A STUDY OF THE MOVING BOUNDARY METHOD OF DETERMINING THE TRANSFERENCE NUMBERS OF ELECTROLYTES AND ITS APPLICATION TO AQUEOUS SOLUTIONS OF SILVER NITRATE AND AMMONIUM NITRATE

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INTRODUCTION

The transference number of an ion is defined as the ratio of the electric current carried by the ion to the current carried by all of the ions of the particular salt. It has been used for several purposes. Probably its most important use has been in the interpretation of conductance data. Thus Arrhenius' theory, which assumed that ionic mobilities were independent of concentration, was proved untenable when accurate transference number determinations showed a change in the transference numbers with concentration. It follows that the ionic mobilities are not independent of the concentration. The Debye-Hückel-Onsager theory which predicts achange in the ionic mobilities with concentration has been quantitatively checked in the low concentration range by transference numbers.

Transference numbers are also useful in determining thermodynamic properties of solutions[13]. Using concentration cells with transference the activity of the ions may be calculated by the use of the following equation:

$$dE = 2\, T_i \frac{RT}{F}\, d \ln a_i$$

where a_i is the mean ionic activity of the solution and T_i the transference number of the ion with respect to which the electrodes are not reversible. Besides activities,

liquid junction potentials, electrode polarizations, e.m.f.'s due to gravity and centrifugal force and diffusion coefficients of salts may be calculated once the appropriate transference numbers are known.

There are four methods for determining transference numbers: Hittorf, concentration cell with transference, e.m.f. of a cell in a high centrifugal field (64, 54, 47) and moving boundary. The first of these requires great experimental skill and much time, and does not give results of the highest accuracy. The interpretation of data from concentration cells is open to question. Great experimental difficulties are involved in the third method, although it is being used to some extent now in non-aqueous solutions where the other methods are not applicable. The moving boundary method gives the most accurate transference numbers and is the least time consuming. A study of this method and the possibility of its application to fairly concentrated solutions of $AgNO_3$ and NH_4NO_3 is the subject of this thesis.

The early work is of historical interest only and will be treated briefly. Lodge (30) was the first to observe the motion of a boundary formed between two solutions, one of which was colored. Whetham (66, 67, 68) and Nernst (52) extended the measurements. Masson (49) gave the first critical analysis of the phenomena involved.

Steele[63] originated the use of boundaries formed between solutions, both of which were colorless but had different refractive indices. Denison and Steele[62,63,7,9,8] obtained transference numbers of the more common electrolytes. Franklin and Cady[12] used this method in a non-aqueous solvent, viz, liquid ammonia.

In the present work only two-salt boundaries were considered. Thus boundaries formed between an indicator and a solution of two or more salts and between solutions of a salt at different concentrations are not considered. In the latter class is included the use of Schlieren methods to determine the concentration distribution in the boundary region.

ELEMENTARY THEORY[46]

The phenomenon on which the determination of transference numbers by the moving boundary method depends may be described as follows. Let figure 1 represent a section of a tube containing solutions of two electrolytes, AR and BR, R being a common ion constituent (either anion or cation).

At an initial time the solutions form a boundary a-b. Let an electric potential be applied so that the A and B ions migrate upwards, the common R ions downwards. After the passage of one faraday of electricity the boundary has the position c-d. The effect of this current passage is to move all of the A ions from the volume between a-b and c-d and to replace them with B ions. If the effect were that only those A ions which are dissociated moved upwards, then the motion of the boundary would give the actual velocity of the A ions under the applied potential gradient, but such is not the case, for as soon as the A ions migrate out of the boundary region, any AR molecules present dissociate forming A ions which migrate upwards. Hence the motion of the boundary is not influenced by the degree of dissociation of the electrolyte. This motion, however, is meaningless unless referred to a specific potential gradient. This gradient is that in the leading solution and is a function of the degree of dissociation. It is

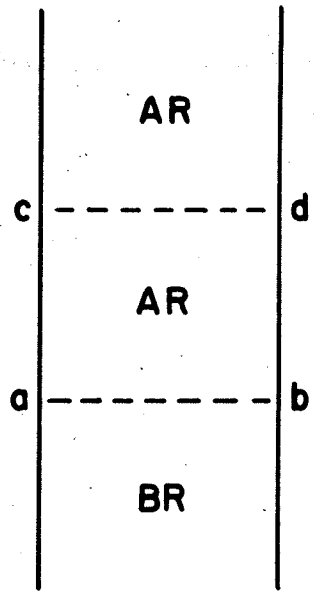


FIG. 1

easily seen that the motion of the boundary gives the same information as regards the velocities of the ions as the combined use of transference numbers and equivalent conductivities.

Let the volume swept out by the boundary in the passage of one faraday be V and the concentration of AR be C_a. Then the transference number of the A ion is:

$$T_a = VC_a. \qquad (1)$$

Experimentally the volume is defined by marks on the tube. Since the volume is taken with respect to the tube rather than with respect to an average solvent molecule as in the Hittorf measurements, the observed moving boundary transference number is not the same as the Hittorf one. The former can be compared to the latter after applying a correction to the moving boundary determination. This correction, discussed in Section V (1) is appreciable only in relatively concentrated solutions ($C_a > 0.1$ N).

If the quantity of electricity passed is not a faraday but rather f coulombs, then:

$$\frac{v}{V} = \frac{f}{F} \qquad (2)$$

v = volume swept out on the passage of f coulombs

F = faraday

and since $f = it$

$$\frac{v}{V} = \frac{it}{F} \qquad (3)$$

i = current in ampreres

t = time in seconds

On eliminating V from (1) and (3)

$$T_a = \frac{v\, C_a\, F}{it}$$

or in general:

$$T = \frac{v\, C\, F}{i\, t} \qquad (4)$$

In this derivation certain assumptions have been made, viz,

a) there are no disturbing effects due to interdiffusion or mixing of the two solutions,

b) the motion of the boundary is uninfluenced by the nature or concentration of the following or indicator ion constituent (B in Figure 1),

c) there are no volume changes in the apparatus that affect the motion of the boundary.

It will be shown that in a properly conducted determination these assumptions are justified or the necessary corrections can be made.

THE PRACTICAL DETERMINATION OF THE TRANSFERENCE NUMBER OF AN ION CONSTITUENT

1. The Indicator Solution

In determining the transference number of an ion constituent, the first consideration is the choice of a suitable electrolyte to act as a following or indicator ion constituent. The possibility of making a determination and the accuracy of the determination depend on the indicator chosen.

Measurements are made with boundaries that fall and also with boundaries that rise during a determination. In the former case the density of the indicator solution must be less, and in the second case greater, than that of the leading solution. Otherwise mixing results at the junction of the solutions and no boundary is formed. Another necessary condition is that the mobility of the indicator ion constituent must be lower than that of the leading ion. The boundary itself must be visible; hence the indicator solution must have a different color, or in general, a different refractive index, from that of the leading solution. Of course there must be no chemical interaction between the two solutions. Although most indicators used have had an ion in common with the leading electrolyte, this is not necessary. This point is clearly discussed by Hartley and Donaldson[15]. They point out that the ion immediately behind the boundary is supplied by the leading solution. Thus any electrolyte which

satisfies the preceding criteria for indicators and which, during the electrolysis, does not form unstable density differences may be used. Thus LiCl may be used above K_2SO_4. After a short period of electrolysis, the graduated tube will contain LiCl above Li_2SO_4 above K_2SO_4, the LiCl being less dense than the Li_2SO_4 solution. LiCl could not be used above Potassium Acetate with positive current flowing downwards since on electrolysis, a rising boundary is formed between LiCl and Lithium Acetate, this boundary being unstable due to the greater density of the LiCl solution. The resulting convection would probably disturb the lower boundary.

There are other requirements for the indicator solution for special cases, and these are discussed in other sections.

2. Method of Observing the Boundary

The method of observing the boundary makes use of the difference in refractive indices of the leading and indicator solutions. The optical system used in all of the work done since 1927 is that of MacInnes, Cowperthwaite, and Huang (45). It is sketched in figure 2. The light source, S , is a cylinder containing a light bulb and with a slit cut in one end. The light is made diffuse by means of a ground glass screen or a piece of 'Kleenex' tissue.

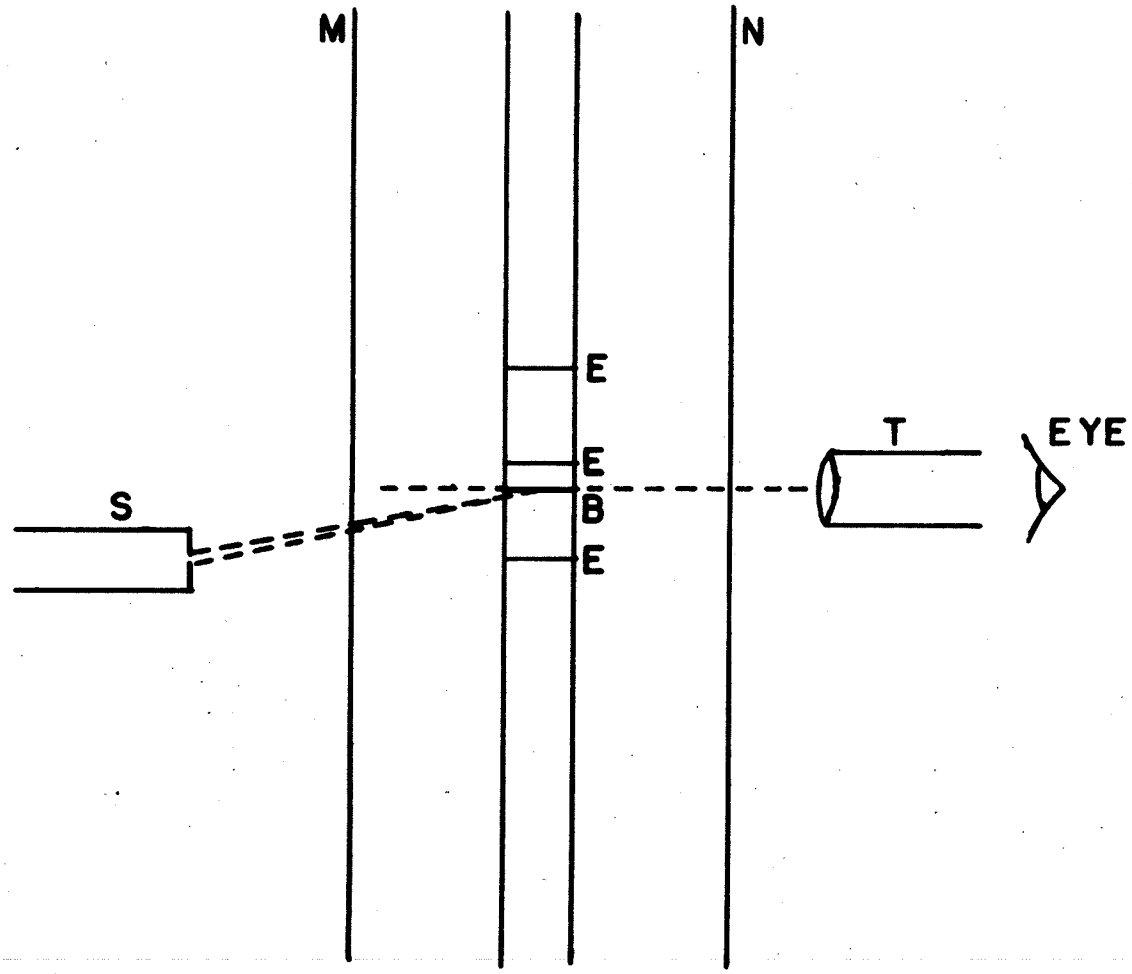


FIG. 2

When the source and the telescope, T , are properly aligned with the boundary, B , some of the light is totally reflected at the boundary due to the refractive index variation. If the source and the telescope are in the same plane as the boundary, the latter appears as a dark line on a bright background. If the relative positions are as shown in the figure the boundary appears as a bright line on a dark background. Whatever alignment is preferred, it should be the same for all readings of the boundary positions. In the figure, M and N are the glass walls of the thermostat; the E's are the etch marks on the capillary tube.

3. Various Moving Boundary Cells

The earliest moving boundary determinations were made using a cell which employed gelatine to separate the solutions initially and to form the boundary. This was unsatisfactory since the gelatine introduced impurities into the solutions. The cells which were subsequently used can be classified into cells which form the boundary by mechanical means and cells which form the boundary by chemical means. The boundary formed by the first method is called a sheared boundary and by the second method, an autogenic boundary.

The original sheared boundary was formed by Denison and Steele[10]. They used a parchment membrane to

separate the solutions and to form the boundary. The method was refined by MacInnes and Smith[48] who substituted rubber for the parchment. The technique was rather crude and formed poor boundaries.

The first apparatus which allowed for a complete initial separation of the solutions and which formed a sharp boundary was that of MacInnes and Brighton[41]. The apparatus has been refined by MacInnes and his school, the latest form of it being described by MacInnes and Longsworth[46]. It is illustrated in figures 3 and 4, the latter figure showing the construction of the plate glass discs, C_1, C_2, C_3, C_4. Discs 1 and 2 bear the same relation to one another as discs 3 and 4. The members of each pair are identical except that at P one has a brass projection and the other a hole into which the projection fits. A channel, J, forms an air insulation from the liquid of the thermostat when the two lubricated discs are in contact. In operation the vessels are filled as in figure 4a, leading solution being placed in the electrode chamber, E, and graduated tube, A, and indicator solution in the electrode chamber, E', if the boundary observed falls; leading solution is placed in E' and A, and indicator solution in E if the boundary rises. For rising boundaries discs 1 and 2, and for falling boundaries discs 3 and 4, are clamped together. The unclamped

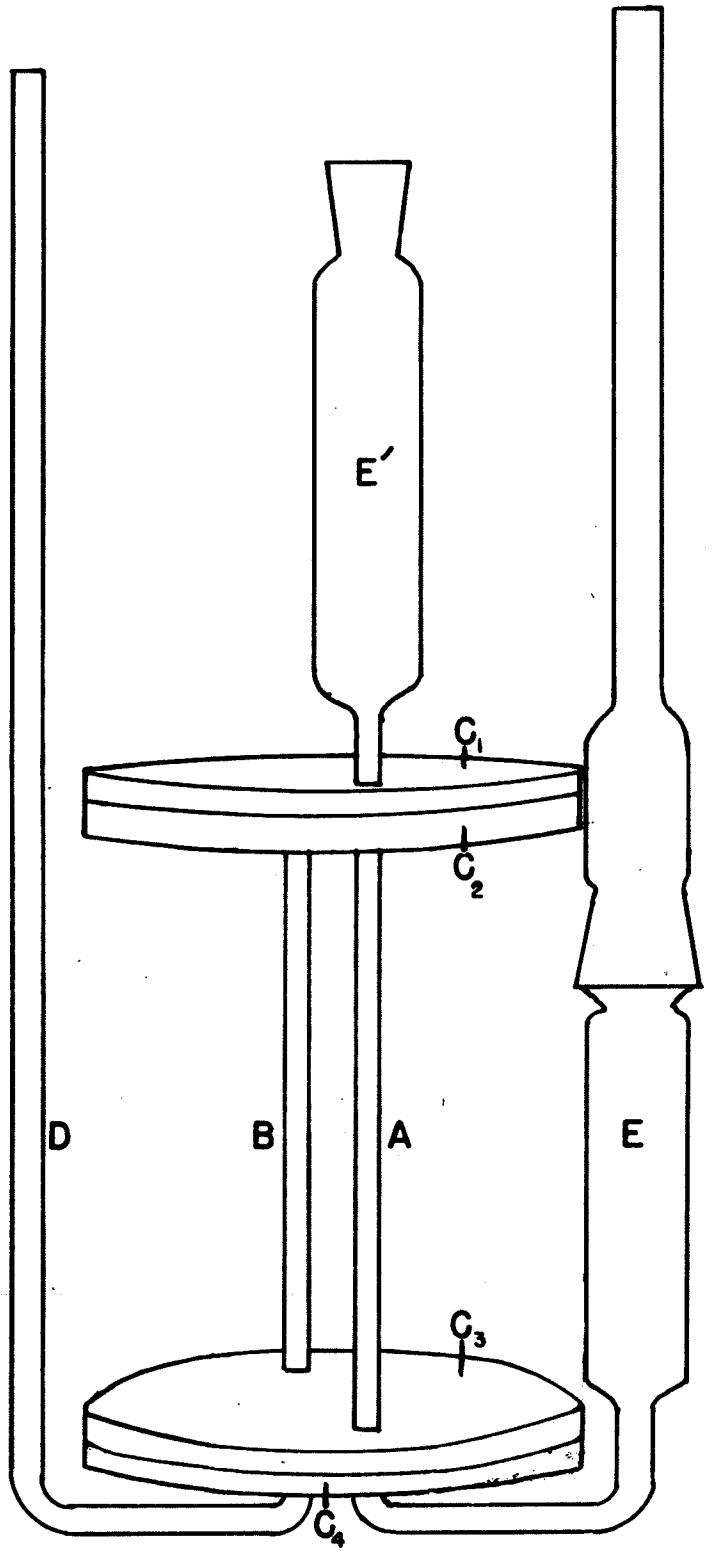
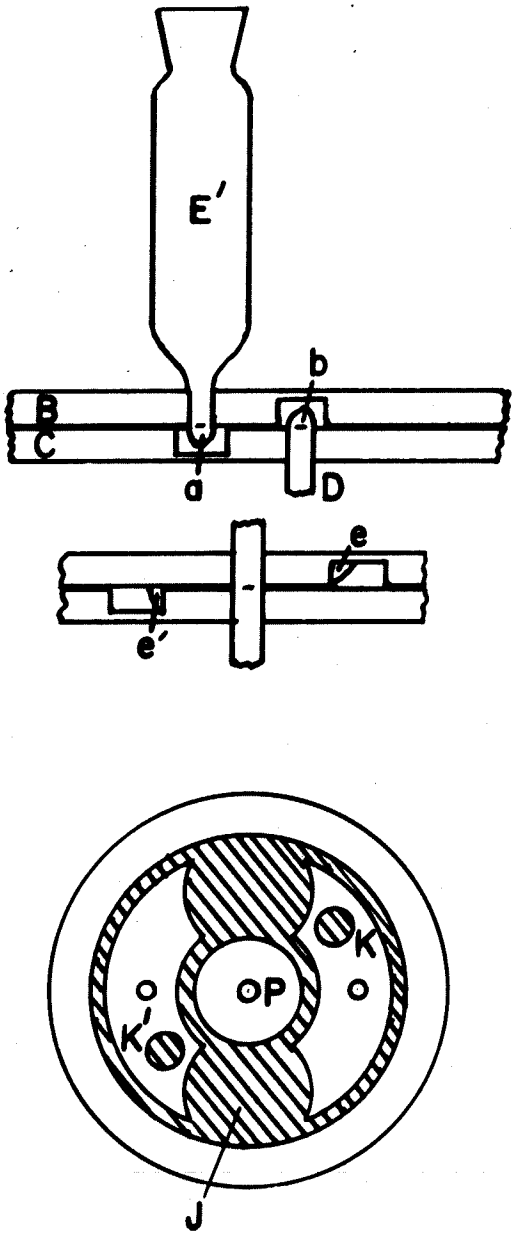


FIG. 3



a

b

c

FIG. 4

discs, adequately lubricated, are then placed at an angle to each other so that the drops on the ends of the tubes project into the appropriate depressions, K, K', of the discs. The discs are then pressed together as in figure 4a and the whole apparatus placed in the thermostat. When temperature equilibrium is reached a spring with a cable release turns disc 1 (if discs 3 and 4 are clamped together) or disc 4 (if 1 and 2 are clamped together) over 2 or 3 respectively to the position shown in figure 4b. The motion is gentle due to the viscosity of the lubricant. The resulting boundary is very sharp.

Gordon and co-workers[2] have developed a cell which is simpler in operation than that described above but which is restricted to rising boundaries. The cell is sketched in figure 5. With the stopcock, S, turned through an angle of 90° from the position shown, the solutions are forced by air pressure through the filling tubes C and D into the electrode vessels A and B and the measuring tube T, indicator solution being placed in A, and leading solution in B and T. To prevent the formation of air bubbles in the apparatus when placed in the thermostat the solutions are degassed by bubbling purified, water-saturated air through them at 200 mm. pressure. When the cell is filled, it is placed in the thermostat. The stopcock is then turned through 90° in a clockwise direction to form the

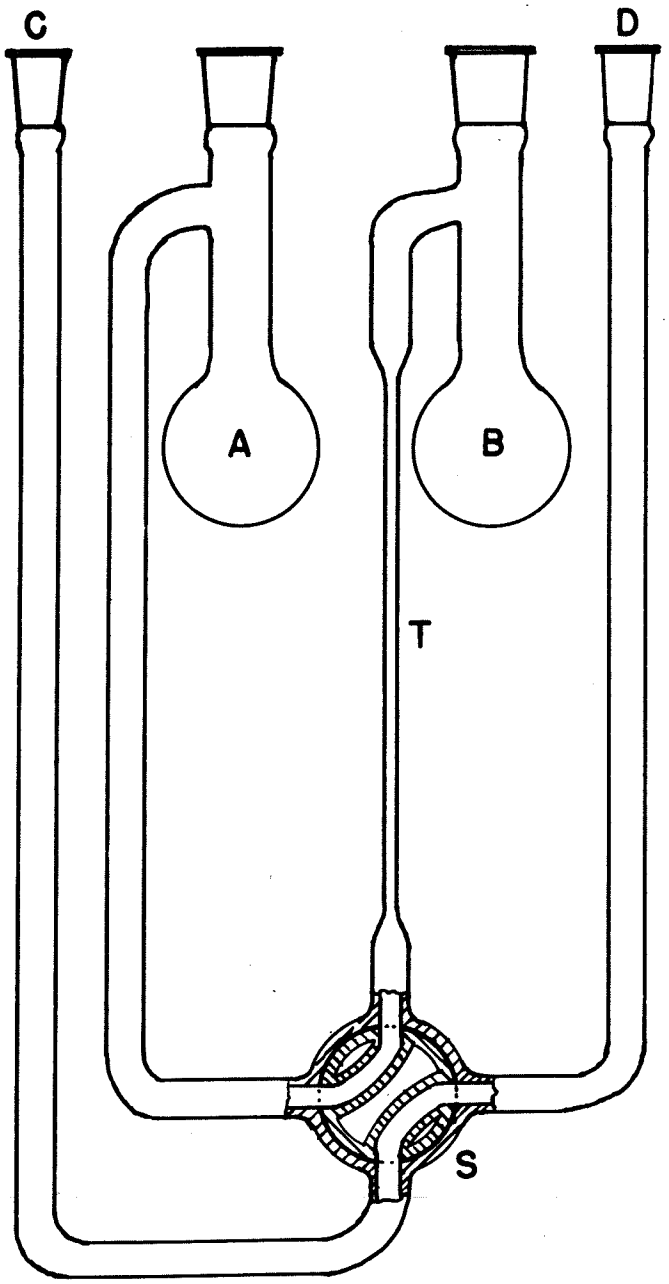


FIG. 5

boundary. The authors state that although the method of forming the boundary is rough, the latter, when it reaches the graduated tube, is sharp.

A type of cell which, when applicable, is much simpler in operation than a sheared cell is the autogenic cell introduced by Franklin and Cady[12] in 1904. No indicator solution as such is used, the indicator ion being formed by solution of the anode. The anodes used have been silver and cadmium. On electrolysis the reaction at a cadmium anode is

$$Cd \rightarrow Cd^{++} + 2 \text{ electrons.}$$

It is, of course, essential that the ions so produced do not form an insoluble salt with the anions of the electrolyte in the cell. If the cation in the cell has a greater mobility than the cadmium ion then a boundary is formed. The net result is the same as the formation of a sheared boundary using the cadmium salt formed as the indicator. The great advantage of the autogenic cell is its simplicity, but it can be used only for the determination of cation transference numbers. The choice of anodes is also severely limited due to interaction with the solvent (as in the case of the alkali metals) and to the fact that the solution produced must possess the properties necessary for an indicator (Section III (1)). All of the autogenic

boundaries produced so far have been rising boundaries.

Two autogenic cells have been extensively used. One is the same as that used by MacInnes and co-workers for sheared boundaries and illustrated in figure 3. To form autogenic boundaries in this apparatus a small cylinder of the metal used is set into a recess in disc 4 directly under tube B. By means of a spring and a soft rubber washer a water-tight connection is made with the bottom of the graduated tube. The tube and an electrode vessel (not in position in the figure) are filled with the observed solution. Contact with the metal cylinder is made by a wire passing through the glass tube D.

The second autogenic cell, drawn in figure 6, is that of LeRoy and Gordon[28]. The anode, of chemically pure cadmium, is carefully machined to fit the lower end of the graduated Pyrex tube, and before each experiment is sealed into the tube with De Khotinsky cement. To do this the lower end of the tube is heated by a small wire resistance bound around it and the anode whose sides have been covered with melted cement is pressed into place. The lowest graduation of the tube is far enough from the heater so that there is no appreciable rise in the temperature of the graduated part of the tube during the brief heating. The tube B is of sufficient length to ensure that none of the products of electrolysis at

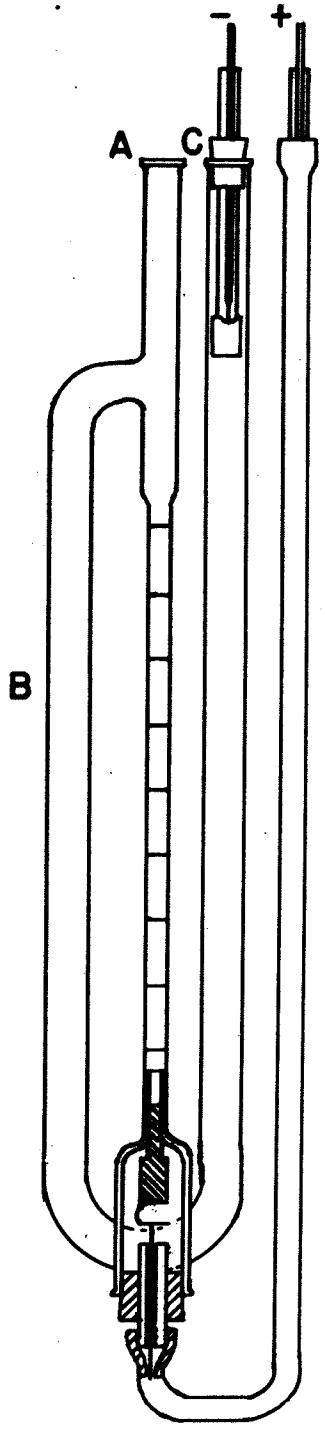


FIG. 6

the cathode can reach the graduated tube during a run. In filling the cell, solution is added at C , any air that might be trapped in the graduated tube being allowed to escape through a narrow capillary inserted at A , the capillary being removed after filling.

4. Electrodes and Electrode Vessels

During a measurement the electrodes must carry currents as high as 20 milliamperes for periods of approximately $2\frac{1}{2}$ hours. The electrodes and electrode vessels must be so designed that the products of electrolysis do not enter the graduated tube. Since one electrode must be closed to facilitate the calculation of the volume correction (Section V (1)) this electrode must be non-gassing during a run.

The commonest electrodes used have been silver and cadmium anodes and silver-silver chloride cathodes. These anodes produce the slow moving silver, cadmium and chloride ions on electrolysis thus helping to fulfill the condition that the electrolysis products should not enter the graduated tube. Cadmium anodes have generally been in rod form[2]. Figure 7 shows the silver electrode used by Smith and MacInnes[61] and by virtually all investigators since. It is formed by electroplating silver on platinum gauze. The wire connecting the gauze to the external power source is placed so as to be in the

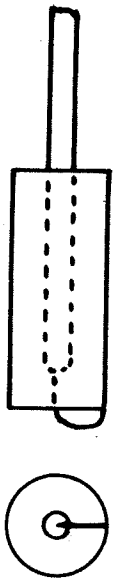


FIG. 7

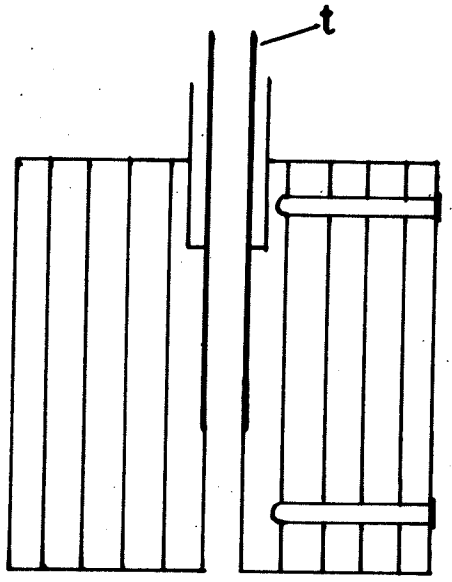
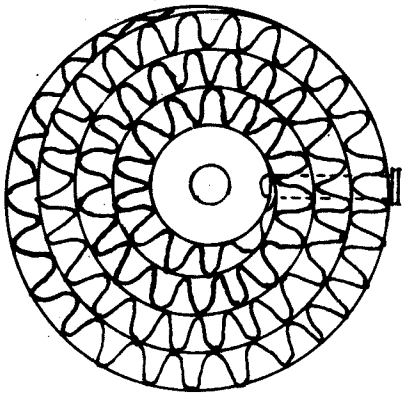


FIG. 8



part of the solution having the lowest current density. Thus the electrode of Figure 7 is used in electrode vessels of the type of Figure 5 and not of the type shown in Figure 3. Otherwise gassing occurs at this wire. Most of the silver-silver chloride electrodes used have been formed from the preceding silver electrode by making it the anode in a chloride solution. Gordon and co-workers[28] have used a platinum wire covered with fused silver chloride. The silver and silver-silver chloride electrodes of the greatest capacity are those of Longsworth[36]; his electrodes are slightly smaller than those of Longsworth and MacInnes[40]. One of these electrodes is sketched in Figure 8. It is made by winding a flat and a corrugated strip of sheet silver together into a tight spiral. The ends of the spiral are anchored to a hollow silver core with silver screws. The silver tube is also threaded into this core. This type of construction exposes a large electrode surface to the electrolyte. The electrodes of this type used by Longsworth had a capacity of 0.2 ampere-hours. To utilize this capacity he immersed the electrode in a 1 normal chloride solution, introduced through the tube t which projected above the apparatus.

A group of English workers under G.S. Hartley have used rather distinctive electrodes. As cathode

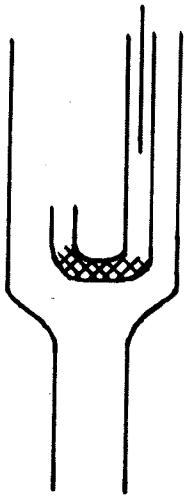


FIG. 9

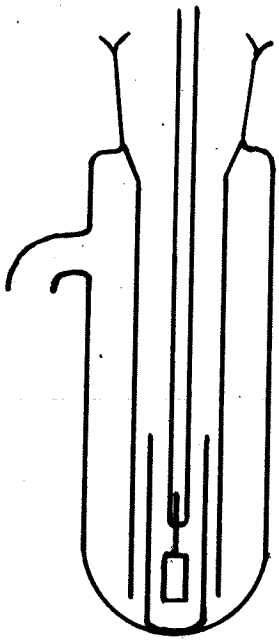


FIG. 10

they have used platinum gauze immersed in a ferric chloride solution[11]. Hartley[15] points out that it is not necessary to have a non-gassing electrode on the open side of the apparatus providing that the hydrogen or hydroxyl ions produced are neutralized. In their work employing lithium chloride as indicator they used the cathode illustrated in Figure 9 in which the shaded part represents solid lithium carbonate. The hydrogen ions produced at the platium wire on passing through the lithium carbonate region combine with the carbonate ions to form bicarbonate ions which move towards the anode. Lithium ions replace the hydrogen ions to carry the current away from the anode. When working with acetate or permanganate ions as indicator ions, these authors used as cathode a platinum wire surrounded by the corresponding acid. A system of guard tubes forced the hydroxyl ions formed by the anode reaction to pass through the acid region.

As mentioned previously, the design of the electrode vessel must be such as to have the electrode as far removed from the graduated tube as feasible. This has been accomplished in two ways. Gordon and co-workers[28] separated the cathode of their autogenic cell from the graduated tube by a tube whose length was twice that of the apparatus (cf. Figure 6). Other

workers have used a system of guard tubes. A typical example is that of Hartley and Donaldson[15]; the apparatus is sketched in Figure 10.

5. The Measured Quantities

a) The concentration.

Since moving boundary measurements have been made accurate to 0.02% the concentration must be known at least this well. Much work with hygroscopic salts has been done using the Richards bottling apparatus[56] by which such salts can be dried and weighed out of contact with air. In this manner the weight per cent of the solution can be accurately determined. Then using density data from the International Critical Tables or other sources the concentration may be calculated. In some cases analyses are sufficiently accurate. This is especially true of acid solutions, the differential electrometric method[43] having been used. However, the concentration is determined, it must be expressed in equivalents per unit volume.

b) The volumes.

The actual transference number determinations are made by determining the time in seconds for the boundary to pass between two etch marks on the measuring tube. The volume between these etch marks must be

known accurately (to $\pm$0.02%). The method used by all workers to achieve this accuracy is that of Longsworth[32]. He made the etch marks by means of hydrofluoric acid, the marks being from six to ten in number and fairly evenly distributed along the tube's length. By choosing appropriate pairs of etch marks it is possible to obtain several transference number determinations during a single run. Thus, if there are six etch marks, three near the bottom and three near the top of the tube, nine values of the transference number can be obtained from a single run using the nine volumes obtained by the combination of the three lower with the three upper marks, each volume having the required accuracy.

The volumes were determined by Longsworth by weighing the amount of mercury contained by the tube between the etch marks concerned. Lack of coincidence of the mercury meniscus with the graduations was allowed for by means of a travelling microscope.

c) The current.

In the equation for the transference number of an ion the product $i\,t$ where i is the current in amperes and t the time in seconds, occurs. If the current remained constant throughout a determination all that would be necessary would be to take one reading of the current and to record the time at which the boundary passed the

graduations, but in a run the cell resistance increases as the leading solution is replaced by a solution of lower conductivity. The simplest way of measuring the product it appears at first sight to be to use a coulometer. This method has been used by Reevely and Gordon[15] who used silver microcoulometers, the silver plated out being weighed on a microbalance, since the weight of silver is very small (approximately 0.015 grams for a 0.1 normal solution in the cell). Hence it is obvious that this method is restricted to relatively concentrated solutions. This method has now been completely discarded in favour of that outlined below.

Instead of determining the product it directly, it is possible to take simultaneous readings of the current and time during the course of a run. This is the technique used in all of the recent work. To increase the accuracy, devices have been developed to keep the current variation as small as possible. MacInnes and co-workers built a device to keep the current constant to $\pm 0.01\%$ during a run. The latest form of this apparatus is given by MacInnes and Longsworth[38]. They placed a large resistance in series with the cell. As the cell resistance increased during a run the decrease in current activated (by means of a potentiometer, galvanometer and photocell) a motor which decreased a series resistance.

The apparatus is quite complicated and has not found favour with other investigators.

An electronic device, much simpler than the one just discussed, was brought out by Hartley and Donaldson[15]. It is illustrated in Figure 11. The apparatus is placed in the plate circuit of a pentode, the one used being a Marconi PT2. For such a tube the plate current is almost independent of the plate voltage when the screen bias is 50 volts or more. The applied voltage V is made up of a 220 volt D.C. line augmented with batteries. The filament heater V_H is a 2 volt high capacity battery. The biases V_G and V_S are made up of dry cells. The grid receives an automatic bias by R_G which is largely cancelled by dry cells V_G. If the current decreases in a run the grid bias becomes more positive thus tending to increase the current. Thus two properties of the circuit help to stabilize the current. The authors found that currents of from 0.5 to 4 milliamps. were maintaned constant to 1 part in 500, the variation being attributed mainly to a drift in the cathode emission. The current is determined at intervals by a potentiometer. No mention is made of their time measurements.

LeRoy and Gordon[28] brought forth a current stabilizer essentially the same as that of Hartley and

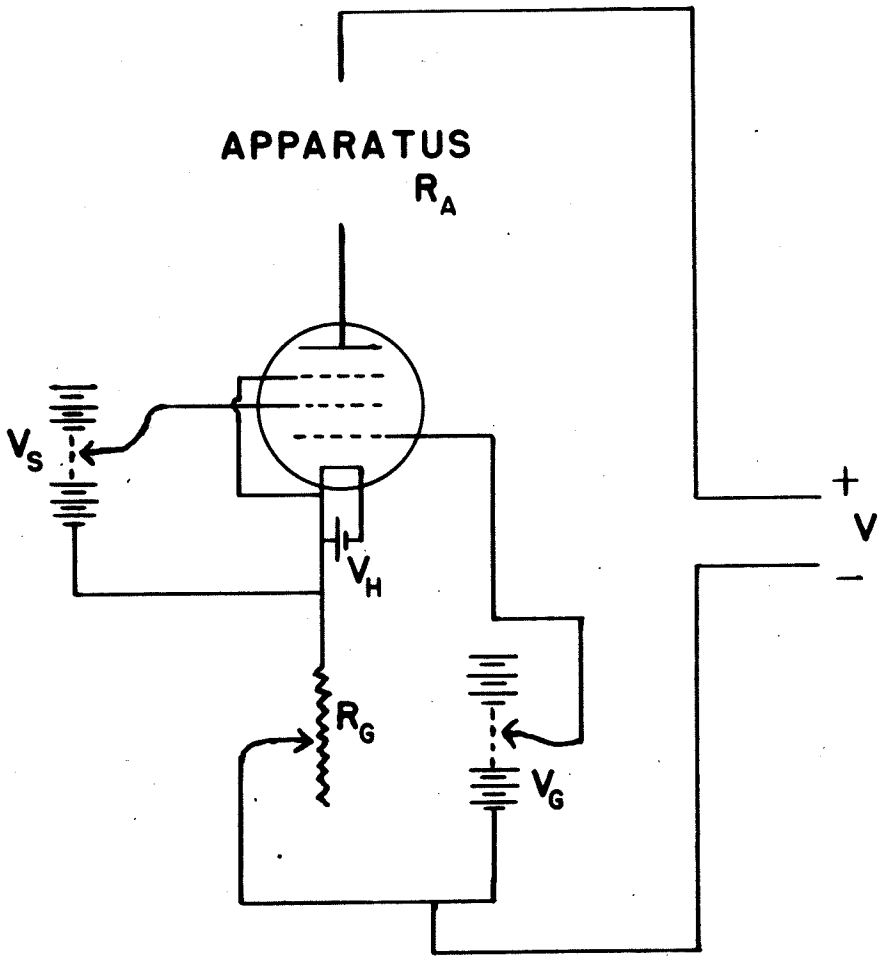


FIG. II

Donaldson. They substiuted a 1B4 pentode for the Marconi PT2 used by the English authors. The screen bias was kept at $^{+}62.5$ volts, the grid bias in the range -2.5 to -4.0 volts. The current was read every 5 or 10 minutes, graphical integration being employed to determine the mean currents.

d) The time.

The measurement of the time at which the boundary passes the graduations and at which the current readings are made must also be extremely accurate. Longsworth and MacInnes[46] employed a magnetic counter operated from the pendulum of an accurate clock. The pendulum periodically introduced a screen between a light source and a slit behind which was a photoelectric cell. With amplification, the resulting change in resistance operated the counter which was started when the boundary passed the first graduation.

Another type of time measuring device, an electrical chronograph, was used by LeRoy and Gordon[28]. No details are given in the paper.

DISTURBING AND RESTORING EFFECTS AT THE BOUNDARY

There are certain effects acting at the boundary, some of which tend to destroy it and some to sharpen it. These are discussed in what follows, taken mainly from reference 46.

1. Convection

During a run, heat is developed in the tube due to the passage of the electric current. This heat introduces two effects which tend to cause mixing at the boundary. Since the indicator solution must have a lower conductivity than the leading solution, more heat is generated in the former than in the latter. As a consequence, at the boundary there is a temperature gradient between the solutions. In certain conditions the flow of heat from the hot solution to the cold one may be accompanied by a tendency of the solutions to mix, this tendency being greater if the hot solution is the lower of the two.

For a discussion of the second heating effect, consider a cross section of one of the solutions which is not near the boundary. There is a temperature gradient set up along the radius of the cross section, the maximum temperature being at the centre (i.e. along the axis of the tube). As a result there is a tendency for the solution in the centre to stream upwards. Such streamers or funnels have been observed using potassium

permanganate as indicator. An analysis of this phenomenon has been accomplished by Mooney[46]. His conclusions are:

"(i) In the usual moving boundary experiment the temperature difference between the solution at the axis of the tube and the thermostat does not amount to more than a few tenths of a degree. Since transference numbers vary but slightly with the temperature this difference is negligible.

"(ii) The temperature of the solution at all points along a radius decreases as the square of the distance from the axis of the tube. Since the flow of solution due to convection decreases with a decrease in the difference in temperature between the solution at the centre and along the inside walls of the tube, this disturbing factor may be decreased by using tubes of small bore.

"(iii) The temperature difference between the axis and inside wall of the tube is independent of the thickness of the glass wall. Of course the mean temperature of the solution is increased by increasing the thickness of the glass wall, but other conditions being the same, the amount of convection which occurs in the solution in the tube is dependent on the bore of the tube and independent of the thickness of the glass wall."

One other point should be noticed about the heating effects. The rate at which heat is produced is Ei watts where E is the voltage drop and i the current. Hence, if for any reason the current is increased without a corresponding decrease in E the heat generated rises. Experimentally the current increases with an increase in the concentrations of the solutions. In none of the literature has a case been mentioned in which it was possible to decrease the applied potential corresponding to the increase in the current. One factor contributing to this effect is the increase in the diffusive forces at the boundary with an increase in concentration. As a result the restoring force must be increased. Thus the heating effect has always increased with increasing concentration. This is probably the reason why no measurements have been made for solutions more concentrated than 2 normal (9, 63).

2. Diffusion

Another factor tending to destroy the boundary is diffusion caused by the concentration gradients at the boundary. This effect increases with the concentration gradients. Hence this also tends to restrict the measurements to fairly dilute solutions. The diffusive and electrical forces have been treated theoretically by Weber (65). and by MacInnes and Longsworth (46). A discussion of their treatment and some experimental verification of their conclusions is given in part 5 of this section.

3. The Restoring Effect

The disturbing effects of convection and diffusion mentioned above are overcome by a restoring effect the nature of which follows. In performing a moving boundary experiment it is necessary for the indicator ion to be slower than the leading ion. As shown in the next part the concentration of the indicator ion in the region immediately behind the boundary is always less than that of the leading ion. Since the same current passes through each solution there is a greater potential gradient in the indicator than in the leading solution. If an indicator ion by convection or diffusion migrates into the leading solution it finds itself in a region of lower potential gradient than previously. Its speed is decreased and the indicator solution catches up to it. Similarly if a leading ion migrates into the indicator solution it is in a higher potential gradient than previously, its velocity increases, and it rejoins its original solution.

This restoring effect has been graphically illustrated by certain experiments of MacInnes and Cowperthwaite[42]. In determinations of the anion transference number of 0.01 normal sodium chloride they interrupted the current for periods of up to 32 minutes. When the current was reapplied the boundary appeared in a short time, the longest interval being 3 minutes for the 32

minute break. It was also found that the motion of the diffuse zone between the solutions was the same as that of the boundary, the transference numbers calculated with the time interval, including that in which no boundary was visible, agreeing within the experimental error with those calculated from the rest of the run. A run was also made in which they reversed the current for certain periods. Thus the sharp boundary was replaced by a diffuse zone of several centimeters in thickness. On returning the current to its original direction and allowing for the volume swept out during the reversal of the current they calculated the anion transference number and found it to agree well with the accepted value. Hence, even with this large diffuse zone, the net ionic motion was the same as if a boundary had been continually present.

Longsworth[33] states that when the restoring effect is greater than the disturbing influence the following conditions are fulfilled:

(i) the boundary appears flat and sharp,

(ii) at constant current it moves with constant velocity,

(iii) the observed transference numbers are, within wide limits, independent of the current density,

(iv) independent observations on cation and anion boundaries for the same solution give consistent results.

4. Adjustment of the Indicator Concentration

Experimentally, the restoring effect discussed in the previous part is powerful enough only if the indicator concentration is within certain limits. The limits depend on several factors but must include the Kohlrausch concentration derived in the next paragraph.

Consider a boundary which has moved from a position near a-b in Figure 12 to c-d. The electrolyte AR has been replaced by BR , the concentration of the latter being in general different from its original value. A concentration boundary is then formed at a-b between the two BR solutions. Consider now the motions on the passage of a faraday. The AR BR boundary goes from c-d to 'c'-d'. The motion of the boundary between the two BR solutions can be neglected as it is very small. The transference number of the A ion is obtained from equation (1).

$$T_A = VC_A \qquad (1)$$

Now the number of equivalents of ion constituent B passing the plane c-d per faraday is given by equation (5).

$$T_B = VC_B \qquad (5)$$

From the ratio of (1) and (5) equation (6) is obtained.

$$\frac{T_A}{C_A} = \frac{T_B}{C_B} \qquad (6)$$

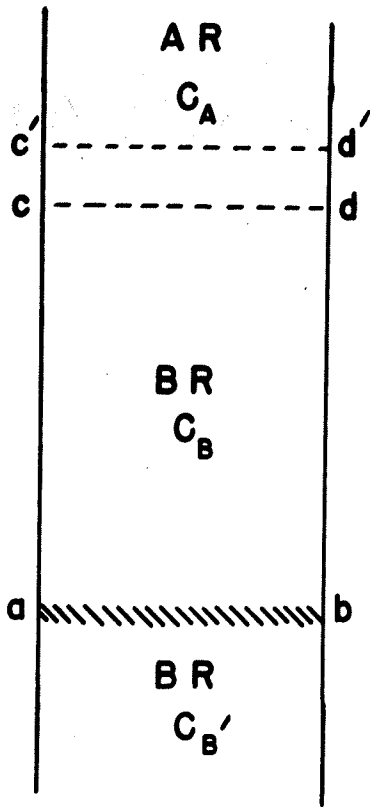


FIG. 12

It will be noted that no assumptions as to ionization of the electrolytes have been made. The reason for the adjustment in the indicator concentration is that the indicator electrolyte must travel at the same velocity at the boundary as the leading electrolyte. This can occur at only one indicator concentration for a given concentration of the leading solution.

This relation (equation (6)) is an application to an ordinary type of boundary of a more general function developed by Kohlrausch[26], This function defines a property of the solution which at any given point retains a constant value independent of changes of concentration caused by electrolytic migration. If as a result of such migration, species of ions different from those initially present appear at a point, their concentrations are adjusted to a value compatible with the constant determined by the initial composition of the solution. Thus the indicator solution concentration immediately behind the boundary is adjusted automatically. It is then obvious that the motion of the boundary gives information directly only for the leading solution and not for the indicator solution, as some of the early investigators thought. Because of Kohlrausch's contribution above, the terms Kohlrausch solution and Kohlrausch concentration are applied to the indicator solution immediately behind the boundary.

This adjustment of the indicator concentration has been used by some workers to determine the transference numbers of the indicator electrolyte. Hartley and Donaldson[15] analyzed the Kohlrausch solution conductimetrically and, using equation (6) together with the known concentration and transference number of the leading solution, calculated the transference number of the Kohlrausch solution. This method is less accurate than the direct moving boundary method but is applicable to ions of low mobility, whereas the direct method is not, Since the indirect method requires a knowledge of the transference number of the leading solution, this having a higher concentration than the Kohlrausch solution, it cannot be extended to solution concentrations greater than those studied by the direct method.

This simple theory of the indicator adjustment predicts no limitations to the adjustment. In practice such limitations are found. Experimentally the initial concentration must not be far removed from the adjusted Kohlrausch concentration. MacInnes and co-workers[61,48,41,59,45] obtained curves similar to Figure 13 when plotting the observed transference number against the initial indicator concentration. The horizontal portion includes the Kohlrausch concentration, C_K. Gordon and co-workers[2] working at 45°C. with potassium chloride followed by

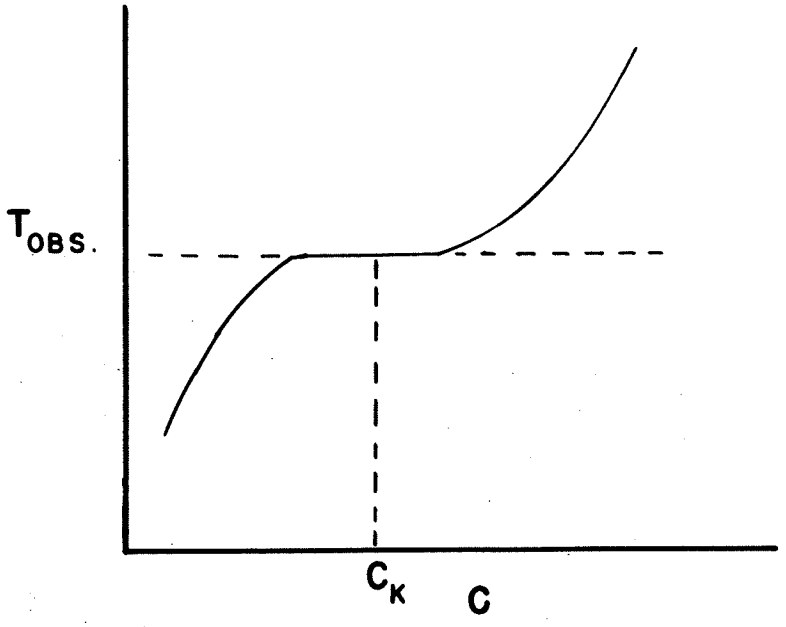


FIG. 13

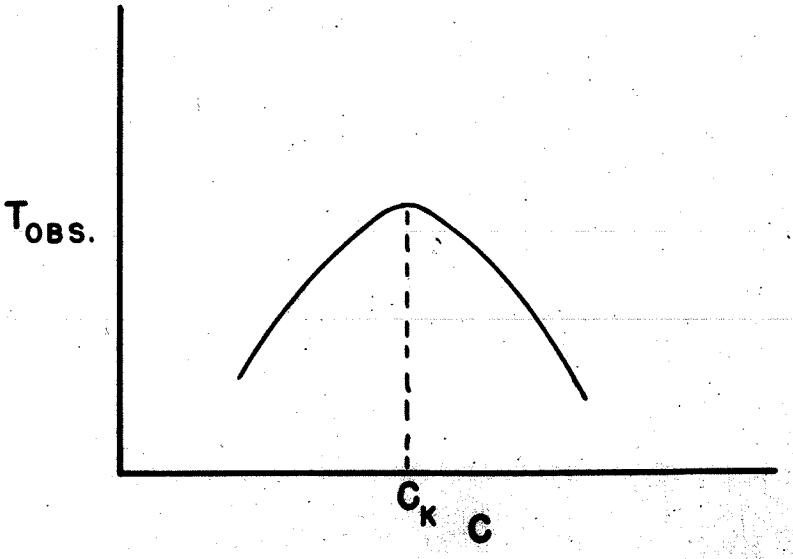


FIG. 14

potassium iodate, obtained the curve drawn in Figure 14. The maximum in the curve occurs at the Kohlrausch concentration. No explanation for the different types of curves is given.

From the various researches certain broad generalizations can be drawn regarding the range of adjustment of the indicator solution. The range is:

i) greater for dilute than for concentrated solutions,
ii) greater for narrow than for wide measuring tubes,
iii) greater for rising than for falling boundaries,
iv) greater at low than at high temperatures.

The indicator concentration must also be chosen so as to avoid unstable density differences. Thus in a rising boundary in which the initial indicator concentration is less than the Kohlrausch concentration an unstable boundary between these solutions is set up. It is quite possible that the resulting convection currents may destroy the boundary under observation. Hence in all measurements except those on the more dilute solutions the indicator concentration for a rising boundary must be greater than, and for a falling boundary less than, the Kohlrausch concentration.

5. Theory of the Effect of Diffusion and of the "Thickness" of the Boundary

Weber[65] was the first to make a theoretical

treatment of the conditions existing at the boundary. His work was reviewed by MacInnes and Longsworth[46], certain unnecessary assumptions being eliminated. The treatment below is that given by the last-named authors.

At a two-salt boundary both electrical and thermodynamic gradients are set up. The latter are due to concentration gradients and are the source of the forces tending to produce diffusion across the boundary. Considering these forces and using the experimental fact that when a steady state is attained the velocity of the boundary is constant, these authors derived equations (4) and (6). Hence, theoretically, the velocity of the boundary is not influenced by the diffusive forces acting at the boundary.

The theory was extended using the assumptions that

$\mu = \mu_o + k \ln c$ — μ = thermodynamic potential; k = Boltzmann constant

$u_\ell = u_c = 2u_i$ — u_ℓ = mobility of leading ion; u_i = mobility of indicator ion; u_c = mobility of common ion

and that these mobilities are independent of concentration (an impossible case but one approached by the LiCl/KCl and KIO_3/KCl boundaries) to compute the concentration gradients in the boundary region. The distribution so found for

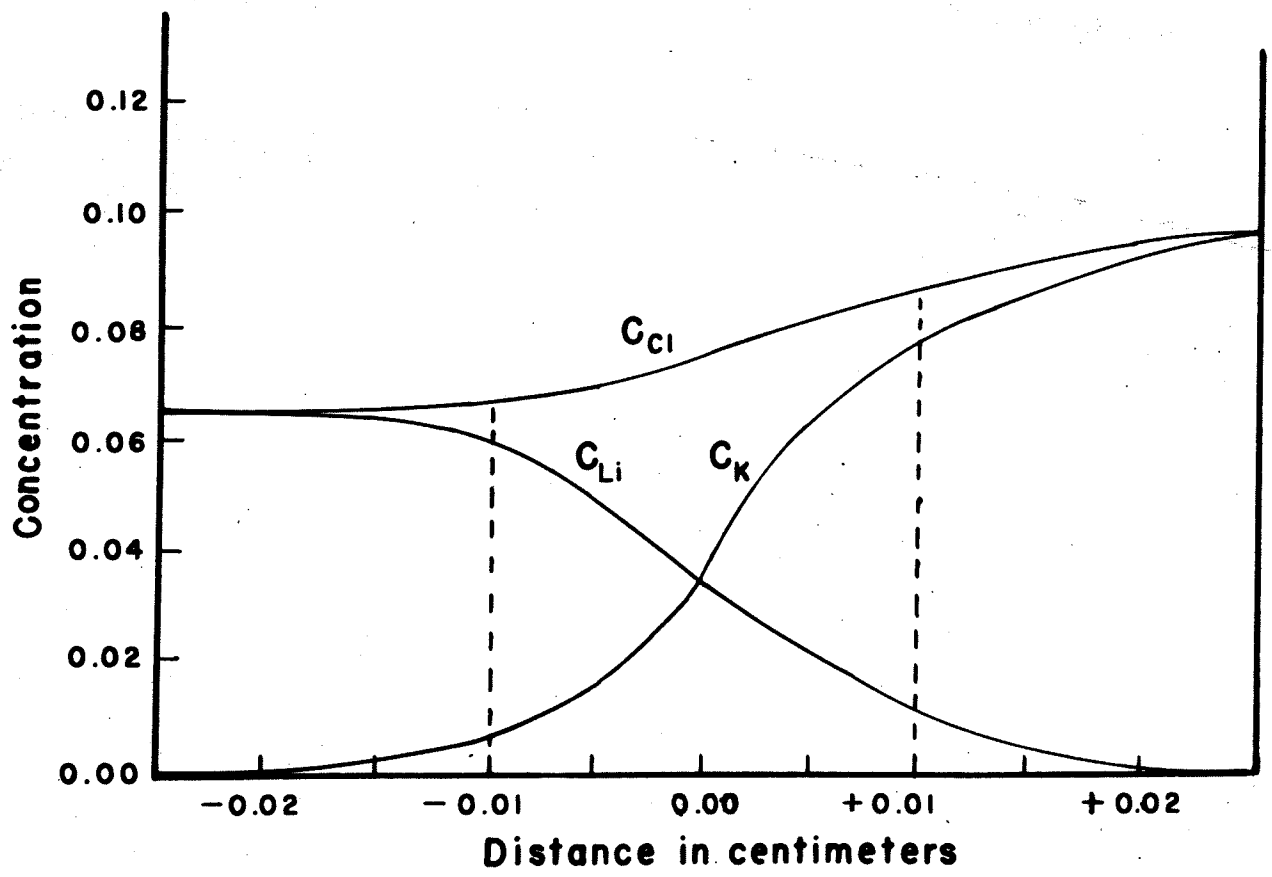

0.12
0.10
0.08
0.06
0.04
0.02
0.00
Concentration
C_{Cl}
C_{Li}
C_K
−0.02
−0.01
0.00
+0.01
+0.02
Distance in centimeters

FIG. 15

0.1 N KCl followed by LiCl is given in Figure 15. A "thickness", represented by dotted lines in the figures, was defined so as to include most of the region of concentration change. From the analytical form of the "thickness" it is seen to be inversely proportional to the velocity, and hence to the current, and to decrease with an increase in the difference between the mobilities of the leading and indicator ions. It should be here noted that the visibility is dependent also on the refractive index gradient in the boundary. Thus a LiCl/KCl boundary is less distinct than a KIO_3/KCl one, although the theory does not predict this.

Using the Schlieren technique which employs an optical system to determine the refractive index gradients in the boundary, Longsworth[59] has confirmed the preceding theory. From his Schlieren scanning patterns he drew the following conclusions.

i) In a two-salt moving boundary experiment two boundaries are formed, the two-salt boundary and a concentration boundary between the initial indicator solution and the Kohlrausch solution. The latter boundary moves almost imperceptibly during a run but becomes broader due to diffusion. The concentration gradients in the two-salt boundary remain unchanged during a run. (In one experiment Longsworth balanced the motion of the

boundary by addition of solution and found that these gradients remained constant for two weeks.

ii) The maximum concentration gradient in a boundary is directly proportional to the current.

iii) When, in the case of a falling boundary, the initial indicator concentration is greater than the Kohlrausch concentration, there are set up at the concentration boundary convection currents which partially penetrate the two-salt boundary and cause its motion to be erratic.

iv) The concentration gradients in a KIO_3/KCl ($c = 0.1$) boundary, as calculated by MacInnes and Longsworth, are in excellent agreement with the experimental gradients. Hence the postulated mechanism, i.e. that the boundary is the result of diffusion and of ionic migration, appears to be confirmed.

Also, from his scanning patterns, Longsworth was able to calculate the Kohlrausch concentration and the transference number of the indicator electrolyte at this concentration with an accuracy of 1%.

CORRECTIONS

1. The Volume Correction

During the early work on the moving boundary method it was noticed that volume changes accompanied the electrode reactions, but at that time the effect on the velocity of the boundary was considered negligible (cf. Denison and Steele[10]). In this early work both electrodes were open to the air and this made impossible an accurate calculation of the correction for the volume changes.

Miller[28] pointed out that "subject to a correction for the expansion and contraction caused by electrolysis" the moving boundary method should give the same results as the Hittorf method. Lewis[29] calculated the necessary corrections in some of the work of Denison and Steele. The treatment following is that of Lewis.

The Hittorf transference number is defined as the number of equivalents of a given ion constituent which, on the passage of one faraday of electricity, cross a boundary fixed with respect to the solvent. The observed moving boundary transference number is the same as this except that the boundary is fixed with respect to the apparatus. Hence, to compare the two, the motion of the solvent with respect to the moving boundary apparatus must be taken into account.

The calculation is facilitated if one electrode chamber is closed as then only the volume change at this electrode need be considered, any volume change at the other electrode having no effect on the motion of the solvent. As an example, consider a rising boundary between barium and potassium chlorides with water as solvent and silver as anode in the closed chamber. Figure 16 a represents the initial conditions in the tube. x represents an average water molecule, or, if one wishes, a plane in the tube below which the mass of solvent remains constant.

On the passage of one faraday the boundary moves from a-b to c-d , the average water molecule from e to e' in Figure 16 b. As the solution between the boundary and average water molecule is homogeneous any volume change near the electrode has the same effect on each. In the electrolysis the following reactions occur.

i) T_K equivalents of K ion pass out of the region between x and the electrode.

ii) T equivalents of Cl ion from the KCl solution pass into the region between x and the electrode.

iii) At the electrode one equivalent of Ag disappears.

iv) At the electrode one equivalent of AgCl appears.

v) One equivalent of Cl ion from the $BaCl_2$ solution disappears due to formation of the AgCl.

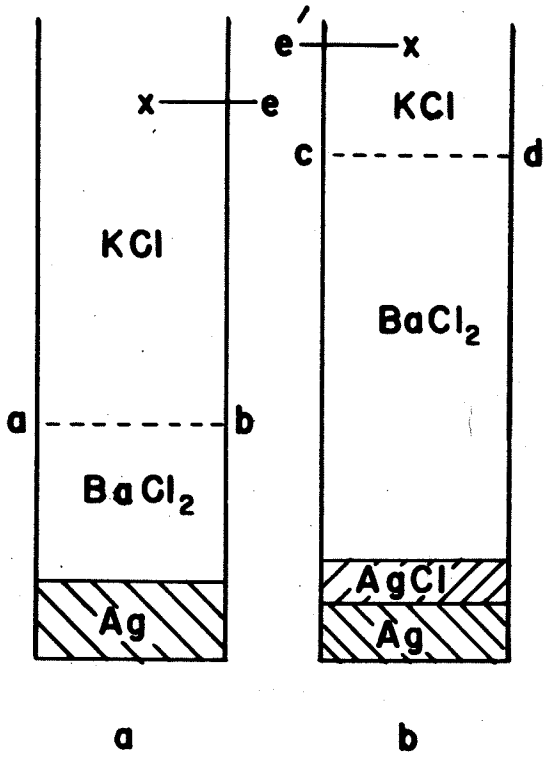


FIG. 16

vi) One equivalent of Cl ion passes from the KCl solution to the $BaCl_2$ solution through the boundary.

The volume increases between x and the electrode due to these reactions are:

i) $-T_K \overline{V}_K^{KCl}$

ii) $+T_{Cl} \overline{V}_{Cl}^{KCl}$

iii) $-V_{Ag}$

iv) $+V_{AgCl}$

v) $-\overline{V}_{Cl}^{BaCl_2}$

vi) $\overline{V}_{Cl}^{BaCl_2} - \overline{V}_{Cl}^{KCl}$

where the $\overline{V}$'s are partial molal volumes. The net increase is then:

$$\Delta V = T_{Cl} \overline{V}_{Cl}^{KCl} - T_K \overline{V}_K^{KCl} - \overline{V}_{Cl}^{BaCl_2} + \overline{V}_{Cl}^{BaCl_2} - \overline{V}_{Cl}^{KCl} + V_{AgCl} - V_{Ag}$$

Using the expressions

$$T_K + T_{Cl} = 1$$

and

$$\overline{V}_{Cl}^{KCl} + \overline{V}_K^{KCl} = \overline{V}_{KCl}$$

this reduces to

$$\Delta V = V_{AgCl} - V_{Ag} - T_K \bar{V}_{KCl}$$

The corrected transference number is then

$$T = VC$$
$$= (V_{obs.} - \Delta V)C$$
$$= T_{obs.} - C\Delta V$$

It is obvious that the correction is small in dilute solutions. However, in concentrated solutions it becomes appreciable and limits the accuracy of the results. The correction itself is only approximate due to several causes. The molar volume of solids depends to some extent on their state and method of preparation and hence in the preceding calculation the molar volumes of silver and silver chloride are not known to a high degree of accuracy. Another disturbing factor is the lack of consideration of the diffusion layers around the electrode. The concentration gradients so formed invalidate the simple expressions involving the partial molal volume at one concentration. Since the partial molal volumes are functions of concentration, integrals[33] of the type

$$\bar{V} = \frac{1}{X_1} \int_0^{X_1} V(x)dx$$

should be used to give the mean partial molal volumes in the

particular region. This calculation requires a knowledge of the concentration gradients present, a knowledge impossible to obtain except in the simplest case of an autogenic boundary. Even with this the calculation is extremely tedious and has never been used, the approximate method invariably being employed. Another factor, not considered in the literature to date, but which could under appropriate experimental conditions contribute an appreciable error to the calculation is the neglect of ionic migration across the concentration boundary in the indicator solution. If the electrode on the indicator side is closed, if the initial indicator concentration is appreciably different from the Kohlrausch concentration and, if the variation of the partial molal volume of the indicator solution with concentration is considerable, additional terms should be added to the volume correction.

These errors, however, are small providing the concentration does not exceed one normal. Smith[60] by means of an electrolysis apparatus in which one electrode could be disconnected and used as a pycnometer, measured the volume change experimentally for a 0.2 N potassium chloride solution with a silver-silver chloride cathode and found it to agree well with the change calculated by the above method. Another check has been furnished by

Longsworth and MacInnes[46] who determined T_+ for potassium chloride at 0.5 and 1.0 N using an autogenic cell with cadmium as anode and a sheared cell with silver as anode and cadmium chloride as indicator. The observed T_+'s by the two methods differed by 2% whereas the corrected T_+'s differed by only 0.1%.

2. The Solvent Correction

The necessity for a correction due to the conductance of the solvent was not recognized in the early work on transference numbers although it was in the work on conductances. Longsworth[33] pointed out in 1932 that the accuracy of the moving boundary method necessitated such a correction for solutions of concentration less than 0.05 N. This correction which should be applied to all transference number determinations, whether moving boundary or Hittorf, is derived as follows.

Let V_+ and V_- represent the actual working velocity of the cation and anion constituents respectively. Since the current I in a linear conductor is equal to the total flux of electricity through a given cross section in unit time, the current through such a conductor of cross section A $cm.^2$ is

$$I = \frac{CFA}{1000}(V_+ + V_-) + \frac{FA}{1000}\sum c_i V_i$$

where C is the concentration of the electrolyte and C_i and V_i refer to the concentration and velocity of the i'th impurity. By multiplying this equation by $\frac{V_+}{V_+ + V_-}$ the following is obtained

$$\frac{V_+}{V_+ + V_-} = T_+ = \frac{CFA\ V_+}{1000\ I} + \frac{FA}{1000\ I}\ T_+ \sum C_i V_i$$

With the assumption that the impurities are completely ionized (as is undoubtedly the case as their concentrations are extremely small) the velocity V_i can be written as

$$V_i = E\ U_i$$

where U_i is the mobility of the i'th ion and E is the field strength. The preceding equation can then be written as

$$T_+ = \frac{CFA\ V_+}{1000\ I} + \frac{FEA}{1000\ I}\ T_+ \sum C_i U_i$$

However, $\frac{I}{EA}$ is the specific conductance of the solution, $K_{solution}$, and $\frac{F}{1000} \sum C_i U_i$ the specific conductance of the solvent, $K_{solvent}$, which may be measured independently. With the assumption the U_i is not changed by the introduction of the electrolyte this equation

becomes

$$T_+ = T_{+(obs.)} + T_+ \frac{K_{solvent}}{K_{solution}}$$

A corresponding equation exists for the anion transference number.

To decrease the solvent effect, Longsworth blew carbon dioxide free nitrogen through the solutions before placing them in the cell, but a correction was still necessary due to contact of the solutions with the air on filling and to electrolytes dissolved in the stopcock grease. The grease that he found most suitable was made by combining five parts of vaseline with one of beeswax, both ingredients having been previously extracted with hot conductivity water.

TRANSFERENCE NUMBER DETERMINATIONS BY THE DIRECT MOVING BOUNDARY METHOD

1. Determinations of the Transference Numbers of Salts with the Exception of $AgNO_3$ and NH_4NO_3

The earliest work that was fairly well done was that of Denison[8] who determined the transference numbers of the chlorides, iodides and bromides of sodium, potassium, rubidium, caesium, magnesium, calcium, strontium, barium and the corresponding ammonium salts by means of sheared boundaries. The indicator ions that he used were lithium and strontium ions for cation boundaries and the acetate ion for anion boundaries. In his calculations he did not take into account either the solvent or volume corrections. Due to this and the relative crudeness of his work as compared with that of later investigators (MacInnes, Longsworth, Gordon) his results are not taken seriously.

Another early investigation was that of Franklin and Cady[12]. Using mercury as the anode in an autogenic cell they determined the cation transference numbers of NH_4NO_3, NH_4I, KNO_3, $NaNO_3$, $NaBrO_3$, and $AgNO_3$ in liquid ammonia. By means of a sheared boundary they determined the anion transference numbers of NH_4NO_3, KNO_3, $NaNO_3$, NH_4Cl, NaCl, NH_4Br, NaBr, NH_4I, and KI, picric acid as an indicator being used for all but the last salts for which iodoeosine was used. The same objection applies to this work as to that of Denison in that no solvent or

volume corrections were made. Both of these early determinations were carried out in such a manner as to make impossible any accurate calculation of the corrections to be applied.

All of the transference number determinations by the direct moving boundary method made since those above are listed in Table I.

TABLE I

Leading electrolyte	Indicator electrolyte	Solvent	Type of boundary	Method of formation*	References
HCl	LiCl	H_2O	cation	s.,r.	57, 59
HCl	$CdCl_2$	H_2O	cation	a.	33
NH_4Cl	$CdCl_2$	H_2O	cation	a.	34
NH_4Cl	NH_4IO_3	H_2O	anion	s.,r.	34
LiCl	$CdCl_2$	H_2O	cation	a.	33
LiCl	$LiIO_3$	H_2O	anion	s.,r.	33
LiCl	$CdCl_2$	H_2O-MeOH	cation	a.	39
NaCl	$CdCl_2$	H_2O	cation	a.	1, 33
NaCl	LiCl	H_2O	cation	s.,f.	59
NaCl	$NaBrO_3$	H_2O	anion	s.,r.	1
NaCl	$NaIO_3$	H_2O	anion	s.,r.	1
NaCl	Sodium tetra-iodofluor-escein	H_2O	anion	s.,r.	33

TABLE I (Continued)

Leading electrolyte	Indicator electrolyte	Solvent	Type of boundary	Method of formation*	References
NaCl	Sodium acetate	H_2O	anion	s.,f.	1
NaCl	$CdCl_2$	H_2O-MeOH	cation	a.	39, 58
NaCl	sodium paratoluene sulfonate	H_2O-MeOH	anion	s.,r.	58
NaCl	sodium paratoluene sulfonate	MeOH	anion	s.,r.	6
Sodium acetate	cadmium acetate	H_2O	cation	a.	34, 28
sodium acetate	lithium acetate	H_2O	cation	s.,f.	28
Na_2SO_4	$CdSO_4$	H_2O	cation	a.	34
KCl	LiCl	H_2O	cation	s.,f.	57,48,61,59,15
KCl	$CdCl_2$	H_2O	cation	a.	58,5,33
KCl	methylene blue	H_2O	cation	s.,r.	15
KCl	KIO_3	H_2O	anion	s.,r.	32
KCl	$KMnO_4$	H_2O	anion	s.,r.	16
KCl	potassium valerate	H_2O	anion	s.,r.	57
KCl	potassium tetra-iodofluor-escein	H_2O	anion	s.,r.	33
KCl	potassium acetate	H_2O	anion	s.,f.	41,15

TABLE I (Continued)

Leading electrolyte	Indicator electrolyte	Solvent	Type of boundary	Method of formation*	References
KCl	potassium paratoluene sulfonate	H_2O MeOH	anion	s.,r.	58
KCl	potassium paratoluene sulfonate	MeOH	anion	s.,r.	6
KCl	potassium triiodo-benzoate	MeOH	anion	s.,r.	6
KCl	potassium dilodo-benzoate	MeOH	anion	s.,r.	6
KBr	LiBr	H_2O	cation	s.,f.	24,48
KBr	$CdBr_2$	H_2O	cation	a.	5,24,34
KBr	KIO_3	H_2O	anion	s.,r.	24,34
KI	potassium acetate	H_2O	anion	s.,f.	34
KI	$K_2C_{20}H_6O_5I_4$	H_2O	anion	s.,r.	34
KNO_3	$Ba(NO_3)_2$	H_2O	cation	s.,r.	34
KNO_3	$LiNO_3$	H_2O	cation	s.,f.	44
KNO_3	$Pb(NO_3)_2$	H_2O	cation	a.	5
KNO_3	$AgNO_3$	H_2O	cation	a.	5
KNO_3	Potassium acetate	H_2O	anion	s.,f.	44
KNO_3	KIO_3	H_2O	anion	s.,r.	34
KNO_3	$K_2C_{20}H_6O_5I_4$	H_2O	anion	s.,r.	34
K_2SO_4	LiCl	H_2O	cation	s.,f.	15
K_2SO_4	$KMnO_4$	H_2O	anion	s.,r.	15

TABLE I (Continued)

Leading electrolyte	Indicator electrolyte	Solvent	Type of boundary	Method of formation*	References
$K_3Fe(CN)_6$	LiCl	H_2O	cation	s.,f.	15
$K_3Fe(CN)_6$	methylene blue	H_2O	cation	s.,r.	15
$K_3Fe(CN)_6$	potassium acetate	H_2O	anion	s.,f.	15
potassium oxalate	potassium valerate	H_2O	anion	s.,r.	57
$CaCl_2$	$CdCl_2$	H_2O	cation	a.	25,34
$CaCl_2$	$CaIO_3$	H_2O	anion	s.,r.	25,34
$CaCl_2$	calcium paratoluene sulfonate	H_2O	anion	s.,r.	25
$ZnBr_2$	zinc dimethyl aniline azo benzyl trimethyl ammonium nitrate	H_2O	cation	s.,r.	57
$ZnBr_2$	Zinc acetate	H_2O	anion	s.,f.	57
$Co(NH_3)_6Cl_3$	LiCl	H_2O	cation	s.,f.	16
$Co(NH_3)_6Cl_3$	$KMnO_4$	H_2O	anion	s.,r.	16
$LaCl_3$	LiCl	H_2O	cation	s.,f.	51
$LaCl_3$	$LaBrO_3$	H_2O	anion	s.,r.	51

*a = autogenic; s = sheared; r = rising; f = falling

In addition to these Longsworth[35], using his previous techniques[32,33], has determined the transference numbers of HCl, KCl and NaCl in deuterium oxide-water mixtures.

2. Transference Number Determinations (by all methods) of Silver Nitrate and Ammonium Nitrate

a) Silver nitrate.

The first work on the transference numbers of silver nitrate was done by the gravimetric method[3,20,21,22,23,27,31,50]. None of this work extended to concentrations beyond 0.5 normal. The best values of the cation transference numbers as determined by these workers and given by Falk in the International Critical Tables [19] are listed in table II.

TABLE II

T°C.	Concentration (equivs./litre)							
	.005	.010	.020	.050	.100	.200	.300	.500
0			.461					
18		.471	.471	.471	.471			
25		.477	.477	.477	.477			
30	.481	.481	.481	.481	.481	.481	.481	.481

The first moving boundary determinations on the transference numbers of silver nitrate were those of Steele[63]. By the crude and inaccurate method of forming boundaries by means of gelatine partitions he obtained a cation transference number of 0.486 for a 1.15 normal solution (the temperature of the measurements was not given). He used copper sulfate and potassium fluoride as indicators for the cation and anion

boundaries respectively.

MacInnes, Cowperthwaite and Huang [45] obtained the first accurate values by using lithium nitrate as a cation indicator for a sheared, falling boundary. The work was extended, the complete results being given in reference 1. They are reproduced in table III.

TABLE III

Concentration (equivs./litre)	T_+
0.01	0.4648
0.02	0.4652
0.05	0.4664
0.10	0.4682

Samis [57], working at 40°C. with lithium chloride as cation indicator in a sheared falling boundary, obtained the results given in table IV.

TABLE IV

Concentration (equivs./litre)	T_+
0.04989	0.4729
0.0914	0.4737
0.1493	0.4739

b) Ammonium nitrate.

The only transference number determination of ammonium nitrate was made by the moving boundary method. Falk in the I.C.T.[19] states this and gives the cation transference number at 25°C. and 0.1 normal concentration as 0.513. The references are not given for each salt but rather as a group for all of the moving boundary determinations. A survey of all but one of the papers failed to reveal any work on ammonium nitrate. A careful search through the American and British Abstracts for the period 1886-1951 also failed to disclose his source. It must be concluded that he obtained the data from the one paper not available - a private communication from D.A. MacInnes of the Rockefeller Institute for Medical Research.

CALIBRATION AND ASSEMBLY OF APPARATUS

1. Calibration of weights

The weights used were calibrated by the method of Pierce and Haenisch[53]. They were determined in absolute grams in vacuo by including in the calibration a 50 gram weight standardized by the National Research Laboratories, Ottawa.

2. Apparatus for Observing the Boundary

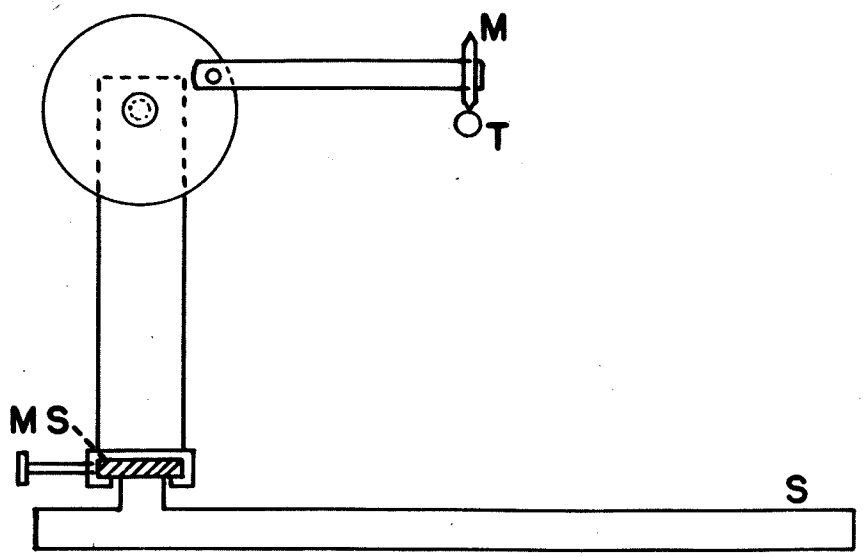
The method of MacInnes, Cowperthwaite and Huang (cf. Section III, (2)) for observing the boundary was used. The light source was a blackened tin can with a rectangular slit cut in one end and containing a 100 watt light bulb. The light was made diffuse by means of a 'Kleenex' tissue fastened over the slit and inside the can. The can was mounted on a framework so that it could be moved upwards or downwards without wobbling. A chain which ran over guide wheels and a sprocket was fastened to the top and bottom of the can. Into the sprocket was threaded a brass rod the other end of which terminated in a wheel at the side of the telescope. Thus an observer at the telescope could move the light source without changing his position. No attempt was made to fasten the light source and telescope together so that the optical system would have the same alignment for each reading of the boundary's position. However in practice such a common alignment was always sought.

3. Calibration of the Volumes

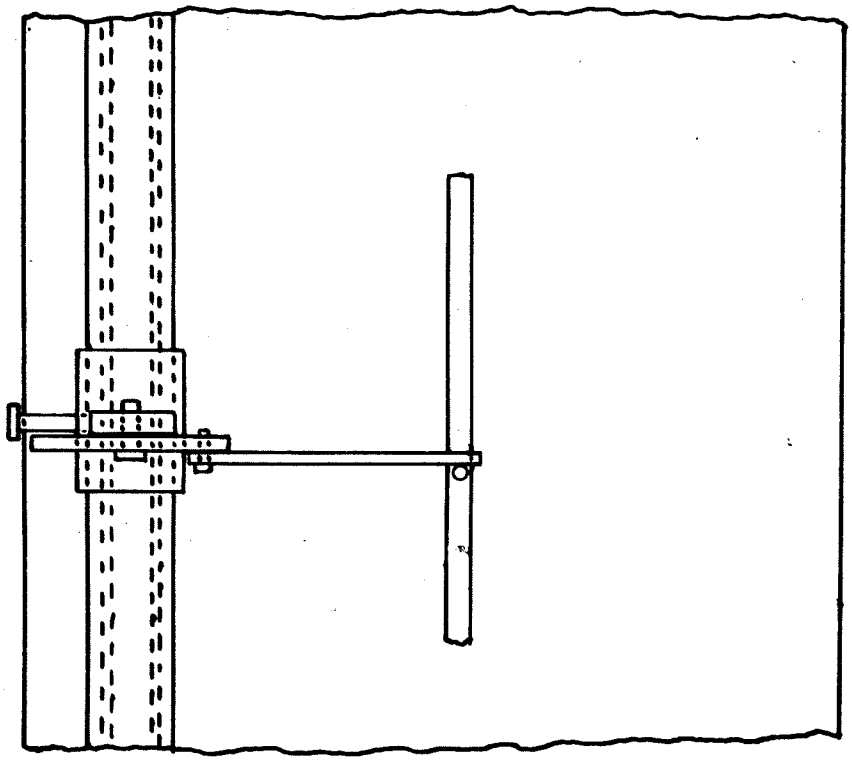
The moving boundary cell which was used in the research was the sheared cell developed by Gordon and co-workers (cf. Section III, (3)). The apparatus was obtained already assembled. If the measuring tube had been separate it would have been a simple matter to coat it with the particular wax used, mount it in a lathe and by means of a pin cut marks in the wax which were perpendicular to the axis of the tube. However, this was not possible so the following procedure was adopted.

The tube was given a thin coating of a 50-50 mixture of beeswax and paraffin. In applying the coat the tube was heated till wax previously placed on it just melted. Molten wax was then poured over it and the cell placed in a vertical position so that a thin even coating was formed on the tube.

The wax coating was cut in fine circles by means of the apparatus sketched in Figure 17(a) and (b). The cell was placed on blocks attached to the stand. It was carefully adjusted till the measuring tube, T, was at right angles to the marking arm. The cell was held firm by means of a rubber band passing around the stopcock and a screw projecting from the stand. When the cell was in position the marker assembly was moved along the meter stick, MS, to the



a



b

FIG. 17

desired position and the marker, M, a steel rod ground to a very fine point at each end, set above the tube. By rotating the brass disc and controlling the marker arm to keep the marker in contact with the tube a circle was cut in the wax coating. The cut was examined with a hand lens to ensure that it was at right angles to the axis of the tube.

When a satisfactory cut was made the tube was etched. This was done by dropping a mixture of 1 part concentrated hydrochloric acid and 1 part anhydrous hydrofluoric acid for a period of two minutes over the mark.

Six such graduations were made, their positions being shown in Figure 18. Henceforth any reference to a particular graduation will use the numbers in the figure.

The volumes were determined by the method of Longsworth (cf. Section III, (5b)). The filling tube for the leading solution was removed from the cell and a 1 mm. stopcock with a capillary tip was sealed on as shown in Figure 18. The volumes between etch mark 6 and each of 1, 2 and 3, between 5 and each of 1, 2 and 3, and between 4 and each of 1, 2 and 3 (henceforth called volumes 6-1, 6-2, 6-3, etc.) were determined directly.

Before the calibration the tube was thoroughly cleaned. Chromic acid cleaning solution was allowed to stand in it for three days, the capillary tip being im-

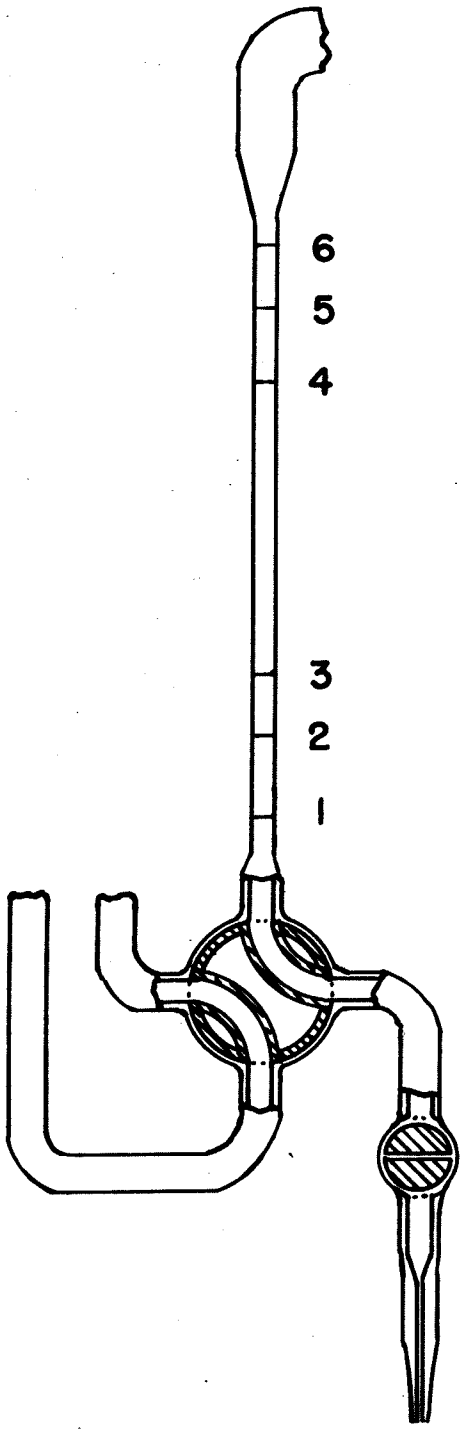
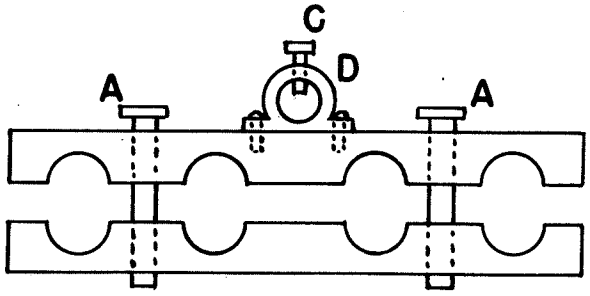


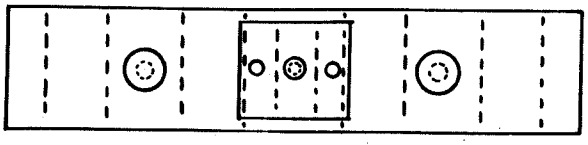
FIG. 18

mersed in the solution. The tube was then emptied and rinsed with tap water, concentrated nitric acid to remove the carbon formed from the stopcock grease distilled water, alcohol and ether successively. The inner parts of the stopcocks were removed and cleaned with ether, concentrated nitric acid, distilled water, alcohol and ether. The outer parts were cleaned with ether. When all parts were dry the inners were given a light coating of a high vacuum silicone stopcock grease manufactured by Dow Corning, the grease being so applied that none could come in contact with the mercury during a calibration. The stopcocks were assembled with the two-way stopcock oriented so as to connect the 1 mm. stopcock and the capillary tip with the measuring tube. A current of air filtered through absorbent cotton was passed through the tube for a few minutes to ensure that it was dry. The cell was then ready to be clamped in position.

Two clamps were used to keep the cell rigid without introducing an undue amount of strain. An oak clamp, illustrated in Figure 19, fitted around the top of the cell. The brass screws, A, were tightened till just snug. The brass sleeve, D, fitted a vertical brass rod on an iron base. At the two-way stopcock a spacer was placed between the cell and the vertical rod. A steel coil spring was looped around the two to keep them firmly attached to one another. For the calibration this spacer was made of cork; however for



a



b

FIG. 19

the actual transference number determinations a brass one was used.

When the cell was clamped to its stand it was filled with mercury. The mercury used was "Nichols mercury metal #1960" which had been redistilled three times, In filling the tube care had to be exercised to avoid the presence of air bubbles in the tube. The cell was tipped to about a 60° angle with the horizontal and a bottle containing the pure mercury placed under the tip so as to cover it. Suction from a water pump was applied to the top of the tube and the mercury was slowly drawn up. Before an actual volume determination the tube was inspected for air bubbles.

When filling had been accomplished with the absence of air bubbles the cell was moved to a position on a soapstone table between a light source identical with the one described in Part 2 of this section and a Gaertner table cathetometer, the scale of which could be read to ±0.0002 cm.; but due to parallax in the optical system cathetometer readings were accurate only to ±0.001 cm. The tube and cathetometer were both levelled, the former by eye and the latter roughly by means of a level on it. An exact level was never obtained on the cathetometer but since the distances read by it were small (about 5 mm.) the resulting error should be negligible.

With everything arranged as above the volume determination was begun. The general procedure was to with-

draw the mercury between two etch marks and to weigh it. From the specific volume of the mercury at the temperature of the calibration the volume of the mercury and hence the volume between the marks was found. However the actual determinations were not this straightforward. The various details follow:

The mercury was withdrawn into a small weighing bottle. This bottle had been initially cleaned with chromic acid cleaning solution. At the start of each day it was cleaned, both inside and out, with alcohol. After that it was never touched by the fingers, 'Kleenex' being used in handling it.

To ensure the same volume of mercury in the capillary tip for each weighing the weighing bottle, containing a small pool of mercury, was raised till the tip was partially immersed in the pool. This procedure was repeated till a constant weight (within 0.1 mg.) was obtained.

In the weighing a weighing bottle of the same dimensions as the one used for the weighing and containing a few ml. of mercury was used as a counterpoise. The balance case was set immediately adjacent to the cathetometer. Thus the balance, weighing bottle and mercury were all at the same temperature and waiting periods for the weighing bottle to attain the temperature of the balance were obviated.

The difficulties attendant on setting the base

of the mercury meniscus on a graduation to ±0.001 cm. necessitated a more lengthy procedure. The mercury column was lowered till the base of the meniscus was just above the particular upper graduation. The weight of the weighing bottle and the height of the base of the meniscus were taken. The column was then lowered to just below the graduation and the same readings made. The height of the graduation was also taken. From the two weights the volume between the two menisci was obtained. From the cathetometer readings the position of the graduation relative to the bases of the two menisci was found. With the assumption that the tube was perfectly cylindrical between the menisci the volume between the graduation and the base of the lower meniscus was calculated. The column was then lowered to a position just above the lower graduation of the volume being determined and the weight of the weighing bottle obtained. From the last two weighings the volume between the base of this meniscus and that of the one immediately preceding was calculated. At this lower graduation the same procedure was followed as at the upper one to obtain the volume between the graduation and the base of the upper meniscus. The sum of the three volumes determined gives the volume between the two graduations. This method would be adequate if the volumes of mercury in the meniscus remained constant; but such was not the case, The necessary corrections are discussed in

the next paragraph.

Variations in the volumes of menisci were caused by variations in their heights and the diameters of their bases. A.R. Gordon, of the University of Toronto, stated in a private communication that he had assumed a spherical meniscus and used the formula $v = \frac{2}{3}\pi r^3$ where r is the tube radius to calculate its volume; but the radius of the tube employed in this research was approximately 1.2 mm. while the heights of the menisci were in the range 0.45-0.65 mm. It was felt that the volume would be more correctly represented by the volume of a paraboloid. The volumes were calculated with the formula $v = \frac{\pi r^2}{2} h$ r being the radius of the base and h the height of the meniscus. The value of r was determined individually for each graduation. From the two or three calibrations involving the particular graduation which had the least difference in its values of h for the menisci above and below the graduation the average cross-sectional area was calculated from the volume and the distance between the menisci. The mean of these cross-sectional areas was taken as the value of πr^2 for that graduation.

The correction for the volume of the meniscus was applied as follows. Let V' be the volume between the menisci above and below a graduation as determined from the weight of mercury withdrawn. Then a correction of $V_2 - V_1$, where V_1 and V_2 are the volumes of the upper and lower

menisci respectively, must be applied to V' to give the true volume between the bases of the menisci.

A disturbing factor in the calibration turned out to be the temperature control. If the temperature was not maintained constant to $\pm 0.05^{\circ}C.$ throughout individual determinations of the same volume then the volumes so found had very poor precision. Therefore before a reading was taken of a meniscus the temperature was checked with that of the previous reading. This was accomplished by setting the cross-hair of the cathetometer on the top of the meniscus immediately after withdrawing the mercury. If the temperature changed during the weighing the cross-hair would no longer be on the top. In such a case the temperature of the room was adjusted till the cross-hair again coincided with the top of the meniscus.

The specific volumes of mercury were obtained from the International Critical Tables.(16).

A correction was also applied to the individual calibrations to allow for expansion or contraction of the glass tube when placed in the 25.0° thermostat. The coefficient of linear expansion of hard glass was found from the Handbook of Chemistry and Physics(14) to be 9.7×10^{-6}. Hence the coefficieht of cubical expansion was 2.9×10^{-5}. The temperature of each determination was recorded from a Cenco thermometer graduated in tenths of a degree Centigrade. The results of the calibration are given in table VI.

As a check on this work the volumes 1-2, 2-3, 4-5 and 5-6 calculated from the above volumes should each be independent of the directly determined volumes chosen. Thus 6-1 - 6-2, 5-1 - 5-2, and 4-1 - 4-2 should give the same volume 1-2. The check is illustrated in table VII.

TABLE VII

Volume sought	Volume Calculated (ml.)	Mean volume (ml.)
1-2	0.0680	
1-2	0.0681	
1-2	0.0683	0.0681
2-3	0.0684	
2-3	0.0681	
2-3	0.0683	0.0683
4-5	0.0671	
4-5	0.0673	
4-5	0.0671	0.0672
5-6	0.0575	
5-6	0.0576	
5-6	0.0579	0.0577

While the agreement is not perfect it is good enough to say that the results are consistent to $\pm$.0001 ml. Since the combinations of the weights, calibrated in terms of absolute grams in vacuo, were different for all weighings any significant error in their values should be revealed in the actual determinations. As for the cathetometer, different

portions of its scale were used for the measurements so that any error in the scale calibration should be evident in the final volumes obtained. It should be noticed that due to the use of the cathetometer to measure relative distances the use of the instrument at a temperature different from that at which the scale was divided off will introduce no error. At any rate, since the cathetometer is used only to obtain corrections to the main volume, the resultant error in the main volume will be extremely small. As stated previously the mercury was extremely pure and corrections were applied to bring the observed volume to that at 25.00°C. Hence it appears reasonable to ascribe an error of $\pm$.0001 ml. to the absolute volumes at 25.00°C. of 1-4, 1-5, 1-6, 2-4, 2-5, 2-6, 3-4 3-5 and 3-6

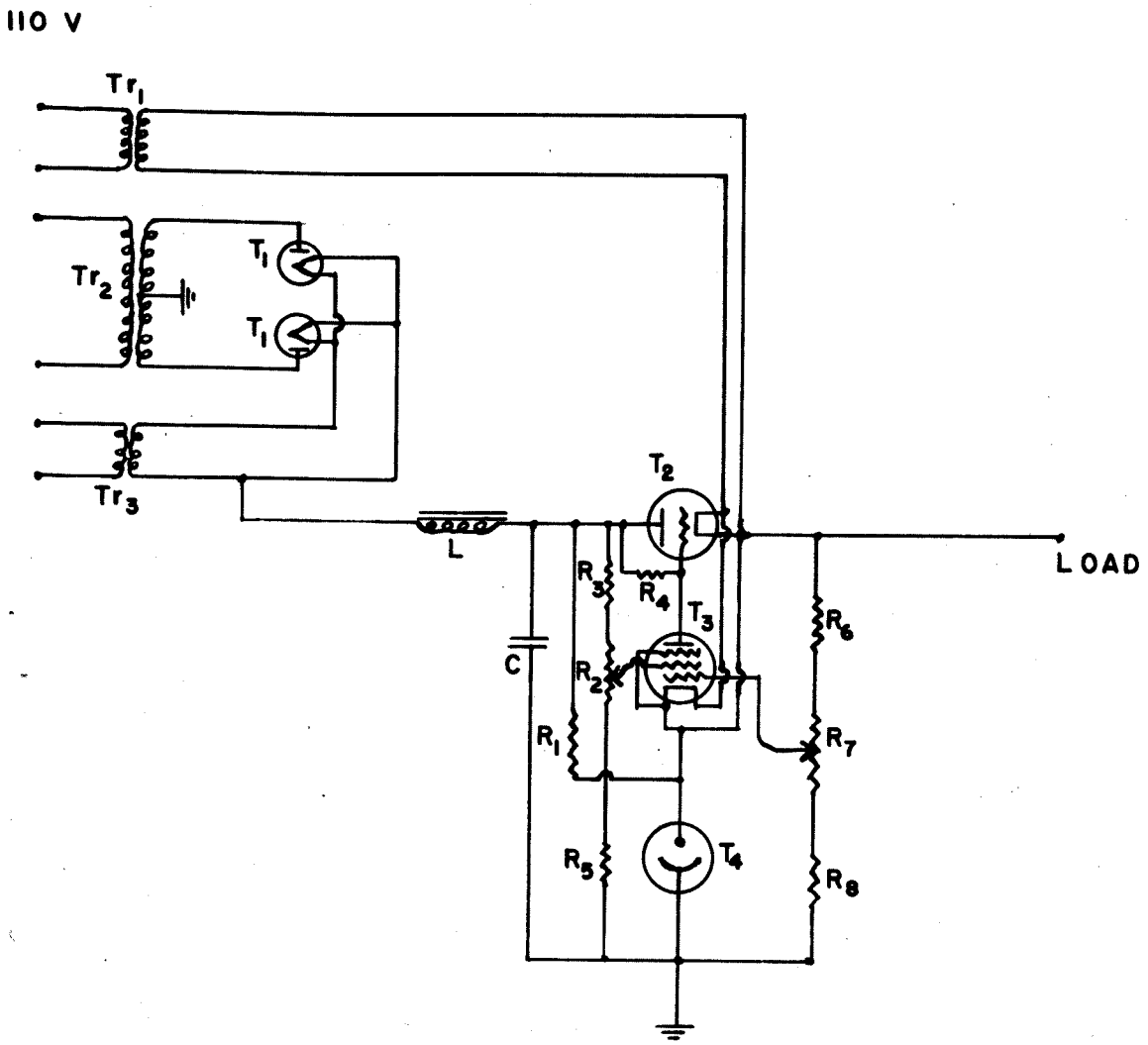
4. The Current

a) The current stabilizer.

It was decided to build an electronic current stabilizer. It was thought that one could be built to give a greater current constancy than those used by other workers (Gordon, Hartley - cf. Section III, (5c)). It was also decided to dispense with the battery source of power previously used and to substitute a D.C. power supply operating off the A.C. main.

It was originally thought that a 400 volt power supply would be big enough for the purpose. Accordingly a standard circuit for such an output was used. The set as

FIG. 20



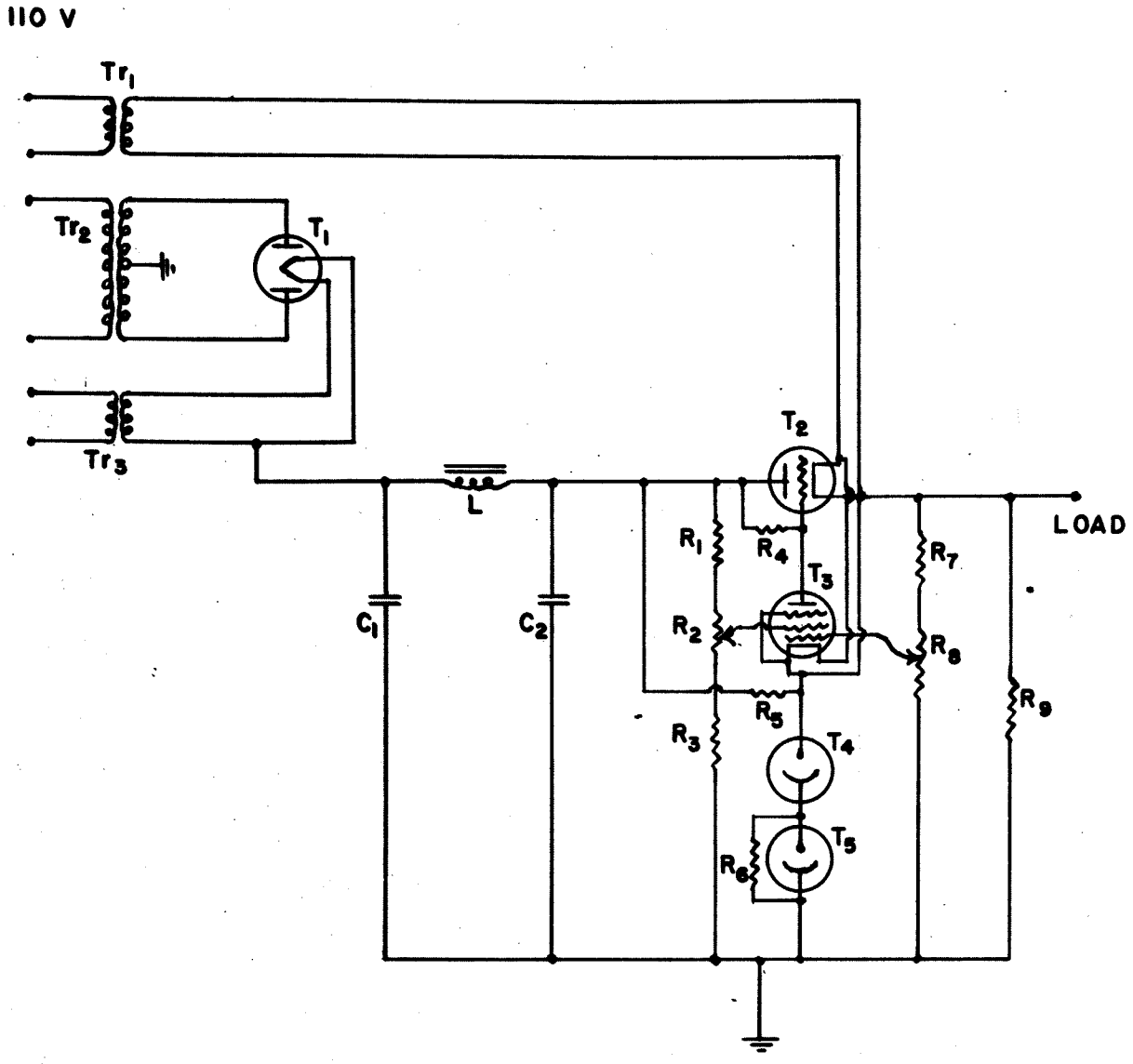
Tr_1 = 6.3 V
Tr_2 = 625 V
Tr_3 = 2.5 V
T_1 = 866 Jr.
T_2 = 6AS7
T_3 = 6SJ7
T_4 = VR 150
R_1 = 25 K
R_2 = 20 K
R_3 = 220 K
R_4 = 200 K
R_5 = 150 K
R_6 = 56 K
R_7 = 50 K
R_8 = 25 K
L = 10 h
C = 16 μf

first built is sketched in Figure 20. It was found that for the current stabilizer then being experimented with the power supply had to be extremely stable. The supply as originally built did not have the necessary stability for voltages of 400 volts and higher. By varying the resistance components various grid biases on the two tubes and feedbacks to the 6SJ7 were tried. Finally the cathode of the 6SJ7 was grounded and B batteries were placed in the tube's cathode grid circuit to give the proper bias. However none of these alterations extended appreciably the stable range of the supply. When the first current stabilizer was discarded in favour of that used by former investigators the power supply was rebuilt to furnish additional voltage.

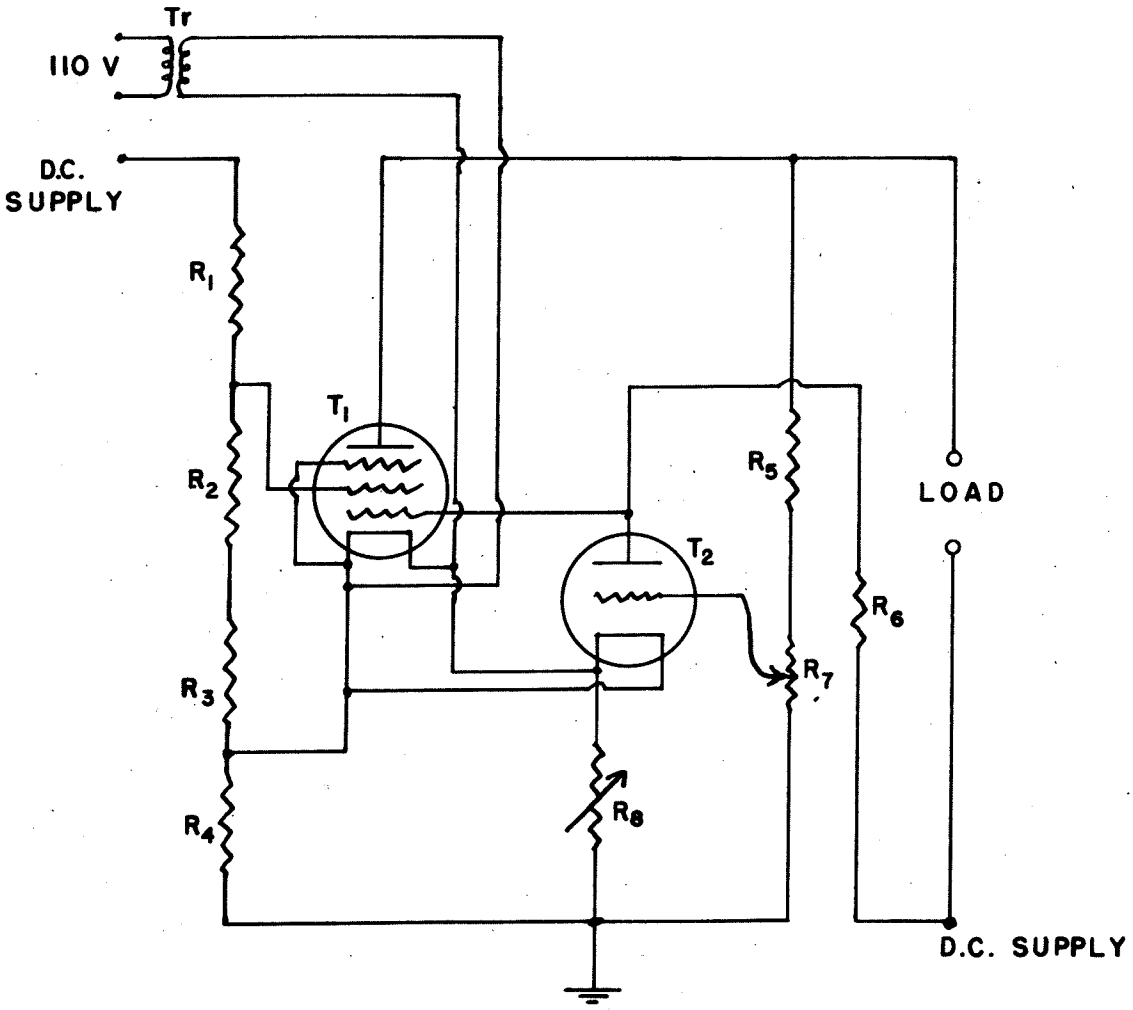
The requirements for the new power supply were that it should furnish up to 700 volts with fair stability. The great stability sought in the first supply was not necessary in this one since the new current stabilizer was markedly independent of the line voltage. The main innovation in the new supply was the use of a 5Z3 full wave rectifier in place of the two 866 Jr.'s in parallel and the use of a condenser input in place of the choke input. This supply is drawn in Figure 21. With it 725 volts was easily obtained.

An attempt was made to build a current stabilizer which would maintain the current during a transference number determination constant to 0.1%. The electronic stabilizers used by Hartley and Donaldson and by Gordon kept it

FIG. 21



Tr_1 = 6.3 V	R_3 = 153 K
Tr_2 = 625 V	R_4 = 70 K
Tr_3 = 5 V	R_5 = 60 K
T_1 = 5Z3	R_6 = 5 M
T_2 = 6AS7	R_7 = 400 K
T_3 = 6SJ7	R_8 = 250 K
T_4 = VR105	R_9 = 300 K
T_5 = VR150	C_1 = 4 µf
R_1 = 250 K	C_2 = 10 µf
R_2 = 20 K	L = 10 h



Tr = 6 V

T_1 = 6AC7

T_2 = 6J5

R_1 = 4 K

R_2 = 2 K

R_3 = 2 K

R_4 = 2 K

R_5 = 5 M

R_6 = 60 K

R_7 = 500 K

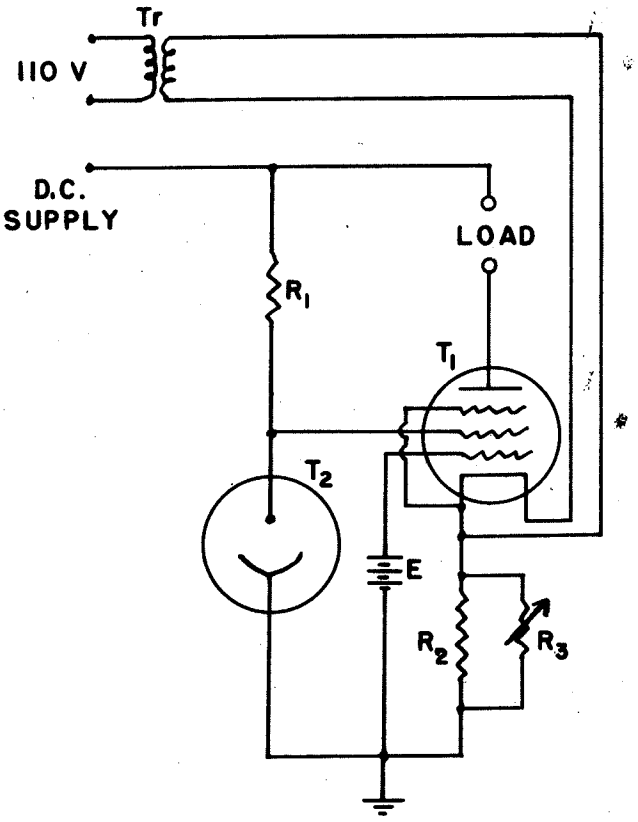
R_8 = 2 K

FIG. 22

constant to 0.6% at best. In a run with 0.1 normal potassium chloride the resistance increases from approximately 80,000 to 150,000 ohms. To keep the current constant in the range 1-10 milliamperes the circuit in Figure 22 was built. Its principle of operation is as follows. A decrease in the current makes the grid of the 6J5 more negative. This causes the plate of this tube and hence the cathode grid of the 6AC7 to become more positive. This in turn decreases the internal resistance of the latter and increases the pentode resistance and tends to decrease the current. By varying the potentiometers settings it was possible to get a constant current of 1.2 ma for a load of 40,000 and 100,000 ohms; but at intermediate resistances the current varied up to 10%. Attempts were made by varying the resistances to overcome this difficulty. No solution was found. A disturbing characteristic of the circuit was its amplification of variations in the line voltage. Since the screen grid bias was set by the line voltage any voltage change affected this bias, the effect being to change the tube resistance out of proportion to the change in the line voltage. An opposing effect is caused by a change in the line voltage on the grid bias of the 6J5. This change is communicated to the 6AC7 so as to oppose the change in the screen grid bias. For example, consider the effect of an increase in the line voltage. Both the screen grid and the cathode of the 6AC7 become more positive to ground, the increase being greater for the former. As a

result the screen grid becomes more positive to the cathode and the tube resistance decreases. The increase in the voltage also causes a momentary increase in the current and hence drives the grid of the 6J5 more positive. This makes the plate of this tube and in turn the cathode grid of the 6AC7 more negative. Thus the resistance of the latter tube is increased, this effect being increased by the increase in the potential of the cathode of the 6AC7. Currents of 1-2 milliamps, showed no signs of oscillations; but at higher currents such oscillations appeared with the galvanometer needle continually going off scale at 4 milliamps. When it was evident that the work involved in perfecting the stabilizer would be considerable it was abandoned in favour of a slight modification of that used by Hartley and Donaldson.

This new stabilizer, Figure 23, was essentially the same as that of the above authors. The only significant difference was the use of a VR150 in place of batteries to produce the screen bias and the use of a 6 volt transformer in place of a battery to heat the filament. Both of these innovations should decrease any drift in the current due to battery decay. On the debit side they could introduce oscillations in the current due to unsteady operations of the VR tube and to fluctuations in the A.C. line voltage operating the transformer. Such oscillations would be most pronounced when the 6AC7 was operating at saturation. In actual practice this was found to be the case, the current



Tr = 6 V

T_1 = 6AC7

T_2 = VR150

E = 45 V

R_1 = 25 K

R_2 = 10 K

R_3 = 500 K

FIG. 23

being very stable for currents of about 5 milliamps, but fluctuating slightly for currents of 8 milliamps. The maximum plate current of the 6AC7 is 10 milliamps. If currents of this magnitude or greater were ever desired this difficulty could be removed by replacing this tube with a 6F6 which has a maximum plate current of 35 milliamps.

To warm the sets up they were put on at a current of about 4 milliamps. for a period of 1-2 hours before a determination was begun.

b) The current measurement.

The current was measured by observing with a standard potentiometer circuit the voltage drop across a calibrated resistance in series with the moving boundary cell. Three General Radio resistances were calibrated - a 1000 ohm, type 500-H; a 500 ohm, type 500-F; a 100 ohm, type 500-D. They were calibrated by comparing them by means of a Leeds and Northrup #776889 which had a resistance according to the company's certificate of 1000.03±.01% absolute ohms as of April 1950. Its catalogue number was 4035-abs. The standard used in the calibration of the 100 ohm resistance was Leeds and Northrup #29233 with a certified resistance of 99.997 absolute ohms in 1916. In the calibrations a slight drift in the potentiometer balance was noticed. Accordingly readings were taken at one minute intervals of the potentiometer balanced alternately against the standard and

the G.R. resistors. For each G.R. resistor potentiometer balances were obtained for approximately seventeen minutes and the appropriate means used in calculating the values of these resistors. Their determined resistances are given in table VIII.

TABLE VIII

Nominal value	Resistance in absolute ohms
100	99.961
500	500.3
1000	999.8

The galvanometer was a table type of low sensitivity. Before the measurement of the current during a determination the potentiometer was always balanced against the standard cell. The high voltage leads from the current stabilizer to the moving boundary cell were encased in glass tubes to minimize the leakages. The potentiometer was a Leeds and Northrup students type; the standard cell was a Weston cell.

5. The Time Measurement

The method of measuring the time at which a boundary passed an etch mark was that in use at the University of Toronto by A.R. Gordon. An Elgin "railroad" watch certified by Birks jewellers to be accurate to 15 seconds in a week was used as the standard of time. An electric metronome made by Central Scientific Company and calibrated against the Elgin watch was set in motion when the boundary was just below an

etch mark and the beats were counted. The beat at which the boundary was exactly on the etch mark was recorded. The time of a subsequent beat was also recorded. From the time between beats the time at which the boundary was at the etch mark was calculated. The metronome was calibrated at two beats by the Elgin watch. For a setting of 60, 563 beats were emitted in ten minutes corresponding to a beat period of 1.066 seconds; for a setting of 120, the beat period as determined from a 5 minute interval was 0.531 seconds.

The watch was also used to record the time of the current measurements. From the current-time readings for a transference number determination a graph was constructed. From it by means of graphical integration the product it was determined for the time intervals which the boundary spent between etch marks.

6. The Temperature Control

As pointed out previously transference numbers do not vary greatly with temperature, but the moving boundary method is such that small temperature differences in the solutions cause density differences with the resulting convection causing erroneous results or destruction of the boundary. Hence fluctuations of the thermostat temperature should not exceed a few thousand'ths of a degree Centigrade.

The thermostat bath that was used was made of copper with two glass windows in it, placed opposite one another.

The thermostating liquid was Bayol F - a water white mineral oil with low viscosity and low flash point. Oil was used instead of water to avoid cell leakage of current and possible electrocution of the operator. A mercury thermoregulator with an adjustable upper contact was used in conjunction with a knife heater and relay to maintain the oil temperature constant. The stirrer motor was mounted on a stand which in turn rested on the floor. Thus very little vibration was communicated to the bath and cell. The temperature control as determined by a Beckmann thermometer was $\pm$ 0.003°C. The temperature itself was measured by a Cenco standard thermometer graduated in tenth's of a degree Centigrade. All determinations were made at 25.00°C.

7. The Electrodes

The electrodes used were those of previous workers, no new ones being tried. For the determination using potassium chloride the electrodes of Smith (Section III, (4)) were employed. The anode was a platinum gauze electroplated with silver and the cathode a platinum gauze electroplated first with silver and then with silver chloride. The silver electroplating was done by the method given by M. Boyd(4). Two grams of $AgNO_3$ and 12 grams of NH_4NO_3 were dissolved in 300 ml. H_2O. A solution of KCN was added till the AgCN just dissolved. The solution was made up to 600 ml. and electrolyzed with the gauze electrode as cathode. A platinum gauze

was the anode. Electrolysis at 3 milliamps. was continued overnight. The silver chloride was plated on by making the silver electrode the anode in a 6N HCl solution with an electrolysis period of two hours at 6 milliamps.

In the unseccessful run with silver nitrate the same electrodes were used as above.

In the NH_4NO_3 run a platinum gauze immersed in a 0.1 normal $AgNO_3$ solution was the cathode and a silver electrode the anode.

All of the above electrodes which formed the closed side of the sheared cell were mounted with DeKhotinsky cement in glass tubes fitted with inner standard tapers which fitted in the outer at the top of the closed side. A silicone high vacuum stopcock grease was applied to the inner before the electrode was placed in the cell. It was held firmly to the latter by rubber bands which passed around a horizontal glass rod of the cell and hooked onto glass tits on the electrode tube.

8. Method of Filling the Cell

The method of filling the cell was that in use at the University of Toronto. The apparatus used is drawn in Figure 24. Before the solutions were introduced into the cell they were degassed. This was accomplished by decreasing the pressure in the flask to about 40 centimeters and swirling the flask till no air bubbles were formed. The apparatus

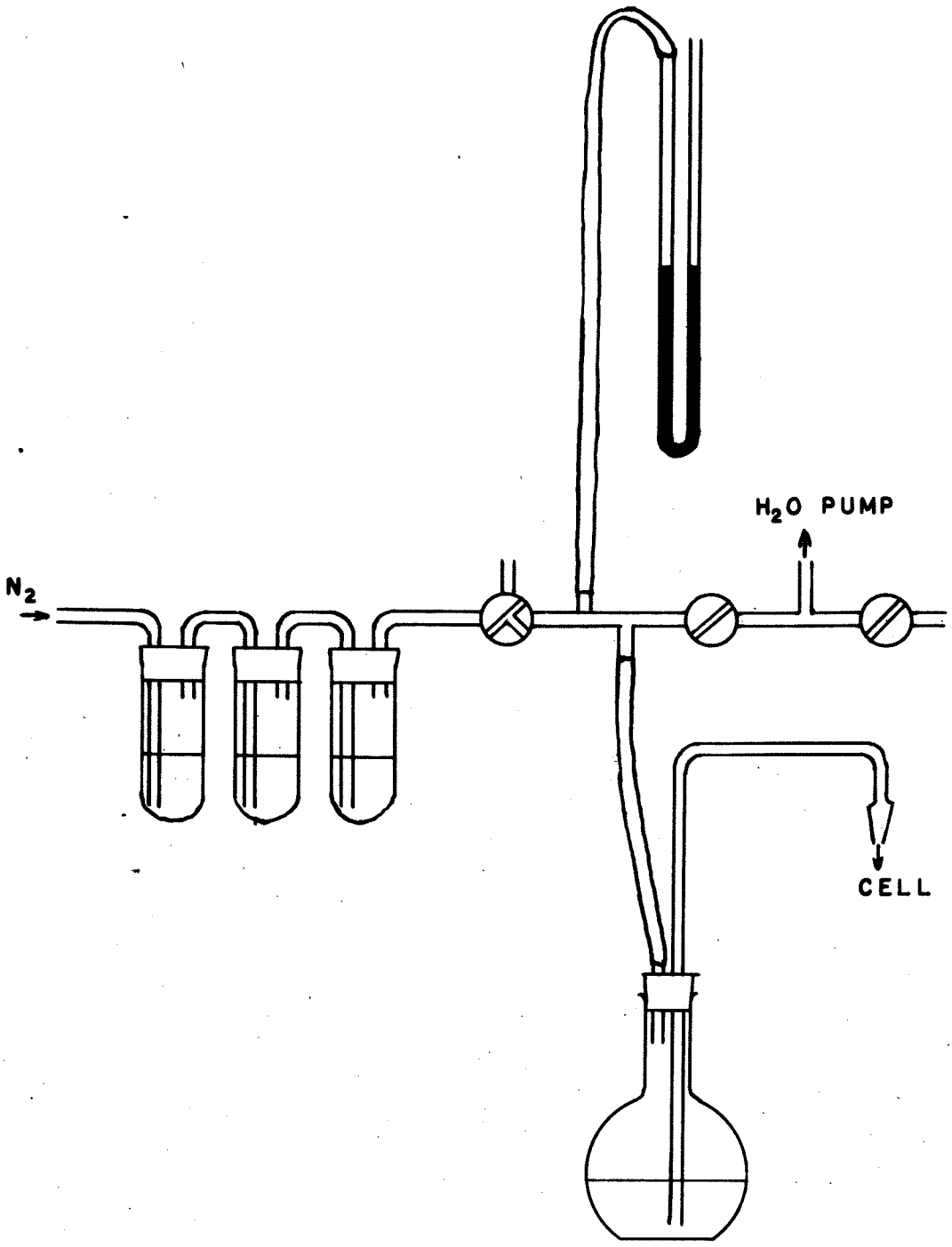


FIG. 24

was then arranged as in the figure and nitrogen, bubbled through concentrated sodium hydroxide, sulfuric acid, and distilled water was used to force the solution through the glass tube and into the cell via the standard taper joint. Any air bubbles trapped in the cell during the filling were removed by a syringe. When the cell was satisfactorily filled the inner joint of the electrode on the closed side of the cell was given a light coating of Dow Corning silicone high vacuum stopcock grease and inserted in the outer part. Enough solution had been added so that there was no air space above the solution in this side.

All glass tubing with which the solution came in contact during the filling was kept in chromic acid cleaning solution when not in use. Before being used it was rinsed thoroughly in tap water and distilled water and then dried by means of a current of air filtered through absorbent cotton. The cell itself was treated in a similar manner.

PURIFICATION OF MATERIALS AND PREPARATION OF SOLUTIONS

1. Purification of Materials

Due to the extreme accuracy attainable with the moving boundary method the materials used must be very pure. This is essentially so for the leading electrolyte since any impurity increases the solvent correction. This is not a serious objection if the impurity concentration is known as is the case for salts of weak acids or bases when the corresponding acid or base is added to decrease the salt hydrolysis. When the impurity is not introduced in this manner the additional solvent correction is unknown. The purity of the indicator electrolyte need not be as high as that of the leading electrolyte since diffusion of the impurity into the leading solution is the sole disturbing factor.

The methods of purification of the various salts used in this research are given below.

a) Potassium chloride.

The purification technique was provided in a private communication from A.R. Gordon of the University of Toronto.

Merck Reagent Grade KCl with maximum impurities of 0.06% was the starting material. It was recrystallized twice from distilled water and then fused in a platinum crucible. The platinum crucible had been cleaned for three days in hot, boiling hydrochloric acid and then rinsed well in tap followed by distilled water.

To weigh a certain amount of anhydrous salt the following procedure was adopted. A platinum boat was cleaned

as above and then heated in a Bunsen flame for fifteen minutes. After this it was placed in a desiccator for thirty minutes, and the balance case for twenty minutes. It was weighed with the calibrated weights. The recrystallized potassium chloride was finely pulverized in an agate mortar and introduced into the boat. The boat was heated over a small Bunsen flame for one hour. It was weighed after standing in a desiccator for thirty minutes and in the balance case for twenty minutes.

b) Potassium iodate.

Merck KIO_3 was recrystallized twice and dried over calcium chloride in vacuo. This was the method employed by Longsworth[32].

c) Silver nitrate.

Merck C.P. $AgNO_3$ was recrystallized once and then centrifuged. It was kept in a desiccator over calcium chloride until needed.

d) Silver perchlorate.

This salt was prepared from the directions of Hill[16]. About 200 gm. of Merck C.P. $AgNO_3$ was dissolved in 500 ml. of water and a slight excess of NaOH in the form of sticks (Merck Reagent) was added. The precipitated silver oxide was filtered through sintered glass and washed repeatedly with distilled water. It was then transferred to a beaker with a little water and treated with a slight excess of

Baker's 70% $HClO_4$. The solution was filtered and evaporated in a porcelain dish upon the water bath until crystals began to appear. After cooling the hot solution, the material was filtered in a centrifuge. It was dried by heating in an electric oven at 120-125°C. for twenty-four hours and was then kept in a desiccator over calcium chloride.

e) Ammonium nitrate.

The ammonium nitrate was supplied by Miss E.Kartzmark. It was the commercial salt which had been recrystallized and then dried for twelve months over concentrated sulfuric acid.

2. Preparation of Solutions

All the leading solutions were prepared by adding a known weight of water to a known weight of salt. Care had to be taken in the handling and weighing of the materials. A one liter flask was cleaned with chromic acid solution and rinsed well with distilled water. The exterior of it was cleaned with alcohol and thenceforth handled with Kleenex tissue. It was weighed against a counterpoise of similar dimensions using calibrated 100 gm. weights in addition to the other calibrated set. The weighed salt was then washed into the bottle with distilled water. The funnel was thoroughly rinsed off and water added till the weight added was within 50 mg. of that calculated to make up a solution of a desired strength. Buoyancy corrections were applied to all weights. Atomic weights were obtained from

the Handbook of Chemistry and Physics[14]. From the density and weight percent data in the International Critical Tables[17] the resultant concentration was calculated. To prevent evaporation of the solution a rubber stopper which had been cleaned in a boiling NaOH solution, rinsed well with distilled water and dried was placed on the flask. This stopper also prevented loss of solution when the flask was swirled to promote a homogeneous solution.

The indicator solutions were made up in a 250 ml. volumetric flask by adding the appropriate amount of solute.

EXPERIMENTAL RESULTS

1. Potassium Chloride

To check the operation of the apparatus a run was made with a 0.1 N solution of potassium chloride as the leading solution and a 0.1 N solution of potassium iodate as the indicator solution. A silver anode and silver-silver chloride cathode were used. These were the conditions in the determination by Longsworth (14) of the transference number of the former salt.

The experimental data follow.

a) Solutions.

KCl

Weight of KCl in vacuo ---- 3.1412 gm.

Weight of H_2O in vacuo ---- 435.7 gm.

Weight % of solution ---- 0.7158

Density (from I.C.T.) ---- 1.00161 gm./ml.

Normality ---- 0.09617 equivs./liter

KIO_3

Weight of KIO_3 ---- 21.4105 gm.

Volume of solution ----- 1 liter

Normality of solution ---- 0.10003 equivs./liter

b) Data from run.

Etch Marks	Volume (ml.)	"it" (abs. coulombs)	$T^- = \frac{VcF}{it}$
1-2	0.0681	12.510	0.5050
2-3	0.0683	12.552	0.5049
3-4	0.6142	11.278	0.5053
4-5	0.0672	12.320	0.5061
5-6	0.0577	10.610	
1-4	0.7510	13.782	0.5056
1-5	0.8181	15.014	0.5056
1-6	0.8756	16.075	0.5054
2-4	0.6827	12.5351	0.5055
2-5	0.7500	13.762	0.5057
2-6	0.8076	14.824	0.5055
3-4	0.6142	11.278	0.5053
3-5	0.6813	12.510	0.5053
3-6	0.7392	13.571	0.5054

The mean of the last nine values of T is 0.5055.

c) Corrections.

1) Solvent correction

$$K_{solvent} = 4 \times 10^{-6} \ \text{ohm}^{-1} \ \text{cm.}^{-1}$$

$$K_{solution} = 1.286 \times 10^{-2} \ \text{ohm}^{-1} \ \text{cm.}^{-1}$$

$$\text{Correction} = 0.5 \times \frac{4 \times 10^{-6}}{1.286 \times 10^{-2}}$$

$$= +0.0001$$

ii) Volume correction

$$\triangle V = V_{AgCl} - V_{Ag} - T_{Cl}^{-} V^{KCl}$$

From Longsworth [14]

$$\bar{V}^{KCl} = 26.65 + 3.21\sqrt{m} \text{ ml. mole}^{-1}$$

$$V_{Ag} = 10.3 \text{ ml.}$$

$$V_{AgCl} = 25.8 \text{ ml.}$$

then $\Delta V = +1.7$ ml.

Volume correction $= +c\Delta V$

$= +0.0002$

Corrected $T_- = 0.5058$

Longsworth gives a value of 0.5102. The transference number as first calculated was 0.5101 but in going over the calculations at the end of the term the present author noticed an error in the calculation of the concentration. There was no time available to repeat the determination or to find the cause of the discrepancy.

2. Silver Nitrate

An attempt was made to determine the anion transference number of 0.1 N silver nitrate with 0.1 N silver perchlorate as indicator. A silver anode and cathode were the electrodes. No boundary was observed for currents of 4-6 milliamps.

3. Ammonium Nitrate

A run was made with 0.1 N ammonium nitrate as the leading and 0.1 N silver nitrate as the indicator solutions, respectively. The electrodes were a silver anode and a platinum gauze immersed in 0.1 $AgNO_3$ as cathode. No boundary was observed for currents in the range 3.5-6 milliamps.

DISCUSSION OF RESULTS

CONCLUSIONS

The necessary apparatus for determining transference numbers by the moving boundary method using A.R. Gordon's cell has been constructed and calibrated. The technique appears to be good except for one disturbing factor which is probably the preparation of the solutions.

Silver perchlorate does not give a rising anion boundary when used as the indicator for silver nitrate. From the literature the most promising indicators for silver nitrate are lithium nitrate in a falling and cadmium nitrate in a rising boundary. To extend the determinations to higher concentrations the differential moving boundary method of Longsworth (36) shows the most promise.

A rising cation boundary is not formed with ammonium nitrate and silver nitrate as the leading and indicator electrolytes respectively. Further investigation is indicated here since this should not be the case.

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