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This Week's Citation Classic®

Butler J N. *Ionic equilibrium: a mathematical approach.*
Reading, MA: Addison-Wesley, 1964. 547 p.
[Tyco Laboratories, Inc., Waltham, MA]

A rigorous use of mass, charge, and equilibrium equations, followed by simplifications based on the relative size of terms, results in a straightforward approach to calculations of pH, titration error, solubility, and complex formation in aqueous solution. [The *SCI*® indicates that this book has been cited in more than 330 publications.]

Mass and Charge Balances Clarify Ionic Equilibrium Calculations

James N. Butler
Division of Applied Sciences
Harvard University
Cambridge, MA 02138

When I was an undergraduate, I was good in math but not in analytical chemistry. Not only did my limestone analysis total 80 percent instead of 100 percent, but, I could not seem to grasp the principles behind weak acid and solubility calculations. The equations given in texts were always for special cases, and, while I could learn them by rote, I could not figure out how they could be generalized to other concentration ranges or mixtures of substances. For example, I could find the pH of 0.01 M acetic acid, but not the pH of a mixture of 0.1 M acetic acid with 0.01 M sulfuric acid.

In graduate school at Harvard, James Lingane showed me a book by J.E. Ricci, *Hydrogen Ion Concentration,*[1] that seemed to have some of the answers, but Ricci had his own notation, and his equations were more complicated than those in the quantum mechanics course I was taking at the same time. This did not seem right to me. I admired Herbert Goldstein's *Classical Mechanics,*[2] which derived its important results directly from Newton's laws and relegated many of the complicated equations to problem sets. I wished that I could find a book like this, only about pH and solubility.

As a young assistant professor at the University of British Columbia, I was asked to teach analytical chemistry—including precisely those problems I had found so difficult as a student. I tried very hard to be rigorous, and I'm sure the students suffered as I learned the pitfalls of such a path. Fortunately, Lars Gunnar Sillen in Stockholm had written a chapter in the M. Kolthoff and P.J. Elving *Treatise on Analytical Chemistry,*[3] which gave me many of the clues I needed. The most important new item was a graphical display of the relative size of all the concentrations in an aqueous system as a function of pH. It even provided a numerical answer to some types of problems at the crossing of two lines.

I set out to write a little book that would explain these things to undergraduate students of analytical chemistry but got so involved that, when I finally felt I was finished, the manuscript was over 700 pages long. Addison-Wesley published this long book as *Ionic Equilibrium.* A few months later, I gave them a 100-page manuscript called *Solubility and pH Calculations, which was the book I had originally set out to write.**

Both these books stayed in print for 22 years—until 1986—and still are cited (27 citations for *Ionic Equilibrium* and 3 for *Solubility andpH\n* 1989). These textbooks have been used by researchers studying topics from acid rain[5] to polymer science to hydrometallurgy. One of the most common reasons for citation is the calculation of activity coefficients for ions in moderately dilute solution—for example, in the limestone neutralization of acid waters.[6] It would be interesting to know in more detail why a book intended for undergraduate analytical chemistry students has been a significant source of information for researchers in many branches of chemistry for over 25 years—but that's another story!

t. **Ricci J E.** *Hydrogen ion concentration.* Princeton. NJ: Princeton University Press, 1952.
2. **Goldstein H.** *Classical mechanics.* Cambridge. MA: Addison-Wesley, 1950. 399 p. (Cited 1,815 times.) [See also: **Goldstein H.** Citation Classic. *Current Contents/Engineering, Technology & Applied Sciences* 12(2): 16, 1981. Reprinted in: *Contemporary classics in engineering and applied sciences.* (Thackray A, comp.) Philadelphia: ISI Press, 1986. p. 47.]
3. Sillen L G. Graphical presentation of equilibrium data. (Kolthoff I M. Elving P J & Sandell E B. eds.) *Treatise on analytical chemistry.* New York: Interscience Encyclopedia, 1959.
4. **Butler J N**. *Solubility and pH calculations.* Reading. MA: Addison-Wesley. 1964.
5. **Tanaka S, Yamanaka K & Hashimoto Y**. Measurement of concentration and oxidation rate of S(IV) in rainwater in Yokahama. Japan. *ACS Symp. Ser.* 349:158-69. 1987.
6. **Santore L, Volpkelli G & Caprio V.** Limestone neutralization of acid waters in the presence of surface precipitates. *Water Res.* 21:641-7, 1987.

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