

usual chemical way. With two samples containing 0.57 and 0.16% of zirconium Hönigschmid and Zintl's results after correction for the zirconium content were 178.64 and 178.57.

Lead.—Permyakov³¹ has determined the atomic weight of lead from both Sadon galena and Khito-Ostrov uraninite by the conventional

Wt. of PbCl ₂	Wt. of Ag	Ratio PbCl ₂ : 2Ag	At. wt. of Pb	Wt. of AgCl	Ratio PbCl ₂ : 2AgCl	At. wt. of Pb
Sadon Galena						
3.9615	3.0733	1.28900	207.20	4.0835	0.97010	207.19
2.2722	1.7628	1.28897	207.19	3.3423	.97008	207.19
3.1425	2.4378	1.28907	207.21	3.2394	.97009	207.19
		1.28901	207.20		.97009	207.19
Khito-Ostrov Uraninite						
1.6599	1.2928	1.28396	206.11	1.7175	0.96646	206.14
2.3032	1.7939	1.28391	206.10	2.3834	.96635	206.12
2.2354	1.7411	1.28390	206.10	2.3132	.96637	206.12
		1.28392	206.10		.96639	206.13

(31) Permyakov, *Bull. acad. sci. U. R. R. S.*, 581 (1941).

chloride-silver-silver chloride method. Weights are corrected to the vacuum standard.

Radium.—Attention is again called to the fact that in the most recent and accurate determination of the atomic weight of radium by Hönigschmid and Sachtleben,³² by conversion of radium bromide to radium chloride, no correction was made for the fact that weights of salt are too low since the temperature of the salts is always higher than that of the balance. The ratio involved is $RaBr_2: RaBr_2 - RaCl_2$, in which the second term is far less affected than the first. In earlier work by Hönigschmid a positive correction of 0.01 unit was used. Although the mass spectrographic value is 226.05, identical with Hönigschmid and Sachtleben's uncorrected result, the application of the above rather uncertain correction produces a discrepancy of 0.01 unit.

(32) Hönigschmid and Sachtleben, *Z. anorg. allgem. Chem.*, **221**, 65 (1934).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Diffusion Coefficient of Potassium Chloride in Dilute Aqueous Solution

BY HERBERT S. HARNED AND RALPH L. NUTTALL

The problem of the determination of diffusion coefficients of electrolytes, particularly in dilute solutions, has perplexed physical chemists for more than sixty years. Indeed, in the past, there has been no experimental evidence to prove the validity of Nernst's¹ fundamental law which predicts the diffusion coefficient at infinite dilution from the electrical properties of the electrolytes.

Recently, Harned and French² have described a conductance method and some preliminary experiments by which they obtained values of the diffusion coefficient of potassium chloride at concentrations between 0.002 and 0.005 *N*. They estimate the accuracy of their final results to be $\pm 0.9\%$ and, in the concluding sentence of their paper, they stated that "our experience indicates that considerable improvement in accuracy can be effected."

We shall now describe an improved apparatus and technique which we believe is an experimental solution to this problem. The results to be described are in the region of concentration 0.001 to 0.01 *N*, suitable for testing the theory. Their accuracy is of the order of 0.1% which is sufficient to assure their use as standards for the calibration of other methods, in particular the diaphragm cell method.

Theory of the Method³

The most important feature of this method is the attainment of maximum simplicity of mathe-

(1) Nernst, *Z. physik. Chem.*, **2**, 613 (1888).

(2) Harned and French, *Ann. N. Y. Acad. Sci.*, **44**, 267 (1945).

(3) The idea of utilizing the difference of conductance at the top and bottom pairs of electrodes was suggested by Professor Lars Onsager some years ago at which time he developed the theory of the method.

matical treatment by the mechanical construction of the apparatus. In the first place, the solution is completely confined in the cell so that "restricted diffusion" occurs. Under this condition, the boundary conditions are such as to render the integral of the differential equation of diffusion both complete and in a form suitable for further simplification.

The simplest form of cell is an accurately machined rectangular parallelepiped with electrodes at top and bottom positions which may be suitably determined by theory. A schematic cross section of the cell with electrodes at distances ξ from the top and bottom is shown in Fig. 1. The electrolyte diffuses in the x direction and the height of the cell is α . Fick's first law of diffusion may be expressed by

$$\mathbf{J} = (c\mathbf{v}) = -D\nabla c \quad (1)$$

where \mathbf{J} is the flow, c the concentration of diffusing component, \mathbf{v} its velocity, D its diffusion coefficient and ∇c the gradient of the concentration. The equation of continuity is

$$\frac{\partial c}{\partial t} + \nabla \cdot (c\mathbf{v}) = 0 \quad (2)$$

and therefore

$$\frac{\partial c}{\partial t} = -\nabla \cdot (c\mathbf{v}) = \nabla \cdot D\nabla c \quad (3)$$

For unidirectional flow in the x direction, we obtain

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} D \frac{\partial c}{\partial x} \quad (4)$$

which is Fick's second law. We shall assume that

the difference in concentration of the solute at the top and bottom is sufficiently small to regard D as constant. Then

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (5)$$

and since $J = 0$ for $x = 0$ and $x = a$, we have the boundary condition that

$$\frac{\partial c}{\partial x} = 0 \quad \begin{cases} x = 0 \\ x = a \end{cases} \quad (6)$$

The solution of equation (5) with these boundary conditions⁴ may be arranged in a series form

$$c = \sum_{n=1}^{\infty} A_n e^{-n^2 \pi^2 D t / a^2} \cos \frac{n \pi x}{a} + c_0 \quad (7)$$

where A_n are the Fourier coefficients which satisfy the boundary conditions. The difference in concentration of electrolyte at the bottom (ξ) and top ($a - \xi$) electrodes is

$$c(\xi) - c(a - \xi) = 2A_1 e^{-\pi^2 D t / a^2} \cos \pi \xi / a + 2A_3 e^{-9\pi^2 D t / a^2} \cos 3\pi \xi / a + 2A_5 e^{-25\pi^2 D t / a^2} \cos 5\pi \xi / a \quad (8)$$

It is important to note that all the even terms have vanished and that the series converges very rapidly because of the nature of the exponential term. In addition, our cell is constructed so that the centers of electrodes are one-sixth the height from the top and bottom. Thus by making $\xi = a/6$ the second term on the right of equation (8) is eliminated and therefore

$$c(\xi) - c(a - \xi) = 2A_1' e^{-\pi^2 D t / a^2} + 2A_5' e^{-25\pi^2 D t / a^2} + \dots \quad (9)$$

where the constants now include the constant trigonometric terms. In this equation only the first term will have significance after a short time. By these devices the whole problem is reduced to a simple first order equation. Let

$$\frac{1}{\tau} = \frac{\pi^2 D}{a^2} \quad (10)$$

and take the logarithm. Then

$$\ln [c(\xi) - c(a - \xi)] = -\frac{t}{\tau} + \text{constant} \quad (11)$$

For many electrolytes, the computations can be further simplified. If K_B and K_T are the reciprocal resistances measured at the bottom and top of the cell, then $c(\xi) - c(a - \xi)$ may be assumed to be proportional to $K_B - K_T$ without introducing an appreciable error. For potassium chloride solu-

(4) For this solution see Byerly, "Fourier's Series and Spherical Harmonics," Chap. IV Section (61), Ginn and Co., 1893; also Houston, "An Introduction to Mathematical Physics," Longmans Green and Co., London, 1912, pp. 88-89. Equation (7) may be obtained without computing the Fourier coefficients if we employ the substitution $c = e^{\alpha x} + \beta t$ in equation (5) whence $\beta = D\alpha^2$. Since α can be any number, convenient trigonometric solutions can be obtained by substituting $i\lambda$ and $-i\lambda$ for α and performing the necessary operations. The solutions become:

$$c = A e^{\beta t} \cos \lambda x \quad \text{and} \quad c = A e^{\beta t} \sin \lambda x$$

The boundary conditions given by equation (6) are satisfied by the cos solution when $\lambda = n\pi/a$ ($n = 0, 1, 2, \dots, \infty$) and the solution given by equation (7) follows. See Mellor, "Higher Mathematics for Students of Chemistry and Physics," Longmans Green and Co., New York, N. Y., 1909, pp. 483-486.

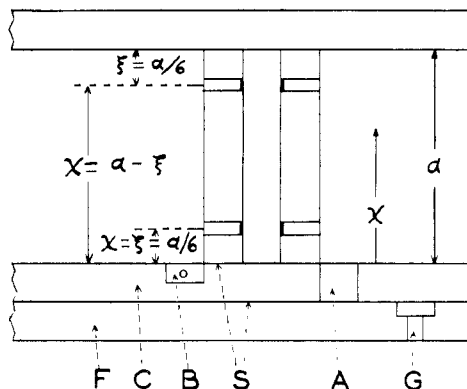


Fig. 1.—Schematic cross section of cell showing essential parts and quantities used in theoretical discussion. Block letters refer to parts discussed under Fig. 2: A, salt cup; B, excess water cup; C, sliding plate; F, bottom plate; G, filling hole for salt cup; S, sliding surfaces.

tion Harned and French² showed by computation of accurate conductance measurements of Shedlovsky, Brown and MacInnes⁵ that, in the range of concentrations used by them, this assumption involved an error not greater than 0.02%. Equation (11) becomes

$$\ln (K_B - K_T) = -\frac{t}{\tau} + \text{constant} \quad (12)$$

and the slope of the line of $\ln (K_B - K_T)$ versus t is $\frac{1}{\tau}$ where

$$D = \frac{a^2}{\pi^2} \frac{1}{\tau} \quad (13)$$

The great simplicity of the method is now apparent since a measurement of the depth of the cell, a , and the conductance difference at the electrodes at suitable time intervals are the only data required for the measurement of the diffusion coefficient. Further, since the measurements are made over a period of days during which the concentrations at the top and bottom approach each other, the assumption that D may be regarded constant is tested for each experiment. If the values of D are constant over a number of days, then we may be sure that the result is a differential diffusion coefficient.

Because of mechanical imperfections in the cell, it is necessary to correct for the ratio of the cell constants at the top and bottom pairs of electrodes. K_B and K_T are conductances corrected for cell constant ratios. Now, let K_B^* and K_T^* equal the actual measured reciprocals of the resistances and consider the equation

$$(K_B^* - K_T^*) - (K_B^\infty - K_T^\infty) = A' e^{-t/\tau} \quad (14)$$

where K_B^∞ and K_T^∞ are the conductances when t is ∞ or when the solution has become uniform in composition. If the cell constant ratio, $k = k_T/k_B$, is introduced in this equation

(5) Shedlovsky, Brown and MacInnes, *Trans. Electrochem. Soc.*, **66**, 165 (1934).

$$(K_B^* - kK_T^*) - (K_B^\infty - kK_T^\infty) = \frac{A'}{k_B} e^{-t/\tau} \quad (15)$$

or

$$(K_B^* - kK_T^*) = (K_B - K_T) = Ae^{-t/\tau} \quad (16)$$

since $(K_B^\infty - kK_T^\infty)$ equals zero. We note that the plots of the logarithms of equations (14) and (16) have identical slopes. If R represents resistance, then in general $K = 1/R$

$$(K_B^\infty - K_T^\infty) = \Delta K \cong -\Delta R_\infty/R_\infty^2 \quad (18)$$

where R_∞ is the mean resistance at top and bottom when t is infinite. The correction ΔK must be determined for each measurement.

Cell Design and Experimental Technique

The most difficult obstacle to the attainment of high accuracy in diffusion measurements is the elimination of turbulent flow. This requires a very constant and uniform temperature throughout the cell and the exclusion of any outside influence which may cause local temperature gradients. To achieve this condition, the cell is mounted on a brass block weighing over forty pounds which is enclosed in a lucite box. This apparatus is placed on a platform in a large thermostat. The platform

is suspended from the ceiling by a three-point (Julius) suspension with springs of suitable size. The lucite box and cell are completely immersed in the thermostat water which is controlled to within $\pm 0.01^\circ$. Since the measurements must extend over a period of a week, the thermostat temperature is continually measured by a recording thermometer. Since the box is an insulator, since the large block of high heat capacity serves to maintain constant temperature within the box, and since the cell itself is made largely of heat insulating material, the fluctuations in temperature of the cell solution are exceedingly small.

In order to reduce convection currents upon introducing the electrolytic solution, a shearing mechanism is employed. The cell employed by Harned and French² was divided into two parts and one of the sliding surfaces was in the center of the cell. Since this surface was greased, there was always the danger that some grease would protrude from the surface of the cell in its final position, thus reducing its width slightly. One of the features of the present cell eliminates this difficulty by allowing the solution to diffuse upward from the bottom before the sliding surface is placed in its final position.

The apparatus is shown in Fig. 2. J is the lucite box and D is the brass block. The cell parts were made of lucite and were carefully machined and lapped. The electrodes, E , were made by soldering a strip of sheet platinum on a copper block which was then machined and lapped to the proper size. The fixed parts were greased with a rubberized stopcock grease and the parts were held together by brass screws. The sliding surfaces, S , were greased with vaseline. The electrodes were platinized rather heavily.

In order to fill, the cell was inverted and the bottom plate F and sliding plate C removed. Conductivity water was then introduced in the cell and the cup B in the plate C was placed over the cell. This cup has the exact area of the diffusing column and the circle shown is open to the air. Thus the excess water in the cell can be sheared off without being forced between the sliding surfaces and without introducing air bubbles into the cell. Next the plate F was fastened in position by the four brass posts H . Cup A was filled with salt solution through the filling hole G which, with plate C in its present position is directly over cup A . The sliding plate C was then moved to the position shown in Fig. 2(a), thus leaving the cell completely filled with water and the cup A with salt solution. The cell was then mounted on the brass block D and the lead wires from the electrodes passed through the holes L in the tapered joint at the top of the box. The lid was then screwed down tightly and the whole apparatus was immersed in the thermostat.

The sliding plate C can be moved by the wire W by turning the capstan K (Fig. 2(b)). This was accomplished by means of a tapered lucite key

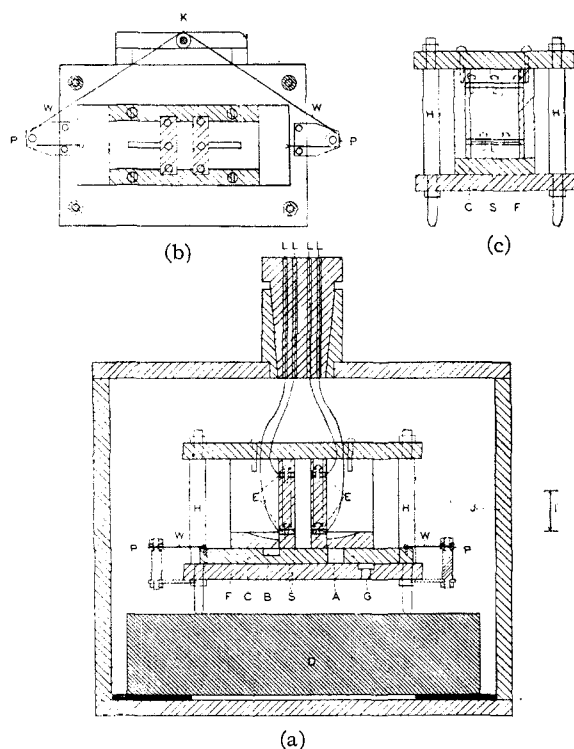


Fig. 2.—Diffusion cell: (a) side view; (b) top view; (c) end view. Cross hatched areas represent central cross sections with wide hatches for lucite and narrow for metal parts: J , lucite box; D , brass block; F , bottom plate; C , sliding plate; S , sliding surfaces; A , salt cup; G , filling hole for salt cup; P , pulleys; W , bronze wire; H , brass corner posts; E , electrodes; L , holes for lead wires; K , brass capstan.

(not shown in figure) extending through the top of the box. After waiting twenty-four hours or more for the attainment of temperature equilibrium, plate C was moved so that the salt solution in A, which has the same horizontal area as the cell, is directly under the cell. The salt was allowed to diffuse into the cell until a desired amount of salt had entered the cell. This was estimated by measurement of the conductance between the bottom pair of electrodes. The cell was then closed off by moving the plate C back to the position shown in Fig. 2(a). After the diffusion had proceeded for about thirty-six hours, the conductance measurements were suitable for computing diffusion coefficients. Five or six measurements were made each day at two-hour intervals over a period of five days.

The conductance measurements were made with a calibrated Leeds and Northrup Jones conductance bridge accurate to 0.01 ohm. The question of local heating at the electrodes during the balancing of the bridge was carefully investigated. It was found that this effect was eliminated when the input voltage to the bridge was low, about 2 volts, and the cell resistance 1000 ohms or greater. For higher salt concentration, additional resistance was placed in series with the cell.

After diffusion had proceeded for a suitable length of time, the solution was stirred by placing a heating lamp near the side of the box. Enough radiant heat was absorbed on the black electrodes to start convection currents in the cell and to produce thorough mixing in a few hours. The final conductance readings, K_B^∞ and K_T^∞ , at top and bottom were made and from these the cell constant ratio determined.

This method yields the diffusion coefficient at the concentration, c , of the salt when t equals infinity or when the solution is completely homogeneous. To determine c , the final solution was removed from the cell and its conductance was measured in a small conductance cell placed in an oil thermostat at 25°. The salt concentration was then determined by employing the data of Shedlovsky, Brown and MacInnes.⁴

The depth, a , of the cell was determined with a depth gage with graduations of 0.001 cm.

Experimental Results

As previously mentioned, conductance measurements were recorded after diffusion in the closed system had proceeded for twenty-four hours. Five or six readings were made each day at two-hour intervals after which the solution was thermally stirred, the infinity readings recorded, ΔK the cell constant correction was computed, and the concentration of the solution determined.

The observed resistances were corrected by use of the bridge calibrations, and lead resistances were taken into account. Corrections were also made for the slight differences in time between the

readings of the top and bottom pairs of electrodes. The reciprocals of these corrected resistances are the conductances K_B^* and K_T^* of the solution at the bottom and top electrode positions, respectively.

Table I contains data which clearly show the characteristic behavior of one of the determinations. The first column contains the time in seconds starting with the readings on the first day. The next two columns record the corrected

TABLE I
DATA FOR THE COMPUTATION OF THE DIFFUSION COEFFICIENT OF POTASSIUM CHLORIDE AT 25°
 $c = 0.00585$; $a = 5.697$ cm.; $\Delta K = 0.1584 \times 10^{-4}$ (ohms)⁻¹.

t	$K_T^* \times 10^4$	$K_B^* \times 10^4$	$D \times 10^6$ (cm. ² sec. ⁻¹)
	0.6449	49.9650	1.9225
7200	.9351	48.2579	1.9263
14400	1.2912	46.6810	1.9293
21600	1.6996	45.2264	1.9281
30000	2.2714	43.5711	1.9348
86400	6.3326	36.1572	1.9350
93600	6.8526	35.4434	1.9316
100800	7.3698	34.7741	1.9316
108000	7.8619	34.1518	1.9341
115200	8.3517	33.5649	1.9330
172800	11.7295	29.7309	1.9305
180000	12.0783	29.3531	1.9310
187200	12.4208	28.9813	1.9303
194400	12.7505	28.6295	1.9309
201600	13.0695	28.3054	1.9325
259200	15.1939	26.0967	1.9310
266400	15.4226	25.8867	1.9334
273600	15.6343	25.6700	1.9305
280800	15.8318	25.4557	1.9286
288000	16.0290	25.2621	1.9301
345600	17.3223	23.9498	
352800	17.4551	23.8146	
360000	17.5821	23.6883	
367200	17.7032	23.4489	
374400	17.8253		
∞	20.5335	20.6919	

conductances in reciprocal ohms during the measurement and the infinity readings. The diffusion coefficient was computed by equation (13) where $1/\tau$ is the slope of the graph obtained by plotting $\ln(K_B^* - K_T^* - \Delta K)$, which equals $\ln(K_B - K_T)$, against t . The values of D recorded in the fourth column were obtained from $1/\tau = \Delta[\ln(K_B - K_T)]/\Delta t$ for each twenty-four-hour period. The constancy of these values shows that the plot mentioned above is essentially a straight line over a five-day period and that the use of such twenty-four-hour slope determinations is justified for the calculation of the differential diffusion coefficient.

Table II contains the values of $D \times 10^6$ at the concentrations recorded in the first column. The notation (1-2), (2-3), etc., are the means of the five or six twenty-four-hour slope determinations

from the first to second, second to third, etc., days, respectively. The last column contains the mean values or the final accepted values. The constancy of these results over a period of five days is very gratifying for it verifies the theory and mechanism of the experiment in every way. The accuracy of the final mean value is of the order of 0.1%.

TABLE II

DAY BY DAY AND MEAN DIFFUSION COEFFICIENTS OF POTASSIUM CHLORIDE AT 25°

(1-2), (2-3), etc., values of $D \times 10^6$ (cm.² sec.⁻¹) obtained from readings taken on first to second, second to third, etc., days.

c	(1-2)	(2-3)	(3-4)	(4-5)	$D \times 10^6$ (mean)
0.00125	1.9615	1.9559	1.9676	1.9600	1.9612
.00194	1.9559	1.9541	1.9536	1.9543	1.9545
.00325	1.9485	1.9454	1.9441	1.9354	1.9433
.00585	1.9282	1.9331	1.9310	1.9307	1.9308
.00704	1.9242	1.9231	1.9251		1.9241
.00980	1.9169	1.9197	1.9175	1.9178	1.9180

Theoretical Considerations⁶

The theory of the variation of the diffusion coefficient with concentration of electrolyte has been developed by Onsager and Fuoss⁷ and their final expression for this variation for a 1-1 electrolyte is

$$D = 16.6288 \times 10^{10} T \left(\frac{\bar{M}}{c} \right) \left(1 + c \frac{\partial \ln \gamma_{\pm}}{\partial c} \right) \quad (18)$$

where

$$\left(\frac{\bar{M}}{c} \right) \times 10^{20} = 1.0748 \frac{\lambda_+^0 \lambda_-^0}{\lambda_+^0 + \lambda_-^0} - \frac{22.148}{\eta_0 (DT)^{1/2}} \left(\frac{\lambda_+^0 - \lambda_-^0}{\lambda_+^0 + \lambda_-^0} \right)^2 \frac{\sqrt{c}}{1 + A'\sqrt{c}} + \frac{9.304 \times 10^7}{\eta_0 (DT)^2} c \phi (A'\sqrt{c}) \quad (19)$$

In these equations λ_+^0 , λ_-^0 are the equivalent conductances at infinite dilution, D is the dielectric constant, η_0 the viscosity of the medium, and c the concentration in moles per liter. When c is zero this reduces to the Nernst limiting equation

$$D_0 = 17.873 \times 10^{-10} (\lambda_+^0 \lambda_-^0 / (\lambda_+^0 + \lambda_-^0)) T \quad (20)$$

The term containing the activity coefficient on the moles per liter scale is given by

$$\left(1 + c \frac{\partial \ln \gamma_{\pm}}{\partial c} \right) = 1 - \frac{1.1514 S_{(1)} \sqrt{c}}{(1 + A'\sqrt{c})^2} + 4.605 BC - c \psi (d) \quad (21)$$

where $A'\sqrt{c} = \kappa a = \kappa \bar{a} \times 10^{-8}$, where a and \bar{a} represent the mean distances of approach of the ions in centimeters and ångström units, respectively, and κ is the Debye and Hückel reciprocal distance. For calculations in dilute solutions, the density term, $C\psi(d)$ is negligible, and the sec-

ond term on the right of equation (19) which involves the square of a small quantity contributes a negligible amount.

Upon introducing the values: $\lambda_+^0 = 73.52$, $\lambda_-^0 = 76.34^8$

$\eta_0 = 8.949 \times 10^{-3}$, $D = 78.54$, $\bar{a} = 3.8$, $B = 0.0202^9$ and the values of $\phi(\kappa a)^{10}$ we obtain the results given in the third column of Table III where they are compared with the observed results. The agreement is remarkable. An even more striking result is obtained by calculating ($D_0 - D$) by equations (19) and (20) and adding this difference to the observed values of D . If the theory is valid, then the resulting values of D_0 should be constant. The fourth column of the table contains the result of such a computation. The mean value of the results at the measured concentration is 1.9966 which confirms the value at infinite dilution, 1.9958 to one in the third decimal place.

TABLE III

OBSERVED AND THEORETICALLY COMPUTED VALUES OF THE DIFFUSION COEFFICIENTS OF POTASSIUM CHLORIDE AT 25°

c	$D \times 10^6$		
	Observed	Theoretical	$D_0 \times 10^6$
0.00000		1.9958	(1.9958)
.00125	1.9612	1.9605	1.9965
.00194	1.9545	1.9531	1.9971
.00325	1.9433	1.9430	1.9961
.00585	1.9308	1.9293	1.9973
.00704	1.9241	1.9246	1.9953
.00980	1.9180	1.9155	1.9986

Summary

1. A conductance method for the determination of the differential diffusion coefficients of electrolytes has been described by Harned and French.² The error of their results was estimated to be $\approx 0.9\%$. In this communication, a new cell and an improved technique is described which reduces the error to approximately $\approx 0.1\%$.

2. The diffusion coefficient of potassium chloride in water at concentrations from 0.001 to 0.01 N at 25° has been determined.

3. These results are the first of sufficient accuracy to test the Onsager and Fuoss theory of electrolytic diffusion. Within this range of concentration excellent agreement between experiment and theory has been obtained.

4. It is important to note that these are the first results which confirm objectively the limiting equation of Nernst for the diffusion coefficient at infinite dilution.

5. These results can be used as standard for the calibration of diaphragm cells used in the determination of diffusion coefficients.

NEW HAVEN, CONN.

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(6) The symbols are those used by Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York, 1943, p. 178-180.

(7) Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

(8) Shedlovsky, *THIS JOURNAL*, **54**, 1423 (1932); Longworth and MacInnes, *ibid.*, **60**, 3073 (1938).

(9) Ref. (5), p. 391.

(10) Ref. (5), p. 130.