Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

KINETIC DATA COMPUTATION FROM NON-ISOTHERMAL THERMOGRAVIMETRIC CURVES OF NON-UNIFORM HEATING RATE

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(Received October 20th, 1970)

ABSTRACT

Correlations which permit computation of the activation energy E, the "reaction order" n, and the frequency factor from non-isothermal thermogravimetric curves have been derived for reactions obeying the relation

$$\frac{d\alpha}{d\tau} = k_x \cdot (1-\alpha)^n \exp\left(-\frac{E}{RT}\right)$$

and for a non-linear temperature rise during the heating of a sample. For the experimental data processing, a corresponding algorithm has been prepared in the GIER-ALGOL language. In order to test the computation program, the published theoretical data for the dehydration of gypsum have been processed. In addition, our thermograms for the dehydration of calcium oxalate monohydrate have been evaluated. All results have been compared with the published values.

INTRODUCTION

When studying the kinetics of the decomposition of solids, a thermogravimetric method is frequently employed in which the temperature is either kept constant or linearly increased. Most decomposition rates of solids may, under certain conditions, be formally described by the differential equation

$$\frac{d\alpha}{d\tau} = k_x \cdot (1-\alpha)^n \exp\left(-\frac{E}{RT}\right) \tag{1}$$

where α is the degree of conversion, τ is the time, T is the absolute temperature, R is the gas constant, and E, n, k are the constants of Eqn. (1), characterizing formally the kinetics of the process studied.

The calculation of the three constants from the measured experimental values of the variables involved in the above equation is relatively time consuming and laborious and, therefore, computer programs have been written for some simplified cases[1,2].

A computer program by Schempf *et al.*[2] permits calculation of the activation energy E and the frequency factor, provided that the order of the reaction studied is equal to unity. Šesták in his papers[3,4a] has required that the experimental device be designed so as to fulfill that the conditions of strictly linear temperature rise in the sample studied. In order to satisfy this requirement, the author[4b] has developed a special experimental technique.

In a large majority of cases, the above-mentioned requirement of a linear rise of the temperature in the sample cannot be practically fulfilled with reactions which can be studied successfully by means of the thermobalance because, owing to the reaction heat, the heating rate of the sample increases and decreases in comparison with the temperature program for the furnace heating or the heating of the standard sample (which is inserted in the furnace together with the sample in a place which has the same temperature conditions as affect the sample). This phenomenon, which manifests itself as a change in the heating rate of a sample taking part in some reaction and is accompanied by heat evolution or absorption, is, as known, the fundamental principle of the differential thermal analysis (DTA). It can, according to the experimental conditions, be either suppressed or, on the contrary, strengthened. When the heat effect is suppressed, the so-called integral method can be employed for the evaluation of the kinetic measurements. However, after such an effect has once occurred during an experimental run, any use of the integral methods in the calculation of the kinetic parameters becomes unusually difficult, because the practical solution of Eqn. (1) by these methods requires the course of the sample temperature to be expressed as a linear function of time. In fact, this requirement cannot be fulfilled with usual thermobalances because of the above-mentioned reasons and this is true especially when the DTA is performed simultaneously with the thermogravimetric measurement. Therefore, we have decided to base the evaluation of our experimental curves for the calculation of the kinetic constants in Eqn. (1) on the employment of the differential method. The relevant mathematical procedure does not require that the special and difficult-to-achieve experimental conditions be strictly maintained, and thus it does not become the controlling factor of the measurement method as has been the case in some cited papers, but, on the contrary, it helps in describing and analyzing the processes in the same manner in which they really proceed.

The differential methods of calculation require data on the instantaneous velocity of the process studied, *i.e.*, the derivative of the dependence of the degree of conversion of the studied substance on time, to be obtained in a convenient way. Unfortunately, it has not yet become customary to produce commercial thermogravimetric devices which, besides recording weight changes, also permit direct recording of their rate. Thus, it is often necessary to employ some frequently laborious numerical or even graphical methods in order to obtain a differential dependence from the integral experimental curves. Some authors who have employed the differential method, *e.g.*, Freeman and Carroll[5], have used in practical calculations only the differences of the changes of the analyzed dependences at given time intervals. This method makes the evaluation of the curves considerably easy, though the accuracy of the results is questionable.

According to the authors of programs[2-4a], it is very convenient to use computers to obtain a derivation curve from discrete values of the degree of conversion, from instantaneous weight changes of a sample, etc. However, we know from our own experience that the accuracy and correctness of the courses of the derivation curves computed in this way depend considerably on the accuracy and carefulness of the reading of individual discrete values from the thermogravimetric curves and on the magnitude of the chosen reading step. This fact has also been reported by Šesták *et al.*[4a]. A small step leads to a large deviation of the computed values and a large step leads to an incorrect course of the derivation curve. A formulation of the courses of the found time dependences of the degree of conversion and the temperature as some functions of time, and a computation of the derivation curves by direct derivation of the found functions or a computation of "corrected" discrete values of the experimental dependences by means of the functions, and a numerical derivation by means of the "corrected" values proved to be most convenient.

This report describes a method which has been used by us for the evaluation of the kinetic constants from thermogravimetric curves in which the differential computation is employed. This method takes also into account the fact that the thermal effects of reactions result in a deviation of the sample temperature from the programmed values of the linear heating.

RELATIONS FOR CALCULATING KINETIC CONSTANTS

As a basis for the derivation of convenient relations for the calculation of the kinetic constants from the experimental data, we regard the differential Eqn. (1). Taking the logarithm of this equation, we obtain

$$\ln\frac{\mathrm{d}\alpha}{\mathrm{d}\tau} = \ln k_\alpha + n\cdot\ln(1-\alpha) - \frac{E}{RT} \tag{2}$$

Considering that α and T are functions of time and differentiating with respect to τ

$$\frac{\dfrac{\mathrm{d}^2\alpha}{\mathrm{d}\tau^2}}{\dfrac{\mathrm{d}\alpha}{\mathrm{d}\tau}} = -\frac{n}{(1-\alpha)}\cdot\frac{\mathrm{d}\alpha}{\mathrm{d}\tau} + \frac{E}{RT^2}\cdot\frac{\mathrm{d}T}{\mathrm{d}\tau} \tag{3}$$

By rearranging this relation, a linear equation can be obtained

$$\frac{\dfrac{\mathrm{d}^2\alpha}{\mathrm{d}\tau^2}\cdot T^2}{\dfrac{\mathrm{d}\alpha}{\mathrm{d}\tau}\cdot\dfrac{\mathrm{d}T}{\mathrm{d}\tau}} = -n\cdot\frac{\dfrac{\mathrm{d}\alpha}{\mathrm{d}\tau}}{(1-\alpha)}\cdot\frac{T^2}{\dfrac{\mathrm{d}T}{\mathrm{d}\tau}} + \frac{E}{R}, \tag{4}$$

by means of which the "reaction order" n can be calculated from its slope and the intercept on the axis of ordinates gives the activation energy E.

For simplicity, the variables in Eqn. (4) will be denoted by simple symbols and thus we write

$$Y = -n \cdot X + \frac{E}{R} \tag{5}$$

When evaluating the thermogravimetric curves, it is more convenient to use directly the experimental data of the sample weight in the calculation. For such a case, Eqn. (1) can be expressed by

$$\frac{\mathrm{d}W}{\mathrm{d}\tau} = k_w \cdot \left(\frac{1}{M_A} \cdot \frac{W_0}{W_\infty - W_0}\right)^{n-1} \cdot (W_\infty - W)^n \cdot \exp\left(-\frac{E}{RT}\right), \tag{6}$$

where M_A is the molecular weight of the initial compound; W_0 is the weighed portion of the sample before the reaction; W is the sample weight at time τ, and W_∞ is the sample weight after the reaction.

Similarly, an equation of a straight line can be obtained

$$\frac{\frac{\mathrm{d}^2W}{\mathrm{d}\tau^2} \cdot T^2}{\frac{\mathrm{d}W}{\mathrm{d}\tau} \cdot \frac{\mathrm{d}T}{\mathrm{d}\tau}} = n \cdot \frac{T^2}{W - W_\infty} \cdot \frac{\frac{\mathrm{d}W}{\mathrm{d}\tau}}{\frac{\mathrm{d}T}{\mathrm{d}\tau}} + \frac{E}{R} \tag{7}$$

which gives after simplification

$$Y_w = n \cdot X_w + \frac{E}{R}. \tag{8}$$

After inserting the calculated values for X and Y, which correspond to certain instants of an experimental run, in Eqn. (5) or (8), we can determine the sought values of n and E; this can be accomplished in the best way by the least-squares method.

Upon expressing numerically the reaction order and the activation energy, we proceed by the same method when determining the k_α and k_w coefficients from modified Eqns. (1) and (6):

$$k_\alpha = \frac{\frac{\mathrm{d}\alpha}{\mathrm{d}\tau}}{(1-\alpha)^n \cdot \exp\left(-\frac{E}{RT}\right)}, \tag{9}$$

and

$$k_w = \frac{\frac{\mathrm{d}W}{\mathrm{d}\tau} \cdot \frac{1}{M_A} \cdot \frac{W_0}{W_\infty - W_0}}{\left[\frac{1}{M_A} \cdot \frac{W_0}{W_\infty - W_0} \cdot (W_\infty - W)\right]^n \cdot \exp\left(-\frac{E}{RT}\right)}. \tag{10}$$

PROGRAM FOR COMPUTING KINETIC CONSTANTS

The simplest procedure of the computation according to relation (8) is our program denoted by VACHVO II[6], which has been prepared for the GIER computer. By this program, the first-order or also the second-order derivatives of the time dependences of the sample weight and temperatures, read at regular time intervals, are computed numerically with respect to time from the experimental values of these quantities. Further, the computer computes the i-th values of X and Y for the corresponding instants, the data being then processed according to Eqn. (5) or (8) using the least-squares method, and it estimates the E and n parameters as well as the corresponding standard deviations. From the expressed E and n values, the computer computes the i-th values for the frequency factor, that are finally also processed by the least-squares method. Besides the estimate of the frequency factor, the computer also estimates the standard deviation of the frequency factor in a manner similar to the above. The computed correlation coefficient r, which indicates the degree of the mutual linear dependence of the experimental values in relation (8), helps in the decision about the applicability of relation (1) to the process studied.

As mentioned earlier, the experimental data need to be read with the maximum possible accuracy in order to obtain a reasonable result from the numerical derivation. This requirement must be fulfilled especially in our computation method, in which even the second-order derivative of the dependence of the weight change on time is computed. Another program, denoted by VYRVACHVON[7], is an improved version of the algorithm VACHVO II, to which a modified procedure has been added[8]. Using the former procedure, a certain polynomic function is laid through the experimental points and its course is determined by means of the least-squares method. The computer then calculates the "corrected" input data from a given expressed function and, using these data, it numerically differentiates. Obviously, the derivatives may also be computed directly by a convenient procedure using the coefficients of the polynomic function, a method which corresponds still better to the logic of the procedure derived by us.

Both the programs mentioned are written in the GIER-ALGOL language. Besides these programs, the CALVACHVO program[9] has been written which includes with the computations a graphical record of the course of the computed dependences according to relation (8).

The input data for the computer evaluation are taken from the thermogravimetric lines by reading the instantaneous values of the sample weight W and the sample temperature t (°C) at regular time intervals. These values are supplemented by other values required for the computation, such as the molecular weight of the initial substance, the initial weighed portion, *etc.* The number and order of the input data is the same for all of the above-mentioned variants of the program.

The input data are inserted in the computer in the following order:

(1) m, the total number of the experimental data for the time—sample weight —temperature triad,

TABLE I

RESULT OF COMPUTATION OF THE EXPERIMENTAL DATA REPORTED BY ŠESTÁK[1] AND PROCESSED BY THE VACHVO II PROGRAM

```
NON-UNIFORM HEATING RATE NON-ISOTHERMAL THERMOGRAVIMETRIC CURVE EVALUATION

      CURVE MARK: LITERAT    EXPER.DATE: 190968   COMPUT.DATE: 190968
      MOL.WEIGHT: 145.150    SAMPLE:    0.1300 GR   CHANGE: -0.00806 GR

J   GRAD,K   CHANGE GR    DW1   SEC     DW2  SEC    DT MIN      X   .      Y

1   394.0   -1.174 ₁₀-3
2   395.0   -1.277 ₁₀-3
3   396.0   -1.388 ₁₀-3
4   397.0   -1.506 ₁₀-3  -6.497 ₁₀-6  -2.302 ₁₀-8   +3.17  -2.953₁₀+3   1.055₁₀+4
5   398.0   -1.633 ₁₀-3  -6.938 ₁₀-6  -2.371 ₁₀-8   +3.17  -3.232₁₀+3   1.023₁₀+4
6   399.0   -1.769 ₁₀-3  -7.395 ₁₀-6  -2.458 ₁₀-8   +3.17  -3.537₁₀+3   9.999₁₀+3
7   400.0   -1.913 ₁₀-3  -7.862 ₁₀-6  -2.488 ₁₀-8   +3.17  -3.868₁₀+3   9.568₁₀+3
8   401.0   -2.066 ₁₀-3  -8.338 ₁₀-6  -2.546 ₁₀-8   +3.17  -4.227₁₀+3   9.280₁₀+3
9   402.0   -2.228 ₁₀-3  -8.823 ₁₀-6  -2.576 ₁₀-8   +3.17  -4.621₁₀+3   8.917₁₀+3
10  403.0   -2.399 ₁₀-3  -9.308 ₁₀-6  -2.553 ₁₀-8   +3.17  -5.048₁₀+3   8.420₁₀+3
11  404.0   -2.580 ₁₀-3  -9.787 ₁₀-6  -2.527 ₁₀-8   +3.17  -5.509₁₀+3   7.965₁₀+3
12  405.0   -2.769 ₁₀-3  -1.027 ₁₀-5  -2.505 ₁₀-8   +3.17  -6.015₁₀+3   7.563₁₀+3
```

```
13   406.0  -2.968 10-3  -1.072 10-5  -2.358 10-8   +3.17  -6.561 10+3   6.849 10+3
14   407.0  -3.175 10-3  -1.116 10-5  -2.271 10-8   +3.17  -7.153 10+3   6.371 10+3
15   408.0  -3.390 10-3  -1.158 10-5  -2.108 10-8   +3.17  -7.800 10+3   5.727 10+3
16   409.0  -3.612 10-3  -1.195 10-5  -1.877 10-8   +3.17  -8.497 10+3   4.963 10+3
17   410.0  -3.841 10-3  -1.229 10-5  -1.647 10-8   +3.17  -9.254 10+3   4.259 10+3
18   411.0  -4.076 10-3  -1.257 10-5  -1.359 10-8   +3.17  -1.008 10+4   3.452 10+3
19   412.0  -4.316 10-3  -1.280 10-5  -9.985 10-9   +3.17  -1.097 10+4   2.503 10+3
20   413.0  -4.560 10-3  -1.295 10-5  -6.318 10-9   +3.17  -1.193 10+4   1.573 10+3
21   414.0  -4.805 10-3  -1.303 10-5  -2.087 10-9   +3.17  -1.297 10+4   5.188 10+2
22   415.0  -5.052 10-3  -1.303 10-5   2.463 10-9   +3.17  -1.410 10+4  -6.155 10+2
23   416.0  -5.297 10-3  -1.294 10-5   6.995 10-9   +3.17  -1.532 10+4  -1.768 10+3
24   417.0  -5.540 10-3  -1.276 10-5   1.233 10-8   +3.17  -1.664 10+4  -3.178 10+3
25   418.0  -5.779 10-3  -1.246 10-5   1.720 10-8   +3.17  -1.806 10+4  -4.554 10+3
26   419.0  -6.011 10-3  -1.210 10-5   2.230 10-8   +3.17  -1.960 10+4  -6.114 10+3
27   420.0  -6.236 10-3
28   421.0  -6.450 10-3
29   422.0  -6.654 10-3


   CORRELATION COEF.: R =  1.000    RESIDUAL SUM OF SQUARES = 3.352 10+4

     ACTIVATION ENERGY: E = 26.817 10+3          ERROR E = 3.446 10+1
     REACTION ORDER    : N =  1.000              ERROR N = 1.683 10-3
     FREQUENCY FACTOR  : K =  5.754 10+11        ERROR K = 2.226 10+7
```

(2) R, the gas constant ($R = 1.987$ cal·grad^{-1}·mole^{-1}),
(3) MVA, the molecular weight of the initial substance A,
(4) WK, the final change in the weight after the reaction ($WK = W_{\infty} - W_0$, the unit—like with W),
(5) p, the range of the graphical record of the weight in grams (g),
(6) d, the range of the graphical record of the weight in the units for W (the unit—like with W),
(7) WP, the initial weighed portion of the sample ($WP = W_0$) (g),
(8) L, the time of the graphical record (the unit—like with q),
(9) A, the time of the graphical record (min),
(10) q, the reading step (the unit is arbitrary but the same as with L),
(11) $\pm W$, a series of m data of weight gains (losses) of the sample determined at individual time intervals (the unit is arbitrary but the same as with WK and d),
(12) T, a series of m temperature data measured at individual time intervals (°C).

Further, words making the experiment description accurate are inserted in the computer input, *viz.*:

(*a*) the designation of the curve (7 letters),
(*b*) the date of the experimental run (6 letters),
(*c*) the date of the computation (6 letters).

These words, enclosed by brackets, which specify the evaluated experiment, are printed by the computer directly into the legend of the computation record.

The complete program VACHVO II, which is the basis for all versions mentioned, is presented in Table II. Sufficiently accurate experimental data can be processed by this program directly. Expanded versions of the programs VYRVACHVON and CALVACHVO can be supplied by the authors of this report on request.

RESULTS AND DISCUSSION

The present method of evaluation of the thermogravimetric curves permits, in contradiction to Refs. 1,2 and 4*a*, processing of the experimental data obtained under usual conditions, when the thermal effects of reactions can fully manifest themselves in the course of the temperature dependence of the sample heating.

The correctness of the procedure suggested has been verified by employing the experimental data and results of Šesták[1]. The experiments described in this paper have theoretically been performed under ideal conditions, the strictly linear rise of the sample temperature being maintained also during the time of the heat effect of the reaction. The data mentioned have been modified to obtain the input data for the VACHVO II program and the computation has been made on the GIER computer similarly to all other computations. The record of the computer output for this computation is shown in Table I.

When comparing the resulting values* of Refs. 1 and 4a with those calculated by means of the VACHVO II program, it is evident that, with all kinetic parameters, an excellent agreement has been reached.

TABLE II

THE VACHVO II COMPUTATION PROGRAM

```
begin real d,p,MVA,WK,WP,n,E,R,SUMX,SUMY,SUMX2,SUMY2,SUMXY,
    L,A,q,SUMZ,SUMZ2,RSCEn,sEn,k,chybaE,chyban,
    chybak,r;
    integer N,j,m,drrev;
    boolean a,b,c;
    real procedure DER(H,K);
    value K; integer K; array H;
    DER:=(H[K+4]-H[K+2])/2-(H[K+5]-2×(H[K+4]-H[K+2])
    -H[K+1])/12+(H[K+6]-4×(H[K+5]-H[K+1])
    +5×(H[K+4]-H[K+2])-H[K])/60;
    real procedure DER2(F,K);
    value K; integer K;array F;
    DER2:=(-2×F[K]+8×F[K+1]+12×F[K+2]-40×F[K+3]+22×F[K+4])/24;
     drrev:=placemin +10000;
AB: printpage;
    input(m);
    begin array T,W,WR[1:m],DW1,DT,X,Y,Z[4:m-3] ,
       DW2[3:m-2];
       input(R,MVA,WK,p,d,WP,L,A,q,W,T);
       reserve(drrev);
       a:=instring; b:=instring; c:=instring;
       printpage;
       printcr;printcr;printcr;printcr;printcr;
       printsp(10);printtext(⟨<print of input data⟩);printcr;printcr;
       print(⟨ndd⟩,m);printcr;
       printcr;printcr;
       print(⟨n.dddd⟩,R);printsp(5);print(⟨ndd.dd⟩,MVA);printcr;
        print(⟨-nd.ddddd⟩,WK,printsp(2));print(⟨-nd.ddddddd⟩,p,printsp(2));
        print(⟨-nd.ddddd⟩,d,
       printsp(2),WP,printsp(2),
       L,printsp(2),A,printsp(2),q);
       printcr;printcr;
       for j:=1 step 1 until m do
       begin print(⟨-n.ddddddd⏨-dd⟩,W[j],printsp(2));
          if j/5=j:5 then printcr;
       end;
       printcr;printcr;
       for j:=1 step 1 until  m do
       begin  print(⟨ndd.ddd⟩,T[j],printsp(2));
          if j/5=j:5 then printcr;
       end;
       printcr;printcr;printtext(a,printcr,b,printcr,c);
       q:=A×q×60/L;
```

---

*$E = 26.82\ 10^{+3}$, err $E = 1.127\ 10^{+3}$, $n = 9.392\ 10^{-1}$, err $n = 2.510\ 10^{-1}$, $Z = 5.789\ 10^{11}$, err $Z = 1.899\ 10^{9}$.

TABLE II (*continued*)

```
WK:=WK×p/d;
for j:=1 step 1 until m do
begin T[j]:=T[j]+273.2;
    W[j]:=W[j]×p/d;
    WR[j]:=WK-W[j];
end;
for j:=1 step 1 until m-6 do
begin DW1[j+3]:=DER(W,j)/q;
    DT[j+3]:=DER(T,j)/q;
end;
for j:=1 step 1 until m-6 do
DW2[j+3]:=DER2(W,j)/q↑2;
SUMX:=SUMY:=SUMX2:=SUMY2:=SUMXY:=SUMZ:=SUMZ2:=0;
N:=m-3;
for j:=4 step 1 until N do
begin Y[j]:=(DW2[j]×T[j]↑2)/(DW1[j]×DT[j]);
    X[j]:=(DW1[j]×T[j]↑2)/(-WR[j]×DT[j]);
    SUMX:=SUMX+X[j];
    SUMY:=SUMY+Y[j];
    SUMX2:=SUMX2+X[j]↑2;
    SUMY2:=SUMY2+Y[j]↑2;
    SUMXY:=SUMXY+X[j]×Y[j];
end;
N:=m-6;
n:=(SUMXY-(SUMX×SUMY)/N)/(SUMX2-(SUMX↑2)/N);
E:=(R×(SUMY-n×SUMX))/N;
RSCEn:=SUMY2-(SUMY↑2)/N-n×(SUMXY-SUMX×SUMY/N);
sEn:=sqrt(abs(RSCEn)/(N-2));
chybaE:=R×sqrt(SUMX2/(N×SUMX2-SUMX↑2))×sEn;
chyban:=sEn/sqrt(SUMX2-(SUMX↑2)/N);
r:=(N×SUMXY- SUMX×SUMY)/sqrt((N×SUMX2-SUMX↑2)×
 (N×SUMY2-SUMY↑2));
N:=m-3;
for j:=4 step 1 until N do
begin Z[j]:=DW1[j]×WP/MVA/WK/(WP/MVA/WK×WR[j])↑n/exp(-E/R/T[j]);
    SUMZ:=SUMZ+Z[j];
    SUMZ2:=SUMZ2+Z[j]↑2;
    DT[j]:=DT[j]×60;
end;
N:=m-6;
k:=SUMZ/N;
chybak:=sqrt((N×SUMZ2-SUMZ↑2)/N↑2/(N-1));
printpage;
printcr;printsp(2);printtext(≮<vachvoII≯);
printcr;printcr;printcr;printsp(3);
printtext(≮<non-uniform␣heating␣rate␣non-isothermal␣thermogravimetric␣
curve␣evaluation≯);
printcr;printcr;printcr;printsp(9);
printtext(≮<curve mark:␣≯,a);
printsp(3);
printtext(≮<exper.date:␣≯,b);
printsp(3);
printtext(≮<comput.date:␣≯,c);
```

TABLE II (*continued*)

```
        printcr;printsp(9);
        printtext(≮<mol.weight:␣≯);print(≮ndd.ddd≯,MVA);
        printsp(3);
        printtext(≮<sample:␣≯);print(≮ndd.dddd≯,WP);
        printsp(1);printtext(≮<gr␣␣␣change:␣≯);
        print(≮+n.ddddd≯,WK);
        printsp(1);printtext(≮<gr≯);
        printcr;printcr;printcr;
        printsp(2);printtext(≮<j≯);
        printsp(3);printtext(≮<grad,k≯);
        printsp(3);printtext(≮<change␣gr≯);printsp(3);
        printtext(≮<dw1␣␣sec␣␣␣␣dw2␣␣sec␣␣␣≯);
        printtext(≮<dt␣min≯);printsp(6);
        printtext(≮<x≯);printsp(10);printtext(≮<y≯);
        printcr;printcr;
        for j:=1 step 1 until  m do
        begin
           printcr;
           printsp(2); print(≮nd≯,j);
           printsp(2);print(≮nddd.d≯,T[j]);
           printsp(2); print(≮+n.ddd⏨-dd≯,W[j]);printsp(2);
           if j>3∧j<m-2 then
           begin
              print(≮-n.ddd⏨-dd≯,DW1[j],printsp(2),DW2[j],
              printsp(2));print(≮+nd.dd≯,DT[j],printsp(2));
              print(≮-n.ddd⏨+d≯,X[j],printsp(2),Y[j])
           end;
        end;
        printcr;printcr;printcr;printsp(6);
        printtext(≮<correlation coef.:␣r␣=␣≯);
        print(≮-n.ddd≯,r);printsp(4);
        printtext(≮<residual sum of squares␣=␣≯);
        print(≮n.ddd⏨-dd≯,RSCEn);
        printcr;printcr;printsp(9);
        printtext(≮<activation energy:␣e␣=␣≯);
        print(≮nd.ddd⏨+dd≯,E);printsp(10);
        printtext(≮<error␣e␣=␣≯);
        print(≮n.ddd⏨+dd≯,chybaE);
        printcr;printsp(9);
        printtext(≮<reaction order␣␣␣:␣n␣=␣≯);
        print(≮-n.ddd⏨+dd≯,n);printsp(10);
        printtext(≮<error␣n␣=␣≯);
        print(≮n.ddd⏨+dd≯,chyban);
        printcr;printsp(9);
        printtext(≮<frequency factor␣:␣k␣=␣≯);
        print(≮-n.ddd⏨+dd≯,k); printsp(10);
        printtext(≮<error k␣=␣≯);
        print(≮n.ddd⏨+dd≯,chybak);
    end;
    goto AB;
end of program;
```

In addition, our experimental data for the dehydration of calcium oxalate monohydrate obtained from the M.O.M. "Derivatograph" have been processed by the VACHVO II program. The M.O.M. Derivatograph permits relatively accurate recording of the temperature of the heated sample and it is suitable for recording sensitively all deviations from the linear temperature rise due to the thermal effects of reactions.

The oxalate samples have been prepared by precipitation from calcium chloride and potassium oxalate solutions. After washing, filtration, and drying in air, they have been ground to give a fine powder, which has been laid in thin layers on little plates of a multiplate platinum boat and inserted in the heated space of the derivatograph. During the heating time, argon has been allowed to pass through this space at a steady flow rate of about 50 ml·min^{-1}. The average rate of the sample heating has been 4.75 °C·min^{-1}. The numerical value of the activation energy of the dehydration of calcium oxalate monohydrate computed by the VACHVO II program equaled 21.6 kcal·mole^{-1} and the "reaction order" $n = 0.98$. For comparison, the values of these quantities determined by the method of differential thermal analysis can be mentioned[10]. The author of the cited paper has reported activation energies of 21.5, 21.6 and 21.8 kcal·mole^{-1}. He has obtained these values by evaluating the DTA experiments, employing three independent methods. The order of the reaction has been found to be $n = 1$. Other authors[10,11] have reported for the activation energy values of 20–22 kcal·mole^{-1}.

As mentioned above, it is not a common practice to measure the temperature directly in the studied sample during the thermogravimetric analysis. Many commercial devices do not permit this measuring and so the measured furnace temperature is taken for the sample temperature. In such a case, the presented linear course of the sample heating is obviously only apparent.

We have been interested in the effect which this incorrect measurement of the sample temperature may have on the computed values of the kinetic parameters. Therefore, we have computed these parameters for the case of the above-mentioned dehydration of calcium oxalate in which we have, of course, substituted another dependence with an average constant rate of the sample heating, *i.e.*, a dependence similar to the course of the furnace heating for the actual temperature dependence. In this case, the result of the computation of the activation energy has been a value of 18.6 kcal·mole^{-1}, *i.e.*, a value 14% lower than that computed earlier; the computed value for the "reaction order" has been $n = 0.86$. The maximum deviation of the "average" temperature from the measured one has been about 2 °C. On the basis of this finding, we may assume that the similar existing differences which occur in the values of the kinetic parameters of some other reactions published by various authors are caused, besides other reasons, primarily by neglecting the deviations of the real values of the sample temperature from the measured data. These differences are obviously greater, the stronger the thermal effects of the heated substance conversion.

As can be seen from relations (4) and (7), the heating rate, expressed in the computations as $dT/d\tau$, is important. Therefore, changes in this rate due to thermal effects cannot be neglected without consequences on the resulting values of the computations. We know from experience that, under entirely common conditions for performing the DTA and TGA, such a change in the course of the effect may attain multifold or only negligible proportions of the initial value of the linear heating rate before the effect occurs. When taking into consideration also the strongly exothermic reactions, then even the sign of the rate of heating of the reaction sample may change under such an effect. Nevertheless, the deviation of the real temperature value from the programmed one may be small and — in comparison with the absolute value of the temperature — negligible.

It may be assumed that the suggested method of evaluation of the thermogravimetric curves will lower the errors in the calculated values of the kinetic parameters because it takes into account also the effects that deform the linearity of the heating.

In addition, the authors are aware that Eqn. (1) has no general validity[1,2] owing to the term $(1-\alpha)^n$. Therefore a more general program is in the course of preparation where the function $\alpha^m (1-\alpha)^n$ is employed. Using identical input data as above, the same values of kinetic parameters have been obtained (including $n \to 1$ and $m \to 0$).

CONCLUSION

A procedure of evaluating the kinetic parameters from the thermogravimetric curves has been suggested for processes obeying the relation

$$\frac{d\alpha}{d\tau} = k_z \cdot (1-\alpha)^n \exp\left(-\frac{E}{RT}\right)$$

and that also for cases when the thermal effects of reactions deform the initially linear course of the rise of the reaction temperature. In order to simplify the processing of the experimental data according to the derived relations, programs have been written for the GIER computer. The results of the evaluations of some dehydration processes by means of the present algorithm agree entirely with the published values obtained by other experimental methods. Moreover, the present method points to one of the possible sources of the deviation in the data of the kinetic parameters of some reactions which appear in the present-day literature.

ACKNOWLEDGMENT

The authors wish to thank Mrs. N. Rykalová for many helpful discussions and assistance with the programming and computations.

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