

# A COMPUTER PROGRAM FOR ZSAKÓ'S INTEGRAL METHOD FOR THERMAL REACTION KINETICS

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Received March 5, 1972

Presented by Prof. Dr. E. Pungor

In recent years there has been a renewed interest in the study of the kinetics of solid state thermal reactions. These reactions can be followed either by isothermal or non-isothermal methods. Methods based on the measurement of weight or enthalpy are generally used. The former one is preferred due to its higher accuracy.

The reaction rate is generally expressed as the derivative of conversion with respect to time. Conversion means the ratio of actual to total weight loss corresponding to a given stage of the reaction

$$\alpha = \frac{W_0 - W}{W_0 - W_f} \quad (1)$$

where  $W$ ,  $W_0$  and  $W_f$  stand for the actual, initial and final weight of the sample, respectively.

Under isothermal conditions the reaction rate depends upon  $\alpha$ :

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \quad (2)$$

where  $k$  is the specific rate constant, and  $f(\alpha)$  is a certain function of  $\alpha$ . Under non-isothermal conditions  $k$  cannot remain constant. The Arrhenius law [1] expressed the temperature dependence of the specific rate constant. Assuming that the temperature increases linearly, the following differential equation can be written:

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{q} \cdot \exp\left(-\frac{E}{RT}\right) dT \quad (3)$$

where  $A$  is the preexponential term,

$q = \frac{dT}{dt}$  is the heating rate,

$E$  is the apparent activation energy,

$R$  is the gas constant.

The kinetic parameters could be obtained by integration of Eq. 3, but the right-hand side of this equation cannot be integrated in finite form. Using the substitution  $u = \frac{E}{RT}$ , Eq. (3) can be transformed as follows:

$$\frac{dx}{f(x)} = - \frac{A \cdot E}{R \cdot q} \cdot \frac{e^{-u}}{u^2} du. \quad (4)$$

This expression can be integrated within a temperature interval from 0 to  $T$

$$\int_0^{\infty} \frac{dx}{f(x)} = g(x) = - \frac{A \cdot E}{R \cdot q} \int_{\infty}^x \frac{e^{-u}}{u^2} du \quad (5)$$

where  $x$  depends on the temperature  $T_x$ , where the fraction of the initial compound decomposed is  $\alpha$ ,  $x = \frac{E}{RT_x}$ .

$$p(x) = - \int_{\infty}^x \frac{e^{-u}}{u^2} du = \frac{e^{-x}}{x} - \int_x^{\infty} \frac{e^{-u}}{u} du = \frac{e^{-x}}{x} + Ei(-x). \quad (6)$$

A number of methods have been introduced to approximate the  $p(x)$  function [2—11].

The integral  $p(x)$  can be resolved in finite form in case where a hyperbolic temperature program is used [12—14] as follows:

$$g(x) \int_0^z \frac{dx}{f(x)} = - \frac{A}{b} \int_{\infty}^{1/T} e^{-\frac{E}{RT}} d\left(\frac{1}{T}\right) = \frac{AR}{b \cdot E} e^{-\frac{E}{RT}} \quad (7)$$

where  $b$  is a constant which depends on the experimental conditions.

The kinetic parameters for the thermal decomposition of solids can be obtained from thermogravimetric  $TG$  curves in the reactions accompanied by weight change. In this case, the series of  $\alpha$  values is given by the  $TG$  curves. The different forms of  $f(x)$  represent the hypothetical models of the reaction mechanism.

The need for the calculation of  $\alpha$  from the weight data of the  $TG$  curve, presentation of the values of the function  $p(x)$ , selection of the suitable kinetic equation, curve fitting and standard deviation calculations make reasonable the application of a computer. Computer technique has already been applied to the estimation of the kinetic parameters of solid state reactions [15—19].

A computer has been used for kinetic studies made on the dehydration of compounds with various contents of water of crystallization [20].

In this computer program the method developed by ZSAKÓ [5] has been used, which provides the apparent activation energy  $E$  and apparent reaction order  $n$  simultaneously on the basis of a single  $TG$  curve.

The essence of the method is contained in Eq. 3, which can also be given in the following form:

$$g(\alpha) = \frac{A \cdot E}{R \cdot q} \cdot p(x). \quad (8)$$

The logarithmic form of the equation is:

$$\log g(\alpha) - \log p(x) = \log \frac{A \cdot E}{R \cdot q} = B. \quad (9)$$

It can be observed that the value of  $B$  depends upon the heating rate, but it is independent of the temperature. In knowledge of the activation energy the preexponential term  $A$  can be calculated as follows:

$$\log A = B + \log R \cdot q - \log E. \quad (10)$$

Further on, let us introduce a computer program for Zsakó's integral method (Table I). The program language is FORTRAN, and it is applicable to the CDC—3300 type computer without alteration.

Table 1

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0001      SUBROUTINE FOPROG
0002      DIMENSION A(100), T(100), BT(100), EN(100), DE(300), W(100),
0003      IZSAK(60,33), ZSA(1980), AM1(6), AM2(6), IM(6)
0004      EQUIVALENCE (ZSAK(1),ZSA(1))
0005      COMMON/C1/A /C2/T /C3/EN /C4BT /C5/DE /C6/N /C7/ZSA
0006      I/C13/KC
0007      EXTERNAL F1,F2,F3,F4,F5,F6
0008 888   FORMAT (/////,20X,I4,* SZ.EXPERIMENT *,////)
0009 31   FORMAT (////)
0010 30   FORMAT (/20X,E14.6)
0011 39   FORMAT (20X,E14.6,4X,F6.2)
0012 990  FORMAT (1H1)
0013 20   FORMAT (13,F7.2,F7.2,1X,I4)
0014 21   FORMAT (F6.2,F7.2)
0015      READ 20,N,WO,WT,KSZ
0016      IT=0
0017      PRINT 990
0018      PRINT 888,KSZ
0019      DO 25 J=1,N,1
0020      READ 21, T (J) ,W(J)
0021      PRINT 39,W (J) ,T (J)
0022 25   CONTINUE
0023      PRINT 31
0024      DO 26 J=1,N,1
0025      A (J) = (WO-W (J)) / (WO-WT)

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0026 26 CONTINUE
0027 460 DO 1 I=1,65,1
0028 EN (1) =I+1
0029 1 CONTINUE
0030 KC=65
0031 PRINT 31
0032 10 FORMAT (25X,19H 0-ORDER REACTION)
0033 41 FORMAT (25X,19H1/3-ORDER REACTION)
0034 51 FORMAT (25X,19H1/2-ORDER REACTION)
0035 61 FORMAT (25X,19H2/3-ORDER REACTION)
0036 71 FORMAT (25X,19H FIRST ORDER REACTION)
0037 81 FORMAT (25X,19H SECOND ORDER REACTION)
0038 600 FORMAT (/////* MINIMUM DELTA :*,E20.14,5X,* ACTIVATION
0039 ENERGY *,F4.1 )
0040 PRINT 990
0041 PRINT 10
0042 CALL DELTA (F1)
0043 PRINT 600,DE (1) ,EN (1)
0044 AM1 (1) =DE (1)
0045 AM2 (1) =EN (1)
0046 PRINT 31
0047 PRINT 41
0048 CALL DELTA (F2)
0049 PRINT 600,DE (1),EN(1)
0050 AM1(2) =DE(1)
0051 AM2(2) =EN(1)
0052 PRINT 31
0053 PRINT 51
0054 CALL DELTA (F3)
0055 PRINT 600,DE (1) ,EN(1)
0056 AM1 (3)=DE(1)
0057 AM2 (3)=EN(1)
0058 PRINT 31
0059 PRINT 61
0060 CALL DELTA (F4)
0061 PRINT 600,DE (1) ,EN(1)
0062 AM1(4)=DE(1)
0063 AM2(4)=EN(1)
0064 PRINT 31
0065 PRINT 71
0066 CALL DELTA (F5)
0067 PRINT 600,DE(1) ,EN(1)
0068 AM1(5)=DE(1)
0069 AM2(5)=EN(1)
0070 PRINT 31
0071 PRINT 81
0072 CALL DELTA (F6)
0073 PRINT 600,DE(1),EN(1)
0074 AM1(6)=DE(1)
0075 AM2(6)=EN(1)
0076 DO 101 I=1,6,1
0077 IM(I)=I
0078 101 CONTINUE
0079 DO 102 I=1,6,1
0080 K=I+1
0081 DO 103 J=K,6,1
0082 IF (AM1(I).LE.AM1(J) GO TO 103
0083 BETA=AM1(I)
0084 AM1(I)=AM1(J)
0085 AM1(J)=BETA
0086 BETA=AM2(I)
0087 AM2(I)=AM2(J)
0088 AM2(J)=BETA

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0089     IBETA=IM(I)
0090     IM(I)=IM(J)
0091     IM(J)=IBETA
0092 103  CONTINUE
0093 102  CONTINUE
0094     DO 115 J=1,20,1
0095     I=J-10
0096     EN(I+Lo)=AM2(1) +0.1*1
0097 115  CONTINUE
0098     KC=20
0099     PRINT 990
0100 191  FORMAT(10X,* ACTIVATION ENERGY : *,F4.1,5X,*MINIMUM DELTA:*,
0101     1E20.14,* 0-ORDER REACTION
0102 192  FORMAT 10X,* ACTIVATION ENERGY : *,F4.1,5X,*MINIMUM DELTA:*,
0103     1E20.14,* 1/3-ORDER REACTION+
0104 193  FORMAT 10X,* ACTIVATION ENERGY : *,F4.1,5X,*MINIMUM DELTA:*,
0105     1E20.14,* 1/2-ORDER REACTION +
0106 194  FORMAT 10X,* ACTIVATION ENERGY : *,F4.1,5X,*MINIMUM DELTA:*,
0107     1E20.14,* 2/3-ORDER REACTION +
0108 195  FORMAT 10X,* ACTIVATION ENERGY : *,F4.1,5X,*MINIMUM DELTA:*,
0109     1E20.14,* FIRST ORDER REACTION *)
0110 196  FORMAT 10X,* ACTIVATION ENERGY : *,F4.1,5X,+MINIMUM DELTA:*,
0111     1E20.14,* SECOND ORDER REACTION *)
0112     PRINT 31
0113     IE ( IM(1) .EQ. 1) PRINT 191,AM2(1),AM1(1)
0114     IF ( IM(1) .EQ. 2) PRINT 192,AM2(1),AM1(1)
0115     IF ( IM(1) .EQ. 3) PRINT 193,AM2(1),AM1(1)
0116     IF ( IM(1) .EQ. 4) PRINT 194,AM2(1),AM1(1)
0117     IF ( IM(1) .EQ. 5) PRINT 195,AM2(1),AM1(1)
0118     IF ( IM(1) .EQ. 6) PRINT 196,AM2(1),AM1(1)
0119     IF ( IM(1) .EQ.1) CALL DELTA (F1)
0120     IF ( IM(1) .EQ.2) CALL DELTA (F2)
0121     IF ( IM(1) .EQ.3) CALL DELTA (F3)
0122     IF ( IM(1) .EQ.4) CALL DELTA (F4)
0123     IF ( IM(1) .EQ.5) CALL DELTA (F5)
0124     IF ( IM(1) .EQ.6) CALL DELTA (F6)
0125 110  FORMAT (////20X,* REFINED VALUES      MINIMUM DELTA *////)
0126     PRINT 110
0127 111  FORMAT (4(4X,E20.14,4X,F4.1))
0128     DO 114 I=1,5,1
0129     J=4*I
0130     PRINT 111,DE(J-3),EN(J-3),DE(J-2),EN(J-2),DE(J-1),EN(J-1),
0131     1DE(J),EN(J)
0132 114  CONTINUE
0133     IF (IT.EQ.1) GO TO 450
0134     GO TO 450
0135     N1=N1-1
0136     K=N2-N1
0137     DO 400 I=1,K,1
0138     N3=N1+I
0139     A(I)=A(N3)
0140     W(I)=W(N3)
0141     T(I)=T(N3)
0142 400  CONTINUE
0143     N=N2-N1
0144     PRINT 990
0145     DO 401 I=1,K,1
0146     PRINT 39,W(I), T(I)
0147 401  CONTINUE
0148     IT=1
0149     GO TO 460
0150 450  RETURN
0151     END

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### Summary

A computer program of Zsakó's integral method for the estimation of kinetic parameters in solid state reactions is described.

### Acknowledgement

The authors thank Mr P. Tóke for valuable advices.

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