

hindrance weakens this bond and makes the compound unstable. If all four H's are substituted by CH₃, no bond can be established and the com-

ound remains a monomeric free radical even in the solid state.

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A Differential Moving Boundary Method for Transference Numbers

BY L. G. LONGSWORTH

Introduction.—A boundary between two different concentrations, c' and c'' , of the same electrolyte, such as 0.2 *N* LiCl:0.5 *N* LiCl, for example, will move, on passage of an electric current, if the corresponding cation transference numbers, T' and T'' , are different. The relation¹ connecting these variables with the displacement, Δv , of the boundary and the number, f , of coulombs passed is

$$T'' - T' = \Delta v(c'' - c')f/F \quad (1)$$

or simply $\Delta T = \Delta V \Delta c$ if ΔV is the displacement per faraday, F . In this expression c is in equivalents per milliliter if ΔV is in milliliters.

These "concentration" boundaries have been studied theoretically by Kohlrausch,² Planck,³ Miller⁴ and von Laue⁵ and experimentally by Smith.⁶ The latter investigation followed the boundary movement with the aid of the simple optical arrangements then in use in this field. As long as a boundary remains uniformly sharp, as do those characteristic of the direct moving boundary method, its movement may be followed accurately without difficulty. At a concentration boundary, on the other hand, the forces counteracting diffusion are relatively weak and, in general, an initially sharp boundary soon becomes indistinct due to the spreading effect of diffusion. By passing sufficiently heavy currents, Smith was able to keep his boundaries visibly sharp during the period of observation and the displacements he observed were, in most instances, in the proper direction and of the right order of magnitude. Under the conditions of his experiments, however, errors due to convection may have been introduced. In the present investigation this diffi-

culty has been overcome by recording photographically, with the aid of the schlieren scanning method,⁷ both the magnitude and the position of the refractive index gradients in the boundaries. Owing to the close proportionality⁸ of the refractive index to the salt concentration the electrolyte distribution may be computed readily from the refractive index gradient curve. As will be shown below, the position of a concentration boundary whose gradients may be spread over several centimeters can be defined with almost the same precision as one in which the change occurs within a small fraction of a millimeter. It is the purpose of this paper to show that this method may be used to determine, with accuracy, the change of the transference number with the concentration and that it is of utility in cases in which the direct moving boundary method is difficult to apply.

Experimental

The solutions were prepared from reagent grade chemicals and their concentrations were checked conductometrically. The quantity of electricity was computed from observations of the time and current. Readings of the latter, determined as the potential drop across a known resistance, were made at intervals during the experiment with a precision of 0.1%. In contrast with the cell containing a regular moving boundary, the resistance of the cell with concentration boundaries changes but slightly during an experiment. These changes, due to polarization of the cell and the B batteries that supply the current, are quite regular and amount to only 1 or 2%. Consequently the averaged value for the current has essentially the same precision as the individual observations and the use of a constant current device is unnecessary. With the differential method described here the concentrations and electrical quantities do not need to be known as precisely as in the case of the direct moving boundary method and the procedure just outlined is adequate for the determination of transference number differences with a precision of $\pm 1 \times 10^{-4}$.

The cell in which the boundaries are formed and observed

(1) For a derivation of this relation, together with a discussion of the various types of moving boundaries, see MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corporation, New York, N. Y., 1939, p. 87.

(2) Kohlrausch, *Ann. Physik*, **62**, 209 (1897).

(3) Planck, *ibid.*, **40**, 561 (1890).

(4) Miller, *Z. physik. Chem.*, **69**, 436 (1909).

(5) von Laue, *Z. anorg. Chem.*, **93**, 329 (1915).

(6) Smith, *Bur. Standards J. Research*, **6**, 917 (1931).

(7) Longworth, *THIS JOURNAL*, **61**, 529 (1939).

(8) Lamm, *Nova Acta Regiae Soc. Sci. Upsaliensis*, Ser. IV, **10**, No. 6 (see p. 64) (1937).

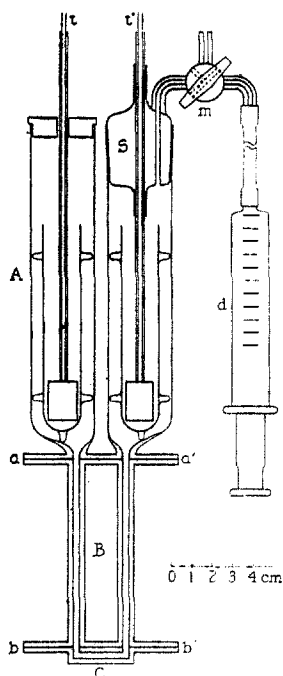


Fig. 1.—The moving boundary cell.

and stopper slowly forces the excess lubricant out and causes disturbing volume changes.

The cell is filled and the boundaries are formed as in work with proteins.¹⁰ The bottom section, C, and the right-hand channel of the center section, B, are filled with the concentrated solution, the remainder of the cell being filled with the dilute solution. In practice the right-hand electrode vessel is closed, care being taken to avoid trapped air bubbles, by means of the ground-glass stopper, S. The silver-silver chloride electrodes used in most of the experiments are of the same design as those previously described,¹¹ although smaller in size. They have a capacity of 0.0075 faraday, *i. e.*, 0.2 ampere-hour, and in order to utilize this capacity it is necessary to immerse the electrodes in a rather concentrated chloride solution. Five ml. of a 1 *N* solution is sufficient in most cases and are introduced through the silver tubes, *t* and *t'* of Fig. 1, that also serve to make electrical connection with the electrodes. A 1 *N* solution does not dissolve appreciable amounts of silver chloride.

The boundaries are formed simultaneously at *a-a'* in the right-hand channel and at *b-b'* in the left-hand side. After forming, the boundaries are brought out from behind the opaque horizontal plates of the cell for a distance of about 2 cm. by slow injection of solution from the syringe, *d*. The piston of the latter is displaced at the desired rate with the aid of a small synchronous motor. The contents of the syringe are then isolated by turning the stopcock, *m*, to the position shown in Fig. 1, after which the potential is applied.

For the first five or six minutes after application of the

is shown in Fig. 1 and, except for the top section A, will be recognized as the Tiselius cell⁹ for studying the electrophoresis of proteins. Since many of the boundary displacements observed in the course of this work have been small, it has been necessary to eliminate the relatively minute volume changes in the closed side of the apparatus that result from an expansion, or contraction, of the rubber connections characteristic of the usual Tiselius assembly. This was accomplished by redesigning the top section to include the electrode cups as shown at A in Fig. 1. For the same reason it has been found necessary to use a minimum of lubricant in assembling the cell. Otherwise the light pressure maintained on the assembled cell

potential the current through the cell increases as the steady state distribution of temperature is established and then changes but slowly, as previously noted. Small volume changes appear to accompany the attainment of the steady state. Consequently the first scanning photograph of the boundaries is not made until the current has been flowing for five or six minutes. All subsequent photographs are also made with the current passing. The movement of the boundary during the scanning interval of one to three minutes is small and introduces a negligible error if the time of the recording is taken as that at which the scanning is half completed. The author has adopted the practice of photographing the boundaries after electrolysis for about two hours and again after four hours. The current is then reversed and a fourth photograph taken after the boundaries have moved in the opposite direction for another interval of two hours. In this manner three values for the velocity of the boundary in each side of the channel are obtained or a total of six values. The constancy of these values affords a check on the experiment that will be discussed later in this paper.

Recording and Locating the Boundary.—The schlieren scanning camera used in this research is the same as that for the electrophoresis of proteins and has been described elsewhere.¹² Exposures were made on Eastman CTC panchromatic plates with the light from an H4 mercury lamp and a Wratten E filter. Prints of typical boundary patterns, obtained with the aid of this camera during the electrolysis of 0.1 *N*:0.2 *N* solutions of calcium chloride, are shown in Fig. 2.¹³ The edge between the light and dark areas of such a pattern is a plot of the refractive index gradient in a thin layer of solution in the cell as ordinate against the height of the layer as abscissa. The edge of the pattern represents the shadow cast by the schlieren diaphragm. Since the latter is not focussed on the photographic plate, a diffraction pattern appears in the illuminated area at the edge. This is illustrated in Fig. 3, which is a microphotometer tracing, obtained through the courtesy of Dr. E. G. Pickels, from the area enclosed by the circle in Fig. 2. Whereas h_0 of Fig. 3 represents the position of the geometrical edge of the shadow,¹⁴ and hence the height in the cell at which the gradient has the value given by the ordinate of h_0 , it has been found experimentally that the position h of the first diffraction minimum can be located with greater precision than h_0 . With the method for locating diffuse boundaries given below the errors

(12) Longworth and MacInnes, *THIS JOURNAL*, **62**, 705 (1940).

(13) The vertical and horizontal striae in the patterns of Fig. 2 are due to traces of dirt, or scratches, on the cell windows and to imperfections in the plate movement, respectively.

(14) Wood, "Physical Optics," The Macmillan Co., New York, N. Y., 1924, p. 192.

(9) Tiselius, *Trans. Faraday Soc.*, **33**, 524 (1937).

(10) Longworth, *Chem. Rev.*, **30**, 323 (1942).

(11) Longworth and MacInnes, *ibid.*, **24**, 271 (1939).

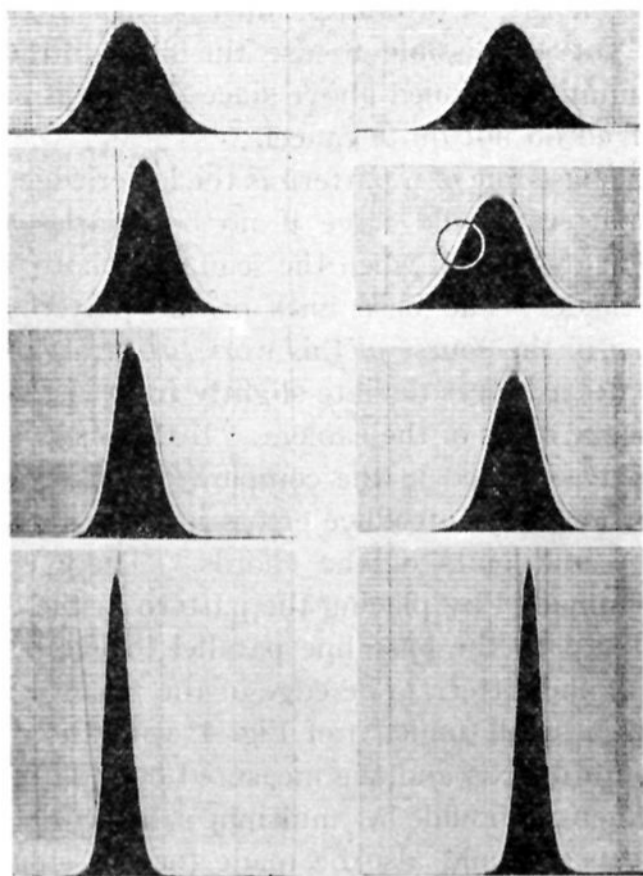


Fig. 2.—Schlieren scanning patterns of the boundaries between 0.1 and 0.2 *N* solutions of calcium chloride.

introduced by using *h* instead of *h*₀ are largely cancelled.

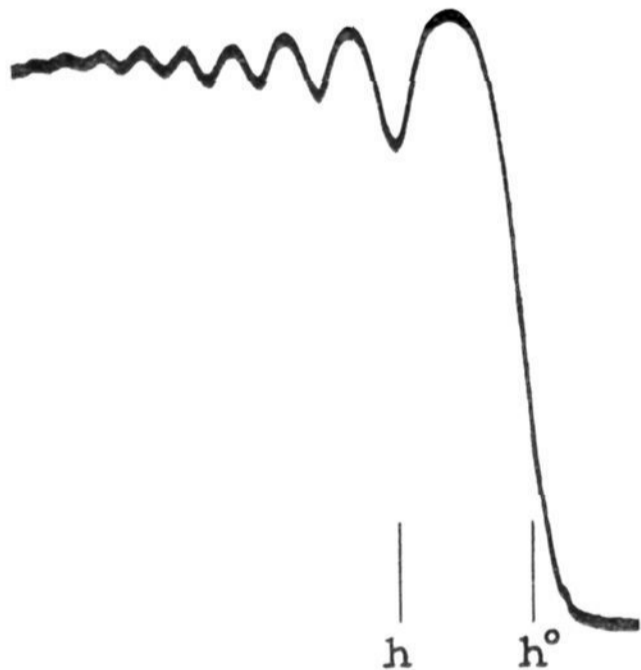


Fig. 3.—Microphotometer tracing of the edge of a schlieren pattern.

The maximum gradient of a boundary which remains uniformly sharp during its motion may, without error, be taken as the correct location of the boundary. If, however, the relative distribution of the gradients is changing, the boundary position requires careful definition. This may be illustrated with the aid of Fig. 4. In this figure the gradient curve, Fig. 4a, for a typical boundary

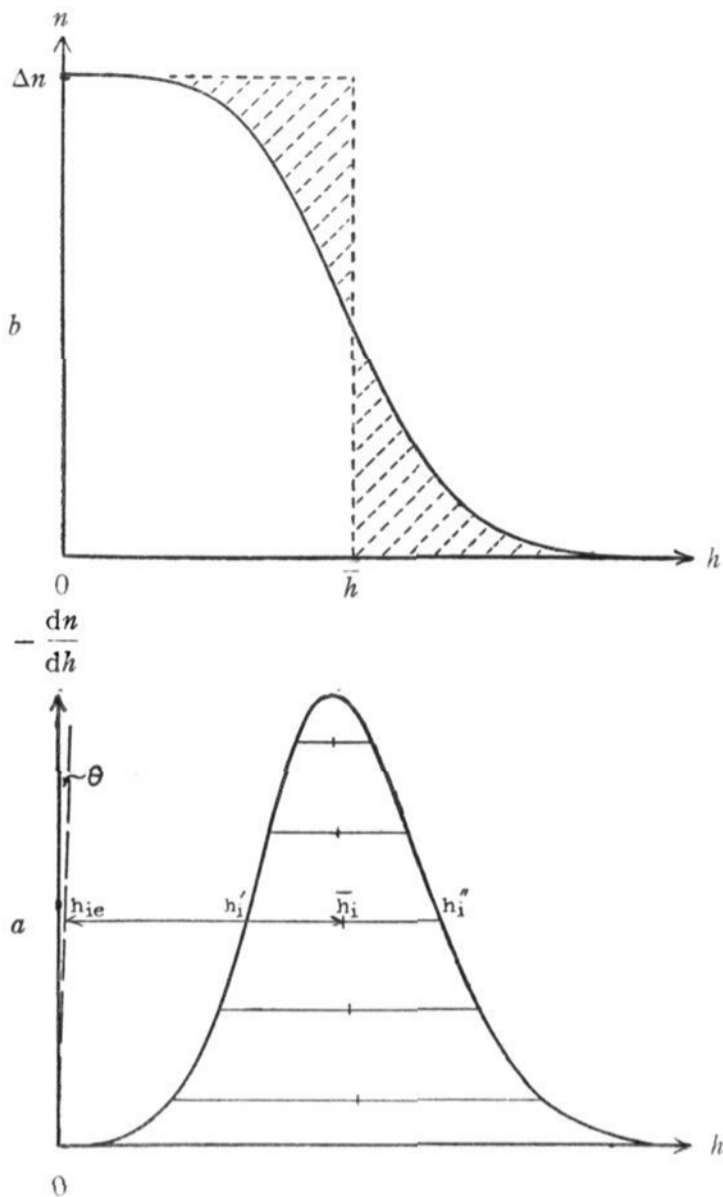


Fig. 4.

has been integrated to give the corresponding integral curve, Fig. 4b, of the refractive index versus the height in the cell. The axis of ordinates for the integral curve has been taken as the refractive index, *n'*, in the body of the dilute solution. The refractive index, *n''*, in the body of the concentrated solution is then *n''* - *n'* or Δn . If an initially sharp boundary between the two solutions started at *h* = 0, for example, and acquired the distribution shown in Fig. 4b on passage of the current, the net quantity of salt transported by the latter would be proportional to the area, $\int_0^\infty n dh$, under the integral curve. Moreover, if the transport had been effected without sacrificing the sharpness of the original boundary the latter would be at the position, \bar{h} , given by the relation

$$\bar{h} \Delta n = \int_0^\infty n dh \tag{2}$$

With this definition of \bar{h} the shaded areas of Fig. 4b cancel each other. It may be noted that there is no net transport of material by diffusion alone.

It is, however, unnecessary to construct the integral curve in order to locate \bar{h} . The right-hand term of equation (2) may be integrated by parts to give $\bar{h}\Delta n = - \int_0^\infty h dn + nh \Big|_0^\infty$. Since h and n vanish at 0 and ∞ , respectively, the last term is zero and this equation may be written $\bar{h}\Delta n = - \int_0^\infty h (dn/dh) dh$. Since Δn is given by the total area, $-\int_0^\infty (dn/dh) dh$, under the gradient curve, Fig. 4a, the expression for \bar{h} becomes

$$\bar{h} = \int_0^\infty h \left(\frac{dn}{dh} \right) dh / \int_0^\infty \left(\frac{dn}{dh} \right) dh \quad (3)$$

The correct boundary position is thus the position of the first moment or centroidal ordinate of the gradient curve and several methods for its evaluation are available.¹⁵

The one adopted was as follows. The photographic plate is placed in a two coordinate comparator¹⁶ with the base line of the pattern parallel to one of the axes. The ordinates of a number of chords, say five, are located, on one scale of the comparator, at equal intervals between the base line and the maximum, as shown in Fig. 4a. On the other scale the abscissas, h_i'' and h_i' , of the ends of each chord, together with the corresponding abscissa, h_{ie} , of the edge of the pattern, are then determined. The abscissa, \bar{h}_i , of the midpoint of a chord is thus $(h_i'' + h_i')/2$. If the distances $\bar{h}_i - h_{ie}$ are the same for each chord the gradients in the boundary are symmetrical about the ordinate through the maximum and $\bar{h} - h_e$ is the position of the boundary referred to a fixed point on the cell since the vertical edge of the pattern corresponds to one end of the channel.

If the distances to the centers of the chords are not equal, the boundary is "skew." If this skewness is not too great, the following relation, which is equivalent to equation (3), may be used: $\bar{h} = \sum_i \Delta h_i (\bar{h}_i - h_{ie}) / \sum_i \Delta h_i$. In this expression Δh_i is the length, $h_i'' - h_i'$, of the i -th chord. In extreme cases, such as the rising boundary of Fig. 9, more tedious methods must, however, be employed. With such a boundary a large num-

ber of chords, or ordinates, must be measured and it is not permissible to use the first diffraction minimum mentioned above since the slight errors involved do not quite cancel.

The base line of a pattern is the lower edge that the pattern would have if no boundaries were present in the cell when the scanning photograph was made. The base lines of the patterns recorded in the course of this work are straight but in some instances deviate slightly from the vertical in the focus of the camera. If the plate is improperly oriented in the comparator this type of distortion may introduce errors into the location of the midpoints of the chords. These errors are eliminated by placing the pattern in the comparator with the base line parallel to one of the axes of the latter. The edge of the pattern then makes a small angle, θ of Fig. 4, with the other comparator axis and the measured boundary displacements should be multiplied by cosine θ . Allowance should also be made for the enlargement factor for the camera if this is not unity.

Results.—The experimental results are given in Table I. The salt is listed in the first column of this table and the concentrations, in equivalents per milliliter, of the two solutions forming the boundaries are given in the next two columns. The current passed through the cell is recorded in the fourth column. The boundary displacement per faraday, ΔV_b , given in column 5 is the mean of the six values obtained as described above. Also included in this column is the average deviation from the mean. If the boundary moves with the current the displacement, ΔV_b , is positive. The correction, ΔV_e , for the volume changes due to the electrode processes is recorded in column 6 and will be discussed later in this paper. The transference number increment, *i. e.*, $\Delta T = (\Delta V_b - \Delta V_e) \Delta c$, is recorded in column 7 and, for comparison, the last two columns of Table I contain values of ΔT computed from existing transference data obtained by the direct moving boundary and Hittorf methods, respectively.

Discussion

If the average deviation of the individual values of ΔT from the mean may be taken as a measure of the precision of the differential method, it is of the order of 1 or 2 units in the fourth decimal place. This compares favorably with the precision of the direct moving boundary method. In this study of the differential method a thermo-

(15) Running, "Empirical Formulae," John Wiley and Sons, Inc., New York, N. Y., 1917, p. 126.

(16) The comparator scales, at right angles to each other, are graduated in millimeters and provided with 10 division verniers. Readings are interpolated to the nearest 0.02 mm. The comparator microscope gives a magnification of 12X. The eyepiece contains a scale whose central line is used as the reference mark. The author takes this opportunity of expressing his appreciation to Mr. Josef Blum of The Rockefeller Institute instrument shop for the care and precision with which this comparator was made.

TABLE I

TRANSFERENCE NUMBER DIFFERENCES FOR AQUEOUS SOLUTIONS OF SOME SALTS AT 0.5°								
1	2	3	4	5	6	7	8	9
Salt	$c'' \times 10^3$	$c' \times 10^3$	Ma.	ΔV_b , ml.	ΔV_e , ml.	$\Delta T \times 10^4$	$\Delta T_{MB} \times 10^4$	$\frac{\Delta T_H}{10^4} \times 10^4$
KCl	0.500	0.200	36	- 1.2 ± 0.3	1.3	- 7 ± 0.9	- 6	
KCl	.500	.200	32	- 10.1 ± 0.5	-7.4	- 8 ± 1.5	- 6	
NaCl	.200	.100	25	- 27.5 ± 1.1	9.2	- 37 ± 1.1	- 33	
NaCl	.500	.100	25	- 14.9 ± 0.4	9.3	- 97 ± 1.6		
NaCl	.500	.200	35	- 11.6 ± 0.4	9.3	- 63 ± 1.2		
LiCl	.502 ₅	.200	32	- 28.2 ± 1.1	9.7	- 115 ± 3.3	-117	-119
KBr	.200	.050	13	- 0.3 ± 1.3	2.4	- 4 ± 2.0	+ 10	
KBr	.500	.200	36	+ 2.0 ± 0.6	2.4	- 1 ± 1.8		
CaCl ₂	.201	.100 ₅	37	- 97.6 ± 1.8	11.3	- 109 ± 1.8	- 107	
BaCl ₂	.200	.100	33	- 87.0 ± 1.0	9.9	- 97 ± 1.0		- 91
CdI ₂	.100	.050	7	-1998 ± 9	20	-1009 ± 5		
CdI ₂	.200	.100	12	-1282 ± 6	0	-1282 ± 6		
CdI ₂	.300	.200	12	- 731 ± 1.7	27.1	- 758 ± 1.7		
LaCl ₃	.100	.050	16	- 209.0 ± 1.8	12.5	- 111 ± 0.9	-107	-130
LaCl ₃	.200	.050	12	- 159.7 ± 2.3	11.6	- 257 ± 3.5	-249	-295
LaCl ₃	.200	.100	30	- 139.6 ± 1.2	11.6	- 151 ± 1.2	-142	-165
LaCl ₃	.200	.400	37	- 85.2 ± 0.9	11.8	- 194 ± 1.8	-198	-205
LaCl ₃	.400	.600	41	- 57.3 ± 0.8	11.9	- 138 ± 1.6		-142
LaCl ₃	.604	.805	42	- 43.5 ± 1.0	12.1	- 112 ± 2.0		-112
LaCl ₃	.805	1.006	35	- 34.3 ± 1.1	12.2	- 93 ± 2.2		- 96

stat temperature of 0.5° was selected in order to reduce the disturbing effects of heat convection. At a temperature of, say 25°, it would doubtless be necessary to use smaller currents than at the lower temperature. The spread of a boundary due to diffusion would thus be greater for a given displacement and the precision of the method might be decreased somewhat as a result. A single experiment at 25° with 0.1 *N*:0.2 *N* solutions of lanthanum chloride gave $\Delta T = -152 \pm 2.2 \times 10^{-4}$ and it will be noted that the average deviation is greater than that, 1.2×10^{-4} , for the same experiment at 0.5°.

In addition to the constancy of the boundary velocity as a check on the experiment, the transference number differences should also be additive, *i. e.*, the sum of the differences for two consecutive concentration intervals should be the same as the difference for the total interval. Sufficient data are given in Table I to permit two tests of this principle. For 0.1 *N*:0.2 *N* and 0.2 *N*:0.5 *N* solutions of sodium chloride the values of ΔT are -0.0037 and -0.0063, respectively, and the sum, -0.0100, may be compared with the value, -0.0097, for the 0.1 *N*:0.5 *N* solutions. Similarly, the sum of the values of ΔT for 0.05 *N*:0.1 *N* and 0.1 *N*:0.2 *N* solutions of lanthanum chloride is -0.0262 whereas that for the 0.05 *N*:0.2 *N* solutions is -0.0257. The deviation from additivity in these two examples indicates a somewhat larger experimental error than does the con-

stancy of the boundary velocity. It may be noted however, that in both cases the average deviation of ΔT from the mean, as given in Table I, is greatest for the wide concentration interval. Possibly because of the great disparity between the amounts of heat generated in two solutions whose concentrations differ widely, it does not appear desirable to have too great a difference of concentration at the boundary.

The recent precise measurements of Allgood and Gordon¹⁷ for sodium chloride indicate that transference number differences are not very sensitive to the temperature although their absolute values may change appreciably with that variable. Consequently the comparison between values of ΔT valid for 0.5°, column 7 of Table I, and those valid at 25°, columns 8 and 9, is justified. The values of column 8 are from the author's earlier work^{18,19} and those of column 9 are due to Jones and his associates.^{20,21,22} The Hittorf values for lanthanum chloride were computed from the equation of Jones and Prendergast.²² In general the differential method yields values in good agreement with those obtained by the direct moving boundary or Hittorf methods. The apparent exception in the case of solutions of potassium bromide may be due to the fact that the mini-

(17) Allgood and Gordon, *J. Chem. Phys.*, **10**, 124 (1942).

(18) Longworth, *THIS JOURNAL*, **57**, 1185 (1935).

(19) Longworth and MacInnes, *ibid.*, **60**, 3070 (1938).

(20) Jones and Bradshaw, *ibid.*, **54**, 138 (1932).

(21) Jones and Dole, *ibid.*, **51**, 1073 (1929).

(22) Jones and Prendergast, *ibid.*, **58**, 1476 (1936).

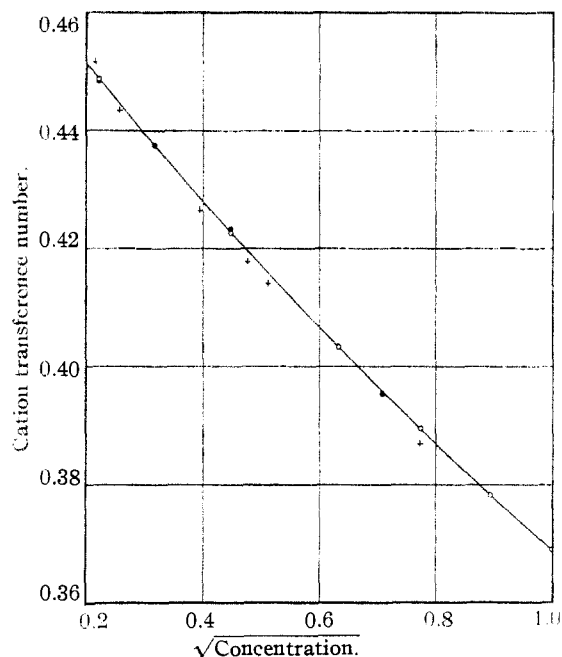


Fig. 5.—Transference numbers of lanthanum chloride as a function of the square root of the concentration: +, Jones and Prendergast; ●, direct moving boundary method; ○, differential moving boundary method.

imum in the T vs. c curve for this salt occurs at a higher concentration at 0 than at 25°.

Although difficulties have been encountered in the application of the differential method at concentrations of 0.02 N and below,²³ the upper limit

(23) The following results for 0.2 N :0.1 N solutions of lithium chloride at 0.021 amp. are typical of those obtained with dilute solutions. The successive values of ΔV_b were $-238 \downarrow$, $-205 \downarrow$ and $-54 \uparrow$ for the boundary in one side of the channel and $-90 \uparrow$, $-94 \uparrow$ and $-172 \downarrow$ for that in the other side, the current having been reversed after the second interval. The arrows indicate the direction in which the boundary moved. The mean of these figures is -142 , with an average deviation of 63, whereas the correct value (Longworth, THIS JOURNAL, 54, 2741 (1932)) is about -107 ml. per faraday. These deviations from normal behavior, which are due to convection, may be explained as follows.

Convective circulation is due both to the heating effect of the current and electro-osmosis. Since streaming due to electro-osmosis depends upon the direction of the current, while that due to heat does not, the two effects enhance each other in one side of the channel and tend to cancel in the other side. Owing to the vertical density gradient a boundary is able to restrict the circulation to the homogeneous solutions above and below but in so doing tends to be "eroded" by the circulation. In the case of concentration boundaries convection is most pronounced in the poorly conducting dilute solution above the boundary. The topmost layers of the latter are, therefore, the first to be disturbed and the more concentrated solution in these layers is carried upward and mixed with the homogeneous solution above. As already noted experimentally, the boundary in one side of the channel thus descends too rapidly while that in the other side rises too slowly. Moreover, the resulting errors do not cancel because of the inequality of the convection in the dilute solution in the two sides of the channel. Experiments with 0.02 N :0.1 N solutions of lithium chloride at other currents, and also in a narrow channel of 1.5×25 mm. cross section, indicate that the contribution of electro-osmosis to the convection is an important one in dilute solutions.

The downward displacement of a concentration boundary due to erosion of its upper layers by convection may even exceed that due to the current. In this event a boundary descends regardless of the di-

rection of concentration has not yet been found. In this respect the differential method is supplementary to the direct method since the application of the latter to concentrated solutions has met with difficulties. A study of concentrated solutions with the aid of the differential method is illustrated by the data of Table I for lanthanum chloride. If the transference numbers of a 0.1 N solution of this salt is assumed to have the same value, 0.4375, at 0.5 as at 25°, the differential method yields the values indicated by the circles in Fig. 5. These values fall on a smooth curve that also includes the directly measured transference numbers, the latter being indicated by the dots. The crosses of Fig. 5 are the Hittorf values of Jones and Prendergast. Although they differ somewhat in magnitude from the moving boundary results, they yield essentially the same slope as the moving boundary methods above a concentration of about 0.1 N .

Owing to the difficulty of finding sufficiently slow indicator ions it is doubtful if the direct moving boundary method could be applied to solutions of cadmium iodide. Concentration boundaries, on the other hand, yield quite satisfactory results. Moreover, the rapid change of the transference number with the concentration of this material gives rise to a phenomenon at one of the boundaries, namely, the movement of the boundary as a steady state, that will be discussed later

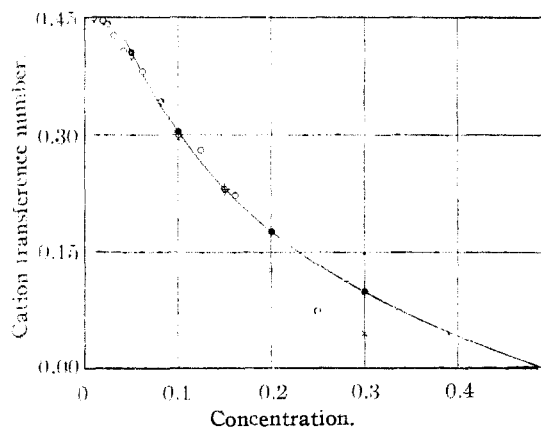


Fig. 6.—Transference numbers of cadmium iodide as a function of the concentration: ○, Redlich; ×, Noyes and Falk's interpolation of Redlich's data; ●, differential moving boundary method.

rection of the current. This phenomenon has been observed with solutions of potassium chloride by both Smith and myself. The disturbance of the boundaries by convection is also evident from the appearance of the schlieren bands. The edges of the latter are not horizontal for those portions of the boundary into which the circulation penetrates.

in this report. The data of Table I for cadmium iodide are indicated by the dots in Fig. 6, 0.3040 having been taken as the transference number of a 0.1 *N* solution of this salt. The curve of the figure was drawn through these points and extrapolates smoothly to Redlich's value at 0.5 *N*. The value 0.3040 was selected on the basis of Redlich's²⁴ data at 18°. The latter are indicated by the circles in Fig. 6. Although most of Redlich's values are reasonably consistent with the concentration boundary results, it is difficult to draw a smooth curve through the data that includes his value at 0.25 *N*. The crosses of Fig. 6 are the values interpolated by Noyes and Falk²⁵ from the data of Redlich and reproduced in the "International Critical Tables." Noyes and Falk apparently gave considerable weight to Redlich's value at 0.25 *N* which now appears to be in error.

The Volume Correction.—As in the direct method, the boundary displacement, Δv_b , is observed with respect to the cell. The displacement required, however, is that with respect to the solvent. Due to the volume changes at the electrodes the solvent itself undergoes a displacement, Δv_e —taken as positive if the solvent moves with the current—and this must be subtracted from Δv_b to give Δv of equation (1). If one electrode chamber is closed only the volume changes in this side of the cell need to be considered. For a silver-silver halide cathode in a halide solution of a *z*-valent cation, X, the changes, per faraday, are

$$\Delta V_e = V_{AgY} - V_{Ag} - T''\bar{V}_{XY_2}/z$$

V_{Ag} and V_{AgY} are the atomic and molecular volumes of silver and silver halide, respectively. T'' is the cation transference number of the more concentrated of the two solutions forming the boundaries. The partial molal volume of the salt, \bar{V}_{XY_2} , corresponds to the concentration of this solution around the electrode. As previously noted²⁶ this concentration changes during electrolysis and there is some uncertainty as to the precise value to be used. In the present investigation this uncertainty is slight since \bar{V} changes relatively slowly with concentration in the strong solutions bathing the electrodes.

The relations of Table II, determined from the best available density data at 0°, were used

(24) Redlich, *Z. physik. Chem.*, **37**, 700 (1901).

(25) Noyes and Falk, *THIS JOURNAL*, **33**, 1436 (1911).

(26) Longworth, *ibid.*, **54**, 2741 (1932).

in computing the values of ΔV_e recorded in column 6 of Table I.

TABLE II
PARTIAL MOLAL VOLUMES, AT 0°, OF SOME SALTS IN AQUEOUS SOLUTION

KCl	$\bar{V} = 23.66 + 3.75 \sqrt{m}$	(1)
NaCl	$= 13.35 + 3.24 \sqrt{m}$	(1)
LiCl	$= 15.40 + 2.85 \sqrt{m}$	(3.2)
KBr	$= 30.22 + 3.42 \sqrt{m}$	(1)
CaCl ₂	$= 13.42 + 10.77 \sqrt{m}$	(2.5)
BaCl ₂	$= 19.85 + 9.78 \sqrt{m}$	(1.2)
CdI ₂	$= 46.40 + 37.20 \sqrt{m}$	(0.3)
LaCl ₃	$= 8.87 + 22.65 \sqrt{m}$	(1)

These relations, in which the concentration, *m*, is expressed as moles of salt per 1000 g. of water, are valid up to the molalities indicated by the figures in parentheses.

A comparison of the values of ΔV_b and ΔV_e of Table I indicates that for many salts the displacement of the solvent is comparable in magnitude with that observed at the boundary. It is essential, therefore, that ΔV_e be known as precisely as ΔV_b . Smith,²⁷ with the aid of an electrolysis apparatus one electrode chamber of which could be disconnected and used as a pycnometer, determined ΔV_e directly for a 0.2 *N* potassium chloride solution and confirmed the computed value to within 0.2 ml. per faraday. In the present investigation indirect confirmation of the validity of the volume correction was obtained as follows. Silver-silver chloride electrodes were used in the first experiment on potassium chloride listed in Table I whereas cadmium electrodes were used in the second experiment on this salt. The volume change at the anode in the latter case is

$$\Delta V_e = \frac{1}{2}\bar{V}_{CaCl_2} - T''\bar{V}_{KCl} - \frac{1}{2}V_{Ca}$$

and has the value, -7.4 ml., which is quite different from that, 1.3 ml., at the silver-silver chloride electrode. Nevertheless the corrected boundary displacements, $\Delta V_b - \Delta V_e$, for the two experiments differ by only 0.2 ml., a discrepancy that is comparable with the uncertainty in ΔV_b . This result, together with that of Smith, indicates that the uncertainty in ΔV_e is probably less than 1 ml. and that, with adequate density data, this quantity can be computed with a precision equal to, or somewhat greater than, that with which the boundary displacement can be measured.

In concluding this discussion of the volume correction it may be noted that ΔV_e is always such that the observed boundary displacement per

(27) Smith, *Bur. Standards J. Research*, **8**, 457 (1932).

faraday is not altered except in direction by reversing the current. This is not the case with other volume changes, such as the gradual solution of a trapped air bubble, that may occur accidentally in the closed side of the cell. If the rate of an accidental volume effect varies with the time, the boundary velocity changes during the passage of current in one direction alone. If the rate is constant the error is revealed on reversal of the current.

Distribution of the Gradients in a Boundary.

Although the method outlined earlier in this paper gives the correct boundary position for the computation of the transference number increment, ΔT , it does not indicate the functional relationship between T and the concentration, c , over the interval, Δc , across the boundary. This additional information is contained in the schlieren photographs since the relationship between T and c , together with the diffusion process, determines the distribution of the gradients in the boundary and the manner in which this distribution changes with the passage of time and current. A complete analysis of the boundary patterns requires a solution of the differential equation describing concentration boundaries and a general solution of this equation is not yet available. It is of interest, however, to formulate the equation and, with its aid, to discuss the patterns.

The differential equation describing concentration boundaries represents but a slight modification of the relations already derived²⁸ in connection with regular boundaries. The ions in the boundary are subject to gradients, $\partial E/\partial h$ and $\partial \mu/\partial h$, of electrical and chemical potentials, respectively. The changes of the concentration, c , of a binary electrolyte with the time, t , and the height, h , in a channel of unit cross section is given by the relation

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial h} \left[\frac{cu_+}{z_+F} \left(\frac{\partial \mu}{\partial h} + z_+F \frac{\partial E}{\partial h} \right) \right] \quad (4)$$

in which u_+ and z_+ are the mobility and valence, respectively, of the cation constituent and F is the faraday. The expression for the current, i , is

$$i = \left(\frac{u_-}{z_-} - \frac{u_+}{z_+} \right) c \frac{\partial \mu}{\partial h} - (u_+ + u_-) c F \frac{\partial E}{\partial h} \quad (5)$$

Elimination of $\partial E/\partial h$ between equations (4) and (5) gives

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial h} \left[\frac{u_+ u_-}{u_+ + u_-} \left(\frac{1}{z_-} + \frac{1}{z_+} \right) \frac{c}{F} \frac{d\mu}{dc} \frac{\partial c}{\partial h} - \frac{u_+}{u_+ + u_-} \times \frac{i}{F} \right] \quad (6)$$

(28) Machines and Longworth, *Chem. Rev.*, **11**, 171 (1932).

Since $u_+/(u_+ + u_-)$ is the cation transference number, T , and the coefficient of $\partial c/\partial h$ is the diffusion constant, D ,²⁹ equation (6) may be written³⁰

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial h^2} - \frac{i}{F} \left(\frac{dT}{dc} \right) \frac{\partial c}{\partial h} \quad (7)$$

Comparison of this expression with Fick's diffusion equation, $\partial c/\partial t = D \partial^2 c/\partial h^2$, indicates that normal diffusion is superimposed on the boundary movement. For the special case in which the transference number is independent of the concentration the last term of equation (7) vanishes and diffusion at the boundary proceeds independently of the current that is flowing. The measurements carried out on solutions of potassium chloride afford an interesting confirmation of this conclusion since the transference number of this salt is very nearly independent of the concentration. Superimposed tracings of the patterns obtained in the first experiment of Table I are shown in Fig. 7. From these a value of 9.9×10^{-6} cm.² per second was computed, using the area and maximum ordinate (see ref. 8, equation 47), for the diffusion coefficient of potassium chloride over the concentration interval from 0.2 *N* to 0.5 *N*. This is but slightly greater than the value, 9.5×10^{-6} , obtained over the same concentration interval in an independent experiment in which no current was passed.

If diffusion at the boundary is neglected equation (7) becomes

$$\frac{\partial c}{\partial t} = - \frac{i}{F} \left(\frac{dT}{dc} \right) \frac{\partial c}{\partial h}$$

a relation that states that each layer of solution in the boundary moves with a velocity proportional to the change, dT/dc , of the transference number with the concentration difference across the layer. For salts whose transference numbers vary with the concentration the following cases may be mentioned.

(29) Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

(30) The error introduced by the approximation that D is constant appears to be small. This conclusion is based on a diffusion experiment between 0.1 *N* and 0.2 *N* solutions of cadmium iodide. The diffusion coefficient for this salt probably changes rapidly with the concentration, as does the transference number, and yet the gradients in the diffusion boundary were symmetrical and deviated but little from the normal Gaussian distribution. On passage of a current, however, the gradients became quite skew as the boundary moved. This is shown in the right-hand patterns of Fig. 9.

Another approximation, tacitly made in the derivation of equation (7), is that the mobility of an ion in a composite gradient of electrical and chemical potentials is the same as in an electric field alone. Since there is no gradient of chemical potential in the homogeneous solutions above and below the boundary, and it is the difference of transference number between these two solutions that determines the boundary displacement, the approximations made here have no effect on the measurements of ΔT . They may, however, introduce small errors into a computation of the gradients through a boundary.

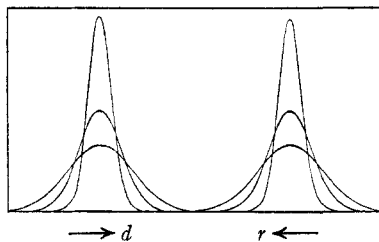


Fig. 7.—Tracings of the patterns obtained during the electrolysis of 0.2 *N* : 0.5 *N* solutions of potassium chloride.

(a) If the transference number varies linearly with the concentration over the given interval, *i. e.*, $T = a_0 + a_1c$, then $dT/dc = a_1$. In this case each layer in the boundary moves with the same velocity, with the current if a_1 is positive, against it if a_1 is negative, normal diffusion is superimposed on the migration and the gradients of the boundaries in both sides of the channel are symmetrical and, at any instant, have the same distribution.

(b) If the transference number over the given concentration interval can be represented by a quadratic in c , *i. e.*, $T = a_0 + a_1c + a_2c^2$, then $dT/dc = a_1 + 2a_2c$. If a_1 and a_2 are of the same sign the magnitude of dT/dc increases with increasing concentration and the concentrated lower layers of a boundary move faster than the dilute upper layers. This has the effect of causing the descending boundary to spread more rapidly, and the rising boundary less rapidly, than from diffusion alone. Thus at any instant the rising boundary is sharper than the descending boundary, provided, of course, that both had the same distribution of gradients initially. If, on the other hand, a_1 and a_2 are of opposite sign the descending boundary is the sharper of the two. This has been the case for most of the patterns obtained in this research. When dT/dc is linear in c , as assumed here, the spreading, or sharpening, effects do not introduce skewness into the gradients.

(c) If powers of c higher than the second are necessary in order to represent the transference number over the given concentration interval, then dT/dc is no longer linear in c and the gradients through the boundary tend to become skew as the latter moves. This, together with the spreading and sharpening effects previously discussed, is illustrated by the patterns of Fig. 2, superimposed tracings of which are shown in Fig. 8. Since the boundary displacement is against the current, dT/dc is negative. Moreover, the

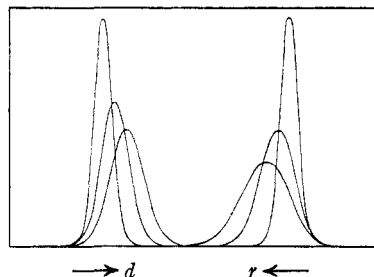


Fig. 8.—Tracings of the patterns obtained during the electrolysis of 0.1 *N* : 0.2 *N* solutions of calcium chloride.

descending boundary is the sharper of the two, from which it follows that d^2T/dc^2 is opposite in sign to dT/dc and hence positive. Although not very apparent in Fig. 8, comparator measurements show that the portion of the rising boundary above the maximum gradient has spread somewhat more rapidly than that below. It can be concluded from this that dT/dc changes more rapidly with the concentration in the dilute layers of the boundary than in the more concentrated ones, *i. e.*, d^2T/dc^2 is negative. Values of the transference number for calcium chloride at a series of concentrations between 0.1 *N* and 0.2 *N* have been interpolated from a large-scale plot of the existing data¹⁸ and are recorded in Table III. It may be noted that the successive differences of these values, given in the last three columns of the table, have the same signs as those predicted from inspection of the patterns.

$c \times 10^3$	T	ΔT	$\Delta^2 T$	$\Delta^3 T$
0.10	0.4060	-0.0025		
.12	.4035	- .0022	+0.0003	-0.0002
.14	.4013	- .0021	+ .0001	.0000
.16	.3992	- .0020	+ .0001	.0000
.18	.3972	- .0019	+ .0001	
.20	.3953			

It is unfortunate that no use readily can be made of the various transference number relations^{21,26,31,32,33} that are based on the Onsager theory of electrolytic conductance since these involve terms in the square root of the concentration and none of the derivatives of T with respect to c is constant. Moreover, the solution of equation (7) for the steady state given below becomes difficult, if not impossible, if T is taken as a function of $c^{1/2}$.

(31) Scatchard, *THIS JOURNAL*, **47**, 696 (1925).

(32) Shedlovsky, *J. Chem. Phys.*, **6**, 845 (1938).

(33) Owen, *THIS JOURNAL*, **57**, 2441 (1935).

Solution for the Steady State.—The sharpening effect at the boundary in one side of the channel has an interesting consequence. With a constant current the sharpening is proportional to the time whereas the diffusion at the boundary proceeds as the square root of the time. Consequently a distribution is eventually established that henceforth moves as a steady state. In all of the experiments reported here, with the exception of those with cadmium iodide, this steady state is not attained during the period of the experiment except for values of the current at which convective disturbances arise. The patterns of the boundaries between 0.1 *N* and 0.2 *N* cadmium iodide solutions are shown in Fig. 9 and it may be noted that the descending boundary moves as a steady state almost from the beginning of the experiment.

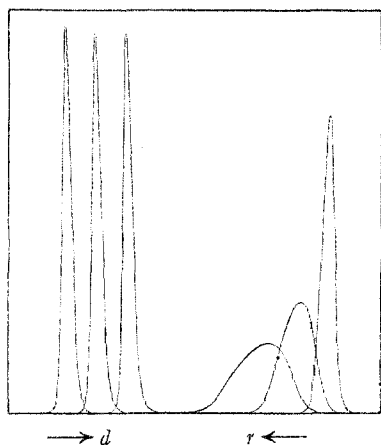


Fig. 9.—Tracings of the patterns obtained during the electrolysis of 0.1 *N*:0.2 *N* solutions of cadmium iodide.

After a balance between the spreading effect of diffusion and the sharpening effect of the transference number variation has been attained, each layer in the boundary then moves, under the influence of a constant current, with the constant velocity *v*. The concentration is thus a function of *h* and *t* of the form *c* = *f*(*h* - *vt*). Since ∂*c*/∂*t* = -*v**f*' = -*v*∂*c*/∂*h*,²⁸ equation (7) becomes

$$-v \frac{dc}{dh} = D \frac{d}{dh} \left(D \frac{dc}{dh} - \frac{i}{F} T \right)$$

This may be integrated to give

$$vc + D \frac{dc}{dh} - \frac{i}{F} T = A \quad (8)$$

The constants *A* and *v* are evaluated from the conditions that

$$\text{at } h = +\infty, c = c', dc/dh = 0 \text{ and } T = T' \quad (9)$$

and

$$\text{at } h = -\infty, c = c'', dc/dh = 0 \text{ and } T = T'' \quad (10)$$

Therefore *v* = *i*Δ*T*/FΔ*c*, which is equivalent to equation (1), and *A* = *v*(*c*' + *c*'')/2 - *i*(*T*' + *T*'')/2F = *v* \bar{c} - *i* \bar{T} /F, in which \bar{c} and \bar{T} denote mean values. In order to integrate equation (8), *T* must be expressed as a function of *c*. As already noted, the simplest relation consistent with the establishment of a steady state is *T* = *a*₀ + *a*₁*c* + *a*₂*c*². Since this relation must satisfy the conditions (9) and (10)

$$a_0 = \bar{T} - i\Delta T'/\Delta c + a_2 c'' c' \quad (11)$$

and

$$a_1 = \Delta T/\Delta c - 2a_2 \bar{c} \quad (12)$$

Making these substitutions in equation (8) and integrating

$$- \frac{2FD}{a_2 i \Delta c} \tanh^{-1} \frac{2c - 2\bar{c}}{\Delta c} = h + B \quad (13)$$

If the origin of coordinates is taken as the position in the boundary for which *c* = \bar{c} the constant of integration, *B*, is zero. Equation (13) may then be written

$$c = \bar{c} - \frac{\Delta c}{2} \tanh \frac{a_2 i \Delta c}{2FD} h \quad (14)$$

which is explicit in *c* and may, therefore, be differentiated to give

$$\frac{dc}{dh} = - \frac{a_2 i (\Delta c)^2}{4FD} \operatorname{sech}^2 \frac{a_2 i \Delta c}{2FD} h \quad (15)$$

The value of the maximum ordinate in the gradient curve represented by equation (15) is

$$(dc/dh)_m = (dn/dh)_m/k = -a_2 i (\Delta c)^2 / 4FD \quad (16)$$

in which *k* is the equivalent refractive increment for the salt.

A current density of 0.0164 ampere was used in the experiment that yielded the patterns of Fig. 9. The height of the maximum of the descending boundary after attainment of the steady state was 7.65 cm. on the plate. This must be divided by the cell length, 2.5 cm., the optical distance from the cell to the schlieren diaphragm, 186 cm., and the ratio, 1.5, of the plate to diaphragm movement to give 0.0110 as the value for -(*dn/dh*)_{*m*}. An independent determination gave 3.7₀ × 10⁻⁶ cm.²/sec. as the value for the diffusion coefficient of cadmium iodide over the same concentration interval, *i. e.*, 0.1 *N*:0.2 *N*. The equivalent refractive increment for cadmium iodide, as determined from the areas of the patterns of either Fig. 9 or those obtained in the diffusion experiment, was 25.1. Substitution of the foregoing values

in equation (16) yields $a_2 = 3.82 \times 10^6$. The boundary displacement shown in Fig. 9 gave a value for $\Delta T = -0.1282$ and hence $a_1 = -2428$ from equation (12). With T for 0.1 N cadmium iodide taken as 0.3040, $a_0 = 0.5086$ from equation (11). The quadratic, $T = 0.5086 - 2428 c + 3.82 \times 10^6 c^2$, should thus touch the actual transference number function at three points in the interval from 0.1 N to 0.2 N . That it does is shown by the fact that a value for T computed for some intermediate concentration, say 0.15 N , falls accurately on the curve of Fig. 6, the computed value being indicated by the crossed circle in that figure.

From the relations derived above, together with the properties of the gradient curve through the boundary when the latter is moving as a steady state, it is thus possible to obtain quantitative information concerning the variation of the transference number over the concentration interval across the boundary. Unfortunately, a concentration boundary moving as a steady state is seldom realized in practice and a more general solution of equation (7) would, therefore, be desirable.

It is a pleasure, indeed, to acknowledge my indebtedness to Dr. D. A. MacInnes of these Laboratories for his interest in this work and

for the care with which he reviewed the manuscript.

Summary

The motion, under the influence of an electric current, of boundaries between two different concentrations of the same electrolyte has been studied with the aid of the schlieren scanning method for recording refractive index gradients. The displacements of such boundaries have been shown to be proportional to the change of the transference number with the concentration. Experiments with several salts have shown that the method compares favorably in precision with the direct moving boundary method and is supplementary to the latter since it is applicable to salts, and at concentrations for which the direct method is not suitable.

The schlieren patterns obtained yield information concerning the manner in which the transference number varies with the concentration in the range included by the boundary. This is discussed with the aid of the differential equation for concentration boundaries. A solution of this equation is given for the case in which one of the boundaries moves as a steady state and is shown to be in agreement with the experiments.

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[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

Values of the Constants in the Debye-Hückel Equation for Activity Coefficients¹

BY GEORGE G. MANOV, ROGER G. BATES, WALTER J. HAMER AND S. F. ACREE

In the determination of ionization constants and the pH values of acids and bases in moderate concentrations, the activity coefficient of an ion is expressed in terms of certain natural and derived constants. The Debye-Hückel equation is most widely used for this purpose. As the National Bureau of Standards is engaged in establishing pH standards, the recent note of Stonehill and Berry² on this subject makes it desirable to record the constants used by the Bureau for this purpose.

(1) (Not copyrighted.) After this manuscript was submitted, the Editor kindly gave us an opportunity to examine the galley proofs of related notes by Van Rysseberghe and by Scatchard (THIS JOURNAL, **65**, 1249, 1249 (1943)).

(2) H. J. Stonehill and M. A. Berry, THIS JOURNAL, **64**, 2724 (1942).

Recent summaries^{3,4} of the values of the general physical constants, together with values of the dielectric constant of water,⁵ permit an accurate calculation of the constants A and B in the Debye-Hückel expression for the activity coefficient of electrolytes in aqueous solutions. The constants A and B may be evaluated for non-aqueous solutions if the dielectric constant of the solvent is known. In general, $A = (1.82455 \times 10^6)/(DT)^{1/2}$ and $B = (50.2904 \times 10^{-8})/(DT)^{1/2}$ for any solvent.

(3) R. T. Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).

(4) H. T. Wensel, *J. Research Natl. Bur. Standards*, **22**, 375 (1939), RP 1189.

(5) J. Wyman and E. N. Ingalls, THIS JOURNAL, **60**, 1182 (1938).