[Contribution from the Stamford Research Laboratories of the American Cyanamid Company]

"Analytical Boundary" Method for the Determination of Transference Numbers

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During the course of the investigation of solutions of colloidal electrolytes in this Laboratory, the need was felt for a fairly simple and rapid method for determining electrical mobilities to an accuracy of about 1%. It was desired to avoid the Hittorf method if possible, not only because of the time involved, but because of the difficulty in analyzing many of these solutions to an accuracy much better than 1%. The use of the moving boundary method with colloidal electrolytes usually involves a difficulty in the choice of a suitable following or "indicator" electrolyte for forming the boundary. The indicator must have a lower conductivity than the salt under investigation in the leading solution; further, the indicating ion must be slower than the leading ion in any possible mixture of the two solutions. The comparatively low conductivity of colloidal ions eliminates the use of simple electrolytes for indicators, and the possibility, or indeed probability, of interaction bars the use of another colloidal electrolyte. Hartley, *et al.*,[2,3] recognized this difficulty, and circumvented it in a study of certain cationic surface active agents by their "balanced boundary" method. Their method, although quite successful in this application, introduces a further complication in apparatus, since the boundary must be kept stationary by mechanical means. Moreover, because of the necessity of analysis *in situ*, the method is inapplicable in the many instances where multiple boundaries are formed.

The purpose of the present paper is to describe the theory and operation of a simpler cell in which, as in the "balanced boundary" method, the roles of the leading and indicating solutions are reversed. Experimental tests of the cell using simple electrolytes will be presented here, and applications to more complex systems given in the following paper.

The apparatus used is shown schematically in Fig. 1. The cell proper is a U tube divided into the two portions A and B by a sintered glass membrane (Pyrex medium grade). Compartment B contains the solution under investigation; the requirements for the solution in A will be referred to in more detail below. The electrode joined to compartment A is of the closed non-gassing type; that at the other leg of the U-tube may gas. The apparatus, called an "analytical boundary" cell for convenience, may be regarded as simply a means for combining the Hittorf and moving boundary methods. The procedure consists essentially of determining analytically the amount of the ion being studied in compartment A that has been transported electrically from compartment B through the boundary created by the membrane.

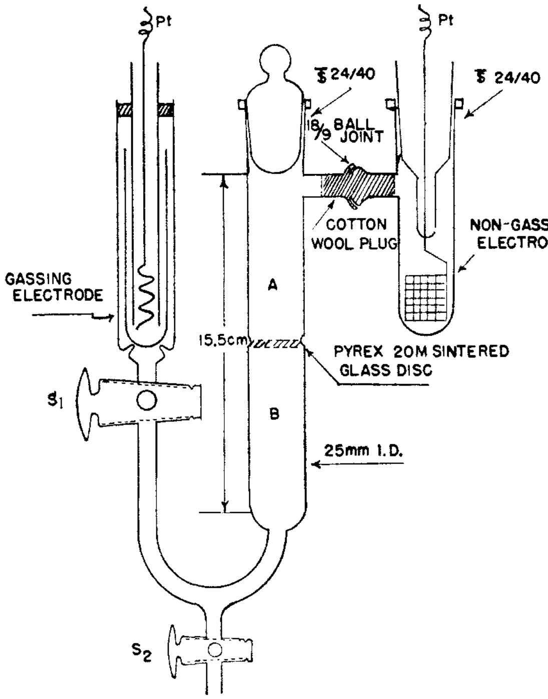

Fig. 1.—Analytical boundary apparatus: A, analytical compartment containing leading electrolyte; B, compartment containing solution under investigation; S_1, S_2, stopcocks.

The operation of the cell can most conveniently be examined from the standpoint of the moving boundary equations. Figure 2 is a diagrammatic representation of a moving boundary experiment. Originally AR and AS (at concentrations C_{AR} and C_{AS}, respectively) form a boundary at ab; after passage of current this boundary moves to cd. As a moving boundary experiment, the arrangement is designed to determine the transport number of S in AS. As an analytical boundary experiment, however, it will be used to determine that of R in AR.

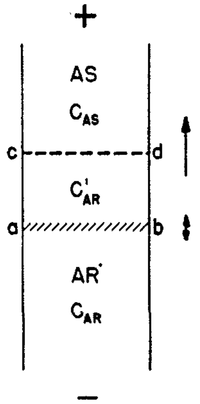

Fig. 2.—Moving boundary experiment.

After a quantity Q of electricity is passed through the solution, the volume V, swept out by

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[2] Hartley, *Trans. Faraday Soc.*, **30**, 648 (1934).

[3] Drew and Hartley, *ibid.*, 653 (1934); Collie and Hartley, *ibid.*, 657 (1934).

the boundary cd is[4]

$$V = \frac{QT_S}{FC_{AS}} \qquad (1)$$

where T_S denotes the transport number of S ion in AS. Equation (1) is the fundamental equation for determining the transport number of S by the moving boundary method. The concentration of AR behind the boundary is no longer the original C_{AR}, but an adjusted value, C'_{AR}, given by the Kohlrausch[5] conditions

$$\frac{T'_R}{C'_{AR}} = \frac{T_S}{C_{AS}} \qquad (2)$$

where T'_R is the transport number of R at the indicator concentration, C'_{AR}. Substitution of equation (2) into equation (1) gives

$$C'_{AR}V = Q\,T'_R/F \qquad (3)$$

Since in general $C'_{AR} \neq C_{AR}$, a slowly moving boundary will remain in the neighborhood of ab. Considering upward movement in Fig. 1 as positive, this boundary will sweep out a volume[4]

$$V' = \frac{Q(T_R - T'_R)}{F(C_{AR} - C'_{AR})} \qquad (4)$$

In the present instance, we are interested in the total quantity of R, M_R, that passes through the plane ab, since this is the quantity that will be determined. If the secondary boundary at ab is stationary or moves downward with time, evidently M_R is given by the left-hand side of equation (3); therefore

$$M_R = QT'_R/F \qquad (5)$$

If, on the other hand, the secondary boundary moves upward with time, then $M_R = C'_{AR}V + (C_{AR} - C'_{AR})V'$, and from equations (3) and (4)

$$M_R = QT_R/F \qquad (6)$$

Thus multiplying the amount of R passing through the plane ab by F/Q gives the transport number of the radical R at the initial or at the adjusted concentration, depending upon whether the secondary boundary moves upward or downward. In the applications to which this cell has so far been put there has been no ambiguity. If such a difficulty did arise, it would be necessary to determine the general shape of the T *vs.* C curve; by using a leading solution of known properties the value of C'_{AR} may be readily approximated from equation (2) and from equation (4) the decision made as to which concentration the observed transference number refers.

An experimental alternative that circumvents the above ambiguity and is convenient and easy to apply, especially in complex systems, is a radiotracer technique. In this method, the leading and unknown solutions are of identical composition, but the latter contains a radioactive isotope of the ion or ions under investigation. There are then no restrictions on the complexity of the system, and, since the "adjusted" concentration is automatically that of the original solution, no complications arise due to motions of secondary boundaries. This technique should find increasing applications as the larger supplies of radioactive elements from uranium piles become available.

The following comments concerning the analytical boundary cell are of importance. First of all, in the derivation of equations (5) and (6) for clarity the assumption was made that stable sharp boundaries are formed. This would require the fulfillment of definite conditions, namely, that the density increase from top to bottom of the cell and that the conductivity of C_{AS} be greater than that of C_{AR}. However, the above assumption is unnecessary since the equations may be derived in terms of the volume velocities past plane ab, and consequently the solution in compartment A does not have to satisfy such rigid requirements. For practical operation of the cell, however, it is necessary to insure that the material transported through the membrane will not be lost in the electrode compartment. Convectional instability is therefore to be avoided. Electrical stability is desirable but not necessary, although again, in order to minimize the possibility of losses the conductivity of the leading solution should not be much less than that of the unknown.

The radical R need not be a single species. However, if it is not, it will usually be necessary to neglect the motion of the secondary boundary, leading to the aforementioned uncertainty as to the exact concentration to which the transport number refers. The error so introduced is usually small. Again, the tracer method overcomes the difficulty.

It is obvious that the migration of foreign ions from either electrode to the neighborhood of the membrane will vitiate results. It is desirable, therefore, although not always necessary, to introduce a small amount of concentrated solution of the unknown around the gassing electrode; it will then be in a region of high conductivity and any hydrogen or hydroxide ion produced in the electrode will have less chance of getting over into compartment B. The baffle system at the gassing electrode is also an aid in this respect. The composition of the non-gassing electrode depends upon that of the leading solution in A and must be so chosen as to introduce no foreign ions into A by electrolytic migration.

Some of the early cells used by Hittorf[6] and by Steele[7] contained membranes. These were abandoned because such materials as fish bladder and gelatin obviously influenced results, either through electroendosmotic streaming or conductivity changes within the membrane. In the present apparatus endosmosis is prevented by the closed system above the membrane, and it is imperative that there be no leakage here. The pore diameter of the membrane is several microns, making the

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(4) MacInnes and Longsworth, *Chem. Rev.*, **11**, 171 (1932).

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

(6) Hittorf, *Z. physik. Chem.*, **39**, 613 (1901); **43**, 239 (1903).

(7) Steele, *ibid.*, **40**, 689 (1902).

TABLE I

TRANSFERENCE NUMBERS OF SOME SIMPLE ELECTROLYTES AT 25° BY THE ANALYTICAL BOUNDARY METHOD

Solution tested	Ion	Solution	Non-gassing electrode	Milliequiv. transported	Coulombs passed	T
0.1 N $AgNO_3$	Ag^+	0.1 N KNO_3	$Pt/Fe(NO_3)_3$	0.208	42.38	0.473
.01 N $AgNO_3$	Ag^+	.01 N KNO_3	$Pt/Fe(NO_3)_3$	.01892	3.892	.469
.1 N KBr	Br^-	.1 N KNO_3	$Pt/K_4Fe(CN)_6$	.2655	49.31	.519
.01 N KBr	Br^-	.1 N KNO_3	$Pt/K_4Fe(CN)_6$	.02356	4.274	.531
.01 N KBr	Br^-	.1 N KNO_3	$Pt/K_4Fe(CN)_6$	.02773	5.006	.527
.05 N NaCl[a]	Cl^-	.05 N NaCl	$Pt/Na_4Fe(CN)_6$	.1369	21.98	.601
.05 N NaCl[a]	Cl^-	.05 N NaCl	$Pt/Na_4Fe(CN)_6$	.1120	17.95	.602
.02 N NaCl[b]	Na^+	.02 N NaCl	Ag/AgCl	.0594	14.478	.396

[a] Radiotracer method; tagged with Br^{82}, see text. [b] Radiotracer method; tagged with Na^{22}.

existence of appreciable surface conductivity improbable. The possibility still exists, of course, but experiments with either uni-univalent electrolytes or solutions of surface active agents (to be presented in a following paper) give no indication of abnormal behavior.

As in the moving boundary method, a small correction in the observed values for the transport number must be made for volume changes above the original boundary during the course of electrolysis, in order to refer the movement to the water rather than the apparatus. The solutions reported here are sufficiently dilute for the correction to be within the experimental error, and it was consequently ignored.

Experimental

Materials.—Reagent grade chemicals were used throughout without further purification. The water used was de-ionized by ion exchange resins, and had a specific conductivity of 2×10^{-6} mho cm.$^{-1}$; this amounted in most cases to about 0.01% of that of the solution tested and never to more than 0.1%.

Radioactive sodium, Na^{22}, was obtained from a magnesium target which had been bombarded with deuterons in the University of California cyclotron. A chemical separation without sodium carrier was made by Mr. R. K. Madison of the Radioactivity Group of these Laboratories. Radiobromine, Br^{82}, was obtained with no carrier by the Szilard-Chalmers procedure[8] from C. P. ethyl bromide bombarded with neutrons from the Columbia University cyclotron. In preparing the tagged solutions, two aliquots of a stock solution were diluted to volume, in one case with a radioactive tracer solution and in the other with water.

Procedure.—The left-hand side of the U-tube, the region below the membrane, and the membrane itself are filled with the solution to be investigated. Compartment B may be rinsed by the use of stopcock S-2; stopcock S-1 is to prevent streaming through the membrane while compartment A is rinsed and filled with the leading solution.

The cell is placed in a thermostat and the desired voltage impressed across the electrodes from storage batteries. A milliammeter and voltmeter serve to check the approximate wattage; no extensive experiments have been made, but the apparatus works satisfactorily up to about 500 milliwatts. The current is read periodically with a Leeds and Northrup type K-2 potentiometer in terms of the voltage across a fixed series resistor. The duration of the experiment depends entirely upon the transference number of the ion under investigation; in the examples given in this paper a calculated movement of about a centimeter for the ion under investigation was found to be satisfactory—tripling this movement gave results several per cent. too low. With the arbitrary limit set on the wattage, this required thirty to ninety minutes, depending upon the concentration.

Analyses.—At the completion of a run the analytical compartment A was rinsed out, then the contents made up to a specified volume. Closing stopcock S-1 prevents streaming during this operation.

Silver and bromide ions were titrated conductometrically with potassium bromide and silver nitrate, respectively (precision *ca.* ±0.2%); the radioactive solutions were counted in a small glass jacketed Geiger counter tube[9] with a conventional amplifying and scaling circuit, and the total number of counts taken on a given sample was sufficient to make the probable counting error less than ±1%.

Results and Discussion

The results of a series of transport determinations in simple electrolytes using the analytical boundary method are given in Table I. The first example, potassium nitrate leading, silver nitrate following, from which T_{Ag^+} was determined, is a system forming a stable boundary. In the second example, potassium nitrate leading, potassium bromide following, from which T_{Br^-} was determined, the boundary is convectionally stable but unstable electrically.

The last three rows in Table I are examples of the radiotracer method. The second of these, in which Na^{22} is used to trace Na^+, is straightforward. In the first, Br^{82} is used to follow Cl^- in NaCl, this combination being adopted to test the general feasibility of using radiobromide to trace chloride ion. The radioisotopes Cl^{34} and Cl^{38} are of too short half life (thirty-three and thirty-seven minutes) for convenient use, and the long lived Cl^{36} (10^3 yr.) was not available to us. The observed migration of radiobromine was divided by the ratio of the equivalent conductivity of Br^- to that of Cl^- at infinite dilution to convert to chloride migration.

In Table II the analytical boundary results are compared with those obtained by the moving boundary[4] and the Hittorf[10] methods. The latter are older values and would be considerably improved by modern techniques, but only with a corresponding increase in manipulative and analytical difficulties. From the results in the table it

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(8) Szilard and Chalmers, *Nature*, **134**, 462 (1934); Seaborg, *Chem. Rev.*, **27**, 260 (1941).

(9) Barnes and Salley, *Ind. Eng. Chem., Anal. Ed.*, **15**, 4 (1943).

(10) Landolt-Börnstein, "Tabellen," HWII, p. 1109.

can be seen that although the listed analytical boundary results are only accurate to about 2%, they are as accurate as a reasonably careful Hittorf determination (taking the moving boundary values as correct), and certainly far less tedious and analytically exacting. The accuracy could be improved by a careful purification of materials and by more precise analytical procedures, but is shown to be sufficient for the purposes for which the cell was designed. The substances listed in Table I were run, of course, only for test purposes, since the moving boundary method gives more accurate results just as quickly. In a following paper (with D. J. Salley), an application to colloidal electrolytes will be presented. It is also obvious that the method is applicable to the study of proteins, dyes (where colorimetric analysis may readily be used), and complex systems such as solutions of acid polymerized trimethylol melamine.

TABLE II

COMPARISON OF ANALYTICAL BOUNDARY RESULTS WITH OTHER METHODS

Solution	Concn.	Cation transference no. Analytical boundary	Moving boundary	Hittorf[a]
$AgNO_3$	0.1	0.473	0.468	0.474
	.01	.469	.465	.474
KBr	.1	.481	.485	...
	.01	.471	.483	.496
NaCl	.05	.399	.390	.396
	.02	.396	.389	.396

[a] These values are at 18°; the temperature correction is small but should tend to *raise* them.

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Summary

1. The design and operation of a cell of simple construction for measuring transference numbers, embodying a combination of the Hittorf and moving boundary techniques, is described. Because of the interchange of the usual roles of the leading and indicator solutions as compared to the moving boundary method, the method is suited for electrolytes containing a colloidal ion.

2. Analytical requirements are much less exacting than in the Hittorf method, permitting a wide choice of methods (*e. g.*, radioactivity counts, conductometric titrations, and colorimetry).

3. In complex systems where the moving boundary results would be difficult or impossible to interpret, radiotracer techniques may be readily applied. Because of the reduced analytical requirements ordinary counting methods may be used.

4. Tests of the cell using solutions of simple electrolytes, employing both analytical and radiotracer methods, indicate an accuracy equivalent to that obtained in reasonably careful determinations by the Hittorf method.

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The Self-diffusion Coefficients and Transference Numbers of the Small Ions in Colloidal Electrolytes

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Introduction

The fraction of small ions associated kinetically with the large aggregates in aqueous solutions of colloidal electrolytes is of general interest for the better understanding of these solutions. The "fraction bound" has been estimated for various colloidal systems from measurement of the thermodynamic properties of the solution, as by freezing point depression[1] or dew point lowering,[2] from the conductivity plus the transference number,[3,4] from e. m. f. measurements,[5,6,7] and from membrane equilibrium.[8] In addition specific methods have been used, such as measuring the *p*H of hexanolamine caprylate solutions containing excess hexanolamine,[9] and the increase of conductivity of lauryl sulfonic acid solutions when potassium nitrate is added.[10] Another general method that suggests itself is self-diffusion, but insofar as the authors are aware it has not yet been applied to this problem.

Any value of the fraction bound derived from experimental data must, of necessity, result from a series of assumptions. Because of this, the values obtained from any one of the above methods may be quite uncertain. This paper compares, under consistent assumptions, the fraction bound as obtained by three methods: self-diffusion, conductivity plus transport, and freezing point lowering.

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(1b) McBain, Laing and Titley, *J. Chem. Soc.*, **115**, 1279 (1919).

(2) McBain and Salmon, THIS JOURNAL, **42**, 426 (1920).

(3) McBain and Thomas, *J. Phys. Chem.*, **40**, 997 (1936).

(4) Hartley, Collie and Samis, *Trans. Faraday Soc.*, **32**, 785 (1936).

(5) Salmon, *J. Chem. Soc.*, **115**, 530 (1920).

(6) Lottermoser and Puschel, *Kolloid Z.*, **63**, 175 (1933).

(7) McBain and Betz, THIS JOURNAL, **57**, 1909 (1935).

(8) Northrup and Kunitz, *J. Gen. Physiol.*, **11**, 481 (1928).

(9) Gonick, THIS JOURNAL, **68**, 177 (1946).

(10) Walton, *ibid.*, **68**, 1182 (1946).