A new predictive formula for calculation of equilibrium pH: a step back in time

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TO THE EDITOR: Nguyen et al. (4) report “the first quantitative approach that can predict the equilibrium [H+] based on the partitioning of H+ buffering among the different buffer pairs in solution.”

To claim no previous method could calculate final equilibrium concentrations from starting preequilibrium concentrations is incorrect, since the ability to perform such calculations was achieved over 50 years ago. None of the classic texts on equilibrium calculations by Bjerrum, Ricci, Stumm, Guenther, Butler, or others (1–3, 6, 9) are referenced, but all of these provide better and more general strategies to accomplish the same goal as Nguyen et al. The classic methods published previously utilize half the number of material balance equations advocated by Nguyen et al. and produce exact, but less cumbersome solutions. These approaches obtain the final equilibrium concentrations more directly and written explicitly in terms of starting concentrations. Nguyen et al. also present a simple titration experiment they imply is novel, although equivalent experiments have been performed before (5). Despite the authors’ claim of physiological relevance, their equation does not explicitly include the carbon dioxide equilibrium, arguably the most important buffer system physiologically.

The authors state that “the Stewart strong ion formulations can only describe (rather than predict) the equilibrium pH,” but the Stewart method (8) for calculating acid-base balance is equivalent to the classic methods (2, 9, 10). They also assert the strong ion difference does not determine a specific proton concentration. For their mixture in Table 3, assuming constant Kw, the strong ion difference, which is numerically equal to the total titratable base, which is numerically equal to the opposite of the total titratable acid, which is numerically equal to the added analytical HCl concentration, which represents the amount of HCl added to the system preequilibrium, will determine the final equilibrium pH (2, 3, 6, 8, 9). Calculation using the Stewart method, or any equivalent relationship, is exact and is predictive. It has also been around for some time. The method Stewart applied to physiology nearly 30 years ago, including the carbon dioxide equilibrium, was known to environmental chemists at least 10 years before that (8, 9).

Nguyen et al. may misunderstand the traditional use of these equations in clinical medicine. The interest in calculating variables such as the base excess and strong ion difference from equilibrium concentrations stems from applying equilibrium equations in the most relevant way. As explained by Siggaard-Andersen and Fogh-Andersen (7), the goal of equilibrium calculations such as the base excess approach or Stewart method in current clinical acid-base assessment is to quantify and characterize the metabolic component of an acid-base disorder, not to calculate final buffer concentrations or pH as implied by the authors. In summary, Nguyen et al. should be congratulated for their interest in applying rigorous chemical principles to physiology, but they have basically taken a step back in time to over a half century ago.

REFERENCES