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Note

COMMENTS ON THE PAPER "ON THE EVALUATION OF KINETIC PARAMETERS FROM THERMOGRAVIMETRIC CURVES" BY J.M. CRIADO AND J. MORALES

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In a recent note to *Thermochimica Acta*, Criado and Morales [1] proposed the following equation for evaluation of kinetic parameters from a TG curve

$$\ln[-\ln(1-\alpha)] - 2n \ln T = -\frac{E}{RT} + n \ln\left[\frac{nRA^{1/n}}{E\beta}\right] \tag{1}$$

where β is the heating rate, n is a number which can take integer values from 1 to 3, and the other symbols have their usual meaning.

If follows, as claimed by the above authors, that the activation energy (E) evaluated from this equation should be independent of n, contrary to the observation reported by Dharwadkar et al. [2]. However, the conclusion of Criado and Morales [1] seems to be a typical one, arising from improper use of units for specific reaction rate. To avoid such a situation, Gomes [3] had cautioned that in any kinetic expression it is necessary to check that the specific reaction rate is expressed in the appropriate units [always containing the factor $(\text{time})^{-1}$] such that the temperature coefficient can be identified as the activation energy for the reaction.

In deriving eqn. (1), Criado and Morales [1] have used Avrami-Erofeyev's equation [4] in the form

$$[-\ln(1-\alpha)] = kt^n \tag{2}$$

where α, t, k and n are the fraction transformed, time, specific reaction rate, and an integer number taking values between 1 and 3, respectively.

Obviously eqn. (2) is dimensionally incompatible except for $n = 1$, where specific reaction rate k is expressible as $(\text{time})^{-1}$. If the proper dimensions are to be maintained, eqn. (2) has to be written as

$$[-\ln(1-\alpha)] = (kt)^n \tag{3}$$

Use of eqn. (3) results in eqn. (4) for the TG curve which shows dependence of activation energy on the value of n, as follows

$$\ln[-\ln(1-\alpha)] - 2n \ln T = \frac{nE}{RT} + n \ln\left[\frac{AR}{E\beta}\right] \tag{4}$$

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Our observations [2] and those of several other investigations [5] are consistent with eqn. (4), which is based on the unambiguous definition of specific reaction rate. Once this basic concept is accepted, there should be no discrepancy in the observations reported by us [2].

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