

DEPENDENCE OF THE PREEXPONENTIAL FACTOR ON TEMPERATURE. ERRORS IN THE ACTIVATION ENERGIES CALCULATED BY ASSUMING THAT A IS CONSTANT.

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ABSTRACT

The dependence of the preexponential factor on the temperature has been examined and the errors involved in the activation energy calculated from isothermal and non-isothermal methods without considering such a dependence have been estimated. It has been shown that the error in the determination of the activation energy calculated ignoring the dependence of A on T can be rather large and it is dependant on $x = E/RT$, but independent of the experimental method used, It has been also shown that the error introduced by omitting the dependence of the preexponential factor on the temperature is considerably larger than the error due to the Arrhenius integral approach used for carrying out the kinetic analysis of TG data.

Keywords: Prexonpetial factor and Temperature, isothermal kinetic analysis, non-isothermal kinetic analysis

INTRODUCTION

Thermally stimulated solid-state reactions, such as decompositions, solid-solid reactions, crystallizations, desorption of gases adsorbed on solid surface and sintering are heterogeneous processes. It has been generally assumed that the reaction rate of such processes can be kinetically described by the following expression [1]:

$$\frac{d\alpha}{dt} = k f(\alpha) = A e^{-E/RT} f(\alpha) \quad (1),$$

where k is the constant rate, A is the preexponential factor, E is the activation energy, R is the gas constant, T is the temperature, t is the time and α is the extent of reaction ranging from 0 before the process starts to 1 when it is over. In the case of desorption of gases adsorbed on solid surfaces [2] the extent of the reaction is defined as a function

of the coverage, θ , and when sintering processes are concerned, the reaction extent is defined by the ratio between the shrinkage, ΔL , and the starting length of the probe, L_0 [3, 4]. Additionally, $f(\alpha)$ (or alternatively, $f(\Delta L/L_0)$ or $f(\theta)$) is a term that describes the dependence of the reaction rate on the reaction mechanism.

Many of the experimental methods used to perform kinetic analysis of solid-state reactions are based in the measurement of the evolution of an integral magnitude, i.e. proportional to the extent of reaction, such as weight loss, released gas, amount of contraction, as a function of temperature. To perform the evaluation of such experimental data, it is necessary to integrate eq. (1). If the reaction is conducted at a constant temperature, the integration of eq. (1) leads to

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \int_0^t A e^{-E/RT} dt = A e^{-E/RT} t = kt \quad (2).$$

The most common heating profile used for studying solid-state reaction is the linear heating program. Under these experimental conditions, T changes in a wide range of values and an entire α - T curve is recorded in a single experiment. For linear heating rate conditions eq. (1) can be written

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} f(\alpha) \quad (3),$$

β being the heating rate.

The integration of eq. (3), after rearranging, leads to

$$g(\alpha) = \frac{AE}{\beta R} \int_x^{\infty} \frac{e^{-x}}{x^2} dx = \frac{AE}{\beta R} p(x) \quad (4),$$

where $x=E/RT$.

Under linear heating rate program, eq. 3 does not have an exact analytical solution to $p(x)$ and, therefore, the solution cannot be expressed in a closed form [5]. Thus, a number of approximated equations have been proposed for $p(x)$ under linear heating program. The number of publications where these integral methods have been used for determining activation energies is vast. Thus, according to *ISI Web of Science* data base, about 4000 citations can be found in the literature for the most popular approaches (Coats and Redfern [6,7], Horowitz and Metzger [8] and Doyle [9, 10]. More than 1200 of these citations have been found in the last 5 years, many of them in this Journal [11-28]. Despite the popularity of these approximations, their accuracies for the estimation

of the kinetic parameters are still in doubt, thus some authors have claimed that these methods are not proper for determining accurate kinetic parameters [29-32]. Some studies have estimated the errors in the approximated $p(x)$ functions by comparing the resulting values with those calculated by numerical integration, concluding that the errors are quite large. These findings have been used as an argument for invalidating these approximated equations in the estimation of the kinetic parameters. Nevertheless, the aim of the aforementioned approximations is the determination of the activation energy and not the accurate computation of $p(x)$. We have shown in recent papers [33, 34] that the error in the determination of the activation energy from the Coats and Redfern approach is lower than 1.3 % even for $x = 10$. According to the Coats and Redfern approach $p(x) \approx e^{-x}/x$ and eq. (3) becomes

$$g(\alpha) = \frac{A_a R}{E_a \beta} T^2 e^{-E_a / RT} \quad (5),$$

where the subscript a refers to the apparent values of the kinetic parameters obtained from the above approach.

It is noteworthy to point out that all the methods of kinetic analysis generally used have been developed by assuming that the preexponential factor can be considered as a constant all over the temperature range investigated. However, several authors [35-37] after extending the theory of the activated complex to the thermal decomposition of single solid state reactions proposed that the preexponential factor is connected with the temperature through the following relationship

$$A = A_0 \cdot T^n \quad (6),$$

where A_0 is a constant and the exponent n is equal either to 1 in the case of the thermal decomposition of a single solid reactive or to 1/2 for reactions between a gas and the surface of a solid. Varhegyi [38], Dollimore [39] and Segal [40] have considered other positive values for this exponent. On the other hand, values of n ranging from 0 to 2.5 have been proposed for the case of reactions of desorption of gases from the surface of solids [41-43]. Moreover, values of n from -3/2 to 0 have been proposed for shrinkage processes depending on the sintering mechanism [4].

The scope of this work is to carry out a systematic analysis of the error involved in the activation energy determined from conventional methods when the preexponential factor is dependant on the temperature.

THEORETICAL

Differential method

If eq. (6) is fulfilled, eq. (1) becomes

$$\frac{d\alpha}{dt} = k f(\alpha) = A_0 T^n e^{-E/RT} f(\alpha) \quad (7).$$

It is a constitutive equation that must be accomplished whatever would be the thermal pathway followed for reaching a particular α - T - t point [44, 45]. Thus, independently if isothermal or non-isothermal methods are used, the slope of the plot of $\ln [(d\alpha/dt)/f(\alpha)]$ versus $1/T$ is connected with the real activation energy, E , through the following expression

$$\frac{d \ln (d\alpha / dt)}{d(1/T)} = \frac{d \ln k}{dt} = -nT - \frac{E}{R} \quad (8).$$

However, if it were omitted the dependence of A on T and were considered that the preexponential factor remains constant all over the temperature range (i.e.; $A = A_0$), according with eq. (1), we get

$$\frac{d \ln (d\alpha / dt)}{d(1/T)} = \frac{d \ln k}{dt} = -\frac{E_a}{R} \quad (9),$$

where E_a represents the apparent activation energy.

The relative error, ε , of the activation energy (E_a) can be defined by the following equation:

$$\varepsilon\% = \frac{E_a - E}{E} 100 = \left[\frac{\frac{E_a}{R}}{\frac{E}{R}} - 1 \right] 100 \quad (10).$$

Thus, from eqs. (8), (9) and (10), we get the following expression for the relative error:

$$\varepsilon\% = \frac{n}{\frac{E}{RT}} 100 \quad (11).$$

The relative error percentages computed from eq. (11) for different values of $x = E/RT$ and the exponent n are shown in table 1.

Integral methods

If the rate constants at different temperatures were determined by the isothermal method and the preexponential factor were changing with the temperature as shown by eq. (6), eq. (2) would become

$$g(\alpha) = A_0 T^n e^{-E/RT} t = kt \quad (12).$$

The rate constant k at a given temperature could be obtained from the slope of $g(\alpha)$ versus t . According to eq. (12), the slope of the plot of the rate constant determined at different temperatures versus $1/T$ (i.e. $\ln k/d(1/T)$) would be connected to the activation energy through a relationship identical to that expressed by eq. (8). Moreover, an expression identical to eq.(9) would be obtained for the relationship between $\ln k/d(1/T)$ and E_a by assuming that A remains constant all over the temperature range following eq. (2). This means that the relative errors in the activation energy calculated from isothermal data by the integral method are identical to those calculated in table 1 for differential methods if it is not taken into account the real correlation between A and T .

Eq. (7) cannot be directly integrated if the conversion as a function of the temperature is recorded under a linear rising temperature. In such a case, under a heating rate $d\alpha/dT = \beta$, eq. (7) would be rearranged in the following form:

$$\frac{d\alpha}{f(\alpha)} = \frac{A_0}{\beta} T^n e^{-E/RT} dT \quad (13).$$

Integration of eq. (12) leads to

$$g(\alpha) = \frac{A_0}{\beta} \int_0^T T^n e^{-E/RT} dT \quad (14),$$

which, after doing the variable change $x = E/RT$, would be rearranged in the following way

$$g(\alpha) = \frac{A_0}{\beta} \left(\frac{E}{R}\right)^{n+1} \int_x^\infty \frac{e^{-x}}{x^{n+2}} dx = \frac{A_0}{\beta} \left(\frac{E}{R}\right)^{n+1} p_n(x) \quad (15).$$

Integrating by part the $p_n(x)$ function results:

$$p_n(x) = \frac{e^{-x}}{x^{n+2}} \left(1 - \frac{n+2}{x} + \frac{(n+2)(n+3)}{x^2} - \frac{(n+2)(n+3)(n+4)}{x^3} + \dots \right) = \frac{e^{-x}}{x^{n+2}} h_n(x) \quad (16),$$

$h_n(x)$ being the series between brackets.

If the preexponential factor were considered as constant and the Coats and Redfern method were used for performing the kinetic analysis, the apparent activation energy, E_a , would be obtained from the slope of the plot of $\ln[g(\alpha)/T^2]$ versus $1/T$:

$$\frac{d \ln[g(\alpha)/T^2]}{d(1/T)} = -\frac{E_a}{R} \quad (17).$$

The real value of the left hand side of eq. (17) as a function of the true activation energy can be easily determined from eqs. (15) and (16):

$$\frac{d \ln[g(\alpha)/T^2]}{d(1/T)} = -\frac{E}{R} \left(1 - \frac{d \ln h_n(x)}{dx} \right) - nT \quad (18).$$

The relative error in the activation energy would be estimated from eqs. (17) and (18) after taking into account the error definition introduced by eq. (10):

$$\varepsilon\% = \left(\frac{n}{x} - \frac{d \ln[h_n(x)]}{dx} \right) \cdot 100 \quad (19).$$

The error percentages determined as a function of $x = E/RT$ from eq. (19), after computing the function $h_n(x)$ using a tolerance of 10^{-5} , are shown in table 2.

The results obtained show that in the case that the preexponential factor were independent of the temperature (i.e; $n = 0$), the error in the activation energy determined from the Coats and Redfern method is very low for $x > 5$. If we bear in mind that values of E/RT lower than 5 have not physical meaning, we can conclude that the Coats and Redfern method is quite accurate for determining the activation energy of heterogeneous processes in spite that the standard deviation of the $p(x)$ function determined from this approach with regards to the true value are rather large [46]. However, table 2 shows that the errors in the activation energy are considerably larger if it is determined by assuming that A is independent of T when it is really dependant on T , according to eq. (6). These results are quite similar to those included in table 1. The slightly larger values of the error shown in table 2 with the regards to the corresponding values shown in table 1 are due to the small additional error introduced by the integral approach of the Arrhenius equation under non-isothermal conditions.

RESULTS

It would be of interest to check the above conclusions by analysing a set of DTG and TG curves simulated by assuming a dependence of A on T according with eq. (6). The DTG and a TG curves have been calculated from eqs. (7) and (14), integrating this last equation by numerical methods with a tolerance of 10^{-5} by means of the MathCad software. Fig. 1 shows the TG and DTG curves simulated by assuming a heating rate $\beta = 10 \text{ K. min}^{-1}$, a first order kinetic (i.e.; $f(\alpha) = (1-\alpha)$ and $g(\alpha) = -\ln(1-\alpha)$) and the

following kinetic parameters: $A = 1.395 \text{ T}^2$ and $E = 74 \text{ kJ. mol}^{-1}$. Then, the kinetic parameters of the DTG curve have been determined from the plot of the $(d\alpha/dt)/f(\alpha)$ values calculated from the α values taken from Fig. 1 as a function of the corresponding values of $1/T$, according with eq. (1). The apparent activation energy and the apparent preexponential factor obtained from the slope and the intercept of this plot are shown in table 3 together with the error given by eq. (10). The apparent kinetic parameters obtained from the TG curve after plotting the values of $\ln [g(\alpha)/T^2]$ calculated from the α values taken from this curve versus $1/T$, according to the Coats and Redfern approach given by eq. (5), are also shown in table 3 together with the error in the activation energy determined from eq. (10).

If we take into account that $x = E/RT \approx 15$ for the TG and DTG simulated curves, we can conclude that the errors in the activation energy reported in table 3 are in excellent agreement with those forecasted in tables 1 and 2, respectively. It is noteworthy to point out that a very good agreement between the errors estimated in table 1 and those calculated from α - t and da/dt - t isothermal plots has been also found, but the analysis of the simulated data has not been included for the sake of the brevity.

The above results point out the error percentages in the calculation of the activation energy would be rather large if the preexponential factor is dependant on the temperature and the kinetic analysis is performed by assuming that A is a constant. Moreover, this error only depends on the value of E/RT and not on the method used for recording the experimental data; in other words, for a given mean value of x , isothermal and non-isothermal methods lead to the same error in the estimation of the activation energy. Moreover, the errors introduced for the most popular approach of the Arrhenius integral (Coats and Redfern) for the kinetic analyses of rising temperature experiments are insignificant when compared with the errors introduced by ignoring the dependence of the preexponential factor on the temperature.

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CAPTION OF FIGURES

Fig. 1. TG and DTG curves simulated by assuming a first order kinetic model, a heating rate $\beta=10 \text{ K min}^{-1}$ and the following kinetic parameters: $A = 1.395 \text{ T}^2 \text{ min}^{-1}$ and $E = 74 \text{ kJ mol}^{-1}$

Table 1. Relative error for the activation energy obtained from isothermal and differential non-isothermal data when the preexponential factor depends on the temperature ($A=A_0T^n$).

	n							
x	-1.5	-1	0	0.5	1	1.5	2	2.5
5	-30.00	-20.00	0	10.00	20.00	30.00	40.00	50.00
10	-15.00	-10.00	0	5.00	10	15.00	20.00	25.00
15	-10.00	-6.67	0	3.33	6.67	10.00	13.33	16.67
20	-7.50	-5.00	0	2.50	5.00	7.50	10.00	12.50
30	-5.00	-3.33	0	1.67	3.33	5.00	6.67	8.33
50	-3.00	-2.00	0	1.00	2.00	3.00	4.00	5.00
100	-1.50	-1.00	0	0.50	1.00	1.50	2.00	2.50

Table 2. Relative errors for the activation energies obtained from the Coats and Redfern approach for the Arrhenius integral and the preexponential factor depends on the temperature ($A=A_0T^n$).

x	n							
	-1.5	-1	0	0.5	1	1.5	2	2.5
5	-30.93	-20.7	6.48	24.54	45.08	66.64	87.63	107.01
10	-15.40	-10.75	-1.23	3.7	8.79	14.1	19.69	25.59
15	-10.19	-7.04	-0.69	2.51	5.73	8.98	12.26	15.58
20	-7.61	-5.22	-0.42	1.99	4.41	6.83	9.26	11.7
30	-5.05	-3.43	-0.2	1.42	3.05	4.67	6.3	7.93
50	-3.02	-2.04	-0.07	0.91	1.89	2.87	3.86	4.84
100	-1.50	-1.01	-0.02	0.48	0.97	1.47	1.96	2.46

Table 3 Results of the analysis of the TG-DTG simulated curves by differential and integral procedures.

	A (min^{-1})	E (kJ mol^{-1})	Relative error in E (%)
Differential	$3.66 \cdot 10^6$	83.9	13.4
Integral	$2.69 \cdot 10^6$	82.9	12.07

