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AN ALTERNATIVE COMPUTATIONAL METHOD TO THAT OF JUDD

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Judd and Norris [1] have dealt with the determination of the reaction order n from the equation

$$(1 - \alpha)^{1-n} = 1 + (n - 1)\,kt \tag{1}$$

They concluded that the only correct method is the application of the least squares principle

$$\sum_i (\delta\alpha_i)^2 = \min \tag{2}$$

where the symbol $\delta\alpha_i$ stands for the difference between the observed and the calculated values of α_i.

Since Eq. (1) is non-linear by two parameters they solved the problem by a general non-linear minimization method.

One of the non-linear parameters, however, can be eliminated if we use the following procedure:

Suppose that n is fixed. Eq. (1) is then linear for k and can be written as

$$Y = 1 + (n - 1)\,kt \tag{3}$$

where

$$Y = (1 - \alpha)^{1-n} \tag{4}$$

If we differentiate Eq. (4), an arbitrary but not too great change of α can be expressed as follows:

$$\delta\alpha \cong \frac{1}{1 - n}(1 - \alpha)^n\,\delta Y \tag{5}$$

Using relation (5), condition (2) can be well approximated:

$$\sum_i (\delta\alpha_i)^2 \cong \sum_i c_i^2(\delta Y_i)^2 = \min \tag{6}$$

where

$$c_i = \frac{1}{1 - n}(1 - \alpha)^n \tag{7}$$

For given n relations (3), (6) and (7) present together an extremely simple linear least squares problem. If the value of n is changed systematically the best value of n can easily be found. The simplest way is to calculate sum (6) for $10-15$ different values of n and choose the least one.

Reference

1. M. D. Judd and A. C. Norris, J. Thermal Anal., 5 (1973) 179.