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DETERMINATION OF THE KINETIC PARAMETERS FROM NON-ISOTHERMAL MEASUREMENTS WITH A GENERAL TEMPERATURE PROGRAM

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ABSTRACT

This paper deals with a new method for the evaluation of the kinetic parameters from thermogravimetric measurements with a general temperature program. The procedure assumes the use of a computer or calculator. In principle, it is an integral method with two variants. The kinetic parameters can be determined from a single and/or from two general temperature programs. This method is free of the shortcomings that the existing method has, i.e. the self-heating and/or self-cooling, resulting in errors in measurements and the limitation of the weight of sample. The two variants of the submitted method have been tested by evaluation of the experimental data of the thermal decomposition of $CaCO_3$.

INTRODUCTION

When considering non-isothermal measurements, the integral and differential methods are widely used for the determination of the kinetic parameters. A review of the methods and modes of evaluation of these parameters is given in a monograph[1] and in ref. 2 where further procedures are also given. In any case it is necessary to keep to the defined temperature program that is expressed as

$$\frac{dT}{dt} = \phi \times T^m \tag{1}$$

where dT/dt is the heating rate, and ϕ and m are coefficients. The simplest and the most frequent case is that for $m = 0$.

This paper presents a practically verified method for the determination of the kinetic parameters of heterogeneous reactions for a general temperature program with the help of a computer. This method is significant especially in the case of the occurrence of self-heating and/or self-cooling in samples and thus the parameter ϕ in eqn. (1) is not constant, but is a function of T.

Deviations from the linear temperature program, shown by the differential method, can be corrected by the procedure described in ref. 3.

THEORY

Let us consider a reaction that can be described by the terms

$$\int_0^{t_0} k\,[T(t)]\mathrm{d}t = \int_0^{\alpha_0} \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} \tag{2}$$

where $k[T(t)]$ is the rate constant depending on the temperature program, α is the degree of transformation, and $\mathrm{f}(\alpha)$ is a function of the instantaneous phase composition of the system providing that the composition is governed by the degree of transformation.

The final relationships for evaluation of the kinetic parameters by a computer will be derived when assuming a general program for function $T(t)$.

For the sake of simplicity, let us analytically express function $k(T)$ by means of the Arrhenius equation

$$k\,[T(t)] = A \times \mathrm{e}^{-E/RT(t)} \tag{3}$$

and the kinetics of the reaction is given by the function

$$\mathrm{f}(\alpha) = \alpha^m (1-\alpha)^n [-\ln(1-\alpha)]^p \tag{4}$$

where m, n and p are apparent exponents of the reaction.

Moreover, let us consider

$$J[E, T_i(t), t_{ij}] = \int_0^{t_{ij}} k\,[T_i(t)]\cdot \mathrm{d}t \tag{5}$$

By calculating the integral of the right-hand side of eqn. (2) and substituting eqn. (4), when assuming $m = 0$, $p = 0$, then

$$\int_0^{\alpha_{i,j}} \frac{\mathrm{d}\alpha}{(1-\alpha)^n} = \begin{cases} -\ln(1-\alpha_{i,j}) & n = 1 \\ \dfrac{1}{1-n}[1-(1-\alpha_{i,j})^{1-n}] & n \neq 1 \end{cases} \tag{6}$$

Further analysis can be divided into two parts. In the first, we deal with the determination of the kinetic parameters E, n and A following from the results measured for two different temperature programs, while in the second, we determine the parameters from a single temperature program.

(*a*) *Determination of the kinetic parameters from two temperature programs*

In this case let us consider two different temperature programs $T_i(t)$, $i = 1, 2$ and for each program we determine the time $t_{i,j}$ referring to the selected degree of

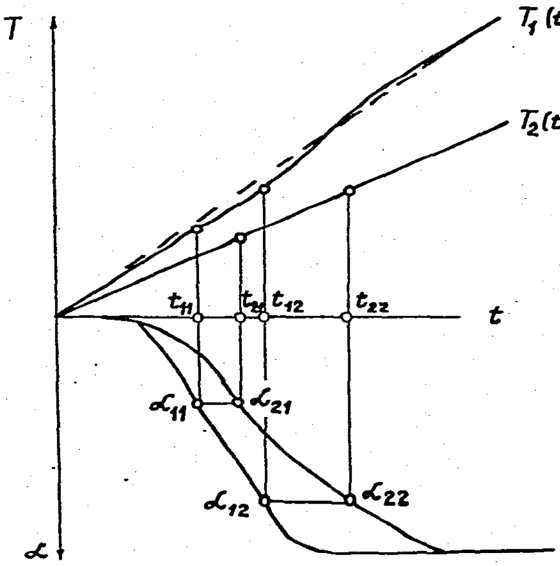

Fig. 1. Designation of the temporal points and the correspondent stages of transformations for the determination of the kinetic parameters from two temperature programs.

transformation $\alpha_{i,j}$. To obtain accurate results, it is necessary to select at least two stages of transformation $\alpha_{i,j}$, the corresponding time intervals being denoted by $t_{i,j}$, $j = 1, 2$ (see Fig. 1). In this respect it is obvious that $\alpha_{11} = \alpha_{21}$, $\alpha_{12} = \alpha_{22}$. It is also obvious from eqns. (2)–(6) that

$$\frac{J[E, T_1(t), t_{ij}]}{J[E, T_2(t), t_{lk}]} = 1 \Rightarrow \begin{array}{l} i,j = 1{,}1\ l,k = 2{,}1\ E = E_1 \\ i,j = 1{,}2\ l,k = 2{,}2\ E = E_2 \end{array} \tag{7}$$

With the help of eqn. (7), it is possible, by means of the given functions $T_i(t)$ (or by given functional values of these functions) to determine the kinetic parameter E as the arithmetic average of the E_i values, unless the E value depends on the rate of linear heating; the difference in E_1 and E_2 values is due to experimental error.

By substitution of eqn. (2) for eqns. (5) and (6) and for the calculated value of E it is possible to calculate the apparent exponent of reaction, n.

$$\frac{1 - (1 - \alpha_{ij})^{1-n}}{1 - (1 - \alpha_{lk})^{1-n}} = \frac{J[E, T_p(t), t_{ij}]}{J[E, T_r(t), t_{lk}]} \tag{8}$$

$i,_i = 1{,}1 \quad l,k = 1{,}2 \quad p = 1,\ r = 1 \Rightarrow n = n_1$
$i,_i = 2{,}1 \quad l,k = 2{,}2 \quad p = 2,\ r = 2 \Rightarrow n = n_2$
$i,_i = 2{,}1 \quad l,k = 1{,}2 \quad p = 2,\ r = 1 \Rightarrow n = n_3$
$i,j = 1{,}1 \quad l,k = 2{,}2 \quad p = 1,\ r = 2 \Rightarrow n = n_4$

The value of n can be determined as the arithmetic average of n_i values for $i = 1$ to 4 unless that parameter depends on the heating rate.

The frequency factor A can be calculated by a combination of eqns. (3), (5) and (6) and of E and n values with eqn. (2)

$$A_{ij} = \frac{1}{1-n}\left[1 - (1 - \alpha_{ij})^{1-n}\right] J^{-1}\left[E, T_r(t), t_{ij}\right] \tag{9}$$

$i,j = 1,1 \quad r = 1 \Rightarrow A = A_{11} \quad i,j = 2,1 \quad r = 2 \Rightarrow A = A_{21}$
$i,j = 1,2 \quad r = 1 \Rightarrow A = A_{12} \quad i,j = 2,2 \quad r = 2 \Rightarrow A = A_{22}$

and by averaging of A_{ij} values. For the calculation of the kinetic parameters n and A by means of eqns. (8) and (9), $\alpha_{11} = \alpha_{21}$, $\alpha_{12} = \alpha_{22}$ need not be valid.

The values of E and n can be reasonably calculated from eqns. (7) and (8) by means of a computer by taking into account the fact that the left-hand side of eqn. (7) is a function of f(E), and the left-hand side of eqn. (8) is a function of f(n) and "the intersection point of these functions with the straight lines parallel with the x-axis" is investigated. For calculation, the input data of a program such as $T_i(t)$, α_{ij}, t_{ij} $i,_i = 1,2$, $E_{\max}$, $E_{\min}$, $n_{\max}$, $n_{\min}$ are used and the calculated values of E_i, E, n_i, n, A_{ij}, A and/or further functional values of f(E) and f(n) are printed. The interval for the calculation of the functional values of f(E) and f(n) functions is confined by $E_{\max}$, $E_{\min}$, $n_{\max}$ and $n_{\min}$ values. The course of $T_i(t)$ may be given in the form of tables and/or graphically if the computer is equipped with a reader (digipost), e.g. immediately from a record of a derivatograph.

(*b*) *Determination of the kinetic parameters from a single general temperature program*

To calculate the kinetic parameters E, n and A of a single temperature program $T(t)$, we apply three stages of transformation α_i corresponding to the time intervals t_i for $i = 1$, 2 and 3 (see Fig. 2). From eqns. (3)–(6) it is obvious that

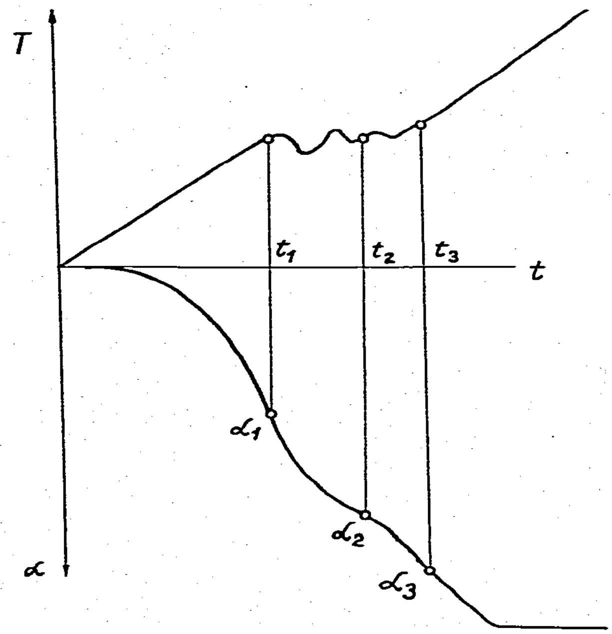

Fig. 2. Designation of the temporal points and the stages of transformations foı the determination of the kinetic parameters from a single general temperature program.

$$\left.\begin{aligned}&\frac{1-(1-\alpha_1)^{1-n}}{1-(1-\alpha_2)^{1-n}}=\frac{J[E,\,T(t),\,t_1]}{J[E,\,T(t),\,t_2]} &&(10\text{a})\\[2ex] &\frac{1-(1-\alpha_1)^{1-n}}{1-(1-\alpha_3)^{1-n}}=\frac{J[E,\,T(t),\,t_1]}{J[E,\,T(t),\,t_3]} &&(10\text{b})\end{aligned}\right\}\Rightarrow\begin{aligned}E&=E_{\mathrm{d}}\\ n&=n_{\mathrm{d}}\end{aligned}$$

$$A_i=\frac{1}{1-n}\left[1-(1-\alpha_i)^{1-n}\right]\cdot J^{-1}\,[E,\,T(t),\,t_i] \tag{11}$$

$$\bar{A}=\sum_{1}^{3}A_i/3 \qquad\qquad i=1,2,3$$

Calculation of the kinetic parameters E_{d}, n_{d} by means of the system of eqn. (10) is again simple. The computer can calculate the left-hand and right-hand sides of eqn. (10), i.e. the functional values of f(n) and f(E) in the interval $n_{\max}$, $n_{\min}$, $E_{\max}$, $E_{\min}$ for given values of n and E. Then, it is possible to express the function $n = F_i(E)$ for $i = 1,2$ corresponding to eqns. (10a) and (10b). The coordinates of the point of intersection of the two functions give the examined values of E_{d} and n_{d} of the kinetic parameters.

In principle, the procedure can be also used for functions other than those given in eqns. (3) and (4). If the number of investigated kinetic parameters is greater (in practice two parameters of function f(α) come into consideration), they can be determined by two different temperature programs in a similar manner to the above-mentioned without any increase of experimental data. For a single temperature program, the calculation is more difficult because of the need for calculation of four stages of transformation and calculation of a system of three equations with three unknown values.

TESTING THE METHOD

The method has been tested by measurement of the thermal decomposition of precipitated $CaCO_3$ (Sojuzchimexport) with the help of MOM-derivatograph (Hungary).

A sample weighing about 0.2 g was put on a multiplate sample holder recommended in ref. 4. The measurements were performed in air with a heating rate of 5 and 10 K min^{-1}. For modelling the general temperature program a Zepafot regulating unit was connected in the control circuit and the temperature was kept constant at 1010 ± 6 K for 10 min before the heating process was continued linearly with an increment identical to that applied up to 1010 K.

The process given in (a) for the two temperature programs ($\phi = 5$ and/or 10 K min^{-1}, $m = 0$, eqn. (1)) was used to determine the values of E and n. First,

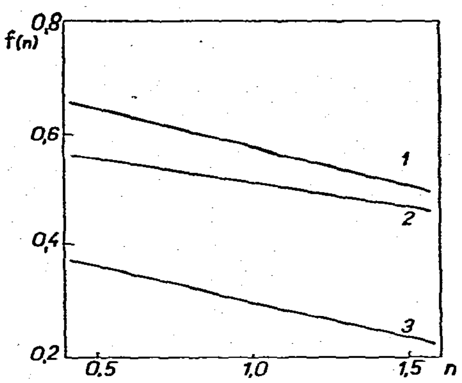

Fig. 3. Graph of function f(n) defined by eqn. (12) where curve 1 is calculated for $\alpha_i = 0.5$; $\alpha_j = 0.7$, 2 – $\alpha_i = 0.3$; $\alpha_j = 0.5$, 3 – $\alpha_i = 0.3$; $\alpha_j = 0.7$.

the calculation was done for the assumed linear temperature program and then the values were corrected for the self-cooling effect, i.e. ϕ = constant. The temperature deviations were determined by calibration of the DTA curve. The actual courses of $T_i = T_i(t)$ were used for calculation by a computer and shall be referred to as the quasi-linear courses in the following.

In a further procedure, the same stages of transformation for the two temperature programs were considered, i.e. $\alpha_{11} = \alpha_{21} = \alpha_1$, $\alpha_{12} = \alpha_{22} = \alpha_2$, and eqn. (8) was reduced to a single equation, and moreover, a further stage of transformation, α_3, was determined. t_i time intervals corresponding to the transformation stages $\alpha_1 = 0.3$; $\alpha_2 = 0.5$; $\alpha_3 = 0.7$ were considered.

The graphs of functions

$$\mathrm{f}(n) = \frac{1 - (1 - \alpha_i)^{1-n}}{1 - (1 - \alpha_j)^{1-n}} \tag{12}$$

are shown in Fig. 3, where curve 1 is calculated for $\alpha_i = 0.5$; $\alpha_j = 0.7$; 2 – $\alpha_i = 0.3$; $\alpha_j = 0.5$; 3 – $\alpha_i = 0.3$; $\alpha_j = 0.7$. The real courses of $T_i(t)$ temperatures are given in Table 1.

The values of E and n calculated according to eqns. (7) and (8) for linear and quasi-linear courses are listed in Table 2.

Although the maximum deviations from the linear temperature program, due to the self-cooling phenomenon, were 4 and 8 K, (i.e. 0.4 and 0.8 %), the mean values calculated from the linear course ($n = 0.54$; $E = 53$ kcal mole^{-1}) and the quasi-linear course ($n = 0.66$; $E = 56.7$ kcal mole^{-1}) were increased by 22 % for the apparent order of reaction and by 7 % for the activation energy.

Let us now consider the calculation of the kinetic parameters from a single temperature program for $\alpha_i = 0.3$, 0.5, and 0.7 by the procedure described in (b). The weight and the sample were identical. The experiments were carried out for a linear temperature program with $\phi = 5$ K min^{-1}, see Table 1 ($T_1(t)$) and for a general temperature program, which in this case was linear with the isotherm illustrated schematically in Fig. 2 and given in Table 3.

TABLE 1

THE REAL TEMPERATURE PROGRAM OF EXPERIMENT (a)

t (sec)	$T_1(t)$ (K)	t (sec)	$T_2(t)$ (K)	t (sec)	$T_2(t)$ (K)
0	921	0	923	675	1043
810	983	150	949	750	1057
1215	1014	300	974	795	1062
1500	1029	450	1001	900	1084
1710	1049	600	1029		

TABLE 2

THE VALUES OF E AND n CALCULATED ACCORDING TO EQNS. (7) AND (8)

$\alpha_i;\alpha_j$		*Linear course*		*Quasi-linear course*	
		n	E(kcal mole^{-1})	n	E(kcal mole^{-1})
0.3	0.5	0.57	53.5	0.73	58
0.5	0.7	0.56	53.5	0.60	56
0.3	0.7	0.50	52	0.66	56

TABLE 3

THE REAL TEMPERATURE COURSE OF EXPERIMENT (b)

t (sec)	$T(t)$ (K)	t (sec)	$T(t)$ (K)	t (sec)	$T(t)$ (K)
0	923	1260	1008	1455	1015
1080	1009	1290	1004	1470	1016
1110	1011	1320	1003	1500	1016
1140	1012	1350	1005	1530	1014
1170	1013	1380	1007	1560	1010
1200	1014	1410	1010	1590	1009
1230	1012	1440	1012	1620	1010

In the first case of assumed linear temperature program, the calculated values were $m = 0.3$ and $E = 47.5$ kcal mole^{-1}. For the actual quasi-linear program, we calculated $n = 0.3$ and $E = 50.5$ kcal mole^{-1}, i.e. the activation energy rose again, namely by 6%.

In the second case of the general temperature program, (see Table 3) the values are $n = 0.44$ and $E = 50.5$ kcal mole^{-1}.

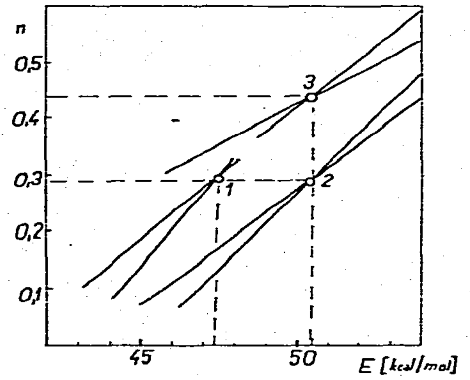

Fig. 4. Graphs of function $n = F_i(E)$ calculated from eqn. (10). 1, linear program; 2, quasi-linear program; 3, general temperature program.

The solution of eqns. (10a) and (10b), i.e. function $n = F_i(E)$ is illustrated in Fig. 4, where 1 refers to the linear program, 2 to the quasi-linear program and 3 to the general temperature program. The numerical calculations were performed by an ODRA 1204 computer and the calculation time of a set was about 10 min. To obtain reasonable data for the computer, the temperature should be given with an accuracy higher than K and $R = 1.9867$ kcal mole^{-1} deg^{-1}.

Let us compare our experimental results with the literature data. The kinetics of the thermal decomposition of $CaCO_3$ have been investigated by numerous authors. A review of these results is given in ref. 5, where the effect of the weight of sample and the heating rate on the value of the kinetic parameter have also been investigated. Our results can be compared with those presented in ref. 6, where analogous experimental conditions have been applied, i.e. $\phi = 3$ K min^{-1}, sample weight of 0.1 g $CaCO_3$, air. The authors[6] have determined the following values: $n = 0.46$; $E = 51.7$ kcal mole^{-1} at α_1 to $\alpha_2 = 0.15$–0.78.

The experimental results obtained by the methods in question underline reasonable conformity with the results achieved by other methods. The proposed method eliminates several shortcomings of other methods so far applied. There is no need to keep to a prescribed temperature program. Furthermore, it is possible to measure the actual parameters with larger sample weights; the apparent values to be influenced by the difference between the actual and the assumed temperature program need not be measured due to thermal effect of reaction.

Moreover, it is opposite to say that the E value determined from two different temperature programs is independent of the prescribed form of function f(α), i.e. independent of the selected mechanism of the heterogeneous reaction, see eqn. (7). Moreover, the dependence of $k[E, T(t)]$ given by eqn. (3) should not be assumed, however, it can have a general program.

In fact, in numerous cases the kinetic parameters determined experimentally vary with the heating rate; this is evidence that the selected form of function f(α) does not describe the reaction and further processes associated with the existing experimental arrangement with reasonable accuracy.

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