

THE APPLICATION OF THE MOVING BOUNDARY METHOD OF
DETERMINING TRANSFERENCE NUMBERS TO DILUTE AQUEOUS
SOLUTIONS OF AMMONIUM NITRATE AT 25°C.

by

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A thesis presented to the
Faculty of Graduate Studies and Research
in partial fulfillment of the
requirements for the degree of
Master of Science

University of Manitoba

April, 1954



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ABSTRACT

The moving boundary method of determining transference numbers of electrolytic solutions was applied to dilute aqueous solutions of ammonium nitrate at 25° C. in order to obtain accurate data for the interpretation of the conductances of these solutions.

To facilitate the determination of the transference numbers by the moving boundary method, a current regulator was designed and constructed. This regulator was capable of maintaining currents of 0.4 to 4 ma. constant to 0.01 per cent during the electrolyses. The potential drop across a calibrated resistor in series with the moving boundary cell was measured with a precision potentiometer, enabling the electrolysis current to be determined to 0.01 per cent.

Rising boundaries with ammonium nitrate solutions and suitable indicator solutions were investigated qualitatively in an air-lock cell, designed and assembled to permit rapid observations. To provide data supplementing the measurements with the sheared boundary cell, an autogenic moving boundary cell was graduated, assembled, and the volume calibrated for quantitative measurements.

Moving boundary measurements with ammonium nitrate solutions in the sheared boundary cell were undertaken using ammonium 3,5-dinitro-

benzoate as the indicator solution. Sharp rising boundaries were obtained. The indicator concentration adjustment range was shown to be extremely critical and was not observed. Rising anion boundaries showing no progression were formed with ammonium iodate as the indicator solution.

Rising cation boundaries of good visibility were obtained with ammonium nitrate and cadmium nitrate as the leading and indicator electrolytes, respectively. Initial measurements in the autogenic cell using cadmium anodes were undertaken. With suitable cadmium anodes, autogenic boundaries showed the most promise for the determination of the transference numbers of dilute aqueous solutions of ammonium nitrate.

ACKNOWLEDGEMENTS

The author wishes to express his sincere thanks to Professor A.N. Campbell for his continued interest and encouragement throughout the investigations described here.

In addition, he wishes to thank Dr. W.J. Biermann, Assistant Professor of Chemistry, for advice in designing and constructing the constant current supply.

The assembling of this thesis in its present form was greatly aided by the many helpful discussions with, and suggestions received from, Dr. G.J. Janz, Professor of Physical Chemistry, Rensselaer Polytechnic Institute, Troy, N.Y., to whom grateful acknowledgement is made.

The author, the recipient of a Bursary and a summer supplement from the National Research Council of Canada, wishes to acknowledge with gratitude this financial assistance which enabled him to carry on his investigations.

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INTRODUCTION

An important property of electrically conducting solutions is the transference number of an ionic constituent of the electrolyte. As defined by Hittorf⁽¹⁶⁾, this is the fraction of the total electrolyzing current carried by that ionic constituent in any given direction. They have been of importance in supporting the interionic attraction theory and find practical application in conductance and electromotive force studies.

The three practical methods which have been used most extensively for determining transference numbers are (1) the Hittorf or analytical method, (2) the electromotive force method, and (3) the moving boundary method. The electromotive force of reversible cells in a high centrifugal field has been used^(56,57) and has recently been re-considered^(42,48), but is experimentally difficult. A procedure based on the analytical and the moving boundary methods has been introduced recently by Brady⁽⁵⁾, but the method lacks the precision of the moving boundary method.

The analytical method was developed by Hittorf⁽¹⁶⁾ in 1853. Although many changes in the design of the apparatus have been made since Hittorf's original work,

the underlying principle remains the same. Concentration changes occur around the electrodes from the differences in the amount of current carried by the cation and anion of electrolyte when a known quantity of electricity is passed through the solution. Transference numbers may be determined from a measure of this concentration change and the total current passed. Accurate transference numbers are difficult to obtain by this method in spite of the apparent simplicity, due to the fact that the change in equivalents per gram of the solvent is small and is obtained by the difference between two large figures. MacInnes and Dole⁽³⁹⁾ clearly indicated these difficulties while showing that the relatively simpler moving boundary method measures the same property of an electrolyte in solution.

The electromotive force of a concentration cell with liquid junction is given by

$$d E = 2 t_1 \frac{RT}{F} d \ln a_1$$

where a_1 is the mean ionic activity of the solution and t_1 is the transference number of the ion with respect to which the electrodes are not reversible, while the expression

$$d E = 2 \frac{RT}{F} d \ln a_1$$

gives the electromotive force of a concentration cell without transference. Transference numbers may then be obtained by a suitable combination of measurements on such cells. This method has two chief drawbacks: (1) the activity coefficient of the salts must be known, and (2) the preparation of concentration cells without transference often present many difficulties particularly in obtaining suitable reversible electrodes.

The theory of the "direct" or moving boundary method has been developed by Kohlrausch⁽²¹⁾, Weber⁽⁵⁸⁾, Masson⁽⁴⁵⁾, and Abegg⁽¹⁾. That the results of the moving boundary method give the actual transference numbers as defined above was first established concisely by Miller⁽⁴⁶⁾ and on this theoretical basis the method has been used.

A complete bibliography of the moving boundary method up to 1939 was given by LeRoy⁽²³⁾. Reviews of the method by MacInnes and Longworth⁽⁴¹⁾ and by Hartley and Moilliet⁽¹⁵⁾ appeared in 1932 and 1933 respectively. A brief treatment will be of interest here.

The first experiments actually designed to observe the migration of ions during electrolysis were those of Lodge⁽³³⁾ in 1886. A gelatin gel impregnated with small amounts of a material which would precipitate or change

color on contact with the ion considered separated the anode and cathode compartment of a cell. Whetham^(59,60,61) followed this work with a series of papers in which he improved on the method, since Lodge's work suffered from a nonuniform potential drop across the cell, and the gelatin gradually exuded from the tube in the direction opposite to that of the current due to electro-osmosis and influenced the motion of the ions. To overcome this difficulty, he eliminated the use of gelatin and employed two electrolytes so chosen that they contained a common ion and one coloured ion. Masson⁽⁴⁵⁾ employed a two indicator scheme in which the electrolyte whose cation and anion transference numbers were to be measured was placed in gelatin between two coloured indicators. Each indicator electrolyte had one ion in common with the electrolyte to be measured. Steele⁽⁵⁵⁾ greatly extended the usefulness of the method by placing a light source behind the measuring tube and observing the discontinuity in the light at the boundary due to the difference in the refractive indices as previously noted by Lenz⁽²²⁾ and Bein⁽³⁾. Denison and Steele⁽¹⁰⁾ avoided the use of gelatin entirely by forming the initial boundary by means of parchment paper. However, it was largely due to the work of MacInnes and Smith^(43,52,53) and numerous co-workers⁽⁴¹⁾

and of Gordon and co-workers^(2,24) that the method has been brought to its present state of high precision.

The only determination of the transference number of ammonium nitrate was reported indirectly by MacInnes and Cowperthwaite⁽³⁵⁾. No details were given except that the moving boundary method was used and that the complete results would be reported at a later date. The single result was 0.5130 for the cation transference number of 0.1 N ammonium nitrate at 25°C. A study of the moving boundary method of determining the transference numbers of electrolytes and the possibility of its application to fairly concentrated solutions of silver nitrate and ammonium nitrate was undertaken in this Laboratory by Rea⁽⁴⁹⁾.

The present thesis presents the results of further studies on the moving boundary method and its application to dilute aqueous solution of ammonium nitrate at 25°C.

I. THEORETICAL CONSIDERATIONS

1. The Fundamental Equation

The elementary theory leading to the fundamental equation connecting the transference number with the quantities measured during a determination was elucidated concisely by Miller⁽⁴⁶⁾ and by Lewis⁽²⁵⁾. A section representing a portion of the tube is shown in Figure 1 in which there are two solutions of electrolytes, AR and BR, with a common (positive or negative) ion constituent R, between which there is the boundary a-b. If the constituents A and B have been properly chosen this boundary will move when current is passed through the tube to another position c-d; all of the ion-constituent A will be swept out of the region between a-b and c-d whether A is or is not present as free ions. Thus, the solution of electrolyte AR in the region between the two positions of the boundary is effectively replaced by another solution containing BR. After the passage of one faraday of current, F, the solution AR retains its original composition, C_{AR} equivalents per liter so that C_{AR} equivalents of A must have passed through any fixed plane M-N in the unchanged portion of the electrolyte solution. V is the volume swept out by the boundary during the passage of the faraday.

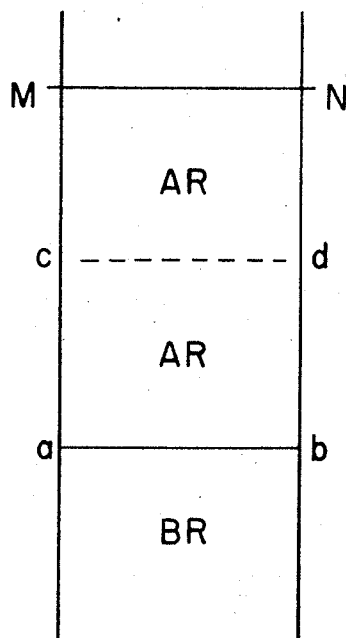


FIG. I. SECTION OF A MOVING BOUNDARY

Then the transference number of the ion-constituent A is given by

$$T_A = \frac{v C_{AR}}{F}$$

For f coulombs of electricity passed through the tube the boundary will sweep out a volume, v , related to V by

$$v/V = f/F$$

so that

$$T_A = \frac{v C_{AR} F}{f}$$

If the current, i , is constant, then $f = it$, where t is the time of current flow. Then,

$$T_A = \frac{v C_{AR} F}{it}$$

This fundamental expression connecting the transference number with the motion of the boundary is subject to corrections due to volume changes occurring within the apparatus during the electrolysis and to residual conductance of the solvent.

2. The Volume Correction

Miller⁽⁴⁶⁾ first pointed out that with the proper volume corrections transference numbers from the moving

boundary method became equal to those obtained by the Hittorf method. Early workers had noticed the volume changes but had regarded them as negligible. With increased precision in measurement, however, these must be taken into account. The magnitude of this correction is relatively unimportant in dilute solutions but becomes a large correction in concentrated solutions. A more complete treatment of the corrections was given by Lewis⁽²⁵⁾. The need for this correction arises from the fact that, on the passage of a current through an electrolytic solution, volume changes result from electrode reactions and ion migration. In the Hittorf method these volume changes are taken into account as one measures the weight changes in concentration around the electrodes per weight of solvent. However, in the moving boundary method, one measures the movement of the boundary with respect to graduations marked on the tube. If volume changes occur due to electrode reactions and ion migration the solvent is moved accordingly and these changes must be taken into account if the movement of the boundary with respect to a fixed amount of solvent is to be treated in a quantitative manner.

Such quantitative treatment is facilitated by considering the volume changes occurring in one closed electrode chamber only, the other chamber being permitted

to be open in such a manner that volume changes at this electrode will not affect the position of the solvent molecules. Consider as an example a boundary between potassium chloride and barium chloride rising from the silver anode in the closed chamber. The initial conditions may be represented diagrammatically as shown in Figure 2a. x denotes the position of an "average" water particle at some point which the boundary does not pass, or it may be considered as a plane in the tube above which the mass of water remains fixed throughout the determination.

With the passage of one faraday the boundary moves to $c-d$ and the "average" water particle moves from e to e' (Figure 2b). This latter movement is caused by the electrode reactions and by the displacement of potassium chloride by barium chloride. Volume changes which displace the reference water molecule will affect the boundary similarly since the solution between the two is uniform and homogeneous. The passage of one faraday causes (1) one equivalent of silver to be oxidized at the electrode, (2) one equivalent of silver chloride to be formed at the electrode, (3) one equivalent of chloride ion to be consumed in the formation of the silver chloride, (4) TK equivalents of potassium ion to pass out of the region between x and the electrode,

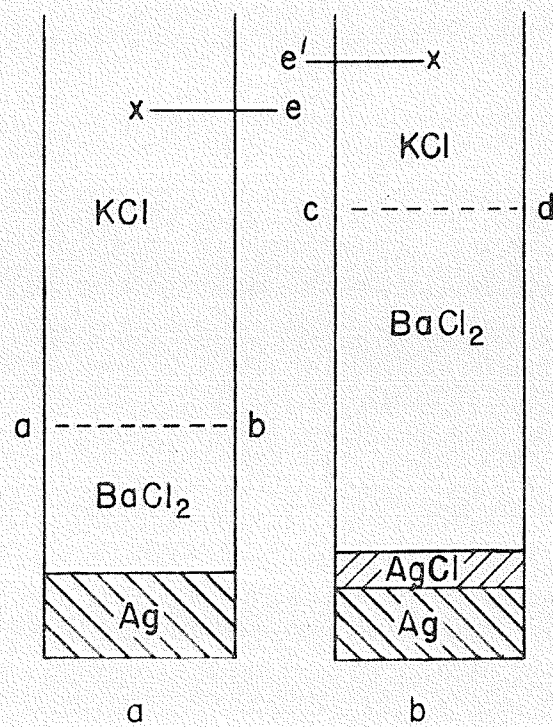


FIG. 2. VOLUME CORRECTION

(5) T_{Cl} equivalents of chloride ion to move into this region, and (6) one equivalent of chloride ion to move downward across the boundary. The volume changes associated with these processes are (1) $-V_{Ag}$, (2) $+V_{AgCl}$, (3) $-V_{Cl}^{BaCl_2}$, (4) $-T_K \bar{V}_K^{KCl}$, (5) $+T_{Cl} \bar{V}_{Cl}^{KCl}$, and (6) $+\bar{V}_{Cl}^{BaCl_2} - \bar{V}_{Cl}^{KCl}$, where \bar{V}_i^j is the partial molal volume of one equivalent of ion i in solution j . The net volume change is

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

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

and

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

this reduces to

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

The observed volume through which the boundary moves is thus greater, by the amount ΔV , than the volume V which was taken with respect to the tube. The corrected transference number is therefore

$$\begin{aligned} T &= CV_{corr.} = C(V_{obs.} - \Delta V) \\ &= T_{obs.} - C \Delta V. \end{aligned}$$

It is seen from the above that the volume correction is proportional to the concentration so that in dilute solutions the correction is small. At higher concentrations, this correction is the main factor which limits the accuracy of the results since the densities of solids vary somewhat depending upon their physical state. Moreover, diffusion effects around the electrodes make an unambiguous evaluation of the partial molal volume difficult⁽²⁷⁾.

The validity of the corrections made as shown has been demonstrated by Smith⁽⁵¹⁾ who made use of an electrolysis apparatus one electrode chamber of which could be disconnected and used as a pycnometer. The electrode chamber contained a silver electrode, covered with silver chloride and potassium chloride solution. On passing the current the chloride was reduced to silver and the potassium chloride increased in concentration. The increase in weight of the electrode portion was equal to that computed within the very small experimental error. These corrections were further supported by MacInnes and Longworth⁽⁴¹⁾ who measured the transference numbers of 0.5 N and 1.0 N potassium chloride using different electrodes which gave rise to different volume corrections. The uncorrected transference numbers observed differed from each other by 2 per cent but when the volume correction was applied, the results differed by

less than 0.1 per cent. The probable errors arising from uncertainties in the densities and partial molal volumes in the computation of the volume corrections must therefore be small since this was an extreme case.

3. The Solvent Correction

The necessity for a correction to transference numbers due to the conductance of the solvent was first recognized by Longworth⁽²⁷⁾. At low electrolyte concentrations, the impurities in the solvent act as a shunt in parallel with the electrolyte solution. With the precision attained by the moving boundary method such a correction is imperative. Moreover, a similar solvent correction should be applied to the results of transference measurements made by all of the available methods where the precision warrants.

The magnitude of the correction may be determined from the conductivity of the solution and that of the solvent, as follows⁽²⁷⁾. The total current, I , is equal to the sum of the current carried by the cation, i_+ , the anion, i_- , and the impurities in the solvent, i_i . Thus,

$$I = i_+ + i_- + i_i.$$

The current carried by the cation is equal to C_+FAV_+ in which C_+ is the equivalents per ml. of the positive ion, V_+ is the velocity of the positive ion, A is the cross sectional area of the tube, and F is the faraday. Similarly,

$$i_- = C_-FAV_-$$

and

$$i_i = FA \sum C_i V_i$$

where C_i and V_i refer to the concentration and velocity of the i 'th impurity. Therefore, for a uni-univalent electrolyte, since

$$C_+ = C_- = C$$

where C is the concentration of the electrolyte in question,

$$I = CFA(V_+ + V_-) + FA \sum C_i V_i.$$

Multiplication of this equation by

$$T_+ = \frac{V_+}{V_+ + V_-}$$

gives

$$T_+ = \frac{CFAV_+}{I} + \frac{FA}{I} T_+ \sum C_i V_i.$$

Since the mobility, U_i , of an ion constituent is given by

$$V_i = EU_i$$

where E is the field strength, this equation may be written as

$$T_+ = \frac{CFAV_+}{I} + \frac{FEA}{I} T_+ \sum C_i U_i.$$

The ratio I/EA is the specific conductance of the solution, K_{solution} , and $F \sum C_i U_i$ is the specific conductance of the solvent, K_{solvent} , which may be measured independently. Assuming that the introduction of the solute into the solution does not alter the concentration and mobilities of the impurities in the solvent, the equation becomes

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

A similar expression may be obtained for T_- .

4. The Kohlrausch Ratio

Kohlrausch⁽²¹⁾ has pointed out that for a steady state with a two-salt boundary, the relation

$$\frac{C_i^*}{C} = \frac{T_i}{T}$$

must hold where C_i^* and C are the concentrations of the indicator ion and the leading ion, respectively, and T_i

and T are the corresponding transference numbers. This ratio is called the Kohlrausch ratio and the concentration of the indicator ion at a stable boundary has been called the adjusted indicator or Kohlrausch solution.

Since the original relations were proposed by Kohlrausch⁽²¹⁾ and Weber⁽⁵⁸⁾ treating ternary ion systems, extensions to more complex systems have been made by Longworth⁽³¹⁾ and by Dole⁽¹¹⁾.

The relation for the ternary ion system may be obtained by consideration of a stable boundary which has moved from a position near a-b to another position c-d as in Figure 3. This movement of the boundary results in the replacement of the electrolyte AR which originally filled the volume between the two positions of the boundary by the indicator electrolyte BR. The concentration C_B^* of BR between a-b and c-d will in general be different from that concentration C_B^0 when the junction is initially formed. The motion of the concentration boundary of these solutions, C_B^*/C_B^0 will be very slow in comparison with the motion of the boundary AR/BR and may be neglected. Under the stable condition, when an additional faraday of current is passed, the boundary at c-d will move to e-f, sweeping through a volume V . The transference number, T , of the leading ion

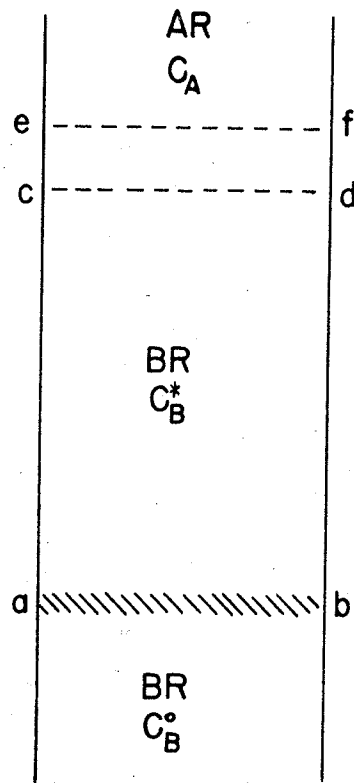


FIG. 3. ADJUSTMENT OF THE INDICATOR SOLUTION

constituent has been shown to be

$$T = C_A V.$$

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

$$T_i = C_B^* V.$$

Since the volume V must be the same, the important relation is obtained by taking the ratio,

$$\frac{C_B^*}{C_A} = \frac{T_i}{T}.$$

No special assumptions as to the ionization of the leading and indicator solutions have been made. The indicator ion constituent at the boundary must move at the same rate as the leading ion constituent in order that the boundary remain stable. For a given concentration of the leading solution this can occur only at one concentration of the indicator solution, necessitating a change of concentration of the indicator solution during the stabilization of the boundary. As Kohlrausch⁽²¹⁾ has pointed out, it is impossible for concentration changes to occur spontaneously in the interior of a homogeneous solution as a result of electrolysis alone. Hence, regions of changed concentration can develop

only at the boundary and only by the indicator solution⁽¹⁵⁾. The velocity of a stable boundary has been shown to be independent of the nature of the indicator radical⁽²⁷⁾ and the concentration of the leading solution has been found experimentally to undergo no adjustment⁽¹⁹⁾. The adjustment of the indicator solution takes place automatically within limits largely determined by experimental conditions.

5. Disturbing effects at the Boundary

Hitherto, it has tacitly been assumed that no disturbing influences occur at the boundary. However, in addition to the uniform velocity of all the individual radicals in the direction of the potential gradient, entirely random thermal motion exists⁽¹⁵⁾. The latter causes interdiffusion of the two electrolytes. The passage of the current through the measuring tube of a transference cell develops a temperature gradient from the leading solution to the indicator solution since the latter must have a higher specific resistance. The resulting flow of heat from the indicator to the leading solution may be accompanied by a tendency of the two solutions to mix. This tendency is greater in rising boundaries where the warmer solution is the lower one.

A second heat effect may arise from any radial temperature gradient arising from a lag in heat dissipation

to the thermostat liquid. The solution in the center of the tube will have the highest temperature and will be, in general, lighter than that along the wall of the tube. This may readily lead to convection currents which will cause enough mixing at a boundary to affect the results. Indeed, with potassium chloride/potassium permanganate rising boundaries, these effects were clearly shown by the upward streaming of the colored indicator⁽³⁸⁾.

In addition to the disturbing effects of convection just discussed, forces of diffusion act at a boundary. Gradients of thermodynamic potential arise from the differences in concentration in successive layers of the boundary and tend to bring about diffusion against the opposition of the viscosity of the medium. However, it has been shown theoretically⁽⁴¹⁾ and verified experimentally⁽³¹⁾ that diffusion influences the thickness of the boundary but not its rate of motion.

6. Restoring Effect

That the boundary remains stable in spite of disturbing effects due to diffusion and convection requires that an appreciable restoring effect be present. The change in potential gradient at the boundary gives rise to this restoring effect. Reference to Figure 4 will

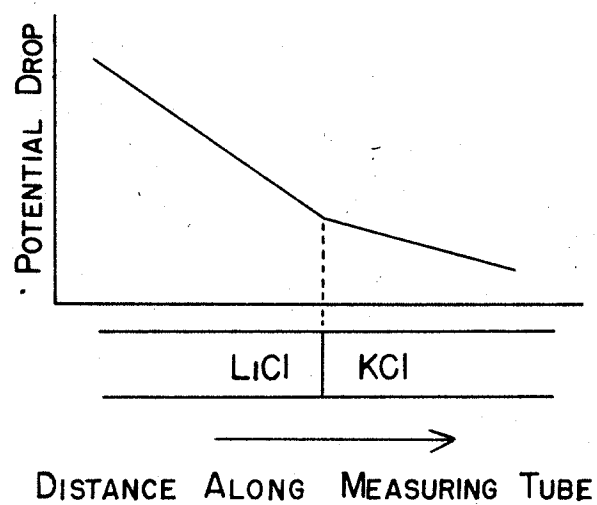


FIG. 4. POTENTIAL DROP IN THE REGION OF
A MOVING BOUNDARY

illustrate this effect in the typical use of a falling boundary between lithium chloride and potassium chloride. 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 must cause a greater potential drop in the lithium chloride solution than in the potassium chloride solution. If some of the relatively fast moving potassium ions diffuse or are carried by convection into the lithium chloride region, the higher potential gradient will return them to the boundary. If lithium ions diffuse into the potassium chloride region they will move more slowly than the potassium ions and will be overtaken by the moving boundary. Miller⁽⁴⁶⁾ predicted that for boundaries of the type acetic acid/sodium acetate, sharp boundaries will occur if the hydrogen ion acts as the indicator in spite of the high mobility of the hydrogen ion. In this case, if the weak acid diffuses forward its ionization is immediately repressed and the diffused acid, ceasing to carry current, would soon be overtaken by the boundary.

The existence and strength of the restoring effect has been strikingly demonstrated by MacInnes and Cowperthwaite⁽³⁶⁾ and by MacInnes and Longworth⁽⁴¹⁾. Diffusion

at the boundary was allowed to occur by stopping the current, or, even more drastic, by actually reversing the direction of the current. On restarting the current, the boundary reformed and became perfectly sharp. Moreover, the diffusion process did not affect the rate of motion of the boundary.

The boundary was observed to move in the direction of the current, and the rate of motion was independent of the current density. The boundary was observed to move in the direction of the current, and the rate of motion was independent of the current density.

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II. EXPERIMENTAL

The apparatus necessary for the practical determination of the transference number of an electrolyte by the moving boundary method consists essentially of (1) a moving boundary cell, (2) suitable electrodes, (3) an apparatus for observing the boundary formed between the indicator solution and the solution under investigation, (4) a constant current source and means of measuring the current, (5) a means of timing the motion of the boundary, and (6) a constant temperature thermostat⁽⁴¹⁾. A discussion of each of these component parts follows in detail.

1. Apparatus

(a) The moving boundary cells

In order to observe the motion of a boundary between two ionic species, some means of forming the boundary initially with a minimum of mixing and diffusion is necessary. Several designs of cells have been used by various investigators in the past. These may be classified generally as (1) sheared boundary cells in which the boundary (rising or falling) is formed mechanically by placing the solutions in contact, and (2) autogenic boundary cells in which the indicator solution is formed by an electrochemical reaction at the electrode. Of the former type, the early cells of

Steele⁽⁵⁵⁾ and of Denison⁽⁹⁾ were unsatisfactory because of the use of a gelatin plug. This was replaced by a parchment closure by Denison and Steele⁽¹⁰⁾ and further improved by MacInnes and Smith^(43,52,53). The first actual shearing mechanism was introduced by MacInnes and Brighton⁽³⁴⁾ with later modifications by MacInnes and associates^(26,27,28,38). A novel apparatus for producing a sheared boundary was developed by Allgood, LeRoy, and Gordon⁽²⁾ in which the essential feature was the use of a four-way stopcock. Simple stopcocks have also found application^(19,54).

Cells producing autogenic boundaries have been designed by Cady and Longworth⁽⁶⁾ and by LeRoy and Gordon⁽²⁴⁾.

Three cells were used in the course of this investigation: (i) a sheared boundary cell, (ii) an air-lock cell, and (iii) an autogenic cell. Each of the cells is discussed in the following.

(i) Sheared boundary cell. The cell used for the greater part of the work described here was already available in this Laboratory⁽⁴⁹⁾. The design of the sheared cell, developed by Allgood, LeRoy, and Gordon⁽²⁾, is shown in Figure 5. With the large hollow stopcock, S, turned 90°

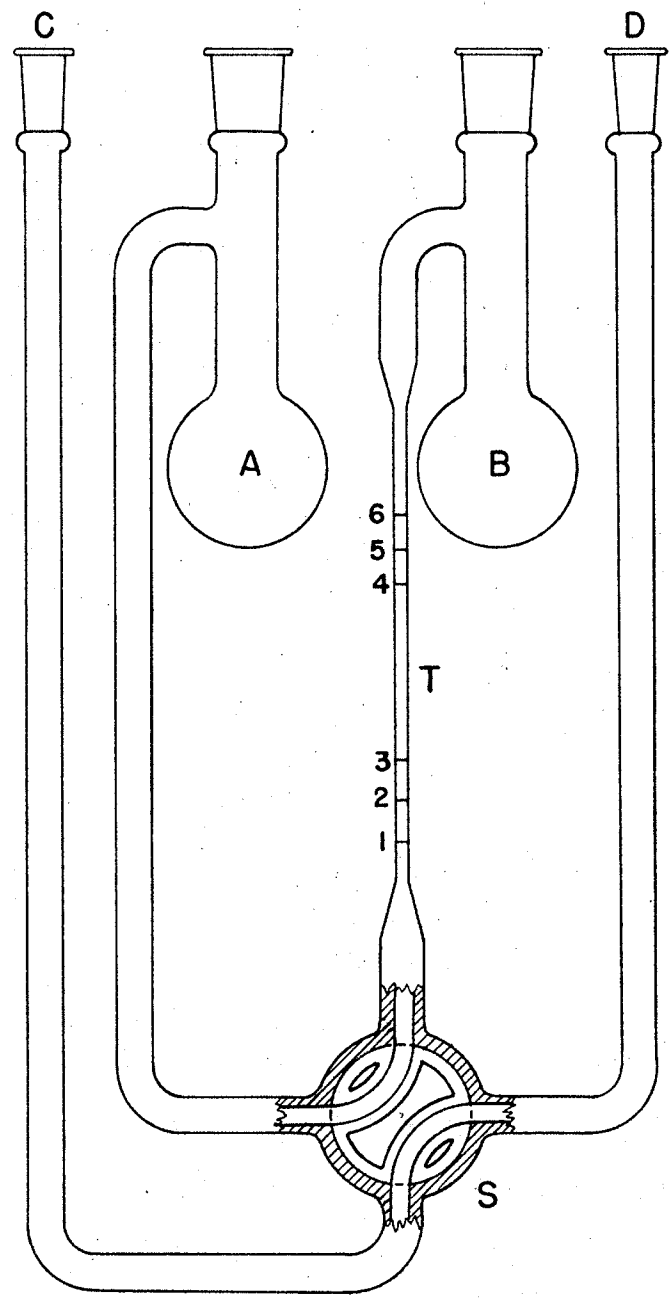


FIG. 5. SHEARED BOUNDARY CELL

counterclockwise from the position indicated in the figure, the leading solution is forced by air pressure into the cell through D and the indicator solution is forced into the cell through C. The anode and cathode (each mounted in a ground glass joint) are placed in B and A. A clockwise rotation of S through 90° forms the junction at the bottom of the graduated tube, T.

The volume calibration used were those determined by Rea⁽⁴⁹⁾ and are given in Table I.

TABLE I
VOLUMES OF THE SHEARED BOUNDARY CELL⁽⁴⁹⁾

Volume Calibrated	Mean Volume (ml)	Volume Calibrated	Mean Volume (ml)	Volume Calibrated	Mean Volume (ml)
6-1	0.8756	5-1	0.8181	4-1	0.7510
6-2	0.8076	5-2	0.7500	4-2	0.6827
6-3	0.7392	5-3	0.6813	4-3	0.6142

(ii) Air-lock cell. The air-lock cell was constructed in the present work for qualitative investigations of the boundaries after the design of Hartley and Donaldson⁽¹⁴⁾. The design as modified is shown in Figure 6. The air-lock method, described below, is much simpler in operation and greatly reduced the time required to make observations of

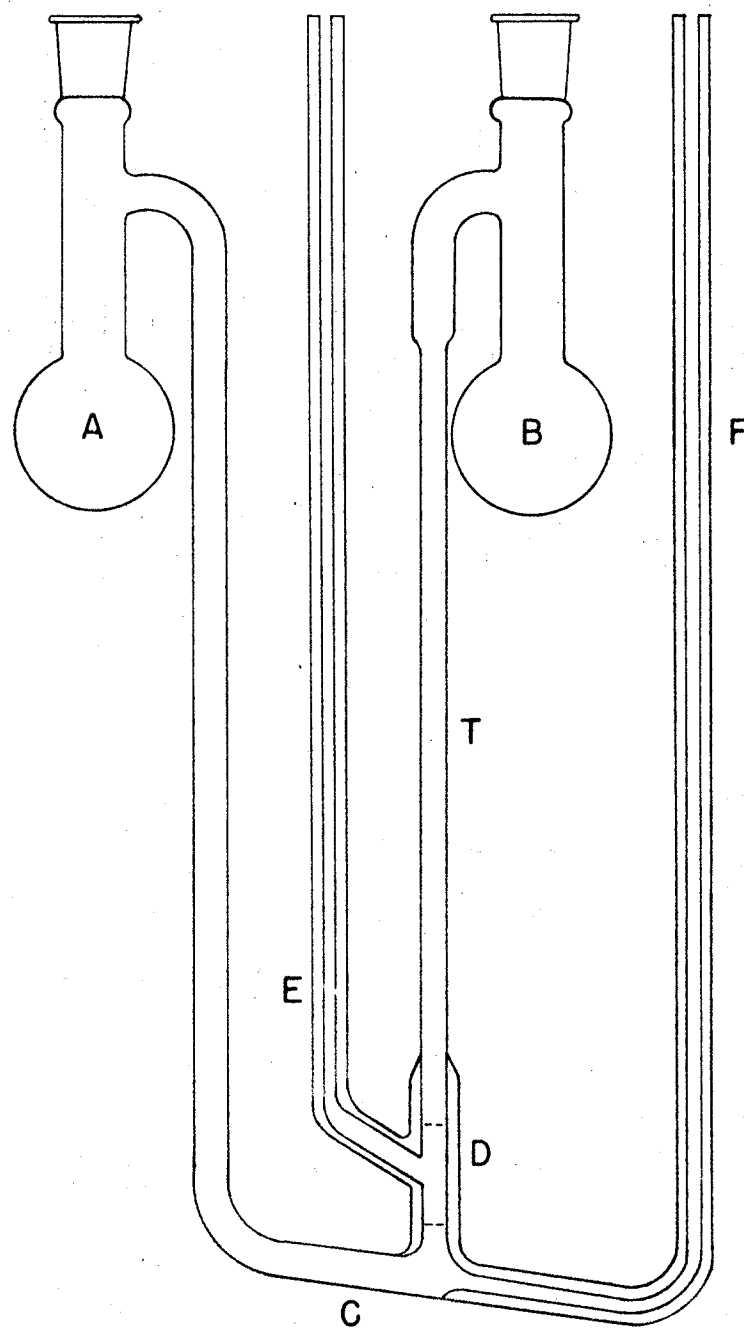


FIG. 6. AIR-LOCK BOUNDARY CELL

the nature of the boundary since the distance between the point of formation of the boundary and the undistorted portion of the measuring tube was only about 1 cm.

The size of the measuring tube, T, was chosen to match closely that of the sheared boundary cell. Other dimensions closely followed those suggested by Hartley and Donaldson.

The boundaries were formed in the following manner. The open end of E was fitted with a short length of pressure tubing with two pinchcocks attached. The apparatus was washed through and filled with leading solution with the upper pinch-cock closed and the lower one half opened. After inserting a suitable electrode in B, and allowing time for thermal equilibrium of the cell with the thermostat, the lower pinch-cock was compressed to force the air column in E into the lower part of T, separating the solution in T and C. Observations of the "heel" of this air column at G were used to detect any leaks or volume changes. The part A C F was then emptied by suction at A and F and washed with indicator solution from A with suction at F. The suction at F was always arrested before the receding meniscus in C reached the junction with T in order not to disrupt the air column. Upon final filling, the electrode was

inserted in A, voltage applied, and the lower pinch-cock on E carefully unscrewed until the air column had receded sufficiently to allow current to flow. A boundary forms immediately and progresses up the measuring tube.

(iii) Autogenic Cell. A different method of forming a boundary is the 'autogenic' boundary first used by Franklin and Cady⁽¹²⁾ in liquid ammonia and in aqueous solution by Cady and Longworth⁽⁶⁾. Figure 7 illustrates the principle of this method. The solution under investigation is placed in the tube B closed by the anode A. With proper choice of the anode, the indicator solution is formed by the anode electrolysis reaction to produce a boundary. The ions produced by the electrolysis must not form an insoluble salt with the anions of the electrolyte in the cell. The choice of the anode is limited by the availability of suitable metals whose solution produced must possess the properties necessary for an indicator. Nevertheless, the simplification introduced by the automatic generation and adjustment of indicator solution recommends it for use when possible. Moreover, sheared boundaries often exhibit anomalous behaviour and should always be verified by means of the autogenic boundary when possible⁽²⁰⁾.

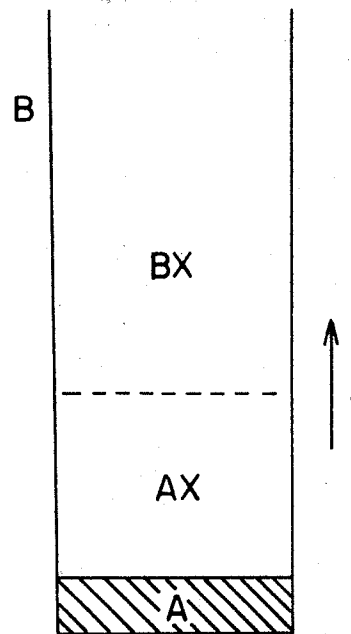


FIG. 7. FORMATION OF THE AUTOGENIC BOUNDARY

The 'autogenic' cell used in this work followed closely the design of that used by LeRoy and Gordon⁽²⁴⁾ and is shown in Figure 8. Before use, the appropriate size measuring tube, T, was graduated by etching, sealed onto the cell, and calibrated with mercury. This is described in the following paragraphs.

A thin-walled tube of well annealed Pyrex tubing formed the measuring tube, T. Prior to sealing this to the rest of the cell, the graduation marks were etched at the appropriate place. This was readily accomplished by coating the tube with a uniform layer of paraffin. The tube was then carefully mounted in a lathe and a fine cut made in the wax coating by means of a razor blade mounted in the tool-post of the lathe. This assured a uniform, fine groove which was perpendicular to the axis of the tube. Subsequent etching for 1 minute with a mixture of one part concentrated hydrochloric acid and one part 48 per cent hydrofluoric acid produced a just perceptible graduation mark. These, however, were amply clear and distinct when viewed under experimental conditions.

The positions of the six graduation marks are shown in Figure 9. The graduation marks were separated by 1.5 cm.

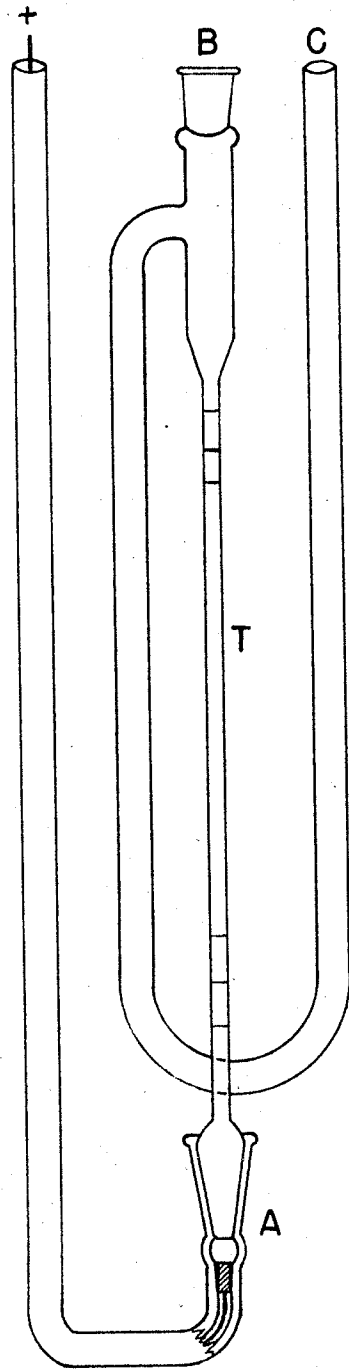


FIG. 8. AUTOGENIC BOUNDARY CELL

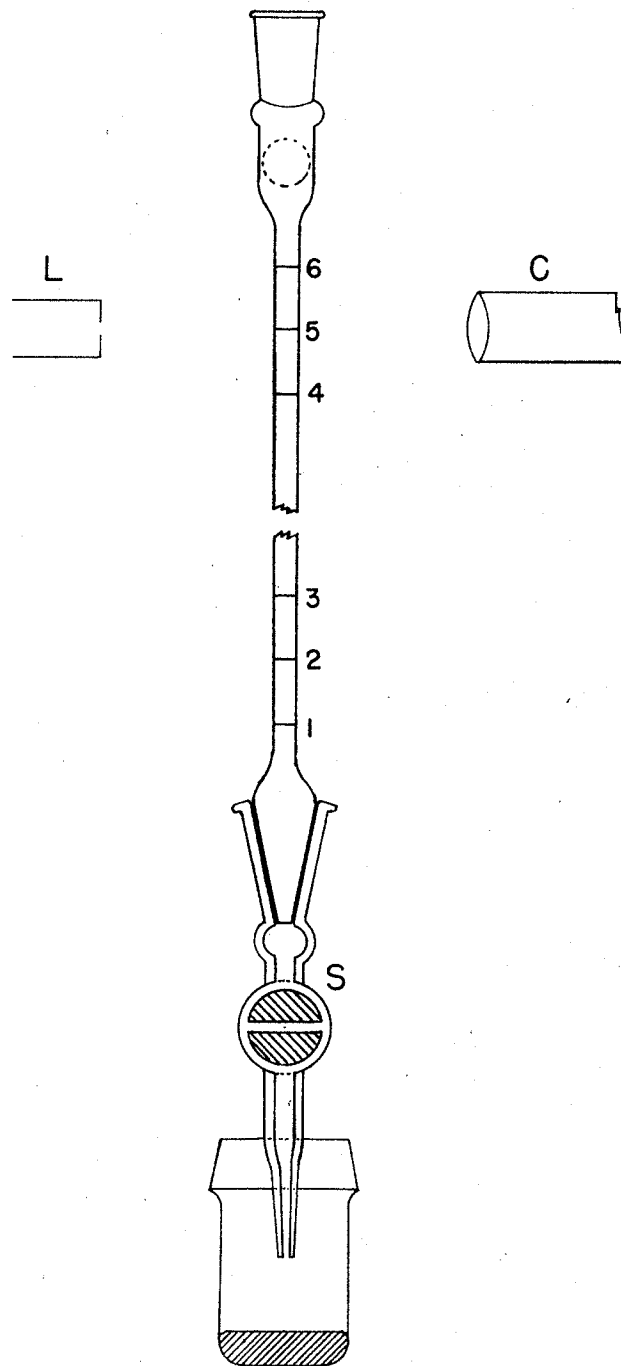


FIG. 9. AUTOGENIC CELL CALIBRATION

except for the 13.5 cm. middle interval. Thus, nine combinations of etch marks, each of 13.5 cm. or more, and six of less precision are possible. With normal progress of the boundary, sufficient time was allowable between the timing operations to make observations of the current, thermostat temperature, and overall progress of the determination.

The volumes were calibrated by the mercury and cathetometer method described by Longworth⁽²⁷⁾ and successfully employed by Rea⁽⁴⁹⁾. For calibration purposes, a 1 mm. stopcock with a capillary tip was sealed to a 10/30 standard taper outer ground glass joint. The stopcock and the standard taper joint were greased sparingly in such a manner as to avoid contamination of the mercury. With the capillary stopcock in place and the cell held rigidly in place on its stand, the mercury (Nichols mercury metal #1960, redistilled three times) was drawn up through the capillary by gentle suction at C, A being closed. Filling with suction ensured that no air bubbles were present.

The cell was illuminated from the back by the light source used in observing the boundary. The positions of the mercury in the measuring tube were determined with a Gaertner table cathetometer to ± 0.001 cm. All weighings

were made with calibrated weights on an analytical balance having a sensitivity of 3.6 divisions per mgm. at zero load. Determinations were carried out in a room with a very high ceiling which showed satisfactory constancy ($\pm 0.1^{\circ}\text{C}$) of temperature.

The procedure followed may be illustrated in detail by reference to the determination of the volume between etch 6 and etch 1 as an example. The mercury meniscus was lowered to just above etch 6. The weighing bottle, containing a small pool of mercury was raised until the tip of the capillary was partially immersed in the pool and the weight of the weighing bottle obtained. A similar weighing bottle containing mercury was used as a counterpoise. This was repeated until constant weight (to 0.03 mgm) was obtained, ensuring a constant volume of mercury in the capillary. The weight of the weighing bottle and the position of the top of the mercury meniscus, the base of the meniscus, and the etch mark were determined. Mercury was then withdrawn dropwise to just below the etch mark, the constant weight of mercury obtained, and the mercury position again measured. The change in mercury height was in general less than 1 cm. so that the corrections were kept to a minimum. The mercury was then withdrawn to just above the lower etch mark and the procedure repeated.

This procedure was necessary because of the difficulty in adjusting the mercury meniscus to coincide exactly with the etch mark and because of the variation in the volume of the meniscus caused by variation in the height and the diameter of the base. The volumes between the etches were calculated from the above observations as follows. The main volume of mercury withdrawn from just below the upper etch mark to just above the lower etch mark was corrected for lack of coincidence in the etch marks by use of the cathetometer readings. Since the radius of the tube was approximately 1.2 mm. and the height of the menisci 0.45 - 0.65 mm., the menisci were considered as paraboloids of volume $v = \pi r^2 h / 2$, where r is the radius of the base and h is the height of the meniscus⁽⁴⁹⁾. From the weight of mercury withdrawn near each etch mark, the average cross-sectional area was determined for each etch mark. The volume not included in the main volume of mercury could then be readily calculated from the distance of the etch mark from the mercury position.

The weights of mercury were converted into volumes from tables of specific volume data in the Handbook of Chemistry and Physics⁽¹³⁾. These tables give the corrected volumes of glass vessels from the weight of the contained mercury when weighed in air with brass weights at various temperatures.

The results of the calibration are given in a following section.

(b) Electrodes

The electrodes used in all experiments with the sheared boundary cell were silver and silver chloride as anode and cathode, respectively. The former was prepared⁽⁴⁹⁾ by electroplating silver onto a 15 mm. square platinum gauze formed into a spherical shell. The solution was prepared from 2 gms. AgNO_3 and 12 gms. NH_4NO_3 dissolved in 300 ml. of water. A solution of KCN was added until the precipitated AgCN just dissolved and the final volume made up to 600 ml. Electrolysis was carried out at 3 ma. at 60°C until sufficient silver was deposited. The electrode was rinsed repeatedly in distilled water and left in slowly circulating distilled water. Prior to use, the electrode was immersed in the solution to be investigated. Silver chloride electrodes were prepared by chloridizing the well washed silver electrode in a 6 N HCl solution for two hours at 6 ma. These were washed with distilled water and stored in the solution to be investigated.

Two types of cadmium anodes were used with the autogenic cell. The initial type was machined from cadmium metal which had been rapidly fused. The machined plug of cadmium

was cemented into place using De Khotinsky cement.

Electroplated cadmium was also used as an anode. Following the procedure of Creighton and Koehler⁽⁸⁾, cadmium was plated onto a platinum wire base from a bath containing 8.5 gms. $\text{Cd}(\text{OH})_2$ and 33.2 gms. KCN in 250 mls. of solution. A uniform deposit was obtained using 2 volts for this operation.

(c) Current supply

(i) Constant current regulator. In a transference number determination, the number of coulombs of electricity required for the boundary to move through a known volume must be determined to an accuracy consistent with the other measured quantities. Early workers^(50,52) used micro-coulometers but these had limited applicability because of the small quantities of electricity involved. Moreover, multiple coulometers are necessary if the full advantage of all the volume combinations is to be utilized. This method has now been completely discarded in favour of simultaneous measurements of the current and the time.

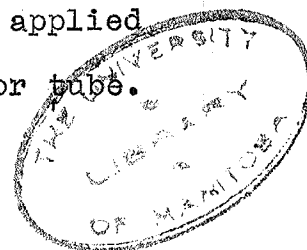
The movement of the boundary in the measuring tube of a moving boundary cell causes an increase in the total cell resistance as the leading solution, necessarily having

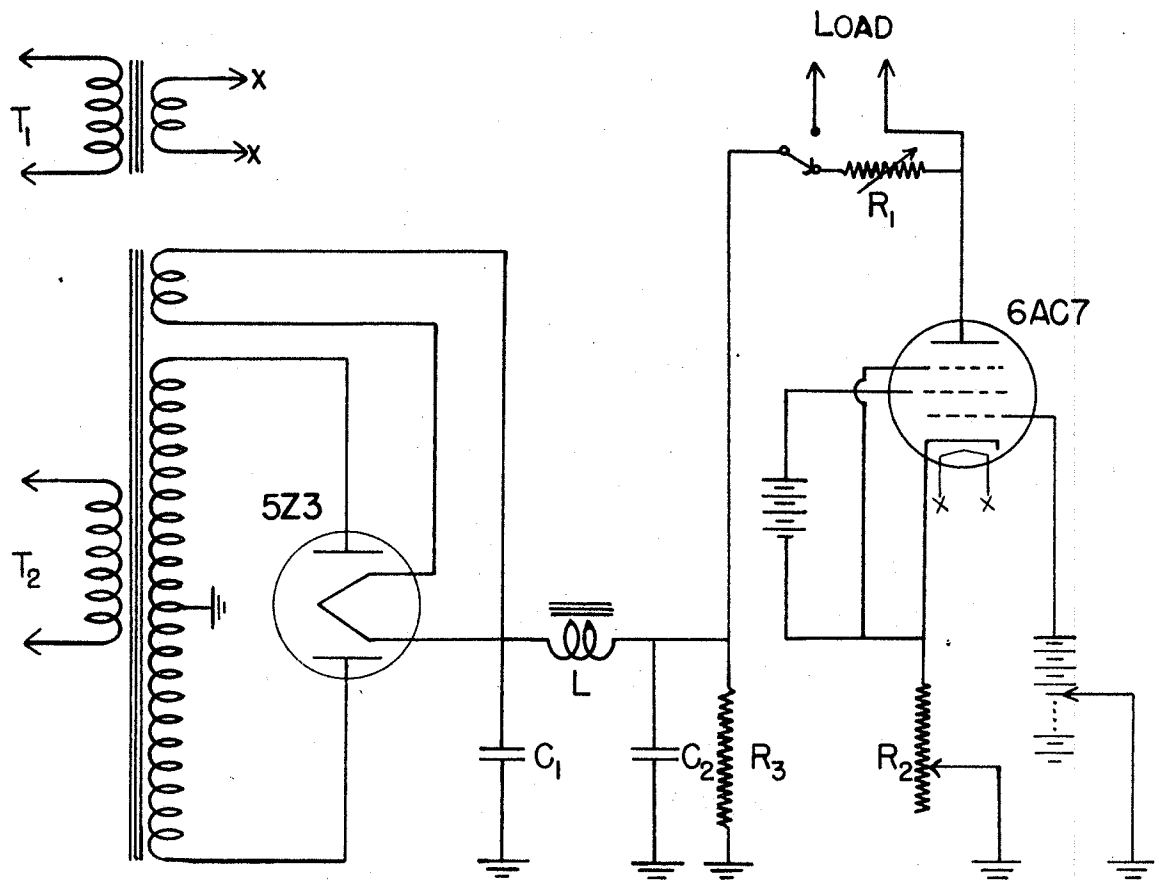
a higher conductivity, is replaced by a solution of lower conductivity. Some suitable auxiliary apparatus must be adopted to maintain the current independent of the resistance of the cell.

A constant current supply capable of maintaining currents up to 4 ma. constant to 0.02% was developed in the course of this investigation. A need for this became evident when in preliminary work the constant current supply available within this Laboratory⁽⁴⁹⁾ did not give the degree of stabilization desired.

Various mechanical^(37,40) and electronic^(4,14,24) devices have been designed to maintain the current constant at any desired value independent of the load resistance. In general, however, these are too cumbersome or require the use of extensive batteries. The circuit adopted, shown in Figure 10, was quite similar to that of LeRoy and Gordon⁽²⁾ and also that of Hartley and Donaldson⁽¹⁴⁾ but does not require the use of a large bank of batteries.

The high voltage supply used was the original one⁽⁴⁹⁾ with the voltage regulating section removed to provide an increased plate voltage as high as 775 volts. The unregulated voltage from the π section filter was applied directly to the load in series with the regulator tube.





T_1 - 6.3 V
 T_2 - POWER TRANS.
 R_1 - "DUMMY" LOAD
 R_2 - 200K, 20W

L - 10h
 C_1 - 4 μ f
 C_2 - 10 μ f
 R_3 - BLEEDER

FIG.10. CONSTANT CURRENT REGULATOR

Any line voltage fluctuation and any residual ripple from the filter appeared at the plate of the 6AC7 regulator tube. For the present case, this is not serious since the voltage drop across the load must change by a much greater amount during a transference number determination due to the change in cell resistance. The stabilization is based on the fact that the plate current of a pentode tube is almost independent of plate voltage beyond a minimum value of plate voltage. To improve the constancy of the plate current, a cathode biasing resistor of large magnitude was included so that any change in plate current must result in a relatively large change in tube bias in such direction as to counteract the change in plate current. Thus, even a substantial increase of resistance in the transference cell (in series with the plate circuit) will result in a very small decrease in plate current because the IR drop across the cathode resistor will become smaller and hence decrease the negative bias on the grid.

The 6AC7 tube was selected because its current handling capacity was suited to the currents employed, and its high transconductance makes the response to small changes in grid bias relatively large. Because the tube will not pass appreciable current if the grid is greater than a few volts negative, it was necessary to put sufficient

positive potential in the grid circuit to raise the grid potential to approximately that of the cathode. Variation of the cathode resistor, the screen voltage, and the grid voltage can then be used to adjust the plate current to any desired value. The screen voltage was maintained by a battery connected between screen and cathode. Some consideration was given to the use of an electronically regulated voltage source to furnish screen voltage, but experience has shown that the batteries could supply the small screen current (less than 1 ma.) without noticeable polarization.

The circuit included a dummy load resistor, R_1 , of approximately the resistance of the cell. A warm-up period of at least an hour was allowed during which time the magnitude of the current was set and the degree of control tested by simulating the actual resistance changes expected during the run with the continuously variable dummy resistor.

Typical performance data of the regulator are given in Table IV later in this thesis.

(ii) Measurement of the current. The current flowing through the transference cell was determined from the potential drop across a calibrated resistor in series with

the cell. The resistors used were obtained from the General Radio Company, and had nominal resistances of 100 ohms (type 500-d) and 1000 ohms (type 500-h). These had been calibrated previously⁽⁴⁹⁾ and the values given in Table II.

TABLE II

CALIBRATED VALUES OF SERIES RESISTORS

Nominal value	Resistance in absolute ohms.
100	99.961
1000	999.8

A Leeds and Northrup type K-1 potentiometer (Serial No. 61167) was used to measure the potential drops as compared with an Eppley Standard Cell (No. 396636). The voltage of this cell was redetermined by comparison with an Eppley Standard Cell recently certified. The potentiometer was compared against a Rubicon Type B high precision potentiometer by measuring on each instrument the potential drop across a variable resistance connected across a 2 volt wet cell. The limit of error in the Rubicon potentiometer, as specified by the manufacturers, including residual errors as well as calibration errors was 0.01% of the readings in this range.

(d) Observation of the boundary

The difference in refractive indices of the leading and indicator solutions permit the boundaries to be readily observed using a relatively simple optical system. The apparatus used was introduced by MacInnes, Cowperthwaite, and Huang⁽³⁸⁾ and was successfully modified by Rea⁽⁴⁹⁾ in this Laboratory. The principle is illustrated in Figure 11. The light source, S, was a blackened cylinder containing a 100 watt light bulb. A rectangular slit 1 cm. by 6 cm. on the end of the cylinder was covered with a "Kleenix" tissue to provide diffuse light. When the relative position of the source, the boundary, B, and the telescope, T, are such that total reflection occurs at the boundary as shown, the boundary appears as a bright line on a dark background. If the source and the telescope are in the same plane as the boundary, the latter appears as a dark line on a bright background. The adjustment of the light source was facilitated by mounting it on a framework which could be moved upwards or downwards smoothly by a chain and sprocket drive actuated from the observer's position.

The Schlieren scanning technique, originally developed by Longworth⁽²⁹⁾ for studying the electrophoresis of proteins has provided a powerful tool with which to investigate in detail the moving boundaries. Information

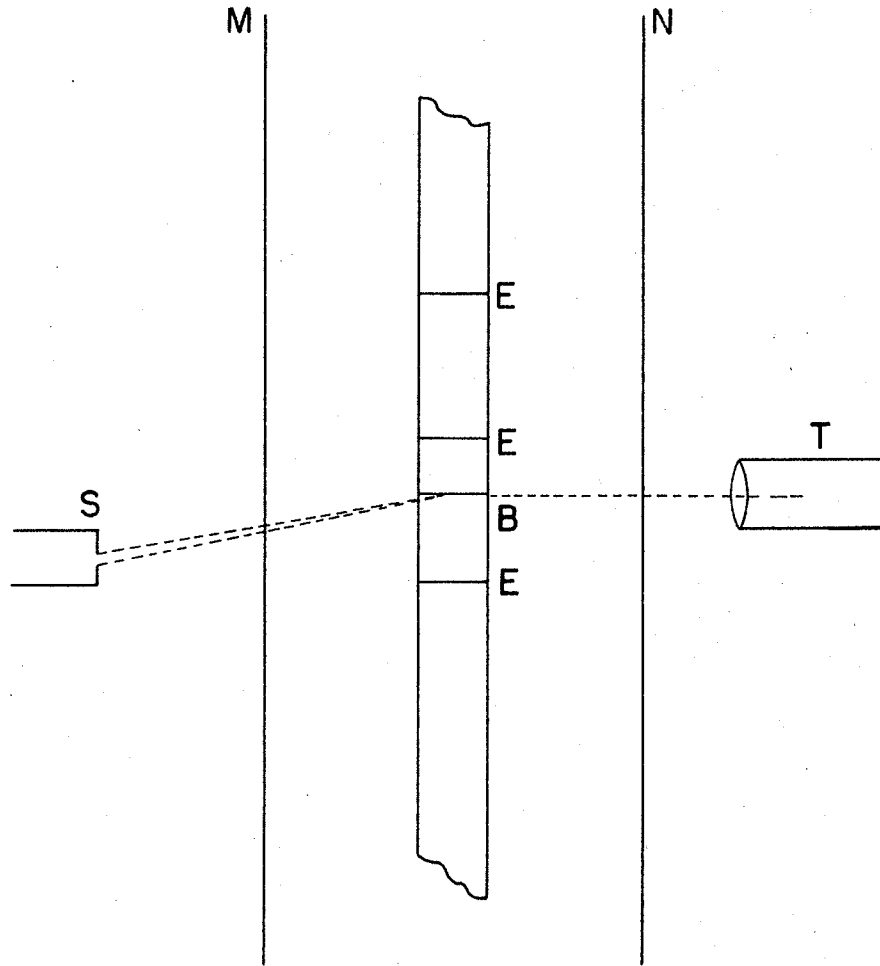


FIG. II. OBSERVATION OF THE BOUNDARY

concerning the magnitude and distribution of the gradients in the boundary and the manner in which these vary with current has been obtained by Longworth^(30,31,32). However, for boundaries encountered in this research the relatively simple optical system employed was entirely adequate.

(e) Measurement of the time

The standard of time used was an Elgin "railroad" watch certified by Birks Jewellers (Winnipeg) to be accurate to 15 seconds in a week. Lesser periods of about three hours were checked repeatedly by means of broadcasted time signals (Washington, D.C.), the deviations found being negligible. The exact moment at which the boundary arrived at an etch mark was interpolated by means of beats from an electric metronome obtained from the Central Scientific Company and calibrated against the Elgin watch⁽⁴⁹⁾. After the initial determinations, the use of the metronome was discontinued since the time at which the boundary reached an etch mark could not be estimated well enough. A stopwatch calibrated against the standard of time was subsequently used by setting it in motion at the moment that the boundary reached the etch mark and stopping it at a known time. The probable error was estimated at ± 0.5 secs.

(f) Temperature control

Although transference numbers do not change critically with temperature, fluctuations of temperature of the thermostat may give rise to serious temperature gradients which cause convection stirring and density stirring of the solutions in the cell. Erroneous results or destruction of the boundary may result, as well as displacement of the boundary due to changes in volume of the electrode chambers from thermal expansion or contraction. Similarly, undue vibration of the cell has been shown to have undesirable effects⁽³⁸⁾.

The thermostat bath used successfully in the first investigation⁽⁴⁹⁾ was employed in the present work. This consisted of a copper bath, with partial glass windows on opposite sides, filled with 'Bayol F' -- a thermostating liquid of water white mineral oil having low viscosity and low flash point. Control was achieved by means of a mercury thermoregulator and mechanical relay controlling a knife heater. The addition of a constant hydrostatic head to the cooling system greatly facilitated the regulation. The stirrer motor stand rested directly on the floor in order that any vibrations would be damped out without being communicated to the bath and cell. The total fluctuation

during any one run was generally less than 0.003°C as determined by means of a Beckmann thermometer. A certified platinum resistance thermometer was used to set the Beckmann thermometer.

2. Preparation of chemicals

In all high precision electrochemical measurements, the purity of the materials used is of utmost importance. Accurate concentrations made up by weight require that the salts be completely anhydrous. These conditions were met adequately in the salts used in this work. For use as indicator solutions in moving boundary measurements, the salt concentration can be varied within limits so that less precision is demanded.

(a) Potassium chloride

The potassium chloride used was that prepared by Rea⁽⁴⁹⁾ and used in previous investigations. It was prepared by twice recrystallizing Merck Reagent grade potassium chloride (maximum impurities of 0.06%) from conductivity water. After drying at 110°C , the salt was fused in a platinum crucible. This yielded a completely anhydrous, neutral salt⁽⁴⁷⁾. It was stored in a ground glass stoppered bottle in a desiccator.

(b) Potassium iodate

Merck potassium iodate was recrystallized twice from conductivity water. After the initial drying, in vacuo, the salt was finely pulverized in an agate mortar. It was stored over anhydrous calcium chloride until required for use.

(c) Ammonium nitrate

The ammonium nitrate was supplied by Dr. E. Kartzmark of this Laboratory. It was the commercial salt⁽⁷⁾ which had been recrystallized and dried for twelve months over concentrated sulfuric acid.

(d) Ammonium propionate

A volume of 100 ml. of propionic acid (Eastman Organic Chemicals) was neutralized with a slight excess of ammonium hydroxide and evaporated to dryness. This was recrystallized from ethyl alcohol and dried over calcium chloride.

(e) Ammonium salicylate

Salicylic acid was neutralized with a slight excess of ammonium hydroxide and the precipitated ammonium salicylate filtered off by suction. After a subsequent recrystallization from slightly basic conductivity water, it was dried over calcium chloride.

(f) Ammonium 3,5-dinitrobenzoate

The ammonium 3,5-dinitrobenzoate was prepared by the method of McMaster and Godlove⁽⁴⁴⁾ by passing NH₃ gas into an ether solution of the acid. A white, amorphous powder having a slight yellowish tinge was precipitated. The salt was obtained by suction filtration from the ethereal solution, further purified by recrystallization from conductivity water, and stored over calcium chloride after oven drying. McMaster and Godlove found that the salt was not deliquescent and was stable in dry air. An aqueous solution was neutral and did not hydrolyse even on long standing.

(g) Ammonium iodate

Iodic acid was neutralized with a slight excess of ammonium hydroxide and the precipitated salt filtered off by suction. A recrystallization from conductivity water was made and the ammonium iodate oven dried before storing over calcium chloride.

(h) Cadmium nitrate

Cadmium nitrate (Merck Reagent grade) was of high purity and was used without further purification. The analysis supplied showed a maximum impurity of 0.07% with no cations of higher mobility present.

3. Preparation of Solutions

All weights used were calibrated in terms of a standard set certified by the National Research Council of Canada. Buoyancy corrections were made in all cases.

(a) Leading solution

The leading solutions were prepared by weight by adding water to a known weight of salt. The final weight of solution was determined rather than adding a known weight of water. This permitted the use of some of the water to rinse the container in which the salt was weighed, and losses of water by evaporation during the preparation of the solution cause no error. Volume concentrations were calculated from the weight concentrations using the density data in the International Critical Tables(17).

(b) Indicator solution

The indicator solutions were made up in calibrated 250 ml. volumetric flasks. The appropriate weight of dry salt was dissolved in conductivity water.

4. Procedure for Cell Filling

The cells were filled using the nitrogen pressure technique recommended by Allgood, LeRoy and Gordon⁽²⁾ as shown in Figure 12. Cylinder nitrogen was passed through a bubbler of concentrated sodium hydroxide to

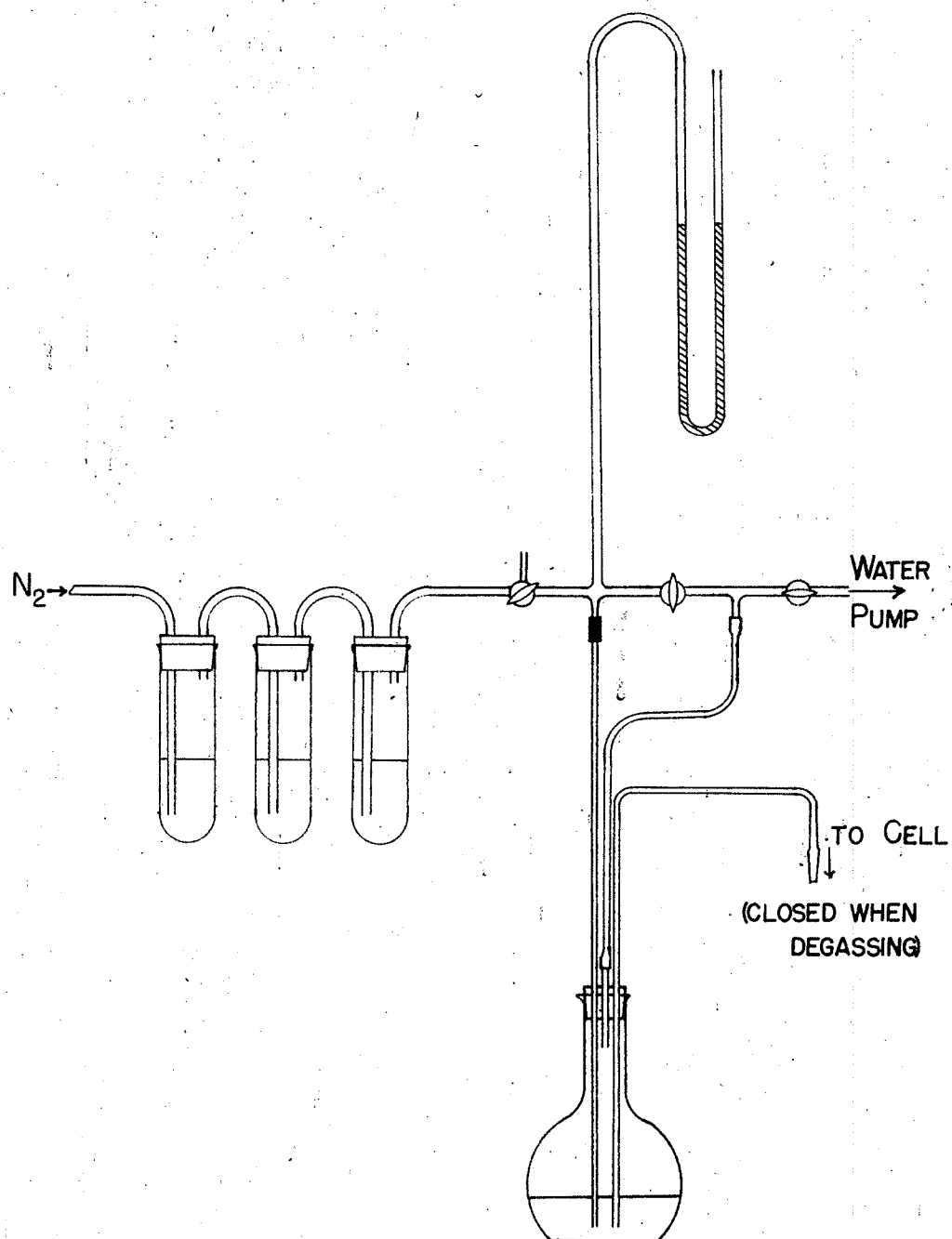


FIG. 12. DEGASSING AND CELL FILLING

remove carbon dioxide and saturated with water by passing through two water bubblers. The water aspirator and the rate of nitrogen flow were adjusted to maintain a slightly reduced pressure of about 500 mm Hg. After degassing, a positive nitrogen pressure was used to force the solution into the cell.

The leading solution of the sheared cell was filled through D, Figure 5, so that the measuring tube was well washed with the solution while filling the anode chamber. The newly silvered anode, which had been resting in part of the leading solution to be used was then carefully seated into place and firmly held in place with springs. Stop-cock grease which had been repeatedly extracted with hot conductivity water was used as a lubricant. The Ag-AgCl cathode was similarly introduced into the cathode chamber after filling with indicator solution. The latter solution was pipetted into the cell.

The autogenic cell was filled by introducing a fine tube through B reaching to the anode. Solution was slowly forced through the fine tube, up the measuring tube and into the side arm. The tube was slowly withdrawn when the cell was almost full, filling the measuring tube. The opening B was closed with a rubber stopper. A silver chloride electrode was used as cathode.

5. Ammonium 3,5-Dinitrobenzoate -- Conductances,
Densities, and Solubility

The conductance and density of a 0.06 N and a 0.10 N solution of ammonium 3,5-dinitrobenzoate were measured to enable an approximation of the proper indicator concentration to be made. A Campbell-Shackelton bridge available in this Laboratory⁽⁷⁾ was used for conductance measurements. Densities were determined with a Weld pycnometer of 5 ml. capacity, calibrated with distilled water.

The solubility of ammonium 3,5-dinitrobenzoate in water at 25°C was determined after equilibrating the salt for twenty-four hours by stirring the thermostated solution with excess solid. Samples for gravimetric analysis of the saturated solution were obtained through sintered glass filters. The weight of residue from a known weight of saturated solution was obtained by slowly evaporating off the water and heating to constant weight at 110°C.

The data and results are listed in Table VI of the next section.

6. Transference Number Measurements

(a) Potassium chloride/potassium iodate sheared boundaries

The transference numbers of potassium chloride have been well investigated^(2,27) and the data are very accurately known. Independent measurements of the transference number of the chloride ion in potassium chloride may serve as a check on the overall method of procedure and the performance of the apparatus. Runs 1, 2, 3, 4, 24, 41 to 44, and 52 using potassium iodate as indicator were carried out on this salt during the investigation for this purpose.

(b) Ammonium chloride/ammonium 3,5-dinitrobenzoate sheared boundaries

The preliminary measurements on the system ammonium nitrate/ammonium 3,5-dinitrobenzoate in the sheared boundary cell showed progression of the rate of movement of the boundary with no appearance of an adjustment range of the indicator. Runs 19, 22, and 23 were made with ammonium chloride and ammonium 3,5-dinitrobenzoate to test the properties of the latter indicator. The transference numbers of ammonium chloride were established by Longsworth⁽²⁸⁾ using the moving boundary method. This ammonium salt thus enabled an independent check on the properties of the 3,5-dinitrobenzoate ion for use as an indicator.

(c) Ammonium nitrate sheared boundaries

(i) Preliminary indicators. The investigation of ammonium nitrate boundaries was initiated with an indicator search in which the ammonium salts of proprionic acid, salicylic acid, and 3,5-dinitrobenzoic acid were used. These indicators were tested in the sheared boundary cell (runs 6 to 10) and in the air-lock cell. Of these, the ammonium 3,5-dinitrobenzoate seemed most promising for use as an indicator.

(ii) Ammonium 3,5-dinitrobenzoate indicator. Sheared boundaries using ammonium 3,5-dinitrobenzoate as indicator were studied systematically with 0.1 N ammonium nitrate and the complete range of indicator concentration from 0.01 N to 0.1 N. These were included in Runs 11, 12, 13, 15 to 18, 20, 21 and 25 to 30.

(iii) Cadmium nitrate indicator. Autogenic boundaries with a cadmium anode give rise to boundaries in which the cadmium salt forms the indicator. Thus, the nature of an autogenic boundary may be investigated by using the proper concentration of the cadmium salt in a rising boundary. Runs 31 to 35 were undertaken with 0.1 N ammonium nitrate and concentrations of cadmium nitrate varying around the Kohlrausch ratio for this purpose.

(iv) Ammonium iodate indicator. The iodate ion has been used with success in rising boundaries (2,27). In the present work, ammonium nitrate/ammonium iodate boundaries were investigated with 0.05 N ammonium nitrate and varying concentrations of ammonium iodate in Runs 45, 46, 50 and 51.

(d) Autogenic boundaries

(i) Potassium chloride. The transference number of the potassium ion in potassium chloride was measured in the autogenic cell to check the calibration of the cell and to test the design of the anode. Runs 36 to 40 were made with 0.1 N potassium chloride using a cadmium anode machined from fused cadmium metal as described previously.

(ii) Ammonium nitrate. The autogenic cell was used to measure the transference number of the ammonium ion in 0.05 N ammonium nitrate. The plated cadmium electrode described in a previous section was used. Three runs (Runs 47, 48, and 49) were made.

III. DATA AND RESULTS

To facilitate the discussion in the next section and in line with the development of the experimental part, the results of this investigation are presented here in the following order: (1) calibration of the autogenic cell, (2) (a) typical performance of the constant current supply, (b) comparison of the Leeds and Northrup Type K-1 potentiometer, (3) properties of the ammonium 3,5-dinitrobenzoate indicator solution, and (4) transference number measurements.

The results of the transference number measurements have been classified further into the types of boundaries investigated: (a) potassium chloride with potassium iodate as indicator in the sheared boundary cell, (b) ammonium chloride in the sheared boundary cell using ammonium 3,5-dinitrobenzoate as indicator, (c) ammonium nitrate in the sheared cell using as indicators (i) ammonium propionate and ammonium salicylate, (ii) ammonium 3,5-dinitrobenzoate, (iii) cadmium nitrate, and (iv) ammonium iodate, and, finally (d) autogenic boundaries with (i) potassium chloride, and (ii) ammonium nitrate.

1. Calibration of the Autogenic Cell

The results of the calibration of the nine volumes are listed in Table III. Each determination is the mean of at least two determinations.

TABLE III

VOLUME CALIBRATION OF AUTOGENIC CELL

Volume Calibrated	Mean Volume ml.	Volume Calibrated	Mean Volume ml.	Volume Calibrated	Mean Volume ml.
6-1	0.9172	5-1	0.8472	4-1	0.7765
6-2	0.8485	5-2	0.7781	4-2	0.7076
6-3	0.7836	5-3	0.7123	4-3	0.6422

(2) Current Supply

(a) The current regulator

The data from two representative runs using the constant current regulator are in Table IV.

TABLE IV

TYPICAL PERFORMANCE OF THE CURRENT REGULATOR

	<u>Trial 1</u>	<u>Trial 2</u>
Time of run, hours	2	2.5
Initial load resistance, ohms	70 K	100 K
Final load resistance, ohms	90 K	155 K
Minimum current, ma.	2.2582	2.2587
Maximum current, ma.	2.2589	2.2593
Maximum deviation from mean	0.016%	0.014%
Average Deviation from mean	0.005%	0.005%

Comparable stabilization was achieved for currents from 0.4 ma. to 4 ma. Currents outside this range were not encountered.

(b) Comparison of the Leeds and Northrup Type K-1 potentiometer

The potential difference in the range 0.4 to 0.6 volts measured on the Leeds and Northrup Type K-1 potentiometer and on the Rubicon Type B potentiometer are given in Table V.

TABLE V

COMPARISON OF POTENTIOMETERS

Measured Potential Drop		
Reference potentiometer (Rubicon)	Compared potentiometer (Leeds & Northrup #61167)	Difference
± 0.00001 Volt	± 0.00001 Volt	mv.
0.60457	0.60455	-0.02
0.48849	0.48851	+0.02
0.46745	0.46745	± 0.00
0.43402	0.43402	± 0.00
0.42426	0.42423	-0.03
0.41410	0.41407	-0.03
0.40472	0.40471	-0.01
0.40194	0.40192	-0.02

(3) Ammonium 3,5-Dinitrobenzoate--Conductances, Densities, and Solubility

The conductivity and density of 0.06 N and 0.1 N solutions and the solubility of ammonium 3,5-dinitrobenzoate in water at 25°C were determined in order to evaluate the

suitability of this salt as an indicator for sheared boundaries with ammonium nitrate. These data are listed in Table VI together with the equivalent conductances⁽¹⁸⁾ and the densities⁽¹⁷⁾ of ammonium nitrate for comparison.

TABLE VI

DENSITIES AND CONDUCTIVITIES OF AMMONIUM 3,5-DINITROBENZOATE AND AMMONIUM NITRATE AT 25°C.

Concentration (Moles/Liter)	Density (gms./ml.)		Λ (mhos cm ²)	
	Benzoate	Nitrate ⁽¹⁷⁾	Benzoate	Nitrate ⁽¹⁸⁾
0.05924	1.0022	0.9990	86.97	126.3
0.09991	1.0063	1.0003	84.04	122.8
0.252*	1.0193	1.0051	-----	114.9

* Solubility of benzoate.

(4) Transference Number Measurements

The results obtained for each series of transference number measurements are tabulated in this section. Rather than presenting all the experimental data required for each determination, for conciseness, only the concentration of the leading solution, the indicator solution, the average current, the observed time, and the computed transference numbers are given. Where graphical integration was employed, the average current given is for the interval 3-4. The volume and solvent corrections have been made where they are applicable.

(a) Potassium chloride/potassium iodate sheared boundaries

The transference number determinations of the chloride ion in 0.01 N, 0.05 N, and 0.1 N potassium chloride are summarized in Table VII. The volume change, ΔV , when silver forms the closed anode is given by

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

The data used for this computation were (27)

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

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

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

The solvent correction, given by $+T_K \frac{K_{\text{solvent}}}{K_{\text{solution}}}$, was computed from the measured conductances when they were significant.

(b) Ammonium chloride/ammonium 3,5-dinitrobenzoate sheared boundaries

Runs 19, 22, and 23 were made in the sheared boundary cell using 0.1 N ammonium chloride as the leading solution and 0.05 N ammonium 3,5-dinitrobenzoate as the indicator solution. The results of Run 22 were invalid because of gassing at the anode and have not been included. The data for Runs 19 and 23 are presented in Table VIII. The

TABLE VII

POTASSIUM CHLORIDE/POTASSIUM IODATE SHEARED BOUNDARIES

Run No.	1	3	4	24	41
CKCl (equiv./liter)	0.09965	0.09926	0.09992	0.09958	0.01012
CKIO ₃ (equiv./liter)	0.1000	0.1000	0.1000	0.1000	0.00700
Mean Current (ma.)	4.165	4.144	4.163	3.924	0.4100
Time (sec.)					
1 - 4		3398	3411	3535	
1 - 5		3703	3718	3856	
1 - 6		3964	3980	4132	
2 - 4	3086	3093	3104	3199	3197
2 - 5	3391	3398	3411	3520	3513
2 - 6	3653	3659	3673	3796	3786
3 - 4	2784	2784	2795	2882	2874
3 - 5	3089	3089	3102	3203	3190
3 - 6	3351	3350	3364	3479	3463
T _{obs.}					
1 - 4		0.5104	0.5096	0.5202	
1 - 5		0.5105	0.5094	0.5194	
1 - 6		0.5105	0.5096	0.5188	
2 - 4	0.5106	0.5099	0.5092	0.5209	0.5086
2 - 5	0.5106	0.5101	0.5092	0.5202	0.5085
2 - 6	0.5105	0.5102	0.5094	0.5195	0.5080
3 - 4	0.5093	0.5098	0.5090	0.5218	0.5090
3 - 5	0.5092	0.5098	0.5088	0.5208	0.5086
3 - 6	0.5094	0.5101	0.5094	0.5202	0.5084
Mean	0.5099	0.5101	0.5093	0.5202	0.5085
Vol. Correction	0.0002	0.0002	0.0002	0.0002	0.0000
Solv. Correction	0.0001	0.0001	0.0001	0.0001	0.0014
T _{corrected}	0.5102	0.5104	0.5096	0.5205	0.5099
T _(2,27)	0.5101	0.5101	0.5101	0.5101	0.5098

TABLE VII (continued)

POTASSIUM CHLORIDE/POTASSIUM IODATE SHEARED BOUNDARIES

Run No.		42	43	44	52
CKCl	(equiv./liter)	0.09986	0.04979	0.009860	0.09981
CKIO ₃	(equiv./liter)	0.07016	0.04006	0.01000	0.07000
Mean Current	(ma.)	3.7493	2.1770	0.41197	3.4732
Time (sec.)	1 - 4	3724	3196	3315	3979
	1 - 5	4061	3480	3610	4336
	1 - 6	4345	3726	3863	4640
	2 - 4	3386	2906	3014	3678
	2 - 5	3723	3190	3309	4035
	2 - 6	4007	3436	3562	4339
	3 - 4	3046	2614	2711	3255
	3 - 5	3383	2898	3006	3612
	3 - 6	3667	3144	3259	3916
T- obs.	1 - 4	0.5182	0.5186	0.5232	0.5234
	1 - 5	0.5177	0.5188	0.5234	0.5232
	1 - 6	0.5179	0.5186	0.5235	0.5233
	2 - 4	0.5182	0.5184	0.5231	0.5232
	2 - 5	0.5177	0.5188	0.5234	0.5232
	2 - 6	0.5180	0.5187	0.5236	0.5234
	3 - 4	0.5182	0.5185	0.5232	0.5232
	3 - 5	0.5176	0.5188	0.5234	0.5231
	3 - 6	0.5180	0.5188	0.5238	0.5235
	Mean	0.5179	0.5187	0.5234	0.5233
Vol. Correction		0.0002	0.0001	0.0000	0.0000
Solv. Correction		0.0001	0.0003	0.0014	0.0014
T- corrected		0.5182	0.5191	0.5248	0.5247
T _{2,27}		0.5101	0.5100	0.5098	0.5101

TABLE VIII

AMMONIUM CHLORIDE/AMMONIUM 3,5-DINITROBENZOATE
SHEARED BOUNDARIES

Run No.	19	23
CNH ₄ Cl (equiv./liter)	0.09979	0.09988
CNH ₄ B (equiv./liter)	0.05000	0.05006
Mean Current (ma.)	3.318	2.695
Time (sec.) 1 - 4	4261	5210
1 - 5	4638	5676
1 - 6	4969	6076
2 - 4	3876	4737
2 - 5	4253	5203
2 - 6	4584	5603
3 - 4	3489	4261
3 - 5	3866	4727
3 - 6	4197	5127
T ₋ obs. 1 - 4	0.5114	0.5154
1 - 5	0.5118	0.5154
1 - 6	0.5113	0.5153
2 - 4	0.5111	0.5154
2 - 5	0.5117	0.5155
2 - 6	0.5112	0.5154
3 - 4	0.5108	0.5155
3 - 5	0.5114	0.5154
3 - 6	0.5111	0.5156
Mean	0.5113	0.5154
Vol. Correction	0.0003	0.0003
Solv. Correction	0.0001	0.0001
T ₋ corrected	0.5117	0.5158
T ₋ (27)	0.5093	0.5093

volume change is given by

$$\Delta V = V_{Ag} - V_{AgCl} + T_{NH_4} \bar{V}^{NH_4Cl}$$

where

$$\bar{V}^{NH_4Cl} = 36.26 + 1.86 \sqrt{m} \text{ ml./mole}^{(27)}.$$

(c) Ammonium nitrate sheared boundaries

(i) Preliminary indicators. The preliminary indicators used with 0.1 N ammonium nitrate were ammonium proprionate at currents of 4 ma. to 6 ma. (Runs 6, 7 and 8) and ammonium salicylate at currents of 3.5 ma. to 5.8 ma. (Runs 9 and 10) in the sheared boundary cell. No boundaries could be observed even though the time of electrolysis and the change in cell resistance showed that sufficient transference had taken place to enable a boundary to move into the field of view. Similarly, no boundaries were obtained with these indicators in the air-lock cell in which the disturbing effects could be operative for only the short interval between the time of formation of the boundary and the time of observation.

Preliminary runs using ammonium 3,5-dinitrobenzoate as indicator, however, produced a very sharp boundary which persisted with a current variation from 3 ma. to 8 ma.

The nature of the boundaries formed between ammonium nitrate and ammonium 3,5-dinitrobenzoate suggested that quantitative investigation of this indicator was warranted.

The results of the transference number measurements using this indicator are summarized in Table IX immediately following.

(ii) Ammonium 3,5-dinitrobenzoate indicator. Runs 11 to 13 and 15 to 18 were made prior to the measurements on ammonium chloride given above, while Runs 20, 21 and 25 to 30 were suggested by the ammonium chloride results. The ammonium nitrate measurements constitute Table IX. The volume and solvent corrections were not determined.

(iii) Cadmium nitrate indicator. Sheared boundaries formed between ammonium nitrate and cadmium nitrate were investigated in Runs 31-35. These results are summarized in Table X. The mean values have not been corrected for change of volume or solvent conductance.

(iv) Ammonium iodate indicator. Ammonium iodate was used as an indicator for 0.05 N solutions of ammonium nitrate in Runs 45, 46, 50 and 51 (Table XI).

TABLE IX

AMMONIUM NITRATE/AMMONIUM 3,5-DINITROBENZOATE
SHEARED BOUNDARIES

Run No.		11	12	13	15	16	
CNH ₄ NO ₃ (equiv./l.)		0.09973	0.09973	0.09971	0.09986	0.09990	
CNH ₄ ^B (equiv./l.)		0.09468	0.08528	0.07587	0.06633	0.04738	
Mean Current (ma.)		3.261	3.329	3.280	3.342	3.343	
Time (sec.)	1 - 4	4410	4291	4405	4350	4309	
	1 - 5	4808	4681	4803	4745	4698	
	1 - 6	5150	5013	5144	5083	5027	
	2 - 4	4021	3912	4018	3966	3926	
	2 - 5	4419	4302	4416	4361	4315	
	2 - 6	4761	4634	4631	4699	4644	
	3 - 4	3623	3526	3621	3578	3542	
	3 - 5	4021	3916	4019	3973	3931	
	3 - 6	4363	4248	4360	4311	4260	
	T- obs.	1 - 4	0.5024	0.5054	0.5001	0.4972	0.5024
		1 - 5	0.5025	0.5047	0.4996	0.4971	0.5022
		1 - 6	0.5017	0.5046	0.4993	0.4968	0.5025
2 - 4		0.5010	0.5041	0.4984	0.4960	0.5011	
2 - 5		0.5008	0.5038	0.4982	0.4961	0.5011	
2 - 6		0.5005	0.5036	0.4980	0.4960	0.5016	
3 - 4		0.5002	0.5035	0.4975	0.4949	0.5000	
3 - 5		0.5000	0.5029	0.4972	0.4948	0.5000	
3 - 6		0.4999	0.5031	0.4973	0.4950	0.4008	

TABLE IX (continued)

AMMONIUM NITRATE/AMMONIUM 3,5-DINITROBENZOATE
SHEARED BOUNDARIES

Run No.		17	18	20	21	25	
CNH_4NO_3 (equiv./l.)		0.09992	0.09990	0.09986	0.09984	0.09992	
CNH_4^{B} (equiv./l.)		0.03009	0.01995	0.06020	0.06001	0.02996	
Mean Current (ma.)		3.328	3.298	3.144	3.355	3.002	
Time (sec.)	1 - 4	4345	4426	4673	4403	4892	
	1 - 5	4741	4833	5095	4808	5330	
	1 - 6	5079	5181	5456	5153	5703	
	2 - 4	3962	3989	4263	4019	4453	
	2 - 5	4358	4395	4685	4424	4891	
	2 - 6	4696	4744	5046	4769	5264	
	3 - 4	3570	3602	3840	3625	4008	
	3 - 5	3966	4008	4262	4030	4446	
	3 - 6	4304	4357	4623	4375	4819	
	T. obs.	1 - 4	0.5003	0.4955	0.4928	0.4892	0.4931
		1 - 5	0.4998	0.4950	0.4925	0.4886	0.4930
		1 - 6	0.4996	0.4947	0.4924	0.4885	0.4932
2 - 4		0.4991	0.4999	0.4908	0.4875	0.4924	
2 - 5		0.4987	0.4991	0.4908	0.4871	0.4926	
2 - 6		0.4987	0.4986	0.4908	0.4872	0.4928	
3 - 4		0.4984	0.4984	0.4901	0.4865	0.4922	
3 - 5		0.4981	0.4975	0.4900	0.4861	0.4923	
3 - 6		0.4983	0.4971	0.4903	0.4864	0.4928	

TABLE IX (Continued)

AMMONIUM NITRATE/AMMONIUM 3,5-DINITROBENZOATE
SHEARED BOUNDARIES

Run No.		26	27	28	29	30
$C_{NH_4NO_3}$ (equiv./l.)		0.09943	0.09987	0.09988	0.09982	0.09992
C_{NH_4B} (equiv./l.)		0.01999	0.01000	0.04998	0.03000	0.02997
Mean Current (ma.)		2.224	2.221	2.1962	2.1960	2.2590
Time (sec.)	1 - 4	6587	6756	6552	6628	6623
	1 - 5	7181	7425	7146	7216	7212
	1 - 6	7687	8004	7651	7724	7717
	2 - 4	6002	6192	5974	6045	6031
	2 - 5	6596	6861	6568	6633	6620
	2 - 6	7102	7440	7073	7141	7125
	3 - 4	5403	5627	5391	5449	5435
	3 - 5	5997	6296	5985	6037	6024
	3 - 6	6503	6875	6490	6545	6529
$T_{obs.}$	1 - 4	0.4918	0.4823	0.5029	0.4969	0.4840
	1 - 5	0.4915	0.4780	0.5024	0.4972	0.4841
	1 - 6	0.4914	0.4746	0.5022	0.4972	0.4842
	2 - 4	0.4907	0.4784	0.5014	0.4953	0.4831
	2 - 5	0.4905	0.4743	0.5010	0.4959	0.4835
	2 - 6	0.4905	0.4710	0.5010	0.4960	0.4838
	3 - 4	0.4904	0.4736	0.4999	0.4944	0.4823
	3 - 5	0.4901	0.4695	0.4995	0.4950	0.4827
	3 - 6	0.4904	0.4665	0.4998	0.4953	0.4823

TABLE X
AMMONIUM NITRATE/CADMIUM NITRATE SHEARED BOUNDARIES

Run No.	31	32	33	34	35
$C_{\text{NH}_4\text{NO}_3}$ (equiv./l.)	0.09980	0.09987	0.09971	0.09981	0.09992
$C_{\text{Cd}(\text{NO}_3)_2}$ (equiv./l.)	0.08000	0.05798	0.05000	0.07000	0.07001
Mean Current (ma.)	2.2584	3.2078	3.2063	3.2038	3.2120
Time (sec.) 1 - 4		4357	4449	4386	4327
1 - 5		4746	4842	4778	4713
1 - 6		5081	5180	5113	5047
2 - 4	5509	3959	4041	3987	3935
2 - 5	6052	4348	4434	4379	4321
2 - 6	6514	4683	4772	4714	4655
3 - 4	4955	3563	3632	3586	3539
3 - 5	5498	3952	4025	3978	3925
3 - 6	5960	4287	4363	4313	4259
T _{obs.} 1 - 4		0.5178	0.5070	0.5147	0.5210
1 - 5		0.5178	0.5070	0.5147	0.5210
1 - 6		0.5176	0.5072	0.5148	0.5208
2 - 4	0.5284	0.5180	0.5069	0.5147	0.5208
2 - 5	0.5284	0.5181	0.5076	0.5149	0.5210
2 - 6	0.5286	0.5180	0.5078	0.5150	0.5208
3 - 4	0.5285	0.5178	0.5074	0.5148	0.5210
3 - 5	0.5283	0.5179	0.5079	0.5148	0.5210
3 - 6	0.5288	0.5179	0.5084	0.5152	0.5210
Mean	0.5285	0.5179	0.5075	0.5148	0.5209

TABLE XI

AMMONIUM NITRATE/AMMONIUM IODATE SHEARED BOUNDARIES

Run No.		45	46	50	51
CNH_4NO_3 (equiv./l.)		0.04988	0.04988	0.05260	0.05260
CNH_4IO_3 (equiv./l.)		0.03499	0.03499	0.03000	0.03000
Mean Current (ma.)		2.0585	2.0576	2.0570	2.0570
Time (sec.)	1 - 4	3458	3507	3709	3755
	1 - 5	3767	3821	4040	4089
	1 - 6	4032	4090	4324	4376
	2 - 4	3145	3187	3372	3414
	2 - 5	3454	3501	3703	3748
	2 - 6	3719	3771	3987	4035
	3 - 4	2830	2868	3033	3070
	3 - 5	3139	3182	3364	3404
	3 - 6	3404	3451	3648	3691
T- obs.	1 - 4	0.5078	0.5009	0.4996	0.4935
	1 - 5	0.5078	0.5009	0.4997	0.4937
	1 - 6	0.5078	0.5008	0.4996	0.4937
	2 - 4	0.5076	0.5011	0.4996	0.4934
	2 - 5	0.5077	0.5011	0.4998	0.4938
	2 - 6	0.5077	0.5010	0.4998	0.4939
	3 - 4	0.5074	0.5010	0.4997	0.4936
	3 - 5	0.5075	0.5009	0.4997	0.4939
	3 - 6	0.5077	0.5011	0.5000	0.4942
	Mean	0.5077	0.5010	0.4997	0.4937

(d) Autogenic Boundaries

(i) Potassium chloride. The autogenic cell was used with 0.1 N KCl in Runs 36-40 with the machined cadmium anode. The results of Runs 38 to 40 are tabulated in Table XII. The two initial measurements suffered from leaks at the anode and have not been included.

TABLE XII

POTASSIUM CHLORIDE/CADMIUM CHLORIDE AUTOGENIC BOUNDARIES

Run No.		38	39	40
CKCl (equiv./liter)		0.09991	0.09982	0.10005
Mean Current (ma.)		3.1807	2.5528	2.0437
Time (sec.)	1 - 4	4732	5894	7276
	1 - 5	5169	6444	7956
	1 - 6	5607	6993	8634
	2 - 4	4333	5405	6675
	2 - 5	4770	5955	7354
	2 - 6	5208	6504	8032
	3 - 4	3947	4932	6093
	3 - 5	4384	5482	6772
	3 - 6	4822	6031	7450
T _{obs.}	1 - 4	0.4973	0.4971	0.5040
	1 - 5	0.4968	0.4961	0.5030
	1 - 6	0.4958	0.4949	0.5017
	2 - 4	0.4949	0.4940	0.5007
	2 - 5	0.4943	0.4930	0.4998
	2 - 6	0.4938	0.4922	0.4990
	3 - 4	0.4932	0.4913	0.4979
	3 - 5	0.4924	0.4903	0.4968
	3 - 6	0.4925	0.4903	0.4968

Machined cadmium anode used.

(ii) Ammonium nitrate. Autogenic boundaries with 0.05 N ammonium nitrate were investigated in Runs 47, 48, and 49. The data from the latter two are listed in Table XIII, but Run 47 was incomplete.

TABLE XIII

AMMONIUM NITRATE/CADMIUM NITRATE AUTOGENIC BOUNDARIES

Run No.	48	49
$C_{\text{NH}_4\text{NO}_3}$ (equiv./liter)	0.05260	0.05260
Mean Current (ma.)	2.0562	2.0568
Time (sec.) 1 - 4	3840	3843
1 - 5	4185	4189
1 - 6	4533	4533
2 - 4	3494	3499
2 - 5	3839	3845
2 - 6	4187	4189
3 - 4	3170	3169
3 - 5	3515	3515
3 - 6	3863	3859
T_+ obs. 1 - 4	0.4991	0.4986
1 - 5	0.4997	0.4990
1 - 6	0.4994	0.4993
2 - 4	0.4999	0.4990
2 - 5	0.5003	0.4994
2 - 6	0.5002	0.4998
3 - 4	0.5000	0.5000
3 - 5	0.5002	0.5000
3 - 6	0.5007	0.5010

Plated cadmium used.

IV. DISCUSSION

The results of the investigation as presented in the previous section may most readily be considered in the order of presentation of the data.

1. Calibration of the Autogenic Cell

The volumes between graduations on the measuring tubes must be known to the precision desired in the transference numbers. As a check on the volume calibration, the volumes 1-2, 2-3, 4-5, and 5-6 may be obtained from suitable combinations of the directly measured volumes. Thus, the volumes between 6-1 and 6-2, 5-1 and 5-2, 4-1 and 4-2, all differ by the same increment, the volume 1-2. This is shown in Table XIV.

TABLE XIV
AUTOGENIC CELL CALIBRATION DERIVED VOLUMES

Volume Sought	Reference Mark	Volume Calculated ml.	Mean Volume ml.
1 - 2	4	0.0689	
1 - 2	5	0.0691	
1 - 2	6	0.0687	0.0689
2 - 3	4	0.0654	
2 - 3	5	0.0658	
2 - 3	6	0.0649	0.0654
4 - 5	1	0.0707	
4 - 5	2	0.0705	
4 - 5	3	0.0701	0.0704
5 - 6	1	0.0700	
5 - 6	2	0.0704	
5 - 6	3	0.0713	0.0706

With the average value for volumes 1-2, 2-3, 4-5 and 5-6 and with the experimental value of the volume 3-4, each of the nine combinations of volumes may be computed. These calculated volumes are compared with the experimental values in Table XV.

TABLE XV
CALCULATED VOLUMES OF AUTOGENIC CELL

Volume Calibrated	Mean Volume		Difference ml. x 10 ⁴
	Experimental ml.	Calculated ml.	
6 - 1	0.9172	0.9175	3
6 - 2	0.8485	0.8486	-1
6 - 3	0.7836	0.7832	-4
5 - 1	0.8472	0.8469	-3
5 - 2	0.7781	0.7780	-1
5 - 3	0.7123	0.7126	3
4 - 1	0.7765	0.7765	0
4 - 2	0.7076	0.7076	0
4 - 3	0.6422	0.6422	0

The volumes calculated show deviations larger than the probable experimental error, but there is no indication that any one particular volume is in error.

In the present investigation the volume calibrations gained experimentally were used. Any recurring differences may be expected to be readily apparent in a transference number determination.

2. Current Supply

(a) The current regulator

With reference to the data in Table IV, the average deviation from the mean, 0.005%, is entirely negligible in comparison with the probable errors associated with the timing of the motion of the boundary. Comparable stabilization was achieved for currents from 0.4 ma. to 4 ma. The marked improvement of the stabilization over the previous regulator(49) may be attributed to the use of (a) batteries for the screen voltage, (b) higher cathode bias resistor, and (c) higher plate voltages. The removal of the voltage regulator tubes increased the voltage output from the filter section to 775 volts.

Although currents outside the above range were not encountered, higher currents up to the maximum rating of 10 ma. as well as lower currents should be equally well stabilized provided that the voltage drop in the load is not too large. Decrease in regulation is expected when the plate voltage falls below the linear portion of the plate characteristic curves.

(b) The Leeds and Northrup Type K-1 potentiometer

The results of the comparison of the Leeds and Northrup Type K-1 potentiometer (Serial No. 61167) with the Rubicon Type B high precision potentiometer showed that the

potentiometer was reliable in this range within the experimental error. The differences are small and, moreover, random.

The resistors used in series with the moving boundary cell (Table II, this thesis) had been calibrated to better than 0.01 per cent⁽⁴⁹⁾. The currents could thus be determined to at least this accuracy.

3. Ammonium 3,5-Dinitrobenzoate--Conductances, Densities and Solubility

The greater density of the indicator solution and its lower conductivity in comparison with ammonium nitrate satisfy two of the necessary conditions for a stable rising boundary.

The transference and conductance data of MacInnes and Cowperthwaite⁽³⁵⁾ on ammonium chloride and ammonium nitrate showed that the ionic conductance of the ammonium ion in these two solutions at 0.1 N was 63.1 mhos cm^{-2} and independent of the solution. From the conductivity of ammonium 3,5-dinitrobenzoate, the transference number of the 3,5-dinitrobenzoate ion in this solution was estimated to be $(84.0-63.1)/84.0$ or 0.25. This assumes the same degree of ionization as in the solutions of ammonium nitrate and ammonium chloride.

The estimated transference number provided an approximate evaluation of the Kohlrausch indicator concentration. This, with the measured solubility, assured that the use of ammonium 3,5-dinitrobenzoate as an indicator for ammonium nitrate would not be limited by solubility factors.

4. Transference Number Measurements

(a) Potassium chloride/potassium iodate sheared boundaries

The transference numbers of potassium chloride have been well established by independent moving boundary measurements^(2,27). Initial measurements were carried out on this system in the sheared cell in this research to evaluate the overall method of procedure and performance of the apparatus. The transference number of the chloride ion in 0.1 N potassium chloride obtained in this work was 0.5101 ± 0.0003 (Runs 1 to 4, Table VII). This value agrees well within the limits of experimental error with the best literature value, $0.5100^{(2)}$ and $0.5102^{(27)}$. In these runs, each determination showed no progression, was self-consistent, and showed that the apparatus was capable of measurements of the desired precision.

During the course of the investigation, additional measurements (Runs 24, 41 to 44, and 52) were made to check on the apparatus and performance. Of these, the

results of Run 41 (0.5099) compared favorably with the established value, 0.5097⁽²⁷⁾ and 0.5098⁽²⁾. The remaining runs also were self-consistent and showed no progression but the transference numbers varied from the literature value by more than the probable experimental error. A consideration of each of the factors entering into the determination of the transference number did not account for the observed discrepancy. The current measurement was shown to be reliable to 0.01 percent (page 80, this thesis). Any shunting of the current caused by the relatively high resistance of the transference cell would result in a lower value rather than the higher values found. Moreover, the use of oil in the thermostat and the shielding of all current leads in glass tubing made any stray current leaks unlikely. The observed discrepancies are too large to be attributed to errors in the concentration.

Some reservations must, therefore, be placed on the results with ammonium nitrate solutions in this work. The results are not conclusive quantitatively but, nevertheless, must be considered to be qualitatively valid. Only a more detailed experimental analysis of the factors can be expected to resolve the observations.

(b) Ammonium chloride/ammonium 3,5-dinitrobenzoate
sheared boundaries

To investigate the ammonium 3,5-dinitrobenzoate indicator, some measurements with a salt other than ammonium nitrate with a known transference number was desirable. If no progression in the observed transference number was obtained, the 3,5-dinitrobenzoate ion would be suitable for indicator use. For this purpose, ammonium chloride was chosen. Longworth⁽²⁸⁾ reports the transference number of the chloride ion in 0.1 N ammonium chloride as 0.5093 at 25°C.

Inspection of the results (Runs 19 and 23, Table XI) shows that the velocity of the ammonium chloride/ammonium 3,5-dinitrobenzoate boundaries remained constant and did not undergo a progression. However, the anion transference numbers (0.5117 and 0.5158) were high. This indicates that the indicator concentration was not within the adjustment range, but suggested that this indicator could be satisfactory if adjustment were obtained.

The preliminary investigations of ammonium nitrate/ammonium 3,5-dinitrobenzoate was extended in view of these results. This is discussed in the next section.

(c) Ammonium nitrate sheared boundaries

(1) Ammonium 3,5-dinitrobenzoate indicator. Among the requirements for a satisfactory boundary, as discussed earlier, is constancy of velocity of the boundary under a constant potential gradient. Experimentally, this is achieved when the conditions of the Kohlrausch ratio are fulfilled. Varying concentrations of ammonium 3,5-dinitrobenzoate as indicator solution for 0.1 N ammonium nitrate sheared boundaries were studied to obtain the concentration within the adjustment range. The results of Runs 11 to 18, in which the concentrations 0.095 N to 0.01 N were investigated, clearly showed that adjustment did not occur with any of the concentrations used. These runs were made before the measurement of the conductance of ammonium 3,5-dinitrobenzoate (Table VI) or Runs 19 and 23 (Table VIII) on ammonium chloride were made. In Runs 20, 21, and 25 to 30, the most promising concentration range was carefully re-investigated.

In each of the fifteen experiments covering a regularly varied indicator concentration, the velocity of the boundary showed a continuous decrease as the boundary moved up the tube. Constancy is approached near the end of the runs. The adjustment can be expected to have occurred to the greatest extent by the time the boundary has moved well up the tube.

The indicator concentration in the system potassium bromide/potassium iodate has been reported to be very critical. Keenan and Gordon⁽²⁰⁾ observed that for 0.05 N potassium bromide, the anion transference number agreed with that required by the autogenic cation transference number at only one concentration of the indicator solution. Moreover, it was only at this particular indicator concentration that the observed anion transference number was independent of the current. At concentrations of 0.07 N and 0.10 N potassium bromide, no indicator concentration could be obtained giving transference numbers independent of the current.

In the present work, the exact concentration of ammonium 3,5-dinitrobenzoate necessary to achieve indicator adjustment in a transference measurement was not achieved. These results suggest that the situation in this system is quite similar to that observed with potassium bromide⁽²⁰⁾. The initial concentration of the ammonium 3,5-dinitrobenzoate solution is quite critical and the indicator adjustment range is very limited. Further measurements to re-investigate the most promising concentration range (0.04 N to 0.06 N) would be of interest with respect to this point.

(ii) Cadmium nitrate indicator. The autogenic cell with a cadmium anode gives rise to a boundary similar to that which would be formed by using the cadmium salt with anion in common with the leading solution. Automatic adjustment of the indicator concentration normally occurs in the autogenic boundary.

The primary information sought -- that suitable boundaries without progression could be formed with ammonium nitrate using cadmium nitrate as indicator-- was established in Runs 31 to 35 (Table X) in the sheared boundary cell. In these, the Kohlrausch indicator concentration calculated from approximate transference number data to be between 0.05 N and 0.08 N cadmium nitrate, was not observed. This showed that the automatic adjustment of the indicator in autogenic cells is an important advantage. The boundaries with ammonium nitrate were sharp and of sufficient quality to warrant the use of the autogenic cell.

(iii) Ammonium iodate indicator. The transference number determinations of 0.05 N ammonium nitrate using ammonium iodate indicator (Runs 45, 46, 50, 51 Table XI) satisfy the criterion of constant velocity under a constant potential gradient. The second criterion of independence of the observed transference number with current density has not been achieved. The results of the autogenic cell

measurements (section (ii) following), however, show that the indicator concentration used lies very nearly in the apparently narrow adjustment range. Small variations of indicator concentration from that in the above runs may be expected to result in complete adjustment to the Kohlrausch concentration.

(d) Autogenic cell

(i) Potassium chloride. Autogenic boundaries have the distinct advantage that the indicator solution, formed by the electrolytic dissolution of the anode, is automatically adjusted to the proper concentration⁽⁴¹⁾. The results of the measurements (Table XII) of 0.1 N potassium chloride in the autogenic cell showed a continual decrease in the measured cation transference number. Since the indicator adjustment is automatic, this effect may not be attributed to lack of adjustment.

The most probable source of error lies in the anode. Low values may result from any leakage of solution at the electrode. The constant difference observed between the values obtained in Runs 39 and 40 does not favour a random error of this nature. Impurities in the cadmium anode may, however, lead to decreased boundary velocity as shown by considerations of polysalt boundaries by Longsworth⁽³²⁾ and Dole⁽¹¹⁾. Those impurities which give rise to ions faster

than cadmium would be particularly harmful since the leading solution would become progressively contaminated.

(ii) Ammonium nitrate. A marked improvement in stability of the boundary was observed in the autogenic boundary measurements when the plated cadmium anode was used (Runs 48 and 49, Table XIII). Moreover, the measured transference numbers were reproducible within the experimental precision. Carefully controlled electroplating from a cyanide bath may be expected to give a cadmium deposit of high purity.

These results of the transference number measurements with the autogenic cell upholds the advantage obtained from automatic adjustment of the indicator concentration. With a suitable electrode, the autogenic cell appears to be the most promising means of obtaining the desired transference numbers of ammonium nitrate.

V. CONCLUSIONS

Transference number measurements by the moving boundary method are greatly facilitated by using a constant current during the electrolysis. A current regulator for this purpose capable of maintaining currents of 0.4 ma. to 4 ma. constant to 0.01 per cent has been constructed.

Additional moving boundary cells were desirable for use in the indicator search for ammonium nitrate and for the direct determination of the cation transference number of ammonium nitrate. An air-lock cell, capable of rapid qualitative investigations of rising sheared boundaries has been designed and assembled. An autogenic moving boundary cell has been graduated, assembled, and calibrated for quantitative measurements.

Moving boundary measurements have been undertaken with ammonium nitrate solutions. Ammonium 3,5-dinitrobenzoate as an indicator produces a sharp rising boundary. The indicator concentration adjustment range was shown to be extremely critical and was not observed. Rising anion boundaries showing no progression are formed with ammonium iodate.

Autogenic boundary cells have the advantage of automatic adjustment of the indicator concentration. Rising cation boundaries of good visibility can be obtained with ammonium nitrate and cadmium nitrate as the leading and indicator electrolytes respectively. With suitable cadmium anodes, autogenic boundaries show the most promise for the determination of the transference numbers of dilute aqueous solutions of ammonium nitrate.

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