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Short communication

A recurrent error which needs to be resolved

A. Ortega

Instituto de Ciencias de Materiales de Sevilla, Centro Mixto C.S.I.C./Universidad de Sevilla, Avda. Americo Vespucio s/n, 41092 Sevilla, Spain

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ABSTRACT

The recent paper by Jankovic et al. [B. Janković, B. Adnađevic, J. Jovanović; Thermochimica Acta 452 (2007) 106] and other similar papers have raised a problem which needs to be resolved. These authors use the method of Kennedy and Clark [J.A. Kennedy, S.M. Clark, Thermochimica Acta 307 (1997) 27] which is conceptually erroneous; this is analyzed in this paper.

In a recent paper in *Thermochimica Acta*, Jankovic et al. [1] have carried out the kinetic study of non-isothermal dehydration of equilibrium swollen poly (acrylic acid) hydrogel. These authors propose the use of the Kennedy–Clark method [2] which is based on the expression:

$$\ln\left(\frac{\beta g(\alpha)}{T-T_0}\right)=\ln(A)-\frac{E}{RT} \tag{1}$$

where T_0 is the initial temperature. The activation energy of the reaction is obtained by plotting the left-hand side of this equation against $1/T$. In others recent papers Bhange et al. [3], Gualtieri et al. [4] and Milanesio et al. [5], Mahfouz et al. [6], etc. have also used this expression to calculated the activation energy of different heterogeneous reactions.

Kennedy–Clark [2] have defined their method from the general equation:

$$g(\alpha)=Kt \tag{2}$$

Taking into account that non-isothermal experiments take place under conditions of constantly ramping temperature, they define T_0 as the temperature at the start of the reaction and the temperature at time t is given by:

$$T=\beta t+T_0 \tag{3}$$

They combine Eqs. (2) and (3) to obtain expression (1) which forms the basis of a general non-isothermal method. Such expression is presented by the authors as "free from any assumptions". The aim of this paper is to show that the use of the Kennedy–Clark method leads to serious errors in the determination of the activation energy of a solid state reaction because Eq. (1) has no real meaning and consequently this method is inadequate for the kinetic analysis of solid state reactions. The reason for this affirmation is that Eq. (1) cannot be used for carrying out the kinetic analysis of non-isothermal data due to the fact that the differential form of the general kinetic equation cannot be integrated without previously taking into account the mathematical function that relates the temperature with the time.

It is well known that the differential general kinetic equation is:

$$\frac{d\alpha}{dt}=Kf(\alpha) \tag{4}$$

where $K=A\exp(-E/RT))$ is the rate constant. Integrating this equation under isothermal conditions we obtain the Eq. (2). Under non-isothermal conditions the time dependence of the temperature must be known. When a linear temperature increase rate is used to perform the kinetic analysis the explicit temporal dependence in Eq. (4) is eliminated through a trivial transformation $dt=dT/\beta$, and to compute the kinetic parameters an approximate form of the temperature integral, $p(x)$, is needed that results from rearrangement and integration of Eq. (4):

$$g(\alpha)=\frac{A}{\beta}\int_0^T\exp\left(-\frac{E}{RT}\right)dT=\frac{AE}{\beta R}p(x) \tag{5}$$

where $p(x)$ is given by:

$$p(x)=\int_x^\infty\frac{\exp(-x)}{x^2}dx \tag{6}$$

Kennedy and Clark eliminate the temperature integral in Eq. (5) by combining Eq. (2) used under isothermal conditions with Eq. (3) used in non-isothermal conditions. Thus, the spurious elimination of the temperature integral is a serious drawbacks to the use of the

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E-mail address: aortega@us.es.

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Table 1
Dependence of the error in the activation energy on the initial temperature T_0 for data in Fig. 1.

T_0	Predicted error from (Eq. (10))	Calculated error from the analysis of the simulated curve (Eq. (7))
700	−13.5	−15.2
600	−7.1	−6.5
500	−2.8	−2.1

method of Kennedy–Clark that surprisingly has not been previously revealed. This is a recurrent error in thermal analysis.

In order to check the error of the method of Kennedy–Clark we have used the following procedure: the relative error $(\delta E/E)\%$ in the activation energy (E_{KC}) calculated by the Kennedy–Clark equation can be defined by the following relationship:

$$\left(\frac{\delta E}{E}\right)\% = \frac{E_{KC}-E}{E}\times 100 = \left(\frac{E_{KC}}{E}-1\right)\times 100 \tag{7}$$

by differentiating Eq. (1) with respect $1/T$ we obtain:

$$\frac{\partial \ln g(\alpha)}{\partial(1/T)} = -\frac{E_{KC}}{R} - \frac{T^2}{T-T_0} \tag{8}$$

On the other hand by differentiating the logarithmic form of Eq. (5) we obtain:

$$\frac{\partial \ln g(\alpha)}{\partial(1/T)} = \frac{\partial \ln p(x)}{\partial(1/T)} = \frac{E}{R}\frac{\partial \ln p(x)}{\partial x} \tag{9}$$

From Eqs. (7)–(9) we obtain the relative error:

$$\left(\frac{\delta E}{E}\right)\% = \left[-\frac{\partial \ln p(x)}{\partial x} - \frac{1}{x}\frac{T}{T-T_0} - 1\right]\times 100 \tag{10}$$

Eq. (10) shows that the relative error in the activation energy depend on $x = E/RT$ and on the initial temperature T_0. The values of the relative error have been computed by numerical integration of $p(x)$. Besides the spurious character of the Kennedy–Clark method, the dependence of the error on the initial temperature T_0 introduces an important ambiguity in the activation energy calculated by this procedure.

To verify this conclusion we have constructed a theoretical first order TG curve [$g(\alpha) = -\ln(1-\alpha)$] with the following kinetic parameters: $E = 150\,\mathrm{kJ\,mol^{-1}}$, $A = 10^8\,\mathrm{min^{-1}}$ and a heating rate $\beta = 10\,^{\circ}\mathrm{C\,min^{-1}}$. Table 1 shows the dependence of the relative error in the activation energy on the initial temperature T_0.

We can see from Table 1 that the small differences between the errors in Table 1 are due to the fact that the error calculated from Eq. (9) has been obtained at a constant value of $x = E/RT$ (the mean value of the range) while the predicted from Eq. (6) do not correspond to a single x value but to the range of x values of Fig. 1. It is noteworthy to point out that the relative error in the activation energy of the Kennedy–Clark method is not high which explains why its conceptual error has not been detected. Most of the time, in non-isothermal kinetic analysis, the KC method gives a good fits to experimental data in comparison with others model fitting method, for example the Coats–Redfernĭs method, it is because similar mathematical equations are used in both methods where the Arrhenius parameters are determined by the form of the $g(\alpha)$ chosen. In non-isothermal experiment both T and α vary simultaneously and the model fitting methods fail to achieve a clean separation between the constant reaction rate, which gives the temperature dependence, and the reaction model $g(\alpha)$. As a result always there is a compensation due to the error in the form of the $g(\alpha)$ assumed. For this reason is better to use an approach that allows for evaluating the activation energy without choosing the $g(\alpha)$ or $f(\alpha)$ functions.

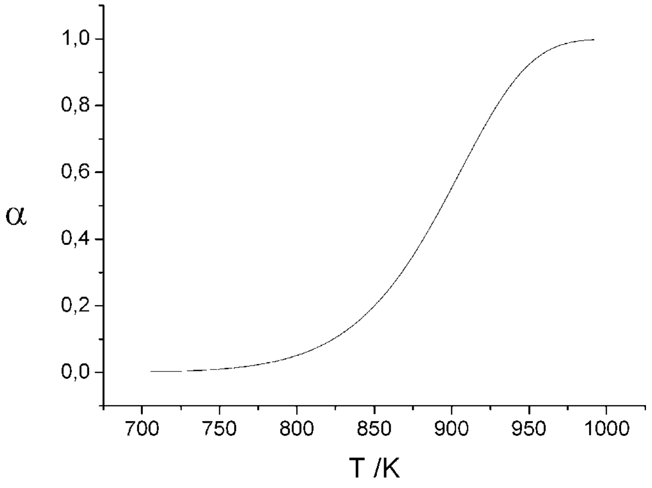

Fig. 1. Theoretical first order curve: $E = 150\,\mathrm{kJ\,mol^{-1}}$, $A = 10^8\,\mathrm{min^{-1}}$ and $\beta = 10\,^{\circ}\mathrm{C\,min^{-1}}$.

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