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Thermochimica Acta 333 (1999) 177–178

thermochimica acta

On the paper "an integral method of non-isothermal kinetic analysis" by R.E. Lyon, which appeared in Thermochimica Acta 297 (1997) 117

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Received 26 March 1999; accepted 17 May 1999

A paper published last year claims the proposal of a new integral method to calculate kinetic parameters from non-isothermal experiments [1]. There are, however, some details that shatter the grounds of the proposed method and we aim to point them out below.

(1) The paper claims the following equation as stating "a new integral method":

$$F(\alpha) \approx \frac{ART^2}{\beta(E+2RT)} \exp(-E/RT), \qquad (1)$$

where $F(\alpha)=\int d\alpha/f(\alpha)$ is the conversion integral, β the heating rate, A the pre-exponential factor, E the activation energy, R the gas constant and T is the temperature. Unfortunately Eq. (1) is not a new one but the well-known Gorbatchev proposed approximation [2] to improve Coats–Redfern method [3] and the method is known as Gorbatchev–Doyle method.

(2) For the calculation of the kinetic parameters the author uses several experiments with linear heating rates and an iso-conversional method based on the logarithmic form of Eq. (1). The result of several approximations leads to

$$\frac{d(\ln\beta)}{d(1/T)} = -\left[\frac{E}{R} + 2T\right], \qquad (2)$$

which is what is usually used both for Coats–Redfern and for Gorbatchev method.

Besides this, as it was shown in previous papers [4–6] the use of the iso-conversional integral methods in the form expressed by Eq. (2) is criticisable. The main reason for this is that Eq. (2) is obtained without any concern of the inferior limit of integration. In other words it is considered that one of the limits for the temperature integral is always zero and this makes the method less accurate when compared to the iso-conversional differential method (Friedman's method [7]). The differences are more evident when the calculated values of the activation energy depends on the degree of conversion, as in the first example given in the discussed paper [1].

(3) In order to obtain a relationship for the pre-exponential factor, A, the author uses a so-called "condition for normalised conversion integral", according to which:

$$\text{for } \alpha = 1 \text{ results that } F(\alpha) = 1. \qquad (3)$$

From Eq. (3) results the following relationship:

$$A = \frac{\beta(E+2RT(1))}{RT^2(1)} \exp(E/RT(1)), \qquad (4)$$

where $T(1)$ is the temperature recorded at α=1.

Condition (3) is quite tricky as a paper of Malek et al. [8] dealing with the boundary conditions for

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PII: S0040-6031(99)00118-5

kinetic model states that

$$\lim_{\alpha\to 1} F(\alpha) = \infty. \tag{5}$$

If by ‘‘normalised conversion integral’’ one means the ratio

$$g(\alpha) = \frac{\int_0^{\alpha} \mathrm{d}\alpha/f(\alpha)}{\int_0^{1} \mathrm{d}\alpha/f(\alpha)}, \tag{6}$$

which indeed ranges from 0 to 1, then, by applying the ratio also to the right-hand term of Eq. (1) one loses just the pre-exponential factor from the final relationship.

As a matter of facts one cannot find any mathematical demonstration to Eq. (4). We can only notice that, according to Eq. (4), the value of the pre-exponential factor changes when the heating rate changes, a fact which contradicts the meaning of the kinetic parameters.

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