

## On the Computerized Refinement of pK Values

G. ANDEREGG

Laboratorium für Anorganische Chemie,  
Eidgenössische Technische Hochschule Zürich,  
CH-8006 Zürich, Switzerland

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The investigation of ionic equilibria by use of potentiometric titrations is often complicated by the presence of systematic experimental errors. This can be overcome by introducing in the mathematical analysis of the data some adjustable parameters. They are: the analytical errors in the composition of the solution and the error in the value of  $E_0$  for the cell used (each assumed to have the same value for all points of a titration curve).

A similar type of refinement was used in a paper<sup>1</sup> published in this journal for the determination of the pK value of 3-bromo-5-sulfosalicylate ion, obtaining a value with a standard deviation of 0.001 log units. We will discuss here, using the same symbols as that work, only the dubiousity in adjusting  $E_0$ . For data referring to one titration curve of a monoprotic acid a change of  $E_0$  by an amount equal to  $\delta E_0$  leads to an equal change of the values of pH and of  $\log \beta_{-11}$ :  $\log \beta_{-11} = \log([C^{-3}]/[HC^{2-}]) - \text{pH}$ , whereas the standard deviation remains constant. Indeed, the values of  $\log([C^{3-}]/[HC^{2-}])$  remain practically unchanged for low values of  $\delta E_0$  of the magnitude of  $\pm 1$  mV. In the cases where different curves are used, this type of adjustment can be carried out in different ways, each giving different mean values for  $\beta_{-11}$ , without any possibility of judging the reliability of the chosen  $\delta E_0$  and of the value of  $\beta_{-11}$ . This can be understood by considering the simple case of two experimental titrations giving without adjustment of  $E_0$ :  $\log \beta_{-11} = -10.470$  and  $-10.480$ , respectively, with a standard deviation in both cases of 0.001. The difference in  $\log \beta_{-11}$  can be eliminated using values of  $\delta E_0$  which compensate for it. With  $\delta E_0 \leq 1.2 \text{ mV}^1$  ( $= 0.02$  log units) and appropriate choice of  $\delta E_0$  for the two titrations, it is possible to obtain for  $\log \beta_{-11}$  mean values which cover approximately the range  $-10.460$  to  $-10.490$ , each with a standard deviation of  $\sim 0.001$ . From all these different values for  $\log \beta_{-11}$  it is impossible to choose the best one and this remains also true if the number of titrations is higher! For this reason this reduction of the standard deviation to 0.001 seems to be an artifact. The whole procedure is further illusory in consideration of the low precision of the pH value of the borax solution used for the cell standardization which is  $9.00 \pm 0.02$ !