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BASIC LANGUAGE PROGRAM TO EVALUATE NON-ISOTHERMAL KINETIC PARAMETERS FROM THERMOANALYTICAL DATA

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ABSTRACT

An improved program for automatic processing of thermoanalytical data to obtain non-isothermal kinetic parameters using the Coats–Redfern method is presented.

INTRODUCTION

According to the integral method of Coats and Redfern [1], the equation used to determine non-isothermal kinetic parameters is:

$$\log\frac{F(\alpha)}{T^2} = \log\frac{AR}{aE} - \frac{E}{4.575}\frac{1}{T} \tag{1}$$

where: α stands for the conversion degree, T for the temperature (K), $F(\alpha)$ for the conversion integral, a for the heating rate, R for the gas constant, A for the pre-exponential factor, and E for the activation energy.

It has been shown that eqn. (1) leads to correct results only for $2RT/E < 1$ [1], a condition which is generally fulfilled. For the "reaction order" model the conversion integral takes the form:

$$F(\alpha) = \frac{1-(1-\alpha)^{1-n}}{1-n} \qquad \text{for } n \neq 1$$
$$F(\alpha) = -\ln(1-\alpha) \qquad \text{for } n = 1 \tag{2}$$

where n stands for the reaction order.

The difficulties connected with the linearisation of eqn. (1) for the correct value of n have been by-passed by using a computer program for automatically processing the experimental data [2–4].

This paper is dedicated to a program written in BASIC, actually dealing with an improved variant of a primary form of the program given in ref. 5, where one calculates the kinetic parameters for all reaction orders between 0 and 2. This program allows the value of the "reaction order" to be selected which corresponds to the most accurate linearisation $[\log[F(\alpha)/T^2], 1/T]$ as well as the intercept and the slope of the corresponding straight line and, thus, the pre-exponential factor and activation energy.

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INPUT DATA

N number of experimental points
W_i weight loss of the sample at temperature T_i
T_i temperature (K)
Z total weight loss of the sample
U heating rate

The value of N was taken as 20. In the vector $\mathbf{Y}(i)$ the values of $\log[F(\alpha_i)/T_i^2]$, with $\alpha_i = W_i/Z$, indexed for a given reaction order n, are calculated, and in the vector $\mathbf{X}(i)$ the values T_i^{-1} are introduced. The correlation index of the linear representation will be denoted by V. In A, B, C, D, E the necessary elements for the least squares method are calculated. In P and Q the slope and the intercept of the straight line are calculated. In K and M the standard deviations for $\mathbf{X}(i)$ and $\mathbf{Y}(i)$ are calculated and V finds the correlation index of the linear representation. The values of the activation energy (kcal mol^{-1}) and pre-exponential factor (s^{-1}) are calculated with the following formulae:

$$E = -4.575\mathrm{P} \tag{3}$$

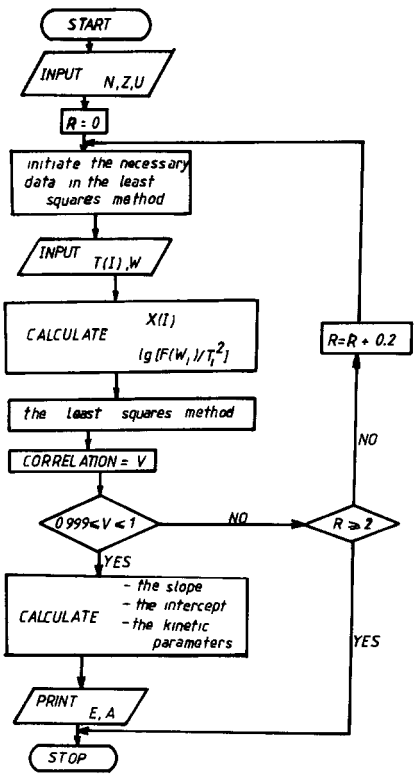

Fig. 1. Flow diagram of computer program.

$$A = 10^{Q} U \frac{E}{60R} \tag{4}$$

($R = 1.986$ cal mol^{-1} K^{-1}).

If the condition:

$$|V| \in (0.999 - 1) \tag{5}$$

is not fulfilled for $0 \leq n \leq 2$, the input data should be re-analysed or the initial and final values of the step for the reaction order should be changed. If condition (5) is fulfilled, the values of E and A are calculated and displayed. In Fig. 1 and the Appendix, the logical diagram and the instructions of the program are given, respectively.

The program is called up by the instruction: RUN (label of the program beginning).

The program was checked with a programmable minicalculator (Sharp PC-1251) to determine the non-isothermal kinetic parameters of the decomposition of some polynuclear coordination compounds [6].

APPENDIX: COMPUTER PROGRAM

```
1  DIM  T(20),W(20),Y(20),X(20)
2  INPUT"OBS NUMBER",N
3  FOR I=1 TO N:PRINT"I=",I
4  INPUT"T?",T(I)
5  INPUT"W?",W(I)
6  NEXT I
7  PRINT"REACTION ORDER"
8  INPUT"W MAXIM=?",Z
9  INPUT"HEATING RATE=?",U
10 INPUT"OBS NUMBER=?",N
11 WAIT 48
12 PAUSE"ENTER",N,"PAIRS"
13 R=0
14 A=0,B=0,C=0,D=0,E=0
15 FOR I=1 TO N
16 WAIT
17 X(I)=1/(T(I)+273)^-1
18 IF(R=0) THEN GOTO 23
19 IF(R=1) THEN GOTO 25
20 H=(1-(W(I)/Z)^(1-R))/((1-R)*(T(I)+273)^2)
21 Y(I)=LOG(H)
22 GOTO 26
23 Y(I)=LOG((-(W(I)-Z)/Z)/((T(I)+273)^2))
24 GO TO 26
25 S=LN(W(I)/Z)    Y(I)=LOG(-S*(X(I)^2))
26 WAIT
27 A=A+X(I)
28 B=B+X(I)^2
29 C=C+Y(I)
30 D=D+Y(I)^2
```

```
31 E=E+(X(I)*Y(I))
32 WAIT 128
33 NEXT I
34 WAIT
35 F=A/N
36 G=C/N
37 J=B-((A^2)/N)
38 K=SQR(J/(N-1))
39 L=D-((C^2)/N)
40 M=SQR(L/(N-1))
41 O=E-(A*C/N)
42 V=O/SQR(J*L)    PRINT"CORRELATION=", V
43 PRINT"REACTION ORDER=", R
44 IF((ABS(V) >=.999) AND (ABS(V)<=1)) THEN GO TO 46
45 GO TO 59
46 P=O/J
47 Q=G-(P*F)
48 WAIT 128
49 PRINT"EQUATION IS="
50 WAIT
51 PRINT" Y=", Q,"+", P,"X"
52 E=4,575*P
53 PRINT"ENERGY=", E
54 WAIT
55 A=(10^Q)*U*E / 120
56 PRINT"FACTOR=", A
57 WAIT
58 IF (R=2) THEN GO TO 61
59 R=R+0.2
60 GO TO 14
61 PRINT= PRINT ' WAIT BEEP 3
62 END
```

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