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PART II

THERMOGRAVIMETRY OF PHENOL-FORMALDEHYDE POLYCONDENSATES

PART II — EMPIRICAL KINETIC PARAMETERS

R. W. FARMER

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ABSTRACT

Empirical kinetic parameters for phenol-formaldehyde polycondensate materials were surveyed for general application to Air Force interests. The ranges of n, A, E for the empirical kinetic model

$$-(dw/dt) = w^n A \exp(-E/RT)$$

where n= 0-5, A = 2.0×10^{-1} to 1.7×10^{16} 1/min, E = 3.7-72kcal/mole, where w ≡ normalized weight, t ≡ time, R ≡ gas constant, T ≡ temperature. The mass spectrometry and thermogravimetry thermal analysis methods used both constant heating rate and isothermal approaches.

Reexamination of data with a new computer program gave reduced variations: n = 1.56±0.07, A = 60.9±41.4, E = 10.38±1.20. The scopes of the comprehensive survey and descriptive thermogravimetry computer analysis were: (22 constant rate + 3 isothermal) vs 6 constant rate experiments by 8 vs 3 investigators using (5 cured + 7 vitreous fiber reinforced) vs 4 cured polycondensates.

Parameter inconsistencies for the survey were partially associated with an atypical polycondensate, laminate and polycondensate particle or laminate powder samples, or a reduced pressure atmosphere. Calculated parameters apparently dependent upon the two latter aspects were not averaged with other values. Small curve-fitting and other errors potentially enhance further disagreement as they often gave large parameter variations.

FOREWORD

This report was prepared by the Thermally Protective Plastics and Composites Section, Plastics and Composites Branch and initiated under Project No. 7340, "Nonmetallic Composites and Materials," Task No. 734001, "Thermally Protective Plastics and Composites." This report was administered under the direction of the Nonmetallic Materials Division, Air Force Materials Laboratory, with Mr. R. Farmer acting as project engineer.

The contributions of Mr. G. L. Denman in supplying samples, Mr. W. E. Huebner in assisting with computer programs, Mr. A. Oliver for computer programming, and Mr. N. J. Olson for many candid technical criticisms are acknowledged with appreciation.

The materials described herein were not formulated for the thermal treatments reported. Results and conclusions should not be misconstrued as reflecting on the characteristics of these materials in different form or under other environmental conditions.

This report covers work conducted from May 1965 to September 1966. Manuscript released by the author September 1966 for publication as an RTD Technical Report.

This technical report has been reviewed and is approved.

R. G. Spain

R. G. Spain, Acting Chief
Plastics & Composites Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

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ILLUSTRATIONS

SYMBOLS

SYMBOL	DEFINITION	SYMBOL UNITS
A	empirical kinetic parameter*	1/min
c	system concentration	
C	solid specific heat at constant pressure	kcal/gm/°K
e	base of natural logarithms	dimensionless
E	empirical kinetic parameter	kcal/gm-mole
exp	exponential function to the base e	dimensionless
f	function	
ΔH	normalized heat of reaction	kcal/gm
k	empirical kinetic parameter*	1/min
K	integral parameter	dimensionless
L	thickness	cm
ln ( )	logarithm to the base e	
$\log_{10}$( )	logarithm to the base 10	
m	series term	dimensionless
n	empirical kinetic parameter	dimensionless
P	pressure	atm
R	gas constant	kcal/gm-mole/°K
S	surface area	cm^2
s_e^2( )	error variance of estimate	
s_p^2( )	population error variance estimate	
T	temperature, degrees absolute*	°K
TS(45°)	tensile strength, 45° to fabric warp	percent
w	reactant (residue-free) weight fraction	dimensionless
w_o	aggregate sample weight fraction	dimensionless
x	reactant (residue-free) weight	gm

SYMBOLS (CONT'D)

SYMBOL	DEFINITION	SYMBOL UNITS
z	oxygen mole fraction	dimensionless
α	thermal diffusivity	cm^2/min
δ, ϵ	increment	dimensionless
θ	temperature	°C

SUBSCRIPTS

SYMBOL	DEFINITION
c	calculated
i	initial
i,j,k	iteration value
I	isothermal
m	maximum rate, maximum value
p,q	limiting value (q span)
r,s	limiting value (s span)
r	residue
1,2	singular value

SUPERSCRIPTS

SYMBOL	DEFINITION
$'$	minimum n error
$-$	mean
$(\dot{\ })$	d( )/dt
$(\dot{\ })_T$	d( )/dT

FUNCTIONAL SYMBOLS

SYMBOL	DEFINING EQUATION	SYMBOL UNITS
a	$\log_{10} r(AR/E\dot{T})$	dimensionless
A'	$-\dot{w}_{Tm} w^{-n} \dot{T} \exp(X_m)$	1/min
a_1	$-\dot{w} = kw^n \exp\left[-(a_1 - a_2/L)\right]$	dimensionless
a_2		cm
a_3	$-\dot{w} = k \exp\left[-a_3(1 - w)\right]$	dimensionless
b	$-E/(R \ln 10)$	°K
c_1, c_2	$TS(45°) = c_1 \exp(c_2 w)$	dimensionless
a_o, b_o, c_o	$g = a_o n^2 + b_o n + c_o$	dimensionless
$F(\ )$	$s_p^2(\ )/s_e^2(\ )$	
G	$L(\alpha CE/\Delta HRL)^{n+1}$	cm^{n+2}/min^{n+1}
g	$\sum (w_{oc} - w_o)^2$	dimensionless
j	$\theta_{p+1} - \theta_p$	°C
k	$\theta_{q+1} - \theta_q$	°C
$p(X)$	$X^{-1}e^{-X} - \int_X^{\infty} X^{-1}e^{-X} dX$	dimensionless
q	$(\theta_p - \theta_q)/j + 1$	°C
r	$X^2 e^X p(X)$	dimensionless
s	$(\theta_r - \theta_s)/k + 1$	°C
$s_e^2(a)$	$s_e^2(w_o)/q$	dimensionless
$s_e^2(b)$	$s_e^2(w_o)/\sum(1/T - \overline{1/T})$	°K
$s_e^2(w_o)$	$g'/(q - 2)$	dimensionless
$s_p^2(w_o)$	$\left[\sum(w_o - \overline{w_o})^2\right]/(q - 1)$	dimensionless

FUNCTIONAL SYMBOLS (CONT'D)

SYMBOL	DEFINING EQUATION	SYMBOL UNITS
w	$x/x_i = (w_o - w_r)/(w_{oi} - w_r)$	dimensionless
X	E/RT	dimensionless
y	$\log_{10}(K/T^2)$	
z	1/T	1/°K
α	$A = \alpha T^{\beta}$	$1/(\text{min-}(°K)^{\beta})$
β		dimensionless
λ	$E = \lambda + \mu T$	kcal/ gm-mole
μ		kcal/gm-mole/°K

COMPUTER PROGRAM DIAGRAMS

*Different units for a symbol are noted with that symbol.

SECTION I

INTRODUCTION

Part I of this report considered procedural variables in the constant heating rate thermogravimetry of phenol-formaldehyde polycondensates (Reference 17). The best sample was an adequately cured and dried molding powder free of any postcure surface product. Powder sieve distribution, pressure or weight effects were small to 500° or 600° C for runs in helium purging flow. Procedural interference increased thereafter to about 4 percent residual weight and 250° near 950°. Fortunately, a change in a procedural variable magnitude gave nearly parallel thermograms. Therefore, the residue-free thermograms were relatively free of procedural biasing. With this result a kinetic model based on a residue-free normalized weight was adopted. Empirical kinetic parameters were calculated for several materials using two new and complimentary curve-fitting methods.

The residue-free thermograms and elemental compositions of five postcured polycondensate powders were nearly identical from 300 to 810° (Reference 37). The empirical kinetic model proved representative for these experiments. Therefore it seemed reasonable that similar empirical kinetic parameters would be found for other polycondensates and fiber reinforced polycondensates. On this basis, a survey was made of previous constant heating rate and isothermal mass spectrometric and thermogravimetric thermal analysis studies.

The phenol-formaldehyde materials survey was disappointing in that the empirical kinetic parameters were inconsistent (Table I). A systematic attempt was made to explain the large differences. First a survey was made of available curve-fitting methods for possible computer program use. Although no entirely satisfactory technique was found, a program was evolved for easy and precise curve-fitting using a dual method approach developed in Part I of this report.

General inspection of computer program or manual calculations for selected experiments revealed significant differences exceeding the normalizing ability of a residue-free basis. Troublesome aspects were reinforced laminate and polycondensate particle or laminate powder samples, an oxidative atmosphere, reduced pressure, and unusual behavior of the sample. The data for some isothermal thermogravimetric and mass spectrometric studies were unsatisfactory for manual calculations and were not amendable to the computer program.

Data clearly disagreeing with likely empirical kinetic parameters for a cured polycondensate powder or unmanageable data was rejected for this study. A computer program analysis was then conducted for the remaining cases. This analysis involved six constant rate runs by three investigators using four materials (Table IX). A markedly reduced spread in the empirical kinetic parameters was encouraging evidence that the simple kinetic model was probably valid for most cured polycondensate powders and reasonable experimental procedures. Several cases of model inconsistency or significant procedural aberrations were also delineated as to probable causes.

Computer parameters were also found representative for seven other materials either by further calculations or residue-free thermogram analogy (References 4 and 37). Further accepting these experiments, the survey and computer study scopes were then respectively (22 constant rate + 3 isothermal) vs 13 constant rate experiments by 8 vs 4 investigators on (5 cured + 7 reinforced) vs 11 cured polycondensate powders.

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*All temperatures in °C unless noted as being °F, °K, or °R.

SECTION II

EMPIRICAL KINETIC PARAMETERS

A. EMPIRICAL MODEL.

Isothermal kinetic relations which empirically represent many physicochemical processes were

$$-\dot{w} = kw^{n} \tag{1}$$

$$k = A \exp(-X) \tag{2}$$

For a constant rate of heating $\dot{T}$

$$-\dot{w}_{T} = (Aw^{n}/\dot{T}) \exp(-X) \tag{3}$$

B. EVALUATION METHODS SURVEY.

Numerous methods were available for extracting empirical kinetic parameters from experimental thermograms. Table III summarized a few examples for constant heating rate thermogravimetry with emphasis on thermosetting polymer studies. The approaches were categorized into first, one or more necessary heating rates and then residual weight, weight loss rate, or a combination of rate and weight as the major temperature (or time) dependent variable. For example, a rearrangement of Equations 1 and 2 gave a method using rate, weight, and an implicit value of n

$$\log_{10}(-\dot{w}w^{-n}) = \frac{-E}{R \ln 10}\left[\frac{1}{T}\right] + \log_{10}A \tag{4}$$

where E, A were respectively evaluated from the slope and intercept of a parametric plot of $\log_{10}(-\dot{w}w^{-n})$ versus 1/T. Other popular methods used a difference or ratio form of the above equation, an integrated version of Equation 3 for a 1/T parametric plot, a maximum rate of weight loss theory. Frequently n could not be evaluated directly thereby requiring special consideration.

The precision and usage of the different methods varied considerably. Critical aspects have been described previously by other authors but will be briefly reviewed here. Multiple temperature point calculation methods had the advantage of being self-checking through visual inspection of a straight-line parametric plot. Unfortunately, such plots were often sensitive to small errors and thereby biased linearity judgment. This difficulty prevailed near the beginning and end of the thermogram. Measuring weight loss rate directly from the thermogram was imprecise and tedious for rapid or slow rates. Aids as computer curve-fitting, electronic differentiation apparatus, optical devices, large and accurate records served to reduce error and time. Integral weight methods, not requiring a rate input, had an advantage although it was usually necessary to determine n by separate means.

Multiple heating rate methods examined kinetics over a wide temperature and time spectrum. On the other hand, they required runs at different rates of heating. In addition, the calculations proved time consuming.

The survey of analysis methods gave nine references for coherent evaluation of the three rate parameters n, A, E. One method required both rate and weight (References 22, 29 and 53).

In addition, the parametric plots were often difficult to interpret. Three other methods used either a computer program or complex manual calculations not otherwise available (References 21, 36 and 44). The two remaining methods specified several rates of heating with a computer program being either necessary or desirable (References 2, 23 and 24).

For our work, no single method was entirely satisfactory for easy and precise curve-fitting. Therefore, three complimentary computer programs based on the Part I theory were developed for this purpose. A maximum rate experimental method (MAXRAX) used data at the point of maximum rate of weight change. This program yielded n and a first estimate for A, E. An integral method program (TRIM) used corresponding values of weight and temperature from the thermogram. A n value was transferred from MAXRAX. This requirement was avoided for the third program (PRIM) where a best apparent value of n was calculated to correspond to the minimum of an overall error term parabolic fit as a function of n (Reference 36). Two additional PRIM features were a comparative pseudo-variance analysis and two temperature spans for A, E evaluation.

C. PHENOL-FORMALDEHYDE MATERIALS SURVEY.

Approximate ranges of experimental conditions and empirical kinetic parameters for the survey were summarized in Table I with detailed results in Table II. In most constant rate work, 5-400 mgm of a fine powder sample was run in a porcelain crucible to about 950° at 3°-10°/min. Bulk material was frequently pulverized under liquid nitrogen to reduce friction heating. A purging flow of inert gas was generally used with a few moderate and high vacuum experiments being reported. Available thermograms and commercial processing suggested a desirable minimum cure or postcure temperature of about 125° with temperature being more important than time for thermogravimetry.* Therefore, the maximum processing temperature was indicated as a crude thermal history index.

The empirical kinetic parameters for constant heating rate thermogravimetry of cured and vitreous fiber reinforced materials overlapped. The higher n, A, E parameters were for reinforced samples. The largest set of values were designated temperature-dependent and varied with each of three curve-fitting methods.

The parameter E for the single isothermal thermogravimetry source for a cured polycondensate was comparable to an isothermal mass spectrometric analysis result, with $n = 0$ in both cases. Constant rate mass spectrometric thermal analysis E values were temperature-dependent, ranging from 16 up to 48 kcal/mole, the highest reported for a cured polycondensate. The parameter n was zero; unfortunately, A results were not given for this study.

The empirical kinetic parameters for the survey were somewhat mutually compensating for different experiments. For a given n, an increase in A gave an increase in E for each investigator with only four close exceptions. For a given n and experimental set, an increase in $\dot{T}$ was consistent with an increase in both A, E with only one minor exception.

For two sets of A, E and with constant n, T identical values of w would correspond to

$$(r_1 A_1 E_2)/(r_2 A_2 E_1) = (\dot{T}_1/\dot{T}_2) \exp\left[(E_1 - E_2)/RT\right] \qquad (5)$$

For $\dot{T}_1 = \dot{T}_2$, there was a single intersection of the two thermograms and large differences were suggested elsewhere. The low precision at hand, however, let sets of A, E and

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*Unpublished work by the author.

especially n, A, E approximate the same thermogram. Thus various parameter sets were dependent upon curve-fitting sensitivity. The same effect clearly existed for different heating rates. This mutual compensation tendency dictated a new and precise curve-fitting technique for the reanalysis of previous data.

A factual heating rate or temperature dependence of A, E was reported by a number of investigators. This was believed to be due in part to mutual compensation from inaccurate curve-fitting as further illustrated in a subsequent section of this report. In a formal sense Equation 3 was invalid for temperature dependent empirical kinetic parameters. The use of this relation and associate curve-fitting techniques gave pseudo-values although the errors involved were probably small. Although at least one partial solution for temperature dependent values of A, E has been obtained, no suitable evaluation method could be derived in detail (Reference 20). Further factual dependence of the empirical kinetic parameters of the invariant model on such procedural aspects as ambient pressure, sample form and weight, and so forth was a major consideration in the reexamination of thermograms using a new computer program.

SECTION III

EXPERIMENTAL MATERIALS AND METHODS

Table IV summarized the major materials for this report. Molding and other samples of Monsanto RI4009 commercial phenol-formaldehyde polycondensate were previously examined (Reference 17). The remaining materials were identical to those of either isothermal thermogravimetry or thermal expansion study (References 12 and 17).

A polycondensate casting and molding were pulverized under liquid nitrogen with a jewelers' cutter (moly-steel 10,000 rpm) and sieved to a standard particle distribution. A reinforced laminate powder was prepared in a similar manner but using a hole saw (moly-steel, 3/4 inch diameter, 780 rpm). Integral glass fabric reinforced samples about one inch square by 1/8 inch thick were used for isothermal air aging.

The modified Aminco Thermo-Grav recording thermobalance and experimental methods for constant heating rate thermogravimetry were described in Part I. Laminate plate aging experiments were conducted in a forced-air convection oven from 300°-800°F (about 150°-430°C) to 1000 hours. The procedures and mechanical property evaluations have been further detailed or referenced elsewhere (Reference 19).

usually agreed with the "best" n value. Small analytical and perhaps experimental errors at the ends of the thermogram severely affected A, E results as the w, K values were especially sensitive here. This was further illustrated by Figures 8 and 9.

The parametric study further suggested that visual inspection of data point deviations from a mean line for a parametric plot was not reliable for the precise evaluation of empirical kinetic parameters. The third computer program PRIM was designed to provide other means for proving reliability.

For PRIM, six incremental values of n were chosen around the MAXRAX n result. Essentially, TRIM was then repeated for these six values. An overall error term g was calculated for each case

$$g = \sum (w_{oc} - w_o)^2 \tag{12}$$

A best value n' was then computed as a minimum for an approximation to g dependence upon n using a parabolic method of least squares

$$g = a_o n^2 + b_o n + c_o \tag{13}$$

Then the result n' was used for calculating corresponding values of A, E using TRIM.

PRIM used two temperature spans. The first or q span was primarily for securing the best value of n. The second or s span was used for calculation of A, E for the entire thermogram. The s range was a compromise between available data and likely pyrolysis, 140° - 1010° in 30° increments. The q span, which also used 30° increments, was roughly chosen for each case using results from an initial parametric study

$$(w_{op}, w_{oq}) \cong (0.98, 0.52) \tag{14}$$

$$(w_p, w_q) \cong (0.95, 0.05) \tag{15}$$

$$(\theta_p, \theta_q) \cong (320°, 880°) \tag{16}$$

A feature of PRIM was evaluation of four indices of conformance for the calculated and experimental thermograms. One was g' and a second was $\pm(w_{oc} - w_o)_m$, this value times 100 giving the maximum sample weight percent error for the s temperature span. Comparative pseudo-variances $s_e^2(a)$, $s_e^2(b)$ were calculated assuming that Equation 11 was valid for a least mean squares analysis (Reference 42). These parameters were respectively indicative of the deviations of A, E and E from a mean (Appendix II).

Absolute methods were not available for either the linear or parabolic approximating least mean squares cases. As the pseudo-methods could fail, several checks were made. A coefficient A' was calculated by an independent relation to confirm the value of A from Equation 10. Several conformance indices were also calculated for the parabolic pseudo-method as further discussed in Appendix II.

The programs were written in Fortran IV for an IBM 7044/7094 system. Depending upon the program, from 2-10 punched input cards were necessary. Only descriptive outlines were given herein as several sets of symbols were used and the programs were not optimized for minimum running time.

SECTION IV

EMPIRICAL KINETICS COMPUTER PROGRAMS

A. THEORY.

The general theory for the computer programs, developed in Part I, was also reviewed herein as Appendix I for reference convenience. Sequential steps for the three programs and a thermogram construction subroutine were summarized using flow sheets (Figures 1-4) and outlines (Appendix II).

The maximum rate experimental program MAXRAX essentially solved four equations using an iterative procedure and two tables

$$n = \frac{\left[\ln r(n^{-1}-1)+1\right]}{\ln w_m} + 1 \tag{6}$$

$$A = w_m^{1-n}(\dot{T}X/nT)_m \exp(X_m) \tag{7}$$

$$E = -\dot{w}_{Tm} R(nT^2/w)_m \tag{8}$$

$$r = X_m^2 e^{X_m} p(X_m) \tag{9}$$

The necessary input data were evaluated at the thermogram maximum rate of weight loss. This point and the associate heating and weight loss rates were visually estimated using a straight edge and an optical device based on the alignment of two partially reflected images of the curve.

The second computer program TRIM solved

$$\log_{10}(K/T^2) = \frac{-E}{R \ln 10}\left[\frac{1}{T}\right] + \log_{10} r(AR/ET) \tag{10}$$

which was derived from the integrated solution of the constant rate kinetic equation. Other than experimental data, the inputs n, r were from MAXRAX and the approximation $\dot{T} = \dot{T}_m$ was made.

For TRIM, the parameters A, E were calculated for an ideal equation

$$y = bz + a \tag{11}$$

by the standard linear method of least squares. This was an approximating pseudo-method as all terms were interdependent, experimental precision was variable and the term r slowly decreased with increasing temperature (about ±2 percent maximum).

Thermograms for -325 sieve molding powder at three heating rates were fairly smooth and consistent excluding the final three percent of weight loss above 700° (Figure 5). A slight discontinuity near 400° for the 9° /min run was also ignored. Using TRIM, systematic variations of n, A, E and the temperature span were used to study these thermograms. The "best" values of A, E for minimum error between calculated and experimental thermograms separation by a constant sample weight difference with a small error occurring at intersections. Thus, inspection of Figure 7 revealed a residue-free resemblance to about 500° with similarity for powder samples to 900°. A particle was an unsatisfactory geometry in agreement with other results (Reference 18). Reference 10 further notes that complete drying would probably have given better agreement to 500°; smaller errors to 900° would also result. The low temperature weight losses also suggested too low a processing temperature with some solvent retention. The small thermogram fluctuations were abnormal and could have been due to an instrument artifact, replotting, or other unknown factors.

PRIM empirical kinetic parameters for polycondensate casting and glass fabric reinforced laminate powders were not the same (Table VII). The laminate powder sample was more stable for a residue-free basis. This apparent stability was believed primarily due to glass particle sintering at the higher temperatures with encapsulation of otherwise decomposable material. For example, a glassy residue with brownish inclusions was found when the laminate powder helium residue was rerun in air. Differences in resin contents calculated for the casting and laminate powders in helium (19.4%), laminate powder in air (24.3%), and a laminate plate (27.0%) were not unreasonable in that any encapsulated material would be ultimately weighed as "glass" and encapsulation would probably be least effective in air. A plate resin content of 27.0 percent was a moisture-free normalized value for long time burnout in air at 540° (Reference 6). Previous results with an uncured resin and heat cleaned 181-"E" glass powder (50/50 mixture, -400 sieve) also suggested encapsulation at temperature above about 500° (Reference 18). The helium residues near 950° were 59.5 percent for the mixture versus 56 percent for the polymer alone.

It proved necessary to "dry" the casting and laminate powders prior to thermogravimetry (Table VII). The conditions were 120° for 25 minutes, which gave an average stabilized weight loss of 1.45 percent. About 25 minutes were used for heating to 120°.

Empirical kinetic parameters were calculated for phenol-formaldehyde polycondensate powder and sized glass fabric reinforced laminate samples (Table VIII). The powder sample was more stable than the plate for both helium purging flow and a moderate vacuum. The spread in A, E was fairly small for all four experiments with n values being similar for plate samples but depending upon environment for powders. Enhanced stability was found under vacuum for both materials. This has been attributed to an increase in pyrolysis product fragmentation with increasing pressure and may be associated with inefficient removal of pyrolysis gases by a purging flow (Reference 18).

PRIM and Reference 53 parameters were not the same for a powder and plate under vacuum (Table VIII). The thermogram error index $\pm(w_{oc} - w_o)_m$ suggested that PRIM was more representative for the powder with PRIM superiority being conclusive for the plate. There were consistent parameter variations for a polycondensate powder versus a plate geometry as compared to a powder versus a laminate powder (Tables VII and VIII). Plate pyrolysis has been suggested to be influenced by catalysis, geometry, glass fabric finish, or possibly other effects (Reference 53). Polycondensate and laminate powder differences were believed primarily due to particulate glass sintering.

Five alkaline catalyzed polycondensate powders have undergone similar gravimetric pyrolysis once curing was complete (Reference 37). PRIM parameters for a sample coded B-C were comparable with other results (Table IX). The necessary thermogram was constructed from tabulated θ - w_o values and extrapolated to 950° (Reference 37). As nearly identical residue-free thermograms were reported for these materials, the sample B-C parameters were also representative for all five. They included three catalyzed by $Ca(OH)_2$ (P/F ratios of 0.36, 0.42, 0.50) and the commercial products CTL-91LD and SC1008.

PRIM curve-fitting indices and empirical kinetic parameters were averaged for six experiments using an inert gas purge (Table IX). A definitive pseudo-variance analysis was intended to aid the selection of experiments but could not be completed for this report. Qualitative results follow:

(a) Molding powder (Tables V and VI). The spread in MAXRAX and TRIM n, A, E values for three heating rates exceeded the spread of the reference set. For PRIM, the 3°/min parameters were adjudged the best of the reference set. The 9°/min results gave upper A, E limits for the reference group although also giving a good calculated-experimental thermogram fit.

(b) Pure polycondensate and glass fabric reinforced powder samples (Table VII). The polycondensate values were used for the reference group subject to being the lowest E case. The high n, A, E laminate powder results were questionable even in view of an excellent overall fit resulting in the lowest conformance indices of any run.

(c) Pure polycondensate powder and glass fabric reinforced plate samples (Table VIII). The helium purge powder parameters were adjudged satisfactory for the reference set. The vacuum results were marginally withheld due to high n, low A values as well as a poor overall fit. Although similar, the plate sample values for both helium and vacuum were not acceptable because of a low n and poor fit.

(d) Polycondensate powder (Table IX). The parameters for the only laboratory synthesized material were used in the reference set subject to being the maximum overall fit error case.

(e) Reference set materials (Table IX). There was still a tendency for mutual compensation of the parameters, especially for A, E between experiments. There were no consistent trends for n, A, E with a change in $\dot{T}$. There was a tendency toward higher values of g', $s_e^2(a)$, $s_e^2(b)$(or average error) but not $\pm(w_{oc} - w_o)_m$ (or maximum error) at the higher values of $\dot{T}$. Within the limited spectrum of experimental conditions, no consistent dependence of the conformance indices or parameters upon other variables as grinding method, sample weight, and so forth was evident. Although the spread in the parameters was low, especially when compared to the initial materials survey, fair errors resulted if one thermogram was predicted using either the reference set parameters or results for another experiment. Rough estimates implied $\pm(w_{oc} - w_o)_m$ of about 0.03-0.06 over a narrow temperature range with up to 0.03 average error. The qualitative selection of experiments for averaging and the averaged set was biased by both low overall accuracy and PRIM limitations to the degree that all observations in the above paragraphs were tentative and subject to future revision.

The residue-free weight w for the empirical kinetic model

$$w = (w_o - w_r)/(w_{oi} - w_r) \tag{17}$$

was for a continuous thermogram. The rate $-\dot{w}_{oT}$ could approximate either zero at two points or one maximum, but could not be a minimum. These rules permitted quick rejection of noncomforming thermograms. For multi-step thermograms (with $-\dot{w}_{oT}$ approaching zero at more than two points) the initial unity value of w_{oi} would have become w_r for each successive step. Equation 17 in a different form permitted easily constructed conversion diagrams for graphical calculations or rapid estimates (Figure 8). General effects of n, w upon K were often pronounced (Figure 9). K values were insensitive to n but strongly dependent upon w for $w \gtrsim 0.8$. This portion of the thermogram was limited for n, A, E evaluation and was unfairly biased by small errors. For a w of less than about 0.2, K was strongly dependent upon both n, w. Although perhaps attractive for n evaluation, small errors also exerted an unfair weighting here.

Accuracy and precision levels for constant heating rate thermogravimetry were reevaluated and the new results summarized as Table X (Reference 17). In addition, slightly revised w_r data were used for some PRIM calculations (Table V).

MAXRAX reflected both experimental and model fitting errors as primarily compared to an overall model error for PRIM. A $\pm(w_{oc} - w_o)_m$ difference between the two was therefore roughly the experimental weight error at the point of maximum rate. Calculated values were reasonable and varied up to twice the estimated experimental precision (Table X). An argument similar to the one above was possible to show that the difference between A, A' approached the error in A associated with the experimental error at the point of maximum rate. In most cases, this difference was encouragingly small (for example, see Table VI).

The program and past studies revealed a variety of troublesome aspects in the evaluation of consistent empirical kinetic parameters for phenol-formaldehyde polycondensate materials (References 17, 18 and 20). Specific examples exceeding the normalizing ability of residue-free empirical kinetics were:

(a) Critical curve-fitting aspects for a single thermogram or similar set including –

1. Data point spacing, reaction rate, or temperature range incorporation and possible magnification of errors (especially near thermogram ends).

2. Improper use of the invariant model in evaluating temperature dependent parameters or thermograms with more than one maximum rate of weight loss, and so forth.

3. Mutual compensation of different sets of parameters permitting approximate representation of a single thermogram.

4. The very flexible nature of the kinetic model for approximate representation of different thermograms.

(b) An oxidative or reduced pressure atmosphere.

(c) Reinforced laminate or polycondensate particle, laminate powder, or polycondensate film samples.

(d) Samples contaminated with postcure surface product or solvent, inadequately cured or dried, or too large.

(e) Two, three, or occasionally many stepped thermograms. This atypical behavior appeared pronounced for large sample particles and perhaps minute thermobalance oxygen contamination; low inert gas flow rates could have resulted in either contamination or inefficient pyrolytic gas removal. Stepping was perhaps accentuated to varying degrees by (b)-(d) items as well as the lack of pressure during sample polymerization.

SECTION V

TYPICAL APPLICATIONS OF EMPIRICAL KINETIC PARAMETERS

A. EMPIRICISM OF n, A, E

The kinetic parameters were strictly empirical. There was no factual significance in terms of classical physicochemical mechanisms (Table XI). Attempts to assign primary governing mechanisms could not resolve complex intra-relations between the sample, experimental method, and possible large numbers of chemical reactions and physical processes during pyrolysis. The kinetic model undoubtably grossly represented a variety of complex mechanisms.

B. RELATIVE THERMAL STABILITY

The empirical kinetic parameter E has often been used as an index of relative thermal stability. For example, this parameter was good for many thermoplastics with a n of a near integer and similar large A values. For thermosets with small values of A, E and high percentage of final residue, the three parameters n, A, E proved closely interrelated. More suitable indices were the maximum rate loss rate and corresponding temperature. The normalized weight at this point proved largely controlled by n, r at about 0.5. For a known n, A, E, $\dot{T}$, the maximum rate indices were only available by interpolation or trial and error calculation

$$T_m^{-2} = n w_m^{n-1} (AR/E\dot{T}) \exp(-X_m) \tag{18}$$

$$K_m = (AE/R\dot{T}) p(X_m) \tag{19}$$

$$-\dot{w}_{Tm} = w_m (X/nT)_m \tag{20}$$

C. HYPERTHERMAL ABLATION

Kinetic models similar to the current one have been used extensively for hyperthermal ablation calculations and computer programs. Three regions were used in one descriptive char-formation ablation analysis (Reference 49). These regions were a carbonaceous char layer, a reaction zone, and the virgin material. A char-reaction zone interface recession rate for the interface temperature was*

$$(\dot{L})^{n+2} = AGn!(1 - w_r)^{2n+1} X^{-2(n+1)} e^{-X} \tag{21}$$

$$G = L(\alpha CE/\Delta HRL)^{n+1} \tag{22}$$

For a given G, the lowest recession rate would result for a large E, w_r and a small A, T. Clearly, small uncertainties in the parameters could give a large $\dot{L}$ error. Some typical parameter values and results from another computer study were summarized by Table XII and Figure 11.

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*This derived form uses the reasonable approximations: $1 \ll \Delta HRX$; $T \rightarrow 0$ as $L \rightarrow \infty$; (wall/pyrolysis) mass flux $\cong (1 - w_r)$. Typically, $\dot{L} \ll 1$.

This application of empirical kinetic parameters to a complex environment appeared primarily because of inadequate experimental methods. The simple thermogravimetry experiment for an isolated, nearly isothermal sample was extrapolated to an internal pyrolysis zone subject to intense and rapidly changing catalytic, compositional, pressure, stress, thermal, volumetric and other gradients. For example, the time for the receding steady temperature distribution of Figure 11 to traverse a pyrolysis zone thickness of about 0.35 mm would be 1.4 second, corresponding to an "average" heating rate of 18,500°/min. In other cases, especially at low heat flux, the heating and recession rate, and temperature distribution was less abrupt with a resultant thick pyrolysis zone. Excluding limited high heating rate and high temperature work, no definitive empirical kinetic model or parameters could be found for this complex environment or a fair experimental simulation.

D. MECHANICAL PROPERTIES.

The use of empirical kinetic models and parameters for the analysis and correlation of mechanical properties has been limited (Reference 16). In one study with this intended goal the present model failed to represent the air aging weight changes of CTL-91LD/Glass Fabric (Figure 12, Reference 19). The isothermal thermograms for this and similar materials suggested two gross controlling mechanisms. There has been evidence for the predominance of diffusive effects at the shorter times and oxidation for longer aging periods with complete oxidative control at the higher temperatures (References 15 and 18).

An encouraging correlation was found for the tensile strength at 45° to the fabric warp for CTL-91LD/Glass Fabric (Figure 13). The empirical result was

$$TS(45^\circ) = c_1 \exp(c_2 w) \qquad (23)$$

A strength retention of only about 10 percent of the average room temperature control (25,260 psi) existed for w = 0.8. The empirical coefficients and other results have been summarized elsewhere for CTL-91LD/Glass Fabric and a second material (Reference 19). Other attempts at mechanical property correlations were not satisfactory if the strength increased with an increase in either temperature of time. Correlations may have been possible over restricted temperature or time regions as suggested by the similarity of the plots of Figure 14.

Other isothermal air aging kinetic experiments for a CTL-91LD polycondensate powder and CTL-91LD/Glass Fabric were informative. A -325 sieve, 100 mgm powder sample had a life-time of two hours at 600°F. The life-time for a -325 sieve 100 mgm laminate powder sample was 48 hours, implying a glass shielding effect. A 100 hour life-time of a 1/8 inch thick laminate plate was undoubtably associated with surface area and/or volume influences. These results suggested a need for a flexible empirical kinetic model properly accounting for surface area, thickness, two controlling mechanisms with a transition region, and probably catalysis, oxygen concentration, and weight. An established model would be necessary prior to any serious attempt to use this approach for the analysis and correlation of the mechanical properties of reinforced laminate plates during long-term air aging.

SECTION VI

SUGGESTIONS FOR FURTHER WORK

Additional work seems necessary to establish ranges of environmental validity for the empirical kinetic model. Particularly questionable aspects include heating rate extremes, isothermal thermogravimetry, micro size powder and large laminate plate samples, purging flow through a powder sample, and reduced and high pressure (Reference 27). Current applications for hyperthermal ablation computer programs, mechanical property correlations, vacuum life-time predictions make realistic environmental simulation an essential need. Table XIII summarized some conditions pertinent to the two above requirements yet within practical experimental capabilities in the near future. Improvements in experimental accuracy of up to an order of magnitude better than for the accuracy values of Table X were desirable although by and large beyond the immediate state of the art of thermogravimetry.

Improved computer programs appeared desirable prior to further study. One outstanding approach gave best empirical kinetic parameters in a least mean squares sense (Reference 43). Additional empirical kinetic models appeared necessary for some critical cases as an oxidative environment or sample other than a fine polymer powder (Table XIV). Particularly desirable features for future computer programs included: (a) constant heating rate and isothermal versions, (b) evaluation of n, A, E in a least mean squares sense, (c) evaluation of confidence limits, variances, and significant digits, (d) experimental corrections, (e) statistical data point weighting for the entire thermogram, and (f) temperature variance options for n, A, E, either singularly or in any combination.

There were a variety of polymers for which definitive kinetic data could prove helpful in ablative, coating, structural, and other aerospace uses. Polymer classes of special interest were summarized by Figure 15. A future goal was kinetic information on the base polymers as well as materials using such reinforcing agents as fibrous carbon, glass, graphite, and silica.

APPENDIX I

GENERAL THEORY

The constant heating rate kinetic relation

$$-\dot{w}_T = (w^n A/\dot{T}) \exp(-X) \qquad \text{(I-1)}$$

was rearranged as

$$K = -\int_1^w w^{-n} dw = (A/\dot{T}) \int_0^T e^{-X} dT \qquad \text{(I-2)}$$

for the assumption of a zero rate at zero degrees. K, a convenient index, became

$$K = (1 - w) \qquad \text{for } n = 0, \qquad \text{(I-3)}$$

$$= -\ln w \qquad = 1, \qquad \text{(I-4)}$$

$$= (w^{1-n} - 1)/(n-1) \qquad \neq 0, 1 \qquad \text{(I-5)}$$

Integration of the other side of Equation I-2 by parts in two different ways gave

$$K = (AE/R\dot{T})\, p(X) \qquad \text{(I-6)}$$

$$p(X) = X^{-1} e^{-X} - \int_X^\infty X^{-1} e^{-X} dX \qquad \text{(I-7)}$$

$$K = (AE/R\dot{T}) \left[1 - \sum_m (-1)^{m+1} X^{-m} (m+1)! \right] X^{-2} e^{-X} \qquad \text{(I-8)}$$

For m = o, a relative error r was defined as

$$r = X^2 e^X p(X) \qquad \text{(I-9)}$$

Therefore

$$K = r (AE/R\dot{T}) X^{-2} e^{-X} \qquad \text{(I-10)}$$

Figure 9 presented K = f(n, w). Figure 10 depicted p(X), r = f(X).

The maximum rate occurred when

$$d(-\dot{w})/dt = d(-\dot{w})/dT = d(-\dot{w})/dw = 0 \qquad \text{(I-11)}$$

Differentiation of Equation I-1 with respect to time gave

$$\left[n\dot{w}w^{n-1} + (\dot{T}/T) w^n X \right]_m = 0 \qquad \text{(I-12)}$$

The maximum rate followed as

$$-\dot{w}_{Tm} = w_m (X/nT)_m \qquad \text{(I-13)}$$

Also

$$k_m = w_m^{1-n} (X/nT)_m \dot{T} = Ae^{-X_m} \qquad (I-14)$$

where n cannot be zero.

The two principal relations for the maximum rate method came from rearrangements of Equations I-13 and I-14

$$E = -\dot{w}_{Tm} nR(T^2/w)_m \qquad (I-15)$$

$$A = w_m^{1-n} (\dot{T}X/nT)_m e^{X_m} \qquad (I-16)$$

The third necessary relationship for n resulted from a comparison of Equations I-10 and I-14

$$K_m = r w_m^{1-n}/n \qquad (I-17)$$

For n = 1

$$w_m = e^{-r} \qquad (I-18)$$

and for $n \neq 0, 1$

$$w_m = \left[r(n^{-1} - 1) + 1)\right]^{1/(n-1)} \qquad I-19)$$

It should be noted that Equation 39 of Reference 17 is in error and should be identical to Equation I-19 above.

APPENDIX II

COMPUTER PROGRAMS OUTLINES

I. Maximum Rate Experimental Method (MAXRAX). See Figure 1.

A. Read input: $R, T_m, \dot{T}, \dot{T}_m, w_m, w_{oi}, -\dot{w}_{Tm}, w_r$

B. Read tables:

1. $r_{j,k} = f_1(X_m)$ (II-1)

2. $w_m = f_2(n_i, r_i)$ (II-2)

C. Read integral values of n_i, r_i for w_m from table.

D. Calculate n_j

$$n_{j,k} = \frac{\ln\left[r_{i,j}(n_{i,j}^{-1} - 1) + 1\right]}{\ln w_m} + 1 \qquad \text{(II-3)}$$

$$(n_{i,j,k} \neq 0, 1) \qquad \text{(II-4)}$$

E. Calculate E, X_m

$$E = -\dot{w}_{Tm} n_{j,k} R (T^2/w)_m \qquad \text{(II-5)}$$

$$X_m = E/RT_m \qquad \text{(II-6)}$$

F. Read r_j from table.

G. Calculate n_k from Equation II-3.

H. Calculate E from Equation II-5. Calculate A

$$A = w_m^{1-n_k} (\dot{T}X/n_k T)_m \exp(X_m) \qquad \text{(II-7)}$$

I. Write output:

1. Run identification.

2. n_k, A, E, r_j, X_m, $\dot{T}_m$

J. Construction subroutine

II. Transfer Resolution Integral Method (TRIM). See Figure 2.

A. Read input:

$$n, r, R, T_m, \dot{T}, \dot{T}_m, w_m, w_{oi}, -\dot{w}_{Tm}, w_r$$

B. Read table:

$$w_o = f_1(\theta) \text{ with } \theta_p \leq \theta \leq \theta_q . \qquad \text{(II-8)}$$

C. Calculate T

$$T = \theta + 273.16 \qquad \text{(II-9)}$$

D. Calculate w

$$w = (w_o - w_r)/(w_{oi} - w_r) \qquad \text{(II-10)}$$

E. Calculate K

$$K = (1 - w) \qquad \text{for } n = 0, \qquad \text{(II-11)}$$

$$= - \ln w \qquad = 1, \qquad \text{(II-12)}$$

$$= (w^{1-n} - 1)/(n-1) \qquad \neq 0, 1 \qquad \text{(II-13)}$$

F. Calculate y, z

$$y = \log_{10} (K/T^2) \qquad \text{(II-14)}$$

$$z = 1/T \qquad \text{(II-15)}$$

G. Calculate A, E by linear pseudo-method of least squares

$$y = bz + a \qquad \text{(II-16)}$$

H. Calculate A'

$$A' = - \dot{w}_{Tm} w^{-n} \dot{T}_m \exp(X_m) \qquad \text{(II-17)}$$

I. Write output:

1. Run Identification.
2. n, A, E, r, $\dot{T}$, A'

J. Construction subroutine.

III. Parabola Resolution Integral Method (PRIM). See Figure 3.

A. Read input: n, r, R, T_m, $\dot{T}$, $\dot{T}_m$, w_m, w_{oi}, $-\dot{w}_{Tm}$, w_r

B. Read tables:

1. $w_o = f_1(\theta)$ with $\theta_p \leq \theta \leq \theta_q$. (II-18)
2. $n_1, n_2 \ldots n_i$, with i = 6 maximum. (II-19)

C. TRIM subroutine.

D. Calculate g

$$g = \sum (w_{oc} - w_o)^2 \tag{II-20}$$

E. If $g = 0$, $n = n'$. Proceed to item (I). (II-21)

F. Calculate a_o, b_o, c_o by parabolic pseudo-method of least squares

$$g = a_o n^2 + b_o n + c_o \tag{II-22}$$

G. If $a \leq 0$, designate. Proceed to item (V). II-23)

H. Calculate n'

$$n' = -b_o / 2 a_o \tag{II-24}$$

I. TRIM subroutine.

J. Calculate g'

$$g' = \sum (w_{oc} - w_o)^2 \tag{II-25}$$

K. Calculate $\overline{w_o}$

$$\overline{w_o} = \left[\sum w_o \right] / q \tag{II-26}$$

L. Calculate $s_e^2 (w_o)$

$$s_e^2 (w_o) = g' / (q - 2) \tag{II-27}$$

M. Calculate $s_p^2 (w_o)$

$$s_p^2 (w_o) = \left[\sum (w_o - \overline{w_o})^2 \right] / q - 1) \tag{II-28}$$

N. Calculate $F(w_o)$

$$F(w_o) = s_p^2 (w_o) / s_e^2 (w_o) \tag{II-29}$$

O. Calculate a, b

$$a = \log_{10} r (AR/E\dot{T}) \tag{II-30}$$

$$b = -E/(R \ln 10) \tag{II-31}$$

P. Calculate $\overline{1/T}$

$$\overline{1/T} = \left[\sum 1/T \right] / q \tag{II-32}$$

Q. Calculate $s_e^2 (a)$

$$s_e^2 (a) = s_e^2 (w_o) / q \tag{II-33}$$

R. Calculate s_e^2 (b)

$$s_e^2(b) = s_e^2(w_o)/\sum(1/T - \overline{1/T}) \tag{II-34}$$

S. Construction subroutine.

T. Substitute s temperature span for q temperature span with

$$\theta_r \le \theta \le \theta_s \tag{II-35}$$

U. Repeat items (I) through (S) for s temperature span.

V. Write output:

1. Run identification.
2. For the q temperature span: n', A, E, R, $\dot{T}$, A', g', $\overline{w_o}$, $s_e^2(w_o)$, $s_p^2(w_o)$, $F(w_o)$, a, b, 1/T, $\overline{1/T}$, $s_e^2(a)$, $s_e^2(b)$;

$$w_{oc} = f_2(\theta) \tag{II-36}$$

3. Item (V.2) for the s temperature span.

IV. Construction Subroutine. See Figure 4.

A. Read input: n, A, E, r, R, $\dot{T}$, $\dot{T}_m$, w_{oi}, w_r

B. Read table: $p(X) = f_1(X)$ (II-37)

C. Calculate K

$$K = (AE/R\dot{T})\,p(X) \tag{II-38}$$

D. Calculate w

$$w = 1 - K \qquad \text{for } n = 0, \tag{II-39}$$

$$= \exp(-K) \qquad = 1, \tag{II-40}$$

$$= \left[K(n-1) + 1\right]^{1/(1-n)} \qquad \neq 0,1 \tag{II-41}$$

E. Calculate w_{oc}

$$w_{oc} = w(w_{oi} - w_r) + w_r \tag{II-42}$$

F. Calculate θ

$$\theta = T - 273.16 \tag{II-43}$$

G. Write output: $w_{oc} = f_2(\theta)$ with $\theta_r \le \theta \le \theta_s$. (II-44)

V. General Notes.

A. Numerical values for this report were:

1. $j = k = 30°$ (II-45)

2. $\epsilon = \delta = 0.001$. (II-46)

3. $w_{oi} = 1$. (II-47)

4. θ_p, θ_q were for the j increment nearest to $w_p \sim 0.95$, $w_q \sim 0.05$, respectively. See Equations 14-16. (II-48)

5. $\theta_r = 140°$, $\theta_s = 1010°$. (II-49)

B. The following was omitted for brevity:

1. Standard tests for avoiding ln 0, ln (-number), etc.

2. For MAXRAX,

   a. Subscript m omitted for n.

   b. Subscripts m, i, j, k, omitted for A, E, X_m.

   c. A manual test assuming $n = 1$ if $n_{j,k} < 0$. (II-50)

   d. A test to insure that

$$\left[r_{i,j} (n^{-1}_{i,j,k} - 1) + 1 \right] \neq 0 \qquad \text{(II-51)}$$

   was positive.

   e. Rules for choosing $+\epsilon$ or $-\epsilon$.

   f. $-\dot{w}_{Tm}$, w_m calculated manually.

3. Linear least mean squares pseudo-method subroutine for TRIM with output A, E.

4. For PRIM,

   a. Parabolic least mean squares pseudo-method subroutine with output n, g, g_c, a_o, b_o, c_o, $\pm(g_c - g)_m$, $s^2_e(g)$, $s^2_p(g)$.

   b. Output: n, A, E and $w_o = f(\theta)$ as an option for each n value. (II-52)

   c. Equations II-26 through II-29 for the flow diagram.

C. For TRIM:

1. $n = n_m$ (MAXRAX), $n = n_i$ (PRIM), or $n = n'$ (PRIM).

2. $r = r_m$ (MAXRAX), and $\dot{T} = \dot{T}_m$ unless noted.

D. For Construction Subroutine:

1. Run identification and n, A, E, r, X_m, $\dot{T}$ included in output when run separately.

2. s temperature span except as a special case for PRIM.

E. Symbols f_m and symbols using subscripts i, j, k usually unique for each program outline.

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53. H. S. Wilson, et al, "Analysis of Thermal Degradation of Glass Reinforced Phenolic and Epoxy Laminates," Wright-Patterson AFB, Ohio, ASD-TDR-62-939(July 1963).

TABLE I

APPROXIMATE RANGES OF LITERATURE EMPIRICAL KINETIC PARAMETERS FOR PHENOL-FORMALDEHYDE POLYCONDENSATE MATERIALS

	Cured Resin		Vitreous Fiber Reinforced Resin
Code	Constant Heating Rate Thermogravimetry*	Isothermal Thermogravimetry*	Constant Heating Rate Thermogravimetry
Sample and Method			
Atmosphere			
Ambient Pressure	He, N_2 purge		He, N_2 purge
Reduced Pressure	10^{-5}, 1 torr	10^{-5} torr	0.5, 1 torr
Crucible	Coors 230 3/0 porcelain	platinum, tungsten	Coors 230 3/0 porcelain
Fabric Reinforcement	none	none	glass, silica
Grinding Method			
Liquid Nitrogen	cutter		end mill
Room Temperature	compaction	ground	
Particle Size	fine, -325 sieve	fine, bulk particle	fine, coarse, thin flakes, plate
Postcure Temperature, °C	178, 204	120, 230	130, 178, 204
Resin Content, %	100	100	23-40
Weight, mgm	100, 200	5-15	100-400
Empirical Kenetic Parameters			
n	0-1.4	0	0-5
A, min^{-1}	1.5-32	4.6×10^3	2×10^{-1}-1.7×10^{16}
E, kcal/mole	5.6-48	18-22	3.7-72
$\dot{T}$, °C/min	2.6-29		2.5-18
T_I, °C		330-430	
T_r, °C	800-950		900-1130
w_r	0.53-0.62		0.57-0.75

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*Constant rate and isothermal mass spectormetric thermal analysis results included for completeness (Reference 51).

TABLE II

SOME LITERATURE EMPIRICAL KINETIC PARAMETERS FOR PHENOL-FORMALDEHYDE POLYCONDENSATE MATERIALS[a]

Reference and Code	Bowen (8) Silica Filled	Farmer (17) Molding Powder			Friedman (25) Glass Fabric Reinforced	Freidman (23,24) Glass Reinforced					
Sample and Method											
Atmosphere	N_2 purge	He purge			N_2 purge	N_2 purge					
Crucible		Coors 230 3/0			Coors 230 3/0	Coors 230 3/0					
Fabric Reinforcement	silica	none			glass	glass					
Grinding Method		cutter;liq N_2			end mill;liq N_2	end mill;liq N_2					
Particle Size	fine	-325 sieve			coarse	thin flakes					
Postcure Temperature[b]		178				130					
Trade Names[c]	MX-2646										
Reinforcement					181-"E" glass						
Resin		RI4009			CTL-91LD	CTL-91LD					
Resin Content, %	22.9	100			40	35-36.1					
Weight, mgm	200	100				200					
Empirical Kinetic Parameters											
n	2	1.4	1.3	1.4	1	5	5	5	5	5	5
A, min^{-1}	3.62×10^4	6.40	31.7	6.87	405	4.09×10^{12}	4.38×10^{13}	7.98×10^{15}	8.55×10^{16}	1.59×10^{15}	1.67×10^{16}
E, kcal/mole	18.2	8.83	10.3	11.1	15.1	61±11	46	55	58	51	55
$\dot{T}$, °C/min	2.5,11,15	2.6	5.0	7.4	3	0.83,1.67,3,6	0.83	1.67	3	6	
T_r, °C	1130	950	950	950	900	900	900	900	900	900	900
w_r	0.567	0.55	0.54	0.54	0.59	0.59-0.61	0.61	0.59	0.61	0.61	
Curve-Fitting Technique[d]	Rate[e]	Maximum Rate, Integral Method[f]			Rate	Multiple Rate[g]	Rate	Rate	Rate	Rate	Four Rates, Averaged[f]

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[a] Constant heating rate thermogravimetry unless noted otherwise.

[b] Maximum postcure (or cure) temperature, °C.

[c] CTL-91LD, CTL, Incorporated; MX-2646, Martin Company; RAD 60 PMTS, Avco RAD: RI4009 and SC1008, Monsanto Research Corporation; V-204, Martin Company

[d] Difference - reaction rate and residual weight ordinate function versus a 1/T abscissa function parametric plot for n, E. Equation for A. Empirical - residual weight ordinate function versus 1/T parametric plot for A, E, n implicit.

TABLE II (CONT'D)

Reference and Code	Levine (36) RAD 60 PMTS Phenolic/Glass Fiber				McGlothlin (38) Silica Phenolic		McGlothlin (38) Silica Phenolic SC-1008		Madorsky (39) Phenolic	Munson (44) Glass Fabric Reinforced
Sample and Method										
Atmosphere	helium				0.5 torr air		0.5 torr air		10^{-5} torr air	N_2 purge
Crucible					Coors 230 3/0		Coors 230 3/0		platinum	Coors 230 3/0
Fabric Reinforcement	glass				silica		silica		none	glass
Grinding Method									none	end mill;liq N_2
Particle Size									bulk particle	coarse
Postcure Temperature[b]										230
Trade Names[c]	RAD 60 PMTS				V-204					
Reinforcement										181-"E" glass
Resin							SC-1008		CTL-91LD	CTL-91LD
Resin Content, %									100	40
Weight, mgm					400.32	369.72	395.27	347.10	5-10	
Empirical Kinetic Parameters[h]										
n	1.7	1.7	1.6	3.0•	2	2	2	2	0	1
A, min^{-1}	0.202	1.16	16.7	361	1.45×10^2	1.07×10^3	4.47×10^2	5.75×10^3	4.6×10^3	21.53
E, kcal/mole	3.71	4.75	6.69	9.10	12.814	13.671	14.576	16.311	18	10.65
$\dot{T}$, °C/min	1.1	2.2	5.5		3	18	3	18		3
T_r, °C					930	930	930	945		900
W_r										0.59
Curve-Fitting Technique[d]	Iterative Calculations (Computer Program)				Rate	Rate	Rate	Rate	Isothermal Thermogravimetry[j]	Iterative Calculations (Manual)[i]

Isothermal mass spectrometric thermal analysis - Arrhenius-type parametric plot for product species, then weighted as a function of molecular weight and molar rate of formation for overall E. n implicit. Integral method - residual weight and T ordinate function versus 1/T parametric plot for E. Maximum rate method for n, equation for A. Iterative calculations - calculated best n, A, E values in a least mean squares sense. Isothermal thermogravimetry - Arrhenius-type parametric plot for E. n implicit, Reference 45 for A. Mass spectrometric thermal analysis - see isothermal mass spectrometric thermal analysis. Maximum rate method - calculated n, A, E values for the point of maximum rate of weight loss. Multiple rate - reaction rate and residual weight ordinate function versus 1/T parametric plots for n, A, E. Rate - Arrhenius-type parametric plot for E, sometimes A. n implicit, usually an equation for A.

• Averaged values for n, A, E for three heating rates.

TABLE II (CONT'D)

Reference and Code	Shulman, Lochte (51) Resins B and D		Wilson (53) Glass Fabric Laminate		Wilson (53) Resin	
Sample and Method						
Atmosphere	high vacuum		1 torr		1 torr	
Crucible	tungsten		Coors 230 3/0		Coors 230 3/0	
Fabric Reinforcement	none		glass		none	
Grinding Method	ground		none		compaction	
Particle Size	fine		plate[m]		fine	
Postcure Temperature[b]	B-232°; D-120°		204		204	
Trade Names[c]						
Reinforcement			181-"E" glass			
Resin			SC1008		SC1008	
Resin Content, %	100		25		100	
Weight, mgm	6-15		200		200	
Empirical Kinetic Parameters						
n	0	0	1	1	1	1
A, min^{-1}			0.49	6.2	1.51	13.2
E, kcal/mole	16 to 48[k]	D-22[l]	4.65	5.12	6.53	5.57
$\dot{T}$, °C/min	12, 29		5	5	5	5
T_r, °C	800		1000	1000	940	940
w_r	D-0.528		0.75	0.75	0.622	0.622
Curve-Fitting Technique[d]	Mass Spectrometric Thermal Analysis	Isothermal Mass Spectrometric Thermal Analysis	Difference	Empirical	Difference	Empirical

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[f] A, E, values also given for a maximum rate method, but omitted here for brevity.

[g] Residual weight dependence of E also given in graphical form.

[h] A value times a sample constant probably necessary to convert to report definition for n different from unity.

[i] Analysis of thermogram of Friedman (Reference 25).

[j] Isothermal experiments at 332°(1200 min), 355°(110 min), 380°C(100 min).

[k] Temperature dependence of E: 300°-16, 350°-19, 400°-26, 450°-44, 500°-48, 550°-38, 600°-34, 650°-43, 700°-42, 725°C-43.

[l] Isothermal experiments at 405°, 415°, 428°C.

[m] About 1/2 x 1/4 x 1/8 inch.

TABLE III

SOME LITERATURE KINETIC METHODS FOR CONSTANT HEATING RATE THERMOGRAVIMETRY

Category	Parameters	Parametric Plot[a]	n Factors[b]	References	Remarks	Specific Materials
Single Heating Rate						
Single Temperature Point						
Maximum Rate Value	A, E	no	implicit	Friedman (23, 24)		glass reinforced phenolic
	A, E	no	unity	Fuoss, et al (26)		Teflon TFE, Lucite, polystyrene, CaC_2O_4(first step)
	n	no		Horowitz, (30), Metzger (41)	critical assumptions	footnote c
Selected Value	A, E	no	implicit	Doyle (14)		Teflon TFE 5
Multiple Temperature Points						
Reaction Rate[d]	n, E	yes		Anderson (1, 3, 5)		Teflon TFE 5, 2 epoxide resins
	n, A, E	yes		Freeburg (21)	computer program	CaC_2O_4 (first step)
	n, A, E	yes		Freeman, Carroll (22)		$CaC_2O_4 \cdot H_2O$
	A, E	yes	implicit or unity	Friedman (25)		glass reinforced phenolic
	n, A, E	yes		Goldstein (29)		nylon, phenolic, composites
	A, E	yes	implicit	Goldstein (29)		nylon, phenolic, composites
	A, E	yes	implicit	McGlothlin (38)		reinforced thermosets
	E	yes	unity	Magnuson (40)		dimethylsiloxane
	E	yes	1/2	Wiedemann (52)		$MgC_2O_4 \cdot H_2O$ (second step)

---

[a] Typically a reaction rate, residual weight, or combined ordinate function versus a 1/T abscissa function.

[b] Implicit - assumed, found by trial and error, or known.

[c] Poly-mixed alky methacrylate ester; lauryl and β-diethylaminoethyl methacrylate copolymer; $CaC_2O_4 \cdot H_2O$ (first step); polyethylene for Reference 30. Polyisobutylene, polypropylene for Reference 41.

[d] Residual weight necessary for parametric plot and to calculate A in certain cases.

[e] Reaction rate not used for parametric plot but necessary to calculate A in certain cases.

TABLE III (CONT'D)

Category	Parameters	Parametric Plot	n Factors	References	Remarks	Specific Materials
Residual Weight^e	A (?), E	yes	implicit	Redfern (48)		$CaC_2O_4 \cdot H_2O$
	A, E	yes	implicit	Doyle (14)		Octamethylcyclotetrasiloxane, Teflon TFE 5
	A, E	yes	implicit	Horowitz (30), Metzger (41)		footnote c
	E	yes	implicit or zero	Ingraham (32)	rate/unit area model	$BaCl_2 \cdot 2H_2O$, $BaCl_2 \cdot H_2O$, $CaCO_3$, $CuSo_4$
	n, A, E	no		Levine (36)	iterative computer program	theory only
	n, A, E	no		Munson (44)	iterative manual calculations	2 reinforced thermosets
	A, E	yes	unity	Wilson, et al (53)	empirical model	phenolic, glass reinforced phenolic
	n, A, E	yes		Wilson, et al (53)		phenolic, glass reinforced phenolic
Thermogram Area	E	no	unity	Doyle (13)		theory only
Multiple Heating Rates						
Single Temperature Point						
Reaction Rate^d	n, A, E	(?)		Anderson (2)	computer program; 3 heating rates	Teflon TFE 5, Teflon FEP 100
Residual Weight^e	n	no		Chaing (11)	derived for isothermal case; 2 heating rates	theory only
Multiple Temperature Points						
Reaction Rate^d	n, A, E	yes		Friedman (23, 24)	5 heating rates	glass reinforced phenolic
	n	yes		Goldstein (29)	2 heating rates	nylon, phenolic, composites
	n, E	yes (2 used)		Lee, et al (34, 35)	2 heating rates	epoxide resins
	n	yes		Lee, et al (35)	2 heating rates	epoxide resins

TABLE IV

EXPERIMENTAL MATERIALS

Code	Molding	Preform	A-4 Casting[b]	A-2 Laminate	CTL-91LD/ Glass Fabric
Fabric Reinforcement	none	none	none		
Finish				A1100	A1100
Layup				Parallel, Back to Back	Parallel, Back to Back
Number of Plies				64	14
Style				112-"E" Glass	181-"E" Glass
Cure Cycle					
Pressure, psi	320[a]	vacuum	1000	to 500[c]	200
Time, hr at Each	0.5-92;	0.75-60	3-93; 1-121	3-93; 1-121,	0.75-132
Temperature, °C	0.5-160		149, 177	149, 177	
Postcure Cycle					
Time, hr at Each	24-149;	none	23-177	23-177	24-121, 149, 177
Temperature, °C	24-177				
Test Laminates					
Barcol Hardness	0	0	0	80	86
Resin Content, %	100	100	100	28.5	37.3
Specific Gravity	1.18		1.19	1.96	1.79
Thickness, inch	0.125	1.25	1.25	1.25	0.125
Void Content, %	nil		0.090	0.124	
Trade Name	RI4009	CTL-91LD	CTL-91LD	CTL-91LD	CTL-91LD
Reference	Farmer (17)	Denman (6,12)	Denman (6,12)	Denman (6,12)	Farmer (19)

---

[a] 0.5 hr at 92° and 160°, heated from 92° to 160° over a 0.25 hr period under pressure.

[b] Preform used as the starting material.

[c] Resin "B"-staged for 0.25 hr at 93°. Pressure applied in 50 psi steps during laminating prior to gelation to 500 psi maximum. Laminate cooled under maximum pressure to 38°, removed from press.

TABLE V

EMPIRICAL KINETIC PARAMETERS FOR A PHENOL-FORMALDEHYDE POLYCONDENSATE MOLDING POWDER AT THREE HEATING RATES USING THREE COMPUTER PROGRAMS[a]

Nominal Furnace Rate, °C/min	3			6			9		
Computer Program	MAXRAX	TRIM	PRIM	MAXRAX	TRIM	PRIM	MAXRAX	TRIM	PRIM
n	1.05571	1.05570	1.48577	1.32683	1.32680	1.46670	1.41220	1.41000	1.47196
A, min^{-1}	4.90932	0.9223229	19.5436	21.7954	17.79772	69.8791	62.6721	70.78961	102.324
A', min^{-1}		1.321482	18.5781		18.53112	58.5909		72.09786	96.8247
E, kcal/mole	8.59391	6.579147	10.1333	9.87088	9.619387	11.2660	10.9420	11.17593	11.5786
q span, °C		350-860	350-860		350-770	260-770		260-770	260-770
r_m	0.780 55	0.780755	0.780755	0.794261	0.794261	0.794261	0.804226	0.804226	0.804226
T_m, °C	500	500	500	510	510	510	520	520	520
$\dot{T}_m$, °C/min	2.55	2.55	2.55	5.04	5.04	5.04	7.4	7.4	7.4
T_r, °C	950	950	950	950	950	950	950	950	950
w_r	0.552	0.552	0.555	0.542	0.542	0.552	0.540	0.540	0.552
$\pm (w_{oc} - w_o)_m$	0.017	0.046	0.005356	0.012	0.015	0.007106	0.010	0.003	0.007472

---

[a] R14009 molding postcured to 178°C and ground with cutter under liquid nitrogen. -325 sieve 100 mgm samples to 950° ± 20°C in helium purging flow using Coors 230 3/0 porcelain crucible.

TABLE VI

P[illegible] I EMPIRICAL KINETIC PARAMETERS FOR A PHENOL-FORMALDEHYDE POLYCONDENSATE MOLDING POWDER AT THREE HEATING RATES[a]

Nominal Furnace Rate, °C/min	3	6	9
A. Empirical Kinetic Parameters[b]			
n	1.48577	1.46670	1.47196
A, min^{-1}	19.5436	69.8791	102.324
E, kcal/mole	10.1333	11.2660	11.5786
q span, °C	350-860	260-770	260-770
r_m	0.780755	0.794261	0.804226
$\dot{T}_m$, °C/min	2.55	5.04	7.40
T_r, °C	950	950	950
w_r	0.555	0.552	0.552
A', min^{-1}	18.5781	58.5909	96.8247
B. Conformance Indices			
$g' \times 10^3$	0.07224	0.2371	0.2840
$s_e^2(a) \times 10^5$	0.02508	0.08232	0.09862
$s_e^2(b) \times 10^2$	-0.02257	-0.06593	-0.07899
$\pm(w_{oc} - w_o)_m$	0.005356(500°)	0.007106(410°)	0.007472(350°)

---

[a] RI4009 molding postcured to 178°C and ground with cutter under liquid nitrogen. -325 sieve 100 mgm samples to 950°±20°C in helium purging flow using Coors 230 3/0 porcelain crucible.

[a] See Table II for results of manual calculations.

TABLE VII

PRIM EMPIRICAL KINETIC PARAMETERS FOR PURE AND GLASS FABRIC REINFORCED PHENOL-FORMALDEHYDE POLYCONDENSATE POWDERS

A. Sample and Method

Atmosphere	He purge	He purge
Code	A-4 Casting	A-2 Laminate
Crucible	Coors 230 3/0	Coors 230 3/0
Fabric Reinforcement	none	yes[a]
Grinding Method	cutter; liquid N_2	hole saw; liquid N_2
Particle Size	-325 sieve	-325 sieve
Postcure Temperature, [b]°C	178	178
Resin Content, %	100	27.0
Trade Name	CTL-91LD	CTL-91LD
Weight, mgm	20	100

B. Empirical Kinetic Parameters

n	1.62580	1.73258
A, min^{-1}	24.234	201.572
E, kcal/mole	9.18206	12.9362
q span, °C	350-770	350-770
r_m	0.787766	0.845028
$\dot{T}$, °C/min	7.7	7.7
T_r, °C	950	950
w_r	0.552	0.8888

C. Conformance Indices

$g' \times 10^3$	0.5973	0.05057
$s_e^2(a) \times 10^5$	0.2667	0.02258
$s_e^2(b) \times 10^2$	-0.2347	-0.01987
$\pm(w_{oc} - w_o)_m$	0.009806(620°)	0.003142(620°)

---

[a] 112-"E" glass fabric with A1100 finish.

[b] Maximum postcure temperature.

TABLE VIII

SUMMARY OF RESULTS FOR REFERENCE 53 PHENOL-FORMALDEHYDE POLYCONDENSATE MATERIALS

Sample and Method						
Atmosphere	He purge	Vacuum		He purge	Vacuum	
Code	Resin	Resin		Laminate	Laminate	
Crucible	Coors 230 3/0	Coors 230 3/0		Coors 230 3/0	Coors 230 3/0	
Fabric Reinforcement[a]	none	none		yes	yes	
Grinding Method	compaction	compaction		none	none	
Particle Size	fine	fine		plate[b]	plate[b]	
Postcure Temperature,[c] °C	204	204		204	204	
Trade Name	SC1008	SC1008		SC1008	SC1008	
Resin Content, %	100	100		25[d]	25[d]	
Weight, mgm	200	200		200	200	
Empirical Kinetic Parameters						
Source	PRIM	PRIM	Ref 53 [e]	PRIM	PRIM	Ref 53 [e]
n	1.56915	1.85899	1	1.29816	1.17066	1
A, min^{-1}	29.9979	13.2415	1.51	46.3025	10.0217	0.49
E, kcal/mole	10.0504	9.24766	6.53	10.5951	9.00476	4.65
q span, °C	350-770	350-770		350-770	350-770	
r_m	0.794261	0.794261		0.794261	0.794261	
$\dot{T}$, °C	5	5	5	5	5	5
T_r, °C	950	950	940	950	950	1000
w_r	0.602	0.610	0.622	0.573	0.573	0.75
Conformance Indices						
$g' \times 10^3$	0.2087	0.6863		1.864	1.365	
$s_e^2(a) \times 10^5$	0.1070	0.3520		0.9558	0.7002	
$s_e^2(b) \times 10^2$	-0.0932	-0.3064		-0.8322	-0.6096	
$\pm (w_{oc} - w_o)_m$	0.007516	0.01134	0.021	0.02558	0.01515	0.080

---

[a] 181-"E" glass fabric with A1100 finish.

[b] About 1/2 x 1/4 x 1/8 inch.

[c] Estimated maximum postcure temperature.

[d] Estimated variation: 25.85 ± 3.25

[e] Method of Freeman and Carroll. See Table II for results for an empirical method.

TABLE IX

MISCELLANEOUS PRIM RESULTS FOR PHENOL-FORMALDEHYDE POLYCONDENSATE POWDERS

A. Sample and Method		
Atmosphere	Ar purge	Ar, He purge
Code	B-C	See Trade Names
Crucible	porcelain	Coors 230 3/0
Grinding Method		
Liquid Nitrogen		cutter, drill
Room Temperature	filing	compaction, filing
Particle Size	fine	fine, -325 sieve
Postcure Temperature[a], °C	230	178,204,230
Trade Name (Or Code)	B-C	B-C, CTL-91LD, RI4009, SC1008
Weight, mgm	200	20, 100, 200
B. Empirical Kinetic Parameters		
n	1.61375[b]	1.55578±0.07002
A, $\min^{-1}$	51.5221	60.9338±41.3902
E, kcal/mole	11.4162	10.38033±1.19827
q span, °C	350-830	560 ± 300
r_m	0.780755	0.7924905 ± 0.0117355
$\dot{T}$, °C/min	3.3	5.125±2.575
T_r, °C	815	882±68
w_r	0.555	0.577±0.025
C. Conformance Indices		
$g' \times 10^3$	0.6770	0.37462±0.30238
$s_e^2(a) \times 10^5$	0.2351	0.14589±0.12081
$s_e^2(b) \times 10^2$	-0.2115	-(0.128635±0.106065)
$\pm(w_{oc} - w_o)_m$	0.01694(440°)	0.011148±0.005792
D. Reference	Lochte, et al (37)	This Report[c]

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[a] Maximum processing temperature.

[b] Approximate estimates for q span, r_m, w_r. w_o values from a smooth curve from tabulated data extrapolated graphically to 950°. A' was not calculated accurately.

[c] Averages from Tables VI (3°, 6°, 9°/min), VII, VIII and IX.

TABLE X

ESTIMATED OVERALL ACCURACY AND PRECISION[a]

Nominal Furnace Rate, °C/min	3		6		9	
Category	Accuracy	Precision	Accuracy	Precision	Accuracy	Precision
Heating Rate						
°C/min	2.7±0.2	2.7±0.2	5.4±0.4	5.4±0.4	8.2±0.8	8.2±0.8
Percent of Average Rate	±7.4	±7.4	±7.4	±7.4	±9.8	±9.8
Temperature						
°C	±8	±5	±8	±5	±8	±5
Percent of 1000°C	±0.8	±0.5	±0.8	±0.5	±0.8	±0.5
Weight						
Percent of Sample Weight	±2	±0.5	±2	±0.5	±2	±0.5
Maximum Rate (Computer Program)						
Percent of Sample Weight	±1.2		±0.5		±0.7	

---

[a] For helium purging flow. Recorder ranges: 0-100 mgm/5 inches and 0-1000°C/10 inches.

TABLE XI

SOME PHYSICOCHEMICAL KINETIC RELATIONS AND MECHANISMS[a]

Isothermal Rate Expression	n Value	Integrated Relation[b]	Controlling Mechanism
$-\dot{c} = kc^n$	0	$kt = (1 - c)$	zero order homogeneous chemical reaction; surface absorption
	1/2	$= 2(1 - c^{1/2})$	interface recession (two dimensions)
	2/3	$= 3(1 - c^{1/3})$	interface recession (three dimensions)
	1	$= -\ln c$	first order homogeneous chemical reaction; random nucleation
$-\dot{c} = (1/2)k(1 - c)^{-1}$		$= c^2$	diffusion in a body
$-\dot{c} = (3/2)kc^{1/3}(1 - c^{1/3})^{-1}$		$= 1 - (2/3)(1 - c) - c^{2/3}$	diffusion in a sphere

---

[a] Adapted in part from Reference 9.

[b] In most cases $k = A \exp(-X)$. For a constant heating rate $\dot{T}$, two substitutions should be made: $-\dot{c}_T = -\dot{c}/\dot{T}$ and $kt = (1/\dot{T}) \int k dT$.

TABLE XII

SOME ADDITIONAL LITERATURE EMPIRICAL KINETIC PARAMETERS FOR PHENOL-FORMALDEHYDE POLYCONDENSATE MATERIALS[a]

Reference and Code	Beecher (7) Glass-Reinforced Phenolic Resin	Hurwicz (31) Silica Reinforced Plastic B	Myers (45) Phenolic Resin	Polezhayev (47) Fiber Glass Reinforced Plastic		Scala (49) Char-Forming Plastic
Sample and Method						
Fabric Reinforcement	glass	silica	none	glass	glass	
Resin Content, %			100		15	
Empirical Kinetic Parameters						
n	0	1	0	1[b]	1[c]	1.0
A, min^{-1}	60×10^6	60×10^6	4.6×10^3	60×10^6	$60 \times 10^4, \times 10^6, \times 10^8$	6.6×10^3
E, kcal/mole	18	22.10	18	46	32, 36, 46	46

---

[a] Most values indicated as being "representative", "typical", and so forth except for References 7 and 45.

[b] Averaged values from References 7 and 49.

[c] n, A, E values used in a parametric ablation study.

TABLE XIII

SOME PROBATIVE KINETIC EXPERIMENTAL RANGES FOR POLYMERS AND REINFORCED PLASTICS[a,f]

Major Variable	Geometry	Heating Rate, °C/min[b]	Isothermal Temperature, °C[c]	Pressure, atm[d]	Purge Rate, Liter/min	Weight
Weight	Powder	3-6	400-600	0.001-1	1-2	0.1-200 mgm
Dynamic Atmosphere	Powder	3-6	400-600	0.5-1	0.1-20	0.1-200 mgm
	Plate	3-6	400-600	0.5-1	0.1-20	1-125 gm
Oxidative Atmosphere	Plate	1-6	150-1350	0.5-1	0.1-20	1-125 gm
Heating Rate	Powder	1-600		0.001-1	1-2	0.1-5 mgm
	Plate	1-6		0.001-1	1-2	1-125 gm
Isothermal Thermogravimetry	Powder		150-1600	0.001-1	1-2	0.1-200 mgm
	Plate		150-1600	0.001-1	1-2	1-125 gm
Pressure[e]	Powder	3-6	400-600	10^{-9}-10^{-3}	0-0.1	0.1-200 mgm
	Plate	3-6	400-600	10^{-9}-10^{-3}	0-0.1	1-125 gm

---

[a] Inert atmosphere and open sample holder unless noted.
[b] Inert atmosphere to 1600°C, oxidative to 1350°C.
[c] Necessary time for weight stabilization or oxidative resin burn-out.
[d] Zero purge rate at 0.001 atm.
[e] Also confined versus open sample holder geometries.
[f] All plate experiments designed for systematic variation in z, P, S, x_i. $S = 15-60\ cm^2$, $L = 0.015-1$ cm. Low L to approach semi-infinite plate, high to approach finite body.

TABLE XIV

SOME PROBATIVE KINETIC RELATIONS FOR EMPIRICAL INVESTIGATION

Atmosphere	Geometry[a]	Hypothetical Mechanism.(s)	Isothermal Rate Expression[b]	k Parameter	Reference (s)	Remarks
Inert	Fine Powder	Physicochemical	$-\dot{w} = kw^n$	$A \exp(-X)$	This Report	
	Semi-Infinite Body Or Plate	Diffusion[c]	$= (1/2)k(1-w)^{-1}$	$A \exp(-X)$	Briendley et al (9)	
			$= kw^n \exp\left[-(a_1 - a_2/L)\right]$	$A \exp(-X)$	Parker & Gloria (46)	
		Interface Recession Or Physicochemical	$= kw^n$	$A \exp(-X)$	Briendley et al (9) This Report	n = 1/2 for interface recession
Oxidative	Finite Plate	Surface Oxidation[d]	$= kS(zP)^n/x_i$	$A \exp(-X)$	Scala (56)	n = 1/2 for carbon. $w_r = 0$.
Inert, Oxidative	Finite Plate	Molecular Evaporation[e]	$= kPS/x_i$	$AT^{-1/2}$		empirical form
		Interface Recession[f]	$= kS/x_i$	$A \exp(-X)$	Ingraham (32)	
		Logarithmic Rate Process	$= k \exp\left[-a_3(1-w)\right]$	$A \exp(-X)$	Doyle (15)	
	All Cases	Temperature Dependent A, E	All Cases	$\alpha T^{\beta} \exp\left[-(\lambda + \mu T)/RT\right]$	Farmer (20)	$A = \alpha T^{\beta}$ $E = \lambda + \mu T$

---

[a] One side only for plate.

[b] Normalized forms. A, k units of 1/min unless noted. Combinations of rate expressions omitted for brevity.

[c] $L \longrightarrow 0$ for zero thickness, semi-infinite plate; $L \longrightarrow \infty$ for semi-infinite body.

[d] A units = k units = $gm/atm^n\text{-}cm^2\text{-}min$.

[e] A units = $gm\text{-}(°K)^{1/2}/atm\text{-}cm^2\text{-}min$; k units = $gm/atm\text{-}cm^2\text{-}min$.

[f] A units = k units = $gm/cm^2\text{-}min$.

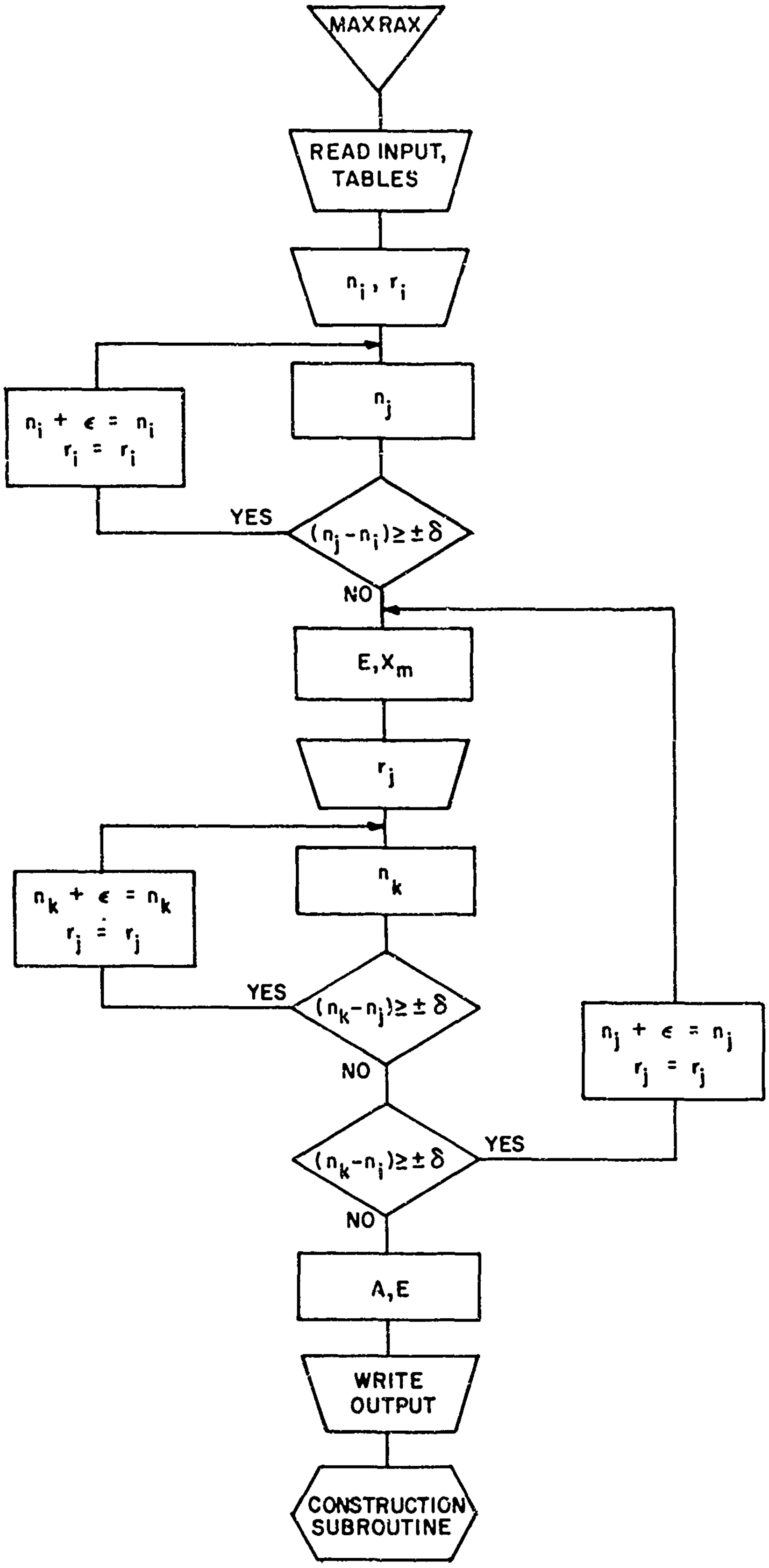


Figure 1. Flow Diagram for the Maximum Rate Experimental Method (MAXRAX) Computer Program

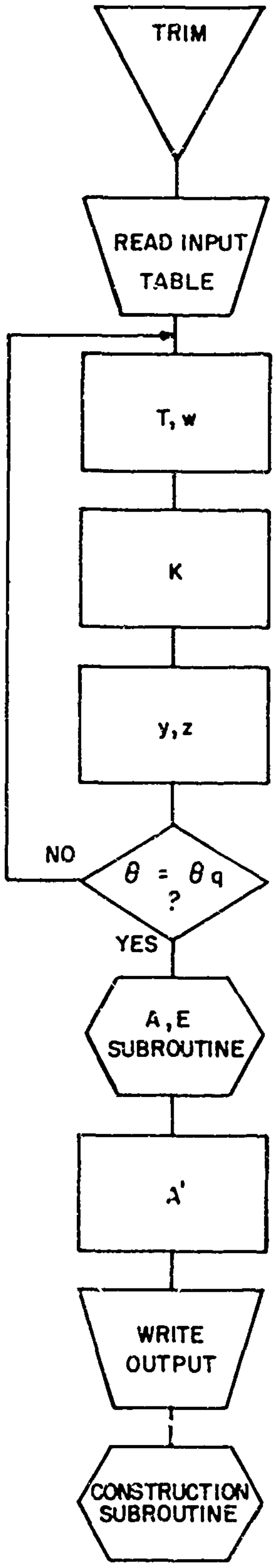


Figure 2. Flow Diagram for the Transfer Resolution Integral Method (TRIM) Computer Program

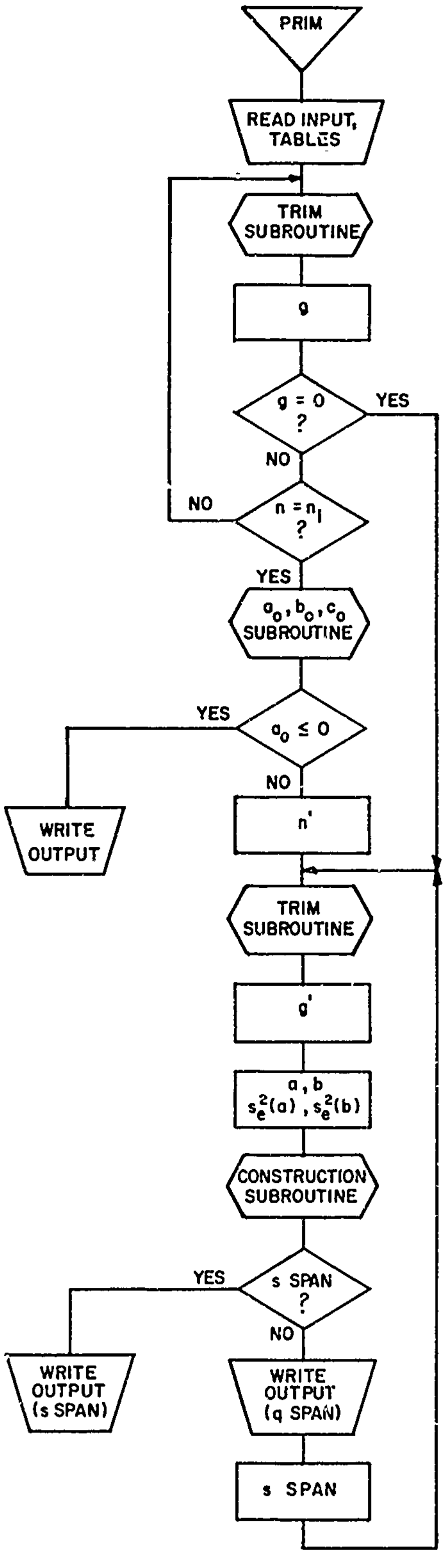


Figure 3. Flow Diagram for the Parabola Resolution Integral Method (PRIM) Computer Program

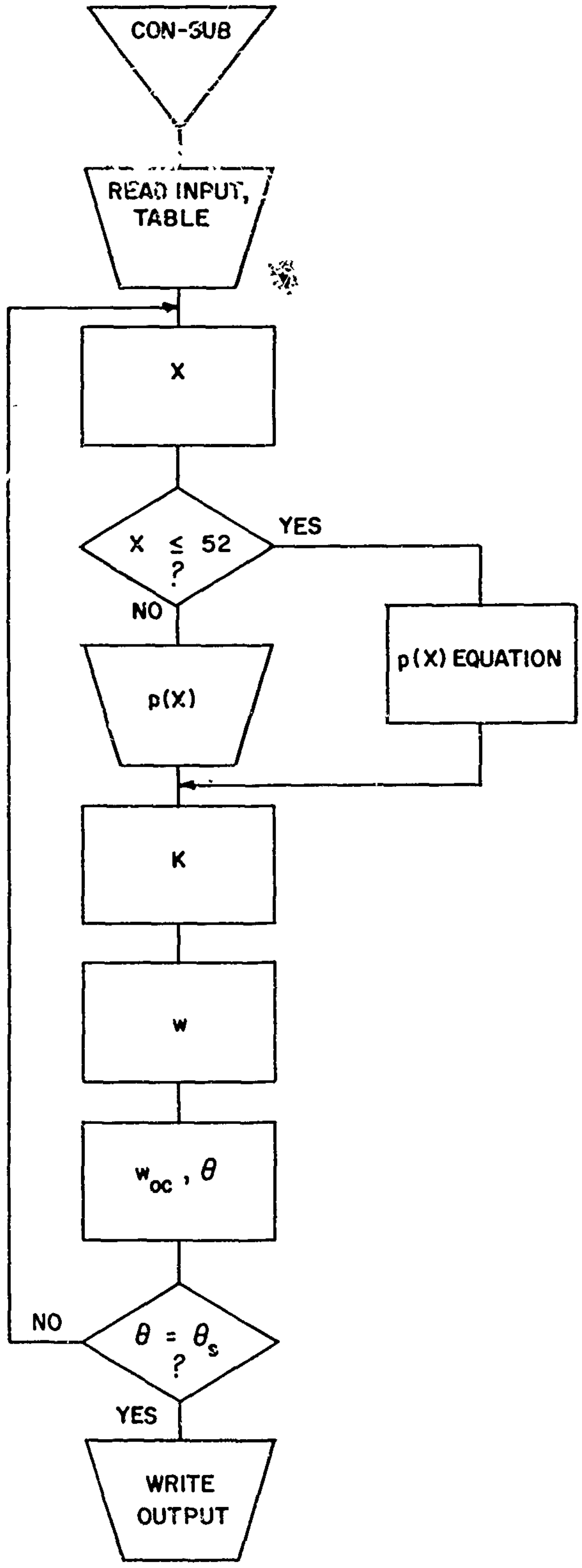


Figure 4. Flow Diagram for the Thermogram Construction Subroutine

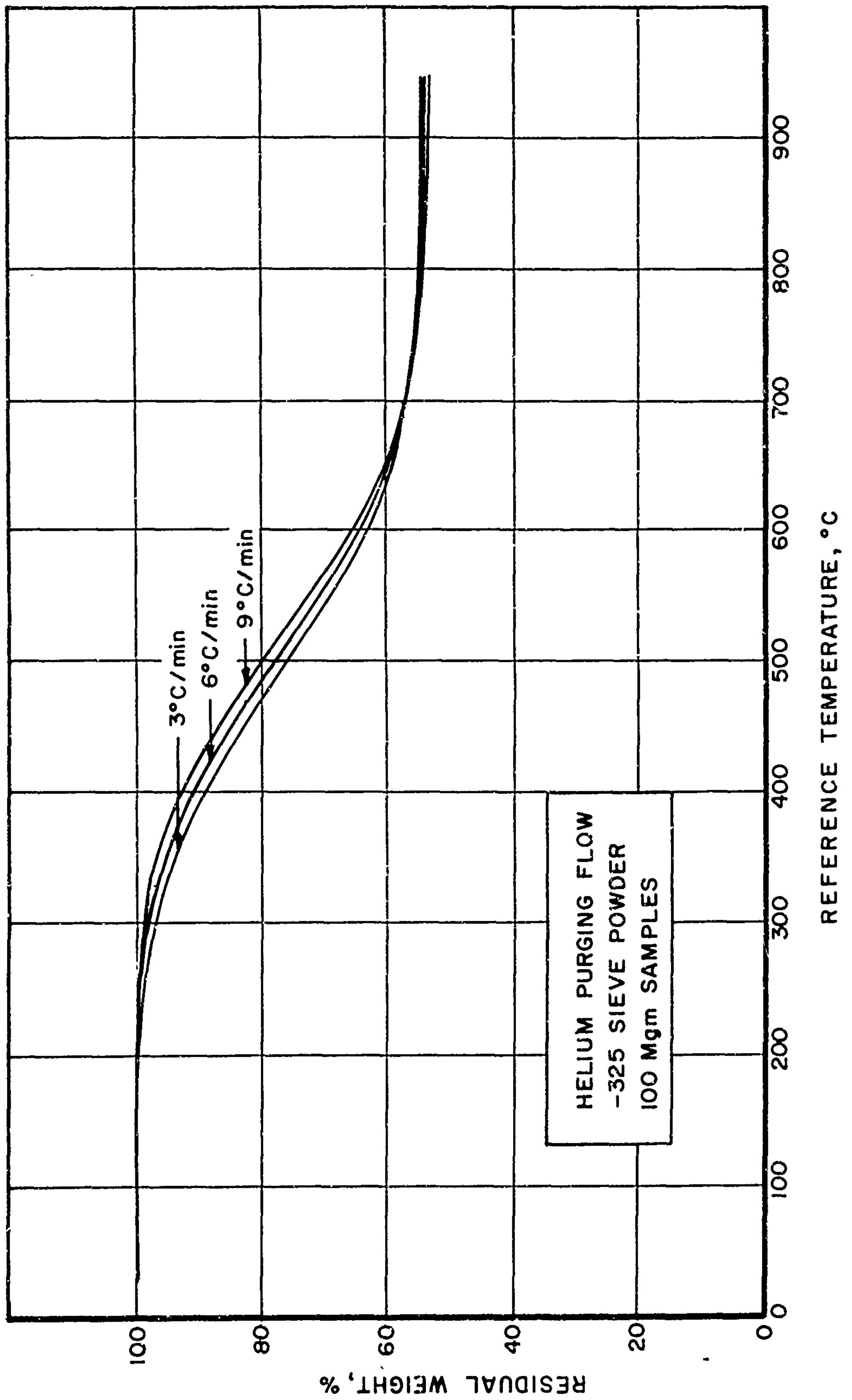


Figure 5. Thermograms for Phenol-Formaldehyde Molding Powder

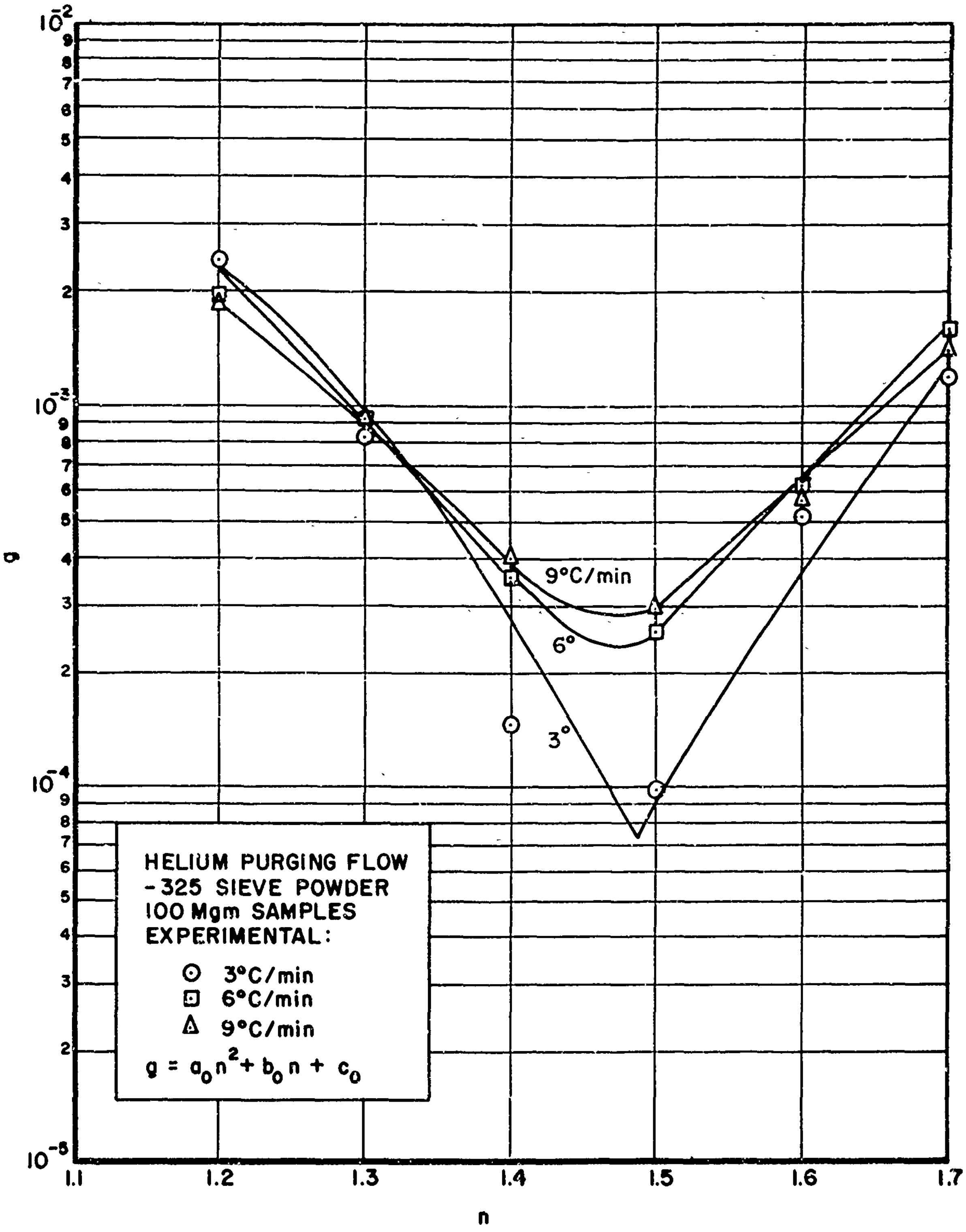


Figure 6. PRIM Parabolic Error Plots for Phenol-Formaldehyde Molding Powder

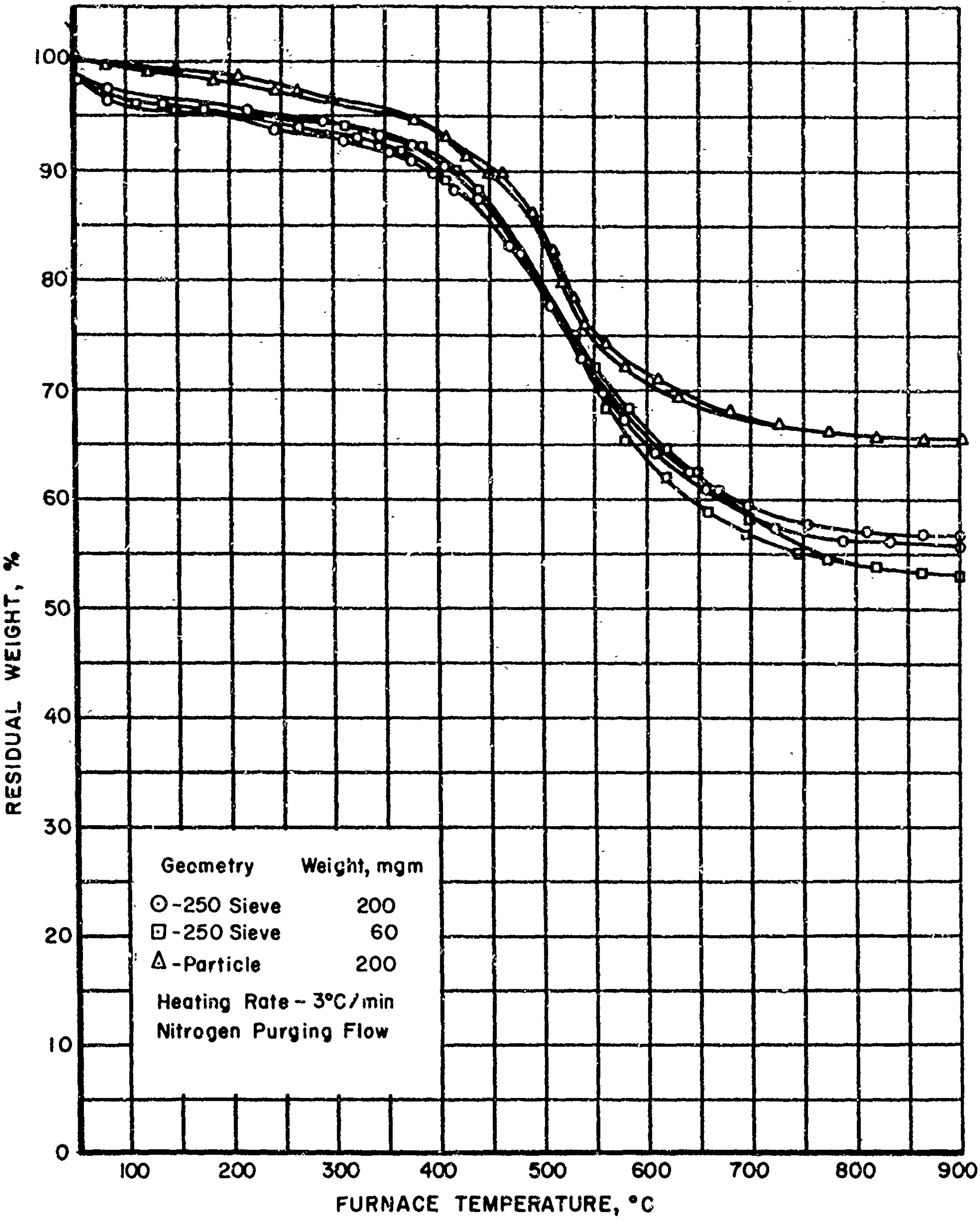


Figure 7. Thermograms for Phenol-Formaldehyde Polycondensate Samples

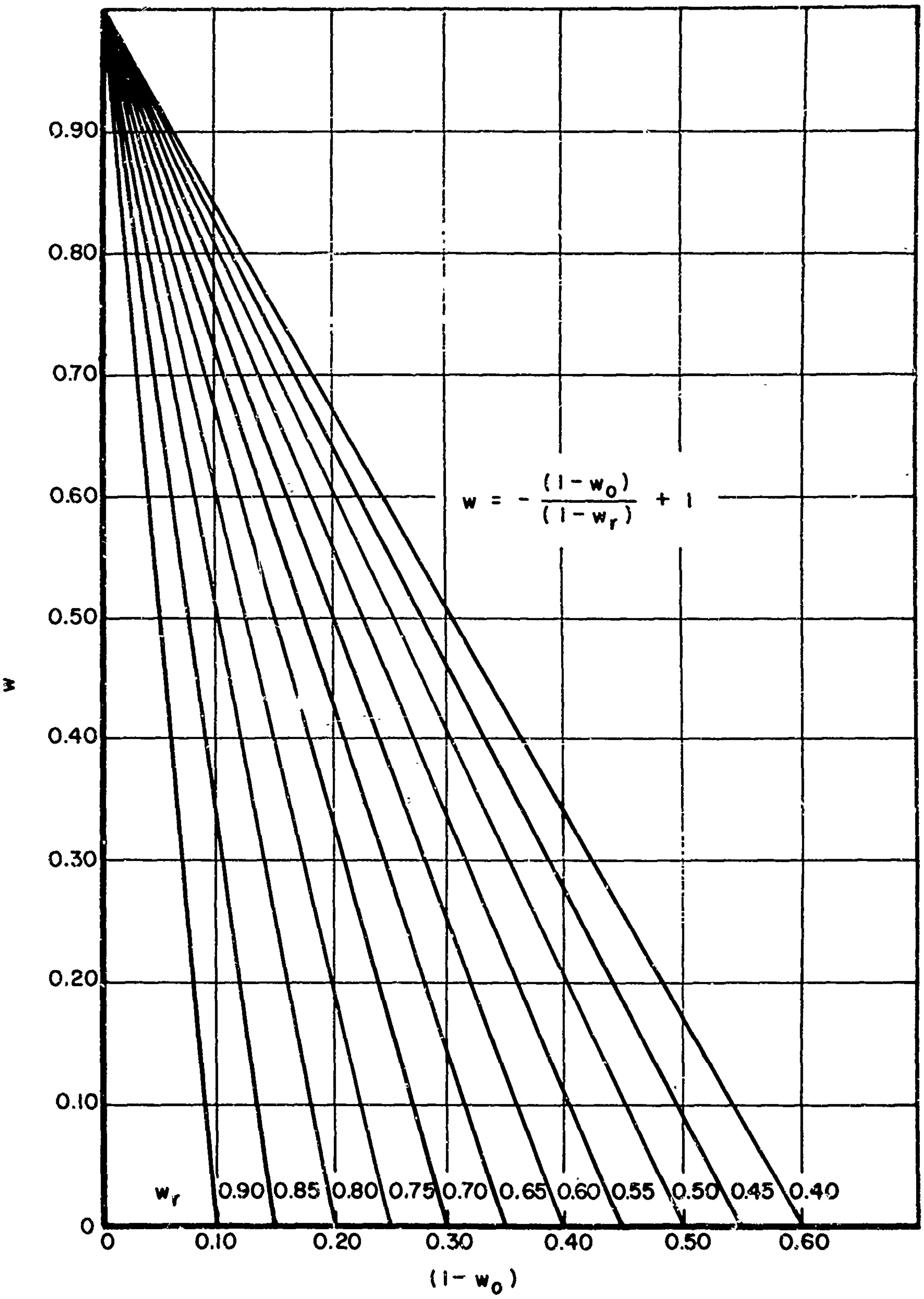


Figure 8. Conversion Diagrams for $(1 - w_o)$ to w

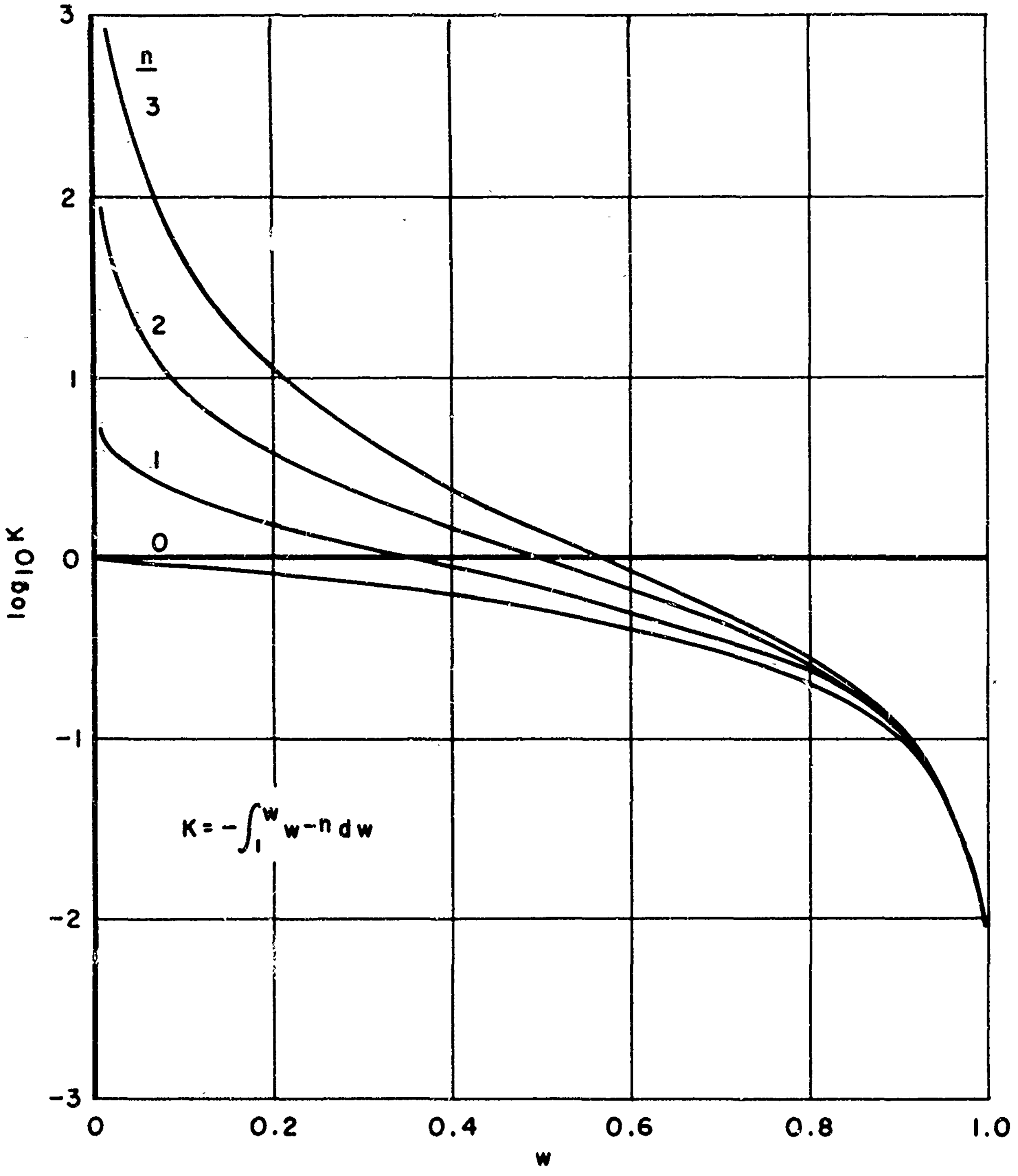


Figure 9. Relationship Between the Integral Parameter K And The Active Weight Fraction

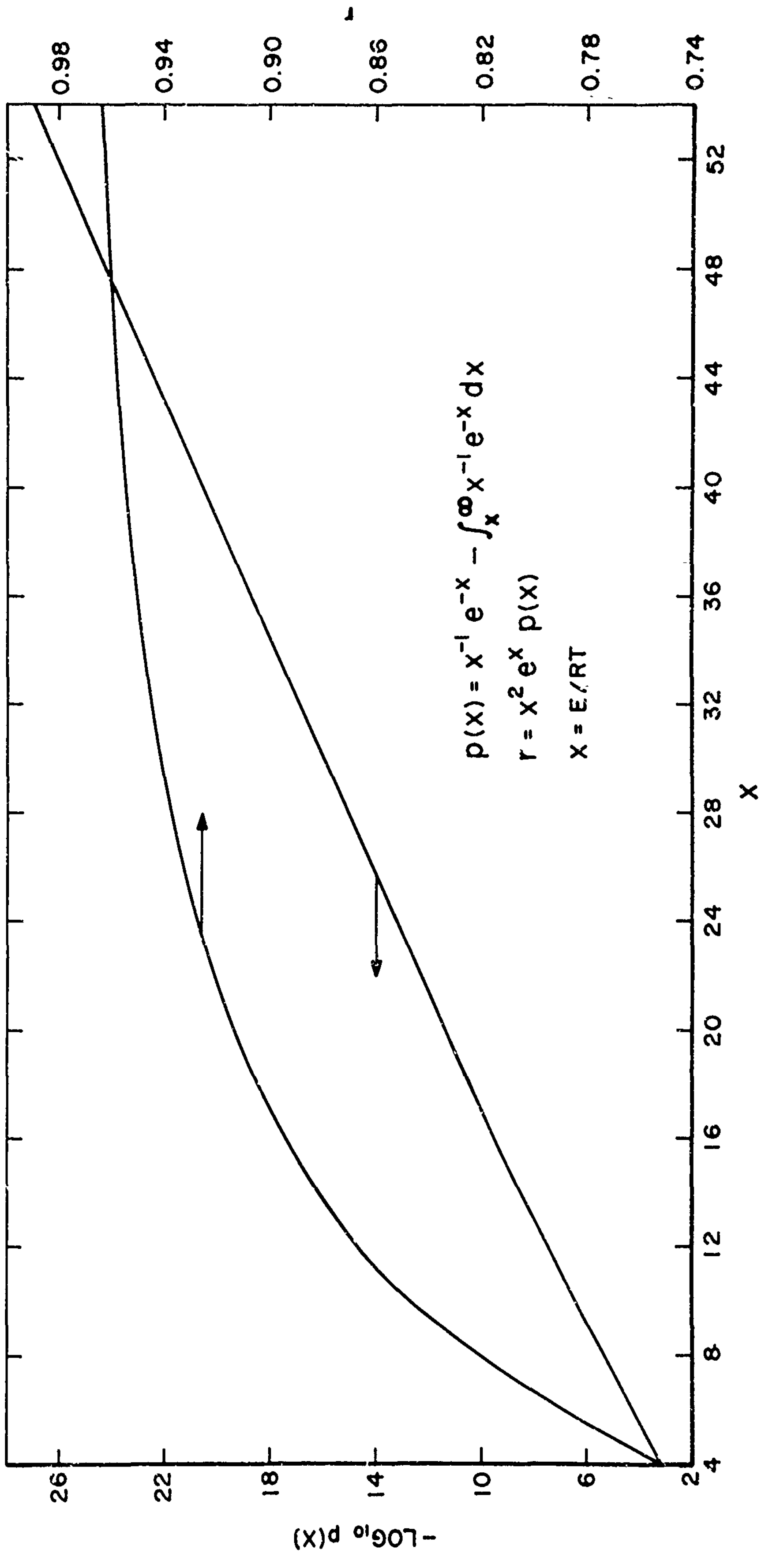


Figure 10. Relationship Between the Terms X, p(X) and r

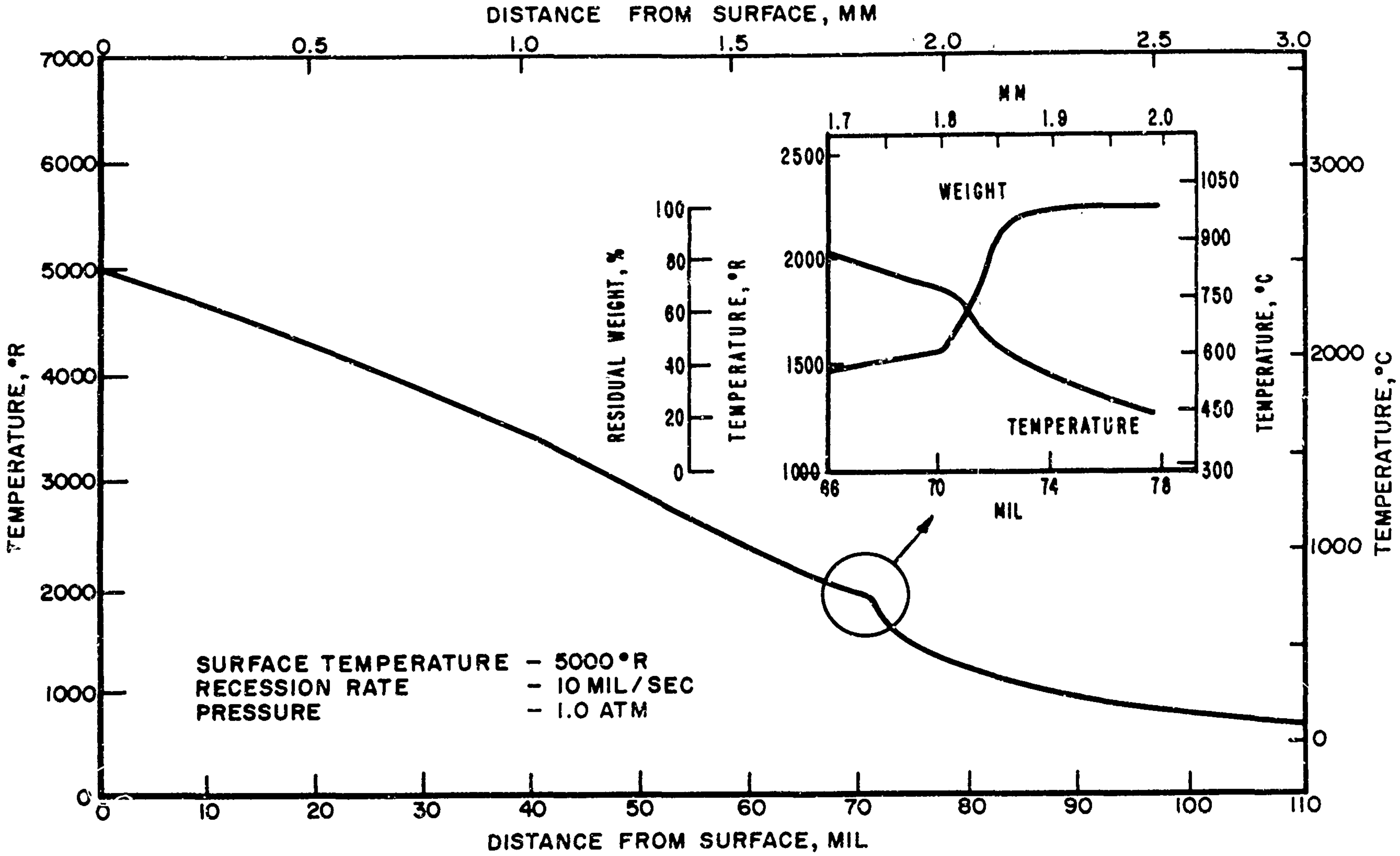


Figure 11. A Typical Temperature Distribution in Nylon Phenolic for Steady Surface Recession Rate(Kratsch)

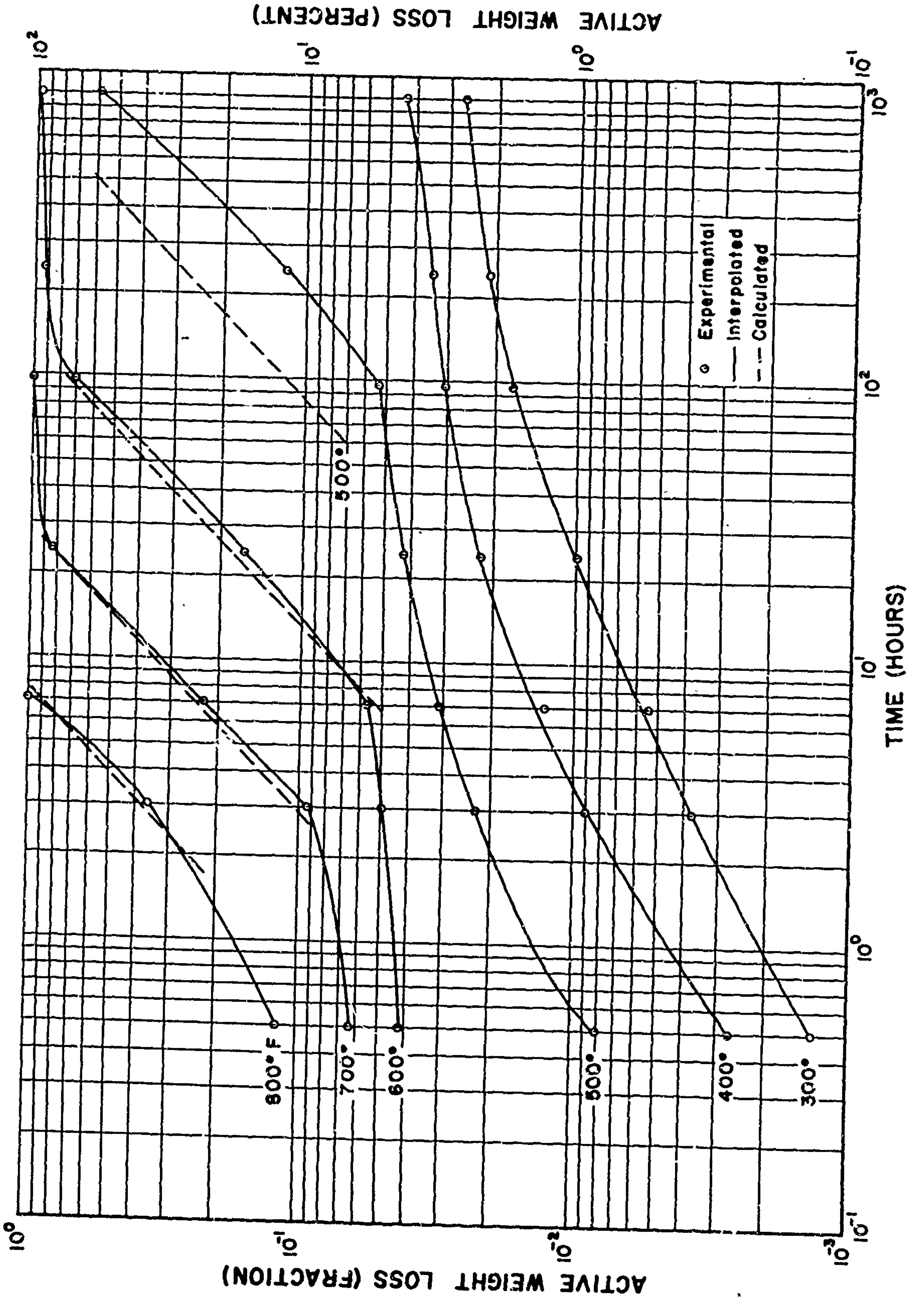


Figure 12. Reduced and Calculated Thermograms for CTL-91LD/Glass Fabric

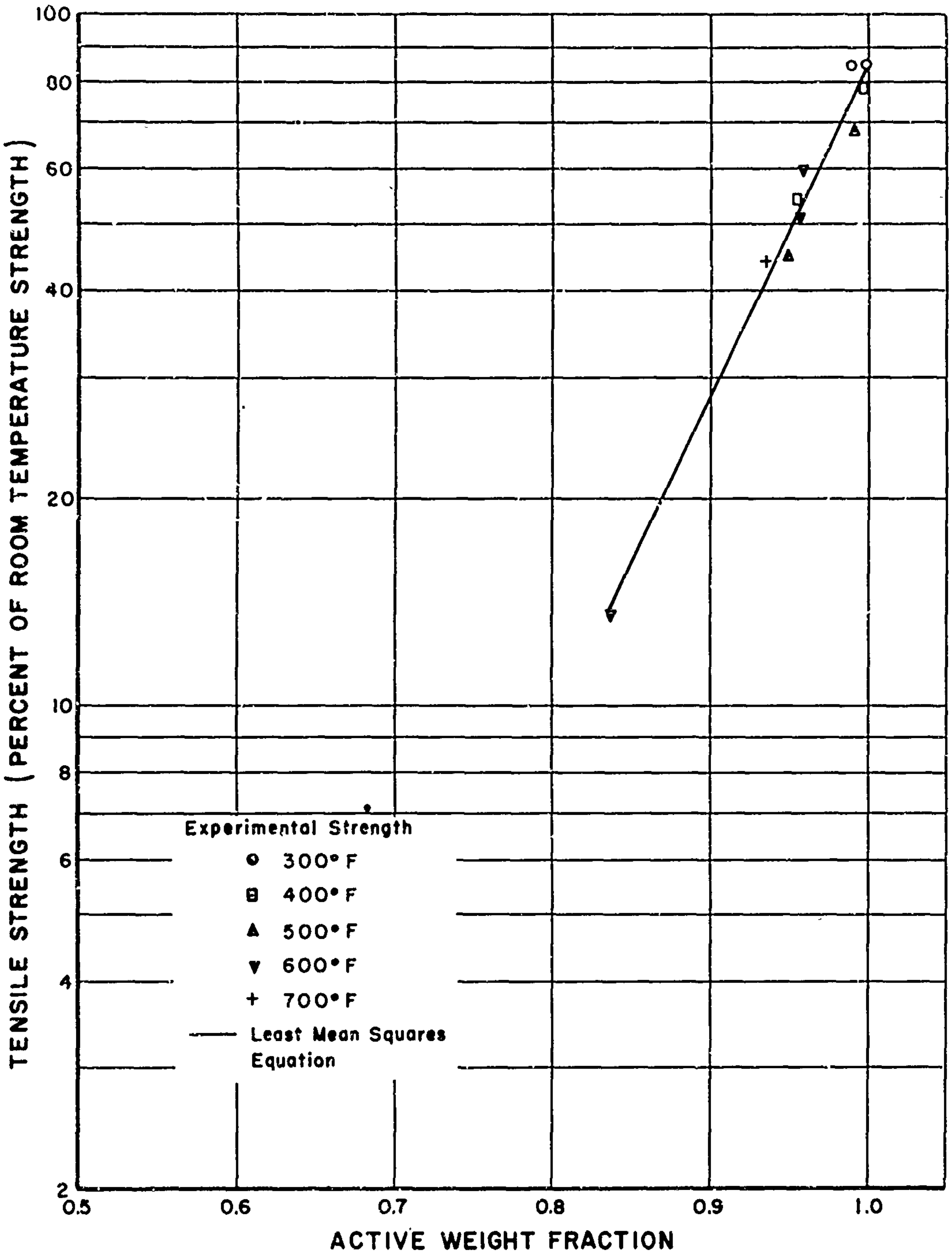


Figure 13. Tensile Strength at 45° to Fabric Warp versus Active Weight Fraction for CTL-91LD/Glass Fabric

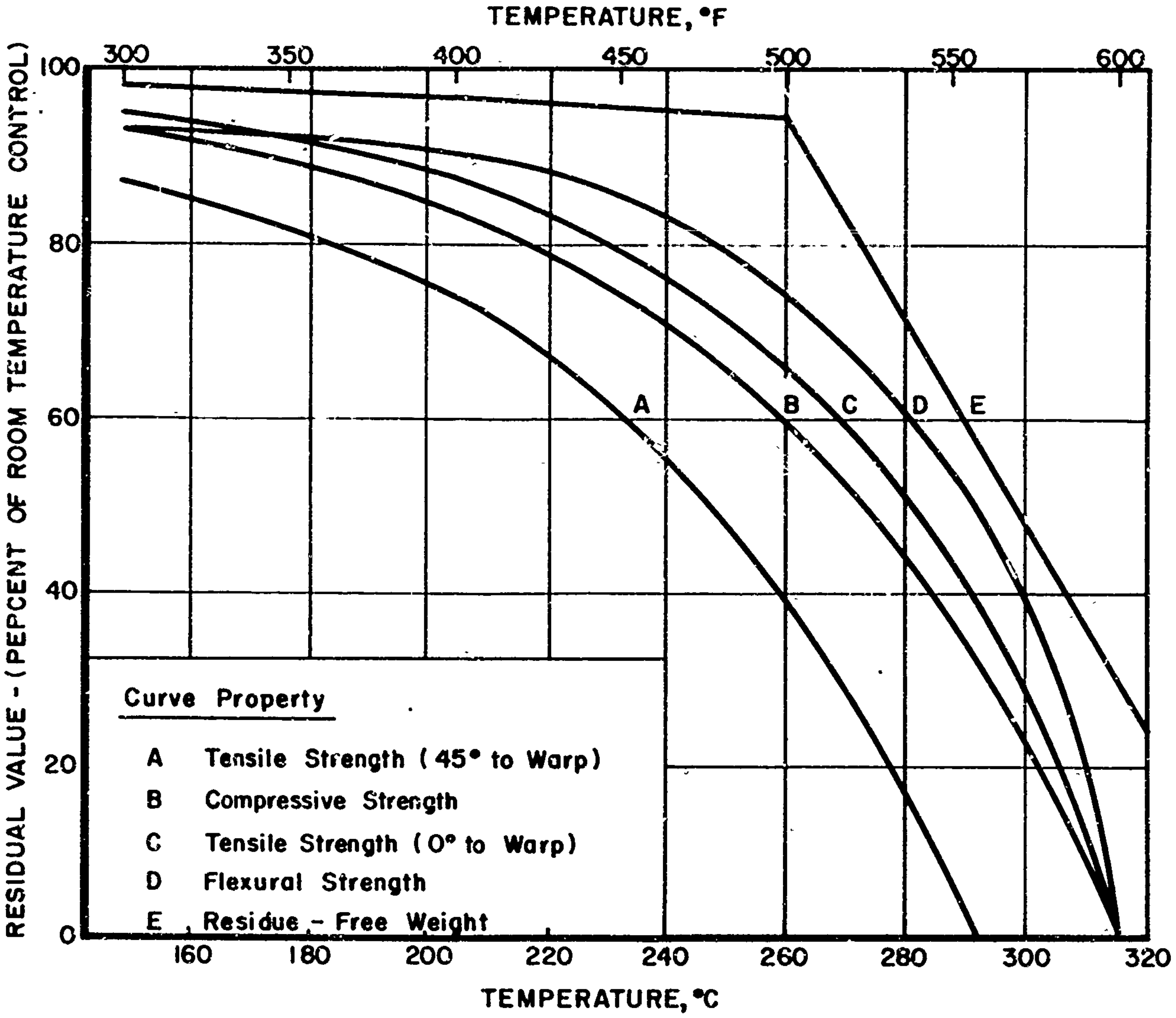
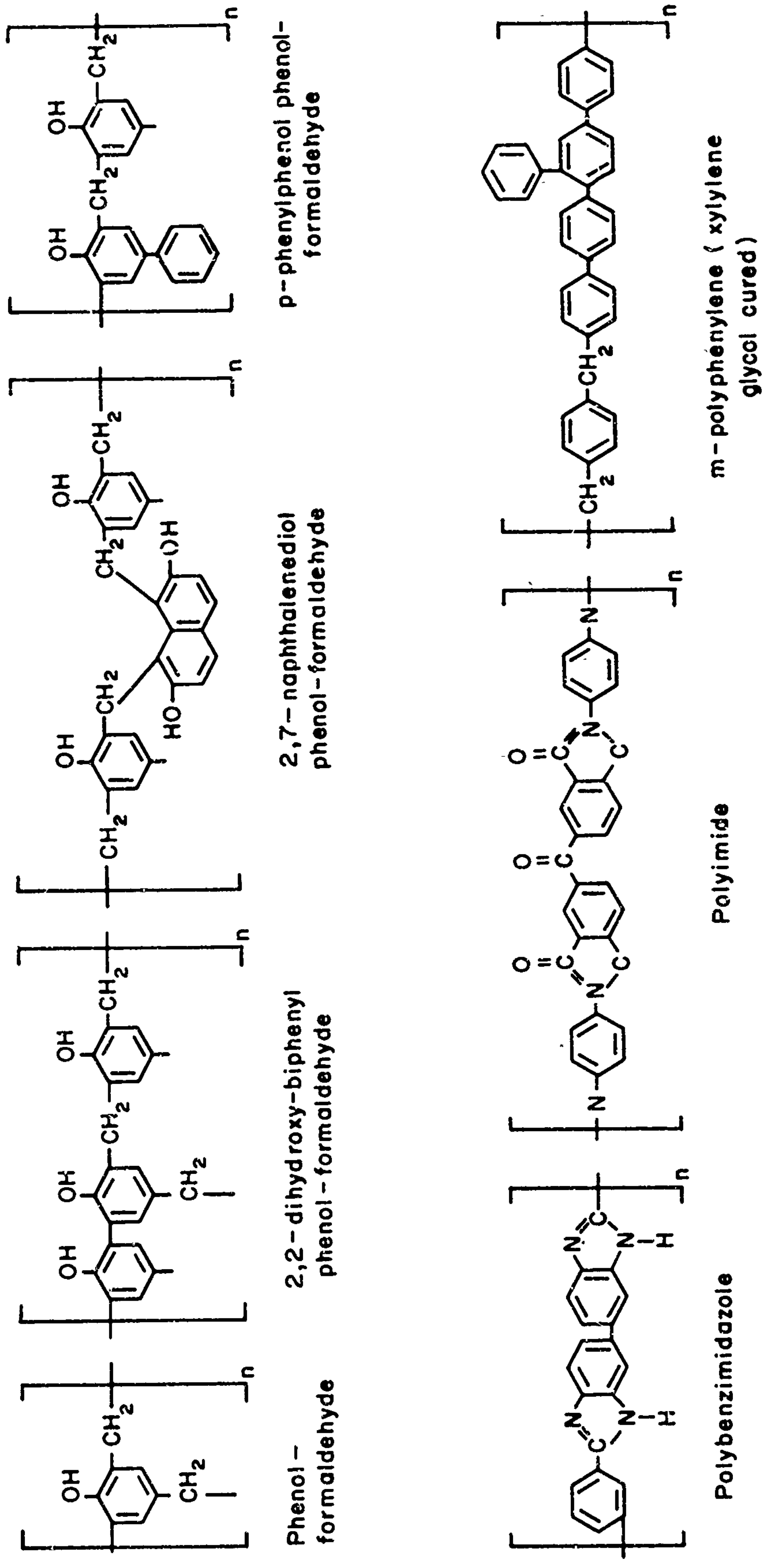


Figure 14. Strength and Weight Retention for 100-Hour Air Aging of CTL-91LD/Glass Fabric



Phenol-formaldehyde

2,2'-dihydroxy-biphenyl phenol-formaldehyde

2,7-naphthalenediol phenol-formaldehyde

p-phenylphenol phenol-formaldehyde

Polybenzimidazole

Polyimide

m-polyphenylene (xylylene glycol cured)

Figure 15. Some Polymers for Future Study

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13. ABSTRACT

Empirical kinetic parameters for phenol-formaldehyde polycondensate materials were surveyed for general application to Air Force interests. The ranges of n, A, E for the empirical kinetic model

$$-(dw/dt) = w^n A \exp(-E/RT)$$

were $n = 0\text{-}5$, $A = 2.0\times10^{-1}$ to 1.7×10^{16} 1/min, $E = 3.7\text{-}72$kcal/mole, where $w \equiv$ normalized weight, $t \equiv$ time, $R \equiv$ gas constant, $T \equiv$ temperature. The mass spectrometry and thermogravimetry thermal analysis methods used both constant heating rate and isothermal approaches.

Reexamination of data with a new computer program gave reduced variations: $n = 1.56 \pm 0.07$, $A = 60.9 \pm 41.4$, $E = 10.38 \pm 1.20$. The scopes of the comprehensive survey and descriptive thermogravimetry computer analysis were: (22 constant rate + 3 isothermal) vs 6 constant rate experiments by 8 vs 3 investigators using (5 cured + 7 vitreous fiber reinforced) vs 4 cured polycondensates.

Parameter inconsistencies for the survey were partially associated with an atypical polycondensate, laminate and polycondensate particle or laminate powder samples, or a reduced pressure atmosphere. Calculated parameters apparently dependent upon the two latter aspects were not averaged with other values. Small curve-fitting and other errors potentially enhance further disagreement as they often gave large parameter variations.

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14. KEY WORDS	LINK A		LINK B		LINK C	
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