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A STUDY OF THE MOVING BOUNDARY METHOD FOR DETERMINING TRANSFERENCE NUMBERS

BY DUNCAN A. MACINNES AND EDGAR REYNOLDS SMITH

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In our study of solutions of strong electrolytes it became desirable to obtain accurate transference numbers of a number of salts throughout a range of concentrations. From its apparent precision and the rapidity with which the measurements can be made, the moving boundary method for obtaining these numbers seemed attractive, and a careful study of the method was accordingly undertaken.

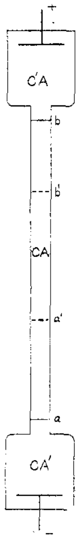

Fig. 1

As usually described, the moving boundary method for determining transference numbers is as follows. The transference number of one of the two ions of a salt is equal to the distance moved by the boundary of one of the ion constituents divided by the distances moved in the same time and under the same potential gradient by the boundaries of both ion constituents. These distances can be measured in an apparatus shown diagrammatically in Fig. 1. A solution of the salt CA under investigation is placed between one of CA' and another of C'A, having, respectively, the same cation and anion as the salt CA. The boundary at *a* and that at *b* are visible because of the different refractive indices of the solutions. On passing current through the apparatus the boundary *a* moves up to *a'* and the boundary *b* moves down to *b'*. The ratio: $aa'/(aa' + bb')$ is equal to the transference number T_a. The solution of C'A must be lighter, and that of CA' heavier, than the solution of CA, and the ions C' and A' have smaller mobilities than the ions C and A, respectively, in order that the boundaries shall persist during the passage of current. The apparatus can also be constructed in the form of a U-tube, in which case both of the following or indicator solutions must be lighter than the solution whose transference number is being measured.

Aside from the purely qualitative early work by Lodge[1] and others, the only workers who have published measurements made by this method are Denison and Steele,[2] and later Denison.[3] These workers obtained a large amount of transference data including measurements on most of the more common strong electrolytes at various concentrations.

The authors of the present article have made an endeavor to extend and amplify Denison and Steele's work. In the first part of the investigation, after obtaining sharp and readily visible boundaries (which proved to be by no means easy), it was found that, although precise measurements could be obtained, the results were not reproducible unless all possible variables, such as impressed e.m.f. and the kind and the concentrations

[1] Lodge, *Brit. Assoc. Repts., Birmingham*, **1886**, p. 389.

[2] Denison and Steele, (a) *Phil. Trans.*, (A) **205**, 449 (1906); (b) *Z. physik. Chem.*, **57**, 110 (1906–7).

[3] Denison, *Trans. Faraday Soc.*, **5**, 165 (1909).

of the salts forming the indicator solutions, were kept constant. Also, the results obtained departed widely and erratically from the accepted values of the transference numbers. A single instance of the difficulties encountered will suffice. Measurements were made on a 0.1 N solution of potassium chloride, using 0.1 N lithium chloride and potassium acetate solutions as indicators. The "transference numbers" at 135, 230 and 325 volts were 0.638, 0.550 and 0.531, respectively. These values were reproducible to about 0.1% at each voltage, though they all depart widely from the correct value, 0.508.[4] It is interesting to note that the values approach nearer to the correct number for the higher potentials. A change of the nature or concentrations of the indicator solutions leads to quite different results from those given.

From these and many other similar discouraging results it became quite evident that either the method was useless or some additional factor must enter. In correspondence with Professor Denison he suggested that the concentrations of the indicator solutions should be adjusted according to the relation,

$$C/T = C'/T' \qquad (1)$$

in which C and T are the concentration and the transference numbers of the solution under observation and C' and T' are the corresponding values for the indicator solution. Kohlrausch,[4] in an early paper, derives this relation as a necessary condition for a stable moving boundary. He states, however, that the condition represented by that equation will automatically be established, if not present at the outset, from which it would be concluded that the initial concentration of the indicator solution is of little importance. Later, it was given a simpler derivation by Denison.[5] Denison and Steele[2a] also state that the condition represented by Equation 1 establishes itself automatically, and give no limits to this spontaneous adjustment. These authors say, "It has been proved that the concentration of the lithium chloride (indicator solution) becomes automatically adjusted, so that the potential gradient is just sufficiently increased to make the lithium ions keep pace with the potassium ions," the latter being the ions of which the transference number is wanted. Denison[5] has shown in his derivation that, under the conditions given, Equation 1 holds.

It became of interest to us therefore to determine (a) whether the boundaries move at the theoretical velocities if the condition given in Equation 1 is fulfilled at the boundaries, and (b) whether any of the automatic adjustment, predicted by Kohlrausch, takes place. It is evident that if the concentrations of the solutions must be *exactly* adjusted according to the ratio given by Equation 1, the moving boundary method is useless for obtaining transference numbers, since these numbers, as well as

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

[5] Denison, *Z. physik. Chem.*, **44**, 581 (1903). See also Miller, *ibid.*, **69**, 436 (1909).

those of the indicator solutions at a series of concentrations, must be known in advance. On the other hand, if there is even a small amount of the automatic adjustment predicted by Kohlrausch the correct transference numbers can be arrived at as the result of a series of experiments which approximate, more and more closely, to the theoretical conditions. This will be discussed more fully, later.

Because of a reduction of the number of variables and the ease of practical manipulation the apparatus we finally used involved only one moving boundary. If the current through the apparatus is kept constant throughout the experiment the transference number can be computed with as great accuracy as from the movement of two boundaries, provided, of course, that the boundary moves at the rate required by the theory under the conditions of the experiment.

The equations involved in the computation of the ionic mobilities and transference numbers when only one boundary is used are obtained as follows: If V is the velocity with which the ion constituent moves and U_1 its mobility, and ϵ the potential gradient then

$$V = U_1\epsilon \qquad (2)$$

Now the current through the tube, i, is determined by Equation 3, in which C is the concentration, A the area of tube and F the Faraday equivalent;

$$i = (U_1 + U_2)\,\epsilon\, CAF \times 10^{-3} = \epsilon\kappa A \qquad (3)$$

since the specific conductance, $\kappa = (U_1 + U_2)CF \times 10^{-3}$. From (2) and (3) then

$$U_1 = V\kappa A/i = l\kappa A/i\,t \qquad (4)$$

in which l is the distance along the tube moved by the boundary in the time t.

From the mobility U_1 the transference number can, of course, be computed, but the transference number can also be computed from the measurements without a knowledge of the specific conductance, since

$$V = U\epsilon = T\Lambda\epsilon/F$$

now $\epsilon = i/\kappa A$ and $\Lambda = 1000\kappa/C$, therefore,[6]

$$T = VCFA/1000i = lCFA/1000\,it \qquad (5)$$

Apparatus and Procedure

The cell shown in Fig. 2 was used for the study of the individual mobility of an ion constituent and the determination of transference numbers by the single boundary method.

Let us consider the case of the measurement of the mobility of the potassium-ion constituent in a solution of potassium chloride. The electrode vessel D and measuring tube T are filled with the potassium chloride solution, which is kept out of

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[6] Since lA is the volume swept through during the time t, and $i\,t$ is the number of coulombs, the transference number can be found by measurement with one boundary and a measurement with a coulometer in series, a principle we may make use of in future work.

B and *A*, and the combination ground glass stopper and electrode tube *C* is put firmly in place. In this case the electrode *E* is a piece of platinum gauze plated electrolytically with silver and then covered with silver chloride by electrolysis. This ground glass stopper *C* was used instead of rubber because the latter, when pushed strongly into the tube, may undergo a slow expansion which would influence the motion of the boundary. The glass rod *R* has a flat circular enlargement, *B*, on the lower end, which is tipped with a circular disk of thin rubber held on by a small central spot of de Khotinsky cement. This rod, which slides easily through the hole in the rubber stopper, is next pressed firmly over the top of *T* and the entrapping of air bubbles under it is avoided. Any excess of solution squeezed out of *T* and into *B* by this action is removed by a capillary pipet thrust through one of the openings, marked *O*, in the rubber stopper. The electrode vessel *A* is then filled with lithium chloride solution and the anode *F*, which consists of a platinum gauze electroplated with silver, is inserted. The apparatus is next placed in a glass walled thermostat (regulated to 25° ± 0.05°), and the connections to the source of voltage are made. Then lithium chloride solution is pipetted through one of the openings marked *O* until *B* is filled. *R* is then gently loosened, but not yet pulled up, so that several milliamperes pass. The boundary between the lithium and potassium ions at once starts down the tube *T*. After the boundary has advanced about a centimeter the rod *R* is carefully pulled up. It was found possible to discard entirely the parchment paper used at the point corresponding to *B* in Denison and Steele's apparatus. The use of this paper is quite objectionable as it soaks up, from the tube *T*, solution which is afterward released into the indicator solution.

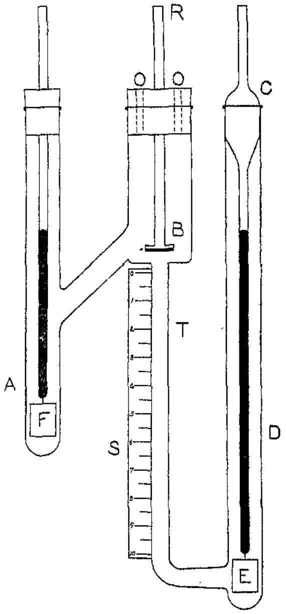

Fig. 2

The boundary was rendered visible by means of an arrangement similar to that used by Denison and Steele. A sheet of white paper was fastened on a frame and placed behind the thermostat. Two electric light bulbs were put behind the paper. By means of a cord and pulley a piece of black cardboard could be raised and lowered between the illuminated paper and the back of the thermostat. When the cardboard was raised to a position just below the boundary the latter became visible and could be read, on the scale *S*, readily to 0.1 millimeter.

The current through the tube, which was of the order of a few milliamperes, was maintained constant, within a few tenths of a per cent. by hand regulation of a rheostat in the circuit. Its value was known from the potential drop, measured with a potentiometer, across a standard resistance. The regulation was effected by observation of the scale of the galvanometer connected with the potentiometer. The source of current was a storage battery yielding 90 volts, to which was occasionally added a battery of dry cells. The volumes, corresponding to readings of the scale *S* in the tube *T* were obtained by means of a calibration with mercury. The length of *T* effective for measuring the motion of the boundary was 9 cm. and the scale *S* was graduated in millimeters. The position of the boundary could be estimated to the nearest 0.1 mm., so the precision of measuring the distance moved by the boundary was 0.2% or better.

The Experimental Results

All the figures obtained in a single experiment, with the apparatus just described, are given in Table. I These results show the constancy of the velocity of the boundary during its whole passage down the tube, provided a constant current is sent through the apparatus. All the results given later in this article are averages of figures obtained as in this typical experiment and having about the same experimental accuracy. In making the readings times were read on the second that the boundary passed a given line on scale *S*.

TABLE I

TYPICAL EXPERIMENTAL RESULTS IN THE DETERMINATION OF A TRANSFERENCE NUMBER

Solution, 0.1 *N* KCl; indicator solution, 0.065 LiCl; current, 0.005893 amp.; potential gradient, in KCl solution, 4 volts per cm.

Scale reading	0.50	5.50	5.80	6.10	6.40	6.70	7.00
Time, sec.	0.0	1900	2016	2130	2243	2357	2472
Velocity, cm./sec., $\times 10^3$	..	2.632	2.629	2.635	2.630	2.630	2.629
					Av. velocity		2.631×10^{-3}
					Av. mobility		0.6578×10^{-3}

In all the experiments the cathode side of the apparatus was closed in order that there might be no movement of the boundary arising from changes of level of the solution due to the electrolysis. It is necessary, however, as G. N. Lewis[7] has pointed out, to consider a correction for the volume change at the cathode during the passage of the current. However, at 0.1 *N* this correction is only one part in 5,000 for both salts.[8]

It will be recalled that the main purpose of this investigation was to determine the effect of the concentration of the indicator solution, and the current density, on the velocities of the boundaries, and the resulting effect on the computed mobilities and transference numbers. In Tables II to V are given the results of measurements on boundaries formed, in each case, with the solution being measured at 0.1 *N* and varying concentrations of the indicator solutions. Tables II and III are the results obtained on the movement of the boundary between potassium and lithium chlorides with two different potential gradients in the tube, and Tables IV and V are corresponding results for potassium bromide solutions. The figures given in Tables IV and V are averages, in each case, of closely agreeing duplicates, whereas the corresponding figures in Tables II and III represent single experiments.

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

[8] Lewis' formula is: $N = N' - vc$, in which N is the Hittorf transference number, N' the uncorrected value from the moving boundary measurements, v the volume change at the electrode due to the passage of a Faraday, and c the concentration. The cathode reaction consists of (a) the formation of 1 equivalent of silver, (b) the formation of N equivalents of potassium halide and (c) the disappearance of an equivalent of AgCl. For KCl the resulting volume changes are (a) 10.3 cc., (b) 13.5 cc. and (c) 25.7 cc., the term (b) being the partial molar volume of KCl in 0.1 *N* solution, computed in the usual way from density measurements, multiplied by 0.49. The net change of volume is therefore 0.002 liter and the correction term 0.0002. The corresponding terms for KBr are (a) 10.5, (b) 17.3 and (c) 29.7.

TABLE II

EFFECT OF CONCENTRATION OF INDICATOR SOLUTION ON MOVEMENT OF BOUNDARY, TENTH NORMAL POTASSIUM CHLORIDE AT 25°

Potential gradient in KCl solution, 4 volts per cm.

Conc. indicator soln. (LiCl)	Velocity Cm. per sec. × 10^3	$10^6 U_K$ in 0.1 N KCl	Transference number of K ion
0.1	2.713	(678)	(0.507)
.0887	2.663	(666)	(.498)
.08	2.654	(664)	(.496)
.075	2.641	(660)	(.494)
.07	2.633	658	.492
.065	2.631	658	.492
.06	2.637	659	.493
.055	2.658	(665)	(.497)
.045	2.622	(656)	(.490)
.035	2.615	(654)	(.489)

TABLE III

EFFECT OF CONCENTRATION OF INDICATOR SOLUTION ON MOVEMENT OF BOUNDARY, TENTH NORMAL POTASSIUM CHLORIDE AT 25°

Potential gradient in KCl solution, 3.5 volts per cm.

Conc. indicator soln. (LiCl)	Velocity Cm. per sec. × 10^3	$10^6 U_K$ in 0.1 N KCl	Transference number of K ion
0.1	2.373	(678)	(0.507)
.0887	2.324	(664)	(.497)
.08	2.312	(661)	(.494)
.075	2.309	(660)	(.493)
.07	2.303	657	.492
.065	2.298	656	.491
.06	2.296	656	.491
.055	2.309	(660)	(.493)
.035	2.287	(653)	(.489)

TABLE IV

EFFECT OF CONCENTRATION OF INDICATOR SOLUTION ON MOVEMENT OF BOUNDARY, TENTH NORMAL POTASSIUM BROMIDE AT 25°

Potential gradient in KBr solution, 3.365 volts per cm.

Conc. indicator soln. (LiBr)	Velocity Cm. per sec. × 10^3	$10^6 U_K$ in 0.1 N KBr	Transference number of K ion
0.1	2.557	(764)	(0.564)
.09	2.373	(709)	(.523)
.08	2.247	(671)	(.495)
.075	2.223	(664)	(.490)
.07	2.202	657	.485
.065	2.201	657	.485
.06	2.272	(680)	(.501)
.05	2.275	(679)	(.501)

Fig. 3 is a typical diagram which represents the data given in the tables. The mobilities computed from the experiments are plotted as ordinates against the corresponding concentrations of indicator solution. A similar plot is obtained if the transference numbers are used instead of the mobilities. The heavy line represents the values obtained at the higher potential gradient used and the lighter line those for a lower gradient. It will be seen from this plot, and also from the tables, that the velocity of the boundary (and therefore the computed mobilities and transference numbers) varies widely with the concentration of the following, or indicator, solution. However, at 0.065 N for potassium chloride and at about the same concentration for potassium bromide there is a minimum in the curves. Within the experimental error the measured mobility at this point is unaffected by changing the potential gradient. In addition, at this point, the relation between the concentrations of the measured and indicator solutions corresponds closely to Equation 1

TABLE V

EFFECT OF CONCENTRATION OF INDICATOR SOLUTION ON MOVEMENT OF BOUNDARY, TENTH NORMAL POTASSIUM BROMIDE AT 25°

Potential gradient in KBr solution, 3.701 volts per cm.

Conc. indicator soln. (LiBr)	Velocity Cm. per sec. × 10^3	10^6 U_K in 0.1 N KBr	Transference number of K ion
0.08	2.465	(669)	(0.494)
.075	2.427	659	.486
.07	2.423	658	.486
.065	2.416	656	.484
.06	2.498	(678)	(.501)
.05	2.497	(678)	(.501)

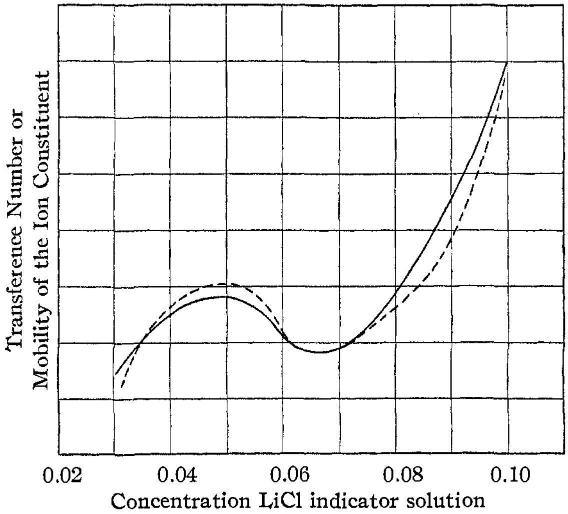

Fig. 3

$$C/T = C'/T'$$

For lithium chloride, for instance, the value for T' computed from Equation 1 is 0.320 whereas the results of MacInnes and Beattie[9] give by inter-

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[9] MacInnes and Beattie, THIS JOURNAL, **42,** 1117 (1920).

polation the value of 0.316 for this concentration. The agreement would be exact if the minimum were taken as 0.064 *N*. In addition it will be seen, from an examination of the tabulated data, that on either side of the minimum there is a range of concentrations of indicator solution (about 5%) in which the measured mobilities and transference numbers are independent of this concentration within the experimental error. Apparently throughout this small range the automatic adjustment of the concentration of the indicator solution, as predicted by Kohlrausch, does take place. Outside this range the adjustment quite as evidently fails to occur. Erroneous values for transference numbers will therefore be obtained if the concentration of the indicator solutions is not adjusted within this range.

Some results have also been obtained which show that if the composition of the indicator solution is adjusted according to Equation 1, the transference number obtained by observation of the moving boundary is, within the experimental error, independent of the potential gradient. The figures are given in Table VI. The boundary becomes invisible, under the conditions of the experiments, with a potential gradient lower than about 2 volts per cm. If too large a potential gradient is used the boundary is distorted by heating effects.

TABLE VI

RESULTS OF MOVING BOUNDARY EXPERIMENTS AT DIFFERENT POTENTIAL GRADIENTS

Concentrations, KCl = 0.1 *N*; LiCl = 0.065 *N*

Current Amp. × 10^3	Gradient (volts/cm.) in KCl solution	$10^6\ U_K$	Transference number of potassium ion
5.893	4	658	0.492
5.156	3.5	657	.491
4.420	3	656	.491
4.051	2.75	660	.494
3.683	2.5	657	.492
3.315	2.25	657	.492
2.951	2	No boundary visible	

In practical use of the moving boundary method for determining transference numbers an estimate of the probable value of the number should be made and the indicator solution concentration should then be computed according to Equation 1, and a measurement made. The indicator concentration should then be varied slightly and the measurement repeated. This should be continued until a portion of a plot similar to Fig. 3, and including the minimum value, can be prepared.

Further, the value obtained should be shown to be independent of the current through the apparatus, that is, to the potential gradients in the solutions. This procedure may sound tedious, but it is far more rapid, and also more accurate, than the determination of the same numbers by the Hittorf method. It also appears desirable that evidence showing that the adjustment of the compositions of the measured solution and the indicator solution has been obtained, should be given in all future work with the moving boundary method.

It does not, at present, appear to be possible to give a clear picture as to why the boundaries move too fast on both sides of the "adjustment" represented by Equation 1, and why, on the side of a too dilute indicator solution, the apparent mobility passes through a maximum and then again decreases. Some experiments under consideration will, we hope, throw light on the subject. It seems probable, however, that if the adjustment to the conditions of Equation 1 cannot take place by the dilution of the indicator solution, the adjustment may occur in the leading solution.

The Transference Numbers

In this investigation we have obtained accurate transference numbers for potassium chloride and potassium bromide solutions at 0.1 *N* and at 25°. The value for potassium chloride, 0.492 ± 0.001, agrees substantially with the value, 0.493, given, by Denison and Steele. It is, however, somewhat lower than the number given by the Hittorf and e.m.f. methods, which average about 0.496.

Our transference number for potassium in potassium bromide, 0.485, lies between the value, 0.480, obtained by Denison and Steele by the moving boundary method, and the number, 0.495, found by Jahn and Bogdan[10] at 18°, and the same value obtained at 25° by Pierce and Hart[11] in an extensive investigation by the electromotive-force method.

This investigation was originally undertaken to obtain data for a further test of the relation

$$T \Lambda \eta^n = K \tag{6}$$

in which T is the transference number, Λ the equivalent conductance, η the relative viscosity, and the exponent n an empirical constant. For the series of alkali chlorides and hydrochloric acid K has been found, by one of the authors,[12] to be a constant at any one concentration. Physically, K is the conductance of the ion in a solution whose relative viscosity is unity. Table VII gives the data and the computation for the potassium ion from the two salts at 0.1 *N* and 25°. The effect of the viscosity is small,

TABLE VII

CONDUCTANCE OF POTASSIUM ION AND THE INFLUENCE OF VISCOSITY

	Λ	T_K	η	$T_K\Lambda$	$T_K\Lambda\eta$
KCl	128.99	0.492	0.9982	63.5	63.4
KBr	131.6[13]	.485	.9946	63.8	63.5

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[10] Jahn and Bogdan, *Z. physik. Chem.*, **37**, 681 (1901).

[11] Pierce and Hart, THIS JOURNAL, **43**, 2483 (1921).

[12] MacInnes, *ibid.*, **43**, 1217 (1921).

[13] Value determined by Stearn, *ibid.*, **44**, 674 (1922), multiplied by 128.99/128.34, the ratio of Stearn's value of Λ for KCl to that recently determined by Kraus, *ibid.*, **44**, 2422 (1922).

but noticeable, at this low concentration. The exponent, n, has been assumed provisionally to be unity. It appears then, for this limited amount of data at least, that within the limit of error Equation 6 holds for the potassium ion as well as for the chloride ion. It is hoped to extend this investigation to cover a wide range of strong electrolytes.

Summary

A modification of the moving boundary method of Denison and Steele for determining transference numbers, involving a single boundary, has been developed.

The boundaries move with the theoretical velocities only when the two solutions in contact at a boundary are adjusted, within about 5%, to the relation $C/T = C'/T'$ in which C and C' are the concentrations and T and T' are the transference numbers. The correct value for T can therefore be obtained by a series of experiments approaching more and more closely to this condition. Unless this adjustment is obtained results are not independent of the composition of the indicator solution, or of the current through the apparatus, and may vary widely and erratically from the true values.

Transference numbers at 25°, for potassium chloride and potassium bromide in 0.1 N solutions have been obtained. These numbers show that the conductance of the potassium ion is the same in these two solutions if correction is made for viscosity.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE AMERICAN TELEPHONE AND TELEGRAPH COMPANY, AND THE WESTERN ELECTRIC COMPANY, INC.]

THE WETTING OF GLASSES BY MERCURY[1]

BY EARLE E. SCHUMACHER

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A number of observers have held that mercury does not wet glass because the latter is always covered by a film of adsorbed gas which prevents the mercury from coming into real contact with the glass. If this view is correct then, as Bancroft[2] has pointed out, mercury should readily wet glass if the adsorbed gas were completely removed. In order to test the accuracy of this hypothesis, a number of experiments were performed in which mercury was placed in glass containers whose walls had been

[1] The term wetting is used in this paper in the sense that wetting is complete when the angle of contact between liquid and solid is zero and the meniscus concave, and that the liquid does not wet the solid in cases in which the angle of contact is zero and the meniscus is convex. In these experiments wetting was considered to have taken place whenever the meniscus of mercury was less convex at the conclusion of the experiment than it was at the start.

[2] Bancroft, *J. Ind. Eng. Chem.*, **13**, 88 (1921).