135. *The Determination of Dissociation Constants of Monobasic Acids. Part II. The Extrapolation Method.*

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An extrapolation method previously proposed is shown to apply accurately to conductivity measurements which are free from systematic errors, and to provide a very accurate interpolation equation of great value in the determination of cell constants. The use of benzoic acid, instead of the usual potassium chloride, is recommended as the standard electrolyte for this purpose. The effect of certain errors on the extrapolation method is discussed.

In a previous paper (Ives, J., 1933, 731; to be considered as Part I), a method was proposed for calculating the equivalent conductivity at zero concentration and the thermodynamic dissociation constant of a weak electrolyte from conductivity data. The method was based on Ostwald's dilution law, Onsager's ionic mobility equation (*Physikal. Z.*, 1927, **28**, 277), and the Debye–Hückel activity equation (*ibid.*, 1923, **24**, 185), and was shown to be capable of giving true dissociation constants independently of the absolute accuracy of the conductivity measurements and without reference to any recorded ionic mobility data. Fuoss and Kraus (*J. Amer. Chem. Soc.*, 1933, **55**, 476), just previously, had also devised a method for solving the same problem, and other modifications, designed to facilitate computation, have been suggested (Fuoss, *ibid.*, 1935, **57**, 488; Shedlovsky and Uhlig, *J. Gen. Physiol.*, 1934, **17**, 549; Shedlovsky, *J. Franklin Inst.*, 1938, **225**, 739).

The sensitivity to various experimental errors of the equation

$$\Lambda + aC_i^{\frac{1}{2}} = \Lambda_0 - \Lambda^2 C \times 10^{-2AC_i^{\frac{1}{2}}}/K(\Lambda_0 - aC_i^{\frac{1}{2}}) \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

(Ives, *loc. cit.*), where a and A are the constant of the Onsager and the Debye–Hückel equation respectively, and the other symbols have their usual significance, has been studied in detail by Kilpatrick (*J. Chem. Physics*, 1940, **8**, 306), with confirmation of the properties originally claimed for this equation. Other similar methods have been examined by Belcher (*J. Amer. Chem. Soc.*, 1938, **60**, 2744). It is now established that these extrapolation methods can be applied satisfactorily to the determination of true dissociation constants and are of unique value when no independent ionic mobility values are available, as in the study of many non-aqueous solutions, and in certain other special cases (see following paper). Restrictions are imposed by the failure of the Debye–Hückel and the Onsager limiting equation at higher concentrations; the use of empirical extensions of these equations is not generally advisable. Nevertheless, equation (1) applies with considerable accuracy up to concentrations of the order of 3—5 × 10^{-3} equiv./l., within a range in which very precise measurements can be made with modern conductivity methods.

The validity of the equation can be tested in two ways. In the above form it can be used for the extrapolation of conductivity data and the determination of Λ_0 and K, which can be compared with the values obtained by the ordinary methods. Alternatively, it can be rearranged into

$$\Lambda = [-K\Lambda_x + \Lambda_x\sqrt{K(K + 4C \times 10^{-2AC_i^{\frac{1}{2}}})}]/2C \times 10^{-2A\sqrt{C_i}} \quad . \; . \; . \; . \; . \quad (2)$$

where $\Lambda_x = \Lambda_0 - aC_i^{\frac{1}{2}}$, and used to calculate values of equivalent conductivity at any concentration, C, from Λ_0 and K determined by the usual methods. Calculated and experimental values of Λ can then be compared. The results of such tests are shown in the following table, the data used being those of Shedlovsky (*J. Amer. Chem. Soc.*, 1932, **54**, 1411) and of Brockman and Kilpatrick (*ibid.*, 1934, **56**, 1483) on acetic and benzoic acids respectively.

Acetic acid.

	Obs.	Calc.
$K \times 10^5$	1·753	1·747
Λ_0	390·59	391·02

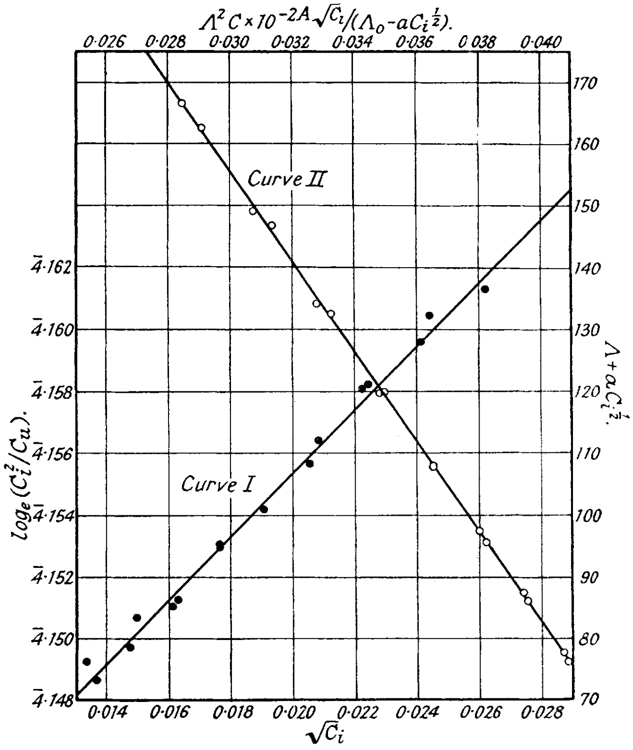
$C \times 10^4$.	Λ, obs.	Λ, calc.	$C \times 10^4$.	Λ, obs.	Λ, calc.
34·4065	27·19	27·21	2·1844	96·47	96·52
24·1400	32·21	32·23	1·5321	112·02	112·09
13·6340	42·215	42·22	1·1135	127·71	127·68
10·2831	48·13	48·16	0·2801	210·32	210·35

Benzoic acid.

	Obs.	Calc.
$K \times 10^5$	6·312	6·314
Λ_0	382·10	382·05

$C \times 10^4$.	Λ, obs.	Λ, calc.	$C \times 10^4$.	Λ, obs.	Λ, calc.
10·729	82·94	82·93	3·8108	127·85	127·85
9·9902	85·54	85·54	2·6281	147·66	147·66
7·6027	96·20	96·19	2·1148	160·14	160·09
3·9045	126·60	126·61	1·9112	166·03	166·07
			0·95887	209·32	209·31

It will be seen that the agreement between Λ, obs. and Λ, calc. at the experimental concentrations is of the highest order of accuracy. There can be no doubt that equation (2) expresses the conductivity of weak uni-univalent electrolytes, within a restricted concentration range, and in the absence of disturbing factors, with very considerable precision. It is strongly urged that this equation, applied to the above data for benzoic acid, provides the best available means of calibrating conductivity cells of low constant, since it permits the accurate interpolation of one of the best series of conductivity measurements which have been made. The equation can be solved for Λ by a fairly simple series of successive approximations. The great advantages of benzoic acid over the usual potassium chloride as a standard electrolyte are immediately obvious. This easily purified, non-hygroscopic substance of low density is a weak electrolyte; the gradient of its specific conductivity–concentration curve is much less than that of a strong electrolyte, the concentrations of the calibration solutions are correspondingly greater, and no solvent correction is necessary. It is clear that these properties provide a very substantial gain in accuracy and ease of manipulation, and facilitate the desirable procedure of covering the widest possible resistance range in the calibration experiments.



A source of error in the application of equation (1) to extrapolation has not hitherto been mentioned. Although an absolute error of 1% in the conductivity measurements has a negligible effect on the value of the dissociation constant obtained (Ives; Kilpatrick; *locc. cit.*), a non-uniform error, affecting one conductivity range more than another, is very much more significant. An error of this type is likely to arise from the direct earthing of the bridge circuit, and the Wagner earthing system (*Z. Elektrochem.*, 1926, **32**, 1001; Jones and Josephs, *J. Amer. Chem. Soc.*, 1928, **50**, 1049; Shedlovsky, *ibid.*, 1930, **52**, 1793) has been designed to deal with this difficulty. Nevertheless, the direct earth is in frequent use, and the errors produced are generally far too small seriously to affect ordinary conductivity measurements and calculations. If, however, extrapolation methods are to be applied to the conductivity measurements, the situation is entirely different, because these methods are peculiarly sensitive to errors of this kind, to a greater extent the weaker the electrolyte and the longer the extrapolation. The conductivity results reported in Part I (*loc. cit.*) were adversely affected in this manner: the dissociation constant of benzoic acid was found to be 6·53 × 10^{-5}, a result confirmed in repeated experiments carried out under the same conditions, but which is in poor agreement with the value for this constant which must now be accepted (6·312 × 10^{-5}, Brockman and Kilpatrick, *loc. cit.*; 6·295 × 10^{-5}, Saxton and Meier, *J. Amer. Chem. Soc.*, 1934, **56**, 1919; 6·373 × 10^{-5}, Jeffery and Vogel, *Phil. Mag.*, 1934, **18**, 901; 6·27 × 10^{-5}, Dippy and Williams, J., 1934, 1888). The measurements reported in the following paper were carried out under the same conditions and will also be subject to this error, which will, however, be negligible in the case of acids with dissociation constants greater than 10^{-3} (cf. Belcher, *loc. cit.*), and probably significant in only one of the cases studied.

A test for constant conductivity errors has been suggested by Kilpatrick (*loc. cit.*) in the linearity of the plot of $\log_{10}(C_i^2/C_u)$ against $C_i^{\frac{1}{2}}$; the application of this to the case of *trans*-1-cyano*cyclo*hexane-2-carboxylic acid ($K = 1{\cdot}365 \times 10^{-4}$) is shown in curve I in the figure. The points are experimental and the continuous line has the theoretical Debye–Hückel slope. Curve II is a graphical representation of equation (1), and should, of course, be strictly linear. Since the result of this test is reasonably satisfactory, the new dissociation-constant data are advanced as being accurate to within 2%, and probably considerably better than this in the case of the stronger acids.

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