TRANSFERENCE NUMBERS BY THE METHOD OF MOVING BOUNDARIES

THEORY, PRACTICE, AND RESULTS

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I. INTRODUCTION

Data on transference numbers have played a relatively small part in the development of the theory of solutions. This is because the available figures have been scattered and, with notable exceptions, have been of doubtful accuracy, owing to the fact that the methods available for the determination of transference numbers have been difficult to carry out and have yielded results of low precision even in the hands of careful workers. The effect has been that theories of solutions of electrolytes have been retained long after transference data that clearly contradicted them have been available. The most notable case of the kind is the theory of dissociation in the quantitative form given it by Arrhenius. This theory requires that the mobilities of ions remain constant, the decrease in equivalent conductance with increasing concentration being ascribed to changes in the number of ions. Now constant ion mobilities require constant transference numbers, though the reverse is not necessarily true. Data, though not of high precision, showing variation of transference numbers with concentration were available, but were apparently ignored, when Arrhenius presented his theory. On the other hand, the modern theory of electrolytic conduction, based on interionic forces, as developed by Debye and Hückel (38) and Onsager (39), requires, in general, changes of transference number with concentration. We will show from data presented later in this article and more fully discussed elsewhere (36) that the recent accurate data are in ample accord with the new theory.

Aside from the interpretation of conductance data, transference numbers are useful in studying the thermodynamic properties of solutions. An early research of this kind was carried out by Jahn (40), who combined measurements of concentration cells "with transference" with determinations of transference numbers, from which he computed the activities of the ion constituents, confusing, however, these activities with ion concentrations. Since we now have at hand data of high accuracy on transference numbers over a range of concentrations

we are in this Laboratory making accurate measurements on concentration cells with transference. For uni-univalent electrolytes, such data may be interpreted by means of the equation

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

in which E is the electromotive force, T_i the transference number, and a_i is the mean ion activity. In the near future transference data will probably be of most service in this field. This method for determining ionic activities has a number of advantages. Only one type of reversible electrode is required, and the measurements are isothermal and can be made in a wide range of temperatures. We already have the necessary data for determining the activities of silver nitrate and sodium chloride in this manner.

In addition, transference numbers are of service in computing liquid junction potentials, electrode polarizations, electromotive forces due to gravity and centrifugal force, diffusion coefficients of salts, etc.

There are three practical methods for determining transference numbers: the Hittorf or analytical, the electromotive force, and the moving boundary methods. The first mentioned requires great skill and precision in analysis, and much time. The second, though useful, is open to difficulties in the interpretation of the experimental data. The third method is the subject of this review, and is, we hope to show, the most useful and precise of the three.

Although this review is concerned only with the present status of the moving boundary method, the researches of the chief workers should be mentioned. The possibility of directly observing the motion of ions was first investigated by Lodge (1). The motion of the boundary between two solutions, one of them having a colored ion, was observed by Whetham (2, 3, 4) and Nernst (5). Masson (8) indicated clearly the conditions necessary for quantitative work with moving boundaries, Steele (9) greatly extended the usefulness of the method by utilizing the observation made by Lenz (41) and Bein (42) that a boundary

between two colorless solutions may be visible as a result of differences in refractive index of the two solutions. Denison and Steele (14) made quantitative measurements with the method, obtaining transference numbers of all the more common electrolytes. An important early research, in which quantitative measurements were made with moving boundaries in liquid ammonia solutions, was carried out by Franklin and Cady (13). This brief summary of the history of the subject may be supplemented by the interested reader by reference to the bibliography, which is complete.

II. ELEMENTARY THEORY

The phenomenon on which the determination of transference numbers by the moving boundary method depends may be described as follows. Let figure 1 represent the section of a tube in which there are two solutions of electrolytes, AR and BR, with a common ion constituent, R, between which there is the boundary $a-b$. If the constituents A and B have been appropriately chosen this boundary will move, when current is passed through the tube, to another position, say $c-d$. Let, for instance, R be the common negative ion constituent and A and B the positive ion constituents; then the boundary will move in the direction of the current and R will move in the reverse direction. The effect of the passage of the current will be to sweep out of the region between $a-b$ and $c-d$ all of the ion constituent A, *whether A is or is not entirely present as free ions*. In other words, the effect of the passage of the current is to replace the solution of electrolyte AR in the region between the two positions of the boundary by another solution containing BR. Thus, under the influence of the passage of a certain number of coulombs, an amount of the ion constituent A, equal to that originally contained in the volume, V, between the two positions of the boundary $a-b$ and $c-d$, must pass any fixed plane, say $M-N$, in the unchanged portion of the electrolyte solution. Let V be the volume in liters swept through by the boundary when one faraday, *i.e.*, 96500 coulombs, of current passes through the tube. The number of equivalents of ion constituent A passing a plane $M-N$ will be VC_A, in which C_A

is the concentration of electrolyte AR in equivalents per liter. Therefore

$$T_A = VC_A \tag{1}$$

in which T_A is a transference number of the constituent A. This transference number differs from the usual Hittorf transference number in that it refers to the number of equivalents passing across a plane stationary with regard to the walls of the tube rather than one stationary with respect to an average solvent particle in the solution. For dilute solutions the two transference numbers are very nearly the same, and the correction of one to obtain the other is fully discussed later in this paper.
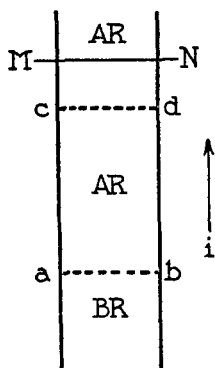
Fig. 1

If another (usually smaller) number, f, of coulombs is passed through the tube, then the boundary will pass through another volume, v, which is related to V by

$$v/V = f/F \tag{2}$$

Eliminating V from equations 1 and 2

$$T_A = \frac{vC_A F}{f} \tag{3}$$

If the current in amperes, i, is constant, then $f = it$, in which t is the number of seconds. Dropping the subscripts,

$$T = \frac{vCF}{it} \tag{4}$$

an equation of which we will make much use in what follows.

In this simplified derivation of the fundamental equation 4 we have made a number of tacit assumptions, the principal of which are as follows; (a) that there are no disturbing effects due to interdiffusion or mixing of the two solutions; (b) that the motion of the boundary is uninfluenced by the nature or concentration of the following or indicator ion constituent (B, of figure 1); (c) that there are no volume changes in the apparatus that affect the motion of the boundary. Later in this article it will be shown that, if the determinations are properly carried out, these assumptions are fully justified or the necessary corrections can be accurately made.

The transference number can also be determined without measurement of current and time by employing two boundaries, one for the cation constituent and one for the anion constituent. For the first we have

$$T_+ = \frac{v_+ CF}{it} \tag{5}$$

where T_+ is the cation transference number and v_+ is the volume swept through by the cation boundary, and

$$T_- = \frac{v_- CF}{it} \tag{6}$$

which contains the corresponding quantities for the anion constituent. Since

$$T_+ + T_- = 1 \tag{7}$$

equations 5 and 6 yield

$$T_+ = \frac{v_+}{v_+ + v_-} \tag{8}$$

since the product it is the same for both boundaries. Most of the early measurements were made using this principle. However, it has several disadvantages. In the first place it is, of course, essential that the two boundaries move at the correct rates. A necessary but not conclusive test that must be applied to these rates is whether the volumes swept out, per coulomb of current passed, are constant. If they are not constant it is probable that mixing of the observed and indicator solution is

taking place. The most convenient method for determining whether a boundary rate is constant is to keep the current constant, and if this current is measured all the data necessary for the use of equation 4 are available. Also, with the two-boundary method it is necessary to select two indicator solutions, which, as will be shown, must have certain definite properties. Such solutions are not always available. For these reasons all the recent work has been made using one boundary. The relation $T_+ + T_- = 1$ has, however, been used to test the results of single boundary measurements.

III. THE PRACTICAL DETERMINATION OF THE TRANSFERENCE NUMBER OF AN ION CONSTITUENT

1. The "indicator" solution

The determination of the transference number of an ion constituent of a solution involves, in the first place, the choice of a solution containing an ion constituent with the necessary properties to serve as a following, or what has been called "indicator," ion constituent. The possibility of making the determination depends upon the existence of the necessary ion constituent, and the accuracy of the determination may depend upon the proper choice when a choice is possible.

Measurements are made with boundaries which fall during the determination and also with boundaries which rise. Since it is always the leading ion constituent whose transference number is determined, the indicator solution must always be lighter if the boundary is of the "falling" type, and heavier if it is of the rising sort; otherwise mixing takes place immediately. A second quite necessary condition is that the mobility of the indicator ion constituent must be lower than that of the leading ion. Thus the lithium ion, being both light and slow, will serve as indicator for most positive ions with falling boundaries, and the cadmium ion constituent will serve in like capacity for many rising boundaries because it is slow and heavy. It must, obviously, be possible to follow the motion of the boundary. For this purpose a difference of color, or far more generally a difference of re-

fractive index of the two solutions in contact, is necessary. Another obvious requirement of the indicator is that it should not react chemically with the solution with which it is in contact. Unless special precautions are taken it is necessary for the leading and indicator solutions to have an ion in common.

There are other requirements necessary to fit special cases, but these will either be obvious to a worker or will be considered under the different topics which will follow.

2. Method for observing the boundaries

The optical system employed for the purpose of locating the boundary is a modification of that suggested by Abegg and Gauss
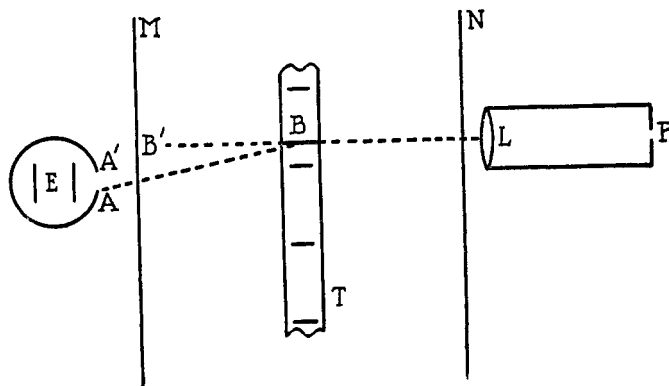
FIG. 2. THE OPTICAL SYSTEM FOR OBSERVING BOUNDARIES

(10) and further improved by MacInnes, Cowperthwaite, and Huang (27). A diagram of the system is given in figure 2. An electric lamp, E, is shaded by a metal shield except for a slit, AA', (seen edgewise in the figure) which is covered by a ground glass screen. Ignoring the effects of the glass walls of the thermostat, MN, and of the measuring tube, T, the path of a beam of light from the lower edge of the illuminated slit is ABL if the angle ABB' is the critical angle for total reflection from the boundary B. Thus the lower illuminated edge A will appear to lie on the line LB, while the light from this edge passing on either side of the tube T will appear to come directly from A. The

boundary thus causes an apparent upward displacement of the illuminated edge, which serves as the means of locating the boundary. The lens, L, which has a focal length of about the distance LB, increases the visibility of the boundary by collecting the light and by throwing the directly viewed edge A out of focus. The tube and aperture, P, provide a constant alignment of the eye with the other optical parts. The lens and source of illumination are mounted upon a rigid framework (not shown in the diagram) which may be raised, or lowered, by means of a thread and screw. The displacement of the boundary may thus be followed continuously with an accurate reproduction of the alignment of the various parts of the optical system.

3. Methods for forming boundaries

The early work involving gelatin, etc., will not be considered in this connection, as it has historical interest only (12).

In order to observe the movement of a boundary between two ion species it is, of course, necessary to form the boundary. An invariable condition is that the lighter solution must be on top. The junction between the leading and indicator solutions must be made with only a slight amount of mixing and diffusion, though, as we shall see, there is a "restoring effect" which overcomes, at least to a limited extent, the results of such disturbances.

The first successful junctions in which one or both of the solutions was not set in a jelly and which were not of the "autogenic" type to be described below, were made by Denison and Steele (14) by means of the scheme shown in figure 3. The solution whose transference number was desired was contained in the tube A. This was separated from the indicator solution in the vessel B by pressing a membrane of parchment paper stretched over the hollow cone, C, onto the shoulder D. On impressing a potential in the appropriate direction, current passed around the edges and through the paper and the boundary started down the tube, after which the cone could be cautiously lifted to the position shown. This device was simplified, as is shown in figure 4, by MacInnes and Smith (21), who replaced the cone and parchment paper by a flattened glass rod and a disk of soft rubber, E.

It was found that with this arrangement there was a more definite initial separation of the solutions, and enough current leaked around the edge between the rubber and the glass shoulder when they were in contact to allow the boundary to move down the tube before the rod and disk were lifted from the shoulder D. Adequate separation of the leading and indicator ion constituents was, however, not easy to obtain with these arrangements.

An apparatus by means of which the two solutions could be kept quite separate until the boundary was formed, and with which a sharper initial boundary could be obtained was developed
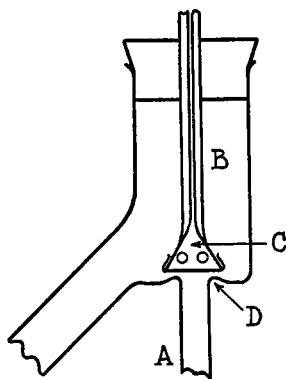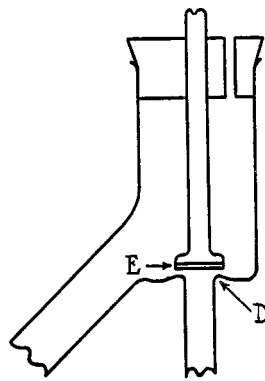
FIG. 3   FIG. 4

FIG. 3. METHOD OF FORMING BOUNDARIES EMPLOYED BY DENISON AND STEELE

FIG. 4. METHOD OF FORMING BOUNDARIES EMPLOYED BY MacINNES AND SMITH

by MacInnes and Brighton (24). This device has been used in most of the recent work. The principle is shown in figure 5a. The electrode vessel, A, is fitted into the disk, B, and the graduated tube, D, into a corresponding disk, C, the disks B and C both having plane surfaces where they meet. The electrode vessel, A, is filled with the proper solution and is closed with a stopper which carries the electrode so that a drop of the solution, a, hangs from the open end of the electrode tube. The graduated tube D is filled with a slight excess of solution so that a drop, b, protrudes. Now if the disk B is slid over the disk C the excess amounts of both solutions are sheared away and a boundary,

very little disturbed by mixing or diffusion, will result when the tubes are in place over each other, as shown in figure 5b. The complete disks, B and C, are of the design shown in figure 6, and are arranged to hold two tubes which may or may not be electrically connected. One of the disks is provided with a brass projection, P, and the other with a hole into which it fits; other-
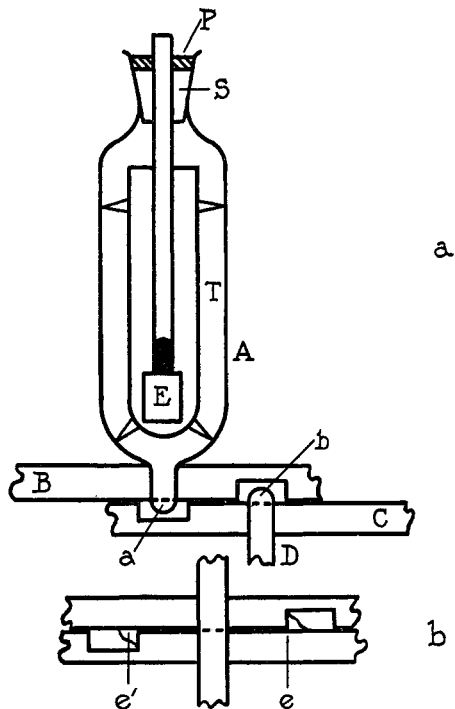
FIG. 5. METHOD OF FORMING BOUNDARIES EMPLOYED BY MacINNES AND BRIGHTON

wise they are identical. A channel, J, forms an air insulation from the water of the thermostat when the two lubricated disks are in contact. In operation the vessels are filled as shown in figure 5a. The disks, adequately lubricated, are then placed at an angle to each other so that the pendant drops from the electrode vessels are over the depressions K and K' (figure 6) on the lower disk, and the drops from the graduated tube D projecting

into the corresponding spaces in the upper disk B. After the assembled apparatus has been allowed to come to temperature equilibrium in the thermostat, one of the disks is turned with the projection P as a center. The excess of liquid and lubricant is sheared off at the edges e and e' (figure 5b). Boundaries formed in the manner just described will be referred to as "sheared boundaries."

Finally there is the "autogenic" boundary first used by Franklin and Cady (13). This method for forming boundaries pre-
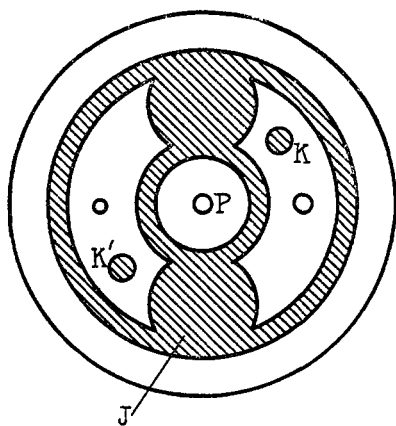
FIG. 6   FIG. 7

FIG. 6. CONSTRUCTION OF THE PLATE GLASS DISKS FOR USE IN FORMING SHEARED BOUNDARIES
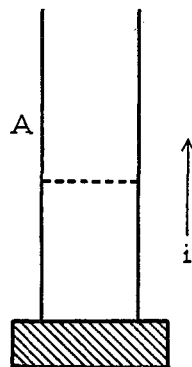
FIG. 7. THE METHOD OF FORMING AUTOGENIC BOUNDARIES DUE TO FRANKLIN AND CADY

ceded that of Denison and Steele (figure 3). The principle of this method is shown in figure 7. The solution under observation is in the tube, A, over the bottom of which is placed a disk of metal which forms a soluble salt in combination with the anion of this solution. For instance, the solution in A may be potassium chloride and the metal cadmium. If now current is passed in the direction indicated by the arrow, cadmium chloride will form at the electrode, and since the cadmium ion constituent is slower than the potassium ion constituent a boundary between these two ions will move up the tube. This method is more

restricted in its application than the others mentioned, but its simplicity recommends it for use when possible.

4. *The complete apparatus*

The apparatus used in most of the more recent work is shown in figure 8. It is fitted to form either falling or rising "sheared" boundaries, or autogenic boundaries.
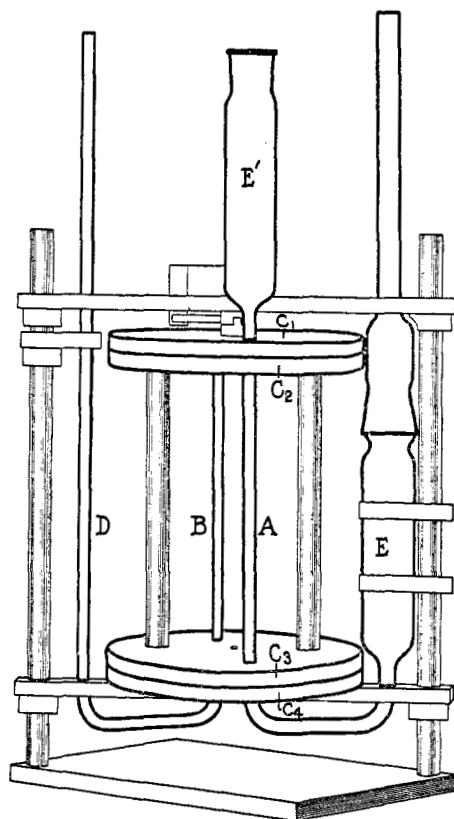
FIG. 8. THE COMPLETE MOVING BOUNDARY CELL

For the sheared boundaries the measurements are made in the graduated tubes, A (or B), which initially hold the solution whose transference number is to be determined. The plate glass disks, C_1, C_2, C_3, and C_4, are of the design shown in figure 6. To form a

falling boundary, disks 3 and 4 are clamped together. The electrode vessel E and tube A are filled with the observed solution. Disk C_1 is placed at approximately 45° to the position shown and is filled with the indicator solution as described in the previous section. The whole apparatus is now placed in the thermostat. When temperature equilibrium is reached, a spring with a cable release turns disk 1 over disk 2. The motion is gentle, owing to the viscosity of the lubricant between the disks.

For a rising boundary the procedure is nearly the same except that disks 1 and 2 are clamped together, the observed solution fills tube A and electrode vessel E', and the indicator solution fills electrode vessel E.

To form autogenic boundaries in this apparatus a small cylinder of metal, usually cadmium, is set into a recess in disk 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 illustration) are filled with the observed solution. Contact with the metal cylinder is made by a wire passing through the glass tube D.

5. The electrodes and electrode vessels

During the measurements it is necessary to carry from one to ten milliamperes for periods up to two hours to and from the electrodes and the solution. Since one of the electrode vessels is closed, any volume change at that electrode and in the intervening solution directly affects the motion of the boundary under observation. It is therefore clearly necessary that no gas be evolved at the electrode, and that any change in volume affecting the boundary displacement be possible of accurate computation. In the early work these important volume changes were given little attention. They will be considered in detail in a later section of this paper. For the more recent determinations silver, cadmium, and silver–silver chloride electrodes have been used, the two first mentioned as anodes and the last as cathode.

The electrode vessel shown in figure 5a has been found to be serviceable. The outer tube, A, is drawn down on its lower end

to the size of the graduated tube in which the boundary is observed.   Inside the tube A is a tube T closed at the lower end and with glass projections as shown.   The electrode E is inserted into this inner tube.   Using cadmium as anode and silver–silver chloride as cathode, the salt concentration around the electrode increases during the passage of current and the tube T prevents the heavier solution from entering the measuring tube.   There are also occasions when it is desirable to surround the electrode with a concentrated salt solution.

If the electrode chamber is kept closed during a determination, it has the following additional features.   The stopper, S, (figure 5a) is ground to fit the neck of the electrode chamber, A, the upper edge of the neck extending a little beyond the top of the stopper.   This leaves a shallow space above the stopper which is sealed over with "Picein", P, after the chamber has been completely filled with solution and the stopper placed in position.

6. The measured quantities

From the equation

$$T = \frac{vCF}{it} \tag{4}$$

it is evident that to determine a transference number by the single boundary method it is necessary to obtain the concentration, C, the current, i, and the volume, v, swept through by the boundary during the time t.   These variables will be discussed in the order given.

The concentration.   This must be known at least to the accuracy to which the transference number is desired.   Since recent measurements have reached an accuracy of 0.02 per cent, the preparation of the solution, or the analysis, must be of high precision.   Much of the recent work has been carried out with the aid of the Richards bottling apparatus (43) by means of which hygroscopic salts may be dried and subsequently weighed without exposing the sample to moist air.   For acids the differential electrometric method (44) has been found to have the necessary precision.   The concentrations must be expressed in equivalents per unit volume.

The volumes. The actual transference number determinations are made by observing the time, t, in seconds necessary for a boundary to move between graduations on the measuring tubes A or B of figure 8. It is thus necessary to know these volumes to the precision desired in the transference numbers. The tubes are graduated (27) as is shown in figure 9. The graduation marks extend on either side, leaving a clear space at front and back. In this way the boundary is always visible, as it is never covered by a graduation mark.

Calibrations of the tubes have been carried out as follows. A stopcock was sealed onto the tube, which was then very carefully

FIG. 9. THE GRADUATION OF TUBES

cleaned. Redistilled mercury was then drawn from a weighing bottle into the tube until the mercury meniscus roughly coincided with a graduation on the tube. A correction for the lack of coincidence was made with a micrometer arrangement (36). This was repeated at another graduation. The weight of mercury necessary to fill the volume between two graduations was thus determined. The graduated portion of the tubes used in all recent work has been ten centimeters long, with graduation marks at every centimeter except at the ends, where there are extra marks at half centimeter intervals. The cross sectional areas have ranged from 0.2 to 0.02 square centimeter.

The current. Although it is theoretically possible to determine

the product which occurs in equation 4 of the current, i, and the time, t, with a coulometer, it has been found necessary to make the actual determinations by keeping the current constant and measuring the time. In the first place, the quantities of electricity involved are in general too small to determine with a coulometer. For instance, in one determination involving 0.02 N sodium chloride the current was 0.0016 ampere and the boundary took 3453 seconds to move the full length of the tube. Under these conditions only 6.2 milligrams of silver would be deposited in a coulometer. Still smaller quantities of electricity are involved when the boundaries move shorter distances or when more dilute solutions are used. It is evident that no available coulometer would yield the required accuracy. An attempt was, however, made by Smith and MacInnes (22) to use coulometers in moving boundary measurements, by using a wide measuring tube, eleven millimeters in diameter. It was found, however, that the large amount of heat generated in these tubes seriously disturbed the boundary; the method is also inconvenient for the reason outlined in the next paragraph.

It has been found important to determine whether a boundary is moving at a uniform rate when a constant current is passing, since, when there are sources of error, such as a progressive mixing of the solutions, there will be changes in this rate as the motion of the boundary proceeds. It is therefore desirable to measure the progress of the boundary at short intervals along the measuring tube. In recent practice readings have been made at every graduation. As has been stated, these are spaced at centimeter intervals except at the ends where there are two extra half centimeter graduations, making fourteen intervals. It is therefore possible to compute the velocity of the boundary for each of these intervals as the experiment is going on. To obtain these data it would require fourteen coulometers. Furthermore, with the present method the necessary computations may be made between readings, thus making the information immediately available.

Some early work was carried out with hand regulation of the current. The inconvenience and comparative inaccuracy of

this method demonstrated the need of a constant current apparatus. Since the motion of a boundary consists of the gradual replacement of a solution of electrolyte by one of lower conductance, to obtain a constant current through the apparatus either the applied potential must be gradually increased or a resistance in series must be progressively diminished. Both these methods have been used, though the former has proved to be the more convenient.

The constant current device (26) in its most recent form is shown diagrammatically in figure 10. The moving boundary apparatus, C, is connected in series with the battery of storage cells, $A–B$, with a maximum potential of about 400 volts. Some of these cells are shunted by the potential divider, DD'. The current through the apparatus is measured by determining the drop of potential across the known resistance, R, by means of the potentiometer, P. The galvanometer, G, used in connection with the potentiometer is of the portable type indicating with a needle. For this work the needle is provided with a vane, V, of aluminum foil. The light from the line filament of the lamp, U, is focussed on the edge of the vane by the lens, L. If not shaded by the vane the light passes to the photoelectric cell, K. The photoelectric cell, three-element tube, O, and the sensitive relay, N, are arranged in the so-called "forward connected" manner (45) so that illumination of the cell causes operation of the relay, N, which in turn operates the relay, J, and the electromagnet, E. This last actuates the following mechanism by which corrections for both positive and negative deviations from the desired current strength may be made. A motor, M, continuously turns a circular leather-faced steel disk, F. A shaft holding the grooved pulley, P_1, and the Bakelite pulleys, P_2 and P_3, is pivoted with bearings above and below the pulley P_1 so that the shaft can swing around an axis at right angles to the axis of the disk F and to the shaft itself. The pulley P_1 is connected by a light belt to the pulley H which operates the potential divider DD' (which is described below). The shaft supporting the pulleys P_1, P_2, and P_3 is normally held by a spring, S, so that pulley P_2 is in contact with the revolving disk

F, thus driving the potential divider in a direction which introduces a higher potential into the circuit. If, however, the electromagnet E receives current through the operation of the

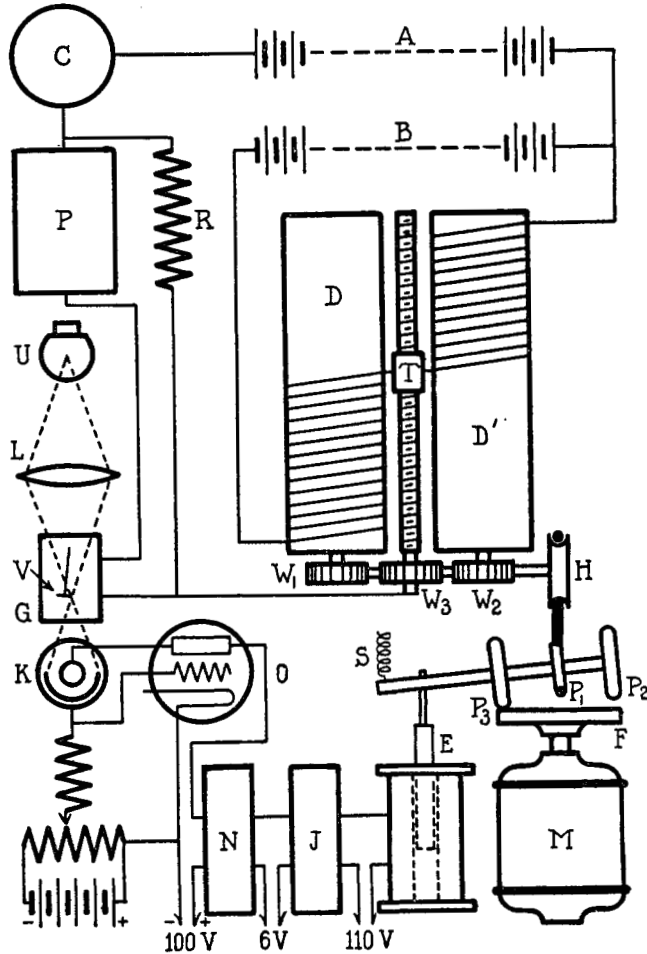
Fig. 10. Diagram of the Constant Current Regulator

relay J, pulley P_3 is brought into contact with F and the motion of the contact point on the current divider is immediately reversed. (When the change of potential required is known to be

in one direction only, it is sometimes desirable to remove this pulley.)

The operation of this apparatus is as follows. If the potential across the resistance R drops, owing to an increase of the resistance of the column of electrolyte at C (or to a running down of the batteries, A–B) the vane V of the galvanometer swings to illuminate the photoelectric cell, thus operating the relays and the magnet E. This permits a forward movement of the contact point T, which soon makes slightly more than the required correction, whereupon the reverse movement of the vane V causes, through the operation of the relay system, the operation of the magnet E and the reversal of the adjustment of the contact T. The sensitiveness of the apparatus is shown by the fact that a reversal of the adjustment occurs if the potential across the terminals of R differs by 0.1 millivolt from the reading of the potentiometer. The total potential across R is usually about 1.5 volts. Thus a variation of less than 0.01 per cent from the correct current will cause the operation of the adjusting system.

The apparatus just described is an improvement over the scheme already published (31) mainly in the use of the potential divider DD' shown diagrammatically in the figure. This device consists of two drums, D and D', covered with an insulating layer, connected to turn in the same direction by a worm and gears, W_1 and W_2. Another gear, W_3, driven by the same worm operates a threaded rod carrying the contact point T. In operation, resistance wire is wound off one drum onto the other past this contact point. Part of the battery A–B is shunted across the whole length of wire on the two drums. These drums carry 500 feet of No. 30 manganin wire having a resistance of approximately 1000 ohms. It is evident that the potential, and thus the current, can be adjusted to almost any degree of accuracy with this arrangement, instead of being limited by the rather large resistance steps of commercially available rheostats.

Time. The measurement of time of passage of a boundary between graduations has been made more convenient by using a magnetic counter, operated from the pendulum of an accurate

clock. The counter thus reads directly in seconds. In order to avoid the necessity for an electrical contact on the pendulum it has been arranged so that the latter periodically places a screen between a light source and a slit, behind which is a photoelectric cell. With amplification the resulting changes in the resistance of the photoelectric cell are made to operate the counter which is started when the boundary passes the first graduation.

TABLE 1

Data and computations for a typical determination. T_+ *at 25°C. for KCl at C =* 0.9992

Sheared boundary—0.80 N BaCl$_2$ indicator. Ag anode, Ag–AgCl cathode, current = 0.014189 ampere

1 x	2 t	3 vCF/i	4 T_+	5 Δx	6 Δt	7 vCF/i	8 T_+
0.0	0			0.0–10.0	3350	1638.8	0.4892
0.5	167			0.5–10.0	3183	1557.1	0.4892
1.0	334	163.3	0.4889	1.0–10.0	3016	1475.5	0.4892
1.5	503			1.5–10.0	2847	1393.8	0.4896
2.0	669	326.8	0.4885	2.0–10.0	2681	1312.0	0.4894
3.0	1004	490.3	0.4884	0.0– 9.5	3181	1557.1	0.4895
4.0	1339	654.1	0.4885	0.5– 9.5	3014	1475.4	0.4895
5.0	1675	818.7	0.4888	1.0– 9.5	2847	1393.8	0.4896
6.0	—	983.4		1.5– 9.5	2678	1312.1	0.4900
7.0	2346	1147.7	0.4892	0.0– 9.0	3016	1475.4	0.4892
8.0	2680	1311.7	0.4894	0.5– 9.0	2849	1393.8	0.4892
8.5	2847			1.0– 9.0	2682	1312.1	0.4892
9.0	3016	1475.4	0.4892	0.0– 8.5	2847	1393.6	0.4895
9.5	3181			0.5– 8.5	2680	1311.9	0.4895
10.0	3350	1638.8	0.4892	0.0– 8.0	2680	1311.7	0.4894
Mean..							0.4894

7. *The results of a typical determination of a transference number*

The greatest advantage of the moving boundary method over the other methods for determining transference numbers is the rapidity with which the measurements can be made. To show the number and relative accuracy of the data obtained in a single determination by the moving boundary method the figures, recorded in a quite typical experiment lasting about 90 minutes, are given in table 1.

Column 2 of the table gives the time required for the boundary to move through the volume between the etch marks spaced by the distance in centimeters given in column 1. Column 3 contains the factor vCF/i, which on division by t in the preceding column gives a value of T_+ (column 4) corresponding to the total volume through which the boundary has moved in that time. The values in column 4 thus constitute a running check on the progress of the experiment. In column 5 there are fifteen combinations of readings in which the boundary has traveled eight or more centimeters, and in column 6 the corresponding times in seconds. Hence, by calculating a value of T_+ for each of these combinations from the data of columns 6 and 7, errors in individual observations are minimized. The probable error of the mean of this typical experiment is 0.00004, corresponding to an error of 0.3 second. This is, of course, merely an indication of the accuracy of the time observations. Errors may also arise from determinations of volumes, current, and concentration. The accuracy of all these measurements has been, in recent work, within 0.02 per cent. Uncertainties in the necessary corrections to be described below may also introduce small errors.

Three runs of this kind can, in general, be made in one day. In contrast, a Hittorf determination in which, at best, two figures are obtained, requires several days, and has not, even in the most skillful hands, reached the precision of the moving boundary method.

IV. DISTURBING AND RESTORING EFFECTS AT THE BOUNDARY

It is quite evident that the reproducibility of the type shown in the preceding section would not be possible if progressive mixing due to diffusion and convection occurs at a boundary. It is the purpose of this section to show that these disturbing effects, though active, are overcome by a powerful restoring effect. *Diffusion* at a boundary is considered theoretically in section IX. We may anticipate that treatment by saying that in a moving boundary experiment a steady state is attained in which diffusion affects the "thickness" of the boundary but not its velocity.

1. Convection

During a determination by the moving boundary method heat is developed in the measuring tube, as a consequence of the resistance of the electrolytic solution to the passage of the current. The temperature gradients which result in the dissipation of heat through the glass wall of the tube into the thermostat liquid introduce two effects which tend to cause mixing at the boundary. The first effect may be considered as due to the fact that a greater quantity of heat per unit of volume is developed in the indicator than in the leading solution, since the former must have a higher specific resistance. The thermal conductivity of both solutions being about the same as that of the pure solvent, the mean temperature of the indicator solution is greater than that of the leading solution. Thus the two solutions meeting at the boundary are at slightly different temperatures and the resulting flow of heat from the indicator to the leading solution may be accompanied by a tendency of the two solutions to mix, the tendency being greater if the hotter solution is the lower one.

For a discussion of the second effect the tube may be considered as having cylindrical symmetry. The flow of heat at points somewhat removed from the boundary is then along radii taken perpendicularly to the axis of the tube. Moreover the temperature of the outside surface of the tube is taken as constant and equal to the temperature of the surrounding thermostat liquid. From symmetry it is evident that the temperature of the solution will have a maximum value at points on the axis and a minimum value at points along the inside surface of the tube. In general, the solution in the center of the tube will be less dense than that along the wall of the tube, with the result that the inner portion will rise and the outer portion will fall. Whether or not these convection currents will cause enough mixing at a boundary to affect the results depends upon the strength of the restoring effects to be described in the next section. By proper choice of the indicator electrolyte and size of measuring tube, the restoring effects can generally be made powerful enough to overcome these disturbing effects.

The problem of thermal distribution in an electrolytic conductor of the type considered here has been studied by Dr. Melvin Mooney. From his analysis (not yet published) the following conclusions may be drawn.

1. 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.

2. The temperature of the solution at 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 center and along the inside walls of the tube, this disturbing effect may be decreased by using tubes of small bore.

3. The temperature difference between the axis and inside wall of the tube is independent of the thickness of the glass wall of the tube. 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. This conclusion is of considerable practical importance since, contrary to the conclusions of many of the early investigators, the use of "quill" tubing for the measuring tubes possesses no advantage over the use of less fragile tubing.

2. Restoring effect

As has already been stated, disturbing effects due to diffusion and convection are overcome by a restoring effect, the nature of which may be made clear from the following example. Consider the case of a boundary between lithium chloride and potassium chloride, shown diagrammatically in figure 11. Since the lithium ion has a lower mobility than the potassium ion and the lithium chloride solution is more dilute than the potassium chloride solution, the passage of current will cause a greater potential drop in the former solution than in the latter. This is also

shown diagrammatically in the figure, where values of the electro-
motive force are plotted as ordinates and distances along the
measuring tube as abscissae.   Now if some of the relatively fast
moving potassium ions diffuse or are carried by convection into
the lithium chloride region, they will encounter a higher potential
gradient and will be sent forward to the boundary.   On the
other hand, if lithium ions diffuse into the potassium chloride
region they will move slower than the potassium ions and will
finally be overtaken by the moving boundary.   After appreciable
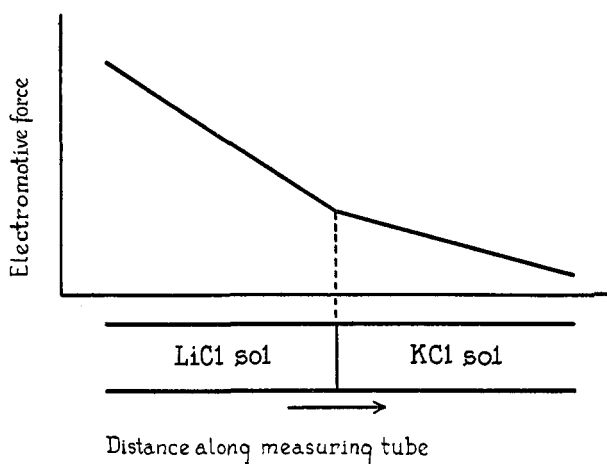
FIG. 11. DISTRIBUTION OF ELECTROMOTIVE FORCE IN THE REGION OF A MOVING
BOUNDARY

diffusion there will not, of course, be a sharp break in the po-
tential lines, such as is shown in figure 11.   However, for this
rectifying action to be effective it is only necessary for the
gradient to be steeper behind a given solution layer than in
front of it.[1]

[1] This explanation does not entirely account for sharp boundaries of the type
$HC_2H_3O_2/NaC_2H_3O_2$ in which the (weak) acid acts as indicator in spite of the
high mobility of the hydrogen ion.   In this case if the acid diffuses forward its
ionization is immediately repressed.   The diffused acid would thus cease to
carry current, and would soon be overtaken by the boundary.   The stability
of this type of boundary was predicted by Miller (17).   Such boundaries have
been found, in an investigation in this laboratory, to be unusually sharp and
readily followed.

That such a mechanism is operative has been demonstrated by MacInnes and Cowperthwaite (29), who showed that a boundary between lithium and silver nitrates will re-form and will move with the correct velocity, even if considerable diffusion has been allowed to occur.   We have repeated these experiments, using other solutions, and a rising instead of a falling boundary.   The solution used in this test was 0.01 N sodium chloride, and the indicator solution was the potassium salt of tetraiodofluorescein, the bright red color of which made the effects of mixing or diffu-

TABLE 2

Test of restoring effect.   Result of interrupting current in determination of T_- for 0.01 N NaCl

TUBE DISTANCE	TIME	$\frac{vCF}{i}$	TRANSFERENCE NUMBER T_-
centimeters	*seconds*		
0	0		
1	326	198.3	0.6083
2	651	396.5	0.6091
3	976	594.8	0.6094
Current interrupted 8 minutes			
4	1303	793.3	0.6088
Current interrupted 16 minutes			
5	1628	991.8	0.6092
6	1955	1190.3	0.6088
Current interrupted 32 minutes			
7	2282 .	1389.3	0.6088
8	2610	1588.5	0.6086
9	2938	1787.7	0.6085
10	3264	1986.9	0.6087

sion visible.   The results of the measurements are shown in table 2.   This determination was carried out in the same way as that described in a previous section, except that during the run the current was interrupted for periods of 8, 16, and 32 minutes. On each interruption the boundary which had been extremely sharp became hazy, owing to diffusion.   In the case of the longest period the color of the indicator solution was visible approximately three millimeters above the position of the boundary when the current was stopped.   On starting the current again, the boundary slowly re-formed and after a period depending upon the time

the current was off, fully recovered its original sharpness. For each interruption an estimate was made of the time necessary for the boundary to return to its original condition. It required about 66 seconds after the 8 minute interval and about 104 and 186 seconds after the 16 and 32 minute intervals. As would be expected, the diffusion is most rapid immediately after the interruption of the current, owing to the steeper concentration gradient at a sharp boundary.

The most surprising observation from this experiment is, however, that the diffuse zone between the two solutions moved, after restarting the current, with the same velocity as the fully formed boundary. This is shown by the constancy of the transference numbers in column 4 of table 2. These numbers are constant within experimental error in spite of the fact that after each interruption the sharp boundary had been replaced by a diffuse layer of from four to six millimeters thickness, which, however, gradually narrowed as the electrolysis proceeded.

A still more drastic test of the rectifying effect was made in an experiment in which the current was reversed for two periods. In this case the solution was 0.2 N NaCl, and the boundary was of the autogenic type. The results are given in table 3. As is indicated in the table, the current was first reversed for 250 seconds. The effect of the reversal, as can be seen from a consideration of figure 11, is to introduce the fast moving ions of the normally leading solution into the high potential gradient existing in the indicator solution, with the result that there is rapidly formed a continuous mixture of both solutions, which is, in this case, several centimeters thick.

On returning the current to its usual direction, the effect of the rectifying action is to narrow the mixture layer to the normal thickness of the boundary. It was interesting to observe that the sharp boundary suddenly reappeared a few seconds after the current in the normal direction had overcome the effects of the reversed current. It is also evident from the constancy of the transference numbers in table 3 that the boundary moved, after this vigorous disturbance, at the same rate as before. The time in seconds has, however, been corrected for *twice* the time of

reversal of current since allowance must be made for the time that the current was reversed and also for the time necessary to overcome the effect of the reversal. Exactly the same result was obtained after a reversal of 500 seconds. Also, in spite of the reversal of the current, the transference number of the sodium ion obtained in this determination agrees excellently with another measurement made in the usual manner on the same solution, the two results being respectively 0.3818 and 0.3814.

That the normally leading ions penetrate deeply into the indicator solution on reversal of current was shown in some quali-

TABLE 3

Test of restoring effect. Result of reversal of current in determination of T_+ for
0.2 N NaCl

TUBE DISTANCE	TIME	$\dfrac{\tau C F}{i}$	TRANSFERENCE NUMBER T_+
centimeters	*seconds*		
1	480	183.3	0.3819
2	958	365.9	0.3819
3	1435	548.0	0.3819
4	1913	730.2	0.3817
5	2390	912.4	0.3818
6	2865	1094.6	0.3821
7	3344	1276.4	0.3817
8	3818	1458.6	0.3820
	Current reversed for 250 seconds		
9	4799–500	1641.5	0.3818
	Current reversed for 500 seconds		
10	6280–1500	1824.6	0.3817

tative experiments with a boundary between hydrochloric acid and cadmium chloride, in which a trace of methyl violet was present. On changing the direction of the current, the sharp color boundary was rapidly transformed into a region several centimeters thick in which the color varied continuously from the blue of the acid solution to violet in the neutral salt solution.

3. Adjustment of the indicator concentration

It will be shown in the following discussion that the restoring effect just described, though powerful, is sufficiently effective

only if there is a preliminary adjustment of the indicator concentration within a certain range. The extent to which the indicator concentration may be varied depends upon a number of factors, but this range must include the value given by equation 10 (below). This relation may be derived as follows.

Consider a boundary which has moved from a position near $a - b$ to another position $c - d$, figure 12. As made clear in section II, the electrolyte AR which originally filled the volume between the two positions of the boundary has been replaced by another electrolyte BR. Now the concentration C_B of BR between $a - b$ and $c - d$ will in general be different from that C'_B behind the
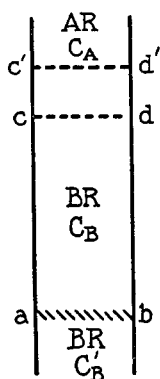
Fig. 12

starting point $a - b$, and there will be a junction of C_B/C'_B between the two solutions of different concentrations. This junction will move, but very slowly compared with that between solutions AR and BR, when current is passed (see section VIII). If, under the new conditions, an additional faraday of current is passed the boundary at $c - d$ will move to $c' - d'$, sweeping through a volume V. As we have already seen, the transference number T_A of the leading ion constituent may be obtained from

$$T_A = C_A V \tag{1}$$

Now the number of equivalents of ion constituent B passing the plane $c - d$, per faraday, will be

$$T_B = C_B V \tag{9}$$

From equations 1 and 9 we obtain the important relation

$$\frac{T_A}{C_A} = \frac{T_B}{C_B} \tag{10}$$

This equation is independent of any special assumption as to the ionization of the leading and indicator solutions. The reason why the "adjusted" concentration C_B of the indicator solution differs from the original concentration C_B' is that the indicator ion constituent at the boundary must move at the same rate as the leading ion constituent. This can occur only at one concentration for a given concentration of the leading solution, and in
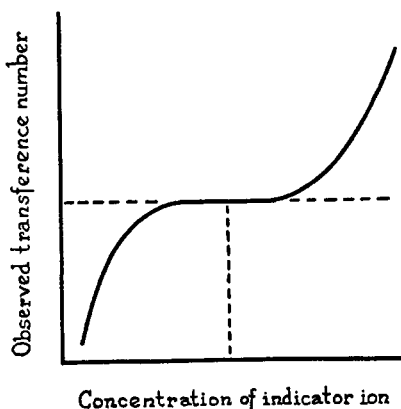
FIG. 13. EFFECT OF THE INDICATOR CONCENTRATION ON THE OBSERVED TRANSFERENCE NUMBER

general requires a change of concentration at a point corresponding to $a - b$. This change takes place automatically within limits which we will presently discuss.

It is evident that the transference number, T_B, of the indicator ion could be found from equation 10. This is, however, inconvenient as C_B would have to be determined, whereas the concentration C_A of the leading solution is known. Nevertheless, a few determinations of the adjusted concentration C_B have been made by indirect methods (30) and the values T_B thus computed from equation 10 were in approximate agreement with data given in the literature.

Although this simple theory indicates no limits to the difference between the initial concentration of the indicator C_B' and the "adjusted" concentration C_B, it has been found experimentally that the initial concentration C_B' must not be too far from that computed for C_B from equation 10. This topic has been studied for falling boundaries by MacInnes and associates (21, 22, 24, 25, 27). These workers found that the observed values of the transference number when plotted against the concentration C_B' of the indicator solution gave curves of the form shown in figure 13. The flat portion of each curve included the correct value of the transference number as ordinate, and the "adjusted" concentration C_B of equation 10 as abscissa. The adjustment range in which correct values of the transference number are obtained and the shape of the curve shown in figure 13, depend upon factors not well understood. However, the range appears to be greater for dilute solutions than for concentrated ones, and for narrow measuring tubes than for wide ones. It also is apparently greater for rising than for falling boundaries. Thus MacInnes and Smith found a range of about 10 per cent in the indicator concentration for the falling boundary LiCl/KCl, whereas Longsworth found that the range was about 40 per cent with the rising boundary KIO_3/KCl. The difference may be at least partly explained as follows.

If a margin is formed, for instance between 0.1 N potassium iodate and 0.1 N potassium chloride, figure 14a represents the initial condition. On passage of a current the boundary will rise, and after some time figure 14b will represent the new conditions in the tube. That is, a concentration gradient between 0.1 N and 0.06 N potassium iodate will remain near the point C. Since the relation of the densities, d, is $d_{0.1\,N\,KCl} < d_{0.06\,N\,KIO_3} < d_{0.1\,N\,KIO_3}$, this distribution will not be disturbed by gravity. On the other hand, consider an analogous case for falling boundaries where the boundary is initially formed between 0.1 N potassium chloride and 0.1 N lithium chloride, figure 15a. After the boundary has fallen some distance, figure 15b would represent conditions were it not for the fact that a denser solution of lithium chloride would thus be left on top. These two solutions of lithium

chloride would consequently tend to mix and destroy the concentration adjustment as fast as it was made. Both rising and falling boundaries are found, however, to give erroneous results when the indicator ion concentration is initially too low.

To a certain extent, then, the finding of the correct indicator concentration is an experimental method of approximations. However, this is not a serious limitation on the method, since the worker usually has at least a rough idea, from conductance or other measurements, of the transference numbers of the leading and indicator solutions from which the concentration
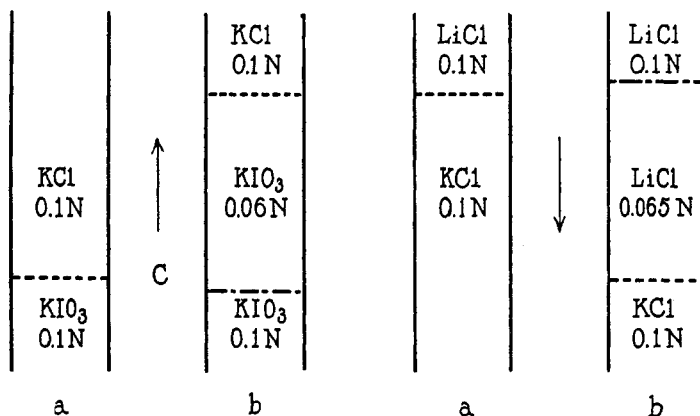
FIG. 14   FIG. 15

relation C_A/C_B can be obtained from equation 10. Furthermore, if the relation C_A/C_B is seriously different from that required by the equation just mentioned, the boundary is usually distorted and its rate of movement varies with time.

4. The regulating function

The relation $C_A/T_A = C_B/T_B$ is an application to an ordinary type of boundary of a more general function first derived by Kohlrausch (6) (see also Longsworth (33)) and named by him the "beharrliche" function. A derivation of the generalized function will not be given in this paper but some of its characteristics will be considered. This function defines a property of the solu-

tion 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 will be adjusted to values compatible with the constant determined by the initial composition of the solution. Thus in an ordinary moving boundary experiment the indicator solution which replaces the leading solution tends to adjust itself *automatically* to the value given by equation 10. Since the leading solution initially occupies the region into which the boundary moves, it has the power to regulate the concentration of the indicator solution which replaces it. This accounts for the fact that a moving boundary gives information directly for only the leading solution.

V. CORRECTIONS

1. The volume correction

In the development of the moving boundary method it was early noticed that the electrochemical reactions which occur at the electrodes on the passage of a current are accompanied by volume changes which affect the observed displacement of the boundary. Denison and Steele (14) considered this effect to be negligible, although subsequently this conclusion was shown to be incorrect. Their experimental arrangement, in which both electrode chambers were open to the atmosphere through capillary tubes, was not adapted to an accurate estimation of the correction after the method of making it had been developed.

Miller (17) was the first to show 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. The computation of this correction was made by Lewis (18) and was applied to some of the results of Denison and Steele. The following treatment is essentially that of Lewis.

As already mentioned, 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 water of the solution. In a determination by the moving boundary method, the position of the boundary is determined with respect to graduations on the tube. Hence, in order to refer the boundary displacement to the water in the apparatus, to obtain a value comparable with the Hittorf transference number, the motion of the water with respect to the tube must be computed.

This computation is greatly facilitated if one electrode chamber is closed throughout the determination, since with this arrange-
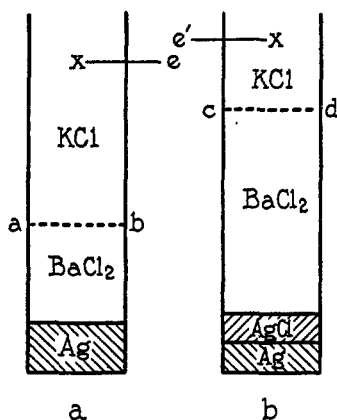
Fig. 16

ment only the volume changes occurring on this side of the moving boundary cell can affect the position of the boundary. As an example we may take a rising cation boundary between potassium and barium chlorides with a silver anode in the closed side of the apparatus. The conditions at the beginning of the experiment may be represented diagrammatically as shown in figure 16a. In this figure x denotes the position of an "average" water particle at some point which the boundary does not pass. As suggested by Lewis, if the concept of such a water particle is obscure, x may also represent a plane in the tube below which the mass of water remains fixed throughout the determination.

On the passage of one faraday the boundary will move from

$a - b$ to $c - d$ and the "average" water particle will move from e to e'. The conditions will then be as shown in figure 16b. Since the solution between the boundary and the "average" water particle is uniform and homogeneous, any volume change which displaces the one will affect the other similarly. During the passage of a faraday T_K equivalents of potassium ion will pass out of the region between x and the electrode. The corresponding loss in volume in this region is $T_K \cdot \overline{V}_K^{KCl}$ where $\overline{V}_K^{KCl}$ denotes the partial molal volume of one equivalent of potassium ions in potassium chloride at the concentration of the leading solution. Similarly, T_{Cl} equivalents of chloride ion will enter this region, corresponding to a volume $T_{Cl} \cdot \overline{V}_{Cl}^{KCl}$. At the electrode one equivalent of silver with a volume V_{Ag} will disappear and one equivalent of silver chloride with a volume V_{AgCl} will be formed. The formation of the solid silver chloride will involve the disappearance of one equivalent of chloride ion from the solution with a volume $\overline{V}_{Cl}^{BaCl_2}$. As the boundary moves from $a - b$ to $c - d$, one equivalent of chloride ion will move downward across this boundary, corresponding to the volume change $\overline{V}_{Cl}^{BaCl_2} - \overline{V}_{Cl}^{KCl}$. It is evident that an entire equivalent of chloride ion will suffer this volume change, since the transference number of this ion constituent referred to the *moving cation boundary* is unity. The net change in volume is

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

Since

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

and

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

this may be reduced to

$$\Delta V = V_{AgCl} - V_{Ag} - T_K \, \overline{V}_{KCl} \tag{11}$$

The observed volume through which the boundary moves is thus greater, by the amount ΔV, than the volume V (equation 1)

which was taken with respect to the water. The corrected transference number is therefore

$$T = V \cdot C = (V_{obs.} - \Delta V)C = T_{obs.} - C \cdot \Delta V \tag{12}$$

It is clear that this correction will be small in dilute solutions, since it is proportional to the concentration. In concentrated solutions, however, the volume correction is the main factor which limits the accuracy of the results. The reasons for this are as follows. The densities of solids are known to vary somewhat with their physical state, and consequently such terms as V_{Ag} and V_{AgCl} cannot be computed with a high degree of accuracy. Moreover, the partial molal volume of the dissolved salt is a function of the concentration, and since the concentrations vary in an unknown manner in the diffusion layers around the electrode, small volume changes would result which have not been considered. The possibility of correction for these small effects has been discussed in an earlier paper (36). Furthermore, it has not yet been definitely established that the partial molal volume and not the "apparent" molal volume is the quantity which should be used in making the correction.

However, these sources of error in the computation of the volume correction must be small, since the validity of the correction has been demonstrated independently by two methods. (a) In an electrolysis apparatus in which one electrode chamber may be disconnected and used as a pycnometer, Smith (35) has electrolyzed a silver–silver chloride cathode into a 0.2 N potassium chloride solution. From the pycnometer readings before and after the passage of a determined quantity of electricity he has experimentally measured the volume change and finds it to be in agreement with the value computed from an equation similar to equation 11. (b) Using tubes of small cross-sectional area the authors have recently been able to obtain satisfactory boundaries for potassium chloride at concentrations of 0.5 and 1.0 N. At these concentrations the volume correction may be quite large depending upon the electrode materials employed. Thus with cation boundaries and a silver anode the

volume change is given by equation 11, while with a cadmium anode this change is

$$\Delta V' = \frac{1}{2} \bar{V}_{CdCl_2} - T_K \bar{V}_{KCl} - \frac{1}{2} V_{Cd}$$

The data necessary for the computation of these corrections in some typical cases are assembled in table 4. The volumes were

TABLE 4

Computation of the volume correction

C_{KCl}	0.512	0.999
$\bar{V}_{KCl}$*	0.02897	0.02991
$\bar{V}_{CdCl_2}$*	0.02772	0.02953
ΔV*	0.0014	0.0009
$\Delta V'$*	−0.0068	−0.0063

* Computed from the equations:
$$\bar{V}_{KCl} = 0.02665 + 0.00321 \sqrt{\text{molality}}$$
$$\bar{V}_{CdCl_2} = 0.02324 + 0.00882 \sqrt{\text{molality}}$$
$$\bar{V}_{Cd} = 0.0130; \quad V_{Ag} = 0.0103; \quad V_{AgCl} = 0.0258$$

TABLE 5

Application of the volume correction

C_{KCl}	0.512	0.999
$C \cdot \Delta V$	0.0007	0.0009
$C \cdot \Delta V'$	−0.0035	−0.0063
T_+ obs. (Ag anode)	0.4894	0.4893
T_+ obs. (Cd anode)	0.4854	0.4817
T_+ corr. (Ag anode)	0.4887	0.4884
T_+ corr. (Cd anode)	0.4889	0.4880

computed from density data taken from the International Critical Tables (46) and are expressed in liters, since the unit of concentration employed throughout this paper is equivalents per liter of solution.

These volume corrections are then applied to the observed transference numbers as shown in table 5.

Thus at the highest concentration the uncorrected cation transference number obtained with a silver anode is about 2 per cent higher than that obtained with a cadmium anode, whereas the corrected values differ by less than 0.1 per cent. The effects here observed are much greater than any possible experimental error and furnish excellent evidence for the validity of the volume correction as here applied.

The discrepancy between the uncorrected transference number as determined by the moving boundary method and the Hittorf value was considered at one time (47, 16) to be due to the fact that the former method gave the "true" transference number. The dependence of the uncorrected value upon the electrode process proves conclusively the fallacy of this view.

2. The solvent correction

In addition to the volume correction discussed in the preceding section, there is also a correction, disregarded by all the earlier workers, which must be made for conducting impurities in the solvent. It should be applied to transference data obtained by any method. In contrast to the volume effect, this correction is important only for data on solutions at low concentrations. The necessity for making this correction, however, may be explained as follows.

In the derivation of equation 4 the assumption was tacitly made that the ions of the solute only were effective in the transport of electricity through the solution. However, in practice the solvent always has a small specific conductance (κ_{solvent}) which in sufficiently dilute solutions is an appreciable fraction of the total conductance. As shown in another publication (36) if κ_{solution} is the specific conductance of the solution, the observed transference number may be corrected by means of the equation

$$T_{\text{corr.}} = T_{\text{obs.}} \left(1 + \frac{\kappa_{\text{solvent}}}{\kappa_{\text{solution}}}\right) \tag{13}$$

For very dilute solutions this correction becomes quite important. Thus, for example, the observed anion transference number for 0.001 N KCl was 0.5052. The specific conductance of the solvent

as measured in the moving boundary cell was 1.3×10^{-6} and that of the solution 1.4×10^{-4}. The corrected anion transference number is 0.509_7, the correction in this rather extreme case amounting to 0.9 per cent of the observed value. Above a concentration of a few hundredths normal the solvent correction is negligible if a good grade of water has been used in the preparation of the solutions.

VI. RESULTS AND THEIR INTERPRETATION

1. Tables of transference data

All transference data obtained by the moving boundary method in which the more recent refinements in experimental technique have been used are given in table 6. The data for silver nitrate, obtained by MacInnes and Cowperthwaite, and some of the values for potassium chloride and potassium bromide have not been previously published. Otherwise the figure to the right of the symbol for each salt is the reference to the bibliography. Data on $CaCl_2$, KBr, KI, and Na_2SO_4 will be published in the near future.

In the interpretation of this data the Onsager theory of electrolytic conductance has been employed. As previously shown (36), this theory requires that the curve obtained by plotting T_+ against the square root of the concentration should go into the axis of zero concentration with the slope

$$\left(\frac{dT_+}{d\sqrt{C}}\right)_{C = 0} = \frac{2\,T_+^0 - 1}{\Lambda_0}\,\beta \tag{14}$$

In this equation T_+^0 and Λ_0 are the limiting cation transference number and equivalent conductance of the salt respectively, and β is a constant of the Onsager conductance equation which, for aqueous solutions of uni-univalent electrolytes at 25°C., has the value 29.9. Since the experimental data do not extend to a dilution where this limiting law is valid, an empirical equation with two adjustable constants has been developed (36) which, however, has the theoretical limiting slope and which may therefore be used for extrapolation of transference data to zero con-

centration. Moreover, this equation appears to be valid for normal electrolytes to a concentration of 0.1 N.

In figure 17 the data which extend over a range of concentration are plotted as ordinates against the square root of the concentration as abscissae. The scale of ordinates is the same for all

TABLE 6

Cation transference numbers of some aqueous solutions of uni-univalent electrolytes at 25°C.

AgNO₃		NaCl (36)		HCl (36)	
C	T_+	C	T_+	C	T_+
0.01	0.4648	0.01	0.3919	0.01	0.8252
0.02	0.4652	0.02	0.3900	0.02	0.8264
0.05	0.4664	0.05	0.3878	0.05	0.8292
0.1	0.4682	0.1	0.3853	0.1	0.8314
		0.2	0.381₄		

KCl (36)		LiCl (36)	
C	T_+	C	T_+
0.001	0.490₃	0.0098356	0.3289
0.002	0.490₃	0.011104	0.3286
0.005	0.490₅	0.018515	0.3264
0.01	0.4902	0.032550	0.3236
0.02	0.4901	0.049942	0.3211
0.05	0.4900	0.064021	0.3196
0.1	0.4898	0.1000	0.3168
0.2	0.489₂	KNO₃ (26)	
0.5	0.488₇		
1.0	0.488₃	0.1	0.5128

NH₄Cl (48)		KBr	
0.1	0.4900	0.1	0.485 (21)
			0.4834

electrolytes, but has been appropriately displaced for each salt in order to make the plot more compact. In the figure the circles represent the experimental points and the continuous curves are the values computed from the empirical equation mentioned above. Except for silver nitrate, the curves approach the limiting slopes which are represented by the straight full

lines. In the case of potassium chloride the limiting slope and the curve given by the empirical equation are coincident to a concentration of several hundredths normal.

The dotted curve through the experimental values for the transference numbers of silver nitrate gives a smooth extrapola-
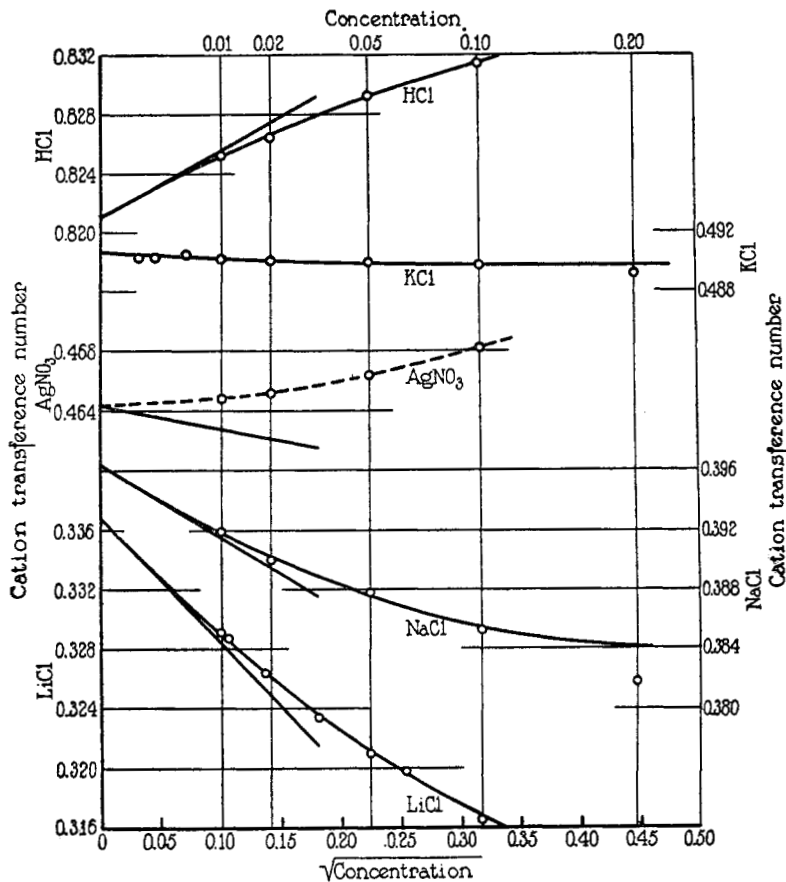

FIG. 17. TRANSFERENCE NUMBERS AS FUNCTIONS OF THE CONCENTRATION

tion to a limiting value which has been computed from the table of ion conductances given elsewhere (37). The apparent limiting slope in this case does not agree with the predictions of the Onsager theory. It is well known, however, that nitrates are abnormal (49, 50).

2. An experimental test of the relation $T_+ + T_- = 1$

The accuracy of some of the recent results obtained by the moving boundary method has been given an additional test in the following manner. From the definition of the transference number it is evident that for a binary electrolyte the sum of the cation and anion transference numbers must be unity. Thus if cation and anion boundaries are independently observed with the same solution, the sum of the transference numbers computed therefrom should be one. Some results of this test are given in table 7. This table, which is self-explanatory, includes results on anion and cation boundaries for various electrolytes and

TABLE 7

Transference numbers from cation and anion boundaries. An experimental test of the relation $T_+ + T_- = 1$

1 SALT	2 CONCEN- TRATION	3 CATION INDICATOR	4 ANION INDICATOR	5 T_+	6 T_-	7 $T_+ + T_-$
KCl	0.5	$BaCl_2$	KIO_3	0.488_4	0.511_0	0.999_4
	0.2	LiCl	KCO_2CH_3	0.490	0.510	1.000
	0.1	$CdCl_2$	KIO_3	0.4898	0.5101	0.9999
	0.01	$CdCl_2$	$K_2C_{20}H_6O_5I_4$	0.4901	0.5097	0.9998
NaCl	0.02	$CdCl_2$	$Na_2C_{20}H_6O_5I_4$	0.3900	0.6099	0.9999
LiCl	0.064021	$CdCl_2$	$LiIO_3$	0.3201	0.6805	1.0006
KBr	0.1	$CdBr_2$	KIO_3	0.4833	0.5165	0.9998
$CaCl_2$	0.019041	$CdCl_2$	$Ca(IO_3)_2$	0.4226	0.5776	1.0002

indicators. In columns 5 and 6 are given independent cation and anion transference numbers and in column 7 the sum of these numbers. As may be seen the values in that column deviate from unity by less than 0.1 per cent, and these deviations are both positive and negative in sign. This test, together with the excellent reproducibility of individual determinations, indicates that the results compiled in table 6 are subject to errors not over 3 or 4 units in the fourth decimal place. Where this figure is given in smaller type the error may be somewhat larger, owing to uncertainties in the volume or other correction.

The indicators which were used in the experiments recorded in table 7 are listed in columns 3 and 4. This list will illustrate

the types of indicator materials used in moving boundary experiments. In instances where a cadmium halide is listed as indicator the boundaries were the autogenic type.

3. Comparison with results obtained by the Hittorf method

It was of great interest to know whether the moving boundary and the Hittorf methods measure the same property of the solution. Although we have assumed this to be the case in our treatment, there has been no adequate test of this assumption until recently. The only measurements of transference numbers by the Hittorf method which are available for this comparison

TABLE 8

Comparison of results by the moving boundary method with recent Hittorf determinations

Potassium chloride					
C	0.02	0.05	0.1	0.5	1.0
T_+ (M. B.)	0.4901	0.4900	0.4898	0.488$_7$	0.488$_3$
T_+ (Hittorf)	0.4893	0.4894	0.4898	0.4896	0.4875
Lithium chloride					
C	0.01	0.02	0.05	0.1	
T_+ (M. B.)	0.329	0.326	0.321	0.317	
T_+ (Hittorf)	0.329	0.327	0.323	0.319	

and in which modern technique has been used are those of MacInnes and Dole on potassium chloride solutions (51) and of Jones and Bradshaw on lithium chloride solutions (52). Data obtained by both methods are arranged for comparison in table 8.

It is evident that agreement between values obtained by the two methods is most satisfactory and furnishes experimental evidence for the assumption that they measure the same property of the solution. The Hittorf transference numbers are, however, probably less accurate, since that method, in spite of its apparent simplicity, is a difficult one and is subject to a variety of errors. The values given for potassium chloride are directly measured ones and involved no interpolation. The figures given for lithium chloride, on the other hand, have been interpolated from empirical equations fitted to the experimental data.

VII. MOVING BOUNDARIES IN MIXTURES OF ELECTROLYTES

The moving boundary method has been used in three researches on solutions containing mixtures of two electrolytes with a common ion. Application of the method to systems containing a larger number of constituents has not yet been attempted. The only ternary ion system investigated by the early workers, Denison and Steele, was that resulting from the hydrolysis of a simple binary salt. More recently mixtures of KCl and NaCl, and of KCl and HCl have been studied; the results obtained are of interest in connection with modern theories of solutions of electrolytes and the concentration changes which take place on electrolysis of salt solutions.

Early in their work on the moving boundary method Steele observed that ordinary boundaries between binary electrolytes moved too slowly if the indicator, aluminum sulfate for example, was hydrolyzed (11). He and Denison utilized this observation in the measurement of the hydrolysis constants of the hydrochlorides of three weak organic bases (15). In these experiments, however, the function of the boundary was merely to effect a partial separation of the hydrogen ion resulting from hydrolysis, the data necessary for the computations being obtained from conductance measurements between small electrodes sealed into the side of the tube in which the boundary moved.

MacInnes, Cowperthwaite, and Shedlovsky (32) have utilized the moving boundary method in a determination of the transference numbers of the chloride ion constituent in mixtures of sodium and potassium chlorides. This work, in which the chloride ion concentration was kept constant at 0.1 N, also included conductance measurements for the mixtures. From these data the chloride ion conductances in the mixtures were computed and found to be very nearly constant. The aspect of this work, however, which is of especial interest in a discussion of the moving boundary method is the fact that the boundaries were normal in their behavior if certain precautions were taken in the preparation of the indicator solutions. Thus the ratio of potassium to sodium in the indicator solutions, which were a mixture of the corresponding acetates, was the same as in the

leading solutions. Moreover, the acetate ion concentration was adjusted approximately to a value required by the regulating function mentioned in section IV, 4, of this paper.

Because of the relatively slight difference in the properties of sodium and potassium ions, these investigators were unable to obtain cation boundaries for the mixtures. In a similar application of moving boundaries to potassium chloride and hydrochloric acid mixtures Longsworth (33) was, however, able to obtain cation boundaries, owing to the greater difference between hydrogen and potassium ions. In addition to obtaining data for the computation of the transference numbers of all three constituents
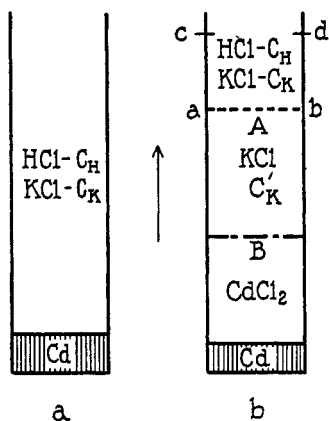

FIG. 18

of the mixtures, the concentration adjustments which occurred spontaneously when cation boundaries were observed have been investigated theoretically. Moreover, the equations resulting from this extension of the moving boundary theory have been completely verified, as will be shown below.

The experiments on the mixtures of potassium chloride and hydrochloric acid using, for instance, a cadmium anode as the source of indicating cations may be represented diagrammatically as follows. The measuring tube was initially filled throughout with the mixture of uniform composition as shown in figure 18a. C_K denotes the concentration of the potassium ion constituent

and $C_{\bar{H}}$ that of the hydrogen ion in the mixtures.   The concentration of the chloride ion, C_{Cl} ($= C_K + C_H$) was 0.1 N throughout.   After the current had passed for a time it was observed that the hydrogen ion constituent originally in the lower part of the tube had forged ahead of a portion of the potassium ion constituent.   Two boundaries, A and B, as shown in figure 18b, were visible.   The boundary A separates the mixture originally placed in the tube from a solution of pure potassium chloride at an "adjusted" concentration, C_K'.   With certain of the mixtures it was necessary to add a trace of methyl violet to the solution in order to make this boundary visible.

The equations describing the motion of this new type of boundary and the concentration adjustment which occurs behind it may be derived as follows.   On the passage of one faraday of electricity in the direction indicated, the boundary A will move from the position $a - b$ to the position $c - d$.   The number of equivalents of potassium ion present in the volume V between $a - b$ and $c - d$ before the passage of the current is VC_K, while the number remaining after the current has passed and the boundary has moved from $a - b$ to $c - d$ is VC_K'.   Moreover T_K equivalents have left this volume through the plane $c - d$, while T_K' equivalents have entered through the plane $a - b$, T_K' denoting the transference number of the potassium ion constituent in the solution of pure KCl at the concentration C_K' and T_K that in the mixture.   Thus the net gain in the number of equivalents, due to migration, is $T_K' - T_K$ so that

$$VC_K' = VC_K + T_K' - T_K \qquad (15)$$

In the case of the hydrogen ion, the number of equivalents initially present in the volume V is VC_H, while the number finally present is zero.   Since no hydrogen enters through the plane $a - b$, but T_H equivalents pass out through the plane $c - d$, we have the relation

$$T_H = VC_H \qquad (16)$$

Elmination of V between equations 15 and 16 gives the expression

$$C_K' = C_K + \frac{T_K - T_K'}{T_H} C_H \qquad (17)$$

by means of which the value of C_K' may be computed if the quantities on the right-hand side are known. According to equation 16, T_H may be computed directly from the observed displacement of the boundary A. T_K is obtained from the relation

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

after the chloride ion transference number, T_{Cl}, of the same mixture of electrolytes has been determined in a separate experiment from anion boundaries using, for instance, an appropriate mixture of potassium iodate and iodic acid as indicator. C_H and C_K are known and T_K' may be obtained from independent measurements on potassium chloride, such as those given in table 6. The data

TABLE 9

Concentration changes on electrolysis of KCl–HCl mixtures

CONCENTRATIONS		TRANSFERENCE NUMBERS			COMPUTED CONCENTRATION. OF INTERMEDIATE SOLUTION	
		Leading solution		Intermediate solution	From leading boundary	From following boundary
C_K	C_H	T_K	T_H	T'_K	C_K'	C_K'
0.025	0.075	0.0503	0.7456	0.4900	0.06923	0.06935
0.050	0.050	0.1242	0.6198	0.4899	0.07950	0.07961
0.075	0.025	0.2477	0.4109	0.4898	0.08973	0.08984

necessary for the computation of C_K' by means of equation 17, together with the values thus computed for the various mixtures (column 6), are given under appropriate headings in table 9.

A very interesting check on the value computed for the concentration, C_K', of the intermediate solution of pure potassium chloride may be obtained by means of data on the motion of the following boundary B. This check, given in columns 6 and 7 of table 9, is almost exact and furnishes a verification of the theory that has been outlined for the leading boundary A. The boundary B lies between the indicating electrolyte, cadmium chloride in this instance, and the solution of potassium chloride which has been progressively separated from the original mixture in the tube. In using equation 4, which is applicable to this boundary, the normal procedure may be reversed, and the con-

centration may be considered the unknown instead of the trans-
ference number, so that

$$C = \frac{Tit}{vF}$$

Thus, since the displacement per coulomb, $\frac{v}{it}$, of the boundary B
has been observed and values of T_K for potassium chloride are
known from independent measurements such as those given in
table 6, values of C_K' may be computed for different compositions
of the leading solution. In general, the transference number
varies with the concentration, and a series of successive approxi-
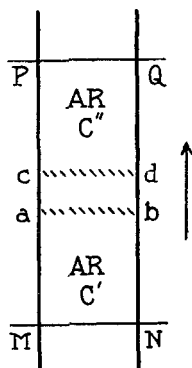
Fig. 19

mations will be necessary in the computation of C_K' by either of
the two methods outlined here, though in the present instance,
in which the transference numbers of potassium chloride are
very nearly constant, no approximations are necessary.

VIII. THE MOTION OF THE BOUNDARY BETWEEN TWO SOLUTIONS OF THE SAME SALT

It has already been mentioned (section IV) that if a boundary
is formed between two solutions of the same salt it will, in general,
move when a current is passed. The subject has been discussed
theoretically by Kohlrausch (6), Miller (17), and von Laue
(19), and has been studied experimentally by Smith (34).

The boundary between two concentrations $C' > C''$ of the electrolyte AR will be a more or less broad diffusion band. If conditions are chosen so that it moves at a uniform speed with the passage of a constant current, the difference between the transference numbers of one of the ion constituents in the two solutions may be computed from the observed motion of the boundary. Let figure 19 represent the tube of uniform cross section in which the boundary displacement occurs. If, on the passage of one faraday of electricity in the direction indicated, the boundary moves from $a - b$ to $c - d$ through a volume V, the product $(C' - C'')V$ must be equal to the difference between the number of equivalents, T'_A, of positive ion constituent passing across a plane $M - N$ in the concentrated solution, and the number T''_A passing across the plane $P - Q$. That is,

$$(C' - C'')V = T'_A - T''_A \tag{18}$$

For a different quantity of electricity, f, the boundary displacement, v, will be $v = Vf/F$ so that

$$v = \frac{T'_A - T''_A}{C' - C''} \cdot \frac{f}{F} \tag{19}$$

The actual motion of the boundaries observed by Smith were in the predicted direction and of the right order of magnitude. This method of obtaining differences of transference numbers with concentration has not yet reached the accuracy of the direct determinations, but is very promising and should receive further study.

IX. THE THEORY OF THE EFFECT OF DIFFUSION AND OF THE "THICKNESS" OF THE BOUNDARY

It will be recalled that in the derivation of the equation

$$T = \frac{vCF}{it} \tag{4}$$

given in section II it was assumed that the diffusion that takes place at the boundary has no influence on its motion. It is the main purpose of section IX to show that this equation still follows

when allowance is made for such diffusion. To anticipate the results of the analysis, diffusion influences the thickness of the boundary but not its rate of motion. The treatment given is based on Weber (7), though his results are generalized by the elimination of unnecessary assumptions.

At a boundary of the type LiCl/KCl there will be gradients both of electric and of thermodynamic potential whether a current is flowing or not. The gradients of thermodynamic potential arise from the differences in concentration in successive layers of the boundary. The thermodynamic potential is, of course, the source of energy tending to bring about diffusion against the opposition of the viscosity of the medium.

The thermodynamic potential of an ion constituent, i, is defined by

$$\mu_i = \mu_i^0 + RT \ln a_i \tag{20}$$

in which a_i is the ion activity and μ_i^0 is a function of the temperature and of the solvent but is independent of the concentration of the ion constituent.

For simplicity it will be assumed that the process here considered takes place in a tube of unit cross-section parallel to the x-axis of coördinates. Then if there is a gradient of concentration in the x-direction, there will be a force per gram-mole of ion constituent equal to $\dfrac{\partial \mu_i}{\partial x}$ tending to produce diffusion. If, in addition, there is a gradient of electric potential, there will be another force per mole equal (for univalent ions to which this treatment will be limited) to $\pm F \dfrac{\partial E}{\partial x}$; the sign of this term will be that of the charge on the ion. Thus the force per mole due to the concentration and the electric potential gradients will be

$$\frac{\partial \mu_i}{\partial x} \pm F \frac{\partial E}{\partial x} \tag{21}$$

As a result of the presence of this gradient the ion constituent will acquire the velocity

$$u_i = -\frac{U_i}{F}\left(\frac{\partial \mu_i}{\partial x} \pm F \frac{\partial E}{\partial x}\right) \tag{22}$$

in which U_i is the ion mobility, *i.e.*, the velocity of an ion constituent per volt per centimeter. The flux $C_i u_i$ of the ion constituent, i, will thus be

$$C_i u_i = -\frac{C_i U_i}{F}\left(\frac{\partial \mu_i}{\partial x} \pm F\frac{\partial E}{\partial x}\right) \tag{23}$$

in which C_i is the concentration of that ion constituent. Since the current density, I, consists of the summation of the flux $C_i u_i$ of each ion multiplied by its charge which is $\pm F$ per gram equivalent we have

$$I = \sum_i \pm FC_i u_i = \mp \sum_i C_i U_i\left(\frac{\partial \mu_i}{\partial x} \pm F\frac{\partial E}{\partial x}\right) \tag{24}$$

With the aid of the equation of continuity[2]

$$-\frac{\partial(C_i u_i)}{\partial x} = \frac{\partial C_i}{\partial t} \tag{25}$$

---

[2] The flux of the constituent, i, at the point x in Δt seconds is

$$C_i u_i \cdot \Delta t$$

and at $x + \Delta x$ it is

$$\left[C_i u_i + \frac{\partial}{\partial x}(C_i u_i) \cdot \Delta x\right]\Delta t$$

The accumulation of this constituent in the region between x and $x + \Delta x$ in Δt seconds is the difference between these two expressions, *i.e.*,

$$-\frac{\partial}{\partial x}(C_i u_i)\Delta x \cdot \Delta t$$

This quantity, divided by the volume (Δx in this case since the tube is of unit cross-section) in which the change occurs is the increment of concentration, ΔC_i, so that

$$\Delta C_i = -\frac{\partial}{\partial x}(C_i u_i)\cdot \Delta t$$

or in the limit

$$\frac{\partial C_i}{\partial t} = -\frac{\partial}{\partial x}(C_i u_i)$$

which is the so-called equation of continuity and is merely a mathematical formulation of the law of conservation of mass.

we obtain

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x}\left[\frac{C_i U_i}{F}\left(\frac{\partial \mu_i}{\partial x} \pm F\frac{\partial E}{\partial x}\right)\right] \tag{26}$$

The general equations 24 and 26, of which use will be made in the following analysis, are also fundamental in the theory of the diffusion of electrolytes and in the theory of the electromotive force of cells with liquid junctions.

We will once more consider a boundary between the electrolytes AR and BR, but instead of ignoring possible mixtures of these two, the boundary is considered to be of finite thickness, the two salt concentrations varying continuously from the constant values C_A' and 0 at "infinity" on one side of the boundary to 0 and C_B'' at "infinity" on the other side. However, as has been shown by experiment, any distribution of the several ion constituents in the boundary, when a steady state is attained, moves with a constant velocity $\mathbf{v}$ when a constant current is passed. The concentrations must therefore be functions of x and t of the form

$$C_i = f_i(x - \mathbf{v}t) \tag{27}$$

Since

$$\frac{\partial C_i}{\partial x} = f_i'(x - \mathbf{v}t) \tag{28}$$

and

$$\frac{\partial C_i}{\partial t} = -\mathbf{v}f_i'(x - \mathbf{v}t) \tag{29}$$

then

$$\frac{\partial C_i}{\partial t} = -\mathbf{v}\frac{\partial C_i}{\partial x} \tag{30}$$

Substituting in equation 26

$$\mathbf{v}\frac{dC_i}{dx} + \frac{d}{dx}\left[\frac{C_i U_i}{F}\left(\frac{d\mu_i}{dx} \pm F\frac{dE}{dx}\right)\right] = 0 \tag{31}$$

in which the use of the total derivative is permissible if our coördinate system moves with the velocity $\mathbf{v}$ in the x direction, as implied in equation 27.

Integrating equation 31 once

$$\mathbf{v}C_i + \frac{C_i U_i}{F}\left(\frac{d\mu_i}{dx} \pm F\frac{dE}{dx}\right) = K_i \qquad (32)$$

in which K_i is a constant of integration. For the cations A and B and the common anion R

$$\mathbf{v}C_A + \frac{C_A U_A}{F}\left(\frac{d\mu_A}{dx} + F\frac{dE}{dx}\right) = K_A \qquad (33a)$$

$$\mathbf{v}C_B + \frac{C_B U_B}{F}\left(\frac{d\mu_B}{dx} + F\frac{dE}{dx}\right) = K_B \qquad (33b)$$

$$\mathbf{v}C_R + \frac{C_R U_R}{F}\left(\frac{d\mu_R}{dx} - F\frac{dE}{dx}\right) = K_R \qquad (33c)$$

From equation 24 the current density under these conditions is equal to

$$I = -C_A U_A\left(\frac{d\mu_A}{dx} + F\frac{dE}{dx}\right) - C_B U_B\left(\frac{d\mu_B}{dx} + F\frac{dE}{dx}\right) + C_R U_R\left(\frac{d\mu_R}{dx} - F\frac{dE}{dx}\right) \qquad (34)$$

Including the condition for electric neutrality

$$C_A + C_B = C_R \qquad (35)$$

it will be seen from equations 33 and 34 that

$$I = (K_R - K_A - K_B)\,F \qquad (36)$$

Now in any mixture of the electrolytes AR and BR the thermodynamic potentials μ_A, μ_B, and μ_R and the mobilities U_A, U_B, and U_R are single valued functions of the concentrations C_A and C_B. To determine the constants K_A, K_B, K_R, and $\mathbf{v}$, three more conditions are necessary. We have, however, four conditions when we assume that for $x = +\infty$ and $x = -\infty$ the concentrations C_A and C_B are known. These values cannot, therefore, be independent; that is to say, there must be a relation connecting them. We have already assumed that on one side of the bound-

ary at "infinity" we have only AR and on the other only BR. Therefore

$$\text{for } x = -\infty \qquad C_A = 0 \qquad C_B = C''_B \qquad (37a)$$

$$\text{for } x = +\infty \qquad C_A = C'_A \qquad C_B = 0 \qquad (37b)$$

in which C'_A and C''_B are the limiting values of the respective concentrations. Since equations 33a and 33b must hold throughout the range of the variables C_A and C_B, including $C_A = 0$ and $C_B = 0$,

$$K_A = K_B = 0 \qquad (38a)$$

and thus from equation 36

$$K_R = I/F \qquad (38b)$$

Since at $x = +\infty$, $C_A = C'_A = C'_R$ and $\dfrac{d\mu_A}{dx} = \dfrac{d\mu_R}{dx} = 0$, and the ion mobilities have the values U'_A and U'_R corresponding to the concentration C'_A, equations 33a and 33c become

$$vC'_A + \frac{C'_A U'_A}{F}\left(\frac{dE}{dx}\right)_{x=\infty} = 0 \qquad (39a)$$

$$vC'_A - \frac{C'_A U'_R}{F}\left(\frac{dE}{dx}\right)_{x=\infty} = \frac{I}{F} \qquad (39b)$$

From which, by eliminating $\dfrac{dE}{dx}$, we obtain

$$\frac{U'_A}{U'_A + U'_R} = \frac{vFC'_A}{I} \qquad (40)$$

Similarly from equations 33b, 33c, and 37a the relation

$$\frac{U''_B}{U''_B + U''_R} = \frac{vFC''_B}{I} \qquad (41)$$

may be obtained. From equations 40 and 41 we have

$$\frac{U'_A}{U'_A + U'_R} : \frac{U''_B}{U''_B + U''_R} = C'_A : C''_B \qquad (42)$$

This is the additional relation, mentioned above, between the limiting concentrations. Since the transference number

$$T_A = \frac{U'_A}{U'_A + U'_R} \tag{43a}$$

and

$$T_B = \frac{U''_B}{U''_B + U''_R} \tag{43b}$$

equation 42 may also be put in the form

$$\frac{T_A}{C'_A} = \frac{T_B}{C''_B} \tag{10}$$

which is identical with equation 10 derived in another manner in section IV.

The current density $I = i/A$, in which i is the total current and A the area of the boundary. Also $v = x/t$, x being the distance moved through by the boundary and t the time. With these substitutions equation 40 becomes

$$T_A = \frac{U'_A}{U'_A + U'_R} = \frac{xAFC'_A}{it} = \frac{vC'_A F}{it} \tag{4}$$

in which T_A is the transference number and v is the volume the boundary sweeps through. *Thus the fundamental equation for obtaining transference numbers from moving boundary measurements, and the equation relating the concentrations of the leading and indicator solutions, have been derived, including a consideration of the forces tending to produce diffusion at a boundary.*

With the aid of simplifying assumptions, further information may be obtained concerning the boundary region, as follows. Using equations 20 and 38a, equations 33a and 33b may be put in the form

$$v + \frac{U_A}{F}\left(RT\,\frac{d \ln a_A}{dx} + F\,\frac{dE}{dx}\right) = 0 \tag{44a}$$

$$v + \frac{U_B}{F}\left(RT\,\frac{d \ln a_B}{dx} + F\,\frac{dE}{dx}\right) = 0 \tag{44b}$$

Eliminating $\dfrac{\mathrm{d}E}{\mathrm{d}x}$ from these equations

$$\frac{\mathrm{d}}{\mathrm{d}x}\,(\ln\,a_\mathrm{A}/a_\mathrm{B}) = \frac{F\,\mathbf{v}}{R\mathbf{T}} \cdot \frac{U_\mathrm{A} - U_\mathrm{B}}{U_\mathrm{A}U_\mathrm{B}} \tag{45}$$

If the mobilities U_A and U_B are *now* assumed to be independent of the concentration, this equation may be integrated to yield a relation for the activity ratio $a_\mathrm{A}/a_\mathrm{B}$ as a function of x and t, which is

$$\ln\frac{a_\mathrm{A}}{a_\mathrm{B}} = \frac{F\mathbf{v}}{R\mathbf{T}} \cdot \frac{U_\mathrm{A} - U_\mathrm{B}}{U_\mathrm{A}U_\mathrm{B}} \cdot (x - K) \tag{46}$$

If the origin of coördinates is taken at the plane in the boundary where the ratio $a_\mathrm{A}/a_\mathrm{B}$ is unity, the constant of integration, K, is zero and equation 46 takes the simpler form

$$\ln\frac{a_\mathrm{A}}{a_\mathrm{B}} = \frac{F\mathbf{v}}{R\mathbf{T}} \cdot \frac{U_\mathrm{A} - U_\mathrm{B}}{U_\mathrm{A}U_\mathrm{B}}\,x \tag{47}$$

which becomes

$$\ln\frac{C_\mathrm{A}}{C_\mathrm{B}} = \frac{F\mathbf{v}}{R\mathbf{T}} \cdot \frac{U_\mathrm{A} - U_\mathrm{B}}{U_\mathrm{A}U_\mathrm{B}}\,x \tag{48}$$

if the activity coefficient ratio is assumed to be unity. The conditions given in equations 37a and 37b require the ratio $C_\mathrm{A}/C_\mathrm{B}$ to become infinite at $x = +\infty$ and zero at $x = -\infty$. If $\mathbf{v}$ is positive this can only be true when $U_\mathrm{A} > U_\mathrm{B}$. That is to say, the following or indicator ion constituent must have the lower mobility if the boundary is to progress as a "steady state." This is the explanation of the fading of a visible boundary on reversal of the current.

The "thickness" of the boundary may be defined for purposes of comparison as follows: From

$$x = -\frac{2\,R\mathbf{T}}{F\mathbf{v}}\frac{U_\mathrm{A}U_\mathrm{B}}{U_\mathrm{A} - U_\mathrm{B}}$$

to

$$x = + \frac{2\,RT}{Fv} \frac{U_A U_B}{U_A - U_B}$$

the value of C_A/C_B varies from e^2 to $1/e^2$ (e is the base of natural logarithms) and includes most of the region of concentration change. Thus we may define the thickness, A, as

$$A = \frac{4\,RT}{Fv} \frac{U_A U_B}{U_A - U_B} \tag{49}$$

The thickness thus varies inversely as the boundary velocity and is thus inversely proportional to the current. Also, the thick-
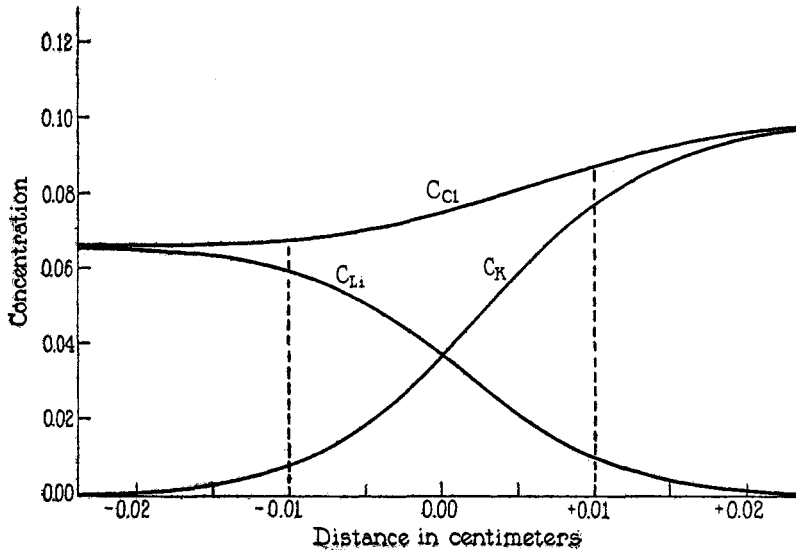

FIG. 20. COMPUTED DISTRIBUTION OF CONCENTRATION IN A TYPICAL MOVING BOUNDARY

ness decreases with an increase of the difference between the mobilities of the leading and indicator ions. This is in agreement with the observation that a boundary is apparently made thinner, *i.e.*, "sharper," by increasing the current density and by increasing the difference of the mobilities of the leading and indicator ions. The visibility also depends upon the difference of refractive indices of the two solutions; thus, a LiCl/KCl

boundary is less visible than a KIO$_3$/KCl boundary although, according to the theory just developed, the concentration distribution in the two cases is about the same.

The computation of the actual distribution of concentration in the boundary presents some difficulty even with the simplifying assumptions already made. However, figure 20 shows very nearly the distribution for a boundary between lithium chloride and potassium chloride solutions. The concentration of the leading solution is assumed to be 0.1 N and the boundary velocity 1/300 centimeter per second. Moreover, in order to evaluate certain integrals it was convenient to take $U_K = U_{Cl} = 2U_{Li}$, which is very nearly the case. The numerical value assigned to the ion mobility U_K was 64/F. The dotted lines indicate the thickness of the boundary as defined by equation 49, which in this instance has a value of 0.02 centimeter. The thickness is considerably greater than that of such boundaries as CdCl$_2$/KCl and much greater than that of a boundary involving a strong acid, as for instance, the combination CdCl$_2$/HCl.

X. SUMMARY AND CONCLUSIONS

The study of solutions of electrolytes has suffered from a lack of data on transference numbers of adequate precision and of sufficient concentration range. This review describes the attempt that has been made, over a number of years, to fill this gap in the available data. An account is given of the determination of transference numbers of a high order of accuracy by the moving boundary method. This includes an outline of the theory of the method, the apparatus, and the most recent procedure. Results are also given of the measurements for a number of electrolytes at a series of dilutions. Additional results will be published in the near future.

These results, together with conductance measurements, have been found to be in excellent accord with the Debye-Hückel-Onsager theory. They have also been found useful, and will be more so in the future, in the study of the thermodynamic properties of solutions.

XI. REFERENCES

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