[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Estimation of Transference Numbers in Dilute Solutions from Limiting Ionic Conductances

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While the known transference data of simple strong electrolytes can be reproduced with high precision by the empirical evaluation of a single parameter in the Longsworth[1] equation, or by the adjustment of two parameters in the equation of Jones and Dole,[2] the semi-empirical relation

$$T_+ = T_+^0 + \frac{(2T_+^0 - 1)\beta\sqrt{C}}{\Lambda^0 - (\alpha\Lambda^0 + 2\beta)\sqrt{C}}\left[1 - (1 - \alpha\sqrt{C})\sqrt{2C}\right] \quad (1)$$

permits the estimation of certain transference numbers from limiting conductances alone.[3] This equation is formally equivalent to that of Longsworth, but a comparison of coefficients shows that the parameter, A, which Longsworth evaluated from the transference data for each individual electrolyte, may be replaced by the quantity $-\beta\sqrt{2}(2T_+^0 - 1)/\Lambda^0$, characteristic of the whole group of electrolytes conforming to the Longsworth equation. Although this replacement is accompanied by a loss in precision, there are obvious practical advantages afforded by the gain in generality.

TABLE I

TEST OF EQUATION (1) AT 25°

Electrolyte	Λ^0	$T_+^{0\,a}$	$(T_+(\text{Eq. (1)}) -$	$T_+(\text{Obs.}))10^4$	
HCl	426.17	0.8209	−6	−11	−24
$NaC_2H_3O_2$	90.99	.5507	−1	1	4
NH_4Cl*	149.94	.4909	−3	− 6	−12
KCl	149.86	.4906	0	− 1	2
KI*	150.29	.4892	2	− 1	− 7
KBr*	151.63	.4849	7	2	− 8
NaCl	126.43	.3963	−2	− 8	4
LiCl	115.03	.3364	−6	− 9	5
Concentration (moles per liter), C =			0.05	0.1	0.2

^{a} $\lambda^0_{Cl^-} = 76.34$.

In Table I are recorded the differences between T_+ calculated by Equation (1) and the smoothed experimental values recently tabulated by Longsworth.[4] The average differences are (with increasing concentration) three, five and eight units in the fourth decimal place of the transference numbers. The maximum individual difference amounts to nearly 0.3%. The necessary values of $\Lambda^0(= \lambda_+^0 + \lambda_-^0)$ and $T_+^0(= \lambda_+^0/\Lambda^0)$ are all computed from the table of limiting ionic conductances given by MacInnes, Shedlovsky and Longsworth,[5] except those indicated with an asterisk. Of these latter, Λ^0(KBr) is due to Jones and Bickford,[6] Λ^0(KI) to Lasselle and Aston,[7] and $\Lambda^0(NH_4Cl)$ is given by Longsworth.[8] All values have been adjusted to conform to the primary conductance standard of Jones and Bradshaw.[9]

Equation (1) is not in accord with the known transference data for silver and potassium nitrates,[4] for calcium[4] and barium[2] chlorides, and for sodium sulfate.[4] Its failure in this respect is parallelled by that of the Longsworth[1] equation, but the results in Table I indicate that we might confidently expect an accuracy of better than one unit in the third decimal place of the transference number when it is applied to *dilute solutions* ($C < 0.15$ normal) *of uni-univalent electrolytes in which ionic association is negligible.* Precise limiting conductances are already available for a number of electrolytes in this category, including the chlorides, bromides, iodides, acetates, propionates, chloro substituted acetates, etc., of lithium, sodium and potassium. The accuracy to be expected in such calculations for the halides of hydrogen and ammonia, and possibly the hydroxides of the alkali metals, would hardly be better than two or three in the third decimal place of the transference numbers at 0.2 normal, but should improve with dilution, because the equation reduces, in the limit, to the theoretical tangent derivable from the Onsager[10] conductance equation. With proper attention to the above limitations, however, it appears that this equation might have considerable application in problems involving diffusion and liquid junction potentials, and in the determination[11] of the activity coefficients of salts (the bromides and iodides of lithium and sodium, for example) at high dilution.

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(1) Longsworth, THIS JOURNAL, **54**, 2741 (1932).
(2) Jones and Dole, *ibid.*, **51**, 1073 (1929).
(3) The constants α and β from the Onsager conductance equation[10] will be taken as 0.2277 and 29.93, respectively (25°), in subsequent calculations.
(4) Longsworth, THIS JOURNAL, **57**, 1185 (1935).
(5) MacInnes, Shedlovsky and Longsworth, *ibid.*, **54**, 2758 (1932).
(6) Jones and Bickford, *ibid.*, **56**, 602 (1934).
(7) Lasselle and Aston, *ibid.*, **55**, 3067 (1933).
(8) This value was obtained by extrapolation from 0.01 normal.[4]
(9) Jones and Bradshaw, *ibid.*, **55**, 1780 (1933).
(10) Onsager, *Physik. Z.*, **28**, 277 (1927).
(11) Brown and MacInnes, THIS JOURNAL, **57**, 1356 (1935).