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An Equation for Transference Numbers

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The following transference number equation is proposed,

$$1/t=1/t_0+AC^{\frac{1}{2}}-BC.$$

The values for the constant A are in accord with the Onsager theory for most uni-univalent electrolytes in water, but not for abnormal salts, such as silver nitrate, or for higher valence salts. However, the transference equation appears to have quite general applicability.

SEVERAL years ago the author proposed an equation for electrolytic conductance[1] which reduces to Onsager's[2] theoretical formulation at high dilutions and is useful for extrapolation purposes. It is applicable to most strong uni-univalent electrolytes up to a concentration of about one-tenth normal. An analogous equation for transference numbers has been proposed by Longsworth.[3] However, these equations have forms which are somewhat unwieldy for practical computations and they fail in the case of higher valence salts. In the present communication a simpler transference number equation is presented.

The Onsager theory for conductance yields the following limiting transference number equation

$$t=\frac{\lambda}{\Lambda}=\frac{\lambda_0(1-\alpha C^{\frac{1}{2}})-\beta(Z_1/Z_1+Z_2)C^{\frac{1}{2}}}{\Lambda_0(1-\alpha C^{\frac{1}{2}})-\beta C^{\frac{1}{2}}}, \quad (1)$$

in which t is the transference number, λ the equivalent conductance of the corresponding ion species of valence Z_1, Z_2 the valence of the other ion species, and α and β are the Onsager constants for the "time of relaxation" and electrophoretic effects, respectively. Neglecting terms of higher order than $C^{\frac{1}{2}}$ in an expansion yields

$$t=t_0-\frac{\beta t_0}{\Lambda_0}\left(\frac{Z_1}{(Z_1+Z_2)t_0}-1\right)C^{\frac{1}{2}}, \quad (1')$$

in which $t_0=\lambda_0/\Lambda_0$. It will be noted that only the electrophoretic term appears in this equation. Plots of t against $C^{\frac{1}{2}}$, however, generally show considerable curvature. To account for this fact, Longsworth[3] proposed the equation

$$t_0'=\frac{t\Lambda'+(\beta/2)C^{\frac{1}{2}}}{\Lambda'+\beta C^{\frac{1}{2}}}=t_0+BC, \quad (2)$$

in which $\Lambda'=\Lambda_0-(\alpha\Lambda_0+\beta)C^{\frac{1}{2}}$, based on the modified Onsager formula[1]

$$\Lambda_0=\frac{\Lambda+\beta C^{\frac{1}{2}}}{1-\alpha C^{\frac{1}{2}}}-BC.$$

He found it applicable to his very accurate measurements on strong uni-univalent electrolytes up to $C=0.10N$.

A simpler equation, also reducing to the theoretical limiting Eq. (1′), is the following

$$1/t=1/t_0+AC^{\frac{1}{2}}-BC, \quad (3)$$

in which $A=(\beta/l_1)[Z_1/(Z_1+Z_2)t_0-1]C^{\frac{1}{2}}$ and B is an empirical constant. For uni-univalent electrolytes in water at 25° $A=(59.79/l_0)(1/2t_0-1)$.

Using Longsworth's[4] transference measurements on NaCl, HCl, LiCl, KCl, KBr, KI, NH_4Cl and $NaC_2H_3O_2$, linear graphs result when the function $(1/t-AC^{\frac{1}{2}})$ is plotted against C, from which the empirical constants B are obtained. In every case the intercepts give values for the limiting transference number, t_0, in accord with those chosen by Longsworth. The comparison in Table I shows the excellent agreement between the experimentally determined values for the transference numbers and the corresponding ones computed from Eq. (3). It is interesting to note that the equation reproduces the slight minima observed for KI, KBr and NH_4Cl.

[1] T. Shedlovsky, J. Am. Chem. Soc. **54**, 1405 (1932).
[2] L. Onsager, Physik. Zeits. **27**, 388 (1926); **28**, 277 (1927).
[3] L. G. Longsworth, J. Am. Chem. Soc. **54**, 2741 (1932). See also, B. B. Owen, *ibid.* **57**, 2441 (1935).
[4] L. G. Longsworth, J. Am. Chem. Soc. **57**, 1185 (1935).

TABLE I. *Cation transference numbers of strong* $1-1$ *electrolytes in water at* 25°.

$1/t^+ = 1/t^+ + AC^{\frac{1}{2}} - BC; \quad A = (\beta/l_0^+)1/2t_0^+ - 1; \quad \beta = 59.79.$

ELECTROLYTE	C EQUIV./LITER	t^+ CAL.	t^+ OBS.
KCl	0.01	0.4903	0.4902
$A = 0.012$	.02	.4902	.4901
$B = .002$	.05	.4900	.4899
$t_0^+ = .4906$	.10	.4897	.4898
	.20	.4894	.4894
	.50	.4888	.4887
	1.00	.4882	.4883
NaCl	.01	.3918	.3918
$A = 0.312$	.02	.3903	.3902
$B = .250$	.05	.3875	.3876
$t_0^+ = .3963$	.10	.3851	.3854
	.20	.3827	.3821
LiCl	.01	.3290	.3289
$A = 0.749$	.02	.3262	.3261
$B = .453$	.05	.3211	.3211
$t_0^+ = .3368$	.10	.3164	.3168
	.20	.3112	.3112
HCl	.01	.8252	.8251
$A = -0.067$	.02	.8267	.8266
$B = -.058$	.05	.8293	.8292
$t_0^+ = .8210$	.10	.8315	.8314
	.20	.8336	.8337
NaAc	.01	.5538	.5537
$A = -0.110$	.02	.5550	.5550
$B = -.070$	.05	.5572	.5573
$t_0^+ = .5507$	.10	.5593	.5594
	.20	.5616	.5610
KI	.01	.4884	.4884
$A = 0.019$	.02	.4883	.4883
$B = .043$	.05	.4882	.4882
$t_0^+ = .4887$	.10	.4883	.4883
	.20	.4887	.4887
KBr	.01	.4832	.4833
$A = 0.027$	.02	.4831	.4832
$B = .069$	.05	.4831	.4831
$t_0^+ = .4837$	.10	.4833	.4833
	.20	.4841	.4841
NH_4Cl	.01	.4906	.4907
$A = 0.015$	.02	.4906	.4906
$B = .039$	.05	.4906	.4905
$t_0^+ = .4909$	.10	.4907	.4907
	.20	.4912	.4911

For higher valence electrolytes and certain abnormal uni-univalent salts such as silver nitrate, Eq. (3) is not in accord with the transference data if the theoretical Onsager values for the coefficients A are used. However, if A, as well as B, is taken as an empirical constant, the equation is useful in many cases. This is shown by the examples listed in Table II for $CaCl_2$,[4] $AgNO_3$ [5] and K_2SO_4.[6] The values for t_0^+ in the "observed" columns were obtained from the limiting conductances and ionic mobilities for these salts,[4, 6] while the constants A and B for Eq. (3) were found from the transference data by the method of least squares. Although the coefficients A are in all these cases considerably lower than would be expected from the Onsager theory, the equation is well in accord with the measurements and gives the correct limiting transference number values. For example, in the case of calcium chloride $t_0^+ = 1 - l_0Cl^-/\Lambda_0 = 1 - 76.34/135.84 = 0.4380$, which is in close agreement with the value 0.4376 obtained from the transference data alone, but the value of $A = 0.6113$ is quite different from the theoretical value $A = 0.965$.

TABLE II. *Cation transference numbers for calcium chloride, silver nitrate and potassium sulfate in water at* 25°.

$1/t^+ = 1/t_0^+ + AC^{\frac{1}{2}} - BC.$

C EQUIV./LITER	t^+					
	$CaCl_2$		$AgNO_3$		K_2SO_4	
	OBS.	CALC.	OBS.	CALC.	OBS.	CALC.
0	(0.4380)	0.4376	(0.4643)	0.4643	(0.480)	0.4780
0.01	.4264	.4264	.4648	.4648	.4829	.4826
.02	.4220	.4221	.4652	.4652	.4848	.4843
.05	.4140	.4141	.4664	.4664	.4870	.4871
.10	.4060	.4057	.4682	.4682	.4890	.4895
.20	.3953	.3952	—	—	.4910	.4916
.50	—	—	—	—	.4909	.4909
A	.6113		−.0085		−.2192	
B	.1411		.155		−.2001	

[5] D. A. MacInnes and L. G. Longsworth, Chem. Rev. **11**, 209 (1932).

[6] G. S. Hartley and G. W. Donaldson, Trans. Faraday Soc. **33**, 457 (1937).