Computation of Dissociation Constants and Equivalent Conductances at Infinite Dilution

Iterative methods [1, 2, 3] are available for the calculation of thermodynamic dissociation constants (K) of weak or moderately strong monoprotic acids in dilute aqueous solution from $(C, \Lambda)_T$ primary data where C is the molarity (g-mole liter^{-1}) and Λ the equivalent conductance (ohm^{-1} cm^2 g-equiv^{-1}) of the acid solution at a given constant temperature (T). These methods are advantageous over the older alternative whereby the equivalent conductance at infinite dilution (Λ_0) is calculated from the individual limiting ionic mobilities of the ions involved, of which that for the anion has to be determined by an additional series of measurements with, for example, the sodium salt.

Accurate K data obtained by the Ives method [1] have been used for the evaluation of standard molar Gibbs free energies, enthalpies, entropies and specific heats of ionisation of the acids concerned [4]. The demand for a sufficiently high level of significance of these functions, which depends on the accuracy of K, necessitates, in turn, a close examination of the calculational accuracies on which the latter depends, and hence a comparison of the results from the various methods available. Where comparison of K and Λ_0 values (and other functions derived from them) of one acid with those of others is of interest, re-calculation, in some instances, of such values which have been based on older values of the constants of the equations used is necessary. Further, alternative calculations are sometimes needed to examine numerically the effect of the *ad hoc* choice of a value for the "ion-size" parameter [5]. These requirements may be met in a practical and efficient way only by use of computers. Three programs have now been written and used by the author for calculations along these lines. Two of these are based on the Ives method, the first being in the *CHLF*3 Atlas Autocode (suitable for the Atlas Computer, University of London) and the latter in ALGOL 803 (suitable for the Elliott 803B, University of Khartoum). The latter of these is more developed than the first inasmuch as it contains a stage for the calculation (from adopted fundamental physical constants and solvent viscosity and dielectric constant at any given working temperature) of the constants (A) of the Debye–Hückel equation for the activity coefficient, and (α) and (β), the relaxation and electrophoretic coefficients in the Debye–Hückel–Onsager limiting law. The values of these constants are not available for all temperatures from tables. The program

further calculates the standard errors of both K and Λ_0 and the value of the $x - y$ correlation coefficient (R) as a test for the extent of distortion from linearity, if any, of the fitted equation. The program also lists out the regression values of y and their deviations from the corresponding experimental values, the deviations being expressed as fractional errors of y. The third program is based on the Shedlovsky method and is similar in its development to the last. It is also in ALGOL 803. All three programs are available with complete description and listing. A fourth program based on the Fuoss–Shedlovsky method [3] is also in preparation along the same lines. Comparison of results obtained for certain chosen acids will be presented elsewhere.

REFERENCES

1. D. J. G. IVES, *J. Chem. Soc.*, (1933), 731.
2. T. SHEDLOVSKY, *J. Franklin Inst.* **225** (1938), 739.
3. R. M. FUOSS, *J. Amer. Chem. Soc.* **57** (1933), 488; H. E. WORTH, *J. Phys. Chem.* **65** (1961), 1441.
4. F. S. FEATES AND D. J. G. IVES, *J. Chem. Soc.*, 1956, 2798; D. J. G. IVES AND P. D. MARSDEN, *J. Chem. Soc.*, 1965, 649; D. J. G. IVES AND P. G. N. MOSELEY, *J. Chem. Soc.*, 1970 (in press).
5. E. J. KING, Acid-base equilibria *in* "The International Encyclopaedia of Physical Chemistry and Chemical Physics," Topic 15, (E. A. GUGGENHEIM, J. E. MAYER, AND F. C. TOMPKINS, eds.), p. 34, Pergamon Press, London/New York, 1965.

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