A CONDUCTIMETRIC INVESTIGATION
OF PHENOMENA IN
EXTREMELY DILUTE AQUEOUS SOLUTIONS

A DISSERTATION
submitted in fulfilment of the requirements
for the degree of
DOCTOR OF PHILOSOPHY
in the Faculty of Science of
RHODES UNIVERSITY

by

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B.Sc. (Hons.) (S.A.)

Pretoria September 1956

ACKNOWLEDGMENTS

The author wishes sincerely to express his gratitude and appreciation to the following persons:-

Prof. W.F. Barker, for his friendly guidance and constant encouragement;

Prof. J.A. Gledhill, for supervising this thesis and for his invaluable criticism and advice;

Dr. A. Faure, for helpful discussions and for his generous assistance in the typing of this manuscript;

Mr. F. van de Water and Mr. G.W. Randell, for ready assistance with the glass-blowing and, in particular, for the patient hours which they spent in making leak-proof conductance cells;

Mr. F.C. Zulch, for his excellent reproduction of the diagrams;

Dr. J.R. Parrish and Mr. J.F. de Wet, M.Sc., for their assistance with the photographs;

Miss P.M. Hughes, B.Sc., for her willing assistance in the tedious task of proofreading this manuscript;

and to all the other people who, by their help in some small way, have each contributed towards the final completion of this thesis.

A grant enabling this investigation to be undertaken was received from the South African Council for Scientific and Industrial Research, to whom the author tenders his thanks for this financial assistance.

SUMMARY

1. The apparatus used in this investigation is fully described, and a new method is outlined for the calibration of bridge resistances "in situ".

2. A chart is given for the accurate correction of weights in air to weights in vacuum for a range of temperatures extending from 10° to 28°C, and for pressures from 690 to 730 mm.

3. An automatic recycling still has been designed for the continuous production of "ultra-pure" water. This still is capable of delivering daily, in routine operation, 16 l. of water of conductivity less than 100 nm/cm after aeration with "CO_2- and NH_3-free" air.

4. A very soluble layer appears to form on the surface of glass when it is dried; this layer is readily removed on contact with water.

5. The removal of carbon dioxide and of ammonia from aqueous solution by aeration with an indifferent gas has been fully investigated, and it has been shown that these gases can be completely eliminated by such a process. Whereas the carbon dioxide is removed fairly rapidly, however, the ammonia, whether present alone or together with carbon dioxide, only goes out of solution rather slowly.

6. It has been shown that ammonia is adsorbed from aqueous solution on the glass walls of the cell.

7. There does not appear to be any ammonium bicarbonate in the residual impurity left in the "ultra-pure" water obtained from the still; the impurity can, in fact, be regarded as neutral salt with sufficient accuracy for most purposes.

8. The resistance change which accompanies any variation in the rate of bubbling of the stirring gas through the water has been investigated, but no solution has been found as to the cause of this change.

9. A comparison has been made of the efficiency of different gases for stirring purposes, and it seems that, for general work, nitrogen is by far the most suitable of the common gases.

10. The extrapolation to be used for converting resistances to their values at infinite frequency appears

which surrounded it. Heat losses by transfer through the bottom of the thermostat were avoided by standing the inner vessel on three ebonite legs. This bath was filled with paraffin, because the conductivity of water gave rise to errors in accurate conductance measurements when it was used as a thermostatic liquid in contact with the cell[4]. The paraffin was stirred by a current of air which first passed through one of the three copper coils in the outer bath before emerging into the oil from a tube near the bottom of the inner vessel. Another of the copper coils was also sealed through the wall of the latter vessel near the top, but it ended in a tube placed above the paraffin level; this was connected by a rubber joint to the side-tube B of the cell (see Fig.1.4), thus enabling gas to be passed over the surface of the liquid in the cell. The third coil in the outer bath was joined via the potash bulb to another coil of copper tubing placed in the paraffin but terminating above the liquid level so that it could be connected to the capillary tube A of the cell by means of pressure tubing: the gas that was used to stir the contents of the cell should therefore have been fully temperature equilibrated after passing through these two coils.

Slight condensation appeared to take place in the coils, particularly in the one in the inner thermostat; then, after some time, small droplets of water were occasionally carried over into the cell by the stirring gas, thus causing the resistance to change suddenly by quite large amounts (see Section 2.424). The coils were therefore cleaned and dried at regular intervals: tap-water was allowed to flow through them for a while, and afterwards dry air was sucked through until tests with weighed calcium chloride tubes showed no more moisture to be present.

1.13 The Thermoregulator.

The thermoregulator (shown in Fig. 1.1) was of the standard pattern employed for conductance work in this laboratory[1,2,3]. The stopcock was well ground to prevent leaks, and it was lubricated with a glycerol-dextrin mixture[5] which was insoluble in the toluene used for filling the regulator. A few other details of the construction may perhaps be stressed, although they are fairly obvious:-

(i) Variations up to 0.005°, and sometimes greater, were found with the first regulator which was used, particularly when the surface of the mercury in the contact tube A had become slightly dirty. Decreasing the diameter of this capillary tube increased the sensitivity of the control and reduced the size of the temperature ripple.

CONTENTS

ABBREVIATIONS, SYMBOLS, AND UNITS.

The following are used throughout the text:-

aq. - aqueous
cc. - cubic centimetre
cm - centimetre
conc. - concentrated
concn. - concentration
c/s - cycles per second
equiv. - equivalent
expt. - experiment
g - gram
G.R. - guaranteed reagent
h - hour
kcal. - kilocalorie
l. - litre
min - minute
mg - milligram
ml - millilitre
mm - millimetre
nm/cm - nanomho per centimetre = 1×10^{-9} ohm^{-1}cm^{-1}
sec - second

Å - ångström
d - density
D - demal solution
m - molar concentration
Q - cell constant
r,R - resistance
W - weight

κ_i - specific conductance (conductivity) of electrolyte species i
Λ_i - equivalent conductance of electrolyte species i
λ_i - equivalent ionic conductance of ionic species i
μg - microgram
μF - microfarad
ρ - resistance of unit length of slidewire

INTRODUCTION.

For many years one of the main fields of research in physical chemistry in the Rhodes University Chemistry Department has been that of the electrical conductances of aqueous solutions. In particular, attempts have been made to increase greatly the precision with which conductimetric titrations may be performed. This programme was initiated by Professor Barker, and has been carried on by several research students in this laboratory. The ultimate aim has been to provide a more accurate interpretation of the curves obtained by this method of analysis, especially where complex solutions are involved. However, the extension of the precision with which the conductance measurements can be made has brought forth a whole host of new problems, which must first be solved before the complete titration of any mixture can be accomplished with the desired accuracy.

Two of these problems have been investigated in this thesis:

(i) the nature of the residual impurities present in the very pure water which has been prepared for routine use (Part 2);

(ii) the adsorption effects which take place in a conductance cell containing very dilute solutions (Part 3).

A considerable amount of specialised apparatus has been used for the precision work involved in these investigations. For convenient reference, and to avoid breaking the trend of the descriptions of actual experimental work, this apparatus has been fully described separately in Part 1. For the same reasons, detailed results of calibrations and of individual experiments have not been included in the general text, but have been placed in several appendices, to which the reader is referred where necessary.

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PART 1

DESCRIPTION, CALIBRATION, AND STANDARDISATION OF THE APPARATUS

1.1 THE TEMPERATURE CONTROL APPARATUS.

The conductivity of any electrolytic solution varies greatly with the temperature; it is therefore essential to keep this constant whenever accurate conductance measurements are being made. A constancy of 0.001°C was deemed desirable for the investigations reported here, and this was attained quite readily.

1.11 The Constant Temperature Room.

The advantages of housing all precision conductance apparatus in a room, which is itself kept at a constant temperature, have been enumerated by Goddard[1] and A. Faure[2]. The second constant temperature room which was built in this laboratory was used for all but the earliest experiments in the present study. This room, which has already been fully described[1,2], was controlled at about 24°C, i.e. 1° below the temperature at which all measurements were being made: the resultant even rate of flow of heat from the thermostat to the surroundings enabled the temperature of the former to be maintained very constant. On the whole the regulation by means of the thyratron-controlled relay worked very satisfactorily, except for a few occasions when the temperature of the room rose to well over 30°C. This took place because the regulator ceased to operate as soon as the temperature exceeded a certain value (about 25-26°); if, therefore, the plant which cooled the air being drawn into the room failed during a spell of hot weather (as happened quite frequently), and the temperature rose sufficiently without it being noticed, it did not automatically return to 25°C. The instability of the cooling system was, in fact, the biggest source of trouble as regards the control of the temperature, and the temperamental behaviour of this unit caused many anxious moments and considerable loss of time during these investigations.

1.12 The Thermostat.

The thermostat was the one employed by Gledhill[3], with a few minor modifications. It was placed on the table provided in the S.W. corner of the room, to the right of the conductance bridge. The complete arrangement of the apparatus in this corner is illustrated in Plate I.

The large outer vessel of the thermostat was kept filled with water, fresh portions being added occasionally to compensate for evaporation losses. When tap-water was used, this

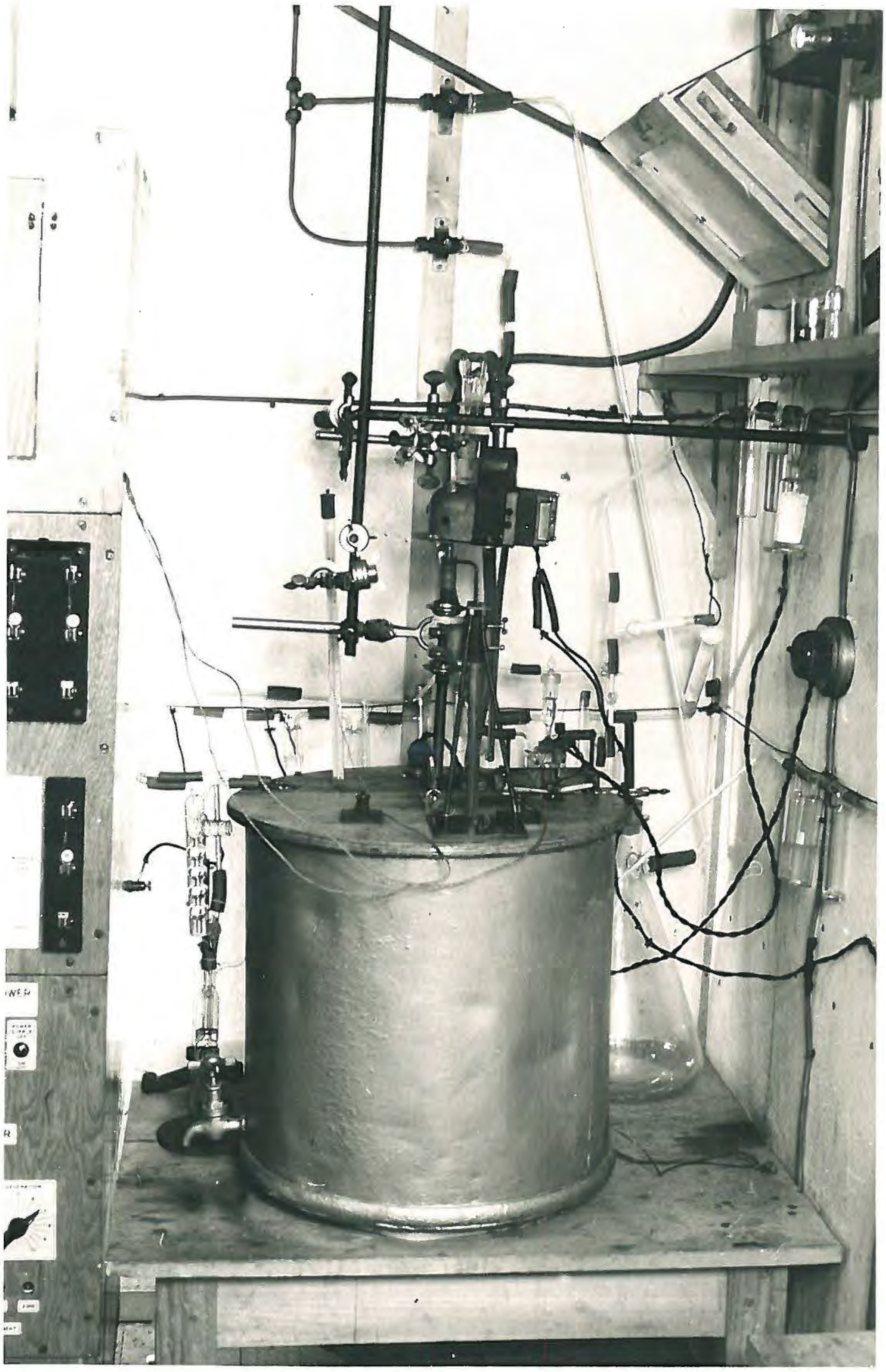

Plate I

replenishing caused a gradual increase in the mineral content, and eventually the various parts of the thermostat in contact with the water became coated with a hard layer that was quite difficult to remove; also, there was a tendency for algae to grow in the water which could, however, be prevented by adding small amounts of mercury or mercuric chloride. This precaution proved unnecessary when a change was made to using distilled or demineralised water for the filling so that the walls would not become coated: the water then remained reasonably clean over long periods. The inner surface of the vessel was painted with Plicote (a chemical-resistant paint) in order to prevent corrosion of the iron. At one stage strips of magnesium foil were also suspended in the water so as to undergo preferential corrosion, but these corroded too rapidly and then fell off into the thermostat where they tended to jam the paddle-stirrer; this caused so much inconvenience that the practice was discontinued.

The heater was a 250-watt Cenco knife type immersion heater, whose wattage was decreased by placing resistances in series. Ordinary electric lamp bulbs, which were plugged in to a board placed below the room so as not to form an additional source of heat inside it, were used for this purpose. These lamps could be shorted out by means of a switch (visible in Plate I on the wall on the right) whenever rapid heating was required, e.g. during the initial warming up of the thermostat. The wattages of the bulbs were chosen by trial and error, the values originally used being such as to give approximately equal "On" and "Off" periods of the heater. Afterwards, however, the heating period was adjusted to be as long and the cooling period as short as possible. This departure from normal practice was made because it was the more logical and effective procedure under the conditions of thermostating described here. With any thermoregulator which depends in principle on the changes occurring in the volume of a liquid with temperature, there must necessarily be a finite time-lag during heating or cooling before the heat exchanges have caused sufficient expansion or contraction for the relay to be operated by the regulator. This lag in time will be approximately constant for a given thermoregulator, depending on its construction, and it may be quite large where poor heat conductors such as glass are being used. There will therefore be a definite overshoot in temperature, depending on the rate of the heating or cooling. With constant temperature surroundings, the thermostat will always cool at a constant rate, and hence the overshoot in this direction will be fixed. The rate of heating, however, may be varied at will, and the faster the heating the greater will be the overshoot. The "ripple effect" will therefore be smallest and the temperature most nearly constant when the rate of heating is maintained just in excess of the cooling rate: ideally they should actually be equal. Slight fluctuations in the temperature of the constant temperature room naturally precluded this possibility, but it was quite easy to regulate the heating to give a long "On" and short "Off" period.

The temperature of the water in the thermostat was kept uniform by stirring it with a large rotating paddle-wheel mounted centrally near the bottom of the vessel. Gledhill[3] used a baffle to isolate the heater from the main part of the thermostat in order to prevent currents of hot water from circulating there. It was shown by A. Faure[2], however, that this was not necessary and that, in fact, it only impeded the circulation. The baffle was therefore omitted in this thermostat. The stirrer was driven at about 100 r.p.m. by a Garrard gramophone motor, which has given remarkably satisfactory service over a number of years of continuous use, although it was never intended to operate under such a heavy load. In order to minimise strain on the bearings of the motor, the latter was connected to the axle of the bicycle hub, which formed the upper end of the stirrer shaft, by means of a short length of pressure tubing. Both the motor and the hub were rigidly clamped to an iron framework mounted onto the wall (see Plate I), in order that no vibration might be transmitted to the thermoregulator. For this same reason, the latter was suspended in the water on rubber bands, and the whole vessel was placed on twelve tennis balls. The constancy of the temperature was controlled by the thermoregulator (see Section 1.13), and by the Sunvic relay and thermionic section described by Goddard[1] and A. Faure[2].

The outer vessel contained also three coils of copper tubing, through which air (or other gases) could be passed in order to reach temperature equilibrium at 25°C before flowing out of the tubes. These coils were connected to an inner vessel, two of them directly while the third was first joined to a potash bulb; the latter was filled with conductivity water so that the gas would bubble through it and thus become saturated at 25° as well.

The inner vessel was much smaller than the outer container, for it was intended primarily to hold only the conductance cell. It had no independent heater, but was constructed of sheet copper for the efficient exchange of heat with the water which surrounded it. Heat losses by transfer through the bottom of the thermostat were avoided by standing the inner vessel on three ebonite legs. This bath was filled with paraffin, because the conductivity of water gave rise to errors in accurate conductance measurements when it was used as a thermostatic liquid in contact with the cell[4]. The paraffin was stirred by a current of air which first passed through one of the three copper coils in the outer bath before emerging into the oil from a tube near the bottom of the inner vessel. Another of the copper coils was also sealed through the wall of the latter vessel near the top, but it ended in a tube placed above the paraffin level; this was connected by a rubber joint to the side-tube B of the cell (see Fig.1.4), thus enabling gas to be passed over the surface of the liquid in the cell. The third coil in the outer bath was joined via the potash bulb to another coil of copper tubing placed in the paraffin but terminating above the liquid level so that it could be connected to the capillary tube A of the cell by means of pressure tubing: the gas that was used to stir the contents of the cell should therefore have been fully temperature equilibrated after passing through these two coils.

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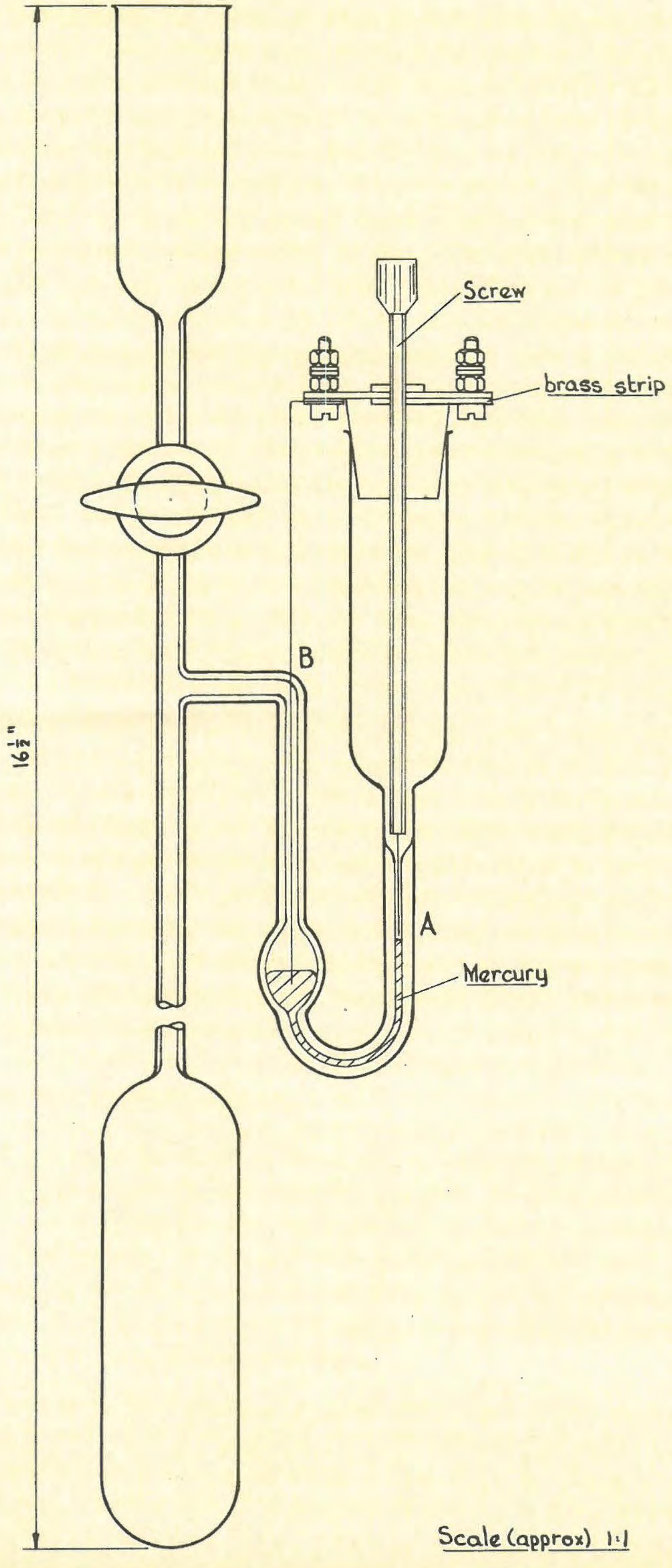
Fig. 1·1 The Thermoregulator



Scale (approx) 1:1

(ii) It is recommended that the regulator be constructed of soda-glass because of the difficulty of obtaining a leak-proof seal of platinum through Pyrex glass, even when thin wires are used. When the first regulator was broken, two new ones were made of Pyrex glass. Although neither of these showed any visible leakage of air during several exhaustive tests with reduced pressures, nevertheless a gradual rise in the temperature of the water bath (about 0.3-0.4° per day) took place when either of them was used in the thermostat. This rise was finally proved to be due to a minute leak at the platinum-glass seal B, because the rate of rise of the temperature dropped markedly when this seal was coated with shellac.

1.14 Standardisation of Temperature.

When the experimental work described in Parts 2 and 3 was commenced, no recently standardised thermometers were available. The standard method of precision temperature measurement at the value being considered (25°C) is, of course, by platinum resistance thermometry: this follows at once from the definition of the International Temperature Scale[6]. The attempts to use this method, however, were not very satisfactory because of the lack of sufficiently sensitive resistance-measuring equipment. An accuracy of temperature measurement of 0.001°C requires a precision of resistance measurement of a few parts per million[7], and the apparatus available was not capable of giving results to better than 0.04°C.

Further attempts at electrical standardisation were made by means of thermoelectric thermometry, but these were even less successful. Tests performed with a 28-junction copper-constantan thermocouple by placing one junction in melting ice (0°C) and the other in sodium sulphate at its transition point (32.383°C) indicated that the equipment was sufficiently sensitive: for each 0.01°C, an e.m.f. of about 4 microvolts was set up, which could readily be measured on a Tinsley Vernier Potentiometer. As is generally the case[8], however, the e.m.f. did not appear to vary linearly with the temperature. The method could therefore not be used satisfactorily, since no intermediate standard temperatures were available for the accurate calibration of the thermocouple over the required range. In any case, it seemed that this particular thermocouple was defective, as tests between 0 and 25°C, and between 25 and 32.38°C indicated that it did not obey the law of successive or intermediate temperatures[8].

The question of temperature standardisation was therefore left over until it was possible to have mercury-in-glass thermometers calibrated by the South African National Physical Laboratory. This method of thermometry is not really suitable for measurements of the highest precision because of slow changes in the volume of the bulb with time[9]; but it was the only method readily available after the failure of the attempts at an electrical standardisation. Several batches of thermometers were sent to the N.P.L. for calibration at various times. A solid-stem mercury-in-glass thermometer (No. 2314) was eventually used for all accurate measurements of the temperature; it was graduated from 17 to 35°C in hundredths of a degree, and calibrated to 0.01°C, although 0.001°C could be estimated by interpolation. Such readings were, in fact, regularly made whenever the temperature of the bath was being measured. This procedure is not generally to be recommended, particularly since the thermometer possessed no reference point by which changes in the volume of the bulb could easily be checked[9]. However, this thermometer was already very old when it was calibrated, and it was permanently kept in the constant temperature room and not subjected to large variations in temperature; it was therefore considered unlikely that its calibration would change by more than 0.01°C in the course of a year or two. The constancy of the cell constant determinations made at various times (see Appendix B) seems to justify this opinion.

For the routine checking of the thermostat temperature and its variations, a 5° Beckmann thermometer, graduated in hundredths, was permanently placed in the water in the outer bath. The use of such a thermometer is not entirely satisfactory for long-term standardisations, because its setting does not remain quite constant over protracted periods of time, particularly when it is subjected to changes in temperature: Tober[10], for instance, found that when a Beckmann thermometer was heated above the temperature for which it had been set, it did not always return to the same reading afterwards. So, too, in the present case it was found that over a period of several years the setting corresponding to 25.00°C varied irregularly by as much as 0.04°. These variations were probably due to changes in the volume of the bulb, the effect being quite pronounced because of the large volume of mercury generally used in Beckmann thermometers and the rather thin walls of their bulbs. Sometimes these changes in the setting seemed to take place in erratic jumps of up to 0.01° each over a period of a few days. Such behaviour was naturally a little annoying in view of the rigorous control of temperature required; it was, however, somewhat exceptional, and in general the thermometer proved extremely useful in indicating small variations in temperature over shorter time intervals (one or two days).

In order to ensure that the setting of the Beckmann thermometer was correct, it was compared with the standard thermometer whenever the thermostat was restarted after a period of disuse, and also at regular intervals between these times. This comparison was always made by placing the standard thermometer directly into the liquid in the cell, with the bulb about $\frac{1}{2}$-inch above the electrodes, while the Beckmann thermometer was left immersed in the water-bath. This procedure was adopted after it had been discovered that there was a distinct difference between the temperatures of the various baths, the paraffin being slightly cooler than the water. By alternately placing the Beckmann thermometer either directly into the cell or in the water-bath, and by taking readings after each change-over at one-minute intervals until the recorded temperature had been constant for at least 10 minutes, it was shown that the temperature inside the cell was actually about 0.008 - 0.010° lower than that in the outer thermostat. The former temperature was, of course, the one which it was desired to maintain constant at 25.00°C -- hence the reason for the method used in standardising the Beckmann thermometer. The standard thermometer was always allowed to equilibrate for 3 - 5 minutes after its immersion in the liquid in the cell before the readings on the two thermometers were compared; also, during the latter stages of this research, it was first warmed or cooled to about 24.8°C before being placed in the cell. These precautions were considered necessary because it had been found that, unless the thermometer was left to equilibrate in the cell for a very long time, the final temperature recorded seemed to depend on the temperature of the thermometer immediately prior to its immersion. Presumably this was due to a slight cooling or heating of the liquid in the cell because of its contact with the thermometer at a different initial temperature.

1.15 Performance of Thermostat.

The largest variations in the recorded temperature of the thermostat were probably not real changes in temperature, but arose from changes in the reading of the thermometer with time, as mentioned above. Apart from these apparent variations, the thermostat temperature was found to remain exceedingly constant for a given setting of the thermoregulator, particularly after the new one with a narrower capillary for the contact tube had been installed. With the previous regulator, for instance, variations of 0.005° (and sometimes larger when the mercury had become dirty) had been observed as the heater was switched on and off; but the later variations seldom exceeded

$0.001^{\circ}C$ over short periods of time. Over longer periods, ranging from several hours to a few days, changes up to 0.004° were noted on the Beckmann thermometer: these were probably real changes in temperature, resulting from variations in the atmospheric pressure, which would affect not only the volume of the thin-walled bulb of the thermometer but also the large volume of toluene in the regulator.

The temperature of the liquid inside the cell naturally remained more constant even than that of the outer water-bath. During the course of the investigations on pure water, changes were observed to take place in the resistance when the bubbling rate through the cell was varied (see Section 2.41). When these changes were first noticed, it was thought that they might be due to an incomplete temperature equilibration of the stirring gas during its passage through the copper coils: this would cause a progressively greater cooling of the liquid in the cell the faster the stirring. The bulb of a 1° Beckmann thermometer, graduated in thousandths, was therefore immersed directly in the cell liquid and left there while changes were made in the bubbling rate. Because of the large volume of mercury in the bulb, ample time was always allowed for the equilibrium value of the temperature, at the new stirring rate, to be recorded on the thermometer. The results of several such tests showed that the temperature inside the cell did not alter even by as much as 0.001° for periods of up to 4 hours, although the rate of bubbling was varied from less than one to about five bubbles per second.

The paraffin in the inner thermostat was stirred by passing a stream of air through it. Originally the main reason for doing this was to keep the liquid mixed at a uniform temperature and to speed up the temperature equilibration between the contents of the cell and the outer bath. That there was a real need to maintain this stirring, however, became apparent when several unexpected small increases in resistance were observed during one of the titrations (Expt. 9 -- see Section 3.325). At the time, these changes could only be correlated with the temporary failure of the compressor which supplied the air. This was confirmed by a series of tests, which showed that, even though the temperature in the outer bath remained quite constant, a distinct decrease in temperature of about $0.010 - 0.012^{\circ}$ occurred inside the cell whenever the stirring of the paraffin was stopped.

1.2 THE CONDUCTANCE BRIDGE.

The bridge used was the one built by Goddard[1] and A. Faure[2]; it has been adequately described by them.

1.21 Calibration of Bridge Resistances.

The resistances had been calibrated by A. Faure, but it was decided to restandardise the bridge when a few discrepancies were found on measuring a given resistance by alternative methods, i.e. by using different combinations of coils in the bridge. Faure's method of calibration[2] was rather long, and it involved the preliminary intercomparison of the resistances in a separate decade resistance box. This intermediate step was apparently included in order to calibrate the bridge resistors "in situ", since the use of a method such as that described by Dike[11] would require the removal of the shielding in order to gain access to the studs to which the individual resistance coils were attached.

The new method of standardisation used was, in effect, the analogue of the standard Richards' method of calibration of weights relative to each other[12]: the resistances of the various coils were intercompared in the bridge itself, and ultimately checked at one point against a standard resistance in order to get absolute values. This method seemed to have several advantages over the one employed by A. Faure: it eliminated the intermediate stage, which was really tantamount to another full standardisation; also, except for an uncalibrated decade resistance box, it required no other additional apparatus, such as a potentiometer and small standard resistance. The whole calibration could be done with the bridge "in situ", and it was possible even to measure the leads resistance of the bridge without having to open the latter at all.

The chief objection to this method seemed to be that it was limited by the accuracy with which the contact resistance on the studs of the various decades could be reproduced. This was true particularly of the smaller resistances, where the value was required to 0.0001 ohm if an accuracy of 0.001% was to be maintained over the full range of the calibration. The manufacturers (General Radio Company) guaranteed the contact resistances of the decades to 0.002 ohm only. These resistances presumably arose mainly from the formation of a thin coating of oxide on the studs when not in use, and possibly also from other minor effects, such as the pressure of the switch-arm contact on the studs. Any resistance due to the latter cause should, however, remain constant for a given switch-arm and stud; in any case, it could not be dissociated from the resistance of the coil itself when the bridge was being used for the normal measurement of resistances, since there would necessarily have to be contact between the arm and the stud. Such contact resistances should therefore be included in the final standardised values for the coils, whatever the method of calibration used. This inclusion was automatically ensured by the "in situ" method employed here.

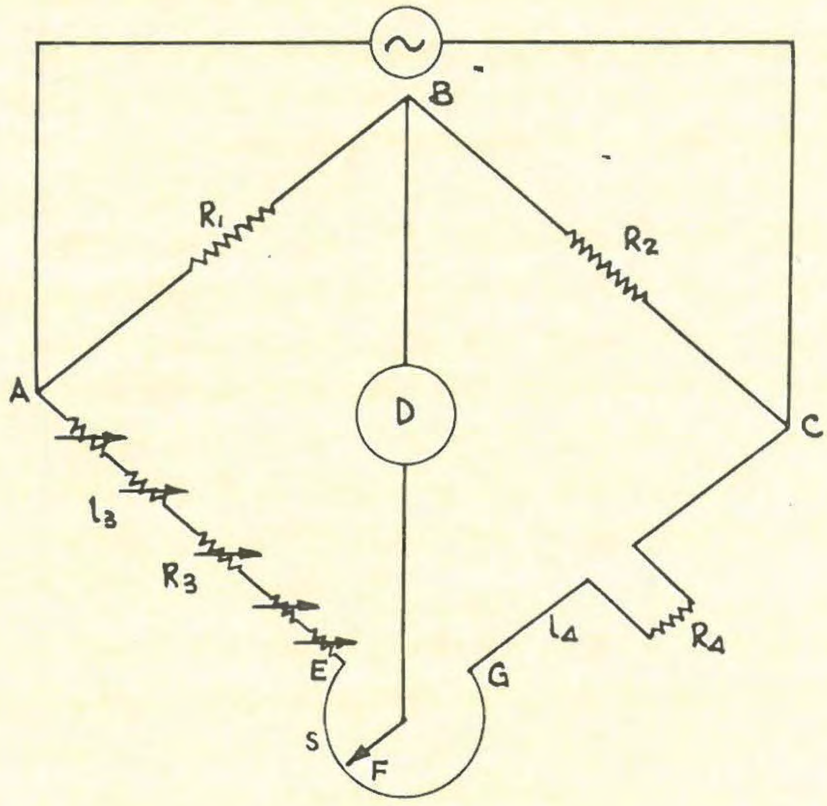
The oxide films, on the other hand, would cause the contact resistance to vary slightly, depending on their thickness. During the calibration only two stud positions were changed for each coil standardised (except for the high resistances, where in any case the contact resistance was negligible); the rest of the contacts in the other decades were not shifted, and hence their resistance should have stayed constant -- one of the essential characteristics required of this method. The Faure-Goddard bridge is very sensitive, particularly at the lower resistances, and it could be balanced and the resistance estimated on the slidewire to 0.0001 ohm for individual settings of the contacts. Before each setting, those contacts which had to be changed were always cleaned by wiping the switch-arm backwards and forwards several times over the stud until the resistance reading obtained was constant; the extreme variations which were observed thereafter for several successive settings of the contact were seldom greater than 0.0004 ohm, and usually less. Since the bridge balancing could be performed quite rapidly and easily, the contacts were normally reset and a new reading taken about 8 - 10 times for each coil standardised: the mean was therefore almost certainly not in error by more than 0.0001 ohm, i.e. within the accuracy required. Hence the variable contact resistance, which constituted the main objection to this method of calibration, could apparently be eliminated quite successfully by this cleaning procedure. A similar cleaning of the contacts is recommended for the accurate measurement of any resistance, especially if the value is low, since the oxide coating on the various studs can cause an appreciable error when its resistance is summed over the contacts of all the decades.

This method of standardisation can be applied to any bridge which possesses a continuously variable small resistance, such as a slidewire. In effect, the resistances are merely being compared in terms of the resistance of different lengths of the slidewire (see later). The latter should be uniform and its resistance should vary linearly with the setting: in this case, an arbitrary assumption (but preferably one which is approximately correct, so that the adjustments to an absolute standard will not be large) may be made about its resistance per unit length, since this will not affect the intercomparisons. The slidewire then automatically becomes standardised as well when the absolute comparison is made at one point. If the wire is not uniform, it may be necessary to calibrate it separately at different settings by a potentiometric method -- relative values are quite sufficient for this purpose; the differences in resistance between various settings of the slidewire may then be obtained from this calibration.

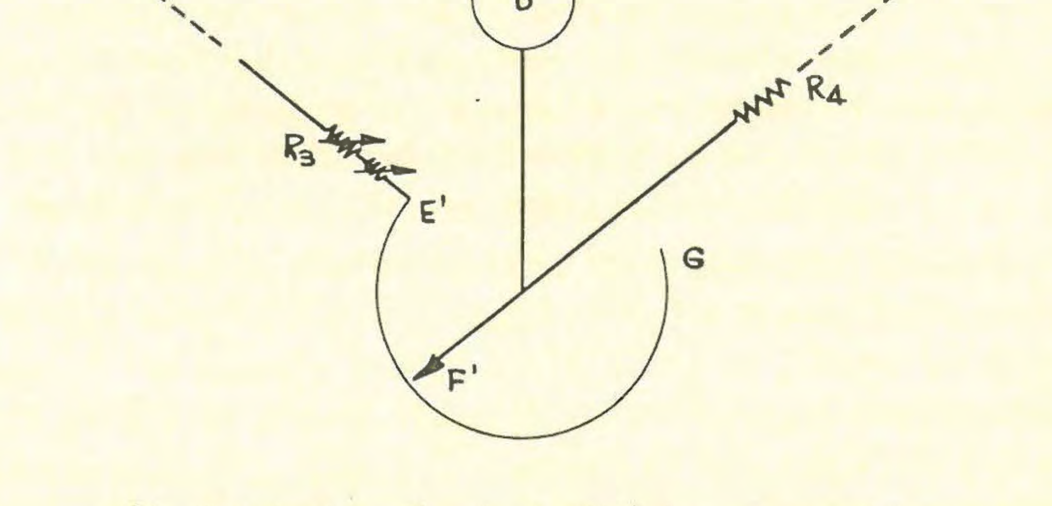
Fig. 1.2 shows the simplified circuit of a typical conductance bridge. Two standard methods by which the slidewire may be connected in to the bridge circuit are depicted here: Fig. 1.2(a) gives the construction used in the Faure-Goddard bridge with which almost all the resistance measurements in the present investigation were made, and which was being recalibrated; and Fig. 1.2(b) illustrates the older method of connection (the whole circuit is not drawn, since the only difference from (a) is in the slidewire connection). The latter method suffers from the serious disadvantage that any resistance arising from a faulty contact on the slidewire will be additive to the measuring arm R_3. Such faults cannot always be avoided, for even with the best-kept slidewires, bad spots develop owing to corrosion, etc.; if this happens frequently, it can be very troublesome. This difficulty can be overcome by making the connection as in the method used by Dike[11], which was also incorporated in the Faure-Goddard bridge: here any contact resistance will be in series with the input to the amplifier and detector (D), and not with the resistances of the bridge; it cannot, therefore, alter the position of balance.

It is easy to see that, when the connection is made as in Fig. 1.2(b), and the value of R_4 is fixed, replacement of one of the 0.1-ohm decade coils in R_3 by nearly the full length of the slidewire (depending on its total resistance) is tantamount to a direct comparison of the resistance of the coil with that of a given length of slidewire, regardless of the equality of the two ratio arm resistances R_1 and R_2. With the connection (a), however, the resistances R_3 and R_4 will both vary with the position of the sliding contact,

Fig. 1·2 - Simplified circuit of conductance bridge



(a) Slidewire connected as in Faure - Goddard bridge



(b) Original method of slidewire connection.

and hence the inequality between the ratio arms will enter into the resistance contributed by the slidewire. This can readily be seen from the following derivation:-

Let: R_1 = total resistance between points A and B (inclusive of connecting leads)

R_2 = total resistance between points B and C (inclusive of connecting leads)

R_3 = resistance read off on measuring arm decade resistances

R_4 = resistance to be measured

l_3 = resistance of leads between points A and E, i.e. of leads used to connect up the measuring arm decades

l_4 = resistance of leads between points E and C, i.e. of leads used to connect the unknown resistance to the bridge <u>plus</u> the full resistance of the slidewire

s = resistance of the slidewire between the fixed end E and the variable contact F

∴ Total resistance of arm (3) $= R_3 + l_3 + s$

" " " " (4) $= R_4 + l_4 - s$

At balance*:

$$\frac{R_3 + l_3 + s}{R_4 + l_4 - s} = \frac{R_1}{R_2} = \text{constant (since } R_1 \text{ and } R_2 \text{ are fixed ratio arms)}$$

$$= X \qquad \text{..........(1.1)}$$

Hence $$R_3 + l_3 + (1+X)s = X(R_4 + l_4) \qquad \text{..........(1.2)}$$

In general, $R_1 \neq R_2$, i.e. $X \neq 1$ because of slight inequalities in the values of the resistances and leads used to construct the two ratio arms of the bridge. This is normally overcome by reversing the ratio arms after R_3 has been determined, and thus obtaining another value, R_3', given by

$$R_3' + l_3 + (1+\tfrac{1}{X})s' = \tfrac{1}{X}(R_4 + l_4) \qquad \text{..........(1.3)}$$

From equations (1.2) and (1.3), it follows that the true value of $(R_4 + l_4)$ is the geometric mean of the two readings (including the leads and slidewire resistances). Generally, however, the arithmetic mean is taken, since it can readily be shown that, in spite of the presence of the inequality ratio X in the term containing the slidewire resistance in equations (1.2) and (1.3), the two means are always in agree-

---

* The condition stated above is, of course, strictly true only for direct current measurements, since with alternating current the quantities which should be compared are the impedances. Equation (1.1) holds good, however, when the resistive components of the impedances are being considered. The resistances used in the bridge were in any case of such low inductance that the accuracy of the calibration was not affected when a.c. was used.

ment with each other to 0.001% or better provided that X lies within the range 0.997 - 1.003, i.e. if resistances R_1 and R_2 do not differ by more than 0.3%. It seems, in fact, desirable in any conductance bridge covering a normal range of resistances to have the ratio arms equal within these limits, so that the bridge will be "direct-reading" insofar as one need only take the arithmetic mean of two resistance measurements made with a direct and a reversed ratio arm respectively. This was the case in the Faure-Goddard bridge -- the difference in resistance of the two ratio arms was actually about 0.043%.

If mean values of the resistances are used, equation (1.2) reduces to the form

$$R_3 + l_3 + 2s = R_4 + l_4 \qquad \text{..........(1.4)}$$

Hence $$R_4 = R_3 + 2s - (l_4 - l_3) \qquad \text{..........(1.5)}$$

It can be seen that, with the connection as shown in Fig. 1.2(a), the slidewire contributes twice its actual value to the measured resistance. Also, the final resistance involves the term $(l_4 - l_3)$, which is equal to the difference in resistance of the various leads used in the two arms of the bridge: since these leads are all fixed, $(l_4 - l_3)$ will be a constant, which may be called the "leads resistance of the bridge". This must be subtracted from the observed resistance $(R_3 + 2s)$ in any accurate determination of a resistance R_4. The value of the leads resistance can be measured "in situ" (see Section 1.212) without having to measure the resistances of all the individual leads and then summing them appropriately.

1.211 Method of calibration of measuring arm resistances.

R_4 must be a variable resistance covering the same range as the bridge resistances, and preferably of rather low inductance: a suitably wound decade resistance box is very satisfactory. In the actual calibration a General Radio Company Type 602-N box with five decades, from tenths to thousands of ohms, was used. It was also found necessary, when very low resistances were being measured with a.c., to introduce extra capacitance into arm (4) of the bridge: a General Radio Company Type 219-M decade condenser box (three decades of total capacity 1.11 μF) was used for this purpose.

Although the inequality of the ratio arms can be eliminated by reversing them and taking the arithmetic mean of the readings, this is not necessary during the standardisation, as will be seen later. In fact, elimination of X (i.e. R_1/R_2)

would merely require duplication of the readings, of which a large number are already necessary for the complete calibration because each resistance coil must be standardised individually. Hence it was thought preferable to take more readings of each resistance setting with the ratio arms in one position only, in order to obtain a more accurate mean value and thus increase the precision of the whole standardisation. For each coil, therefore, 8 - 10 sets of readings were taken: each set comprised two resistance measurements, the decade switch-arm being placed alternately on each of the two studs to which the coil was attached. These studs were always first cleaned by being wiped with the switch-arm, and hence it may be assumed that all the contact resistances were negligible.

The following general notation will be used in the discussion:-

(i) $r_{0.n}$, r_n, r_{n0}, r_{n00}.... are the individual resistances of the *n*th coils of the 0.1-, 1-, 10-, 100-....ohm decades respectively.

(ii) $R_{0.n}$, R_n, R_{n0}, R_{n00}.... are the total resistances of the first *n* coils of the 0.1-, 1-, 10-, 100-....ohm decades respectively, i.e. the resistances of the individual decades when the switch-arms are set at position *n*.

(iii) $s_{n(n-1)}$ and s_{nn} are the resistances of the slidewire at various settings. The first figure *n* denotes the number of the coil which is being calibrated in the decade under consideration; the second figure, (n-1) or *n*, gives the number of the stud on which the switch-arm of the decade is set. For example, when the sixth coil of a decade is being standardised, *n* = 6, and it will be necessary to set the switch-arm alternately on the 5th and 6th studs of this decade: s_{65} and s_{66} will therefore denote the two positions of the contact on the slidewire in this case.

(a) Comparison of 0.1-ohm decade coils with the slidewire.

R_4 was adjusted to a small value so that balance to 0.0001 ohm could be effected very easily. The actual value was chosen so that, with the switch-arm of the 0.1-ohm decade in arm (3) set on stud 0, at balance the slidewire was set near its maximum G. All the other decades were left with their settings unchanged throughout the calibration of the 0.1-ohm decade: let their total resistance be R_3.

For the calibration of the first coil, the decade switch-arm was set alternately on studs 0 and 1: the corresponding slidewire resistances were therefore s_{10} and s_{11} respectively. Hence, from equation (1.2),

$$\begin{aligned} R_3 + l_3 + (1+X)s_{10} &= X(R_4 + l_4) \\ &= R_3 + l_3 + r_{0.1} + (1+X)s_{11} \end{aligned}$$

$$\therefore \quad r_{0.1} = (1+X)(s_{10} - s_{11}) \qquad \text{..........(1.6)}$$

For the second coil, R_4 was increased by 0.1 ohm, and two new slidewire resistances s_{21} and s_{22} determined for stud positions 1 and 2 on the decade respectively. This gave

$$r_{0.2} = (1+X)(s_{21} - s_{22})$$

In general:

$$r_{0.n} = (1+X)(s_{n(n-1)} - s_{nn}) \qquad \text{..........(1.7)}$$

$$\text{and } R_{0.n} = (1+X)\sum_{n=1}^{n=n}(s_{n(n-1)} - s_{nn}) \qquad \text{..........(1.8)}$$

(b) Comparison of 1-ohm decade coils with the sum of the 0.1-ohm decade ($R_{\Sigma 0.1}$).

R_4 was adjusted so that the bridge could be balanced with the slidewire when the switch-arm of the 1-ohm decade was set on stud 0 and the switch-arm of the 0.1-ohm decade on stud 10: the slidewire resistance was therefore s_{10}. This changed to s_{11} when a new balance was made after the positions of the switch-arms had been altered to 1 and 0 on the 1- and 0.1-ohm decades respectively. Equation (1.2) gives (if R_3 = unchanged resistance of the other decades)

$$R_3 + l_3 + R_{\Sigma 0.1} + (1+X)s_{10} = X(R_4 + l_4)$$

$$= R_3 + l_3 + r_1 + (1+X)s_{11}$$

$$\therefore \quad r_1 = R_{\Sigma 0.1} + (1+X)(s_{10} - s_{11}) \qquad \text{..........(1.9)}$$

In general:

$$r_n = R_{\Sigma 0.1} + (1+X)(s_{n(n-1)} - s_{nn}) \qquad \text{..........(1.10)}$$

$$\text{and} \quad R_n = nR_{\Sigma 0.1} + (1+X)\sum_{n=1}^{n=n}(s_{n(n-1)} - s_{nn}) \qquad \text{..........(1.11)}$$

(c) Further comparisons.

This procedure was extended further to the standardisation of the higher resistances; each coil was compared with the sum of the ten coils in the next lower decade, giving

$$R_{n0} = nR_{\Sigma 1} + (1+X)\sum_{1}^{n}(s_{n(n-1)} - s_{nn}) \qquad \text{..........(1.12)}$$

$$R_{n00} = nR_{\Sigma 10} + (1+X)\sum_{1}^{n}(s_{n(n-1)} - s_{nn}) \qquad \text{..........(1.13)}$$

and so on.

The range of the slidewire was naturally rather limited (a little over 0.1 ohm). Not surprisingly, therefore, it was found that, as the resistance was increased, it was no longer always possible to balance the bridge by adjusting the contact on the slidewire alone when the position of the switch-arm was interchanged between studs (n-1) and n during the calibration of the nth coil of a decade. By a suitable choice of R_4, however, the resistance of any coil could still be compared with the sum of the resistances of the ten coils in the lower decade by varying not only the position of the slidewire slider, but also that of the switch-arm in the 0.1- (and, if necessary, even the 1-) ohm decade. This merely meant that these additional resistances, which had already been compared with the slidewire, had to be added to or subtracted from the recorded differences in the slidewire resistance -- the correct sign was easily obtained by common-sense, or by application of equation (1.2).

In the calibration of the 0.1-ohm decade, the term $(s_{n(n-1)} - s_{nn})$ in equation (1.7) represents the resistance of the length of slidewire between the two slider settings which correspond to the decade switch-arm being placed in positions (n-1) and n respectively, i.e. the resistance of the nth coil is proportional to the resistance of a certain length of slidewire. Hence, in equation (1.8), $\sum(s_{n(n-1)} - s_{nn})$ represents the resistance of another length of slidewire (=S_a, say): this equation is therefore actually of the form

$$R_{0.n} = (1+X)S_a \qquad \text{..........(1.14)}$$

Similarly, for equation (1.11) we may write

$$R_n = n(1+X)S_b + (1+X)S_a \qquad \text{..........(1.15)}$$

This is generally true for all the values determined by this method, so that any resistance R_x will be given by

$$R_x = (1+X)S_x \qquad \text{..........(1.16)}$$

where S_x = resistance of the corresponding length of slidewire.
If l_x = length of slidewire of resistance S_x
and ρ = resistance of unit length of slidewire,
equation (1.16) becomes

$$R_x = (1+X)\rho l_x \qquad \text{..........(1.17)}$$

Since X and ρ are constants for the bridge,

$$(1+X)\rho = \text{constant} = W \qquad \text{..........(1.18)}$$

$$\text{and} \qquad R_x = W.l_x \qquad \text{..........(1.19)}$$

Hence all the resistances will have been intercompared, in effect, in terms of the resistance of an equivalent length of slidewire. The unit of length may be taken as one division on the slidewire scale, and any arbitrary value W' may be chosen for W without affecting the values of the resistance coils relative to each other. The absolute values may then be obtained by determining the ratio $^W/_{W'}$ for one resistance and multiplying all the other relative values by this factor.

(d) Determination of the ratio $^W/_{W'}$.

One standard resistance is necessary in order to obtain absolute resistance values. The standard used for the calibration was a 10-ohm oil-immersed resistor of the Reichsanstalt pattern (manufactured by Hartmann and Braun A.G., Frankfurt A.M.), which had been standardised by the S.A. National Physical Laboratory: the value given was 10.0018 ohms. at 24°C. For 0.001% accuracy in the calibration, therefore, this would have to be measured to 0.0001 ohm. Since this was the limit of measurement which could be made on the bridge, and since it necessitated taking the mean of numerous readings in order to achieve this accuracy, a larger resistance would have been preferable as the standard, say 100 ohms. This, however, was not available, and so a number of readings was taken, all of which were very consistent. Because the standard resistor was not specially non-inductively wound), the standardisation was performed with both a.c. and d.c.; but the discrepancy was only 0.0002 ohm.

This resistance was compared with the sum of the 1-ohm decade coils. For this purpose, it was placed in series with another resistance R_4 in order to eliminate the unknown leads resistance; also, the contacts of the standard resistor were dipped into two mercury cups to avoid uncertain contact resistances. First the two leads, i.e. from the bridge and from R_4 (for which the same decade box was used as previously -- see p. 15) were dipped into the same cup and the value of R_4 adjusted, at approximately 10 ohms, until the bridge could be balanced with the slidewire when the switch-arm of the 1-ohm decade was set on stud 0. A number of readings was taken with the ratio arms direct and reversed, and the arithmetic mean (=Z) obtained: this eliminated any inequalities in the ratio arms. The standard resistor was then placed in series with R_4 by moving one of the leads into the other mercury cup, and the mean resistance (=Y) again determined with the 1-ohm decade switch-arm now set on stud 10. The values obtained for the bridge resistances during the arbitrary relative calibration were used in calculating both the measured resistances; the difference (Y - Z) then gave R_s', the apparent value of the standard resistance on this arbitrary scale. Therefore, if R_s = true value of the standard resistance,

$$\frac{W}{W'} = \frac{R_s}{R_s'} \qquad \text{..........(1.20)}$$

Hence all the other relative values could be corrected to absolute values by multiplying by this factor.

(e) Calibration of the slidewire.

From equation (1.5), it was seen that, when the arithmetic mean of the readings for ratio arms direct and reversed had been taken, the slidewire contributed twice its actual resistance to the measured value, i.e.,

$$\text{Effective resistance of slidewire} = 2s = 2\rho.1 \quad \ldots\ldots\ldots\ldots(1.21)$$

From equations (1.18) and (1.20), we get

$$\rho = \frac{W}{1+X} = \frac{R_s.W'}{R_s'(1+X)} \quad \ldots\ldots\ldots\ldots(1.22)$$

W' is the arbitrary value chosen initially for the constant W in equation (1.19), and R_s/R_s' can be determined as just described. X can also readily be determined by measuring a fairly large resistance with ratio arms direct and reversed. Hence ρ can be obtained from equation (1.22), and the slidewire calibrated for direct reading, with an effective resistance of 2ρ for each slidewire division.

1.212 Methods of determination of leads resistance of bridge.

The leads resistance can also be determined with the bridge "in situ", by utilising either the standard resistance or another resistance decade (preferably one of low value, so as to get very sensitive balancing of the bridge). As in the calibration and use of the bridge resistances, so too in both these methods the studs should be thoroughly cleaned by wiping the switch-arm over them: the contact resistances are therefore assumed to be negligible.

(a) By using a standard resistance.

The bridge leads were connected directly to the standard resistance R_s, via mercury cups, i.e. resistance R_4 in Fig. 1.2(a) was equal to R_s. Measurements were made with the ratio arms both direct and reversed, and the arithmetic mean taken, $= [R_3 + 2s]_s$. Then, from equation (1.5),

$$(l_4 - l_3) = \text{Leads resistance of bridge} = [R_3 + 2s]_s - R_s \quad \ldots\ldots\ldots\ldots(1.23)$$

(b) By using a non-inductive resistance decade.

The possibility of an error in a.c. measurement by method (a) owing to the standard resistance not being specially wound for such purposes could easily be avoided by using a non-inductive resistance decade in its place. A General Radio Company Type 510-B 1-ohm decade was actually used. Short thick copper leads were soldered to the two end-contacts and to the switch-arm contact; one bridge lead was connected to the latter throughout the whole standardisation, while the other bridge lead was connected alternately to the two end copper leads, i.e. to points X and Y in Fig. 1.3. Then if:

l_x = copper leads resistance when connection is made at X
l_y = copper leads resistance when connection is made at Y
r_n = resistance of the *n*th coil in the decade
$[R_3 + 2s]_x^n$ = measured resistance when connection is made at X and switch-arm is on stud *n*
$[R_3 + 2s]_y^n$ = measured resistance when connection is made at Y and switch-arm is on stud *n*,

from equation (1.4) we shall have:

$$[R_3 + 2s]_x^n + l_3 = \sum_1^n r_n + l_4 + l_x \quad \text{..........(1.24)}$$

$$[R_3 + 2s]_y^n + l_3 = \sum_{(n+1)}^{10} r_m + l_4 + l_y \quad \text{..........(1.25)}$$

Also $$[R_3 + 2s]_y^0 + l_3 = \sum_1^{10} r_m + l_4 + l_y \quad \text{..........(1.26)}$$

Subtracting equation (1.25) from (1.26) gives

$$[R_3 + 2s]_y^0 - [R_3 + 2s]_y^n = \sum_1^{10} r_m - \sum_{(n+1)}^{10} r_m$$

$$= \sum_1^n r_n \quad \text{..........(1.27)}$$

Hence, by substituting in equation (1.24), we get

$$(l_4 - l_3) = \text{Leads resistance of bridge}$$

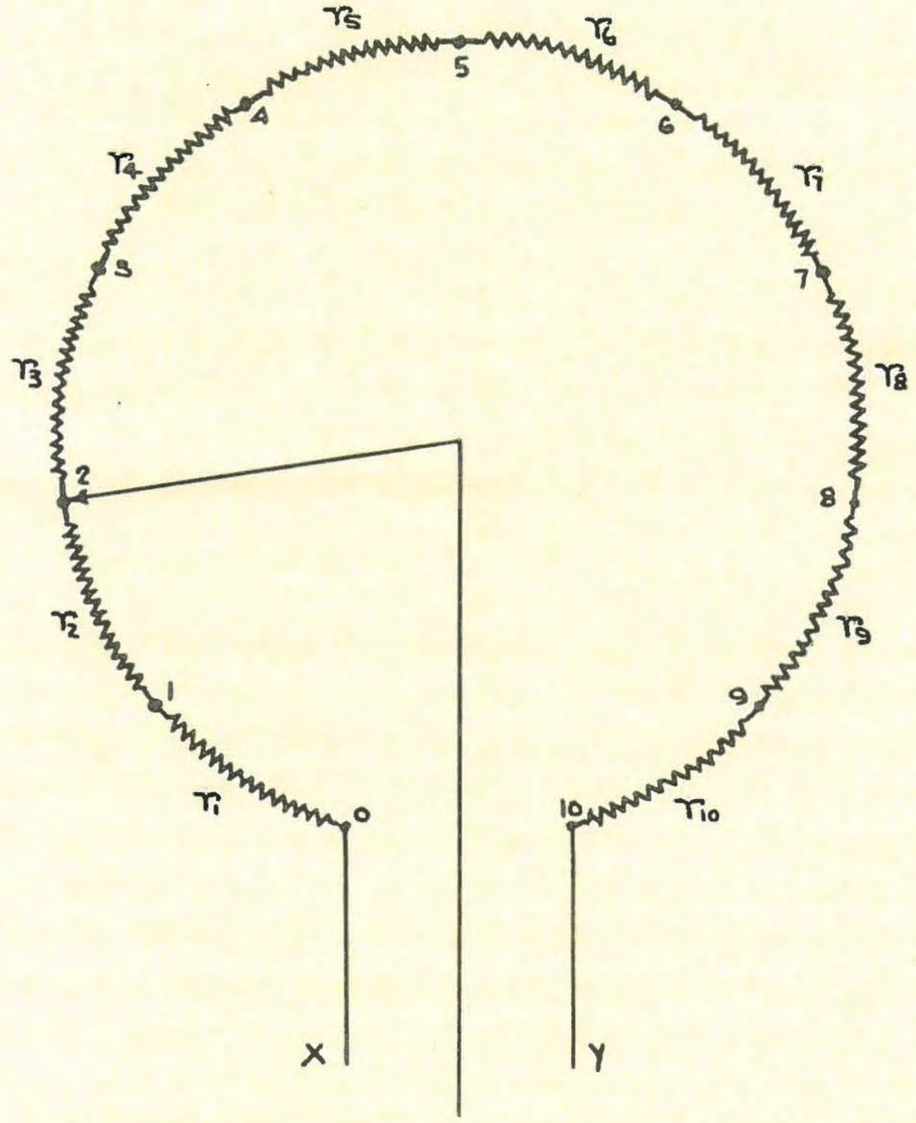
$$= [R_3 + 2s]_x^n + [R_3 + 2s]_y^n - [R_3 + 2s]_y^0 - l_x \quad \text{...(1.28)}$$

Thus the leads resistance of the bridge can be determined by making three resistance measurements:-

(i) With the switch-arm on the *n*th stud and the lead connected to X;
(ii) With the switch-arm on the *n*th stud and the lead connected to Y;
(iii) With the switch-arm on the zero stud and the lead connected to Y.

Effectively the first two terms of equation (1.28) give the total resistance of the decade when measured in two steps, so that the bridge and copper leads resistances will be duplicated: from the total determined in this way is subtracted the third term of the equation, which is the total

Fig. 1·3- Determination of leads resistance with a decade resistance.



resistance measured in one step, i.e. with the leads resistance taken only once. If the copper leads are thick and they are kept short, their resistance l_x may be neglected; otherwise a correction must be applied to the measured resistances as indicated in equation (1.28).

Ten different determinations of the leads resistance were made by this method, by measuring the resistances in turn for each of the stud settings 1 to 10; the extreme values thus obtained differed by only 0.001 ohm, so that the mean was probably quite accurate. This value also agreed with that determined by method (a) to 0.001 ohm.

The results obtained on calibration of all the bridge resistances are given in Appendix A.

1.22 Calibration of Bridge Condensers.

In order to obtain balance with a.c., small variable air condensers had been built into the bridge in parallel with the measuring arm (C_3) and with the cell arm (C_4); there were also two terminals on the front panel of the bridge, marked "additional capacity", to which extra condensers could be connected in parallel with C_3.

The built-in condensers were recalibrated by a method similar to that used by Goddard[1] and A. Faure[2] when the bridge was initially built, except that C_4 was not disconnected. The bridge leads were connected to a non-inductive 10,000-ohms resistor (General Radio Company Type 500-J), and a standard variable air condenser (C_s) was placed in parallel with this. C_3 was set to zero, C_s to some fixed starting value, and a small mica condenser (of value depending on the setting of C_s) was connected across the terminals marked "additional capacity"; the bridge was then balanced by varying C_4. Thereafter C_4 and the additional capacitance were left unaltered while C_s was set to various fixed values, for each of which the bridge was rebalanced by means of C_3. Since any change made in the capacitance of arm (4) of the bridge would have to be compensated by an equal change in arm (3) in order to restore balance, the various readings obtained on C_3 would correspond to capacitances which were equal to the differences in value between the initial setting and each of the new positions of C_s respectively. These differences could readily be calculated from the calibration curve of C_s.

An alternative method of utilising C_s for the calibration of C_3 "in situ" was to connect the former to the bridge as the "additional capacity", i.e. in parallel with C_3, and to place a mica condenser in parallel with the 10,000-ohms resistor, i.e. with C_4 -- about 500 pF was found to be sufficient for this purpose, since the maximum value of C_3 was only about 320 pF. The initial balance of the bridge was again made with C_4 after C_3 had been set to zero and C_s to a known value; as before, too, the balance was then maintained by varying C_3 as C_s was altered by fixed steps. This time, however, since the capacitance in arm (4) of the bridge remained constant, and since C_3 and C_s were present in the same arm, the sum of the capacitances of the latter two condensers had to be kept constant, i.e. C_s had to be decreased for increasing values of C_3. As in the previous standardisation, the capacitances corresponding to the readings taken on C_3 could be obtained from the calibration curve of C_s. The results of the two methods of calibration agreed very well.

The standardisation of condenser C_4 was carried out by exactly similar methods, i.e. by first balancing the bridge with C_3 and then keeping this constant while corresponding settings of C_4 and C_s were determined. Alternatively, C_4 could be compared directly with the previously calibrated C_3, by varying the setting on one of these and rebalancing the bridge with the other.

These methods of calibration do not necessarily give the absolute capacitances which correspond to the scale readings of the condensers; in fact, this is the case only when the condenser has zero capacitance at a setting of zero -- a condition generally not satisfied -- because the capacitances which are being measured are actually the increases above the "zero value" as the setting is changed from this position. The "in situ" method does not allow the residual capacitances of the individual condensers at zero setting to be measured. Fortunately, however, such values are of no real significance: the only important factor is the difference between the zero values of the condensers in the two arms, and this can be determined. For this purpose the bridge leads were left unconnected and one of the knife-switches in the 10,000-ohms section of the bridge was left in the open position, i.e. an infinite resistance was placed in each of the arms (3) and (4) of the bridge. It was then necessary to set either C_3 or C_4 to zero (whichever had the larger residual capacitance at zero setting), and to balance the bridge by varying the other condenser: in the bridge used, the residual zero capacitance of C_3 was the larger, and this condenser was therefore left on zero while C_4 was varied.

The actual difference between the zero values was about 11 pF. Hence, for any given settings of the two condensers, the effective capacitance in parallel with the measuring arm would be

$$C = C_3 - C_4 + 11 \text{ pF} \qquad \text{..........(1.29)}$$

This was the value to be used in the $p^2C^2R^2$ correction term (see Section 3.21).

After the calibration of the bridge condensers, several of the small mica radio condensers, which were normally used as the additional capacities, were also standardised in a similar manner: the bridge was balanced with condensers C_3 and C_4 before and after the extra condenser was connected to the "additional capacity" terminals, and the capacitance of the latter condenser was calculated from the previously calibrated values of the former two. Of all the capacitors which were thus tested, only those which were best insulated were chosen for general use. The basis of this selection was very simple, since the finite resistance of the condenser caused a small change in the measured value of the 10,000-ohms resistor in arm (4) when the capacitor was connected in parallel with the measuring arm of the bridge: obviously, therefore, those condensers which produced the smallest change had the highest leak resistance, and hence were the most suitable.

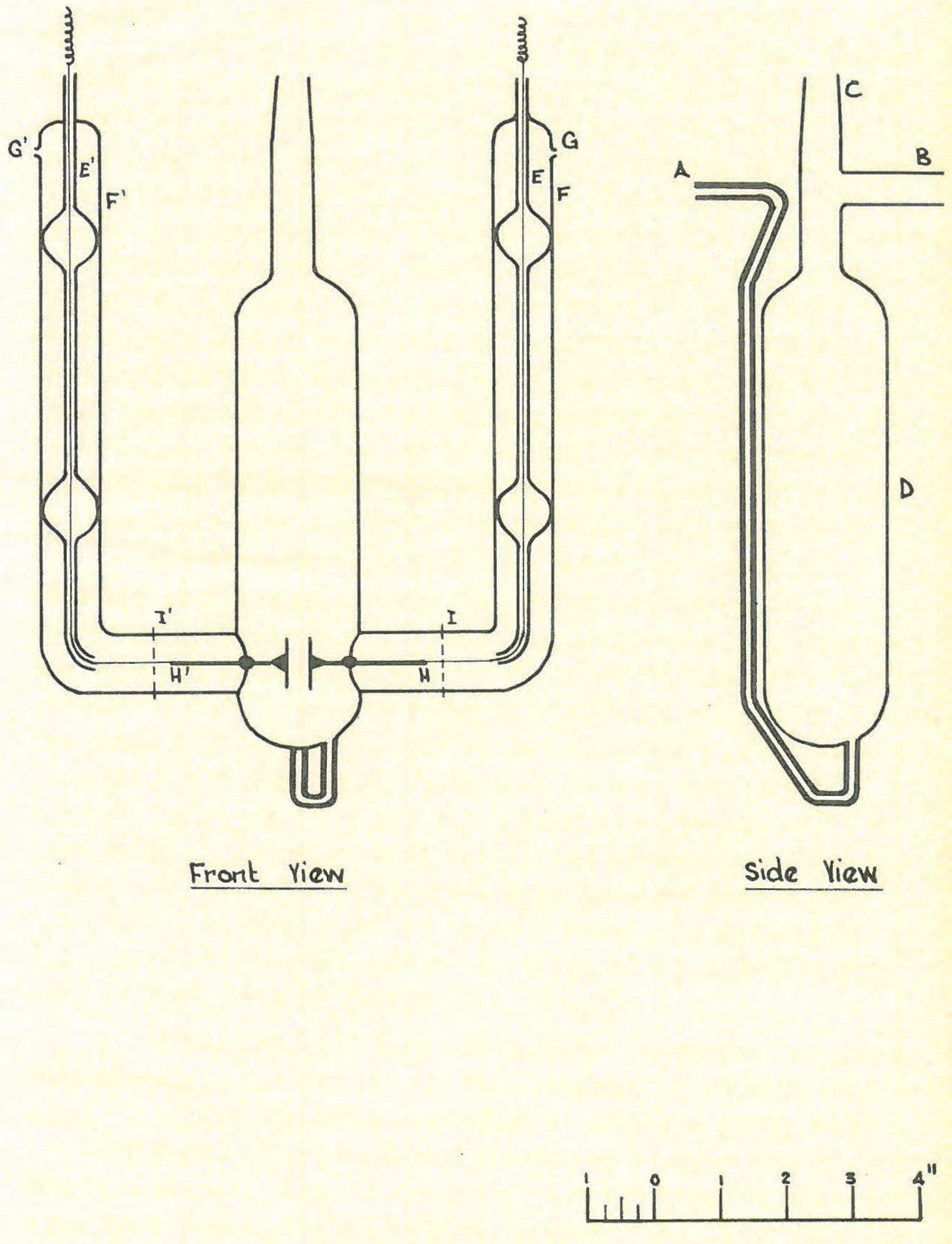
1.3 THE CONDUCTANCE CELLS.

1.31 Construction of the Cells.

Two conductance cells made of Pyrex were used throughout this investigation; Fig. 1.4 shows their design, and Cell II is illustrated in Plate II. They were similar to the cell described by Gledhill[3], with a few minor modifications. Although the design was independently developed in this laboratory for use in conductimetric titrations, cells of the same basic form had actually been reported in the literature a few years earlier by Johnson and Hulett[13]; unfortunately no details were given regarding dimensions, etc. From these authors' figure of a typical cell, however, it seems that the electrodes were sealed into the main body much higher than in the present design: in general, therefore, they would not be as well covered with liquid as the electrodes of a Gledhill type cell -- a defect when accurate conductimetric determinations are to be made, since errors can arise owing to the spreading out of the current between the electrodes if the latter are not immersed to a sufficient depth. A further difference appears to be that the side-arms were not spaced so far away from the body in the Johnson-Hulett cells, and that they were much narrower and probably filled with mercury for making connection to the electrodes. Gledhill had spaced the lead-wires well away from the solution under investigation in order to eliminate "Parker effect"[14], and he increased the effective separation by placing the leads inside a wider tube filled with air[3]. With this construction, the cell should certainly be free from "Parker effect", since even Johnson and Hulett's design seemed to be successful in reducing it to negligible proportions: they reported, for instance, that their cell constant ratios were independent of frequency over a wide range of resistances. The absence of "Parker effect" in cells of the Gledhill type has, in fact, been confirmed by A. Faure[2].

Since this type of cell was designed primarily for use in conductimetric titrations, it was necessary to provide some means of mixing the solutions after an addition which would not at the same time allow the atmosphere to come into contact with the liquid. Gas stirring was used for this purpose, and also for removing carbon dioxide, ammonia, and other volatile impurities from the water in the cell. The bubbles of purified gas were introduced to the liquid via the capillary tube A, which was connected with pressure tubing to the copper coil placed in the inner thermostat (see Section 1.12 for details

Fig. 1·4 - The conductance cell



Front View

Side View

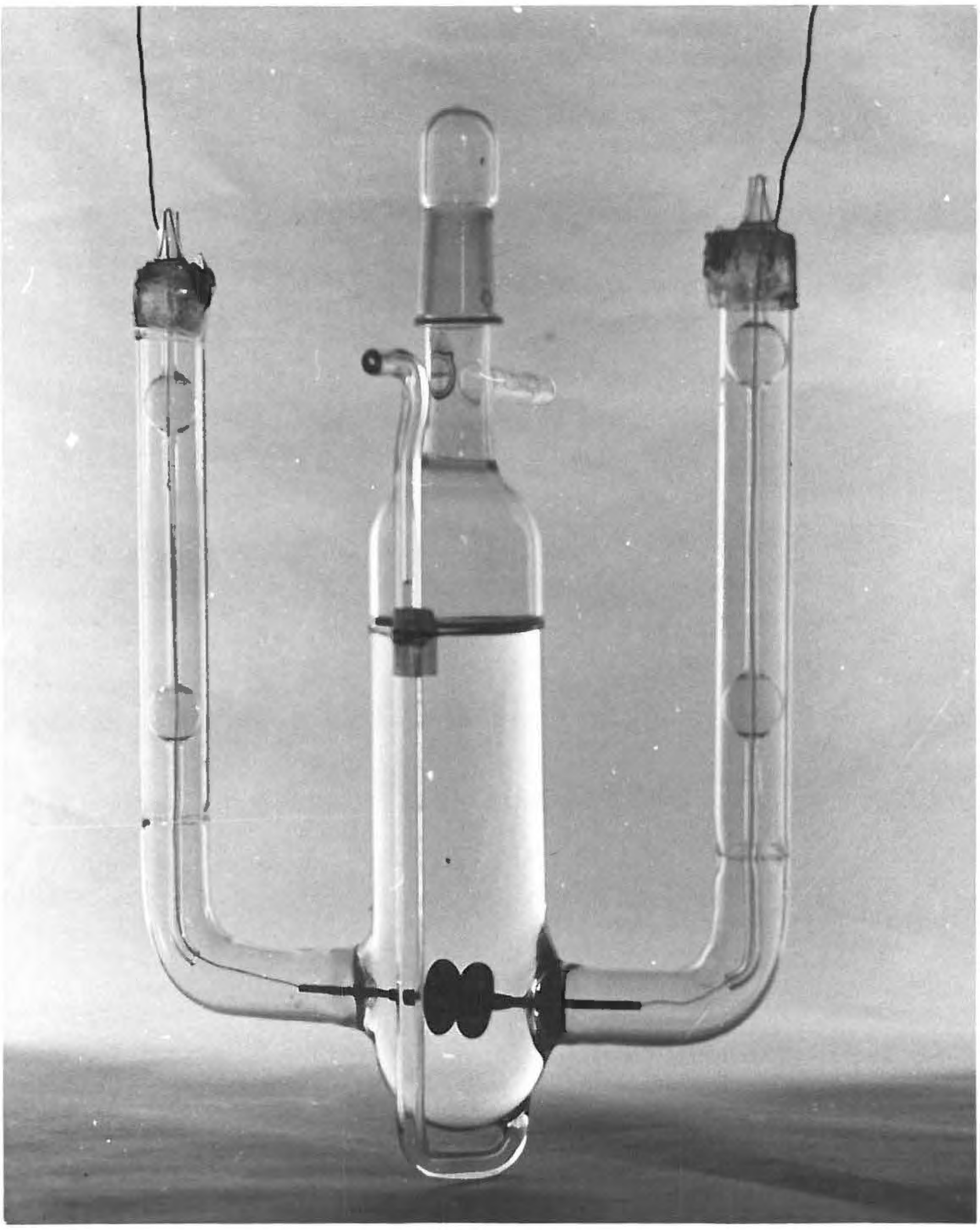


Plate II

of thermostat construction). Gas could also be passed over the top of the liquid in the cell via the side-tube B sealed to the neck C; B was joined to the end of the copper coil in the outer bath that terminated inside the inner vessel. (The two rubber connections actually served the dual purpose of forming a joint and of suspending the cell in the paraffin thermostat.) The secondary gas-stream was used to prevent back-diffusion of the atmosphere into the cell during periods when it was necessary to stop the bubbling through the solution, e.g. during the taking of resistance readings. Since the mouth of the cell had to be reasonably wide so that a burette could be introduced for the titrations, back-diffusion might still have been possible even while the gas was emerging from the cell; a close-fitting glass cap was therefore placed over the neck C of the cell whenever the latter was in the thermostat. A series of experiments showed that this precaution was sufficient to prevent carbon dioxide from the atmosphere from diffusing back into the cell, and that it was not necessary to protect the mouth with a soda-lime guard tube[15] (see Section 2.41). In later cells of this type, the neck was modified to terminate in a standard ground glass B19 cone, and the cap was made from the corresponding socket with a small hole in it to allow for the escape of the gas (see Plate II).

The most important modification of Gledhill's design was in the manner of joining the capillary tube A to the main body D of the cell. Originally it had been sealed centrally through the bottom of the cell and the internal portion bent to follow the contour of the wall closely; the tube then ended at the same level as the electrodes, so that the emerging bubbles would not pass these at all and perhaps, in doing so, cause changes in the cell constant -- the possibility of the bubbles displacing the electrodes was quite real in view of the rather flimsy nature of the initial electrode supports. It was suspected, however, that some of the very slow changes in resistance observed by Gledhill after he had added hydrochloric acid to water in the cell[3] were due to poor mixing of the solution at the bottom of the cell because of this construction. This suspicion was confirmed by various tests. For instance, the cell was filled to the usual level with water and a small amount of permanganate solution was carefully placed at the bottom before the stirring was started; mixing was found to be exceedingly slow at slow bubbling rates, and even at a rate of 5 - 6 bubbles per second about 35 minutes were required before the permanganate appeared visually to be uniformly dispersed throughout the solution. With this fast rate of bubbling, however, a considerable amount of spraying was observed as the bubbles broke the liquid surface, and it seemed that losses due to this source could be quite large. For quantitative work where further additions had to be made, therefore, such rapid bubbling was not to be recommended. Other visual tests, using a similar procedure, showed that mixing took place very much faster when the capillary tube was sealed flush with the bottom of the cell, either centrally or off-centre; with the latter seal, for instance, mixing appeared to be complete in 3 - 5 minutes for a rate as slow as 1 bubble per second, and in about 1 minute when this rate was doubled. Spraying was also, of course, much less at these slower rates, though still apparent. The off-centre seal was considered preferable to the central one for the construction of these cells, since it would still allow the bubbles to by-pass the electrodes to some extent and thus minimise any possibility of the latter being displaced. This seal was therefore adopted as standard for all future cells. Since the passage of bubbles of gas between the electrodes caused momentary changes in the resistance of the solution and hence necessitated stopping the stirring whenever accurate readings had to be taken, an attempt was made to avoid this need by placing the seal about 45° behind one of the electrodes (i.e. between the supporting tube and the electrode itself) instead of between them. The desired object was not achieved, however, because the bubbles rose too irregularly and the changes produced by their passage past the electrodes were still too large.

Because of the strains imposed on the capillary tube A whenever connections to it were being made or broken, it was rigidly bound to the body of the cell with thin wire. This wire also served as a convenient guide for the filling of the cell, since it was placed at a level corresponding to about 200 ml of liquid in the cell. In order to keep the whole assembly secure, a spacer was required between the capillary tube and the body. Originally it was made of cork, but this proved unsatisfactory when it became necessary to weigh the cell: the dry weight did not remain quite constant, and the small variations were tracked down to changes in the weight of the cork spacer resulting from its absorption of paraffin from the inner thermostat and the subsequent evaporation thereof. Various tests were made with Perspex, in which weighed pieces of the material were immersed in paraffin for several weeks, during which they were periodically removed from the liquid, wiped dry, and weighed; no significant changes in weight were observed. The spacer was therefore made from this material; it was shaped to fit the capillary tube and the cell body closely so that there would be no large gaps to trap paraffin which could subsequently evaporate. The remaining gaps were closed with Duco cement which, in similar weight tests, had also proved satisfactory in its resistance towards paraffin. In other cells of this design which have subsequently been constructed in this laboratory, the need for a spacer has been eliminated altogether by securing the capillary tube rigidly to the body by means of a solid glass seal between the top bend of the tube A and the neck C.

Further modifications of the original cell design included the application of a more elegant glass-blowing technique for centring the inner tubes E,E' of the side-arms F,F', through which the lead-wires passed. This was done by means of the bulbs shown in Fig. 1.4 instead of with mica discs as used by Gledhill. The small holes G,G' at the tops of the side-arms were retained to facilitate the cleaning and drying of the latter should they become wet inside owing to leakage at the electrode seals. When the lead-wires were left loose where they emerged from the side-arms, there was always a danger that the welded connections at H,H', where the wires had been joined to the platinum tubes of the electrodes, might be pulled apart; also, the wires tended to break at the point of emergence as a result of the constant bending there during use of the cell. Both these contingencies involved the breaking and re-sealing of the side-arm in order to effect repairs. To forestall such an eventuality, the wires were secured externally, with a small piece in reserve, by binding them back on to the tops of the side-arms. Cellophane tape was originally used for this purpose, but it was not entirely satisfactory: for instance, tests showed that the tape seemed to lose weight slowly, particularly when it was fresh; there was also the risk of getting it wet, especially while the side-arms were being cleaned -- the tape soaked very readily, and thereafter did not return to the same weight. Both these possibilities could be avoided fairly easily, the first by allowing the tape to age for some time after the binding before the cell was used, and the second by careful manipulation. However, further tests showed that nylon thread did not suffer from either of these disadvantages, and its use is therefore recommended for securing the leads on to the side-arms.

Gledhill had made his electrodes by welding a piece of platinum foil to a thin platinum tube, via several intermediate steps[3]. By the time that these cells were constructed, however, it was possible to have the complete electrodes manufactured by Messrs. Johnson, Matthey and Co., Ltd. A circular disc of thick platinum foil, 2 cm in diameter, was joined by means of a hollow platinum cone to a drawn platinum tube 2 mm in diameter and of wall thickness 0.1 mm (length about 5 cm, but immaterial). These tube dimensions were in accordance with those given by Wichers and Saylor[16] for the satisfactory sealing of platinum into Pyrex glass. The lead-wires were joined to the back ends of these tubes before the glass-blowing was done. Platinum wire was originally used for these leads, but it was too springy to lie centrally inside the glass tubes. It was therefore replaced by gold wire (26 S.W.G.), which was much softer, and which also had a very low resistance so that the correction for the cell leads resistance was fairly small. Longish leads were needed on the cell for making connections while it was in the thermostat, but the gold (or platinum) wire was not used throughout because the expense was unnecessary in view of the occasional breaking which occurred. Instead, copper wire (22 S.W.G.) was brazed to the nobler metal outside the side-arm (this wire was not joined directly to the platinum and used for the whole lead because the Cu-Pt joint tended to oxidise and break during the final sealing of the side-arm into the body).

Cell I was the first cell constructed according to the modified design, and it still had platinum leads welded to the platinum tubes. It was used for all the experiments on water described in Part 2, but not with the solutions in Part 3 because of leakages into the side-arms. A special feature of this cell was the method used for obtaining leak-proof seals of the electrodes. Although the platinum tubes conformed to the recommended diameter/wall-thickness ratio[16], and although successful seals into the side-arm tubes alone were effected fairly readily, the final sealing of these tubes into the body of the cell invariably resulted in a separation of the glass from the metal. No matter how small this was, capillary flow then caused the liquid to leak from the body of the cell into the side-arms. Such leaks were obviously undesirable. When all normal glass-blowing techniques had failed to produce a satisfactory seal, the rear end of the glass collar round the platinum tube was blocked with fused silver chloride. This substance had previously been used for high-temperature vacuum-tight seals of sodium chloride[17] and of fluorite[18] to glass, and also for metal-to-glass seals[19]. Tests showed it to wet and to adhere tenaciously to both glass and platinum; further, it had a high melting point (about

450°C) -- an essential property because the electrodes had first to be sealed into the body and the silver chloride applied to them before the final sealing of the side-arms was completed at I,I' (Fig. 1.4). The seals thus made proved very satisfactory, and leakage through them was almost negligible. Unfortunately the capillary tube A was broken near the bottom after the conclusion of the experiments in Part 2, and the strong heating required during the repair caused a slight flow of the silver chloride away from the seals. The leaks then increased somewhat, but were still fairly small; in fact, the cell was quite satisfactory for use with water provided that the side-arms were occasionally cleaned and dried (a rinse with acetone, followed by suction of air, was used). The leaks were considered too large, however, for quantitative work where it was necessary to know accurately the amount of liquid in the cell at all times.

Cell II is illustrated in Plate II; it was used for all the titration experiments described in Section 3.3. The silver chloride was no longer necessary in the construction of this cell, for by this time completely leak-proof platinum-to-Pyrex seals were being obtained in this laboratory. These were made by putting a sleeve of Intasil GS1 (a Chance Bros. Ltd. glass) of wall thickness 1 - 1½ mm on to the platinum, then sealing this straight into the Pyrex and letting it cool in asbestos-wool. This glass is actually the right intermediate for sealing tungsten into Pyrex, and it was tried after numerous unsuccesful attempts with the Corning-707-to-uranium-glass-to-Pyrex seal recommended for platinum. With the latter seal, the glass invariably separated from the metal, as had occurred with Pyrex alone. The thickness quoted above for the Intasil sleeve was apparently fairly critical, and it is possible that the failure of the Corning 707 seal was due to some lack of technique in regard to the right thickness of the various glasses required. This cell had gold wire leads which were joined to the platinum tubes with copper solder. A new device was tried for protecting them against undue strain and possible breakage, viz. a glass binding-post sealed to the top of each side-arm, around which the leads were wound. This proved unsatisfactory because the various coils of the winding shorted each other out to different extents as the wire was moved around, and so caused the leads resistance to be variable; even the soft gold wire had sufficient spring not to remain in a fixed position round the binding-posts during handling of the cell. The leads were therefore bound to the side-arms with Cellophane tape as before, and this was not removed when the more desirable properties of nylon thread for this purpose were realised; by then the weight of the cell seemed to have settled to a steady value, and changing the binding would have required a redetermination of the cell leads resistance at a stage when no time could be spared for the subsequent cleaning of the cell.

The determination of the cell constants of these cells is described fully in Section 3.2, and the values obtained are given in Appendix B.

1.32 Leads Resistance of the Cells.

The resistance of the cell leads was determined by placing sufficient pure dry mercury in the cell to cover the electrodes completely. Since the resistance was too low to be measured directly on the bridge with a.c., a small resistor (about 5 ohms) was used in series with the cell. The ends of all leads were amalgated and dipped into mercury cups to eliminate contact resistances. Determinations were then made of the resistance of the added resistor alternately with and without the cell in series, to give the resistance of the cell leads by difference; no change was found when either a.c. or d.c. was employed. The values obtained for Cells I and II are given in Appendix B. These values, suitably corrected for the resistance of the portions of the leads not actually connected in the measuring circuit (the connections to the bridge leads were usually made as close to the tops of the side-arms as possible), were always subtracted from the measured resistance of the cell in order to obtain the true value for the solution.

After the determination it was necessary to clean the cell, since not all the mercury could be removed by pouring. The last droplets were dissolved out with nitric acid, and the glass was then thoroughly cleaned with an alcohol-nitric acid mixture which had been allowed to react and cool; this latter mixture, as well as the chromic acid cleaning mixture, was fairly frequently used to clean the cell internally during the titration experiments (see Section 3.323). The electrodes, which had been bright before their contact with the mercury, still seemed a little gray even after the nitric acid treatment; they were therefore cleaned with a mixture of equal parts of concentrated hydrochloric acid and 30% hydrogen peroxide, the mixture being left in contact with the electrodes for 1 - 2 minutes only, as it dissolved the platinum. Finally the cell had to be leached for 10 - 14 days with repeated changes of fresh water before it was ready for use. This process could be hastened by steaming out the cell, but such heating was inadvisable once the cell constant had been determined.

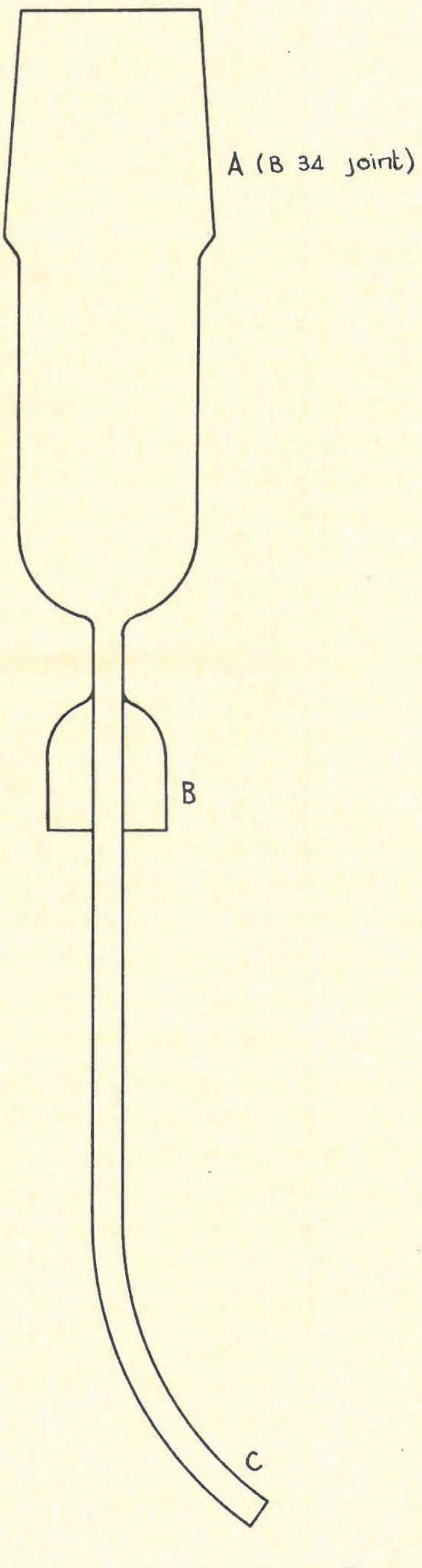
1.33 Drying, Filling, and Weighing of the Cells.

In order to know exactly how much liquid was placed in the cell during volumetric procedures, it was necessary first to dry the cell completely. Even if a titration were to be done gravimetrically, it was still essential to weigh the cell dry before filling it with water to ensure that no changes in weight had occurred, e.g. owing to wetting of the material used for securing the leads to the side-arms, or to absorption of paraffin by the spacer between the capillary tube and the body. Less frequent drying would be required for gravimetric procedures, however, for once it had been established that the weight remained fairly constant, these checks would not need to be made before every filling of the cell. For this reason, and because of its greater general accuracy over the volumetric method, the gravimetric procedure was chosen for performing the conductimetric titrations described in Section 3.3. This choice proved to be a wise one for another reason, for it was subsequently observed that the conductivity water always appeared to be of a poorer quality when it was placed in a completely dry cell.

The internal drying of the cell was effected by draining it in an inverted position, and at the same time sucking a stream of air through it by means of a vacuum pump; about $\frac{1}{2}$ - 1 hour was usually sufficient, depending on the relative humidity of the atmosphere. Although the interior of the cell was dried only occasionally, it was of course necessary to dry the exterior before every weighing. If the cell had just been taken out of the thermostat, it was first drained for a short while and wiped roughly to get rid of the large excess of paraffin, then left for a further 10 - 15 minutes. The last traces of oil were always removed by wiping very thoroughly over the whole outer surface with a clean cloth or handkerchief; particular attention was paid to any little crevices, etc., where the paraffin might be retained and so change the weight of the cell. Thereafter the cell was left in the balance-room for a further $\frac{1}{2}$ - 1 hour to attain complete equilibrium after the wiping before it was finally weighed. During these last wiping and the subsequent weighing operations, clean white cotton gloves were used for handling the cell.

The normal method of filling the cell with water or solutions, viz. by pouring them in directly from the flask, could not be used for the titrations, since it was obviously undesirable to have water adhering to the upper walls and neck of the cell: this would be weighed as if it were in the bulk of the liquid. At first, therefore, the cell was dried internally before each filling (as would have been necessary for volumetric procedures), and the upper portions were kept dry by pouring the water in through a glass funnel which had been cut so that it ended just above the required 200-ml level. Invariably, however, the water so placed in the cell seemed to be of poor quality. Since it was thought that this resulted from the introduction of impurities during the transfer via the funnel, a new cell-filling device was designed which would enable water to be distilled directly into the cell. This device (shown in Fig. 1.5) could be attached to the still in place of the usual collecting flask by means of the ground-glass joint A (for details of the still see reprint at the back of this thesis). The neck of the cell was connected by means of rubber tubing to the wide tube B, thus sealing the contents of the cell from the atmosphere while water was being distilled through the narrow tube C; the latter was bent so as to touch the wall of the cell just above the 200-ml level and thus prevent splashing on to the upper portions. Some difficulty was experienced owing to condensation of moisture on these colder upper parts, but this could be overcome by warming the top half of the cell, and by cooling the distillate more thoroughly with colder condenser water. However, although this device was steamed out for long periods before the cell was connected, the quality of the water so collected still remained poor. This poorness was finally correlated with the internal drying of the cell, though the probable reason for the phenomenon was only realised later (see Section 2.32). The cell was therefore no longer dried completely before being filled for a titration, but merely drained very well; if the inside were quite clean, a few minutes drainage left very little water adhering to the upper parts of the cell. Since filling the cell with the special device was rather slow and would still require precautions to prevent condensation, the device was discarded at this stage, and the water was placed in the cell by using the funnel exclusively. This was kept permanently immersed in frequently changed conductivity water, and just before use it was wiped lightly on the inside and outside with a clean handkerchief to dry it. Any foreign matter which might have remained in the funnel from this wiping

Fig. 1·5 Device for filling the cell.



Scale (approx) 1:1

was washed through with some freshly distilled water, and then the funnel was placed in the cell and water poured in from a normal collecting flask up to the required level. With careful manipulation, the funnel could again be readily removed from the cell without leaving any water on the upper walls or the neck.

The cell was weighed on balance BIII (see Section 1.41), being held in place on the pan with a wire hook. Although the weight was always determined at the beginning and end of each titration to check on any losses by evaporation and spraying, the weighing was done without the rubber connections used for suspending the cell in the thermostat, as it was found that these changed in weight, presumably due to absorption of paraffin vapour. Steps had to be taken, of course, to prevent evaporation of the liquid in the cell during the weighing procedure. For this purpose the side-tube B and capillary tube A (Fig. 1.4) were blocked with a small rubber stopper and with a rubber tube and glass plug respectively, and the glass cap (p. 26) was placed over the neck C. These same accessories (including the wire hook) were kept specially for all weighings of the cells, both dry and with liquid. The efficiency of the wiping operations previous;y described is shown by the constancy of the weight of Cell II, the dry weight of which only varied between 289.408 and 289.459 g during 15 months of use. Even Cell I only changed in weight between 308.641 and 308.694 g in 4 months after the broken capillary had been repaired, in spite of the fact that its side-arms had then also to be cleaned and dried periodically.

1.34 Platinisation of the Electrodes.

After the titrations with bright platinum electrodes (Expts. 1 to 10, Section 3.325) had been completed, the electrodes of Cell II were platinised fairly heavily in order to investigate the adsorption of potassium chloride on platinum black. Jones and Bollinger[20] had found that platinising solutions containing no lead acetate yielded unsatisfactory results, particularly for large deposits, and their solution (0.3% platinum chloride and 0.025% lead acetate in 0.025 N hydrochloric acid) was therefore used. During the electrolysis the direction of the current was automatically reversed every 10 seconds to ensure an equal deposit on each electrode. The exact amount of platinum black deposited is not known, because the current decreased so rapidly during these short time-intervals as the electrodes became polarised that only a very approximate estimate of the mean current could be made; also, the total platinisation was performed in several stages, and at times it appeared that a current was flowing without any actual deposition occurring. During the first step, for instance, a very low current (approximately 5 milliamps) was employed, since it was desired to get a firmly adherent deposit by slow platinisation; but after 4 hours the electrodes appeared as bright as before, and the polarisation correction (see Section 3.22) was found to be still very large. The average current was therefore increased to about 25 milliamps, when the electrodes blackened very nicely, mainly on the front faces but also somewhat on the backs and on the platinum cones and tubes. The electrolysis was carried on for about an hour, but the amount of deposit at this stage was estimated at only 35 - 40 coulombs per electrode, not 45 as given by calculation: this was based on the fact that, although the electrodes had seemed to become progressively blacker during most of this period, their appearance did not change visibly when the platinisation was continued for a further spell at the same current in order to obtain a heavier deposit. Yet the blackness intensified almost immediately when, after two hours, the current was increased to 50 milliamps. This current was passed until no further visible change was apparent; it was then increased again in two more steps, to 60 and 70 milliamps respectively for several minutes each, before the electrolysis was finally stopped. An even, sooty black deposit resulted, which seemed quite thick and firmly adherent; the total amount was estimated at about 150 coulombs per electrode. (See also Section 3.222.)

After the platinisation the products of the electrolysis which had been adsorbed on the platinum black (chiefly chlorine) were removed by electrolysing a dilute solution of sulphuric acid in the cell[21]. 1N-acid was used at 150 - 200 milliamps for 3 hours, the current being reversed every 5 minutes. Even then the cell still had to be leached out for several days with numerous changes of water before it was again ready for use in further titrations. The electrodes were always kept immersed in water when the cell was not in actual use, and were only dried completely on the few occasions when it was necessary to check the weight of the cell after the platinisation. Thereafter, since dry platinised electrodes are apparently not easily wetted by water, they were first soaked in absolute alcohol for a few minutes before water was again placed in the cell[22].

1.4 BALANCES AND WEIGHTS.

1.41 Balances.

Three balances were used during the various experiments described in Part 3.

BI was a Kuhlmann microbalance, of beam length 7 cm. Weights larger than 10 mg had to be added from a box, but additions from 1 to 10 mg could be made to the right-hand pan, with the balance-case closed, by external manipulation of four riders (originally 1, 2, 2, and 5 mg, but later one of the 2 mg riders was replaced by a 3 mg rider). Smaller weights, from 1 µg to 1 mg, could be estimated from a telescopically-viewed 100-division scale. The maximum load was 20g, but this balance was not in perfect condition, and sudden erratic shifts, sometimes as large as 30 - 40 µg, were occasionally found under such a heavy load. With lighter loads, however, successive readings were invariably reproducible to 10 µg or better. Since this balance was used only for weighing out KCl for the preparation of standard solutions, in portions of 0.5g or more, and since the mean of three settings was usually taken, any errors due to inconstancy of the weighing would be quite negligible. Care had to be taken, however, that no large fluctuations in the ambient temperature occurred during a weighing, as the balance was very sensitive to such changes.

BII was an Oertling automatic air-damped balance (Model 62FM), of maximum load 100g. All fractional weights, from 10 mg upwards, could be added by external manipulation of riders, without opening the balance. The third and fourth decimal places were read off from a projection scale, whose divisions were large enough for the fifth place to be estimated too. Such estimation was perhaps straining the limits of precision of the balance, for which an accuracy of 0.1 mg was claimed by the manufacturers. However, the aliquots of the KCl stock solution added to the cell during the titration experiments (Section 3.3) were only about 0.2g each, and these weights were determined on this balance as the difference between two large weights (the burette weighed approximately 40g). Hence, if each of the latter quantities was determined to an accuracy of 0.1 mg only, it was still possible for the required weight to be in error by as much as 0.1%. Since it was hoped to achieve a better overall precision than this in the performance of the experiments, it was essential to be able to estimate the weights to five decimal places. Unfortunately, the balance was by no means as stable as could have been desired: with no load on the pans, shifts of up to 0.1 mg were found between successive readings, while under 40 g load the sudden jumps were occasionally as large as 0.2 mg. The practice was therefore adopted of taking the mean of at least five successive settings of the balance, and more if an erratic change had become apparent; between each of these the burette was removed from and replaced on the supporting hook. This procedure was rather tedious, since the balance was slow in settling down to a final steady value (it usually took 1 - 2 minutes per reading). However, numerous tests showed that the mean value of such a set of weighings was almost certainly correct to 0.05 mg or better, i.e. under these conditions, the error in the weight of an individual addition would not be more than 0.05%: this was the maximum error, and it would arise only if the separate errors of the two weighings of the burette were 0.05 mg each, but in opposite directions. With increasing numbers of additions, the total error was probably less than this, since it is statistically unlikely that all the individual errors would have been additive.

Very accurate weighing on this balance was further hampered on occasions because of its situation. It was, of course, essential to have it inside the constant temperature room, and it was placed on the slate slab provided there for this purpose. This slab had been mounted directly to one of the walls of the building in an effort to minimise the vibrations which would occur if it were in contact with the floor of the room. The choice of wall, however, was rather unfortunate. Presumably in order to avoid the larger fluctuations in temperature which would be found at an outer wall of the building, an inner one had been chosen; but this wall was situated immediately below the departmental store, and it also formed part of a long corridor wall. Hence the movements in the former or the occasional slamming of doors in the latter resulted in the transmission of vibrations to the balance, which made precision weighing very trying at times. Several methods of damping these vibrations were tried, but none of them met with much success.

<u>B III</u> was a large Sartorius balance, undamped, and of maximum load 1000 g. It was used for weighing all large objects, such as the cell and the flasks in which solutions were prepared.

Because weights, which had been determined on three different balances, were to be intercompared, it was necessary to determine the differences in length of the arms of the various balances in order to maintain the desired precision. This was done by Gauss's method of double weighing[23], and the results are given in Appendix C. A suitable correction was then applied to all weighings.

Experience has shown that, when an object is weighed on a balance that has been arrested for a while, the initial weight changes slightly as successive weighings of the same object are repeated, and a constant weight is recorded only after some time. This is believed to be due to some fatiguing effect of the metal beam. The effect is admittedly small, but in order to eliminate as many sources of error as possible for the sake of precision, the standard practice was adopted, especially with heavier loads, of first "fatiguing" the balances by several preliminary weighings before making any precise determination.

1.42 Weights.

Several different sets of weights were used in conjunction with the various balances.

WI was a box of Oertling micro-weights (1 mg to 50g) kept specially for balance BI. Only the fractional weights (10 to 500 mg) from this box were used: of these, the 50 to 500 mg weights were gold-plated, but not the 20 and 10 mg pieces. Below 10 mg the riders supplied with the balance were used.

WII was a box of Grade A Sartorius weights (1 mg to 100g -- Box No. 7). The larger weights, from 1g upwards, were made of chromium-plated brass: they were used with all the balances. The fractional weights (10 and 20 mg -- aluminium; 50 to 500 mg -- platinum-plated nickelin) were used with balance BIII.

WIII was a box of Sartorius weights (10 mg to 1000g), of which the brass weights from 100g upwards were used for weighings on balance BIII.

WIV was the set of riders supplied with balance BII (10 to 500 mg): these were used for all weighings on this balance.

All weights used were calibrated by a modification of the Richards' method[12]. Balance BI was used for intercomparing all the weights up to 20g, balance BII for weights from 20 to 100g, and balance BIII for the larger weights. Although this intercomparison was sufficiently accurate in itself, since it gave all the weights relative to one another, the calibration was completed by comparing the 10 and 20g weights against two similar weights which had been standardised by the S.A. National Physical Laboratory. The calibration was repeated several times, and the results of the most recent calibration are given in Appendix C.

1.43 Conversion of Weights to Vacuum.

The standard equation for the reduction of weights in air to vacuum is given by[24]

$$W_v = W_a + d_a\left(\frac{W_v}{d_b} - \frac{W_a}{d_w}\right) \qquad \text{..........(1.30)}$$

where W_v = true weight in vacuum
W_a = apparent weight in air
d_a = density of air
d_b = density of the body
d_w = density of the weights.

Since W_v and W_a are so nearly equal, equation (1.30) reduces to

$$W_v = W_a(1 + C) \qquad \text{..........(1.31)}$$

where C = vacuum correction factor

$$= d_a\left(\frac{1}{d_b} - \frac{1}{d_w}\right) \qquad \text{..........(1.32)}$$

The density of air, d_a, depends on the temperature, pressure, and humidity. C, therefore, involves so many variables that the tabulated values are normally based upon a constant air density, no allowance being made for local daily variations in atmospheric conditions. These values were considered not precise enough for the conductance work described here, since it was desired to obtain an overall accuracy of 0.01%, or at least as close to this as could be achieved. All likely sources of error had therefore to be minimised as much as possible.

Thacher[25] constructed a nomographic chart from which the correction factors for certain atmospheric conditions could be obtained fairly readily and precisely. This chart covered quite a wide range of temperatures, pressures, and body densities. Unfortunately the range of pressures considered (730 - 790 mm) did not include the normal pressures prevailing in Grahamstown (about 700 - 720 mm). Although the chart could have been extended to take in these pressures, this would have caused the slope of the interpolation line, which had to be drawn in order to determine the correction, to become steeper: it would then no longer have been possible to read off the intercept with the same precision.

An accurate correction could, of course, always have been obtained by direct calculation of C from equation (1.32), using the exact value of d_a for the given temperature and pressure. Such a procedure, however, would have been rather tedious where many weighings were being performed, and in order to avoid this the chart shown in Fig. 1.6 was constructed. In effect, this chart merely represents lines of constant air density which will, on calculation, give certain values for C when water (or a fairly dilute aqueous solution of density d_b = 1.00 g/cc. approx.) is weighed against brass weights (density d_w = 8.4 g/cc.). The air density values were obtained for different temperatures and pressures from tables[26]. A constant relative humidity of 50% was assumed, as was done by Thacher[25] too, since changes in the humidity do not appreciably affect the density of air. The corrections read off from Fig. 1.6 must be added to the apparent weights obtained in air.

The chart can also be used for obtaining the correction when bodies of density other than 1.00 g/cc. are weighed against brass weights. Thus the following formula is easily derived from equation (1.32):-

$$C = C_1\left(\frac{1.1351}{d_b} - 0.1351\right) \qquad \text{..........(1.33)}$$

where C = correction factor for body of density d_b
and C_1 = " " " " " 1.00 g/cc.

C_1 can be obtained from the chart, and hence C by calculation from equation (1.33). In particular, for potassium chloride (the electrolyte used in this investigation), d_b = 1.984 g/cc.[27], and equation (1.33) therefore simplifies to

$$C = 0.437\ C_1 \qquad \text{..........(1.34)}$$

1.5 THE WEIGHT BURETTE.

1.51 Construction of the Burette.

The design of the weight burette, which was made of Pyrex glass, is shown in Fig. 1.7. Its special feature was the presence of the controlling stopcock D at the top instead of in the more conventional position at the bottom of the burette. This principle had been used previously in a weight burette by Shedlovsky and Brown[28], and also in this laboratory for burettes of similar design by Festenstein[29] and A. Faure[2]. The primary purpose of this construction was to avoid contamination by grease of the solution to be dispensed from the burette; but this design also allowed the burette to be made with a rather long jet, which could be inserted well into the the cell, without its total length becoming too great for it to be placed on the balance. These two considerations of length actually governed the final dimensions of the burette. The jet in particular had to be long enough so that the tip could be lowered to within $\frac{1}{4}-\frac{1}{2}$ inch of the 200-ml level in the cell (this was the usual amount used for a filling): this ensured that no splashing of the solution would occur while an addition was being made.

Two burettes were constructed, to deliver approximately 2 ml and 0.2 ml respectively. The original intention was to make additions of about 2 ml during the titrations, since this quantity of solution could be weighed quite accurately by difference on the balance B II (see Section 1.41), which was the only automatic analytical balance available. This volume of solution, however, was large enough to introduce appreciable amounts of dissolved carbon dioxide into the liquid in the cell, and also, if it were not itself at 25°C before addition, to change the temperature inside the cell noticeably. For instance, changes in conductivity of the order of 10 - 20 nm/cm were observed during several experiments in which blank additions were made to the cell (2 ml pure water added to 200 ml previously equilibrated water). These variations arising from temperature equilibration and the removal of carbon dioxide were considered too large for the projected experiments, where it was hoped to investigate the adsorption of potassium chloride by observing the immediate changes in conductivity which occurred when this electrolyte was added to water (see Section 3.31). 0.2 ml was therefore chosen as the standard addition, in spite of the fact that this amount could not be weighed out with the same accu-

Fig. 1·6 - Chart for correcting weights to vacuum

For aqueous solutions (density 1·000 g/cc.) weighed against brass weights. Correction must be *ADDED* to apparent weight in air to give weight "in vacuo"

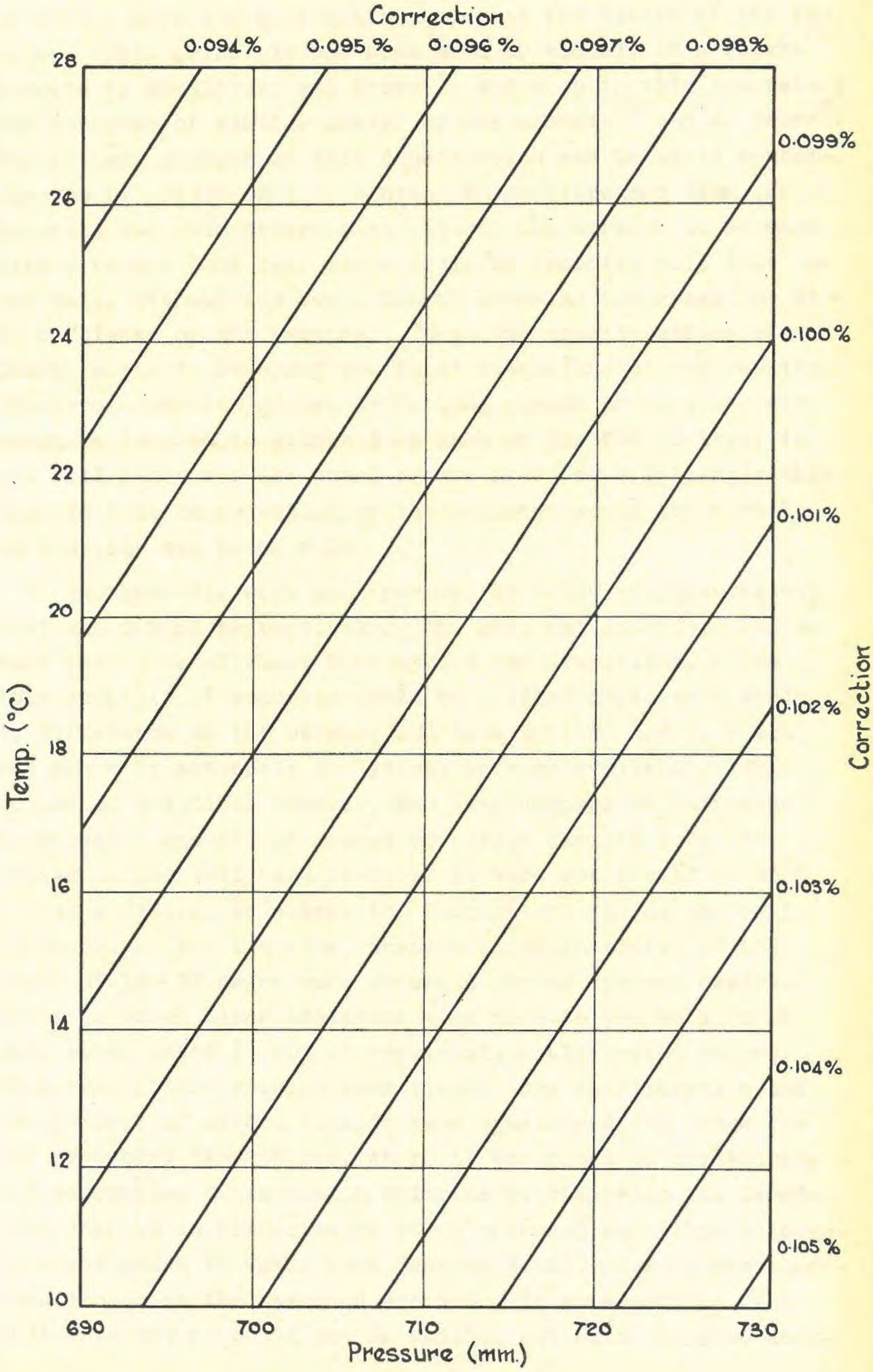
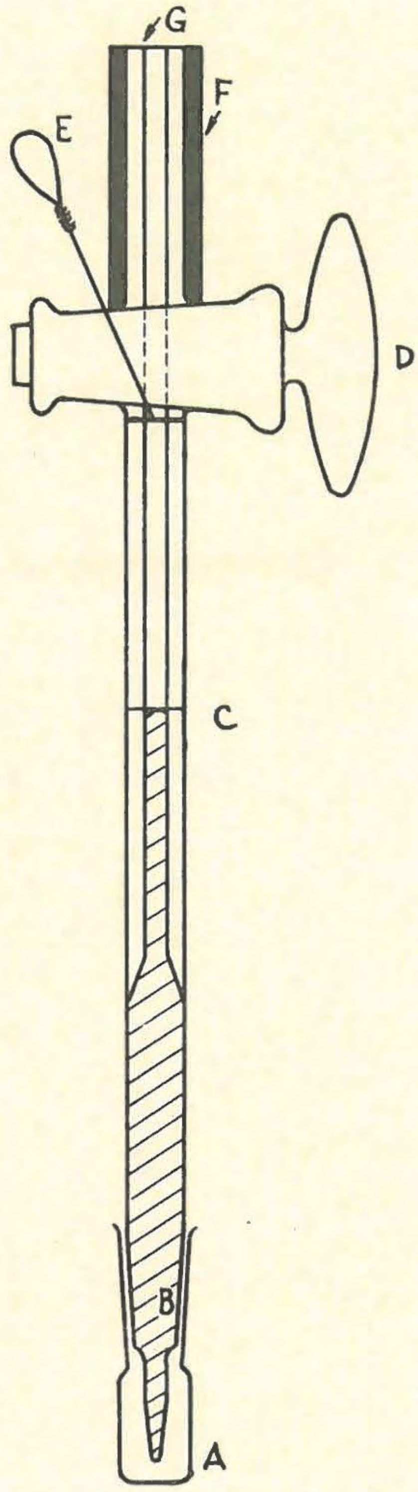


Fig. 1·7 The Weight Burette



Scale (approx) 1:1

racy as a larger volume.

These burettes were constructed with a ground glass cap A, which could be placed over the jet to prevent evaporation during weighing, etc. No grease was used on this joint, to avoid contamination should the jet accidentally be touched against it; the cap was held in place quite satisfactorily merely by friction, without the aid of hooks and springs. This cap A and the corresponding joint B were made from a Quickfit A7 socket and cone respectively. Since the internal volume of the latter joint was itself more than 0.2 ml, it was not possible to construct a burette which had a total capacity of this amount, no matter how short the jet was made: the graduation mark for 0.2 ml would, in fact, have to be made on the ground glass joint B, which was rather unsatisfactory. To avoid this, the tube was drawn down just below the end of the joint to an extremely fine jet. This was then gradually ground back, with frequent testing of the rate at which water flowed out of the burette when it was filled to about the level C and the stopcock D was opened fully; the orifice was considered large enough when approximately 0.2 ml of liquid flowed out in 10 seconds. The graduation mark was then made at C (three marks were actually made, corresponding roughly to deliveries of 0.23, 0.20, and 0.18 ml in 10 secs), and the jet was bevelled off to a fine tip so that the liquid would flow out in very small drops.

A Pyrex capillary stopcock (external diameter of tube 6½ mm and internal diameter 2½ mm) was used for the body of the burette. The top end G was made just long enough so that the burette could be clamped securely while it was being lowered into or raised from the cell. Since the tube was actually rather narrow for firm clamping, the whole end G was sheathed in a piece of rubber tubing F to ensure that the burette would not slip in the clamp. The choice of rubber for this purpose was perhaps not the best in view of its tendency to change in weight (see Section 1.54), and some plastic tubing might well be tried instead in future burettes; however, it served satisfactorily with careful handling. The looped copper wire E (about 20 S.W.G.) enabled the burette to be suspended on balance BII; it was fastened around the stem just below the stopcock D and sealed in place with a blob of de Khotinsky cement.

The burette is illustrated (together with its clamp) in Plates III a and III b.

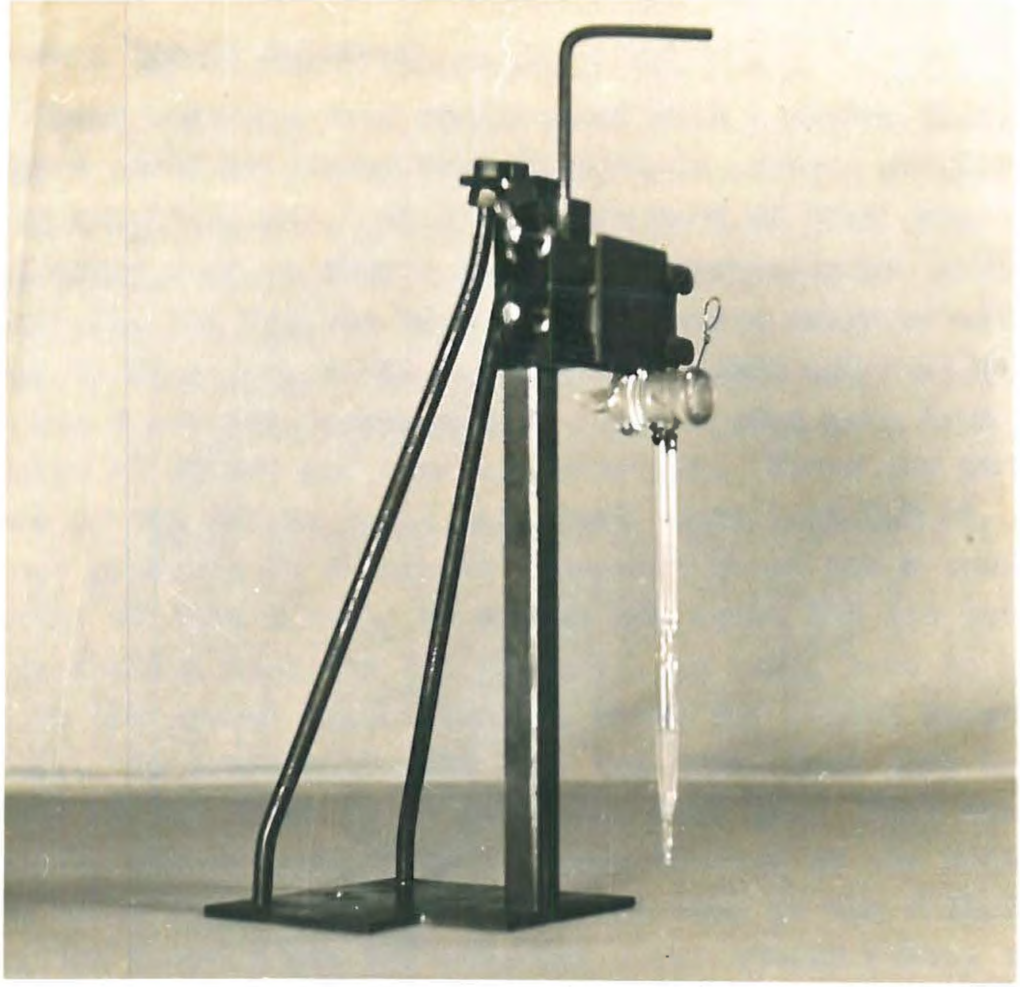


Plate III a

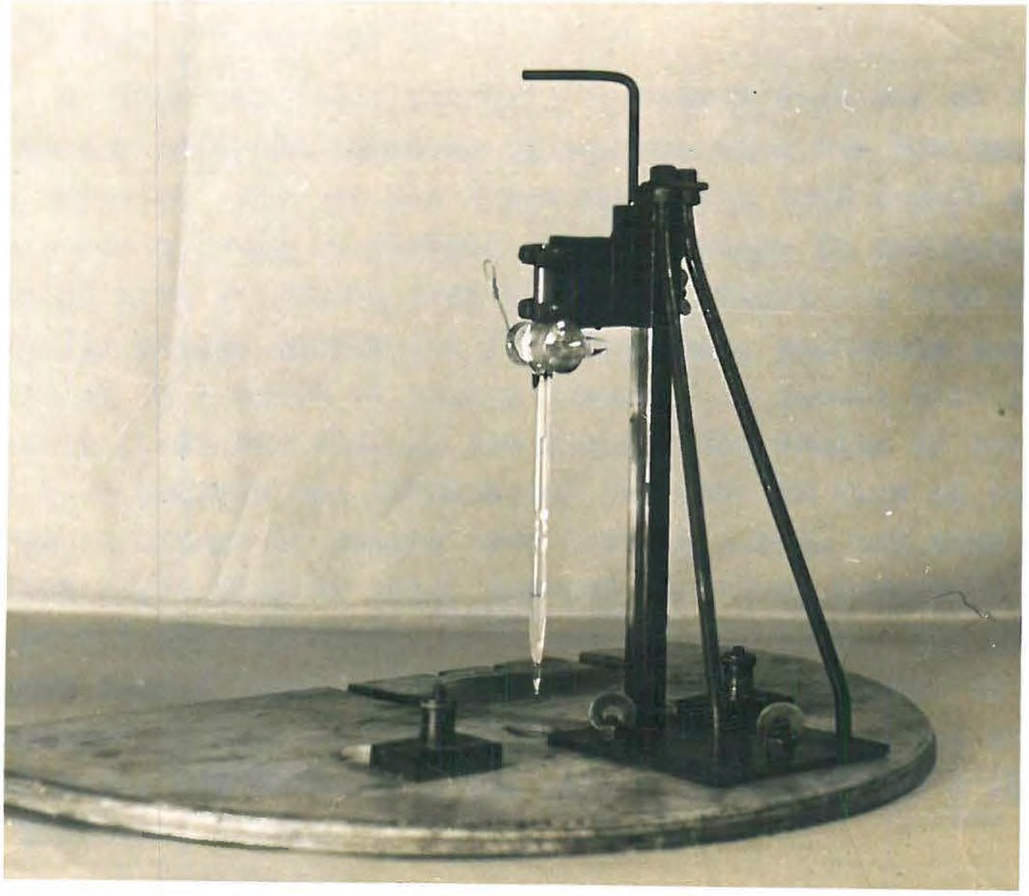


Plate III b

1.52 Use of the Burette.

After its construction the burette was left overnight filled with chromic acid solution, and was then steamed out for several hours*. Thereafter it was further leached out with several changes of water and of the potassium chloride stock solution (Section 3.321). When not in actual use, the burette was kept filled with this solution almost up to the stopcock D, and left suspended in the constant temperature room.

The normal method of filling the burette was to place the tip of the jet directly into the solution and then to apply a gentle suction (usually with the mouth, since it allowed of better control) via a long piece of rubber tubing fixed over the end of the tube F. Great care was taken not to let the liquid rise as high as the stopcock. If this did happen, the burette was first cleaned by sucking pure water through it with a filter-pump, and subsequently dried by air-suction; the stopcock was also regreased.

When the burette had been filled to a given mark, delivery of the required 0.2 ml was effected by opening the stopcock fully for a suitable period (in this case, 8½ seconds).

1.53 The Burette Clamp.

When an addition of solution was made to the cell, the burette was lowered well down into the latter, until the tip was within ¼ - ½ inch of the liquid surface. This eliminated the risk of drops of the solution falling on to the walls of the cell and then draining only slowly and incompletely into the liquid; at the same time, the possibility of losses resulting from splashing on to the walls as the drops fell directly into the liquid was reduced to a minimum. During the raising and lowering of the burette, it was necessary to avoid contact, especially of the tip, with the drops of liquid which frequently adhered to the inside of the neck of the cell (see Section 3.323), and with the liquid itself. A special clamp was therefore used for holding the burette centrally in the neck during these operations.

The details of construction and use of this clamp may be seen in Fig. 1.8 and Plates III a and III b. In essence it

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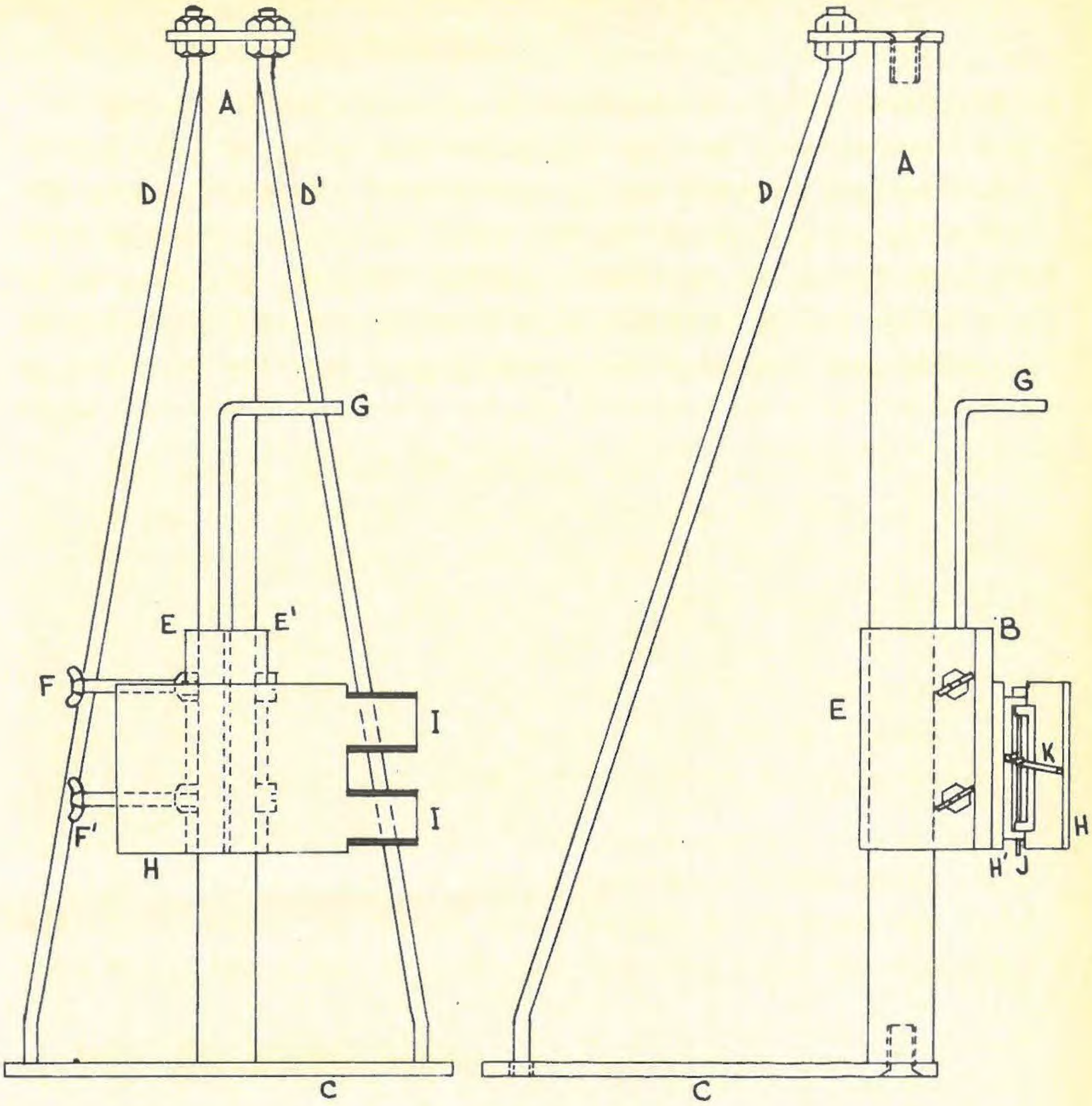
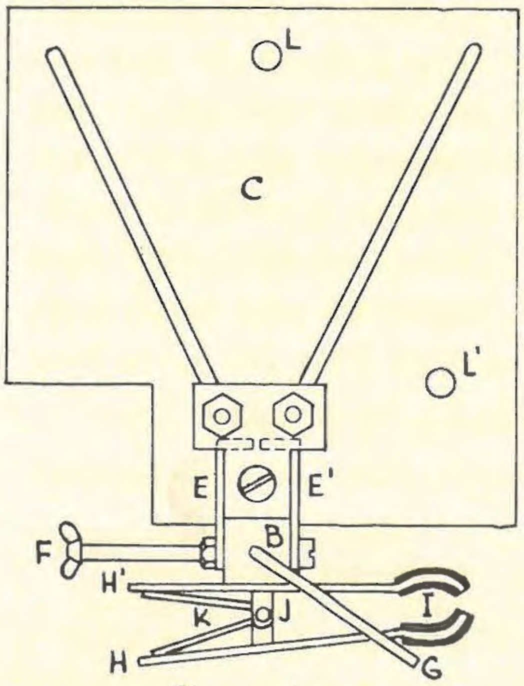
* Great care should be taken in fastening the burette firmly to the steaming apparatus, as the very narrow jet causes a considerable steam pressure to be built up!

Fig. 1·8 The Burette Clamp.



Elevation

Side elevation



Plan view

Scale (approx) 1:2

consisted of a length of $\frac{1}{2}$-inch square brass rod A along which a shorter piece of similar rod B could be slid. A was bolted to a square brass base-plate C (the gap cut in the one corner was merely to allow space for the one terminal block on the thermostat lid when the clamp was fixed there -- see Plate III b), and it was held firmly and vertically by means of the two stay-rods D,D'. B was held in contact with A by means of two pieces of angle-iron E,E' bolted to it; these also served to clamp B in any desired position by friction when the bolts were tightened. The long-shafted wing-bolts F,F' facilitated the clamping and unclamping; when these were loosened slightly, B could be raised or lowered very smoothly and easily. The bent rod G, which was screwed into B, provided a convenient handle for this purpose. The clamp itself was bolted to the front face of B: it consisted of two brass plates H,H' with the jaws I cut out at one end and bent to shape. These plates pivoted about a rod J, and the jaws were pressed close by means of a coiled spring K. The jaws were covered with rubber to give a better friction grip on the burette.

The whole burette clamp could be bolted to the thermostat lid (see Plate III b): two bolts were fixed into the lid for this purpose. The clamp was not permanently fastened to the lid, because the position of the cell mouth varied slightly each time it was placed in the thermostat owing to the manner of its suspension. Obviously it was desirable to position the burette so that it could be lowered as centrally as possible into the cell, and the two holes L,L' in the base-plate were therefore made with diameter a little larger than that of the bolts projecting from the lid, in order to allow some latitude in the positioning of the clamp. The latter was fastened to the lid with wing-nuts and spring-washers, so that minor adjustments of its position could readily be made. Whenever a titration was to be performed, the clamp was positioned as soon as the cell had been put in the thermostat and the lid had been replaced, and it was then left undisturbed for the whole experiment.

1.54 Weighing the Burette.

This was probably the most important procedure affecting the general accuracy of the titrations, as can readily be seen when it is realised that the whole burette weighed approximately 40 g, while the additions to be made from it were only about 0.2 g. Since these had to be determined by difference, errors in the larger weights, which would normally be regarded as insignificant, could obviously become quite appreciable in estimating the smaller weight accurately. Apart from the errors which could arise from the general instability of the balance available (see Section 1.41), there was also the question of the effect of the various handling operations on the constancy and reproducibility of the weight of so large an object. It was, for instance, necessary to wipe the burette clean and dry after it had been filled; but the weight immediately after this had been done was found to increase during the first 10 minutes by about 0.3 mg (an average value, for it was not completely reproducible) owing to adsorption of moisture on the cleaned glass surface and dissipation of the electrification produced by the rubbing. This increase appeared to continue for quite a long while, though at a diminishing rate. Numerous tests were therefore performed to determine the effects of wiping and handling the burette, and to find under what conditions a reproducible weight could be expected. Apart from the increase in weight with time already mentioned, the following are some of the results obtained:-

(i) The need for the use of a cap over the jet to prevent evaporation was clearly demonstrated. Without a cap and with no drop visible on the end of the jet, the orifice was so narrow that the weight decreased at an almost negligible rate (0.02 mg per minute or less); but as long as any semblance of a drop was present on the tip, there was a steady decrease of about 0.16 mg per minute when the burette was left exposed in the room, i.e. almost 0.1% of the total weight of an addition per minute. Since it could not be guaranteed that the last drop would be broken off cleanly during an addition, it was obviously essential to have a cap, and to replace it quite rapidly after the addition had been made. While the cap was on the burette, the weight remained quite steady, except on a few occasions when the jet had accidentally been touched against the cap as the latter was being replaced after an addition, and a thin layer of liquid had thus spread over the ground glass surface (a very steady hand was required to avoid doing this!): then a slow, but much smaller, loss by evaporation did become detectable.

(ii) It was deemed desirable to handle the burette as far as possible with clean white cotton gloves, and light handling in this manner of both the glass and rubber parts did not seem to alter the weight appreciably. Since, however, this made manipulation of the burette and its clamp during an addition rather clumsy, a number of tests were carried out to ascertain the effects of direct handling with bare fingers. Rather surprisingly, it was found that, once the weight of the burette had become constant, the glass stopcock and stem could be touched more than was necessary for normal operation, and even with fairly clammy hands, without producing changes in weight outside the limits of reproducibility of the balance. This was not, however, true of the rubber above the stopcock: successive weighings of the burette, during which it was removed from and immediately replaced on the balance by taking the rubber between bare fingers, showed a gradual but definite increase (about 0.03 mg per handling).

(iii) A similar difference in behaviour of glass and rubber was found on wiping the burette. When the glass parts were wiped repeatedly with either a cloth or chamois leather and the burette was weighed immediately after each wiping, the weight soon became constant within the balance error (the number of wipes required depended on how vigorously they were made). Gentle wiping of the rubber also resulted in a constant weight, but more vigorous rubbing caused definite and permanent decreases (up to 0.3 mg) to occur.

From (ii) and (iii) it was obvious that the rubber should be handled with care, but that, if this were done, its presence would not impair the accuracy with which the burette could be weighed.

Although a constant weight could be obtained for the burette immediately after wiping, this whole procedure would have to be repeated several times to allow for balance variations if an accuracy of better than 0.1 mg was to be achieved (see Section 1.41). This was time-consuming and very inconvenient, especially after an addition, when the resistance was also being closely followed. Fortunately further tests showed that fairly reproducible weights were obtained on leaving the burette for equal times (from 15 minutes onwards) after a thorough wiping of the glass, in spite of the normal gradual increase in weight. The standard procedure adopted, therefore, was to wipe the burette well, first with a clean handkerchief and then with a chamois leather for about a minute each, and immediately afterwards to take a rapid check on the weight; thereafter the burette was left suspended on the balance for 20 - 25 minutes before its weight was finally and accurately determined as the mean of at least five settings. The actual length of time was governed by the time required to take a final set of resistance readings on the solution obtained from the previous addition in the titration, which was done during this interval. The burette was handled with gloves during all these operations as a precautionary measure, in spite of the findings in (ii) above. It was later realised that this wiping and weighing procedure is, of course, very similar to the standard method of weighing absorption tubes in organic combustion microanalysis[30].

1.6 THE GAS-PURIFICATION TRAINS.

The use of a Gledhill-type cell required, as standard practice, that a current of gas be bubbled through the liquid contained therein. The function of this was intended to be be twofold: not only was it meant to keep the contents well stirred, but it was hoped that it would also remove any volatile impurities remaining in the water after distillation. Both these aims were successfully realised (see Sections 1.31 and 2.3). For the latter purpose, of course, it was essential that the gas be very carefully purified before entry into the cell, so that it would neither introduce new impurities which could increase the conductivity of the liquid, nor merely set up a steady state with those impurities already present instead of removing them completely. Several gases were used for bubbling through the cell at various times; they were purified by being passed through a train containing suitable reagents.

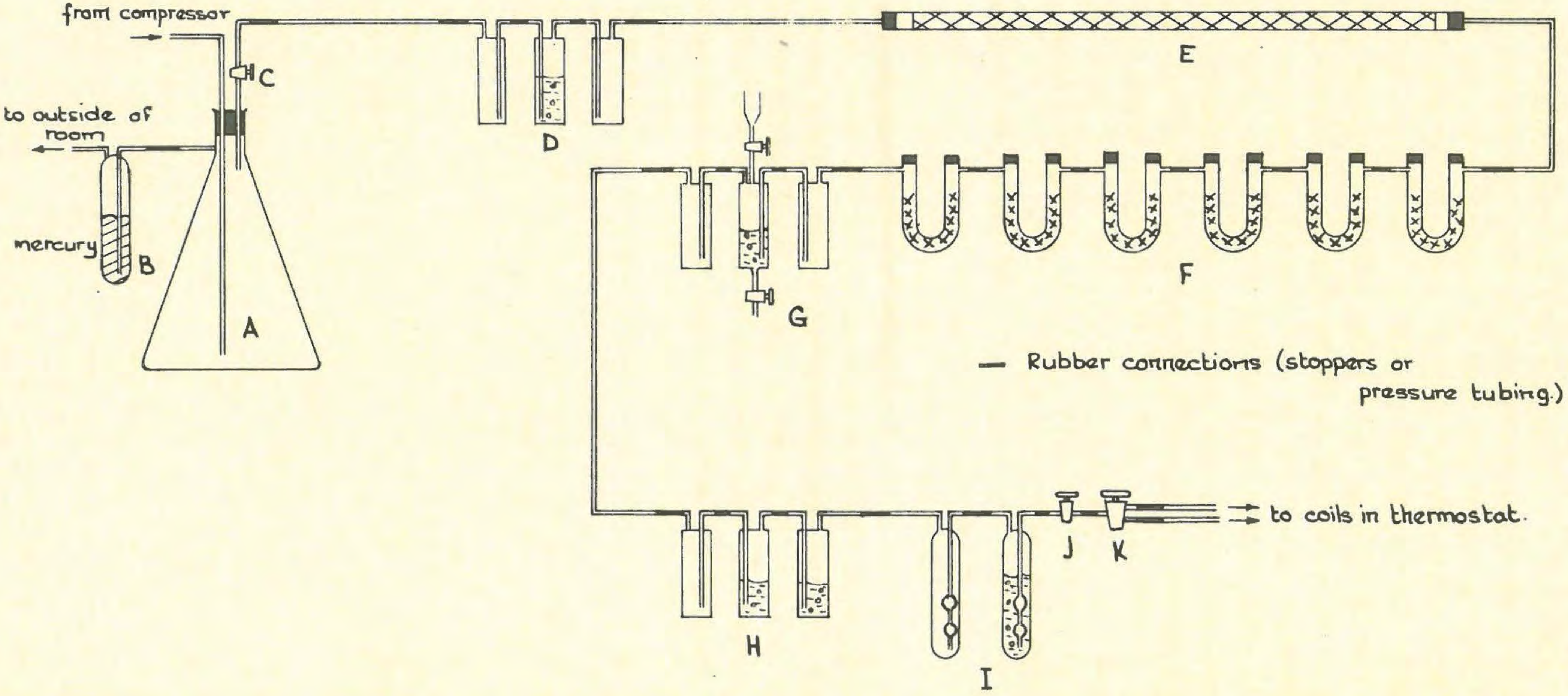
1.61 The Air-purification Train.

This train, which is sometimes also referred to as the "long purification train", was originally assembled for purifying the compressed air which it was intended to use for all general stirring, but later the other gases were also passed through it after some prior purification. The final train is depicted in Fig. 1.9. It may perhaps seem unnecessarily long, but several factors were responsible for its eventual form: thus:

(i) Renewal of the whole train was obviously necessary whenever the reagents in it had become spent. Sometimes, too, smaller parts of the train were renewed separately, either for the same reason or because some of the reagents had accidentally become contaminated. These renewals were usually rather tedious processes, partly because of the difficulty encountered in removing the materials from the tubes, which were then always thoroughly cleaned and dried as well, and also because some sections of the train could only be removed and replaced with considerable difficulty owing to the rather cramped space around the thermostat (see Plate I). Large amounts of purifying materials were therefore used so that, in the normal course of events, their renewal would only have to be performed infrequently. The efficient purification of the air passing through these substances was ensured by arranging them so as to provide a long path, thus increasing the time of contact between the gas and the reagents. The sectional arrangement of this long train facilitated the occasional renewal of shorter portions thereof.

(ii) The liquid reagents were placed in small gas-washing bottles, of standard pattern as illustrated. If, for some reason, the pressure at the beginning of the train

Fig. 1-9 The Air-Purification Train.



dropped for any length of time, the liquid was always sucked back from the bubbler. Alternatively, when a very rapid stream of gas was passed through the train, either continuously by design or in a large burst by accident (usually the result of turning a wrong control stopcock and applying too much pressure), it was found that some of the liquid was carried forward in the form of spray. Both these occurrences originally caused contamination of the reagents in other sections of the train, with the resulting bother outlined in (i). The dictates of experience soon showed the wisdom of including in the train two extra bottles for each liquid, placed empty before and after the reagent bubbler respectively in the manner indicated in Fig. 1.9.

(iii) Changes were occasionally made to the composition of the original train as new purifying materials were tested and incorporated. Though these sometimes involved replacement of one section by another, this was not always the case, especially where the original portion was not too readily accessible; then the new part merely became an addition to the train. The latter, in fact, just tended to grow by an evolutionary process into its final, more or less permanent state.

The air supply was obtained from a compressor situated in the workshop of the department and connected to the constant temperature room by a long length of copper tubing. The probable impurities in this air were considered to be: oil-vapour and -spray (from the compressor itself); water-vapour and -spray (from the condensed water in the supply tank and the pipe-line), which might contain dissolved impurities as well; and volatile materials such as might be found in any normal laboratory air. Of the latter impurities the major component by far was naturally carbon dioxide, and most of the train was intended for the elimination of this gas. Ammonia was another gas to whose removal special attention was paid, as well as any acid or other fumes which might be present in the building at the time of compression, and which might contribute to the conductance of the liquid in the cell.

The various reagents used in the train were:

(a) Soda-lime - This was intended mainly to remove carbon dioxide, but it also served to retain any other volatile acidic impurities, such as HCl, etc. Very occasionally, too, a small amount of pure sodium hydroxide pellets was used, usually for testing purposes.

(b) Phosphoric acid - When phosphoric acid appeared so successful in holding back ammonia during the preparation of pure water (see Section 2.2), it was incorporated in the purification train for the same purpose. At first syrupy phosphoric acid was used, but later it was thought that a solid reagent might be more efficient than a liquid, since the air would stay in contact with the reagent for a longer time. Phosphorus pentoxide, however, was considered unsuitable because of its very hygroscopic nature and the consequent tendency of the fine powder to clog the train. Solid metaphosphoric acid seemed much superior in respect of these properties; its efficiency was therefore tested by bubbling air through an ammonium hydroxide solution (about 1N), then passing it through a small U-tube containing metaphosphoric acid which had been crushed somewhat to increase its surface area, and finally into Nessler's reagent. After several hours there was still no precipitate, although air which was passed through the ammonia solution, but not through the U-tube, produced a thick precipitate within a few seconds. Crushed solid metaphosphoric acid was therefore included as part of the regular filling of the train.

(c) Sulphuric acid - The concentrated acid used also removed ammonia and other possible alkaline impurities, but its chief function was actually as a dehydrating agent, otherwise the solid reagents absorbed the water vapour. This very soon resulted in a pasty mess and blocking of the train.

(d) Cupric chloride - A very small amount of the crystals of this substance was placed in the train as a precautionary measure against hydrogen sulphide, which might be present in the laboratory air.

When the train was first assembled, the bubblers D (in Fig. 1.9) were connected directly to a compressed air point in the constant temperature room. It was found, however, that the control stopcocks had to be adjusted continually in order to keep the rate of bubbling through the cell constant. The fluctuations in rate occurring at a constant setting were eventually correlated with the cycles of the air compressor: because of the length of the purification train, the rate of bubbling at the end was quite sensitive to changes in the pressure at the beginning of the train, and it decreased markedly as the pressure in the air pipe-line dropped until the next "On" period of the compressor motor, when the rate rapidly increased again. In many of the experiments which were performed in Part 2, however, it was necessary to maintain a very constant bubbling rate; further, since the final conductivity of the water in the cell appeared to be dependent on the rate of bubbling being employed (see Section 2.41), the constancy of the latter seemed generally desirable. This was achieved by first leading the air into a 5-litre filter flask A, the outlet of which was connected to a bubbler B containing mercury, i.e. the initial pressure was kept constant. The height of the mercury was adjusted so that the pressure was slightly larger than the minimum value required to force the air through the whole train when the cell was in the thermostat. A sufficient flow of air had always to be maintained into A to prevent the pressure dropping below this value. The excess air which was needed to do this then escaped via B whence, because of the mercury vapour present in it after its passage through this liquid in B, it was led away out of the room for the vapour to be dissipated in the outer atmosphere.

With this arrangement very constant rates of bubbling could be maintained through the cell for long periods without attention. The flow of air out of the constant pressure reservoir into the train was controlled by means of the stopcock C set into the rubber stopper with which A was covered. From here the air went to the bubbler D containing sulphuric acid. This served several functions: it acted as a bubble counter to give an idea of the approximate rate of flow at the beginning of the train, and as such was very useful in indicating the presence of leakages further on; it trapped the last amounts of spray and solid particles which might have progressed thus far, although the introduction of A had made such a possibility most unlikely; and it dried the air before its passage through the solid reagents. Since there was quite a considerable amount of water vapour present in the air from the compressor, the acid in D had to be renewed frequently, because the level soon rose to the point where danger of spraying was rather large. From D the air passed to the long tube E (about 3 feet long and ½ inch internal diameter), which contained about 6 inches of crushed phosphoric acid at the beginning, and for the rest was packed with soda-lime. The U-tubes F were also filled with soda-lime, although one of them was a general purpose tube which contained a little phosphoric acid and some cupric chloride as well; it could be rapidly removed and renewed for testing when there was some doubt about the efficiency of the reagents in the train. Ordinary soda-lime was used for the most part, but a small amount of self-indicating material was placed at the end of the long tube and of each of the U-tubes to indicate the progress of the spent portions and thus show when renewal was necessary. Next came the bubbler G, which had been specially made with a stopcock at the top and at the bottom for easy filling and draining respectively. It was incorporated because at one stage the only soda-lime available was a "non-deliquescent" type, which actually saturated the dry air passing through it; this water was subsequently being absorbed by the phosphoric acid, the frequent renewal of which was rather expensive. Sulphuric acid was therefore used to dehydrate the air again, and the tedium of its constant renewal was overcome by the installation of G. Thereafter the air passed to the bubblers H containing syrupy phosphoric acid, and thence to I, which served a dual purpose. Firstly, the conductivity water with which this bubbler was kept filled pre-saturated the air at room temperature before its passage into the potash bubbler situated inside the thermostat (see Section 1.12), where it was finally saturated at 25°C prior to its entry into the cell; the need for refilling the potash bubbler was therefore cut down considerably at the expense of frequent replenishing of the much more readily accessible bubbler I. Secondly, I was the bubble counter to which all the rates of bubbling used throughout these investigations were referred. These rates were always determined and recorded as the number of bubbles passing through I in 30 seconds, and hence the standard convention has been adopted of expressing bubbling rates in the form x/30, meaning that x bubbles were counted in 30 seconds. This method of expression will be adhered to throughout the text, except where otherwise stated. The volume of each bubble was roughly 0.4 ml, though it varied slightly with the bubbling rate being used -- the faster the stirring, the larger the bubble. The rate was controlled by the stopcock J placed immediately after bubbler I and before the two-way stopcock K. By means of the latter, the air could be made to pass either through the liquid in the cell for stirring it (after first going through the two copper coils and the potash bubbler in the thermostat -- see Section 1.12), or over the top of the cell liquid after temperature equilibration in another copper coil.

The various parts of the train were all connected with rubber pressure tubing, the joints being made glass-to-glass as nearly as possible. At one stage these joints and the rubber stoppers used in the long tube E and the U-tubes F were coated with wax to prevent any diffusion into the train, but this precaution proved unnecessary (see Section 2.41).

1.62 The Nitrogen-, Oxygen-, and Hydrogen-purification Train.

Nitrogen was used for all general stirring after it had been shown to be more suitable for this purpose than air (see Section 2.423). The gas was obtained from a cylinder of commercial "dry nitrogen". The chief impurity appeared to be a small amount of oxygen, which was considered undesirable; it was therefore removed by passing the gas from the cylinder over hot copper. The latter, in the form of turnings, was placed in a long Vitreosil tube, which was heated in an ordinary electric combustion furnace. Because past experience had shown that any unnecessary source of heat either inside or even below the constant temperature room was most undesirable for maintaining good control of the temperature, and because a pipe-line was already available from this room to another small laboratory situated at the end of the same corridor, the furnace was set up permanently in the latter room.

The nitrogen was taken directly from the cylinder to the heated copper. This gradually became oxidised, but it was regenerated whenever the empty nitrogen cylinder was exchanged for a fresh one, and also occasionally at other times when it appeared necessary, by passing a stream of hydrogen through the heated tube. During this process, and while the tube was subsequently being flushed out again with nitrogen, a two-way stopcock placed at the end of the tube was turned to let the gases pass out into the atmosphere: in this way the gas inside the train was kept free from contamination whenever the oxide had to be reduced or the cylinder changed. Normally this stopcock was turned to let the nitrogen flow into a bubbler containing concentrated sulphuric acid, on which the rate of flow of the gas could be observed, for purposes both of adjustment of the cylinder valve and of the detection of possible leaks along the train. Thereafter the gas went through a tube containing soda-lime and crushed metaphosphoric acid for preliminary purification before entering the copper tubing (about 50 feet long) which led to the constant temperature room. Inside this room the gas passed into a constant pressure reservoir similar to the one used for the air-purification train. The rubber stopper which closed this flask was fitted with four well-ground stopcocks, so that four different supplies of nitrogen would be available in the room if necessary; each of these stopcocks was connected to a U-tube containing both soda-lime and solid phosphoric acid. The nitrogen supply was then joined to the ordinary train shown in Fig. 1.9 just before the bubblers I by means of a two-way stopcock so that either air or nitrogen could be sent through the cell. Later a similar two-way connection was made before the bubblers D, so that the nitrogen would have to pass through the whole of the long train first before it finally reached the cell: this was done by exchanging the ordinary stopcock C for a three-way stopcock. This latter arrangement was eventually used as the standard path for the purification of nitrogen (see Section 2.425).

The use of the two-way stopcock K (Fig. 1.9) meant that the air or gas could be passed either through the liquid in in the cell or over the top of it, but only as alternatives. It was afterwards found desirable to be able to pass the nitrogen along both these paths simultaneously. K was therefore replaced by an ordinary stopcock, which was connected directly to the copper coil leading to the capillary tube of the cell; this stopcock was included purely as an "On-Off" control so that, once the bubbling rate had been adjusted to a given value by means of J, it would not be necessary to interfere with the setting of J whenever it was desired to stop the stirring through the cell completely, as during the accurate measurement of the resistance of a solution (see Section 3.21). One of the other supplies from the constant pressure reservoir was then connected via a bubbler containing conductivity water (to saturate the gas at room temperature) to the other copper coil leading to the side tube of the cell: gas could therefore be passed independently over the top of the liquid in the cell.

The oxygen and hydrogen used were also obtained from cylinders of commercial gas. For their purification, the nitrogen cylinder was merely interchanged with a cylinder of the desired gas, and the same train was employed since it was thought that this already contained sufficient reagents to remove any impurities which might be present in the commercial gases. Naturally, of course, the copper was not heated when oxygen was being used, although heating was still continued during the passage of the hydrogen.

1.63 Other Trains.

Two minor purification trains were also employed during these investigations:

1.631 The auxiliary air-purification train.

This was used chiefly during the additions of small amounts of ammonia to water in the cell for the experiments where the removal of this substance by aeration* was being studied (see Sections 2.34 and 2.35). The train consisted of: a small U-tube with solid phosphoric acid; a large U-tube containing soda-lime; an empty gas-washing bottle (to act as a liquid trap); a bubbler containing syrupy phosphoric acid; and a bubbler filled with pure conductivity water. The purified air emerging from this train was led to another bubbler (made of Quickfit parts), in which about 50 ml of conductivity water was aerated prior to the addition of a small amount

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* In this thesis, the word "aeration" denotes the passage of a current of highly purified air (or any other sparingly soluble, non-conducting gas) through a liquid.

of conc. G.R. ammonium hydroxide. A standard procedure was then used for passing the air-ammonia mixture from this solution into the water in the cell by means of a tube kept specially for this purpose (see Section 2.32).

1.632 The short all-glass train.

This was temporarily installed in order to reduce to one the number of rubber joints which the air had to pass after its final purification and before its entry into the cell. It is more appropriately described under the experiments performed to test for the diffusion of carbon dioxide into the air-stream through the joints in the train (see Section 2.41).

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PART 2

THE PREPARATION AND STUDY OF "ULTRA-PURE WATER"

2.1 INTRODUCTION.

In all accurate conductimetric determinations, the problem of the correction which must be applied for the conductance of the solvent has always been rather a perplexing one. It was realised even by the earliest investigators in this field that, in order to obtain the true conductance of the dissolved electrolyte in a solution, allowance must be made for the contribution of the solvent to the total measured conductance; but the method of application of this correction seems to have been very arbitrary. Initially the conductance of the solvent was determined separately, and the whole amount subtracted from the conductance of the solution. Although this answered fairly well for neutral salts, it led to anomalous and obviously incorrect results for acids and bases, particularly in the more dilute solutions: the molecular conductance, for instance, instead of tending towards a maximum, showed values decreasing with increasing dilution[31]. This was obviated by the empirical procedure of applying either half the solvent correction or none at all! Since there was no foundation for adopting such a procedure, Kohlrausch rejected these suggestions as meaningless. He recognised that the difficulties experienced in obtaining accurate results at high dilutions were due to the disturbing influence of the acidic and basic impurities in the water, and very prophetically remarked in one article that "the last word upon the subject of dilute acids and bases will certainly not be spoken until we have succeeded in investigating the solutions in pure water"[32].

In the case of aqueous solutions, there will always be some solvent conductance because of the presence of the ions formed by the dissociation of the water itself, i.e.,

$$H_2O \rightleftharpoons H^+ + OH^- \qquad \text{..........(2.1)}$$

The specific conductance of pure water can readily be calculated. The ionic concentrations are so small that they may be taken as equal to the activities with sufficient accuracy for this purpose. Hence we have

$$\begin{aligned} K_w &= [H^+] \times [OH^-] \qquad \text{..........(2.2)} \\ &= 1.008 \times 10^{-14} \text{ at } 25^\circ C. \end{aligned}$$

But since the ions are present in equal concentrations,

$$[H^+] = [OH^-] = 1.004 \times 10^{-7} \text{ g-ions/l.}$$

The specific conductance of water κ_{H_2O}, which is due to the presence of H^+ and OH^- ions only, is then given by the standard equation

$$\kappa_{H_2O} = \frac{c.\Lambda^o_{H_2O}}{1000}, \qquad ....(2.3)$$

where c = concn. of dissolved electrolyte in g-equiv./l.
= 1.004×10^{-7} in this case,

and $\Lambda^o_{H_2O}$ = limiting equivalent conductance of water
= 548.3 (Value computed from Glasstone[33])*

$$\therefore \kappa_{H_2O} = \frac{1.004 \times 10^{-7} \times 548.3}{1000}$$

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

Absolutely pure water, therefore, will have a specific conductance of about 55 nm/cm at 25°C. Although this is small, it would still represent almost 4% of the total conductance of a 10^{-5}N potassium chloride solution. Water of this degree of purity has never yet been prepared. The best sample reported still remains that of Kohlrausch and Heydweiller[34] in their classical experiment which involved 42 distillations in vacuo; this water had a conductivity of 61 nm/cm (recalculated to 25°C). The quantity was very small, and the conductivity rose rapidly again on exposure to the air. Because of this rapid contamination, Kohlrausch and his co-workers did not attempt any refinements in the purification of the water used for their ordinary experiments, but prepared their solutions with water of conductivity approximately 800 - 2000 nm/cm at 18°C.

The first really systematic analysis of the "water correction" was made by Kendall[35]. The relatively high conductivity of distilled water is due mainly to dissolved carbon dioxide, which must be eliminated when preparing very pure water. Kendall stressed the difficulties of this procedure and of all the subsequent manipulations (such as

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* For convenience, all ionic conductances have been referred to a single table in the literature rather than to individual papers, since for some ions, e.g. hydroxyl, computation of the value is required from as many as four different sources. The table selected comes from Glasstone's "Elements of Physical Chemistry". This is admittedly an elementary textbook; but it must be pointed out that the values have all been checked and that, although numerous more authoritative works on electrochemistry were also consulted, this was the only reference available which contained all the required conductances accurately in one table.

preparation of solutions and measurement of conductances); these operations would require elaborate precautions to prevent contact of the liquid with the air again. He therefore advocated the use of purified water which had been allowed to become saturated with atmospheric carbon dioxide (so-called "equilibrium water"), since it seemed preferable to use a stable sample of water for which an exact correction could be made, rather than a purer sample for which the correction was less certain because of the possible absorption of CO_2. On the assumption that carbon dioxide was then the only impurity in the water, he proceeded to apply a "carbonic acid correction", based upon the law of mass action, to all the types of solutions likely to be encountered in conductance work -- acids and bases, both weak and strong, and the salts of these.

Kendall's application of this correction to previous measurements made by other investigators certainly did lead to more consistent results, although the equivalent conductances of strong acids still showed a maximum at about 0.0001 to 0.0002N, thereafter decreasing again. Washburn[36] concluded from this that Kendall had not been justified in assuming that the whole of the impurity in the conductivity water was carbonic acid, and that this behaviour was actually due to the added presence in the water of basic or saline impurities, or both, in amounts which were far from negligible. This conclusion was strongly supported by the later work of Kraus and Parker[37] on the conductance of iodic acid solutions; when water of conductivity above 100 - 200 nm/cm was used, a maximum was found in the conductance curve which they correlated with the presence of impurities in the water. They also found that alkaline impurities derived from the glass cells seemed to have a very pronounced effect in producing this maximum.

Washburn further pointed out that "equilibrium water" was not sufficiently stable to warrant its use in measuring the conductances of very dilute solutions. In an experiment in which filtered air was drawn through a large sample of conductivity water in a quartz vessel, the conductivity was found to vary erratically between 797 and 865 nm/cm over a period of less than a day. Obviously considerable errors could result from using such water for measurements with dilute solutions, the conductivities of which were themselves only of the same order of magnitude as that of the water. The solution would therefore still have to be protected against atmospheric contamination during its preparation and measurement, even if "equilibrium water" were used instead of "ultra-pure water"*. The difficulties involved would probably be no greater in the latter case than in the former, and the absolute changes in conductivity, owing to chance contamination with CO_2, would be approximately of the same magnitude in both cases. Since the accuracy of the final correction for dissolved CO_2 depended only on these absolute changes, there seemed to be no logical reason for preferring "equilibrium water" to "ultra-pure water".

The "water correction" is not a constant quantity, equal to the measured conductivity of the water or some fixed fraction thereof, but it depends on the nature of the impurity (whether acidic, basic, or saline) and of the solution being considered. Interactions can obviously occur between the electrolyte and the water or the impurity in it. Since these will cause varying amounts of change in the ionisation of the conducting material present, the size of the correction, for the same sample of water, can differ greatly in different solutions. A full discussion of the methods of application of the correction in the various cases has been given by Washburn[36].

In making any accurate conductimetric measurements, therefore, it is necessary to know both the amount and the nature of the residual impurities present in the water. Information regarding the nature is usually derived by inference, since the actual amounts of material being considered are invariably too small for analysis. The uncertainty of the correction arising from this source is therefore probably equally great whether "equilibrium water" or "ultra-pure water" is used. A distinct advantage of the latter procedure, however, is that the total correction is much smaller, and hence it can probably be applied with greater certainty. When the correction is large and impurities other than CO_2 are present, such as is usual with "equilibrium water", it is obviously difficult to decide what proportion of the correction is due to dissolved carbon dioxide. With a small correction, however, the errors in estimating the amounts of the other impurities are likely to be much smaller, particularly if the CO_2 can be eliminated completely.

In spite of the desirability of keeping the solvent correction at the lowest possible level and so increasing

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* The term "ultra-pure water" is usually taken as meaning water having a conductivity of 100 nm/cm or less.

the accuracy of its application, very few workers in the conductance field seem to have used "ultra-pure water" in their determinations, even though the preparation of very pure samples has frequently been described in the literature (see Section 2.2). Weiland[38] reported the use of water of conductivity 53 - 70 nm/cm at 18°C, while values of 95 - 500 and 80 - 150 nm/cm at 25°C were mentioned by Kraus and Parker[37], and by Krieger and Kilpatrick[39] respectively. Very recently, too, Ives and Pryor[40] prepared all their solutions with water of average specific conductance 100 nm/cm (presumably an average value for the various temperatures, from 15° to 35°C, at which their measurements were made). In general, however, much precision work has been described in which the water had a conductivity of over 100 nm/cm, going up to 500 nm/cm (and sometimes even more!). Most of this conductance was probably due to dissolved carbon dioxide, present because of the difficulty of working completely out of contact with the atmosphere. These relatively high water conductivities have not always been significant. For instance, in measurements such as those of Grindley and Davies[41], Shedlovsky[42], Davies[43], and Owen and Zeldes[44], where the electrolyte (potassium chloride) was the salt of a strong acid and strong base, the correction, although large, could still be applied accurately even to the results obtained with dilute solutions. But in numerous other determinations, where there was a possibility of reaction between the electrolyte and impurity, or between the electrolyte and water (hydrolysis), the final accuracy has depended on a knowledge of the amount and the nature of all the impurities responsible for the comparatively high conductivity of the water. Sometimes it has been possible to obtain some of this information experimentally, as in the work of MacInnes and Shedlovsky[45] on acetic acid and sodium acetate. Frequently, however, an arbitrary assumption regarding the proportions of possible impurities seems to have been made: the measurements of Robinson and Davies[46] on thallous salts are a case in point.

Apart from the slight inaccuracy which may arise, particularly with very dilute solutions, from the approximations which must be made when the solvent correction is large, there is another possible source of error in these cases. This is due to the large number of extra ions present in the water. Davies[47] has shown that both the mobilities and activities of the solute and solvent ions may be affected by each other's presence, and that the true solvent correction should take into account the interionic attraction effects as well. If these factors are ignored, a small error can result even in the case of potassium chloride and other neutral salts.

It seems, therefore, that the use of water of a relatively high conductivity requires the introduction of several corrections and approximations. Though these can often be made quite accurately, their application would almost certainly lead to more exact results if water of the purest quality were used. In this laboratory, a large amount of work which involved conductimetric measurements on extremely dilute solutions was in progress and in prospect. It was therefore decided to try to have available for routine use a very pure grade of water, and also, if possible, to determine the nature of the residual impurity, so that accurate corrections could be made to measurements on even the most dilute solutions.

2.2 PREPARATION OF "ULTRA-PURE WATER".

Numerous stills for the preparation of "ultra-pure water" have been described in the literature. In many of these a continuous stream of purified air was used during the distillation process in order to remove volatile impurities. Sometimes the air was passed upwards through the condenser, where it mixed with the vapour and the distillate and thus freed the latter from dissolved gases. This method was used in Bourdillon's still[48], and in later modifications thereof by Bengough, Stuart, and Lee[49], and by Stuart and Wormwell[50]. Weiland[38], however, passed the purified air through the water in the distilling flask, which was maintained at a temperature a few degrees below the boiling point. The first portion of the distillate was then discarded on the grounds that it would contain all the gaseous impurities in the original water.

In Kraus and Dexter's method of preparation[51], the use of pure air during the distillation was eliminated. Instead they effected a purification by a fractional condensation process, which was based on the fact that, at the boiling point of water, the concentration of carbon dioxide in the vapour phase is about five times as great as that in the liquid phase. The still was designed so that complete condensation of the steam could take place in two stages. About 20 - 25% of the steam was allowed to escape uncondensed from the first condenser, and this vapour carried with it practically all the carbon dioxide and the other volatile impurities in the water, i.e. the steam itself performed the function of the purified air employed by Bourdillon and by Weiland.

Each of these stills, and numerous others, was described as being capable of delivering daily several litres of water of conductivity less than 70 nm/cm. However, the water they provided, judged by reports of subsequent experimental work emanating from the same laboratories, seems invariably to have had a rather higher conductivity, presumably arising from atmospheric contamination after the distillation.

Since carbon dioxide can apparently be removed fairly readily from water by passing a stream of purified "CO_2-free" gas through it, the policy in this laboratory has been to effect its removal in the conductance cell itself rather than in the still. This procedure eliminates the necessity for many of the precautions found necessary in all the above-mentioned stills; at the same time it avoids the risk of contamination of the water during handling operations and before the actual conductance measurement, and thus minimises the uncertainty of the solvent correction. The effectiveness and completeness of this means of removing carbon dioxide from water has been carefully studied in this work.

Originally a single distillation of ordinary distilled water from alkaline permanganate was used, according to the method of Kraus and Dexter[51]. However, even the best water obtained by Festenstein[29] had a conductivity of 121 nm/cm after it had been aerated in the cell, and the quality was usually much worse.

Ellis and Kiehl[52] used a combination Bourdillon and Weiland still for the preparation of pure water in order to determine its pH. They found that the most persistent volatile impurity was ammonia, any carbon dioxide remaining being easily eliminated by aeration. The first fraction of distillate obtained from a single distillation from either water or alkali invariably had a high pH (8.5 or more). The pH dropped in the succeeding fractions, but it only became constant (at just over 7) after half the distillation had been completed. The presence of ammonia in the initial fractions was confirmed by Nessler tests. The addition of Nessler's reagent to the boiling flask failed to hold back the ammonia for the early fractions; but when phosphoric acid was added to the boiler, all the fractions had about the same pH (6.94 - 7.15), showing that this acid retained all the ammonia.

Phosphoric acid was therefore tried in the distilling flask instead of alkaline permanganate, and a pear-bulb fractionating column was connected to the flask to act as a spray-trap and reflux device. With this apparatus, the first distillate collected had a conductivity of 150 nm/cm after aeration. Later, values as low as 96 nm/cm were obtained, but the quality of the water still seemed to be very variable. The variations were believed to arise from a contaminating effect caused by fumes of various kinds which had spread from the general laboratory to the room in which the still was placed. Since such contamination could not be avoided completely, and since it was desired to have a still which would produce good quality water under all operating conditions, it was decided to put guard-tubes on the still to prevent entry of any volatile impurities likely to contribute to the conductance (CO_2, NH_3, H_2S and other impurities present in normal laboratory air). The distillation would also be performed in two stages -- first from ordinary distilled water containing alkaline permanganate, to eliminate acid and organic impurities, and then from phosphoric acid to retain the ammonia and other basic impurities.

With this still, water of about 100 nm/cm was obtained consistently. However, it was noticed that, after the still had been started up in the morning, there was a tendency for the quality of the water to improve during the day. A similar effect has been reported by Thiessen and Hermann[53] who found that, after cleaning and reassembling the parts of their still, they had to run it for several days before water of the highest grade of purity was again obtained. The effect is probably due to the leaching out of those parts of the still which have not been in contact with water for some time. In order to test this hypothesis, the still was operated continuously for 36 hours, and periodic checks were made on the quality of the water coming from it. A definite, progressive decrease in conductivity was found, and the final distillate had a conductivity of 73 nm/cm -- about 10 - 12 nm/cm better than had previously been obtained from this still.

In view of the improved quality of the water after prolonged distillation, it seemed desirable to design a still which would be fully automatic in operation and which could be left running continuously. Apart from the fact that this would provide a better quality of water, there was also the obvious advantage that it would not be necessary to wait each day after the still had been started in the morning for sufficient water to become available: a flask of good water would be ready for immediate use whenever required. Such a still was duly designed and constructed: it is illustrated in Plate IV, and a full description of it is given in the reprint at the back of this thesis. The best water obtained from this still had a conductivity of 62.8 nm/cm at 25°C after aeration in the cell: this is not much worse than that of the best water prepared by Kohlrausch and Heydweiller[34], although its preparation was considerably easier. The usual quality of water obtained, however, had a conductivity within the range 80 - 100 nm/cm.

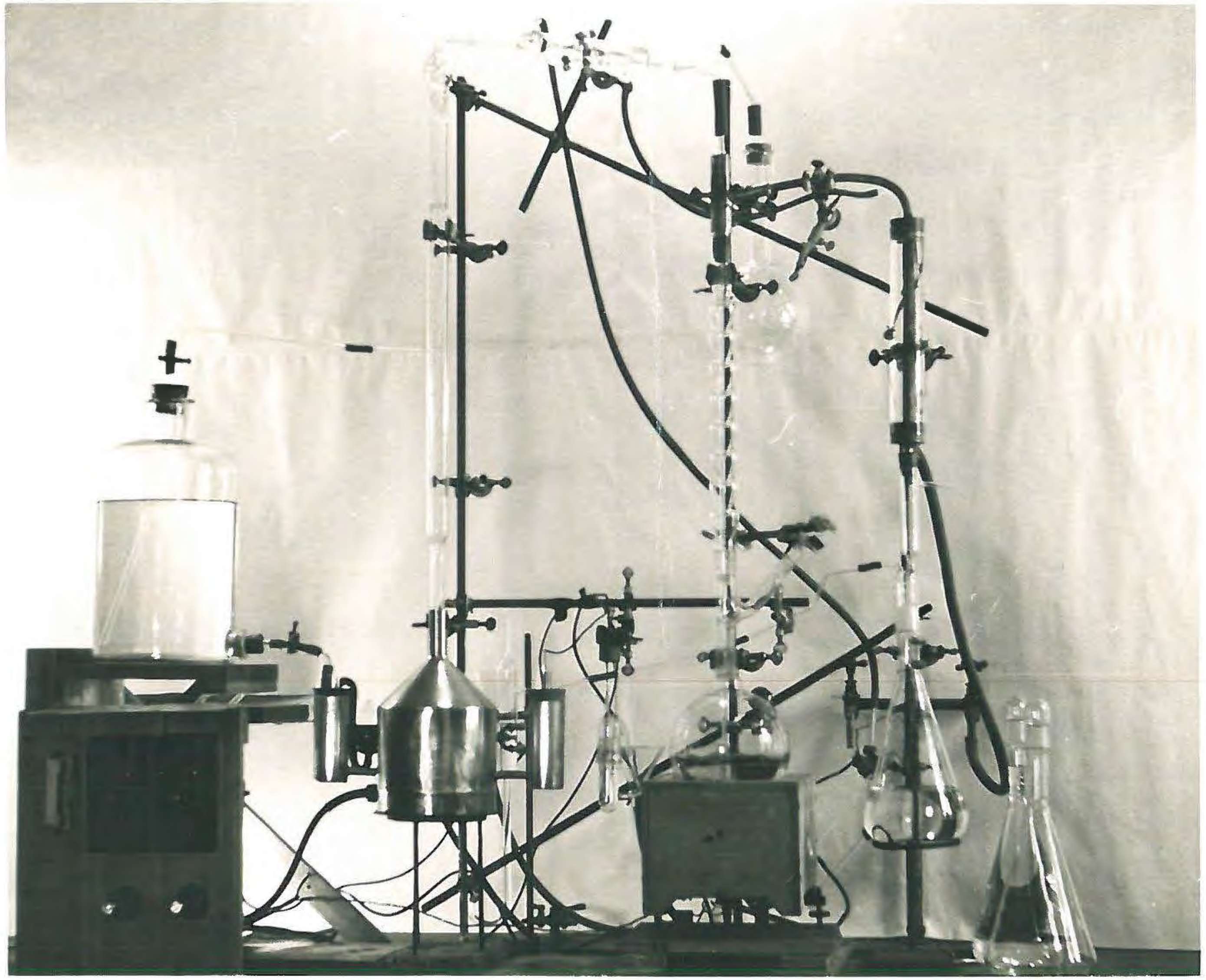


Plate IV

2.3 DETERMINATION OF THE RESIDUAL IMPURITY IN "ULTRA-PURE WATER".

2.31 Behaviour of Pure Water on Aeration.

Cell I was used for all the experiments on pure water. After it had been rinsed several times and filled to about the 200-ml level, it was placed in the inner thermostat. Here a stream of purified air was bubbled through the water in the cell (see Section 1.31).

The range of the bridge was not large enough to allow a direct determination of the extremely high resistance of the cell when it was filled with pure water (about 1.2 megohm for water of conductivity 100 nm/cm). For all measurements made on water, therefore, the cell was shunted with a non-inductive 10,000-ohm resistor (cf. Shedlovsky[42]). The resistor used (a General Radio Company Type 500-J) had a very low temperature coefficient. Its resistance, which was frequently checked, remained very constant under all conditions -- an essential requirement in the investigation described here, in order that the numerous very small changes in resistance which were observed might be attributed definitely to corresponding variations in the conductance of the water, and so that these changes could be compared. The measured value of the resistance was 10,003.0 ohms at 24°C. The resistance of the water in the cell is then given by

$$R_{H_2O} = \frac{10{,}003.0 \times R_m}{10{,}003.0 - R_m} \qquad \text{..........(2.4)}$$

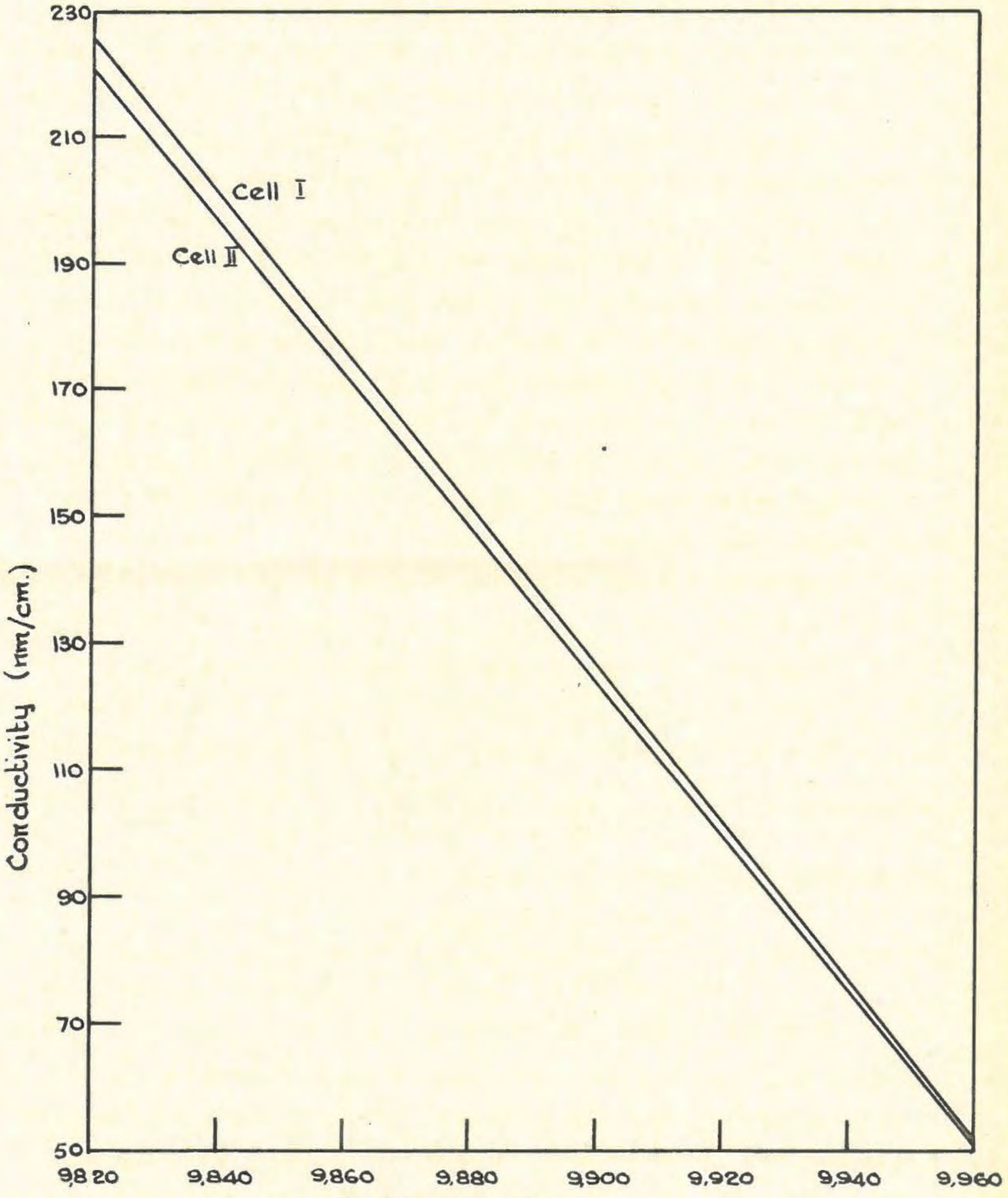
where R_m = measured resistance

Hence $$\kappa_{H_2O} = \frac{(10{,}003.0 - R_m) \times Q}{10{,}003.0 \times R_m} \qquad \text{..........(2.5)}$$

where Q = cell constant

The measured resistances when Cell I or Cell II was filled with pure water and placed in parallel with this resistor were usually within the range 9800 - 9950 ohms. With such large values of R_m, small variations will not appreciably affect the product in the denominator in equation (2.5), so that the conductivity of the water in either of these cells will vary approximately linearly with the measured resistance over the above range. This linearity of the $\kappa_{H_2O} - R_m$ relationship can be clearly seen in Fig. 2.1, where the accurate conductivities, calculated from equation (2.5), are plotted against the measured resistance for Cells I and II. The actual values for various resistances are given in Appendix D.

Fig. 2·1 - Variation of water conductivity with measured resistance.



Further, since the usual values of R_m were so nearly 10,000 ohms, equation (2.5) may be reduced to

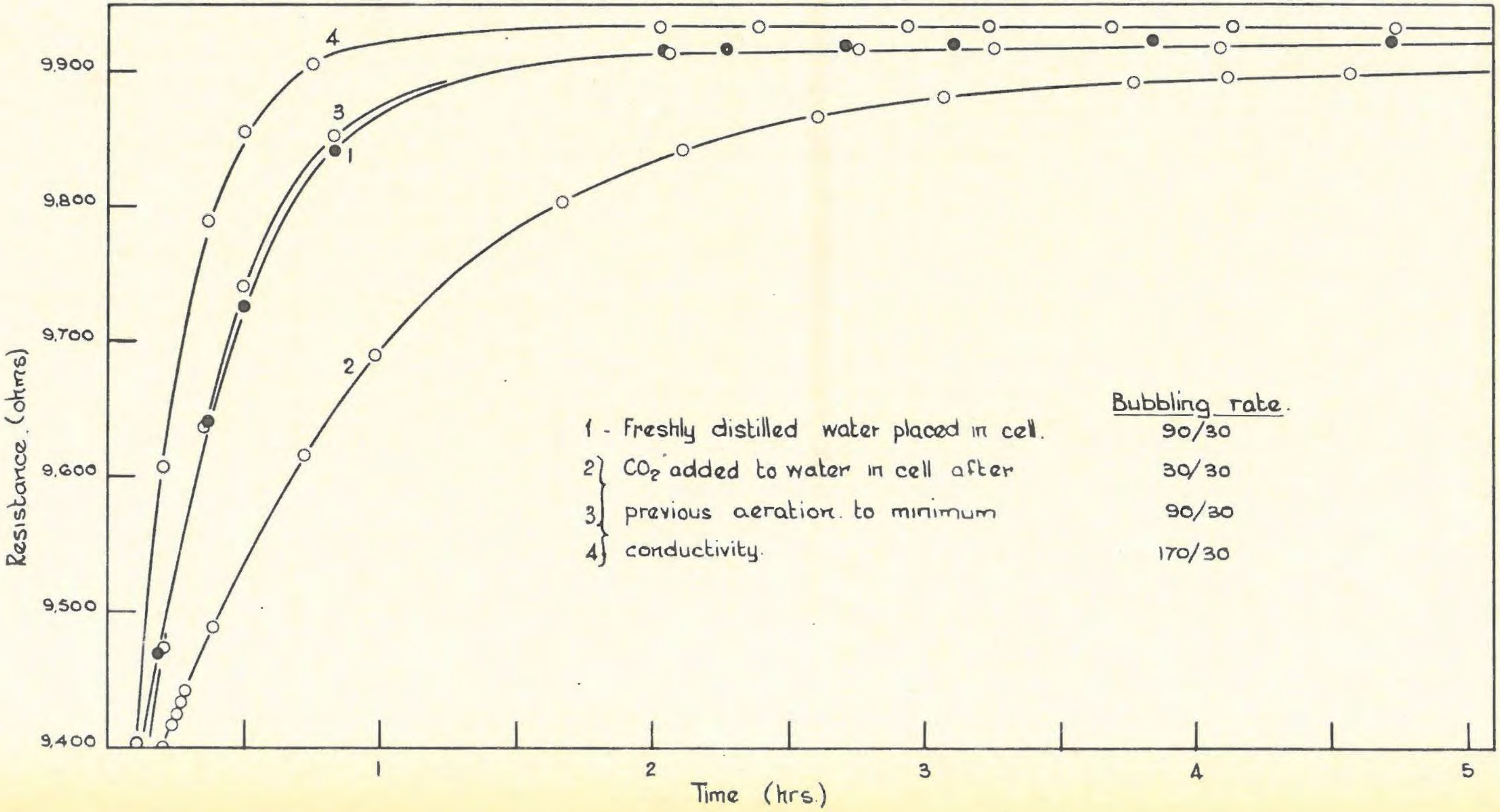
$$\kappa_{H_2O} \approx (10{,}003.0 - R_m) \times 10 \times Q \quad \text{nm/cm} \quad ....(2.6)$$

The respective constants of Cells I and II were approximately 0.12 and 0.11 cm^{-1}. It will therefore be seen that, when either of these cells was filled with water, a drop in resistance of 1 ohm corresponded to an increase of just over 1 nm/cm in the conductivity. This approximation served as a useful and rapid guide to the size of the conductivity changes which were being observed in this investigation of pure water. Since these changes were actually of greater significance than the absolute conductivities of the water, the latter values were usually computed only when they were required for more comprehensive calculations. In general, however, the numerous resistance readings were not converted to the corresponding conductivities, but the variations in the latter were always followed by plotting the resistances directly. All changes were reflected quite adequately by this procedure, which saved a considerable amount of time and which was justified by the linearity between the conductivity and the measured resistance over the range normally encountered.

The removal of volatile impurities from water by a purified gas was followed by observing the changes in resistance which took place on aeration. In this part of the work, the resistances were determined at one frequency only (900 c/s) and for a single setting of the ratio arms and supply voltage. These readings could be taken accurately even while the air was being bubbled through the water in the cell (cf. Section 3.21, when there was solution in the cell). It was therefore not necessary to stop the stirring while following the course of the removal. The initial resistance of the cell with the resistor in parallel was usually about 9300 - 9400 ohms, i.e. the water conductivity was about 800 - 900 nm/cm -- roughly that of "equilibrium water". On aeration, the resistance rose, fairly rapidly at first but at a gradually diminishing rate, until after several hours it reached a maximum value; the time taken varied with the rate of bubbling, from about 3 hours for a rate of 170/30 to 12 hours or more for a rate of 30/30 (see p.51 for convention used to express bubbling rates). A typical curve of the variation of resistance with time is shown in Fig 2.2, line (1).

After reaching a maximum value and staying there for a little while, the resistance began to decrease again on continued aeration, i.e. the conductance reached a minimum and

Fig. 2·2 - Variation of resistance of conductivity water on initial aeration.

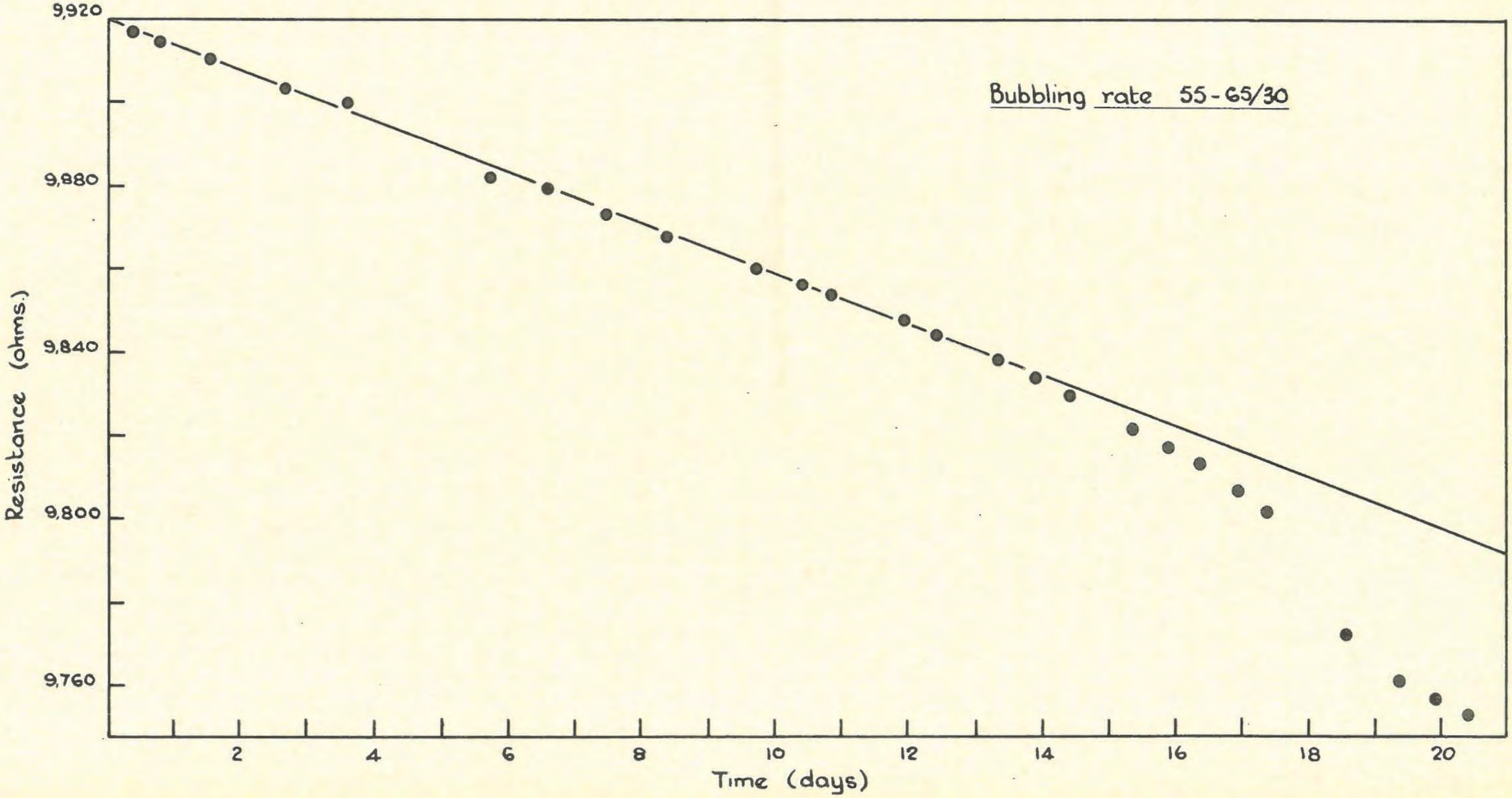


then increased. The rate of decrease of resistance remained fairly constant for a fixed stirring rate, as can be seen from Fig 2.3; this shows the change in resistance which occurred when a sample of water was left in the cell for 20 days with air bubbling through it at a rate of about 60/30. In this instance, the resistance dropped fairly uniformly at an approximate rate of 0.25 ohm/h, i.e. the conductivity increased at about 0.3 nm/cm/h. After about the thirteenth day, however, the rate at which the resistance fell gradually became higher, and it continued to increase as time passed. This was finally ascribed to the slow saturation with paraffin of the pressure tubing used for connecting the capillary tube of the cell to the copper tube in the inner thermostat. This tubing was definitely somewhat swollen at the end of the experiment, and it might well have been allowing a slight but gradually increasing amount of paraffin vapour to diffuse into the stirring air. It seemed, therefore, inadvisable to let any experiment run for longer than about ten days.

In addition to this eventual slow increase in the rate at which the resistance fell, several other factors seemed to influence the rate of drop. The latter always remained constant for any given sample of water, provided the stirring rate was kept at a fixed value; but variations occurred with different samples of water. There appeared to be some correlation between the rate of decrease and the quality of the water used -- the former was usually higher the poorer the latter -- but changes were found even when using samples of equal conductivity. For example, different portions of water, which had approximately the same conductivity, gave rates varying from 0.25 - 0.5 ohm/h for a bubbling rate of 60/30 (the same as was used in the 20-day experiment). Increasing the stirring rate invariably increased the rate of decrease of the resistance. The nature of the gas being bubbled through the cell was also found to have some effect (see Section 2.42).

This slow increase in conductivity, which becomes apparent after the removal of the volatile impurities, is probably due to the highly complex process commonly called the "solution of glass". According to Morey[54], when complex silicates such as glasses are treated with water, they do not dissolve in the normal manner. The process is rather one of slow decomposition, the end result of which, if true equilibrium could be attained, would be that practically all the SiO_2 would be left behind while the alkaline constituents would have passed into solution. The correctness of the results

Fig. 2·3 - Variation of resistance of conductivity water on prolonged aeration



of decomposition was confirmed by an actual analysis of some conductivity water which had been left standing in this laboratory in a large Pyrex flask for four years: practically no silica was found, but there were distinct traces of Na, K, Ca, Mg, and Fe, all of which are present in ordinary Pyrex glass[55]. Such a decomposition process accounts quite satisfactorily for the slightly increased rate of drop of resistance of water produced by faster stirring, since an increase in the rate of bubbling through the water would cause a more rapid rate of removal of the reaction products formed at the glass-water interface.

Morey[54] has stated further that the presence of an acid or alkali will often profoundly affect the rate of decomposition or "solution" of the glass, and that the effect will be dependent both on the composition of the glass and on the dissolved material. Frequently the rate is found to increase quite appreciably. The conductance of such solutions should therefore increase more rapidly than that of pure water. This is in agreement with the marked increase in the rate of change of conductance which has frequently been found in this laboratory with dilute solutions of acids, alkalies, and even salts[15, 29, 56, 57].

Malan[15] has suggested that, since the greater rate of change of conductance is found when a larger number of ions is present in the solution, the "solution of glass" process is due to an ion-exchange between the solution and the glass. This explanation may suffice for pure water, where the solution could become alkaline due to the exchange of H^+ ions from the water with the alkali ions (chiefly Na^+) from the glass: because this would upset the balance of equation (2.2), more water would then ionise to restore the equilibrium. The nett result would be the addition of small quantities of soluble ionic constituents from the glass to the water, and hence an increase in conductivity. However, a similar ion-exchange would not satisfactorily explain the increase found, for instance, with dilute solutions of acids such as HCl, since the replacement of fast-moving H^+ ions by slower-moving Na^+ ions would not be completely compensated by subsequent restoration of the water equilibrium. Rather, in fact, would a decrease in conductance be expected under these circumstances. Also, with salt solutions, an exchange between ions from the salt and the glass would merely mean a replacement of one ion with another of similar mobility. Such an exchange can be reconciled with the greater rate of increase of conductivity which is observed only if the removal of ions from the solution itself initiates some secondary reaction which will replace those ions lost by the exchange, e.g. in the determination of the solubilities of sparingly soluble salts, where the excess solid present in contact with the solution provides further ions in order to keep the concentrations up to equilibrium values.

Whatever the mechanism of the "solution of glass", it seems certain that some such process takes place in the cell and causes the conductance of the water or the solution to rise slowly but steadily after the minimum value has been reached by aeration. By extrapolating the steady rate of decrease of resistance to the time when the water was placed in the cell, the resistance at zero time (with volatile impurities removed) can be determined. Hence the additional conductivity resulting from the solution of glass during the time taken for the minimum value to be reached can readily be obtained. In general, this extra conductance was rather small, of the order of 2 nm/cm (the average values of the time taken for a maximum resistance to be reached and of the subsequent rate of decrease were about 4 hours and 0.4 ohm/h respectively). The solution of glass could therefore not account completely for the relatively large difference between the minimum conductivity found after aeration of the water taken from the still (usually about 80 - 100 nm/cm) and the theoretical value for pure water (55 nm/cm).

In view of the method of preparation of the water by distillation from both alkaline permanganate and phosphoric acid, it was felt unlikely that the residual impurities could be any volatile acids or bases. They might, however, result from a solution effect occurring after the final condensation, either from the tin condenser or from subsequent glass parts of the still, or even from the collecting flask. There was also the possibility that all the carbon dioxide was not being swept out by the stream of purified air. Finally, too, it was possible that, since ammonia is so very soluble in water, a small amount of atmospheric ammonia was dissolved during the process of filling the cell, and was not subsequently removed during the aeration process: it would presumably then be present in the form of ammonium bicarbonate. In order to test these latter theories, it was decided to add both CO_2 and NH_3, separately and together, to water which had already been aerated to a minimum conductivity, and then to study the rates and the completeness of the removal of these added gases.

ADDED IN TYPING: A very recent paper[106] raises the possibility that the faster change in conductivity of solutions may be due to ion-exchange between the electrolyte and H^+ and OH^- ions in the diffuse layer surrounding the silica (see Section 3.333).

2.32 Effect of Immersion of a Glass Tube in Water.

The method proposed for the addition of carbon dioxide and ammonia to the liquid in the cell was to lead a few bubbles of the purified gas into the water, after this had attained its maximum resistance, via a clean Pyrex glass tube dipping below the surface. This tube would obviously have to be dry too, to avoid extra impurities, which might be dissolved in the liquid adhering to the moist glass, being introduced into the water at the same time.

In a blank run a tube of about 8 mm external diameter was dried inside with a pipe-cleaner and outside with a clean handkerchief, and used for passing a few bubbles of purified air into the water. The resistance was measured immediately before and after addition, and was found to have dropped by more than 7 ohms; thereafter it remained constant at the new value. Repeat experiments, with rigid adherence to cleanliness, confirmed this relatively large change in resistance, decreases of as much as 18 ohms being observed. In some instances the resistance did not remain constant afterwards but increased again slightly, as if some carbon dioxide were being removed from the water in the cell.

Since the passage of purified air through the tube was fairly slow (about 1 bubble per second), and since the opening of the tube was rather wide, there seemed a possibility that some CO_2 could diffuse back into the tube and then dissolve in the water on immersion. A new tube was therefore drawn down to a 1 - 2 mm jet. This tube was thoroughly cleaned by immersion in hot chromic acid followed by steaming for several hours with the tube itself standing in water in order to leach out its external surface as well. Finally it was suspended in conductivity water in a cleaned Pyrex boiling tube in such a way that it made no contact with the walls of the boiling tube. The gas-leading tube was kept permanently in this manner between additions, with frequent changes of the water in the boiling tube, from which it was only removed just before it was required for an experiment. Since it was still necessary to have the tube dry before making an addition, the outside was wiped with a clean handkerchief as before, but the narrow end now made it difficult to dry the inside similarly with a pipe-cleaner: this was therefore done by sucking air through the tube.

In spite of all this attention to cleanliness, falls of resistance of the same order as before were still observed. It was suggested that these might result from the wiping procedure used to dry the outside of the tube, but several tests, in which both the inside and the outside were dried merely by leaving the tube suspended in the air, showed no significant differences in the results. The purity of the air being added to the water was also checked by renewing the phosphoric acid, soda-lime, etc. of the auxiliary purification train through which the air was being passed (see Section 1.631), but again there was no improvement.

It seemed that the source of this resistance drop would have to be tracked down by elimination, and the whole addition procedure was therefore standardised as far as possible. Before the tube was removed from the water in which it was suspended, a fairly fast stream of purified air (about 4 bubbles per second) was passed through it for at least 30 minutes to ensure that it contained no volatile impurities. Immediately on removal the tube was attached to a vacuum pump and air sucked through it for exactly 30 minutes: this was in all cases found to be sufficient to dry the inside completely. The outside was then wiped quite dry with a clean handkerchief, and the tube reattached to the air-stream (still at the same rate) for exactly 5 minutes. The bubbling rate was reduced to about 1 per second just before immersion of the tube, and 4 bubbles of air were passed into the water in the cell; the actual time of immersion was noted. During this operation the stirring through the cell was not stopped, so that it would prevent CO_2 from diffusing back into the cell while it was open. Afterwards the cap was replaced on the cell as soon as possible.

A positive result was at last found, although it gave no indication of the cause of the resistance change, when the depth to which the tube was immersed was varied. Thus for a depth of immersion of about 1 inch, the resistance drop was about 2 ohms, as against about 8 - 10 ohms for a 4 inch immersion; intermediate values were obtained for 3 and 2 inches. This correlation was by no means quantitative, for in spite of the rigorous standardisation of procedure the actual individual drops were rather erratic. However, a number of tests showed a definite qualitative correlation between the magnitude of the drop and the depth of immersion. The latter was therefore also standardised in subsequent tests.

This result seemed to indicate that some sort of a surface effect involving the walls of the glass tube was taking place. The first possibility considered was that some substance was being condensed or adsorbed on either the inner or the outer surface of the tube during its long exposure to the air, and was subsequently being removed therefrom by the water. As regards the inner surface, this substance might come from the moist air which was passed through the tube after it had been dried and before its immersion. However, considerable variation of the length of time for which this moist air was allowed to pass (the outer surface was always wiped just before the addition) produced no trend in the resistance changes. A similar result was found after varying the length of time for which the outer surface was exposed to the air after it had been wiped dry. It seemed unlikely, therefore, that these surfaces were introducing to the water any impurity which they had acquired from external sources.

The other possibility was that the impurity actually came from the glass surfaces, i.e. that the effects were due to solution of glass from the walls of the tube. Since the solution of the cell walls, which had a considerably larger surface area than those of the tube, only resulted in a relatively small rate of fall of resistance (about 0.4 ohm/h), this explanation did not appear to be very probable. However, it was felt that, if such a process were responsible for the decreases in resistance occurring on immersion of the tube, then the magnitude of the drop should be dependent on the length of time of immersion. This had so far been more or less constant at 7 - 11 seconds, but was now varied from about 2 seconds (the tube was just dipped into the water and one bubble of air allowed to pass) to 2 minutes. No corresponding variations were observed in the amounts by which the resistance dropped. Thus neither the length of time of immersion nor the total number of bubbles of air passed appeared to have any significance; nor did the rate of passage of the bubbles, which was also varied.

At this stage no further avenues of approach were tried, but several later observations have thrown a new light on this subject. Thus, in the course of the investigations on the adsorption of potassium chloride (Section 3.3), the cell was frequently dried in order to obtain its dry weight; it was invariably found that the first portion of water placed in the cell after drying had a rather high conductivity -- usually about 60 - 70 nm/cm more than normal, though sometimes even higher -- whereas the second portion, which was frequently taken from the same flask of water and put into the cell without further rinsing, showed a more normal value.

Similar increases in conductivity resulting from the contact of pure water with a dried surface have occasionally been reported in the literature as well. Weiland[38], for instance, investigated the adsorption of potassium chloride by quartz by determining the change in conductance produced on adding ground quartz powder, which had been well washed and dried at 300°C, to the potassium chloride solutions. He remarked that it was necessary to correct for the "polluting effect" of the quartz. Blanks were therefore run in which equal weights of quartz were added to the conductivity water alone and the resulting increase in conductance of the water was noted; the experimental figures showed this increase to be of the order of 100 nm/cm.

Recently, too Benton and Elton[58], using a conductimetric technique for a similar study of the adsorption of ions from electrolytic solutions by silica, observed an immediate and considerable increase in the conductivity of their water after adding ground fused silica which had been well cleaned, washed, and dried at 120°C in an air-oven. This phenomenon persisted, to the same extent, in spite of further repeated washing of the silica with boiling conductivity water and redrying of the powder. Nor was it affected by outgassing the silica at 100°C in vacuum: it could therefore not have been due to the dissolution of gases (e.g. CO_2) adsorbed on the dried surface. Successive replacement of the water without intermediate drying of the silica eventually gave a sample which, in equilibrium with the silica, had a conductivity nearly as low as that of the freshly prepared water. This suggested that the phenomenon was due to the dissolution of a soluble surface layer which formed at the dried surface and which was very readily removed on contact with water, dissolving to give mainly colloidal silica. Benton and Elton also showed that, after dissolution in a neutral or acid medium, this layer was readily regenerated by redrying the silica at 120°C.

The increase in conductivity of the water was found by Benton and Elton to vary linearly with increasing area of silica present, the proportionality factor being about 1.2 nm/cm/θ (where $\underline{\theta}$ is the ratio of the silica surface area to the volume of water). Calculation from Weiland's figures[38] yields a rather similar value of about 1.4 nm/cm/θ. No exact measurements have been made with glass, and most of the readings in the experiments described earlier were rather erratic; but if the glass surface is assumed to be smooth, then a rough average of the values obtained for the resistance drop indicates a much higher value of about 50 nm/cm/θ for the proportionality factor. It is unlikely that this large discrepancy is entirely due to the assumption that the glass surface is smooth, and it therefore appears that this effect is much greater with glass than with pure silica. The increased effect may be due to the presence of alkaline and other constituents in smaller proportions than the 80% SiO_2 which Pyrex glass contains[55]: possibly these minor constituents migrate more readily to the dry surface and are more easily removed by dissolution. Thus it has also been observed that new Pyrex flasks apparently "age" rapidly: for instance, in one estimation of the "solubility" of new Pyrex glass, the amount of dissolved material (expressed as mg Na_2O) was found to drop from 0.40 to 0.03 in four successive tests[54].

A theoretical consideration of the magnitude of the increases in conductivity which are found certainly does not exclude the possibility of a soluble surface layer forming on the dry surface of the glass and dissolving as soon as water is added. Rough calculation shows that the number of ions required to produce a change of 70 nm/cm (such as was sometimes found on refilling the cell after it had been dried) would occupy an area of about 150 cm^2 if they were spread in a monolayer: this is based on the assumption that the average ionic conductance is 70 and the ionic radius 2 Å. If, further, it is once again assumed that the glass surface is smooth, the area thereof which is in contact with 200 ml water contained in the cell would be about 200 cm^2. Since the actual area is likely to be larger than this, and since some ions do not come from the glass which is finally in contact with the water, but from the neck and upper walls of the cell during the filling process, the surface area required for the ions is certainly not greater than the available exposed glass surface.

The effects observed with silica and glass are probably related to the fact that a better quality of water is obtained from the still only after it has been operated continuously for some time (see Section 2.2). When the still is not in use, a soluble surface layer may be formed on those parts of the surface which become dry. On then restarting the still, the early portions of water collected will have a rather higher conductivity than those obtained later, when removal of the surface layer has again been completed.

Very recently Holt and King[59], using labelled (^{31}Si) silicic acid in solution in contact with silica, have shown that a layer of silicic acid normally exists on silica surfaces. It is present as an incomplete monolayer covering about one-sixth of the surface, and is much more soluble than the rest of the material; in fact, it dissolves extremely rapidly in both water and dilute alkaline solutions, but not in acid solutions. Even after this layer has been removed by treatment with alkali, some degree of dissolution of silica and readsorption of silicic acid may occur if the sample is dried. These facts are in accord with the deductions which had already been made. It is possible that the whole soluble surface layer in the dried cell may be silicic acid: since it is acidic and yields the fast-moving H^+ ion, which has a much higher mobility than the average value of 70 that was assumed, the number of ions and hence the surface required will be much less than previously calculated. However, the possibility of some alkali ions being present on the surface in the case of glass is not quite excluded.

2.33 Removal of Dissolved Carbon Dioxide from Aqueous Solution.

2.331 Experimental.

Water was aerated in the cell and the resistance followed for some time after the maximum had been reached in order to determine its rate of decrease: this was necessary so that the completeness of the removal of any added volatile impurity could later be checked by suitable extrapolation of this resistance line. Carbon dioxide was then added to the water by the standard procedure previously described for air (see Section 2.32). The purified air stream was replaced by a stream of carbon dioxide which was obtained from a Kipps apparatus containing marble chips and hydrochloric acid; the gas was first washed by passing it through two bubblers containing conductivity water before it was allowed to enter the cell. A standard depth of immersion of 1 inch was adopted, and 3 bubbles of gas were usually passed into the cell, since it was found that this reduced the resistance to about the same value as that obtained when fresh water was placed in the cell. The removal of this added CO_2 by the air-stream was then followed by observing the resistance changes which occurred on continued aeration of the water.

The rate of removal was studied for different rates of bubbling, and some typical curves are shown in Fig 2.2, lines (2), (3), and (4); line (1) represents the corresponding variation of resistance occurring on aeration of a sample of freshly-distilled water. It will be noticed that the latter curve is very similar to (3), i.e. when the bubbling rates are the same (90/30 in this case), the rate of increase of resistance of fresh conductivity water from which the volatile impurities are being removed is approximately the same as that found for water to which CO_2 has been added. This is to be expected if the impurity originally present was almost entirely carbon dioxide dissolved from the atmosphere. Similar results were found for the other stirring rates.

The times taken for the maximum resistance to be reached were also nearly the same when corresponding bubbling rates were used. Sometimes the fresh water had to be aerated for slightly longer: this may have been due to some extra impurity being occasionally introduced into the water, but the results were not consistent enough to allow of any definite conclusions being drawn. Naturally the slower the rate of bubbling the longer it took for the resistance to rise to a maximum again, but the time was not quite inversely proportional to the bubbling rate, e.g. it required about 3 hours at 170/30, 4½ - 5 hours at 90/30, and 10 - 12 hours at 30/30. It seems, therefore, that when a fixed volume of air is passed through the water, the removal of the CO_2 is more **efficient at a** slower stirring rate.

The completeness of the removal of added carbon dioxide was judged from a graphical comparison between the resistances measured after the maximum had been passed and the values obtained at corresponding times from the extrapolated line which was drawn through the initial water resistances. A typical example is illustrated in Fig. 2.4. If the removal were complete, and no other effects had occurred, the resistances would be expected to fall again on the extrapolated line AB. Actually they were found to lie on a line CD which was parallel to AB, but about 1.6 ohms lower, i.e. the resistance decreased again at the same rate after the addition and removal of CO_2, but there had been a small drop in resistance owing to the addition. This, however, almost certainly arises from the immersion of the glass tube into the water when making the addition: it has already been shown (see Section 2.32) that this causes a decrease in resistance of approximately 2 ohms for a depth of immersion of 1 inch, so that, even if all the CO_2 were removed, a small change in resistance would be expected. It seems, therefore, that carbon dioxide can be removed completely from water by aeration.

2.332 Calculation of concentration of carbon dioxide.

When carbon dioxide is dissolved in water, in addition to the ionic dissociation of the water (equation (2.1)), the following equilibria take place in the solution:-

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad \ldots\ldots\ldots\ldots(2.7)$$

The mass action equations are

$$[H^+][OH^-] = K_w \qquad \text{..........(2.2)}$$

and $$\frac{[H^+][HCO_3^-]}{[CO_2]} = K_a \qquad \text{..........(2.8)}$$

Also, for electrical neutrality,

$$[H^+] = [OH^-] + [HCO_3^-]$$

Hence $$[HCO_3^-] = [H^+] - \frac{K_w}{[H^+]} \qquad \text{..........(2.9)}$$

Now κ = specific conductance of the solution

$$= \sum_i \frac{c_i \lambda_i}{1000} \qquad \text{..........(2.10)}$$

where c_i = concentration of ionic species i in g-equiv./l.
and λ_i = equivalent conductance of ionic species i.

The values of λ for the ions present are[33]:-

$$\lambda_{H^+} = 349.8$$
$$\lambda_{OH^-} = 198.5$$
$$\lambda_{HCO_3^-} = 44.5$$

Hence $$\kappa = 10^{-3}\left(349.8[H^+] + 198.5[OH^-] + 44.5[HCO_3^-]\right)$$

$$= 10^{-3}\left[349.8[H^+] + 198.5 \times \frac{K_w}{[H^+]} + \left(44.5\ [H^+] - \frac{K_w}{[H^+]}\right)\right]$$

from equations (2.2) and (2.9)

$$\therefore \quad 0.3943[H^+]^2 - \kappa[H^+] + 0.1540K_w = 0$$

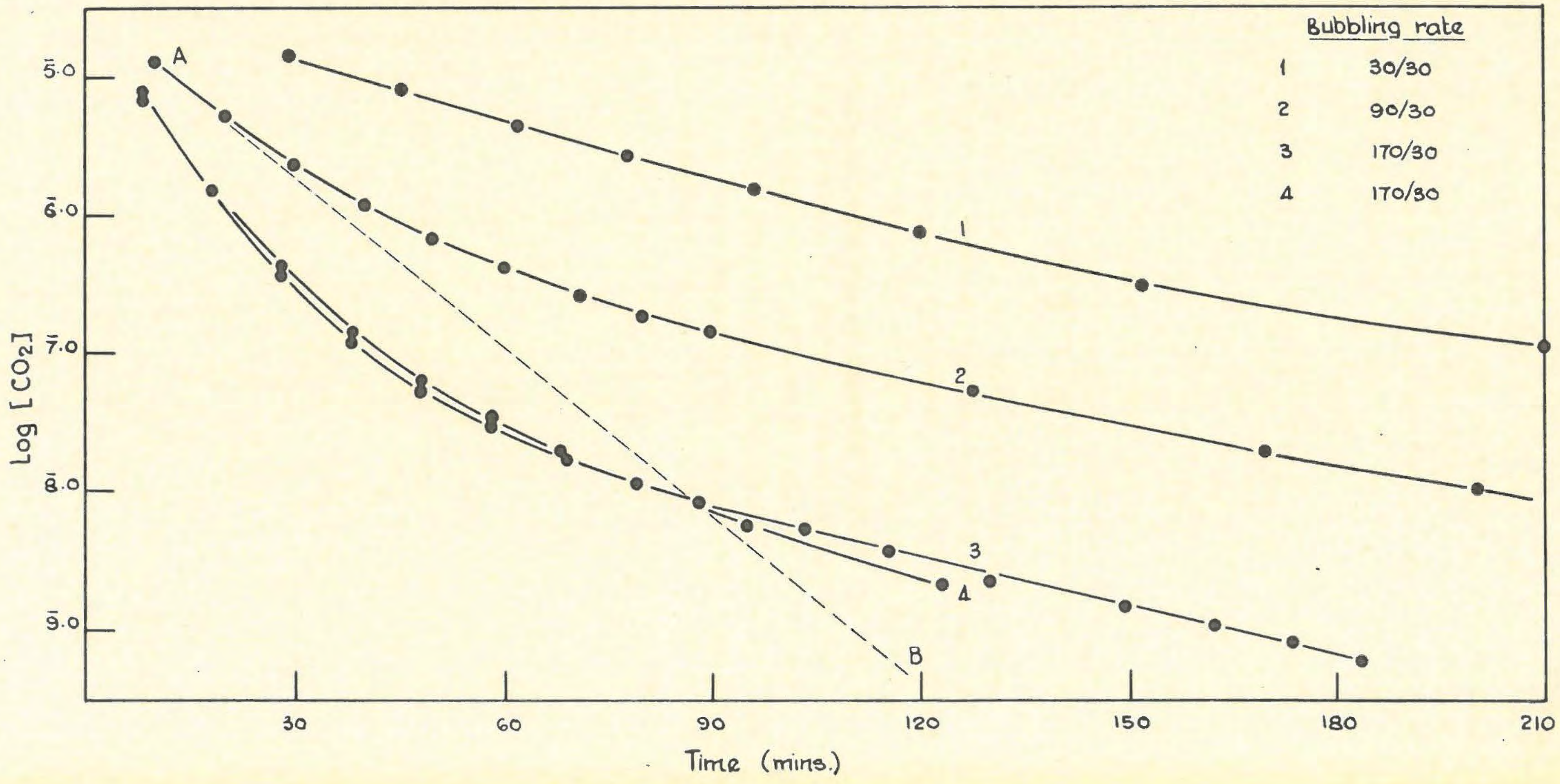
Taking $K_w = 10^{-14}$, we get

$$[H^+] = \frac{\kappa \pm \sqrt{\kappa^2 - 2.429 \times 10^{-15}}}{0.7886} \qquad \text{..........(2.11)}$$

Substitution of this value of $[H^+]$ in equation (2.9) gives $[HCO_3^-]$; these two values may then further be substituted in equation (2.8), together with the value[60] $K_a = 4.452 \times 10^{-7}$, to give $[CO_2]$, the concentration of undissociated CO_2.

In this derivation, it is assumed that the carbon dioxide is added to absolutely pure water of conductivity 55 nm/cm, so that the final conductivity of the CO_2 solution is due only to the presence of H^+, OH^-, and HCO_3^- ions. This was, of course, never true in actual practice, since the water conductivity was usually within the range 80 - 100 nm/cm. The concentration of CO_2 left in the water at various times during the course of the aeration could therefore not be calculated directly from the measured conductivities; the latter values had first to be corrected for the small amount of impurity present in the water. For this purpose it was assumed that

Fig. 2·5 – Plot of Log [carbon dioxide] v. time for different bubbling rates.



the impurity did not react with the water or with the CO_2, and hence the correction could be subtracted directly from the measured conductivity. Since the value of this correction gradually increased as the conductivity of the water rose owing to the solution of glass, the method of application was to extrapolate line CD backwards, and then to read off the resistance of the water E corresponding to the resistance of the carbonic acid solution F measured at the same time (see Fig. 2.4). The conductivity of the water of resistance E (= $\underline{x}$ nm/cm) was calculated (see values in Appendix D), and the difference $(x - 55)$, due to the presence of the impurity, was subtracted from the conductivity corresponding to resistance F to give the true conductivity of the carbonic acid solution. This value was then used for calculating the concentration of undissociated CO_2.

2.333 Theoretical analysis of results.

The fundamental law governing the distribution of a solute gas between the gaseous and solution phases is Henry's Law. This may be expressed in the simple form:-

At equilibrium: $p = K.m$ ....(2.12)

where p = partial pressure of the gas above the liquid
m = molar concn. of dissolved gas
K = constant (Henry's Law Constant)

Hence, for a fixed value of $\underline{p}$, the larger the value of $\underline{K}$ the smaller will $\underline{m}$ become, i.e. the less the solubility of the gas. $\underline{K}$ as used here is, in fact, inversely proportional to the solubility coefficient.

When a stream of an indifferent gas is passed through a solution of a volatile solute, the dissolved material will pass into the bubbles of the aerating gas and will gradually be removed from the solution. If it is assumed that each bubble attains complete equilibrium with the solution and becomes saturated according to equation (2.12) before it finally leaves the solution, then it is possible to calculate the rate at which the removal of the volatile solute will occur.

Solution phase:

Let: m = concentration of dissolved gas (in moles/l.) at any time $\underline{t}$ during the course of the removal
$-dm$ = decrease in concentration occurring in time $\underline{dt}$ (from $\underline{t}$ to $\underline{t+dt}$)
V_1 = total volume of solution (in litres)

Then: No. of moles solute which enters the gas phase in time dt

= No. of moles solute which is removed from the solution in time dt

$= -V_1.dm$ ....(2.13)

Gas phase:
(Air will be taken as the indifferent gas)

If p = partial pressure (in mm) of the solute gas in the air at time t,

then since complete equilibrium is assumed at all times,

$$p = K.m \qquad \text{from eqn. (2.12).}$$

Let: n = number of bubbles of air passing per second

V_b = volume of each bubble of air passed (in ml)

Then: Total volume occupied by solute gas which enters the air in time dt

= Total volume of air which passes through the solution in time dt

$= nV_b.dt$ ....(2.14)

The values obtained from equations (2.12), (2.13), and (2.14) may be substituted in the General Gas Equation (PV = nRT) to give

$$(K.m)(nV_b.dt) = (-V_1.dm).RT \qquad \text{..........(2.15)}$$

where T = Absolute Temperature
R = Gas Constant in ml-mm/$^\circ$C/mole
= 6.236×10^4 " " "

$$\therefore \quad -\frac{dm}{dt} = \frac{nV_b.K}{V_1.RT} \times m \qquad \text{..........(2.16)}$$

Hence the rate of decrease in concentration of the volatile solute at any time is proportional to the concentration m at that time and to the rate of flow of air through the solution (nV_b); it is also proportional to K, i.e. inversely proportional to the solubility of the solute gas.

In any one removal at constant temperature, K, V_1, and T will be fixed. If the rate of flow of the air (or indifferent gas) is also kept constant, then

$$J = \frac{nV_b.K}{V_1.RT} = \text{constant} \qquad \text{..........(2.17)}$$

J will be called the "Removal rate-constant". If, further, the initial concentration is m_o, integration of equation (2.16) between the limits m and m_o, and t and 0, will give

$$\ln m = -Jt + \ln m_o \qquad \text{..........(2.18)}$$

A plot of log m versus t should therefore give a straight line.

In all cases of the distribution of a solute between two phases, the equilibrium laws are valid only for molecules of the same species. Where a gaseous solute ionises in solution, therefore, only the unionised molecules should be considered when Henry's Law is applied: it was shown, for instance, that apparent deviations from this law which were found for dilute aqueous solutions of ammonia were due to neglecting the ionisation[61]. In the present investigation on the removal of carbon dioxide from solution, the range of concentrations considered was so small (10^{-5} to 10^{-9}M) that, although carbonic acid is only a very weak acid, an appreciable change in dissociation would occur, from about 20 - 80%. It is therefore essential in the application of equation (2.18) to this removal to consider the concentration of undissociated CO_2 molecules only, and not the total concentration of dissolved carbon dioxide.

When these concentrations were calculated from the measured conductivities for a bubbling rate of 90/30, and $\log[CO_2]$ was plotted against $\underline{t}$, instead of the expected straight line, a line of distinct positive curvature was obtained (see Fig. 2.5, line (2)). Plots made for other stirring rates gave similar curves, e.g. in Fig. 2.5, line (1) is for a rate 30/30, and lines (3) and (4) for 170/30. The nature of these curves is such that the slope, which is equal to the removal rate-constant $\underline{J}$, is continually decreasing with time. Since $\underline{n}$, V_b, V_1, $\underline{R}$, and $\underline{T}$ are all constant in any one determination, such a decrease could occur only if $\underline{K}$ decreased with dilution, which seems most unlikely.

Alternatively, if equation (2.16) is valid and $\underline{J}$ really is constant, there is the possibility that the concentration of undissociated carbon dioxide was not only decreasing because of the removal of the gas by the air-stream, as has been assumed in the foregoing derivation, but that it was also being changed by some other process which was not taken into consideration. For instance, the residual impurity initially present in the water might also be causing a displacement of the equilibrium (2.7). It was hoped that, if such a correlation could be made, it would throw some light on the nature of this impurity.

Whatever the cause of the disturbance of the equilibrium, it is necessary that the displacement should be such as to produce more ions, so that the actual concentration of undissociated carbon dioxide corresponding to a given conductivity of the solution would be less than the amount calculated as in Section 2.332. This can perhaps be most readily seen by considering Fig. 2.5. Presumably the effect would become more pronounced as the concentration of carbon dioxide diminished, so that the value of $\underline{J}$ calculated for the beginning of any removal should be more accurate than later values. Since $\underline{J}$ is assumed to be constant, the plot of $\log[CO_2]$ versus $\underline{t}$ should be a straight line of slope equal to this value; for example, in Fig. 2.5, for a bubbling rate of 90/30, the true values of $\log[CO_2]$ during the removal should lie on the straight line AB having the same slope as the initial value for line (2). The relative positions of these two lines indicate that the true concentrations are in all cases less than the values calculated from the measured conductivities at corresponding times. Equilibrium (2.7) must therefore be displaced to the right to account for the curvature of the lines in Fig. 2.5. The presence of impurities, however, can only cause a displacement in the reverse direction, or none at all. Thus, if the original impurity were acidic, the H^+ ions would repress the ionisation of the CO_2 and increase the concentration of undissociated molecules. Repression would also result from the presence of alkaline impurities (whether in the water originally or introduced to it subsequently by solution from the glass) because of the extra bicarbonate ions formed by reaction between the alkaline material and the excess CO_2. A neutral impurity, on the other hand, would not affect the dissociation at all.

Consideration of lines (3) and (4) in Fig. 2.5 lends further support to the idea that it is not the impurity present in the water which is responsible for the curvature in the $\log[CO_2]$-t plots. The bubbling rates in these two cases were approximately the same(170/30), but for line (3) the water used was very good --- it had a conductivity of 77 nm/cm at minimum. The total amount of residual impurity, therefore, must have been very small, so that the error introduced in the calculation of the true conductivity of the CO_2 solution could not have been very large even if the assumptions regarding the nature of the impurity and the method of correction outlined in Section 2.332 were wrong. For line (4), the water conductivity was somewhat higher (about 108 nm/cm); nevertheless this line is, if anything, straighter than line (3), in spite of the poorer quality of the water. It would definitely seem, therefore, that it is not the impurity in the water, nor a faulty correction for its presence, which produces the curvature in the plots in Fig. 2.5.

The possibility that this curvature was caused by surface activity was also considered. Carbon dioxide, however, lowers

Fig. 2·4 - Variation of resistance of conductivity water on aeration, before & after the addition of carbon dioxide.

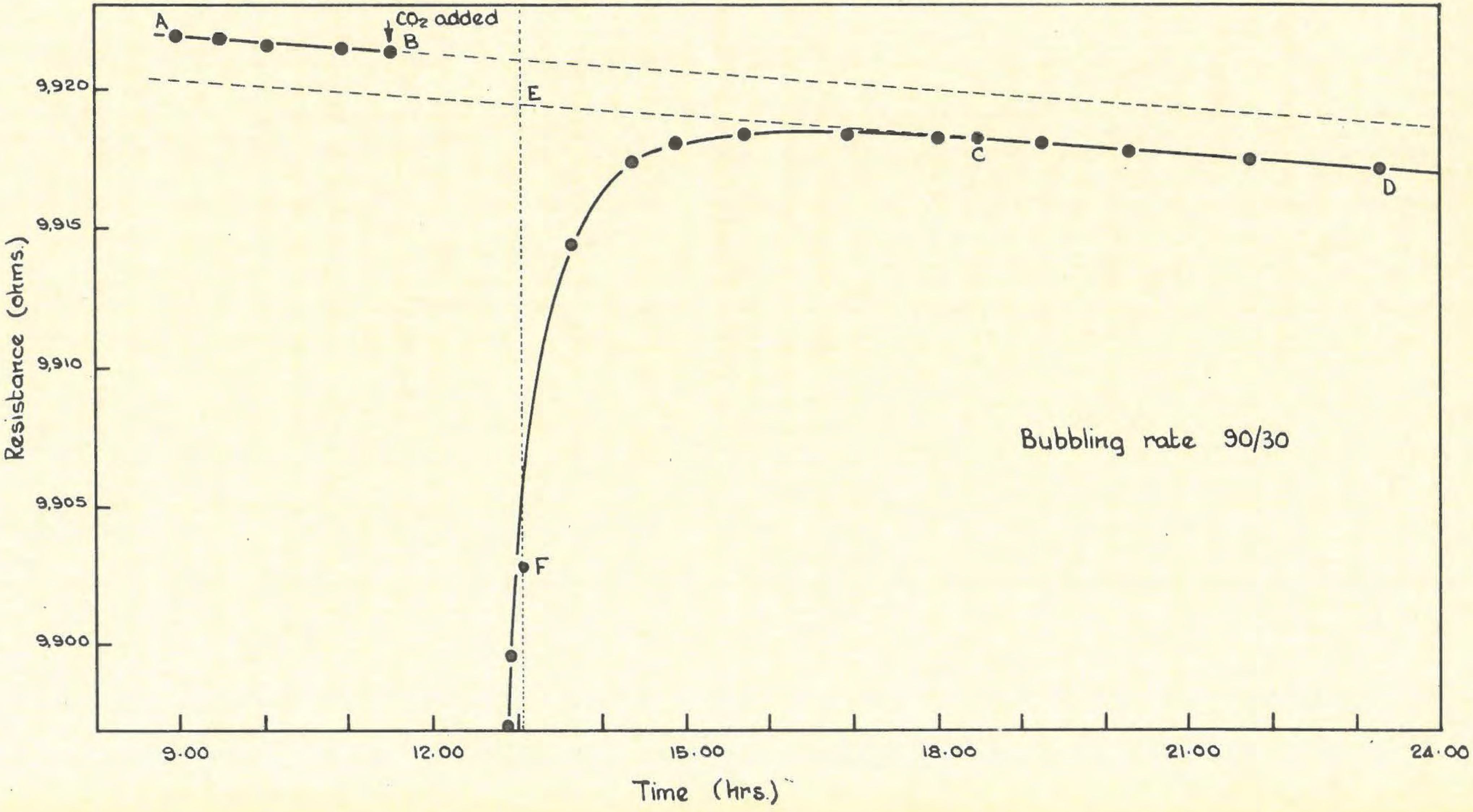
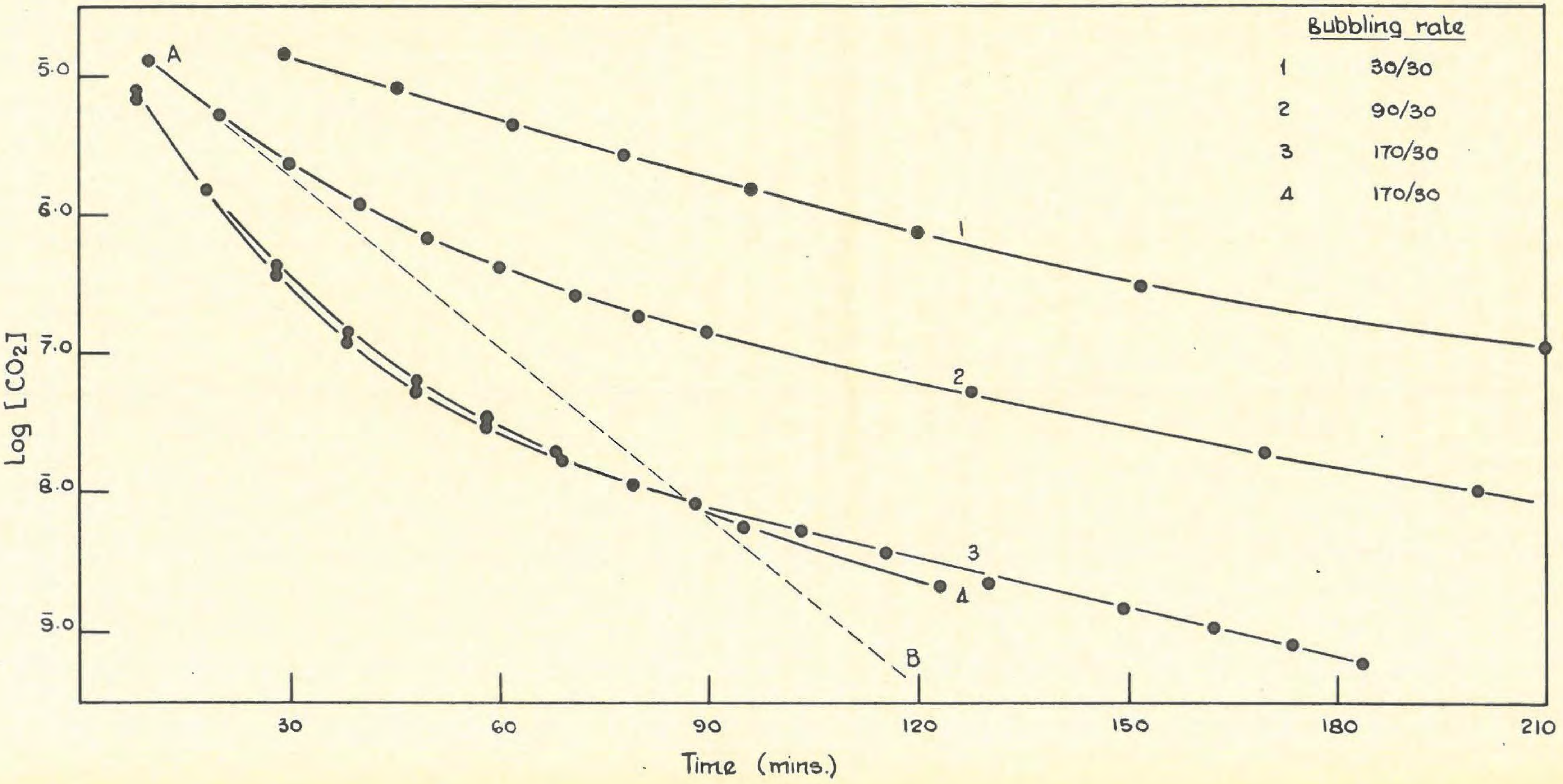


Fig. 2·5 – Plot of Log [carbon dioxide] v. time for different bubbling rates.



the surface tension of water: hence, according to the Gibbs adsorption theory, its concentration would tend to increase in the boundary layer of the solution adjacent to the bubble. The effect is, therefore, again in the wrong direction, as a decrease in $[CO_2]$ is being sought.

A few roughly quantitative calculations, based on the equations derived earlier, further revealed the inadequacy of their derivation for describing completely the phenomena encountered during the removal of CO_2 from aqueous solutions. Equation (2.18), for instance, may be rewritten as

$$\begin{aligned} t &= \frac{1}{J}\cdot\ln\frac{m_o}{m} \\ &= \frac{V_1.RT}{nV_b.K}\ln\frac{m_o}{m} \qquad \text{..........(2.19)} \end{aligned}$$

Hence, if the same volume of solution containing the same volatile solute is being aerated at a constant temperature, the time taken for the concentration to be reduced by a given amount, i.e. for the ratio $\frac{m_o}{m}$ to reach a fixed level, should be inversely proportional to the rate of flow of the air through the liquid (nV_b): in particular, since the latter quantity is determined as the number of bubbles of a constant size passing in unit time, the time required for all the dissolved gas to be removed and a maximum resistance to be reached should vary inversely as the bubbling rate. This time can be calculated from equation (2.19). For example, consider a typical case during the present investigation, viz. the removal of carbon dioxide from 200 ml water (V_1 = 0.2 l.) at a bubbling rate of 90/30 ($\underline{n}$ = 3 bubbles per second). A rough measurement gave the volume of each bubble of air as about 0.4 ml (= V_b); also, the initial concentration (m_o) of CO_2 was usually about 10^{-5} M (approximately the concentration in "equilibrium water"), and removal was regarded as complete when the concentration had dropped to 10^{-9}M. A time of 21½ minutes is obtained on calculation from these figures and from the value $K = 2.21 \times 10^4$ (derived from the solubility coefficient of CO_2 at 25°C given by Harned and Davis[60]). In actual practice, however, it required nearly 4 hours for the maximum resistance to be reached at this stirring rate. It seems, therefore, that the bubbles of air were not being fully saturated with carbon dioxide in their passage through the liquid, but passed through too fast to allow equilibrium to be established completely.

This conclusion is supported by the values of $\underline{K}$ calculated from the initial slopes of the $\log[CO_2]$-t curves in Fig. 2.5, i.e. from the lines corresponding to AB. From equation (2.18), these slopes = J, and hence K can be determined from equation (2.17). The following values were obtained:-

Bubbling Rate	K
30/30	6500
90/30	5400
170/30	4200 and 3850

These values are much lower than the true equilibrium value of 22,100 for CO_2 and water[60]. It again appears, therefore, that the air bubbles passing through the water were only partially saturated, from about one-fifth to one-third, depending on the bubbling rate. The trend in these values is in agreement with the previous observation that the efficiency of removal of dissolved carbon dioxide seemed to be greater the slower the rate of bubbling (p. 76).

Although only a partial saturation of the bubbles appears to have taken place, Henry's Law must still apply to the concentrations at the solution-air boundary layers. Since the time of contact of the air bubbles with the solution was not long enough to allow true equilibrium conditions to be set up throughout the bulk phases, the controlling factors in the rate of removal were probably the rates of diffusion of the carbon dioxide to and from these layers.

The problem of the removal of a volatile solute by an indifferent gas was treated as a pure diffusion process by Luther and MacDougall[62], on the basis of the following assumptions:-

(i) that the distribution equilibrium at the liquid-gas boundary was established instantaneously;

(ii) that the bubbles of gas which were passed through the liquid were all of uniform size, and were spherical;

(iii) that, because of the stirring set up by the passage of the bubbles through the liquid, the concentration of volatile material at any time was uniform throughout the whole solution;

(iv) that practically stationary conditions existed in the solution over a finite period of time, insofar as the concentration of volatile material remained constant in the solution during the time of passage of a bubble: hence the concentration would also remain constant in the outermost layer of the bubble.

Application of Fick's Laws to the inward diffusion of the solute gas from the outermost layers of the spherical bubbles eventually led to the general solution (the symbols have been changed to conform to those previously used in the present discussion):

$$-\frac{dm}{dt} = \frac{nV_b \cdot K}{V_1} \times L \times m \qquad \text{..........(2.20)}$$

where

$$L = 1 - 24 \sum_{n=0}^{n=\infty} e^{-\frac{k(2n+1)^2\pi^2 t}{4r^2}} \left(\frac{1}{(2n+1)^2\pi^2} - \frac{8}{(2n+1)^4\pi^4} \right) \qquad \text{..........(2.21)}$$

where k = diffusion coefficient of the solute gas in air (or in the indifferent gas)
t = time of contact of the bubble with the liquid
r = radius of the bubbles

For given experimental conditions, k, t, and r will be constant, hence L will also be constant.

The similarity between equations (2.20) and **(2.16) is** immediately obvious. However, the theoretical removal rate-constant will now have a different value, because the former equation takes into account the time of contact of the bubble with the liquid. In fact, the trend in the values which have been calculated for K at different stirring rates may be qualitatively explained by this equation. Thus a number of observations of gas bubbles emerging from a glass tube immersed in water showed that they became slightly smaller as the rate of flow was decreased. Presumably the same is true of the bubbles in the cell. r will therefore be smaller for a bubbling rate of 30/30 than for 170/30. Further, Allen[63] found that the speed of a bubble rising in a liquid was proportional to its radius. Since the bubble must pass through a fixed height of water in the cell, the time of contact t before it escapes from the surface must be slightly larger for a slower rate of bubbling; also, under these conditions, the bubble remains in contact with the liquid somewhat longer while it is being formed at the mouth of the capillary tube before it finally breaks away. The nett effect of a larger t and smaller r is that L becomes larger, so that the removal rate-constant (and hence, apparently, the value of K) will be greater for the slower stirring rates: this is in accord with the observed results.

Since the only difference between equations (2.16) and (2.20) lies in the value of the constant, further deductions from the latter equation must lead to the same results as those found for the former. In particular, it still seems that the plot of log[CO_2] versus t should be a straight line. The diffusion theory of Luther and MacDougall therefore does not account for the curves which were actually obtained. Implicit in their treatment of the problem, of course, was the assumption that no mixing of the gases took place inside each bubble because of stirring effects, but that the removal of the solute gas from the outermost layer into the bulk of the bubble was controlled entirely by diffusion. This assumption of still conditions within the bubble is probably invalid: in fact, visual observations made on bubbles rising in liquids seemed to indicate that a considerable amount of stirring must take place. Also, assumption (iii), that the concentration of the solute was uniform throughout the solution, may not be quite true. It is possible that the limiting factor in the removal process is not the diffusion which takes place within the bubble, but the diffusion of the solute into the surface layer of the solution in order to replace the material which has escaped into the bubble. If this is the case, the position as regards the removal of carbon dioxide would be further complicated by the fact that undissociated CO_2 molecules lost in this manner could be replaced either by diffusion of other CO_2 molecules from the main bulk of the solution, or by recombination of ions in the surface layer in order to restore the equilibrium (2.7); these ions would then, in turn, have to be replaced by further ions by diffusion. This problem has so far proved insoluble, and no explanation has been found to account for the curvature of the $\log[CO_2]$-t plots.

2.34 Removal of Dissolved Ammonia from Aqueous Solution.

It has already been shown that the removal of a dissolved gas from solution by aeration under fixed conditions is proportional to its Henry's Law Constant $\underline{K}$ (as expressed in equation (2.12)), i.e. inversely proportional to its solubility (see equations (2.16) and (2.20)). Ammonia is more soluble in water than is carbon dioxide, and its value for $\underline{K}$ is considerably smaller -- about 1,000 (derived from values given in tables[64]) as against 22,100 for the latter gas[60]. Hence it may be expected that the elimination of ammonia from aqueous solution by aeration will take much longer than that of carbon dioxide. In practice, the removal was found to occur extremely slowly. For instance, in one early experiment in this series, sufficient ammonia was introduced to the water in the cell to lower the measured parallel resistance to about 9650 ohms, i.e. the conductivity was about 450 mm/cm. The conductance, therefore, had not been increased nearly as much as was usual for additions of CO_2; yet, after two days with fast stirring, the resistance had only increased by about 120 ohms and was rising very slowly, even though it was still about 150 ohms below the initial value. The experiment was discontinued at this stage as it was obviously going to take a considerable time before a maximum resistance was reached.

Since the aim of these experiments was to study the completeness of the removal of ammonia, and since this removal was so very slow, it was decided to try to introduce to the water in the cell only enough gas to lower the measured resistance by about 100 ohms. Calculation along similar lines to those outlined for CO_2 solutions in Section 2.332 shows that this would correspond to a total ammonia concentration of about 5.5×10^{-7} equiv./l.

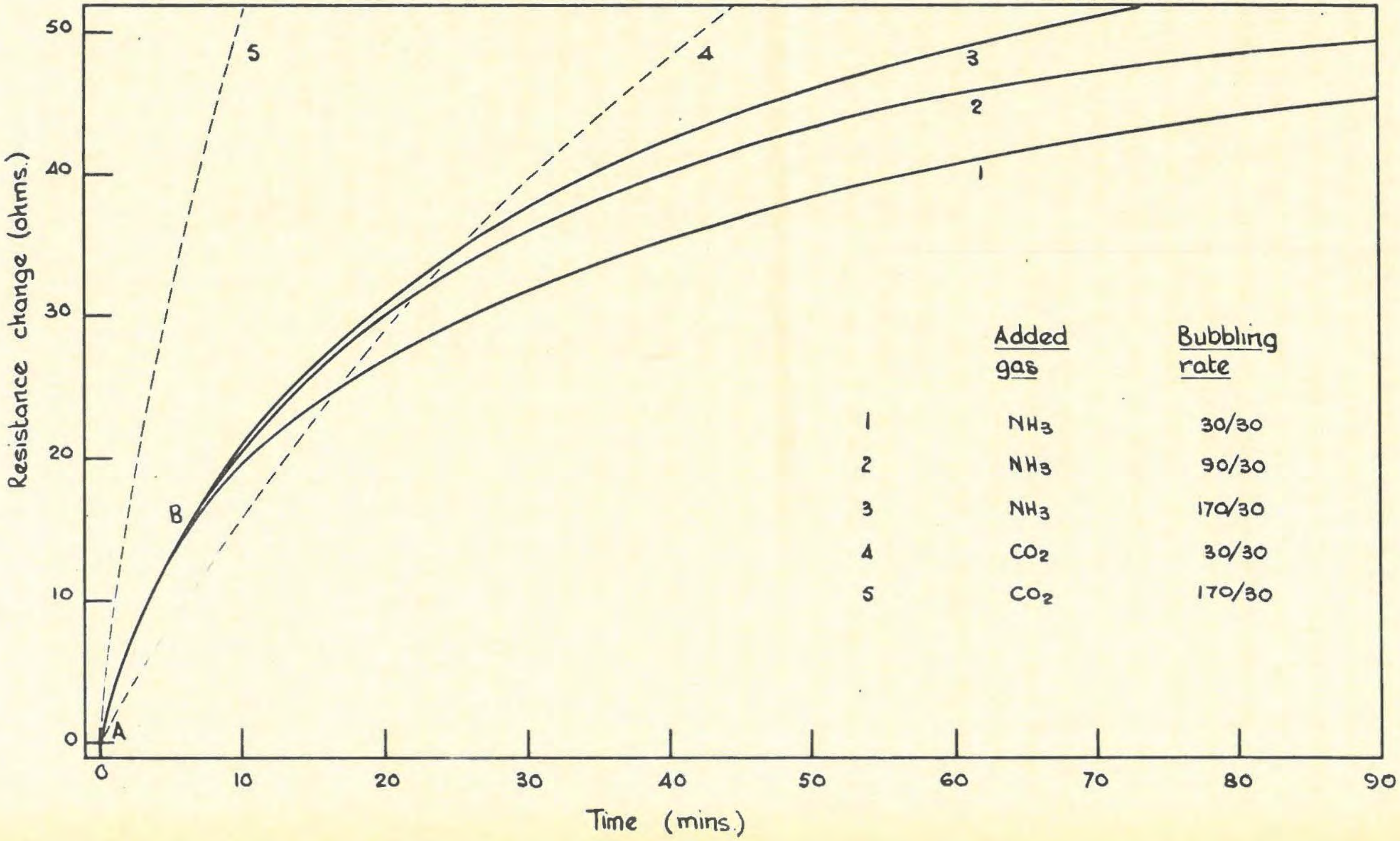
The addition of ammonia, which was obtained by passing purified air from the auxiliary train (see Section 1.631) through an extremely dilute ammonium hydroxide solution, was made by the standard procedure previously described (see Section 2.32). The solution was prepared by placing about 50 ml conductivity water in a bubbler and aerating it for several hours to ensure that all traces of CO_2 had been removed; then, immediately before the addition tube was removed for drying from the water in which it was normally kept, about 0.3 ml conc. G.R. ammonia was added to the water in the bubbler, and the passage of air was continued for the 30 minutes during which the addition tube was being sucked dry. The depth of immersion used was 1 inch, and 20 bubbles of the air-ammonia mixture were passed into the water. This generally produced a resistance drop of 80 - 100 ohms; but in spite of all the rigorous standardisation of procedure there was no certainty about the magnitude of the decrease, values varying from 30 to 150 ohms being found on different occasions.

This inconstancy of the resistance drop was but one of the many examples of inconsistent behaviour which were found throughout these ammonia investigations. In all, 40 additions of ammonia were made, and the subsequent changes in resistance of the cell were followed for periods varying from two hours to ten days. The curves obtained were not very reproducible, even for similar conditions of stirring rate and resistance drop. However, certain general conclusions did become apparent.

As in the case of carbon dioxide, so the removal of ammonia was also studied at different bubbling rates. With the CO_2 solutions, when approximately equal concentrations were being considered, i.e. at nearly equal values of the measured resistance, it was found that the rate at which the resistance increased on aeration was dependent on the bubbling rate, to which it was roughly proportional. With the ammonia solutions, however, the behaviour was rather different. The readings taken at one-minute intervals showed that the resistance invariably increased quite rapidly immediately after the addition, irrespective of the rate of bubbling being used. The initial rates of rise were in all cases much faster than had been expected; also, they appeared to be very similar even for widely differing stirring rates. This similarity was confirmed by plotting the changes in resistance observed with different rates of aeration, and by comparing the curves so obtained. For example, in Fig. 2.6 the continuous lines (1), (2), and (3) show, for three different bubbling rates, the changes which occurred immediately after the addition of ammonia; in each case the decrease in resistance, due to the addition, was about 100 ohms. As a comparison, the broken lines (4) and (5) show the corresponding changes in resistance which took place on aeration of water (at a slow and a fast rate respectively) which contained sufficient CO_2 to reduce the resistance below its maximum value by a similar amount. Fig. 2.6 has not been plotted on an absolute resistance and time scale, but only the actual changes in resistance from the time of addition have been considered, in order that all the curves may start from a common point and hence may be more easily compared. It will be seen that the rate of increase of resistance for water containing CO_2 was always less, at corresponding resistances, for the slower bubbling rate. After additions of ammonia, however, the resistance increased initially (from A to B in the diagram) at about the same speed irrespective of the stirring rate; furthermore, this rate of increase was faster than that found, for example, for the removal of CO_2 at a bubbling rate of 30/30. The ammonia therefore seems to have been removed from the solution, initially at any rate, not only by being swept out by the air-stream, but also by some other mechanism. It is believed that these observed effects were due to adsorption of the ammonia on the glass walls of the cell.

Gaseous ammonia is one of the most readily adsorbed gases on glass: for instance, Evans and George[65] calculated that, in one of their experiments at constant pressure, there were 39.9 molecular layers of ammonia adsorbed by the glass, as against 5.5 for CO_2. Since the affinity of glass for ammonia is so strong, it is not unlikely that it would still be noticeable even when the ammonia was present, not as a gas, but in solution. The resulting adsorption could cause quite an appreciable change in the concentration if the solution was extremely dilute, as was the case with the solutions from which the removal of ammonia was being studied. In fact, a quantitative consideration certainly does not exclude the possibility that

Fig. 2·6 – Initial variation of resistance of conductivity water on aeration, after additions of ammonia & carbon dioxide.



the observed changes of resistance were being caused by such an adsorption. Thus it has already been mentioned that the concentration of ammonia corresponding to a 100-ohm decrease in the measured resistance of the water is about 5.5×10^{-7} equiv./l. (p.86): in these experiments, therefore, 1.1×10^{-7} equiv. must have been added to the 200 ml water in the cell. The area of glass surface in contact with these solutions was about 200 cm^2 (see Section 2.32, p.74). This area is capable of carrying a considerably larger amount of adsorbed ammonia than the 1.1×10^{-7} equiv. which was added. Crespi and Moles[66], for instance, found that on saturation and under 1 atmosphere pressure (temperature not stated, but presumably room temperature) the walls of a 1-litre flask adsorbed 1.8×10^{-4} g, i.e. about 10^{-5} equiv. ammonia: this amount would therefore be present on an area of 480 cm^2, if it is assumed that the flask was spherical and the glass quite smooth. If, further, the molecular diameter of NH_3 is taken as 3 Å[67], it will be seen that this adsorption corresponded to a multimolecular layer (about 10 molecules thick). The concentration of the ammonia gas in this case was, of course, approximately $\frac{1}{22.4}$ equiv./l. -- much higher than that of the ammonia in the solutions being considered. Naturally, therefore, the amount of adsorption would be much less in the latter cases, though it would not be proportionately smaller because, from the nature of the general adsorption isotherm, the quantity of substance adsorbed becomes much greater relative to the total concentration as the latter is made very small. Hence it is to be expected that a larger fraction of the total amount of NH_3 present would be adsorbed from the dilute solutions than from the more concentrated gas phase of Crespi and Moles. In fact, though the actual fraction adsorbed was rather small in the latter case, it is conceivable that, in view of the extreme dilution of the solutions, the fractions adsorbed during these experiments were considerably larger. A coverage of the glass surface in contact with the solution with a monomolecular layer of ammonia (if the same assumptions are made as previously) would require about 0.27×10^{-7} equiv., i.e. about $\frac{1}{4}$ of the total amount present. This would therefore correspond to an increase in resistance of about 25 ohms owing to removal by adsorption, which appears to be of the right order of magnitude for the resistance changes which were observed after an addition.

The question of the speed of the reaction must also be considered. Burt[68] has stated that the adsorption of ammonia by glass is a slow process, which takes a long time before complete saturation is reached. Nevertheless, it is to be expected that the initial adsorption will take place reasonably fast when the glass is quite free of ammonia; and it must be remembered that the walls of the cell were usually well leached and free from adsorbed material because the water in the cell was normally changed several times between experiments and aerated to a maximum resistance each time. Furthermore, calculation indicates that the rate of removal of ammonia by aeration would definitely be much too slow to account for the rapid increases in resistance which were observed. It seems more likely, therefore, that the primary removal taking place immediately after the addition of ammonia was due to adsorption. As this would not be influenced by the rate of stirring in the cell (except insofar as the stirring aided diffusion in replenishing the depleted layers of solution in contact with the glass), the initial rise in resistance would then be the same regardless of the bubbling rate. Only when the rate of removal by aeration had become comparable with that by adsorption would any difference become noticeable in the rate at which the resistance rose with varying stirring rates.

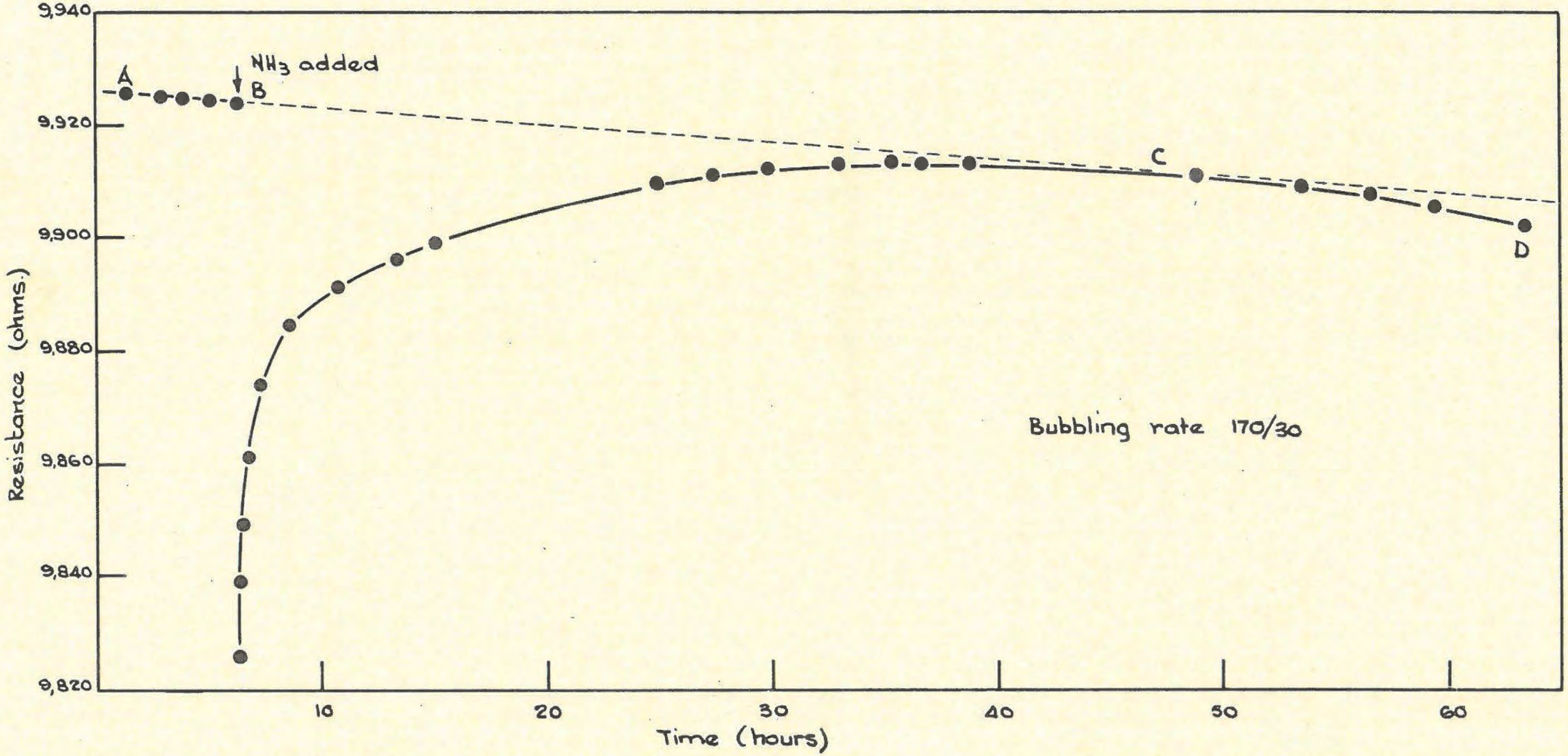
Further confirmation of the adsorption of ammonia on the glass walls of the cell was furnished by the unusual behaviour on aeration of a sample of water which had been placed in the cell immediately after one of the early experiments on the removal of ammonia. Too much ammonia had been added to the water in this instance, but the dilute ammonia solution had still been left in the cell for one day before it was emptied out and replaced by fresh water. The initial changes on aeration of this water were similar to those normally observed. After the conductivity had fallen fairly rapidly to about 175 nm/cm, however, it increased over a period of five hours to 253 nm/cm, and finally again began to drop, though rather slowly. This behaviour can readily be explained if the walls of the cell were still contaminated with ammonia adsorbed thereon during the previous experiment. Thus the first decrease in conductivity was probably due to the normal removal of CO_2 from the water. As the rate of this removal slowed down, the simultaneous increase in conductance resulting from the desorption of ammonia from the walls gradually became more pronounced, until eventually it exceeded the decrease and caused the measured conductivity to rise; this rise continued until a new equality had been established between the rate of desorption of ammonia from the walls and the rate of its removal from the solution by aeration. Finally, when the latter had become predominant, a slow decrease in conductivity again took place.

The relatively rapid increase of resistance observed after an addition of ammonia to water in the cell usually persisted (to a gradually diminishing extent) for a few hours, when presumably adsorption saturation was more or less reached. Thereafter the resistance still continued to rise for a long time, although very slowly, until finally it reached a maximum and began to fall again. This whole process was followed for a number of additions. It was found that, for an initial fall in resistance of 80 - 100 ohms when the ammonia was added, the time taken for the subsequent attainment of the maximum resistance varied from about 1 day at a bubbling rate of 170/30 to 4 - 5 days at a 30/30 rate; the exact time, however, was very variable, even at a fixed stirring rate and for the same decrease in resistance, e.g. times ranging from 18 to 29 hours were found with 170/30 bubbling.

The resistance-time curve obtained for one experiment on the removal of added ammonia is shown in Fig. 2.7. In this example, the extrapolated line AB drawn through the initial resistances of the water before the addition passes through the maximum resistance C reached after the addition. This is the criterion which was used for checking the completeness of the removal of added carbon dioxide (see Section 2.331): hence it seems that in this experiment the ammonia was also completely removed from the solution. This method of checking, however, could not in general be applied to the additions of ammonia with as great a certainty as to those of CO_2 because of the long extrapolations which were necessary -- the time required for the removal of ammonia was always much larger, even though the falls in resistance due to the addition were only about 100 ohms as against the approximately 10 times greater decreases used for carbon dioxide. Nor would it have been more expedient to have added smaller quantities of ammonia to the water in order to shorten the time taken for the maximum resistance to be reached, since most of the ammonia would then have been removed by adsorption.

A second check could also be made on the completeness of the removal of carbon dioxide, viz. by extrapolating the line of the decrease of resistance observed after the maximum back to the time of addition, and then comparing the resistance thus obtained with the measured value at this time. Although a similar procedure worked satisfactorily in a few cases with ammonia, sometimes it was found that the rate of decrease of resistance after the maximum, instead of being equal to the

Fig. 2·7 - Variation of resistance of conductivity water on aeration, before & after the addition of ammonia.



rate of drop observed for the fresh water before the addition was made, was now greater; also, the final rate found for the aerated solution was not always constant, but frequently appeared to be increasing, thus causing the plotted line to become curved (CD in Fig. 2.7). The reason for these effects is not known, but they may have been associated with the fact that, by the time the maximum resistance had been reached and passed, the water had already stood in the cell for several days and its conductivity was by then considerably higher than at the start of the experiment (cf. the faster rate of decrease of resistance observed with water of poorer quality, which has previously been mentioned -- p.67). Whatever their cause, these effects seemed to render invalid the additional method of checking the completeness of the removal of added ammonia: the curved line in particular could naturally not be extrapolated to the time of addition with any accuracy. However, from all the experiments which were performed, it did seem that ammonia was completely removed from dilute aqueous solution if sufficient time was allowed.

Although the forward extrapolation of the water line was generally a little uncertain, in a few cases it appeared definitely to pass 3 or 4 ohms below the maximum resistance found after the addition of ammonia. This, of course, corresponds to a "more than complete" removal of the added material. Various explanations of this effect have been suggested. It may be that the adsorbed layer of ammonia partially screened the glass surface from attack by the water and thus prevented, or at least slowed down, the decomposition or "solution" of the glass. In this case extrapolation of the water line would not be valid, since this construction is based on the assumption that the conductivity of the water increases at the same constant rate throughout the experiment.

Another possibility is that the effect was due to neutralisation by the added ammonia of a very small amount of acid impurity present in the water: such a process would involve the replacement of fast-moving H^+ ions by slower NH_4^+ ions, with a consequent reduction in conductivity. In one experiment, for instance, where the amount of ammonia added was so small that it caused the resistance to drop by only 5 ohms, within 2 hours a maximum was reached which was about 1 ohm higher than the initial water resistance. This cannot be accounted for by the previous explanation, but calculation shows that only a very small amount of acid would need to be present in the water originally in order to produce such a change. For example, suppose that during aeration water of conductivity 100 nm/cm remains unaffected by the solution of glass or other processes which might change its conductance; and suppose that finally, after ammonia has been added and the excess has been removed by aeration, the conductivity drops to 97 nm/cm (this decrease is about the same as those which were actually found in a few experiments when the extrapolation was made). Further,

let: X = contribution to total conductivity by neutral salt impurity (which will remain constant),

x = concn. (in equiv./l.) of acid impurity anion A^-,

and $\lambda_{A^-} = 70$ (an approximately average value for many ions).

Before addition:

From equations (2.2) and (2.10), and using the λ-values already quoted (p.77), we get

$$\begin{aligned}\kappa_{H_2O} &= \text{initial conductivity of water}\\ &= 100\\ &= 0.3498[H^+] + 0.1985\,\frac{10^{-14}}{[H^+]} + 0.070\,x + X \quad \ldots\ldots(2.22)\end{aligned}$$

Also, for electrical neutrality, we have

$$x = [H^+] - \frac{10^{-14}}{[H^+]} \quad \ldots\ldots\ldots\ldots(2.23)$$

After addition:

If, in order to avoid complications due to complex hydrolysis effects, we assume the acid to have the same ionisation constant as ammonia, the pH of the solution will be 7.0, and hence the conductivity due to the H^+ and OH^- ions in this solution will be 54.83 nm/cm.

Using the value[33] $\lambda_{NH_4^+} = 73.4$, we then get

$$\begin{aligned}\kappa'_{H_2O} &= \text{conductivity after addition and removal of ammonia}\\ &= 97\\ &= 54.83 + 0.070\,x + 0.0734\,x + X \quad \ldots\ldots\ldots\ldots(2.24)\end{aligned}$$

Solution of equations (2.22), (2.23), and (2.24) gives the approximate values X = 33 nm/cm and x = 6.5×10^{-8} equiv./l.: the latter, then, is the amount of acid impurity required to make the final conductivity, after ammonia has been added and removed, 3 nm/cm less than it was initially. Further calculation shows that varying the strength of the acid does not greatly change these values for X and x. Hence it will be seen that, if acid impurity present in the water was indeed the factor responsible for the occasional "more than complete" removal of added ammonia, the water would need to contain only a very small amount thereof in order to produce effects of similar magnitude to those which were observed. In the example considered above, for instance, if one excludes the contribution made by the H^+ and OH^- ions to the total conductivity of the water, the "solvent correction" to be applied for the presence of residual impurities in the water would be mainly a correction for neutral impurities; in fact, the amount of acid impurity is small enough for all the impurity to be regarded as neutral and for the total correction therefor to be taken as 100 - 55 = 45 nm/cm without any appreciable error being introduced, except when determinations are being made of the conductivities of extremely dilute solutions of acids and bases.

The theoretical treatment of the results of these experiments with ammonia along lines similar to those used for the removal of carbon dioxide (see Section 2.333) becomes even more complicated because of the adsorption taking place, which must now also be considered. No serious attempt has therefore been made to derive a mathematical relationship which will describe the observed variations of resistance with time, especially since it was in any case almost impossible, owing to the uncertainty of the various extrapolations, to estimate accurately the concentration of the ammonia at any given time during the removal. Also, the results themselves were not really reproducible enough to warrant a quantitative analysis. For instance, although the curves in Fig. 2.6 show the immediate increases of resistance to be fairly uniform irrespective of the bubbling rate, more rapid rises were frequently observed even when the actual decrease of resistance on addition had been much smaller than in these cases. There were also numerous discrepancies from the removal pattern shown in Fig. 2.7. Thus in one experiment the resistance increased normally for about 8 hours after the addition; but it then remained constant, within 1 or 2 ohms, for seven days before starting to decrease more or less along the extrapolated water line (AB). By contrast with this case, on four other occasions (they were actually in succession) the resistance rose very rapidly to a false maximum instead of following the usual steady change of resistance shown in Fig. 2.7; thereafter it dropped fairly fast until it again coincided approximately with the expected curve -- twice before the usual maximum was reached, but in the other two cases there was no second maximum. In all four cases prolonged aeration eventually resulted in the normal slow decrease of resistance lying more or less along the extrapolated water resistance line. The bubbling rate in these four experiments was 170/30; at this rate the time taken for the maximum to be reached was usually about 20 hours, but this false maximum was reached in a mere 3 to 6 hours. On one of these occasions, too, the resistance at this maximum was actually 8 ohms higher than the initial water resistance! These inconsistencies turned up despite all attempts at an extremely rigorous standardisation of the various procedures used in the many experiments performed with ammonia. They may have been caused by the effects which the physical condition and the previous history of the glass walls had on the adsorption on the adsorption occurring there, but no definite correlation between these factors could be obtained.

In spite of the erratic behaviour encountered during this investigation on the removal of ammonia from water by aeration, the following three general conclusions do appear to be valid:-

(i) Ammonia is adsorbed from solution by the glass walls of the cell.

(ii) All the ammonia added to water can be removed by aeration, but the process is very slow.

(iii) Since, in general, the maximum reached after an addition did not exceed the corresponding value found by extrapolating the water resistance line, it seems that the residual impurity in the water is not acidic in nature. Traces of acid may appear occasionally, but the amounts seem usually to be so small that in most determinations no appreciable error would be introduced in the solvent correction by regarding all the residual impurity as neutral. This conclusion has been supported by the subsequent determination of the solubility of calomel by conductimetric methods performed by Dry[57,69] in this laboratory.

2.35 Removal of Dissolved Carbon Dioxide and Ammonia When Present Together in Aqueous Solution.

It has been shown that dissolved ammonia can be removed completely from very dilute solution by aeration. If, however, owing either to its incomplete removal during distillation or to subsequent atmospheric contamination, there was still ammonia present in traces in the water that was placed in the cell, it would presumably have been present not as the hydroxide but as the bicarbonate, formed by combination with the dissolved carbon dioxide which, throughout this investigation, was removed from the water only after the latter had been put into the cell. It seemed possible, therefore, that some of the residual conductivity which was found after the water had been aerated to a minimum conductance, i.e. some of the amount by which this minimum exceeded the theoretical value of 55 mμ/cm for pure water, might be due to the presence of ammonium bicarbonate as impurity. At the low concentrations which would prevail under these circumstances, however, hydrolysis would occur to an appreciable extent, thus:-

$$\begin{array}{lcc} \mathrm{NH_4^+ + HCO_3^- + H_2O} \rightleftharpoons \mathrm{NH_4OH} & + & \mathrm{H_2CO_3} \\ \qquad\qquad\qquad\qquad\quad \upharpoonleft\downharpoonright & & \upharpoonleft\downharpoonright \\ \qquad\qquad\qquad\quad \mathrm{NH_3 + H_2O} & & \mathrm{CO_2 + H_2O} \end{array} \quad \ldots\ldots.(2.25)$$

Both the products could be removed separately by aeration; hence it seemed likely that such a procedure might also completely eliminate the ammonium bicarbonate, since removal of the ammonia and the carbon dioxide in equilibrium (2.25) would result in a continued displacement to the right until all the reactants on the left had disappeared. In order to test this theory, it was decided to add both gases together to water in the cell and then to investigate the completeness of their removal by aeration.

The carbon dioxide and ammonia were added by the standard methods previously described (see Sections 2.32, 2.33, and 2.34). Because of the time required to ensure that the tube was thoroughly clean and dry for each addition, it was not possible to add both gases simultaneously; but such a procedure was, in any case, not advisable, since it would not indicate which gas was present in excess nor how much of each there was in combination. These were factors which should be known and controllable. For instance, it seemed desirable to have the combined gases present in very low concentrations, because it was unlikely that the rate of removal of the two gases together would be any faster than that of ammonia alone -- probably slower, if anything. The accurate control of the small amounts required could be achieved only by putting in one gas first and allowing it to be removed to some known concentration, as indicated by the resistance of the solution, and then introducing an excess of the second gas. In practice, the second addition was usually made when the resistance had risen to about 30 ohms below the initial value at the time of the first addition: this meant that the concentration of dissolved gas had fallen to about $2 - 3 \times 10^{-7}$ equiv./l. -- large enough for the ammonium bicarbonate formed still to give reasonable resistance changes on aeration, but without making the completion of the experiment unduly long (several days were usually required in any case!).

Obviously the addition of two gases in succession can be made in two different ways. The primary interest of this study was to determine whether ammonium bicarbonate was still present as an impurity in the water obtained from the still after it had been aerated in the cell to a minimum conductance.

Since such an impurity would have arisen from the combination of a small trace of ammonia with a large excess of carbon dioxide, the more logical approach was to add the ammonia first, followed by the CO_2 when the concentration of the former gas had been reduced to a very low value by aeration. This sequence, however, suffered from the disadvantage that it was not usually possible to add just a small excess of CO_2: even the addition of only one or two bubbles caused the resistance to drop by a few hundred ohms, and several hours then elapsed before it had again risen to its former value at the time of the addition. This meant that it was not possible to follow any immediate small changes in resistance occurring just after the addition in order to observe the effect which the added CO_2 had on the removal of the ammonia. However, a few additions of this nature were made, and the curve obtained for one such experiment is shown in Fig. 2.8.

Line AB gives the decrease in resistance of the water alone. When this had been observed long enough for the slope of the line to be established reasonably accurately, ammonia was added (at B -- the resistance was then about 9932 ohms), and the resistance dropped about 73 ohms to C. A fairly rapid rise in resistance followed (CD), such as was usually found on the addition of NH_3: this was presumably due chiefly to adsorption of ammonia on the glass. At D, when the resistance was still about 32 ohms below the extrapolated water value corresponding to this time (F), CO_2 was passed into the cell; the resistance dropped below 9300 ohms, but it immediately began to rise again at a very rapid rate as the excess CO_2 was removed by the fast air stirring (170/30). The values obtained during the latter part of this rise (from about 9820 ohms) are shown by the plotted points along GHJK. The actual line GH and its extension to I was drawn from data obtained in an earlier experiment on the removal of carbon dioxide alone at a similar bubbling rate -- a section of the curve was chosen such that the resistance corresponding to G was the same amount below the resistance of the water at the time of the addition as G was below F. It will be seen that the rise observed in the present experiment was quite normal for the removal of CO_2 at the bubbling rate being used until the resistance reached a value H which was just less than that of the solution at the time that the second addition was made (D). Had the removal of CO_2 still proceeded normally, the resistance would then have continued to rise as shown by the broken line HI. At H, however, the rate of rise began to deviate from the normal, and at the value J, which was almost equal to that of the solution when the CO_2 was added, it decreased quite markedly, and seemed to become more nearly similar to that usually observed for the removal of ammonia alone (cf. the broken line DE that was drawn, as an extension to the line CD, from data previously obtained during the experiments with ammonia by itself); the experimental curve from J onwards, in fact, appeared to very nearly an extension of CD, being just an ohm or two lower at each point. The resistance eventually rose to a maximum (K), which was reached about 29 hours after the first addition had been made, and afterwards it began to drop again at a uniform rate. This decrease, given by LM, coincided with the extrapolated line AB for the initial water resistance. Removal of all the added ammonia and carbon dioxide seems therefore to have been complete, and to have taken about the same time as that required for ammonia alone.

The fact that, in the example chosen, the curve JK for the removal of ammonium bicarbonate (or ammonia and carbon dioxide present together in equivalent quantities) lay almost along the continuation DE of the curve for the removal of ammonia alone is probably not generally true, but it appears rather to be coincidental as a result of several factors. The main reason for this phenomenon seems to be the arbitrary choice of approximately 30 ohms for the difference between the initial water resistance (B) and the resistance of the ammonia solution at the time of the CO_2 addition (D). This can be demonstrated quite readily by a consideration of the specific conductances of ammonia and ammonium bicarbonate solutions at the extreme dilutions encountered in these experiments. These conductivities* are shown in Fig. 2.9, together with the corresponding changes in measured resistance which would occur if the solutions were placed in Cell I†. It will be seen that the values for these two substances do not differ much for concentrations from zero up to about 2.5×10^{-7} equiv./l., i.e. the measured resistances of solutions formed by the addition of either ammonia or ammonium bicarbonate to water would be nearly the same, for equal concentrations, provided the amount of solute added did not cause a change in the resistance of Cell I larger than about 25 ohms. This range almost completely covers the

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* The calculation of the specific conductances of ammonium hydroxide solutions can be most easily performed by calculating the concentrations of ammonia which correspond to various conductivities in a manner similar to that previously described for CO_2 (see Section 2.332); and Malan[15] has outlined a method for calculating the specific conductances of solutions of ammonium bicarbonate.

† These resistance changes may be obtained by interpolation of the values given in Appendix D.

Fig. 2·9 - Specific conductances of dilute solutions of carbon dioxide, ammonia & ammonium bicarbonate.

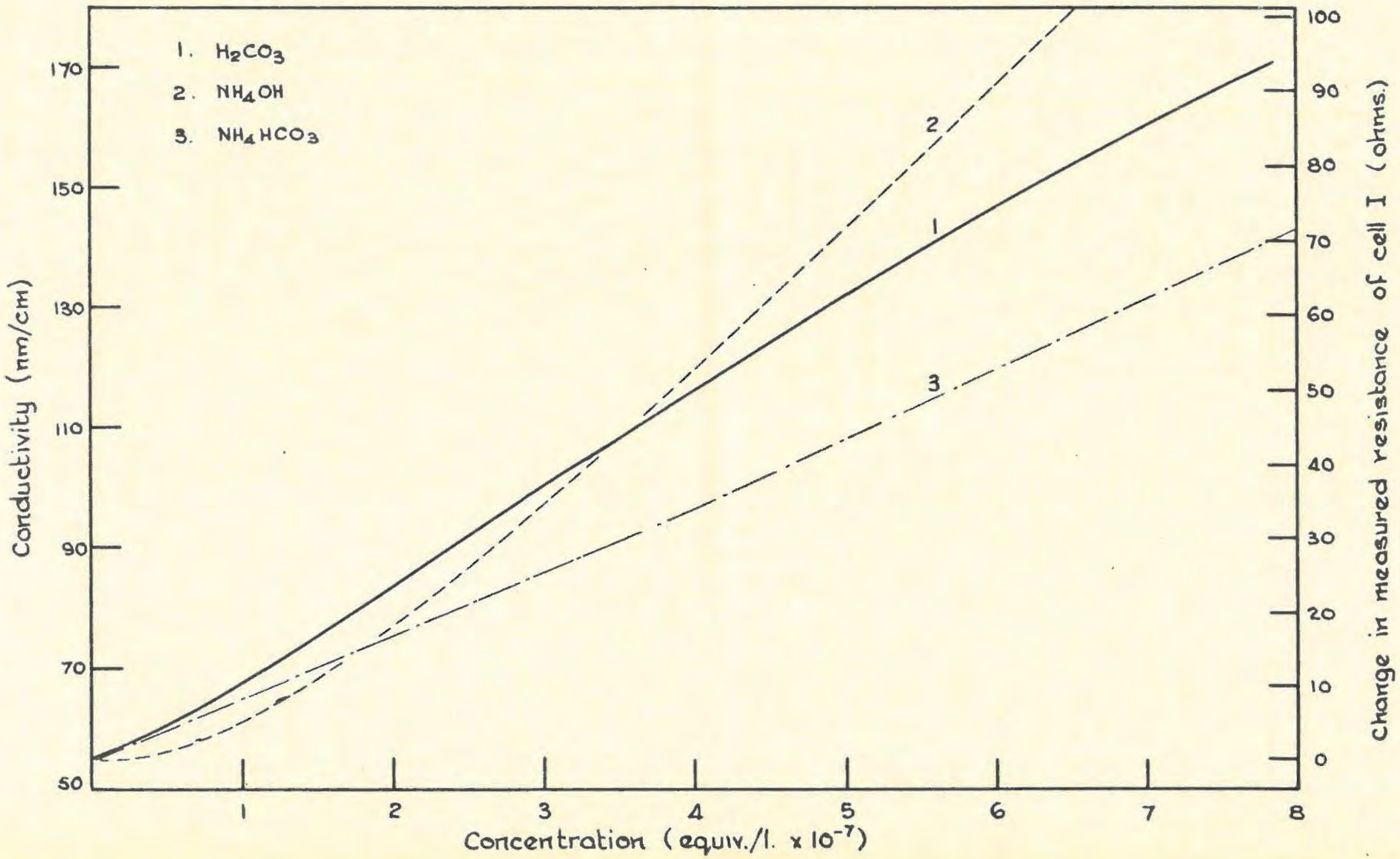
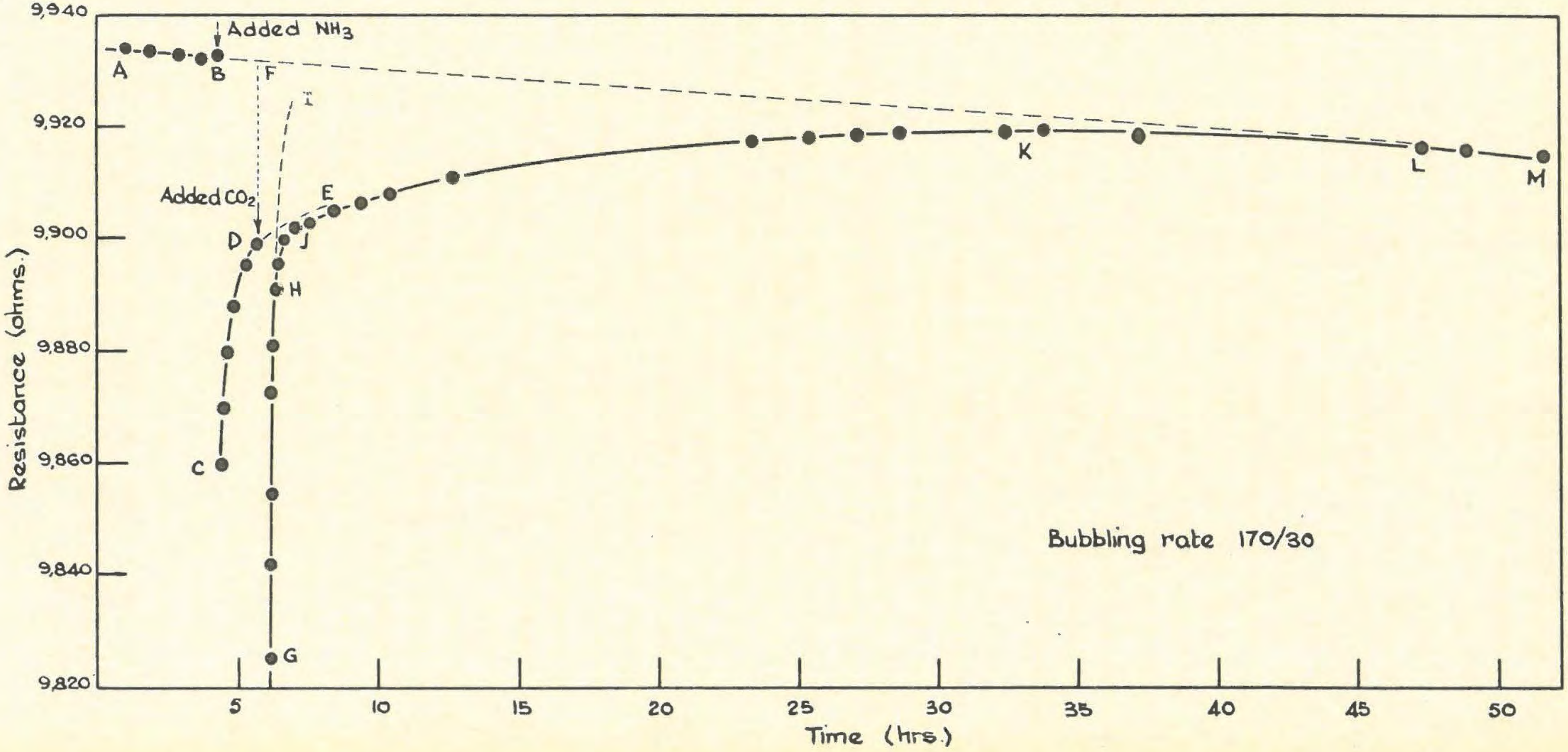


Fig. 2.8 - Variation of resistance of conductivity water on aeration, before & after the successive addition of (i) ammonia & (ii) carbon dioxide.



various resistance changes (usually about 30 ohms or less) which were being considered in these experiments on the removal of ammonium bicarbonate by aeration. It is not surprising, therefore, that in these particular cases the curves obtained before the addition and after the removal of excess carbon dioxide respectively should nearly have coincided.

Other factors contributing to the pattern of Fig. 2.8 probably include the hydrolysis effects which were present in this experiment. The large excess of CO_2 added at D would repress practically all the hydrolysis of the ammonium bicarbonate formed, so that one would expect the resistance to rise at first in the manner normally observed when CO_2 alone has been added. Such an increase, however, would continue only until most of the carbon dioxide in excess of that required to form the bicarbonate had been removed, at which stage the hydrolysis given by equilibrium (2.25) would take place to an appreciable extent. Removal of the products of this hydrolysis would then still cause the resistance to keep rising, but at a much slower rate. This is probably the reason for the large change in the slope found at J.

The repression of hydrolysis of the ammonium bicarbonate which was taking place while the excess CO_2 was being removed would presumably prevent the simultaneous removal of the former during this period; for some time, therefore, its concentration would remain virtually constant at a value equal to that of the ammonia which was still present when the carbon dioxide was added to the solution. If this concentration was such that the ammonium hydroxide and the ammonium bicarbonate solutions that were formed had exactly the same conductivity, the resistance after the excess CO_2 had been removed would be the same as it had been before the addition. Nevertheless, the time-lag between these two points would cause a definite discontinuity in the resistance-time curves, similar to the one appearing in Fig. 2.8, i.e. with JK lying just below the extension DE for the removal of ammonia alone. It must be remembered, however, that in this particular case there was a difference in resistance of about 32 ohms between D and F. Inspection of Fig. 2.9 shows that the concentration of ammonia corresponding to this is about 2.9×10^{-7} equiv./l., and that the change in the measured resistance of water caused by an ammonium bicarbonate solution of the same concentration would be about 7 - 8 ohms less than that due to the ammonium hydroxide. It seems, therefore, that the resistance should actually have been 7 - 8 ohms higher after the excess CO_2 had been removed than it was at the time that this addition was made, i.e.

the curve JK should really have lain somewhere above DE rather than below it. Its observed position can, however, still be explained by considering two other factors: the immersion of the glass tube while the second addition was being made would cause a resistance decrease of approximately 2 ohms and thus generally lower the line by this amount; also, there would be a drop in resistance owing to the slow desorption of some ammonia which had previously been adsorbed on the glass walls of the cell. The latter factor would be one of considerable uncertainty. Nevertheless, it does seem likely that the repression of hydrolysis (2.25) by the excess CO_2 present would lower the concentration of NH_3 in the solution so much that it would, in turn, disturb the adsorption equilibrium which had been established prior to the addition. The ammonia desorbed from the walls as a result of this would combine with the carbon dioxide in solution, thus increasing the concentration of ammonium bicarbonate: the nett effect, therefore, would be a slight decrease of the measured resistance. By chance, the amount involved in this experiment seems to have been just about right to make the resistance curves CD and JK appear almost continuous.

The alternative method of making successive additions of carbon dioxide and ammonia to the water, viz. by adding the former first, followed by a slight excess of the latter, was also used in this study of the removal of these two gases by aeration when they were present together in solution. In aqueous solutions containing both these substances, the following equilibria can occur:-

$$NH_3 + CO_2 + H_2O \rightleftharpoons NH_4^+ + HCO_3^- \qquad \text{..........(2.26)}$$

$$NH_3 + NH_4^+ + HCO_3^- \rightleftharpoons 2NH_4^+ + CO_3^= \qquad \text{..........(2.27)}$$

Hence, while there is excess ammonia, the normal ammonium carbonate may be expected to be present in the solution*.

Fig. 2.10 illustrates the results of one of these experiments. AB and CD are the lines for the change of water resistance and for the latter part of the normal removal of carbon dioxide respectively (the resistance had actually dropped to

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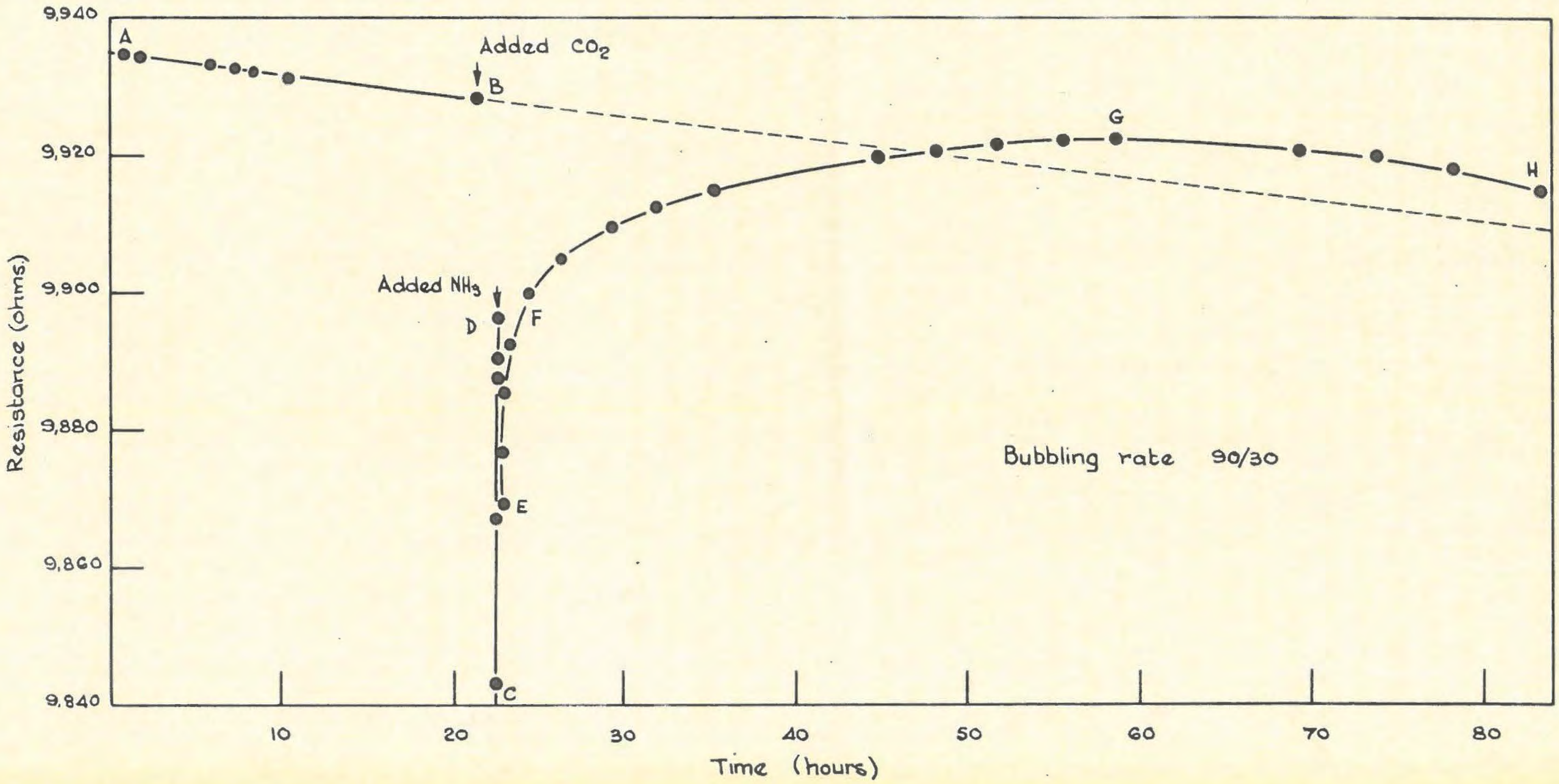
* The possibility of the formation of ammonium carbamate was also considered, but was discarded as improbable under the conditions of these experiments because of the extensive hydrolysis of the salt to the normal carbonate which takes place in aqueous solution: for instance, in a solution consisting of 1 part carbamate to 200 parts water, the degree of hydrolysis was already 74.9%, and this increased to 96.6% on further dilution to 1:500 (Mellor[70]). It seems most unlikely, therefore, that there would be any ammonium carbamate present in the extremely dilute solutions which were being considered in this investigation.

Fig. 2·10 - Variation of resistance of conductivity water on aeration, before and after the successive additions of (i) carbon dioxide & (ii) ammonia



about 9100 ohms on the addition of CO_2 at B). At D, which was about 32 ohms below the initial resistance B, ammonia was added. The specific conductances of dilute solutions of carbon dioxide (calculated as outlined in Section 2.332), and the changes in the measured resistance of Cell I which would correspond to these, are shown in Fig. 2.9. It will be seen that, at the very low concentrations corresponding to the small resistance changes which were generally considered in these experiments, the conductivities of ammonium bicarbonate solutions are invariably less that those of carbonic acid solutions of equal concentration; this is true, too, of the conductivities of ammonium carbonate solutions, which do not differ greatly from those of the bicarbonate. Hence the decrease in resistance (from D to E) caused by the addition of the ammonia is a certain indication that excess ammonia was added, otherwise the resistance would have increased owing to the lower conductivity of the bicarbonate and/or carbonate formed as in equations (2.26) and (2.27): at E, therefore, the solution probably consisted chiefly of a mixture of ammonium carbonate and hydroxide. Immediately after the addition, the resistance began to rise again (EF). As in the experiments where ammonia alone was added to water, this rise was fairly rapid at first, and presumably it was again due mainly to the removal of NH_3 by adsorption on the glass. It seems likely that, as the excess ammonia was being removed, both by adsorption and by aeration, it would be replaced in part by the hydrolysis of the ammonium carbonate solution, thus:-

$$\begin{array}{l} 2NH_4^+ + CO_3^= + H_2O \rightleftharpoons NH_4^+ + HCO_3^- + NH_4OH \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \updownarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad NH_3 + H_2O \quad \text{........(2.28)} \end{array}$$

Continued removal of the ammonia would therefore cause all the carbonate to be converted eventually into bicarbonate. This, in turn, would hydrolyse according to equation (2.25) to yield further volatile products, which could also be removed by aeration; hence the resistance should continue to rise on prolonged aeration. Such an increase was actually found in this experiment (curve EFG). The rise, as one would expect, was quite continuous because each of the processes mentioned would gradually merge into one another: it was not possible, therefore, to assign various portions of this curve to any of the individual reactions. On the whole, EFGH rather resembled the curves found when solutions of ammonia alone were being aerated, and the time taken for the maximum resistance to be reached (about 1½ days in this particular example) was also of the same order as that required for the removal of dissolved ammonia only at an equal stirring rate (90/30).

The similarity between the behaviour observed during the experiments with ammonia alone and that found in this instance where carbon dioxide and ammonia were present together in the solution appeared to be general for the various experiments performed on the simultaneous removal of these two gases, irrespective of the order in which they had been added to the water. Thus in all cases, as long as there was no excess CO_2 left, there was a close resemblance between the changes in resistance which occurred in the two series of experiments during aeration of the solutions; the maxima, too, were invariably reached in approximately the same times (at equal stirring rates) whether carbon dioxide was present with the ammonia or not. The similarity extended even to the occurrence of erratic variations, such as those described in Section 2.34. For instance, the maxima sometimes coincided with the extrapolated water resistance line (as shown in Fig. 2.8), and sometimes lay slightly above it (as in Fig. 2.10). But one point of difference -- and this was an additional inconsistency encountered during the experiments with the combined gases -- was that on a few occasions the resistance reached at maximum was still definitely below the corresponding extrapolated value, i.e. the water line neither touched nor intersected the curve for the removal of the gases, but lay above it at all points. The similarity between the two sets of experiments was again evident, however, in the way in which the rate of decrease of the water resistance after the maximum had been passed was not always the same as that observed before any additions were made, but sometimes tended to increase gradually.

The numerous inconsistencies and erratic variations which were encountered in these experiments made any quantitative analysis of the results very uncertain. In general, however, it did appear that small amounts of ammonium bicarbonate were completely removed from solution by a current of purified air, although the process was rather slow. This result, taken in conjunction with the behaviour normally observed when fresh samples of water from the still were aerated in the cell, seems to indicate that the residual impurity present in this water at minimum conductance was not ammonium bicarbonate. For instance, it has already been seen (in Section 2.331) that, when similar stirring rates were used, the aeration of this water to a minimum conductivity generally took just about the same time as was required for the removal of CO_2 which had been added to previously aerated water -- sometimes, perhaps, just a little longer, but never very much. In all cases the minimum conductance was reached in considerably less time than was necessary for even small amounts of ammonium bicarbonate in solution to be removed completely by aeration. This was true not only of the numerous samples of water that were used in these aeration experiments, but also of the hundreds of samples that were aerated in conductivity cells throughout both this investigation and those conducted in this laboratory by other workers[2,15,56]. Hence it seems that the volatile impurity which remained in the water generally delivered by the still was almost entirely carbon dioxide; at most there could have been but a trace of ammonium bicarbonate. Apparently, therefore, the phosphoric acid used in the distillation process very effectively retained all the ammonia originally present in the water.

2.4 INVESTIGATION OF VARIOUS FACTORS AFFECTING THE CONDUCTIVITY OF "ULTRA-PURE" WATER.

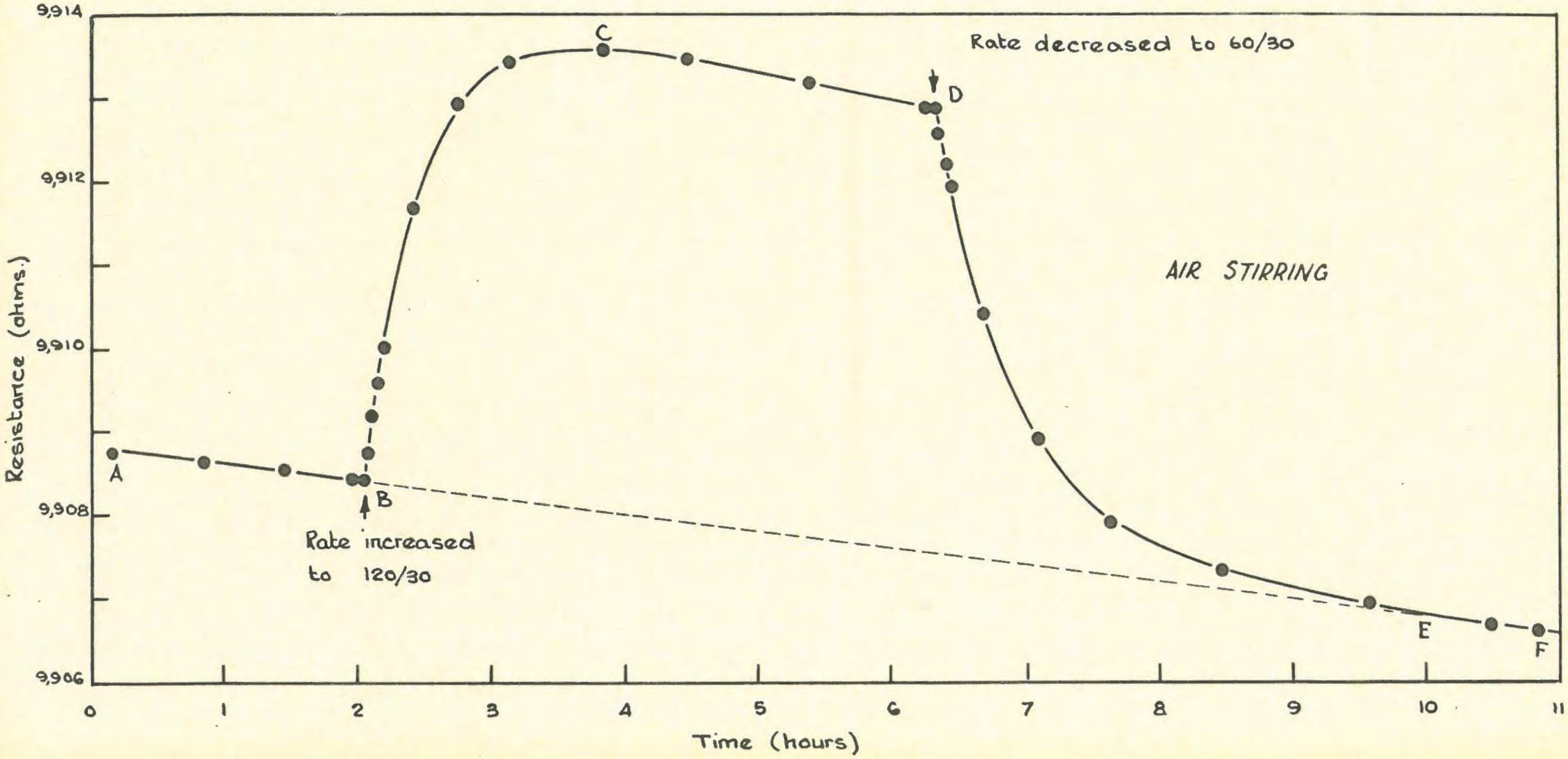
2.41 Effect of Bubbling Rate.

Very early in these investigations on "ultra-pure" water it was found that the final conductivity of the water, after elimination of the volatile impurities, depended on the rate of bubbling of the purified air through the liquid: for a given sample of water, for instance, the resistance rose, i.e. the conductance decreased as the bubbling rate was increased. When this effect was examined quantitatively, it was found that, as in so many other instances during this extremely precise conductance work at the high dilutions being considered, the changes obtained were not always completely reproducible: thus variations in resistance from about 2½ to 8 ohms were observed on different occasions when the bubbling rate was changed either from 60/30 to 120/30 or vice versa. Nevertheless, the effect was quite definite. It was particularly noticeable at the slower stirring rates (about 1 bubble per second), where a small absolute change in rate would naturally mean a larger relative change than when the rate was high. However, variations in the measured resistance of as much as ½ - 1 ohm were detected even when the bubbling rate was varied from 120/30 to 150/30. The actual changes in conductivity were usually only a few nm/cm; but although these were small in themselves, they were still appreciable in comparison with the conductivity of the water being investigated, which was usually about 80 - 100 nm/cm.

The remarkable feature about this effect was the immediacy with which it became evident. If, for instance, the resistance trend after the maximum was closely followed for a while at a fixed stirring rate, and if the rate was then increased or decreased, the corresponding change in the resistance would already be distinctly noticeable within a minute of the adjustment of the bubbling rate. This can be clearly seen in Fig. 2.11, which shows the resistance readings obtained on a sample of water over a period of about 11 hours, during which two different rates of stirring were used; besides the occasional measurements made in order to determine the general trend of the resistance, a number of readings were taken at intervals of exactly one minute for a short while immediately before and after each of the two changes of bubling rate.

Although the effect manifested itself so rapidly, the

Fig. 2·11 – Variation of resistance of conductivity water with changes in the bubbling rate.



complete change usually took one or more hours before steady conditions had again been set up and the resistance was once more dropping at a uniform rate. The eventual rate of decrease of the resistance depended on the new bubbling rate being used (cf. the observation made in Section 2.31, p.67). The latter rate also seemed to govern the time required for the attainment of the new steady state -- the faster the stirring, the shorter the time.

This effect has also been observed by several other workers in this laboratory[2,15]. It did not affect the results of the experiments on the removal of carbon dioxide and ammonia (Sections 2.33, 2.34, and 2.35), since in each experiment the bubbling rate was maintained at a constant value. However, because it meant that in any determination the exact correction for the residual impurity would be a variable quantity depending on the rate of stirring being used, it was decided to try to find out what was causing this effect.

At first it was thought that the effect might be due to temperature variations, i.e. that when the gas flowed rapidly, it was not being properly equilibrated to 25°C in the copper coils through which it was passing. Since the gas was usually colder than this at the beginning of the air-purification train, such incomplete equilibration would cause a slight cooling of the liquid in the cell, which would become greater the faster the rate of flow: the resistance would therefore rise when the bubbling rate was increased. Experiment showed, however, that the temperature of the water in the cell varied by less than 0.001°C for stirring rates from 30/30 to 150/30 (see Section 1.15): this was far too little to bring about the observed resistance variations.

The nature of the rise in resistance obtained on increasing the stirring rate rather resembled that found for the removal of the last traces of carbon dioxide from water: this seemed to suggest that somehow carbon dioxide was entering the cell in increasing amounts as the rate of passage of air through the cell was decreased. Two possible methods by which this could occur readily presented themselves:-

(i) By back-diffusion of atmospheric CO_2 past the cap placed over the mouth of the cell (see Section 1.31). This diffusion was normally prevented by the rapid flow of air in the opposite direction out of the cell, but it might have increased to an appreciable extent as this flow was diminished.

(ii) By diffusion of CO_2 into the stream of purified air through the rubber joints used in the later stages of

> the purification train (i.e. after the last soda-lime tube -- see Section 1.61). Since the partial pressures of CO_2 inside and outside the tubes were constant, this process would occur at a constant rate: hence the slower the flow of air through the train, the larger would be the concentration of CO_2 that would build up in the air-stream before it entered the cell.

Both these processes would require that, when changes were made in the bubbling rate, a new steady state be set up between the water in the cell and the air in contact with it (either above it, as in (i), or passing through it, as in (ii)). Since the air in both cases would contain more CO_2 the slower the stirring, a decrease in resistance would result when the rate was reduced.

The possibility of either of these two processes occurring to a sufficient extent to cause the relatively large changes in resistance that were sometimes observed was considered rather remote in view of the general precautions taken against the intrusion of carbon dioxide. Even if this was possible, however, there was still the far more important criterion of the immediacy of the observed effects to be satisfied in any explanation of the phenomenon; but it seemed very doubtful whether either of these mechanisms could produce a change in resistance within the first minute which was at least as great as those occurring in subsequent minutes, as was usually the case in practice. Nevertheless, in spite of these theoretical objections, the two hypotheses were put to the practical test.

The glass cap which was normally placed over the mouth of the cell had been specially selected for its very close fit to the neck of the cell in order to minimise back-diffusion as much as possible. If this cap was removed after the water resistance had settled down to a steady rate of fall for a given stirring rate (which was maintained constant), and if there was then any unusual drop in the measured resistance, such a decrease would presumably be an approximate measure of the back-diffusion (chiefly of CO_2) taking place through the much larger opening presented to the atmosphere by the exposed mouth of the cell. Several experiments conducted along these lines showed that the difference between the initial resistance and the final value, after steady conditions had again been attained, was appreciable only when very slow bubbling rates were being used: for instance, when the rate was 30/30, drops of over 25 ohms were obtained; but the decrease was only $\frac{1}{2}$ - 1 ohm at 60/30 bubbling, and at 90/30 or faster it was 0.1 ohm or less. When the cap was replaced on the cell, the resistance rose again by similar amounts, i.e. the changes were reversible, as one would expect if they were due to the introduction of CO_2 into the water in the cell. It seemed, therefore, that even with the cell completely open to the atmosphere very little back-diffusion took place except at rather slow bubbling rates. Also, the resistance changes observed at these slower rates did not appear to be so large that they could not be diminished appreciably by a moderate reduction in the aperture of the mouth of the cell. Hence, since the cap actually fitted the neck very closely indeed, back-diffusion should have been negligible while the cap was on the cell, even when the bubbling rate was slow.

This conclusion was confirmed by replacing the cap with a guard-tube containing soda-lime and phosphoric acid. Two similar experiments were performed, in one of which the cell mouth was covered with the cap and in the other with the guard-tube; the latter was attached to the cell with rubber tubing, the joint being made as nearly glass-to-glass as possible. In each case the resistance of a sample of water, which had previously been aerated to a minimum conductance, was followed for a period of 10 - 11 hours, during which the bubbling rate was changed from 30/30 to 150/30 in a series of four steps. For each step the variations of resistance obtained in the two tests were found to be similar. Since the guard-tube would definitely have prevented the entry of carbon dioxide into the water via the mouth of the cell during the control experiment, this similarity in behaviour was taken as a clear indication that back-diffusion was just as effectively stopped by having the cap on the cell as by the guard-tube, and that it was therefore negligible under normal operational conditions.

Attention was therefore directed to the second possibility, viz. that carbon dioxide was present in the purified air-stream which was entering the cell: this could result either from the incomplete removal of CO_2 by the purifying materials in the early part of the air-purification train, or from subsequent diffusion of the gas into the later stages of the train, i.e. after the last soda-lime tube (see Section 1.61 for details of the train). The former possibility was easily ruled out when renewal of the soda-lime, and also replacement of some of it by sodium hydroxide, both solid and solution, failed either to eliminate or even to diminish the effect observed on varying the bubbling rate.

In the purification train which had been assembled, there were, in all, 17 rubber connections between the last soda-lime tube and the cell itself; these were used to join up the various bubblers, stopcocks, etc. The joints were all made with pressure tubing, as nearly glass-to-glass as possible. A rough calculation on the basis of the value 5.94×10^{-5} cc./min for the specific permeability of rubber to CO_2 at $25^{\circ}C$ (Edwards and Pickering[71]) showed that the amount of carbon dioxide which could diffuse through these joints from the atmosphere would produce at most a variation of 0.1 ohm in the water resistance when the bubbling rate was changed from 60/30 to 120/30. It did not seem likely, therefore, that such diffusion could be the cause of the observed variations in resistance. However, this theoretical figure was not regarded as conclusive, and a practical test was performed to see whether carbon dioxide was indeed entering the air-stream through the rubber joints in the train. Another soda-lime tube was placed in the one arm of the two-way stopcock K in Fig. 1.9, and connected with a T-piece to the main air-path through the cell in such a way that it was possible either to send the air through this additional CO_2-trap or to by-pass it. With this arrangement the number of joints which the air had to pass after its final purification could be reduced at will to 5, as against the normal 17. If, therefore, carbon dioxide was diffusing through the rubber connections, the resistance should rise or fall according to whether the path selected for the air included or excluded this trap; furthermore, the variations in resistance which were observed whenever the bubbling rate was altered should be smaller (for equal changes in stirring rate) when the trap was linked in the train than when it was not.

A few experiments performed along the above lines at once both proved and disproved the proposed theory! For instance, when the path of the air was changed at a constant bubbling rate (two different values -- 60/30 and 130/30 -- were actually used), the resistance was found to vary by 3 to 5 ohms, increasing when the trap was included, and decreasing when this was again by-passed: this result was consistent with the removal of traces of carbon dioxide in the air by the additional soda-lime. However, the presence of the trap in the air-stream did not diminish the resistance variations to the anticipated one-third of their normal value (for diffusion through 5 joints instead of 17); in fact, the changes observed when, under these circumstances, the bubbling rate was either increased from 60/30 to 120/30 or vice versa appeared to be still as large as always!

In order to obtain more positive evidence whether it was possible for carbon dioxide to leak through the joints and thereby cause appreciable changes in the resistance, a test joint was prepared in which the connection was not glass-to-glass, as usual, but where the ends of the two tubes were still about half-an-inch apart; the gap was merely covered with the pressure tubing which was used to make the connection. This joint was placed in the train just in front of the phosphoric acid bubblers H in Fig. 1.9 (see also Section 1.61), i.e. well ahead of the two-way stopcock K leading to the additional soda-lime tube; hence the air emerging from the joint could still either be sent directly into the cell along the normal route, or else be by-passed to go through the trap. The whole rubber connection was encased in a wide glass tube, so that it could be surrounded with any desired gas. A sample of water was aerated at a constant rate (120/30) under normal conditions (direct air-path and air around the joint) for some time, and when its resistance was dropping steadily, the joint was bathed in an atmosphere of CO_2 (from a Kipps apparatus). Several hours later, the resistance was found to have dropped quite markedly. When steady conditions had once more been attained, the test which had been made in the previous experiments was again carried out, viz. changing the path of the air so that it alternately went through the CO_2-trap or by-passed it: the changes in resistance were found to have increased to about 20 ohms. Hence it seemed that CO_2 could diffuse through the rubber appreciably enough to produce marked variations in the water resistance. It must be remembered, however, that the joint in this case was placed in an atmosphere containing carbon dioxide not in the small quantity in which it is normally present in ordinary air (about 0.03 - 0.05%), but at a very much higher pressure (about 700 mm). Proportionately, therefore, diffusion under the normal operating conditions should only have produced negligible resistance changes, as the theoretical consideration had predicted.

Similar joints were made with various other materials, and these were tested by the same procedure to see whether the substances were more impervious to carbon dioxide than the rubber. Tygon tubing was tried first, but the resistance changes found with this were again about 20 ohms. Next a piece of pressure tubing was impregnated by immersing it in molten paraffin wax under reduced pressure for 5 minutes, and then rapidly increasing the pressure again (Pregl[30] recommends a similar impregnation in the preparation of the rubber connections for combustion microanalysis). The test joint made with this tubing showed a considerable improvement over the previous ones -- the corresponding resistance change was now only about 7½ ohms. All five joints after the additional soda-lime tube were therefore changed to impregnated rubber connections, and a test was made of the resistance changes produced by varying the bubbling rate. The effect was found to be still there, and present to the same extent as before!

In general, the results of the experiments thus far did not seem to favour the diffusion of carbon dioxide into the air-stream as being the factor responsible for the dependence of the water resistance on the stirring rate. Unfortunately this conclusion was drawn largely from evidence of a negative character, viz. the failure to eliminate or even to diminish the effect being investigated by means of the precautions which had been taken to prevent such a diffusion. At no stage, however, had the possibility of a CO_2-diffusion into the train been entirely excluded, either by 100% protection against exposure to carbon dioxide of all the joints after the last soda-lime tube or by complete elimination of these connections. This possibility, though remote, was nevertheless real, as had been clearly demonstrated by the experiment in which the test joint was surrounded with CO_2. Furthermore, there was support for the diffusion theory in the change of resistance which had occurred when the air-stream was diverted from its normal path through the additional trap (p. 107): this change, which had not yet been satisfactorily accounted for, was similar to the one found when the joint was bathed in CO_2, though it was somewhat smaller (as one would expect if diffusion had taken place, to a lesser extent, through all the joints as a result of their normal exposure to atmospheric carbon dioxide).

In order to ascertain conclusively whether the presence of joints in the train after the last CO_2-removal stage had any connection with the effects observed when the rate of bubbling was changed, it was decided to reduce the number of these joints to the minimum possible, viz. one -- the cell still had to be connected by means of rubber (or other) tubing. This was achieved by making a short all-glass train, which consisted of a tube about 15" long sealed to a bubbler. The tube was filled chiefly with both soda-lime and solid NaOH, to ensure the complete removal of carbon dioxide; as with the main purification train, some solid phosphoric acid and a little cupric chloride were included to remove traces of ammonia and H_2S respectively should these be present in the air supply. Pure water was placed in the bubbler, which was immersed in the thermostat: the stirring air would therefore be both temperature equilibrated and saturated with water vapour at 25°C. This train was then connected directly to the cell. Yet even with this arrangement, where there was only one rubber joint left after the final purification of the air, the resistance was still found to change with the stirring rate. As a final measure, therefore, this joint, and also the other rubber connection by which the cell was normally suspended in the paraffin bath (see Section 1.31), were both packed completely in moist soda-lime to ensure that no carbon dioxide could even reach the joints in order to diffuse into the air. It was actually not anticipated that this would make the effect disappear, as indeed proved to be the case: changes in the bubbling rate still caused the resistance to vary to about the same extent as always. Definitely, therefore, diffusion of carbon dioxide into the train could not have been the reason for these variations.

A suggestion that the changes were due to H_2S given off by the rubber[72] had previously been disproved as well. In order to magnify the effect (i.e. if it really was due to H_2S), a long length of new rubber tubing was inserted in the train in the place where the test joint was usually placed; also, the additional CO_2-trap just before the thermostat was replaced by an H_2S-trap -- an acidified solution of copper sulphate was used. No significant changes in resistance were observed when the path of the air was alternated so that it either went through the trap or by-passed it; if anything, in fact, the resistance in the latter case was lower than in the former, rather than higher as would be expected.

The experiments described so far all had one factor in common: although the bubbling rate had been varied, in some cases quite considerably, there was always some stirring of the contents of the cell. It was decided at this stage to see what would happen if the passage of the air through the cell were stopped completely. For this experiment the short glass train just described was used for the purification of the air; the two rubber connections by which the cell was suspended in the paraffin thermostat were again packed with soda-lime; also, the mouth of the cell was covered with a soda-lime guard-tube joined to the neck, as nearly glass-to-glass as possible, by means of a short rubber connection which was itself coated ("in situ") with molten paraffin wax. Presumably, therefore, it would not be possible for any carbon dioxide to leak into the system while there was no air flowing through the cell. The sample of water in the cell was aerated beyond its minimum conductance, and when its resistance had been dropping steadily for some time, the bubbling was cut off completely. Immediately (readings were being taken, as usual, at one-minute intervals) the resistance began to drop much more rapidly, at a rate of about 0.4 ohm/min -- the rate prior to stopping the stirring was 0.005 ohm/min. Although the initial rate soon diminished to 0.1 - 0.2 ohm/min, after 3 hours the total drop of resistance was already about 40 ohms. The change was followed for seven days, by which time the resistance had fallen by 220 ohms in all; even then, however, it had not yet reached a constant value, but was still decreasing slowly by about 6 ohms/day (see Fig 2.12, on which the results of this experiment are plotted). At this stage the stirring was restarted at a rate of about 110/30. After an initial small decrease of about 3 ohms (presumably owing to a mixing effect), the resistance began to rise quite rapidly, and within three hours it had reached a maximum which was only 2.7 ohms less than the value seven days earlier when the stirring had been stopped. The nature of this rise seemed very similar to that obtained for the removal of carbon dioxide alone from water by aeration: this can readily be seen in Fig. 2.13, in which the plotted points are the resistance readings taken in this experiment, and the continuous curve shows the resistance changes observed previously when CO_2 was being removed at a bubbling rate of 90/30 (unfortunately no data were available for a rate of 110/30, as was used in this last experiment).

Although the resistance dropped continuously throughout the seven days, the decrease was not quite regular: thus a lack of smoothness was apparent when the curve shown in Fig. 2.12 was examined on a large-scale plot. The irregularities were noticeable especially during several periods (varying in length from 10 - 40 minutes each) near the beginning of the the experiment, when readings were being taken at intervals of exactly one minute in order to follow the changes of the resistance more closely. These fluctuations in the rate of drop seemed to suggest that some mixing process was taking place in the liquid of pockets of the electrolyte responsible for the observed decrease in resistance.

Fig. 2·12 – Variation of resistance of conductivity water with & without aeration.

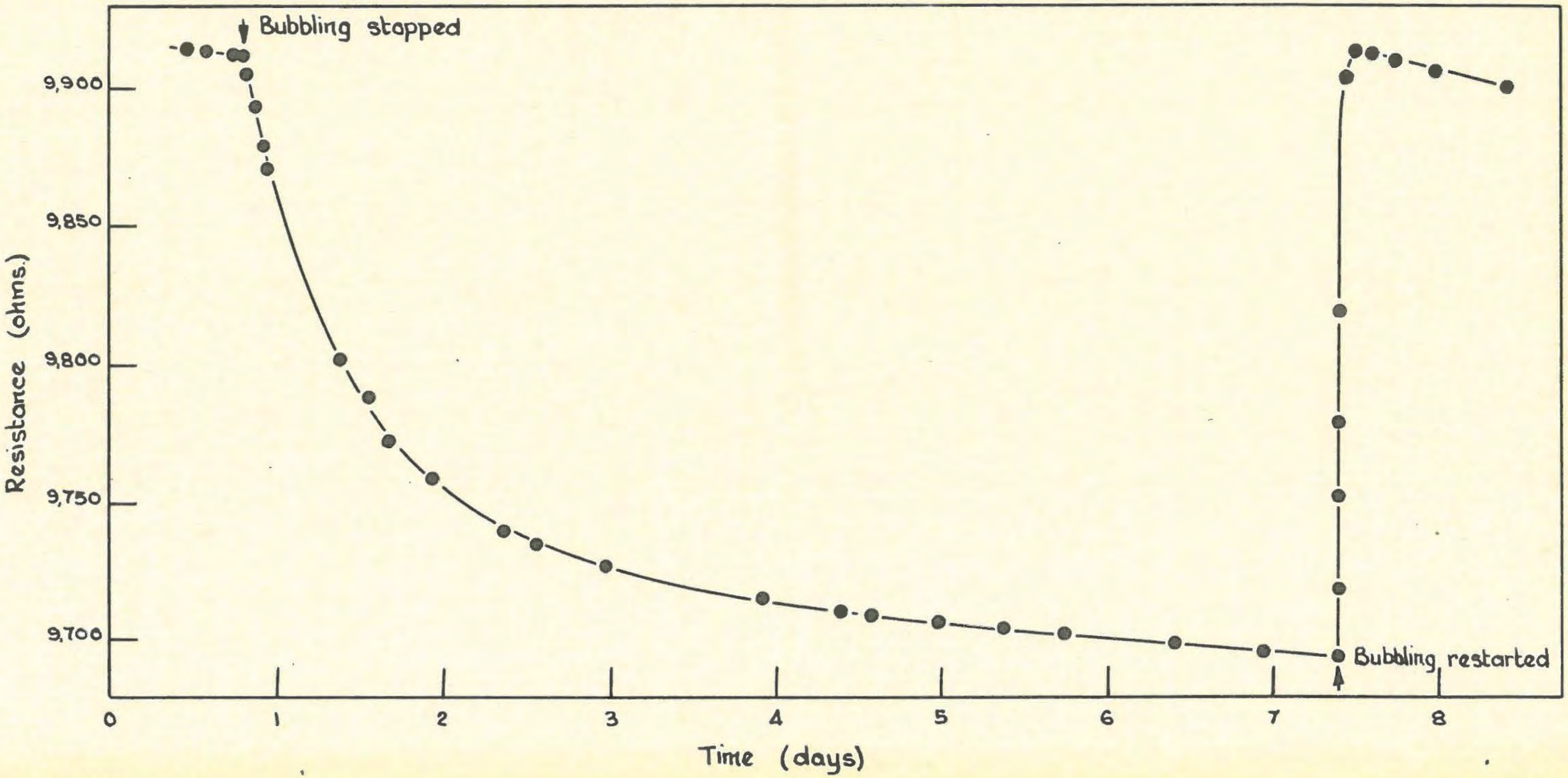
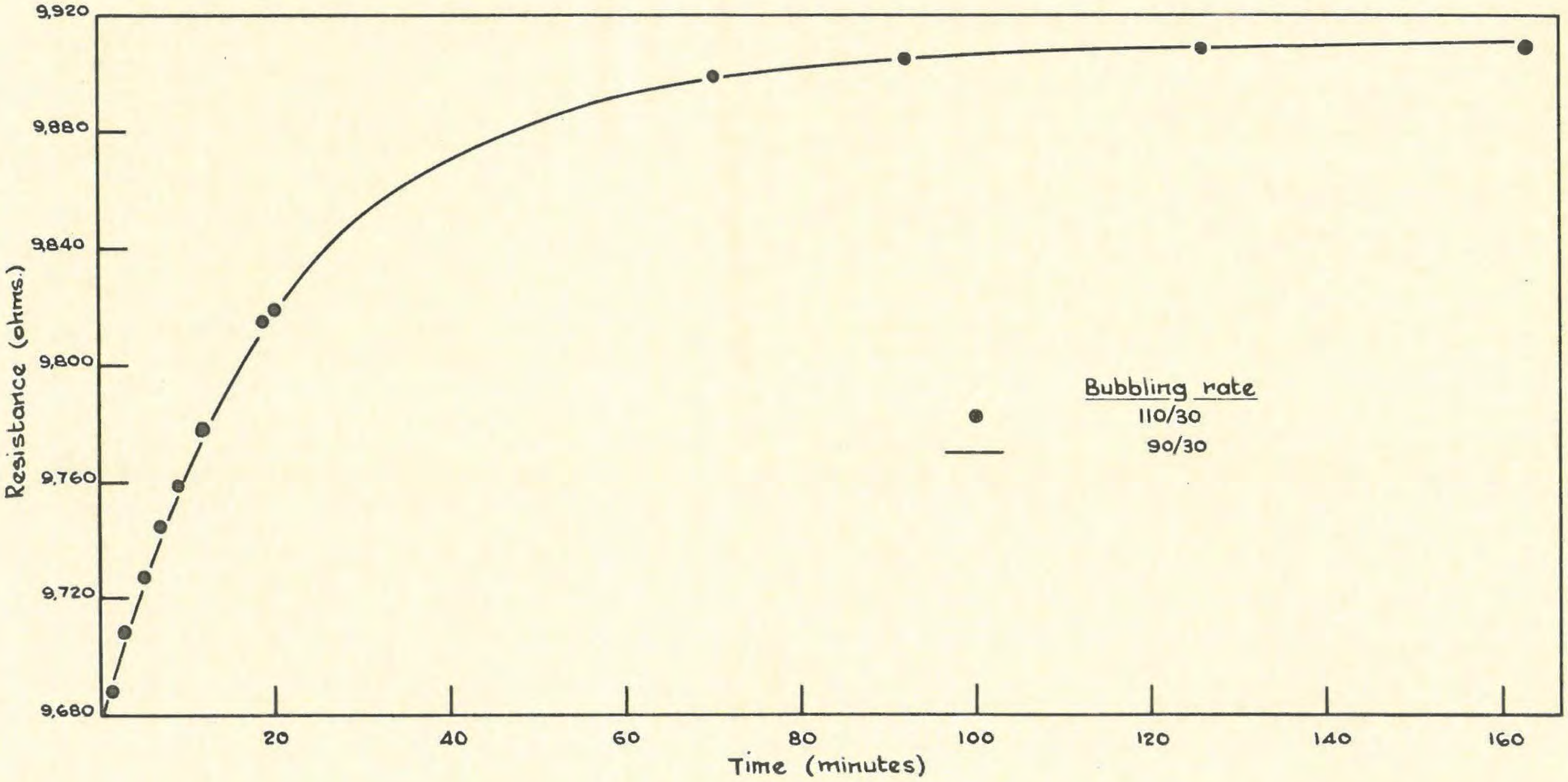


Fig. 2·13 - Comparison of resistance changes occurring on aeration of
(i) water which had not been stirred for seven days,
(ii) water to which carbon dioxide had been added.



In order to see how homogeneous the solution was at various stages throughout the large drop in resistance which occurred when the stirring was stopped, a further test was performed on the same sample of water. It has been mentioned that, at the end of the seven days, this water was aerated to a maximum resistance. When the resistance was once more dropping at a slow steady rate, the bubbling was again stopped, and the water was left for a further three days without stirring. During this period, however, thorough mixing of the liquid was ensured by the occasional application of a short rapid burst of bubbling lasting for either 5 or 10 seconds; usually this was repeated several times in succession at one-minute intervals until the resistance, which was measured after each burst, either remained constant or began increasing by a constant amount per burst as a result of the stirring (such rises occurred when the resistance had already dropped considerably below the value at maximum). The general decrease in resistance was found to follow much the same pattern as before, a total drop of 204 ohms being recorded after three days. As to the changes in resistance produced by the short bursts of stirring, those which were definitely due to a mixing effect were usually only very small -- seldom more than 2 ohms, and on the whole much less. It seemed, therefore, that in spite of the absence of stirring the solution remained fairly homogeneous throughout the course of the experiment.

From the homogeneity of the liquid it was inferred that the large decrease in resistance was probably not due to any solution effect taking place at one of the various boundaries of the water, i.e. at the liquid-air surface, the liquid-glass interface, or the liquid-electrode interface. If such a solution were occurring, the concentration of electrolyte in the boundary layer should slowly have increased in the absence of stirring, and the subsequent dissipation of this layer caused by the mixing should therefore have produced marked changes in the resistance. Also, as far as the first two boundaries are concerned, there would almost certainly have been an initial delay before any drop in the measured resistance became apparent after the stirring had been stopped, because the "solute" would first have had to reach the electrode level by diffusion through the liquid in order to register its presence.

That any effect taking place at the liquid-air surface would be manifested only after some delay was clearly demonstrated by two experiments. In each of these, the bubbling was stopped completely once the resistance had started to decrease steadily after passing its maximum, i.e. the initial procedure was the same as in the two previous experiments. As before, the resistance at once began to drop at a more rapid and somewhat erratic rate of approximately 0.4 ohm/min. But when this decrease had been observed closely for a while by taking readings at one-minute intervals, a small quantity of carbon dioxide was introduced into the air-space above the liquid in the cell. On both occasions it was found that the resistance continued to decrease at an unchanged rate for a further 10 - 11 minutes, and then it suddenly began to drop very much faster -- decreases of as much as 47 ohms in one minute were observed shortly afterwards. Obviously this sharp change was due to the fact that the CO_2 dissolved in the surface layers had then diffused sufficiently far into the liquid to have a marked effect on the resistance measured between the electrodes.

The immediacy with which the resistance changes were normally observed whenever the stirring was stopped, as opposed to the distinct delay encountered in these last two experiments, definitely ruled out any liquid-air boundary effects as the cause of the decrease of resistance. Similarly, liquid-glass effects were just as unlikely to be responsible in view of the layer of water separating the glass from the electrodes. This left the possibility of a reaction occurring either at the electrodes themselves or throughout the bulk of the liquid. The homogeneity of the solution at all times rather favoured the latter idea. But what reaction could take place in pure water that would cause the observed phenomena? The similarity of the curves shown in Fig. 2.13 still suggested that the electrolyte concerned was carbon dioxide. No direct check could be made on this, for calculation showed that only about 18 micrograms of dissolved CO_2 would be required for the resistance in the cell to be decreased by 200 ohms, i.e. by the amount which was normally observed only after several days. Nevertheless, if carbon dioxide were in some way being formed in the water, it might cause the resistance to drop in a manner similar to that which was found. Thus, even if its production were continuous, the CO_2 would not keep increasing in concentration, because there would also be a tendency for it to be slowly removed again by the soda-lime in the guard-tube on the cell. That such a removal would occur was observed in one of the two experiments where CO_2 was introduced into the air-space in the cell. In this instance, after sufficient readings had been taken to confirm the delay period, the liquid was vigorously stirred to produce thorough mixing; it was then left without stirring again, whereupon the resistance was found to rise slowly, presumably because of diffusion of the carbon dioxide out of the solution. This removal of the CO_2 by the guard-tube would act in opposition to the production of the gas in the water, so that an equilibrium concentration would eventually be established when the rates of the two processes were equal. Hence the decrease in resistance owing to the presence of carbon dioxide would also proceed at a progressively slower rate, and the resistance itself would tend to finally reach an equilibrium value, exactly as had been found in practice.

Although the formation of CO_2 in the body of the liquid could explain qualitatively the nature of the observed drop in resistance, this theory merely posed yet another difficult question: What can cause the liberation of carbon dioxide in "ultra-pure" water? The only feasible possibility appeared to be that it was due to some form of bacterial action. But this would presumably require the presence of oxygen, as would any other mechanism for the production of CO_2. However, all the experiments thus far described had been performed with air stirring, which would provide the necessary oxygen. It was decided, therefore, to test the effect of bubbling nitrogen through the cell, in order to see whether it was possible by this means to eliminate the changes in resistance which occurred whenever the bubbling rate was varied.

2.42 Effect of Different Stirring Gases.

2.421 Nitrogen.

For the preliminary experiments with nitrogen stirring, the gas from a cylinder of dry nitrogen was passed over heated copper turnings to remove oxygen, and through a bubbler containing silver nitrate solution, whose purpose was partly to remove any H_2S but chiefly to act as a bubble-counter. The gas was then led into the constant pressure reservoir normally used for the air, and passed through the same purification train. Later, the permanent train was set up as described in Section 1.62.

The first tests were merely qualitative ones in order to see whether the resistance still changed when the bubbling rate was varied. Although they were rapidly performed, however, they were sufficient to indicate at once that the nitrogen stirring would probably not be completely effective in eliminating the changes in resistance. Afterwards a more exact test was made, in which the cell was again closed with a guard-tube, as in several previous experiments (see Section 2.41). Nitrogen was bubbled through the water and the resistance followed until it had passed its maximum and had been dropping steadily for some time. The bubbling was then stopped completely. At once the resistance began to drop at a considerably faster rate, though not quite as rapidly as in the experiments where the air stirring had been stopped (the initial rates in the two cases were about 0.1 and 0.4 ohm/min respectively). However, after 1 - 1½ hours the rate of fall seemed to increase to about 0.2 ohm/min, i.e. to nearly the same value as had been observed at a corresponding time after the stopping of the air stirring; thereafter the decrease in resistance followed a rather similar pattern to that found in in the previous experiments -- if anything, the resistance fell a bit faster later on, for in this experiment there was a total drop of 220 ohms after only two days. When the stirring was restarted at this time, the resistance began to rise again quite rapidly; as before, the rise looked much as if carbon dioxide were being removed. A repeat of this experiment yielded very similar results.

The guard-tube placed over the mouth of the cell had been filled with soda-lime, and was intended to prevent the entry of carbon dioxide only. It was possible, therefore, that oxygen might have diffused back into the cell and caused the change in the rate of decrease of the resistance which had been observed about an hour after the stirring had been stopped. The bubbling had so far always been cut off by turning the control stopcock J in the train (see Section 1.61 and Fig. 1.9) to the completely closed position, so that no gas entered the cell at all. For the next experiment, however, the passage of gas was not entirely stopped through the whole cell, but it was only prevented from going through the water so that this would not be stirred: this was done by turning the two-way stopcock K in the train so that the nitrogen merely flowed over the top of the liquid and then out of the cell via its mouth and the guard-tube. Since the bubbling rate being used was 120/30, this procedure should effectively have prevented the back-diffusion of all gases into the cell, or at least have diminished it very considerably (see Section 2.41, p. 106). When the stirring of the water was stopped in this manner, there was an immediate increase in the rate at which the resistance had been falling. However, this new rate (about 0.05 ohm/min) was definitely less than the initial values obtained previously when the passage of gas through the cell had been completely stopped; nor did the rate show any signs of increasing later, even though the resistance trend was followed for 33 hours. In fact, the total decrease during this period was only 19.7 ohms. It seemed likely, therefore, that the decrease in resistance found with no stirring was caused very largely by oxygen from the air; at the same time, however, oxygen could not have been entirely responsible, because the effect was not completely eliminated, but only considerably reduced by the use of pure nitrogen.

Further tests confirmed that nitrogen stirring was not wholly effective in eliminating the variations in resistance which accompanied changes made in the bubbling rate. These tests were performed by allowing the resistance of a sample of water being stirred with nitrogen to become constant (except for the very slow decrease due to the "solution of glass") at a fixed bubbling rate; the latter was then altered, and the consequent change in resistance followed until a new steady state had been established. Two bubbling rates were used mainly -- 60/30 and 120/30 -- and the rate was alternately increased and decreased from the one value to the other. The resistance was found to start changing immediately after the bubbling rate had been altered, just as with air stirring; but the amount of change seemed to be somewhat less -- about $1\frac{1}{2} - 2\frac{1}{2}$ ohms for a variation between the rates mentioned, as against $2\frac{1}{2} - 8$ ohms for air. Quantitative determination of these small changes was once again rather uncertain because of the appearance of numerous odd effects. Thus, ideally, graphs similar to Fig. 2.11 were obtained on plotting the resistances; but sometimes, when the stirring rate was decreased, a "false minimum" appeared, i.e. instead of the resistance decreasing and slowly settling to a new steady rate of fall (DEF), it first dropped about $1\frac{1}{2} - 2$ ohms in about $2\frac{1}{2}$ hours, remained constant for a short while, and then gradually increased again by an ohm or more (but never enough to rise above the initial value); thereafter the behaviour returned to normal, and the resistance decreased steadily at the slow rate expected for 60/30 stirring. These unusual changes occurred on several random occasions, which were interspersed with the more usual changes depicted by Fig. 2.11: there seemed to be no explanation for them, because all the working conditions appeared to have been thoroughly standardised and rigorously observed.

A few experiments were also performed to see whether the simultaneous passage of nitrogen over the top of the liquid in the cell, as well as through it, would diminish the amount by which the resistance changed whenever the bubbling rate was varied. This was tried because both the rate and the magnitude of the resistance drop, which normally occurred whenever the bubbling through the water was stopped completely, had been successfully reduced by allowing a current of purified nitrogen to continue flowing through the top of the cell. In the first experiments, the rate of flow over the liquid was maintained constant while the usual variations were made in the rate of bubbling through the water. No significant reduction in the resultant changes of resistance seemed to be obtained, i.e. there did not appear to be any real advantage in using a simultaneous flow of gas both through and over the liquid. The comparison of these results was not quite certain, however, because once again, as in practically all these experiments, the small changes were not quantitatively reproducible. The conclusion was therefore confirmed in another way. This time the rate of bubbling of nitrogen through the water was kept constant at 120/30 for three days, during which there were alternate periods when there was either a fairly rapid rate of flow of gas over the top of the liquid as well, or else none at all. The resistance, which was determined at frequent intervals throughout this time, was found to drop at a constant rate that was not affected by the stopping and restarting of the stream of nitrogen through the top of the cell. Presumably, therefore, when the cap was on the cell (as in normal use), the bubbling taking place through the water was quite sufficient to prevent all back-diffusion -- a conclusion which had been reached previously when considering the diffusion of carbon dioxide into the cell (p.106).

It has been mentioned that, for equal changes in the bubbling rates, the resultant variations in resistance were found to be smaller with nitrogen stirring than with air. In general, too, when nitrogen was used for the aeration of water, a higher maximum resistance seemed to be reached, and the subsequent rate of decrease also appeared to be less. For instance, the lowest conductivity that had been measured with air stirring was 68.1 nm/cm (on the only occasion that a value below 70 nm/cm was obtained); yet at this stage of the work minimum conductivities below the latter value were frequently being recorded with nitrogen stirring, and the rates of increase of conductance were sometimes as low as 0.15 nm/cm/h. Unfortunately the usual inconsistencies were also apparent, for rates of increase of more than 1 nm/cm/h were obtained too! Such a high rate was quite inexplicable: it could not even be correlated with the fact that the quality of the water was poor -- a general conclusion which had been drawn on previous occasions -- because in one of these cases the minimum conductivity reached on aeration had been 68 nm/cm. It was, in fact, but another example of the peculiarly erratic behaviour which dogged the whole of this precise (perhaps too meticulous!) investigation. However, the general behaviour on aeration with nitrogen did appear to indicate that it was a more efficient stirring gas to use than air. This conclusion was later confirmed by a direct comparison of the two gases (see Section 2.423).

2.422 Oxygen.

From the first experiments performed with nitrogen stirring, it seemed that the large drop in resistance which normally occurred whenever the passage of gas through the cell was stopped completely was due chiefly to the presence of oxygen. If this were the case, then presumably the use of oxygen as the stirring gas would magnify all the effects accompanying a change in the bubbling rate, and thus provide a more positive proof that this substance was really responsible for the observed phenomena. It was therefore decided to repeat some of the previous experiments, but with pure oxygen instead of air or nitrogen as the stirring gas.

Oxygen from a cylinder was passed through the same train as had been used for the nitrogen, but in this case the copper was not heated. The first significant effect which was noticed was that, on continued aeration after the maximum resistance had been passed, the rate of decrease of the resistance seemed to be much faster than usual -- about $1\frac{1}{4}$ ohm/h, whereas normally it was seldom larger than about $\frac{1}{2}$ ohm/h. When the resistance was dropping at quite a steady rate, the stirring of the water was stopped completely, as in the later experiments with nitrogen, by turning the two-way stopcock K (see Fig. 1.9) so that the oxygen was by-passed over the top of the liquid. At once the resistance began to decrease much more rapidly, at a rate which was fairly similar to that found after the stopping of the air stirring, and much faster than in the similar experiment with nitrogen stirring. This initial result rather confirmed the idea that the variations of resistance which were being encountered were in some way associated with the presence of oxygen in the cell. Unfortunately the rate of decrease of the resistance later slowed down appreciably, and the total drop after two days was only about 110 ohms, as against the values of about 200 ohms which had been observed in previous cases. This was quite contrary to expectation, which predicted a much larger decrease rather than a smaller one. In spite of this anomalous change, however, all the evidence taken together (e.g., the fact that the water resistance after maximum fell so rapidly with oxygen stirring; the results of the direct comparison made later (Section 2.423) between nitrogen and air stirring; and various other minor observations) still suggested that the presence of oxygen contributed greatly, though not entirely, to the peculiar phenomena which had been observed. Also, it seemed that the use of oxygen was not to be recommended for general stirring purposes.

Quite how the presence of oxygen could cause the resistance of the water to change was not clear. In the experiment just described, the stirring was restarted after the resistance trend had been followed for two days. Once again it was found that the resistance rose in a manner resembling that observed on the removal of CO_2. Since oxygen was present in this instance, the observed change in resistance might have been due to the formation of carbon dioxide in the water, presumably by bacterial action as proposed earlier. However, the weight of evidence gathered in other experiments was still very much against the possibility of CO_2 being present in the cell.

It has been suggested that hydrogen peroxide might be formed by reaction of the water with the oxygen present:

$$O_2 + 2H_2O \rightleftharpoons 2H_2O_2(aq.) \qquad \text{..........(2.29)}$$

and that this subsequently ionises thus:

$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \qquad \text{..........(2.30)}$$

For reaction (2.29), however, $\Delta F^o = 50.44$ kcal.[73]. Hence, from the well-known equation

$$\Delta F^o = -RT.\ln K \qquad \text{..........(2.31)}$$

we get, for the equilibrium constant of this reaction at 25°C,

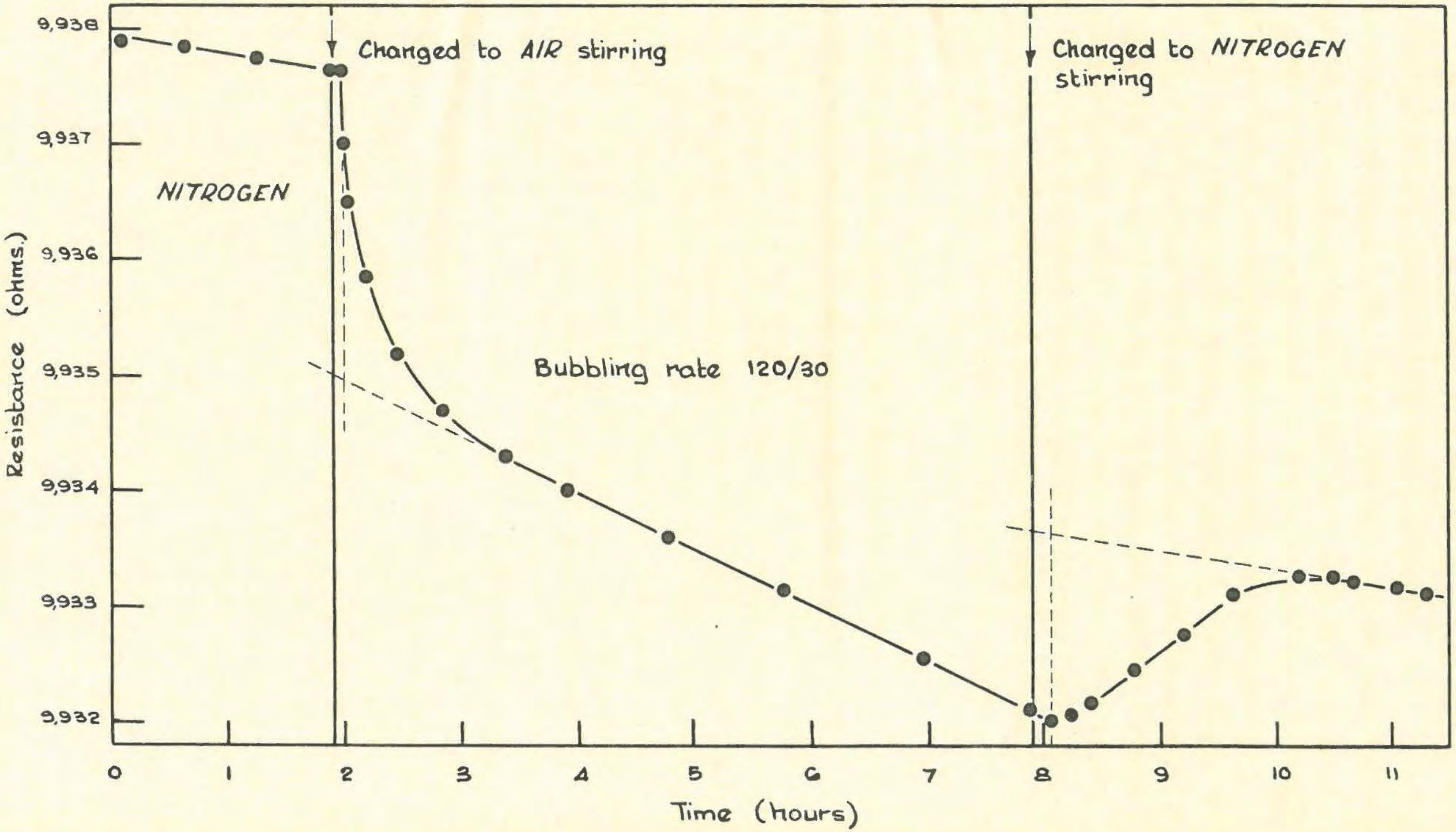
$$K = 10^{-37}$$

It appears therefore that the equilibrium concentration of the hydrogen peroxide would be negligibly small even if the oxygen were present at 1 atmosphere pressure. Hence this suggestion cannot account for the observed variations of resistance.

2.423 Comparison of nitrogen and air stirring.

In order to confirm the idea that the use of nitrogen for stirring purposes was more effective than that of air, a direct comparison was made between these two gases. This was done by bubbling them alternately, but at the same rate, through the same sample of water; meanwhile a close check was kept on the resistance, which was allowed to settle down to a new steady rate of decrease after each change of gas before the next change was made. The switch-over from the one gas to the other was facilitated by joining the two trains together with a two-way stopcock, which could be turned to allow the flow of either gas through the cell at will. Several tests were made with this stopcock connected in various positions: in some experiments, for instance, it was put in the place of the ordinary stopcock C (Fig. 1.9) at the beginning of the long air-purification train, so that the nitrogen, already purified in its own short train, still had to pass through the long train as well before it finally reached the cell; in other cases, the nitrogen received no further purification, the linkage being made just before the final bubbler I in the train (see Section 1.61 for full details of the air-purification train). There did not appear to be much difference in the general behaviour observed with the stopcock placed in either of these two positions except that, in the former case, it took longer before any effects of the change-over became noticeable, as one would naturally expect since the new gas had first to sweep out the long train before it entered the cell. It was found, however, that the change from nitrogen to air stirring was invariably accompanied by a drop in resistance -- usually about 3 ohms in all: this value was obtained by letting the resistance settle down to a new steady rate of decrease, which generally took several hours, and then extrapolating this rate of fall back to the time when the departure from the original resistance trend could first be detected. The resistance change was reversible, though not quite quantitatively: thus, on going back to nitrogen stirring, the resistance first rose to a maximum before decreasing again at the same steady rate previously observed for this gas; extrapolation as before gave an average increase of about 2 ohms. Fig. 2.14 shows the changes which took place in one of these experiments. It will be noticed that the slope of the line for air stirring was considerably greater

Fig. 2·14 – Variation of resistance of conductivity water on stirring alternately with Nitrogen & Air



than for nitrogen -- the respective values in this instance were about 0.5 and 0.2 ohm/h. The difference was not always quite so marked, but it seemed to be generally true that the resistance decreased more rapidly when air stirring was being used than when nitrogen was being bubbled through the water.

The higher maximum resistances and the slower rates of decrease of resistance obtained by the use of nitrogen stirring meant that, in general, the impurity correction would be smaller under these circumstances than with air stirring. Also, it had been found earlier that the changes in resistance which occurred whenever the bubbling rate was varied were appreciably smaller with the former gas than with the latter. It was therefore concluded that, for general use, nitrogen would be a more suitable gas to bubble through the liquid in the cell than the air which had previously been naïvely employed.

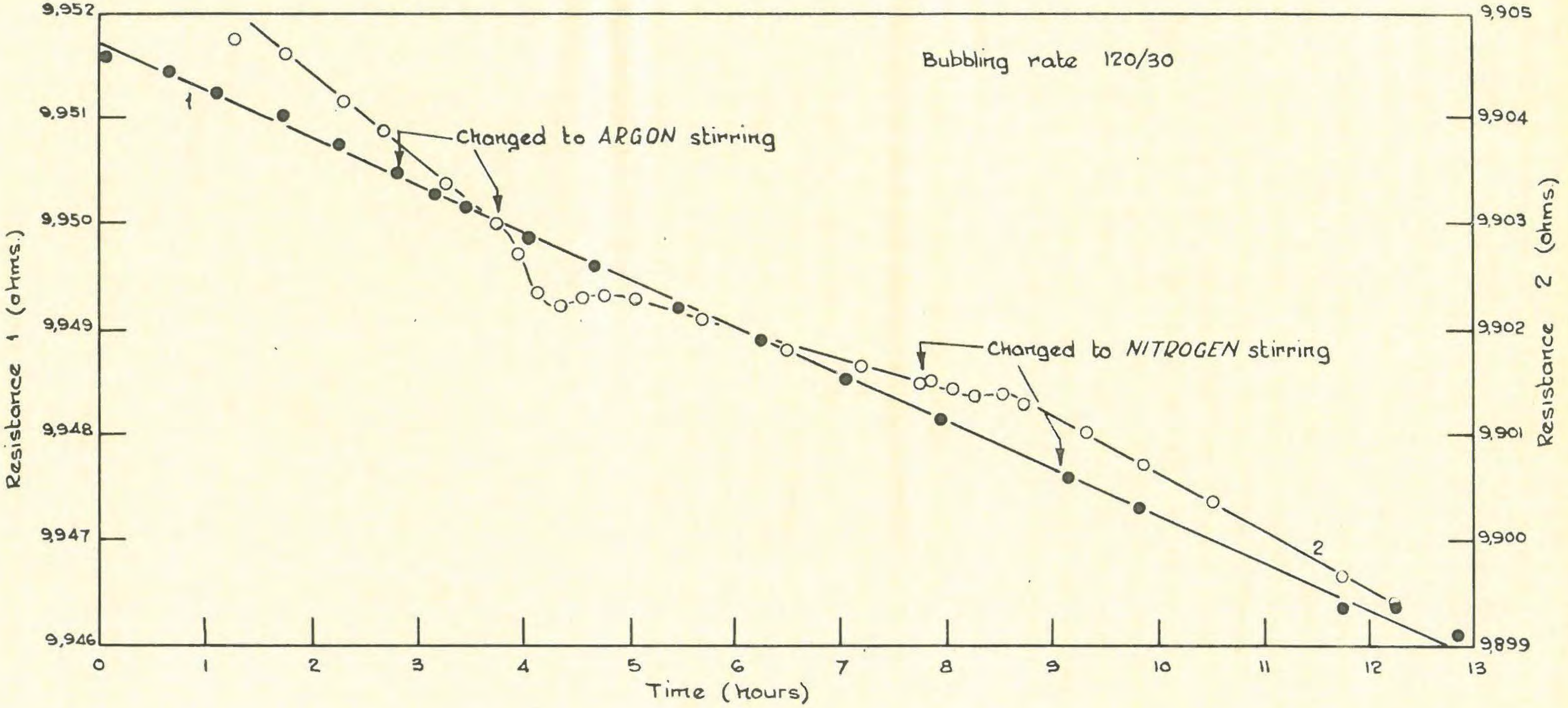
2.424 <u>Comparison of nitrogen and argon stirring.</u>

The use of an inert gas in place of nitrogen seemed a logical further step in the process of the elimination of all the odd resistance variations. A small cylinder of argon was kindly placed at our disposal by The Electric Lamp Manufacturers of South Africa (Pty.) Ltd., so that the efficiency of this gas for stirring purposes could be examined. The experiments performed with the gas were mainly comparative tests with nitrogen along the lines just described in the previous section.

The argon supplied was stated to be 93% pure, the remainder being nitrogen. However, when it was used in the first test without further purification, the change from nitrogen to argon stirring caused the resistance to drop, rather unexpectedly, by about 30 ohms. On reversal of the change of gases, the resistance rose again to its original value in a manner which resembled that observed during the removal of a small amount of carbon dioxide from the water. Presumably this substance was present in the argon to a small extent, because the large change in resistance did not reappear when the test was repeated with the argon first passing through the normal air-purification train.

The results of this comparison of argon and nitrogen stirring were not too conclusive, mainly because of the usual manifestation of inconsistencies. This can be seen in Fig. 2.15, which illustrates the results of two of these experiments. In the first, shown by line (1), the water used was

Fig. 2·15 – Variation of resistance of conductivity water on stirring alternately with Nitrogen & Argon



exceedingly good -- it was, in fact, the best sample measured in this laboratory, its conductivity at minimum being only 62.8 nm/cm; yet the rate of decrease of the resistance (0.43 ohm/h) was relatively high for nitrogen stirring. The change from the one gas to the other was, in this case, effected by replacing the nitrogen cylinder itself by the argon cylinder, so that the two gases actually went through the same train. The disadvantage of this was, of course, that there would be a considerable time-lag each time the two cylinders were interchanged before the new gas reached the cell, because it would first have to pass through the whole train -- in this case there was the long copper tube leading to the constant temperature room and the 5-litre constant pressure reservoir to be filled, as well as the normal air train (see Sections 1.61 and 1.62 for details of the trains). However, it was estimated that, if the new gas pushed the previous one out completely before it reached the cell itself, its passage should not take more than 2 hours at the bubbling rate being used (120/30). In the experiment, the argon cylinder was actually left attached for 6½ hours. Even allowing for any mixing of the gases, which was almost bound to occur, the gas entering the cell by the end of this period should have been fairly pure argon (it could never, of course, be quite pure, since the original gas contained 7% nitrogen). Yet there was no indication from the trend of the measured resistance that any change had been made in the nature of the gas bubbling through the water; the resistance continued to fall at the same steady rate, and any fluctuations which did occur were of the order of 0.2 ohm or less. The same result was true of the reverse change of the stirring, from argon back to nitrogen. In the latter case, there was absolutely no doubt that all the argon had been swept out of the system, for further resistance measurements were made on this sample of water on the next day as well; although these readings are not shown in Fig. 2.15, they actually lay on the same line. From this experiment, therefore, it appeared that it was immaterial which of the two gases was used for stirring the water.

Shortly before the performance of the other experiment, shown in Fig. 2.15 by line (2), considerable difficulty was experienced in obtaining from the still a sample of water of the usual high quality. Since time was very limited at this stage, a portion of water was eventually taken for this experiment which was not nearly as good as that used for line (1): its conductivity at minimum was actually about 120 nm/cm.

The argon cylinder was connected to the beginning of the normal air-purification train (i.e. just before the bubblers D in Fig. 1.9) by means of a two-way stopcock, the other arm of which was joined to the purified nitrogen supply coming from the constant pressure reservoir (see Section 1.62). The argon and nitrogen could therefore be selected at will, and they shared the long air-purification train; however, the argon now no longer passed over the heated copper, as it had done in the previous experiment. This arrangement considerably reduced the time-lag occurring after a change-over of the gases before the new gas reached the cell -- it was estimated that it would take 15 - 20 minutes to flush out the train at a bubbling rate of 120/30. By contrast with the previous experiment, however, it was found that now the change from nitrogen to argon stirring definitely had some effect on the resistance: thus, very soon after the switch-over had been made, the rate of fall of the resistance began to increase slightly; after the resistance had dropped to a minimum in about $\frac{3}{4}$ hour, however, it again rose a little, and then settled down to a new steady rate of fall which was lower than the rate previously being maintained with the nitrogen stirring. The total drop of resistance, from the time of its beginning to the minimum, was actually less than 1 ohm -- small enough to be evident more as a kink in the resistance-time curve rather than as a distinct decrease and increase, even on fairly large-scale plots. Nevertheless, the drop illustrated in this diagram was quite definite. Similar effects were also frequently found in other experiments of this type, though not always -- the inconsistency just had to be there! The cause of this decrease is unknown: it could not have been due to a temporary decrease in the stirring rate, for this was not altered at all during or after the change-over from nitrogen to argon; nor, presumably, did it have any connection with the entry of argon into the cell, because the effect usually started so soon after the switch-over that the argon could certainly not have traversed the train in the time available. The reverse change of gases, from argon back to nitrogen, caused the resistance to settle down once again, after a few minor fluctuations but with no definite maximum appearing, to the same steady rate of decrease as had been maintained with nitrogen stirring previously in the experiment, i.e. to a somewhat faster rate than with the argon stirring. The various increases and decreases in resistance which were observed during this comparison were never as large nor as definite as those which occurred during the similar comparison made between nitrogen and air stirring (Section 2.423). Nevertheless, it did appear from the different rates of decrease of the resistance observed with argon and with nitrogen stirring that the former gas was slightly the better to use for aeration of the liquid -- a result which was not in agreement with the findings from the experiment shown by line (1).

In previous considerations of the efficiency of a gas for stirring purposes, a further test had been applied, viz. the size of the change in resistance which occurred when the bubbling rate was varied between fixed limits, e.g. between 60/30 and 120/30. No measurements were made of the magnitude of this effect when argon stirring was being used, however, because the attempts to do so were nullified by the appearance of various sudden decreases of the resistance. These occurred while the slow steady fall of resistance due to the "solution of glass" was being followed, and they were sometimes as large as 20 ohms or more. At the time that these experiments were being performed, no explanation could be found for these sudden changes. It was later realised, however, that they were probably due to small droplets of water being carried over into the cell from the copper coil situated in the inner thermostat: presumably the water had gradually collected in this coil over a long period of time, possibly as a result of condensation or by being sprayed in from the potash bubbler (see Section 1.12 for details of the thermostat construction).

The supply of argon made available initially was rather limited, and it was soon exhausted. It was realised that the experiments which had been performed with the gas by no means constituted a thorough and exhaustive test of the efficiency of argon for stirring purposes. However, the results thus far appeared to indicate that it was not sufficiently superior to nitrogen to justify obtaining a larger quantity, either for making further tests or for routine use. The comparison of the two gases was therefore discontinued at this stage, and the tentative conclusion was drawn that argon was at least as efficient for stirring purposes as nitrogen; it might even be just a bit better, but not sufficiently so as to warrant its general use.

2.425 Comparison of the use of short and long purification trains.

The original short train used for purification of the nitrogen is described in Section 1.62. When this train was first set up permanently, the gas emerging from it went directly to the final water bubbler I placed just before the thermostat (see Fig. 1.9). During the course of the various stirring experiments and comparisons described in the preceding sections, however, it sometimes appeared almost as if the resistance of the water was dependent not only on the stirring gas, but also to some extent on the purification train through which this gas was being passed. Tests were therefore made in which the nitrogen from the short train was passed alternately into the cell, either directly or else first via the whole air-purification train as well. During these changes of path, a close check was kept on the resistance. In general, the variations of resistance observed in these experiments were only very small, and there did not seem to be any real difference between the two gas-paths; however, a careful study of several experiments did suggest that, if anything, passage of the gas through the long train might be preferable. From this time on, therefore, the full train was used as the standard train for all gases.

2.5 SUMMARY AND CONCLUSIONS.

Whenever the rate of bubbling of the gas passing through the water was altered, the measured resistance of the cell was found to vary as well. In spite of an exhaustive investigation of this phenomenon, it has not been possible either to trace its cause or to eliminate the changes in resistance. The numerous experiments did show, however, that stirring with nitrogen was superior in all respects to stirring with air: it is recommended, therefore, that the former gas be used in all routine measurements of conductance where a technique similar to the one utilised in this investigation is employed for the removal of carbon dioxide from the water.

The use of nitrogen stirring did not eliminate the variations of resistance, but only diminished them. The final conductivity of the water therefore still remained slightly variable, i.e., the correction to be applied for the residual impurity present in a given sample of water varied with the rate of stirring being used. Hence, in all accurate work, the same constant rate of bubbling should always be maintained during aeration of both the pure solvent and the solution.

The nature and the constitution of the residual impurity remain matters of speculation. To some extent, at least, this is due to the extreme purity of the water which was being prepared by routine operation of the specially constructed still: the concentration of the impurity in the water, for instance, was generally of the order of 10^{-7} equiv./l. after all the volatile matter had been removed by aeration. As regards the volatile impurities, it has been shown that carbon dioxide and ammonia can be completely removed from water by aerating it with a current of purified gas. When these gases were present individually in the water, the carbon dioxide was removed quite rapidly, but the ammonia was eliminated much more slowly; in each other's presence, the removal was also fairly slow, and resembled that found for ammonia alone. From this last fact, and from the fact that the removal of the carbon dioxide which was originally present in the distilled water generally took about the same time, at equal bubbling rates, as was required for the removal of an equal amount of CO_2 added to pure water, it has been deduced that there was no ammonium bicarbonate (or at most a trace) present in the residual impurity.

There seems no possibility that the residual impurity after aeration of the water to a minimum conductivity was alkaline. If this were so, then any carbon dioxide which was added to such water would not be completely removed again, as happened frequently, because some of the acidic gas would have combined with the basic impurity. In any case, even if there was such an impurity present in the water at the time of its condensation in the still, the water had sufficient contact with the atmosphere for all basic material to be converted to the bicarbonate by the excess carbon dioxide which would have been dissolved in the liquid. As a matter of fact, from a consideration of conductimetric and pH data, it is even possible that all the residual impurity in the water at its minimum conductance could have been sodium bicarbonate (the sodium having come from the "solution" of the glass). Ellis and Kiehl[52], for instance, found that the individual pH values at 25°C of various fractions of water distilled from phosphoric acid ranged from 6.94 to 7.15; these results were confirmed in other determinations of the pH of pure water by Cranston and Brown[74], and by Edwards and Evans[75]. The procedure used by the latter workers for the purification of their water is particularly interesting: traces of volatile acid in their laboratory distilled water were removed by preliminary distillation from alkaline permanganate before they distilled off the final product from phosphoric acid solution in a special still; afterwards, purified air (from a train containing soda-lime, sodium hydroxide solution, dilute phosphoric acid, and conductivity water) was passed through the water for some time before the pH was eventually measured. It seems, in fact, that the whole procedure was very similar to that which was employed in the present investigation, even to the method of purification of the air. Presumably, therefore, the water aerated in the conductance cell would have the same pH as the water used in the determinations of Edwards and Evans. Calculation shows that the pH of a sodium bicarbonate solution, whose conductivity is 100 nm/cm at 25°C, would be about 7.15; for lower conductivities approaching that of pure water (55 nm/cm), the pH would, of course, be less and would tend towards the value 7.0. Hence the results of the various pH measurements, taken in conjunction with the fact that the water generally had a conductivity well below 100 nm/cm at minimum, seem to corroborate the contention that all the residual impurity in the water in the cell could have been sodium bicarbonate. However, it is possible that traces of the alkali constituents of Pyrex glass other than sodium were also present, and perhaps minute amounts of silicate as well.

The experiments performed on the removal of ammonia appear to exclude the possibility that the residual impurity was acidic, except occasionally when it might have been present in amounts so small that there would have been no need to make any special allowance for it in the application of the solvent correction. The general conclusion may therefore be drawn that, although the exact nature of the residual impurity in water that has been prepared and aerated to a minimum conductivity as in this investigation is not known, the impurity should all be treated simply as neutral salt and the solvent correction made accordingly. Hence, for neutral salt solutions, the measured solvent conductivity should be subtracted 'in toto'; for acidic or basic solutions, however, only the measured value in excess of 55 nm/cm (the conductivity due to the H^+ and OH^- ions resulting from the dissociation of pure water) should be subtracted, and a suitable adjustment should be made for the repression of the ionisation of water. The application of this method of correction has proved very successful in various conductimetric determinations performed in this laboratory, e.g. in the solubility measurements made by Malan on silver chloride[15,76] and silver bromide[15,77], and by Dry on calomel[57,69].

The conclusion that has been drawn may, of course, be valid only because the water which was used was so very pure and the amount of residual impurity in it so small that any error made in correcting for the conductance of this impurity could never have been very large. If this is so, then it only lends further support to the initial argument, that it is better to prepare the water as pure as possible and have a very small solvent correction to apply, rather than to have to make a relatively large correction which still involves some speculation regarding the exact nature and amount of the residual impurity. In fact, the time spent on the present investigation has been amply justified by the very close agreement obtained, for the first time, between the conductimetric and the potentiometric methods of determination of the solubilities of both silver chloride[76] and silver bromide[77]. This is true particularly of the latter substance, for which no other published contimetric values were found by Malan[15,77]. Presumably no determinations had previously been made by this method because the solubility of silver bromide is so low that the Ag^+ and Br^- ions do not contribute a large amount to the measured conductivity of the solutions: even with this very pure water, for instance, the solvent correction constituted 45 - 50% of the total measured conductance. It can safely be said, therefore, that the success of the determination was due very largely to the excellent quality of the water used.

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PART 3

THE INVESTIGATION OF THE ADSORPTION OF POTASSIUM CHLORIDE IN CONDUCTANCE CELLS

3.1 INTRODUCTION.

The possibility of the occurrence of adsorption in conductance cells has been recognised since the early days of Kohlrausch. This great pioneer of accurate conductimetric determinations showed a truly remarkable insight into the many difficulties with which this type of measurement abounds, and his practical ability in overcoming them enabled him to achieve a degree of accuracy which would even today be very creditable. Thus he showed, for instance, that HCl gradually went out of solution into the electrodes, and was held there with great tenacity in spite of the presence of water; and that, in order to remove this HCl, many washings were required[78].

Sorption effects in conductimetric determinations cause changes in the concentration of the original solution, and so give rise to a possible source of error which has become increasingly more important with improvements in the accuracy of measurement, and particularly with the extension of the range of determinations to the region of very dilute solutions. That this effect can be quite large in such cases is apparent, for instance, from the work of Cox, Kraus, and Fuoss[79] on non-aqueous solutions: thus, in one example, they stated that, for a 0.82×10^{-6} N solution of tetrabutylammonium nitrate in anisole, "the initial resistance was 2.2 megohms and increased to 6.0 megohms in the course of an hour; on mixing the contents of the cell, the conductance (sic!) returned to 2.3 megohms". For measurements on aqueous solutions, there have also been frequent references in which changes in the conductance with time were actually ascribed by the authors as being probably due to some adsorption effect[3,29,42,80-82]; and in other cases, where changes of a somewhat similar nature were reported, although the authors did not specifically mention adsorption, it seems likely from the general descriptions that this was again responsible for these changes[83-85].

The caution of the latter writers is perhaps justified. Frequently adsorption has been labelled as the scapegoat to explain some odd behaviour in conductimetric determinations merely for want of a more suitable explanation: the "Parker effect" is an outstanding example. Parker[86] compared the resistances of several potassium chloride solutions when measured in different cells; these solutions covered a wide range of concentrations, and he showed that the cell constant appeared to vary with the concentration. Similar variations were subsequently found for several other electrolytes by Randall and Scott[87], who agreed with Parker that the change occurring in dilute solutions, when the resistance being measured was high, was probably due to adsorption. Shedlovsky[88], however, using a multiple-electrode cell in which several comparisons could be made on the same solution, also observed these apparent changes in cell constant, but found that they were larger with bright platinum than with unplatinised electrodes. Adsorption, therefore, could almost certainly not have accounted entirely for the variations. The real reason, as was eventually pointed out by Jones and Bollinger[14], arose from an electrical effect due to the design of the cells used. As a result of the close proximity of the cell-filling tube and the leads to the electrodes, a resistive-capacitative shunt was effectively set up, which became more noticeable as the resistance being measured was increased.

Nevertheless, anyone wishing to determine conductances accurately should always consider the possible occurrence of adsorption and effects arising therefrom. Almost invariably, where this has been done, the references seem to indicate that the electrodes only were regarded as the seat of adsorption; and the precautions taken were obviously designed to prevent, eliminate, or allow for any effects occurring at these. This conception probably arose because in most cases the electrodes had been platinised, and it is, of course, well known that platinum black forms a very good adsorbent because of its extended surface area. Frumkin and Donde[89], for instance, found that even a solution of sodium sulphate in contact with platinum black in a hydrogen atmosphere developed a pronounced acid reaction, probably due to adsorption of the alkali from the solution by the platinum black. Later Kolthoff and Kameda[90], using a cylinder of platinised platinum foil, demonstrated its adsorbent properties for strong acids, strong alkalies, and a number of salts in both hydrogen and oxygen atmospheres; they found definite evidence of adsorption in many cases, up to as much as 22% for a dilute solution of hydrochloric acid in the presence of oxygen.

The two essential features of a conductance cell are the electrodes and the containing vessel, and although it seems likely that most of the adsorption, if any, will take place at the former, the walls of the latter cannot be ignored. In the present work, for instance, evidence of the occurrence of adsorption on the glass walls of the cell has already appeared (during the experiments on the addition and removal of ammonia from solution -- see Section 2.34); also, it was often found that, immediately after a cell had been cleaned with strong acid, such as the chromic acid cleaning mixture, the conductivity of very good quality water seldom dropped, on aeration, below about 400 nm/cm at minimum, and then rose again very rapidly, presumably due to the desorption of acid from the glass walls of the cell. Only after numerous portions of water had been allowed to stand in the cell did it begin to behave normally again. Yet it appears, from a thorough survey of the conductance literature, that very little attention has been paid to the possibility of adsorption on the cell walls. Even Cox, Kraus, and Fuoss[79] seem to have considered their sorption effects in the cell itself to be occurring at the electrodes only -- this in spite of the fact that they were using bright platinum electrodes and that there was far more definite evidence that sorption was actually taking place at glass surfaces. For aqueous solutions, only two cases could be found in the literature where the matter was mentioned at all. Weiland[38] determined a correction for the adsorption of potassium chloride by quartz to be applied to his measurements of the conductivities of solutions of this electrolyte, but found it to be negligible; and Randall and Scott[87] produced evidence for the adsorption of the same electrolyte on the glass walls of a flask used for storing the solution.

If it is desired only to determine accurately the conductance of a given solution, adsorption effects can usually be eliminated by the well-known "wash-out" technique, whereby the cell is rinsed and left standing with at least one, but preferably several fillings of the solution before taking the final resistance readings. In this way, the various parts of the cell reach adsorption equilibrium at the concentration of the solution being studied before the final filling is made, so that no further losses occur from the final portion of solution used for measurement. This technique is effective in preventing adsorption losses both at the walls of the cell and at the electrodes, and since it has been widely used, it may seem to contradict the previous statement that the cell walls have usually been overlooked in allowing for sorption effects. However, the method necessarily involves the preparation of a bulk solution in some other vessel, where adsorption is just as likely to occur on the walls as in the cell unless the flask has first been "seasoned" by allowing a solution of the same concentration to stand in it for some time. Only then will the concentration of the solution used in the final resistance measurement be known with certainty. The importance of this "seasoning", especially for very dilute solutions, can be seen from the figures quoted by Cox, Kraus and Fuoss[79]. This method was successfully used by A. Faure[2] in his accurate redetermination of the conductivities of dilute potassium chloride solutions.

The "wash-out" technique has certain disadvantages. It gives very accurate results for the conductance of a solution, but no indication of the total amount of adsorption which occurs in the preparation flask and in the cell. Where there is a considerable amount of adsorption, the method can be rather tedious and wasteful, for the preparation of solutions and filling of the cell must be continued until the final conductances, after equilibration, of two successive solutions are the same. This is true for every new solution measured, be it of a different electrolyte or only just a different concentration of the same electrolyte. On the other hand, where there is no adsorption, these precautions are unnecessary; yet the preparation and measurement would still have to be repeated at least once in order to show this.

The method frequently used in the determination of the conductance of a given electrolyte at different concentrations is the addition or concentration technique. Here successively more concentrated solutions are prepared by the repeated addition of weighed amounts of solid electrolyte, or of aliquots of some stronger stock solution, to a given amount of solvent placed either in the cell[79] or in some adjoining flask, as in the Shedlovsky cell[42]. This is, of course, the same procedure as is used in conductimetric titrations, and it is obviously liable to adsorption errors which are likely to differ in magnitude for each addition until the concentration is high enough for saturated adsorption to have been reached. For accurate work, therefore, it becomes necessary to know something about the nature and extent of the adsorption occurring in each case considered, and also to perform the measurements under such conditions that any errors are minimised as much as possible.

Since it was desired in this laboratory to improve considerably the accuracy of conductimetric titrations, the initial investigation performed by Gledhill[3] was extended by the author to a consideration of the effects of adsorption, and of the partial or complete elimination of these. A full investigation of this problem would eventually cover the whole field of strong and weak acids, strong and weak alkalies, and the various salt combinations of these. The simplest case seems to be that of the neutral salts of strong acids and bases; of these, potassium chloride was chosen for the first investigation into methods and techniques of determining adsorption, because it is so widely used in conductimetric measurements.

In spite of the frequent use of potassium chloride, very little mention seems to have been made of its adsorption, and even the few references which have been found appear to be rather conflicting. Thus Kohlrausch[91] concluded that no appreciable error was to be feared from adsorption of neutral salts by the electrodes. de Brouckère[80], however, found that even in relatively concentrated (N/100) solutions of the chlorides of lithium, sodium, potassium, copper, and nickel, the initial conductivity of the first batch of solution placed in a cell with freshly platinised electrodes slowly decreased in each case, and after about 12 hours reached a constant value which was some tenths of a percent lower than the original value. She showed too that this change in conductivity was due to adsorption by the electrodes. Kolthoff and Kameda, in their studies on the adsorbent properties of platinised platinum, showed that adsorption by the platinum black occurred from potassium chloride solutions in a hydrogen or oxygen atmosphere[90], but stated that there was no adsorption in a nitrogen atmosphere[92]. Festenstein[29], however, on titrating a concentrated potassium chloride solution into water in a conductance cell with lightly platinised electrodes, using purified air to stir the solution, found that the cell constant values showed a small downward drift with increasing number of additions; these changes were still apparent, though to a smaller extent, when nitrogen was used for stirring instead of air, and they seemed to be best explicable as due to adsorption occurring in the cell. A critical survey of this work, however, has shown that the results were a little erratic and inconsistent, and it is not quite certain whether these small changes were real or possibly due to slight experimental errors.

References to the adsorption of potassium chloride elsewhere than on the electrodes have already been mentioned: this was the electrolyte used in the only two instances where the possibility of such adsorption has been considered for aqueous solutions. Weiland[38] found a negligible adsorption on quartz, while Randall and Scott[87] stated that there was some adsorption of potassium chloride on the glass walls of the storage flask, but they did not indicate to what extent this occurred.

The method proposed initially for this investigation was similar to Weiland's[38], viz., to wait for the attainment of steady conditions after making an addition of potassium chloride to water in the cell, then to add either glass beads or pieces of platinum foil, of known surface area in each case, and to observe any changes in conductivity resulting from this. However, early trials along these lines, using the conductance bridge described by Gledhill[3], did not give very promising results. The added materials in these experiments were carefully cleaned and treated in a manner similar to that used for the cell. On adding the glass beads to the cell, there was an immediate rise in resistance, while the addition of the platinum foil caused a decrease. Both these changes were on some occasions quite large, though by no means consistent. They were definitely not associated with any adsorption effect, but were more probably due to changes in the cell characteristics because the electrodes in the type of cell used were sealed in very near the bottom (see Section 1.31). Hence any pieces of platinum foil lying in the cell would act as a low resistance shunt and cause a decrease in resistance of uncertain magnitude, depending on their proximity and positions relative to the electrodes: somewhat erratic readings were actually obtained on stirring, the resistance occasionally showing a **sudden,** very large change (about $\frac{1}{4} - \frac{1}{2}\%$). The glass beads, on the other hand, would displace some of the conducting solution, to give an unknown increase in resistance. This decreased conductance would probably be offset very slightly by the existence of a surface conductivity near the boundary between potassium chloride solutions and glass, as demonstrated by McBain, Peaker and King[93]. With glass beads of relatively small surface area, such as were actually used, the latter effect would doubtless be very small indeed; but if the surface area were increased, say by the use of powdered glass, in order to show up any adsorption effects more clearly, the surface conductivity would also increase, and the whole issue would become exceedingly complicated. Although large amounts of adsorption could easily be demonstrated qualitatively by this method[79], it did not appear to be very satisfactory for a quantitative investigation, particularly where the adsorption was likely to be small.

The tests with the glass beads and platinum foil were designed to check the correctness of Festenstein's deduction that the apparent variation in cell constant on titrating potassium chloride into water was due to adsorption[29]. Shortly afterwards, a second precision conductance bridge was built in this laboratory by A. Faure[2] and Goddard[1], which incorporated a cathode-ray oscilloscope as detector instead of the more conventional earphones used in the previous bridge. With this visual method, the balancing of the bridge could be made much more rapidly and with considerably less fatigue to the operator than with the audio-detector. It therefore became possible to follow the resistance of the cell very soon after making an addition, and so to observe any immediate changes which might occur, without interrupting the stirring for periods long enough to allow secondary effects to take place. If several additions were to be made, as during a titration, these changes could be followed until constant conditions were re-established each time, and this would probably provide another check on possible adsorption, supplementary to any surmises made from changes in the cell constant such as were found by Festenstein[29]. It was therefore decided to investigate the adsorption of potassium chloride by repeating the titration into water, but with much greater attention to the effects occurring immediately after addition and to the general accuracy. Also, the titration would be performed with different stirring gases (nitrogen, oxygen, and hydrogen), using both bright and platinised electrodes, so that the adsorption could be studied under varying conditions of measurement.

3.2 DETERMINATION OF THE CELL CONSTANTS.

3.21 Experimental.

The cell constants of the two cells were determined by the usual method of measuring the resistance of a solution of very accurately known conductivity. In this case, the 0.01D KCl solution described by Jones and Bradshaw[94] was used: this contains 0.745263 g KCl per 1000 g solution (both weights in vacuo), and has a conductivity of 0.00140877 $ohm^{-1}cm^{-1}$ at 25°C, to which must also be added the conductivity of the water. The latter was not usually measured for each solution prepared, but just taken as 100 nm/cm, since numerous resistance determinations on water obtained from the still had shown that its conductivity was almost invariably within 30 nm/cm of this value: any error in this assumed value would therefore cause at most an error of 0.002% in the calculated conductivity of the 0.01D KCl solution.

At different times, various batches of potassium chloride were used for the preparation of standard solutions. These had all been purified by other conductance workers in this laboratory, the first step being two or three recrystallisations of G.R. material from conductivity water. Thereafter A. Faure[2] fused the crystals in a nitrogen atmosphere, and obtained a water-white product: this was taken as a standard for all these measurements. Festenstein's fusion was done in air[29], and the final product was very slightly discoloured, but only the portions showing the least colour were used. Taylor[56] merely heated the recrystallised material to 600°C in a dry nitrogen atmosphere, following a statement by Addink[95] that fusion was unnecessary to expel the last traces of water adhering to KCl crystals. No significant differences in cell constant values were found on using these three different batches of potassium chloride.

A 1-litre Pyrex flask with ground-glass stopper was kept specially for the preparation of 0.01D KCl solutions. Before the flask was used for any standard solution, it was first cleaned and then thoroughly "seasoned" by letting an approximately 0.01D KCl solution stand in it. When any fresh standard solution was prepared, the previous solution was poured out and the flask allowed to drain for about 30 seconds, then stoppered, wiped, and weighed on balance

BIII. The potassium chloride was weighed on balance BI, using a small silver dish and tare. In accordance with the deduction made by A. Faure[2], that even fairly long exposure to the atmosphere resulted in water absorption of not more than 0.02%, provided that the relative humidity was less than 75%, no special precaution was taken to keep the salt out of contact with the atmosphere. On very humid days, the humidity could usually be lowered sufficiently by warming the whole balance-room with several radiators. The temperature and pressure were noted to enable conversion of the KCl weight to vacuum, and the final weight in air of solution required to make an exactly 0.01D solution was calculated (see Section 1.43). Sufficient water was then added directly from a collecting flask to the preparation flask until the weight was less than the required weight by something under 50 g. Any water adhering to the ground-glass joint was then wiped off with a clean cloth and the stopper was replaced, care being taken that the solution in the flask was not shaken on to the joint or stopper. An accurate weight check on balance BIII now showed how much water was still required, and this exact amount was added from a 50-ml Normax burette which had been carefully cleaned and which was kept specially for this purpose. To prevent contamination of the water, the tap was not greased. The burette was kept permanently filled with conductivity water. By this method an exactly 0.01D solution could be prepared quite rapidly, one addition from the burette invariably proving sufficient to give a solution correct within 0.01%. The final weight was, however, always determined and the exact conductivity of the solution calculated: a proportional correction was made to the value 0.00140877 $ohm^{-1}cm^{-1}$ for an exactly 0.01D solution[94] to allow for any small deviations from this concentration. Only then was the solution thoroughly shaken to mix, and it was usually left standing for a while in the constant temperature room to reach approximate temperature equilibrium.

Unless the cell had just previously contained 0.01D KCl, it was first rinsed three or four times and then filled with the freshly-prepared solution (about 200 ml). All transfers were made by pouring directly from the preparation flask into the cell, and the room fans were always switched off whenever the flask was opened, in order to minimise evaporation. This solution was left in the cell, which was usually immersed in the thermostat, for several hours, until the resistance drift due to temperature equilibration and removal of CO_2 had ceased. Thereafter the cell was emptied and drained for a few seconds, then refilled with a fresh portion of the same solution and returned to the thermostat. With all fillings where the resistance was to be measured accurately, the bubbling rate was kept very slow at first (one bubble per second or less): this was sufficient to keep the solution slightly stirred without causing changes in concentration due to initial temperature differences between the stirring gas (saturated at 25°C) and the solution. After about half-an-hour, however, when temperature equilibrium was more or less established, the rate was increased to 60/30, and the resistance was measured occasionally until it remained constant; the accurate set of readings was then taken. It was found necessary to stop the stirring completely for the final balancing of the bridge, otherwise the resistive and capacitative changes produced by the passage of bubbles past the electrodes in the solution made accurate measurement impossible; the stirring gas was therefore by-passed over the top of the cell to prevent back-diffusion of carbon dioxide during this short period. The equilibration usually took 3 - 4 hours, but in cases where greater speed was required, the bubbling rate was sometimes increased to 120/30 or more after the initial slow period, kept there for about 1½ hours, and then reduced to 60/30 again for about 30 minutes before the final readings were taken. A check which was once made on the same solution equilibrated at both these rates actually showed no significant difference in resistance: the lower rate, however, was generally preferred because it caused less spraying, and because it was the standard rate chosen for the titration experiments (see Section 3.322).

If the resistance of a further portion of the same solution was measured as a check, the cell was refilled without intermediate rinsing: for a completely new solution, no further "seasoning" was necessary, and one rinsing was usually sufficient because the concentrations of all the solutions prepared were so nearly the same.

The resistance measurements taken during the period of equilibration were made at one frequency only (900 c/s) and for a single setting of the ratio arms and supply voltage (this was merely to detect whether the resistance was still changing or not). For the final accurate measurement, however, readings were taken at the five different frequencies given by the oscillator, so that the true resistance of the solution in the cell could be obtained by applying a suitable polarisation correction (see Section 3.22). Initially four measurements were made at each frequency, with both the ratio arms and the supply voltage direct and reversed, the arithmetic mean of these readings being taken. Later, however, when it had been shown that reversing the supply voltage did not cause any significant change in resistance, only the ratio arms were reversed and two readings taken; and sometimes, for rough checks or when a rapid set of readings was required, the resistance was only measured for one ratio arm setting at each frequency, since the extrapolated value could readily be corrected for any inequality in the two ratio arms if this were accurately known. During each set of measurements, the individual frequencies were rapidly checked on the oscilloscope using a 50 c/s circular time-base: the approximate frequency was given in multiples of 50 by the number of peaks (Z), while a more exact value was obtained by observing how many revolutions a single peak made round the circular scale in Z seconds, and then adding this to or subtracting it from the approximate value, according to the dictates of experience. The five frequencies were usually adjusted to within 10 c/s of the values 500, 650, 900, 1300, and 1950 c/s. These were the original frequencies to which the oscillator and amplifier had been set accurately when the bridge was built (except that initially the highest value was 2000 c/s), and the values could then be obtained quite readily by merely changing the position of a selector switch, without adjustment of the regeneration; with the aging of components in the circuit, however, it had become necessary to make small regeneration adjustments with each change, and the frequencies were also found to be no longer exactly at their original values. It was for this reason, and because the polarisation correction was dependent on the frequency, that this check was deemed desirable; with unplatinised electrodes, for instance, polarisation sometimes caused a difference of as much as 1.3 ohms (or 1.7% of the measured value) between the resistances at 900 c/s and those at infinite frequency, and a fairly accurately known correction was therefore required.

With the relatively small resistances measured and so much polarisation, it was necessary to increase the parallel capacitance in the measuring arm of the bridge very considerably -- more than could be obtained with the small mica radio condensers which were normally used. A General

Radio Co. Type 219-M decade condenser box, with a range from 0.001 to 1.11 µF, was therefore used as well. For each resistance reading taken, the total parallel capacity (C) was also noted, since with alternating current determinations the measured resistance (R_m) is not necessarily the true resistance (R_t) because of inductive and capacitative effects. According to Gledhill[3], Goddard[1], and A. Faure[2], if the equivalent cell circuit is assumed as a first approximation to be a pure resistance in series with a pure capacitance, then the true resistance may be calculated from the measured value by means of the equation

$$R_t = \frac{R_m}{1 + p^2C^2R_m^2} \qquad \text{..........(3.1)}$$

where $p = 2\pi \times$ (the a.c. frequency)

If the correction term is very small, this may be expanded to the simpler form

$$R_t = R_m(1 - p^2C^2R_m^2) \qquad \text{..........(3.2)}$$

The initial and final readings of each set of resistances for a given solution were always taken at the same frequency (900 c/s), in order to check that no large change had occurred during the time of measurement. Only very small changes were occasionally found, which might possibly have been due to slight heating effects arising from the continued passage of current through the cell (cf. A. Faure[2]). These drifts in resistance were assumed to be uniform throughout the period of the determination, and a small proportional correction was accordingly made to the resistance at each frequency, depending on the order in which the readings were taken.

The temperature of the outer thermostat was also checked at the beginning and the end of each set of readings.

3.22 The Polarisation Correction.

The resistance of a solution found from a.c. measurements varies with the frequency of the applied voltage, owing to the effects of polarisation at the electrodes. Jones and Christian[96], during a study of galvanic polarisation, eliminated these effects by using a cell with variably spaced electrodes: they showed that the electrode effects caused a constant positive polarisation resistance, which depended on the frequency, and that the true resistance of a solution varied linearly with the distance between the electrodes and was independent of the frequency. They also found that, for a given separation between the electrodes, the resistance measured at different frequencies varied approximately linearly with the reciprocal square root of the frequency; and when the straight line obtained by plotting R v. $f^{-\frac{1}{2}}$ (where R = resistance of cell, and f = oscillator frequency) was extrapolated to infinite frequency, where the polarisation resistance would be expected to be negligible, the value given was very nearly the same as the true resistance of the solution for the same electrode spacing. Obviously it involves less in the way of practical difficulties to vary the measuring frequency of an a.c. bridge than to use a cell with movable electrodes in order to determine the true resistances of solutions. Accordingly the $R\text{-}f^{-\frac{1}{2}}$ extrapolation to infinite frequency became the standard method of polarisation correction in the accurate determination of electrolytic conductances.

Although this method was recommended by Jones and Christian because of its simpler experimental technique, they stated that it was probably not quite as reliable as their first method for cases in which the polarisation resistance was a substantial fraction of the measured resistance. The values of the true resistance thus obtained were usually slightly lower than those found by varying the distance between the electrodes. This was because the experimental points, plotted against $f^{-\frac{1}{2}}$, did not lie completely on a straight line, but showed indications of a small positive curvature in the line connecting the points. This curvature was mentioned several times by these authors, but the impression gained from their paper is that it was very slight and caused only a very small error when a best straight line was drawn through the $R\text{-}f^{-\frac{1}{2}}$ points to give the resistance at infinite frequency. When a five-frequency bridge was built in this laboratory, however, Goddard[1] found a very distinct positive curvature during his cell constant determinations with 0.01D KCl in a cell with unplatinised platinum electrodes (resistance about 111 ohms), and the true resistance could not be computed easily; only when the polarisation had been greatly diminished by a light platinisation could an accurate cell constant be determined. A similar pronounced curve was obtained by A. Faure[2]. He found that a plot of R v. f^{-1} gave points which lay much better on a straight line, particularly in the case of unplatinised electrodes; with platinised electrodes the results appeared to be rather more erratic, but since the correction in these cases was small anyway, he used an R-f^{-1} plot for all extrapolations to infinite frequency.

In the present work, it was desired to use both unplatinised and heavily platinised electrodes, in order to compare the adsorption effects occurring under these differing conditions. It was therefore necessary to determine the cell constant accurately in both cases, and it was found that the polarisation correction appeared to depend very much on the state of the electrodes.

3.221 Unplatinised electrodes.

The results with unplatinised electrodes were very similar to those of A. Faure[2]. A typical set of resistance readings obtained for 0.01D KCl in cell II is shown plotted against f^{-1} in Fig. 3.1, and against $f^{-\frac{1}{2}}$ in Fig. 3.2. In both these figures line (1) gives the mean resistance obtained at each frequency, with no corrections applied other than for bridge calibration. Line (2) gives the same resistances with the $p^2C^2R_m^2$ correction applied (see p.142). It will be seen that, although the resistance being measured was fairly small (ca. 78 - 80 ohms), the correction was quite large (almost 0.6 ohms at 500 c/s), and the more accurate form given by equation (3.1) was therefore used in calculating the corrected values. The estimated limits of error in these values are indicated in Fig 3.1 by plotting them as rhomboids, derived on the following assumptions:-

(i) that the frequency was measured with an accuracy of 1%. This gives a variation of ±1% in the f^{-1} value, and also causes small changes in the resistance for each possible frequency within this range owing to differing values of the $p^2C^2R_m^2$ correction term: the total variation, therefore, is represented by a sloping line through the plotted point;

(ii) that the capacity was measured with an accuracy of 1%: this is the accuracy which was specified by the manufacturers of the decade condenser box, and it was assumed to be correct since no standards were available for calibration. It appeared later from certain inconsistencies that the 0.1 µF decade was not quite so correct, but slightly greater errors do not affect the final results appreciably. The small mica radio condensers which were used were all calibrated. Small errors in the measured capacity cause slight changes in the $p^2C^2R_m^2$ correction term, and hence in the plotted resistances;

(iii) that the resistance was measured with an accuracy of 0.003 ohms (0.005 ohms for 1950 c/s). Since the bridge was calibrated, this error was determined solely by the accuracy with which balance could be obtained.

Fig. 3·1 – R. v. f^{-1} extrapolation curves with unplatinised electrodes.

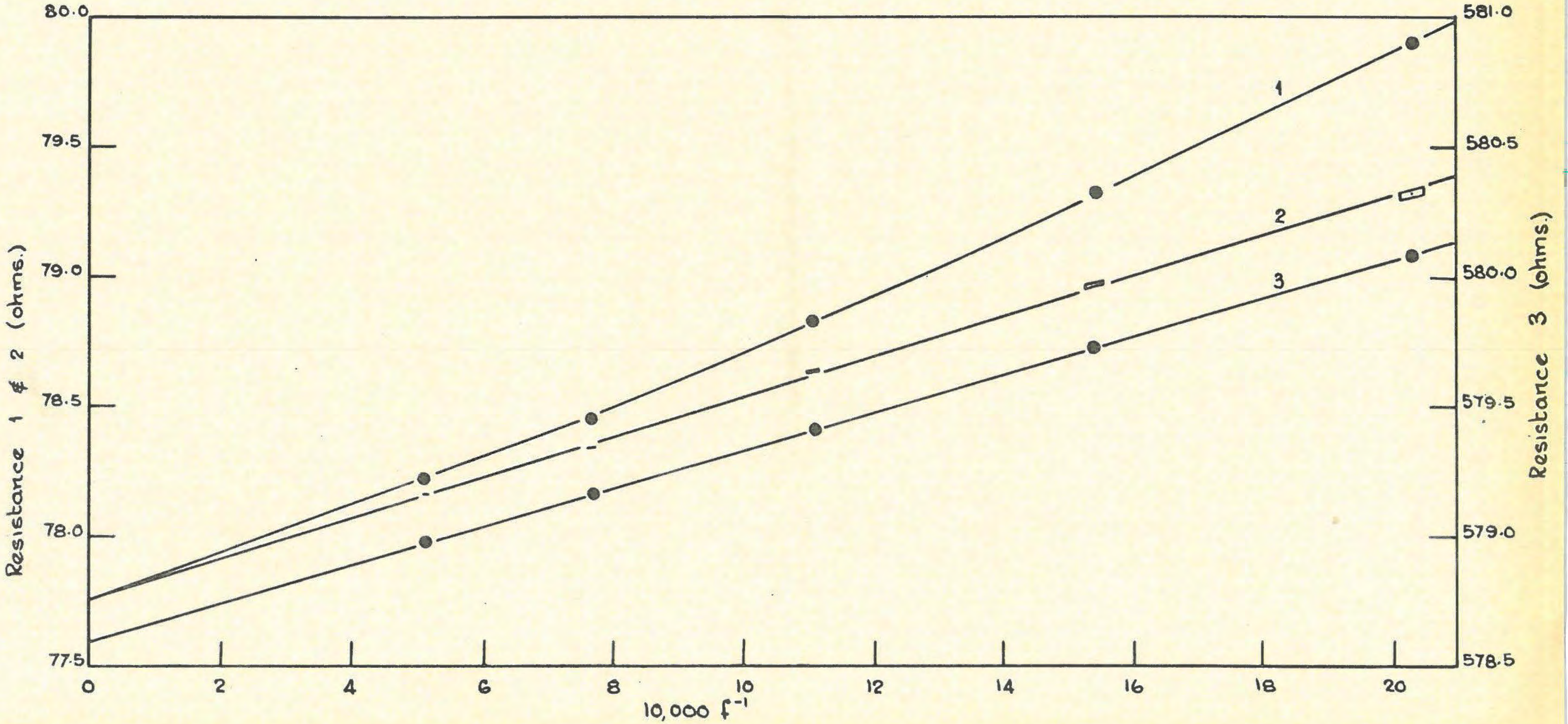
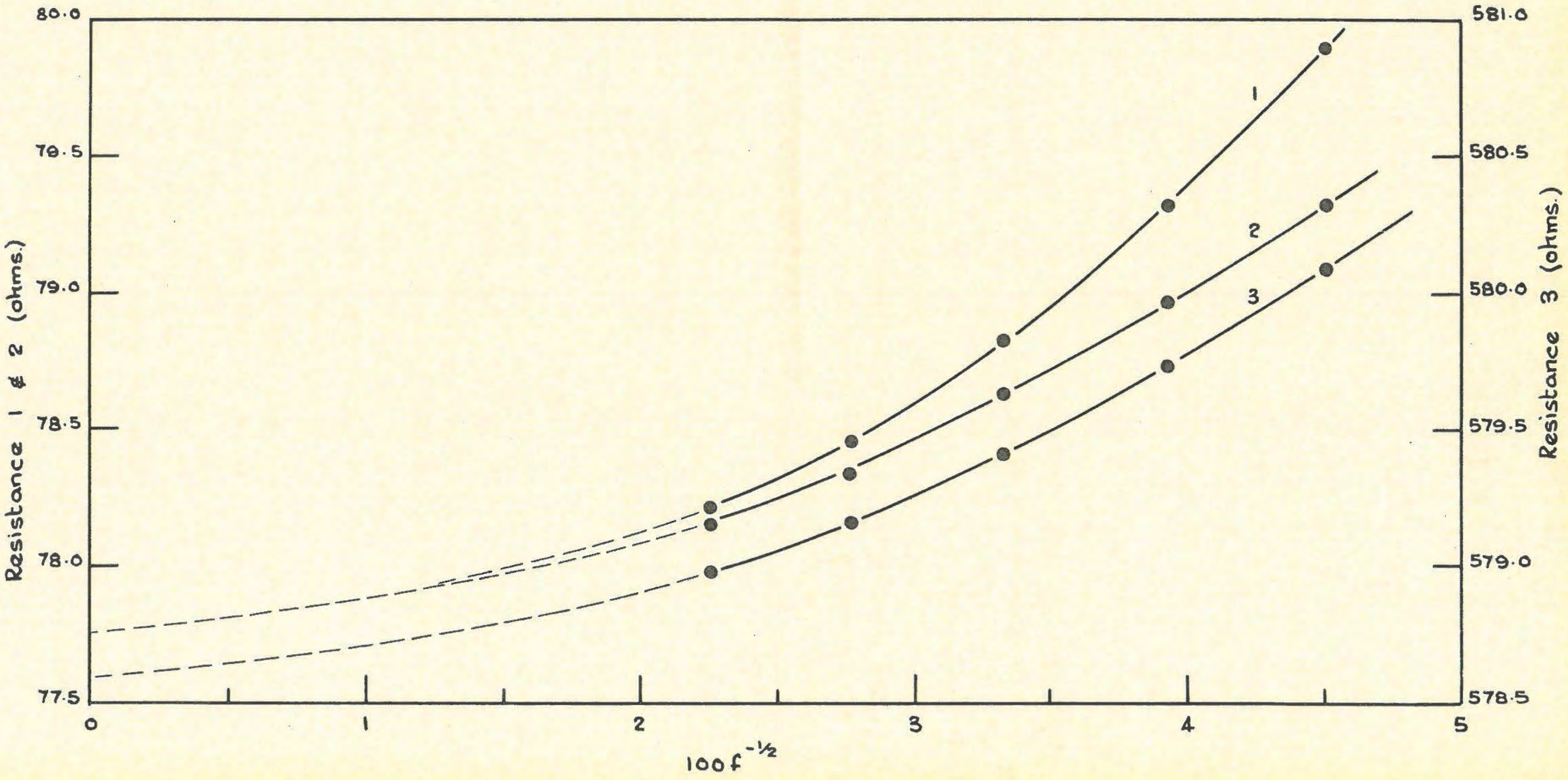


Fig. 3·2 – R. v. $f^{-1/2}$ extrapolation curves with unplatinised electrodes.



Errors (ii) and (iii) are additive and result in a range of r sistances for each possible frequency within the limits set by (i): the nett effect gives rhomboidal plots as shown.

Both lines for the plots against $f^{-\frac{1}{2}}$ are very distinctly curved, and line (1) in Fig. 3.1, for the uncorrected resistances, also shows a slight positive curvature. When the corrected resistances are plotted against f^{-1}, however, the points appear to lie very closely on a straight line, which can readily be extrapolated to $f^{-1} = 0$. The value obtained, after correction for the resistance of the bridge leads (see Section 1.212) and of the cell leads (Section 1.32), was taken as the true resistance of the solution. The extrapolation was always done graphically; in drawing the best straight line, the various points were weighted differently to conform to the assumptions of accuracy mentioned previously. These different weights, and the fact that the points were not equally spaced along the f^{-1} axis, made it very difficult to fit a best straight line by the method of least squares[97]. However, a few comparisons between the mathematical and graphical computations of the resistance showed agreement within 0.01%, and since the latter method was simpler, it was adopted as standard.

Although the points lay on a straight line within the estimated limits of experimental error, in general they were just slightly displaced from the line, possibly owing to the lack of calibration of the decade condenser box. The best straight line therefore had to be drawn very carefully, since even very small variations in slope could cause quite appreciable changes in the extrapolated resistance because of the large polarisation correction and consequent steep slope of the line. The agreement of results found with different solutions, however, showed that, with due care, it was possible to obtain the resistance at infinite frequency within the required accuracy of 0.01%.

It has been standard practice in this laboratory to use a resistance in series with the cell when measuring fairly low resistances[1,3,29]. This was because the bridge could not be balanced at the lower frequencies owing to the high parallel capacitance required, especially with unplatinised electrodes. An objection to this practice, which applies particularly where the bridge resistances have not been calibrated, is that the determination of a small resistance as the difference between two larger ones can give rise to another possible source of error, unless the value of the series resistor is very carefully chosen[29]. In the present work, the decade condenser box was available, and it was possible with the visual balance to measure even low resistances quite accurately. The parallel capacitance was, however, very large: for the case shown in Figs. 3.1 and 3.2, for instance, it varied from 0.028 µF at 1950 c/s to 0.344 µF at 500 c/s. Sometimes it was even higher than this, for it was found that the parallel capacitance and the slope of the $R\text{-}f^{-1}$ line varied with time; they were both considerably less just after the cell had been well cleaned, e.g. with alcohol and nitric acid or with chromic acid cleaning mixture, but gradually increased as the cell was used, or even if KCl solution were allowed to stand in it. It has already been pointed out that this large capacitance caused quite an appreciable $p^2C^2R_m^2$ correction, and it might therefore be the reason for the corrected resistances usually being slightly displaced from the best straight line in the $R\text{-}f^{-1}$ extrapolation. Since the bridge used had been calibrated and accurate resistance differences could be obtained, it was decided to see whether measuring the cell resistance with a series resistor would give points lying more exactly on a straight line, which could then be more accurately extrapolated.

The resistance used was a General Radio Co. Type 510-D hundred-ohm decade: this was chosen because

(i) the value of the series resistance could be easily varied;

(ii) its resistance was independent of frequency over the range used: actual measurement showed the variation to be less than 0.002 ohms;

(iii) it had a very low temperature coefficient (0.002% per °C). This was essential if the resistance was to remain constant during a series of measurements, and not to show fluctuations due to possible body radiation from the operator or other persons in the the room. As an additional precaution, the whole decade was placed in a box insulated with cotton-wool.

Measurements were made using both 500 and 1000 ohms in series with the cell. The introduction of the series resistance caused a very great decrease in the size of the parallel capacitance, e.g. only 0.0005 to 0.0067 µF was required for the full frequency range when 500 ohms* was placed in series with the same solution for which the capacitance values were previously quoted. The resistances (corrected for $p^2C^2R_m^2$) obtained in this determination are

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* The exact value of the series resistance was 500.805 ohms.

plotted against f^{-1} and $f^{-\frac{1}{2}}$ as line (3) in Figs. 3.1 and 3.2 respectively. In the latter plot the line is still distinctly curved, and exact extrapolation is therefore no easier than for lines (1) and (2); but there is a marked improvement in the way in which the points plotted against f^{-1} lie on a straight line. This was found to be generally true for all the cases considered, and the lines could be extrapolated more accurately to $f^{-1} = 0$ than those obtained for the cell alone. The lines appeared to have about the same slope with and without the series resistor present, i.e. the polarisation correction was not changed. However, the value obtained for the cell resistance, after suitable deductions had been made for the leads and series resistances, was always found to be 0.04 - 0.06 ohm higher than when the cell was used alone. This difference was quite definite, and far larger than any possible error resulting from incorrect extrapolation. It occurred whether the series resistance was attached to the cell leads on the oscillator side or the earth side (see diagram of Faure-Goddard bridge[2]), no significant difference being found between these two cases. The reason is probably connected with the equivalent circuit of a conductance cell, which has not yet been accurately established. Further investigation of this effect was not possible in the present study. It was therefore decided merely to accept the value obtained with no resistance in series, even though this extrapolation might not be quite so exact, because in the later measurement of KCl solutions during the titrations no series resistance would be used.

It is interesting to note that recently Nichol and Fuoss[98] have also reported a similar curvature in the R-$f^{-\frac{1}{2}}$ plots when using bright platinum electrodes for the determination of the resistances of dilute non-aqueous solutions. They state that the data can be represented by the quadratic equation

$$R = R_{\infty} + ax + bx^2 \qquad \text{..........(3.3)}$$

where $x = f^{-\frac{1}{2}}$, and they calculate R_{∞}, the resistance at infinite frequency, from this equation. In an example depicted graphically, where the points lie on a distinct curve for an R-$f^{-\frac{1}{2}}$ plot, the value of R_{∞} calculated as above is about 0.6 ohm higher than that obtained by a straight line fitted to the points by the method of least squares: this is quite an appreciable error in the resistance of about 1090 ohms being determined. If the values of these points are measured from the published graph and plotted on an R-f^{-1} scale instead, they are found to lie quite well on a straight line which extrapolates to a value only 0.2 ohm higher than that calculated by Nichol and Fuoss, i.e. the difference is now only 0.02%. Of course, in the extreme cases, equation (3.3) would reduce to

(i) $R = R_\infty + af^{-\frac{1}{2}}$ when $b = 0$,
i.e., the Jones-Christian recommendation,

or (ii) $R = R_\infty + bf^{-1}$ when $a = 0$,
i.e., the present recommended plot.

3.222 Platinised electrodes.

The very marked decrease in polarisation caused by platinisation of the electrodes is shown by the resistance and parallel capacitance values given in Table 3.1, column (b). For comparison, the values obtained before platinisation, which have been plotted in Fig. 3.1, are also quoted in this table, column (a).

TABLE 3.1

Approx. frequency (c/s)	Before platinisation (a)		After platinisation (b)		(c)	
	Cap. (µF)	Resis. (ohms)	Cap. (µF)	Resis. (ohms)	Cap. (µF)	Resis. (ohms)
500	0.3443	79.897	0.00500	77.928	0.00280	77.910
650	0.2061	79.322	0.00300	77.925$_5$	0.00175	77.906$_5$
900	0.1112	78.828	0.00137	77.924	0.00090	77.902
1300	0.0589	78.451	0.00064	77.922	0.00052	77.897
1950	0.0280	78.217	0.00022	77.920$_5$	0.00020	77.892$_5$

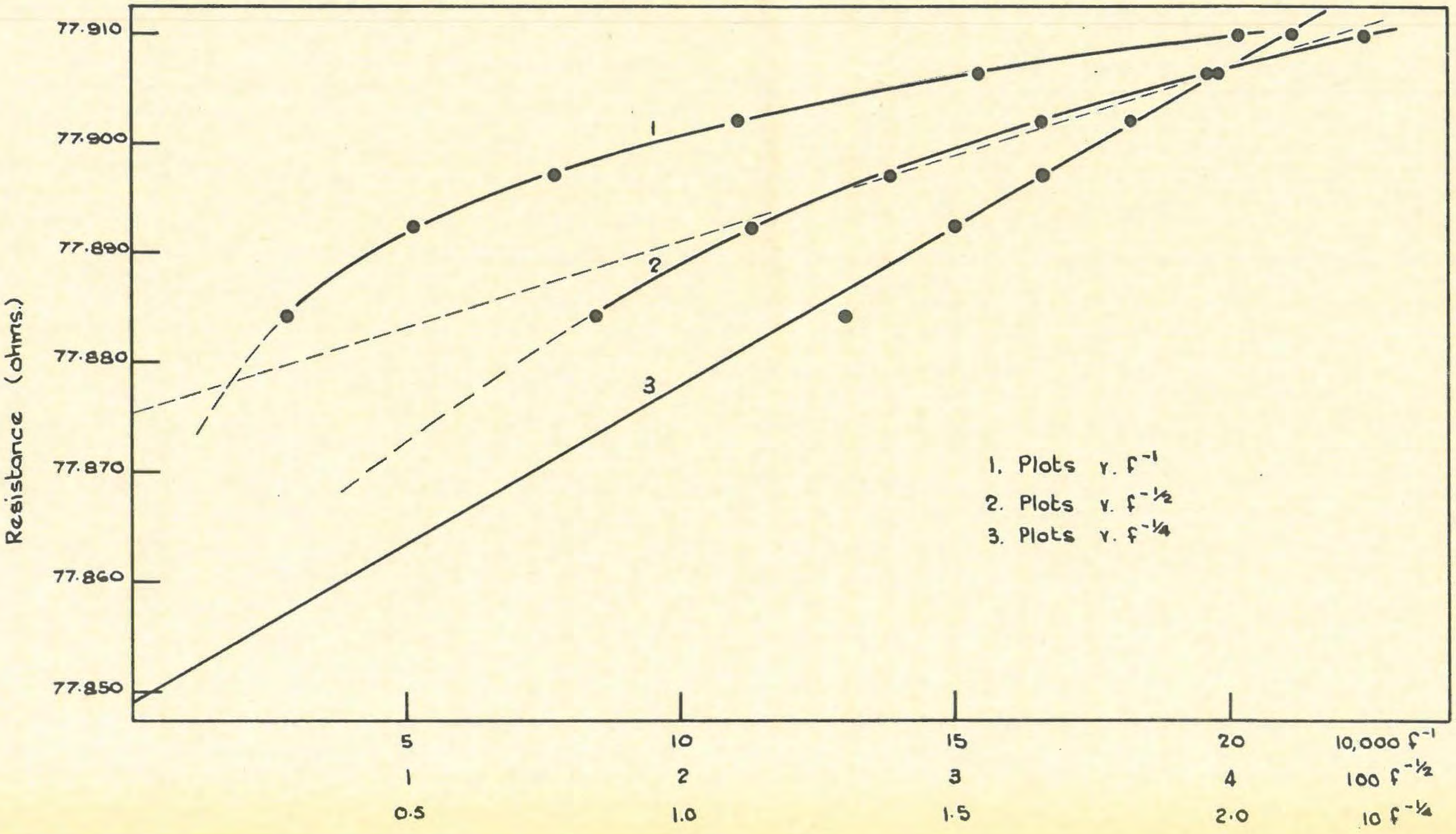
In (b), the $p^2C^2R_m^2$ correction is now completely negligible, and the resistance values vary so little that they may be plotted against either f^{-1} or $f^{-\frac{1}{2}}$, to give a straight line. The two extrapolated values are 77.918 and 77.913 ohms respectively, i.e. there is a difference of less than 0.01%; and even if no extrapolation were made and the resistance were taken as that at the highest frequency used, no appreciable error would be introduced.

The values in Table 3.1, column (b) were obtained for an approximately 0.01D KCl solution; the resistances were measured as an intermediate check on the progress of the platinisation of Cell II (see Section 1.34). It was estimated that each electrode had then received about 35 - 40 coulombs as a cathode, but the exact density of the deposit was not known because it was not confined to the front faces of the electrodes, but also occurred to a lesser extent on the back faces and the supporting cones and tubes. The electrode diameter was 2 cm, and the total surface area per electrode (including the cone and tube) was therefore about $7\frac{1}{2}$ cm^2; hence it is likely that the deposit on the front faces was equivalent to about 6 coulombs per cm^2. This is of the same order as that which Jones and Bollinger[20] found to be about the minimum required for the most effective diminution of polarisation. In the example given by them, further platinisation up to ten times this amount did not change the polarisation resistance appreciably, but the parallel capacitance definitely still decreased somewhat; thereafter excessive platinisation caused these both to increase a little again.

The polarisation resistance of Cell II at this stage was quite small and the platinisation would normally have been considered to be satisfactory, even though the parallel capacitance did not seem to have been decreased by as much as Jones and Bollinger had found at optimum platinisation, but still appeared to be fairly large. Since the purpose of this investigation, however, was to study the adsorption effects of potassium chloride at both bright and platinised electrodes, it was decided to continue the platinisation to obtain a heavy deposit and so exaggerate any possible adsorption. It was hoped that this would also decrease the capacitance still further, but that the polarisation resistance would remain the same, or possibly show a very slight improvement as well. The results obtained for 0.01D KCl when each electrode had received about 150 coulombs are given in Table 3.1, column (c): it will be seen that, although the expected decrease in capacitance was observed, the polarisation resistance was quite obviously a bit larger. When these points were plotted against f^{-1} in order to extrapolate to infinite frequency, it was found that they lay on a line of distinct negative curvature: this was still so, though to a lesser extent, when the plots were made against $f^{-\frac{1}{2}}$. The curves obtained are shown in lines (1) and (2) of Fig. 3.3.

The actual variations of resistance with frequency were rather small and these plots are therefore shown on a very enlarged scale, but there is little doubt that the curvature is real. Occasionally in an individual determination it did appear as if the R-$f^{-\frac{1}{2}}$ graph might be a straight line, since the curvature was really so slight that it only needed the measured resistance at one or two of the frequencies to be out by 0.002 ohm or less in order to straighten the line: this was within the limits of experimental error. The majority of plots, however,

Fig. 3.3 - Extrapolation curves with platinised electrodes.



appeared to be curved, and the values quoted in Table 3.1 and plotted in Fig 3.3 are actually the mean values at each frequency obtained from eight different determinations. The chance errors which might accompany a single measurement are therefore eliminated, and the presence of the slight negative curvature definitely confirmed. In order to establish this still further, attempts were made in four of the determinations to measure the resistance with an even higher frequency than was available on the bridge. For this purpose an oscillator was borrowed from another bridge which had been built to study polarisation, and this was connected in parallel with the built-in unit and a frequency of 3500 c/s used. Unfortunately balance could not be obtained as exactly as for the actual bridge frequencies because of excessive a.c. pick-up, and because the built-in amplifier was not tuned for this frequency and hence had to be used at its 2000 c/s setting. The mean value of the resistance at 3500 c/s seemed to confirm the curvature; in fact, it appeared even to be about 0.002 ohm lower than might be expected, perhaps because of the slight inaccuracy in its determination, and it was therefore not considered in the final extrapolation.

A similar curvature was reported by A. Faure[2] for a modified Jones type cell with platinised electrodes. The platinisation was by no means as heavy as in the present case, but previous measurements by A. Faure with a similar cell of about the same dimensions, but having electrodes which were more lightly platinised, had given a straight line when R was plotted against f^{-1}. The result had been ascribed to ineffective platinisation, and the erratic effects were circumvented by using unplatinised electrodes.

In the present case, it was necessary to use the heavily platinised electrodes, and therefore essential to be able to extrapolate to infinite frequency with reasonable accuracy. The appearance of the curvature in the $R\text{-}f^{-1}$ and $R\text{-}f^{-\frac{1}{2}}$ graphs was probably due to the effects of excessive platinisation on the values of the equivalent cell circuit, but this could not be investigated here. Nor was it possible to extrapolate these lines with accuracy because their curvature caused them to approach the $f^{-1} = 0$ and $f^{-\frac{1}{2}} = 0$ axes fairly steeply and so gave rise to much uncertainty in the value of R_{∞} in spite of the comparatively small polarisation correction involved. A plot was tried against $f^{-\frac{1}{4}}$, and this appeared to give quite a good straight line (line (3), Fig. 3.3). Although the extrapolation which had to be made on this scale was quite long, it could very easily be done with an accuracy of better than 0.01%. The value thus obtained (77.849 ohms) was actually only 0.26 ohm (or just over 0.03%) lower than that given by the best straight line extrapolation for the corresponding $R\text{-}f^{-\frac{1}{2}}$ plot; when the slight curve of the latter is considered, the former value is probably very little in error. There is no theoretical justification for assuming that an $R\text{-}f^{-\frac{1}{4}}$ extrapolation is correct, but since it was necessary to find the resistance at infinite frequency, and since this appeared to give a more consistent value than could be obtained from the $R\text{-}f^{-1}$ and $R\text{-}f^{-\frac{1}{2}}$ curves, it was decided to use these plots for extrapolation in all measurements made with the heavily platinised electrodes.

3.23 Results.

In order to obtain consistent results, it was found advisable not to leave the 0.01D KCl in the cell unnecessarily long. This was because, not only did the parallel capacitance increase gradually with time, thereby causing a larger polarisation correction (see p.146), but the resistance was also found to change slowly -- in this case, a decrease which was quite appreciable: in one determination, for instance, a drop of about 0.05 ohm was observed after the solution had been left in the cell for a week, i.e. a change of about 0.01% per day. Variations of a similar order of magnitude were found on several other occasions as well, so that it appeared that all measurements made within one day of filling the cell were still within the limits of accuracy desired. It was thought that the effect might be due to the greater rate of increase of conductance of water which has been observed when solutes are present (cf. the remarks made on p.68, and also the increased rate found after KCl had been added to water during the titration experiments -- see Section 3.333). However, the change could also have been caused by evaporation. Although no specific mention was made of gas being passed continuously over the top of the solution in the cell during these particular determinations, it seems likely, from a careful scrutiny of all the relevant notes, that such flow was indeed taking place. If so, then evaporation would definitely have occurred, to the extent of almost 0.01% per day (see Section 3.322), i.e. about the same amount as would be required to produce the observed resistance changes. Very probably, therefore, the resistance would show much smaller variations if only the gas, which had been passed through the water in the potash bubbler and hence was saturated at 25°C, were allowed to pass through the cell.

The cell constant found for Cell II was 0.10899 cm^{-1} with bright electrodes, and 0.10892 cm^{-1} after platinisation. Since the cell constant $Q = \frac{l}{a}$ (where $\underline{l}$ = distance between electrodes, and $\underline{a}$ = area of electrodes), this decrease is to be expected, because the heavy coating of platinum black will effectively bring the electrodes closer together without changing their area appreciably.

The individual values determined at various times for the constants of Cells I and II, together with the sources of the potassium chloride used, are given in Appendix B. No significant changes were found to occur over any length of time, not even after Cell II had been placed in a thermostat at 45°C to hasten its leaching out (see p. 186), nor when it had once been accidentally heated to 55°C. Malan[15] has stated that the maximum change in cell constant over this range of temperatures is 0.04% of the value at 25°C; hence no appreciable permanent change would be expected in the latter value as a result of the heating which the cell received, even though there was some hysteresis during the subsequent contraction of the glass.

3.3 TITRATION OF POTASSIUM CHLORIDE INTO WATER.

3.31 Outline of Method.

The aim of these experiments was to investigate the adsorption effects which take place when a very dilute solution of potassium chloride is placed in a conductance cell. The method of approach, as outlined briefly in Section 3.1, was to add small amounts of potassium chloride to conductivity water which had already been aerated in the cell to beyond its minimum conductance (see Section 2.31). Immediately after each addition the resistance would be determined, and further measurements would be made at frequent intervals with the minimum amount of interruption of the passage of stirring gas through the liquid. Also, the theoretical resistance of the cell corresponding to each addition would be calculated and compared with the measured value. It was hoped that, if adsorption did take place in the cell, any deviations revealed by this comparison, taken in conjunction with the results of the close following of the resistance trends after the additions, would yield information regarding the nature of the adsorption process(es). These titrations were to be performed under a variety of conditions, in which all possible combinations of three different stirring gases (nitrogen, oxygen, and hydrogen) and of two electrode conditions (unplatinised and heavily platinised) would be used.

In order to calculate the resistance of the solution in the cell at any time, it was necessary to know: the concentration of the solution, i.e. the exact volume of the solution and the exact weight of potassium chloride present; the conductivity of the water; and the cell constant. Of these quantities, the determination of the last-mentioned has already been fully discussed in Section 3.2.

The volume of the solution (about 200 ml) could be calculated if either a known volume or a known weight of conductivity water was placed in the cell originally. The gravimetric procedure was preferred because it was considered to be more accurate than the volumetric method, and also because the latter procedure would entail drying the inside of the cell each time that water was to be introduced for a titration. Of course, such drying would also be necessary in the gravimetric method, since the dry weight of the cell would have to be known before the weight of water placed in it could be determined. However, drying would not have to be performed as frequently, provided that the weight of the cell remained reasonably constant over long periods of use. This was shown to be the case: the extreme variation found in the dry weight of the cell, which was determined periodically over 15 months, was 0.051 g in a total of 289 g. This would correspond to a maximum error of 0.025% in the weight of the 200 g of liquid in the cell.

Although the gravimetric procedure was chosen for the above reasons, the real wisdom of the choice only became apparent when it was noticed that the quality of the first portion of water placed in the cell immediately after it had been dried on the inside was always rather poor -- the conductivity was often about 60 - 70 nm/cm higher than normal, and sometimes even more; subsequent portions, though taken from the same flask of water, again had more or less normal conductivities. This phenomenon, the reason for which has been discussed in Section 2.32, would have rendered the volumetric method unsuitable if the titration were to be performed with water of the best quality in the cell.

The choice of method also proved to be good for another reason. During the course of these experiments it was found that, when the solution was left in the cell for some time, the weight of the bulk of the liquid in the cell gradually tended to change. Usually it decreased owing to losses by evaporation and by spraying of the liquid as a result of the stirring gas passing through it; but in some cases there was even an increase in weight! These phenomena, which will all be described more fully in Section 3.322, made it essential to weigh the cell at the end of a titration as well as at the beginning, in order to determine the magnitude of any changes which had occurred. The gravimetric procedure, therefore, was actually the only accurate method of performing these titrations.

The concentration range which was to be investigated was from 10^{-4} to 10^{-3} equiv./l. Since it was desired to cover this range in ten additions to the cell, the weight of potassium chloride required for each addition (about 1.5 mg) was obviously too small to be weighed and added accurately. The titration was therefore performed by adding aliquots of a more concentrated stock solution of potassium chloride. Once again the gravimetric method was preferred for determining the amounts added, because the small volumes required could not be measured volumetrically with the same accuracy. The weight burette used for this purpose has been fully described in Section 1.51. The standard aliquot chosen was approximately 0.2 ml, although a larger amount could obviously be weighed with greater accuracy on the only balance available (balance BII -- see Section 1.41); but several blank tests had shown that the resistance changes which occurred immediately after the addition of 2-ml portions of conductivity water were rather large (10 - 20 ohms) and would tend to mask the other immediate effects (if any) which were being sought. These changes resulted mainly from the removal of appreciable amounts of dissolved carbon dioxide added with the water, and partly from fresh temperature equilibration since the aliquot was seldom at exactly 25°C. The addition of 0.2-ml portions, however, would cause hardly any change in the temperature of the solution inside the cell -- only 0.001° for each 1° by which the temperature of the stock solution differed from 25°. Four further blank tests were performed in which this quantity of conductivity water was added to water, which had been aerated in the cell, by the standard procedure to be adopted during the titrations. In each case, the first reading after restarting the stirring showed a drop in resistance, which varied from 1.1 to 2.4 ohms, i.e. the conductivity had changed by approximately 1.3 - 2.9 nm/cm (see Appendix D). With the stirring rate being used (about 90/30), mixing appeared to be complete within 2 - 3 minutes, as indicated by the constancy of the resistance. This time was about the minimum required to perform all the operations necessary during an addition, so that the resistance was, in fact, already constant by the time that the first reading could be taken (in all cases but one, when it changed by 0.1 ohm only). With continued stirring the resistance soon began to rise very slowly, and in about 1 - 1½ hours a maximum was reached which was within a few tenths of an ohm of the value that the resistance would have had had no addition been made (this value was obtained by extrapolation of the water resistance line -- see Section 2.31). Hence it appeared that the addition of 0.2-ml aliquots would cause only very small immediate changes in the observed resistance, and negligibly small permanent changes. This volume was therefore chosen as standard for all additions. The methods of delivering this small amount from the burette and of determining its weight with reasonable accuracy (0.05% or better) have been described in Sections 1.52 and 1.54.

The preliminary titrations (Expts. 1 to 3 -- see Section 3.325), in which single aliquots were added on separate days, were performed for a dual purpose: firstly, to acquire technique in making an addition accurately to the cell, since this involved a very rapid but quite complicated sequence of operations if the immediate effects were to be observed and at the same time all precautions were to be taken in order to maintain the high standard of precision desired; and secondly, to see what sort of effects could be expected and for how long they persisted, because at this stage there was no information whatever available on the behaviour of the resistance after such additions. It was anticipated that, if any changes did occur, they would be greatest after the first additions, and these solutions were therefore always left in the cell for two days before proceeding further; during this time, frequent resistance measurements were made, particularly shortly after the addition. Subsequent additions were also at first left for two days each, but later the aliquots were added on successive days.

It soon became evident that the changes occurring after the first addition were indeed the largest, though even they were not very big (of the order of 0.1% or less of the measured resistance during the first few hours after addition); also, although erratic variations appeared every now and again, all regular changes other than the dropping of the resistance at a more or less steady rate definitely came to an end in well under a day. From the second addition onwards the changes were still smaller, and it appeared (if erratic variations were neglected) that, within 3 - 4 hours after the addition, the resistance was once again dropping slowly but steadily. It seemed, therefore, that it was not necessary to leave the later additions in the cell for long periods before proceeding to the next addition. This was very important, for these preliminary experiments revealed what would probably be the major uncertainties in the titrations which were envisaged.

One of the chief factors affecting the accuracy of the calculation of the resistances was the correction for the solvent conductance. It had, of course, been realised that the latter would increase as the liquid was left in the cell due to the "solution of glass". But it was intended to use for the titrations only very good quality water (conductivity less than 100 nm/cm, and changing by about 0.5 nm/cm/h or less): the total change during several days should therefore still be fairly small, and hence slight errors in estimating the water correction on the basis of its initial rate of change would not appreciably affect the much larger conductivity of the solution. However, it appeared that not only was the rate of increase of conductance much faster for the potassium chloride solutions, but it differed between additions as well -- variations from $1\frac{1}{2} - 5$ times the rate for water were obtained. Since the reason for this faster rate of increase was not known, it was a little difficult to see quite how to allow for it in calculating the conductivity of the solvent for each addition.

The two solutions to the problem of the solvent correction seemed to be: either to perform the whole titration as rapidly as possible, thereby not allowing time for the solvent conductivity to change much from its initial value at the time of the first addition, and hence diminishing the error in its estimation; or to assume that the uniform rate of decrease of resistance observed with each solution resulted merely from a normal increase in the solvent conductivity, and then to correct the latter accordingly by leaving each addition in the cell for long enough to give an accurate estimate of the rate of change of the conductivity, i.e. till the resistance had been dropping steadily for quite a while. There were, however, objections to both these solutions. The first would defeat the aim of the experiments, which was partly to follow the changes in resistance after each addition until steady conditions had been re-established; whereas the second, although fully realising this aim, meant that each experiment would take very long to be completed. Apart from the obvious disadvantage inherent in the length of time required, such protracted experiments tended to introduce a whole host of new troubles. Thus erratic variations, up to 0.05% of the measured resistance, had already been encountered in the preliminary titrations. These not only spoilt any smooth trend shown by the resistance, but they were also large enough to be disturbing in view of the precision being sought (0.01% or better in the constancy of the resistance, which could itself be measured accurately to 0.001%).

Variations of resistance of differing degrees of magnitude could arise from any one of a number of causes: inconstancy of the temperature, either of the thermostat, which would change the temperature and hence the conductivity of the solution, or of the room, which would affect the values of the bridge resistances; inconstancy of the bubbling rate; gradual saturation of the rubber connections with paraffin vapour (see p.67); drops of liquid being blown into the cell from the copper coils (p.124); drops of liquid running back into the solution from the upper walls of the cell, where they had been deposited by spraying or condensation; and so on. In each case the possibility of the effect occurring during the course of a titration was enhanced by lengthening the time that the cell was in the thermostat. In fact, so many of the large number of conditions which had to be maintained constant throughout these experiments were normally controlled automatically that the risk of the results of an experiment being vitiated owing to the failure of one or other of the controls increased greatly with time. This had already been clearly demonstrated by several such troubles encountered during Expt. 2: for instance, the stirrer of the thermostat was jammed several times by a piece of loose magnesium foil in the outer bath, and the resultant lack of stirring caused large fluctuations in the temperature of the solution; then the refrigeration unit used to cool the air being drawn into the room did not function satisfactorily during a spell of warm weather, and made it very difficult to keep the room and thermostat temperatures down to 25°C; and when this had been fixed, the experiment still had to be abandoned shortly afterwards because the relay controlling the room temperature failed, and had to be dismantled and repaired.

Troubles of the above nature could perhaps be avoided, even during a lengthy experiment, by frequent careful checking of the numerous factors involved in maintaining completely constant conditions for all the resistance measurements; yet even then, it seemed, a fair share of good fortune was required! But the preliminary titrations revealed another major uncertainty, viz. the calculation of the exact concentration of the solution at any time, for it was found that the weight of the bulk of the liquid in the cell did not remain constant throughout the experiment (allowance was made, of course, for the increase owing to the known weight of KCl solution added). In Expt. 1, for instance the weight of liquid at the end of the 14 days for which the cell was in the thermostat was almost 1.4 g lower than the combined weight of water initially plus all the additions. That this loss was real and not due to weighing errors was confirmed in the two subsequent titrations. It seemed to arise from evaporation and spraying of the liquid as a result of the continuous passage of gas through the cell. Whatever the cause, however -- it was ascertained and will be discussed later --, it was obvious that, with such a large loss, any correction made in order to estimate the concentration of the solution after each addition could entail quite a considerable error; also that, if the loss could not be entirely eliminated (which did not seem possible), then the error in correcting for it could at least be diminished by shortening the whole experiment and thus reducing the size of the change in weight.

The various considerations just discussed suggested the best procedure to be followed for these titrations. This was naturally a compromise between an unduly long experiment with all its undesirable features, and one which was too short to allow all the possible changes in resistance to be observed closely. A standard bubbling rate of 60/30 was chosen (also a compromise, for reasons given in Section 3.322); with this stirring rate the maximum resistance of the water was usually reached in about 6 - 8 hours. In order to make quite sure that all volatile impurities had been removed, however, and also so that the rate of change of the water conductivity might be known, it was necessary to leave the water alone in the cell for rather longer than this time. It was decided, therefore, always to place the cell in the thermostat on the day preceding the first addition, and to follow the changes in the resistance of the water after maximum until the addition was made. During the preliminary titrations, the observed changes in resistance, even after the first additions, had been rather small and apparently complete within about 8 hours. This would not necessarily be the case in the other titrations, however, since the first experiments had been performed with nitrogen stirring and unplatinised electrodes -- the conditions under which adsorption was expected to be least. Nevertheless, it seemed certain that the largest changes would still take place after each first addition. It was therefore proposed to add only one aliquot to the water on the second day of the experiment, and to follow the variations in resistance, closely at first and later at longer intervals, for about a full day. Then on the third day all the remaining additions would be made (if possible), because it seemed that the changes taking place would be much smaller and would go to completion much more rapidly.

The procedure outlined became the standard method of performing these titrations. The programme proved to be very exacting because of the high standard of precision which had to be maintained throughout the whole experiment: an error in any of the additions, for instance, whether in determining its weight or in the actual adding of the aliquot to the cell, would be reflected not only in the addition concerned, but also to a diminishing extent in all subsequent ones. The titration would therefore have to be abandoned at the first obvious mistake, while unobserved errors would become apparent only when the results had been calculated. The last day in particular was very exhausting, and tended almost to make these titrations tests of endurance rather than of skill: the outstanding example was during the prototype experiment, when nine additions were made in one day. It was discovered that, what with having to rinse and fill the burette, weigh it accurately twice, make the addition, measure the resistance every few minutes, keep a constant check on the bubbling rate, record all readings, and make notes of any irregularities, the shortest interval between any two successive additions was 85 minutes -- this in spite of working at top speed all the time. In fact, the first two minutes of complete rest taken on this day were snatched more than eight hours after the start, and then only as a result of judicious planning for more than an hour beforehand! The full titration required the author's presence in the constant temperature room for a continuous spell of 14 hours, after which the cell still had to be removed from the thermostat and weighed by the normal procedure. This experiment, however, indicated that it was probably not necessary to do as many as ten additions in all, and the standard number aimed at later was five -- one on the second day and four on the third. Each of the latter additions could then be left in the cell for 2½ - 3 hours, which made the work not quite so rushed and also allowed a longer time for the resistance to attain a steady state. Even this programme, however, was quite tiring, because the continual occurrence of unforeseen events and the random appearance of unusual resistance variations made it desirable in the later experiments to check the resistance after the first addition occasionally during the night as well. Only one experiment deviated considerably from this general procedure. In this case (Expt. 12), circumstances had indicated that it might be wiser to do the whole titration as rapidly as possible, and it was therefore performed from start to finish in 31 hours; but this involved a spell (from before the first addition to the end of the experiment) which required the author's presence in the laboratory for 21¼ hours! Although this was not as continuous as in the previous case mentioned, it was nevertheless pretty exhausting, and the procedure was obviously impractical as a routine method; in fact, despite the successful completion of the experiment, it seemed that the titrations were really best performed over three days if this could be arranged. Needless to say, no other marathons of this nature were attempted!

3.32 Experimental.

3.321 Stock solution of potassium chloride.

Since the aliquots to be used had a volume of 0.2 ml, the stock solution of potassium chloride had to be about 0.1 N in order that each addition might change the concentration of the liquid in the cell by approximately 10^{-4}N. This solution was stored in a 250-ml Pyrex flask which had a B 34 cone sealed to the neck, and which was covered with a cap made from the corresponding socket: an outside ground glass joint was used so that the solution would not come into contact with it. Before the solution was prepared, the flask was well cleaned with both the alcohol-nitric acid and the chromic acid cleaning mixtures, and steamed out for several hours; it was then left standing for five weeks filled first with fresh conductivity water, followed by five changes of approximately 0.1 N KCl. This "seasoning" process ensured that the walls of the flask would not adsorb any K^+ or Cl^- ions on preparation of the final solution, and also removed all traces of other adsorbed material, such as acids from the cleaning process. Thereafter the stock solution was prepared with A. Faure's potassium chloride[2], the method used being similar to that described for the preparation of the standard 0.01 D KCl solutions (see Section 3.21). However, no great care was taken to make the solution exactly 0.1 N, as the size of the aliquots would in any case be variable; in fact, the exact normality was not even calculated, but only the number of equivalents which would be added to the approximately 200 g liquid in the cell (as weighed on balance B III) if exactly 1 g of stock solution were weighed on balance B II and added to the cell (both weights corrected to vacuum). No further correction for the different inequalities of beam-length of the various balances (given in Appendix C) had therefore to be made to the weight of solution (in vacuo) obtained on balance B II, since these corrections were all taken into account when the conversion factor, from weight of solution to number of equivs. KCl added was derived for these particular titrations.

This stock solution was used over a period of 15 months for all the Expts. 1 to 13 (Section 3.325) and for innumerable other trial additions and measurements. Throughout the whole of this time the flask was kept in the constant temperature room, and it was only opened, after the room fans had been stopped, for as short a while as possible whenever it was necessary either to rinse or to fill the burette: in this way it was hoped to keep evaporation from the solution down to a negligible amount. Immediately before each occasion on which the solution was used, uniformity of the concentration was ensured by shaking the flask well in order to mix the water, which had evaporated from the solution and condensed on the upper walls and cap during the previous periods of standing, with the main bulk of the solution. For the rest, however, there was no agitation of the flask at all.

In spite of the precautions taken during its preparation and of the careful treatment which it received in all subsequent operations, the solution did not maintain a constant conductivity throughout the period of its use. This change was first suspected about the time that Expt. 10 was completed, because there seemed to be a trend in the end results of the various experiments (see Section 3.34). Nevertheless, since numerous difficulties had been encountered during the performance of many of these titrations, and since it was by no means certain that the effects observed did not reflect the true results of the experiments -- the eventual general pattern of results was not yet quite clear --, the same stock solution was still used for the titrations with platinised electrodes as well (Expts. 11 - 13). The persistence of the trend through these experiments too, however, led to an investigation whether the stock solution still had the same conductivity as at the time of its preparation. This check was performed by preparing two 0.01D KCl solutions by suitable dilution of aliquots of the stock solution, and then comparing the cell constants obtained with these diluted solutions with the values determined with similar solutions prepared directly from purified potassium chloride crystals. It was very disconcerting indeed to find that the mean of the former two values was only 0.10820 cm^{-1}, i.e. 0.66% lower than the true constant of 0.10892 cm^{-1}, for this meant that the stock solution was then in error by the same amount, its conductivity having increased since its preparation. This result was contrary to the observation made by Randall and Scott[87], who found that the conductivity of a potassium chloride solution which they had prepared diminished considerably after it had been left standing for several months. Their solution, however, was not disturbed during this period, and it was not even shaken before the required quantity was pipetted out for the final resistance determination, so that the conditions in the two cases were not exactly analogous.

The reason for the comparatively large change in the conductance of the stock solution is not quite clear, but several factors might have been responsible. Thus it might have arisen from the frequent insertion into the solution of the tip of the burette, which was always first wiped dry with a clean handkerchief: the dried surface would have caused some increase in the conductivity (see Section 2.32); also, when the remaining solution in the flask was examined closely, a number of tiny threads were seen which probably came from the wiping procedure and which might have contributed to the conductance, either by themselves or through introducing other impurities adhering to them. Then, too, slight evaporation might have taken place during the frequent but necessary opening of the flask, in spite of the precautions observed: this would have concentrated the solution and hence increased its conductivity. Finally, the increase might also have been due to the greater rate of change of solvent conductivity which occurred in potassium chloride solutions by ion-exchange with the glass walls (see Section 3.333); this would have been assisted by the periodical shaking and mixing of the contents of the flask. Probably the total increase of the conductance resulted from a combination of all these factors.

Whatever the cause of the change in conductivity, it seems advisable in future work along these lines to prepare the stock solution in smaller amounts than the 250 odd ml used in this investigation, and not to keep it so long; fresh portions could be made up if the previous lot were more than, say, a month old when required for an experiment. A new solution was, in fact prepared and used in Expt. 14. This was a repeat of Expt. 13, and it was performed both in order to check the correctness of the results of the latter, which were so very different from those obtained for all the other experiments, and also to show that the trend which had been found in all the end results was really associated with the change observed in the conductivity of the stock solution.

3.322 Rate of passage of gas through cell.

The loss in weight of the bulk of the liquid in the cell, which occurred while the first preliminary titration (Expt. 1) was being performed, has already been mentioned in Section 3.31. During the course of this experiment, and also of all the others in which the cell was in the thermostat for more than a day, liquid accumulated gradually inside the cap on the cell, until eventually it tended to run down the sides and out of the cap when this was removed in order to make an addition; also, at the conclusion of the titration, an appreciable amount of liquid was observed to be adhering to the neck of the cell. Some of the loss in weight during Expt. 1 was due to occasionally wiping out the liquid in the cap in order to prevent its running back into the cell, and also to removing the liquid from the neck at the end of the experiment. The estimated weights of these quantities of liquid, however, were definitely not large enough to account for the total loss found. The same appeared to be true for Expts. 2 and 3 as well -- in each case there seemed to be a distinct loss in weight from the bulk of the liquid of 0.3 - 0.4 g.

During these preliminary titrations, nitrogen was passed continuously over the top of the liquid in the cell (rate about 120/30) as well as through it. The former gas-stream, unlike the latter, did not flow through a bubbler filled with conductivity water placed inside the thermostat, but only passed through a water-filled bubbler in the constant temperature room (see Section 1.62). It was therefore saturated only at about 24°C, and hence it seemed likely that evaporation losses resulting from the passage of this gas over the liquid in the cell at 25°C might have been the reason for the comparatively large decrease in weight which was observed. This was tested by leaving the cell in the thermostat for three periods of four days each, during which the contents of the cell were not stirred at all but nitrogen was merely passed over the top (4 - 5 bubbles per sec). At the end of each of these periods, slight but definite traces of moisture were visible on the inside of the cap and of the upper portions of the cell, which had all been quite dry at the start of the experiment; the amounts, however, were very much less than in the case of Expts. 1 to 3, and they had presumably resulted from condensation on those parts of the cell which were not immersed in the thermostat liquid and hence may have been slightly cooler. A definite loss in weight also occurred in each test, but it was only about 17 mg (approx. 0.01% of the total weight) per day. This was not large enough to explain fully the changes actually found. Nevertheless, since some loss was taking place by evaporation, in future the passage of gas over the top of the liquid in the cell was used only during the actual additions of KCl solution, and sometimes during the final resistance measurements over the range of frequencies.

Since the weight did not remain constant even after the stopping of the secondary gas-stream, the only remaining possibility was that the decreases were associated with the passage of gas through the liquid. Losses could occur by two mechanisms -- either by evaporation, if the air were not fully saturated, or as a result of the spraying of drops of liquid out of the main bulk by the bubbles breaking through the surface. The former was unlikely, in view of the fact that the stirring gas was passed through two bubblers with water at 24° and 25°C respectively prior to its entry into the cell: it should therefore have been sufficiently well saturated not to cause any large loss by evaporation, especially since the gas passing over the top, which had been saturated only once (and that at 24°C), caused but a relatively small decrease in weight. In any case, it was quite impossible to separate and distinguish losses by this mechanism from those occurring as a result of spraying from the liquid surface -- a process which definitely did take place.

The spraying phenomenon was first observed very early in these investigations -- in fact, during the tests which were made before the construction of Cell I in order to determine the positioning of the capillary tube (see Section 1.31): small droplets of water were seen to be deposited every now and again on the bare walls of the test vessel, some as high as three inches above the level of the liquid surface. This occurred with a very rapid bubbling rate (about 5 - 6 per sec), but it seemed to be almost absent at slower rates of 1 - 2 per sec. These observations were recalled when it was noticed that the condensed film of liquid, which was found on the exposed parts of the cell after the experiments on the passage of gas over the top of the solution only, was very much less than the amounts which normally accumulated in the cap and neck of the cell whenever a titration was performed. It seemed hardly likely that the latter quantities could all have been due to condensation, even from the more saturated gas emerging from the solution. A visual test was therefore made in which the cell was filled to the usual level with water but left outside the thermostat for about $\frac{3}{4}$ hour after it had been connected to the normal gas-stream. This test showed that at a bubbling rate of 90/30 some spraying of the liquid was definitely taking place: during the period of observation, quite a large number of water drops formed on the bare walls of the body of the cell above the level of the liquid surface, some were deposited on the inside of the neck, and a few very tiny droplets even settled on the inside of the cap placed over the neck (about 4½ inches above the surface). The effects were obviously being caused by the bursting of the bubbles of gas through the surface of the liquid. It is interesting to note that the mechanism by which the bursting of bubbles in the surface of liquids results in the vertical projection of one or more fairly large drops of liquid has been clearly demonstrated (subsequently to the completion of the experimental work in this thesis) by the high-speed photographic studies of Blanchard and co-workers[99,100], Newitt and co-workers[101], and Mason[102]. Apparently the liquid rushing into the crater that is left in the surface at the site of the burst bubble ejects an unstable jet, which then breaks up into discrete drops. The mean diameter of the drops produced by a breaking jet was roughly 15% of the diameter of the parent bubble[102], and the heights of projection ranged from about 0.5 to 15 cm[99].

These conclusions reached from high-speed photography agree very well with the observations made during the visual test in particular and all the experiments in general. Since the mere bursting of the bubble in the surface is sufficient to form a droplet which may occasionally be deposited on the upper walls or neck of the cell, or inside the cap, the spraying effects can obviously never be completely eliminated as long as stirring by a current of gas is employed, but can only be reduced by slowing down the rate of bubbling. This had been found to be the case, and it seemed desirable from this point of view to use a very slow stirring rate. However, too slow a rate might allow back-diffusion to occur despite the presence of the cap over the cell-mouth; also, the initial removal of carbon dioxide from the water would take very long, and mixing after each addition would not be too rapid, so that the immediate resistance changes might perhaps escape detection. As a compromise between all these factors, a standard bubbling rate of 60/30 (about 45 ml gas per minute) was finally chosen, except immediately after each addition, when a rate of 120/30 was used for five minutes: this had previously been shown to be more than ample to ensure complete mixing of the solution.

Under these conditions of passage of gas through the cell -- 60/30 bubbling through the liquid and none over the top -- the changes in weight during an experiment were found to diminish appreciably. Nevertheless, there still appeared to be a nett loss in weight from the bulk of the liquid of about 0.2 - 0.3 g, and this increased to over 0.7 g in Expt 6. Most of this large loss was accounted for by the considerable amount of liquid which had been deposited on the upper portions of the cell by the spraying and which was still adhering there at the end of the experiment. However, even though the total weight was almost constant, the weight of liquid in the bulk was the significant factor in calculating concentrations, and a state of affairs in which liquid was permanently separated from the main bulk after it had been removed by the somewhat diminished but not completely avoidable spraying was obviously rather unsatisfactory. When this had been remedied (see next section), the weight of the bulk of the liquid in the cell changed only very slightly during an experiment, and the total weight (inclusive of liquid adhering to the neck and inside the cap) was found to be almost constant in most cases; in fact, there was sometimes even a tendency for the weight to increase a little, particularly when hydrogen stirring was being used -- the total weight in these cases was on an average about 80 mg larger at the end of the titration than it should have been! The reason for this gain in weight, which appeared in each of the experiments with hydrogen, is not known. It was noticed, however, that spraying seemed to be much more pronounced when hydrogen was used for stirring than with the other gases, for liquid definitely accumulated in the cap much faster: possibly, therefore, the increase in weight was due to water being carried over from the potash bubbler in the form of spray, though how it managed to traverse the copper coil without settling out before it entered the cell remains a mystery.

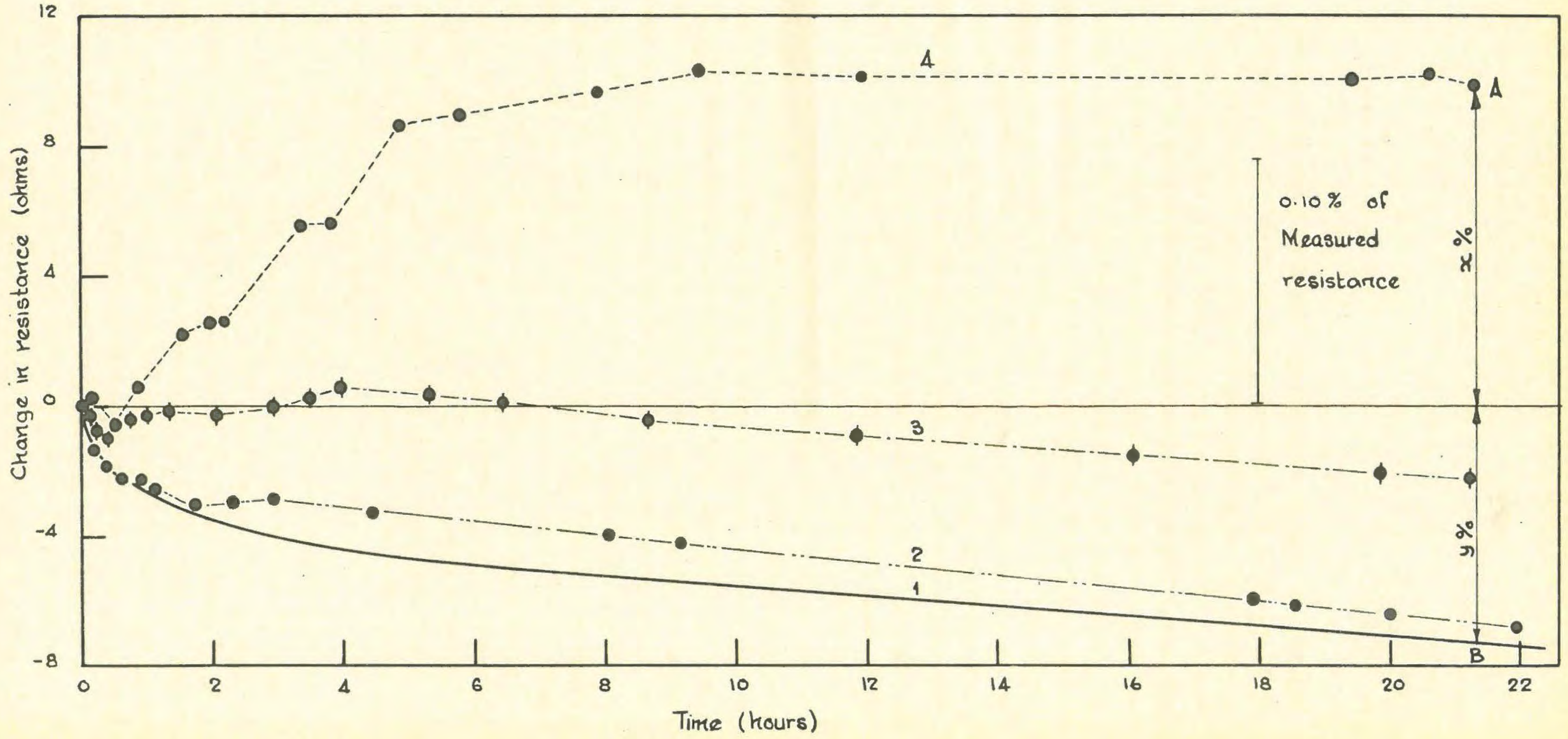
3.323 Cleaning the cell.

The cleanness of the internal surface of the cell, especially of the upper portion above the normal level of the liquid, was a factor of major importance in the successful performance of these titrations. It had been realised at the outset of these experiments that the significant factor when determining the weight of the liquid placed in the cell was the weight of the bulk, since the resistance changes of this portion would be observed after each addition, and hence the weights both of water and of KCl present here would have to be known accurately in order to do the calculations. For this reason, tests were made of ways and means of filling the cell with water without wetting the upper portions. The final method adopted was by means of a funnel specially kept for this purpose (see Section 1.33 for filling of cell).

Although the cell had been very well cleaned after its construction, and although it was never filled with anything but conductivity water and very dilute solutions (maximum concentration 0.01D), its internal surface gradually became contaminated in some way over a period of several months of use, and drainage of liquid from the walls, particularly at points just above the normal surface level, was no longer as good as in the beginning. This was evident from the solution which was always found adhering to the upper walls and neck of the cell at the end of an experiment. Also, in one of the experiments, the cell was carefully filled and weighed, but was then accidentally shaken as it was being transferred to the thermostat; this caused the liquid to run a little way up the sides, and subsequently a ring of water remained on the glass about 1 cm above the general surface level. Effects such as these were considered most undesirable, but at first they seemed also to be unavoidable; empirical corrections were therefore made for them during the calculation. Thus the solution adhering to the upper portions of the cell was assumed to have been deposited there by spraying at a uniform rate, and a proportional correction for such losses was applied to the weight of the liquid (and of the KCl) in the cell at any time; the ring of water, on the other hand, was disregarded, partly because its weight was estimated to be less than 0.05% of the total weight of liquid, and also because more water would in any case have been sprayed on to the walls by the time that the first addition was made. These corrections proved suitable for a while, until further effects resulting from poor drainage became apparent, for which no accurate correction was possible.

From a study of the results of all the experiments, it seems that under ideal conditions the typical curve for the change in resistance after the first addition of potassium chloride to water should be as shown by the continuous line (1) in Fig. 3.4. But, as has already been mentioned in Section 3.31, erratic variations of the resistance were frequently encountered in the early experiments; this can be seen from the results shown by the various dotted lines in Fig. 3.4. Sometimes the variations were small and did not affect the

Fig. 3·4 - Variation of resistance after several first additions of potassium chloride to water.



general trend of the resistance, e.g. line (2) (from the results of Expt. 2). In line (3) (Expt. 5), the deviations were more marked, but the true pattern is still apparent in the initial and final behaviour of the resistance, although the rise in the middle destroys the picture as a whole. The climax of the irregular behaviour, however, is shown in line (4) (Expt. 6): the general trend of this graph appears at first sight to indicate a continuous rise in resistance -- irregular perhaps, but nevertheless different to the trends observed in all the previous experiments. This was unfortunate, because it happened to be the first titration performed with a gas other than nitrogen for stirring, viz. oxygen, and the difference was therefore originally attributed to a real difference in behaviour resulting from the change of the stirring gases; in fact, it seemed that in this case an adsorption was taking place, which was causing the resistance to increase after the addition. However, when the cell was removed at the end of the experiment and the large amount of liquid adhering to the walls was observed, and when it was seen how some of the large drops looked almost ready to run back into the liquid, the reason for many of the previous odd variations became clear. Because the drainage from the upper walls of the cell was not good, the liquid which was sprayed out of the main bulk by the bursting bubbles of stirring gas tended to adhere to the glass in the form of small droplets instead of running back into the cell and leaving only a thin film of liquid on the glass walls. With the passage of time, the size of these droplets naturally increased as close neighbours coalesced, until eventually the stage was reached where a drop had become so large that it could no longer stick on the glass, and hence it ran back into the main body of the cell. Since the liquid on the walls was almost invariably less concentrated than the solution in the central bulk, particularly shortly after an addition, this "run-back" into the solution of large discrete drops, instead of a general steady draining back into the cell, manifested itself by sudden increases in the measured resistance, such as can clearly be seen in line (4).

This theory received full support from a few simple calculations and deductions. For instance, the discontinuous changes of resistance in the experiment shown by line (4) were about 2 - 3 ohms: if it is assumed that the liquid running back was pure water -- a justifiable assumption for the first few changes, since these occurred shortly after the addition when very little KCl would yet have been sprayed out of the solution --, then about 0.05 - 0.08g would be required for each variation. This is a reasonable value for the weight of a single drop; the latter value may perhaps seem a bit high, but it must be remembered that the size of the drop entering the solution would almost certainly depend on its point of origin. Thus a drop starting just above the liquid level would be smaller than one which started higher up, since the latter would, in the course of its progress down the side, produce a sort of "snowballing" effect by which it would carry with it some of the liquid adhering to the walls lower down in its path. Secondly, the magnitude of the resistance changes appeared to diminish with time. Such a decrease would be expected, however, even though the drops running back remained constant in size, because the liquid on the walls would gradually become more concentrated as the weaker solution ran back and was replaced by solution of the same concentration as that inside the cell; if the addition were left in the cell long enough, in fact, the water originally present on the walls would eventually be replaced completely by the KCl solution formed by the addition, and further "run-back" would no longer be evident as a change in resistance. Finally, too, there was the fact that these sudden changes occurred at intervals which had some semblance of regularity, but with quite a wide latitude in time -- in various experiments intervals from $1\frac{1}{2}$ - 4 hours were found: this is what one would expect from a phenomenon as outlined. The time interval actually corresponded quite well with the average rate of loss by spraying, which was calculated for Expt. 6 as 0.023 g/h -- a very approximate figure, since several assumptions had to be made; but it definitely agreed with the calculated value given above for the size of the drops, and thus lent further support to the spraying and "run-back" theory.

Besides tending to obscure any changes in resistance due to other causes, the effects which have been described diminished the accuracy of the titrations. Although a remarkably simple and reasonably accurate method of correction for these effects was discovered (see Section 3.334), the better solution to the problem nevertheless seemed to be to eliminate them if possible. This was finally accomplished by very thorough cleaning of the cell walls.

Just before Expt. 6, great difficulty was experienced in obtaining a sample of water of good quality from the still. In an effort, therefore, to improve the quality of the water placed in the cell by cutting out all intermediate steps, the water for Expts. 6 and 7 was not poured in via the usual funnel, but directly from the collecting flask; the excess water adhering to the upper walls of the cell was then wiped off with the aid of a bent wire and a handkerchief which had been specially cleaned for this purpose. Similar wiping had also been used occasionally at the end of various experiments to remove the liquid on the inside of the neck and upper walls before the cell was weighed: in this way the weight of solution left in the bulk could be determined. It appeared, however, from the vast amount of liquid adhering to the upper parts of the cell at the end of these two experiments in particular, and also from other later observations, that such wiping was about the worst method of treatment which could be given to the cell. In spite of the cleanness of the cloth and of the care taken on each occasion, the wiping seemed to leave some sort of a film on the glass surface, so that it was no longer effectively wetted by the water; hence, instead of the water (and solution) draining back evenly, it merely stuck to the surface as individual drops. These were just the right surface conditions to favour retention of the sprayed droplets and cause "run-back" troubles.

Thorough cleaning of the internal surface was eventually effected by resorting to the well-known alcohol-nitric acid and chromic acid cleaning mixtures. The disadvantage of treatment with these reagents was the long period for which the cell could not be used afterwards because of all the acid which had been adsorbed on the walls. The cell was first rinsed with the alcohol-nitric acid mixture (after it had reacted and been allowed to cool, so as not to alter the cell constant); then the chromic acid was poured in, and the cell stoppered and left inverted overnight -- it was, of course, more essential to clean the upper portions, which would not be in contact with the central bulk of the liquid during an experiment, than the main body of the cell. After the acid had been emptied out, the cell was usually connected to the municipal water supply and running water passed through it for about two days. Then it was filled with frequent changes of conductivity water until all the adsorbed material had been removed again: this was tested by placing the cell in the thermostat and observing the resistance of each change of water. At first the resistance did not reach the normal high values, and it also dropped at a much faster rate than usual (see Section 2.31). The criterion of cleanness, however, was that the observed resistance should be normal in both these respects. This always took at least a few days, but in general an average of about 10 days was required for the complete cleaning of the cell before it was again ready for use.

After the cell had been treated in this manner, the drainage appeared to be excellent. In fact, the droplets which were sprayed out of the solution seemed then to drain back steadily, and at the end of an experiment there were usually only a few smallish drops adhering to the glass; also, the weight of the bulk of the liquid no longer changed by more than 0.1 g, and usually by less than 0.05 g. Corrections for any losses could therefore be made very accurately when calculating the concentration of the solution at any time. The cell could be used for several successive titrations before it had to be cleaned again, provided that due care was observed whenever it was necessary to wipe the small droplets out of the neck in order to obtain the exact weights of the liquid in the various parts of the cell.

3.324 General procedure*.

Before every experiment, the bubblers containing conductivity water for saturating the stirring gas were checked to see that there was sufficient water to last through the experiment; if necessary they were filled with fresh water. Any reagents in the purification train about whose effectiveness there was some doubt were renewed as well. The copper coils were also frequently sucked dry (sometimes after being first washed with running water) to ensure that no droplets of liquid would be blown into the cell during the course of an experiment; this was essential particularly when hydrogen stirring was being used, because of the greater amount of spraying which seemed to occur with this gas.

It has already been mentioned (Section 3.31) that the method to be adopted for these titrations was to place the water in the cell on one day, make the first addition of KCl stock solution on the next day, and (if possible) four more on the third day. This general plan was followed in all the later titrations, except where circumstances dictated some other course -- usually a shortening of the time factor of the whole experiment, either because of the poor internal

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* The following sections should be consulted in conjunction with this one:-

(i) Section 1.33 -- for the method of drying and weighing the cell, and of filling it with water for a titration.

(ii) Section 1.5 -- for the description and method of use of the weight burette; in particular, see Section 1.54 for the handling and accurate weighing of the burette.

(iii) Section 1.41 -- for further details of the weighing procedure used in order to obtain accurate weights on balance BII.

(iv) Section 3.2 -- for the method of determination of resistances at infinite frequency.

condition of the cell, or because of the poor quality of the water placed in it. These deviations from the proposed method, as well as any others which were necessary, are mentioned in the short descriptions of the individual experiments (Section 3.325).

In all cases, irrespective of deviations as regards the number of additions or the length of time for which the resistance variations were observed after each addition, a standard procedure was followed for the various operations involved. This procedure was gradually developed as increasing experience and technique were gained from the early experiments, and it was successfully used during all the later titrations.

(a) <u>At beginning of experiment.</u>

The cell, which had been well cleaned and whose dry weight was accurately known, always contained water just prior to the performance of a titration. This was poured out and the cell inverted for a few minutes to let most of the water drain out; the large drops which collected at the mouth were touched off with a clean cloth. The whole cell was then wiped well on the outside to remove all traces of paraffin, after which it was left standing empty in the constant temperature room for about $\frac{1}{2}$ - 1 hour so that its surface could re-equilibrate with the atmosphere and any charge could be dissipated before the weighing was performed. During this period, some condensation of the remaining liquid frequently occurred on the upper portions of the cell, where it was least wanted; this was easily prevented, however, by draping a cloth loosely over these parts. From the time that the cell had been wiped until it was weighed it was handled only with gloved hands; thereafter, of course, the method of handling was immaterial. Just before it was removed to the balance-room for weighing, the cell was filled with water via the special funnel to the 200-ml level, and then stoppered in the normal manner. The temperature and pressure in the balance-room were noted so that the weight of water taken could be corrected to vacuum (see Section 1.43). Immediately after the weighing, the cell was transferred to the thermostat, new pieces of rubber tubing being used for connecting it to the gas lines and for suspending it in the inner bath. Its position in the thermostat was adjusted, as well as that of the burette clamp on the lid, until the burette could be slid centrally in and out of the cell mouth. During all these operations some gas was passed over the top of the liquid in the cell, but not through it in case drops should splash up on to the burette and then run back again, thus contaminating the water. As soon as everything had been centred, the cap was put on the cell, the passage of gas over the top stopped, and bubbling through the water started at a rate of 60/30. The time of starting was noted, so that the length of time of stirring would be known if corrections had to be made for spraying and other losses. Resistance measurements, with the 10,000-ohm resistor in parallel with the cell as usual (see Section 2.31), were taken periodically while the water was in the cell in order to check its quality and to determine the rate of increase of its conductivity.

(b) Addition of KCl stock solution.

Quite a complicated sequence of operations was necessary in order that an addition might be made to the cell with the desired accuracy. Many of the steps had to be performed in rapid succession, and this was possible, without error or omission, only after complete familiarity with the routine had been acquired, as well as a considerable amount of technique. The latter, of course, was gained by practice and experience; the former came from constant repetition of the following detailed procedure:-

(i) The room fans were switched off while the burette was rinsed and filled. Excess liquid was wiped off the jet and ground joint, and the caps replaced on both the burette and the flask of stock solution before the fans were switched on again.

(ii) The burette was well wiped and immediately weighed once in order to obtain a check on its weight. It was then left suspended on the balance for 20 - 25 minutes -- the exact period was usually governed by the time required for operation (iii).

(iii) If the addition was the first of the titration, the time-interval was normally utilised in checking the sensitivity of the automatic balance BII under the load of the weight burette. This was not necessary every time, but it served to restandardise the projection scale reading and ensured that this had not changed since the previous experiment.

For all subsequent additions, the time was spent in determining the resistance at infinite frequency of the solution formed in the cell by the previous addition. Readings were taken at all five frequencies, the values of which were also checked. It was found necessary always to stop the stirring for the final accurate balancing of the bridge; this was done for as short a time as possible. Each series of readings was started and ended at 900 c/s, in order to check whether any drift in the resistance had occurred during the measurements; if there was any, a proportional correction was made to the individual readings. To save time, only one reading (with the ratio arms and the supply voltage direct) was taken at each frequency, except at 900 c/s: at this frequency readings were taken at the end of the series with the ratio arms both direct and reversed. This yielded a correction for ratio arm inequality, which was applied to the value obtained by extrapolating the various resistance readings to infinite frequency (see Section 3.331 for methods of extrapolation used). Hence an overall correction was calculated by means of which any reading during the particular addition could be converted to the corresponding resistance at infinite frequency.

(iv) Immediately after the resistance determinations the burette was accurately weighed; at least five separate weighings were made, and more if any irregularities took place. During these operations the burette was handled with gloves.

(v) The various bridge circuits were switched on.

(vi) The passage of gas over the top of the liquid in the cell was started at a fairly fast rate (about 120 - 150/30).

(vii) The control stopcock in the main gas-stream was adjusted so that the bubbling rate through the cell was increased to about 120/30. As soon as it had been confirmed that the rate was approximately correct, stirring was cut off completely by means of the "On-off" stopcock (there could be no stirring during an addition, in case liquid was sprayed on to the burette).

(viii) A last check reading of the resistance of the previous addition was taken at 900 c/s.

(ix) The room fans were switched off.

(x) The caps on the cell and the burette were carefully removed, and the burette placed in its clamp. From here onwards the burette was handled with bare fingers, as this allowed of better control during the subsequent delicate operations.

(xi) The burette was lowered into the cell to the right depth, clamped in position, and the stopcock turned fully open for $8\frac{1}{2}$ seconds (this was the time which was finally found to result in delivery of about 0.2 ml when the burette was filled to a given level). Sometimes the liquid did not begin to flow spontaneously because the jet was so very fine; it then became necessary to tap the burette until flow started. After an estimated $8\frac{1}{2}$ seconds of flow, the burette was raised from the cell, but only sufficiently to enable its jet to be observed. If a drop of solution was visible there, it was necessary first to remove this, as experience showed it to be almost impossible to replace the narrow burette cap without touching off the drop; the burette was therefore relowered, and the stopcock turned rapidly through 180° before the burette was raised again. This procedure was repeated several times if necessary, until the drop had grown large enough to fall off into the solution. It was deemed unwise to dislodge the drop by too vigorous tapping of the burette, as it might then settle on the walls of the cell instead of in the liquid.

(xii) When no drop, or at most a very tiny one, was present on the jet, the burette was removed from the clamp. Any liquid droplets adhering to it (should it accidentally have touched the neck of the cell) were wiped off lightly, care being taken not to touch the solution on the jet with the cloth. The cap was then replaced as rapidly as possible to prevent evaporation losses from the burette before it could be weighed.

(xiii) The cap was replaced on the cell.

(xiv) The stirring of the liquid was restarted by opening the "On-off" stopcock; the rate was controlled at about 120/30 by the setting which had been made in step (vii).

(xv) The passage of the gas over the top of the liquid was stopped.

(xvi) The room fans were switched on again.

(xvii) The burette was immediately weighed to obtain a check-weight for the addition.

(xviii) The first resistance reading was taken as soon as possible. Thereafter readings were repeated exactly on the minute at two-minute intervals; the interval was gradually lengthened, however, as the changes in resistance between successive readings became smaller. All resistance measurements were made at 900 c/s only, with the ratio arms and supply voltage both direct.

(xix) Five minutes after the stirring had been restarted, its rate was reduced again to 60/30. This rate was checked at frequent intervals during the subsequent period for which the changes in resistance were being followed; a close watch was kept on the temperature of the thermostat as well.

(xx) As soon as the numerous operations allowed a chance (usually about 8 - 10 minutes after the addition), a second check-weighing of the burette was made. If there was no loss -- decreases sometimes occurred by evaporation, but normally only if a drop on the jet had been touched off on the ground glass of the cap -- the burette was well wiped again, and its accurate weight taken after a further 20 - 25 minutes (the same time-interval as with the initial weighing for the addition). The pressure was noted, so that the weight of solution could be corrected to vacuum; the the temperature was, of course, 24°C.

The times corresponding to all readings (resistance, bubbling rate, temperature, etc.) and to the various operations were always recorded; also, wherever possible, notes were made of any troubles which were experienced or peculiarities which were observed during the course of the addition, so that attempts could be made to correct for them, if necessary, during the calculation of the results. Most operations were performed as rapidly as possible, particularly those concerned with the actual addition. Thus steps (vi) to (xviii) took 6 - 6½ minutes on the average -- the times required actually varied from 5 - 8 minutes, being dependent largely on the success of operation (xi), i.e. on how soon the liquid began to flow from the burette and how quickly the drop on the end (if any) was induced to fall off. The resistance readings, too, were taken extremely fast, with the stirring off for the shortest time possible. This was essential, since in many cases, particularly when hydrogen was being used, the resistance changed rapidly as soon as the stirring was stopped; yet it was necessary to do this in order to determine the resistance accurately. The first reading immediately after each addition naturally took the longest, since the value of the resistance was then unknown. With practice, however, and by first balancing the bridge roughly with the stirring still going, it was afterwards possible to take even these readings with the bubbling stopped for only 15 - 20 seconds, and sometimes less. Subsequently, when the value of the resistance was already fairly well known, the readings could be taken accurately and exactly on the minute with the stirring off for as little as three seconds.

(c) At end of experiment.

As soon as the last series of resistance measurements at different frequencies had been completed, the cell was removed from the thermostat and clamped above it to let the excess paraffin drain off. The rubber connections were immediately cut off and replaced by the usual weighing stoppers and cap used to prevent evaporation of the contents of the cell. The cap that was placed over the cell whenever it was in the thermostat was also stoppered; then, in order to determine the weight of solution which had been sprayed into it during the experiment, it was weighed before and after the liquid in it was wiped out. After draining for 10 - 15 minutes, the cell was well wiped on the outside to remove all traces of paraffin, and it was then left standing in the constant temperature room for the usual $\frac{1}{2}$ - 1 hour before being weighed. During the wiping, care was taken not to let the solution in the cell run up the sides and remove any liquid adhering to the upper parts; a close inspection was also made of these parts to see how much solution was adhering there. If there was only a small amount, its weight was merely estimated; but if large, this liquid was carefully wiped out with a clean handkerchief immediately after the cell had been weighed, and the latter was then reweighed to obtain both the true weight of liquid left in the bulk and the weight adhering to the walls. In the later experiments, such wiping was avoided as much as possible because of its deleterious effect on the draining properties of the glass surfaces. As usual, the temperature and pressure were noted in order to correct the weights to vacuum.

3.325 Individual experiments.

The experiments described here are placed in chronological order. Although numbered consecutively, however, they are not necessarily successive, for these are only all the completed titrations in which several additions were made to the water in the cell. Besides these, there were quite a number of others in which, for various reasons, a full titration was not performed. Since their results are of no significance in the final evaluation, they have not been included in this description.

Cell II was used for all the titrations. In general, these were performed according to the procedure outlined in the previous section, and therefore only features which may have a bearing on the final result and irregularities which occurred during the experiments will be mentioned here.

(a) Experiments with unplatinised electrodes.

The first experiments were performed with unplatinised electrodes, since smaller adsorption effects were expected under these conditions. The electrodes received special treatment only once: shortly after the construction of the cell they were cleaned with a mixture of equal parts of 30% hydrogen peroxide and conc. hydrochloric acid, because their surfaces were not very bright after being in contact with the mercury used for the determination of the resistance of the cell leads. This mixture was left in the cell, with continuous shaking, for one minute only; after being rinsed with water, the electrodes then seemed quite clean and bright. They were used in this condition for all the experiments with unplatinised electrodes, and were almost always immersed in liquid, being dried only occasionally when it was necessary to determine the dry weight of the cell. Apart from water, the only liquids with which the electrodes came into contact were the dilute KCl solutions, and very infrequently the strong acids used for cleaning the inside of the cell; after the latter treatment, however, they were always soaked in water for several days so that any adsorbed material could be removed before they were used again.

Experiment 1. Stirring gas: Nitrogen
No. of additions: 5

The additions were made on alternate days, i.e. each addition was left in the cell and its resistance changes followed for two days. The bubbling rate through the liquid in the cell was 90/30, and gas was also passed continuously over the top (rate not recorded). A considerable amount of liquid collected in the cap during this lengthy experiment; to prevent this from running back into the cell, some of it was shaken out at the time of the third addition, and the cap was wiped out when the fifth addition was made.

Experiment 2. Stirring gas: Nitrogen
No. of additions: 3

It was intended to leave the first addition for two days, and then to make several more on successive days. Unfortunately this addition had to be left for one extra day, because the paddle-stirrer in the thermostat was jammed several times by a loose piece of magnesium foil in the outer bath (see Section 1.12); the resultant lack of stirring caused the temperature to fluctuate considerably, and it was deemed inadvisable to proceed with the titration until the loose foil had been located and removed. Hence the second and third additions were only made on the fifth and sixth days respectively. During the third addition, the refrigeration system used for cooling the air which was drawn into the constant temperature room did not function properly on a rather warm day, and both the room and thermostat temperatures were above 25°C for quite a long time. The blocked expansion valve, which was responsible for this trouble, was temporarily repaired; but on the following day the temperatures again lacked control, this time because the thyratron-controlled thermionic regulator for the room[2] had failed. No further additions were therefore made, but the third one was left in the cell for five days while the regulator and refrigeration system were thoroughly overhauled. This experiment was the first titration in which the standard bubbling rate of 60/30 was used; contrary to the eventual procedure, however, gas was also passed continuously over the top of the cell (rate about 120/30).

Experiment 3. Stirring gas: Nitrogen
No. of additions: 5

The first addition was left for two days, during which the changes in resistance were followed; thereafter the remaining four aliquots were added on successive days. The final solution was left in the cell for four days before the latter was removed from the thermostat, so that the whole experiment lasted for nine days. During all this time gas was passed over the top of the cell at a rate of about 120/30, in addition to being bubbled through the liquid at the standard (60/30) rate. On the whole, the temperature and other conditions remained reasonably constant.

Experiment 4. Stirring gas: Nitrogen
No. of additions: 6

This was intended to be a trial run for the first full-scale titration by the projected method, i.e. one addition would be made on the second day, and nine more on the following day. The experiment was abandoned after the sixth addition, however, when the bridge suddenly went completely out of balance while the set of readings at different frequencies was being taken. No immediate attempt was made to trace the fault and continue the titration because, in any case, the sample of water used had been of very poor quality -- its conductivity after aeration was about 265 nm/cm at minimum, as against the normal value of below 100 nm/cm; also, the five additions on the third day had taken rather longer than had been anticipated, and there seemed little chance of completing four more additions on that day. Nevertheless the experiment was very useful as a trial run, and it indicated where the technique could be improved and the operations perhaps speeded up in future attempts at a full-scale titration.

This experiment was the first in which no gas was passed over the top of the cell, except during actual additions;in fact, from this time onwards, the flow of gas through the cell always took place in accordance with the standard procedure.

Experiment 5. Stirring gas: Nitrogen
No. of additions: 10

This was the only titration in which ten additions were made -- the first one on the morning after the water had been placed in the cell, and the remaining nine on the following day. The experiment was very fatiguing on the last day, but everything went off fairly smoothly. The water used was of good quality (about 80 nm/cm), and although there were occasional indications of "run-back" of solution, the changes were very small. The final calculation of results could therefore be done with complete confidence in their correctness.

Experiment 6. Stirring gas: Oxygen
No. of additions: 4

The initial filling of the cell was not performed by the usual funnel technique; instead, in an attempt to improve the quality of the water placed in the cell by eliminating all intermediate steps, the water was poured in directly from the collecting flask (even then its conductivity was only 126 nm/cm just before the first addition). The drops of liquid adhering to the upper walls and neck of the cell were then naïvely wiped off with a clean handkerchief, so that the weight of this water, which was already separated from the main portion to which the KCl would be added, would not be included in the weight determined for the water placed in the cell. Because of this treatment, "run-back" of solution was prevalent in this titration (see line (4), Fig. 3.4), and at the end of the experiment a great deal of liquid was found adhering to the upper parts of the cell in the form of large drops; about 0.73g of solution was, in fact, wiped off at this stage. For the rest, the titration proceeded more or less normally along the standard procedure; bubbling through the cell was 60/30, and oxygen was passed over the top during additions only.

Experiment 7. Stirring gas: Oxygen
No. of additions: 5

As in the preceding experiment, the funnel was not used for filling the cell with water, which was again poured in directly from the storage flask. Although the cell had been cleaned after the previous titration, the drainage from the walls was still somewhat uneven. Once more, therefore, the mistake -- it was realised to be such only subsequently to this experiment -- was made of wiping out the excess water adhering to the walls and neck of the cell. The titration exhibited considerable "run-back", though not quite as bad as in Expt. 6; after the experiment, too, about 0.63g of liquid was removed from the upper parts of the cell. Otherwise the titration was quite normal, even to the presence of the troubles usually experienced while the additions, weighings, resistance measurements, etc., were being made -- minor ones, but nevertheless irritating.

Experiment 8. Stirring gas: Hydrogen
No. of additions: 3

The cell was well cleaned before this experiment in the manner already described (Section 3.323), and it was once again filled via the funnel. No troubles were experienced with the drainage from the walls, but the use of hydrogen introduced new complications. All three additions, for instance, were made by the normal procedure (p. 175); yet although this had so far proved quite satisfactory, it was apparently not good enough under the changed conditions to prevent carbon dioxide from entering the cell. The cap, which was placed on the cell whenever the latter was in the thermostat, fitted the neck very closely, and it had been shown that back-diffusion would not take place as long as the normal passage of gas (60/30) was maintained through the cell: this seemed to be true even when the gas used was hydrogen. But the cap had to be removed for the addition to be made, and although the passage of hydrogen was then still continued over the top of the cell at an even faster rate, the gas was so light that it all escaped from the space above the liquid and was immediately replaced by air. Consequently some carbon dioxide was dissolved in the solution each time that an addition was made, and this had to be removed by the aeration before a steady state was once again set up inside the cell -- a slow process with a stirring rate of only 60/30. The occurrence of this phenomenon was deduced from the fact that, immediately after each of the additions, the resistance began to rise from its initial value, and continued to do so slowly but steadily for about 3 - 4 hours; after the first addition, the total increase was actually over 40 ohms (almost 0.6% of the measured resistance), but in the other two cases the percentage change was less because the addition procedure was speeded up as much as possible, especially as regards the period for which the cell had to remain open. Since these rises in resistance appeared to be due to the removal of carbon dioxide which had entered the cell during the additions, several blank tests were performed after the conclusion of the experiment: these tests confirmed the deduction made about the origin of the unexpected resistance changes. The latter did not affect the comparison of the calculated resistances with the measured values, for each addition was left long enough for the resistance to pass its maximum and start dropping steadily again; the line of decrease was then extrapolated back to the time of the addition to give the immediate value of the resistance. The prolonged aeration required, however, meant that the additions could not be made in rapid succession on the last day; in fact, only two were possible, and the titration was therefore stopped after all measurements on the third addition had been completed. In any case, it did not seem worth while to continue with the experiment, since the observed changes in resistance obviously arose from a side effect, but were nevertheless large enough to obscure other changes which might have been occurring immediately after the additions.

In this experiment, two other phenomena were also encountered for the first time -- the increase in the total weight of the liquid which was contained in the cell and its cap, and the changing of the resistance when the stirring was stopped. The former effect, and the greater amount of spraying which seemed to take place with hydrogen bubbling, have already been mentioned (Section 3.322); the total increase in weight during this particular titration was estimated at 85 mg.

As regards the latter effect, very small decreases in the resistance had almost invariably been found whenever the stirring of the liquid was stopped completely, not only with the water alone (see Section 2.41), but also with potassium chloride solutions. In the latter cases, the downward drift of the resistance had been ascribed by A. Faure[2] to a local heating effect as a result of the passage of current between the electrodes; this explanation seemed quite plausible, for the resistance usually reassumed its original value when stirring was restarted and the whole solution was again efficiently mixed. But the effect observed during this titration, when hydrogen was being used as the stirring gas, was something definitely different. It was, for instance, much faster and more marked, and the resistance had to be measured rapidly in order to get accurate values, particularly shortly after an addition. Usually, therefore, the bubbling was interrupted for as short a time as possible; but about 20 minutes after the first addition, the stirring was left off for rather longer than normal in order to examine the nature and magnitude of the changes which resulted. By this time the effect appeared already to have diminished considerably; nevertheless the resistance (about 7300 ohms) first rose quite fast by about 0.2 ohm, and then proceeded to drop as rapidly; the value when the stirring was restarted after 55 seconds was 0.6 ohm lower than the value immediately after the bubbling had been stopped. This general pattern was repeated in several subsequent readings in which the stirring was shut off for periods of 30 seconds each; on every occasion there was a definite tendency for the resistance to increase during the first 5 - 10 seconds by about 0.1 - 0.2 ohm, but at the end of the 30 seconds it was always 0.2 - 0.3 ohm below the immediate value. The magnitude of the effect gradually diminished with time, however, and the initial increase of resistance later disappeared, leaving only the decrease. The stirring was not left off for longer periods during the early stages of the addition because the back-diffusion of carbon dioxide as a result of the displacement of the lighter hydrogen gas would have interfered with the close following of the resistance trend. About 8 hours after the addition, however, when the resistance had passed its maximum and was dropping at a slow steady rate, the bubbling was completely stopped for five minutes, and readings were taken at $\frac{1}{2}$-minute intervals: the resistance then dropped more or less regularly at about 0.3 ohm/min. This decrease could not have been due to the entry of carbon dioxide into the cell, since more than five minutes were required before the presence of this gas above the liquid would be registered by any marked change in the conductivity (see p.113).

The changing of the resistance whenever the stirring was stopped was not confined to the first addition. Thus similar variations were observed after both the second and the third additions; in each case the effect was again most marked immediately after the addition, and then diminished slowly with time. However, although the general pattern was the same as in the first addition, the actual changes were much smaller in proportion to the resistance of the solution (the total change shortly after the second addition was less than 0.005% during 30 seconds of no stirring).

Because of this change in resistance when the stirring was stopped, no sets of resistance readings were taken at different frequencies during this titration. The measured values were merely corrected to infinite frequency by using the mean corrections obtained in the determinations of resistances of similar magnitudes during previous experiments.

Experiment 9. Stirring gas: Hydrogen
No. of additions: 5

The troubles encountered in the preceding experiment owing to carbon dioxide entering the cell while additions were being made were eliminated by a modification of the standard procedure: instead of hydrogen being passed over the top of the cell for the short period of the addition, purified air from the auxiliary train (Section 1.631) was used (nitrogen would have been preferable, but this was not possible because the nitrogen- and hydrogen-purification trains were common). The effectiveness of this measure had been demonstrated by performing several mock additions, in which water had been placed in the cell and the full addition procedure had been followed except that the stopcock was not turned open and hence no liquid was actually added to the water; the immediate changes in resistance were equivalent to 0.01% or less of the conductivity changes which resulted from any normal addition of the stock solution. This modification was therefore adopted as standard for all titrations in which hydrogen was used as the stirring gas.

This experiment was performed very shortly after the previous titration with hydrogen stirring, without further cleaning of the cell; the drainage, however, was still very good. During the experiment a total increase of 65 mg occurred in the weight of the liquid.

As in Expt. 8, the resistance changed quite noticeably as soon as the stirring was stopped for an accurate reading to be taken. The largest variations in each addition occurred just after it had been made, and they gradually diminished with time; also, the relative changes at corresponding times after each addition decreased with successive additions. The general pattern and the magnitude of the variations were similar to those described in Expt. 8. Again no sets of readings were taken at different frequencies for the correction of the resistances to infinite frequency.

During this titration, several odd rises and falls in resistance were observed. These were correlated with the temporary failure and restarting of the compressor which supplied air for the stirring of the inner paraffin thermostat. It appeared that the lack of stirring caused the temperature inside the cell to drop by about 0.010 - 0.012°: such a decrease would, of course, result in a rise in measured resistance of about 0.03%.

<u>Experiment 10.</u> Stirring gas: Oxygen
No. of additions: 5

Another titration with oxygen stirring seemed desirable in view of the very large amount of "run-back" of solution which occurred during Expts. 6 and 7. The drainage from the upper walls of the cell was now very good, but some drops of liquid were still found adhering to the inside of the neck at the end of this experiment; this was because it had been necessary to wipe it lightly at the conclusion of each of the two preceding titrations. However, only one instance of a small drop running back into the solution was apparent from the resistance-time graphs for the various additions; this occurred during the second addition, and the change produced in the measured resistance was only about 0.01%.

During this titration several details were watched more closely than before because of the phenomena which were observed in the preceding experiments when hydrogen stirring was being used. Thus the liquid in the cell was weighed very carefully at the beginning and end of the experiment: an increase definitely occurred, but the amount (23 mg) was negligible in comparison with the total weight of the solution. The behaviour of the resistance when the stirring was stopped was also followed closely, but there appeared to be only the usual mild downward drift; certainly there were no marked changes such as had been found with the hydrogen stirring.

(b) Experiments with platinised electrodes.

The platinisation of the electrodes has been described in Section 1.34. After the platinisation, the resistance of water placed in the cell was found to drop extremely rapidly because of desorption of the products of the electrolysis: thus, instead of the rate of decrease being less than 1 ohm/h, as had been the case before, it was now almost 20 ohm/h, and it diminished only very slowly from this value with repeated changes of water. The procedure recommended for removing the adsorbed products of platinisation, viz. the electrolysis of a dilute solution of sulphuric acid in the cell[21], helped considerably in reducing the rate at which the resistance dropped; but even then it was still 5 - 6 ohm/h. This meant that the conductivity of the water at minimum did not reach the low values which had previously been considered normal, and also that the quality of the water in the cell deteriorated rapidly. Since only a limited time was available for the performance of the remaining experiments, the cell was kept at 45°C in another thermostat and filled with frequent changes of conductivity water in an attempt to speed up the leaching-out process. However, several days of this treatment did not cause the rate of change of the water resistance to drop much.

Not all the trouble with the rapid change of the resistance seemed to arise from the internal condition of the cell after the platinisation. When the rate of decrease remained so high in spite of both the still and the purification train being dismantled and cleaned, and despite all their reagents being renewed, tests were made of the quality of the water being collected from the still by placing samples thereof in Cell I and then observing the changes in resistance which occurred with nitrogen stirring. This cell had been standing filled with water for a long time, and it was known to be clean inside. The normal rate of decrease of resistance when water was placed in this cell was about 0.3 - 0.5 ohm/h, and it had seldom gone as high as 1 ohm/h; yet in these tests rates from 1.5 - 2 ohm/h were found. The reason for the poor quality of the water is not known, for every piece of apparatus had been cleaned; in fact, some of the reagents in the still and in the train were even replaced again, the copper coils were thoroughly cleaned and dried, and many of the joints in the train were wired fast, without any improvement. Because of the limited time available, therefore, it was decided to carry on with the experiments with platinised electrodes in spite of the apparently poor quality of the water and the much larger rate of decrease of its resistance as against that of the water which had been used in the previous titrations. The experiments would then be performed as rapidly as possible in order that the changes in the solvent conductivity might be kept small.

These difficulties with the internal condition of the cell and the quality of the water did not end the troubles which were experienced during this very trying period. Although it was earnestly desired to begin the titrations as soon as possible, the start was actually scheduled for the latest date which would still allow sufficient time (including a day or two as a safety margin) for the completion of all the remaining experiments; the leaching-out of the cell and the attempts to obtain a good sample of water could then be continued for the longest time possible, in the hope that this would result in an improvement in the solvent conductivity. This hope was not realised; instead it became necessary to postpone the scheduled beginning for a further day because, when everything at last seemed set for the start, the refrigeration unit and the thermionic regulators for both thermostats in the constant temperature room all failed within the space of a few hours. Frantic efforts were made to rectify the faults, the thermostat meanwhile being controlled manually so that its temperature would not drift too far from 25°C and thus destroy the thermoregulator setting. Under the summer conditions already prevailing, it was essential to be able to cool the air which was drawn into the room; yet although the cooling unit had been functioning quite satisfactorily for several weeks, it was now found to have developed both mechanical and electrical faults -- an expansion valve which was no longer efficient and kept getting blocked, and bad contacts which persistently threw out the master switch of the refrigerator. The unit was repaired after much difficulty, but it continued to behave temperamentally throughout these experiments in spite of the frequent attention of the technicians. The thermionic regulators too had given little trouble till this time, and if only the one in normal use with the author's thermostat had failed, it would have been possible to use long leads to the other, which was then available; but both failed! Fortunately the fault in one of them could soon be traced and rectified.

Prior to the first titration with each of the stirring gases, a trial addition was made in order to gain some idea of the resistance behaviour which could be expected in these experiments. The results of these tests will be described under the appropriate experiments.

Experiment 11. Stirring gas: Nitrogen
No. of additions: 5

The trial addition showed that there was a marked tendency for the resistance to rise as soon as the stirring was stopped. The first few readings were taken rapidly, with the bubbling off for as short a time as possible. About 20 minutes after the addition had been made, however, the passage of gas through the solution was stopped completely for a further 20 minutes during which resistance readings were taken very frequently (5-second intervals at first, gradually lengthening to one minute); nitrogen was allowed to pass over the top of the cell during this period in order to prevent back-diffusion of carbon dioxide. The resistance increased very rapidly in the beginning -- a rise of 2.8 ohms was obtained after the first 30 seconds. But the rate of rise gradually diminished with time, and after 13 minutes the resistance reached a maximum: it had then increased from 7640.3 to 7655.8 ohms. Thereafter it began to decrease again, very slowly at first but at a gradually increasing rate. The resistance was 7653.6 ohms, and dropping at about 0.6 ohm/min, when the stirring was restarted 7 minutes after the maximum had been attained. A minute later the reading was 7638.6 ohms, which was roughly the value that the resistance would have had if there had been no cessation of the stirring (estimated from the rate at which the resistance was dropping before the bubbling was stopped).

In the actual titration, the resistance after the first addition also showed a marked tendency to rise as soon as the stirring was stopped, but these changes were not followed for any length of time, the bubbling being interrupted only long enough for the readings to be taken. Nevertheless it was obvious that the magnitude of the variations was diminishing all the time: about 4¼ hours after the aliquot had been added, for instance, the effect had become so small that, when the stirring was stopped for a bit longer than usual, the resistance stayed constant for about 15 seconds before it started to rise slowly. This tendency for the resistance to increase when the solution was not being stirred was noticed in the subsequent additions as well, but to a less marked degree with each succeeding one; in fact, it had virtually disappeared by the fourth addition.

Despite the many difficulties which had beset the preparations for this titration, the experiment went off very well. The water, of course, was not as good as could have been desired, and the first addition was therefore made as soon as possible; even so, the conductivity of the water was then already 156 nm/cm. Because the conductance was also increasing very rapidly (about $4\frac{1}{2}$ nm/cm/h), the whole titration was speeded up somewhat: the first addition, for instance, was left in the cell for only 17 hours instead of the more usual 22 - 24 hours. The drainage from the cell walls was really excellent -- the best of the whole series of experiments.

Experiment 12. Stirring gas: Oxygen
No. of additions: 5

After the preceding experiment the cell was leached out for two days with frequent changes of conductivity water, the process again being speeded up by placing the cell in a thermostat at 45°C for part of the time. During this cleaning period a trial addition was made (at 25°C). Immediately after the addition the resistance dropped so rapidly when the stirring was stopped that it was impossible to take an accurate reading: four minutes after the addition had been made, for instance, the rate of drop was about 1 ohm in 10 - 15 seconds, and it had been even faster before this. The rate of decrease slowed down appreciably, however, being 0.5 ohm in 15 seconds eight minutes after the addition, and 0.9 ohm in 1 minute after the sixteenth minute. At this stage the stirring was left off completely for 10 minutes, during which the resistance dropped continuously at a gradually diminishing rate (0.65 ohm/min at the end of the period); the total drop was 7.4 ohms (from 7368.9 to 7361.5 ohms). When the bubbling was then restarted, the resistance at once rose to 7367.1 ohms. As in the case of the trial addition with nitrogen stirring, this value was roughly the resistance which the solution would have had if the bubbling had not been stopped. In a similar stoppage of the stirring $1\frac{1}{3}$ hours later, the resistance dropped 3.0 ohms in 6 minutes, but a burst of bubbling for 10 seconds was then sufficient to restore the resistance to its extrapolated value for uninterrupted stirring.

During the leaching period, the rate of increase of conductivity of the water in the cell was exceptionally high (about 13 nm/cm/h -- 1 nm/cm/h or less was regarded as normal for oxygen stirring). This meant that the solvent correction would not only be large, but would also be changing very rapidly, and hence could not be applied with the same accuracy as in previous experiments. In order to minimise this error, it was decided to depart from the standard procedure used in other titrations, and not to leave the first addition in the cell overnight, but to perform the whole experiment as rapidly as possible. Actually the sample of water used in the experiment was of better quality than had been anticipated -- its conductivity at the time of the first addition was 145 nm/cm and increasing then at a rate of about 5¼ nm/cm/h. Nevertheless the original plan was adhered to, and when the resistance of the water had been observed for a few hours after it had passed its maximum, the first addition was made and left for about 7 hours, followed by the remaining four additions at intervals of about 2½ hours each -- a continuous sequence of operations requiring about 21¼ hours before the final weighing of the cell was completed. The troubles experienced during this period were fortunately minor ones resulting mainly from a slight lack of co-ordination brought on by fatigue. The drainage from the upper portions of the cell was still very good.

Very careful checking of the weights of liquid in the cell before and after the titration revealed a gain in weight of 28 mg -- not as much as in the experiments with hydrogen stirring (even allowing for the shorter duration of this experiment), but the increase was nevertheless quite definite. It was, however, only just over 0.01% of the total weight, and hence could not cause an appreciable error even if it were neglected.

As regards the resistance, a similar behaviour was observed after the first addition as was found during the trial addition, although the changes were not quite as marked. Nevertheless, whenever the stirring was stopped in order to determine the resistance accurately, the readings had to be taken very fast. The magnitude of the variations diminished fairly rapidly after the first addition. The effect was also noticeable, to a decreasing extent, after the second and third additions, but thereafter it was quite absent.

Experiment 13. Stirring gas: Hydrogen
No. of additions: 5

The cell was again leached out for two days (part of the time at 45°C) with several portions of fresh conductivity water. The trial addition made during this period revealed an extremely rapid decrease of the resistance as soon as the stirring was stopped in order to take a reading. In fact, it dropped at such a tremendous rate immediately after the addition that, when the first reading was being taken, it was impossible to track the resistance even with the 1-ohm decade. During the second reading, which was taken two minutes after the addition -- because of the large changes, readings were being taken at one-minute intervals instead of the usual two minutes --, the resistance could be measured more rapidly because its approximate value was already known, and it was then found to drop by 4 ohms in about 15 seconds. Fortunately the rate of drop itself decreased quite rapidly, and it was possible to estimate the resistance roughly to a tenth of an ohm by interpolation on the 1-ohm decade after about four minutes, and to determine it on the 0.1-ohm decade after seven minutes. After the eighteenth minute the stirring was left off completely for a further 15 minutes (air was passed over the top of the cell during this period in order to prevent any back-diffusion of CO_2 into the cell): the resistance dropped by 0.8 ohm during the first minute, but the rate was still decreasing, and the drop during the last minute was only 0.15 ohm; the total drop was 4.8 ohms (from 8232.7 to 8227.9 ohms). The stirring was then restarted for 10 seconds only, but this proved sufficient to restore the resistance to its normal value had the bubbling been continued all the time; further bursts of stirring in quick succession produced no more change in the resistance.

A similar behaviour was observed during the actual experiment, although the changes appeared to be less marked. This could not be confirmed, however, since the initial variations were still quite large and hence all the readings were being taken (at one-minute intervals at first) as rapidly as possible -- often within two seconds of stopping the stirring; thereafter the bubbling was at once restarted, and was never left off for any length of time because of the risk of back-diffusion of CO_2 taking place. The effect diminished quite rapidly with time during the first addition, and was hardly noticeable after 25 minutes. It also became smaller with succeeding additions, and was barely evident during the third addition, even immediately after the aliquot had been added. However, other troubles on the second day of the experiment precluded observing this effect very closely during all the later additions.

The experiment was once again performed fairly rapidly, though not as continuously as Expt. 12. During the leaching process, the quality of the water had appeared to have improved somewhat, but the sample finally used was not very good -- its conductivity at the time of the first addition was only 177 nm/cm, although it was increasing at a more reasonable rate of $2\frac{1}{2}$ nm/cm/h. Most of the trouble in this experiment arose from the failure (once again!) of the refrigeration unit on the second day. Since it was a rather warm day -- the temperature outside the room was already 23°C at 10 a.m. -- it was essential for the incoming air to be cooled if the room temperature were not to rise. But since it was also a Sunday, it was impossible to obtain the assistance of technicians to effect the necessary repairs; nor was it possible to do the repairs personally, although the fault was obvious. The experiment could not be abandoned, however, for it was already half-completed, and there was no time for a repeat. Fortunately the departmental refrigerator was in operation, and some degree of cooling was obtained by placing a large tray of ice inside the room, and also by packing ice-cubes at frequent intervals on the cooling fins of the evaporator over which the air was normally drawn into the room. At the same time an attempt was made to stick as closely as possible to the normal procedure with all the attention to detail which this invariably required. The task was successfully accomplished, and although the temperature of the room varied rather more than usual, that of the thermostat remained quite constant throughout the experiment.

As in Expt. 9, air was passed over the top of the cell during the actual additions to prevent CO_2 from diffusing in while the cap was off. A similar flow of air was also used during the taking of the final set of resistance readings at different frequencies, when the bubbling had frequently to be stopped for the accurate balancing of the bridge.

Despite thorough cleaning and drying of all the copper coils and other tubes before the titration was started, there was an increase in weight of the liquid in the cell of 83 mg during the experiment. The drainage inside the cell was still good, though not as good as in Expt. 11; in fact, it was readily obvious that it was deteriorating with each experiment.

<u>Experiment 14.</u> Stirring gas: Hydrogen
No. of additions: 5

This experiment was performed about a month after Expt. 13, mainly because calculation of the results of the latter had shown that they differed considerably from those obtained in all the other titrations. However, it was not certain that this difference was real and not perhaps due to some experimental error, since a constant correction to all the calculated conductivities yielded results more in agreement with the normal. Also, it had meanwhile been shown that the KCl stock solution definitely no longer had the same conductivity as when it had been prepared (see Section 3.321). It was therefore decided to repeat Expt. 13 with a new KCl solution.

No trial addition was performed, since the changes in resistance which could be expected were now known. The behaviour when the stirring was stopped was, in fact, similar to that found before, and again readings had to be taken very rapidly, especially just after the additions had been made. This time it was possible to observe the behaviour more closely after each aliquot was added, and although the effect diminished considerably with succeeding additions, it was definitely still noticeable even after the fifth one. In all cases, however, its magnitude decreased rapidly with time, and the resistance very soon stayed constant for quite a while when the stirring was stopped.

During most of the month which elapsed between the performance of Expt. 13 and this one, the cell had stood filled with conductivity water. It was also leached with several changes of fresh water just before the experiment, and the still was again cleaned and its reagents renewed. Nevertheless, the water used had a conductivity of 164 nm/cm at the time of the first addition. Rather oddly, the conductivity was still decreasing at a steady rate of about 0.7 nm/cm/h at this time, although the water had then been aerated for 12½ hours (the minimum was normally reached in 8 - 9 hours at a 60/30 bubbling rate). A similar odd behaviour was observed after the first addition: the resistance fell initially in the manner expected, but after an hour it began to rise slowly, and eventually it exceeded the initial value at the time of the addition (6749 ohms); in fact, when the second aliquot was added after 12 hours, the resistance was actually 2 ohms higher than this value. The two effects are probably related to each other, but the reason for them is not known.

Again the liquid in the cell increased in weight during the experiment (85 mg), although the final parts of the train had been thoroughly dried just prior to the titration. The drainage was poorer than in the previous three experiments, but there was only one indication of "run-back", and then the change in resistance was less than 0.005%. Air was again passed over the top of the cell while the additions were being made and while the resistances at different frequencies were being determined. Much trouble was experienced both with the weighings (the balance appeared to be particularly unstable during this experiment) and in maintaining the bubbling rate constant: it is possible that these factors were contributory to the experimental error which, from the calculated results, obviously took place during the fourth addition (see Section 3.34 and Appendix E).

3.33 Calculation of Results.

3.331 Resistance at infinite frequency.

When the sets of readings taken at different frequencies during the early experiments with unplatinised electrodes were plotted against f^{-1}, the plots for the first additions (average resistance about 7500 ohms) invariably showed a slight but distinct negative curvature. This curvature gradually disappeared as more KCl was added, and usually from the fourth addition onwards the plots against f^{-1} appeared definitely to be straight lines. This result was in agreement with the observation made by A. Faure, who also found that, with a Gledhill-type cell, the R-f^{-1} plots for KCl solutions became curved at lower concentrations, although they were straight lines at higher values[2].

The resistances of the first additions lay more nearly on a straight line when they were plotted against $f^{-\frac{1}{2}}$, as recommended by Jones and Christian[96]. However, similar plots made for the other additions exhibited a definite tendency towards increasing positive curvature as the solution became more concentrated. Such a curvature had also been found in the R-$f^{-\frac{1}{2}}$ plots for the 0.01D KCl solutions used for the determinations of the cell constants (see Section 3.221), and the correction for polarisation resistance in these cases had therefore been determined by extrapolating to infinite frequency the straight lines which resulted from plotting the readings against f^{-1}. Since the value of the cell constant had to be used in the calculation of the theoretical resistances which were eventually to be compared with the measured resistances, it was decided to determine the values of the latter at infinite frequency by a similar straight-line extrapolation of the R-f^{-1} plots for all the additions, whether the lines appeared curved or not. Actually the curvature even for the first additions was so little and the polarisation correction for these solutions so small in comparison with their actual resistance that the difference resulting from the best-straight-line extrapolations of either the $R\text{-}f^{-1}$ or the $R\text{-}f^{-\frac{1}{2}}$ plots was generally only about 0.03%, which was still within the limits of experimental error of the weighings for these additions; whereas for the second and third additions it was usually debatable whether the decreasing negative curvature of the $R\text{-}f^{-1}$ graphs was any greater than the increasing positive curvature of the $R\text{-}f^{-\frac{1}{2}}$ plots. No $p^2C^2R_m^2$ correction was applied to the resistance readings as had been done for the 0.01D KCl solutions (see p. 142) because the parallel capacities required for balance at the higher resistances of the solutions formed during the titrations were so low that the correction to individual readings was virtually negligible, and the lines for the corrected and the uncorrected resistances extrapolated to the same value at infinite frequency.

With platinised electrodes, the necessary extrapolation was performed by plotting the readings against $f^{-\frac{1}{4}}$ (again as had been done for the cell constant determinations). Plots were actually tried against f^{-1}, $f^{-\frac{1}{2}}$, and $f^{-\frac{1}{4}}$, but the polarisation correction was still small although the resistances being determined were now much larger than for the 0.01D KCl solutions; consequently the experimental errors of the measurements were comparable in order with the correction itself, and so the plots were rather erratic. For the first additions, for instance, the resistances could only be measured to 0.1 ohm, and the various readings seemed so randomly distributed that a straight line could equally well have been drawn through each of the three plots. With succeeding additions, however, it was possible to determine the resistances more exactly as their value decreased, and a distinct negative curvature became apparent in the plots against f^{-1}; the lines in the $f^{-\frac{1}{2}}$ graph also appeared to be negatively curved, though not as definitely, while the $f^{-\frac{1}{4}}$ lines seemed to be the straightest of the three sets -- exactly the same behaviour as had been found for the more concentrated KCl solutions used for the cell constant determinations. Although the $f^{-\frac{1}{4}}$ extrapolation was finally chosen as standard for these titrations, it would actually not have mattered much which plot had been used, because the corrections were so small in comparison with the resistances themselves that the maximum variations (i.e. those between the f^{-1} and the $f^{-\frac{1}{4}}$ plots) were generally not larger than 0.04%.

When the resistance at infinite frequency for any addition had been obtained from the graph, the value was corrected for the ratio arm inequality of the bridge (all sets of readings at different frequencies during the titrations were taken at one ratio arm setting only) and for the leads resistances of the bridge and of the cell. The difference was then calculated between this corrected resistance and the value actually measured at 900 c/s during the set of readings to give a correction term which could be applied to all the readings which had been taken during this particular addition.

3.332 Concentration of the solution.

Ideally no liquid should enter or leave the bulk of the solution inside the cell during the course of a titration (other than that introduced during the additions), and the weight of solution at any time should be equal to the weight of water originally placed in the cell plus that of all the additions of stock solution already made. This condition was sometimes approximated when the inner walls of the cell had been well cleaned and drainage was very good. But, in general, changes in weight of various kinds were found to occur, mainly due to liquid being sprayed out of the bulk by the bursting bubbles of stirring gas and then not returning again to the solution; also, there were the unexplained increases in weight occurring particularly when hydrogen stirring was being used. All such changes were assumed to have taken place at a uniform rate, and a correction was applied proportionally to the length of time for which the experiment had been going (except, of course, in the cases where "run-back" had obviously occurred: this necessitated a special correction, which will be discussed later).

In order to make these corrections, the cell was always carefully weighed at the end of a titration both before and after the liquid adhering to its upper portions had been wiped out; the weight of liquid inside the cap that normally covered the cell whenever the latter was in the thermostat was also determined. If there had been no change in the total weight, or if there had been a decrease, the loss in weight from the bulk of the solution was calculated as the difference between (initial weight of water placed in the cell plus all additions) and (weight of solution left in the cell after it had been wiped on the inside at the end of the experiment); a proportional correction for spraying losses, based on the quantity so determined, was then applied both to the weight of liquid in the cell and to the weight of electrolyte present therein, since obviously some of the KCl must have been carried out by the spray as well. If, however, the total weight had increased during the titration, the same method of correction was still used for the weight of solution inside the cell, but this was obviously not valid for the weight of electrolyte as well. The correction for the latter case was calculated from the weight of liquid which was known to have been separated from the bulk of the solution, i.e. the weight of the liquid present in the cap and that which was wiped out from the upper portions of the cell, as well as the weight of any drops which may have been removed on the stem of the burette if it had accidentally been touched against the sides during the additions (the latter quantity had to be estimated, but tests showed that it never amounted to more than a few milligrams). In most of the titrations, if the drainage had been at all reasonable, the total correction throughout the whole experiment was usually only about 0.10 - 0.15% -- sometimes even considerably less, especially during the later titrations, when the technique for cleaning the cell had been improved. The adjusted weights for each individual addition are therefore probably correct to 0.01% or better.

In the calculation of the results, it is not really the weight of the solution which is required, but its volume, in order that the concentration after each addition may be calculated in equiv./l. The exact densities of the various solutions formed during a titration could be determined from the formula given by Li and Fang[103] for the variation of density of KCl solutions at 25°C:-

$$d = 0.99707 + 0.00635\,f \quad \text{g/ml} \qquad \dots\dots\dots\dots(3.4)$$

where f = weight percentage of KCl

However, this was not generally done, as the concentrations being considered were so low and their range so small that it was sufficiently accurate to assume that all the solutions had the same density as water, viz. 0.99707 g/ml at 25°C. It can, in fact, readily be shown that such an approximation merely results in a constant absolute error in all the calculated resistances, regardless of the number of additions which have already been made; and this error is negligibly small even in the most concentrated solution considered. For the simplest derivation, the following assumptions may be made:-

(i) that the weight of solution in the cell ($\underline{W}$ g) remains constant (the actual change during a titration of ten additions was only 1%);

(ii) that the same number of equivalents of KCl ($\underline{E}$) is added to the cell each time;

(iii) that the electrolyte in the cell is always dissociated to the same extent, i.e. that the equivalent conductance of the KCl (Λ) is the same for all the solutions (this was approximately true in these titrations, where the actual concentrations were so low that dissociation was nearly complete and the range of concentrations was so small that Λ varied by only $1\frac{1}{3}$% for ten additions to the cell);

(iv) that the conductivity of the water is negligibly small compared with that of the electrolyte.

After nth addition:

c_n = concn. of the solution in equiv./l.

$$= \frac{1000nE.d_n}{W} \qquad \text{..........(3.5)}$$

where d_n = density of this solution

Also, from the standard conductance equation,

κ_n = conductivity of the solution

$$= \frac{c_n.\Lambda}{1000} \qquad \text{..........(3.6)}$$

Substitution from equations (3.5) and (3.6) in the equation

R_n = resistance of the solution

$$= \frac{Q}{\kappa_n} \qquad \text{where } Q = \text{cell constant,}$$

gives $$R_n = \frac{QW}{\Lambda nE.d_n} \qquad \text{..........(3.7)}$$

Equation (3.4) may be reduced to the form:

$$d_n = d_w(1 + nx) \qquad \text{..........(3.8)}$$

where d_w = density of water
and x = correction factor for a single addition.

Hence equation (3.7) becomes

$$R_n = \frac{QW}{\Lambda nE.d_w}(1 + nx)^{-1}$$

which may be expanded (since nx is very small) to give

$$R_n = \frac{QW}{\Lambda nE.d_w} - \frac{QWx}{\Lambda E.d_w} \qquad \text{..........(3.9)}$$

The first term on the right-hand side of equation (3.9) is the resistance of the solution as normally calculated, the density being taken as equal to the density of water; the second term is the correction which must be applied to this calculated resistance to allow for the differing densities of the KCl solutions. It will be seen that the latter factor consists entirely of constants, so that the correction will have the same absolute value for all the additions. This value was about 0.035 ohm for the titrations as normally performed, i.e. less than 0.005% of the resistance being measured even after ten additions had been made to the cell.

3.333 Correction for solvent conductance.

Since the electrolyte being used was the salt of a strong acid and a strong base, the method of application of the solvent correction was extremely simple, viz. to add the conductivity of the water to the calculated conductance of the KCl in the solution. The difficulty in these titrations, however, lay in the fact that the conductivity of the solvent was not constant, but changed continuously throughout the experiment owing to "solution of glass" and other effects. The original intention was to assume that the water conductivity continued to increase during the titration at the same rate after the KCl had been added as when the water alone was in the cell. The first additions were therefore not made immediately after the resistance of the water had passed its maximum value, but the water was always first left in the cell long enough for the rate of change of its conductivity to be determined, so that the conductance after each of the additions could be calculated. However, it soon became apparent that the assumption was incorrect, since the conductivities of the potassium chloride solutions invariably increased more rapidly than that of the water alone. There did not seem to be a consistent relationship between the rates: they varied, for example, for different additions, but not proportionally to the number of additions -- rates ranging from $1\frac{1}{2} - 5$ times that of the water alone (which itself varied with different samples) were found.

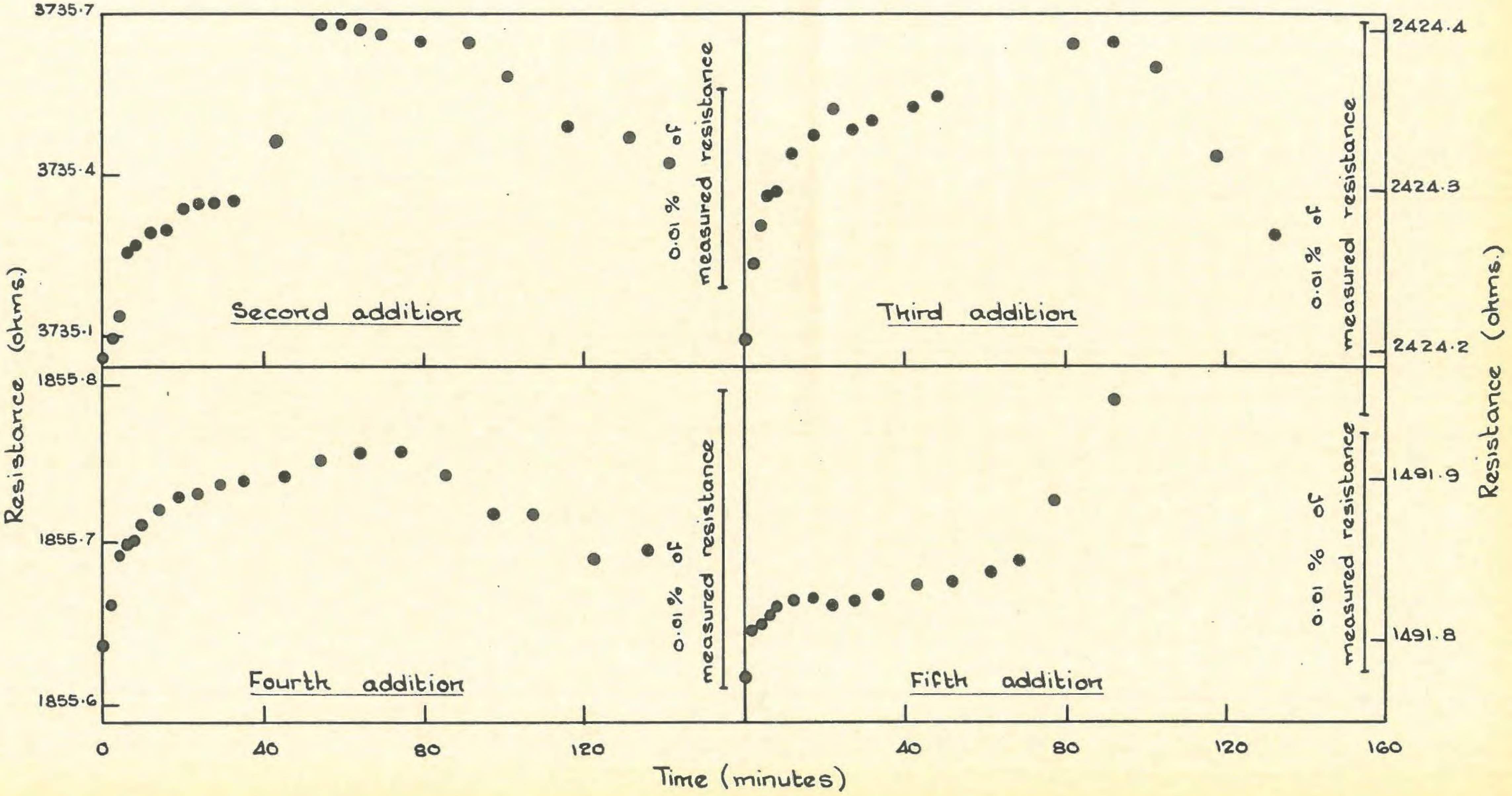
The most probable reason for the faster rate of increase of conductivity of the potassium chloride solutions appeared to be an ion-exchange whereby, for example, K^+ ions were being replaced by more highly-conducting H^+ ions. This idea was supported by the general slope of the typical curve for the change in resistance found after a first addition of stock solution to the water in the cell (see line (1), Fig. 3.4). If irregularities were neglected, a decrease in resistance seemed to occur immediately after the addition which was fairly fast at first, but gradually slowed down until a more or less constant rate was reached: this is the sort of behaviour to be expected if an interchange was occurring between the newly-added electrolyte and a previously denuded surface. From the similarity of the curves obtained before and after platinisation of the electrodes (the general shape was the same with platinised electrodes, though the changes were faster and greater; but then the conductivity of the water alone had also been increasing considerably faster than usual), it was inferred that the surface concerned with this reaction was the glass wall of the cell, and not the electrodes. The mechanism of the exchange, however, was not certain. Gaudin et al. had shown, by using radioactive tracer techniques, that barium[104] and sodium[105] ions are adsorbed from solution on to the surfaces of quartz particles, and presumably therefore the potassium ions would also be adsorbed on to the glass, which is mainly silica. But adsorption alone would mean a decrease in resistance due to removal of conducting material, whereas the resistance actually increased, so that an exchange process seemed far more likely. This hypothesis has now received confirmation from a paper published very recently, in which O'Connor and Buchanan[106] have interpreted Gaudin et al.'s results as due to a cation exchange involving the hydroxyl groups of the hydrated surface layer which is possessed by silica and other insoluble oxides when in contact with water. Such oxides undergo reaction with the water, giving hydroxyl groups which may ionise either as weak acids or weak bases, depending on the circumstances, i.e. an electrical double layer is established which will have either hydrogen or hydroxyl ions in the diffuse layer. In the case of quartz, the surface is invariably acidic, so that cation exchange will be much more probable than anion exchange. The replacement of K^+ ions by H^+ ions will cause the resistance of the solution to decrease, fairly fast immediately after the addition of the first portion of KCl, but gradually slowing down until a constant rate of exchange is reached.

How should this ion exchange be allowed for in the final calculation of the results? This was obviously a question of major importance, since the method of correction would affect the values obtained for the calculated resistances -- not so much, perhaps, in cases where the rates of change of conductivity were fairly slow, but quite appreciably in the experiments with platinised electrodes, when the conductances were changing relatively rapidly. In Expt. 11 (nitrogen stirring), for instance, the rate of change for water alone was 0.03% of the conductivity of the first addition per hour, but the total change in conductance which occurred during the 17½ hours that the first addition was left in the cell was 0.71%. The value calculated for the resistance of the second addition would therefore vary by about 0.1% depending on whether the solvent conductivity was assumed to increase at the same uniform rate found before the addition was made, or at the rate occurring after the addition. If the former assumption were followed (as had been the original intention) and there had been no adsorption or other effect taking place at the electrodes, then the difference between the calculated and measured resistances would, of course, give a measure of the amount of ion-exchange which had occurred relative to each of the additions. But such a result would be rather meaningless, partly because the calculated magnitude of the effect would depend on the length of time for which each addition was left in the cell (since the process was not going to completion, but was occurring continuously all the time), and also because the rates of change were in any case so variable. In fact, a better idea of the ion-exchange effect could be obtained by comparing the actual rate of change of conductivity of the solution with that of the water. It seemed preferable, therefore, to recognise the ion-exchange process as definitely taking place, and then to calculate the total change in the conductivity of the solvent (whether due to ordinary "solution of glass" or to ion-exchange) on the basis of the changes occurring after each addition. In this way any difference obtained between the calculated and measured resistance would not include a term due to ion-exchange effects at the glass surface, but would presumably be due entirely to effects occurring at the electrodes.

Even though the method of correction had been decided on in principle, the actual application was still not straightforward because the variations of resistance after an addition were usually not regular. Thus the erratic behaviour sometimes encountered after the first additions has already been illustrated in Fig. 3.4. Fig. 3.5 shows the changes which occurred in one titration (Expt. 10) after the second to fifth additions; it will be seen that these were fairly regular, but this particular set of readings was specially chosen to illustrate what is believed to be the ideal behaviour (i.e. when no external effects have influenced the values of the resistances) during the later stages of a titration. In most cases, however, the variations were not nearly as uniform as this. Because of the irregularities which so frequently occurred in all additions, therefore, the final correction which was applied usually had to be suited to the circumstances not just of each experiment, but sometimes even of each individual addition. Hence a brief outline only of actual methods can be given.

The first additions were the ones which were left in the cell longest, since the largest changes (if any) were expected in these cases. Consequently it was usually possible to get some idea of the rate of change of conductivity of the

Fig. 3.5 – Variation of resistance after second to fifth additions of potassium chloride to water.



solutions formed by these additions, though even this was not always true, e.g. where "run-back" was prevalent, as in Expt. 6 (illustrated by line (4), Fig. 3.4), no regular decrease was found even after one day; but these cases were exceptional and were treated specially (see next section), since the weight of solution in the cell also had to be carefully considered. In general, where the rate of increase of conductance of the solution was obtainable, the change in solvent conductivity over the whole period of the first addition could be determined either by graphical extrapolation or by calculation. However, these methods still involved the assumption that the rate of increase was constant; and although steady conditions were frequently set up in the experiments with unplatinised electrodes, after platinisation the actual rates of change were so high that they seemed to take longer to settle down and were, in fact, still decreasing slowly when the second addition was made to the cell: no accurate extrapolation was therefore possible in these instances. In any case, as can be seen from the typical curve given by line (1) in Fig. 3.4, the extrapolation of an eventual steady rate of change will neglect the more rapid decrease in resistance occurring just after the addition; yet this is presumably also caused by ion-exchange, i.e. the same process for which allowance is being made in calculating the change of conductivity, but it is merely taking place at a faster rate while the glass surface is still bare of K^+ ions until a steady state has been established. Neglect of this factor in the typical case shown (the line was actually drawn from the results of Expt. 1) would cause the calculated conductivity at the time of the second addition to be in error by about 0.05% of the total conductivity of the first addition (the difference between the extrapolated resistance and the actual resistance at the time of the first addition); hence the calculation for the second addition would show an error of 0.025% only, and this would become proportionately less for subsequent additions. The errors are small, but it seems preferable to calculate the total change in conductivity for a first addition as the difference between the final and initial values for this addition, as long as the variations in resistance that have occurred are more less normal, e.g. as in line (2), Fig. 3.4. In line (3), however, it would be better to make the necessary correction by calculation from the uniform rate of change of conductivity occurring after the unusual variations, since the rise in resistance which took place during this addition would result in a larger error if the initial and final values of the conductivity were considered.

From the second addition onwards the resistance usually rose at first from its initial value immediately after the addition. This was probably due to the removal of a small amount of carbon dioxide introduced to the solution in the cell with the aliquot of stock solution. The rise was not evident in the first addition, although presumably a similar removal was effected there as well, because it was masked by the more rapid decrease in resistance resulting from the ion-exchange. This should constitute another correction to the change in conductivity of the first addition, but it was so small (of the order of 0.01% of the total conductance) that it was invariably neglected.

Although small, the rise usually persisted for quite a while before the resistance began to drop at the steady rate resulting from the ion-exchange. Where the addition had been left long enough and the rate could be determined (as in Fig. 3.5), the change in conductivity during the addition could readily be calculated; also the resistance at the time of the addition (i.e. without CO_2 present) could be obtained by extrapolation. This value of the resistance was obviously the correct one to be used as the measured value for the addition, rather than the immediately determined resistance. Where the addition was not left for long enough or where the points were too erratic to give the rate of change of conductivity, the highest measured value was usually taken as correct, since at least all the CO_2 would have been removed, and the error involved between the highest value and the extrapolated value was small (it can be seen from Fig. 3.5 that this was less than 0.01%). As regards the conductivity correction under these circumstances, either this was calculated as the difference between the conductances corresponding to the highest and the final resistances, or the rate of change of conductivity for the first addition (if determined) was assumed to apply to the other additions too -- the method was dictated always by a consideration of the actual case. Both methods were not quite correct, since the highest resistance was not the true resistance of the solution formed in the addition concerned, nor were the rates of change of conductivity the same for different additions; but the changes were so small because of the short period for which all additions but the first were left in the cell that the errors caused by these assumptions would be less than 0.01% for any addition.

3.334 Corrections for "run-back" of solution.

The methods of calculation of the concentration of the solution and the conductivity of the solvent outlined in the two preceding sections are obviously valid only as long as the variations which occur during the titration are regular. Special corrections will, however, have to be applied whenever large erratic changes are encountered, such as were caused by solution running back off the upper walls of the cell after being deposited there by spraying. Where the "run-back" is small and infrequent, so that the regular change of conductivity of each solution can still be distinguished and its rate determined, the conductivity correction may, of course, be applied as before. But the total loss in weight occurring during the titration as a result of spraying will not be equal to the difference between the initial and final weights, nor can the weights of solution or of electrolyte in the cell at any time be assumed to have changed at a uniform rate: a proportional correction is therefore no longer satisfactory. However, a fairly accurate approximation can still be made in the cases where "run-back" is limited to two or three drops during the experiment, by assuming the rate of deposition of spray (whether of water or of the solution in the cell during any given addition) to have taken place uniformly: hence the concentration of solution on the walls can be calculated from the time for which the experiment as a whole has been proceeding and from the amounts of electrolyte which have been deposited. Then the weight of solution of given concentration at the time of the "run-back" can be obtained from the change in resistance which it has produced. The weights of all the drops which have run back are then added to the total loss in weight as normally determined, to give a more accurate estimate of the loss in weight which has actually taken place during the experiment. If necessary, a second approximation can be made; but since the method is valid only when the number of cases of "run-back" are few, the corrections involved are usually small and one approximation is invariably sufficient. From the corrected rate of loss of solution by spraying, the weights of solution and of electrolyte in the cell at any time can now be calculated proportionally as before, with appropriate allowance being made during those additions where a "run-back" has occurred.

This approximation method does not hold where "run-back" has been very prevalent, since it is essentially based on an assumption that the changes during a titration occur continuously; but the process of "run-back" being considered here is in every respect a discontinuous one. This is caused by the dropwise instead of the steady return of liquid which has left the solution continuously at a rate which, because the spray droplets are so small, can still be regarded as uniform. The liquid on the walls of the cell can therefore be considered to increase uniformly in concentration as more spray is deposited, but only until the first large drop runs back. Then one portion of the wall will be bare, and fresh solution deposited there will have a higher concentration than in other places where it is being diluted by water and more dilute solutions already present on these sites. It is likely that the concentration will be most uniform, and will increase most regularly, right at the top of the cell, since less drops will return from there than lower down, and hence the conditions will approximate most closely to the ideal rates of change previously assumed. However, there will almost certainly be a non-uniform gradation of concentration as one progresses above the liquid surface level, for the liquid situated lower down on the walls can not only be caused to return to the solution by virtue of the drops having grown to flowing size by themselves, but it may also be carried back by the "snowballing" effect resulting when drops from higher up flow down the walls.

It is quite obvious from the actual graphs and from a general consideration of the problem that the drops do not return at absolutely regular intervals, nor are they all of exactly the same size. This irregularity both in the size and in the time of return of the drops only further complicates the issue. It would, of course, be possible to follow the resistance variations very closely (which would involve numerous readings to be taken right through the night as well!) and thus observe each individual "run-back" by the erratic change which it produced; but this would only indicate how many drops had returned and when -- the weight of each drop could still not be calculated from the size of the resistance change because of the uncertainty of the concentration of the liquid which has run back. At best a series of approximations could be made (and a large number would be required!) along the lines suggested for cases where "run-back" occurred only two or three times during the whole experiment. Besides the tedium of this procedure, however, an uncertainty would even then remain, viz. how much water had run back before the first addition was made, since this could not be assessed at all.

The weights of liquid actually wiped off the walls of the cell at the end of the experiments where "run-back" had been prevalent were about 0.3 - 0.4% of the total weight. Since a considerable amount of liquid had also returned to the solution during the titrations, the error involved by using the ordinary methods of correction outlined in Sections 3.332 and 3.333 would obviously be large. It seemed, therefore, that the results of these experiments would have to be discarded. But fortunately a remarkably simple and reasonably accurate solution to this problem was found.

The proposed solution is based on one assumption only, viz. that the walls of the cell have already reached a saturated condition when the first addition is made. It seems justifiable to assume this, since the indications of "run-back" were usually evident within a couple of hours (the time-interval normally found between successive drops running back) of this addition being made. If this is so, then it follows that any liquid which is subsequently sprayed out of the solution on to the upper walls will return again fairly soon (at most within a few hours), and hence the weight of liquid adhering to the walls must stay more or less constant throughout the addition, i.e. the weight of solution in the cell will also remain constant. The limit of variation here will be one drop: if the weight of this is taken as 0.1g (a very liberal estimate), then the error in the weight of solution may vary up to 0.05%. The actual weight of liquid on the walls necessary to produce saturated conditions may be estimated from the weight wiped off at the end of the experiment.

Consider now the curves in Fig. 3.4, where line (1) represents an ideal case and line (4) a typical example of much "run-back". In the latter case the resistance has risen in stepwise fashion to a value A at the end of the addition which is x% higher than the initial value when the aliquot was added, instead of its having dropped normally by y% to B, i.e. the conductance, instead of increasing owing to the "solution of glass" and ion-exchange, has effectively dropped by (x+y)%: this results from the dilution which occurs when the solution (and hence the KCl) is sprayed out and is then replaced by the water (or a more dilute solution) previously present on the walls. Since the weight of solution has been assumed to remain constant, the amount of KCl left on the walls will be (x+y)% of the total amount added. Hence, if normal changes in solvent conductivity are assumed to have occurred during this addition, i.e. if an estimate of y% is made from other titrations, then the weight of solution, the weight of KCl lost, and the solvent conductivity at the start of the second addition will all be known: these are the only factors from the titration which are required for the calculation.

The solution to the corrections for "run-back" may even be carried a stage further, in order to eliminate the uncertainty of estimation of y. Thus the y% increase in conductivity of the solution which normally occurs may be offset by removing y% of the added KCl, so that the total conductance will not have changed at all. Hence we shall have exactly the same situation if we assume that the conductivity of the water has remained quite constant throughout the addition and only x% of the KCl has been left behind on the walls, as we should get by letting the solvent conductivity increase by y% and the amount of KCl be reduced by (x+y)%. All that is required in the calculation of the resistances of subsequent additions, therefore, is that the weight and the conductivity of the solution in the cell be taken as remaining constant throughout the first addition, during which x% of the total amount of KCl added is lost by spraying.

For subsequent additions, the same method of correction can be used, but x% should be calculated as the change occurring, not from the initial resistance, but from the highest measured resistance, since this is regarded as the more correct value for the addition (see previous section).

3.335 Typical calculation.

A typical example of the method of calculating the theoretical resistance of the solution for each addition during a titration is given below. Expt. 9 has been chosen because hydrogen stirring was used, and the example therefore illustrates, in addition to the other corrections, the method employed when an increase in the total weight has taken place.

The equivalent conductances of the solutions formed by the various additions have been calculated from the equation proposed by Davies[43] for KCl solutions:-

$$\Lambda = 149.92 - 93.85\,c^{\frac{1}{2}} + 50\,c \qquad \ldots\ldots\ldots\ldots(3.10)$$

where c = concn. in g-equiv./l.

<u>At beginning of expt.</u> (15.11 hrs. on 14/10/53):-

Wt. (in air) of water placed in cell = 490.167 - 289.447 g
= 200.720 g
Vacuum correction factor for water = 0.0990%
∴ Wt. (in vacuo) of water in cell = 200.720 x 1.000990 g
= <u>200.919</u> g

<u>Additions made</u>:-

Addn. No.	Made at Date	 Time	Wt. of KCl soln. added In air	 In vacuo	10^4 x No. of equiv. KCl added
1	15/10	11.08	0.19889 g	0.19908 g	0.19907
2	16/10	09.19	0.22066	0.22088	0.22086
3	16/10	11.51	0.23097	0.23120	0.23118
4	16/10	14.47	0.21868	0.21889	0.21888
5	16/10	16.46	0.21234	0.21255	0.21253
			<u>TOTALS</u>	1.08260	1.08252

∴ Total wt. soln. in cell at end should be 200.919 + 1.083 g
= <u>202.002</u> g

<u>At end of expt.</u> (18.18 hrs. on 16/10/53):-

Total wt. (in air) of soln. left in cell after wiping = 491.073 - 289.445 g
= 201.628 g
Vacuum correction factor for water = 0.1003%
∴ Wt. (in vacuo) of soln. in cell = 201.628 x 1.001003 g
= <u>201.830</u> g

∴ Total nett loss in weight = 202.002 - 201.830 g
= 0.172 g

Time for which cell was in thermostat = 48' + 18'18" - 15'11"
= 51'07"

∴ Nett rate of loss in wt. of liquid from cell = $\frac{0.172}{51.1}$ g/h
= <u>0.0033_7</u> g/h

Total wt. of liquid lost from cell (in cap, on walls, etc.)
= 0.237 g

∴ Rate of loss of wt. of soln. by spraying = $\frac{0.237}{51.1}$ g/h
= <u>0.0046_4</u> g/h

<u>First addition</u>:

Wt. water in cell at time of addn. = 200.919 - (20 x 0.00337) g
= 200.919 - 0.067 g
= 200.852 g
Wt. KCl soln. added = 0.199 g
∴ Total wt. soln. in cell = 201.051 g
∴ Vol. soln. in cell = $\frac{201.051}{0.99707}$ = 201.642 ml

$$\therefore \text{Concn. soln.} = \frac{0.19907 \times 10^{-4} \times 1000}{201.642} = 9.8725 \times 10^{-5} \text{ equiv./l.}$$

$$\begin{aligned}\therefore \Lambda &= 149.92 - 93.85\,(9.8725 \times 10^{-5})^{\frac{1}{2}} + 50 \times 9.8725 \times 10^{-5} \\ &= 149.92 - 0.932 + 0.005 \\ &= 148.993\end{aligned}$$

$$\begin{aligned}\therefore \kappa \text{ for this soln.} &= \frac{9.8725 \times 10^{-5} \times 148.993}{1000} \\ &= 1.4709_3 \times 10^{-5} \text{ ohm}^{-1}\text{cm}^{-1}\end{aligned}$$

But $\kappa_{H_2O} = 93.5$ nm/cm

$$\begin{aligned}\therefore \kappa_1 &= \text{conductivity of soln. formed in first addition} \\ &= 1.4802_8 \times 10^{-5} \text{ ohm}^{-1}\text{cm}^{-1}\end{aligned}$$

$$\therefore R_1 = \frac{0.10899}{1.4802_8 \times 10^{-5}} = \underline{\underline{7363.2}} \text{ ohms.}$$

Second addition:

$$\begin{aligned}\text{Wt. soln. in cell at time of addn.} &= 201.051 - (22.2 \times 0.00337)\text{ g} \\ &= 201.051 - 0.075 \text{ g} \\ &= 200.976 \text{ g} \\ \text{Wt. KCl soln. added} &= 0.221 \text{ g} \\ \therefore \text{Total wt. soln. in cell} &= 201.197 \text{ g} \\ \therefore \text{Vol. soln. in cell} = \frac{201.197}{0.99707} &= 201.788 \text{ ml}\end{aligned}$$

$$\begin{aligned}\text{Equiv. KCl added} &= 10^{-5}\left(1.9907 + 2.2086 - \frac{22.2 \times 0.00464 \times 9.8725}{1000}\right) \\ &= 10^{-5}(4.1993 - 0.0010) \\ &= 4.1983 \times 10^{-5}\end{aligned}$$

$$\therefore \text{Concn. soln.} = \frac{4.1983 \times 10^{-5} \times 1000}{201.788} = 2.0805 \times 10^{-4} \text{ equiv./l.}$$

$$\begin{aligned}\therefore \Lambda &= 149.92 - 93.85\,(2.0805 \times 10^{-4})^{\frac{1}{2}} + 50 \times 2.0805 \times 10^{-4} \\ &= 149.92 - 1.354 + 0.010 \\ &= 148.576\end{aligned}$$

$$\begin{aligned}\therefore \kappa \text{ for this soln.} &= \frac{2.0805 \times 10^{-4} \times 148.576}{1000} \\ &= 3.0911_5 \times 10^{-5} \text{ ohm}^{-1}\text{cm}^{-1}\end{aligned}$$

$$\begin{aligned}\text{But } \Delta\kappa_{H_2O} &= 22.2 \times 1.28 \text{ nm/cm} \\ &= 28.4 \text{ nm/cm}\end{aligned}$$

$$\therefore \quad \kappa_{H_2O} = 93.5 + 28.4 = 121.9 \text{ nm/cm}$$

$$\therefore \kappa_2 = 3.1033_4 \times 10^{-5} \text{ nm/cm}$$

$$\therefore R_2 = \frac{0.10899}{3.1033_4 \times 10^{-5}} = \underline{\underline{3512.2}} \text{ ohms}$$

Subsequent additions are calculated exactly as for the second.

3.34 Discussion of Results.

One of the results observed during these experiments, wherein potassium chloride was titrated into water, has already been mentioned, viz. the ion-exchange occurring at the glass walls of the cell, presumably between the K^+ ions from the solution and the H^+ ions from the diffuse layer surrounding the silica (see Section 3.333). This effect needs no further discussion, other than to state that it appears to be the only effect taking place at the glass surface of the conductance cell.

Further results of the experiments were evaluated by comparing the calculated resistance for each addition (R_c) with the measured resistance (R_m). The values used for the latter were either those taken immediately after the addition (always the case for the first additions) or, for subsequent solutions, the highest values if the resistances rose owing to the removal of CO_2 after the aliquots had been added; the measured values were always corrected to infinite frequency, as outlined in Section 3.331. A complete list of the results of all the experiments described in Section 3.325 is tabulated in Appendix E.

The accuracy of the results has been fully discussed in the appropriate sections, and need therefore only be summarised here. The measured resistances are in all cases believed to be accurate to 0.01%, because any uncertainties in the extrapolation to infinite frequency are offset by the fact that the resistances themselves were large and hence even the total polarisation correction was relatively small. The calculated values, however, are not as accurate, owing to limitations either of the apparatus or of the corrections. The resistances of the first additions are, in general, probably correct to 0.05% -- the estimated limit of accuracy of the weight of the aliquot and hence of the KCl (see Section 1.41) -- since the conductivity of the solvent and the weight of the water at this stage were usually known quite accurately; in cases where "run-back" was prevalent, the error may be a bit larger. The same weighing error can apply to all other additions, but it seems statistically unlikely that all weights would be in error by the maximum amount and always in the same direction; hence it is felt that the weight of KCl becomes more exactly known as the titration progresses. The weight of solution at any time is still known quite accurately in later additions (again with the exception of "run-back" cases), but there is a greater doubt about the conductivity of the solvent. This error will be largest for the second addition, owing to the longer time for which the first addition is left in the cell; thereafter the solvent conductivity error decreases, since subsequent additions are not only made much more rapidly and hence the conductance cannot change as much, but the actual conductivity of these solutions becomes greater, i.e. the relative contribution of the solvent becomes less, with increasing number of additions. It is difficult to place a general assessment on these errors because of the peculiarities which arose in individual experiments. However, it is felt that the second additions were also accurate to 0.05%, and that the error probably diminished to 0.03% or less by the fifth addition; and in some of the experiments, where irregularities were absent, the overall accuracy may well have been much better than this. Of course, for the experiments with "run-back" a constant error of 0.05%, arising from the estimation of the weight of the solution, must be assumed for all additions; to this amount must be added the error for the weighing of the KCl aliquots.

Since the ion-exchange has already been allowed for in the calculation of the theoretical resistances, any differences found between R_c and R_m should be due to effects occurring at the electrodes -- the only solid-solution interface present in a conductance cell other than the glass walls. The results of Expt. 1 seemed rather odd, showing first a negative and then, with increasing KCl concentration, a positive difference between the calculated and measured resistances, but this was probably due to experimental error while technique was still being gained in the performance of these titrations. In fact, in all succeeding experiments with unplatinised electrodes and nitrogen stirring, the calculated resistance was always greater than the measured value for every addition -- about 0.2% for the first, but gradually diminishing as the concentration was increased. This seemed a little strange at first, for it was anticipated that any adsorption would result in a higher measured resistance owing to removal of some of the conducting material from the solution. However, A. Faure[2] had found during his redetermination of the accurate conductivities of dilute potassium chloride solutions that the results obtained with a Gledhill-type cell differed both from those obtained with a modified Jones cell and from those calculated from equation (3.10). Since the latter values agreed with each other, it seems that the former cell was at fault. The reason for this is not known, but as A. Faure's measurements were all performed by the "wash-out" technique, any effects due to ion-exchange or adsorption at the electrodes would presumably be absent. His results were therefore accepted as indicating standard behaviour for the Gledhill-type cell. These results were given in terms of the equivalent conductances of the solutions, whereas in the present investigation the resistances have been considered, the final comparison being of the form:

$$\% \text{ Difference} = \frac{100(R_c - R_m)}{R_c} \qquad \ldots\ldots\ldots\ldots(3.11)$$

However, it can readily be shown, by substitution from the standard conductance equations, that

$$\frac{R_c - R_m}{R_c} = \frac{\Lambda_m - \Lambda_c}{\Lambda_m} \qquad \ldots\ldots\ldots\ldots(3.12)$$

where Λ_c = calculated equiv. cond.
and Λ_m = measured equiv. cond.

A. Faure's results were therefore expressed in percentage form similar to the present ones, and these are also given in Appendix E. These results and the ones obtained from the full-scale ten-addition titration with nitrogen stirring (Expt. 5) have been plotted in Fig. 3.6, from which the close agreement between the two sets of measurements can be seen (the plot is on a very large scale of percentages, and the deviations between the two curves are within the limits of experimental error, in spite of line (1) (for Expt. 5) lying a bit above line (2) (A. Faure) at higher concentrations: the probable reason for this is given below). This behaviour was therefore accepted as typical for the results of a titration exhibiting no adsorption.

The next experiments with unplatinised electrodes yielded similar curves, but the actual differences kept getting larger with each succeeding experiment (see Fig. 3.7, in which some of the results are plotted). Since different stirring gases were being used, it was not certain that this behaviour did not result from changing the gas: for instance, some adsorption might be taking place. However, the effect of any adsorption should have been relatively smaller the more concentrated the solution became; yet the difference found between corresponding higher additions was the same as for the lower ones. This trend in the end results (i.e. the results for the most concentrated solutions in the various titrations) persisted even through the experiments with platinised electrodes, in some of which other effects were definitely occurring. Since the calculated differences showed a progressive, though not quite regular, increase with each experiment, it seemed that the stock solution might be changing slowly in conductivity. This was proved to be the case, the conductivity after Expt. 13 being 0.66% in error (see Section 3.321). The deviation was in agreement with the end results of the last few experiments

Fig. 3·6 – Comparison of results obtained by titration (Expt. 5) & by "wash-out" technique (A. Faure)

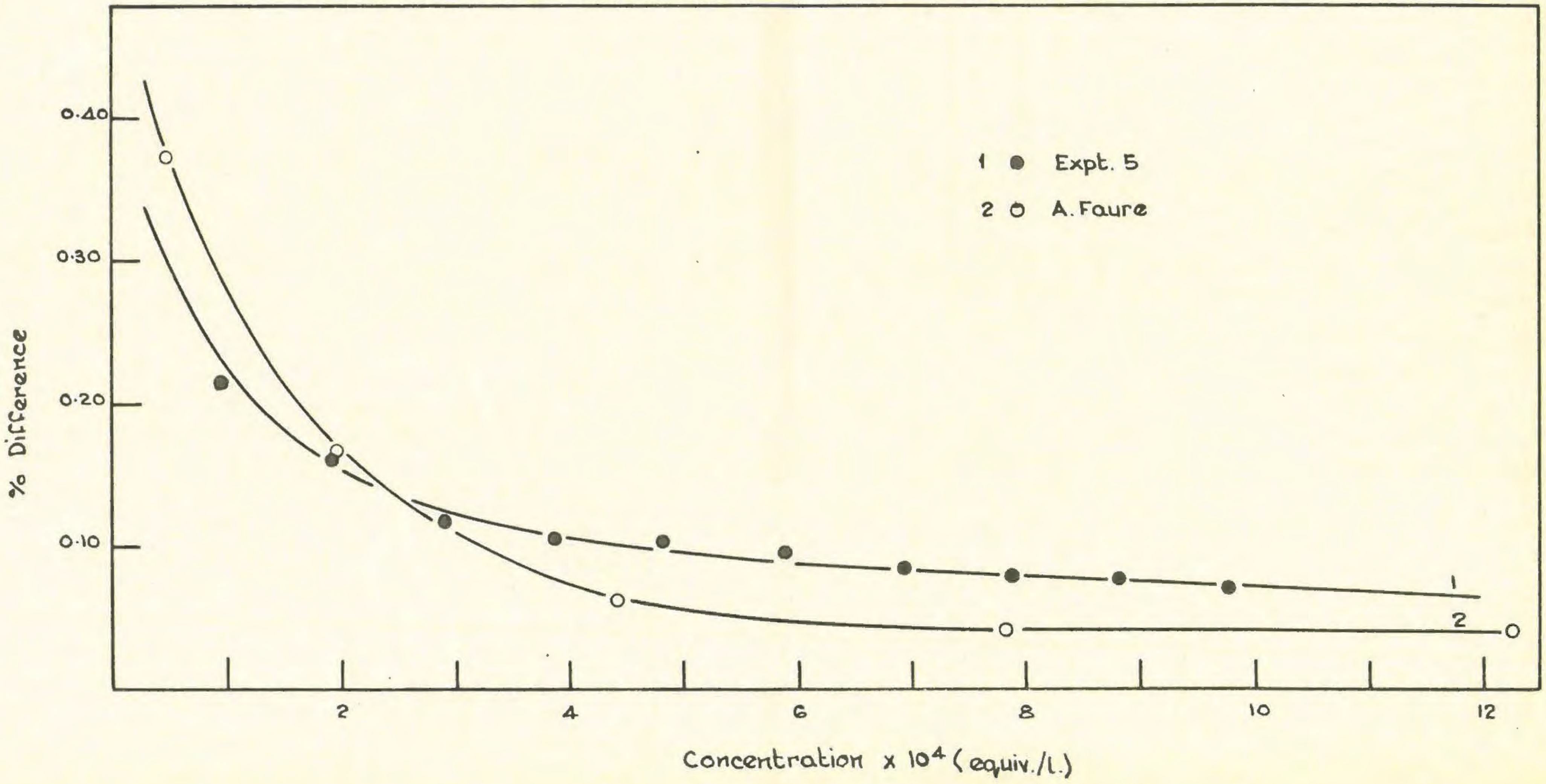
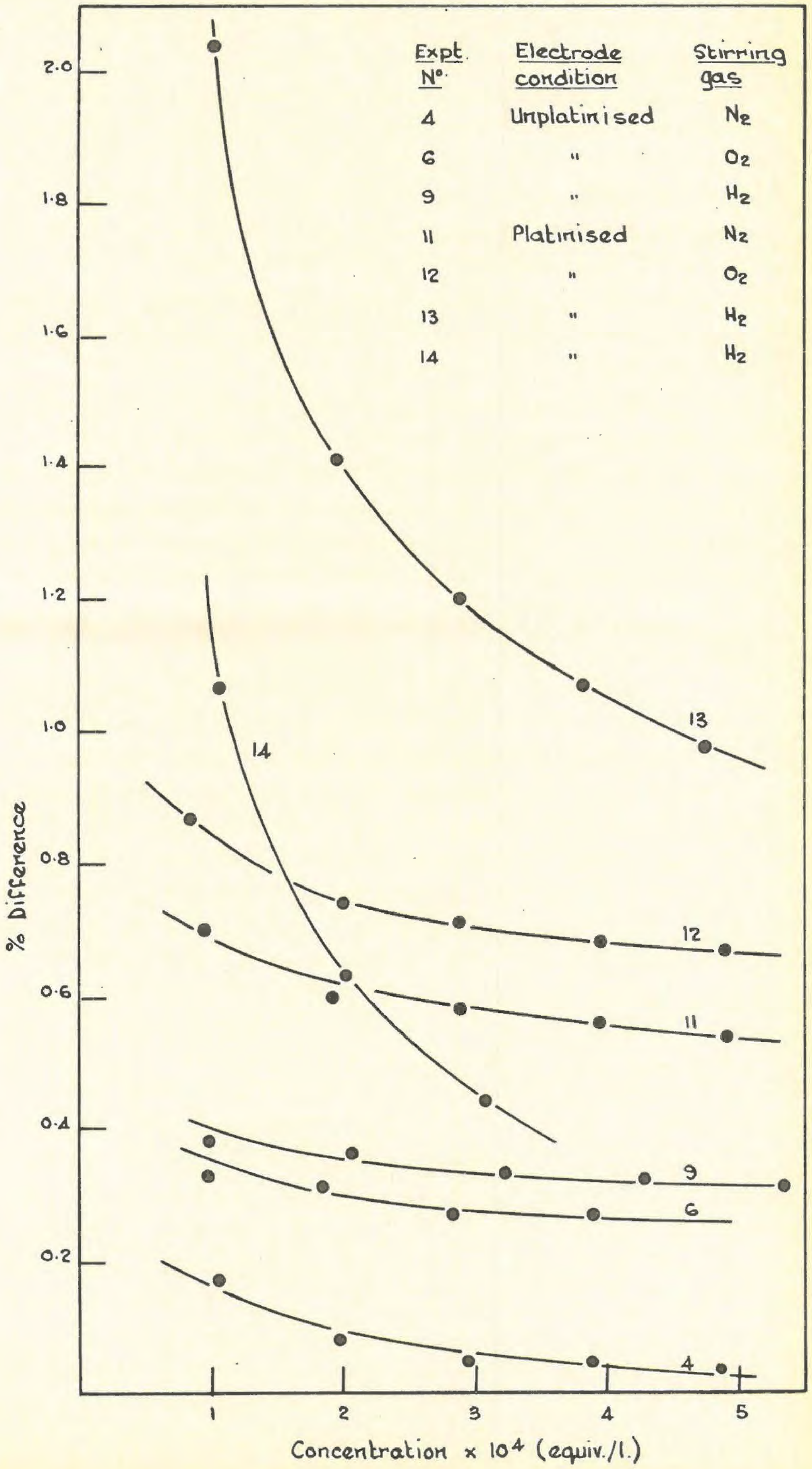


Fig. 3·7 - Results of titrations performed under varying conditions.



performed with this solution (though Expt. 13 obviously showed other effects as well). That the upward trend of the lines in Fig. 3.7 was due to this cause was then confirmed by repeating Expt. 13. The line for Expt. 14 follows the same shape as Expt. 13, but it lies about 0.7% lower at all points -- the exact difference is difficult to measure with such a steep and changing slope, and unfortunately the results for the fourth and fifth additions of Expt. 14 show definite signs of an experimental error (see Appendix E). The negative values found for the percentage difference in these last two instances can, in fact, be readily explained if some KCl were weighed out for the fourth addition but did not actually enter the solution, e.g. if it were accidentally deposited on the walls of the cell.

If the upward trend of the results, owing to the conductance of the stock solution changing with time, is neglected, it will be seen that all the experiments with unplatinised electrodes show similar curves, i.e. no adsorption occurs when the electrodes are bright, irrespective of the stirring being used.

As regards the platinised electrodes, it is probably best to consider first the experiments with hydrogen stirring, in which very large deviations from the normal are apparent (the results of Expt. 14 confirmed that those found in Expt. 13 were not due to experimental error). Frumkin and Donde[89], and Kolthoff and Kameda[90] found that platinised platinum can adsorb alkali from neutral salt solutions in a hydrogen atmosphere, the solution itself becoming acidic. The latter authors suggested that, under these conditions, a double layer is formed around the platinum particles, the metal being negative and the layer of hydrogen ions at the liquid side forming the positive part. Cations from the solution may then displace hydrogen ions in the double layer, which results in an adsorption of the cation and an equivalent amount of hydrogen ions going into solution. Since the deviations observed in the present experiments show the calculated resistance to be higher than the measured value, i.e. the solution is actually more highly conducting than it should be theoretically, the above explanation is very probably correct. Further confirmation, in fact, comes from the behaviour found in these experiments as soon as the stirring was stopped in order to take a reading (see descriptions of Expts. 13 and 14). The immediate and very rapid decrease of the resistance had suggested that a reaction was taking place in the solution -- probably at the electrodes, thus causing a localised change in the conductivity. This idea was supported by the immediacy with which the resistance resumed its true value when even a short burst of stirring was applied to the solution: any mixing would tend to remove the more highly-conducting layer quite rapidly from the vicinity of the electrodes, where it had a large effect on the measured resistance, and distribute it more uniformly throughout the solution, whose conductivity would still be almost unchanged. The replacement of K^+ ions by H^+ ions at the platinised surface therefore fits in very well with all the observations. It is possible that the much smaller decreases in resistance found when the hydrogen stirring was stopped in the experiments with unplatinised electrodes (Expts. 8 and 9) might also have resulted from a similar adsorption and exchange occurring even with bright platinum, but to a considerably lesser extent. Thus the adsorption could not be detected in the final curves, whereas with the platinised electrodes, the adsorption error was of the order of 1% for the first addition (concentration about 10^{-4}N).

With oxygen stirring, the sharp decrease in resistance found when the bubbling was stopped and the immediate return to the correct value when the stirring was restarted also suggests some exchange process taking place at the electrodes, though the plot of the results of the experiment is not as unusual as with hydrogen. There is a suspicion that the line is slightly more curved at the beginning (i.e. at low concentrations), but this cannot be stated definitely without more sets of readings being taken in order to reduce the experimental error. Kolthoff and Kameda[90] did find an adsorption of potassium ions on platinised platinum from KCl solution in an oxygen atmosphere, the solution itself becoming slightly acidic. The proposed mechanism in this case was the initial formation of hexahydroxyplatinic acid, $H_2Pt(OH)_6$, by oxidation of the platinum black. This acid is very slightly soluble and remains for the main part on the electrode, where it then reacts with the K^+ ions in the solution to form an insoluble salt: these ions are therefore effectively replaced by H^+ ions. This explanation does fit the observed results: thus the changes in resistance found whenever the stirring was stopped during the trial addition were never as large as those occurring with hydrogen, but they seemed to be far more persistent. For instance, when the bubbling was left off for ten minutes, the resistance decreased at an almost steady rate, which had not diminished much even 1⅓ hours later; whereas with hydrogen, the changes were very large immediately after the addition, but soon became smaller. The latter behaviour is to be expected if the process is merely an exchange, in which an equilibrium will tend to be set up; but the production of the hexahydroplatinic acid, although it may take place slowly, will presumably be far more continuous. From the results of the experiment, it appears that the amount of adsorption of KCl on platinised electrodes in an oxygen atmosphere is very slight -- perhaps of the order of 0.1% for the first addition; but it may be that the 1½ days leaching with pure water which the cell received before the actual experiment was not sufficient to remove all the material which had been adsorbed during the trial addition.

The plot of Expt. 11, where nitrogen stirring was used, shows no signs at all of adsorption -- a result in agreement with that of Kolthoff and Kameda[92]. There was, however, a rapid change in resistance when the bubbling was stopped in order to take readings, and the increase which was found suggests the occurrence of some adsorption on the electrodes, e.g. of the K^+ ions, which would cause the conductance to decrease. But a secondary reaction must also have been taking place, since the resistance afterwards dropped at quite a rapid rate. No satisfactory explanation can be given for these changes in resistance.

3.4 SUMMARY AND CONCLUSIONS.

For this investigation of the adsorption of potassium chloride from aqueous solution, a conductance cell has been used with unplatinised and with heavily platinised electrodes. The resistances taken at different frequencies during the determinations of the cell constant before platinisation were plotted against both f^{-1} (as suggested by A. Faure[2]) and $f^{-\frac{1}{2}}$ (as recommended by Jones and Christian[96]). The latter plot is widely used by conductance workers in order to correct for the polarisation resistance at the electrodes by extrapolation to infinite frequency. However, such plots gave lines of very distinct positive curvature, whereas the points lay very closely on a straight line when plotted against f^{-1}; an extrapolation on this basis was therefore used for the measurements made with unplatinised electrodes.

The heavy platinisation certainly caused a large decrease in the polarisation correction, but the plots of the readings at different frequencies gave negatively curved lines for both f^{-1} and $f^{-\frac{1}{2}}$ graphs. In spite of the smallness of the actual correction, these curvatures were quite definite. The plots tried against $f^{-\frac{1}{4}}$ appeared to be more nearly straight, and this was therefore used for the extrapolations to infinite frequency of the readings taken with the platinised electrodes, although there is no theoretical justification for doing so.

Similar results to the above were found for both unplatinised and platinised electrodes during the measurement of the resistances of the various solutions which were formed during the titrations, even though the actual values of these resistances were now considerably higher. The extrapolations to infinite frequency were therefore made in the same way as for the determinations of the cell constants.

The investigation of the adsorption effects which take place inside a conductance cell has been successfully performed by a titration method. For this purpose, aliquots of a stock solution of potassium chloride were added to water in the cell under a variety of conditions, and the changes in resistance which followed each addition were closely observed. The experiments have shown that the conductivities of solutions of potassium chloride increase at a faster rate than that of pure water, owing to an ion-exchange process occurring at the glass walls of the cell: H$^+$ ions in the diffuse layer surrounding the silica are apparently replaced by K$^+$ ions from the solution.

No adsorption occurs at the electrodes when these are unplatinised, irrespective of the gas being used for stirring the potassium chloride solutions. There is also no adsorption in a nitrogen atmosphere even with heavily platinised electrodes; but some adsorption takes place in an oxygen atmosphere, and quite a considerable amount when hydrogen is used for stirring the contents of the cell. In each case K$^+$ ions are adsorbed on the platinum black and replaced by H$^+$ ions in the solution, but the mechanism of the reaction is quite different in the two cases. In the case of the hydrogen atmosphere, the reaction apparently goes to completion fairly rapidly: thus the difference between the calculated and the measured resistances after the first addition was about %, even though the latter value was taken within two minutes of the potassium chloride being added to the water; also, the changes in resistance which occurred subsequently were of the same order as those which were found in all the other experiments, and could quite satisfactorily be accounted for by the ion-exchange at the glass surface.

The major errors in these experiments arose from difficulties encountered in the weighing of the small aliquots of stock solution used, and from losses occurring as a result of spraying of the liquid when the bubbles of stirring gas burst at the surface. For future work along similar lines to these, therefore, it is recommended that:

(i) a somewhat lighter weight burette be constructed, and a semi-micro balance be used for weighing it, so that the weight of each aliquot can more easily be obtained with an accuracy of 0.05% or better;

(ii) an attempt be made to design a cell in which spraying losses can be eliminated, and which does not suffer from the defect that the Gledhill-type cell apparently has, viz. an apparent change in cell constant with decreasing concentration.

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APPENDIX

A. CALIBRATION OF BRIDGE RESISTANCES.

The values given below were obtained in June 1952 when the bridge resistances were calibrated as described in Section 1.21. For comparison, the values found for the decade resistances by A. Faure[2] in August 1951 (by means of an intermediate step involving the calibration of another resistance box) are also shown, together with the differences between the two calibrations (A. Faure's values for the 1- and 10-ohm decades were obtained in 1949).

(a) Bridge Decade Resistances.

1000-ohm Decade

Setting	Correction(ohms)		% Diff.
	(1952)	(A.Faure 1951)	
1	+0.54	+0.73	0.019
2	+1.07	+1.46	0.020
3	+2.13	+2.72	0.020
4	+2.56	+3.35	0.020
5	+3.36	+4.35	0.020
6	+4.44	+5.62	0.020
7	+4.90	+6.29	0.020
8	+5.63	+7.25	0.020
9	+6.42	+8.29	0.021
10	+7.27	+9.44	0.022

100-ohm Decade

Setting	Correction(ohms)		% Diff.
	(1952)	(A.Faure 1951)	
1	+0.090	+0.107	0.017
2	+0.178	+0.211	0.017
3	+0.302	+0.350	0.016
4	+0.378	+0.447	0.017
5	+0.402	+0.488	0.017
6	+0.462	+0.563	0.017
7	+0.603	+0.719	0.017
8	+0.690	+0.825	0.017
9	+0.820	+0.966	0.016
10	+0.970	+1.130	0.016

10-ohm Decade

Setting	Correction(ohms)		% Diff.
	(1952)	(A.Faure 1951)	
1	+0.0199	+0.0199	0.000
2	+0.0418	+0.0425	0.004
3	+0.0614	+0.0628	0.005
4	+0.0792	+0.0815	0.006
5	+0.0981	+0.1016	0.007
6	+0.1236	+0.1285	0.008
7	+0.1431	+0.1497	0.009
8	+0.1628	+0.1719	0.011
9	+0.1802	+0.1918	0.013
10	+0.2029	+0.2166	0.014

1-ohm Decade

Setting	Correction(ohms)		% Diff.
	(1952)	(A.Faure 1951)	
1	+0.0007	+0.0017	0.100
2	+0.0002	+0.0002	0.000
3	-0.0006	-0.0005	0.003
4	-0.0012	+0.0018	0.075
5	-0.0015	+0.0021	0.072
6	-0.0010	+0.0024	0.057
7	-0.0014	+0.0017	0.044
8	-0.0019	+0.0014	0.041
9	-0.0025	+0.0008	0.037
10	-0.0034	-0.0019	0.015

0.1-ohm Decade

Setting	Correction(ohms)		% Diff.
	(1952)	(A.Faure 1951)	
1	+0.0006	+0.0006	0.000
2	+0.0003	+0.0005	0.100
3	+0.0003	+0.0007	0.133
4	+0.0003	+0.0009	0.150
5	+0.0004	+0.0012	0.160
6	+0.0005	+0.0015	0.167
7	+0.0008	+0.0018	0.143
8	+0.0010	+0.0023	0.162
9	+0.0010	+0.0028	0.200
10	+0.0007	+0.0030	0.230

(b) The Slidewire.

NOTE: The values below represent the resistance as measured on the bridge for a given setting of the slidewire, i.e. twice the actual resistance of the wire for the setting in question (see p.20). They are set out in the same way as logarithm tables. The units are ohms $\times 10^{-4}$.

	0	1	2	3	4	5	6	7	8	9
0	-	-	-	-	-	-	0000	0012	0024	0036
1	0048	0060	0072	0083	0095	0107	0119	0131	0143	0155
2	0167	0179	0191	0203	0215	0226	0238	0250	0262	0274
3	0286	0298	0310	0322	0334	0346	0358	0370	0381	0393
4	0405	0417	0429	0441	0453	0465	0477	0489	0501	0513
5	0524	0536	0548	0560	0572	0584	0596	0608	0620	0632
6	0644	0656	0667	0679	0691	0703	0715	0727	0739	0751
7	0763	0775	0787	0799	0811	0822	0834	0846	0858	0870
8	0882	0894	0906	0918	0930	0942	0954	0965	0977	0989
9	1001	1013	1025	1037	1049	1061	1073	1085	1097	1109
10	1120	1132	-	-	-	-	-	-	-	-

(c) Bridge Leads Resistance.

The leads resistance of the bridge on the right-hand side was 0.283 ohms.

(d) Ratio Arm Inequality.

Readings taken with the ratio arms direct were 0.085% higher than those with ratio arms reversed: the inequality ratio of the ratio arms (X in equation (1.1)) was therefore approximately 0.043%.

B. STANDARDISATION OF THE CONDUCTANCE CELLS.

(a) Cell Constants.

The values obtained for the cell constants of Cells I and II at various times are given below. For Cell I, only the values determined after the capillary tube had been broken and subsequently repaired on 28/3/1952 are quoted. The potassium chloride used had been purified by A. Faure[2], Festenstein[29], or Taylor[56].

Cell	Source of KCl	Date	Cell Constant
Cell I	A. Faure	26/8/1952	0.12118
	"	27/8/1952	0.12119
	"	27/8/1952	0.12120
	"	9/9/1952	0.12122
	"	10/9/1952	0.12121
	"	10/9/1952	0.12123
Cell II (Before platinisation)	A. Faure	6/8/1952	0.10899
	Taylor	8/8/1952	0.10899
	"	17/8/1952	0.10898
	A. Faure	8/9/1952	0.10899
	"	8/9/1952	0.10900
	"	9/9/1952	0.10900
	Festenstein	3/7/1953	0.10901
	"	3/7/1953	0.10900
	"	4/7/1953	0.10900
	"	4/7/1953	0.10898
	"	9/11/1953	0.10898
	"	11/11/1953	0.10898
	"	12/11/1953	0.10897
	"	12/11/1953	0.10899
(After platinisation)	Festenstein	6/12/1953	0.10893
	"	7/12/1953	0.10892
	"	21/12/1953	0.10892
	"	21/12/1953	0.10892
	A. Faure	22/12/1953	0.10892

(b) Cell Leads Resistances.

Cell I -- 0.635 ohms (August 1952)

Cell II -- 0.119_5 " (June 1952)

Both these values were the total leads resistance measured from 1 cm from the ends of the wires. For connections at other points, 0.0004_4 ohm was subtracted for each 1 cm of lead which was unconnected.

B. STANDARDISATION OF THE CONDUCTANCE CELLS.

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The values obtained for the cell constants of Cells I and II at various times are given below. For Cell I, only the values determined after the capillary tube had been broken and subsequently repaired on 28/3/1952 are quoted. The potassium chloride used had been purified by A. Faure[2], Festenstein[29], or Taylor[56].

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Cell I	A. Faure	26/8/1952	0.12118
	"	27/8/1952	0.12119
	"	27/8/1952	0.12120
	"	9/9/1952	0.12122
	"	10/9/1952	0.12121
	"	10/9/1952	0.12123
Cell II (Before platinisation)	A. Faure	6/8/1952	0.10899
	Taylor	8/8/1952	0.10899
	"	17/8/1952	0.10898
	A. Faure	8/9/1952	0.10899
	"	8/9/1952	0.10900
	"	9/9/1952	0.10900
	Festenstein	3/7/1953	0.10901
	"	3/7/1953	0.10900
	"	4/7/1953	0.10900
	"	4/7/1953	0.10898
	"	9/11/1953	0.10898
	"	11/11/1953	0.10898
	"	12/11/1953	0.10897
	"	12/11/1953	0.10899
(After platinisation)	Festenstein	6/12/1953	0.10893
	"	7/12/1953	0.10892
	"	21/12/1953	0.10892
	"	21/12/1953	0.10892
	A. Faure	22/12/1953	0.10892

(b) Cell Leads Resistances.

Cell I -- 0.635 ohms (August 1952)

Cell II -- 0.119_5 " (June 1952)

Both these values were the total leads resistance measured from 1 cm from the ends of the wires. For connections at other points, 0.0004_4 ohm was subtracted for each 1 cm of lead which was unconnected.

C. STANDARDISATION OF BALANCES AND WEIGHTS.

(a) Corrections for Inequality of Length of Balance-arms.
(May 1952)

All weighings were performed in the conventional manner, with the object to be weighed on the left-hand pan and the weights on the right-hand pan.

The following corrections for inequality of length of the balance-arms had to be applied to the observed weights on the different balances in order to obtain the true weights:-

Balance	Correction
B I	- 0.0146%
B II	+ 0.0075%
B III	+ 0.0025%

However, for the intercomparison of weighings done on two different balances, it was not necessary to convert all weighings to true weights. Instead, the corrections given in the table below were used: the correction was applied to the apparent weight of the body observed on balance Y (i.e. in the left-hand column) in order to obtain its apparent weight on balance X (i.e. in the top row).

Balance X / Balance Y	B I	B II	B III
B I	---	- 0.0221%	- 0.0171%
B II	+ 0.0221%	---	+ 0.0050%
B III	+ 0.0171%	- 0.0050%	---

(b) Calibration of Weights.

Weights WI (Fractional weights in box (10 - 500 mg) -- May 1952
Riders on balance (1 - 5 mg) -- November 1953)

Nominal Wt. (mg)	Correction (μg)	Nominal Wt. (mg)	Correction (μg)
1	+ 1	20	- 16
2	+ 13	50	- 37
3	- 1	100	- 29
5	- 4	100*	- 31
10	+ 16	200	- 15
10*	+ 26	500	- 51

Weights WII (May 1952)

Nominal Wt. (g)	Correction (mg)	Nominal Wt. (g)	Correction (mg)
0.01	- 0.02	1	0.00
0.01*	- 0.07	1*	+ 0.02
0.02	- 0.05	1**	+ 0.03
0.05	+ 0.01	2	+ 0.05
0.1	+ 0.02	5	- 0.01
0.1*	+ 0.03	10	+ 0.07
0.2	+ 0.05	10*	+ 0.15
0.5	+ 0.06	20	+ 0.03
		50	+ 0.04
		100	+ 0.62

Weights WIII (May 1952)

Nominal Wt. (g)	Correction (mg)
100	- 0.8
100*	- 1.1
200	- 2.5
500	- 3.5
1000	- 5.5

Weights WIV (March 1953)

Nominal Wt. (mg)	Correction (mg)	Nominal Wt. (mg)	Correction (mg)
10	0.00	100	- 0.01
20	+ 0.04	200	- 0.01
30	+ 0.06	300	- 0.02
40	+ 0.06	400	- 0.03
50	- 0.03	500	+ 0.06
60	+ 0.01	600	+ 0.06
70	- 0.01	700	+ 0.04
80	0.00	800	+ 0.02
90	+ 0.03	900	+ 0.02

D. VARIATION OF CONDUCTIVITY OF WATER WITH MEASURED RESISTANCE.

All resistances were measured with the ratio arms and the supply voltage in the direct position, using a frequency of 900 c/s. The value of the resistance used in parallel with the cell, measured under the same conditions was 10,003.0 ohms at 24°C.

Measured Resistance (ohms)	Conductivity (nm/cm) of Water in	
	Cell I	Cell II
9958.0	54.8_4	-
9956.9_5	-	54.8_3
9950	64.7	63.2
9940	76.9	75.2
9930	89.2	87.2
9920	101.5	99.2
9910	113.9	111.3
9900	126.3	123.4
9890	138.7	135.5
9880	151.1	147.6
9870	163.5	159.8
9860	176.0	172.0
9850	188.5	184.2
9840	201.0	196.4
9830	213.6	208.7
9820	226.2	221.0
9810	238.8	233.3
9800	251.4	245.6
9780	276.7	270.4
9760	302.2	295.2
9740	327.7	320.2
9720	353.4	345.2
9700	379.1	370.4
9680	405.0	395.6
9660	430.9	421.0
9640	457.0	446.5
9620	483.2	472.0
9600	509.5	497.7
9550	575.7	562.4
9500	642.6	627.8
9450	710.2	693.8
9400	778.5	760.6
9350	847.6	828.1
9300	917.4	896.2
9250	988.0	965.2
9200	1059.3	1034.9
9100	1204.3	1176.5
9000	1352.5	1321.3
8800	1659.1	1620.8
8600	1979.9	1934.2
8400	2316.0	2262.6
8200	2668.5	2607.0
8000	3038.6	2968.6

E. RESULTS OF THE TITRATION EXPERIMENTS.

The detailed results of the various experiments described in Section 3.325 are given in the table below. The abbreviations and symbols mean as follows:-

Plat. - platinised electrodes
Unplat. - unplatinised electrodes
R_c - calculated resistance (see Section 3.
R_m - measured resistance

The measured resistances are in all cases either the values obtained immediately after the addition (for the first additions and some of the others) or, where a slight increase in resistance has subsequently occurred which is obviously due to the removal of a small amount of carbon dioxide, the highest resistance reached after the addition. The solvent corrections for each of the solutions have not been included.

Expt. No.	Electrode condition	Stirring gas	Addn. No.	Concn. x 10^4 (equiv./l.)	Resistance (ohms)		% Diff. $\frac{100(R_c-R_m)}{R_c}$
					R_c	R_m	
1	Unplat.	Nitrogen	1	0.9729_6	7469.4	7498.5	-0.39_0
			2	1.9480	3751.6	3754.2	-0.06_9
			3	2.8705	2553.4	2553.8	-0.01_6
			4	3.8426	1911.5	1910.8	0.03_7
			5	4.7890	1536.5	1536.1	0.02_6
2	Unplat.	Nitrogen	1	0.9776_8	7436.2	7425.6	0.14_3
			2	2.0402	3582.2	3577.8	0.12_3
			3	2.9978	2444.4	2441.9	0.10_2
3	Unplat.	Nitrogen	1	0.9584_7	7587.7	7572.9	0.19_5
			2	1.8876	3869.8	3864.8	0.12_9
			3	2.8351	2584.5	2581.8	0.10_4
			4	3.7578	1954.1	1952.8	0.06_6
			5	4.7163	1559.7	1559.1	0.03_8
4	Unplat.	Nitrogen	1	1.0527	6834.1	6822.2	0.17_4
			2	1.9797	3669.9	3666.9	0.08_2
			3	2.9321	2490.2	2489.0	0.04_8
			4	3.8939	1881.0	1880.2	0.04_3
			5	4.8574	1511.5	1511.0	0.03_3
			6	5.7866	1271.1	1270.5	0.04_7
5	Unplat.	Nitrogen	1	0.9560_1	7607.9	7591.5	0.21_6
			2	1.9272	3793.6	3787.4	0.16_3
			3	2.8878	2539.1	2536.1	0.11_8
			4	3.8677	1900.0	1898.0	0.10_5
			5	4.8145	1528.9	1527.3	0.10_4
			6	5.8763	1254.7	1253.5	0.09_5
			7	6.9221	1066.6	1065.7	0.08_4
			8	7.8692	939.3_9	938.6_6	0.07_8
			9	8.8110	839.8_6	839.2_2	0.07_6
			10	9.7724	758.0_3	757.5_0	0.07_0
6	Unplat.	Oxygen	1	0.9838_7	7371.6	7347.4	0.33
			2	1.8541	3936.5	3924.1	0.31
			3	2.8375	2581.4	2574.5	0.27
			4	3.9088	1878.8	1873.8	0.27

Expt. No.	Electrode condition	Stirring gas	Addn. No.	Concn. x 10^4 (equiv./l.)	Resistance (ohms) R_c	Resistance (ohms) R_m	% Diff. $\frac{100(R_c-R_m)}{R_c}$
7	Unplat.	Oxygen	1	0.9833_3	7386.5	7360.1	0.36
			2	1.8501	3947.9	3934.9	0.33
			3	2.9073	2521.0	2512.9	0.32
			4	3.8865	1890.0	1884.1	0.31
			5	4.9281	1493.2	1488.7	0.30
8	Unplat.	Hydrogen	1	0.9868_0	7364.9	7339.4	0.35
			2	2.0648	3538.2	3528.0	0.29
			3	3.0473	2404.3	2396.9	0.31
9	Unplat.	Hydrogen	1	0.9872_5	7364.0	7336.0	0.38
			2	2.0805	3512.1	3499.3	0.36
			3	3.2225	2275.4	2267.8	0.33
			4	4.3015	1708.7	1703.3	0.32
			5	5.3469	1376.9	1372.6	0.31
10	Unplat.	Oxygen	1	0.9839_9	7377.2	7348.7	0.39
			2	1.9467	3748.8	3735.1	0.37
			3	3.0121	2431.9	2423.5	0.35
			4	3.9444	1861.2	1855.0	0.33
			5	4.9163	1496.1	1491.2	0.33
11	Plat.	Nitrogen	1	0.9563_8	7560.1	7506.9	0.70
			2	1.9278	3767.6	3745.0	0.60
			3	2.9026	2513.9	2499.3	0.58
			4	3.9511	1852.9	1842.5	0.56
			5	4.9100	1494.3	1486.2	0.54
12	Plat.	Oxygen	1	0.9848_0	7350.3	7286.4	0.87
			2	2.0089	3624.2	3597.5	0.74
			3	2.8951	2523.6	2505.7	0.71
			4	3.9593	1850.5	1837.9	0.68
			5	4.9043	1496.9	1486.9	0.67
13	Plat.	Hydrogen	1	1.0101	7153.7	7007.7	2.04
			2	1.9573	3714.1	3661.8	1.41
			3	2.8912	2525.0	2494.7	1.20
			4	3.8243	1914.4	1894.0	1.07
			5	4.7601	1541.4	1526.3	0.98
14	Plat.	Hydrogen	1	1.0608	6821.8	6749.1	1.07
			2	2.0324	3587.4	3564.9	0.63
			3	3.0922	2367.0	2356.6	0.44
			4	4.0166	1826.5	1845.1	- 1.02
			5	4.9894	1473.2	1484.6	- 0.77
A. Faure's Results^2.					Equiv. Cond. Λ_c	Λ_m	$\frac{100(\Lambda_m-\Lambda_c)}{\Lambda_m}$
				0.49	149.27	149.83	0.37_4
				1.96	148.62	148.87	0.16_8
				4.41	147.97	148.06	0.06_1
				7.84	147.33	147.39	0.04_1
				12.25	146.70	146.76	0.04_1

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Reprinted from THE JOURNAL OF THE SOUTH AFRICAN CHEMICAL INSTITUTE, New Series, June 1951, Vol. IV, No. 1, *pp.* 19–24

Oorgedruk uit DIE JOERNAAL VAN DIE SUID-AFRIKAANSE CHEMIESE INSTITUUT, Nuwe Serie, Junie 1951, Deel IV, No. 1, *bl.* 19–24

AN AUTOMATIC RECYCLING CONDUCTANCE WATER STILL

by

A. FAURE, P. K. FAURE and J. A. GLEDHILL

With the author's compliments
Met die komplimente van die skrywer

W. LTD

AN AUTOMATIC RECYCLING CONDUCTANCE WATER STILL.

by

A. FAURE, P. K. FAURE AND J. A. GLEDHILL

OPSOMMING

'n Elektries verhitte distilleerapparaat waarin die water in twee stadia gedistilleer word, eers uit alkaliese permanganaat en dan uit fosforsuur, word beskryf. Toebehore wat 'n konstante waterpeil en veiligheid verseker word gebruik sodat die apparaat lang tydperke sonder aandag kan werk. 'n Outomatiese toestel laat die water sirkuleer as dit nie uit die opvangsfles verwyder word nie; gevolglik word die lang opwarmingsperiode wat noodsaaklik is in die geval van die gewone distilleerapparate, vermy. Daar word ook aangetoon dat die verwydering van ammoniak uit die distilleerketel gevolg deur die verwydering van koolstofdioksied uit die geleiding-sel beter resultate lewer as wanneer albei gasse tegelyk uit die distilleerketel verwyder word. Hierdie distilleerapparaat lewer water met 'n geleidings vermoë van minder as 0·09 mikromhos per centimeter; die beste monsters het 'n waarde van 0·071 bereik. Die apparaat verskaf ongeveer 16 liter water per dag.

SUMMARY

An electrically heated still is described in which the water is distilled in two stages, first from alkaline permanganate and then from phosphoric acid. Constant-level and safety devices are employed to enable the still to run for long periods without attention. An automatic device allows the water to be recycled when none is being taken from the still, thus avoiding the long "warm-up" period necessary with conventional stills. It is pointed out that removal of ammonia in the still and of carbon dioxide in the conductance cell gives better results than removal of both gases in the still. When used in this way the water from the still has a conductivity below 0·09 micromhos per centimetre, the best water obtained reaching 0·071. The still will deliver up to 16 litres of such water per day.

The work reported in this paper is part of a research programme originated by Professor W. F. Barker in this laboratory.

In the execution of this programme, recent measurements of the conductances of very dilute aqueous solutions of electrolytes have necessitated the use of water of the lowest conductance attainable in routine work. The literature abounds with descriptions of stills for the production of conductance water; in their original forms several of these are capable of delivering daily several litres of "ultra-pure" water of conductivity better than 100 nm. per cm. (1 nm per .cm. = 1 nanomho per centimetre = 10^{-9} ohm^{-1}cm^{-1}) at 25° C. In general use, however, these stills do not seem to perform quite as well as this, and the common range of conductivity of the water used in precision conductance research has been from 200 to 600 nm. per cm.

It is commonly found that the water obtained from a still improves in quality from the time of starting the distillation, and reaches its lowest conductivity after several hours; this effect is probably due to the leaching out of those parts of the still which have not been in contact with water for some time. The still described in this paper is arranged to operate automatically for several weeks, the water, once it has filled the collecting vessel, being siphoned back into the reservoir. In this way it is possible to obtain water of excellent quality as it is required, without having to wait for the still to be leached out.

The hydrogen and hydroxyl ions present in water contribute 55 nm. per cm. to its conductivity at 25° C.; it is generally believed that the remainder is due to carbon dioxide in the water. Work carried out in this laboratory has suggested that a large part of the residual conductivity is due to the ammonium and bicarbonate ions formed from the small amounts of ammonia and carbon dioxide in the air. This work, to be published later, also suggests that, while residual carbon dioxide is easily removed from the water by a current of carbon-dioxide-free gas, this procedure does not effectively remove it if ammonia is present. Hence it is desirable to remove all the ammonia before the water is used, a fact which has been stressed by Bjerrum[1] and by Ellis and Kiehl[2] among others.

In the present still a second distillation of the water from phosphoric acid solution is used to accomplish this end. The use of this acid in the preparation of conductance water has been suggested from time to time (e.g., by Bourdillon[3]), but the decision to use it in the present case was taken on the basis of the excellent results obtained by Ellis and Kiehl[2] in their work on the pH of distilled water, and has been fully justified by the performance of the still.

By the technique in which the ammonia is removed in the still and the carbon dioxide is removed later in the cell we have found it possible to use water of conductance 80—90 nm. per cm. as a routine practice. Many stills previously described in the literature as capable of delivering water of conductivity less than 70 nm. per cm. use a counter-current of purified air or condense only a fraction of the steam in order to free the water from gaseous impurities. The water is then used in the conductance cell without further blowing out. Careful study of later papers from those laboratories in which such stills were used, however, has failed to disclose any reports of experimental work in which the conductivity of the water was less than 120 nm. per cm.[4]

Description of the still

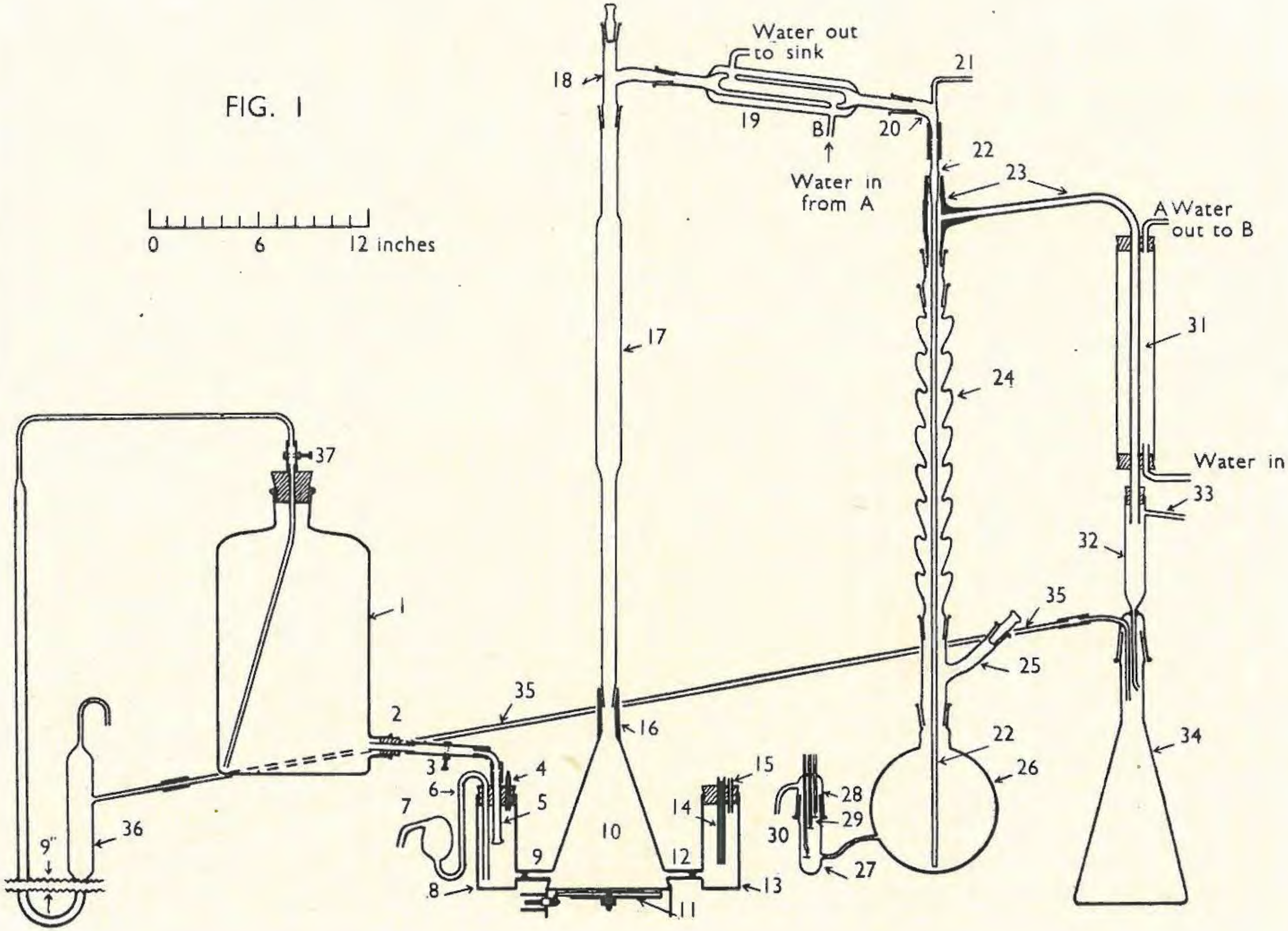
Figure 1 is a diagram of the still. The water for distillation is contained in the 10 litre Pyrex aspirator 1, from which it flows through the constant-level device to the boiler 10. The latter is an 18—8 stainless steel conical vessel with two side cups 8 and 13 of the same material, which are welded to the connecting tubes 9 and 12. These connecting tubes are made of $\frac{1}{2}$-inch stainless steel rod and have for $\frac{1}{2}$ inch of their length holes of diameter 1/32 inch, connecting the $\frac{3}{8}$ inch holes from either end; the purpose of the small holes is to permit slow transfer of liquid through the tubes without allowing the level in the cups to change rapidly as the liquid in 10 swishes round when boiling.

The cup 8 carries, through a rubber stopper, the inlet tube 5, the height of which determines the level of liquid in 8, 10 and 13. It also carries the level-indicator tube 6 and the air-leak tube 4 which consists of a short length of capillary tubing drawn to a diameter of about 0·3 mm. The tube 5 is flared at its lower end and has a spout like that of a beaker at one side. When the level in 8 falls below the end of this tube, bubbles of air enter and travel up into 1 by way of the slightly inclined tube 2, allowing water to enter 8 and so hold the liquid level constant. By having the small air leak 4 and the wide portion 7 on the level-indicator, liquid flows back from 7 into 8 during the bubbling process and so limits the amount of water entering to a quantity which can be handled by the cup and connecting tube 9. The overflow on 7 is a safety device in case air should get into 1 by some mishap; it discharges into a sink.

The boiler 10 contains enough sodium hydroxide to make the solution about normal, and enough potassium permanganate to make it about decinormal; the purpose of this mixture is to oxidize organic matter in the water and to hold back acid impurities. Because of the rapid action of the mixture on glass, it is essential to have the boiler made of some resistant material: the 18—8 stainless steel has been found eminently satisfactory for this purpose. The boiler is heated by a 900 watt urn element 11, which is controlled through a safety relay in conjunction with the electrode 14 as described later.

At the top of the boiler is the standard-taper socket 16, turned from stainless steel and welded to the boiler; it is designed to take the B24 joint at the foot of the spray trap and reflux column 17. This is surmounted by the stillhead 18, condenser 19 and adapter 20, all of which have standard-taper joints. The adapter connects with the inlet tube 22

FIG. 1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to the second boiler 26 by a glass-to-glass joint in pressure tubing, which gives a little flexibility when assembling the still. The lower end of 22 is drawn down to about 1mm. diameter to prevent solution from 26 blowing up and back into 10 if severe bumping should develop. The adapter carries also a tube 21 which is connected to a 2 litre flask (not shown) which communicates with the air. This flask acts as a buffer to prevent excessive "breathing" of laboratory air during boiling. Provision is made for a guard tube on the inlet.

The second boiler 26 is a 2 litre round-bottomed flask with the control device 27 sealed on by way of a length of 0·7 mm. capillary tubing, and is heated by a two-element flask-heating oven of special design. This flask contains approximately 0·1 M. phosphoric acid solution. It is connected by means of a B34 joint to the adapter 25, which carries the pear-bulb fractioning column 24 to act as a spray trap and reflux device, and which also has a side arm through which a porcelain chip may be inserted if bumping commences. Above the fractionating column is the cast block-tin stillhead 23, which has standard half-taper joints to fit the column and to carry the inlet tube 22. The tin take-off pipe from the stillhead is inclined upwards so that the first condensate will return to 26. The steam is finally condensed in the vertical portion 31, from which it falls through the adapter 32 into the 2 litre conical collecting flask 34, which has a B34 cone joint to fit the cap on the adapter as shown. The tube 33 connects with a 1 litre buffer flask which communicates with the air through a guard tube containing soda lime (for CO_2 and HCl), cupric chloride dihydrate (for H_2S), solid metaphosphoric acid (for NH_3) and more soda lime, in that order from the inside.

When the flask 34 has filled, the water is forced through the recycling tube 35 by the head which builds up in 32, and siphons intermittently down the sloping tube into the bulb 36. Since the latter is connected with the reservoir 1 by way of 37, the natural level of the water in 36 is the same as that in 8; thus when returned water runs into 36 it is eventually transferred to 1 to take the place of water leaving through 2, and becomes recycled. Provision is made for a guard tube at the top of 36.

The apparatus is mounted on a framework of three cross-braced retort stands screwed to a wooden base; a wooden stand is provided for the aspirator 1.

The electrical control apparatus

Since the still is required to operate unattended for long periods it is necessary that it should be protected against various kinds of fault which may develop. Also, it will be evident that some means is necessary for ensuring that water distils off from the second boiler 26 at a rate equal to that at which it enters from 10, otherwise 26 will fill and overflow or boil dry and crack. Both these ends are achieved by the use of a simple electrical control system.

The boiler 26 is heated by a specially made hotplate containing two elements, one o 750 watts and one of 600, spirally wound on an alundum base shaped to fit the flask. The 750 watt element is permanently on, but both it and the 900 watt element 11 of the first boiler form the load of a Sunvic type F 102–4 hot-wire relay. The control circuit of this relay is modified so as to connect to the line on one side and to the electrode 30 in the control device 27 on the other side. Electrode 29 is connected to the stainless steel electrode 14 in the control device 13 of the first boiler, and the metal boiler itself is earthed (Figure 2). This ensures that the permanent heaters will only function if the liquid level in 13 is above the end of the electrode 14 and if the level in 26 is sufficiently high to cover electrode 29. If the supply of water from 1 should fail for any reason, or if 26 should crack, this control circuit will at once switch off the heaters. Also, because of the connexion *via* earth and the neutral wire, the still cannot be put into operation if the earth contact on 10 is faulty, nor if the mains plug is inserted the wrong way round.

An automatic recycling conductance water still

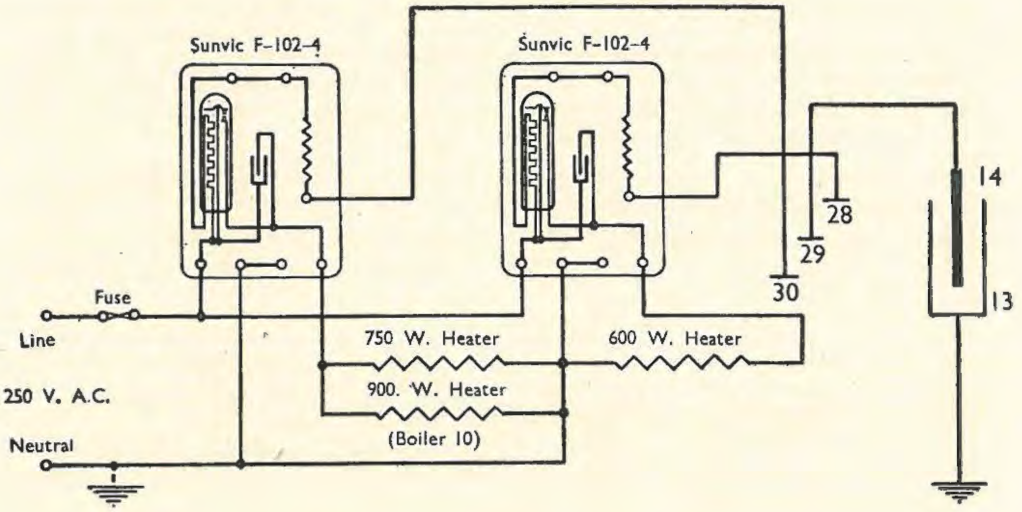

FIG. 2. Electric control circuit

The 600 watt intermittent heater for flask 26 is controlled through a similar Sunvic relay, the control circuit of which operates through electrodes 28, 29 and 14 to earth. Thus when the fast distillation from 10 brings the liquid level in 26 to that of electrode 28, the second heater is energized and, since the total wattage input to 26 now exceeds that to 10, the level falls again until contact with 28 is broken, and flask 26 refills until the cycle starts again.

The electrodes 28, 29 and 30 are horizontal pieces of thick platinum foil of area about $\frac{1}{4}$ square centimetre, with stout leads which are sealed to the mercury-filled Pyrex lead-tubes by Corning 707 glass and uranium glass.[5] The lead-tubes are brought out by internal seals through a cap with a B34 socket, making the electrode assembly easily removable when the still is to be cleaned. Electrode 14 was originally constructed in a similar way, but was found to be attacked by the caustic soda so that the platinum wire became loose and the electrode fell out of the glass tube. It was replaced, therefore, by a stainless steel rod as shown. It is not practicable to have this electrode in cup 8 and thus to eliminate one of the two cups, because when the still recycles, 8 is full of very pure water which does not conduct well enough to close the circuit.

Performance

The still delivers 2 litres of water into the receiving flask in 3 hours, so that 16 litres a day may be obtained from it if desired. Normally it is allowed to recycle overnight, and the convenience of having a flask full of good conductance water first thing in the morning would alone justify the continuous operation principle. Ordinary laboratory distilled water is used to fill the reservoir 1 when necessary. The pinchcocks 3 and 37 are first closed and afterwards opened slowly to prevent overflow of solution from 7. When poured from the flask into the cell in the air of the laboratory the water has a conductivity of about 800 nm. per cm.; after blowing out with carbon-dioxide-free air for about an hour, the time depending on the bubbling rate, the conductivity falls to a minimum which is between 80 and 90 nm. per cm. The best sample measured had a conductivity of 71 nm. per cm. This may be compared with the value of 62 nm. per cm. (recalculated to 25° C.) reached by Kohlrausch and Heydweiller in their classical experiment which involved 42 distillations *in vacuo*,[6] and with the figure of 66 nm. per cm. for the best water obtained by Kraus and Dexter from their still.[7]

When the water is kept in well-seasoned Pyrex flasks with tinfoil-covered rubber stoppers its conductivity increases by less than 1 nm. per cm. per day at 24° C. In a cell where it is agitated by bubbling the rate of increase is somewhat higher.

The chemicals in the boilers need replacing every month, or whenever the quality of the water starts to fall off.

Work on the early forms of the still was done in conjunction with Mr. G. N. Festenstein, MSc.

We are indebted to Mr. G. McP. Malan, BSc. for criticism and suggestions, and for a large number of measurements of the conductivities of samples of water.

One of us (A.F.) held a research studentship awarded by African Explosives and Chemical Industries during the period of development of the still, and wishes to express his gratitude to that company.

Note added in proof: Since submitting this paper the figure of 71 nm. per cm. for the best water has been improved upon by using purified nitrogen instead of air for the stirring gas. The best water obtained in this way reached 62 nm. per cm.

To guard against failure of the town water supply to the condensers a perforated bucket on a pivoted arm carrying a mercury switch has been inserted between electrodes 29 and 14, and the outflow water from the condensers passes through this bucket. This device has proved its worth on several occasions.

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Received December 4, 1950.

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