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A THEORETICAL ANALYSIS OF THE MOVING BOUNDARY MEASUREMENT OF TRANSFERENCE NUMBERS

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(Master's Thesis)

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A Theoretical Analysis of the Moving Boundary Measurement of Transference Numbers

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September 1967

Abstract

A moving boundary system is analyzed and an equation for the transference number is derived. The equation is valid for concentrated as well as dilute solutions. When the partial molal volume of the solvent is constant through the boundary, the equation reduces to the approximate equation now in common use.

The cation transference number in 0.213M NH_4NO_3 was experimentally determined and found to be equal to 0.5140±0.0024.

Introduction

The moving boundary method for measuring transference numbers is well established. Investigation of moving boundaries dates back to the 19th century[1], and the method is still used today[2]. Over this period of time improvements have been made in the mechanics of forming and observing the boundary[1,3,4], and the accuracy in measuring the variables involved has been increased. The procedure, though, has remained as follows:

A boundary is somehow formed in a tube or channel between two ionic solutions which have one common ion. A measured quantity of electrical charge is passed through the solutions, and the displacement of the boundary is measured.

Treatment of the data has undergone little refinement. It was early realized that the electrochemical reactions which occur at the electrodes affect the movement of the boundary and must be accounted for. G. N. Lewis[5] in 1910 presented an approximate analysis which corrected for this movement. His equation was thought to be restricted to dilute solutions[1]. No improvement in the calculation has yet been suggested, although Bearman[6] in 1962 showed that the Lewis correction is actually not restricted to dilute solutions, but applies to systems in which the partial molal volumes through the boundary are constant - a slightly less stringent requirement.

In what follows, a detailed analysis of the moving boundary system is made. An expression for the transference number is derived which is applicable at any concentration and which reduces to an expression of the type proposed by Lewis when the partial molal volume of the solvent is

constant through the boundary. The accuracy of the expression depends, to some extent, upon the accuracy to which the density of the following solution can be linearly related to its concentration over the range of interest. It is shown that this range can be made small, and a linear representation is quite justified.

The transference number of the NH_4^+ ion in 0.213M NH_4NO_3 at 25°C was experimentally determined with $AgNO_3$ as a following solution. The value obtained is 0.5140±0.0024.

Theoretical Development

The System Described

In moving boundary transference number determinations a boundary between two salt solutions having a common ion is formed in a tube or channel. Current is passed through the solution forcing the boundary to move up (or down) the channel. (In practice it is observed that if current is passed in one direction the boundary soon reaches a steady state where compositions vary only in a thin boundary region, while if the current is reversed, the boundary is destroyed and becomes progressively more diffuse.) Figure 1 shows the system after the boundary has been formed and current has passed for some time, long enough for the system to have reached steady state. Solution A is composed of ions 1 and 3 and, being the lighter of the two solutions, is above solution B, which is composed of ions 2 and 3. The common ion is denoted by "3." For the case in which the boundary progresses up the channel, the leading ion is "1" and the following ion is "2." When the boundary falls, the opposite designation applies. The solvent is referred to by "0."

The derivation of an equation for the transference number will begin by considering just the 2-salt boundary of Figure 1. Much useful information can be extracted from this simple figure, but to arrive at the transference number the system will have to be expanded to include one of the electrode chambers (not pictured in Figure 1). Thus different possibilities must be considered depending upon the actual experimental arrangement. One arrangement will be chosen, others lead to analogous results.

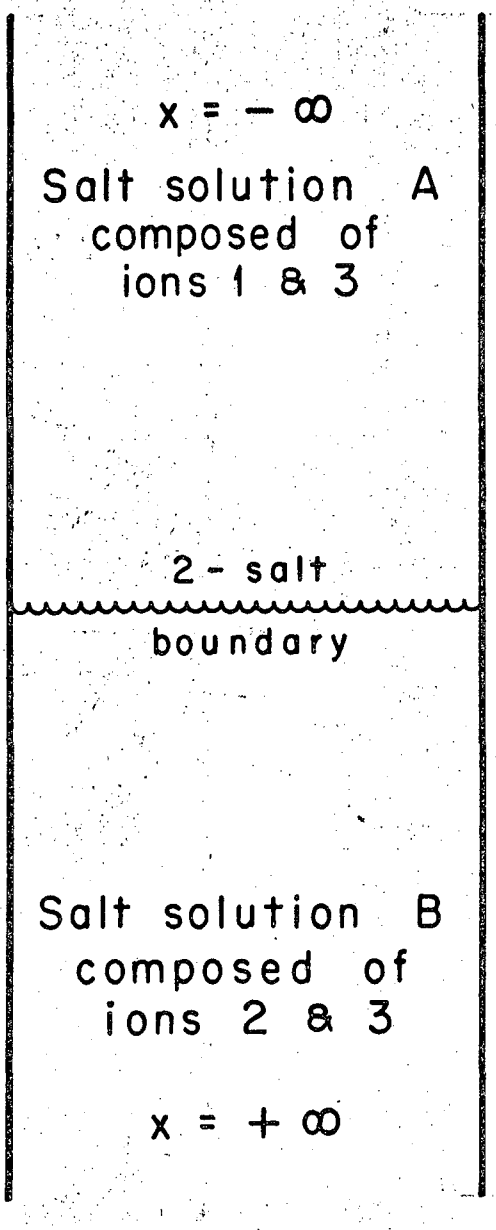

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Figure 1. The 2-salt boundary.

Equations

Four equations are necessary to describe the moving boundary system. They are the continuity equation or material balance,

$$\frac{\partial C_i}{\partial t} = -\nabla \cdot \underline{N}_i = -\nabla \cdot (C_i \underline{v}_i) , \tag{1}$$

an equation relating the current density to the fluxes,

$$\underline{i} = F \sum_i z_i \underline{N}_i , \tag{2}$$

a mathematical statement of electroneutrality,

$$\sum_i z_i C_i = 0 , \tag{3}$$

and a flux or transport equation,

$$C_i \nabla \mu_i = RT \sum_j \frac{C_i C_j}{C_T \mathcal{D}_{ij}} (\underline{v}_j - \underline{v}_i) . \tag{4}$$

These equations are discussed in detail by Newman[7]. Their one dimensional form will be used in later developments.

Definition of Transference Number

The transference number of an ionic species in a given electrolytic solution of uniform composition is the fraction of current carried by that ionic species when current is passed through the solution. The motion of the ions must be referred to some reference for the transference number to be completely defined. If that reference is chosen to be the solvent velocity, the moving boundary transference number and the Hittorf transference number become the same. This reference is the one commonly used in the literature, and it is adapted here.

For a single salt solution this definition can be expressed by

$$t_+ = \frac{z_+ C_+ (v_+ - v_o)}{z_+ C_+ (v_+ - v_o) + z_- C_- (v_- - v_o)} \quad . \tag{5}$$

It is convenient to relate the transference number so defined to the transport properties $\mathcal{D}_{ij}$ defined by equation (4).[8] Written for the solvent of a single salt solution, the one dimensional form of equation (4) is

$$C_o \frac{d\mu_o}{dx} = RT \left[\frac{C_o C_+}{C_T \mathcal{D}_{o+}} (v_+ - v_o) + \frac{C_o C_-}{C_T \mathcal{D}_{o-}} (v_- - v_o) \right] . \tag{6}$$

Since the composition is uniform and since the solvent is an uncharged species, $d\mu_o/dx = 0$ and equation (6) becomes

$$0 = \frac{C_+}{\mathcal{D}_{o+}} (v_+ - v_o) + \frac{C_-}{\mathcal{D}_{o-}} (v_- - v_o) , \tag{7}$$

or,

$$C_- (v_- - v_o) = - \frac{\mathcal{D}_{o-}}{\mathcal{D}_{o+}} C_+ (v_+ - v_o) . \tag{8}$$

Substitution into equation (5) yields

$$t_+ = \frac{z_+ \mathcal{D}_{o+}}{z_+ \mathcal{D}_{o+} - z_- \mathcal{D}_{o-}} \quad . \tag{9}$$

This expression will be used in the later development.

The Analysis

At the 2-salt boundary

The approach in deriving an expression for the transference number is to inspect the appropriate equations as applied to Figure 1 using a coordinate frame which moves at the steady state velocity of the boundary v_b. That is, the velocities of all the species present will

be compared to that quantity which is measured in the laboratory determination of a transference number, v_b. Using this coordinate frame equation(1) becomes

$$C_i(v_i-v_b) = \text{constant} . \tag{10}$$

Since C_1=0 below the boundary, $C_1(v_1-v_b)$ must equal zero, or

$$v_1 = v_b . \tag{11}$$

Similarly, C_2=0 above the boundary and

$$v_2 = v_b . \tag{12}$$

From equation (2),

$$v_3 = v_b + \frac{i}{Fz_3C_3} . \tag{13}$$

The independent transport relations, equations (4), are:

$$\left.\begin{aligned} \frac{d\mu_1}{dx} &= \frac{RT}{C_T}\left[\frac{C_o(v_o-v_b)}{\mathcal{D}_{10}} + \frac{C_3(v_3-v_b)}{\mathcal{D}_{13}}\right] \\ \frac{d\mu_2}{dx} &= \frac{RT}{C_T}\left[\frac{C_o(v_o-v_b)}{\mathcal{D}_{20}} + \frac{C_3(v_3-v_b)}{\mathcal{D}_{23}}\right] \\ \frac{d\mu_3}{dx} &= \frac{RT}{C_T}\left[\frac{C_o(v_o-v_b)}{\mathcal{D}_{30}} - \left(\frac{C_o}{\mathcal{D}_{30}} + \frac{C_1}{\mathcal{D}_{31}} + \frac{C_2}{\mathcal{D}_{32}}\right)(v_3-v_b)\right] . \end{aligned}\right\} \tag{14}$$

The ion electrochemical potentials can be combined into salt chemical potentials by defining

$$\left.\begin{aligned} \mu_A &= \nu_1\mu_1 + \nu_3^A\mu_3 = \nu_1(\mu_1 - z_1\mu_3/z_3), \text{ where } \nu_3^A = -z_1\nu_1/z_3 \\ \mu_B &= \nu_2\mu_2 + \nu_3^B\mu_3 = \nu_2(\mu_2 - z_2\mu_3/z_3), \text{ where } \nu_3^B = -z_2\nu_2/z_3 . \end{aligned}\right\} \tag{15}$$

Combining equations (14) and (15) yields

$$\frac{d\mu_A}{dx} = \frac{\nu_1 RT}{C_T}\left[(v_o-v_b)\left(\frac{C_o}{\mathcal{D}_{10}} - \frac{z_1}{z_3}\frac{C_o}{\mathcal{D}_{30}}\right) + (v_3-v_b)\left(\frac{z_1}{z_3}\frac{C_o}{\mathcal{D}_{30}} + \frac{z_1}{z_3}\frac{C_1}{\mathcal{D}_{31}} + \frac{z_1}{z_3}\frac{C_2}{\mathcal{D}_{32}} + \frac{C_3}{\mathcal{D}_{13}}\right)\right] \tag{16}$$

$$\frac{d\mu_B}{dx} = \frac{\nu_2 RT}{C_T}\left[(v_o-v_b)\left(\frac{C_o}{\mathcal{D}_{20}} - \frac{z_2}{z_3}\frac{C_o}{\mathcal{D}_{30}}\right) + (v_3-v_b)\left(\frac{z_2}{z_3}\frac{C_o}{\mathcal{D}_{30}} + \frac{z_2}{z_3}\frac{C_1}{\mathcal{D}_{31}} + \frac{z_2}{z_3}\frac{C_2}{\mathcal{D}_{32}} + \frac{C_3}{\mathcal{D}_{23}}\right)\right]. \quad (17)$$

As $x \to -\infty$, just salt solution A is present. Then $C_2=0$ and $d\mu_A/dx = 0$ and equation (16) becomes

$$\left.\frac{v_o-v_b}{v_3-v_b}\right|_{x=-\infty} = \frac{\frac{z_1}{z_3}\left(\frac{C_o}{\mathcal{D}_{30}} + \frac{C_1}{\mathcal{D}_{31}}\right) + \frac{C_3}{\mathcal{D}_{13}}}{\frac{z_1}{z_3}\frac{C_o}{\mathcal{D}_{30}} - \frac{C_o}{\mathcal{D}_{10}}} = \frac{\frac{z_1 C_o}{z_3 \mathcal{D}_{30}} + \left(\frac{z_1 C_1}{z_3} + C_3\right)\frac{1}{\mathcal{D}_{13}}}{\frac{z_1}{z_3}\frac{C_o}{\mathcal{D}_{30}} - \frac{C_o}{\mathcal{D}_{10}}}. \quad (18)$$

Here the identity $\mathcal{D}_{ij}=\mathcal{D}_{ji}$ has been used.[8] The subscript $(x=-\infty)$ is included to stress the fact that v_o and v_3 must be evaluated far above the boundary of Figure 1.

From equation (3), $z_1C_1/z_3+C_3=0$ and equation (18) becomes

$$\left.\frac{v_o-v_b}{v_3-v_b}\right|_{x=-\infty} = \frac{z_1\mathcal{D}_{10}}{z_1\mathcal{D}_{10}-z_3\mathcal{D}_{30}}. \quad (19)$$

From the definition of the transference number, equation (9), this is the transference number of ion 1. Hence

$$\left.\frac{v_o-v_b}{v_3-v_b}\right|_{x=-\infty} = t_1. \quad (20)$$

Substituting equation (13) into equation (20) yields

$$t_1 = \frac{Fz_3}{i}\left[C_3(v_o-v_b)\right]_{x=-\infty} \quad (21)$$

This can be rewritten as

$$t_1 = \frac{Fz_3}{i}\left.\frac{C_3}{C_o}\right|_{x=-\infty}\left[C_o(v_o-v_b)\right]_{x=-\infty} \quad (22)$$

or, since $C_i(v_i-v_b)$ = constant,

$$t_1 = \frac{Fz_3}{i}\frac{C_3}{C_o}\bigg|_{x=-\infty}\left[C_o(v_o-v_b)\right]. \qquad (23)$$

A similar expression can be derived for t_2 from equation (17) by noting that as $x \to +\infty$, $C_1=0$ and $d\mu_B/dx=0$. The result is

$$t_2 = \frac{Fz_3}{i}\frac{C_3}{C_o}\bigg|_{x=+\infty}\left[C_o(v_o-v_b)\right]. \qquad (24)$$

Equations (23) and (24) require the calculation of v_o for the transference numbers to be determined. Thus the system must here be expanded to include the experimentally closed electrode chamber where a relation involving v_o can be set up.

Before doing this, however, it is interesting to note that the Kohlrausch regulating function[1] can be derived directly from equations (23) and (24):

$$\frac{t_1}{t_2} = \frac{[C_3/C_o]_{x=-\infty}}{[C_3/C_o]_{x=+\infty}}. \qquad (25)$$

This equation is identical to the one derived by Smits and Duyvis[9] in their criticism of earlier work done separately by Bearman[6], Haase[10], and Spiro[11].

Further investigation of the 2-salt boundary is left to appendix A where an insight into the experimentally observed fact that the current can be passed in only one direction is presented, and an approximate numerical solution to equations (16) and (17) for the concentration profile is outlined.

At the closed electrode

Let the electrode in contact with solution B be the closed electrode,

as represented in Figure 2, which also shows the 2-salt boundary and includes the possibility of a concentration boundary being present. The cross sectional area of the channel is A. For the sake of concreteness, let the reaction at the electrode be that of a metallic ion dissolving. Then solution A is the leading solution, and the 2-salt boundary is progressing up the tube. This is the usual arrangement for determining t_1, and C_1 in this case is known. Suppose the current has been passed for some time so that a steady state has been established in the 2-salt boundary.

Consider a solvent plane initially at level x_i far below the 2-salt boundary but far above any concentration disturbances taking place at the electrode or at a concentration boundary. The amount of solvent below the plane remains constant. The number of moles of ion 2 initially present below x_i is equal to the volume integral on concentration in the space below x_i, here represented by $\int_o^{x_i} C_{2i}dV$. If current I is passed for a time t, the solvent plane originally at x_i will move to some x and the amount of ion 2 then present below x can be represented by $\int_o^{x} C_2 dV$. During this time, $\frac{It}{z_2F}$ moles of ion 2 enters the system at the electrode and $(It/z_2F)t_2$ moles leaves across the solvent plane. Thus

$$\int_o^{v_i} C_{2i}dV + \frac{I(1-t_2)t}{z_2F} = \int_o^{x} C_2 dV \ . \qquad (26)$$

As the amount of solvent below the plane remains constant,

$$\int_o^{x_i} C_{oi}dV = \int_o^{x} C_o dV \ . \qquad (27)$$

An assumption is now made which allows for the explicit determination of the transference number. Assume that the density of solution B

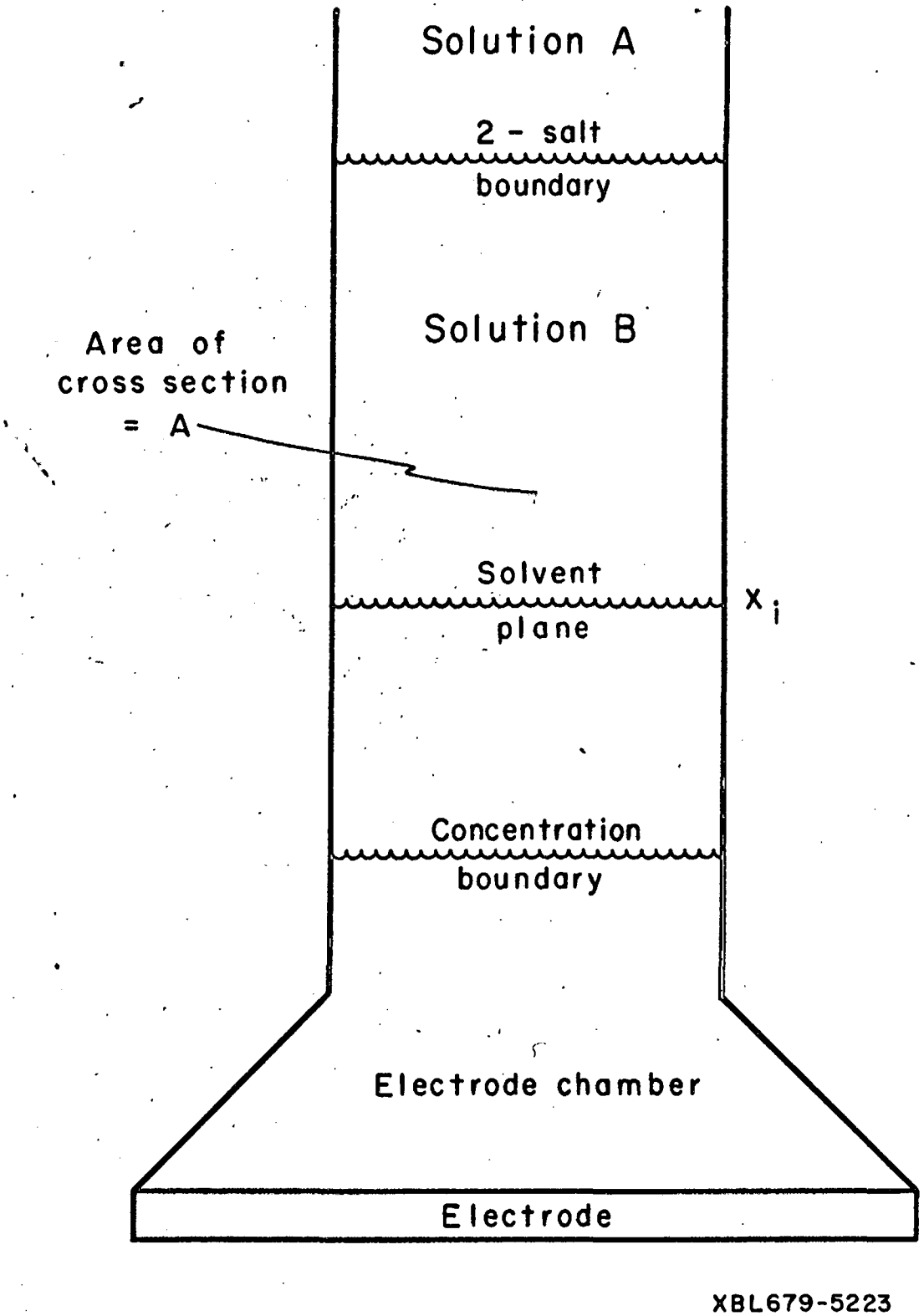


Figure 2. The closed electrode.

below the solvent plane at x is linearly related to its concentration. (We do not here assume that the density-concentration curve is straight over all concentrations, only over the concentration range present below the plane at x. As will be shown later, this concentration range can be made small and the assumption is warranted.) Then in this region

$$\rho_B = \alpha_B + \beta_B C_B \ . \tag{28}$$

An exact expression for the density is

$$\rho_B = M_B C_B + M_o C_{oB} \ . \tag{29}$$

Solving equations (28) and (29) for C_{oB} yields

$$C_{oB} = a_B + b_B C_B = a_B + \frac{b_B C_2}{\nu_2} \tag{30}$$

where $$a_B = \alpha_B / M_o \text{ and } b_B = (\beta_B - M_B)/M_o \ . \tag{31}$$

Putting equation (30) into equation (27) yields

$$a_B \left[\int_o^x dV - \int_o^{x_i} dV \right] = \frac{b_B}{\nu_2} \left[\int_o^{x_i} C_{2i} dV - \int_o^x C_2 dV \right] \ . \tag{32}$$

The quantity in brackets on the right-hand side of equation (32) is given by equation (26). The quantity in brackets on the left-hand side of equation (32) is the change in volume that has taken place below the solvent plane at x. This change is the net result of the movement of the electrode and the movement of the solution and is precisely equal to

$$\left[\int_o^x dV - \int_o^{x_i} dV \right] \leq (x - x_i)A + \frac{It}{z_2 F} \frac{M_e}{\rho_e} \ . \tag{33}$$

Putting equations (26) and (33) into equation (32) yields

$$\frac{x - x_i}{t} = - \frac{I}{A z_2 F} \left[\frac{(1 - t_2)}{\nu_2} \frac{b_B}{a_B} + \frac{M_e}{\rho_e} \right] \tag{34}$$

But $(x-x_i)/t$ is the solvent velocity, v_o, and I/A is the current density in the channel, i, so equation (34) becomes

$$v_o = -\frac{i}{F}\left[\frac{(1-t_2)}{z_2\nu_2}\frac{b_B}{a_B} + \frac{M_e}{z_2\rho_e}\right]. \tag{35}$$

This is the desired result to be substituted into equations (23) and (24) to yield equations for the transference numbers. Recall that the C_o in the brackets of equations (23) and (24) must be evaluated at the same place as v_o, which when using equation (35) is at $x=+\infty$. Thus the equations become

$$t_1 = -z_3\frac{C_3}{C_o}\bigg|_{x=-\infty} C_o\bigg|_{x=+\infty}\left[\frac{v_b F}{i} + \frac{(1-t_2)}{z_2\nu_2}\frac{b_B}{a_B} + \frac{M_e}{z_2\rho_e}\right] \tag{36}$$

$$t_2 = -z_3 C_3\bigg|_{x=+\infty}\left[\frac{v_b F}{i} + \frac{(1-t_2)}{z_2\nu_2}\frac{b_B}{a_B} + \frac{M_e}{z_2\rho_e}\right]. \tag{37}$$

The quantity v_b/i is what is measured during a laboratory determination of a transference number and is equal to

$$\frac{v_b}{i} = \frac{V}{It}, \tag{38}$$

where V is the volume through which the boundary moves when current I is passed for time t. Putting equation (38) into equations (36) and (37) yields

$$t_1 = -\frac{z_3 C_3}{C_o}\bigg|_{x=-\infty} C_3\bigg|_{x=+\infty}\left[\frac{FV}{It} + \frac{M_e}{z_2\rho_e} + \frac{(1-t_2)}{z_2\nu_2}\frac{b_B}{a_B}\right] \tag{39}$$

$$t_2 = -z_3 C_3\bigg|_{x=+\infty}\left[\frac{FV}{It} + \frac{M_e}{z_2\rho_e} + \frac{(1-t_2)}{z_2\nu_2}\frac{b_B}{a_B}\right]. \tag{40}$$

Equation (40) can be solved for t_2 to yield

$$t_2\left[1 - \frac{z_3C_3\Big|_{x=+\infty}}{\nu_2 z_2}\frac{b_B}{a_B}\right] = -z_3C_3\Big|_{x=+\infty}\left[\frac{FV}{It} + \frac{M_e}{z_2\rho_e} + \frac{b_B}{z_2\nu_2 a_B}\right] . \qquad (41)$$

But $$-\frac{z_3C_3\Big|_{x=+\infty}}{\nu_2 z_2} = C_B\Big|_{x=+\infty}, \text{ and } 1 + \frac{C_B\Big|_{x=+\infty} b_B}{a_B} = \frac{C_o\Big|_{x=+\infty}}{a_B}$$

(from equation (30)). Therefore,

$$t_2 = -\frac{a_B z_3 C_3}{C_o}\Bigg|_{x=+\infty}\left[\frac{FV}{It} + \frac{M_e}{z_2\rho_e} + \frac{b_B}{z_2\nu_2 a_B}\right] . \qquad (42)$$

Putting equation (42) into (39) or (25) yields

$$t_1 = -a_B\frac{z_3C_3}{C_o}\Bigg|_{x=-\infty}\left[\frac{FV}{It} + \frac{M_e}{z_2\rho_e} + \frac{b_B}{z_2\nu_2 a_B}\right] . \qquad (43)$$

Equations (42) and (43) are the desired equations for the transference number. Equation (43) is the more useful of the two as C_3/C_o is known for the leading solution ($x=-\infty$), but must be experimentally determined for the following solution.

The problem of accurately calculating a_B and b_B still exists. This is the topic of the next section.

Determination of a_B and b_B

Density concentration data are often presented in the literature as a power series in concentration:

$$\rho = k_1 + k_2C + k_3C^{3/2} + k_4C^2 . \qquad (44)$$

Solving equations (29) and (44) for C_o yields

$$C_o = e + fC + gC^{1/2} + hC^2 \qquad (45)$$

where
$$\left.\begin{aligned} e &= k_1/M_o \quad , \quad f = (k_2 - M)/M_o \\ g &= k_3/M_o \quad , \quad h = k_4/M_o . \end{aligned}\right\} \qquad (46)$$

In the analysis to determine the transference number, equation (45) was approximated by

$$C_o^{approx} = a + bC \tag{30}$$

over a range of concentration from $C_{initial}$ to C_{final}. As the transference number is directly proportional to a, it is important that it be accurately determined. A least square fit of equation (45) to yield accurate values of a and b in equation (30) can be accomplished by defining the integral J:

$$J = \int_{C_{initial}}^{C_{final}} (C_o - C_o^{approx})^2 dC \ . \tag{47}$$

Then the value of a when $\partial J/\partial a = 0$ is the required value. Also, b can be determined from the equation $\partial J/\partial b = 0$. The results of this procedure are

$$a = e - \frac{4gC_{initial}^{3/2}}{35} \frac{(Q^{9/2}+Q^{7/2}-14Q^{5/2}+14Q^2-Q-1)}{(Q-1)^3}$$

$$- \frac{hC_{initial}^2}{6} \frac{(Q^5+Q^4-8Q^3+8Q^2-Q-1)}{(Q-1)^3} \tag{48}$$

$$b = f - \frac{12gC_{initial}^{1/2}}{35} \frac{(-3Q^{7/2}+7Q^{5/2}-7Q+3)}{(Q-1)^3}$$

$$-hC_{initial} \frac{(-Q^4+2Q^3-2Q+1)}{(Q-1)^3} \tag{49}$$

where $Q = C_{final}/C_{initial}$. (50)

The sensitivity of a to the determination of C_{final} can best be seen by substituting $1 + \epsilon = Q$ into equation (48) and expanding in a power series for small ϵ. The result is

$$a = e - \frac{1}{2} g C_{initial}^{3/2} \left(1 + \frac{3}{4} \epsilon + \frac{1}{80} \epsilon^2 + O(\epsilon^3)\right)$$

$$-h C_{initial}^{2} \left(1 + \epsilon + \frac{1}{6} \epsilon^2\right) . \qquad (51)$$

[The expression for b in terms of ϵ is

$$b = f + \frac{3}{2} g C_{initial}^{1/2} \left(1 + \frac{1}{4} \epsilon + O(\epsilon^2)\right) + 2h C_{initial} \left(1 + \frac{1}{2} \epsilon\right)]. \qquad (52)$$

When one realizes that the value of the quantity a calculated from equation (51) is not usually much different from the concentration of pure water, e = 55.3439M, and that the terms involving g and h are merely correction terms to e, one sees that ϵ need not be determined very accurately for the quantity a to be satisfactorily determined. For example, the density of NH_4NO_3 solutions at 25°C is given by[12]

$$\rho = 0.997077 + 0.032628\ C - 9.63 \times 10^{-4} C^{3/2} - 4.73 \times 10^{-5} C^2,$$

which yields g = -0.0535 and h = -0.00263. For a concentrated solution, say $C_{initial}$ = 2M, a varies only from 55.4301 M to 55.4436 M, a change of 0.025%, as ϵ varies from 0 to 0.2 (C_{final} varies from 2M to 2.4M). Thus, a is insensitive to the determination of C_{final}.

As ϵ need not be precisely determined, it is useful to estimate the value of ϵ that results in the electrode chamber for different electrode geometries to help in the design of transference number apparatus. This is the topic of the next section.

Geometry Requirements for Measuring Transference Numbers

For the analysis which led to the equations for the transference number to be fruitfully applied to a real system, the system must be designed so that the ϵ in equation (51) is small. Then a in equations (42) and (43) is accurately determined by equation (51). Thus an estimate

of ϵ for different experimental arrangements is appropriate. Consider, still, a closed anode chamber and a rising boundary. For simplicity, let $z_1=z_2=-z_3=1$ throughout. An anode chamber of uniform concentration is considered, then a vertical plate anode, and then a horizontal anode.

Anolyte of uniform concentration

Consider an anode chamber of fixed volume U. Initially $C_2^i U$ moles of salt B are present. Pass current I for time t, and $It(1-t_2)/F$ moles of salt B are added to the chamber (disregarding, here, the correction for the movement of the solvent). If the liquid in the anode chamber can now be considered to be of uniform concentration, $C_2^f U$ moles of salt B will finally be present. Thus:

$$C_2^i U + It(1-t_2)/F = C_2^f U ,$$

or

$$\epsilon = \frac{C_2^f - C_2^i}{C_2^i} = \frac{It}{F} \frac{(1-t_2)}{C_2^i U} . \qquad (53)$$

But, again disregarding correction terms,

$$It/F = C_1 V/t_1 ,$$

and

$$\epsilon = \frac{C_1}{C_2^i} \frac{(1-t_2)}{t_1} \frac{V}{U} . \qquad (54)$$

Since $C_1 \cong C_2^i$ and $(1-t_2) \cong t_1$,

$$\epsilon \cong V/U . \qquad (55)$$

This says that if uniform concentration in the anode chamber can be achieved, ϵ can be made as small as desired by having a large anode chamber.

In practice, uniform concentration could be achieved only by

mechanical stirring, and the possibility of disturbing the 2-salt boundary would exist. An alternative might be to use a vertical plate anode.

Vertical plate anode, uniform surface flux

Sparrow and Gregg[14] have determined the temperature profile for free convection from a vertical plate with uniform surface heat flux, as a function of the Prandtl number, Pr. At high Pr their solution is indistinguishable from the solution by Sparrow[15] using the von Kármán-Pohlhausen method:

$$\frac{T_w - T_\infty}{qx/k}\left[\frac{g\beta q x^4}{k\nu^2}\right]^{1/5} = f(Pr) = \frac{(360)^{1/5}}{2}\left[\frac{0.8+Pr}{Pr^2}\right]^{1/5} . \qquad (56)$$

By analogy:

$$\frac{C_w - C_\infty}{x\left(\frac{\partial C}{\partial y}\right)\Big|_{y=0}}\left[\frac{g\beta x^4}{\nu^2}\left(\frac{\partial C}{\partial y}\right)\Big|_{y=0}\right]^{1/5} = f(Sc) = \frac{(360)^{1/5}}{2}\left[\frac{0.8+Sc}{Sc^2}\right]^{1/5} \qquad (57)$$

applies at high Schmidt number, Sc. An expression from dilute solution theory for $(\partial C/\partial y)\big|_{y=0}$ is (see reference 7, equations 1 and 15):

$$\left.\frac{\partial C}{\partial y}\right|_{y=0} = -\frac{t_- i}{DF} . \qquad (58)$$

Then

$$(C_w - C_\infty)\left(\frac{g\beta}{\nu^2 x}\right)^{1/5}\left(\frac{DF}{t_- i}\right)^{4/5} = f(Sc),$$

or

$$\epsilon = [f(Sc)]\left[\frac{I t_-}{C_\infty A_e DF}\right]^{4/5}\left[\frac{\nu^2 L}{C_\infty g\beta}\right]^{1/5} , \qquad (59)$$

where A_e is the area of the anode and L is its length. To get an idea of the size of ϵ, substitute into equation (59) the values Sc = 1000, $D = 10^{-5}$cm^2/sec, $F = 10^5$coul/eq, $t_- = 0.5$, $g = 10^3$cm/sec^2 and $\nu = 10^{-2}$cm^2/sec.

Then

$$\epsilon = 0.01 \left(\frac{I}{2A_e C_\infty}\right)^{4/5} \left(\frac{11.25L}{\beta C_\infty}\right)^{1/5}, \qquad (60)$$

where C_∞ is in moles/ℓ, L is in cm, β is in ℓ/mole, A_e is in cm^2 and I is in milliamps. Practical considerations limit the value of I for a given C_∞. The current must be high enough to maintain a sharp boundary but low enough to allow the heat generated to be conducted to the channel walls. Thus when C_∞ is low, I must be low as the solution resistance is high. When C_∞ is high, I must be high to maintain a distinguishable boundary. For illustrative purposes, suppose I can be 40 ma when C_∞ = 1M. Suppose, also, the values A_e = 10 cm^2, L = 5 cm, $\beta = 0.1M^{-1}$. Then the ϵ for this system, according to equation (60) is equal to 0.06177, and the system is well suited to the theory.

It should be realized that the use of a vertical electrode necessitates forming a sheared boundary. A concentration boundary is then set up in the following solution between the original solution B and the solution B which is required by the Kohlraush relation, equation (25). The difference in concentration across the concentration boundary must be estimated or measured and its effect must be added to the ϵ calculated above. In concentrated solutions this second effect is the predominant one, and it could also be even in dilute solutions.

Vertical plate electrode; uniform surface concentration

As current distribution on a vertical electrode is not, in general, uniform, the analysis based on Sparrow's equation does not apply exactly. A second approximate analysis of the vertical plate can be made, based on an equation presented by Newman[16], for a vertical plate of uniform surface concentration. This analysis, then, assumes that the flux at the electrode is not uniform, but that the concentration there is. According

to Newman

$$\left.\frac{\partial C}{\partial y}\right|_{y=0} = \frac{3}{4} K(Sc)\left[\frac{g\beta}{\nu Dx}\right]^{1/4} (C_\infty - C_o)^{5/4} \qquad (61)$$

where y is perpendicular to the electrode, x is parallel to it, and K(Sc) is tabulated. Solving equations (58) and (61) for ϵ yields

$$\epsilon = \left[\frac{4}{3K(Sc)}\right]^{4/5} \left[\frac{It}{A_e DFC_\infty}\right]^{4/5} \left[\frac{\nu Dx}{g\beta C_\infty}\right]^{1/5} . \qquad (62)$$

This can be compared to equation (59) for the uniform flux case:

$$\frac{\epsilon|_{\text{uniform concentration}}}{\epsilon|_{\text{uniform flux}}} = \left[\frac{4}{3K(Sc)}\right]^{4/5} \frac{1}{Sc^{1/5} f(Sc)} . \qquad (63)$$

For Sc = 1000, K(Sc) = 0.6649 (based on work by Ostrach[17]), and

$$\frac{\epsilon|_{\text{uniform concentration}}}{\epsilon|_{\text{uniform flux}}} = 1.075. \qquad (64)$$

Thus the two cases yield results only 7.5% different from each other. Since ϵ is small, and since the analyses are only approximate, it makes little difference which expression is used to calculate ϵ, equation (59) or equation (62).

Horizontal electrode

At a horizontal anode, the worst possible situation exists when one considers that uniform concentration in the anode chamber is desirable. Here a stratified liquid exists with a very concentrated solution at the electrode. At a horizontal electrode the uniform flux condition is likely to be met. Then the diffusion equation

$$\frac{\partial C_2}{\partial t} = D \frac{\partial^2 C_2}{\partial x^2} \qquad (65)$$

can be solved by making the substitution $q = \partial C_2/\partial x$ into (65). The

equation becomes

$$\frac{\partial q}{\partial t} = D \frac{\partial^2 q}{\partial x^2} \tag{66}$$

with

$$q = -t_- i/DF = B \text{ at } x = 0. \tag{58}$$

Then the solution to equation (66),

$$q = \frac{2B}{\sqrt{\pi}} \int_{\eta}^{\infty} e^{-\eta^2} \, d\eta = \frac{\partial C_2}{\partial x} \quad ,$$

where $\eta = x/2\sqrt{Dt}$ can be integrated to yield the solution to equation (65):

$$C_2 = C_\infty - 2B \text{ ierfc } \eta \, , \tag{67}$$

where ierfc η is the integral of the error function complement. At $x = 0$, $\eta = 0$, and ierfc$(0) = 1/2\ \Gamma(\frac{3}{2}) = 1/\sqrt{\pi}$. Thus

$$\epsilon = \frac{2t_- i}{C_\infty F} \sqrt{\frac{t}{D\pi}} = \frac{2t_- I}{C_\infty F A_e} \sqrt{\frac{t}{D\pi}} \, . \tag{68}$$

If it is assumed that the transference numbers involved are 0.5, and a sheared boundary is formed, then $t \cong \frac{C_\infty FV}{0.5I}$ and equation (68) becomes

$$\epsilon = \frac{1}{A_e} \sqrt{\frac{2IV}{C_\infty F D \pi}} \, . \tag{69}$$

If the same values are substituted into equation (69) as were used in equation (59) for the vertical electrode case, and V, the volume through which the boundary moves, is taken to be 0.5 cc, then $\epsilon = 0.3568$. This ϵ is over five times larger than the one calculated for the vertical electrode case, and illustrates that extreme care must be taken in designing an apparatus which employs a horizontal electrode. It should be pointed out that an autogenically formed boundary cannot be used, as then either 1) the electrode area is equal to the channel cross section and a very large ϵ results (see equation (68)), or 2) a large electrode

is used which necessitates t being large and hence a large ϵ.

Comparison between Lewis Equation and Present Equation

Equation (43) would give a transference number identical to that calculated using the Lewis volume correction[1] if the a_B outside the brackets were replaced by a_A where

$$C_{oA} = a_A + b_A C_A \quad . \tag{70}$$

This can be seen as follows:

The volume correction, ΔV, to the Lewis equation,

$$t_1^L = - \frac{z_3 C_3 \big|_{x=-\infty}^{(V+\Delta V)F}}{It} \quad , \tag{71}$$

for the case of a dissolving anode is

$$\Delta V = \frac{It}{F} \left[\frac{\bar{V}_e}{z_2} + \frac{t_1^L \bar{V}_A}{z_1 \nu_1} - \frac{\bar{V}_B}{z_2 \nu_2} \right] , \tag{72}$$

where the $\bar{V}_i$'s are partial molal volumes. Thus the "Lewis transference number" is

$$t_1^L = - \frac{z_3 C_3 \big|_{x=-\infty}}{1 - C_A \bar{V}_A} \left[\frac{FV}{It} + \frac{\bar{V}_e}{z_2} - \frac{\bar{V}_B}{z_2 \nu_2} \right] . \tag{73}$$

Substituting the identities

$$\bar{V}_e = M_e / \rho_e \tag{74}$$

and

$$1 - C_A \bar{V}_A = C_{oA} \bar{V}_{oA} \tag{75}$$

into equation (73) yields

$$t_1^L = - \frac{z_3 C_3 \big|_{x=-\infty}}{\bar{V}_{oA} C_o \big|_{x=-\infty}} \left[\frac{FV}{It} + \frac{M_e}{z_2 \rho_e} - \frac{\bar{V}_B}{z_2 \nu_2} \right] . \tag{76}$$

For a single salt solution, the partial molal volume of the salt is given by

$$\overline{V}_s = \frac{M_s - \frac{\partial \rho}{\partial C_s}}{\rho - C_s \frac{\partial \rho}{\partial C_s}} , \tag{77}$$

where C_s is the salt concentration and ρ is the solution density. The partial molal volume of the solvent is given by

$$\overline{V}_o = \frac{M_o}{\rho - C_s \frac{\partial \rho}{\partial C_s}} . \tag{78}$$

(See Appendix B for the proof of equations (77) and (78).

Thus $\overline{V}_B$ in equation (76) is

$$\overline{V}_B = \frac{M_B - \beta_B}{\alpha_B + \beta_B C_B - \beta_B C_B} = \frac{M_B - \beta_B}{\alpha_B} , \tag{79}$$

and from equations (31),

$$\overline{V}_B = \frac{M_B - \beta_B}{\alpha_B} = - \frac{b_B}{a_B} . \tag{80}$$

Equation (76) becomes

$$t_1^L = - \frac{z_3 C_3 \big|_{x=-\infty}}{\overline{V}_{oA} C_o \big|_{x=-\infty}} \left[\frac{FV}{It} + \frac{M_e}{z_2 \rho_e} + \frac{b_B}{z_2 \nu_2 a_B} \right] . \tag{81}$$

Thus, from equations (43) and (81)

$$\frac{t_1^L}{t_1} = \frac{1/\overline{V}_{oA}}{a_B} . \tag{82}$$

The meaning of equation (82) can best be seen by linearizing C_{oA} about C_A in a fashion analogous to that done with solution B. Then $\rho_A = \alpha_A + \beta_A C_A$, and

$$C_{oA} = a_A + b_A C_A , \tag{70}$$

where $a_A = \alpha_A/M_o$ and $b_A = (\beta_A - M_A)/M_o$. Then from equation (78),

$$\frac{1}{\overline{V}_{oA}} = \frac{\alpha_A + \beta_A C_A - C_A \beta_A}{M_o} = \frac{\alpha_A}{M_o} = a_A \ , \tag{83}$$

and equations (81) and (82) become, respectively,

$$t_1^L = -a_A z_3 \frac{C_3}{C_o}\bigg|_{x=-\infty} \left[\frac{FV}{It} + \frac{M_e}{z_2 \rho_e} + \frac{b_B}{z_2 \nu_2 a_B}\right] \tag{84}$$

and

$$\frac{t_1^L}{t_1} = \frac{a_A}{a_B} \ . \tag{85}$$

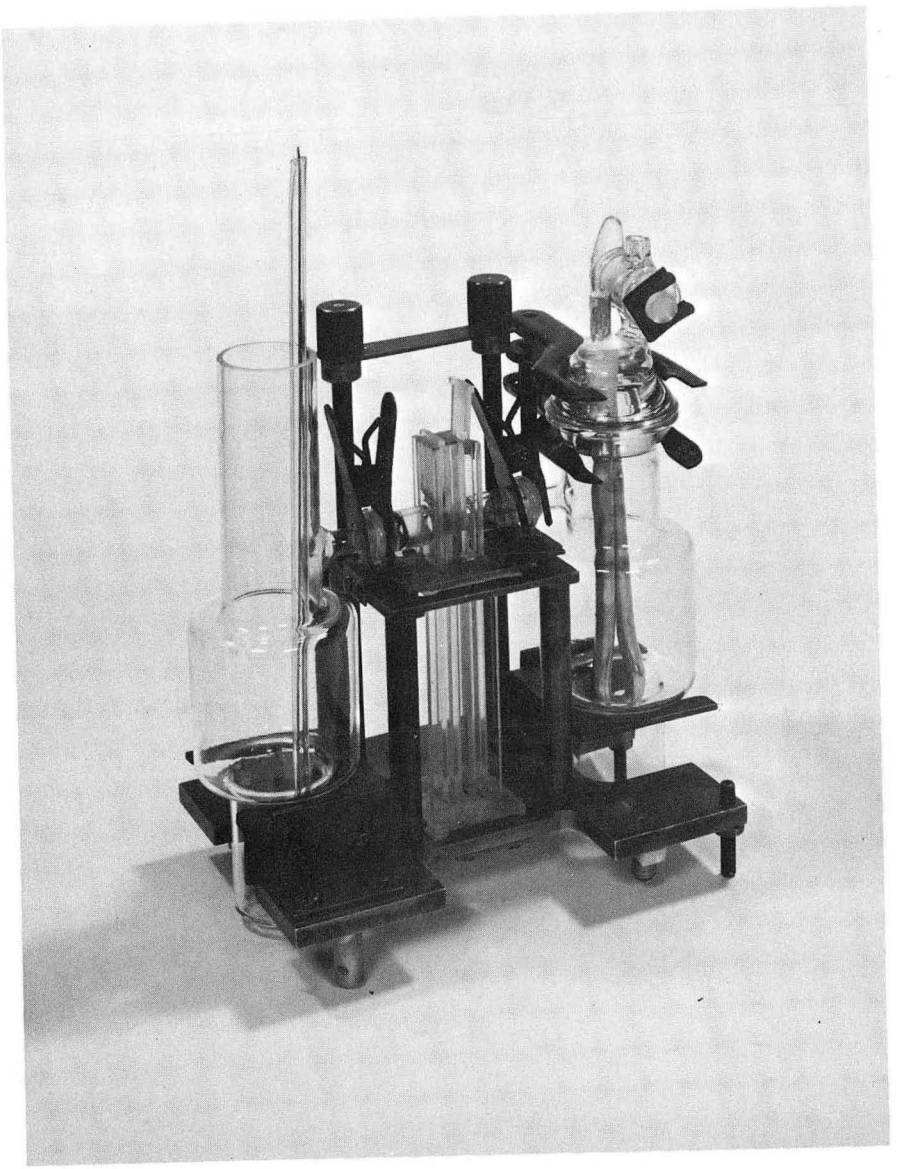
Thus when the partial molal volume of the solvent is constant through the boundary, $\overline{V}_{oA} = \overline{V}_{oB}$, $a_A = a_B$, and $t_1^L = t_1$.

Experimental

The transference number of 0.213M NH_4NO_3 was determined at 25°C. The pertinent features of the experimental work were as follows: Silver nitrate was used as following solution to a rising boundary. A vertical silver anode was used in a closed anode chamber. A standard Tiselius cell[13] (as used in electrophoresis experiments[18]) was used to form and contain the boundary. The cell and electrode chambers are pictured in Figures 3, 4, and 5. Figure 3 shows the cell in the holder, Figure 4 is a blowup of the cell, Figure 5 is a close-up of the cell without the electrode chambers.

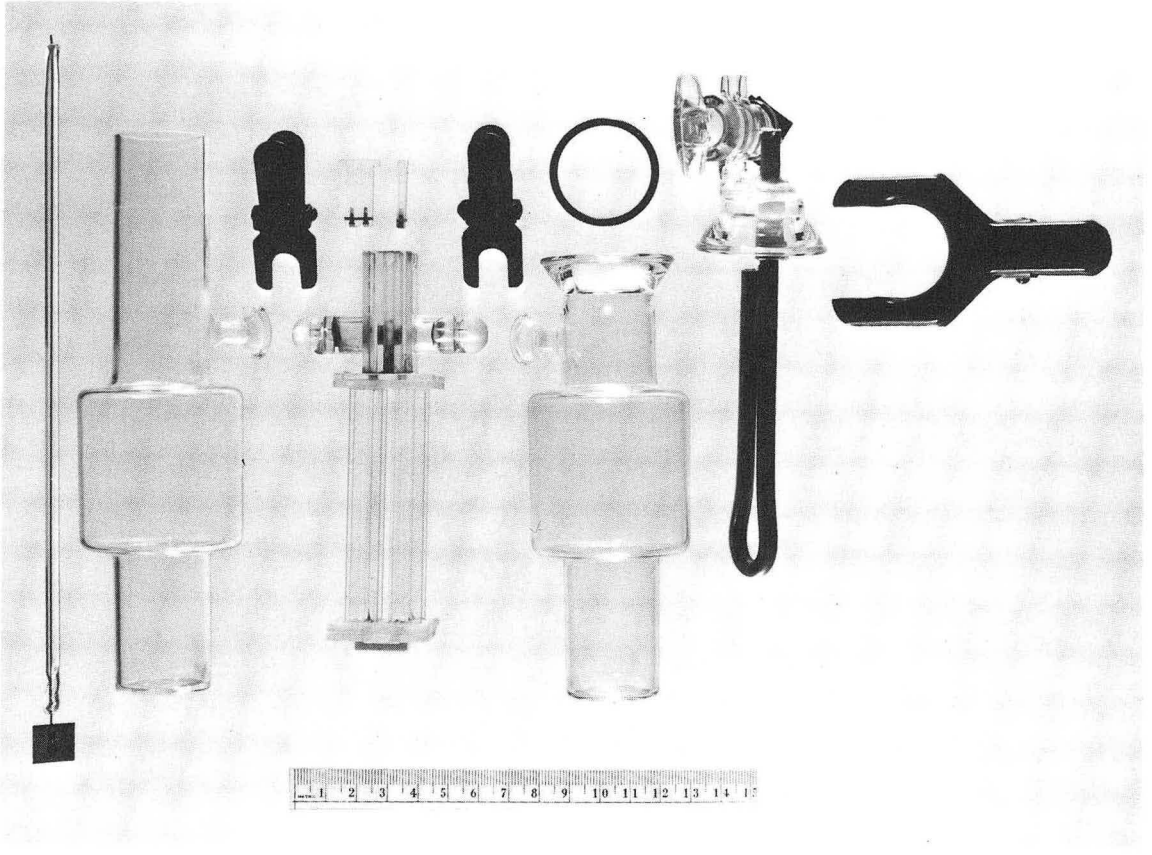
The Tiselius cell was modified so that the anode chamber was closed. The silver anode was cemented to the anode chamber top. The flange between the chamber and the chamber top was grooved to hold a rubber "O" ring. The clamp on the flange compressed the "O" ring and insured a tight seal. The top section of the cell was fitted with two removable lucite plugs which had slightly enlarged, hard rubber sheets built into them to ensure a tight seal. Apiezon grease (grade N) was used on the plugs, and also on the cell flanges and the clamped ball joints joining the electrode chambers to the cell top. A platinum cathode was used.

The movement of the boundary was followed using the Schlieren optical system built into an electrophoresis apparatus purchased from the Perkin-Elmer Corporation, Norwalk, Connecticut. Photographs of the boundary were taken at measured time intervals with the Polaroid camera built into the electrophoresis apparatus in order to determine the volume through which the boundary moved. The base volume was determined by a mercury calibration, and corrections for the boundary being slightly



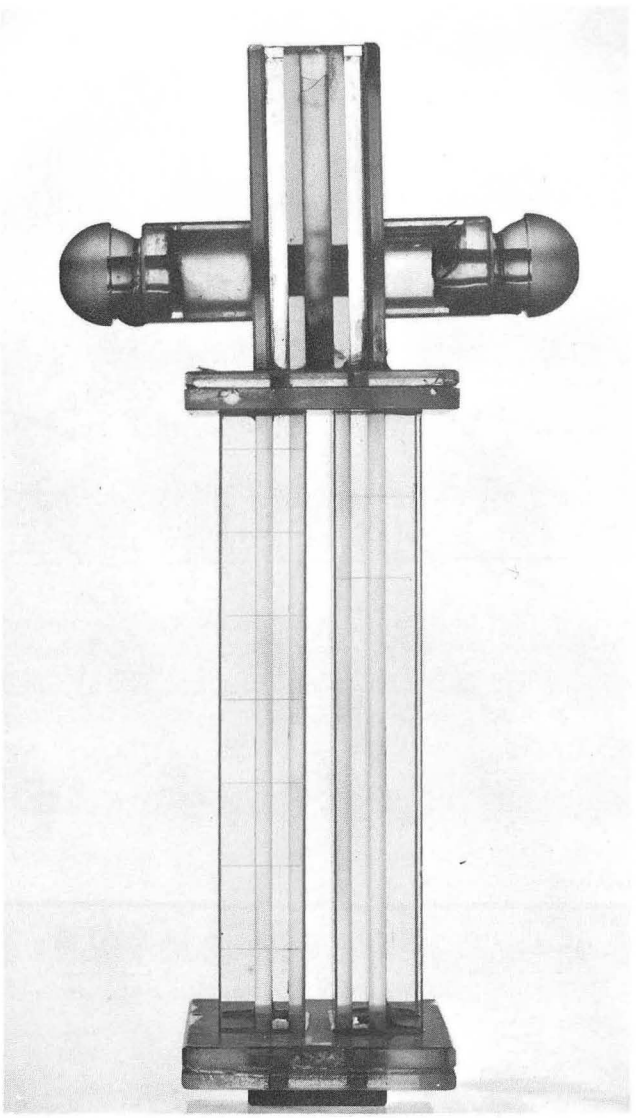
XBB 679-5169

Fig. 3 Tiselius cell in holder.



XBB 679-5170

Fig. 4 Blow-up of Tiselius cell.



XBB-679-5168

Fig. 5 Close-up of Tiselius cell without electrode chambers.

removed from the reference marks when the photos were taken were made. By using an external heater and the cooling system built into the bath of the electrophoresis apparatus, temperature was controlled to within 0.02°C, or better. Current was supplied by a constant current power source, and was monitored by continuously recording the voltage difference between a standard resistor placed in series with the cell and a highly stable bucking voltage supplied by a differential voltmeter. Time lapse between photographs was measured with an electric timer. Solutions were made up by weight, and were transferred to the cell through syringes and platinum-rhodium hypodermic needles.

The cell was tested for leaks just before and again just after each run, while the cell was in place in the bath. A large voltage (≈300 volts) was imposed across 1) the two cell electrodes, 2) the anode and a bath electrode, 3) the cathode and the bath electrode. The resulting current was always less than 1 μA.

The transference number of NH_4NO_3 measured in this system is calculated from the equation

$$t_1 = - \left. \frac{z_3 C_3}{C_o} \right|_{x=-\infty} a_B \left[\frac{FV}{It} + \frac{M_e}{\rho_e} + \frac{b_B}{\nu_2 z_2 a_B} \right], \qquad (43)$$

where here "1" refers to the NH_4^+ ion, "3" to the NO_3^- ion, B to the $AgNO_3$ solution, "e" to the silver anode, and "2" to the Ag^+ ion. Hence, $-z_3 = z_2 = \nu_2 = 1$. The "$x = -\infty$" refers to the fact that C_3/C_o must be evaluated in the NH_4NO_3 solution rather than in the $AgNO_3$ solution. The values $M_e = 107.880$, $\rho_e = 10.492$ gm/cc, and $F = 96{,}493$ coul/eq. are used.

A detailed explanation of the measurement of the remaining variables

in the equation for the transference number is given in the next few sections.

Measurement of C_3/C_o

Reagent grade NH_4NO_3 purchased from Merck & Co., Inc., Rahway, N. J., was used to prepare the solution. The salt was stored in a vacuum oven at 80°C until it was needed. As NH_4NO_3 is hydroscopic in nature, pains were taken to insure that it was dry when weighed. To prepare the solution, the oven was cooled to room temperature and then brought to room pressure by bleeding air into it through a tube containing Drierite ($CaSO_4$). Salt was weighed into a weighing bottle by means of a Mettler balance. The weighing bottle was then returned to the vacuum oven and heated at 80°C under vacuum over night. The oven was then cooled to room temperature, and air was again bled into it through Drierite. The oven door was opened and the weighing bottle immediately covered tightly. The weighing bottle was weighed, and the desired weight of salt was known. The salt was then transferred to a 750 ml flat bottomed flask, and distilled water was weighed into the flask. Thus $C_3/C_o\big|_{x=-\infty}$ was determined.

The solution was stored in a 750 ml flask with a rubber stopper. Glassware was cleaned with soap solution, H_2SO_4-K_2SO_4 solution, rinsed with distilled water, and oven dried at 90°C. From that time on it was handled only with tongs or Kimwipes.

The solution, the transference number of which was measured, was composed of 12.5687 g NH_4NO_3 and 727.3068 g H_2O. Thus

$$\left.\frac{C_3}{C_o}\right|_{x=-\infty} = \frac{12.5687/80.048}{727.3068/18.0160} = 3.88939 \times 10^{-3} .$$

Although $C_3\big|_{x=-\infty}$ and $C_o\big|_{x=-\infty}$ are not needed separately, they were

calculated from the equations[12] $\rho = 0.997077 + 0.032628C - 9.63 \times 10^{-4}C^{3/2} - 4.73 \times 10^{-5}C^2$, and equation (29), $\rho = M_oC_o + MC$. The results are $C_3\big|_{x=-\infty} = 0.213052M$ and $C_o\big|_{x=-\infty} = 54.7778M$. ($\rho = 1.00393$ g/cc)

Measurement of V

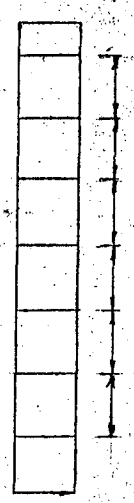
Base volume

Seven lines were scribed on the cell approximately 1 centimeter apart (see Figure 5). The distances between the lines were then measured on a platform microscope. The measurements are listed in Table 1.

To find the volume between the top and bottom lines, a sheet of hard rubber backed with a lucite plate, both of about the same size and shape as the cell bottom flange, was attached to the cell bottom with rubber bands. This closed off the cell. Mercury, the meniscus of which was close to the bottom line, was weighed into the cell. The cell was then placed into the electrophoresis apparatus bath, which was maintained at 25°C. (The cell without the electrode chambers attached can be supported in the bath without using the cell holder by sliding the top flange of the cell over the flat mirror at the rear of the bath. The cell is then in the same position as when it is in the holder.) After waiting to be sure that the mercury had reached 25°C, a photograph of the cell was taken. Then the volume present below the bottom line, $V_{o:1}$, is equal to the volume occupied by the mercury, $V_{o:1^-}$, plus the volume between the mercury meniscus and the bottom line, $V_{1^-:1} = Ah$, where A is the cross sectional area of the cell and h is the distance between the meniscus and the bottom line. The same procedure was followed to get the volume present below the top line, $V_{o:7} = V_{o:7^-} + V_{7^-:7}$. Then the desired volume, the volume between the top and bottom lines, was equal

Table 1. Distance measurements on cell.
(all numbers are in centimeters)

The first three values of "overall length" represent single measurements from line 1 to line 7. The fourth is the sum of two measurements, one from line 1 to line 4 and one from line 4 to line 7.

Line	Cell	5-4-67 (1)	5-4-67 (2)	5-4-67 (3)	10-14-66	8-31-66	Average
7							
6		0.9965	0.9940	0.9952	0.9972	0.9982	0.9962
5		0.9974	0.9954	0.9951	0.9962	0.9957	0.9960
4		1.0072	1.0081	1.0083	1.0090	1.0071	1.0079
3		1.0023	1.0028	1.0044	1.0033	1.0033	1.0032
2		0.9934	0.9944	0.9931	0.9944	0.9957	0.9942
1		1.0013	1.0021	0.9995	1.0020	1.0000	1.0010
	Sum	5.9981	5.9968	5.9956	6.0021	6.0000	5.9985
Overall Length		5.9982	5.9968	5.9956	5.9989		5.9974

to $V_{1:7} = V_{o:7} - V_{o:1}$. As $V_{1:7}$ is the difference between two volume measurements, it is not affected by the shape of the mercury meniscus.

The value of h was determined by viewing the photograph under a platform microscope. An enlargement factor, or film factor, was determined by comparing the distance between the two lines nearest the meniscus on the photograph with the actual cell distance. This allowed the determination of the cross sectional area, A, and hence the volume, $V_{1:7} = 5.9974A$. Later results obtained by measuring the boundary velocity over each centimeter as it progressed up the channel showed that A was not actually constant, but varied from 0.17733 to 0.18065 cm^2 between the top and bottom lines, with a median value of 0.17898 cm^2. The volume $V_{1:7}$ was thus found to be equal to 1.07343 cm^3 with a standard deviation for 5 trials of 0.00037 cm^3. Table 2 lists the data.

Corrections to the base volume

When measuring the transference number, transparency type photographs of the Schlieren pattern were taken when the boundary was near line 1 and again when it was near line 7. Synchronized with the taking of the photographs was the starting and stopping of an electric timer. As the boundary was not precisely at a reference mark when the photo was taken, correction terms had to be added to the base volume. Then the volume through which the boundary moved, V, was equal to $V = V_{1:7} + \Delta V_1 + \Delta V_2$, where ΔV_1 is the correction for the boundary not being at line 1 when the timer was started and ΔV_2 the correction for the boundary not being at line 7 when the timer was stopped. The ΔV's were obtained by analyzing the photographs on a microphotometer. The microphotometer records the intensity of light which is transmitted through a small

Table 2. Base volume data.
(all numbers are in cubic centimeters)

Trial	2A	$3A_1$	$3A_2$	4A	$5A_1$	$5A_2$	Average	Standard Deviation
$V_{o:1^-}$	0.116455	0.117993	---	0.123659	0.110935	0.115627		
$V_{1^-:1}$	0.006654	0.004588	---	-0.000913	0.011878	0.007308		
$V_{o:1}$	0.123109	0.122581	---	0.122746	0.122813	0.122935	0.122837	0.000198
$V_{o:7^-}$	1.193874	1.197927	1.194563	1.190461	1.186353	---		
$V_{7^-:7}$	0.002247	-0.001523	0.002021	0.005956	0.009445	---		
$V_{o:7}$	1.196121	1.196404	1.196584	1.196417	1.195798	---	1.196265	0.000310
$V_{1:7}$							1.07343	0.00037

area of the film. The film is clear over all its area except where the cell reference marks and the boundary are. The film was passed under the microphotometer beam at a constant velocity and a recording of intensity versus position was made. The peaks so recorded due to the reference marks allowed absolute distances to be determined. The boundary was recorded as two peaks close together. The center of the two peaks was taken as the boundary. The distance from the boundary to the nearest reference mark was measured, and ΔV was determined. Table 3 shows the volume through which the boundary moved, V, for the 5 trials. (For runs 2 and 3, two timers were used and two sets of photographs were taken.)

Table 3. Volume through which the boundary moved.
(all numbers are in cubic centimeters)

Run	$V_{1:7}$	$-\Delta V_1$	$-\Delta V_2$	V
1	1.0734	0.3602	0.0180	0.6752
2A	1.0734	0.0203	0.0210	1.0321
2B	1.0734	0.1926	0.0210	0.8598
3A	1.0734	-0.0134	0.0243	1.0625
3B	1.0734	0.0143	0.0243	1.0348

Measurement of I

Current was supplied by a constant current power source, Model C612, purchased from Electronics Measurements, Co., Inc., Eatontown, N. J. A standard resistor of 100.000 ohms, purchased from Leeds and Northrup Co., Philadelphia, Pa., was placed in series with the cell. The voltage drop across the resistor was measured with a differential voltmeter, Model 887A, purchased from the John Fluke Co., Seattle, Washington.

A voltage signal supplied by the voltmeter which was equal to the difference between the voltmeter setting and the voltage being measured at that instant was continuously recorded on a Model SR recorder purchased from E. H. Sargent & Co., Chicago, Ill. The recorder was calibrated using a standard cell purchased from the Eppley Laboratory, Inc., Newport, R. I. (cat. no. 100), so that its range was from -1.00 mV to +1.00 mV.

At the beginning of a run the voltmeter was set at a value E_o so that the recorder was at 0.00. As the run progressed, the current supplied by the power source tended to drift slightly, and this drift was recorded as a voltage change across the resistor. This voltage change was averaged over the length of the run by integrating the recorder output with K & E Polar Planimeter, model 620005. The resulting voltage change, ΔE, was added to E_o to give the time average voltage drop across the 100 ohm resister, E. Then the current was equal to I = E/100.000. The experimental results are listed in Table 4.

Table 4. Time averaged current.

Run	E_o volts	ΔE volts	E volts	I milliamps
1	1.031500	+.000356	1.031856	10.31856
2A	1.031100	+.000490	1.031590	10.31590
2B	1.03110	+.000548	1.031648	10.31648
3A	0.516800	-.000092	0.516708	5.16708
3B	0.516800	-.000095	0.516705	5.16705

Measurement of t

Time elapsed between the photographs taken of the boundary at the bottom line of the cell and at the top line of the cell was measured

with an electric timer purchased from the Precision Scientific Co. (cat. no. 69235). Exposure time for the photographs was on the order of 2 seconds. The procedure was to open the shutter, start (or stop) the timer, and then close the shutter. Thus uncertainty in t was introduced, as the reproducibility of the procedure could not be checked.

Table 5 lists the times required for the runs.

Table 5. Time of runs.

Run	Time (minutes)
1	43.79_1
2A	66.48_2
2B	55.48_0
3A	137.86_0
3B	134.30_6

Measurement of a_B and b_B

The density of $AgNO_3$ solutions is given by the equation[12]

$$\rho = 0.997074 + 0.141956 \cdot C - 0.002603\ C^{3/2} .$$

Thus the values to substitute into equations (51) and (52) for a_B and b_B are (see equations (46)) e = 55.3438 moles/ℓ, f = -1.5504, g = -0.1445 (moles/ℓ)$^{-1/2}$, and h = 0. The concentration $C_{initial}$ was found by making up the solution in exactly the same manner as described in the section on the measurement of C_3/C_o, and was found to be $C_{initial}$ = 0.201799 M. Thus a_B and b_B are to be determined from the equations

$$a_B = 55.3438 + 0.00655\ [1 + \tfrac{3}{4}\ \epsilon + \tfrac{1}{80}\ \epsilon^2] \qquad (86)$$

$$b_B = -1.5504 - 0.09737\ [1 + \tfrac{1}{4}\ \epsilon]. \qquad (87)$$

An estimate of the value of ϵ due just to the electrode reaction can be obtained from equation (60):

$$\epsilon = 0.01 \left[\frac{I}{2A_e C_\infty}\right]^{4/5} \left[\frac{11.25L}{\beta C_\infty}\right]^{1/5} .$$

The values $A_e = 5\ cm^2$, $C_\infty = 0.2M$, $L = 3$ cm, $\beta = \frac{1}{\rho}\frac{d\rho}{dC} = \frac{0.1419C - 0.0039C^{1/2}}{\rho} \cong 0.027$ (where A and L are estimated effective values, not the geometric values) were used. For I = 10 mA, this yields $\epsilon \cong 0.21$, for I = 5 mA, $\epsilon \cong 0.12$.

An estimate of the ϵ due to the concentration boundary caused by the following solution adjusting to the concentration required by the Kohlrausch regulating function, equation (25), was made as follows: After the run was completed, the concentration boundary was forced up into the center of the cell. A photograph of the concentration boundary was taken using the Rayleigh interference optics[18] available in the electrophoresis apparatus. As each "fringe shift" corresponds to a certain concentration change, counting the fringes and knowing the proportionality constant yields the concentration change. The fringes were counted using the microphotometer; the proportionality constant was determined by forming concentration boundaries between two solutions of known concentrations and counting the fringe shifts recorded on the Rayleigh photograph. Its value was found to be 0.00170 M/fringe in the range of 0-0.2 M. In this way the ϵ at the concentration boundary was found to be approximately 0.03. (The value of ϵ for the concentration boundary is as small as it is because some attention was devoted in earlier experiments to determining the correct value of the concentration of the following solution.)

Thus the value of ϵ to be used in equations (86) and (87) is 0.24 for I = 10 ma and 0.15 for I = 5 ma. The resulting values of a_B

and b_B are listed in Table 6.

Table 6. Values of a_B and b_B.

Run	I_{ma}	ϵ	a_B	b_B
1	10	0.24	55.3515	-1.6536
2A	10	0.24	55.3515	-1.6536
2B	10	0.24	55.3515	-1.6536
3A	5	0.15	55.3511	-1.6514
3B	5	0.15	55.3511	-1.6514

Resulting value of t_1

The transference number of the NH_4^+ ion in 0.21305 M NH_4NO_3 is 0.5140±0.0024. The 5 separate determinations are listed in Table 7.

The uncertainty was determined as follows: The scatter in the data has a standard deviation of 0.00218. If it is assumed that this is a result of the uncertainties in I, t, and V, then the percentage uncertainty due to them is 0.424%. (This is more than can be theoretically accounted for.) To this is added the uncertainties in $V_{1:7}$ and C_3/C_o. Using the standard deviation $V_{1:7}$ as its uncertainty, the percentage uncertainty due to it is 0.035%. The uncertainty in C_3/C_o is taken as the uncertainty in the weight of salt, and is estimated to be 0.001 g, or 0.008%. The sum of the uncertainties is 0.467%, or an absolute amount of 0.0024.

The transference number of the following solution can be estimated from equation (25):

$$t_2 = \frac{[C_3/C_o]|_{x=+\infty}}{[C_3/C_o]|_{x=-\infty}} t_1 . \qquad (25)$$

The value $C_3|_{x=+\infty}$ was measured and found to be equal to 0.1950 M. The density of the $AgNO_3$ solution is calculated from the equation of Campbell,

et al[12] and found to be equal to 1.024531 g/ml. Thus $C_o|_{x=+\infty}$ can be determined from equation (29), and the result is $C_o|_{x=+\infty}$ = 55.029 M. Substituting these values, and the values previously given for $[C_3/C_o]|_{x=-\infty}$ and t_1, into equation (25) yields the result t_2 = 0.467. Due to the uncertainties involved in $C_3|_{x=+\infty}$, and t_1, this result is accurate only to within about 2%, i.e., t_2 = 0.467±0.009. This value can be compared to the values measured by Haase, et al[2], at a concentration of 0.1995 M, 0.4708 and 0.4723 (two determinations). Haase's values were calculated using a Lewis type volume correction. If they are corrected by employing equation (85), the values become 0.4701 and 0.4716, respectively.

Table 7. Transference number of NH_4^+ in 0.213 M NH_4NO_3 at 25°C.

Run	$a_B C_3/C_o$	FV/It	M_e/ρ_e	b_B/a_B	t_1
1	.215284	2.4031	0.0103	-0.0299	0.51313
2A	.215284	2.4202	0.0103	-0.0299	0.51681
2B	.215284	2.4158	0.0103	-0.0299	0.51586
3A	.215282	2.3987	0.0103	-0.0298	0.51220
3B	.215282	2.3981	0.0103	-0.0298	0.51207
Average					0.51401
Standard Deviation					0.00218

Summary and Conclusions

An equation for the transference number as determined by the moving boundary method has been derived:

$$t_1 = -\left.\frac{z_3 C_3}{C_o}\right|_{x=-\infty} a_B \left[\frac{FV}{It} + \frac{M_e}{z_2 \rho_e} + \frac{b_B}{z_2 \nu_2 a_B}\right] . \qquad (43)$$

The expression is valid for concentrated as well as dilute solutions. It requires a knowledge of the quantities a_B and b_B, which were not heretofore determined. They are defined by the expression

$$C_{oB} = a_B + b_B C_B , \qquad (30)$$

which is equivalent to a linear density correlation. Expressions for a_B and b_B are presented which relate them to nonlinear density correlations:

$$a_B = e - \frac{1}{2} g C_{initial}^{3/2} \left[1 + \frac{3}{4}\epsilon + \frac{1}{80}\epsilon^2 + O(\epsilon^3)\right] - h C_{initial}^2 \left[1 + \epsilon + \frac{1}{6}\epsilon^2\right] \qquad (51)$$

$$b_B = f + \frac{3}{2} g C_{initial}^{1/2} \left[1 + \frac{1}{4}\epsilon + O(\epsilon^2)\right] + 2h C_{initial} \left[1 + \frac{1}{2}\epsilon\right] . \qquad (52)$$

Equations are presented which give estimates of the value of ϵ which results in the electrode chamber for both horizontal and vertical electrodes, and which can be used in the design of experimental equipment so that ϵ is minimized and the highest possible accuracy in the determination of a_B is attained. For a vertical electrode:

$$\epsilon = 0.01 \left(\frac{I}{2A_e C_\infty}\right)^{4/5} \left(\frac{11.25L}{\beta C_\infty}\right)^{1/5} . \qquad (60)$$

For a horizontal electrode:

$$\epsilon = \frac{1}{A_e}\left[\frac{2IV}{C_\infty \pi}\right]^{1/2} . \qquad (69)$$

The transference number of the NH_4^+ ion in 0.213 M NH_4NO_3 at 25°C was determined and found to be 0.5140±.0024. The cation transference number in the following $AgNO_3$ solution was estimated to be 0.467±0.009 at a concentration of 0.195 M.

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Nomenclature

a_I - defined by equation (30).

$\bar{a}_I$ - activity of solution I, moles/cm^3.

A - cross-sectional area of cell channel, cm^2.

A_e - defined by equation (A15)

A - surface area of electrode, cm^2.

b_I - defined by equation (30).

B - defined by equation (A17).

C_i - concentration of species i, moles/cm^3.

C_T - total solution concentration, moles/cm^3.

$C_{initial}$ - lowest concentration of following solution removed from the 2-salt boundary, moles/cm^3.

C_{final} - highest concentration of following solution removed from the 2-salt boundary, moles/cm^3.

C_p - specific heat, cal/g-deg.

D - diffusion coefficient, cm^2/sec.

$\mathcal{D}_{ij}$ - diffusion coefficient for binary interactions, cm^2/sec.

e - defined by equations (45) and (46).

f - defined by equations (45) and (46).

F - Faraday's constant, 96,493 coul/eq.

f(Pr) - function dependent upon Pr, defined by equation (56).

f(Sc) - function dependent upon Sc, defined by equation (57).

g - defined by equations (45) and (46).

g - acceleration of gravity, cm/sec^2.

h - defined by equations (45) and (46).

i - current density, amps/cm^2.

I - current, amps.

J - integral defined by equation (47).

k - thermal conductivity, cal/deg·cm·sec.

k_1, k_2, k_3, k_4 - defined by equation (44).

$K(Sc)$ - function dependent upon Sc, defined by equation (61).

L - electrode length, cm.

M - molarity of solution, moles/ℓ.

M_I - molecular weight of substance I, g/mole.

n_i - number of moles of species i.

N_i - flux of species i, moles/cm^2-sec.

Pr - Prandtl number = $C_p\mu/k$.

q - heat flux, cal/cm^2-sec.

q - defined by equations (65) and (66).

Q - $C_{final}/C_{initial}$.

R - universal gas constant, joule/mole-deg.

Sc - Schmidt number = ν/D.

t - time, sec.

t_i - transference number of species i.

t_i^L - transference number of species i as calculated using a Lewis-type volume correction, see equation (71).

T - temperature, deg K.

U - volume of anode chamber, cm^3.

v_b - velocity of the 2-salt boundary, cm/sec.

v_i - velocity of species i, cm/sec.

V - volume through which the 2-salt boundary moves, cm^3.

V - volume, cm^3.

$\bar{V}_I$ - partial molal volume of substance I, cm^3/mole.

w - $xiC_o/Fz_3C_T\mathcal{D}_{o3}$, see equation (A10), eq/cm^3.

x - distance variable, cm.

X - $C_1/C_1\big|_{x=-\infty}$

y - distance variable, cm.

Y - $C_2/C_2\big|_{x=+\infty}$

z_i - charge number of species i.

$\alpha_1,\alpha_2,\alpha_3$ - defined by equations (A20).

α_I - defined by equation (28).

β - coefficient of expansion, $(1/\rho)(\partial\rho/\partial C)$, see equation (57), cm^3/mole.

β - coefficient of thermal expansion $(1/\rho)(\partial\rho/\partial T)$, see equation (56), deg^{-1}.

β_I - defined by equation (28).

δ_{jk} = 1 for $j \neq k$, = 0 for $j \neq k$.

ϵ = Q-1.

μ - viscosity, g/cm-sec.

μ_i - electrochemical potential of species i, joule/mole.

μ_I - chemical potential of salt I.

ν - kinematic viscosity, cm^2/sec.

ν_+,ν_- - numbers of cations and anions produced by the dissociation of one molecule of electrolyte.

$\nu_I=\nu_++\nu_-$ - total number of ions produced by the dissociation of one molecule of salt I.

ρ_e - density of electrode material, g/cm^3.

ρ_I - density of solution I, g/cm^3.

Subscripts

0 - solvent.

1 - leading ion when boundary rises, following ion when boundary falls.

2 - following ion when boundary rises, leading ion when boundary falls.

3 - common ion.

b - 2-salt boundary.

e - electrode.

s - salt.

w - at the wall.

∞ - far removed.

$x=-\infty$ - evaluated in solution A at concentration required by Kohlrausch relation.

$x=+\infty$ - evaluated in solution B at concentration required by Kohlrausch relation.

A - salt or salt solution composed of ions 1 and 3.

B - salt or salt solution composed of ions 2 and 3.

+ - cation.

- - anion.

$\underline{\ \ }$ - a line under a variable indicates that the variable is a vector.

Superscripts

A - salt solution composed of ions 1 and 3.

B - salt solution composed of ions 2 and 3.

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Appendix A

Approximate Concentration Profile in 2-salt Boundary

A concentration profile in the 2-salt boundary can be determined by eliminating the distance variable in equations (16) and (17) and solving for $d\mu_B/d\mu_A$. Once C_A and C_B are related, a spatial distribution can be determined by solving either equation (16) or (17). The two equations can be rewritten as

$$\frac{d\mu_A}{dx} = \frac{i}{F}\frac{\nu_1 z_1}{z_3^2 C_3}\frac{C_o}{C_T}\frac{RT}{\mathcal{D}_{30}}\left[\frac{(v_o-v_b)}{(v_3-v_b)}\left(\frac{z_3\mathcal{D}_{30}-z_1\mathcal{D}_{10}}{z_1\mathcal{D}_{10}}\right)\right.$$

$$\left. + \frac{\mathcal{D}_{30}}{C_o}\left(\frac{C_o}{\mathcal{D}_{30}} + \frac{C_1}{\mathcal{D}_{31}} + \frac{C_2}{\mathcal{D}_{32}} + \frac{z_3 C_3}{z_1\mathcal{D}_{13}}\right)\right] , \qquad (A1)$$

$$\frac{d\mu_B}{dx} = \frac{i}{F}\frac{\nu_2 z_2}{z_3^2 C_3}\frac{C_o}{C_T}\frac{RT}{\mathcal{D}_{30}}\left[\frac{(v_o-v_b)}{(v_3-v_b)}\left(\frac{z_3\mathcal{D}_{30}-z_2\mathcal{D}_{20}}{z_2\mathcal{D}_{20}}\right)\right.$$

$$\left. + \frac{\mathcal{D}_{30}}{C_o}\left(\frac{C_o}{\mathcal{D}_{30}} + \frac{C_1}{\mathcal{D}_{31}} + \frac{C_2}{\mathcal{D}_{32}} + \frac{z_3 C_3}{z_2\mathcal{D}_{32}}\right)\right] . \qquad (A2)$$

It is clear from equations (A1) and (A2) that the current density, i, enters only as a scaling factor for x. This means that the sharpness of the boundary depends on i. When i=0, there can be no steady state boundary, and the solutions diffuse into each other. That a further restriction exists can be seen as follows:

As $x \to +\infty$, $C_1 \to 0$, and the activity of solution A, $\bar{a}_A$, approaches zero, $\bar{a}_A \to 0$. Then $\mu_A = \nu_A RT \ln \bar{a}_A$ approaches $-\infty$, and $d\mu_A/dx < 0$.

$$\frac{d\mu_A}{dx} < 0 \quad \text{at} \quad x \to +\infty . \qquad (A3)$$

At $x \to +\infty$, equation (A1) becomes (using equation (13))

$$\frac{d\mu_A}{dx} = \frac{i}{F}\frac{\nu_1 z_1}{z_3^2 C_3}\frac{C_o}{C_T}\frac{RT}{\mathcal{D}_{30}}\left[\frac{F(v_o-v_b)z_3C_3}{i}\left(\frac{z_3\mathcal{D}_{30}-z_1\mathcal{D}_{10}}{z_1\mathcal{D}_{10}}\right)+\frac{\mathcal{D}_{30}}{C_o}\left(\frac{C_o}{\mathcal{D}_{30}}+\frac{C_2}{\mathcal{D}_{32}}+\frac{z_3C_3}{z_1\mathcal{D}_{13}}\right)\right]$$

$$= \frac{i}{F}\frac{\nu_1 z_1}{z_3^2 C_3}\frac{C_o}{C_T}\frac{RT}{\mathcal{D}_{30}}\left[t_2\left(\frac{z_3\mathcal{D}_{30}-z_1\mathcal{D}_{10}}{z_1\mathcal{D}_{10}}\right)+1+\frac{C_2\mathcal{D}_{30}}{z_1C_o}\left(\frac{z_1}{\mathcal{D}_{32}}-\frac{z_2}{\mathcal{D}_{13}}\right)\right]. \qquad (A4)$$

In view of equation (A3),

$$iz_1t_2 > iz_1\left(\frac{z_1\mathcal{D}_{10}}{z_1\mathcal{D}_{10}-z_3\mathcal{D}_{30}}\right)\left[1+\frac{C_2\mathcal{D}_{30}}{C_oz_1}\left(\frac{z_1}{\mathcal{D}_{32}}-\frac{z_2}{\mathcal{D}_{13}}\right)\right]. \qquad (A5)$$

If $z_1\mathcal{D}_{10}/(z_1\mathcal{D}_{10}-z_3\mathcal{D}_{30})$ in this equation is regarded as being equal to t_1 (equation (9)) even though $C_1 = 0$ in solution B, equation (A5) becomes

$$iz_1t_2 > iz_1t_1 + \frac{it_1C_2\mathcal{D}_{30}}{C_o}\left(\frac{z_1}{\mathcal{D}_{32}}-\frac{z_2}{\mathcal{D}_{13}}\right). \qquad (A6)$$

The analogous result obtained by letting $x \to -\infty$ in equation (A2) and noting that $d\mu_B/dx > 0$ is

$$iz_2t_2 > iz_2t_1 + \frac{it_2C_1\mathcal{D}_{30}}{C_o}\left(\frac{z_1}{\mathcal{D}_{32}}-\frac{z_2}{\mathcal{D}_{31}}\right). \qquad (A7)$$

These relations mean that passage of current in one direction will help maintain the sharpness of the boundary, while a sharp boundary cannot be achieved if the current passes in the other direction. In dilute solutions equations (A6) and (A7) become

$$iz_1t_2 > iz_1t_1. \qquad (A8)$$

This might be regarded as the mathematical statement of the experimentally observed fact that the leading ion must have a higher transference number than the following ion for the boundary to remain distinct.

An approximate concentration profile through the 2-salt boundary can be calculated as follows: Assume

$$\mu_A = \nu_A RT \ln C_A \quad , \quad \mu_B = \nu_B RT \ln C_B \; . \tag{A9}$$

Treat C_T, C_o, and $\mathcal{D}_{ij}$ as constant. Define

$$w = \frac{i\, C_o}{F z_3 C_T \mathcal{D}_{03}}\, x \tag{A10}$$

where i/z_3 is taken as positive. (Then $w = +\infty$ when $x = +\infty$.) Then equation (A1) becomes

$$\frac{dC_1}{C_1 dw} = \frac{\nu_1 z_1}{\nu_A z_3 C_3}\left[\frac{(v_o - v_b)}{(v_3 - v_b)}\left(\frac{z_3\mathcal{D}_{30} - z_1\mathcal{D}_{10}}{z_1\mathcal{D}_{10}}\right) + 1 + \frac{\mathcal{D}_{30}}{C_o}\left(\frac{1}{\mathcal{D}_{32}} - \frac{z_2}{z_1\mathcal{D}_{13}}\right) C_2\right]. \tag{A11}$$

From equations (23) and (13),

$$\frac{(v_o - v_b)}{(v_3 - v_b)} = \frac{C_o(v_o - v_b)}{C_o(v_3 - v_b)} = \frac{\dfrac{it_1}{Fz_3}\left.\dfrac{C_o}{C_3}\right|_{x=-\infty}}{\dfrac{C_o i}{F z_3 C_3}} =$$

$$= t_1 \frac{C_3}{C_3\big|_{x=-\infty}} = \left(\frac{z_1\mathcal{D}_{10}}{z_1\mathcal{D}_{10} - z_3\mathcal{D}_{30}}\right)\left.\frac{C_2 z_2 + C_1 z_1}{z_1 C_1}\right|_{x=-\infty} . \tag{A12}$$

Putting equation (A12) into equation (A11) yields

$$\frac{dX}{X dw} = \frac{\nu_1 z_1}{\nu_A z_3 C_3}\,[1 - X - AY] \tag{A13}$$

where

$$X = C_1/C_1\big|_{x=-\infty}, \qquad Y = C_2/C_2\big|_{x=+\infty} \tag{A14}$$

and

$$A = \frac{z_2 C_2\big|_{x=+\infty}}{z_1 C_1\big|_{x=-\infty}} - \frac{C_2\big|_{x=+\infty}}{C_o}\,\mathcal{D}_{30}\left(\frac{1}{\mathcal{D}_{32}} - \frac{z_2}{z_1\mathcal{D}_{31}}\right). \tag{A15}$$

Analogously, equation (A2) becomes

$$\frac{dY}{Y dw} = \frac{\nu_2 z_2}{z_3 C_3 \nu_B}\,[1 - Y - BX] \tag{A16}$$

where

$$B = \frac{z_1 C_1\big|_{x=-\infty}}{z_2 C_2\big|_{x=+\infty}} - \frac{C_1\big|_{x=-\infty}}{C_o}\,\mathcal{D}_{30}\left(\frac{1}{\mathcal{D}_{31}} - \frac{z_1}{z_2\mathcal{D}_{32}}\right). \tag{A17}$$

When C_3 is eliminated from equations (A13) and (A16), the results are

$$\frac{dX}{dw} = \frac{\alpha_1(AY + X - 1)\,X}{\alpha_3 Y + X} \tag{A18}$$

$$\frac{dY}{dw} = \frac{\alpha_2\alpha_3(BX + Y - 1)Y}{\alpha_3 Y + X} \tag{A19}$$

where

$$\alpha_1 = \nu_1/\nu_A C_1\Big|_{x=-\infty} \quad , \quad \alpha_2 = \nu_2/\nu_B C_2\Big|_{x=+\infty}$$
$$\alpha_3 = z_2 C_2\Big|_{x=+\infty}/z_1 C_1\Big|_{x=-\infty} . \tag{A20}$$

The FORTRAN IV computer program listed below[19] solves equations (A18) and (A19) to give the concentration profiles in the 2-salt boundary. The input data A, B, ALPHA1, ALPHA2, and ALPHA3 are the same as defined above by equations (A15), (A17), and (A20). The input H is the increment on X in the range from X=0 to X=0.100. The input E is the increment on X in the range from X=0.100 to X=1.000. The values H=0.0010 and E=0.0100 were used successfully by the author. The outputs X, Y, and w are the same as defined above by equations (A14) and (A10). The output CT is the concentration of the common ion, C_3. In the program presented, a separate card (numbered 6 in the program) defining CT from the equation

$$C_3 = -\frac{z_2 C_2\Big|_{x=+\infty}}{z_3} Y - \frac{z_1 C_1\Big|_{x=-\infty}}{z_3} X$$

must be inserted into the program deck for each system investigated.

In A and B there appear $\mathcal{D}_{32}$ and $\mathcal{D}_{31}$. Values for these are essentially unknown in multicomponent solutions[20], and the values should probably depend on the concentration. However, the main contributions to A and B in moderately dilute solutions come from the first terms in equations (A15) and (A17), the second terms being perhaps 2 orders of magnitude smaller.

```
      DIMENSION X(190), Y(190), W(190), CT(190)
   70 FORMAT (1H1)
   71 FORMAT (7F10.0)
   72 FORMAT (11X2H X, 11X2H Y, 9X2H W, 11X3H CT //)
   73 FORMAT(F15.3,F15.5,E15.5,F15.5)
   74 FORMAT(1H1,5X,1HA,9X,1HB,7X,6HALPHA1,4X,6HALPHA2,4X,
     26HALPHA3,6X,1HH,8X,1HE/7F10.4//)
      PRINT 70
   10 READ 71 ,A,B,ALPHA1,ALPHA2,ALPHA3,H,E
      PRINT 74,A,B,ALPHA1,ALPHA2,ALPHA3,H,E
      PRINT 72
      C=(ALPHA2/ALPHA1)*ALPHA3
      G=-B/((1.-A)/C+1.)
      P1=H*G
      X1=H/2.
      Y1=1.+P1/2.
      P2=H*C*(1.-Y1-B*X1)*Y1/((1.-X1-A*Y1)*X1)
      Y1=1.+P2/2.
      P3=H*C*(1.-Y1-B*X1)*Y1/((1.-X1-A*Y1)*X1)
      Y1=1.+P3
      X1=H
      P4=H*C*(1.-Y1-B*X1)*Y1/((1.-X1-A*Y1)*X1)
      Y(1)=1.+(P1+2.*P2+2.*P3+P4)/6.
      DO 1 J=1,99
      X(J)=FLOAT(J)*H
      P1=H*C*(1.-Y(J)-B*X(J))*Y(J)/((1.-X(J)-A*Y(J))*X(J))
      X1=X(J)+H/2.
      Y1=Y(J)+P1/2.
      P2=H*C*(1.-Y1-B*X1)*Y1/((1.-X1-A*Y1)*X1)
      Y1=Y(J)+P2/2.
      P3=H*C*(1.-Y1-B*X1)*Y1/((1.-X1-A*Y1)*X1)
      Y1=Y(J)+P3
      X1=X(J)+H
      P4=H*C*(1.-Y1-B*X1)*Y1/((1.-X1-A*Y1)*X1)
    1 Y(J+1)=Y(J)+(P1+2.*P2+2.*P3+P4)/6.
      DO 4 J=100,189
      X(J)=FLOAT(J-100)*E+0.1
      P1=E*C*(1.-Y(J)-B*X(J))*Y(J)/((1.-X(J)-A*Y(J))*X(J))
      X1=X(J)+E/2.
      Y1=Y(J)+P1/2.
      P2=E*C*(1.-Y1-B*X1)*Y1/((1.-X1-A*Y1)*X1)
      Y1=Y(J)+P2/2.
      P3=E*C*(1.-Y1-B*X1)*Y1/((1.-X1-A*Y1)*X1)
      Y1=Y(J)+P3
      X1=X(J)+E
      P4=E*C*(1.-Y1-B*X1)*Y1/((1.-X1-A*Y1)*X1)
    4 Y(J+1)=Y(J)+(P1+2.*P2+2.*P3+P4)/6.
      W(140)=0.
      D=ALPHA1
      R=ALPHA3
      DO 2 J=140,188
      G1=(1.+R*Y(J-2)/X(J-2))/(D*(A*Y(J-2)+X(J-2)-1.))
      G2=(1.+R*Y(J-1)/X(J-1))/(D*(A*Y(J-1)+X(J-1)-1.))
      G3=(1.+R*Y(J  )/X(J  ))/(D*(A*Y(J  )+X(J  )-1.))
      G4=(1.+R*Y(J+1)/X(J+1))/(D*(A*Y(J+1)+X(J+1)-1.))
    2 W(J+1)=W(J)+E*(9.*G4+19.*G3-5.*G2+G1)/24.
      DO 5 J=1,40
```

```
      JA=141-J
      G1=(1.+R*Y(JA+2)/X(JA+2))/(D*(A*Y(JA+2)+X(JA+2)-1.))
      G2=(1.+R*Y(JA+1)/X(JA+1))/(D*(A*Y(JA+1)+X(JA+1)-1.))
      G3=(1.+R*Y(JA  )/X(JA  ))/(D*(A*Y(JA  )+X(JA  )-1.))
      G4=(1.+R*Y(JA-1)/X(JA-1))/(D*(A*Y(JA-1)+X(JA-1)-1.))
    5 W(JA-1)=W(JA)-E*(9.*G4+19.*G3-5.*G2+G1)/24.
      DO 3 J=40,139
      JA=141-J
      G1=(1.+R*Y(JA+2)/X(JA+2))/(D*(A*Y(JA+2)+X(JA+2)-1.))
      G2=(1.+R*Y(JA+1)/X(JA+1))/(D*(A*Y(JA+1)+X(JA+1)-1.))
      G3=(1.+R*Y(JA  )/X(JA  ))/(D*(A*Y(JA  )+X(JA  )-1.))
      G4=(1.+R*Y(JA-1)/X(JA-1))/(D*(A*Y(JA-1)+X(JA-1)-1.))
    3 W(JA-1)=W(JA)-H*(9.*G4+19.*G3-5.*G2+G1)/24.
      X(190)=1.
      DO 6 J=1,190
    6 CT(J)=0.1950*Y(J)+0.21305*X(J)
      PRINT 73,(X(J),Y(J),W(J),CT(J),J=1,190)
      GO TO 10
      END
```

Appendix B

Relation between Density and Partial Molal Volume

The density of a solution is given by the equation

$$\rho = \sum_{i}^{n} C_i M_i = \frac{1}{V} \sum_{i}^{n} n_i M_i \qquad (B1)$$

where here V is the total volume of the system, M_i is the molecular weight of species i, $n_i = C_i V$ is the number of moles of species i present, and the total number of species present is equal to n. The density of the solution is also given by the experimental correlation

$$\rho = \rho(C_1, C_2, \ldots C_{n-1}) . \qquad (B2)$$

The partial molal volume of species j is given by

$$\bar{V}_j = \partial V / \partial n_j \qquad (B3)$$

which, from equation (B1) is

$$\bar{V}_j = \frac{1}{\rho} \frac{\partial}{\partial n_j} \sum_{i}^{n} n_i M_i + \sum_{i}^{n} n_i M_i \frac{\partial (\frac{1}{\rho})}{\partial n_j}$$

$$= \frac{M_j}{\rho} - \frac{1}{\rho^2} \sum_{i}^{n} n_i M_i \frac{\partial \rho}{\partial n_j}$$

$$= \frac{M_j}{\rho} - \frac{V}{\rho} \frac{\partial \rho}{\partial n_j} . \qquad (B4)$$

From equation (B2),

$$\frac{\partial \rho}{\partial n_j} = \sum_{k=1}^{n-1} \frac{\partial \rho}{\partial C_k} \frac{\partial C_k}{\partial n_j} = \sum_{k=1}^{n-1} \frac{\partial \rho}{\partial C_k} \frac{\partial (n_k / V)}{\partial n_j}$$

$$= \sum_{k=1}^{n-1} \frac{\partial \rho}{\partial C_k} \left[\frac{1}{V} \frac{\partial n_k}{\partial n_j} - \frac{n_k}{V^2} \frac{\partial V}{\partial n_j} \right] = \sum_{k=1}^{n-1} \frac{\partial \rho}{\partial C_k} \left[\frac{\delta_{jk}}{V} - \frac{C_k \bar{V}_j}{V} \right] ; \qquad (B5)$$

where $\delta_{jk}=1$ for $j=k$ and $\delta_{jk}=0$ for $j\neq k$. Substituting equation (B5) into equation (B4) yields

$$\bar{V}_j = \frac{M_j}{\rho} - \frac{1}{\rho}\sum_{k=1}^{n-1}\frac{\partial\rho}{\partial C_k}\left[\delta_{jk} - C_k\bar{V}_j\right]$$

$$= \frac{M_j}{\rho} - \frac{1}{\rho}\sum_{k=1}^{n-1}\frac{\partial\rho}{\partial C_k}\delta_{jk} + \frac{1}{\rho}\sum_{k=1}^{n-1}\frac{\partial\rho}{\partial C_k}C_k\bar{V}_j \quad . \qquad \text{(B6)}$$

Solving equation (B6) for $\bar{V}_j$ yields

$$\bar{V}_j = \frac{M_j - \sum_{k=1}^{n-1}\frac{\partial\rho}{\partial C_k}\delta_{jk}}{\rho - \sum_{k=1}^{n-1}C_k\frac{\partial\rho}{\partial C_k}} = \frac{M_j - \frac{\partial\rho}{\partial C_j}[1-\delta_{jn}]}{\rho - \sum_{k=1}^{n-1}C_k\frac{\partial\rho}{\partial C_k}} \quad . \qquad \text{(B7)}$$

For a single salt solution the density of which is given by $\rho = \rho(C_s)$, where C_s is the concentration of the salt, equation (B7) yields

$$\bar{V}_s = \frac{M_s - \frac{d\rho}{dC_s}}{\rho - C_s\frac{d\rho}{dC_s}}$$

and

$$\bar{V}_o = \frac{M_o}{\rho - C_s\frac{\partial\rho}{\partial C_s}} \quad ,$$

where the subscript s refers to the salt and the subscript o refers to the solvent.