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Data Acquisition and Reduction Program for Thermogravimetry

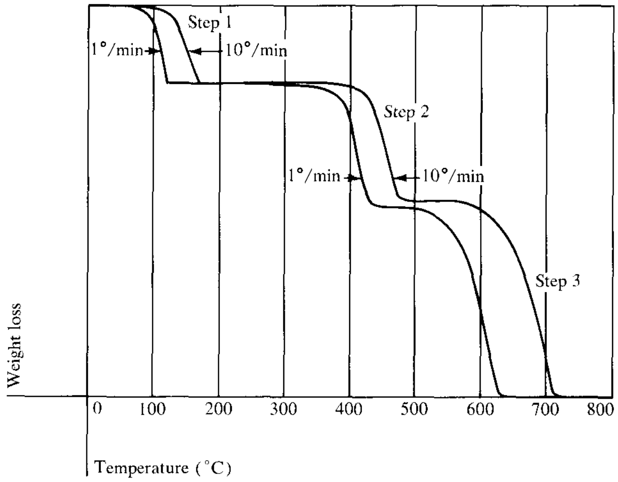
Abstract: An on-line data acquisition system for thermogravimetry using the IBM S/7 computer followed by data reduction on a 360/195 is described by means of flow charts. The system is designed so that no knowledge of programming is required to acquire, display and manipulate data on an interactive graphics terminal. The program not only extracts weight loss data, but also computes the energies of activation, E, for any selected weight loss interval by two methods, i.e., tabular integral and derivative. The system is demonstrated by a study of the activation energies for loss of water, loss of carbon monoxide, and loss of carbon dioxide during the thermal decomposition of calcium oxalate monohydrate. The results are in good agreement with the best literature values. The derivative method was found to give more consistent results than the tabular integral approach because of problems encountered in the precise measurement of temperature in the thermobalance.

Introduction

Thermogravimetry (TGA) is an established technique for following weight loss or gain of a sample as a function of temperature or time at a fixed temperature. This technique has been widely applied to the study of both organic and inorganic decompositions, oxidations and other reactions [1]. There are essentially five types of reaction which TGA will follow (see Table 1). All involve some loss or gain in weight. In some cases it is possible to follow processes which have no weight loss or gain when the no-weight loss/gain reaction produces a solid product that decomposes at a different temperature or at a different rate from the reactants that produced the new solid [2]. Also, the no-weight loss/gain process should have a much different rate from the weight loss/gain process.

The programmed temperature mode of TGA operation (weight loss or gain vs temperature) produces curves similar to those in Fig. 1. In theory, such a curve contains all of the information necessary to determine the energy of activation E, kinetic order n, and frequency factor Z, from the well-known Arrhenius equation. Approaches to a solution of the weight loss function have been developed by a number of workers in the past 25 years [1, 3–6]. These are of two essential types, derivative and tabular integral. The derivative solutions usually require, in addition to the integral weight loss vs time curve, the first derivative of that curve (DTG) or rate of weight loss as a function of temperature/time. Tabular methods attempt to fit the integral curve to some integral function whose solution is known [4, 7]. Recently, a tabular integral approach using two TGA curves taken at two heating rates has been published [4]. This solution appears to be general and involves a minimum of assumptions. Single point methods for determining E will not be considered since most of the

Figure 1 Typical TGA scan on two samples of calcium oxalate monohydrate in flowing nitrogen taken from graphics display.



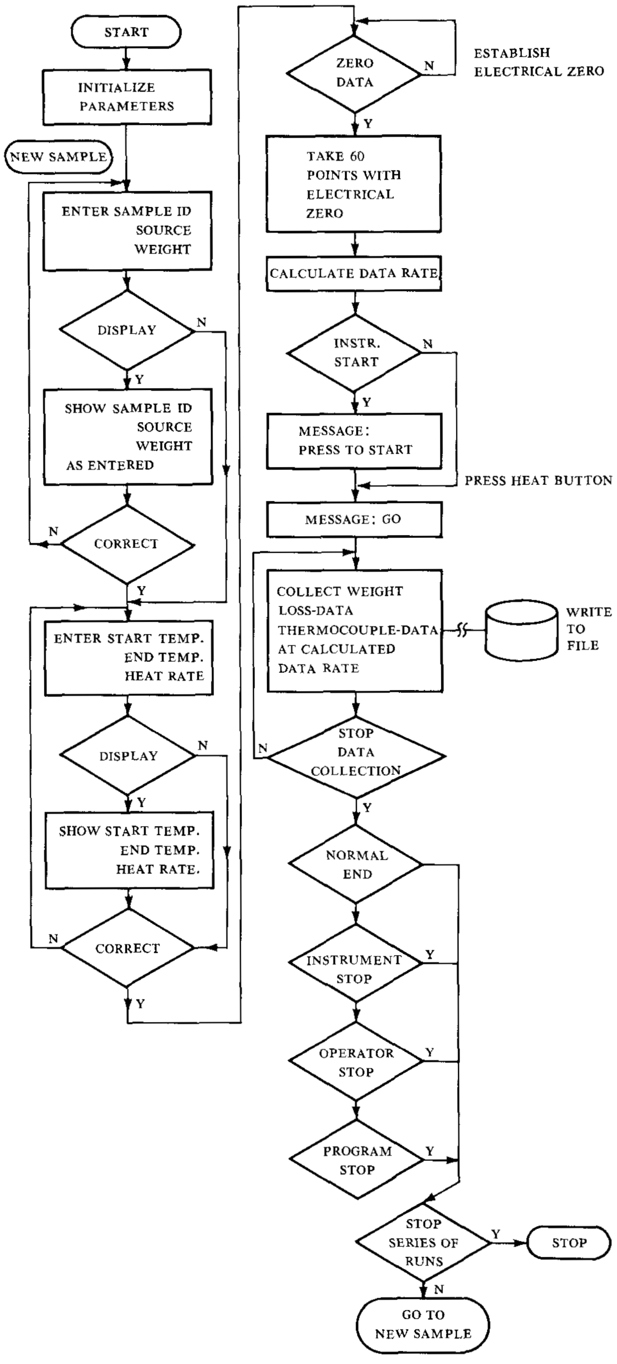


Figure 2 Flow diagram of TGA—data collection.

materials to which TGA is usually applied will proceed by at least two values of E from onset to conclusion of the weight loss. For reference to single point methods see [5].

In any of the methods suggested to date, various assumptions are made concerning the experimental parameters, kinetic equations, and mathematical validity of the fitting process. Therefore, the values of E, n and A are highly dependent upon how closely the system agrees with these assumptions. A partial list of potential errors is given in Table 2. A study of that table indicates that there are many places where the various methods can be in serious error. The most important among these, when attempting to design an experiment to test the methods of data reduction, are those errors which are due to instrumental factors. Primary among those is the measurement of effective sample temperature. In most cases the TGA temperature is measured external to the sample at some point in the furnace. In some equipment (Mettler and Rigaku, for example) the sample temperature is measured by a thermocouple in contact with the sample. The important temperature is the one that controls the weight loss process. This may be the surface temperature (oxidations and reductions) or the internal temperature (decompositions). The location of the reaction zone will change as the process continues.

Table 1 Processes which may be studied by conventional TGA. TGA.

*Reaction type**	*Examples*
1. $S_1 \rightarrow G_1\uparrow$	Anaerobic decomposition of polyethylene, boiling or evaporation of a liquid or solid, G_1 can be several gases.
2. $S_1 + G_1 \rightarrow G_2\uparrow$	Aerobic pyrolysis of many polymers.
3. $S_1 + G_1 \rightarrow S_2 + G_2\uparrow$	Char formation in polymers, conversion of oxides.
4. $S_1 + G_1 \rightarrow S_2$	Oxidation processes.
5. $S_1 \rightarrow S_2 + G_2\uparrow$	Dehydrations, calcinations.

*S—a solid or nonvolatile liquid. G—an incondensable gas at the operating temperature. Subscripts differentiate solid and gas types.

The above problems aside, TGA is a method widely employed throughout the world; it deserves a detailed study. An inherent stumbling block to such a study in the past has been the extremely tedious nature of the data reduction process from analog curves. Numerous ruler measurements, normalizations and table citations are required for even the simplest method for deriving the apparent activation energy. On-line data acquisition and data reduction offer a solution to the problem of TGA data management and manipulation.

The authors recently described a program for connecting the IBM S/7-360/195 system to an E. I. du Pont 990 thermoanalyzer for quantitative differential thermal analysis (QDTA) [8]. This system features interactive manipulation of QDTA data on a Tektronix display and makes minimum demands on the user's normal operating procedures. The system has now been extended to cover TGA data collection and manipulation by the integral [4] and the derivative [9] methods.

Table 2 A partial list of errors in thermogravimetry.

I. Instrumental
   A. Inaccurate temperature measurement
   B. Drift in balance mechanism
   C. Nonlinear effective heating rate
   D. Loss of sample by nonvolatile mechanisms (spattering)
   E. Condensation of decomposition products on the balance mechanism

II. Chemical
   A. Quasi-equilibrium is not attained.
   B. Reaction *path* is heating rate sensitive.
   C. Rate of weight loss is not determined by chemical decomposition.
   D. Arrhenius equation does not apply to the process.

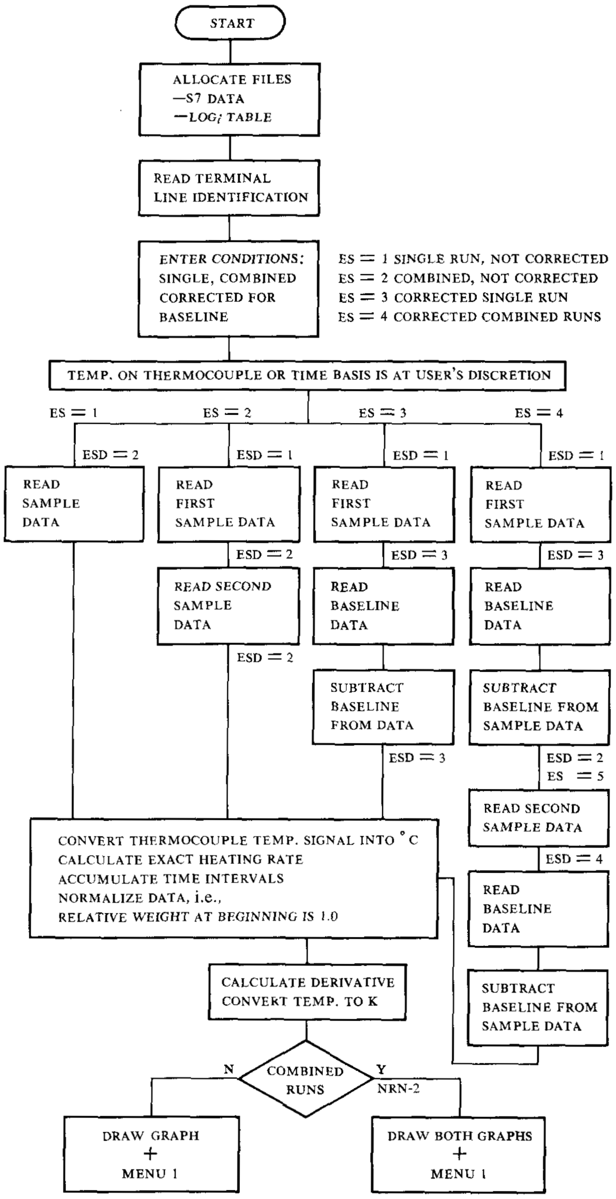
Data acquisition

An IBM S/7 Computer is used for weight data collection by following many of the same principles employed previously for QDTA data collection from the E. I. du Pont 990 [8]. The same interface and hardware are used. Just as QDTA must have the isothermal baseline established prior to temperature programming, the thermobalance must have the electrical zero (zero weight) signal established at the beginning of a run. This is done by depressing the TGA zero button while data are being taken before the beginning of the program.

The TGA sample temperature, unlike that of the QDTA, does not experience a completely linear temperature change with respect to time. Thus, in addition to the weight signal, the sample thermocouple signal must be taken and written into the file. The nonlinearity of the temperature change is due to the thermal magnitude of endothermal or exothermal weight loss or gain processes. These are much larger than normal heats of fusion, solid-solid phase transitions, and glass transitions usually studied by QDTA.

Data reduction

The primary commands for data reduction are entered by means of an interactive display device (Tektronix 4013 Scope) supported by an IBM 360/195. The data from the S/7 are transmitted to the 360/195 on command. The program that reads the data file allows it to be combined with that of another run (at a different heating rate) or with an empty pan run. This combinatory function is required both to calculate an activation energy by the method of Gyulai and Greenhow [4] and to correct any sample run for base or zero line drift. This drift is caused by the inevitable change in balance atmosphere density as the temperature increases. Prior to display, all weight loss data are normalized on the basis of the sample weight and the total measured weight loss from zero to 100 percent. The program also calculates the first derivative of the integral of weight loss vs time. The first display function draws either one or two normalized weight loss curves as a func-



THE MENU ALLOWS THE FOLLOWING FUNCTIONS

LOGIC FUNCTIONS:	STOP RETURN (TO SELECT ANOTHER RUN)
DRAWING FUNCTIONS GENERAL:	REGION DRAW ALL REDR. SAME DRAW REST
SPECIFIC IN TIME BASE:	TIME BASE TEMP BASE DERIVATIVE (DY-DT)
CALCULATING FUNCTIONS:	WEIGHT LOSS KINETICS
COMBINED:	TWO-INT. METHOD

Figure 3 Flow diagram of TGA—990 data reduction.

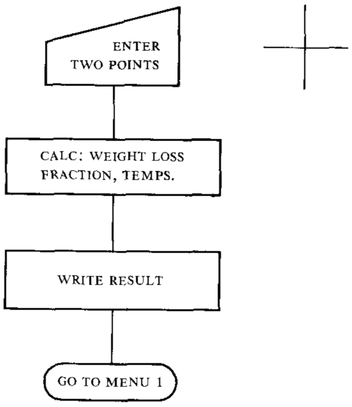


Figure 4 Flow chart for the function WEIGHTLOSS.

Table 3 Drawing and calculation functions.

Drawing function	*Purpose*
REGION	Permits the selection of any section of a TGA chart for display on the basis of temperature interval.
DRAWALL	Displays all of the TGA chart.
REDRAW-SAME	Redisplays TGA chart less added numbers or lines from calculation.
DRAWREST	Draws the higher temperature portion of the TGA chart not shown when REGION was used.
TIME-BASE	Displays weight loss as a function of time.
TEMP-BASE	Displays weight loss as a function of temperature.
TEMP-TIME	Displays temperature as a function of time.
DY-DT	Displays the derivative of weight loss as a function time (rate of weight loss) vs time superimposed on the integral curve.

Calculation function	*Purpose*
WEIGHT LOSS	Calculates between selected limits: weight loss in mg, weight loss fraction of the total weight, temperatures of the selected limits.
KINETICS	Calculates the energy of activation E between selected limits by the derivative method [9]. E is then displayed as a function of temperature.
2-INTM	Calculates E between selected limits using the weight loss as a function of temperature taken at two heating rates and the tabular integral method [4].
E/REGION	Displays numerical E values for selected sections on the $\ln\left(\frac{-Rate}{Wt_{obs}-X}\right)$ vs $1/T$ graph.

tion of temperature plus a menu of functions. Logic and drawing functions are equivalent to those of the previously described QDTA programs [8].

- *Calculation functions*

Three calculation functions are described.

1. *Weight loss* This function calculates the absolute and relative weight loss that occurs between two points selected by the operator on the TGA curve, as first displayed on the graphics terminal.
2. *Kinetics* The calculation of activation energy by the first derivative method uses Eq. (1) [9]:

$$\ln \frac{-Rate}{(Wt_{obs} - X)} = -\frac{E}{RT} + \ln (Z/a), \qquad (1)$$

   where *Rate* is the rate of weight change or slope of the integral curve at any point; $(Wt_{obs} - X)$ is the weight observed at time t minus the weight of any residue remaining after the reaction; E is the activation energy in Kcal/mol; R is the gas constant; T is the temperature at time t in K; Z is the preexponential function from the familiar Arrhenius equation; and a is the heating rate in °C/min. A plot of $\ln[-Rate/(Wt_{obs} - X)]$ vs $1/T$ gives a line or lines whose slopes are $-E/R$ for that temperature region. Several linear regions are usually found because of the nature of the weight loss process. By selecting E/REGION from the function menu the operator may choose relevant linear segments from the above plot as shown on the graphics display. Results written at this point to the screen are activation energy, temperature boundaries and fraction of weight loss remaining.
3. 2-INTM This function calculates the value of E using the double heating rate method [4]; it is available only when two runs have been combined. The section of weight loss of interest is chosen from both curves with the cross hairs, and the program normalizes these sections to a common base. These normalized curves are divided into 100 fractions. At each fraction, the temperature T is calculated on each of the two curves. Also, the log of the quotient of the slower heating rate divided by the faster heating rate is calculated and stored as B_1.

The program uses a file that contains a table of log i values for temperature (in steps of 20 degrees from 260 to 1200 K) as a function of values of E (from 20 to 90 Kcal/mol in steps of 10 Kcal/mol). The values of log i are derived from the tabular integration used by Gyulai and Greenhow [4]. The computer assumes two values for E, 40 and 70 Kcal/mol, and calculates the ratio log (i_1/i_2) at these two values, using the temperature at a certain conversion (100 steps as given above) at the slower heating rate to find log i_1 and the temperature at the *same* con-

Table 4 Selected values of the activation energy for the three-stage decomposition of calcium oxalate monohydrate.

Reference	*Energy of activation (Kcal/mol)* *Loss 1*	*Loss 2*	*Loss 3*
9	21.2	76.3	42.0
10	21.6 ± 15.0%	—	43.3 ± 15.0%
11	21.5	—	45.0
12	21.0 ± 20.0%	—	—
13	20.6	—	—
14	20.2	—	—
3	21.4	62.0	51.7
15	27.0	85.0	—
16	22.0	74.0	39.0
17	—	—	43.0
Average	21.8	71.9	45.1
Derivative method, temperature base	33.4 ± 12.0%	62.9 ± 2.0%	54.7 ± 1.3%
Derivative method, time base	32.0 ± 13.0%	64.0 ± 2.3%	53.4 ± 3.2%
Tabular integral method, temperature base	23.3 ± 7.0%	47.5 ± 10.0%	42.4 ± 15.0%
Tabular integral method, time base	21.4 ± 11.0%	54.8 ± 14.0%	51.2 ± 38.0%

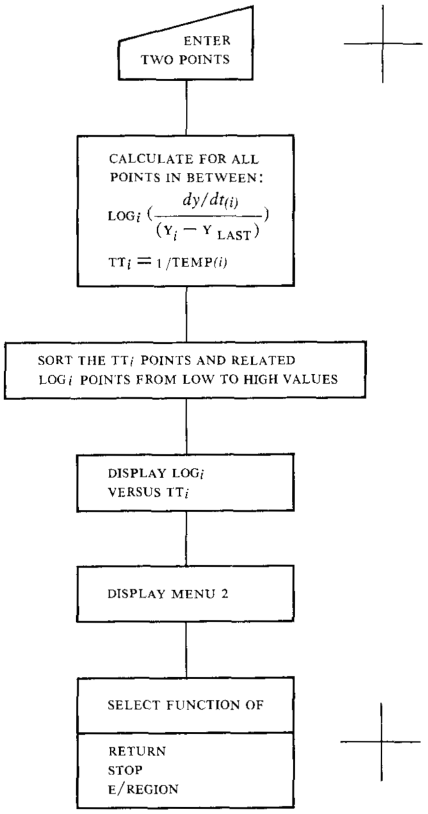
version at the faster heating rate to find log i_2. The values of log $(i_1/i_2)_{40}$ and log $(i_1/i_2)_{70}$ are compared to B_1. For this method, the correct value of E is found at the log (i_1/i_2) value, which equals B_1. From this first pass, an approximate value of E is determined by interpolation between 40 and 70 Kcal/mol, and the limits of E are narrowed around the approximate value. If the value of E is lower than 40 or higher than 70 Kcal/mol, this range is automatically shifted down or up in the next cycle of calculation. The whole process is repeated and a more accurate approximation of E is calculated. This is done for each percent of weight loss. These results are displayed on the graphics screen as a plot of E as a function of percent conversion. The menu function POINT permits the operator to request the exact value of E for any point on this graph by using the movable cross hairs.

Flow diagrams

- *Data collection*

As explained previously, instructions to the S/7 are entered by means of an ASK/7 terminal located near the TGA [8]. The guiding principle of the data collection program is one of interaction and flexibility with the human operator. It should be noted in the flow diagram, Fig. 2, that at several steps the program displays previously entered data for user verification. The program also has several exits to compensate for instrument and/or hardware

Figure 5 Flow chart for the function KINETICS.



FUNCTION RETURN WILL DISPLAY THE DRAWING FUNCTIONS OF MENU 1.

Table 5 Activation energy of oxalate decomposition as a function of systematic variables calculated by the tabular integral method [4].

Heating rate ratio	*Energy of activation* (Kcal/mol)					
	Temperature calculated from elapsed time			*Temperature based on thermocouple*		
	Loss 1	*Loss 2*	*Loss 3*	*Loss 1*	*Loss 2*	*Loss 3*
2.0 (1 : 0.5)	—	107.0*	75.0	—	47.7	45.0
(2 : 1)	35.5	63.1	57.9	33.2	52.3	48.6
(10 : 5)	22.6	73.9	79.5	23.5	59.7	59.9
2.5 (5 : 2)	14.8	41.0	28.0	18.3	36.9	29.1
5.0 (5 : 1)	18.0	47.4	36.4	22.2	42.4	35.6
(10 : 2)	17.9	50.2	38.8	20.2	45.8	37.9
10.0 (10 : 1)	19.5	53.0	43.1	22.4	46.8	40.8
Average	21.4	54.8	51.2	23.3	47.5	42.4
Range	14.8 to 35.5	41.0 to 73.9	28.0 to 79.5	18.3 to 33.2	36.9 to 59.7	29.1 to 59.9
	<20.7>	<32.9>	<51.9>	<14.9>	<22.8>	<30.8>
Range	17.9 to 22.6	47.4 to 63.1	36.4 to 75.0	20.2 to 23.5	42.4 to 52.3	35.6 to 48.6
>L, <H	<4.7>	<15.7>	<38.6>	<3.3>	<9.9>	<13.0>
**Best Value	21.4 ± 2.4	54.8 ± 7.9	51.2 ± 19.3	23.3 ± 1.7	47.5 ± 5.0	42.4 ± 6.5
	or ± 11.0%	or ± 14.0%	or ± 38.0%	or ± 7.0%	or ± 10.0%	or ± 15.0%

*Not included in the average.
**The average which includes the range distribution mean.

Table 6 Activation energy of oxalate decomposition as a function of systematic variables calculated by the derivative method [9].

Heating rate (°C/min)	*Energy of activation* (Kcal/mole)					
	Temperature calculated from elapsed time			*Temperature based on thermocouple*		
	Loss 1	*Loss 2*	*Loss 3*	*Loss 1*	*Loss 2*	*Loss 3*
0.5	48.9	58.0	55.8	50.0	51.8	55.7
1.0	33.1	62.0	51.6	34.5	65.6	53.0
2.0	29.6	65.5	55.4	30.8	67.3	55.2
5.0	24.9	70.5	52.0	26.5	65.3	55.4
10.0	23.6	64.2	52.3	25.3	64.3	54.0
Average	32.0	64.0	53.4	33.4	62.9	54.7
Range	23.6 to 48.9	58.0 to 70.5	51.6 to 55.8	25.3 to 50.0	51.8 to 67.3	53.0 to 55.7
	<25.3>	<12.5>	<4.2>	<24.7>	<15.5>	<2.7>
Range	24.9 to 33.1	62.0 to 65.0	52.0 to 55.4	26.5 to 34.5	62.9 to 65.6	54.0 to 55.4
>L, <H	<8.2>	<3.0>	<3.4>	<8.0>	<2.7>	<1.4>
**Best Value	32.0 ± 4.1	64.0 ± 1.5	53.4 ± 1.7	33.4 ± 4.0	62.9 ± 1.4	54.7 ± 0.7
	or ± 13.0%	or ± 2.3%	or ± 3.2%	or ± 12.0%	or ± 2.1%	or ± 1.3%

*Not included in the average.
**The average which includes the range distribution mean.

failure. This results in a "user friendly" program, the operation of which requires no real knowledge of computer programming.

- *Data reduction*

Data reduction is carried out on the 360/195 through the interactive graphics display and keyboard. The menu format permits the selection of a number of modes of operation. The hard copy feature of the display permits the storage of curves and results in a convenient and accessible format. The high degree of interaction and the several exit modes make this program very forgiving of operator error. Again, knowledge of computer programming is not required at any step. The general functions of the program are shown in flow diagram form in Fig. 3.

The TGA program, like the QDTA program, makes use of a menu of functions that may be selected with the cross hair cursor of the display screen. The designation and purpose of each function are given in Table 3. Flow charts of the programs for each calculation function are given in Figs. 4 through 7. The two methods for the extraction of E were chosen as being the most reliable and/or widely used of their type. In the case of the double heating rate method, the tabular integral values i were stored as tables and not as equations. In Fig. 7, the variable B_1 is

$$B_1 = \log\left(\frac{heat\ rate\ 1}{heat\ rate\ 2}\right) = \log\left(\frac{i_{11}}{i_{21}}\right), \tag{2}$$

and

$$i_{11} = \int_0^{T_{11}} e^{-E/RT}dt; \tag{3}$$

$$i_{21} = \int_0^{T_{21}} e^{-E/RT}dt. \tag{4}$$

Results

The test of a data acquisition and reduction program is its ability to handle a well-known sample and produce reliable results. As we have seen in an earlier section, TGA can suffer from many sources of error. The test of this set of programs, after reliable operation has been obtained, is a test of the TGA method for the extraction of activation energies from decomposition weight loss data.

Calcium oxalate has been studied by many authors [10–18] by means of the thermogravimetric approach (see Table 4). Although there are no certified standards for TGA, this material has become the usual subject for testing thermobalance performance. The reactions studied are

$CaC_2O_4 \cdot H_2O \xrightarrow[\Delta]{} CaC_2O_4 + H_2O \uparrow$ weight loss 1

$CaC_2O_4 \xrightarrow[\Delta]{} CaCO_3 + CO \uparrow$ weight loss 2

$CaCO_3 \xrightarrow[\Delta]{} CaO + CO_2 \uparrow$ weight loss 3

The weight losses 1, 2, and 3 refer to those steps marked in Fig. 1. In the past, calculation of E from thermogravimetric curves has been a tedious and complicated process. There are many opportunities for error, and the ultimate accuracy can be no better than the ability of the operator to measure curve heights with a ruler. Until recently, the first derivative of the integral weight loss curve was obtainable only by mechanical means, i.e., mirror and ruler. The E. I. du Pont 990 gives an analog derivative also, but finding corresponding points is tedious. Such conditions and difficulties are not conducive to the application of most methods of calculation for E on a general or repeat basis. Therefore, the computer TGA system gives a unique opportunity to study TGA processes free from computational aberration.

TGA curves were acquired on 5-mg samples of Baker analytical grade calcium-oxalate monohydrate at heating rates of 0.5, 1, 2, 5 and 10°C/min. The E. I. du Pont 990 module and 951 TGA was operated as suggested by the manufacturer by using a dry nitrogen purge at 20 ml/min. The TGA data were compared by extracting the activation energy of losses 1, 2 and 3 by a factorial combination. That is, for the tabular integral or dual heating rate methods, E was calculated by using all possible heating rate combinations and both the time and the temperature base (Table 5). The derivative method was also applied to the same data using the time and the temperature base (Table 6). Although both methods can calculate E at any desired conversion, E was determined only during the main portion of the reaction for comparison to literature results. In general, with solid decompositions the values of E at the beginning of the weight loss are low because of the decomposition of very small particles. The values of E are usually low at the end of the reaction because of a deficiency of product gases near the individual particles for back reaction. In other studies where high temperature liquids (polymer melts) were used, low initial values of E were obtained as a result of boil-off of oligomers [9]. With char formation, the value of E becomes very large (> 100 Kcal/mol), which may or may not be valid.

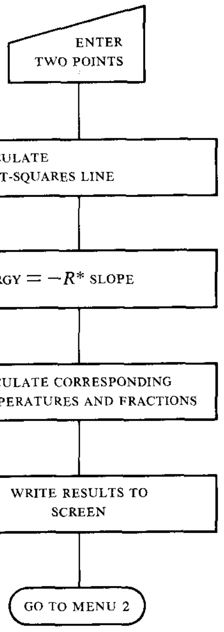
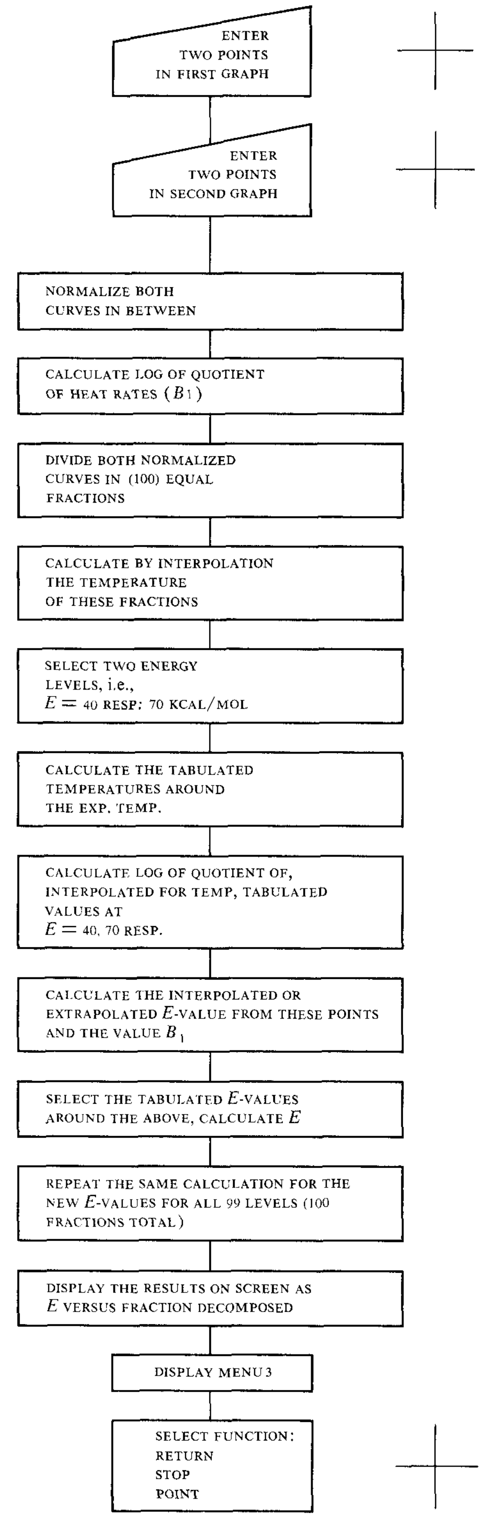


Figure 6 Flow chart for the function E/REGION.

Under normal circumstances a ten-inch deflection is equivalent to a load of 5 mg. With a ruler and hand magnifying glass the analog chart can be read to 0.01 in. (0.25 mm—about the width of the recorder penline). This gives a weighing accuracy of 0.1 percent or one part in 1000. The S/7 analog to digital converter plus the line noise from various sources gives a point scatter under isothermal conditions equivalent to 10^{-7} g between maxima and minima and an average error band of $\approx 5 \times 10^{-8}$ g. Thus, the digital data system has an in-group precision of 0.001 percent or one part in 100 000. Unfortunately, the balance mechanism, quartz beam clip and nulling errors reduce the absolute accuracy to one part in 10 000. This latter value was obtained by repeatedly weighing a stand-



RETURN WILL DISPLAY THE DRAWING FUNCTIONS. POINT WILL WRITE TO THE SCREEN THE E-VALUE AND PERCENT DECOMPOSED AT THE POINT SELECTED ON THE SCREEN GRAPH.

Figure 7 Flow sheet for the function 2-INTM.

ard one-mg weight under static-free conditions in still air. However, since most TGA measurements are relative, the more optimistic "precision" of one part in 100 000 can be read as relative accuracy. Thus, the digital system has resulted in a ten- to 100-fold improvement in accuracy and precision over the analog procedure. A comparable improvement was noted in differential thermal analysis and differential scanning calorimeter data when recorded by a similar S/7 computer and program [8].

In general, the energies obtained at the slowest heating rate compare less consistently with the body of data collected at heating rates of 1°C/min or more. The trend with the derivative method is toward unusually high values of E. This could be due to forcing the reaction by unusual loss of products during the very long period of the 0.5°C/min experiment. The tabular integral method gave badly scattered values at 0.5° and 1°C/min rates. The integral method appears to suffer from errors in temperature measurement and shows broad scatter of E values when the time base is employed. Inspection of Fig. 1 in the region of sharp weight loss indicates how a small error in temperature measurement can cause a serious displacement of the indicated conversion. The derivative method appears to be relatively insensitive to errors in temperature measurement. The results for E appear to be independent of the assumed time or temperature base. High heating rates, above 5°C/min, increase the scatter of both methods of calculation, with the derivative method being the least sensitive. For the integral method, difference in heating rate between the two TGA runs compared appears to be as important as temperature measurement for heating rates of 1°/min or faster.

The results of this study on calcium oxalate monohydrate are compared in Table 4 with values taken from the extensive TGA literature. Although simple averaging gives E values of 21.8, 71.9 and 45.1 Kcal/mol for loss of water, carbon monoxide and carbon dioxide, respectively, the values of Coats and Redfern [3] (21.4, 62.0 and 51.7 Kcal/mol) are frequently cited as the most reliable. Speros and Woodhouse [19] have found a value of 44 Kcal/mol for step 3. The derivative analysis appears to be the more accurate for the carbon monoxide and dioxide losses. However, the integral method produced the best results for the dehydration, especially at higher heating rates. This may be a statistical artifact. However, dehydrations do appear to be of a special nature in TGA [1]. Back reaction at low conversion is probably more important in dehydration processes than in chemical decompositions.

Conclusions

On-line data acquisition and interactive data reduction offer real advantages in TGA studies. Not only is the weight loss-temperature relationship more accurately recorded in the digital system, but also the convenience of reduction permits a far more thorough treatment of data than do manual methods. Digital weight loss data may also be conveniently converted to the first derivative of weight vs time or temperature. This permits the direct application of any one of several kinetic treatments which require dw/dt as a function of percent conversion [20]. The present study has also indicated that this derivative method is more accurate than the dual heating rate tabular integral method, since it is less sensitive to errors in sample temperature measurement at high rates of conversions with E. I. du Pont type TGA equipment (thermocouple external to the sample).

This study has little to say about the merits of the TGA method for determining energies of activation. It is obvious that the weakest portion of the treatment is temperature measurement in the reaction zone. For the processes studied here, the sample temperature and the system temperature appear to be nearly equal, as demonstrated by the equivalency of the temperature and time base results. However, this need not always be true, and each system must be evaluated on the basis of the process studied.

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