

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WESTERN AUSTRALIA]

## The Variation of Transference Numbers with Concentration

BY R. H. STOKES

RECEIVED JULY 7, 1953

The interionic attraction theory leads to an expression for the transference number of an ion in a single electrolyte, in which the relaxation effect cancels out. If the uncertain influence of the change in macroscopic viscosity is assumed to be the same for both ions, this also cancels from the transference number expression, which then contains only electrophoretic terms. These can be evaluated in a similar way to the electrophoretic terms in diffusion.<sup>1</sup> The resulting formula is convergent for aqueous 1:1 electrolytes, but not for unsymmetrical types, and gives an excellent reproduction of the observed values for 1:1 electrolytes. The values of the ion size parameter (distance of closest approach) required are similar to those determined from activity data.

### Introduction

The motion of an ion under an external field is complicated by two effects arising from interionic forces, the relaxation and electrophoretic effects. The former may be regarded as an electrostatic drag operating between oppositely charged ions moving in opposite directions; the latter arises from force transfer between the ions as a result of a viscosity mechanism. Another factor which may influence the velocity of ions is the bulk viscosity of the solution, but there is no agreement on the precise form in which this should be introduced. In this paper it is shown that in the theory of the transference number the relaxation effect and the bulk viscosity effect may be eliminated, so that the concentration-dependence of the transference number provides an interesting test of the theory of the electrophoretic effect.

**The Relaxation Effect.**—The relaxation effect gives rise to an additional field  $\Delta X$  at the ion, which is thus subject to a total electric field  $X + \Delta X$ , where  $X$  is the intensity of the applied field. This relaxation field was evaluated by Onsager<sup>2</sup> for the case of a single electrolyte in very dilute solutions as

$$\frac{\Delta X}{X} = \frac{z_1 z_2 e^2}{3ekT} \frac{q\kappa}{1 + \sqrt{q}} \quad (1)$$

where

$$q = \frac{|z_1 z_2|}{(|z_1| + |z_2|)(|z_2| \rho_1 + |z_1| \rho_2)} \left( = \frac{1}{2} \text{ for symmetrical valence-types} \right)$$

and the other symbols have the meanings defined in a previous article.<sup>1</sup> Expression 1 is valid only as a limiting law, no account having been taken in its derivation of the finite size of the ions. Recently Falkenhagen and collaborators<sup>3</sup> have given a more complete formula in which the ions are treated as spheres of diameter  $a$ . In their formula  $\kappa$  has a slightly different significance owing to the use of a different ionic distribution-function from the Boltzmann distribution conventionally employed in the interionic attraction theory. However, since in the end this new function has to be approximated to a linear form in the solution of the equation for the potential, and this approximation

(1) R. H. Stokes, *THIS JOURNAL*, **75**, 4563 (1953). (a) In order to avoid confusion between the proton charge and the base of natural logarithms, the symbol for the proton charge has been given as a bold-face  $e$  in this paper. (b) In reference (1): the last factor on the right of equation (12) should read  $(z_1^m v_1^m + z_2^m v_2^m) / \bar{A}^m$ . On p. 4565, col. 2, line 4, the expression should be  $(1 + C \ln y_{\pm} / d_1)$ . In Fig. 1, the reference to Harned and Levy should be (7).

(2) L. Onsager, *Physik Z.*, **28**, 277 (1927).

(3) H. Falkenhagen, M. Leist and G. Kelbg, *Ann. Physik*, [B] **11**, 51 (1952).

neglects quantities larger than the difference between the Boltzmann and the new distribution-functions, it seems safe to ignore the parts of Falkenhagen's expression arising from the change in the distribution-function, and examine his formula as it would stand if obtained from the usual distribution-function. It would then be

$$\frac{\Delta X}{X} = \frac{z_1 z_2 e^2}{3ekT} \frac{q\kappa}{1 - q} \frac{e^{(1 - \sqrt{q})\kappa a} - 1}{\kappa a (1 + \kappa a)} \quad (2)$$

We need not for the moment consider this expression in detail; it is sufficient to note that, like Onsager's limiting form (1), (and also like Falkenhagen's more elaborate formula based on the new distribution-function), *it is the same for both ions*.

**The Electrophoretic Effect.**—In the treatment of the electrophoretic effect given by Onsager and Fuoss,<sup>4</sup> the velocity of the solution in the neighborhood of the ion is determined from the ionic distribution function and the Debye-Hückel expression for the potential, in terms of the forces  $\mathbf{k}_1$  and  $\mathbf{k}_2$  acting on the cation and anion, respectively. This velocity is then superimposed on the velocity which the ion would attain under these forces in the absence of the electrophoretic effect. In Onsager's treatment, since only a limiting law is sought, it is legitimate to take the forces  $\mathbf{k}_1$  and  $\mathbf{k}_2$  as  $Xz_1\mathbf{e}$  and  $Xz_2\mathbf{e}$ , respectively; but if more concentrated solutions are of interest one should write

$$\mathbf{k}_1 = (X + \Delta X)z_1\mathbf{e} \text{ and } \mathbf{k}_2 = (X + \Delta X)z_2\mathbf{e} \quad (3)$$

In a previous paper,<sup>1</sup> the general ( $n$ 'th) electrophoretic term arising from a Boltzmann distribution was evaluated for the case of diffusion; this course facilitated the investigation of convergence problems, though on grounds of mathematical self-consistency no more than two terms can be accepted for symmetrical electrolytes, and no more than one for unsymmetrical electrolytes. If one neglects the effect on the electrophoretic terms of the asymmetry of the ionic distribution in the conductance problem, a similar computation of the electrophoretic contributions  $\Delta v_1$  and  $\Delta v_2$  to the velocities of the ions may be made. One obtains for these the results

$$\begin{aligned} \Delta v_1 &= \sum A_n \frac{z_1^n (z_1^{n-1} \mathbf{k}_1 - z_2^{n-1} \mathbf{k}_2)}{\bar{a}^n (z_1 - z_2)} \\ \Delta v_2 &= \sum A_n \frac{z_2^n (z_1^{n-1} \mathbf{k}_1 - z_2^{n-1} \mathbf{k}_2)}{\bar{a}^n (z_1 - z_2)} \end{aligned} \quad (4)$$

where the quantities  $A_n$  are functions of solvent

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

properties and the dimensionless quantity  $(\kappa a)$  only, and are given by

$$A_n = \frac{(-1)^n 10^{8n}}{n!} \frac{e^2}{6\pi\eta} \left(\frac{e^2}{\epsilon k T}\right)^{n-1} \phi n(\kappa a) \quad (5)$$

$\phi n(\kappa a)$  being the function defined and tabulated in the previous paper.<sup>1</sup> Now substituting the values (3) for  $\mathbf{k}_1$  and  $\mathbf{k}_2$ , one obtains

$$\begin{aligned} \Delta v_1 &= (X + \Delta X) e \Sigma A_n \frac{z_1^{2n} - z_1^n z_2^n}{\hat{a}^n (z_1 - z_2)} \\ \Delta v_2 &= (X + \Delta X) e \Sigma A_n \frac{z_1^n z_2^n - z_2^{2n}}{\hat{a}^n (z_1 - z_2)} \end{aligned} \quad (6)$$

If  $u_1^0$  and  $u_2^0$  be the mobilities of the ions at infinite dilution, in absolute c.g.s. units (cm. sec.<sup>-1</sup> dvne<sup>-1</sup>), and  $v_1^0, v_2^0$ , be their velocities (in cm. sec.<sup>-1</sup>) under the external field  $X$ , we have

$$v_1^0 = X z_1 e u_1^0, v_2^0 = X z_2 e u_2^0 \quad (7)$$

The velocities of the ions relative to the solution, under the combined influence of the applied field  $X$  and the relaxation field  $\Delta X$ , are

$$\begin{aligned} v'_1 &= (X + \Delta X) z_1 e u_1^0 \text{ and} \\ v'_2 &= (X + \Delta X) z_2 e u_2^0 \end{aligned} \quad (8)$$

The absolute velocities  $v_1$  and  $v_2$  of the ions are therefore obtained by adding expressions (6) and (8); the results may be written

$$\begin{aligned} \frac{v_1}{v_1^0} &= \left(1 + \frac{\Delta X}{X}\right) \left[1 + \frac{1}{z_1 u_1^0} \Sigma A_n \frac{z_1^{2n} - z_1^n z_2^n}{\hat{a}^n (z_1 - z_2)}\right] \\ \frac{v_2}{v_2^0} &= \left(1 + \frac{\Delta X}{X}\right) \left[1 + \frac{1}{z_2 u_2^0} \Sigma A_n \frac{z_1^n z_2^n - z_2^{2n}}{\hat{a}^n (z_1 - z_2)}\right] \end{aligned} \quad (9)$$

Now the velocity ratios  $v_1/v_1^0$  and  $v_2/v_2^0$  may be replaced by the equivalent conductance ratios  $\lambda_1/\lambda_1^0$  and  $\lambda_2/\lambda_2^0$ , and  $u_1^0$  and  $u_2^0$  by  $6.468 \times 10^6 \lambda_1^0/|z_1|$  and  $6.468 \times 10^6 \lambda_2^0/|z_2|$ , respectively; and the equivalent conductance of the whole electrolyte,  $\Lambda$  can be obtained as the sum of  $\lambda_1$  and  $\lambda_2$ . We have therefore

$$\begin{aligned} \lambda_1 &= \left[\lambda_1^0 + 1.546 \times 10^{-7} \Sigma A_n \frac{z_1^{2n} - z_1^n z_2^n}{\hat{a}^n (z_1 - z_2)}\right] \left(1 + \frac{\Delta X}{X}\right) \\ \Lambda &= \left[\Lambda^0 + 1.546 \times 10^{-7} \Sigma A_n \frac{(z_1^n - z_2^n)^2}{\hat{a}^n (z_1 - z_2)}\right] \left(1 + \frac{\Delta X}{X}\right) \end{aligned} \quad (10)$$

These expressions, if used at fairly high concentrations, may require modification to allow for the changed bulk viscosity of the solution; this question will be examined in a later paper. However, if we make the reasonable assumption that any such effect will alter the velocities of both ions in the same proportion, we can compute the transference number  $t_1$  of the cation as the ratio of  $\lambda_1$  to  $\Lambda$  without worrying about the detailed form of the viscosity-dependence; and furthermore, since the relaxation effect appears as the same factor in both  $\lambda_1$  and  $\Lambda$ , this too will cancel, leaving us with

$$t_1 = \frac{\lambda_1^0 + 1.546 \times 10^{-7} \Sigma A_n (z_1^{2n} - z_1^n z_2^n) / [\hat{a}^n (z_1 - z_2)]}{\Lambda^0 + 1.546 \times 10^{-7} \Sigma A_n (z_1^n - z_2^n)^2 / [\hat{a}^n (z_1 - z_2)]} \quad (11)$$

We shall now examine the applicability of equation 11 to various electrolytes.

**1:1 Electrolytes.**—For uni-univalent electrolytes ( $z_1 = -z_2 = 1$ ) all terms for even values of  $n$  are zero in both the numerator and the denominator of 11, and the odd values of  $n$  give the result

$$t_1 = \frac{\lambda_1^0 + 1.546 \times 10^{-7} \sum_{\text{odd } n} (A_n/\hat{a}^n)}{\Lambda^0 + 1.546 \times 10^{-7} \sum_{\text{odd } n} (2A_n/\hat{a}^n)} \quad (12)$$

(For higher *symmetrical* valence types, with  $z_1 = -z_2 = z$  say, a further factor  $z^{2n}$  multiplies  $A_n$  in both the numerator and denominator, all terms in even  $n$  still vanishing. The actual behavior of bivalent and higher symmetrical types is complicated by ion-pair formation, but these formula should be applicable to the non-paired content of ions in such cases.)

It has been pointed out in the previous paper that on grounds of mathematical self-consistency only the first two terms ( $n = 1$  and  $n = 2$ ) of the series in 11 are acceptable for symmetrical electrolytes; we now see that in the conductance formulas, in contrast to the diffusion case, the second-order electrophoretic terms vanish identically for symmetrical electrolytes; therefore only the term for  $n = 1$  need be considered. It is however gratifying to find that the third-order term ( $n = 3$ ) is much smaller than the first-order term. This may be seen as follows: the function  $A_n$  in the equations above is, from equation 5, directly proportional to the function  $F_n(\kappa a)$  defined and tabulated in the previous paper.<sup>1</sup> At a given  $(\kappa a)$ ,  $A_n$  is therefore of a constant order of magnitude for  $n$  up to at least 5, so that  $A_3$  is less than  $A_1$  by a factor of at least  $1/\hat{a}^2$  for 1:1 electrolytes. Since  $\hat{a}$  lies in the range 3.5–5 for most fully-dissociated 1:1 electrolytes (such as alkali halides), it follows that the electrophoretic terms converge rapidly.  $A_1$  is always negative,  $A_2$  is identically zero, and  $A_3$  is negative and much smaller than  $A_1$ . Thus the course demanded by mathematical self-consistency, of accepting only the first two electrophoretic terms for 1:1 electrolytes, is also adequate; and in reality one needs only the first-order term, the second-order term being zero. For symmetrical electrolytes of higher valency type, the ratio of successive non-vanishing terms is of the order of  $z^2/\hat{a}^2$ ; in these cases the theory would therefore be on a less satisfactory basis unless the ions were unusually large. It should also be noted that in solvents of lower dielectric constant the presence of the factor  $(e^2/\epsilon k T)^{n-1}$  in  $A_n$  (see equation 5) would make the convergence slower even in the case of 1:1 electrolytes. For unsymmetrical electrolytes, the degree of self-consistency of the entire interionic attraction theory is lower, only first-order terms being logically justifiable; unfortunately at the same time the formulas lead to only slow convergence, the terms for even values of  $n$  not vanishing, and the ratio of successive terms being much larger than for 1:1 electrolytes. Thus it seems that good agreement with the theory can be expected only for 1:1 electrolytes.

The formula 11 for the transference number of a 1:1 electrolyte can now be drastically simplified, since only the first-order electrophoretic term need be used. Using the definition of  $A_1$  (see equation 5 and ref. 1) the result is found to be

$$t_1 = \frac{\lambda_1^0 - 41.25 \sqrt{\epsilon} / [\eta(\epsilon T)^{1/2} (1 + \kappa a)]}{\Lambda^0 - 82.5 \sqrt{\epsilon} / [\eta(\epsilon T)^{1/2} (1 + \kappa a)]} \quad (13)$$

which for aqueous solutions at 25° becomes

$$t_1 = \frac{\lambda_1^0 - 30.15\sqrt{c}/(1 + .3286 \hat{a}\sqrt{c})}{\lambda^0 - 60.3\sqrt{c}/(1 + .3286 \hat{a}\sqrt{c})} \quad (14)$$

These results differ from the formulas obtained from Onsager's limiting law only by the presence of the factor  $(1 + \kappa a)$  in the denominator of the electrophoretic term, a factor dropped in the derivation of the limiting law because at the dilutions there considered the condition  $\kappa a \ll 1$  was fulfilled. The appearance of this factor as a correction for finite ionic size is of course familiar in the theory of the activity coefficient; it is also noteworthy that Falkenhagen's expression (2) for the relaxation effect, if the exponential is expanded to the first-order term, likewise differs from Onsager's limiting expression by the same factor.

Equation 14, with the allocation of reasonable values to the ion size parameter  $\hat{a}$ , is capable of representing the observed transference numbers with excellent accuracy. In Table I are given the observed and calculated values for hydrochloric acid solutions. The value  $\hat{a} = 4.4$  is in striking agreement with the value obtained from activity data,<sup>5</sup> viz.,  $\hat{a} = 4.47$ . The success of the theory in

are at any given moment traveling like normal ions, the proton being surrounded by a cluster of water molecules; the electrophoretic correction applicable to this part of the process would be normal, as would that for the chloride ion.

Equally good agreement is found with other 1:1 electrolytes in which ion-pair formation is believed to be absent or slight, as shown in Table II.

The agreement with the theory is of course most significant for those cases where the transference number differs considerably from 0.5. In the case of potassium chloride where  $t_1$  is nearly 0.5, almost any value of  $\hat{a}$ , including zero, would serve, but in the other cases a change of a few tenths of an ångström in  $\hat{a}$  appreciably alters the quality of the agreement.

For calcium chloride, one finds that the electrophoretic contributions do not converge satisfactorily after the first-order term as would be necessary if the theory could be expected to succeed, for only the first-order term is really consistent with the approximate distribution function which has to be used; it is however encouraging to find that the results calculated by the present theory at least lie nearer to the observed values than do those given by the limiting law, and that the remaining deviations are of similar magnitude to the rejected higher terms.

**Conclusion.**—The quantitative success of the present treatment of the concentration-dependence of the transference numbers of uni-univalent electrolytes is due to the rapid convergence of the electrophoretic terms, combined with the fact that for symmetrical electrolytes the self-consistency of the entire body of interionic attraction theory extends as far as the second-order terms in the potential. Its inadequacy for unsymmetrical electrolytes is attributable to the approximations de-

TABLE I  
CATION TRANSFERENCE NUMBERS IN AQUEOUS HYDROCHLORIC ACID AT 25°;  $\hat{a} = 4.4$

$c$ , moles/l.	$t_1^a$	$t_1^c$	$c$ , moles/l.	$t_1^a$	$t_1^c$
0.01	0.8251	0.8249	0.5	0.838	0.838
.02	.8266	.8263	1.0	.841	.841
.05	.8292	.8287	2.0	.843	.843
.1	.8314	.8310	3.0	.843	.845
.2	.8337	.8337			

<sup>a</sup> Observed values up to 0.2 *M* from L. G. Longworth, THIS JOURNAL, 54, 2741 (1932), by the moving-boundary method; above 0.2 *M* from H. S. Harned and E. C. Dreby, *ibid.*, 61, 3113 (1939), by the e.m.f. method.

TABLE II

CATION TRANSFERENCE NUMBERS OF AQUEOUS 1:1 ELECTROLYTES AT 25°, TESTS OF EQUATION 14

The following accepted values of  $\lambda^0$  have been used in computing the values in Tables I and II: H<sup>+</sup>, 349.82; Li<sup>+</sup>, 38.68; Na<sup>+</sup>, 73.50; Cl<sup>-</sup>, 76.35; Ac<sup>-</sup>, 40.98.

$c$ , moles/l.	LiCl <sup>a</sup>		NaCl <sup>b</sup>		NaAc <sup>a</sup>		KCl <sup>b, d</sup>		KAc <sup>c</sup>	
	Obsd.	$t_1$ Calcd.	Obsd.	$t_1$ Calcd.	Obsd.	$t_1$ Calcd.	Obsd.	$t_1$ Calcd.	Obsd.	$t_1$ Calcd.
0.01	0.3289	0.3285	0.3918	0.3918	0.5537	0.5538	0.4902	0.4901	0.6498	0.6495
.02	.3261	.3258	.3902	.3902	.5550	.5550	.4901	.4900	.6523	.6521
.05	.3211	.3211	.3876	.3875	.5573	.5573	.4899	.4898	.6569	.6570
.1	.3168	.3165	.3854	.3849	.5594	.5596	.4898	.4895	.6609	.6619
.2	.3112	.3112	.3821	.3819	.5610	.5626	.4894	.4892	.....	.....
$\hat{a}$	5.2		5.2		3.7		3.7		3.7	

<sup>a</sup> Observed values by moving-boundary method: L. G. Longworth, THIS JOURNAL, 54, 2741 (1932), and 57, 1185 (1935). Ac = acetate. <sup>b</sup> Moving-boundary method: R. W. Allgood, D. J. Leroy and A. R. Gordon, *J. Chem. Phys.*, 8, 418 (1940), and 10, 124 (1942). <sup>c</sup> Moving-boundary method: D. J. Leroy and A. R. Gordon, *ibid.*, 6, 398 (1938). <sup>d</sup> For KCl at 0.5 *M*,  $t_1$ (obsd.) = 0.4888,  $t_1$ (calcd.) = 0.4887; at 1.0 *M*,  $t_1$ (obsd.) = 0.4882,  $t_1$ (calcd.) = 0.4883.

this case is actually rather disturbing, since it is recognized that the high mobility of the hydrogen ion is due to an abnormal transport mechanism available to the proton. However, it can perhaps be argued that the great majority of hydrogen ions

manded by the need for self-consistency in the fundamental equations, which do not permit the consideration of higher electrophoretic terms, although these can be shown to be comparable to the first-order term if the Boltzmann distribution is retained.

(5) R. H. Stokes and R. A. Robinson, THIS JOURNAL, 70, 1870 (1948).