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The Differential Diffusion Coefficients of Lithium and Sodium Chlorides in Dilute Aqueous Solution at 25°

BY HERBERT S. HARNED AND CLARENCE L. HILDRETH, JR.

Recent accurate measurements^{1,2,3} of the diffusion coefficients of potassium chloride in water from 4 to 30° have shown excellent agreement with the theory⁴ at concentrations from 0 to 0.3 molar. As a further test of the theory for 1-1 electrolytes, we have employed the conductometric method for measuring the diffusion of lithium and sodium chlorides in dilute aqueous solutions. The results obtained by this method for potassium chloride solutions have received excellent verification by their agreement with values obtained by Gosting³ who employed the Gouy layer optical method. This agreement increases our confidence in the value of the conductometric method for the investigation of the theoretical aspects of electrolytic diffusion in dilute solution.

Theoretical Calculations

The theoretical values of the diffusion coefficients were computed by the following equations⁵ applicable to 1-1 electrolytes:

$$\mathfrak{D} = 16.629 \times 10^{10} T \frac{\bar{M}}{c} \left(1 + c \frac{\partial \ln y_{\pm}}{\partial c} \right) \quad (1)$$

$$\frac{\bar{M}}{c} \times 10^{20} = 1.0748 \left(\frac{\lambda_1^0 \lambda_2^0}{\Lambda^0} \right) - \frac{22.148}{\eta_0 (DT)^{1/2}} \left(\frac{\lambda_1^0 - \lambda_2^0}{\Lambda^0} \right)^2 \frac{\sqrt{c}}{1 + A' \sqrt{c}} + \frac{9.304 \times 10^7}{\eta_0 (DT)^2} c \phi(A' \sqrt{c}) \quad (2)$$

where $\Lambda_0 = \lambda_1^0 + \lambda_2^0$; $\kappa a = A \sqrt{\Gamma} = A' \sqrt{c}$; $A = a35.559 \times 10^8 / (DT)^{1/2}$. \mathfrak{D} is the diffusion coefficient in $\text{cm}^2 \text{sec}^{-1}$, λ_1^0 and λ_2^0 and the equivalent limiting ionic conductances of the cation and anion, η_0 is the viscosity of the solvent, D is the dielectric constant of water, T is the absolute temperature, $\phi(A' \sqrt{c})$ is an exponential integral function which can be obtained from a table,^{6,6} κ is the reciprocal distance of the Debye and Hückel theory, a is the mean distance of approach of the ions in cm. and Γ is the ionic concentration. The thermodynamic term in equation (1) was calculated by the equations

$$\left(1 + c \frac{\partial \ln y_{\pm}}{\partial c} \right) = 1 - \frac{1.1514 S_{(D)} \sqrt{c}}{(1 + A' \sqrt{c})^2} + \frac{2.303(2B)c - c\psi(d)}{2.303(2B)c - c\psi(d)} \quad (3)$$

$$\psi(d) = \frac{\partial d / \partial c + 0.001 (2M_1 - M_2)}{d + 0.001c(2M_1 - M_2)} \quad (4)$$

$$d = d_0 + \frac{(M_2 - d_0 \phi_{\pm}^0)}{1000} c - \frac{S_v d_0}{1000} c^{1/2} \quad (5)$$

where y_{\pm} is the mean activity coefficient of the electrolyte on the molar concentration scale, $S_{(t)}$ is the limiting theoretical expression of the Debye and Hückel theory for activity coefficients, and B is an empirical constant. The density term, $c\psi(d)$, in equation (3), was calculated by equations (4) and (5)^{6a} in which d is the density of the solution, d_0 the density of the solvent, M_1 and M_2 are the molecular weights of the solvent and solute, respectively, ϕ_{\pm}^0 is the apparent molal volume at infinite dilution and S_v is the experimental slope of the apparent molal volume versus \sqrt{c} .

The limiting value of the diffusion coefficient, \mathfrak{D}_0 , may be obtained from

$$\mathfrak{D}_0 = 17.872 \times 10^{-10} T \left(\frac{\lambda_1^0 \lambda_2^0}{\Lambda_0} \right) \quad (6)$$

and the slope, $S_{(D)}$, of the limiting law

$$\mathfrak{D} = \mathfrak{D}_0 - S_{(D)} \sqrt{c} \quad (7)$$

may be computed by

$$S_{(D)} = \frac{3.754 \times 10^{-8}}{D^{1/2} T^{1/2}} \left(\frac{\lambda_1^0 \lambda_2^0}{\Lambda_0} \right) + \frac{3.683 \times 10^{-8}}{D^{1/2} T^{-1/2}} \left(\frac{\lambda_1^0 - \lambda_2^0}{\Lambda_0} \right) \quad (8)$$

The numerical coefficients in these equations were evaluated by using the universal constants of Birge.⁷ The quantities required for the calculations and their sources are recorded in Table I.

TABLE I
CONSTANTS AND PARAMETERS EMPLOYED IN THEORETICAL CALCULATIONS

		LiCl	NaCl
T	298.16	λ_1^0	38.69 ^a 50.11 ^c
$S_{(t)}$	0.5091 ^a	λ_2^0	76.34 ^c 76.34 ^c
d_0	0.97707 ^b	$a \times 10^8$	4.25 ^a 4.0 ^a
η_0	8.949×10^{-30} , ^b	4.606 B	0.2740 0.1287
D	78.54 ^d	M_2	42.40 58.45
		S_v	1.488 ^a 2.153 ^a
		ϕ_v^0	17.00 ^a 16.40 ^a

^a Ref. (6). ^b "International Critical Tables," Vol. 3, p. 24 (1928), McGraw-Hill Book Co., Inc., New York, N. Y. ^c MacInnes, Shedlovsky and Longworth, THIS JOURNAL, 54, 2758 (1932). ^d Wyman, Phys. Rev., 35, 613 (1930).

(6a) Ref. (6), p. 250.

(7) Birge, Rev. Mod. Phys., 13, 233 (1941).

(1) Harned and Nuttall, THIS JOURNAL, 71, 1460 (1949).

(2) Harned and Blake, *ibid.*, 72, 2265 (1950).

(3) Gosting, *ibid.*, in press.

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

(5) Harned, Chem. Revs., 40, 461 (1947).

(6) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950, p. 130.

TABLE II

OBSERVED AND CALCULATED DIFFERENTIAL DIFFUSION COEFFICIENTS OF LITHIUM AND SODIUM CHLORIDES AT 25°

c mole/l.	$\mathfrak{D} \times 10^5$ (obs.)	$\mathfrak{D} \times 10^5$ (theoretical)	$\mathfrak{D}' \times 10^5$	c	$\mathfrak{D} \times 10^5$ (obs.)	$\mathfrak{D} \times 10^5$ (theoretical)	$\mathfrak{D}' \times 10^5$
0.0000	...	(1.368)	(1.368)	0.0000	...	(1.612)	(1.612)
.000634	1.348	1.349	1.367	.000746	1.586	1.589	1.609
.00179	1.331	1.339	1.360	.00161	1.576	1.580	1.608
.00229	1.335	1.335	1.368	.0033	1.576	1.568	1.620
.00235	1.335	1.335	1.368	.0045	1.562	1.563	1.611
.00263	1.334	1.334	1.368	.0052	1.559	1.560	1.611
.00302	1.331	1.331	1.368	.0065	1.557	1.556	1.613
.00339	1.327	1.329	1.366	.0077	1.555	1.552	1.615
.00496	1.326	1.323	1.371	.0090	1.544	1.549	1.607
.00568	1.319	1.321	1.366	.0093	1.544	1.548	1.608
.00732	1.320	1.317	1.371	.0100	1.547	1.546	1.613
.00792	1.315	1.316	1.367	.01473	1.542	1.537	1.617
.00834	1.313	1.315	1.368				
.00935	1.312	1.313	1.367				
.01100	1.313	1.310	1.371				
		Mean	1.368				Mean 1.612

Experimental Results

The experimental results were obtained by the same procedure as previously described¹ and are of the same order of accuracy as those obtained for potassium chloride. The observed results are compared with those computed by equations (1) to (6) and are found to agree very satisfactorily with the theoretical values from 0 to somewhat over 0.01 molar concentration. This calculation also confirms the limiting value of the diffusion coefficient as computed by equation (6) or the equation of Nernst. In columns (4) and (8) of Table II, the quantity $\mathfrak{D}' = (\mathfrak{D}_0 - \mathfrak{D})_{\text{calc.}} + \mathfrak{D}_{\text{obs.}}$ is recorded. If the theory is correct, this quantity should be constant for each salt and equal the value at zero concentration given in parentheses. As is to be noticed, the mean values of \mathfrak{D}' are equal to the computed values of \mathfrak{D}_0 which is further confirmation of the validity of the theory. The deviations of the values of \mathfrak{D}' from their mean is of course an indication of the experimental errors in these determinations.

Since these calculations involve data derived from many sources, and the requirements of accuracy are so high, one cannot be certain that the evaluation of the mobility term, \overline{M}/C , in equation (1) is exact. A closer examination of the situation will disclose the difficulties. The first term on the right of equation (2) is constant, the second term is negative and the third term is positive. The conductances of potassium and chloride ions are very nearly the same so that for this salt the second term becomes negligible and the whole variation of \overline{M}/C with concentration depends on the third term. For lithium chloride solutions, which we chose for this discussion, the ionic conductances are sufficiently different to cause the second term to nearly cancel the $\phi(A'\sqrt{c})$ term. Upon introduction of the numerical values in Table I, equation (2) for lithium chloride reduces to

$$\overline{M}/c \times 10^{20} = 27.5973 - 1.7326 \frac{\sqrt{c}}{(1 + A'\sqrt{c})} + \frac{18.9590c}{\phi(A'\sqrt{c})} \quad (9)$$

We record in Table III values of the second and third terms on the right of this equation at a few

TABLE III

DETAILS OF THE THEORETICAL COMPUTATION OF THE DIFFUSION COEFFICIENT OF LITHIUM CHLORIDE AS A FUNCTION OF CONCENTRATION

c	$\frac{1.73259}{\sqrt{c}} \frac{18.959c}{\phi(A'\sqrt{c})} \left((1 + c \frac{\partial \ln \gamma_{\pm}}{\partial c}) \right) \mathfrak{D} \times 10^5$	$\mathfrak{D} \times 10^5$ ($\overline{M}/c = \text{const.}$)
0.000	0.0000	0.0000
.001	.0524	.0367
.002	.0729	.0619
.005	.1115	.1179
.007	.1298	.1477
.01	.1520	.1845
		1.0000
		.9832
		.9773
		.9669
		.9625
		.9574
		1.3683
		1.3446
		1.3367
		1.3234
		1.3178
		1.3100

round concentrations and also the thermodynamic term in equation (1). We note that both the results in the second and third column are relatively small compared with 27.5973 and since they are of opposite sign will cause very little effect on the mobility term when they are combined. This fact is apparent from the last two columns of the table which contain the results computed by the complete theory (fifth column) and the values computed by keeping \overline{M}/c constant and equal to its limiting value (last column). Consequently, the whole variation of \mathfrak{D} with concentration may be computed by the thermodynamic term which decreases about 4% between 0 and 0.01 molar concentration.

In spite of these difficulties, the results for lithium, sodium and potassium chlorides contribute evidence for the correctness of the mobility term. For potassium chloride, this term varies 0.5% from 0 to 0.1 molar concentration. Since the results on this salt have an accuracy of the order of $\approx 0.1\%$, they seem to be accurate enough to indicate the essential validity of the theory. For the lithium and sodium chlorides, the fact that the thermodynamic term accounts for practically the entire variation of the diffusion coefficients with concentration is also contributing evidence for the theory since it predicts that the mobility term is nearly constant.

It is important to note that the theory may be expected to hold only in dilute solutions. In-

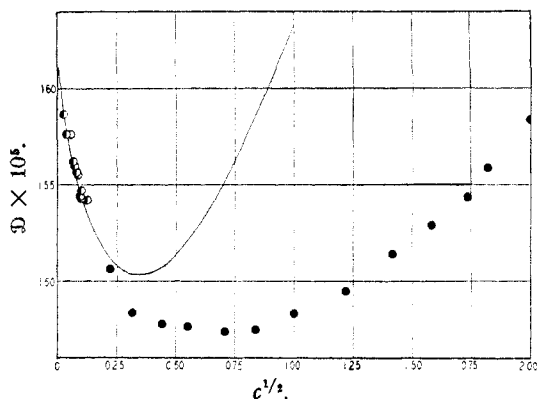


Fig. 1.—The diffusion coefficient of sodium chloride at 25° from conductance and diaphragm cell measurements. The curve represents the theoretical calculation according to equations (1) to (6): ○, conductance; ●, diaphragm cell; —, theory.

deed, the agreement with the theory of our results on potassium chloride up to 0.3 to 0.5 molar concentration was entirely unexpected. A more normal condition occurs with the diffusion coefficients of lithium and sodium chlorides. As an illustration, the diffusion coefficient of sodium

chloride up to 4 molar has been plotted against \sqrt{c} in Fig. 1. The half-linked circles are our results and the dots represent values at high concentrations recently obtained by Stokes⁸ who has developed an improved diaphragm cell method. His cell was calibrated by using the results of Harned and Nuttall¹ on potassium chloride. The experimental values approach the theoretical curve (represented by the solid line) as the concentration decreases. If the lowest point of Stokes at 0.05 molar is correct, then a curve through his results should coincide with the theoretical curve somewhat below 0.04 molar.

Summary

1. The differential diffusion coefficients of lithium and sodium chlorides from 0.001 to 0.01 molar concentrations have been determined by the conductance method.

2. Excellent agreement with the theoretical computation is obtained at these concentrations. Recent diaphragm cell measurements indicate that departure from the theoretical predictions will begin to occur in the neighborhood of 0.02 to 0.04 molar concentration.

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The Differential Diffusion Coefficient of Potassium Nitrate in Dilute Aqueous Solutions at 25°

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Values of the differential diffusion coefficients of lithium, sodium and potassium chlorides^{1,2,3} at concentrations between 0.0005 and 0.015 molar have been shown to conform to the theory of Onsager and Fuoss.⁴ On the other hand, values of the diffusion coefficient of calcium chloride at these low concentrations deviated considerably from the theoretical prediction.⁵ Apart from the fact that calcium chloride is an unsymmetrical electrolyte, one might correlate the above non-conformity with theory with the anomalous behavior of the cation transference number of calcium chloride.⁶ Although the equivalent conductance of this salt approaches the Onsager theory as the concentration approaches zero, the cation transference number lies considerably above the theoretical prediction and, at concentrations at which it has been determined, does not appear to approach the theoretical estimation.

The cation transference number of potassium nitrate behaves similarly to that of the calcium ion since it lies above the theoretical prediction. The equivalent conductance of this salt approaches the

limiting law from below, a fact which has been interpreted as indicating slight ionic association. Since this behavior is different from that of the chlorides of lithium, sodium and potassium, we thought that possibly the diffusion coefficient of potassium nitrate might disagree with theory in a manner similar to that of calcium chloride.

Experimental Results and Theoretical Calculations.—In the determination of the diffusion coefficient by the conductometric method, it is assumed that the difference in conductances at the bottom and top electrodes is proportional to the difference in salt concentrations at these two electrodes. That no appreciable error is caused by this assumption is proved by the data in Table I which were derived from the conductance measurements of Shedlovsky.⁷ In Table I, the specific conductances, L_1 and L_2 , at round concentrations, c_1 and c_2 , are recorded. In the last column, the

TABLE I

SPECIFIC CONDUCTANCES OF POTASSIUM NITRATE AT 25°

c_1	$L_1 \times 10^3$	c_2	$L_2 \times 10^3$	$(L_1 - L_2)/(c_1 - c_2)$ $c_1 + c_2 = 0.011$
0.01	1.3578	0.001	0.1418	0.1351
.009	1.2285	.002	.2810	.1354
.008	1.0955	.003	.4187	.1354
.007	0.9621	.004	.5558	.1354
.006	0.8276	.005	.6922	.1354

(1) Harned and Nuttall, *THIS JOURNAL*, **71**, 1460 (1949).

(2) Harned and Blake, Jr., *ibid.*, **72**, 2265 (1950).

(3) Harned and Hildreth, *ibid.*, **73**, 650 (1951).

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

(5) Harned and Levy, *THIS JOURNAL*, **71**, 2781 (1949).

(6) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950, pp. 163-164.

(7) Shedlovsky, *THIS JOURNAL*, **54**, 1411 (1932).