CHEMICAL KINETICS OF SOLID REACTIONS BY FLUIDIZED BED DIFFERENTIAL THERMAL ANALYSIS

A Thesis

Presented to

The Faculty of the Department of Chemical Engineering

University of Houston

In Partial Fulfillment

of the Requirements for the Degree Master of Science in Chemical Engineering

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Leonard Kristian Schuster

May, 1970

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ABSTRACT

An experimental technique for conducting fluidized bed differential thermal analysis (DTA) was tested and shown to be suitable for quantitative determination of the kinetic parameters of certain chemical reactions of Essential features of the fluidized bed DTA appasolids. ratus include a fluidized bed heat bath, fluidized DTA cells and a standard DTA unit for temperature programming and measurement. A number of DTA curves for the dehydration of calcium oxalate monohydrate were obtained with the equipment. In these experiments nitrogen was used to fluidize mixtures of the reactant oxalate and inert aluminum oxide. Individual DTA runs were made with initial oxalate concentrations from 5.00 to 15.00 weight per cent and heating rates from 4.67 to 11.85 ^oC/min.

A method, suitable for computer application, was developed whereby the activation energy, frequency factor and reaction order can all be determined from a single DTA curve. Theoretical basis for the method, which assumes uniform temperature and gas-solid temperature equilibrium in the fluidized DTA cells, is more fundamental than other widely accepted theories of DTA for solid reactions. Significant differences between kinetic parameters determined by fluid bed DTA and data obtained by other investigators with more conventional methods were observed. The fluid bed DTA equations were integrated numerically to generate theoretical DTA curves. These theoretical curves agreed well with the corresponding experimental curves, thus verifying important aspects of the theoretical approach employed in this study. Applicability of the fluidized bed DTA method to reactions more complex than the simple sort of decomposition typified by the oxalate dehydration is also briefly discussed.

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CHAPTER 1

INTRODUCTION

Differential thermal analysis (DTA) is an experimental technique for observing the physical or chemical transitions that a substance undergoes on heating or cooling. Specific designs of DTA equipment vary widely depending on the particular application, but general features of the method are briefly summarized as follows. The reactive material to be studied is placed in a sample cell, and an inert material is placed in a reference The inert material is chosen so that its heat cell. capacity and thermal conductivity approximate those of the reactive material. Both cells are immersed in a heat bath. Heat is then supplied to the bath so that the temperature in the reference cell, T_{p} , increases linearly with time. In the absence of reaction the sample temperature, T_S , will also increase linearly with time and equal T_R . When reaction commences in the sample cell, the heat liberated or absorbed causes the sample temperature to differ from the reference temperature. This difference, $\Delta T = T_S - T_R$, is recorded by means of a differential thermocouple. The actual reference temperature, T_R , is simultaneously recorded. The result of the DTA experiment is then a graph of ΔT vs. time, t, as shown in Figure 1.1.



Figure 1.1. DTA Curve for a Simple Reaction

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Applications of DTA are so numerous that a recent survey of the literature by Smothers and Chiang (17) produced a bibliography of over four thousand publications. DTA is extensively used for qualitative and quantitative characterization of various materials such as minerals, coals, catalysts, oils, and polymers. Specific problems to which DTA has been applied include the determination of fusion temperatures, heat capacities, thermal conductivities, and heats of reaction. Examples of DTA applications at temperatures as high as 3000°C and pressures to 12,000 psia might be cited from the literature to further illustrate the versatility of the method.

Most recently several methods have been suggested for using DTA to determine quantitatively the kinetic parameters for certain types of reactions (5, 6, 12, 21). The most fundamental approach is that of Borchardt and Daniels (6). These investigators applied DTA to study simple homogenous liquid-phase reactions and were thus able to employ an all-liquid system with stirred heat bath and stirred sample and reference cells. With such a system the temperatures of reference, sample, and heat bath are almost uniform. This permits the system to be described in terms of very elementary heat balances. For the case of a single irreversible reaction, of order

n with respect to only one component, Borchardt and Daniels developed a straightforward procedure whereby the activation energy, frequency factor and order of the reaction are all computed from a single DTA curve.

Primarily because of its fundamental nature, the theory of Borchardt and Daniels is readily adaptable to a variety of reaction systems, and later investigators have proposed various modifications and extensions of this theory. Blumberg (5) modified the Borchardt and Daniels method to study the kinetics of a heterogenous system, vitreous silica and hydrofluoric acid. Reed et al. (16) developed additional aspects of the Borchardt and Daniels theory and also carried out an experimental study which verified the essential features predicted by this theory. More recently Yamamoto (22) has investigated the applicability of the Borchardt and Daniels method to more complex systems of simultaneous, concurrent, and consecutive reactions.

DTA has also been used to study simple solid decompositions of the type

For such reactions there is no fundamental theory of DTA which parallels that of Borchardt and Daniels for liquid

systems. In DTA investigations involving solid materials it is usual to employ packed sample and reference cells so that a temperature gradient develops between the cell walls and the center where the temperatures are measured. To avoid the mathematical difficulties inherent in accurately accounting for these complex temperature gradients, Kissinger (12) argued that the maximum reaction rate must occur at the peak of the DTA curve. Under this condition, a simple procedure was proposed whereby data from several DTA curves obtained at different heating rates are used to compute the activation energy for the reaction.

Kissinger's approach is attractive because of its simplicity, but the theoretical basis for the method is very fragile. Reed et al. (16) have shown that Kissinger's assumption that the maximum reaction rate coincides with the peak of the DTA curve is incorrect. Furthermore, it was demonstrated very clearly that the method can result in large errors in computed kinetic parameters, even though the reaction rate may occur very close to the peak of the DTA curve.

Other investigators, for lack of a more fundamental approach than Kissinger's method, have completely neglected the complex temperature gradients which develop in stagnant sample and reference material. Wendlandt (21), for example,

has applied the Borchardt and Daniels method to DTA curves obtained with packed sample and reference. However, such a simplification is not justified. With the usual sample size and heating rates employed in conventional DTA, gross temperature differences of 20°C or more can develop in the DTA cells (18).

Thus, while there are many interesting problems in the kinetics of noncatalytic heterogeneous reactions wherein quantitative DTA would prove to be an extremely useful experimental tool, the need still exists for a correct and practical theory of DTA for such reaction systems. The results of many experimental studies(1,10,14) show that, even under very severe conditions of heating or cooling, a gas-fluidized bed of solid particles can be characterized by essentially uniform temperatures throughout. In a further study Eichhorn and White(7) employed dielectric heating to generate heat continuously in a system of gas-fluidized plastic particles. Their experiments show that, for solid particles less than 250 micron in size, the temperature of solid and fluidizing gas are essentially identical throughout the entire bed. Uniformity of temperature and gas-solid temperature equilibrium are properties of the fluidized state which can be used to good advantage in DTA studies involving solid materials. When the stagnant sample and reference materials employed

in conventional DTA are replaced by fluidized beds, it is possible to extend the fundamental analysis of Borchardt and Daniels to reactions of solids. Basden (2,3) also recognized the benefits of a fluidized system in DTA and attempted to qualitatively characterize various types of coals by a fluid bed DTA method. However, Basden's apparatus was not suitable for quantitative analysis, and no conclusive results were ever reported.

The object of this work is to investigate the feasibility of using fluid bed DTA to study quantitatively certain reactions of solids. A fluid bed system suitable for quantitative DTA is used to obtain a number of DTA thermograms for a simple solid decomposition reaction. Kinetic parameters for the reaction are computed from the experimental curves by means of a theory which assumes temperature uniformity and gas-solid temperature equilibrium in the fluidized DTA cells. Important features predicted by this theory are verified by detailed examination of the experimental DTA curves. Since accurate mathematical description of the fluid bed DTA system is relatively straightforward, it will be evident that the theory and methods of analysis developed for a simple decomposition are readily extended to more complex reactions such as that between a gas and a solid.

CHAPTER II THEORY AND BASIC EQUATIONS FOR FLUID BED DTA

Theoretical considerations and basic equations for obtaining kinetic data by a fluidized bed DTA technique will be developed in this chapter. This development will be carried out specifically for the case of a simple irreversible reaction of the form

A(solid) ------ B(solid) + C(gas)

However, extension of the theoretical results obtained here to more complex reaction systems does not appear too difficult and is briefly discussed in Chapter V.

The experimental scheme referred to in the development which follows consists of two identical fluidized bed DTA cells which replace the sample holders used in conventional DTA. The reference cell, R, contains only an inert fluidizing solid. The sample cell, S, contains the inert material plus a small amount of the reacting substance to be studied such that the total heat capacities of the material in the sample and reference cells are approximately equal. Both cells are immersed in a heat bath at a uniform temperature, T_B . The solids in the cells are fluidized by an inert gas which enters each cell with flow rate m_g and temperature T_0 . Heat is supplied to the bath so that T_B , T_0 , T_S , and T_R , all increase with time. During the course of the experiment, the actual temperature in the reference cell and the temperature difference, $\Delta T = T_S - T_R$, due to reaction in the sample cell are simultaneously recorded.

When a solid reaction, which consumes or evolves gaseous components, takes place in a fluid bed the solids concentration will be uniform due to solids mixing. The concentrations of the various gaseous components may vary in a complicated manner with position in the bed, depending on gas flow rate, bed height, bed diameter, and other fluidization parameters. However, for the case of a simple irreversible decomposition, the gas phase concentrations will not influence the reaction rate. Thus. if the temperature is uniform throughout the bed, the reaction rate will also be uniform. With the additional assumption of temperature equilibrium between solid particles and fluidizing gas, theoretical description of the DTA curve then becomes relatively straightforward.

Under the conditions noted above, a heat balance on the material in the reference cell gives

$$\left[(1-\epsilon)Pc_{p} + \epsilon P_{g}c_{pg} \right]_{S} V_{S} \frac{dT_{s}}{dt} = m_{g}c_{pg}(T_{o} - T_{s}) - K_{s}(T_{s} - T_{s}) + r(-\Delta H_{r})$$

where

$$E = \text{fraction of voids in fluidized cell}$$

$$\rho c_p = \text{heat capacity per unit volume of solid}$$

$$\text{material in the cell, cal/cm3 °C}$$

$$P_S c_{Pg} = \text{heat capacity per unit volume of fluid-izing gas in the cell, cal/cm3 °C}$$

$$V_S = \text{volume of fluidized bed in the sample}$$

$$\text{cell, cm3}$$

$$K_S = \text{heat transfer coefficient for the sam-ple cell, cal/min °C}$$

$$\Delta H_{\gamma} = \text{heat of reaction, cal/mole}$$

$$\gamma = -dN/dt = \text{rate of disappearance of reac-tant, moles/min}$$

The term in brackets to the left of Equation (2) can be written in the form

$$(1-\epsilon)PCp\left[1 + \left(\frac{\epsilon}{1-\epsilon}\right)\left(\frac{P_{g}C_{pq}}{P_{cp}}\right)\right]$$

For values of bed voidage normally encountered in dense phase fluidization, \in will have a value near 0.5. Also, at ordinary pressures $\rho_{C_P} >> \rho_g c_{\rho g}$ so that

$$\left(\frac{\epsilon}{1-\epsilon}\right)\left(\frac{\rho_{a}c_{pa}}{\rho_{cp}}\right) << 1 \tag{1}$$

and the heat capacity of the gas in the fluidized bed can

be neglected. Equation (1) can then be written simply as

$$(Mc_p)_{s} \frac{dT_s}{dt} = m_g c_{pg} (T_o - T_s) - K_s (T_s - T_B)_{(2)}$$
$$+ \gamma (-\Delta H_{\gamma})$$

A similar heat balance on the reference cell, where no reaction occurs, results in

$$(Mc_{P})_{R} \frac{dT_{R}}{dt} = m_{g}c_{Pg}(T_{o}-T_{R}) - K_{R}(T_{R}-T_{B}) \quad (3)$$

The heat transfer coefficients, K_{S} and K_{R} , will depend primarily on the area of the cell walls, the film coefficients at the inner and outer surfaces of the walls, and possibly the material of construction and thickness of the cell walls. If the cells are immersed in a uniform bath, then for identical fluidization conditions within each cell, one would expect that $K_S = K_R = K$. Moreover, the inert material can be chosen so that its heat capacity is nearly equal to that of the reacting substance and solid products of the reaction. Then, if relatively small amounts of reactant are used, the total heat capacities of the material in each cell will be approximately equal, i.e. $(Mc_p)_R \simeq (Mc_p)_S = Mc_p$. With these simplifications Equation (3) can be subtracted from Equation (2) to give

$$\gamma(-\Delta H_{\gamma}) = Mc_p \frac{d\Delta T}{dt} + (K + Mgc_{pg})\Delta T \quad (4)$$

where $\Delta T = T_S - T_R$, the temperature difference due to reaction in the sample cell. Equation (4) is then the differential equation proposed to describe the observed DTA curves.

From an experimental viewpoint, exact matching of the DTA cells may not always be necessary to obtain useful thermograms. For example, if the total heat capacities within each cell are not exactly equal, Equation (4) will become

$$r(-\Delta H_{A}) + \left[(mc_{p})_{s}^{-} (Mc_{p})_{R} \right] \left(\frac{dT_{R}}{dt} \right) =$$

$$(Mc_{p})_{s} \frac{d\Delta T'}{dt} + (K + m_{q}c_{pq})\Delta T'$$

$$(5)$$

where again $\Delta T' = T_S - T_R$, but now includes the temperature difference due to reaction plus that due to thermal imbalance between the cells. Assuming a linear temperature rise in the reference cell, no reaction in the sample cell, and the initial conditions that $\Delta T' = 0$ at t = 0, Equation (5) has the solution

$$\Delta T' = \left[(Mc_p)_s - (Mc_p)_R \right] \left(\frac{dT_R}{dt} \right) \left[1 - e^{-\alpha t} \right]$$

where

$$\chi = \frac{(k + m_g c_{pg})}{(M c_p)s}$$

Thus, $\Delta T'$ will reach a constant value given by

$$\Delta T_{c} = \frac{\left[(Mc_{p})_{s} - (Mc_{p})_{R} \right]}{\left[K + m_{g} C_{p} g \right]} \left(\frac{dT_{R}}{dt} \right)$$
(6)

Letting $\Delta T = \Delta T' - \Delta T_C$ and substituting Equation (6) into Equation (5) yields again Equation (4). Hence, in lieu of exact matching of the cells, ΔT_C can be taken as the baseline as shown in Figure 2.1.

In any case, Equation (4) will be the basic relationship used to analyze the DTA curve. The parameter K can be eliminated by further manipulation of Equation (4), which if K, \triangle H_r, c_p, c_{pg} are all constant, can be written as

$$-\int_{N_{0}}^{N_{0}} dN = \frac{Mc_{p}}{(-\Delta H_{\gamma})} \int_{0}^{\Delta T_{0}} \frac{dT_{o}}{(-\Delta H_{\gamma})} \int_{0}^{\Delta T_{o}} \frac{dt}{(-\Delta H_{\gamma})} \int_{t=0}^{t=\infty} \frac{dT_{o}}{dt}$$

where t = 0 is the time at which the first observable temperature deflection occurs. Performing the integration and noting that $N_{\infty} = \Delta T_{\infty} = 0$, one obtains

$$A_{\tau} = \frac{(-\Delta H_{\tau})N_{o}}{(K + n n_{g} c_{pg})}$$
(7)



t - Time

Figure 2.1. DTA Curve When Cells are not Matched

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where A_{T} is the total area under the DTA curve. Substitution of Equation (7) into (4) results in

$$-\frac{1}{N_{o}}\left(\frac{dN}{dt}\right) = \delta \frac{d\Delta T}{dt} + \frac{\Delta T}{A_{T}}$$
(8)

where

$$\delta = \frac{MCP}{(-\Delta H_{\gamma})(N_{o})}$$

The parameter δ must be determined from the DTA curve as well as the kinetic parameters involved in the rate expression. When substantially all of the reactant is consumed, $dN/dt \simeq 0$ and Equation (8) can be integrated between some point on the 'cooling' portion of the curve and t = ∞ to yield

$$\left(1 - \frac{A_{\pm}}{A_{\pm}}\right) = \delta \Delta \top \tag{9}$$

where ΔT and A_t are any temperature deflection and cumulative peak area sufficiently beyond the high temperature inflection point so that $dN/dt \approx 0$. Equation (8) predicts that a plot of various values of $(1-A_t/A_T)$ against ΔT taken from the cooling portion of the curve should have a linear portion the slope of which determines δ .

Up to this point nothing has been said of the

particular form of the rate expression, r, or kinetic parameters involved. Unfortunately, no single, comprehensive theory describes the behavior of solid decompo-and experimental results of numerous studies of solid decomposition mechanisms are summarized by Garner (9). The main theories are founded on the notion that solid decomposition begins at positions of strain on the sur-These nuclei or active sites grow in number and face. size in a manner dependent on the microscopic structure of the solid. The manner of nucleation then leads to any one of numerous specific rate laws. As an example, in one study (23) no less than four distinct rate expressions were required to precisely describe experimental results obtained for the pyrolisis of magnesium oxalate over the entire range of temperatures and conversions examined.

Wen (19) points out that, regardless of the detailed mechanism, the kinetics of many heterogenous solid reactions can be adequately described by simple n th order rate laws. For a simple decomposition reaction such as that considered here an appropriate rate law is

$$-\frac{1}{N_o}\left(\frac{dN}{dt}\right) = k \left(\frac{N}{N_o}\right)^n \tag{10}$$

where n is an empirical reaction order and k is assumed to have the usual Arrhenius temperature dependence:

$$k = 2 \cdot e^{\frac{-E}{PT}}$$
(11)

where E and Z are the activation energy and frequency factor, respectively. In view of the exploratory nature of this work, it will now be assumed that an n th order rate law such as Equation (10) is sufficient to describe the decomposition kinetics.

The problem of determining the parameters E, Z, and n can then be formulated in general terms without, at this point, going into the details of the numerical procedure. The reaction rate at any time can be computed using information easily obtained from the DTA curve by means of Equation (8). Moreover, Equation (8) can be integrated between the limits t = 0 and any time, t, during the experiment. The result is

$$\left(\frac{N}{N_0} \right) = 1 - \left(\delta \Delta T + \frac{A_+}{A_T} \right)$$
 (12)

Thus, the normalized concentration, N/N_0 , while not conveniently measured during the experiment, can also be inferred from the DTA curve. The actual temperature in the sample cell is computed from the recorded temperature

deflection and reference cell temperature. Thus, reaction rates at various times during the DTA experiment can be be tabulated together with the corresponding sample temperatures and reactant concentrations. A suitable parameter estimation method will then determine E, Z, and n.

In summary, Equations (8), (9), and (12) are the basic relationships whereby the kinetic parameters can be computed from a single DTA curve. These relationships were all obtained from Equation (4) which, in turn, depends on the validity of the simple heat balances, Equations (2) and (3). Obviously, the preceding analysis constitutes the simplest approach that still maintains the essential features of the the problem. The limitations and and difficulties in application of these results will be reviewed after some experimentation involving a simple reaction system.

CHAPTER III

EXPERIMENTAL EQUIPMENT AND METHODS

The experimental work summarized in this thesis was conducted with two primary objectives:

- To explore the experimental difficulties which might arise in application of the proposed fluidized bed DTA technique.
- To obtain sufficient data to test the validity of the theory given in Chapter II and allow comparison of the kinetic results with those obtained by other methods.

The reaction selected for quantitative study was the thermal decomposition of calcium oxalate monohydrate. Decomposition of the hydrate becomes appreciable above 100°C and occurs according to the equation

 CaC_20_4 ·H₂0 (solid) ----- CaC_20_4 (solid) + H₂0(gas)

This particular reaction was chosen over others mainly because it occurs at low enough temperature so that the difficulties in constructing and operating higher temperature equipment could be avoided. Moreover, the kinetics of the reaction have been determined by Freeman and Carroll (8), who used a thermogravimetric analysis technique, and also by Wendlandt (21), who used a conventional DTA method. Hence, the results obtained with the fluidized bed technique could be directly compared with results obtained by more conventional methods.

Thermograms could be easily generated by numerical solution* of the basic heat balance, Equation (4). Preliminary computations of this type were carried out using the kinetic parameters reported by Freeman and Carroll and estimates of the heat of reaction and the cell heat transfer coefficient. The results of these computations predicted that, with reasonable initial reactant concentrations, heating rates of 2 to 10°C/min would produce fluidized bed DTA peaks suitable for quantitative study. Moreover, theory predicted that these peaks would occur within the temperature range of 100 to 200°C. This information was then used to design the experimental apparatus described in the following section.

*See Appendix D for details of the numerical method.

A. Description of Experimental Equipment

For purposes of discussion the experimental equipment can be divided into three sections:

- Two 0.80 inch I.D. nitrogen fluidized beds which served as the DTA cells.
- A 7-inch diameter air fluidized bed which served as the heat bath for the DTA cells.
- 3. An R. L. Stone Model 202 Differential Thermal Analysis System to perform temperature programming and recording functions.

DTA Cells and Heat Bath

The construction of the fluid bed DTA cells is illustrated in Figure 3.1. Each of the cells was fabricated from nominal 3/4 inch type 304 stainless steel pipe fitted with a porous stainless steel bed support. After the bed supports were welded in place, the entire assembly was machined to remove excess metal and reduce the wall thickness of the cells to 0.05 inches. Actual and differential temperatures were measured with 32 gauge chromel-alumel thermocouples. These thermocouples were of the stainless steel sheathed type with an outer diameter of 0.063 inches. Each of



the cells was fitted with two such thermocouples, vertically inserted into the cells, so that the bare measuring junctions were immersed directly in the fluid bed portion of the cells as shown in Figure 3.1.

Figure 3.2 shows the air fluidized heat bath and physical arrangement of the DTA cells in the bath, together with some pertinent dimensions. The heat bath consisted of an insulated vessel with an inside diameter of 7 inches and a height of 15 inches. The conical inlet section was filled with 1/32 inch diameter steel shot to promote good air distribution. Heat was supplied to the bath by means of two symmetrically positioned, U-shaped tubular heating elements. The two elements together had a maximum power rating of 1.5 KW at 120 VAC. Before entering the cells. the nitrogen to each cell was heated to the bath temperature by flowing through a five-foot length of 1/8 inch diameter, standard weight stainless steel tubing shaped into a 2.5 inch diameter coil. Two of these coils, one for each cell, were symmetrically located in the heat bath as shown in Figure 3.2. The DTA cells, heating elements, and nitrogen heating coils were mounted on the heat bath cover so that the entire assembly could be easily inserted into and removed from the bath.

Figure 3.3 is a schematic flow and equipment diagram.



Figure 3.2. DTA Cells and Heating Bath





Nitrogen was delivered from a compressed gas cylinder equipped with a two-stage regulator adjusted so that delivery pressure into the system was 125 psig. After leaving the cylinder the nitrogen passed through a 1.5 inch diameter, 1 foot high bed of 1-16 mesh, grade 05 silica gel dessicant. The nitrogen was then split into two streams metered with two Fisher and Porter flow meters calibrated for a maximum flow of 1400 cc/min nitrogen at 75°F and 14.7 psia. The nitrogen then flowed through the heating coils immersed in the bath and into the DTA cells. After passing through the cells nitrogen was simply vented to the room.

Local compressed air, available at 100 psig, was used to fluidize the heat bath. The air was metered with a Fisher and Porter flowmeter with a maximum flow rating of 6.00 cu ft/min of air at 70° F and 14.7 psia. The air entered the bath at room temperature, passed through a dust filter, and was then vented to the room.

Model 202 DTA System

The Model 202 Differential Thermal Analysis System is a standard item manufactured by Tracor, Inc. (Austin, Texas). However, the unit used in this study included several modifications which should be noted, since later

references to this equipment may apply only to the modified version of the standard apparatus. All modifications were made by the manufacturer on request.

The standard Model 202 comes equipped with an X-Y recorder so that the differential temperature can be recorded directly against either sample temperature or reference temperature. This procedure is common practice in conventional, qualitative DTA, although it can lead to serious errors in interpretation of the DTA peaks if small irregularities in the heating rate occur. A much sounder procedure is to record the differential temperature directly against time, while independently recording the reference temperature. For this reason, and simply because the DTA curves are then more conveniently analyzed in terms of the theory given in Chapter II, the X-Y recorder was replaced with a 10 millivolt strip-chart recorder. The unit was then equipped with a temperature readout module to visually indicate the reference cell temperature and simultaneously activate an event marker which would record the reference temperature on the same chart as the differential temperature.

At comparable heating rates, the heat load required for the fluid bed DTA experiment is greater than required for
conventional DTA. Therefore, the Model 202 used in this study was equipped with an auxilliary silicon controlled rectifier power unit which increased the maximum programmed power output to 2KW.

The modifications noted above were the only changes required to adapt the Model 202 to the fluid bed DTA experiment. The unit can now be described in more detail. Major components of the system and their functions are:

- A DC amplifer and strip chart recorder to record the differential temperature.
- 2. A temperature readout unit to record the actual reference cell temperature.
- 3. A temperature programming circuit to control the power input to the heaters immersed in the bath so that the reference cell temperature increases at a constant rate.

The simplified block diagram shown in Figure 3.4 illustrates how the individual components of the Model 202 DTA System enter into the overall experimental scheme.

The differential temperature signal is obtained from two opposed thermocouples, one located in each cell. This signal is then transmitted to a DC amplifier with a maximum gain of 10 millivolt output for a 5 microvolt input. The



Figure 3.4. Instrumentation and Control System

amplified differential signal is then recorded by the 10 millivolt strip-chart recorder.

One of the two thermocouples located in the reference cell provides the reference temperature signal which is transmitted to the temperature readout module and recorded. This same thermocouple also serves as the sensing element for the temperature programming circuit. The programming circuit is basically an anologue circuit which simulates a physical system in which the temperature increases linearly with time. The input to the programming circuit is the desired heating rate. The selected heating rate then determines the rate at which a motor-driven potentiometer linearly increases a reference voltage. For a given heating rate, this reference voltage is equivalent to the desired reference cell temperature at any time. This temperature equivalent voltage is then transmitted to an emf generator capable of reproducing the non-linear temperature-emf relationship of a standard chromel-alumel thermocouple. The output of the emf generator is then compared with the actual emf of the reference couple immersed in the reference cell. Whenever the emf of the reference couple falls below the generated emf, the resulting positive error signal is amplified and transmitted to the SCR power control. The SCR unit then supplies power

to the heaters immersed in the bath in proportion to the magnitude of the error signal. Fower is supplied until the actual reference cell temperature approaches the required reference temperature and the error signal to the SCR unit diminishes. The control system, operating continuously in this manner, then provides a linear temperature rise in the reference cell.

The Model 202 DTA System also comes equipped with sample holder, furnace, and furnace platform for conducting standard DTA analyses. These components are used to analyze stagnant samples in the conventional manner and need not be described here.

B. Calibration of Equipment

<u>Reference Thermocouple</u>--As pointed out previously, the reference couple was used to measure the actual temperature in the reference cell and also as a sensing device for the temperature programming circuit. One of nine previously prepared chromel-alumel thermocouples was selected and its emf, with respect to a reference at 0 °C, was determined at each of four standard calibration temperatures. Emf's were measured with a

model X-2, NSL Digital Voltmeter, read to the nearest 0.01 millivolt. The temperature-emf relationship of this couple, shown in Figure B.1 in Appendix B, deviates by less than 1°C from that of the standard* chromel-alumel thermocouple over the temperature range 0-327°C. During these tests, the calibration of the Model 202 temperature readout module was also checked by directly inputting the emf of the reference couple at each of the test temperatures. Again, within 1°C, no correction to the manufacturer's calibration was required.

<u>Differential Thermocouples</u>--Since the maximum expected differential temperatures were only about 3 or 4° C, it was considered essential that the differential couples be well matched in the sense that, when both are at the same temperature, the emf output of the differential circuit be negligibly small. To find a suitable pair of thermocouples, each of the remaining eight couples, in turn, was connected in a differential circuit with the reference couple. The test and reference couple were then allowed to come to equilibrium with boiling water. At equilibrium, the differential emf of the circuit was measured using the DC amplifier and recorder

^{*}Temperature-Millivolt Reference Tables for Thermocouples, Honeywell Bulletin 16735526-001

supplied with the Model 202 DTA System. This procedure was then repeated with each of the thermocouples at the boiling point of analine. These measurements, shown in Table B.l in Appendix B, indicated that the thermocouples labeled '2' and '4' when used in the differential temperature measuring circuit, would give a matching error of less than 1 microvolt. These two thermocouples were used throughout, and the matching error given above, equivalent to less than 0.025°C, is a reasonable estimate of greatest error expected in measuring the differential temperature.

<u>Flowmeters</u>--Calibration curves for the nitrogen flow meters are shown in Figure B-2 in the Appendix. Calibration was performed by water displacement after the meters were installed in the system. The actual air flow to the heat bath did not have to be accurately known, and thus the manufacturer's calibration was used without correction.

C. Materials

Chromatographic grade aluminum oxide, purchased from J. T. Baker Chemical Company, served as the inert solid fluidized in the DTA cells. Nitrogen to fluidize the DTA cells was purchased from Union Carbide, Linde Division. This grade of nitrogen was oil free and had a maximum specified moisture content of less than 25.5 parts per million.

Reagent grade calcium oxalate monohydrate was obtained from the Matheson Chemical Company. This material was available only in a finely powdered form which could not be fluidized with the alumina without excessive loss from the cell. After some experimentation, a procedure was found which would produce large conglomerated oxalate crystals suitable for fluidization. Approximately 19 grams of the purchased oxalate was dissolved in 1.0 N boiling HCL to produce a saturated solution. This saturated solution was then allowed to cool slowly to room temperature. The oxalate crystals which formed over a period of several days were then collected, washed several times with water, and then air dried for 24 hours at room temperature.

Standard DTA analyses were made to compare the purchased powder and crystallized form of the oxalate. These thermograms, shown in Figures 3.5 and 3.6 were obtained with the aluminum dish sample holders supplied with the DTA unit. The first peak at 185°C is due to the <u>endo-</u> <u>thermic</u> dehydration reaction. The second peak near 450°C corresponds to the net <u>exothermic</u> reaction

 $CaC_2O_4(s) + \frac{1}{2}O_2 \longrightarrow CaCO_3(s) + CO_2(g)$



Figure 3.5. Standard DTA Thermogram for Calcium Oxalate Powder



As is readily apparent, there is little difference in the DTA patterns obtained from the two forms of the oxalate.

During the course of the experimental work, three batches of oxalate crystals were prepared in the manner previously described. As a further check on the purity of this material, weight loss determinations were made on the first and last batch. Weighed samples from these batches were first maintained at 200°C for one hour, and the weight loss due to removal of water was determined. The dehydrated samples were then maintained at 500°C for one hour and the weight loss due to the oxalate decomposition was determined. For the two batches, the weight loss due to dehydration was 12.12 and 13.05 per cent; whereas, the theoretical weight loss is 12.33 per cent. For the high temperature oxalate decomposition, weight losses were found to be 32.24 and 32.12 per cent, which compares favorably with the theoretical weight loss of 31.50 per cent.

D. Preliminary Experiments and Final Operating Conditions

Before any quantitative results could be obtained some preliminary work was required to insure proper performance of the equipment and arrive at a suitable set of operating conditions. Reasonable values had to be selected

for such variables as nitrogen flow rate to the DTA cells, air flow rate to the heat bath, and weight of solids used in the DTA cells. All of these variables directly affect fluidization performance and a reasonable amount of care was necessary in fixing them.

Leva (14) discusses the numerous factors which affect fluidization performance. Good heat transfer and temperature uniformity are generally attributed to the excellent solids circulation which can be attained at proper fluidization conditions. Based on Leva's detailed discussion, some qualitative guidelines for achieving good fluidization performance can be listed:

- The gas flow rate should be at least 2 to 3 times the minimum fluidization velocity.
- The solid should possess a wide range of particle sizes.
- The expanded bed height should be less than twice the bed diameter.

Fluidization characteristics of the aluminum oxide were studied in a 0.80 inch diameter Plexiglass bed similar in construction to the DTA cells, so that fluidization could be visually observed. The purchased alumina had a very narrow particle size distribution with about 60 per cent

of the material in the range 53 to 74 microns and 10 per cent less than 37 microns. At flow rates high enough to give adequate solids circulation, the fine material was continuously lost from the bed. Therefore the fraction less than 37 microns was removed completely. With this modification, the alumina could be fluidized at gas rates as high as 1200 cc/min for 30 minutes with less than 1 per cent loss of material.

Following the suggestions of Leva, some experimentation with particle size distribution was done. The particle size distribution of the alumina was made more uniform by reducing the large fraction in the range 53-74 microns. At the same nitrogen flow rate this adjusted material gave noticeably more uniform fluidization with less slugging and more vigorous solids circulation than the unmodified alumina. Thus, enough material to last throughout the tests was prepared with the following parricle size distribution

Particle Size (microns)	Weight per cent
37- 53	23.1
53-74	30.7
74-105	23.1
105-125	15.4
125-149	7.7

The average particle size¹ of this material is 69 microns while the minimum fluidization gas rate² is approximately 250 cc/min.

The total weight of material used in the DTA cells also affects fluidization performance, since this weight will directly determine the expanded bed height. Using the plexiglass bed with a nitrogen flow of 950 cc/min, a series of experiments was conducted in which alumina was slowly added to the cells in increments of 1.0 gram and the affect on fluidization noted. Up to a total weight of 4 to 5 grams, which corresponds to an expanded bed height of about 1 inch, fluidization remained fairly uniform. With 6 or more grams of material, slugging tended to become excessive, and particle circulation in the bottom of the bed was noticeably restricted.

Initially, a fine silica sand was fluidized in the bath. Test runs made with this material, with no reactant in the sample cell, resulted in an erratic, continuously shifting baseline which would clearly be unacceptable for quantitative DTA. As shown in Chapter II, a

Calculated using the method recommended by Leva, p.61
Calculated from the correlation given by Leva, p.64

baseline at Δ T=0 is not necessary; however, it is essential that the baseline offset reach a constant value to avoid errors in interpretation of the DTA patterns. This difficulty was finally traced to the poor fluidization characteristics of the silica sand. The sand was replaced with a silica-alumina catalyst* having the following particle size distribution:

Particle Size (microns)	Weight per cent
37	4.62
37-44	1.95
44-63	42.04
63-74.	37.08
74-88	3.15
88-125	11.16

This catalyst was especially designed for use in fluid bed cracking units, and its use in the heat bath resulted in a dramatic improvement in the baseline as illustrated in Figure 3.7. The solid line in the figure is an actual

* Obtained from Shell Chemical Company, Deer Park, Texas

baseline obtained with the catalyst at a heating rate of approximately 12°C per minute, air flow of 3.3 cu ft/min, and approximately 4 grams of alumina in each cell. The dashed line, shown for comparison, roughly indicates the type of baseline obtained previously with the silica sand at similar conditions. With the catalyst in the heat bath, the lowest air rate which would yield a steady baseline was about 3.0 cu ft/min. The lowest feasible air rate is, of course, desirable to reduce solids loss from the bath during a run and to minimize the load on the heaters immersed in the bath.

As illustrated in Figure 3.7, once the thermal inertia of the system was overcome, the temperature programming circuit functioned satisfactorly. With an air flow of 3.3 cu ft/min, the maximum attainable heating rate was about 12° C per minute with less than 2 per cent deviation from linearity up to a temperature of 220° C. At lower heating rates temperature control was even more precise.

These preliminary experiments served to determine the capabilities of the equipment and led to a feasible set of operating conditions. Unless otherwise noted, all of the results presented in the next chapter were taken at the fixed conditions described here. Nitrogen flow to the DTA





cells was 950 cc/min, or 3.8 times the minimum fluidization velocity. The thermocouples were positioned so that the measuring junctions would be located in the central portion of the bed, 1/2 inch above the bed support. Air flow to the heat bath was 3.3 cu ft/min, which corresponds to 5.5 times the minimum fluidization velocity.

CHAPTER IV

EXPERIMENTAL RESULTS AND DISCUSSION

Table 4.1 summarizes the experimental conditions at which thermograms for the oxalate dehydration were obtained. With the exception of Run 9, all runs were made with a total mass of 4.000 gm in each cell and oxalate particle size between 44 and 88 micron. For Run 9 the total mass in each cell was 5.000 gm, and reactant particle size was 125-250 micron. Runs 1 through 5 were made with varying amounts of initial reactant at approximately the same heating rate. Runs 6, 7, and 8 were made with the same initial reactant concentration but different heating rates. Run 9 was made to test particle size and diffusion effects.

A. Qualitative Comments

Figures 4.1 and 4.2 show two actual thermograms obtained with the fluid bed DTA technique. The small, short-term oscillations superimposed on the DTA patterns are due to slight non-uniformities caused by gas bubbling which cannot be entirely eliminated in fluidization. Further experimentation with particle size distribution and other fluidization parameters aimed at improving fluidization efficiency might serve to reduce these oscillations. For the numerical computations, the original

Table 4.1. Fluid Bed DTA Experiments with Calcium Oxalate Monohydrate

Run no.	Heating Rate (^o C/min.)	Initial Reactant Concentration (wt. per cent)		
l	11.85	5.00		
2	12.00	7.50		
3	11.50	10.00		
4	11.70	12.50		
5	11.85	15.00		
6	4.67	10.00		
7	9.07	10.00		
8	11.85	10.00		
9.	7.50	10.00		

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Figure 4.1 Experimental Fluid Bed DTA Thermogram - Run 3





thermograms were simply smoothed as illustrated in Figures 4.1 and 4.2.

The two curves shown were obtained from Runs 3 and 8, and thus roughly indicate the sort of reproducibility resulting in DTA patterns generated at similar conditions of heating rate and initial reactant concentration. Differences in the general shape of the two curves can be attributed to the slightly different heating rate for the two runs. More precise reproducibility in the actual DTA curves is difficult to demonstrate, since heating rates could not be duplicated within limits better than those indicated in Table 4.1. Exact reproducibility in the DTA patterns is not essential. It is more desirable to have an adequate theory which accounts for the effect of experimental variables such as heating rate, and thus be able to demonstrate reproducibility in the final kinetic constants.

B. Numerical Analysis of DTA Curves

A brief description of the methods used to process experimental DTA curves is given in this section. The actual computations were programmed in Fortran IV for a digital computer. A listing of the computer program, together with some example output is given in Appendix C.

The differential temperature and corresponding sample temperature at various times during the DTA experiment constitute the basic information required to analyze the DTA curves according to the theory developed in Chapter II. Peak heights were measured to the nearest 0.01 inch directly from the thermograms at 2°C intervals in reference temperature, T_R . Over the temperature range 100-200°C, the emf-temperature relationship of the chromel-alumel thermocouple is sufficiently linear so that an average emf of 40 micro-volts/°C can be assumed with less that 3 per cent error. Measured peak heights were then converted to differential temperature using this conversion factor together with the known recording sensitivity:

$$\Delta T = \text{peak height} \\ \text{(inches)} X \begin{bmatrix} \text{sensitivity} \\ \frac{(\text{microvolts/inch})}{40 \text{ microvolts/}^{\circ}C} \end{bmatrix}$$

Sample temperatures were computed as the sum of the recorded reference temperature, the differential reaction temperature, ΔT , and the constant baseline offset, ΔT_C :

$$T_S = T_R + \Delta T + \Delta T_C$$

Corresponding values of A_t were determined by numerical integration of the peak using Simpson's Rule. The required derivatives, d $\Delta T/dt$, were computed using the five point differentiation formulas recommended by Walas(1).

The proposed theory assumes that all heat capacities are constant over the temperature range of interest. In practice, all heat capacities were evaluated⁽²⁾ at a mean temperature of 140° C. In the temperature interval $100-200^{\circ}$ C the heat capacity of aluminum oxide deviates by less than 10 per cent from its value at 140° C; while the same deviation for nitrogen is less than 1 per cent.

The actual calculation procedure begins with the determination of the unknown parameter δ . Pairs of points, ΔT and A_t , are selected from the cooling portion of the curve, beyond the high temperature inflection point. δ is then estimated from a least squares approximation to Equation (9):

$$\left(1 - \frac{A_t}{A_T}\right) = \delta \Delta T \qquad (9)$$

The reaction rate and normalized reactant concentration at various points on the DTA curve are then computed from Equations (8) and (12):

S. M. Walas, "Reaction Kinetics for Chemical Engineer's", p. 301, McGraw-Hill Book Company, Inc., New York, 1959.

J. H. Perry, "Chemical Engineers Handbook", 4th. ed., pp. 3-116, 3-119, McGraw-Hill Book Company, Inc., 1963.

$$-\frac{1}{N_{o}}\left(\frac{dN}{dt}\right) = S\left(\frac{dAT}{dt}\right) + \frac{\Delta T}{A_{T}}$$
(8)

$$\begin{pmatrix} N \\ N_0 \end{pmatrix} = I - \left(S \Delta T + \frac{A_t}{A_T} \right)$$
(12)

These values are tabulated together with the corresponding sample cell temperature, T_S . At this point, a nonlinear parameter estimation technique developed by Marquardt (15) is used to determine the constants E, Z, and n in the assumed rate equation

$$-\frac{1}{N_{o}}\frac{dN}{dt} = Z \mathcal{L}^{-\frac{E}{RT_{s}}} \left(\frac{N}{N_{o}}\right)^{M}$$

Marquardt's method is an iterative procedure which, starting with some initial estimate of the unknown constants, produces successively better approximations to the unknown parameters. Iteration stops when the current values of the parameters result in deviations between calculated and observed reaction rates which satisfy the minimum sum of squares criterion. Additional details of the method and its application to the particular problem of interest here are given in Appendix C.

To obtain some idea of the precision of the computations, the entire procedure was first applied to several theoretical DTA curves generated numerically with known input parameters. Differential temperatures were taken directly from plots of these theoretical thermograms. The resulting calculated values of S, $\log_{10} 2$, and n were always within 10 per cent of the input values; whereas, the activation energy, E, could always be computed to within 5 per cent of the input value. Differences between the calculated and input values merely reflect the effect of small errors in measuring peak heights and the limited precision of the methods used to numerically integrate and differentiate the DTA peaks. Since these computations simulate ideal experiments, with a minimum of experimental error, it should be quite clear that greater precision than indicated above cannot be expected in any results derived from actual experimental DTA curves.

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C. Calculated Results

The method of analysis described in the previous section was first applied to the thermograms obtained from Runs 1 through 5. These thermograms are plotted in Figure 4.3 against reference cell temperature, corrected for the constant baseline offset. Clearly, even a relatively small increase in initial reactant résults in a pronounced increase in the magnitude of the peak maximum, as well as a shift of the peak maximum to a



Figure 4.3 DTA Thermograms - Runs 1 to 5

higher reference temperature. Regardless of the differences in shape and location of the peaks shown in Figure 4.3, if the same rate equation applies in all instances, a correct theory and numerical analysis must produce very nearly the same kinetic constants from all of the data.

Before presenting the final kinetic parameters computed for Runs 1 through 5, further aspects of the proposed theory and numerical analysis will be illustrated with some typical intermediate results. Figure 4.4 shows the plot of $(1-A_t/A_T)$ against ΔT taken from the cooling portion of the thermogram obtained in Run 3. As predicted by Equation (9), the plot is linear with intercept through the origin. A value of $\delta = -0.055^{\circ}C^{-1}$ was calculated from the specific data shown in Figure 4.4.

Provided that ΔH_r , K, and $m_g c_{pg}$ do not vary, Equation (7) predicts a linear relationship between A_T and N_o for a series of thermograms obtained with increasing initial reactant concentration. Figure 4.5 shows such a plot of total peak area against initial moles of reactant for Runs 1 to 5. The linear relation predicted by Equation (7) is in fact observed.

Since no obvious discrepancy between theory and experiment has yet been uncovered, it seems appropriate to





Figure 4.4. Determination of § from Cooling Portion of DTA Curve-Run 3



Figure 4.5. Linear Relation Between Total Peak Area and Initial Reactant Concentration

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proceed to the determination of the kinetic parameters. Practical considerations limit the portion of any DTA curve which can yield useful data for the kinetic calculations. All of the experimental thermograms exhibited the instability near 100 ^OC illustrated by the curves shown in Figures 4.1 and 4.2. Presumably this initial disturbance was due to desorption of surface water from the oxalate. Because of the uncerainty in measuring the differential temperature in this region, the initial portion of the DTA curves was not used to determine the kinetic constants. On the other hand. according to Equation(12), the oxalate dehydration is essentially complete immediately after the maximum in the DTA curve. Attempts to apply Equation (12) much beyond the maximum temperature deflection can result in small, negative values for the reactant concentration due to small errors in evaluating the individual terms of the equation. Points used to calculate the kinetic constants were therefore confined to regions of the curves immediately after the initial disturbance to just beyond the peak maximum. Thus, each curve yielded from 20 to 30 points, spaced at 2 $^{\circ}$ C intervals in T_P.

The results of some intermediate reaction rate calculations for Run 3 are shown in Table 4.2. The range of

normalized concentration and reaction rate illustrated in the table is representative of the results obtained for Runs 1 to 5. Marguardt's method applied to the data from Run 3 gave final values of $E = 22.6 \text{ kcal/mole}, Z = 1.58X10^{11}$ min⁻¹, and n = 0.486. It should be noted that only alternate points actually used in the determination of these constants are shown in the table. This editing was done merely for convenience of presentation and does not alter the conclusions to be made. Corresponding rates predicted with the derived constants are also shown in Table 4.2. The last column in the table lists the percentage deviation between observed and predicted rates at each temperature and concentration. Over most of the course of dehydration, the observed rates are within 10 per cent of the rates predicted by the derived rate equation. However, the initial portion of the reaction is poorly represented by the assumed n th order rate law. Essentially the same precision of fit was obtained for all the data in this set of runs. In view of the empirical nature of such a simple rate law and the wide range of conversion to which it has been applied, the absence of a more precise fit to the data should not be too surprising.

Table 4.3 summarizes the final results of interest calculated for Runs 1 through 5. The values of ΔH_r shown in the table were calculated from the definition

Table 4	.2. R	eaction	Rate	Data-Run	3
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$(0.1)^{TS}$. <u>N</u>	Reaction R	Reaction Rate, $\frac{1}{N}$ $\left(\frac{dN}{d+1}\right)$		
(°K)		Observed	Predicted		
394.1	• 0•936	0.062	0.045	37.8	
398.0	0.913	0.077	0.059	• 30.5	
401.9	0.883	0.092	0.076	21.0	
405.8	0.848	0.106	0.098	8.1	
409.7	0.806	0.130	0.124	4.8	
413.6	0.760	0.153	0.156	-1.9	
417.4	0.699	0.183	0.194	-5.7	
. 421.2	0.630	0.220	0.235	-6.4	
425.0	0.545	0.266	0.279	-4.7	
428.7	0.445	0.302	0.319	-5.3	
432.4	0.332	0.343	0.348	-1.4	
436.2	0.206	0.379	0.346	9.5	
440.2	0.083	0.304	0.282	7.8	
444.8	0.012	0.094	0.144	-34.8	

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$$\begin{cases} = \underline{Mcp} \\ (-\Delta H_{n}) No \end{cases}$$

The individual cell heat transfer coefficients were then computed from Equation (7), rearranged to read

$$K = -\left[\frac{\Delta H_{T} N_{O}}{A_{T}} + m_{g} c_{P} g\right]$$

The heats of reaction and heat transfer coefficients computed from the individual thermograms should be identical within reasonable limits of experimental error. Discounting Run 2, the average heat of reaction computed from the data in Table 4.3 is 5.93 kcal/mole, with a maximum deviation from this average of only 7.9 per cent. The average cell heat transfer coefficient is 2.25 cal/min, with a maximum deviation of 9.6 per cent. Considering the differences in magnitude and general shape of the original thermograms shown in Figure 4.3, the reproducibility with which the heat of reaction and heat transfer coefficients can be extracted from the individual thermograms verifies that both the theory and numerical approach are basically correct.

Table 4.3 also lists the activation energies, frequency factors, and reaction orders calculated from each of the thermograms from Runs 1 through 5. These runs were

Table 4.3 Calculated Results - Runs 1 to 5

Run no.	<u>δ</u> (°c ⁻¹)	Δ_{H_r}	K <u>(cal/min)</u>	E <u>(kcal/mole)</u>	<u>(min⁻¹)</u>	<u>`n</u> _
1	-1.06	6.15	2.23	30.5	7.13x10 ¹⁶	0.876
2	-1.11	3.96	1.58	27.0	.4.90x10 ¹³	0.734
3	-0.055	6.04	2.24	22.6	1.58x10 ¹¹	0.486
4.	-0.048	5.46	2.09	22.1	7.46x10 ¹⁰	0.371
5	-0.036	6.06	2.45	23.4	3.18x10 ¹¹	0.404
Averag	;e (without Run 2)	5.93	2.25			

1 2 3 3 4.51x10¹⁵ 0.849 28.0 1.64x10¹⁴ 0.867 22.5 1.32x10¹¹ 0.474 22.2 9.00x10¹⁰ 0.386 5 Average (without Runs 1 & 2) $\delta = \frac{-1.53x10^{-4}}{N_0} \begin{cases} 30.2 & 4.51x10^{15} & 0.849\\ 28.0 & 1.64x10^{14} & 0.867\\ 22.5 & 1.32x10^{11} & 0.474\\ 22.7 & 1.78x10^{11} & 0.420 \end{cases}$ made principally to determine if the same set of kinetic constants could be calculated from the individual thermograms. Such a demonstration of reproducibility alone would verify that the equations developed in Chapter II adequately describe the experimental fluid bed thermograms. However, comparison of the tabulated results will show that the activation energies determined from Runs 1 and 2 are significantly higher than calculated from Runs 3, 4, and 5. The frequency factor and reaction order show similar behavior. In contrast, reproducibility is excellent for Runs 3, 4, and 5. For these experiments the variation between individual runs is within the expected limits of precision previously derived.

The calculations were repeated in an attempt to bring the kinetic constants from the individual runs into closer agreement. The average heat of reaction indicated in Table 4.3 together with the constant known total heat capacity of the material in the sample cell can be used to arrive at an average value for $Mc_p/(-\Delta H_r)$ of -1.53×10^{-4} moles/°C. Instead of using the cooling portions of the individual thermograms, this average was used to calculate δ for each run from the equation

$$\delta = \frac{-1.53 \times 10^{-4}}{N_0}$$
The resulting kinetic constants, again listed in Table 4.3, are not very different from those calculated previously. It appears that the kinetic parameters, in particular the activation energy, are not overly sensitive to small errors in the determination of S. The overall spread in kinetic constants has been decreased slightly by using the averaging procedure to determine S, but still the results for Runs 1 and 2 differ significantly from the remaining values.

The exact reason for the apparently different kinetics at the lower initial reactant concentration is not known. However, the weaker heat effect associated with using smaller amounts of reactant almost certainly results in thermograms which are less suitable for reliable quantitative analysis. This point is illustrated by comparison of the thermograms shown in Figure 4.3. The DTA patterns for Runs 1 and 2 exhibit an erratic behavior which contrasts with the regular transition of the thermograms for Runs 3, 4, and 5. The weak thermograms from Runs 1 and 2 may have been too poorly defined to yield reliable kinetic constants.

The data summarized in Table 4.3 resulted from thermograms obtained at essentially identical heating rates but varying initial reactant concentration. Using input parameters derived from the experiments conducted at constant heating rate, it is interesting to see how well theory

predicts the effect of increasing heating rate on the location and magnitude of the DTA curves. Disregarding the results of Runs 1 and 2, the variance in kinetic parameters is sufficiently small so that values of E = 22.7kcal/mole, $A = 1.78 \times 10^{11} \text{ min}^{-1}$, and n = 0.420 can be computed by simply averaging the results of Runs 3, 4, and These average kinetic parameters, together with the 5. average values for ΔH_r and K indicated in Table 4.3, were used to generate a series of theoretical thermograms corresponding to the reactant concentration and heating rates of Runs 6, 7, and 8. The appropriate theoretical thermograms are compared with experiment in Figures 4.6, 4.7, and 4.8. Agreement between theory and experiment is quite good. In all three cases theory predicts almost exactly the correct increase in magnitude of the peaks as well as the shift of the DTA peaks to higher temperatures with increased heating rate.

Table 4.4 lists the kinetic constants computed directly from the thermograms of Runs 6, 7, and 8. The results from these experiments at different heating rates are in good agreement with the average constants from Runs 3, 4, and 5 which were all made at a heating rate of 12 °C/min, but different initial oxalate concentrations. For Runs 7 and 8 the calculated activation energies are within 5 per cent of the average 22.7 kcal/mole obtained







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Run no.	△H _r (kcal/mole)	E (kcal/mole)	(min ⁻¹)	<u>n</u>
6	5.70	19.3	2.30X10 ⁹	0.356
7	6.65	23.5	4.63X10 ¹¹	0.458
8	5.55	23.8	6.89X10 ¹¹	0.421
9	5.75	20.5	8.69x10 ⁹	0.204

Table 4.4 Calculated Results - Runs 6 to 9

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from Runs 3, 4, and 5. The low heating rate employed in Run 6 gave a weak, poorly defined thermogram; consequently, agreement with the previous set of runs is less precise.

All of the data reported thus far were taken with the oxalate particle size between 44 and 88 microns. For Run 9 the particle size was increased to the range 125-250 microns. Table 4.4 again summarizes the computed results for this run. Increasing the particle size has not appreciably affected the activation energy. The computed value of 20.5 kcal/mole is within 10 per cent of the average 22.7 kcal/mole obtained from Runs 3, 4, and 5. However, as a result of the increased particle size, the reaction order has been significantly reduced to 0.204 from the average 0.420 previously determined from Runs 3, 4, and 5.

The observed decrease in reaction order with increasing particle size is an interesting result which merits some further discussion. Such an effect of particle size on reaction order would be anticipated if diffusion of product water vapor through the reacting particles has been a controlling step in the rate of dehydration. Any effect, such as an increase in particle size, which enhances the importance of diffusion will lessen the rate dependence on reactant concentration and thus result in a lower apparent reaction order. The temperature dependence of the

reaction is characterized by the activation energy according to the Arrhenius equation, while the rate of diffusion is relatively insensitive to changes in tempeature. Thus, if diffusion is a controlling step, an increase in particle size will cause a decrease in the apparent activation energy. However, when the reactant particle size was increased for Run 9, the computed activation energy was not significantly different from the previous runs with the smaller particle size. It is therefore unlikely that diffusion was a limiting factor for the range of particle size used in this study.

Even if diffusion is not a controlling factor, the reaction order is related to the shape of the reactant particles. Berlin and Robinson (4) point out that the decomposition of many hydrates and carbonates is governed by the progression of the interface between reactant and product solids toward the center of the reacting particle. For such a mechanism they developed a theoretical rate model which is equivalent to the n th order rate expression adopted in this study. The order of reaction, n, relates the surface area of the reactant-product interface to the concentration of reactant by

$$\frac{S}{S_o} = \left(\frac{N}{N_o}\right)^m$$
(13)

where S_0 is the initial surface area of the particles, and S is the area at the reactant-product interface at any time after decomposition begins.

Berlin and Robinson were not immediately concerned with the reaction order. However, probable values of n can be inferred from the geometry of the reacting particles. According to Equation (13), reaction of spherical or cubical particles should result in n = 2/3. Long. needle-like particles would give n=1/2. Thin, flat particles for which the surface area is nearly independent of conversion should yield a reaction order n = 0. Presumably, more complicated shapes would result in intermediate values for the reaction order. Grinding a sample of coarse, irregularly shaped particles has the general effect of causing the particles to assume a more nearly spherical or cubical shape. As a result, the finer material should yield a higher reaction order which is nearer the value of 2/3 predicted for spherical or cubical particles. Such an effect of particle size on reaction order is precisely the result obtained experimentally in this study.

D. Comparison of Results with Literature Values

Freeman and Carroll (8) employed a thermogravimetric analysis (TGA) technique to study the kinetics of simple

solid decomposition reactions. Their method has gained wide acceptance because it is easy to carry out experimentally. The test material is heated at a known and constant rate, while the weight loss due to reaction is simultaneously recorded. Freeman and Carroll assumed that the sample temperature remains uniform during heating and that an n th order rate law applies. Appropriate manipulation of the rate equation then resulted in the relation

$$-\frac{E}{R}\left[\frac{\Delta(+)}{\Delta \ln(\frac{N}{N_{o}})}\right] = \left[\frac{\Delta \ln - \frac{1}{N_{o}}\left(\frac{dN}{dt}\right)}{\Delta \ln(\frac{N}{N_{o}})}\right] - n \quad (14)$$

The differences indicated in Equation (14) are taken directly from the weight-temperature curve obtained in the TGA experiment. Freeman and Carroll concluded that a plot of the bracketed terms in Equation (14) should give a straight line such that the slope determines the activation energy, and the intercept yields the reaction order.

Wendlandt (21) has proposed that the theory of Borchardt and Daniels is also applicable to the study of solid decomposition reactions by conventional DTA where stagnant sample and reference materials are used. Wendlandt assumed that n = 1, and further simplified the basic equation

of Borchardt and Daniels to

$$k = \frac{\Delta T}{(A_T - A_t)}$$
(15)

Equation (15), together with the required data from a DTA curve, can then be used to construct an Arrhenius plot which determines the activation energy and frequency factor.

Freeman and Carroll and also Wendlandt applied their respective methods to the dehydration of calcium oxalate monohydrate. In Table 4.5 a comparison is made between the kinetic parameters reported by these investigators and the results obtained in this study by fluid bed DTA. For the comparison, only the average constants for Runs 3, 4, and 5 are given in the table.

The activation energy determined by fluid bed DTA is in good agreement with that obtained by the TGA method of Freeman and Carroll. It is evident that the conventional DTA method of Wendlandt gives an activation energy about 20 per cent higher than either fluid bed DTA or TGA. Both the methods of Freeman and Carroll and that of Wendlandt neglect the temperature gradients which develop in the sample due to heating and reaction. A 10°C/min heating rate was used in both studies. However,

Method	Source	E <u>(kcal/mole)</u>	Z-l	<u>`n</u>
Fluid Bed DTA	This work	22.7	1.78X10 ¹¹	0.42
TGA	Freeman and Carroll (8)	22.0		1.0
Conventional DTA	Wendlandt (21)	27.0	1.52X10 ¹²	1.0 (assumed)

•

Table 4.5. Comparison of Results with Literature Values

from Wendlandt's description of his DTA apparatus, it appears that he used much larger amounts of material than did Freeman and Carroll. Perhaps the higher activation energy obtained by Wendlandt reflects the effect of temperature gradients which were more pronounced in his experiments because of the larger amounts of material used.

The reaction order determined by fluid bed DTA is clearly different from the TGA value reported by Freeman and Carroll. The exact reason for this disagreement is not known; however, Reed, et. al. (16) found experimental scatter can be so large when data is plotted according to the method of Freeman and Carroll that several TGA curves must be used to obtain a reliable value of n. Since Freeman and Carroll analyzed only one TGA curve, it is difficult to be overly confident in the resulting value of n. Certainly, on the basis of the foregoing comparison, there is no reason to suspect that the reaction order determined by fluid bed DTA is grossly in error.

No direct determination of the heat of reaction for the oxalate dehydration could be found in the literature. However, standard heat of formation data* at 25° C can be used to compute a heat of reaction of 9.1 kcal/mole for the reaction

 $CaC_{2}O_{4} \cdot H_{2}O(s) \longrightarrow CaC_{2}O_{4}(s) + H_{2}O(g)$

^{*}Handbook of Chemistry and Physics, 48th ed., Published by Chemical Rubber Co., pp. D-38 to D-51.

The average heat of reaction computed from the experiments summarized in Table 4.3 was 5.93 kcal/mole. It appears then that the heat of reaction obtained by fluid bed DTA is much too low. It is unlikely that significantly better agreement could be obtained by correcting the DTA value to the 25°C reference temperature.

In deriving the basic heat balance equation it was assumed that the rate of heat loss from the material in the cells could be expressed in terms of an overall conductance, K, and the total temperature difference between the cell and heat bath. For unsteady state heat transfer, such a formulation is only an approximation. The cell wall itself may absorb a significant portion of the heat transferred between the heat bath and cell, so that the rate of heat transfer is not simply proportional to the overall temperature difference. The somewhat more detailed development which follows will illustrate exactly how the heat absorbed by the cell wall causes the heat of reaction determined by DTA to be low.

If the thermal resistance of the cell wall is small, its temperature can be assumed uniform at T_W . The rate of heat loss from the material in the reference cell, q, can then be expressed by the two equations

$$q = h_i a_i (T_R - T_W) \tag{16}$$

and

$$q = h_0 a_0 \left(T_W - T_B \right) + q_a \qquad (17)$$

where

- q_a = rate at which heat is accumulated by cell wall, cal/min.

Equations (16) and (17) can be combined to give

$$q = K(T_R - T_B) + \frac{K}{h_o a_o} q_a \qquad (18)$$

where

$$K = \frac{1}{\left[\frac{1}{k_i a_i} + \frac{1}{k_o a_o}\right]}$$

If the inner and outer heat transfer coefficients are nearly equal and the cell wall is not too thick, then

hoao ~ hiai

and therefore

K ~ 1/2

Equation (18) for the rate of heat loss then becomes

g=K(TR-TB)+1/2 ga (19)

The rate at which heat is accumulated by the cell wall is approximately

$$q_a = M_W C_{PW} \frac{dT_W}{dt}$$

where M_W and c_{pW} are the mass and heat capacity of the cell walls, respectively. The wall temperature will be very nearly the average of T_R and T_B so that

$$g_a = \frac{1}{2} M_w c_{pw} \left[\frac{dT_R}{dt} + \frac{dT_B}{dt} \right]$$

Equation (19) for the rate of heat loss from the cell then becomes

$$q = K(T_R - T_B) + \frac{1}{4} M_W c_{pW} \left[\frac{dT_B}{dt} + \frac{dT_B}{dt} \right]$$
(20)

Using Equation (20) to reformulate the total heat balance for the reference cell results in

$$\left[Mc_{p} + \frac{1}{4}Mwc_{pw}\right]\frac{dT_{P}}{dt} = Mgc_{pg}(T_{6}-T_{R})_{(21)}$$

The same procedure repeated for the sample cell gives

$$[Mc_{p} + \frac{1}{4}Mw c_{pn}] \frac{dT_{s}}{dt} = Mgc_{pg}(T_{o} - T_{s})$$
$$-K(T_{s} - T_{B}) - \frac{1}{4}Mw c_{pn} \frac{dT_{B}}{dt} + r(-\Delta H_{r})^{(22)}$$

Subtracting Equation (21) from Equation (22) to obtain the differential equation which describes the DTA curve gives

 $r(-\Delta H_{x}) = (M c_{p} + \frac{1}{4} M_{W} c_{pW}) \frac{d \Delta T}{dt}$ + (K+ mg cpg) AT (23)

Equation (23) has the same form as Equation (4) which was used to analyze the experimental DTA curves. The important difference is that Equation (23) also includes a term involving the heat capacity of the cell wall. This equation suggests that, to account for the heat absorbed or released by the cell wall, the parameter δ should be redefined as

 $\delta = \frac{\left[Mc_{p} + \frac{1}{4}MwC_{pw}\right]}{\left(-\Delta H_{n}\right)N_{o}}$

The reason for the apparent error in the heats of reaction determined by fluid bed DTA is now obvious. § is determined directly from an experimental DTA curve, and its value does not depend on how it is defined. However, the value of ΔH_r computed from the definition of § will always be low unless the wall heat capacity is taken into account.

Because of the simplifications made in the above

derivation, the modified definition of δ probably does not represent the cell wall effect well enough to permit accurate determinations of the heat of reaction. Reliable values of the heat of reaction might be obtained if the cells are constructed so that the mass of the cell walls is completely negligible compared to the mass of solids contained in the cells. This was not the case in the present experiments. For 4.00 gm of aluminum oxide at 140°C, $Mc_n = 1.00 \text{ cal/}^{\circ}C$. Based on a 1.0 in. fluid bed height and an 0.05 in. cell wall thickness, $M_W c_{pW} = 1.20 \text{ cal/}^{\circ}C$. Using these values in the modified definition of δ , the average heat of reaction becomes 7.7 kcal/mole. This value is still about 15 per cent lower than that computed from heat of formation data, but it is important to note that correction for the wall effect has resulted in a heat of reaction considerably higher than the 5.93 kcal/mole which was obtained previously.

The heat of reaction need not be known to carry out a kinetic study by DTA. However, with some additional experiments it may be possible to determine an accurate value for this parameter. A series of DTA thermograms can be obtained with varying amounts of some standard material for which the heat of reaction is well known. These data, plotted in the form of Equation (7), can then be used to determine the cell heat transfer coefficient. The data from another series of thermograms made with the material for which the heat of reaction is unknown can again be plotted according to Equation (?). This plot, together with the known heat transfer coefficient, can then be used to determine the unknown heat of reaction. Borchardt and Daniels used a similar procedure with apparent success. Since the heat of reaction and heat transfer coefficient will be somewhat temperature dependent, correct application of the above method will require the availability of a standard material which decomposes over very nearly the same temperature interval as does the test material. Especially at higher temperatures, where the fluid bed DTA method is likely to prove most useful, such a standard material may not always be available.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

From a practical standpoint it is possible to obtain fluid bed DTA thermograms which are suitable for quantitative analysis. The experimental scheme which was successfully employed in this study consisted of a fluid bed heat bath, fluid bed DTA cells, and a standard DTA unit to perform temperature programming and recording functions. Provided that good fluidization performance is maintained in the heat bath, the fluid bed technique is no more difficult to carry out experimentally than standard DTA.

Since standard DTA equipment can be adapted for use in the fluid bed method, any laboratory equipped with a good DTA unit can conduct fluid bed DTA experiments with little additional cost and effort. Wendlandt (20) has developed an inexpensive temperature programming system for use in standard DTA. If a standard DTA unit is not available, it may be possible to adapt Wendlandt's system for temperature control of a fluid bed heat bath. In this case, the only additional equipment required for fluid bed DTA would be a good amplifier and recorder.

A serious limitation on the usefulness of fluid bed

DTA arises from the requirement that the particle size of the solid reactant be suitable for fluidization. Many materials of interest occur only as fine powders, and at gas rates high enough to promote good solids circulation, such materials cannot be retained in the fluidized DTA cells without significant loss during the experiment. In the case of calcium oxalate monohydrate, it was possible to increase the particle size by recrystallizing the material from an acid solution. This procedure will not always be applicable, but other techniques for rendering the material suitable for fluidization suggest themselves. For example, some fine powders are conveniently pelletized. The pellets might then be crushed to obtain particles having the size required for In other cases it will be feasible to impregfluidization. nate a fluidizing, inert solid with a solution of the reactant to be studied, much in the same way that certain catalysts are prepared. In any case, when working with very fine materials, some method for physically keeping the reactant in the DTA cell must be found before fluid bed DTA can be considered for a kinetic study.

Experimental DTA curves are accurately described by a simple theory which assumes gas-solid temperature equilibrium and temperature uniformity in the fluid bed DTA cells. Important features predicted by this theory were verified by detailed examination of a number of thermograms

for the dehydration of calcium oxalate monohydrate. Furthermore, meaningful kinetic parameters can be computed from the experimental curves by suitable numerical analysis. Activation energies determined by fluid bed DTA were found to be in very good agreement with the activation energy obtained by the TGA method of Freeman and Carroll. Maximum reproducibility and reliability of the fluid bed method is achieved by employing high initial reactant concentrations and high heating rates.

The walls of the DTA cells contribute an interfering heat effect which makes it difficult to reliably compute the heat of reaction from a single DTA curve. The thermal capacitance of the cell wall and solids contained in the cells are approximately additive so that the wall effect can be minimized by constructing the cells of thin-walled tubing. The heat of reaction is not needed to compute kinetic parameters from the experimental DTA curves. However, if a very accurate value for the heat of reaction is desired, the calibration procedure of Borchardt and Daniels should be used.

The experimental work with the oxalate dehydration was sufficient to demonstrate the feasibility of using fluid bed DTA to study the kinetics of simple decomposition reactions. However, it should not be too difficult to apply

the method to certain other reaction systems which have the general form

A(solid) + B(gas) _____ gaseous and/or solid products

These reactions are of great industrial importance and include such varied processes as the combustion of solid fuels, the roasting and smelting of ores, the regeneration of catalysts, and the chemisorption of gases on solid adsorbents.

Despite the importance of gas-solid reactions, there have been relatively few conclusive experimental studies involving such heterogenous noncatalytic systems. Partly, this is due to the difficulty of isolating such purely physical effects as diffusion and gas-solid heat transfer from the chemical kinetics. However, because of the small particle size and efficient convective heat and mass transfer encountered in fluidization, these physical limitations will often be eliminated in a kinetic study by fluid bed DTA.

Many investigators, for example Gilliland (10) and Handlos (11), have studied gas mixing in fluidized beds. Their experiments show that the gas flow pattern approaches that of perfect mixing as the solid particle size and fluid bed height to diameter ratio decrease. This is, of course, an important result as concerns the application of fluid

bed DTA to the study of gas-solid reactions. Under the conditions of perfect mixing and uniform temperature, the rate of a gas-solid reaction will also be uniform throughout the DTA cell. As a result, all of the equations previously derived for a simple decomposition reaction are also valid for the case of a gas-solid reaction. No doubt, many problems will arise in such an application of fluid bed DTA. If successful, however it would prove to be an interesting and extremely useful extension of the DTA method.

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APPENDIX .

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APPENDIX A

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NOMENCLATURE

Α	area under the DTA curve			
a	heat transfer area of the DTA cell			
cp	constant pressure heat capacity			
E	activation energy			
h	film heat transfer coefficient for the DTA cell			
∆H _r	heat of reaction			
К	overall heat transfer coefficient for the DTA cell			
k	reaction rate constant			
М	mass of solids in the DTA cell			
mg	flow rate of fluidizing gas			
N	moles of solid reactant			
n	reaction order			
q	rate of heat loss from the DTA cell			
R	ideal gas constant			
r	rate of reaction			
S	total surface area of the reactant-product interface			
Т	temperature			
t	time			
ΔT	differential temperature			
v	volume of the DTA cell			
Z	frequency factor			
8	parameter defined by Equation (8)			

e fraction of voids in the fluidized DTA cell

 ρ density

.

Subscripts:

.

В	heat bath				
С	constant value reached after large time interval				
g	gas ,				
0	gas entering DTA cell				
0	initial value				
R	reference cell				
S	sample cell				
t	function of time				
т	total area under DTA curve				
W	cell wall				
∞	value computed after large time interval				

.

APPENDIX B

CALIBRATION DATA



Figure B.l. Reference Thermocouple Calibration



Figure B.2. Nitrogen Flowmeter Calibration

	emf with respect to Reference Thermocouple $(\mathcal{AN},)$					
TC no.	T _{bath} =100.0 °C	T _{bath} =184.4 °C				
).	-32	-32				
2	- 2	+ 1				
3	-13	-70				
4	· - 1	+ 2				
5	- 1	- 1				
6	-10	-12				
7	+ 2	+ 4				
8	+12	+20				

.

Table B.1 Differential Thermocouple Calibration

APPENDIX C

MARQUARDT'S METHOD

Briefly, the general parameter estimation problem consists of fitting some mathematical model which contains the unknown parameters to a set of measured data. In matrix notation* this model can be written as

$$\gamma = f(\underline{5}, \underline{B})$$

where $\underline{\xi}$ is the vector of independent variables such as temperature, concentration or pressure, and $\underline{\beta}$ is a k x l vector of the parameters to be estimated. The usual criterion used when adjusting $\underline{\beta}$ so that the model will give a good representation of the observed data is to choose the parameter values which minimize the sum of residuals

$$\Phi(\underline{\beta}) = \sum_{k=1}^{m} \left[f_{jk} - f(\underline{\beta}, \underline{\beta}) \right]^2 \quad (C-1)$$

where y_u is the value of y measured for the u th experiment, and is the total number of measurements taken. To find the least squares estimates of $\underline{\beta}$ Equation (C-1) can be differentiated with respect to each $\beta_{\underline{c}}$ and the derivatives set equal to zero. If the assumed model is linear in each of the para-

^{*}Variables underlined with a single bar are vectors. Variables underlined with a double bar are matrices.

meters, the result is a system of k linear equations which are easily solved for the unknown parameters. However, if the model is not linear, taking the derivatives of $\oint (\underline{\beta})$ will generate a system of non-linear equations which, in general, must be solved by some iterative technique. Thus, the numerical aspects of non-linear parameter estimation theory are primarily concerned with developing efficient schemes for finding the minimum of the least squares function, $\oint (\underline{\beta})$.

One accepted solution to the problem involves making a Taylor series expansion of the assumed model about a set of parameter values. If only the linear terms in the expansion are retained, this procedure will generate a system of linear equations which, given an initial estimate of β , are solved iteratively to give successively better approximations to the parameters. This linearization method converges rapidly if the initial parameter estimates are near the minimum of $\overline{\Phi}(\hat{F})$; otherwise, the method diverges.

An entirely different approach to finding the parameter values which will minimize $\overline{\Phi}(\underline{\beta})$ can be visualized by considering the sum of squares function to be a surface in a space where the parameters are variable. The minimum of $\overline{\Phi}(\underline{\beta})$ is then found by some form of the gradient search method, wherein corrections to the parameters are always made in the direction

of steepest descent on the sum of squares surface. In theory this method converges for all problems, regardless of the initial parameter estimates. Convergence is extremely slow, however, as the minimum of $\overline{\Phi}(\underline{\beta})$ is approached.

A non-linear parameter estimation method developed by Marquardt(15) combines the best features of the linearization method and the steepest descent method but avoids the chief limitations of both. According to Marquardt's algorithm, successively better approximations to the parameters are computed from the relation

$$\underline{B}^{(n)} = \underline{B}^{(n-1)} + \left(\underline{X}^{T} \cdot \underline{X} + 2 \underline{I}\right) \cdot \left(\underline{X}^{T} \cdot \underline{Z}\right) \quad (C-2)$$

where X is an m x k matrix of the derivatives

$$X_{u,i} = \begin{bmatrix} \frac{\partial f(\underline{x}_{u}, \underline{\beta})}{\partial \beta_{i}} \end{bmatrix} \begin{pmatrix} i = 1 \dots k, \\ n = 1 \dots m \end{pmatrix}$$

$$p = \underline{\beta}^{(n)} \quad n = 1 \dots m$$

and \underline{Z} is an m x l vector whose general element is computed from

$$Z_{\mathcal{M}} = \left[\gamma_{\mathcal{M}} - f\left(\frac{\beta}{m}, \beta^{(n)}\right) \right] (\mathcal{M} = 1, \dots, m)$$

At each step in the iterative procedure λ is chosen in prescribed fashion as follows:
Let $\gamma > 1$

Let $\lambda^{(n-1)}$ denote the value of λ from the previous iteraion (Marquardt suggests $\lambda^{(o)} = 10^{-2}$).

Compute
$$\overline{\Phi}(\lambda^{(n-1)})$$
 and $\overline{\Phi}(\lambda^{(n-1)})$
1. If $\overline{\Phi}(\lambda^{(n-1)}) \leq \overline{\Phi}^{(n)}$, let $\lambda^{(n)} = \lambda^{(n-1)}/\gamma$.
2. If $\overline{\Phi}(\lambda^{(n-1)}/\gamma) > \overline{\Phi}^{(n)}$, and $\overline{\Phi}(\lambda^{(n-1)}) \leq \overline{\Phi}^{(n)}$, let $\lambda^{(n)} = \lambda^{(n-1)}$.
3. If $\overline{\Phi}(\lambda^{(n-1)}/\gamma) > \overline{\Phi}^{(n)}$, and $\overline{\Phi}(\lambda^{(n-1)}) > \overline{\Phi}^{(n)}$ increase λ by successive multiplication by γ until for some smallest ψ , $\overline{\Phi}(\lambda^{(n-1)}) \leq \overline{\Phi}^{(n)}$. Then let $\lambda^{(n)} = \lambda^{(n-1)}/\gamma$.

According to the foregoing strategy, λ decreases if the calculations are converging, i.e. if Φ is decreasing. For small λ Equation (C-2) reduces to the linearization method, and thus rapid convergence is assured near the minimum of the least squares surface. On the other hand, if the iterative process is diverging, λ is automatically increased. Since $\underline{X}^{T} \cdot \underline{Z}$ is the vector of steepest descent on the least squares surface, Equation (C-2) reduces to the gradient search method for large λ , and thus convergence is assured even if the initial guess of parameters is beyond the range of convergence of the linearization technique.

The calculations required to derive kinetic parameters from DTA curves were programmed in Fortran IV for an SDS . Sigma 7 computer. Program listings are included in this section, together with some computed results for Run 4.

The main program receives the necessary input data and calculates reaction rates as outlined in Chapter IV. Numerical integration and differentiation of the DTA peaks are done by subroutines INT and DER. The rate data is then passed to subroutine BSOLVE* where Marquardt's method is used to compute the activation energy, frequency factor and reaction order. Subroutine DERIV computes elements of the \underline{X} matrix as requested by BSOLVE. For the rate equation

$$\lambda = A \cdot e^{-\frac{E}{RT_{s}}} \left(\frac{N}{N_{o}}\right)^{m}$$

the required derivatives are computed as follows:

$$X_{m_{1}} = \left(\frac{\partial x_{m}}{\partial A}\right) = e^{-\frac{E}{RT_{su}}} \left(\frac{N}{N_{o}}\right)_{m}^{m}$$

$$X_{m_{2}} = \left(\frac{\partial x_{m}}{\partial E}\right) = -\frac{A}{RT_{m}} e^{-\frac{E}{RT_{su}}} \left(\frac{N}{N_{o}}\right)_{m}^{m}$$

$$X_{m_{3}} = \left(\frac{\partial x_{m}}{\partial M}\right) = A e^{-\frac{E}{RT_{su}}} \left(\frac{N}{N_{o}}\right)_{m}^{m} \cdot \ln\left(\frac{N}{N_{o}}\right)_{m}^{m}$$

Subroutine FUNC returns functional values

$$r_{n} = A e^{-\frac{E}{RT_{SN}}} \left(\frac{N}{N_{o}}\right)_{n}^{M}$$

^{*}This subprogram was adapted from a program written by Dr. W. E. Ball, Washington University, St. Louis, Missouri.

used in computing elements of the \underline{Z} vector and the least squares function, $\overline{\Phi}$.

:

	WELLCTT DEAL +STANDA 71	103
-		
	EXTERNAL FUNCIPERIVIARUUS	
		<u>),</u>
	1RK(100);X(100);Y(100);NREACT(9);NINERT(9);NGAS(9)	
	DIMENSION B(10), Z(100), DUMMY1(100), DUMMY2(100), IBCODE(10),	
	18MIN(10), BMAX(10)	
C		
č.	LARREREESE STAN INDIT DAYA BELEREESEESEESEESEESEESEESEESEESEESEESEESEE	
č	ANANYANANANANANANANANANANANANANANANANAN	7 # 7 # * * *
100	READ(5)500) (NREACIVI)/191/9)	
	READ(5,500)_(NINERT(I),I=1,9)	
	READ(52500) (NGAS(I)) I=129)	
500	FORMAT (9A4)	
	READ(5,501) NRUN	
	READ(5,501) N, NRI, NR2, NC1, NC2	
501	FARMAT (5110)	
	READIS, 5021 H.SE.TH.TINC.DTC	
502	EADMAT/5015.51	
202	DEVOLE EVOL END DIT TH	
	READ(5)5021 SMM/RMM/GMM/GD	
	READ(5,502) (DI(1), I=1, N)	
C	******	* * * * * * *
	DTC=SF*DTC	
	Q(1)≓0,000D+00	
	DT(1)=SF*DT(1)	
	TR(1)=T0+DTC	
	00 9 1=2/N	
	Q(I)=D(I=1)+H	
	DT(I)=SF*DT(I)	
	TR(I)=TR(I=1)+TINC	
9	CONTINUE	
С	tenne 🍸 en ge ge ² an men mendendede die die die die die die die die die	
č	******************* PRINT INPUT NATA ***********************	* * * * * * * *
<u> </u>		
C	WRITE(6.601) NRUN	
601	EARMAT (141 A1X A TAPHIT DATA - RUN NR. 1.15///)	
001	write(4,400) (Nreact(1), t=1.9)	
602	EARMATIANY TREACTING CHROMANCE I AAA //	
002	$\frac{1}{2} = \frac{1}{2} = \frac{1}$	
	WRITE VOIGUST VINERI (17)1=1797	
603	FORMATIONS/INCRE REFERENCE SUBSTANLE='J9A4J/)	
·/··	WRILE(6)604) (NGAS(1),1=1,9)	
604	FORMAT(10X) 'FLUIDIZING GAS='/9A4////	
	NR = (NR2 = NR1) +1	
	ARITE(6,605) N/NRI/NR2/NC1/NC2	
605	FORMAT(10x, IND. OF DATA POINTS = 1,15,/,10x, IFIRST DATA PO	INT USED
	119 CALCULATE KINETIC PARAMETERS = 1,15,/,10X,1LAST DATA POI	NT USED
	279 CALCULATE KINETIC PARAMETERS= 1,15,/,10X,1 FIRST DATA P	BINT USE
	3019 CALCULATE CELL HEAT TRANSFER COEFFICIENT= 1,15,/,10x,11	LAST DAT
	4A POINT USED TO CALCULATE CELL HEAT TRANSFER COFFFICIENT =	1.15,//)
	WRITE(6,606) SM, RN9, GM, PHI, TM	
605	FORMAT(10X, WEIGHT OF INERT REFERENCE= 1.D12.5.1 GRAMS1./.	1 A X .
	11 INITIAL WT. OF REACTANTE LADI2.5. GRAMS! . /. 10X. IGAS FLAW	RATE 1
	2.012.5. 1 STD CC/MINI. /. 108. THEATING RATE = 1.012.5.1 DEG C	ZMINIA
	3 /10X, MEAN TEMPERATURE = 1.012.5. 1 DEG C1.///)	
	= 2012402 + 000 = 2012402 + 000 = 2010402 + 000 = 0000 = 000 = 000 = 000 = 000 = 000 = 000 = 000 = 000 = 000 = 000 = 000 = 000 = 0000 = 0000 = 0000 = 0000 = 0000 = 0000 = 0000 = 0000 = 0000 = 0000	
607-	EADMATING AVEN PORTA DATA DATATO TAKINI PORM DTA CUDURAL ACORY A	TIME
007	- FUNNALIZIZAT DATA FUINTO TANEN FRUM DIA LURVESTTATZAZIT 2478-1011-408-1101-2-008-124101-248 12000 011 408 12000 01	1 1 1 1 E 1
*** ********	C1/A/ UI'JIAA/ 'IK'J/JC8A) '(MIN/'J14A) '(UEG C) 'J13A) '(UEU C)	12///
	$\frac{1}{2} \left(\frac{1}{2} \right) = \frac{1}{2} \left(\frac{1}{2} \right) = \frac{1}$	
008	- FJKMAI(15X)JU24+7)	
	1M31M+d/d0160+00	
	DU & I=1+N	

		•
	$TR(1) = TR(1) + 2/3 \cdot 16D + 00$	3.04
<u> </u>		104
	SMESM/SMW	
 . 		
~	RNJ=RNU/RMW	
c c	ANALALALA CALCOLATE HEAT CAPACITIES AT MEAN TEMPERATURE	*****
- <u>c</u>		
C	CPS=2.2080+01+8.9710-03*TM-5225.00+02/TM-*2	
	CPG=6+4570+00+1+3890=03*TM=0+0690=06*TM**2	
C		
~~c~~~~~		
č	CALCULATE AND PRINT SAMPLE TEMPERATURES. AREAS. AND DERIV	VATIVES
C		· · · · · · · · · · · · · · · · · · ·
č		
	DB 10 1=1,N	<u> </u>
	TS(I) = TR(I) + DT(I)	
10	CONTINUE	
	CALL INTIDT, AREA, H, N)	
	CALL DER(DT,DTD,H,N)	
	WRITE(6,609)	
609	FORMAT(1H1,25X, 'TIME', 18X, 'DT', 18X, 'TS', 16X, 'AREA', 17X, 'I	DTD11///)
	WRITE(6,610) (D(I), DT(I), TS(I), AREA(I), DTD(I), I=1,N)	
610	FORMAT(10X,5D20.7)	
_C	**********	****
ç		
<u></u>	DETERMINE DELTA FROM COOLING PORTION OF CURVE	و المراجع الم
C		
		·····
	NN-NC2-1+1	
		· · · · · · · · · · · · · · · · · · ·
•	$Y(T) = 1 \cdot 000 + 00 - AREA(NN) / AREA(N)$	
80	CANTINUE	
•••	CALL LSOR1 (X+Y+DFLTA+NC)	
	WRITE(6,618) DELTA	
618	FORMAT(1H1,9X, 'DELTA= ', D15+5,//)	
	HR==(SM*CPS)7(DELTA*RN0)	
	WRITE(6,616) HR	
616	FORMATIIOX, HEAT OF REACTION= 1015.7. CAL/GM=MOLE'///)	
	HK=-HR*RNO/AREA(N)-GM*CPG	
	WRITE (6,615) HK	•
615	FORMAT(10X, ICELL HEAT TRANSFER COEFFICIENT: 1, D15.7, ' CAL	_/MIN DEG
_	101,///)	
<u> </u>		
	CHECK FIL LA CAALING PARILAN AF CORVE	
619	$= RRRAT(//.17X,DT),SY,I(I-A/T)/AT)I,SY,I(I-A/T)/AT)I,I\mathcal{P}Y,I(I-A/T)/AT)I,I\mathcal{P}Y,I(I-A/T)/AT)I,I\mathcal{P}Y,I(I-A/T)/AT)I,I\mathcal{P}Y,I(I-A/T)/AT)I,I\mathcal{P}Y,I(I-A/T)/AT)I,I(I-A/T)/I,I(I-A/T)/I)I,I(I-A/T)/I,I(I-A/T)/I,I(I-A/T)/I)$	IDEVI+//.
	132X + FXPI - 11X - CALCI - 2)	
	SUM=0+00	
	DA 30 I=1.NC	
	YC=DELTA*X(I)	
	DEV=Y(I)+YC	
	SUM=SUM+DEV *DEV	
	WRITE(6,620) X(1),Y(1),YC,DEV	· · · · · · · · · · · · · · · · · · ·
620.	FORMAT(3X, 4D15+5)	
30	CONTINUE	
	SUM=DSGRT(SUM)/FLOAT(NC)	
	WRITE (6, 621) SUM	
621	FORMAT(//,10X, 'RMS DEV = +,D15,5,/)	

с с_ с	CALCULATE REACTION RATES AND REACTANT CONCENTRATIONS 105
•	
	DR 40 I=NR1+NR2
	V(X,R) = DETTA = DT(T) + DT(T) / A REA(X)
	$\frac{1}{1} \frac{1}{1} \frac{1}$
	DUMPTENNE / TEUDUTUUTUUTUUTIATUINTAREA(I)/AREA(N)/
<u>40</u>	
<u> </u>	INITIALIZE PARAMETERS FOR MARQUARDI'S METHOD
Ç	
	K=3
	INDEX=0
	<u>KP1=4</u>
	ENU=0+00D+00
	FLAMDA=0:00D+00
	TAU=0.00D+00
	EPSILN=0:00D+00
	PHIMIN=0:00D+00
	B(1)=1=000+16
	B(2)=2:500D+4
	B(3)=1+000D+00
	DA 50 1=1,K
	TBC0DE(I)==1
	BMIN(1)=0.00D+00
ອິດ	CANTINUE
	BMAX(1)=1.00D+20
	BMAX(2)=1.00D+05
	BMAX(3)+5,000+00
c	DURY (D / * D # D OD * 4 D
č	APPLY MAPOLARDITE ITEPATTAN UNTIL CANVEDOENCE
	ANTER PARADANDERS TIERATION DIALTE CONVERGENCE
40	
6 V	CALL REPLACE /K.R. NO. 7. V. CÚMER CULLE [®] ANDA ⁻ TALL CROTLAN RUTATA
	LALL DOULVE AND AND AND ADD SWIP AUTELANDA, LAUTEPSTENTHIMINA A ADEV. KADE DEMMYA, DEMMYA - DEADE DMAN DMAN KDA ELNE DEDAU ADDOOL
	TINDEXTRUETOUNTTITUUNHTZTICCODETBUINTBUAXIKPITFUNCTUERIVIARCOST
(WRITE (6/622) INDEX
622	FORMATTINI, MA OF TIERATIONS FOR CONVERGENCE= 1, 15,//)
	WRITE(6,623) (5(1),I=1,K)
623	FORMAI(//,10X,'Z=',D10+4,/,10X,'E=',D10+4,/,10X,'N=',D10+4,//)
	WRITE(6,624)
624	FORMAT(//,18X, 'TS',9X, '(N/NO)',7X, 'EXP RATE',6X, 'CALC RATE',/)
	WRITE(6,625) (DUMMY1(I),DUMMY2(I),Y(I),Z(I),I=1,NR)
625	FORMAT(5X,4D15+5)
	G8 T9 100
	END

	-
	SUBROUTINE INT(Y,Z,H,N)
	IMPLICIT REAL +8(A-H, 8-2)
	DIMENSION Y(100).Z(100)
C	THIS SUBROUTINE CALCULATES THE INTEGRAL HE & TABULATED FUNCTION
С	BETWEEN THE INITIAL VALUE AND FACH TABULATED VALUE BY DEPENTED
°C · · · · ·	APPLICATION OF SIMPSONIS DUE
č	Y=FUNCTIAN VALUE
č	H=INTERVAL OF TABULATION
č	7=INTEGRAL AT THE EUNETIAN VALUE. Y
	7(1)=0.000+00
	7(2)=0.50D+00+H*(Y(1)+Y(2))
	NN=N=2
	7/1+2)=+33333333333333333333333333333333333
10	CB/LIMIE CB/LIMIE
10	
	7/1+21 222222222222222222222222222222222
20	Z(1+2/++3222222222222222220+00*H*(+(1/+4+0D+00*+(1+1)++(1+5))+Z(1)
20	
	ENU

	SUBROUTINE DER(Y,Z,H,N)
	IMPLICIT REAL +8(A-H, 0-Z)
	DIMENSION Y(100), Z(100)
С	THIS SUBROUTINE CALCULATES THE DERIVATIVE OF A TABULATED FUNCTION
С	USING FIVE PUINT DIFFERENCE FORMULAS
C	Y=FUNCTION VALUE
С	H=INTERVAL OF TABULATION
C	Z=DERIVATIVE AT FUNCTION VALUE,Y
	XX=1+/(12+*H)
	2(1)=XX*(-25**Y(1)+48**Y(2)-36**Y(3)+16**Y(4)-3*Y(5))
	Z(2)=XX*(=3**Y(1)=10**Y(2)+18**Y(3)=6**Y(4)+Y(5))
	NN=N=2
	D8 10 I=3,NN
	$Z(I) = X \times (Y(I = 2) - 8 \cdot Y(I = 1) + 8 \cdot Y(I + 1) - Y(I + 2))$
10	CONTINUE
	Z(NN+1) = XX*(-Y(N-4)+6*Y(N-3)-18*Y(N-2)+10*Y(N-1)+3*Y(N))
	Z(N)=XX*(3e*Y(N=4)=16e*Y(N=3)+36e*Y(N=2)=48e*Y(N=1)+25e*Y(N))
	RETURN
	ÉND -

-

	IMPLICIT REAL *8 (A +H, 0 - Z) DIMENSION X(100), Y(100)
•	THIS SUBROUTINE CALCULATES B1 FOR A LEAST SQURES FIT OF THE FORM
	Y = B1 * X
	SUM1=0:00D+00
	SUM2=0+00D+00
	D8 10 I=1,N
	SUM1=SUM1+X(I)*Y(I)
	SUM2=SUM2+X(I)*X(I)
.0	CONTINUE
	B1=SUM1/SUM2
	RETURN
	END
	-

	SUBRAUTINE	BSOLVE (K.B.N.7.Y.PHT.ENU.FLAMDA.TAU.EPSTIN. PHIMIN.
	1 INDEX KODE	, DUMMY1, DUMMY2, 13CODF, BMIN, BMAX, KP1, FUNC, DERIV, ARCOS)
	IMPLICIT R	$EAL * \delta(A-H_2 \theta = Z)$
С		
С		
Ç	K	= NUMBER OF UNKNOWNS - INPUT
C	B(I)	= VECTOR OF UNKNOWNS - DIMENSION K
C		ON FIRST ENTRY + ORIGINAL ESTIMATES - INPUT
<u>ل</u>		UN FINAL EXIT = ANSWERS = BUTPUT
c	N	THE ANDUR OF EQUATIONS - MUST BE OREATER THAN OR EQUAL
č	7(1)	= VECTOR OF FUNCTIONAL VALUES - DIMENSION N - OUTPUT
c	2.147	DESTRE $Z(T) = Y(T)$
C	Y(I)	= VECTOR OF GIVEN VALUES . DIMENSION N . INPUT
С	PHI	= FUNCTION TO BE MINIMIZED = SUM OF (Y(I)=Z(I))**2
C	•••	OUTPUT
C	FNU	= NU FACTOR (SET TO 10.0 IF LESS THAN OR EQUAL TO 0.0)
C	a transformation and the second s	INPUT
<u> </u>	FLAMDA	= LAMBUA FACTOR (SET TO D:01 IF LESS THAN OR EQUAL
c c	TA 11	THE OUT A INPUT
<u>ک</u>		TH OAD A THRUT
č	FPSTIN	= FPSTLAN FACTAR (SET TO 0.00002 TE LESS THAN AR FOUND
C		TO 0.0) - INPUT
Ċ	PHIMIN	= CUT OFF POINT FOR RECALCULATING JACOBIAN MATRIX
C	·	USUALLY MAY BE SET TO D.O - INPUT
<u>C</u>	INDEX	= ITERATION COUNTER = MUST BE INITIALIZED AT ZERO
C		
<u> </u>	KOUE	F NUMBER OF UNKNOWNS NOT SATISFYING THE CONVERGENCE
č		= 0 _ ANSWERS FAIND
č		= -1 - NO FUNCTION IMPROVEMENT POSSIBLE
č		= -2 - MORE UNKNOWNS THAN FUNCTIONS
C		= -3 - TOTAL NUMBER OF VARIABLES IS ZERO
С		= -4 - CORRECTIONS SATISFY CONVERGENCE REQUIREMENT
C	** *	BUT LAMBDA IS STILL LARGE
C	DUMMY1	= DUMMY VECTOR PASSED ON TO DERIV AND FUNC
C C	DUMMY2	= DUMMY VECTOR PASSED ON TO DERIV
~	IBCODEILI	- O BTILLS EVEN
č		= 1 - B(T) IS VARIABLE AND NUMERICAL DERIVATIVES
č	· · · · · · · · · · · · · · · · · · ·	ARE TO BE USED FOR JACOBIAN MATRIX
С		= -1 - B(I) IS VARIABLE AND ANALYTICAL DERIVATIVES
C		ARE TO BE USED FOR JACOBIAN MATRIX . SUBROUTINE
<u>C</u>	BMIN(I)	= MINIMUM VALUES OF B(I) = DIMENSION K = INPUT
C	D	DERIV IS REQUIRED
د د	BMAX(1)	F MAXIMUM VALUES OF B(I) + DIMENSION K + INPUT
c c		- INTÉRNAL CTRRACE VECTROS
с	7574(1)	- TULENNE STORAGE VECTORS
č	AMEGA(1)	•
C	A(IJ)	= INTERNAL STORAGE FOR CORRECTION EQUATIONS
C	DELTA(I)	
C	G(I)	
<u>C</u>	ASCALE(I,J	I = MATRIX COMPOSED OF SCALED A MATRIX AND SCALED
с c		
č	GAMMA	ANGLE IN DEGREES RETWEEN THE MADIFIED NEWTON EADUSAN
č	MACHE A	DIRECTION AND STEEPEST DESCENT DIRECTION
C	ÎTER	= ITERATION COUNTER IN SEARCH FOR LAMODA THAT
C		REDUCES PHI

C	109
č	FUNC = NAME OF SUBRALITINE OF FUNCTIONS TO BE WRITTEN BY
r -	USER - NAME MUST APPEAR IN LEVIEDNALL STATEMENT
r r	IN CALLING PRAGRAM - THIS PALITING MUST ALWAYS
<u>-</u>	RE CHERITED
r	
~~~·	CALL FUNCIK NAA 77 DIMMY1V
č	CHEL FORCKRYNARAELDO HHTY K
с	N = NUMBER OF UNNIVENS = INPUT
r r	N THURDER OF EQUALIONS TINFUL AATTN - VECTOD OF EQUALIONS TINFUL
<u> </u>	$\frac{2711}{7711} = \frac{1}{1000} = $
ĉ	22/17 = VELION OF FUNCTIONAL VALUES # DIFENSION N
c	DURATI DURAT VECTOR TRANSMITTED TO FUNC
	TO DE USED AS DESTRED
с С	
<u> </u>	UERIV = NAME OF SUBROUTINE TO EVALUATE DERIVATIVES IF
	INDICATED BY IDCOUP(I) = #1 = WRITTEN BY USER + NAME
<u> </u>	MUST APPEAR IN 'EXTERNAL' STATEMENT IN LALLING
	PROGRAM
<u> </u>	
	LALL DERIV(JJKINJBBJXXJJTESTJDUMMY1JDUMMY2)
<u> </u>	J = INDEX OF THE VARIABLES FOR WHICH
	DERIVATIVES ARE TO BE CALCULATED - INPUT
<u>.</u>	K = NUMBER OF UNKNOWNS = INPUT
	N = NUMBER OF EQUALIENS - INPUT
	BB(I) = VECTOR OF UNKNOWNS = DIMENSION K = INPUT
	XX(I) = VECTOR OF DERIVATIVES = DIMENSION N
<u> </u>	THIS IS THE J-TH COLUMN OF THE JACOBIAN
C	MATRIX = BUTPUI
	JIEST = INDICATOR TO NOTE IF DERIVATIVES HAVE BEEN
	LALCULATED - IF NOT, A RETURNED VALUE OF
<u>.</u>	-1 WILL CAUSE NUMERICAL DERIVATIVES TO BE
	CALCULATED - OTHERWISE, JTEST = C = OUTPUT
<u> </u>	DUMMY1= DUMMY VECTURS TRANSMITTED TO DERIV TO
	DUMMY2 BE USED AS DESTRED
- <u>C</u>	
	ARCOS = NAME OF FUNCTION SUBPROGRAM TO CALCULATE THE
<u> </u>	ARC COSINE . NAME MUST APPEAR IN AN IEXTERNAL'
C	STATEMENT IN THE CALLING PROGRAM
. <u>C</u>	
	THE CALLING PROGRAM SHOULD CONTAIN THE APPROPRIATE INITIALIZING
ر م	AND 'EXTERNAL' STATEMENTS PRIOR TO EXECUTION OF THIS
	SUBRAUTINE - AFTER EXECUTION OF THIS SUBPROGRAM A CHECK SHOULD
- <u>_</u>	BE MADE ON THE VALUE OF THE OUTPUT VARIABLE TRODET - IF RODE IS
	GREATER THAN ZERA THIS SUBROUTINE SHOULD BE REREXECUTED
- <u>C</u>	
	REFERENCE: MARJUARDI, DANALD W., JAN ALGORITHM FOR LEAST-SCUARES
- <u>_</u>	ESTIMATION OF NONLINEAR PARAMETERS, J. SCC. INCUST.
	APPL MATH VOL 11 NO 2 JUNE 1963
<u> </u>	
	DIMENSION IBLOUE (10), ALPHA (10), $B(10)$ , $ZETA(100)$ , $Z(100)$ ,
	1Y(100), DUMMY1(100), DUMMY2(100), AJACOB(100,10), BMAX(10), BMIN(10),
•	2G(10),A(10,10),UMEGA(10),ASCALE(10,11),DELTA(10)
C	
C .	INITIALIZATION OF TEST AND CORRECTION PARAMETERS
<u>C</u>	
•	IF (FLAMDA+LE+0+00D+00)FLAMDA=0+01D+00
<u>C</u>	
	IF(INDEX:GT.0) G9 T0 300
	IE(FNU+LE+0+COD+00)
· <u> </u>	IF(TAU+LE+C+00D+00) TAU=1+00D=03

	IF (EPSILN.L IF (PHIMIN.L	LE:0:00D+00) EPSILN=2:00D-05 LT:0:00D+00) PHIMIN=0:00D+00	110
Г С   С	COUNT OF B	IS WHICH ARE VARIABLES (NOT FIXED BY INPUT)	
_ C 	KEY=0		
; ;	Q8 100 J=1, 100 IF(1BC8DE(,	#K J) • NE • 0) KEY=KEY+1	
C C	CHECK IF AL	LL VARIABLES ARE FIXED	
C	IF (KEY+GT+C	O) G8 T8 101	
	EXIT - ALL	VARIABLES FIXED	
	KODE = - 3		
		UMBER OF FOUNTIONS TO LESS THAN NUMBED OF UNK	19 IN 6
<u> </u>	101 TEINGERKEN	VI 63 TA 102	
	EXIT - NUMP	BER OF EQUATIONS IS LESS THAN NUMBER OF UNKNOW	ik s
Č	KADE==2		· · · · · · · · · · · · · · · · · · ·
С С	G8 T9 1500		·····
C	102 IF (INDEX.GT	T.O) G9 T8 300	
C	ON FIRST IT	TERATION, STORE BIS (ORIGINAL ESTIMATES) IN AL	РНА
	D9 200 J=1; 200 ALPHA(J)=B(	,K (J)	
	ON FIRST IT	TERATION, CHECK IF BIS (ORIGINAL ESTIMATES) AR	E CORRECT
	G8 T8 90C		
	TEST FOR RE EQUAL TO SO GREATER THA	ECALCULATION OF JACOBIAN MATRIX IF PHI GREATER OME (SPECIFIED) MINIMUM PHI AND ITERATION COUN AN ONE	THAN OR T (INDEX)
C	300 IF(PHIMIN.G	GT+PHI+AND+INDEX+GT+1) G9 T0 400	
C C	CALCULATION	N OF JÁCOBIAN MÁTRIX COLUMN BY COLUMN	
C	D8 307 J=1,	, K	
	CHECK IF B	(J) IS FIXED ER VARIABLE	
	· ĬF(IBC0DE(J	J)) 301,307,303	
	CALCULATION	N OF DERIVATIVES ANALYTICALLY USING SUBROUTINE	DERIV
	301 CALL DERIV	(J:K:N,B,ZETA, JTEST, DUMMY1, DUMMY2)	-
	302 AJAC9B(I)	)=ZETA(I)	
C		NOF DERIVATIVES NUMERICALLY	
Ċ	CALCUENTION	T OF DENITATIVES NUMERICALLY	

		TBCADE(1)=1	
, ,	222		
_ '	3J3		L
		IF (DABS(B(J))+5(+1+00D=04) DEL=1+00D=05	
_		IF (B(J)+DEL+LE+BMAX(J)) G0 T0 304	
		ALPHA(J)=B(J)=DEL	
	304	ALPHA(J)=B(J)+DEL	
	305	CALL FUNC(K)NJALPHAJZETAJDUMMY1JDUMMY2)	
		AI PHA(.1) = B(.1)	
1		Da 308 1=11N	
	306_	AJAC9B(I,J)=(ZLTA(I)-Z(I))/DEL	
	307	CONTINUE	
	r		
	~	CCT UD CODECTION COUNTIONS	
		SET OF CORRECTION EQUATIONS	
	<u>C</u>		
	400	D8 406 LL=1/K	
: (	r i		
	~	CULCY IF PULLY TO VADIABLE AD ETVED	
		CHECK IN DILLY IS VARIABLE OR FIXED	
	C		
		IF(IBCODE(LL)) 401,404,401	
. 1	C		
	~	BULLA TO VADIABLE	
		B(LL) IS VARIABLE	
(	C	· · · · · · · · · · · · · · · · · · ·	
- (	C	CALCULATION OF G VECTOR	
	C		
		C(1) L X 2 - 00D + 00	
	101		
	402	G(LL)=G(LL)+AJAC0B(JJ,LL)*(Y(JJ),Z(JJ))	
. (	C.		
··		CALCULATION RE A MATRIX	
	~	CALCOLATION OF A DATATA	
(	Ç		
		D9 403 JJ=1,K	
		$A(1 + 1, 1) = 0.000 \pm 0.0$	
		DB 403 MM=IIN	
	403	A(LL,JJ)=A(LL,JJ)+AJAC9B(MM,LL)+AJAC8B(MM,JJ)	
		IF (A(LL/LL) • GT • 1 • 00D=70) G8 T8 406	
(	~		
- )	~	DULLA TO ETVEN BU DIACHALL ELEMENT OF A WARDLY TO NEADLY TO DE	
•	-	B(CL) IS FIXED OR DIAGONAL ELEMENT OF A MATRIX IS NEARLY ZERO	
_ (	<u> </u>		
	404	D8 405 JJ=1,K	
	405	A(1 1,1,1)=0.000+00	
		G(LL)=0,00D+C0	
(	C		
	404	CANTINUE	
(	<b>_</b>		
. (	2	CALCULATION OF SQUARE OF NORM OF G VECTOR	
<u> </u>			
	-	GN8RM=0-00D+00	
	407	GNORM=GNORM+G(I)**2	
(	<u>`</u>	•	
7	-	SCALING BE CARRECTIAN SCHATIANS	
····· .	~ ~	SOURTHA AL CAULERIAN CRAVITAD	
(		•	
(	5	CALCULATION OF SQUARE ROOTS OF DIAGONAL FLEMENTS OF A MATRIX	
- (	c		
•	-	DA 500 1-1.K	
·		UB JUV I FIIN	
-	20Q	OMEGA(I)=DSGRT(A(I,I))	
0			
		D8 501 1=1.K	
	~		
	-		

C		SCALING OF G VECTOR	112
<u> </u>		G(1)=G(1)/OMEGA(1)	
Ċ		SCALING OF A MATRIX	
	501	$\frac{1}{1} \frac{1}{1} \frac{1}$	······
C			
		ITER=1 68 T8 503	
с.	502	FLAM#FLAM*FNU	
č ⊂		ADDITION OF LAMBDA FACTOR TO SCALED & MATRIX	
	503 504	D0 504 I=1,K A(I,I)=A(I,I)+FLAM	
C		D8 506 I=1,K	
	505	D8 505 J=1,K ASCALE(I,J)=A(I,J)	
с	506	ASCALE(I,KP1)=G(I)	
¯Ċ C		SOLUTION TO CORRECTION EQUATIONS	······
		D0 603 L=1,K LL=L+1	
-	600	DO 600 M=LL,KP1 ASCALE(L,M)=ASCALE(L,M)/ASCALE(L,L)	
•		D9 603 M=1,K IF(L-M) 601,603,601	
	601 602	DO 602 J=LL,KP1 ASCALE(M,J)=ASCALE(M,J)=ASCALE(L,J)*ASCALE(M,L)	
c	603	CONTINUE	
-с с		LAST COLUMN (K+1) OF ASCALE MATRIX CONTAINS SCALED DELTA VECTOR	
		DLN8RM=0:00D+00 DGPR8D=0:00D+00	
C		D9 701 I=1,K	
C C		CALCULATION OF UNSCALED DELTA VECTOR	
ے 		DELTA(I)=ASCALE(I,KPI)/OMEGA(I)	
<u> </u>		PUT CORRECTED BIS INTO ALPHA	
С 		IF(IBCODE(I)+EQ+0) GO TO 700	
<u> </u>		ALPHA(I)=DMAA1(BMIN(I))DMIN1(BMAX(I))B(I)+DELTA(I)))	
_C	2	CALCULATION OF SQUARE OF NORM OF DELTA VELTOR	
_ <u>c</u> _	/00		
с с		LALUULATION OF PRODULT OF DELTA AND UNSCALED & VELTORS	<u></u>
<u></u>	<u></u>	DGPRBD=DGPRBD+DELIA(I)*G(I)*BMEGA(I)	
С С		REPLACE DELTA'S WITH ACTUAL DIFFERENCES USED	

701	DELTA(I) = ALPHA(I) = B(I)	113
	COSINE GAMMA = (DELTA)(G)/(NORM DELTA)(NORM G)	· · · · · ·
; ; ;	C8SGAM=DGPR0D/(DSGRT(DLN0RM*GN0RM))	n a caso a faaranse so as
	DETERMINATION OF QUADRANT IN WHICH SAMMA LIES	·
· · · · · · · · · · · · · · · · · · ·	JGUAD=1 IF(CBSGAM) 800,801,801	
800	COSGAM=-COSGAM	
	DETERMINATION OF GAMMA IN DEGREES	
801	COSGAM=DMIN1(COSGAM,1.000+00) GAMMA=ARCOS(COSGAM)*1.80D+02/3.14159265D+00 IF(JQUAD.GT.1) GAMMA=1.80D+02-GAMMA	
<u>ج</u>	FUNCTIONAL EVALUATION WITH CORRECTED BIS	
2 C 900	CALL FUNC(K, N, ALPHA, ZETA, DUMMY1, DUMMY2)	
C C C	CALCULATION OF PHI	
C	XPHI=0+00D+00	· <u></u>
901	D0 901 I=1/N xpHI=xpHI+(y(1)=zETA(I))**2	
i U.	CHE I HIEETS CRITE RION OF SUCCESS	
	IF (XPHI .LT . 1. 00D-30) G8 T8 1400	
	SUCCESS CRITERION NOT MET	
i L 	IF(INDEX,GT.0) G0 T0 1000	
	Ge Te 1404	
C C	CHECK IF NEW PHI IS LESS THAN PREVIOUS PHI	
 	IF (XPHI+GE+PHI) GO TO 1300	
C	ÉPSILON TEST	
;	K8DE=0	
_ 1100	IF (DABS (DELTA(I))/(TAU+DABS(ALPHA(I))).GT.EPSILN) KODE = KODE +1 IF (KODE + EG.O) GO TO 1200	
	GAMMA - LAMBDA TEST	
	IF (FLAM.GT.1.00D+00.AND.GAMMA.GT.9.00D+01) KODE==1 G0 T0 1401	`.
	GAMMA - EPSILON TEST	·
_1200_	IF (FLAM.GT.1.00D+00.AND.GAMMA.LE.4.50D+01) KODE==4 G0 T0 1401	
C	ITERATION TO FIND A LAMBDA THAT REDUCES PHI	

21	1300	IF (FLAM+GE+1+00D+08) G8 T8 1301
31		1TER=ITER+1
4		G9 T9 502
51	1301	K9DE=-1
6		G8 T9 1500
71	С	
8 :	1400	K0DE=0
ЭL		IF (INDEX, EQ. 0) G9 T9 1402
0;	С	
11	С	REPLACE LAMBDA WITH NEW VALUE
2:	C	
3:	1401	FLAMDA=FLAM
4:	С	
51	C	REPLACE BIS WITH NEW VALUES
6;	C	
71	1402	D8 1403 1=1.K
81	1403	B(I)=ALPHA(I)
91		
01	С	REPLACE Z'S WITH NEW VALUES
11	<u>C</u>	
2;	14C4	D0 1405 J=1,N
3 ;	1405	Z(J) = ZETA(J)
4:	С	· • •
51	C	REPLACE PHI WITH NEW VALUE
6;	Ç	
71		PHI=XPHI
8 ;	С	
91	<u> </u>	INCREASE ITERATION COUNTER
0:	С	
11		INDEX=INDEX+1
21	С	
3	1500_	
4 :		END

	DIBRANTING DERIVITIK, N. RE. XX. ITERT. DUMMY1. DUMMY21
· · · · · · · · · · · · · · · · · · ·	IMPLICIT REAL*8(A=HJ9=Z)
	DIMENSION BB(10), XX(100), DUMMY1(100), DUMMY2(100)
1	JTEST=0
I	G8 T8 (1,2,3) J
1	D8 10 I=1,N
<b>!</b>	XX(I)=DEXP(-BB(2)/DUMMY1(I))*(DUMMY2(1))**BB(3)
10	CONTINUE
	RETURN
2	D8 20 I=1,N
;	XX(I)=+BB(1)*DEXP(+BB(2)/DUMMY1(I))/DUMMY1(I)*(DUMMY2(I))**B3(3)
20	CONTINUE
	RETURN
3	
<u> </u>	XX(1)=00(1)+DEAP(=00(2)/DUMMY1(1))*(DUMMY2(1))**00(3)*
<u> </u>	
) <u>*</u>	RETURN
' <b>i</b>	<u> </u>
•••••	
	SUBRBUTINE FUNC(KINIAAIZZ, DUMMY1, DUMMY2)
	IMPLICIT REAL * 8 (A-H/9-Z)
	DIMENSION_AA(10), 22(100), DUMMY1(100), DUMMY2(100)
i I	
10	
10	
1	
1 1	EINCTION ACCORS (X)
• I > !	IMPLICIT REAL +8/A+H+8_7
3:	$\frac{1}{10} = \frac{1}{10} $
- <u></u>	$\frac{1}{16} \frac{1}{16} \frac$
5:	1 = 1 = 1 = 1 = 1 = 1 = 1 = 1 = 1 = 1 =
5 :	ARC8s=0.000+00
7:	RETURN
3 5	ARC0S=1+5707963D+00
3	RETURN
0; 10	$ARC \Theta S = DATAN (DS \Theta RT (1 \cdot 00D + 00 - X * X) / X)$
	RETURN
5; 20	WRITE(6,25) X
31_25	FORMAT(1HO, LARGOS ERROR= 1, D15.7)
+ :	G8 18 5
51	END
	· · ·
	·
-	

INPUT C	DATA+RÜN NO+ 4	
	REACTING SUBSTANCE = CALCIUM ØXALATE_MØN9HYDRATE	
· · ·	INERT REFERENCE SUBSTANCE + ALUMINUM OXIDE	
	FLUIDIZING GAS #_NITROGEN	
- '	NO: OF DATA POINTS = 49 FIRST DATA POINT USEDTO CALCULATE KINETIC PARAMETERS= 11 LAST DATA POINT USED TO CALCULATE KINETIC PARAMETERS= 37 FIRST DATA POINT USEDTO CALCULATE CELL HEAT TRANSFER COEFFICIENT= 42 LAST DATA POINT USED TO CALCULATE CELL HEAT TRANSFER COEFFICIENT= 46 WEIGHT OF INERT REFERENCE= .40000D 01 GRAMS	
 · · ·	GAS FLOW RATE = +95000D 03 STD CC/MIN HEATING RATE = +11700D 02 DEG C /MIN MEAN TEMPERATURE = +14000D 03 DEG C	
	· ·	
· · ·		
-		-
400 <b></b>	· · · ·	
••••••		611

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PATA POINTS	S TAKEN FROM DIA_C	URVEJ	117
	TIME		TR
	(MIN)	(DEG C)	(DEG C)
			9916250D C2
	·17100000 00	500000D-01	+1011625D 03
	<u>.3420000000</u>	<u>**8750000D-01</u>	
	•5130000 <u>0</u> 00	-,1125000D 00	·1051625D C3
		1375000D_00	- 1071625D 03
	·85500000 00	1500000D 00	·1091625D 03
		• 1875000D_00	11116250_03
	•1197000D 01	= 2125000D 00	•1131625D 03
		- 21250000 00	
	+15390000 01	- 2875000D 00	
	•20520000 01	=+3375000D 00 =•3876000D 00	1231625D 03
	•22230000 01	# 4250000D 00	•1251625D 03
	·23940200 01	- 4875000D 00	•1271625D 03
	2565000D 01	+ 5375000D 00	12916250 03
	.27360000_01	- 5875000D 00	1311625D C3
	+2907000D 01	-,6375000D 00	<b>1331625D 03</b>
			<b>1</b> 351625D 03
	*3249000D 01	<b>-</b> ,7500000D 00	<b>1371625D 03</b>
		8125000D_00	13916250 03
	·35910000 01	# *8875000D 00	<pre>+1411625D 03</pre>
***		9750000D_00	1431625D 03
	·3933000D 01	-,1087500D 01	1451625D 03
			14/16/50 03
	+42750000 01	- 1497500D 01	14910250 U3
	46170000_01		15316250 03
	+47880000 01	••1887500D 01	+1551625D 03
	•49590000 01	* 2137500D 01	•15716250 03
	.5130000n 01	- 2287500D 01	•1591625D C3
	•53010000 01	- 2475000D 01	16116250 03
	.54720000_01	26250000_01	1631625D C3
	•5643000D 01	2737500D 01	·1651625D 03
	5814000D 01		
	•5985000D 01	-:2825000D 01	·1691625D C3
	•632/000D 01	<b>★</b> •2512500D 01	•1731625D Q3
	<u>•64980000 01</u>	-1387500D 01	1751625D 03
	•66690000 01	= #113/503D 01	17/16/50 03
	•71820000 01		18316250 V3
	.73530000 01	••23750000 00	+10010200 00
	•7524000n 01	-1625000D 00	•1871625D 03
	•76950000 01	=:1125000D 00	18916250'03
	• <b>7</b> 8660000 01	-•500000D-01	19116250 03
	80370000 01	• 1250000D-01	•1931625D C3
	•82080000 01 ·		1951625D 03

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······	. TIME .		.DT		TS	AR	EA	DŢD
	•0000000D 00	•0000000D,	00 _	• 3723225D	03	•0000000D	00	••3106725D 00
	•3420000D 00	- 8750000D-	-01	•3762350D	03	₩₩₩275000De	01	*•1766569D 00
	•5130000D 00 _*6840000D 00	*•1125000D *•1375000D	00 00	•3782100D •3801850D	03	=•3348750D= ••5486250D=	01 01	-•1461988D 00 
	.85500000 00 .1026000D 01	-,1500000 -,18750000	00 00	•3821725D •3841350D	03 03	₹•7980000D+ ₹•1075875D	01 00	.1461988D 00 .1949318D 00
	•1197000D 01 •1368000D 01	+.2125000D	00	•3861100D	03 03	•1432125D	00	=•1401072D 00
	•1539000D 01	• 2625000D	00	•3900600D	03	= • 2244375D	00	r•1340156D 00
	•1881000D 01 •2052000D 01		00		03	• 3241875D	00	
	•2223000D 01	++4250000D	00	•3978975D	03	• 4560000D	00	-•2923977D 00
	•254000D 01	€ • 5375000D	00	• 4017850D	03	• 6220125D	00	₹•34113060 00 ₹•28630600 00
	-•2736000D_01 •2907000D_01		_00 00	+4037350D +4056850D	03_ 03	■•7160625D ■•8229375D	00 00	
	•3078000D 01 •3249000D 01		00/	+4076350D +4095725D	03 03	• • 9340875D • • 1058775D	00 01	-•3289474D 00 -•3654971D 00
	•3420000D 01 •3591000D 01	- 8125000D		+4115100D +4134350D	03	* • 1190587D	01	**3959552D 00
	•3762000D 01	-•9750000D	00 /	•4153475D	03	•1494825D	01	#•6030702D 00

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	•3933000D 01	*•1087500D 01	•4172350D 03	* 1672237D 01	+•5726121D 00
	+4104000D 01	1175000D 01	•4191475D 03	•1865325D 01	-+6274366D 00
	•4275000D 01	+.1312500D 01	,4210100D 03	₹¢2076937D 01	-9259259D 00
_	+4446000D 01	<b>•</b> •14375000 01	•4228350D 03	••2316337D 01	-+1114766D 01
-	•4617000D 01	<b>*</b> •16875000 01	+4246350D 03	<b>*</b> ∗2587087D 01	# • 1157407D 01
	•4788000D 01				1364522D 01
	•4959000D 01	- 2137500D 01	,42818500 03	#•3235462D Q1	••1175682D 01
-	•5130000D 01	••2287500D 01	<b>,</b> 4300350D 03	₹•3618787D 01	••9563840D 00
-	•5301000D 01	2475000D 01	•4318475D 03	₹•4019925D 01	10233920 01
	•5472000D 01	#•2625000D 01	+4336975D 03	■•4463100D 01	<b>••77972710 00</b>
	,5643000D 01	-,2737500D 01	4355850D 03	■•4915537D 01	-+4629630D 00
•	•5814000D 01	2787500D 01	+4375350D 03	<b>*</b> •5395762D 01	#•2680312D_00
	•5985000D 01	• 28250000 01	+43949750 03	*•5868150D 01	-•6091618D-01
	•6156000D 0 <b>1</b>	••2775000D 01	•4415475D 03	₩•6356925D 01	•7797271D 00
	•6327000D 01	<b>■</b> •25125000 01	•4438100D 03	••6805087D 01	•2637671D 01
_	•6498000D 0 <b>1</b>	<b>≠</b> •1887500D 01	•4464350D O3	••7195537D 01	•4355507D 01
	•6669000D_01	••1137500D 01	•4491850D 03	™•7443487D 01	•3594055D 01
	•6840000D 01	<b>••7125000D 00</b>	•4516100D 03	<b>*</b> •7603087D 01	•1778752D 01
	•7011000D 01	-+48750000 00	+538350D 03	e • 7698562D 01	•1023392D 01
	•7182000D 01	33750000 00	•4559850D Q3	<b>■•7774087D 01</b>	•7066277D 00
	•7353000D 01	=.2375000D 00	•4580850D O3	<b>*•7816837D 01</b>	•4995127D 00
	•7524000D 01	+•1625000D 00	•4601600D 03	<b>*</b> •7856737D 01	•3472222D 00
	•7695000D 01	1125000D_00	•4622100D 03	♥•7873837D 01	•3289474D 00
	•7866000D 01	-• 500000D+01	+4642725D 03	#•7894500D 01	•3106725D 00
	•80370000 01	- • 1250000D=01	•4663100D 03	*•78923620 01	•1279240D 00
	•8208000D 01	•0000000D 00	•4683225D 03	<b>≈</b> •7900200D 01	•5482456D=01

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DELTA: ++48331D=01

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	HEAT OF REAC	TION= .53918	99D 04 CAL/GM-MOLE			
	CELL HEAT TR	ANSFER GOEFFICI	ENT2063101D 0	1 CALZMIN DEG C		
	_ DT	(1-A(T)/AT)	_ (1-A(T)/AT)			· ·
		EXP	CĂĹC			
	••11250D 00 ••16250D 00 ••23750D 00 ••33750D 00 -•48750D 00	.33369D-02 .55014D-02 .10552D-01 .159630-01 .25523D-01	.54373D-02 .78538D-02 .11479D-01 .16312D-01 .23561D-01	21003D-02 23524D-02 92672D-03 34858D-03 19616D-02	• • · ·	
	RMS DEV ■	•768720=03				
• -				···	-	
					·	
******				an an Arthur an Indiana a tha an		120

	Z= •7465D 11					
	E= +22070 05		-	<b>.</b>		
	N# •3707D 00					
					արիների հիշինությունը արդերիները, որ հարար օ անդերերումը, հետո տեն ուր տես երելից, հետո ու հար օպտուս ու օ	
	· · ·					
	<b>R</b> •TS	(N/NO)	EXP RATE	CALC RATE		
	•77897D 03	·951920 00	•46990D-01	•36356D=01		
	•78285D 03	942650 00	•57736D=01	.41678D-01		******
	·78672D 03	+93248D 00	+60826D-01	.47693D-01		
	·79062D 03	·92174D 00	.679280-01	•54536D-01		
	•79447D 03	•90907 <u>0</u> 00	•78195D+01	.62115D-01		
	•79835D 03	<b>895290 00</b>	•81874D=01	.706790-01		
	•80222D 03	·880970 00	•88497D-01	·80294D-01		
	•80610D 03	+86502D 00	•94532D=01	.91028D-01		
	•80997D 03	84854D 00	.102920 00	.10303D 00		
	•81382D 03	.82973D QQ	•11260D 00	.11623D 00		
•• •• ••	•817670 03	•81003D 00	•12198D 00	.13089D 00		
	•82150D 03	•78782D 00	13501D 00	.14690D OO		
	•825300_03	_,76366 <u>0</u> _00	.15256D 00	+16433D 00		
	•82905D 03	.73577D 00	•16533D 00	182920 00		
	+83285D Q3	.70710D 00	•179060 00	·20353D 00		
	•83655D 03	•67367D 00	•21089D 00	.22477D 00		
	•84017D 03	•63491D QO	•24216D 00	.24641D 00		
	•84375D 03	•59097D 00	·269540 00	•56850D 00		
······	_•84733D_03	.542520 00	.30487D_00			
	•85080D 03	+487155 00	•32738D_00	.310130 00		
	•85448D 03	<b>,</b> 43138 <u></u> ,00	•33577D 00	.331460 00		
	•858080 03	37154D 00	•36274D 00	·34952D 00		
-	•86176D 03 .	*30850D 00	•36996D 00	·363930 00		
	•86551D 03	•24549D 00	•36889D 00	,373/60 00		
	-86938D 03	·18229D 00	•36579D 00	.37499D 00		
	•873280 03	.120680_00	.360530_00	.360450 00		an a
	·877360 03	.61227n=01	.313570 00	-31518D CO		

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## APPENDIX D

## NUMERICAL GENERATION OF FLUID BED DTA CURVES

Equation (4), the basic heat balance, can be written in the form

$$-\frac{dN}{dt} = \frac{Mc_p}{(-\Delta H_1)} \frac{d\Delta T}{dt} + \frac{(K+m_g c_{pg})}{(-\Delta H_1)} \Delta T \quad (D-1)$$

Assuming an n th order rate law applies, the rate of disappearance of solid reactant is

$$-\frac{dN}{dt} = N_o Z e^{-\frac{E}{RT_s}} \left(\frac{N}{N_o}\right)^m \qquad (D-2)$$

Equation (D-1) and (D-2) combined give

$$\beta \frac{d\Delta T}{dt} + \gamma \Delta T = N_o \mathcal{Z} \mathcal{L} \frac{-\mathcal{L}}{RT_s} \left(\frac{N}{N_o}\right)^{m} \quad (D-3)$$
  
ere  $\beta = \left(\frac{Mc_P}{-\Delta H_A}\right)$ 

whe

$$\gamma = \frac{(K + m_g C_{Pg})}{(-\Delta H_r)}$$

The moles of reactantremaining is given by Equation (12) written in the form

$$N = N_0 - \beta \Delta T - \gamma A_{\pm} \qquad (D-4)$$

When Equation (D-4) is substituted into Equation (D-3) the

result is

$$\frac{d\Delta T}{dt} = \frac{N_0^{l-m} z e^{\frac{-E}{RT}s} [N_0 - \beta \Delta T + \delta A_{\pm}] - \frac{N}{\beta} \Delta T (D-5)}{\beta}$$

Furthermore, the differential temperature and peak area are related by

$$\frac{dA_{t}}{dt} = \Delta T \qquad (D-6)$$

Equations(D-5) and (D-6) form a system of simultaneous differential equations which, together with the appropriate initial and auxiliary conditions, mustbe solved in order to generate theoretical DTA curves. If t=0 is taken as the time at which the first observable temperature deflection occurs, the initial conditions are simply

$$\Delta T = 0$$

$$A_{\pm} = 0$$

A linear heating rate is specified by the condition that

$$T_R = T_{Ro} + \Theta t$$

where  $T_{RO}$  is the reference cell temperature at the initial temperature deflection and  $\Theta$  is the constant heating rate. Due to non-linearity of the system, exact analytical solution of the DTA equations is not possible; however, the equations are easily solved numerically. Primarily because of its simplicity and known error behavior, a fourth order Runge-Kutta integration technique was employed in this study. The entire solution procedure was programmed in Fortran IV, and a listing of the program follows. The calculated results included with the program listing were obtained using the average kinetic parameters obtained from Runs 3, 4 and 5, while the heating rate and initial reactant concentration correspond to those employed in Run 7.

		~	195
11		IMPLICIT_REAL #8(A+H+0+Z)	
21		DIMENSION Y(2),F(2)	
		REAU (5,501)E,2,4 AN, ANO, BETA, GAMMA	
9 i 5 i	50.	READ(DIDUI) IDIPHIIMIUMAX	
.). بر ک			
71	502	READIDIDUE) FREM	
: : 2 :			
01	601	CREMATICHI, SX. IINPUT DATAHI. ///)	
10:		URITE (6.602) F.7. AN. ANA. BETA, GAMMA	
11:	602	$= FRRMAT(10X_*   E = 1 \cdot D15_5 \cdot I - CAL/M31 FL_{*} 10X_*   Z = 1 \cdot D1$	5.5.1 DER MINUTEL
121		1./.10X.1AN= '.D15.5./.10X.1AN8= 1.D15.5.1 GRAMS1.	2, $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ , $10$ ,
131		-2015.5.1_MBLES/DEG_CL//10X+1GAMMAz-1.015.5.1_MBLE	SIDEG MINI. //)
141		WRITE(6,603) TO, HIDMAX, PHI	
15	603		15.5,
161	-	1/,10X, 'TIME INCREMENT= ',D15,5, ' MIN',/,10X, MAXI	MUM TIME = 1,
_171		-2015+5,MIN! , /, 10X, HEATING-RATE=- , D15, 5, 1-DEG-	C/MIN1///)
18;		T0=T0+273+16D+00	
		D=0+000D+00	
20;		AN0=AN0/1+4612D+02	
_21;	·····		
55!		T∓T8	
		DELTA = GAMMA/BETA	
24;		D9 10 I=1,2	
251		<u>Y(I)≡0+00D+00</u>	
201	10		
201		17=V 1017=14,400)	
.30!	604	EROMAT/141.12Y.ITIVEL.15Y.ITPL.15Y.IDFL.15Y.ITCL.	17V. LAREAL OV.
31:	004	11RXT_RATE!.13X/1N/N01.//)	1344, AKEN, 3344
321	200	CONTINUE	
33:		IR=I=Y(2)=273+160±00	
34		XX=1.987D+00#T	
351			
36:		CONFANT/AND	
37;		DN=AN8+Z/DEXP(ZZ)+(C8N)++AN	
38;		WRITE(6,605) DITRIY(2)JTIY(1)JDN2CON	
391	_605_	E0RMAT(7(5X)D12.5))	
40;	300	M=M+1	
41;		CALL RUNGE (MAKAY, FADAH)	
421		IF(K+EG+1) GD 10 15	
431			
44i	10	T=[U+PHI+U+T1C/	
45.i			
40 i 1 •		225C/AA C/11-V/21	
¶/∔_ 0•			•
491		$IF(ANT \bullet I T \bullet C \bullet OD \pm OO) ANT=0 \bullet OD \pm OO$	
50:		CAN=ANT/ANG	
51:		E(2)=1:000D+00/BETA*AN3*Z/EXP(77)*C9N**AN+DELTA*Y	((2)
52;		G8 T9 300	- • • • • • • • • • • • • • • • • • • •
531	17	M=0	
54:		IF (D.GT.DMAX) GO TO 100	
55:		ICOUNT = ICOUNT +1	
56		IF(ICOUNT.EG.IFREG) GO TO 20	
57		G9T0_300	
58	20	ICOUNT=0	
59;		G8T9_200	
60;		END	

			126
1;		SUBRBUTINE_RUNGE(MIKIYIFIXIH)	120
21		IMPLIUII KEAL*O(AFH/0+2) DIMENSIAN SAVEY(SO), PUI(SO), V(S) S(S)	
		GA TA 11.2.3.4451 M	
51	_1		
6;	·	G8 T8 15	
	2	D8_30_J=1,2	
8;		SAVEY(J) = Y(J)	
91		PH1 (J)=F-(J)	
101	20	Y(J)=SAVEY(J)+0+500D+00*H*F(J) CRNTINUC	
12:		UONTINUE	
13		K=1	
14;		G8 T8 15	
151	3	_D0_40_J=1,2	
16;		PHI(J)=PHI(J)+S•000+00+L(J)	
17‡		Y(J)=SAVEY(J)++500D+00*H*F(J)	
181	40	CONTINUE	
131			
201	h	60 10 15 DB 50 1-1-2	
221			
231			**
24	50	CONTINUE	
25;		X=X+0,500D+00*H	
261		K=1	
27:	·····		
201	5	DU 60 J#1/2 N/ 1)-SAVEN/ 1)-(DUT/ 1)-E/ 1)-N/1// 000-00	
	60		
31	00	K=S	
32;	15	CONTINUE	
33‡		RETURN	
34;		END	
			·
·····			
•	<u> </u>		<b></b>
			•

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INPUT DATA:	127
E=22700D_05_CAL/MOLE Z= .17800D_12_PER_MINUTE AN=42000D_00	
ANDE +4000CD OU GRAMS BETA= +•15300D+03 M9LES/DEG_C GAMMAE +•43200D+03 M0LES/DEG MIN	
TEMPERATURE AT BEGINNING OF PEAK=       •90000D 02 DEG C         TIME INCREMENT=       •10000D-01 MIN         MAXIMUM TIME=       •15000D 02 MIN         HEATING RATE=       •90200D 01 DEG C/MIN	
	· · · · · · · · · · · · · · · · · · ·
•	

TIME	TR	DT		<b>T</b> \$-	AF	REA-	RXT-RATE	N/NO
•00000D 00	•90000D 02	•00000D 00	.36316D	03	. 00000D	00	•10611D=04	•10000D 01
	•93606D 02	.=•20019D=01	+36675D	03		•02 ·		•99818D 00 -
•80000D 00	•972160 02		•37034D	03	• 152030	•01	•19496D=04	•99572D 00
120000_01	•10084D 03	##47374D#01	•37394D	03	_==:313300:	•01_	•26188D=04	-•99241D 00-
•16000D 01	•10443D 03	++641720+01	•37753D	03	#+53508D+	•01	•34955D=04	•98797D 00
20000D01	10804D_03	_ <b>=</b> \$85699D+Q1_	•38111D	03-	<b>8</b> 3299D•	•01_	• #6354D=04	-•,98206D-00-
+24000D 01	•11165D 03	=•11349D 00	•38469D	03	122900	00	•61064D=04	•97426D 00
•28000D 01	•115260 03	<b>••14923D 00</b>	•38827D	03	_==1/515D	00	• 79895D = 04	-•96402D 00
•320000 01	•11886D 03	<b>*</b> •19485D 00	•39183D	03	- 243600	00	+10379D#03	•95067D 00
	•12247D 03 .	-•25258D 00	•39538D	03	••332640	00 -	•13382D=03	•93339D 00 -
+40000D 01	•1260 ⁸ D 03		•39892D	03	**44761D	00	•17114D=03	•91120D 00
	•12969D-03	_= • 41445D-QO	+ 40243D	03-	• 59486D-	-00-	•21694D=03	-•88296D-00-
•48000D 01	•13330D 03	<b>••</b> 523910 00	•40593D	03	-•781820	00	•272320=03	•84734D DO
+ •52000D 01	•13690D 03	••655620 00	•40941D	03	-+10170D	01		-•80287 <u>0</u> 00 -
•56000D 01	•14051D 03	-+81108D 00	•41286D	03	-•13095D	01	•41445D=03	•74802D 00
600000 01_	•1441CD 03	# \$99016D 00	_•41629D	03	-##16690D	01	•50050D=03-	-•68128D 00
•64000D 01	•14//3D 03	••11898D Q1	+41970D	03	=+21044D	01	•59354D=03	•60141D 00
	•15134D-03	-••14023D 01-	+42309D-	.03-		-01—	+68778D+03-	-•50776D-00-
•72000D 01	•15494D 03	••16114D Q1	•42649D	03	322580	01	•77230D+03	•40087D 00
•76000D 01 ·	•15855D 03	17872D 01	•42992D	03	-+390740	01 -		+28349D 00
•80000D 01	•16216D 03	••18725D 01	.43345D	03	<b>-+</b> 46438D	01	•81238D=03	·16251D 00
	•16577D Q3	174790 01	- •43718D	QЗ	••53781D	01 -	•63845D+03	•535880-01
+88000D 01	•16938D 03	-•10371D Q1	•44150D	03	<del>,</del> • 59696D	01	•00000D 00	•00000D 00
920000_01	-17298D_03		+44581D-	-03-		-01		-+00000D-00-
9600CD 01	•17659D 03	<b>••10834D 00</b>	•44964D	03	++62986D	01	•00000D 00	•00000D 00
	•18020D 03	<b>+,</b> 35019D#01	. •45332D	03	• • 632450	01	000000 00	•000000 00
+10400D 02	18381D 03	••11319D-01	,45696D	03	- 633290	01	•00000D 00	•00000D 00
10800D 02	18742D 03.	_ <b>#</b> #36586D=02 _	+46057D	03	. <b>⊭</b> :63356D	01_	•00000D_00	_•00000D _00_
11200D 02	•19102D 03	<b>*</b> *11825D <del>*</del> 02	+46418D	03	e 63365D	01	•00000D 00	•00000D 00
11600D_02	.19463D_03		+ 46779D	03.	63368D_	01-		-+00000D-00-
•12000D 02	19824D 03	-12354D-03	•47140D	03	<b>**63369D</b>	01	•00000D 00	+00000D 00
+12400D 02	·201850 03.	= 39932D=04 .	•47501D	03	+633690	01_	• 00000D - 00	-•00000D 00 .
·12800D 02	·20546D 03	-,12907D-04	•47862D	03	••63369D	<b>01</b>	•00000D 00	•00000D 00
13200D 02	.20906D 03	-+417190-05	. +48222D	03	+63369D	01_	• 000000 _ 00	-00000D 00 -
•13600D 02	•21267D 03	-,13484D-05	+48583D	QЗ	<b>#\$</b> 63369D	01	+00000D 00	•00000D 00
14000D_02	.21628D_03_	_+ + 43585D-06_	+48944D	03		01_	•00000D_00	_• 00000D00_
•14400D 02	•21989D 03	+.14088D=06	•49305D	QЗ	- • 63369D	01	•00000D 00	•00000D 00
14800D 02	•22350D 03	- 455350-07	,49666D	03	-+633690	01 _	•00000D.00	-•00000D 00