

THE MOVING BOUNDARY METHOD FOR DETERMINING
TRANSFERENCE NUMBERS

by

L. G. Longworth,

A. B. - Southwestern College, 1925

M. A. - University of Kansas, 1927

Submitted to the Department of
Chemistry and the Faculty of
the Graduate School of the
University of Kansas in partial
fulfillment of the requirements
for the degree of Doctor of
Philosophy.

Approved by:-

H. P. Cady
Instructor in Charge

May 15, 1928

H. P. Cady
Head or Chairman of Dept.

The opportunity is taken
at this point of thanking Dr. H. P. Cady,
under whom this thesis was worked out,
for the helpful suggestions and kind
assistance so graciously given.

TABLE OF CONTENTS

	Page
BIBLIOGRAPHY	i
TABLE OF SYMBOLS	iv
INTRODUCTION	1
HISTORICAL	6
THEORETICAL	11
Conditions and Restrictions	11
The Diffusion Layer	21
Derivation of Equations	23
Analysis of Results	24
EXPERIMENTAL	31
Preliminary	31
Tables of Preliminary Results	37
Description of Apparatus	40
Method of Recording Results	44
Anion Margins	49
Acetic Acid as Solvent	51
Results in Acetic Acid	60
Discussion of Results	61
SUMMARY	62

BIBLIOGRAPHY

1. "Moving Boundary Method for the Determination of Transference Numbers". A novel form of apparatus. MacInnes and Brighton, J.A.C.S. 47, 994, (1925)
2. "The Transference Numbers of Some Chloride Solutions" MacInnes and Smith, J.A.C.S. 47, 1009, (1925)
3. "Accurate Measurement of Ionic Velocities, with Applications to Various Ions" Denison and Steele, Philosophical Trans., 205, 449, (1906)
4. "Moving Boundary Method for Determining Transference Numbers" Smith and MacInnes, J.A.C.S. 46, 1398, (1924)
5. "Ionic Velocities" Masson, Philosophical Trans., 192, 331, (1899)
6. "Theory of the Determination of Transference Numbers by the Method of Moving Boundaries" G. N. Lewis, J.A.C.S. 32, 862, (1910)
7. "New Method for the Measurement of Ionic Velocities in Aqueous Solutions" B. D. Steele, Journal Chemical Soc. (London) 79, 414, (1901)

8. "Moving Boundaries and the Phase Rule"
E. R. Smith, J.A.C.S. 47, 795, (1925)
9. "Ionic Velocities"
W. C. Whetman, Philosophical Trans., 337, (1893)
10. "Ionic Velocities" Second Article
W. C. Whetman, Philosophical Trans., 186, 507, (1895)
11. "Moving Boundary Method for Determining Transference Numbers"
Smith and MacInnes, J.A.C.S. 46, 2246, (1923)
12. "Ion Velocities in Liquid Ammonia"
Franklin and Cady, J.A.C.S. 26, 499, (1904)
13. "The Theory of the Direct Method of Determining Transport Numbers"
W. Lash Miller, Zett. Fur Phys. Chem., 69, 436, (1909)
14. "Migration of Ions in Aqueous Solutions"
R. B. Denison, Trans. of the Faraday Society, 5, 165, (1909)
15. "Discussion of the Direct Method for Measuring Ionic Velocities"
Abegg and Gause, Zeit. fur Phys. Chem., 44, 575, (1903)

16. "Discussion of the Direct Measurement of Transport Numbers"
R. B. Denison, Zeit. fur Phys. Chem., 44, 575, (1903)
17. "The Measurement of Ionic Velocities in Aqueous Solution, and the Existence of Complex Ions"
B. D. Steele, Philosophical Trans., 198, 105, (1902)
18. "Application of the Phase Rule to Galvanic Cells"
J. A. Beattie, J. A. C. S., 46, 2211, (1924)
19. "Mathematical Theory of the Changes of Concentration on Electrolysis"
Miller and Rosebrough, J. Phys. Chem., (1910)
20. "Concentration at the Electrode in a Solution"
Sand, Philosophical Magazine, 6, 1, 45, (1901)
21. "The Moving Boundary Method for Determining Transference Numbers. A Constant Current Apparatus"
MacInnes, Cowperthwaite, and Blanchard, J.A.C.S., 48, 1909, (1926)
22. "The Moving Boundary Method of Determining Transference Numbers", MacInnes, Cowperthwaite, and Huang, J. A. C. S. 49, 1710, 1927

Symbols Employed and their Significance,

- A = cross sectional area in square centimeters.
- C = concentration in gram equivalents per liter.
- c = concentration in gram equivalents per c.c.
- E = electromotive force in volts.
- F = the Faraday equivalent = 96,500 coulombs.
- γ = degree of dissociation.
- I = the current (constant) in amperes.
- i = the current (variable) in amperes.
- k = specific conductance = conductance in mhos of a solution placed between opposite insulated faces of a centimeter cube.
- L = conductance in mhos.
- Λ = equivalent conductivity.
- m = number of ions into which an electrolyte dissociates.
- μ = molecular conductivity = conductance in mhos of a solution containing one gram mole of solute when placed between two parallel electrodes 1 cm. apart and of indefinite area.
- N = volume normality
- n = total charge associated with the cation constituent.
- n_c = the cation transference number.
- n_a = anion transference number = $1 - n_c$.

R = resistance in ohms.

R_0 = specific resistance = reciprocal of specific conductance.

R = gas constant in calories per degree.

T = absolute temperature.

t = time in seconds.

U_{c+} = velocity of cation under unit potential slope.

U_{c-} = velocity of anion under unit potential slope.

U_c = velocity of cation constituent under unit potential slope.

U_a = velocity of anion constituent under unit potential slope.

u_c = observed velocity of cation constituent.

u_a = observed velocity of anion constituent.

x = distance in centimeters.

Fundamental Relationships,

$$E = IR$$

$$u_c = U_c \frac{dE}{dx} = \frac{U_c}{U_{c+}} \frac{dE}{dx}$$

$$C = 1000 \text{ c}$$

$$\mu = n \Lambda$$

$$\Lambda = 1000 \kappa / C$$

$$R = R_0 x / A$$

$$L = \kappa A / x$$

INTRODUCTION

The conduction process in metals and in solutions of electrolytes, that is, in conductors of the first and second class respectively, is essentially different. In the first case the assumption is generally made, and is justified experimentally that the free electrons within the metal, which seem to be chiefly responsible for the common metallic properties of the metals, are the sole carriers of the electric current and it is the motion of these charged particles with respect to the stationary crystal lattice of the metal that constitutes the passage of a current through the metal. The Waterman equilibrium theory of metallic conduction presents the most acceptable picture of metallic conduction, to the chemist at least, since it assumes an equilibrium between metal atoms, metal ions, and free electrons, analogous completely to the Ostwald dilution law for electrolytic conduction. The relatively high ratio of charge to mass of the free electrons compared with the metal ions and the crystal forces bearing upon these metal ions prevent them from sharing in the conduction process as do the cations in solutions

of electrolytes and the anions, or electrons, are the sole carriers.

In second class conduction, free electrons are absent, and it is the simultaneous motion of two different kinds of electricity in opposite directions and very often at quite different rates which constitutes the passage of the current through a conductor of the second class, and it is this difference in the conduction process in the two classes of conductors which lead to such phenomena as are always observed at the interface between a conductor of the first and a conductor of the second class. The two kinds of electricity set in motion in an electrolytic conductor upon the application of an electric field are associated with relatively large masses and the frictional resistance of these charged bodies or ions is very large compared with that of the very minute free electrons of metals, thus accounting for the lower order of magnitude of the conductivity of solutions of electrolytes compared with that for metals. But it is just these things, the relative sluggishness of the current carriers, and the optical properties of these systems which contain no free electrons, that make investigation of these conductors

more accessible. The general subject of the present paper deals with a particular method of ascertaining the velocities with which these current carriers move. One point on which the two processes do not differ, however, is the fact that an adequate theory for either type of conduction has not been developed as yet. In the one field theories differ as to whether the number or mean free path of the conducting electrons is variable or whether both vary, while in the other the dilution law of Ostwald clashes with the inter-ionic attraction theories of Debye, Hückel, and Onsager.

There are three different methods of measuring the transport numbers and the ratio of ion velocities in second class conductors. The Hittorf or gravimetric method is the oldest chronologically and depends on the quantitative analysis of either the anolyte or catholyte before and after the passage of a definite quantity of electricity, to determine which species of ion has carried that fraction of the total quantity into or out of this region. The moving boundary method depends on the absolute motion of the solvated ions and in the method whereby both cation and anion boundaries are accounted

for, a solution of the electrolyte whose transference numbers are being determined is placed between two other solutions of electrolytes in the same solvent. On the passage of a current the cations of all three solutions begin moving toward the cathode and the anions toward the anode. If the two end solutions fulfill certain conditions there will be a discontinuity or boundary between the cations of the central electrolyte and the trailing or indicator cations of the outer electrolyte, and similarly for the anions at the other junction. The third general method for the determination of transference data is by the measurement of the electromotive force of concentration cells with and without diffusion. The difference of potential set up at the junction of a solution of the same electrolyte at two different concentrations is caused by the difference in the rates of migration of the two ions, the more dilute solution acquiring a charge corresponding to that of the ion with the greater velocity. A possible fourth method has occurred to the author. If a strong magnetic field could be impressed across an electrolyte carrying a current, the stream lines of current represented by the ions in motion would be deflected to one side

and this deflection would continue until the diffusion potential from the side of higher concentration just balanced (plus a second effect to be considered shortly) the deflecting force of the magnetic field. Suitable electrodes placed on opposite sides of the tube containing the electrolyte might then register the potential of this concentration gradient. Superimposed upon this concentration potential, there would be a potential due to the space charge from the fact that the slower species of ions would not be deflected as much as the faster species, account being taken of their relative masses - this second effect would be completely analogous to the Hall effect in first class conductors. If this second potential could be differentiated from the first it would give us immediately the relative velocities of the two ionic species.

HISTORICAL

The possibility of measuring the velocity of ionic migration directly by the observation of the displacement of a plane of separation between two ionic species originates with Sir Oliver Lodge, and his experiments utilizing this idea are recorded in the British Association Reports of 1886. Whetman,^{9,10} in two papers dated 1893 and 1895 respectively, improves somewhat on the method of Lodge by avoiding the use of gelatine. To accomplish this he arranged the specifically lighter solution over the heavier one in a vertical tube, choosing the two solutions such that the potential gradient in the tube would be as nearly uniform as possible and consequently amenable to calculation from the potential drop across the entire tube. He was the first to realize the necessity of the indicator ion being specifically slower than the ion whose velocity was being measured if the boundary was to remain sharp.

The chief contribution of Orme Masson in⁵ perfecting and developing the method was in making available for observation a wider range of substances.

He reverted back to the use of gelatine for initial formation and maintenance of the boundaries and depended upon colored indicators for the location of the margin. He observed both anion and cation boundaries simultaneously and hence no measurements of current or assumptions regarding distribution of potential were necessary. He showed, theoretically and experimentally, that the concentration of the indicator ions was automatically adjusted behind the boundary to such a value that the potential gradient acting on the indicator ions was just sufficient to cause them to keep pace with the boundary.

3, 7, 14, 16, 17

Denison and Steele, working both individually and together over a period of years from 1902 to 1909, then developed and refined the method to such a point that the transport numbers obtained by its use were of the same order of accuracy as those determined by the Hittorf method. In their first article they describe an extension of the method in two directions, first, the substitution of aqueous for gelatine solutions, and second, the location of the margin as a result of

the different indices of refraction on the two sides of the margin, thus rendering available colorless indicator ions. At first their margins were initially formed with the aid of a gelatine partition but Abegg and Gaus¹⁵ showed that endosmosis and cataphoresis took place at this partition, and henceforth Dennison and Steele used a purely mechanical method of initially forming the boundary. Steele found that it was only over a comparatively narrow range of potential gradients that their boundaries were stable, although there was no theoretical justification for this restriction. With the refinements which these men introduced in the formation, maintenance, and detection of the boundary, the results obtained by them compared very favorably with the "best" Hittorf values and the agreement was still better after Miller and Lewis¹³ in 1910 showed that a correction must be applied to the results of Dennison and Steele, taking into account the volume changes at the electrodes.

The work of Franklin and Cady¹² in liquid ammonia as solvent which was reported in 1904 has a more direct bearing on the present research than any other, since they were the first to use

ascending boundaries with an anode soluble under the action of the electric current as the source of indicator ions. They derived the equation for the velocity and transport number of a given ion from observations upon a single boundary and were the first to utilize this method quantitatively in a non-aqueous solvent.

From 1910 to 1923 the method of moving boundaries lay unused until in the latter year Smith and MacInnes² published the results of their preliminary studies on this method. In their effort to extend and amplify the work of Denison and Steele they encountered difficulties in obtaining reproducible results unless the concentration of the indicator ion was previously adjusted to the value demanded by the relation $c/c' = N_c/N_c'$ which will be derived in a subsequent paragraph. Kohlrausch derived this relation in an early paper and predicted the adjustment to these relations would automatically take place, which automatic adjustment was found to take place by Denison and Steele.

The subsequent work of MacInnes and co-

1, 2, 4, 8, 11, 21, 22
workers would indicate that with the experimental conditions under which they were operating, this automatic adjustment of the indicator ion concentration does not take place except when the concentration of the indicator solution is previously adjusted to within approximately 5% of the value required by theory. Within these comparatively narrow limits the automatic adjustment predicted by Kohlrausch actually does take place. According to these authors, once the adjustment of the indicator concentration has been effected, the boundary is stable throughout a large range of potential gradients. Denison and Steele were restricted in the potential gradient employed without theoretical justification while MacInnes and co-workers are similarly restricted in the case of the indicator ion concentration. It should be noted before leaving this brief review of the work by these men that they have worked entirely with descending boundaries and any automatic concentration adjustment which might have taken place would be susceptible of destruction by gravity currents. Their results, however, represent the highest accuracy yet obtained by this or any other method for that matter.

THEORETICAL

We have found that, with one or two exceptions, a boundary which travels with a uniform velocity under a constant potential gradient or where the change of velocity is proportional to the change in the potential gradient is one whose velocity can be relied upon to give the true velocity of the preceding ion constituent. For the production and maintenance of a good boundary, Franklin and Cady¹² prescribe the following conditions, and they will here be taken up and discussed in some detail.

1. The indicator ion and indicator ion constituent must be specifically slower than the ion whose speed is being measured. If the indicator ion was faster than the ion under observation, the potential gradient in the indicator solution would be lower than that in the preceding solution (assuming a common ion of opposite charge and equal concentrations in both solutions), and once an indicator ion had crossed the surface of separation of the two solutions thus passing into a region of higher potential, its velocity would be

increased, it would pass the ions it was supposed to trail, diffusion of the two phases would result and the boundary destroyed. If, on the other hand, the following ions were specifically slower, the distribution of gradient would be reversed and, if an indicator ion penetrated the preceding solution, the gradient acting on it would be lessened and it would lag behind until it fell back of the boundary into a region of such potential slope that it could keep up with the boundary.

Experimental evidence of the justification of this condition is found in the case of thalous ion as indicator for the potassium ion. In water the Tl^+ ion is very slightly faster than the K^+ ion and the former would not serve as an indicator for the latter, whereas in anhydrous acetic acid as solvent the reverse is the case and a boundary, though not very sharp, was still observable.

2. If the meniscus is to travel up the tube, then the indicator solutions must be heavier than the superimposed solution. Most of the work performed in this research was upon ascending boundaries with anodes soluble under the action of the electric current as the source of indicating

ions and the necessity of this restriction was apparent on several occasions. Let the boundary in question be that between two different cation constituents travelling with the current and matched by anions, all of one kind, travelling against it. Since the current in the circuit is the same throughout,

$$C'FA (u'_c + u'_a) = CFA(u_c + u_a) = 1000I(1)$$

but at the boundary $u'_c = u_c$

$$\begin{aligned} \frac{C'}{C} &= \frac{u_c + u_a}{u'_c + u'_a} \cdot \frac{u'_c}{u_c} \quad \text{since} \quad \frac{u'_c}{u_c} = 1 \\ &= \frac{u_c + u_a}{u_c} \cdot \frac{u'_c}{u'_c + u'_a} = \frac{N'_c}{N_c} \end{aligned} \quad (2)$$

and we have here the derivation of a condition previously mentioned. This relation also emphasizes the point that when comparing the specific gravities of the preceding and following solutions, equimolar concentrations must not be compared, but the adjusted concentrations. Thus, $\text{Cu}(\text{NO}_3)_2$ is specifically heavier than KNO_3 at equal concentrations but at the adjusted concentrations which occur in a moving boundary experiment the specific gravity of KNO_3 at C is slightly greater than the specific

gravity of $\text{Cu}(\text{NO}_3)_2$ at C' , which accounts for the fact that the blue color of the Cu^{++} ion diffused rapidly through the tube when the attempt was made to utilize this ion as indicator for the potassium ion in 0.1 N potassium nitrate.

3. The current must not be strong enough to develop so much heat that the boundary will be distorted or destroyed. This is an extremely important restriction and, although convection currents are not amenable to quantitative treatment, the qualitative conclusions are of considerable significance. MacInnes and co-workers²² have drawn the conclusion, from experiments with ascending boundaries utilizing the permanganate ion as the indicating anion, that the type of boundary is impracticable due to convection currents in the indicator solution. The specific resistance of the adjusted indicator solution is greater than that of the observed solution, the magnitude of this difference depending on the relative velocities of the following and preceding ions, and consequently the heat developed (the I^2R) in this portion of the tube is greater than that in the other portions of the tube.

Convection currents undoubtedly alter the boundary velocity at high current densities and this is evidenced by the extreme convexity of the margin and its acceleration under a constant potential gradient, but at low current densities the boundary is remarkably flat and its specific velocity independent of the current density over a considerable range, if indicator ions are properly chosen. That these conclusions are correct will be shown later in connection with the experimental part. For the present it will suffice to say that it may become necessary on occasion to determine the boundary velocity at a series of concentrations and extrapolate to zero current density where convection currents could not possibly effect the progress of the boundary.

4. The fall of potential along the tube must be large enough to bring out a good meniscus. There seem to be two factors affecting the sharpness and ease of detection of a refraction margin, firstly, the difference in the indices of refraction of the two solutions forming the boundary, this being roughly proportional to the difference in specific gravities of the two solutions, and secondly, the

relative velocities of the preceding and indicator ions. The plane of separation of the two solutions is not a mathematical plane, that is to say, the optical characteristics of the two solutions forming the boundary do not suffer an abrupt change at the boundary but the optical properties of the one merge more or less gradually into those of the other. The electrolyte in each phase has a certain tendency to diffuse into the other phase, which tendency is counteracted only by the potential drop in the two phases at the boundary. The method of detecting the boundary is to move a black opaque screen vertically on an illuminated ground glass background with the apparatus, in which the boundary is ascending, between the eye of the observer and this background until the black-white margin on the screen is sustained by the refraction margin. If the black-white edge is then still further lowered the refraction margin appears as a sustained black line, due probably to total reflection, since the edge is well within the critical angle for the boundary in which the medium of lower index is above and into which the light from the edge of the

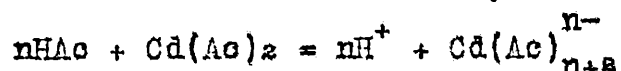
screen does not penetrate. If experimentally possible it would be interesting to determine the ellipticity of the light reflected from this interface when the incident light is plane polarized at 45° and, hence, the thickness of the transition layer between the two media. In any event, it is an experimental observation that the boundary sharpens with increasing current density and that the more nearly the velocities of the preceding and indicating ion constituents are to each other the higher the current density necessary to bring out a sharp refraction margin.

5. The electrode action must be such as not to introduce new ions, faster than the ones being measured. Two methods are usually employed in overcoming the possibility of electrode reactions introducing ions faster than the ions under observation. The one is to so construct the apparatus that the tube in which the boundary moves is far removed from the electrodes, thus minimizing the possibility of ions formed at the electrode penetrating the solution being observed and altering the boundary velocity. The other method used in combination with the above is to make the electrodes of such materials and dipping

into such solutions that there is no gas evolution and either no ions of high velocity are formed or, if formed, they are disposed of before leaving the immediate neighborhood of the electrode. Particular types of electrodes are described in the experimental part.

6. The electrolyte furnishing the indicator ion must not be subject to hydrolysis since, if this occurred to any appreciable extent, there would be released either H^+ or OH^- ions, the two fastest ions, and although these ions would not destroy the boundary, they would penetrate the preceding solution, rendering this an isohydric solution, and the velocity of the margin would lose its significance. This, moreover, is one case in which a margin can travel with a velocity strictly proportional to the potential gradient acting on the preceding solution and yet not measure the true velocity of the preceding ion constituent. Cadmium as indicator for K^+ in KNO_3 gave small but consistent deviations and this was ascribed to a slight hydrolysis of the $Cd(NO_3)_2$ forming the indicator solution. With cadmium as indicator for the K^+ in KAc in anhydrous acetic acid as solvent, the boundary velocities were consistently low though moving with uniform

velocity. Complex ion formation, which certainly characterizes cadmium salts in water, of a type



would account for the behavior of Cd in acetic acid. Another example was furnished by the attempt to utilize Hg as a source of indicator ions for the K^+ ion in KNO_3 . The hydrolysis occurring here was so marked as to slow down the $\text{Hg}^{++}/\text{K}^+$ margin very materially.

7. The potential slope of that portion of the tube in which the boundary moves must be known, and this is readily ascertained from the specific conductivity of the solution when no concentration changes take place in the solution. Kohlrausch has shown that unless an initial concentration difference and a variation of transference ratio with concentration both exist simultaneously, prolonged electrolysis will not alter the concentration of that portion of any second class conductor far enough removed from the electrodes to be able to neglect diffusion effects from these. Such are the conditions under which the observed solution is electrolyzed in a moving boundary experiment and, since the specific resistance of this solution is known and remains constant throughout the experiment,

(since the concentration remains constant and uniform) the potential gradient in this solution is readily calculated from this resistance and the total current in the circuit.

$$\begin{aligned}
 E &= IR \\
 R &= \frac{x}{KA} \\
 E &= \frac{Ix}{KA} \\
 \frac{dE}{dx} &= \frac{I}{KA} \qquad (3)
 \end{aligned}$$

8. In the case where soluble electrodes are used in the initial formation of the boundary and as a source of the indicating ions, a further restriction must be imposed that the electrode material must be pure, entirely soluble, and no other electrode reactions take place than the one wherein the indicating ions are generated. The necessity of this restriction is apparent when we consider the possibility of a discharge of one of the ions of the solvent with subsequent gas evolution and disruption of the boundary by ascending bubbles of the gas. It has been noted in the use of certain metals as anodes, that, as the electrolysis was continued and the concentration of the ion reversible with respect to that metal continued to increase around the

electrode, the electrode potential was built up to such a value that gas evolution took place with a resulting destruction of the boundary. Further, the electrode reaction must not give rise to any ions faster than the ions under observations, an example of the results of a violation of this restriction being offered by the attempt to make the second class electrode $\text{Ag} - \text{AgBrO}_3$ a source of the indicating anions, BrO_3^- . A partial reduction of the bromate to bromide must have taken place in addition to the expected reduction of the silver ion since the boundary, $\text{NO}_3^-/\text{BrO}_3^-$, moved abnormally slowly.

In this method of moving boundaries which observes but a single boundary and uses a soluble electrode as the source of indicator ions, the passage of 1 faraday brings about the solution of one equivalent weight of the metal (in the case of a boundary between cations) as ion. Of this amount passing into the ionic state only n'_c equivalents are transported away from the electrode by the electrolyzing current, leaving $1 - n'_c$ or n'_a equivalents, electrically compensated by the downward migration of n'_a equivalents of the common anion into this region. This accumulation of electrolyte

next to the electrode is taken care of entirely by diffusion (possibly convection at higher current densities) and, since this diffusion layer is characteristic of this particular adaptation of the moving boundary method it was considered necessary to investigate this more in detail. Resort was had to a solution of Fick's diffusion law^{19,20} by means of Fourier series and the equation finally obtained was,

$$C = C_0 + \frac{G}{\sqrt{\pi k}} \int_0^t \frac{1}{\sqrt{t}} e^{-\frac{x^2}{4kt}} dt$$

where k = diffusion coefficient of electrolyte in question

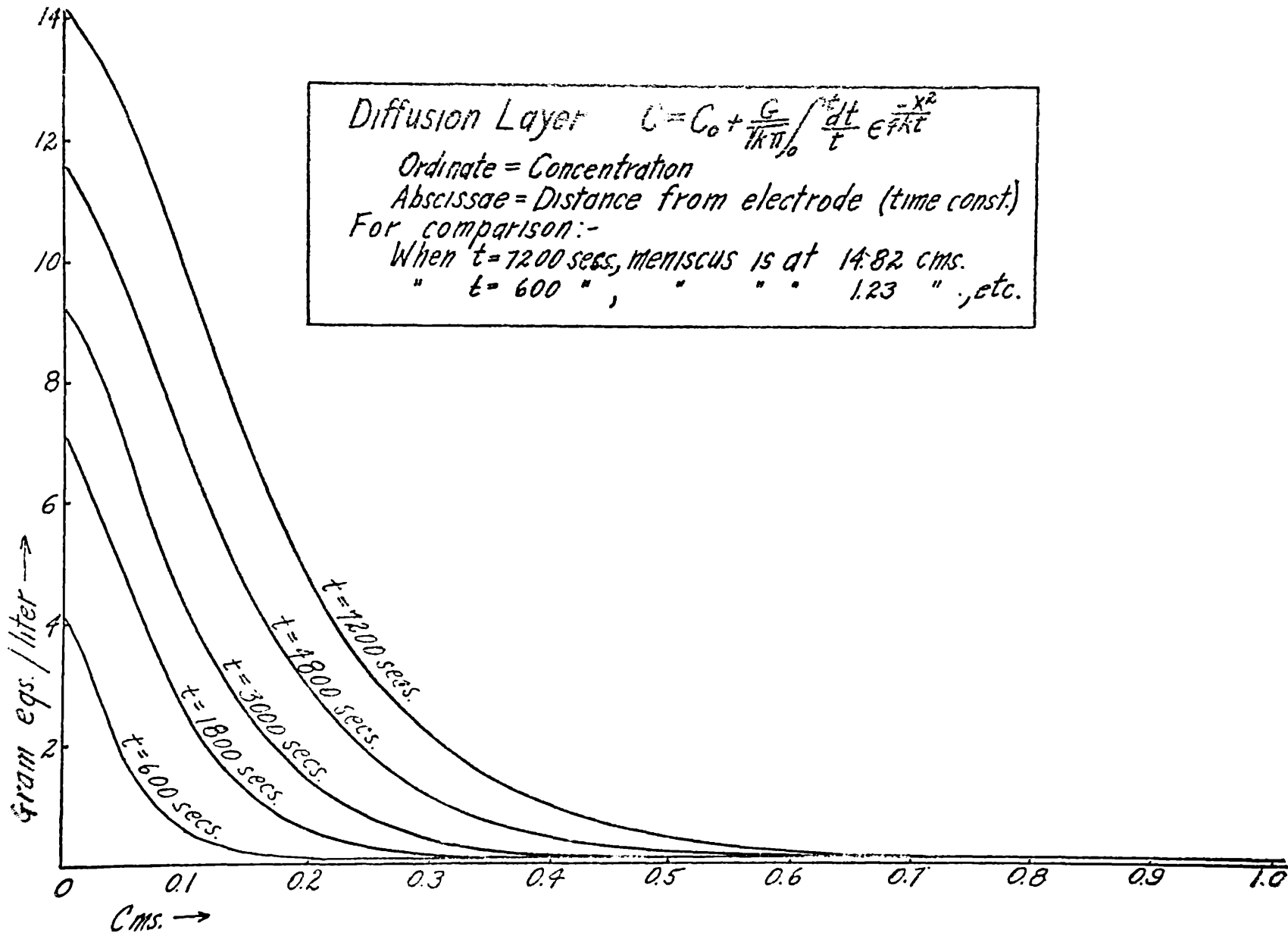
$$G = \frac{I(1 - n_c)}{FA}$$

x = distance from electrode

t = time

C_0 = initial concentration.

The accompanying plot, Figure I, of this equation for a typical case shows that at no time (in aqueous solutions, at least) does diffusion from the electrode alter the adjusted concentration of the indicator ion behind the boundary since by the time the edge of the diffusion layer has advanced a few mm. the boundary will have advanced several centimeters.



22-9

The equations used in calculation of results are most easily derived from the general equation (1).

$$I = cAF(u_c + u_a) \quad (1)$$

$$\frac{u_c}{u_c + u_a} = \frac{u_cAFc}{I} = n_c$$

$$u_c = \frac{x}{t} \quad (4)$$

$$n_c = \frac{xCAF}{It} = \frac{xCAF}{1000It} \quad (5)$$

$$u_c = u_c \frac{dE}{dx} = \frac{u_c I}{kA} \quad (6)$$

$$u_c = \frac{kAx}{It} \quad (7)$$

Since the total resistance of the cell increases as the boundary ascends the tube, as the indicator ion constituent must be specifically slower, a rheostat resistance in the circuit must be continually decreased and the time rate of this decrease is indication of the velocity of the indicator ion constituent and, hence, its transport number. Consider a tube of length l in which the boundary is at a position x cms. from the bottom of the tube, then

$$R_{\text{tube}} = R_{l-x} + R_x, \text{ assuming } I \text{ constant,}$$

$$R = \frac{x}{kA}, \quad k = \frac{u_c It}{Ax} \quad (7)$$

$$n_c = \frac{xCAF}{It} \quad (5)$$

Eliminating between (5) and (7)

$$k = \frac{c u_c F}{n_c}$$

$$R_{tube} = \frac{l-x}{hA} + \frac{x}{h'A} = \frac{(l-x) n_c}{c u_c F A} + \frac{x n_c'}{c' u_c' F A} \quad \text{but } \frac{n_c}{c} = \frac{n_c'}{c'}$$

$$R_{tube} = \frac{l n_c}{c u_c F A} - \frac{x n_c}{c u_c F A} + \frac{x n_c}{c u_c' F A}$$

$$\frac{dR}{dx} = \frac{n_c}{c F A} \left(\frac{1}{u_c'} - \frac{1}{u_c} \right) = \frac{n_c}{c F A u_a} \left(\frac{u_a}{u_c'} + 1 - \frac{u_a}{u_c} - 1 \right)$$

$$= \frac{n_c}{c F A u_a} \left(\frac{1}{u_c'} - \frac{1}{u_c} \right), \quad \text{solving for } n_c'$$

$$n_c' = \frac{n_c}{1 + c F A u_a \frac{dR}{dx}} \quad (9)$$

$$\text{But } \frac{dR}{dx} = \frac{dR}{dt} \frac{dt}{dx} \quad \text{and} \quad \frac{dt}{dx} = \frac{c A F}{I n_c}, \quad u_a = u_c \frac{n_a}{n_c} = u_c \frac{1-n_c}{n_c}$$

$$n_c' = \frac{n_c}{c^2 A^2 F^2 u_c \frac{1-n_c}{n_c^2 I} \frac{dR}{dt} + 1} \quad (10)$$

Note:- See page 25-4

Equations (9) and (10) are alternative forms of the same equation depending on whether one wishes to determine the $\frac{dR}{dt}$ coefficient or the $\frac{dR}{dx}$ coefficient. Before attempting to apply this development, let us

It is to be noted that in the derivation of Equations 9 and 10 that the assumption is implicitly made that the specific velocity of the common ion constituent is the same in both the preceding and the indicator electrolytes. Such is actually the case only in very special combinations of electrolytes, and we must seek a more general relation for the general case.

$$R = \frac{l-x}{kA} + \frac{x}{k'A}$$

$$\frac{dR}{dx} = \frac{1}{k'A} - \frac{1}{kA}$$

$$k' = \frac{k}{1 + kA \frac{dR}{dx}}$$

10-a

which relation gives us the value of the adjusted concentration when k' is known as a function of the concentration and then from Equation 2 the value of N_c' may be computed. Silver as indicator ion is the only case tested which even approximately fulfills the conditions stipulated above and the value of N_c' for AgNO_3 calculated by means of Equation 9, 0.4608, is in fair agreement with the value quoted by Jones and Mather for 0.1 N AgNO_3 at 30° of 0.4683.

consider the conditions actually existent in the tube in which the boundary ascends. We have not in this development taken into account the effect of the diffusion layer next to the electrode, which will be to reduce the value of the $\frac{dR}{dx}$ coefficient since the conductance of this portion of the tube is relatively high and becomes more appreciable the lower the velocity of the boundary. In other words, the $\frac{dR}{dx}$ coefficient which we must substitute in Equation 9 is the one we would get if we could cause the boundary to ascend the tube instantaneously and yet have no convection currents since, under these conditions, the time would be zero and no diffusion could take place. It is an experimental observation that at high current density, convection currents undoubtedly penetrate this diffusion layer and tend to distribute the electrolyte in this layer uniformly throughout the region of indicator electrolyte so that when this begins to take place the $\frac{dR}{dx}$ coefficient will suffer a corresponding decrease. Now if we plot the $\frac{dR}{dx}$ coefficient as ordinate against the reciprocal of the current density as abscissa and extrapolate a tangent to this curve at low current densities (before convection sets in) to zero value

of abscissal, we will have the desired value of the $\frac{dR}{dx}$ coefficient for substitution in Equation (9), since a zero value for the reciprocal of the current density corresponds to an infinite current density. This method was applied to some rather rough data on the Pb^{++} ion following K^+ ion in KNO_3 , and the truth of the above argument tentatively verified. The results are recorded in the following paragraphs and it is interesting to note that the $\frac{dR}{dx}$ versus $\frac{1}{\frac{dE}{dx}}$ curves leaves the extrapolating tangent at about the same value of $\frac{dE}{dx}$ as the n_c versus $\frac{dE}{dx}$ leaves the straight line in the plot described in a later paragraph. This work further indicates a consistent value of the $\frac{dR}{dx}$ coefficient as a possible criterion of a correctly functioning boundary.

Figure 2 gives the value of the $\frac{dR}{dx}$ coefficient for Pb as indicator for the K^+ ion in 0.1 N KNO_3 at 25°C and a series of potential gradients. From these curves we get the data,

$\frac{dR}{dx}$	158 $\frac{\Omega}{cm.}$	166	133	126	96
$\frac{dE}{dx}$	4.329 $\frac{volts}{cm.}$	8.658	12.99	17.32	21.64
$1/\frac{dE}{dx}$	0.231	0.1155	0.0770	0.0577	0.0461

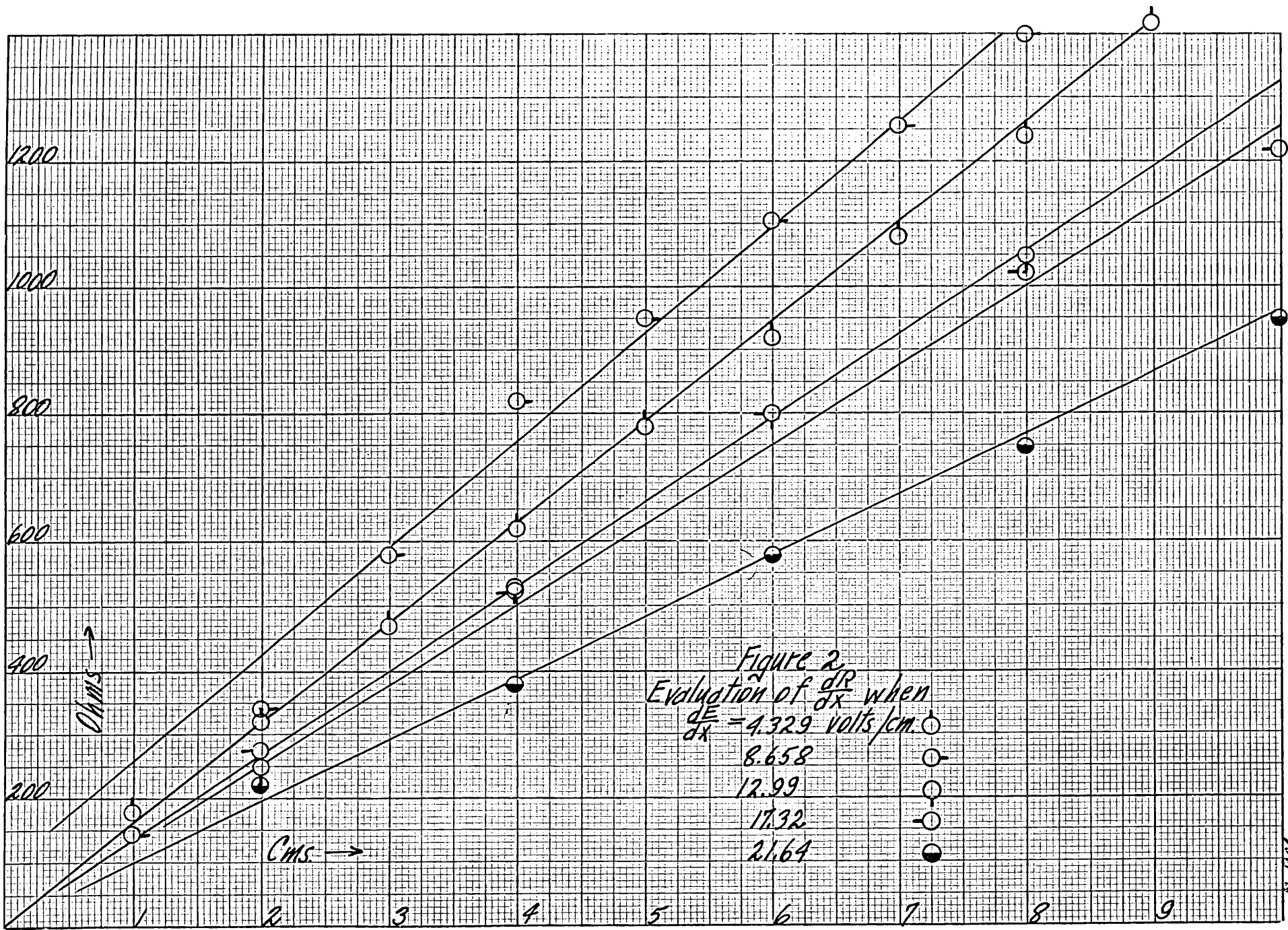
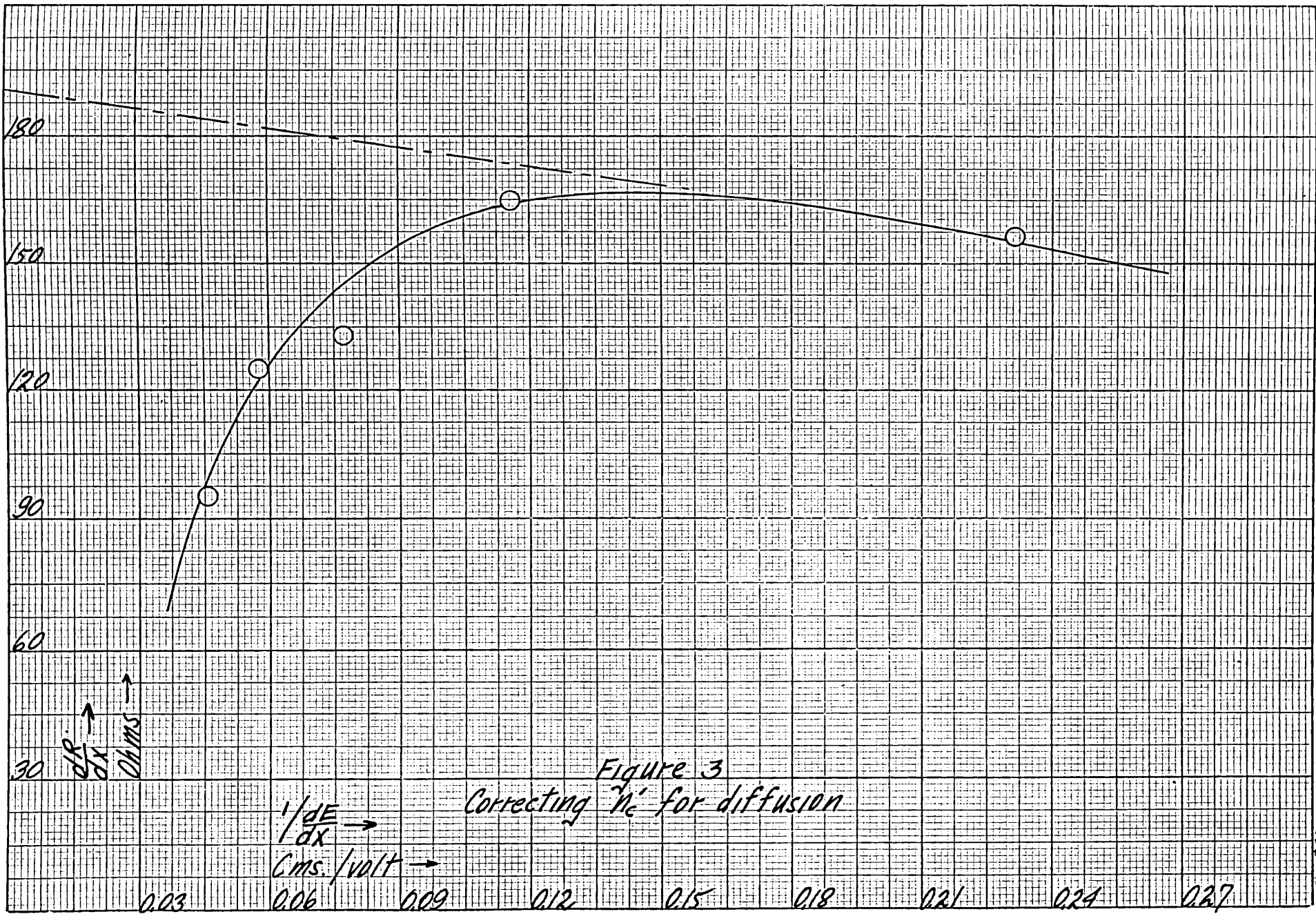


Figure 2
 Evaluation of $\frac{dR}{dx}$ when
 $\frac{dE}{dx} = 4.329$ volts/cm.

- 8.658 ○
- 17.32 ○
- 21.64 ○
- 21.64 ●



Plotting dR/dx against $\frac{1}{dR/dx}$, we get the plot shown in Figure 3 and the extrapolated value of dR/dx is about 190 ohms per cm. Substituting this value in equation 10-a we obtain the value for k' , 0.00835. From a specific conductance - concentration plot we find that this corresponds to a value of $\phi/00925$ for the concentration, and this value substituted in Equation 2 gives for N_0' the value 0.474 which is lower than the value of 0.487 quoted by Noyes and Falk. When the largest value of dR/dx obtained in any of this series of runs was substituted directly in Equation 10-a without correcting for diffusion a value of N_0' was obtained which was slightly higher than the accepted value --- which probably means that in our somewhat arbitrary choice of the limiting value of dR/dx we chose a value too high. For $AgNO_3$ at the adjusted concentration and uncorrected for diffusion we get from Equations 2 and 10-a the value 0.477 which agrees rather closely with the value 0.468 quoted by MacInnes and Cowperthwaite.

MacInnes, Cowperthwaite, and Huang²² have made the statement and advanced evidence to show that ascending boundaries are impracticable due to convection currents in the indicator solution, To meet these arguments we ran a series of

determinations on the same solution over a large range of potential gradients and plotting transport number against potential gradient found that the transport number was independent of potential gradient up to fairly high current densities where convection behind the boundary became very noticeable and hence extrapolation to zero current density where convection could not possibly alter the boundary velocity was both expedient and accurate.

In our work in acetic acid as solvent where the boundaries move verly slowly relative to their velocities in water, it was impracticable to attempt to maintain a constant current through the apparatus and so the current change under a constant potential was recorded in addition to the position of the meniscus. The method of analyzing the results in acetic acid is as follows. The current was plotted as ordinate against time as abcissa \AA and on the same plot the total distance the boundary had travelled was also plotted as ordinate against the same time abscissa \AA . Ordinates were erected at equal time intervals and the average current over one of these intervals (as taken from the curve) was divided

into the distance travelled by the margin in the same interval. The constancy of this ratio was taken as an indication of a correctly moving boundary and from it the transport ratio. The curves were drawn on a large scale and the values used in calculating this ratio were taken from the smoothed curves through the plotted points. Since in this solvent of low dielectric constant, and hence of low ionizing power, the refraction margins move so slowly that to observe them travel for more than a few centimeters introduces a prohibitive time element, it was thought that taking the values from the smoothed curve would partially eliminate accidental errors in the estimation of the position of the meniscus.

This method in effect is thus merely an integration of the current-time curve for total quantity of electricity passed in the given interval by the trapezoidal rule. On one occasion the attempt was made to fit an empirical equation to this $I = f(t)$ and the following forms were found to fit rather closely.

$$I = a + b \log(1+t) + c \log^2(1+t) + d \log^3(1+t) \quad (11)$$

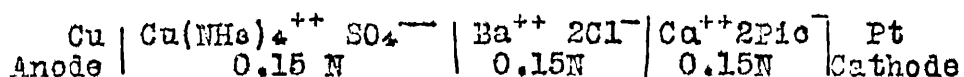
and,

$$I = a + b \log^c(1+t) \quad (12)$$

The evaluation of the constants in equation (11) is quite laborious and the equation difficult to integrate as a definite integral even after the constants have been evaluated. The constants of equation (12) are rather easily determined by choosing proper points on the curve for their evaluation, but this equation can be integrated only by development into a power series and term by term integration, the series at first diverging and only converging slowly after several terms, thus making the number of terms necessary to take into account prohibitive. In one case this method of determining the total quantity of electricity passed was utilized and agreed excellently with the graphical method, but the much less work involved in the latter case led to its adoption for the general case.

EXPERIMENTAL

The preliminary work began with a critical study of the moving boundary experiment as performed in the regular laboratory course in Electrochemistry here at the University of Kansas. This experiment is of essentially the same type as those performed by Masson in that horizontal boundaries supported by agar are utilized with colored ions as indicator ions. The arrangement of ions was as follows:



Upon application of a constant potential across the system the blue $\text{Cu}(\text{NH}_3)_4^{++}/\text{Ba}^{++}$ boundary and the yellow Pic^-/Cl^- boundary moved out from opposite ends of the tube, the relative velocities indicating the transference number for BaCl_2 at this concentration. It was found that this method had two grave faults, aside from cataphoresis in the agar, first, the presence of NH_4^+ ions which are faster than Ba^{++} ions in the $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ solution serving as the source of indicating cations and secondly, the release of the fast hydroxyl ions at the cathode as a result of the discharge of the cation of the solvent. The apparatus

was so constructed that the cathode was not far removed from the anion boundary and these hydroxyl ions soon penetrated this region and slowed up the Cl^-/Pic^- boundary. The first vitiating factor was eliminated by using Cu^{++} ion alone as indicating cation and the second by introducing solid picric acid around the cathode. The values then obtained were more consistent but still deviated widely from the accepted values.

In connection with this preliminary work it might be said that this experiment has been substituted in the Electrochemistry laboratory by one which grew out of subsequent work on this subject. In the new laboratory exercise the refraction margin between solutions of lead and potassium nitrate formed by the solution of a lead anode under the action of the current is observed by the student. Agar is dispensed with and a single ascending boundary observed. The author constructed eight sets of apparatus similar to the one to be described later, Figure 5, and these have been used with considerable success in giving the student a physical concept of ionic velocities and at the same time furnishing an exercise which is capable of highly quantitative results. At first

the student experiences some difficulty in locating the refraction margin since he does not know what to look for or expect but once located, he is usually surprised at the extreme sharpness of it.

An apparatus was then constructed with electrodes farther removed from the boundaries and the results became more consistent and reproducible. Work was then begun on a single boundary, the "modus operandi" being as follows, the tube of known cross-sectional area was filled with BaCl₂ - Agar solution, the anode chamber with a CuSO₄ solution, and in the cathode chamber a few c.c. of dilute acetic or hydrochloric acid were introduced before filling with BaCl₂ solution of the same concentration as that in the Agar-gel in the tube. The cathode was platinum and the anode of copper, and on application of a potential across the system, the Cu⁺⁺/Ba⁺⁺ boundary moved out into the tube containing the BaCl₂-Agar gel with a velocity approximately proportional to the potential gradient in the preceding solution.

In four of the experiments, performed as indicated in the preceding paragraph, advantage was taken of the opportunity of testing the statement of

Kohlrausch relative to the automatic concentration adjustment of the indicator solution behind the boundary. In each of these four cases a given volume of the tube contents was analyzed for chlorides, by the Volhard method, immediately before and after the advance of the $\text{Cu}^{++}/\text{Ba}^{++}$ boundary through the volume analyzed. The following table incorporates the results of these analyses,

$$n_c \text{ (for BaCl}_2 \text{ at } 25^\circ \text{ and 0.1N from Noyes), } = 0.427$$

$$n_c \text{ (for CuCl}_2 \text{ at } 25^\circ \text{ and 0.064 from Bein) } = 0.404$$

Initial Conc. of CuCl_2	Initial Conc. of BaCl_2	Final Conc. of CuCl_2	$n_c' = c'n_c/c$
0.15	0.1006	0.09267	0.394
0.09	0.1006	0.09442	0.400
0.09	0.1050	0.09980	0.406
0.085	0.1050	0.10050	0.408
			Mean = 0.402

The agreement is much better than was expected since the errors introduced in analyzing such a small amount of these comparatively dilute solutions in the presence of Agar are possibly pretty large.

The preliminary work thus far indicated that the development and maintenance of a boundary between aqueous solutions could best be effected by a method identical in principle with that used by Franklin and

12

Cady in their work in liquid ammonia, in which a single boundary is developed at the junction of the anode and the solution, the anode consisting of some metal which will pass into the ionic state under the action of the current and these cations, electrically balanced by the inward migration of anions from the superimposed solution under observation, will form a solution of higher specific gravity and consequently a sharp refraction margin will be immediately developed between the two solutions. The conditions to be fulfilled by this anode material have been discussed in connection with the theoretical part of this paper and nothing further will be said except that cadmium, silver, and lead proved experimentally to be the best for this purpose, excluding the possibility of slight hydrolysis in the case of the cadmium, where potassium nitrate solutions were under observation -- lead probably giving the best results from every point of view since the velocity of this ion is less than that of the potassium ion but the difference is not so great as to cause undue convection, and the higher specific gravity of the lead nitrate solution formed giving a very sharp and easily detectable refraction margin over a greater range of current densities and concentrations.

The apparatus and method involved in these earlier experiments is essentially the same as that to be described later. The current in the circuit was maintained constant by hand regulation of a rheostat and the current flowing measured by means of a milliammeter provided with appropriate shunts. The following tables give a summary of the results obtained.

TABLE I

Potassium Nitrate Solutions at 30°C.

No.	C	Indicator	dE/dx	u_c	U_c
65	0.1 N	Ag	8.743	0.006132	0.0007013
66	"	"	8.334	5818	6981
71	"	"	4.089	2859	6992
72	"	"	2.035	1424	6995
73	"	"	12.27	8541	7002
74	"	Pb	8.242	5725	6947
75-a	"	"	4.098	2861	6998
75-b	"	"	2.035	1426	7006
76	"	"	8.136	5722	7033
78-a	"	"	4.036	2805	6953
78-b	"	"	2.009	1403	6982
77	"	"	4.036	2829	7010
80	"	"	14.16	9986	7050
81	"	"	14.16	10010	7069
82-a	"	"	8.066	5678	7039
82-b	"	"	4.036	2819	6986
83	"	Cd	4.036	2835	7023
84	"	"	8.066	5640	6993
85	0.02 N	Pb	9.088	6944	7641
86	"	"	17.02	13140	7718
87	"	"	17.02	13110	7703
89	0.2 N	Pb	8.696	5753	6616
90-a	"	"	2.167	1389	6410
90-b	"	"	1.079	06979	6470
90-c	"	"	2.167	1403	6474
91	"	Cd	4.331	3015	6280
92	"	"	8.696	5675	6678
93	"	"	2.167	1405	6487
94	"	Ag	8.696	5639	6485
95	"	"	8.696	5711	6567
96	"	"	8.696	5817	6690
97	"	"	4.331	2881	6653
98	"	Pb	4.331	2833	6543
99-a	"	Cd	8.696	5644	6490
102	"	Pb	15.12	.01005	6648
103	1.0 N	Ag	5.417	2903	5359
104	"	"	5.417	2861	5282

TABLE II

Velocity of the Potassium Ion Constituent,
 U_c , in 0.1 N KNO_3 at 30°C.

dE/dx (approx.)	Indicators		
	Silver	Lead	Cadmium
2 volts/cm.	<u>0.0006995</u>	0.0007006 6982	_____
4 " / "	<u>0.0006992</u>	0.0006998 6953 7010 6986	<u>0.0007023</u>
8 " / "	<u>0.0007013</u> 6981	0.0006947 7033 7039	<u>0.0006993</u>
14 " / "	<u>0.0007002</u>	0.0007050 7069	_____

Velocity of the Potassium Ion Constituent,
 U_c , in 0.02 N KNO_3 at 30°C.

9 volts/cm.	_____	0.0007641	_____
17 " "	_____	0.0007718 7703	_____

Velocity of the Potassium Ion Constituent, U_c ,
in 0.2 N KNO_3 at 30°C.

1 volt/cm.	_____	0.0006470	_____
2 volts/cm	_____	0.0006410 6474	<u>0.0006487</u>
4 " "	0.0006653	0.0006543	0.0006280
8 " "	0.0006485 6567 6690	0.0006416	0.0006678 6490
15 " "	_____	0.0006648	_____

Velocity of the Potassium Ion Constituent, U_c ,
in 1.0 N KNO_3 at 30°C.

5 volts/cm.	0.0005359 0.0005282	_____	_____
-------------	------------------------	-------	-------

TABLE III

Summary of Transference Data

dE/dx (approx.)	Solution	U_0 (mean)	n_0	n (best value)
2	0.1 N KNO_3	0.0006994	0.5097	0.5097
4	"	6994	0.5097	
8	"	7001	0.5103	
14	"	7040	0.5131	
1	0.2 N KNO_3	6470	0.5064	0.5122
2	"	6442	0.5042	
4	"	6543	0.5121	
8	"	6616	0.5178	
15	"	6648	0.5203	
9	0.02 N KNO_3	7641	0.5033	0.5050
17	"	7710	0.5084	
5	1.0 N KNO_3	5321	0.5221	0.5221

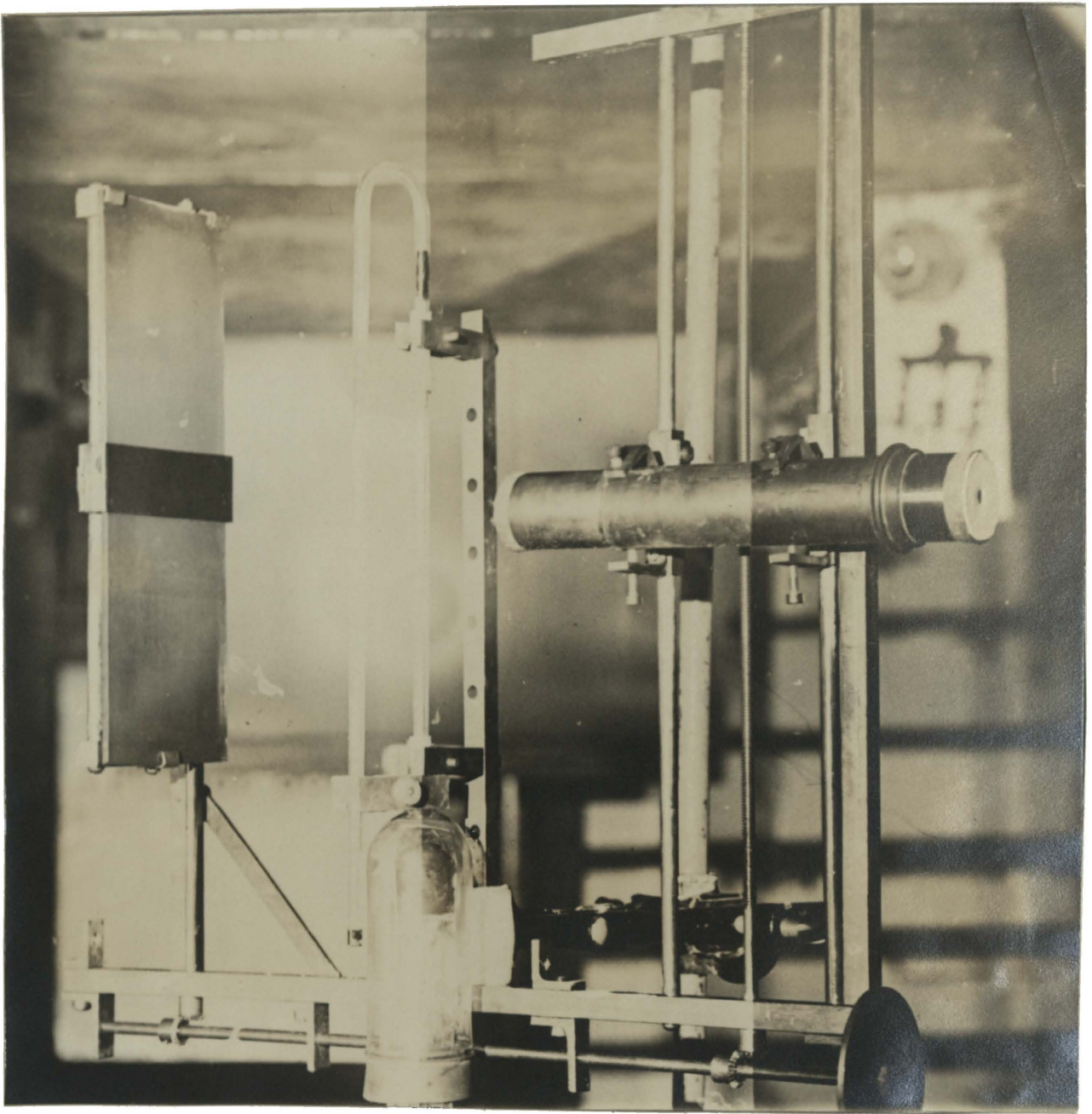
Notes on Table III,

1. In the case of the 0.1 N solutions, the average or mean values given are those obtained giving the results from all three indicators the same weight.

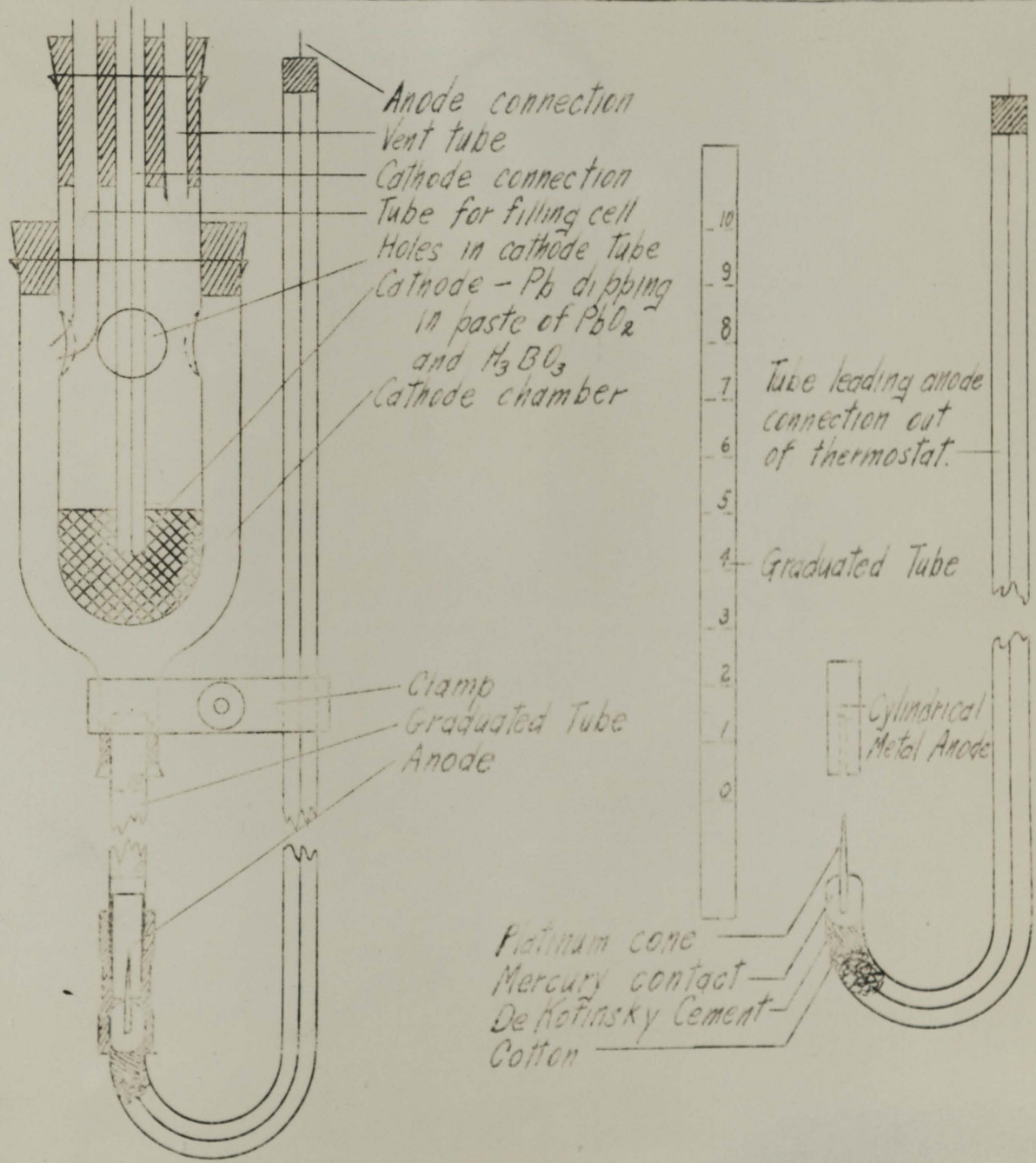
2. In the case of the 0.2 N solutions, the mean values given are those obtained by averaging only the data in which lead served as indicator, since the other values using the other two indicators are erratic and do not show the regularity that characterizes the values obtained using lead.

3. The "best value" of n_0 is given taking into consideration the fact that the values of n_0 obtained at the lower potential slopes will probably be the most accurate.

The apparatus shown in Figure 4 was then constructed and consists of a system of threaded rods and bevel pinions so arranged that a telescope and opaque screen on a ground glass background can be raised or lowered simultaneously and equipped with a clamp to hold the tube assemblage shown in Figure 5. This entire system is then fastened to a thermostat with parallel glass sides, the moving boundary apparatus and background being immersed in the water of the thermostat while the telescope is outside. A source of illumination is then placed behind the glass background and as previously suggested it is the distortion of the movable black margin on this background by the boundary which permits its detection. This mechanical synchronism of the distorted margin image with the position of the telescope renders it much easier for the operator to keep track of the boundary and still have time to make the other observations which are necessary in a moving boundary determination. A telescope could only be used when solutions of high concentrations were being investigated, at lower concentrations a hollow tube was substituted for the telescope merely to insure that the boundary was being located with the eye at a constant angle



90-a



to the perpendicular. The inability to use a telescope at ordinary concentrations is due to the fact that the reflection image of the boundary and the graduation marks on the tube cannot be gotten simultaneously into the focal plane of the telescope. In future work it is proposed to interpose a convex lens between the background and the tube so as to bring the reflection image of the margin to focus on the tube so that both the graduations on the tube and the boundary can be brought to focus in the observing telescope.

The apparatus in which the boundaries were run is shown in Figure 5 and is self-explanatory. The cylindrical metal anode is machined to fit the calibrated tube rather snugly and the approximate anode is wedged on to the platinum tip and slipped into the lower end of the tube in which the boundary is to run with the rubber connection so adjusted that there is but slight opportunity for the solution to slip down between the sides of the tube and the metal anode and no opportunity for the solution to work its way down and come in contact with the platinum tip. The electrode was ordinarily moistened with solution before adjustment so that

when the solution was introduced into the tube from above there would be little tendency for air bubbles to remain attached to the metal electrode, a bothersome occurrence in earlier work. The cathode chamber is much the same as the one recommended by MacInnes and Brighton¹ and is so constructed as to remove the cathode to quite a distance from the tube in which the boundary travels. The cathode proper is so arranged as to prevent gas evolution and also to prevent release of the fast hydroxyl ions.

An experiment is performed by assembling the apparatus, filling with the solution whose transference data is to be determined, adjusting in place in the thermostat and allowing to come to the temperature of the latter. The apparatus is then connected in series with a 400 volt "B" battery, arranged to give potentials from 200 to 400 volts in 2 volt steps, a rheostat or variable resistance, and a standard resistance connected to a potentiometer for determining the current in the circuit. The potential is then adjusted, with some resistance cut in, to give the current at which the boundary is to be run, and this resistance is then

gradually cut out as the boundary ascends the tube so as to keep the current in the circuit a constant and hence the potential acting on the preceding ions. The tube is graduated according to MacInnes, Cowperthwaite, and Huang²², which method has the advantage that at no time is the boundary directly behind a graduation mark on the tube, and by means of a pair of stop watches, the time required for the boundary to move from one centimeter mark to the next is recorded. The following data shows the method of tabulating results and indicates the constancy with which the boundary moves under a constant potential gradient.

Experiment Number _____ Date 2/16/28 Tube Number 11

Anode Pb Solution 0.1N KNO₃ Cathode PbO₂ } Pb
H₂BO₃

K 0.01200 C 0.100 l 1.00 A 0.1927 I 0.01 t 363.5

A 120.0 dE/dx 4.329 dx/dt 0.00275 u_0 0.635 \bar{v}_0 0.5110

0.5119 - corr.

Δt	Current	R	Distance
<u>0 SECS.</u>	<u>0.01 amp.</u>	<u>2890.52</u>	<u>0.00 CMS.</u>
<u>6:04</u>	<u>"</u>	<u>2710</u>	<u>1.00</u>
<u>6:00</u>	<u>"</u>	<u>2590</u>	<u>2.00</u>
<u>6:00</u>	<u>"</u>	<u>2420</u>	<u>3.00</u>
<u>6:05</u>	<u>"</u>	<u>2270</u>	<u>4.00</u>
<u>6:03</u>	<u>"</u>	<u>2110</u>	<u>5.00</u>
<u>6:05.4</u>	<u>"</u>	<u>1970</u>	<u>6.00</u>
<u>6:05.4</u>	<u>"</u>	<u>1810</u>	<u>7.00</u>
<u>6:06</u>	<u>"</u>	<u>1650</u>	<u>8.00</u>
<u>6:03</u>	<u>"</u>	<u>1480</u>	<u>9.00</u>
<u>6:03</u>	<u>"</u>	<u>1300</u>	<u>10.00</u>
<u>AV=6:03.48</u>			

Experiment Number _____ Date 2/22/28 Tube Number 12
 Anode Pb Solution 0.1N KNO₃ Cathode PbO₂ } Pb
H₂SO₄
H. 0.01200 G. 0.100 l. 1.00 A. 0.1100 I. 0.01 t. 207.6
Δ 120.0 dE/dx 7.576 dx/dt _____ u. 0.009817 U. 0.006357 n. 0.5112
0.5121-corr.

<u>Δt</u>	<u>Current</u>	<u>R</u>	<u>Distance</u>
<u>0 secs.</u>	<u>0.01 amp</u>	<u>_____</u>	<u>0.00 CMS</u>
<u>3:35.5</u>	<u>"</u>	<u>_____</u>	<u>1.00</u>
<u>3:30</u>	<u>"</u>	<u>_____</u>	<u>2.00</u>
<u>3:32.8</u>	<u>"</u>	<u>_____</u>	<u>3.00</u>
<u>3:28.8</u>	<u>"</u>	<u>_____</u>	<u>4.00</u>
<u>3:25</u>	<u>"</u>	<u>_____</u>	<u>5.00</u>
<u>3:25</u>	<u>"</u>	<u>_____</u>	<u>6.00</u>
<u>3:28</u>	<u>"</u>	<u>_____</u>	<u>7.00</u>
<u>3:25</u>	<u>"</u>	<u>_____</u>	<u>8.00</u>
<u>3:26.5</u>	<u>"</u>	<u>_____</u>	<u>9.00</u>
<u>3:27.2</u>	<u>"</u>	<u>_____</u>	<u>10.00</u>
<u>Av-3:27.6</u>	<u>_____</u>	<u>_____</u>	<u>_____</u>

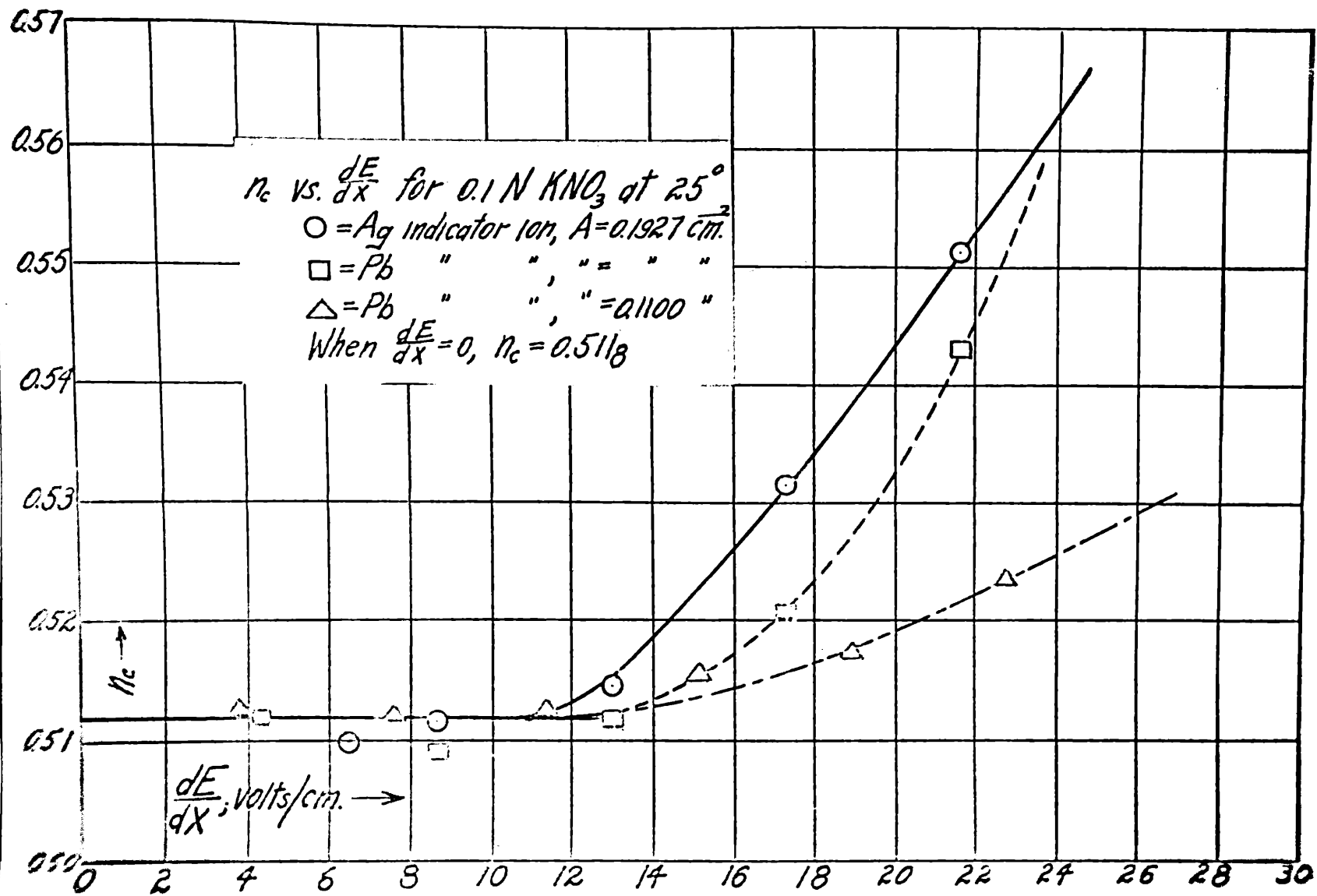
Not recorded yet
 this run

Experiment number _____ Date 2/15/28 Tube No. 11
 Anode Ag Solution 0.1N KNO₃ Cathode PbO₂ } Pb
H₂SO₄
 K_e 0.0200 C 0.100 l 1.00 A 0.1927 I 0.02 t 181.86
 Λ 120.0 dE/dx 8.658 dx/dt _____ u 0.5499 v 0.635 n_0 0.5107

0.5117-corr.

Δt	Current	R	Distance
<u>0.5secs</u>	<u>0.02 amp.</u>	<u>2800 Ω</u>	<u>2.00 cms.</u>
<u>2:57</u>	"	_____	<u>3.00</u>
<u>3:01</u>	"	_____	<u>4.00</u>
<u>3:02</u>	"	_____	<u>5.00</u>
<u>3:02</u>	"	_____	<u>6.00</u>
<u>3:03</u>	"	_____	<u>7.00</u>
<u>3:01</u>	"	_____	<u>8.00</u>
<u>3:02</u>	"	_____	<u>9.00</u>
<u>3:02</u>	"	_____	<u>10.00</u>
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____

A series of observations of this type were made upon 0.1 N KNO₃ at 25° with silver and lead as indicator ions and two different sizes of tubes in which the boundaries moved, and at a variety of potential gradients with the object in mind of ascertaining the effect on the boundary velocity and the stability of the boundary under various gradients. The results are shown graphically in Figure 6 from which we can conclude that over a considerable range of potential gradients, the specific boundary velocity is quite independent of the gradient. At higher current densities where convection currents begin to become appreciable, the boundary velocity is too high. A possible explanation is that at the higher current densities the increased convection penetrates the diffusion layer next to the electrode and carries solution of higher concentration up to the boundary, thus altering the automatically adjusted concentration behind the boundary. The values of n_0 determined at the higher current densities were calculated taking an average velocity of the boundary during the run. That the boundary velocity, however, suffers a slight acceleration during the run is shown by



47-d

reference to Figure 7 where the slight curvature denotes acceleration. If we take the slope of this curve at zero distance or time and use it in calculating the transport number, we get a value, $n_c = 0.521$ but slightly higher than the extrapolated value, indicating that at high current densities the vitiating effect of convection increases with the increasing zone of indicator electrolyte, which is rather what would be expected.

The chief attributes of the method as thus far developed are the extreme ease of initially forming the boundary and the absence of any necessity of previous adjustment of the indicator ion concentration. In opposition to these advantages, however, is the rather serious objection that it is limited to cation boundaries and to salts containing only anions that will not precipitate with the available indicating cations. It occurred to the author that since electrodes of the first class had been such a successful source of indicating cations, electrodes of the second class might be an equally successful source of indicating anions. The full consequences of this

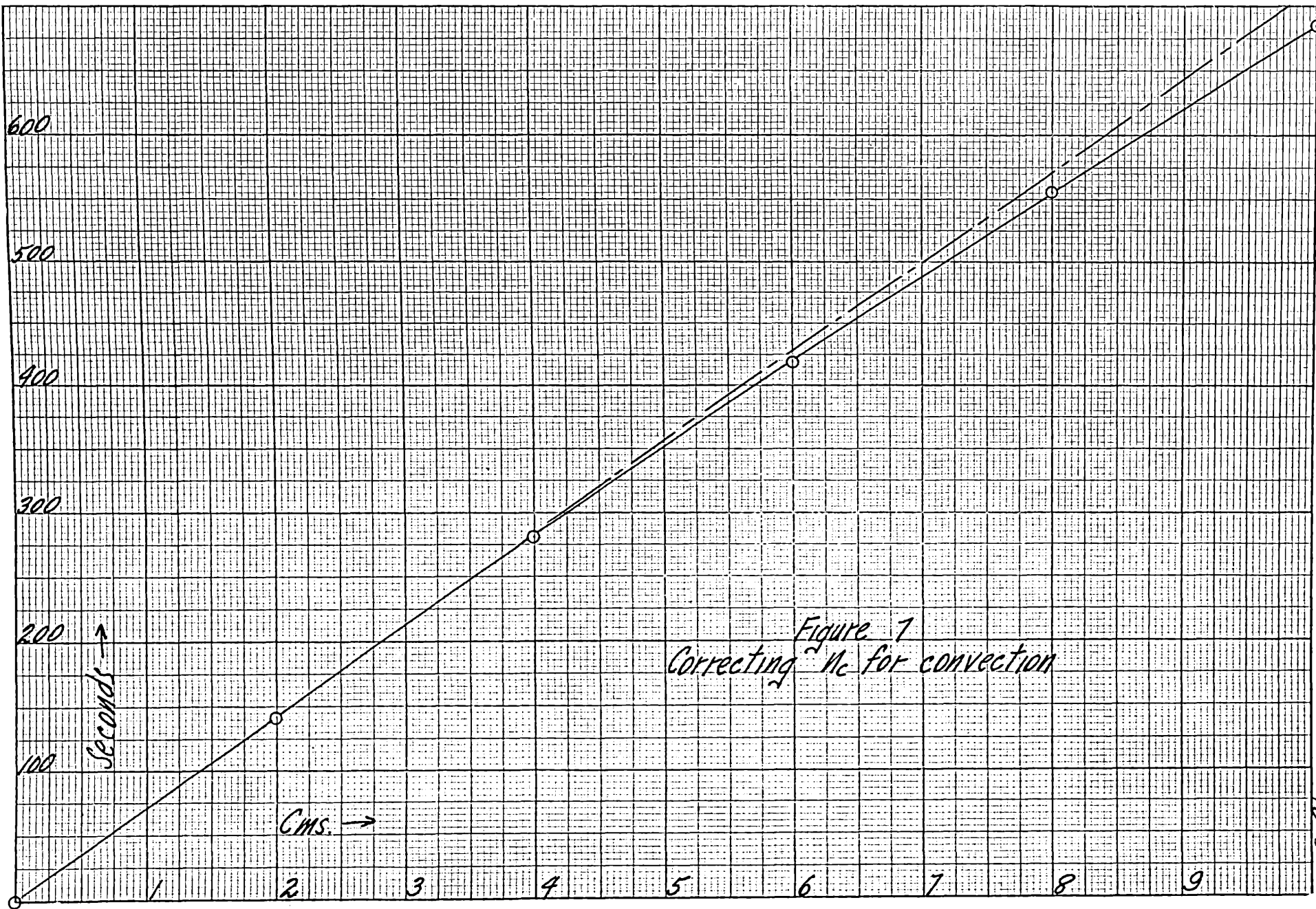


Figure 7
Correcting n_c for convection

possibility have not been determined as yet, but enough has been done to indicate the greatly enhanced range of the method by the use of electrodes of this type.

The first anion boundary attempted was a qualitative one in which an Hg - HgI paste in contact with an Hg cathode was made the source of indicating iodide ions to follow the hydroxyl ions in KOH. Upon application of a potential across the cell OH^-/I^- boundary moved away from the liquid paste interface just as the cation boundaries move away from the liquid metal interface, and the same diffusion layer next to this electrode is developed as in the case of cation boundaries. In connection with this particular boundary it should be noted that in addition to the preceding OH^-/I^- margin there were two fainter margins trailing behind at lower velocities, due possibly to margins of the type $\text{I}^-/\text{HgI}_2^-$.

The following anion margins were then investigated quantitatively. $\text{Ag}-\text{Ag}_2\text{C}_2\text{O}_4$ with 0.1 N KCl - Resistance of the cell increased normally but no boundary appeared. $\text{K}_2\text{C}_2\text{O}_4$ probably not dense enough

at the adjusted concentration. The cathode showed normal reduction, there was no gas evolution and the tube was clear throughout. Silver permanganate was not sufficiently stable to permit its use as a source of indicator ions. No boundaries were obtainable with AgSCN or Ag_2SO_4 in 0.1 N KCl although the cathodes behaved normally, specific gravity probably accounting for this failure also. Silver iodide served as an excellent source of indicating anions for the bromide ion in 0.1 N KBr and the mean of two closely agreeing determinations at the lowest current densities at which sharp margins were obtainable gave the value $n_a = 0.5208$ for 0.1 N KBr at 25°C , which is in very good agreement with the value of 0.519 given by Dennison and Steele. The chromate ion from Ag_2CrO_4 gave excellent boundaries with the anions of KCl and KNO_3 respectively, but determinations over a large enough range of potential gradients were not run from which to draw any final conclusions. It is noteworthy, however, that the refraction margin was exactly coincident with the color margin and at no time was the slightest tinge of yellow evident above the boundary. When the attempt was made to get the

chromate ion to follow the bromide ion in KBr, the yellow color soon diffused throughout the tube, due to the fact that the K_2CrO_4 solution at the adjusted concentration was specifically lighter than the superimposed solution of KBr. Qualitative boundaries were developed with several organic anions, and this is the most promising source of indicating anions since the silver salts of these anions are usually insoluble, and the anions themselves are heavy and slow. In the development of an anion boundary, a paste of finely powdered precipitated silver and the insoluble silver salt of the anion to act as indicator is made and packed in around a spiral of silver wire sealed into the lower end of the tube in which the boundary is to move. A small piece of filter paper is then tamped on top of this paste to prevent stirring up of the paste when the solution of electrolyte is introduced into the tube. As the silver is reduced and the anions released, the ever increasing region of reduced silver at the top of the paste is readily visible.

The major portion of the work performed since that done for the Master's degree has been

in anhydrous acetic acid as solvent. This solvent was chosen largely because of its availability in a relatively pure state, because it is more or less representative of solvents of low dielectric constant in which anomalies occur in conductivity - concentration curves, and because other properties of this substance as a solvent are being studied here at Kansas University.

The alkali acetates were chosen as solutes because of their high solubility and the data available on the conductance of these solutions. Sodium and potassium acetate were prepared by neutralizing the corresponding hydroxide in water solution by an excess of glacial acetic acid and evaporating the resulting solution to dryness and heating for some time at a temperature somewhat above the boiling point of the saturated solution. Their melting point was taken as the standard of their purity and both of the anhydrous salts melted rather sharply at the correct temperature.

The solutions were prepared by direct weighing and no attempt was made to adjust the concentration to an even fractional value. A glass

stoppered Erlenmeyer flask was dried and weighed, some of the anhydrous acetate introduced and heated to a constant weight. The solvent was then introduced and again the weight recorded. To find the volume concentration of the resulting solutions it was necessary to know the density of the solution, and this was determined by means of an Ostwald-Sprengel pyknometer at 25°C.

The viscosity of these solutions was determined at the same temperature by means of an Ostwald pipette, using 5 c.c. portions of the solution and with a pipette of such dimensions that the time of efflux varied from about one hundred to two hundred seconds in the range of concentrations used. The density-concentration plot closely approximates a straight line and accurately extrapolates to the density of anhydrous acetic acid found in the tables. The viscosity-concentration plot shows a convexity toward the concentration axis, but all points fell rather accurately on a smooth curve which readily extrapolates to the viscosity of the pure solvent found in the literature. Since all the concentrations measured are fractional ones the following tables

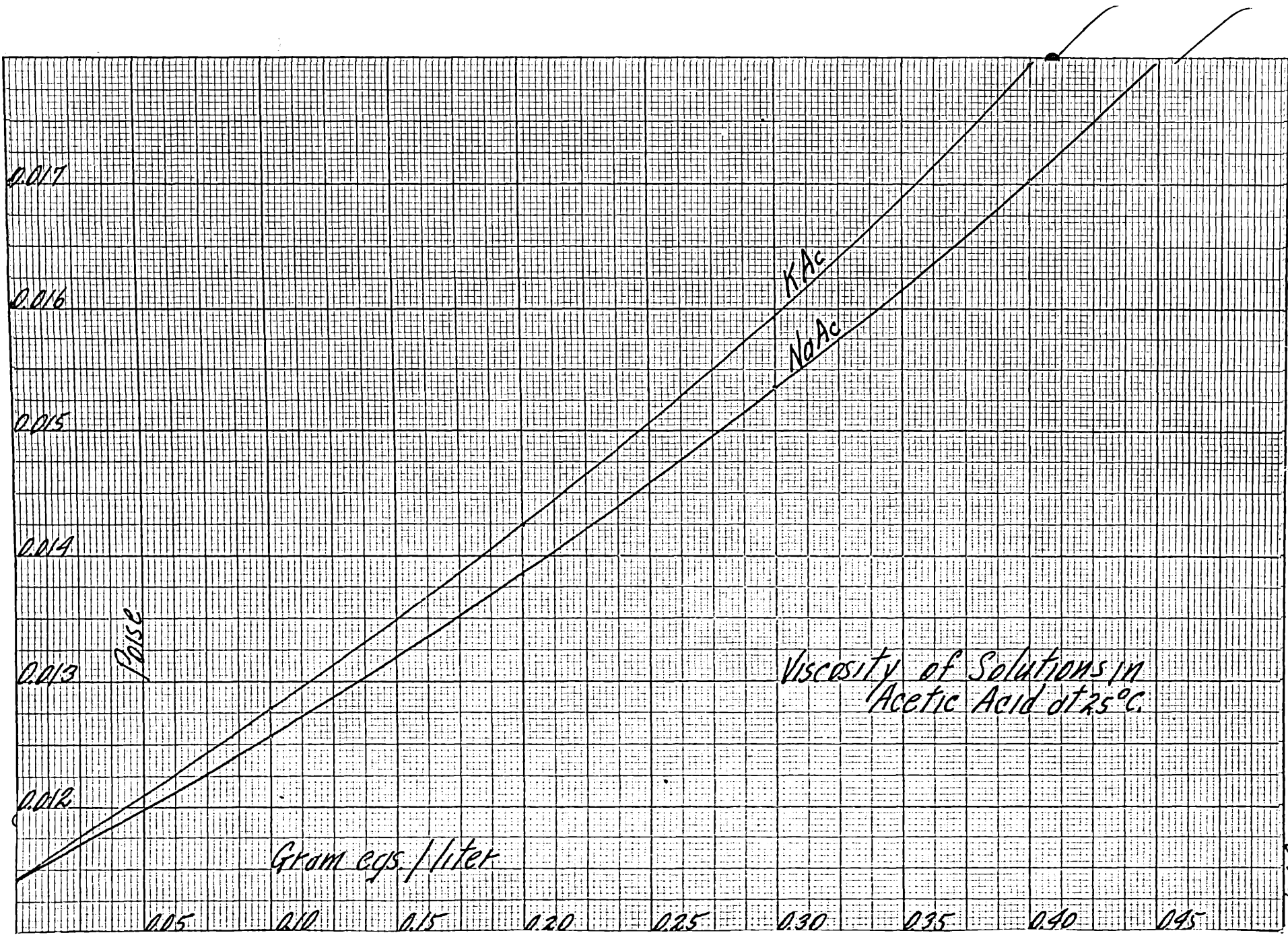
are interpolated values taken from the smoothed curves at the integral fractional concentration listed.

VISCOSITY

Conc.	KAc	NaAc
0.0	0.01141 poise	0.01141 poise
0.1	1277	1257
0.2	1424	1384
0.3	1592	1536
0.4	1795	1703
0.5	2035	1894
0.6	2293	2105

DENSITY

Conc.	KA ₀	NaAc
0	1.0445 /c.c.	1.0445 /c.c.
0.1	1.0498	1.0487
0.2	1.0551	1.0529
0.3	1.0604	1.0570
0.4	1.0658	1.0612
0.5	1.0711	1.0654
0.6	1.0765	1.0696



54-D

Density of solutions in
Acetic Acid at 25°C.

KAc ○

NaAc ●

1.070

1.065

1.060

1.055

1.050

1.045

Grams/cm³

Gram eqs./liter

0.05

0.10

0.15

0.20

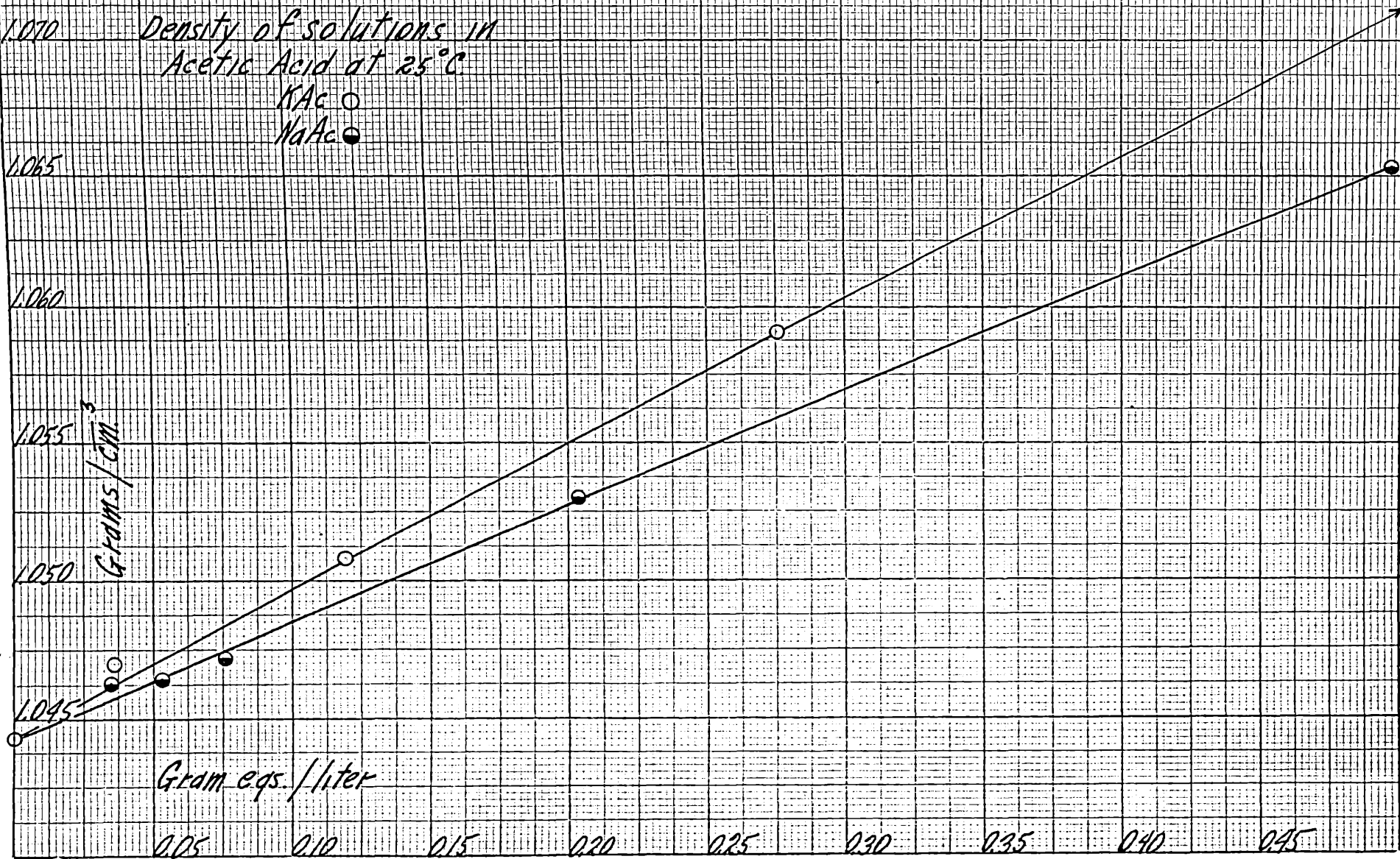
0.25

0.30

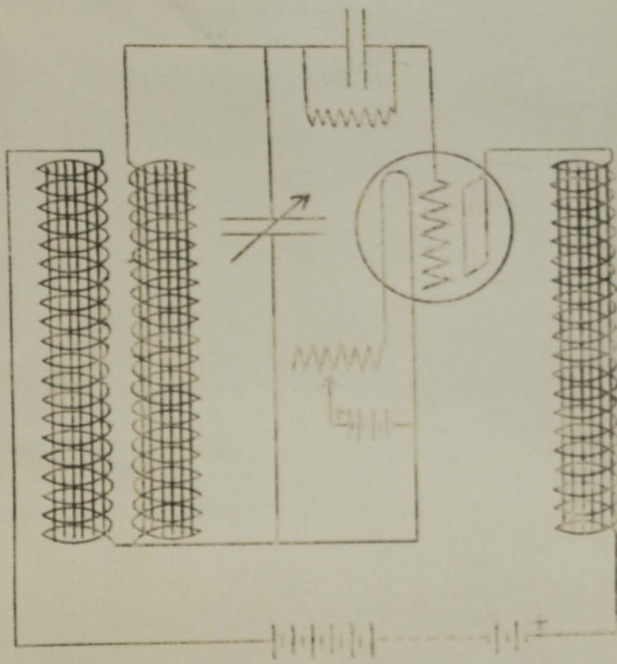
0.35

0.40

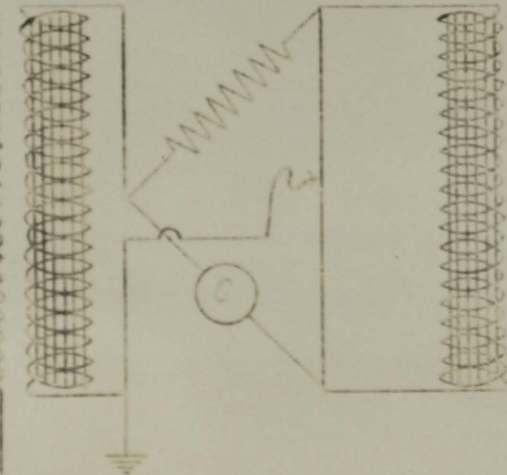
0.45



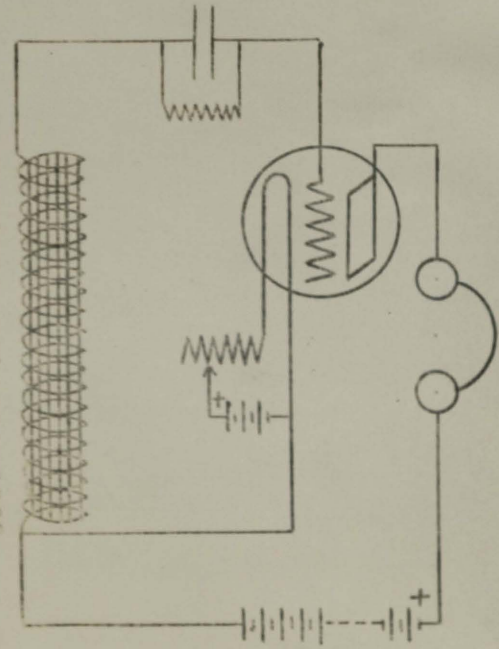
The conductivities were measured by means of the bridge system diagrammed in Figure 8. The source of bridge potential is an audion oscillator whose frequency is variable and the output from the bridge is passed through one stage of audio-frequency amplification before detection in the phones. The audion oscillator is the source of a remarkably pure sine wave potential, and this probably accounts for the unusually quiet and sharp minima obtainable in the conductance measurements. One small defect of this arrangement is the variation of the frequency with the load but this was largely eliminated by inserting the transformer between the output of the oscillator and the input of the bridge. A cell of constant about 0.1 was used in measuring the conductivities of the solutions in acetic acid while a cell whose constant was about 0.4 was used in measuring the conductivities in water. The conductivity of the acetic acid employed as solvent was well below that of the best conductivity water available and this, together with the freezing point, was taken as the criteria of the "electrical" purity of the acetic acid. The acid used had a higher



Oscillator



Bridge



Amplifier

melting point (16.46°) and a lower conductivity than the C.P. "Special" brand sold by Baker. The equivalent conductance of the solutions in acetic acid agree very well with the values of Hopfgartner quoted in Walden "Das Leitvermögen der Lösungen" except at the higher concentrations where our values are slightly but consistently higher. The data quoted by Völlmer is considerably at variance with either of the preceding sets.

The equivalent conductivity of KAc goes through a minimum at about 0.03 N and that of NaAc at about 0.05 N. Since the method of moving boundaries is available from concentrations of this order on up, (the upper limit is a matter of question - with very small bore tubes it may be possible to run up to as high as one or two normal) we endeavored to choose concentrations such that some light might possibly be thrown on this anomaly which characterizes solutions of electrolytes in many solvents of low dielectric constant.

Sharp, stable, refraction margins were obtained with both Cd and Pb as a source of indicator ions, and the results of a typical determination are recorded in the following tables.

Moving Boundary Determination on Solution of
 $\text{HA}_2(518.802) + \text{NaAc}(8.3613)$.

Time	Time	Distance	Current	Remarks
1:26 P.M.	0 hrs.	0.00 cms.	0.1499 M.A.	Pb anode
3:36	2.17	0.090	1365	Tube #1,
5:04	3.63	0.148	1282	A = 0.1872
7:09	5.71	0.250	1182	emf const.
9:38	8.20	0.395	1091	at ca.200
7:11 A.M.	17.75	0.790	0860	volts
10:44	21.30	0.918	0803	2/28/28
12:22 P.M.	22.93	0.950	0780	
4:09	26.71	1.070	0734	
5:35	28.15	1.125	0717	
10:21	32.91	1.245	0669	
8:23 A.M.	42.93	1.525	0594	

This data is then plotted on a large scale as described in a previous section and the following values taken from the smoothed curves through the plotted points. In this case a four hour period was taken as the time interval. The first column is the median hour of the interval, the second the position of the meniscus at the end of the given interval, the third the distance travelled during the interval, the fourth the mean current during the interval, and the fifth is the ratio of the distance travelled to the mean current.

Hour	x_2	Δx	I_{Average}	$\frac{\Delta x}{I}$
2	0.200 cms.	0.200 cms.	0.1368 M.A.	1.46
6	0.386	186	1178	1.58
10	0.555	169	1041	1.62
14	0.711	156	0939	1.66
18	0.855	144	0864	1.67

Hour	x_2	Δx	$I_{AV.}$	$\frac{\Delta x}{I}$
22	0.990	0.135	0.0785	1.70
26	1.114	124	742	1.67
30	1.228	114	699	1.63
34	1.335	107	660	1.62
38	1.437	102	630	1.62
42	1.535	098	600	1.63
46	1.630	095	573	1.65

Best mean = 1.641 ± 0.006

$$1.641 \frac{\text{cms.}}{4 \text{ hr. M.A.}} = \frac{1.641}{14.4} \frac{\text{cms.}}{\text{amp.-sec.}} = 0.1140$$

$$N_c = \frac{0.2036 \times 96494 \times 0.1872}{1000} \times 0.1140 = 0.4191$$

$$\text{Since } N_c = \frac{x \text{CFA}}{1000it} = \frac{\text{CFA}}{1000} \cdot \frac{x}{it}$$

The constancy of the $\frac{\Delta x}{I}$ coefficient is taken as indicating that the boundary is a correct one and is not being vitiated by convection. The values obtained with lead as indicator ion were consistently reproducible while those obtained with cadmium were much lower and fluctuated violently, though in any one determination the ratio $\frac{\Delta x}{I}$ might be as constant as in the lead determinations. The attempt was made, therefore, to obtain a check on the values obtained with the lead as indicator using a different indicator. ~~then~~ Thallium proved to be the desired source of indicator ions and the corrected value obtained with this ion as indicator agreed very well with the value obtained with lead for the same solution.

The term "corrected value" requires an explanation. At the relatively high concentration of KAc at which the thallium and lead values were compared, there is considerable convection in the indicator solution at the current density necessary to bring out a sharp margin and analogous to similar conditions in water solutions the K^+/Tl^- boundary was accelerated and the value quoted is that obtained by taking the value of $\frac{\Delta x}{I}$ from the smoothed plot of $\frac{\Delta x}{I}$ versus time at zero time. Since the accuracy of these results is not very high, it being feasible to observe the boundary only for one or two centimeters as a rule, this method of correcting for convection is probably within the limits of error.

Under a constant potential across the apparatus and using lead as a source of indicator ions the current drop as the boundary ascends the tube is very large, indicating that $Pb(Ac)_2$ (the analogue of $Pb(OH)_2$ in water solutions) is a very weak base. On the same argument we must conclude that $TlAc$ is almost as strong a base as KAc since the current drops but little as the K^+/Tl^+ boundary ascends the tube. From conductance data we must likewise conclude that NaAc while still a stronger

base than $\text{Pb}(\text{Ac})_2$ is weak as compared with KAc . The choice of these electrolytes as solutes is possibly unfortunate since their conductance is considerably lower than that of salt electrolytes at the same concentration, thus increasing the time required in making observations upon a single boundary.

Solution	Conc.	Eq. cond.	Pb	$\frac{n_0}{\text{Cl}}$	Cd
KAc	0.2765	0.493 ₆	0.430	0.426	
	0.1193	0.262 ₄	0.437 ₈		0.1202
			0.438 ₄		
			0.438 ₀		
	0.0383	0.153 ₂	0.450		0.317
0.5554	1.153	No reliable data obtained on this conc. as yet.			
NaAc	0.0530	0.083 ₆	0.430 ₆		
	0.0760	0.089 ₂₈			0.1925
					0.2313
	0.2036	0.148 ₂	0.419 ₁		
			0.413 ₀		
	0.4965	0.428 ₆	0.420 ₂		
0.0350	0.079 ₆	No margins visible at this conc.			

The abnormal behavior of the Cd as source of indicator ion may be explained in a manner suggested in a previous section, that is, complex ion formation with liberation of the fast hydrogen ion. The data is too meagre as yet to draw any definite conclusions in this connection.

Tentatively accepting the values obtained with lead as indicator ion and checked with thallium as the correct values, we are forced to conclude that though the equivalent conductance of the solution is undergoing an anomaly the transference numbers are behaving perfectly normally, that is, approaching 0.5 as the concentration decreases, and that the minimum in the conductance - concentration function is not due to either ionic species in particular but is affecting both ion constituent velocities to about the same extent. Before we can get a positive clue to the cause of this anomaly, other properties, particularly the molecular refraction and molecular polarization of the solutions in this concentration region must be determined.

SUMMARY

A method of ascending boundaries has been developed with metallic electrodes of the first class as the source of indicating cations and insoluble salt electrodes of the second class as the source of indicating anions.

The various factors influencing the initial development and maintenance of a boundary or refraction margin have been studied and methods of attack and treatment developed wherever possible.

The value of the transport number of the potassium ion in 0.1 N KNO_3 at 30° has been found to be 0.5097 and at 25° , 0.5118, which variation is in agreement with the temperature coefficient for the conductance of the potassium ion over this temperature interval.

The method has been applied to a solvent of low dielectric constant, acetic acid, and with certain minor modifications, has been found available in the study of ionic velocities in a solvent of this type.

The transference data of solutions of KAc

and NaAc solutions in acetic acid have been determined and found to be nearly independent of concentration over the range studied, a range in which the equivalent conductance of these same solutions is undergoing marked changes.