Thermochimica Acta, 33 (1979) 367—369

Note

A NEW METHOD FOR THE EVALUATION OF KINETIC CONSTANTS FROM THERMOGRAVIMETRIC DATA

V. SWAMINATHAN and N.S. MADHAVAN

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

(Received 5 December 1978)

Several methods have been described in the literature for evaluating the kinetic parameters of chemical reactions from thermogravimetric data [1]. The object of this note is to present the salient features of a technique which is simple and versatile and which can be employed with advantage for evaluating the frequency factor, energy of activation and order of reaction of chemical reactions. The values of kinetic parameters obtained by this method appear to be reasonably consistent with those obtained by standard procedures such as the Freeman and Carroll method [2]. The details of the method are as follows.

The general rate equation of non-isothermal kinetics assuming the reaction order model has the well-known form

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

where, α = weight fraction of chemical decomposed, t = time, A = pre-exponential factor, ϕ = heating rate, E = energy of activation, R = universal gas constant, T = temperature (absolute), and n = order of reaction.

Equation (1) on integration yields (cf. ref. 1, p. 450)

$$\mathrm{g}(\alpha, n) = \frac{AE}{R\phi} \mathrm{P}(x) \tag{2}$$

where

$$\mathrm{g}(\alpha, n) = [1-(1-\alpha)^{1-n}]/(1-n)$$

$$\mathrm{P}(x) = \int_x^\infty \exp(-u)/u^2 \,\mathrm{d}u$$

and

$$x = E/RT$$

The kinetic data analysis is aimed at evaluating the values of the constants A, E and n which satisfy eqn. (2).

Suppose that n observations relating to α and T are available. The problem reduces to one of evaluating the kinetic constants which minimize the sum of residues

$$S = \sum_{i=1}^{n} |g(\alpha_i, n) - \frac{AE}{R\phi} P(x_i)| \qquad (3)$$

An analytical approach to this minimization problem is fraught with difficulties but the method of direct random search and systematic reduction of the size of the search region can be quite helpful in this case. To start with, a set of initial estimates P_i^0 ($i = 1, 2, 3$) for the kinetic parameters A, E and n, with ranges R_i^0 ($i = 1, 2, 3$) which, in all probability, will contain the actual values of the parameters are chosen and the corresponding residual sum S^0 evaluated. Also, using any standard method (cf. ref. 3, p. 225), three random numbers N_i^0 ($i = 1, 2, 3$) such that $-0.5 < N_i^0 < +0.5$ are generated. New estimates for the parameters are then obtained from the previous set of values by the use of the formula

$$\ln P_i^1 = \ln P_i^0 + N_i^0 R_i^0 \qquad (4)$$

and the error sum S^1 determined. If $S^1 < S^0$, the trial can be regarded as a success and new estimates P_i^2 are obtained by using

$$\ln P_i^2 = \ln P_i^1 + N_i^1 R_i^1$$

where N_i^1 are again three pseudo-random numbers and $R_i^1 = R_i^0 \epsilon$ where ϵ is a proper fraction, the multiplication by which reduces the range systematically after each iteration. If, on the other hand, $S^1 \geqslant S^0$, the trial is a failure and second estimates are generated by

$$\ln P_i^2 = \ln P_i^0 + N_i^1 R_i^0$$

The procedure, described above, is repeated until R_i^n becomes so small that subsequent trials do not appreciably change the values of the kinetic parameters.

The convergence thus obtained may not lead to the actual values of the parameters, since the range may soon become small and possibly exclude the actual values. To obviate this difficulty, the whole process may have to be repeated with P_i^n as the initial estimates and R_i^0 as the ranges and a few such trials may be required before attaining values that are sufficiently accurate.

A computer program was developed in FORTRAN IV language for the

TABLE 1

Sample data

T (K)	α	T (K)	α	T (K)	α	T (K)	α
713	0.956	743	0.778	757	0.538	769	0.217
723	0.924	748	0.706	760	0.461	772	0.135
733	0.870	751	0.656	763	0.383	775	0.055
738	0.828	754	0.598	766	0.304		

TABLE 2

A comparison of kinetic parameters obtained by the two methods

Parameter	Dimension	Magnitude		
		Initial estimates	By the method described in this note	By the Freeman and Carroll method
Energy of activation, E	(kcal mole^{-1})	20.0	56.7	52.8
Order of reaction, n		0.7	0.26	0.37
Pre-exponential factor, A		10^9	0.37×10^{16}	

analysis of the thermogravimetric data using the random search technique and was run on the IBM 360/Model 44 Computer at Vikram Sarabhai Space Centre, Trivandrum, for a number of sets of experimental data. The subroutine RANDU (IX, IY, YFL), available in the System Subroutine Package of IBM 360, was employed for generating the necessary pseudo-random numbers and a computer time extending to roughly 2 min was needed to obtain reasonably accurate values for the kinetic parameters. A major advantage of this technique appears to be its simplicity, together with its capability to yield the three chief kinetic constants all at once. A sample set of data taken for our analysis is given in Table 1, while Table 2 presents the initial estimates and final values of the kinetic parameters obtained by the technique elucidated in this note, together with those obtained by the Freeman and Carroll method. The sum of the residues which, in this case, has a value of 0.1657×10^6 corresponding to the initial estimates, is found to reduce ultimately to 0.0459.

ACKNOWLEDGEMENT

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

REFERENCES

1 J. Šesták, V. Satava and W.W. Wendlandt, Thermochim. Acta, 7 (1973) 333.
2 E.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
3 R.V. Andree, J.P. Andree and D.D. Andree, Computer Programming: Techniques, Analysis, and Mathematics, Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1973, p. 225.