well tested experimentally on mixtures of the simple electrolytic ions to permit its application, with confidence, to the quantitative interpretation of the relatively complex protein patterns.

Acknowledgment.—The author is indebted to Dr. D. A. MacInnes of these laboratories for his continued interest in the work and for his care in reviewing the manuscript.

Summary

If disturbances due to convection and gravity are avoided, an initially sharp boundary between two solutions containing n species of ions will split, on passage of an electric current, into not more than $n - 1$ separate boundaries, each of which moves at a different rate. In this research ions differing by only a few per cent. in mobility and systems containing as many as six species have been studied with the aid of the new procedures in which the refractive index gradients in the boundaries are photographed with the schlieren scanning camera during substantially convection-free electrolysis at 0° in the Tiselius cell.

The fundamental moving boundary equation, $\Delta T_j/\Delta C_j = V$, in which V is the displacement of the boundary across which the differences of transference number and concentration of the jth ion are ΔT_j and ΔC_j, respectively, has been shown to be valid for all cases in which accurate transference data were available. The more complex boundary patterns have been interpreted, using the theory of Vincent P. Dole given in the following paper, with the aid of the assumption that relative ion mobilities are independent of the concentration. Within the limits of error imposed by this approximation it has been shown, for all cases studied, that a boundary can remain stationary on passage of the current only if all constituents are in the same relative proportions on either side. At a moving boundary, on the other hand, no two species can exist in the same proportion on the two sides unless their mobilities are identical.

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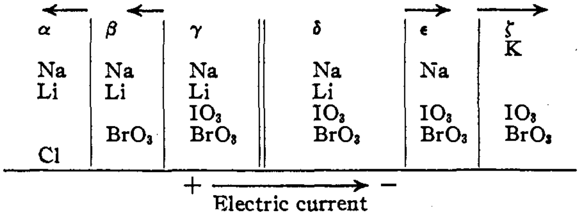
A Theory of Moving Boundary Systems Formed by Strong Electrolytes[1]

BY VINCENT P. DOLE[2]

In an accompanying paper by Longsworth[3] it is shown experimentally that the passage of an electric current across an initially sharp junction between two electrolyte solutions may cause new concentration gradients to form and to move away from the original gradients. From a single original boundary there will thus be formed a system of boundaries. The motion of these boundaries and the composition of the solutions between them may be predicted from the theory to be outlined below, for strong electrolytes, if the disturbing effects of thermal and gravitational convections are avoided. An example of such a system is given schematically in Fig. 1. This system, taken from Fig. 1 of the accompanying paper,[3] involves a total of six different ion species and has one less than that number of boundaries, as will be found to be generally true. Of the five boundaries, one is stationary, indicated by the double bars, and four move, two toward the anode and two toward the cathode, as would be expected from the presence of three anions and three cations. The fact that some of the six ions are missing in the different phases, $\alpha \ldots \zeta$, is not of general significance since a similar system would be developed with all ions present in each phase if the two original solutions, α and ζ, both contained all the ion species.



← α	← β	γ	δ	ϵ →	ζ →
					K
Na	Na	Na	Na	Na	
Li	Li	Li	Li		
		IO_3	IO_3	IO_3	IO_3
	BrO_3	BrO_3	BrO_3	BrO_3	BrO_3
Cl					

Fig. 1.—Schematic representation of a particular six ion system.

A complete description of such a system—boundary velocities and concentration distributions—could, in principle, be obtained from the compositions of the original solutions with the differential equations of continuity, the electroneutrality requirement and a specification of ion mobilities as functions of composition. This approach to the problem, however, would fail to yield practically useful, general results, because of mathematical complexity and lack of data for specification of the mobilities.

Since the mathematical difficulties arise chiefly in the description of concentration distributions through the boundaries, a simplification is obtained if the continuity equations are developed in a form independent of the particular path by which an ion concentration changes between phases. This device eliminates the complica-

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[1] The Bureau of Medicine and Surgery does not necessarily undertake to endorse views or opinions which are expressed in this paper.

[2] Lieutenant Commander Medical Corps, United States Naval Reserve.

[3] Longsworth, THIS JOURNAL, 67, 1109 (1945).

tions due to diffusion, since that process cannot affect the homogeneous phases, and has been used in most of the earlier developments of the theory of moving boundaries.[4,5]

Fortunately for the present analysis, it is sufficient to specify mobilities as relative mobilities. To the extent, therefore, that mobilities are varied by the same proportional factor with change in composition the variation does not enter the analysis. Later in this paper the assumption will be made that the relative mobilities are constant. This assumption represents a close approximation for aqueous solutions of the strong electrolytes at the concentrations encountered in moving boundary experiments, as is shown by the satisfactory agreement, reported in the accompanying paper,[3] between the theory and experiment. It is to be anticipated that considerable deviations from theory would be found with solutions of the weak electrolytes, for which such an assumption would, in many instances, be a poor approximation.

Definitions and Notation.—The equivalent volume concentration of an ion of the j species, C_j, the mobility, u_j, and the relative mobility, r_j, will all be taken as signed quantities, negative for an anion and positive for a cation. Only ions with different mobilities will be considered distinct species. The positive direction in the cell will be taken as that given by the motion of positive ions in the electric field. Both the total flux (current density) due to flow of all ions, i, and the partial flux due to flow of ions of the j species, i_j, are positive in homogeneous solutions for which only the fluxes will be defined. The dimensions of these variables are current/area.

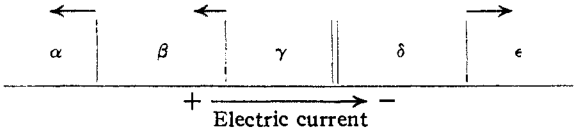

Fig. 2.—General schematic representation of a moving boundary system. The double line indicates the stationary boundary.

In a one dimensional potential gradient ($\mathrm{d}E/\mathrm{d}x$) the following equation serves to define the mobility, u_j

$$i_j = -u_j C_j \frac{\mathrm{d}E}{\mathrm{d}x} \tag{1}$$

From Ohm's law the potential gradient is given by

$$\frac{\mathrm{d}E}{\mathrm{d}x} = -\frac{i}{\kappa} \tag{2}$$

where κ is the specific conductance of the solution. This, in turn, is given from the fact that the total flux, i, is the sum of all partial fluxes, i_j, so for n ions

$$\kappa = u_1C_1 + u_2C_2 + \cdots + u_nC_n \tag{3}$$

The transference number of the j ion species, T_j, may be defined and evaluated from the preceding relations

$$T_j = \frac{i_j}{i} = \frac{u_jC_j}{\kappa} = \frac{u_jC_j}{u_1C_1 + u_2C_2 + \cdots + u_nC_n} \tag{4}$$

Since the mobilities enter the present analysis only through the transference number, in which they appear as ratios, it is sufficient to specify the relative mobilities, r_j, which may be obtained by dividing through the set of mobilities, $u_1 \cdots u_n$, by the absolute magnitude of any one member of the set. It will be convenient for subsequent analysis to consider the set of relative mobilities, $r_1 \cdots r_n$, as ordered from the most negative to the most positive. In terms of relative mobilities, the transference number is unchanged in form

$$T_j = \frac{r_jC_j}{r_1C_1 + r_2C_2 + \cdots + r_nC_n} = \frac{r_jC_j}{\sigma} \tag{5}$$

The denominator, σ, of the last expression is seen to be similar in form to the specific conductance, κ, except that the mobilities involved are relative mobilities. For this reason it will be called the relative conductance.

Under the convention of signed equivalent concentrations the condition of electroneutrality is given by

$$C_1 + C_2 + \cdots + C_n = 0 \tag{6}$$

For any system of boundaries (Fig. 2), the homogeneous phases will be indicated by Greek letter superscripts on appropriate variables. A variable associated with a boundary will be identified by a pair of superscripts, obtained from the phases on either side. The ion species will be denoted by subscript numerals or lower case letters.

The Moving Boundary Equation.—Consider two homogeneous solutions, α and β, in a cell of uniform cross-sectional area (Fig. 3). In the transition region between these two phases, indicated by the shaded area, the plane, $\bar{x}$, is located at the first moment of the concentration gradient of the considered ion species. Let two reference planes, x_1, x_2, stationary with respect to average solvent molecules, be placed in the homogeneous solutions, one on either side of the boundary, and at a sufficient distance apart that any motion of the boundary in a time interval, Δt, will not bring a plane into the boundary region. Since the transference numbers of an ion species are, in general, different in the solutions on either side, there will be for any ion species a difference between the fluxes through the two reference planes. During

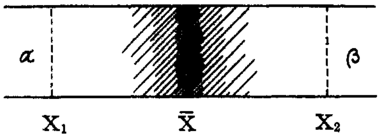

Fig. 3.—The neighborhood of a boundary. The cross hatching symbolizes concentration gradients.

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

(5) H. Weber, "Die partiellen Differential-Gleichungen der mathematischen Physik," 5th edition, chapter 24, Braunschweig, 1910; von Laue, *Z. anorg. Chem.*, **93**, 329 (1915); Henry and Brittain, *Trans. Faraday Soc.*, **29**, 798 (1933). Svensson, *Arkiv Kemi, Mineral. Geol.*, **17A**, No. 14, 1 (1943)

the time interval, Δt, the volume enclosed by the cell walls and the reference planes will thus gain an amount, $G_j(\Delta t)$, of the ions of the j species, given by

$$G_j(\Delta t) = a\int_t^{t+\Delta t} [i_j(x_2) - i_j(x_1)]\mathrm{d}t = a[T_j(x_2) - T_j(x_1)]\int_t^{t+\Delta t} i\mathrm{d}t \quad (7)$$

where x_1 and x_2 locate the reference planes along the cell axis, and a is the cross-sectional area of the cell.

The first moment of the concentration gradient in the boundary has the useful property[6] that, if the ions of a given species were rearranged to eliminate concentration gradients between the two homogeneous solutions, the location of this ideal boundary would be at the first moment. The position of the first moment, $\bar{x}_j(t)$, for the ion species, j, at time, t, is given by the following expression, wherein the numerator is integrated by parts

$$\bar{x}_j(t) = \frac{\int_{x_1}^{x_2} x\frac{\partial C_j(x,t)}{\partial t}\,\mathrm{d}t}{\int_{x_1}^{x_2}\frac{\partial C_j(x,t)}{\partial t}\,\mathrm{d}t} = \frac{x_2C_j(x_2,t) - x_1C_j(x_1,t) - \int_{x_1}^{x_2}C_j(x,t)\mathrm{d}x}{C_j(x_2,t) - C_j(x_1,t)} \quad (8)$$

On rearrangement, this becomes

$$\int_{x_1}^{x_2} C_j(x,t)\mathrm{d}x = [x_2 - \bar{x}_j(t)]C_j(x_2) - [x_1 - \bar{x}_j(t)]C_j(x_1) \quad (9)$$

The integral, multiplied by the cross-sectional area a, gives the quantity of ion species, j, enclosed at time, t, by the reference planes and the cell walls. With the concentrations at the reference planes independent, by hypothesis, of time, the enclosed volume will gain an amount of the ion species during Δt

$$G_j(\Delta t) = a[\bar{x}_j(t) - \bar{x}_j(t+\Delta t)][C_j(x_2) - C_j(x_1)] \quad (10)$$

Since the points x_1 and x_2 are arbitrarily located in the phases, α and β, it is sufficient to label concentrations and transferences by a superscript for the phase. Equating, with this simplification equations 7 and 10, we obtain

$$V_j^{\alpha\beta}\left(C_j^\alpha - C_j^\beta\right) = T_j^\alpha - T_j^\beta \quad (11)$$

The function, $V_j^{\alpha\beta}$, introduced into this equation, is given by

$$V_j^{\alpha\beta} = \frac{\bar{x}_j(t+\Delta t) - \bar{x}_j(t)}{\int_t^{t+\Delta t} i\mathrm{d}t} = \frac{1}{i}\frac{\mathrm{d}\bar{x}_j}{\mathrm{d}t} \quad (12)$$

where the second form is obtained as a limit as Δt approaches zero. It will be seen that $V_j^{\alpha\beta}$ has the physical significance of the boundary velocity per unit total flux across it, or, equivalently, of the volume swept out by a plane at the first moment per unit quantity of current passed. This will be constant for a boundary, regardless of variations in the current or in the cell dimensions, since the concentrations and transference numbers in the phases at either side cannot vary with time.

Since the boundary under consideration does not split on passage of the current there can be no relative motion of the first moments of any two ion species. The function, $V_j^{\alpha\beta}$, has, therefore, the same value, $V^{\alpha\beta}$, for all species. Diffusion in the boundary, moreover, cannot shift the first moment of any species, since, as previously seen, such a shift in the moment would imply a net transfer of material through a reference plane in a homogeneous solution. Consequently, the moving boundary equation, which is simply a statement of the conservation of mass, becomes

$$V^{\alpha\beta}\left(C_j^\alpha - C_j^\beta\right) = T_j^\alpha - T_j^\beta \quad (13)$$

The following special forms of this relation, equations 14 and 15, will be used later in this paper. Equation 14 is obtained by the elimination of the transference numbers between equations 13 and 5, while elimination of the concentrations between these two relations gives equation 15, after multiplication of both sides by r_j.

$$\left(\frac{r_j}{\sigma^\alpha} - V^{\alpha\beta}\right)C_j^\alpha = \left(\frac{r_j}{\sigma^\beta} - V^{\alpha\beta}\right)C_j^\beta \quad (14)$$

$$\left(r_j - V^{\alpha\beta}\sigma^\alpha\right)T_j^\alpha = \left(r_j - V^{\alpha\beta}\sigma^\beta\right)T_j^\beta \quad (15)$$

The relative mobilities, r_j, bear no phase superscript since they are to be assumed constant throughout the system.

The Frame of Reference.—Although the total flux of all ions, *i. e.*, the current density, is independent of the reference plane, the partial flux of any particular species is not thus independent. For this reason a transference number, defined by the ratio of a partial to the total flux, will have meaning only in reference to some element which is considered as stationary. The transference numbers used in this analysis are the same as those obtained by the Hittorf method, since they are referred to the solvent as the fixed element.

Since the transference number of any ion species gives the flux per unit current density, the condition of continuity could be succinctly expressed by the equality of transference numbers referred to the boundary as the fixed element. A transformation can then be made to the set of Hittorf transference numbers by taking into account the relative motion of the boundary and the solvent. As was first shown by Lewis,[7] such a transformation is effected for the j species by the equation

$$T_j' = T_j - VC_j \quad (16)$$

where T_j' and T_j are referred to the boundary and to the solvent, respectively, V is the boundary velocity per unit current density referred to the solvent, and C_j is the concentration. Thus equality of the primed transference numbers in

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[6] Longsworth, THIS JOURNAL, **65**, 1755 (1943).

[7] Lewis, *ibid.*, **32**, 862 (1910).

adjacent phases implies the moving boundary equation 13, providing that the average solvent molecules in the two phases are not in motion relative to each other.

Actually, there must be slight relative motion, as will be seen below. Since the transference numbers in any phase should be referred to the solvent in that phase, the moving boundary equation would properly be written, for, say, the $\gamma\delta$ boundary

$$T_j^\gamma - T_j^\delta = C_j^\gamma V^{\gamma\delta}(\gamma) - C_j^\delta V^{\gamma\delta}(\delta) \qquad (17)$$

where $V^{\gamma\delta}(\gamma)$ and $V^{\gamma\delta}(\delta)$ are, respectively, the displacements of the boundary with respect to the solvent of the γ and the δ phases. If displacements are measured, primarily, with respect to the apparatus, the transference numbers in the phase toward the closed end must be corrected for any significant displacement of solvent due to volume changes at the electrode in the closed end and at all boundaries intervening between this electrode and the $\gamma\delta$ boundary. The transference numbers in the more distant phase require these corrections plus a correction for volume changes around the $\gamma\delta$ boundary itself.

The volume change around the electrode in the closed end of the cell is small, and may be calculated with sufficient accuracy under the assumption that the partial molar volumes of the reactants are constant over the concentration range involved.[7]

Volume effects about the boundaries appear to be of a lower order of magnitude than the errors introduced by the assumption of constant relative ion mobilities. The first effect is due to differences in the solvent concentration in the phases. If a boundary region is so defined that it includes all boundary gradients within it, and moves along with the boundary in such a way as to enclose a constant mass of solvent, then the flux of solvent into the region must be the same as the flux out. The flux, however, may be calculated as the product of volume concentration times velocity, so inequalities in the concentration of solvent in the adjoining phases imply reciprocal inequalities in velocities. Thus the solvent molecules of the two phases are in relative motion.

The second effect can occur only with boundaries in which the concentration distributions change with time, and so is absent in the steady state boundaries usually studied. Any volume change which occurs on redistribution of constituents in the boundary region of constant mass as a result of deviations from ideal behavior probably is small in systems for which the assumption of constant relative mobilities is an adequate approximation. Both types of volume change around the boundaries have been neglected in the present analysis.

As will be shown later in this paper, the assumption of constant relative mobilities implies that the boundary at the original site remains stationary with respect to the solvent. For systems to which the present analysis is applicable, therefore, reference to this boundary as the stationary element implies Hittorf transference numbers without the need of any volume correction.

Dimensions of the Variables.—The transference number, as implied by its name and by equation 5, is dimensionless. Therefore, from equation 13, products of the form $V^{\alpha\beta}C_j^\alpha$ are also dimensionless. Since, by equation 12, $V^{\alpha\beta}$ has the dimensions of volume per quantity of electricity, it could simply be expressed in cu. cm./coulomb, while concentration of the ions would be given in coulombs/cu. cm. For practical calculations it will be found to be more convenient to express concentration in gram equivalents/liter, in which case numerical factors will be avoided in equation 13 by expressing $V^{\alpha\beta}$ in liters/96,500 coulombs.

Since the relative mobilities, r_j, are dimensionless by definition, the relative conductance, σ^α, has the same dimensions as are used for concentration. For this reason, products of the form $V^{\alpha\beta}\sigma^\alpha$ are dimensionless, in accord with the requirements of equation 15.

General Theory.—In the following development the relative mobilities of all species present in the system, and the compositions of the two end solutions forming the original boundary, are considered to be known. The data sought are the concentrations and transference numbers of the ions in all of the newly formed phases and the displacements, V, of the separated boundaries.

In a preliminary survey of the problem it can be seen that the specification of one phase containing n species is not sufficient to determine the n concentrations of the next adjacent phase, together with the boundary displacement, V, since the number of conditions sought will generally be one more than the number given in the original specification. Consequently it is necessary to use data from both original solutions to make complete calculations for any boundary in the system. As will be seen later, for the special case in which one of the ions, present in the known phase, is absent in the unknown phase, it is possible to calculate both the composition and the boundary displacement, V. Even in this case, however, one datum has been taken from the original solution at the other end of the system, namely, the absence of some particular ion.

The following considerations indicate that a system that involves a total of n ions will, in general, have $n - 1$ boundaries. To specify the composition of a solution containing n ions, $n - 1$ independent concentrations must be given, one having been eliminated by the electroneutrality condition. If it is imagined that the $n - 1$ given conditions for one original solution are applied to the calculation of the n variables involved in the first boundary ($n - 1$ to specify the next phase, and 1 to give V), it will be clear that one variable is left undetermined. If this process is repeated through $n - 1$ boundaries, there will be thus accumulated $n - 1$ undetermined variables—just sufficient to allow an arbitrary composition for the other original solution. If there were less than $n - 1$ boundaries, the two original solutions could not have had arbitrary compositions; if there were more than $n - 1$ boundaries, the system would not be determinate.

Two practical difficulties are encountered in calculation. One is the fact, just mentioned, that data from both original solutions must be used for each boundary. The second is that each continuity equation involves two phase variables, the relative conductances (σ^α and σ^β, for the boundary between phases α and β), each of which is a function of all the concentrations in its phase (equations 14 and 15). Both of these difficulties are resolved by dealing with products of the form $V^{\alpha\beta}\sigma^\alpha$, $V^{\alpha\beta}\sigma^\beta$, etc., as single variables.

There are $2(n - 1)$ of these products in a system of $n - 1$ boundaries, since for each boundary the displacements, V, may be multiplied by the relative conductance, σ, of either adjoining phase. The first step in the solution is the calculation of the entire set of $V\sigma$ products from the known $2(n - 1)$ independent transference numbers of ions in the two original solutions. In any phase, β for example, the transference number of the j ion is related to the transference number of that ion in the α phase by the corresponding continuity equation (15), and to its transference number in the γ phase by a second similar equation. If the transference number in the β phase is eliminated between these two equations, a relation is obtained between transference numbers in the α and γ phases

$$(r_j - V^{\alpha\beta}\sigma^\alpha)(r_j - V^{\beta\gamma}\sigma^\beta)\,T_j^\alpha = (r_j - V^{\alpha\beta}\sigma^\beta)(r_j - V^{\beta\gamma}\sigma^\gamma)\,T_j^\gamma \quad (18)$$

Repetition of this elimination between successive phases leads to a relation between the transference numbers of any ion, j, in the two known end phases. If these end phases be denoted by α and η, with any number of boundaries intervening, this relation will be

$$(r_j - V^{\alpha\beta}\sigma^\alpha)(r_j - V^{\beta\gamma}\sigma^\beta)\cdots(r_j - V^{\zeta\eta}\sigma^\zeta)\,T_j^\alpha = (r_j - V^{\alpha\beta}\sigma^\beta)(r_j - V^{\beta\gamma}\sigma^\gamma)\cdots(r_j - V^{\zeta\eta}\sigma^\eta)\,T_j^\eta \quad (19)$$

It may be noted that on each side of the equation the superscripts of V run in consecutive alphabetical pairs, corresponding to the successive boundaries that are encountered between the α and η phases. On the left side of the equation the superscripts of the σ factor correspond to the left member of the pair on V, while on the right side of the equation the correspondence is with the right. If there are n ions in the system, there are n such equations.

It will be shown below that the two polynomials, equation 20, each of which involves the known transference numbers of an end phase have the property that their roots, $x_1, x_2 \cdots$ and $y_1, y_2 \cdots$, give the desired set of $2(n - 1)$ values for the different $V\sigma$ products. These polynomials, for the α and η phases, respectively, are

$$\left.\begin{aligned}\frac{T_1^\alpha}{r_1 - x} + \frac{T_2^\alpha}{r_2 - x} + \cdots + \frac{T_n^\alpha}{r_n - x} &= 0\\ \frac{T_1^\eta}{r_1 - y} + \frac{T_2^\eta}{r_2 - y} + \cdots + \frac{T_n^\eta}{r_n - y} &= 0\end{aligned}\right\} \quad (20)$$

Let it be granted, for the moment, that each of these polynomials always has $n - 1$ distinct real roots. The set of $n - 1$ roots from the first polynomial, $x_1, x_2, \cdots x_{n-1}$, with the additional relation that the sum of all transference numbers in a phase is unity (from equation 5), leads to a set of n linear equations in the n transference numbers. For the first polynomial this set of equations is

$$\left.\begin{aligned}\frac{T_1^\alpha}{r_1 - x_1} + \frac{T_2^\alpha}{r_2 - x_1} + \cdots + \frac{T_n^\alpha}{r_n - x_1} &= 0\\ \frac{T_1^\alpha}{r_1 - x_2} + \frac{T_2^\alpha}{r_2 - x_2} + \cdots + \frac{T_n^\alpha}{r_n - x_2} &= 0\\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots&\cdots\\ \frac{T_1^\alpha}{r_1 - x_{n-1}} + \frac{T_2^\alpha}{r_2 - x_{n-1}} + \cdots + \frac{T_n^\alpha}{r_n - x_{n-1}} &= 0\\ T_1^\alpha + T_2^\alpha + \cdots + T_n^\alpha &= 1\end{aligned}\right\} \quad (21)$$

Such a set of equations can be solved by standard methods,[8] to give values for the T_j^α variables in terms of the coefficients. A typical solution is

$$T_j^\alpha = \frac{(r_j - x_1)(r_j - x_2)\cdots(r_j - x_{n-1})}{(r_j - r_1)(r_j - r_2)\cdots(r_j - r_n)} \quad (22)$$

in which there are $n - 1$ factors in both the numerator and the denominator, the zero factor, $r_j - r_j$, being absent in the denominator.

By identical procedures, an equivalent expression for T_j^η is obtained from the second polynomial

$$T_j^\eta = \frac{(r_j - y_1)(r_j - y_2)\cdots(r_j - y_{n-1})}{(r_j - r_1)(r_j - r_2)\cdots(r_j - r_n)} \quad (23)$$

Finally, by elimination of the denominators, which are common to the two equations, there results the relation

$$(r_j - y_1)(r_j - y_2)\cdots(r_j - y_{n-1})T_j^\alpha = (r_j - x_1)(r_j - x_2)\cdots(r_j - x_{n-1})T_j^\eta \quad (24)$$

Comparison of this equation with equation 19 shows that the sets $y_1 \cdots y_{n-1}$ and $x_1 \cdots x_{n-1}$ are actually the desired $V\sigma$ products.. It should be noted that the $V\sigma$ terms multiplying the α phase transference number, T_j^α in equation 19, are given by the roots of the polynomial from the η phase, and *vice versa*.

It remains to be shown that all roots of the polynomial are real, as supposed, and that a rule can be given whereby the roots can be ordered to correspond with successive $V\sigma$ products. Since

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(8) Bôcher, "Introduction to Higher Algebra," The Macmillan Co., New York, N. Y., 1922.

the transference numbers are always positive, the polynomial

$$z = \frac{T_1^\alpha}{r_1 - x} + \frac{T_2^\alpha}{r_2 - x} + \cdots + \frac{T_n^\alpha}{r_n - x} \quad (25)$$

will have the general form of Fig. 4, which is drawn for the special case of three anions (relative mobilities r_1, r_2, r_3), and two cations (r_4, r_5). The functions must thus cross the x axis, *i. e.*, have a root, somewhere between each successive pair of relative mobility values. Between the least negative relative mobility and the least positive one, it must pass through the origin since one root is always zero to satisfy equations 5 and 6.

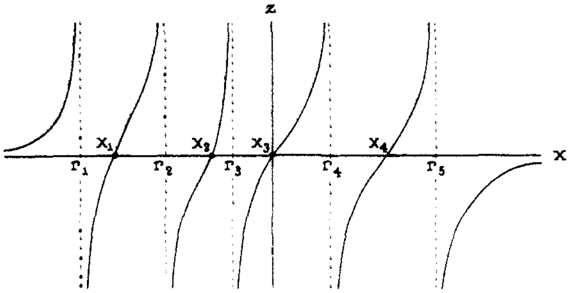

Fig. 4.—The graphical form of the function given in equation 25.

Now consider the continuity equations for any boundary, say the $\beta\gamma$ boundary

$$\left(r_j - V^{\beta\gamma}\sigma^\beta\right) T_j^\beta = \left(r_j - V^{\beta\gamma}\sigma^\gamma\right) T_j^\gamma \quad (15)$$

Since the transference numbers are both positive, the factors in parentheses must have the same sign. In other words, both $V^{\beta\gamma}\sigma^\beta$ and $V^{\beta\gamma}\sigma^\gamma$ must have values such that they fall in the same interval between two successive relative mobilities. If the designations of the system are such that $V^{\alpha\beta}$ has the most negative value, *i. e.*, the $\alpha\beta$ boundary in Fig. 2, then $V^{\alpha\beta}\sigma^\beta$ will be more negative than $V^{\beta\gamma}\sigma^\beta$, since $V^{\alpha\beta} < V^{\beta\gamma}$ and σ^β is always positive by equation 5. But $V^{\beta\gamma}\sigma^\beta$ and $V^{\beta\gamma}\sigma^\gamma$ have just been shown to fall in the same interval between two consecutive relative mobilities, so that we have

$$V^{\alpha\beta}\sigma^\beta < V^{\beta\gamma}\sigma^\gamma \quad (26)$$

From these considerations, we see that the roots of each polynomial, if ordered from the extreme negative to the most positive, will correspond to the appropriate set of $V\sigma$ products, similarly ordered. This order will, moreover, correspond to the actual order of boundaries in the system, from the one with the greatest negative velocity to the one with the most positive, *i. e.*, from left to right in Fig. 2.

When one or more of the n ions in a system is absent from one original solution, the calculations are somewhat simplified but involve the same principles. In such a case the polynomial for the original solution in which an ion is missing is reduced in degree, by the absence of the corresponding term, and the additional values required for $V\sigma$ products are obtained directly from the fact that the $V\sigma$ term must equal the relative mobility of each ion missing, *i. e.*, $r_j - V\sigma = 0$. This follows from the necessity that an ion present in one original solution, but absent from the other, must disappear over a boundary in the system. At this boundary a continuity equation, in the form of equation 15, will then have one transference number equal to zero and one not zero, so that the factor $(r_j - V\sigma)$ for the second must vanish. The boundary over which the ion will disappear will be determined by the position of the ion in the ordered set of relative mobilities of all ions in the system.

Corollaries.—It will be apparent from the foregoing analysis that a system that contains n ions will, in general, form $n - 1$ boundaries, whether or not any ions disappear over a boundary. If the system contains p anions and q cations, there will generally be $p - 1$ boundaries with negative velocities, and $q - 1$ with positive velocities.

A system containing n ions may, however, form less than $n - 1$ boundaries under special conditions. If the $V\sigma$ products for a moving boundary are equal, *e. g.*, $V^{\beta\gamma}\sigma^\beta = V^{\beta\gamma}\sigma^\gamma$, the consequent equality of σ functions of adjacent phases would, by equation 14, imply equal concentrations for each ion species in the two phases, so that no boundary would exist. Equality of corresponding non-zero roots of the two polynomials (20), implies, therefore, the disappearance of a boundary.

A boundary cannot disappear by equality of the velocities of two adjacent boundaries. Such an event would imply either that an ion is absent from both original solutions (in which case it is absent from the entire system), or that two relative mobilities are identical (in which case the two ions would be classed as one species).

The condition for disappearance of the stationary boundary is most easily given in terms of the regulating function. This function, originally defined by Kohlrausch[4] under the more restrictive assumption of constant ion mobilities, may be redefined in terms of relative mobilities, the constancy of which has been found to be sufficient for the present analysis. Expressed in terms of relative mobilities, the regulating function, ω, becomes

$$\omega = \frac{C_1}{r_1} + \frac{C_2}{r_2} + \cdots + \frac{C_n}{r_n} \quad (27)$$

Like σ, this function is always positive and has the dimensions of concentration. If each member of the set of equations, represented by equation 14, is divided through by the corresponding relative mobility, and the set then added, one obtains

$$V^{\alpha\beta}(\omega^\alpha - \omega^\beta) = 0 \quad (28)$$

This result is obtained by the use of the electroneutrality condition (6) and the above definition of ω. In the case of a moving boundary ($V^{\alpha\beta} \neq 0$), the regulating function must have the same value in the two adjoining phases. As a consequence, this function must have the same value in every phase on one side of the stationary boundary, regardless of the number of boundaries and phases, since the reasoning applies to all moving boundaries.

The stationary boundary, on the other hand, must have unequal values of the regulating function in adjoining phases for its existence. If, in equation 14, the V term is set equal to zero, and the relative mobilities cancelled, one obtains

$$\frac{C_1^\alpha}{C_1^\beta} = \frac{C_2^\alpha}{C_2^\beta} = \cdots = \frac{C_n^\alpha}{C_n^\beta} = \frac{\sigma^\alpha}{\sigma^\beta} = \frac{\omega^\alpha}{\omega^\beta} \qquad (29)$$

The last term, involving the regulating function ratio, can be justified by substituting the preceding terms into equation 27. It is thus seen that the stationary boundary is not only always a dilution boundary, but also that the dilution factor can be calculated from the values of the regulating function in each of the two original solutions. Since a more concentrated solution usually has the greater density, the original solution having the higher value for the regulating function should be placed below the other in a moving boundary experiment in order to avoid gravitational convection at the stationary boundary.

In contrast to the stationary boundary, a moving boundary cannot have any pair of ions maintain their relative proportions across it. Such an event would, by equation 14, imply either that their relative mobilities are equal (which is excluded by definition) or that no concentration changes occur for any ion species, since the relative conductance must change across any real boundary. For both moving and stationary boundaries, equation 14 also implies that there is either some change in concentration for every ion species or no change in any concentration across the boundary.

Equations Convenient for Calculation.—In the calculation of single boundaries in the system, an especially simple case arises when two ions disappear across a boundary, for example Cl and BrO_3 at the $\alpha\beta$ boundary in Fig. 1, since both the $V\sigma$ products required for this boundary are given by the relative mobilities of the disappearing ions. It is to be noted that, while only one ion species can disappear across a boundary in a given direction (for the disappearance of two would, by equation 14, imply equality of their relative mobilities), it is possible for one ion to disappear in one direction and the second ion in the other direction. This occurs when an ion is absent from one original solution, and another ion which is next to it in the ordered sequence of relative mobilities, is absent in the other original solution. If g and h are the ions that disappear under these circumstances, the concentrations of ions, j, in the two phases, say α and β, are given by a special form of equation 14, where $V^{\alpha\beta}\sigma^\alpha = r_g$ and $V^{\alpha\beta}\sigma^\beta = r_h$. Substitution of these values leads to

$$C_j^\beta = \frac{r_h(r_g - r_j)}{r_g(r_h - r_j)}\, C_j^\alpha \qquad (30)$$

The next special case in order of difficulty occurs when one ion, present in the known phase, is absent in the otherwise unknown phase. Let the known phase be α and the unknown, β, with the g ion species absent in β. Then $V^{\alpha\beta}\sigma^\alpha = r_g$, and for other ions, j, equation 14 becomes

$$C_j^\beta = \frac{(V^{\alpha\beta}\sigma^\beta)(r_g - r_j)}{r_g(V^{\alpha\beta}\sigma^\beta - r_j)}\, C_j^\alpha \qquad (31)$$

Finally, for the general case in which all ions are present, it is necessary to obtain both $V\sigma$ products from the polynomials of the known end phases. Equation 14 may, for moving boundaries, be used in the form

$$C_j^\beta = \frac{(V^{\alpha\beta}\sigma^\beta)(V^{\alpha\beta}\sigma^\alpha - r_j)}{(V^{\alpha\beta}\sigma^\alpha)(V^{\alpha\beta}\sigma^\beta - r_j)}\, C_j^\alpha \qquad (32)$$

Alternative means of calculating the system from the determined $V\sigma$ products are also available: the transference numbers may be first calculated with equation 15, or the displacements, V, may be evaluated as an initial step by use of the known values of σ^α and σ^η in the end phases. The regulating function may be used to facilitate evaluation of the stationary boundary.

The polynomials used for calculating the $V\sigma$ products may be brought into a more useful form by expression in terms of concentrations, and elimination of any one concentration by use of the electroneutrality condition (*i. e.*, elimination of the zero root). Equation 20 then becomes

$$\left.\begin{aligned} \frac{r_1 - r_n}{r_1 - x}\, C_1^\alpha + \frac{r_2 - r_n}{r_2 - x}\, C_2^\alpha + \cdots + \frac{r_{n-1} - r_n}{r_{n-1} - x}\, C_{n-1}^\alpha &= 0 \\ \frac{r_1 - r_n}{r_1 - y}\, C_1 + \frac{r_2 - r_n}{r_2 - y}\, C_2^\eta + \cdots + \frac{r_{n-1} - r_n}{r_{n-1} - y}\, C_{n-1}^\eta &= 0 \end{aligned}\right\} \qquad (33)$$

In the most general case of an n ion system, in which every ion is present in each phase, it will be necessary to solve two polynomials of degree $n - 2$. For each absence of an ion from one original solution, the degree of that polynomial is reduced by 1. If only two ions are present in one original solution, there is no equation for that phase, since the set of $V\sigma$ products is given by the set of relative mobilities, with the zero root for the stationary boundary.

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Summary

A theory is developed to account for the formation of a system of moving boundaries when an electric current is passed across an initial sharp

junction between two salt solutions of arbitrary composition. The analysis is restricted to the class of strong electrolytes for which it may be assumed that the relative mobilities of the ions are constant through the system.

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Electron Deficient Molecules. I. The Principles of Hydroboron Structures

BY KENNETH S. PITZER

Atoms such as boron and aluminum with fewer valence electrons than valence shell orbitals do not complete their valence shells by electron sharing of the usual type. While many compounds of such elements are metallic and others are salt-like or ionic, still others consist of essentially non-polar molecules. Such molecules can be termed electron deficient. In some cases the simple molecules predicted by conventional valence theory actually combine further. The most extensive series of this type is the subject of this paper.

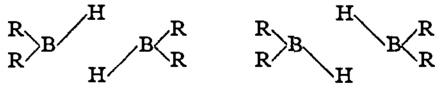
The compounds of hydrogen with boron have long been a puzzle in valence theory. In 1942 Bauer[1] summarized the most fully developed theory of that time, which assumed hydrocarbon-like structures. Since too few electrons are present for electron pair bonds, resonance is assumed among structures with one electron and no electron bonds in various positions. The net results with this point of view are unsatisfying. At many points the natural, expected result is not found and the theory must be strained to fit the facts. One may mention the infrared spectrum[2] of B_2H_6, which is quite unlike that of C_2H_6, and the need of assuming a higher potential barrier to internal rotation[2] in B_2H_6, than in C_2H_6, in spite of larger distances and fewer electrons in the former. Other points will be noted below. However, possibly a more serious failure of the hydrocarbon-like structural theory is its failure to give any adequate reasons for the existence of the particular hydroborons that are found, and for the absence of any others in the lower molecular weight range. For example, why should there be no molecule with three boron atoms?

Very recently Nekrasov,[3] Syrkin and Dyatkina[4] and Longuet-Higgins and Bell[5] have revived and discussed the structure proposed earlier by Dilthey[6] and by Core.[7] This structure places two of the hydrogen atoms of B_2H_6 between the boron atoms, one above and one below the plane of the rest of the molecule. Thus a small, four-membered ring bond or bridge is formed. The evidence as presented by these authors[3,4,5] is most favorable to this point of view. Indeed the theory presented below develops in part from this structure and is entirely consistent with it. However, several additional elements are needed before all hydroboron chemistry is brought into a coherent picture.

The first important addition is the recognition that this ring bond is not inconsistent with the essentials of the Wiberg[8] structure, which so ably explained certain reactions of the hydroborons. The present picture is much more specific than Wiberg's, and differs from it in many ways. Hellriegel[9] proposed somewhat similar structures to those given below, but his postulate of K shell binding is totally different and is not acceptable. Let us now proceed with a logical exposition of the theory.

The Protonated Double Bond.—The first element of the theory is the new type of bond. It can form between electron pair bonded groups of the general formula R_nMH where $n + 1$ is less than the number of valence shell orbitals of the atom M. Thus in $(CH_3)_2BH$ or BH_3 all atoms are bonded with electron pair bonds, but the boron atom has one vacant orbital, and there is at least one hydrogen atom bonded to boron. The formation of this bond uses one hydrogen atom and one vacant orbital in each group.

As two such groups come together with a hydrogen of one group near the vacant orbital of the other, the following resonance can occur



I

where we have taken boron with its valence shell of four orbitals as the example. Ionic forms are also possible.

II

These forms will be particularly important if one central atom is more electronegative than the

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