Thermochimica Acta, 39 (1980) 329—333

Note

THE DETERMINATION OF THE MECHANISM OF SOLID STATE REACTIONS FROM THERMOGRAVIMETRIC DATA

V. SWAMINATHAN, N.S. MADHAVAN and D. RADHAMONY

Chemicals and Materials Group, Vikram Sarabhai Space Centre, Trivandrum-695 022 (India)

(Received 7 January 1980)

The object of this note is to present the salient features of a generalized computer program that was developed with a view to determining the most likely reaction mechanism from thermogravimetric data and also the kinetic parameters of relevance. The data are fitted to different kinds (as many as 13) of mechanistic equations and a residue analysis is carried out. The goodness of fit of the data to the equations has finally been used as a measure to arrive at conclusions regarding the most probable reaction mechanism and the corresponding equation yields the values of the kinetic constants.

While carrying out the actual computations, care was taken to ensure that the cases of those equations which lead to unrealistic or irrational values for the kinetic parameters, such as activation energy and pre-exponential factor, were neglected for the purpose of our analysis. Such situations often become possible on account of the fact that the technique applied for determining the reaction mechanism in the program is essentially mathematical in character and also due to the fact that the weight losses which are considered for the analysis are susceptible to experimental errors. The details of the method used in the computer program are as follows.

It is well known that the mechanistic equations corresponding to different types of reactions are generally of the form

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\phi} \exp(-E/RT)\, \mathrm{f}(\alpha)$$

where α is the weight fraction of chemical decomposed, T the absolute temperature of the reaction environment, A the pre-exponential factor, ϕ the heating rate, E the energy of activation, R the universal gas constant, and $\mathrm{f}(\alpha)$ a function of α. A number of possible reactions and the functions, $\mathrm{f}(\alpha)$, connected with them are shown in Table 1 (cf. ref. 1, pp. 7—10). The computer program endeavours to fit the given data to all these equations and calculates, in each case, the sum of squares of the residuals. It then becomes a relatively simple matter to determine which of the equations leaves the least residue and, as a consequence, characterizes the reaction in question.

TABLE 1

List of mechanisms of reactions and corresponding f(α)

Reaction mechanism	f(α)
(a) Phase-boundary controlled processes	
(1) One-dimensional movement (and some cases of evaporation)	α^0
(2) Two-dimensional movement (for cylinder or prism)	$(1-\alpha)^{1/2}$
(3) Three-dimensional movement (a sphere reacting from all surfaces inwards)	$(1-\alpha)^{2/3}$
(b) Reactions controlled by nucleation	
(4) Nucleation according to the power law	α^m
(5) Nucleation according to the exponential law	$\alpha^m(1-\alpha)^n$
(c) Process governed by nucleation followed by bulk growth of nuclei	
(6) Induction stage	α^m
(7) Two-dimensional growth of nuclei	$(1-\alpha)[-\ln(1-\alpha)]^{1/2}$
(8) Three-dimensional growth of nuclei	$(1-\alpha)[-\ln(1-\alpha)]^{2/3}$
(9) Later stages (unimolecular decay law)	$(1-\alpha)$
(d) Process controlled by nucleation followed by the linear growth of nuclei	
(10) Chain growth of nuclei	α
(11) Branching nuclei interacting during their growth	$\alpha(1-\alpha)$
(12) Later stages of (10) and (11)	$\alpha^m(1-\alpha)^n$
(e) Diffusion-controlled reactions	
(13) One-dimensional transport process with constant diffusion coefficient	α^{-1}
(14) Two-dimensional transport process	$[-\ln(1-\alpha)]^{-1}$
(15) Three-dimensional transport process	$(1-\alpha)^{1/3}[-\ln(1-\alpha)]^{-1}$
(16) Growth of spherical particles	$\alpha^m(1-\alpha)^n$

As a typical example, we may consider the case of nucleation according to the exponential law, wherein we have [1]

$$\frac{d\alpha}{dT}=\frac{A}{\phi}\exp(-E/RT)\,\alpha^m(1-\alpha)^n$$

m and n being constants. Taking logarithms

$$\ln\left(\frac{d\alpha}{dT}\right)=\ln\left(\frac{A}{\phi}\right)-\frac{E}{R}\frac{1}{T}+m\ln\alpha+n\ln(1-\alpha)$$

which is clearly of the form

$$u=a+bx+my+nz$$

where

$$u=\ln(d\alpha/dT)\,,\qquad x=1/T\,,\qquad y=\ln\alpha\,,\qquad z=\ln(1-\alpha)\,,$$

and

$$a=\ln(A/\phi)\qquad\text{and}\qquad b=-E/R$$

TABLE 2

Sample thermogravimetric data

T (K)	$1-\alpha$	T (K)	$1-\alpha$	T (K)	$1-\alpha$
742	0.959	787	0.755	812	0.384
757	0.923	792	0.695	817	0.239
767	0.894	797	0.625	822	0.204
777	0.839	802	0.552	827	0.130
782	0.803	807	0.460	832	0.072

are parameters to be estimated.

From thermogravimetric data consisting of T_i and the corresponding α_i [and possibly $(\mathrm{d}\alpha/\mathrm{d}T)_i$ also], the magnitudes of u_i, x_i, y_i, z_i (where the subscript i refers to the ith value of the relevant variable) are obtained. The values of a, b, m and n are now determined by applying the principle of least squares [2]. The constants A and E follow immediately.

The data are again fitted in like manner to all other mechanistic equations and the sum of the squared residues for each equation is worked out by using the expression

$$S=\sum_i \left\{\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{i(\text{actual})}-\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{i(\text{predicted})}\right\}^2$$

From the different values of S obtained as above, the equation (and thus the reaction mechanism) which suits the data best is easily the one which corresponds to the minimum value of S unless, of course, the corresponding kinetic parameters are too unrealistic to characterize the situation.

A computer program * employing the above technique, was developed in FORTRAN IV and was run on the IBM-360 Model-44 Computer at Vikram Sarabhai Space Centre, Trivandrum, for determining the reaction mechanism of a number of chemicals from their thermogravimetric data. The program consists of a main program together with 13 subprograms, each of these corresponding to the curve-fitting and residue evaluation for one particular mechanistic equation. Table 3 exhibits the results obtained for a typical set of input data shown in Table 2. A glance at Table 3 reveals that the least residue is 0.1389×10^{-3} corresponding to the mechanistic equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A}{\phi}\exp(-E/RT)\,\alpha^m(1-\alpha)^n$$

The relevant kinetic parameters, however, are somewhat abnormal and hence

---

* The computer program is readily available from the authors and will be supplied on request.

TABLE 3

Results obtained from the computer program for sample data

Serial no.	$f(\alpha)$	A	E	m	n	Residue
1	$(1-\alpha)^{1/3}[-\ln(1-\alpha)]^{-1}$	0.1403×10^{25}	89.36			0.4963×10^{-3}
2	$(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	0.5706×10^{8}	26.46			0.2080×10^{-3}
3	$(1-\alpha)$	0.8816×10^{16}	56.99			0.1864×10^{-3}
4	$\alpha(1-\alpha)$	0.1254×10^{4}	8.300			0.1964×10^{-3}
5	$(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	0.8816×10^{16}	56.99			0.5828×10^{-3}
6	α^{0}	0.1937×10^{5}	28.27			0.2555×10^{-2}
7	$(1-\alpha)^{2/3}$	0.5385×10^{10}	47.38			0.2390×10^{-3}
8	$(1-\alpha)^{1/2}$	0.2340×10^{9}	42.60			0.2792×10^{-3}
9	α	0.2836×10^{-8}	−20.37			0.3973×10^{-3}
10	$\alpha^{m}(1-\alpha)^{n}$	0.1939×10^{44}	172.43	−2.019	1.599	0.1389×10^{-3}
11	α^{-1}	0.1320×10^{18}	76.92			0.6118×10^{-3}
12	$[-\ln(1-\alpha)]^{-1}$	0.4442×10^{21}	89.27			0.3890×10^{-3}
13	α^{m}	0.1192×10^{-29}	−101.38	2.664		0.3464×10^{-3}

unsatisfactory, E being 172.43 kcal mole^{-1} and A 0.1939 × 10^{44}. We have recourse to the next best equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A}{\phi}\exp(-E/RT)(1-\alpha)$$

which corresponds to a residue of 0.1864 × 10^{-3}, yielding kinetic parameters E = 56.99 kcal mole^{-1} and A = 0.8816 × 10^{16} which are more reasonable. This suggests that the reaction is governed by the later stage of nucleation (unimolecular decay law). Once the mechanism of reaction and approximate values for the parameters have been obtained, more sophisticated techniques may be employed, if needed, to improve the constants [3,4].

ACKNOWLEDGEMENTS

The authors are grateful to Dr. Vasant R. Gowariker, Director, Vikram Sarabhai Space Centre and Mr. M.R. Kurup, Director, Chemicals and Materials Group, Vikram Sarabhai Space Centre, Trivandrum, for their kind encouragement in the preparation of this paper.

REFERENCES

1 J. Šesták and G. Berggren, Thermochim. Acta, 3 (1971) 1.
2 C.F. Gerald, Applied Numerical Analysis, Addison-Wesley, Reading, MA, 1973, p. 284.
3 V. Swaminathan and N.S. Madhavan, Thermochim. Acta, 33 (1979) 367.
4 E.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.