

## **A GENERAL DIFFERENTIAL TECHNIQUE FOR THE DETERMINATION OF PARAMETERS FOR**

$$d(\alpha)/dt = f(\alpha)A \exp(-E/RT)$$

**Energy of activation, preexponential factor and order of reaction (when applicable)**

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A general differential method is developed and described which determines the Arrhenius parameters, energy of activation and the preexponential factor, as functions of degree of conversion from sets of two or more experiments with differing thermal programs. (These experiments may be performed at any combination of isothermal, constant heating rate or other temperature programs.) The method tests to see whether or not the kinetics follow the equation,

$$f(\alpha) = (1-\alpha)^n,$$

and calculates the correct reaction order,  $n$ , when such an equation is applicable. The correct energy of activation,  $E$ , is determined as a function of both temperature and conversion. The correct preexponential term,  $A$ , is calculated for all cases described by equation,  $d(\alpha)/dt = f(\alpha)A \exp(-E/RT)$ , except for the 'autocatalytic' case in which  $f(\alpha) = 0$ . Calculation of parameters for equations involving other functions for  $f(\alpha)$  will be described in a subsequent paper.

In the analysis of the kinetics of heterogeneous condensed phase reactions, it is found convenient to define an extent of reaction or fractional conversion term,  $f(\alpha)$ , where

$$\alpha = (x_i - x) / (x_i - x_f) \quad (1)$$

and the fraction remaining is given by

$$(1-\alpha) = (x - x_f) / (x_i - x_f) \quad (2)$$

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where  $x$  is the measured value for the extensive variable (mass, enthalpy, volume, etc.) and  $x_i$  and  $x_f$  are respectively its initial and final values at the beginning and at the end of the reaction of interest. It is often convenient to use this extent of reaction variable when only a part of the experimental data range is being analyzed or several different experiments are being compared. The equations and methods are developed in terms of  $\alpha$  in this paper. However, one may substitute for  $\alpha$ , mutatis mutandis, the values for the measured change in the extensive variable,  $x$ , (i.e., mass, volume, enthalpy, etc.) without any loss of general applicability.

The most general differential equation commonly used to describe the reaction rate is

$$d\alpha / dt = f(\alpha)k(T) \quad (3)$$

where rate of change of alpha is expressed as a product of separable functions for alpha and temperature.

The term,  $f(\alpha)$ , can be fitted occasionally by the equation

$$f(\alpha) = (1-\alpha)^n \quad (4)$$

and in some other cases by more complex expressions. (It is probably impossible to overemphasize the fact that the kinetics of most of the reactions in thermal analysis are not described well by Eq. (4). Analysis for other forms of  $f(\alpha)$  are described in a subsequent paper [1]. Fortunately, the method developed herein tests the assumption in Eq. (4) and calculates the Arrhenius parameters independently of the form of  $f(\alpha)$ .)

A fit of the temperature dependent expression,  $k(T)$ , by the Arrhenius equation,

$$k(T) = A \exp(-E/RT), \quad (5)$$

is almost always attempted. In Eq. (5),  $A$  is the preexponential factor,  $E$  is the energy of activation,  $R$  is the gas constant, and  $T$  is the absolute temperature.

The differential method is fully developed here so as to apply to any set of experiments with differing temperature programs. The constancy of  $E/R$  with  $\alpha$  and temperature is tested. If  $E/R$  is constant, the correct value for  $A$  is determined, and then the applicability of Eq. (4) is tested. Methods to

determine the parameters of several other forms of  $f(\alpha)$  are given in a subsequent paper [1].

A differential method for the analysis of reaction kinetics was first developed by van't Hoff [2]. In his method, if two experiments are carried out at different initial concentrations,  $c_1$  and  $c_2$ , their rates are  $-dc_1/dt = k c_1^n$  and  $-dc_2/dt = k c_2^n$ . If one takes logarithms, then upon rearrangement, it is found that,

$$n = \left( \ln(-dc_1/dt) - \ln(-dc_2/dt) \right) / (\ln c_1 - \ln c_2) \quad (6)$$

from which  $n$ , the order of reaction, is calculated.

This differential method later was extended by Letort [3] to apply to a single isothermal experiment. If Eq. (4) is substituted into Eq. (3) and logarithms taken, one obtains

$$\ln d\alpha/dt = n \ln(1-\alpha) + \ln k(T) \quad (7)$$

Therefore, one may plot the logarithm of the rate,  $\ln d\alpha/dt$ , as a function of the logarithm of the fraction remaining,  $\ln(1-\alpha)$ , and obtain the logarithm of the rate constant,  $\ln k(T)$ , from the intercept at  $\alpha$  equal zero. If the plot is linear, then its slope is equal to the reaction order,  $n$ . Letort [3] pointed out the superiority of this technique over those which apply integrated forms of the  $f(\alpha)$  equations. The order is determined directly (not assumed as in integral methods) so that fractional orders may be obtained. Also any change in the order during the reaction is observed directly from changes in the slope from the plot of Eq. (7). Letort also pointed out that the "initial rate",  $v_0$ , is obtained from this method so that if initial rates are obtained from several experiments performed at differing initial concentrations,  $c_0$ , then one may write

$$\ln v_0 = n_0 \ln c_0 + \text{constants} \quad (8)$$

and  $n_0$ , the "order as a function of initial data", may be compared with  $n$ , the "order as a function of time". The two orders may differ in cases for which the reaction kinetics is complex, that is, cases where intermediates and products affect the form of the rate equation and value of  $n$ . Thus this distinction between the two orders can be useful in establishing reaction mechanism. ("Concentrations" are seldom meaningful or calculable in thermal analysis experiments. However, this distinction between the two reac-

tion orders may have some application in thermal analysis as a test for complexities in the kinetics. For example, the "order as a function of initial data" may be calculated from a series of thermogravimetric experiments which are performed at differing initial specimen weights and this value compared with the "order as a function of time" to test whether the reaction is irreversible or reversible, i.e., whether the reaction kinetics are affected by the products.)

The application of the differential technique for determining kinetics parameters to the nonisothermal experiments of thermal analysis was developed in the landmark paper in 1965 by Friedman [4]. In his method, Eqs (3) and (5) may be combined to obtain

$$d\alpha / dt = f(\alpha)A \exp(-E/RT) \quad (9)$$

One obtains, upon taking logarithms, for a value of  $\alpha$ ,  $\alpha_i$ ,

$$\ln (d\alpha / dt)_i = \ln f(\alpha_i)A - E/RT_i, \quad (10)$$

where the subscript,  $i$ , refers to the value of the variable at  $\alpha_i$  degree of conversion.

Thus Friedman demonstrated that, from Eq. (10), a plot of  $\ln d\alpha / dt$  vs.  $1/T$  values at the same degree of conversion from a series of experiments at differing constant heating rates would result in a straight line with a slope of  $-E/R$  and an intercept of  $\ln Af(\alpha)$  for cases in which the Arrhenius Eq. (5) was followed. This procedure could be repeated at various degrees of conversion and resulting parallel straight lines would prove the constancy of  $E/R$  as the reaction proceeds. This was the first published "isoconversional" method for the determination of  $E/R$  from thermoanalytical data. It was followed closely by papers by Ozawa [5] and Flynn [6] who independently developed a similar 'integral' method in which data (logarithm heating rate,  $1/T$ ) from integral curves were plotted at constant conversion to obtain  $E/R$  without the necessity of first determining  $d\alpha / dt$ .

The first critical discussion of Friedman's method was made by Flynn [7] in 1966, the year following its publication. He pointed out the advantages of the method (over the Ozawa-Flynn method), viz.,

- 1) successive approximations from the Doyle equation for the temperature integral are unnecessary,
- 2) differential methods give instantaneous values for the kinetics parameters and are not subject to cumulative errors, and

3) initial (boundary) conditions which are often poorly defined in thermal analysis and are needed for integral methods are unnecessary for differential methods. The chief disadvantages of Friedman's method (in 1966) were that it was tedious to obtain derivative values from thermal analysis curves and that such derivative curves often exhibited considerable experimental scatter. These disadvantages undoubtedly were the reason for the much wider use and the much wider acceptance of the integral method over the differential isoconversional method in the 1970 and 80's. However, the advent of computer interfacing with integrating and smoothing capabilities has rendered the disadvantages mentioned above irrelevant and several recent papers have emphasized the advantages of the Friedman differential method for calculating  $E/R$  [8-10].

There were two facets of the differential isoconversional method of Friedman which have been generally ignored. First of all, it is not necessary to use differing constant heating rates for the several experiments which are to be compared at various degrees of conversion, that is, any combination of differing temperature programs can be used. Secondly, in this method, the preexponential factor,  $A$ , can be separated from  $f(\alpha)$  and independently determined under rather general conditions. The general differential isoconversional method which is developed in the following section will include these two greater capabilities.

#### *A general differential isoconversional method*

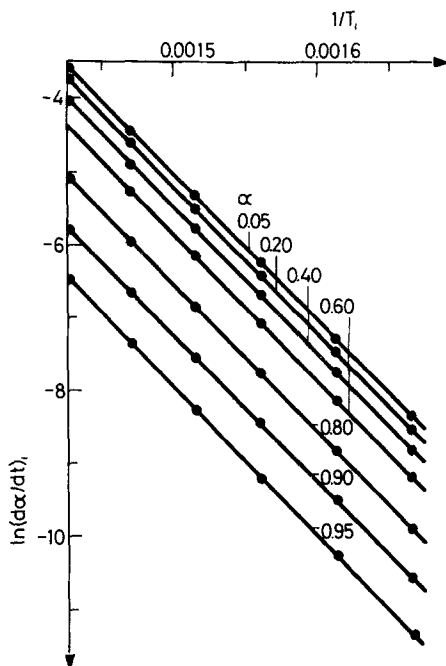
##### a) Calculation of the energy of activation:

The basic equation for the differential isothermal method is Eq. (10). Two or more experiments are performed at differing temperature programs. For each experiment, values for temperature and  $d\alpha/dt$  are obtained for various values of  $\alpha_i$  (e.g.  $\alpha_i = 0.05, 0.10, 0.20, \dots, 0.90, 0.95$ ) covering the experimental range. Values for  $E/R$  and  $\ln Af(\alpha_i)$  at each value of  $\alpha_i$  are obtained from the slope and intercept of Eq. (10), or from the intercept and slope of Eq. (11), which is obtained from Eq. (10) from multiplication by temperature.

$$T_i \ln (d\alpha / dt)_i = T_i \ln Af(\alpha_i) - E/R \quad (11)$$

For an example, we take data for a first order reaction,  $f(\alpha) = (1-\alpha)$ , performed isothermally at temperatures of 600, 620, 640, 680, and 700 K. Figure 1 is a plot of  $\ln (d\alpha / dt)_i$  vs.  $1/T_i$  for values of  $\alpha_i = 0.05, 0.20, 0.40, 0.60, 0.80, 0.90$  and  $0.95$ . The parallel slopes of lines for each value of  $\alpha_i$  give,

from Eq. (10), values for  $E/R$  of 20.000 K. The intercepts (at  $1/T_i = \text{infinity}$  or  $T_i = 0$ ) give values for  $\ln Af(\alpha)$  for each of the above  $\alpha$ 's. (These values will be used later to determine  $A$  and the form of  $f(\alpha)$ .)



**Fig. 1**  $\ln(d\alpha/dt)$  vs.  $1/T$  for a first order reaction,  $E/R=20.000$  K,  $\ln A=25$ , at isothermal temperatures of 600, 620, 640, 660, 680 and 700 K,  $\alpha=0.05, 0.20, 0.40, 0.60, 0.80, 0.90$  and  $0.95$

Figure 2 is a plot of  $T_i(d\alpha/dt)_i$  vs.  $T_i$  for the same data and conditions as in Fig. 1. The slopes of the constant  $\alpha$  lines are not parallel and, from Eq. (11), we see that these isoconversional lines intersect at  $T_i = 0$  to give a value for  $E/R$  of 20.000 K. In Fig. 2, the slopes give values for  $\ln Af(\alpha)_i$ , and these values will be used subsequently to determine  $A$  and  $f(\alpha)$ .

The two ways of plotting ( $\alpha_i, d\alpha/dt_i, T_i$ ) data, illustrated in Figs 1 and 2 are equivalent. If one uses the same sort of regression analysis on the same sets of data, then, of course, the two plots will yield identical values for the parameters,  $E/R$  and the various  $\ln Af(\alpha)_i$ .

The first important feature of isoconversional methods such as this one is that the applicability of the basic equation, Eq. (9) is tested. If the isoconversional lines in Figs 1 and 2 are curved, then the kinetics are too complex to be described by Eq. (9) and meaningful values for the parameters  $E/R$  and  $\ln A$  can not be obtained. (However, if the data are extensive enough, there may be regions in  $\alpha$ -temperature space in which sets of straight isoconversional lines can be found and values of  $E/R$  and  $A$  calculated for that portion of the reaction.)

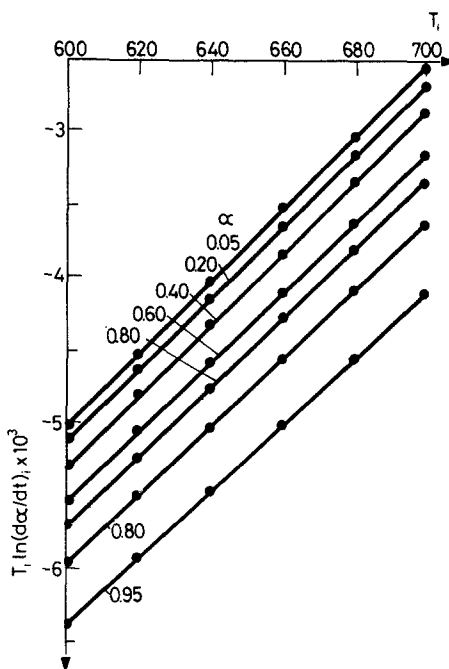


Fig. 2  $T_i \ln(d\alpha/dt)_i$  vs.  $T_i$  for a first order reaction,  $E/R=20.000$  K,  $\ln A=25$ , at isothermal temperatures of 600, 620, 640, 660, 680 and 700 K,  $\alpha=0.05, .0.20, 0.40, 0.60, 0.80, 0.90$  and 0.95

The examples given above are for a series of isothermal experiments at differing temperatures. It is more common to perform thermal analysis experiments at constant heating rate. An isoconversional plot for a series of experiments at differing constant heating rates will differ from Figs 1 and 2 in that, as  $\alpha$  increases, the  $T$  and  $1/T$  points will be skewed to higher temperatures especially at faster heating rates. An example of such a plot is

shown in Fig. 3 for an autocatalytic reaction [7]. The rates for autocatalytic reactions are the greatest during a middle portion of the reaction, in this case, for  $\alpha = 0.5$  to  $0.7$ . However, one does not obtain a neat progression of decreasing parallel isoconversional lines even for kinetics in which the isothermal rate decreases monotonically with time since the rate is accelerated through a maximum value in all constant heating rate experiments.

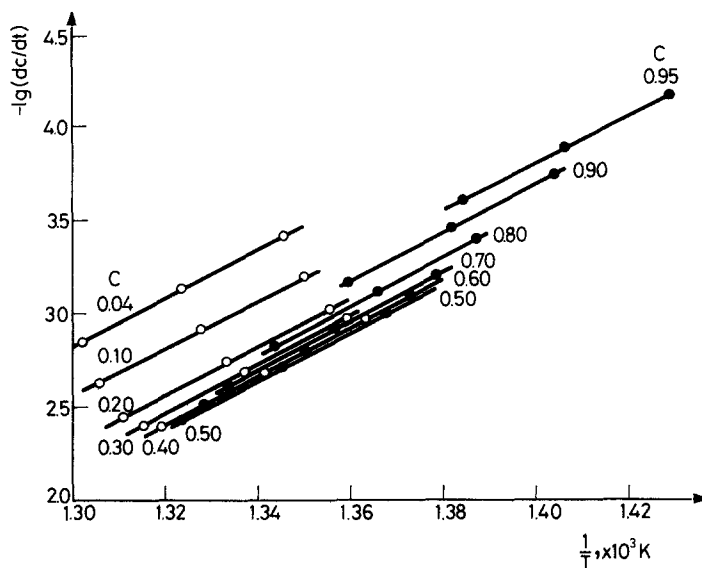


Fig. 3  $\ln(d\alpha/dt)_i$  vs.  $1/T_i$  for an autocatalytic reaction,  $E/R = 30.196$  K,  $\ln A = 34.54$ , at heating rates of 0.05, 0.10 and 0.20 deg/sec.  $C = 1 - \alpha = 0.04, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90$  and  $0.95$ . (See Ref. 7, p. 511, Fig. 16)

As was pointed out earlier, data from any set of experiments performed under differing temperature programs (isothermal, constant heating rate, stepwise, or whatever) may be plotted in the above manner so that  $E/R$  and  $\ln Ad(\alpha)/dt$  values can be obtained over the temperature - conversion range covered by the experimental data. The advantage of using data from sets of isothermal experiments performed at various temperatures or constant heating rate experiments performed at various heating rates is that a systematic distribution of data points over the experimental ranges is obtained in such plots as shown in Figs 1, 2 and 3.



## b) Point of intersection (concurrency):

However, one should not use only a set of isothermal experiments or a set of constant heating rate experiments. When sets of experiments with mixed temperature programs are employed in obtaining thermal analytical data, points of degeneracy will occur which have identical values for temperature and conversion,  $(1-\alpha)$ . These points of intersection or concurrency can be used to test the assumption of equation (9) that the rate of reaction depends only upon the analytical forms of  $k(T)$  and  $F(\alpha)$  and, therefore, is path independent [11, 12]. If two or more experiments which differ only in their temperature programs come to the same temperature at the same degree of conversion, then their rates of conversion at that point should be equal if the kinetics follow Eq. (9). If the values for the rate at this point are significantly different from one another, then the true rate equation must be more complex than Eq. (9) and the significance of the parameters  $(E/R$  and  $\ln A)$  obtained from Eq. (9) are suspect.

Therefore it should be standard practice to include one isothermal experiment with a set of constant heating rate experiments or one constant heating rate experiment with a set of isothermal experiments. In the former case, a properly chosen isothermal curve will intersect each of the constant heating rate curves in conversion-temperature space and the independence of the value for the rate from its thermal history tested at each of these intersections. In the latter case, the constant heating rate curve will intersect each of the isothermal curves producing similar points at which to test the thermal path independence of the rate.

c) Calculation of the preexponential factor,  $A$ :

Once the constancy of the parameter,  $E/R$ , has been established, the values of  $\ln Af(\alpha_i)$  from the differential isoconversional method can be extrapolated to zero  $\alpha$  to obtain the preexponential factor,  $A$ , for many cases, viz., whenever the limit of  $f(\alpha)$  as  $\alpha$  approaches zero is unity as in Eq. (12).

$$\lim_{\alpha \rightarrow 0} f(\alpha) = f(\alpha = 0) = 1 \quad (12)$$

This condition is met for many of the equations used for  $f(\alpha)$  in thermal analysis kinetics including Eq. (4) for a  $n$ th order reaction. Moreover, the definition of  $\ln A$  is empirical in thermal analysis kinetics, so if the limit of  $f(\alpha)$  in Eq. (12) is equal to any constant,  $\ln B$ , then  $\ln A$  may be redefined to incorporate this constant. This is permissible since  $A$  is not a simple "fre-

quency factor" in thermal analysis but may include other geometrical and physical factors which affect the rate. The distinction between the  $\ln A$  value from the extrapolation in Fig. 4 (below) and some "true" value for  $\ln A$  would matter only in a detailed modeling of the reaction mechanism and not in the analytical curve fitting described in this paper.

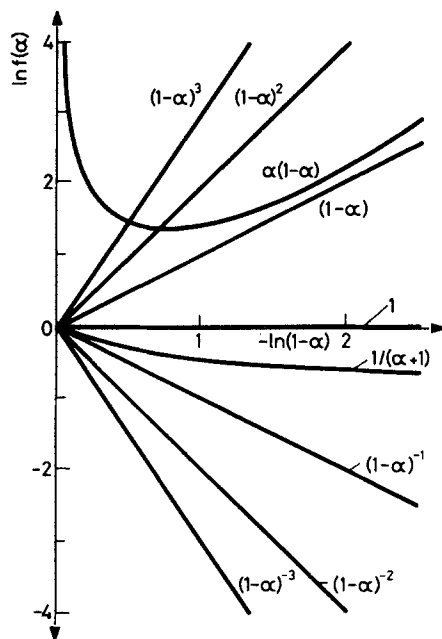


Fig. 4  $\ln f(\alpha)$  vs.  $\ln(1-\alpha)$  for  $f(\alpha) = (1-\alpha)^3, (1-\alpha)^2, (1-\alpha), 1, (1-\alpha)^{-1}, (1-\alpha)^{-2}, (1-\alpha)^{-3}, 1/(1+\alpha)$  and  $\alpha(1-\alpha)$

Thus, if one obtains values of  $\ln Af(\alpha)_i$  from the intercepts of Fig. 1 or from the slopes of Fig. 2 for various values of  $\alpha_i$ , then a plot of  $\ln Af(\alpha)_i$  as a function of  $\ln(1-\alpha)_i$ , as shown in Fig. 4, will have an extrapolated intercept at  $\alpha = 0$  equal to  $\ln A$ .

All of the "nth order" curves and one other thrown in as an example,  $f(\alpha) = 1/(1-\alpha)$ , in Fig. 4 are "well behaved", that is, they satisfy the criterion of Eq. (12). The chief type of functions for  $f(\alpha)$  which do not follow the condition defined by Eq. (12) are those used to describe the kinetics of some autocatalytic reactions. These reaction are often fitted to an equation such as

$$f(\alpha) = (1-\alpha)^n(\alpha)^m \quad (13)$$

The plot of such an autocatalytic function, for the equation  $f(\alpha) = (1-\alpha)(\alpha)$ , is shown by the curving line in Fig. 4. Extrapolation to  $\alpha$  equal zero can not be performed for this case since the logarithm of zero is minus infinity. It is, of course, obvious that Eq. (13) can not possibly describe the kinetics at  $\alpha$  equal zero and it has been suggested that a better expression for this type of kinetics behavior is

$$f(\alpha) = (1-\alpha)^n(\alpha + \varepsilon)^m \quad (14)$$

where  $\varepsilon \ll 1$ . This form may be more satisfying mathematically but does not help in the extrapolation since this function changes very rapidly until  $\alpha$  approaches  $\varepsilon$  in magnitude at which point  $\alpha$  is at too small a value to permit measurement of the rate.

(There are many autocatalytic reactions for which the initial rate is large enough to be measured so that  $\ln A$  can be determined by the above method. Weight loss reactions for the random degradation of polymers are autocatalytic. However, the magnitude of the initial rate is often about a third of the maximum rate as the former depends upon the maximum size of fragments which can distill from the reacting system. See, for example, cases B and C in Ref. [7].)

In general, the above extrapolation can be performed for most of the forms of  $f(\alpha)$  used in thermal analysis kinetics including those for  $n$ th order reactions shown in Fig. 4. The chief advantage of this method for determining  $\ln A$  over others is it that the algebraic form of  $f(\alpha)$  need not be known. This has been a flaw of many previous methods for determining  $\ln A$  which posit first order kinetics during its calculation.

#### d) Calculation of order of reaction, $n$ :

In Fig. 4,  $\ln f(\alpha)_i$  is plotted vs.  $\ln(1-\alpha)_i$  for reaction orders,  $n = 3, 2, 1, 0, -1, -2$ , and  $-3$ . From the logarithm of Eq. (4),

$$\ln f(\alpha) = n \ln(1-\alpha), \quad (12)$$

it is obvious that, as a bonus from the above method for determining  $\ln A$ , the slopes of these curves are equal to the reaction order,  $n$ . Therefore, we have a method for determining the reaction order in a nonsubjective manner, that is, without "testing various integer orders for fit" as is done when

integrated equations are used. Thus noninteger orders can be determined and any deviation from the simple  $n$ th order kinetics of Eqs (4) and (12) will be exposed immediately by the nonlinearity of the slope.

The extrapolation of  $\ln Af(\alpha)$  vs. (other functions of  $\alpha$ ) curves to  $\alpha = 0$  in order to determine the parameters for other more complex mathematical expressions for the reaction kinetics will be discussed in a subsequent publication [1].

## Conclusions

The general differential isoconversional method for the determination of parameters for thermal analysis kinetics contains many safeguards against its misuse; a) the linearity of the isoconversional curves (as in Figs. 1, 2 and 3) test the constancy of  $E/R$  and  $\ln A$ , b) the linearity of the  $\ln Af(\alpha)$  vs.  $\ln(1-\alpha)$  curves (as in Fig. 4) test the applicability of the  $n$ th order equation, and c) points of intersection test thermal history independence of the rate of reaction.

## References

- 1 J. H. Flynn, to be published.
- 2 J. H. van't Hoff, *Etudes de dynamique chimique*, F. Müller and Company, Amsterdam 1884, p. 87.
- 3 M. Letort, *J. Chim. Phys.*, 34 (1937) 206.
- 4 H. Friedman, *J. Polym. Sci.*, 50 (1965) 183.
- 5 T. Ozawa, *Bull. Chem. Soc. Japan*, 38 (1965) 1881.
- 6 J. H. Flynn and L. A. Wall, *Polym. Lett.*, 4 (1966) 191.
- 7 J. H. Flynn and L. A. Wall, *J. Res. Nat. Bur. Standards A Phys. Chem.*, 70A (1966) 487.
- 8 J. H. Flynn, *J. Thermal Anal.*, 27 (1983) 95.
- 9 T. Ozawa, *J. Thermal Anal.*, 31 (1986) 547; *Thermochim. Acta*, 100 (1986) 109.
- 10 J. Elder, *J. Thermal Anal.*, 36 (1990) 1077.
- 11 J. H. Flynn, *Analysis of Thermogravimetric Kinetics - Overcoming Complications of Thermal History*, Chapter 3 in *Thermal Analysis in Polymer Characterization*, ed. E. A. Turi, Hayden, London, 1981, pp. 43-58.
- 12 J. H. Flynn, *J. Thermal Anal.*, 34 (1988) 367.

**Zusammenfassung** — Es wurde ein allgemeines Differentialverfahren entwickelt und beschrieben, das die Arrheniusschen Parameter, namentlich die Aktivierungsenergie und den präexponentiellen Faktor, als Funktion des Umsetzungsgrades aus Angaben über zwei oder mehrere Experimente mit verschiedenen Temperaturprogrammen beschreibt. (Diese Experimente können mit beliebigen Kombinationen aus isothermen Temperaturprogrammen, solchen mit konstanter Aufheizgeschwindigkeit oder anderen Temperaturprogrammen durchgeführt werden.) Das Verfahren überprüft, ob die Kinetik durch die Gleichung  $f(\alpha) = (1-\alpha)^n$  beschrieben werden kann und berechnet die richtige Reaktionsordnung  $n$ , wenn eine solche Gleichung anwendbar ist. Die richtige Aktivierungsenergie  $E$  wird als

Funktion von Temperatur und Umsatz bestimmt. Der richtige präexponentielle Ausdruck wird für alle beschriebenen Fälle mittels der Gleichung  $d(\alpha)/dt = f(\alpha) A \exp(-E/RT)$  berechnet. Eine Ausnahme bildet der Fall "Autokatalyse", wobei  $f(\alpha = 0) = 0$  gilt. Die Berechnung der Parameter für Gleichungen mit anderen Funktionen für  $f(\alpha)$  wird in einem späteren Manuskript beschrieben.