NOTE ON THE MOVING BOUNDARY METHOD FOR MEASURING TRANSFERENCE NUMBERS

A PYCNOMETER FOR DETERMINING THE VOLUME CHANGE OCCURRING AT AN ELECTRODE AND ITS APPLICATION TO A CATHODE OF SILVER CHLORIDE IN A SOLUTION OF POTASSIUM CHLORIDE

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ABSTRACT

Transference numbers, measured by the moving boundary method, must be corrected for the change in volume which occurs at the electrode on the closed side of the transference cell. It has been customary to compute this volume correction from the densities of the electrode materials and of the solution, together with a value for the transference number. A method for measuring the volume correction is described. Measurements of the correction to be applied in the case of a silver-silver chloride electrode in potassium chloride solution show that the computed value is correct up to concentrations of 0.2 molal, to within the precision required.

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I. NOTATION

Δn_w, moles of water transferred from anode to cathode portion, per faraday.
T_x, "true" transference number of the ion x.
N_x, "Hittorf" transference number of the ion x.
r, ratio of moles of salt to moles of water in the original solution.
D, density of the original solution.
V, volume.
$\overline{V}_s$, partial molal volume of salt in the solution.
$\overline{V}_w$, partial molal volume of water in the solution.
ΔV_e, volume change of the electrode material, per faraday.
M_x, weight of one equivalent of ion x.
M = weight of one equivalent of salt.
Δm, change in total weight of the cathode tube and solution, per faraday.

II. INTRODUCTION

The volume change which occurs when electricity is passed across the junction between an electrode and an electrolytic solution is, in general, the result of several factors. Faraday's law governs the change in state at the electrode proper, while in the solution, the ions move in accordance with the phenomenon of transference. Consider,

for example, a cathode of silver coated with silver chloride and immersed in a solution of potassium chloride. When 1 faraday of electricity is passed from the solution to the electrode, one equivalent of solid silver chloride having a volume of V_{AgCl} disappears, one equivalent of solid silver having a volume of V_{Ag} appears, the amount of salt in the cathode portion is increased by T_K equivalents and the amount of water is increased by Δn_w moles. The volume change at the cathode is the resultant of all these effects and is therefore given by the equation

$$\Delta V = (V_{Ag} - V_{AgCl}) + T_K \overline{V}_s + \Delta n_w \overline{V}_w \tag{1}$$

in which $\overline{V}_s$ and $\overline{V}_w$ are the partial molal volumes of salt and water, respectively. It was first shown by G. N. Lewis [1] that the moving boundary method of measuring transference numbers gives the Hittorf number when the proper correction is made for the volume changes at the electrodes. The volume correction to be made in order to obtain the Hittorf number, as Lewis showed, is not the sum of all the terms comprising ΔV in equation (1), but is the sum

$$V_{Ag} - V_{AgCl} + N_K \overline{V}_s \text{ or } \Delta V_e + N_K \overline{V}_s \tag{2}$$

This volume correction can easily be calculated from density data, but with no assurance that the value so calculated is correct. Thus, from density values in International Critical Tables, $\Delta V_e = 10.3 - 25.8 = -15.5$ cm^3, from the tabulation of partial molal volumes by V. K. Lamer and T. H. Gronwall,[2] $\overline{V}_s = 27.81$ cm^3 for 0.2 molal potassium chloride solution, and from the precise measurements of D. A. MacInnes and M. Dole,[3] $N_K = 0.4897$ at 25°. The volume correction is therefore computed to be -1.9 cm^3, the negative sign denoting a decrease in volume at this electrode. However, it is well known that the densities of solids vary somewhat according to their physical state. The density of silver has been reported at values between about 9.8 and 10.6 and of silver chloride between 5.46 and 5.56, depending on the method of preparation and physical treatment.[4] Furthermore, at a silver-chloride cathode in potassium chloride solution, the increase in concentration of the solution occurs locally at the surface and in the pores of the silver chloride electrode. Since the transference number of potassium chloride is practically the same at all concentrations,[5 6] there is no tendency for the concentrated portion produced at the electrode to distribute by electrolytic migration, for the same number of ions of each kind migrate in or out of any portion of the solution. Consequently, except for the influences of gravity, diffusion and convection, a more and more concentrated solution surrounds the silver-chloride cathode as the electrolysis progresses. In addition to the slight change in partial molal volume of the salt with increase in concentration, it is quite possible that some silver chloride dissolves in the concentrated solution formed in the pores of the cathode and produces an added change in volume.

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[1] G. N. Lewis, J. Am. Chem. Soc., vol. 32, p. 862, 1910.
[2] V. K. Lamer and T. H. Gronwall, J. Phys. Chem., vol. 31, p. 393, 1927.
[3] D. A. MacInnes and M. Dole, J. Am. Chem. Soc., vol. 53, p. 1357, 1931.
[4] J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, vol. 3, pp. 323 and 393. Longmans, Green & Co., London, 1923.
[5] E. R. Smith, B. S. Jour. Research, vol. 6, p. 917, 1931.
[6] See footnote 3.

In view of these uncertainties in the calculated volume corrections for moving boundary determinations, especially for junctions between solutions of the same salt at different concentrations where the correction may be of the same order of magnitude as the motion observed,[7] it appeared desirable to attempt the direct measurement of these volume corrections for comparison with the computed values.

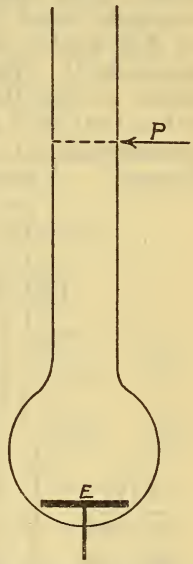

FIGURE 1.—*Removable electrode portion*

III. THEORY OF THE METHOD

Consider an electrode portion which can be separated from the remainder of the cell, by a method such as described in the next section, at a fixed plane P on the cell. (Fig. 1.) All of the concentration and chemical changes due to transference and the electrode reaction take place at the electrode E below the plane P. The resultant volume change around the electrode forces an equal volume of the unchanged middle portion of the solution in or out of the removable electrode portion; that is, past the plane P. At the same time, if E is a cathode, cations move into the portion and anions move out and, since the ions are hydrated, water will also be transferred past P. The change in weight of the electrode portion after the passage of one faraday will therefore be

$$\Delta m = M_c T_c - M_a T_a + 18.016 \Delta n_w - (\Delta V_e + \overline{V}_s T_c + \overline{V}_w \Delta n_w) D \qquad (3)$$

The true transference numbers can be expressed in terms of the Hittorf numbers by the relations.[8]

$$T_c = N_c + r\Delta n_w \text{ and } T_a = 1 - N_c - r\Delta n_w \qquad (4)$$

Making this substitution and noting that $M = M_c + M_a$, we obtain the equation

$$\Delta m = MN_c - M_a - (\Delta V_e + \overline{V}_s N_c) D + \Delta n_w [18.016 + Mr - (\overline{V}_w + \overline{V}_s r) D] \qquad (5)$$

For dilute solutions, in the case of the alkali chlorides below about 0.5 molal,

$$18.016 + Mr - D(\overline{V}_w + \overline{V}_s r) = 0.000 \qquad (6)$$

and hence

$$(\Delta V_e + N_c \overline{V}_s) = \frac{MN_c - M_a - \Delta m}{D} \qquad (7)$$

From equation (7) it is seen that the desired volume correction, $(\Delta V_e + N_c \overline{V}_s)$, can be obtained by measuring Δm for a solution for which the density and Hittorf transference number are known.[9]

[7] See footnote 5, p. 458.
[8] E. W. Washburn, Principles of Physical Chemistry, p. 233, McGraw-Hill Book Co., New York, 1914.
[9] It is interesting to note that equation (5) may be used for the determination of Δn_w in any case where equation (6) can be evaluated, if the volume changes are known.

IV. APPARATUS

The pyrex glass cell, shown in Figure 2, was made in two parts which fitted together by means of the ground glass joint *E*. The electrode vessel *B* was essentially a pycnometer, of the type described by J. Johnston and L. H. Adams, [10] containing a sealed-in tungsten electrode *D*. The under side of the circular cap *A* and the top of the flange around the opening of *B* were ground and polished optically flat so that they made a precise fit for the pycnometer measurements, corresponding to separating the electrode portion at the plane *P* of Figure 1. A piece of platinum gauze was fitted on the tungsten wire and fastened in place by electroplating with a heavy deposit of silver. It was then coated electrolytically with chloride and covered with a layer of precipitated silver chloride *C*, prepared as described by Washburn.[11] The tube and stopcock *F* permitted the insertion of a pipet for the removal of a middle portion of the solution for analysis after an electrolysis.

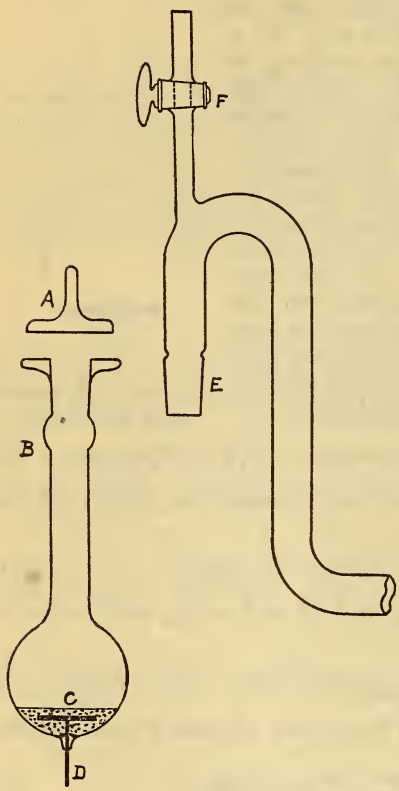

FIGURE 2.—*Electrode pycnometer and connecting portion*

Before electrolysis, the electrode pycnometer was filled with solution and immersed in a thermostat containing distilled water, an electrical heater, a motor-driven stirrer and a mercury regulator, the latter connected with a vibrator and an electron tube circuit for sensitive regulation. The temperature was held constant to within 0.01°. After allowing a half hour for the attainment of temperature equilibrium, the cap *A* was slid into place with a slight rotary motion, shearing off the projecting small portion of the solution. The tube was then removed from the thermostat, dried and weighed. The cap *A* was next removed and the whole cell fitted together by the ground joint *E*. The electrolyses were carried out over night at room temperature with a current of about 30 milliamperes. A small copper coulometer was used to measure the amount of electricity. After electrolysis, a middle portion was pipetted out for analysis, the cell separated into its two parts, and the pycnometer tube again brought to 25° in the thermostat, dried and weighed as before.

The potassium chloride was prepared by recrystallizing the c. p. salt, drying and heating to incipient fusion in a platinum dish. The solutions were prepared by weighing out the requisite quantities of salt and water.

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[10] J. Johnston and L. H. Adams, J. Am. Chem. Soc., vol. 34, p. 563, 1912.
[11] E. W. Washburn, J. Am. Chem. Soc., vol. 31, p. 331, 1909.

V. EXPERIMENTAL RESULTS

It has not yet been found possible to get accurate transference numbers by the moving boundary method at concentrations above about 0.2 molal[3]. This concentration was chosen for the measurements on the silver-silver chloride electrode since if disturbing effects, such as the dissolving of silver chloride in the solution, occur they would be more apparent in the more concentrated solutions.

TABLE 1.—*The volume change at a silver-chloride cathode in 0.2 molal KCl solution at 25°*

	Experiment No.		
	1	2	3
Weight of electrode tube and solution before electrolysis	140.0662	139.7643	139.6352
Weight of electrode tube and solution after electrolysis	140.1382	139.8374	139.7037
Weight of Cu deposited in coulometer	.8885	.7888	.7751
Number of faradays	.02795	.02482	.02439
Δm	2.58	2.95	2.81
Composition of the original solution. g KCl/g solution	.01469	.01469	.01470
Composition of the middle portion. g KCl/g solution	.01468	.01467	.01474
$\Delta V_e + N_c \overline{V}_s$	−1.52	−1.89	−1.75

The experimental results are shown in Table 1. The average of the three measured values of $(\Delta V_e + N_c\overline{V}_s)$ is -1.7_2 as compared with the calculated value of -1.9 cm³. Considering that both the measured and calculated value are uncertain in the second significant figure, the agreement is good. The equation for the correction of a moving boundary transference number is

$$N_c = N'_c \pm (\Delta V_e + N_c\overline{V}_2)C$$

in which N'_c is the uncorrected value of the transference number and C is the concentration of the solution expressed in equivalents per cubic centimeter. For example, the measured value of N'_c in one experiment[12] was 0.4904 for 0.2 molal potassium chloride, in which $C = 0.1983 \times 10^{-3}$, with the use of a silver chloride cathode at the closed side of the cell. The measured correction to be applied is therefore $-1.7 \times 0.1983 \times 10^{-3} = -0.00034$ and the calculated correction is $-1.9 \times 0.1983 \times 10^{-3} = -0.00037$. The corrected value of the transference number is therefore 0.4900_6 or 0.4900_3, respectively. The difference is outside the precision of the measurement of transference numbers and leads to the conclusion that the computed corrections may be applied with confidence in the case of potassium chloride solutions up to 0.2 molal.

The author desires to express appreciation to E. W. Washburn, for suggesting the design of apparatus and the method used in this research and for helpful advice and interest during the course of the measurements.

WASHINGTON, January 21, 1932.

[12] E. R. Smith and D. A. MacInnes, J. Am. Chem. Soc., vol. 47, p. 1013, 1925.