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Note

A CRITICAL STUDY OF THE REICH AND STIVALA METHOD OF KINETIC ANALYSIS OF TG TRACES

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The method of Coats and Redfern [1] has been widely used in literature for performing the kinetic analysis of "n order" reactions from TG traces. This method implies the use of the approximate equations

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{1-n}\cdot\frac{1}{T^2}\right]\simeq\ln\frac{AR}{E\beta}-\frac{E}{RT},\ n\neq 1 \tag{1}$$

$$\ln\left[\frac{1}{1-\alpha}\cdot\frac{1}{T^2}\right]\simeq\ln\frac{AR}{E\beta}\cdot\frac{E}{RT},\qquad n=1 \tag{2}$$

where α is the reacted fraction, β is the heating rate, E is the activation energy and A is the pre-exponential factor of Arrhenius.

In a very recent paper, Reich and Stivala [2] have derived, starting from eqn. (1)

$$\ln\left[\frac{1-(1-\alpha_1)^{1-n}}{1-(1-\alpha_2)^{1-n}}\cdot\left(\frac{T_2}{T_1}\right)^2\right]=\frac{-E}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right] \tag{3}$$

α_1, and α_2 being the reacted fraction recorded on a single TG curve at temperatures T_1 and T_2, respectively.

Reich and Stivala [2] propose a method for determining both the activation energy and the reaction order by correlating the left-hand side of eqn. (3) with $(1/T_1 - 1/T_2)$ by employing successively increasing values of n and a least squares treatment. Values of n and $-E/R$ are considered to be final when the intercept of the plot of the left-hand side of eqn. (3) against $(1/T_1 - 1/T_2)$ is closest to zero.

The scope of the present work is to show that eqn. (3) is not only accomplished by kinetic data of n order reactions but also by those corresponding to thermal decomposition reactions of solids following other reaction mechanisms.

It is known [3,4] that the Coats and Redfern equation can be written in the general form

$$\ln\frac{g(\alpha)}{T^2}=\ln\frac{AR}{E\beta}-\frac{E}{RT} \tag{4}$$

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where $g(\alpha)$ is a function depending on the reaction mechanism.

If the following relationship applies

$$\ln g(\alpha) = a \ln[1-(1-\alpha)^{1-n}] + b \tag{5}$$

we would obtain from eqns. (4) and (5)

$$\ln \frac{1-(1-\alpha)^{1-n}}{T^{(2/a)}} = \frac{1}{a}\left[\ln \frac{AR}{E\beta} - b\right] - \frac{1}{a} \cdot \frac{E}{RT} \tag{6}$$

which, following Reich and Stivala's calculation method becomes

$$\ln \frac{[1-(1-\alpha_1)^{1-n}]}{[1-(1-\alpha_2)^{1-n}]} \cdot \left(\frac{T_2}{T_1}\right)^{2/a} = \frac{-E'}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{7}$$

where a and b are constants and E' is E/a.

Therefore, if we plot the left-hand side of eqn. (7) against $(1/T_2 - 1/T_1)$, by employing successively increasing values of n we would obtain a straight line whose intercept is zero when the value of n which fits relationship (5) is reached. On the other hand, we would take into account that the numerical value of the slope of the plot of eqn. (7) is nearly independent of $(T_2/T_1)^{2/a}$ because thermal decompositions of solids under a linear heating program occur in a narrow temperature range and the ratio (T_2/T_1) remains almost constant (and very close to 1) throughout the reactions.

The above considerations mean that if relationship (5) applies, eqn. (3) must be fulfilled. Accordingly, kinetic data of reactions following a mechanism represented by a $g(\alpha)$ function, different from $[1-(1-\alpha)^{1-n}]$, would be erroneously interpreted as an n order reaction. Moreover, an apparent activation energy $E' = E/a$ would be obtained from Reich and Stivala's method.

Equation (5) has been checked for α values ranging from 0.05 to 0.95 by considering the $g(\alpha)$ functions commonly used for representing the kinetic laws of solid state reactions. The values of n giving the best fit to eqn. (5) are included in Table 1 together with those obtained for both a and the linear correlation coefficient, r.

The results in Table 1 demonstrate rather clearly that if reactions fulfilling a diffusion mechanism are analysed by means of eqn. (3), they would be erroneously considered as n order reactions and an apparent activation energy above half the actual one would be obtained.

TABLE 1

Fitting of diffusion kinetic laws to eqn. (5)

Mechanism *	Apparent order (n)	$a \simeq E/E'$	r
D_1	0.000	2.00	1.0000
D_2	0 300	2.01	1 0000
D_3	2/3	2.00	1 0000
D_4	0.430	2.00	1.0000

* The symbols of Sharp et al [9] have been used.

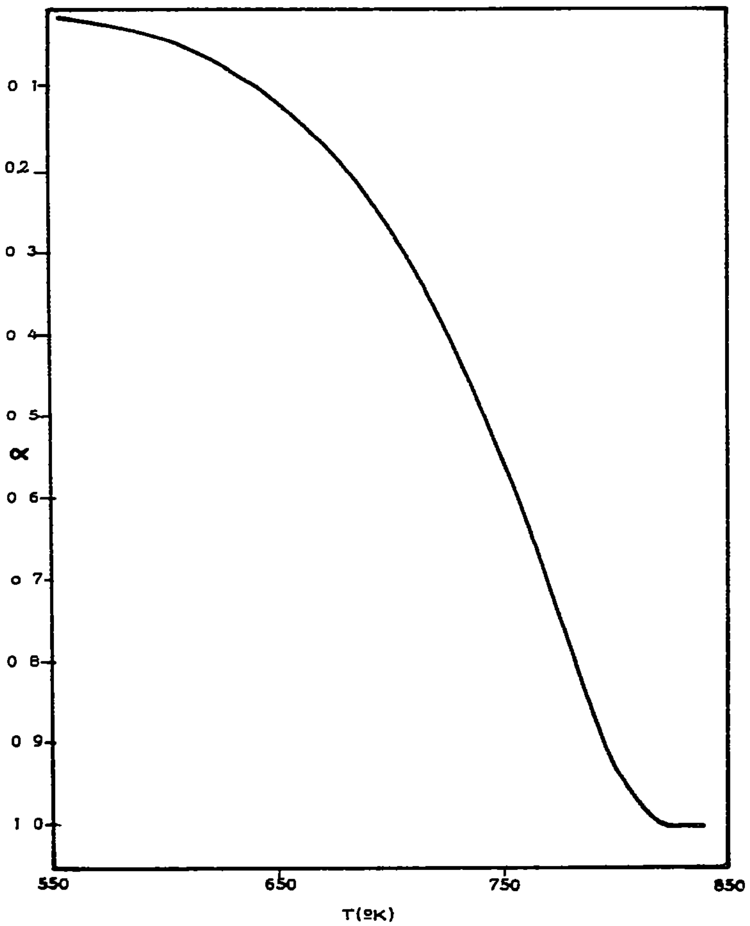

Fig. 1. Theoretical TG curve constructed for a two-dimensional diffusion mechanism by assuming the following kinetic parameters: $E = 30$ kcal mole^{-1}, $A = 3 \times 10^6$ min^{-1}, β = 1°C min^{-1}

In the case of thermal decomposition reactions taking place through the Avrami—Erofeev mechanism it has been shown in previous papers [5—7] that their TG and DTG traces have the same shape as a first order reaction. Thus, a value of n close to 1 would be calculated from the Reich and Stivala method (n cannot be exactly equal to unity, in which case eqn. (3) is no longer valid [2]).

In order to check the validity of the above considerations we have constructed the TG curve included in Fig. 1 by assuming a bidimensional diffusion mechanism, D_2, (i.e., $g(\alpha) = (1-\alpha)\ln(1-\alpha) + \alpha$) and the following kinetic parameters: $E = 30$ kcal mole^{-1}, $A = 3 \cdot 10^6$ min^{-1}; heating rate β = 1°C min^{-1}. The Arrhenius equation has been integrated by means of the 4th

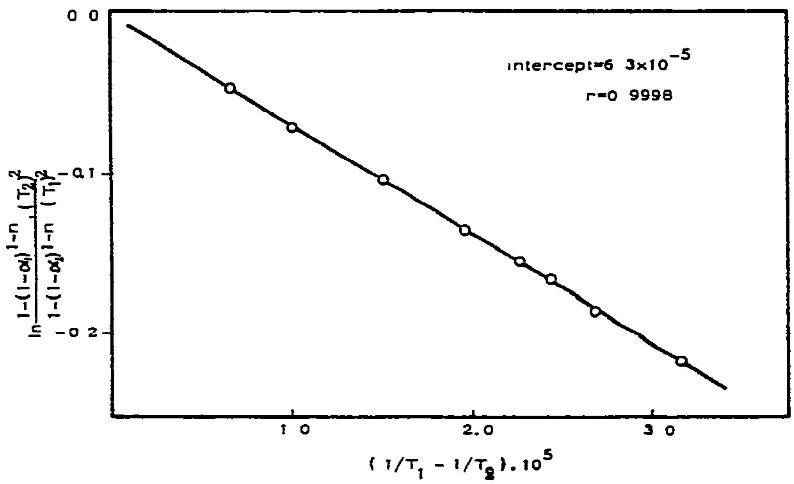

Fig. 2. Kinetic analysis of data in Fig. 1 by means of eqn. (3).

degree rational approximation proposed by Senum and Yang [8]

$$\int_0^T \exp\left(-E/RT\right) dT = \frac{E}{R} \cdot \frac{\exp(-x)}{x} \cdot \frac{(x^3 + 18x^2 + 88x + 96)}{x^4 + 20x^3 + 120x^2 + 240x + 120},$$

$$x = E/RT \tag{8}$$

which involves an error less than $10^{-3}\%$

The kinetic analysis of data in Fig. 1 has been carried out using Reich and Stivala's method by successively increasing the value of n in steps of 0.001 until obtaining the plot included in Fig. 2, which gives an intercept closest to zero.

The values of the kinetic parameters calculated from Fig. 2 are $E' = 13.5$ kcal mole^{-1} (which gives a ratio $E/E' = 30/13.5 = 2.2$) and $n = 0.32$. These results are in excellent agreement with the values previously calculated in Table 1.

In summary, we can conclude that Reich and Stivala's method [2] makes possible the assignment of an "n order" to a reaction that is following a quite different mechanism. In such a case this method of kinetic analysis gives, in addition, erroneous values of the activation energy of the reaction.

REFERENCES

1 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
2 L. Reich and S.S. Stivala, Thermochim. Acta, 36 (1980) 103.
3 M.C. Ball and M.J. Casson, Thermochim. Acta, 27 (1978) 387.

4 S.R. Dharwadkar, M.S. Chandrasekharaiach and M.D. Karkhanavala, Thermochim. Acta, 25 (1978) 372.
5 J.M. Criado, F. Gonzalez and J. Morales, An. Quim., 70 (1974) 787
6 J.M. Criado and J. Morales, Thermochim. Acta, 16 (1976) 382.
7 J.M. Criado, R. García and F. Gonzalez, An. Quim., 75 (1979) 179.
8 G.I. Senum and R.T. Yang, J. Therm. Anal., 11 (1977) 445.
9 J.H. Sharp, G.W. Brindley and N.N. Achar, J. Am. Ceram. Soc., 47 (1966) 379.