Numerical Differentiation Of Equally Spaced And Not Equally Spaced Experimental Data [3]

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NUMERICAL DIFFERENTIATION OF EQUALLY SPACED AND NOT EQUALLY SPACED EXPERIMENTAL DATA

SIR: Table I in our paper showed the effect of round-off error on the least square coefficients. The possibility of obtaining poor estimates of these coefficients was illustrated by contrasting coefficients which were calculated in single precision arithmetic by elimination with a second set of coefficients which were calculated by scaling and using double precision arithmetic. Scaling helps to reduce round-off error when the range is narrow. However, the range of experimental data often covers several orders of magnitude, in which case scaling is of little help (Draper and Smith, 1967, p. 144). Table I clearly makes the point that the investigator should be certain that he is really obtaining meaningful coefficients by his computational procedure.

In regard to Winski's other point, ϵ was carefully defined as the error in the model, Equation 2 (Graybill, 1961). Our quoted statement is correct as stands, because the only way to reduce ϵ for a given set of data is to increase m. As m increases, the value of the determinant of $(X' X)$, which is equal to the product of the eigenvalues of $(X' X)$ (Hildebrand, 1963), also decreases. Ralston (1965) shows that $(X' X)$ when normalized can be approximated by the principal minor of the Hilbert matrix, which is the classic example of an ill-conditioned matrix. The value of the determinant of $(X' X)$ approaches zero as m increases because the value of the smallest eigenvalue decreases (Lapidus, 1962). The solution to Equation 3 in the paper

$$(X' X)\,(\hat{B}) = (X' Y) \qquad (1)$$

may be written as:

$$(\hat{B}) = (X' X)^{-1}\,(X' Y) \qquad (2)$$

where the inverse $(X' X)^{-1}$ is defined as the adjoint of $(X' X)$ divided by the determinant of $(X' X)$ (Hildebrand, 1963). Obviously as the determinant of $(X' X)$ approaches zero, the inverse elements increase in magnitude and thus become more sensitive to round-off error.

Thus, we feel the points raised by Winski were correctly handled in our paper.

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MECHANISM IN THE OXIDATION OF PARTS-PER-MILLION QUANTITIES OF NITRIC OXIDE

SIR: In a paper by Morrison, Rinker, and Corcoran (1966), the empirical equation for the rate of oxidation of parts-per-million quantities of nitric oxide in the presence of nitrogen and oxygen was found to be of the following form:

$$-dC_{NO}/dt = 2k_7K_3C_{NO}^2C_{O_2} + k_6K_4K_5C_{NO}C_{NO_2}C_{O_2} \qquad (1)$$

A mechanism was proposed. In later correspondence Norman Cohen and Julian Heicklen of the Aerospace Corp. noted that the proposed mechanism could produce both asymmetrical and symmetrical NO_3. The asymmetrical NO_3 can be formed from the reaction:

$$NO + O_2 \rightarrow asym\text{-}NO_3 \qquad (2)$$

and symmetrical NO_3 in accord with the equation

$$N_2O_5 \rightarrow NO_2 + sym\text{-}NO_3 \qquad (3)$$

If that information in combination with the concept of the steady state for reactive intermediates is superimposed upon the analysis given by Morrison *et al.*, Equation 1 becomes

$$-dC_{NO}/dt = 2k_7K_3C_{NO}^2C_{O_2} + 2k_6K_4K_5C_{NO}C_{NO_2}C_{O_2} \qquad (4)$$

The only difference between Equations 1 and 4 is the factor of 2 in the second term on the right-hand side of Equation 4. The analysis still does not necessarily provide any definitive answer for the mechanism of the proposed reaction.

Because some 500 data points at 26.5° C. and atmospheric pressure were used to establish Equation 1, the form of the empirical equation for the conditions involved appears to be based upon a good foundation. Absolute definition of the mechanism would require further study of the system with special reference to the real presence of intermediates such as asymmetric NO_3, symmetric NO_3, N_2O_3, and N_2O_5.

The consideration of Cohen and Heicklen in bringing the problem to our attention is much appreciated.

Literature Cited

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