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A new point of view on the evaluation of the temperature integral[1]

A. Ortega *, L.A. Pérez-Maqueda, J.M. Criado

Departamento de Química Inorgánica e Instituto de Ciencias de Materiales. Centro Mixto Coordinado
C.S.I.C y Universidad de Sevilla. Aptdo. 1115, 41080 Sevilla, Spain

Abstract

The accuracy of the approximation of the temperature integral of the Arrhenius law proposed by Coats and Redfern, which is one of the simplest and most popular, has been tested. It has been demonstrated that this method leads to accurate values of sufficiently the activation energy of solid state reactions. This means that the use of a tedious and sophisticated approximation of the temperature integral is not necessary.

Keywords: Arrhenius law; Activation energy; Solid state reactions; Temperature integral

1. Introduction

Recent interest in a highly accurate, rational computation of the temperature integral can be observed [1]. This interest is connected with improved computer programs. Today the $p(E/RT)$ function can be calculated with simple computer routines to great accuracy.

Some approximations of the $p(E/RT)$ function leading to linear correlation between $\ln p(E/RT)$ and the reciprocal of the temperature have been developed in order easily to obtain the activation energy. These expressions have been obtained either by simplifying the series expansions or in an empirical way. The most simple and popular among them is that of Coats and Redfern [2].

It should be pointed out that there is a controversy regarding the accuracy of the approximations generally used for evaluating the temperature integral in order to calculate the activation energy of chemical reactions. According to Hajduk and

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* Corresponding author.

[1] Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

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Norwisz [3] and Flynn [4], the approximations of Coats and Redfern [2], Doyle [5], MacCallum and Tanner [6] and others do not allow proper values of the kinetic parameters to be obtained.

Several authors [7, 8] have compared the values of $p(E/RT)$ calculated from the approximations commonly used in the literature with those computed numerically with an accuracy better than $10^{-5}\%$ by means of Simpson's procedure. The conclusion has been drawn that the error involved in the $p(E/RT)$ function calculated from the above approximations is very large (of the order of several hundred percent). This strongly restricts the possibility of their use in performing the kinetic analysis of solid-state reactions. However, it must be pointed out that these approximations have been developed for determining the kinetic parameters (E and A) of the reaction from the plots of $\ln g(\alpha)$ against $1/T$, rather than for generating theoretical α–T curves.

The scope of the present paper is to determine the error involved in the activation energy calculated from the Coats–Redfern approximation as a function of the parameter E/RT in order to determine its range of applicability in kinetic studies, because there is no evidence that the same error would be implied in the determination of both the value of the $p(E/RT)$ function and the activation energy. This means that sophisticated approximations of the function $p(E/RT)$, which require the use of tedious non-linear optimisation for calculating the kinetic parameters, are not necessary.

2. Theoretical

Combining the Arrhenius law with the equation for the rate in terms of α, the fraction conversion, we obtain the following relationship for the calculation of the kinetic parameters of a solid-state reaction from non-isothermal data

$$\frac{d\alpha}{dt} = \frac{A}{\beta} f(\alpha) \exp(-E/RT) \tag{1}$$

where $f(\alpha)$ is a function depending on the reaction mechanism (Table 1).

By integrating Eq. (1) we get

$$g(\alpha) = \frac{AE}{\beta R} \int_x^{\infty} \frac{\exp(-x)}{x^2} dx = \frac{AE}{\beta R} p(x) \tag{2}$$

with $x = E/RT$. Or in logarithmic form:

$$\ln g(\alpha) = \ln \frac{AE}{\beta R} + \ln p(x) \tag{3}$$

For a nonisothermal system, a constant heating rate is often used

$$\beta = dT/dt \tag{4}$$

A difficulty in non-isothermal kinetic methods is that there is no exact analytical solution of the $p(x)$ function and therefore the solution cannot be expressed in a closed form, although there exist several convergent series for its approximation with a high level of accuracy. These approximations, reviewed in Ref. [9], may be used to determine

Table 1
Algebraic expressions of the $g(\alpha)$ functions commonly used for reaction kinetics

Mechanism	Symbol	$g(\alpha)$
Phase-boundary-controlled reaction (contracting cylinder)	R_2	$2(1-(1-\alpha)^{1/2})$
Phase-boundary-controlled reaction (contracting sphere)	R_3	$3(1-(1-\alpha)^{1/3})$
Random nucleation, unimolecular decay law (first order)	F_1	$-\ln(1-\alpha)$
n-Dimensional growth of nuclei (Avrami–Erofeev equation)	A_n	$(-\ln(1-\alpha))^{1/n}$
Two-dimensional diffusion	D_2	$(1-\alpha)\ln(1-\alpha)+\alpha$
Three-dimensional diffusion (Jander equation)	D_3	$(1-(1-\alpha)^{1/3})^2$
Three-dimensional diffusion (Ginstling–Brounstein equation)	D_4	$(1-2\alpha/3)-(1-\alpha)^{2/3}$

the kinetic parameters of the reaction by an iterative method that requires the use of computers.

In this paper, the reference values of the temperature integral were computed numerically by means of the fourth Senum and Yang approximation [7] which allows an accuracy better than $10^{-5}\%$ for $E/RT = 20$

$$p(x) = \frac{\exp(-x)}{x^2} h(x) \tag{5}$$

where

$$h(x) = \frac{x^4 + 18x^3 + 88x^2 + 96x}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{6}$$

Let us call $p(x_a)$ the approximation of the $p(x)$ function given by Coats and Redfern

$$p(x_a) = \frac{\exp(x_a)}{x_a^2}\left(1 - \frac{2}{x_a}\right) \tag{7}$$

where the subscript a refers to the approximate value of x. However, the expression commonly used in the literature is the simplest and most popular form

$$p(x_a) = \frac{\exp(-x_a)}{x_a^2} \tag{8}$$

leading to a linear correlation.

The above considerations suggest that calculations of the error involved in the determination of the activation energy by using the approximations of the $p(x)$ function developed by Coats and Redfern is required in order to draw a conclusion with regards to the applicability of this approximation to the kinetic analysis of reactions under a linear heating rate.

3. Calculation of the error

Let us call $x_a = E_a/RT$ the apparent value of x obtained from the approximation of the $p(x)$ function. The error ε of x_a with respect to the true value of x can be defined by the following relationships.

$$\varepsilon\% = \frac{E_a/RT - E/RT}{E/RT}100 = \frac{E_a - E}{E}100 \tag{9}$$

By introducing the exact expression of $p(x)$, Eq. (5), into Eq. (3), it becomes

$$\ln g(\alpha) = \ln\frac{AR}{E\beta} - x - 2\ln x + \ln h(x) \tag{10}$$

By differentiating the logarithmic form with respect $1/T$, we obtain

$$\frac{\partial \ln g(\alpha)}{\partial 1/T} = -\frac{E}{R} - 2T + \frac{\partial \ln h(x)}{\partial 1/T} \tag{11}$$

Using the above procedure with the Coats–Redfern approximation $p(x_a)$, we get, after introducing Eq. (8) into Eq. (3)

$$\ln g(\alpha) = \ln\frac{A_a R}{E_a \beta} + 2\ln T - \frac{E_a}{RT} \tag{12}$$

By differentiating Eq. (12) we obtain

$$\frac{\partial \ln g(\alpha)}{\partial 1/T} = \frac{E_a}{R} - 2T \tag{13}$$

Combining Eqs. (11) and (13) gives

$$E_a/R - E/R = -\frac{\partial \ln h(x)}{\partial 1/T} \tag{14}$$

Eq. (14) may be rewritten as

$$\varepsilon\% = \frac{E_a - E}{E}100 = -\frac{\partial \ln h(x)}{\partial x}100 \tag{15}$$

We can see that the error yielded in the activation energy by the Coats–Redfern approximation is dependent only on the parameter E/RT and not on the kinetic law obeyed by the reaction.

The errors in x obtained from the Coats–Redfern approximation are shown in Table 2 as a function of the values of x taken as the accurate ones for computing $p(x)$. The results included in Table 2 point out that the activation energy can be determined from

Table 2
The errors ε in x (or E) calculated for the Coats–Redfern approximation as a function of E/RT

$x = E/RT$	2	5	10	15	20	50	70	100
ε	−19.89	−4.67	−1.42	−0.68	−0.41	0.07	−0.038	−0.019

the Coats–Redfern method with an accuracy better than 5%, even for x values lower than 5. This seems to indicate that this method can be used for performing the kinetic analysis in a range of x larger than that proposed by the authors [2].

In order to check the above conclusions, we have used this approximation of the function $p(x)$ for performing the kinetic analysis of the series of theoretical curves shown in Fig. 1, calculated by assuming a random nucleation unimolecular decay law (F1), e.g. $g(\alpha) = -\ln(1-\alpha)$, a heating rate of 4 K min^{-1}, and a range of values of the activation energy and pre-exponential factors selected in such a way as to cover a wide range of x and T values. These curves have been computed by numerical integration of Eq. (2) from Simpson's procedure with an accuracy better than 10^{-5}%.

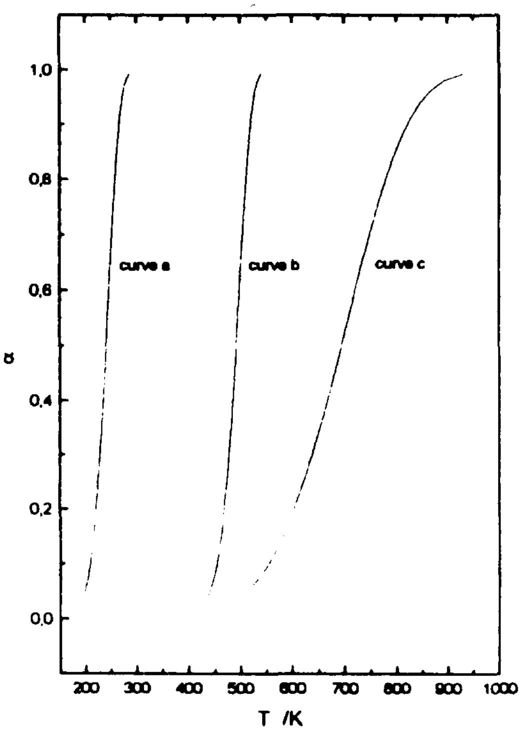

Fig. 1 Theoretical α–T curves calculated by assuming a random nucleation unimolecular decay law (first-order kinetic F_1), a heating rate $\beta = 4$ and the following kinetic parameters: (a), $E = 21$ kJ mol^{-1}, $A = 5 \times 10^3$ min^{-1}. (b), $E = 83.6$ kJ mol^{-1}, $A = 10^8$ min^{-1}. (c); $E = 33.5$ kJ mol^{-1}, $A = 10^{-1}$ min^{-1}.

Table 3
Errors $\varepsilon(\%)$ in the activation energy determined from the kinetic analysis of Fig. 1 by means of the Coats–Redfern method as a function of E/RT

E/RT	6	10	20
$\varepsilon(\%)$	-3.80	-1.22	-0.55

The activation energies determined from the slope of the plots of the values of $\ln(g(\alpha)/T^2)$ calculated from the TG traces of Fig. 1, as a function of $1/T$, according to the Coats–Redfern method, Eq. (12), are collected in Table 3, together with the calculated values of the pre-exponential factor and the error determined from Eq. (15).

The results collected in Table 3 demonstrate that, in general, the errors involved in the determination of the activation energy with the aid of the Coats–Redfern method are in good agreement with those forecasted in Table 2. The small differences between the two series of values are due to the fact that the errors included in Table 3 do not correspond to a single value of E/RT but represents the average of ε in the range of temperature at which the TG curves in Fig. 1 have been recorded.

Similar results have been obtained from the analysis of the theoretical curves calculated by assuming any of the kinetic models included in Table 1. However, for the sake of brevity, these results have not been shown in the present article.

4. Conclusion

In summary, it can be concluded that the approximation of the temperature integral developed by Coats and Redfern investigated here leads to reasonably good results. Therefore, this approximation can be used for determining the activation energy of solid-state reactions, in spite of giving poor accuracy when used for calculating the $p(x)$ function.

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