The Shedlovsky Extrapolation Function

By Harry M. Daggett, Jr.1

In a recent note, Fuoss and Shedlovsky² have shown that in evaluating the limiting equivalent conductance, Λ_0 , and the dissociation constant, K, from conductance data of electrolytes in non-aqueous solutions, it is preferable to use the Shedlovsky³ extrapolation function rather than that⁴

a table of the function S(z) similar to that given by Fuoss⁴ for F(z).

Such a table has been constructed in the course of another investigation. Values of the function S(z) for the range $0.000 \leqslant z \leqslant 0.209$ are presented in Table I. Linear interpolation in this table is readily carried out to give S(z) for any z in this range. The values of S(z) so obtained should be significant to ± 1 in the fourth decimal.

TABLE 1

Values of the Shedlovsky Extrapolation Function, $S(z)$											
z	0.000	0.001	0.002	0.003	0.004	0.005	0.006	0.007	0.008	0.009	Diff.
0.000	1.0000	1.0010	1.0020	1.0030	1.0040	1.0050	1.0060	1.0070	1.0080	1.0090	10
.010	1.0101	1.0111	1.0121	1.0131	1.0141	1.0151	1.0161	1.0171	1.0182	1.0192	10
.020	1.0202	1.0212	1.0222	1.0233	1.0243	1.0253	1.0263	1.0274	1.0284	1.0294	10
.030	1.0305	1.0315	1.0325	1.0335	1.0346	1.0356	1.0367	1.0377	1.0387	1.0398	10
.040	1.0408	1.0418	1.0429	1.0439	1.0450	1.0460	1.0471	1.0481	1.0492	1.0502	11
.050	1.0513	1.0523	1.0534	1.0544	\mathbf{f} . 0555	1.0565	1.0576	1.0586	1.0597	1.0608	11
.060	1.0618	1.0629	1.0640	1.0650	1.0661	1.0671	1.0682	1.0693	1.0704	1.0714	11
. 070	1 , 0725	1.0736	1.0746	1.0757	1.0768	1.0779	1.0789	1.0800	1.0811	1.0822	11
.080	1.0833	1.0843	1.0854	1.0865	1.0876	1.0887	1.0898	1.0909	1.0920	1.0930	11
.090	1.0941	1.0952	1.0963	1.0974	1.0985	1.0996	1.1007	1.1018	1.1029	1.1040	11
.100	1.1051	1.1062	1.1073	1.1084	1.1095	1.1107	1.1118	1.1129	1.1140	1.1151	11
.110	1.1162	1.1173	1.1184	1.1196	1.1207	1.1218	1.1229	1.1240	1.1252	1.1263	11
. 120	1.1274	1.1285	1.1297	1.1308	1.1319	1.1331	1.1342	1.1353	1.1365	1.1376	11
. 130	1.1387	1.1399	1.1410	1.1421	1.1433	1.1444	1.1456	1.1467	1.1479	1.1490	11
. 140	1.1501	1.1513	1.1524	1.1536	1.1547	1.1559	1.1570	1.1582	1.1594	1.1605	12
. 150	1.1617	1.1628	1.1640	1.1652	1.1663	1.1675	1.1686	1.1698	1.1710	1.1721	12
. 160	1.1733	1.1745	1.1757	1.1768	1.1780	1.1792	1.1803	1.1815	1.1827	1.1839	12
.170	1.1851	1.1862	1.1874	1.1886	1.1898	1.1910	1.1922	1.1934	1.1945	1.1957	12
.180	1.1969	1.1981	1.1993	1.2005	1.2017	1.2029	1.2041	1.2053	1.2065	1.2077	12
. 190	1.2089	1.2101	1.2113	1.2125	1.2137	1.2149	1.2161	1.2174	1.2186	1.2198	12
.200	1.2210	1.2222	1.2234	1.2246	1.2259	1.2271	1.2283	1.2295	1.2308	1.2320	12

proposed by Fuoss. The values obtained for Λ_0 by these two procedures are identical, but those for K are sometimes significantly different. In the range $10^{-3} \leqslant K \leqslant 1$, the value of K obtained through the Shedlovsky function is preferable, while for $K \leqslant 10^{-3}$ either procedure is satisfactory.

The method of Shedlovsky is based on the solution of the equation⁵

$$\Lambda = \theta \Lambda_0 - \alpha (\Lambda/\Lambda_0) \sqrt{c\theta}$$

in terms of the function

$$S(z) = \left[\frac{z}{2} + \sqrt{1 + (\frac{z}{2})^2} \right]^2$$

= 1 + z + z²/2 + z³/8 - z⁵/128 + z⁷/1024 - ...

where $z = \alpha \sqrt{c\Lambda}/\Lambda_0^{3/2}$ (for details see ref. 2 or 3). While it is a relatively easy matter to calculate the required values of S(z) from the expanded form, the procedure is rather time-consuming when a large number of calculations are to be made. It would, therefore, be convenient to have available

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 (2) R. M. Fuoss and T. Shedlovsky. This Lournal. 71, 1496
- (2) R. M. Fuoss and T. Shedlovsky, This Journal, 71, 1496 (1949).
- (3) T. Shedlovsky, J. Franklin Inst., 225, 739 (1938).
- (4) R. M. Fuoss, This Journal, 57, 488 (1935).
- (5) The symbols used in this note are the same as those of Fuoss and Shedlovsky, ref. 2.
- (6) Ordinarily, it is not necessary to employ terms higher than z^2 in evaluating S(z) [H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed., Reinhold Publishing Corporation, New York, N. Y., 1950, p. 189; also cf. ref. 3, p. 742].

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RECEIVED MAY 28, 1951

Identification of Histidine and Tyrosine by Partition Chromatography of Their Azo Dyes^{1a}

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The identification of histidine and tyrosine in biological materials by paper partition chromatography has proven difficult because these aminoacids give weak color reactions with ninhydrin. A more sensitive spot-test method was described by Dent² who coupled histidine and tyrosine with diazobenzene-p-sulfonic acid to reveal their presence after separating them on a one-dimensional paper chromatogram.

One difficulty encountered in applying Dent's method² was that other amino-acids such as glycine and alanine gave yellow-orange spots when treated with diazotized sulfanilic acid and sodium carbonate and thus interfered with the identification of histidine which gave an orange-red spot. When irrigated with Dent's collidine-lutidine mixture on a one-dimensional chromatogram these

^{(1) (}a) Paper No. 2635 Scientific Journal Series, Minnesota Agricultural Experiment Station. (b) Aided by a grant from the U.S. Atomic Energy Commission, Contract No. AT(11-1)-42.

⁽²⁾ C. E. Dent, Biochem. J., 41, 240 (1947).