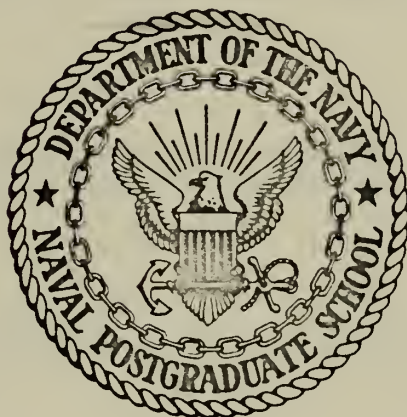THE THERMAL DECOMPOSITION OF RDX

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# NAVAL POSTGRADUATE SCHOOL
## Monterey, California

# THESIS

THE THERMAL DECOMPOSITION OF RDX

by

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ABSTRACT

Cyclotrimethlenetrinitramine (RDX or Cyclonite) exists in two poly-
morphic species, α and β. The α-form is stable under normal conditions,
whereas β-RDX is formed by recrystallization from high boiling solvents.
It immediately transfers to the α-form in the presence of excess α-RDX,
and it is therefore assumed that RDX as it exists in its normal state
consists solely of the α polymorph.

The thermal decomposition of RDX has been comprehensively studied
at Picatinny Arsenal by means of quantitative measurements of the de-
composition products. The thermal stability of explosive compositions
has also been investigated by measuring the rate of gas evolution during
decomposition.

It was the purpose of this work to obtain thermal and kinetic data
for RDX using Differential Thermal Analysis (DTA) experimental methods.
These results and techniques were compared with those obtained using
the other methods and with theoretical values. The favorable results
lend credibility to the DTA method and suggest that further development
in the technique will prove useful in providing a fast and reasonably
accurate method of characterizing the thermal and kinetic properties of
new explosives and propellants.

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## TABLE OF SYMBOLS

A     =   Arrhenius frequency factor.

c     =   Heat capacity.

$dq/dt$ =   Chemical energy generated by decomposition.

DTA     =   Differential Thermal Analysis.

$dx/dt$ =   Rate of reaction.

$E_a$     =   Activation energy, calories/mole.

k     =   Rate constant.

MAA     =   Microimmersion Autocatalytic Analysis.

n     =   Empirical order of reaction.

R     =   Gas constant, 1.987 calories/mole °K.

T     =   Temperature in degrees Kelvin.

$T_m$     =   The sample temperature at which the peak in the DTA thermogram occurs.

$T_o$     =   Temperature at the outside of the sample or reference cylinder.

$T_r$     =   Temperature of the reference material.

$T_s$     =   Temperature of the sample material.

$t_o$     =   Induction time.

x     =   Fraction of material reacted.

$\theta$     =   Differential temperature $\Delta T$.

$\kappa$     =   Thermal conductivity.

$\rho$     =   Sample density.

$\tau$     =   Time-to-deflagration.

$\phi$     =   $dT/dt$, heating rate supplied to sample explosive, °K/min.

## ACKNOWLEDGMENT

# I.  INTRODUCTION

Explosives undergo thermal decomposition at temperatures far below those at which spontaneous explosion may occur.  The decomposition reaction is important in determining the stability of the explosive.  A considerable amount of heat energy is liberated in the decomposition process.  This highly exothermic reaction accelerates to a high velocity culminating in deflagration or detonation when the rate of heat production is greater than the rate of heat loss to the surroundings by conduction and convection.  Explosives in their normal state are metastable, the free energy of the explosive being considerably higher than its decomposition products.  For an explosive to remain stable at ordinary temperatures, its decomposition reaction must depend on relatively high activation energies.

Kinetic studies are therefore important in the study of explosive reaction mechanisms.  The Differential Thermal Analysis technique is one of several that is used to study reaction kinetics.  When a reaction occurs in DTA, the change in heat content and in the thermal properties of the sample is indicated by a deflection in the thermogram.  For reactions that possess activation energies and thereby proceed at a rate varying with temperature, the position of the peak varies with the heating rate.  The activation energy and Arrhenius frequency factor can be determined from this experimental information.

Cyclotrimethylenetrinitramine (RDX or Cyclonite) is an important explosive used in many military composite explosives.  RDX melts at 203°C, and the decomposition of liquid cyclonite follows the unimolecular rate

equation over the range of temperatures 213-299°C.  [Robertson 1949].
The Arrhenius frequency factor is large, and the activation energy is
of the order of 50 kcal/mole.  The high value of the Arrhenius frequency
factor is a possible indication of self heating.

The purpose of this work was to investigate the thermal decomposi-
tion of RDX using DTA experimental techniques.  In the decomposition
of 1,3,5,7-Tetranitro-1,3,5,7-Tetrazacyclooctane (HMX), three separate
peaks were observed in the DTA thermogram, and three separate activa-
tion energies obtained from the DTA data [Hondee 1971].  It was of
interest to determine whether these phenomena were evident in the de-
composition of RDX, to detect any evidence of self-heating, and to
compare the kinetic data obtained with that found in the literature.

## II.  THERMAL DECOMPOSITION OF EXPLOSIVES

The investigation of the thermal behavior of explosives involves both the study of chemical kinetics and the theory of transport properties. The chemical kinetics of explosive reactions are not fully understood due to the high reaction rates and temperatures involved and the complexity of the products of the reaction.  The decomposition of RDX may be written:

$$C_3H_6O_6N_6 + O_2 \rightarrow 3CO_2 + 3H_2O + 6NO_2$$

This reaction may be accurate for detonation but is unlikely to occur thermally due to the large number of bonds which must be broken in the parent molecule.  Attempts to study these reactions require that measurements of the decomposition rates be made at relatively low temperatures.

Thermal decomposition is essentially a heat-balance problem.  The heat loss to the surroundings and the accumulation of heat in the explosive equals the chemical energy generated by the decomposition of the explosive.

$$\kappa \nabla^2 T + \rho c \phi = dq/dt$$

This can be written simply as F + G = H.  The chemical energy generated by the decomposition, H, increases exponentially with temperature.  The heat loss, F, consists of thermal conduction, which is proportional to the thermal gradient, and radiation, which follows the Stefan-Boltzmann $T^4$ law.  The heat loss therefore increases at a slower rate, especially since the heats of activation of explosives are of the order of 50 kcal/mole.  The accumulation of heat in the explosive, G, becomes more important as the temperature increases, causing acceleration of the decomposition.

Some explosives liberate energy in their interior due to a slow chemical reaction that is often a decomposition reaction. This is known as self-heating and causes the temperature of the material to increase, resulting in an increase in the rate of reaction. Dynamic equilibrium is reached when the heat is removed as fast as it is generated. If heat is generated faster than it can be removed, the temperature increases more rapidly and the reaction accelerates. The maximum temperature of the surroundings for which a steady state is possible is called the critical temperature for the explosive. Above this temperature, the material will self-heat until ignition or explosion occurs [Longwell 1961].

Decomposition reactions are sometimes autocatalytic or catalyzed by small amounts of impurities. The decomposition products or impurities in the explosive may act as a catalyst in that the reaction rate is increased as more products are produced. The decomposition rates of these materials then become a function of the duration or extent of the decomposition.

# III. REACTION KINETICS IN DTA

The material of this section is a summary of Kissinger's work on the theory of differential thermal analysis [Ref. 2]. DTA techniques produce a deflection or peak ($\Delta T$) in the thermogram due to a change in heat content and thermal properties of the active sample during a reaction. This peak temperature is affected by experimental technique, and is often higher than known transition or decomposition temperatures.

The temperature of maximum deflection is defined by kinetic constants and the heating rate. If a reaction posses an activation energy, it will proceed at a rate varying with temperature and the position of the peak will vary with the heating rate. The temperature of maximum deflection in DTA is also the temperature at which the reaction rate is a maximum. The temperature distribution of the sample explosive obeys the general heat flow equation;

$$\frac{\partial T}{\partial t} - \frac{\kappa}{\rho c} \nabla^2 T = \frac{1}{\rho c} \frac{dq}{dt} \tag{1}$$

where the rate of heat generated due to chemical reaction per unit volume of the sample is equal to zero in the inert reference. The temperature distribution in the reference material is then given by;

$$\frac{\partial T}{\partial t} = \frac{\kappa}{\rho c} \nabla^2 T \tag{2}$$

Assuming the sample to be a cylinder of radius a and of infinite length, integration of equation 2 yields;

$$T_r = T_O + \phi t - \frac{\phi \rho c a^2}{4\kappa} \tag{3}$$

where $\phi = dT/dt$ and the outside temperature is given by $T = T_O + \phi t$. The rate of heat generated due to chemical reaction is a function of

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temperature in the active sample. Equation 1 is therefore a non-linear partial differential equation. Assuming that the temperature of the outside of the tube rises at a linear rate, the solution for the temperature at the center of the sample will be of the form;

$$T_s = T_h + \phi t - f(dq/dt) \tag{4}$$

where $f(dq/dt)$ is a function of the reaction rate and includes secondary effects of the reaction such as changes in volume, density and thermal properties.

The differential temperature is the difference between temperatures at the centers of the two samples;

$$\theta = f\left(\frac{dq}{dt}\right)_{sample} - \left(\frac{\phi \rho c a^2}{\kappa}\right)_{reference} \tag{5}$$

and is a maximum at the temperature of maximum deflection where $d\theta/dt$ is zero.

$$d\theta/dt = f'(dq/dt)\ d^2q/dt^2 \tag{6}$$

When the derivative of the rate of heat absorption is zero it can be seen from Equation 6 that $d\theta/dt$ is also zero. Since the rate of heat absorption is proportional to the rate of reaction, Equation 6 shows that the peak differential deflection occurs when the reaction rate is a maximum. It should be noted that the heating rate must be constant for this to hold and that Equation 6 is valid for a sample of any shape.

The rate law for the thermal decomposition of explosives can be described by the equation;

$$(\partial x/\partial t)_T = k_T\ (1-x)^n \tag{7}$$

where $k_T = A\ \exp(-E_a/RT)$ and temperature is a function of time.

$$\frac{dx}{dt} = \left(\frac{\partial x}{\partial t}\right)_T + \left(\frac{\partial x}{\partial T}\right)_t\ \frac{dT}{dt} \tag{8}$$

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The rate of change of x with respect to temperature, with the time coordinates fixed, is equal to zero because the number and positions of the particles of the reactant are also fixed with time. The only effect of instantaneous change in temperature is in the velocities of thermal motion of the reactant particles. Equation 7 can now be written;

$$dx/dt - A(1-x)^n \exp(-E_a/RT) \tag{9}$$

which holds for any temperature as long as the fraction of reactant decomposed and temperature are measured at the same instant. It is assumed that the empirical order of the reaction remains constant through the greater part of the reaction.

When the temperature rises during the reaction, the reaction rate will rise to a maximum value, then return to zero as the reactant is exhausted. This maximum rate occurs when d/dt(dx/dt) is zero. Providing the temperature rises at a constant rate, the differentiation of Equation 9 yields;

$$\frac{d}{dt}\left(\frac{dx}{dt}\right) = \frac{dx}{dt} \left[ \frac{E_a \phi}{RT^2} - An(1-x)^{n-1} e^{-E_a/RT} \right] \tag{10}$$

Setting this equation equal to zero defines the temperature at which the maximum rate occurs.

$$\frac{E_a \phi}{RT_m^2} = An(1-x)_m^{n-1} e^{-E_a/RT_m} \tag{11}$$

$T_m$ is the sample temperature at which the peak in the DTA thermogram occurs. The quantity of material left unreacted, $(1-x)_m$, is not determined by the DTA method.

To obtain the extent of reaction as a function of temperature, Equation 9 can be integrated. The resulting exponential integral does

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not yield a simple expression.  Previous work has resulted in a satis-
factory approximation by successive integration by parts.  Higher order
terms were neglected, and the simplified expression becomes;

$$n(1-x)_m^{n-1} = 1 + (n-1) \frac{2RT_m}{E_a} \qquad (12)$$

The heating rate does not appear except as a result of $T_m$, which varies
with heating rate.  The product $n(1-x)_m^{n-1}$ is independent of heating rate
and nearly equal to unity.  Equation 11 now becomes;

$$\phi = \frac{ART_m^2}{E_a} e^{-E_a/RT_m} \qquad (13)$$

Taking the natural logarithm of both sides and differentiating;

$$\frac{d \ln(\phi/T_m^2)}{d(1/T_m)} = \frac{d \ln (AR/E_a \ e^{-E_a/RT_m})}{d(1/T_m)}$$

$$= \left(\frac{E_a}{AR}\right) e^{+E_a/RT_m} \left(\frac{AR}{E_a}\right) \left(\frac{-E_a}{R}\right) e^{-E_a/RT_m}$$

$$\frac{d \ln(\phi/T_m^2)}{d(1000/T_m)} = \frac{-E_a}{R} \qquad (14)$$

By experimentally obtaining DTA thermograms at different heating rates,
the activation energy for the decomposition reaction can be determined
by Equation 14, regardless of reaction order.

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## IV.   EXPERIMENTAL PROCEDURE

### A.   APPARATUS

The differential thermal analysis reaction was obtained by use of
the DuPont 900 Differential Thermal Analyzer shown in Figure 1.  A re-
mote cell unit, shown in Figure 2, was used in this work due to the
nature of the samples being studied.

DTA uses a differential thermocouple arrangement consisting of two
thermocouples wired in opposition as shown in Figure 3.
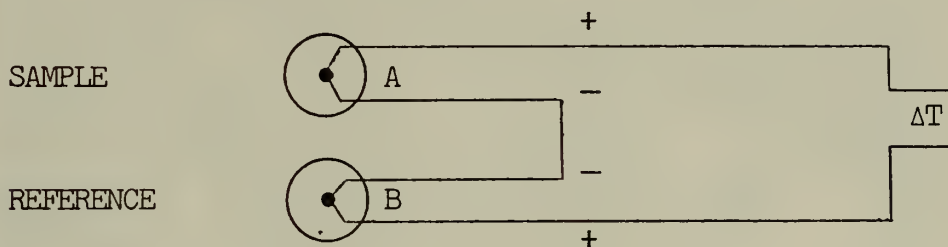
FIGURE 3   DIFFERENTIAL THERMOCOUPLE

Thermocouple A is placed in the sample to be analyzed.  Thermocouple B
is placed in an inert reference material.  When the temperature of the
sample equals the temperature of the reference, the thermocouples pro-
duce identical voltage, and the net voltage output, $\Delta T$, is zero.  When
a physical or chemical reaction occurs in the sample, a differential
signal is received and recorded.  Figure 4 shows a schematic of the DTA
system.

A silver heating block is mounted in the remote cell assembly.
This block contains the sample, reference, and controlling chromel-
alumel thermocouples as shown in Figure 5.  The block is designed to
provide for equal heating rates for both the reference and sample ma-
terials.  The temperature of the reference is less than the temperature

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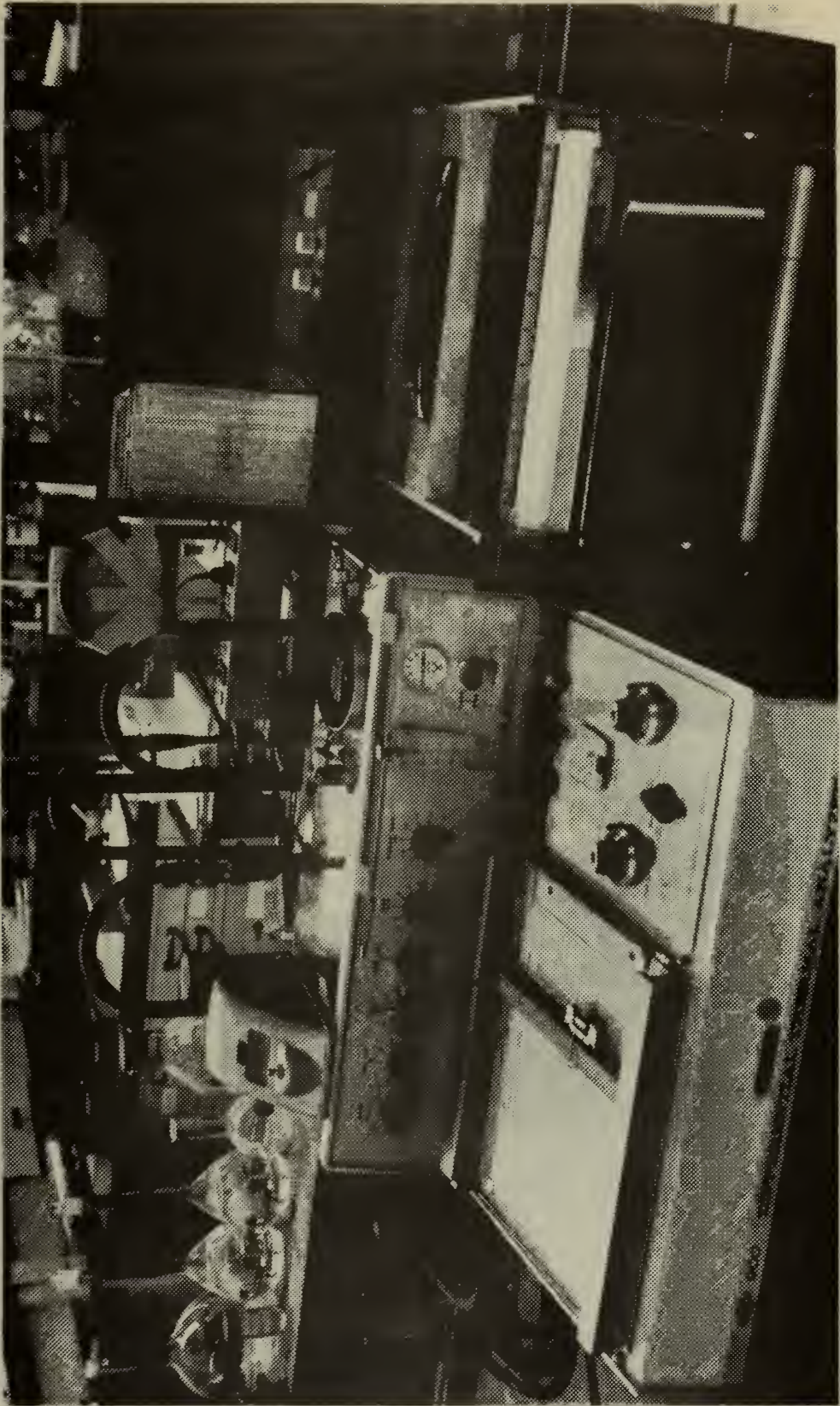
FIGURE 1: DuPont 900 Differential Thermal Analyzer
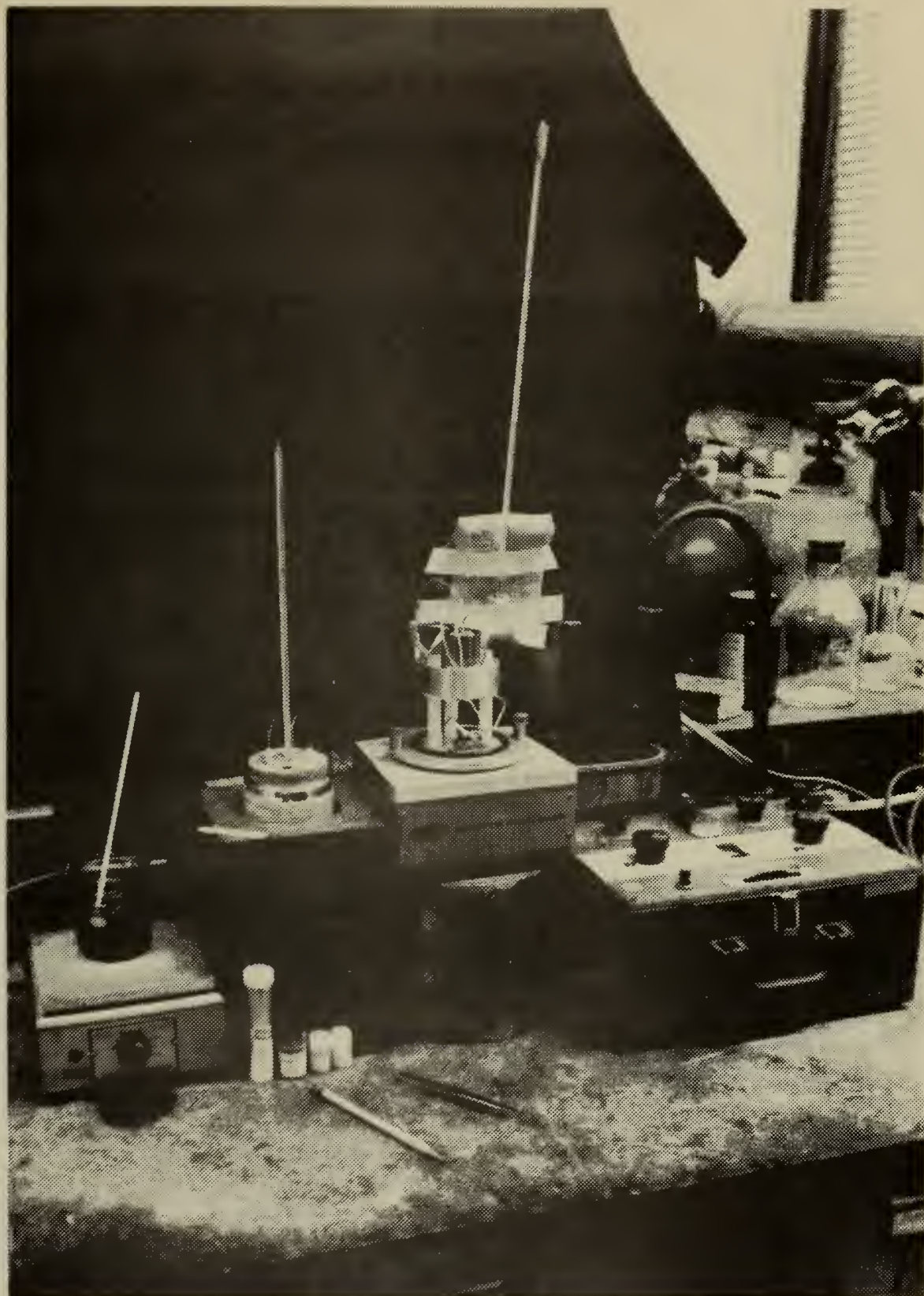
FIGURE 2: Remote Cell Assembly
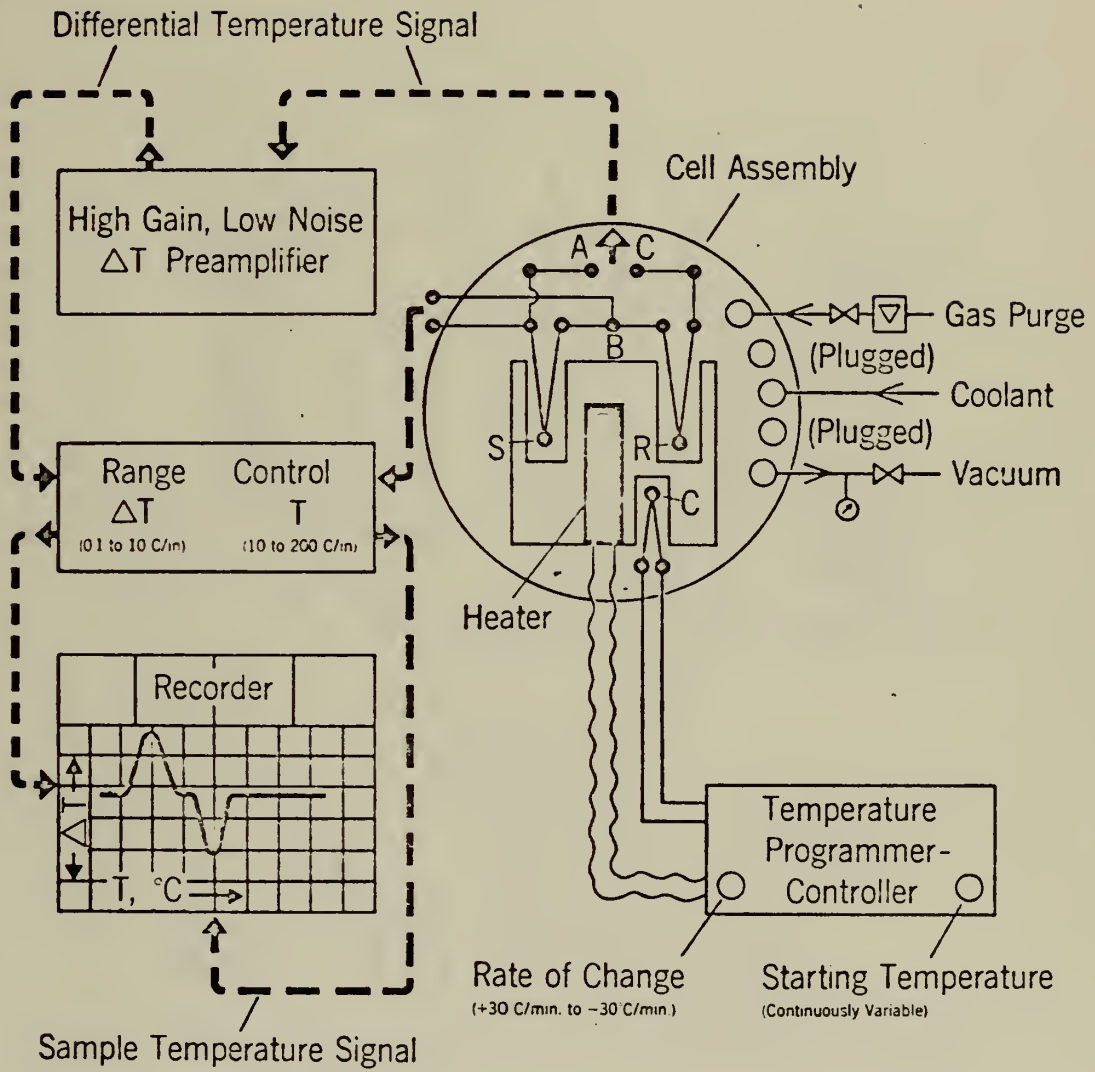
FIGURE 4: DTA System Schematic

(taken from ref. 10, pg. 3-2)
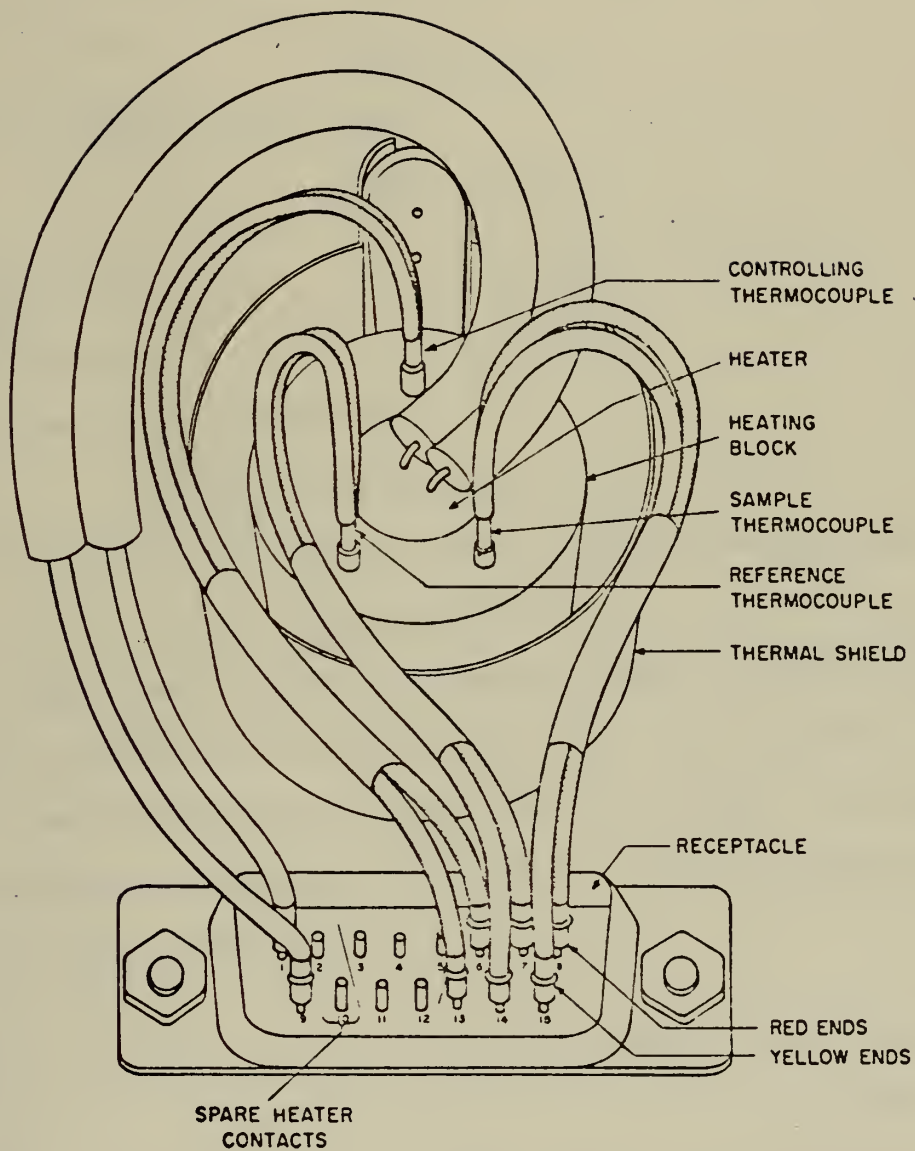
FIGURE 5:  Heating Block and Thermocouple Arrangement

(taken from ref. 10, pg. 3-4)

of the block by a constant amount that is directly proportional to the
heating rate, weight and heat capacity of the reference material, and
inversely proportional to the thermal conductivity of the reference ma-
terial, plus a complex exponential function which can be neglected for
simplification.

$$T_R \simeq T_B - \phi_R (Wc/\kappa)_R$$

Assuming a thermally inert sample,

$$T_S \simeq T_B - \phi_S (Wc/\kappa)_S$$

| | |
|---|---|
| T = temperature | $\kappa$ = thermal conductivity |
| $\phi$ = heating rate | S = sample |
| W = weight | R = reference |
| c = heat capacity | B = block |

The differential temperature is:

$$\Delta T = T_S - T_R \simeq \phi_R (Wc/\kappa)_R - \phi_S (Wc/\kappa)_S$$

The heating block in the DuPont 900 is designed such that $\phi_S = \phi_R$:

$$\Delta T \simeq (Wc/\kappa)_R - (Wc/\kappa)_S$$

If the weight, heat capacity and thermal conductivity of the sample and
reference material are the same, $\Delta T$ is zero. The $\Delta T$ signal as a func-
tion of sample temperature is sent to the X-Y recorder. Any change in
the properties of the sample results in a positive or negative value
for $\Delta T$ as shown in Figure 6.



POSITIVE SIGNAL: $(Wc/\kappa)_R > (Wc/\kappa)_S$

$$c, \kappa \neq f(T)$$

ZERO SIGNAL: $(Wc/\kappa)_R = (Wc/\kappa)_S$

NEGATIVE SIGNAL: $(Wc/\kappa)_R < (Wc/\kappa)_S$

$$c, \kappa \neq f(T)$$
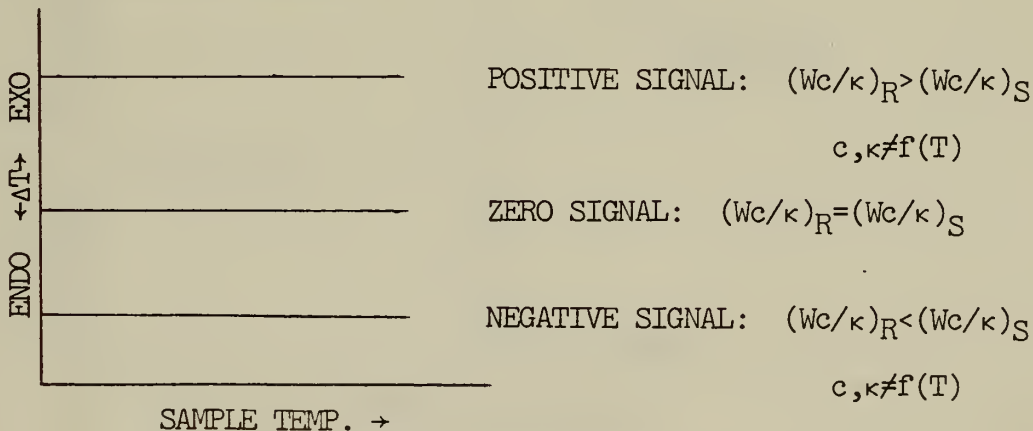
FIGURE 6   DTA THERMOGRAM

A thermally active material will experience a change in heat capacity and thermal conductivity over a temperature range. The $\Delta T$ trace will be a sloping straight line if the properties change linearly with temperature, and curved if the change with temperature is quadratic or of higher order. Figure 7 exhibits this relationship, where the curved line would have a positive slope if $(Wc/\kappa)_R > (Wc/\kappa)_S$.



$$\begin{cases} (Wc/\kappa)_R < (Wc/\kappa)_S \\ c,\kappa = \text{linear } f(T) \end{cases}$$

$$\begin{cases} (Wc/\kappa)_R < (Wc/\kappa)_S \\ c,\kappa = \text{quadratic } f(T) \end{cases}$$
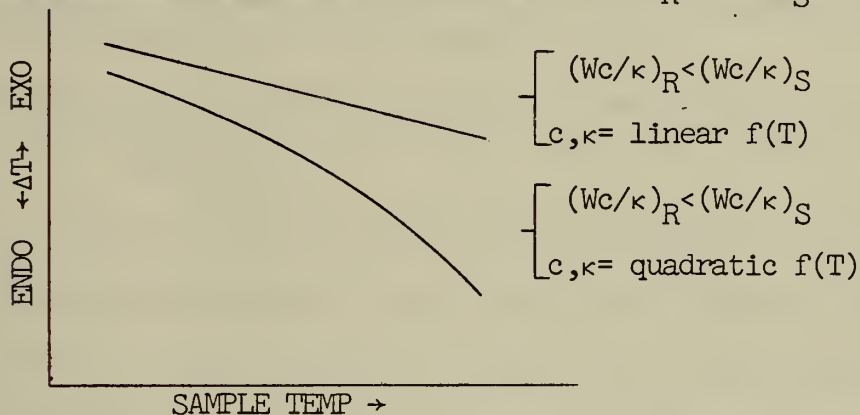
FIGURE 7   DTA THERMOGRAM

The DTA thermogram of a thermally active sample will exhibit endotherms and exotherms where the temperatures of interest are defined in Figure 8.
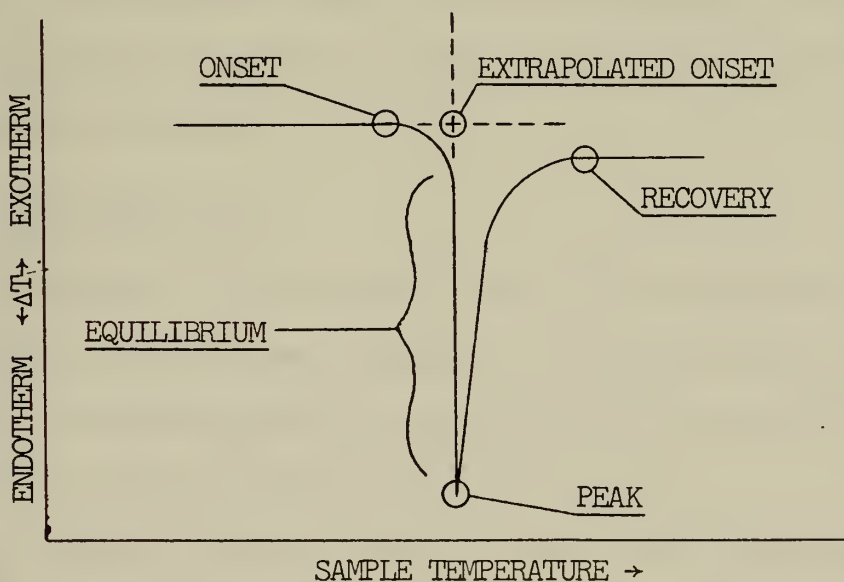


FIGURE 8   TRANSITION TEMPERATURES

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## TRANSITION TEMPERATURE DEFINITIONS USED IN FIGURE 8.

ONSET: The temperature at which the thermogram starts to depart from the base line.

EXTRAPOLATED ONSET: The temperature corresponding to the intersection of extrapolations of the base line and the longest straight-line section of the low-temperature side of the peak.

PEAK: The temperature of reversal.

RECOVERY: The temperature at which the thermogram returns to either the same or a different base line.

EQUILIBRIUM: The region where the state or form of the sample before transition is in equilibrium with its state or form after transition.

For the purposes of this work, a fourth well was drilled in the silver heating blocks to cross check the temperature scale on the DTA 900 X-Y plotter. A single chromel-alumel thermocouple was set in inert glass beads and connected to a Varian recorder. This gave a millivolt versus time chart to check the heating block temperatures and heating rate. The Varian thermocouple was calibrated with a millivolt potentiometer and temperatures were verified through the use of a hot oil bath. The temperature scale of the DTA thermogram is calibrated to the chromel-alumel millivolt output to give direct temperature readings in degrees centigrade.

## B. SAMPLE PREPARATION

The samples of RDX that were used in the experimental runs were prepared by drying a small quantity of pure RDX that was stored in water. The sample appeared to be pure RDX as its melting temperature of 204°C compared favorably with listed values.

Two separate heating blocks were used in the experimental work. In the variable heating rate runs, a silver block with wells to accept two

millimeter diameter capillary tubes was used. The RDX sample was
tapped down into one of the four capillary tubes to a depth of four
millimeters, which was calculated to be 19.3 milligrams of RDX. The
three remaining capillary tubes contained equal levels of inert finely
ground glass beads .05 millimeters in diameter. These tubes contained
the reference, controlling, and Varian recorder chromel-alumel thermo-
couples. All four capillary tubes were then cut to 1-1/8 inch. Care
was taken when placing the thermocouples to insure that they were
pushed to the full depth of the material. The capillary tubes were
then placed in their respective wells, and the thermocouple leads were
folded under the rim of the remote cell unit to insure that they re-
mained completely seated throughout the run. This was especially im-
portant in the case of the RDX sample since the reactant gases given
off during the exothermic decomposition tended to push the thermo-
couple out of the tube. The sample depth of four millimeters was
critical for satisfactory results. A quantity larger than this would
push the thermocouple out of the tube, giving erroneous readings. A
smaller quantity would not provide complete coverage of the thermo-
couple probe. The fineness or texture of the sample in this work was
not considered since the reactions occurred above the melting tempera-
ture, or in all cases for the variable heating rate runs, in the liquid
phase.

The second silver heating block was identical to the first with the
exception of the sample and reference wells which were designed to hold
four millimeter diameter test tubes. The RDX sample was measured in
the same manner as before to a depth of four millimeters, which in

this case gave a sample of 43.32 milligrams of RDX. The second four millimeter test tube contained an equal volume of inert glass beads and served as the reference. Both four millimeter tubes were covered with small metal caps through which the thermocouples were inserted. This reduced losses to the atmosphere during reaction. The controlling and Varian thermocouples were inserted in the remaining two small capillary wells in the same manner as in the variable heating rate block. This second heating block was used in the isothermal portion of the experimental work.

C. VARIABLE HEATING RATE EXPERIMENT

The DTA 900 control panel contains dials to set starting temperatures and heating rates. It was determined that there was no apparent difference in the thermogram presentation for a sample that was heated from room temperature at an established rate through decomposition or for one which was heated at an accelerated rate (50°C/min.) to 200°C, then slowed to the established rate through the decomposition reaction. In order to expedite the runs, this latter procedure was adopted.

The full range of the DTA 900 heating rate capability was utilized. In order to establish consistency in the procedure, an outline was set down and followed in each run.

EXPERIMENTAL PROCEDURE FOR VARIABLE HEATING RATE EXPERIMENT

(1) Turn DTA 900 power knob to STANDBY, allow five minute warm up.

(2) Place inert reference and sample material in the capillary tubes, tap and measure to a depth of four millimeters. Cut to 1-1/8 inch.

(3) Insert corresponding thermocouples, insuring that the thermocouple probe is completely immersed in the material. A new thermocouple is used for the RDX sample in each run.

(4)  Insert capillary tubes into the correct wells of the heating block.

(5)  Bend the leads of the thermocouples under the remote cell rim.

(6)  Insure that the zero temperature ice bath reference thermocouples are fully inserted into their glass tubes, which in turn are immersed in the ice and distilled water solution at 0°C.

(7)  Place a thermogram grid on the X-Y plotter.

(8)  Set the pen to room temperature on the T-scale.

(9)  Set the DTA 900 upper panel knobs:

(a)  T-zero shift.
(b)  T-scale, °C/in.
(c)  ΔT-zero shift.
(d)  ΔT-scale, °C/in.
(e)  Baseline slope.

(10) Set the DTA 900 lower panel dials:

(a)  Temperature heating rate, range 0-30°C/min.
(b)  Set starting temperature dial to minimum setting to get the minimum voltage reading on the heater voltage indicator.

(11) Set the program mode to HEAT.

(12) Push RESET to erase previous program memory.

(13) Place recorder pen to the DOWN position.

(14) Place power knob to RECORD.

(15) Start timer and Varian recorder.

Figure 9 shows a sample thermogram for a heating rate of 20°C/min. beginning at room temperature. The endotherm at 204°C shows transformation to the liquid phase, followed immediately by the exothermic decomposition with the peak in the exotherm at 251°C. Figure 10 shows a thermogram for ammonium nitrate. The endotherm at 40°C shows a transition from rhombic I to rhombic II. At 91°C, a crystalline change to tetragonal occurs, then to cubic at 130°C. Melting occurs at 174°C followed by decomposition in the liquid phase. This run was made to

check the calibration of the machine, to give an indication of the
sensitivity of the analyzer, and for use in a method of estimating the
heat of reaction of RDX, to be described in the recommendations. The
thermogram was compared with the ammonium nitrate thermogram presented
on page 5-7 of the DTA Instruction Manual [Ref. 10]. The comparison
showed a disparity in temperature for the peak exotherm, where that of
Figure 10 showed a temperature approximately 10°C higher than that of
the reference thermogram. This was corroborated by the Varian recorder,
and subsequent temperature readings were taken from the Varian recorder.

D.  ISOTHERMAL EXPERIMENT

A time base adaptor for the DTA 900 provides for maintaining the
heating block at set temperatures over long periods of time. The X-Y
plotter now provides for time in minutes on the abscissa and as before,
ΔT on the ordinant. Experimental runs were made using the four mil-
limeter test tube macro heating block. A variation of a method used
in determining the effects of thermal aging of propellants was followed
[Kuletz and Pakulak 1962]. This technique is known as microimmersion
autocatalytic analysis (MAA). In this work, the sample of RDX was
dropped into the well of the macro heating block after the block had
been established at a desired temperature. The procedure followed is
listed below.

EXPERIMENTAL PROCEDURE FOR ISOTHERMAL EXPERIMENT

(1)  Turn DTA 900 power knob to STANDBY, allow one to two hours warm up.

(2)  Place inert reference material in both 4mm test tubes, tap and
     measure to a depth of four millimeters.

(3)  Place metal thermocouple holder caps over test tubes and insert
     thermocouples, insuring complete immersion.

(4) Insert reference and sample 4mm test tubes in the large wells of the macro heating block. Two small capillary tubes are used for the controlling and Varian recorder thermocouples.

(5) Bend the thermocouple leads under the remote cell rim.

(6) Check the zero temperature ice bath and thermocouples.

(7) Place a thermogram grid on the X-Y plotter.

(8) Set the time base adaptor to TIME.

(9) Set the DTA 900 upper panel knobs:

    (a) T-zero shift.
    (b) T-scale, Min./in.
    (c) ΔT-zero shift.
    (d) ΔT-scale.
    (e) Baseline slope.

(10) Set the DTA 900 lower panel dials:

    (a) Set temperature heating rate at zero.
    (b) Set the starting temperature dial according to the scale of Figure 3G of section 3, DTA Instruction Manual [Ref. 10].

(11) Set the program mode to ISOTHERMAL.

(12) Allow the temperature to stabilize at the desired setting and record the Varian reading.

(13) Place a sample test tube of RDX in the macro heating block and reset the corresponding thermocouple. (Wear protective shield)

(14) Push RESET to start zero time at the left end of the scale.

(15) Place recorder pen to the DOWN position.

(16) Record time and start timer.

(17) Monitor Varian recorder.

The resulting thermogram plots ΔT versus time.

# V.   RESULTS AND DISCUSSION

The series of thermograms obtained from the variable heating rate method using RDX samples are reproduced in Figures 11-17.  During each of these runs, temperatures were recorded at 5°C intervals and at significant points on the thermogram (melting, peak exotherm) with the corresponding time in seconds.  This data is plotted in Figures 18-36.  An $n^{th}$ order regression analysis program of the WANG 700 was used to calculate the least squares fit to the data points, the slope of which is the actual heating rate for that run.  The resulting equation gives the temperature at any time during each run for the programed heating rate.  The calculated heating rates, along with the sample temperature of the peak in the exotherm $T_m$, are the required data for determining the kinetic parameters of the decomposition by Kissinger's method [Ref. 2].  These data are summarized in Table I.

The kinetic data for the decomposition reaction of RDX were determined from the plot of the variable heating rate experimental data of Table I.  The natural logarithm of the rate factor $\phi/T_m^2$ was plotted versus the reciprocal of the Kelvin temperature of the heating block, as shown in Figure 37.  The WANG 700 was used to calculate a least squares fit to the experimental data points.  The slope of this line determines the activation energy which was calculated to be 49.4713 kcal/mole.  The Arrhenius frequency factor was determined from Equation 13, averaged over the temperature range of the experiment.  The average value was $6.9199 \times 10^{20}$, which varied from the fastest heating rate value by $1.1501 \times 10^{20}$ and from the lowest by $0.1415 \times 10^{20}$.  These values compare favorably with those of previous works [Rauch and

Wainright 1969, Robertson 1948]. The kinetic parameters are summarized in Table II. There is a 1.6% error in the value for the activation energy when compared with that of Rauch and Wainright's work for Picatinny Arsenal.

Appendix A is an IBM 360 computer readout which tabulates values for the heating rate with incremental increase in the peak temperature $T_m$. The experimentally determined values of activation energy and Arrhenius frequency factor were used in Equation 13 to generate values of the heating rate $\phi$. Appendix B tabulates the same information for comparison using the kinetic data determined by Rauch and Wainright. This data is presented in Table III along with values from the experimental runs for comparison. At higher heating rates, the experimental and calculated data differ to a larger extent. This is probably due to experimental time lag at the higher heating rates which caused lower temperature readings at the higher rates. Although the values of activation energies compare favorably, Table III shows that the experimentally determined temperatures of the peak in the exotherms at the various heating rates would have to be approximately 30°C higher to give heating rates comparable to the Picatinny data.

The rate constant k over the experimental temperature range was calculated using the Arrhenius equation. Appendix C tabulates values of k using the experimentally determined values of $E_a$ and A. Appendix D presents the same data using the kinetic data determined in the study made for Picatinny Arsenal. These values are compared in Table IV. The smaller values for the rate constant resulting from the Picatinny data correspond with the lower heating rate values shown in Table III.

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Some variation existed in the peak temperature of the exotherms as evidenced in Table I. This resulted in the scatter noted in Figure 37. An attempt to reproduce the peak temperature at a given heating rate was made over three consecutive runs using the standard experimental technique. Results are shown in Figure 38, where the three runs were carried out at a heating rate of 6°C/min. The maximum variation in the peaks was 4°C. This compares with the variation in temperatures for the experimental and calculated values of $T_m$ shown in Table III. The maximum deviation approaches .8% error, which is well within the accur- of the experiment. There is a definite increase in $T_m$ with heating rate as proposed by the DTA kinetic theory [Kissinger 1957]. The ef- fect of sample size appeared to be only an increase in the quantity of heat liberated, as shown in Figure 39. The peak temperature did not vary to any greater degree than in the normal manner with equivalent volumes of material.

The isothermal data gave somewhat less conclusive results. The thermograms, Figures 40-44, show a difinite exothermic decomposition reaction which occurs at a constant block temperature after an induc- tion time which decreases with increased temperature. A temperature range of 192-210°C was investigated. The time elapsed to initiation of the exothermic reaction, or induction time, and the time elapsed to the peak in the exotherm, the time-to-deflagration, were observed and recorded. Table V summarizes the isothermal data. It was noted that although these reactions occur at or below the normal melting tempera- ture they occurred in the liquid phase. A physical observation during one of the runs confirmed a liquid phase decomposition with decomposi- tion gases bubbling off. The sample at 192°C showed no evidence of

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reaction after six and one-half hours. Near the melting temperature (204°C) and above, the sample changed to the liquid phase immediately upon reaching block temperature with the exothermic decomposition ensuing. The microimmersion autocatalytic analysis (MAA) method was used to determine kinetic data from the isothermal phase of the experiment. This method is based on the equation;

$$\frac{T^2}{\tau} = \frac{AQE_a}{cR} \, e^{-E_a/RT} \qquad (15)$$

where Q is the heat of reaction. A plot of the natural logarithm of the rate factor $(\tau/T^2)$ versus the reciprocal of the constant block temperature gives a slope equal to $E_a/R$. In addition, an Arrhenius plot using the reciprocal of the time data versus 1000/T was made [Kuletz and Pakulak 1962]. Both induction time and time-to-deflagration data were used. Table VI lists the induction time data. Two plots were made using these data. The natural logarithm of the reciprocal of the induction time versus the reciprocal of the isothermal block temperature in degrees Kelvin is presented in Figure 45. The MAA procedure, plotting the natural logarithm of the rate factor $(t_o/T^2)$ versus 1000/ T°K, is shown in Figure 46. This was done again using the time-to-deflagration. The data for time-to-deflagration are listed in Table VII. The plots of these data are shown in Figures 47 and 48 respectively. The results are shown in Table VIII. In all cases the WANG 700 was used to determine a least squares fit to the data points and the resulting slopes. It can be seen that both the reciprocal time and MAA rate factor methods produce nearly identical results. The values obtained for $E_a$ are far too high for activation energies.

# VI. CONCLUSIONS AND RECOMMENDATIONS

Experimental work done on HMX [Suryamarayana and Graybush 1967] suggested that materials which exhibit sigmoid pressure-time curves generally involve three stages in the decomposition reaction. The first stage is the induction period. This is followed by an acceleration period where the rate reaches a maximum. The material is consumed in the decay period. Even with this mass spectrometric study, the conclusions were limited due to the several decomposition products formed. It was observed that each product reached a constant rate of formation after an acceleratory stage which appeared due to autocatalysis. It was found that HMX exhibited different modes of decomposition. The kinetic data changed in different discrete temperature ranges. These findings were supported in a DTA analysis of HMX [Hondee 1971], where three separate activation energies were found during three discrete stages of the decomposition process.

Causes for acceleration of the decomposition of HMX to a constant rate can be attributed to [Suryamarayana and Graybush 1967]:

(1) Progressive melting as a result of lowered melting point by the decomposition products.
(2) Self-heating.
(3) Autocatalysis by products.
(4) Acceleration due to structural factors such as the increase in the number of nuclei.

During this experimental study of the decomposition of RDX there was no evidence of different activation energies since the heating rate in all runs remained constant over the entire decomposition. The peak exotherm, although somewhat variable, did not exhibit more than one sharp peak. The thermograms for the variable heating rate experiments

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(Figures 11-17) show that the exothermic decomposition reached a peak which was in most cases followed by a second peak. This second peak is probably a result of the capillary action of the liquid sample causing the thermocouple to rise in the tube, then drop back down just before the reaction completes causing another jump in the thermogram.

The isothermal experiment thermograms (Figures 40-44) show a definite decomposition reaction after an induction time at lower temperatures. This is in agreement with previous studies which have found evidence of self-heating and autocatalysis in the decomposition of RDX and other explosives. These data can be applied to estimates of the sensitivity of explosives and propellants.

Several reasons may be proposed for the discontinuities in the variable heating rate experiment. Although the RDX sample was assumed homogeneous and pure, it may well have been nonuniform in nature and composition. Possible water content in the samples was neglected. DTA results vary between laboratories due to the difference in experimental techniques and equipment as well as in the interpretation of the results. Standardization of method would be beneficial.

Explosive decomposition rates vary rapidly with temperature and for ideal results the temperature of the sample should at all times be uniform. This is not the true situation due to thermal conduction in the sample and self-cooling or self-heating effects arising from the reaction. Robertson [Ref. 9] showed that errors in the values of the kinetic parameters occur due partly to autocatalysis and self-heating. Autocatalysis increases the activation energy value by approximately 2000 cal/mole as a maximum error and causes a corresponding

variation in the Arrhenius frequency factor by as much as a factor of 10. Errors due to self-heating are also incurred and tend to increase $E_a$ and A as well. This effect increases with increased temperature.

Experimental errors are also induced by the apparatus. The accuracy of the DTA method depends on the precision with which a uniform heating rate can be maintained. Although the DTA 900 provides for a constant rate to the heating block, the exterior of the sample is hotter than the interior and reacts sooner and faster. This causes additional autocatalytic and self-heating effects which are accented by an increased heating rate. Another source of error in this work was the uncontrolled atmosphere. This provides for possible variations in the data from day to day. Bubbles of the decomposition gases which formed on the thermocouples caused the high intensity chatter on the thermograms. Capillary action of the melt during decomposition caused it to climb the walls of the tube surrounding the thermocouple sleeve. This drew the material away from the thermocouple probe. Care had to be taken to keep the level of the liquid below the sleeve in order to minimize this effect.

Notwithstanding these adverse and random effects, the dominant factor in controlling the shape and position of the endotherms and exotherms is the nature of the reaction itself. The favorable results obtained lend credibility to the DTA method and suggest that further development in the technique will prove useful in providing a fast and reasonably accurate method of characterizing the thermal and kinetic properties of new explosives and propellants.

Areas for further study are wide and varied. Considerably more information as to the mechanisms of the reaction can be obtained by

combining the DTA method with one or more of several more precise analytical techniques such as thermogravimetry, infrared spectrometry, mass spectrometry, X-ray measurements, and visual observations.

More information may be determined from the DTA thermograms themselves. It has been shown that the area under the peak in the thermogram is proportional to the heat of reaction [Rivette and Besser 1961]. This provides a means to quickly estimate the heats of reaction of the sample. The shape of the exotherm provides a means to estimate the reaction order [Kissinger 1957]. Rough estimations using this method showed the reaction order to vary from 0.2 to 0.8 over the range of heating rates considered. Further analysis of the isothermal thermograms appears warranted to discover the significance of the two slopes on the low temperature side of the exotherm and the shape and extent of the decay pattern on the high temperature side, as well as the significance of the high values obtained for $E_a$ from the Arrhenius and MAA plots of the induction time and time-to-deflagration data.

## TABLE I

### EXPERIMENTAL DATA, VARIABLE HEATING RATE THERMAL ANALYSIS

| RUN # | $\phi$,°C/MIN | $T_m$ °K | $\ln(\phi/T_m^2)$ | $(1/T_m) \times 10^3$ |
|-------|---------------|----------|-------------------|------------------------|
| 1 | 2.431 | 504.00 | -11.5601 | 1.9802 |
| 2 | 2.880 | 501.00 | -11.3754 | 1.9960 |
| 3 | 3.333 | 509.00 | -11.2610 | 1.9646 |
| 4 | 3.8571 | 513.00 | -11.1306 | 1.9493 |
| 5 | 4.3636 | 505.25 | -10.9768 | 1.9792 |
| 6 | 4.6957 | 509.00 | -10.9183 | 1.9646 |
| 7 | 5.1940 | 510.50 | -10.8233 | 1.9589 |
| 8 | 5.6552 | 514.50 | -10.7538 | 1.9436 |
| 9 | 6.2069 | 515.25 | -10.6636 | 1.9408 |
| 10 | 6.8182 | 513.00 | -10.5610 | 1.9493 |
| 11 | 7.9149 | 517.25 | -10.4283 | 1.9333 |
| 12 | 8.8696 | 510.75 | -10.2891 | 1.9579 |
| 13 | 9.7143 | 511.50 | -10.2011 | 1.9550 |
| 14 | 10.5556 | 512.75 | -10.1229 | 1.9503 |
| 15 | 11.6471 | 519.00 | -10.0488 | 1.9268 |
| 16 | 16.5217 | 517.00 | -9.6914 | 1.9342 |
| 17 | 21.0000 | 524.50 | -9.4804 | 1.9066 |
| 18 | 26.0769 | 523.25 | -9.2591 | 1.9111 |
| 19 | 30.0000 | 528.00 | -9.1370 | 1.8939 |

## TABLE II

### KINETIC PARAMETERS

|  | $E_a$(kcal/mole) | A (sec$^{-1}$) | |
| --- | --- | --- | --- |
| EXPERIMENTAL | 49.5 | $6.9 \times 10^{20}$ | $10^{20.8}$ |
| RAUCH & WAINRIGHT | 48.7 | $1.7 \times 10^{19}$ | $10^{19.2}$ |
| ROBERTSON | 47.5 | $3.16 \times 10^{18}$ | $10^{18.5}$ |

## TABLE III

### HEATING RATE DATA COMPARISON

| PEAK TEMPERATURE $T_m$ | HEATING RATE $\phi$ | | |
| --- | --- | --- | --- |
| | EXPERIMENTAL | CALCULATED | PICATINNY |
| 504.00 | 2.4310 | 2.4817 | 0.1338 |
| 509.00 | 4.6957 | 4.1122 | 0.2200 |
| 513.00 | 6.8182 | 6.1167 | 0.3253 |
| 524.50 | 21.0000 | 18.5317 | 0.9694 |
| 528.00 | 30.0000 | 25.7247 | 1.3391 |

## TABLE IV

### RATE CONSTANT DATA COMPARISON

| PEAK TEMPERATURE $T_m$ | RATE CONSTANT k (sec$^{-1}$) | |
| --- | --- | --- |
| | EXPERIMENTAL | PICATINNY |
| 504.00 | 0.2433 | 0.0129 |
| 509.00 | 0.3952 | 0.0208 |
| 513.00 | 0.5787 | 0.0303 |
| 524.50 | 1.6772 | 0.0864 |
| 528.00 | 2.2974 | 0.1177 |

## TABLE V

### EXPERIMENTAL DATA, ISOTHERMAL ANALYSIS

| RUN # | T (°C) | T (°K) | INDUCTION TIME $t_0$ (min) | $t_0$ (sec) | DEFLAGRATION $\tau$ (min) | $\tau$ (sec) | $\Delta T_{max}$ |
|---|---|---|---|---|---|---|---|
| 1 | 192.00 | 465.00 | EXCESS OF 6-1/2 HRS. | | | | |
| 2 | 194.25 | 467.25 | 192.0 | 11,520 | 238.5 | 14,310 | .39 |
| 3 | 196.75 | 469.75 | 130.0 | 7,848 | 145.6 | 8,736 | .30 |
| 4 | 198.00 | 471.00 | 85.0 | 5,100 | 107.5 | 6,450 | .66 |
| 5 | 198.50 | 471.50 | 37.5 | 2,250 | 58.5 | 3,510 | 1.30 |
| 6 | 199.50 | 472.50 | 15.0 | 900 | 34.8 | 2,088 | 1.50 |
| 7 | 204.50 | 477.50 | 10.8 | 648 | 19.2 | 1,152 | 1.60 |
| 8 | 206.75 | 479.75 | 0.0 | 0 | 0.0 | 0 | 3.20 |

## TABLE VI

### ISOTHERMAL ANALYSIS, INDUCTION TIME DATA

| RUN # | 1000/T | $t_0$ sec | $1/t_0$ | $\ln(1/t_0)$ | $\ln(t_0/T^2)$ |
|---|---|---|---|---|---|
| 2 | 2.1402 | 11,520 | $.8681 \times 10^{-4}$ | -9.3518 | -2.9419 |
| 3 | 2.1288 | 7,848 | $.1274 \times 10^{-3}$ | -8.9680 | -3.3364 |
| 4 | 2.1231 | 5,100 | $.1961 \times 10^{-3}$ | -8.5370 | -3.7727 |
| 5 | 2.1209 | 2,250 | $.4444 \times 10^{-3}$ | -7.7187 | -4.5932 |
| 6 | 2.1164 | 900 | $.1111 \times 10^{-2}$ | -6.8024 | -5.5137 |
| 7 | 2.0964 | 648 | $.1543 \times 10^{-2}$ | -6.4739 | -5.8611 |

# TABLE VII

## ISOTHERMAL ANALYSIS, TIME-TO-DEFLAGRATION

| RUN # | 1000/T | $1/\tau(sec^{-1})$ | $\ln(\tau/T^2)$ | $\ln(1/\tau)$ |
|-------|--------|---------------------|------------------|----------------|
| 2 | 2.1402 | $.6988 \times 10^{-4}$ | $-6.8194$ | $-5.4744$ |
| 3 | 2.1288 | $.1145 \times 10^{-3}$ | $-7.3235$ | $-4.9809$ |
| 4 | 2.1231 | $.1550 \times 10^{-3}$ | $-7.6322$ | $-4.6775$ |
| 5 | 2.1209 | $.2849 \times 10^{-3}$ | $-8.2428$ | $-4.0690$ |
| 6 | 2.1164 | $.4789 \times 10^{-3}$ | $-8.7665$ | $-3.5496$ |
| 7 | 2.0964 | $.8681 \times 10^{-3}$ | $-9.3801$ | $-2.9549$ |

# TABLE VIII

## ISOTHERMAL RESULTS

| | INDUCTION TIME | | TIME-TO-DEFLAGRATION | |
|---|---|---|---|---|
| | $1/t_o$ | $t_o/T^2$ | $1/\tau$ | $\tau/T^2$ |
| $E_a$ (kcal/mole)→ | 159.0282 | 160.9012 | 131.0144 | 132.8778 |

FIGURE 9: Thermogram of RDX, Heating Rate 20°C/min.

$\Delta T = 1.0°C$

T°C (CORRECTED FOR CHROMEL ALUMEL THERMOCOUPLES)

EXO ←——— $\Delta T$ ———→ ENDO
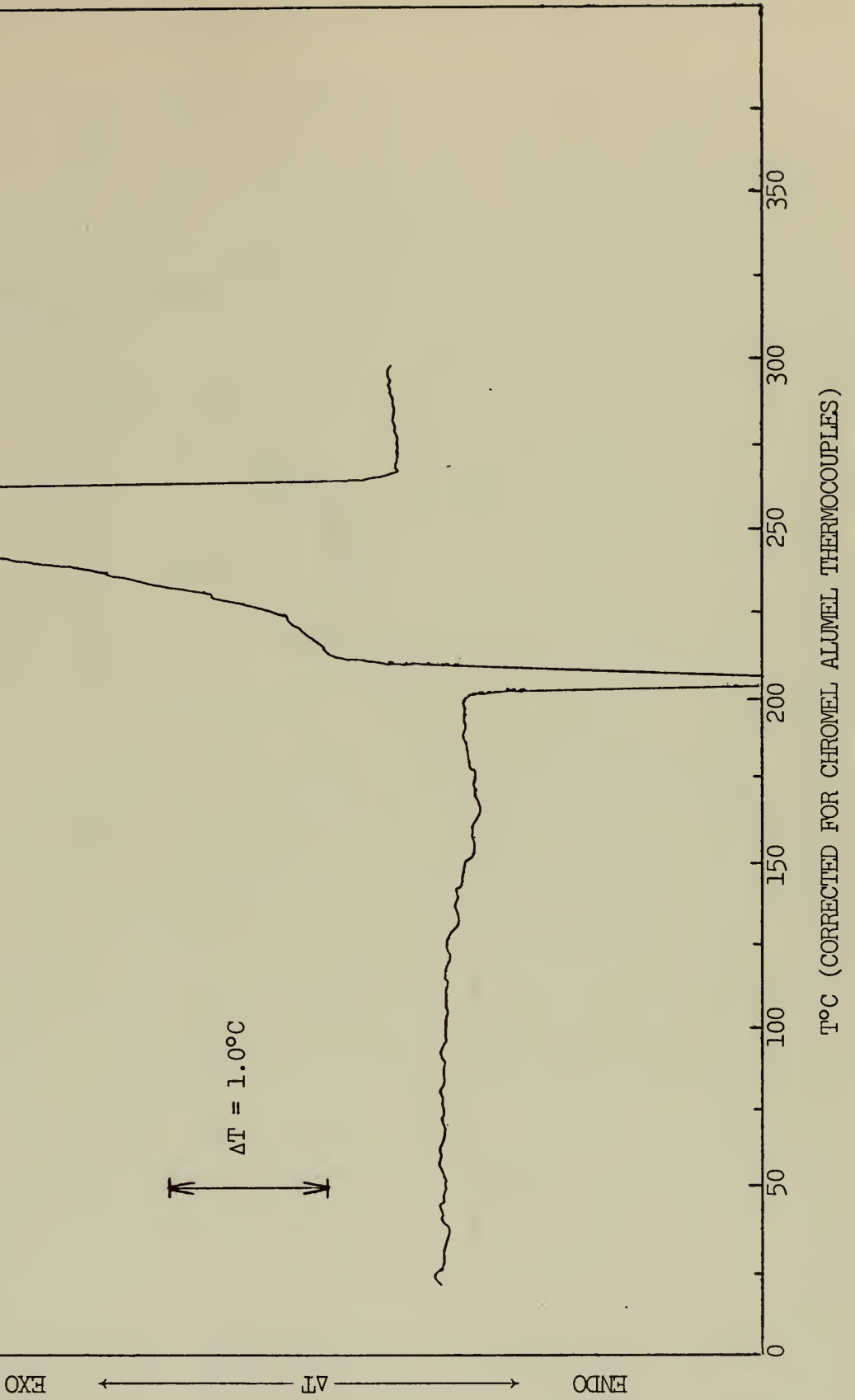
FIGURE 10: Thermogram of Ammonium Nitrate, Heating Rate 20°C/min.

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heating rate = 2.43° C/min.

heating rate = 2.88° C/min.

heating rate = 3.33° C/min.

0.2° C

204        220        240        260        280        300° C
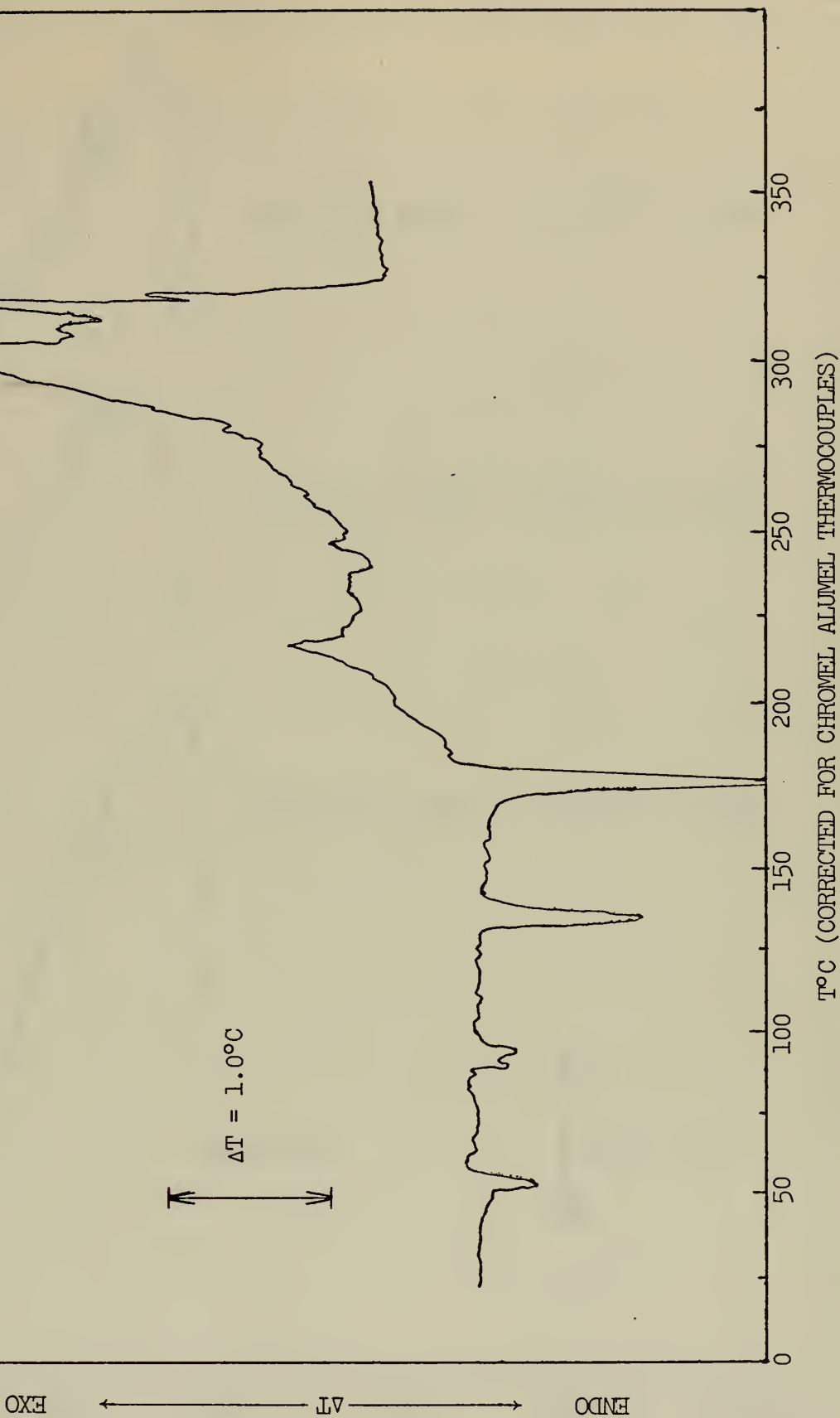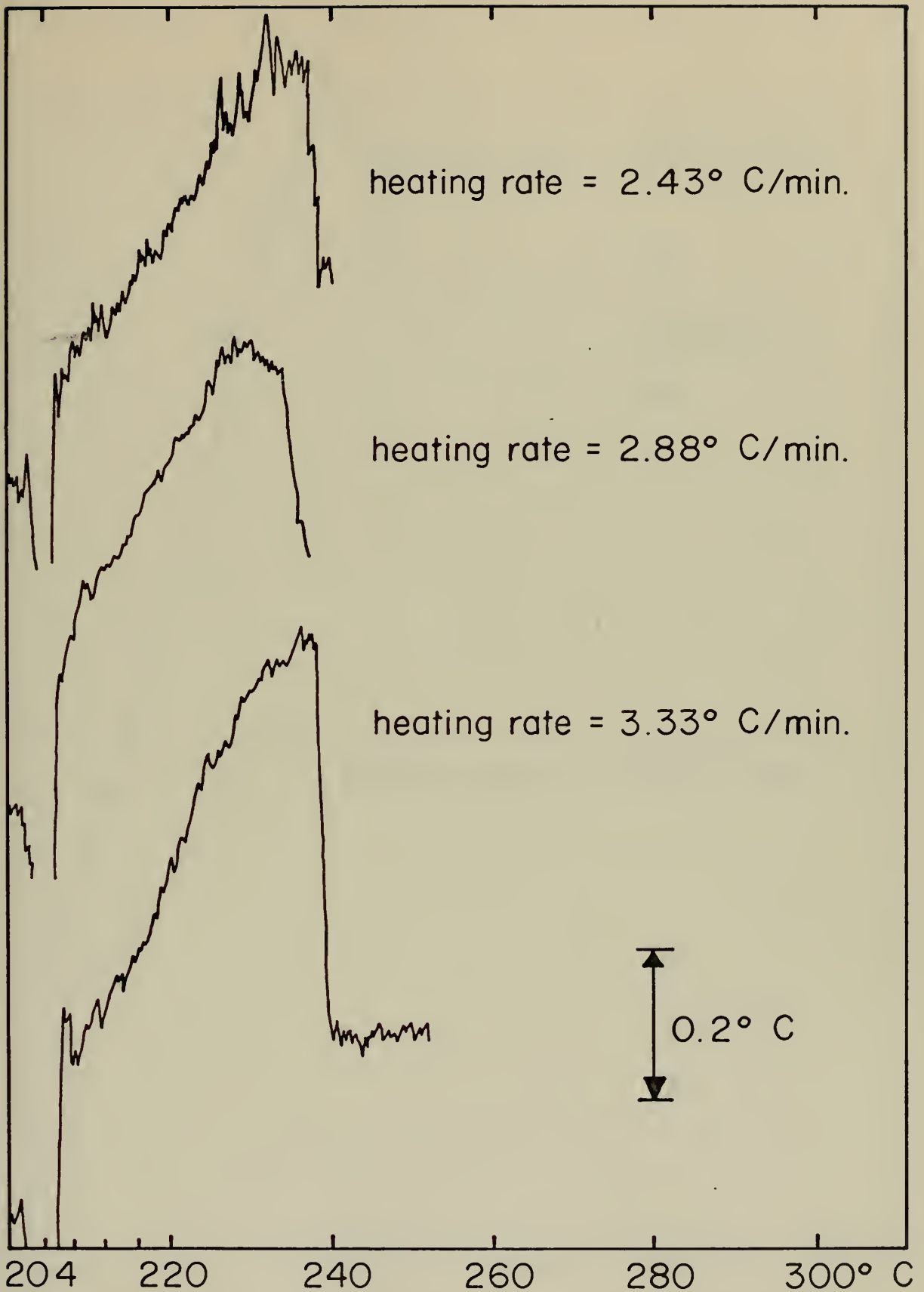
Figure II. Variable Heating runs I-3.

Figure 12. Variable Heating rate runs 4 & 5.

heating rate = 4.70° C/min.

heating rate = 5.19° C/min.

heating rate = 5.66° C/min.

0.5°C

204        220        240        260        280        300° C
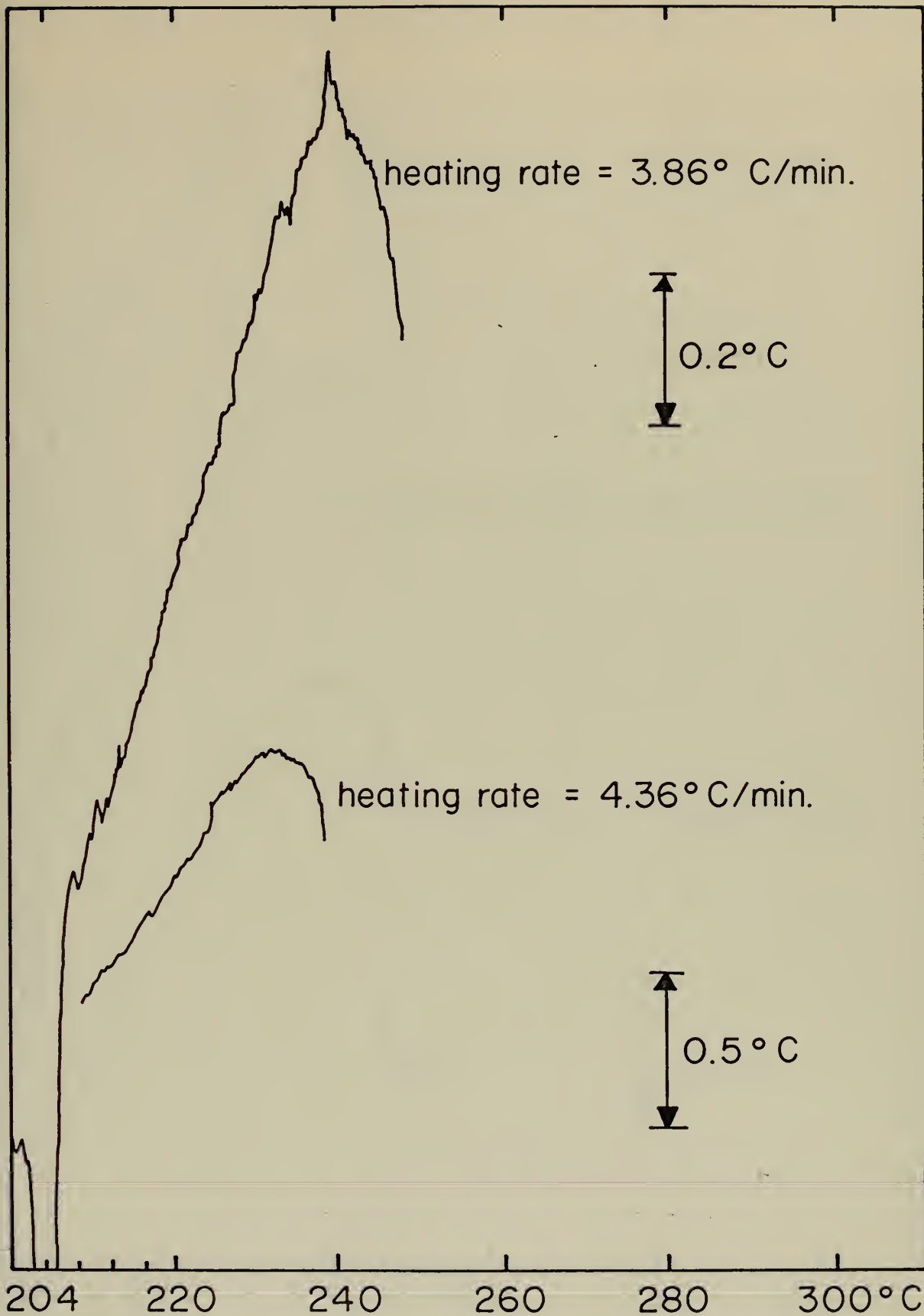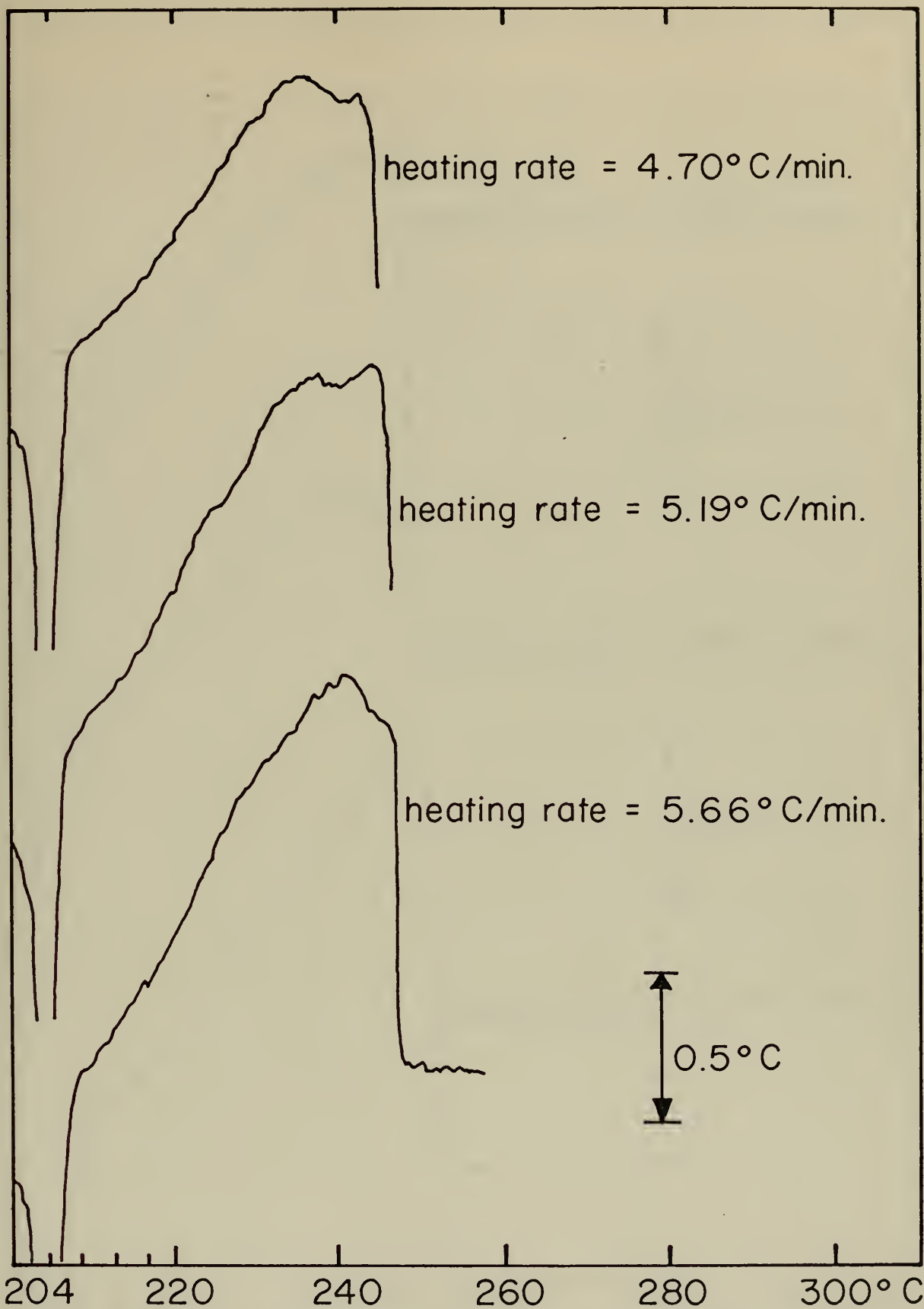
Figure 13. Variable Heating Rate Runs 6-8.

heating rate = 6.21° C/min.

0.5° C

heating rate = 6.82° C/min.

1.0° C

heating rate = 7.92° C/min.

204    220    240    260    280    300° C
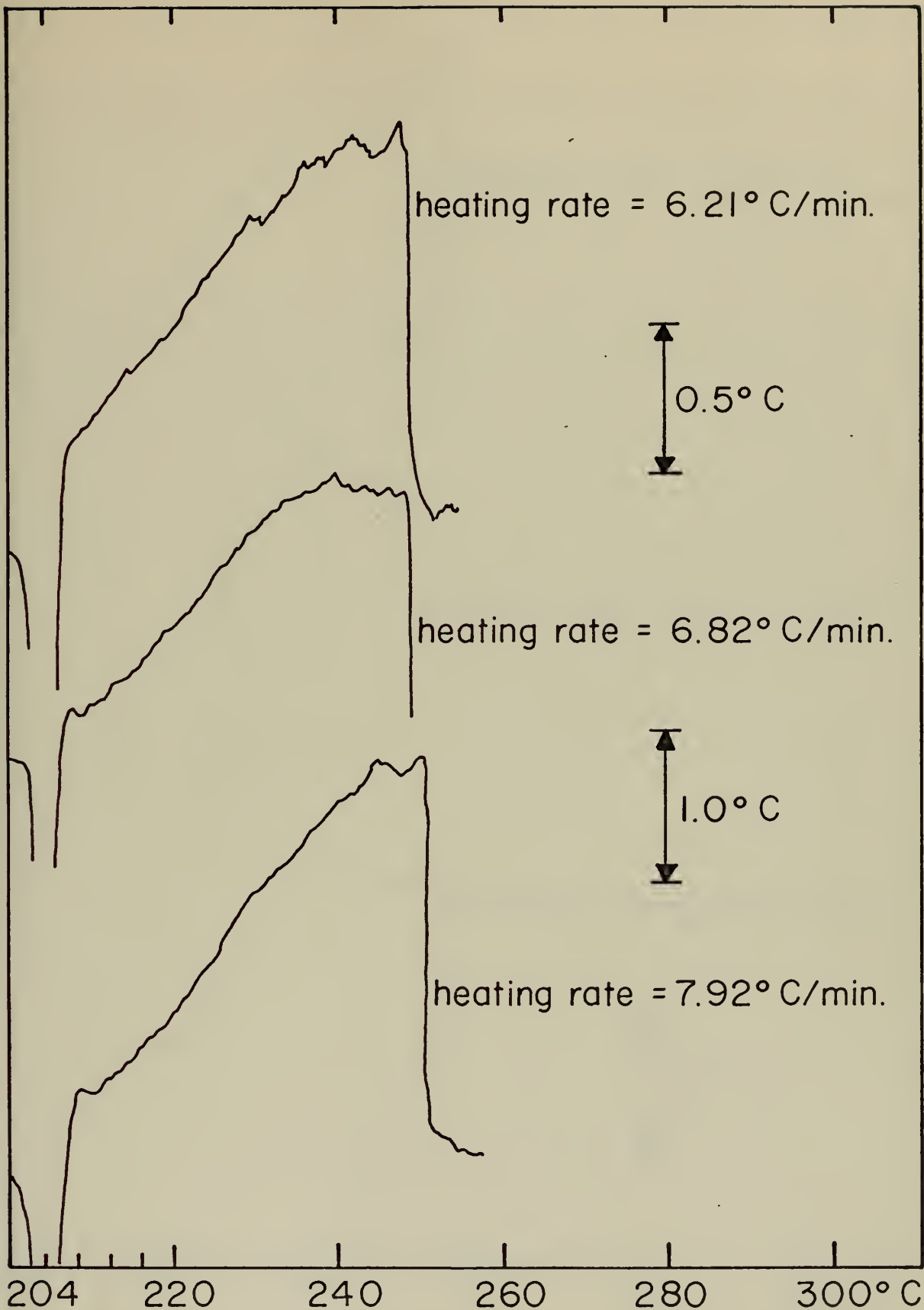
Figure 14. Variable Heating Rate Runs 9–11.

heating rate = 8.87° C/min.

heating rate = 9.71° C/min.

heating rate = 0.56° C/min.

1.0° C

204      220      240      260      280      300° C
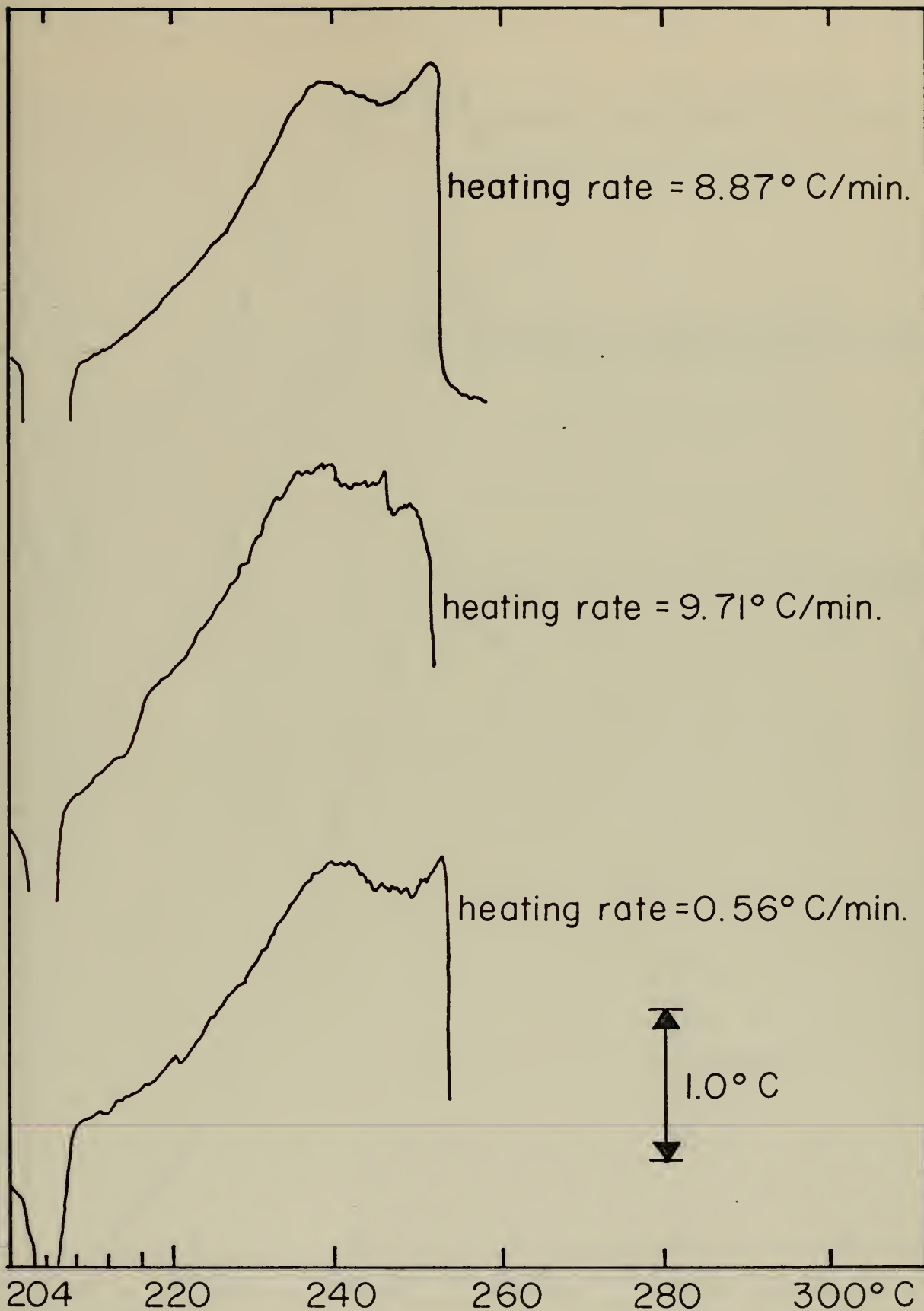
Figure 15. Variable Heating Rate Runs 12-14.

47
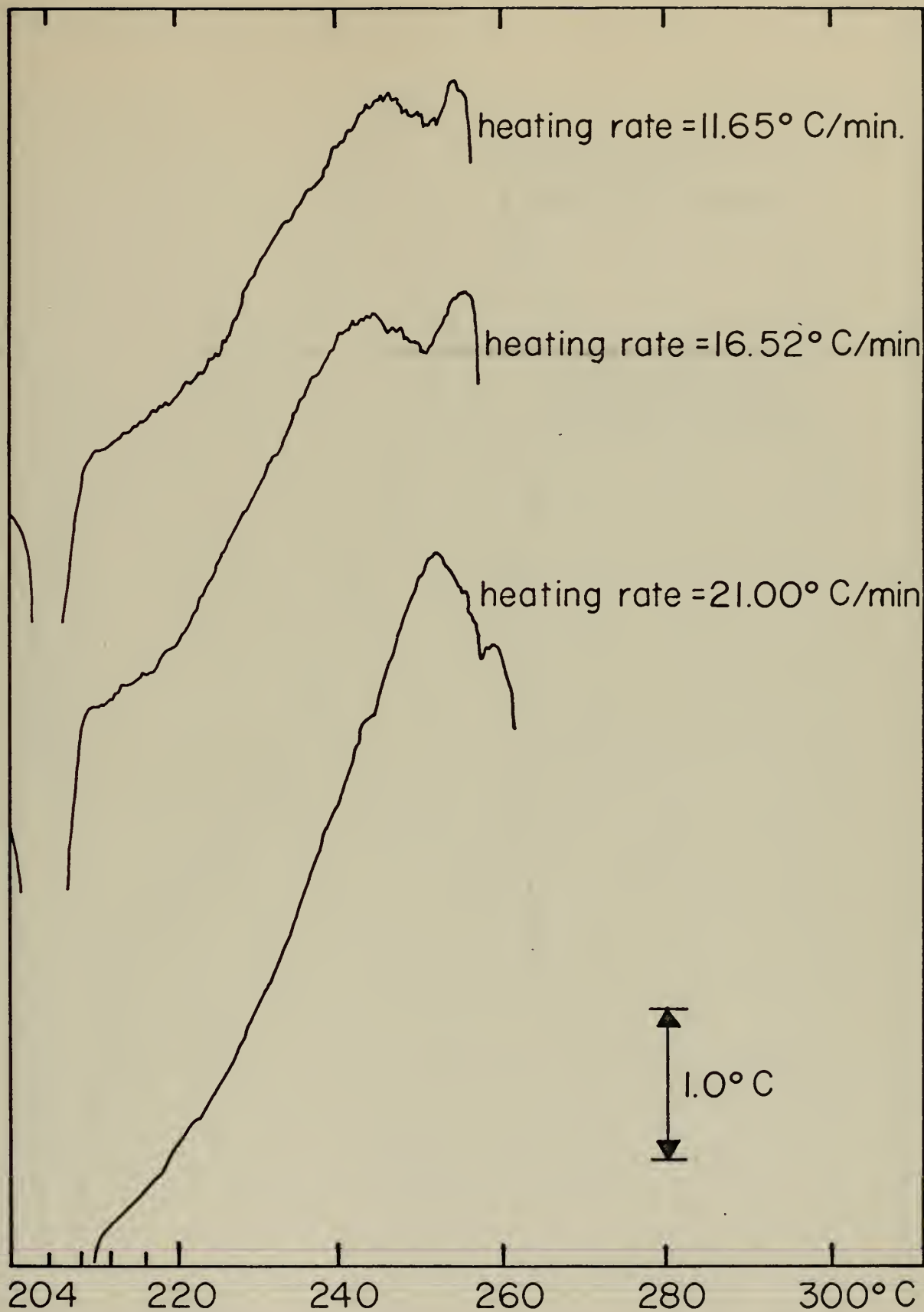
Figure 16. Variable Heating Rate Runs 15-17.
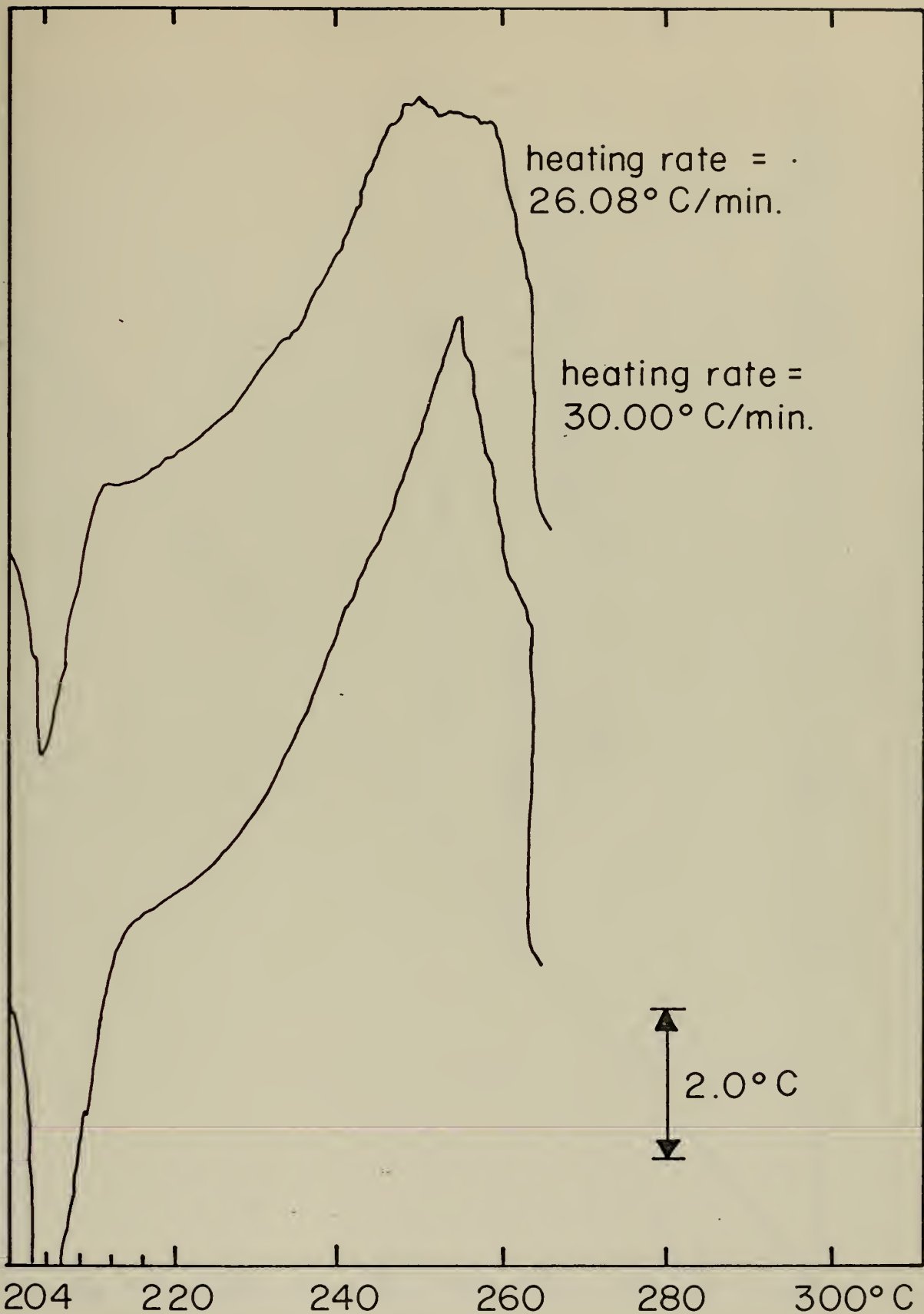
Figure 17. Variable Heating Rate Runs 18 & 19.

slope = 0.04077 °K/sec

WANG 700 PROGRAM:

$T = 463.425 + .1786t - .8974 \times 10^{-3} t^2 + .1997 \times 10^{-5} t^3$
$- .1801 \times 10^{-8} t^4 + .5666 \times 10^{-12} t^5$
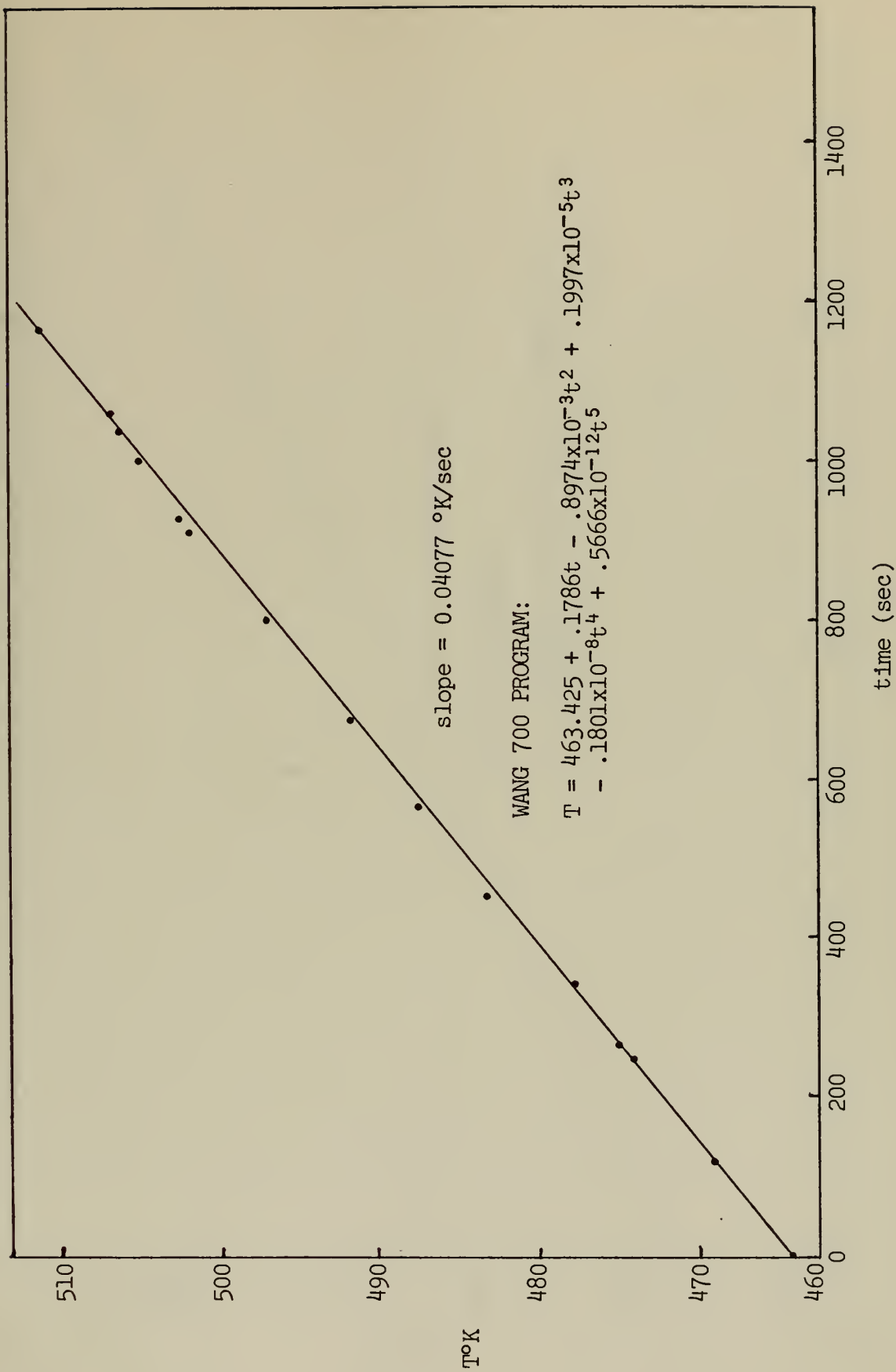
FIGURE 18: T°K vs. time, heating rate 2.43°C/min.

50

slope — 0.04800 °K/sec

WANG 700 PROGRAM:

$T = 464.0894 + .4290 \times 10^{-1}t + .1879 \times 10^{-4}t^2 - .1307 \times 10^{-7}t^3 - .5904 \times 10^{-11}t^4 + .4352 \times 10^{-14}t^5$

time (sec)

T°K

500

490

480

470

460

100   200   300   400   500   600   700   800
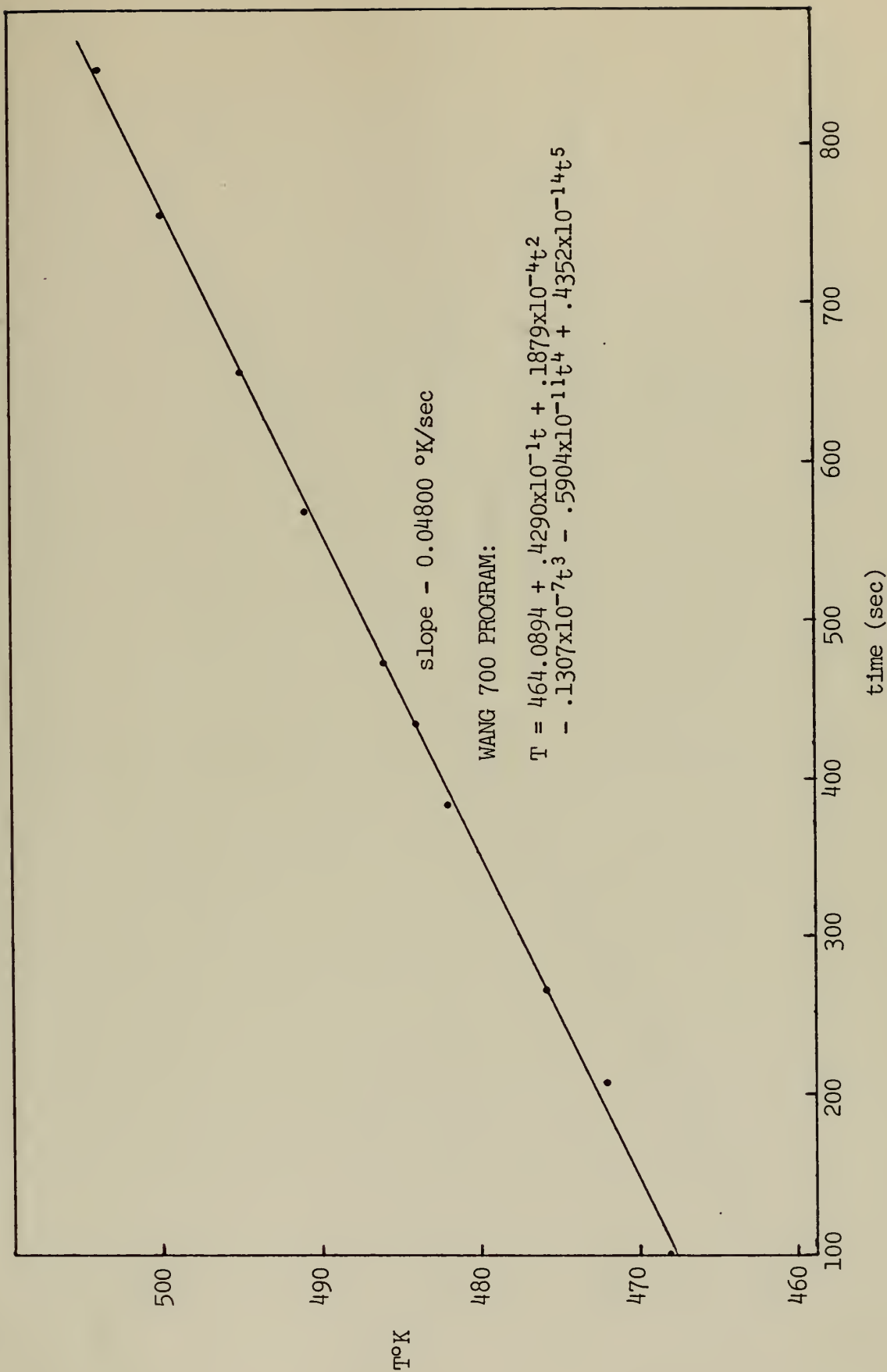
FIGURE 19: T°K vs. time, heating rate 2.88°C/min.

51
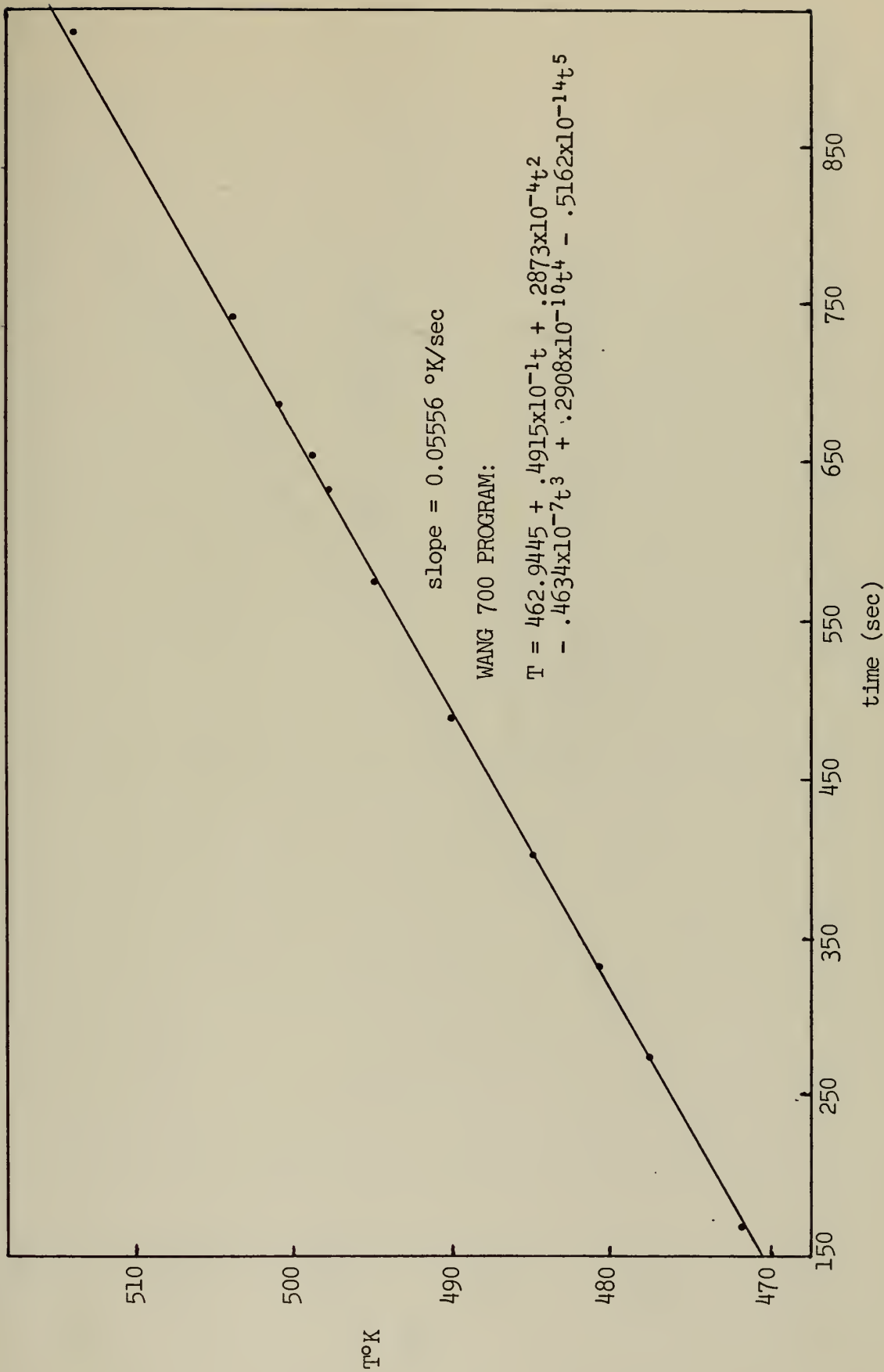
FIGURE 20: T°K vs. time, heating rate 3.33°C/min.

slope = 0.05556 °K/sec

WANG 700 PROGRAM:

$$T = 462.9445 + .4915 \times 10^{-1} t + .2873 \times 10^{-4} t^2 - .4634 \times 10^{-7} t^3 + .2908 \times 10^{-10} t^4 - .5162 \times 10^{-14} t^5$$

52

slope = 0.06430 °K/sec

WANG 700 PROGRAM:

$T = 466.0017 + .7358 \times 10^{-1} t - .8636 \times 10^{-4} t^2$
$+ .2648 \times 10^{-6} t^3 - .3223 \times 10^{-9} t^4 + .1364 \times 10^{-12} t^5$
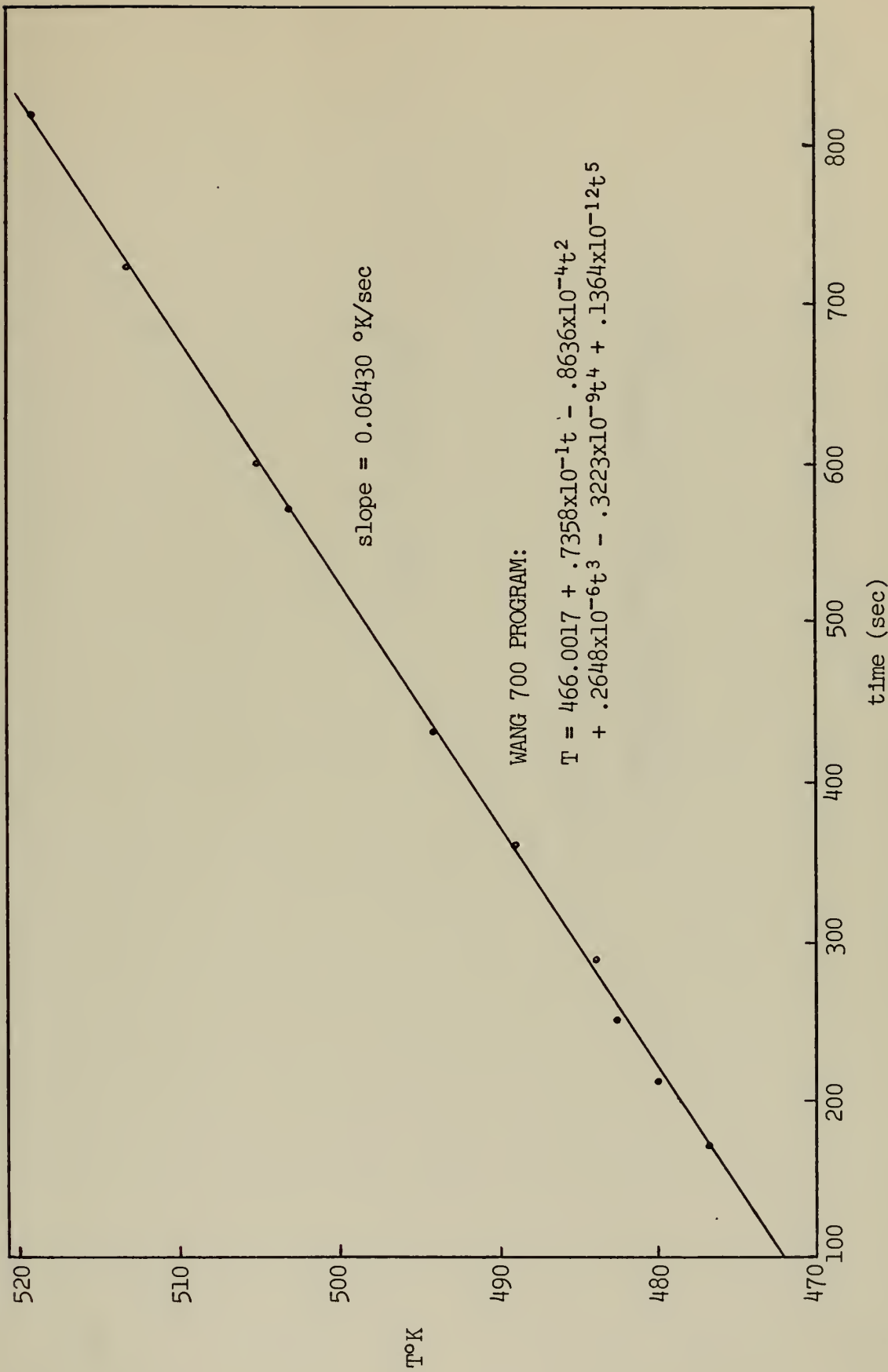
FIGURE 21: T°K vs. time, heating rate 3.86°C/min.

53

slope = 0.07273 °K/sec

WANG 700 PROGRAM:

$T = 465.2145 + .7830 \times 10^{-1}t - .4030 \times 10^{-4}t^2 + .1477 \times 10^{-6}t^3 - .2472 \times 10^{-9}t^4 + .1482 \times 10^{-12}t^5$
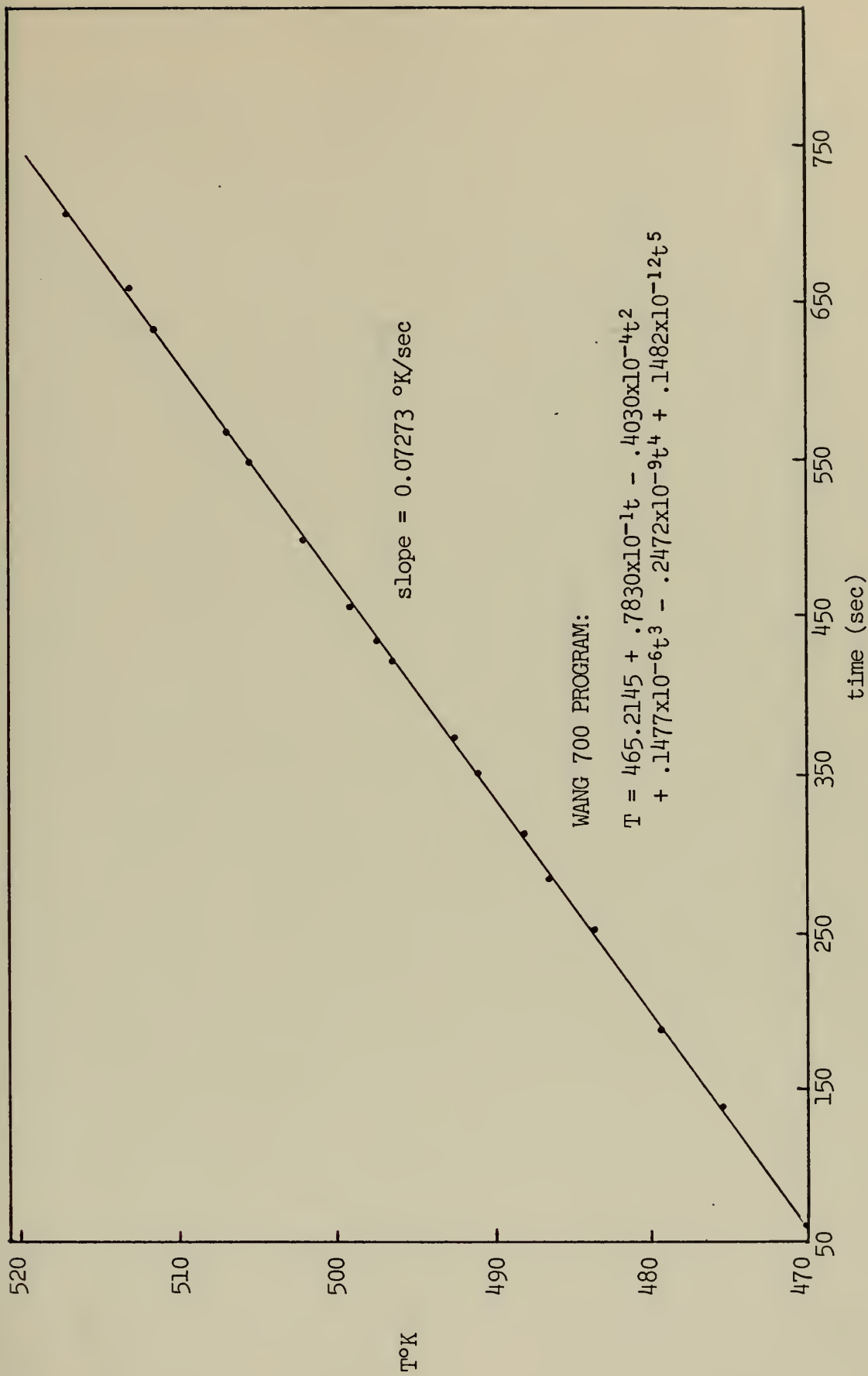
FIGURE 22: T°K vs. time, heating rate 4.36°C/min.

54

slope = 0.0783 °K/sec

WANG 700 PROGRAM:

$T = 462.9910 + .8495 \times 10^{-1}t - .1158 \times 10^{-3}t^2 + .4745 \times 10^{-6}t^3 - .7345 \times 10^{-9}t^4 + .3924 \times 10^{-12}t^5$

time (sec)

T°K
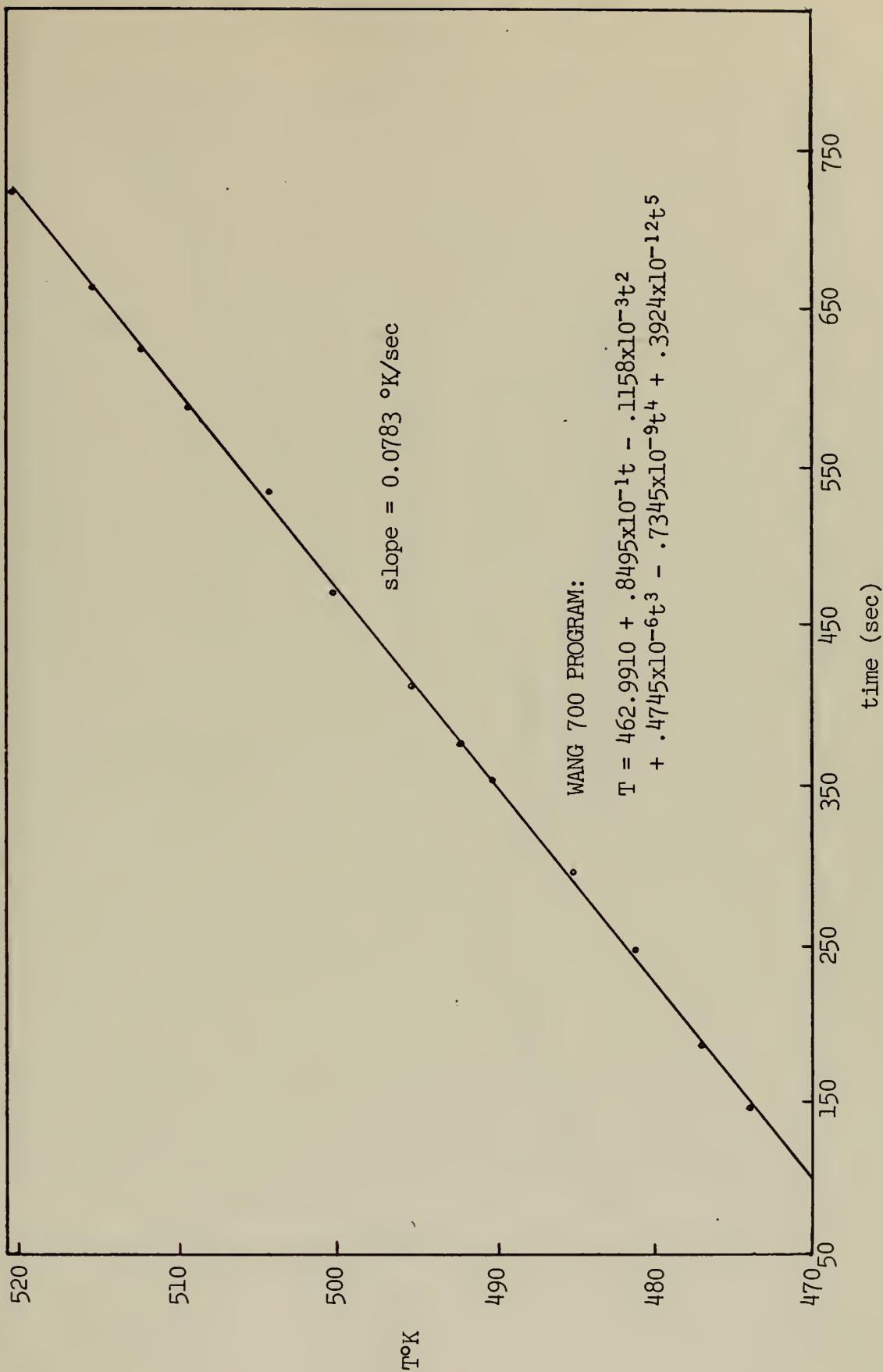
FIGURE 23: T°K vs. time, heating rate 4.70°C/min.

55

slope = 0.0866 °K/sec

WANG 700 PROGRAM:

$T = 475.4787 + .9684 \times 10^{-1} t - .2127 \times 10^{-3} t^2$
$+ .1550 \times 10^{-5} t^3 - .4344 \times 10^{-8} t^4 + .4077 \times 10^{-11} t^5$
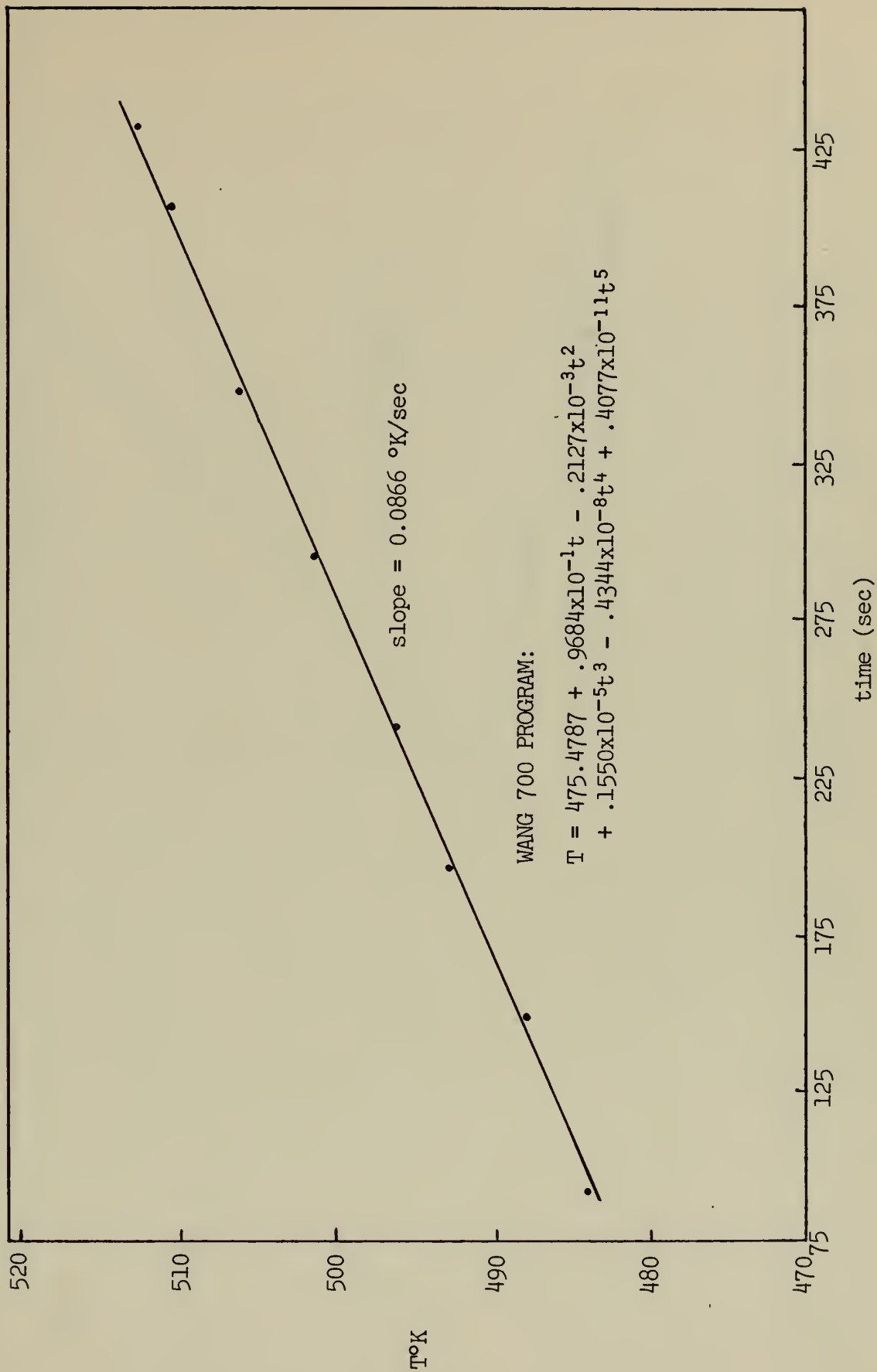
FIGURE 24: T°K vs. time, heating rate 5.19°C/min.

slope = 0.0943 °K/sec

WANG 700 PROGRAM:

$T = 462.3624 + .1049t - .1074 \times 10^{-3}t^2$
$+ .4228 \times 10^{-6}t^3 - .7148 \times 10^{-9}t^4 + .4291 \times 10^{-12}t^5$
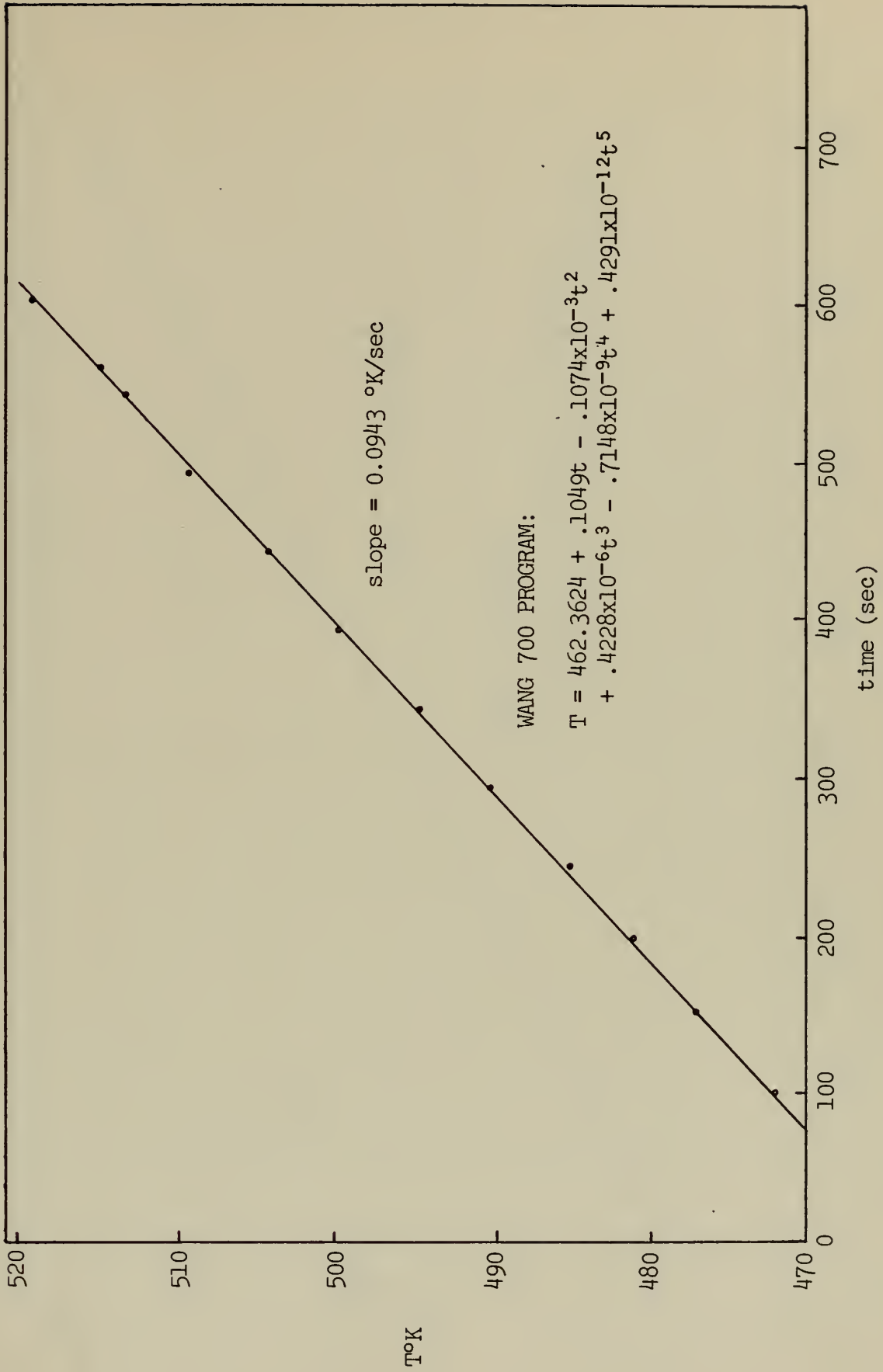
FIGURE 25: T°K vs. time, heating rate 5.66°C/min.

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slope = 0.1035 °K/sec

WANG 700 PROGRAM:

$T = 469.4820 + .8434 \times 10^{-1} t + .1237 \times 10^{-3} t^2$
$- .1738 \times 10^{-6} t^3 - .3607 \times 10^{-9} t^4 + .7437 \times 10^{-12} t^5$
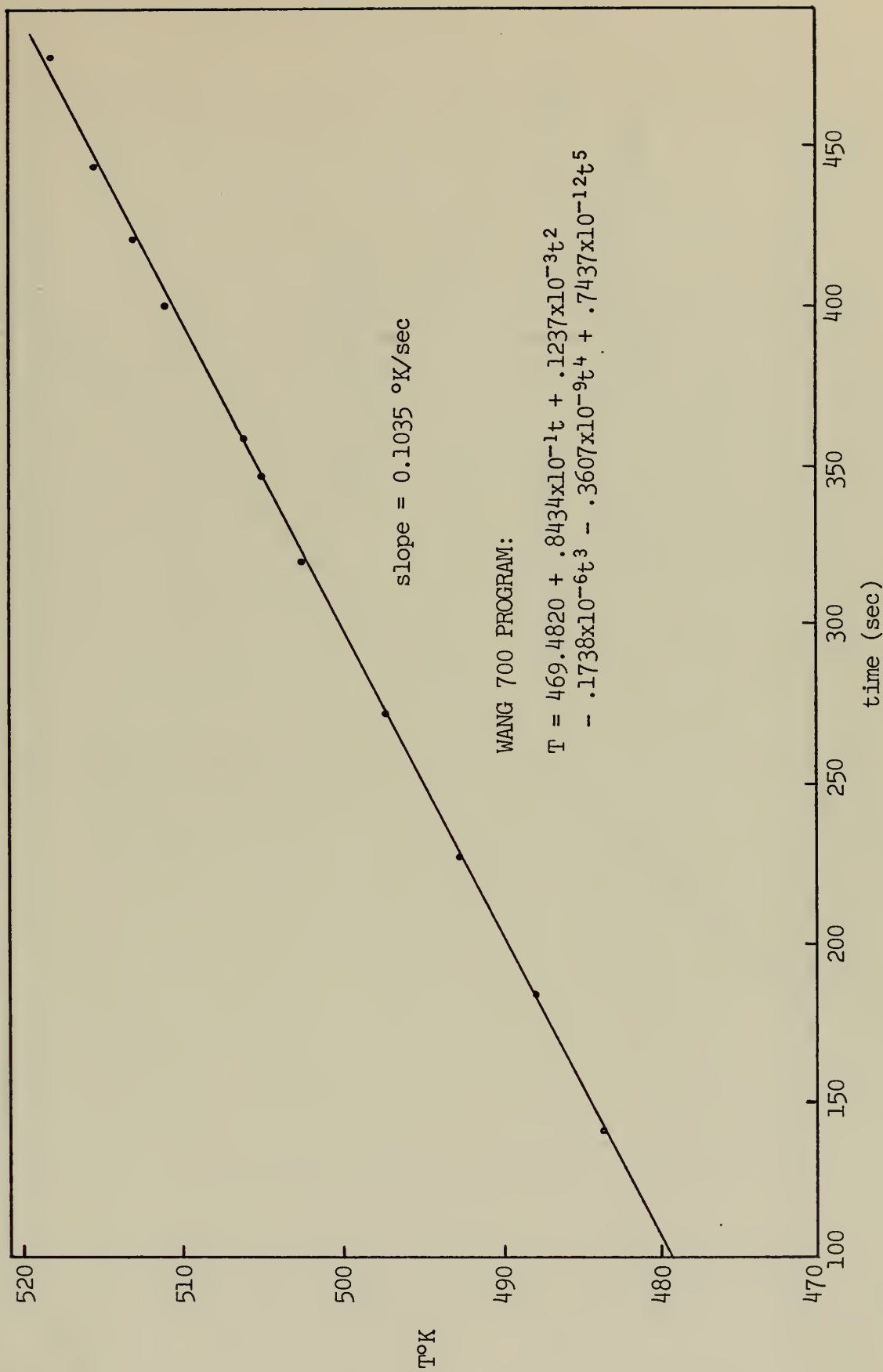
FIGURE 26: T°K vs. time, heating rate 6.21°C/min.

slope = 0.1136 °K/sec

WANG 700 PROGRAM:

$T = 463.0536 + .1191t - .2283 \times 10^{-3} t^2$
$+ .1598 \times 10^{-5} t^3 - .4035 \times 10^{-8} t^4 + .3396 \times 10^{-11} t^5$
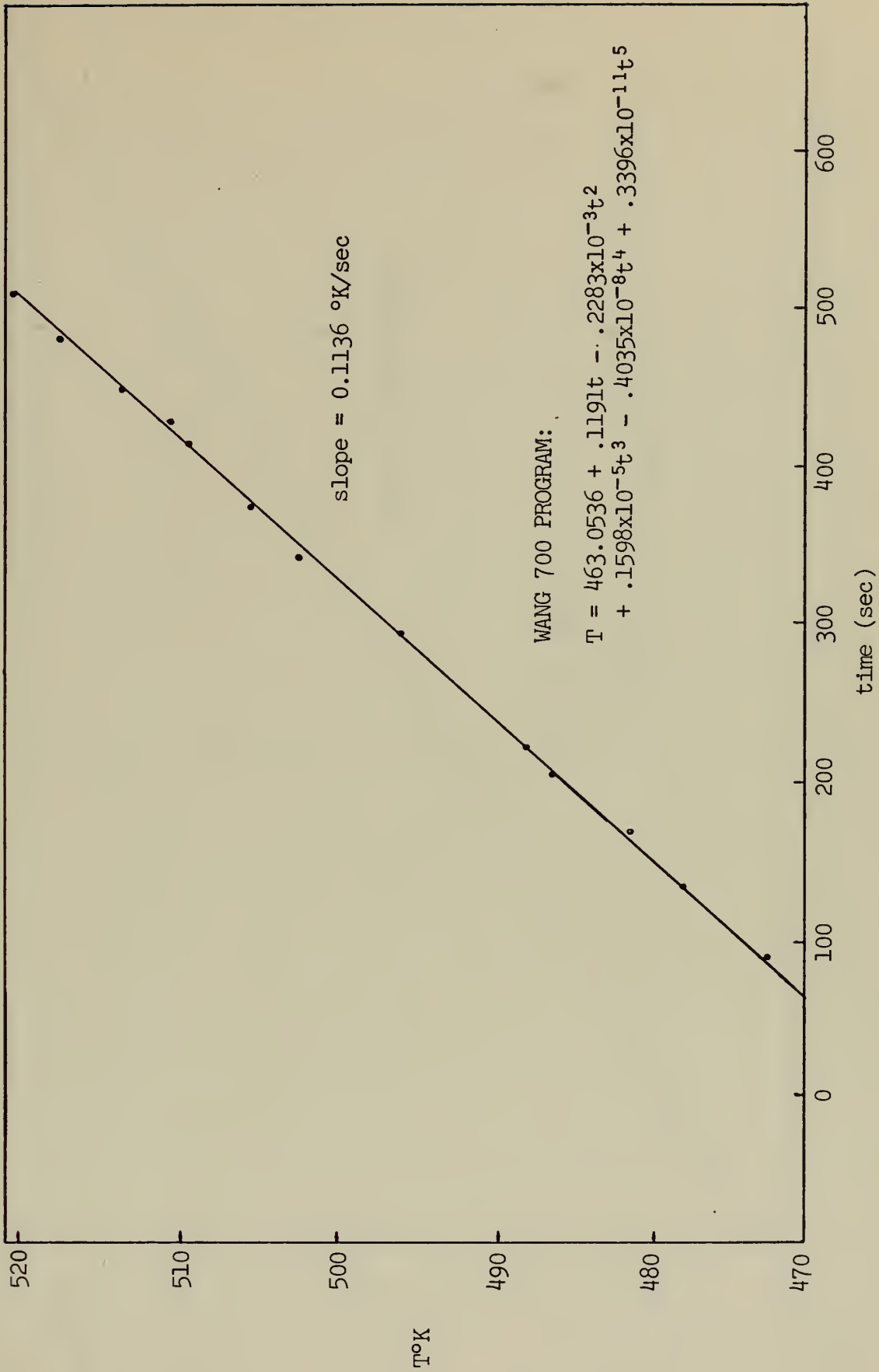
FIGURE 27: T°K vs. time, heating rate 6.82°C/min.

59
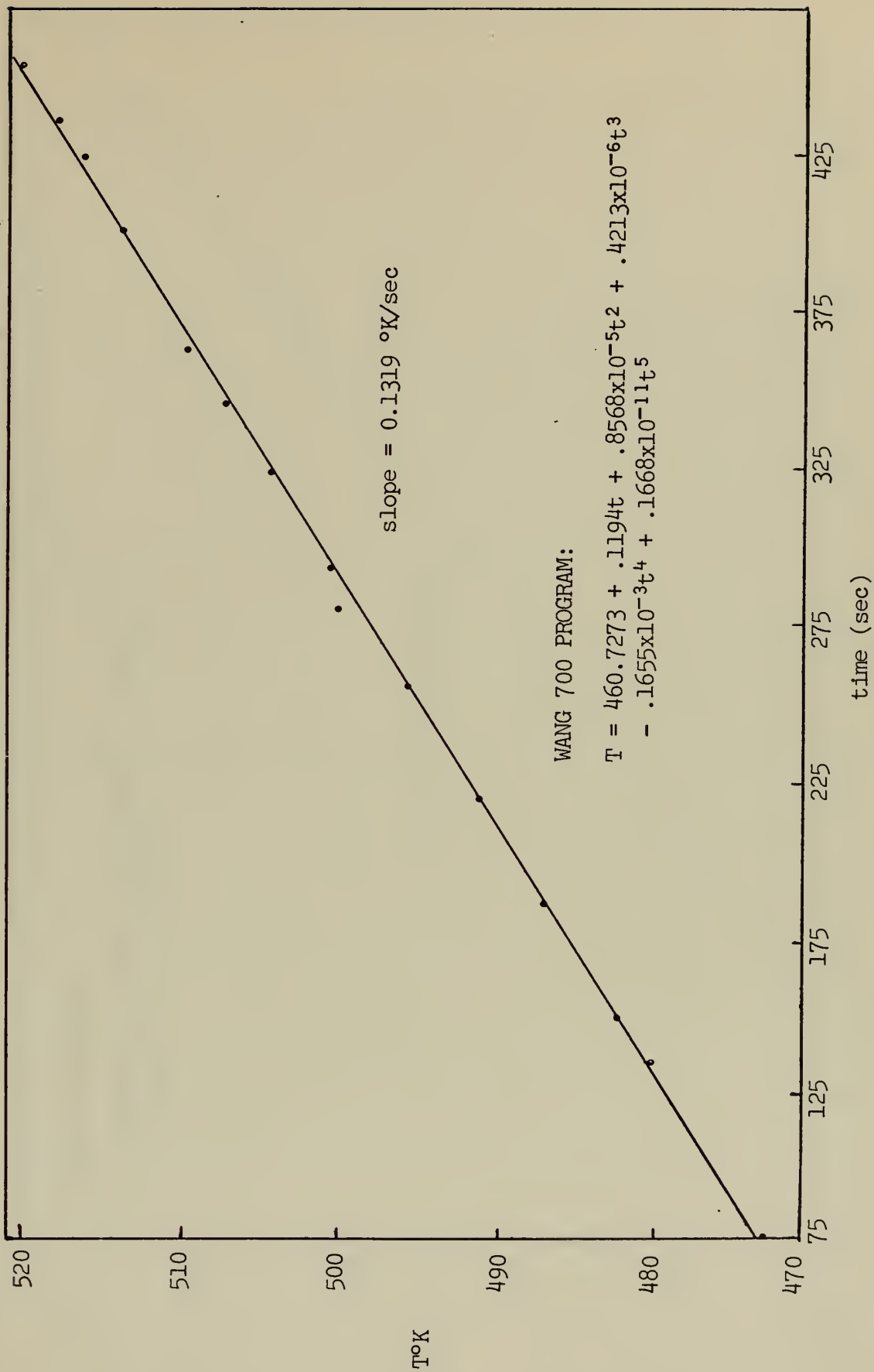
FIGURE 28: T°K vs. time, heating rate 7.92°C/min.

slope = 0.1319 °K/sec

WANG 700 PROGRAM:

$T = 460.7273 + .1194t + .8568 \times 10^{-5}t^2 + .4213 \times 10^{-6}t^3$
$\quad - .1655 \times 10^{-3}t^4 + .1668 \times 10^{-11}t^5$

60
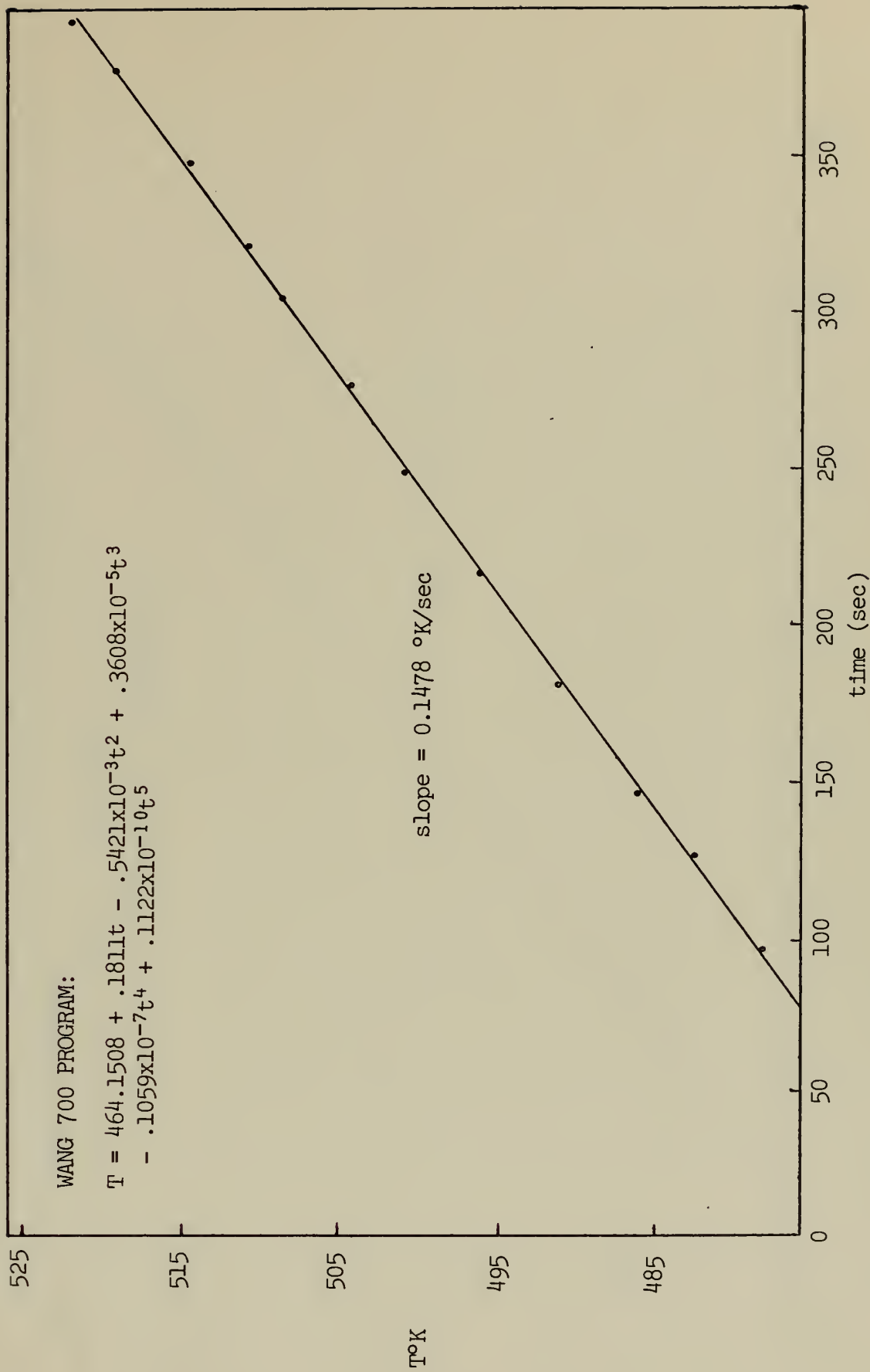
FIGURE 29: T°K vs. time, heating rate 8.87°C/min.

WANG 700 PROGRAM:

$T = 464.1508 + .1811t - .5421 \times 10^{-3}t^2 + .3608 \times 10^{-5}t^3$
$- .1059 \times 10^{-7}t^4 + .1122 \times 10^{-10}t^5$

slope = 0.1478 °K/sec

WANG 700 PROGRAM:

$T = 468.1176 + .0650t + .3154 \times 10^{-2} t^2$
$\quad - .3222 \times 10^{-4} t^3 + .1298 \times 10^{-6} t^4 - .1798 \times 10^{-9} t^5$

slope = 0.1619 °K/sec
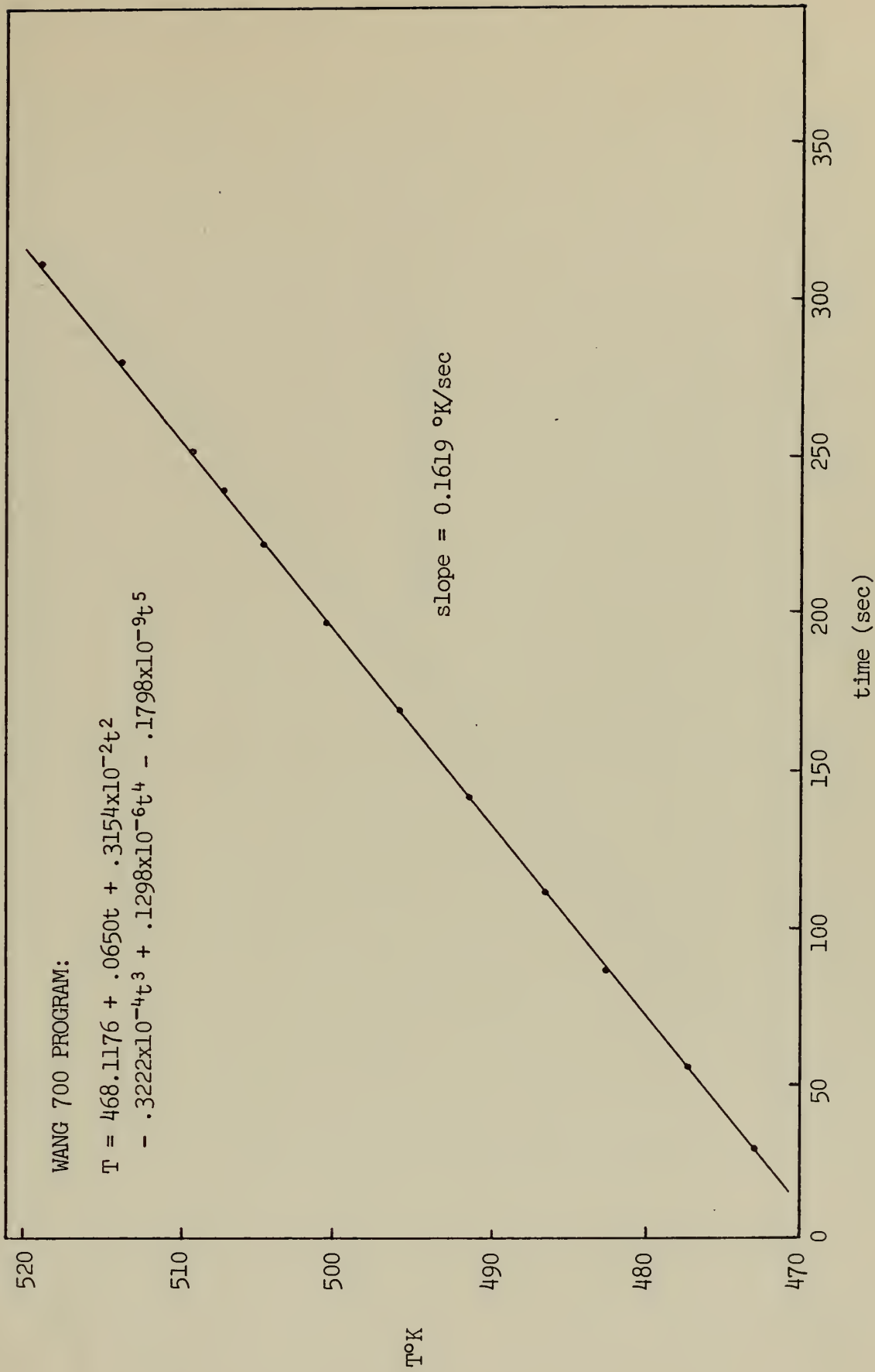
FIGURE 30: T°K vs. time, heating rate 9.71°C/min.

62

WANG 700 PROGRAM:

$T = 462.4540 + .1800t - .1625 \times 10^{-3} t^2$
$+ .2109 \times 10^{-5} t^3 - .9478 \times 10^{-8} t^4 + .1366 \times 10^{-10} t^5$

slope = 0.1759 °K/sec

T°K

time (sec)

520

510

500

490

480

470

0    50   100  150  200  250  300  350
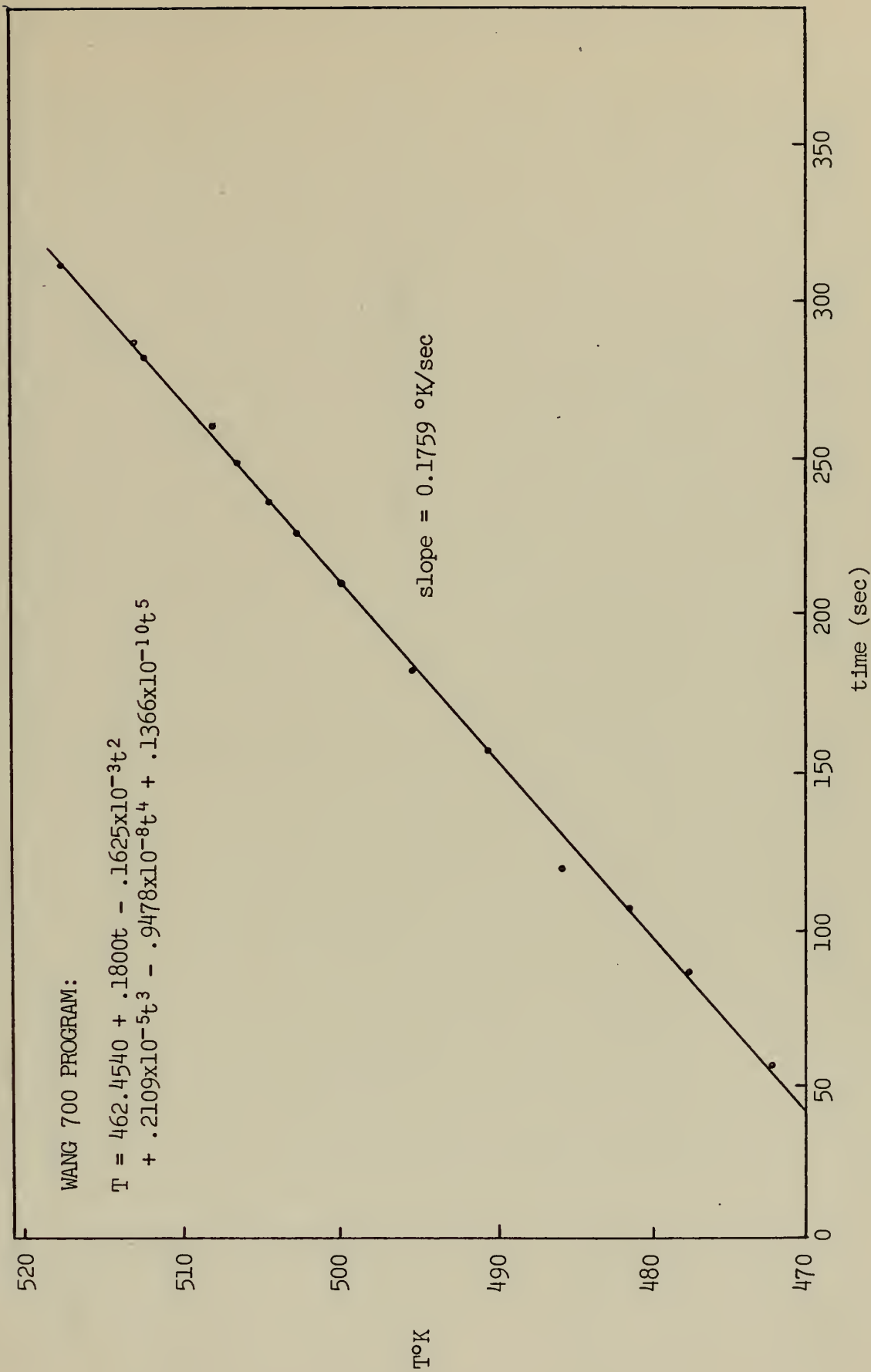
FIGURE 31: T°K vs. time, heating rate 10.56°C/min.

WANG 700 PROGRAM:

$T = 463.0963 + .1740t + .5270 \times 10^{-3}t^2$
$- .4575 \times 10^{-5}t^3 + .1629 \times 10^{-7}t^4 - .2054 \times 10^{-10}t^5$

slope = 0.1941 °K/sec
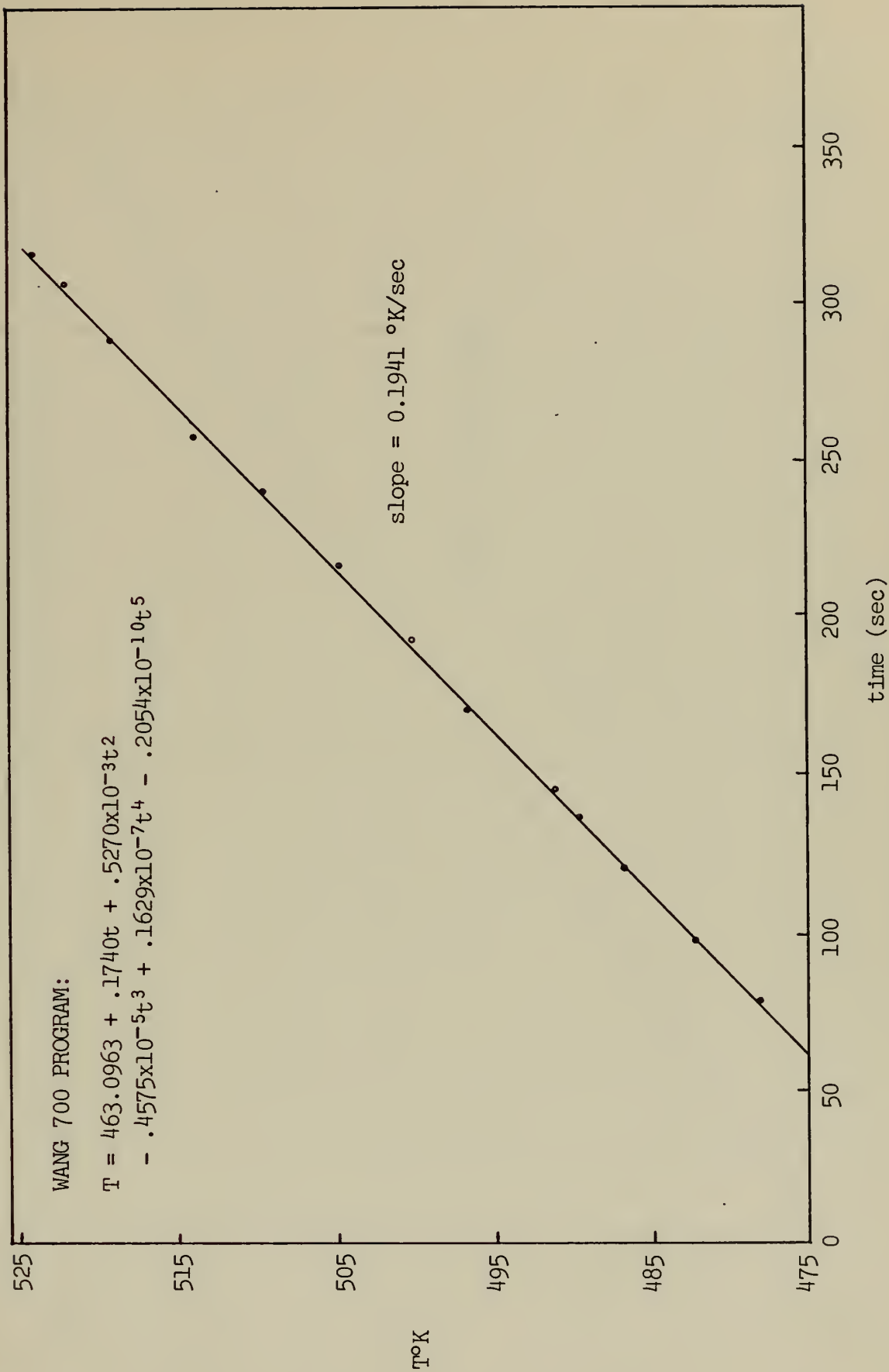
FIGURE 32: T°K vs. time, heating rate 11.65°C/min.

64

WANG 700 PROGRAM:

$T = 465.0456 + .2503t + .1219 \times 10^{-2} t^2$
$- .1584 \times 10^{-4} t^3 + .8030 \times 10^{-7} t^4 = .1410 \times 10^{-9} t^5$

slope = 0.2754 °K/sec
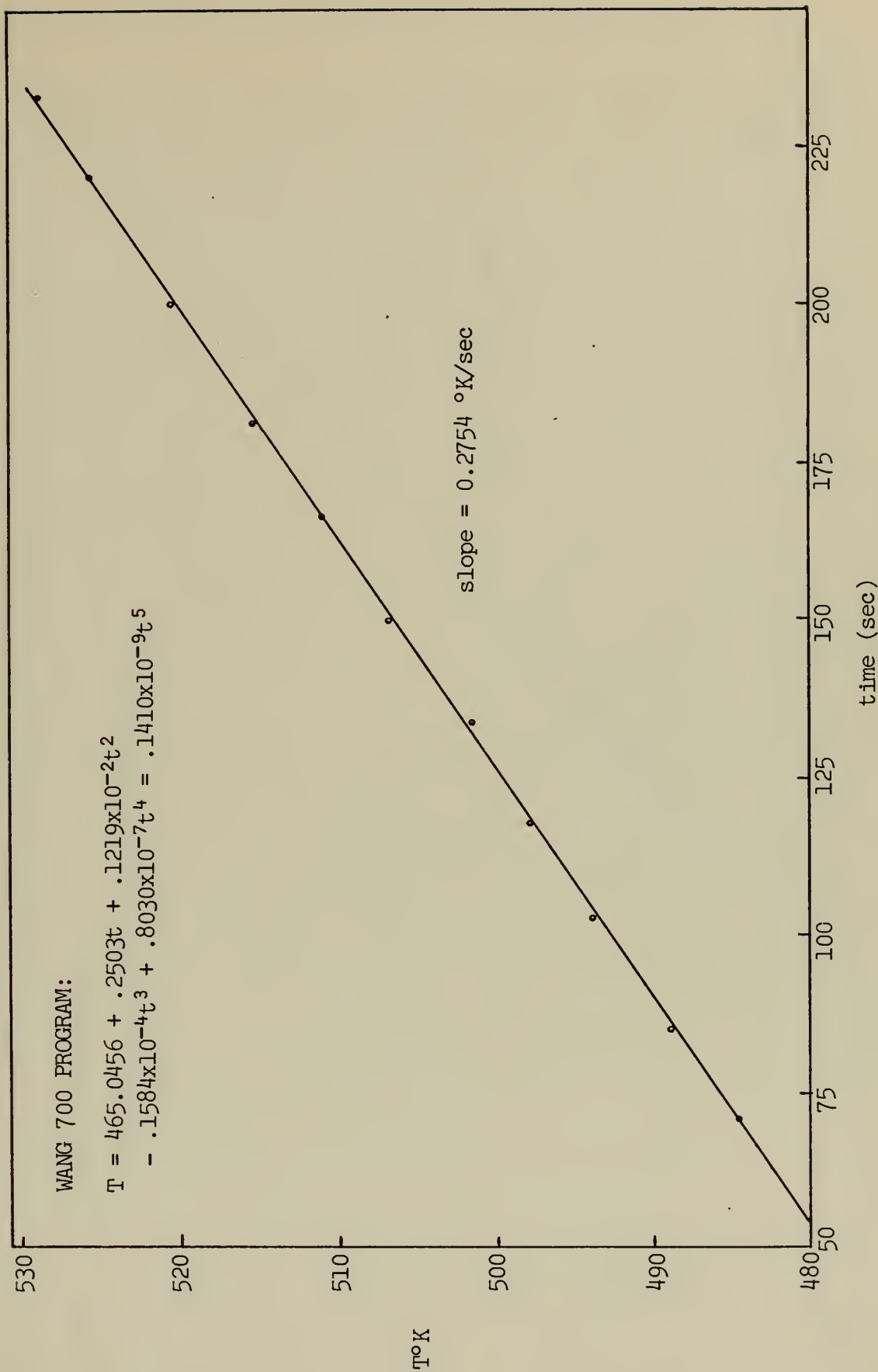
FIGURE 33: T°K vs. time, heating rate 16.52°C/min.

65

WANG 700 PROGRAM:

$T = 385.1072 + 3.9709t - .6274 \times 10^{-1} t^2$
$+ .5079 \times 10^{-3} t^3 - .1913 \times 10^{-5} t^4 + .2668 \times 10^{-8} t^5$

slope = 0.3500 °K/sec

time (sec)

T°K
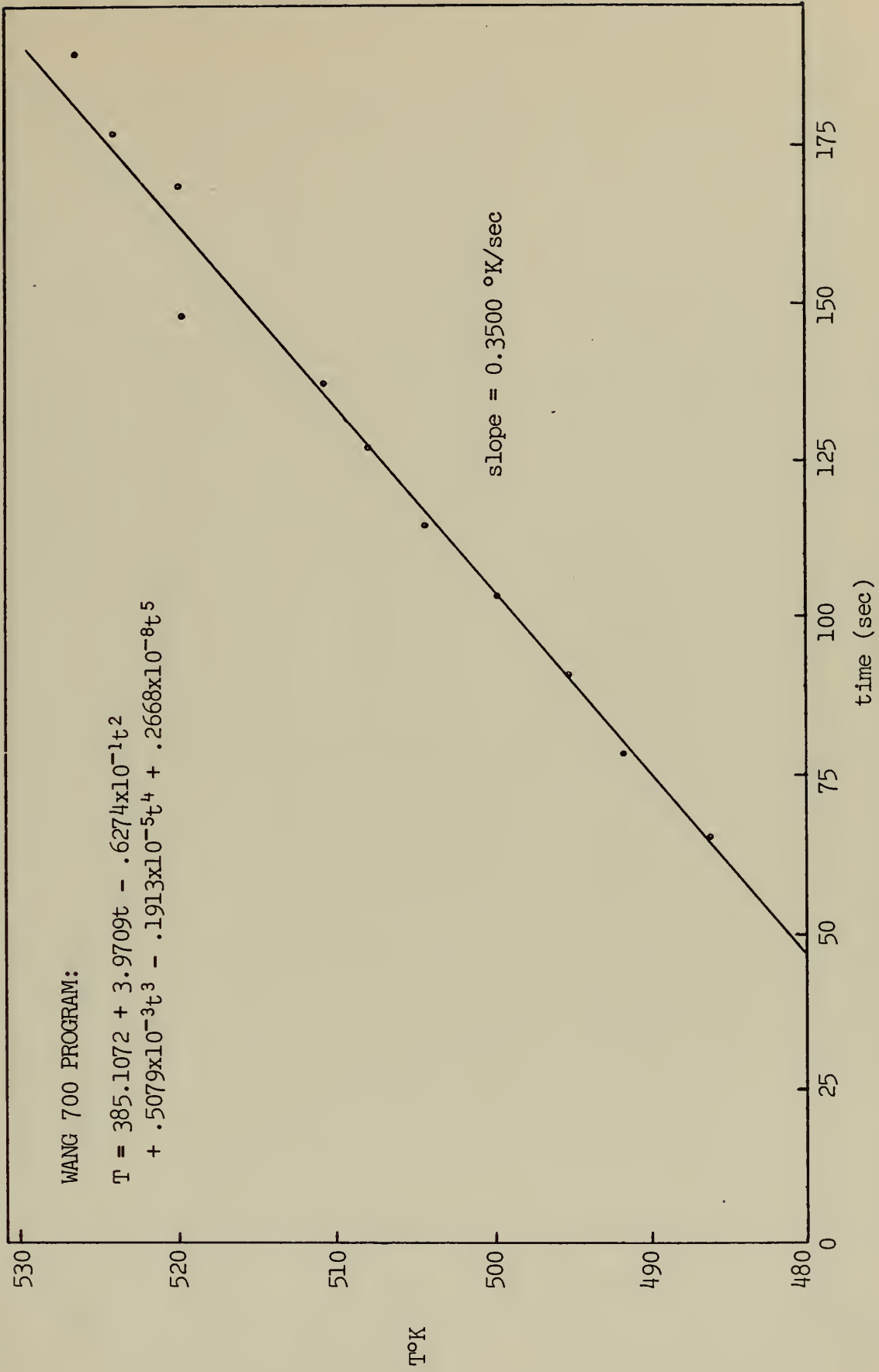
FIGURE 34: T°K vs. time, heating rate 21.00°C/min.

66

WANG 700 PROGRAM:

$T = 465.0032 + .3181t + .7594 \times 10^{-2}t^2$
$- .1551 \times 10^{-3}t^3 + .1270 \times 10^{-5}t^4 - .3604 \times 10^{-8}t^5$

slope = 0.4346 °K/sec

time (sec)

T°K
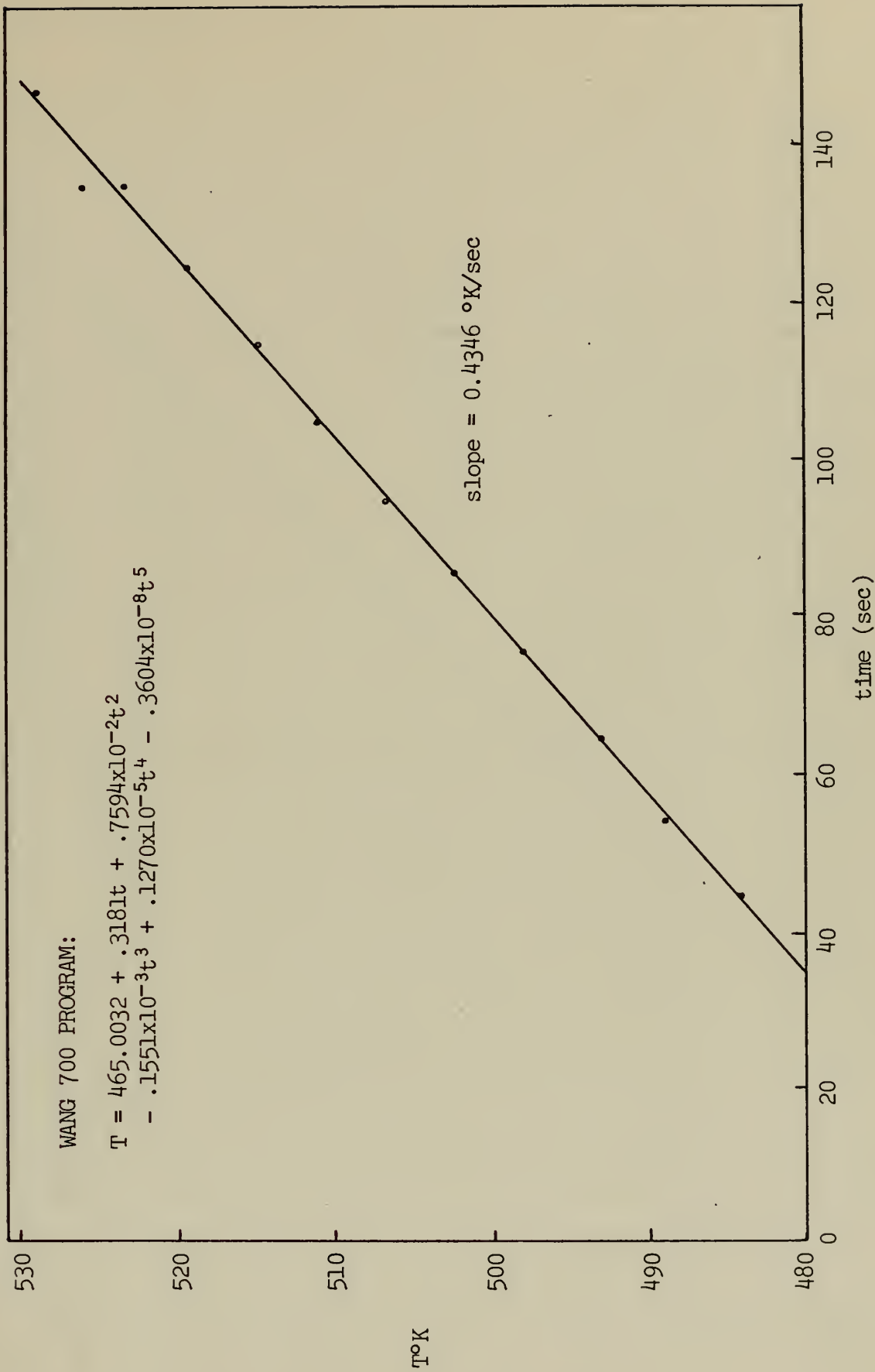
FIGURE 35: T°K vs. time, heating rate 26.08°C/min.

WANG 700 PROGRAM:

$T = 464.9626 + .4765t + .7926 \times 10^{-3}t^2$
$- .5774 \times 10^{-5}t^3 + .3909 \times 10^{-7}t^4 - .3254 \times 10^{-9}t^5$

slope = 0.5000 °K/sec
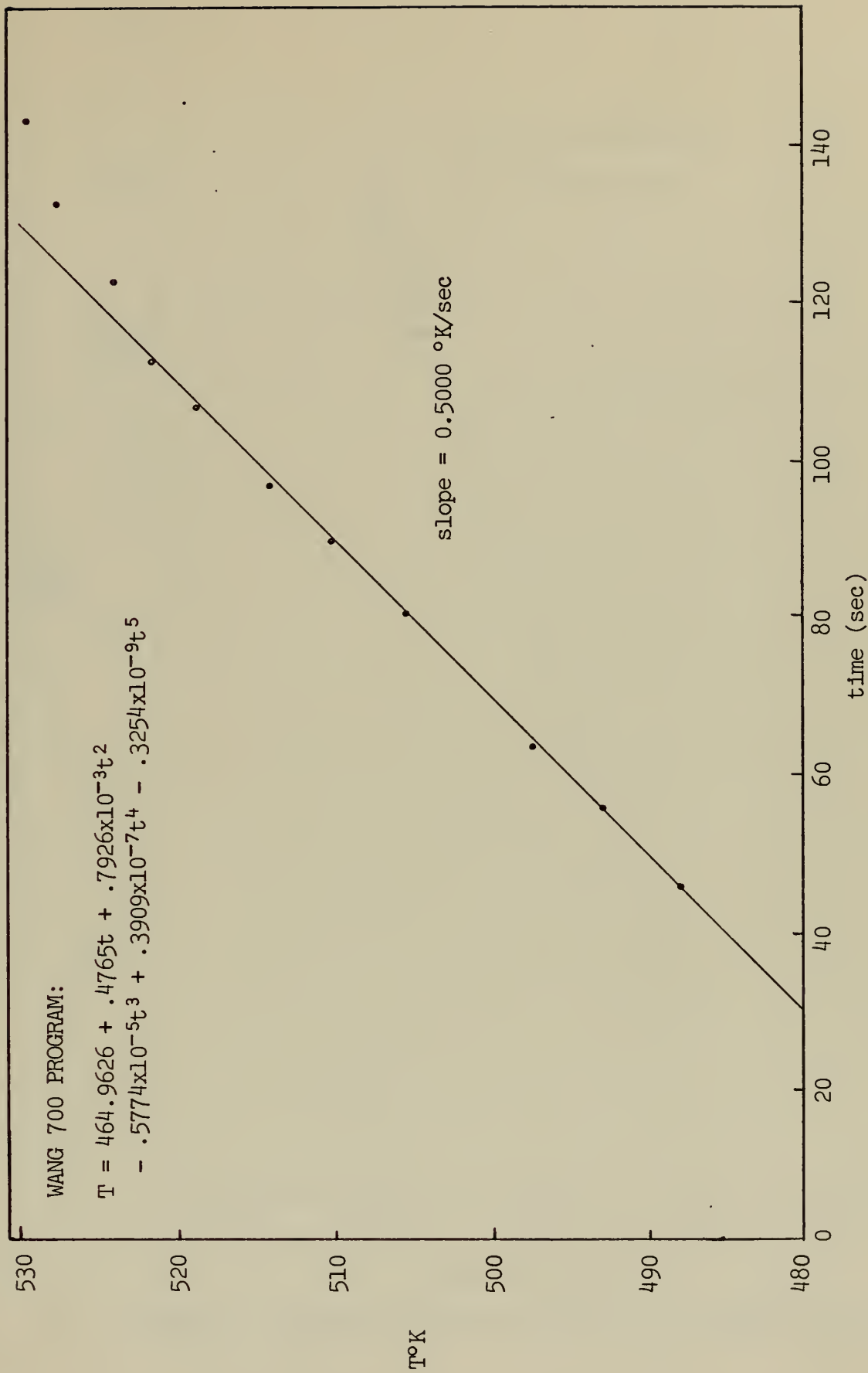
FIGURE 36: T°K vs. time, heating rate 30.00°C/min.

68
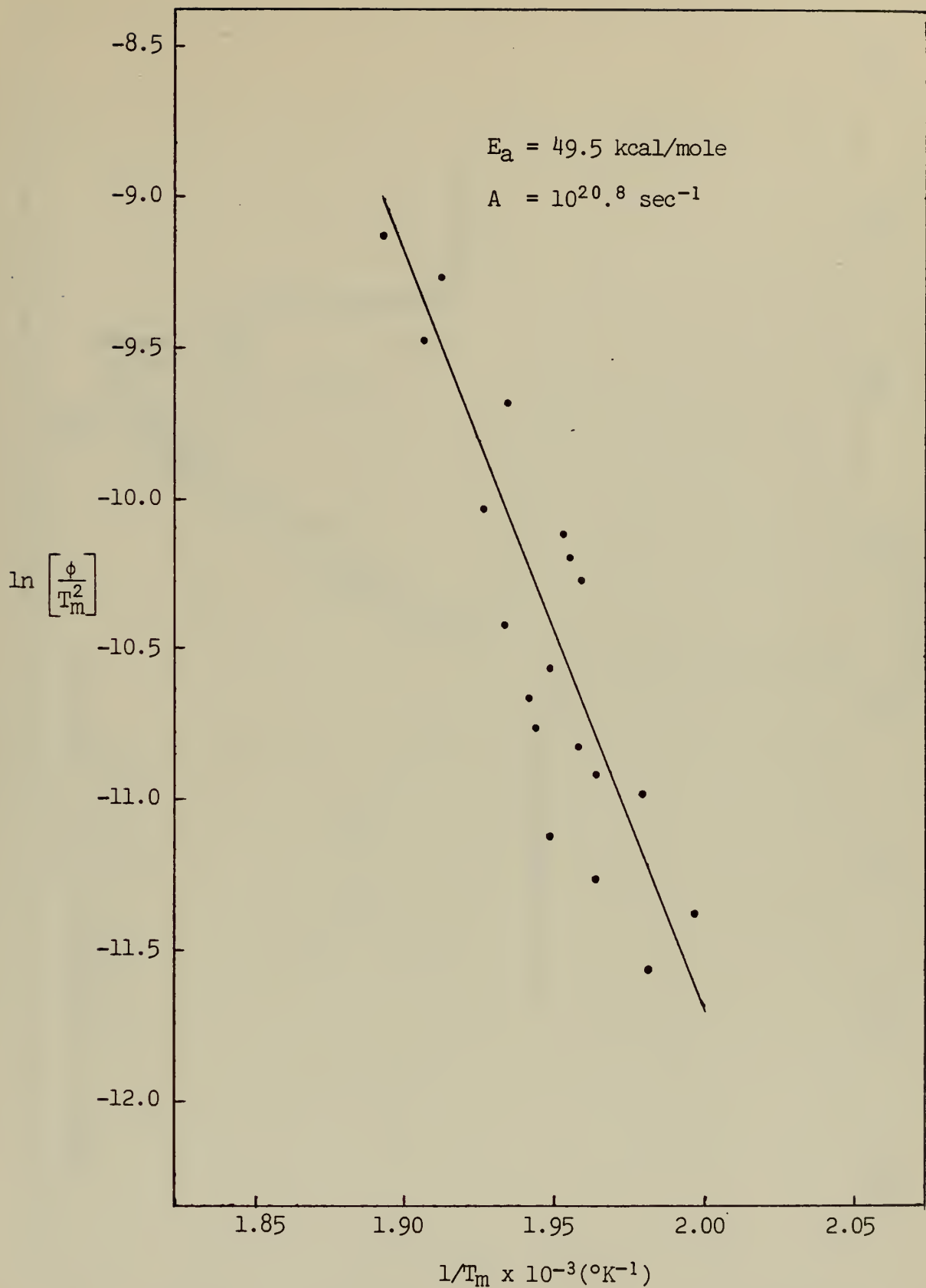
FIGURE 37:  Variable heating rate plot of $\ln\left[\phi/T_m^2\right]$ vs. $1000/T_m$

The y-axis is labeled $\ln\left[\dfrac{\phi}{T_m^2}\right]$

The x-axis is labeled $1/T_m \times 10^{-3}(°K^{-1})$

$E_a$ = 49.5 kcal/mole

$A$ = $10^{20.8}$ sec$^{-1}$

FIGURE 38: Thermogram of RDX. Three runs at 6°C/min. Heating Rate

ΔT = 2.0°C

Temperature °C
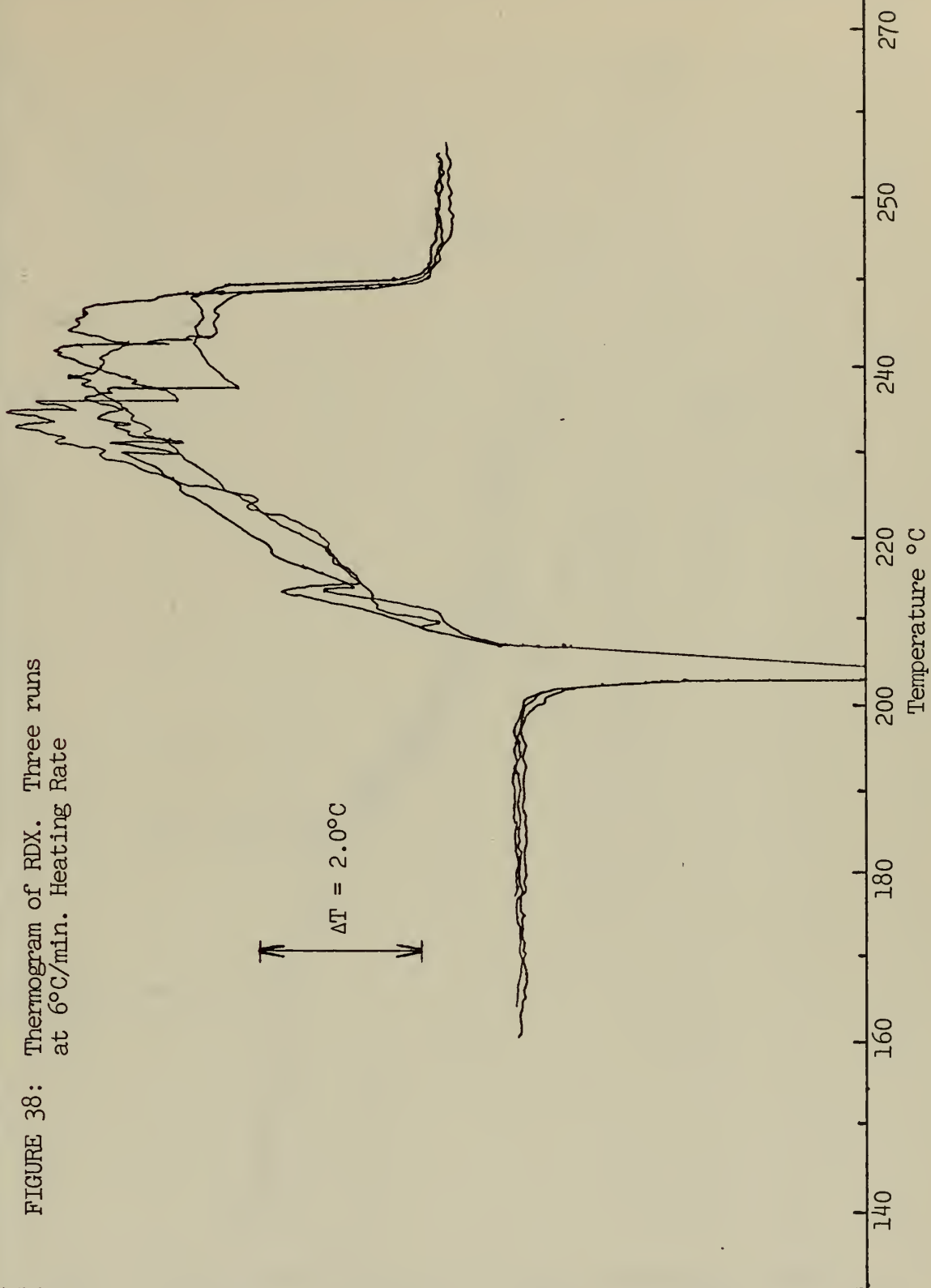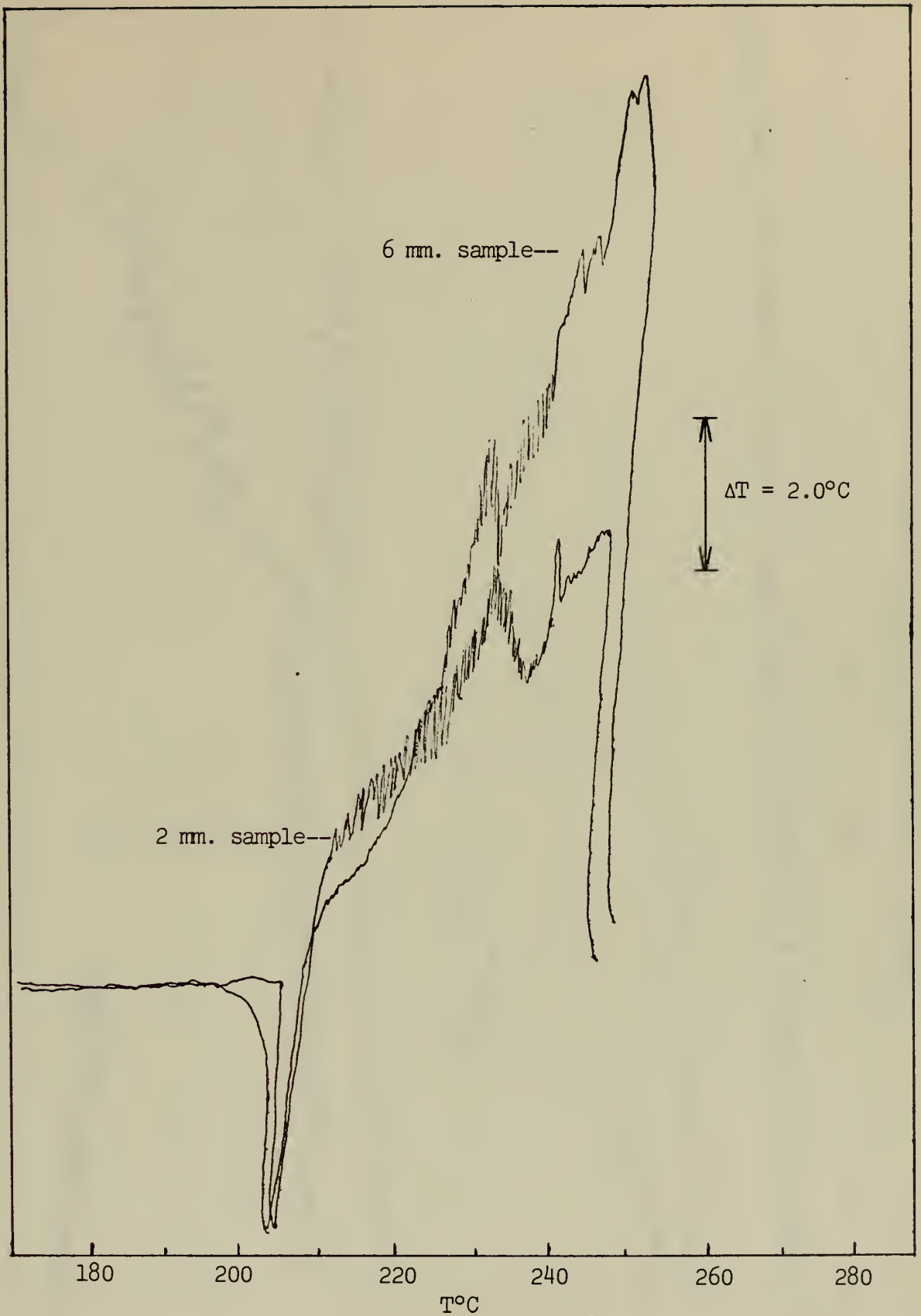
FIGURE 39: Thermogram of RDX, 4°C/min.

71
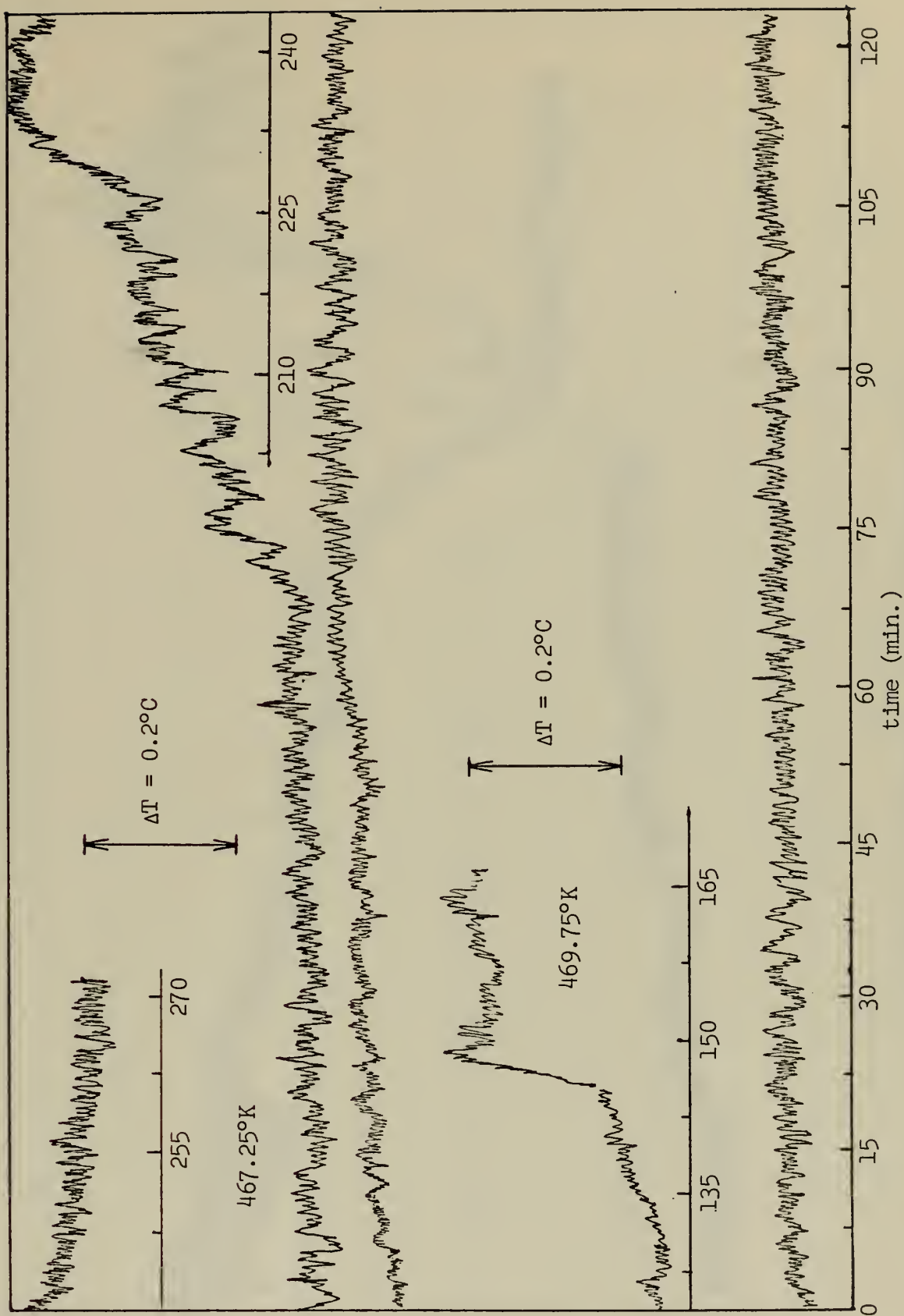
FIGURE 40: Thermograms of RDX, Isothermal runs 2 & 3.

72
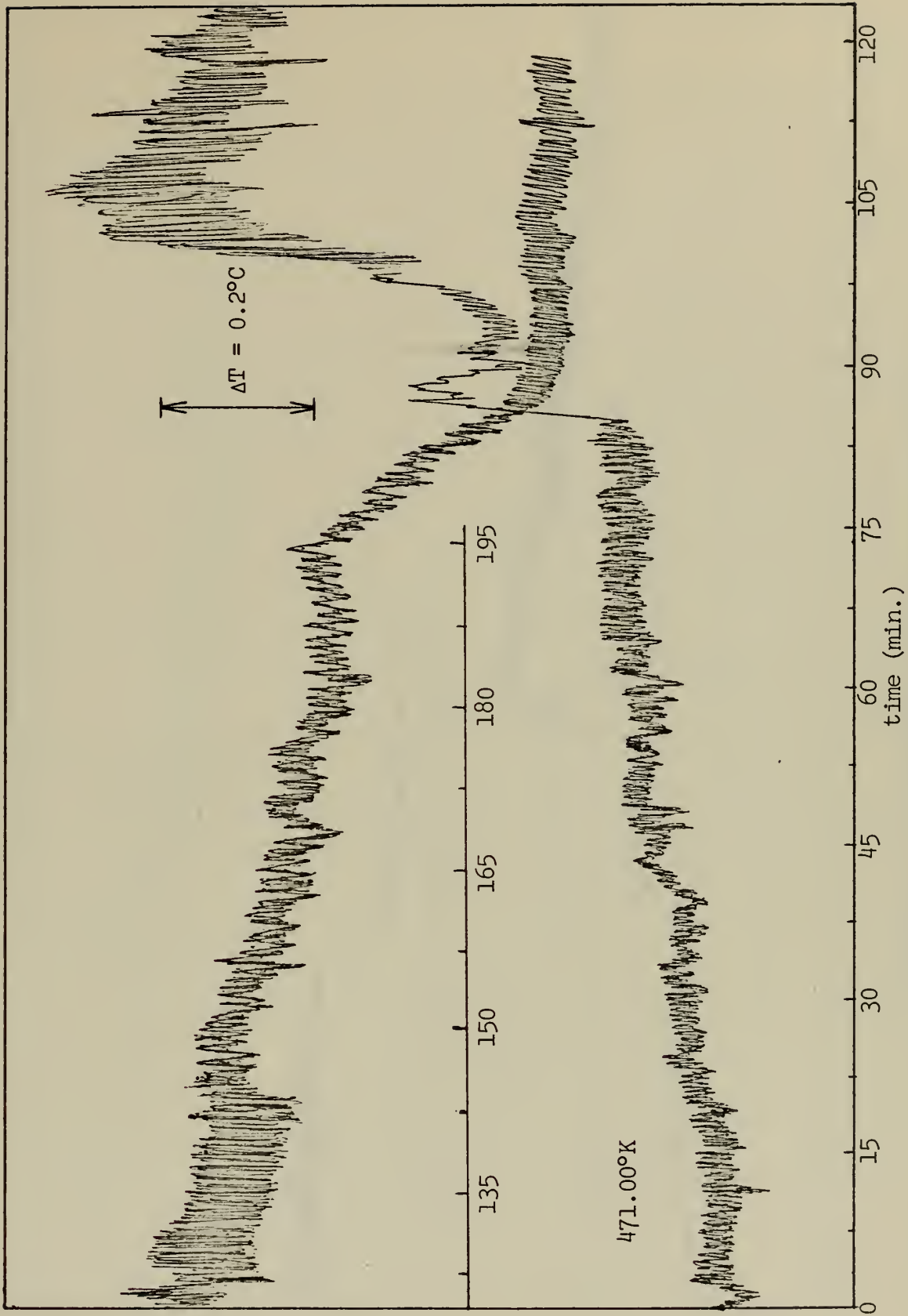
FIGURE 41: Thermogram of RDX, Isothermal run 4.

73
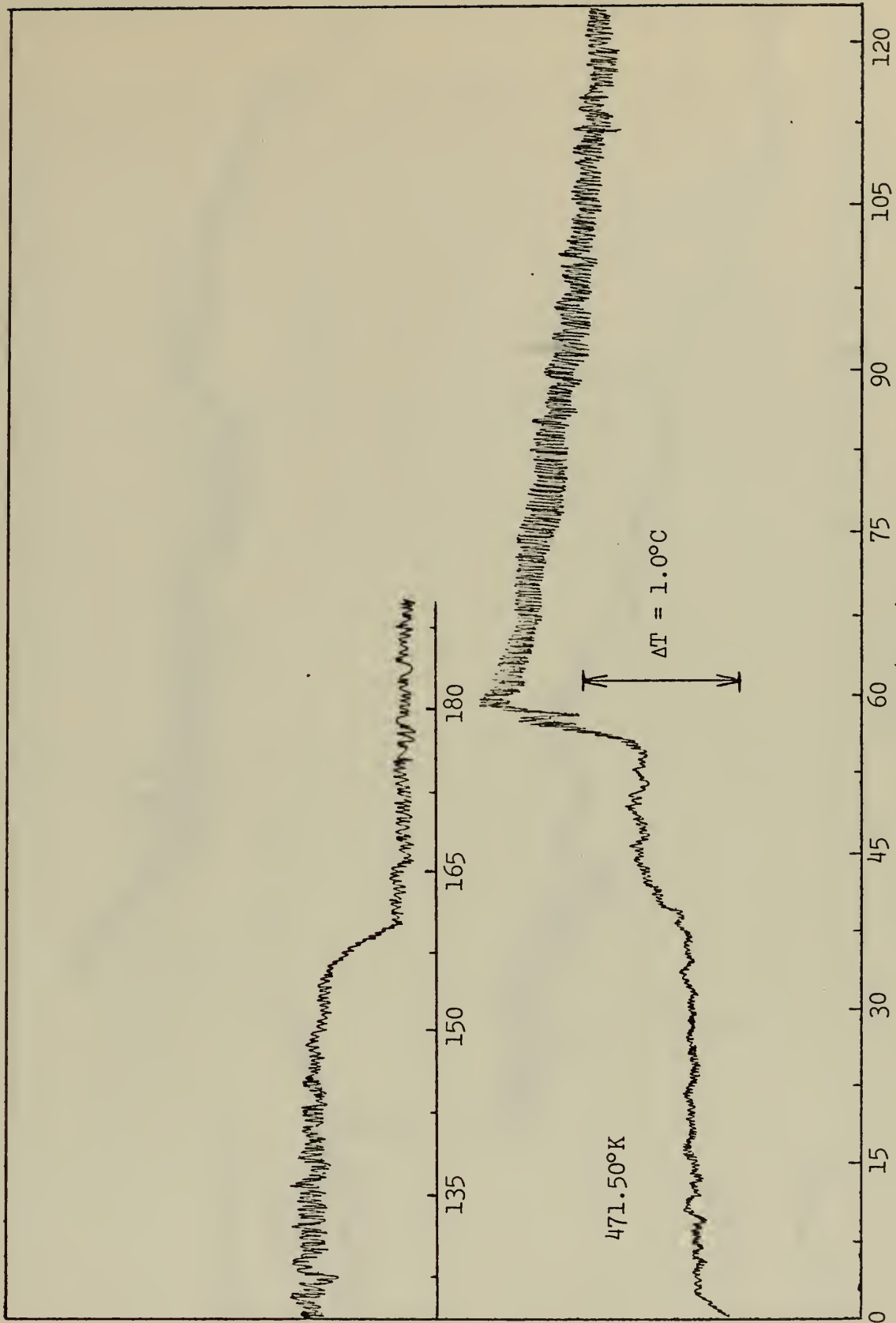
FIGURE 42: Thermogram of RDX, Isothermal run 5.

471.50°K

ΔT = 1.0°C

time (min.)

74
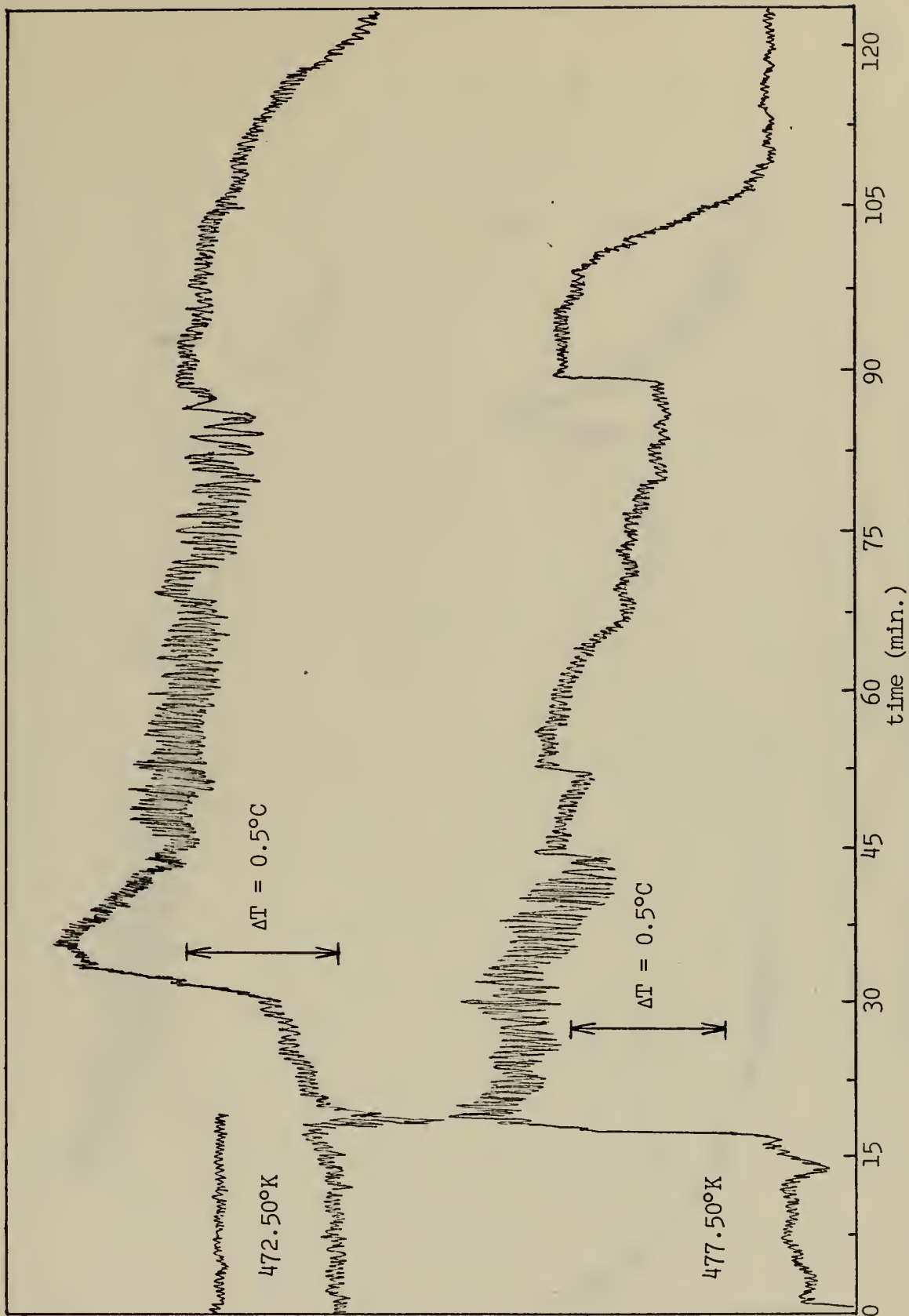
FIGURE 43: Thermograms of RDX, Isothermal runs 6 & 7.

$\Delta T = 0.5°C$

472.50°K

$\Delta T = 0.5°C$

477.50°K

time (min.)

75
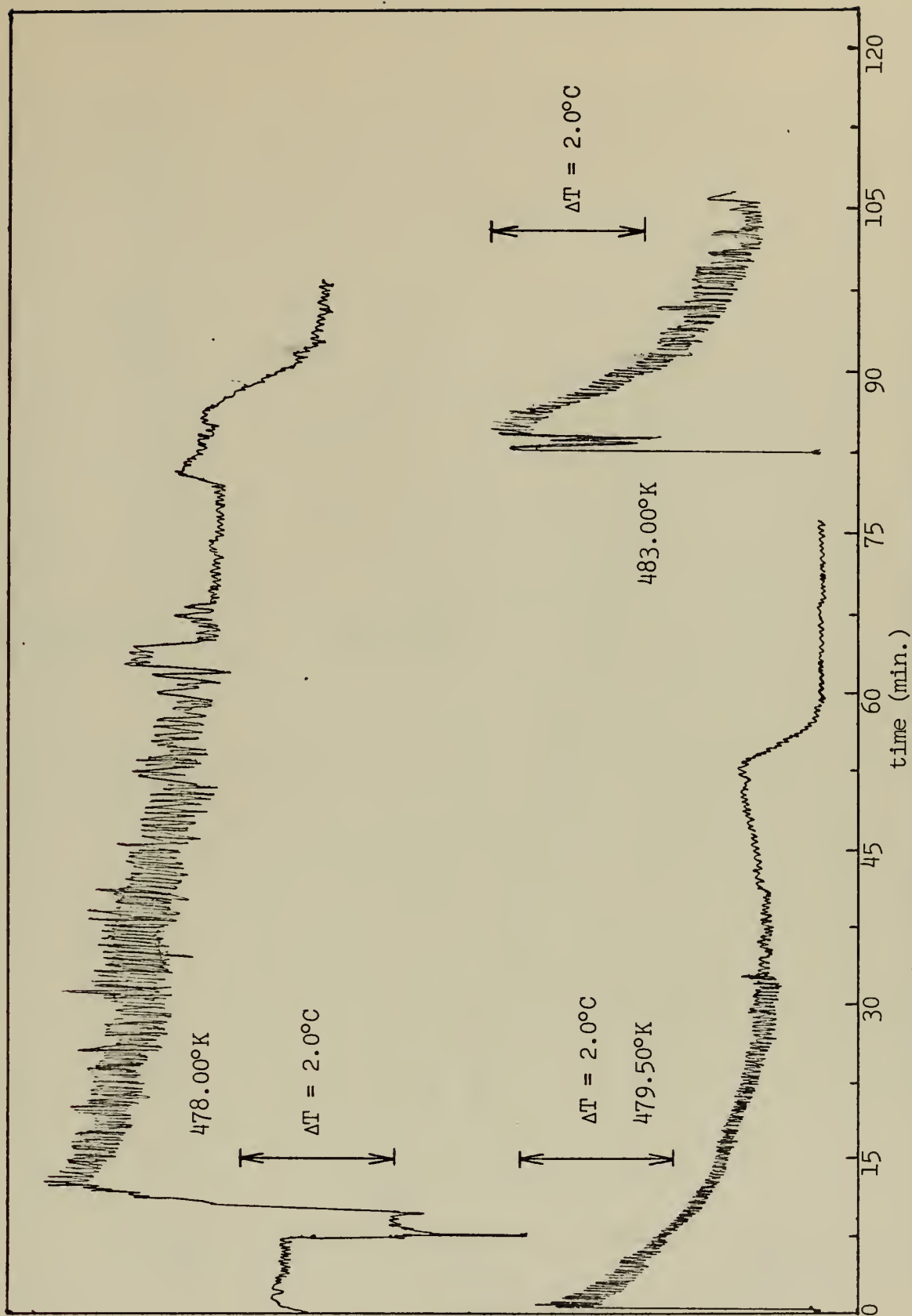
FIGURE 44: Thermograms of RDX, Isothermal runs 8, 9, & 10.
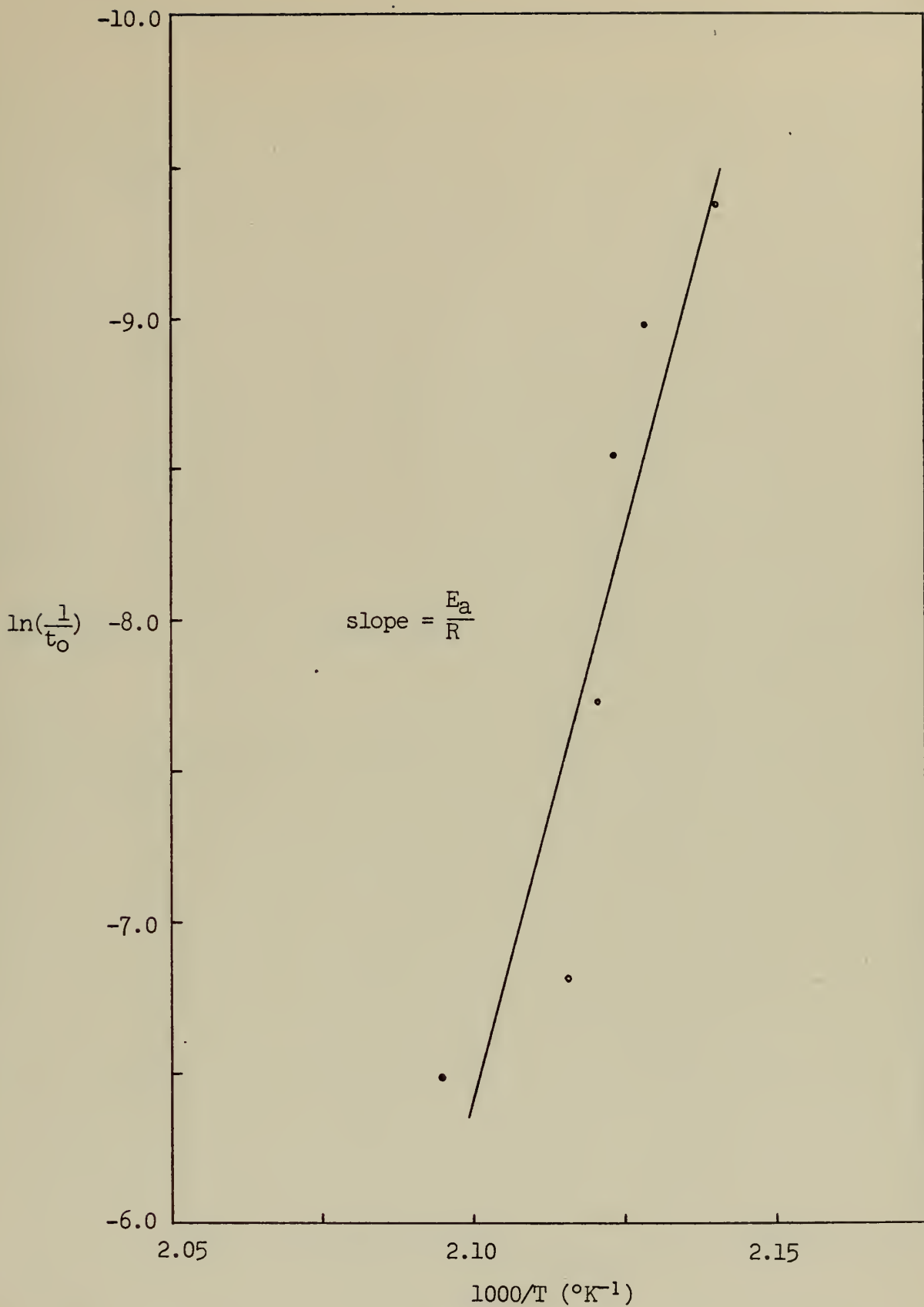
76

FIGURE 45:   ln (1/$t_o$) vs. 1000/T

FIGURE 46: $\ln (t_o/T^2)$ vs. $1000/T$

slope = $E_a/R$

$\ln (t_o/T^2)$

$1000/T$ $(^{\circ}K^{-1})$

78

FIGURE 47: ln (1/τ) vs. 1000/T

FIGURE 48: ln ($\tau/T^2$) vs. 1000/T

The y-axis is labeled $\ln(\frac{\tau}{T^2})$ with values -6.0, -7.0, -8.0, -9.0, -10.0.

The x-axis is labeled 1000/T (°K$^{-1}$) with values 2.05, 2.10, 2.15.

slope = $E_a/R$
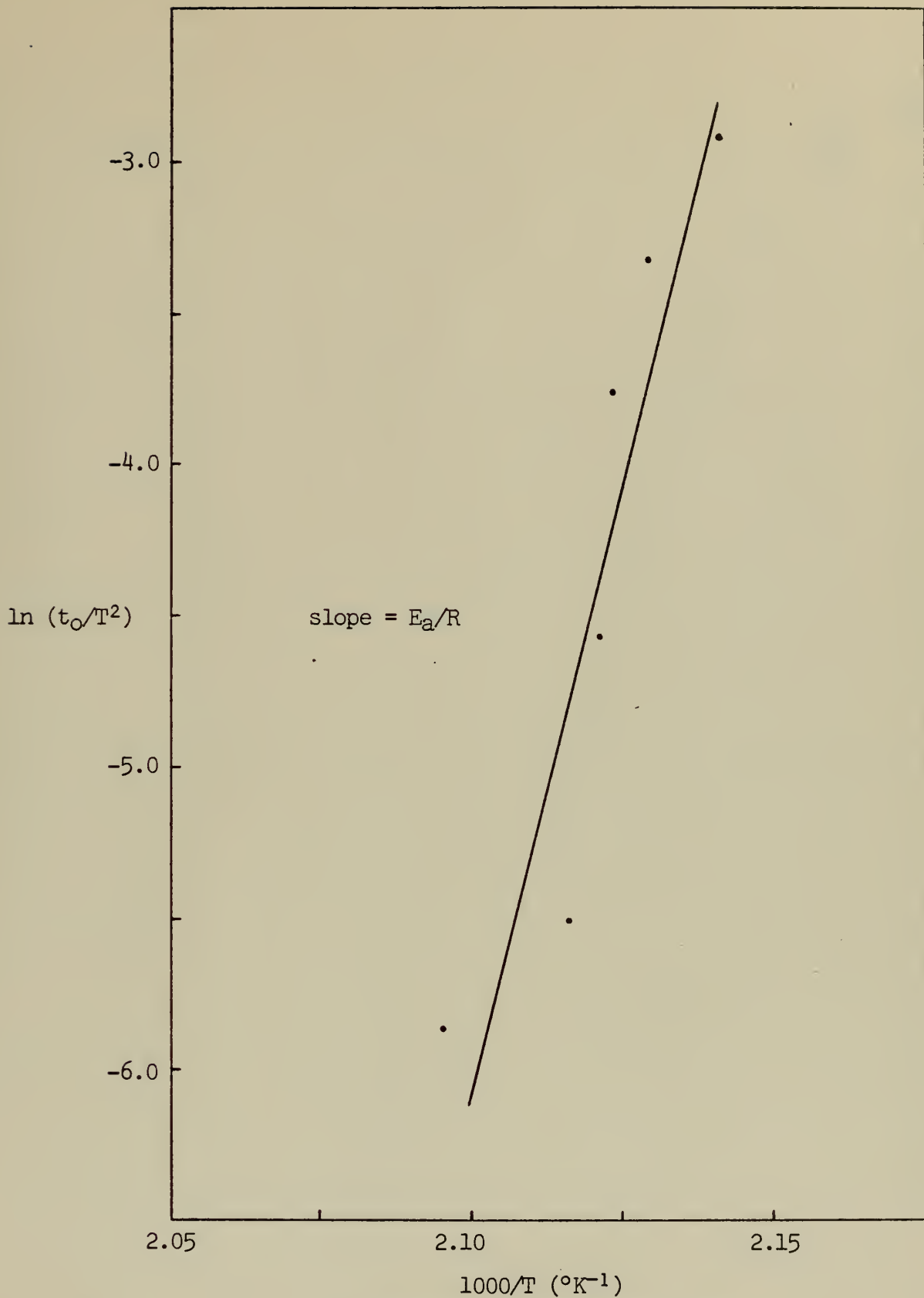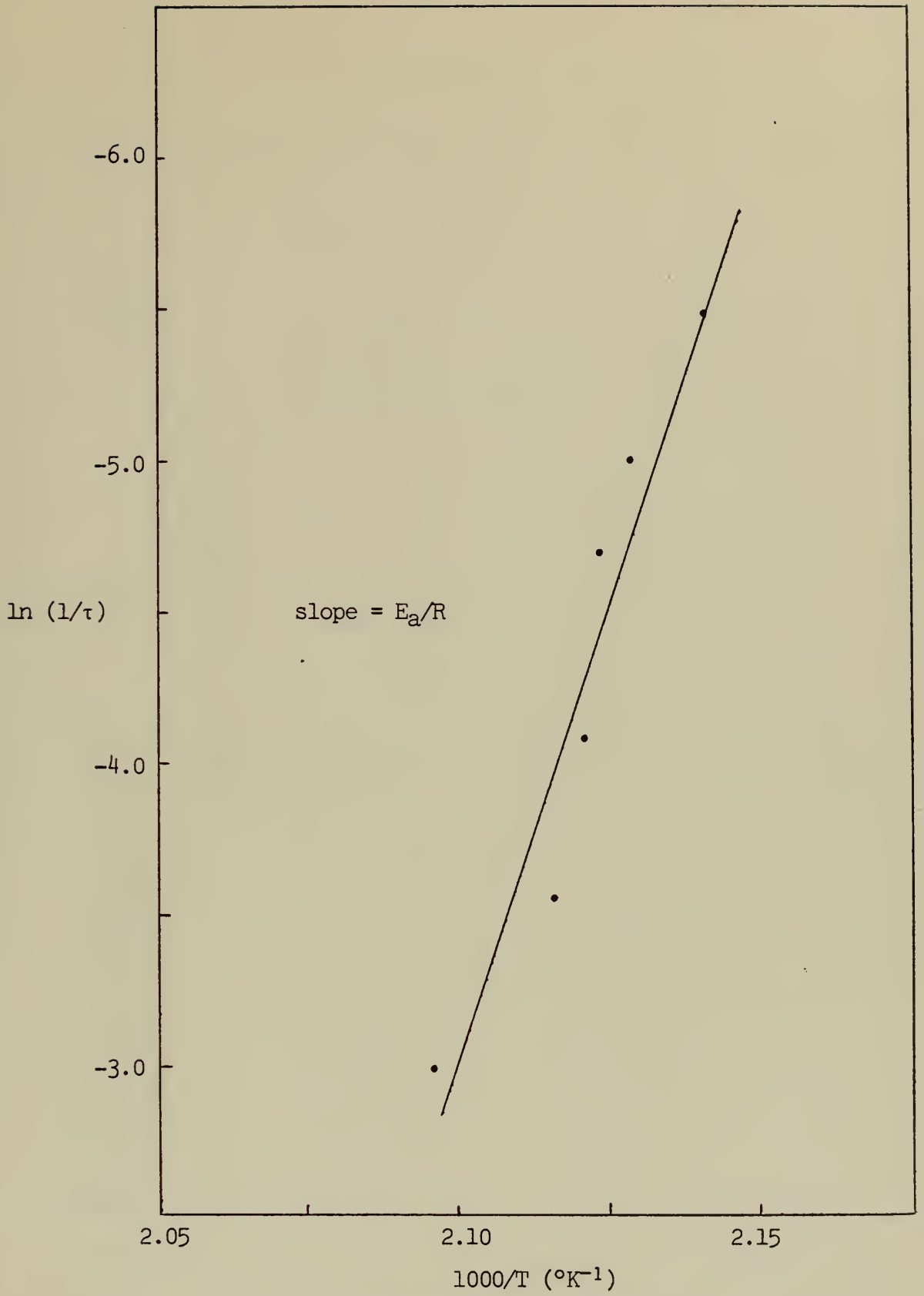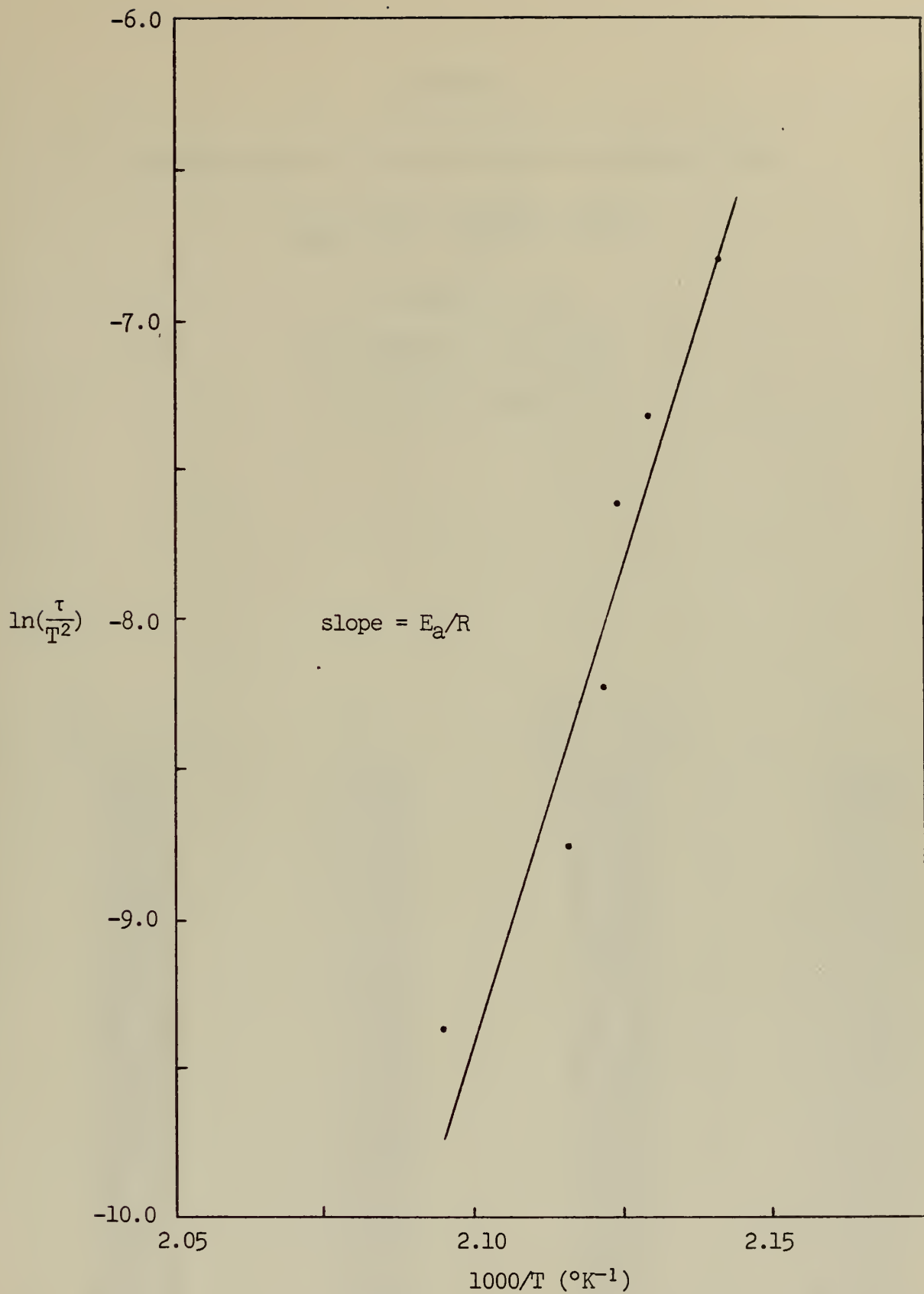
## APPENDIX A

HEATING RATE VS. PEAK TEMPERATURE, 500.00–530.50°K

$$\text{HEATING RATE} = \frac{ARТ_m^2}{E_a}\, e^{-E_a/RT_m}$$

$$A = 6.91985 \times 10^{20}$$

$$E_a = 49{,}471.30 \text{ cal/mole}$$

$$R = 1.987 \text{ cal/mole } °K$$

| TEMP. DEG K | | RATE | TEMP. DEG K | | RATE |
|---|---|---|---|---|---|
| 500.00 | – – – | 1.64513 | 515.50 | – – – | 7.81557 |
| 500.50 | – – – | 1.73252 | 516.00 | – – – | 8.20592 |
| 501.00 | – – – | 1.82433 | 516.50 | – – – | 8.61496 |
| 501.50 | – – – | 1.92082 | 517.00 | – – – | 9.04354 |
| 502.00 | – – – | 2.02223 | 517.50 | – – – | 9.49271 |
| 502.50 | – – – | 2.12876 | 518.00 | – – – | 9.96309 |
| 503.00 | – – – | 2.24069 | 518.50 | – – – | 10.45597 |
| 503.50 | – – – | 2.35825 | 519.00 | – – – | 10.97204 |
| 504.00 | – – – | 2.48174 | 519.50 | – – – | 11.51268 |
| 504.50 | – – – | 2.61146 | 520.00 | – – – | 12.07884 |
| 505.00 | – – – | 2.74766 | 520.50 | – – – | 12.67184 |
| 505.50 | – – – | 2.89069 | 521.00 | – – – | 13.29251 |
| 506.00 | – – – | 3.04084 | 521.50 | – – – | 13.94250 |
| 506.50 | – – – | 3.19853 | 522.00 | – – – | 14.62290 |
| 507.00 | – – – | 3.36404 | 522.50 | – – – | 15.33508 |
| 507.50 | – – – | 3.53773 | 523.00 | – – – | 16.08067 |
| 508.00 | – – – | 3.72009 | 523.50 | – – – | 16.86069 |
| 508.50 | – – – | 3.91143 | 524.00 | – – – | 17.67717 |
| 509.00 | – – – | 4.11222 | 524.50 | – – – | 18.53172 |
| 509.50 | – – – | 4.32292 | 525.00 | – – – | 19.42580 |
| 510.00 | – – – | 4.54399 | 525.50 | – – – | 20.36110 |
| 510.50 | – – – | 4.77592 | 526.00 | – – – | 21.33943 |
| 511.00 | – – – | 5.01914 | 526.50 | – – – | 22.36304 |
| 511.50 | – – – | 5.27426 | 527.00 | – – – | 23.43390 |
| 512.00 | – – – | 5.54182 | 527.50 | – – – | 24.55339 |
| 512.50 | – – – | 5.82250 | 528.00 | – – – | 25.72473 |
| 513.00 | – – – | 6.11673 | 528.50 | – – – | 26.94904 |
| 513.50 | – – – | 6.42524 | 529.00 | – – – | 28.22940 |
| 514.00 | – – – | 6.74866 | 529.50 | – – – | 29.56830 |
| 514.50 | – – – | 7.08771 | 530.00 | – – – | 30.96779 |
| 515.00 | – – – | 7.44310 | 530.50 | – – – | 32.43098 |

# APPENDIX B

## HEATING RATE VS. PEAK TEMPERATURE, 500.00–530.50°K

$$\text{HEATING RATE} = \frac{ARTm^2}{E_a} e^{-E_a/RT_m}$$

$$A = 1.70000 \times 10^{19}$$

$$E_a = 48{,}700.00 \text{ cal/mole}$$

$$R = 1.987 \text{ cal/mole °K}$$

| TEMP. DEG K | | | RATE | TEMP. DEG K | | | RATE |
|---|---|---|---|---|---|---|---|
| 500.00 | – | – | – | 0.08924 | 515.50 | – | – | – | 0.41415 |
| 500.50 | – | – | – | 0.09390 | 516.00 | – | – | – | 0.43452 |
| 501.00 | – | – | – | 0.09880 | 516.50 | – | – | – | 0.45585 |
| 501.50 | – | – | – | 0.10395 | 517.00 | – | – | – | 0.47818 |
| 502.00 | – | – | – | 0.10935 | 517.50 | – | – | – | 0.50156 |
| 502.50 | – | – | – | 0.11502 | 518.00 | – | – | – | 0.52603 |
| 503.00 | – | – | – | 0.12098 | 518.50 | – | – | – | 0.55165 |
| 503.50 | – | – | – | 0.12723 | 519.00 | – | – | – | 0.57847 |
| 504.00 | – | – | – | 0.13379 | 519.50 | – | – | – | 0.60654 |
| 504.50 | – | – | – | 0.14067 | 520.00 | – | – | – | 0.63590 |
| 505.00 | – | – | – | 0.14790 | 520.50 | – | – | – | 0.66665 |
| 505.50 | – | – | – | 0.15548 | 521.00 | – | – | – | 0.69880 |
| 506.00 | – | – | – | 0.16343 | 521.50 | – | – | – | 0.73244 |
| 506.50 | – | – | – | 0.17177 | 522.00 | – | – | – | 0.76763 |
| 507.00 | – | – | – | 0.18053 | 522.50 | – | – | – | 0.80446 |
| 507.50 | – | – | – | 0.18971 | 523.00 | – | – | – | 0.84296 |
| 508.00 | – | – | – | 0.19933 | 523.50 | – | – | – | 0.88323 |
| 508.50 | – | – | – | 0.20943 | 524.00 | – | – | – | 0.92535 |
| 509.00 | – | – | – | 0.22002 | 524.50 | – | – | – | 0.96939 |
| 509.50 | – | – | – | 0.23112 | 525.00 | – | – | – | 1.01545 |
| 510.00 | – | – | – | 0.24275 | 525.50 | – | – | – | 1.06359 |
| 510.50 | – | – | – | 0.25495 | 526.00 | – | – | – | 1.11392 |
| 511.00 | – | – | – | 0.26774 | 526.50 | – | – | – | 1.16653 |
| 511.50 | – | – | – | 0.28114 | 527.00 | – | – | – | 1.22153 |
| 512.00 | – | – | – | 0.29518 | 527.50 | – | – | – | 1.27901 |
| 512.50 | – | – | – | 0.30990 | 528.00 | – | – | – | 1.33906 |
| 513.00 | – | – | – | 0.32532 | 528.50 | – | – | – | 1.40185 |
| 513.50 | – | – | – | 0.34147 | 529.00 | – | – | – | 1.46742 |
| 514.00 | – | – | – | 0.35840 | 529.50 | – | – | – | 1.53594 |
| 514.50 | – | – | – | 0.37613 | 530.00 | – | – | – | 1.60753 |
| 515.00 | – | – | – | 0.39470 | 530.50 | – | – | – | 1.68233 |

RATE CONSTANT VS. ISOTHERMAL TEMPERATURE, 470.00-550.00 °K

$$k = A \, e^{-E_a/RT}$$

$$A = 6.91985 \times 10^{20}$$

$$E_a = 49{,}471.30 \text{ cal/mole}$$

$$R = 1.987 \text{ cal/mole } °K$$

| TEMP. DEG K | | | | K | TEMP. DEG K | | | | K |
|---|---|---|---|---|---|---|---|---|---|
| 470.00 | - | - | - | 0.00682 | 510.50 | - | - | - | 0.45627 |
| 470.50 | - | - | - | 0.00722 | 511.00 | - | - | - | 0.47857 |
| 471.00 | - | - | - | 0.00764 | 511.50 | - | - | - | 0.50191 |
| 471.50 | - | - | - | 0.00808 | 512.00 | - | - | - | 0.52634 |
| 472.00 | - | - | - | 0.00854 | 512.50 | - | - | - | 0.55192 |
| 472.50 | - | - | - | 0.00903 | 513.00 | - | - | - | 0.57868 |
| 473.00 | - | - | - | 0.00955 | 513.50 | - | - | - | 0.60669 |
| 473.50 | - | - | - | 0.01010 | 514.00 | - | - | - | 0.63599 |
| 474.00 | - | - | - | 0.01067 | 514.50 | - | - | - | 0.66664 |
| 474.50 | - | - | - | 0.01128 | 515.00 | - | - | - | 0.69871 |
| 475.00 | - | - | - | 0.01192 | 515.50 | - | - | - | 0.73225 |
| 475.50 | - | - | - | 0.01259 | 516.00 | - | - | - | 0.76733 |
| 476.00 | - | - | - | 0.01331 | 516.50 | - | - | - | 0.80402 |
| 476.50 | - | - | - | 0.01406 | 517.00 | - | - | - | 0.84239 |
| 477.00 | - | - | - | 0.01485 | 517.50 | - | - | - | 0.88252 |
| 477.50 | - | - | - | 0.01568 | 518.00 | - | - | - | 0.92446 |
| 478.00 | - | - | - | 0.01656 | 518.50 | - | - | - | 0.96833 |
| 478.50 | - | - | - | 0.01749 | 519.00 | - | - | - | 1.01416 |
| 479.00 | - | - | - | 0.01846 | 519.50 | - | - | - | 1.06209 |
| 479.50 | - | - | - | 0.01949 | 520.00 | - | - | - | 1.11218 |
| 480.00 | - | - | - | 0.02058 | 520.50 | - | - | - | 1.16454 |
| 480.50 | - | - | - | 0.02172 | 521.00 | - | - | - | 1.21923 |
| 481.00 | - | - | - | 0.02292 | 521.50 | - | - | - | 1.27640 |
| 481.50 | - | - | - | 0.02418 | 522.00 | - | - | - | 1.33613 |
| 482.00 | - | - | - | 0.02552 | 522.50 | - | - | - | 1.39852 |
| 482.50 | - | - | - | 0.02692 | 523.00 | - | - | - | 1.46371 |
| 483.00 | - | - | - | 0.02840 | 523.50 | - | - | - | 1.53179 |
| 483.50 | - | - | - | 0.02995 | 524.00 | - | - | - | 1.60290 |
| 484.00 | - | - | - | 0.03159 | 524.50 | - | - | - | 1.67718 |
| 484.50 | - | - | - | 0.03331 | 525.00 | - | - | - | 1.75475 |

| TEMP. DEG K | | | K | TEMP. DEG K | | | K |
|---|---|---|---|---|---|---|---|
| 485.00 | - | - | - | 0.03512 | 525.50 | - | - | - | 1.83574 |
| 485.50 | - | - | - | 0.03703 | 526.00 | - | - | - | 1.92029 |
| 486.00 | - | - | - | 0.03904 | 526.50 | - | - | - | 2.00858 |
| 486.50 | - | - | - | 0.04115 | 527.00 | - | - | - | 2.10077 |
| 487.00 | - | - | - | 0.04337 | 527.50 | - | - | - | 2.19696 |
| 487.50 | - | - | - | 0.04570 | 528.00 | - | - | - | 2.29741 |
| 488.00 | - | - | - | 0.04816 | 528.50 | - | - | - | 2.40220 |
| 488.50 | - | - | - | 0.05074 | 529.00 | - | - | - | 2.51157 |
| 489.00 | - | - | - | 0.05345 | 529.50 | - | - | - | 2.62573 |
| 489.50 | - | - | - | 0.05630 | 530.00 | - | - | - | 2.74482 |
| 490.00 | - | - | - | 0.05930 | 530.50 | - | - | - | 2.86910 |
| 490.50 | - | - | - | 0.06246 | 531.00 | - | - | - | 2.99872 |
| 491.00 | - | - | - | 0.06577 | 531.50 | - | - | - | 3.13397 |
| 491.50 | - | - | - | 0.06925 | 532.00 | - | - | - | 3.27501 |
| 492.00 | - | - | - | 0.07291 | 532.50 | - | - | - | 3.42214 |
| 492.50 | - | - | - | 0.07675 | 533.00 | - | - | - | 3.57555 |
| 493.00 | - | - | - | 0.08079 | 533.50 | - | - | - | 3.73556 |
| 493.50 | - | - | - | 0.08503 | 534.00 | - | - | - | 3.90243 |
| 494.00 | - | - | - | 0.08949 | 534.50 | - | - | - | 4.07638 |
| 494.50 | - | - | - | 0.09417 | 535.00 | - | - | - | 4.25776 |
| 495.00 | - | - | - | 0.09908 | 535.50 | - | - | - | 4.44687 |
| 495.50 | - | - | - | 0.10424 | 536.00 | - | - | - | 4.64402 |
| 496.00 | - | - | - | 0.10965 | 536.50 | - | - | - | 4.84947 |
| 496.50 | - | - | - | 0.11534 | 537.00 | - | - | - | 5.06354 |
| 497.00 | - | - | - | 0.12131 | 537.50 | - | - | - | 5.28675 |
| 497.50 | - | - | - | 0.12757 | 538.00 | - | - | - | 5.51929 |
| 498.00 | - | - | - | 0.13414 | 538.50 | - | - | - | 5.76161 |
| 498.50 | - | - | - | 0.14104 | 539.00 | - | - | - | 6.01412 |
| 499.00 | - | - | - | 0.14828 | 539.50 | - | - | - | 6.27721 |
| 499.50 | - | - | - | 0.15587 | 540.00 | - | - | - | 6.55121 |
| 500.00 | - | - | - | 0.16384 | 540.50 | - | - | - | 6.83666 |
| 500.50 | - | - | - | 0.17220 | 541.00 | - | - | - | 7.13399 |
| 501.00 | - | - | - | 0.18096 | 541.50 | - | - | - | 7.44369 |
| 501.50 | - | - | - | 0.19015 | 542.00 | - | - | - | 7.76624 |
| 502.00 | - | - | - | 0.19979 | 542.50 | - | - | - | 8.10215 |
| 502.50 | - | - | - | 0.20990 | 543.00 | - | - | - | 8.45181 |
| 503.00 | - | - | - | 0.22050 | 543.50 | - | - | - | 8.81602 |
| 503.50 | - | - | - | 0.23160 | 544.00 | - | - | - | 9.19509 |
| 504.00 | - | - | - | 0.24325 | 544.50 | - | - | - | 9.58973 |
| 504.50 | - | - | - | 0.25546 | 545.00 | - | - | - | 10.00054 |
| 505.00 | - | - | - | 0.26825 | 545.50 | - | - | - | 10.42831 |
| 505.50 | - | - | - | 0.28165 | 546.00 | - | - | - | 10.87339 |
| 506.00 | - | - | - | 0.29570 | 546.50 | - | - | - | 11.33659 |
| 506.50 | - | - | - | 0.31042 | 547.00 | - | - | - | 11.81863 |
| 507.00 | - | - | - | 0.32584 | 547.50 | - | - | - | 12.32022 |
| 507.50 | - | - | - | 0.34199 | 548.00 | - | - | - | 12.84212 |
| 508.00 | - | - | - | 0.35891 | 548.50 | - | - | - | 13.38532 |
| 508.50 | - | - | - | 0.37663 | 549.00 | - | - | - | 13.95021 |
| 509.00 | - | - | - | 0.39518 | 549.50 | - | - | - | 14.53783 |
| 509.50 | - | - | - | 0.41461 | 550.00 | - | - | - | 15.14928 |

# APPENDIX D

RATE CONSTANT VS. ISOTHERMAL TEMPERATURE, 470.00-550.00 °K

$$k = A \ e^{-E_a/RT}$$

$$A = 1.7000 \times 10^{19}$$

$$E_a = 48,700.00 \ \text{cal/mole}$$

$$R = 1.987 \ \text{cal/mole} \ °K$$

| TEMP. DEG K | | K | TEMP. DEG K | | K |
|---|---|---|---|---|---|
| 470.00 | - - - | 0.00038 | 510.50 | - - - | 0.02398 |
| 470.50 | - - - | 0.00040 | 511.00 | - - - | 0.02513 |
| 471.00 | - - - | 0.00043 | 511.50 | - - - | 0.02634 |
| 471.50 | - - - | 0.00045 | 512.00 | - - - | 0.02760 |
| 472.00 | - - - | 0.00048 | 512.50 | - - - | 0.02892 |
| 472.50 | - - - | 0.00050 | 513.00 | - - - | 0.03030 |
| 473.00 | - - - | 0.00053 | 513.50 | - - - | 0.03174 |
| 473.50 | - - - | 0.00056 | 514.00 | - - - | 0.03325 |
| 474.00 | - - - | 0.00059 | 514.50 | - - - | 0.03483 |
| 474.50 | - - - | 0.00063 | 515.00 | - - - | 0.03647 |
| 475.00 | - - - | 0.00066 | 515.50 | - - - | 0.03820 |
| 475.50 | - - - | 0.00070 | 516.00 | - - - | 0.04000 |
| 476.00 | - - - | 0.00074 | 516.50 | - - - | 0.04188 |
| 476.50 | - - - | 0.00078 | 517.00 | - - - | 0.04385 |
| 477.00 | - - - | 0.00082 | 517.50 | - - - | 0.04590 |
| 477.50 | - - - | 0.00087 | 518.00 | - - - | 0.04805 |
| 478.00 | - - - | 0.00092 | 518.50 | - - - | 0.05029 |
| 478.50 | - - - | 0.00097 | 519.00 | - - - | 0.05264 |
| 479.00 | - - - | 0.00102 | 519.50 | - - - | 0.05508 |
| 479.50 | - - - | 0.00108 | 520.00 | - - - | 0.05764 |
| 480.00 | - - - | 0.00113 | 520.50 | - - - | 0.06031 |
| 480.50 | - - - | 0.00120 | 521.00 | - - - | 0.06310 |
| 481.00 | - - - | 0.00126 | 521.50 | - - - | 0.06601 |
| 481.50 | - - - | 0.00133 | 522.00 | - - - | 0.06905 |
| 482.00 | - - - | 0.00140 | 522.50 | - - - | 0.07222 |
| 482.50 | - - - | 0.00148 | 523.00 | - - - | 0.07553 |
| 483.00 | - - - | 0.00156 | 523.50 | - - - | 0.07899 |
| 483.50 | - - - | 0.00164 | 524.00 | - - - | 0.08260 |
| 484.00 | - - - | 0.00173 | 524.50 | - - - | 0.08637 |
| 484.50 | - - - | 0.00182 | 525.00 | - - - | 0.09030 |

| TEMP. DEG K | K | TEMP. DEG K | K |
|---|---|---|---|
| 485.00 – – – | 0.00192 | 525.50 – – – | 0.09440 |
| 485.50 – – – | 0.00202 | 526.00 – – – | 0.09868 |
| 486.00 – – – | 0.00213 | 526.50 – – – | 0.10314 |
| 486.50 – – – | 0.00224 | 527.00 – – – | 0.10780 |
| 487.00 – – – | 0.00236 | 527.50 – – – | 0.11266 |
| 487.50 – – – | 0.00249 | 528.00 – – – | 0.11772 |
| 488.00 – – – | 0.00262 | 528.50 – – – | 0.12301 |
| 488.50 – – – | 0.00276 | 529.00 – – – | 0.12852 |
| 489.00 – – – | 0.00290 | 529.50 – – – | 0.13427 |
| 489.50 – – – | 0.00306 | 530.00 – – – | 0.14026 |
| 490.00 – – – | 0.00322 | 530.50 – – – | 0.14651 |
| 490.50 – – – | 0.00339 | 531.00 – – – | 0.15303 |
| 491.00 – – – | 0.00356 | 531.50 – – – | 0.15982 |
| 491.50 – – – | 0.00375 | 532.00 – – – | 0.16690 |
| 492.00 – – – | 0.00394 | 532.50 – – – | 0.17427 |
| 492.50 – – – | 0.00415 | 533.00 – – – | 0.18196 |
| 493.00 – – – | 0.00436 | 533.50 – – – | 0.18998 |
| 493.50 – – – | 0.00459 | 534.00 – – – | 0.19833 |
| 494.00 – – – | 0.00482 | 534.50 – – – | 0.20703 |
| 494.50 – – – | 0.00507 | 535.00 – – – | 0.21609 |
| 495.00 – – – | 0.00533 | 535.50 – – – | 0.22553 |
| 495.50 – – – | 0.00561 | 536.00 – – – | 0.23537 |
| 496.00 – – – | 0.00589 | 536.50 – – – | 0.24562 |
| 496.50 – – – | 0.00619 | 537.00 – – – | 0.25629 |
| 497.00 – – – | 0.00651 | 537.50 – – – | 0.26741 |
| 497.50 – – – | 0.00684 | 538.00 – – – | 0.27899 |
| 498.00 – – – | 0.00719 | 538.50 – – – | 0.29104 |
| 498.50 – – – | 0.00755 | 539.00 – – – | 0.30359 |
| 499.00 – – – | 0.00793 | 539.50 – – – | 0.31665 |
| 499.50 – – – | 0.00833 | 540.00 – – – | 0.33026 |
| 500.00 – – – | 0.00875 | 540.50 – – – | 0.34442 |
| 500.50 – – – | 0.00919 | 541.00 – – – | 0.35916 |
| 501.00 – – – | 0.00965 | 541.50 – – – | 0.37451 |
| 501.50 – – – | 0.01013 | 542.00 – – – | 0.39047 |
| 502.00 – – – | 0.01064 | 542.50 – – – | 0.40710 |
| 502.50 – – – | 0.01116 | 543.00 – – – | 0.42439 |
| 503.00 – – – | 0.01172 | 543.50 – – – | 0.44238 |
| 503.50 – – – | 0.01230 | 544.00 – – – | 0.46110 |
| 504.00 – – – | 0.01291 | 544.50 – – – | 0.48058 |
| 504.50 – – – | 0.01355 | 545.00 – – – | 0.50084 |
| 505.00 – – – | 0.01421 | 545.50 – – – | 0.52192 |
| 505.50 – – – | 0.01491 | 546.00 – – – | 0.54383 |
| 506.00 – – – | 0.01564 | 546.50 – – – | 0.56664 |
| 506.50 – – – | 0.01641 | 547.00 – – – | 0.59034 |
| 507.00 – – – | 0.01721 | 547.50 – – – | 0.61501 |
| 507.50 – – – | 0.01805 | 548.00 – – – | 0.64065 |
| 508.00 – – – | 0.01893 | 548.50 – – – | 0.66731 |
| 508.50 – – – | 0.01985 | 549.00 – – – | 0.69502 |
| 509.00 – – – | 0.02081 | 549.50 – – – | 0.72384 |
| 509.50 – – – | 0.02182 | 550.00 – – – | 0.75378 |

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13. ABSTRACT

Cyclotrimethlenetrinitramine (RDX or Cyclonite) exists in two polymorphic species, α and β. The α-form is stable under normal conditions, whereas β-RDX is formed by re-crystallization from high boiling solvents. It immediately transfers to the α-form in the presence of excess α-RDX, and it is therefore assumed that RDX as it exists in its normal state consists solely of the α polymorph.

The thermal decomposition of RDX has been comprehensively studied at Picatinny Arsenal by means of quantitative measurements of the decomposition products. The thermal stability of explosive compositions has also been investigated by measuring the rate of gas evolution during decomposition.

It was the purpose of this work to obtain thermal and kinetic data for RDX using Differential Thermal Analysis (DTA) experimental methods. These results and techniques were compared with those obtained using the other methods and with theoretical values. The favorable results lend credibility to the DTA method and suggest that further development in the technique will prove useful in providing a fast and reasonably accurate method of characterizing the thermal and kinetic properties of new explosives and propellants.

A-31408

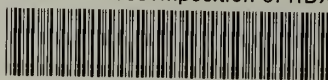| 14. KEY WORDS | LINK A | | LINK B | | LINK C | |
|---|---|---|---|---|---|---|
| | ROLE | WT | ROLE | WT | ROLE | WT |
| autocatalytic | | | | | | |
| cyclotrimethlenetrinitramine (RDX) | | | | | | |
| differential thermal analysis | | | | | | |
| explosive | | | | | | |
| induction time | | | | | | |
| thermal decomposition | | | | | | |
| time-to-deflagration | | | | | | |

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