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THE MOVING-BOUNDARY METHOD FOR DETERMINING TRANSFERENCE NUMBERS. VI. FURTHER DEVELOPMENTS IN EXPERIMENTAL TECHNIQUE

BY D. A. MACINNES, IRVING A. COWPERTHWAITE AND T. C. HUANG

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1. Introduction

Many of our experimental methods in the use of the moving boundary for measuring transference numbers have been described in the earlier papers of this series.[1] Recently, however, we have made a number of changes and improvements in the apparatus that seem worthy of record as they have resulted in greatly increased accuracy and convenience, in the possibility of use of the method through wider ranges of concentration and materials, and in the use of the method under unfavorable circumstances.

2. Changes in the Design of the Cell

All of our recent work has been carried out with the type of cell designed by MacInnes and Brighton[1c] in which the boundary is formed by means of a shearing motion. The improved apparatus is shown in Fig. 1. The disks B and C are now made of plate glass, instead of the hard rubber formerly used. The glass does not warp after a little use as the rubber did. It also has a smoother surface, and its transparency is frequently of service. The channels, etc., in the surfaces of the plates that are in contact were etched out with hydrofluoric acid.

Since the motion of a boundary through 10 cm. of the measuring tube involves a volume of only 1.7 cc., and in our most recently constructed cell only 0.32 cc., it is evident that all precautions must be taken to prevent slight volume changes in the apparatus that would, ever so slightly, affect the motion of the boundaries. In pressing the lubricated plates together a small amount of air was included under a slight excess of pressure. This was occasionally sufficient to form a bubble at the junction of the measuring tube and apparently produced irregularities in the readings. This difficulty was overcome by placing a vent, F in Fig. 1, which releases the pressure by leading off the excess of air from the space between the plates to a point above the level of the thermostat water.

It has been our practice to have one of the electrode vessels completely

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[1] (a) MacInnes and Smith, THIS JOURNAL, **45**, 2246 (1923). (b) Smith and MacInnes, *ibid.*, **46**, 1398 (1924). (c) MacInnes and Brighton, *ibid.*, **47**, 994 (1925). (d) Smith and MacInnes, *ibid.*, **47**, 1009 (1925). (e) MacInnes, Cowperthwaite and Blanchard, *ibid.*, **48**, 1909 (1926).

filled with solution. The moving-boundary results are corrected, according to the method of Lewis,[2] for volume changes at this closed end of the apparatus. The other electrode vessel contains a bubble of air to allow for possible expansions and contractions during the electrolysis. Originally this bubble was at the top of the vessel which projected into the air and was thus exposed to changes of temperature. This was probably the cause of some irregularities in our measurements. At present, however, one of the tubes holding the electrodes is left hollow and holds a small volume of air under the solution where it encounters a uniform temperature.

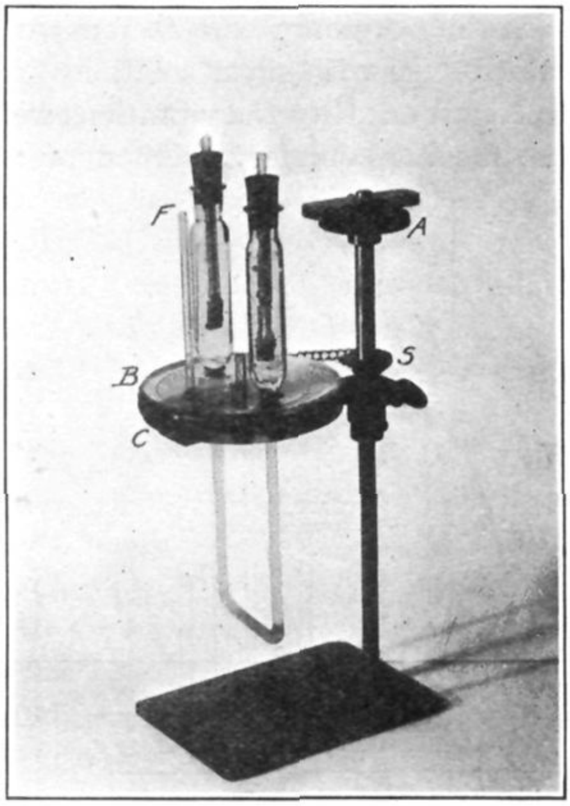

Fig. 1.

An added convenience, which makes possible the turning Disk B over Disk D with a minimum of mixing due to shaking, is furnished by the chain and sprocket arrangement also shown in Fig. 1. The brass Disk A which extends beyond the water of the thermostat is connected to a small sprocket S by means of a brass tube which encircles the upright of the stand. The sprocket engages a chain which is passed around Disk B. The chain is held in place by means of a rubber band which is slipped over a strip of brass holding a pin which, in turn, is inserted into a hole bored in the glass disk. Thus by turning the brass Disk A, the glass Disk B can be swung into place.

The convenience in measuring the time required in the passage of a boundary between graduations of the measuring tube has been greatly increased by substituting a Veeder magnetic counter for the watch previously used. The counter is operated once per second, by an accurate pendulum clock. Electrical contacts with the pendulum have been avoided by making the pendulum interpose a screen between a light and photo-electric cell once per second. By amplification this is made to operate the electric counter. The latter is started when the boundary passes the first graduation mark, and readings are made directly in seconds thereafter. A large amount of burdensome computation (subtractions, and changing of hours and minutes into seconds) is thus avoided.

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

3. The Effect of Vibration

In our earlier experiments in Cambridge we found that erratic results were obtained if there were a large difference between the densities of the leading and indicator solutions, such as exists between silver or cesium nitrates and lithium nitrate. The boundary usually started at nearly the correct rate but gradually slowed down toward the end of the determination. This effect is undoubtedly due to mixing caused by waves, over the surface of the boundary, generated by external vibrations. By exercising ordinary care to remove sources of vibration, results were obtained even with silver solutions. However, after moving the apparatus to New York City the vibrations were found to be intense enough to make the moving-boundary method quite useless, even for pairs of solutions without large differences in density.

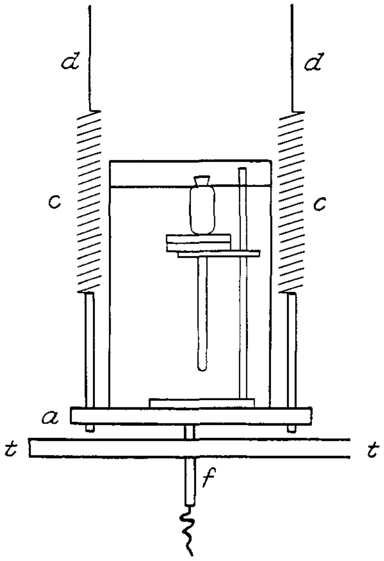

Fig. 2.

This serious difficulty was overcome, after a series of preliminary experiments, by the use of a modified Julius suspension for the thermostat. A diagram of the arrangement is shown in Fig. 2. The thermostat is placed on a cast-iron plate, *a*, from which four heavy bolts extend to about the level of the center of gravity of the suspended system. From these bolts extend four 4 cm. heavy coil springs, *c*, about 45 cm. long which, in turn, are supported by four light ropes, *d*, tied to hooks fixed in a heavy beam in the ceiling. Under these conditions no external vibrations of any strength reach the thermostat, as is shown by the steadiness of a beam of light reflected from the surface of a dish of mercury. Although these are ideal conditions for the progress of the measurements it is necessary to commence the determination, that is, to turn the electrode vessels into place over the measuring tube, without starting vibrations in the system. This we have accomplished as follows. The lower edge of the suspended system is hung very near to the table top *t*. From the center of the cast-iron plate, *a*, extends an iron rod, *f*, which passes through a hole in the table top and to which is attached a rope which is connected to a foot treadle (not shown in the figure). By pressing on this treadle the suspended system is temporarily placed in contact with the table. Choosing a moment when vibration is feeble, the boundary is made by turning Disk B (Fig. 1) on Disk C. The treadle is then carefully released. This can be done without causing the suspended system to swing.

It has been our frequent observation that a boundary which starts at an incorrect rate (due presumably to a very slight initial mixing of the solutions) will gradually approach the correct rate as the experiment proceeds, unless there is an additional source of disturbance. It appears, therefore, that the vibration during the time that the boundary is being formed and the suspended system is released cannot have an appreciable effect.

4. Experiments with Rising Boundaries

So far all our work has been carried out with indicator solutions which are lighter than the solution of which the transference number is to be measured. The indicator solution must therefore be on top of the leading solution and the boundary must descend during the determination. It seemed probable that a greater range of indicators would be available, including, possibly, some colored materials which might be visible at great dilutions, if a cell could be constructed which would utilize indicator solutions which are heavier than the measured solution. This would, of course, involve rising boundaries. Experiments were therefore carried out with an apparatus which was substantially the cell shown in Fig. 1 inverted, although a number of details had to be changed.

Observations were made on the boundaries $KMnO_4$ 0.07 $N \longrightarrow KCl$ 0.1 N, and $BaCl_2$ 0.07 $N \longrightarrow KCl$ 0.1 N. In both cases the boundaries were relatively sharp at the start, although somewhat convex upward. As they progressed, however, they became increasingly diffuse and instead of maintaining a steady motion as would be expected, the current being kept constant, both boundaries slowed down. It was evident that some additional condition governed the phenomenon when the boundaries were rising.

With the permanganate-chloride boundary there was another effect which was visible, due to the color of the indicator solution. A representation of the effect is shown in Fig. 3, in which the heavily shaded region, C, represents the portion of the tube containing the potassium permanganate indicator solution and the unshaded, B, the potassium chloride solution. Rising from the boundary was a faintly pink region of chimney shape, the color of which became more intense as the electrolysis proceeded, and finally not only this region but all of the potassium chloride region became colored. It immediately became of interest to find out whether a similar effect is to be observed with a descending boundary, and it was a relief to find that with permanganate as the leading solution and an acetate as indicator, a perfectly sharp boundary was formed with no pink color in the acetate solution. Furthermore, the boundary moved at the normal uniform rate.

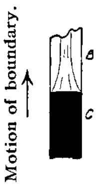

Fig. 3.

The explanation of the disturbing effect with rising boundaries appears to be as follows. Since the indicator solution contains ions which have lower mobility than the ions of corresponding charge in the leading solution, and is further diluted according to the relation[1a,3] $C/T = C'/T'$, the conductance of the indicator solution must be lower than that of the measured solution. The result is therefore that due to the higher potential gradient, more heat is generated in the indicator solution than in the solution it follows. The effect shown in Fig. 3 is due to the fact that a small amount of the potassium chloride solution immediately in contact with the boundary became warmed and rose, carrying a small amount of permanganate with it. A similar effect must have occurred in the barium chloride-potassium chloride boundary, but it was not visible. In the case of the descending boundary, on the other hand, the warmer indicator solution is on top, and the difference of temperature tends to keep the two solutions separate, if it has any effect at all.

It is evident, therefore, that in all moving-boundary measurements the solution of lower conductance must be on top. Some of the early work with the moving boundary must be in error on account of failure to observe this effect. An additional effect of heat generated in the apparatus will be given in Section 6.

5. The Visibility of the Boundary

In all our measurements we read, to the nearest second, the time when the boundary passes a given graduation mark. An increase of accuracy has been attained by graduating the tube as is shown in Fig. 4. The graduation marks extend on either side, one-fourth or less of the distance around the tube, leaving a clear space in front and back. In this way the boundary is always visible, and is never covered by the graduation mark. With faint boundaries, such as are obtained with dilute solutions, this arrangement is entirely necessary.

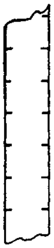

Fig. 4.

The possibility of distinguishing the junction of two transparent solutions depends upon the differences in their refractive indices. The arrangement now used for viewing the boundary is shown diagrammatically in Fig. 5. An electric lamp E is shaded by a metal screen except for a slit, a–b (seen edgewise in the figure) which is covered by a translucent screen. By means of a rack, sprockets and chain this slit can be moved vertically. Ignoring the effects of the glass walls of the thermostat M–M′ and N–N′ and of the measuring tubes, the path of a beam of light from the lower edge b of the illuminated slit is b, B, J. Thus, the edge b, viewed *through the boundary*, appears as if it were at b′. At a certain limiting value of the angle b B b′ we have the condition for total reflection. At this point the boundary appears as a sharp dark line at b′ with an illuminated area below it due to the fact that the illuminated slit can also be viewed directly through the lower solution. The apparent separation

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[3] C, C', T and T' are, respectively, the concentrations and transference numbers of the measured and indicator solutions.

of the direct and refracted images depends on the differences of the indices of refraction of the solutions meeting at the boundary.

A very surprising increase in the visibility of boundaries is obtained by the simple device of placing a lens at the point J as shown in the figure. The lens must have a focal length reaching only to the region of the boundary. The effect of this arrangement is to throw the directly viewed edge of the slit b out of focus. The edge of total reflection, which constitutes the boundary, can thus be much more readily distinguished. Other optical systems that we have tried have been less effective than the simple one just described.

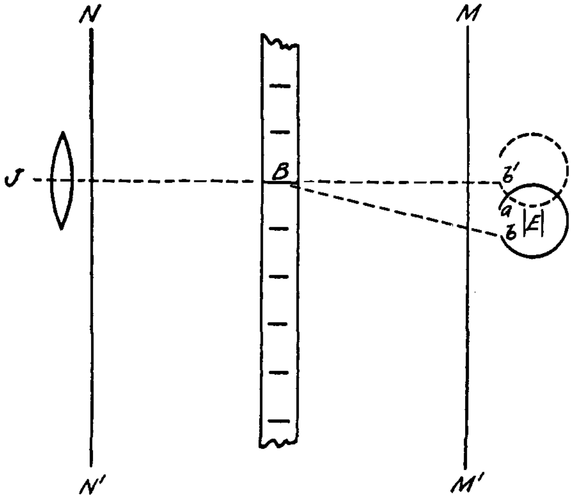

Fig. 5.

6. Conditions Governing "Adjustment"

As explained in previous papers in this series, the ions of the leading solution and the indicator move at the same rate when the solutions are adjusted to the condition

$$C/T = C'/T' \tag{1}$$

which must be, in general, obtained by a series of experiments. A curve of the apparent transference numbers as ordinates against the indicator concentrations C' as abscissas takes an upward slope in the dilute region, then a horizontal portion followed by a slope for more concentrated indicators. The correct transference number, and the values fulfilling the condition of Equation 1 are on the flat portion of the curve.[1d] Now the relative width of this flat portion is an important matter, since it determines the number of determinations that must be made in order to establish the shape of the curve. According to Kohlrausch[4] and others

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

the condition represented by Equation 1 should establish itself automatically, no limits of initial concentration being stated. However, we have found in general that this can only be relied on for deviations of 3 to 5% from the correct concentration. There are apparently additional influences, including diffusion, that limit the range of adjustment. We have found, for one thing, that adjustment is considerably modified by the amount of heat developed in the measuring tube. Some experiments already published[1b] have shown that with an apparatus involving the use of a wide tube (10 mm.) the flat spot in the curve nearly disappeared. In that case, due to the relatively low ratio of external surface to area of tube, the heat had little opportunity to be conducted away. We have recently observed much the same effect with a 6mm. tube with more concentrated solutions, and thus necessarily higher currents than were used in the earlier experiments. On the other hand, we have found adjustment over wide ranges of indicator concentrations under two conditions, (a) very dilute solutions, and (b) solutions of electrolytes having high equivalent conductances. In the first of these cases it is evident that little heat is developed because small currents pass through the apparatus. The measurements with highly conducting solutions (for example, 0.1 *N* hydrochloric acid or 0.1 *N* nitric acid) can be explained in the same way. Since the resistance is relatively low, less heat is generated. However, this latter case is complicated by the fact that the solution is followed by an unusually dilute indicator solution (0.03 to 0.05 *N*) in which, due to the high potential gradient, the heating effect must be unusually large. However, this hotter solution is on top rather than on the bottom in contrast to the experiments described in Section 4, so that the small difference of temperature apparently increases the stability of the system rather than otherwise.

For use with solutions above 0.1 *N* we have constructed a cell with a thin-walled measuring tube with an internal diameter of only 2 mm. At the same rate of motion of the boundary this smaller tube requires only one-ninth of the current used in the 6mm. tube, whereas the surface exposed is one-third. A distinct increase of the range of indicator concentrations yielding adjustment has been observed, as would be expected. However, other factors not yet clearly understood affect adjustment. We expect to make this matter the subject of future investigations.

7. The Transference Number of 0.05 *N* Silver Nitrate Solution

The data we have accumulated on transference numbers will be published in an article dealing with the question of the ionization of strong electrolytes. It may be of interest, however, to give an example of the precision attainable, under favorable circumstances, by the moving-boundary method. A plot of the data on 0.05 *N* silver nitrate solution is given in Fig. 6, in which the observed transference numbers are plotted as ordinates and the indicator concentrations as abscissas. The concentration of the indicator solution (lithium nitrate) varied from 0.0385 N to 0.0410 N. It will be seen that adjustment was attained through nearly all of this range within about 0.02%. A slight drop in the transference number can be observed in the region of the dilute indicator solutions. Experiments were not carried out at higher values of the indicator solution than those shown, but from analogy to other cases studied the curve would eventually ascend. The value for the transference number obtained, 0.4664 at 25°, is lower than published values by the Hittorf method, which are nearer 0.470.

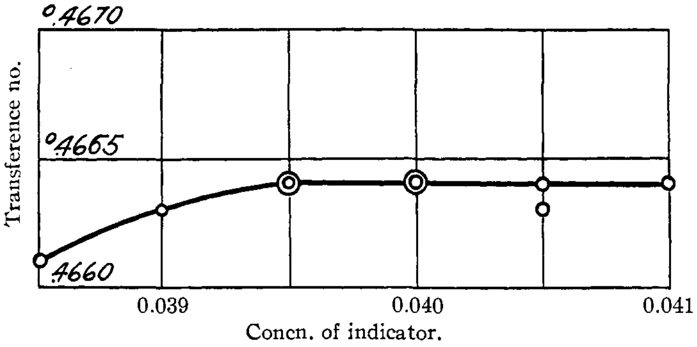

Fig. 6.

Summary

Improvements in the moving-boundary apparatus for determining transference numbers, leading to greater accuracy and convenience in the use of the method, are described.

The measurements have been found to be much influenced by vibrations, particularly where there is much difference in density of the solutions at the boundary. Our method for eliminating this difficulty is outlined.

Experiments are described with indicate that boundaries must be descending during the determinations. Ascending boundaries give rise to heat effects which cause mixing.

The conditions governing the visibility of boundaries are outlined.

Some of the factors governing "adjustment," that is, the dependence of the motion of the boundary on the indicator concentration, are outlined.

The precision of the method now attainable is shown by measurements of the transference number of 0.05 N silver nitrate solution.

New York, N. Y.