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A NEW TECHNIQUE FOR DETERMINATION OF THE POSSIBLE REACTION MECHANISM FROM NON-ISOTHERMAL THERMOGRAVIMETRIC DATA

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ABSTRACT

A new technique for the selection of the most probable reaction mechanism utilising non-isothermal thermogravimetric data has been developed. The proposed method utilises the isoconversional activation energy, i.e. the apparent activation energy evaluated using the isoconversional method, as an indicator for distinguishing between mechanism types. An added advantage of this novel technique is that it allows an accurate recognition of non-isokinetic processes. Our investigation also reveals that the constancy of the pre-exponential factor over a range of heating rates is not peculiar to a single reaction mechanism; consequently, it is not a sufficient criterion for establishing the most appropriate reaction mechanism. This work also demonstrates the sensitivity of the apparent activation energy and pre-exponential factor to the accuracy of temperature measurement and re-emphasises the inaccuracy of drawing conclusions about reaction mechanisms using the correlation coefficient as the sole criterion.

INTRODUCTION

The difficulties of evaluating kinetic parameters for solid state processes from rising temperature thermogravimetric data have led to the publication of numerous conflicting kinetic equations and calculation techniques. This has invariably sparked off debate within the scientific community thus compelling the International Confederation for Thermal Analysis (I.C.T.A.) to appoint a sub committee on kinetics [1] under the chairmanship of Professor J.H. Flynn to look into the issue.

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BACKGROUND TO THE PROBLEMS

To describe the kinetics of a process, it is desirable to know the dependence of the reaction rate on the parameters which characterise the system. Unfortunately, in the case of heterogeneous systems there is hardly a single process that can adequately describe the rate-limiting step in the entire region of investigation. To circumvent this difficulty, experiments should be designed in such a way that would allow the investigation of a single partial process. Provided this can be achieved, it can be assumed that the rate of the process is a unique function of temperature (T) and degree of conversion (α), in which case the rate is formally expressed as

$$\text{rate} = \mathrm{d}\alpha/\mathrm{d}t = k(T)f(\alpha) \tag{1}$$

or according to ref. 2, as

$$\text{rate} = \mathrm{d}\alpha/\mathrm{d}t = k(T)f(\alpha)\phi(\alpha, T) \tag{2}$$

where $\phi(\alpha, T)$ is equated to unity for isokinetic processes, $k(T)$ is a temperature dependent rate constant, $f(\alpha)$ is the conversion function which is assumed to describe the reaction mechanism and α is a dimensionless quantity referred to as the degree of conversion.

To solve the differential equation given in eqn. (1) above, it is imperative to know: the functional dependence of the rate constant on temperature, $k(T)$; and the analytical form of the conversion function $f(\alpha)$.

The various approaches employed to obtain this information have led to a proliferation of equations and calculation techniques for the determination of kinetic parameters from thermogravimetric data.

The complete success achieved in extracting similar information for homogeneous systems was so overwhelming that concepts and reaction mechanisms used in homogeneous kinetics were used to treat kinetic data for heterogeneous processes under non-isothermal conditions. Consequently, the validity of the Arrhenius equation was presumed and the thermal dependence of the rate constant, $k(T)$, is accordingly expressed as

$$k(T) = A\exp(-E/RT) \tag{3}$$

or according to some authors [3,4]

$$k(T) = AT^{b}\exp(-E/RT) \tag{4}$$

where A is the "pre-exponential factor", E is the "apparent activation energy" and b is a constant. In this communication, eqn. (3) will be used because, in our opinion, the constant b only complicates an already difficult problem and, moreover, there is no satisfactory method for its determination. For a linear temperature program, eqn. (3) can be combined with eqn. (1) to obtain

$$\mathrm{d}\alpha/\mathrm{d}t = A/\beta\exp(-E/RT)f(\alpha) \tag{5}$$

where β is the heating rate in °C min^{-1}.

Equation (5) is the fundamental equation that forms the basis of both the differential and integral methods of analysing thermoanalytical data obtained from thermogravimetric curves. It is also the focus of most of the controversies in non-isothermal solid state kinetics. The major areas of disagreement amongst thermal analysts are:

(a) the consistency of the calculation techniques currently in use for evaluation of the apparent activation energy and pre-exponential factor [5];
(b) the appropriateness of the existing methods for elucidation of the most probable reaction mechanism describing the process [5];
(c) the existence or otherwise of the total differential of $\alpha = f(t, T)$, in other words the relationship between $\mathrm{d}\alpha/\mathrm{d}T$ and $\mathrm{d}\alpha/\mathrm{d}t$ [6];
(d) the validity of expressing the thermal dependence of the rate constant in terms of the Arrhenius equation [7–14].

We shall address ourselves to items (a) and (b) leaving items (c) and (d) for further consideration in a subsequent communication. It is widely accepted within the thermal analysis community that the parameters E and A in eqn. (5) have little physical significance apart from being empirical constants [15,16]. This view is held because of the following observations: (i) the values of these parameters obtained for the same substance by different workers, and sometimes by the same worker, often vary widely [17,18]; (ii) these parameters have been reported to vary with experimental factors such as heating rate, furnace atmosphere, packing density of sample, shape and nature of crucible, sample size and even the history of the sample preparation [19–21].

In our opinion the above observations are at the root of the current debate regarding the non-isothermal kinetics of solid state processes: it was on these grounds that researchers started to question the rationale of using the Arrhenius equation and the rate expression as given in eqn. (1).

METHOD FOR EVALUATION OF THE APPARENT ACTIVATION ENERGY

Of the various calculation techniques that have been reported, we consider the isoconversional method as the most suitable despite Zsako and Arz's criticism of this method [17]. The isoconversional method was first formulated independently by Ozawa [22] and Flynn and Waal [23]. Its attraction derives mainly from its ability to give activation energy values without the necessity of presuming the analytical form of the controversial conversion function $f(\alpha)$. A published method [24] based on the Ozawa [22] technique and an improved version of the Coats–Redfern equation [25] will be utilised in this work. The details of the calculation technique are given below.

In order to improve the Coats–Redfern equation [25] for use with the Ozawa technique [22], Fatemi [26] modified and transposed the Coats–Redfern equation to get

$$\log_{10}\left\{\frac{\beta_i}{T_{ij}^2\phi(E, T_{ij})}\right\} = \log_{10}\left\{\frac{AR}{g(\alpha_j)E}\right\} - \frac{E}{2.303RT_{ij}} \tag{6}$$

where $\phi(E, T_{ij})$ is an asymptotic series given as:

$$\phi(E, T_{ij}) = 1 - \frac{2!}{X} + \frac{3!}{X^2} - \ldots + \frac{(-1)^n(n+1)!}{X^n} \tag{7}$$

For efficient evaluation of the above series, we combined two successive terms to give a new series as follows

$$\phi'(E, T_{ij}) = (1 - 2/X) + \frac{3!}{X^2}(1 - 4/X) + \frac{(2n+1)!}{X^{2n}}\left\{1 - \frac{2n+2}{X}\right\} \tag{8}$$

Replacing $\phi(E, T_{ij})$ with $\phi'(E, T_{ij})$ in eqn. (6) gives

$$\log_{10}\left\{\frac{\beta_i}{T_{ij}^2\phi'(E, T_{ij})}\right\} = \log_{10}\left\{\frac{AR}{g(\alpha_j)E}\right\} - \frac{E}{2.303RT_{ij}} \tag{9}$$

A term in the new series is the sum of two terms in the former series; consequently, each term in the new series is smaller in magnitude than either of its components in the original series. Hence, not only has this eliminated the alternating sign between terms in the original series, but also may accelerate the attainment of the limiting conditions, that is, in reaching the negligible term of the series or the approach to the asymptotic condition.

Although eqn. (9) contains the apparent activation energy (E) in an asymptotic series, it is easy to solve for E using an iterative technique. Basically, the iterative procedure consists of two loops. The iteration is initialised by taking $E = 10^{10}$ in $\phi'(E, T_{ij})$ which then becomes unity: a first approximation to E is thus obtained which is then substituted into eqn. (9). At this point, a second loop is used to evaluate the sum of the asymptotic series as described in the next paragraph. The sum is then resubstituted into the main loop and the equation solved to give values of the left-hand-side corresponding to each reciprocal temperature ($1/T_{ij}$) and heating rate (β_i), for the jth degree of conversion, α_j. A plot of the left-hand-side against $1/T_{ij}$ is made and the best straight line is drawn through the points using a least-squares fit analysis. The apparent activation energy (E) is then calculated from the slope ($-E/2.303\ R$) of this line. The difference between the newly evaluated activation energy and its predecessor is compared with an assigned value of the acceptable truncation error (ERROR $= 10^{-6}$). If this difference is greater than ERROR, the current activation energy is recycled as the approximate value and the computation repeated until the condition is satisfied and we obtain the activation energy for the given degree of conversion α_j. The whole procedure is repeated for each degree of conversion chosen and the mean is calculated and reported as the apparent activation energy for the particular process. In subsequent references, this mean apparent activation energy will be called the isoconversional activation energy.

The sum of the asymptotic series is obtained by splitting the sum into the first term plus the sum of the remaining terms. The first term is stored and each subsequent term of the series is calculated from its predecessor using an iterative loop. Once a term is calculated its magnitude is compared with the truncated error; if it is larger than ERROR, it is added to the store and the next term is calculated and tested similarly. This sequence of computation is repeated until a term is obtained with a magnitude less than or equal to ERROR; the loop is then terminated and the sum is used in solving eqn. (9) as described above.

GENERATION OF THEORETICAL DATA

To test the consistency of the above technique, theoretical data were generated as follows. Equation (9) is generally quoted as

$$g(\alpha) = (AE/R\beta)P(X) \tag{10}$$

where by definition

$$g(\alpha) = \int_0^{\alpha} \mathrm{d}\alpha/f(\alpha) \tag{11}$$

$$P(X) = \int_{\infty}^{X} X^{-2}\,\mathrm{e}^{-X}\,\mathrm{d}X \tag{12}$$

$$X = E/RT \tag{13}$$

TABLE 1

Refined data: theoretical data generated by assuming $E = 125.520$ kJ mol^{-1}, $A = 6.667 \times 10^8$ min^{-1}, $g(\alpha) = [-\ln(1-\alpha)]^{\frac{1}{2}}$ and $\beta_i = 1, 2, 4, 6, 8$ °C min^{-1}

α	T (K) at $\beta = 1$ °C min^{-1}	T (K) at $\beta = 2$ °C min^{-1}	T (K) at $\beta = 4$ °C min^{-1}	T (K) at $\beta = 6$ °C min^{-1}	T (K) at $\beta = 8$ °C min^{-1}
0.1	614.06505	630.53379	647.87588	658.45268	666.16084
0.2	622.87542	639.80870	657.65209	668.54073	676.47904
0.3	628.50665	645.74007	663.90762	674.99803	683.08533
0.4	632.88629	650.35488	688.77657	680.02523	688.22942
0.5	636.65415	654.32628	672.96800	684.35374	692.65920
0.6	640.13757	657.99886	676.84518	688.36841	696.75808
0.7	643.58128	661.63053	680.68020	692.32020	700.81356
0.8	647.28140	665.53364	684.80303	696.58003	705.17467
0.9	651.90380	670.41116	689.95679	701.90611	710.62817

TABLE 2

Apparent activation energies evaluated from theoretical data for $E = 41.840$, 125.520 and 209.200 kJ mol^{-1}, $A = 6.667 \times 10^8$ min^{-1}, $\beta_i = 1, 2, 4, 6, 8$ °C min^{-1} and $g(\alpha) = (-\ln(1-\alpha))^{\frac{1}{2}}$

Alpha (α)	Activation energy E (kJ mol^{-1})	Correlation coefficient r
0.1	41.84001	−1.00000
0.2	41.83999	−1.00000
0.3	41.83999	−1.00000
0.4	41.84001	−1.00000
0.5	41.84001	−1.00000
0.6	41.83999	−1.00000
0.7	41.83999	−1.00000
0.8	41.84000	−1.00000
0.9	41.84001	−1.00000
Average	41.84000	
Standard deviations	0.00001	
Absolute error	0.00000	
0.1	125.51998	−1.00000
0.2	125.52001	−1.00000
0.3	125.52001	−1.00000
0.4	125.51998	−1.00000
0.5	125.51999	−1.00000
0.6	125.52000	−1.00000
0.7	125.51999	−1.00000
0.8	125.52000	−1.00000
0.9	125.52000	−1.00000
Average	125.52000	
Standard deviation	0.00001	
Absolute error	0.00000	
0.1	209.20001	−1.00000
0.2	209.20000	−1.00000
0.3	209.19999	−1.00000
0.4	209.20000	−1.00000
0.5	209.20001	−1.00000
0.6	209.20001	−1.00000
0.7	209.19999	−1.00000
0.8	209.20000	−1.00000
0.9	209.20000	−1.00000
Average	209.20000	
Standard deviation	0.00001	
Absolute error	0.00000	

and $R = 8.3143$, is the gas constant. Transposing eqn. (10) and taking logarithms yields

$$\log_{10}(P(X)) = \log_{10}(R/AE) + \log_{10}(\beta_i) + \log_{10}(g(\alpha_j)) \qquad (14)$$

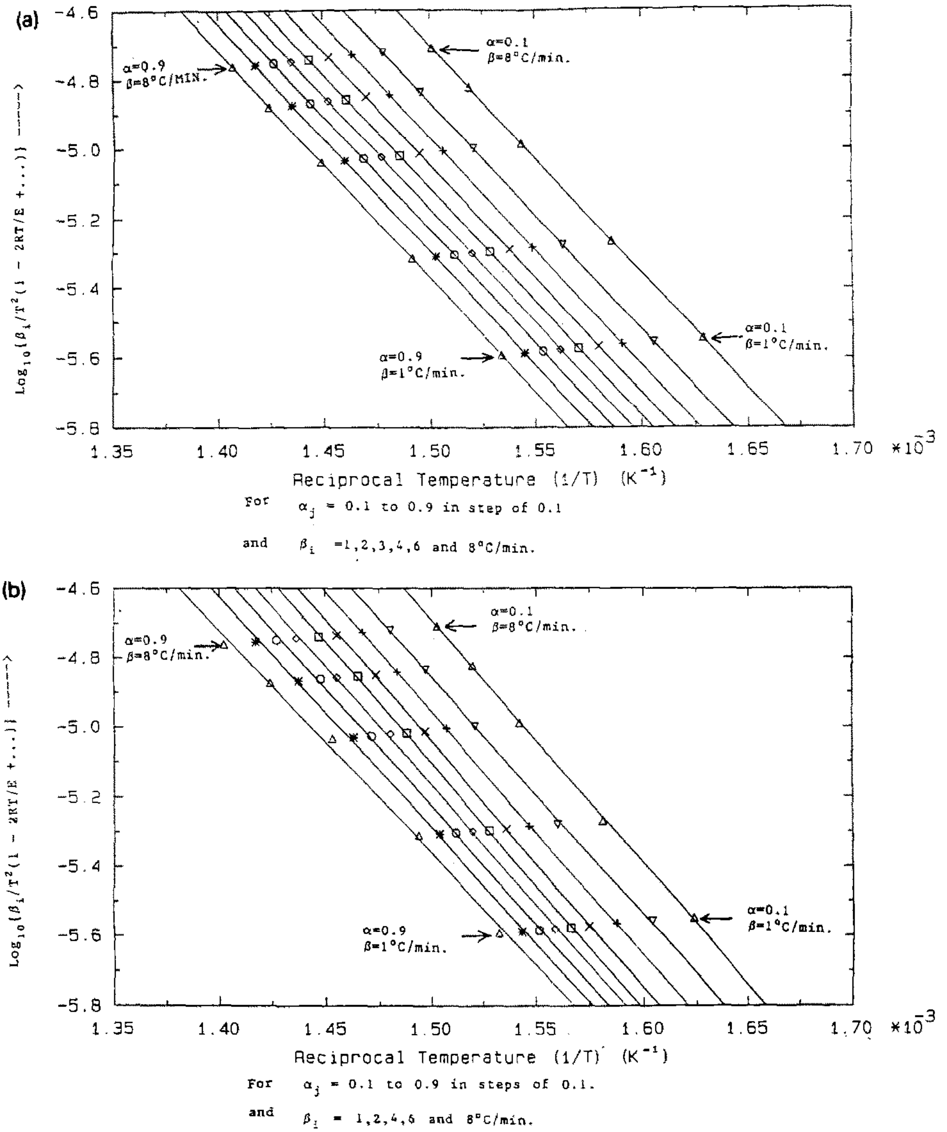

Fig. 1. Isoconversional plots obtained using (a) refined and (b) unrefined data.

For the ith heating rate $\beta_i = 1$, 2, 4, 6 and 8°C min^{-1}, and the assigned values of $E = 41.840$ kJ mol^{-1} and $A = 6.667 \times 10^8$ min^{-1}, eqn. (14) was solved for values of $g(\alpha_j)$ at each α_j from 0.1 to 0.9 in steps of 0.1 with $g(\alpha_j)$ arbitrarily chosen as $g(\alpha_j) = (-\ln(1 - \alpha_j))^{1/2}$. To obtain the temperature values corresponding to each value of $-\log_{10}(P(X))$, we utilised the fact that

$$P(X) = \int_{\infty}^{X} X^{-2}\,\mathrm{e}^{-X}\,\mathrm{d}X = X^{-2}\,\mathrm{e}^{-X}\phi'(E, T_{ij}) \qquad (15)$$

TABLE 3

Unrefined data: theoretical data obtained by adding a random error of between −2°C to +2°C to the refined data given in Table 1

α	T (K) at $\beta = 1$°C min^{-1}	T (K) at $\beta = 2$°C min^{-1}	T (K) at $\beta = 4$°C min^{-1}	T (K) at $\beta = 6$°C min^{-1}	T (K) at $\beta = 8$°C min^{-1}
0.1	616.00000	632.50000	648.50000	658.00000	665.50000
0.2	623.50000	641.00000	657.50000	668.00000	675.50000
0.3	630.00000	646.50000	663.50000	674.00000	681.50000
0.4	635.00000	651.00000	668.00000	678.50000	687.00000
0.5	638.50000	654.50000	672.00000	682.50000	691.00000
0.6	641.50000	658.00000	675.50000	687.00000	696.00000
0.7	644.50000	661.50000	679.50000	690.50000	700.50000
0.8	648.00000	665.00000	683.50000	695.50000	705.50000
0.9	652.50000	669.50000	688.00000	702.00000	713.00000

where $\phi'(E, T_{ij})$ is as defined by eqn. (8) above. Taking logs and transposing eqn. (15) gives

$$X = 2.303\left[-\log_{10}P(X) - 2\log_{10}X + \log_{10}\phi'(E, T_{ij})\right] \tag{16}$$

Equation (16) was evaluated using an iterative technique to give X and hence T_{ij}.

Two more sets of temperature data were similarly obtained for the same mechanism type, at the same heating rates with the same pre-exponential

TABLE 4

Apparent isoconversional activation energy evaluated from unrefined data (Table 3) using the isoconversional method

α	Activation energy E (kJ mol^{-1})	Correlation coefficient r
0.1	133.84440	−0.99979
0.2	130.33073	−0.99975
0.3	133.69150	−0.99999
0.4	135.18901	−0.99982
0.5	135.06386	−0.99984
0.6	131.65479	−0.99961
0.7	130.10900	−0.99945
0.8	127.53769	−0.99932
0.9	122.83806	−0.99771
Average	131.13989	
Standard deviation	4.02332	
Absolute error	5.61989	

TABLE 5

Theoretical data generated by assuming $E = 83.68$ kJ mol^{-1}, $A = 1.0 \times 10^{12}$ min^{-1} and $g(\alpha) = -\ln(1-\alpha)$; $\beta_i = 1$, 2, 5, 10, 20, 50 and 100 °C min^{-1}

α	T (K) at $\beta = 1$ °C min^{-1}	T (K) at $\beta = 2$ °C min^{-1}	T (K) at $\beta = 5$ °C min^{-1}	T (K) at $\beta = 10$ °C min^{-1}	T (K) at $\beta = 20$ °C min^{-1}	T (K) at $\beta = 50$ °C min^{-1}	T (K) at $\beta = 100$ °C min^{-1}
0.1	313.54965	320.06221	329.08553	336.24632	343.71584	354.09801	362.36442
0.2	320.61217	327.41573	336.85162	344.34752	352.17387	363.06428	371.74554
0.3	325.18524	332.18051	341.88848	349.60567	357.66790	368.89473	377.85097
0.4	328.77423	335.92174	345.84598	353.73920	361.98921	373.48412	382.65970
0.5	331.88477	339.16550	349.27911	357.32658	365.74125	377.47141	386.83961
0.6	334.77951	342.18528	352.47674	360.66917	369.23866	381.19017	390.73975
0.7	337.65938	345.19056	355.66051	363.99851	372.72355	384.89760	394.62966
0.8	340.77394	348.44189	359.10661	367.60355	376.49854	388.91589	389.84760
0.9	344.69462	352.53643	363.44889	372.14816	381.25963	393.98715	404.17358

TABLE 6

Data reported by Samosekharan and Kalpagam in ref. 27

α	T (K) at $\beta = 1°$ C min^{-1}	T (K) at $\beta = 2°$ C min^{-1}	T (K) at $\beta = 5°$ C min^{-1}	T (K) at $\beta = 10°$ C min^{-1}	T (K) at $\beta = 20°$ C min^{-1}	T (K) at $\beta = 50°$ C min^{-1}	T (K) at $\beta = 100°$ C min^{-1}
0.1	313.549	320.062	329.085	336.245	343.715	354.097	362.363
0.2	320.612	327.415	336.851	344.346	352.173	363.063	371.744
0.3	325.185	332.180	341.888	349.604	357.666	368.893	377.849
0.4	328.774	335.921	345.845	353.738	361.988	373.482	382.657
0.5	331.884	339.165	349.278	357.325	365.740	377.469	386.837
0.6	334.779	342.184	352.476	360.668	369.237	381.188	390.737
0.7	337.659	345.190	355.659	363.997	372.722	384.895	394.627
0.8	340.773	348.441	359.105	367.602	376.497	388.913	398.844
0.9	344.694	352.535	363.447	372.146	381.257	393.984	404.170

factor but different apparent activation energies, namely $E = 125.520$ kJ mol^{-1} and 209.200 kJ mol^{-1}: typical data are given in Table 1 and will be referred to as refined data. The results of applying our technique to these data are shown in Table 2.

To examine the sensitivity to temperature of the kinetic parameters calculated using our method, errors ranging from $-2°\text{C}$ to $+2°\text{C}$ were randomly introduced into the refined data (Table 1). The resultant data (Table 3) will be referred to as unrefined data and may be considered as the theoretical equivalent of the experimental data. The result of applying eqn. (9) to the unrefined data is given in Table 4 which clearly shows that our method is quite sensitive to the accuracy of temperature measurement.

Typical plots given by the isoconversional method are demonstrated in Figs. 1a and 1b for the refined and unrefined data respectively.

As a check on our method of generating temperature data, we calculated the temperature data for $g(\alpha_j) = -\ln(1-\alpha_j)$, $E = 83.680$ kJ mol^{-1}, $A = 1.0 \times 10^{12}$ min^{-1}, $\beta_i = 1, 2, 5, 10, 20, 50$ and $100°\text{C min}^{-1}$ and $\alpha_j = 0.1\text{–}0.9$ in steps of 0.1. This was done in order to compare the resulting temperature data with that reported by Somasekharan and Kalpagam [27] for the same parameters and kinetic mechanism. The data (Table 5) calculated using our technique is in excellent agreement with the reported data (Table 6).

COMPARISON OF KINETIC EQUATIONS USING OUR TECHNIQUE

Many amendments to the original equation reported by Coats and Redfern [25] have appeared in the literature [28–31]. Basically all the amendments were aimed at obtaining better approximate solution of the temperature integral. Since our approach is essentially the same, it was imperative to compare our approximation with those already reported. To achieve this, the approximations to the temperature integral reported by Coats and Redfern [25], Gorbachev [28], Balarin [29], Li [30], Agrawal [31] and the one obtained by Zuru [32] using the first five terms in the Schlölimch series, have been adapted to give the following equations. When put into a standard form, the various approximations give:

Coats and Redfern

$$\log_{10}\left\{\frac{\beta_i}{T_{ij}^2(1-2RT_{ij}/E)}\right\} = \log_{10}\left\{\frac{AR}{g(\alpha_j)E}\right\} - \frac{E}{2.303RT_{ij}} \tag{17}$$

Gorbachev

$$\log_{10}\left\{\frac{\beta_i}{T_{ij}^2\left(1/(1+2RT_{ij}/E)\right)}\right\} = \log_{10}\left\{\frac{AR}{g(\alpha_j)E}\right\} - \frac{E}{2.303RT_{ij}} \tag{18}$$

Balarin

$$\log_{10}\left\{\frac{\beta_i(1+4RT_{ij}/E)^{1/2}}{T_{ij}^2}\right\} = \log_{10}\left\{\frac{AR}{g(\alpha_j)}\right\} - \frac{E}{2.303RT_{ij}} \tag{19}$$

Li

$$\log_{10}\left\{\frac{\beta_i\left(1-6(RT_{ij}/E)^2\right)}{T_{ij}^2(1-2RT_{ij}/E)}\right\} = \log_{10}\left\{\frac{AR}{g(\alpha_j)E}\right\} - \frac{E}{2.303RT_{ij}} \tag{20}$$

Agrawal

$$\log_{10}\left\{\frac{\beta_i\left(1-5(RT_{ij}/E)^2\right)}{T_{ij}^2(1-2RT_{ij}/E)}\right\} = \log_{10}\left\{\frac{AR}{g(\alpha_j)E}\right\} - \frac{E}{2.303RT_{ij}} \tag{21}$$

Zuru and Whitehead

$$\log_{10}\left\{\frac{\beta_i}{T_{ij}\Theta(U)}\right\} = \log_{10}\left\{\frac{A}{g(\alpha_j)}\right\} - \frac{E}{2.303RT_{ij}} \tag{22}$$

where

$$\Theta(U) = \frac{U}{U+1} - \frac{U^2}{(U+1)(U+2)} + \frac{2U^3}{(U+1)..(U+3)} - \frac{4U^4}{(U+1)..(U+4)} + \frac{14U^5}{(U+1)..(U+5)} \tag{23}$$

and U is defined as

$$U = RT/E \tag{24}$$

Equations (17)–(22) were used to calculate the apparent activation energy (E) using the data generated with $E = 48.840$, 125.520 and 209.200 kJ mol^{-1} as well as the unrefined data given in Table 3. The isoconversional activation energies obtained for each equation are summarised in Table 7.

IDENTIFICATION OF PROBABLE REACTION MECHANISM

In their paper [27], Somasekharan and Kalpagam implied that the trial and error technique could be used to calculate both the apparent activation energy and pre-exponential factor. The same authors suggested that the

TABLE 7

Apparent isoconversional activation energies evaluated using equations (6) and (22)–(27) with theoretical data generated by assuming $E = 41.840$, 125.520 and 209.200 kJ mol^{-1}, $A = 6.667 \times 10^{8}$ min^{-1} and $\beta_i = 1, 2, 4, 6$ and 8 °C min^{-1}

Equation used	Isoconversional activation energy (kJ mol^{-1})	Absolute error (kJ mol^{-1})	Standard deviation (kJ mol^{-1})
Fatemi/Whitehead	41.84003	0.00003	0.00001
Agrawal	41.83966	0.00034	0.00044
Balarin	41.83548	0.00452	0.00081
Gorbachev	41.84771	0.00771	0.00056
Li	41.83157	0.00843	0.00142
Zuru/Whitehead	41.81171	0.02829	0.00210
Coats/Redfern	41.87946	0.03946	0.00433
Fatemi/Whitehead	125.52000	0.00000	0.00001
Agrawal	125.52000	0.00000	0.00048
Balarin	125.50848	0.01152	0.00101
Gorbachev	125.54159	0.02159	0.00178
Li	125.49839	0.02161	0.00178
Zuru/Whitehead	125.44057	0.07943	0.00284
Coats/Redfern	125.62678	0.10678	0.00585
Fatemi/Whitehead	209.20000	0.00000	0.00001
Agrawal	209.20088	0.00088	0.00069
Balarin	209.18249	0.01751	0.00151
Li	209.16697	0.03303	0.00268
Gorbachev	209.23464	0.03464	0.00128
Zuru/Whitehead	209.07245	0.12755	0.00446
Coats/Redfern	209.36785	0.16785	0.00940
With unrefined data			
Zuru/Whitehead	131.06302	5.54302	4.02720
Li	131.12086	5.60086	4.02652
Balarin	131.12984	5.60984	4.60984
Fatemi/Whitehead	131.13989	5.61989	4.02332
Agrawal	131.14080	5.62080	4.02434
Gorbachev	131.16066	5.64066	4.02652
Coats/Redfern	131.23925	5.71925	4.01371

probable reaction mechanism could be deduced from the constancy of the pre-exponential factor over the heating rates considered. Accordingly, we tried to predict the correct reaction mechanism as well as to reproduce the kinetic parameters assumed in generating the data shown in Table 1 using their suggestion and, in addition, using the technique we have developed. To achieve this, eqn. (9) was rearranged to give

$$\log_{10}\left\{\frac{g(\alpha_j)}{T_{ij}^2\phi'(E,T_{ij})}\right\} = \log_{10}\left\{\frac{AR}{\beta_i E}\right\} - \frac{E}{2.303RT_{ij}} \tag{25}$$

where all symbols retain their earlier definition.

TABLE 8

Table of average apparent activation energies, average pre-exponential factors and standard deviations from isoconversional activation energy for the 25 reaction models (see Appendix A) from refined data

Equation No.	Mean activation energy (kJ mol^{-1})	Mean pre-exponential factor (min^{-1})	Deviation from isoconversional energy (kJ mol^{-1})
1	39.83782	0.54372E+02	95.79561
2	55.51900	0.10658E+04	78.26360
3	87.89625	0.45241E+06	42.06472
4	185.93886	0.29421E+14	67.55049
5	284.18442	0.19370E+22	177.39265
6	382.47751	0.14146E+30	287.28794
7	220.00227	0.20943E+17	105.63464
8	232.96332	0.25462E+18	120.12557
9	207.86643	0.20191E+16	92.06632
10	498.49346	0.51224E+40	416.99804
11	261.44743	0.61731E+20	151.97185
12	310.65348	0.82043E+24	206.98602
13	367.24165	0.46197E+29	270.26367
14	170.79410	0.29968E+13	50.61810
15	125.52000	0.66670E+09	0.00001
16	80.36795	0.14262E+06	50.48163
17	57.97088	0.20308E+04	75.52232
18	423.87691	0.22473E+33	333.57399
19	441.20753	0.21803E+34	352.95026
20	476.60920	0.21377E+37	392.53064
21	364.53658	0.14637E+27	256.04895
22	597.54664	0.23512E+47	527.74314
23	111.31581	0.24765E+08	15.88080
24	70.95686	0.15651E+05	61.00355
25	345.56840	0.11183E+26	246.02220

Using essentially the same iteration technique described earlier, the apparent activation energies (E) and pre-exponential factors for the 25 different analytical forms of $g(\alpha_j)$ given in the Appendix were evaluated using eqn. (25) above. For each of the 25 reaction mechanisms, the apparent activation energy corresponding to each ith heating rate, $\beta_i = 1, 2, 4, 6$ and $8°C\ min^{-1}$, was evaluated. For each mechanism type, the standard deviation of the activation energies (calculated for each heating rate) was computed from the isoconversional energy (not from their mean). The results obtained for the refined and unrefined data are given in Tables 8 and 9 respectively.

DISCUSSION

Although an accuracy of up to two decimal places in activation energy is hardly practicable in solid state kinetics, nevertheless, as we are using

TABLE 9

Table of average apparent activation energies, average pre-exponential factors and standard deviations from isoconversional activation energy for 25 reaction models (Appendix A) from unrefined data

Equation No.	Mean activation energy (kJ mol^{-1})	Mean pre-exponential factor (min^{-1})	Deviation from isoconversional energy (kJ mol^{-1})
1	40.75309	0.63571E+02	101.08653
2	56.77021	0.14317E+04	83.22407
3	89.79089	0.84672E+06	46.53997
4	189.74565	0.18531E+15	66.37204
5	289.90035	0.40309E+23	178.19890
6	390.10193	0.86661E+31	290.28594
7	224.75768	0.20226E+18	105.36023
8	238.09126	0.28823E+19	120.22516
9	212.27839	0.16772E+17	91.43956
10	511.78474	0.10216E+43	426.16144
11	267.41126	0.98302E+21	152.96072
12	318.10136	0.22993E+26	209.59910
13	376.43336	0.24007E+31	274.80682
14	174.76547	0.15649E+14	49.62022
15	128.49420	0.19769E+10	7.49037
16	82.34221	0.25105E+06	54.75324
17	59.43965	0.28596E+04	80.23795
18	432.62637	0.21144E+35	337.83467
19	450.45296	0.24462E+36	357.76708
20	486.87548	0.34211E+39	398.49473
21	361.50982	0.66525E+28	258.30824
22	611.40238	0.12272E+50	537.75397
23	113.87173	0.61535E+08	20.31679
24	72.65136	0.24796E+05	65.52987
25	352.33372	0.46111E+27	248.04640

theoretical data, we have chosen to quote our results to five decimal places in order to demonstrate the accuracy and internal consistency of our calculation method.

Inspection of the results given in Table 2 clearly shows the accuracy and consistency of our calculation technique over all ranges of $X(E/RT)$ considered.

The isoconversional activation energies evaluated using eqns. (9) and (17)–(22) from the data generated with $E = 41.840$, 125.520 and 209.200 kJ mol^{-1}, and those calculated from the unrefined data, are all summarised in Table 7. It is obvious from these results that all the approximations lead to practically the same apparent activation energies to the nearest kilojoule. This reinforces Gorbachev's [33] suggestion that there is little value in trying to find more accurate approximations to the temperature integral. Nevertheless, without unduly overemphasising the slight differences in isoconversional activation energies between the equations, we wish to observe that while the Fatemi and Whitehead approximation leads to the most accurate and precise isoconversional activation energy with the refined temperature data, the Zuru and Whitehead approximation leads to the best result with

TABLE 10

Extract of the kinetic parameters obtained from the refined data (Table 1) by applying the trial and error technique using the 25 reaction models given in Appendix A

Equation No.	Heating rate β (°C min^{-1})	Activation energy E (kJ mol^{-1})	Pre-exponential factor A (min^{-1})	Correlation coefficient r
11	1.0	260.98578	0.14441E+21	−1.00000
11	2.0	261.24515	0.75878E+20	−1.00000
11	4.0	261.51780	0.39914E+20	−1.00000
11	6.0	261.68380	0.27426E+20	−1.00000
11	8.0	261.80463	0.21021E+20	−1.00000
Average		261.44743	0.61731E+20	
Standard deviation		151.97185	0.50859E+20	
Absolute error		135.92743	0.61731E+20	
14	1.0	170.64356	0.42112E+13	−1.00000
14	2.0	170.72819	0.33975E+13	−1.00000
14	4.0	170.81709	0.27420E+13	−1.00000
14	6.0	170.87117	0.24193E+13	−1.00000
14	8.0	170.91050	0.22138E+13	−1.00000
Average		170.79410	0.29968E+13	
Standard deviation		50.61810	0.81343E+12	
Absolute error		45.27410	0.29961E+13	
15	1.0	125.51999	0.66670E+09	−1.00000
15	2.0	125.52000	0.66670E+09	−1.00000
15	4.0	125.52001	0.66670E+09	−1.00000
15	6.0	125.52001	0.66670E+09	−1.00000
15	8.0	125.52000	0.66670E+09	−1.00000
Average		125.52000	0.66670E+09	
Standard deviation		0.00001	0.10832E+04	
Absolute error		0.00000	0.12894E+03	
16	1.0	80.50408	0.95911E+05	−1.00000
16	2.0	80.42714	0.11901E+06	−1.00000
16	4.0	80.34691	0.14763E+06	−1.00000
16	6.0	80.29839	0.16745E+06	−1.00000
16	8.0	80.26322	0.18310E+06	−1.00000
Average		80.36795	0.14262E+06	
Standard deviation		50.48163	0.35424E+05	
Absolute error		45.15205	0.66656E+09	

the unrefined data. This observation suggests that the Schlömilch expansion of the temperature integral may lead to comparatively more accurate activation energies with experimental data than the semi-divergent asymptotic expansion: a view already held by some authors [34–36].

Table 8 contains the kinetic parameters obtained when eqn. (25) was applied to the refined data with the 25 different analytical forms of $g(\alpha_j)$

TABLE 11

Extract of the kinetic parameters obtained from the unrefined data (Table 1) by applying the trial and error technique using the 25 reaction models given in Appendix A

Equation No.	Heating rate β ($^\circ$C min^{-1})	Activation energy E (kJ mol^{-1})	Pre-exponential factor A (min^{-1})	Correlation coefficient r
11	1.0	268.30616	0.53263E+21	−0.99896
11	2.0	282.00497	0.36291E+22	−0.99997
11	4.0	276.98337	0.71691E+21	−0.99992
11	6.0	262.59687	0.34831E+20	−0.99886
11	8.0	247.16493	0.16097E+19	−0.99787
Average		267.41126	0.98302E+21	
Standard deviation		152.96060	0.15114E+22	
Absolute error		141.89126	0.98302E+21	
14	1.0	175.51418	0.10124E+14	−0.99893
14	2.0	184.55347	0.45753E+14	−0.99997
14	4.0	181.12095	0.19133E+14	−0.99991
14	6.0	171.48076	0.28409E+13	−0.99881
14	8.0	161.15798	0.39244E+12	−0.99776
Average		174.76547	0.15649E+14	
Standard deviation		49.62010	0.18342E+14	
Absolute error		49.24547	0.15648E+14	
15	1.0	129.16450	0.12936E+10	−0.99889
15	2.0	135.87411	0.47603E+10	−0.99997
15	4.0	133.23966	0.28977E+10	−0.99991
15	6.0	125.97760	0.75274E+09	−0.99875
15	8.0	118.21513	0.17996E+09	−0.99765
Average		128.49420	0.19769E−10	
Standard deviation		7.49042	0.18567E+10	
Absolute error		2.97420	0.13102E+10	
16	1.0	82.91842	0.15005E+06	−0.99881
16	2.0	87.29745	0.44926E+06	−0.99997
16	4.0	85.47112	0.39870E+06	−0.99990
16	6.0	80.60305	0.18175E+06	−0.99862
16	8.0	75.42102	0.75500E+05	−0.99740
Average		82.34221	0.25105E+06	
Standard deviation		54.75336	0.16348E+06	
Absolute error		43.17779	0.66645E+09	

given in Appendix A. A more informative tabulation of the results is given in Table 10. Careful scrutiny of the results reveals the following observations.

(a) Of the 25 mechanism types tried, only the appropriate analytical form, namely, $g(\alpha_j) = (-\ln(1-\alpha))^{1/2}$, reproduced the assumed kinetic parameters, i.e. $E = 125.520$ kJ mol^{-1} and $A = 6.667 \times 10^8$ min^{-1}.

(b) All the 25 reaction mechanisms gave distinctly different apparent activation energies.

(c) The lowest standard deviation from the isoconversional activation energy is associated with mechanism 15, $g(\alpha) = (-\ln(1-\alpha))^{1/2}$, which was the reaction mechanism used in generating the data.

(d) Of the 25 mechanisms considered, mechanisms 11, 14, 15 and 16 gave a correlation coefficient (r) of -1.00000, as shown in Table 10.

(e) Also, mechanisms 14, 15 and 16 all gave reasonably constant pre-exponential factors over all the heating rates considered.

The kinetic parameters evaluated from the unrefined data are displayed in Tables 9 and 11. Inspection of these tables reveals the same trend as observed above with the refined data. In addition it can be seen that the random error has distorted the pre-exponential factor by more than an order of magnitude and introduced an absolute error of about 3.0 kJ mol^{-1} into the apparent activation energy. From the above observations, we have extracted the following findings.

(i) The isoconversional method is capable of producing the apparent activation energy without the necessity of assuming the analytical form of the conversion function.

(ii) Only in the case of the appropriate reaction mechanism did the trial and error method give apparent activation energies which were in good agreement with the values obtained using the isoconversional technique.

(iii) As reported by other workers [37–40], the correlation coefficient is not a sufficient criterion for judging the 'best' mechanism $f(\alpha)$.

(iv) Contrary to the claim by Somasekharan and Kalpagam [27], constancy of the pre-exponential factor is not unique to one mechanism type.

PROPOSED METHOD FOR THE EVALUATION OF KINETIC PARAMETERS AND DETERMINATION OF REACTION MECHANISM

Because all the mechanism types tried gave different apparent activation energies with the trial and error method and only the 'true' reaction mechanism gave activation energies in good agreement with values obtained using the isoconversional method, we strongly feel that this agreement could be utilised to identify the most probable reaction mechanism and to thus obtain a most probable pre-exponential factor in addition to the apparent activation energy. To achieve this we recommend the following steps.

(a) Sufficient data should be collected at different heating rates to warrant a straight line plot.

(b) The isoconversional method should be used, without reference to any mechanism, to calculate the apparent activation energies corresponding to various degrees of conversion (α) at suitable intervals and the mean evaluated. The mean was referred to as the isoconversional activation energy in the text.

(c) The trial and error technique should then be applied to evaluate the apparent activation energies corresponding to each heating rate for various reaction mechanisms.

(d) For each mechanism type, the standard deviation of the apparent activation energies evaluated for each heating rate from the isoconversional activation energy (not their mean) should be computed.

Provided the reaction is essentially isokinetic over all heating rates and temperature range covered, the reaction mechanism that gave the least standard deviation from the isoconversional activation energy may be considered as the most probable mechanism type. Once the most probable reaction mechanism has been established, the associated kinetic parameters could be regarded as the apparent activation energy and pre-exponential factor for the process.

CONCLUSION

The apparent activation energy evaluated using the isoconversional method has proved a successful reference for the determination of the most probable reaction mechanism in this theoretical investigation. The constancy of the pre-exponential factor and the correlation coefficient cannot be used as sufficient criteria for distinguishing between some reaction mechanisms. We wish to reiterate that the reported method may not apply if: (i) the mechanism of the process alters with changes in heating rate; and (ii) the reaction is not isokinetic over the temperature range considered.

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APPENDIX A

Reaction mechanisms used with trial and error method

Corresponding number	Mechanism type
1	$\alpha^{\frac{1}{4}}$
2	$\alpha^{\frac{1}{3}}$
3	$\alpha^{\frac{1}{2}}$
4	α
5	$\alpha^{\frac{3}{2}}$
6	α^2
7	$2.0\{1-(1-\alpha)^{\frac{1}{2}}\}$
8	$3.0\{1-(1-\alpha)^{\frac{1}{3}}\}$
9	$1.5\{1-(1-\alpha)^{\frac{2}{3}}\}$
10	$0.5\{1/(1-\alpha)^2-1\}$
11	$-\ln(1-\alpha)$
12	$2.0\{1/(1-\alpha)^{\frac{1}{2}}-1\}$
13	$\alpha/(1-\alpha)$
14	$\{-\ln(1-\alpha)\}^{\frac{2}{3}}$
15	$\{-\ln(1-\alpha)\}^{\frac{1}{2}}$
16	$\{-\ln(1-\alpha)\}^{\frac{1}{3}}$
17	$\{-\ln(1-\alpha)\}^{\frac{1}{4}}$
18	$(1-\alpha)\ln(1-\alpha)+\alpha$
19	$1.5\{1-(2/3)\alpha-(1-\alpha)^{\frac{2}{3}}\}$
20	$1.5\{1-(1-\alpha)^{\frac{1}{3}}\}^2$
21	$\{(1+\alpha)^{\frac{1}{2}}-1\}^2$
22	$\{(1+\alpha)^{-\frac{1}{3}}-1\}^2$
23	$\{1-(1-\alpha)^{\frac{1}{3}}\}^{\frac{1}{2}}$
24	$\{1-(1-\alpha)^{\frac{1}{3}}\}^{\frac{1}{3}}$
25	$\{(1+\alpha)^{\frac{1}{3}}-1\}^2$

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