very satisfactory results with volumes up to 250 cc. With more dilute solutions the end-point is a violet in place of a deep blue obtained in a volume of about 150 cc. Dilution of over 300 cc. is not to be recommended. Over 0.4 cc. of indicator should not be used. In using 0.4 cc. of reagent the solution acquires a greenish hue with the addition of permanganate. This is very predominant with larger amounts of indicator and is evidently due to the action of permanganate on the indicator rather than to the iron in the solution. The green produced by adding an excess of diphenylamine to the blue solution of a completed titration bears out this conclusion.

Summary

Diphenylamine indicator, shown by Knop to be valuable in titration of iron by potassium dichromate, may also be applied in potassium permanganate titrations of iron. The presence of hydrochloric acid, stannic chloride and mercurous chloride do not interfere, thus enabling potassium permanganate titrations to be made where formerly they were not possible.

GOLDEN, COLORADO

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 159]

THE MOVING-BOUNDARY METHOD FOR DETERMINING TRANSFERENCE NUMBERS. II

BY EDGAR R. SMITH AND DUNCAN A. MACINNES

RECEIVED MARCH 18, 1924

This article describes a test of a simplification of the moving-boundary method for determining transference numbers. The method depends upon measuring, with a silver coulometer, the number of coulombs that pass through the circuit during the time it takes a single-boundary to sweep through a known volume.

The transference number T obtained by the single-boundary method is given by the equation

$$T = \frac{V}{\phi}\frac{F}{Q} \qquad (1)$$

in which V is the volume passed through by the boundary, ϕ is the volume of the solution which contains one equivalent, F is 96,500 coulombs, and Q is the number of coulombs passed during the measurement. The derivation of this equation is very simple. If F coulombs were passed, the single boundary would sweep through a volume of $T\phi$, and for a different number of coulombs, Q, the volume traversed will be $V = T\phi Q/F$ which is Equation 1.

It has been shown theoretically[1] that if a boundary is to move at its

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[1] Kohlrausch, *Ann. Physik*, **62**, 209 (1897). Masson, *Z. physik. Chem.*, **29**, 501 (1899). Denison, *ibid.*, **44**, 581 (1903). Miller, *ibid.*, **69**, 436 (1909).

theoretical velocity the concentrations of the measured and of the indicator solutions (C and C', respectively) must conform to the relationship,

$$C/C' = T/T' \tag{2}$$

in which T and T' are the transference numbers of the leading and following ions. Previous investigators have assumed an automatic adjustment of the indicator solution to take place which fulfills this requirement.[2] In the first paper of this series[3] the authors showed that the observed "transference number" varies markedly with the concentration of the indicator solution, except for a short range on each side of the theoretical concentration as calculated from Equation 2. The work to be described includes a further study of this variation, with a different design of apparatus, for the case of potassium chloride solutions, with lithium chloride solutions of various concentrations as indicators. In order to obtain sufficient current to give, in the coulometers, a deposit of silver which could be weighed with the required accuracy, the moving-boundary apparatus had to be made much larger than has been the usual practice. This change led to effects, described below, which convince us that the greatest usefulness of the method will not be obtained along the lines described in this research. The results, however, are interesting and will be given in some detail.

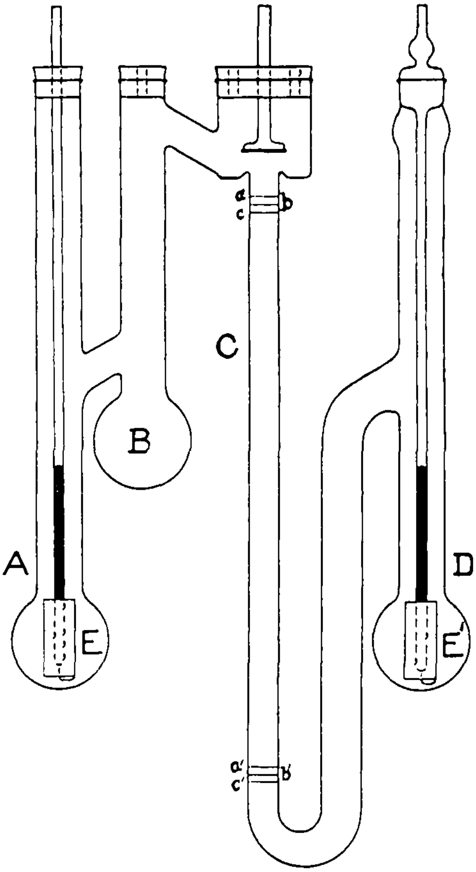

Fig. 1.

Apparatus and Manipulation

The apparatus used differs in many details from the one described in our previous article,[3] and is shown in Fig. 1.

The electrode tubes, A and D, are far enough removed from the measuring tube C

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[2] Denison and Steele, *Phil. Trans.*, **205A**, 449 (1906).

[3] MacInnes and Smith, This Journal, **45**, 2246 (1923).

so that the concentration changes taking place in the electrode tubes during the electrolysis cannot possibly alter the concentration of the solution in C. The electrodes, E and E′, are made of platinum gauze, coated electrolytically with silver, the cathode E′ being also coated with silver chloride. Trouble was experienced due to the evolution of gas at the electrodes when these were of the form shown in Fig. 2a, the gas being mainly evolved on the wire used for sealing into the tube. This was overcome by making the electrodes in the form of a cylinder surrounding the lower end of the tube, as shown in Fig. 2b, thus reducing the current density on the upper part of the electrode where it was first attacked by the current. It was also found necessary to fill the bulb of Tube A with a more concentrated solution of lithium chloride (about 0.5 N) to supply the anode with sufficient chloride for the electrode reaction. Tube B acted as a trap to prevent this concentrated solution from reaching the measuring tube C. This tube had an inside diameter of 1.1 cm. as compared to one of 0.3 cm. diameter in our first apparatus. It was calibrated with mercury for three volumes between the marks a and a′, b and b′, c and c′. These marks were etched completely around the tube to eliminate errors due to parallax. The methods of filling the apparatus, forming and illuminating the boundary, etc., were the same as described in our first paper.

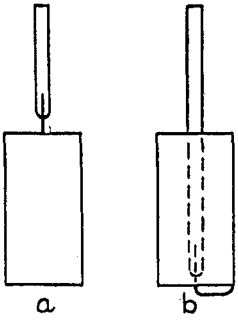

Fig. 2.

Three silver coulometers of the porous-cup type were connected in series with the apparatus in such a way that each could be independently thrown in or out of the circuit without interrupting the electrolysis. As the boundary passed each of the upper marks on the Tube C of the apparatus a coulometer was thrown into the circuit, and as it crossed each of the lower marks the corresponding coulometer was disconnected from the circuit, thus giving three independent measurements in each experiment. The general specifications for silver coulometers recommended by the Bureau of Standards[4] were followed. A current of about 35 milliamperes was used and was kept nearly constant by means of an adjustable resistance and a milliammeter in series. The weight of silver deposited was about 0.5 g. in each coulometer.

Purification of Materials

The potassium chloride used was a C. P. product and was further purified by recrystallization and fusion. The lithium chloride was prepared from C. P. lithium carbonate and hydrochloric acid, and purified by recrystallization. The silver nitrate for the coulometers was recrystallized from slightly acid solution, and fused.

Experimental Results

In every experiment the concentration of potassium chloride was 0.1 weight normal, that is, 7.456 g. of salt per 1000 g. of water. The density of this solution[5] at 25° is 1.0017, and therefore $\phi = 10058$ in Equation 1. Vacuum corrections have been made on the weights and the density. A series of measurements was made on this solution using, as indicators, lithium chloride solutions at a series of concentrations. All the results are given in Table I, three significant figures only being retained in the averages. A graph in which the concentrations of indicator solution are

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[4] Rosa and Vinal, *Bur. Standards Bull.*, **13**, 479 (1916–17).

[5] Stearn, THIS JOURNAL, **44**, 670 (1922).

plotted as abscissas and the corresponding "transference numbers" as ordinates is shown in Fig. 3.

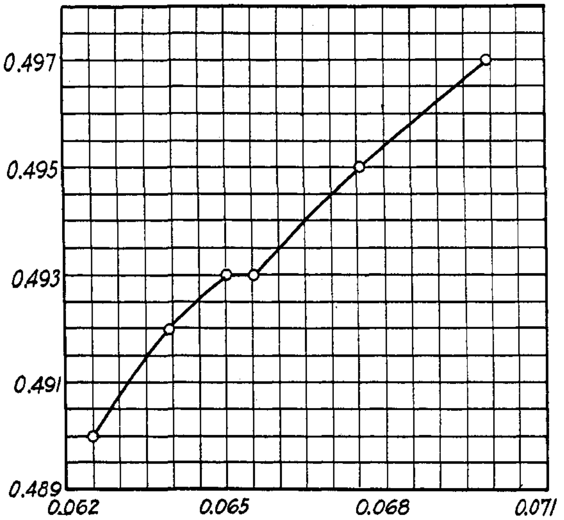

Fig. 3.

TABLE I

EFFECT OF CONCENTRATION OF INDICATOR SOLUTION ON CATION "TRANSFERENCE NUMBER" OF 0.1 N POTASSIUM CHLORIDE SOLUTION AT 25°

Concn. of LiCl	0.06250 T_k	0.06394 T_k	0.06500 T_k	0.06548 T_k	0.06750 T_k	0.06991 T_k
	0.4894	0.4915	0.4925	0.4927	0.4938	0.4966
	.4894	.4926	.4934	.4928	.4943	.4966
	.4900	.4921	.4928	.4927	.4950	.4977
	.4896	...	.4927	...	.4946	...
	.4899	...	.4925	...	.4946	...
	.4906	...	.4934	...	.4953	...
Av. T_k	.490	.492	.493	.493	.495	.497

Discussion

It will be seen that the observed "transference number" changes fairly rapidly with the concentration of the indicator solution, as was found in our previous communication.[3] In our earlier results, however, the curve which corresponds to Fig. 3 had a minimum at the point where Equation 2, $C/T = C'/T'$, holds, followed by a maximum on the side of more dilute indicator solutions. The minimum furnished a clear indication that adjustment to Equation 2 had been reached. In the present results, on the other hand, there is merely a break, or flat space, in the curve at and near the point where the concentrations fulfil the condition of that equation. (This point, for the solutions under consideration, corresponds to a

0.065 *N* lithium chloride solution.) With the smaller apparatus the indicator solutions had to be within about 5% of this concentration before adjustment was obtained. With this larger apparatus the indicator concentration must be apparently within 1% or less of that value before the nature of the curve gives any indication that adjustment has been reached. This would make the determination of an unknown transference number very tedious, since many more measurements would be necessary. The difference of behavior of the two pieces of apparatus was a puzzle to us until it was found that the heating effect of the current in the wider tubes is much greater than in the smaller ones. By trial it was found that the temperature of the solution in the tube was more than 1° above that of the thermostat. For some of the experiments the thermostat temperature was lowered to 23.7° so that the temperature in the tube would be about 25°. No appreciable difference was found between the results in which this was and was not done, as would be expected, since the transference numbers of potassium chloride have very low temperature coefficients.

Since the heat-radiating surface of the measuring tubes increases directly as the diameter, and the heat generated, at equal current density, as the square of the diameter, it is to be expected that this heating effect will be considerably greater in the larger tubes. Taking into account the fact that the glass walls of the tube in the smaller instrument were thinner, it is improbable that in our earlier experiments the temperature of the solution during a measurement was over 0.1° higher than the thermostat. It is this heating effect, and the unfavorable nature of the change of the "transference number" with the indicator concentration which make it appear that the larger apparatus is not the best for further work. We have not been able to suggest an explanation of the results obtained when the relation between the concentrations is not that given by Equation 2. These results when compared with our earlier ones make it appear, however, that especially when the indicator solutions are more dilute than required by that equation, the measurements are affected by the heating effect of the current.

It is of particular interest to note, however, that the transference number of potassium ion in potassium chloride, 0.493, obtained when the solutions were adjusted closely to Equation 2, agrees within the experimental error with the value, 0.492 ± 0.001, reported as a result of our previous investigation, and with the value 0.493 obtained by Denison and Steele, also by the moving-boundary method. The Hittorf and e.m.f. methods have given a somewhat higher value, 0.496, for this constant.

Summary

A test is reported of a simplification of the moving-boundary method of determining transference numbers, which consists of measuring, with

a coulometer, the number of coulombs passed while the boundary sweeps through a measured volume. Since an enlarged apparatus was necessary, heating effects were encountered which diminish the usefulness of the method. The values for the transference numbers, however, agree with those previously obtained by this method.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

A STUDY OF IONIZATION PRODUCED IN CERTAIN GASEOUS REACTIONS[1]

BY A. KEITH BREWER

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Is chemical action accompanied by ionization? This question, important as it is, has not been answered definitely in the case of gaseous reactions. A complete answer will help to explain the mechanism of chemical reaction. It is believed that electrons are transferred from one atom to another during chemical reaction, and it is likely that they are loosened at the moment of transfer. The displacement of these electrons should result in ionization. Although the evidence for ionization in reacting gases has been unsatisfactory, the present investigation shows that ionization may be detected in every reaction studied, if proper precautions are observed.

Improvements which have made possible a greater precision are (1) a chamber of special design in which electrical leakage is eliminated; (2) a sensitive electrical system which makes possible the measurements of currents as small as 5×10^{-15} ampere; (3) a construction which permits heating the chamber to red heat in order to diminish the adsorption of gases on the electrodes; (4) a 2200-volt battery.

J. J. Thomson[2] was one of the first to investigate this problem. Using a small gold-leaf electroscope in the reacting gases he concluded that no ionization is produced. Reboul[3] failed to detect ionization in gaseous reactions. Haber and Just,[4] using a galvanometer sensitive to 10^{-9} ampere per scale division found that a metal emits electrons when it reacts with a gas. In all the experiments the quantities of electricity emitted were much less than the Faraday equivalents. Bloch[5] found that no ionization was produced, except in the oxidation of phosphorus.

Pinkus[6] carried out extensive experiments in which the change in the rate of fall

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[1] A portion of a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy. A preliminary report was published by Brewer and Daniels in (a) *Trans. Am. Electrochem. Soc.*, **44**, 257 (1923).

[2] Thomson, *Proc. Cambridge Phil. Soc.*, **11**, 90 (1901).

[3] Reboul, *Compt. rend.*, **149**, 110 (1909); **151**, 311 (1910).

[4] Haber and Just, *Z. Elektrochem.*, **20**, 783 (1914).

[5] Bloch, *Compt. rend.*, **150**, 694 (1910); *Ann. phys. chim.*, **22**, 370, 441 (1911).

[6] Pinkus, *J. chim. phys.*, **16**, 201 (1918); **18**, 366, 412 (1920). *Helvetica Chim. Acta*, **1**, 141 (1918).