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Note

ON THE THEORETICAL BASIS OF THE HANCOCK AND SHARP "ln.ln METHOD" OF KINETIC ANALYSIS OF ISOTHERMAL DATA

J.M. CRIADO

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

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Hancock and Sharp [1] have introduced a method for performing the kinetic analysis of isothermal data of solid state reactions based on the generalized Avrami—Erofeev plots that take the form

$$1 - \alpha = \exp(-kt^n) \qquad (1)$$

or

$$\ln[-\ln(1-\alpha)] = n \ln t + B \qquad (2)$$

where B is a constant which depends on the constant rate k, n is a constant that can vary according to the nucleation and growth mechanism, α is the reacted fraction and t is the time. The value of n can be calculated from the slope of the plot of the left-hand side of eqn. (2) against $\ln t$.

Hancock and Sharp [1] calculated a series of α—t curves from the different kinetic equations proposed in the literature for analysing solid state reactions and they realized that the kinetic data following any of these equations also lead to linear plots when $\ln[-\ln(1-\alpha)]$ is plotted against $\ln t$ for α values ranging from 0.05 to 0.65 [1,2]. Moreover, they found that the slopes are characteristic of the reaction mechanism, which allows the actual kinetic law followed by the reaction to be determined. It is, however, an empirical method with, as yet, no theoretical basis [2].

The aim of the present note is to suggest a possible interpretation of the behaviour described above.

It is well known that the kinetics of a solid state reaction can be represented in a general way by the equation

$$g(\alpha) = kt \qquad (3)$$

or

$$\ln g(\alpha) = \ln k + \ln t \qquad (4)$$

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

If the function $g(\alpha)$ were linearly correlated with $\ln[-\ln(1-\alpha)]$, we could write

$$\ln g(\alpha) = a \ln[-\ln(1-\alpha)] + b \qquad (5)$$

TABLE I

Calculation of the kinetic constants of Hancock and Sharp's ln · ln method

Mechanism [a]	n	$-b$	r	n (ref. 1)
Zero order	1.18	0.381	0.9979	1.24
R_2	1.09	0.197	0.9994	1.11
R_3	1.06	0.134	0.9997	1.07
F_1	1.00	0.000	1.0000	1.00
D_1	0.59	0.763	0.9977	0.62
D_2	0.56	1.219	0.9989	0.57
D_3	0.53	2.464	0.9997	0.54
D_4	0.55	2.637	0.9993	0.57
A_2	2.00	0.000	1.0000	2.00
A_3	3.00	0.000	1.0000	3.00

[a] Hancock and Sharp's symbols [1] have been used.

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

$$\ln[-\ln(1-\alpha)] = \frac{1}{a}(\ln k - b) + \frac{1}{a}\ln t \tag{6}$$

where a and b are constants.

Therefore, from a comparison of eqns. (2) and (6) we would obtain

$$n = \frac{1}{a} \tag{7a}$$

and

$$B = n(\ln k - b) \tag{7b}$$

In order to see if the above assumptions work, we have plotted α data ranging from 0.05 to 0.65 according to eqn. (5), after considering the functions $g(\alpha)$ more commonly used for representing the kinetic laws of solid state reactions; the values of n and b obtained are included in Table 1 together with the linear correlation coefficients.

We can see that the values of n calculated from eqn. (5) agree very well with those reported by Hancock and Sharp (see Table 1). In addition, we must point out that the kinetic analysis carried out in the present paper also allows calculation of the constant rate, k, from the intercept of the Hancock and Sharp plots by means of eqn. (7b), once the value of n is known. The value of k would, alternatively, be determined from the slope of the plot of $\ln[-\ln(1-\alpha)]/\ln t$ against $1/\ln t$. In this way, the extrapolation needed for calculating the constant k from the intercept would be avoided.

REFERENCES

1 J.D. Hancock and J.H. Sharp, J. Am. Ceram. Soc., 55 (1972) 74.

2 C.J. Keatch and D. Dollimore, An Introduction to Thermogravimetry, London, 1975, p. 73.