Thermochimica Acta, 41 (1980) 125—127
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

Note

ON THE EVALUATION OF KINETIC PARAMETERS FROM THERMOGRAVIMETRIC CURVES

J.M. CRIADO and J. MORALES

Departamento de Química Inorgánica, Facultad de Química de la Universidad de Sevilla y Departamento de Investigaciones Físicas y Químicas, Centro Coordinado del C.S.I.C., Seville (Spain)

(Received 20 February 1980)

We concluded in a previous work [1] that it is not possible to determine the kinetic law followed by a thermal decomposition reaction of a solid from the kinetic analysis of a single TG curve. It is necessary to carry out at least one isothermal run to determine the actual reaction mechanism without ambiguity.

It was shown from a theoretical analysis [1] that TG data of reactions following an Avrami—Erofeev law necessarily fit a first-order kinetic equation. However, it was concluded that very similar activation energies would be obtained whatever the value of the exponent n (1, 2 or 3) in the Avrami—Erofeev equation.

Dharwadkar et al. [2] have studied the mechanism of the thermal decomposition of $CdCO_3$ and, from the analysis of both a single TG diagram and a single isothermal curve, they find that the reaction mechanism is described by an Avrami—Erofeev equation with $n = 3$, concluding that their results support, in part, our theoretical conclusions. However, they state [2] that the apparent activation energies calculated from a TG diagram are quite different for different values of n, which is not in agreement with our theoretical deduction [1].

The aim of the present note is to show that the apparent contradiction between the statement of Dharwadkar et al. and our conclusion is due to the different ways of defining the constant rate.

Thus, Dharwadkar et al. [2] seem to express the Avrami—Erofeev isothermal in the form

$$[-\ln(1-\alpha)] = (kt)^n \tag{1}$$

This can be written as

$$[-\ln(1-\alpha)]^{1/n} = \int_0^t k \, \mathrm{d}t \tag{2}$$

where α is the reacted fraction, n a constant concerned with the nucleation and growth mechanism and k the constant rate that depends on the temperature T according to the Arrhenius equation

$$k = A \exp(-E/RT) \tag{3}$$

E being the activation energy and A Arrhenius the pre-exponential factor.

By using a linear heating rate, $\beta = \mathrm{d}T/\mathrm{d}t$, to perform the kinetic analysis the relationship

$$[-\ln(1-\alpha)]^{1/n} = \int_0^T \frac{A}{\beta} \exp(-E/RT)\,\mathrm{d}T \tag{4}$$

can be obtained from eqns. (2) and (3). By integrating eqn. (4) according to Coats and Redfern [3], taking logarithms and rearranging we obtain

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

or (5)

$$\ln[-\ln(1-\alpha)] - 2n\ln T = -\frac{nE}{RT} + n\ln\frac{AR}{E\beta}$$

Dharwadkar et al. [2] evaluated the activation energy from the plot of the left-hand side of eqn. (5) against $1/T$. If we consider that a solid decomposition reaction at programmed temperature occurs in a narrow range of temperature, the corresponding values of $\ln T$ would be nearly constants. Therefore, regardless of the value given to n, this plot would give a straight line whose slope would be nE/R. Accordingly, the activation energies calculated for different values of n would be closely related through the expression

$$\frac{E_2}{E_1} = \frac{n_1}{n_2} \tag{6}$$

In fact, the values of the activation energy of the thermal decomposition of $CdCO_3$ calculated by Dharwadkar et al. [2] from the Avrami—Erofeev equation by assuming different values of n (1, 2 and 3) are in good agreement with eqn. (6).

However, it is necessary to claim that eqn. (1) does not express in a proper way the kinetic law of reactions following the Avrami—Erofeev mechanism. On the contrary, it has been shown in a number of papers [4—6] that it must be represented in the form

$$-\ln(1-\alpha) = kt^n \tag{7}$$

that would be written in the form

$$[-\ln(1-\alpha)]^{1/n} = \int_0^t k^{1/n}\,\mathrm{d}t \tag{8}$$

Substituting eqn. (3) into eqn. (8), taking into account that $\beta = \mathrm{d}T/\mathrm{d}t$ and integrating as shown previously [1], we obtain

$$[-\ln(1-\alpha)]^{1/n} = \frac{nA^{1/n}RT^2}{E\beta}\exp(-E/nRT) \tag{9}$$

TABLE 1

Kinetic analysis of the TG curve of $CdCO_3$ reported by Dharwadkar et al. [2] by means of eqn. (10)

n	E (kJ mole^{-1})	Correlation coefficient
1	143	—0.9997
2	134	—0.9997
3	121	—0.9997

which, on taking logarithms and rearranging, becomes

$$\ln[-\ln(1-\alpha)] - 2n \ln T = -\frac{E}{RT} + n \ln \frac{nA^{1/n}R}{E\beta} \tag{10}$$

Therefore, if we bear in mind that $\ln T$ remains almost constant, we can conclude that the plot of the left-hand side of eqn. (10) against $1/T$ would be a straight line of slope E/R whatever the value of n.

In summary, we must emphasize that the kinetic analysis of reactions following an Avrami—Erofeev mechanism from TG data leads to a value of the activation energy very close to the actual one, independently of the value previously given to n.

In order to prove the previous assertions we have analysed by means of eqn. (10) the TG data reported by Dharwadkar et al. [2] for the thermal decomposition of $CdCO_3$. The results obtained (Table 1) show that both the activation energies and the correlation coefficients calculated for different values of n are close, in agreement with our previous theoretical analysis [1].

On the other hand, if we take into account that Dharwadkar et al. have proved from the kinetic analysis of one isothermal run of $CdCO_3$ that $n = 3$, we must conclude that the actual value of the activation energy of the thermal decomposition of $CdCO_3$ is $E = 121$ kJ mole^{-1} instead of 41 kJ mole^{-1} as the above authors have reported [2]. Furthermore, the value calculated in the present paper is near to the standard enthalpy of the reaction (100 kJ mole^{-1}).

REFERENCES

1 J.M. Criado and J. Morales, Thermochim. Acta, 16 (1976) 382.
2 S.R. Dharwadkar, M.S. Chandrasekharaiah and M.D. Karkhanavala, Thermochim. Acta, 25 (1978) 372.
3 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
4 B.V. Erofeev, C.R. Acad. Sci. URSS, 52 (1946) 511.
5 M. Avrami, J. Chem. Phys., 7 (1941) 177.
6 D.A. Young, Decomposition of Solids, Pergamon Press, London, 1966.