

## The Adjustment for Systematic Errors in pH Measurements

G. ANDEREGG

Laboratorium für Anorganische Chemie  
Eidgenössische Technische Hochschule Zürich,  
CH-8092 Zürich, Switzerland

Dr. Lee's reply<sup>1</sup> to my comments<sup>2</sup> on the computerized refinements of pK values can lead to the unreliable conclusion that this type of improvement is feasible and appropriate. To avoid misunderstandings and because of the wide use of computerized methods, it seems worthwhile to come back to this question.

In her paper Dr. Lee,<sup>3</sup> as a result of a first refinement from two series of measurements with 3-bromo-5-sulfosalicylate ion (HC), reports the following constants:

- I series (128 points)  
 $\log \beta_{-11} = -10.473 \pm 0.002$   
II series (219 points)  
 $\log \beta_{-11} = -10.464 \pm 0.001$ .

As "best value" the "mean" value of these two results was given as:

$$\log \beta_{-11} = -10.467 \pm 0.001.$$

As the difference of 0.009 in  $\log \beta_{-11}$  for the two series is likely to arise from a systematic error, it is not justified to give such a low "standard deviation". Indeed, one has no possibility of knowing the exact value of  $\log \beta_{-11}$  and the sign of the systematic error in each single series! Calculating the mean value, one makes a precise but arbitrary choice of the values of these errors. This makes the "mean" value and its standard deviation doubtful.

Concerning the reply given by Dr. Lee to my comments, I should like to point out that the arguments of Sillén<sup>4</sup> which are quoted refer to analytical errors and not to  $E_0$  values. With the exclusion of that case, the error sum  $U = \sum (E_{\text{calc}} - E_{\text{exp}})^2$  can be used confidently:<sup>5-7</sup>

Returning to the question of elimination of systematic errors, what, therefore, can be done? We have to distinguish between (a) errors in analytical concentrations and (b) errors in  $E_0$ . The errors under (a) can be eliminated by variation of the values for the analytical concentrations: this occurs also if only data of a single titration curve are considered. Inserting the exact concentrations of the components, the involved constants show a lower standard deviation. It is then possible to find

the "best values" for the analytical concentrations of each titration, which correspond to a new lower minimum of  $U$ .<sup>4</sup> The situation is very different for (b) as already discussed. The systematic error for emf measurements with the glass electrode seems to be connected with the properties of this electrode, which shows fluctuations in  $E_0$  with time.<sup>8</sup> Even if other sources of errors<sup>9,10</sup> have been fully experimentally eliminated, the calibration and actual determination, which involve two or more measurements, already give a systematic error of at least 0.01–0.02 pH unit.<sup>9</sup> For instance, in the case considered of the determination of a pK value of a monoprotic acid, an error of 0.01–0.02 pK unit is to be expected. The equilibrium data obtained in this way are normally sufficiently accurate for the usual applications and goals. To obtain more exact values other devices have been proposed.<sup>8</sup> This can be done for pH measurements with glass electrodes<sup>11</sup> by correcting for the time dependence of the cell potential<sup>8</sup> or using electrodes with low resistance<sup>11</sup> as well as with hydrogen electrodes because in these cases no systematic error seems to be present in the emf measurements.

1. Lee, Y.-H. *Acta Chem. Scand. A* 33 (1979) 75.
2. Anderegg, G. *Acta Chem. Scand. A* 33 (1979) 74.
3. Lee, Y.-H. *Acta Chem. Scand. A* 30 (1976) 586.
4. Brauner, P., Sillén, L. G. and Whiteker, R. *Ark. Kemi* 31 (1969) 365.
5. Sillén, L. G. *Acta Chem. Scand.* 16 (1962) 159.
6. Gabon, S. *Acta Chem. Scand.* 17 (1963) 2181.
7. Schorsch, G. and Ingri, N. *Acta Chem. Scand.* 21 (1967) 2727.
8. Baes, C. F., Jr. and Meyer, N. J. *Inorg. Chem.* 1 (1962) 780.
9. Bates, R. G. *Determination of pH, Theory and Practice*, Wiley, New York 1964.
10. Bates, R. G., Vega, C. A. and White, D. R., Jr. *Anal. Chem.* 50 (1978) 1295.
11. Covington, A. K. and Prue, J. E. *J. Chem. Soc.* (1955) 3696, 3701.

Received January 25, 1980.