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A COMPUTER PROGRAM FOR KINETIC ANALYSIS OF NON-ISOTHERMAL THERMOGRAVIMETRIC DATA

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ABSTRACT

A computer program in BASIC which enables regression analysis and determination of kinetic and thermodynamic parameters from experimental TG/DTG non-isothermal thermogravimetric data is presented. This program allows the Freeman–Carroll, Horowitz–Metzger, Coats–Redfern and Doyle (modified by Zsakó treatments) methods to be performed for up to 14 different solid-state rate-controlling reactions, including *n*th-order, Avrami–Erofeev, phase boundary movement and diffusional models. Data from the literature and the dehydration of calcium oxalate monohydrate were tested as examples of the application of this program.

INTRODUCTION

During recent years, determination of kinetic parameters by non-isothermal methods has been used extensively as this method has several advantages over isothermal methods [1,2]. Many authors have employed different computational methods, among which the Freeman–Carroll [3], Coats–Redfern [4], Horowitz–Metzger [5], Doyle [6] modified by Zsakó [7] and Šatava–Škvará [8] methods are well known and have been tested by several researchers [9–11].

Zsakó and Zsakó [12] have described a FORTRAN program system for the determination of kinetic parameters from non-isothermal TG data describing solid-state degradative reactions. Their methods were based on the use of the integral form of the basic rate equations, and their procedure was limited to *n*th-order reactions. Reich and Stivala [13] have presented a program, written in BASIC, for such analysis. Their approach covers up to ten different kinetic models of the type discussed by Brown et al. [14].

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Recently, Elder [15] presented a FORTRAN program system for the determination of kinetic parameters from non-isothermal TG data for Arrhenius, Friedman and Kissinger analysis for up to nine different solid-state rate-controlling reactions.

Although, strictly speaking, standardized FORTRAN has a more powerful structure than BASIC, it is less portable between different computers. This paper therefore presents a computer program written in advanced BASIC for computing kinetic and thermodynamic parameters using different computational methods [3–5,7,12]. The computer program can be run on IBM PCs or IBM PC compatibles using the advanced BASIC interpreter (BASICA version 2.0 or higher). It is capable of performing kinetic analysis of values for the extent of reaction and the rate of reaction obtained from experimental non-isothermal TG data and of subjecting the data to regression analysis (least-squares method), hence calculating the kinetic and thermodynamic parameters.

A BRIEF SUMMARY OF THE FIVE METHODS FOR OBTAINING KINETIC PARAMETERS

Theory

In a solid state reaction leading to the evaluation of a gaseous product, the conversion can be defined as

$$\alpha = (W_0 - W)/(W_0 - W_f) \tag{1}$$

where W_0, W and W_f are the initial, actual and final sample weights respectively. The rate of the reaction depends on the conversion, according to

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{2}$$

where the rate constant k is frequently assumed to obey the Arrhenius law

$$k = A\, e^{-E/RT} \tag{3}$$

A is the pre-exponential factor, E is the apparent activation energy, R is the gas constant and T is absolute temperature.

Integral methods use the equation of thermogravimetry in its integral form

$$g(\alpha) = \frac{ZE}{R\phi} p(x) \tag{4}$$

where $g(\alpha)$ is the conversion integral

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} \tag{5}$$

where ϕ is the heating rate dT/dt and $p(x)$ is the exponential integral

$$p(x) = \int_x^{\alpha} \frac{e^{-u}}{u^2}\, du \tag{6}$$

where $u = E/RT$.

The conversion integral $g(\alpha)$ can be calculated easily if the conversion function $f(\alpha)$ is assumed to be of the form

$$f(\alpha) = (1-\alpha)^n \tag{7}$$

where n is the apparent reaction order.

Method 1—Freeman and Carroll treatment

The final equation derived by this method is

$$\frac{\Delta \log[dW/dT]}{\Delta \log W_r} = -\frac{E}{2.303R}\frac{\Delta(1/T)}{\Delta \log W_r} + n \tag{8}$$

where $W_r = W_c - W_t$ (W_c is the weight loss at the completion of the reaction and W_t is the total weight loss up to time t and dW/dT is proportional to the rate of the reaction, which is measured from the slope of the tangent to the reaction curve at temperature T. From eqn. (8), a plot of

$$\frac{\Delta \log(dW/dT)}{\Delta \log W_r} \text{ vs. } \frac{\Delta(1/T)}{\Delta \log W_r}$$

results in a straight line, the slope of which equals $-E/2.303R$ from which the activation energy E can be calculated. The intercept of the line at the ordinate gives the order of reaction n.

Method 2—Horowitz and Metzger treatment

These workers defined a reference temperature T_m at the point of inflexion of the reaction curve and changed the variable T to Θ using $\Theta = T - T_m$. The value of α at the point of inflexion, α_m, determines the order of reaction. A plot of log n versus $1 - \alpha_m$ is almost linear for $0.5 \leqslant n \leqslant 5$. If $1 - \alpha_m = 1/e$ where e is the base of the natural logarithm, then $n = 1$ and the following expression holds:

$$\ln[-\ln(1-\alpha)] = [E/(RT_m^2)]\Theta \tag{9}$$

Thus a plot of $\ln[-\ln(1-\alpha)$ versus Θ should give a straight line with a slope of $E/2.303RT_m^2$. For $n \neq 1$, the following equation is derived:

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{1-n}\right] = [E/(RT_m^2)]\Theta \tag{10}$$

A plot of $\ln\{[1-(1-\alpha)^{1-n}]/(1-n)$ versus Θ should then be a straight line of slope $E/(2.303RT_m^2)$.

Method 3—Horowitz and Metzger method modified by Dharwadkar and Karkhanavala [16]

For first-order kinetics the modified equation is

$$\ln\left[\ln(1-\alpha)^{-1}\right] = E/RT_i^2\left[100/(T_f - T_i)\right]\Theta + C \qquad (11)$$

where T_i and T_f are the initial and the final temperature respectively. C is a constant which is numerically different for different heating rates and has no effect on the slope and hence on the activation energy.

The activation energy can be computed from the slope of the unmodified Horowitz and Metzger plot via

$$E = \text{Slope}\frac{(T_f - T_i)}{100}RT_i^2 \qquad (12)$$

Dharwadkar and Karkhanavala have modified the equation for first-order kinetics, and the modifications apply equally well for other reaction orders.

Method 4—Coats and Redfern treatment

The equation derived using this method is

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right] = \frac{E}{2.303RT} + \log\frac{AR}{\phi E} \qquad (13)$$

where A is the frequency factor in the Arrhenius equation and ϕ is the heating rate. A plot of $\log\{[1-(1-\alpha)^{1-n}]/[(1-n)T^2]\}$ versus $1/T$ should give a straight line with a slope of $E/2.303R$ for any value of n except 1. For $n = 1$, $\log[-\log(1-\alpha)/T^2]$ against $(1/T)$ is plotted which gives a straight line with slope $E/2.303R$.

Method 5—Doyle method modified by Zsakó [17] and Zsakó–Zsakó [12]

For the calculation of the exponential integral $p(x)$, a good [18] empirical formula has been proposed by Zsakó [17]

$$p(x) = \frac{e^{-x}}{(x+2)(x-d)} \qquad (14)$$

where $d = 16/(x^2 - 4x + 84)$.

The basic idea behind the method concerns the constancy of the magnitude

$$B = \log\frac{AE}{R\phi} = \log g(\alpha) - \log p(x) \qquad (15)$$

resulting from eqn. (10). The integrals $g(\alpha)$ and $p(x)$ have different values for each point of the TG curves, but their ratio is constant.

Utilizing

$$g(\alpha) = \frac{1-(1-\alpha)^{1-n}}{1-n} \qquad \text{for } n \neq 1 \tag{16}$$

and

$$g(\alpha) = -\ln(1-\alpha) \qquad \text{for } n = 1 \tag{17}$$

Zsakó [7] and Zsakó [12] used minimization δ and double minimization D of the standard deviation

$$\delta = \left[\frac{\sum (B_i - \bar{B})^2}{M}\right]^{1/2} \tag{18}$$

$$D = \left[\frac{\sum (B_i - \bar{B})^2}{M\bar{B}^2}\right]^{1/2} \tag{19}$$

where B_i stands for the B value calculated from a single point of the TG curve by means of eqn (15), $\bar{B}$ represents the arithmetic mean of the individual B_i values and M stands for the number of experimental points used. In order to determine the most probable n-values, the above minimization and double minimization are performed for the following n-values: 0, $\frac{1}{3}$, $\frac{1}{2}$, $\frac{2}{3}$, 1 and 2. The minimum of the $\delta_{\min}$ and $D_{\min}$ values indicates the best n-value.

The pre-exponential factor can be obtained from

$$\log A = \bar{B} + \log(RQ) - \log E \tag{20}$$

DETERMINATION OF THERMODYNAMIC PARAMETERS

The entropy of activation S, the free energy of activation G, and the enthalpy of activation H were calculated starting from [19]

$$S = 2.303 \log(A * h/kT_i) \tag{21}$$

where h and k are Planck's and Boltzmann's constants respectively. As the reaction rate mainly depends on the free energy of activation, the entropy of activation S should decide the magnitude of G according to

$$G = E - T_i S \tag{22}$$

The enthalpy of activation was calculated using

$$E \approx H + RT_i \tag{23}$$

hence

$$H \approx E - RT_i \tag{24}$$

RESULTS AND DISCUSSION

Prior to the execution of the program some adjustments had to be made in lines 40 (number of data), 50 (number of kinetic models), 2150 (sample name), 2170 (introducing the values of Q, W_0, W, W_f, T_i, T_m, T_f and ALMX which is the value of α_m), 2220 (introducing data, i.e. temperature, weight at the time) and 2230 (introducing data, i.e. rate), see Appendix A.

The data from the literature [7,20] and the experimental TG/DTG data (obtained on a MOM Derivatograph) for the dehydration of calcium oxalate monohydrate were tested on this program. The program and some of the results obtained from it are shown in Appendix A. The program in Appendix A is for hard copy. However, with the slight modification to the program of changing LPRINT to PRINT and deleting the REM from lines 650–670, the program is executable on monitor. If the input is "Y" in line 200, then evaluation of the data by all the methods takes 1 min 51 s; if the input is "N" then methods 1–4 take 7–10 s each and method 5 takes 1 min 20 s on an IBM PS2/Model 60. These methods require double the time on compatible computers. However, execution time also depends on the number of data. The rates at different points of the TG curve for calcium oxalate monohydrate were calculated by the cubic spline method [21].

The results obtained from the computer program are summarized in Table 1, and are comparable with the values reported in the literature except

TABLE 1

Kinetic parameters from different methods [a]

Method		Complex I	Complex II	A [b]	B [b]
	n	–	–	1.32	0.22
FC	E (kcal mol^{-1})	–	–	26.96	71.43
	log A (s^{-1})	–	–	9.01	5.86
	n	2	1	1	0.67
HM	E (kcal mol^{-1})	43.11	32.89	26.58	64.48
	log A (s^{-1})	17.72	12.89	10.01	14.40
	n	2	1	1	0.67
DK	E (kcal mol^{-1})	21.67	22.57	22.36	82.95
	log A (s^{-1})	7.52	7.95	8.03	19.36
	n	2	0.67	0.67	0.67
CR	E (kcal mol^{-1})	39.25	25.86	18.28	58.13
	log A (s^{-1})	8.78	5.73	6.09	7.38
	n	2	0.67	0.67	0.67
ZZ	E (kcal mol^{-1})	40.00	26.00	25.00	59.00
	log A (s^{-1})	19.55	12.48	12.23	15.99

[a] Abbreviations: FC, Freeman–Carroll [3]; HM, Horrowitz–Metzger [5]; DK, Dharwadkar–Karkhanavala [16]; CR, Coats–Redfern [4]; ZZ, Zsakó–Zsakó [12].

[b] A, Calcium oxalate monohydrate; B, tris-thallium(III) glycollate.

for the kinetic parameters for tris-thallium(III) glycollate reported by Khadikar [20]. Evaluating the data from ref. 20 using the Coats–Redfern treatment for nine data and for all the kinetic models included in the program, the results obtained were: $E = 499.9395$ kJ mol^{-1} [119.49 kcal mol^{-1}]; kinetic model KM = 14 (D3); and correlation coefficient $r = 0.99611$ (maximum). By limiting the kinetic models (KM) to 13 in line 50, thus excluding the D3 model, the results obtained were: $E = 243.2199$ kJ mol^{-1} [58.129 kcal mol^{-1}]; and KM = 8 (R3), which is equivalent to $n = \frac{2}{3}$. The criterion for the Horowitz–Metzger and Dharwadkar modified treatments is not the maximum correlation coefficient having to give the correct values of the kinetic parameters. The calculated values of $C_s = 1 - \alpha_m$ were compared with those reported by Horowitz and Metzger [5], and selection for the kinetic parameters was made accordingly. Results from Zsakó and Zsakó's treatment agree well with those of the Coats–Redfern treatment in each case.

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APPENDIX A

Program

```
10                              FILE NAME: KIN
20 ' Regression analysis kinetic and thermodynamic parameters from TG curve
30 CLEAR:CLS :KEY OFF
40 ND=9: ' Number of data
50 KM=14: ' Number of kinetic models
60 DIM W(ND),T(ND),RATE(ND),ALFA(ND),KM$(KM),B(ND),X(100),Y(100),G(ND),M(KM+1),C
(KM+1),E(KM),R(KM+1),Z(60),LGZ(KM+1),S(KM+1),ZZD(60),MPE(60),MZ(60)
70 DIM K(60),PE(60),LZZD(KM+1),ZZMPE(KM),MNZZ(KM)
80 ' Selection of method
90 PRINT "________________________________________________________________
100 PRINT :PRINT "                KINETIC AND THERMODYNAMIC PARAMETERS"
110 PRINT "                     FROM NON-ISOTHERMAL TG DATA "
120 PRINT "                                KIN.BAS "
130 PRINT "______________________________________________________________
140 PRINT
150 PRINT "                  1. Freeman-Carroll's treatment(1958)"
160 PRINT "                  2. Horowitz-Metzger's treatment(1963)"
170 PRINT "                  3. Dharwadker's treatment(1969)"
180 PRINT "                  4. Coats-Redfern's treatment(1964)"
190 PRINT "                  5. Zsakó-Zsakó's treatment(1958,1980)" :PRINT
200 INPUT "Do you wish to evaluate the data by utilising all the methods Y/N";Q$
210 IF Q$="y" OR Q$="Y" THEN GOTO 230
220 IF Q$="n" OR Q$="N" THEN GOTO 270 ELSE 280
230 FOR METH= 1 TO 5
240 GOSUB 290
250 NEXT METH
260 CLS:LOCATE 12,30 :PRINT "End of the session" :END
270 INPUT "Enter your choice";METH
280 IF METH<1 OR METH>5 THEN GOTO 260 : PRINT
290 CLS:LOCATE 12,20:PRINT "Please wait for some moments..........."
300 GOSUB 2120:                         'TG data treatment
310 IF METH=1 THEN GOSUB 1460:          'Freeman-Carroll's treatment
320 IF METH=1 THEN GOSUB 1250:          'regression analysis
330 IF METH=1 THEN GOSUB 1150:          'kinetic parameters calculation
340 IF METH=1 THEN GOTO 480
350 IF METH>1 THEN GOTO 360
360 FOR J = 1 TO KM
370 IF J=J THEN KM=J
380 GOSUB 1940:                         'kinetic models
390 IF METH=2 OR METH=3 THEN GOSUB 1570: 'Horowtz-Metzger's treatment
400 IF METH=4  THEN GOSUB 1620:         'Coats-Redfern's treatment
410 IF METH=5  THEN GOSUB 1690:         'Zsako-Zsako treatment
420 IF METH<>5 THEN GOSUB 1250:         'regression analysis
430 IF METH<=4 THEN GOSUB 1150:         'kinetic parameters calculation
440 IF METH=5  THEN LZZD(J)=LZZD:E(J)=ZZMPE:LGZ(J)=MNZZ
450 NEXT J
460 IF METH<>5 THEN GOSUB 910
470 IF METH=5  THEN GOSUB 980
480 GOSUB 1050:                         'thermodynamic calculation
490 RESTORE
500 CLS:LPRINT :LPRINT
510 IF METH=1 THEN LPRINT TAB(10)"Freeman-Carroll treatment for ";S$
520 IF METH=2 THEN LPRINT TAB(10)"Horowitz-Metzger treatment for ";S$
530 IF METH=3 THEN LPRINT TAB(10)"Dharwadkar's treatment for ";S$
540 IF METH=4 THEN LPRINT TAB(10)"Coats-Redfern's treatment for ";S$
550 IF METH=5 THEN LPRINT TAB(10)"Zsakó-Zsakó's treatment for ";S$
560 LPRINT TAB(10)"_______________________________________________" :LPRINT
570 IF METH=1 THEN LPRINT TAB(9)" δ(1/T)"TAB(25)"α"TAB(30)"δ(1/T)/δlog(1-α)"TAB(
52)"δLog(dα/dT)/δlog(1-α)":LPRINT
580 FOR I=2 TO ND:IF METH=1 THEN LPRINT TAB(10)USING"#.####      #.####      #.
####                 ###.####";DELT(I);ALFA(I);X(I);Y(I):NEXT I
590 IF METH>1 AND METH<>5 THEN LPRINT "KM   n";TAB(9)"Mode";TAB(15)"Activation E
nergy";TAB(38)"log A";TAB(52)"m";TAB(62)"c";TAB(74)"r"
600 IF METH>1 AND METH<>5 THEN LPRINT TAB(15)"kJ/mol";TAB(24)"kcal/mol"
610 FOR J=1 TO KM:IF METH>1 AND METH<>5 THEN LPRINT KM$(J);TAB(9)J;TAB(13)USING"
  ###.##   ###.##      ##.##       ###.####   ##.####      #.#####";E(J);E(J)*.23
9;LGZ(J);M(J);C(J);R(J):NEXT J
620 IF METH=5 THEN LPRINT TAB(10)"KM   n";TAB(21)"Mode";TAB(32)"E";TAB(40)"log A
";TAB(60)"Dm"
630 IF METH=5 THEN LPRINT TAB(28)"kcal/mol"
640 FOR J=1 TO KM:IF METH=5 THEN LPRINT TAB(10)KM$(J);TAB(21)USING"##        ##.#
#    ###.##              #.####";J;E(J);LGZ(J);LZZD(J):NEXT J
```

```
650 'IF Q$="n" OR Q$="N" THEN GOTO 660 ELSE 680
660 'LOCATE 24,55:COLOR 31:PRINT "Press <C> To Continue...":COLOR 7
670 'IF INKEY$ <> "C" THEN 670 ELSE 680
680 CLS:LPRINT:LPRINT
690 IF METH=1  THEN LPRINT TAB(10)"Correlation coefficient r="USING"#.#####";HV
700 IF METH>1 AND METH<>5 THEN LPRINT TAB(10)"For maximum correlation coefficien
t r="USING"#.#####";HV
710 IF METH<=4 THEN LPRINT TAB(10)"Slope m="USING" ###.####";HM
720 IF METH<=4 THEN LPRINT TAB(10)"Intercept c="USING" ##.####";HC :LPRINT
730 IF METH<>5 THEN LPRINT TAB(10)"Activation energy E=";HE;"kJ/mol [";.239*HE;"
kcal/mol ]"
740 IF METH<>5 THEN LPRINT TAB(10)"Frequency factor log A="USING" ###.##";HLGZ
750 IF METH=1  THEN LPRINT TAB(10)"Order of reaction="USING" #.##";C
760 IF METH>1 AND METH<5 THEN LPRINT TAB(10)"Kinetic model=";HKM$
770 IF METH=5  THEN LPRINT TAB(10)"For minimum standard deviation Dm="USING"#.##
##";LD
780 IF METH=5  THEN LPRINT TAB(10)"Activation energy E=";HE*4.184;"kJ/mol [";HE;
"kcal/mol ]"
790 IF METH=5  THEN LPRINT TAB(10)"Frequency factor log A="USING"###.##";LGA
800 IF METH=5  THEN LPRINT TAB(10)"Kinetic model=";HKM$
810 LPRINT :LPRINT TAB(10)"Entropy of activation S="USING"###.##";S
820 LPRINT TAB(10)"Free energy of activation G="USING"###.##";G
830 LPRINT TAB(10)"Enthalpy of activation H="USING"###.##";H
840 LPRINT :LPRINT :LPRINT TAB(10)"logA in /s, S in J/mol K, G & H are in kJ/mol
850 IF Q$="n" OR Q$="N" THEN 860 ELSE 900
860 LOCATE 24,55:COLOR 31:PRINT "Press <C> To Continue...":COLOR 7
870 IF INKEY$ <> "C" THEN 870 ELSE 10
880 LOCATE 24,55:COLOR 31:PRINT "Press <C> To Continue...":COLOR 7
890 IF INKEY$ <> "C" THEN 890 ELSE 900
900 IF Q$="y" OR Q$="Y" THEN RETURN
910 ' For maximum r value
920 HV=R(J)
930 LV=R(J)
940 FOR MXM = 1 TO KM
950 IF R(MXM) > HV THEN HV=R(MXM):HM=M(MXM):HC=C(MXM):HE=E(MXM):HLGZ=LGZ(MXM):HK
M$=KM$(MXM)
960 NEXT MXM
970 RETURN
980 ' For minimum of mimimum D value
990 HD=LZZD(1)
1000 LD=LZZD(1)
1010 FOR MNM = 1 TO KM
1020 IF LZZD(MNM)<LD THEN LD=LZZD(MNM):HE=E(MNM):LGA=LGZ(MNM):HKM$=KM$(MNM)
1030 NEXT MNM
1040 RETURN
1050 'Calculation of thermodynamic parameters
1060 PLANK=6.6262*10^(-34)
1070 BOLTZ=1.3807*10^(-23)
1080 IF METH<>5 THEN S=(HLGZ+LOG(PLANK/(BOLTZ*TS))/2.303)*8.3144
1090 IF METH=5  THEN S=(LGA+LOG(PLANK/(BOLTZ*TS))/2.303)*8.3144
1100 IF METH<>5 THEN G=HE-S*TS/10^3
1110 IF METH=5  THEN G=HE*4.184-S*TS/10^3
1120 IF METH<>5 THEN H=HE-8.314*TS/10^3
1130 IF METH=5  THEN H=HE*4.184-8.314*TS/10^3
1140 RETURN
1150 'Calculation of kinetic parameters
1160 IF METH=1 THEN HE=-(8.3144*2.303)*M
1170 IF METH=2 THEN E(J)=8.3144*(TS^2)*M(J)/(10^3)
1180 IF METH=3 THEN E(J)=8.3144*(TF-IT)*(IT^2)*M(J)/(10^5)
1190 IF METH=4 THEN E(J)=-(8.3144*2.303)*M(J)
1200 IF METH=1 THEN HLGZ=-((8.314*TS)/HE)*(LOG(.4435)/2.303-ALMX*(LOG(ALMX)/2.30
3))
1210 IF METH=2 OR METH=3 THEN Z(J)=(Q*E(J)*10^3/(8.314*TS^2))*EXP((E(J)*10^3)/(8
.314*TS))
1220 IF METH=4 THEN Z(J)=((Q*E(J)*(10^3))/8.314)*EXP(C(J))
1230 IF METH>1 OR METH=4 THEN LGZ(J)=(LOG(Z(J)))/2.303
1240 RETURN
1250 'Regression analysis (least squares method)
1260 Z1=0:Z2=0:Z3=0:Z4=0:Z5=0
1270 IF METH=1 THEN GOTO 1280 ELSE 1350
1280 FOR I=2 TO ND
1290 Z1=Z1+X(I):Z2=Z2+Y(I):Z3=Z3+X(I)*Y(I):Z4=Z4+X(I)^2:Z5=Z5+Y(I)^2
1300 NEXT I
1310 M=((ND-1)*Z3-Z1*Z2)/((ND-1)*Z4-(Z1^2))
1320 C=(Z2-M*Z1)/(ND-1)
1330 D=SQR((Z4-Z1^2/(ND-1))/(Z5-(Z2^2)/(ND-1)))
1340 IF METH=1 THEN GOTO 1410
```

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1350 FOR I=1 TO ND
1360 Z1=Z1+X(I):Z2=Z2+Y(I):Z3=Z3+X(I)*Y(I):Z4=Z4+X(I)^2:Z5=Z5+Y(I)^2
1370 NEXT I
1380 M(J)=(ND*Z3-Z1*Z2)/(ND*Z4-(Z1^2))
1390 C(J)=(Z2-M(J)*Z1)/ND
1400 D=SQR((Z4-Z1^2/ND)/(Z5-(Z2^2)/ND))
1410 IF METH=1 THEN R=-M*D
1420 IF METH=4 THEN R(J)=-M(J)*D
1430 IF METH=2 OR METH=3 THEN R(J)=M(J)*D
1440 IF METH=1 THEN HV=R:HM=M:HC=C
1450 RETURN
1460 'Data treatment for Freeman-Carroll's equation
1470 FOR I=1 TO ND
1480 T(I)=(1/T(I))*10^3:DELT(I)=(T(I-1)-T(I))
1490 WR(I)=1-ALFA(I):LGWR(I)=LOG(WR(I))/2.303:DLGWR(I)=LGWR(I-1)-LGWR(I)
1500 LGRATE(I)=LOG(RATE(I))/2.303:DLGRATE(I)=LGRATE(I-1)-LGRATE(I)
1510 NEXT I
1520 FOR I=2 TO ND
1530 X(I)=DELT(I)/DLGWR(I):Y(I)=DLGRATE(I)/DLGWR(I)
1540 NEXT I
1550 RETURN
1560 'Horowitz-Metzger and its modified equation by Dharwadkar
1570 FOR I=1 TO ND
1580 X(I)=T(I)-TS
1590 Y(I)=LOG(G(I))
1600 NEXT I
1610 RETURN
1620 'Coats-Redfern's equation
1630 FOR I=1 TO ND
1640 X(I)=(1/T(I))*10^3
1650 IF KM=1 THEN Y(I)=LOG(G(I)/(2.303*(T(I)^2)))/2.303
1660 IF KM<>1 THEN Y(I)=LOG(G(I)/T(I)^2)/2.303
1670 NEXT I
1680 RETURN
1690 'Zsako-Zsako treatment (1980)
1700 PE = 19000
1710 FOR K=1 TO 41
1720 PE=PE + 1000
1730 FOR I=1 TO ND
1740 X(I)=PE/(1.9872*T(I))
1750 PX(I)=.43429*X(I)+LOG((X(I)+2)*(X(I)-16/(X(I)^2-4*X(I)+84)))/2.303
1760 GX(I)=LOG(G(I))/2.303
1770 B(I)=GX(I)+PX(I)
1780 NEXT I
1790 MB=0
1800 FOR I=1 TO ND:MB=MB+B(I):NEXT I
1810 MEANB=MB/ND
1820 B1=0
1830 FOR I=1 TO ND:B1=B1+(B(I)-MEANB)^2:NEXT I
1840 DMD=SQR(B1/(ND*MEANB^2))
1850 Z=MEANB+LOG(8.314*Q)/2.303-LOG(4.184*(PE/10^3))/2.303
1860 ZZD(K)=DMD:MPE(K)=PE/10^3:MZ(K)=Z
1870 NEXT K
1880 HZZD=ZZD(1)
1890 LZZD=ZZD(1)
1900 FOR MNM=2 TO 41
1910 IF ZZD(MNM) < LZZD THEN LZZD=ZZD(MNM) :ZZMPE=MPE(MNM):MNZZ=MZ(MNM)
1920 NEXT MNM
1930 RETURN
1940 ' different kinetic models and calculation of g(α)
1950 FOR I=1 TO ND
1960 IF KM=1  THEN G(I)= -1*LOG(1-ALFA(I))                     :'Fn  n=1
1970 IF KM=2  THEN G(I)=ALFA(I)                                :'Fn  n=0
1980 IF KM=3  THEN G(I)=(1-(1-ALFA(I))^(2/3))/(2/3)            :'Fn  n=1/3
1990 IF KM=4  THEN G(I)=(1-(1-ALFA(I))^(1/2))/(1/2)            :'Fn  n=1/2
2000 IF KM=5  THEN G(I)=(1-(1-ALFA(I))^(1/3))/(1/3)            :'Fn  n=2/3
2010 IF KM=6  THEN G(I)=(1-(1-ALFA(I))^(-1))/(-1)              :'Fn  n=2
2020 IF KM=7  THEN G(I)=(1-(1-ALFA(I))^(1/2))                  :'R2
2030 IF KM=8  THEN G(I)=(1-(1-ALFA(I))^(1/3))                  :'R3
2040 IF KM=9  THEN G(I)=(-1*LOG(1-ALFA(I)))^(1/2)              :'A2
2050 IF KM=10 THEN G(I)=(-1*LOG(1-ALFA(I)))^(1/3)              :'A3
2060 IF KM=11 THEN G(I)=(-1*LOG(1-ALFA(I)))^(1/4)              :'A4
2070 IF KM=12 THEN G(I)=(1-ALFA(I))*(LOG(1-ALFA(I)))+ALFA(I)   :'D2
2080 IF KM=14 THEN G(I)=(1-(1-ALFA(I))^(1/3))^2                :'D3
2090 IF KM=13 THEN G(I)=1-(2/3)*ALFA(I)-(1-ALFA(I))^(2/3)      :'D4
2100 NEXT I
2110 RETURN
```

```
2120 'TG data treatment for calculation of kinetic parameters using
2130 'different kinetic models for different methods used in this program
2140 'S$="Complex I"
2150 S$="Tris-thallium(III) glycollate"
2160 'Q=.066:WO=100:WF=79.4:IT=160+273:TS=200+273:TF=220+273:'Complex I Zsako
2170 Q=.066:WO=100:RW=27.14:WF=0:IT=350+273 :TS=560+273 : TF=580+273:ALMX=.7286:
'Tris-thallium(III) glycollate (Khadikar)
2180 FOR I=1 TO ND:READ T(I),W(I):T(I)=T(I)+273:ALFA(I)=(WO-W(I))/(WO-WF):NEXT I
2190 FOR I=1 TO ND :READ RATE(I):NEXT I
2200 FOR J=1 TO KM:READ KM$(J):NEXT J
2210 'DATA 160,99.3,170,97.9,180,95.9,190,92.4,200,87.9,210,82.1,220,81.1:'Compl
ex I (Zsako)
2220 DATA 500,95.003,510,89.286,520,82.501,530,74.289,540,63.93,550,50.715,560,2
7.143,570,5,580,1.075:'tris-thallium (III) glycollate (Khadikar)
2230 DATA .02016,.0252,.09482,.1501,.22772,.82822,.4435,.240,.125:'RATE(I) Tris-
thallium(III) glycollate (Khadikar)
2240 DATA "Fn  1","Fn  0","Fn 1/3","Fn 1/2","Fn 2/3","Fn  2","R2","R3","A2
","A3","A4","D2","D4","D3"
2250 RETURN
```

Some results from the program

Freeman–Carroll treatment for tris-thallium(III) glycollate

$\delta(1/T)$	α	$\delta(1/T)/\delta\log(1-\alpha)$	$\delta\log(\mathrm{d}\alpha/\mathrm{d}T)/\delta\log(1-\alpha)$
0.0165	0.1071	0.6131	−3.5954
0.0161	0.1750	0.4693	−16.7666
0.0157	0.2571	0.3449	−4.3809
0.0153	0.3607	0.2349	−2.7755
0.0149	0.4929	0.1486	−5.5758
0.0146	0.7286	0.0537	0.9992
0.0142	0.9500	0.0194	0.3630
0.0139	0.9893	0.0208	0.4244

Correlation coefficient $r = 0.62313$
Slope $m = -16.1761$
Intercept $c = -0.0619$

Activation energy $E = 309.7412$ kJ mol^{-1} (74.02815 kcal mol^{-1})
Frequency factor log $A = 5.65$ s^{-1}
Order of reaction $= -0.06$

Entropy of activation $S = -63.05$ J mol^{-1} K^{-1}
Free energy of activation $G = 362.26$ kJ mol^{-1}
Enthalpy of activation $H = 302.82$ kJ mol^{-1}

Omitting the first two lines of the above table and subjecting to least squares method by adjusting subroutine 1250 the following result is obtained.

Correlation coefficient $r = 0.721\,19$
Slope $m = -15.608\,4$
Intercept $c = 0.228\,4$

Activation energy $E = 298.870\,5$ kJ mol^{-1} (71.430 04 kcal mol^{-1})
Frequency factor log $A = 5.86$ s^{-1}
Order of reaction = 0.23

Entropy of activation $S = -61.34$ J mol^{-1} K^{-1}
Free energy of activation $G = 349.97$ kJ mol^{-1}
Enthalpy of activation $H = 291.94$ kJ mol^{-1}

Horowitz–Metzger treatment for tris-thallium(III) glycollate

KM	n	Mode	Activation energy		log A	m	c	r
			(kJ mol^{-1})	(kcal mol^{-1})				
Fn	1	1	311.60	74.47	17.09	0.0540	0.3772	0.99546
Fn	0	2	211.47	50.54	10.64	0.0367	−0.4266	0.98024
Fn	$\frac{1}{3}$	3	237.03	56.65	12.29	0.0411	−0.2120	0.98937
Fn	$\frac{1}{2}$	4	252.38	60.32	13.28	0.0437	−0.0870	0.99286
Fn	$\frac{2}{3}$	5	269.78	64.48	14.40	0.0468	0.0519	0.99523
Fn	2	6	492.03	117.60	28.60	0.0853	1.7252	0.96240
R2		7	252.38	60.32	13.28	0.0437	−0.7802	0.99286
R3		8	269.78	64.48	14.40	0.0468	−1.0467	0.99523
A2		9	155.80	37.24	7.02	0.0270	0.1886	0.99546
A3		10	103.87	24.82	3.59	0.0180	0.1257	0.99545
A4		11	77.90	18.62	1.83	0.0135	0.0943	0.99546
D2		12	469.34	112.17	27.16	0.0814	−1.1499	0.98835
D4		13	491.66	117.51	28.58	0.0852	−2.4743	0.99140
D3		14	539.57	128.96	31.62	0.0935	−2.0935	0.99523

Maximum correlation coefficient $r = 0.995\,46$
Slope $m = 0.027\,0$
Intercept $c = 0.188\,6$

Activation energy $E = 155.801\,7$ kJ mol^{-1} (37.236 6 kcal mol^{-1})
Frequency factor log $A = 7.02$ s^{-1}
Kinetic model = A2

Entropy of activation $S = -51.69$ J mol^{-1} K^{-1}
Free energy of activation $G = 198.86$ kJ mol^{-1}
Enthalpy of activation $H = 148.88$ kJ mol^{-1}

Dharwadkar treatment for tris-thallium(III) glycollate

KM	n	Mode	Activation energy (kJ mol^{-1})	Activation energy (kcal mol^{-1})	log A	m	c	r
Fn	1	1	311.60	74.47	17.09	0.0540	0.3772	0.99546
Fn	0	2	211.47	50.54	10.64	0.0367	−0.4266	0.98024
Fn	$\frac{1}{3}$	3	237.03	56.65	12.29	0.0411	−0.2120	0.98937
Fn	$\frac{1}{2}$	4	252.38	60.32	13.28	0.0437	−0.0870	0.99286
Fn	$\frac{2}{3}$	5	269.78	64.48	14.40	0.0468	0.0519	0.99523
Fn	2	6	492.03	117.60	28.60	0.0853	1.7252	0.96240
R2		7	252.38	60.32	13.28	0.0437	−0.7802	0.99286
R3		8	269.78	64.48	14.40	0.0468	−1.0467	0.99523
A2		9	155.80	37.24	7.02	0.0270	0.1886	0.99546
A3		10	103.87	24.82	3.59	0.0180	0.1257	0.99545
A4		11	77.90	18.62	1.83	0.0135	0.0943	0.99546
D2		12	469.34	112.17	27.16	0.0814	−1.1499	0.98835
D4		13	491.66	117.51	28.58	0.0852	−2.4743	0.99140
D3		14	539.57	128.96	31.62	0.0935	−2.0935	0.99523

Maximum correlation coefficient $r = 0.995\,46$
Slope $m = 0.027\,0$
Intercept $c = 0.188\,6$

Activation energy $E = 200.440\,8$ kJ mol^{-1} (47.905 34 kcal mol^{-1})
Frequency factor log $A = 9.93$ s^{-1}
Kinetic model = A2

Entropy of activation $S = -27.51$ J mol^{-1} K^{-1}
Free energy of activation $G = 223.36$ kJ mol^{-1}
Enthalpy of activation $H = 193.52$ kJ mol^{-1}

Coats–Redfern treatment for tris-thallium(III) glycollate

KM	n	Mode	Activation energy (kJ mol^{-1})	Activation energy (kcal mol^{-1})	log A	m	c	r
Fn	1	1	282.34	67.48	8.42	−14.7448	11.6685	0.99381
Fn	0	2	188.48	45.05	5.69	−9.8432	5.7972	0.98269
Fn	$\frac{1}{3}$	3	212.48	50.78	6.44	−11.0969	7.3955	0.99134
Fn	$\frac{1}{2}$	4	226.91	54.23	6.88	-11.8500	8.3540	0.99436
Fn	$\frac{2}{3}$	5	243.20	58.13	7.38	−12.7011	9.4360	0.99586
Fn	2	6	450.86	107.76	13.62	−23.5462	23.1812	0.95319
R2		7	226.90	54.23	6.75	−11.8496	8.0525	0.99431
R3		8	243.20	58.13	7.18	−12.7011	8.9590	0.99587
A2		9	134.42	32.13	4.19	−7.0202	2.6723	0.99324
A3		10	85.13	20.35	2.64	−4.4459	−0.4464	0.99271
A4		11	60.47	14.45	1.81	−3.1578	−2.0069	0.99181
D2		12	434.10	103.75	12.61	−22.6706	20.8888	0.99111
D4		13	455.02	108.75	12.95	−23.7630	21.6252	0.99356
D3		14	499.91	119.48	14.28	−26.1077	24.6053	0.99611

Maximum correlation coefficient $r = 0.99611$
Slope $m = -26.1077$
Intercept $c = 24.6053$

Activation energy $E = 499.9113$ kJ mol^{-1} (119.4788 kcal mol^{-1})
Frequency factor log $A = 14.28$
Kinetic model = D3

Entropy of activation $S = 8.69$ J mol^{-1} K^{-1}
Free energy of activation $G = 492.67$ kJ mol^{-1}
Enthalpy of activation $H = 492.99$ kJ mol^{-1}

Zsakó–Zsakó treatment for tris-thallium(III) glycollate

KM	n	Mode	E (kcal mol^{-1})	log A	D_m
Fn	1	1	60.00	16.34	0.0048
Fn	0	2	47.00	12.55	0.0049
Fn	$\frac{1}{3}$	3	52.00	13.99	0.0035
Fn	$\frac{1}{2}$	4	55.00	14.85	0.0029
Fn	$\frac{2}{3}$	5	59.00	15.99	0.0025
Fn	2	6	60.00	16.66	0.0260
R2		7	55.00	14.55	0.0029
R3		8	59.00	15.51	0.0025
A2		9	33.00	8.99	0.0029
A3		10	21.00	5.63	0.0028
A4		11	21.00	5.63	0.0064
D2		12	60.00	15.44	0.0217
D4		13	60.00	14.83	0.0246
D3		14	60.00	14.93	0.0294

Minimum standard deviation $D = 0.0025$
Activation energy $E = 246.856$ kJ mol^{-1} (59 kcal mol^{-1})
Frequency factor log $A = 15.99$ s^{-1}
Kinetic model = Fn $\frac{2}{3}$

Entropy of activation $S = 22.87$ J mol^{-1} K^{-1}
Free energy of activation $G = 227.81$ kJ mol^{-1}
Enthalpy of activation $H = 239.93$ kJ mol^{-1}