

Citation Classics

Paul M A & Long F A. H_o and related indicator acidity functions.
Chem. Rev. 57:1-45, 1957.

The authors review the literature pertaining to indicator acidity functions and their applications to elucidating the mechanisms of acid catalysis. [The SC[®] indicates that this paper was cited 699 times in the period 1961-1976.]

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"This article, together with a companion article on the application of the H_o acidity function to kinetics and mechanisms of acid catalysis,¹ reviewed twenty-five years of research stemming from the establishment by L.P. Hammett and A.J. Deyrup in 1932² of quantitative means of extending acidity measurements to highly acid solutions through a sequence of indicators with progressively decreasing base strengths, selected according to criteria minimizing extraneous medium effects not immediately related to acidity. Conspicuous among such medium effects are those associated with the charge type of the indicator; Hammett and Deyrup's H_o acidity

function (a logarithmic measure of acidity reducing to pH in dilute aqueous solutions) is derived from indicators of charge type: $B^{\ominus} + H^{\oplus} \rightleftharpoons BH^{\oplus}$

"In concentrated aqueous solutions of strong acids, H_o is observed to decrease (indicating increasing acidity) with increasing acid concentration C significantly more rapidly than does $-\log C$, and furthermore the H_o values for the different strong acids are spread apart. Since the rates of certain acid-catalyzed reactions were found to correlate rather well with the behavior of H_o whereas the rates of others showed poor correlation, interest grew in the possibility of using the presence or absence of such correlation as evidence for the particular mechanism of acid catalysis involved. Our review was prepared at a time when interest in acid catalysis had been renewed by the ideas of C.K. Ingold and his associates on the mechanisms of homogeneous organic reactions in general. By assembling and critically evaluating the published data on acidity functions and their applications to the study of acid catalysis (252 references), we evidently helped many investigators in further research on the subject. Indicator acidity functions of various types have since been determined and redetermined with improved precision by modern spectrophotometric methods, and found to be less general than was originally hoped. Also, many interesting complexities have been discovered in the mechanisms of acid-catalyzed reactions. An updated review of the field is now available, published in 1970 by C.H. Rochester.³

REFERENCES

1. Long F A & Paul M A. Application of the H_o acidity function to kinetics and mechanisms of acid catalysis. *Chem. Rev.* 57:955-1010, 1957.
2. Hammett L P & Deyrup A J. A series of simple basic indicators.
 1. The acidity functions of mixtures of sulfuric and perchloric acids with water; 2. Some applications to solutions in formic acid. *J. Am. Chem. S.* 54:2721-39, 4239-47, 1932.
3. Rochester C H. *Acidity functions*. New York: Academic Press, 1970. 310 pp.