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BASIC program to discriminate among mechanisms of solid–gas decomposition (DISCRIM 2)

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Abstract

This paper describes a program to evaluate automatically the experimental data for nonisothermal kinetic analysis. The program is based mainly on a least-squares procedure.

INTRODUCTION

Mathematical treatment of the results of thermogravimetric experiments to determine the kinetic parameters of thermal decomposition of substances is a tedious and time consuming operation. To overcome these difficulties, in recent times there have been developed computer programs [1–9] that describe and test many kinetic expressions.

Zsako and Zsako [1] used a FORTRAN program to estimate kinetic parameters (preexponential factor, activation energy), the method being limited to the "reaction order" model. The program written in BASIC by Reich and Stivala [3] allows the calculation of preexponential factor and activation energy from nonisothermal data in solid–gas decompositions. The methods were based upon application of the integral form of the basic rate equation, covering ten different kinetic models of the type discussed by Brown et al. [10]. Other solid state kinetic models were tested by Elder [9] using a FORTRAN computer program.

PRINCIPLE TO EVALUATE THE NONISOTHERMAL KINETIC PARAMETERS

Using as a starting point the general isothermal kinetic equation

$$\frac{d\alpha}{dt} = A\ e^{-E/RT} f(\alpha) \qquad (1)$$

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where all the notation has known meanings, and introducing into it the heating rate β defined by

$$\beta = \frac{dT}{dt} \tag{2}$$

one obtains

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} f(\alpha) \tag{3}$$

Considering the function

$$\psi(\alpha,T) = \psi[\alpha(T),T] = \psi(T) = \frac{1}{f(\alpha)} \frac{d\alpha}{dT} \tag{4}$$

and taking into account eqn. (3), we get

$$\frac{1}{f(\alpha)} \frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} \tag{5}$$

The correct reaction mechanism expressed through the differential conversion function $f(\alpha)$ (or the integral conversion function $g(\alpha)$) [11] will be obtained in the following steps suggested by us.

1. For various conversion functions, after evaluating by a numerical procedure the derivative $d\alpha/dT$, the left-hand term of eqn. (5) is calculated.
2. By fitting the function from the right-hand term of eqn. (5) with experimental data (as expressed by its right-hand term), applying the least-squares method, the preexponential factor A and the activation energy E are obtained.
3. The mean deviations of the theoretical points with respect to the experimental ones are evaluated for each of the 23 mechanisms given in Table 1.
4. The correct mechanism corresponds to the minimal value of the mean deviation.

In order to evaluate the kinetic parameters A and E we introduce the relationship $\varphi(T) = \ln \psi(T)$. Taking into account relationships (4) and (5) one can write the function $\varphi(T)$ as

$$\varphi(T) = \ln\frac{A}{\beta} - \frac{E}{RT} \tag{6}$$

By introducing the notations

$$x = \ln\frac{A}{\beta}$$

$$y = \frac{E}{R} \tag{7}$$

eqn. (6) can be written in the form

$$\varphi(T) = x - \frac{y}{T} \tag{8}$$

TABLE 1

Forms of functions $f(\alpha)$ and $g(\alpha)$ for various mechanisms of solid–gas decomposition [12]

No.	Reaction mechanism	$f(\alpha)$	$g(\alpha)$	
1–6	Power law	$\frac{1}{n\alpha^{1-n}}$	α^n	$n = 1/4; 1/3; 1/2; 1; 3/2; 2$
7	Mampel unimolecular law	$1-\alpha$	$-\ln(1-\alpha)$	
8–11	Avrami–Erofeev nuclei growth	$\frac{1}{n}(1-\alpha)[-\ln(1-\alpha)]^{1-n}$	$[-\ln(1-\alpha)]^n$	$n = 1/4; 1/3; 1/2; 2/3$
12	Prout–Tompkins branching nuclei	$\alpha(1-\alpha)$	$\ln[\alpha/(1-\alpha)]$	
13	Jander, three-dimensional diffusion	$(1-\alpha)^{-1/3}[1-(1-\alpha)^{-1/3}]^{-1}$	$\frac{3}{2}[1-(1-\alpha)^{1/3}]^2$	
14	Anti-Jander, three-dimensional counter diffusion	$(1+\alpha)^{1/3}[1-(1+\alpha)^{-1/3}]^{-1}$	$\frac{3}{2}[(1+\alpha)^{1/3}-1]^2$	
15	Brounshtein–Ginstling, three-dimensional diffusion	$[(1+\alpha)^{1/3}-1]^{-1}$	$\frac{3}{2}[1-2/3\alpha-(1-\alpha)^{2/3}]$	
16	Valensi, two-dimensional diffusion	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$	
17–18	Exponential	$1/n\alpha$	$\ln \alpha^n$	$n = 1; 2$
19	Contracting sphere	$(1-\alpha)^{2/3}$	$3[1-(1-\alpha)^{1/3}]$	
20	Contracting cylinder	$(1-\alpha)^{1/2}$	$2[1-(1-\alpha)^{1/2}]$	
21–23 [12]	Reaction order	$\frac{1}{2}(1-\alpha)^{1-n}$	$1-(1-\alpha)^n$	$n = 2; 3; 4$

the function $\varphi(T)$ being obtained by experiment. As far as the right-hand term of eqn. (8) is concerned, the coefficients x and y should be determined.

The deviation of the function $x - y/T$ from the experimental data $\varphi(T)$ is defined through the relationship

$$\varepsilon^2 = \left[\varphi(T_k) - \left(x - \frac{y}{T_k}\right)\right]^2 \tag{9}$$

where k is the number corresponding to a given experimental point from the total number of experimental points n; the values of x and y should be chosen in the way which minimizes the sum σ

$$\sigma = \sum_{k=1}^{n} \varepsilon^2 = \sum_{k=1}^{n} \left[\varphi(T_k) - \left(x - \frac{y}{T_k}\right)\right]^2 \tag{10}$$

By solving the system

$$\begin{aligned} \frac{\partial \sigma}{\partial x} &= -2 \sum_{k=1}^{n} \left[\varphi(T_k) - x + \frac{y}{T_k}\right] = 0 \\ \frac{\partial \sigma}{\partial y} &= -2 \sum_{k=1}^{n} \frac{1}{T_k}\left[\varphi(T_k) - x + \frac{y}{T_k}\right] = 0 \end{aligned} \tag{11}$$

with respect to x and y one obtains

$$\begin{aligned} x &= \frac{\left[\sum \frac{1}{T_k}\varphi(T_k)\right]\left[\sum \frac{1}{T_k}\right] - \left[\sum \varphi(T_k)\right]\left[\sum \frac{1}{T_k^2}\right]}{\left(\sum \frac{1}{T_k}\right)^2 - n\sum \frac{1}{T_k^2}} \\ y &= \frac{n\sum \frac{\varphi(T_k)}{T_k} - \left(\sum \frac{1}{T_k}\right)\left[\sum \varphi(T_k)\right]}{\left(\sum \frac{1}{T_k}\right)^2 - n\sum \frac{1}{T_k^2}} \end{aligned} \tag{12}$$

By introducing into eqn. (12) relationships (4), (5) and (6), and taking into account eqn. (7), we obtain

$$\begin{aligned} A_j &= \beta \exp \frac{\left\{\sum\left[\frac{1}{T_k}\ln\frac{1}{f_j(\alpha_k)}\left.\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right|_{T_k}\right]\right\}\left[\sum \frac{1}{T_k}\right] - \left\{\sum\left[\ln\frac{1}{f_j(\alpha_k)}\left.\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right|_{Tk}\right]\right\}\left[\sum \frac{1}{T_k^2}\right]}{\left[\sum \frac{1}{T_k}\right]^2 - n\sum \frac{1}{T_k^2}} \\ E_j &= R\frac{\left\{n\sum\left[\frac{1}{T_k}\ln\frac{1}{f_j(\alpha_k)}\left.\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right|_{Tk}\right]\right\} - \left[\sum \frac{1}{T_k}\right]\left[\sum \ln\frac{1}{f_j(\alpha_k)}\left.\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right|_{T_k}\right]}{\left(\sum \frac{1}{T_k}\right)^2 - n\sum \frac{1}{T_k^2}} \end{aligned} \tag{13}$$

where $(\mathrm{d}\alpha/\mathrm{d}T)|_{T_k}$ means the derivative of α with respect to T at temperature $T = T_k$, and j the number of the reaction mechanism from Table 1.

Using the x and y values given by eqn. (12), the values of deviation σ according to relationship (9) are calculated. As shown, these values are used as a criterion for the most probable mechanism.

To confirm the results, a procedure given by Phandis and Desphande [12] was used. According to their procedure

$$f(\alpha)g(\alpha) = \frac{RT^2}{E}\frac{\mathrm{d}\alpha}{\mathrm{d}T} \quad (14)$$

thus the linearity of the plot $\{[f(\alpha)g(\alpha)], T^2\,\mathrm{d}\alpha/\mathrm{d}T\}$ allows one to decide on the most nearly correct mechanism.

To process the experimental data automatically according to the two described procedures, a program writen in BASIC language was worked out.

THE PROGRAM AND ITS USE

The program allows calculation of the values of the activation energy E, the preexponential factor A and the mean deviation σ according to the relationship (10) for both procedures.

The input data are: number of experimental points, heating rate (K min^{-1}), and total weight (or a magnitude directly proportional to it). Each experimental point is characterized by temperature and weight (or a magnitude directly proportional to it).

In order to test the 23 conversion functions, the temperature range in which the investigated reactions occurs should be divided into a number of intervals between 1 and 30; the number is decided according to the input data. The number of intervals is different from the number of intervals which separates the experimental points. For the ΔT specific intervals, the cubic spline interpolation coefficients are calculated according to a cubic spline interpolation [13].

For each function, the preexponential factor, activation energy and mean deviation are listed, for our method as well as for that of Phandis and Desphande. After recording the results, the mechanism with minimal σ_j and θj (θ_j = deviation from linearity of Phandis' plot) will be selected.

For conversation with the computer, the operator should use the key 1 for YES and the key 0 for NO. In order to evaluate the kinetic parameters over a restricted or extended range of the conversion degree α, the input data can be handled as follows:

- an experimental point with coordinates w and T can be:
  maintained, by pressing key 1;
  changed, by pressing key 2; or
  erased, by pressing key 3.

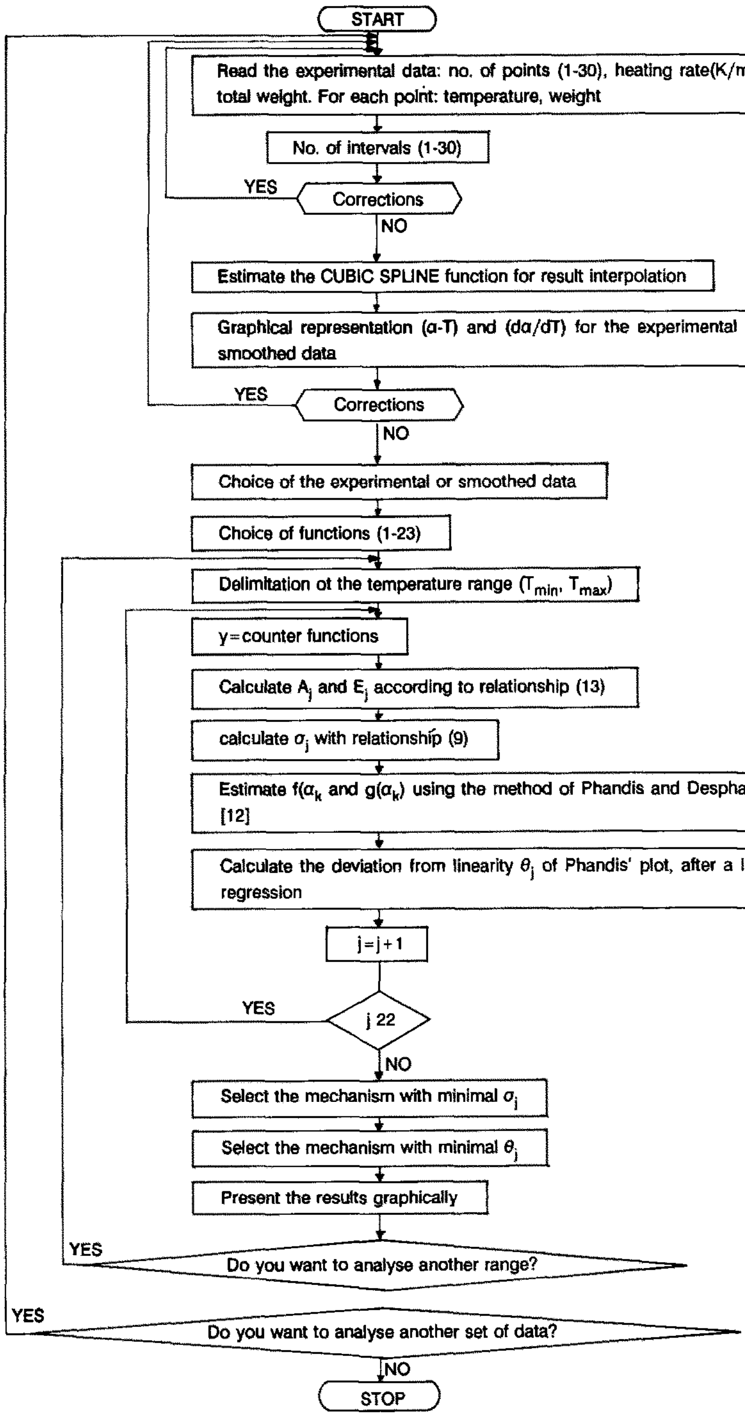

Fig. 1. Flow chart of the program.

TABLE 2

α	extent of reaction (conversion) (dimensionless)
$d\alpha/dt$	rate of reaction (s^{-1})
$f(\alpha)$	differential conversion function
$g(\alpha)$	integral conversion function
T	absolute temperature (K)
E	activation energy (kJ mol^{-1})
A	preexponential factor (min^{-1})
R	universal gas constant (8.13 kJ mol^{-1} K^{-1})
β	heating rate (K min^{-1})

• for an experimental point (w,T), intermediate points between it and the previous point can be added by pressing key 4.

Taking into account that, for $\alpha = 0$ and $\alpha = 1$, some of the tested functions could be undefined, it is recommended that the chosen temperature intervals for calculating A, E and σ should not contain these extreme values.

The program was written according to the flow chart shown in Fig. 1. and contains the instructions shown in Appendix 1. The main symbols used in the program are shown in Table 2.

The program was run on a TIM S computer. Both the applied methods select the same reaction mechanism. For the activation energy, the difference between the values obtained by these methods does not exceed 10%. Our procedure allows the value of the preexponential factor and the activation energy to be obtained.

CONCLUSIONS

(1) A procedure to discriminate between the mechanisms of solid–gas decomposition was selected.

(2) A computer program written in BASIC and based on this procedure was worked out.

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APPENDIX 1

```
  5 REM Program to discrimi-
      nate the mechanism of
      solid-gas decomposions


 10 DIM a(61)
 15 DIM b(30)
 20 DIM c(30)
 24 CLS
 25 DIM d(30)
 30 DIM e(30)
 35 DIM f(23,30)
 40 DIM g(23,30)
 45 DIM h(23)
 46 DIM i(23)
 47 DIM j(23)
 48 DIM k(23)
 49 DIM l(6)
 50 DIM m(23)
 51 DIM n(6)
 54 DIM o(23)
 55 DIM p(23)
 60 DIM q(23)
 65 DIM r(23)
 70 DIM s(23)
 75 DIM t(30)
 80 DIM u(30)
 85 DIM v(61)
 90 DIM w(61)
 95 DIM x(30)
100 DIM y(30)
105 DIM z(23)
106 BORDER 0
107 PAPER 0
108 INK 7
110 REM
115 REM Title page
120 REM
125 CLS
130 PRINT AT 2,1;
     "Program to discriminat";"e
";AT 3,1;
  "the mechanism of solid-ga";"s
";AT 4,5;
  "decomposions"
135 PRINT AT 7,10; INVERSE 1;
           "*** DISCRIM 2 ***"
140 REM
145 REM
150 REM
155 PRINT AT 21,1;
     "Press ENTER to continue"

160 PRINT " "
165 CLS
170 PRINT AT 13,13;"NOTE";
     AT 15,1;
     "During the conversation";
" the ";AT 16,1;
 "following convention will be";
     AT 17,5;"adopted:";AT 20,5;
          "0=NO";AT 21,5;
          "1=YES"
175 REM Acquisition of initial
          data
180 REM
185 INPUT "Number of points";
   " (1-30) :";n
186 INPUT "No. of intervals:";
                   npz
190 INPUT "Heating rate"     ;"
(K/min) :";hr
191 INPUT "Total weight : ";mto
t
195 FOR i=1 TO n:
      CLS
200 PRINT "Point No. ";i
205  INPUT "Temperature (C)";
          " : ";tcel
206  LET x(i)=tcel+273.15
210  INPUT "Weight :";
 mrea
211  LET y(i)=mrea/mtot
215 NEXT i
220 CLS
221 INPUT "Corrections ? (0/1)
: ";ans
222 IF ans<>0 AND ans<>1 THEN
         GO TO 221
223 IF ans=1 THEN GO TO 6000
224 CLS
225 REM
230 REM
235 REM
240 LET npm=n
245 LET npg=60
247 LET npzm1=npz-1
250 LET flgini=1
255 LET up3=1/3
260 LET dp3=2/3
265 LET init=1
270 LET tmin=x(1)
275 FOR i=1 TO n
280  LET t(i)=x(i)
285  LET u(i)=y(i)
290  LET e(i)=y(i)
295 NEXT i
296 FOR i=1 TO 23:
     LET m(i)=1:
    NEXT i
300 REM
305 REM Plot
310 REM
315 LET xstg=5
320 LET xdrp=125
325 LET yjos=7
330 LET ysus=167
335 LET patern=1
340 PRINT AT 1,1;
    "The initial data will be";
```

```
     AT 2,1;" represented as fol
lows:";
     AT 4,5;
     "-left         -experimental
";   AT 6,5;
    "-right         -smoothed";
     AT 8,5;
    "-white circle -alfa";
     AT 10,5;
    "-black circle -derivative";
 341 REM
 345 PRINT AT 21,1;
     "Press ENTER to continue"
 350 PAUSE 0
 355 CLS
 360 PRINT "Calculation of the";
" interpolation coefficients":
     LET flggrf=1
 365 GO SUB 5000:
     IF flggrf=1 THEN
     PRINT "Plot preparation"
 370 LET pasg=(t(n)-t(1))/
              (npg-1)
 375 FOR i=1 TO npg
 380  LET v(i)=(i-1)*pasg+t(1)
 385  LET u=v(i)
 390  GO SUB 5067
 395  IF seval<0 THEN
                 LET w(i)=0
 400  IF seval>1 THEN
                 LET w(i)=1
 405  IF seval>=0 AND seval<=1
          THEN LET w(i)=seval
 410  IF dseval<0 THEN
                  LET a(i)=0
 420  IF dseval>=0 THEN
                 LET a(i)=dseval
 425 NEXT i
 430 IF flggrf=1 THEN CLS
 431 LET comuta=1
 435 GO SUB 4000
 450 LET patern=2
 455 FOR i=1 TO npm
 460  LET u(i)=b(i)
 465 NEXT i
 470 FOR i=1 TO npg
 475  LET w(i)=a(i)
 480 NEXT i
 481 LET comuta=0
 485 GO SUB 4000
 490 IF flggrf=2 THEN GO TO 565
 495  LET flggrf=2
 496  LET patern=1
 500  LET xstg=130
 505  LET xdrp=250
 510  LET yv=y(1)
 515  LET u(1)=y(1)
 520  LET u(npm)=y(npm)
 525  LET nm1=n-1
 530  FOR i=2 TO nm1
 535   LET yn=y(i)
 540   LET y(i)=(yv+y(i)+y(i+1))
                /3
 545   LET yv=yn
 550   LET u(i)=y(i)
 555  NEXT i
 560  GO TO 365
 565 INPUT "Smoothed data ?";
        " (0/1) : ";ans
 566 IF ans<>0 AND ans<>1
           THEN GO TO 565
 570 IF ans=1 THEN GO TO 591
 575  FOR i=1 TO n
 580   LET y(i)=e(i)
 585  NEXT i
 590  GO SUB 5000
 591 INPUT "Corrections ? (0/1)
: ";ans
 592 IF ans<>0 AND ans<>1 THEN
        GO TO 591
 593 IF ans=1 THEN GO TO 6000
 594 INPUT "Selection of functio
ns ? (0/1) : ";ans
 595 IF ans<>0 AND ans<>1 THEN
           GO TO 594
 596 IF ans=0 THEN GO TO 600
 597 FOR i=1 TO 23:
       CLS :
       PRINT AT 1,10;
       "Function no.";i:
       INPUT "Selected ? ";
      "(0/1) : ";m(i):
    NEXT i
 599 REM
 600 REM Zone cycle starting
 605 REM
 606 LET nz=1
 607 LET comuta=1
 610 IF tmin>=x(n) THEN
                 GO TO 1290
 615  CLS
 616  PRINT AT 2,11;"Zone ";
          ;nz;AT 3,1;" "
 619  INPUT "Minimal temperature
"             ;" (C) : ";tmin
 620  PRINT "Minimal temperature
"             ;" : ";tmin;" C":
               LET tmin=tmin+273.
15
 625  INPUT "Maximal temperature
"             ;" (C) : ";tmax
 626  PRINT "Maximal temperature
"             ;" : ";tmax;" C":
               LET tmax=tmax+273.
15
 630  LET past=(tmax-tmin)/npzm1
 635  REM
 640  REM Generation of the con-
         version function values
           its integral and de-
```

```
          termination of some
          preliminary data
 645  REM
 646  PRINT " "
 650  PRINT "Generation of ";
          "conversion function
";    AT 9,1;"No. of function  (
1-23)"     ;" :";AT 10,1;
          "No. of interval  (1-
";npz;") :"
 655  LET s1=0
 660  LET s2=0
 661  LET s5=0
 662  LET s6=0
 665  FOR t=1 TO npz:
       PRINT AT 10,26;t
 670   LET t(t)=tmin+(t-1)*past
 675   LET u=t(t)
 680   LET aux=1000/u
 685   LET s1=s1+aux
 690   LET s2=s2+aux/u
 695   GO SUB 5067
 700   IF seval<0 THEN
                LET a(t)=0
 705   IF seval>1 THEN
                LET a(t)=1
 710   IF seval>=0 AND seval<=1
          THEN LET a(t)=seval
 715   LET alfa=a(t)
 720   IF dseval<1e-6 THEN
                LET e(t)=1e-6
 725   IF dseval>=1e-6 THEN
             LET e(t)=dseval
 726   PRINT AT 9,26;"  "
 727   LET aux=t(t)^2/1000*e(t)
 728   LET s6=s6+aux^2
 729   LET s5=s5+aux
 730   FOR f=1 TO 23
 731    IF m(f)=0 THEN GO TO 755
 732    PRINT AT 9,26;f
 735    LET ifu=f
 740    GO SUB 3000
 745    IF falfa>=1e-6 THEN
              LET f(f,t)=falfa
 746    IF falfa<1e-6 THEN
              LET f(f,t)=1e-6
 750    LET g(f,t)=galfa
 755   NEXT f
 760  NEXT t
 765  LET det1=s1*s1-npz*s2*1000
 766  LET det4=s5*s5-npz*s6*1000
 770  REM
 775  REM The testing of the 23
          functions
 780  REM
 781  PRINT AT 13,1;
      "Testing of the function
      "
 785  FOR f=1 TO 23
 790   PRINT AT 13,25;f
 791   IF z(f)=0 OR m(f)=0
            THEN GO TO 920
 795   LET s3=0
 800   LET s4=0
 801   LET s7=0
 802   LET s8=0
 810   FOR t=1 TO npz
 815    LET aux=1000*
             LN (e(t)/f(f,t))
 820    LET s3=s3+aux
 825    LET s4=s4+aux/t(t)
 830    LET aux=f(f,t)*g(f,t)
             /1000
 831    LET s8=s8+aux*t(t)^2
             *e(t)
 832    LET s7=s7+aux
 835   NEXT t
 840   LET det2=s1*s4-s2*s3
 845   LET det3=npz*1000*s4-s1*
             s3
 846   LET det5=s5*s7-npz*s8
5*s8-1000*s6*s=s5*s8-1000*s6*s7
 850   LET aux=det2/det1
 851   IF aux<73.66-LN (hr)
        THEN LET h(f)=hr*EXP
        (aux)
 852   IF aux>=73.66-LN (hr)
        THEN LET h(f)=1e32
 855   LET o(f)=8314*det3/det1

 860   LET j(f)=det5/det4
 861   LET k(f)=det6/det4
 865   IF ABS (j(f))>1e-28 THEN
          LET q(f)=8314/j(f)
 866   IF ABS (j(f))<1e-28 THEN
          LET q(f)=1e32
 870   LET p(f)=0
 875   LET r(f)=0
 880   LET s(f)=0
 885   FOR t=1 TO npz
 890    LET p(f)=p(f)+q(f)/8314/
             t(t)+LN (hr*e(t)
             /f(f,t))
 895    LET r(f)=r(f)+ ABS (
          LN (ABS (h(f)*f(f,t)/
          hr/e(t)))-o(f)/8314/
          t(t))
 900    LET s(f)=s(f)+
          ABS (LN (ABS ((j(f)*t
          (t)^2*e(t)+k(f))/
          f(f,t)/g(f,t))))
 905   NEXT t
 906   LET p(f)=p(f)/npz
 907  IF p(f)>=73.66 THEN
                LET i(f)=0
 908  IF p(f)<73.66 THEN
                LET i(f)=1
 909  IF p(f)<73.66 THEN
          LET p(f)=EXP (p(f))
 910   LET aux=r(f)/npz
```

```
911>   IF aux<=73.66 THEN
          LET r(f)=ABS (
          EXP (r(f))-1)
 912   IF aux>73.66 THEN
          LET r(f)=1e32
 915   LET aux=s(f)/npz
 916   IF aux<=73.66 THEN
          LET s(f)=ABS (
          EXP (s(f))-1)
 917   IF aux>73.66 THEN
          LET s(f)=1e32
 920  NEXT f
 925  REM
 930  REM Results listing
 935  REM
 940  PRINT AT 17,1;
     "End of testing"
 941  PRINT AT 21,1;
      "Press ENTER to ";
      "continue"
 945  PAUSE 0
 950  IF nz<>1 THEN GO TO 980
 955   CLS
 960   PRINT AT 2,1;
      "Result listing";AT 5,1;
      "Please draw a table";
       AT 6,1;"With following ";
" headings:";AT 8,5;
      "1 No.of function";AT 9,5;
      "2 Preexponential factor";
       AT 10,7;"DISCRIM 2";
       AT 11,5;
      "3 Activation energy DISCR
IM "
 965  PRINT AT 12,5;"4 Mean devi
ation DISCRIM 2";   AT 13,5;
    "5 Preexponential factor";
     AT 14,7;"Phandis";AT 15,5;
    "6 Activation energy Phandis
";   AT 16,5;
    "7 Mean deviation Phandis"
 970  PRINT AT 21,1;
    "Press ENTER to";
    "continue"
 975   PRINT " "
 980  FOR f=1 TO 23
 985   CLS
 987   IF m(f)=1 THEN GO TO 989
 988    CLS :
        PRINT AT 3,5;
        "Function ";f;
         " unselected";
        AT 20,1;"ENTER to";
        " continue":
      PAUSE 0:
      GO TO 1040
 989   IF z(f)=0 THEN GO TO 1027
 990   PRINT AT 2,1;
       "No.heading";AT 2,15;
       "Value"
 995   PRINT AT 5,4;"1";AT 5,15;
       INVERSE 1;" ";f;" "
1000   PRINT AT 7,4;"2";AT 7,15;
       h(f)
1005   PRINT AT 8,4;"3";AT 8,15;
       o(f)/1000
1010   PRINT AT 9,4;"4";AT 9,15;
       r(f)
1015   IF i(f)=1 THEN
       PRINT AT 11,4;"5";AT 11,1
5;       p(f)
1016   IF i(f)=0 THEN
       PRINT AT 11,4;"5";AT 11,1
5;       "incalculable"
1020   PRINT AT 12,4;"6";
       AT 12,15;q(f)/1000
1025   PRINT AT 13,4;"7";
       AT 13,15;s(f)
1026   GO TO 1030
1027   PRINT AT 7,1;
       "Function ";f;
        " indefinite"
1030   PRINT AT 21,1;
      "Press ENTER to";
       "continue"
1035   PRINT " "
1040  NEXT f
1041  LET nz=nz+1
1045  CLS
1050  INPUT "Satisfactory resul"
;     "ts ?","            ";
 "        (0/1) : ";ans
1055  IF ans<>0 AND ans<>1
           THEN GO TO 1050
1060  IF ans=0 THEN GO TO 610
1070  INPUT "Plot? (0/1) : ";ans
1075  IF ans<>0 AND ans<>1
         THEN GO TO 1070
1080  IF ans=0 THEN GO TO 1275
1085   REM
1090   REM Plot
1095   REM
1100   CLS
1105   PRINT AT 1,1;
       "Plot description:";
       AT 4,3;
       "a) Left : d(Alfa)/dT";
       AT 6,6;"- Circle - exper"
;      "imental";AT 7,15;"value"
;      "s";AT 8,6?;"- Line- ";
        "calculed values"
1110   PRINT AT 11,3;"b) Right:
"       ;"Phandis plot";
       AT 13,6;"- Circle - exper
";     " imental";AT 14,15;
       "values";AT 15,6;
       "- Line- liniar";
       AT 16,15;"regresion"
1115   PRINT AT 21,1;
       "Press ENTER to";
```

```
        " continue".
1120    PRINT " "
1121    LET npgv=npg
1125    CLS :
      ? INPUT "No.of function :
";              f:
         PRINT "Plot preparatio"
;              "n"
1126    GO TO 6500
1127    LET ifu=f
1128    LET npg=npgv
1129    LET xstg=5
1130    LET xdrp=125
1131    LET npm=npz
1132    LET patern=1
1135    FOR i=1 TO npm
1139     LET t(i)=(i-1)*past+tmin
1140     LET u(i)=e(i)
1150    NEXT i
1151    LET pasg=(tmax-tmin)/
                 (npg-1)
1155    FOR i=1 TO npg
1156     LET ifu=f
1157     LET flgini=1
1160     LET v(i)=tmin+(i-1)*pasg
1165     LET u=v(i)
1166     GO SUB 5067
1167     LET alfa=seval
1170     GO SUB 3000
1175     LET w(i)=h(f)/hr*falfa*
                 EXP (-o(f)/8314
                 /v(i))
1180    NEXT i
1185    CLS
1190    GO SUB 4000
1195    LET npg=2
1196    LET tminv=tmin
1197    LET tmaxv=tmax
1200    LET xstg=130
1205    LET xdrp=250
1206    LET tmin=1e32
1207    LET tmax=-1e32
1210    FOR i=1 TO npm
1220     LET t(i)=t(i)^2*e(i)
1222     IF t(i)<tmin THEN
             LET tmin=t(i)
1224     IF t(i)>tmax THEN
           LET tmax=t(i)
1225     LET u(i)=f(f,i)*g(f,i)
1230    NEXT i
1235    LET v(1)=tmin
1240    LET v(2)=tmax
1245    LET w(1)=j(f)*v(1)+k(f)
1250    LET w(2)=j(f)*v(2)+k(f)
1255    GO SUB 4000
1256    LET npg=npgv
1257    LET tmax=tmaxv
1258    LET tmin=tminv
1260    INPUT "Another plot ?";
          " (0/1)  : ";ans
1265     IF ans<>0 AND ans<>1
              THEN GO TO 1260
1270     IF ans=1 THEN GO TO 1125
1275    INPUT "Another zone ? (0/1
)"        ;" : ";ans
1280    IF ans<>0 AND ans<>1
                THEN GO TO 1275
1285    IF ans=1 THEN GO TO 610
1290 INPUT "Another set of data
?"        ;" (0/1) : ";ans
1295 IF ans<>0 AND ans<>1
          THEN GO TO 1290
1300 IF ans=0 THEN GO TO 1309
1301 INPUT "Out on the existent
ones? (0/1) : ";ans
1302 IF ans<>0 AND ans<>1 THEN
             GO TO 1301
1303 IF ans=0 THEN GO TO 185
1304 GO TO 6000
1309 CLS
1310 REM
1315 STOP
3000

   REM Subroutine for esti-
     mating the conversion
        function and its
            integral
3002 REM
3004 IF flgini=2 THEN GO TO 3018
3006  LET uma=1-alfa
3008  LET upa=1+alfa
3010  IF alfa<>1 THEN
             LET luma=LN (uma)
3012  LET umau=uma^up3
3014  LET upau=upa^up3
3016  LET flgini=2
3018 IF ifu<=23 THEN GO TO 3026
3020  CLS
3022  PRINT "change '3000'!"
3024  STOP
3026 LET z(ifu)=1
3028 IF ifu>6 THEN GO TO 3086
3030  IF ifu>1 THEN GO TO 3036
3032   LET r=0.25
3034   GO TO 3080
3036  IF ifu>2 THEN GO TO 3042
3038   LET r=up3
3040   GO TO 3080
3042  IF ifu>3 THEN GO TO 3048
3044   LET r=0.5
3046   GO TO 3080
3048  IF ifu>4 THEN GO TO 3060
3050   IF alfa<>0 THEN
                GO TO 3056
3052    LET z(ifu)=0
```

```
3054>    RETURN
3056   LET r=1
3058   GO TO 3080
3060  IF ifu>5 THEN GO TO 3072
3062   IF alfa<>0 THEN
                    GO TO 3068
3064    LET z(ifu)=0
3066    RETURN
3068   LET r=1.5
3070   GO TO 3080
3072  IF alfa<>0 THEN
                   GO TO 3078
3074   LET z(ifu)=0
3076   RETURN
3078  LET r=2
3080  LET falfa=alfa^(1-r)/r
3082  LET galfa=alfa^r
3084  RETURN
3086 IF ifu>7 THEN GO TO 3100
3088  IF alfa<>1 THEN GO TO 3094
3090   LET z(ifu)=0
3092   RETURN
3094  LET falfa=uma
3096  LET galfa=-luma
3098  RETURN
3100 IF ifu>11 THEN GO TO 3134
3102  IF alfa<>1 THEN GO TO 3108
3104   LET z(ifu)=0
3106   RETURN
3108  IF ifu>8 THEN GO TO 3114
3110   LET r=0.25
3112   GO TO 3128
3114  IF ifu>9 THEN GO TO 3120
3116   LET r=up3
3118   GO TO 3128
3120  IF ifu>10 THEN GO TO 3126
3122   LET r=0.5
3124   GO TO 3128
3126  LET r=dp3
3128  LET falfa=uma*(-luma)^
                (1-r)/r
3130  LET galfa=(-luma)^r
3132  RETURN
3134 IF ifu>12 THEN GO TO 3148
3136  IF alfa<>0 AND alfa<>1
                  THEN GO TO 3142
3138   LET z(ifu)=0
3140   RETURN
3142  LET falfa=alfa*uma
3144  LET galfa=LN (alfa/uma)
3146  RETURN
3148 IF ifu>13 THEN GO TO 3162
3150  IF alfa<>0 AND alfa<>1
                  THEN GO TO 3156
3152   LET z(ifu)=0
3154   RETURN
3156  LET falfa=1/(umau-1)
3158  LET galfa=1.5*(1-umau)^2
3160  RETURN
3162 IF ifu>14 THEN GO TO 3176
3164>   IF alfa<>0 THEN GO TO 317
0
3166    LET z(ifu)=0
3168    RETURN
3170   LET falfa=upau^2/(upau-1)
3172   LET galfa=1.5*(upau-1)^2
3174   RETURN
3176 IF ifu>15 THEN GO TO 3190
3178  IF alfa<>0 AND alfa<>1
                  THEN GO TO 3184
3180    LET z(ifu)=0
3182    RETURN
3184   LET falfa=umau/(1-umau)
3186   LET galfa=1.5*(1-dp3*alfa
                -umau^2)
3188   RETURN
3190 IF ifu>16 THEN GO TO 3204
3192  IF alfa<>1 AND alfa<>0
                  THEN GO TO 3198
3194    LET z(ifu)=0
3196    RETURN
3198   LET falfa=-1/luma
3200   LET galfa=alfa+uma*luma
3202   RETURN
3204 IF ifu>18 THEN GO TO 3226
3206  IF alfa<>0 THEN GO TO 3212
3208    LET z(ifu)=0
3210    RETURN
3212  IF ifu>17 THEN GO TO 3218
3214    LET r=1
3216    GO TO 3220
3218   LET r=2
3220   LET falfa=alfa/r
3222   LET galfa=r*LN (alfa)
3224   RETURN
3226 IF ifu>19 THEN GO TO 3234
3228  LET falfa=umau^2
3230  LET galfa=3*(1-umau)
3232  RETURN
3234 IF ifu>20 THEN GO TO 3242
3236  LET falfa=SQR (uma)
3238  LET galfa=2*(1-falfa)
3240  RETURN
3242 IF alfa<>1 THEN GO TO 3248
3244  LET z(ifu)=0
3246  RETURN
3248 IF ifu>21 THEN GO TO 3254
3250  LET r=2
3252  GO TO 3264
3254 IF ifu>22 THEN GO TO 3260
3256  LET r=3
3258  GO TO 3264
3260 LET r=4
3262 LET flgini=1
3264 LET falfa=0.5*uma^(1-r)
3266 LET galfa=1-uma^r
3268 RETURN
3608 PRINT "Calculation of the";
" interpolation coefficients":
    LET flgrf=1
```

```
4000 REM
        Subroutine for plot
         representation
4002 REM
4004 REM Frame drawing
4006 REM
4008 PLOT xstg,yjos
4010 DRAW xdrp-xstg,0
4012 DRAW 0,ysus-yjos
4014 DRAW xstg-xdrp,0
4016 DRAW 0,yjos-ysus
4018 REM
4020 REM Stepp calculation
4022 REM
4026 LET ymax=-1e32
4027 LET xmax=-1e32
4028 LET ymin=1e32
4029 LET xmin=1e32
4030 FOR i=1 TO npm
4031  IF xmax<t(i) THEN
                  LET xmax=t(i)
4032  IF ymax<u(i) THEN
                  LET ymax=u(i)
4033  IF xmin>t(i) THEN
                 LET xmin=t(i)
4034  IF ymin>u(i) THEN
                  LET ymin=u(i)
4036 NEXT i
4038 FOR i=1 TO npg
4039  IF xmax<v(i) THEN
                 LET xmax=v(i)
4040  IF ymax<w(i) THEN
                  LET ymax=w(i)
4041  IF xmin>v(i) THEN
                 LET xmin=v(i)
4042  IF ymin>w(i) THEN
                  LET ymin=w(i)
4044 NEXT i
4045 LET scrx=(xmax-xmin)/
          (xdrp-xstg)
4046 LET scry=(ymax-ymin)/
          (ysus-yjos)
4047 IF comuta=0 THEN
       LET scry=scry*4
4048 REM
4050 REM Trace drawing
4052 REM
4054 FOR i=1 TO npm
4056  LET xm=xstg+(t(i)-xmin)/
          scrx:
      LET ym=yjos+(u(i)-ymin)/
          scry:
      CIRCLE xm,ym,2:
      IF patern=2 THEN
       CIRCLE xm,ym,1:
      IF patern=2 THEN
        PLOT xm,ym
4058 NEXT i
4060 REM
4062 REM Plot drawing
4064 REM
4066 PLOT xstg,yjos+(w(1)-ymin)/
          scry
4068 FOR i=2 TO npg
4070  DRAW (v(i)-v(i-1))/scrx,
          (w(i)-w(i-1))/scry
4072 NEXT i
4074 RETURN
5000 REM
       Subroutine for the de-
     termination of the cubi-
     cal SPLINE interpolation
          coefficients
5001 LET nm1=n-1
5002 IF n<2 THEN RETURN
5003 IF n<3 THEN GO TO 5059
5004 REM
5005 REM Building of the three
        diagonal system
5006 REM
5007 LET d(1)=x(2)-x(1)
5008 LET c(2)=(y(2)-y(1))/d(1)
5009 FOR i=2 TO nm1
5010  LET d(i)=x(i+1)-x(i)
5011  LET b(i)=2*(d(i-1)+d(i))
5012  LET c(i+1)=(y(i+1)-y(i))
          /d(i)
5013  LET c(i)=c(i+1)-c(i)
5014 NEXT i
5015 REM
5016 REM Border conditions
5017 REM
5018 LET b(1)=-d(1)
5019 LET b(n)=-d(nm1)
5020 LET c(1)=0
5021 LET c(n)=0
5022 IF n=3 THEN GO TO 5030
5023  LET c(1)=c(3)/(x(4)-x(2))-
          c(2)/(x(3)-x(1))
5024  LET c(n)=c(nm1)/(x(n)-
          x(n-2))-c(n-2)/
          (x(nm1)-x(n-3))
5025  LET c(1)=c(1)*d(1)*d(1)/
          (x(4)-x(1))
5026  LET c(n)=-c(n)*d(nm1)*
          d(nm1)/
          (x(n)-x(n-3))
5027 REM
5028 REM Forward elimination
5029 REM
5030 FOR i=2 TO n
5031  LET t=d(i-1)/b(i-1)
5032  LET b(i)=b(i)-t*d(i-1)
5033  LET c(i)=c(i)-t*c(i-1)
```

```
5034>NEXT i
5035 REM
5036 REM Backward substitution
5037 REM
5038 LET c(n)=c(n)/b(n)
5040 FOR k=1 TO nm1
5041  LET i=n-k
5042  LET c(i)=(c(i)-d(i)*
           c(i+1))/b(i)
5043 NEXT k
5044 REM
5045 REM Polynomial coefficients
         calculation
5046 REM
5047 LET b(n)=(y(n)-y(nm1))/
          d(nm1)+d(nm1)*
          (c(nm1)+2*c(n))
5048 FOR i=1 TO nm1
5049  LET b(i)=(y(i+1)-y(i))/
           d(i)-d(i)*
           (c(i+1)+2*c(i))
5050  LET d(i)=(c(i+1)-c(i))/
           d(i)
5051  LET c(i)=3*c(i)
5052 NEXT i
5053 LET c(n)=3*c(n)
5054 LET d(n)=d(nm1)
5055 RETURN
5056 REM
5057 REM Case "n=2"
5058 REM
5059 LET b(1)=(y(2)-y(1))/
          (x(2)-x(1))
5060 LET c(1)=0
5061 LET d(1)=0
5062 LET b(2)=b(1)
5063 LET c(2)=0
5064 LET d(2)=0
5065 RETURN
5066 REM
5067 REM Subroutine for esti-
       mation of the SPLINE
       and its derivate
5068 REM
5069 IF init>=1 THEN
            LET init=1
5070 IF u<x(init) THEN
              GO TO 5075
5071 IF u<=x(init+1) THEN
                 GO TO 5084
5072 REM
5073 REM Bynary search
5074 REM
5075 LET init=1
5076 LET j=n+1
5077 LET k=INT ((init+j)/2)
5078 IF u<x(k) THEN LET j=k
5079 IF u>=x(k) THEN LET init=k
5080 IF j>init+1 THEN GO TO 5077
5081 REM
5082 REM Estimation
5083 REM
5084 LET dx=u-x(init)
5085 LET seval=y(init)+dx*(
            b(init)+dx*(
            c(init)+dx*
            d(init)))
5086 LET dseval=b(init)+dx*(
             2*c(init)+3*
             dx*d(init))
5087 RETURN
6000 REM
```

Adding for the editing
the initial set of data

```
6005 REM
6006 LET l(1)=6175
6007 LET l(2)=6185
6008 LET l(3)=6220
6009 LET l(4)=6260
6010 FOR i=1 TO n
6015  LET x(i)=x(i)-273.15
6020  LET y(i)=y(i)*mtot
6025 NEXT i
6030 CLS
6035 PRINT "Heating rate :  ";TAB
 25;INT (hr*100)/100
6040 INPUT "Modify ? (0/1) : ";a
ns
6045 IF ans<>0 AND ans<>1 THEN
         GO TO 6040
6050 IF ans=0 THEN GO TO 6060
6055 INPUT "Heating rate (K/min)
 : ";hr
6056 PRINT AT 1,25;INT (hr*100)/
100
6060 PRINT "No.of intervals : ";
TAB 25;npz
6065 INPUT "Modify ? (0/1) : ";a
ns
6070 IF ans<>0 AND ans<>1 THEN
         GO TO 6065
6075 IF ans=0 THEN GO TO 6085
6080 INPUT "No.of intervals : ";
npz
6081 PRINT AT 2,25;npz
6085 PRINT "Total weight : ";TAB
 25;mtot
6090 INPUT "Modify ? (0/1) : ";a
ns
6095 IF ans<>0 AND ans<>1 THEN
         GO TO 6090
6100 IF ans=0 THEN GO TO 6110
6105 INPUT "Total weight: ";mtot
6106 PRINT AT 3,25;mtot
```

```
6110>CLS
6115 PRINT AT 2,5;"Point no."
6116 PRINT AT 4,1;"Temperature "
;TAB 15;":"
6117 PRINT AT 5,1;"Weight";TAB 1
5;":"
6120 PRINT AT 8,1;"1 - Will be
                     kept"
6125 PRINT AT 10,1;"2 - Will be
                     modified"
6130 PRINT AT 12,1;"3 - Will be
                     erased"
6135 PRINT AT 14,1;"4 - Will be
                   added in ";
         AT 16,1;"front of";
        AT 17,1;?"previous data"
6140 LET i=1
6141 IF i>n THEN GO TO 6325
6145 PRINT AT 1,20;"  ";AT 2,20;
i
6150 PRINT AT 4,17;"
 ";AT 4,17;x(i)
6155 PRINT AT 5,17;"
 ";AT 5,17;y(i)
6160 INPUT "Option (1/2/3/4) : "
;j
6165 IF j<>1 AND j<>2 AND
        j<>3 AND j<>4 THEN
        GO TO 6160
6170 GO TO 1(j)
6174 REM
6175 REM Will be kept
6176 REM
6180 LET i=i+1
6181 GO TO 6141
6184 REM
6185 REM Will be modified
6186 REM
6190 INPUT "Temperature (C) : ";
x(i)
6191 IF i=1 THEN GO TO 6195
6192 IF x(i)<x(i-1) THEN
              GO TO 6190
6195 PRINT AT 4,17;"
 ";AT 4,17;x(i)
6200 INPUT "Weight : ";y(i)
6201 IF i=1 THEN GO TO 6205
6202 IF y(i)<y(i-1) THEN
             GO TO 6200
6205 PRINT AT 5,17;"
 ";AT 5,17;y(i)
6210 LET i=i+1
6215 GO TO 6141
6219 REM
6220 REM Will be erased
6221 REM
6225 LET n=n-1
6230 FOR j=i TO n
6235  LET x(j)=x(j+1)
6240  LET y(j)=y(j+1)
6245 NEXT j
6255 GO TO 6141
6259 REM
6260 REM Will be added in front
        of the previous data
6261 REM
6265 IF n<30 THEN GO TO 6290
6270 PRINT AT 20,1;"You can not
          anymore!";AT 21,1;"Pr
ess ENTER to continue"
6275 PAUSE 0
6280 PRINT AT 20,1;"
   ";AT 21,1;"
         "
6285 GO TO 6141
6290 FOR j=1 TO n-i+1
6291  LET k=n-j+1
6295  LET x(k+1)=x(k)
6300  LET y(k+1)=y(k)
6305 NEXT j
6310 LET n=n+1
6320 GO TO 6185
6324 REM
6325 REM Normalization
6326 REM
6330 FOR i=1 TO n
6335  LET x(i)=x(i)+273.15
6340  LET y(i)=y(i)/mtot
6345 NEXT i
6350 GO TO 224
6500 REM

        Adding to check,select,
           verify the function
           before potting
6505 REM
6510 IF m(f)=1 AND z(f)=1 THEN
        GO TO 1127
6515  CLS
6520  PRINT "Function ";f;
            " indefinite or ",
          "     unselected";
        AT 20,1;
        "Press ENTER to continue"
6525  PAUSE 0
6530  GO TO 1125
```