This Week's Citation Classic®


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The book is a practical manual intended for those who, without previous experience, wish to determine ionization constants (pKₐ values). More advanced instruction is also provided for those who wish to extend their range of techniques. [The SCI® indicates that this book has been cited in over 3,130 publications.]

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In the first half of the 1940s mass production of glass-electrode potentiometer assemblies (also known as "ion activity meters" or "pH kits"), followed by production of the ultraviolet spectrometer, made it easier to determine ionization constants accurately and quickly. Soon, textbooks of physical chemistry and monographs on electrochemistry began to describe these methods. Unfortunately, the examples that they provided were too few to illustrate the full scope of the methods, and they lamentably failed to record the many precautions and checks that must be observed to obtain acceptable results.

After 20 years of experience with these methods, during which we came face to face with many snags that were eventually overcome, my colleague E.P. Serjeant and I were prevailed upon to publish a practical manual that would describe and evaluate all known methods. Our first edition (1962)—the Classic—was entitled Ionization Constants of Acids and Bases and was published by Methuen in London and then by Wiley in New York.

As time went by, we took the opportunity to improve the book by including computer programs to replace the more difficult calculations. We also described newer methods, such as Raman and nuclear magnetic resonance spectrometry, and thermometric titrations, which offer help in difficult cases. In addition, we incorporated methods for determining the stability constants of the complexes that metal cations form by chelation with organic ligands. The second and third editions of the book were retitled The Determination of Ionization Constants.1,2

We took pains to write our book in simple language so that any chemist or biochemist who needed a hitherto unrecorded ionization constant could quickly and easily learn how to determine it. Because no previous experience is necessary in determining ionization constants, researchers have often used the book for this purpose. It has also served well for the in-service training of those technicians and technical officers who are required to provide an institute with an ionization constant service. The book offers help in selecting apparatus, setting out the experimental results, making the calculations from these results, and finally, checking them for consistency and reliability. A much-appreciated feature is our incorporation of a course for beginners, so that they can gain experience with inexpensive materials before tackling precious unknowns.3

The book also provides guidance on the interpretation of ionization constants. We show how they relate to solubility, how the degree of ionization at any pH value can be calculated (a feature that biologists like), and how ionization constants can help decipher unknown chemical structures. We note, after examining papers that cite our book, that many authors are seeking to improve the properties of a known drug or trying to discover a new one. These are activities in which knowledge of ionization constants is accorded much importance. Because our book is a practical manual, best kept on the laboratory bench, we discuss the theory of ionization only briefly, but we refer readers to the excellent monographs by King4 and Bates.5

Both authors of this Classic book are now officially retired, but we feel lucky that we can continue our work.