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Moving Boundary Measurement of Transference Numbers

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Abstract

A moving-boundary system is analyzed, and an equation, valid

for concentrated as well as dilute solutions, is obtained for the

transference number. When the partial molal volume of the sol-

vent is constant through the boundary, the equation reduces to

the approximate equation now in common use. The cation trans-

ference number in 0.213 $\underline{M}$ NH_4NO_3 was experimentally determined

at 25°C and found to be 0.5140 ± 0.0024.

Introduction

Moving-boundary measurements date back to the nineteenth century.[1] The two-salt boundary was analyzed in 1900 by the mathematician Weber.[2] In 1910 the chemist Lewis[3] presented an analysis which corrected for the boundary movement caused by the electrode reaction. His equation was thought to be restricted to dilute solutions[1] until Bearman[4], in 1962, showed that it actually applies to systems in which the partial molal volumes are constant through the boundary--a slightly less stringent condition. No other theoretical progress has yet been made, and Lewis's equation is still used today.[5] In the present work a more detailed analysis of the moving-boundary system yields an expression of more general validity for the transference number.

Theoretical Development

Figure 1 shows the two-salt boundary at 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 solvent is referred to by "0".

The equations necessary to describe the moving-boundary system are the continuity equation or material balance,

$$\frac{\partial c_i}{\partial t} = - \frac{\partial c_i v_i}{\partial x} ,$$

(1)

an equation relating the current density to the fluxes,

$$i = F \sum_i z_i c_i v_i ,$$

(2)

$$x = -\infty$$

Salt solution A
composed of
ions 1 & 3

2 - salt

boundary

Salt solution B
composed of
ions 2 & 3

$$x = +\infty$$
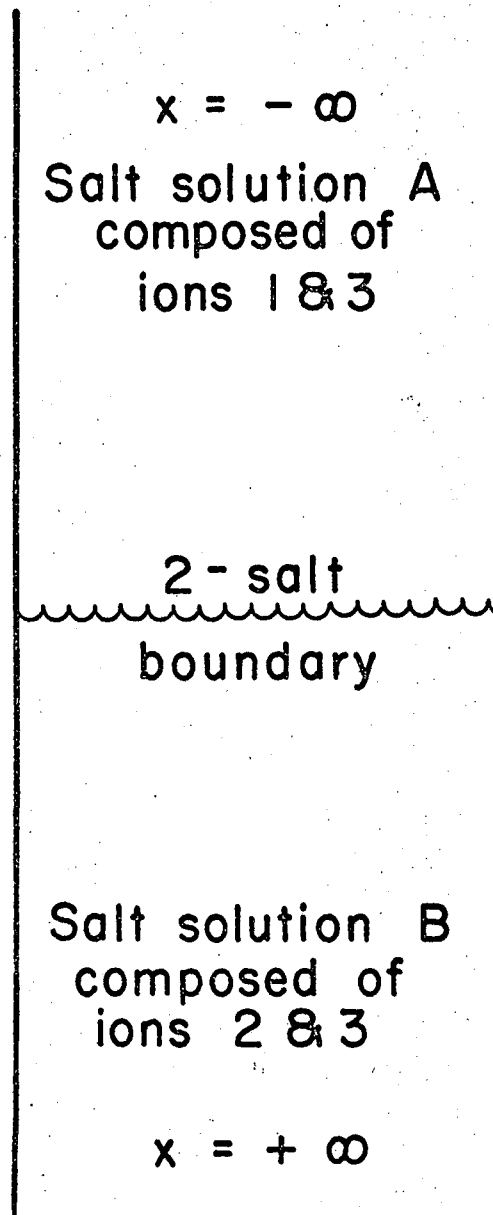
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Figure 1.   The 2-salt boundary.

a statement of electroneutrality,

$$\sum_i z_i c_i = 0 \;, \tag{3}$$

and a flux or transport equation,

$$c_i \frac{\partial \mu_i}{\partial x} = RT \sum_j \frac{c_i c_j}{c_T \mathcal{D}_{ij}} (v_j - v_i) \;, \tag{4}$$

where μ_i is the electrochemical potential. These equations are dis-
cussed in detail by Newman.[6] When the motion of the ions is referred
to the solvent motion, the definition of the transference number becomes

$$t_+ = \frac{z_+ c_+ (v_+ - v_o)}{z_+ c_+ (v_+ - v_o) + z_- c_- (v_- - v_o)} = \frac{z_+ \mathcal{D}_{o+}}{z_+ \mathcal{D}_{o+} - z_- \mathcal{D}_{o-}} \;. \tag{5}$$

Equations (1) to (5) can be manipulated to yield the exact rela-
tionships[7]

$$t_1 = \frac{F}{i} \frac{z_3 c_3}{c_o} \bigg|_{x=-\infty} [c_o (v_o - v_b)] \tag{6}$$

and

$$t_2 = \frac{F}{i} \frac{z_3 c_3}{c_o} \bigg|_{x=+\infty} [c_o (v_o - v_b)] \;, \tag{7}$$

where v_b is the velocity of the boundary, the subscript $x = -\infty$ indicates
that c_3/c_o must be evaluated in solution A above the boundary, and the
subscript $x = +\infty$ indicates that c_3/c_o must be evaluated in solution B
below the boundary.

These equations immediately yield the Kohlrausch regulating function[1]

$$\frac{t_1}{t_2} = \frac{[c_3/c_o]_{x=-\infty}}{[c_3/c_o]_{x=+\infty}} \;. \tag{8}$$

This is identical to the relation derived by Smits and Duyvis[8] in their

criticism of work done separately by Bearman,[4] Haase,[9] and Spiro.[10]
If the concentration of the solution following the boundary does not
initially satisfy the Kohlrausch regulating function, it will adjust
itself so that it does. In this case a concentration boundary between
the initial solution and that following the boundary will be left behind
as the two-salt boundary progresses up or down the channel. This boun-
dary between solutions of two different concentrations of the following
ion has been studied optically by Longsworth.[11]

In equations (6) and (7), the term $c_o(v_o-v_b)$ is the solvent flux
relative to the boundary and is constant through the boundary. The
application of these equations requires the determination of v_o either
above or below the two-salt boundary. Usually one electrode is selected
with a well-defined reaction, and this electrode chamber is tightly closed
so that the volume changes at the electrode can be assessed. Thus the
system shown in figure 1 must be expanded to include the closed electrode
chamber. Figure 2 shows this arrangement with the two-salt boundary and
a concentration boundary, formed as described in the preceding paragraph.

Let the electrode reaction be that of metal dissolution, with the
two-salt boundary progressing up the channel, so that solution A is the
leading solution. This is the usual arrangement for determining t_1. On
account of the dissolution process, the concentration of solution B
near the electrode will be higher than its initial value. The solvent
velocity v_o in the solution below the two-salt boundary can be calculated
by means of material balances over the region below a plane x fixed in the
solvent (see figure 2), allowance being made for the dissolution of the
anode, the concentration dependence of the density of solution B, and
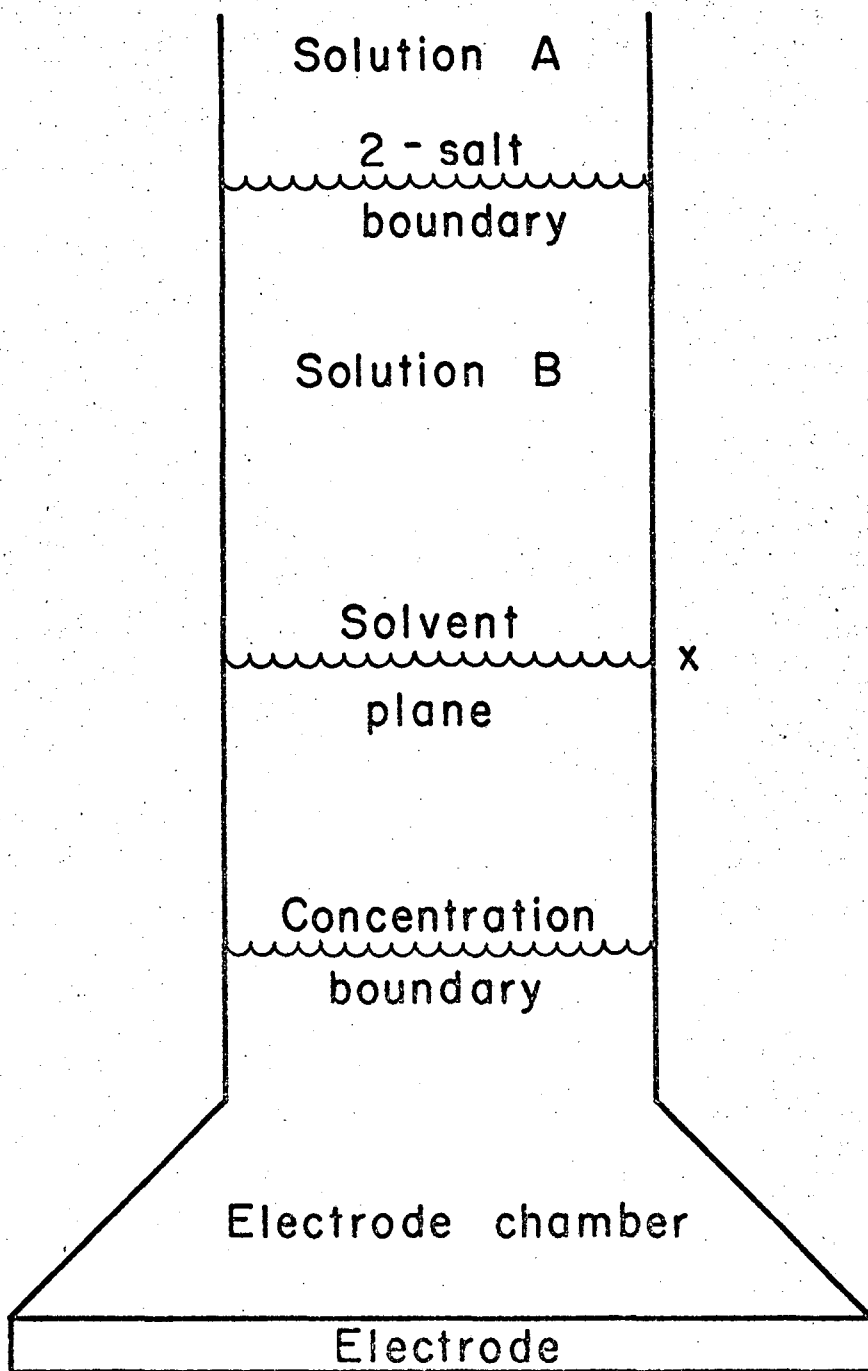
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Figure 2. The closed electrode.

transference of ions across the solvent plane. With a linear approximation to the concentration dependence of the density, the result is[7]

$$v_o = -\frac{i}{F}\left[\frac{M_e}{z_+\rho_e} + \frac{1-t_+}{z_+\nu_+}\frac{b_B}{a_B}\right],\qquad(9)$$

where a_B and b_B are defined by

$$c_{oB} = a_B + b_B c_B .\qquad(10)$$

This last equation is equivalent to a linear density-concentration relationship over the range of interest, that range covering the concentrations present in solution B from the electrode to the solvent plane x.

Substitution of equation (9) into equation (6) with elimination of t_+ (here ion 2 is the cation reacting at the electrode) by means of equation (7) yields[7]

$$t_1 = -a_B \left.\frac{z_3 c_3}{c_o}\right|_{x=-\infty}\left[\frac{FV}{It} + \frac{M_e}{z_2\rho_e} + \frac{b_B}{z_2\nu_2 a_B}\right],\qquad(11)$$

where V is the volume through which the boundary moves when current I is passed for time t.

For equation (11) to be fruitfully applied to a system, equation (10) must be a good approximation. If the density of the following solution is given by

$$\rho = k_1 + k_2 c + k_3 c^{3/2} + k_4 c^2 ,\qquad(12)$$

then the solvent concentration is

$$c_o = e + fc + gc^{3/2} + hc^2 ,\qquad(13)$$

where

$$\left.\begin{array}{ll} e = k_1/M_o, & f = (k_2-M)/M_o , \\ g = k_3/M_o, & h = k_4/M_o , \end{array}\right\}\qquad(14)$$

rather than equation (10). A least squares fit of equation (10) to equation (13) over the concentration range of interest, from c to $(1+\epsilon)c$, yields

$$a = e - \frac{1}{2} gc^{3/2}[1+ \frac{3}{4} \epsilon + \frac{1}{80} \epsilon^2 + 0(\epsilon^3)] - hc^2(1+\epsilon+ \frac{1}{6} \epsilon^2) \qquad (15)$$

and

$$b = f + \frac{3}{2} gc^{1/2}[1+ \frac{1}{4} \epsilon + 0(\epsilon^2)] + 2hc(1+ \frac{1}{2} \epsilon) , \qquad (16)$$

where 0 indicates the order of neglected terms.

Application

If the following solution is initially prepared so that its concentration is less than that required by the Kohlrausch relation, equation (8), then equations (15) and (16) are immediately applicable with the initially prepared value of the concentration equal to c and with ϵ equal to either ϵ_1 in the anode chamber or ϵ_2 across the concentration boundary, whichever is larger.

If the initially prepared following solution is of higher concentration than that required by the Kohlrausch relation, one can, with little error, approximate ϵ by $\epsilon_1+\epsilon_2$ and take c to be the initially prepared concentration (rather than the lowest concentration of solution B present).

The value ϵ_2 due to the Kohlrausch adjustment must be experimentally minimized or measured. The part ϵ_1 due to the electrode reaction can be calculated from one of the following approximate equations:[7]

For a uniform concentration in the anode chamber (an unlikely situation),

$$\epsilon_1 \approx V/U , \qquad (17)$$

where U is the volume of the anode chamber.

If the anode can be treated as a vertical electrode with free convection,

$$\epsilon_1 = \frac{1.62}{c} \left(\frac{It_-}{z_+\nu_+FDA_e}\right)^{0.8} \left(\frac{\nu DL}{g}\frac{1}{\beta}\right)^{0.2} \approx \frac{0.00932}{c} \left(\frac{I}{z_+\nu_+A_e}\right)^{0.8}\left(\frac{L}{\beta}\right)^{0.2} , \quad (18)$$

where in the latter expression I is the current in mA, A_e is the effective electrode area in cm^2, c is in moles/ℓ, L is the effective electrode height in cm, and $\beta = (1/\rho)d\rho/dc$ is in ℓ/mole. The latter expression is based on a diffusion coefficient D of 10^{-5} cm^2/sec, a transference number t_- of 0.5, a kinematic viscosity ν of $10^{-2} cm^2$/sec, and a gravitational acceleration g of $10^3 cm/sec^2$.

For a horizontal electrode,

$$\epsilon_1 \approx \frac{1}{A_e}\sqrt{\frac{2IV}{\pi z_+\nu_+FDc}} \approx \frac{0.8}{A_e}\sqrt{\frac{IV}{z_+\nu_+c}} , \quad (19)$$

where in the latter expression A_e is in cm^2, I is in mA, V is in cm^3, c is in moles/ℓ, and the value $t_- = 0.5$ has been assumed.

Discussion

Equations (6) and (7) are exact relationships describing the two-salt boundary. Equation (11), relating the transference number to the experimentally measured quantities, depends additionally only on the very good approximation of a linear concentration dependence of the density of solution B over the range of concentrations encountered between the electrode and the two-salt boundary.

For the system being analyzed, the equation of the type derived by Lewis[1,3] is

$$t_1^L = -\frac{z_3 c_3(-\infty)}{1-c_A\bar{V}_A}\left[\frac{FV}{It} + \frac{\bar{V}_e}{z_2} - \frac{\bar{V}_B}{z_2\nu_2}\right] . \quad (20)$$

It can be shown[7] that

$$t_1^L/t_1 = a_A/a_B = \overline{V}_{oB}/\overline{V}_{oA} \, , \tag{21}$$

where a_A is given by an equation analogous to equation (10). Thus equation (11) reduces to a Lewis-type equation in the case where the partial molal volume of the solvent is constant through the boundary.

In applications, equation (11) is not very sensitive to the value of ϵ, but it is of course better to keep ϵ small. For most situations encountered, equations (18) and (19) indicate that the use of a vertical anode results in an appreciably smaller value of ϵ_1 than a horizontal electrode. Then the linear approximation, equation (10), is better, and a_B is more accurately known. This should be expected since with a vertical electrode there is a tendency toward a uniform concentration in the anode chamber (the optimum case), while with the horizontal electrode stratified layers of solution form with very little mixing. Equation (19) suggests that an autogenic boundary (one formed with solution A initially adjacent to the electrode surface) should not be used since then ϵ_1 is very large--either A_e is small or V is large--and the analysis is not applicable.

In the derivation of equation (11), it was assumed that ion 2 is the cation reacting at the electrode. If, on the other hand, the common ion 3 is positive, equation (11) should be replaced by

$$t_1 = a_B \left. \frac{z_3 c_3}{c_o} \right|_{x=-\infty} \left[-\frac{F v_b}{i} - \frac{M_e}{z_3 \rho_e} \right] \, , \tag{22}$$

where v_b and i now have opposite signs. If the boundary moves down the channel, equation (11) or (22) is still applicable, but now the concentration boundary is above the two-salt boundary, and ion 2 is the leading

ion. If the electrode operates as a cathode, ϵ_1 should be taken to be negative.

The analysis treats an electrode involving metal dissolution or deposition. The analysis can be modified to treat other cases with well-defined volume changes at the electrode.

The transference number of the leading ion can always be determined more accurately than that of the following ion, since the concentration is known. The transference number of the following ion can be calculated from equation (8) if the concentration difference across the concentration boundary is determined, say, in the manner of Longsworth.[11] The uncertainty in the concentration so determined must be added to the uncertainty in the transference number of the leading ion in order to determine the uncertainty in the following-ion transference number.

Experiment

The transference number of 0.213 $\underline{M}$ NH_4NO_3 at 25°C was determined[7] with $AgNO_3$ as the following solution. A standard Tiselius cell with a closed vertical silver anode was used. Equation (15) was used to calculate a_B, with equation (18) being used to calculate ϵ_1 and ϵ_2 being measured by a Rayleigh interference optical method. All other procedures were standard methods for moving-boundary measurements.

Equation (11) yielded the result $t_+ = 0.5140 \pm 0.0024$. Other than the value $t_+ = 0.5130$ at 0.1 $\underline{M}$ listed by Milazzo[12], for which the present authors could discover no original source, this is the only value measured for NH_4NO_3. The value at infinite dilution, calculated from the limiting ionic mobilities of the ions,[12] is 0.507.

Equation (8) was used to estimate the cation transference number of the following $AgNO_3$ solution. The result $t_+ = 0.467 \pm 0.009$ at a concentration of 0.195 $\underline{M}$ can be compared with the work of Haase, et al.,[5] 0.4708 and 0.4723 (two determinations) at 0.1995 $\underline{M}$, calculated from a Lewis-type equation. If reasonable values are assumed for the concentration range of the following solution used by Haase, his data can be re-evaluated with equation (11) to yield the results 0.4693 and 0.4708, respectively.

Summary

An equation for the transference number, applicable at high as well as low concentrations, was presented. The difference between the present equation and the approximate equation now in common use lies in the calculation of the volume changes which accompany transference number measurements.

The equation in common use is arrived at by an intuitive approach, and accounts for volume changes across the two-salt boundary. Approximations are thus introduced which limit the usefulness of the equation to dilute solutions.

The present equation is derived from fundamental equations. It is seen that once a steady-state concentration profile is established in the two-salt boundary, no changes take place across the two-salt boundary which affect the determination of the transference number. Rather, the volume corrections are dependent only upon what takes place in the region from the electrode in the closed electrode assembly to, but not including,

the two-salt boundary. The approximation is made that, in this region, the concentration of solvent is linear with respect to the concentration of solute, $c_o = a + bc$. This approximation does not greatly limit the usefulness of the transference number equation.

Equations are presented which allow the calculation of the quantities a and b if the density of the solution is known as a function of concentration and the concentrations on both sides of the Kohlrausch concentration boundary are known.

The transference number of 0.213 $\underline{M}$ NH_4NO_3 was measured at 25°C.

Acknowledgment

Nomenclature

a_B	- defined by equation (10).
A_e	- surface area of electrode, cm^2.
b_B	- defined by equation (10).
c_i	- concentration of species i, $mole/cm^3$.
c_T	- total solution concentration, $mole/cm^3$.
D	- diffusion coefficient of salt, cm^2/sec.
D_{ij}	- diffusion coefficient for binary interactions, cm^2/sec.
e,f,g,h	- defined by equations (13) and (14).
F	- Faraday's constant, 96,493 coul/equiv.
g	- acceleration of gravity, cm/sec^2.
i	- current density, amp/cm^2.
I	- current, amp.
k_1, k_2, k_3, k_4	- defined by equation (12).

L   - electrode height, cm.

M_i - molecular weight of substance i, g/mole.

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

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 (20).

T   - temperature, deg K.

U   - volume of anode chamber, cm^3.

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

v_i - velocity of species i, cm/sec.

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

$\overline{V}_i$ - partial molal volume of component i, cm^3/mole.

x   - distance variable, cm.

z_i - charge number of species i.

β - coefficient of expansion, cm^3/mole.

ϵ - range of concentrations of solution B present below the two-salt boundary, relative to the lowest concentration in that range.

ϵ_1 - relative concentration range in electrode chamber.

ϵ_2 - relative concentration change across concentration boundary.

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

ν - kinematic viscosity, cm^2/sec.

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

ρ - density of solution, g/cm^3.

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

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