A NEW INTEGRAL METHOD FOR THE KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA

G. GYULAI and E. J. GREENHOW

Chemistry Department, Chelsea College, University of London, England

Methods for the calculation of activation energies, pre-exponential factors and reaction orders from thermogravimetric data are briefly reviewed. A new integral method is proposed for the determination of these kinetic parameters, using data from pairs of TG curves produced at different heating rates. Employing accurate values of the temperature integral of the Arrhenius equation, tabulated over a range of E and T, and a simple graphical procedure, the method offers advantages of speed and accuracy over those previously reported. It is suggested that at least one of the kinetic parameters should be allowed to move freely in order to achieve the best possible fit between calculated and experimental traces.

If the thermal decomposition of a material is accompanied by weight loss, the changes of weight can be followed by thermogravimetric measurements and, from the data produced, valuable information can be obtained concerning the thermal decomposition process itself.

During the course of the thermogravimetric studies the sample is heated at elevated temperatures and the weight loss is recorded as a function of time. A constant heating rate is usually employed, and in this case the time units can easily be transformed into temperature units.

To obtain kinetic data (activation energy, pre-exponential factor, reaction order) from the recorded curves, the well known kinetic equation:

$$\mathrm{d}x/\mathrm{d}t = Ae^{-E/RT} f(x) \tag{1}$$

or its modification containing the constant heating rate:

$$\mathrm{d}x/\mathrm{d}T = (A/a)e^{-E/RT} f(x) \tag{2}$$

serves as a basis for calculations, where $a = \mathrm{d}T/\mathrm{d}t$ is the linear heating rate, A the pre-exponential factor, E the activation energy, and x the fractional weight of the reacted material related to the total weight loss, while R, T and t are the gas constant, the absolute temperature and the time, respectively. The term $f(x)$ is a function of the weight loss and its analytical form depends on the mechanism of the reaction in question. In some cases $f(x)$ can be expressed as $(1-x)^n$ where n is the reaction order. It must be pointed out that in stepwise decomposition, such as occurs when, for example, calcium oxalate is heated, the above equations can be used only for analysis of the separate steps.

The evaluation of thermoanalytical data has been discussed in several review articles [1−3]. These show two distinct approaches for the determination of kinetic parameters from thermogravimetric measurements. Thus, the Arrhenius-type expressions (Eqs 1 and 2) may be treated either

(a) by integral analysis, which considers the expressions as differential equations and obtains the kinetic constants from their integrated forms, or

(b) by obtaining the data in a differential form and setting the values of dx/dt, x, and T into a suitably derived form of the expressions.

The choice between the two approaches is not simply a matter of taste since, in the differential approach, (b), the determination of the apparent reaction rates requires either a special derivative thermogravimetric (DTG) apparatus or a not too accurate and lengthy procedure of graphical differentiation of the TG curve, whereas when integral methods are used the weight loss-temperature curves are sufficient.

The main difficulties arising in the application of integral methods are that in the rearranged form of Eq. (2):

$$dx/f(x) = (A/a)e^{-E/RT} \, dT \qquad (3)$$

neither the analytical form of $f(x)$ is known nor the right hand side of the expression can be integrated in a finite form.

The differences between the integral methods reported in the literature are those of the approach to, and the solution of, the integral equation:

$$F(x) = \int_{x_0}^{x} dx/f(x) = (A/a) \int_{T_0}^{T} e^{-E/RT} \, dT \qquad (4)$$

where x_0 and T_0 are the corresponding values of the initial conversion and absolute temperature.

The methods suggested for the solution of Eq. (4) are of two different types as far as the integration of the right hand side is concerned. One group of authors [4−7] suggests approximate expressions for the exponential integral, while others [8−10] recommend the use of numerically integrated and tabulated values of it. Although the approximative methods are generally easier to use, for more accurate results those methods using the accurate integral values are to be preferred.

Doyle [8] has suggested a curve fitting method for analysing thermogravimetric data from decomposition reactions having a known analytical form of $f(x)$. He assumes that the values of $F(x)$, for the materials under consideration, are very small at low temperatures and substitutes 0 for T_0. Thus:

$$(A/a) \int_{T_0}^{T} e^{-E/RT} \, dT = (A/a) \int_{0}^{T} e^{-E/RT} \, dT \qquad (5)$$

By modifying Eq. (4) as shown in Eq. (5), and using the notation: $u = E/RT$, we obtain:

$$F(x) = (-AE/aR) \int_{\infty}^{z} (e^{-u}/u^2) \, du \qquad (6)$$

where z is the value of u at the temperature corresponding to the apparent value of x.

Introducing the notation:

$$p(z) = - \int_{\infty}^{z} (e^{-u}/u^2)\mathrm{d}u \qquad (7)$$

the equation of the TG curves is obtained:

$$F(x) = (AE/aR)p(z) \qquad (8)$$

The values of $-\log p(z)$ have been given by Doyle for E/RT values ranging from 10 to 50.

Starting with an approximate value of E and an assumed analytical form for $F(x)$, an approximate $x-T$ curve can be calculated with the aid of the tabulated $-\log p(z)$ values and compared with the experimental curve. The procedure can be repeated with other E values until the possible best agreement of the calculated and experimental curves has been achieved and the best-fit E value thereby obtained.

A may be determined simultaneously with E, and is calculated on the basis of the equation of the TG curve slope. The main drawbacks of this method are that $f(x)$ must be known or assumed and that the procedure is lengthy.

A more convenient and elegant procedure has been suggested by Zsakó [9]. He rearranges Eq. (8) and takes logarithms to obtain the expression:

$$\log (AE/aR) = \log F(x) - \log p(z) = B \qquad (9)$$

where B is a constant containing A, E, R and the heating rate, the last named remaining constant in a particular determination.

By assuming different reaction mechanisms and activation energies, series of values for B can be calculated using the tabulated values of $\log p(z)$, which have been given by Zsakó for different temperatures and activation energies. The validity of the assumptions can be characterised by the standard deviation of B. Thus the minimum standard deviation (maximum consistency) of B would show the best E value and the maximum consistency of the decomposition process with the assumed $f(x)$ function. With a knowledge of the $f(x)$ and E values the pre-exponential factor, A, can easily be determined. The main achievement of Zsakó's method is that it allows three characteristics of the decomposition process to be determined simultaneously. The required calculations are, however, still lengthy.

Satava and Skvara [10] have simplified Zsakó's treatment and use a graphical curve fitting method for the simultaneous determination of the $f(x)$ function and the values of E and A. The method is based upon Eq. (9). Values of $\log p(z)$ have been calculated and plotted against the absolute temperature for various activation energies. Log $F(x)$ values corresponding to various mechanisms have been calculated for a wide range of values of x and given in a tabulated form. Diagrams of $F(x)$ versus T are then constructed for assumed reaction mechanisms

and drawn on transparent paper. By shifting this paper along the log $p(z)$ versus T diagram until the log $p(z)$ and log $F(x)$ graphs correspond perfectly, one is able to determine the activation energy and the $F(x)$ ($f(x)$) function.

More recently Satava [11] has described an improved method for determining the $f(x)$ function.

The advantage of the methods described by Satava and Skvara is that they allow for identification of curve portions characterised by different reaction mechanisms and/or activation energies. However, since the procedure used is based on curves corresponding to discrete E values and assumed $f(x)$ functions, it is hardly faster than that suggested by Zsakó.

In the present paper a new method is described for the kinetic analysis of thermogravimetric data. The method is more rapid and, in some aspects, more advantageous than those described above. In the method we use the notation:

$$i = \int_0^T e^{-E/RT} \, \mathrm{d}T \tag{10}$$

Eq. (4) can be written:

$$F(x) = (A/a)i \tag{11}$$

For two points of the same conversion, x, but obtained from two different TG curves of the same material produced at different heating rates and from samples preferably of the same initial weight, the following expressions can be written:

$$i_{11} = \int_0^{T_{11}} e^{-E/RT} \, \mathrm{d}T \;;\;\; i_{21} = \int_0^{T_{21}} e^{-E/RT} \, \mathrm{d}T \tag{12}$$

$$F(x)_{11} = (A/a_1)i_{11} \;;\;\; F(x)_{21} = (A/a_2)i_{21} \tag{13}$$

$$F(x)_{11} = F(x)_{21} \tag{14}$$

where the first figure in the subscript indicates the TG curve and the second a particular conversion value. Combining (13) and (14) we can write:

$$F(x)_{11}/F(x)_{21} = (a_2/a_1)/(i_{11}/i_{21}) = 1 \tag{15}$$

and hence:

$$a_1/a_2 = i_{11}/i_{21} \tag{16}$$

or generally expressed:

$$a_k/a_1 = i_{k1}/i_{11} = i_{k2}/i_{12} = \ldots\ldots = i_{kn}/i_{1n} \tag{17}$$

The i values can be calculated numerically and given in tabulated or diagrammatic forms. For calculation purposes it is more convenient to have values of log i.

For determination of the activation energy, the method is applied as follows: two points of the same conversion are chosen on two TG curves obtained at different heating rates (a_1 and a_2) and the corresponding temperatures, T_{11} and T_{21} noted. The values of log i corresponding to these temperatures at various

activation energies can be obtained from the tabulated values. If we plot log (i_1/i_2) (here the subscripts 1 and 2 refer to the values corresponding with T_{11} and T_{21}) against E, the unknown E can be located as that value of E corresponding to log $(a_1/a_2) = $ log (i_1/i_2).

If we consider the simple cases of $f(x)$, where $f(x) = (1-x)^n$, we can determine the reaction order, n, in the following way, using either of the two TG curves employed for determination of the activation energy:

When $f(x) = (1-x)^n$, the conversion integral is given by:

$$F(x) = \int_{x_0}^{x} \mathrm{d}x/(1-x)^n \tag{18}$$

where x_0 is usually chosen as zero. The expression for $F(x)$ when $n \neq 1$ is then:

$$F(x) = \big(1/(n-1)\big)\big(1/(1-x)^{n-1}\big) - 1) \tag{19}$$

If $n = 1$:

$$F(x) = -ln(1-x) = 2.3 \ \log(1-x) \tag{20}$$

In the subsequent calculations the pre-exponential factor is assumed to be constant, although this does not mean that the results should necessarily be given in terms of A remaining constant in the entire reaction range.

Now, for two points on the same TG curve, we may write:

$$F(x_1) = (A/a)i(E_1, T_1); \quad F(x_2) = (A/a)i(E_2, T_2) \tag{21}$$

$$F(x_1)/F(x_2) = i(E_1, T_1)/i(E_2, T_2) \tag{22}$$

assuming, as noted above, A to be constant in the conversion region x_1 to x_2.

Eq. (22) can be solved for n using a simple graphical procedure. Thus, one chooses x_2 to be a constant reference conversion, such as 0.1, 0.5, or 0.9, and calculates the ratio log $(F(x)/F(x_2))$ for a range of values for the conversion x. This ratio is then plotted against n, on the basis of Eq. (19). The apparent order for a given conversion x_1 can be obtained from the graph as the value of n corresponding to $x = x_1$ and log $(F(x_1)/F(x_2)) = $ log $(i(E_1, T_1)/i(E_2, T_2))$. The right hand side of Eq. (22) can be calculated on the basis of the tabulated log i values.

Having determined the analytical form of $f(x)$ (and $F(x)$), the pre-exponential factor can be calculated from the rearranged form of Eq. (11):

$$A = (a/i)F(x) \tag{23}$$

or

$$\log A = \log a - \log i + \log F(x) \tag{24}$$

Calculations and discussion

Values of log i have been calculated on a computer utilising a 32-point Gaussian numerical integration formula. Their negative logarithms for several temperatures and activation energies are given in Table 1.

Table 1

Values of $-(\log i)$

T, Kelvin	E, kcal/mol								
	20	30	40	50	60	70	80	90	100
260	16.005444	24.580245	33.107265	41.607643	50.090994	58.562518	67.025343	75.530771	
280	14.741837	22.715749	30.642112	38.541931	46.424775	54.295821	62.158187	70.013898	
300	13.642769	21.095851	28.501613	35.880928	43.243319	50.593940	57.935900	65.271218	72.601444
320	12.677647	19.674947	26.625153	33.549009	40.455990	47.351231	54.237829	61.117797	67.992517
340	11.823045	18.418133	24.966351	31.488313	37.993451	44.486877	50.971678	57.449863	63.922808
360	11.060719	17.298238	23.489107	29.653815	35.801747	41.937996	48.065639	54.186677	60.302484
380	10.376247	16.293792	22.164904	28.009947	33.838264	39.654926	45.463001	51.264482	57.060741
400	9.758077	15.387604	20.970912	26.528243	32.068896	37.597923	43.118380	48.632256	54.140920
420	9.196846	14.565746	19.888638	25.185645	30.466021	35.734800	40.995026	46.248684	51.499005
440	8.684881	13.816811	18.902942	23.963278	29.007030	34.039212	39.062861	44.079953	49.091849
460	8.215838	13.131370	18.001308	22.845540	27.673236	32.489390	37.297028	42.098122	46.894028
480	7.784422	12.501556	17.173299	21.819426	26.449062	31.067185	35.676808	40.279899	44.877811
500	7.386180	11.920757	16.410144	20.874002	25.321416	29.757343	34.184789	38.605715	43.021470
520	7.017338	11.383372	15.704414	20.000014	24.279215	28.546957	32.806235	37.059005	41.306613
540	6.674680	10.884628	15.049779	19.189574	23.313016	27.425026	31.528589	35.625655	39.717568
560	6.355442	10.420426	14.440807	18.435917	22.414719	26.382115	30.341082	34.293564	38.240901
580	6.057241	9.987234	13.872815	17.733208	21.577339	25.410091	29.234430	33.052296	36.865026
600	5.778008	9.581986	13.341739	17.076389	20.794821	24.501899	28.200583	31.892804	35.579898
620	5.515940	9.202009	12.844040	16.461050	20.061886	23.651396	27.232527	30.807208	34.376768
640	5.269455	8.844964	12.376617	15.883332	19.373917	22.853201	26.324123	29.788607	33.247979
660	5.037163	8.508790	11.936744	15.339841	18.726851	22.102585	25.469976	28.830939	32.186797
680	4.817835	8.191672	11.522015	14.827581	18.117103	21.395376	24.665321	27.928850	31.187283
700	4.610381	7.891997	11.130296	14.343897	17.541497	20.727874	23.905939	27.077600	30.244173
720	4.413832	7.608331	10.759689	13.886428	16.997208	20.096790	23.180077	26.272971	29.352785
740	4.227322	7.339396	10.408501	13.453067	16.481715	19.499191	22.508388	25.511202	28.508945
760	4.050075	7.084044	10.075217	13.041927	15.992762	18.932449	21.863874	24.788928	27.708917
780	3.881393	6.841247	9.758475	12.651316	15.528323	18.394208	21.251846	24.103124	26.949347

800	3.720649	6.610078	9.457047	12.279707	15.086574	17.882343	20.669882	23.451071	26.227213
820	3.567275	6.389698	9.169829	11.925725	14.665869	17.394939	20.115795	22.830314	25.539792
840	3.420756	6.179351	8.895816	11.588122	14.264716	16.930261	19.587608	22.238628	24.884615
860	3.280626	5.978346	8.634099	11.265767	13.881673	16.486735	19.083524	21.673997	24.259445
880	3.146459	5.786059	8.383851	10.957632	13.515781	16.062930	18.601912	21.134588	23.662248
900	3.017869	5.601917	8.144318	10.662779	13.165648	15.657541	18.141283	20.618729	23.091167
920	2.894499	5.425399	7.914808	10.380350	12.830340	15.269377	17.700278	20.124895	22.544510
940	2.776027	5.256028	7.694693	10.109563	12.508919	14.897346	17.277653	19.651687	22.020727
960	2.662153	5.093364	7.483392	9.849697	12.200526	14.540450	16.872269	19.197825	21.518396
980	2.552604	4.937004	7.280375	9.600091	11.904371	14.197769	16.483078	18.762133	21.036211
1000	2.447127	4.786578	7.085150	9.360138	11.619727	13.868458	16.109114	18.343528	20.572972
1020	2.345490	4.641743	6.897267	9.129275	11.345924	13.551736	15.749490	17.941012	20.127570
1040	2.247477	4.502184	6.716308	8.906987	11.082342	13.246886	15.403384	17.553662	19.698984
1060	2.152889	4.367607	6.541889	8.692792	10.828411	12.953239	15.070038	17.180627	19.286267
1080	2.061541	4.237741	6.373650	8.486248	10.583598	12.670181	14.748749	16.821117	18.888544
1100	1.973262	4.112335	6.211260	8.286941	10.347412	12.397138	14.438864	16.474400	18.505002
1120	1.887892	3.991155	6.054412	8.094491	10.119396	12.133579	14.139777	16.139795	18.134887
1140	1.805283	3.873984	5.902818	7.908541	9.899126	11.879011	13.850926	15.816671	17.777497
1160	1.725297	3.760617	5.756211	7.728759	9.686205	11.632973	13.571785	15.504437	17.432178
1180	1.647804	3.650868	5.614342	7.554835	9.480263	11.395035	13.301865	15.202546	17.098322
1200	1.572684	3.544558	5.476978	7.386482	9.280956	11.164796	13.040709	14.910483	16.775359

When the log i values were plotted against the activation energy straight lines were obtained. A similar, linear, relationship was found to obtain between log i and the reciprocal of the absolute temperature. In a recent work [12] we have evaluated these relationships and found that the linearity of the log $i - E$ and log $i - 1/T$ plots can be characterised by correlation coefficients better than 0.999991 and 0.999969 respectively.
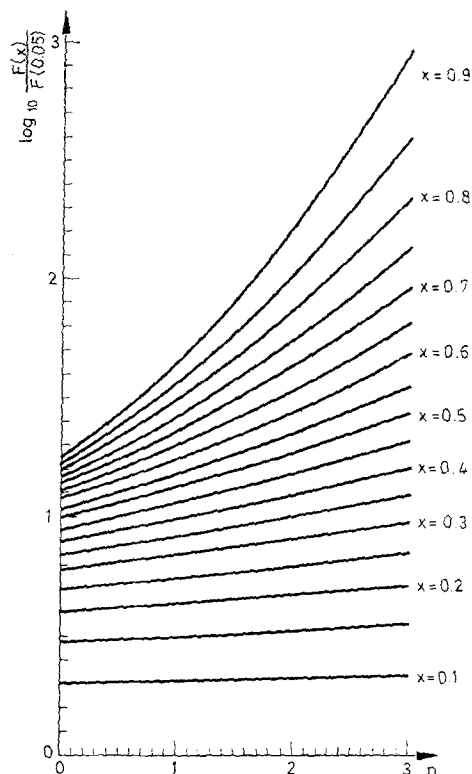

Fig. 1. Curves for determining reaction order. Reference conversion 0.05

These linear relationships are useful in expediting the calculation of activation energy, since it is now sufficient to calculate the log i values for only two different activation energies; the log $(i_{11}/i_{21}) - E$ plot can be obtained by simply laying a straight line through these two points. Furthermore, the linearity allows the calculation of log i values corresponding to any temperature by reciprocal interpolation of data in Table 1. These data are given in such a manner that log i values can be determined to an accuracy of 10^{-4} per cent by linear interpolation of the reciprocal temperature.

For determination of the reaction order, n, several reference conversions can be used. Figs 1, 2, and 3 are based on reference conversions 0.05, 0.5, and 0.9, respectively, and cover reaction order in the range $0-3$. Whenever practicable, it is preferable to use Fig. 3 since with a reference conversion of 0.9 due to the stronger curvature the method is less sensitive to experimental scatter.
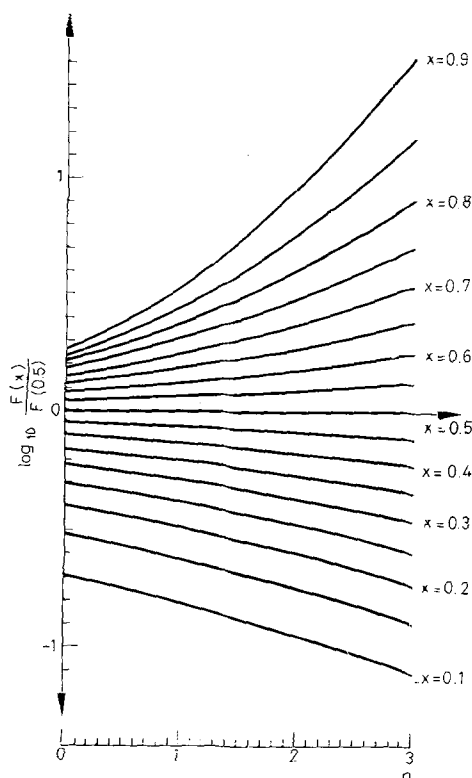

Fig. 2. Curves for determining reaction order. Reference conversion 0.5

To demonstrate the theoretical accuracy of this evaluation method, values of the kinetic constants were calculated from theoretical curves that had been computed in such a way as to restrict the error in the temperature integral to within 10^{-3} per cent. The parameters used to construct these theoretical curves were as follows: $E = 60$ kcal/mol; $n = 1$; $A = 10^{14}$ min^{-1}; $a = 2$ and 4 deg/min. The log $(i_{11}/i_{21}) - E$ curves were calculated from log i values obtained at 50 and 70 kcal/mol activation energies for the given temperatures. For determination of the order, 0.9 was chosen as the reference conversion.

The calculations were carried out on the computer, including the simulation of the graphical procedures to approximate the theoretical accuracy of the method.

The temperature data were fed into the computer with an accuracy of three decimal places.

Results obtained between the conversion limits 0.1 and 0.9 are shown in Table 2. The seventh and eighth columns of Table 2 show a modification of the calculations in which the values of the pre-exponential factor are given in terms of a constant order. This approach is discussed below.
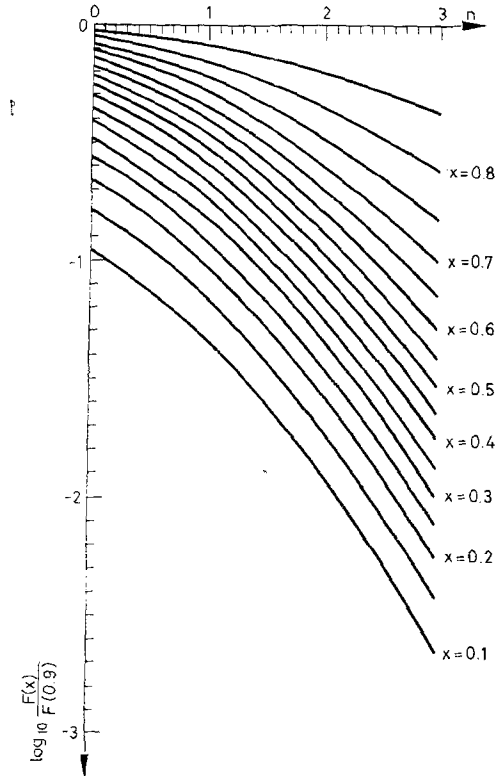

Fig. 3. Curves for determining reaction order. Reference conversion 0.9

Although activation energy, pre-exponential factor, and order of reaction are widely used to characterise processes followed by thermogravimetry and related techniques, there has been some confusion as to the nature of these kinetic parameters. In their methods for the interpretation of thermoanalytical data, Doyle [7, 8] and Zsakó [9] treat all three parameters as constants, while Ozawa [13] assumes the reaction order to be constant and calculates $E - A$ data pairs for points on a master curve.

A serious drawback of the integral evaluation techniques reported in the literature is in the assumption that the kinetic parameters do not change in the

Table 2

Kinetic parameters calculated from theoretical data

x	T_2, K	T_4, K	E, kcal/mole	n	A, min$^{-1} \times 10^{-14}$	$\bar{n}$	A', min$^{-1} \times 10^{-14}$
0.1	819.493	843.394	60.0024	1.0006	1.002	0.9983	1.001
0.2	835.649	851.134	59.9998	0.9990	0.999	0.9983	1.000
0.3	846.066	861.933	59.9994	0.9986	0.999	0.9983	1.000
0.4	854.217	870.386	59.9992	0.9984	0.999	0.9983	0.999
0.5	861.264	877.696	60.0002	0.9991	1.000	0.9983	1.000
0.6	867.807	884.486	59.9975	0.9967	0.997	0.9983	0.998
0.7	874.304	891.225	60.0023	1.0009	1.002	0.9983	1.000
0.8	881.314	898.507	59.9976	0.9934	0.993	0.9983	0.997
0.9	890.117	907.648	60.0014	—	—	0.9983	0.999

Theoretical data: $E = 60$ kcal/mole; $n = 1$; $A = 10^{14}$ min^{-1}; $a = 2$ and 4°/min. A', column 8, is calculated on the basis of $\bar{n}$. T_2 and T_4 refer to heating rates of 2 and 4°/min, respectively.

integration range. If they do, and the changes are not taken into consideration, results obtained by these techniques will be cumulative ones, and values obtained for a given $x - T$ point will be characteristic only of that point on the TG curve itself, but not of the $x - T$ point in the actual reaction path. Thus results obtained in this way merely describe the TG curve, and the question as to which parameter or parameters should be given as constants loses its relevance.

Techniques assigning single values to the three kinetic parameters are generally less successful from the point of view of curve fitting than those letting at least one of the parameters move freely. The procedures described in this paper for the determination of reaction order and pre-exponential factor can be used with variables modified according to the required form of data interpretation. The seventh and eighth columns of Table 2 show an example of this; here the results are given in terms of a constant reaction order, which has been produced as an average of orders belonging to different conversions.

Compared to integral procedures previously described, ours has several advantages. For example, the activation energy can be determined from point to point; this gives an indication as to whether or not the reaction can be characterised by a single E value. There is no limitation concerning the reaction mechanism, thus complicated reactions can also be investigated by compiling the appropriate graphs. It is possible to establish the order or other parameters of the analytical form of $f(x)$ by a continuous method thus avoiding the time consuming trial-and-error curve-fitting procedures.

The calculations to establish the parameters are carried out by using full integrals instead of approximate equations.

Several workers [13—15] have reported methods for the determination of kinetic parameters which employ two or more TG curves in the evaluation procedure. Ozawa's method [13] is generally regarded as being the most reliable.

In this he utilises Doyle's approximation [4] for the logarithm of the $p(z)$ term in Eq. (8):

$$\log p(z) \simeq -2.315 - 0.4567E/RT \tag{25}$$

and obtains the following expression for points of identical conversion on TG curves obtained at different heating rates:

$$d \log a/d \frac{1}{T} \simeq 0.4567E/R$$

He then calculates the activation energy from the slope of the $\log a - 1/T$ linear relationship. Doyle [7] obtained the coefficients of Eq. (25) by evaluating the $\log p(z) - E/RT$ relationship over the range $20 < E/RT < 60$. Since this relationship is not completely linear, the use of the coefficients so calculated gives rise to errors in the approximation [12] and, therefore, in any kinetic parameters determined with its aid.

In our method we have assumed that the $\log i - E$ relationship is linear. Errors are insignificant if this assumption is applied to the vicinity of the unknown activation energy.

The superiority of the $\log i - E$ linear approximation over the $\log i - 1/T$ approximation, which is in fact that employed by Ozawa, is discussed elsewhere [12]. However, on statistical grounds, Ozawa's use of more than two TG curves in the evaluation will reduce the error arising from the scatter of experimental results.

An approximate value for the error originating from incorrect temperature measurement or an erroneous a_1/a_2 value can be assessed from a formula obtained by applying Doyle's approximation [7] to the conditions of the present evaluation method:

$$E \simeq \log (a_2/a_1)(R/0.4567)(T_1 T_2/(T_2 - T_1))$$

This expression shows that deviations from the assumed heating-rate ratio or errors affecting equally the absolute values of T_1 and T_2 give rise only to moderate changes in the calculated activation energy. The method is, however, very sensitive to errors in the difference $T_2 - T_1$. Thus if the value of $T_2 - T_1$ corresponding to a particular a_2/a_1 ratio is 20° and the value obtained experimentally is 19°, the apparent activation energy, E', is given by:

$$E' = (20/19) E$$

which represents an error of about 5 per cent.

The bigger the difference between the two temperatures the smaller the significance of an error in the temperature reading or of a shift which might be due to the slow diffusion of gaseous products. It is, therefore, advantageous to carry out measurements at heating rates which differ as much as possible, i.e. at the largest practicable a_2/a_1 ratio $(a_2 > a_1)$.

To diminish the effects of inadequate removal of gaseous products, low heating rates, small sample size, and the application of vacuum, are recommended.

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RÉSUMÉ — On passe brièvement en revue les méthodes de calcul des énergies d'activation, des facteurs préexponentiels et des ordres de réaction à partir des données thermogravimétriques. On propose une nouvelle méthode d'intégration pour déterminer ces paramètres cinétiques en utilisant les données fournies par des courbes TG groupées par paires et obtenues avec différentes vitesses de chauffage. En employant des valeurs précises de l'intégrale de la température de l'équation d'Arrhenius, fournies par un tableau donnant différentes valeurs de E et de T ou obtenues par un procédé graphique simple, la méthode offre des avantages de rapidité et d'exactitude supérieurs à ceux décrits auparavant. On propose qu'au moins l'un des paramètres cinétiques puisse varier librement afin d'assurer le meilleur ajustement possible entre les courbes expérimentales et calculées.

ZUSAMMENFASSUNG — Eine kurze Übersicht über die Berechnungsmethoden von Aktivierungsenergien, preexponentiellen Faktoren und Reaktionsordnungen aus thermogravimetrischen Daten wird gegeben. Eine neue Integralmethode zur Bestimmung dieser kinetischen Parameter wird vorgeschlagen, die Daten von durch verschiedene Aufheizungsgeschwindigkeiten aufgenommenen Paaren von TG-Kurven verwendet. Durch Anwendung genauer Temperatur-Integralwerte der Arrhenius-Gleichung, welche in einem gewissen E und T Bereich in eine Tabelle eingetragen werden, sowie durch ein einfaches graphisches Verfahren gestattet die Methode Geschwindigkeit und Genauigkeit, die den früher beschriebenen überlegen sind. Die freie Variationsmöglichkeit wenigstens eines der kinetischen Parameter wird vorgeschlagen, um die bestmögliche Anpassung der berechneten und experimentellen Linien zu erhalten.

Резюме — Дан краткий обзор методов расчета энергии активации, предэкспоненциальных факторов и порядка реакции на основе термогравиметрических данных. Предложен новый интегральный метод для определения этих кинетических параметров, используя данные пар кривых ТГ, снятых при различных скоростях нагрева. При применении точных значений температупного интеграла уравнения Аррениуса, стабулированных по диапазону E и T, и простого графического приема, данный метод, по сравнению с ранее предложенными, имеет преимущества в скорости и точности.