[CONTRIBUTION FROM STANFORD UNIVERSITY]

The Diffusion of Ions in Supporting Electrolytes[1]

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It has been recognized since the time of Nernst that electrical attraction between ions of opposite sign forces the separate ions of a single salt to diffuse at the same rate in water regardless of differences in the individual ionic mobilities. The electrical potential difference set up when a salt diffuses is the familiar diffusion potential or liquid junction potential. It is also well known that the diffusion potential can be reduced by the addition of a salt in high concentration that of itself produces little or no diffusion potential such as potassium chloride, potassium nitrate or ammonium chloride.[3] The diffusion potential can also be reduced by the addition of any electrolyte in uniform high concentration to both sides of the diffusion layer.

The corresponding effects produced by the addition of salts to diffusing systems on the diffusion mobility of the separate ions have been comparatively neglected. It is generally realized (for example, see [4]) that the presence of a large excess of salt will effectively liberate the diffusing ions from electrical effects and allow them to diffuse at almost the same velocity they would have if uncharged. Hartley and Robinson in 1931[5] derived an equation for the true (or differential) diffusion coefficient of an anion diffusing in a salt solution of uniform concentration. They also pointed out that large errors are to be expected when a dye containing an impurity such as sodium chloride diffuses into pure water. Vinograd and McBain[6] examined the diffusion of mixed salts into pure water both theoretically and experimentally and derived an equation for the differential diffusion coefficient of any ion in terms of the mobilities, valences, concentrations and concentration gradients of all other ions present. Their equation neglects the changes of activity and mobility with concentration but, as is pointed out by Hartley and Robinson,[5] these properties of the diffusing ions will change very little with concentration in salt solutions appreciably more concentrated than the diffusing ions.

I. Theoretical Formulation

The author proposes to use the term "supporting electrolyte" to designate electrolytes initially present at the same concentration throughout the diffusing system. The term is already used in polarography to refer to the electrolyte added to carry the current up to the mercury drops. There should be no confusion in the use of the term since the supporting electrolytes have similar functions in the two systems.

The equivalent ionic mobilities that apply in diffusion are in general greater than the corresponding equivalent ionic conductances calculated from transference and conductivity measurements since the electrophoretic effect and the time of relaxation effect are absent when both ions move in the same direction and at the same velocity. As a first approximation it is usual to use the limiting ionic conductances at infinite dilution in diffusion equations such as Henderson's.[7] However, when diffusion takes place in a supporting electrolyte the diffusing ions are not necessarily moving at the same velocity. The effect of interionic attractions and changes in hydration probably outweigh the electrophoretic and time of relaxation effects at concentrations of supporting electrolyte usually employed. It would seem better therefore when possible to calculate the ionic mobilities directly from transference and conductivity measurements of the diffusing salt at the concentrations in question.

The completely general determination of the integrated diffusion coefficient of one ion in a salt mixture cannot be solved without some assumption as to the structure of the diffusing layers. When diffusion takes place in bulk solution the concentration gradient varies continuously in time and space. The classical method as used by Öholm[8] as well as the modern scale method devised by Lamm[9] is not directly applicable to substances whose diffusion coefficients vary with concentration. The Northrup diffusion cell,[10] improved by McBain and his students,[6] lends itself more readily to measurements of substances whose diffusion coefficients vary with concentration. In these cells diffusion takes place at essentially a steady state through a sintered glass membrane.[11] Under these conditions the integral diffusion coefficient is defined as

$$\bar{D} = \frac{\mathrm{d}Q}{\mathrm{d}t}\,\frac{K}{\Delta c} \qquad (1)$$

where $\mathrm{d}Q/\mathrm{d}t$ is the rate of movement of the diffusing substance across the membrane, Δc is the difference in concentration across the membrane and K is a constant depending on the geometry

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[1] The material in this paper was presented at the Colloid Division of the American Chemical Society meeting in Cleveland, April 6, 1944.

[2] Bristol Myers Co. Fellow in Chemistry, 1941–44.

[3] MacInnis, "The Principles of Electrochemistry," Reinhold Publ. Co., New York, N. Y., 1939, p. 243.

[4] Svedberg and Pederson, "The Ultracentrifuge," Oxford University Press, New York, N. Y., 1940, p. 23.

[5] Hartley and Robinson, *Proc. Roy. Soc.* (London), **A134**, 20 (1931).

[6] Vinograd and McBain, THIS JOURNAL, **63**, 2008 (1941). In this reference, on page 2011, *N* should be in moles, not in equivalents.

[7] Henderson, *Z. physik. Chem.*, **59**, 118 (1907).

[8] Öholm, *ibid.*, **70**, 378 (1910).

[9] Lamm and Poulson, *Biochem. J.*, **30**, 528 (1936).

[10] Northrup and Anson, *J. Gen. Physiol.*, **12**, 543 (1929).

[11] Barnes, *Physics*, **5**, 4 (1934).

of the cell and determined from the diffusion of a reference substance such as 0.1 N potassium chloride. The units of concentration cancel if concentration is expressed on a volume basis.

When a steady state of diffusion has been reached across a membrane[12]

$$\bar{D} = \frac{1}{c}\int_{c_1}^{c_2} D \, \mathrm{d}c \qquad (2)$$

where D is the true or differential diffusion coefficient. C_1 is usually taken to be zero unless otherwise stated.[13] Likewise

$$D = \bar{D} + c\,(\mathrm{d}\bar{D}/\mathrm{d}c) \qquad (3)$$

The general equation for the diffusion of a given ion in a mixture of salts has been derived by Vinograd and McBain[6] following the method of Nernst, and may be written

$$D_+G_+ = \frac{RT}{F^2}\frac{u_+}{n_+}\left(G_+ - n_+c\,\frac{\Sigma u_+G_+/n_+ - \Sigma u_-G_-/n_-}{\Sigma uc}\right) \qquad (4)$$

D_+ is the diffusion coefficient of the cation, n_+ its valence, u_+ its equivalent conductance and $G = \mathrm{d}c/\mathrm{d}x$, the gradient of concentration of the ion with respect to distance. Again the units of concentration cancel out. The negative term inside the brackets is positive for anions.

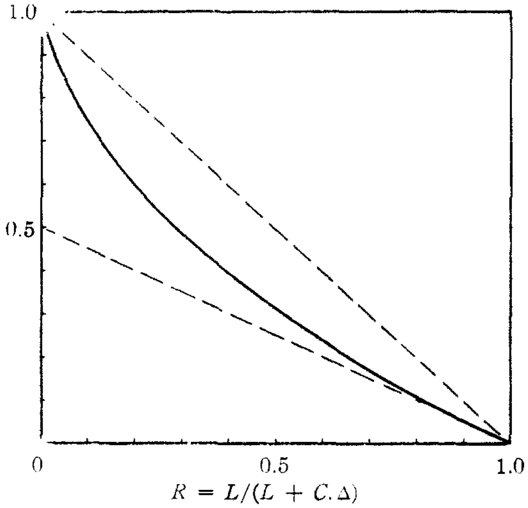

Fig. 1.—Theoretical relation between the conductivity ratio, R, and the electrical contribution to the diffusion of an ion, F. $F = 1 - R/(1 - R) \ln R$.

When only one salt is diffusing, equation 4 reduces (as it should) to the Haskel equation[14]

$$D = \frac{RT}{F}\left(\frac{1}{n_+} + \frac{1}{n_-}\right)\Big/\left(\frac{1}{u_+} + \frac{1}{u_-}\right) \qquad (5)$$

It is in general impossible to integrate equation 4 when more than one salt is present without making some assumption about the concentration of the supporting electrolyte at all parts throughout the region in which diffusion is taking place. If we were to assume that a steady state existed within the membrane and that the supporting electrolyte is free to move, then the integration, if possible, would probably resemble that obtained by Planck[15] for the diffusion potentials and would probably be even more cumbersome to calculate. As a first approximation we can use the same assumptions that lead to the relatively simple Henderson equation for diffusion potentials which in this special case amounts to the assumption that the supporting electrolyte does not move and therefore that G_s remains zero for all ions of the supporting electrolyte and the necessary corollary that $G_+ = G_-$ for the two ions of the diffusing electrolyte. G can then be removed from equation 4 leaving

$$D_+ = D_{+0}\left(1 - n_+c_+\frac{u_+/n - u_-/n}{c(u_+ + u_-) + \Sigma u_sc_s}\right) \qquad (6)$$

where $D_{+0} = \dfrac{RT}{F^2}\dfrac{u_+}{n_+}$ the free diffusion coefficient of the cation in the absence of an electric field. The subscript s now refers to the ions of the supporting electrolyte. The term Σu_sc_s is equal to L the conductance of the supporting electrolyte. The term Σuc is equal to Λ_0, the equivalent conductance of the diffusing salt. When the value for D_+ from equation 6 is introduced into equation 2 we get

$$\bar{D}_+ = \frac{D_{0+}}{c}\int_0^{c_0}\left(1 - \frac{nc(u_+/n_- - u_-/n_-)}{\Lambda_0\,c + L}\right)\mathrm{d}c \qquad (7)$$

Integrating between limits we get

$$\bar{D}_+ = D_{0+}\left[1 - \frac{n_+(u_+/n_+ - u_-/n_-)}{(u_+ + u_-)}\left(1 - \frac{L}{\Lambda_0c_0}\ln\frac{L + \Lambda_0C_0}{L}\right)\right] \qquad (8)$$

Let $R = L/(L + \Lambda_0C_0)$, the ratio of the conductance of the supporting electrolyte alone to the conductance of the supporting electrolyte plus the diffusing electrolyte and let

$$\frac{u_+/n_+ - u_-/n_-}{u_+ + u_-} = H$$

which is equal to $t_+/n_+ - t_-/n_-$ when u_+ and u_- are independent of concentration. Equation 8 reduces to

$$\bar{D}_+ = \bar{D}_0\,[1 - n_+H(1 - R(\ln R)/(1 - R))] \qquad (8')$$

The factor $[1 - R(\ln R)/(1 - R)]$ depends only upon the relative conductances of the two solutions on either side of the diffusion membrane and measures the electrical contribution to the diffusion of an ion. This function, which may be replaced by the symbol F, has been calculated for values of R from 0 to 1. Selected values are given in Table I and the function F is plotted in Fig. 1. In the derivation of equation 8 the term

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[12] Hartley and Runnicles, *Proc. Roy. Soc.* (London), **A168**, 401 (1938).

[13] Equation 1 assumes that the diffusion coefficient is measured by the diffusion of an infinitesimal amount of solute. In practice, up to 10% is allowed to diffuse. According to unpublished calculations by the author the maximum error that can be produced in D, calculated from equation 3 on the assumption that $\bar{D}$ is actually being measured by 10% diffusion, is slightly more than 5% of the highest value of D, except in the immediate vicinity of a sharp change in D.

[14] Haskel, *Phys. Rev.*, **21**, 149 (1908).

[15] See ref. 3, page 401.

Σuc arises from the conductivity of the system and therefore in real solutions where the conductivity of the solution is not given accurately by Σuc of the pure components[16] it is correct to use the measured conductivity ratio $L/(L + \Lambda_0 C_0)$ rather than the calculated value.

The function $F = [1 - R \ln R/(1 - R)]$ is independent of the relative mobilities of the ions making up the supporting electrolyte. Equation 8 therefore predicts that the diffusion of a given ion should be the same in different supporting electrolytes having the same conductivity but varying relative ionic mobilities.

TABLE I

VALUES OF THE FUNCTION $F = 1 - R(\ln R)/(1 - R)$ WHERE R IS THE RATIO OF THE CONDUCTIVITY OF THE SUPPORTING ELECTROLYTE TO THE CONDUCTIVITY OF THE DIFFUSING ELECTROLYTE IN THE SUPPORTING ELECTROLYTE, AND F IS THE ELECTRICAL CONTRIBUTION TO THE DIFFUSION OF AN ION

R	F	R	F
0	1.000	0.6	0.234
0.1	0.744	.7	.168
.2	.598	.8	.109
.3	.484	.9	.050
.4	.398	1.0	.000
.5	.307		

The viscosity of the supporting electrolyte, if different from pure water, will change the true diffusion coefficients of the ions in proportion to the relative fluidity (inverse viscosity) of the supporting electrolyte. Equation 8 when corrected for viscosity becomes

$$\overline{D}_+ = \eta_0/\eta \; D_{0+} \, (1 - n_+ HF) \qquad (9)$$

where η_0 is the viscosity of pure water and η is the viscosity of the supporting electrolyte. Although there has been some question as to the exact form the viscosity correction should take,[17] the simple correction factor used is justified by experiments with potassium chloride in magnesium sulfate described in part III b of this paper.

The theory so far presented is admittedly inexact, although the main error, introduced by assuming that the supporting electrolyte does not move, obviously tends to zero at the limit $R = 1$. Therefore it seems impractical at present to allow for minor factors such as change of activity or ionic mobility with concentration for an approximate theory of this sort. The second part of this paper presents experimental data which follow the predictions of equation 9 to a satisfying degree. Equation 9 should therefore have practical value when determining the diffusion mobility of charged ions in the presence of supporting electrolytes.

II. Experimental

Diffusion was measured in Northrup–McBain double-ended sintered glass cells.[18] The sintered glass membranes were carefully flushed with boiled-out distilled water to remove air bubbles. The more concentrated solution was placed in the upper compartment and diffusion was allowed to proceed in a thermostat at 25° until the rate of diffusion was within 1% of the steady state. This occurs when $Dt/h^2 \geqslant 0.55$[19] where h is the maximum pore length in the membrane. The membranes are about 2 mm. thick and a value of $h^2 = 0.10$ cm. was taken equivalent to a total pore length of 0.316 mm. The solutions in the two compartments were replaced by fresh solutions at 25° after a steady state had been reached. Time was measured from the time the lower compartment was refilled to the time it was emptied. Stock solutions were made up on a volumetric basis and diluted as needed. Cell constants were determined with 0.1 N potassium chloride using the value $\overline{D} = 1.631$ cm.^{2}/day at 25° obtained from Cohen and Bruins'[20] value at 20°. Analyses were compared with the original solution used to fill the upper compartment diluted 1:10 with the original solution used to fill the bottom compartment. Chlorides were determined by a microelectrometric titration using a micrometer buret[21] containing a solution of silver nitrate in 0.05 N nitric acid and 0.5 N potassium nitrate. The buret tip contained a silver wire at its upper end connected to a potentiometer and dipped into the liquid being titrated. A 5-cc. sample of chloride solution was diluted with 10 cc. of water and 2 cc. of saturated potassium nitrate. A silver wire plated with silver chloride completed the circuit through a potentiometer. After preliminary titrations established the potential of the end-point, the potentiometer was set to that potential and silver nitrate added until the galvanometer indicated zero current flow. This method enables 5 cc. of approximately 0.01 N chlorine to be determined to 0.5% in less than five minutes. Copper was determined colorimetrically; 10 cc. of approximately 0.01 N copper was placed in a one ounce screw-top bottle and one cc. of 33% ammonium hydroxide added. The bottle was shaken and the color determined on a "Lumetron" colorimeter using a narrow band filter having a maximum at 590 mμ. Citrate was determined by wet oxidation with potassium dichromate in 12 N sulfuric acid at 100° for fifteen minutes followed by electrometric back titration with ferrous ammonium sulfate.

High grade analytical reagents were used except for copper perchlorate which was prepared from perchloric acid and an excess of basic copper carbonate. The stock solution was filtered and diluted for use. The concentration was determined colorimetrically as above by comparison with copper wire dissolved in nitric acid.

The analytical methods were chosen for their convenience and rapidity. Conductivities were in general calculated from published data for pure solutions on the assumption that conductivities are additive in mixture. Although it has been shown[16] that the conductivities of mixtures are not strictly additive, the errors introduced are not great and are probably negligible for large values of the conductivity ratio R. The conductivity ratio of copper perchlorate in perchloric acid to perchloric acid was measured in conventional conductivity cells.

Viscosities likewise were not measured except for magnesium sulfate solutions. The fluidities were calculated by making use of Bingham's principle of additive ionic fluidities[22] for solutions not listed as such in the "International Critical Tables."

III. Results

a. The diffusion of chloride in 0.1 N lithium chloride was measured in various concentrations of potassium nitrate and nitric acid, Fig. 2 and

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(16) Van Rysselberghe and Nutting, THIS JOURNAL, **59**, 333 (1937).

(17) Van Rysselberghe, *ibid.*, **60**, 2326 (1938).

(18) McBain and Dawson, *Proc. Roy. Soc.* (London), **A148**, 32 (1935).

(19) Jacobs, *Ergeb. Biol.*, **12**, 62 (1935).

(20) Cohen and Bruins, *Z. physik. Chem.*, **113**, 159 (1924).

(21) Dean and Fetcher, *Science*, **96**, 237 (1942).

(22) Bingham, *J. Phys. Chem.*, **45**, 885 (1941).

TABLE II

DIFFUSION OF CHLORIDE WHEN 1.0 N LiCl DIFFUSES THROUGH A SUPPORTING ELECTROLYTE. EACH VALUE IS THE MEAN OF 2 OR 3 DETERMINATIONS

Supporting electrolyte	D obs., cm.^{2}/day	D cor. for η	Λ_s	R	F^b	$\bar{D}$ calcd., cm.^{2}/day	$\frac{D \text{ cor.}}{D \text{ calcd.}}$
0.00	1.15^a	..	(Λ_0 = 9.6)	0	1.00	1.15	(1.00)
.03 N KNO$_3$	1.36	..	4.1	.299	.484	1.41	.96
.01 N HNO$_3$	1.33	..	4.0	.294	.489	1.41	.94
.1 N KNO$_3$	1.50	..	12.0	.555	.265	1.52	.99
.5 N KNO$_3$	1.63	1.61	57	.855	.072	1.62	.99
	1.66	..		1.000	0.0	1.66	(1.00)

^{a} See ref. 6. ^{b} Calculated, see text.

Table II. F was calculated from R using a large scale graph of Fig. 1. D_{0Cl} was obtained from the accurately known values of u_+ and u_-[23] and $\bar{D}$ for potassium chloride by means of equation 8. The theoretical curve for $\bar{D}$ vs. R based on $\bar{D}$ for lithium chloride and D_{0Cl} is shown as a solid line in Fig. 2. It will be seen that the value for $\bar{D}$ when nitric acid is used as the supporting electrolyte is not greatly different from the value at the same R when potassium nitrate is used. The greatest deviation from the theory would be expected in this region where the concentration of the supporting electrolyte is much less than the concentration of the diffusing electrolyte.

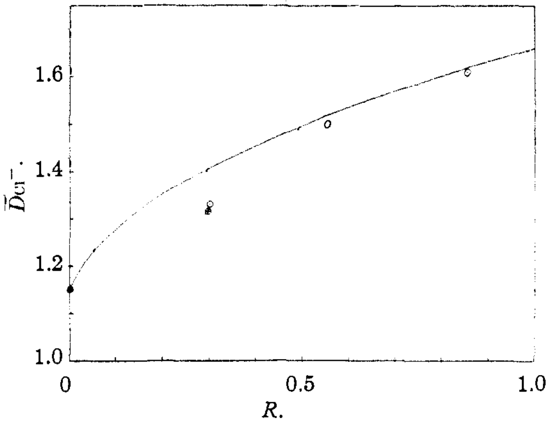

Fig. 2.—Diffusion of Cl$^-$ as 0.1 N LiCl in: ⊙, KNO$_3$; ⊕, HNO$_3$.

b. The effect of the viscosity of the supporting electrolyte on the mobility of Cl$^-$ ion was tested using 0.1 N potassium chloride in 0.2 M magnesium sulfate. $\bar{D}_{Cl}$ was found to be 1.47. For these conditions $R = 0.435$ and $F = .35$. Since $\bar{D}_{KCl} = 1.63$ and $\bar{D}_{0Cl} = 1.66$ (IIIa) the expected value of $\bar{D}_{Cl}$ would be 1.65 in this case if there were no viscosity change. If equation 9 represents the facts then the ratio of 1.47 to 1.65 = 0.891 should equal the relative fluidity of 0.2 M magnesium sulfate. The viscosity of this solution of magnesium sulfate was measured at 25° in an Ostwald viscometer and the relative fluidity found to be $\eta_0/\eta = 0.894$. The excellent agreement between the relative diffusion mobility and the relative fluidity justifies the use of the fluidity correction in the other tables of this paper.

c. The diffusion of divalent cupric ions as 0.1 N copper nitrate in potassium nitrate or nitric acid and as copper perchlorate in perchloric acid has been measured; see Table III and Fig. 3. The calculated value for $\bar{D}_{0Cu^{++}}$ obtained from $\bar{D}$ and $t+$ for 0.1 N copper sulfate is $\bar{D}_{0Cu^{++}} = 0.48$ cm./day. The calculated value for $\bar{D}_{0Cu^{++}}$ obtained from $\bar{D}$ for 0.1 N copper nitrate and infinite dilution values for $u_{Cu^{++}}$ and $u_{NO_3^-}$ is $\bar{D}_{0Cu^{++}} = 0.24$. Actually Cole and Gordon[24] found that $\bar{D}_{CuSO_4}$ is hardly changed by addition of sulfuric acid at 18°. This means that $u_{Cu^{++}} = u_{SO_4^{-}}$ in this supporting electrolyte. The value for $\bar{D}_{Cu}$ obtained from their one value at 25° after correcting for viscosity is $\bar{D}_{Cu^{++}} = 0.65$. See Table IIIc. The limiting value found in this work on copper nitrate and copper perchlorate is $\bar{D}_{0Cu^{++}} = 0.66$ in agreement with Cole and Gordon.

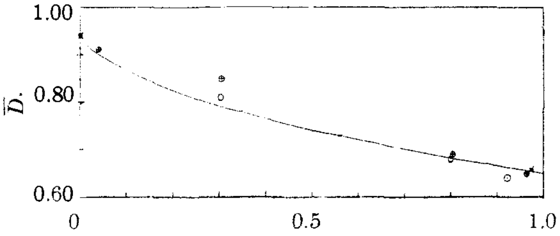

Fig. 3.—Diffusion of Cu^{++} as 0.1 N Cu(NO$_3$)$_2$ in HNO$_3$. ⊕. 0.1 N Cu(NO$_3$)$_2$ in KNO$_3$. O; 0.1 N Cu(ClO$_4$)$_2$ in HClO$_4$. ✦.

Table III shows that divalent diffusing ions agree with equation 9 to a good approximation. The difference between values of $\bar{D}_{Cu^{++}}$ obtained in nitric acid and potassium nitrate as supporting electrolytes is not large. In general the potassium nitrate values fall closer to the theoretical curve. The marked disagreement of all the diffusion data with the value for $\bar{D}_{0Cu^{++}}$ obtained from transport numbers is perhaps one more indication that Cu^{++} associated to form complex ions in solution.

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[23] See ref. 3, p. 340.

[24] Cole and Gordon, *J. Phys. Chem.*, **40**, 737 (1936).

TABLE III

DIFFUSION OF 0.1 N Cu^{++}

Supporting electrolyte	$C_S\Lambda_S$	R	F	D obs.	D cor. for η	D calcd.	$\frac{D\text{ cor.}}{D\text{ calcd.}}$
0	0	0	1.00	0.94[a]	..	(0.94)	
a. $Cu(NO_3)_3$ in supporting electrolytes; $C_0\Lambda_0 = 9.3$							
0.001 N HNO_3	0.4	.041	0.86	.91	..	.90	1.01
.01 N HNO_3	4.07	.305	.48	.85	..	.79	1.08
.03 N KNO_3	4.05	.303	.48	.81	..	.79	1.03
0.1 N HNO_3	38.6	.805	.104	.69	..	.68	1.02
0.3 N KNO_3	37.2	.800	.108	.69	0.68	.68	1.00
1.0 N KNO_3	111.9	.923	.037	.66	.64	.66	0.97
0.8 N HNO_3	269	.965	.018	.62	.65	.65	1.00
∞	∞	1.00	.00	..	..	(.65)	
b. $Cu(ClO_4)_2$ in $HClO_4$. R determined conductimetrically							
0	0	0	1.00	.94	..	(.94)	
0.5 N $HClO_4$		0.974	0.013	.66	.66	.65	1.02
c. $CuSO_4$ in H_2SO_4. Data of Cole and Gordon[24]							
0 at 18°				0.52 at 18°	..		
0.5 N H_2SO_4 at 18°				.532 at 18°	..		
1.0 N H_2SO_4 at 18°				.512 at 18°	..		
0.1 N H_2SO_4 at 25°		.68	.18	.65	.67		

[a] Öholm[25] found D for 0.1 N copper nitrate = 0.94 corrected to 25° from values near 20°.

The diffusion of 0.1 N potassium citrate was measured in water and in 0.1 N potassium chloride and 0.13 N lithium chloride and the results are listed in Table IV. Values of $\overline{D}_0$ are based on the relative ionic mobilities at infinite dilution.

TABLE IV

Supporting electrolyte	R	E	D obs.	D calcd.	$D_{obs.}/D_{calcd.}$
0	0	1	0.90	(90)	(1.00)
0.1 N KCl	0.5	0.3	.57	0.58	0.98
0.13 N LiCl	.5	.3	.61	.58	1.06

In the case of 0.13 N lithium chloride the change in concentration of chloride was also measured. When an average of 0.0106 mole per liter of the citrate had diffused from the upper to the lower chamber the chloride movement averaged 0.0051 mole per liter in the same direction. Thus the chloride movement is half the citrate movement but even in this case the change in the concentration of the supporting electrolyte is only four per cent. This experiment helps to justify the admittedly false assumption that the supporting electrolyte does not move, since it shows that the movement of the supporting electrolyte has only a small effect on the relative conductivities of the diffusing and supporting electrolytes. The fact that the chloride movement was half the citrate movement shows how unreliable any nonspecific analysis such as refractive index must be in the presence of supporting electrolytes.

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Summary

1. A "supporting electrolyte" is defined as the electrolyte or mixture of electrolytes initially present at uniform concentration throughout a system in which diffusion takes place.

2. An equation is developed relating the integral diffusion coefficient of any ion to the conductivities of the supporting and diffusing electrolytes.

3. The diffusion of chloride, copper and citrate ions has been measured in various supporting electrolytes and the results agree satisfactorily with the theory.

4. The diffusion of ions is nearly independent of the relative ionic mobilities of the supporting electrolyte but depends almost entirely on the conductivity of the latter.

5. When the supporting electrolyte has ten times the conductivity of the diffusing electrolyte, an ion diffuses at a rate that still differs from its ideal rate if uncharged by 5 per cent. of the difference between the ideal rate and the rate in the absence of supporting electrolyte. For larger conductivity ratios the deviation will be proportionately less.

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(25) Öholm. *Finska Kemistsamfunds Medd.*, **46**, 124 (1937); *Chem. Abs.*, **33**, 9094 (1939).