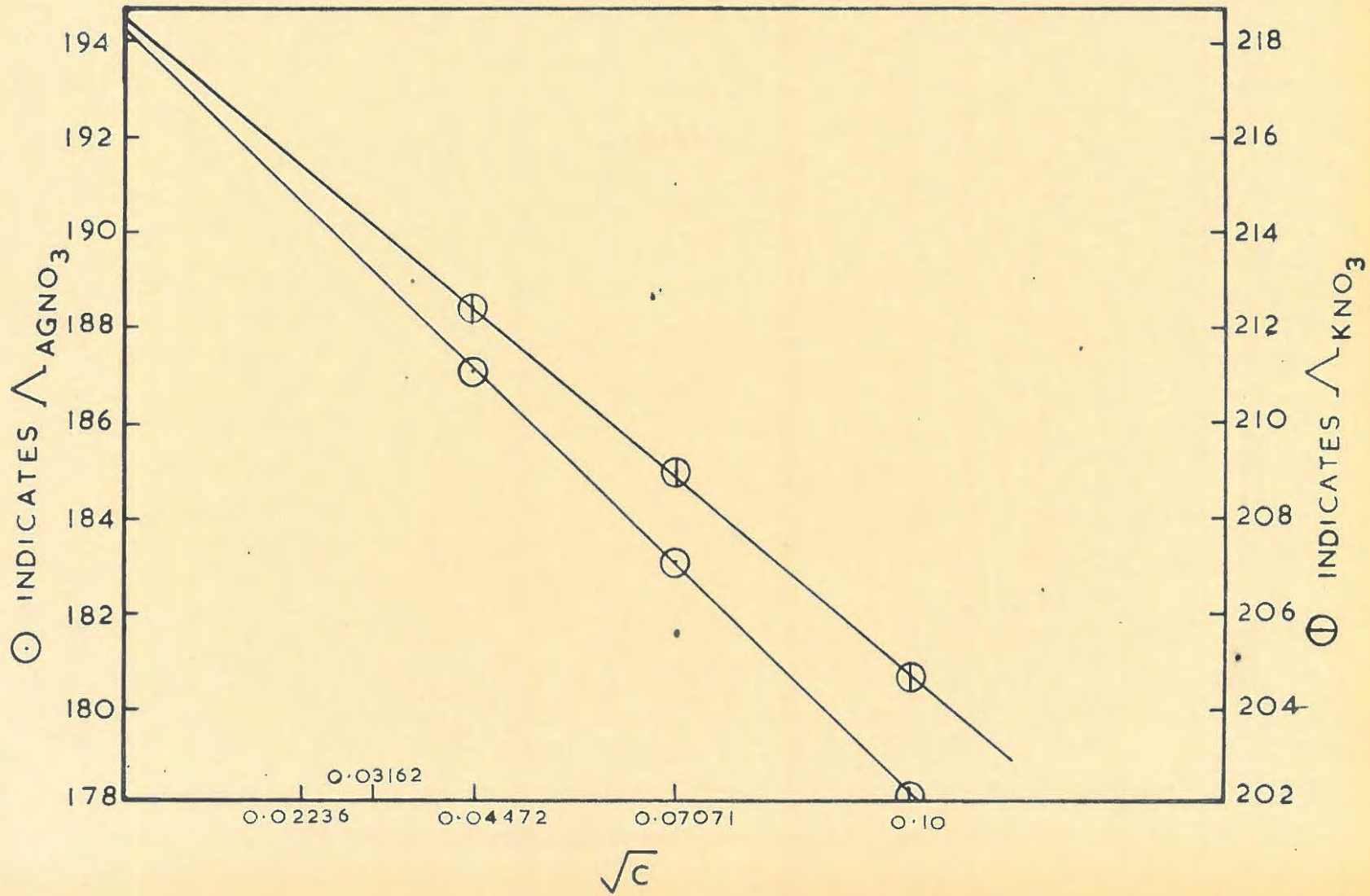
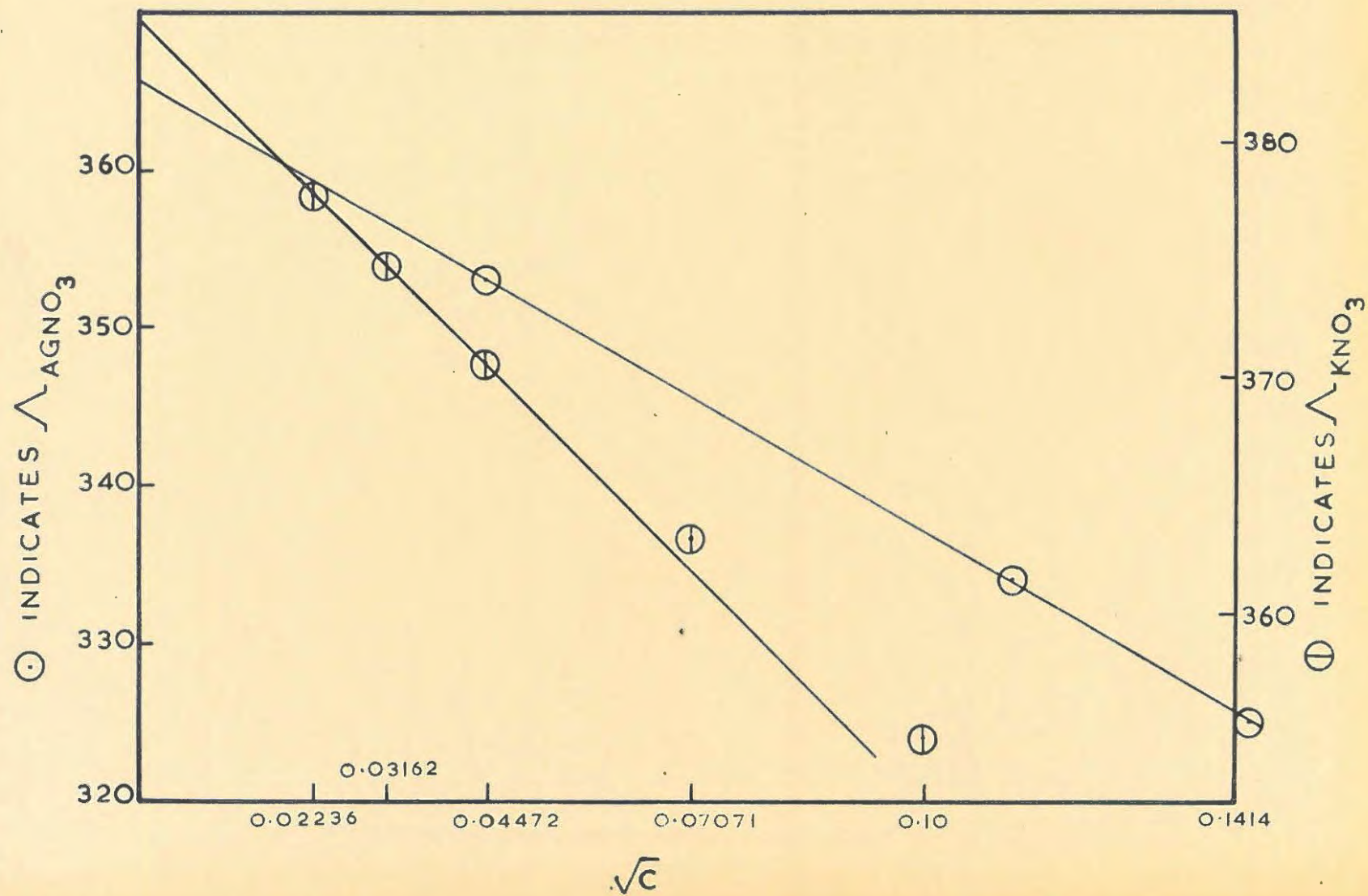


FIG. 17. EVALUATION OF Λ_0 FOR AgNO_3 AND KNO_3 AT 100°C BY EXTRAPOLATION TO ZERO CONCENTRATION.



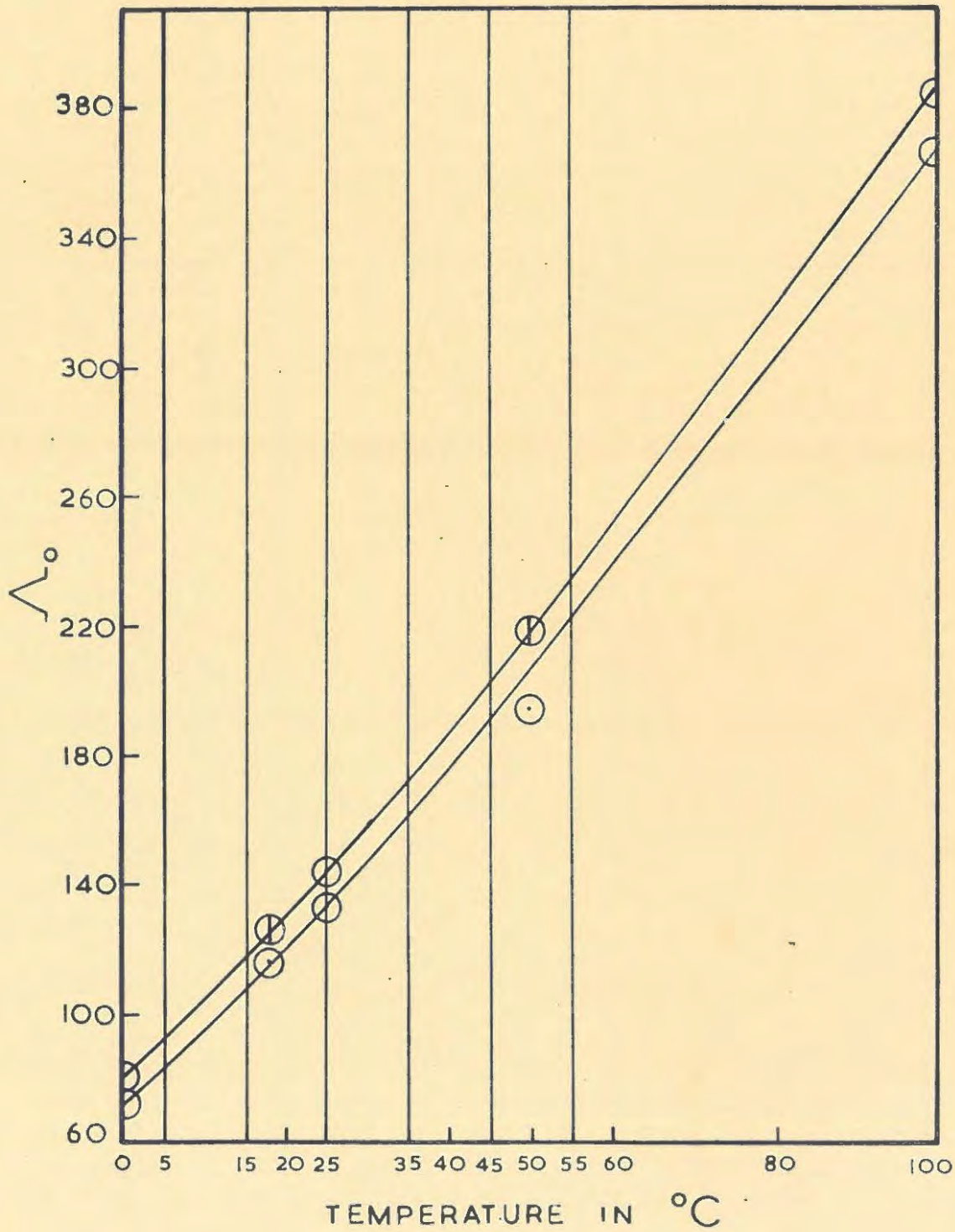
equivalent conductances Λ° of these electrolytes were determined by graphical extrapolation to zero concentration of the plot of Λ against $c^{1/2}$. The data from the Int. Crit. Tables are recorded in table 18, and the graphical extrapolations at the various temperatures are shown in fig. 13, 14, 15, 16 and 17.

TABLE 18. - VARIATION OF EQUIVALENT CONDUCTANCE OF
POTASSIUM NITRATE AND SILVER NITRATE
WITH CONCENTRATION FROM 0 TO 100°C.

| Salt | temp. (°C) | concentration c in milliformula weights/litre solution | | | | | | | |
|-------------------|---------------|--|--------|--------|--------|--------|--------|--------|--------|
| | | 0.1 | 0.2 | 0.5 | 1.0 | 2.0 | 5.0 | 10.0 | 20.0 |
| KNO ₃ | 0.0 | | | 79.29 | 78.89 | 78.25 | 77.09 | 75.60 | 73.70 |
| | 18.0 | 125.2 | 124.9 | 124.6 | 123.37 | 122.32 | 120.21 | 117.93 | 114.96 |
| | 25.0 | | | | | 140.5 | 138.3 | 135.7 | 132.31 |
| | 50.0 | | | | | 212.4 | 208.9 | 204.6 | 199.0 |
| | 100.0 | | 380.2 | 377.7 | 374.7 | 370.6 | 363.3 | 354.8 | 344.1 |
| AgNO ₃ | 0.0 | | | 72.4 | 71.9 | 71.2 | 70.0 | 68.8 | 66.9 |
| | 18.0 | 114.85 | 114.40 | 113.72 | 113.0 | 111.92 | 109.88 | 107.62 | 104.9 |
| | 25.0 | | | | 130.1 | 128.7 | 126.6 | 124.1 | 120.9 |
| | 50.0 | | | | | 187 | 183 | 178 | 173 |
| | 100.0 | | | | | 353 | | 334 | 325 |

The equivalent conductances in table 18 are only given at 0, 18, 25, 50 and 100°C, but the values of Λ° at 5, 15, 35, 45 and 55°C were interpolated from

FIG. 18. GRAPH OF Λ_0 VALUES FOR AgNO_3 AND KNO_3 AGAINST TEMPERATURE.



the plot of Λ° against temperature in fig. 18. The limiting equivalent conductances obtained in this way by extrapolation and interpolation are given in table 19.

TABLE 19. - VARIATION WITH TEMPERATURE OF THE LIMITING EQUIVALENT CONDUCTANCE OF POTASSIUM NITRATE AND SILVER NITRATE.

| Temperature ($^{\circ}\text{C}$) | $\Lambda^\circ_{\text{AgNO}_3}$ | $\Lambda^\circ_{\text{KNO}_3}$ |
|------------------------------------|---------------------------------|--------------------------------|
| 0.0 | 73.7 | 80.3 |
| 5.0 | 85.5 | 93.5 |
| 15.0 | 108.5 | 118.5 |
| 18.0 | 115.5 | 126.0 |
| 25.0 | 133.4 | 144.9 |
| 35.0 | 159.5 | 174.5 |
| 45.0 | 186.5 | 204.0 |
| 50.0 | 194.4 | 218.6 |
| 55.0 | 215.0 | 234.5 |
| 100.0 | 366.0 | 384.5 |

Because of the limitations imposed by the graphical extrapolations, and particularly the interpolations in fig. 18, it is unlikely that an accuracy of greater than $\pm 1\%$ can be claimed for the above values.

From the data thus assembled it is now possible to calculate the limiting equivalent conductances of

silver chloride and silver bromide, as well as the limiting ionic mobilities of the silver ion, from 5 to 55°C. They are recorded in table 20.

TABLE 20. - LIMITING EQUIVALENT CONDUCTANCES AND IONIC MOBILITIES OF SILVER CHLORIDE AND SILVER BROMIDE FROM 5 TO 55°C.

| Temp. (°C) | $\Lambda_{\text{AgNO}_3}^\circ$ | + | $\Lambda_{\text{KCl}}^\circ$ | - | $\Lambda_{\text{KNO}_3}^\circ$ | = | $\Lambda_{\text{AgCl}}^\circ$ | $\lambda_{\text{Cl}^-}^\circ$ | $\lambda_{\text{Ag}^+}^\circ$ |
|---------------|---------------------------------|---|------------------------------|---|--------------------------------|---|-------------------------------|-------------------------------|-------------------------------|
| 5.0 | 85.5 | + | 94.3 | - | 93.5 | = | 86.3 | 47.0 | 39.3 |
| 15.0 | 108.5 | + | 121.1 | - | 118.5 | = | 111.1 | 61.2 | 49.9 |
| 25.0 | 133.4 | + | 149.9 | - | 144.9 | = | 138.4 | 76.3 | 62.1 |
| 35.0 | 159.5 | + | 180.4 | - | 174.5 | = | 165.4 | 92.5 | 72.9 |
| 45.0 | 186.5 | + | 212.4 | - | 204.0 | = | 194.9 | 109.5 | 85.4 |
| 55.0 | 215.0 | + | 245.7 | - | 234.5 | = | 226.2 | 127.4 | 98.8 |
| | $\Lambda_{\text{AgNO}_3}^\circ$ | + | $\Lambda_{\text{KBr}}^\circ$ | - | $\Lambda_{\text{KNO}_3}^\circ$ | = | $\Lambda_{\text{AgBr}}^\circ$ | $\lambda_{\text{Br}^-}^\circ$ | $\lambda_{\text{Ag}^+}^\circ$ |
| 5.0 | 85.5 | + | 96.0 | - | 93.5 | = | 88.0 | 48.8 | 39.3 |
| 15.0 | 108.5 | + | 122.8 | - | 118.5 | = | 112.8 | 63.2 | 49.6 |
| 25.0 | 133.4 | + | 151.6 | - | 144.9 | = | 140.1 | 78.3 | 61.8 |
| 35.0 | 159.5 | + | 182.2 | - | 174.5 | = | 167.2 | 94.0 | 73.2 |
| 45.0 | 186.5 | + | 214.2 | - | 204.0 | = | 196.7 | 110.7 | 86.0 |
| 55.0 | 215.0 | + | 247.2 | - | 234.5 | = | 227.7 | 128.9 | 98.8 |

In the last column $\lambda_{\text{Ag}^+}^\circ$ values have been obtained from two different sets of data, and are indicative

of the uncertainty of these values when obtained by indirect methods. The ones eventually used were the arithmetic means (to the first decimal place) of the two sets of data given above. To ensure self-consistent values as much as possible, Owen and Sweetons' data (81) for $\lambda_{\text{Cl}^-}^{\circ}$, and Benson and Gordons' (86) and Gunning and Gordons' data (87) for $\lambda_{\text{Br}^-}^{\circ}$ throughout the whole temperature range were preferred. These limiting ionic mobilities, together with the limiting equivalent conductances of the silver halides finally used, are given in table 21.

TABLE 21. - FINALLY ACCEPTED VALUES OF THE LIMITING EQUIVALENT CONDUCTANCES AND IONIC MOBILITIES OF THE SILVER HALIDES.

| Temp. (°C) | $\lambda_{\text{Ag}^+}^{\circ}$ | $\lambda_{\text{Cl}^-}^{\circ}$ | $\lambda_{\text{Br}^-}^{\circ}$ | $\Lambda_{\text{AgCl}}^{\circ}$ | $\Lambda_{\text{AgBr}}^{\circ}$ |
|---------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 5.0 | 59.3 | 47.0 | 48.7* | 86.3 | 88.0 |
| 15.0 | 49.8 | 61.2 | 63.2 | 111.0 | 113.0 |
| 35.0 | 73.0 | 92.5 | 94.0 | 165.5 | 167.0 |
| 45.0 | 85.7 | 109.5 | 110.7 | 195.2 | 196.4 |
| 55.0 | 96.8 | 127.4 | 128.9* | 226.2 | 227.7 |

4. . DESCRIPTION, CALIBRATION AND STANDARDISATION OF APPARATUS.

4.1 Thermostats.

The thermostat was completely redesigned to enable it to operate at any temperature from 5 to 55°C. A circular copper outer vessel, of similar dimensions to the one previously used, was built. It was fitted with a 5-turn helical copper cooling coil connected to a Frigidaire compressor unit driven by a $\frac{1}{3}$ horsepower motor. The unit operates on the pressure cut-out system. An adjustable stopcock in the liquid line regulates the "on-off period" so that the thermostat is kept approximately 0.3° below the required temperature. With the additional aid of the ordinary temperature control heater the thermostat can be run at required temperatures below 24°C (room temperature).

An auxiliary 250 watt knife heater was installed to run the thermostat above 25°C. This heater operated continuously, and its wattage was cut down by a Variac until it kept the temperature approximately 0.3° below the required value. The thermostat was brought up to the working temperature and kept there by the ordinary temperature control heater.

Because of the large differences in temperature

between the room air and the thermostat, the latter was lagged with a thick layer of granulated cork. The wooden lid previously used became saturated with condensed water when working above 30°C. It was replaced by a Perspex lid which is water-repellent and has the additional advantage of being transparent.

The temperature of the outer bath of the thermostat was measured by immersing in it two standard thermometers No. 244 and 245 (described in part I, section 3.212). They were calibrated at 10° intervals from 5 to 95°C to an accuracy of $\pm 0.02^\circ$ by the National Physical Laboratory, Pretoria. The fluctuations in temperature were measured on six 5° Beckmann thermometers graduated to 0.01° (one was set for each temperature).

When the thermostat is operating at 25°C the difference in temperature between the outer water bath, the inner paraffin bath and the cell contents is negligible. This is so because the gas used for stirring the paraffin and the cell contents is at 24°C before entering the thermostat. It then passes through copper coils in the outer bath, and because of the small temperature difference equilibrates readily to 25°C before entering the paraffin bath or the cell contents. However, when operating the thermostat at the other temperatures the stirring gas enters the thermostat

at 24°C, but has to equilibrate to temperatures considerably removed from 24°C in the thermostat. At the stirring rates employed in this work the gas does not quite attain temperature equilibrium. Consequently the outer water bath (mechanically stirred), the inner paraffin bath and the cell contents show slight differences in temperature at any one setting of the thermostat. These differences become more pronounced as the difference between the working temperature of the thermostat and the room temperature is increased. They remained quite constant, however, at any one setting of the thermostat provided the stirring rate was kept constant. Table 22 shows these differences in temperature at each setting of the thermostat, and also indicates the temperature fluctuations as recorded on the six Beckmann thermometers.

TABLE 22. - THERMOSTAT TEMPERATURES.

| Temp. (°C) nominal | corresponding reading Beckmann | observed Beckmann thermometer reading | | |
|-----------------------|--------------------------------------|---------------------------------------|------------------------|---------------|
| | | outer water bath | inner paraffin bath | cell contents |
| 5.0 | A ₁ 5.300 | 5.130 ± 0.005 | 5.220 ± 0.005 | 5.500 ± 0.007 |
| 15.0 | A ₂ 2.990 | 2.920 ± 0.005 | 2.970 ± 0.005 | 2.990 ± 0.005 |
| 25.0 | A ₃ 4.115 | 4.115 ± 0.002 | 4.115 ± 0.002 | 4.115 ± 0.002 |
| 35.0 | A ₄ 3.930 | 4.020 ± 0.005 | 3.930 ± 0.005 | 3.780 ± 0.005 |
| 45.0 | A ₅ 5.630 | 5.765 ± 0.005 | 5.630 ± 0.005 | 5.400 ± 0.007 |
| 55.0 | A ₆ 2.420 | 2.750 ± 0.005 | 2.420 ± 0.005 | 2.120 ± 0.007 |

When the temperature differences between the outer water bath and the inner paraffin bath were first observed, it was confidently expected that the paraffin and the cell contents would have the same temperature at any one setting of the thermostat. This was found not to be the case. As can be seen from table 22 the inner paraffin bath was set to precisely 35, 45 and 55°C. In actual fact the cell contents were in each case at a slightly lower temperature. This discrepancy was discovered before the runs at 5 and 15°C were done, and in these cases the thermostat was set so that the cell contents were at the required temperature.

The failure to obtain reproducible results from the high temperature side (see part I) was due to the fact that the suspensions were preheated at 90°C. At this temperature the solvent correction became quite irreproducible due to the greatly increased rate of solution of glass. It was hoped to eliminate this danger in the present work by preheating the salt suspensions at only 5° from the working temperature. Similarly approaches from the low temperature side would be made by precooling the salt suspensions at 5° from the working temperature.

For this purpose a second thermostat was constructed. It was designed to run at 30, 40, 50 and 60°C, and was

heated by a 250 volt - 250 watt knife heater controlled to $\pm 0.1^\circ$ by a Sunvic bi-metallic spiral thermoregulator. The water was mechanically stirred by a paddle stirrer, and the walls were lagged with a thick layer of granulated cork.

For the runs at 5 and 15°C the salt suspensions were pretreated in cold water baths kept at 0, 10 and 20°C . The temperature was regulated by manual addition of ice cubes and thorough stirring. In this way temperature control to $\pm 0.2^\circ$ could be obtained, quite sufficient for the purpose.

4.2 Variation with temperature of the cell constants.

The cell constants of conductance cells I and II at 25°C have previously been determined (see part I, section 3.43). The values at the other temperatures are calculated from the geometry of the cells and the coefficients of expansion of platinum (79) and of Pyrex glass (90). At no time was the change in the cell constants found to be greater than 0.04%, well within the limit of accuracy of the present work. The values of the cell constants determined at 25°C were therefore used unchanged throughout the whole temperature range.

4.3 Variation with temperature of the 10,000
ohm shunt resistor.

The 10,000 ohm (nominal) shunt resistor was placed on the lid of the thermostat. Due to thermal conduction through the Perspex lid it experienced slight temperature variations at each new setting of the thermostat. Consequently its resistance changed slightly. The true value of the parallel resistor at each of the six thermostat settings are recorded in table 23. These values were checked frequently during a series of runs, and were found to be constant at any one setting of the thermostat.

TABLE 23. - OBSERVED RESISTANCE OF SHUNT RESISTOR.

| Thermostat setting (°C) | True shunt resistance (ohms) |
|----------------------------|---------------------------------|
| 5.0 | 9999.8 |
| 15.0 | 10,000.2 |
| 25.0 | 10,000.4 |
| 35.0 | 10,000.8 |
| 45.0 | 10,000.9 |
| 55.0 | 10,001.2 |

5. PREPARATION AND STANDARDISATION OF MATERIALS.

5.1 Nitrogen.

For reasons given part I, section 3.425, purified nitrogen was employed to remove the volatile impurities and stir the cell contents in all the conductance measurements in part II. It was purified as described in part I, section 4.32. After saturation with water vapour at room temperature (24°C) it was passed through a trap in the thermostat to collect any condensed water. This was essential when the thermostat was operating at temperatures below 24°C in order to avoid this water from being carried over into the conductance cell. Finally the nitrogen was saturated with water vapour in a potash bulb in the thermostat.

6. EXPERIMENTAL RESULTS AND DISCUSSION.

Note: The techniques and treatment described below are employed throughout the temperature range work, and are grouped here to avoid repetition.

6.1 Experimental technique.

(a) Treatment of salt suspensions.

In approaching saturation from the low temperature side the salt suspensions were precooled at 5° from the working temperature for exactly 30 minutes with

constant shaking. The suspensions were kept in the same conical Pyrex flasks in which they had been washed. After 30 minutes they were rapidly transferred to conductance cell II, and purified nitrogen was bubbled through the contents at 7 bubbles per sec. The resistance was measured at regular intervals until it was dropping at a steady rate.

In the approaches from the high temperature side the salt suspensions were preheated at 5° from the working temperature for 30 minutes, and then subsequently treated in the same way.

(b) Treatment of conductivity water.

Because of the very rapid increase in the rate of solution of glass with temperature, the conductivity water samples used in each run were treated in exactly the same way as the corresponding salt suspensions.

(c) Treatment of silver halide precipitates.

The silver halide precipitates were washed 50 - 60 times by decantation with conductivity water, and were aged for periods varying from 3 to 7 days.

6.11 Treatment of results.

The results were interpreted graphically. Once again it was found that the conductance of the saturated silver halide solutions increased at a greater rate

FIG. 19. GRAPH OF RESISTANCE AGAINST TIME
FOR CONDUCTANCE WATER AT 5°C.

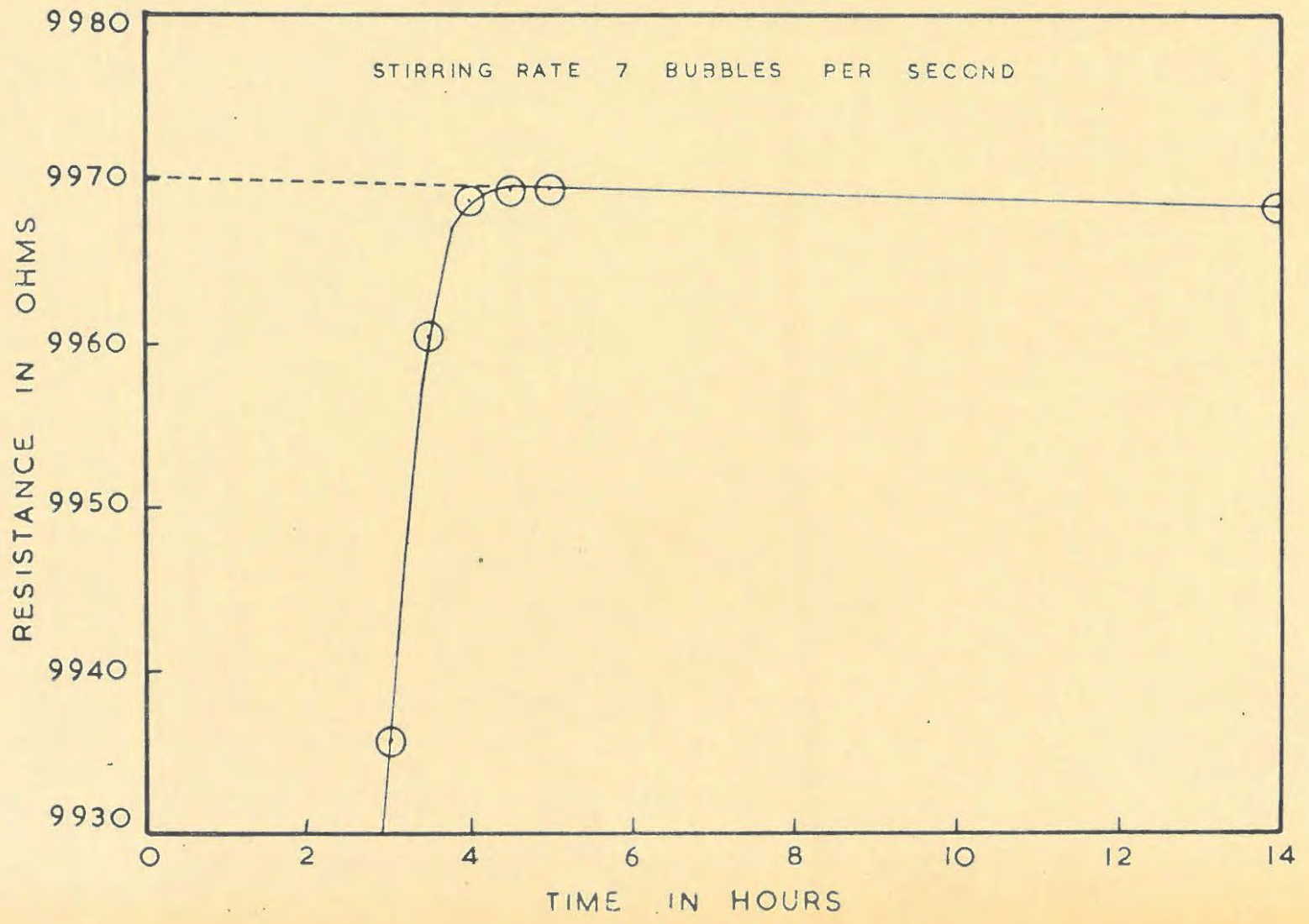
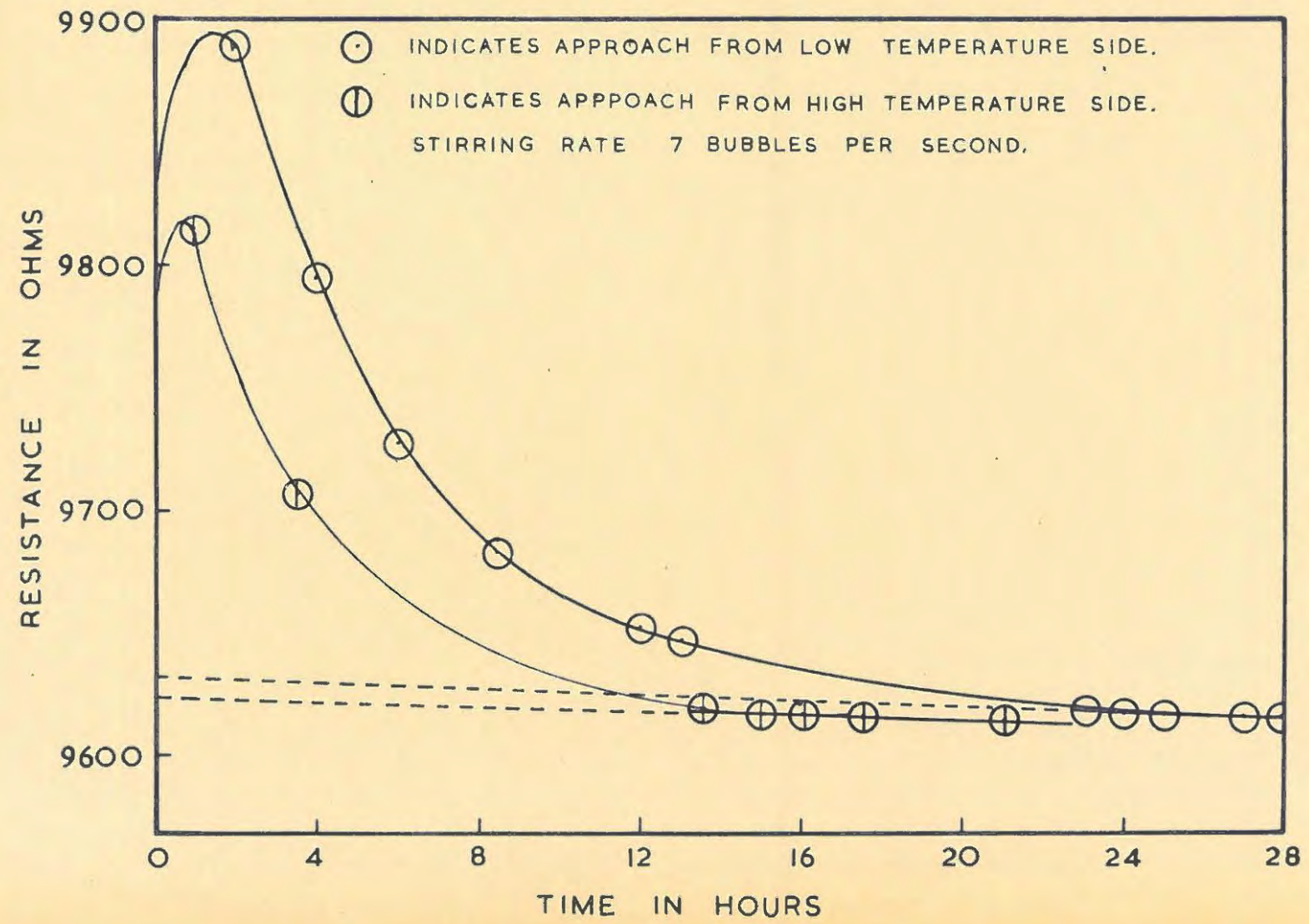


FIG. 20. GRAPH OF RESISTANCE AGAINST TIME
FOR SATURATED AGCL SOLUTION AT 5°C.



than that of water alone. Since the drop in resistance was linear with time, the observed resistances were extrapolated back to zero time both for the water and for the silver halide solutions.

6.2 Determinations at 5°C.

6.21 Silver chloride results.

For experimental data see appendix E.

Fig. 19 shows a typical graph of resistance against time for conductivity water. The resistance of the water rose rapidly to a maximum value after about 4.5 hours, and then dropped steadily at the rate of about 0.1 ohm/hr. corresponding to an increase in the conductance of about 0.1 nm./cm.hr. There was no noticeable difference in the conductance of samples of water from the same batch which had been precooled on the one hand, and preheated on the other. The very slow rate of solution of glass at these low temperatures probably accounts for this.

Fig. 20 illustrates the typical variation of resistance with time for a saturated silver chloride solution. In approaches from the low temperature side the saturation point was reached after about 22 hours, whereas it took only about 14 hours to attain saturation from the high temperature side. After saturation was

complete the resistance fell steadily at about 0.35 ohm/hr., corresponding to an increase in the conductance of 0.45 nm./cm.hr.

The solubilities were calculated in the usual way using the Onsager equation

$$\Lambda_{\text{AgCl}} = 86.3 - 54.25 s^{\frac{1}{2}}$$

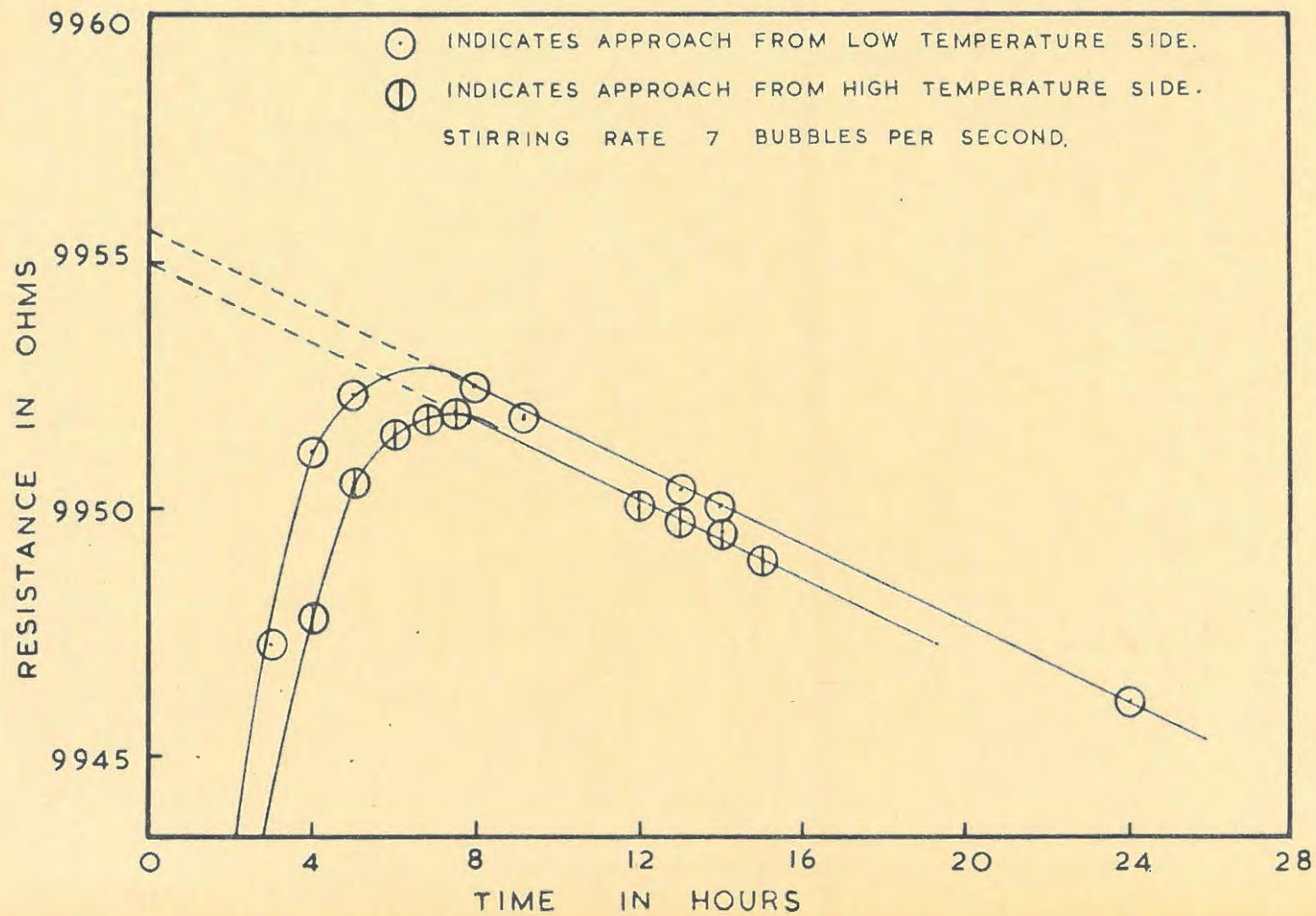
The results are recorded in table 24.

TABLE 24. - SOLUBILITY OF SILVER CHLORIDE AT 5°C.

| No. of expt. | extrapolated to zero time | | | mean solubility equiv./l. x 10 ⁻⁵ | mean solubility product K x 10 ⁻¹⁰ |
|--------------|--------------------------------------|---------------------------------------|--------------------------------|--|---|
| | κ_{AgCl} soln. nm./cm. | $\kappa_{\text{H}_2\text{O}}$ nm./cm. | κ_{AgCl} nm./cm. | | |
| 17 L | 465 | 31 | 434 | | |
| 17 H | 466 | 31 | 435 | | |
| 18 L | 469 | 31 | 438 | | |
| 18 H | 470 | 31 | 439 | ± 0.507 ± 0.01 | ± 0.256 ± 0.02 |
| 19 L | 471 | 32 | 439 | | |
| 19 H | 470 | 32 | 438 | | |
| 20 L | 465 | 29 | 436 | | |
| 20 H | 465 | 29 | 436 | | |

The limits of error have been estimated from the uncertainty in the extrapolations and the values of the limiting equivalent conductances and ionic mobilities. The solvent correction amounts to 6 - 7% of the total conductivity. It is significant that

FIG. 21. GRAPH OF RESISTANCE AGAINST TIME
FOR SATURATED AGR SOLUTION AT 5°C.



approaches of the saturation point from the high temperature side yielded solubility values which agreed with those obtained from the low temperature side to within the limit of experimental error.

6.22 Silver bromide results.

For experimental data see appendix F.

Fig. 21 refers to the experimental results for a saturated silver bromide solution in a typical case.

TABLE 25. - SOLUBILITY OF SILVER BROMIDE AT 5°C.

| No. of expt. | extrapolated to zero time | | | mean solubility equiv./l. $\times 10^{-7}$ | mean solubility product $K \times 10^{13}$ |
|--------------|------------------------------------|-------------------------------------|------------------------------|--|--|
| | χ_{AgBr} soln. nm./cm. | $\chi_{\text{H}_2\text{O}}$ nm./cm. | χ_{AgBr} nm./cm. | | |
| 21 L | 50.8 | 32.6 | 18.2 | | |
| 21 H | 51.2 | 32.6 | 18.6 | | |
| 22 L | 49.0 | 30.2 | 18.8 | | |
| 22 H | 49.5 | 30.2 | 19.2 | ± 2.17 ± 0.10 | 0.470 ± 0.02 |
| 23 L | 50.6 | 31.5 | 19.1 | | |
| 23 H | 50.8 | 31.5 | 19.3 | | |
| 24 L | 51.9 | 32.4 | 19.5 | | |
| 24 H | 52.5 | 32.4 | 20.1 | | |

The resistance rose rapidly to a maximum value after about 7 - 8 hours both for approaches from the high and the low temperature sides. It then dropped regularly

at the rate of about 0.4 ohm/hr. This is equivalent to an increase in the conductance of 0.4 nm./cm.hr. The solubilities were calculated using the Onsager equation

$$\Lambda_{\text{AgBr}} = 88.0 - 54.62 s^{\frac{1}{2}}$$

The results are recorded on the previous page in table 25. Although the conductivity water had a specific conductance of only about 30 nm./cm., the solvent correction still amounted to about 60% of the total conductivity. The solubility was not affected by the method of approaching the saturation point.

6.3 Determinations at 15°C.

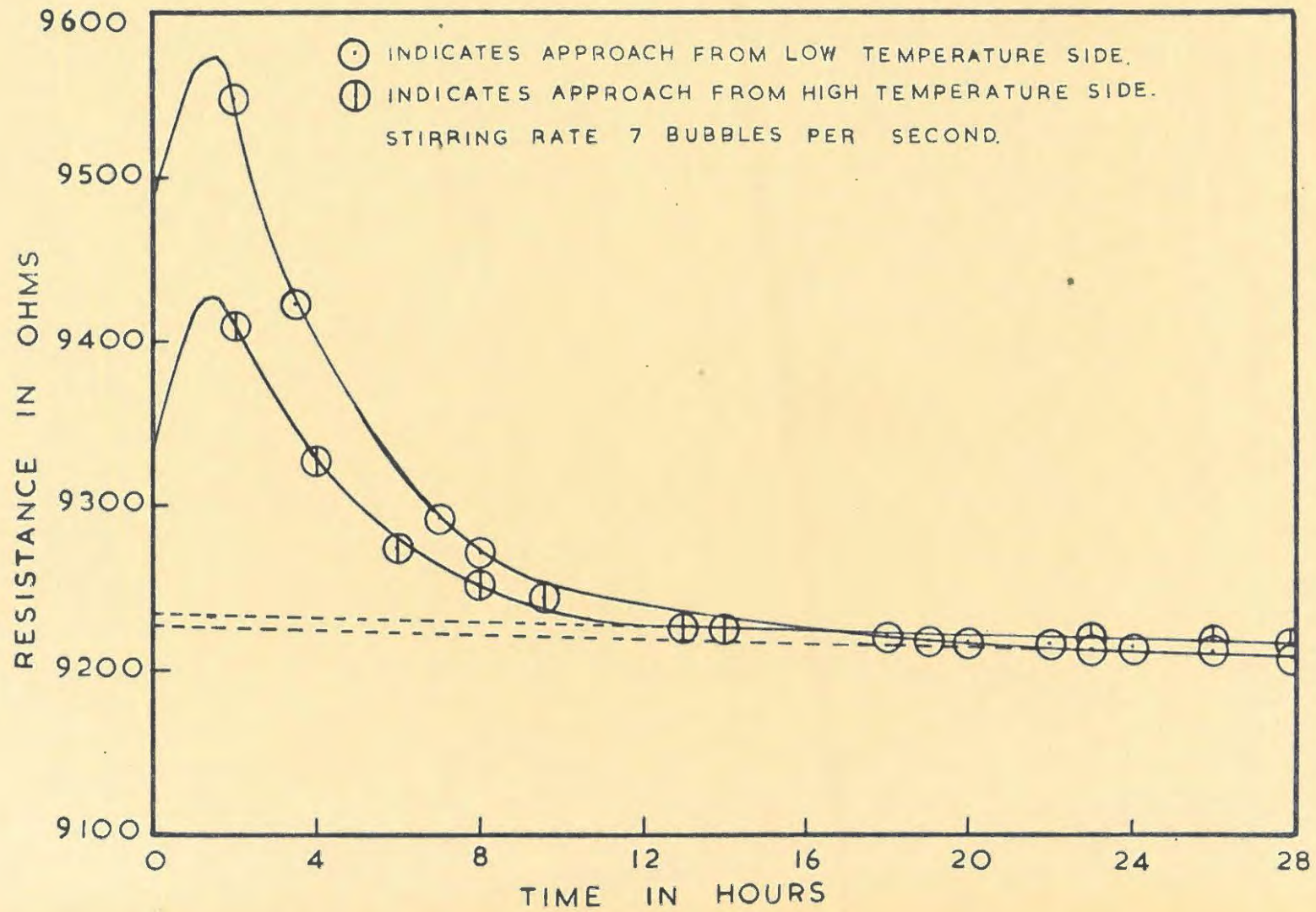
6.31 Silver chloride results.

For experimental data see appendix G.

The variation of resistance with time for conductivity water is shown in fig. 22. After reaching a maximum value the resistance fell at a steady rate of 0.2 - 0.3 ohm/hr., corresponding to an increase in the conductance of 0.3 nm./cm.hr. Samples of water from the same batch showed no difference in conductance whether preheated or precooled.

Fig. 23 shows a typical graph for a saturated silver chloride solution. Preheated samples reached saturation point after about 11 hours, whereas precooled samples took about 20 hours. After saturation the resistance

FIG. 23. GRAPH OF RESISTANCE AGAINST TIME
FOR SATURATED AGCL SOLUTION AT 15°C.



of the solutions fell steadily at about 0.9 - 1.0 ohm/hr. This represents a steady increase in the conductance of about 1.2 nm./cm.hr.

The solubilities were calculated using the Onsager equation $\Lambda_{\text{AgCl}} = 111.0 - 71.81 s^{1/2}$

The results are given in table 26.

TABLE 26. - SOLUBILITY OF SILVER CHLORIDE AT 15°C.

| No. of expt. | extrapolated to zero | | | mean solubility equiv./l. $\times 10^{-5}$ | mean solubility product $K \times 10^{-10}$ |
|--------------|--------------------------------------|---------------------------------------|--------------------------------|--|---|
| | κ_{AgCl} soln. nm./cm. | $\kappa_{\text{H}_2\text{O}}$ nm./cm. | κ_{AgCl} nm./cm. | | |
| 25 L | 975 | 40 | 935 | | |
| 25 H | 970 | 40 | 930 | | |
| 26 L | 983 | 44 | 939 | | |
| 26 H | 980 | 44 | 936 | ± 0.859 ± 0.017 | 0.700 ± 0.035 |
| 27 L | 968 | 50 | 918 | | |
| 27 H | 975 | 50 | 925 | | |
| 28 L | 970 | 45 | 925 | | |
| 28 H | 973 | 45 | 928 | | |

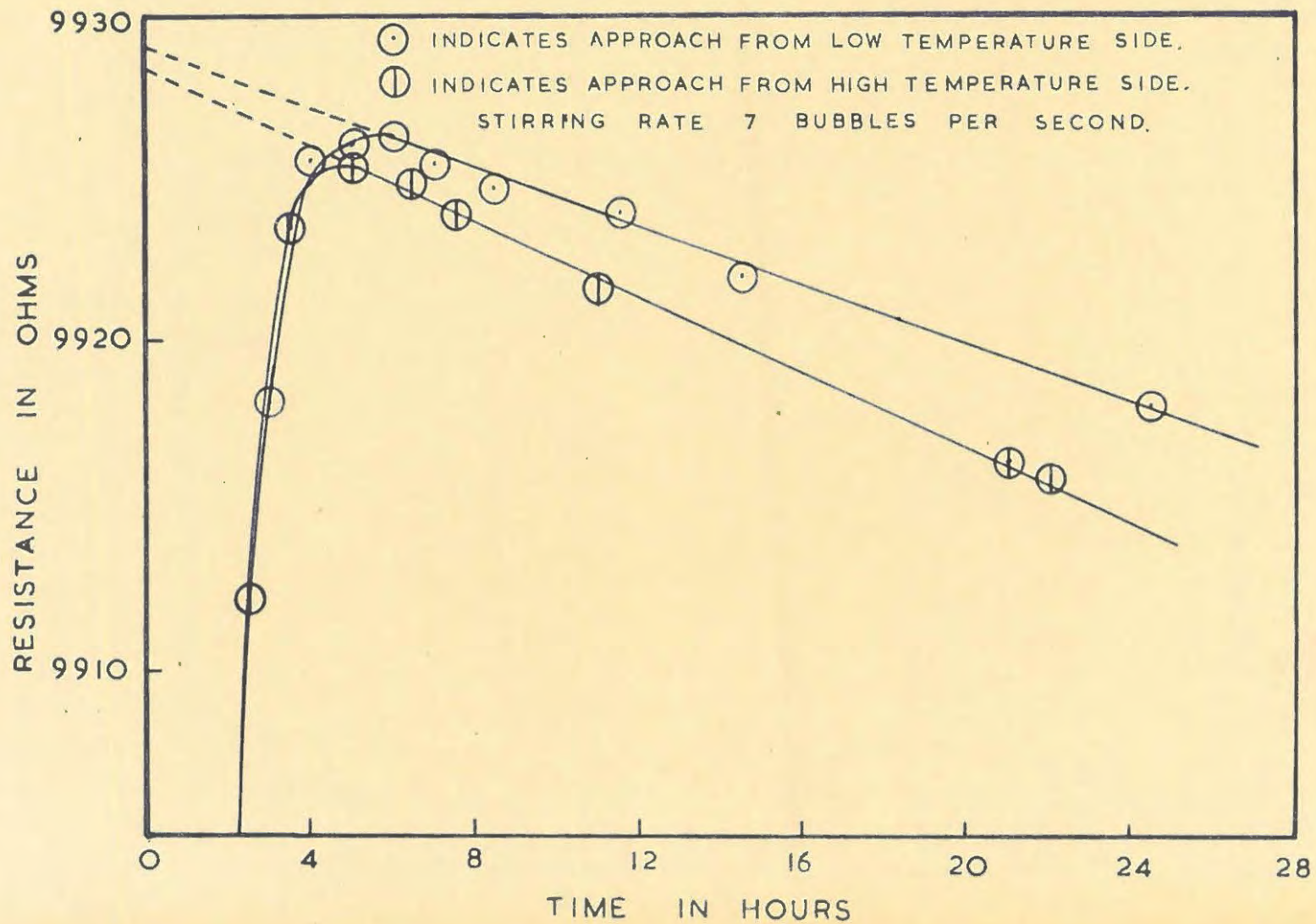
The solvent correction amounted to about 5 - 6% of the total conductivity.

6.32 Silver bromide results.

For experimental data see appendix H.

Fig. 24 refers to a typical set of experimental

FIG. 24. GRAPH OF RESISTANCE AGAINST TIME
FOR SATURATED AGR SOLUTION AT 15°C.



results. Saturation was attained after about 6 - 7 hours both for approaches from the high and the low temperature sides. The resistance then fell steadily at a rate of about 0.6 ohm/hr., although the rate of drop between individual runs varied slightly. This drop corresponds to an increase in the conductance of 0.7 nm./cm.hr. The Onsager equation

$$\Lambda_{\text{AgBr}} = 113.0 - 72.26 s^{\frac{1}{2}}$$

was used to calculate the results which are given in table 27.

TABLE 27. - SOLUBILITY OF SILVER BROMIDE AT 15°C.

| No. of expt. | extrapolated to zero | | | mean solubility equiv./l. $\times 10^{-7}$ | mean solubility product $K \times 10^{15}$ |
|--------------|--------------------------------------|---------------------------------------|--------------------------------|--|--|
| | κ_{AgBr} soln. nm./cm. | $\kappa_{\text{H}_2\text{O}}$ nm./cm. | κ_{AgBr} nm./cm. | | |
| 29 L | 96 | 54 | 42 | | |
| 29 H | 98 | 54 | 45 | | |
| 30 L | 90 | 45 | 45 | | |
| 30 H | 87 | 45 | 42 | 3.85 ± 0.14 | 1.48 ± 0.28 |
| 31 L | 83 | 39 | 44 | | |
| 31 H | 84 | 39 | 45 | | |
| 32 L | 87 | 45 | 44 | | |
| 32 H | 87 | 45 | 44 | | |

The solvent correction amounted to about 50% of the total conductivity.

FIG. 25. GRAPH OF RESISTANCE AGAINST TIME
FOR CONDUCTANCE WATER AT 35°C.

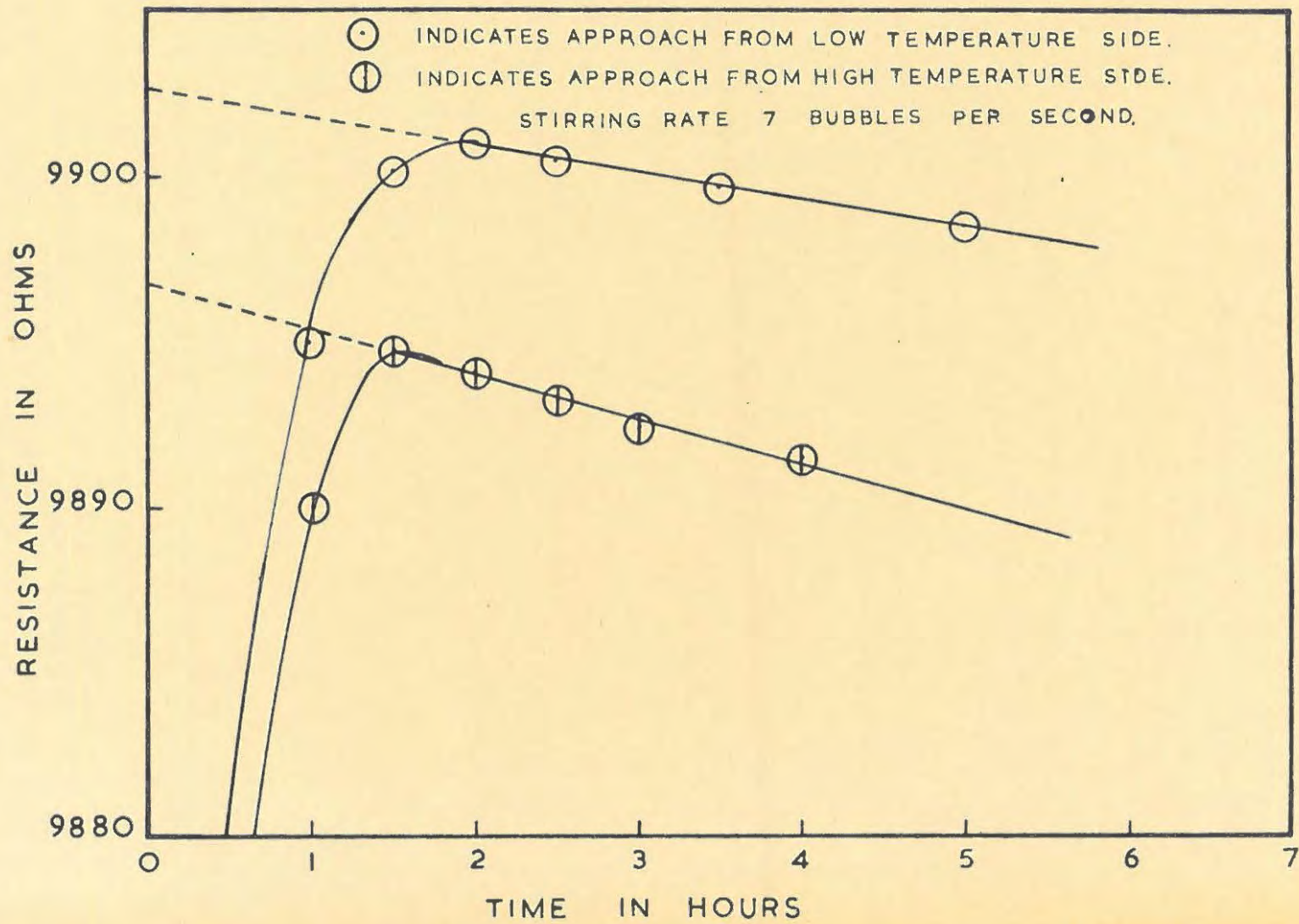
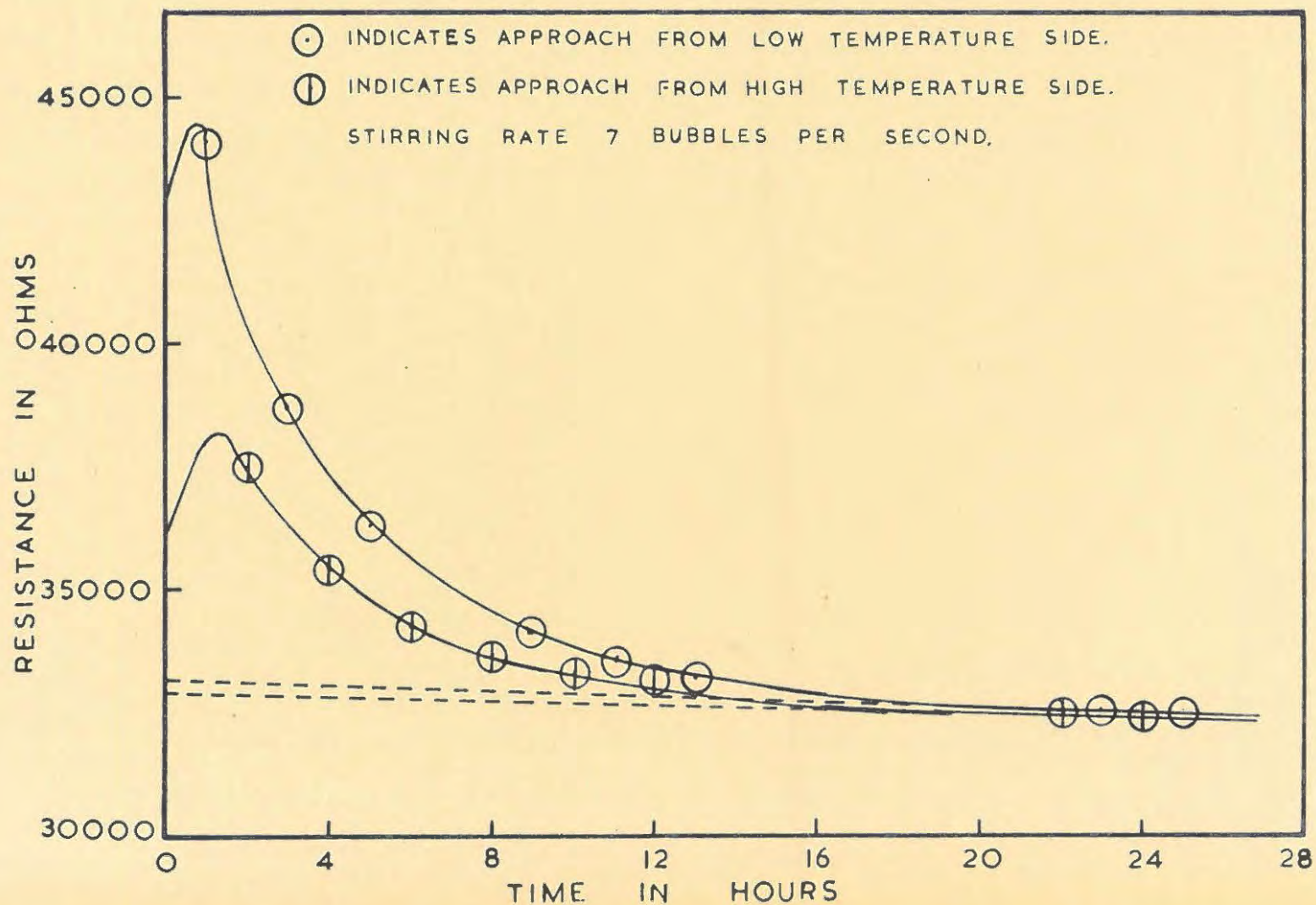


FIG. 26. GRAPH OF RESISTANCE AGAINST TIME
FOR SATURATED AGCL SOLUTION AT 35°C.



6.4 Determinations at 35°C.

6.41 Silver chloride results.

For experimental data see appendix I.

The variation of resistance with time for conductivity water follows a typical curve shown in fig. 25. At higher working temperatures the conductance of the water is no longer independent of the method of pretreatment. Samples from the same batch always have a higher specific conductance when preheated than when precooled. This is to be expected since the rate of solution of glass increases as the temperature is raised, and the effect becomes noticeable when working above room temperature. In both cases the resistance rose rapidly to a maximum value after about 1.5 - 2 hours, and then fell at a uniform rate of about 1 ohm/hr. This represents a steady increase in the conductance of 1 - 2 nm./cm.hr.

Fig. 26 refers to the experimental results for a saturated silver chloride solution. Precooled samples reached saturation point after about 18 hours, whereas preheated samples took only 12 - 13 hours. After saturation the resistance fell steadily at the rate of approximately 60 ohms/hr., corresponding to an increase in the conductance of about 6 nm./cm.hr.

It should be noted that for runs on silver chloride at 35, 45 and 55°C the resistance of the saturated solutions is sufficiently low to enable it to be measured directly without using the 10,000 ohm shunt resistor.

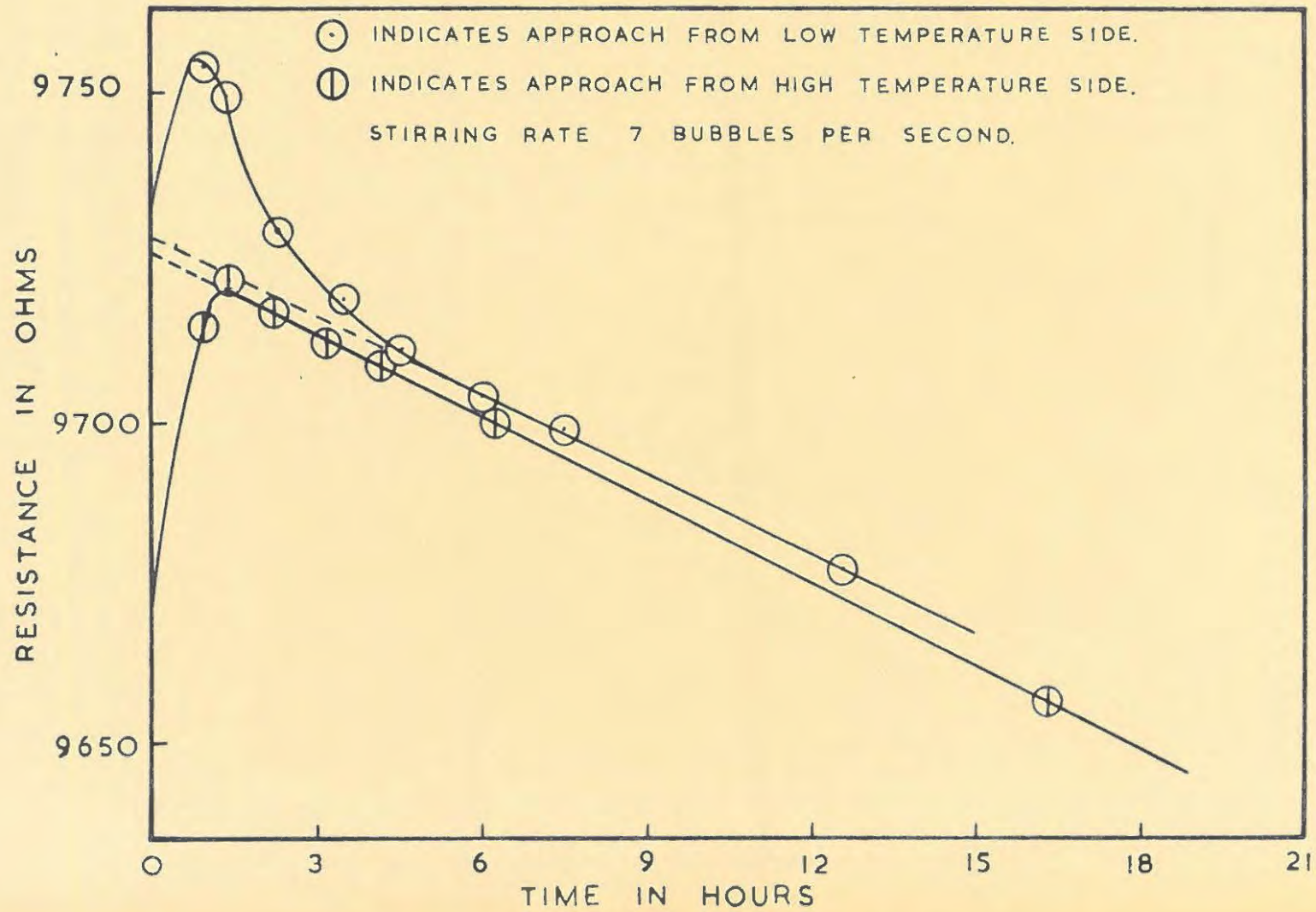
The results were calculated in the usual way using the Onsager equation $\Lambda_{\text{AgCl}} = 165.5 - 113.9 s^{1/2}$ and are given in table 28.

TABLE 28. - SOLUBILITY OF SILVER CHLORIDE AT 35°C.

| No. of expt. | extrapolated to zero time | | κ_{AgCl} nm./cm. | mean solubility equiv./l. $\times 10^{-5}$ | mean solubility product $K \times 10^{10}$ |
|--------------|--------------------------------------|---------------------------------------|--------------------------------|--|--|
| | κ_{AgCl} soln. nm./cm. | $\kappa_{\text{H}_2\text{O}}$ nm./cm. | | | |
| 33 L | 3471 | 122 | 3349 | | |
| 33 H | 3476 | 128 | 3348 | | |
| 34 L | 3479 | 128 | 3351 | | |
| 34 H | 3492 | 135 | 3357 | ± 2.032 ± 0.04 | ± 4.13 ± 0.08 |
| 35 L | 3478 | 119 | 3359 | | |
| 35 H | 3481 | 130 | 3351 | | |
| 36 L | 3481 | 124 | 3357 | | |
| 36 H | 3488 | 133 | 3355 | | |

The specific conductance of the silver halides increases much more rapidly than that of water alone as the working temperature is raised. Consequently the solvent correction decreases with rise in temperature, and is here only about 4% of the total conductivity.

FIG. 27. GRAPH OF RESISTANCE AGAINST TIME
FOR SATURATED AGR SOLUTION AT 35°C.



6.42 Silver bromide results.

For experimental data see appendix J.

The curves in fig. 27 show the typical variation of resistance with time for a saturated silver bromide solution. Preheated samples reached saturation after only 1.5 - 2 hours, but the precooled samples appeared to be unsaturated initially and the resistance reached a higher maximum. It then fell rapidly, as in the case of the silver chloride runs, until the saturation point was finally reached after 5 - 6 hours.

TABLE 29. - SOLUBILITY OF SILVER BROMIDE AT 35°C.

| No. of expt. | extrapolated to zero time | | | mean solubility equiv./l. x 10 ⁻⁷ | mean solubility product K x 10 ⁻¹³ |
|--------------|--------------------------------------|---------------------------------------|--------------------------------|--|---|
| | $\kappa_{\text{AgBr soln.}}$ nm./cm. | $\kappa_{\text{H}_2\text{O}}$ nm./cm. | κ_{AgBr} nm./cm. | | |
| 37 L | 526 | 116 | 210 | | |
| 37 H | 328 | 120 | 208 | | |
| 38 L | 315 | 106 | 209 | | |
| 38 H | 322 | 114 | 208 | ± 12.51 ± 0.25 | ± 15.8 ± 0.5 |
| 39 L | 330 | 122 | 208 | | |
| 39 H | 337 | 122 | 215 | | |
| 40 L | 315 | 107 | 208 | | |
| 40 H | 318 | 112 | 206 | | |

After saturation the resistance of both preheated and precooled samples fell steadily at about

FIG. 28. GRAPH OF RESISTANCE AGAINST TIME
FOR CONDUGTANCE WATER AT 45°C.

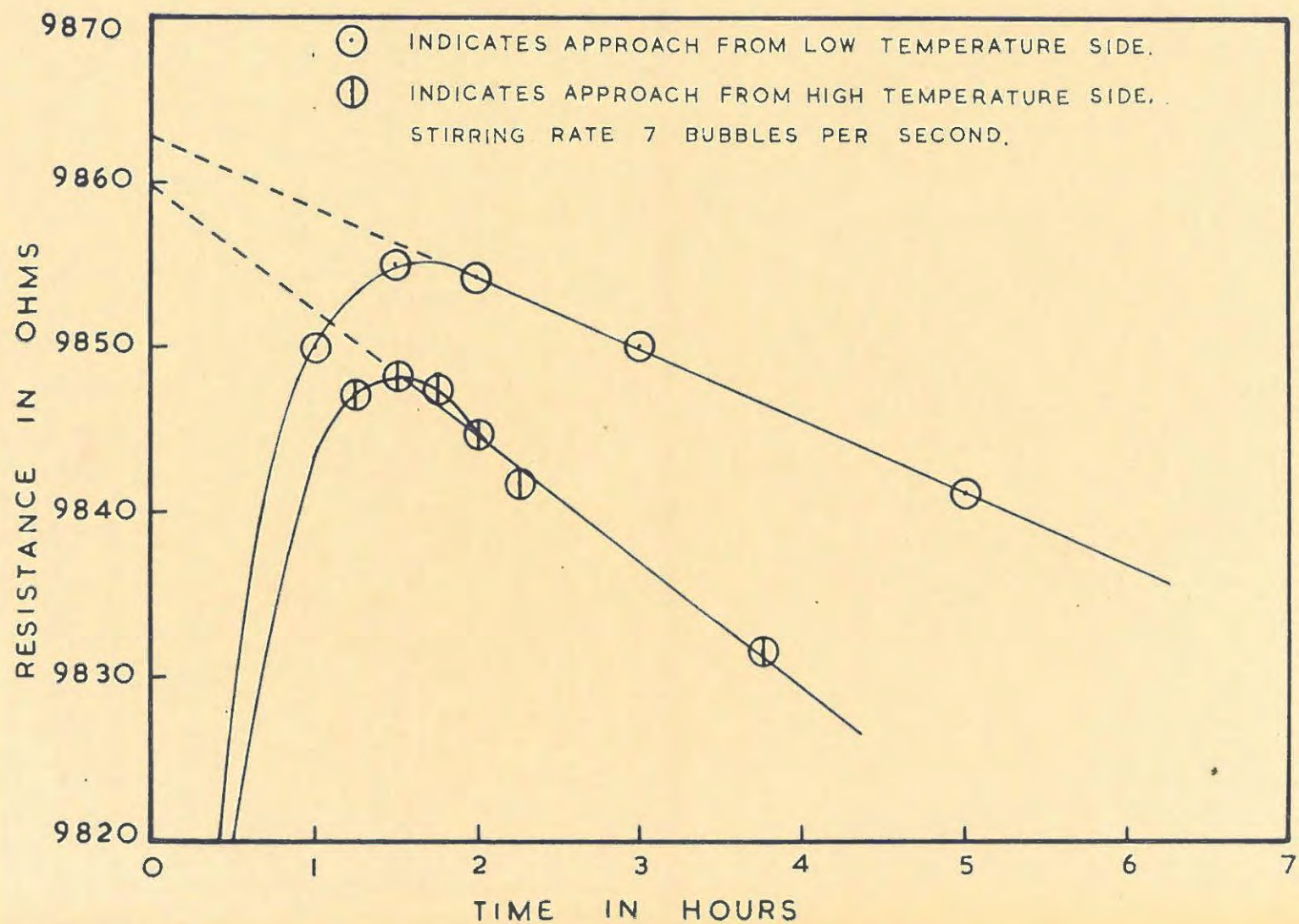
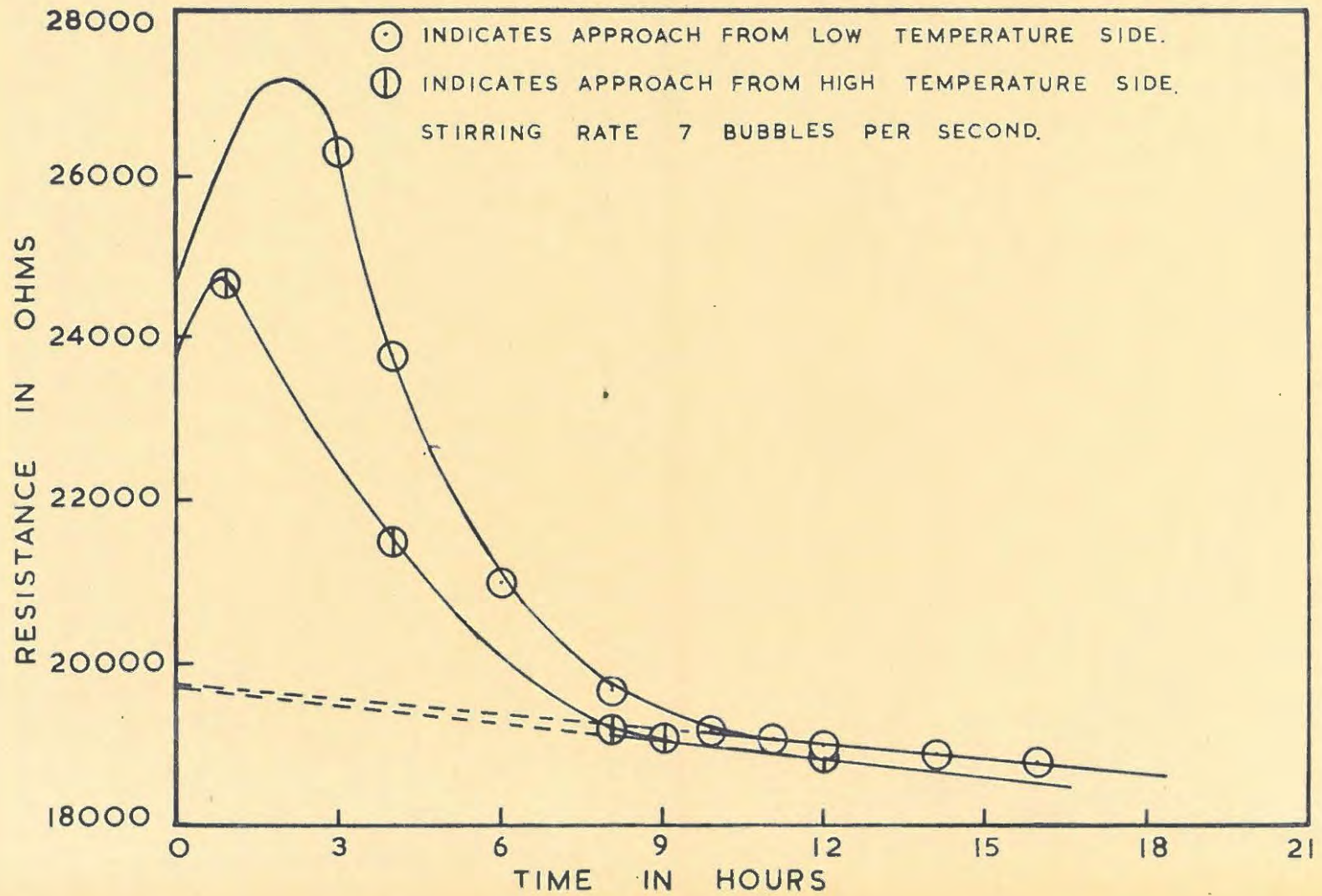


FIG. 29. GRAPH OF RESISTANCE AGAINST TIME
FOR SATURATED AGCL SOLUTION AT 45°C.



4.5 ohm/hr., corresponding to an increase in the conductance of about 3 - 4 nm./cm.hr.

The solubilities were calculated using the Onsager equation $\Lambda_{\text{AgBr}} = 167.0 - 114.3 s^{\frac{1}{2}}$ and the results are given on the previous page in table 29.

Although the solvent correction has decreased, it is still 35 - 40% of the total conductivity.

6.5 Determinations at 45°C.

6.51 Silver chloride results.

For experimental data see appendix K.

A typical set of experimental data for water is shown in fig. 28. Preheated samples again have a higher conductance than those which have been precooled; the difference being even greater than in the runs at 35°C. After rising rapidly to a maximum value after 1.5 - 2 hours, the resistance fell steadily at the rate of 4 ohm/hr. This represents a steady increase in the conductance of about 6 nm./cm.hr.

Fig. 29 refers to a typical set of experimental results for a saturated silver chloride solution. It is noticed that the time taken to reach saturation decreases as the working temperature is increased. This is true both for approaches from above and below.

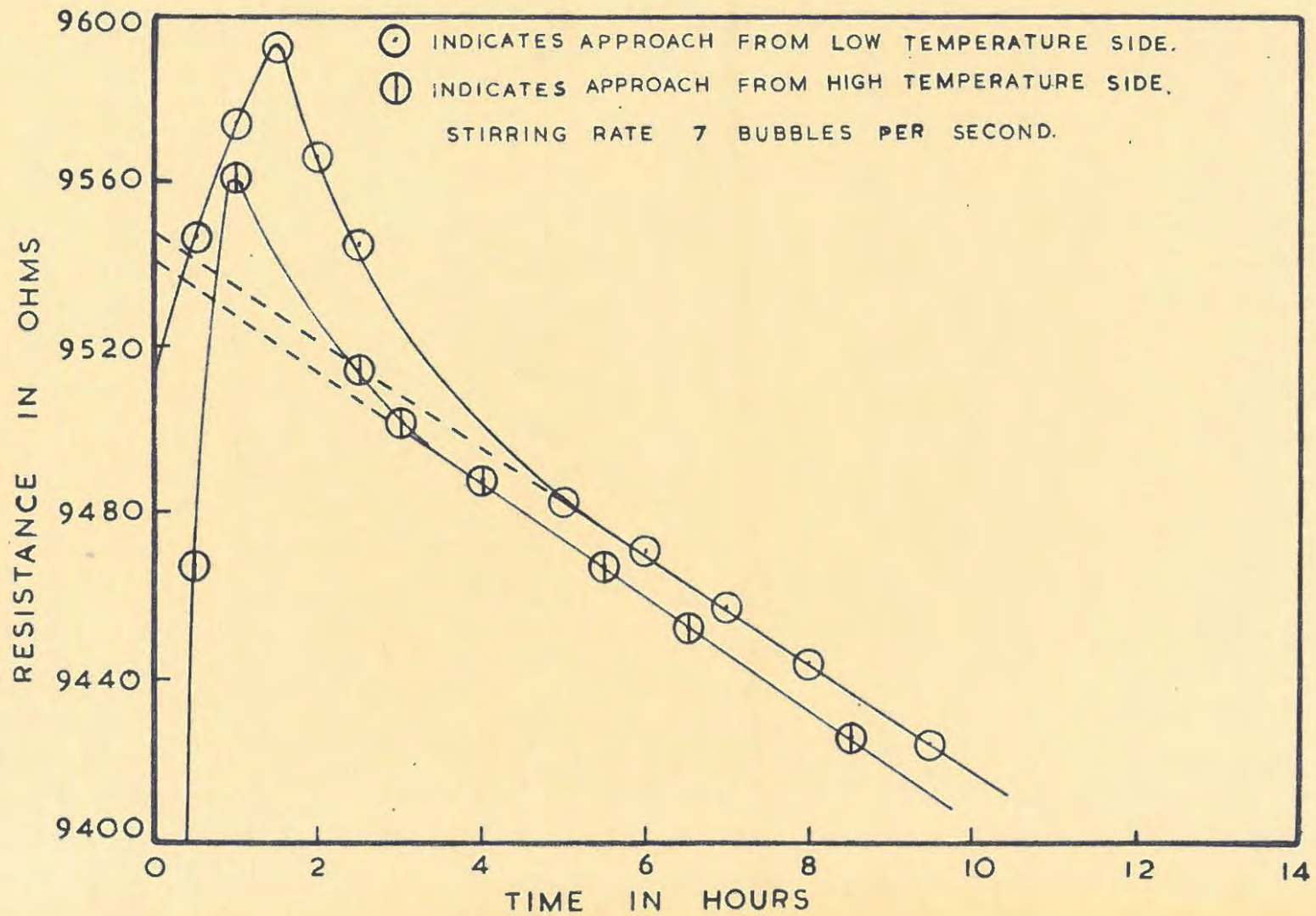
Furthermore, the rise in conductance after saturation, though still linear with time, is rapidly increasing with temperature. Precooled samples reached saturation after approximately 12 hours; on the other hand preheated samples required only about 8 - 9 hours. After saturation the resistance fell steadily at about 56 ohm/hr., corresponding to an increase in the conductance of 18 nm./cm.hr. The solubilities were calculated using the Onsager equation $\Lambda_{\text{AgCl}} = 195.2 - 158.2 s^{\frac{1}{2}}$ and the results are grouped in table 30.

TABLE 30. - SOLUBILITY OF SILVER CHLORIDE AT 45°C.

| No. of expt. | extrapolated to zero time | | κ_{AgCl} nm./cm. | mean solubility equiv./l. $\times 10^{-5}$ | mean solubility product $K \times 10^{10}$ |
|--------------|--------------------------------------|---------------------------------------|--------------------------------|--|--|
| | κ_{AgCl} soln. nm./cm. | $\kappa_{\text{H}_2\text{O}}$ nm./cm. | | | |
| 41 L | 5984 | 152 | 5882 | | |
| 41 H | 6019 | 161 | 5861 | | |
| 42 L | 5991 | 152 | 5839 | | |
| 42 H | 6013 | 163 | 5853 | ± 3.010 | ± 9.11 |
| 43 L | 6015 | 158 | 5857 | ± 0.06 | ± 0.12 |
| 43 H | 6031 | 167 | 5864 | | |
| 44 L | 6008 | 157 | 5851 | | |
| 44 H | 6025 | 166 | 5859 | | |

The solvent correction amounted to only 2.5 - 3% of the total conductivity.

FIG. 30. GRAPH OF RESISTANCE AGAINST TIME
FOR SATURATED AGR SOLUTION AT 45°C



6.52 Silver bromide results.

For experimental data see appendix I.

Typical resistance - time graphs for a saturated silver bromide solution are shown in fig. 30. Precooled samples took about 5 - 6 hours to reach saturation, whereas preheated samples were saturated after 3 - 4 hours. In approaches from both the high and the low temperature sides the resistance of the solutions fell rapidly after the maximum value was reached due to unsaturation and further solution of silver bromide.

TABLE 31. - SOLUBILITY OF SILVER BROMIDE AT 45°C.

| No. of expt. | extrapolated to zero | | | mean solubility equiv./l. x 10 ⁻⁷ | mean solubility product K x 10 ⁻¹³ |
|--------------|--------------------------------------|---------------------------------------|--------------------------------|--|---|
| | κ_{AgBr} soln. nm./cm. | $\kappa_{\text{H}_2\text{O}}$ nm./cm. | κ_{AgBr} nm./cm. | | |
| 45 L | 557 | 152 | 405 | | |
| 45 H | 556 | 153 | 413 | | |
| 46 L | 555 | 143 | 412 | | |
| 46 H | 563 | 151 | 412 | 20.9 ± 0.4 | 44.4 ± 0.8 |
| 47 L | 560 | 153 | 407 | | |
| 47 H | 574 | 159 | 415 | | |
| 48 L | 574 | 156 | 418 | | |
| 48 H | 571 | 167 | 404 | | |

After saturation, however, the resistance fell at a uniform rate of about 12 ohm/hr., which represents

an increase in the conductance of about 15 nm./cm.hr.

The Onsager equation $\Lambda_{\text{AgBr}} = 196.4 - 138.5 s^{\frac{1}{2}}$ was used to calculate the results which are given in table 31 on the previous page.

The water accounted for about 30% of the total conductivity.

6.6 Determinations at 55°C.

6.61 Condensation of water in the lead-out tube.

When measuring the resistance of samples of conductivity water at 55°C it was found that the resistance, after passing through a maximum value, fell very erratically. A fall of 200 ohms in 30 minutes was not uncommon. This effect was eventually traced to the condensation of water from the exit stirring gas on the cooler portions of the lead-out tube of the cell. When sufficient droplets had formed they ran back into the conductance cell carrying with them impurities dissolved from the unleached glass walls of the lead-out tube. This accounts for the sudden rapid falls in the resistance. The effect had not been experienced in the previous runs because the temperature difference between the saturated stirring gas and the cooler portions of the lead-out tube had not been sufficiently great.

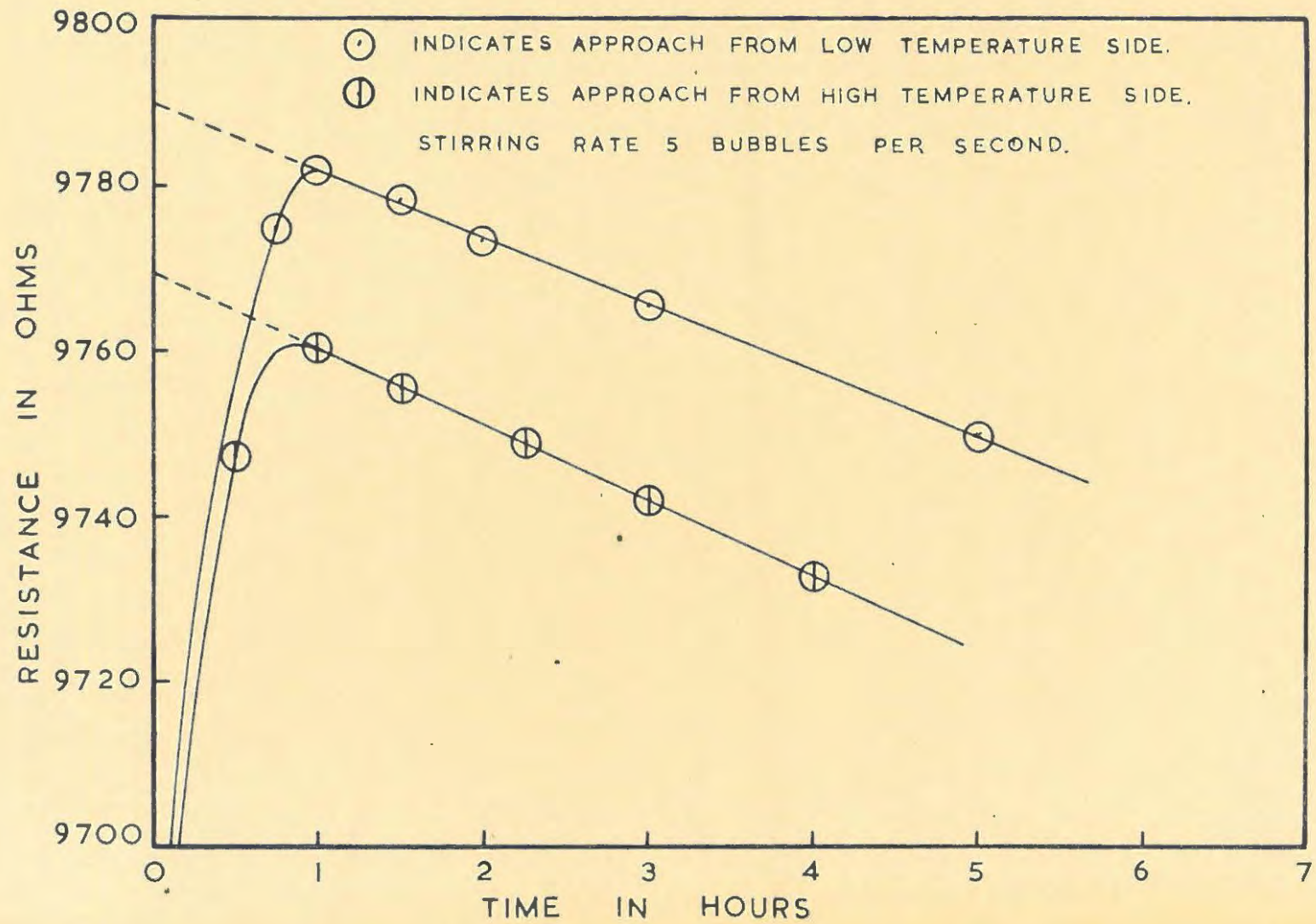
To prevent condensation the lead-out tube was fitted

with an electrically heated jacket. It consisted of a length of Pyrex tubing of slightly larger diameter than the lead-out tube. The jacket was insulated with asbestos paper, and wound with 7 feet (28 turns) of 36 gauge manganin resistance wire (total resistance 80 ohms) attached at each end to 16 gauge copper wire terminals. The A.C. mains supply, stepped down to 15 volts by means of a Variac, maintained the temperature of the jacket at about 60°C and very effectively prevented any condensation in the lead-out tube.

It was realised that heating the lead-out tube might raise the temperature of the cell contents due to thermal conduction along the glass walls of the cell. This was tested by measuring the temperature of the cell contents with a Beckmann thermometer. The thermometer showed a 0.4° rise in temperature when the lead-out tube was heated, but this was found to be due to heating of the mercury thread above the bulb and not to an actual rise in the temperature of the cell contents.

Since the uniform fall of the resistance after saturation at 55°C was considerable, the stirring rate was reduced from 7 to 5 bubbles/sec. both for the runs on the conductivity water and the saturated silver halide solutions.

FIG. 31. GRAPH OF RESISTANCE AGAINST TIME
FOR CONDUCTANCE WATER AT 55°C.



6.62 Silver chloride results.

For experimental data see appendix M.

Note: The resistances of the saturated silver chloride solutions in expt. 49 and 50 were measured using the 10,000 ohm shunt resistor, whereas in expt. 51 and 52 they were measured directly.

Fig. 31 refers to the variation of resistance with time for conductivity water. The resistance of both the precooled and the preheated samples rose steeply to a maximum value after approximately 1 hour, and then fell steadily at about 9 ohm/hr. This is equivalent to an increase in the conductance of 12 nm./cm.hr. Preheated

TABLE 32. - SOLUBILITY OF SILVER CHLORIDE AT 55°C.

| No. of expt. | extrapolated to zero time | | κ_{AgCl} nm./cm. | mean solubility equiv./l. $\times 10^{-5}$ | mean solubility product $K \times 10^{10}$ |
|--------------|--------------------------------------|---------------------------------------|--------------------------------|--|--|
| | κ_{AgCl} soln. nm./cm. | $\kappa_{\text{H}_2\text{O}}$ nm./cm. | | | |
| 49 L | 10,394 | 220 | 10,174 | | |
| 49 H | 10,430 | 254 | 10,196 | | |
| 50 L | 10,402 | 219 | 10,183 | | |
| 50 H | 10,432 | 230 | 10,202 | 4.52 ± 0.09 | 20.7 ± 0.18 |
| 51 L | 10,405 | 228 | 10,177 | | |
| 51 H | 10,440 | 244 | 10,196 | | |
| 52 L | 10,400 | 231 | 10,169 | | |
| 52 H | 10,410 | 247 | 10,163 | | |

FIG. 32. GRAPH OF RESISTANCE AGAINST TIME
FOR SATURATED AGCL SOLUTION AT 55°C.

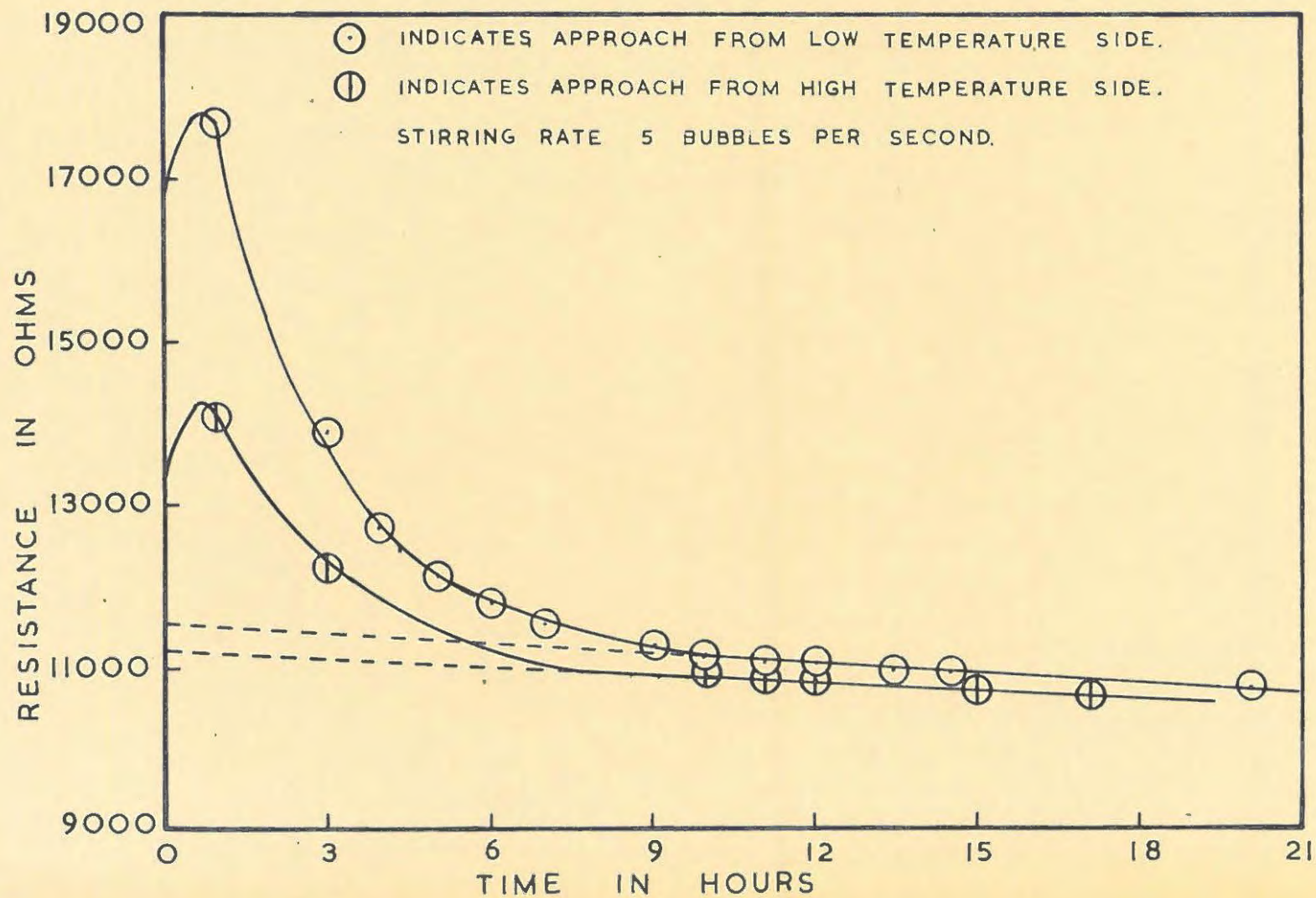
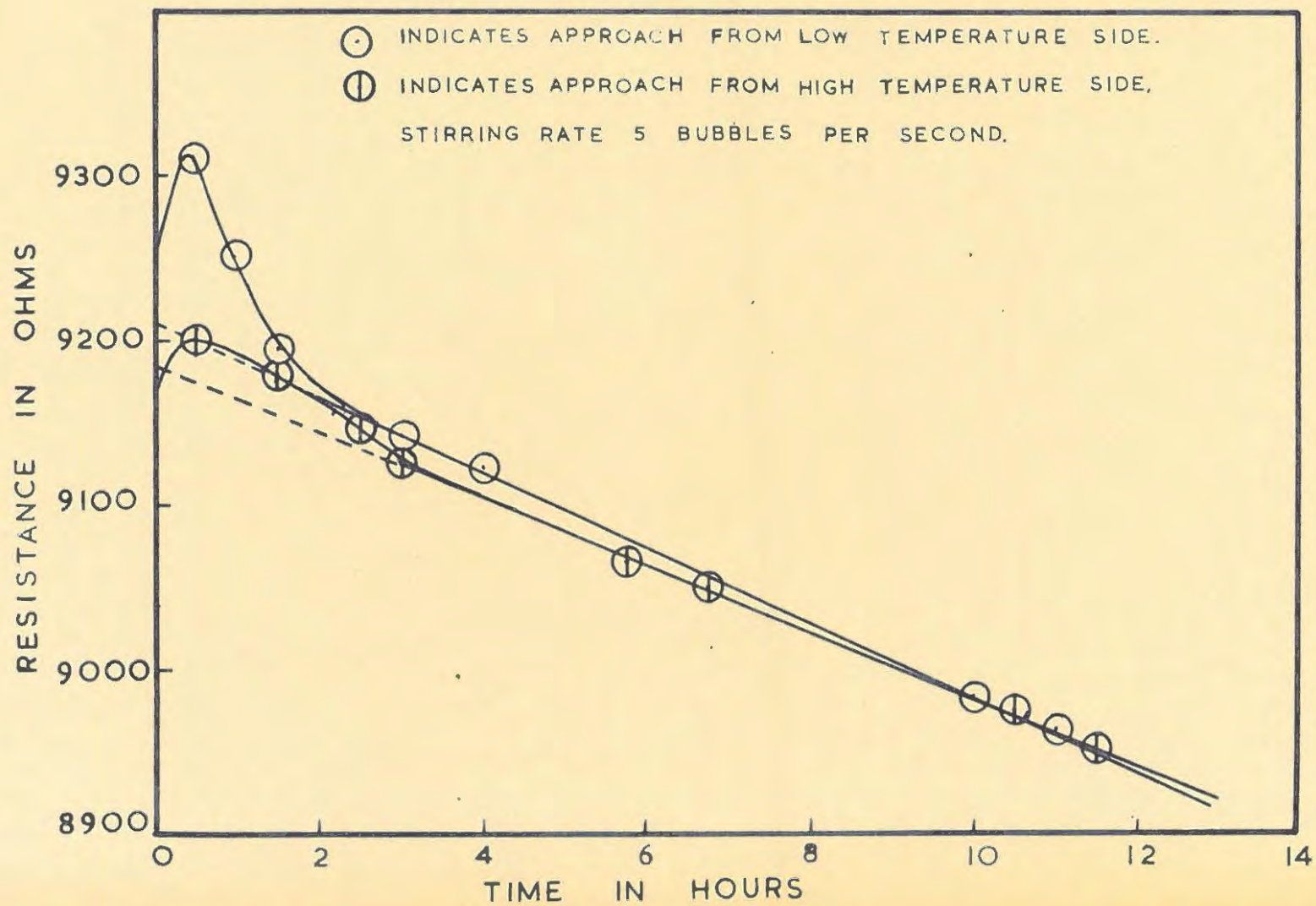


FIG. 33. GRAPH OF RESISTANCE AGAINST TIME
FOR SATURATED AGR SOLUTION AT 55°C.



samples always had a higher conductance than those which had been precooled.

The variation of resistance with time for a saturated silver chloride solution follows the typical curve of fig. 32. When approached from below saturation was reached after about 10 hours; preheated samples, on the other hand, were saturated after only 8 - 9 hours. After saturation the resistance fell at a uniform rate of about 9 ohm/hr. (when using the 10,000 ohm shunt resistor), and at 36 ohm/hr. when the resistance was measured directly. These rates of fall represent an increase in the conductance of 36 - 40 nm./cm.hr.

The results were calculated using the Onsager equation $\Lambda_{\text{AgCl}} = 225.1 - 163.9 s^{\frac{1}{2}}$ and are given in table 32 on the previous page.

The water contributed only 2 - 2.5% to the total conductivity.

6.63 Silver bromide results.

For experimental data see appendix N.

A typical set of experimental data is shown in fig. 35. Saturation was reached in about 3 hours both for precooled and preheated samples. Thereafter the resistance fell steadily at about 20 ohm/hr. corresponding to an increase in the conductance of 28 nm./cm.hr.

The Onsager equation $\Lambda_{\text{AgBr}} = 227.7 - 164.3 s^{1/2}$ was used to calculate the results which are given in table 33.

TABLE 33. - SOLUBILITY OF SILVER BROMIDE AT 55°C.

| No. of expt. | extrapolated to zero time | | | mean solubility equiv./l. $\times 10^{-7}$ | mean solubility product $K \times 10^{13}$ |
|--------------|--------------------------------------|---------------------------------------|--------------------------------|--|--|
| | κ_{AgBr} soln. nm./cm. | $\kappa_{\text{H}_2\text{O}}$ nm./cm. | κ_{AgBr} nm./cm. | | |
| 53 L | 1009 | 233 | 776 | | |
| 53 H | 1048 | 258 | 790 | | |
| 54 L | 1037 | 248 | 789 | | |
| 54 H | 1048 | 257 | 791 | 34.7 ± 0.7 | 123.4 ± 1.4 |
| 55 L | 1016 | 228 | 788 | | |
| 55 H | 1033 | 241 | 792 | | |
| 56 L | 1028 | 239 | 789 | | |
| 56 H | 1043 | 253 | 790 | | |

The solvent correction amounted to 20 - 25% of the total conductivity.

6.7 Correction of the observed solubilities in sections 6.4, 6.5 and 6.6 to values at the integral temperatures.

In the experiments performed at 35, 45 and 55°C the temperature of the cell contents was in each case slightly lower than the nominal value (see part II,

section 4.41). Since the limiting equivalent conductances of the silver salts in table 21 are stated for exact integral temperatures, it is preferable to correct the values of the specific conductances to the integral temperatures. The correction is complicated by the fact that the specific conductances are by no means linear functions of temperature. Even a fourth order equation does not fit well enough for interpolation.

On the other hand, the logarithms of the specific conductances vary almost linearly with temperature. The second differences are only about one tenth of the first order ones, so that a linear interpolation over a short interval can be made. The variation of $\log \kappa_{\text{AgCl}}$ and $\log \kappa_{\text{AgBr}}$ with temperature is shown in tables 34 and 35 respectively, which also include the first, second and third differences.

TABLE 34. - VARIATION OF $\log \kappa_{\text{AgCl}}$ WITH TEMPERATURE.

| Temp. (°C) | $\log \kappa_{\text{AgCl}}$ | Δ^1 (+) | Δ^2 (-) | Δ^3 (-) |
|---------------|-----------------------------|----------------|----------------|----------------|
| 25.00 | 3.26553 | 0.25990 | 0.01802 | 0.01667 |
| 34.85 | 3.52543 | 0.24188 | 0.00135 | - |
| 44.77 | 3.76731 | 0.24053 | - | - |
| 54.70 | 4.00784 | - | - | - |

TABLE 35. - VARIATION OF $\log \kappa_{\text{AgBr}}$ WITH TEMPERATURE.

| Temp. (°C) | $\log \kappa_{\text{AgBr}}$ | Δ^1 (+) | Δ^2 (-) | Δ^3 (-) |
|---------------|-----------------------------|----------------|----------------|----------------|
| 25.00 | 2.00000 | 0.32015 | 0.02646 | 0.01656 |
| 54.85 | 2.32015 | 0.29369 | 0.00990 | - |
| 44.77 | 2.61384 | 0.28379 | - | - |
| 54.70 | 2.89764 | - | - | - |

The corrected values for the specific conductances, together with the corresponding solubilities and solubility products, are given in table 36.

TABLE 36. - CORRECTED SOLUBILITIES OF SILVER CHLORIDE AND SILVER BROMIDE AT 35, 45 AND 55°C.

| | Temp. (°C) | mean κ_{AgCl} corrected | solubility 10^{-5} equiv./l corrected | soly. prod. $K \times 10^{10}$ corrected |
|------|---------------|---|---|--|
| AgCl | 35.00 | 3381 | 2.049 ± 0.04 | 4.20 ± 0.08 |
| | 45.00 | 5928 | 3.049 ± 0.06 | 9.35 ± 0.12 |
| | 55.00 | 10350 | 4.60 ± 0.09 | 21.40 ± 0.18 |
| | Temp. (°C) | mean κ_{AgBr} corrected | solubility 10^{-7} equiv./l corrected | soly. prod. $K \times 10^{13}$ corrected |
| AgBr | 35.00 | 211 | 12.63 ± 0.25 | 16.0 ± 0.5 |
| | 45.00 | 417 | 21.2 ± 0.4 | 45.6 ± 0.8 |
| | 55.00 | 806 | 35.4 ± 0.7 | 128.2 ± 1.4 |

7. SUMMARY AND CONCLUSIONS.

The best values for the solubility of silver chloride and silver bromide from 5 to 55°C are given in tables 37 and 38. Owen and Brinkley's figures (18) for silver chloride and silver bromide are included for comparison.

TABLE 37. - SOLUBILITY AND SOLUBILITY PRODUCT OF SILVER CHLORIDE FROM CONDUCTANCE MEASUREMENTS.

| Temp. (°C) | solubility g.equiv./l. x 10 ⁻⁵ | | K _{AgCl} x 10 ¹⁰ | |
|---------------|---|-------------------|--------------------------------------|-------------------|
| | author | Owen and Brinkley | author | Owen and Brinkley |
| 0.0 | 0.42 ± 0.03 | | | |
| 5.0 | 0.507 ± 0.01 | 0.506 | 0.256 ± 0.020 | 0.254 |
| 10.0 | 0.62 ± 0.02 | | | |
| 15.0 | 0.839 ± 0.017 | 0.842 | 0.700 ± 0.035 | 0.705 |
| 18.0 | 0.95 ± 0.03 | | | |
| 20.0 | 1.02 ± 0.03 | | | |
| 25.0 | 1.337 ± 0.004 | 1.337 | 1.780 ± 0.010 | 1.782 |
| 30.0 | 1.64 ± 0.05 | | | |
| 35.0 | 2.049 ± 0.04 | 2.038 | 4.20 ± 0.08 | 4.16 |
| 40.0 | 2.50 ± 0.07 | | | |
| 45.0 | 3.049 ± 0.06 | 3.002 | 9.35 ± 0.12 | 9.07 |
| 50.0 | 3.70 ± 0.10 | | | |
| 55.0 | 4.60 ± 0.09 | | 21.40 ± 0.18 | |

FIG. 34. SOLUBILITY CURVE FOR
AGCL FROM 5 TO 55°C.

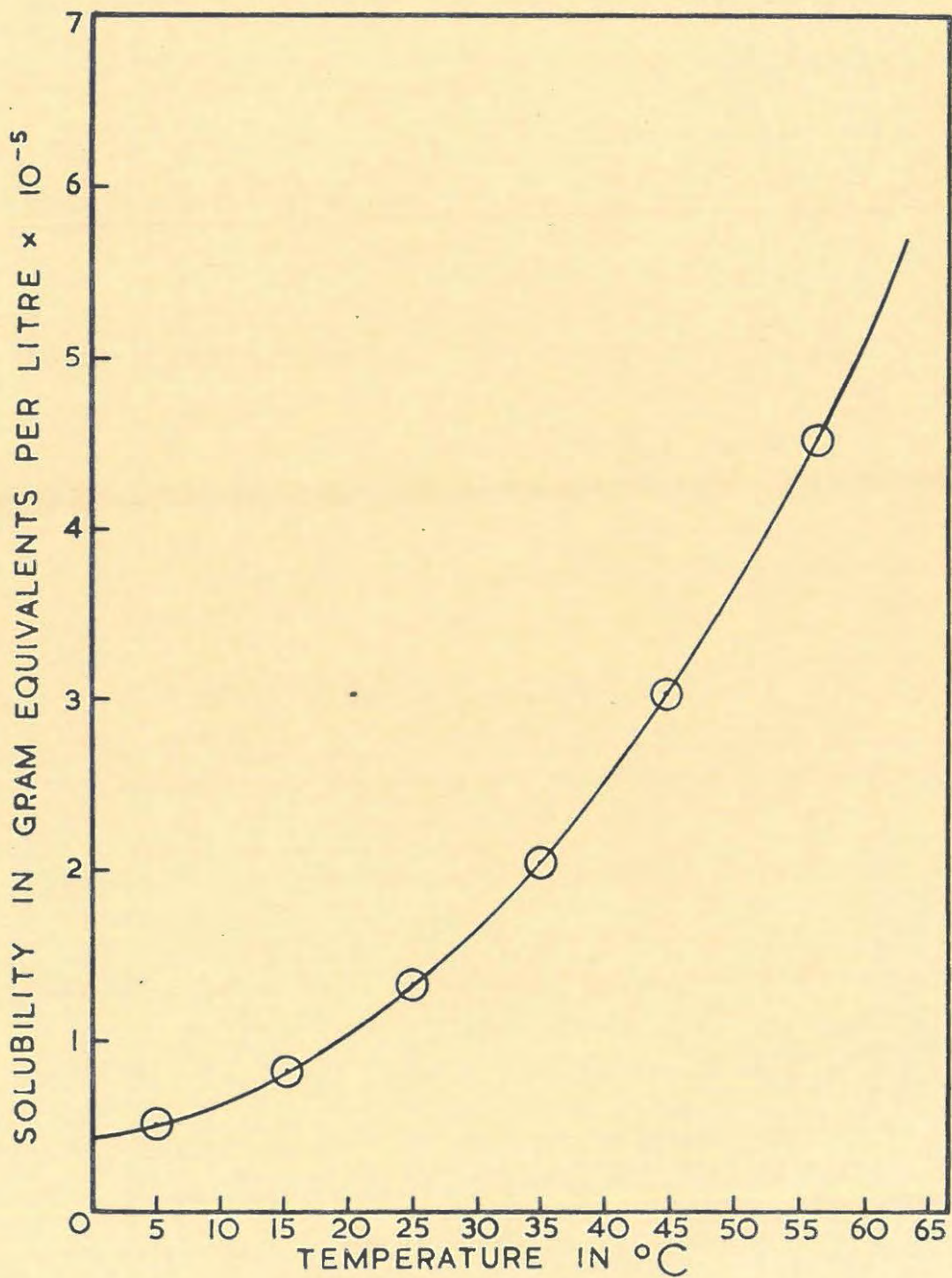


FIG. 35. SOLUBILITY CURVE FOR
AGBR FROM 5 TO 55°C

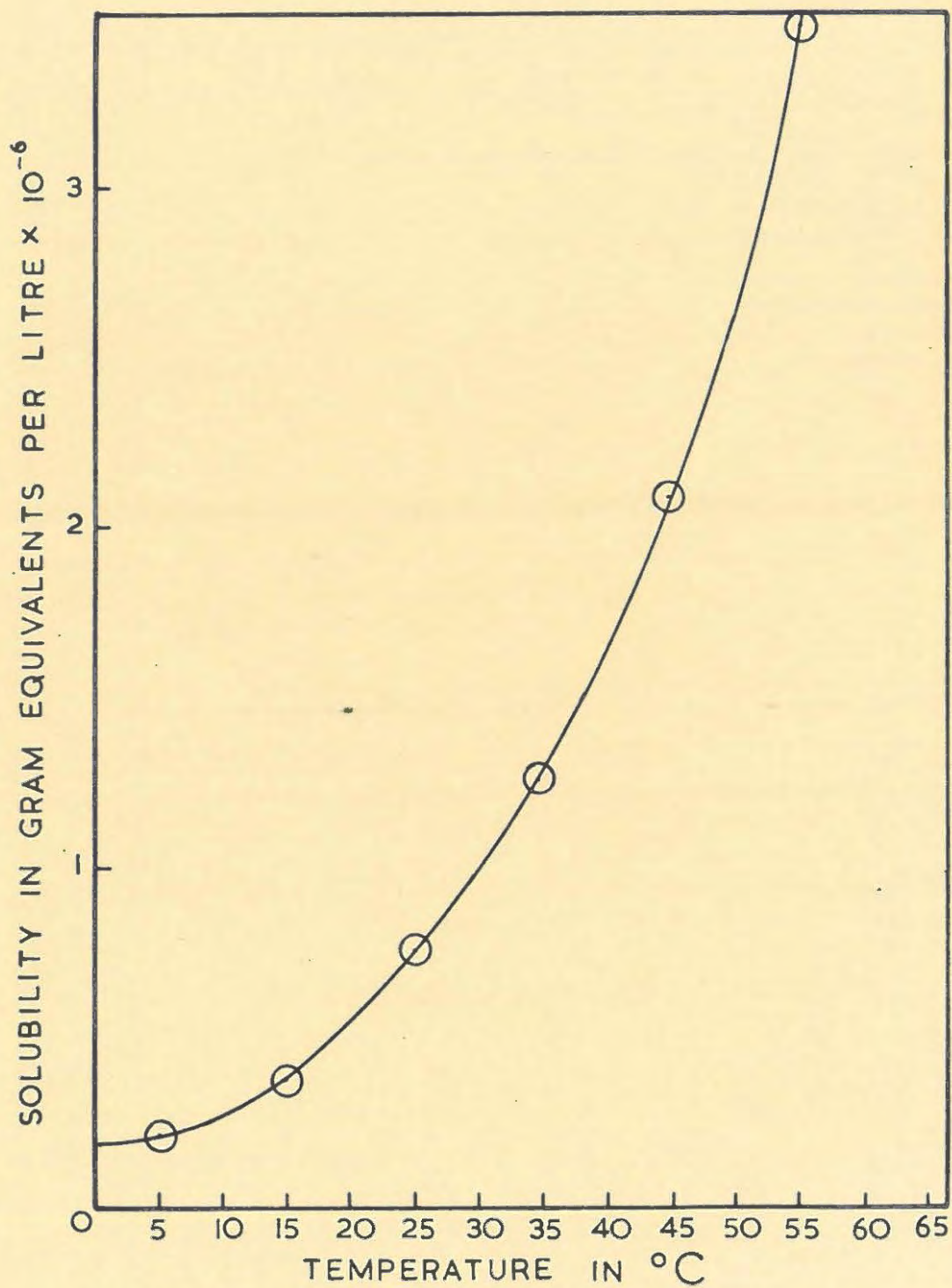


TABLE 38. - SOLUBILITY AND SOLUBILITY PRODUCT OF SILVER
BROMIDE FROM CONDUCTANCE MEASUREMENTS.

| Temp. (°C) | solubility g.equiv./l. x 10 ⁻⁷ | | K _{AgBr} x 10 ¹³ | |
|---------------|---|----------------------|--------------------------------------|----------------------|
| | author | Owen and Brinkley | author | Owen and Brinkley |
| 0.0 | 1.8 ± 0.30 | | | |
| 5.0 | 2.17 ± 0.10 | 2.03 | 0.47 ± 0.02 | 0.41 |
| 10.0 | 2.8 ± 0.20 | | | |
| 15.0 | 3.85 ± 0.14 | 3.80 | 1.48 ± 0.28 | 1.51 |
| 18.0 | 4.7 ± 0.20 | | | |
| 20.0 | 5.3 ± 0.25 | | | |
| 25.0 | 7.15 ± 0.20 | 7.04 | 5.20 ± 0.40 | 4.98 |
| 30.0 | 9.6 ± 0.30 | | | |
| 35.0 | 12.63 ± 0.25 | 12.13 | 16.0 ± 0.5 | 14.9 |
| 40.0 | 16.5 ± 0.5 | | | |
| 45.0 | 21.2 ± 0.4 | 19.97 | 45.6 ± 0.8 | 40.6 |
| 50.0 | 26.0 ± 1.0 | | | |
| 55.0 | 35.4 ± 0.7 | | 128.2 ± 1.4 | |

The solubility curves for these salts are given in fig. 34 and 35. From these curves additional values have been obtained by interpolation and extrapolation, and these are included in tables 37 and 38. The limits of error have been extended accordingly.

It is significant that the solubilities for silver chloride agree with Owen and Brinkleys' figures (18)

FIG. 36. GRAPH OF LOG K AGAINST $\frac{1}{T}$
FOR SILVER CHLORIDE

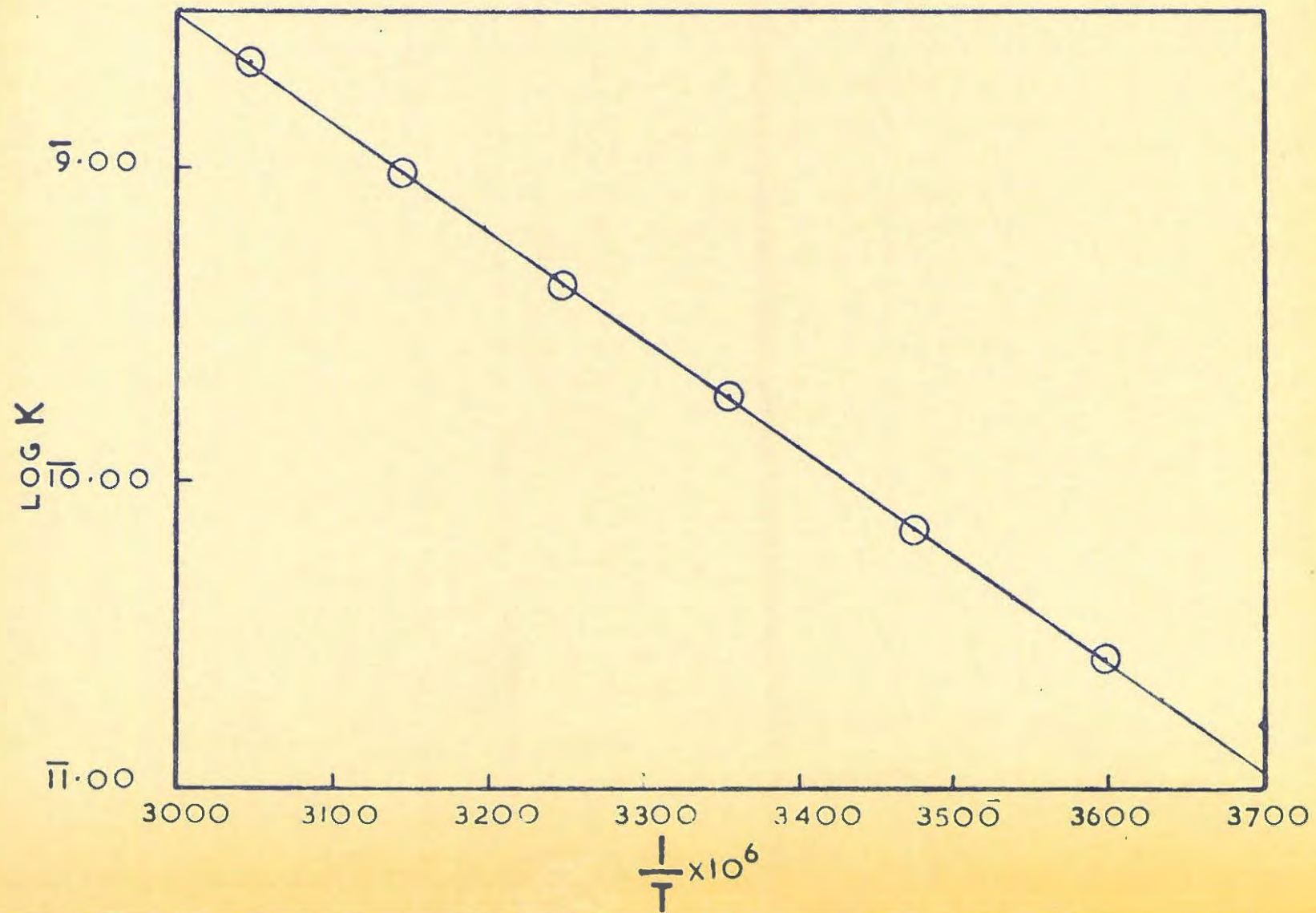
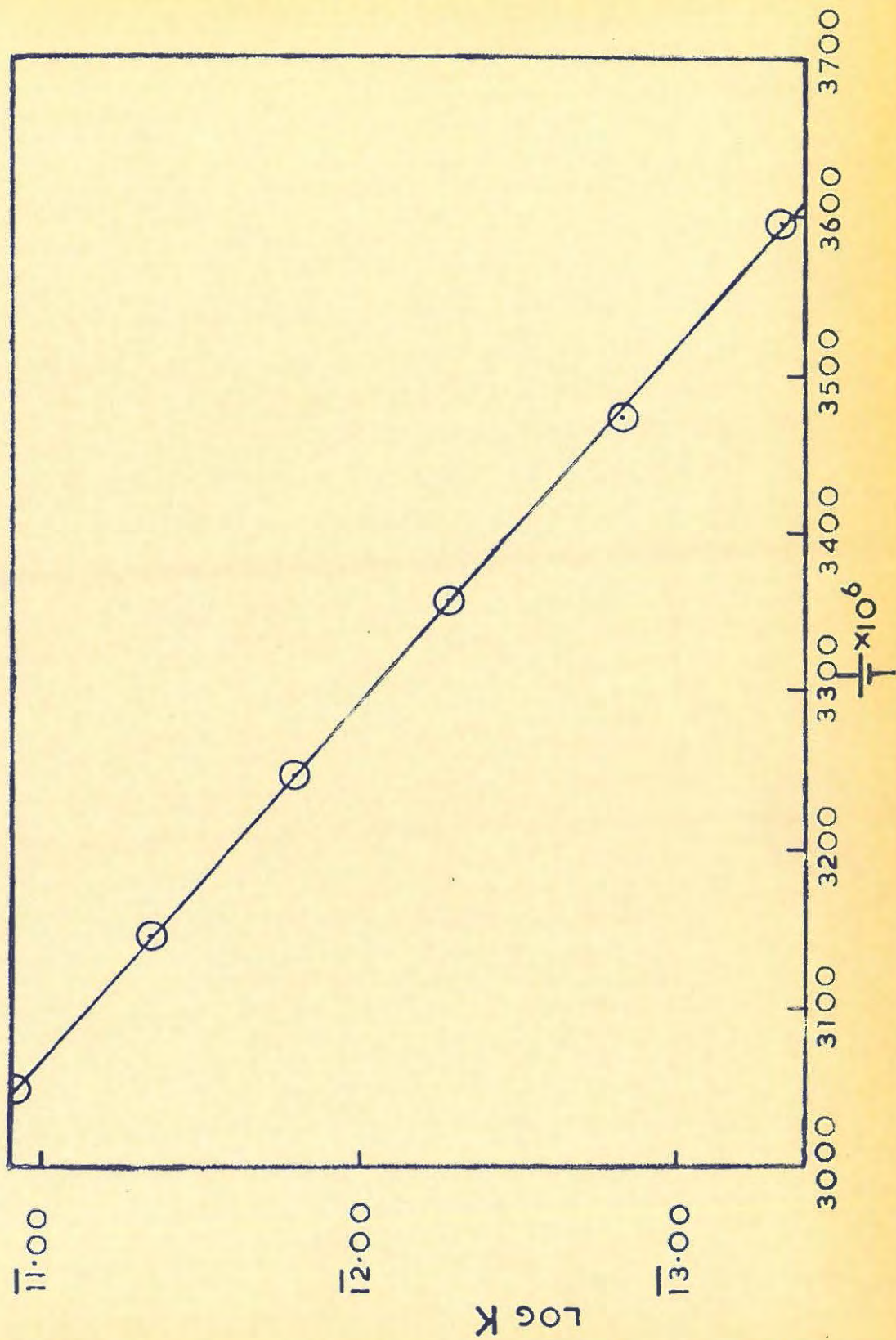


FIG. 37. GRAPH OF LOG K AGAINST $\frac{1}{T}$
FOR SILVER BROMIDE



to within the estimated limits of experimental error. For silver bromide the discrepancies are slightly greater than the experimental error; the conductometric values being definitely higher than the potentiometric ones, especially at the upper temperatures. However, an uncertainty of $\pm 1\%$ in the values for the limiting equivalent conductances in table 21 may account for this. Nevertheless, the agreement is sufficiently close to suggest that samples of the two salts prepared either by electrolysis or precipitation show no real difference in solubility.

An alternative way of expressing the results graphically is shown in fig. 36 and 37, where $\log K$ is plotted against $\frac{1}{T}$. The variation is almost linear both for silver chloride and silver bromide, which is what one would expect thermodynamically by inspection of the van't Hoff isochore

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta H^\circ}{RT^2} \dots\dots\dots 43.$$

At the extreme dilutions encountered in this work the solutions approximate to ideal behaviour. If the coefficient of thermal expansion of the solutions is neglected, and ΔH° is assumed to remain constant over the whole temperature range, integration of eqn. 43 yields

$$\ln K = - \frac{\Delta H^\circ}{RT} + I \quad \dots\dots\dots 44.$$

or

$$\log K = - \frac{\Delta H^\circ}{2.303R} \cdot \frac{1}{T} + I \dots\dots\dots 45.$$

Equation 45 and fig. 36 and 37 permit evaluation of ΔH° (the standard heat of reaction) for the reaction



This leads to the values

$\Delta H^\circ = 15.77$ k.cal./mole for silver chloride
and $\Delta H^\circ = 20.25$ k.cal./mole for silver bromide.

In view of the simplifying assumptions made above these figures are only averages for the temperature range from 5 to 55°C. An uncertainty in the limiting equivalent conductances of the silver halides does not justify a more rigorous evaluation of ΔH° .

APPENDIX.

Note: In numbering the experiments L indicates approach of the saturation point from the low temperature side, whereas H indicates approach from the high temperature side.

A. Variation with time of the resistance of
conductivity water at 25°C.

EXPERIMENT 1.

| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| 0.0 | 9560.2 | 28.5 | 9910.6 |
| 1.0 | 9800.0 | 31.5 | 9910.2 |
| 2.0 | 9850.1 | 34.5 | 9909.3 |
| 2.5 | 9870.4 | 47.5 | 9905.1 |
| 2.75 | 9890.7 | 50.5 | 9904.3 |
| 3.0 | 9905.8 | 52.5 | 9903.4 |
| 3.5 | 9915.2 | 55.5 | 9902.8 |
| 4.0 | 9917.0 | 58.5 | 9902.5 |
| 4.5 | 9917.1 | 71.5 | 9898.4 |
| 5.5 | 9917.0 | 74.5 | 9897.3 |
| 8.5 | 9916.5 | 76.5 | 9896.6 |
| 23.5 | 9911.8 | 79.5 | 9896.1 |
| 26.5 | 9911.0 | 81.5 | 9895.2 |

B. Silver chloride data at 25°C.

EXPERIMENT 4.

$$\kappa_{\text{H}_2\text{O}} = 95 \text{ nm./cm.}$$

L. Saturated silver chloride solution.

| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| 0.0 | 8974.1 | 61.0 | 8655.1 |
| 4.0 | 9016.4 | 64.0 | 8640.1 |
| 8.0 | 8975.9 | 72.0 | 8610.2 |
| 10.0 | 8959.8 | 78.0 | 8600.4 |
| 24.0 | 8862.4 | 82.0 | 8595.5 |
| 29.0 | 8837.1 | 86.0 | 8585.9 |
| 34.0 | 8820.0 | 96.0 | 8575.4 |
| 37.0 | 8807.3 | 101.0 | 8573.0 |
| 48.0 | 8775.7 | 105.0 | 8571.1 |
| 53.0 | 8683.9 | 109.0 | 8570.0 |
| 57.0 | 8670.5 | 120.0 | 8567.1 |

EXPERIMENT 5.

$$\kappa_{\text{H}_2\text{O}} = 96 \text{ nm./cm.}$$

H. Saturated silver chloride solution.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 0.5 | 7350.0 |
| 5.0 | 8020.1 |
| 11.0 | 8110.4 |
| 21.0 | 8235.5 |
| 23.0 | 8260.2 |
| 27.0 | 8290.0 |
| 32.0 | 8330.9 |
| 45.0 | 8410.4 |
| 48.0 | 8420.3 |
| 53.0 | 8435.5 |
| 57.0 | 8450.6 |
| 61.0 | 8465.1 |
| 69.0 | 8470.1 |
| 72.0 | 8468.6 |
| 80.0 | 8464.0 |

127.

EXPERIMENT 6.

$$\kappa_{\text{H}_2\text{O}} = 82 \text{ nm./cm.}$$

L. Saturated silver chloride solution.

| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| 0.0 | 8996.0 | 5.5 | 8614.0 |
| 0.5 | 8015.0 | 5.83 | 8611.0 |
| 2.16 | 8738.5 | 7.5 | 8600.0 |
| 2.5 | 8705.5 | 10.75 | 8599.5 |
| 3.25 | 8650.0 | 21.0 | 8596.2 |
| 4.0 | 8633.4 | 23.0 | 8595.8 |
| 4.83 | 8621.0 | | |

EXPERIMENT 7.

$$\kappa_{\text{H}_2\text{O}} = 87 \text{ nm./cm.}$$

L. Saturated silver chloride solution.

| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| 0.0 | 8800.0 | 17.0 | 8595.4 |
| 0.34 | 8860.0 | 18.0 | 8594.0 |
| 0.67 | 8794.3 | 19.0 | 8593.4 |
| 1.34 | 8693.4 | 20.5 | 8593.0 |
| 3.5 | 8650.1 | 22.0 | 8592.5 |
| 7.0 | 8625.2 | 26.0 | 8591.1 |

128.

EXPERIMENT 8.

$$\kappa_{\text{H}_2\text{O}} = 89 \text{ nm./cm.}$$

L. Saturated silver chloride solution.

| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| 0.0 | 8830.0 | 9.0 | 8596.1 |
| 1.5 | 8810.1 | 10.5 | 8591.5 |
| 3.0 | 8700.4 | 12.0 | 8589.3 |
| 4.0 | 8670.2 | 14.0 | 8588.9 |
| 5.0 | 8650.0 | 24.0 | 8586.3 |
| 6.0 | 8630.0 | 27.0 | 8585.4 |

EXPERIMENT 9.

$$\kappa_{\text{H}_2\text{O}} = 96 \text{ nm./cm.}$$

L. Saturated silver chloride solution.

| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| 0.0 | 8990.4 | 28.0 | 8590.3 |
| 4.0 | 8870.0 | 30.0 | 8586.1 |
| 9.0 | 8709.8 | 33.0 | 8583.0 |
| 14.0 | 8645.2 | 36.0 | 8582.2 |
| 24.0 | 8600.4 | 49.0 | 8579.5 |
| 23.0 | 8594.0 | | |

EXPERIMENT 10.

$$\kappa_{\text{H}_2\text{O}} = 95 \text{ nm./cm.}$$

H. Saturated silver chloride solution.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 0.0 | 7994.0 |
| 26.0 | 8240.1 |
| 52.0 | 8380.6 |
| 66.0 | 8446.4 |
| 68.0 | 8455.4 |
| 72.0 | 8455.7 |
| 82.0 | 8445.9 |
| 94.0 | 8439.2 |
| 100.0 | 8455.8 |

130.

C. Silver bromide data at 25°C.

EXPERIMENT 12.

L. Conductivity water.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 0.75 | 9868.5 |
| 1.5 | 9898.5 |
| 2.5 | 9913.0 |
| 3.5 | 9914.5 |
| 4.5 | 9914.8 |
| 6.5 | 9914.5 |

L. Saturated silver bromide solution.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 0.67 | 9702.0 |
| 1.67 | 9821.5 |
| 1.92 | 9826.3 |
| 2.18 | 9830.3 |
| 2.42 | 9831.8 |
| 2.67 | 9832.5 |
| 3.17 | 9831.6 |
| 3.67 | 9832.7 |
| 5.16 | 9831.0 |
| 19.5 | 9804.3 |
| 22.5 | 9798.6 |

EXPERIMENT 13.

L. Conductivity water.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 1.0 | 9758.5 |
| 1.5 | 9888.5 |
| 2.5 | 9902.0 |
| 5.0 | 9907.3 |
| 8.5 | 9911.0 |
| 19.5 | 9907.5 |

L. Saturated silver bromide solution.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 1.0 | 9786.5 |
| 1.5 | 9820.5 |
| 2.25 | 9829.1 |
| 3.0 | 9829.5 |
| 3.5 | 9827.7 |
| 5.0 | 9825.3 |
| 6.5 | 9821.0 |
| 11.5 | 9809.3 |

EXPERIMENT 14.

L. Conductivity water.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 1.0 | 9908.5 |
| 1.75 | 9918.0 |
| 2.5 | 9918.6 |
| 3.0 | 9918.8 |
| 3.5 | 9918.7 |
| 5.0 | 9918.3 |

L. Saturated silver bromide solution.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 0.5 | 9781.7 |
| 1.34 | 9831.9 |
| 1.67 | 9835.0 |
| 2.5 | 9836.2 |
| 3.0 | 9835.5 |
| 10.0 | 9821.6 |
| 22.5 | 9796.1 |

EXPERIMENT 15.

L. Conductivity water.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 1.0 | 9908.5 |
| 1.75 | 9918.0 |
| 2.5 | 9918.6 |
| 3.0 | 9918.8 |
| 3.5 | 9918.7 |
| 5.0 | 9918.3 |

L. Saturated silver bromide solution.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 1.25 | 9811.5 |
| 1.75 | 9829.1 |
| 2.25 | 9834.0 |
| 2.5 | 9834.5 |
| 3.0 | 9834.5 |
| 4.5 | 9832.6 |
| 6.5 | 9834.5 |
| 13.5 | 9815.4 |

EXPERIMENT 16.

L. Conductivity water.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 1.0 | 9885.0 |
| 2.0 | 9910.4 |
| 3.0 | 9915.0 |
| 4.5 | 9914.7 |
| 5.5 | 9914.6 |
| 6.5 | 9914.3 |

L. Saturated silver bromide solution.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 1.25 | 9821.9 |
| 1.75 | 9830.3 |
| 2.5 | 9832.8 |
| 3.75 | 9833.9 |
| 4.75 | 9833.5 |
| 6.0 | 9829.5 |
| 10.75 | 9821.5 |
| 20.75 | 9805.0 |
| 22.75 | 9801.9 |

D. Calibration of Tinsley potentiometer.

Medium coil.

| Setting | correction | Setting | correction |
|---------|------------|---------|------------|
| 0.00100 | 0.00000 | 0.02100 | - 0.00001 |
| 0.00200 | 0.00000 | 0.02200 | - 0.00001 |
| 0.00300 | 0.00000 | 0.02300 | - 0.00001 |
| 0.00400 | 0.00000 | 0.02400 | - 0.00001 |
| 0.00500 | 0.00000 | 0.02500 | - 0.00001 |
| 0.00600 | 0.00000 | 0.02600 | - 0.00001 |
| 0.00700 | 0.00000 | 0.02700 | - 0.00001 |
| 0.00800 | 0.00000 | 0.02800 | - 0.00001 |
| 0.00900 | 0.00000 | 0.02900 | - 0.00001 |
| 0.01000 | 0.00000 | 0.03000 | - 0.00001 |
| 0.01100 | 0.00000 | 0.03100 | - 0.00001 |
| 0.01200 | 0.00000 | 0.03200 | - 0.00001 |
| 0.01300 | 0.00000 | 0.03300 | - 0.00001 |
| 0.01400 | 0.00000 | 0.03400 | - 0.00001 |
| 0.01500 | 0.00000 | 0.03500 | - 0.00001 |
| 0.01600 | 0.00000 | 0.03600 | - 0.00001 |
| 0.01700 | 0.00000 | 0.03700 | - 0.00001 |
| 0.01800 | 0.00000 | 0.03800 | - 0.00001 |
| 0.01900 | 0.00000 | 0.03900 | - 0.00001 |
| 0.02000 | 0.00000 | 0.04000 | - 0.00001 |

Medium coil. (cont'd.)

| Setting | correction | Setting | correction |
|---------|------------|---------|------------|
| 0.04100 | - 0.00001 | 0.06099 | - 0.00001 |
| 0.04200 | - 0.00001 | 0.06199 | - 0.00001 |
| 0.04300 | - 0.00001 | 0.06299 | - 0.00001 |
| 0.04400 | - 0.00001 | 0.06399 | - 0.00001 |
| 0.04500 | - 0.00001 | 0.06499 | - 0.00001 |
| 0.04600 | - 0.00001 | 0.06599 | - 0.00001 |
| 0.04700 | - 0.00001 | 0.06699 | - 0.00001 |
| 0.04800 | - 0.00001 | 0.06799 | - 0.00001 |
| 0.04900 | - 0.00001 | 0.06899 | - 0.00001 |
| 0.05000 | - 0.00001 | 0.06999 | - 0.00001 |
| 0.05100 | - 0.00001 | 0.07099 | - 0.00001 |
| 0.05200 | - 0.00001 | 0.07199 | - 0.00001 |
| 0.05300 | - 0.00001 | 0.07299 | - 0.00001 |
| 0.05400 | - 0.00001 | 0.07399 | - 0.00001 |
| 0.05500 | - 0.00001 | 0.07499 | - 0.00001 |
| 0.05600 | 0.00000 | 0.07599 | - 0.00001 |
| 0.05700 | 0.00000 | 0.07699 | - 0.00001 |
| 0.05800 | - 0.00001 | 0.07799 | - 0.00001 |
| 0.05900 | - 0.00001 | 0.07899 | - 0.00001 |
| 0.05999 | - 0.00001 | 0.07998 | - 0.00001 |

Medium coil. (cont'd.)

| Setting | correction | Setting | correction |
|---------|------------|---------|------------|
| 0.08099 | - 0.00001 | 0.09098 | 0.00000 |
| 0.08199 | - 0.00001 | 0.09198 | 0.00000 |
| 0.08299 | - 0.00001 | 0.09298 | 0.00000 |
| 0.08399 | - 0.00001 | 0.09398 | 0.00000 |
| 0.08499 | - 0.00001 | 0.09498 | 0.00000 |
| 0.08598 | 0.00000 | 0.09598 | 0.00000 |
| 0.08698 | 0.00000 | 0.09698 | 0.00000 |
| 0.08798 | 0.00000 | 0.09798 | 0.00000 |
| 0.08898 | 0.00000 | 0.09898 | 0.00000 |
| 0.08998 | 0.00000 | 0.09998 | 0.00000 |

Large coil.

| Setting | correction | Setting | correction |
|---------|------------|---------|------------|
| 0.09999 | - 0.00001 | 0.99995 | + 0.00002 |
| 0.20000 | - 0.00001 | 1.09998 | - 0.00003 |
| 0.50002 | - 0.00002 | 1.19997 | - 0.00001 |
| 0.40007 | - 0.00001 | 1.29996 | + 0.00002 |
| 0.50006 | - 0.00001 | 1.39995 | + 0.00008 |
| 0.60005 | - 0.00001 | 1.50001 | + 0.00001 |
| 0.70004 | - 0.00001 | 1.60002 | - 0.00001 |
| 0.80006 | 0.00000 | 1.70003 | - 0.00003 |
| 0.89999 | + 0.00001 | 1.80002 | + 0.00001 |

E. Silver chloride data at 5°C.

EXPERIMENT 17.

L. Conductivity water.

| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| 2.0 | 9821.5 | 4.5 | 9970.9 |
| 3.0 | 9937.1 | 5.0 | 9971.0 |
| 3.5 | 9961.9 | 14.0 | 9969.9 |
| 4.0 | 9970.4 | | |

Saturated silver chloride solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 0.0 | 9804.0 | 0.0 | 9784.0 |
| 2.0 | 9890.7 | 1.0 | 9815.6 |
| 4.0 | 9795.4 | 2.5 | 9727.5 |
| 6.0 | 9726.7 | 3.5 | 9706.7 |
| 8.5 | 9681.6 | 13.5 | 9617.8 |
| 13.0 | 9646.9 | 15.0 | 9616.3 |
| 23.0 | 9616.1 | 16.0 | 9615.6 |
| 24.0 | 9615.2 | 17.5 | 9615.0 |
| 25.0 | 9615.1 | 18.5 | 9614.3 |
| 27.0 | 9614.5 | 19.5 | 9614.3 |
| 28.0 | 9614.4 | 21.0 | 9615.6 |
| 31.0 | 9613.7 | 22.0 | 9613.4 |

EXPERIMENT 18.

H. Conductivity water.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 3.75 | 9970.5 |
| 4.25 | 9970.7 |
| 4.75 | 9970.7 |
| 14.75 | 9969.8 |
| 15.75 | 9969.8 |

Saturated silver chloride solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 16.0 | 9610.9 | 13.0 | 9611.2 |
| 17.0 | 9609.8 | 14.0 | 9610.4 |
| 18.0 | 9609.2 | 15.0 | 9610.0 |
| 20.0 | 9608.7 | 16.75 | 9608.7 |
| 21.0 | 9608.2 | 19.5 | 9607.4 |
| 30.0 | 9603.7 | 21.5 | 9606.9 |
| | | 23.0 | 9605.8 |

EXPERIMENT 19.

L. Conductivity water.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 2.0 | 9842.1 |
| 3.0 | 9959.3 |
| 4.0 | 9970.3 |
| 5.0 | 9970.2 |
| 6.0 | 9970.0 |

Saturated silver chloride solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 16.0 | 9611.6 | 14.0 | 9613.4 |
| 17.0 | 9610.8 | 15.0 | 9612.7 |
| 18.0 | 9610.5 | 16.0 | 9612.4 |
| 20.0 | 9610.2 | 18.0 | 9612.2 |
| 21.0 | 9609.9 | 19.0 | 9611.8 |
| 22.0 | 9609.2 | 21.5 | 9611.0 |
| 24.0 | 9608.7 | 23.5 | 9610.1 |
| | | 27.0 | 9608.9 |
| | | 28.0 | 9608.8 |

EXPERIMENT 20.

H. Conductivity water.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 2.0 | 9872.1 |
| 3.0 | 9956.3 |
| 4.0 | 9972.9 |
| 5.0 | 9972.9 |
| 6.0 | 9972.8 |
| 8.0 | 9972.7 |

Saturated silver chloride solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 16.0 | 9615.5 | 14.0 | 9614.9 |
| 17.0 | 9614.9 | 15.0 | 9613.9 |
| 18.0 | 9614.1 | 16.0 | 9613.4 |
| 19.5 | 9613.8 | 18.0 | 9612.9 |
| 21.5 | 9612.7 | 19.0 | 9612.3 |
| 23.5 | 9612.2 | 20.5 | 9611.3 |
| 25.0 | 9611.3 | 23.5 | 9609.9 |
| | | 27.0 | 9608.7 |

F. Silver bromide data at 5°C.

EXPERIMENT 21.

H. Conductivity water.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 3.0 | 9960.1 |
| 4.0 | 9969.5 |
| 5.0 | 9969.3 |
| 6.0 | 9969.2 |
| 6.5 | 9969.2 |
| 8.0 | 9969.0 |

Saturated silver bromide solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.5 | 9877.9 | 3.0 | 9937.6 |
| 3.0 | 9948.7 | 4.0 | 9949.3 |
| 4.0 | 9952.6 | 5.0 | 9952.0 |
| 5.0 | 9953.8 | 6.0 | 9953.0 |
| 8.0 | 9953.9 | 6.75 | 9953.3 |
| 9.25 | 9953.2 | 7.5 | 9953.4 |
| 13.0 | 9951.8 | 12.0 | 9951.5 |
| 14.0 | 9951.5 | 13.0 | 9951.2 |
| 24.0 | 9947.6 | 14.0 | 9951.0 |
| | | 15.0 | 9950.4 |

EXPERIMENT 22.

H. Conductivity water.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 3.0 | 9967.1 |
| 4.0 | 9971.3 |
| 4.5 | 9971.7 |
| 5.0 | 9971.7 |
| 5.5 | 9971.6 |
| 6.0 | 9971.6 |
| 7.5 | 9971.4 |

Saturated silver bromide solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 2.0 | 9913.5 | 2.0 | 9906.3 |
| 3.0 | 9947.0 | 3.0 | 9938.2 |
| 4.0 | 9951.8 | 4.0 | 9945.7 |
| 5.5 | 9954.8 | 5.0 | 9953.0 |
| 6.5 | 9955.7 | 7.0 | 9954.5 |
| 7.5 | 9955.7 | 8.0 | 9954.6 |
| 14.5 | 9953.2 | 9.0 | 9954.3 |
| 16.0 | 9952.6 | 17.0 | 9950.9 |
| 18.0 | 9952.1 | 18.0 | 9950.7 |
| 21.0 | 9951.0 | 19.5 | 9949.0 |

EXPERIMENT 23.

H. Conductivity water.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 2.0 | 9922.5 |
| 3.0 | 9967.9 |
| 4.5 | 9970.4 |
| 5.0 | 9970.5 |
| 6.0 | 9970.4 |
| 7.0 | 9970.2 |
| 8.0 | 9970.2 |

Saturated silver bromide solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 9.0 | 9954.6 | 10.0 | 9953.4 |
| 11.0 | 9954.0 | 11.0 | 9953.0 |
| 12.0 | 9953.7 | 12.0 | 9952.8 |
| 13.0 | 9953.4 | 13.0 | 9952.5 |
| 14.0 | 9953.2 | 14.0 | 9952.2 |
| 16.0 | 9952.7 | 16.0 | 9951.3 |
| 17.5 | 9952.3 | 18.0 | 9950.6 |

EXPERIMENT 24.

L. Conductivity water.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 3.0 | 9963.9 |
| 4.0 | 9969.6 |
| 5.0 | 9969.7 |
| 6.0 | 9969.5 |
| 6.5 | 9969.5 |
| 12.5 | 9968.9 |

Saturated silver bromide solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 10.0 | 9952.2 | 10.0 | 9951.2 |
| 11.0 | 9951.5 | 11.0 | 9950.6 |
| 13.0 | 9950.9 | 12.0 | 9950.4 |
| 14.0 | 9950.4 | 14.0 | 9949.5 |
| 15.5 | 9950.0 | 15.0 | 9949.0 |
| 18.0 | 9948.9 | 16.0 | 9948.3 |
| 20.0 | 9947.8 | 18.0 | 9947.5 |
| 22.0 | 9947.2 | 19.5 | 9947.2 |

G. Silver chloride data at 15°C.

EXPERIMENT 25.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 2.0 | 9952.1 | 3.5 | 9962.5 |
| 3.0 | 9961.5 | 4.0 | 9962.6 |
| 3.5 | 9962.5 | 4.5 | 9962.5 |
| 4.0 | 9962.7 | 5.5 | 9962.2 |
| 5.0 | 9962.5 | 6.5 | 9962.1 |
| 6.0 | 9960.8 | | |

Saturated silver chloride solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 0.0 | 9490.0 | 0.0 | 9330.0 |
| 2.0 | 9551.1 | 2.0 | 9411.5 |
| 3.5 | 9425.4 | 4.0 | 9330.5 |
| 7.0 | 9292.7 | 6.0 | 9274.0 |
| 8.0 | 9271.5 | 8.0 | 9252.9 |
| 18.0 | 9221.6 | 9.5 | 9242.5 |
| 19.0 | 9220.4 | 13.0 | 9230.2 |
| 20.0 | 9218.5 | 14.0 | 9228.0 |
| 22.0 | 9217.2 | 23.0 | 9218.8 |
| 23.0 | 9216.6 | 24.0 | 9217.8 |

Saturated silver chloride solution. (cont'd.)

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 24.0 | 9215.7 | 25.0 | 9215.9 |
| 26.0 | 9213.2 | 26.0 | 9215.1 |
| 28.0 | 9211.1 | 28.0 | 9213.4 |

EXPERIMENT 26.

H. Conductivity water.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 2.0 | 9951.1 |
| 3.0 | 9953.8 |
| 3.5 | 9955.0 |
| 4.0 | 9957.5 |
| 4.5 | 9957.1 |
| 5.0 | 9957.1 |
| 6.0 | 9956.8 |
| 8.0 | 9956.2 |

Saturated silver chloride solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 12.0 | 9220.9 | 12.0 | 9220.8 |
| 13.0 | 9219.4 | 13.0 | 9220.3 |
| 14.0 | 9218.3 | 15.0 | 9217.8 |
| 16.0 | 9217.0 | 16.0 | 9216.1 |
| 17.0 | 9215.6 | 17.5 | 9214.5 |
| 19.0 | 9214.1 | 18.5 | 9213.4 |
| 21.5 | 9210.9 | 20.0 | 9211.6 |
| 25.0 | 9207.6 | 22.0 | 9210.0 |
| 26.0 | 9207.4 | 23.0 | 9208.9 |

EXPERIMENT 27.

H. Conductivity water.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 2.0 | 9948.2 |
| 3.0 | 9951.9 |
| 3.5 | 9953.0 |
| 4.0 | 9954.0 |
| 5.0 | 9953.9 |
| 6.0 | 9953.5 |

Saturated silver chloride solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 14.0 | 9229.4 | 12.0 | 9225.5 |
| 16.0 | 9227.4 | 14.0 | 9224.6 |
| 17.0 | 9226.6 | 15.0 | 9223.4 |
| 19.0 | 9223.5 | 16.0 | 9221.7 |
| 20.0 | 9223.2 | 17.0 | 9220.6 |
| 21.5 | 9222.1 | 18.5 | 9219.9 |
| 23.0 | 9220.2 | 19.5 | 9217.7 |
| 25.0 | 9218.5 | 22.0 | 9216.1 |

EXPERIMENT 28.

L. Conductivity water.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 2.0 | 9949.4 |
| 3.0 | 9953.5 |
| 4.0 | 9959.1 |
| 5.0 | 9958.7 |
| 6.0 | 9958.5 |
| 7.0 | 9958.4 |

Saturated silver chloride solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 12.0 | 9233.5 | 12.0 | 9230.0 |
| 13.0 | 9231.9 | 14.0 | 9227.4 |
| 15.0 | 9230.0 | 15.0 | 9227.0 |
| 16.0 | 9228.5 | 17.0 | 9226.0 |
| 17.5 | 9228.0 | 18.0 | 9224.2 |
| 21.0 | 9225.2 | 21.0 | 9222.6 |
| 22.0 | 9223.6 | 24.0 | 9219.3 |
| 23.0 | 9222.9 | | |

H. Silver bromide data at 15°C.

EXPERIMENT 29.

L. Conductivity water.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 2.0 | 9944.6 |
| 3.0 | 9951.4 |
| 3.5 | 9952.0 |
| 4.75 | 9953.8 |
| 6.25 | 9953.7 |
| 10.75 | 9953.1 |
| 14.25 | 9949.0 |

Saturated silver bromide solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 2.0 | 9913.7 | 1.5 | 9899.0 |
| 3.25 | 9917.7 | 2.25 | 9910.3 |
| 4.0 | 9917.5 | 3.25 | 9914.6 |
| 5.75 | 9916.0 | 3.75 | 9915.6 |
| 6.75 | 9915.5 | 5.0 | 9916.5 |
| 7.75 | 9915.0 | 6.75 | 9915.7 |
| 19.0 | 9907.5 | 9.25 | 9915.0 |
| 20.5 | 9906.1 | 20.0 | 9911.5 |
| 22.0 | 9905.6 | 22.0 | 9910.5 |

EXPERIMENT 30.

L. Conductivity water.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 2.0 | 9955.3 |
| 3.25 | 9958.7 |
| 5.75 | 9958.7 |
| 7.75 | 9958.5 |
| 8.75 | 9958.4 |
| 9.75 | 9958.4 |

Saturated silver bromide solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 3.0 | 9883.7 | 2.25 | 9896.5 |
| 4.0 | 9890.7 | 6.0 | 9920.5 |
| 6.5 | 9920.7 | 8.25 | 9920.0 |
| 8.0 | 9919.9 | 10.75 | 9918.0 |
| 16.5 | 9914.5 | 23.75 | 9908.0 |
| 18.5 | 9913.7 | 25.75 | 9906.2 |

EXPERIMENT 31.

H. Conductivity water.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 1.75 | 9960.0 |
| 2.5 | 9963.0 |
| 4.0 | 9963.7 |
| 5.0 | 9963.7 |
| 6.75 | 9963.4 |
| 9.25 | 9962.5 |
| 11.25 | 9959.9 |

Saturated silver bromide solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 2.0 | 9900.5 | 2.5 | 9913.6 |
| 3.0 | 9919.7 | 3.5 | 9925.0 |
| 4.0 | 9927.0 | 5.0 | 9926.9 |
| 5.0 | 9927.5 | 6.5 | 9926.4 |
| 6.0 | 9927.7 | 7.5 | 9925.0 |
| 7.0 | 9926.9 | 11.0 | 9923.1 |
| 8.5 | 9926.2 | 21.0 | 9917.9 |
| 11.5 | 9925.5 | 22.0 | 9917.3 |
| 14.5 | 9923.5 | | |
| 24.5 | 9919.6 | | |

EXPERIMENT 32.

H. Conductivity water.

| Time from start of experiment (hours) | resistance (ohms) |
|--|-------------------|
| 2.0 | 9951.6 |
| 3.0 | 9959.3 |
| 4.0 | 9959.9 |
| 4.5 | 9959.9 |
| 5.5 | 9959.7 |
| 8.5 | 9959.3 |
| 19.5 | 9956.6 |

Saturated silver bromide solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 2.0 | 9905.0 | 2.5 | 9915.1 |
| 3.0 | 9917.5 | 3.5 | 9921.6 |
| 4.0 | 9923.9 | 4.5 | 9923.3 |
| 5.0 | 9924.9 | 6.0 | 9923.5 |
| 6.5 | 9925.1 | 7.5 | 9922.9 |
| 7.5 | 9924.3 | 9.0 | 9922.3 |
| 8.5 | 9924.1 | 12.5 | 9920.1 |
| 10.0 | 9923.8 | 23.5 | 9915.5 |
| 13.5 | 9922.2 | | |
| 23.5 | 9918.8 | | |

I. Silver chloride data at 35°C.

EXPERIMENT 33.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9880.6 | 1.0 | 9872.1 |
| 1.5 | 9886.0 | 1.5 | 9877.7 |
| 2.0 | 9888.5 | 2.0 | 9883.0 |
| 2.5 | 9888.1 | 2.5 | 9882.6 |
| 3.0 | 9887.6 | 3.0 | 9882.1 |
| 4.0 | 9886.7 | 4.0 | 9881.2 |

Saturated silver chloride solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 0.0 | 42,900 | 0.0 | 36,100 |
| 1.0 | 44,045 | 2.0 | 37,505 |
| 3.0 | 38,765 | 4.0 | 35,497 |
| 5.0 | 36,245 | 6.0 | 34,311 |
| 7.0 | 34,785 | 8.0 | 33,761 |
| 9.0 | 34,115 | 10.0 | 33,366 |
| 11.0 | 33,605 | 11.0 | 33,293 |
| 12.0 | 33,347 | 12.0 | 33,254 |
| 13.0 | 33,295 | 22.0 | 32,605 |

Saturated silver chloride solution. (cont'd.)

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 14.0 | 33,218 | 23.0 | 32,520 |
| 23.0 | 32,698 | 24.0 | 32,460 |
| 24.0 | 32,631 | | |
| 25.0 | 32,575 | | |

EXPERIMENT 34.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9878.3 | 1.0 | 9863.5 |
| 1.5 | 9880.9 | 1.5 | 9872.9 |
| 2.0 | 9883.5 | 2.0 | 9876.7 |
| 2.5 | 9883.1 | 2.5 | 9876.2 |
| 3.0 | 9882.6 | 3.0 | 9875.8 |
| 4.0 | 9881.6 | 4.0 | 9874.7 |

Saturated silver chloride solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 10.0 | 33,586 | 9.0 | 33,423 |
| 11.0 | 33,428 | 10.0 | 33,343 |
| 12.0 | 33,334 | 11.0 | 33,268 |
| 14.0 | 33,226 | 12.0 | 33,216 |
| 15.0 | 33,147 | 14.0 | 33,128 |
| 17.0 | 33,044 | 15.0 | 33,077 |
| 19.0 | 32,933 | 17.5 | 32,956 |
| 22.0 | 32,795 | 19.5 | 32,827 |

EXPERIMENT 35.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9879.8 | 1.0 | 9871.9 |
| 1.5 | 9883.9 | 1.5 | 9878.0 |
| 2.0 | 9891.6 | 2.0 | 9881.5 |
| 2.5 | 9891.0 | 2.5 | 9881.1 |
| 3.0 | 9890.5 | 3.0 | 9880.5 |
| 4.0 | 9889.6 | 4.5 | 9879.0 |

Saturated silver chloride solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 12.0 | 33,242 | 11.0 | 33,242 |
| 13.0 | 33,186 | 12.0 | 33,199 |
| 14.0 | 33,106 | 14.0 | 33,072 |
| 15.0 | 33,041 | 15.0 | 33,005 |
| 17.0 | 32,940 | 16.0 | 32,926 |
| 19.0 | 32,816 | 17.0 | 32,857 |
| 21.0 | 32,668 | 18.0 | 32,794 |
| | | 20.0 | 32,693 |

EXPERIMENT 36.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9873.1 | 1.0 | 9864.7 |
| 1.5 | 9882.9 | 1.5 | 9875.7 |
| 2.0 | 9886.5 | 2.0 | 9878.6 |
| 2.5 | 9885.9 | 2.5 | 9878.0 |
| 3.0 | 9885.6 | 3.0 | 9877.6 |
| 4.0 | 9884.5 | 4.0 | 9876.7 |
| 5.0 | 9883.6 | | |

Saturated silver chloride solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 11.0 | 33,396 | 10.0 | 33,326 |
| 12.0 | 33,343 | 11.0 | 33,265 |
| 13.0 | 33,289 | 12.0 | 33,182 |
| 15.0 | 33,164 | 13.0 | 33,154 |
| 16.0 | 33,114 | 15.0 | 33,044 |
| 17.0 | 33,058 | 17.0 | 32,902 |
| 18.0 | 33,009 | 18.5 | 32,845 |
| 20.5 | 32,885 | 21.0 | 32,693 |
| 24.0 | 32,683 | | |

J. Silver bromide data at 35°C.

EXPERIMENT 37.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9885.0 | 1.0 | 9881.5 |
| 1.5 | 9892.2 | 1.5 | 9889.7 |
| 2.0 | 9893.8 | 2.0 | 9890.5 |
| 2.5 | 9893.0 | 2.5 | 9890.0 |
| 4.0 | 9891.4 | 4.0 | 9888.6 |
| 6.0 | 9889.5 | | |

Saturated silver bromide solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9755.5 | 1.0 | 9716.5 |
| 1.5 | 9751.0 | 1.5 | 9723.7 |
| 1.65 | 9730.5 | 2.5 | 9719.0 |
| 3.5 | 9721.4 | 3.5 | 9715.0 |
| 4.5 | 9712.7 | 4.5 | 9711.0 |
| 6.0 | 9706.0 | 6.5 | 9701.6 |
| 7.5 | 9700.5 | 16.5 | 9759.6 |
| 12.5 | 9677.5 | | |

EXPERIMENT 38.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9896.9 | 1.0 | 9891.5 |
| 1.5 | 9901.6 | 1.5 | 9896.1 |
| 2.0 | 9902.5 | 2.0 | 9895.5 |
| 2.5 | 9903.0 | 2.5 | 9894.7 |
| 3.5 | 9901.1 | 3.0 | 9893.8 |
| | | 4.0 | 9892.9 |

Saturated silver bromide solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9757.6 | 1.0 | 9731.6 |
| 1.5 | 9749.5 | 1.5 | 9729.3 |
| 2.0 | 9741.5 | 2.0 | 9727.5 |
| 2.5 | 9735.4 | 2.5 | 9725.7 |
| 3.0 | 9731.8 | 3.0 | 9723.3 |
| 4.0 | 9729.3 | 4.0 | 9719.6 |
| 5.0 | 9725.6 | 5.0 | 9716.4 |
| 6.0 | 9721.7 | 6.0 | 9711.8 |
| 8.0 | 9715.6 | 8.0 | 9704.6 |
| 10.0 | 9709.3 | 10.0 | 9695.8 |
| 14.0 | 9695.8 | | |

EXPERIMENT 39.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9891.6 | 1.0 | 9882.6 |
| 2.0 | 9895.5 | 1.5 | 9884.9 |
| 2.5 | 9895.5 | 2.0 | 9888.5 |
| 3.5 | 9894.2 | 2.5 | 9888.1 |
| 4.5 | 9893.1 | 3.5 | 9887.2 |

Saturated silver bromide solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9754.0 | 1.0 | 9700.5 |
| 1.5 | 9741.6 | 1.5 | 9713.8 |
| 2.5 | 9726.5 | 2.25 | 9710.1 |
| 3.5 | 9714.5 | 3.0 | 9705.9 |
| 5.0 | 9702.7 | 6.0 | 9687.0 |
| 5.5 | 9699.7 | 10.0 | 9662.5 |
| 8.0 | 9687.3 | 20.0 | 9601.6 |
| 10.0 | 9675.6 | | |

EXPERIMENT 40.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 0.5 | 9900.1 | 1.5 | 9894.0 |
| 2.0 | 9902.3 | 2.0 | 9897.5 |
| 2.5 | 9901.9 | 2.5 | 9897.3 |
| 3.5 | 9901.2 | 3.0 | 9896.7 |
| 5.5 | 9899.8 | 5.0 | 9894.9 |

Saturated silver bromide solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9748.5 | 1.0 | 9735.0 |
| 1.5 | 9744.5 | 1.5 | 9732.0 |
| 2.0 | 9739.0 | 2.0 | 9726.5 |
| 2.5 | 9729.5 | 2.5 | 9723.5 |
| 3.25 | 9723.2 | 5.5 | 9705.6 |
| 5.25 | 9713.3 | 7.0 | 9697.1 |
| 7.25 | 9701.9 | | |
| 9.25 | 9693.0 | | |

K. Silver chloride data at 45°C.

EXPERIMENT 41.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9856.1 | 1.0 | 9851.1 |
| 1.5 | 9857.6 | 1.5 | 9848.5 |
| 2.5 | 9852.7 | 2.0 | 9846.1 |
| 3.5 | 9848.5 | 3.5 | 9838.5 |
| 4.5 | 9843.8 | 7.0 | 9821.6 |
| 5.5 | 9839.6 | | |

Saturated silver chloride solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 0.0 | 24,750 | 0.0 | 23,990 |
| 3.0 | 26,207 | 1.0 | 24,605 |
| 4.0 | 23,723 | 4.0 | 21,464 |
| 6.0 | 20,940 | 8.0 | 19,104 |
| 8.0 | 19,604 | 9.0 | 19,008 |
| 10.0 | 19,106 | 10.0 | 18,936 |
| 11.0 | 19,030 | 12.0 | 18,813 |
| 12.0 | 19,001 | 21.0 | 18,224 |
| 14.0 | 18,855 | 22.0 | 18,153 |
| 16.0 | 18,728 | | |

EXPERIMENT 42.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9851.5 | 1.0 | 9849.5 |
| 1.5 | 9857.7 | 2.0 | 9847.6 |
| 2.0 | 9855.1 | 2.5 | 9844.7 |
| 2.5 | 9852.7 | 3.5 | 9840.1 |
| 3.5 | 9847.9 | 4.5 | 9835.5 |
| 4.5 | 9843.2 | 5.5 | 9830.7 |

Saturated silver chloride solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 10.0 | 19,204 | 12.0 | 18,929 |
| 11.0 | 19,129 | 13.0 | 18,875 |
| 12.0 | 19,078 | 14.0 | 18,785 |
| 13.0 | 19,041 | 15.0 | 18,753 |
| 14.0 | 18,985 | 16.0 | 18,686 |
| 15.0 | 18,923 | 17.0 | 18,627 |
| 16.0 | 18,874 | 18.0 | 18,538 |
| 17.0 | 18,823 | | |

EXPERIMENT 43.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9850.2 | 1.0 | 9846.1 |
| 1.5 | 9851.5 | 1.5 | 9843.6 |
| 2.0 | 9849.1 | 2.0 | 9840.8 |
| 2.5 | 9846.6 | 2.5 | 9838.5 |
| 4.0 | 9839.2 | 3.5 | 9833.6 |
| 5.0 | 9834.4 | 7.0 | 9816.1 |

Saturated silver chloride solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 10.0 | 19,245 | 10.0 | 19,078 |
| 11.0 | 19,140 | 12.0 | 18,977 |
| 12.0 | 19,097 | 14.0 | 18,868 |
| 14.0 | 19,027 | 15.0 | 18,812 |
| 15.0 | 18,978 | 16.0 | 18,754 |
| 16.0 | 18,930 | 18.5 | 18,652 |
| 17.0 | 18,887 | 20.0 | 18,554 |
| 19.0 | 18,784 | | |

EXPERIMENT 44.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9851.6 | 1.0 | 9846.9 |
| 1.5 | 9853.5 | 1.5 | 9844.5 |
| 2.0 | 9851.5 | 2.0 | 9842.2 |
| 2.5 | 9849.3 | 3.0 | 9837.4 |
| 3.5 | 9844.5 | 4.5 | 9829.9 |
| 4.5 | 9840.6 | | |

Saturated silver chloride solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 10.0 | 19,279 | 10.0 | 19,106 |
| 11.0 | 19,193 | 11.0 | 19,032 |
| 12.0 | 19,140 | 12.0 | 19,003 |
| 13.0 | 19,079 | 13.0 | 18,893 |
| 14.0 | 19,030 | 14.0 | 18,839 |
| 16.0 | 18,954 | 16.0 | 18,740 |

L. Silver bromide data at 45°C.

EXPERIMENT 45.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 0.5 | 9781.9 | 0.5 | 9801.5 |
| 1.0 | 9851.5 | 1.25 | 9848.5 |
| 1.5 | 9856.5 | 1.5 | 9849.5 |
| 2.0 | 9855.6 | 2.0 | 9848.8 |
| 3.0 | 9851.5 | 2.5 | 9846.0 |
| 5.0 | 9842.5 | 3.0 | 9843.0 |
| | | 4.5 | 9832.5 |

Saturated silver bromide solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 0.5 | 9547.7 | 0.5 | 9568.9 |
| 1.0 | 9615.5 | 1.0 | 9562.0 |
| 1.5 | 9593.7 | 2.5 | 9515.2 |
| 2.0 | 9567.7 | 3.0 | 9502.5 |
| 2.5 | 9545.9 | 4.0 | 9489.1 |
| 5.0 | 9483.6 | 5.5 | 9467.7 |
| 6.0 | 9471.9 | 6.5 | 9452.8 |
| 7.0 | 9457.7 | 8.5 | 9426.8 |
| 8.0 | 9444.6 | 11.5 | 9384.6 |
| 9.5 | 9435.7 | | |

EXPERIMENT 46.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9858.0 | 0.5 | 9763.5 |
| 1.5 | 9866.0 | 1.0 | 9853.0 |
| 2.0 | 9864.9 | 1.5 | 9855.8 |
| 3.0 | 9860.5 | 2.0 | 9855.0 |
| 5.5 | 9860.0 | 2.5 | 9855.5 |
| | | 3.5 | 9848.5 |

Saturated silver bromide solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9583.5 | 0.75 | 9542.7 |
| 1.5 | 9560.7 | 1.25 | 9562.3 |
| 2.0 | 9537.7 | 1.5 | 9557.0 |
| 2.5 | 9522.9 | 2.0 | 9540.0 |
| 5.75 | 9506.3 | 3.0 | 9525.1 |
| 5.0 | 9490.0 | 4.0 | 9508.6 |
| 7.0 | 9466.7 | 5.0 | 9500.0 |
| 9.0 | 9441.3 | 6.0 | 9490.4 |
| | | 7.0 | 9481.3 |
| | | 10.5 | 9447.8 |

EXPERIMENT 47.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9851.8 | 1.0 | 9841.4 |
| 1.5 | 9856.0 | 1.5 | 9849.9 |
| 2.5 | 9855.5 | 2.0 | 9849.5 |
| 3.0 | 9853.6 | 2.5 | 9847.6 |
| 3.5 | 9851.9 | 7.5 | 9825.7 |
| 4.0 | 9849.4 | | |

Saturated silver bromide solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9568.5 | 0.5 | 9506.1 |
| 1.5 | 9542.6 | 1.75 | 9527.5 |
| 2.0 | 9525.1 | 2.25 | 9511.1 |
| 3.5 | 9507.7 | 2.75 | 9498.8 |
| 4.0 | 9501.6 | 3.75 | 9485.1 |
| 5.0 | 9490.6 | 5.0 | 9466.3 |
| 6.0 | 9478.0 | 6.0 | 9451.8 |
| 7.0 | 9467.3 | 11.0 | 9371.5 |
| 9.0 | 9444.1 | | |

EXPERIMENT 48.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.5 | 9851.5 | 1.0 | 9832.9 |
| 2.0 | 9851.5 | 1.5 | 9843.5 |
| 2.75 | 9848.7 | 2.0 | 9843.3 |
| 4.0 | 9845.8 | 3.0 | 9840.7 |
| 5.0 | 9839.4 | 3.75 | 9837.5 |

Saturated silver bromide solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9616.8 | 1.0 | 9609.5 |
| 2.0 | 9554.7 | 1.5 | 9586.6 |
| 3.0 | 9521.7 | 2.0 | 9566.0 |
| 3.5 | 9506.3 | 2.5 | 9544.3 |
| 4.5 | 9491.5 | 4.0 | 9515.1 |
| 5.5 | 9480.5 | 5.25 | 9493.7 |
| 6.5 | 9469.5 | 6.0 | 9493.8 |
| 11.3 | 9420.3 | 7.5 | 9481.8 |
| | | 10.5 | 9456.6 |

M. Silver chloride data at 55°C.

EXPERIMENT 49.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9792.7 | 1.0 | 9780.9 |
| 1.5 | 9788.5 | 1.5 | 9775.4 |
| 2.0 | 9783.6 | 2.0 | 9770.5 |
| 2.5 | 9778.4 | 2.5 | 9764.7 |
| 3.0 | 9773.3 | 3.0 | 9759.1 |
| 4.0 | 9763.1 | 4.0 | 9747.7 |

Saturated silver chloride solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 0.0 | 6300.0 | 3.0 | 5426.6 |
| 0.5 | 6356.6 | 3.5 | 5382.2 |
| 9.0 | 5257.0 | 4.5 | 5346.3 |
| 10.0 | 5236.6 | 5.0 | 5325.6 |
| 11.0 | 5223.9 | 6.0 | 5299.1 |
| 12.0 | 5211.3 | 7.0 | 5282.3 |
| 14.0 | 5197.5 | 8.0 | 5257.7 |
| 15.0 | 5184.6 | 9.0 | 5236.9 |
| 16.0 | 5178.9 | 10.0 | 5221.4 |

Saturated silver chloride solution (cont'd).

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 17.0 | 5170.0 | 13.0 | 5191.9 |
| 18.0 | 5159.0 | 14.0 | 5184.5 |
| | | 15.0 | 5170.3 |
| | | 25.0 | 5080.3 |

EXPERIMENT 50.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9794.5 | 1.0 | 9784.5 |
| 1.5 | 9790.5 | 1.5 | 9779.6 |
| 2.0 | 9785.6 | 2.0 | 9775.0 |
| 3.0 | 9775.9 | 3.0 | 9765.3 |
| 4.0 | 9765.5 | 6.5 | 9730.2 |

Saturated silver chloride solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 6943.9 | 1.0 | 6150.2 |
| 9.0 | 5286.6 | 4.0 | 5421.9 |
| 10.0 | 5256.4 | 5.0 | 5357.2 |
| 11.0 | 5233.9 | 6.0 | 5301.5 |
| 12.0 | 5216.2 | 7.0 | 5276.3 |
| 13.0 | 5202.5 | 8.0 | 5251.5 |
| 14.0 | 5193.6 | 9.5 | 5234.2 |
| 15.0 | 5189.2 | 11.0 | 5222.4 |
| 24.0 | 5109.6 | 13.0 | 5205.6 |
| | | 14.0 | 5197.5 |

EXPERIMENT 51.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9786.8 | 1.0 | 9773.5 |
| 1.5 | 9782.5 | 1.5 | 9768.6 |
| 2.0 | 9777.8 | 2.0 | 9763.0 |
| 3.0 | 9768.3 | 3.0 | 9755.5 |
| 3.5 | 9763.5 | 6.5 | 9719.5 |
| 4.0 | 9758.7 | | |
| 5.0 | 9749.0 | | |

175.

Saturated silver chloride solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 0.0 | 18,521 | 0.0 | 14,108 |
| 9.0 | 11,333 | 10.0 | 10,920 |
| 10.0 | 11,057 | 11.0 | 10,865 |
| 11.0 | 10,931 | 12.0 | 10,824 |
| 12.0 | 10,873 | 14.0 | 10,751 |
| 14.0 | 10,793 | 15.0 | 10,711 |
| 15.0 | 10,765 | 16.5 | 10,633 |
| 16.0 | 10,722 | 18.0 | 10,590 |
| 17.0 | 10,682 | 20.0 | 10,512 |
| 18.0 | 10,640 | 22.0 | 10,435 |
| 20.0 | 10,575 | | |

EXPERIMENT 52.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9784.0 | 1.0 | 9771.9 |
| 1.5 | 9781.6 | 1.5 | 9767.5 |
| 2.0 | 9776.5 | 2.0 | 9762.9 |
| 2.5 | 9771.2 | 3.0 | 9753.8 |
| 3.5 | 9761.1 | 4.0 | 9745.1 |
| 4.5 | 9751.3 | 5.0 | 9735.3 |

Saturated silver chloride solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 0.0 | 16,990 | 0.0 | 13,350 |
| 1.0 | 17,657 | 1.0 | 14,058 |
| 3.0 | 13,820 | 5.0 | 12,252 |
| 4.0 | 12,342 | 10.0 | 10,979 |
| 5.0 | 12,182 | 11.0 | 10,938 |
| 6.0 | 11,800 | 12.0 | 10,883 |
| 7.0 | 11,585 | 13.0 | 10,863 |
| 9.0 | 11,243 | 14.0 | 10,804 |
| 10.0 | 11,123 | 15.0 | 10,772 |
| 11.0 | 11,052 | 16.0 | 10,748 |
| 12.0 | 11,021 | 18.0 | 10,673 |
| 13.5 | 10,980 | | |
| 14.5 | 10,941 | | |
| 20.0 | 10,794 | | |

N. Silver bromide data at 55°C.

EXPERIMENT 53.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 0.75 | 9776.6 | 0.5 | 9750.7 |
| 1.0 | 9784.0 | 1.0 | 9762.0 |
| 1.5 | 9779.5 | 1.5 | 9757.0 |
| 2.0 | 9775.1 | 2.25 | 9749.9 |
| 3.0 | 9766.3 | 3.0 | 9743.5 |
| 5.0 | 9750.9 | 4.0 | 9734.2 |

Saturated silver bromide solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 0.0 | 9260.0 | 0.0 | 9170.0 |
| 0.5 | 9311.6 | 0.5 | 9201.5 |
| 1.0 | 9252.1 | 1.5 | 9181.5 |
| 1.5 | 9196.7 | 2.5 | 9151.0 |
| 1.75 | 9176.6 | 3.0 | 9128.9 |
| 2.0 | 9168.7 | 5.75 | 9067.6 |
| 3.0 | 9144.6 | 6.75 | 9051.8 |

Saturated silver bromide solution (cont'd.)

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 3.5 | 9132.2 | 10.5 | 8976.7 |
| 4.0 | 9124.5 | 11.5 | 8952.5 |
| 10.0 | 8985.7 | | |
| 11.0 | 8966.6 | | |

EXPERIMENT 54.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9772.6 | 1.0 | 9751.6 |
| 1.5 | 9772.0 | 1.5 | 9757.9 |
| 2.0 | 9767.2 | 2.0 | 9754.3 |
| 3.0 | 9748.3 | 2.5 | 9749.6 |
| 6.0 | 9720.7 | 4.0 | 9736.7 |
| 7.0 | 9712.1 | 5.0 | 9727.8 |

Saturated silver bromide solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 0.5 | 9194.7 | 0.5 | 9156.0 |
| 1.0 | 9191.0 | 1.0 | 9186.2 |
| 2.0 | 9159.7 | 2.0 | 9166.4 |
| 2.5 | 9146.9 | 2.5 | 9161.4 |
| 3.0 | 9138.6 | 4.0 | 9141.7 |
| 4.0 | 9121.2 | 6.0 | 9119.6 |
| 5.0 | 9102.3 | 12.0 | 9052.3 |
| 7.5 | 9057.0 | 13.5 | 9034.5 |
| 10.0 | 9011.4 | | |

EXPERIMENT 55.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9773.5 | 1.0 | 9757.8 |
| 1.5 | 9784.9 | 1.5 | 9773.6 |
| 3.5 | 9766.6 | 2.0 | 9769.5 |
| 5.0 | 9758.0 | 2.5 | 9765.1 |
| 6.0 | 9748.7 | 4.0 | 9753.5 |
| | | 5.0 | 9745.6 |

Saturated silver bromide solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9296.7 | 0.5 | 9231.3 |
| 1.5 | 9221.7 | 1.0 | 9201.5 |
| 2.0 | 9181.3 | 1.5 | 9176.3 |
| 2.5 | 9161.9 | 2.0 | 9160.4 |
| 3.0 | 9146.9 | 2.5 | 9141.8 |
| 3.5 | 9136.3 | 3.0 | 9131.7 |
| 4.0 | 9126.2 | 4.0 | 9109.4 |
| 5.0 | 9109.5 | 5.0 | 9091.3 |
| 6.0 | 9084.2 | 6.0 | 9064.0 |
| 7.0 | 9061.8 | 8.0 | 9025.6 |
| 8.0 | 9046.0 | | |
| 10.0 | 9004.1 | | |

EXPERIMENT 56.

Conductivity water.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 1.0 | 9770.0 | 1.0 | 9752.6 |
| 1.5 | 9774.0 | 1.5 | 9761.9 |
| 2.0 | 9769.5 | 2.0 | 9757.5 |
| 2.5 | 9765.2 | 3.0 | 9748.7 |
| 3.5 | 9756.5 | 4.0 | 9739.6 |
| 4.5 | 9747.8 | 5.0 | 9731.0 |
| | | 6.0 | 9722.3 |

Saturated silver bromide solution.

| L. | | H. | |
|---------------------------------------|----------------------|---------------------------------------|----------------------|
| Time from start of expt. (hrs.) | resistance (ohms) | Time from start of expt. (hrs.) | resistance (ohms) |
| 0.5 | 9231.7 | 0.5 | 9206.4 |
| 1.0 | 9241.3 | 1.0 | 9196.6 |
| 1.5 | 9211.2 | 1.5 | 9176.3 |
| 2.0 | 9182.2 | 2.0 | 9159.7 |
| 3.0 | 9151.7 | 3.0 | 9140.6 |
| 4.0 | 9126.0 | 4.0 | 9127.5 |
| 5.0 | 9107.6 | 5.0 | 9115.4 |
| 6.0 | 9092.5 | 7.0 | 9078.9 |
| 7.0 | 9074.9 | 9.0 | 9053.9 |
| 10.0 | 9019.0 | 10.0 | 9034.5 |

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