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KINETIC ANALYSIS OF THERMOGRAVIMETRY

Part III: Experimental Modifications

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AIR FORCE MATERIALS LABORATORY
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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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.

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ABSTRACT

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.

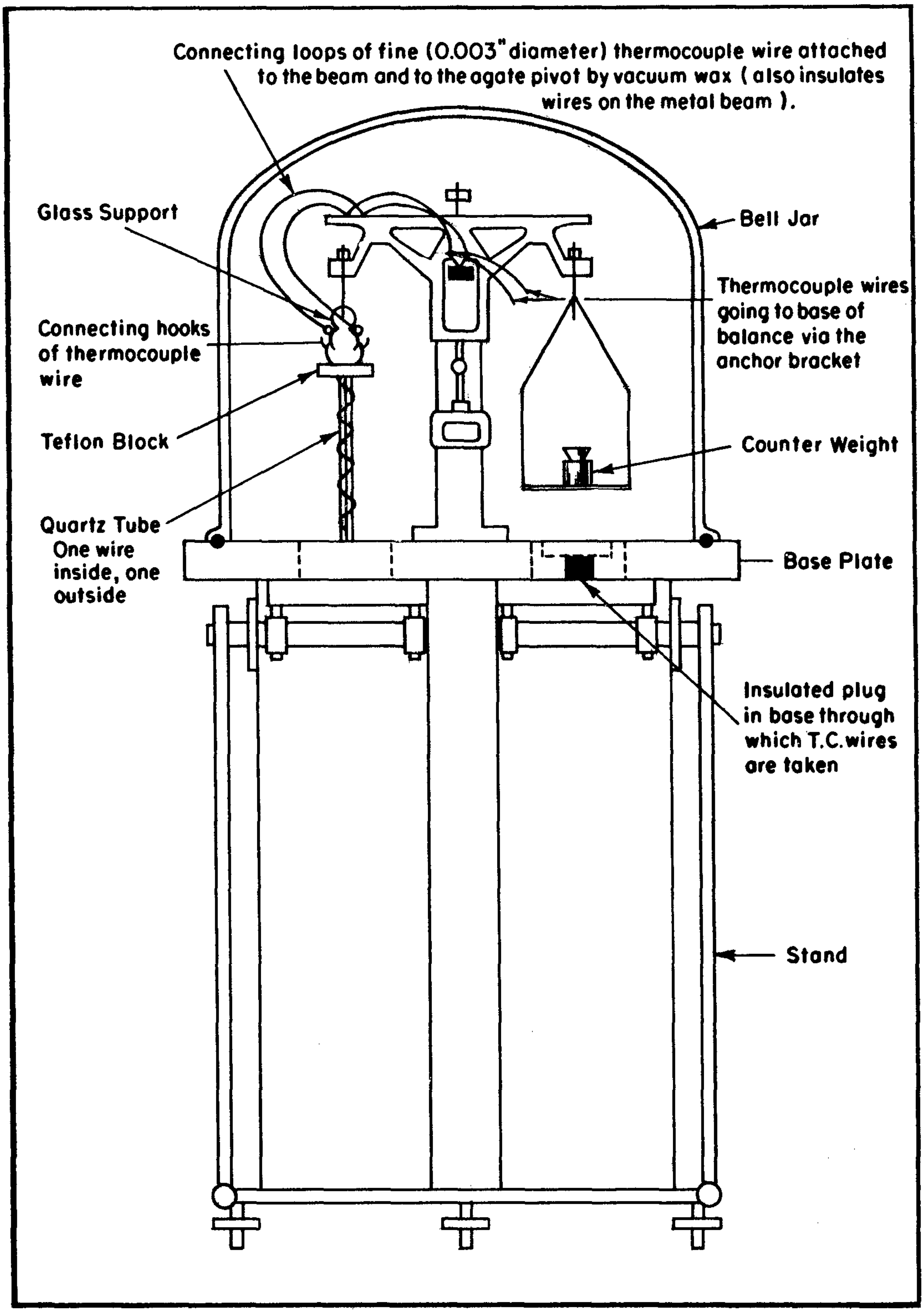

Figure 1. Ainsworth RV Balance - General Arrangement with Wires and Thermocouple Support System

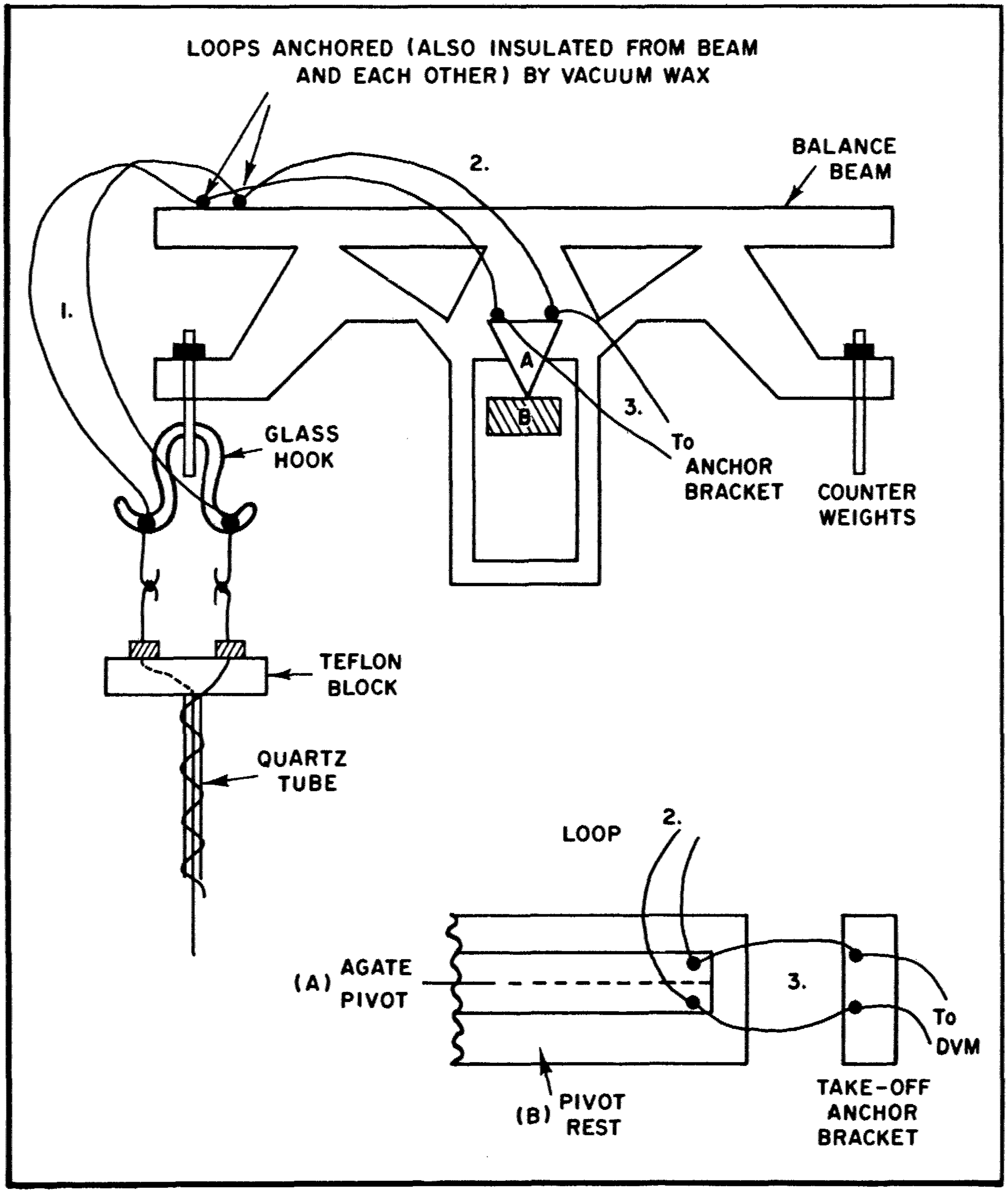

Figure 2. Details of Wires Attached to Balance Beam and the Thermocouple/Support Arrangement

Originally the balance was wired with Chromel/Alumel wire because of its high millivolt per degree output (0.04 mv/^{o}C), but because the wire is magnetic there was considerable interaction with the furnace electrical supply up to 300^{o}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. α_1, is the angle between the beam and suspension, initially, and α_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.

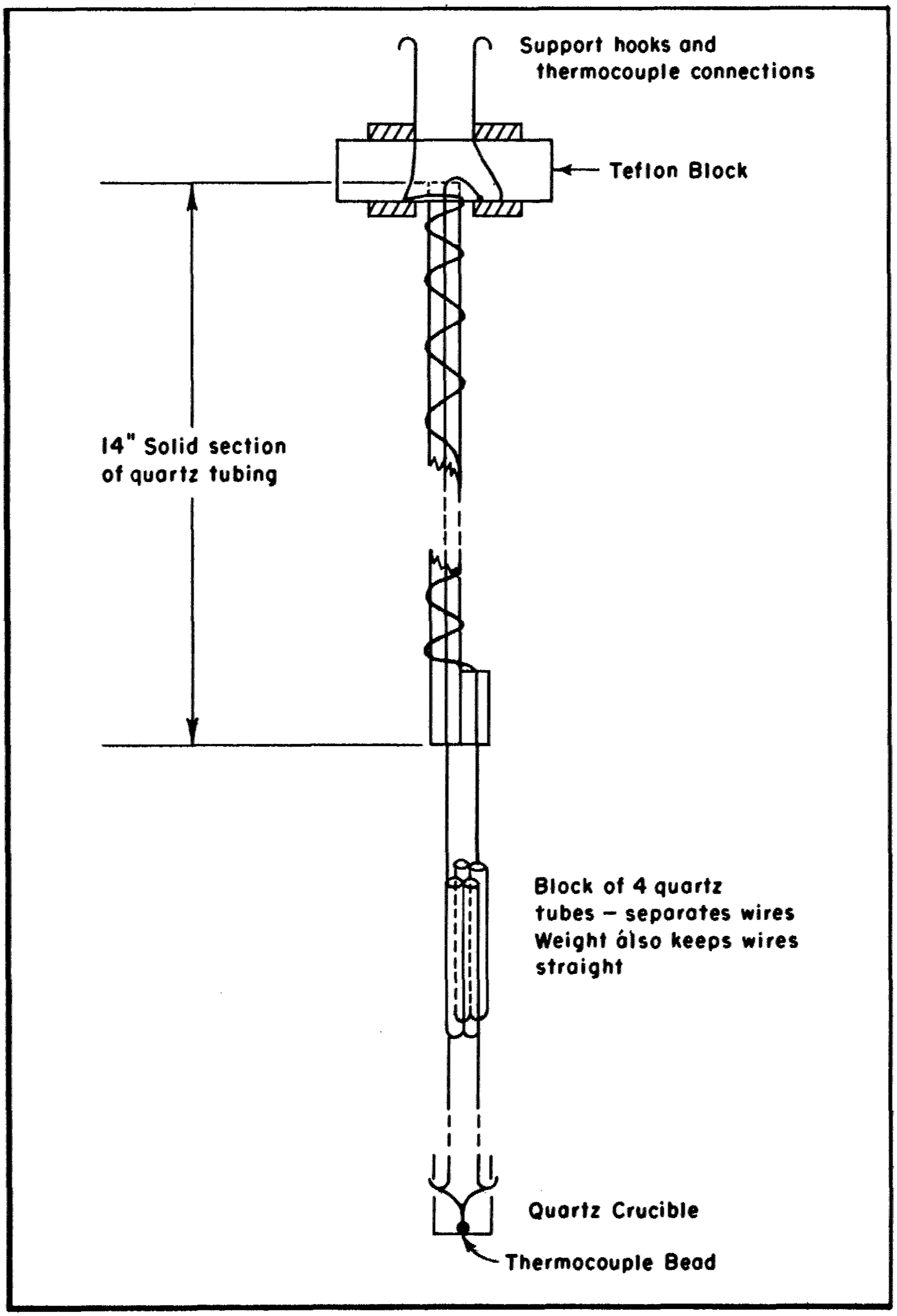

Figure 3. The Thermocouple/Support

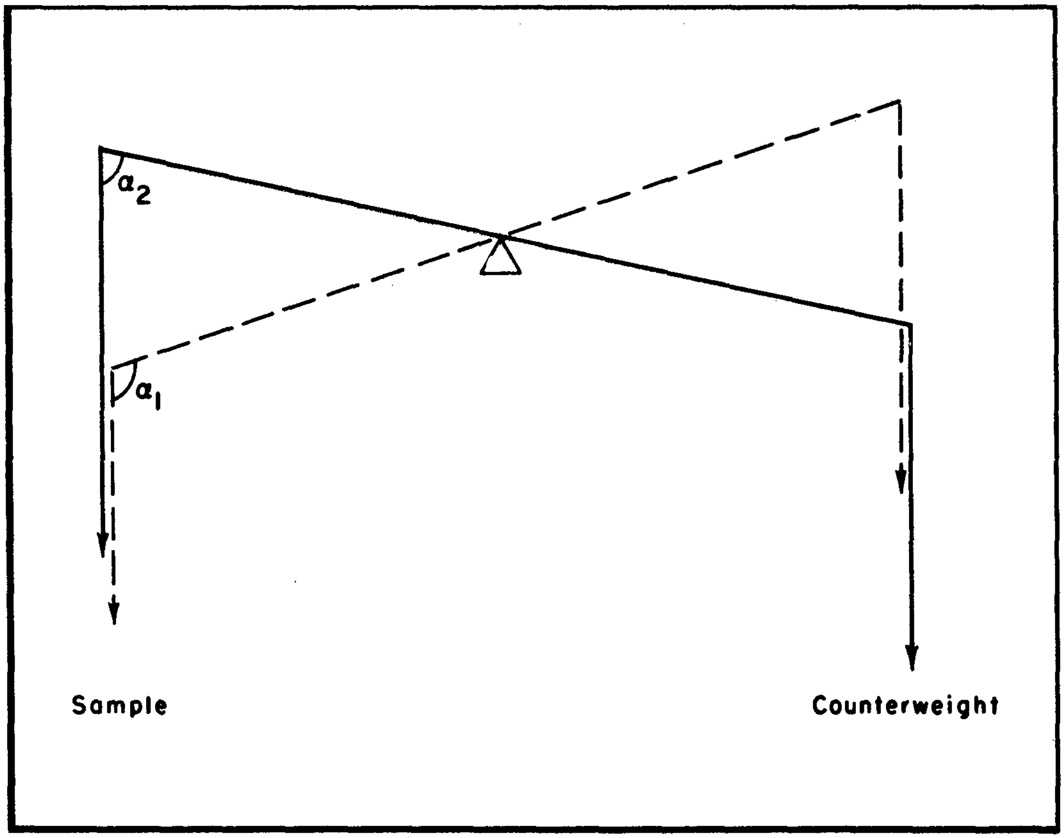

Figure 4. Effect of Sample Weight Changes on Beam Position

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 $1^{\circ}C$ at $600^{\circ}C$.

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 $450^{\circ}C$/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.

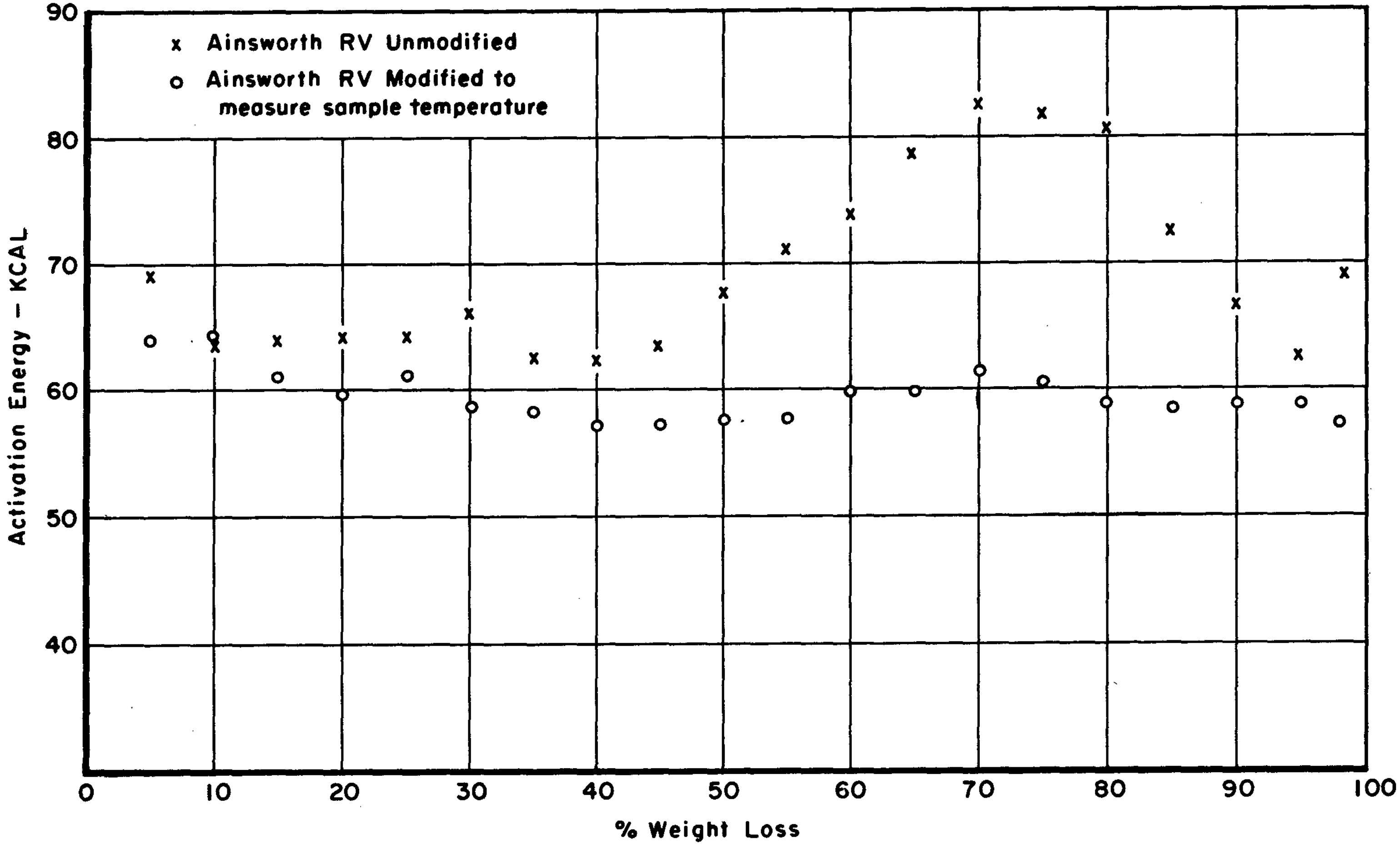

Figure 5. Activation Energy as a Function of Weight Loss for Polytetrafluoroethylene

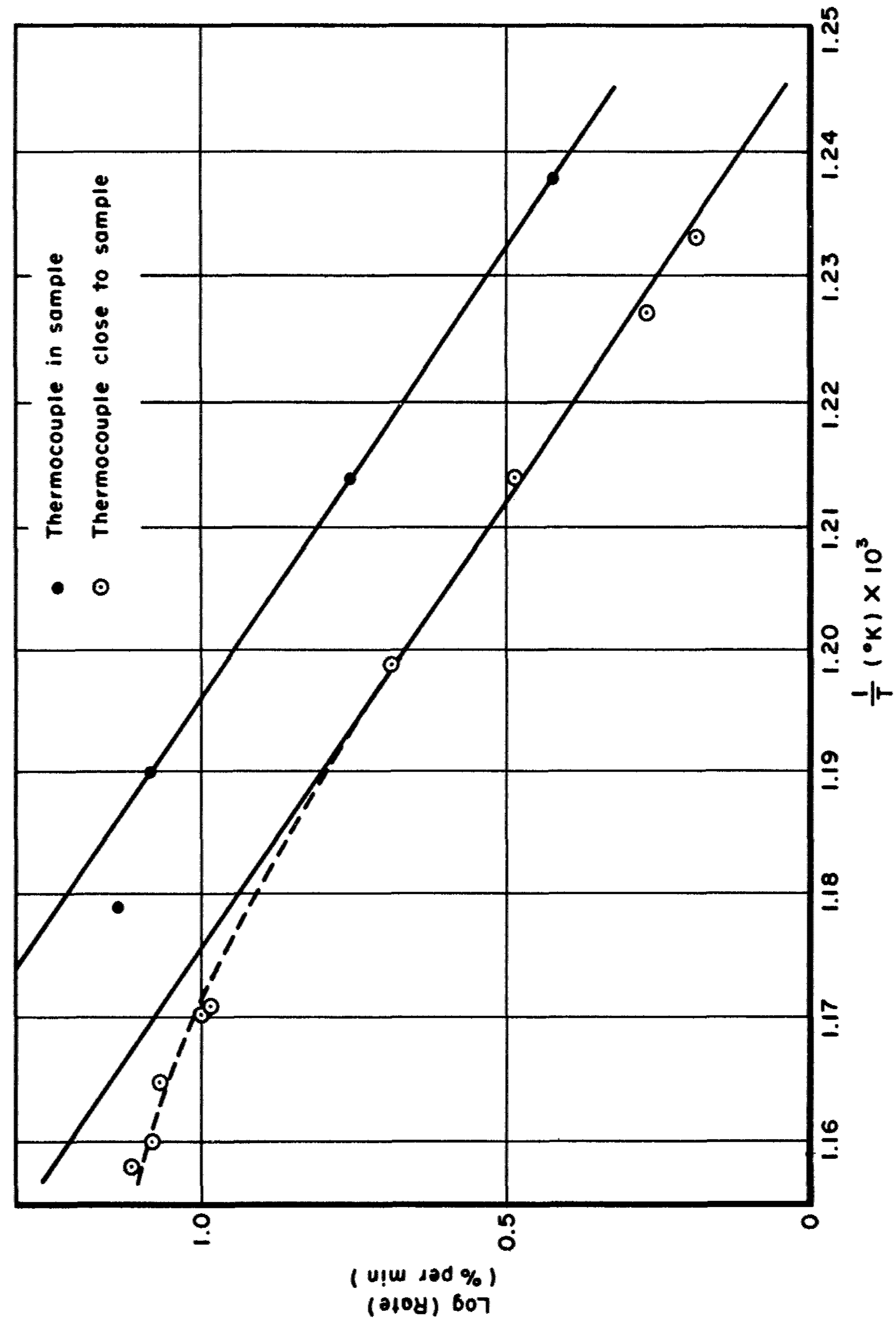

Figure 6. Arrhenius Plots for PTFE at 50% Weight Loss

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 Aquisition System was acquired. This is described in the next section.

2. THE SRL MODEL 837 DATA AQUISITION 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.
2. A model X-2P Digital Voltmeter - Non-Linear Systems, Inc.
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

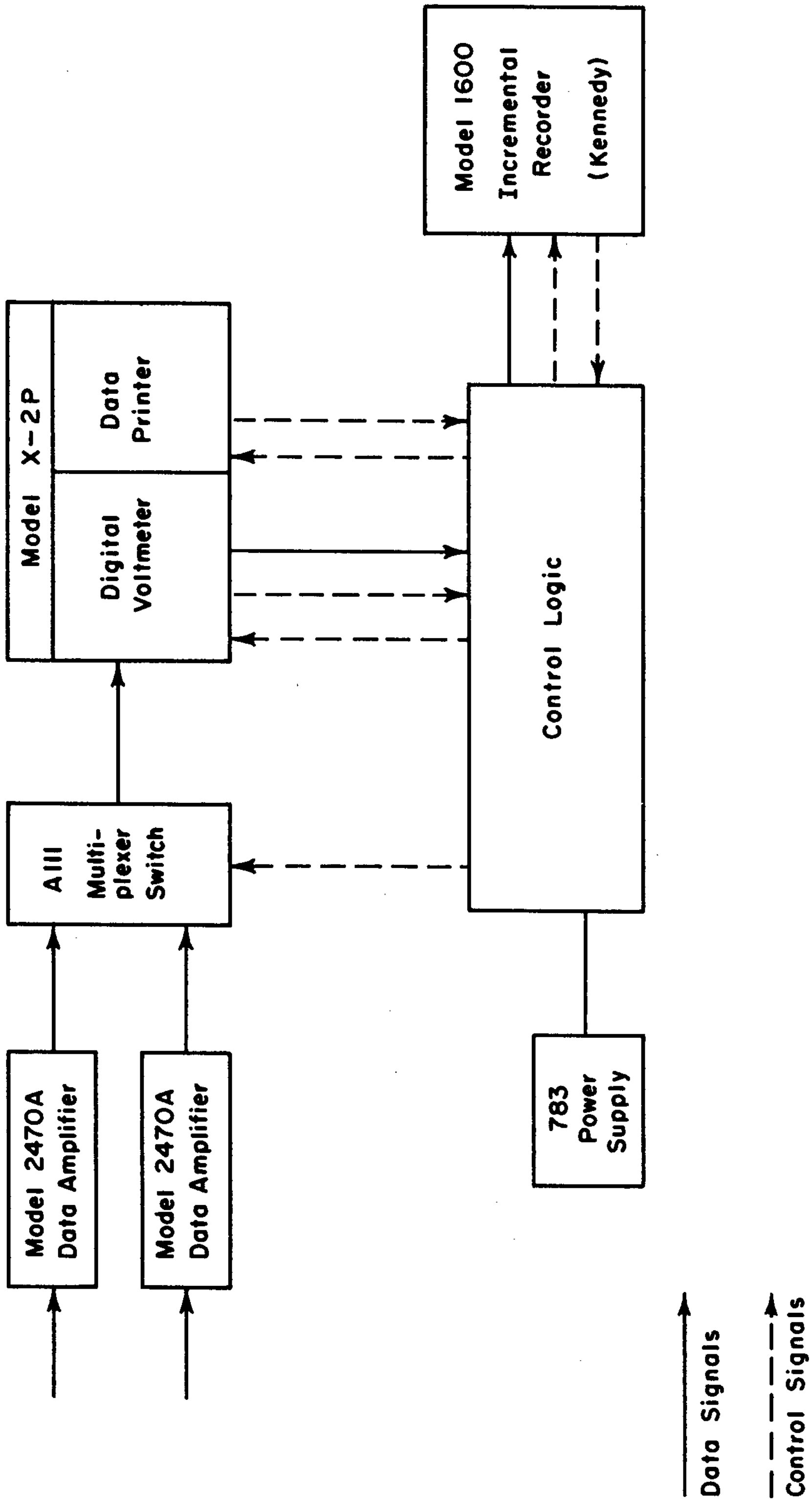

Figure 7. Model 837 Dual Channel Data Aquisition System Block Diagram

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.

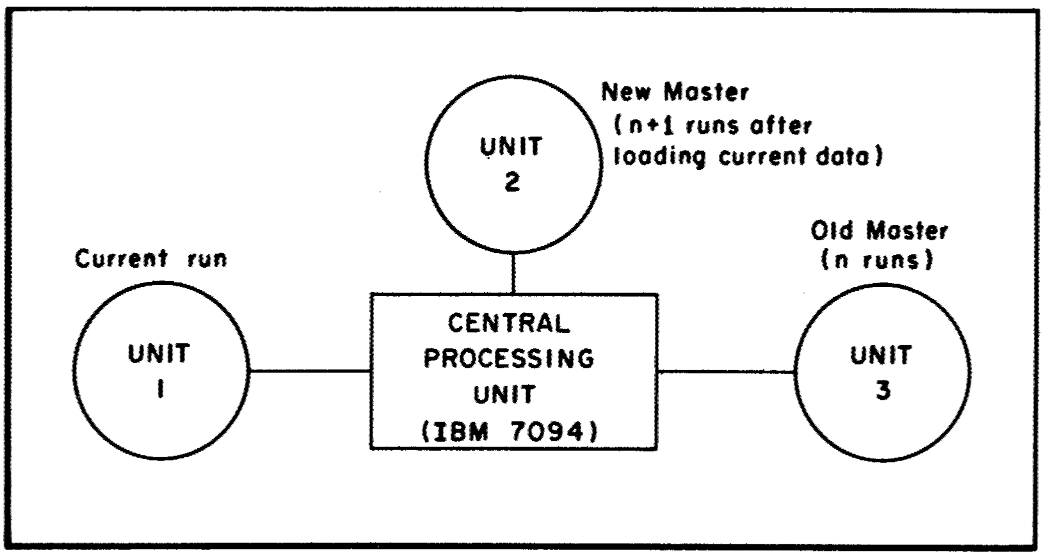

Figure 8. Transfer of Data From Small Tape to the Master Storage Tape

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^{o}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

1. I. J. Goldfarb, A. C. Meeks, R. McGuchan, AFML-TR-68-181, Part II.

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

3. I. J. Goldfarb, A. C. Meeks, AFML-TR-68-367, Part I.

4. H. C. Anderson, in Thermal Analysis, Vol. 1, Ed. P. E. Slade and L. T. Jenkins.

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.

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

C       PROGRAM 1  TAPE PREPARATION AND INITIAL EXAMINATION OF DATA
C       PROGRAM TO READ CURRENT DATA AND TRANSFER IT TO THE MASTER TAPE
C       ALONG WITH ALL THE DATA ON THE OLD MASTER
C       THE PROGRAM ALSO PRINTS OUT THE DATA OF THE CURRENT RUN AND
C       DETERMINES RATE OF WEIGHT LOSS AT ONE PER CENT INTERVALS
C       UNIT 1 = SMALL TAPE WITH CURRENT RUN
C       UNIT 2 = NEW MASTER TAPE
C       UNIT 3 = OLD MASTER TAPE (CAN BE READ ONLY)
C       PROGRAM USES SUBROUTINE EOF TO PERMIT READING OF A NUMBER OF
C       FILES SEPARATED BY END OF FILE MARKERS
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       W = WEIGHT DATA POINT READ OFF TAPE
C       T = TEMPERATURE DATA POINT READ OF TAPE(IN MV.)
C       TI =TIME DATA POINT CALCULATED FROM TIME INTERVAL AND NO OF DATA POINTS
C       TINT=TIME INTERVAL
C       WW =WEIGHT LOSS AT 1 PER CENT INTERVALS
C       DWDT=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       PLOT =DIMENSIONS FOR GRAPH PLOT SUBROUTINE
C       B = COEFFICIENTS OF 10TH ORDER POLYNOMIAL FITTING TEMP/EMF DATA FOR
C           PLATINUM*PLATINUM 10PER CENT RHODIUM
C       C = COEFFICIENTS OF WEIGHT/TIME PLSQ QUADRATIC
C       D = 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))
       1,(COM1,JZ(4)),(COM2,JZ(5)),(COM3,JZ(6)),(COM4,JZ(7)),(TINT,JZ(8))
        DIMENSION TI(5500),WW(101),TNW(101),DWDT(101),Y(120),C(6),A(1),
       1W(5500),T(5500),Z(42),X(36),PLOT(50,110),TDER(101),TPOLY(101),
       1RTEMP(101),B(11),D(6),JZ(8)
        INTEGER DUMMY
        DATA DUMMY/4HZERO/
     98 CALL READ(3,JZ,8,J)                                                2
        IF (ID.EQ.DUMMY)GO TO 114
        CALL WRITE(2,JZ,8)                                                 7
     97 CALL READ(3,X,18,J)                                                9
        IF (J-1) 111,112,113
    111 CALL WRITE(2,X,18)                                                13
        GO TO 97
    112 CALL CLOSE(2,2)                                                   16
        GO TO 98
    113 WRITE(6,115)JZ(1)                                                 18
    115 FORMAT(2X,A5,39HREDUNDANCY ENCOUNTERED - RUN TERMINATED)
        STOP
    114 READ(5,1000)ID,DATE1,DATE2,COM1,COM2,COM3,COM4,TINT               19
   1000 FORMAT(8X,A5,1X,A6,A2,2X,3A6,A3,6X,F6.4)
        CALL WRITE(2,JZ,8)                                                21
```

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

        L=C
        ASSIGN 20 TC IEOF
        CALL EOF(IECF)                                                    25
 10     L=L+1
        N=18*L
        IF(N.GT.55CC)GC TO 400
        M=N-17
        READ(1,1002)(W(I),T(I),I=M,N)                                     32
  1002  FORMAT(36(F6.2,1X))
    19  CALL WRITE(2,W(M),18)                                             42
        CALL WRITE(2,T(M),18)                                             45
        GO TC 10
 20     L=L-1
        N=18*L
        CALL CLOSE(2,2)                                                   50
        CALL WRITE(2,DUMMY,8)                                             52
   25   LK=L-5
        DO 38C K=1,LK,5
        WRITE(6,4)IC,K                                                    57
     4  FORMAT(1H1,10X,A5,5X,6HREC NO,I3//38X,3(1HW,11X,1HT,11X))
        KT=K+4
        DO 370 J=K,KT
        KB=18*J-17
        KE=18*J-12
        DO 365 I=KB,KE
   365  WRITE(6,5)W(I),T(I),W(I+6),T(I+6),W(I+12),T(I+12)                65
     5  FORMAT(35X,6(F7.2,4X))
        WRITE(6,381)                                                      72
   381  FORMAT(1H0)
   370  CONTINUE
   38C  CONTINUE
        LR=L-(L/5)*5
        IF(LR.EQ.0)LR=5
        M=L-LR+1
        WRITE(6,4)IC,M                                                    81
        DO 385 J=M,L
        KB=18*J-17
        KE=18*J-12
        DO 395 I=KB,KE
   395  WRITE(6,5) W(I),T(I),W(I+6),T(I+6),W(I+12),T(I+12)                89
        WRITE(6,381)                                                      96
   385  CONTINUE
    51  JJ=.C1C*FLCAT(N)
        LL = MAXO(JJ,1C)
C
C       JJ = 1 PERCENT OF NO. OF DATA SETS READ IN
C       LL = NO. OF CURVE FIT POINTS (LATER = NN)
C
        WRITE (6,3CCO)                                                   102
  3000  FORMAT (1H1)
        WRITE (6,3C50) ID,DATE1,DATE2,COM1,COM2,COM3,COM4                103
  3050  FORMAT(4X,A5,8X,A6,A2,1CX,A6,A6,A6,A3//)
        WRITE(6,306C)TINT                                                104
  3060  FORMAT(10X,14HTIME INTERVAL=,F6.4)
        WRITE (6,3170) LL                                                105
  3170  FORMAT (10X,25HNC CF PTS IN CURVE FIT = ,I2)
```

```
      TGTAPE                                                                   09/17/70
          TGTAPE       -  EFN    SOURCE STATEMENT   -   IFN(S)   -

      WRITE (6,3010) N                                                                  106
 3010 FORMAT (10X,21HTOTAL NO OF POINTS = ,I4)
      NN = LL
C
C     K = POLYNOMIAL ORDER,NEEDED FOR PLSQ SUBROUTINE. LIST = 0 FOR NO ERROR
C     ANALYSIS OF PLSQ
C     D = TOTAL WEIGHT LOSS
C
      LINDA = 1
      D = W(1) - W(N)
      B(1)=-6.885309E-6
      B(2)=3.521905E-4
      B(3)=-7.783805E-3
      B(4)=9.75327E-2
      B(5)=-7.656367E-1
      B(6)=3.943215E0
      B(7)=-1.367422E1
      B(8)=3.274186E1
      B(9)=-5.749016E1
      B(10)=1.819171E2
      B(11)=3.812777E-2
      DO 55 I=1,N
      W(I) = 100.-(100.*(W(I)-W(N))/D)
      TI(I)=(2.*FLOAT(I)-1.)*TINT/60.
      POLY=B(1)
      DO 300 J=2,11
  300 POLY=POLY*I(I)/10.+B(J)
      T(I)=POLY
   55 CONTINUE
C
C     CURVE FIT OF TIME AND TEMPERATURE DATA
C
      K = 5
      LIST = 0
      CALL PLSQ(TI,T,N,K,D,LIST,EMAX,ERMS,EMEQ)                                         129
      WRITE (6,5100) EMAX                                                               130
 5100 FORMAT (10X,17HMAX TEMP ERROR = ,F10.6)
      WRITE (6,5200) ERMS                                                               131
 5200 FORMAT (10X,30HTEMP ROOT MEAN SQUARE ERROR = ,F10.6)
      WRITE (6,5300)                                                                    132
 5300 FORMAT (10X,15HTEMP POLY COEFF)
      WRITE (6,5400) (D(I),I=1,6)                                                       133
 5400 FORMAT(13X,E12.6)
C
C     START MAJOR LOOP
C
      DO 100 NW = 1,99
   58 II = LINDA-1
      WW(NW) = FLOAT(NW)
C
C     SCAN WEIGHT DATA FOR ONE CLOSE TO BUT JUST GREATER THAN ONE PERCENT WEIGHT
C     LOSS. II =INDEX OF THAT POINT
C
      DO 60 I=LINDA,N
      II = II+1
      IF (W(I).GT.WW(NW)) GO TO 70
```

```
      TGTAPE                                                        09/17/70
         TGTAPE      -  EFN   SOURCE STATEMENT  -  IFN(S)  -

   60 CONTINUE
   70 LINDA = II-(LL/2)
C
C     LINDA = INDEX OF FIRST DATA TO BE USED BY PLSQ
C
      DO 80 J=1,LL
      JI = LINDA+J-1
      TI(J)=(2.*FLOAT(JI)-2.)*TINT/60.
      Y(J) = W(JI)
   80 CONTINUE
C
C     CURVE FIT OF TIME AND WEIGHT DATA
C
      K = 2
      LIST = 0
      CALL PLSQ(TI,Y,NN,K,C,LIST,EMAX,ERMS,EMEQ)                        168
      KK = 1
C
C     START LOOP TO CHECK FOR BAD INPUT DATA
C
      DO 81 J=1,LL
      JI = LINDA+J-1
C
C     WE = WEIGHT CALCULATED FROM POLYNOMIAL
C
      WE=C(1)*TI(J)**2+C(2)*TI(J)+C(3)
C
C     COMPARE CALCULATED AND ORIGINAL DATA
C
      IF (ABS(WE-W(JI)).GT.1.) GO TO 82
      GO TO 81
   82 WRITE (6,4000) JI,W(JI),WE                                        182
 4000 FORMAT (10X,9HAT PT NO ,I4,10H WEIGHT = ,F5.1,13H REPLACED BY ,
     .F5.1)
C
C     REPLACE BAD DATA BY CALCULATED VALUES
C
      W(JI) = WE
      KK = 2
   81 CONTINUE
      GO TO (83,58),KK
C
C     CHECK FOR IMAGINARY ROOTS IN SOLUTION OF QUADRATIC
C
   83 SCREW = C(2)*C(2)-4.0*C(1)*(C(3)-WW(NW))
      IF (SCREW.LT.0.0) GO TO 90
C
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
C     DWDT = RATE OF WEIGHT LOSS
C                                                                       194
      DWDT(NW) = 2.0*C(1)*TNW(NW) + C(2)
      GO TO 100
   90 TNW(NW)=(2.*FLOAT(II)-4.)*TINT/60.
```

```
      TGTAPB                                                           09/17/7C
          TGTAPE       -  EFN    SOURCE STATEMENT   -   IFN(S)   -

      DWCT(NW) = C.0
C
C     WRITE OUT ICENTIFICATION AND LOCATION OF BAD DATA
C
      WRITE(6,316C)NW,II,TNW(NW),W(II)                                       202
 3160 FORMAT(2X,17HSCREW LESS THAN 0,1CX,3HNW=,I3,10X,3HII=,I4,10X,
     .2HT=,F6.2,1CX,2HW=,F5.1)
  100 CONTINUE
      WRITE (6,3110)                                                          207
 3110 FORMAT(//3X,11HWEIGHT LOSS,6X,8HDWDT(NW),14X,4HTEMP,6X,
     .4HTDER,11X,5HRTEMP,16X,4HTIME)
      DO 12C NW=1,99
      CT=TNW(NW)
      TSTOR = D(1)
C
C     LOOP TO EVALUATE TEMPERATURE POLYNOMIAL FOR EACH VALUE OF CT
C
      DO 2C0 I=2,6
  200 TSTOR = TSTOR*CT+D(I)
      TPOLY(NW) = TSTOR
      TSTOR = 5.*D(1)
      DO 250 I=2,5
      J = 6-I
  250 TSTOR = TSTOR*CT+FLOAT(J)*D(I)
C
C     TDER = TEMPERATURE DERIVATIVE
C     RTEMP = RECIPROCAL OF ABSOLUTE TEMPERATURE
C
      TDER(NW) = TSTOR
      RTEMP(NW) = 1.0/(TPOLY(NW)+273.16)
      WRITE (6,3120) NW,DWDT(NW),TPOLY(NW),TDER(NW),RTEMP(NW),CT             226
 3120 FORMAT (6X,I3,10X,E12.5,7X,F9.3,2E15.5,5X,F7.2)
  120 CONTINUE
      STDER = 0.C
C
C     CALCULATE AVERAGE TEMPERATURE DERIVATIVE (AVE)
C
      DO 125 I=1,99
      STDER = STDER + TDER(I)
  125 CONTINUE
      AVE = STDER/99.0
      WRITE (6,3125) AVE                                                      241
 3125 FORMAT (//1CX,27H AVERAGE TEMP DERIVATIVE = ,E15.5)
C
C     SET UP DUMMY POINTS FOR GRAPH PLOTTING SUBROUTINE (GP)
C
      WW(1CC) = C.0
      DWDT(100) = C.C
      TNW(1C0) = TNW(99)
      TDER(1C0) = 0.C
      WW(1C1) = 1C0.C
      DWDT(1C1) = C.C
      TNW(1C1) = TNW(99)
      TDER(1C1) = TDER(99)
      WRITE (6,3CC0)                                                          242
      WRITE (6,313C)  ID                                                      243
```

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

  313C FORMAT (1CX,19HDWDT VS WEIGHT LOSS,20X,A5)
       L = 3
       LS = 5
       LW = 1C1
       LN = 5C
       M = 1C1
       DATA A/1H./
       JN = 1
C
C      PLCT GRAPH CF RATE OF WEIGHT LOSS AGAINST PERCENT WEIGHT LOSS
C
       CALL GP (WW,DWCT,L,LS,M,JN,LW,LN,A,PLOT)                               250
       WRITE (6,3CCO)                                                         251
       WRITE (6,3140) ID                                                      252
  3140 FORMAT (10X,19HWEIGHT LOSS VS TIME,20X,A5)
C
C      PLCT GRAPH CF PERCENT WEIGHT LOSS AGAINST TIME
C
       CALL GP (TNW,WW,L,LS,M,JN,LW,LN,A,PLOT)                                253
       WRITE (6,3CCO)                                                         254
       WRITE (6,3150) ID                                                      255
  3150 FORMAT (1CX,12HTDER VS TIME,20X,A5)
C
C      PLCT GRAPH CF TEMPERATURE DERIVATIVE AGAINST TIME
C
       CALL GP (TNW,TDER,L,LS,M,JN,LW,LN,A,PLCT)                              256
       GO TC 500
   400 WRITE(6,6CCC)                                                          258
  6000 FORMAT(10X,48HNUMBER OF DATA POINTS EXCEEDS NUMBER DIMENSIONED)
   50C STCP
       ENC
```

PROGRAM 2

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

```
     TGTAPE                                                                   09/17/70
         TGTAPE     -  EFN   SOURCE STATEMENT  -  IFN(S)  -

C      PRCGRAM 2  CUT OFF AND RATE CATA FOR A SERIES OF RUNS
C      FRCGRAM TC REAC A SERIES OF RUNS FROM THE MASTER FILE,APPLY THE
C      APPRCPRIATE CUT OFF VALUE, AND OUTPUT THE RATE OF WEIGHT LCSS 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 TC A
C      CUACRATIC BY PLSC.
C      INPUT WEIGHTS DIFFERING FROM FITTED LINE BY MORE THAN ONE PERCENT CF THE
C      TCTAL WEIGHT LOSS ARE REPLACED BY THE CURVE FIT VALUE.
C      CUTPLT DATA IS PUNCHED ON TO CARDS FOR FURTHER PROCESSING (TO CALCULATE
C      ACTIVATION ENERGY ETC).
C      W = WEIGHT DATA POINT READ OFF TAPE
C      T = TEMPERATURE DATA POINT READ OF TAPE(IN MV.)
C      TI =TIME CATA POINT CALCULATED FROM TIME INTERVAL AND NO OF DATA POINTS
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      TPCLY=TEMPERATURE CORRESPONDING TO EACH PER CENT WEIGHT LOSS,CALCULATED BY
C      PLSC
C      TNW= TIME CORRESPONDING TO EACH PER CENT WEIGHT LOSS
C      PLCT =DIMENSIONS FOR GRAPH PLOT SUBROUTINE
C      B = CCEFFICIENTS OF 10TH ORDER POLYNOMIAL FITTING TEMP/EMF DATA FOR
C         PLATINUM*PLATINUM 10PER CENT RHODIUM
C      C = CCEFFICIENTS OF WEIGHT/TIME PLSQ QUADRATIC
C      D = CCEFFICIENTS 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))
      1,(COM1,JZ(4)),(COM2,JZ(5)),(COM3,JZ(6)),(COM4,JZ(7)),(TINT,JZ(8))
       DIMENSION TI(5500),WW(101),TNW(101),DWDT(101),Y(120),C(6),A(1),
      1W(5500),T(5500),Z(42),X(36),PLOT(50,110),TDER(101),TPOLY(101),
      1RTEMP(101),B(11),D(6),JZ(8)
       DIMENSION IDA(12),DCA(12)
       INTEGER DUMMY
       DATA DUMMY/4HZERO/
       NF=1
    15 READ(5,1010)IDA(NF),DCA(NF)                                               2
  1010 FORMAT(8X,A5,1X,F5.3)
       IF(IDA(NF).EQ.DUMMY)GO TO 20
       NF=NF+1
       GO TO 15
    20 NF=NF-1
       DO 5 INF=1,NF
    99 CALL READ(3,JZ,8,J)                                                       16
       IF(ID.EQ.DUMMY)GO TO 101
       IF(ID.EQ.IDA(INF))GO TO 97
    98 CALL READ(3,W,18,J)                                                       26
       IF(J-1)98,99,98
   101 WRITE(6,4500)                                                             29
  4500 FORMAT(10X,25HSEARCH EXCEEDS VALID FILE)
       STOP
    97 DC=DCA(INF)
       L=0
```

```
      TGTAPE                                                          09/17/70
         TGTAPE      -  EFN   SOURCE STATEMENT  -  IFN(S)  -

   25 M=18*L+1
      CALL READ(3,W(M),18,J)                                                34
      IF(J-1)10,51,30
   10 CALL READ(3,T(M),18,J)                                                39
      IF(J-1)40,50,30
   50 WRITE(6,1000)ID,L                                                     43
 1000 FORMAT(2X,21HOUT OF PHASE DATA IN ,A6,18H, AFTER RECORD NO ,I3)
      STOP
   40 L=L+1
      N=18*L
      GO TO 25
   30 WRITE(6,6)(Z(I),I=1,42)                                               47
    6 FORMAT(1H1,10X,39HTAPE READ ERROR IN THE FOLLOWING RECORD/(8X,14(A
     16,2X)))
      STOP
   51 JJ=.010*FLOAT(N)
      LL = MAX0(JJ,10)
C
C     JJ = 1 PERCENT OF NO. OF DATA SETS READ IN
C     LL = NO. OF CURVE FIT POINTS (LATER = NN)
C
      WRITE (6,3000)                                                        54
 3000 FORMAT (1H1)
      WRITE (6,3050) ID,DATE1,DATE2,COM1,COM2,COM3,COM4                     55
 3050 FORMAT(4X,A5,8X,A6,A2,10X,A6,A6,A6,A3//)
      WRITE(6,3060)TINT                                                     56
 3060 FORMAT(10X,14HTIME INTERVAL=,F6.4)
      WRITE (6,3170) LL                                                     57
 3170 FORMAT (10X,25HNO OF PTS IN CURVE FIT = ,I2)
      WRITE (6,3010) N                                                      58
 3010 FORMAT (10X,21HTOTAL NO OF POINTS = ,I4)
      NN = LL
      WRITE(6,3020)DC                                                       59
 3020 FORMAT(10X,9HCUT OFF =,F5.3)
C
C     K = POLYNOMIAL ORDER,NEEDED FOR PLSQ SUBROUTINE. LIST = 0 FOR NO ERROR
C     ANALYSIS OF PLSQ
C     D = TOTAL WEIGHT LOSS
C
      LINCA = 1
      D = W(1) - W(N)
      B(1)=-6.885309E-6
      B(2)=3.521905E-4
      B(3)=-7.783805E-3
      B(4)=9.75327E-2
      B(5)=-7.656367E-1
      B(6)=3.943215E0
      B(7)=-1.367422E1
      B(8)=3.274186E1
      B(9)=-5.749016E1
      B(10)=1.819171E2
      B(11)=3.812777E-2
      DO 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                                                                 09/17/70
          TGTAPE      -   EFN    SOURCE STATEMENT  -   IFN(S)   -

      POLY=B(1)
      DO 300 J=2,11
  300 POLY=POLY*T(I)/10.+B(J)
      T(I)=POLY
   55 CONTINUE
C
C     CURVE FIT OF TIME AND TEMPERATURE DATA
C
      K = 5
      LIST = 0
      CALL PLSQ(TI,T,N,K,D,LIST,EMAX,ERMS,EMEQ)                                  81
      WRITE (6,5100) EMAX                                                        82
 5100 FORMAT (10X,17HMAX TEMP ERROR = ,F10.6)
      WRITE (6,5200) ERMS                                                        83
 5200 FORMAT (10X,30HTEMP ROOT MEAN SQUARE ERROR = ,F10.6)
      WRITE (6,5300)                                                             84
 5300 FORMAT (10X,15HTEMP POLY COEFF)
      WRITE (6,5400) (D(I),I=1,6)                                                85
 5400 FORMAT(13X,E12.6)
C
C     START MAJOR LOOP
C
      DO 100 NW = 1,99
   58 II = LINDA-1
      WW(NW) = FLOAT(NW)
C
C     SCAN WEIGHT DATA FOR ONE CLOSE TO BUT JUST GREATER THAN ONE PERCENT WEIGHT
C     LOSS. II =INDEX OF THAT POINT
C
      DO 60 I=LINDA,N
      II = II+1
      IF (W(I).GT.WW(NW)) GO TO 70
   60 CONTINUE
   70 LINDA = II-(LL/2)
C
C     LINDA = INDEX OF FIRST DATA TO BE USED BY PLSQ
C
      DO 80 J=1,LL
      JI = LINDA+J-1
      TI(J)=(2.*FLOAT(JI)-2.)*TINT/60.
      Y(J) = W(JI)
   80 CONTINUE
C
C     CURVE FIT OF TIME AND WEIGHT DATA
C
      K = 2
      LIST = 0
      CALL PLSQ(TI,Y,NN,K,C,LIST,EMAX,ERMS,EMEQ)                                117
      KK = 1
C
C     START LOOP TO CHECK FOR BAD INPUT DATA
C
      DO 81 J=1,LL
      JI = LINDA+J-1
C
C     WE = WEIGHT CALCULATED FROM POLYNOMIAL
```

```
      TGTAPE                                                          09/17/70
         TGTAPE      -  EFN    SOURCE STATEMENT  -  IFN(S)  -
C
      WE=C(1)*TI(J)**2+C(2)*TI(J)+C(3)
C
C     COMPARE CALCULATED AND ORIGINAL DATA
C
      IF (ABS(WE-W(JI)).GT.1.) GO TO 82
      GO TO 81
   82 WRITE (6,4000) JI,W(JI),WE                                          132
 4000 FORMAT (10X,9HAT PT NO ,I4,10H WEIGHT = ,F5.1,13H REPLACED BY ,
     .F5.1)
C
C     REPLACE BAD DATA BY CALCULATED VALUES
C
      W(JI) = WE
      KK = 2
   81 CONTINUE
      GO TO (83,58),KK
C
C     CHECK FOR IMAGINARY ROOTS IN SOLUTION OF QUADRATIC
C
   83 SCREW = C(2)*C(2)-4.0*C(1)*(C(3)-WW(NW))
      IF (SCREW.LT.0.0) GO TO 90
C
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
C     DWDT = RATE OF WEIGHT LOSS
C                                                                         144
      DWDT(NW) = 2.0*C(1)*TNW(NW) + C(2)
      GO TO 100
   90 TNW(NW)=(2.*FLOAT(II)-4.)*TINT/60.
      DWDT(NW) = 0.0
C
C     WRITE OUT IDENTIFICATION AND LOCATION OF BAD DATA
C
      WRITE(6,3160)NW,II,TNW(NW),W(II)                                    152
 3160 FORMAT(2X,17HSCREW LESS THAN 0,10X,3HNW=,I3,10X,3HII=,I4,10X,
     .2HT=,F6.2,10X,2HW=,F5.1)
  100 CONTINUE
      WRITE (6,3110)                                                      156
 3110 FORMAT(//3X,11HWEIGHT LOSS,6X,8HDWDT(NW),14X,4HTEMP,6X,
     .4HTDER,11X,5HRTEMP,16X,4HTIME)
      DO 120 NW=1,99
      CT=TNW(NW)
      TSTOR = D(1)
C
C     LOOP TO EVALUATE TEMPERATURE POLYNOMIAL FOR EACH VALUE OF CT
C
      DO 200 I=2,6
  200 TSTOR = TSTOR*CT+D(I)
      TPOLY(NW) = TSTOR
      TSTOR = 5.*D(1)
      DO 250 I=2,5
      J = 6-I
  250 TSTOR = TSTOR*CT+FLOAT(J)*D(I)
```

```
     TGTAPE                                                                  09/17/70
        TGTAPE      -  EFN    SOURCE STATEMENT  -  IFN(S)  -

C
C     TDER = TEMPERATURE DERIVATIVE
C     RTEMP = RECIPROCAL OF ABSOLUTE TEMPERATURE
C
      TDER(NW) = TSTOR
      RTEMP(NW) = 1.0/(TPOLY(NW)+273.16)
      WRITE (6,3120) NW,DWDT(NW),TPOLY(NW),TDER(NW),RTEMP(NW),CT              174
 3120 FORMAT (6X,I3,10X,E12.5,7X,F9.3,2E15.5,5X,F7.2)
  120 CONTINUE
      STDER = 0.0
C
C     CALCULATE AVERAGE TEMPERATURE DERIVATIVE (AVE)
C
      DO 125 I=1,99
      STDER = STDER + TDER(I)
  125 CONTINUE
      AVE = STDER/99.0
      WRITE (6,3125) AVE                                                       186
 3125 FORMAT (//10X,27H AVERAGE TEMP DERIVATIVE = ,E15.5)
C
C     SET UP DUMMY POINTS FOR GRAPH PLOTTING SUBROUTINE (GP)
C
      WW(100) = 0.0
      DWDT(100) = 0.0
      TNW(100) = TNW(99)
      TDER(100) = 0.0
      WW(101) = 100.0
      DWDT(101) = 0.0
      TNW(101) = TNW(99)
      TDER(101) = TDER(99)
      WRITE (6,3000)                                                           187
      WRITE (6,3130)  ID                                                       188
 3130 FORMAT (10X,19HDWDT VS WEIGHT LOSS,20X,A5)
      L = 3
      LS = 5
      LW = 101
      LN = 50
      M = 101
      DATA A/1H./
      JN = 1
C
C     PLOT GRAPH OF RATE OF WEIGHT LOSS AGAINST PERCENT WEIGHT LOSS
C
      CALL GP (WW,DWDT,L,LS,M,JN,LW,LN,A,PLOT)                                 195
      WRITE (6,3000)                                                           196
      DWDT(100) = 0.0
      TPOLY(100) = 0.0
C
C     PUNCH OUTPUT CARDS CONTAINING PERCENT WT. LOSS(NW) THEN THREE PAIRS OF
C     TEMPERATURE AND RATE OF WEIGHT LOSS DATA
C
      DO 150 NW=1,100,3
      PUNCH 5000,ID,NW,DWDT(NW),TPOLY(NW),DWDT(NW+1),TPOLY(NW+1),
     .DWDT(NW+2),TPOLY(NW+2)                                                   198
 5000 FORMAT (1X,A5,I4,E13.5,F6.1,E13.5,F6.1,E13.5,F6.1)
  150 CONTINUE

     TGTAPE                                                                  09/17/70
        TGTAPE      -  EFN    SOURCE STATEMENT  -  IFN(S)  -

    5 CONTINUE
      STOP
      END
```

PROGRAM 3

Arrhenius Program. Calculates E_a at 1% intervals.

```
      TGA                                                                  05/04/70
          PLCT        -  EFN   SOURCE STATEMENT  -  IFN(S)  -

C     PROGRAMME TO DETERMINE TGA PARAMETERS BY FRIEDMANS METHOD
C     PROGRAMME ACCEPTS DATA CARDS HAVING THREE SETS OF DATA PER CARD.
C     LAST CARD OF EACH DECK MUST HAVE A ONE IN COLUMN1. LAST CARD OF
C     LAST DECK FOR ONE POLYMER SYSTEM MUST HAVE A TWO IN COLUMN 1 INSTEAD
C     TO RUN A SECOND SET OF DECKS, PUNCH A CARD WITH A THREE IN COLUMN 1
C     AND PLACE BETWEEN SETS
C     AT THE END OF ALL DECKS PLACE A BLANK CARD  THEN AN  $EOF
C
C     SYMBOLS  DWDT = RATE OF WEIGHT LOSS, RTEMP = RECIPROCAL OF ABSOLUTE
C     TEMPERATURE, RATE = LOG RATE OF WEIGHT LOSS, SLOPE = SLOPE OF ARRHENIUS
C     PLOT, PREX =PRE-EXPONENTIAL FACTOR, PLOT = DIMENSION OF GP SUBROUTINE
C     ACTE = ACTIVATION ENERGY, X AND Y REPRESENT DATA TREATED BY GP
C     TPOLY = INPUT TEMPERATURES, ID = IDENTIFICATION, A = NO. OF SYMBOLS IN GP
C     AA = PERCENT WEIGHT LOSS, AFW = FUNCTION FROM FRIEDMANS EQUATION
C     FW = AVERAGE AFW, BB = LOG (PERCENT RESIDUE), WF = AVERAGE AFW
C
      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(10),A(1),AA(101),AFW(10),FW(100),BB(95),WF(95),
     .SPS(100),SDS(100),SDI(100),B(8)
    1 READ (5,1000) IG,COM1,COM2,COM3,COM4,COM5,COM6,COM7,COM8                 1
      WRITE (6,3000)                                                           3
      WRITE (6,1100) IG,COM1,COM2,COM3,COM4,COM5,COM6,COM7,COM8                4
    2 J = 0
   10 J = J+1
C
C     START LOOP TO READ IN DATA
C
      DO 20 NW = 1, 97,3
C
C     LBJ = 1 IN COLUMN 1 OF LAST CARD OF A DECK, LAST CARD OF LAST DECK FOR
C     ONE POLYMER SYSTEM NEEDS LBJ = 2.
C
      READ (5,1200) LBJ,ID(J),IW,DWDT(NW,J),TPOLY(NW,J),DWDT(NW+1,J),
     .TPOLY(NW+1,J),DWDT(NW+2,J),TPOLY(NW+2,J)
C
C     CHECK THAT INPUT CARDS ARE IN CONSECUTIVE ORDER
C                                                                             10
      IF (IW-NW)3,4,3
    3 WRITE (6,1900) NW,ID(J),IW                                              21
      STOP
    4 AA(NW) = FLOAT(NW)
      AA(NW+1) = FLOAT(NW+1)
      AA(NW+2) = FLOAT(NW+2)
      IF (LBJ.EQ.1) GO TO 10
   20 IF (LBJ.EQ.2) GO TO 25
   25 XJ =J
C
C     WRITE LIST OF RUN IDS
C
      WRITE (6,1800)(ID(I),I=1,J)
C
C     CHECK FOR AT LEAST THREE DATA DECKS
C                                                                             36
      IF(J-3) 30,35,35
```

```
        TGA                                                                  05/04/70
              PLCT          -  EFN    SOURCE STATEMENT   -   IFN(S)   -

   30 WRITE (6,2000)                                                             44
      GO TO 300
   35 WRITE (6,1500)                                                             46
      TSUM = 0
      N = 0
      SPREX = 0.0
C
C     START LOOP TO CALCULATE LEAST SQUARES LINE OF LOG(RATE) VS.  RTEMP
C
      DO 45 NW = 4,98
      SUMXX = 0
      SUMYY = 0
      SUMX = 0
      SUMY = 0
      SUMXY = 0
      DO 40 K = 1,J
C
C     CHECK FOR ZERO RATES
C
      IF(DWDT(NW,K).LT.1.0E-10) GO TO 65
      RATE(NW,K) = ALOG10(DWDT(NW,K))                                            58
      RTEMP(NW,K) = 1.0/(TPOLY(NW,K)+273.16)
C
C     SUMXX = PARTIAL SUM OF X SQUARED ETC.
C
      SUMXX = SUMXX + RTEMP(NW,K)**2
      SUMYY = SUMYY + (RATE(NW,K))**2
      SUMX = SUMX + RTEMP(NW,K)
      SUMY = SUMY + RATE(NW,K)
   40 SUMXY = SUMXY + RTEMP(NW,K)*RATE(NW,K)
      GO TO 55
C
C     SET UP DUMMY POINTS FOR GP IF A DWDT VALUE IS ZERO
C
   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) =((SUMYY-(SUMY*SUMY/XJ)-((XJ*SUMXY-SUMX*SUMY)**2/
     .(XJ*XJ*SUMXX-XJ*SUMX*SUMX)))/(XJ-2.0))
      ALPHA = (SPS(NW)/(SUMXX-(SUMX*SUMX/XJ)))*4.576
      IF(ALPHA) 58,58,57
   57 SDS(NW) = SQRT(ALPHA)                                                      85
      GO TO 59
   58 SDS(NW) = 0.0
   59 BETA = (SPS(NW)*SUMXX/(XJ*SUMXX-SUMX*SUMX))
      IF(BETA) 62,62,61
   61 SDI(NW) = SQRT(BETA)                                                       94
      GO TO 63
   62 SDI(NW) = 0.0
   63 ACTE(NW) = -SLOPE(NW)*4.576
      PREX(NW) = (SUMXX*SUMY-SUMX*SUMXY)/(XJ*SUMXX-SUMX**2)
      IF(NW.LT.20) GO TO 45
      IF(NW.GT.60) GO TO 45
```

```
        TGA                                                                05/04/70
             PLCT        -  EFN   SOURCE STATEMENT  -  IFN(S)  -

        TSUM = TSUM-SLCPE(NW)
        SPREX = SPREX + PREX(NW)
        N = N+1
     45 CONTINUE
C
C       CALCULATE AVERAGE ACTIVATION ENERGY AND PRE-EXPCNENTIAL FACTOR
C
        AVPREX = SPREX / FLOAT(N)
        AVEA = TSUM/FLCAT(N)
        AVACTE = AVEA*1.987*2.303
C
C       START LOCP TC CALCULATE AFW
C
        DO 70 NW = 4,98
        Z = 0
        DO 90 K = 1,J
        AFW(K) = RATE(NW,K) + AVEA*RTEMP(NW,K)
     90 Z = Z + AFW(K)
        FW(NW) = Z/XJ
        WN = FLCAT(NW)
        GG = ALCG10(100.-WN)                                                    126
        SD = 0
        DO 93 K = 1,J
     93 SD = SD + (FW(NW)-AFW(K))**2
        YK = J-1
        SDAFW = SQRT(SD/YK)
C
C       WRITE OUT RESULTS' PERCENT WT. LOSS, ACTIVATION ENERGY, PRE-EXPONENTIAL
C       FACTOR, AVERAGE FW, AND STANCARD DEVIATIONS, ALSC LOG WEIGHT REMAINING(GG)
C                                                                               133
     70 WRITE (6,1400) NW,ACTE(NW),SDS(NW),PREX(NW),SDI(NW),FW(NW),SDAFW,
       .GG                                                                      134
        WRITE (6,1425) AVACTE                                                   141
        WRITE (6,1435) AVPREX                                                   142
        WRITE (6,1440)
C
C       SET UP INFORMATION FOR GP SUBROUTINE, SEE OTHER PROGRAMS
C                                                                               143
        L = 3
        LS = 5
        LW = 100
        LN = 50
        M = J
        DATA A/1H./
        JN = 1
C
C       START LCCP FCR PLOTTING GRAPHS AT 10 PERCENT WEIGHT LOSS INTERVALS
C
        DO 200 NW = 10,99,10
        DO 100 K = 1,J
        X(K) = RTEMP(NW,K)
    100 Y(K) = RATE(NW,K)
        WRITE (6,3000)                                                          160
        WRITE (6,1700) NW
C
C       PLOT GRAPH OF LOG (RATE OF WEIGHT LOSS) AGAINST  RECIPROCAL
```

```
        TGA                                                              05/04/70
            PLOT         -  EFN   SOURCE STATEMENT  -  IFN(S)  -

 C      OF TEMPERATURE
 C                                                                          161
   200 CALL GP (X,Y,L,LS,M,JN,LW,LN,A,PLOT)                                 163
       M = 100
       WRITE (6,3000)                                                       167
       WRITE (6,3100)
 C
 C      PLOT GRAPH OF ACTIVATION ENERGY AGAINST PERCENT WT. LOSS
 C                                                                          168
       CALL GP (AA,ACTE,L,LS,M,JN,LW,LN,A,PLOT)                             169
       WRITE (6,3000)                                                       170
       WRITE (6,3200)
 C
 C      PLOT GRAPH OF PRE-EXPONENTIAL FACTOR AGAINST PERCENT WEIGHT LOSS
 C                                                                          171
       CALL GP (AA,PREX,L,LS,M,JN,LW,LN,A,PLOT)                             172
       WRITE (6,3000)                                                       173
       WRITE (6,3300)                                                       174
       DO 75 I=1,87
       BB(I) = ALOG10(100.-AA(I+3))                                         179
    75 WF(I) = FW(I+3)
       LW = 95
       M = 87
 C
 C      PLOT GRAPH OF LOG(AFW) AGAINST LOG(PERCENT RESIDUE WEIGHT)
 C
       CALL GP(BB,WF,L,LS,M,JN,LW,LN,A,PLOT)                                188
       WRITE (6,3000)                                                       189
       LW = 101
       M = 101
       DATA B/1H1,1H2,1H3,1H4,1H5,1H6,1H7,1H8/
       AA(100) = 0.0
       AA(101) = 100.0
       DO 101 K=1,J
       DWDT(100,K) = 0.0
   101 DWDT(101,K) = 0.0
       WRITE (6,3400)                                                       199
       CALL GP (AA,DWDT,L,LS,M,J,LW,LN,B,PLOT)                              200
       WRITE (6,3000)
 C
 C      LOOK FOR FURTHER SETS OF DATA
 C                                                                          201
   300 READ (5,1300) MORE                                                   202
       IF(MORE.EQ.3) GO TO 1
    80 STOP
  1000 FORMAT (2X,A3,2X,8A6)
  1100 FORMAT (10X,A3,2X,8A6)
  1200 FORMAT (I1,A5,I4,E13.5,F6.1,E13.5,F6.1,E13.5,F6.1)
  1300 FORMAT (I1)
  1400 FORMAT (10X,I3,4X,-3PF7.3,5X,F6.3,5X,0PF6.3,2(5X,F6.3),2(5X,F6.4))
  1425 FORMAT (//10X,29H AVERAGE ACTIVATION ENERGY = ,-3PF7.3)
  1435 FORMAT (10X,17H AVERAGE LOG PREX,10X,2H= ,F6.3)
  1440 FORMAT(10X,34HBOTH FOR 20-60 PERCENT WEIGHT LOSS)
  1500 FORMAT (/8X,7HWT LOSS,2X,8HEA(KCAL),3X,8HST.DEVN.,3X,8HLOG PREX,
      .3X,8HST.DEVN.,2X,10HAV.LOG AFW,2X,8HST.DEVN.,2X,11HLOG RES.WT.)
  1700 FORMAT (10X,18HLOG RATE VS 1/TEMP/10X,14HWEIGHT LOSS = ,I4)
```

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        TGA                                                              05/04/70
               PLCT          -  EFN   SOURCE STATEMENT  -  IFN(S)  -

 1800 FORMAT (/10X,11HRUN IC NOS ,9(A5,2H, ))
 1900 FORMAT (10X,13HERROR FOR W =,I4,7HRUN NO ,A3,6H READ ,I3,
     .9H INSTEAD.)
 2000 FORMAT (10X,25HLESS THAN 3 HEATING RATES/1H1)
 3000 FORMAT (1H1)
 3100 FORMAT (10X,32HACTIVATION ENERGY VS WEIGHT LOSS)
 3200 FORMAT (10X,22HPRE-EXP VS WEIGHT LOSS)
 3300 FORMAT(10X,46HAVER LOG AF(W) VS LOG PERCENT WEIGHT REMAINING)
 3400 FORMAT (10X,48HCOMPOUNDED RATE OF WT. LOSS VS. PERCENT WT. LOSS )
      END
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13. ABSTRACT

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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