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Note

A RANDOM SEARCH TECHNIQUE FOR FINDING THE MECHANISM OF SOLID STATE REACTIONS FROM THERMOGRAVIMETRIC DATA

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The determination of the mechanism of solid state reactions from thermogravimetric data is a subject of considerable importance. The present note is concerned with a direct random search technique for arriving at conclusions regarding the mechanism of the reaction and also for evaluating with reasonable accuracy the constants that occur in the relevant kinetic equation. The determination of the specific reaction mechanism in the paper is based on a hypothesis proposed by Sestak and Berggren [1] that almost all the mechanistic equations can be represented as special cases of a very general equation containing various functions of the instantaneous weight fraction. In the algorithm developed herein, the general kinetic equation is fitted to the experimentally obtained thermogravimetric data, and by changing the values of the constants involved using a random search procedure, the equation is modified to best fit the data; this equation, incidentally, is the most probable mechanistic equation. The sum of the squares of the residuals (or errors) has been used as a criterion for measuring the 'goodness of fit' of the equation to the data in question. The salient features of the theory and the associated algorithm are presented below.

The various kinetic reaction mechanisms may be classified into one or other of the following five broad categories:

(1) phase-boundary controlled processes;

(2) reactions controlled by nucleation;

(3) process governed by nucleation followed by the bulk growth of nuclei;

(4) process controlled by nucleation followed by the linear growth of nuclei; and

(5) diffusion-controlled reactions.

A consideration of the above reaction mechanisms seems to indicate that the kinetic equation can, with analytic advantage, be expressed in the general form

$$\frac{d\alpha}{dt} = K(1-\alpha)^n \alpha^m [-\ln(1-\alpha)]^p ,$$

where k = rate constant, α = weight fraction of chemical decomposed, t = time of reaction and n, m and p are constants. The various combinations of

TABLE 1

Combination of exponent factors for possible reaction mechanisms

Sl No.	Reaction mechanism	n	m	p
1	Phase boundary reaction (one-dimensional movement)	X	X	X
2	Phase boundary reaction (unimolecular decay)	√	X	X
3	Nucleation, linear growth of nuclei, linear diffusion	X	√	X
4	Diffusion	X	X	√
5	Nucleation, latter stages of linear growth of nuclei	√	√	X
6	Growth of nuclei diffusion	√	X	√

Note: The equations containing m and p only and m, n and p are not justified.

the exponents m, n and p correspond to the different reaction mechanisms as shown in Table 1. It may further be noted, as suggested in ref. 1, that the use of the Arrhenius equation

$$K = A \exp(-E/RT)$$

where, A = the pre-exponential factor, E = the energy of activation, R = the universal gas constant, and T = the absolute temperature, is justified. For known reactions, the thermogravimetric data can be fitted [2] to the general equation with that combination of the indices which corresponds to the relevant mechanism and thus E and A can be evaluated. The algorithm developed in the present paper is based on the converse assumption, viz., that the combination of the indices in the above equation, which best fits the data, will throw adequate light on the reaction mechanism, and consequently may be used to pinpoint, at least qualitatively, the most probable mechanism which has generated the experimental data. For n data points consisting of α, T and $d\alpha/dt$, the residue

$$R = \sum_{i=1}^{n} \left[\left(\frac{d\alpha}{dt}\right)_i - A \exp(-E/RT_i)\, \alpha_i^m (1-\alpha_i)^n \{-\ln(1-\alpha_i)\}^p \right]^2$$

can reasonably be regarded as a measure of the goodness of fit of the equation to the data [3].

The method of random search with systematic reduction of the size of the search region constitutes an elegant procedure for optimization and may be utilized for minimizing R to arrive at a suitable combination of m, n and p. The process is started with an initial set of values A^0, E^0, m^0, n^0 and p^0 for the kinetic parameters and ranges R_A^0, R_E^0, R_m^0, R_n^0 and R_p^0 are defined to restrict the magnitudes of the corrections to the values of the respective parameters during each iteration. The residue R^0 is then evaluated. Using any standard method, five pseudo-random numbers N_j^0 ($j = 1, 2, \cdots, 5$), such that $-0.5 < N_j^0 < 0.5$, are generated and new estimates for the parameters determined using the relations

$$A^1 = A^0 + N_1^0 R_A^0$$

$$E^1 = E^0 + N_2^0 R_E^0$$

$$m^1 = m^0 + N_3^0 R_m^0$$

$$n^1 = n^0 + N_4^0 R_n^0$$

$$p^1 = p^0 + N_5^0 R_p^0$$

and the residue R' corresponding to the above new values is obtained. In general, however, R' may or may not be less than R^0. If $R' < R^0$, the trial can be regarded as a success and new estimates for the parameters obtained by using

$$A^2 = A^1 + N_1^1 R_A^1$$

and so on, where N_i^1 are again five random numbers and $R_A^1 = R_A^0 \times \epsilon$ where $0 < \epsilon < 1$. The multiplication by a proper fraction has the effect of reducing the range in a systematic fashion after each successful iteration. If, however, $R' > R$, the trial is a failure and second estimates are generated by $A^2 = A^0 + N_1^2 R_A^0$

The above procedure is continued till such time as $R_A^{(n)}$, $R_E^{(n)} \cdots R_p^{(n)}$ become extremely small and the subsequent trials do not affect the values of the parameters significantly. The value of R thus obtained may not be the minimum, since the intervals may possibly become quite small soon and exclude the most probable values of the parameters. With a view to avoiding this possibility, the whole process of minimizing the residue is repeated with $A^{(n)}$, $E^{(n)}$, ... as initial values and R_A^0, R_E^0 ... as ranges. Several trials of this kind may be needed to obtain a sufficiently small value of R.

The above algorithm was coded in FORTRAN language and the program was run on the IBM 360/Model 44 Computer of Vikram Sarabhai Space Centre, Trivandrum, for numerous sets of thermogravimetric data. The subroutine RANDU (IX, IY, YFL), available in the Scientific Subroutine Package of IBM 360 (also described in ref. 4), was employed for generating pseudo-random numbers to be used in the procedure. A sample set of data together with the relevant results, obtained by this method, are exhibited in Tables 2 and 3.

TABLE 2

Sample data

T (K)	$1-\alpha$	T (K)	$1-\alpha$	T (K)	$1-\alpha$
419.0	0.9665	459.0	0.7224	482.0	0 3913
429.0	0.9331	462.0	0.6890	485.0	0.3361
434.0	0.9114	465.0	0.6522	488.0	0.2761
439.0	0.8863	468.0	0.6104	491.0	0.2308
444.0	0.8562	471.0	0.5686	494.0	0.1789
447.0	0.8328	474.0	0.5234	497.0	0.1304
450.0	0.8110	477.0	0.4732	500.0	0.0870
453.0	0.8080	479.0	0.4398	503.0	0.0502
456.0	0.7542				

TABLE 3

Initial values, some intermediate computed values and final values of the parameters

	A	E (kcal mole^{-1})	Exponent factors			Residue
			n	m	p	
Initial values	0.1000×10^{14}	25.000	1.000	1.000	1.000	2862.907
Intermediate computed values	0.9893×10^{13}	27.260	0.980	1.118	1.126	32.681
	0.9459×10^{13}	30.747	1.373	1.120	0.352	0.001
	0.9546×10^{13}	31.585	0.902	0.153	—0.545	0.0002
Final [a] values	0.8233×10^{13}	31.976	0.466	0.0	—0.842	0.00014

[a] The equation corresponding to the final values is

$$\frac{d\alpha}{dt} = 0.8233 \times 10^{13} \exp(-31976/RT)(1-\alpha)^{0.466}[-\ln(1-\alpha)]^{-0.842}$$

suggesting the mechanism to be possibly a three-dimensional transport process.

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