KINETIC ANALYSIS OF THERMOGRAVIMETRY

Part III: Experimental Modifications

IVAN J. GOLDFARB

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials", Task No. 734203, "Fundamental Principles Determining the Behavior of Macromolecules" with Dr. I. J. Goldfarb (AFML/LNP) acting as task scientist. The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio.

The author wishes to thank Dr. D. R. Bain for his many helpful suggestions and the late Mr. R. R. Luthman, Jr., for his valuable assistance in the experimental work.

This report covers research conducted from September 1968 to July 1970. This report was submitted by the author in March 1971 for publication as a technical report.

This technical report has been reviewed and is approved.

R. L. VAN DEUSEN
Chief, Polymer Branch
Nonmetallic Materials Division
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The experimental apparatus for temperature programmed thermogravimetry has been modified to more effectively obtain kinetic parameters for the degradation of polymers. The thermobalance was modified to incorporate direct sample temperature measurement thereby to minimize temperature measurement errors. An automatic data acquisition system was incorporated into the apparatus and appropriate computer programs to handle the magnetic tape data were written. The modified apparatus has been tested with several polymer systems and it was demonstrated that the use of the magnetic tape data recording system permitted greatly increased output from the thermobalance.
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SECTION I
INTRODUCTION

In the previous report (Reference 1) a method of obtaining kinetic parameters for the degradation of polymers using temperature programmed thermogravimetry was described. The experimental procedures and a method of processing TGA data on the computer were described including the application of the technique to several polymers. The technique has since been applied to a variety of polymer systems with considerable success (References 2 and 3). Routine operation of the system revealed two possible limitations to the accuracy and usefulness of the apparatus in its present form.

1. The temperature of the degrading sample was assumed to be that of a thermocouple placed near the crucible with some temperature correction applied.

2. The output was limited by the speed at which data could be read off the chart and prepared for processing by the computer.

Since the system had been shown to be capable of producing high quality data, it seemed desirable to redesign the apparatus to remove these limitations on its use. This is described in detail in the following sections.
SECTION II

MODIFICATION TO THE AINSWORTH RV THERMOBALANCE TO INCORPORATE DIRECT SAMPLE TEMPERATURE MEASUREMENT

1. INTRODUCTION

In TGA it is customary to calibrate the temperature inside the sample holder against an external thermocouple placed as close to the operating position of the sample holder as possible, under normal run conditions (heating rate, etc.) except that weight is not being recorded. Providing the same conditions are observed during the normal run there is no reason to suppose this technique is inaccurate. However, for a large number of samples, heating rates, etc., this represents an inordinately large number of calibrations and this still presupposes absolute reproducibility of the two runs. A much more satisfactory method is to measure the temperature of the sample directly during the degradation, particularly in kinetic studies where temperature is so important. The evaporation of material from degrading polymers can cause considerable decrease in sample temperature, particularly when rate of weight loss is high. For example, polytetrafluoroethylene loses 16%/minute at its maximum rate of weight loss under the conditions used to study this polymer.

2. MODIFICATIONS

The Ainsworth RV thermobalance used in this work is particularly suitable for conversion to direct sample temperature measurement. All of the parts are accessible when the cover is removed. The fact that the balance is not the null deflection type poses some problem since, at some stage, wires have to be taken from the beam to a measuring device thereby interfering with the normal free swing of the balance. The configuration of the wires described in this section was arrived at by trial and error.

Figure 1 shows a general view of the balance with the bell jar in place. Figure 2 shows the detailed arrangement of the connecting wires.
Connecting loops of fine (0.003" diameter) thermocouple wire attached to the beam and to the agate pivot by vacuum wax (also insulates wires on the metal beam).

Figure 1. Ainsworth RV Balance - General Arrangement with Wires and Thermocouple Support System
Figure 2. Details of Wires Attached to Balance Beam and the Thermocouple/Support Arrangement
Originally the balance was wired with Chromel/Alumel wire because of its high millivolt per degree output (0.04 mv/°C), but because the wire is magnetic there was considerable interaction with the furnace electrical supply up to 300° C. Weight readings below this temperature could not be used. The balance was later rewired with platinum-platinum/10% rhodium wires which are nonmagnetic. The lower EMF was measured with a Digital Voltmeter. The real problem in direct sample temperature and weight measurement is in finding some way of transferring the EMF signal from the balance beam without interfering with the weighing characteristics. Any attachments to the beam have the potential of upsetting both the sensitivity and the zero of the balance, especially as the Ainsworth is not a null deflection balance. The wire attachments are shown in Figure 2. Loop 1 joins the thermocouple/suspension to the beam. Consider the effect of changes in sample weight on this loop. The situation is shown in Figure 4. $\alpha_1$, is the angle between the beam and suspension, initially, and $\alpha_2$ the angle after the sample has lost weight. It can be seen that the arrangement of Loop 1 will tend to restrict this motion and cause anomalous weight readings. The arrangement of Loops 2 and 3 will have a similar effect. Loop 3 was found to have a profound effect on the zero of the balance. Careful arrangement of the length and position of the wires resulted in a stable system provided certain limitations were recognized. Although this balance can follow weight changes up to 200 mg using multiple chart scans the weight loss that could be followed was less than 10 mg, i.e. one span of the recorder chart. Some relaxation effects were noted when the beam was switched from one position to another by adding or subtracting 10 mg to the counter weight. This limitation of 10 mg samples is of little importance since heating effects and diffusion usually restrict sample size. A detailed drawing of the support suspension is given in Figure 3. Removing and rehanging the suspension was found to give small variations in readings so the balance could not be used to measure absolute sample weight. In practice this was not a problem since either the sample degraded completely or the weight added to the crucible could be measured with sufficient accuracy.
Figure 3. The Thermocouple/Support
Figure 4. Effect of Sample Weight Changes on Beam Position
The operation of the balance is very convenient for checking zero and sensitivity, and long-term drift in both. If the balance is adjusted to give a zero or 100% reading on the chart, adding or subtracting 10 mg by the remote control switches the balance from one extreme to the other. In this way changes in zero and sensitivity can be detected and adjusted. In practice, as well as checking the sensitivity before a run, the weight was arranged such that, at the end of the degradation, the balance was close enough to the zero position to allow switching and a further check. Sensitivity variations were usually less than 1%. The constancy of buoyancy correction is another "built-in" check on the accuracy of operation.

The weight of the Teflon block and quartz rod in the suspension was found to give good electrical contact at the hooks. The black wax used as an anchor for the wires on the balance beam also acted as an effective insulator. To check the electrical integrity of the system, the sample temperature as measured by the suspension was checked against an independent thermocouple in the crucible. Variation was less than 1°C at 600°C.

3. TESTING UNDER RUN CONDITIONS

Since an extensive study of the degradation of polytetrafluoroethylene had been made on the unmodified balance (Reference 1) a complete kinetic analysis was carried out on the polymer using the balance with the wires attached.

Samples of Teflon molding powder (8-9 mgs) were degraded at nominal heating rates of 75, 150, 300, and 450°C/hour. The data was analyzed by the standard procedures detailed in Reference 1.

A plot of Activation Energy against % weight loss is shown in Figure 5, before and after balance modifications. The results of this work show an average activation energy of 59.5 kcal compared with 69.3 kcal for the previous work (both for 10-80% of the reaction). The earlier results, however, show a considerable increase in activation energy after 50% weight loss.
Figure 5. Activation Energy as a Function of Weight Loss for Polytetrafluoroethylene
Figure 6. Arrhenius Plots for PTFE at 50% Weight Loss
A better comparison of the result is obtained by comparing the Arrhenius plots for the two series at 50% weight loss. The points at lower heating rates in both cases fall on parallel straight lines indicating the same activation energy. The separation of the lines represent a temperature difference of 13°C, the sort of difference one might expect between thermocouples placed in and adjacent to the sample. It is interesting to note that, with the thermocouple in the sample, the data at 300°C/hour heating rate falls on the straight line whereas it does not in the previous data. This is probably due to the temperature in the sample being lower than that recorded in the earlier work. Deviations occur in both cases at 450°C/hour. At this heating rate the rate of volatilization is of the order of 16% per minute and questions of how well the thermocouple can respond to the changes and how the sample is distributed with respect to the thermocouple arise. There also exists the possibility of lower rates due to diffusion effects at high heating rates, particularly in the larger samples used in the earlier work (100 mg). This effect of sample size may have something to do with the otherwise unexplained increase in activation energy after 50% reaction, observed in the earlier work.

4. CONCLUSION

In general the agreement in the two sets of data is good indicating that the attachments to the balance beam have had little effect on the accuracy of the system. The modified system is, however, inherently more accurate since the temperature sensor is inside the crucible, although question may still arise about contact with the sample, thermal conductivity of the sample, temperature gradients and heat being conducted away from the sample by the wires (Reference 4).

Confidence in the stability and response of the balance was further increased when a set of data obtained with a chromel-alumel system with manual reading of data from a recorder chart, gave the same kinetic parameters for BBB degradation as the same balance wired with platinum-platinum/10% rhodium and using a magnetic tape recording of the data.
SECTION III
COLLECTION, PROCESSING AND ANALYSIS OF TGA DATA

1. INTRODUCTION

In the previous reports (References 1 through 3) TGA data was obtained by reading several hundred sets of weight/temperature data points from the recorder chart, and having the data transferred to punched cards for processing by the computer. This operation was both time consuming and tedious and considerably reduced the amount of data that could be produced. The method had also considerable potential for human error. Modern advances in instrumentation have suggested the replacement of the chart recorder by another device such as a magnetic tape or paper tape recorder which can be read directly by the computer. For this purpose an SRL Model 837 Data Acquisition System was acquired. This is described in the next section.

2. THE SRL MODEL 837 DATA ACQUISITION SYSTEM

A block diagram of the apparatus is shown in Figure 7. The system consists of the following components:

1. Two model 2670 Data Amplifiers - Hewlett-Packard.
3. A model 1600 Incremental Tape Recorder - Kennedy.
4. Scanner and Counter Logic - SRL design using Digital Equipment Corporation Flip Chip Modules and power supply.

The complete system is housed in a 67-inch Honeywell modu-mount enclosure and each basic component has its own power supply, switch, and fuse.

Electrical signals proportional to the weight and temperature are fed to the two Data Amplifiers, the levels of which can be adjusted to send a measurable output to the digital voltmeter. The two signals are scanned alternately, the scanning interval varying from 0.5 to 10 seconds (i.e. the interval between two successive weight or temperature readings can be varied from 1 to 20 seconds). If necessary a permanent record of the data can be obtained from the printer in which case the
Figure 7. Model 837 Dual Channel Data Acquisition System Block Diagram
lower limit of the scan interval is governed by the tracking speed of the printer. In practice the printer is only used during testing or trouble-shooting. The amplified signals are fed to the magnetic tape recorder. Data is recorded in records of a length determined by the control logic, with a record gap at the end of each record. At present the apparatus is set up to receive 18 sets of weight/temperature data but this can be varied. This short length is very suitable for correction as will be discussed later. When the "Stop" button of the system is activated, recording continues to the end of the record. At the end of the last record an "End of File" code must be recorded. This is used by the computer to detect the end of the data and without it data cannot be recovered.

Once the data is recorded it is now in a form suitable for processing on the IBM 7094 computer.

To minimize the loss of data which could occur due to various failures, each run is recorded on a separate magnetic tape (Ampex Data Mailer, 200 ft). Since it is necessary to retain data for some time but undesirable to accumulate numerous magnetic tapes, the data is transferred to a master storage tape during the initial processing. A block diagram of the tape manipulation is shown in Figure 8.

![Figure 8. Transfer of Data From Small Tape to the Master Storage Tape](image)
Transfer and storage of data is carried out when the data is sent for preliminary examination using Program 1 (Appendix). To minimize loss of data due to machine or operation error, three master tapes and at least the six most recent runs are retained. The three storage tapes have n, n-1 and n-2 runs. When hung in the configuration shown, the tape with the largest number of runs is the old master tape which is read only. The tape with the least number is the new master. The n-1 tape is meanwhile safely stored. The data from the old master is written on the new master (Step 1) followed by the current run data (Step 2). This tape then becomes the main master storage. The method also allows the erasure of the latest record should the output show the data was unsatisfactory.

As well as handling the storage of data, Program 1 also displays the weight loss, temperature, and rate of weight loss at each of the weight losses, along with a record by record account of the data as stored on the tape. Both the records and the number of data points are counted and those figures are particularly useful for identification purposes in the case of bad data. Three types of bad data have been encountered and Program 1 is available with modification to cope with each:

1. Redundant records caused by write errors, eg parity errors, in the recording. Provided they do not occur at critical stages in the degradation up to nine records can be discarded. This type of failure is recognized by the computer in reading the tape and the number of redundant records is shown on the initial print out.

2. Records which have bad data but which are not redundant and are not detected by the machine. If they do not occur at a critical stage in the degradation they can be discarded.

3. Bad data points in a record. These can be replaced by values in keeping with the rest of the data.

Once a set of satisfactory runs have been loaded on to the master tape, the data is reprocessed using Program 2. This program, provides a print out of the rate of weight loss at 1% intervals and also gives the output on IBM punched cards for use in the Arrhenius Program (Program 3, Appendix).
3. CONCLUSION

The complete series of modifications to the thermogravimetric system described in this report have been tested on a series of styrene-acrylonitrile copolymers. These copolymers have a very high rate of weight loss providing an effective test for the direct sample temperature measurement. As with the degradation of Teflon, it was shown that good Arrhenius plots could be obtained provided the heating rate did not exceed 300°C/hour. The short degradation time was useful in testing the efficiency of the data recording system. It was clearly demonstrated that the use of the magnetic tape data recording system permitted maximum output from the thermobalance. The system is set up such that if the output is to be further increased a second thermobalance could be readily accommodated, one balance being loaded and evacuated while the other is being used. Detailed results of the analyses of the kinetics of degradation of the styrene-acrylonitrile copolymers will be described in another report.
REFERENCES


2. I. J. Goldfarb, R. McGuchan, AFML-TR-68-182, Parts I and II.


APPENDIX

PROGRAMS 1 - 3
PROGRAM 1

This program transfers current run data to master storage tape, provides record by record output of data as it appears on the tape, and provides a preliminary print out of the rates for examination.
PROGRAM 1: TAPE PREPARATION AND INITIAL EXAMINATION OF DATA

PROGRAM TO READ CURRENT DATA AND TRANSFER IT TO THE MASTER TAPE

ALONG WITH ALL THE DATA ON THE OLD MASTER

THE PROGRAM ALSO PRINTS OUT THE DATA OF THE CURRENT RUN AND

DETERMINES RATE OF WEIGHT LOSS AT ONE PER CENT INTERVALS

UNIT 1 = SMALL TAPE WITH CURRENT RUN

UNIT 2 = NEW MASTER TAPE

UNIT 3 = OLD MASTER TAPE (CAN BE READ ONLY)

PROGRAM USES SUBROUTINE EOF TO PERMIT READING OF A NUMBER OF

FILES SEPARATELY BY END OF FILE MARKERS

INPUT TEMPERATURES ARE FITTED TO A FIFTH DEGREE POLYNOMIAL USING A

LEAST SQUARES SUBROUTINE (PLSQ).

WEIGHTS CORRESPONDING TO SHORT TEMPERATURE RANGES ARE FITTED TO A

QUADRATIC BY PLSQ.

INPUT WEIGHTS DIFFERING FROM FITTED LINE BY MORE THAN ONE PERCENT OF THE

TOTAL WEIGHT LOSS ARE REPLACED BY THE CURVE FIT VALUE.

W = WEIGHT DATA POINT READ OFF TAPE

T = TEMPERATURE DATA POINT READ CF TAPE (IN MW).

T = TIME DATA POINT CALULATED FROM TIME INTERVAL AND NO OF DATA POINTS

TINT = TIME INTERVAL

WW = WEIGHT LOSS AT 1 PER CENT INTERVALS

DWT = RATE OF WEIGHT LOSS AT 1 PER CENT INTERVALS

TDER = HEATING RATE AT 1 PER CENT INTERVALS

TDP = TEMPERATURE CORRESPONDING TO EACH PER CENT WEIGHT LOSS, CALCULATED BY

PLSQ.

T = TIME CORRESPONDING TO EACH PER CENT WEIGHT LOSS.

PLOT = DIMENSIONS FOR GRAPH PLOT SUBROUTINE

B = COEFFICIENTS OF 10TH ORDER POLYNOMIAL FITTING TEMP/EMF DATA FOR

PLATINUM/PLATINUM IC PER CENT RHODIUM

C = COEFFICIENTS OF WEIGHT/TIME PLSQ QUADRATIC

D = COEFFICIENTS OF 5TH ORDER PLSQ USED TO FIT TIME/TEMP. DATA

R = 1/RHODIUM ABSOLUTE TEMPERATURE

EQUIVALENCE (1,(1,1),PLUT(1),,(1,1,JZ(1)),(DATE1,JZ(2)),(DATE2,JZ(3)),

1,(COM1,JZ(4)),(COM2,JZ(5)),(COM3,JZ(6)),(COM4,JZ(7)),(TINT,JZ(8)))

DIMENSION (1,5500),NULL(101),TNULL(101),DNULL(101),Y(120),C(6),A(11),

1W(5500),T(5500),Z(42),X(36),PLOT(90,110),TDER(101),TPOLY(101),

1BT(101),B(111),D(6),JZ(8)

INTEGER DUMMY

98 CALL READ2(2,JZ,8,J)

IF (ID.EQ.DUMMY) GO TO 114

97 CALL WRITE(2,JZ,8)

96 CALL READ2(3,X,18,J).

IF (J-1) 111,112,113

111 CALL WRITE(2,X,18)

GO TO 97

112 CALL CLOSE(2,Z)

GO TO 98

113 WRITE(6,115,JZ(1))

115 FORMAT(2X,A5,39HREduNCANCY ENCOUNTERED - RUN TERMINATED)

114 READ(5,1CC)ID,DATE1,DATE2,COM1,COM2,COM3,COM4,TINT

1000 FORMAT(2X,A5,1X,A6,2X,A7,2X,366,366,6X,F6.4)

CALL WRITE(2,JZ,8)
TCTAPE

TCTAPE  -  EFN  SOURCE  STATEMENT  -  IFN(S)  -  09/17/7C

L=C
ASSIGN 20 TC IEOF
CALL EDI(TECF)

10  L=L+1
N=N#1
IF(M+GT.55CC)GC TO 400
M=M-17
READ(I1,IOG2)(W(I),T(I),I=M,N)
1002 FORMAT(36F6.2,IX))
19  CALL WRITE(2,W(M),18)
CALL WRITE(2,T(M),18)
GO TO 10

20  L=L-1
N=N#1
CALL CLOSE(2,2)
CALL WRITE(2,DUMMY,8)
25  LK=1-L-5
DO 380 K=1,1K,5
WRITE(6,4)IC,K
4  FORMAT(11H1,10X,A5,5X,6HREC NO.,13/38X,31IHw,11X,1HT,11X))
KT=K+4
DO 370 J=K,KT
KD=18#J-17
KE=18#J-12
DO 365 I=KE,KE
WRITE(6,5)W(I),T(I),W(I+6),T(I+6),W(I+12),T(I+12)
5  FORMAT(35X,6(F7.2,4X))
WRITE(6,381)72
381  FORMAT(1HOH)
370  CONTINUE
390  CONTINUE
3  LR=L-(L/5)*5
IF(LR,EQ,0)LR=5
M=L-LR+1
WRITE(6,4)IC,M
3  FORMAT(11H1,10X,A5,5X,6HREC NO.,13/38X,31IHw,11X,1HT,11X))
KT=K+4
DO 370 J=K,KT
KD=18#J-17
KE=18#J-12
DO 365 I=KE,KE
WRITE(6,5)W(I),T(I),W(I+6),T(I+6),W(I+12),T(I+12)
WRITE(6,381)96
385  CONTINUE
51 JJ=CC10#FLCAT(N)
LL = MAX0(JJ,10)

C  JJ  =  1  PERCENT  OF  NO.  OF  DATA  SETS  READ  IN
C  LL  =  NO.  OF  CURVE  FIT  POINTS  (LATER  =  NN)
C
WRITE (6,3CCQ)

3000  FORMAT (1H1)
WRITE (6,3CSO) ID,DATE1,DATE2,COM1,COM2,COM3,COM4
3050  FORMAT(4X,A5,8X,A6,A2,1CX,A6,A6,A6,A37/))
WRITE(6,30CC)TINT
3060  FORMAT (10X,14HTIME INTERVAL=F6.4)
WRITE (6,J10) LL
3170  FORMAT (10X,25HAC CF PTS IN CURVE FIT = ,I2)

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**Part III**

**TC-TAPE**

09/17/7C

C **K = POLYNOMIAL ORDER, NEEDED FOR PLSQ SUBROUTINE, LIST = 0 FOR NO ERROR**

C **ANALYSIS OF PLSQ**

C **D = TOTAL WEIGHT LOSS**

C

**LINEA = 1**

**D = w(1) - w(N)**

B(1) = -6.885309E-6

B(2) = 3.521556E-4

B(3) = -7.783805E-3

B(4) = 9.753717E-2

B(5) = 1.955367E-1

B(6) = 3.54215E0

B(7) = 1.367622E1

B(8) = 3.74106E1

B(9) = 5.745C16E1

B(10) = 1.815117E2

B(11) = 3.812777E-2

**DD 55 I = 1, K**

**W(I) = 100.-(100.*w(I)-w(N))/D)**

**T(I)=(2.*FLOAT(I)-1.)*TINT/60.**

**POLY = B(I)**

**DD 30C J=2, 11**

**30C POLY = POLY+I(I)/1C+B(J)**

**T(I) = POLY**

**55 CONTINUE**

C **CURVE FIT CF TIME AND TEMPERATURE DATA**

C

**K = 5**

**LIST = 0**

**CALL PLSQ(I1,Ta,N,K,D,LIST,FMAX,FRMS,EMEQ)**

**WRITE (6,5100) EMAX**

**5100 FORMAT (10X,17MAX TEMPERATURE ERROR = \*F10.6)**

**WRITE (6,5200) FRMS**

**5200 FORMAT (10X,30TH ROOT MEAN SQUARE ERROR = \*F10.6)**

**WRITE (6,5300) (D(I),I=1,6)**

**5300 FORMAT (10X,15H TEMPERATURE COEFFF)**

**WRITE (6,5400) (D(I),I=1,6)**

**5400 FORMAT (13X,F12.6)**

C **START MAJOR LOOP**

C

**GO 10C NW = 1, 99**

**59 II = LINDA-1**

**WW(NW) = FLCAT(NW)**

C **SCAN WEIGHT DATA FOR ONE CLOSE TO BUT JUST GREATER THAN ONE PERCENT WEIGHT**

C **LOSS, II = INDEX OF THAT POINT**

C **DO 6C I=LINEA,N**

**IF (w(I).GT.WW(NW)) GO TO 70**

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TOTAPE 09/17/70

CONTINUE

7C LINDA = II-(LL/2)

C LINDA = INDEX OF FIRST DATA TO BE USED BY PLSQ

DO 8C J=1,LL
   JI = LINDA+J-1
   Y(JI) = W(JI)

8C CONTINUE

C CURVE FIT CF TIME AND WEIGHT DATA

K = 2
LIST = C
CALL PLSQ(TII,Y,NW,K,C,LIST,EMAX,ERMS,EMEQ)
KK = 1

C START LCOP TO CHECK FOR BAD INPUT DATA

DO 81 J=1,LL
   JI = LINDA+J-1
   W(J) = WEIGHT CALCULATED FROM POLYNOMIAL
   W(E) = (TII(JI)**2*C(2)+C(3))
   C COMPARE CALCULATED AND ORIGINAL DATA
   IF (ABS(W(E)-W(JI)).GT.1.) GO TO 82

C WE = WEIGHT CALCULATED FROM POLYNOMIAL
   IF (ABS(WE-W(JI)).GT.1.) GO TO 82

C WE = WEIGHT CALCULATED FROM POLYNOMIAL
   IF (ABS(WE-W(JI)).GT.1.) GO TO 82

C START LCOP TO CHECK FOR BAD INPUT DATA

DO 81 J=1,LL
   JI = LINDA+J-1
   W(J) = WEIGHT CALCULATED FROM POLYNOMIAL
   W(E) = (TII(JI)**2*C(2)+C(3))
   C COMPARE CALCULATED AND ORIGINAL DATA
   IF (ABS(W(E)-W(JI)).GT.1.) GO TO 82

C WE = WEIGHT CALCULATED FROM POLYNOMIAL
   IF (ABS(WE-W(JI)).GT.1.) GO TO 82

C WRITE (6,4CC,DO) JI,W(JI),WE
   WRITE (6,4CC,DO) JI,W(JI),WE

C REPLACE BAD DATA BY CALCULATED VALUES
   W(JI) = WE
   KK = 2

81 CONTINUE

C CHECK FOR IMAGINARY ROOTS IN SOLUTION OF QUADRATIC

C SCR.EW = C(2)*C(2)-4.0*C(1)*(C(3)-WW(NW))
   IF (SCR.EW.LT.0.0) GO TO 90

C USE REAL ROOT TO DETERMINE TIME CORRESPONDING TO EACH PERCENT WEIGHT LOSS

C TNW(NW) = (SQRT(C(2)*C(2)-4.0*C(1)*(C(3)-WW(NW)))-C(2))/(2.0*C(1))

C DWCT = RATE OF WEIGHT LOSS

C DWCT(NW) = 2.0*C(1)*TNW(NW) + C(2)

90 TNW(NW) = (2.*FLOAT(Il)-4.)*TINT/6C.
C WRITE OUT IDENTIFICATION AND LOCATION OF BAD DATA
C
C WRITE (6, 316) NW, II, 'NW(NW), M(II)
3160 FORMAT (2X, 17HSCREW LESS THAN 0, 1CX, 3HWN = , 13, 10X, 3HNI = , 14, 10X,
        2HTE = F6.2, 1CX, 2HN = F5.1)
100 CONTINUE
WRITE (6, 3110)
3110 FORMAT (3X, 11HWEIGHT LOSS, 6X, $; NWDT(NW), 14X, 4HTEMP, 6X,
        4HTC = 11X, 5HTEMP, 16X, 4HTIME)
C 120 NW = 1, 99
CT = NW(NW)
TSTCR = D(1)
C
C DO 200 I = 2, 6
    TSTCR = TSTCR * CT * D(I)
120 CONTINUE
C
C WRITE (6, 3120) NW, 'NW, NW(NW), TPCLY(NW), TDPOLY(NW), TDER(NW), RTEMP(NW), CT
3120 FORMAT (6X, 13, 10X, E12.5, 7X, F9.3, 2E15.5, 5X, F7.2)
120 CONTINUE
C
C STEER = 0, C
C
C AVERAGE TEMPERATURE DERIVATIVE (AVE)
C
C 125 1 = 1, 99
STEER = STEER + TDER(I)
125 CONTINUE
AVE = TDER / 99.0
WRITE (6, 3125) AVE
3125 FORMAT (6X, 13, 10X, 'AVE', 27, 10X, 'AVERAGE TEMP DERIVATIVE =', E15.5)
C
C SET LP DUMMY POINTS FOR GRAPH PLOTTING SUBROUTINE (GP)
C
C kW(1CC) = C, 0
CDWT(1CC) = C, C
TNK(1CC) = TNW(99)
TDER(1CC) = 0, C
kW(1CC) = 1CC, C
CDWT(1CC) = C, C
TNK(1CC) = TNW(99)
TDER(1CC) = TDER(99)
WRITE (6, 3130)
3130 FORMAT (3X, 10X, 'WRITE (6, 3130) 10')
Tape -  EFN  SOURCE STATEMENT  -  IFN(S)  -  09/17/70

313C FORMAT (1CX,10X,DWOT VS WEIGHT LOSS,20X,A5)

L = 3
LS = 5
LW = 1C1
LN = 50
M = 1C1
DATA A/1H,

JN = 1

PLCT GRAPH CF RATE OF WEIGHT LOSS AGAINST PERCENT WEIGHT LOSS

CALL GP (WW,DWOT,L,LS,M,JN,LW,LN,A,PLOT)
WRITE (6,3C00)
WRITE (6,3140) ID
3140 FORMAT (1,11F-WEIGHT LOSS VS TIME,20X,A5)

PLCT GRAPH CF PERCENT WEIGHT LOSS AGAINST TIME

CALL GP (THN,WW,L,LS,M,JN,LW,LN,A,PLOT)
WRITE (6,3C00)
WRITE (6,3150) ID
3150 FORMAT (10X,12HTDER VS TIME,20X,A5)

PLCT GRAPH CF TEMPERATURE DERIVATIVE AGAINST TIME

CALL GP (THN,TDER,L,LS,M,JN,LW,LN,A,PLCT)
GO TO 500

GO TO 500

WRITE (6,6DDD)
600 FORMAT (10X,48HNUMBER OF DATA POINTS EXCEEDS NUMBER DIMENSIONED)
500 STCP
ENC
PROGRAM 2

This program provides print out of rates also rate and temperature on punched cards for use in Program 3.
TGTAPE

STATEMENT - IFN(S)

C PROGRAM 2 CUT OFF AND RATE DATA FOR A SERIES OF RUNS
C PROGRAM TO READ A SERIES OF RUNS FROM THE MASTER FILE, APPLY THE
C APPROPRIATE CUT OFF VALUE, AND OUTPUT THE RATE OF WEIGHT LOSS AT
C 1 PER CENT INTERVALS ON CARDS FOR USE IN THE ARRHENIUS PROGRAM
C INPUT TEMPERATURES ARE FITTED TO A FIFTH DEGREE POLYNOMIAL USING A
C LEAST SQUARES SUBROUTINE (PLSQ),
C WEIGHTS CORRESPONDING TO SHORT TEMPERATURE RANGES ARE FITTED TO A
C QUADRATIC BY PLSQ.
C INPUT WEIGHTS DIFFERING FROM FITTED LINE BY MORE THAN ONE PERCENT OF THE
C TOTAL WEIGHT LOSS ARE REPLACED BY THE CURVE FIT VALUE.
C CUTPUT DATA IS PUNCED ON TO CARDS FOR FURTHER PROCESSING (TO CALCULATE
C ACTIVATION ENERGY ETC).
C
C W = WEIGHT DATA POINT READ OFF TAPE
C T = TEMPERATURE DATA POINT READ OFF TAPE(IN MV.)
C TI = TIME DATA POINT READ OFF TAPE(IN MV.)
C TINT = TIME INTERVAL
C WW = WEIGHT LOSS AT 1 PER CENT INTERVALS
C CWCT = RATE OF WEIGHT LOSS AT 1 PER CENT INTERVALS
C TDER = HEATING RATE AT 1 PER CENT INTERVALS
C TPOLY = TEMPERATURE CORRESPONDING TO EACH PER CENT WEIGHT LOSS, CALCULATED BY
C PLSQ
C TNW = TIME CORRESPONDING TO EACH PER CENT WEIGHT LOSS
C PLCT = DIMENSIONS FOR GRAPH PLOT SUBROUTINE
C R = COEFFICIENTS OF 10TH ORDER POLYNOMIAL FITTING TEMP/EMF DATA FOR
C PLATINUM*PLATINUM 10 PER CENT RHODIUM
C C = COEFFICIENTS OF WEIGHT/TIME PLSQ QUADRATIC
C C = COEFFICIENTS OF 5TH ORDER PLSQ USED TO FIT TIME/TEMP. DATA
C RTEMP = RECIPROCAL ABSOLUTE TEMPERATURE
C EQUIVALENCE (TI(1),PLOT(1)),(ID,JZ(1)),(DATE1,JZ(2)),(DATE2,JZ(3))
C (DATE1,JZ(4)),(COMA,JZ(5)),(CO,HM,JZ(6)),(COM,JZ(7)),(TINT,JZ(8))
C DIMENSION TI(5500),WW(101),TNW(101),DHDT(101),Y(120),C(6),A(1),
C YW(5500),T(5500),Z(42),X(36),PLOT(0,110),TIER(101),TPOLY(101),
C IRTEMP(101),B(101),D(101),JZ(8)
C DIMENSION IDA(12),DCA(12)
C INTEGER DUMMY
C DATA DUMMY/4+ZERO/
C NF=1
15 REAC(5),1010,IDA(NF),CCA(NF)
1010 FORMAT((K,A5,1X,F5.3))
IF (IC.EQ.CUMMY) GO TO 20
NF=NF+1
GC TC 15
20 NF=NF-1
GC 5 INF=1,NF
99 CALL READ(3,JZ,8,J)
IF (IC.EQ.Cdummy) GO TO 101
IF (IC.EQ.ICCA(INF)) GO TO 97
98 CALL READ(3,W,18,J)
IF (J=1198,99,98
101 WRITE(6,4500)
4500 FORMAT(10X,25HSEARCH EXCEEDS VALID FILE)
STOP
97 CC=CCA(INF)
L=0

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25 F=18*L+1
   CALL READ(3,W(M),18,J)
   IF(J-1)10,51,30
10 CALL READ(3,Y(P),18,J)
   IF(J-1)40,50,30
50 WRITE(5,1000),L,L
1000 FORMAT(2X,2I10,"OUT OF PHASE DATA IN A6,18H, AFTER RECORD NO. I3")
   STOP
40 L=L+1
   GC TC 25
30 WRITE(6,61)(2(I),I=1,42)
6 FORMAT(1H1,10X,39HTAPE READ ERROR IN THE FOLLOWING RECORD/10X,14(A
   16,2X)/)
   STOP
51 JJ=.010*FLOAT(N)
   LL = MAX(0,JJ,10)

C JJ = 1 PERCENT OF NO. OF DATA SETS READ IN
C LL = NO. OF CURVE FIT POINTS (LATER = NN)
C WRITE (6,3000)
3000 FORMAT (1H1)
   WRITE (6,3050) ID,CATE1,CATE2,COM1,COM2,COM3,COM4
3050 FORMAT (4X,A5,8X,A6,A2,10X,A6,A6,A6,A6,A6,A6,A3/)]
   WRITE(6,3060)TINT
3060 FORMAT (10X,14HTIME INTERVAL=,F6.4)
   WRITE (6,3170) LL
3170 FORMAT (10X,25HTOTAL NO OF PTS IN CURVE FIT = ,I2)
   WRITE (6,3010) N
3010 FORMAT (10X,21HTOTAL NO OF POINTS = ,I4)
   NN = LL
   WRITE(6,3020)DC
3020 FORMAT (10X,9HCUT OFF =,F5.3)
C K = POLYNOMIAL ORDER, NEEDED FOR PLSQ SUBROUTINE. LIST = 0 FOR NO ERRCR
C ANALYSIS OF PLSQ
C WRITE (6,3030) LINEC = 1
3030 FORMAT (1X)
   C = W(I) - W(N)
   E(1)=-5.883309E-6
   E(2)=3.521905E-4
   E(3)=-7.783805E-3
   E(4)=9.75327E-2
   E(5)=7.656367E-1
   E(6)=3.943215E0
   E(7)=-1.367422E1
   E(8)=3.274108E1
   E(9)=-5.749016E1
   E(10)=1.819171E2
   E(11)=3.812777E-2
   DC 55 I=1,N
   W(I) = 100.-(100.-(W(I)-W(N))/D)
   W(I)=W(I)/DC
   TI(I)=(2.*FLOAT(I)-1.)*TINT/60.
TGTape
TGTape - EFN Source Statement - IFN(S) - 09/17/71

FCLY=E(1)
CC 3CO J=2,11
300 FCLY=POLY*T(I)/10.+B(J)
T(I)=POLY
55 CONTINUE

Curve fit of time and temperature data

K = 5
LIST = 0
81 CALL PLSC(T,I,TN,K,D,LIST,E-MAX,ERM,EMEQ)
WRITE (6,5100) EMAX
5100 FORMAT (10X,17HMAX TEMP ERROR = ,F10.6)
WRITE (6,5200) ERM
5200 FORMAT (10X,17HTEMP ROOT MEAN SQUARE ERROR = ,F10.6)
WRITE (6,5300)
5300 FORMAT (10X,15HTEMP POLY COEFF)
WRITE (6,5400)
5400 FORMAT (13X,12,I)

START MAJOR LOOP

II = LINDA-1
88 NW=FLOAT(NW)

Scan weight data for one close to but just greater than one percent weight
LASS. II = INDEX OF THAT POINT

89 I=LINDA,N
II = II+1
IF (W(II)*WT-WNW(NW)) GO TO 70
60 CONTINUE
70 LINDA = II-(LL/2)

LINDA = INDEX OF FIRST DATA TO BE USED BY PLSQ

CC 9C J=1,LL
90 J = LINDA+J-1
TI(J)=(2.*FJCAT(JI)-2.)*TINT/60.
Y(J) = W(J)

Curve fit of time and weight data

K = 2
LIST = 0
117 CALL PLSC(T,I,TN,K,D,LIST,E-MAX,ERM,EMEQ)

Start loop to check for bad input data

CC 81 J=1,LL
82 J = LINDA+J-1

WE = weight calculated from polynomial
C WE=CI(J)*TI(J)+2*C(2)*TI(J)+C(3)
C CCMARE CALCULATED AND ORIGINAL DATA
C IF (ABS(WE=W(J)),GT.1) GO TO 82
C TC 81
82 WRITE (6,4000) JJ,W(JJ),WE
4000 FORMAT (10X,9HT,PT NO ,14,10H WEIGHT = ,F5.1,13H REPLACED BY ,
*F5.1)
C REPLACE BAC DATA BY CALCULATED VALUES
C JJ=WE
KK = 2
81 CONTINUE
C TC (83,88),KK
C C CHECK FOR IMAGINARY ROOTS IN SOLUTION OF QUADRATIC
C 83 SCREW = C(2)*C(2)-4.0*C(1)*(C(3)-Wt(NW))
 IF (SCREW.LT.0.0) GO TO 90
C USE REAL ROCT TO DETERMINE TIME CORRESPONDING TO EACH PERCENT WEIGHT LOSS
C TNW(NW) = (SORT(C(2)*C(2)-4.C*C(1)*C(3)-Wt(NW))=C(2))/(2.0*C(1))
C CWCT = RATE OF WEIGHT LOSS
C CWCT(NW) = 2.0*C(J)*TNW(NW) + C(2)
C TC 100
90 TNW(NW) = (2.*FLOAT(J)-4.)*TINT/60.
 CWCT(NW) = 0.0
C C WRITE OUT IDENTIFICATION AND LOCATION OF BAD DATA
C WRITE (6,3160)NW,II,TNW(NW),W(JJ)
3160 FORMAT(12X,17HS) SCREW LESS THAN 0,10X,3HNN=,1J,10X,3HTI=,14,10X,
 2HT=,F6.2,10X,2HM=,F6.1)
100 CONTINUE
C WRITE (6,3110)
3110 FORMAT(12X,17H WEIGHT LOSS,6X,8HD WT(NW),14X,4HT TEMP,6X,
 4HT DC,11X,4HT TIME)
C TC 120 M=1,99
CT=TNW(NW)
TSTCR = (11)
C C LCCP TO EVALUATE TEMPERATURE POLYNOMIAL FOR EACH VALUE OF CT
C CC 250 I=2,6
200 TSTCR = TSTOR*CT*D(I)
 TPCLY(NW) = TSTOR
 TSTCR = 5.*D(1)
 CC 250 I=2,5
 J = 6-I
250 TSTCR = TSTOR*CT+FLOAT(J)*D(I)
C TGER = TEMPERATURE DERIVATIVE
C RTMP = RECIPROCAL OF ABSOLUTE TEMPERATURE
C
TGER(NW) = TSTOR
RTMP(NW) = 1.0/(TPOLY(NW)+273.16)
WRITE (6,3120) NW, DWDT(NW),TPOLY(NW),TDER(NW),RTMP(NW), CT

3120 FORMAT (6X,10X,E12.5,7X,F5.3,2E15.5,5X,F7.2)

120 CONTINUE
STDER = 0.0,

C CALCULATE AVERAGE TEMPERATURE DERIVATIVE (AVE)
C
EC 125 I=1,99
STDER = STDER+TDER(I)
125 CONTINUE
AVE = STDER/99.0
WRITE (6,3125) AVE

3125 FORMAT (6X,10X,27H AVERAGE TEMP DERIVATIVE = ,E15.5)

C SET UP DUMMY POINTS FOR GRAPPLING SUBROUTINE (GP)
C
WK(100) = 0.0
EWET(100) = 0.0
TAW(100) = TAW(99)
TGER(100) = 0.0
WK(101) = 100.0
EWET(101) = 0.0
TAN(101) = TAN(99)
TCEP(101) = TCEP(99)
WRITE (6,3130) 186

3130 FORMAT (6X,19H MAT VS WEIGHT LOSS,20X,A5)
L = 3
LS = 5
LW = 101
LN = 50
M = 101
DATA A/1H./
JN = 1

C FLCT GRAPPLING RATE OF WEIGHT LOSS AGAINST PERCENT WEIGHT LOSS
C
CALL GP (NW, EWET, L, LS, M, JN, LN, A, PLOT)
WRITE (6,3000) 195
EWET(100) = 0.0
TPOLY(100) = 0.0

C PUNCH OUTPUT CARDS CONTAINING PERCENT WT. LOSS(NW) THEN THREE PAIRS CF
C TEMPERATURE AND RATE OF WEIGHT LOSS DATA
C
EC 150 NW=1,100,3
PUNCH 5000,ID,NW,DWDT(NW),TPOLY(NW),DWDT(NW+1),TPOLY(NW+1),
,CNCT(NW+2),TPOLY(NW+2)


150 CONTINUE

5 CONTINUE
STCF
EAC
PROGRAM 3

Arrhenius Program. Calculates $E_a$ at 1% intervals.
PROGRAM TO DETERMINE TGA PARAMETERS BY FRIEDMAN'S METHOD

PROGRAM ACCEPTS DATA CARDS HAVING THREE SETS OF DATA PER CARD.

LAST CARD OF EACH DECK MUST HAVE A ONE IN COLUMN 1. LAST CARD OF

LAST DECK FOR ONE POLYMER SYSTEM MUST HAVE A TWO IN COLUMN 1 INSTEAD

TO RUN A SECOND SET OF DECKS, PUNCH A CARD WITH A THREE IN COLUMN 1

AND PLACE BETWEEN SETS

AT THE END OF ALL DECKS PLACE A BLANK CARD THEN AN $EOF$

SYMBOLS

_ DWDT = RATE OF WEIGHT LOSS, _ RTEMP = RECIPROCAL OF ABSOLUTE

TEMPERATURE, _ RATE = LOG RATE OF WEIGHT LOSS, _ SLOPE = SLOPE OF ARRHENIUS

PLOT, _ PREX = PRE-EXPONENTIAL FACTOR, _ PLOT = DIMENSION OF GP SUBROUTINE

_ACTE = ACTIVATION ENERGY, _ X AND Y REPRESENT DATA TREATED BY GP

_TPOLY = INPUT TEMPERATURES, _ID = IDENTIFICATION, _ A = NO. OF SYMBOLS IN GP

_AA = PERCENT WEIGHT LOSS, _ AFH = FUNCTION FROM FRIEDMAN'S EQUATION

_FW = AVERAGE AFH, _BB = LOG (PERCENT RESIDUE), _WF = AVERAGE AFH

DIMENSION _ DWDT(100, 10), _ RTEMP(100, 10), _ RATE(100, 10), _SLOPE(100),

*PREX(100), _PLOT(50, 100), _ACTE(100), _X(10), _Y(10),

*TPOLY(100, 10), _ID(100), _ AA(100), _ AFH(100), _ FW(100), _ BB(95), _ WF(95),

*SPL(100), _ SDS(100), _ SD(100), _B(8)

1 READ (5, 1000) _ IG, _ COM1, _ CCM2, _ CCM3, _ COM4, _ COM5, _ COM6, _ CCM7, _ COM8

1 WRITE (6, 3000) 1

2 WRITE (6, 1100) _ IG, _ COM1, _ COM2, _ CCM3, _ COM4, _ COM5, _ COM6, _ CCM7, _ COM8

J = 0

10 IF (LBJ.EQ.2) GO TO 25

25 XJ = J

WRITE LIST OF RUN IDS

WRITE (6, 1800)(ID(J), J = 1, 10)

CHECK FOR AT LEAST THREE DATA DECKS

IF(J = 3), 30, 35, 35
IAG  
PLCT  
EFN  
SOURCE STATEMENT  
IFn(s)  

30 WRITE (6,2000) 44  
GO TO 300  

35 WRITE (6,1500)  
TSUM = 0  
N = 0  
SPRX = 0.0  

C  
START LOOP TO CALCULATE LEAST SQUARES LINE OF LOG(RATE) VS. RTemp  

DO 45 NW = 4,98  
SUMXX = 0  
SUMYY = 0  
SUMX = 0  
SUMY = 0  
DO 40 K = 1,J  

C  
CHECK FOR ZERO RATES  

IF(DWDT(NW,K) .LT. 1.0E-10) GO TO 65  
RATE(NW,K) = ALOG10(DWDT(NW,K))  
RTemp(NW,K) = 1.0/(1.0ELY(NW,K)+273.16)  

C  
SUMXX = PARTIAL SUM OF X-SQUARED ETC.  

SUMXX = SUMXX + RTemp(NW,K)**2  
SUMYY = SUMYY + (RATE(NW,K))**2  
SUMX = SUMX + RTemp(NW,K)  
SUMY = SUMY + RATE(NW,K)  
SUMXY = SUMXY + RTemp(NW,K)*RATE(NW,K)  
GO TO 55  

C  
SET UP GLMAY FCINTS FCR GP IF A DWCT VALUE IS ZERO  

65 ACTE(NW) = 0.  
PREX(NW) = 0.  
RATE(NW,K) = 0.  
RTemp(NW,K) = 0.0015  
GO TO 45  

55 SLOPE(NW) = (XJ*SUMXY-SUMX*SUMY)/(XJ*SUMXX-SUMX**2)  
SPS(NW) = 1/(SUMYY-(SUMX*SUMY/XJ)-((XJ*SUMXY-SUMX*SUMY)**2/  
(XJ*SUMX-UMXX-2*XJ))/XJ-2.0))  
ALPHA = (SPS(NW)/(SUMXX-(SUMX*SUMY/XJ)))*4.576  
IF(ALPHA) 58,58,57  

57 SDSL(NW) = SCRT(ALPHA)  
GO TO 59  

58 SDIS(NW) = 0.  
59 BETA = (SPS(NW)*SUMXX/(XJ*SUMXX-SUMX*SUMX))  
IF(BETA) 62,62,61  

61 SDO(NW) = SCRT(BETA)  
GO TO 63  

62 SDO(NW) = 0.  
63 ACTE(NW) = -SLOPE(NW)*4.576  
PREX(NW) = (SL*SUMX*SUMY-SUMXY)/(XJ*SUMXX-SUMX**2)  
IF(NW.LT.20) GC TO 45  
IF(NW.GT.60) GC TO 45
TGA

PLCT - EFN SOURCE STATEMENT - IFN(S) -

TSUM = TSUM-SCPE(NW)
SPEX = SPEX + PREX(NW)
N = N+1
45 CONTINUE
C
CALCULATE AVERAGE ACTIVATION ENERGY AND PRE-EXPONENTIAL FACTOR
C
AVPRES = SPEX / FLQT(N)
AVEA = TSUM/FLCAT(N)
AVACTE = AVEA*1.987*2.303
C
START LOOP TO CALCULATE AFW
C
DO 70 NW = 4,98
DO 90 K = 1,J
AFW(K) = RATE(NW,K) + AVEA*RTEMP(NW,K)
90 Z = Z + AFW(K)
FW(NW) = Z/XJ
WN = FLQT(N)
GG = ALCG10(1.00-WN)
SD = 0
DO 93 K = 1,J
93 SD = SD + (FW(NW)-AFW(K))**2
YK = J-1
SDAFW = SQRT(SD/YK)
C
WRITE OUT RESULTS* PERCENT WT. LOSS, ACTIVATION ENERGY, PRE-EXPONENTIAL
C
FACTOR, AVERAGE FW, AND STANDARD DEVIATIONS, ALSO LOG WEIGHT REMAINING(GG)
C
70 WRITE (6,1400) NW,ACTE(NW),SES(NW),PREX(NW),SDI(NW),FW(NW),SDAFW,
GG
WRITE (6,1425) AVACTE
WRITE (6,1435) AVPRES
WRITE (6,1440)
C
SET UP INFORMATION FOR GP SUBROUTINE, SEE OTHER PROGRAMS
C
143
L = 3
LS = 5
LM = 100
LN = 50
M = J
DATA A/1K.1/
JN = 1
C
START LOOP FOR PLOTTING GRAPHS AT 10 PERCENT WEIGHT LOSS INTERVALS
C
DO 200 NW = 1C,99,10
DO 100 K = 1,J
X(K) = RTEMP(NW,K)
100 Y(K) = RATE(NW,K)
WRITE (6,3000)
WRITE (6,1700)
C
PLOT GRAPH OF LOG (RATE OF WEIGHT LOSS) AGAINST RECIPROCAL
C OF TEMPERATURE

200 CALL GP (X,Y,L,LS,M,JN,LW,LN,A,PLOT)
M = 100
WRITE (6,3000)
WRITE (6,3100)

C PLOT GRAPH OF ACTIVATION ENERGY AGAINST PERCENT WT. LOSS

CALL GP (AA,ACTE,L,LS,M,JN,LW,LN,A,PLOT)
WRITE (6,3000)
WRITE (6,3200)

C PLOT GRAPH OF PRE-EXPOENTIAL FACTOR AGAINST PERCENT WEIGHT LOSS

CALL GP (AA,PREX,L,LS,M,JN,LW,LN,A,PLOT)
WRITE (6,3000)
WRITE (6,3300)
WRITE (6,3400)
DO 75 I=1,87
BB(I) = ALOG10(100.-AA(I+3))
75 IF(1) = FW(I+3)
LW = .95
M = 87

C PLOT GRAPH OF LOG(AFW) AGAINST LOG(PERCENT RESICLE WEIGHT)

CALL GP(BB,WF,L,LS,M,JN,LW,LN,A,PLOT)
WRITE (6,3000)
LW = 101
M = 101
DATA 0.1,1,1.2,1.3,1.4,1.5,1.6,1.7,1.8/
AA(1001) = 0.0
AA(101) = 100.0
DO 101 K=1,1
DWD(1000,K) = 0.0
101 DWD(101,K) = 0.0
WRITE (6,3400)
CALL GP (AA,DWD,L,LS,M,J,LW,LN,B,PLOT)
WRITE (6,3000)

C LOOK FOR FURTHER SETS OF DATA

300 READ (5,1300) MORE
IF (MORE.EQ.3) GO TO 1

80 STOP

1000 FORMAT (2X,A3,2X,8A6)
1100 FORMAT (10X,A3,2X,8A6)
1300 FORMAT (11)
1400 FORMAT (10X,13,4X,-3PF7.3,5X,F6.3,5X,0PF6.3,2(5X,F6.3),2(5X,F6.41)
1425 FORMAT (/10X,29H AVERAGE ACTIVATION ENERGY = -3PF7.3)
1435 FORMAT (10X,17H AVERAGE LOG PREX,10X,2H= ,F6.3)
1440 FORMAT(10X,34H BOTH FOR 20-60 PERCENT WEIGHT LOSS)
1500 FORMAT (10X,17H HT ACTIVITY,2X,8HEXPKCAL)/3X,8HST. DEVN.,3X,8HLOG PREX,
+3X,8HST. DEVN.,2X,10HAV.,LOG AFW,2X,8HST. DEVN.,2X,11HLOG RES. WT.)
1700 FORMAT (10X,18HLG RATE VS 1/TEMP,10X,14HWEIGHT LOSS #14)
TGA

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1800 FORMAT (/10X,11HRUN IC NOS *9(A5,2F4.1))
1900 FORMAT (10X,13ERROR FOR W = *14,7THRUN NO. A3,6H READ *13,9H INSTEAD.)
2000 FORMAT (10X,25H LESS THAN 3 HEATING RATES/1H1)
3000 FORMAT (1H1)
3100 FORMAT (10X,32H ACTIVATION ENERGY VS WEIGHT LOSS)
3200 FORMAT (10X,22HPRE-EXP VS WEIGHT LOSS)
3300 FORMAT (10X,46H AVER LOG AF(W) VS LOG PERCENT WEIGHT REMAINING)
3400 FORMAT (10X,48H COMPOUNDED RATE OF WT. LOSS VS. PERCENT WT. LOSS)

END
The experimental apparatus for temperature programmed thermogravimetry has been modified to more effectively obtain kinetic parameters for the degradation of polymers. The thermobalance was modified to incorporate direct sample temperature measurement thereby to minimize temperature measurement errors. An automatic data acquisition system was incorporated into the apparatus and appropriate computer programs to handle the magnetic tape data were written. The modified apparatus has been tested with several polymer systems and it was demonstrated that the use of the magnetic tape data recording system permitted greatly increased output from the thermobalance.
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<thead>
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<th>KEY WORDS</th>
<th>LINK A</th>
<th>LINK B</th>
<th>LINK C</th>
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<tbody>
<tr>
<td>Thermogravimetry (TGA)</td>
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<td>Polymer Degradation</td>
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<td>Kinetics</td>
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