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Wentworth W E. Rigorous least squares adjustment: application to some non-linear equations, I and II. *J Chem. Educ.* **42**:96-103, 162-7, 1965
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Many equations in chemistry and related physical sciences are non-linear with respect to various parameters This article describes how a least squares adjustment can be carried out rigorously using properly weighted observations The procedure is illustrated by application to a kinetic rate expression and the Arrhenius Equation [The *SCI*® indicates that these papers have been cited in over 340 and 115 publications, respectively]

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While I was a graduate student in chemistry, I had several occasions to fit data to equations using the principle of least squares. However, I noticed that upon rearrangement of the equation I would obtain a different least squares solution. This was puzzling to me and I never could get the problem resolved.

Upon leaving graduate school in 1956, I decided to work as an applied mathematician in the "new" missile industry. Recall that digital computers were in their infancy at that time and all programming was carried out in machine language. It was during this employment as an applied mathematician that I was introduced to the generalized least squares adjustment. It became immediately apparent that there was only one least squares adjustment and the different least squares solutions that I had obtained in graduate school were simply the neglect of *weighting the residuals*. Once the appropriate weighting factors are used there is only one solution. This assumes that the errors are sufficiently small that a Taylor's Series expansion including only the first order terms is satisfactory. Generally, this is the case if the parameters are to be defined with reasonable precision.

The generalized least squares adjustment was described thoroughly in a book by Deming,[1] which was written in 1943, well before the advent of digital computers. Since the calculations required to carry out non-linear least squares adjustments are very tedious, it is understandable that the technique was not used extensively. In retrospect, I believe the reason for the attention given to my paper was a matter of timing. In the early to mid-1960s digital computers were finding their way into universities, and it was only natural that non-linear least squares would appeal to experimentalists who for years had struggled with less satisfactory approximation methods.

My intent in writing the article was to present the subject at a level that the average experimental chemist could understand. Most chemists at that time did not have a background in matrix algebra, and for that reason I tried to avoid the extensive use of matrices. The popularity of the article was apparent when 250 reprints were exhausted within two months and another 250 at the end of a year. Even today I get an occasional reprint request. A recent book based on this paper has been written by Edwin Meyer of DePaul University.[2] Also, there is a computer software package written using this non-linear least squares adjustment.

1 **Deming W E.** *Statistical adjustment of data* New York Wiley, 1943. 261 p (Cited 695 times since 1955)
2 **Meyer E F.** *A practical guide to curve-fitting for chemists*
Chicago Department of Chemistry, DePaul University, 1984 207 p