A New Method of Analyzing Thermogravimetric Data

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Various kinds of materials have been studied by thermogravimetric analysis, in which is recorded the weight-change of a sample heated at a constant rate of heating. Thermogravimetry has an advantage over measurement at a constant temperature, because in the latter a part of the sample may change while the sample is heated to the desired temperature. Especially at the degradation of high polymers, this initial structure change in the sample complicates the isothermal data and makes it difficult to analyze.

The many methods proposed for obtaining the kinetic parameters from the thermogravimetric data, though rather complicated, may be classified into two classes, in both of which the rates of decomposition must have the following form:

$$-\frac{\mathrm{d}W}{\mathrm{d}t}=A\exp\left(-\frac{\Delta E}{\boldsymbol{R}T}\right)W^n \qquad (1)$$

where W is the fractional residual weight of the sample; T, the absolute temperature; $\boldsymbol{R}$, the gas constant; t, the time, and A, ΔE and n, the pre-exponential factor, the activation energy and the order of the reaction respectively.

In the first class of the analyzing method,[1-5] Eq. 1 is treated as a differential equation, and the fractional weight is derived by integration as a function of the temperature. In the other method,[6-10] from the plots of the logarithms of the terms of Eq. 1 the kinetic constants are obtained. These analyses are usually cumbersome. Complex quantities must be derived from the data or the trial-and-error fitting of the curve is required in the former cases, while the weight-temperature curve must be differentiated graphically in the latter cases. Furthermore, these methods are applicable only to the decomposition expressed by Eq. 1.

This paper will propose an approximate integral method similar to, but even simpler than, that of Doyle.[2] This method is more widely applicable than the others. For example, the random degradation of high polymers[11] can be analyzed by this treatment.

A few methods of estimating the thermal stability of polymeric materials have been reported.[12,13] In these papers, however, the effect of the heating rate has not been considered. In this paper these methods will be revised, considering the effect of heating rates, and it will be shown that a master curve may be derived from the data at different heating rates.

The applications of the method to the decomposition of calcium oxalate and to the degradation of nylon 6 will be shown. Finally, the applicability of the method to other types of thermal analyses and the possibility of extending it to thermal behavior under various conditions of temperature change will be discussed.

Theoretical Consideration

Generally, the fractional weight, W, of a reacting material is expressed as a function of the fraction of a structural quantity, such as a group, a constituent, a broken bond, etc., which is represented by x:

$$W=\boldsymbol{f}(x) \qquad (2)$$

where x changes according to the ordinary kinetic equation:

$$-\frac{\mathrm{d}x}{\mathrm{d}t}=A\exp\left(-\frac{\Delta E}{\boldsymbol{R}T}\right)\boldsymbol{g}(x) \qquad (3)$$

By integration,

$$-\int_{x_0}^{x}\frac{\mathrm{d}x}{\boldsymbol{g}(x)}=A\int_{t_0}^{t}\exp\left(-\frac{\Delta E}{\boldsymbol{R}T}\right)\mathrm{d}t \qquad (4)$$

where x_0 is the value of x at $t=t_0$. In most cases, the kinetics of the weight-change can be expressed as Eq. 1, where x is equal to W.

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TABLE I. SEVERAL FORMS OF $\boldsymbol{f}(x)$, $\boldsymbol{g}(x)$ AND $\int dx/\boldsymbol{g}(x)$

Type of reaction	$\boldsymbol{f}(x)$	$\boldsymbol{g}(x)$	$\int dx/\boldsymbol{g}(x)$
0th order reaction	W	1	W
1st order reaction	W	W	$\ln W$
2nd order reaction	W	W^2	$-1/W$
3rd order reaction	W	W^3	$-2/W^2$
Random degradation[11]	$(1-x)^{L-1}\left\{1+x\frac{(N-L)(L-1)}{N}\right\}^*$	$-(1-x)$	$-\ln(1-x)$

* N is the initial degree of polymerization and L is the least number of repeating units of polymer not volatilized. Following approximation can be made for $N \gg L$:

$$\boldsymbol{f}(x)=(1-x)^{L-1}\{1+(L-1)x\}$$

In the random degradation of high polymers,[11] x is a fractional number of the broken bond.

When the temperature of the sample is raised at a constant rate, a, the change in x is given by Eq. 5:

$$-\int_{x_0}^{x}\frac{dx}{\boldsymbol{g}(x)}=\frac{A}{a}\int_{T_0}^{T}\exp\left(-\frac{\Delta E}{\boldsymbol{R}T}\right)dT \qquad (5)$$

where T_0 is the value of T at $t=t_0$. Ordinarily, the rate of the reaction is very low at low temperatures. Therefore, the next approximation is valid:

$$\int_{T_0}^{T}\exp\left(-\frac{\Delta E}{\boldsymbol{R}T}\right)dT=\int_{0}^{T}\exp\left(-\frac{\Delta E}{\boldsymbol{R}T}\right)dT \quad (6)$$

The value of the right side of Eq. 6 is expressed and tabulated by Doyle[2] as the following function, $\boldsymbol{p}$:

$$\frac{\Delta E}{\boldsymbol{R}}\boldsymbol{p}\left(\frac{\Delta E}{\boldsymbol{R}T}\right)=\int_{0}^{T}\exp\left(-\frac{\Delta E}{\boldsymbol{R}T}\right)dT \qquad (7)$$

If $\Delta E/\boldsymbol{R}T$ is larger than 20, $\boldsymbol{p}(\Delta E/\boldsymbol{R}T)$ can be approximated by the following formula:[3]

$$\log\boldsymbol{p}\left(\frac{\Delta E}{\boldsymbol{R}T}\right)\fallingdotseq -2.315-0.4567\frac{\Delta E}{\boldsymbol{R}T} \qquad (8)$$

Now, for a given value of W, a single-valued function of x, the left side of Eq. 5 is a constant which does not depend on the heating rate. Therefore, if the weight decreases to a given fraction at the temperature, T_1, for the heating rate of a_1, at T_2 for a_2, and so on, the following equations can be obtained;

$$\frac{A\Delta E}{a_1\boldsymbol{R}}\boldsymbol{p}\left(\frac{\Delta E}{\boldsymbol{R}T_1}\right)=\frac{A\Delta E}{a_2\boldsymbol{R}}\boldsymbol{p}\left(\frac{\Delta E}{\boldsymbol{R}T_2}\right)=\cdots \qquad (9)$$

Using Eq. 8, the following linear relations can easily be derived:

$$-\log a_1-0.4567\frac{\Delta E}{\boldsymbol{R}T_1}= -\log a_2-0.4567\frac{\Delta E}{\boldsymbol{R}T_2}=\cdots \qquad (10)$$

Thus, the plots of $\log a$ versus the reciprocal absolute temperature for a given value of W must give a straight line, the slope of which gives the activation energy. In other words, if the thermogravimetric curves are given as a plot of W versus the reciprocal absolute temperature for various heating rates, the curves can be superposed upon each other by shifting them along the abscissa. The length of the lateral shift is proportional to the logarithm of the corresponding heating rate of the curve. By these superpositions there is obtained the master thermogravimetric curve, which is a standard and more accurate curve than individual ones; this procedure makes possible the mutual comparison of the thermogravimetric data at different heating rates.

The next step of the analysis is the determination of A, $\boldsymbol{f}(x)$ and $\boldsymbol{g}(x)$. For some typical kinetic processes, $\boldsymbol{f}(x)$, $\boldsymbol{g}(x)$ and $\int dx/\boldsymbol{g}(x)$ are given in Table I, where L is the

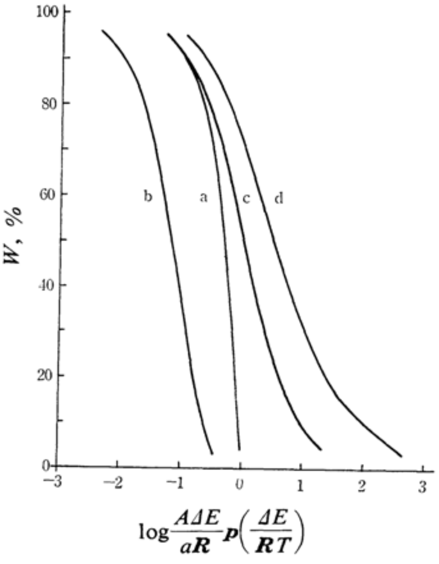

Fig. 1. The theoretical thermogravimetric curves for;
a, 0th order reaction; b, 1st order reaction; c, 2nd order reaction; d, 3rd order reaction.

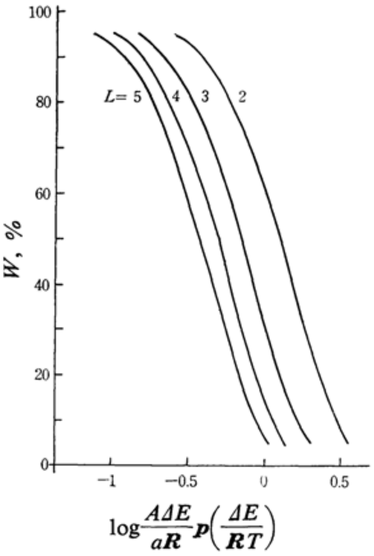

Fig. 2. The theoretical thermogravimetric curves of the random degradation of high polymers with the indicated values of L. Approximation is made for $N \gg L$.

least number of repeating units of the polymer not volatilized.[11] As $\int \mathrm{d}x/\boldsymbol{g}(x)$ is a function of x, which is equal to $(A\Delta E/\boldsymbol{aR})\boldsymbol{p}(\Delta E/\boldsymbol{RT})$, and W is a single-valued function of x, W can be calculated as a function of log $\{(A\Delta E/\boldsymbol{aR})\boldsymbol{p}(\Delta E/\boldsymbol{RT})\}$, as is shown in Figs. 1 and 2. The plots of W against $\log\{(\Delta E/\boldsymbol{aR})\boldsymbol{p}(\Delta E/\boldsymbol{RT})\}$ by using the experimental master thermogravimetric curve and the activation energy determined as shown above must be superposed upon one of the curves in Figs. 1 and 2 by a lateral shift. By this procedure the forms of $\boldsymbol{f}(x)$ and $\boldsymbol{g}(x)$ are determined, and the length of the lateral shift is found to be equal to $\log A$. An analogous, but more precise determination of A can be made by the subtraction of $\log\{(\Delta E/\boldsymbol{aR})\boldsymbol{p}(\Delta E/\boldsymbol{RT})\}$ from the $\int \mathrm{d}x/\boldsymbol{g}(x)$ of the determined form of $\boldsymbol{g}(x)$, as is shown in Tables II and III.

TABLE II. THE KINETIC PARAMETERS OF THE DECOMPOSITION OF CALCIUM OXALATE

W	ΔE kcal./mol.	$\log A$*
0.95	87.4	28.60
0.90	80.3	28.57
0.85	76.7	28.56
0.80	82.7	28.56
0.75	74.8	28.58
0.70	77.9	28.58
0.65	76.9	28.59
0.60	77.0	28.62
0.55	79.2	28.63
0.50	80.1	28.64
0.45	80.1	28.64
0.40	82.1	28.67
0.35	78.0	28.67
0.30	78.7	28.68
0.25	76.3	28.69
0.20	75.6	28.70
0.15	77.0	28.72
0.10	73.7	28.69
0.05	67.0	28.69
mean	78.0±1.0	28.64±0.012

* The dimension of A is min^{-1}.

TABLE III. THE KINETIC PARAMETERS OF THE DEGRADATION OF NYLON 6

W	ΔE kcal./mol.	$\log A$*
0.95	29.7	11.11
0.90	35.0	10.98
0.85	35.9	10.96
0.80	35.7	10.95
0.75	36.2	10.94
0.70	35.3	10.92
0.65	35.7	10.91
0.60	36.5	10.90
0.55	36.0	10.91
0.50	35.5	10.90
0.45	36.3	10.89
0.40	36.3	10.90
0.35	36.5	10.88
0.30	36.5	10.88
0.25	37.2	10.88
0.20	37.0	10.88
0.15	37.8	10.87
0.10	39.2	10.88
0.05	40.1	10.84
mean	36.2±0.5	10.91±0.014

* The dimension of A is min^{-1}.

Thus, the kinetic parameters, e. g., ΔE, A, $\boldsymbol{f}(x)$ and $\boldsymbol{g}(x)$, are determined; from these parameters, a theoretical curve can be drawn and compared with the experimental master thermogravimetric curve. If the successive adjustments of the parameters are made, more accurate values will be obtained.

Experimental

The method was applied to two reactions: the decomposition of calcium oxalate into calcium carbonate and carbon monooxide, and the degradation of nylon 6. The calcium oxalate monohydrate was of a G. R. grade, purchased from the Showa Chemical Co., Ltd., and used without further purification. The nylon 6, kindly supplied by the Toyo Rayon Co., Ltd., was dissolved in formic acid, reprecipitated by water, and dried in vacuo. The viscosity-average molecular weight of 10300, was obtained from the intrinsic viscosity as measured in formic acid at 25°C. The amino groups at the chain ends of the polymer were partly acetylated.

A 300 mg. sample of calcium oxalate monohydrate or a 100 mg. sample of nylon 6 was weighed in a glass sample pan 15 mm. in diameter and 10 mm. in depth. The sample of nylon 6 was dried in the sample pan at 180°C for one hour under a pressure of less than 1×10^{-3} Torr. prior to the measurements.

A null-type continuously-recording thermobalance supplied by the Ohyo Rika Kogyo Co., Ltd., was employed for the thermogravimetric measurements. A chromel-alumel thermocouple was located directly above the sample. The linear increase in the furnace temperature was regulated by a PI-type program controller and a SCR regulator purchased from the Ohkura Electric Co., Ltd. The pyrolysis of calcium oxalate monohydrate was carried out in air at an ambient pressure, and that of nylon 6, under a pressure of less than 1×10^{-3} Torr. The heating rates were varied from 12°C per hour to 140°C per hour. The samples were weighed before and after heating by an analytical balance.

Results and Discussion

The results of the thermogravimetry at various heating rates are plotted against the reciprocal absolute temperature in Figs. 3 and 4. It is apparent that these curves can be superposed by lateral shifts. The logarithms of the heating rates are plotted against the reciprocal absolute temperature, until which point the weight of the sample decreases to a given fraction, as Figs. 5 and 6 show. Straight lines are drawn by the method of the least squares; from these lines the activation energies are determined as listed in Tables II and III.

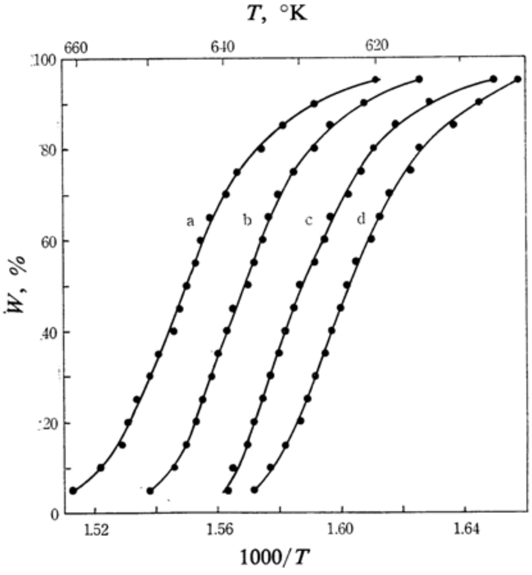

Fig. 3. The thermogravimetric curves of decomposition of calcium oxalate plotted against the reciprocal absolute temperature. Heating rate; a, 108°C/hr.; b, 54°C/hr.; c, 24.4°C/hr.; d, 12.5°C/hr.

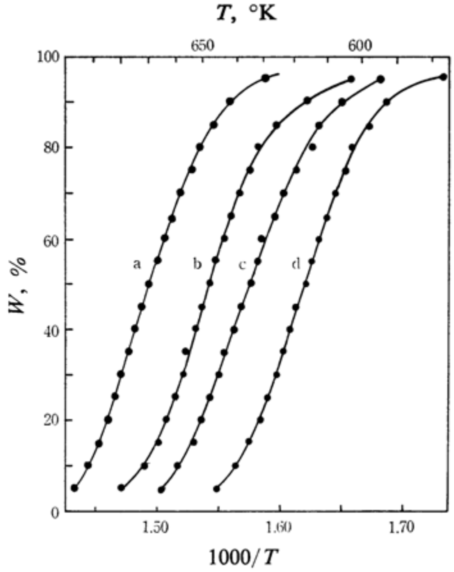

Fig. 4. The thermogravimetric curves of nylon 6 plotted against the reciprocal absoute temperature. Heating rate; a, 140°C/hr.; b, 48°C/hr.; c, 28°C/hr.; d, 14.3°C/hr.

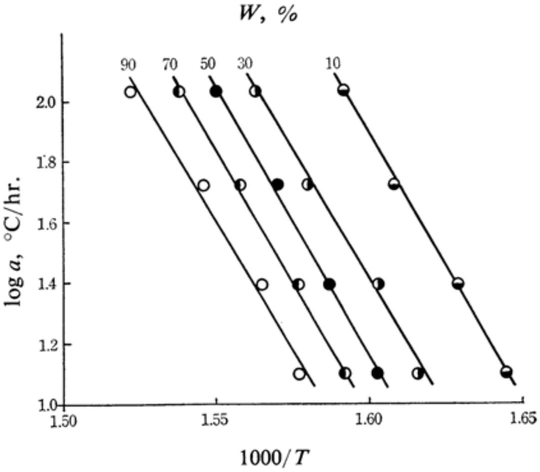

Fig. 5. The plots of logarithms of heating rate versus the reciprocal absolute temperature for indicated conversions of the decomposition of calcium oxalate.

By using the activation energies thus determined, the weight changes are plotted against $\log\{(\Delta E/a\boldsymbol{R})\boldsymbol{p}(\Delta E/\boldsymbol{R}T)\}$ and compared with the curves in Figs. 1 and 2. From these comparisons, the mechanism of the decomposition of calcium oxalate may be elucidated to be of the 1st order; it is also found that the

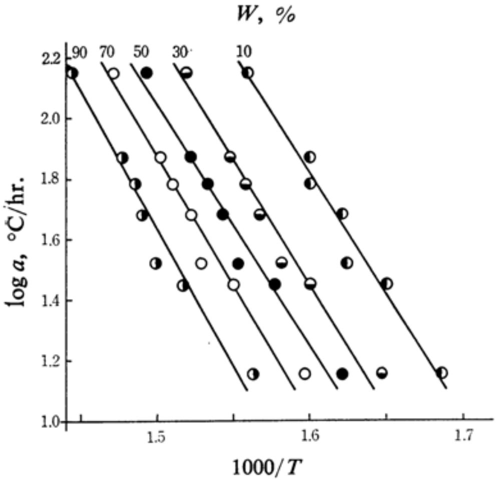

Fig. 6. The plots of logarithms of heating rate versus the reciprocal absolute temperature for indicated conversions of the degradation of nylon 6.

theoretical curve of random degradation with $L=2$ is best fitted to the experimental curve of nylon 6. A is determined by comparing $\log\{(\Delta E/aR)p(\Delta E/RT)\}$ with $\log\int dx/g(x)$ at every 5% of conversion; this tabulation is also in Tables II and III. In Freeman and Carrol's paper,[7] the activation energy and the order of the reaction of the decomposition of calcium oxalate were reported to be 74 kcal./mol. and 0.7 respectively, but the pre-exponential factor could not be evaluated by their method. The agreement between the results of this paper and theirs is good. For nylon 6, the activation energy and the order of the reaction were evaluated to be 37.0 kcal./mol. and 0 in Inoue and Sumoto's paper,[14] in which the mechanism of the unzipping of the monomer from carboxyl ends was postulated, whereas Straus and Wall[15] reported a mechanism of random degradation in which the activation energy is about 30 kcal./mol., the pre-exponential factor is of the order of 10^5—10^7, and L is 5. In both papers, the results were obtained by isothermal measurements, which contain some errors, as has been pointed out above. Considering these facts, the agreement seems fairly good. The experimental master curves at the heating rate of 60°C per hour are shown in Figs. 7 and 8, where they are also compared with the theoretical curves on the basis of the kinetic parameters obtained by the above analyses. The agreements between them are also good.

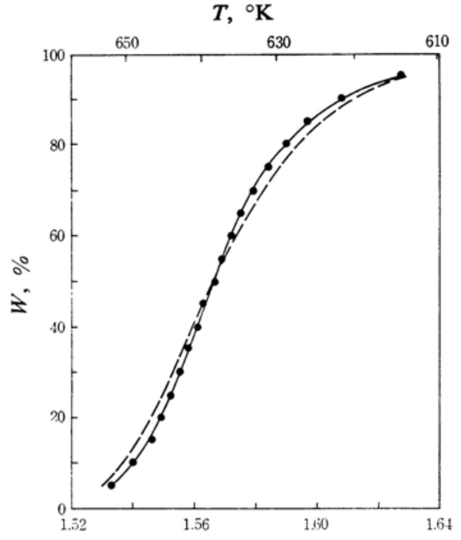

Fig. 7. The comparison of the experimental master curve (——) and the theoretical curve (----) of the decomposition of calcium oxalate.

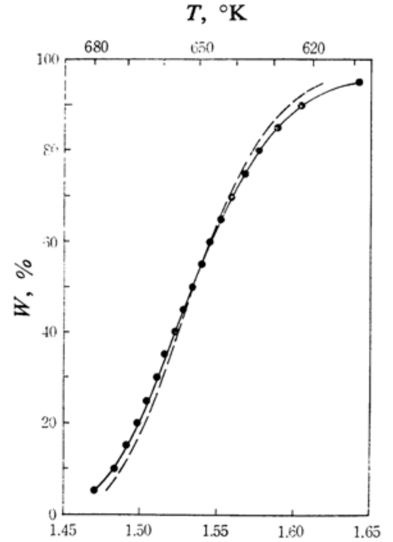

Fig. 8. The comparison of the experimental master curve (——) and the theoretical curve (----) of the degradation of nylon 6.

As may be seen in the above procedure, the method described in this paper is simple and applicable to the random degradation of polymers and other complicated reactions which can not be analyzed by other methods. However, if the weight changes in the manner of parallel reactions or consecutive reactions (in other words, if the weight-change is governed by two or more activation energies), the curves of the weight versus the reciprocal

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absolute temperature at different heating rates can not be superposed, and the analysis mentioned above can not be applied. This is also the case for the other methods of analyzing thermogravimetric data.

Now we would like to discuss the applicability of the method to other types of thermal analyses, in which is recorded the change, or the rate of the change, of some property of the material heated at a constant rate.[16,17] If the property measured is a function of x only, the change in the property can be treated similarly to the change in weight at the random degradation of polymers, and even if the exact form of $\boldsymbol{f}(x)$ and/or $\boldsymbol{g}(x)$ is unknown, the activation energy of the thermal behavior of the property can be estimated by a plot similar to Figs. 5 and 6. Furthermore, the change in the property under different conditions of temperature change can be predicted. Namely, the conversion of the property depends on the integral of the right side of Eq. 4, which has the dimension of time and which could be called "reduced time," θ:

$$\theta=\int_{t_0}^{t}\exp\left(-\frac{\Delta E}{\boldsymbol{R}T}\right)\mathrm{d}t \tag{11}$$

When the change in the property is plotted against the logarithm of the reduced time by using the activation energy thus determined, the master curve of the change in the property under the various conditions of temperature change will be obtained. Below are shown the expressions of the reduced time, some of which have already been calculated in the literature.[18] (i) If the temperature is maintained at T from time 0 to time t:

$$\theta=t\exp\left(-\Delta E/\boldsymbol{R}T\right) \tag{12}$$

(ii) If the temperature is raised from T_1 to T_2 at the rate of a and cooled from T_2 to T_3 at the rate of b:

$$\begin{aligned}\theta=&(\Delta E/a\boldsymbol{R})\{\boldsymbol{p}(\Delta E/\boldsymbol{R}T_2)-\boldsymbol{p}(\Delta E/\boldsymbol{R}T_1)\}\\&+(\Delta E/b\boldsymbol{R})\{\boldsymbol{p}(\Delta E/\boldsymbol{R}T_2)-\boldsymbol{p}(\Delta E/\boldsymbol{R}T_3)\}\end{aligned} \tag{13}$$

(iii) If the temperature is changed from T_1 to T_2 according to Eq. 14:

$$T=a+b\exp\left(-\alpha t\right) \tag{14}$$

$$\begin{aligned}\theta=&\left(\frac{1}{\alpha}\right)\left\{\boldsymbol{Ei}\left(-\frac{\Delta E}{\boldsymbol{R}T_2}\right)-\boldsymbol{Ei}\left(-\frac{\Delta E}{\boldsymbol{R}T_1}\right)\right\}\\&-\left(\frac{1}{\alpha}\right)\exp\left(-\frac{\Delta E}{a\boldsymbol{R}}\right)\left\{\boldsymbol{Ei}\left(\frac{\Delta E}{a\boldsymbol{R}}-\frac{\Delta E}{\boldsymbol{R}T_2}\right)\right.\\&\left.-\boldsymbol{Ei}\left(\frac{\Delta E}{a\boldsymbol{R}}-\frac{\Delta E}{\boldsymbol{R}T_1}\right)\right\}\end{aligned} \tag{15}$$

where:

$$\boldsymbol{Ei}(x)=\frac{\exp(x)}{x}\left\{1+\frac{1}{x}+\frac{2!}{x^2}+\frac{3!}{x^3}+\cdots\right\} \tag{16}$$

(iv) If the temperature is changed from T_1 to T_2 according to Eq. 17:

$$1/T=1/T_0-at \tag{17}$$

$$\theta=\left(\frac{\boldsymbol{R}}{a\Delta E}\right)\left\{\exp\left(-\frac{\Delta E}{\boldsymbol{R}T_2}\right)-\exp\left(-\frac{\Delta E}{\boldsymbol{R}T_1}\right)\right\} \tag{18}$$

For the more complicated changes in the temperature, θ can be calculated according to its additivity, or according to its linearity in integration. It is also apparent from the above discussions that the thermal stability of the materials should be defined by using θ and ΔE.

Summary

A new method of obtaining the kinetic parameters from thermogravimetric curves has been proposed. The method is simple and applicable to reactions which can not be analyzed by other methods. The effect of the heating rate on thermogravimetric curves has been elucidated, and the master curve of the experimental curves at different heating rates has been derived.

The applications of the method to the pyrolyses of calcium oxalate and nylon 6 have been shown; the results are in good agreement with the reported values.

The applicability of the method to other types of thermal analyses has been discussed, and the method of the conversion of the data to other conditions of temperature change has been suggested. From these discussions, the definition of the thermal stability of materials has been criticized.

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