

KINETIC ANALYSIS OF DERIVATIVE CURVES IN THERMAL ANALYSIS

T. OZAWA

Electrotechnical Laboratory, Tanashi, Tokyo, Japan

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Two methods of obtaining kinetic parameters from derivative thermoanalytical curves are proposed. The methods are based on the general form of kinetic formulae and are applicable to general types of reactions governed by a single activation energy. One method utilizes the linear relation between peak temperature and heating rate in order to estimate the activation energy, and only the information of the rate of conversion versus the temperature is necessary. The other method needs the information of both the conversion and the rate of conversion versus the temperature, and the Arrhenius plot is made for an assumed kinetic mechanism.

Various types of thermal analysis have been applied in almost all fields of material research. The thermoanalytical method, in which the properties of a sample heated at a constant rate of heating are observed continuously, is an effective method when the thermal response time is large compared with the rate of the process and considerable change occurs during the period of heating the sample up to the desired temperature in an isothermal measurement. For kinetic investigation of the pyrolysis of a substance, thermogravimetry has been utilized mainly, and many methods of obtaining kinetic parameters from thermogravimetric data have been proposed. These have been thoroughly reviewed by Flynn and Wall [1].

Recently mass-spectrometric thermal analysis (MTA) was proposed [2] and has been applied to the thermal degradation of polymeric materials [3–6]. This technique has some advantages over thermogravimetry since the volatilized products can be identified by mass-spectroscopy and the rate of the volatilization of each product is also recorded simultaneously. Thus, we can obtain kinetic information as well as a knowledge of the products, and if the reaction proceeds in parallel reactions, these can be distinguished by identification of the products; this is not possible with thermogravimetry.

However, a method of kinetic analysis of such derivative types of thermoanalytical curves as are obtained by MTA and differential scanning calorimetry (DSC) has not yet been proposed. Methods of kinetic analysis using data of both the conversion and the rate of conversion are reported for thermogravimetry, but these are only applicable to reactions of the n -th order, and hence can-

not be applied to high polymers, some of which are decomposed by other mechanisms such as random degradation, in which the rate of scission is followed by a first order reaction. The scission occurs at random points of the main-chain in equal probability, and the rates of volatilization of the products are quite different from that of the first-order reaction. Moreover, these methods need data of both conversion and rate of conversion. In a previous paper [7], the author proposed a method of kinetic analysis of thermogravimetric data which has wide applicability and needs only data of conversion. However, although we can observe the rate of conversion by MTA and DSC, integration of the derivative curve is not always equal to the conversion, because of the presence of an additional minor reaction, especially when the latter becomes dominant as the temperature is raised.

In the present paper, methods of kinetic analysis of derivative curves are proposed which are also applicable to the above-mentioned complex process. Some of the methods are examined by using the derivative curve calculated theoretically by machine.

Theoretical considerations

In thermal analysis, properties of the sample, P , or the rate of change of the properties, dP/dt (or dP/dT), are recorded as a function of temperature, T , or time, t . In order to estimate the kinetic parameters with thermal analysis, the properties measured should be independent of the temperature and the experimental time scale, and depend only on the structural quantity of the sample, x . Hence, properties such as viscoelastic or dielectric properties are not suitable for this purpose. The conversion, C , which is equal to $(P - P_0)/(P_\infty - P_0)$, is a function of x :

$$C = f(x) \quad (1)$$

In thermal analysis we cannot utilize the observations of the change of other properties, such as volume in dynamic dilatometry and relative modulus in torsional braid analysis, since the volume and modulus depend on the temperature and the experimental time scale, as well as on the structure. The kinetic parameters cannot be obtained unless we can obtain or derive the structural quantity, x , from these measurements. The modulus in the rubbery region may be utilized for this purpose, since the ratio of the modulus to the temperature depends only on the cross-linking density of the polymer.

The structural quantity is assumed to change following ordinary reaction kinetics:

$$dx/dt = A \exp(-\Delta E/RT) g(x) \quad (2)$$

where A , ΔE and R are the frequency factor, the activation energy and the gas

constant, respectively. The above assumption may generally hold. The temperature changes linearly:

$$T = T_0 + at \quad (3)$$

where T_0 and a are the initial temperature and the rate of heating (or cooling), respectively.

In the previous paper [7], the author derived C as a function of T :

$$\int_0^x \frac{dx}{g(x)} = A \int_0^t \exp(-\Delta E/RT) dt \quad (4)$$

$$G(x) = A \Theta \quad (5)$$

where $G(x)$ equals $\int_0^x dx/g(x)$ and Θ was defined as the reduced time [7]. When the temperature is increased at a constant rate and the reaction barely occurs at the initial temperature, Θ is given by the following equation:

$$\Theta = \frac{\Delta E}{aR} p \left(\frac{\Delta E}{RT} \right) \quad (6)$$

where the p -function is given by:

$$p(y) = - \int_0^y \frac{\exp(-y)}{y^2} dy \quad (7)$$

If y is larger than 15, then the following approximation can be applied:

$$p(y) = \frac{\exp(-y)}{y} \left[\frac{1}{y+1} - \frac{1}{(y+1)(y+2)} + \frac{2}{(y+1)(y+2)(y+3)} - \frac{4}{(y+1)(y+2)(y+3)(y+4)} + \frac{14}{(y+1)(y+2)(y+3)(y+4)(y+5)} - \frac{38}{(y+1)(y+2)(y+3)(y+4)(y+5)(y+6)} + \frac{216}{(y+1)(y+2)(y+3)(y+4)(y+5)(y+6)(y+7)} - \frac{600}{(y+1)(y+2)(y+3)(y+4)(y+5)(y+6)(y+7)(y+8)} \right] \quad (8)$$

$(y \geq 15)$

and

$$\log p(y) = -2.315 - 0.4567y \quad (9)$$

The approximation may be applicable to the ordinary reaction, since y is usually greater than 15.

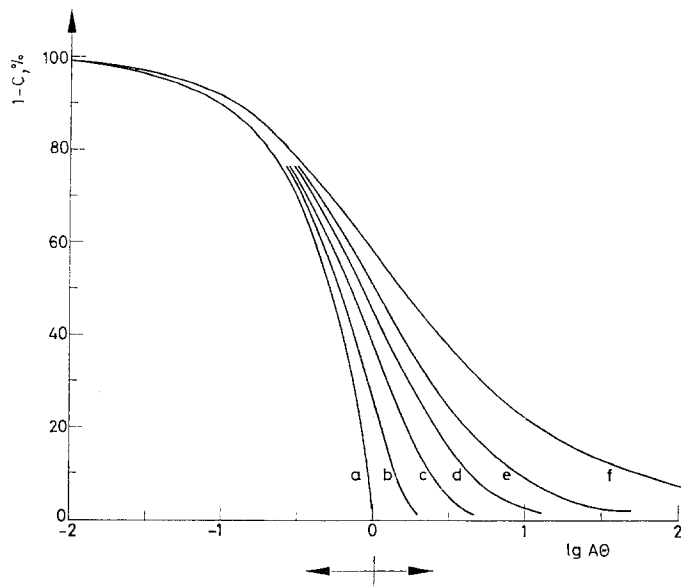


Fig. 1. The relation between the conversion, C , and $A\theta$ for the reactions of the n -th order; a) 0th, b) 0.5th, c) 1st, d) 1.5th, e) 2nd, f) 3rd

From Eqs (1) and (5), we can derive the relation between P and $A\theta$, because the relation between C and $g(x)$ is equal to the relation between C and $A\theta$. The relations between C and $A\theta$ are dependent only on the functions f and g , i.e. the mechanism of the reaction and the relation of P with x , and they can be theoretically derived. Some of the typical relations are shown in Figs 1* and 2. For the weight change in the random degradation of a high polymer, C is given by Simha and Wall [8]:

$$1 - C = (1 - x)^{L-1} \left[1 + x \frac{(N-1)(L-1)}{N} \right] \quad (10)$$

$$\frac{dx}{dt} = A \exp \left(-\frac{\Delta E}{RT} \right) (1 - x) \quad (11)$$

* Similar curves are shown in the previous paper. However, the present graphs are revised ones.

where x , N and L are the fraction of bonds broken, the initial degree of polymerization and the least length of the polymer not volatilized, respectively. The right side of Eq. (10) is approximately equal to $(1 - x)^{(L-1)}[1 + (L - 1)x]$, since L is negligibly small compared with N . The relations between C and x are

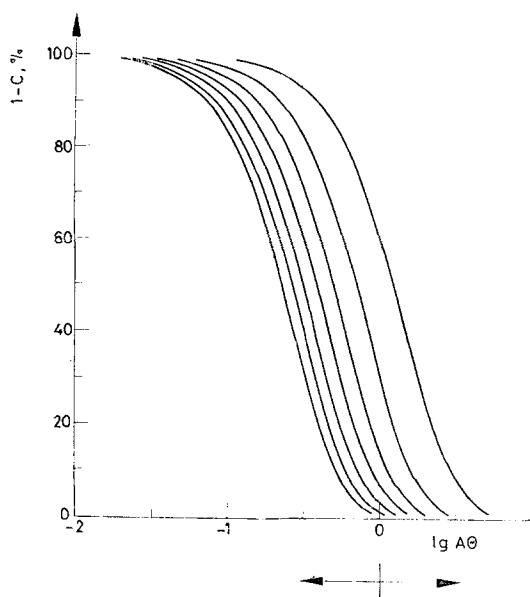


Fig. 2. The relation between the conversion, C , and $A\theta$ for the random degradation of high polymers; from right to left, $L = 2, 3, 4, 5, 6, 7$ and 8

obtained by resolving the equation for a given conversion by using Newton's method of approximation; they are shown in Fig. 3. Utilizing the relations in Fig. 3, the curves in Fig. 2 can be drawn. Thus, we can obtain the theoretical integral types of curve for given values of the kinetic parameters of A and ΔE and a given mechanism of f and g , by using these theoretical relations and Eq. (8).

On the other hand, the similar theoretical relations of derivative type are also derived:

$$\frac{dC}{dA\theta} = \frac{df(x)}{dx} \cdot \frac{dx}{dA\theta} \tag{12}$$

$$= \frac{df(x)}{dx} \cdot \frac{dx}{dt} \cdot \frac{dt}{dA\theta} \tag{13}$$

$$= g(x) \frac{df(x)}{dx} \tag{14}$$

because

$$dA\Theta/dt = A \exp(-\Delta E/RT) \quad (15)$$

Thus, the theoretical relations between $dC/dA\Theta$ and C are derived from Eqs (1) and (14). The theoretical relations between $dC/dA\Theta$ and $A\Theta$ are derived from Eqs (5) and (14). These relations are the theoretical ones depending only on the functions f and g .

The derivative curves are similarly obtained for a particular set of the kinetic parameters, because

$$\frac{dC}{dT} = \frac{dC}{dA\Theta} \frac{dA\Theta}{dT} = A \exp\left(-\frac{\Delta E}{RT}\right) g(x) \frac{df(x)}{dx} \quad (16)$$

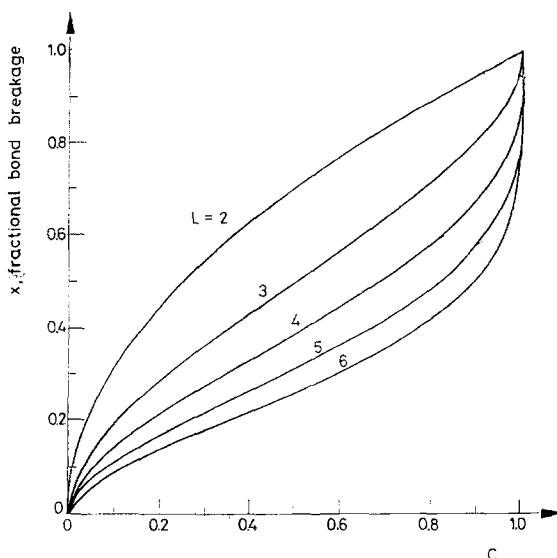


Fig. 3. The relation between C and x for the random degradation of high polymers

For the random degradation of high polymers, the weight changes are shown above, and the rates of weight loss can be calculated by using the above equations, but the theoretical relations of the volatilization rate of each product must be known, since in MTA and evolved gas analysis one observes not the rate of the total weight change but the volatilization rates of the individual products.

Now let us consider the probability of the formation of each product. For the random degradation of high polymers, the products of the repeating unit from one to $L - 1$ are formed. The probabilities of the formation of each product from a polymer larger than $(2L - 1)$ -mer are equal to each other, since the i -th bond from the end should be broken for the volatilization of the i -mer ($i \leq L - 1$),

and the number of such bonds to be broken is two for each product. The probabilities of formation of each product from the j -mer ($L \leq j < 2L - 1$) must be considered. A simple approach is made after Mejlzer et al. [9]. If the i -th bond

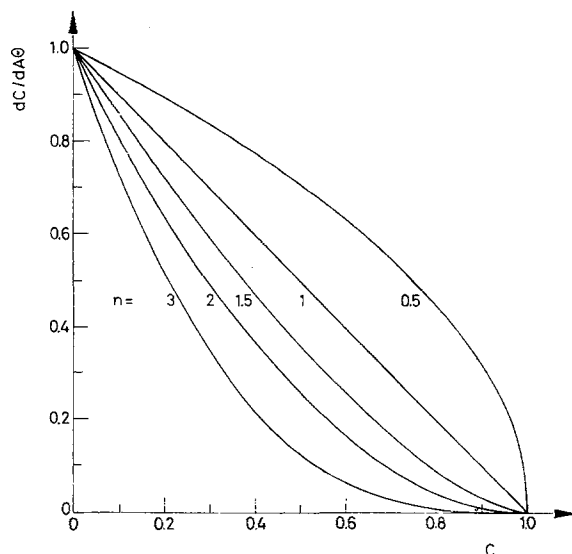


Fig. 4. The relation between $dC/dA\theta$ and C for the reaction of the order indicated in the Figure

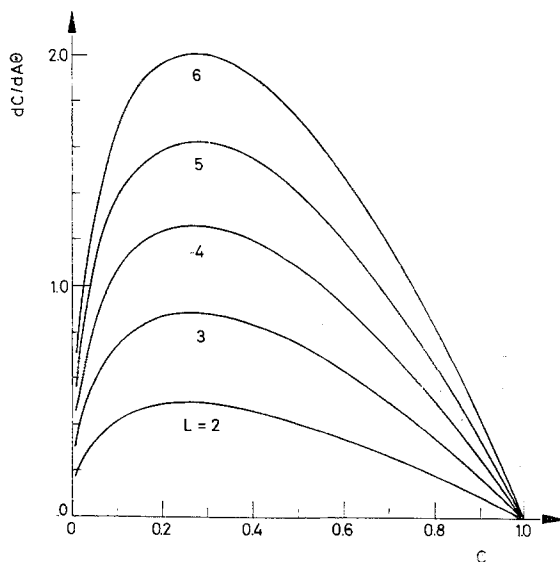


Fig. 5. The relation between $dC/dA\theta$ and C for the random degradation of high polymers with L indicated in the Figure

from one end is broken, the i -mer and $(j - i)$ -mer are produced. If the i -th bond from the other end is broken, the situation is the same. If the i -th bond from the ends of the $(2i)$ -mer is broken, two molecules of the i -mer are formed by the breaking of one bond. Thus, the number of ways of producing i -mer from j -mer is independent of i and equal to 2. As the probability of breaking is equal for all bonds, the probabilities of formation of the volatilized products are equal to each other, and the conversion of volatilized products corresponds to the weight change of Eq. (9).

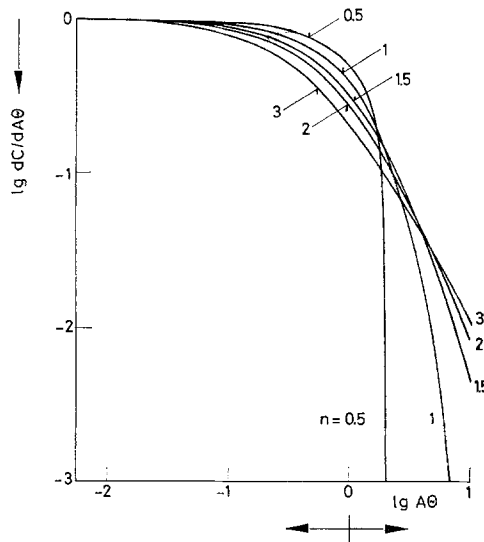


Fig. 6. The relation between $dC/dA\theta$ and $A\theta$ for the reaction of the order indicated in the Figure

Hence, $dC/dA\theta$ can be derived for the volatilization rate in the random degradation of high polymers.

For some of the typical cases, $dC/dA\theta$ is shown as functions of $A\theta$ and C in Figs 3, 4, 5 and 6 and in Table 1.

Now let us consider the peak of the curve. Shulman and Lochte [10] suggested that the logarithm of the heating rate is in a linear relation with the reciprocal value of the peak absolute temperature in first order reactions and that the activation energy can be estimated from the slope. This was based on two facts: the conversion at the peak is almost constant and independent of the heating rate, as shown by Horowitz and Metzger [11]; and the logarithm of the heating rate is in a linear relation with the reciprocal absolute temperature for the given conversion as suggested by the author [7].

Table 1
Typical forms of $f(x)$, $g(x)$, $G(x)$ and $-dC/dA\theta$

Type of reaction	$f(x)$	$g(x)$	$G(x)$	$-dC/dA\theta$
n -th order ($n \neq 1$)	x	$(1 - C)^n$	$\frac{1}{n-1}[(1 - C)^{1-n} - 1]$	$[1 + (n - 1)A\theta]^{n/(1-n)}$
1st order	x	$(1 - C)$	$-\ln(1 - x)$	$\exp(-A\theta)$
Random degradation	$(1 - x)^{L-1}[1 + (L - 1)x]$	$(1 - x)$	$-\ln(1 - x)$	$\frac{L(L-1)\exp[-(L-1)A\theta]}{\times [1 - \exp(-A\theta)]}$
Parabolic law	x	$\frac{1}{2C}$	C^2	$\frac{1}{2\sqrt{A\theta}}$

On the other hand, Murray and White [12] pointed out another linear relationship between the logarithm of the heating rate divided by the square of the peak absolute temperature and the reciprocal peak absolute temperature for first order reactions. Kissinger [13] suggested that the linear relationship is also applicable to reactions of different order for differential thermal analysis (DTA) data.

However, the above-mentioned relationships hold for wider varieties of reaction, as elucidated below, but the relations cannot generally be applied for DTA data, as seen in the discussion.

At the peak:

$$\frac{d^2C}{dT^2} = 0 \quad (17)$$

then:

$$\frac{\Delta E}{RT_m^2} \left[\frac{df(x)}{dx} \right]_{x=x_m} + \frac{A}{a} \exp \left(-\frac{\Delta E}{RT} \right) \left[\frac{dg(x)}{dx} \right]_{x=x_m} \left[\frac{df(x)}{dx} \right]_{x=x_m} + \left[\frac{d^2f(x)}{dTdx} \right]_{x=x_m} = 0 \quad (18)$$

where suffix m denotes the peak. If the following approximation is made (the approximation is examined by Doyle [14]):

$$p(y) = \exp(-y)/y^2 \quad (19)$$

then:

$$\frac{ART_m^2}{a\Delta E} \exp \left(-\frac{\Delta E}{RT_m} \right) = A\Theta_m = G(x_m) \quad (20)$$

Thus, Eq. (18) reduces to the following equation containing only x_m :

$$\left[\frac{df(x)}{dx} \right]_{x=x_m} + G(x_m) \left[\frac{dg(x)}{dx} \right]_{x=x_m} \left[\frac{df(x)}{dx} \right]_{x=x_m} + g(x_m) G(x_m) \left[\frac{d^2f(x)}{dx^2} \right]_{x=x_m} = 0 \quad (21)$$

and x_m is approximately independent of the heating rate. According to Eq. (5), $A\Theta_m$ is equal to $G(x_m)$, and the method of obtaining the activation energy from the integral thermoanalytical curve proposed previously by the present author, is also applicable to the peak of the derivative curve. Namely:

$$\log a = -0.4567 \Delta E/RT_m - 2.315 + \log A\Delta E/R - \log G(x_m) \quad (22)$$

Thus, $\log a$ is in linear relation with $1/T_m$, and the "Ozawa plot" proposed by Shulman and Lochte [10] has wide applicability; if the reaction observed is consistent with Eqs (1) and (2), we can estimate the activation energy of the

reaction by using the linear dependency of the reciprocal absolute peak temperature on the logarithm of the heating rate. In order to obtain a more correct value of the activation energy, the following correction proposed by Flynn and Wall [15] is applicable:

$$\Delta E_c = \Delta E \frac{\log p(\bar{y} - 0.5) - \log p(\bar{y} + 0.5)}{0.4567} \quad (23)$$

where ΔE_c is the corrected activation energy and \bar{y} is the average value of $\Delta E/RT$.

The following equation is also derived by using Eq. (19):

$$\ln(a/T_m^2) = -\Delta E/RT_m + \ln(AR/\Delta E) - \log G(x_m) \quad (24)$$

This method of obtaining the activation energy is equivalent to that proposed by Kissinger for the DTA data, but it is applicable not to DTA but to the above-mentioned types of thermal analysis and to wider varieties of reaction.

When the conversion follows a reaction of the n -th order:

$$C = x \quad (25)$$

and

$$g(x) = (1 - x)^n \quad (26)$$

the following equations are derived from Eq. (20):

$$1 - C_m = \begin{cases} 1/e & \text{for } n = 1 \\ n^{1/(1-n)} & \text{for } n \neq 1 \end{cases} \quad (27)$$

since

$$\frac{df(x)}{dx} = 1 \quad (28)$$

$$\frac{d^2f(x)}{dx^2} = 0 \quad (29)$$

and

$$\frac{dg(x)}{dx} = -n(1 - x)^{n-1} \quad (30)$$

From Eqs (20) and (28),

$$A\Theta_m = 1. \quad (31)$$

In this case, the following two equations can also be derived from Eq. (31):

$$\log a = -0.4567\Delta E/RT_m - 2.315 + \log(A\Delta E/R) \quad (32)$$

$$\ln(a/T_m^2) = \ln(AR/\Delta E) - \Delta E/RT_m \quad (33)$$

The latter equation holds without any approximation for reactions of the first order.

For the volatilization of the random degradation of high polymer, the following equation holds:

$$x_m - (1 - Lx_m) \ln(1 - x_m) = 0 \quad (34)$$

The roots of the equation and the values of C_m are tabulated in Table 2, and Eqs (32) and (33) are also approximately applicable, since $G(x_m)$ can be neglected compared with the other terms.

Table 2
Conversions and fractions of bonds broken
at the peak of the derivative curve
of the random degradation of polymers

L	x_m	C_m (%)
2	0.7644	58.43
3	0.5606	59.04
4	0.4398	59.22
5	0.3612	59.29
6	0.3063	59.32
7	0.2658	59.35
8	0.2347	59.36

Methods of kinetic analysis

Two methods are derived from the above theoretical consideration. The one is based on the approximate relation between the peak temperature and the heating rate, and the other is applicable to the case when we can obtain the conversion as well as the rate of conversion, i.e., the case when the effect of the minor side reaction can be neglected and the integral of the rate of conversion is equal to the conversion. In the first method, the logarithm of the heating rate or the logarithm of the heating rate divided by the square of the absolute peak temperature is plotted against the reciprocal absolute peak temperature, and from the slope of this plot we obtain the activation energy by using Eqs (22), (23) and (24). Then, unless the conversion can be obtained, we cannot normalize the rate with the total amount of the change, $P_\infty - P_0$, and since the height of the curve is proportional to dC/dt and

$$dC/d\Theta = dC/dt \cdot \exp(AE/RT)/a \quad (35)$$

the rate proportional to $dC/d\Theta$ is derived. We can also calculate Θ by using Eq. (6).

The relation between $dC/d\Theta$ and Θ is the experimental master relation, and the curves obtained at the different heating rates can be superimposed on each other by converting them to the relation of $dC/d\Theta$ with Θ . The curve thus obtained is the experimental master curve and equivalent to the generalized isothermal rate of the process, since Θ is proportional to the actual time under the isothermal condition and is equal to the reduced time elapsed in the isothermal process. Then $dC/d\Theta$ is the reduced (or generalized) rate of the process. As mentioned above, we cannot always obtain $dC/d\Theta$ itself but the rate proportional to it. If we plot the logarithms of the rate reduced by Θ as a function of Θ , the curves obtained at the different heating rates can be superimposed on each other by longitudinal shifts. If they cannot be superimposed on each other, the process does not proceed by a single simple mechanism but is governed by two or more activation energies; by this superimposition we can examine the reality of the activation energy obtained by using the peak temperatures at several heating rates.

The superimposed experimental master curve is compared with the similar curve drawn theoretically for the assumed kinetics, such as Figs 5 and 6, and the type of kinetics can be determined, if the experimental curve can be superimposed on one of the theoretical curves. The frequency factor, A , is obtained by the length of the lateral shift of the superimposition.

The second method is the generalized one of the method proposed by Sharp and Wentworth [16], and applied to the case in which both the rate of conversion and the conversion are obtained as a function of the temperature. If we can obtain the activation energy from the plot of the logarithm of the heating rates against the reciprocal absolute peak temperature, we can obtain $dC/d\Theta$ as a function of C and T . The relation of $dC/d\Theta$ with C is also the experimental master curve, and it is the generalized form of the relation of dC/dt vs. C proposed by Simha and Wall [8] to distinguish the kinetic mechanisms. Then, we can compare it with the theoretically obtained curve of $dC/dA\Theta$ against C . Furthermore, an Arrhenius plot can be made, since for a given conversion

$$\ln (dC/dt) - \ln (dC/dA\Theta) = \ln A - \Delta E/RT \quad (36)$$

where the first and second terms of the left side are the experimental rate and the rate calculated theoretically for the assumed kinetics. If the assumed kinetics are correct, the Arrhenius plot should be quite linear and we obtain a set of reasonable values for the kinetic parameters.

Accuracy of the methods of obtaining the activation energy

As the linear relationship between the logarithm of the heating rate and the reciprocal absolute peak temperature and the similar relationship between the logarithm of the heating rate divided by the square of the absolute peak temperature and the reciprocal absolute peak temperature elucidated above are based

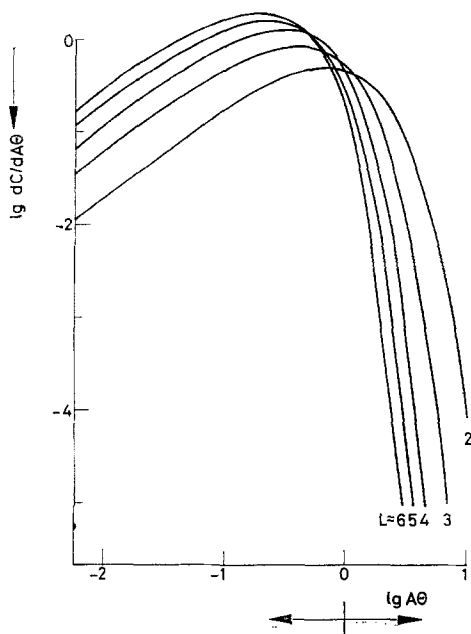


Fig. 7. The relation between $dC/dA\theta$ and $A\theta$ for the random degradation of the high polymers with L indicated in the Figure

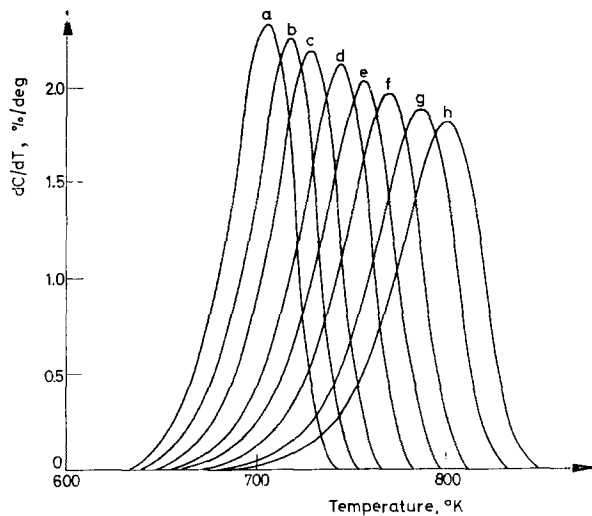


Fig. 8. Theoretical derivative curves calculated for a first order reaction with $A = 10^{15} \text{ sec}^{-1}$ and $\Delta E = 60 \text{ kcal/mole}$; a) $0.25^\circ/\text{min}$, b) $0.5^\circ/\text{min}$, c) $1^\circ/\text{min}$, d) $2.5^\circ/\text{min}$, e) $5.0^\circ/\text{min}$, f) $10^\circ/\text{min}$, g) $25^\circ/\text{min}$, h) $50^\circ/\text{min}$

on roughly approximated formulae, the critical examination of the methods should be made; the derivative curve is obtained with an electronic digital computer by using Eq. (16) and Eq. (8) for $p(y)$ to a much higher approximation, and the peak temperature is obtained to an accuracy of the 0.5th, 1st, 1.5th, 2nd and 3rd order and random degradation with $L = 2, 3, 4, 5$ and 6 , where the heating rate is $0.25, 0.5, 1.0, 2.5, 5.0, 10, 25$ and $50^\circ/\text{min}$ and where most of the

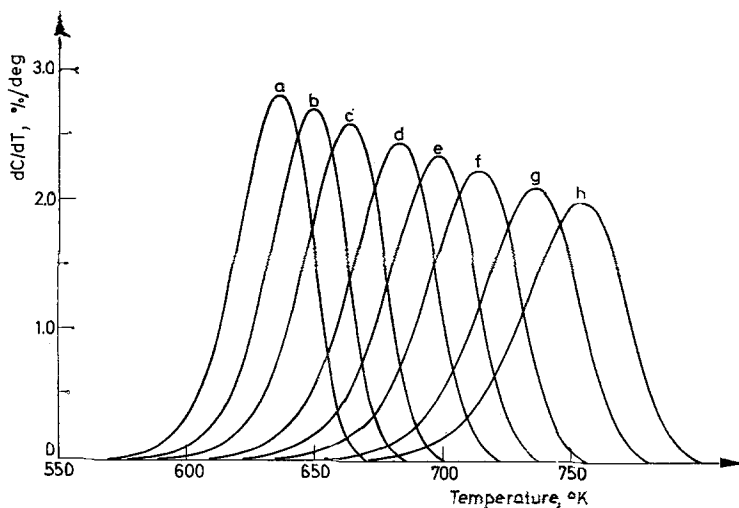


Fig. 9. Theoretical derivative curves calculated for the random degradation of a high polymer with $A = 10^{10} \text{ sec}^{-1}$, $\Delta E = 40 \text{ kcal/mole}$ and $L = 3$; a) $0.25^\circ/\text{min}$, b) $0.5^\circ/\text{min}$, c) $1.0^\circ/\text{min}$, d) $2.5^\circ/\text{min}$, e) $5.0^\circ/\text{min}$, f) $10^\circ/\text{min}$, g) $25^\circ/\text{min}$, h) $50^\circ/\text{min}$

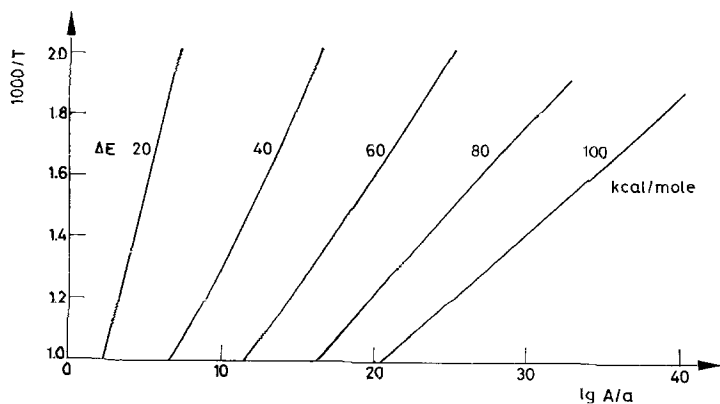


Fig. 10. The dependency of peak temperature upon A/a for a first order reaction with the indicated activation energy

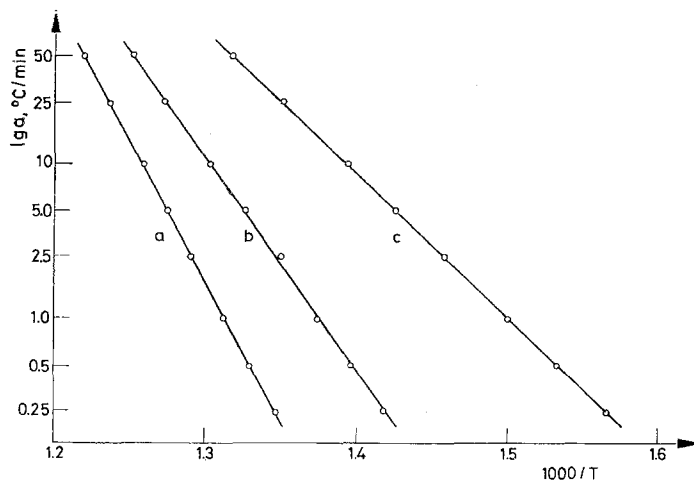


Fig. 11. Typical plots of the logarithm of the heating rate versus the reciprocal absolute peak temperature; a) second order reaction with $A = 10^{20} \text{ sec}^{-1}$ and $\Delta E = 80 \text{ kcal/mole}$; b) first order reaction with $A = 10^{15} \text{ sec}^{-1}$ and $\Delta E = 60 \text{ kcal/mole}$; c) 0.5th order reaction with $A = 10^{10} \text{ sec}^{-1}$ and $\Delta E = 40 \text{ kcal/mole}$

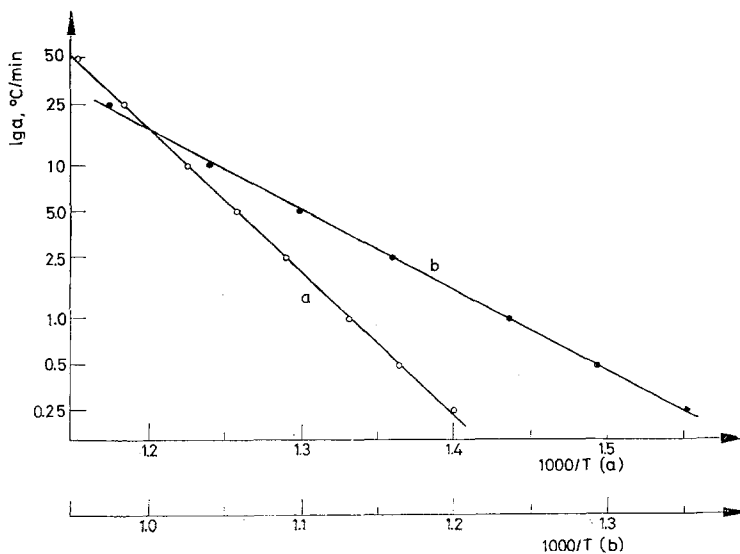


Fig. 12. Typical plots of the logarithm of the heating rate versus the reciprocal absolute peak temperature; a) the random degradation of a high polymer with $A = 10^{10} \text{ sec}^{-1}$, $\Delta E = 40 \text{ kcal/mole}$ and $L = 6$; b) the random degradation of a high polymer with $A = 10^2 \text{ sec}^{-1}$, $\Delta E = 20 \text{ kcal/mole}$ and $L = 2$

peak temperatures are in the range 500–1000 °K. Some of the curves thus obtained are shown in Figs 8 and 9. The peak temperatures are plotted against A/a for reactions of the first order in Fig. 10; the peak temperatures for other types of kinetics are almost the same as those for the first order reactions.

Typical examples of plots of the logarithm of the heating rate against the reciprocal absolute peak temperature are shown in Figs 11 and 12. The activation energies and the frequency factors are estimated by using Eqs (32), (33) and (23), and some of them are tabulated in Tables 3 and 4; the other results are similar to those listed. The results are in very good agreement with each other and with the theoretical values, and the differences between the estimated values and the theoretical ones are due to the approximations in the utilized equations and the precision of the calculated peak temperatures of 0.1 °K.

Discussion

As seen in Tables 3 and 4, the accuracy of the methods for the estimation of the activation energy is high, though the approximation utilized in the methods is a rough one. Even the frequency factor is estimated to relatively high accuracy. But the conversions estimated at the peaks of the calculated curves are rather different from those derived from Eqs (27), (28) and (34). These differences may be ascribed to the facts that the former methods are based on the peak temperatures and that a small variation of the temperature causes a large variation of the conversion near the peak.

Next, we must discuss the differential curve obtained with DTA, which resembles the derivative curve discussed above. The differential curve is not the derivative curve since in DTA the heat evolved or absorbed during the process is supplied in the following two forms:

(1) the heat flowing into or out of the sample along the temperature gradient is different from the steady state, which appears as the difference of the differential temperature from the base line of the steady state;

(2) the heat stored or consumed in the form of the temperature gradient is different from the steady state, which causes the tailing of the differential curve.

In other words, the difference between the differential curve and the derivative curve is clearly shown in the fact that after the completion of the process the temperature difference decays exponentially to the base line in DTA [17]. Thus the height of the temperature difference from the base line is not proportional to the rate of the process. Kissinger asserted that the height is proportional to the rate according to the expression that the temperature measured is a function of the time, the position of the temperature-measurement and the rate of conversion, but the temperature is a function of the conversion, the rate of conversion, the time and the position as shown in the above discussion.

Table 3A
 The difference between the estimated activation energy, ΔE_{est} , and the theoretical one, ΔE_{theo} , for an n -th order reaction

ΔE_{theo} Kcal/mole	$\log A$ sec ⁻¹	$\Delta E_{\text{est}} - \Delta E_{\text{theo}}$											
		$n = 0.5$		$n = 1$		$n = 1.5$		$n = 2$		$n = 3$			
		COP	KP	COP	KP	COP	KP	COP	KP	COP	KP		
20	2	+0.45	-0.10	+0.56	+0.01	+0.63	+0.10	+0.70	+0.17	+0.82	+0.30		
	4	+0.24	-0.06	+0.29	-0.01	+0.35	+0.05	+0.41	+0.11	+0.48	+0.19		
	6	+0.14	-0.04	+0.19	+0.01	+0.22	+0.04	+0.25	+0.07	+0.32	+0.14		
40	8	+0.17	-0.05	+0.22	0.00	+0.27	+0.06	+0.32	+0.10	+0.39	+0.18		
	10	+0.12	-0.02	+0.15	+0.01	+0.20	+0.06	+0.21	+0.07	+0.29	+0.15		
	12	+0.07	-0.02	+0.11	+0.02	+0.13	+0.04	+0.18	+0.09	+0.18	+0.09		
60	14	+0.01	-0.05	+0.06	0.00	+0.07	+0.01	+0.07	+0.01	+0.16	+0.10		
	10	+0.13	-0.07	+0.22	+0.01	+0.24	+0.04	+0.35	+0.14	+0.41	+0.22		
	14	+0.09	0.00	+0.10	+0.01	+0.14	+0.05	+0.20	+0.11	+0.21	+0.12		
80	18	+0.02	-0.01	+0.02	-0.01	+0.08	+0.04	+0.07	+0.03	+0.10	+0.07		
	22	+0.01	+0.01	-0.05	-0.05	+0.04	+0.04	+0.06	+0.05	+0.07	+0.06		
	16	+0.04	-0.03	+0.10	+0.03	+0.14	+0.06	+0.16	+0.08	+0.20	+0.13		
100	20	+0.04	+0.02	+0.07	+0.05	+0.05	+0.03	+0.13	+0.11	+0.08	+0.06		
	24	-0.03	-0.02	-0.07	-0.06	+0.07	+0.07	-0.04	-0.03	+0.11	+0.12		
	20	-0.03	-0.06	+0.01	-0.01	0.00	-0.02	+0.15	+0.13	+0.19	+0.17		
32	26	-0.05	-0.03	0.00	+0.02	+0.07	+0.09	+0.02	+0.05	+0.14	+0.16		
	32	+0.05	+0.09	+0.02	+0.06	-0.01	+0.03	-0.04	0.00	-0.11	-0.07		

KP is the Kissinger plot and COP is the corrected Ozawa plot.

Table 3B

The difference between the estimated activation energy, ΔE_{est} , and the theoretical one, ΔE_{theo} , for the random degradation of a polymer

ΔE_{theo} Kcal/mole	$\log A$ sec ⁻¹	$\Delta E_{est} - \Delta E_{theo}$											
		L = 2		L = 3		L = 4		L = 5		L = 6			
		COP	KP	COP	KP	COP	KP	COP	KP	COP	KP		
20	2	+0.47	-0.11	+0.42	-0.11	+0.40	-0.11	+0.26	-0.23	+0.38	-0.10		
	4	+0.25	-0.07	+0.24	-0.06	+0.22	-0.06	+0.36	+0.08	+0.21	-0.06		
	6	+0.15	-0.04	+0.13	-0.04	+0.15	-0.02	+0.13	-0.04	+0.14	-0.03		
40	8	+0.37	+0.15	+0.15	-0.06	+0.38	+0.18	-0.14	-0.34	-0.01	-0.19		
	10	+0.11	-0.03	+0.10	-0.04	+0.08	-0.05	+0.15	-0.02	+0.40	+0.28		
	12	+0.08	-0.01	+0.09	0.00	+0.07	-0.02	-0.41	-0.50	+0.05	-0.03		
60	14	+0.01	-0.05	+0.02	-0.04	+0.02	-0.03	+0.50	+0.46	+0.05	0.00		
	10	+0.15	-0.06	+0.15	-0.05	+0.16	-0.03	-0.09	-0.28	+0.15	-0.04		
	14	+0.07	-0.03	+0.05	-0.03	+0.04	-0.05	+0.08	0.00	+0.05	-0.03		
80	18	+0.02	-0.01	+0.03	0.00	+0.04	+0.01	-0.05	-0.08	0.00	-0.03		
	22	-0.04	-0.04	-0.01	-0.02	-0.01	-0.01	-0.06	-0.06	+0.01	+0.01		
	16	+0.04	-0.04	+0.06	-0.02	+0.05	-0.02	+0.06	-0.02	+0.03	-0.04		
100	20	-0.01	-0.01	+0.01	-0.01	+0.04	+0.02	+0.07	+0.05	-0.05	-0.07		
	24	+0.04	+0.04	-0.01	+0.01	-0.08	-0.07	+0.01	+0.01	+0.01	+0.01		
	20	-0.01	-0.01	+0.03	+0.01	+0.01	+0.09	+0.03	+0.01	+0.01	-0.01		
32	26	0.00	+0.02	-0.08	-0.06	-0.03	-0.01	-0.10	-0.08	0.00	+0.02		
	32	+0.07	+0.11	+0.11	+0.16	+0.01	+0.06	-0.03	+0.01	-0.20	-0.16		

KP is the Kissinger plot and COP is the corrected Ozawa plot.

Table 4A
 The difference between the logarithm of the estimated frequency factor, $\log A_{est}$, and the theoretical one, $\log A_{theo}$,
 for an n -th order reaction

AE_{theo} Kcal/mole	$\log A$ sec ⁻¹	$\log A_{est} - \log A_{theo}$											
		$n = 0.5$		$n = 1$		$n = 1.5$		$n = 2$		$n = 3$			
		KP	COP	KP	COP	KP	COP	KP	COP	KP	COP		
20	2	-0.058	+1.005	+0.003	+1.060	+0.053	+1.106	+0.099	+1.146	+0.183	+1.225		
	4	-0.046	+0.754	-0.003	+0.794	+0.040	+0.834	+0.082	+0.874	+0.148	+0.936		
	6	-0.039	+0.554	+0.003	+0.595	+0.033	+0.623	+0.066	+0.654	+0.131	+0.716		
40	8	-0.131	+0.370	-0.101	+0.399	-0.070	+0.429	-0.044	+0.454	+0.005	+0.500		
	10	-0.123	+0.238	-0.100	+0.260	-0.071	+0.288	-0.053	+0.306	-0.003	+0.354		
	12	-0.123	+0.117	-0.096	+0.143	-0.086	+0.162	-0.049	+0.189	+0.023	+0.213		
60	14	-0.126	-0.003	-0.102	+0.030	-0.089	+0.043	-0.079	+0.052	-0.020	+0.110		
	10	-0.031	+0.219	0.000	+0.249	+0.020	+0.264	+0.054	+0.302	+0.094	+0.340		
	14	-0.014	+0.009	+0.001	+0.024	+0.020	+0.043	+0.048	+0.070	+0.071	+0.092		
80	18	-0.017	-0.175	-0.008	-0.166	+0.019	-0.139	+0.024	-0.135	+0.052	-0.107		
	22	-0.009	-0.317	-0.027	-0.335	+0.017	-0.292	+0.031	-0.278	+0.048	-0.261		
	16	-0.021	-0.098	+0.003	-0.075	+0.020	-0.058	+0.034	-0.044	+0.064	-0.016		
100	20	-0.006	-0.242	+0.009	-0.232	+0.012	-0.229	+0.042	-0.199	+0.043	-0.199		
	24	-0.020	-0.399	-0.025	-0.404	+0.026	-0.354	-0.002	-0.382	+0.061	-0.319		
	20	-0.026	-0.270	-0.007	-0.252	-0.002	-0.247	+0.038	-0.206	+0.063	-0.183		
32	26	-0.021	-0.466	0.000	-0.444	+0.026	-0.419	+0.019	-0.425	+0.065	-0.380		
	32	+0.019	-0.589	+0.013	-0.594	+0.008	-0.600	+0.003	-0.605	-0.008	-0.616		

KP is the Kissinger plot and COP is the corrected Ozawa plot.

Table 4B
 The difference between the logarithm of the estimated frequency factor, $\log A_{est}$, and the theoretical one, $\log A_{theo}$,
 for the random degradation of a polymer

ΔE_{theo} Kcal/mole	$\log A$ sec ⁻¹	$\log A_{est} - \log A_{theo}$											
		L = 2		L = 3		L = 4		L = 5		L = 6			
		KP	COP	KP	COP	KP	COP	KP	COP	KP	COP		
20	2	-0.221	+0.866	+0.023	+1.073	+0.175	+1.202	+0.257	+1.267	+0.377	+1.376		
	4	-0.209	+0.609	+0.038	+0.828	+0.190	+0.963	+0.359	+1.119	+0.389	+1.140		
	6	-0.186	+0.413	+0.046	+0.631	+0.205	+0.776	+0.311	+0.873	+0.404	+0.958		
40	8	-0.234	+0.279	-0.049	+0.446	+0.171	+0.654	+0.141	+0.616	+0.272	+0.739		
	10	-0.237	+0.085	-0.043	+0.313	+0.104	+0.450	+0.244	+0.583	+0.146	+0.749		
	12	-0.279	-0.030	-0.030	+0.204	+0.115	+0.341	+0.064	+0.283	+0.310	+0.526		
60	14	-0.293	-0.153	-0.045	+0.083	+0.109	+0.230	+0.433	+0.547	+0.321	+0.432		
	10	-0.188	+0.072	+0.057	+0.302	+0.214	+0.449	+0.275	+0.502	+0.412	+0.634		
	14	-0.180	-0.149	+0.062	+0.081	+0.210	+0.222	+0.334	+0.341	+0.414	+0.416		
80	18	-0.176	-0.327	+0.071	-0.089	+0.227	+0.060	+0.309	+0.138	+0.412	+0.237		
	22	-0.188	-0.491	+0.064	-0.248	+0.219	-0.093	+0.311	+0.009	+0.429	+0.106		
	16	-0.182	-0.252	+0.068	-0.013	+0.218	+0.131	+0.330	+0.238	+0.414	+0.317		
100	20	-0.444	-0.680	+0.069	-0.175	+0.229	-0.021	+0.351	+0.097	+0.405	+0.148		
	24	-0.158	-0.532	+0.072	-0.310	+0.201	-0.186	+0.855	+0.494	+0.799	+0.406		
	20	-0.477	-0.716	+0.075	-0.173	+0.251	-0.002	+0.338	+0.080	+0.422	+0.161		
32	26	-0.165	-0.605	+0.057	-0.390	+0.222	-0.229	+0.313	-0.142	+0.431	-0.026		
	32	-0.134	-1.053	+0.126	-0.798	+0.244	-0.684	+0.343	-0.588	+0.371	-0.562		

KP is the Kissinger plot and COP is the corrected Ozawa plot.

Other investigators [18–23] also postulated the approximate proportionality between the height and the reaction rate without considering the heat flow into the sample. However, the proportionality holds approximately only when the second form mentioned above can be neglected, when the temperature gradient indispensable for DTA measurement exists within material of high thermal diffusivity and of low heat capacity. In the case of Borchardt and Daniels [18], the temperature gradient exists within the thin layer of the glass sample cell and the solution sample is stirred. In short, the methods of Kissinger [13], Borchardt [19], Piloyan et al. [20], Reich [21] and Taylor et al. [23] are applicable for these particular cases of DTA, as is clear in a recent argument [24–26], and if these methods should be applied to normal cases, false results would be obtained. Thus, these methods are generally applicable not to the differential curve but to the derivative curve such as that obtained with DSC.

Now let us discuss the problems of the kinetic analysis of thermoanalytical data, which have not yet been pointed out or solved. Most methods of the kinetic analysis of thermoanalytical data proposed so far are based on particular kinetic formulae, such as a reaction of the n -th order and the parabolic law [16]. These methods involve the dangerous tendency to study (unjustifiably) processes of great variety within the limited framework of the particular specialized formulae, and to lead to false results. On the other hand, the present methods and the method proposed previously by the author are based on the general form of the kinetics and the general relation of the observed properties to the structure reacting in the thermal analysis. Therefore, the methods have general applicability. Moreover, in the course of the application of the methods, the validity of the application of the methods to the analyzed process is examined with the experimental master curve; if one can draw a smooth experimental master curve, this is evidence of the validity. In order to obtain the real kinetic parameters, it is necessary, at least to compare the kinetic analyses of the curves of the different heating rates, as Flynn and Wall pointed out [1].

There are some reactions which consist of a few consecutive elementary reactions and which proceed as a whole following one order of reaction or kinetics such as Eq. (2) under isothermal conditions. Typical processes are depolymerization of high polymers [27], dehydrochlorination of polyvinyl chloride [28] and diffusion-controlled decomposition of a solid substance [16]. For the kinetic analysis of the thermoanalytical data of such processes we must consider the rate of each elementary reaction; false results are obtained if the process is treated as a whole according to the overall isothermal kinetics. However, for the depolymerization of a high polymer the treatment of the process as a whole according to the overall isothermal kinetics may be reasonable, since the time interval from the formation of a propagating radical to its annihilation is small compared with the temperature-rise during the time interval; a quasi-stationary state may exist such as the stationary state of the amount of the radical in isothermal depolymerization; and the amount of the radical and its kinetic chain length may be the same as those in the isothermal process at the same temperature. The kinetic

analysis of the curve of parallel reactions is discussed by Chatterjee [29] only for limited cases. However, it would be very difficult and complicated to analyse the parallel reactions in the general form.

The second point to be considered in the kinetic analysis of thermoanalytical data is the effect of the temperature gradient within the sample. In all methods including the present ones, the temperature is assumed to be uniform within the sample. If the sample is heated at a higher heating rate, there exists a relatively larger temperature gradient in the sample, and this broadens the curve. The effect is non-linear in its nature, because the rate of the process depends on the temperature non-linearly. Thus, the reduction of a curve deformed by the effect of the temperature gradient to the substantial curve without temperature gradient by using Laplace transformation and transfer function, such as is proposed by Tateno [30], is not reasonable, since the procedure is based on the linearity or the superimposition principle of the phenomenon.

As the effect is non-linear, it is impossible by the simple procedure to obtain the substantial curve from the deformed one, and if the mathematical procedure becomes resolved, it may probably need the thermophysical data of the reacting sample. Thus, it seems more reasonable to perform the thermal analysis with a small amount of sample at a relatively slow heating rate in order to diminish the effect of the temperature gradient; the effect could be detected by tracing the experimental master curve. Another problem of the thermal analysis of a reaction is diffusion of the volatilized products from the relatively thick layer of the sample. The effect of the diffusion could also be checked by inspection of the experimental master curve.

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In our laboratory, the mass-spectrometric thermal analysis of the degradation of high polymers is now in progress. We shall report the results in the near future. The author acknowledges the help of Mr. Kiyoshi Sakakibara and Mr. Koji Yada in the machine computation.

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RÉSUMÉ — On propose deux méthodes pour déduire les paramètres cinétiques des thermogrammes dérivés. Elles reposent sur des formules cinétiques générales applicables aux réactions correspondant à une seule valeur d'énergie d'activation. L'une de ces méthodes utilise la relation linéaire entre la température du pic et la vitesse de chauffage pour estimer la valeur de l'énergie d'activation; seule la vitesse de conversion en fonction de la température nécessite d'être connue. L'autre méthode demande de connaître à la fois le taux et la vitesse de conversion en fonction de la température, et l'on effectue le tracé de l'équation d'Arrhénius pour le mécanisme cinétique supposé.

ZUSAMMENFASSUNG — Zwei neue Methoden zur Ermittlung von kinetischen Parametern wurden auf Grund von derivierten Kurven vorgeschlagen. Die Verfahren benutzen allgemeine kinetische Formeln, die anwendbar sind für alle Reaktionstypen, welche von einer einzigen Aktivierungsenergie beherrscht sind. Die eine Methode bedient sich der linearen Beziehung zwischen Spitzentemperaturen und Aufheizraten zur Errechnung der Aktivierungsenergie, allein in Kenntnis der Umwandlungsgeschwindigkeit als Funktion der Zeit. Die andere Methode benötigt die Kenntnis des Umwandlungsgrades und der Umwandlungsgeschwindigkeit als Funktion der Temperatur und ermittelt die Arrhenius'sche Gleichung für den vorausgesetzten kinetischen Mechanismus.

Резюме. — Описано два метода получения кинетических параметров по данным дифференциальной кривой. Методы основаны на общей форме кинетических формул и их можно применять для реакций общего типа, направляемых единственной энергией активации. В одном из этих методов для расчета энергии активации используется линейное соотношение между температурой пиков и скоростями нагрева, и таким образом необходима только информация о зависимости скорости превращения от температуры.

Другой метод требует информации о превращении и о зависимости скорости превращения от температуры и график Аррениуса построен по предположенному кинетическому механизму.