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Note

COMPUTER EVALUATION OF NON-ISOTHERMAL KINETIC PARAMETERS FROM TG DATA

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ABSTRACT

A FORTRAN-77 program for evaluation of non-isothermal kinetic parameters from thermogravimetric data using Coats-Redfern equation has been developed.

Schlempf et al. [1] have described a program to calculate thermodynamic constants from thermogravimetric curves, to determine A (the pre-exponential factor) and E (the energy of activation). This program performed a least-squares fit of time t and sample weight w to a polynomial. Recently, a program written in BASIC to obtain non-isothermal kinetic parameters using the Coats-Redfern equation [2] has been developed by Eftimie and Segal [3]. Since the program was written for a programmable minicalculator (Sharp PC-1251), the BASIC program seems to have limited scope. Furthermore, many of the statements in the program are not used in the ADVANCED BASIC language and do not seem to be necessary. This BASIC program [3] has been tested on a BBC microcomputer and produced erroneous results, since many of the statements such as "WAIT 48", "WAIT 128", "PAUSE" and "WAIT" are not accepted by the computer. Hence, a FORTRAN-77 version of the BASIC program of Eftimie and Segal [3] has been developed and is presented in this paper. The program is so designed that non-isothermal kinetic parameters for all reaction orders between 0 and 2 can be calculated with the help of this program, and choice of the reaction order has been made from the most accurate linearization of $[\log F(\alpha)/T^2, 1/T]$, the degree of which is known from the correlation index of the linear representation, V. The symbols used for the input data, the logical diagram and other conditions remain the same as in ref. 3. The FORTRAN-77 program has been checked on an IBM PC. The non-isother-

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mal kinetic parameters for thermal decomposition of some cobaloxime complexes [4] have been determined with the help of our program.

NIK.FOR

```
C     COMPUTER PROGRAM ( FORTRAN 77 ) FOR EVALUATION
      OF NON-ISOTHERMAL KINETIC PARAMETERS FROM TG DATA
C     BY COATS-REDFERN EQUATION
C
      INTEGER T(2Ø)
      DIMENSION W(2Ø),X(2Ø),Y(2Ø),XX(2Ø),YY(2Ø)
      OPEN ( 7,FILE = 'UU1.DAT',STATUS = 'OLD' )
      READ(7,1Ø) N
1Ø    FORMAT(13)
      DO 5Ø I = 1,N
      READ(7,15) T(I),W(I)
15    FORMAT(14,2X,F1Ø.4)
5Ø    CONTINUE
      WRITE(*,2Ø)
2Ø    FORMAT(1X, 'INPUT Z')
      READ(*,25) Z
25    FORMAT(F7.4)
      WRITE(*,3Ø)
3Ø    FORMAT(1X, 'INPUT U')
      READ(*,35) U
35    FORMAT(F6.2)
      R = Ø.Ø
4Ø    SUMX = Ø.Ø
      SUMY = Ø.Ø
      SUMXY = Ø.Ø
      SUMX2 = Ø.Ø
      SUMY2 = Ø.Ø
      DO 1ØØ I = 1,N
      X(I) = 1./(T(I) + 273.)
      IF ( R . EQ. Ø ) GO TO 45
      IF ( R . EQ. 1.Ø ) GO TO 6Ø
      P = (1. - R)*2.3Ø3*ALOG(W(I)/Z)
      Q = EXP(P)
      H = (1. - Q)/((1.Ø - R)*(T(I) + 273.Ø)**2)
      Y(I) = ALOG(H)
      GO TO 65
45    Y(I) = ALOG(((-W(I) - Z)/Z)/((T(I) + 273.Ø)**2))
      GO TO 65
6Ø    S = 2.3Ø3*ALOG(W(I)/Z)
      Y(I) = ALOG(-S*(X(I)**2))
C
```

```
C     LEAST-SQUARE FIT
C
65    SUMX = SUMX + X(I)
      SUMX2 = SUMX2 + X(I)**2
      SUMY = SUMY + Y(I)
      SUMY2 = SUMY2 + Y(I)**2
      SUMXY = SUMXY + (X(I)*Y(I))
      XX(I) = X(I)
      YY(I) = Y(I)
1ØØ   CONTINUE
      XBAR = SUMX/N
      YBAR = SUMY/N
      A = SUMX2 - (SUMX**2/N)
      B = SUMY2 - (SUMY**2/N)
      C = SUMXY - (SUMX*SUMY/N)
C
C     CORRELATION INDEX, 'V'
C
      V = C/SQRT(A*B)
C
C     Ø.999 < ABS(V ) < 1.Ø
C
      IF ((ABS(V). GT. Ø.999) .AND. (ABS(V) .LT. 1.Ø) GO TO 7Ø
      GO TO 95
C
C     CALCULATION OF 'REACTION ORDER', 'CORRELATION
      INDEX'
C     'PRE-EXPONENTIAL FACTOR' AND 'ENERGY'
C
7Ø    SLOPE = (N*SUMXY - SUMX*SUMY)/(N*SUMX2 -
      SUMX**2)
      AINT = YBAR - XBAR*SLOPE
      ENG = 4.576*SLOPE
      QQ = 2.3Ø3*(AINT + ALOG(U) + ALOG(ENG) - ALOG(12Ø.Ø))
      FACT = EXP(QQ)
      WRITE(*,75)
75    FORMAT(5X,'REACTION ORDER', 5X,'VALUE OF V',5X,'FACT'
      1ØX,
      1'ENERGY'/)
      WRITE(*,8Ø)R,V,FACT,ENG
8Ø    FORMAT(11X,F4.2,9X,E1Ø.4,2X,E1Ø.4,4X,F1Ø.4/)
C
C     CALCULATED X AND Y VALUES FOR GRAPHICAL PLOT
C
      WRITE(*,13Ø)
```

```
13Ø   FORMAT(1ØX,'X(I)',1ØX,'Y(I)'/)
      DO 12Ø I = 1,N
      WRITE(*,125) XX(I),YY(I)
125   FORMAT(5X,F1Ø.6,5X,F1Ø.6)
12Ø   CONTINUE
95    R = R + Ø.2
      IF ( R .GT. 2.Ø ) GO TO 11Ø
      GO TO 4Ø
11Ø   CLOSE(7)
      STOP
      END
```

In order to execute the program (NIK.FOR), a separate program (DATAETRY.FOR) for creation of a datafile has been written, as shown below. The DATAETRY.FOR program when executed will demand number of observation, N and the values of 'T' and 'W', thereafter will create a datafile called "uu1.dat". This has been done more for convenience such that the main program need not be changed for different set of input data, since the set of data will be stored in the form of a file. And thus, this program has been developed so as to offer greater flexibility to a user.

DATAETRY.FOR

```
      INTEGER T(2Ø)
      DIMENSION W(2Ø)
      OPEN ( 7, FILE = 'UU1.DAT',STATUS = 'NEW' )
      WRITE (*,1)
1     FORMAT(1X,'INPUT N')
      READ(*,2) N
2     FORMAT(I3)
      WRITE(7,2) N
      DO 5 I = 1, N
      WRITE (*,6)
6     FORMAT(1X,'INPUT T')
      READ(*,1Ø) T(I)
1Ø    FORMAT(14)
      WRITE(*,7)
7     FORMAT(1X,'INPUT W')
      READ(*,8) W(I)
8     FORMAT(F1Ø.4)
      WRITE(*,11)
11    FORMAT(1X.'OVER')
      WRITE(7,3Ø) T(I), W(I)
3Ø    FORMAT( I4,2X,F1Ø.4)
5     CONTINUE
      CLOSE ( 7 )
```

```
      WRITE(*,2Ø)
2Ø    FORMAT(1X,'DONE')
      STOP
      END
```

An example showing evaluation of non-isothermal kinetic parameters for thermal decomposition of a cobaloxime complex [4] from thermogravimetric data with the help of computer program, as given above, is presented here.

The output data appear as follows:

Reaction Order	: Ø.2
Correlation Index	: Ø.9993
Pre-exponential Factor	: Ø.1118E − Ø8 (1 / sec)
Energy	: 6.694 kcal / mol
Reaction Order	: Ø.4
Correlation Index	: Ø.9991
Pre-exponential Factor	: Ø.1147E − Ø8 (1 / sec)
Energy	: 7.294 kcal / mol

The graphical plot showing linearization of $Y(I)$, $X(I)$ is presented in Fig. 1. This program has also been used to calculate the above parameters in respect of several coordination complexes of uranium(VI) [4].

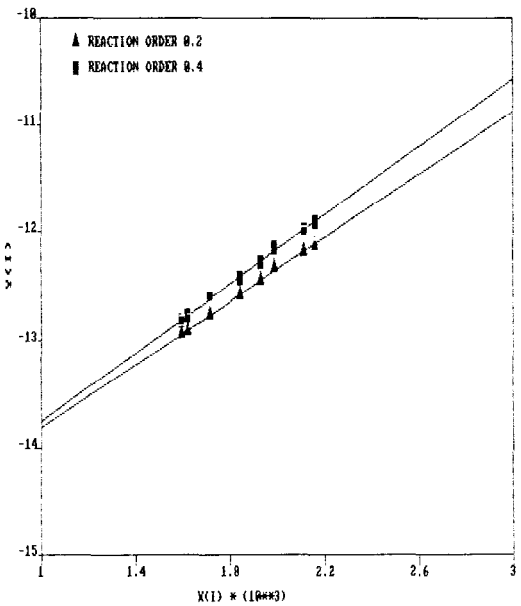

Fig. 1. Non-isothermal kinetic parameters. The regression polynomial of line 1, $(-1.527\text{E}+01)+(1.462\text{E}+00)X$; variance, 1.199E − 04. The regression polynomial of line 2, $(-1.535\text{E}+01)+(1.593\text{E}+00)X$; variance, 1.789E − 04.

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