spectively. The coördination number of the metal is six in ferric chloride[15] and aluminum chloride.[16] The structure of gallium chloride has not been determined. The relatively great range in melting points of the trichlorides is then explained on the basis that metal–chlorine bonds must be broken to some extent in melting, at least in the case of aluminum chloride and ferric chloride.

An interesting property of the compounds $M'M'''Cl_4$ is the high solubility of some of them in anhydrous ether. Some observations on these solutions, particularly those of NH_4GaCl_4, will be reported in a separate communication.

Acknowledgment.—This research was supported by funds from the Office of Naval Research under Contract No. N6-ori-20. Some of the experiments with NH_4AlCl_4 were performed by Mr. William Korst, and with NH_4FeCl_4, by Mr. Robert A. Plane.

Summary

Observations have been made on the chemistry of some compounds of the type $M'M'''Cl_4$ with $M' = NH_4$, Li, K, Cs and $M''' =$ Ga, Fe, Al. Five more or less general methods of preparation of this class of compounds and the applicability of these methods to the compounds studied are described. Measurements were made of the melting points, densities and solubilities in ether of these compounds.

Some differences in stability were noted. $LiGaCl_4$ and $LiAlCl_4$ undergo the reaction $M'M'''Cl_4(l) \rightarrow M'Cl(l) + M'''Cl_3(g)$ more readily on heating than do the corresponding potassium compounds. NH_4GaCl_4 is completely volatilized on heating, and the dissociation $NH_4GaCl_4(l) \rightarrow HCl(g) + NH_3GaCl_3(g)$ takes place. The system in liquid vapor equilibrium is divariant, the vapor phase being enriched in hydrogen chloride.

NH_3GaCl_3 in the vapor is monomeric. Above about 450° at atmospheric pressure the dissociation becomes appreciable. The heat of vaporization of the liquid is 17.7 kcal. per mole. This value, together with other data, leads to ΔH for the reaction $NH_3GaCl_3(g) \rightarrow NH_3(g) + GaCl_3(g)$. The value is +33 kcal., which may be compared with +41 reported by Klemm and coworkers for the corresponding reaction with NH_3AlCl_3.

On heating, ammonia replaces potassium chloride from $KGaCl_4$, forming gallium trichloride amines. NH_4GaCl_4 can be oxidized by chlorine at about 450°, yielding gallium chloride. Formation of NH_4GaCl_4 from aqueous solution followed by oxidation of the substance with chlorine is a convenient method for preparing gallium chloride from aqueous systems.

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[15] Klemm and Krose, *Z. anorg. allgem. Chem.*, **253**, 218 (1947).

[16] Ketelaar, *Rec. trav. chim.*, **66**, 501 (1947).

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF CAMBRIDGE, ENGLAND]

The Diffusion Coefficients of Eight Uni-univalent Electrolytes in Aqueous Solution at 25°

BY R. H. STOKES[1]

In a previous paper[2] it was shown that the improved porous-diaphragm cell technique there described is capable of yielding accurate values for the diffusion coefficients of electrolyte solutions in the concentration-range above 0.05 normal, and some limitations of the method were examined. The present paper describes diffusion measurements on the chlorides and bromides of potassium, sodium, lithium and hydrogen at concentrations up to four normal.

Experimental

The cell and its manipulation and calibration have been described.[2] The water used in making up solutions was double-distilled and had a conductivity $\sim 10^{-6}$ mho/cm. Potassium and sodium chlorides, hydrochloric acid and hydrobromic acid were of analytical quality, used without further purification. Potassium bromide was recrystallized once from the analytical quality salt, and sodium bromide three times from the ordinary supply. The lithium salts were prepared by dissolving the hydroxide in the appropriate pure acid until neutral, followed by three crystallizations; the hot solutions were re-neutralized before crystallizing, as some loss of acid occurred during evaporation. The 4 *N* stock solutions were filtered through sintered-glass. Times were measured on a reliable pocket-watch checked twice daily against the radio time-signals from Greenwich Observatory. The temperature was maintained within 0.01° as indicated on a Beckmann thermometer, and was known to be within 0.03° of the true 25°. Since the method is a relative one, no detectable error should arise from an uncertainty of 0.03° in the absolute temperature.

The final concentrations of the lower (more concentrated) and upper (less concentrated) cell compartments (c_3 and c_4, respectively) were determined by potentiometric titration of weighed samples against silver nitrate, using a capillary reference electrode[3] with a valve voltmeter as null indicator. Duplicate analyses were made and agreed to 0.1%. The resulting weight-concentrations were converted to volume-concentrations for 25° by means of the standard density data.

Wear of the Diaphragm.—The cell constant showed a slow increase, amounting to 0.5–1% per thousand hours

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[2] R. H. Stokes, THIS JOURNAL, **72**, 763 (1950).

[3] H. Muller, *Z. physik. Chem.*, **135**, 102 (1928).

of use. This was attributed to wearing away of the diaphragm as the result of the rapid stirring adopted. This was allowed for by frequent recalibrations (about every ten runs), and by the use of a large-scale graph of cell-constant *versus* cell life to interpolate the cell-constant for each run. Since few of the runs exceeded seventy hours duration, no correction for the change of cell constant during any individual run was necessary.

Method of Calculation.—From the measured final volume concentrations c_3 and c_4, the initial concentration c_1 of the lower compartment was calculated by the conservation-equation given by Gordon.[4] (The volumes of the compartments and the diaphragm were measured by weighing with the various parts filled with water, and were reproducible to 0.02 ml.) In all but a few of the runs, the upper compartment at the beginning of the run was filled with pure water, (*i. e.*, $c_2 = 0$). The reason for this choice will now be discussed.

Effect of Analytical Errors on the Accuracy of the Diffusion Coefficient.—The fundamental equation for the diaphragm-cell integral diffusion coefficient $\bar{D}$

$$\bar{D} = \frac{1}{\beta t} \log \frac{c_1 - c_2}{c_3 - c_4} \tag{1}$$

where β is the cell constant and t the time, becomes, taking for the sake of simplicity the hypothetical case of exactly equal compartment volumes, and expressing c_1 in terms of the quantities c_2, c_3 and c_4 (c_1 not being conveniently measurable in the present design of cell)

$$\bar{D} = \frac{1}{\beta t} \log \frac{c_3 + c_4 - 2c_2}{c_3 - c_4} \tag{2}$$

Denoting relative errors in the concentration measurements by $\delta c/c$, differentiation of (2) yields for the relative error in $\bar{D}$

$$\frac{\delta\bar{D}}{\bar{D}} = 2\,\frac{\frac{\delta c_2}{c_2}(c_4 - c_3)c_2 + \frac{\delta c_3}{c_3}(c_2 - c_4)c_3 + \frac{\delta c_4}{c_4}(c_3 - c_2)c_4}{(c_3 - c_4)(c_3 + c_4 - 2c_2)\ln\,[(c_3 + c_4 - 2c_2)/(c_3 - c_4)]} \tag{3}$$

Since the relative error in the concentrations is, for the method of analysis adopted here, practically independent of the actual concentration, we may write

$$|\delta c_2/c_2| \approx |\delta c_3/c_3| \approx |\delta c_4/c_4| \approx p$$

Now the experimental conditions demand that $c_3 > c_4 > c_2$; hence we see from (3) that if the errors in c_2 and c_3 have one sign, and that in c_4 the opposite sign, the errors accumulate, and the resulting error in $\bar{D}$ is

$$\left|\frac{\delta\bar{D}}{\bar{D}}\right| = 4p\,\frac{c_4(c_2 - c_3)}{(c_3 - c_4)(c_3 + c_4 - 2c_2)\ln\,[(c_3 + c_4 - 2c_2)/(c_3 - c_4)]} \tag{4}$$

Graphs of the function (4) for various values of the initial concentration ratio $(c_3 + c_4 - c_2)/c_2$ plotted against the extent to which diffusion is allowed to proceed, show a minimum which indicates an optimum duration for an experiment with any given initial concentration ratio. The error at this optimum duration is given in Table I.

TABLE I

ERROR ($\delta\bar{D}/\bar{D}$) RESULTING FROM VARIOUS INITIAL CONCENTRATION RATIOS $(c_3 + c_4 - c_2)/c_2$

Concn. ratio	1.1	1.2	1.3	2.0	3.0	4.0	10.0
Resultant error	80p	37p	25p	10p	6p	5p	3p

Thus even for an experiment in which the compartments are initially filled with 2*N* and 1*N* solution, there may be a tenfold magnification of analytical errors; while if the initial concentrations are made closer, with the object of obtaining "differential" diffusion coefficients directly, the resulting uncertainty in $\bar{D}$ becomes much more serious. However, for the cases where $c_2 = 0$, the function (4) shows no minimum, and the relative error in $\bar{D}$ rises only slowly as the run proceeds, and scarcely exceeds 2p for runs of normal duration. Therefore, the present measurements were made as integral diffusion coefficient determinations for diffusion from a solution into (initially) pure water. The differential diffusion coefficients required for comparison with theory are readily derived from these results by the method now described and exemplified for the case of hydrochloric acid.

Table II gives the initial concentration c_1 in the lower compartment for the runs with hydrochloric acid, and the integral diffusion coefficient $\bar{D}$ calculated by equation (1). Now Gordon[4] has shown that $\bar{D}$ is related to the true or differential diffusion coefficient D by the equation

$$\bar{D} = \frac{1}{c_m' - c_m''} \int_{c_m''}^{c_m'} D\,\mathrm{d}c \tag{5}$$

where $c_m' = (c_1 + c_3)/2$, and $c_m'' = (c_2 + c_4)/2$ ($= c_4/2$ here.) This equation, though not quite theoretically exact, is not in error by more than 0.02%, as Gordon has shown, and the writer has verified for wider concentration ranges than Gordon considered. The differential diffusion coefficient D commonly varies with concentration in the manner shown in Fig. 1, where the full ordinates are drawn at the concentrations for the beginning and end of a run, and the dashed ordinates correspond to c_m' and c_m'' as defined above. Figure 1 refers to the case where $c_2 = 0$. Now, if we define a new integral diffusion coefficient $\bar{D}^0$ as that which would be found in a run of vanishingly short duration, with initial concentrations c and zero on the two sides of the diaphragm, we have from (5)

$$\bar{D}^0 = \frac{1}{c} \int_0^c D\,\mathrm{d}c \tag{6}$$

We shall denote by $\bar{D}^0(c_m')$ and $\bar{D}^0(c_m'')$ the values

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[4] A. R. Gordon, *Ann. N. Y. Acad. Sci.*, **46**, 285 (1945). The equation is: $(v_1 + v_3/2)c_3 + (v_2 + v_3/2)c_4 = (v_1 + v_3/2)c_1$ where v_1, v_2 and v_3 are the volumes of the lower and upper compartments and the diaphragm, respectively.

TABLE II

INTEGRAL DIFFUSION COEFFICIENTS FOR HYDROCHLORIC ACID AT 25°

$\overline{D}$ = coefficient calculated from equation (1), in cm.^{2} sec.$^{-1}$ × 10^{-5}. $\overline{D}^0(c_m')$ = coefficient for diffusion from concentration c_m' into water for vanishingly short time. (See text.) Concentration in moles per liter.

c_1	$\overline{D}$	c_m'	$\overline{D}^0\ (c_m')$
0.01013	3.198	0.00864	3.212
.01047	3.198	.00907	3.211
.01072	3.197	.00921	3.210
.02056	3.182	.01893	3.190
.02079	3.152	.01765	3.170
.04798	3.110	.04080	3.130
.04866	3.121	.04434	3.133
.07926	3.095	.06871	3.112
.09722	3.066	.08386	3.086
.1959	3.061	.1787	3.073
.2020	3.058	.1840	3.070
.3030	3.055	.2628	3.066
.3042	3.060	.2639	3.071
.4997	3.083	.4580	3.087
.5131	3.094	.4756	3.097
.8476	3.163	.7814	3.158
.9334	3.166	.8507	3.160
1.023	3.201	.9479	3.192
1.841	3.402	1.643	3.362
1.906	3.439	1.634	3.377
2.489	3.603	2.221	3.538
2.756	3.678	2.471	3.609
3.422	3.874	3.090	3.788
3.448	3.886	3.062	3.786
4.559	4.209	4.094	4.100
4.585	4.230	4.039	4.061

of $\overline{D}^0$ in such hypothetical experiments with initial concentrations c_m' and c_m'' respectively. The geometry of Fig. 1 shows that

$$\overline{D}^0{}_{(c_m')} = \overline{D} - (c_m''/c_m')\,[\overline{D} - \overline{D}^0{}_{(c_m'')}] \qquad (7)$$

Hence from the observed integral diffusion coefficient $\overline{D}$ we can calculate $\overline{D}^0$ for the concentration c_m', provided we know it for the lower concentration c_m''. Now it turns out that the curve of $\overline{D}^0(c_m')$ against c_m' lies within 1% of that of $\overline{D}$ against c_1, which makes possible the solution of equation (7) by a short series of approximations. First the curve of $\overline{D}$ against $\sqrt{c_1}$ is plotted and extrapolated smoothly to the Nernst limiting value at infinite dilution. From this curve, a first approximation to $\overline{D}^0(c_m'')$ is read for each run, and substituted into the square bracket of equation (7). The resulting values of $\overline{D}^0{}_{(c_m')}$ are then plotted against $\sqrt{c_m'}$, and this new curve gives a second approximation to $\overline{D}^0{}_{(c_m'')}$ which is again substituted into equation (7). The resulting second approximation to $\overline{D}^0{}_{(c_m')}$ does not change on continuing the process. The "crude" $\overline{D}$ values and the final $\overline{D}^0{}_{(c_m')}$ values are plotted in Figure 2 for hydrochloric acid over a part of the range studied, and c_m' and $\overline{D}^0(c_m')$ are listed in the last two columns of Table II. For the sake of brevity, only c_m' and $\overline{D}^0(c_m')$ are given for the remaining seven electrolytes, in Table III. The data are thus all adjusted to a common basis of comparison, and show less scatter than the original D *versus* $\sqrt{c_1}$ results, which contain a certain amount of artificial scatter because of the varying duration of runs. The inherent experimental scatter may be judged from the following table, which gives the average and maximum deviations of the $\overline{D}^0(c_m')$ values from the smooth curves drawn through them.

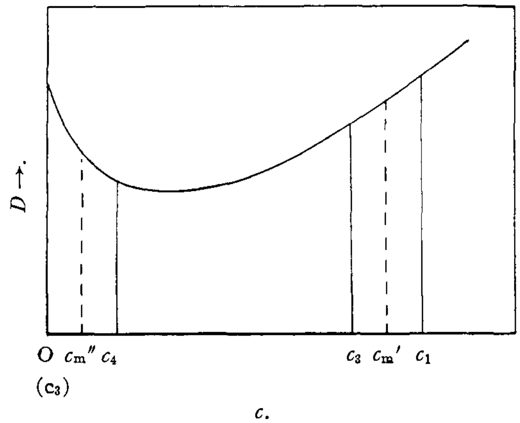

Fig. 1.—Initial and final conditions in a diaphragm-cell diffusion.

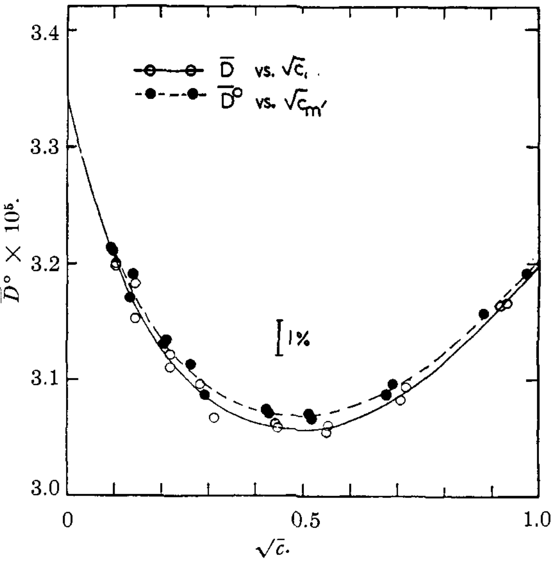

Fig. 2.—Hydrochloric acid at 25°: correction of observed diffusion coefficients to refer to runs of zero duration (see text for details).

Electrolyte	HCl	HBr	LiCl	LiBr	NaCl	NaBr	KCl	KBr
Av. devn., %	0.16	0.13	0.34	0.33	0.17	0.21	0.13	0.14
Max. devn., %	0.4	0.3	0.4	0.7	0.4	0.6	0.3	0.3

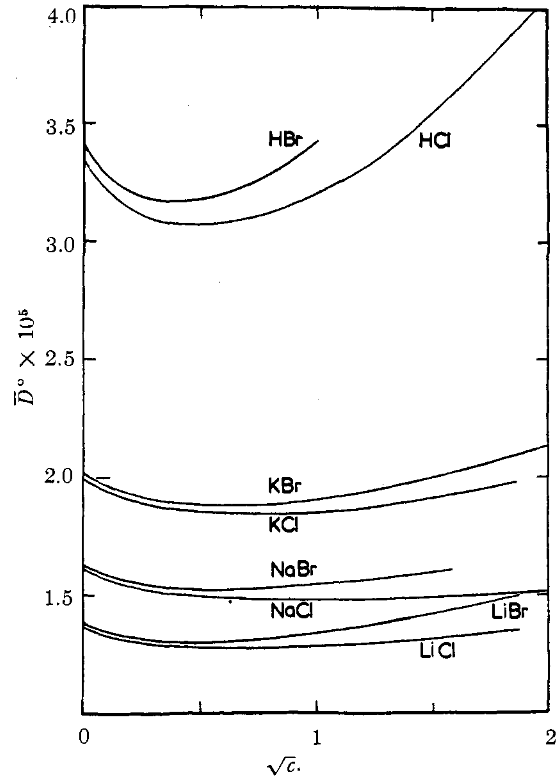

Fig. 3.—Integral diffusion coefficients (corrected to zero duration of run) at 25°; c = moles/liter.

From these $\overline{D}^0$ data, which are plotted in Fig. 3, the differential diffusion coefficient D is readily obtained, since equation (6) is immediately differentiable to yield

$$\left.\begin{aligned} D &= \overline{D}^0 + c\,\frac{\mathrm{d}\overline{D}^0}{\mathrm{d}c} \\ &\text{or} \\ D &= \overline{D}^0 + \frac{\sqrt{c}}{2}\,\frac{\mathrm{d}\overline{D}^0}{\mathrm{d}\sqrt{c}} \end{aligned}\right\} \qquad (8)$$

(This differentiation is of course not possible in equation (5), since there the integral runs from a variable lower limit.) The slopes $\mathrm{d}\overline{D}^0/\mathrm{d}c$ or $\mathrm{d}\overline{D}^0/\mathrm{d}\sqrt{c}$ of (8) are obtained by graphical or tabular means, and lead to the differential diffusion coefficients of Table IV. These are plotted in Fig. 4.

TABLE III

INTEGRAL DIFFUSION COEFFICIENTS FOR RUNS OF VANISHINGLY SHORT DURATION

c_m' in moles per liter; $\overline{D}^0(c_m')$ in cm.^{2} sec.$^{-1}$ × 10^{-5}

HBr		LiCl		LiBr	
c_m'	$\overline{D}^0$ (c_m')	c_m'	$\overline{D}^0$ (c_m')	c_m'	$\overline{D}^0$ (c_m')
0.00854	3.278	0.0489	1.304	0.0468	1.326
.00865	3.275	.0495	1.304	.0512	1.329
.0178	3.247	1.008	1.287	.0942	1.306
.0179	3.254	.0994	1.289	.1023	1.306
.0464	3.203	.1746	1.280	.1956	1.293
.0450	3.199	.1797	1.278	.1914	1.293
.0816	3.189	.4900	1.272	.4693	1.302
.0820	3.182	.4978	1.277	.4803	1.297
.0906	3.176	1.008	1.286	.930	1.329
.1559	3.170	0.988	1.279	.968	1.336
.1789	3.161	1.965	1.305	.985	1.326
.3544	3.197	1.968	1.304	1.705	1.373
.4055	3.217	2.753	1.330	1.850	1.388
.6352	3.282	2.851	1.335	1.870	1.405
.9173	3.396	3.430	1.346	2.599	1.447
.9380	3.395			2.642	1.439
				3.372	1.493
				3.612	1.499

NaBr		KCl		KBr	
c_m'	$\overline{D}^0$ (c_m')	c_m'	$\overline{D}^0$ (c_m')	c_m'	$\overline{D}^0$ (c_m')
0.0394	1.563	0.0414	1.905	0.0443	1.931
.0396	1.560	.0423	1.912	.0452	1.925
.0483	1.554	.0875	1.877[a]	.0913	1.907
.0769	1.543	.1641	1.862	.0887	1.903
.0771	1.548	.1672	1.865	.1637	1.888
.0886	1.541	.4337	1.844	.1675	1.890
.0858	1.550	.4336	1.840	.1697	1.891
.2021	1.531	.8374	1.842	.4608	1.881
.2007	1.523	.9221	1.842	.4771	1.878
.2600	1.517	1.290	1.866	.9075	1.901
.2662	1.523	1.312	1.868	.9884	1.896
.4770	1.519	1.699	1.878	1.748	1.963
.5073	1.527	1.825	1.884	1.884	1.971
.7849	1.535	2.504	1.930	2.799	2.042
1.021	1.548	2.573	1.934	2.951	2.047
1.743	1.569	3.455	1.978	3.802	2.112
1.758	1.589	3.480	1.973	3.832	2.120
2.379	1.609				
2.539	1.603				

		NaCl			
c_m'	$\overline{D}^0$ (c_m')	c_m'	$\overline{D}^0$ (c_m')	c_m'	$\overline{D}^0$ (c_m')
0.0428	1.534	0.4455	1.486	1.914	1.491
.0851	1.520	.4267	1.487	1.959	1.491
.0868	1.520	.9384	1.479	2.757	1.499
.0889	1.522	.9597	1.484	2.673	1.497
.1652	1.506	.9844	1.479	3.749	1.512
.1746	1.497	1.856	1.493	3.774	1.509
.1752	1.502	1.892	1.485	4.534	1.532
		1.824	1.483	4.576	1.522

[a] Calibration runs.

As a check on the data and the computational procedure leading to these D values, a few measurements were made in which the upper compartment at the beginning of the run contained instead of water a solution of known concentration; *i. e.*, $c_2 \neq 0$. Equation (4) now demands higher analytical accuracy than for the case $c_2 = 0$, and also requires that the concentrations c_1 and c_2 at the beginning of the run should not be too close together, as this leads to excessive magnification of the analytical errors. The analyses were made by the orthodox gravimetric procedure of precipitating and weighing the silver halide. The measurements were made with sodium chloride, one of the slowest-diffusing solutes studied, and with hydrochloric acid, one of the fastest-diffusing. The observed $\overline{D}$ values may now be compared with those calculated from equation (5), by graphical or tabular integration of the differential diffusion coefficients D of Table IV. This comparison,

TABLE IV

DIFFERENTIAL DIFFUSION COEFFICIENTS AT 25°

c = moles solute per liter; D in cm.^{2} sec.$^{-1}$ × 10^{-5}

c	HCl	HBr	LiCl	LiBr	NaCl	NaBr	KCl	KBr
0.00[a]	3.339	3.403	1.368	1.379	1.612	1.627	1.995	2.018
.05	3.073	3.156	1.280	1.300	1.506	1.533	1.863	1.892
.1	3.050	3.146	1.269	1.279	1.484	1.517	1.848	1.874
.2	3.064	3.190	1.267	1.285	1.478	1.507	1.835	1.870
.3	3.093	3.249	1.269	1.296	1.477	1.515	1.826	1.872
.5	3.184	3.388	1.278	1.328	1.474	1.542	1.835	1.885
.7	3.286	3.552	1.288	1.360	1.475	1.569	1.846	1.917
1.0	3.436	3.869	1.302	1.404	1.483	1.596	1.876	1.975
1.5	3.743		1.331	1.473	1.495	1.629	1.951	2.062
2.0	4.046		1.363	1.542	1.514	1.668	2.011	2.132
2.5	4.337		1.397	1.597	1.529	1.702	2.064	2.199
3.0	4.658		1.430	1.650	1.544		2.110	2.280
3.5	4.920		1.464	1.693	1.559		2.152	2.354
4.0	5.17				1.584			2.434

[a] Nernst limiting values.

made in Table V, reveals excellent agreement. Since the diffusion process in these latter measurements does not involve the dilute region where D is changing very rapidly, the agreement provides considerable justification for Gordon's assumption of a steady state in the diaphragm, from which equation (5) is derived.[4] It also confirms that the surface-effect found in the earlier paper[2] is not making any significant contribution to the transport of solute for the concentrations of this investigation.

TABLE V

c in moles/liter, $\bar{D}$ in cm.^{2} sec.$^{-1}$ × 10^{-5}

Solute	c_1	c_2	c_3	c_4	$\bar{D}_{\text{obs.}}$	$\bar{D}_{\text{calcd.}}$
HCl	2.829	0.5578	2.246	1.1335	3.859	3.861
HCl	0.5447	.1120	0.4667	0.1900	3.100	3.109
NaCl	4.761	.9971	4.157	1.6075	1.536	1.542
NaCl	1.9928	.4976	1.6234	0.8637	1.489	1.489

Detailed theoretical discussion of the results reported here will be reserved for a later publication. In the meantime, the following remarks may be of interest: (a) The diffusion coefficients of Table IV fall increasingly *below* the predictions of the Onsager–Fuoss theory as the concentration increases. The relative deviations are greatest for the lithium salts, followed by the acids, the sodium salts, and the potassium salts in that order. (b) Up to one normal, the deviations may be represented by multiplying the Onsager–Fuoss expression by a factor of the form $(1 - 0.018nm)$ where m is the molality, and n is a parameter independent of concentration for each solute. This factor can be accounted for by assuming that each molecule of salt transports with it n molecules of water of hydration. The n values which fit the data are: LiCl, 9.9; LiBr, 9.0; HCl, 6.8; HBr, 5.9; NaCl, 5.0; NaBr, 4.1; KCl, 1.2; KBr, 0.3. These n values seem reasonable, except for the two acids, where they imply an amount of transport of hydrate water quite inconsistent with the observed high mobility of the hydrogen ion. (c)

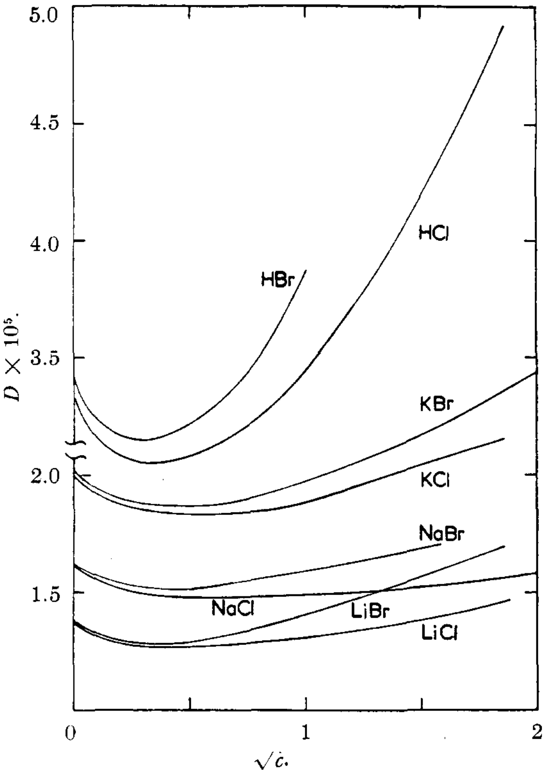

Fig. 4.—True or differential diffusion coefficients at 25°; c = moles/liter.

The viscosity-corrected equation proposed by Gordon[5] is inadequate to account for the deviations from the Onsager–Fuoss theory up to 1N, except in the case of sodium chloride. (d) Omission of the Onsager–Fuoss electrophoretic corrections leads to difficulty in extrapolating the data to the Nernst limiting value. (e) There is no evidence of the anomaly reported by Gordon and co-workers[6] in the diffusion data for hydrochloric acid.

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Summary

The magnetically-stirred diaphragm-cell described earlier is applied to measurements of the integral diffusion coefficients of eight uni-univalent electrolytes in the range 0.05 to 4N at 25°. A simple method is developed for deriving from these data the differential diffusion coefficients as a function of concentration. These are tabulated at round concentrations and a preliminary account of their theoretical implications is given.

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(6) W. A. James, E. A. Hollingshead and A. R. Gordon, *ibid.*, **7**, 89 (1939).