[CONTRIBUTION NO. 1247 FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Diffusion Coefficient of Calcium Chloride in Dilute and Moderately Dilute Solutions at 25°

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The diffusion coefficient of calcium chloride has been determined by the conductometric method at concentrations between 0.001 and 0.02 molar. The results are higher than those obtained by Harned and Levy but lower than those computed by the Onsager and Fuoss theory. At the higher concentrations the values obtained conform closely to those finally obtained by Lyons and Riley by Gouy diffusiometry.

Measurements of the diffusion coefficient of calcium chloride in dilute solution determined by the conductometric method by Harned and Levy[1] differ considerably from those predicted by the Onsager and Fuoss[2] theory. These experimental results were in agreement with those of Hollingshead and Gordon[3] derived from diaphragm cell measurements. This deviation from theory has stimulated further experimental studies. Measurements of the diffusion coefficient of this salt at higher concentrations by Hall, Wishaw and Stokes[4] by Gouy diffusiometry are in agreement with those of Harned and Levy. This agreement was also indicated by an early series of values determined by Lyons and Riley in this Laboratory by the optical interference method but later more accurate determinations by these investigators[5] definitely show that the results of Hall, Wishaw and Stokes and those of Harned and Levy are low. Further, the conductometric determination by Harned and Polestra[6] of the diffusion coefficients of magnesium, strontium and barium chlorides are in accord with the theory of Onsager and Fuoss. This confusing situation has made it imperative for us to redetermine the diffusion coefficient of calcium chloride by the conductometric method.

Theoretical Considerations

Upon substitution of $\lambda_1^0 = 76.34$,[7] $\lambda_2^0 = 59.50$,[7] $\eta_0 = 8.949 \times 10^{-3}$, $D = 78.54$, $a = 4.944$ Å,[8] for the limiting conductances of the chloride and calcium ions, the viscosity, dielectric constant and distance parameter, respectively, in the theoretical equations for the concentration dependence of the diffusion coefficient, the following numerical equations were obtained.[9]

$$\mathfrak{D} = 24.943 \times 10^{10} T(\mathfrak{M}/c)\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right) \quad (1)$$

$$(\mathfrak{M}/c) \times 10^{20} = 17.970 - \frac{4.393\sqrt{c}}{(1 + 2.814\sqrt{c})} + 136.77c\phi(\kappa a) \quad (2)$$

$$\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right) = 1 - \frac{2.0165\sqrt{c}}{(1 + 2.814\sqrt{c})^2} + 6.3385c \quad (3)$$

In equation 2, $\phi(\kappa a)$ is the exponential integral function of the theory.

Experimental Results

These conductometric determinations were carried with the same purified calcium chloride as was

TABLE I

OBSERVED AND CALCULATED DIFFUSION COEFFICIENTS OF CALCIUM CHLORIDE AT 25°

The data in parentheses were obtained by Drs. Philip A. Lyons and J. F. Riley in this Laboratory by Gouy diffusiometry.[5]

	$\mathfrak{D} \times 10^5$			$\mathfrak{D} \times 10^5$	
c	Obsd.	Calcd.	c	Obsd.	Calcd.
0.000	...	(1.336)	0.0120	1.183	1.196
.0017	1.251	1.254	.0139	1.175	1.190
.0021	1.236	1.249	.0162	1.167	1.184
.0032	1.227	1.237	.0281	(1.153)	1.170
.0043	1.214	1.228	.0547	(1.136)	1.173
.0054	1.209	1.220	.1020	(1.122)	1.194
.0070	1.200	1.212			

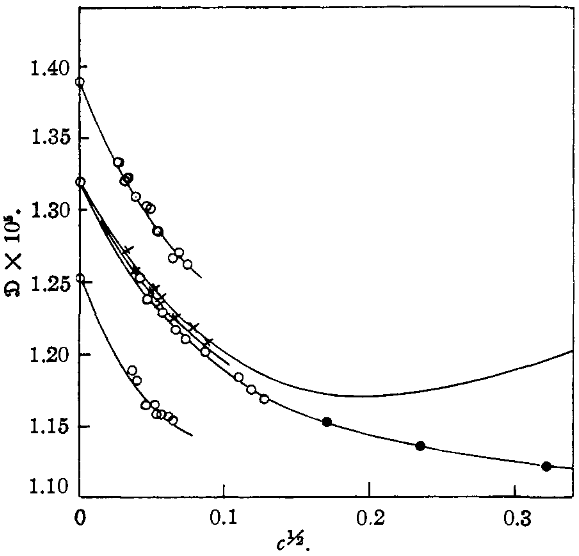

Fig. 1.—The diffusion coefficients of the alkaline earth chloride in dilute solutions at 25°. The top curve and circles represent the theoretical and observed results, respectively, for barium chloride. The second and third curves from the top represent the calculated values for calcium and strontium chlorides, respectively. The crosses represent the observed values for strontium chloride. The fourth curve from the top represents the observed results of this investigation, circles, and three results, dots, obtained by Gouy diffusiometry by Lyons and Riley. The bottom curve and circles represent the theoretical and observed results for magnesium chloride.

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(1) H. S. Harned and A. L. Levy, THIS JOURNAL, **71**, 2781 (1949).

(2) L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

(3) E. A. Hollingshead and A. R. Gordon, *J. Chem. Phys.*, **9**, 152 (1941).

(4) J. R. Hall, B. F. Wishaw and R. H. Stokes, THIS JOURNAL, **75**, 1556 (1953).

(5) P. A. Lyons and J. F. Riley, *ibid.*, **76**, 261 (1954).

(6) H. S. Harned and F. M. Polestra, *ibid.*, **75**, 4168 (1953); **76**, 2064 (1954).

(7) T. Shedlovsky and A. S. Brown, *ibid.*, **56**, 1066 (1934).

(8) D. A. MacInnes, "Principles of Electrochemistry," Reinhold Publ. Corp., New York, N. Y., 1939, p. 164.

(9) Compare reference 1.

used by Lyons and Riley[5] for their optical measurements. Careful examination was made to assure the same temperature in both series of determinations. The results at the molar concentrations designated are given in Table I. Three of the values obtained by Gouy diffusiometry are recorded in parentheses in this table. In the last column of the table, the diffusion coefficient calculated by equations 1, 2 and 3 are presented. Although the present results are higher than those obtained by Harned and Levy, they are still lower than the theoretical values.

Further Considerations Regarding the Diffusion Coefficients of the Alkaline Earth Chlorides.—In Fig. 1, the experimental diffusion coefficients of the alkaline earth chlorides are plotted against the square root of the molar concentration. The curves at the top and bottom represent the calculated values for barium and magnesium chlorides, respectively.[10] As evidenced by the circles representing the experimental results, the theory is confirmed for these salts. The second and third curves from the top are plots of the theoretical values for calcium and strontium chlorides, respectively. It appears that the strontium chloride diffusion coefficients, represented by crosses, lie near the theoretical curve and that the calcium chloride values, represented by circles, lie below the curve computed theoretically. The three results at the higher concentrations were obtained by Gouy diffusiometry and are seen to be in accord with the conductometric values.

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[10] In Table I, H. S. Harned and F. M. Polestra, This Journal, **76**, 2064 (1953), under $MgCl_2$, the following corrections should be made. At $c = 0.00205$, the observed result should be 1.163 and the calculated value 1.168 and at $c = 0.004$ the observed value should be 1.155 and the calculated 1.150.

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[Contribution from the Metcalf Chemical Laboratories of Brown University]

The Structure of the Aqueous Borate Ion

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The Raman spectrum of the borate ion in aqueous solution has been reinvestigated. The number, shapes and positions of the lines indicate that this ion has tetrahedral symmetry and is $B(OH)_4^-$. The infrared spectrum of a synthetic sample of the mineral teepleite, reported to contain this ion, confirms the Raman data. The Raman spectrum of the fluoborate ion has been reinvestigated.

The structure, in aqueous solution, of the conjugate base of boric acid has remained a mystery in spite of attempts to obtain a definitive answer to the problem. One can conceive of three possible structures for a *monomeric* borate ion of single negative charge; the differences between these structures lie primarily in the coördination number of the boron atom.

The first possibility, the metaborate ion BO_2^-, is unlikely on chemical grounds. There are no known compounds in which tripositive boron has a coördination number of two. For example, the anhydrous alkali metaborates contain cyclic triborate ions in which the boron atoms have a coördination number of three.[2] The second possible structure, which is $H_2BO_3^-$, would be the most reasonable possibility if boric acid were a Brönsted-Lowry acid (*i.e.*, a proton donor). On the other hand, if boric acid acts as a Lewis acid (an electron pair acceptor) as does boron trifluoride, then the most reasonable possibility for the structure of the conjugate base is $B(OH)_4^-$. Since some boron-oxygen compounds have a coördination number of three and others of four and since most solid borates contain polymeric anions, the chemical evidence available does not discriminate between the latter two structures.[3]

It is necessary, therefore, to rely on physical measurements which do not alter the equilibrium position in order to study this aqueous system; the Raman effect, it was felt, was most applicable to this problem. Previous work on the Raman spectra of various borate solutions has been done by three groups[5-7]; the results of these studies have been summarized by Hibben.[7] (The work of Ghosh and Das[5] is in complete disagreement with all of the other studies including the present one. As they gave no details on their preparation of "sodium metaborate," their work will not be considered further.) The fact that the borate ion has only one strong Raman line led to the conclusion that it has the metaborate structure; however, this conclusion was later questioned on the discovery of other weaker Raman lines.[6,7]

Recently, it has been found by Fornaseri[8] through X-ray studies on the minerals teepleite (analysis gives $NaBO_2 \cdot NaCl \cdot 2H_2O$) and bandylite (analysis gives $Cu(BO_2)_2 \cdot CuCl_2 \cdot 4H_2O$) that the borate ion in each of these solids has four oxygens situated about each trivalent boron. From the symmetry and the numbers of oxygens and hydrogens present, it was borne out by Fourier analysis that

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[1] Senior Research Assistant, 1953–1954.

[2] W. H. Zachariasen, *J. Chem. Phys.*, **5**, 919 (1937).

[3] This is, in large measure, a result of the rapid rate of replacement reactions involving ligands in the coördination sphere of the borate ion.[4]

[4] J. O. Edwards, This Journal, **75**, 6151 (1953); *J. Chem. Educ.*, **31**, 270 (1954).

[5] J. C. Ghosh and S. K. Das, *J. Phys. Chem.*, **36**, 586 (1932).

[6] (a) J. R. Nielsen and N. E. Ward, *J. Chem. Phys.*, **5**, 201 (1937); (b) J. R. Nielsen, N. E. Ward and H. Dodson, *Phys. Rev.*, **53**, 331 (1938).

[7] (a) J. H. Hibben, *Am. J. Sci.*, **35A**, 113 (1938); (b) J. H. Hibben, "The Raman Effect and its Chemical Applications," Reinhold Publ. Corp., New York, N. Y., 1939, pp. 430–439.

[8] M. Fornaseri, *Periodica mineral. Rome*, **18**, 103 (1949); **19**, 157 (1950); *La Ricerca Scientifica*, **21**, No. 7 (1951).