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CORRELATION COEFFICIENTS AND MECHANISM USING TG DATA

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ABSTRACT

The use of linear correlation coefficients to ascertain mechanism from TG data was shown to be unsatisfactory This is in agreement with results reported by others who also indicated the necessity of using additional isothermal techniques for determining mechanism.

Two methods, Reich—Stivala (R—S) and double-log (D-L), were employed to distinguish one mechanism from among 15 theoretical possibilities for heterogeneous solid-state reactions using theoretical TG data. With a certain degree of accuracy of TG data and for relatively large E/RT values (above 18), the R—S method was shown to be superior to the D-L method and a good indicator of a most probable mechanism. In this respect, the utilization of supplemental isothermal techniques may not be necessary when the R—S method is used under certain conditions.

INTRODUCTION

The linear correlation coefficient (r) has been employed by various workers as an adjunct in the estimation of kinetic parameters, i.e., activation energy (E) and reaction order (n) from TG data. In this respect, Fong and Chen [1] attempted to determine which of 17 possible expressions for heterogeneous decompositions best fit their TG data for the thermal dehydroxylation of magnesium hydroxide by using r values. These authors found that it was very difficult to determine the probable mechanism (and hence values of E and n) based on r values since at least half of the expressions tested gave values of r above 0.995. Other workers found similar results. Thus, Heide and co-workers [2,3] found that linear correlation coefficients were not satisfactory for ascertaining the kinetic mechanism from among various theoretically possible mechanisms postulated. Criado and Morales [4,5] and Dharwadkar et al. [6] also reported that high r values do not necessarily lead to the establishment of mechanism using TG data. These workers [4—6] were in agreement that supplemental isothermal runs were also necessary in mechanism studies. Thus, Dharwadkar et al. [6] studied the decomposition of cadmium carbonate in argon by TG techniques. The TG curves obtained were analyzed using a combination of the Coats—Redfern

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[7] and Avrami-Erofeyev [8,9] expressions, i.e.

$$\log\left(\frac{g(\alpha)}{T^2}\right) = -\frac{E}{RT} + \log\left(\frac{ARP}{(\mathrm{RH})E}\right) \tag{1}$$

where, $P = 1 - 2X + 6X^2 - 24X^3 + 120X^4 + \cdots$; $X = RT/E$; $g(\alpha) = F[\int d\alpha/f(\alpha)]$; T = temperature (K); A = frequency factor; (RH) = heating rate; α = fractional conversion; R = gas constant. In eqn. (1), $g(\alpha)$ was set equal to $[-\log(1-\alpha)]^{1/N}$, where N could equal 1, 2 or 3. Dharwadkar et al. [6] found that plots of eqn. (1) (P assumed to be constant) were linear for all three values of N and that the r values obtained were almost unity (0.997—0.998). However, additional isothermal runs were carried out and clearly indicated that the value of N should be 3.

The preceding results with regard to r values may not be surprising when it is considered that the r value is only a relative term. The square of r is proportional to the ratio, explained data variation to total data variation, when least squares analysis of data is used. Thus, while a high r value indicates a good fit of data to a least squares line, it does not necessarily mean that an expression which afforded this value is more likely than one which gave a somewhat lower r value.

The purpose of this paper is to extend a method previously reported by Reich and Stivala (R—S) [10,11] to three mechanisms and, based on these cases, ascertain whether or not it is necessary to supplement TG techniques with isothermal techniques in order to establish a probable mechanism (and consequently values of kinetic parameters) The R—S method was initially applied to TG data (presumably obtained from heterogeneous decompositions) utilizing the well-known expression for homogeneous kinetics

$$\frac{d\alpha}{dT} = \frac{A}{(\mathrm{RH})}\exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \tag{2}$$

Despite its apparent limitations, eqn. (2) has been employed by numerous workers for analyzing TG data (it is theoretically valid for heterogeneous reactions with values of n = 0, 1/2, 2/3, 1) In this paper, the R—S method and a double-log (D-L) method will be applied to 15 kinetic functions which are mechanistically possible for heterogeneous reactions.

SOME THEORETICAL BACKGROUND

From eqn. (1), the following eqn. (3) can readily be obtained. In this equation, P terms are not included. At relatively high E/RT values, P is approximately constant; further, P ratios are close to unity. However, at relatively low E/RT values this is no longer true, so that eqn. (3) becomes less accurate and/or invalid, depending upon the E/RT value. Generally, the E/RT value should be greater than 18.

$$\log\left[\frac{g(\alpha_1)}{g(\alpha_2)}T(1)\right]U(1) = \frac{E}{R} \tag{3}$$

where, $T(1) = (T_2/T_1)^2$; $U(1) = T_1T_2/(T_2 - T_2)$. From eqn. (3), the double-log expression can be derived

$$\frac{\log[K_R G(\alpha_1)]}{\log[K_R G(\alpha_2)]}(TR) = Z_1 \tag{4}$$

where, $K_R = T_R^2/g(\alpha_R)$; T_R and α_R denote an arbitrary reference temperature and its corresponding conversion, respectively; $G(\alpha_1) = g(\alpha_1)/T_1^2$, $G(\alpha_2) = g(\alpha_2)/T_2^2$; $TR = T_1\ (T_R - T_2)/T_2(T_R - T_1)$. In eqn. (4), Z_1 should theoretically be equal to unity.

Equations (3 and 4) will be applied to the following 15 possible kinetic functions. As previously indicated in the R—S method [10,11], the most probable function will be that whose E/R and/or Z_1 values have the lowest mean deviations (MD).

TESTING THE R—S AND D-L METHODS

Fifteen theoretically possible kinetic functions for describing solid-state processes were tested. In the following are listed, in order, the function number and corresponding expression for g(α)

1, α; 2, α^2; 3, $\alpha^{1/2}$; 4, $\alpha^{1/3}$; 5, $\alpha^{1/4}$; 6, $1-(1-\alpha)^{1/2}$; 7, $1-(1-\alpha)^{1/3}$;
8, $-\log(1-\alpha)$; 9, $[-\log(1-\alpha)]^{2/3}$, 10. $[-\log(1-\alpha)]^{1/2}$;
11, $[-\log(1-\alpha)]^{1/3}$; 12, $[-\log(1-\alpha)]^{1/4}$: 13, $\alpha + (1-\alpha)\log(1-\alpha)$;
14, $1 - 2\alpha/3 - (1-\alpha)^{2/3}$: 15. $[1-(1-\alpha)^{1/3}]^2$.

In the preceding, Nos. 1, 3—5 denote a power law mechanism, 6 and 7, a contracting geometry mechanism; 8—12, Avrami—Erofeyev expressions (nucleation): 2, 13 and 14, one-dimensional diffusion, two-dimensional (cylindrical symmetry) diffusion and three-dimensional (spherical symmetry) diffusion (Ginstling—Brounshtein equation), respectively; 15, three-dimensional (spherical symmetry) diffusion (Jander equation).

The 15 expressions were tested with three sets of theoretical $\alpha - T$(K) data generated by means of eqn. (1) and various kinetic parameters (this derived data as well as that which follows was obtained by means of a computer; see ref. 12 for a description of a computer program involving the R—S method). Derived $\alpha - T$ data was obtained using function Nos. 7, 10, and 15 along with various parameters and eqn. (1). In this equation, P was calculated to the 24th power, and E/RT values were greater than 18. When E/RT values are less than ca. 18, the utilization of eqn. (3) (and eqn. (1)) becomes moot.

In the first set of data (DS-1), E/R = 23500 cal mole^{-1}, log $AR/(\mathrm{RH})\ E$ = 10, $g(\alpha) = 1-(1-\alpha)^{1/3}$, to yield the following values of α and T(K), respectively: 0.0606723, 860; 0.0842361, 870; 0.115733, 880; 0.157228, 890; 0.210970, 900; 0.279156, 910; 0.363471, 920; 0.464322, 930; 0.579673, 940; 0.703513, 950; 0.824309, 960; 0.924655, 970. For the second set of data (DS-2), E/R = 15 000 cal mole^{-1}, log $AR/(\mathrm{RH})\ E$ = 11, $g(\alpha) = [-\log(1-\alpha)]^{1/2}$, to yield the following values of $\alpha - T$(K), respectively.

0.00454777, 570; 0.01200787, 580; 0.0305348, 590; 0.0743169, 600; 0.170412, 610; 0.355785, 620; 0.635114, 630; 0.895963, 640; 0.992717, 650; 0.999973, 660. For the third, and final, set (DS-3) of theoretical $\alpha - T(\text{K})$ data generated, $E/R = 15\,000$, $\log AR/(\text{RH})\,E = 4$, $g(\alpha) = [1 - (1-\alpha)^{1/3}]^2$, to yield: 0.0719718, 620; 0.106950, 640; 0.154388, 660; 0.216610, 680; 0.295332, 700; 0.390990, 720; 0.501860, 740; 0.623082, 760; 0.745873, 780; 0.857461, 800; 0.942786, 820. Typical results obtained are listed in Table 1 for DS-1.

From Table 1, it is evident that the most probable mechanism involves function No. 7 and $E/R = 23439 \pm 3$, as anticipated. The only other possible mechanism that came reasonably close involved the Jander diffusion expression (No. 15). These results are based on an accuracy of α to six significant figures (s.f.). When this accuracy was reduced to 4 s.f., MD (7) = 13 and MD (15) = 44 for the R—S method. However, at this accuracy of α, the D-L method failed, i.e. for the D-L method, MD (7) = 1.24×10^{-4} and MD (15) = 1.17×10^{-4}. When α was reduced to 3 s.f., for the R—S method, MD (7) = 126 and MD (15) = 261. Thus, whereas the R—S method could distinguish mechanism No. 7 from 14 other mechanisms down to an accuracy of α to 3 s.f., the D-L method could not distinguish between Nos. 7 and 15 at α to 4 s.f. It may also be noted here that least squares plots were carried out using eqn. (1), DS-1, and the $g(\alpha)$'s for Nos. 7, 14, and 15. The following values of E/R, $\log AR/(\text{RH})\,E$, and r were obtained, respectively: 23428, 9.85, —0.9998; 45606, 31.8, 0.9993; 48683, 35.3, —0 9998. From the preceding, it is vir-

TABLE 1

Values of average E/R and MD and Z_1 and MD for DS-1 by R—S and D-L methods

Function No.	Method			
	R—S		D-L [a]	
	E/R (cal mole^{-1})	MD	Z_1	MD
1	19 534	2713	1.081	0.0476
2	40 889	5379	1 075	0.0429
3	8 857	1381	1.098	0.0606
4	5 298	936	1 124	0.0841
5	3 519	714	1.174	0.135
6	22 374	775	1.017	0.00859
7	23 439	3	1 000	0.00000184
8	25 752	1740	0 972	0.0129
9	16 561	1144	0.972	0.0133
10	11 966	846	0.971	0.0137
11	7 371	548	0.969	0.0145
12	5 073	400	0.967	0.0155
13	44 371	3116	1 038	0 0219
14	45 797	2082	1.023	0 0128
15	48 697	44	1.000	0.00000339

[a] $T_R = 970$, $\alpha_R = 0\ 924655$.

tually impossible to predict the most probable mechanism based on *r* values, as previously contended.

From the DS-2 data, values obtained from function Nos. 8—12 were of a similar order of magnitude. Thus, for α to 6 s.f., the R—S method yielded the following values for E/R and MD: E/R (8) = 31134 ± 35, E/R (9) = 20349 ± 10, E/R (10) = 14957 ± 3, E/R (11) = 9565 ± 15, E/R (12) = 6869 ± 21. However, at this level of accuracy of α, the D-L method failed, e.g., MD (8) = 2.12×10^{-4}, MD (10) = 2.27×10^{-4}. When α was reduced to 4 s.f., mechanism No. 10 still prevailed in the R—S method. However, at α to 3 s.f., the R—S method failed, e.g., MD (10 = 48 and MD (12) = 25 (it may be noted here that although function No. 12 appears to be the most probable mechanism by the R—S method, at an α of 3 s.f., the lowest E/RT value would be less than 10, making this mechanism suspect).

Finally, from the DS-3 data, values obtained for function No. 15 were reasonably close only to values obtained for the similar function No. 7. Thus, at α of 6 s.f., the R—S method yielded E/R (15) = 14943 ± 7 and E/R (7) = 6761 ± 48; for the D-L method, MD (15) = 2.93×10^{-6} and MD (7) = 6.33×10^{-5}. When α was reduced to 4 s f., for the R—S method, MD (15) = 9 and MD (7) = 48, while for the D-L method, MD (15) = 9.96×10^{-5} and MD (7) = 1.04×10^{-4}. Thus, for α to 4 s.f., both methods afforded the mechanism anticipated. However, at an α of 3 s.f., for the R—S method, MD (15) = 84 and MD (7) = 63. The R—S method now fails (the E/RT value for mechanism No. 7 is less than 9, which should make this mechanism suspect). However, the D-L method still applies, i.e., MD (15) = 1.80×10^{-3} and MD (7) = 2.01×10^{-3}.

From the preceding, it can be stated, generally, that the R—S method is more reliable than the D-L method. Thus, for an α of 4 s.f., the R—S method is valid for all the cases tested, whereas the D-L method is not. Below 4 s.f., the R—S method may not be reliable and additional techniques (e.g. isothermal) may be necessary in order to distinguish a mechanism. As previously noted, when the R—S method is employed, the function indicated should possess a minimum value of E/RT greater than 18, and the minimum MD obtained should not be of relatively large magnitude; otherwise, the function should be considered suspect, and other techniques (e.g., isothermal) should be utilized. Also, the functions listed are not all-inclusive, e.g., the Prout—Tompkins function was omitted. Conclusions regarding a correct mechanism should be confirmed, if possible, by means of X-ray diffraction and/or microscopy. Lastly, in the previous treatment, temperatures have been tacitly assumed to be accurate

Some other methods proposed for ascertaining a mechanism using dynamic thermogravimetry will be mentioned. Thus, Criado [13] proposed a method whereby a series of master curves were devised in order to readily determine the mechanism in the thermal decomposition of solids from differential thermogravimetry (DTG) data. However, this method requires accurate measurements of steep slopes and can only distinguish 6 of the 15 functions previously listed (the remaining functions yielding duplicate or identical reduced rate functions of conversion). Also, Criado et al. [14] explored the possibility of distinguishing theoretical mechanisms, using TG data, from the fraction of solid reacted at maximum reaction rate (α_M). These workers concluded that determination of order of thermal decomposition of solids by means of α_M values would lead to misinterpretation of results. Thus, they could find no important differences among corresponding theoretical values of α_M arrived at using various mechanisms, e.g., Jander diffusion mechanism and 2/3-order reactions (cf. function Nos. 7 and 15 previously listed). Gallagher and Johnson [15] also attempted to distinguish theoretical kinetic rate laws. They used, as a criterion for the most acceptable rate law, a minimum standard deviation obtained from the least squares fit of the best straight line. Others [16,17] used an approach similar to that of Gallagher and Johnson and found they could distinguish individual model equations, with statistical significance, from among 11 theoretically possible expressions, using theoretical α — T data. Satava and Skvara [18] proposed master curves to ascertain mechanism and kinetic parameters from TG data. Thus, when a particular plot coincided with a certain master curve, the most probable mechanism and E could be determined. Further manipulations of the graphs allowed for the estimation of A.

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