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Calculation of activation energy and pre-exponential factors from rising temperature data and the generation of TG and DTG curves from *A* and *E* values

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Abstract

After reviewing present methods of evaluating E, the activation energy, and A, the pre-exponential constant, and pointing out some of the inherent weaknesses of the method, a technique is outlined whereby a DTG and/or TG curve may be produced for direct comparison with experimental curves by assuming values for A and E and using finite difference techniques to produce such a curve.

INTRODUCTION

In isothermal studies of solid state decompositions, the rate constant k is usually represented by an equation of the form

$$g(\alpha) = kt \tag{1}$$

where $g(\alpha)$ is some function of the fraction reacted at time t at some constant temperature T (in degrees absolute). The function $g(\alpha)$ can take different forms depending on the reaction occurring, and such forms have been summarized by Keattch and Dollimore [1] and by Brown [2]. The value of k at different temperatures for the same reaction is generally assumed to be governed by the Arrhenius equation

$$k = A \exp(-E/RT) \tag{2}$$

where E is the activation energy associated with the process, R is the gas constant and A is the pre-exponential constant. In using rising temperature kinetic evaluations, the function $g(\alpha)$ is usually not known, and one way of designating $g(\alpha)$ is to perform calculations of k using all available functions $g(\alpha)$ and determine which gives the best Arrhenius plot. This is a tedious procedure and necessitates computer programming. Alternatively, one may run a single isothermal experiment and determine the form of $g(\alpha)$ by the method of Jones et al. [3] or Sharp et al. [4]. However, there is no guarantee that the kinetics of isothermal decomposition follow the same $g(\alpha)$ as in

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rising temperature experiments. In deducing the kinetic evaluation of rising temperature data, one further difficulty is the evaluation of the integral

$$\int_0^T e^{-E/RT}\, dT$$

which arises if the integral equation (eqn. (1)) is used in the calculations. In the method described here, a computer program is outlined which allows a TG curve (or α–T curve) to be reconstructed and compared with experimental data. Furthermore, the method is based not on the integral equation (eqn. (1)) but on the differential form of the equation.

THEORY AND CALCULATION

If eqn. (1) is differentiated

$$\frac{1}{f(\alpha)} \cdot \frac{d\alpha}{dt} = k = A \exp\left(\frac{-E}{RT}\right) \tag{3}$$

where $f(\alpha)$ is the reciprocal of the differentiation of $g(\alpha)$ with respect to α and $d\alpha/dt$ is the differentiation of α with respect to time.

In the rising temperature experiments the time is not explicit; temperature is used as one axis, so it is necessary to know the relationship of T with t, and this is usually of the form

$$T = T_0 + \beta t \tag{4}$$

where β is the rate of heating (in degrees per second) and T_0 is the starting temperature; t is the time of heating. By differentiation

$$\frac{dT}{dt} = \beta \tag{5}$$

It is possible to write

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT} \cdot \frac{dT}{dt} \tag{6}$$

or

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT} \cdot \beta \tag{7}$$

Using eqn. (7) in eqn. (3)

$$\frac{(d\alpha/dT) \cdot \beta}{f(\alpha)} = k \tag{8}$$

or

$$\frac{d\alpha}{dT} = \frac{A \exp(-E/RT) \cdot f(\alpha)}{\beta} \tag{9}$$

Taking logarithms gives

$$\ln k = \ln(\mathrm{d}\alpha/\mathrm{d}T) - \ln f(\alpha) + \ln \beta \qquad (10)$$

giving the relationship between the rising temperature and k. The final term is a constant, $\mathrm{d}\alpha/\mathrm{d}T$ is the slope of the plot of α against T, and $f(\alpha)$ can be calculated at each point at which $\mathrm{d}\alpha/\mathrm{d}T$ is measured by using that particular value of α. The values of A and E can then be calculated by plotting $\ln k$ against $1/T$ using the logarithmic form of eqn. (2).

FINITE DIFFERENCE METHODS

Although most of the differential equations discussed cannot be solved by standard mathematical techniques, very close approximations to such solutions can be obtained using finite difference methods. One of the present authors (F.W.W.) has used the method successfully to predict the effect of heat transfer on a typical DTA curve [5].

The method consists essentially of taking very small increments in the variable, in this case time, and calculating the fractional amount reacted in that increment of time. Initially α is given the value zero, or a very small value, should zero make the solving of the reaction equation impossible, and a suitably low temperature is chosen at which the reaction rate is negligible. The time is incremented and the value of the fractional amount reacted is calculated. Time is again incremented, adjustments being made to the temperature, where $T = T_0 + \beta t$.

The previous value of $\mathrm{d}\alpha$ is added to α and this is used as the new value of α for the next calculation. The process is repeated until α equals or approaches unity. The process is one of iteration, and would be very time consuming if carried out manually. It is an ideal situation for a computer and programs have been developed to accommodate most of the suggested reaction equations.

There are, however, a number of points which need careful consideration when using the technique. The time step chosen must be as small as possible. Large time steps can lead to distorted and erroneous results. Unfortunately, the smaller the time step, the slower is the completion of the program. Hence values of the time step must be chosen as a compromise. A comparison of the results using two different time steps, one an order of magnitude greater than the other, will ascertain whether a given choice is suitable. If the results are widely different then a comparison between the lower value and another an order of magnitude less should be made. The process is repeated until there are no significant differences between the results, using both time steps. It is then safe to use the higher value.

Errors can arise if the chosen starting temperature is too high. This will distort the whole curve, but the error can be detected by a close examination of the initial part of the $\mathrm{d}\alpha/\mathrm{d}T$ vs. temperature curve (the DTG curve). If

TABLE 1

Values of α at $(d\alpha/dT)_{max}$ for different equations at different heating rates (β)

Equation		β	α at $(d\alpha/dT)_{max}$
1. A_2	$[-\ln(1-\alpha)]^{1/2}$	5	0.6247
A_2		10	0.6245
A_2		15	0.6250
2. A_3	$[-\ln(1-\alpha)]^{1/3}$	5	0.6295
A_3		10	0.6306
A_3		15	0.6312
3. A_4	$[-\ln(1-\alpha)]^{1/4}$	10	0.6340 [a]
4. B_1	$\ln[\alpha/(1-\alpha)]$	10	0.5422
5. D_1	α^2	10	1.0000
6. D_2	$(1-\alpha)\ln(1-\alpha)+\alpha$	10	0.8151
7. D_3	$[1-(1-\alpha)^{1/3}]^2$	10	0.6762
8. D_4	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	10	0.7541
9. E_1	$\ln\alpha$	10	1.0000
10. F_1	$-\ln(1-\alpha)$	10	0.6149
F_1		15	0.6142
11. F_2	$1/(1-\alpha)$	10	0.4783
12. F_3	$[1/(1-\alpha)]^2$	10	0.3963
13. P_1	$\alpha^{1/n}$ $(n=1)$	10	1.0000
14. R_2	$1-(1-\alpha)^{1/2}$	10	0.7384
15. R_3	$1-(1-\alpha)^{1/3}$	10	0.6903

[a] See ref. 6.

the initial part of the curve has a slope greater than most of the early part of the curve, this indicates that the starting temperature chosen was too high. The initial part of the curve should increase in slope gradually.

THE COMPUTER PROGRAM

The program prints out a list of temperature (°C), α (fraction reacted) and $(d\alpha/dt)/\beta$ i.e. $d\alpha/dT$ (T being temperature). If $d\alpha/dt$ is required then this can easily be accomplished. The graph-drawing program prints out the maximum value of $d\alpha/dt$ or $d\alpha/dT$. The curves can be normalized by dividing the values of $d\alpha/dt$ (or $d\alpha/dT$) by $(d\alpha/dt)_{max}$ (or $(d\alpha/dT)_{max}$).

A brief description of the program is as follows. Equation (9) is rewritten in the form

$$d\alpha = A\exp(-E/RT)\cdot f(\alpha)\,dt \tag{11}$$

The required function $f(\alpha)$ is used and the iteration process is commenced by giving E, R and T initial values. α is set at zero, unless by so doing the equation will not operate, when a small value, say 0.00001, is used. Using these values the value of $d\alpha$ is computed. This value of $d\alpha$ is added to that of α and used in the next computation in $f(\alpha)$. Temperature (absolute) is upgraded by adding β times dt to the T used in the previous calculation. Again $d\alpha$ is computed. This value is again added to α to make the value of α to be used in the next calculation. Again T is upgraded as before and a new value of $d\alpha$ is calculated. The process is repeated until the temperature reaches the final temperature. The results are stored on a disc, usually at every $2°C$ step, although at longer intervals when there is little reaction occurring. The data stored is α, $d\alpha/dT$ (that is, the computed value of $d\alpha$ divided by dT). The process can be repeated for any given values of A and E, for as many different functions $f(\alpha)$ as required to be tested. In drawing the graphs it may be better to normalize them for comparison purposes. This can be achieved by dividing each value of $d\alpha/dT$ by $(d\alpha/dT)_{max}$ so that the height of the y axis is unity. As this value of $(d\alpha/dT)_{max}$ is given in the print-out it is an easy matter to estimate other values on the graph. The program is constantly updated, so requests for the print-out should be made to the authors in order to obtain the latest version. An appendix gives the current status of this program.

RESULTS

Some early results using the 15 equations suggested by Keattch and Dollimore [1] and those suggested by Brown [2] have indicated (although further work is necessary to confirm this) that the value of α at which the maximum value of $(d\alpha/dT)$ occurs is dependent on the reaction equation only, being sensibly independent of heating rate, as Table 1 would suggest.

Figure 1 shows the correlation between TG plot and the DTG plot. In the program both plots are presented superimposed. The diagram is schematic

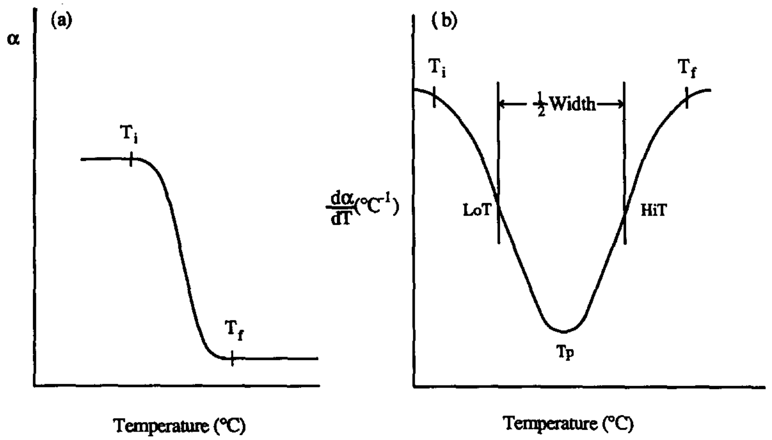

Fig. 1. Schematic plots of TG and DTG curves showing data which can be ascertained from computer curves. T_i and T_f are the initial and final temperatures respectively. HiT and LoT are the high and low temperature ends of the halfwidth respectively. T_p is the peak temperature of a DTG curve.

only and the footnote indicates the parameters which can be reported from the computer program.

APPENDIX: LISTINGS OF COMPUTER PROGRAMS

RISTEMP.BAS

```
10  REM Program to Re-construct Rising Temperature Curve from A and E values
20  REM FREDB
30  LPRINT"Programs to Re-construct Rising Temperature TG & DTG curves "
40  LPRINT "  from Reaction Equations and A and E Values"
50  LPRINT "        (C)by F.W.Wilburn,June 1989  "
60  LPRINT
70  INPUT "Name for File Please";N$
80  LPRINT "File for Results: ";N$
90  LPRINT
100 OPEN N$ FOR OUTPUT AS #1
110 INPUT "VALUE of A please(Recip Secs)?";A
120 INPUT "VALUE of E please(joules/mole)?";E
130 INPUT  "Starting Temperature(deg C.) please?";TS
140 INPUT  "Final Temperature(deg C.) please?";TF
150 INPUT "Heating Rate (Deg/min) ";BETA
160 PRINT #1,A;",";E;",";TS;",";TF;",";BETA
170 X=0: DX=0
180 TEMP =TS + 273
190 CLS
200 PRINT " Functions Available"
210 PRINT "1.P1 f(x) = x^(1/n)
220 PRINT "2.E1 f(X) = ln X"
230 PRINT "3.A2 f(X) = [-ln(1-X)]^0.5"
240 PRINT "4.A3 f(X) = [-ln(1-x)]^0.33"
250 PRINT "5.A4 f(X) = [-ln(1-X)]^0.25"
260 PRINT "6.B1 f(X) = ln[x/(1-x)]"
270 PRINT "7.R2 f(x) = 1-(1-x)^0.5"
280 PRINT "8.R3 f(x) = 1-(1-x)^0.33"
290 PRINT "9.D1 f(x) = x^2"
300 PRINT "10. D2 f(x) = (1-x)ln(1-x) + x "
310 PRINT "11. D3 f(x) = [1-(1-x)^0.33]^2"
320 PRINT "12. D4 f(x) = (1-2x/3) - (1-x)^2/3"
330 PRINT "13. F1 f(x) = -ln(1-x)"
340 PRINT "14. F2 f(x) = 1/(1-x) "
350 PRINT "15. F3 f(x) = [1/(1-x)]^2"
360 INPUT "Number of Equation Required? ";NUM
370 PRINT #1,NUM
380 IF NUM =1 THEN  INPUT "Value of n Please ";N :LPRINT "N = ";N
390 LPRINT "Equation Selected - ";
400 ON NUM GOTO  410, 420, 430, 440, 450, 460, 470, 480, 490, 500, 510, 520,
    530, 540, 550
410 LPRINT " P1 f(x) = X^(1/n) ":GOTO  560
420 LPRINT " E1 f(x) = ln x   ":GOTO  560
430 LPRINT " A2 f(x) = [-ln(1-x)]^0.5 ":GOTO  560
440 LPRINT " A3 f(x) = [-ln(1-x)]^0.33 ":GOTO  560
450 LPRINT " A5 f(x) = [-ln(1-x)]^0.2 ":GOTO  560
460 LPRINT " B1 f(x) = ln[x/(1-x)]  ":GOTO  560
470 LPRINT " R2 f(x) = 1-(1-x)^0.5 ":GOTO  560
480 LPRINT " R3 f(x) = 1-(1-x)^0.33 ":GOTO 560
490 LPRINT " D1 f(x) = x^2 ":GOTO 560
500 LPRINT " D2 f(x) = (1-x)ln(1-x) + x ":GOTO 560
510 LPRINT " D3 f(x) = [1-(1-x)^0.33]^2 ":GOTO 560
520 LPRINT " D4 f(x) = (1-2x/3)-(1-x)^2/3 ":GOTO 560
530 LPRINT " F1 f(x) = -ln(1-x) ":GOTO 560
540 LPRINT " F2 f(x) = 1/(1-x) ":GOTO 560
550 LPRINT " F3 f(x) =[1/(1-x)]^2 "
560 X = .00001:DXMAX = 0
570 DT =.1:BETA=BETA/60:R = 8.314:TS =TS + 273:TF=TF+273
580 ON NUM GOSUB 770, 790, 810, 830, 850, 870, 890, 910, 930, 950, 970, 1000,
    1020, 1040, 1060
590 DX = A*P1*EXP(-E/(R*TS))*DT
600 X = X + DX: IF X => .9999 THEN  X=.9999:DX=0
610 IF DX/(DT*BETA) > DXMAX AND X > .05 THEN  DXMAX =
    DX/(DT*BETA): XMAX = X:TMAX = TS -273
620 IF X >.1 AND X < .9999 THEN  SPAN = 2 ELSE  SPAN = 10
630 IF TS>TEMP THEN PRINT"X= ";X;TAB(25);"TS= ";TS-273;TAB(50)
    "DX/DT= ";DX/(DT*BETA):TEMP=TEMP+SPAN :GOSUB 1080
640 TS =TS + BETA*DT
650 IF TS<TF  THEN  GOTO  580
660 U= LEN(N$):U=U-4
670 P$= MID$(N$,5,U)
680 Q$ ="NAME" + P$
690 OPEN Q$ FOR OUTPUT AS #2
700 PRINT #2,DXMAX;",";TMAX
710 CLOSE #2
720 LPRINT "Max Rate occurs at a Value of X =";XMAX;" and at ";TMAX;" deg C."
730 LPRINT "Max Rate is  ";DXMAX
740 CLOSE
750 CHAIN "CURVE"
760 END
```

```
770 P1 = N*(X)^((N-1)/N)
780 RETURN
790 P1 = X
800 RETURN
810 P1 = 2*(1-X)*(-LOG(1-X))^.5
820 RETURN
830 P1 = 3*(1-X)*(-LOG(1-X))^(2/3)
840 RETURN
850 P1 = 4*(1-X)*(-LOG(1-X))^.75
860 RETURN
870 P1 = X*(1-X)
880 RETURN
890 P1 = 2*(1-X)^.5
900 RETURN
910 P1 = 3*(1-X)^(2/3)
920 RETURN
930 P1 = 1/(2*X)
940 RETURN
950 P1 =1/(-LOG(1-X))
960 RETURN
970 A1=(1-X)^(-2/3):B1=(1-X)^(1/3):C1=1-B1
980  P1=1.5/(A1*C1)
990  RETURN
1000 P1 =1.5/((1-X)^(-1/3)-1)
1010 RETURN
1020 P1 =1-X
1030 RETURN
1040 P1 =(1-X)^2
1050 RETURN
1060 P1 =.5*((1-X)^3)
1070 RETURN
1080 LPRINT"X= ";X;TAB(25);"TS= ";TS-273;TAB(50)"DX/DT=";DX/(DT*BETA)
1090 PRINT #1, TS-273;",";X;",";DX/(DT*BETA)
1100 RETURN
1110 LPRINT  CHR$(27);"K";CHR$(224);CHR$(1);
1120 FOR J=1 TO 40:FOR I= 1 TO 12
1130 READ R:LPRINT CHR$(R);
1140 NEXT
1150 LPRINT
1160 RESTORE
1170 NEXT
1180 DATA  4,10,26,58,103,231,231,103,58,26,10,4
1190 RETURN
```

CURVE.BAS

```
10  REM Program to Draw Curves From Data in a File(Curvex1)
20  INPUT "Filename Please? = ";N$
30  OPEN N$ FOR INPUT AS #1
40  INPUT  #1,D$,E$,F$,G$,H$,J$
50  D=VAL(D$):LPRINT "Value of A = ";D;" Recip. Secs "
60  E=VAL(E$):LPRINT "Value of E = ";E;" Joules/mole"
70  TA=VAL(F$):LPRINT "Value of Start Temp = ";TA;"deg C. "
80  TF=VAL(G$):LPRINT "Value of Final Temp = ";TF;"deg C. "
90  H=VAL(H$):LPRINT "Value of Heating Rate = ";H; "deg/min "
100 J=VAL(J$):LPRINT "Number of Equation Chosen ";J
110 U = LEN(N$):U=U-4
120 P$ = MID$(N$,5,U)
130 Q$ = "NAME" + P$
140 OPEN Q$ FOR INPUT AS #3
150 INPUT #3,K$,L$:K=VAL(K$):L=VAL(L$)
160 CLOSE #3
170 D = 10:F =10:G = 10:DT =.1
180 CLS
190 SCREEN 1
200 LINE (10,1)-(10,160)
210 LINE (10,160)-(299,160)
220 LOCATE 1,1:PRINT "0"
230 LOCATE 10,1:PRINT "X"
240 LOCATE 20,1:PRINT "1"
250 R=(TF-TA)/100:P=36/R:S=1:N=1:TS1=TA
260 LOCATE 22,1:PRINT TA
270 TS1=TS1+100:IF TS1>TF THEN GOTO  310
280 S=P*N
290 LOCATE 22,S:PRINT TS1
300 N=N+1:GOTO 270
310 LINE -(0,0),,,&H0
320 IF EOF (1) THEN CLOSE:GOTO 400
330 INPUT  #1,A$,B$,C$
340 TS = VAL (A$):X = VAL (B$):DX = VAL (C$)
350 LINE (D,F) - (((TS-TA)*299)/(TF-TA),160*X),2
360 LINE (D,G) - ((TS-TA)*299/(TF-TA),(DX*160)/K),3
370 LINE  ((TS-TA)*299/(TF-TA),(DX*160)/K) - (((TS-TA)*299)/(TF-
    TA),160*X),,,&H0
380 D = (TS-TA)*299/(TF-TA):F = 160*X : G = (DX*160)/K
390 GOTO 320
400 LOCATE  5,1:PRINT
410 END
```

RETREV.BAS

```
10  REM Data Retrieval RETREV
20  INPUT "Filename Please ";N$
25  LPRINT "Filename - ";N$
30  OPEN N$ FOR INPUT AS #1
40  INPUT #1,D$,E$,F$,G$,H$,J$
50  D=VAL(D$):LPRINT "VALUE of A = ";D;"secs-1"
60  E=VAL(E$):LPRINT "VALUE of E = ";E;"J/mole"
70  F=VAL(F$):LPRINT "VALUE of Start Temp = ";F;"deg C."
80  G=VAL(G$):LPRINT "VALUE of Final Temp = ";G;"deg C."
90  H=VAL(H$):LPRINT "VALUE of Heating Rate = ";H;"deg/Min"
100 J=VAL(J$):LPRINT "Equation Selected - ";
110 ON J GOTO 120, 130, 140, 150, 160, 170, 180, 190, 200, 210, 220, 230, 240,
    250, 260
120 LPRINT "P1 f(x) = X^(1/n) ":GOTO 270
130 LPRINT "E1 f(x) = ln x ":GOTO 270
140 LPRINT "A2 f(x) =[-ln[1-x]^0.5 ":GOTO 270
150 LPRINT "A3 f(x) =[-ln[1-x]^0.33 ":GOTO 270
160 LPRINT "A4 f(x) =[-ln[1-x]^0.25 ":GOTO 270
170 LPRINT "B1 f(x) =ln[x/(1-x)] ":GOTO 270
180 LPRINT "R2 f(x) = 1-(1-x)^0.5 ":GOTO 270
190 LPRINT "R3 f(x) = 1-(1-x)^0.33 ":GOTO 270
200 LPRINT "D1 f(x) = x^2 ":GOTO 270
210 LPRINT "D2 f(x) =(1-x)ln(1-x) + x ":GOTO 270
220 LPRINT "D3 f(x) =[1-(1-x)^0.33]^2 ":GOTO 270
230 LPRINT "D4 f(x) =(1-2x/3)-(1-x)^0.66] ":GOTO 270
240 LPRINT "F1 f(x) =-ln(1-x) ":GOTO 270
250 LPRINT "F2 f(x) =1/(1-x) ":GOTO 270
260 LPRINT "F2 f(x) =[1/(1-x)]^2 ":GOTO 270
270 LPRINT
280 LPRINT "  Temp";TAB(24);"X";TAB(45);"DX"
290 IF EOF(1) THEN CLOSE: END
300 INPUT #1,A$,B$,C$
310 A=VAL(A$)
320 B=VAL(B$)
330 C=VAL(C$)
340 LPRINT A;TAB(20);B;TAB(40);C
350 GOTO 290
```

WIDTH.BAS

```
10  REM Program to Find Half Width of DTG Curve(WIDTH)
20  INPUT "Filename Please? = ";N$
30  OPEN N$ FOR INPUT AS #1
40  INPUT #1,D$,E$,F$,G$,H$,J$
50  D=VAL(D$):LPRINT "Value of A = ";D;" Recip. Secs "
60  E=VAL(E$):LPRINT "Value of E = ";E;" Joules/mole"
70  TA=VAL(F$):LPRINT "Value of Start Temp = ";TA;"deg C. "
80  TF=VAL(G$):LPRINT "Value of Final Temp = ";TF;"deg C. "
90  H=VAL(H$):LPRINT "Value of Heating Rate = ";H; "deg/min "
100 J=VAL(J$):LPRINT "Number of Equation Chosen ";J
110 U = LEN(N$):U=U-4
120 P$ = MID$(N$,5,U)
130 Q$ = "NAME" + P$
140 PRINT Q$;" brings DXMAX to this Program "
150 OPEN Q$ FOR INPUT AS #3
160 INPUT #3,K$,L$:K=VAL(K$):L=VAL(L$)
170 IF EOF (3) THEN  CLOSE #3
180 D = 0:F = 0:G = 0:DT =.1
190 CLS
200 N=0
210 IF EOF (1) THEN CLOSE:GOTO 290
220 INPUT  #1,A$,B$,C$
230 TS = VAL (A$):X = VAL (B$):DX = VAL (C$)
240 IF N=1 GOTO 260
250 IF DX >K/2 AND TS < L THEN N=1:W1=TS:LPRINT "LoTS=";W1:GOTO 210
260 IF DX <K/2 AND TS > L  THEN GOTO 280
270 GOTO 210
280 W2=TS:LPRINT "HiTS= ";W2:CLOSE
290 LPRINT "Half Width = ";W2-W1;" with Peak at ";L
300 END
```

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