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CRITICAL ANALYSIS OF THE ISOCONVERSIONAL METHODS FOR EVALUATING THE ACTIVATION ENERGY

I. Theoretical background

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Abstract

It is demonstrated that, if the activation energy depends on the degree of conversion, its values obtained by isoconversional differential and integral methods are different.

Keywords: isoconversional methods, kinetics

Introduction

The kinetics of the heterogeneous condensed phase reactions is usually described [1] by the equation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=Af(\alpha)\exp\left(-\frac{E}{RT}\right) \tag{1}$$

where α is the degree of conversion, t is the time, A is the pre-exponential factor, E is the activation energy, R is the gas constant and $f(\alpha)$ is the differential conversion function.

For non-isothermal conditions with a linear heating program (the heating rate is $\beta=\mathrm{d}T/\mathrm{d}t=\text{const.}$) relation (1) becomes:

$$\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}=Af(\alpha)\exp\left(-\frac{E}{RT}\right) \tag{2}$$

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Relations (1) and (2) ground the procedures for evaluation of the kinetic parameters of heterogeneous condensed phase reactions under isothermal (Eq. (1)) and non-isothermal (Eq. (2)) conditions.

Critical analyses of methods for the evaluation of kinetic parameters under non-isothermal conditions are to be found in some recent papers [2–5].

In the present paper we focus on the isoconversional methods which are known to permit a model independent estimate of the activation energy. Use of these methods allows the dependence of the activation energy on the degree of conversion to be taken into account. Dowdy [6] showed that, for systems of competitive or independent reactions, the Friedman isoconversional differential method (Fr) [7] and Flynn–Wall–Ozawa isoconversional integral method (FWO) [8, 9] lead to different values of the activation energy. These values were compared with the instantaneous mean activation energy given by Dowdy [6], whose expression corresponds to an open system of either parallel or independent reactions.

Recent papers [5, 10] have demonstrated that, for the dehydration of calcium oxalate monohydrate and for the thermal degradation of polychloroprene rubber, the activation energy depends on the degree of conversion and $E_{FWO} \neq E_{FR}$ (E_{FWO} and E_{FR} are the activation energy values determined by means of the Flynn–Wall–Ozawa and Friedman methods). On the other hand, if E is independent on α, then the two methods lead to practically the same activation energy value. These results [5] and the theoretical considerations based on them were the subject of a recent critical analysis by Criado *et al.* [11].

The reasons for the differences between E_{FWO} and E_{FR} observed for $E=E(\alpha)$ could be that

a) the numerical instability of the differential method could lead to high errors in the estimation of E_{FR} values;

b) the use of Doyle's approximation [12] for the temperature integral could result in errors in E_{FWO}.

As pointed out by Flynn [13], the possibility a) is valid only when the derivative values are obtained from thermal analysis curves, which often exhibit considerable experimental scatter. The advent of computer interfacing with integrating and smoothing capabilities has greatly reduced this disadvantage of the Friedman method [13].

In order to reveal that possibility b) does not cause the differences between E_{FWO} and E_{FR}, due to the dependence of E on α, in this paper we shall present a critical discussion of the isoconversional methods used to process the non-isothermal data.

However, in the first section of this work, use of the isoconversional methods to evaluate the activation energy for isothermal data will be discussed.We consider such an analysis to be necessary for an understanding of the critical analysis of the isoconversional methods applied to non-isothermal data.

Isoconversional methods for evaluation of the activation energy

Isothermal conditions

The differential method for evaluation of the activation energy is based on the logarithmic form of equation (1):

$$\ln\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\ln Af(\alpha)-\frac{E}{RT} \tag{3}$$

For α=const., a plot of ln $\mathrm{d}\alpha/\mathrm{d}t$ *vs.* $1/T$ should be a straight line whose slope allows an evaluation of the activation energy.

A variant of this method suggested by Flynn [13] is based on the following form of Eq. (3):

$$T\ln\frac{\mathrm{d}\alpha}{\mathrm{d}t}=T\ln Af(\alpha)-\frac{E}{R} \tag{4}$$

For α=const., a plot of $T\ln(\mathrm{d}\alpha/\mathrm{d}t)$ *vs.* T should be a straight line whose intercept allows evaluation of the activation energy.

According to Flynn [10] if the isoconversional lines $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ *vs.* $1/T$ and $T\ln(\mathrm{d}\alpha/\mathrm{d}t)$ *vs.* T are bent, then the kinetics is too complex to be described by Eq. (1).

The integral method uses the integral form of equation (1):

$$g(\alpha)\equiv\int_0^\alpha\frac{\mathrm{d}\alpha}{f(\alpha)}=At\exp\left(-\frac{E}{RT}\right) \tag{5}$$

from which it emerges that:

$$\ln t=\ln\frac{g(\alpha)}{A}+\frac{E}{RT} \tag{6}$$

For α=const., a plot of $\ln t$ *vs.* $1/T$ should be a straight line whose slope allows evaluation of the activation energy.

Obviously, application of the differential and integral methods to the same isothermal data should lead to the same value of the activation energy. However, such an agreement should be expected only if E does not depend on α. The dependence $E=E(\alpha)$ is characteristic for complex processes (parallel, successive or reversible reactions). In such cases, for the large temperature range in which the reaction isotherms were recorded, bending of the isoconversional lines should be observed, i.e. the activation energy becomes dependent on temperature. For a given (α, T) pair, the activation energy can be evaluated through differentiation of the isoconversional curve $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ *vs.* $1/T$ for the differential method, or of the isoconversional curve $\ln t$ *vs.* $1/T$ for the integral method:

$$E_{\mathrm{dif}}^{\alpha,\mathrm{T}}=-R\left[\frac{\mathrm{d}\left(\ln\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)}{\mathrm{d}\left(\frac{1}{T}\right)}\right]_{\alpha,\mathrm{T}} \tag{7}$$

$$E_{\mathrm{int}}^{\alpha,\mathrm{T}}=R\left[\frac{\mathrm{d}\ln t}{\mathrm{d}\left(\frac{1}{T}\right)}\right]_{\alpha,\mathrm{T}} \tag{8}$$

Relation (6) was derived through the integration of Eq. (1) for activation parameters which do not depend on α. If this condition is not fulfilled, the integration of Eq. (1) is no longer correct. This is the reason why in such cases it must be expected that $E_{\mathrm{dif}}^{\alpha,\mathrm{T}}\neq E_{\mathrm{int}}^{\alpha,\mathrm{T}}$.

For real cases, the kinetic investigation of heterogeneous condensed phase reactions is performed in rather narrow ranges of temperature. Under such conditions, the isoconversional plots $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ *vs.* $1/T$ and $\ln t$ *vs.* $1/T$ are practically linear. Even in these cases, however, the condition $E_{\mathrm{dif}}\neq E_{\mathrm{int}}$ should be fulfilled.

Non-isothermal conditions

If isoconversional methods are to be used, thermal analysis curves must be recorded at several heating rates. It is presumed that the kinetic parameters of the investigated change do not depend on the heating rate.

Friedman's isoconversional method [7] is based on Eq. (2) written in the following form:

$$\ln\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\ln Af(\alpha)-\frac{E}{RT} \tag{9}$$

For α=const., a plot of $\ln\beta(\mathrm{d}\alpha/\mathrm{d}T)$ *vs.* $1/T$ should be a straight line whose slope allows evaluation of the activation energy.

Some integral methods are based on the following relation, which is obtained from Eq. (2) through integration:

$$g(\alpha)=\frac{A}{\beta}\int_0^{\mathrm{T}}\left[\exp\left(-\frac{E}{RT}\right)\right]\mathrm{d}T\equiv\frac{AE}{\beta R}p(x) \tag{10}$$

where $x=E/RT$ and $p(x)$ is the temperature integral which can not be calculated exactly.

The isoconversional integral methods differ according to the approximation used to calculate the temperature integral.

The isoconversional integral method given independently by Flynn and Wall [8] and Ozawa [9] uses the Doyle approximation [12]:

$$\ln p(x) = -5.331 - 1.052x \tag{11}$$

Relations (10) and (11) lead to:

$$\ln\beta = \ln\frac{AE}{Rg(\alpha)} - 5.331 - 1.052\frac{E}{RT} \tag{12}$$

Thus, for α=const., a plot of $\ln\beta$ *vs.* $1/T$, obtained from thermal curves recorded at several heating rates, should be a straight line whose slope allows evaluation of the activation energy. As far as, the pre-exponential factor is concerned, its value can be obtained from the intercept if the form of the integral conversion function is known. For $x<20$, Doyle's approximation leads to errors higher than 10%. For such cases Flynn [14] suggested corrections in order to obtain correct activation energy values.

Agrawal [15] suggests the following approximation for the temperature integral:

$$p(x) = \left[\frac{\exp(-x)}{x^2}\right]\left(1 - \frac{2}{x}\right)\left(1 - \frac{m}{x^2}\right) \tag{13}$$

where m is a parameter specific for other approximations previously suggested (for $m=0$, the known Coats–Redfern approximation [16] is obtained).

Vyazovkin and Dollimore [17] have shown that, for $x>10$, $(1-2/x)(1-m/x^2)\approx 1$. Under such conditions, relations (10) and (13) lead to:

$$\ln\frac{\beta}{T^2} = \ln\frac{AR}{Eg(\alpha)} - \frac{E}{RT} \tag{14}$$

Thus, for α=const., a plot of $\ln(\beta/T^2)$ *vs.* $1/T$, obtained from thermal curves recorded at several heating rates, is a straight line whose slope allows evaluation of the activation energy and whose intercept allows the value of the pre-exponential factor to be obtained for a known analytical form of the integral function of conversion.

Li and Tang [18, 19] recently suggested an isoconversional integral method which involves no approximation to the temperature integral and is easy to implement on the computer. The relation on which this method is based results from using the α integral of both sides of Eq. (9) :

$$\int_0^\alpha \left(\ln\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)\mathrm{d}\alpha = G(\alpha) - \frac{E}{R}\int_0^\alpha \left(\frac{1}{T}\right)\mathrm{d}\alpha \tag{15}$$

where $G(\alpha) = \alpha\ln A + \int_0^\alpha (\ln f(\alpha))\mathrm{d}\alpha$.

A plot of $\int_0^\alpha [ln\beta(\mathrm{d}\alpha/\mathrm{d}T)]\mathrm{d}\alpha$ *vs.* $\int_0^\alpha (1/T)\mathrm{d}\alpha$ for a given α for a set of β's will therefore have the slope $(-E/R)$.

Obviously, the different isoconversional methods applied to the same non-isothermal data should lead to the same activation energy value. Nevertheless, in a previous paper [5] we have shown that $E_{\mathrm{FR}} = E_{\mathrm{FWO}}$ only if E does not depend on α. It was demonstrated that, if E depends on α, $E_{FR} \neq E_{FWO}$. The question next arises as to whether, under such conditions, E_{FR} differs not only from E_{FWO}, but also from E_V and E_{LT} (E_V and E_{LT} are the activation energies obtained by using relation (14) and relation (15), respectively); in other words, whether the previously reported differences between E_{FR} and E_{FWO} [5] are due to the use of Doyle's approximation only. We consider that the existence of significant differences between E_{FR} and E calculated by using integral methods are due to the mode of derivation of the relations, on which the integral methods are based. These relations are derived by considering that the activation parameters do not depend on α. Obviously, if $E=E(\alpha)$ and $A=A(\alpha)$, these derivations are not correct. The dependences of the activation energy and the pre-exponential factor on the degree of conversion generally reflects the existence of a compensation effect which corresponds to the validity of the following relation [20–24]:

$$\ln A = aE + b \tag{16}$$

where a and b are constants.

Conclusions

The relations on which the isoconversional methods for determination of the kinetic parameters of heterogeneous condensed phase reactions are based for both isothermal and non-isothermal data have been presented and analysed.

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