

AD-A119 300

NAVAL WEAPONS CENTER CHINA LAKE CA
DATA PROCESSING FOR THE DETERMINATION OF CHEMICAL KINETIC PARAM--ETC(U)
AUG 82 G A VERNON
NWC-TP-6337

F/G 9/2

UNCLASSIFIED

NL

1-1

Aug 82

11:00

11:00



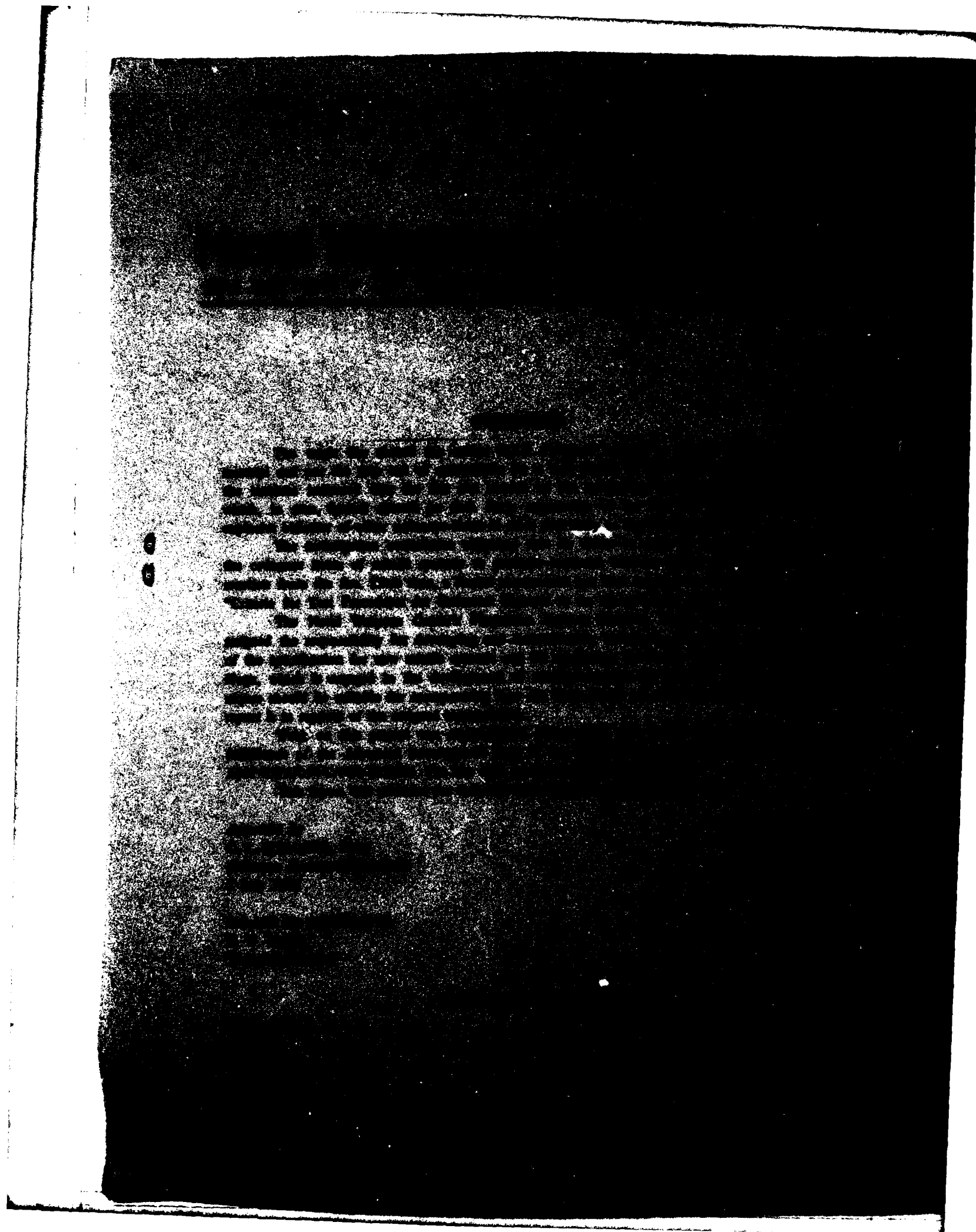
END

DATE

10.82

OTIC

AD A119300



DISCLAIMER NOTICE

**THIS DOCUMENT IS BEST QUALITY
PRACTICABLE. THE COPY FURNISHED
TO DTIC CONTAINED A SIGNIFICANT
NUMBER OF PAGES WHICH DO NOT
REPRODUCE LEGIBLY.**

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NWC TP 6337	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) DATA PROCESSING FOR THE DETERMINATION OF CHEMICAL KINETIC PARAMETERS		5. TYPE OF REPORT & PERIOD COVERED Final Report FY 1981
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Gregory A. Vernon		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Weapons Center China Lake, California 93555		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS AIRTASK A03P-03PA/054-C/1W0- 592-001
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Weapons Center China Lake, California 93555		12. REPORT DATE August 1982
		13. NUMBER OF PAGES 70
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Chemical Kinetics Nonequilibrium Thermodynamics Differential Scanning Calorimetry Nucleation Differential Thermal Analysis Thermal Analysis Gibbs-Helmholtz Equation Thermogravimetric Analysis		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) See reverse side of this form.		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

(U) *Data Processing for the Determination of Chemical Kinetic Parameters*, by Gregory A. Vernon. China Lake, Calif., Naval Weapons Center, August 1982. 70 pp. (NWC TP 6337, publication UNCLASSIFIED.)

(U) Renewed interest in thermal analysis has stimulated development of new computer-compatible techniques for data analysis and reduction. Application of these techniques is intended for use in the determination of chemical kinetic parameters of rocket motor and warhead liners, propellants, and explosives in an effort to increase the safety of handling this hardware.

(U) The numerical methods for data reduction in the field of thermal analysis have had to be updated due to new instrumentation and increasing computer technology. Chemical kinetics subroutines have been developed for isothermal and nonisothermal differential scanning calorimetry and for differential thermal analysis by digitizing analog outputs. Mathematic interpretation of thermodynamic data is accomplished with application of the Gibbs-Helmholtz equation.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

CONTENTS

Introduction	3
Theoretical Background	4
Analytical Techniques	5
General	5
Nonisothermal DSC	6
Isothermal DSC	8
Thermogravimetric Analysis	10
Conclusions	11
References	32
Appendixes:	
A. Program for Acquisition and Analysis of Constant Heating Rate Differential Scanning Calorimeter Data	33
B. Program for Acquisition of Isothermal DSC Data	43
C. Program for Acquisition and Analysis of Thermogravimetric Data	57
Nomenclature	69

Figures:

1. DSC Plot of RDX Class 5	12
2. Plot of RDX Class 5 with a Linear Baseline Correction	13
3. Plot of RDX Class 5	14
4. Plot of $\ln D$ vs $1/T$ to Determine Activation Energy E^*	15
5. Kinetic Plot of RDX Class 5 at 10 deg/min	16
6. Isothermal Run of RDX Class 5 on Perkin Elmer DSC II	17
7. Isothermal Run of RDX Class 5 on Perkin Elmer DSC II	18
8. Plot of the Rate of Change of the Area Fraction vs Area Fraction	19
9. Graphics of Linear Regression Analysis of Linear Portion of Curve in Figure 8	20
10. A Plot of Fraction Unreacted (1-X) vs Time for RDX Class 5	21

Figures (Contd.)

11. Plot of $\ln D$ vs Time	22
12. "Order" Plot for RDX Class 5	23
13. Graphics of Thermogravimetric Analysis of RDX Class 5	24
14. Computer-Generated Plot of the Derivative of the TGA Curve in Figure 13	25
15. Graphics of TGA Plot of Figure 13 Showing % Mass Loss	26

Tables:

1. Computer Printout of Data used to Determine Kinetic Parameters	27
2. Computer Printout of Data used for Graphics and Kinetic Parameter Calculations	29
3. Computer Printout of Time, Temperature, Mass Loss Data for TGA Program	31



Accession No.	
NTIS GRA&I	
DTIC TAB	
Unannounced	
Justification	
By	
Distribution	
Availability	
Dist	Avail. or Special
A-23	GP

INTRODUCTION

The determination of physical properties of liners, explosives, and propellants is important for the characterization of cook-off behavior, aging processes, and the mathematic modelling of the thermal responses of warheads and rocket motors.

The development of test hardware, data acquisition, and numerical methods for data reduction and analysis is of considerable importance. Thermal analysis techniques such as Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), and Differential Thermal Analysis (DTA) have traditionally been used to determine the thermal characteristics and decomposition kinetics of reactive substances.

As compared with other analytical techniques, thermal analysis has until recently received little attention in chemical research. This is primarily due to instrument insensitivity and the laborious task of manually reducing data. More sensitive techniques, usually spectroscopic in nature, were opted for in the determination of chemical kinetics.

There has recently been a resurgence of interest in thermal analysis due to the increased safety awareness of both the industrial and military sectors. This is due to the development of new materials for use in energy development, and for extraterrestrial and military applications.

Considerable activity has been generated in the area of the application of known numerical techniques to thermal analysis. This has been made possible with the development of new thermal analysis techniques, the availability of microprocessor-controlled analysis instrumentation, and the development of small computer technology for the acquisition and reduction of large quantities of data.

As a part of an ongoing process of upgrading the Naval Weapons Center's analytical capabilities, the Explosives Formulation Branch has written computer software to acquire and analyze data from laboratory instruments. These programs include routines to input digital data from interfaced digitizers and various numerical analysis and graphics subroutines to reduce, display, and analyze the data.

Chemical kinetics subroutines have been developed for nonisothermal DSC, isothermal DSC, and for TGA. This has been accomplished through the digitization of the analog outputs of the laboratory instrumentation which is achieved by interfacing with a Fluke 7600A scanning digital multimeter or Fluke 8520A digital multimeter. Transfer to the Hewlett-Packard 9845T computer is achieved via the IEEE-488 interface bus either by direct computer command or by use of service

request interrupts. The rate of data acquisition is programmed via command string to the microprocessor control units of the digital multimeters.

THEORETICAL BACKGROUND

Mathematical interpretation of thermodynamic data is accomplished through the application of the Gibbs-Helmholtz equation, usually stated as:

$$\frac{\partial \Delta G/T}{\partial (1/T)} = \Delta H$$

where G is the Gibbs free energy, H is the enthalpy, and T the absolute temperature. Kinetic data may be determined from the relationship $\Delta G^\circ = -RT \ln K(T)$, $K(T)$ being the equilibrium constant at temperature T . For a reaction such as $A \rightleftharpoons B$, the equilibrium constant may be written $K(T) = k_2(T)/k_1^*(T)$ where $k_2(T)$ is the rate of the forward reaction and $k_1^*(T)$ is the rate of the reverse reaction.

Arrhenius first gave the expression for these rate constants as:

$$k_2(T) = Z \cdot \exp(-E^*/RT)$$

where Z is an experimentally determined rate constant with the dimensions mole/sec and E^* is the activation energy. The form of this equation was taken as a logical extension of the Gibbs-Helmholtz equation and is used presently in experimental determinations. Current interpretation of E^* is that of an energy barrier or depth of a potential well, and the factor $\exp(-E^*/RT)$ is the probability per unit time that a molecule will penetrate the barrier.

From the Gibbs-Helmholtz equation, the temperature dependence of the equilibrium constant is given as:

$$\ln \frac{K(T_2)}{K(T_1)} = \frac{\Delta H}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Unfortunately, when dealing with highly energetic materials, the chemical reactions are irreversible. The temperatures and pressures are not uniform and, in fact, have severe gradients throughout the material, presenting a problem in nonequilibrium thermodynamics. When dealing with small samples, temperature and pressure gradients are usually assumed to be negligible and a rate equation may be written for the reaction. For the reaction $B \rightarrow \text{Products}$:

$$\text{Rate} = \frac{dX}{dt} = k(T) \cdot f(X)$$

where X is the fraction of B that has reacted and $f(X)$ is some function which depends upon the mechanism by which the reaction takes place.

For simple liquid and gaseous reactions, $f(X)$ takes the form $(1-X)^n$, where n is referred to as the reaction order, n is usually 2 or less. A set of coupled reactions will yield fractional n 's while reactions which occur in the solid state via diffusion or nucleation mechanisms take on complex algebraic forms with n usually less than 1.

When looking at energetic materials, $n=1$ works quite well in the higher temperature ranges where $B \rightarrow \text{Products}$ is an accurate representation of the reactions taking place. However, at lower temperatures, nucleation reactions are present. They are dependent upon the surface free energy of the material which is affected by such factors as physical state, impurities, and method of preparation. Thus, a study of reaction rates at higher temperatures may give a somewhat limited view of the manner in which a material might behave.

For nonhomogeneous materials such as propellants, reaction rates are diffusion controlled and highly pressure-dependent. For materials of current interest, $f(X)$ will stand for $(1-X)$ for simple reactions and $X(1-X)$ for the autocatalytic reactions which occur in many explosives.

For materials which melt with decomposition, complex kinetics occur in the initial stages of the decomposition reaction. Behavior beyond the exotherm maximum is usually more typical of the first order reaction, $B_{(\text{liquid})} \rightarrow \text{Products}$. The first stages of the decomposition process frequently draw the most interest in the thermal stability studies. Investigation of this behavior will give a more complete description of how a particular substance reacts.

ANALYTICAL TECHNIQUES

GENERAL

Ordinate data points are obtained by digitizing millivolt output from the instrumentation with the sensitivity of the instruments selectable by the operator. The analog output of the DSC represents energy absorption (endotherm) or release (exotherm) in units of millicalories per second. The TGA output represents milligrams.

Abscissa data points are obtained as time from the Real Time Clock interfaced to the HP 9845T computer. Temperature is obtained as the product of time and heating rate. Extremely accurate temperature

tracking has been achieved in the case of the DSC, while less favorable results have been obtained from the TGA. This is due to the heating rates deviating from programmed values. The problem has been eliminated by manually entering data into a separate computer program after the TGA run is complete.

Data points (X_j, Y_j) are curve-fitted using a precise continuous cubic polynomial, or cubic spline, algorithm. Ordinate values are represented as:

$$Y_j = \sum_{k=0}^3 M_{jk} X^k$$

where the coefficient matrix M is determined by demanding continuity of the polynomial and its first derivative at each data point.

Use of this algorithm allows facile differentiation and integration of the data curves and is relatively insensitive to noise in the instrumental output.

NONISOTHERMAL DSC

Graphics output of a DSC run of RDX Type II Class 5 is shown in Figure 1. Figure 2 is the data after a linear baseline correction has been made.

For a nonisothermal DSC run, the ordinant displacement dH/dt is given as:

$$D(t) = \Delta H \cdot \text{rate} = \Delta H \frac{dX}{dt} = \Delta H \cdot k(t)(1 - X)^n \quad (1)$$

where ΔH is the total enthalpy change for the reaction, represented as the area A , under the displacement - temperature curve. Thus $dX/dt = 1/A \cdot dH/dT$. If this equation is integrated, the result is $X = \Delta Hx(T)/A$ where ΔHx is the heat released due to the fraction X reacting. This is represented by the area $a(T)$, under the peak up until the temperature in question. Thus $X(T) = a(T)/A$ may be determined graphically or by a numerical integration technique as is done by the computer program which has been developed (Figure 3).

Borchardt and Daniels¹ have shown that the rate constant may be expressed as:

$$k(T) = A^{n-1} \frac{dH(T)}{dt}$$

¹Hans J. Borchardt and Farrington Daniels. "The Application of Differential Thermal Analysis to the Study of Reaction Kinetics," Journal of the American Chemical Society, Vol. 79, No. 4, July 1956, p. 41.

Comparing the rate constants at two temperatures gives:

$$\frac{k(T_2)}{k(T_1)} = \frac{(dH/dt)(T_2)}{(dH/dt)(T_1)} \cdot \left[\frac{A-a(T_1)}{A-a(T_2)} \right]^n$$

Since dH/dT is the ordinate deflection $D(T)$, and $X = a(T)/A$, this relation may be rewritten:

$$\frac{k(T_2)}{k(T_1)} = \frac{D(T_2)}{D(T_1)} \cdot \left[\frac{1-x(T_1)}{1-x(T_2)} \right]^n$$

Assuming only one chemical reaction takes place, $k(T)$ may be written:

$$k(T) = Z \cdot \exp(-E^*/RT)$$

and thus:

$$\frac{\exp(-E^*/RT_2)}{\exp(-E^*/RT_1)} = \exp\left[\frac{E^*}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] = \frac{D(T_2)}{D(T_1)} \cdot \left[\frac{1-x(T_2)}{1-x(T_1)} \right]^n$$

and:

$$-E^* \left[\frac{1}{T_2} - \frac{1}{T_1} \right] = R \ln \left[\frac{D(T_2)}{D(T_1)} \right] + nR \ln \left[\frac{1-x(T_1)}{1-x(T_2)} \right]$$

Thus the activation energy may be calculated from ordinate displacement and partial areas. In fact, for closely spaced data points, the last term approaches zero.²

The frequency factor Z , and thus the rate constant may be calculated using partial areas and known values. With ϕ as the heating rate:

$$\frac{dX(r)}{dt} = \phi \cdot \frac{dX(r)}{dT} = Z \cdot \exp[-E^*/RT(r)] \left[1 - \frac{a(r)}{A} \right]$$

In the computer implementation of this method, E^* is calculated from a linear least squares (linear regression) algorithm which fits the curve of $\ln D$ versus $1/T$ (Figure 4).

²Jen Chiu. "Dynamic Differential Calorimetric Technique for Measuring Heat of Polymerization," in Proceedings of the Second Symposium on Analytical Calorimetry, ed. by Roger S. Porter, New York Plenum, 1970, p. 171-183.

Figure 5 shows a plot of the reaction rate versus fraction decomposed. Ideally, the plot should provide some idea of the algebraic form of the rate equation, with a straight line indicating a first order reaction. For an autocatalytic reaction, a straight line would result from plotting rate versus $X(1-X)$. In the case of solids, there are several processes occurring simultaneously and a clear and precise interpretation of this plot would be difficult to achieve. In a homogeneous liquid, such as is present to the right of the exotherm maximum in the case of RDX, a portion may be represented by

RDX (Liquid) $\rightarrow$ Products:

$$\text{Rate} = k(T)(1 - X) \quad (2)$$

and appears as a virtually linear portion of the curve. This portion may be selected for determination of kinetics for the first order reaction of Equation 2.

Kissinger³ has devised a method based upon variable heating rates to determine the activation energy. This method is independent of reaction order and should give an accurate value for E^* assuming that only one chemical reaction is taking place at a time. The basic equation is given as:

$$d(\ln \phi/T_m)/d(1/T) = -E^*/R$$

where T_m is the temperature at which the maximum exotherm or endotherm occurs. A plot of $\ln \phi/T_m$ versus $1/T_m$ from several runs will have slope $-E^*/R$.

ISOTHERMAL DSC

The software developed for nonisothermal DSC has been modified to allow for the treatment of the isothermal case.

Because the temperature is constant in an isothermal DSC, the equation:

$$\frac{dX}{dt} = \lim_{t_2 \rightarrow t_1} \frac{a(t_2) - a(t_1)}{A \cdot (t_2 - t_1)} = k(T) \cdot f(x) \quad (3)$$

may be solved directly for $k(T)$.

³Homer E. Kissinger. "Reaction Kinetics in Differential Thermal Analysis," Analytical Chemistry, Vol. 29, June 1957, p. 1702.

For closely spaced data points, dX/dt is reasonably approximated as $\Delta a/\Delta t \cdot A$. A plot of $\Delta a/A/\Delta t$ versus a/A will indicate the nature of $f(X)$, and k is calculated directly by linear regression analysis for the linear portion of this curve when first order kinetics are observed. One could plot rate versus different algebraic forms of $f(X)$ to see if a straight line results. Again, $f(X)$ would be expected to take the form $(1-X)$ or $X(1-X)$ for explosives.[†] Figures 6 to 9 are graphic output examples of this program and Tables 1 and 2 provide examples of numeric outputs.

The activation energy is calculated by plotting the values of $k(T)$ obtained at several temperatures versus $1/T$. The slope of this plot is E^*/R .

Previous isothermal kinetic determinations have used the portion of data to the right of the exothermic peak. By integrating Equation 3, a plot of fraction unreacted versus time should have the form:

$$1 - X = \exp [-k(T) \cdot t] \quad (4)$$

for a first order reaction (Figure 10).⁴

From Equation 1, the ordinate displacement $D(t)$ is given as $\Delta H \cdot k(T) \cdot (1-x)$. For a first order reaction:

$$D(t) = \Delta H \frac{dX}{dt} = \Delta H \cdot k(T) \cdot (1 - x)$$

Substituting Equation 4 for $(1-x)$ gives:

$$D(t) = \Delta H \cdot k(T) \cdot \exp[-k(T) \cdot t]$$

or

$$\ln[D(t)] = \ln[\Delta H \cdot k(T)] - k(T) \cdot t$$

[†]Jamey and Rodgers. Los Alamos Scientific Laboratory, Private Communication.

⁴Ray N. Rogers. "Differential Scanning Calorimetric Determination of Kinetics Constants of Systems That Melt With Decomposition," Thermochemical ACTA, Vol. 3, 1972, p. 437-447.

Thus a plot of $\ln D$ versus time should have slope $k(T)$ for a first order reaction.⁵ Figure 11 shows the plot of $\ln D$ versus time for RDX Class 5. The linear portion of this curve was used for determination of first order kinetics for $\text{RDX}_{(1)} \rightarrow \text{Products}$.

From the form of Equation 1, it is seen that $\ln D = n \ln(1-a) + \text{constants}$, so a plot of $\ln D$ versus $\ln(1-a)$ should yield the reaction order n . Figure 12 represents this plot. Calculation of the slope in the region from which kinetic data were calculated gives a value of 1.05, which agrees with the assumption of a first order reaction.

Both the partial area technique and the old technique of plotting $\ln D$ versus t give essentially the same answer in the region chosen. The partial area technique is more dynamic in that the fraction of material reacted can be calculated at any point. Thus, if some reaction mechanism is hypothesized, it may be verified with actual experimental numbers.

THERMOGRAVIMETRIC ANALYSIS

While the DSC data are useful for describing the thermodynamics of a system, TGA is necessary for correlating weight loss with temperature. For reactions of the type solid $\rightarrow$ gas, TGA may be used for kinetic determinations. The fraction X , given as $X = M-m/M$, M = original mass, and the reaction rate dx/dt may be taken directly from the TGA data.

Numerical analysis for TGA data is the same as that for nonisothermal DSC. Because the temperature rise rate in the TGA instrument is nonlinear, temperature must be calculated after the run is completed. Temperature/mass data are then manually entered into the computer. Temperature is accurately determined by entering millivolt values from strip chart output and converting to temperature values using a standard National Bureau of Standards interpolating polynomial. Data for RDX Class 5 is shown in Table 3 and is plotted in Figures 13 through 15.

This program was developed primarily to investigate the decomposition of rocket motor liners where time, temperature, and mass values are important. If only mass and temperature are needed, the software is easily modified to allow entry of approximately ten times the number of data points. The acquisition of computer compatible thermogravimetric equipment will also allow acquisition of more data points when all three reference points are required.

⁵Ray N. Rogers. "Simplified Determination of Rate Constants by Scanning Calorimetry", Analytical Chemistry, Vol. 44, December 1971, p. 1336.

NWC TP 6337

CONCLUSIONS

The acquisition and analysis of large amounts of data with a digital computer has opened a new field in the area of thermal analysis. Plotting and numerical analysis software allow the data to be reduced in a fraction of the time previously needed and permit use of a larger number of data points.

In addition, fast integrating algorithms allow use of partial area techniques which will prove to be very influential in future analytical procedures.

The successful application of these computer techniques in the determination of isothermal kinetics should prove extremely useful in determining the cook-off hazards from aging studies and understanding cook-off behavior.

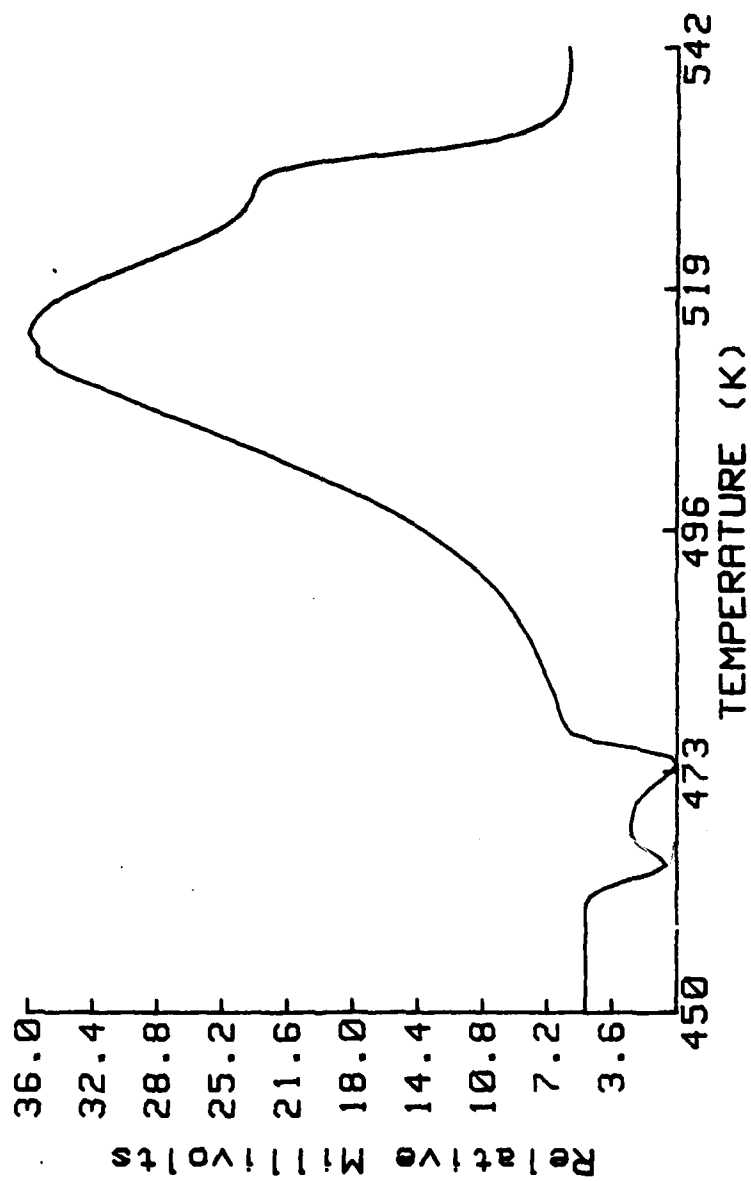


FIGURE 1. DSC Plot of RDX Class 5. (Scanning Rate is 10 deg/min.)

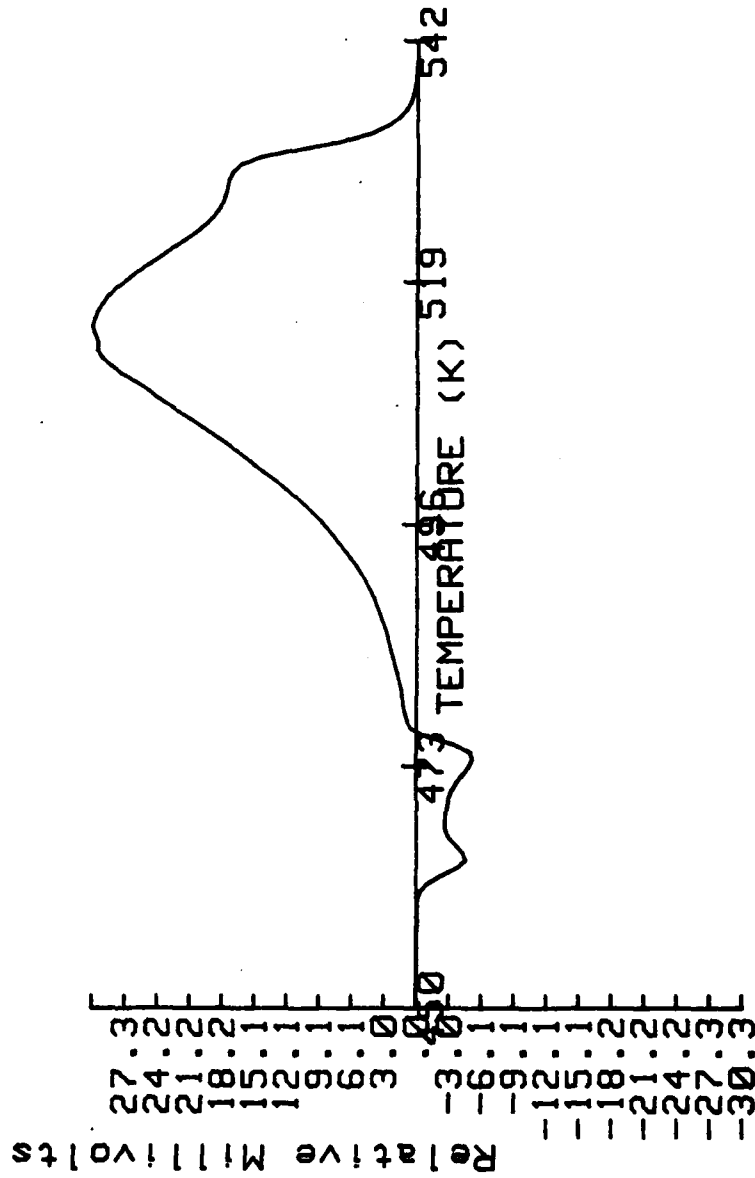


FIGURE 2. Plot of RDX Class 5 with a Linear Baseline Correction.

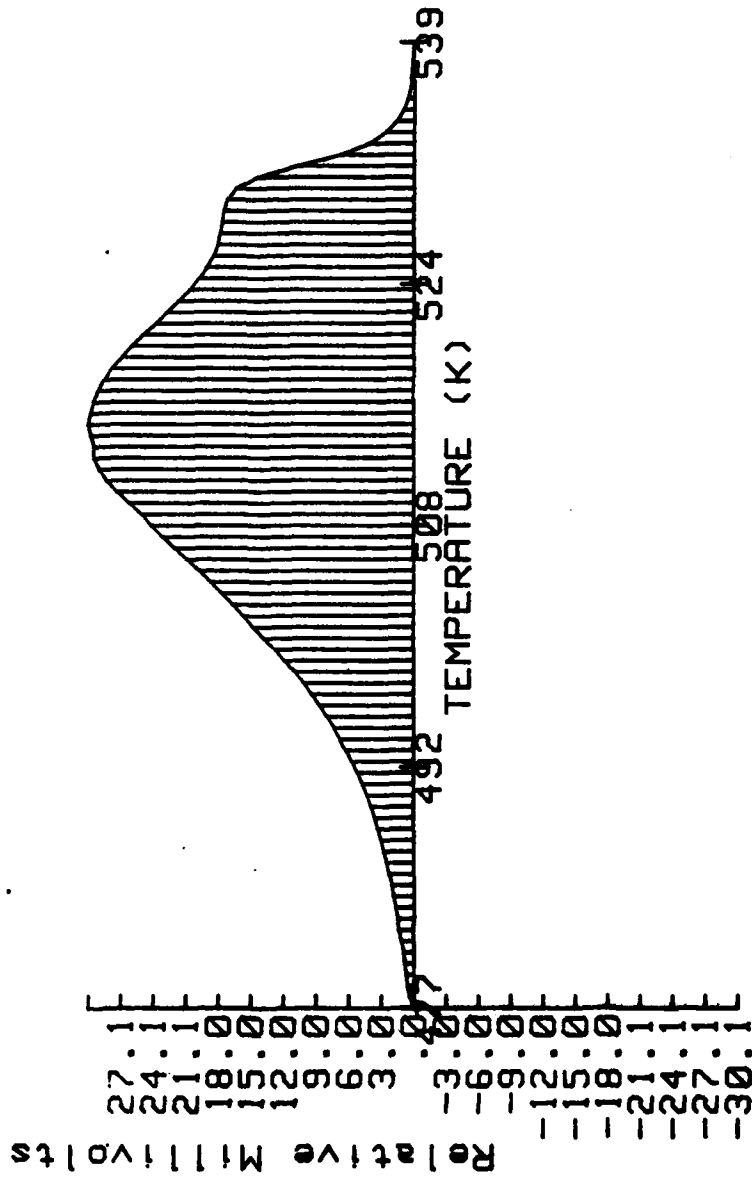


FIGURE 3. Plot of EDX Class 5. (Shaded region denotes area calculated by the computer. Ratios of partial areas to total area gives fraction reacted. The actual value of energy released may be obtained by comparison with a primary standard.)

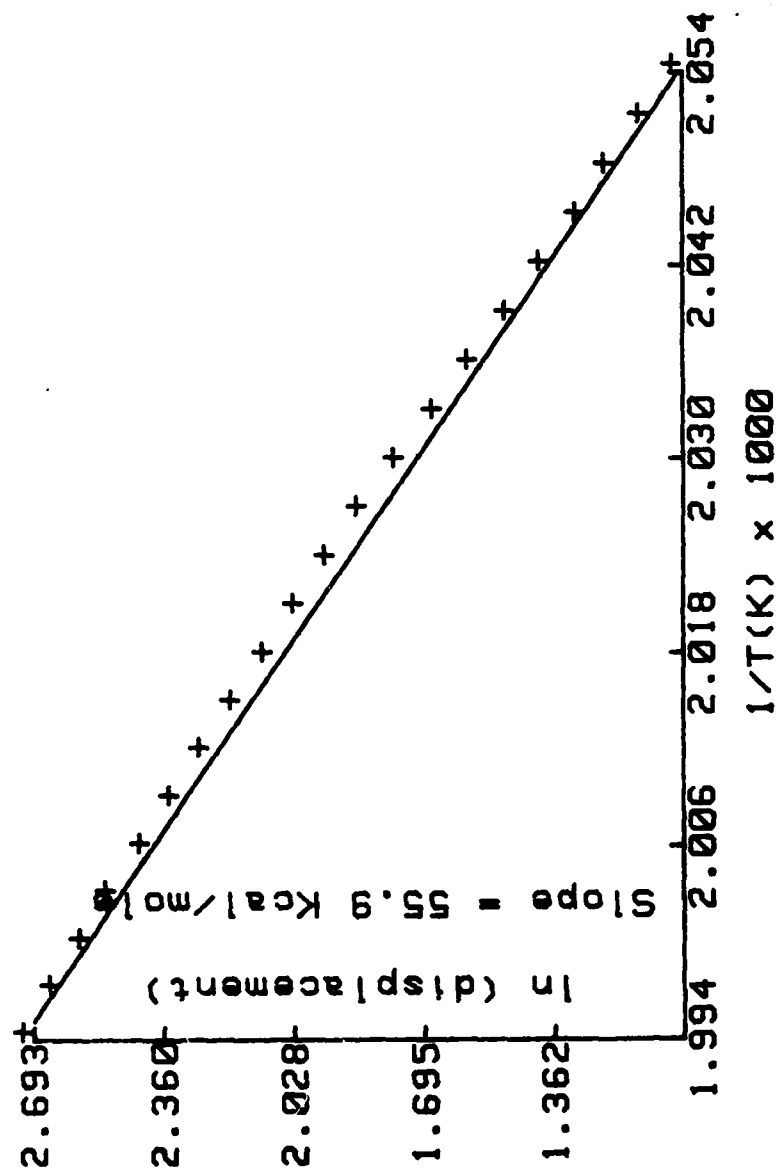


FIGURE 4. Plot of $\ln D$ vs $1/T$ to Determine Activation Energy E^* .

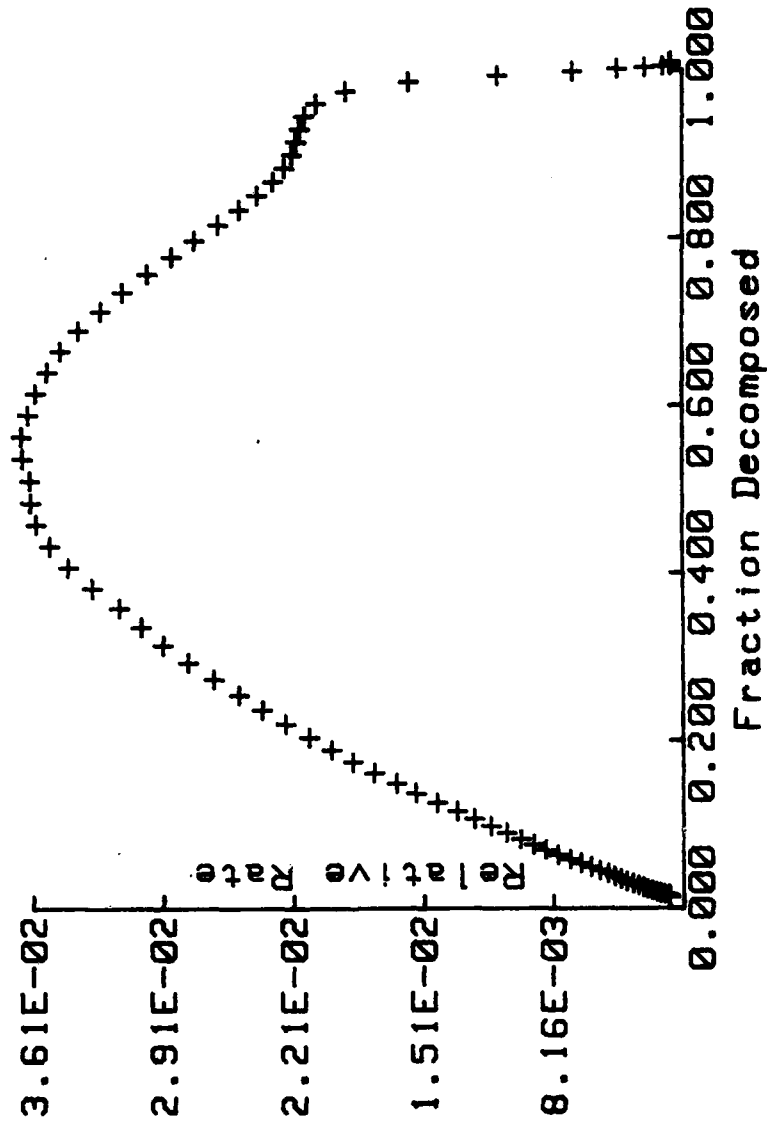


FIGURE 5. Kinetic Plot of RDX Class 5 at 10 deg/min.

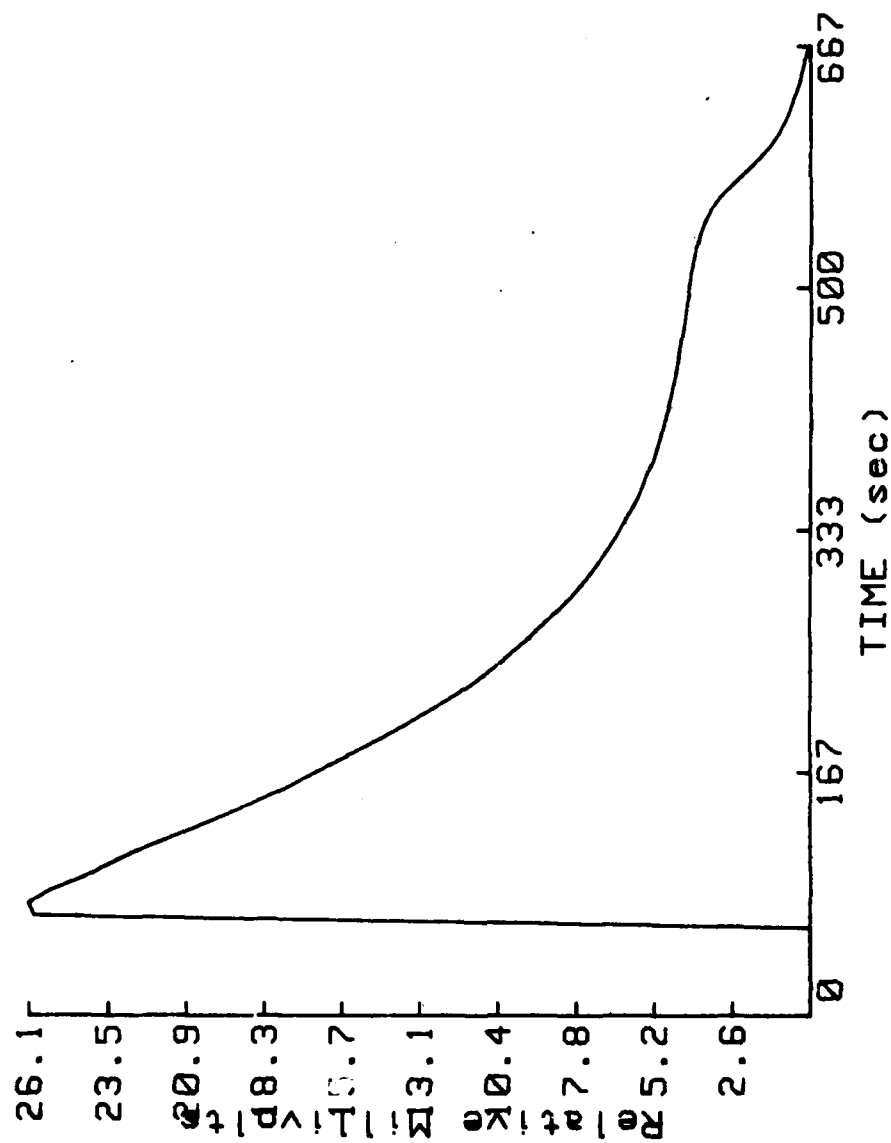


FIGURE 6. Isothermal Run of RDX Class 5 on Perkin Elmer DSC II. (Temperature is 504 K.)

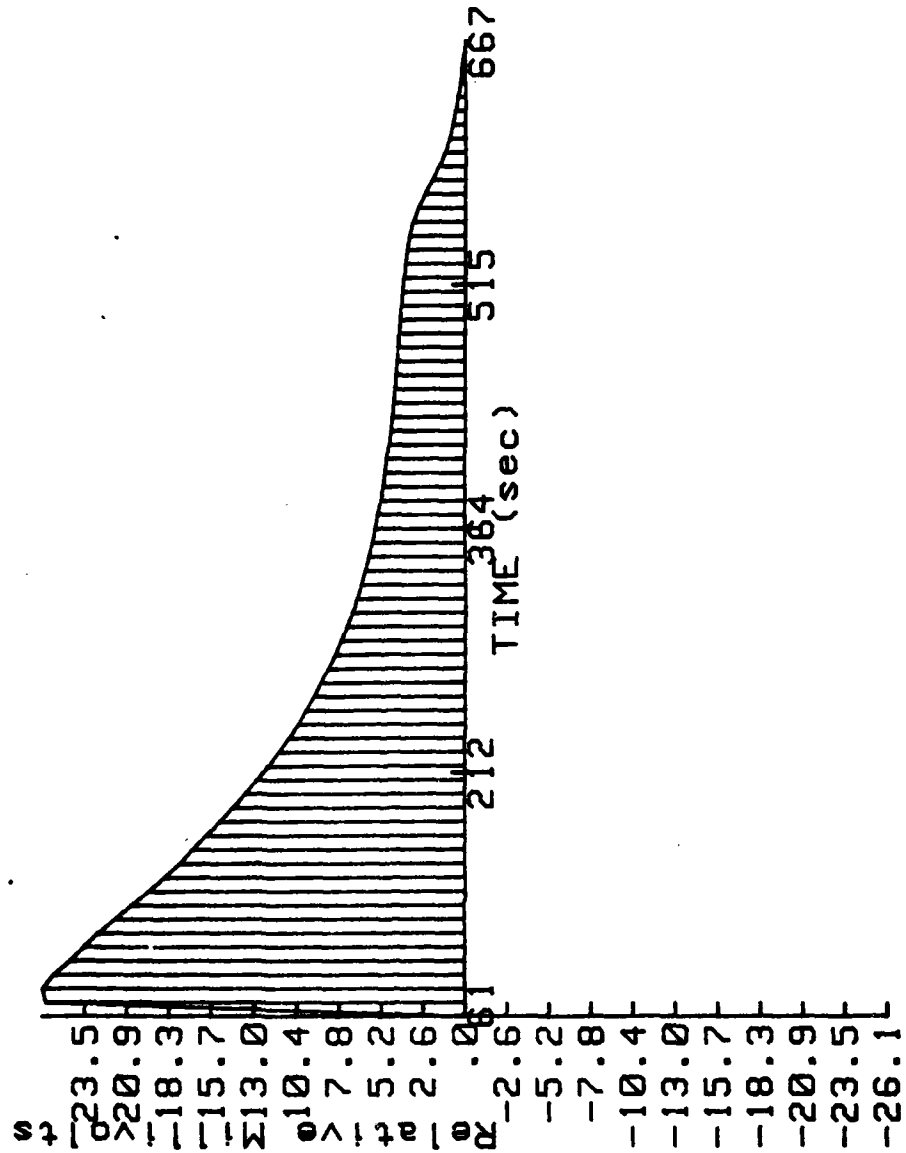


FIGURE 7. Isothermal Run of RDX Class 5 on Perkin Elmer DSC II. (The shaded area represents the area calculated by the computer. Endpoints for the determination as well as points used for baseline determination are operator selected.)

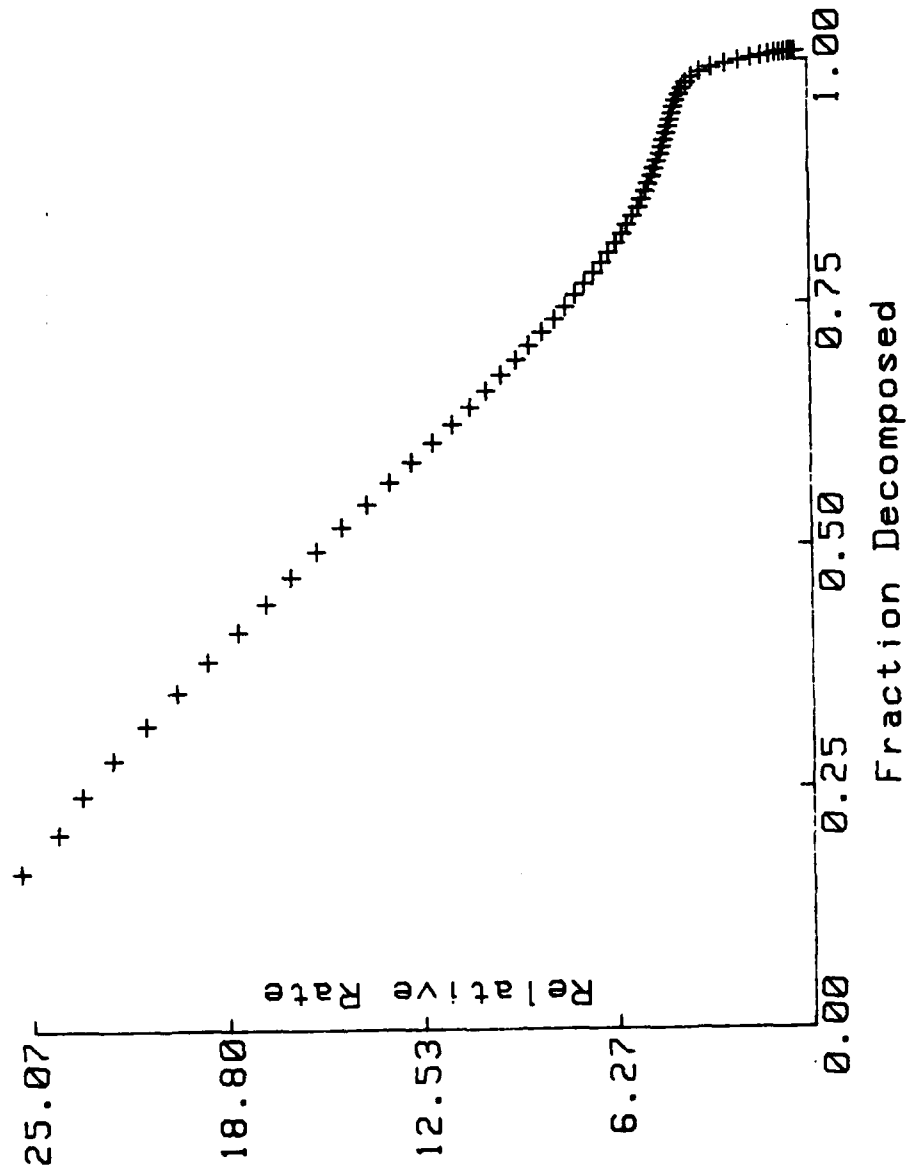
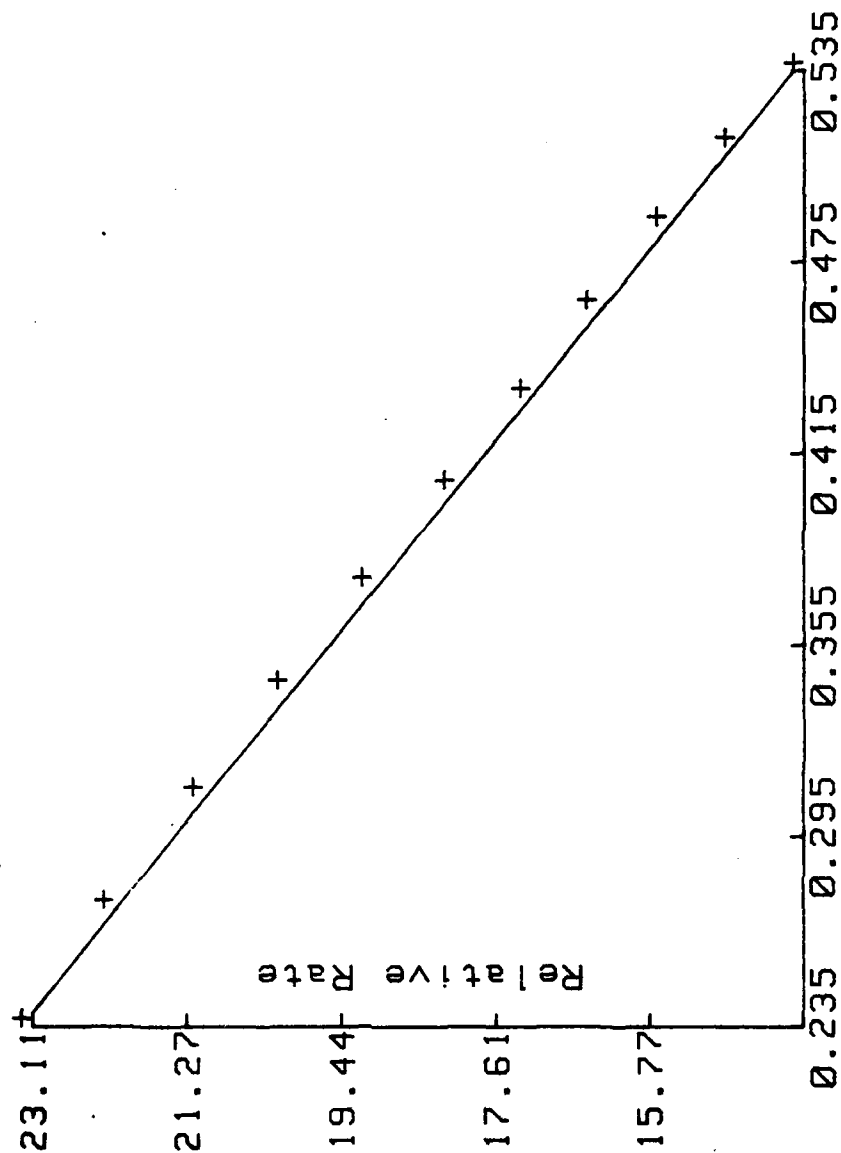


FIGURE 8. Plot of the Rate of Change of the Area Fraction vs the Area Fraction. (The linear portion of the curve is chosen for the determination of kinetic parameters.)



Fraction Decomposed

FIGURE 9. Graphics of Linear Regression Analysis of Linear Portion of Curve in Figure 8. (The calculated slope is $30.6 \pm 0.2 \text{ sec}^{-1}$. Dividing this by the total area (Table 2) yields a rate constant of $0.00595 \pm 0.00004 \text{ sec}^{-1}$.)

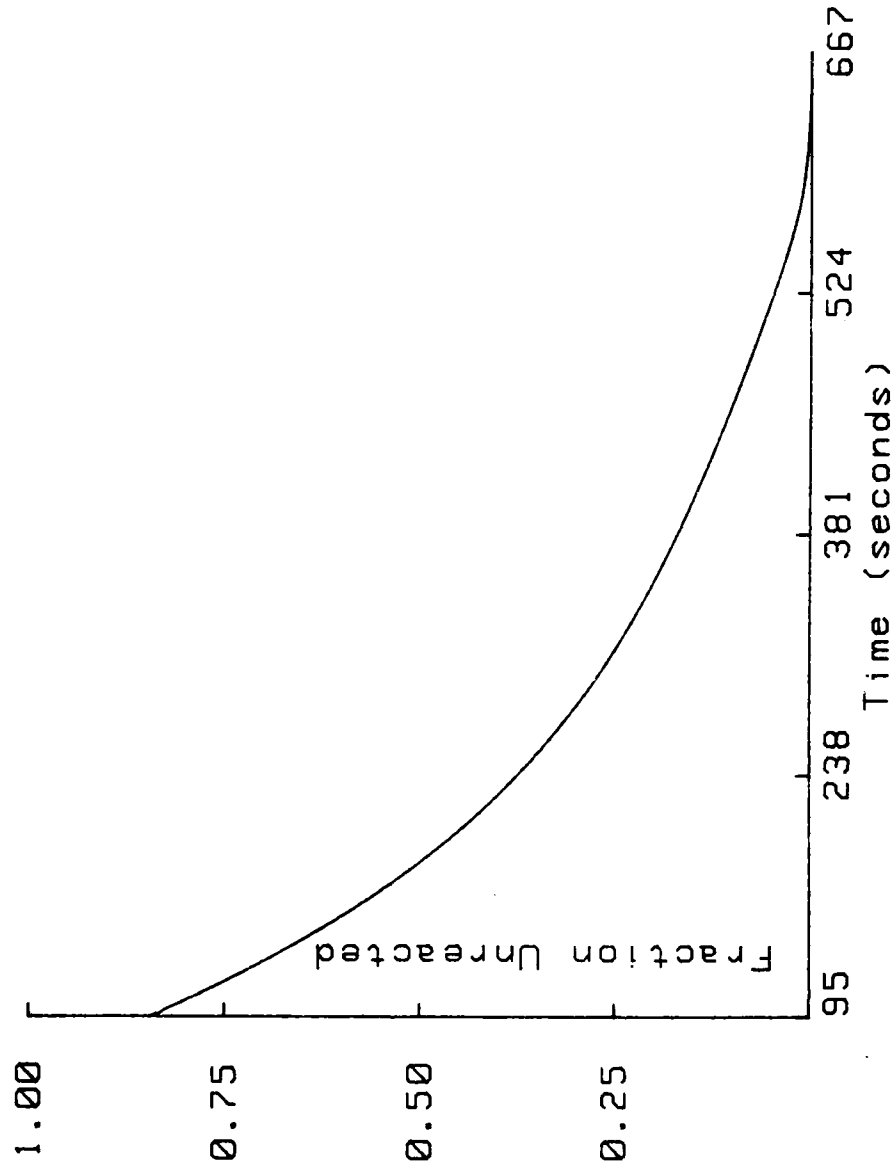


FIGURE 10. A Plot of Fraction Unreacted (1-x) vs Time for DX Class 5. (The plot has the shape expected from theory for a first order reaction.)

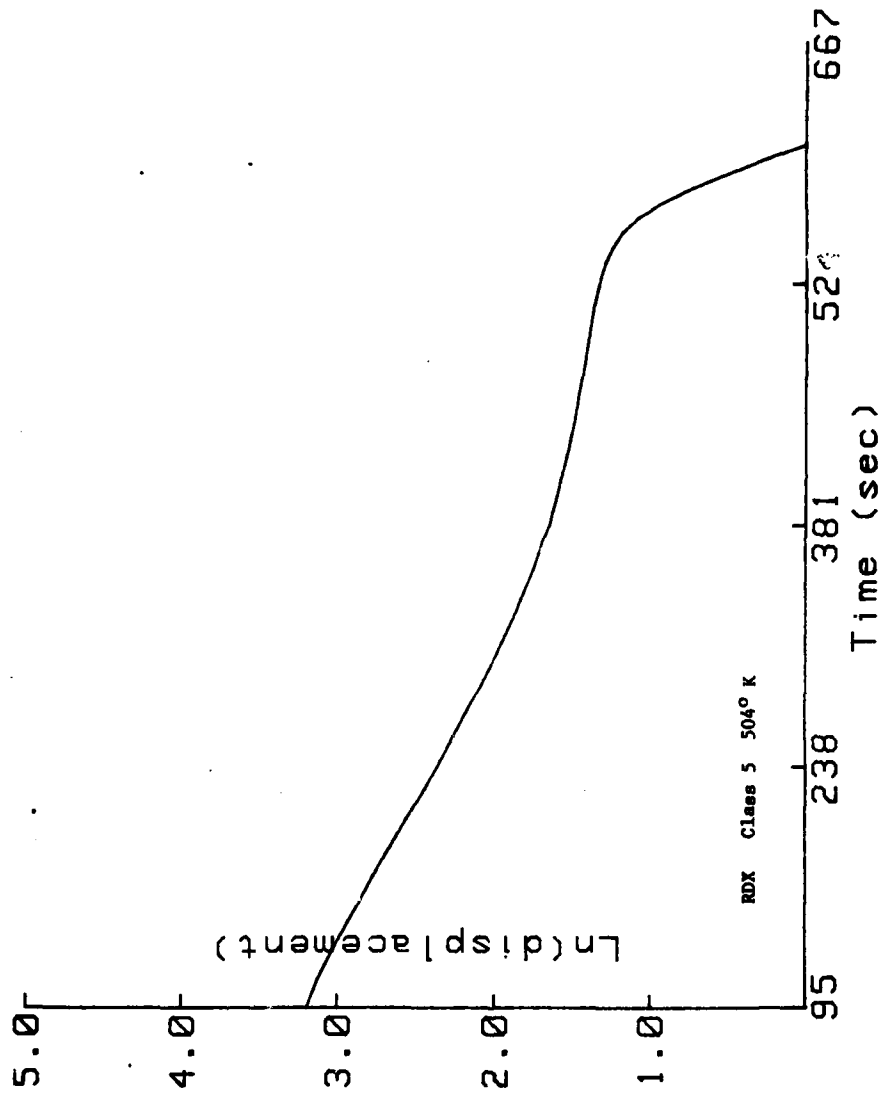


FIGURE 11. Plot of $\ln D_1$ vs Time. (The slope of the linear portion was calculated to be 0.00604 sec⁻¹. This is in excellent agreement with the rate constant calculated in Figure 9.)

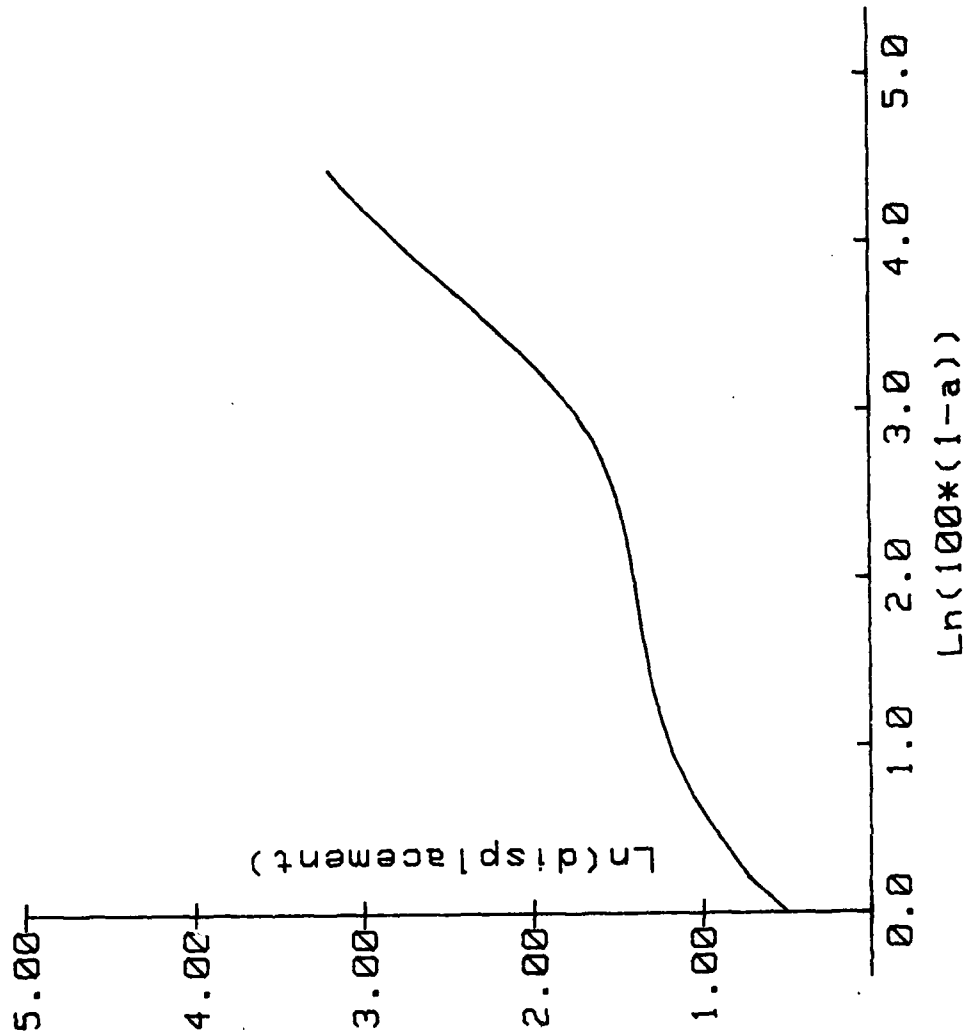


FIGURE 12. "Order" Plot for RDX Class 5. (Slope of linear portion is 1.05 ± 0.01 .)

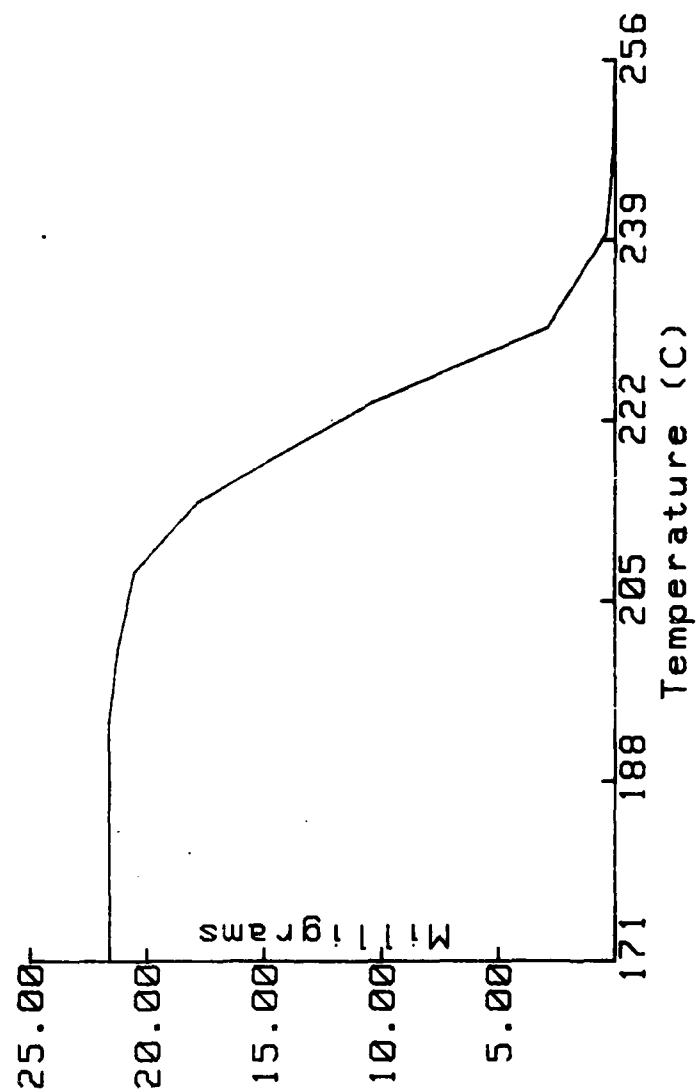


FIGURE 13. Graphics of Thermogravimetric Analysis of RDX Class 5. (Scan rate is 3 deg/min.)

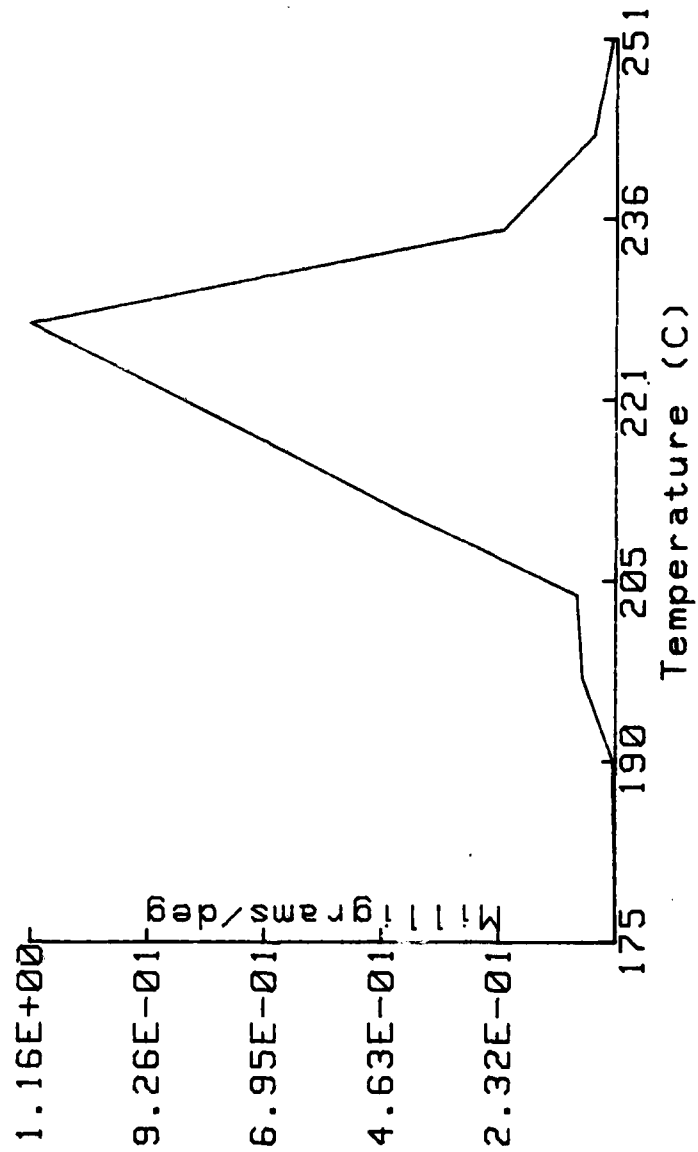


FIGURE 14. Computer-Generated Plot of the Derivative of the TGA Curve in Figure 13.

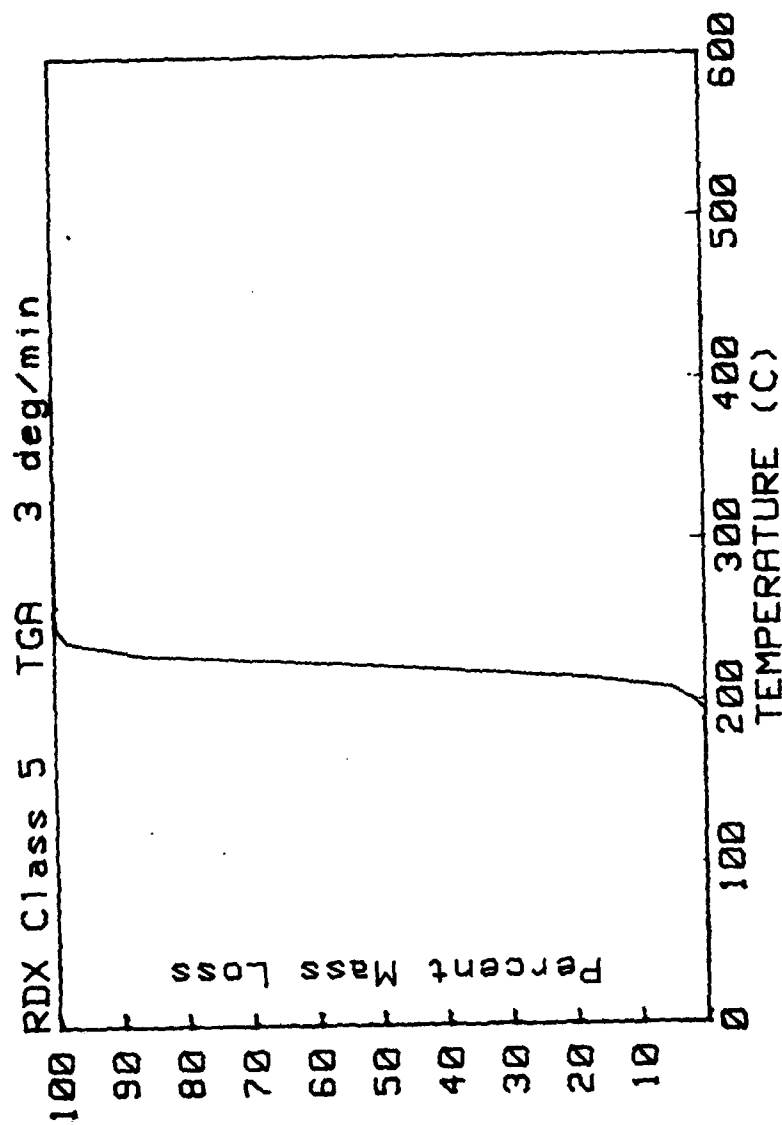


FIGURE 15. Graphics of TGA Plot of Figure 13 Showing % Mass Lost. (For gaseous products, this indicates fraction reacted. This type of plot is useful when comparing different materials.)

NWC TP 6337

TABLE 1. Computer Printout of Data Used to Determine Kinetic Parameters. (The section of the data that is used for the calculations is operator selectable.)

RDX Class 5 10 deg/min 2 kcal/sec 2.32 mg
October 2, 1981
Kinetics determination

Temp(K)	1/T	Area Fract.	LN(ordinate)	Relative Rate	Pts
479	2.09E-03	0.004	.001	1.30E-03	5
480	2.08E-03	0.005	.001	1.30E-03	6
481	2.08E-03	0.006	.126	1.36E-03	7
482	2.08E-03	0.007	.203	1.57E-03	8
482	2.07E-03	0.008	.415	1.80E-03	9
483	2.07E-03	0.010	.525	2.02E-03	10
484	2.07E-03	0.011	.646	2.24E-03	11
485	2.06E-03	0.013	.734	2.49E-03	12
485	2.06E-03	0.015	.830	2.71E-03	13
486	2.06E-03	0.017	.923	2.97E-03	14
487	2.05E-03	0.020	1.029	3.27E-03	15
487	2.05E-03	0.022	1.117	3.60E-03	16
488	2.05E-03	0.025	1.203	3.91E-03	17
489	2.05E-03	0.028	1.279	4.24E-03	18
490	2.04E-03	0.032	1.372	4.59E-03	19
490	2.04E-03	0.035	1.461	5.03E-03	20
491	2.04E-03	0.039	1.557	5.50E-03	21
492	2.03E-03	0.044	1.647	6.04E-03	22
493	2.03E-03	0.049	1.745	6.61E-03	23
493	2.03E-03	0.054	1.840	7.20E-03	24
494	2.02E-03	0.060	1.922	7.95E-03	25
495	2.02E-03	0.066	2.001	8.60E-03	26
496	2.02E-03	0.073	2.080	9.31E-03	27
496	2.01E-03	0.080	2.161	1.01E-02	28
497	2.01E-03	0.088	2.242	1.09E-02	29
498	2.01E-03	0.097	2.318	1.18E-02	30
498	2.01E-03	0.106	2.395	1.27E-02	31
499	2.00E-03	0.116	2.481	1.38E-02	32
500	2.00E-03	0.127	2.549	1.49E-02	33
501	2.00E-03	0.139	2.624	1.60E-02	34
501	1.99E-03	0.152	2.693	1.72E-02	35
502	1.99E-03	0.165	2.754	1.83E-02	36
503	1.99E-03	0.179	2.814	1.95E-02	37
504	1.99E-03	0.194	2.874	2.07E-02	38
504	1.98E-03	0.210	2.932	2.19E-02	39
505	1.98E-03	0.227	2.986	2.32E-02	40
506	1.98E-03	0.245	3.039	2.44E-02	41
507	1.97E-03	0.264	3.092	2.58E-02	42
507	1.97E-03	0.284	3.142	2.71E-02	43
508	1.97E-03	0.305	3.190	2.85E-02	44
509	1.97E-03	0.327	3.223	2.97E-02	45
509	1.96E-03	0.349	3.269	3.08E-02	46
510	1.96E-03	0.373	3.312	3.23E-02	47
511	1.96E-03	0.398	3.347	3.36E-02	48
512	1.95E-03	0.423	3.372	3.46E-02	49
512	1.95E-03	0.449	3.388	3.53E-02	50
513	1.95E-03	0.475	3.387	3.56E-02	51
514	1.95E-03	0.501	3.397	3.56E-02	52
515	1.94E-03	0.527	3.405	3.60E-02	53
515	1.94E-03	0.554	3.399	3.61E-02	54
516	1.94E-03	0.580	3.389	3.58E-02	55
517	1.94E-03	0.606	3.374	3.53E-02	56
518	1.93E-03	0.631	3.356	3.47E-02	57
518	1.93E-03	0.656	3.332	3.40E-02	58
519	1.93E-03	0.680	3.296	3.30E-02	59

NWC TP 6337

TABLE 1. (Contd.)

520	1.92E-03	0.704	3.261	3.19E-02	60
520	1.92E-03	0.726	3.220	3.07E-02	61
521	1.92E-03	0.748	3.173	2.93E-02	62
522	1.92E-03	0.768	3.130	2.80E-02	63
523	1.91E-03	0.788	3.083	2.68E-02	64
523	1.91E-03	0.806	3.034	2.56E-02	65
524	1.91E-03	0.824	2.992	2.44E-02	66
525	1.91E-03	0.841	2.952	2.34E-02	67
526	1.90E-03	0.858	2.921	2.26E-02	68
526	1.90E-03	0.874	2.899	2.20E-02	69
527	1.90E-03	0.890	2.885	2.16E-02	70
528	1.89E-03	0.906	2.875	2.14E-02	71
529	1.89E-03	0.921	2.867	2.12E-02	72
529	1.89E-03	0.936	2.849	2.09E-02	73
530	1.89E-03	0.951	2.803	2.03E-02	74
531	1.88E-03	0.965	2.673	1.87E-02	75
531	1.88E-03	0.976	2.376	1.53E-02	76
532	1.88E-03	0.984	1.920	1.05E-02	77
533	1.88E-03	0.989	1.443	6.47E-03	78
534	1.87E-03	0.992	.990	4.07E-03	79
534	1.87E-03	0.994	.515	2.58E-03	80
535	1.87E-03	0.995	.052	1.60E-03	81
536	1.87E-03	0.996	.001	1.18E-03	82
537	1.86E-03	0.996	.001	1.22E-03	83
537	1.86E-03	0.997	.001	1.20E-03	84
538	1.86E-03	0.998	.001	1.20E-03	85
539	1.86E-03	0.999	.001	1.20E-03	86
539	1.85E-03	1.000	.001	1.20E-03	87

NWC TP 6337

TABLE 2. Computer Printout of Data Used for Graphics and Kinetic Parameter Calculations.

TIME s	AREA	FRACT A	AREA INCREMENT	RATE OF INCREASE	Pts
95	800	0.156	216.982	25.067	5
104	1007	0.196	206.605	23.863	6
113	1207	0.235	200.003	23.106	7
121	1398	0.272	191.548	22.124	8
130	1581	0.307	182.245	21.057	9
139	1754	0.341	173.670	20.059	10
147	1919	0.373	164.955	19.061	11
156	2076	0.404	156.694	18.094	12
165	2225	0.432	148.803	17.191	13
173	2367	0.460	142.030	16.403	14
182	2502	0.486	134.618	15.572	15
191	2619	0.511	127.725	14.754	16
199	2750	0.535	120.645	13.939	17
208	2864	0.557	114.329	13.202	18
217	2973	0.578	108.207	12.499	19
225	3075	0.598	102.229	11.819	20
234	3172	0.616	96.785	11.183	21
242	3264	0.634	91.899	10.614	22
251	3351	0.651	87.456	10.100	23
260	3434	0.668	83.277	9.617	24
268	3513	0.683	78.980	9.123	25
277	3589	0.698	75.347	8.702	26
286	3660	0.711	71.571	8.269	27
294	3728	0.723	68.069	7.861	28
303	3793	0.737	65.031	7.512	29
312	3856	0.749	62.191	7.183	30
320	3915	0.761	59.541	6.877	31
329	3972	0.772	57.043	6.587	32
338	4027	0.783	54.783	6.329	33
346	4080	0.793	52.794	6.099	34
355	4130	0.803	50.711	5.856	35
364	4179	0.812	48.898	5.646	36
372	4227	0.822	47.532	5.491	37
381	4273	0.831	45.991	5.313	38
390	4317	0.839	44.415	5.129	39
398	4361	0.848	43.472	5.021	40
407	4402	0.856	42.417	4.897	41
416	4445	0.864	41.502	4.795	42
424	4485	0.872	40.514	4.678	43
433	4525	0.879	39.628	4.577	44
442	4564	0.887	38.837	4.486	45
450	4602	0.894	38.068	4.395	46
459	4639	0.902	37.564	4.338	47
468	4676	0.909	36.961	4.269	48
476	4712	0.916	36.286	4.191	49
485	4748	0.923	35.751	4.129	50
494	4784	0.930	35.279	4.074	51
502	4818	0.937	34.702	4.000	52
511	4852	0.943	34.209	3.951	53
520	4886	0.950	33.559	3.876	54
528	4919	0.956	32.772	3.786	55
537	4951	0.962	31.952	3.690	56
546	4982	0.968	30.791	3.556	57
554	5011	0.974	29.172	3.368	58
563	5038	0.979	26.901	3.107	59
571	5061	0.984	23.672	2.734	60
580	5081	0.988	19.826	2.290	61
589	5097	0.991	16.030	1.853	62
597	5110	0.993	12.610	1.457	63
606	5120	0.995	9.003	1.132	64
615	5127	0.997	7.634	0.882	65
623	5133	0.998	5.936	0.686	66
632	5139	0.999	4.587	0.530	67
641	5141	0.999	3.329	0.385	68
649	5143	1.000	2.106	0.243	69
658	5144	1.000	1.339	0.155	70
667	5145	1.000	0.346	0.040	71

NWC TP 6337

TABLE 2. (Contd.)

Pts	Time(sec)	Y	Log(Y)	a	(1-a)	Ln 100*(1-a)
5	95	24.4	3.193	0.156	0.844	4.436
6	104	23.5	3.158	0.196	0.804	4.387
7	113	22.6	3.120	0.235	0.765	4.338
8	121	21.6	3.071	0.272	0.728	4.288
9	130	20.6	3.023	0.307	0.693	4.238
10	139	19.6	2.973	0.341	0.659	4.188
11	147	18.6	2.922	0.373	0.627	4.138
12	156	17.6	2.868	0.404	0.596	4.088
13	165	16.0	2.822	0.432	0.568	4.039
14	173	16.0	2.771	0.460	0.540	3.989
15	182	15.2	2.719	0.486	0.514	3.939
16	191	14.3	2.662	0.511	0.489	3.890
17	199	13.6	2.607	0.535	0.465	3.840
18	208	12.0	2.553	0.557	0.443	3.792
19	217	12.2	2.498	0.578	0.422	3.743
20	225	11.5	2.441	0.598	0.402	3.695
21	234	10.9	2.388	0.616	0.384	3.647
22	242	10.3	2.336	0.634	0.366	3.599
23	251	9.9	2.289	0.651	0.349	3.551
24	260	9.4	2.236	0.668	0.332	3.504
25	268	8.9	2.188	0.683	0.317	3.457
26	277	8.5	2.138	0.698	0.302	3.409
27	286	8.1	2.096	0.711	0.289	3.362
28	294	7.7	2.039	0.725	0.275	3.315
29	303	7.3	1.994	0.737	0.263	3.268
30	312	7.0	1.950	0.749	0.251	3.221
31	320	6.7	1.906	0.761	0.239	3.174
32	329	6.4	1.864	0.772	0.228	3.126
33	338	6.2	1.827	0.783	0.217	3.079
34	346	6.0	1.788	0.793	0.207	3.030
35	355	5.7	1.747	0.803	0.197	2.981
36	364	5.6	1.717	0.812	0.188	2.932
37	372	5.4	1.689	0.822	0.178	2.882
38	381	5.2	1.649	0.831	0.169	2.838
39	390	5.1	1.626	0.839	0.161	2.778
40	398	5.0	1.600	0.848	0.152	2.724
41	407	4.8	1.579	0.856	0.144	2.668
42	416	4.7	1.555	0.864	0.136	2.611
43	424	4.6	1.531	0.872	0.128	2.551
44	433	4.5	1.512	0.879	0.121	2.489
45	442	4.4	1.489	0.887	0.113	2.425
46	450	4.4	1.474	0.894	0.106	2.357
47	459	4.3	1.460	0.902	0.098	2.285
48	468	4.2	1.442	0.909	0.091	2.209
49	476	4.2	1.425	0.916	0.084	2.129
50	485	4.1	1.412	0.923	0.077	2.042
51	494	4.0	1.396	0.930	0.070	1.949
52	502	4.0	1.382	0.937	0.063	1.848
53	511	3.9	1.365	0.943	0.057	1.737
54	520	3.8	1.343	0.950	0.050	1.616
55	528	3.7	1.320	0.956	0.044	1.488
56	537	3.6	1.298	0.962	0.038	1.320
57	546	3.5	1.244	0.968	0.032	1.155
58	554	3.3	1.181	0.974	0.026	0.958
59	563	2.9	1.078	0.979	0.021	0.734
60	571	2.5	0.922	0.984	0.016	0.485
61	580	2.1	0.726	0.988	0.012	0.214
62	589	1.6	0.497	0.991	0.009	-0.076
63	597	1.3	0.248	0.993	0.007	-0.303
64	606	1.0	-0.003	0.995	0.005	-0.711
65	615	.8	-0.253	0.997	0.003	-1.070
66	623	.6	-0.508	0.998	0.002	-1.488
67	632	.5	-0.760	0.999	0.001	-1.970
68	641	.3	-1.215	0.999	0.001	-2.608
69	649	.2	-1.567	1.000	0.000	-3.419
70	658	.1	-2.416	1.000	0.000	-5.003

NWC TP 6337

TABLE 3. Computer Printout of Time, Temperature, Mass Loss Data for TGA Program.

RDX Class 5 TGA 3 deg/min.
Initial mass is 21.59 mg. Heating rate is 3 deg/min
Sensitivity is 10 μ g/mv

Temperature (C)	Time(min)	Mass(mg)	% Mass Loss	Data Pt #
36	0.00	21.6	0.00	1
37	2.50	21.6	0.00	2
38	5.00	21.6	0.00	3
41	7.50	21.6	0.00	4
45	10.00	21.6	0.00	5
49	12.50	21.6	0.00	6
55	15.00	21.6	0.00	7
61	17.50	21.6	0.00	8
67	20.00	21.6	0.00	9
74	22.50	21.6	0.00	10
82	25.00	21.6	0.00	11
90	27.50	21.6	0.00	12
99	30.00	21.6	0.00	13
106	32.50	21.6	0.00	14
117	35.00	21.6	0.00	15
126	37.50	21.6	0.00	16
134	40.00	21.6	0.00	17
142	42.50	21.6	0.00	18
149	45.00	21.6	0.00	19
157	47.50	21.6	0.00	20
164	50.00	21.6	0.00	21
171	52.50	21.6	0.00	22
179	55.00	21.6	0.00	23
187	57.50	21.6	0.00	24
194	60.00	21.6	0.00	25
201	62.50	21.2	1.95	26
208	65.00	20.5	5.09	27
214	67.50	17.8	17.60	28
224	70.00	10.4	51.88	29
231	72.50	2.9	86.61	30
239	75.00	.4	98.19	31
246	77.50	.1	99.58	32
256	80.00	0.0	100.00	33
264	82.50	0.0	100.00	34
272	85.00	0.0	100.00	35
281	87.50	0.0	100.00	36
291	90.00	0.0	100.00	37

REFERENCES

1. Hans J. Brochardt and Farrington Daniels. "The Application of Differential Thermal Analysis to the Study of Reaction Kinetics," Journal of the American Chemical Society, Vol. 79, No. 4, July 1956, p. 41.
2. Jen Chiu. "Dynamic Differential Calorimetric Technique for Measuring Heat of Polymerization," Proceedings of the Second Symposium on Analytical Calorimetry, ed. by Roger S. Porter, New York, Plenum, 1970, p. 171-83.
3. Homer E. Kissinger. "Reaction Kinetics in Differential Thermal Analysis," Analytical Chemistry, Vol. 29, June 1957, p. 1702.
4. Ray N. Rogers. "Differential Scanning Calorimetric Determination of Kinetics Constants of Systems That Melt with Decomposition," Thermochemica ACTA, Vol. 3, 1972, p. 437-447.
5. Ray N. Rogers. "Simplified Determination of Rate Constants by Scanning Calorimetry," Analytical Chemistry, Vol. 44, No. 7, December 1971, p. 1336.

NWC TP 6337

APPENDIX A

**Program for Acquisition and Analysis of Constant Heating Rate
Differential Scanning Calorimeter Data**

NWC TP 6337

PROGRAM FOR ACQUISITION AND ANALYSIS OF THERMOGRAVIMETRIC DATA

```

10  OPTION BASE 1
20  COM T(300),Mass(300),Mass1(300),Time(300),N,M0,A$(80),B$(80)
25  COM A(300),B(300),Anew(300),Bnew(300),Deriv(300)
30  COM Aa(0:9) ! Coefficients for interpolating polynomial
40  MAT READ Aa for type S thermocouple.
45  INPUT "ENTER RUN IDENTIFIER",B$
50  Plot=1
60  IF Plot>1 THEN INPUT "DO YOU WANT TO PLOT ANOTHER RUN?",Cont$
62  IF (Plot/1) AND (Cont$(1,1)<>"Y") THEN GOSUB Continue
65  INPUT "ENTER NUMBER OF DATA POINTS",N
70  REDIM T(N),Mass(N),Mass1(N),Time(N)
80  INPUT "ENTER MILLIVOLT READING FOR INDIUM MELT",Mp
90  INPUT "ENTER THERMOCOUPLE GAIN (1 OR 5)",Gain
100 INPUT "ENTER INITIAL MASS",M0
105 INPUT "ENTER HEATING RATE",Hrate
110 INPUT "ENTER MILLIVOLT VALUE FOR INITIAL MASS",Mv
115 INPUT "ENTER MASS SENSITIVITY (mg/mv): 1 or 10 ",Sens
120 PRINTER IS 16
130 FOR I=1 TO N
140 PRINT LIN(6)
150 PRINT USING 220;I
160 INPUT X,Y
170 X=(X-Mp)/Gain+1.082 ! Calculate S thermocouple output.
180 T(I)=FN$CAL(X/1000) ! Calculate Temperature.
190 Mass(I)=M0+Sens*(Y-Mv) ! Calculate Mass For (Sens)mg/mv sensitivity.
195 Time(I)=(I-1)*2.5 ! Time in minutes: 5 min/inch chart speed.
200 Mass1(I)=(M0-Mass(I))/M0*100 !Percent Mass Loss.
202 PRINT PAGE
205 PRINT USING 225;T(I),Mass(I),Time(I)
210 NEXT I
220 IMAGE "ENTER MILLIVOLT READINGS FOR POINT #",DD," (Temp.,Mass)"
225 IMAGE "Temperature is ",DDD," C; Mass is ",DD.DD," mg.; Time is ",DDDD
    ".D." min."
230 GOSUB Printer
235 INPUT "DO YOU WANT THE DATA STORED?",Stores
236 IF Stores$(1,1)="Y" THEN CALL Store(T(*),Mass(*),M0,N,B$)
240 IF Plot>1 THEN GOSUB S
245 REM Plot % Mass loss vs Temperature
250 INPUT "ENTER PLOTTER CODE: 1=CRT; 2=9872A",Plotter
260 IF Plotter=1 THEN PLOTTER IS "GRAPHICS"
270 IF Plotter=2 THEN PLOTTER IS 7,5,"9872A"
280 GRAPHICS
290 LOCATE 15,90,20,70
295 INPUT "ENTER HIGHEST PERCENTAGE DESIRED ON PLOT",Q
300 SCALE 0,600,0,Q
310 INPUT "ENTER PLOT LABEL",A$
320 Xname$="TEMPERATURE (C)"
330 Yname$="Percent Mass Loss"
340 AXES 100,Q/10,0,0
350 FRAME
360 MOVE T(1),Mass1(1)
370 FOR I=2 TO N !PLOT FIRST ARRAY.
380 DRAW T(I),Mass1(I)
390 NEXT I
400 PENUP
410 LORG 6 ! Label X Axis
420 FOR I=0 TO 600 STEP 100

```


NWC TP 6337

```

430 MOVE I,-2
440 LABEL I
450 NEXT I
460 LOGO 3 'Label Y Axis
470 FOR I=0:10 TO 0 STEP 0:10
480 MOVE 0,I
490 LABEL I
500 NEXT I
510 LOGO 1 'Label Plot.
520 MOVE 0,1.02*Q
530 LABEL AS
540 LOGO 6
541 MOVE 300,-.08*Q
542 LABEL Xname$
543 MOVE 25,0/2
544 LDIR PI/2
545 LABEL Yname$
547 PENUP
548 LDIR 0
550 PAUSE
553 IF Plotter=1 THEN DUMP GRAPHICS
555 LINUT "WOULD YOU LIKE TO REPEAT THIS PLOT?",Pp:3
560 IF Rpt$(1,1)="Y" THEN GOTO 250
565 Plot=Plot+1
568 GOTO 60
570 5: 'Plot other arrays
580 IF Plot=2 THEN LINE TYPE 4
590 IF Plot=3 THEN LINE TYPE 6
600 IF Plot=4 THEN LINE TYPE 8
610 MOVE T(1),Mass(1)
620 FOR I=2 TO N
630 DRAW T(I),Mass(I)
640 NEXT I
650 PENUP
660 Plot=Plot+1
670 GOTO 60
700 Exit: IF Plotter=2 THEN OUTPUT 7,5;"SP0-IN"
710 IF Plotter=2 THEN STOP
720 DUMP GRAPHICS
730 EXIT GRAPHICS
740 GCLEAR
750 END
760 Printer: PRINTER IS 0
765 PRINT PAGE
770 PRINT LIN(2)
780 PRINT B$
785 PRINT USING 790;M0,Hrate,Sens
790 IMAGE "Initial mass is ",DDD.DD," mg. Heating rate is ",DD," deg min",
    "Sensitivity is ", DD," mg/mu"
800 PRINT LIN(2)
910 PRINT "Temperature (C) Time(min) Mass(mg) % Mass Loss
    Data Pt #
820 PRINT
830 FOR I=1 TO N
835 IF Mass(I)=0 THEN Mass(I)=0
836 IF Mass(I)>100 THEN Mass(I)=100
840 PRINT USING 860;T(I),Time(I),Mass(I),Mass(I),I
850 NEXT I
860 IMAGE DDDD16X,DDD.DD8X,DD.D10X,DDD.DD12X,DDD
870 PRINT PAGE
880 RETURN
1000 DATA .927763167,169526.515,-31569363.94,3990730633,-1.63565E12,1.88027E14
    ,-1.27241E16,6.17501E17,-1.56105E19,1.69535E20
1050 DEF FN$cal(2)
1075 COM A(0:9)

```

NWC TP 6337

```

1085 Interpolating polynomial for converting millivolts to degrees
1095 For type S (platinum-10%rhodium - platinum) thermocouple.
1105 S:1=A(0)+Z*(A(1)+Z*(A(2)+Z*(A(3)+Z*(A(4)+Z*(A(5)+Z*(A(6)+Z*(A(7)+Z*(A(8)+
Z*(A(9)+Z*(A(10))))))
1115 RETURN S:1
1125 F:END
1135 SUB Store(X(*),Y(*),Y0,N,Id$)
1145 S=OPT A=N,R(N)
1175 MAT A=X
1185 MAT B=Y
1195 INPUT "ENTER FILE NAME",D$
1210 INPUT "ENTER MASS STORAGE MEDIUM",E$
1215 CREATE D$:"\%E$,N 16+2
1225 ASSIGN #4 TO D$:"%E$
1235 PRINT #4;Id$,Y0,N
1245 MAT PRINT #4;A,B
1255 ASSIGN #4 TO *
1265 SUBEXIT
1275 SUBEND
1300 F:CONTINUE
1305 OPTION BASE 1
1310 DIM T(*),Mass(*),Mass1(*),Time(*),N,M0,A$,B$
1320 DIM A(*),B(*),Anew(*),Bnew(*),Deriv(*)
1325 DIM Page$(80)
1330 CALL Plotter(B$,Time(*),Mass1(*),N,2)
1340 PRINT PAGE
1350 INPUT "DO YOU WANT TO CONTINUE WITH DATA ANALYSIS?",Y$
1360 IF Y$(1,1)<>"Y" THEN SUBEXIT
1370 INPUT "ENTER BEGINNING AND ENDING POINT FOR DATA ANALYSIS",P1,P2
1380 Dim=P2-P1+1
1390 REDIM A(Dim),B(Dim),Deriv(Dim-1),Anew(Dim-1),Bnew(Dim-1)
1400 FOR K=1 TO Dim
1410 A(K)=T(P1+K-1)
1420 B(K)=Mass(P1+K-1)
1430 NEXT K
1440 FOR I=1 TO Dim-1 ! Calculate derivatives at midpoints.
1450 Anew(I)=(A(I+1)+A(I))/2
1460 NEXT I
1470 Eps=1E-6
1480 PRINT PAGE
1490 PRINT LIN(3)
1500 PRINT B$
1510 PRINT "Subset Output"
1520 PRINT LIN(2)
1530 CALL Spline(Dim,Dim-1,A(*),B(*),Anew(*),Bnew(*),Deriv(*),01,Eps)
1540 MAT Deriv=ABS(Deriv)
1550 Page$="Temperature(C)   Mass(mg)   -dM/dT   ln(dM/dT)"
1560 PRINT Page$
1570 PRINT LIN(2)
1580 FOR I=1 TO Dim-1
1590 PRINT USING 1670;I,Anew(I),Bnew(I),Deriv(I),LOG(Deriv(I))
1600 IF I MOD 50<>0 THEN GOTO 1660
1610 PRINT PAGE
1620 PRINT B$
1630 PRINT LIN(2)
1640 PRINT Page$
1650 PRINT LIN(2)
1660 NEXT I
1670 IMAGE DDDYXX,DDDDXXXXXXXX,MDD,DDDDXXXXXXXX,MD,DDXXXXXXXX,MZ,DDD
1680 CALL Plotter(B$,A(*),B(*),Dim,0)
1690 CALL Plotter(B$,Anew(*),Deriv(*),Dim-1,1)
1700 PRINT PAGE
1710 PRINT LIN(2)
1720 INPUT "DO YOU WANT TO CALCULATE KINETIC PARAMETERS FROM THE DATA?",S$
1730 IF S$(1,1)="Y" THEN CALL kinetics(B$,Anew(*),Bnew(*),Deriv(*),Dim,M0)

```

NWC TP 6337

```

1740 GOTO 1350
1750 SUBEND
1800 SUB Plotter(A$,X(*),Y(*),N,Flag)
1801 INPUT "ENTER PLOTTER CODE: 1=CRT 2=9872A",Plotter
1802 IF Plotter=2 THEN PLOTTER IS 7,5,"9872A"
1803 IF Flag=2 THEN G$="Time:minutes:"
1805 IF Flag=2 THEN G$="Temperature (C)"
1806 IF Flag=0 THEN H$="Milligrams"
1807 IF Flag=1 THEN H$="Milligrams/deg"
1808 IF Flag=2 THEN H$="Percent Mass Loss"
1810 PRINTER IS 0
1811 PRINT PAGE
1812 PRINT
1813 PRINT A$
1814 IF Flag=1 THEN PRINT "Derivative Plot"
1815 PRINT LIN(2)
1816 IF Flag=0 THEN INPUT "ENTER MAXIMUM ORDINATE VALUE (mg)",C
1817 D=0
1818 IF Flag=2 THEN C=100
1819 IF Flag=1 THEN GOTO 1821
1820 INPUT "DO YOU WANT COMPUTER CALCULATED ORDINATE TICKS?",Axis$
1821 IF Flag=1 THEN Axis$="Y"
1825 A=FNMax(X(*),N)
1830 B=FNMin(X(*),N)
1835 IF Axis$[1,1]<>"Y" THEN GOTO 1860
1840 C=FNMax(Y(*),N)
1850 D=FNMin(Y(*),N)
1860 E=(A-B)/10
1870 F=(C-D)/10
1871 IF Plotter=1 THEN PLOTTER IS "GRAPHICS"
1872 GRAPHICS
1880 IF Plotter=1 THEN LOCATE 20,90,20,90
1885 IF Plotter=2 THEN LOCATE 20,90,20,65
1890 SCALE B,A,D,C
1900 AXES 2+E,2+F,B,D
1910 MOVE X(1),Y(1)
1920 FOR I=1 TO N
1930 DRAW X(I),Y(I)
1940 NEXT I
1950 MOVE B,D-F
1960 LORG 6 ! LABEL X AXIS
1970 FOR I=B TO A STEP 2+E
1980 MOVE I,D-.1+F
1990 LABEL USING "DDD";I
2000 NEXT I
2010 MOVE B,D-F
2020 DEG
2030 LORG 8 ! LABEL Y AXIS
2040 FOR I=D+2+F TO C STEP 2+F
2050 MOVE B-.1+E,I
2055 IF Flag=1 THEN LABEL USING "D.DDE";I
2060 IF Flag=0 THEN LABEL USING "DDD.DD";I
2065 IF Flag=2 THEN LABEL USING "DDD";I
2070 NEXT I
2080 LORG 6
2090 MOVE B+5+E,D-.8+F
2100 LABEL G$
2110 MOVE B+.4+E,D+5+F
2115 LORG 4
2120 LDIR 90
2130 LABEL H$
2131 LDIR 0
2132 IF Plotter=2 THEN OUTPUT 7,5;"IN"
2133 INPUT "DO YOU WANT GRAPHICS OUTPUT ON THERMAL PRINTER",Print$
2134 IF Print$[1,1]<>"N" THEN DUMP GRAPHICS

```

NWC TP 6337

```

2135 GLEAP
2136 E IT GRAPHICS
2139 INPUT "DO YOU WANT THE PLOT REPEATED?",Rpt$
2144 IF Rpt$(1,1)="Y" THEN GOTO 1901
2149 E,BEXIT
2150 E,END
2160 DEF FNMax(X(*),N)
2170 Max=X(1)
2180 FOR I=2 TO N
2190 IF X(I)>Max THEN Max=X(I)
2200 NEXT I
2210 RETURN Max
2220 FNEND
2230 DEF FNMin(X(*),N)
2240 Min=X(1)
2250 FOR I=2 TO N
2260 IF X(I)<Min THEN Min=X(I)
2270 NEXT I
2280 RETURN Min
2290 FNEND
2300 SUB Insert(B$,X(*),Y(*),N)
2390 E,BEXIT
2400 E,END
2500 DEF FNScale(X)
2900 E,B Spline=N,Nang,X(*),Y(*),Domain(*),Func(*),Deriv(*),Int,Eps)
2880 BadSta=Eps/0
2890 IF BadSta=0 THEN 2990
2920 PRINT LIN(2),"ERROR IN SUBPROGRAM Spline."
2930 PRINT "Eps=";Eps,LIN(2)
2940 PAUSE
2950 GOTO 2880
2990 OPTION BASE 1
3000 DIM S(N),G(N-1),Work(N-1)
3010 FOR I=2 TO N-1
3020 X1=X(I)
3030 X11=X(I-1)
3040 X12=X(I+1)
3050 Y1=Y(I)
3060 Y11=Y(I-1)
3070 Y12=Y(I+1)
3080 H=X1-X11
3090 H=X12-X11
3100 Work(I)=.5*X/H
3110 T=(Y12-Y1)*(X12-X1)-(Y1-Y11)*(X1-X11)/H
3120 S(I)=2*T
3130 G(I)=3*T
3140 NEXT I
3150 E 1=S(N)=0
3170 W=8-4*SQR(3)
3180 U=0
3190 FOR I=2 TO N-1
3200 T=W*(-S(I)-Work(I)+S(I-1)-(W-Work(I))*S(I+1)+G(I))
3210 H=ABS(T)
3220 IF H>U THEN U=H
3230 S(I)=S(I)+T
3240 NEXT I
3250 IF U=Eps THEN 0180
3260 FOR I=1 TO N-1
3270 G(I)=(S(I+1)-S(I))/(X(I+1)-X(I))
3280 NEXT I
3290 IF Nang=0 THEN 3600
3330 FOR J=1 TO Nang
3340 Connector: I=1
3350 T=Domain(J)
3360 IF T=X(1) THEN 3430
3370 PRINT LIN(2),"ERROR IN SUBPROGRAM Spline."

```

```

3380 PRINT "ARGUMENT OUT OF BOUNDS."
3390 PRINT "X(I)=";X(I),"X(N)=";X(N),"Domain(";J;")=";Domain(J),LIN(2)
3400 PAUSE
3430 I=I+1
3440 IF I>N THEN 3370
3450 IF T>X(I) THEN 3430
3460 I=I-1
3470 H=Domain(J)-X(I)
3480 T=Domain(J)-X(I+1)
3490 X=H+T
3500 S=S(I)+H*G(I)
3510 Z=1+6
3520 U=Z*(S(I)+S(I+1)+S)
3530 W=(Y(I+1)-Y(I))/(X(I+1)-X(I))
3540 Func(J)=W*H+Y(I)+X*U
3550 Deriv(J)=H*(H+T)*U+Z*X*G(I)
3560 NEXT J
3600 Int=0
3610 FOR I=1 TO N-1
3620 H=X(I+1)-X(I)
3630 Int=Int+.5*H*(Y(I)+Y(I+1))-1/24*H^3*(S(I)+S(I+1))
3640 NEXT I
3650 SUBEND
3800 SUB Kinetics(As,X(*),Y(*),Z(*),N,Mz)
3802 REM X=TEMP, Y=MASS, Z=dM/dT
3804 OPTION BASE 1
3809 DIM Ff(N),Tinv(N),Xx(N),Yy(N),Dm(N)
3814 INPUT "ENTER RESIDUE MASS (mg)",Residue
3820 Mr=Mz-Residue ! Total mass reacted.
3824 INPUT "ENTER POINT NUMBERS FOR KINETICS PLOTS",P1,P2
3829 Datapoints=P2-P1+1
3831 REDIM Ff(Datapoints),Tinv(Datapoints),Xx(Datapoints),Yy(Datapoints),Dm(Datapoints)
3834 FOR I=1 TO Datapoints
3839 Xx(I)=X(P1+I-1)+273 ! Compute array and change to Kelvin.
3842 Yy(I)=Mz-Y(P1+I-1) ! Compute mass reacted array.
3844 Ff(I)=Yy(I)/Mr ! Calculate fraction decomposed.
3845 Tinv(I)=1/Xx(I) ! Calculate reciprocal temperature.
3846 NEXT I
3850 CALL Spline(Datapoints,Datapoints,Xx(*),Ff(*),Xx(*),Ff(*),Dm(*),Q2,1E-6) ! Fit curve and calculate d(frac)/dT
3855 MAT Dm=ABS(Dm)
3860 CALL Plotz(Datapoints,Xx(*),Ff(*),Dm(*),As) ! Print and plot dx/dT vs x
3864 FOR I=1 TO Datapoints
3869 IF Dm(I)>.001 THEN Dm(I)=LOG(1000*Dm(I))
3874 NEXT I
3880 PRINT PAGE
3885 PRINT As
3886 PRINT LIN(2)
3890 PRINT "Linear regression analysis of TGA data between Temperatures"
3900 PRINT USING 3910;Xx(1),Xx(Datapoints)
3910 IMAGE DDDD," and ",DDDD," degrees Kelvin."
3920 PRINT
3930 CALL Regress(Tinv(*),Dm(*),Datapoints,A,B,C1,C2,C3,C4,C5,C6,C7,C8,C9,C0,Var)
3940 PRINT USING 3950;ABS(B*1.9872),Var
3950 IMAGE "CALCULATED ACTIVATION ENERGY IS ",MD.DDE," Cal./mole "," +/- ",D.DDE
3951 PRINT
4110 PRINT PAGE
4120 PRINT LIN(3)
4130 PRINT As
4140 PRINT
4150 PRINT "KINETICS DATA PLOT"
4160 PRINT LIN(2)
4170 Xmax=FNMax(Tinv(*),Datapoints)

```

NWC TP 6337

```

4190 Xmin=FNMin(Tinv(*),Datapoints)
4190 Ymax=FNMax(Dm(*),Datapoints)
4200 Ymin=FNMin(Dm(*),Datapoints)
4210 E=(Xmax-Xmin)/10
4220 F=(Ymax-Ymin)/10
4222 INPUT "ENTER PLOTTER CODE: 1=CRT; 2=9872A",Code
4224 IF Code=2 THEN PLOTTER IS 7,5,"9872A"
4230 IF Code=1 THEN PLOTTER IS "GRAPHICS"
4240 GRAPHICS
4250 LOCATE 10,90,15,75
4260 SCALE Xmin,Xmax,Ymin-F,Ymax+F
4270 AXES 2+E,2+F,Xmin,Ymin-F
4280 FOR I=1 TO Datapoints
4290 MOVE Tinv(I),Dm(I)
4300 LABEL "+"
4310 NEXT I
4320 FOR J=1 TO Datapoints
4330 Dm(J)=B+Tinv(J)+A
4340 NEXT J
4350 MOVE Tinv(1),Dm(1)
4360 FOR I=1 TO Datapoints
4370 DRAW Tinv(I),Dm(I)
4380 NEXT I
4390 MOVE Xmin,Ymin-F
4400 LOG 6
4410 FOR I=Xmin TO Xmax STEP 2+E
4420 MOVE I,Ymin-1.1*F
4430 LABEL USING "D.DDD";I*1000
4440 NEXT I
4450 MOVE Xmin,Ymin-F
4460 LOG 8
4470 FOR I=Ymin+F TO Ymax+F STEP 2+F
4480 MOVE Xmin-.04+E,I
4490 LABEL USING "D.DDD";I
4500 NEXT I
4510 LOG 6
4520 MOVE Xmin+5+E,Ymin-2+F
4530 LABEL "1/T(K) x 1000"
4540 MOVE Xmin+.4+E,Ymin+5+F
4550 LDIP PI/2
4560 LABEL "ln (dm/dT) x 1000"
4570 PRUSE
4574 INPUT "DO YOU WANT TO REPEAT THE PLOT?",Rpt$
4579 IF Rpt$(1,1)="Y" THEN GOTO 4222
4584 IF Code=1 THEN DUMP GRAPHICS
4594 EXIT GRAPHICS
4600 GCLEAR
4604 INPUT "DO YOU WANT TO REPEAT USING DIFFERENT POINTS?",Again$
4608 IF Again$(1,1)="Y" THEN GOTO 3824
4610 SUBEXIT
4620 SUBEND
4700 SUB Regress(X(*),Y(*),N,A,B,Regss,Resss,Totalss,Regms,Resms,F,Dfreg,Dfres,B
ftot,Abort,Dev)
4710 : *** MODEL: Y=A+B*X ***
4720 ON ERROR GOTO Bomb
4730 Abort=0
4740 Y1=X1=Z=X2=Y2=0
4750 FOR I=1 TO N
4760 X1=X1+X(I) ! Sum of X's
4770 Y1=Y1+Y(I) ! Sum of Y's
4780 X2=X2+X(I)*X(I) ! Sum of X squares
4790 Y2=Y2+Y(I)*Y(I) ! Sum of Y squares
4800 Z=Z+X(I)*Y(I) ! Sum of XY's
4810 NEXT I
4820 X1=X1/N ! Mean X
4830 Y1=Y1/N ! Mean Y

```

NWC TP 6337

```

4840 B=(Z-N*X1*Y1)/(X2-N*X1*X1)
4850 A=Y1-B*X1
4860 Totals=Y2-N*Y1*Y1      ! Total Sum of Squares
4870 Regss=(Z-N*X1*Y1)^2/(X2-N*X1*X1) ! Regression Sum of Squares
4880 Resss=Totals-Regss      ! Residual Sum of Squares
4890 Regms=Regss              ! Regression Mean Squares
4900 Resms=Resss/(N-2)       ! Residual Mean Squares
4904 Dev=SQR(Resms)          ! Mean Square Deviation
4910 OFF ERROR
4920 DEFAULT ON
4930 F=Regms/Resms           ! F Ratio
4940 DEFAULT OFF
4950 Dfreg=1                  ! Degrees of Freedom
4960 Dfres=N-2
4970 Dftot=Dfreg+Dfres
4980 SUBEXIT
4990 Bomb: Abort=1
5000 SUBEND
5330 SUB Exponential(X(*),Y(*),N,A,B,Regss,Resss,Totals,Regms,Resms,F,Dfreg,Dfres,Dftot,Abort)
5340 ! *** MODEL: Y=A*EXP(B*X) ***
5350 ON ERROR GOTO Bomb
5360 Abort=0
5370 X1=X2=Z=Y1=Y2=0
5380 FOR I=1 TO N
5390   Logy=LOG(Y(I))
5400   X1=X1+X(I)      ! Sum of X's
5410   X2=X2+X(I)*X(I) ! Sum of X squares
5420   Y1=Y1+Logy      ! Sum of Y's
5430   Y2=Y2+Logy*Logy ! Sum of Y squares
5440   Z=Z+X(I)*Logy   ! Sum of XY's
5450 NEXT I
5460 X1=X1/N           ! Mean X
5470 Y1=Y1/N           ! Mean Y
5480 B=(Z-N*X1*Y1)/(X2-N*X1*X1)
5490 A=EXP(Y1-B*X1)
5500 Totals=Y2-N*Y1*Y1      ! Total Sum of Squares
5510 Regss=(Z-N*X1*Y1)^2/(X2-N*X1*X1) ! Regression Sum of Squares
5520 Resss=Totals-Regss      ! Residual Sum of Squares
5530 Regms=Regss              ! Regression Mean Squares
5540 Resms=Resss/(N-2)       ! Residual Mean Squares
5550 OFF ERROR
5560 DEFAULT ON
5570 F=Regms/Resms           ! F Ratio
5580 DEFAULT OFF
5590 Dfreg=1                  ! Degrees of Freedom
5600 Dfres=N-2
5610 Dftot=Dfreg+Dfres
5620 SUBEXIT
5630 Bomb: Abort=1
5640 SUBEND
5650 SUB Plotz(N,T(*),X(*),Y(*),AS)
5660 OPTION BASE 1
5670 PRINT PAGE
5680 PRINT LIN(3)
5690 PRINT AS
5695 INPUT "DO YOU WANT THE DATA PRINTED?",Prints
5696 IF Prints(1,1)="Y" THEN GOSUB Print
5700 PRINT "Kinetics plot of dx/dt vs. x.  x= fraction decomposed"
5710 PRINT LIN(3)
5720 C=FNMax(Y(*),N)
5730 D=FNMin(Y(*),N)
5740 E=.1
5750 F=(C-D)/10
5754 INPUT "ENTER PLOTTER CODE: 1=CRT; 2=9872A ",Code

```

NWC TP 6337

```

5760 IF Code=1 THEN PLOTTER IS "GRAPHICS"
5764 IF Code=2 THEN PLOTTER IS 7,5,"9872A"
5770 GRAPHICS
5780 LOCATE 25,90,15.75
5790 SCALE 0,1,D,C
5800 AXES .2,2*F,0,D
5810 FOR I=1 TO N
5820 MOVE X(I),Y(I)
5830 LABEL "+"
5840 NEXT I
5850 LOG 6
5860 FOR I=0 TO 1 STEP .2
5870 MOVE I,D-.1*F
5880 LABEL USING "Z.DDD";I
5890 NEXT I
5900 LOG 8
5910 FOR I=D+2*F TO C STEP 2*F
5920 MOVE -.01,I
5930 LABEL USING "D.DDE";I
5940 NEXT I
5950 LOG 6
5960 MOVE .5,D-.8*F
5970 LABEL "Fraction Decomposed"
5990 LDIR PI/2
6000 MOVE .025,D+.5*F
6010 LABEL "Rate (mg/deg)"
6020 LDIR 0
6030 PAUSE
6040 IF Code=1 THEN DUMP GRAPHICS
6050 GCLEAR
6054 LINPUT "DO YOU WANT TO REPEAT THE PLOT?",Rpt$
6055 IF Rpt$(1,1)="Y" THEN GOTO 5700
6060 EXIT GRAPHICS
6070 SUBEXIT
6080 Print: PRINTER IS 0
6090 PRINT "Temperature(K) Fraction decomposed Rate (deg-1)"
6100 PRINT
6110 FOR I=1 TO N
6120 PRINT USING 6150;T(I),X(I),Y(I)
6130 NEXT I
6150 IMAGE DDDDDXXXXXXXXXXXXX,Z.DDDDDXXXXXXXXXXXXXXXXXXXX,D.DDDE
6160 PRINT PAGE
6170 PRINT LIN(3)
6180 PRINT AS
6190 RETURN
6200 SUBEND

```


NWC TP 6337

Appendix B

Program for Acquisition of Isothermal DSC Data

NWC TP 6337

PROGRAM FOR ACQUISITION AND ANALYSIS OF ISOTHERMAL DSC DATA

```

10 OPTION BASE 1
20 DIM Y(1000),Time(1000),X3(1000),Y3(1000)
30 PRINTER IS 16
40 PRINT LIN(4)
50 PRINT "Data aquisition program for the Scanning Differential"
60 PRINT "Calorimeter. Use scanning digital voltmeter line"
70 PRINT "9. Ordinate axis is calibrated for 10 millivolts"
80 PRINT "full scale."
90 PRINT "Data is taken at the approximate rate of one point"
100 PRINT "per 4 seconds. Edit line 313 to change rate"
110 PRINT
120 PRINT "Follow the CRT prompts. Press CONT to enter data"
130 PRINT "into the computer or to have a plot on the CRT put"
140 PRINT "onto the thermal printer. Terminate the program by pressing"
145 PRINT "STOP."
146 PRINT
150 PRINT "EDIT THE PROGRAM AND PRESS CONT"
155 PAUSE
160 PRINT PAGE
170 PRINTER IS 0
180 DIM A$(60),B$(60),C$(80)
190 INPUT " ENTER TEST IDENTIFIER, LINE 1",A$
200 INPUT "ENTER TEST IDENTIFIER, LINE 2",B$
210 INPUT " ENTER TEMPERATURE OF THE RUN",Tinit
225 INPUT "ENTER MASS OF SAMPLE (mg)",Samplemass
235 INPUT "ENTER SENSITIVITY (mcal/sec)",Sensitivity
240 PRINT LIN(3)
250 PRINT A$
260 PRINT B$
270 PRINT USING 200;Tinit
275 PRINT USING 285;Samplemass,Sensitivity
280 IMAGE "Temperature is ",DDD," K "
285 IMAGE "Mass of sample is ",DD.DDD," mg. Sensitivity is ",DD," mcal/sec"
290 PRINT LIN(2)
300 REM The following lines configure the scanning digital voltmeter and time
clock and set key interrupts.
310 OUTPUT 701;"R H2 0"Configure DVM for interrupt transfer.
320 ON ERROR GOSUB EscapeEnable run errors to be corrected.
330 ON KEY #7 GOSUB EndOperator termination of data aquisition.
335 ON KEY #8 GOSUB Exit
340 ON INT #7 GOSUB ReadBranching routine for data transfer.
350 OUTPUT 9;"A/U1=12"Configure clock.
360 CONTROL MASK 7;128Look for interrupt flag.
370 PRINT LIN(2)
375 PRINT "Time(sec)      Ordinate      Points"
380 PRINT
385 I=1
390 DISP "Press CONT to begin data aquisition"
400 PAUSE
410 OUTPUT 9;"U1G"Start the clock
420 DISP "PRESS K7 TO TERMINATE DATA GATHERING"
430 CARD ENABLE 7Allow DVM interrupts to take place.
440 IF I<1000 THEN GOTO 440
450 DISABLE
460 PRINTER IS 16
470 PRINT "ALLOCATED CORE STORAGE IS FULL"
480 PRINTER IS 0

```

NWC TP 6337

```

490 GOSUB End
500 E 11: OUTPUT 701;"+"
505 STOP
510 Read: INPUT DATA FROM DSC
520 ENTER 701;71:
525 Y(I)=Y(I)+1000+20 (Convert millivolts to a 0 to 10 scale.
530 OUTPUT 9;"UIV"
540 ENTER 9;Time(I)
550 Time(I)=Time(I)+1000 (Convert milliseconds to seconds.
560 PRINT USING 570;Time(I),Y(I),I
570 IMAGE DDDDDXXXXXXXXXXXX,MDD.DDDDDDDDDDD
580 I=I+1
650 OUTPUT 701;"0" (Trigger Digital Voltmeter
660 CARD ENABLE 7 (Re-Enable Interrupts
670 RETURN
680 End: Process Data
685 INPUT "ENTER POINT NUMBER OF STABLE ORDINATE",R
687 FOR K=1 TO R-1
690 Y(K)=Y(P) (Eliminate initial transient
695 NEXT K
700 Npts=I-2 (Eliminate extraneous data points
710 REDIM Y(Npts),Time(Npts) (Condense the arrays.
720 Minimum=FNMin(Y*),Npts) (Calculate lowest voltage output from DSC.
730 MAT Y=Y-(Minimum) (Set zero point as lowest output voltage
740 CALL Graph(A$,B$,Time(*),Y(*),Npts) (Plot the data.
750 INPUT "DO YOU WANT THE DATA STORED?",C$
760 IF C$(1,1)="Y" THEN CALL Store(A$,B$,Time(*),Y(*),Npts)
770 INPUT "DO YOU WANT TO EXPAND THE PLOT",D$
780 IF D$(1,1)="Y" THEN CALL Expand(A$,B$,Time(*),Y(*))
790 INPUT "DO YOU WANT TO MAKE A LINEAR BASELINE CORRECTION?",E$
800 IF E$(1,1)="Y" THEN CALL Transform(A$,B$,Time(*),Y(*),Npts)
835 PRINTER IS 16
836 PRINT PAGE
837 PRINT "Peak integrator using an arbitrary baseline correction"
838 PRINT
839 PRINT "Data point numbers correspond to original data list"
840 PRINT LIN(2)
841 PRINT "The baseline is calculated using a straight line from the first to
the last data point"
842 PRINT LIN(3)
843 PRINT "Press STOP if you wish to terminate the program. Press CONT if
you wish to continue."
844 PAUSE
845 PRINT PAGE
846 INPUT "ENTER BEGINNING AND ENDING POINTS FOR NUMERICAL INTEGRATION".Begin,
End
850 Qpts=End-Begin+1
852 PRINT USING 854;Qpts
854 IMAGE "ENTER 1 AND ",DDD," FOR INTEGRATION LIMITS"
856 REDIM X3(Qpts),Y3(Qpts)
858 FOR L=1 TO Qpts
860 Y3(L)=Y(L+Begin-1)
862 X3(L)=Time(L+Begin-1)
864 NEXT L
866 Slope2=(Y3(Qpts)-Y3(1))/(X3(Qpts)-X3(1))
867 B=Y3(1)
868 FOR L=1 TO Qpts
870 Y3(L)=Y3(L)-Slope2*(X3(L)-X3(1))-B
872 NEXT L
874 C$=B$&" Expanded plot peak integration"
876 CALL Graph2(A$,C$,X3(*),Y3(*),Qpts,Area)
878 INPUT "DO YOU WANT TO TERMINATE THE PROGRAM?",Stop$
880 IF Stop$(1,1)="Y" THEN GOSUB Exit
881 CALL Kinetics(X3(*),Y3(*),Qpts,Area)
884 GOTO 300
885 Escape: (Correct any run errors.

```

NWC TP 6337

```

590 PRINTER IS 10
900 PRINT EPROMS GENERATED. EDIT PROGRAM AND PRESS CONT.
910 PAUSE
920 PRINTER IS 0
930 RETURN
1000 SUB Store(A$,B$,X(+),Y(+),N)
1010 OPTION BASE 1 'Subroutine for storing data from X-Y plotter input.
1011 SHORT U$ND,V$ND
1012 MAT U=X
1013 MAT V=Y
1020 INPUT "ENTER MASS STORAGE MEDIUM",F$
1030 INPUT "ENTER 6 CHARACTER FILE NAME",G$
1040 J$=G$+"":I$F$
1050 CREATE G$,N$F$
1060 ASSIGN #2 TO G$
1070 PRINT #2;A$,B$,N
1080 MAT PRINT #2;X,Y
1090 PRINT LIN=5
1095 PRINT USING 1100;I$F$:G$
1100 IMAGE "DATA IS STORED IN FILE " "I$,N," "
1110 ASSIGN #2 TO *
1120 SUBEXIT
1130 SUBEND
1200 SUB Graph(A$,B$,X(+),Y(+),N)
1210 PRINT PAGE 'Subroutine for plotting data from an X-Y plotter
1220 PRINT LIN(3) 'Using the internal thermal printer.
1230 OPTION BASE 1
1240 PRINT A$
1250 PRINT B$
1260 PRINT LIN(3)
1270 DIM D$(19)
1275 C$="TIME (sec)"
1278 D$="Relative Millivolts"
1280 A=F$ND*(Y(+)-N,1)
1290 B=N$ND-X(1)
1300 A=F
1310 INPUT "DO YOU WANT A MAXIMUM Y USED FOR THE GRAPH INSTEAD OF THE CALCULAT
ED MA. IMUM",J$
1320 IF J$(1,1)="Y" THEN INPUT "ENTER Ymax",H
1325 IF J$(1,1)="Y" THEN A=H
1330 INPUT "ENTER PLOTTER CODE: CRT=A, 9872A=B",Plot$
1340 IF Plot$(1,1)="B" THEN PLOTTER IS 7.5,"9872A"
1350 IF Plot$(1,1)="A" THEN PLOTTER IS "GRAPHICS"
1360 GRAPHICS
1370 LOCATE 18,83,10.75
1380 SCALE X(1),X(N),0,A
1390 AXES B/4,A/10,X(1),0
1400 MOVE X(1),Y(1)
1410 FOR I=1 TO N
1420 DRAW X(I),Y(I)
1430 NEXT I
1440 PENUP
1450 LOGO 5
1490 FOR I=X(1) TO X(N) STEP B/4
1500 MOVE I,-A/100
1510 LABEL USING 1530;I
1520 NEXT I
1530 IMAGE DDD
1540 LOGO 8
1550 FOR I=A/10 TO A STEP A/10
1560 MOVE -B/100+X(1),I
1570 LABEL USING 1590;I
1580 NEXT I
1590 IMAGE DD.D
1600 LOGO 5
1610 MOVE B/2+X(1),-A/15

```

NWC TP 6337

```

1620 LABEL C#
1630 LDIR P1/2
1640 LOGP 4
1650 MOVE -B/9+(X1),R/2
1660 LABEL D#
1670 INPUT "DO YOU WANT GRAPHICS PRINTOUT VIA THE THERMAL PRINTER?",L#
1680 IF L#(1,1)="Y" THEN DUMP GRAPHICS
1690 EXIT GRAPHICS
1700 GCLEAR
1705 IF Plot#(1,1)="B" THEN OUTPUT T05;"SP0:IN"
1710 SUBEXIT
1720 SUBEND
1730 DEF FNMax(A+1,N,Start)
1740 Max=A(Start)
1750 FOR I=Start TO N
1760 IF A(I)>Max THEN Max=A(I)
1770 NEXT I
1780 RETURN Max
1790 FEND
2000 SUB Expand(C#,D#,X(+),Y(+))
2010 OPTION BASE 1
2020 DIM Z(1000),T(1000),R(1000),W(1000)
2025 DIM I$(90),R$(90)
2030 INPUT "ENTER LOWEST AND HIGHEST DATA POINTS FOR PLOT EXPANSION (P1,P2)",P1
,P2
2040 N=ABS(P2-P1)+1
2050 REDIM Z(N),T(N)
2060 FOR I=1 TO N
2070 Z(I)=X(I+P1-1)
2080 T(I)=Y(I+P1-1)
2090 NEXT I
2100 I$=D#0:"Expanded Plot"
2110 INPUT "IS THIS A BASELINE CORRECTED PLOT?",M#
2120 IF M#(1,1)<>"Y" THEN GOTO 2175
2130 IF M#(1,1)="Y" THEN CALL Printz(C#,I$,Z(+),T(+),N)
2140 IF M#(1,1)="Y" THEN CALL Graph2(C#,I$,Z(+),T(+),N,Area)
2141 PRINTER IS 16
2142 PRINT "DO YOU WANT TO INTEGRATE THIS EXPANDED PLOT USING ANOTHER BASELINE
CORRECTION?"
2144 INPUT N#
2145 PRINT PAGE
2146 IF N#(1,1)<>"Y" THEN GOTO 2170
2147 INPUT "ENTER THE DATA POINT NUMBERS (new list) FOR ORDINATE POINTS ",P3,P4
2148 Mx=P4-P3+1
2149 REDIM R(Mx),W(Mx)
2150 PRINT USING 2152;Mx
2152 IMAGE "USE 1 AND ",DDD," FOR INTEGRATION LIMITS"
2153 FOR K=1 TO Mx
2154 P/K/=Z(K+P3-1)
2155 W(K)=T(K+P3-1)
2156 NEXT K
2157 R$="Expanded Plot: Arbitrary baseline connection"
2158 Slope2=(W(Mx)-W(1))/(R(Mx)-R(1))
2159 Bb=W-1
2160 FOR K=1 TO Mx
2161 W(K)=W(K)-Slope2*(P(K)-R(1))-Bb
2162 NEXT K
2163 CALL Graph2(C#,R$,R(+),W(+),Mx)
2170 IF M#(1,1)="Y" THEN SUBEXIT
2175 CALL Graph(C#,I$,Z(+),T(+),N)
2180 SUBEXIT
2185 SUBEND
2190 SUB Transform(F#,G#,X(+),Y(+),N)
2200 OPTION BASE 1 ' Linear baseline correction for 2 variable plots.
2210 DIM Ynew(N)
2215 DIM H$(90)

```

NWC TP 6337

```

2220 B=(Y(6)+Y(7)+Y(8)+Y(9)+Y(10))/5 : Average the first and last 5 points and
take initial dip into consideration.
2230 M=(Y(N)+Y(N-1)+Y(N-2)+Y(N-3)+Y(N-4))/5 : For slope calculation.
2240 Slope=(Y(5)-Y(1))/(X(5)-X(1))
2250 FOR I=1 TO N
2260 NewY(I)=(Y(I)-Slope*(X(I)-X(1)))/S
2270 NEXT I
2280 H$=GET$("Linear Baseline Connection")
2290 CALL Graph2(F$,H$,X(1),NewY(1),N,Area)
2300 INPUT "DO YOU WANT THE PLOT EXPANDED?";N$
2310 IF N$(1,1)="Y" THEN CALL Expand(F$,H$,X(1),NewY(1))
2320 SUBEND
2330 SUBEND
2400 DEF FNMaxabs(A$(1),N)
2410 Ma=ABS(A(1))
2420 FOR I=2 TO N
2430 IF ABS(A(I))>Ma THEN Ma=ABS(A(I))
2440 NEXT I
2441 RETURN Ma:abs
2442 FEND
2450 DEF FNMin(B$(1),N)
2460 Min=B(1)
2470 FOR I=2 TO N
2480 IF B(I)<Min THEN Min=B(I)
2490 NEXT I
2500 RETURN Min
2510 FEND
2600 SUB Graph2(F$,B$,X(1),X(2),N,Integral)
2605 PRINT IS:0
2610 PRINT PAGE : (Subroutine for plotting data from an X-Y plotter
2620 PRINT LINK3 : (using the internal thermal printer.
2630 OPTION BASE 1
2640 PRINT B$
2650 PRINT B$
2660 PRINT LINK3:
2670 DIM D$(10),U$(1000),V$(1000)
2671 FEDIM U$(N),V$(N)
2675 C$="TIME (sec)"
2678 D$="Relative Millivolts"
2680 F=FNMaxabs(A$(1),N)
2690 B=X(2)-X(1)
2700 A=F
2710 INPUT "DO YOU WANT A MAXIMUM USED FOR THE GRAPH INSTEAD OF THE CALCULAT
ED MAXIMUM?";J$
2720 IF J$(1,1)="Y" THEN INPUT "ENTER Max",H
2740 IF J$(1,1)="Y" THEN A=H
2745 INPUT "ENTER PLOTTER CODE: CRT=A, 9872A=B",Plot$
2750 IF Plot$(1,1)="A" THEN PLOTTER IS "GRAPHICS"
2755 IF Plot$(1,1)="B" THEN PLOTTER IS 7,5,"9872A"
2760 GRAPHICS
2770 LOCATE 17,92,10,75
2780 SCALE X:10,X:N0,-A:A
2790 ACES B:4,A:10,X(1):0
2800 MOVE (X(1),Y(1))
2810 FOR I=1 TO N
2820 DRAW (X(I),Y(I))
2830 NEXT I
2840 PENUP
2850 LOGO 6
2860 FOR I=X(1) TO X(N) STEP B:4
2870 MOVE I,-A:100
2880 LABEL USING 2930:I
2890 NEXT I
2900 IMAGE DDD
2910 LOGO 8
2920 FOR I=-A TO A STEP A:10

```

NWC TP 6337

```

2960 MOVE -B/100+X(I),I
2970 LABEL USING 2990:I
2980 NEXT I
2990 IMAGE MDD.D
3000 LOGS 2
3010 MOVE B/2+X(I),-A/15
3020 LABEL C#
3030 LDIR PI/2
3040 LOGS 4
3050 MOVE -B/9+X(I),A/2
3060 LABEL D#
3062 INPUT "DO YOU WANT TO INTEGRATE PART OF THE CURVE",O#
3065 IF O#(1,1)="/Y" THEN GOTO 3085
3066 INPUT "ENTER BEGINNING AND ENDING DATA POINT NUMBERS(FROM NEW SET IF EXPA
DED)",Start,Finish
3067 REDIM Ux(Finish-Start+1),Vy(Finish-Start+1)
3068 J=1
3069 FOR I=Start TO Finish
3070 Ux(J)=X(I)
3071 Vy(J)=Y(I)
3072 MOVE X(I),Y(I)
3073 DRAW X(I),0
3074 PENUP
3075 J=J+1
3076 NEXT I
3077 Epsilon=1E-6
3078 CALL Intun(J-1,Epsilon,Ux(*),Vy(*),Integral)
3079 PRINT USING 3080;Ux(1),Ux(J-1),Integral
3080 IMAGE "THE AREA REPRESENTED BY THE SHADED REGION BETWEEN DOMAIN VALUES ",
DDD.DD," AND ",DDD.DD," IS ",MD.DDE
3081 PRINT LIN(2)
3085 INPUT "DO YOU WANT GRAPHICS PRINTOUT VIA THE THERMAL PRINTER?",L#
3090 IF L#(1,1)="/Y" THEN DUMP GRAPHICS
3095 EXIT GRAPHICS
3100 GCLEAR
3105 IF Plot#(1,1)="/B" THEN OUTPUT 7,5;"SP0-IN"
3110 SUBEXIT
3120 SUBEND
3130 SUB Printz(A#,B#,X(*),Y(*),N)
3140 OPTION BASE 1
3145 INPUT "DO YOU WANT THIS PRINTED ON THE TYPEWRITER?",Printer#
3146 IF Printer#(1,1)="/Y" THEN PRINTER IS 7,4
3147 GOTO 3160
3150 PRINT PAGE
3160 PRINT "DATA POINT RENUMBERING FOR BASELINE CORRECTED , EXPANDED PLOT"
3170 PRINT A#
3180 PRINT B#
3190 PRINT
3200 PRINT "DOMAIN VALUE      RANGE VALUE      NEW DATA POINT NUMBER"
3210 PRINT
3220 FOR I=1 TO N
3230 PRINT USING 3250;X(I),Y(I),I
3240 NEXT I
3250 IMAGE DDD.DDXXXXXXXXXXXX,DD.DDXXXXXXXXXXXX,DDD
3260 PRINT LIN(5)
3270 SUBEXIT
3280 SUBEND
3400 SUB Intun(N,Eps,X(*),Y(*),Int) : Cubic Spline Integrator
3480 Eaddra=N/3: OR (X(1)=X(N)) OR (Eps=0)
3490 IF Baddra=0 THEN 3600
3520 PRINT LIN(2),"ERROR IN SUBPROGRAM Intun."
3530 PRINT USING 3540;N,Eps,X(1),X(N)
3540 IMAGE "N=",DDD.DD,"Eps=",MZ.DDE,/, "X(1)=",MZ.DDE.DD,"X(N)=",MZ.DDE.DD
3550 PAUSE
3560 GOTO 3480
3600 OPTION BASE 1

```

NWC TP 6337

```

3610 DIM B(2:N-1),S(N),G(2:N-1)
3620 FOR I=2 TO N-1
3630   H=X(I+1)-X(I-1)
3640   C=X(I)-X(I-1)
3650   B(I)=.5*X/H
3660   T=(Y(I+1)-Y(I))-(X(I+1)-X(I))*C/(Y(I)-Y(I-1))/X/H
3670   S(I)=2+T
3680   G(I)=3+T
3690 NEXT I
3700 S(1)=S(N)=0
3720 W=8-4*SQR(3)
3740 U=0
3760 FOR I=2 TO N-1
3770   T=W*(-S(I)-B(I)+5*S(I-1)-(C-5-B(I))+S(I+1)+G(I))
3780   H=ABS(T)
3800   IF H>U THEN U=H
3820   S(I)=S(I)+T
3830 NEXT I
3850 IF U=Eps THEN 3740
3860 Int=0
3920 FOR I=1 TO N-1
3930   H=X(I+1)-X(I)
3940   Int=Int+.5*H*(Y(I)+Y(I+1))-1/24*H*3*(S(I)+S(I+1))
3950 NEXT I
3960 SUBEND
4000 SUB Kinetics(X2(*),Y2(*),N,D)
4010 OPTION BASE 1
4020 PRINTER IS 0
4040 DIM X4(N),Y4(N),R4(4:N),Frac(4:N),Da(5:N),Deriv(5:N),Logd(N)
4090 Epsilon=1E-6 ! Establish tolerance for convergence
4110 FOR I=1 TO 3
4120   X4(I)=X2(I)
4130   Y4(I)=Y2(I) ! Begin generating partial area arrays.
4140 NEXT I
4150 FOR J=4 TO N
4160   PEDIM X4(J),Y4(J) ! Incrementally generate partial area arrays.
4170   X4(J)=X2(J)
4180   Y4(J)=Y2(J)
4190 CALL Intun(J,Epsilon,X4(*),Y4(*),R4(J))
4200   Frac(J)=R4(J)/D ! Calculate fractional areas.
4210 DISP "Generating Areas",J,R4(J),Frac(J)
4215 NEXT J
4220 FOR K=5 TO N
4230   Da(K)=R4(K)-R4(K-1)
4240   Deriv(K)=Da(K)/(X2(K)-X2(K-1))
4250 NEXT K
4270 PRINT "TIME(s)  AREA  FRACT A  AREA INCREMENT  RATE OF INCREAS
E  Pt#"
4280 PRINT LINK2)
4290 FOR I=5 TO N
4300 PRINT USING 4320;X2(I),R4(I),Frac(I),Da(I),Deriv(I),I
4310 NEXT I
4320 IMAGE DDDDDXXXXX,DDDDXXXXX,Z.DDDDDXXXXX,DDZ.DDDDDXXXXXXXXXX,DDZ.DDDDDXXXXXXXXXX
,DDD
4330 CALL Plot(Frac(*),Deriv(*),N)
4340 MAT Y2=Y2+(1E-6) ! Insure nonzero arguments
4350 MAT Logd=LOG(Y2)
4365 CALL Printer(X2(*),Y2(*),Frac(*),Logd(*),N)
4370 CALL Plot2(X2(*),Frac(*),N)
4375 PRINT PAGE
4380 CALL Plot3(X2(*),Logd(*),N)
4390 PRINT PAGE
4400 CALL Plot4(Frac(*),Logd(*),N)
4490 SUBEXIT
4500 SUBEND
5000 SUB Linear(X(*),Y(*),N,A,B,Regss,Reass,Totals,Regms,Resms,F,Dneg,Dfres,Df

```


NWC TP 6337

```

tot,Abort, Variance)
5010 ! *** MODEL: Y=A+B*X ***
5020 ON ERROR GOTO Bomb
5030 Abort=0
5040 Y1=X1=Z=X2=Y2=0
5050 FOR I=1 TO N
5060     X1=X1+X(I)           ! Sum of X's
5070     Y1=Y1+Y(I)           ! Sum of Y's
5080     X2=X2+X(I)*X(I)       ! Sum of X squares
5090     Y2=Y2+Y(I)*Y(I)       ! Sum of Y squares
5100     Z=Z+X(I)*Y(I)         ! Sum of XY's
5110 NEXT I
5120 X1=X1/N                 ! Mean X
5130 Y1=Y1/N                 ! Mean Y
5140 B=(Z-N*X1*Y1)/(X2-N*X1*X1)
5150 A=Y1-B*X1
5160 Totalss=Y2-N*Y1*Y1      ! Total Sum of Squares
5170 Regss=(Z-N*X1*Y1)^2/(X2-N*X1*X1) ! Regression Sum of Squares
5180 Resss=Totalss-Regss      ! Residual Sum of Squares
5190 Regms=Regss              ! Regression Mean Squares
5200 Resms=Resss/(N-2)        ! Residual Mean Squares
5205 Variance=SQR(Resms/(X2-N*X1*X1))
5210 OFF ERROR
5220 DEFAULT ON
5230 F=Regms/Resms           ! F Ratio
5240 DEFAULT OFF
5250 Dfreg=1                  ! Degrees of Freedom
5260 Dfres=N-2
5270 Dftot=Dfreg+Dfres
5280 SUBEXIT
5290 Bomb: Abort=1
5300 SUBEND
5310 SUB Plot1(X(*),Y(*),N)
5320 ! Plot fraction reacted vs rate of reaction.
5330 Xmax=FNHMax(X(*),N)
5340 Xmin=FNHMin(X(*),N)
5350 Ymax=FNHMax(Y(*),N)
5360 Ymin=FNHMin(Y(*),N)
5370 LINUT "ENTER PLOTTER CODE:A=CRT,B=9872A",Plotters
5380 IF Plotters(1,1)="A" THEN PLOTTER IS "GRAPHICS"
5390 IF Plotters(1,1)="B" THEN PLOTTER IS 7,5,"9872A"
5400 GRAPHICS
5410 LOCATE 5,90,10,75
5420 SCALE Xmin,Xmax,Ymin,Ymax
5430 AXES (Xmax-Xmin)/4,(Ymax-Ymin)/4,Xmin,Ymin
5440 FOR I=1 TO N
5450 PLOT X(I),Y(I)
5460 NEXT I
5470 LORG 6
5480 FOR J=Xmin TO Xmax STEP (Xmax-Xmin)/4
5490 MOVE J,Ymin-Ymin/20
5500 LABEL USING "D.DDE";J
5510 NEXT J
5520 LORG 8
5530 FOR K=Ymin+(Ymax-Ymin)/4 TO Ymax STEP (Ymax-Ymin)/4
5540 MOVE Xmin-Xmin/20,K
5550 LABEL USING "D.DDE";K
5560 NEXT K
5570 MOVE Xmin,Ymin-(Ymax-Ymin)/8
5580 LORG 3
5590 LABEL "Plot of fraction reacted vs rate"
5595 PAUSE
5600 IF Plotters(1,1)="A" THEN DUMP GRAPHICS
5605 IF Plotters(1,1)="B" THEN OUTPUT 7,5;"SP0-IN"
5610 EXIT GRAPHICS
5615 GCLEAR

```

NWC TP 6337

```

5616 SUBEXIT
5620 SUBEND
5630 SUB Plot2(X(*),Y(*),N)
5640 ! Plot (1-fraction reacted) vs time
5650 INPUT "ENTER PLOTTER CODE: A=CRT, B=9872A",Plotter$
5660 IF Plotter$(1,1)="A" THEN PLOTTER IS "GRAPHICS"
5670 IF Plotter$(1,1)="B" THEN PLOTTER IS 7,5,"9872A"
5680 IF Plotter$(1,1)="A" THEN PRINT PAGE
5690 GRAPHICS
5700 LOCATE 10,90,10,75
5710 SCALE X(5),X(N),0,1
5720 AXES (X(N)-X(5))/4,.25,X(5),0
5730 FOR I=5 TO N
5740 PLOT X(I),1-Y(I)
5750 NEXT I
5760 LOG 6
5770 FOR J=X(5) TO X(N) STEP (X(N)-X(5))/4
5780 MOVE J,-.02
5790 LABEL USING "DDDD";J
5800 NEXT J
5810 MOVE (X(N)-X(5))/2+X(5),-.07
5820 LABEL "Time (seconds)"
5830 LOG 8
5840 FOR K=.25 TO 1 STEP .25
5850 MOVE (X(N)-X(5))/20+X(5),K
5860 LABEL USING "2.DD";K
5870 NEXT K
5880 LOG 3
5890 LDIR PI/2
5900 MOVE (X(N)-X(5))/20+X(5),.05
5910 LABEL "Fraction Unreacted"
5915 PAUSE
5920 IF Plotter$(1,1)="A" THEN DUMP GRAPHICS
5925 IF Plotter$(1,1)="B" THEN OUTPUT 7,5;"SP0/IN"
5930 EXIT GRAPHICS
5931 GOCLEAR
5935 SUBEXIT
5940 SUBEND
5950 SUB Plot3(X(*),Y(*),N)
5960 ! Plot of log displacement vs time
5970 DIM A(N),B(N) ! Partial Arrays for Kinetics Calculations
5980 INPUT "ENTER PLOTTER CODE: A=CRT, B=9872A",Plotter$
5990 IF Plotter$(1,1)="A" THEN PLOTTER IS "GRAPHICS"
6000 IF Plotter$(1,1)="B" THEN PLOTTER IS 7,5,"9872A"
6010 GRAPHICS
6020 LOCATE 10,90,10,75
6030 SCALE X(5),X(N),0,5
6035 LDIR 0
6040 AXES (X(N)-X(5))/4,1,X(5),0
6050 FOR I=5 TO N
6060 DRAW X(I),Y(I)
6070 NEXT I
6080 LOG 6 ! Label the axes
6090 FOR I=X(5) TO X(N) STEP (X(N)-X(5))/4
6100 MOVE I,-.05
6110 LABEL USING "DDD";I
6120 NEXT I
6130 MOVE (X(N)-X(5))/2+X(5),-.3
6140 LABEL "Time (sec)"
6145 LOG 8
6150 FOR J=1 TO 5
6160 MOVE X(5)+.01*(X(N)-X(5)),J
6170 LABEL USING "D.D";J
6180 NEXT J
6190 LDIR PI/2
6200 LOG 6

```

NWC TP 6337

```

6210 MOVE X(5)+.05*(X(N)-X(5)),2.5
6220 LABEL "Ln(displacement)"
6230 LDIR 0
6240 PAUSE
6250 IF Plotter$(1,1)="A" THEN DUMP GRAPHICS
6255 IF Plotter$(1,1)="B" THEN OUTPUT 7,5;"SP0-IN"
6260 EXIT GRAPHICS
6265 GCLEAR
6270 PRINTER IS 0
6275 INPUT "ENTER TWO POINT NUMBERS FOR THE SLOPE CALCULATION",S,T
6280 Nptsd=T-S+1
6285 REDIM A(1:Nptsd),B(1:Nptsd)
6290 PRINT LIN(3)
6295 FOR I=1 TO Nptsd
6300 A(I)=X(S+I-1)
6305 B(I)=Y(S+I-1)
6310 NEXT I
6320 CALL Linear(A(*),B(*),Nptsd,Int,Slp,C0,C1,C2,C3,C4,C5,C6,C7,C8,C9,Var)
6330 PRINT USING 6340;A(1),A(Nptsd),Slp,Var
6340 IMAGE "Slope of plot between times ",DDDD," and ",DDDD," seconds is "/D.DDE
," +/- ",D.DDE," sec-1"
6350 PRINT LIN(3)
6360 INPUT "DO YOU WANT TO REPEAT THE CALCULATION USING OTHER POINTS?",Rpt$
6370 IF (Rpt$(1,1)="Y") OR (Rpt$(1,1)="y") THEN GOTO 6275
6375 SUBEXIT
6380 SUBEND
6600 SUB Plot(X(*),Y(*),N)
6610 REM Plot dA/dt vs A and choose linear portion for kinetics
6620 PRINT PAGE
6625 OPTION BASE 1
6630 PRINT LIN(3)
6640 PRINT "Kinetics plot of dx/dt vs x. x = fraction decomposed"
6650 DIM X1(N),Y1(N)
6660 C=FNMax(Y(*),N,5)
6690 F=C*.10
6700 PLOTTER IS "GRAPHICS"
6710 GRAPHICS
6720 LOCATE 10,90,10,75
6730 SCALE 0,1,0,C
6740 AXES .25,2.5*F,0,0
6750 FOR I=5 TO N
6760 MOVE X(I),Y(I)
6770 LABEL "+"
6780 NEXT I
6790 LOG 6
6800 FOR I=0 TO 1 STEP .25
6810 MOVE I,-.1*F
6820 LABEL USING "2.DD";I
6830 NEXT I
6840 LOG 8
6850 FOR I=2.5*F TO C STEP 2.5*F
6860 MOVE -.01,I
6870 LABEL USING "D2.DD";I
6880 NEXT I
6890 LOG 6
6900 MOVE .5,-.8*F
6910 LABEL "Fraction Decomposed"
6920 LDIR P1/2
6930 MOVE .025,D+S*F
6940 LABEL "Relative Rate"
6950 LDIR 0
6960 PAUSE
6970 DUMP GRAPHICS
6980 GCLEAR
6990 EXIT GRAPHICS
7000 PRINT PAGE

```

NWC TP 6337

```

7010 PRINT LIN(2)
7020 PRINT "Linear Regression Analysis of the Data"
7030 PRINT LIN(2)
7040 INPUT "ENTER BEGINNING AND ENDING POINT FOR CURVE FITTING",Begin,End
7050 Pts=End-Begin+1
7060 PEDIM X1(1:Pts),Y1(1:Pts)
7070 FOR I=1 TO Pts
7080   X1(I)=X(Begin+I-1)
7090   Y1(I)=Y(Begin+I-1)
7100 NEXT I
7110 PRINT USING 7120;X1(1),X1(Pts)
7120 IMAGE "Plot is between times ",DDDD.D," seconds and ",DDDD.D," seconds."
7130 PRINT LIN(2)
7140 CALL Linear(X1(*),Y1(*),Pts,A,B,C0,C1,C2,C3,C4,C5,C6,C7,C8,C9,V)
7150 PRINT USING 7160;ABS(B),V
7160 IMAGE "Rate Constant is ",D.DDE," sec-1.      Mean Variance is ",D.DDE
7170 PRINT LIN(3)
7180 Xmax=FNMax(X1(*),Pts,1)
7190 Ymax=FNMax(Y1(*),Pts,1)
7200 Xmin=FNMin(X1(*),Pts)
7210 Ymin=FNMin(Y1(*),Pts)
7220 E=(Xmax-Xmin)*10
7230 F=(Ymax-Ymin)*10
7240 PLOTTER IS "GRAPHICS"
7250 GRAPHICS
7260 LOCATE 20,100,20,90
7270 SCALE Xmin,Xmax,Ymin,Ymax
7280 AXES 2+E,2+F,Xmin,Ymin
7290 FOR I=1 TO Pts
7300   MOVE X1(I),Y1(I)
7310   LABEL "+"
7320 NEXT I
7330 FOR J=1 TO Pts
7340   Y1(J)=X1(J)*B+A
7350 NEXT J
7360 MOVE X1(1),Y1(1)
7370 FOR I=1 TO Pts
7380   DRAW X1(I),Y1(I)
7390 NEXT I
7400 LOG 6
7410 FOR I=Xmin TO Xmax STEP 2+E
7420   MOVE I,Ymin-.1*F
7430   LABEL USING "D.DDD";I
7440 NEXT I
7450 LOG 8
7460 FOR I=Ymin+2*F TO Ymax STEP 2+F
7470   MOVE Xmin-.04+E,I
7480   LABEL USING "DZ.DD":I
7490 NEXT I
7500 LOG 6
7510 MOVE Xmin+.5+E,Ymin-F
7520 LABEL "Fraction Decomposed"
7530 LDIR PI/2
7540 MOVE Xmin+.4+E,Ymin+.5*F
7550 LABEL "Relative Rate"
7560 PAUSE
7570 DUMP GRAPHICS
7580 GCLEAR
7590 EXIT GRAPHICS
7600 INPUT "DO YOU WANT TO REPEAT THE CALCULATION?",Repeat$
7610 IF Repeat$(1,1)="Y" THEN GOTO 7000
7620 SUBEXIT
7630 SUBEND
7700 DEF FNMon(A(*),N)
7710   Min=A(1)
7720   FOR I=1 TO N

```

NWC TP 6337

```

7730 IF A(I)<Min THEN Min=A(I)
7740 NEXT I
7750 RETURN Min
7760 FEND
7770 SUB Printer(Time(*),Disp(*),Frac(*),Logd(*),N)
7780 ! Print out values used in kinetics calculations
7790 DISP "CHOOSE PRINTER AND PRECS CONT"
7800 PAUSE
7810 PRINT "Ptb      Time(sec)      Y      Log(Y)      a      (1-a)      L
n 100*(1-a)"
7820 PRINT
7830 FOR I=5 TO N
7835 IF Frac(I)=1 THEN GOTO 7870
7840 PRINT USING 7860;I,Time(I),Disp(I),Logd(I),Frac(I),1-Frac(I),LOG(100*(1-Frac(I)))
7850 NEXT I
7860 IMAGE DDDXXXXX,DDDDXXXXXX,DDD.DXXXXX,MZ.DDDXXXXX,Z.DDDXXX,Z.DDDXXXXX,MZ.Z
DD
7870 PRINT PAGE
7880 SUBEXIT
7890 SUBEND
7900 SUB Plot4(X(*),Y(*),Z)
7901 DIM U(Z),V(Z)! order plot of log(displacement) vs log(100*(1-a))
7905 INPUT "ENTER PLOTTER CODE: CRT=A, 9872A=5",Plotters
7910 IF Plotters[1,1]="A" THEN PLOTTER IS "GRAPHICS"
7915 IF Plotters[1,1]="B" THEN PLOTTER IS 7,5,"9872A"
7920 MAT X=(1)-X
7925 MAT Y=(100)*X ! Eliminate negative logarithms
7930 FOR I=5 TO Z
7933 IF X(I)=0 THEN GOTO 7937
7935 X(I)=LOG(X(I))
7937 NEXT I
7940 A=5
7950 C=5
7970 LOCATE 15,90,10,80
7980 SCALE 0,A,0,C
7985 SHOW 0,A,0,C
7990 AXES 1,1,0,0
8000 FOR I=5 TO Z
8002 IF Y(I)<0 THEN Y(I)=0 ! ignore negative logarithms.
8003 IF X(I)<0 THEN X(I)=0
8010 PLOT X(I),Y(I)
8020 NEXT I
8025 LOG 6
8030 FOR I=0 TO A
8040 MOVE I,-.02+C
8050 LABEL USING "Z.D";I
8060 NEXT I
8070 MOVE A/2,-.08+C
8080 LABEL "Ln(100*(1-a))"
8085 LOG 8
8090 FOR I=1 TO 5
8100 MOVE -.02+A,I
8110 LABEL USING "D.DD";I
8120 NEXT I
8130 LDIR PI/2
8140 MOVE .05+A,.5+C
8150 LOG 6
8160 LABEL "Ln(displacement)"
8170 PAUSE
8180 IF Plotters[1,1]="A" THEN DUMP GRAPHICS
8190 IF Plotters[1,1]="B" THEN OUTPUT 7,5;"SP0/IN"
8200 LDIR 0
8210 EXIT GRAPHICS
8220 GCLFAP
8230 INPUT "ENTER TWO POINTS FOR SLOPE CALCULATION",B,D

```

NWC TP 6337

```

8240  Qpts=D-B+1
8250  PEDIM U(1:Qpts),V(1:Qpts)
8260  FOR I=1 TO Qpts
8270    U(I)=X(B+I-1)
8280    V(I)=Y(B+I-1)
8290  NEXT I
8300  CALL Linear(U(1),U(Qpts),Int,Slope,C0,C1,C2,C3,C4,C5,C6,C7,C8,C9,Var)
8310  PRINT LINK3)
8320  PRINT USING 8320;U(1),U(Qpts),Slope,Var
8330  IMAGE "Slope of order curve between values ",D.DD," and ",D.DD," is ",D.DD,
" +
",D.DD
8340  INPUT "DO YOU WANT TO REPEAT THE CALCULATION? ,Again?
8350  IF Again$(1,1)="" THEN GOTO 8230
8360  SUBEXIT
8370  SUBEND

```

NWC TP 6337

APPENDIX C

Program for Acquisition and Analysis of Thermogravimetric Data

NWC TP 6337

PROGRAM FOR ACQUISITION AND ANALYSIS OF CONSTANT HEATING RATE
DIFFERENTIAL SCANNING CALORIMETER DATA.

```

10 OPTION BASE 1
20 DIM Y(1000),Temp(1000),X(1000),Y3(1000)
30 PRINTER IS 16
40 PRINT LIN(4)
50 PRINT "Data acquisition program for the Scanning Differential"
60 PRINT "Calorimeter. Use scanning digital voltmeter line"
70 PRINT "9. Ordinate axis is calibrated for 10 millivolts"
80 PRINT "full scale. Temperature is calculated as TIME * "
90 PRINT "HEATING RATE. Data is taken at the approximate rate"
100 PRINT "of one point per 4 seconds. Edit line 310 to change rate"
110 PRINT
120 PRINT "Follow the CRT prompts. Press CONT to enter data"
130 PRINT "into the computer or to have a plot on the CRT put"
140 PRINT "onto the thermal printer. Terminate the program by pressing"
145 PRINT "STOP. Edit K5 if you want additional graphics features."
146 PRINT
150 PRINT "EDIT THE PROGRAM AND PRESS CONT"
155 PAUSE
160 PRINT PAGE
170 PRINTER IS 0
180 DIM A$(60),E$(60),C$(80)
190 INPUT " ENTER TEST IDENTIFIER, LINE 1",A$
200 INPUT "ENTER TEST IDENTIFIER, LINE 2",B$
210 INPUT " ENTER INITIAL TEMPERATURE OF THE RUN * ",Tinit
220 INPUT "ENTER THE HEATING RATE IN DEGREES C per MINUTE",Rate
225 INPUT "ENTER MASS OF SAMPLE (mg)",Samplemass
226 INPUT "ENTER SENSITIVITY (mcal/sec)",Sensitivity
230 Rate=Rate*60 !Convert rate to degrees per second.
240 PRINT LIN(3)
250 PRINT A$
260 PRINT B$
270 PRINT USING 280:Tinit,Rate*60
275 PRINT USING 285:Samplemass,Sensitivity
280 IMAGE "Initial Temperature is ",DDD," K Heating Rate is ",DD," deg/min"
285 IMAGE "Mass of sample is ",DD.DDD," mg. Sensitivity is ",DD," mcal/sec"
290 PRINT LIN(2)
300 REM The following lines configure the scanning digital voltmeter and time
clock and set key interrupts.
310 OUTPUT 701:"R H0 0"!Configure DVM for interrupt transfer.
320 ON ERROR GOSUB Escape!Enable run errors to be corrected.
330 ON KEY #7 GOSUB End!Operator termination of data acquisition.
335 ON KEY #8 GOSUB Exit
340 ON INT #7 GOSUB Read!Branching routine for data transfer.
350 OUTPUT 9:"A-U1=12"!Configure clock.
360 CONTROL MASK 7:128!Look for interrupt flag.
370 PRINT LIN(2)
375 PRINT "TEMPERATURE (K) ORDINATE POINT#"
380 PRINT
385 I=1
390 DISP "Press CONT to begin data acquisition"
400 PAUSE
410 OUTPUT 9:"UI0"!Start the clock
420 DISP "PRESS K7 TO TERMINATE DATA GATHERING"
430 CARD ENABLE 7!allow DVM interrupts to take place.
440 IF I<1000 THEN GOTO 440
450 DISABLE

```


NMC TP 6337

```

460  PRINTER IS 16
470  PRINT "ALLOCATED CORE STORAGE IS FULL"
480  PRINTER IS 0
490  GOSUB End
500  Exit:  OUTPUT 701;"*
505  STOP
510  Read:  INPUT DATA FROM DSC
520  ENTER 701;Y(I)
525  Y(I)=Y(I)+1000+20 'Convert millivolts to a 0 to 10 scale.
530  OUTPUT 9;"UIV"
540  ENTER 9;Time
550  Temp(I)=Time+Rate/1000+Tinit
560  PRINT USING 570;Temp(I),Y(I),I
570  IMAGE DDDDDXXXXXXXXXXXXXXXXX,MDD.DDDXXXXXXXXX,DDDD
580  I=I+1
590  OUTPUT 701;"0"
600  CARD ENABLE 7
610  RETURN
620  End:  Process Data
630  Y(1)=Y(2) 'Bad data point eliminator
640  Temp(1)=Tinit 'Make sure first point is correct
650  Npts=I-2 'Eliminate extraneous data points
660  REDIM Y(Npts),Temp(Npts) 'Condense the array.
670  Minimum=FNMin(Y(*),Npts) 'Calculate lowest voltage output from DSC.
680  MAT Y=Y-(Minimum) 'Set zero point as lowest output voltage
690  CALL Graph(As,Bs,Temp(*),Y(*),Npts)
700  INPUT "DO YOU WANT THE DATA STORED?",Cs
710  IF Cs(1,1)="Y" THEN CALL Store(As,Bs,Temp(*),Y(*),Npts,Tinit,Rate,Samples,
720  Ss,Sensitivity)
730  INPUT "DO YOU WANT TO EXPAND THE PLOT",Ds
740  IF Ds(1,1)="Y" THEN CALL Expand(As,Bs,Temp(*),Y(*))
750  INPUT "DO YOU WANT TO MAKE A LINEAR BASELINE CORRECTION?",Es
760  IF Es(1,1)="Y" THEN CALL Transform(As,Bs,Temp(*),Y(*),Npts)
770  PRINTER IS 16
780  PRINT PAGE
790  PRINT "Peak integrator using an arbitrary baseline correction"
800  PRINT
810  PRINT "Data point numbers correspond to original data list"
820  PRINT LIN(2)
830  PRINT "The baseline is calculated using a straight line from the first to
840  the last data point"
850  PRINT LIN(3)
860  PRINT "Press STOP if you wish to terminate the program. Press CONT if
870  you wish to continue."
880  PAUSE
890  PRINT PAGE
900  INPUT "ENTER BEGINNING AND ENDING POINTS FOR NUMERICAL INTEGRATION",Begin,
910  End
920  Opts=End-Begin+1
930  PRINT USING 954;Opts
940  IMAGE "ENTER 1 AND ",DDD," FOR INTEGRATION LIMITS"
950  REDIM X3(Opts),Y3(Opts)
960  FOR L=1 TO Opts
970  Y3(L)=Y(L+Begin-1)
980  X3(L)=Temp(L+Begin-1)
990  NEXT L
1000  Slope3=(Y3(Opts)-Y3(1))/(X3(Opts)-X3(1))
1010  B=Y3(1)
1020  FOR L=1 TO Opts
1030  Y3(L)=Y3(L)-Slope3*(X3(L)-X3(1))-B
1040  NEXT L
1050  Cs=999: Expanded plot peak integration"
1060  CALL Graph2(As,Cs,X3(*),Y3(*),Opts,Area)
1070  INPUT "DO YOU WANT TO CONTINUE WITH KINETICS?",Stops
1080  IF Stops(1,1)="Y" THEN GOSUB Exit
1090  CALL Kinetics(As,Cs,X3(*),Y3(*),Opts,Area)

```

MWC TP 6337

```

884 GOTO 300
885 Escape: 1 Correct any run errors.
890 PRINTER IS 16
898 PRINT ERRMSG: "GENERATEI. EDIT PROGRAM AND PRESS CONT."
910 PAUSE
920 PRINTER IS 0
930 RETURN
1000 SUB Store(A$,B$,X(*),Y(*),N,T0,R,Sm,Sens)
1010 OPTION BASE 1 'Subroutine for storing data from X-Y plotter input.
1015 SHORT R=N,SEN
1020 INPUT "ENTER MASS STORAGE MEDIUM",FS
1030 INPUT "ENTER 6 CHARACTER FILE NAME",GS
1040 GS=GS$:"LFS
1050 CREATE GS,N/9
1060 ASSIGN #2 TO GS
1070 PRINT #2;A$,B$,N,T0,R,Sm,Sens
1075 MAT R=X
1076 MAT S=Y
1080 MAT PRINT #2;R,S
1090 PRINT LIN(5)
1100 PRINT "DATA IS STORED IN FILE "&CHR$(34);GS;CHR$(34)
1110 ASSIGN #2 TO *
1120 SUBEXIT
1130 SUBEND
1200 SUB Graph(A$,B$,X(*),Y(*),N)
1201 OPTION BASE 1
1205 INPUT "ENTER PLOTTER CODE: 1=CRT; 2=9872A",Code
1206 IF Code=2 THEN GOTO 1270
1210 PRINT PAGE 'Subroutine for plotting data from an X-Y plotter
1220 PRINT LIN(3) 'using the internal thermal printer.
1240 PRINT A$
1250 PRINT B$
1260 PRINT LIN(3)
1270 DIM C$(60),D$(60)
1275 INPUT "ENTER X AXIS LABEL IF OTHER THAN TEMPERATURE (K)",CS
1276 IF CS="" THEN CS="TEMPERATURE (K)"
1277 INPUT "ENTER Y AXIS LABEL IF DESIRED",DS
1278 IF DS="" THEN DS="Relative Millivolts"
1280 F=FNMax(Y(*),N)
1290 B=X(N)-X(1)
1300 A=F
1310 INPUT "DO YOU WANT A MAXIMUM Y USED FOR THE GRAPH INSTEAD OF THE CALCULAT
ED MAXIMUM",JS
1320 IF JS(1,1)="Y" THEN INPUT "ENTER Ymax",H
1330 IF JS(1,1)="Y" THEN A=H
1340 IF Code=2 THEN PLOTTER IS 7,5,"9872A"
1350 IF Code=1 THEN PLOTTER IS "GRAPHICS"
1360 GRAPHICS
1370 LOCATE 15,90,15,75
1380 SCALE X(1),X(N),0,A
1390 AXES B/4,A/10,X(1),0
1400 MOVE X(1),Y(1)
1410 FOR I=1 TO N
1420 DRAW X(I),Y(I)
1430 NEXT I
1440 PENUP
1480 LOG 6
1490 FOR I=X(1) TO X(N) STEP B/4
1500 MOVE I,-A/100
1510 LABEL USING 1530;I
1520 NEXT I
1530 IMAGE DDD
1540 LOG 8
1550 FOR I=A/10 TO A STEP A/10
1560 MOVE -B/100+X(1),I
1570 LABEL USING 1590;I

```

NWC TP 6337

```

1580 NEXT I
1590 IMAGE DD.D
1600 LOG 6
1610 MOVE B/2+X(1),-A-15
1620 LABEL TRIM$(C$)
1630 LDIR PI/2
1640 LOG 4
1650 MOVE -B/10+X(1),A/2
1660 LABEL TRIM$(D$)
1670 PAUSE
1680 IF Code=1 THEN DUMP GRAPHICS
1690 EXIT GRAPHICS
1700 GCLEAR
1710 SUBEXIT
1720 SUBEND
1730 DEF FNMax(A(*),N)
1740 Max=A(1)
1750 FOR I=2 TO N
1760 IF A(I)>Max THEN Max=A(I)
1770 NEXT I
1780 RETURN Max
1790 FNEED
2000 SUB Expand(C$,D$,X(*),Y(*))
2010 OPTION BASE 1
2020 DIM Z(1000),T(1000),R(1000),W(1000)
2025 DIM IS(80),RS(80)
2030 INPUT "ENTER LOWEST AND HIGHEST DATA POINTS FOR PLOT EXPANSION (P1,P2)",P1
,P2
2040 N=ABS(P2-P1)+1
2050 REDIM Z(N),T(N)
2060 FOR I=1 TO N
2070 Z(I)=X(I+P1-1)
2080 T(I)=Y(I+P1-1)
2090 NEXT I
2100 IS=D$+"-EXPANDED PLOT"
2110 LINPUT "IS THIS A BASELINE CORRECTED PLOT?",N$
2120 IF N$(1,1)="" THEN GOTO 2175
2130 IF N$(1,1)="Y" THEN CALL Printz(C$,IS,Z(*),T(*),N)
2140 IF N$(1,1)="Y" THEN CALL Graph2(C$,IS,Z(*),T(*),N,Area)
2141 PRINTER IS 16
2143 PRINT "DO YOU WANT TO INTEGRATE THIS EXPANDED PLOT USING ANOTHER BASELINE
CORRECTION?"
2144 LINPUT N$
2145 PRINT PAGE
2146 IF N$(1,1)="" THEN GOTO 2170
2147 INPUT "ENTER THE DATA POINT NUMBERS (new list) FOR ORDINATE POINTS ",P3,P4
2148 Mx=P4-P3+1
2149 PEDIM R(Mx),W(Mx)
2150 PRINT USING 2152;Mx
2152 IMAGE "USE 1 AND ",DDD," FOR INTEGRATION LIMITS"
2153 FOR K=1 TO Mx
2154 R(K)=Z(K+P3-1)
2155 W(K)=T(K+P3-1)
2156 NEXT K
2157 RS="Expanded plot: Arbitrary Baseline correction for curve integration."
2158 Slope2=(W(Mx)-W(1))/(R(Mx)-R(1))
2159 Bb=W(1)
2162 FOR K=1 TO Mx
2163 W(K)=W(K)-Slope2*(R(K)-R(1))-Bb
2164 NEXT K
2165 CALL Graph2(C$,RS,R(*),W(*),Mx,Area)
2170 IF N$(1,1)="Y" THEN SUBEXIT
2175 CALL Graph(C$,IS,Z(*),T(*),N)
2180 SUBEXIT
2185 SUBEND
2190 SUB Transform(F$,G$,X(*),Y(*),N)

```

NWC TP 6337

```

2200 OPTION BASE 1 ' Linear baseline correction for 2 variable plots.
2210 DIM Ynew(N)
2212 INPUT "ENTER POINT NUMBER TO BEGIN BASELINE CORRECTION",Qpt
2215 DIM H$(80)
2220 S=(Y(Qpt)+Y(Qpt+1)+Y(Qpt+2))/3 ' Average three points
2230 V=(Y(N)+Y(N-1)+Y(N-2))/3 ' for slope calculation.
2240 Slope=(V-S)/(X(N)-X(1))
2250 FOR I=1 TO N
2260 Ynew(I)=Y(I)-Slope*(X(I)-X(1))-S
2270 NEXT I
2280 H$=G$: "Linear baseline correction"
2290 CALL Graph2(F$,H$,X(*),Ynew(*),N,Area)
2300 INPUT "DO YOU WANT THE PLOT EXPANDED?",N$
2335 IF H$(1,1)="Y" THEN CALL Expand(F$,H$,X(*),Ynew(*))
2340 SUBEXIT
2350 SUBEND
2400 DEF FNMaxAbs(A(*),N)
2410 Ma:=ABS(A(1))
2420 FOR I=2 TO N
2430 IF ABS(A(I))>Ma THEN Ma:=ABS(A(I))
2440 NEXT I
2441 RETURN Ma
2442 FEND
2450 DEF FNMin(B(*),N)
2460 Mi:=B(1)
2470 FOR I=2 TO N
2480 IF B(I)<Mi THEN Mi:=B(I)
2490 NEXT I
2500 RETURN Mi
2510 FEND
2600 SUB Graph2(A$,B$,X(*),Y(*),N,Integral)
2601 OPTION BASE 1
2605 PRINTER IS 0
2610 INPUT "ENTER PLOTTER CODE: 1=CRT; 2=9872A",Code
2615 IF Code=2 THEN GOTO 2670
2620 PRINT PAGE 'Subroutine for plotting data from an X-Y plotter
2630 PRINT LIN(3) 'using the internal thermal printer.
2640 PRINT A$
2650 PRINT B$
2660 PRINT LIN(3)
2670 DIM C$(80),D$(80),Ux(1000),Vy(1000)
2671 REDIM Ux(N),Vy(N)
2675 INPUT "ENTER X AXIS LABEL IF OTHER THAN TEMPERATURE (K)",C$
2676 IF C$="" THEN C$="TEMPERATURE (K)"
2677 INPUT "ENTER Y AXIS LABEL IF DESIRED",D$
2678 IF D$="" THEN D$="Relative Millivolts"
2680 F=FNMaxAbs(Y(*),N)
2690 B=X(N)-X(1)
2700 A=F
2710 INPUT "DO YOU WANT A MAXIMUM Y USED FOR THE GRAPH INSTEAD OF THE CALCULATED MAXIMUM",J$
2720 IF J$(1,1)="Y" THEN INPUT "ENTER Ymax",H
2740 IF J$(1,1)="Y" THEN A=H
2750 IF Code=1 THEN PLOTTER IS "GRAPHICS"
2755 IF Code=2 THEN PLOTTER IS 7,5,"9872A"
2760 GRAPHICS
2770 LOCATE 15,90,15,75
2780 SCALE X(1),X(N),-A,A
2790 AXES B/4,A/10,X(1),0
2800 MOVE X(1),Y(1)
2810 FOR I=1 TO N
2820 DRAW X(I),Y(I)
2830 NEXT I
2840 PENUP
2880 LOG 6
2890 FOR I=X(1) TO X(N) STEP B 4

```

NWC TP 6337

```

2900 MOVE I,-A/100
2910 LABEL USING 2930:I
2920 NEXT I
2930 IMAGE DDD
2940 LOG 8
2950 FOR I=-A TO A STEP A/10
2960 MOVE -B/100+X(I),I
2970 LABEL USING 2990:I
2980 NEXT I
2990 IMAGE MDD,D
3000 LOG 6
3010 MOVE B/2+X(I),-A/15
3020 LABEL TRIM$(C$)
3030 LDIR PI/2
3040 LOG 4
3050 MOVE -B/10+X(I),A/2
3060 LABEL TRIM$(D$)
3062 LINPUT "DO YOU WANT TO INTEGRATE PART OF THE CURVE",C$
3065 IF C$(1,1)="/" THEN GOTO 3085
3066 INPUT "ENTER BEGINNING AND ENDING DATA POINT NUMBERS FROM NEW SET IF EXPLAN
DED",Start,Finish
3067 REDIM Ux(Finish-Start+1),Vx(Finish-Start+1)
3068 J=1
3069 FOR I=Start TO Finish
3070 Ux(J)=X(I)
3071 Vx(J)=Y(I)
3072 MOVE X(I),Y(I)
3073 DRAW X(I),0
3074 PENUP
3075 J=J+1
3076 NEXT I
3077 Epsilon=1E-6
3078 CALL Intun(J-1,Epsilon,Ux(1),Vx(1),Integral)
3079 PRINT USING 3080:Ux(1),Ux(J-1),Integral
3080 IMAGE "THE AREA REPRESENTED BY THE SHADED REGION BETWEEN DOMAIN VALUES ",
DDD.DD," AND ",DDD.DD," IS ",MD.DDDE
3081 PRINT LIN(2)
3085 LINPUT "DO YOU WANT GRAPHICS PRINTOUT VIA THE THERMAL PRINTER",L$
3090 IF (L$(1,1)="Y") AND (Code=1) THEN DUMP GRAPHICS
3095 EXIT GRAPHICS
3100 GCLER
3110 SUBEXIT
3120 SUBEND
3130 SUB Printz(A$,B$,X$,Y$,N)
3140 OPTION BASE 1
3150 PRINT PAGE
3160 PRINT "DATA POINT RENUMBERING FOR BASELINE CORRECTED , EXPANDED PLOT"
3170 PRINT A$
3180 PRINT B$
3190 PRINT
3200 PRINT "DOMAIN VALUE      RANGE VALUE      NEW DATA POINT NUMBER"
3210 PRINT
3220 FOR I=1 TO N
3230 PRINT USING 3250:X(I),Y(I),I
3240 NEXT I
3250 IMAGE DDD.DDXXXXXXXXXX,DD.DDXXXXXXXXXX,DDD
3260 PRINT LIN(6)
3270 SUBEXIT
3280 SUBEND
3400 SUB Intun(N,Eps,X(*),Y(*),Int) ! Cubic Spline Integrator
3430 Baddta=(N<3) OR (X(1)=X(N)) OR (Eps=0)
3490 IF Baddta=0 THEN 3600
3520 PRINT LIN(2),"EPROR IN SUBPROGRAM Intun."
3530 PRINT USING 3540:N,Eps,X(1),X(N)
3540 IMAGE "N=",DDD,5X,"Eps=",MD,6DE,5,"X(1)=",MD,6DE,5,"X(N)=",MD,6DE,5
3550 PAUSE

```

NWC TP 6337

```

3500 GOTO 3480
3600 OPTION BASE 1
3610 DIM B(2:N-1),S(0),G(2:N-1)
3620 FOR I=2 TO N-1
3630   H=X(I+1)-X(I-1)
3640   X=X(I)-X(I-1)
3650   B(I)=.5*X/H
3660   T=(Y(I+1)-Y(I))*X(I+1)-X(I)-(Y(I)-Y(I-1))*X(I)
3670   S(I)=2*T
3680   G(I)=3+T
3690 NEXT I
3700 S(0)=S(N)=0
3720 W=5-4*SQR(3)
3740 U=0
3760 FOR I=2 TO N-1
3770   T=W*(S(I)-B(I)*S(I-1)-(1.5-B(I))*S(I+1)+G(I))
3780   H=ABS(T)
3800   IF H>U THEN U=H
3820   S(I)=S(I)+T
3830 NEXT I
3850 IF U=EPS THEN 3740
3860 Int=0
3920 FOR I=1 TO N-1
3930   H=X(I+1)-X(I)
3940   Int=Int+.5*H*(Y(I)+Y(I+1))-1.24*H*(S(I)+S(I+1))
3950 NEXT I
3960 SUBEND
4000 SUB Kinetics(R$,B$,X(0),Y(0),N,Area) (Nonisothermal DSC Kinetics)
4010 OPTION BASE 1
4015 ON ERROR GOSUB Trap
4020 DIM Logd(N),Fract(0:N),Temp(N),A(4:N),D(N),Dfract(5:N),C(N)
4030 CALL Printz(R$,B$,X(0),Y(0),N)
4040 PRINT PAGE
4050 PRINT LINK(2)
4060 PRINT A$
4070 PRINT B$
4080 PRINT "Kinetics determination"
4090 PRINT
4100 PRINT "Temp(K)   1/T   Area Fract.   LN(ordinate)   Relative P
ate Pres"
4110 PRINT
4130 MAT Temp=(1)/X : Calculate 1/T(K)
4132 FOR I=1 TO N : INSURE NON NEGATIVE ARGUMENT
4134 IF Y(I)<1 THEN GOTO 4140
4136 Logd(I)=LOG(Y(I))
4138 GOTO 4145
4140 Logd(I)=0
4145 NEXT I
4180 FOR I=1 TO 3 : SET UP ARRAYS
4190 C(I)=X(I)
4200 D(I)=Y(I)
4210 NEXT I
4220 Epsilon=1E-6
4230 FOR I=4 TO N : CALCULATE PARTIAL AREAS
4235 REDIM C(I),D(I)
4240 C(I)=X(I)
4250 D(I)=Y(I)
4270 CALL Intun(I,Epsilon,C(0),D(0),Partial_area)
4280 Fract(I)=Partial_area/Area
4285 DISP Partial_area,Fract(I),I
4290 NEXT I
4300 FOR I=5 TO N
4310 Dfract(I)=Fract(I)-Fract(I-1)*(C(I)-C(I-1))
4320 NEXT I
4330 FOR I=5 TO N
4340 PRINT USING 4360;(I,Temp(I),Fract(I),Logd(I),Dfract(I),I

```

NWC TP 6337

```

4350 NEXT I
4355 PRINT
4360 IMAGE DDDXXXXX,D,DDEXXX,Z,DDDDXXXXXXXXXX,MD,DDDDXXXXXXXXXX,D,DDEXXX,DDD
4370 ! PLOT Dfract vs Fract AND CHOOSE LINEAR SECTION FOR KINETICS
4380 PRINT PAGE
4390 PRINT LIN(3)
4400 PRINT "Kinetics plot of dx/dt vs x. x = fraction decomposed"
4410 PRINT LIN(3)
4440 C=FNMaxy(Dfract(*),N)
4450 D=FNMiny(Dfract(*),N)
4460 E=.1
4470 F=(C-D)/10
4475 INPUT "ENTER PLOTTER CODE: 1=CRT; 2=9872A",Code
4480 IF Code=1 THEN PLOTTER IS "GRAPHICS"
4485 IF Code=2 THEN PLOTTER IS 7,5,"9872A"
4490 GRAPHICS
4500 LOCATE 15,90,15,75
4510 SCALE 0,1,D,C
4520 AXES .2,2*F,0,D
4530 FOR I=5 TO N
4540 MOVE Fract(I),Dfract(I)
4550 LABEL "+"
4560 NEXT I
4570 LOGO 6
4580 FOR I=0 TO 1 STEP .2
4590 MOVE I,D-.1*F
4600 LABEL USING "Z.DDD";I
4610 NEXT I
4620 LOGO 8
4630 FOR I=D+2*F TO C STEP 2*F
4640 MOVE -.01,I
4650 LABEL USING "D.DDE";I
4660 NEXT I
4670 LOGO 6
4680 MOVE .5,D-.8*F
4690 LABEL "Fraction Decomposed"
4700 LDIR PI/2
4710 MOVE .025,D+.5*F
4720 LABEL "Relative Rate"
4730 LDIR 0
4740 PAUSE
4750 IF Code=1 THEN DUMP GRAPHICS
4760 GCLEAR
4770 EXIT GRAPHICS
4780 PRINT PAGE
4790 PRINT LIN(2)
4800 PRINT "LINEAR REGRESSION ANALYSIS OF DATA"
4810 PRINT LIN(2)
4820 INPUT "ENTER BEGINNING AND ENDING POINTS FOR CALCULATION",Begin,End
4830 Pts=End-Begin+1
4840 REDIM T2(Pts),F2(Pts)
4850 IMAGE "Plot is between temperatures ",DDDD," and ",DDDD," Kelvin"
4860 FOR I=1 TO Pts
4861 T2(I)=Temp:Begin+I-1)
4862 F2(I)=Logd(Begin+I-1)
4865 NEXT I
4866 PRINT USING 4850;1/T2(1),1/T2(Pts)
4870 PRINT
4880 CALL Linear(T2(*),F2(*),Pts,A,B,C0,C1,C2,C3,C4,C5,C6,C7,C8,C9,V)
4890 PRINT USING 4900;-B*1.9872!Activation energy in cal./mole
4905 PRINT USING 4905;V
4900 IMAGE "Calculated activation energy (linear regression) is ",D,DDE," cal/mole"
4905 IMAGE "Mean slope variance is ",D,DDE," cal/mole"
4910 PRINT LIN(3)
4920 Cma=FNMax2(T2(*),1,Pts)

```

NWC TP 6337

```

4930 Xmin=FNMin2(T2(*),1,Pts)
4940 Ymax=FNMax2(F2(*),1,Pts)
4950 Ymin=FNMin2(F2(*),1,Pts)
4960 E=(Xmax-Xmin)/10
4970 F=(Ymax-Ymin)/10
4980 IF Code=1 THEN PLOTTER IS "GRAPHICS"
4985 IF Code=2 THEN PLOTTER IS 7,5,"9872A"
4990 GRAPHICS
5000 LOCATE 15,90,15,75
5010 SCALE Xmin,Xmax,Ymin,Ymax
5020 AXES 2+E,2+F,Xmin,Ymin
5030 FOR I=1 TO Pts
5040 MOVE T2(I),F2(I)
5050 LABEL "+"
5060 NEXT I
5070 FOR J=1 TO Pts
5080 F2(J)=B+T2(J)+A
5090 NEXT J
5095 MOVE T2(1),F2(1)
5100 FOR J=2 TO Pts
5110 DRAW T2(J),F2(J)
5120 NEXT J
5140 LOG 6
5150 FOR I=Xmin TO Xmax STEP 2+E
5160 MOVE I,Ymin-.1+F
5170 LABEL USING "D.DDD";I+1000
5180 NEXT I
5200 LOG 8
5210 FOR I=Ymin+2+F TO Ymax STEP 2+F
5220 MOVE Xmin-.04+E,I
5230 LABEL USING "MD.DDD";I
5240 NEXT I
5250 LOG 6
5260 MOVE Xmin+5+E,Ymin-F
5270 LABEL "1-T(K) x 1000"
5280 MOVE Xmin+.4+E,Ymin+5+F
5290 LDIP PI/2
5300 LABEL "In (displacement)"
5310 PAUSE
5320 IF Code=1 THEN DUMP GRAPHICS
5330 GCLEAR
5340 EXIT GRAPHICS
5344 INPUT "DO YOU WANT TO REPEAT THE CALCULATION?",Repeat$
5345 IF Repeat$(1,1)="Y" THEN GOTO 4780
5350 SUBEXIT
5351 Trap: DISP ERRMS
5352 PAUSE
5355 GOTO 4040
5360 DEF FNMaxy(X(*),N)
5370 Maxy=X(5)
5380 FOR I=5 TO N
5390 IF X(I)>Maxy THEN Maxy=X(I)
5400 NEXT I
5410 RETURN Maxy
5420 FNEND
5430 DEF FNMiny(X(*),N)
5440 Miny=X(5)
5450 FOR I=5 TO N
5460 IF X(I)<Miny THEN Miny=X(I)
5470 NEXT I
5480 RETURN Miny
5490 FNEND
5500 SUBEND
5700 SUB Linear(X(*),Y(*),N,A,B,Regss,Reass,Totalss,Regms,Reams,F,Dfreg,Dfres,Df
tot,Abort,Variance)

```


NWC TP 6337

```

5710 ! *** MODEL: Y=A+B*X ***
5720 ON ERROR GOTO Bomb
5730 Abort=0
5740 Y1=X1-Z=X2=Y2=0
5750 FOR I=1 TO N
5760   X1=X1+X(I)           ! Sum of X's
5770   Y1=Y1+Y(I)           ! Sum of Y's
5780   X2=X2+X(I)*X(I)      ! Sum of X squares
5790   Y2=Y2+Y(I)*Y(I)      ! Sum of Y squares
5800   Z=Z+X(I)*Y(I)        ! Sum of XY's
5810 NEXT I
5820 X1=X1/N               ! Mean X
5830 Y1=Y1/N               ! Mean Y
5840 B=(Z-N*X1*Y1)/(X2-N*X1*X1)
5850 A=Y1-B*X1
5860 Totalss=Y2-N*Y1*Y1    ! Total Sum of Squares
5870 Regss=(Z-N*X1*Y1)^2/(X2-N*X1*X1) ! Regression Sum of Squares
5880 Resss=Totalss-Regss    ! Residual Sum of Squares
5890 Regms=Regss            ! Regression Mean Squares
5900 Resms=Resss/(N-2)     ! Residual Mean Squares
5905 Variance=SQR(Resms/(X2-N*X1*X1)) ! Slope Variance
5910 OFF ERROR
5920 DEFAULT ON
5930 F=Regms/Resms         ! F Ratio
5940 DEFAULT OFF
5950 Dfreg=1                ! Degrees of Freedom
5960 Dfres=N-2
5970 Dftot=Dfreg+Dfres
5980 SUBEXIT
5990 Bomb: Abort=1
6000 SUBEND
6010 DEF FNMax2(X(*),A,B)
6020   Max2=X(A)
6030   FOR I=A+1 TO B
6040     IF X(I)>Max2 THEN Max2=X(I)
6050   NEXT I
6060   RETURN Max2
6070 FNEND
6080 DEF FNMin2(X(*),A,B)
6090   Min2=X(A)
6100   FOR I=A+1 TO B
6110     IF X(I)<Min2 THEN Min2=X(I)
6120   NEXT I
6130   RETURN Min2
6140 FNEND
6200 SUB Polynomial(X(*),Y(*),N,Degree,Coeffs(*),Regss,Resss,Totalss,Regms,Resms
,F,Dfreg,Dfres,Dftot,Abort)
6210 ON ERROR GOTO Bomb
6220 Abort=0
6230 OPTION BASE 0
6240 DIM Matrix(Degree,Degree),Inv(Degree,Degree),B(Degree)
6250 REDIM Coeffs(Degree)
6260 IF Degree>N-2 THEN SUBEXIT ! Check for higher degree than possible
6270 Dfreg=Degree
6280 Dfres=N-1-Degree
6290 Dftot=Dfreg+Dfres
6300 FOR K=0 TO Degree      ! Set up system of equations
6310   FOR J=K TO Degree
6320     Matrix(K,J)=0
6330     FOR I=1 TO N
6340       Matrix(K,J)=Matrix(K,J)+FNG(K)*FNG(J)
6350     NEXT I
6360     Matrix(J,K)=Matrix(K,J)
6370   NEXT J
6380   B(K)=0
6390   FOR I=1 TO N

```

NWC TP 6337

```

6400     B(K)=B(K)+Y(I)*FNG(K)
6410     NEXT I
6420 NEXT K
6430 MAT Inv=INV(Matrx)      ! Solve the system of equations
6440 MAT Coeffs=Inv*B
6450 FOR I=1 TO N
6460   X1=X1+X(I)
6470   X2=X2+X(I)*X(I)
6480   Y1=Y1+Y(I)
6490   Y2=Y2+Y(I)*Y(I)
6500   Z=Z+X(I)*Y(I)
6510 NEXT I
6520 Y1=Y1/N
6530 X1=X1/N
6540 Totalss=Y2-N*Y1*Y1      ! Total Sum of Squares
6550 GOSUB Regss             ! Regression Sum of Squares
6560 Fesss=Totalss-Regss    ! Residual Sum of Squares
6570 Regss=Regss/Dfreg
6580 Resms=Resss/Dfres
6590 OFF ERROR
6600 DEFAULT ON
6610 F=Regms-Resms
6620 DEFAULT OFF
6630 SUBEXIT
6640 Regss=Regss*0
6650 FOR I=1 TO N
6660   J=0
6670   FOR L=0 TO Degree
6680     J=J+X(I)^L*Coeffs(L)
6690   NEXT L
6700   Regss=Regss+(J-Y1)^2
6710 NEXT I
6720 RETURN
6730 SUBEXIT
6740 DEF FNG(M)=X(I)^M
6750 Bomb: Abort=1
6760 SUBEND
6770 SUB Quad(X(*),Y(*),Z)
6780 PRINT LIN(2)
6785 OPTION BASE 1
6790 DIM A(3)
6800 CALL Polynomial(X(*),Y(*),Z,2,A(*),C0,C1,C2,C3,C4,C5,C6,C7,C8,C9)
6810 PRINT USING 6820;-A(2)+1.9872,A(1)+1.9872
6811 PRINT A(3)
6820 IMAGE "THE QUADRATIC COEFFICIENTS ARE ",MD.DDE," and ",MD.DDE
6830 PRINT
6840 SUBEXIT
6850 SUBEND

```

NWC TP 6337

NOMENCLATURE

A	Total Area
a	Partial Area
D(t)	Ordinate Deflection
E*	Activation Energy
f(x)	Algebraic Function of Fraction Reaction
G	Gibbs Free Energy
H	Enthalpy
K(T)	Equilibrium Constant
k(T)	Rate Constant
R	Universal Gas Constant
T	Temperature
T _m	Temperature of Maximum Exotherm
t	Time
X	Fraction Reacted
Z	Preexponential Factor in Arrhenius Equation
φ	Heating Rate

INITIAL DISTRIBUTION

- 4 Naval Air Systems Command
 - AIR-00D4 (2)
 - AIR-03P (1)
 - AIR-350 (1)
- 4 Chief of Naval Operations (OP-03)
- 8 Chief of Naval Material
 - NSP-00 (1)
 - NSP-27 (1)
 - NSP-270 (1)
 - NSP-273 (3)
 - NSP-274 (1)
 - PM-23 (1)
- 7 Naval Sea Systems Command
 - SEA-03 (1)
 - SEA-04H3, A. Daugherty (1)
 - SEA-64E, R. L. Beauregard (1)
 - SEA-99E (1)
 - SEA-9913 (1)
 - SEA-99612 (2)
- 1 Chief of Naval Research, Arlington
- 1 Commander in Chief, U.S. Pacific Fleet (Code 325)
- 1 Commander, Third Fleet, Pearl Harbor
- 1 Commander, Seventh Fleet, San Francisco
- 1 Fleet Anti-Air Warfare Training Center, San Diego (Guided Missile Section)
- 1 Naval Air Engineering Center, Lakehurst
- 1 Naval Air Test Center, Patuxent River (CT-252, Building 405 (Aeronautical Publication Library))
- 1 Naval Avionics Center, Indianapolis (Technical Library)
- 1 Naval Ocean Systems Center, San Diego (Code 133)
- 1 Naval Ordnance Station, Indian Head
- 1 Naval School Explosive Ordnance Disposal, Indian Head
- 3 Naval Ship Weapon Systems Engineering Station, Port Hueneme
 - Code 5711, Repository (2)
 - Code 5712 (1)
- 1 Naval War College, Newport
- 1 Naval Weapons Evaluation Facility, Kirtland Air Force Base (Code 401)
- 1 Operational Test and Evaluation Force, Atlantic
- 1 Operational Test and Evaluation Force, Pacific
- 1 Pacific Missile Test Center, Point Mugu (Code 2145, P. McQuaide)
- 1 Naval Plant Branch Representative, Magna (Hercules, Inc.)
- 1 Naval Plant Representative Office, Sunnyvale (Lockheed Missiles and Space Company)
- 1 Army Armament Research and Development Command, Dover (DRDAR-LCE, H. J. Matsuguma)
- 1 Army Ballistic Research Laboratory, Aberdeen Proving Ground (DRDAR-TSB-S (STINFO))

- 1 Tactical Air Command, Langley Air Force Base (TAC-40000)
- 1 Air University Library, Maxwell Air Force Base
- 3 Air Force Armament Division, Eglin Air Force Base
- HLO (2)
- Dr. L. O. Ekins (1)
- 1 Edwards Air Force Base (D. Hart)
- 1 Air Force Plant Representative Office, Sacramento (Aircraft Component Corporation)
- 12 Defense Technical Information Center
- 2 Lockheed Missiles and Space Company, Sunnyvale, CA
- J. Hainhart (1)
- Technical Reports Library (1)
- 1 Los Alamos National Laboratory, Los Alamos, NM (Code W-2, Dr. R. M. Rogers)
- 1 The Bunker-Ramo Corporation, Westlake Village, CA (Technical Information Services)
- 110 Chemical Propulsion Mailing List dated December 1961, including categories 1, 2, 3, 4, 5

FILME
10-8