Thermochimica Acta, 185 (1991) 129–134
Elsevier Science Publishers B.V., Amsterdam

BASIC VERSATILE program for nonisothermal kinetics Part II

N. Dragoe [a] and E. Segal [b]

[a] *Department of Inorganic Chemistry, Faculty of Chemistry, University of Bucharest, Str. Dumbrava Roşie nr. 23, Bucharest (Romania)*
[b] *Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, Bulevardul Republicii 13, Bucharest (Romania)*

(Received 27 November 1990)

Abstract

A program to evaluate nonisothermal kinetic parameters by means of nine methods selected from the literature, in addition to generating the thermogravimetric curves, is presented.

INTRODUCTION

In a previous paper [1], a VERSATILE program was presented for automatically processing thermogravimetric data to estimate values of the nonisothermal kinetic parameters with the aid of six methods: those according to Kissinger [2], Freeman–Carroll [3], Coats–Redfern [4], Flynn–Wall for $\alpha = \text{const.}$ (α, degree of conversion) [5], Flynn–Wall for $\beta = \text{const.}$ (β, heating rate) [5] and Flynn–Wall for $T = \text{const.}$ [5]. Later on, programs to evaluate nonisothermal kinetic parameters using a variant of the Coats–Redfern method [6] according to Urbanovici and Segal [7], as well as to generate TG and DTG curves using the estimated values of the nonisothermal kinetic parameters [8], were worked out. All these programs are based mainly on the optimization of the kinetic parameter values using the least squares method. The optimum values of the nonisothermal kinetic parameters correspond to the maximum absolute value of the correlation coefficient of the linear regression.

THE PROGRAM

In this paper, a perfected variant of the previous programs, VERSATILE 2, is presented. The following advantages recommend the use of this variant.

0040-6031/91/$03.50

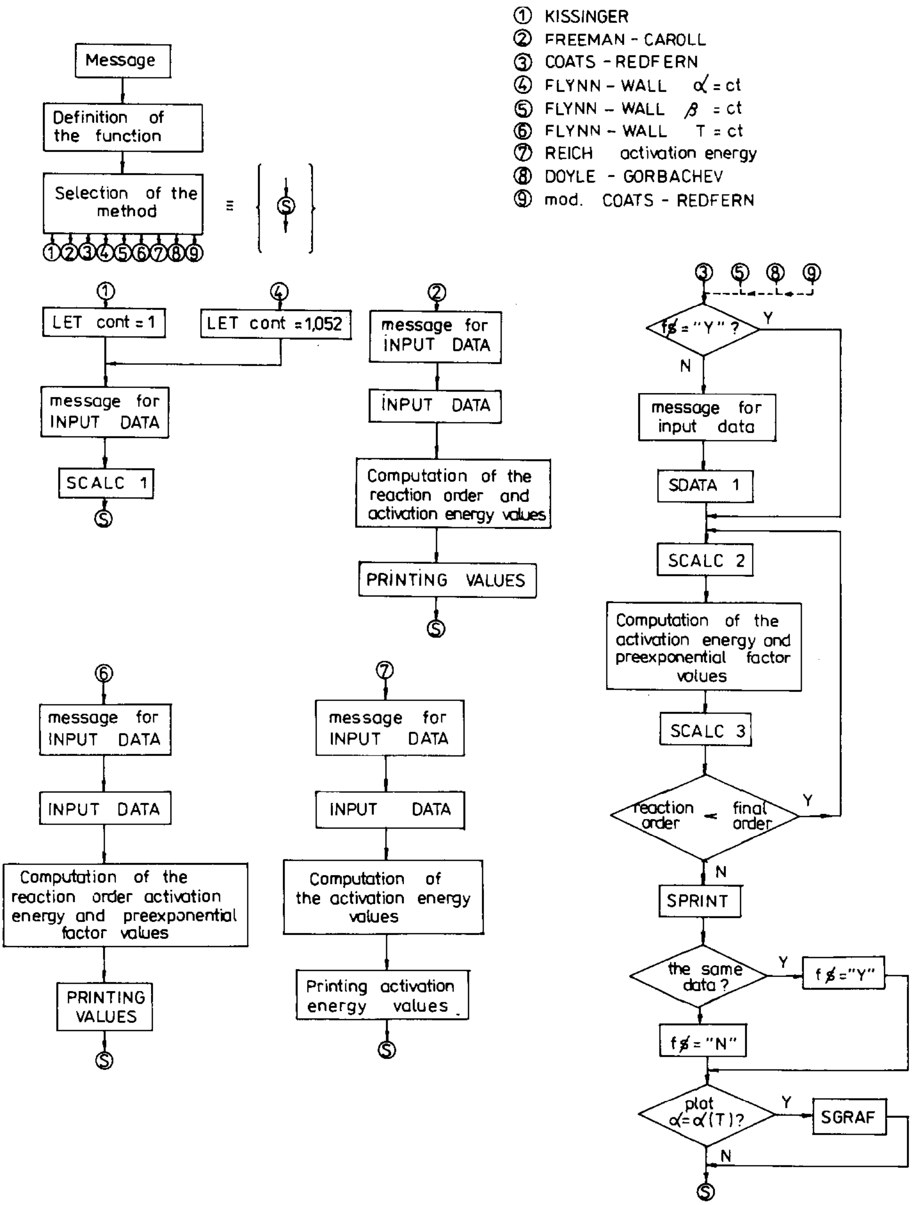

Fig. 1. Flow chart.

1. Nine methods are used to evaluate the nonisothermal kinetic parameters, the modified Coats–Redfern method [7], Reich method [9] and Doyle–Gorbachev method [10] being added to the old program [1].

2. For the integral methods, the experimental data are introduced only once.

3. After the evaluation of the nonisothermal kinetic parameters by means of the Coats–Redfern and Flynn–Wall (β = const.) methods, at the wish of

TABLE 1

Selection of the method

SCALC 1	Subroutine for calculation of the activation energy and printing its value; if the variable cont equals unity the E value according to Kissinger's method is calculated, and if cont = 1.052 the E value according to the Flynn–Wall method for isoconversion is calculated
$f\$$	Alphanumeric variable used in the storage of data
SDATA 1	Subroutine for input data (integral methods)
SCALC 2	Subroutine for calculation of the slope and intercept of the straight line $y = y(x)$; for each method the values y and x are initialized
SCALC 3	Subroutine which calculates the correlation coefficient and retains the values E, n and A for the best correlation
SPRINT	Subroutine for printing values
SGRAF	Subroutine for generation of $\alpha = \alpha(T)$ curves according to the Coats–Redfern method and the Flynn–Wall method for constant heating rate

the operator the computer generates the TG curve on which the experimental points could be placed.

The flow chart is given in Fig. 1, the selection procedure is shown in Table 1, and the program is given in Appendix 1.

The program is conversational. The selection of the method for computers from the ZX SPECTRUM family is made by moving a pointer using the keys 6 (to move the pointer down) and 7 (to move the pointer up). After the operator presses the key W, the computer starts to work out the data by means of the chosen methods.

The program was run on a TIM S computer, and was used for the estimation of the nonisothermal kinetic parameters of the thermal decomposition of some coordination compounds [11]

REFERENCES

1 E. Segal and T. Coseac, Rev. Roum. Chim., 34 (1989) 287.
2 M.E. Kissinger, Anal. Chem., 29 (1957) 1702.
3 E.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
4 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
5 J.H. Flynn and L.A. Wall, Polym. Lett., 4 (1966) 68.
6 T. Coseac and E. Segal, Bul. Inst. Politeh. Bucureşti Ser. Chim.-Metal. (in press).
7 E. Urbanovici and E. Segal, Thermochim. Acta, 80 (1984) 389.
8 T. Coseac and E. Segal, Rev. Roum. Chim. (in press).
9 L. Reich, Polym. Lett., 2 (1964) 621.
10 (a) C.D. Doyle, Nature (London), 207 (1965) 290; (b) V.M. Gorbachev, J. Therm. Anal., 8 (1975) 340.
11 N. Dragoe, M. Andruch, A. Meghea and E. Segal, Thermochim. Acta, 161 (1990) 259.

APPENDIX 1

```
--------------------------------

        ESTIMATION OF
    NON-ISOTHERMAL KINETIC
         PARAMETERS

--------------------------------

   3 CLS : LET f$="n": LET lin=2

   4 BORDER 5: PAPER 5: INK 1
  15 FOR i=0 TO 7
  16 READ m
  18 POKE USR "a"+i,m: NEXT i
  20 DATA 0,BIN 10,BIN 01100100,
BIN 10011000,BIN 10011000,BIN 10
010100,BIN 1100010,0
  25 CLS : PRINT AT 0,0; BRIGHT
1;"          VERSATILE 2        "'"s
election of the methods "; BRIGH
T 0;AT 3,1;"KISSINGER";AT 4,1;"F
REEMAN-CAROLL";AT 5,1;"COATS-RED
FERN";AT 6,1;"FLYNN-WALL,alpha=c
onst";AT 7,1;"FLYNN-WALL,heating
 rate=const";AT 8,1;"FLYNN-WALL,
T=const";AT 9,1;"REICH,act. ener
gy";AT 10,1;"DOYLE-GORBACHEV";AT
 11,1;"COATS-REDFERN,mod.";AT 13
,1;"STOP";AT 18,0;"7-UP"'"6-DOWN
"'"w-WORK  "
  26 DEF FN m(a,b,c,e,n)=(e-a*c/
n)/(b-a*a/n)
  27 DEF FN o(a,b,c,e,n)=(c*b-a*
e)/(n*b-a*a)
  28 DEF FN r(a,b,c,d,e,n)=(e-a*
c/n)/SQR (b-ABS a^2/n)/(SQR (d-A
BS c^2/n))
  29 DEF FN f(a,n)=(1-(1-a)^(1-n
))/(1-n)
  30 DEF FN g(a)=-LN (1-a)
  50 PRINT AT lin,0;">": PAUSE 2
5: BEEP .005,-10
  51 FOR i=2 TO 14: PRINT AT lin
,0;" ": NEXT i
  55 IF INKEY$="w" OR INKEY$="W"
 THEN  GO TO (lin-2)*100+46
  58 IF INKEY$="6" THEN  IF lin<
>14 THEN  LET lin=lin+1
  60 IF INKEY$="7" THEN  IF lin<
>2 THEN  LET lin=lin-1
  70 GO TO 50
 150 CLS : PRINT AT 3,1; BRIGHT
1;"KISSINGER"; BRIGHT 0;'''"numb
er of points"'"values(T,heating
rate)"
 151 LET cont=1
 155 GO SUB 2000
 160 BEEP .08,-10: PRINT '; FLAS
H 1;"press any key": FLASH 0: PA
USE 0: CLS : GO TO 25
 250 CLS : PRINT AT 3,1; BRIGHT
1;"FREEMAN-CAROLL"; BRIGHT 0;'''
';" number of points"'" heating
rate"''" values (T,TG,DTG)"'''''
'"OBS:"''"first value for alpha=
0"'"last value for alpha=1"

 255 INPUT vm,v
 260 DIM t(vm): DIM a(vm): DIM m
(vm)
 265 FOR i=1 TO vm: PRINT i: INP
UT t,m(i),a(i): LET t(i)=t+273:
NEXT i
 266 CLS : PRINT AT 9,5;"ATENTIO
N - WORKING !"
 270 LET s6=0: LET s1=0: LET s2=
0: LET s3=0: LET s4=0: LET s5=0
 280 FOR i=2 TO vm-1
 285 LET a1=(m(i)-m(1))/(m(vm)-m
(1))
 286 FOR j=i+1 TO vm-1
 287 LET a2=(m(j)-m(1))/(m(vm)-m
(1))
 290 LET x=(1/t(j)-1/t(i))/LN ((
1-a2)/(1-a1))
 295 LET y=LN (a(j)/a(i))/LN ((1
-a2)/(1-a1))
 300 LET s1=s1+x: LET s2=s2+x*x:
 LET s3=s3+y: LET s4=s4+y*y: LET
 s5=s5+y*x: LET s6=s6+1
 310 NEXT j: NEXT i
 320 LET n=FN o(s1,s2,s3,s5,s6):
 LET e=-1.986*FN m(s1,s2,s3,s5,s
6): LET r=FN r(s1,s2,s3,s4,s5,s6
): LET zm=0
 335 FOR i=1 TO vm-1
 336 LET z=v*(m(i+1)-m(i))/(t(i+
1)-t(i))/(m(vm-m(1))*EXP (e/1.98
6/t(i))/((m(vm)-m(i))/(m(vm)-m(1
)))^n)/60
 338 LET zm=zm+z: NEXT i
 339 LET zm=zm/(vm-1)*10^-20
 340 PRINT "VALUES"'"AE-20=";z'"
n=";n'"E=";e
 341 GO TO 160
 348 IF f$="y" OR f$="Y" THEN  G
O SUB 2125
 349 LET cont=1: IF f$="y" OR f$
="Y" THEN  GO TO 361
 350 CLS : PRINT AT 3,1; BRIGHT
1;"COATS-REDFERN"; BRIGHT 0;'''"
 number of points"'"first value
n (reaction order)"'"last value
n"'" step n"'"heating rate "'''"
VALUES (T,TG)"''''"OBS:"'"first v
alue for alpha=0"'"last value fo
r alpha=1"
 360 GO SUB 2100
 361 GO SUB 2135
 365 LET j=j+1: LET e(j)=-1.986*
FN m(s1,s2,s3,s5,s6): LET z(j)=e
(j)*v*EXP (FN o(s1,s2,s3,s5,s6)-
20*LN 10)/1.986/60
 370 GO SUB 1920
 385 IF n<=nms+.0001 THEN  GO TO
 361
 395 GO SUB 1950
 396 GO SUB 1900
 397 INPUT "graphic alpha=f(T)?
(y/n)";a$
 405 IF a$="y" THEN  GO TO 1700
 406 GO TO 160
 450 CLS : PRINT AT 3,1; BRIGHT
1;"FLYNN-WALL,alpha=ct."; BRIGHT
 0;'''"conversion"''''"values(te
mp.,heating rate)"

 455 INPUT a
 460 LET cont=1.052
 470 GO SUB 2000
 475 GO TO 160
 546 LET cont=0
 547 IF f$<>"y" THEN  IF f$<>"Y"
 THEN  GO TO 550
 548 GO SUB 2125
 549 GO TO 571
 550 CLS : PRINT AT 3,1; BRIGHT
1;"FLYNN-WALL
         alpha=const          ";
 BRIGHT 0;'''" number of points"
```

```
'"first value n (reaction order)
"'"last value n"'" step n"'"heat
ing rate "''''"VALUES (T,TG)"''''"
OBS:"'"first value for alpha=0"'
"last value for alpha=1"
 570 GO SUB 2100
 571 GO SUB 2135
 580 LET j=j+1: LET e(j)=-1.986/
1.052*FN m(s1,s2,s3,s5,s6): LET
z(j)=1.986/60*v*EXP (FN o(s1,s2,
s3,s5,s6)-20*LN 10+5.33)/e(j)
 585 GO SUB 1920
 595 IF n<(nms+.001) THEN  GO TO
 571
 596 GO SUB 1950
 600 GO SUB 1900
 601 INPUT "graphic alpha=f(T)?
(y/n)";a$
 610 IF a$="y" OR a$="Y" THEN  G
O TO 1700
 620 GO TO 160
 650 CLS : PRINT AT 3,1; BRIGHT
1;"FLYNN-WALL,T=ct."; BRIGHT 0;'
'"number of points"'"first value
 for n"'"last value for n"'"step
 n"'"temp."''''"  VALUES "'"heati
ng rate"'"mass gas"
 655 INPUT vm,nm,nms,p,t: LET nr
=INT ((nms-nm)/p+1)
 656 DIM v(vm): DIM c(vm): DIM a
(vm): DIM b(vm): DIM m(nr): DIM
n(nr): DIM r(nr)
 660 FOR i=1 TO vm: PRINT i: INP
UT v(i),c(i),a(i),b(i): NEXT i
 665 LET r=0: LET m2=10^10: LET
n=nm: LET j=0
 667 LET s1=0: LET s2=0: LET s3=
0: LET s4=0: LET s5=0
 668 PRINT AT 8,4;"            ";A
T 8,4;"order=";n
 669 FOR i=1 TO vm
 670 LET x=LN v(i): LET a=(c(i)-
a(i))/(b(i)-a(i))
 675 IF ABS (n-1)<.0001 THEN  GO
 TO 685
 680 LET y=LN (FN f(a,n)): GO TO
 690
 685 LET y=LN (FN g(a))
 690 LET s1=s1+x: LET s2=s2+x*x:
 LET s3=s3+y: LET s4=s4+y*y: LET
 s5=s5+x*y
 691 NEXT i
 692 LET j=j+1: LET n(j)=n: LET
m(j)=FN m(s1,s2,s3,s5,vm): LET r
(j)=FN r(s1,s2,s3,s4,s5,vm)
 695 IF r(j)>r THEN  GO TO 705
 700 LET r=r(j): LET no=n(j): LE
T m1=m(j)
 705 IF ABS (m(j)+1)>ABS (m2+1)
THEN  GO TO 715
 710 LET m=m(j): LET nov=n(j): L
ET r1=r(j): LET m2=m(j)
 715 LET n=n+p: IF n<=nms+.001 T
HEN  GO TO 667
 720 PRINT "VALUES"''''''"report
ed to r:"''"n=";no'"m=";m1'"r=";
r''''"reported to m"''"n=";nov'"
m=";m2'"r=";r1
 725 PRINT ''; FLASH 1;"press an
y key": PAUSE 0: FLASH 0: RUN
 750 CLS : PRINT AT 3,1; BRIGHT
1;"REICH, activation energy"; BR
IGHT 0;''"alpha=constant"''''''"
number of curves"''"VALUES:"'"he
ating rate"'"temp."
 755 INPUT q
 760 DIM a(q): DIM t(q): FOR i=1
 TO q: INPUT a(i),t: LET t(i)=t+
273: NEXT i
 785 LET num=0: LET e=0: DIM e(q
,q)
 786 CLS
 790 FOR i=1 TO q
 795 FOR j=i+1 TO q
 800 LET e(i,j)=(1.986*LN ((a(j)
*t(i)^2)/a(i)/t(j)^2))/(1/t(i)-1
/t(j))
 805 PRINT e(i,j): LET num=num+1

 810 LET e=e+e(i,j)
 815 NEXT j: NEXT i
 820 PRINT : PRINT "on an averag
e"';e/num
 825 GO TO 160
 846 IF f$="y" OR f$="Y" THEN  G
O SUB 2125
 847 LET cont=1: IF f$="y" OR f$
="Y" THEN  GO TO 865
 850 CLS : PRINT AT 3,1; BRIGHT
1;"  DOYLE-GORBACHEV "; BRIGHT 0
;'''" number of points"'"first v
alue n (reaction order)"'"last v
alue n"'" step n"'"heating rate
"''''"VALUES (T,TG)"''''"OBS:"'"fi
rst value for alpha=0"'"last val
ue for alpha=1"
 860 GO SUB 2100
 865 GO SUB 2135
 870 LET j=j+1: LET e(j)=-1.986*
FN m(s1,s2,s3,s5,s6): LET z(j)=(
e(j)+2*1.986*(ABS (t(vm)-t(1))/2
))*v*EXP (FN o(s1,s2,s3,s5,s6)-2
0*LN 10)/1.986/60
 880 GO SUB 1920
 890 IF n<=(nms+.0001) THEN  GO
TO 865
 895 GO SUB 1950
 896 GO SUB 1900
 898 INPUT "graphic  ~ Coats-Red
f. ? (y/n)";a$: IF a$="y" OR a$=
"Y" THEN  GO TO 1700
 900 GO TO 160
 946 IF f$<>"y" OR f$="Y" THEN
GO TO 950
 947 GO SUB 2125
 948 GO TO 956
 950 CLS : PRINT AT 3,1; BRIGHT
1;"  COATS-REDFERN  (mod)"; BRIG
HT 0;'''" number of points"'"fir
st value n (reaction order)"'"la
st value n"'" step n"'"heating r
ate "''''"VALUES (T,TG)"''''"OBS:"
'"first value for alpha=0"'"last
 value for alpha=1"
 955 GO SUB 2100
 956 DIM I(vm-1)
 960 LET I(1)=0: LET r=2
 970 LET s1=0: LET s2=0: LET s3=
0: LET s4=0: LET s5=0
 975 FOR i=2 TO vm-1
 980 LET x=1/t(i): LET a=(m(i)-m
(1))/(m(vm)-m(1))
 985 LET b=(m(i-1)-m(1))/(m(vm)-
m(1))
 995 LET I(i)=I(i-1)+(a-b)/2*(1/
(1-a)^n/t(i)^2+1/(1-b)^n/t(i-1)^
2)
1000 LET y=LN I(i)
1009 PRINT AT 8,4;"            ";A
T 8,4;"order=";n
1010 LET s1=s1+x: LET s2=s2+x*x:
 LET s3=s3+y: LET s4=s4+y*y: LET
 s5=s5+x*y
1011 NEXT i
1020 LET j=j+1: LET e(j)=-1.986*
FN m(s1,s2,s3,s5,vm-2): LET z(j)
```

```
=e(j)*v*EXP (FN o(s1,s2,s3,s5,vm
-2)-20*LN 10)/1.986/60
1030 GO SUB 1920
1040 IF n<=(nms+.001) THEN  GO T
O 970
1041 GO SUB 1950
1042 GO SUB 1900
1050 GO TO 25
1150 CLEAR : STOP
1250 GO TO 25
1700 CLS : BEEP .05,20: LET z=z*
10^20
1704 IF lin=7 THEN  GO TO 1905
1705 IF no<>1 THEN  GO TO 1730
1706 RESTORE 1710: READ h$
1710 DATA "1-EXP (-z*1.986*x^2*6
0*EXP (-e/1.986/x)/v/e)"
1725 GO TO 1740
1730 RESTORE 1732: READ h$
1732 DATA "1-(1-(1-no)*z*1.986*6
0*x*x*EXP (-e/1.986/x)/v/e)^(1/(
1-no))"
1740 PLOT 31,168: DRAW 0,-153 :
DRAW 216,0
1745 FOR i=0 TO 3
1746 PLOT 31+52.5*i,12: DRAW 0,3
: PAUSE 3
1747 PRINT AT 21,(2+7*i);(INT (t
(1)+i*(t(vm)-t(1))/4))-273
1750 NEXT i
1760 PRINT AT 1,0;"(a)";AT 2,1;"
%";AT 21,28;"T(C)": REM
*******************************

 this "a" is alpha !!  ( PRESS
KEY "a" OR "A" in GRAPHIC MODE )
,   and anywhere in this program
 , when you would  like to use
the   charachtere  alpha

          //for example in the ti
tle of the methods //

1770 FOR i=0 TO 3
1775 PRINT AT 19-4.25*i,1;25*i
1780 PLOT 28,16+36*i: DRAW 3,0
1790 NEXT i
1800 PLOT 28,167: DRAW 3,0
1805 FOR i=0 TO 207
1810 LET x=t(1)+i*(t(vm)-t(1))/2
07
1811 PLOT 32+i,15+152*VAL h$
1840 NEXT i
1860 FOR i=1 TO vm
1865 LET w=31+((t(i)-t(1))/(t(vm
)-t(1))*207): LET wy=15+((m(i)-m
(1))/(m(vm)-m(1))*152)
1867 INK 2: PLOT w,wy: CIRCLE w,
wy,2
1870 NEXT i
1880 STOP
1890 INK 1: CLS : GO TO 21
1900 INPUT "       KEEP THE DATA
?                  (y/n)  ";f$
1901 RETURN
1905 IF no<>1 THEN  GO TO 1915
1906 RESTORE 1910: READ h$
1910 DATA "1-EXP (-z*e/v/1.986*6
0*(10^(-2.315-0.457*e/1.986/x)))
"
1911 GO TO 1740
1915 RESTORE 1918: READ h$
1918 DATA "1-((no-1)*z/1.986/v*6
0*e*(10^(-2.315-0.457*e/1.986/x)
)+1)^(1/(1-no))"
1919 GO TO 1740
1920 LET r(j)=FN r(s1,s2,s3,s4,s
5,vm-2)
1921 IF r(j)>r THEN  GO TO 1930
1925 LET e=e(j): LET r=r(j): LET
 z=z(j): LET no=n
1930 LET n=n+p
1935 RETURN
1950 BEEP .8,10: PRINT  BRIGHT 1
;'"VALUES"'' BRIGHT 0;"Ea(cal/mo
l)=";e'"AE-20(1/sec)=";z'"reacti
on order=";no'"correlation coeff
icint r=";r
1960 RETURN
2000 INPUT vm
2002 DIM t(vm): DIM v(vm): LET s
t=1
2010 FOR i=1 TO vm: PRINT i: INP
UT t,v(i): LET t(i)=t+273: NEXT
i
2020 PAUSE 10: CLS : PRINT AT 9,
3;"   ATENTION - WORKING  !"
2030 LET s1=0: LET s2=0: LET s3=
0: LET s4=0: LET s5=0
2035 FOR i=1 TO vm
2037 IF cont=1 THEN  LET st=t(i)
^2
2038 LET x=1/t(i): LET y=LN (v(i
)/st)
2045 LET s1=s1+x: LET s2=s2+x*x:
 LET s3=s3+y: LET s4=s4+y*y: LET
 s5=s5+y*x
2050 NEXT i
2060 LET e=-1.986/cont*FN m(s1,s
2,s3,s5,vm): LET r=FN r(s1,s2,s3
,s4,s5,vm)
2070 PRINT "E=";e'"r=";r
2075 RETURN
2100 INPUT vm,nm,nms,p,v
2110 LET nr=INT ((nms-nm)/p+1)
2115 DIM t(vm): DIM m(vm): DIM e
(nr): DIM r(nr): DIM z(nr)
2120 FOR i=1 TO vm: PRINT i: INP
UT t,m(i): LET t(i)=273+t: NEXT
i
2125 CLS : PRINT AT 6,3;"  ATENT
ION - WORKING !"
2130 LET s6=vm-2: LET r=0: LET n
=nm: LET j=0
2132 RETURN
2135 LET s1=0: LET s2=0: LET s3=
0: LET s4=0: LET s5=0
2140 FOR i=2 TO vm-1
2141 LET st=1
2142 IF cont=1 THEN  LET st=t(i)
^2
2145 LET x=1/t(i): LET a=(m(i)-m
(1))/(m(vm)-m(1))
2149 PRINT AT 8,4;"           ": P
RINT AT 8,4;"order=";n
2150 IF ABS (n-1)<10^-4 THEN  GO
 TO 2160
2155 LET y=LN ABS ((FN f(a,n)/st
)): GO TO 2165
2160 LET y=LN (FN g(a)/st)
2165 LET s1=s1+x: LET s2=s2+x*x:
 LET s3=s3+y: LET s4=s4+y*y: LET
 s5=s5+y*x
2170 NEXT i
2175 RETURN
2180 REM  nov.1989

---------------------------------

           GOOD LUCK !

---------------------------------
```