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# METHODS TO DETERMINE THE TEMPERATURE DEPENDENCE OF THE PRE-EXPONENTIAL FACTOR OF THE ARRHENIUS EQUATION FROM THERMOGRAVIMETRIC DATA*

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The well-known methods of Coats–Redfern, Freeman–Carroll, and Achar et al. are modified to include the temperature dependence of the pre-exponential factor in the Arrhenius expression for the rate constant. These modifications serve to cast these methods into their most general Arrhenius form. Suggestions are given regarding various numerical methods for extracting the temperature dependence of the pre-exponential factor from thermogravimetric and derivative thermogravimetric data.

There have been numerous proposals which relate thermogravimetric (TG) and derivative thermogravimetric (DTG) data to kinetic parameters of solid-state decompositions [1–7]. In these proposals, it is assumed that the pre-exponential factor of the Arrhenius equation is temperature independent. It has been shown experimentally, however, for a number of gas and solution phase reactions that the extended form of the Arrhenius equation, $\ln k = \ln Z + (C/R)\ln T - E/RT$, is necessary to explain the kinetic data [8]. The basis of this equation in statistical mechanics is well known [9]. Even though TG and DTG data often span wide temperature ranges, there has yet been no quantitative test of the temperature dependence of the pre-exponential factor. In some cases where the activation energy is small, this temperature dependence may be observable. We propose extensions of the methods of Freeman and Carroll [1], Coats and Redfern [2], and Achar et al. [3] to include this effect. These extensions serve to put these methods into the most general Arrhenius form.

## Theory

The disappearance of the reactant in a solid-state decomposition may be represented by

$$d\alpha/dt = k(1 - \alpha)^n \tag{1}$$

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where $d\alpha/dt$ is the decomposition rate, $\alpha$ is the fraction of the original material reacted, $k$ is the rate constant, and $n$ is the order of the reaction.

To develop our generalized approaches, we write the Arrhenius equation as

$$k = ZT^{(C/R)} \exp(-E/RT) \tag{2}$$

where $Z$ = constant, $T$ = temperature, $C$ = constant, $R$ = gas constant, and $E$ = activation energy.

As usual, temperature and time are related by

$$a = dT/dt \tag{3}$$

where $a$ is the linear heating rate.

## Modification of the Coats and Redfern method

The method devised by Coats and Redfern has been frequently employed to determine kinetic parameters. This is an integral method; hence, DTG data are unnecessary. In this method, one generally assumes that the reaction has an order of 0, 1/2, 2/3, or 1. The most nearly linear Coats and Redfern plot is then chosen to correspond to the correct values of $n$, $E$, and $Z$.

By combining Eqs (1), (2), and (3) and integrating, we immediately see that

$$\int_0^{\alpha} \frac{d\alpha'}{(1-\alpha')^n} = \frac{Z}{a} \int_0^{T} T'^{b} \exp(-E/RT')\, dT' \tag{4}$$

where $b = C/R$.

When $n \neq 1$, the left-hand side $I(\alpha)$ of Eq. (4) is simply

$$I(\alpha) = \frac{1-(1-\alpha)^{1-n}}{1-n}. \tag{5a}$$

However, if $n = 1$, we have

$$I(\alpha) = \ln(1-\alpha). \tag{5b}$$

With the substitution $x = \frac{E}{RT'}$, the right-hand side $J(T)$ of Eq. (4) may be written as

$$J(T) = \frac{Z}{a}\left(\frac{E}{R}\right)^{b+1} \int_{E/RT}^{\infty} x^{-(b+2)} \exp(-x)\, dx. \tag{6}$$

For particular values of $b$, the integral in Eq. (6) can be related to certain special functions such as the incomplete gamma function and the exponential integral [10]. If in Eq. (6) we expand the integral by repeated integration by parts, we find

$$J(T) = \frac{Z}{a}\left(\frac{R}{E}\right)T^{b+2}\left[1 - \frac{b+2}{(E/RT)} - \frac{(b+2)(b+3)}{(E/RT)^2} - \ldots\right]\exp(-E/RT) \qquad (7)$$

Eq. (7) is an asymptotic (semiconvergent) series [11]. The series is finite and exact, however, when $b$ is a negative integer less than $-2$. In this case, Eq. (6) becomes

$$J(T) = \frac{Z}{a}\left(\frac{R}{E}\right)^{|b|-1}(|b|-2)!\ \exp(-E/RT)\sum_{k=0}^{|b|-2}\frac{(E/RT)^k}{k!}\,. \qquad (8)$$

When $b = -2$, Eq. (7) is a simple exponential function. When $b = 0$, Eq. 7 corresponds to the result found by Coats and Redfern. It is noteworthy that in Eqs (5a) and (7), $n$ and $b$ are not restricted to the integers but may be allowed to take on any real values.

If we include only the first two terms in Eq. (7), we may combine it with Eq. (5a) to obtain

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = \frac{ZRT^{b+2}}{aE}\left[1 - \frac{RT(b+2)}{E}\right]\exp(-E/RT) \qquad (9)$$

TG data may be analyzed according to Eq. (9) in a number of ways. Of these, we consider two.

First, we follow Coats and Redfern and write Eq. (9) in the form

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^{b+2}}\,\frac{aE}{R\left(1-\dfrac{(b+2)RT}{E}\right)}\right] = \ln Z - \frac{E}{RT}\,. \qquad (10)$$

If $n$ and $b$ are given assumed values, the quantities $E$ and $Z$ may be obtained by the method of least squares by iterating on $E$.

Secondly, Eq. (9) may be written in the form

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{1-n}\,\frac{aE}{R\left(1-\dfrac{(b+2)RT}{E}\right)}\right] = \ln Z + (b+2)\ln T - \frac{E}{RT}\,. \qquad (11)$$

If $n$ is given an assumed value, then $E$, $Z$, and $b + 2$ may be determined by the method of least squares by iterating on $E$ and $b$. The success of this method will depend upon whether $\ln T$ varies enough so that the value of the determinant of the least-squares matrix is not dominated by the random errors in the measurements of $\alpha$ and $T$.

## Modification of the Freeman and Carroll method

The method discussed by Freeman and Carroll is unique in that it allows for the direct determination of the order of the reaction. Although this approach possesses several difficulties, it is still frequently employed. It has been especially successful in solution studies [12].

The Eqs (1) and (2) may now be combined to eliminate $k$ resulting in

$$ZT^{b} \exp(-E/RT) = \frac{d\alpha/dt}{(1-\alpha)^{n}}. \tag{12}$$

Differentiating the logarithmic form of Eq. (12) with respect to $T$ gives

$$d \ln (d\alpha/dt) = \frac{EdT}{RT^2} + \frac{bdT}{T} + nd \ln(1-\alpha). \tag{13}$$

The values of $E$, $b$, and $n$ may be obtained from a least-squares fit of the data to Eq. (13). Alternatively, if $b$ is chosen to have a specific value, a plot of

$$\frac{d \ln (d\alpha/dt) - b(dT/T)}{d \ln(1-\alpha)} = n + \frac{E}{R} \frac{dT}{T^2 d \ln(1-\alpha)} \tag{14}$$

will yield a straight line with a slope of $E/R$ and an intercept of $n$. Several values of $b$ should be used to find the best fit of the data. The factor $Z$ may be evaluated by the use of Eq. (12).

## Modification of the Achar, Brindley, and Sharp method

Uniting Eqs (1), (2), and (3), rearranging and taking logs we find

$$\ln\left[\frac{a d\alpha}{T^{b}(1-\alpha)^{n} dT}\right] = \ln Z - \frac{E}{RT}. \tag{15}$$

It can easily be seen that a plot of ln $[a d\alpha/T^{b}(1-\alpha)^{n} dT]$ as a function of $1/T$ results in a straight line from which the values of $E$ and $Z$ can be determined. Values of $n$ and $b$ may be obtained from iterative calculations. Clearly, it is also possible to expand Eq. (15) and employ $b$ as a least-squares parameter.

## Least-squares analysis

The ordinary least-squares methods assume that the random error is present in only one axis [13, 14]. However, from relations such as Eqs (11) and (13), it is obvious that both ordinate and abscissa may contain error. It is possible for these errors to be of similar importance in influencing the values of the least-squares parameters. To alleviate this problem, least-squares techniques which consider uncertainties in both variables may be used [13–16].

When least-squares methods are used in conjunction with equations such as Eqs (10), (11), (13), and (15), the nonlinear transformation to ln space introduces some uncertainty concerning the exact values of the parameters. The residuals based upon the initial relation [see Eqs (9) and (12)] will yield kinetic factors different from that found using the logarithmic expression. In general, the discrepancy is relatively small. However, the range of the variables may cause this difference to become appreciable. A generalized computer search routine can be employed to examine this situation.

## Conclusions

Several methods of kinetic analysis from TG and DTG studies have been put into forms so that the temperature dependence of the Arrhenius pre-exponential factor may be determined. Methods of working with these forms were considered. Attention was given to difficulties which arise during the least-squares analysis of data.

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Résumé — Les méthodes bien connues de Coats—Redfern, Freeman—Carroll et Achar et al. ont été modifiées afin de tenir compte du fait que le facteur préexponentiel donnant la constante de vitesse dans l'expression d'Arrhenius est une fonction de la température. Ces modifications permettent d'exprimer l'équation d'Arrhenius sous une forme plus générale. Plusieurs méthodes numériques sont proposées pour exprimer la relation du facteur préexponentiel avec la température à partir des données TG et des courbes TG dérivées.

ZUSAMMENFASSUNG — Die bekannten Methoden von Coats—Redfern, Freeman—Carroll sowie Achar und Mitarbeiter wurden auf solche Weise modifiziert, dass sie die Temperaturabhängigkeit des präexponentiellen Faktors in der Arrhenius-Gleichung für die Geschwindigkeitskonstante enthalten. Durch diese Abänderungen werden diese Methoden in ihre ganz allgemeine Arrhenius-Form überführt. Vorschläge betreffs verschiedener numerischer Methoden zur Ermittlung der Temperaturabhängigkeit des präexponentiellen Faktors aus thermogravimetrischen und derivierten thermogravimetrischen Angaben werden gemacht.

Резюме — Хорошо известные методы Коутса—Редферна, Фримэн—Каролла и Ашара с сотр., модифицированы с целью включения температурной зависимости предэкспоненциального фактора в уравнении Аррениуса для константы скорости. Эти изменения служат для того, чтобы выразить эти методы в их наиболее общей аррениусовской форме. Высказаны предположения, касающиеся различных числовых методов выделения температурной зависимости предэкспоненциального фактора из данных ТГ и ДТГ.