

Comments on the Refinement of pK Values

Y. H. LEE

Swedish Water and Air Pollution Research
Laboratory (IVL), P.O.Box 5207,
S-402 24 Gothenburg, Sweden

I would like to thank Professor Anderegg for his interest in my paper.¹ Attempting to adjust possible systematic errors, Lars Gunnar Sillén and his school introduced in the sixties a general minimizing program, LETAGROP, which was used in my paper. According to this method the $\beta_{-1,1}$ were sought as the value, which gave a minimum for the error squares sum $U_H = \sum (H_{\text{calc}} - H_{\text{exp}})^2$. The program also permits adjustment of systematic errors, such as E_0 , etc. In different combinations of parameters adjusted, a corresponding error squares sum U was obtained. That combination, giving the lowest error squares sum, U_{min} , was considered to be the "best" one.

As Sillén *et al.* point out,² if U is defined instead by the deviation in E , i.e. $U_E = \sum (E_{\text{calc}} - E_{\text{exp}})^2$, then there would be an infinity of sets of values that would give the same U' , corresponding to a level valley bottom in multidimensional space. Thus, there would be obviously no real improvement of the fit. This is also the simplified case that Professor Anderegg mentioned in his comment.

After adjusting systematic errors and finding $\log \beta_{-1,1}$, the calculation also gives the standard deviation $\sigma(\log \beta_{-1,1})$. The obtained "best" value was taken to be $\log \beta_{-1,1} \pm 3\sigma$, where 3σ indicated random errors. For definitions of the standard deviation, see Sillén.³

1. Anderegg, G. *Acta Chem. Scand. A* 33 (1979) 74.
2. Brauner, P., Sillén, L. G. and Whiteker, R. *Ark. Kemi* 31 (1969) 365.
3. Sillén, L. G. *Acta Chem. Scand.* 16 (1962) 159.

Received October 27, 1978.