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SOME PROPERTIES OF A COMPOSITE SOLID PROPELLANT

by

Gordon A. Campbell

A thesis submitted in partial fulfillment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in the

DEPARTMENT OF CHEMICAL ENGINEERING

UNIVERSITY OF OTTAWA

Ottawa, Canada

1968

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TABLE OF CONTENTS

TABLE OF CONTENTS	ii
LIST OF TABLES	iii
LIST OF FIGURES	v
NOMENCLATURE	xiii
ACKNOWLEDGMENTS	xxi
ABSTRACT	xxii
INTRODUCTION	1
LITERATURE SURVEY	3
THEORETICAL CONSIDERATIONS	40
EXPERIMENTAL	76
CALCULATIONS	95
RESULTS	121
DISCUSSION	157
CONCLUSIONS	238
REFERENCES	240
APPENDIX - 1 Statistical Analysis of the Results	250
APPENDIX - 2 Computer Programs	277
APPENDIX - 3 Solution of the Heat Conduction Equation with a Constant Temperature Boundary	306
APPENDIX - 4 Solution of the Heat Conduction Equation with a Film Boundary	311

LIST OF TABLES

I The Relationship between the Burning Rate and Radius for Polyurethane Propellant - 5" diameter cylinder	122
II The Relationship between the Burning Rate and Radius for the Thin Walled Hollow Cylinder	125
III The Values of ΔH for the Polymerization of the Polyurethane Polymer, obtained from the Microcalorimeter	126
IV Temperature History of a small sample of Polyurethane during Polymerization - 1	128
V Temperature History of a small sample of Polyurethane during Polymerization - 2	130
VI Temperature History for a 19mm diameter Brass Cylinder cooling in air	133
VII A sample of the recorder readings taken on Calorimeter #1 at 47.32°C.	134
VIII Determination of Constants a_1 and w_1 in the function $\theta = a_1 e^{w_1 t}$ by the Method of Least Squares	135
IX An exponential decay, where $\theta = a_2 e^{w_2 t}$	136
X Determination of Constants a_2 and w_2 in the function $\theta = a_2 e^{w_2 t}$ by the Method of Least Squares	137
XI Calculated Values of q for comparison with the experimental Curve	138
XII The Constants for the equation $a_1 e^{w_1 t} - e^{w_2 t}$	140
XIII Exponential Constants in the Heat Source Equation	142
XIV The Constants in the $\frac{\partial H}{\partial t}$ Equations	142

LIST OF TABLES CONTINUED

XV A Cooling Curve for Polyurethane Propellant in Air - 1	143
XVI A Cooling Curve for Polyurethane Propellant in Air - 2	144
XVII A Cooling Curve for Polyurethane Propellant in Air - 3	145
XVIII A Cooling Curve for Polyurethane Propellant in Air - 4	146
XIX A Cooling Curve for Polyurethane Propellant in Air - 5	147
XX A Cooling Curve for Polyurethane Propellant in Air - 6	148
XXI A Cooling Curve for Polyurethane Propellant in Air - 7	149
XXII A Cooling Curve for Polyurethane Propellant in Air - 8	150
XXIII Propellant Thermal Diffusivity	151
XXIV The Effect of the Variation in k and $(h_c + h_r)$ on Thermal Diffusivity	151
XXV The Effect of the Variation in Thermal Diffusivity on Heat Capacity	152
XXVI The Estimation of the Heat Transfer Constants, λ , k , ρ , and c_p for the 20% Aluminum case	152
XXVII Computation for the Rank-Difference Method of Correlation between the Burning Rate and the Maximum Temperature Curve for $\lambda = 0.008, 104 \text{ ft}^2/\text{hr}$, 122°F boundaries, Positive Initial Slope and Top Alfa	153
XXVIII The Product-Moment Method of Correlation of the Burning Rate and the Maximum Temperature for the Top Value of Alfa and $\lambda = 0.008, 104 \text{ ft}^2/\text{hr}$	154
XXIX Product-Moment Correlation Coefficients between Burning Rate and Polymerization Temperature	156
XXX The Results of the Statistical Analysis	251

LIST OF FIGURES

1. A Plot of two exponentials where $w_2 = 10w_1$	47
2. A Plot of $\phi = \theta_1 - \theta_2$ to illustrate the combination of two exponentials	47
3. A Schematic Diagram of the Strand Burner	78
4. A Schematic Diagram of the Strand Burner Timing Circuits	78
5. A Schematic Diagram of the Photoelectric Recording Circuits	79
6. A Schematic Diagram of the Strand Burner Cards	80
7. A Schematic Diagram of the Strand Burner Firing Circuit	80
8. A Schematic Diagram of the Microcalorimeter Calibration Circuit	87
9. A Schematic Diagram of the Resistance Thermometer Bridge	87
10. The Time Constants from Exponential Curves	90
11. Curves for the Determination of the Calorimeter Constants	92
12. Schematic Diagram of the Microcalorimeter and Recording Circuits	94
13. Comparison of the Calculated and Experimental Curves for q	96
14. A Semilogarithmic Plot of a sample of the Recorder Readings on Microcalorimeter #1 at 47.32°C	97
15. A Curve of q versus time to illustrate ΔH calculation	100
16. A Semilogarithmic Plot of ϕ versus Temperature	105
17. A Semilogarithmic Plot of w_1 versus Temperature	106
18. Comparison of the Burning Rate and Temperature for the 5 inch diameter Solid Cylinder	158
19. Comparison of the Burning Rate and Temperature for the 5.25" O.D. and 3" I.D. Hollow Cylinder	160

LIST OF FIGURES CONTINUED

20. Temperature Gradients for the 6" diameter Solid Cylinder with α top, and $X = 0.008,104 \text{ ft}^2/\text{hr}$	164
21. Temperature Gradients for the 5" diameter Solid Cylinder with α top, and $X = 0.006,8 \text{ ft}^2/\text{hr}$	165
22. Temperature Gradients for the 5" diameter Solid Cylinder with α average and $X = 0.006,8 \text{ ft}^2/\text{hr}$	166
23. Temperature Gradients for the 5" diameter Solid Cylinder with α top, and $X = 0.008,104 \text{ ft}^2/\text{hr}$	167
24. Temperature Gradients for the 5" diameter Solid Cylinder with α average and $X = 0.008,104 \text{ ft}^2/\text{hr}$	168
25. Temperature Gradients for the 5" diameter Solid Cylinder with α top and $X = 0.011,413 \text{ ft}^2/\text{hr}$	169
26. Temperature Gradients for the 5" diameter Solid Cylinder with α average and $X = 0.011,413 \text{ ft}^2/\text{hr}$	170
27. Temperature Gradients for the Thin Walled Hollow Cylinder with α top and $X = 0.006,8 \text{ ft}^2/\text{hr}$	173
28. Temperature Gradients for the Thin Walled Hollow Cylinder with α average and $X = 0.006,8 \text{ ft}^2/\text{hr}$	174
29. Temperature Gradients for the Thin Walled Hollow Cylinder with α top and $X = 0.008,104 \text{ ft}^2/\text{hr}$	175
30. Temperature Gradients for the Thin Walled Hollow Cylinder with α average and $X = 0.008,104 \text{ ft}^2/\text{hr}$	176
31. Temperature Gradients for the Thin Walled Hollow Cylinder with α top and $X = 0.011,413 \text{ ft}^2/\text{hr}$	177

LIST OF FIGURES CONTINUED

- | | |
|--|-----|
| 32. Temperature Gradients for the Thin Walled Hollow Cylinder
with α average and $\kappa = 0.011,413 \text{ ft}^2/\text{hr}$ | 178 |
| 33. Temperature Gradients for the Thick Walled Hollow Cylinder
with α average and $\kappa = 0.006,8 \text{ ft}^2/\text{hr}$ | 180 |
| 34. Temperature Gradients for the Thick Walled Hollow Cylinder
with α average and $\kappa = 0.006,8 \text{ ft}^2/\text{hr}$ | 181 |
| 35. Temperature Gradients for the Thick Walled Hollow Cylinder
with α top and $\kappa = 0.008,104 \text{ ft}^2/\text{hr}$ | 182 |
| 36. Temperature Gradients for the Thick Walled Hollow Cylinder
with α average and $\kappa = 0.008,104 \text{ ft}^2/\text{hr}$ | 183 |
| 37. Temperature Gradients for the Thick Walled Hollow Cylinder
with α top and $\kappa = 0.011,413 \text{ ft}^2/\text{hr}$ | 184 |
| 38. Temperature Gradients for the Thick Walled Hollow Cylinder
with α average and $\kappa = 0.011,413 \text{ ft}^2/\text{hr}$ | 185 |
| 39. Isotherms for the Star Shaped Centre Hollow Cylinder with
$T(r, \theta, 0) = 77^\circ\text{F.}$, α top, $\kappa = 0.008,104 \text{ ft}^2/\text{hr}$ and $t = 0.504,61$
hours | 187 |
| 40. Isotherms for the Star Shaped Centre Hollow Cylinder with
$T(r, \theta, 0) = 77^\circ\text{F.}$, α top, $\kappa = 0.008,104 \text{ ft}^2/\text{hr}$ and $t = 0.999,70$
hours | 188 |
| 41. Isotherms for the Star Shaped Centre Hollow Cylinder with
$T(r, \theta, 0) = 77^\circ\text{F.}$, α top, $\kappa = 0.008,104 \text{ ft}^2/\text{hr}$ and $t = 1.504,32$
hours | 189 |

LIST OF FIGURES CONTINUED

42. Isotherms for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 77^{\circ}\text{F.}$, α top, $\kappa = 0.008,104 \text{ ft}^2/\text{hr}$ and $t = 2.008,93$
 hours 190
43. Isotherms for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 77^{\circ}\text{F.}$, α top, $\kappa = 0.008,104 \text{ ft}^2/\text{hr}$ and $t = 2.504,02$
 hours 191
44. Isotherms for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 77^{\circ}\text{F.}$, α top, $\kappa = 0.008,104 \text{ ft}^2/\text{hr}$ and $t = 3.170,49$
 hours 192
45. Isotherms for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 77^{\circ}\text{F.}$, α top, $\kappa = 0.008,104 \text{ ft}^2/\text{hr}$ and $t = 3.808,49$
 hours 193
46. Isotherms for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 122^{\circ}\text{F.}$, α top, $\kappa = 0.008,104 \text{ ft}^2/\text{hr}$ and $t = 0.504,61$
 hours 194
47. Isotherms for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 122^{\circ}\text{F.}$, α top, $\kappa = 0.008,104 \text{ ft}^2/\text{hr}$ and $t = 0.999,70$
 hours 195
48. Isotherms for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 122^{\circ}\text{F.}$, α top, $\kappa = 0.008,104 \text{ ft}^2/\text{hr}$ and $t = 1.504,32$
 hours 196
49. Isotherms for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 122^{\circ}\text{F.}$, α top, $\kappa = 0.008,104 \text{ ft}^2/\text{hr}$ and $t = 2.008,93$
 hours 197

LIST OF FIGURES CONTINUED

50. Isotherms for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 122^{\circ}\text{F.}$, α_{top} , $\kappa = 0.008, 104 \text{ ft}^2/\text{hr}$ and $t = 2.504, 02$
 hours 198
51. Isotherms for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 122^{\circ}\text{F.}$, α_{top} , $\kappa = 0.008, 104 \text{ ft}^2/\text{hr}$ and $t = 3.170, 49$
 hours 199
52. Isotherms for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 122^{\circ}\text{F.}$, α_{top} , $\kappa = 0.008, 104 \text{ ft}^2/\text{hr}$ and $t = 3.808, 40$
 hours 200
53. Sector Diagram for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 77^{\circ}\text{F.}$, α_{top} , $\kappa = 0.008, 104 \text{ ft}^2/\text{hr}$ and $t = 0.504, 61$
 hours 201
54. Sector Diagram for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 77^{\circ}\text{F.}$, α_{top} , $\kappa = 0.008, 104 \text{ ft}^2/\text{hr}$ and $t = 0.999, 70$
 hours 202
55. Sector Diagram for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 77^{\circ}\text{F.}$, α_{top} , $\kappa = 0.008, 104 \text{ ft}^2/\text{hr}$ and $t = 1.504, 32$
 hours 203
56. Sector Diagram for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 77^{\circ}\text{F.}$, α_{top} , $\kappa = 0.008, 104 \text{ ft}^2/\text{hr}$ and $t = 2.008, 93$
 hours 204
57. Sector Diagram for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 77^{\circ}\text{F.}$, α_{top} , $\kappa = 0.008, 104 \text{ ft}^2/\text{hr}$ and $t = 2.504, 02$
 hours 205

LIST OF FIGURES CONTINUED

58. Sector Diagram for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 77^{\circ}\text{F.}$, α_{top} , $\kappa = 0.008, 104 \text{ ft}^2/\text{hr}$ and $t = 3.170, 49$
 hours 206
59. Sector Diagram for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 77^{\circ}\text{F.}$, α_{top} , $\kappa = 0.008, 104 \text{ ft}^2/\text{hr}$ and $t = 3.808, 40$
 hours 207
60. Sector Diagram for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 122^{\circ}\text{F.}$, α_{top} , $\kappa = 0.008, 104 \text{ ft}^2/\text{hr}$ and $t = 0.504, 61$
 hours 208
61. Sector Diagram for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 122^{\circ}\text{F.}$, α_{top} , $\kappa = 0.008, 104 \text{ ft}^2/\text{hr}$ and $t = 0.999, 70$
 hours 209
62. Sector Diagram for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 122^{\circ}\text{F.}$, α_{top} , $\kappa = 0.008, 104 \text{ ft}^2/\text{hr}$ and $t = 1.504, 32$
 hours 210
63. Sector Diagram for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 122^{\circ}\text{F.}$, α_{top} , $\kappa = 0.008, 104 \text{ ft}^2/\text{hr}$ and $t = 2.008, 93$
 hours 211
64. Sector Diagram for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 122^{\circ}\text{F.}$, α_{top} , $\kappa = 0.008, 104 \text{ ft}^2/\text{hr}$ and $t = 2.504, 02$
 hours 212
65. Sector Diagram for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 122^{\circ}\text{F.}$, α_{top} , $\kappa = 0.008, 104 \text{ ft}^2/\text{hr}$ and $t = 3.170, 49$
 hours 213

LIST OF FIGURES CONTINUED

66. Sector Diagram for the Star Shaped Centre Hollow Cylinder with
 $T(r, \theta, 0) = 122^{\circ}\text{F.}$, α top, $\kappa = 0.008, 104 \text{ ft}^2/\text{hr}$ and $t = 3.808, 40$
 hours 214
67. End Effect Diagrams for the 6" diameter Solid Cylinder with
 $T(r, z, 0) = 77^{\circ}\text{F.}$, α top, $\kappa = 0.008, 104 \text{ ft}^2/\text{hr}$ and N from
 12 to 33 216
68. End Effect Diagrams for the 6" diameter Solid Cylinder with
 $T(r, z, 0) = 77^{\circ}\text{F.}$, α top, $\kappa = 0.008, 104 \text{ ft}^2/\text{hr}$ and N from
 44 to 65 217
69. End Effect Diagrams for the 6" diameter Solid Cylinder with
 $T(r, z, 0) = 122^{\circ}\text{F.}$, α top, $\kappa = 0.008, 104 \text{ ft}^2/\text{hr}$ and N from
 12 to 33 218
70. End Effect Diagrams for the 6" diameter Solid Cylinder with
 $T(r, z, 0) = 122^{\circ}\text{F.}$, α top, $\kappa = 0.008, 104 \text{ ft}^2/\text{hr}$ and N from
 44 to 65 219
71. End Effect Diagrams for the 5" diameter Solid Cylinder with
 $T(r, z, 0) = 77^{\circ}\text{F.}$, α top, $\kappa = 0.008, 104 \text{ ft}^2/\text{hr}$ and N from
 12 to 33 221
72. End Effect Diagrams for the 5" diameter Solid Cylinder with
 $T(r, z, 0) = 77^{\circ}\text{F.}$, α top, $\kappa = 0.008, 104 \text{ ft}^2/\text{hr}$ and N from
 44 to 65 222
73. End Effect Diagrams for the 5" diameter Solid Cylinder with
 $T(r, z, 0) = 122^{\circ}\text{F.}$, α top, $\kappa = 0.008, 104 \text{ ft}^2/\text{hr}$ and N from
 12 to 33 223

LIST OF FIGURES CONTINUED

74. End Effect Diagrams for the 5" diameter Solid Cylinder with
 $T(r,z,0) = 122^{\circ}\text{F.}$, α top, $\kappa = 0.008,104 \text{ ft}^2/\text{hr}$ and N from
 44 to 65 224
75. The Quenched Grain Surface 226
76. Temperature Gradients for the Solid Cylinder with 20% Aluminum,
 α average and $\kappa = 0.476 \text{ ft}^2/\text{hr}$ 228
77. Temperature Gradients for the Solid Cylinder with 20% Aluminum,
 α top and $\kappa = 0.476 \text{ ft}^2/\text{hr}$ 229
78. Scatter Diagrams to illustrate Correlation with $T(R,0) = 122^{\circ}\text{F.}$,
 α top and $\kappa = 0.008,104 \text{ ft}^2/\text{hr}$ 232
79. Scatter Diagrams to illustrate Correlation with $T(R,0) = 122^{\circ}\text{F.}$,
 α average and $\kappa = 0.008,104 \text{ ft}^2/\text{hr}$ 233

NOMENCLATURE

		<u>Remarks (Equation No)</u>
A	a constant	20, 126, 127, 161, 178, 179
A	the burning surface area	1
A_E	area of the nozzle at the exit	2, 5, 6, 7
A_s	burning surface area	
A_T	area of the nozzle at the throat	
B	a constant	
C	a constant	
C'	a constant equal to h/k	
D_o	diameter in inches	
E_{exp}	experimental energy of activation	
F	thrust in lbs force	
F_o	power in watts	157, 158
H	enthalpy	
H_1	a constant	
H_2	a constant	
I	current in amperes	129, 158
$I_p(x)$	a modified Bessel function of the first kind of order p	
I_{sp}	specific impulse	
K	modulus in the θ direction	99, 109
$K_n(x)$	a modified Bessel function of the second kind of order n	
M	mass	3
M	modulus in the r direction	

NOMENCLATURE CONTINUED

		<u>Remarks (Equation No)</u>
M_p	mass of the propellant	
M_r	mass of the rocket (less fuel)	
N	total number	170
P	Peltier heat	132
P_{at}	atmospheric pressure	2
P_{exit}	gas pressure at the nozzle exit	2
P_{eq}	pressure at equilibrium	15
Q'	heat source term	
R	gas constant	7, 8, 16, 17
R	a root of a quadratic equation	118
R	resistance in ohms	129, 158
R	outer radius	
S	burning surface	15
S	entropy	16, 17
T	time constant	134
T	temperature	
T_o	initial temperature	
T_l	surface temperature	
T_A	air temperature	
T_B	net point temperature	
T_c	chamber temperature	
T_i	a base temperature	
T_R	temperature at the outer surface	

NOMENCLATURE CONTINUED

		<u>Remarks (Equation No)</u>
T_s	surface temperature	
V	velocity in ft/sec	
V_c	volume of the chamber	
V_1	velocity at the nozzle entrance	
V_E	velocity at the nozzle exit	
$V_{\text{Brenschluss}}$	velocity at end of burning	
W	power	132, 133
W	a weight	19, 20
Z	modulus in the z direction	
a	a constant	10, 11, 14
a	acceleration in ft/sec ²	
a_1	an exponential decay constant	
a_2	an exponential decay constant	
b	a constant	
b'	a constant at the base temperature	
c	a constant	55, 55a, 96, 101, 108, 109, 110, 111, 112, 113, 114, 115, 116
c	specific heat	
c_p	specific heat at constant pressure	7, 55a, 128
c_v	specific heat at constant volume	
g	a constant	132, 133, 134
g	gravitational constant	2, 5, 6, 7, 8

NOMENCLATURE CONTINUED

		<u>Remarks (Equation No)</u>
h	Planck's constant	16, 17
h	air film coefficient	181, 183
h	cylinder height	156
h_c	cone height	156
h_c	film heat-transfer coefficient	
h_r	radiation coefficient	
j	a constant	
k	a constant	13, 20
k	specific reaction rate	16, 17, 18
k	Boltzmann's constant	16, 17
k	thermal conductivity	27, 28, 29, 32, 33, 157, 181
m	plane m	
$\dot{m}$	mass rate of flow	
n	an exponent	9, 11, 13
n	a direction	27, 28a, 29, 31
n	a number	165, 166, 167, 168, 169
n	a time plane	
o	plane o	
p	plane p	86, 87, 88, 89, 90, 93, 96, 100, 101, 109, 112, 113, 114
p	pressure	9, 10, 11, 13, 14
p	a constant	132, 133, 134
p	a complex constant	

NOMENCLATURE CONTINUED

		<u>Remarks (Equation No)</u>
p_c	chamber pressure	
p_E	pressure at the nozzle exit	
q	a constant	19
q	a heat flow vector	28, 28a, 29, 31
q	instantaneous heat	135
q''	an instantaneous heat source	165, 166
q_r	heat transferred by radiation	163
r	burning rate	1, 8, 9, 10, 11, 13, 14
r	Spearman's correlation coefficient	171
r	radius	
r_1	radius at position 1	
r_2	radius at position 2	
r_c	radius of the cone	
r_s	Spearman's rank correlation coefficient	
s_z	sample estimate of the variance	172, 173
t	Student's "t"	169, 173
t	time	
t'	duration of the heat pulse	
u_1	rank number of the first variable	167, 168
v	gas velocity parallel to the surface	
v_1	temperature at radius 1	
v_2	temperature at radius 2	
v_i	rank number of the second variable	167, 168

NOMENCLATURE CONTINUEDRemarks (Equation No)

w_1	an exponential constant	
w_2	an exponential constant	
x	distance	
x'	standardized variable for correlation	
y'	standardized variable for correlation	
y_1	a least squares variable	
z	a symmetrical function of r_s	171
z	a direction	
$\bar{z}$	sample average	173
$\bar{\bar{z}}$	population average	173
α	a constant	
α_1	a constant	55, 55a, 96, 100, 108
ρ	a constant	
ρ	an eigenvalue	126, 127
ρ_n	a general eigenvalue	126, 127, 161
γ	ratio of specific heats	7, 8
δ	a constant	
ϵ	emissivity	
θ	temperature	19
θ	an exponential constant	136
θ	an exponential curve	141
θ	theta direction	
θ_1	an exponential decay	47, 49, 136

NOMENCLATURE CONTINUED

		<u>Remarks (Equation No)</u>
Θ_2	an exponential decay	48, 49, 50
κ	thermal diffusivity	
λ	an eigenvalue	42, 183
λ_n	a general eigenvalue	41, 44, 45, 159, 160, 182
μ	a constant	
ρ	Spearman's population rank correlation	
	coefficient	167
ρ	a constant	55, 55a, 96, 101, 108, 109, 110, 111, 112, 114, 115, 116
ρ	density	
ρ_c	density of the gases in the chamber	
ρ_g	density of the gas	
ρ_p	density of the propellant	
σ	a surface	27, 29
τ	an arbitrary volume	30, 31, 32, 33
ϕ	the difference of two exponentials	46, 49, 51
ϕ	an exponential growth curve	130
ϕ	an exponential decay curve	131
ϕ	an exponential constant	130, 131
ϕ	an exponential	148, 150, 154
Δ	height	132, 133
$\Delta H^\ddagger$	enthalpy of activation	16, 18
Δt_s	temperature difference	162

NOMENCLATURE CONTINUED

		<u>Remarks (Equation No)</u>
$\Delta S^\ddagger$	entropy of activation	16, 17
∇	del	28, 32
∇^2	del squared	33, 34, 35, 36
T	dimensionless number	127

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ABSTRACT

Temperature profiles during polymerization , for the infinite solid cylinder, the infinite hollow cylinder and the star perforated infinite cylinder of polyurethane ammonium perchlorate solid propellant; have been determined. They show that the temperature across the solid rises considerably above the wall temperature and exceeds the 60°C (140°F) limit, recommended for the polyurethane propellants, by a considerable margin, often as much as 25°F .

An end effect test indicated that a hot region of fleeting duration is present near the ends of the solid.

Burning rates, measured radially across a piece of solid propellant, showed that a variation of burning rate with radius is present. The burning rates across a thin walled hollow cylinder of propellant did not vary radially.

Correlation coefficients between the burning rate and the maximum temperature gradient for the solid cylinder are of the order of 0.92, indicating that a high degree of correlation is present between burning rate and polymerization temperature. Correlation coefficients of this magnitude also show that one of the real causes of uneven burning in rocket motors is high temperature during polymerization.

INTRODUCTION

Uneven burning has plagued the solid propellant field from the very beginning. Often a certain configuration of motor and grain would work on a small scale but for some reason would become unstable as the rocket was made larger. Many reasons have been advanced for this phenomenon - most involving an explanation based on the flow of gases from the burning surface to the nozzle and vortices in the flow field. In spite of much good work along these lines, it seemed that the true explanation might lie elsewhere. In this study it was decided to focus attention on the solid propellant itself and to divine what might have happened in its preparation that could cause uneven burning. It was likely to be due to some oversight in preparation or some variable introduced in the scale up. In brief, attention was focused on the temperature, a factor easily controlled on laboratory scale where the quantities involved are small but not so easily controlled in a large solid, necessary for a rocket grain. Also, it is known that some polymerizations give off a considerable quantity of heat. In addition, plastics and rubbers are good heat insulators. This means that when a viscous solid propellant mixture is placed in a mould the temperature across it will vary greatly even though the outer surfaces may be kept constant. The result is that the temperature in the centre region could rise and approach decomposition temperatures. Therefore it was decided to investigate the heat of polymerization, evaluate the temperature gradients using the heat conduction equation with active sources present,

and compare the curves with actual radial propellant burning rates obtained in a strand burner for possible correlations.

LITERATURE SURVEY

Introduction

Combustion instability has been a problem for rocket designers throughout the history of rocketry. In the early days, experimenters always had a number of unexplained explosions among their successful designs, explosions which seemed to be due to a failure in the metal wall. To avoid this difficulty a number of nondestructive tests such as X-rays, the fluoroscope, and magnaflux were introduced to catch the flaws in the metal components before the rocket was assembled. This helped to some extent but still a number of rockets blew up - rockets whose design should have been satisfactory since all the equations for burning rate, maximum pressure and flow through the nozzle checked out and whose pressure time curves were normal. This difficulty could only be avoided by putting more metal in the wall with consequent loss in range. As technology advanced the method of measuring pressure was changed from a Bourdon gauge with an oil or grease filled tube to damp out the oscillations to a system with much faster response with pressure transducers, oscilloscopes and cameras. Then for the first time the reason for the unexplained blow ups became apparent. The pressure in the rocket was not nearly as steady as had been thought but showed unexplained peaks which could easily blow the casing to pieces. Immediately a new avenue of research had to be opened to find the explanation.

The survey made in this investigation consists of the following:

1. Basic Equations in Rocketry.
2. Burning Rate Fundamentals.
3. Acoustic Instability.
4. Vortices.
5. The solution of the heat conduction equation with chemical heat sources.
6. Chemical reactions in propellant formation.
7. Experimental Methods.
8. Circuits and Electronics.

Basic Equations in Rocketry.

The velocity at which a solid propellant was consumed during operation was called the burning rate. It was measured in a direction normal to the propellant surface and was usually expressed in inches per second, as stated by Sutton (112a). The burning rate was a factor in determining the mass rate of flow of gases according to the equation

$$\dot{m} = \rho_p \cdot A \cdot r \dots\dots\dots (1)$$

given in Sutton (112b), where $\dot{m}$ was the mass rate of flow in lbs./sec., ρ_p was the density of the propellant in lbs./ft³, A was the burning surface area in ft² and r was the rate in ft./sec. The mass velocity was one of the factors which determined the thrust of the rocket motor

according to the formula

$$F = \frac{\dot{m} \cdot V_e}{g} - (P_e - P_{at})A_e \dots\dots\dots(2)$$

given in Sutton (112b) where F was the thrust in lbs force, $\dot{m}$ was the mass rate of flow in lbs mass/sec., V_e was the velocity of the gas at the nozzle exit in ft/sec., g was the gravitational constant in ft/sec², P_e was the pressure of the gases at the exit of the nozzle, P_{at} was the atmospheric pressure and A_e was the area of the nozzle at the exit in ft².

Mass velocity also helped to determine the maximum velocity a chemical rocket could attain. Consider a rocket in flight in a vacuum. At time t consider the conditions during an increment of time dt . First a puff of gas flows from the nozzle of mass equal to dM . The impulse imparted is $I_{sp} \cdot dM$. Let the mass of the rocket be M and its velocity V .

$$\text{Impulse} = F \cdot t = \Delta MV = M \cdot a \cdot \Delta t = I_{sp} \cdot \Delta M \dots\dots\dots(3)$$

Equating the last two terms gives

$$M \cdot a \cdot \Delta t = I_{sp} \Delta M$$

$$M \cdot \frac{dV}{dt} \cdot dt = I_{sp} (-dM)$$

$$M \cdot dV = -I_{sp} \cdot dM$$

$$dV = -I_{sp} \cdot \frac{dM}{M}$$

$$\int_0^V dv = \int_{M_r + M_p}^{M_r} -I_{sp} \cdot \frac{dM}{M}$$

where M_r was the mass of the rocket and M_p was the mass of the propellant

$$[v]_0^V = -I_{sp} \left[\ln M \right]_{M_r + M_p}^{M_r}$$

$$[v - 0] = I_{sp} \cdot \ln \left[\frac{M_r + M_p}{M_r} \right] \dots\dots\dots(4)$$

$$V_{Brenschluss} = I_{sp} \cdot \ln \left[\frac{M_r + M_p}{M_r} \right] \dots\dots\dots(4)$$

$V_{Brenschluss}$ was the velocity at the end of burning. Sutton (112c) gave the formula

$$I_{sp} = \frac{V_{exit}}{g} \dots\dots\dots(5)$$

Substituting (5) in (4) gives

$$V_{Brenschluss} = \frac{V_e}{g} \cdot \ln \left[\frac{M_r + M_p}{M_r} \right] \dots\dots\dots(6)$$

The nozzle exhaust velocity V_{exit} was also given by Sutton (112c) as

$$V_{exit} = \sqrt{\frac{2g\gamma}{\gamma-1} \cdot R T_c \left[1 - \left[\frac{p_e}{p_c} \right]^{\frac{\gamma-1}{\gamma}} \right] + v_1^2} \dots\dots\dots(7)$$

where g = the acceleration due to gravity

γ = the ratio of the specific heats c_p/c_v

T_c = chamber temperature

R = gas constant

p_e = pressure at the exit

p_c = chamber pressure

V_1 = velocity at the nozzle entrance

If the chamber cross section was large compared to the nozzle then V_1^2 could be neglected.

The basic performance relation was derived by Sutton (112d) from the principle of conservation of matter. The propellant mass burned per unit time had to equal the sum of the increase in gas mass per unit time in the combustion chamber and the mass flowing through the nozzle per unit time.

$$A_s \cdot r \cdot \rho_p = \frac{d(\rho_c \cdot V_c)}{dt} + A_t \cdot p_c \sqrt{\frac{g \gamma}{RT_c} \left(\frac{2}{\gamma+1} \right)^{\frac{\gamma+1}{\gamma-1}}} \dots\dots\dots(8)$$

The term on the left hand side of the equation gave the rate of gas generation. The term on the right gave the change in propellant mass in the combustion chamber, and the last term gave the nozzle flow.

Burning Rate Fundamentals

It has been known for some time that the propellant burning rate was dependent on the working pressure. St. Robert's (110) law

$$r = b p^n \dots\dots\dots(9)$$

where $0.3 \leq n \leq 0.7$, was often used to describe the relationship for double-base propellant - a homogeneous mixture of nitrocellulose and nitroglycerine. Mureour's law (90,91)

$$r = a + bp \dots\dots\dots(10)$$

could also be used to describe the burning of double-base propellants, and sometimes a combination of both these empirical laws,

$$r = a + bp^n \dots\dots\dots(11)$$

was used. Ambient temperature was accounted for by Gibson (55) in the correlation

$$b = \frac{b'}{T_1 - T} \dots\dots\dots(12)$$

where T_1 was the initial temperature and b' was the constant thereat. If erosive burning was to be considered Gibson (55) gave

$$r = bp^n (1 + kv) \dots\dots\dots(13)$$

where k was a constant and v was the velocity of the gases parallel to the surface. When composite propellants, such as ammonium perchlorate with polyurethane binder, were considered; these equations did not work very well over a wide pressure range and therefore Summerfield (111)

developed the relationship

$$\frac{1}{r} = \frac{a}{p} + \frac{b}{p^{1/3}} \dots\dots\dots(14)$$

In this equation a was a constant determined by the chemical kinetics of the combustion which were rate-controlling at low pressures, and b was a constant determined by the diffusion characteristics of the fuel and oxidizer vapors, which were rate-controlling for combustion at high pressures.

The structure of one-dimensional flames was studied by Boys and Corner (14), who showed that they were completely determined by constants such as those of heat conductivity, of diffusion, and of the homogeneous reaction rates. The mathematical problem in the most general case was intractable, but three simple cases were fully solved by a mathematical method of successive approximations. The three cases were those in which diffusion is neglected compared with heat conductivity and in which the reaction velocities of the following type were considered: unimolecular, bimolecular, and the quasimolecular form of a unimolecular reaction at low pressure. The method of mathematical approximations was shown to involve errors of the order of only 10% in some actual cases, an error which is negligible compared with other uncertainties of the problem. In these simple cases it was impossible to solve all details of the structure such as the variation of composition and temperature through the flame.

Gibson (55) states that it has long been known that a solid

propellant was satisfactory only if it obeys the "law of burning in parallel layers"; this was to say that the self-oxidation reaction, i.e. the "burning" took place only on the exposed surfaces and that the rate at which the burning progressed normal to itself into the powder grain was the same at all points. This rate of progression was called the "linear burning rate" of the powder.

It was seen from the foregoing that control of the rate of generation of hot gases by a solid propellant was definitely a complicated problem. Basically the principal factors involved were the product of the density ρ , the burning surface S , and the linear burning rate r . The burning surface was controlled by the geometry of each single grain of the propellant charge and must be known at every instant of the reaction. The linear burning rate depended on the following factors and was under control only when these factors were under control: (1) chemical composition; (2) chamber pressure; (3) initial powder temperature; (4) radiation from the environment; and (5) the tangential velocity of propellant gases. It was only recently that the significance of these last three variables was recognized and investigated. Generally speaking, the empirical understanding of these factors had advanced to a point where the equation (Gibson (55))

$$P_{\text{equilibrium}} = \frac{S_b (\rho - \rho_{\text{gas}}) \frac{1}{1-n}}{A_t C_D} \dots\dots\dots (15)$$

could be set up to give quite accurately the equilibrium pressure in a rocket from a knowledge of the properties of the propellant. Here b

and n came from the equation

$$r = bp^n \dots\dots\dots(9)$$

The mechanism of the burning of double-base propellants was studied by Crawford, Huggett and McBrady (28). Such propellants burned by layers. Thus they maintained their shape. The function of an increase in pressure was to compress the reaction zone into a smaller distance about the burning surface. This took place through an acceleration of the chemical processes and also through the compression of the gaseous products. The detailed structure of the reaction zone and the form of the temperature gradient through it depended on the compositions of the propellant.

Parr and Crawford (93) developed a physical theory of burning of double-base rocket propellants. Considerable experimental evidence indicated that the burning of double-base propellants was a step-wise process. It was generally believed that three main stages were involved: (a) primary solid-phase decomposition giving organic fragments and nitrogen dioxide; (b) nonluminous gas-phase reactions of the products of (a) to give nitric oxide and aldehydic molecules; and (c) luminous gas-phase reaction of the products of (b) to give the final products. These stages might be called the foam, fizz, and flame reactions respectively.

The task of treating this burning mechanism quantitatively was really twofold. A definite model had first to be set up, and then the means devised for treating it mathematically. The model had to

include detailed kinetics of individual steps and various thermal quantities - several unknown parameters - and hence at best could only be a crude approximation. Starting from an assumed model and with a suitable choice of parameters, theoretical results could be obtained which should be close to those obtained experimentally. If this attempt was successful, it was possible to claim that the model had some use; if not, it might be hoped that the mathematical treatment would have value elsewhere.

The burning of double-base powder appeared to occur in three stages, according to Rice and Ginell (101), all with the evolution of heat. The first stage occurred at the surface of, or just within, the solid powder, and resulted in the formation of unsaturated fragments which were ejected into the gas phase normal to the surface. In the second stage, these fragments reacted in the gas phase in an assumed second-order reaction. These two stages constituted what together was called "fizz burning"; the gases produced were still capable of further reaction. At low pressures (from 1 to a few atmospheres) the only heat reaching the surface is that produced by the reaction at the surface, which was thus self-sustaining at a definite (limiting low pressure) rate. At higher pressures heat generated from the gas phase reaction reached the surface and the reaction rate then increased with pressure. The reactions thus far considered produced no visible light.

The third stage of the reaction consisted of the flame, which appeared only at pressures exceeding about 20 atmos., and apparently did not affect the rate of reaction below about 100 atmos. The flame exhibited a very striking appearance. The edge of the luminous

zone was fairly sharp. The base of the flame at the burning end of a long cylindrical stick of powder appeared no larger in diameter than the powder. Beyond this, however, the flame flared out, frequently exhibiting signs of turbulence. This appearance suggested that the second gas-phase reaction resembled a branching-chain explosion.

Type of Theory: There were two distinct possibilities as regards gas-phase reactions, which would make a considerable difference in the nature of the theory to be applied:

1) If the energy of activation of a gas-phase reaction was small, the average distance from the surface and the average time at which it would occur would be determined by a reaction rate which would not be strongly dependent on temperature.

2) If the energy of activation was high the average distance and time would not depend directly on the rate constant, but rather on the time required for any particular portion of the gas to be carried into a region where temperature is high enough for reaction to occur at an appreciable speed.

Case 1 was the theory considered here. Among contemporary developments of this type might be mentioned the work of Daniels (122).

Case 2 has been considered in detail by Boys and Corner (14). In this case the gas-phase reaction was completely rate determining; the zone of reaction merely moved forward or away from the surface, so that the temperature of the latter was adjusted to eject reactive fragments into the gas, at the required rate for maintenance of a steady state. This theory made the slope of the $\log M$ vs. $\log p$ curve (p = pressure, M = mass rate) equal to one-half the order of the gas-phase reaction

(14, 101) while the theory of case 1 indicated that the slope of the curve might be a much more complicated matter.

Penner (93a) reviewed the literature on propellant burning.

Wilfong, Penner and Daniels (122) found that when nitrocellulose "burned" the surface underwent violent decomposition and evolved large quantities of hot gases which could be used for propulsion purposes. At the surface, molecules were decomposed and ejected, fresh layers of molecules were exposed successively deeper and deeper in the propellant. The rate of regression or "peeling off" of one molecular layer after another, were measured directly and found to be of the order of 2 cms/sec at a pressure of 1500 lbs/in². A small bomb was developed by Crawford et al (27) for the rapid determination of the linear burning rate of experimental propellants under pressure, making use of fuse wires and timing circuits. The linear rate of burning depended greatly on the pressure of the gases surrounding the propellant and to a small extent on the initial temperature of the propellant.

The rate determining step was the isothermal unimolecular rupture of the oxygen-nitrogen bonds at the surface. The general equation for the reaction



in terms of the thermodynamic functions was given by Laidler (76a)

$$k = \frac{kT}{h} e^{\frac{\Delta S^{\ddagger}}{R}} e^{\frac{-\Delta H^{\ddagger}}{RT}} \dots\dots\dots(16)$$

If the reaction was unimolecular Leidler (76b) gave the relationship

$$k = e \frac{kT}{h} e^{\frac{\Delta S^\ddagger}{R}} e^{\frac{-E_a}{RT}} \dots\dots\dots(17)$$

Here k was the specific reaction rate k, R, T and h were Boltzmann's constant, the gas constant, absolute temperature, and Planck's constant, respectively, and $\Delta S^\ddagger$, $\Delta H^\ddagger$ and E_a were the entropy, heat and experimental energy of activation, respectively. $\Delta S^\ddagger$ might be regarded as essentially zero for the breaking of a bond, and at 1000°C the formula became

$$k = 3 \cdot 10^{13} \cdot e^{\frac{-\Delta H^\ddagger}{RT}} \dots\dots\dots(18)$$

$E_a = 46,700$ calories per mole and therefore $k = 5.5 \cdot 10^5 \text{ sec}^{-1}$ at 1000°C. The numerical value of the frequency factor was discussed extensively by Huggett (67a).

Radiation effects in propellant burning were investigated by Avery (2). In an effort to explain the action of added potassium salts upon the burning rate of propellants, an examination was made of the factors that could affect the shape of the pressure-time curve of a rocket fired statically under standard conditions. Of the variables considered, it was most reasonable to assume that the warming of the powder (1) through heat conduction or (2) through radiation caused the burning rate, and hence the pressure, to increase with time of burning.

A roughly quantitative treatment was also made by Avery (2) which showed that the effect of heat conduction was negligible but that warming of the powder by radiation might be appreciable. The radiation

effect was studied in some detail and the changes in shape of the pressure-time curves investigated theoretically for two cases in which the postulated conditions were (a) a constant radiation intensity and a constant absorptivity of the powder; (b) a radiation constant with time but distributed spectrally according to Planck's radiation law for a black body at 3000°K ., the absorption coefficient of the powder being given as a function of the wave length from experimental data.

Pressure-time curves calculated by the formulae developed were presented for radiation intensities corresponding to several different fractions of the radiation from a black body at 3000°K .

Bircumshaw and Newman (7) investigated the thermal decomposition of ammonium perchlorate in vacuo in the temperature ranges 220 to 280°C and 380 to 450°C . Small initial pressures of nitrogen were used to suppress sublimation. The experimental techniques for following the decomposition and subsequent analysis of the products were described and gas analysis results given.

In the low temperature range only 30% decomposition occurred though the "residue" was still ammonium perchlorate. In vacuo sublimation occurred all the time and also after decomposition has ceased which indicated that the reaction was not in the vapour phase. Some of the properties of the sublimated material and the "residue" were investigated; in particular, it was found that the residue which was porous in texture (the decomposition had occurred throughout the crystal) could be "rejuvenated" by exposure to solvent vapour.

The crystal transformation at 240°C from orthorhombic to cubic, the addition of some metallic oxide catalysts, were also investigated.

A thermal model of solid propellant burning was postulated by Green (56), in which the complex chemical reaction and heat conduction problem in the gas phase were replaced by a simplified boundary condition, which assumed convective heat transfer to the surface from a parallel flow of gas at flame temperature. The effective heat transfer coefficient was assumed to be an inverse function of propellant burning rate, which in turn was assumed to be an Arrhenius function of the surface temperature. This model permitted calculation of steady-state propellant temperatures, burning rates and temperature gradients which showed the proper qualitative dependence upon the propellant and gas flow parameters and which, for the assumed values of these parameters appeared to be of the proper order and magnitude. The non-steady behaviour of the model was analyzed, assuming that the nonsteady variations in heat flux, surface temperature, and burning rate may be expressed as small perturbations from the steady-state values, and considering that a small time interval is required for completion of the phase change or disordering of the propellant matter from the solid to homogeneous, gaseous state in a thin zone comprising the burning "surface". The results indicated that, when the simplified transfer coefficient assumed to govern heat flow to the surface was subject to fluctuations at high frequencies as a result of "sonance" in the grain cavity, conditions could exist under which a coupling between the heat transfer fluctuation and the decomposition reaction could cause large-amplitude oscillations of the surface temperature. In such a "resonance" condition, significant deviations in the burning rate from its nominal steady-state value may be effected.

The determination of the radiation from a composite propellant flame has been carried out by Blair (10, 11, 12, 100).

Hermance and Summerfield (61) have compared the burning rates in strands and rocket motors and have found that, in general, the burning rate in the rocket motor at any specified pressure was less than that of a strand burning at the same pressure.

In their propellant ignition studies, Hermance, Shinnar, Wenograd and Summerfield (60) have investigated the ignition of the reaction field adjacent to the surface of a solid propellant.

Denison and Baum (40) have worked out a simplified model of unstable burning in solid propellants, wherein an analysis of the surface temperature, and hence mass flux, response of a solid propellant to a disturbance in gas pressure has been developed. Time lags in the gas phase were neglected while transient heat conduction in the solid was considered. The results were obtained by perturbing the conservation equations in both the gas phase and the solid phase. Stability conditions were obtained in terms of a few dimensionless parameters which depended upon the steady state conditions.

Bastress and Summerfield (6) have studied the modification of burning rates of ammonium perchlorate solid propellants by particle size control.

The mechanism of accelerated burning of ammonium perchlorate at high pressures was investigated by Irwin, Salzman, and Andersen (71). The linear burning rate of ammonium perchlorate previously has been shown to undergo a marked increase in pressure dependence at high pressures.

The effect was considered to result from an increased burning surface area formed by a shear process at the burning surface as a result of high pressure. The possibility that the steep thermal gradient which existed at the burning surface at high pressures also could have lead to the shear stress responsible for cracking, was investigated. The analysis indicated that the thermal stress was almost solely responsible for the cracking over the entire pressure range of the burning rate experiments.

Chuffing and nonacoustic instability phenomena was studied by Yount and Angelus (126), and nonacoustic combustion pulsations of ammonium perchlorate containing aluminum was investigated by Inani and Shanfield (69).

The performance of solid propellants containing metal additives was studied by Cheung and Cohen (21). Test firings of solid propellant research rockets were made to study effects of propellant composition, pressure; and engine size on the exhaust oxide particle size, and on the composition of the solid exhaust products. The experimental results of this work and those reported by others were analysed collectively to provide a reasonable description of aluminum combustion and oxide condensation processes in solid propellant motors. Combustion of aluminum was found to occur in the vapour phase, and was essentially complete in the engines studied although some combustion took place in the nozzle. The experimental results indicated that the condensation of the oxide vapour could be described by first-order chemical kinetics. Further particle growth by agglomeration appeared likely. The effect of two phase flow was found to be significant in the motors tested and

reached a maximum in motors of a certain size. In motors where this loss was large, significant improvement in delivered performance could be realized by reducing the aluminum content.

Lindsey and Williams (79) investigated the structural integrity of an ablating rocket subjected to axial acceleration.

Schappery and Cantey (105) did thermochemical response studies of solid propellants subjected to cyclic and random loading.

The relationship between filler distribution and uniaxial rupture was studied by Fishman (52).

Acoustic Instability

A study of the damping of sound by mists and tiny solid particles was carried out by Epstein and Carhart (49) and strong transverse waves without shocks in a circular cylinder were investigated by Maslen and Moore (81).

Zucrow and Osborn (128) did an experimental study of high-frequency combustion pressure oscillations. The paper reports the results of some experiments conducted to investigate the influence of the length of the combustion chamber, the steady-state chamber pressure, the shape of the nozzle, and the equivalence ratio on high-frequency combustion pressure oscillations. The experiments were conducted with a rocket motor burning pre-mixed gases, thereby simplifying the experimental work and eliminating the effects of such variables as atomization, vapourization, mixing, etc. The pre-mixed gaseous

propellants used were superheated propane and air, ethane and air, methane and air, hydrogen and air, and ethylene and air. For the longitudinal mode of combustion pressure oscillation and frequencies ranged from 570 to 1750 cycles per second. The results indicated that a relationship existed between the amplitude and frequency of the combustion pressure oscillations, the combustion chamber geometry, and the burning rate of the propellants.

Combustion instability in solid propellant rocket motors was studied by Price and Sofferis (99) and later Price (95) alone using a T-burner.

Hart and McClure (59) investigated the acoustic interaction with the burning surface. A theory of the response of a burning solid to a sound wave was developed, based on time-dependent solutions of the transport equations relevant to a combustible having idealized physical and chemical properties. The development was restricted to small perturbations about the steady-state conditions for a rather simple model whose parameters had either a direct or physical significance, or were experimentally determinable. The introduction of ad hoc time delays or other phenomenological parameters was entirely avoided. Kinetics was also avoided by considering only those cases whose volumetric rate of reaction corresponded to instantaneous steady state. The predictions of the theory were discussed briefly, and several rather general observations were made. However, in view of the complexity inherent in the phenomenon and the inadequate state of empirical knowledge at the time the work was done, it was not yet possible to make a quantitative comparison between theory and experiment.

An experimental investigation, by Brownlee and Marble, (15) on finite-wave axial combustion instability was carried out and Crump and Price (35) looked at "catastrophic" changes in burning rate.

McClure, Hart and Bird (85) considered solid propellant motors as acoustic oscillators and Price (96) reviewed the experimental research on combustion instability. Later Price (97) did an experimental investigation on the same subject.

Bird, Haar, Hart and McClure (8) studied the effect of solid propellant compressibility on combustion and Kogaro (75) investigated the amplification of compression waves in the combustion zone.

The effect of the acoustic environment on the burning rate of double-base propellants was considered by Crump and Price (36), while McClure, Hart and Bird (86) investigated the heat release rate, temperature and pressure on instability.

Price, Mathes, Crump and McGie (98) found that 1) tangential rather than axial vibrations were primarily responsible for instability, 2) the rate decreased in regions where severe pressure oscillations and only mild velocity oscillations occurred, 3) the burning response to periodic disturbances was independent of the frequency.

The field of irregular burning in solid propellants was surveyed by Vandenkerckhove (119).

Watermeier (120) also studied combustion instability. Double-base rocket propellant slabs were burned in a transparent walled chamber which was vented to the atmosphere through a nozzle. The slabs were ignited at ambient nitrogen pressures of 200 to 800 psi. Pressure waves

were produced normal to the burning surface by a siren operating at frequencies of 100 to 1400 cps. Photographs revealed an increased burning rate as the siren approached the resonant frequency of the chamber. Large pressure variations recorded during this process present evidence of possible acoustic interaction with the burning surface. When 3% aluminum was added to the powder, each particle seemed to act like a flame holder and no instability was present.

The effects of gas phase and solid phase damping on instability of low frequency modes was investigated by Deters (41).

The initiation of finite wave axial instability by firing black powder charges was carried out by Dickinson (42) who also, together with Jackson (44) wrote a general paper on instability.

The acoustic admittance of a burning solid propellant surface was measured by Horton (63), while Horton and Price (66) measured the dynamic characteristics of propellant combustion.

McClure, Bird and Hart (84) determined the erosion mechanism for nonlinear instability in axial modes and Ryan, Coates and Baer (103) investigated the participation of the solid phase in oscillatory burning.

Virtual specific acoustic admittance measurements were made by Strittmater, Watermeier and Pfaff (109) while Trubridge and Badham (117) described the experimental methods used to suppress unstable combustion.

Watermeier, Aungst and Pfaff (121) did an experimental study of the aluminum additive role in unstable combustion. Composite-double base rocket propellant slabs which contained different concentrations and particle sizes of aluminum were burned in a transparent walled chamber. The chamber was exhausted to the atmosphere. The slabs were

ignited in cigarette fashion and burned under ambient nitrogen pressures of 200-900 psi. Experimental runs were made under steady flow conditions and under oscillating conditions with a siren rotating over the exhaust port.

Motion pictures were taken of the burning process at high framing rates. Data on droplet burning and concentrations in various regions above the propellant surfaces were obtained from individual frames of the film.

Wood (125) also investigated oscillatory burning and McClure et al (83) held a panel discussion on the subject.

Culick (38) studied the stability of high frequency pressure oscillations while Hart and Cantrell (58) investigated the amplification and attenuation of sound by burning propellants.

Particulate damping experiments on oscillatory combustion were done by Horton and McGie (65).

The interaction between sound and flow and the stability of the T-burner was done by McClure, Hart and Cantrell (87).

Linear acoustic gains and losses were investigated by Cantrell, Hart and McClure (18) and Coates, Horton and Ryan (22) determined the acoustic admittance by the T-burner method, while Crump and Price (37) noted the effects of the acoustic environment on the burning rate.

Dobbins and Temkin (45) measured particulate acoustic attenuation while Eisel, Horton, Price and Rice (46) studied the preferred frequency of oscillatory combustion and Engler and

Nachbar (48) did experiments with a solid propellant acoustic oscillator.

Admittance measurements of solid propellants by an acoustic oscillator technique were done by Foner, Hudson and Hall (54).

Nonlinear effects in instability were studied by Hart, Bird, Cantrell and McClure (57) while Horton (64) used a one-dimensional T-burner to investigate oscillatory combustion. Later Horton and Rice (67) noted the effect of compositional variables upon oscillatory combustion and the influence of the solid phase was done by Ryan and Coates (103).

Bird, Hart and McClure (9) studied finite acoustic oscillations and erosive burning in solid fuel rockets while the effects of thermal radiation on the acoustic response was noted by Cantrell, McClure and Hart (19).

Imber (70) worked out the stability criteria using transient effects and Trubridge (116) discusses the empirical methods which have been adopted to eliminate the effects of instability.

The response of a burning fuel plate to sound vibrations has been studied by Williams (123).

A theoretical study of superficial gaseous discharge with high frequency oscillations was done by Crocco (29) who worked out a number of complex frequencies which should be present. Crocco (30) did not agree with Zucrow and Osborn (128) in their conclusion that a relationship existed between the amplitude and frequency of the combustion pressure oscillations, the combustion chamber geometry, and the burning rate of the propellants. The importance of the sensitive time lag in longitudinal

high-frequency combustion instability was investigated by Crocco, Grey and Harrje (31) and later Crocco, Grey and Harrje (32) worked out a theory of liquid propellant rocket combustion instability and verified it experimentally. Crocco, Harrje and Reardon (33) developed a theoretical formulation of stability criteria for purely transverse modes of high frequency combustion instability, based on the time lag theories.

Osborn (92) questioned the validity of the time lag theory as experimental work did not verify the upper critical length. In reply, Crocco (34) stated that it was necessary to avoid confusion between liquid propellant rockets and premixed gas rockets. The behaviour of the two was generally quite different. Liquid propellant rockets did exhibit, almost invariably, the so-called "time-lag behaviour".

Sirignano and Crocco (106) developed a shock wave model of unstable rocket combustors and Bowman, Glassman and Crocco (13) discussed combustion instability and concluded that observations could be explained in terms of an instability model in which the driving mechanism depended on chemical kinetic factors.

Vortices

Jenkins and Swithenbank (73) and later Swithenbank and Sotter (113) discussed vortices in solid propellant rocket motors. Studies of combustion instability revealed an interesting interaction between the flow pattern and the combustion chemistry. This took the form of strong vortices in the acoustic cavity which lead to several remarkable effects.

Swithenbank and Sotter (114) found that vortices are generated by acoustic oscillations as a second-order viscous effect. Travelling tangential modes in an axially perforated solid propellant rocket gave a single vortex swirling about the axis. Tangential velocity at the periphery, typically a few hundred feet per second, could be predicted approximately using acoustic streaming theory modified by heat addition and radial flow effects. Serious consequences of the vortex were 1) torque, which gave undesired roll, especially in large vehicles as torque varies as the radius, and 2) pressure rise caused largely by reduction in effective area of the nozzle throat. Standing tangential modes produced a pair of vortices rotating in opposite directions for each pressure antinode. These gave no net torque and were much less destructive. Experimental data included 3200 frames per second cine-films of the vortices, torque measurements, and radial pressure gradient determinations in the head end of a motor. The travelling tangential modes could be initiated readily by tangential injection of nitrogen into the motor.

Flandro (53) found that roll torque of considerable magnitude was generated in some solid propellant rocket motors during periods of high-intensity acoustic combustion instability. Forces normal to the motor axis sometimes accompanied roll perturbations. These effects appeared to result from nonlinear viscous phenomena (acoustic streaming) that occurred in the presence of intense acoustic wave motion in combustion gases. Direct measurements of the moments and associated vortex flow disturbances originating within the burning cavity verified this theoretical description. Unstable motors using a cylindrical grain

perforation geometry were especially subject to roll torque generation. However, similar effects were exhibited in more complex grain configurations. Star-perforated cavities were capable of producing several levels of roll torque, depending upon the number of star-points. The secondary force effects were sensitive to initial grain temperature and thus could be minimized in some motors by prerun temperature conditioning.

The Solution of the Heat Conduction Equation with Chemical Heat Sources.

An experimental and theoretical investigation of the combustion of slabs of dry wood was made by Bamford, Crank and Malan (4), including spontaneous and forced burning of the surface. A minimum heating time was required to produce spontaneous burning. For sheets of different thickness the temperature at the centre of the block at the minimum heating time was about 480°K . The final temperature at the centre of the block was about 780°K . A mathematical treatment considered heat liberated by the exothermic decomposition reaction superimposed on the expression for heat conduction. Simplifying assumptions about the rate of escape and calorific value of the decomposition products were necessary. Decomposition was considered to be a simple reaction of the first order. Equations were derived for the rise of the central temperature with time during spontaneous burning, for the rate of gas evolution, and for the thickness of the combustion zone. In forced burning the surface was exposed to external radiant heat. Slow decomposition began at the surface, and the products might be ignited. The flame died out unless

the intensity of radiation exceeded a critical value. The rate of evolution of gases calculated for experimental conditions under radiation rose to a maximum and diminished.

Crank and Nicolson (26) devised a practical method for numerical evaluation of solutions of partial differential equations of the heat-conduction type which arose when a chemical reaction was treated as a heat source. This paper was concerned with methods of evaluating numerical solutions of the nonlinear partial differential equation

$$\frac{\partial \theta}{\partial t} = \frac{\partial^2 \theta}{\partial x^2} - q \frac{\partial w}{\partial t} \dots\dots\dots(19)$$

where

$$\frac{\partial w}{\partial t} = -k.w. e^{-A/\theta} \dots\dots\dots (20)$$

subject to the boundary conditions

$$\left. \begin{aligned} \theta &= f_1(x) \\ w &= f_2(x) \\ \frac{\partial \theta}{\partial x} &= H_1(\theta) \quad \text{at } t = 0 \text{ for } t \geq 0 \\ \frac{\partial \theta}{\partial x} &= H_2(\theta) \quad \text{at } t = 1 \text{ for } t \geq 0 \end{aligned} \right\} \text{ at } t = 0 \text{ for } 0 < x < 1 \dots\dots\dots (20a)$$

A, k, and q are constants.

Equation (19) was of a type which arose in problems of heat flow when there was an internal generation of heat within the medium; if the heat was due to a chemical reaction proceeding at each point at a rate dependent upon the local temperature, the rate of heat generation was often defined by an equation such as (20).

Chemical Reactions in Propellant Formation

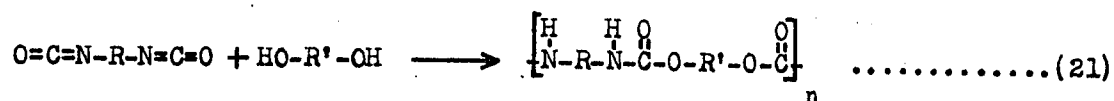
Evans and Tyrall (51) in an investigation of the heats of polymerization of acrylic acid and its derivatives, found 18.49 kcals/mole, 15.84 kcals/mole, 20.19 kcals/mole and 12.9 kcals/mole for acrylic acid, methacrylic acid, methyl acrylic ester, and methyl methacrylate, respectively.

A method of determining the alcoholic hydroxyl group in organic compounds using phthalic anhydride and pyridine was developed by Elving and Warshowsky (47).

The additive calculation of the heat of combustion was improved to such an extent by Klages (74) that it was possible to calculate the total heat of combustion of aliphatic and simple alicyclic hydrocarbons to within 0.5 parts per thousand, in some cases even to 0.2 parts per thousand, of the truth.

The preparation of some oxycyclobutane polymer was reported by Farthing (51a) who used boron trifluoroetherate as a catalyst.

Wittbecker and Katz (124) gave the following general reaction for the production of polyurethanes from a diisocyanate and a glycol



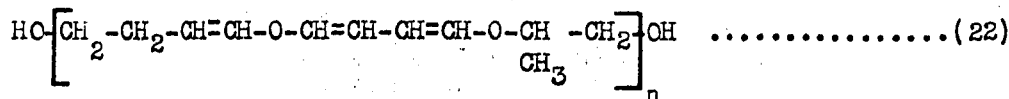
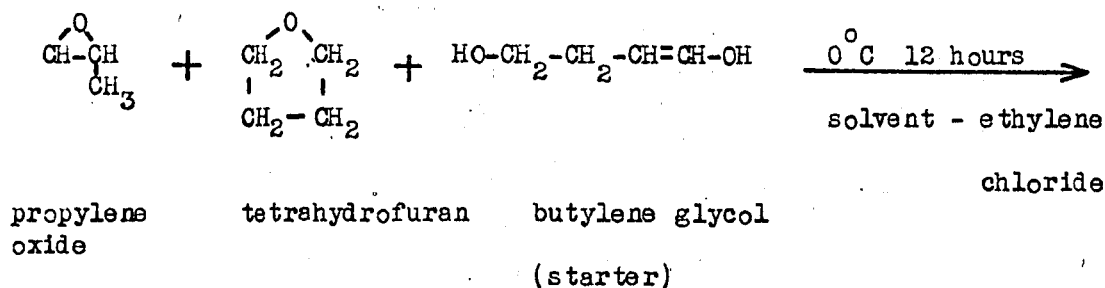
It was found also that the resulting polymers were not too stable to heat.

The vapour pressures and heats of mixing in the systems polyglycols-methanol were studied by Lakhanpal and Conway (77) and the

thermodynamic functions of the system polyglycols-methanol were also studied by Conway and Lakhanpal (24). The equilibrium swelling of crosslinked polyurethane elastomers was investigated by Conway and Tong (25) and Conway (23) determined the elastic properties of the derived elastomers.

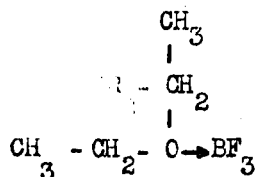
Dickinson (43) derived new elastomers from the copolymers of tetrahydrofuran and propylene oxide. The reactions were as follows:

1) a cationic catalysis to produce a difunctional diol



the diol - polyoxypropylenetetramethylene glycol M.Wt. 2100

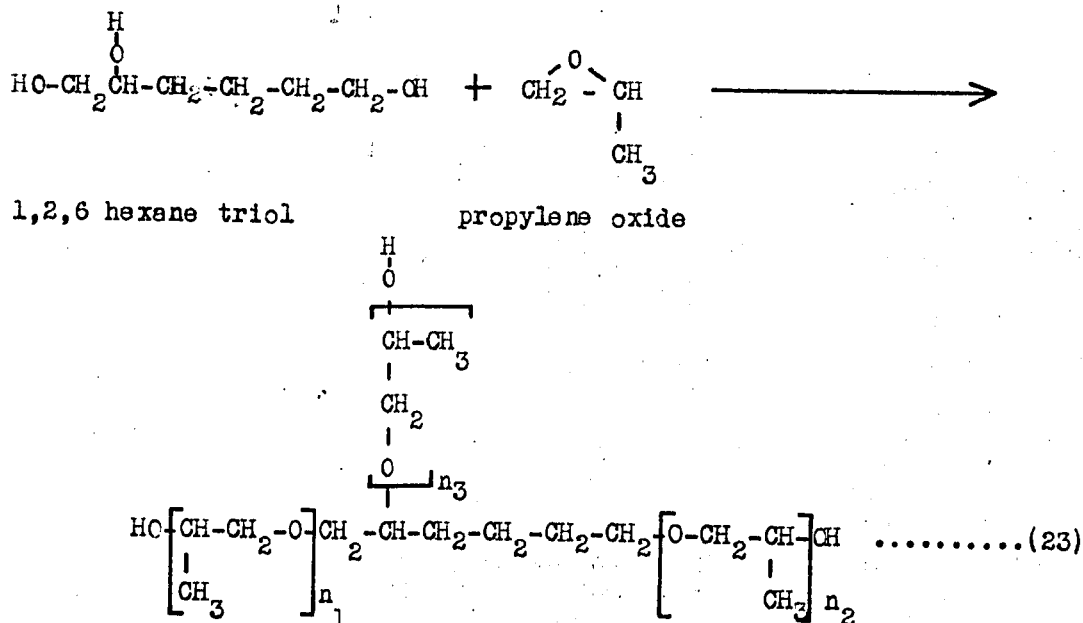
The polymerization was done in a solution of ethylene chloride using boron trifluoride etherate as a catalyst



boron trifluoride etherate

The crosslinking triol was a propylene oxide addunct of 1, 2, 6 hexane triol with a molecular weight of 1500 (Union Carbide Niox Triol LHT 112).

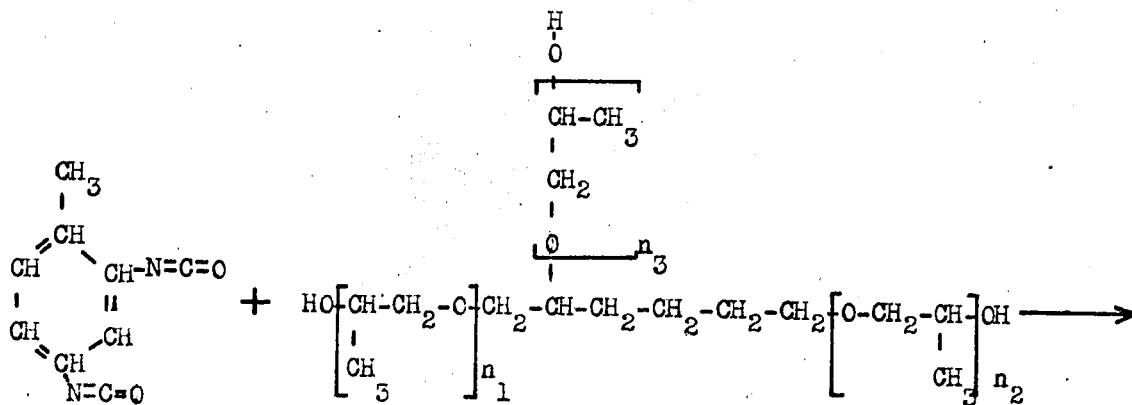
The reaction was 2)



polyoxypropylene hexane triol M.Wt. 1500

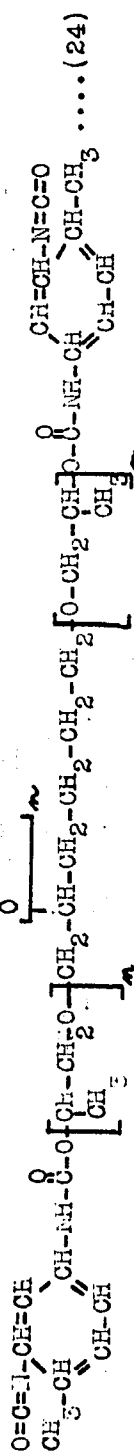
Niox Triol LHT 112

3) The next step was to treat the crosslinker with toluene 2,4 diisocyanate



2,4 toluene diisocyanate

polyoxypropylene triol

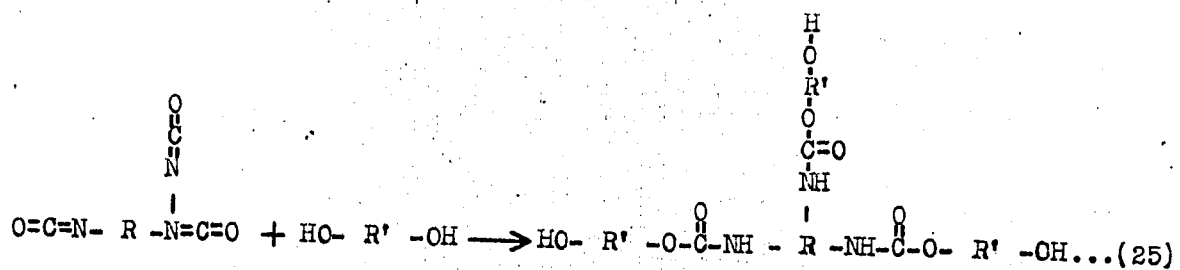


The cross linker

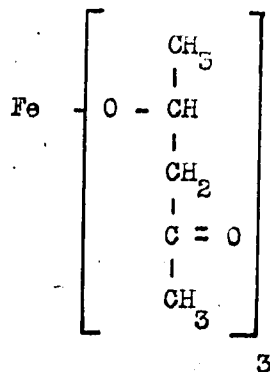
Let the cross linker be written as



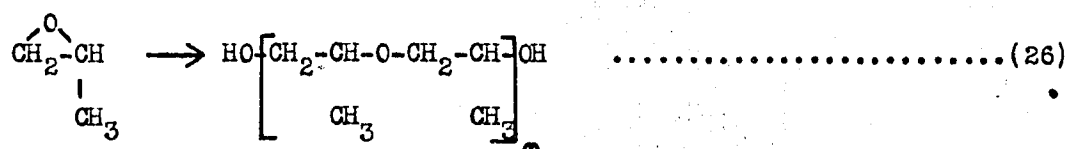
and the diol as $\text{HO}-\text{R}'-\text{OH}$, then these two when reacted together give the elastomeric unit



The catalyst was Ferric AcetylAcetonate



Carde uses the same method with the exception that the diol is a polyoxypropylene. The equation for its production was



Experimental Methods

Crawford (27) developed a small bomb, pressurized with nitrogen, to burn small strips of propellant, and formally called a strand burner.

A method of measuring erosive burning using tiny pieces of propellant was perfected by Marklund and Lake (80).

Ives, Dominik and Proell (72) developed a heat sink strand bomb for determining ballistic properties of solid propellants.

An experimental method of measuring intensity of turbulence in a rocket chamber photographically was worked out by Hersch (62).

Bastress, Hall and Summerfield (6) described a method for particle size analysis of ammonium perchlorate by liquid sedimentation.

The thermal diffusivity of ammonium perchlorate has been found by Rosser, Inani and Wire (102).

A discussion of methods of determining the heat of polymerization was given by McCurdy (82) under the following headings:

1. Combustion Method: The heat of polymerization was found by subtracting the heat of combustion of the monomer from the heat of combustion of the polymer. Since heats of combustion were many times larger than the heats of polymerization, high precision was required.

2. Direct Calorimetry:

a) Non-isothermal Methods

1) Integral Method: This method involved the measurement of the amount of heat corresponding to the formation of a certain weight of polymer.

ii) Differential Method: The amount of heat evolved and a physical property related to the extent of the reaction were measured at convenient time intervals.

iii) Self Heating Method: If a reaction was initiated photochemically the centre of the illuminated volume element might remain adiabatic long enough for this element to be used as its own calorimeter.

b) Vaporization Method: The heat of polymerization was used to evaporate a liquid in equilibrium with its vapor at the boiling point. The weight of the liquid evaporated was directly proportional to the heat.

c) Fusion Method: An isothermal calorimeter was used with diphenyl ether as the working substance.

3. Other Methods:

a) Thermodynamic Method: A long chain polymer could be in thermodynamic equilibrium with monomer only at a certain activity, similar to the fact that a solid or a liquid has a definite equilibrium vapour pressure at a given temperature. Measurement of this activity at different temperatures permitted the evaluation of the heat of polymerization by the application of the isochore.

b) Semi-Empirical Methods: This method depended on the fact that heats of formation were approximately additive.

Circuits and Electronics

Dauphinee (39) has designed an isolating potential comparator with which electromotive forces could be compared accurately without making any direct electrical connection between them. A double-pole, double throw chopper, having a condenser connected between the vibrating contacts, was used with a galvanometer or electronic amplifier to indicate any inequality between e.m.f's. without allowing any net flow of current between the circuits.

A differential microcalorimeter of the Tian-Calvet type has been designed and constructed by Attree, Cushing, Ladd and Pieroni (3). The galvanometers previously employed have been replaced by a DC amplifier, which materially simplified the construction and operation of the instrument. In addition this allowed an electrical analog integrator to be used which gave directly the heat of the reaction.

Sensitivity of the instrument in the range from 0.01 to 2 calories was such that measurements could be made with a precision of 1% or better. Measurements have been made, under ideal conditions, of 0.002 calories with a standard deviation of 0.1%.

Mueller (88,89) developed a special form of the Wheatstone bridge for measuring the resistance of a resistance thermometer with four leads.

The analog integrator was described by Albert (1).

An improved resistance thermometer bridge was developed by Evans (50).

Summary:

In all this there seems to be no realization that the burning rate and the polymerization temperature at different positions radially across the grain may not be constant. Should this be the case, another explanation for uneven burning is a real possibility. Therefore, it was decided 1) to measure the linear burning rates radially across the grain 2) to set up a mathematical model for the heat during polymerization 3) to measure the heat of polymerization at different temperatures in the microcalorimeter, 4) to measure the appropriate heat transfer constants, 5) to solve the mathematical model for instantaneous temperatures on the computer, 6) to draw curves from these instantaneous temperatures, 7) to attempt to correlate the temperature and the burning rate, 8) to attempt another explanation for uneven burning.

THEORETICAL CONSIDERATIONS

The Effect of Heat on the Temperature Distribution

The differential equation governing heat flow in a solid was developed in Sokolnikoff and Redheffer (107). The development given below is for the case where heat sources are present. It was known from empirical results that heat will flow from points at higher temperatures to those at lower temperatures. At any point the rate of decrease of temperature varied with direction, and it was generally assumed that the amount of heat ΔH crossing an element of surface $\Delta \sigma$ in Δt seconds was proportional to the greatest rate of decrease of the temperature T ; that is

$$H = k \cdot \Delta \sigma \cdot \Delta t \left| \frac{dT}{dn} \right| \dots\dots\dots(27)$$

A vector q , representing the flow of heat, was defined by the formula

$$q = -k \nabla T \dots\dots\dots(28)$$

where k was a constant of proportionality known as the thermal conductivity of a substance. The negative sign was chosen in the definition because heat flows from points of higher temperature to those of lower, and the vector ∇T was directed normally to the level surface $T = \text{a constant}$ in the direction of increasing T . Then the total amount of heat H flowing out in Δt seconds from an arbitrary volume τ bounded by a closed surface σ was

$$H \doteq -\Delta t \int_{\sigma} k \frac{dT}{dn} d\sigma = \Delta t \int_{\tau} q \cdot n d\sigma \dots\dots\dots(29)$$

Since $q \cdot n = -k \frac{dT}{dn}$ by equation (28). On the other hand, the amount of heat lost by a body τ could be calculated as follows: In order to increase the temperature of a volume element by ΔT^0 , it is necessary to supply an amount of heat that is proportional to the increase in temperature and to the mass of the volume element plus the contribution of the continuously distributed heat sources, $Q'(x,y,z,t)$. Hence

$$\Delta H = c \Delta T \rho \Delta \tau + Q'(x,y,z,t)$$

where c was the specific heat of the substance and ρ was its density. Therefore, the total heat loss from the volume τ in Δt seconds was

$$H = -\Delta t \int_{\tau} \frac{\partial T}{\partial t} c \rho d\tau + \Delta t \int_{\tau} Q'(x,y,z,t) d\tau \dots\dots\dots(30)$$

Equating (29) and (30) gave

$$\Delta t \int_{\sigma} q \cdot n d\sigma = -\Delta t \int_{\tau} \frac{\partial T}{\partial t} c \rho d\tau + \Delta t \int_{\tau} Q'(x,y,z,t) d\tau$$

The application of the Divergence Theorem given below

$$\int_{\sigma} q \cdot n d\sigma = \int_{\tau} \text{div } q d\tau$$

to the left hand side gave

$$\int_{\tau} \text{div } q \, d\tau = - \int_{\tau} \frac{\partial T}{\partial n} c \rho \, d\tau + \int_{\tau} Q'(x,y,z,t) \, d\tau \dots\dots\dots(31)$$

and since $q = -k \nabla T$, the foregoing equation assumed the form

$$\int_{\tau} \left[\text{div}(-k \nabla T) + c \rho \frac{\partial T}{\partial t} - Q'(x,y,z,t) \right] d\tau \equiv 0 \dots\dots\dots(32)$$

if k was a constant

$$\text{div}(k \nabla T) = k \nabla^2 T$$

and (32) became

$$\int_{\tau} \left[-k \nabla^2 T + c \rho \frac{\partial T}{\partial t} - Q'(x,y,z,t) \right] d\tau \equiv 0 \dots\dots\dots(33)$$

Since this integral must vanish for an arbitrary volume τ and the integrand is a continuous function, it follows that the integrand must be equal to zero, for if such were not the case, τ could be so chosen as to be a region throughout which the integrand has a constant sign. But if the integrand had one sign throughout this region, then the integral would have the same sign and would not vanish as required by equation (33).

Therefore

$$-k \nabla^2 T + c \rho \frac{\partial T}{\partial t} - Q' = 0$$

$$-k \nabla^2 T = -c \rho \frac{\partial T}{\partial t} + Q'$$

$$k \nabla^2 T = c \rho \frac{\partial T}{\partial t} - Q'$$

$$\frac{k}{c \rho} \nabla^2 T = \frac{\partial T}{\partial t} - \frac{Q'}{\rho c}$$

Let $\kappa = \frac{k}{c \rho}$, where κ is the thermal diffusivity, then

$$\kappa \nabla^2 T = \frac{\partial T}{\partial t} - \frac{Q'}{c \rho} \dots\dots\dots(34)$$

If no heat sources are present this equation reduces to

$$\kappa \nabla^2 T = \frac{\partial T}{\partial t} \dots\dots\dots(35)$$

If the solid has a cylindrical shape ∇^2 in cylindrical coordinates equals

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial z^2} \dots\dots\dots(36)$$

as given by Mickley (87b). If no heat sources are present in a solid cylinder of infinite length the differential equation is

$$\kappa \left[\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right] = \frac{\partial T}{\partial t} \dots\dots\dots(37)$$

with the boundary conditions

$$T(r,0) = T_0 \dots\dots\dots(38)$$

$$T(R,t) = T_1 \text{ where } t > 0 \dots\dots\dots(39)$$

$$\left[\frac{\partial T}{\partial r} \right]_{r=0} = 0 \dots\dots\dots(40)$$

Carslaw and Jaeger (20a) gave the solution as

$$\frac{T - T_0}{T_1 - T_0} = 1 - \frac{2}{R} \sum e^{-\lambda_n^2 t} \frac{J_0(\lambda_n r)}{\lambda_n J_1(\lambda_n R)} \dots\dots\dots(41)$$

where λ_n , $n = 1, 2, 3, \dots$, are the roots of

$$J_0(\lambda R) = 0 \dots\dots\dots(42)$$

When heat sources are present, Thews (115) gave the solution of the differential equation as

$$x \left[\frac{\partial^2 T}{\partial r^2} + \frac{\partial T}{r \partial r} \right] = \frac{\partial T}{\partial t} - \frac{Q'}{\rho c} \dots\dots\dots(43)$$

with the boundary conditions given below

$$T(r,0) = T_0 \dots\dots\dots(38)$$

$$T(R,t) = T_1 \text{ where } t > 0 \dots\dots\dots(39)$$

$$\left[\frac{\partial T}{\partial r} \right]_{r=0} = 0 \dots\dots\dots(40)$$

$$\text{as } \frac{T-T_0}{T_1-T_0} = 1 - 2 \sum_{n=1}^{\infty} e^{-\kappa \lambda_n^2 t} \frac{J_0(\lambda_n r)}{\lambda_n^3 J_1(\lambda_n R)} + \frac{a}{4\kappa} \frac{(R^2 - r^2)}{(T_1 - T_0)} - \frac{2a}{\kappa R (T_1 - T_0)} \sum_{n=1}^{\infty} e^{-\kappa \lambda_n^2 t} \frac{J_0(\lambda_n r)}{\lambda_n^3 J_1(\lambda_n R)} \dots\dots\dots(44)$$

where λ_n are the roots of

$$J_0(\lambda R) = 0 \dots\dots\dots(42)$$

if $T_1 = T_0$ then the solution as given by Carslaw and Jaeger (20b) was

$$(T-T_0) = \frac{Q'(R^2-r^2)}{\rho c 4\kappa} - \frac{2}{R\kappa} \frac{Q'}{\rho c} \sum_{n=1}^{\infty} e^{-\kappa \lambda_n^2 t} \frac{J_0(\lambda_n r)}{\lambda_n^3 J_1(\lambda_n R)} \dots\dots\dots(45)$$

where $\pm \lambda_n, n = 1, 2, 3, \dots$ were the roots of

$$J_0(\lambda R) = 0 \dots\dots\dots(42)$$

The Mathematical Representation of the Heat Source

In this work the overall heats of polymerization were measured by the integral method while simultaneously the deflection

corresponding to the instantaneous q was recorded. The deflection curve was represented mathematically as the difference of two exponential decays, (17),

$$\phi = a_1 e^{w_1 t} - a_2 e^{w_2 t} \dots\dots\dots (46)$$

which it closely resembles. This will become clear by glancing at Figures 1 and 2. On Figure 1 the exponential decay (17b)

$$\theta_1 = a_1 e^{w_1 t} \dots\dots\dots (47)$$

is plotted together with the second exponential decay (17b)

$$\theta_2 = a_2 e^{w_2 t} \dots\dots\dots (48)$$

with a value of $w_2 = 10w_1$. The second exponential θ_2 is plotted on the negative side since it is to be subtracted. When the curve representing the difference of the two is plotted, (Figure 2), it is soon evident that a curve closely resembling the deflection curve results. But since only a fraction of the total amplified signal was sent to the deflection recorder, a constant c must be placed in front as the integrator works on the total amplified signal. The individual constants w_1 and w_2 were found by plotting the deflection against time on semilogarithmic paper. Taking the slope of the early part of the main decay, and working out the best fit by the method of least squares gave w_1 and a_1 . To get w_2 , as a first

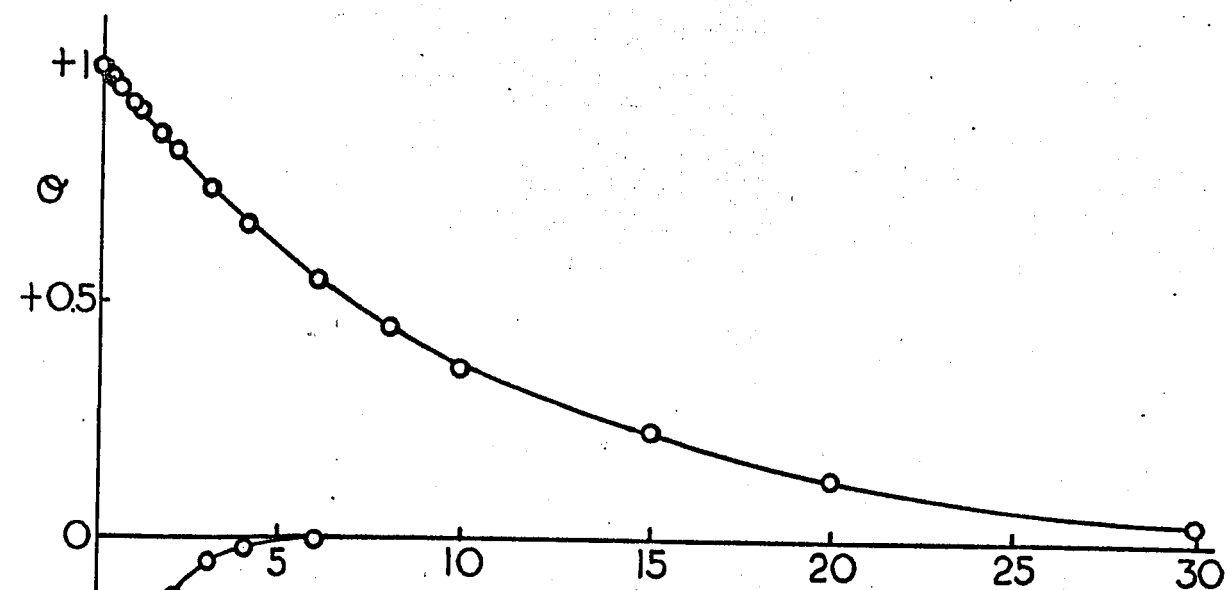


Figure 1 A Plot of two exponentials where $w_2 = 10w_1$

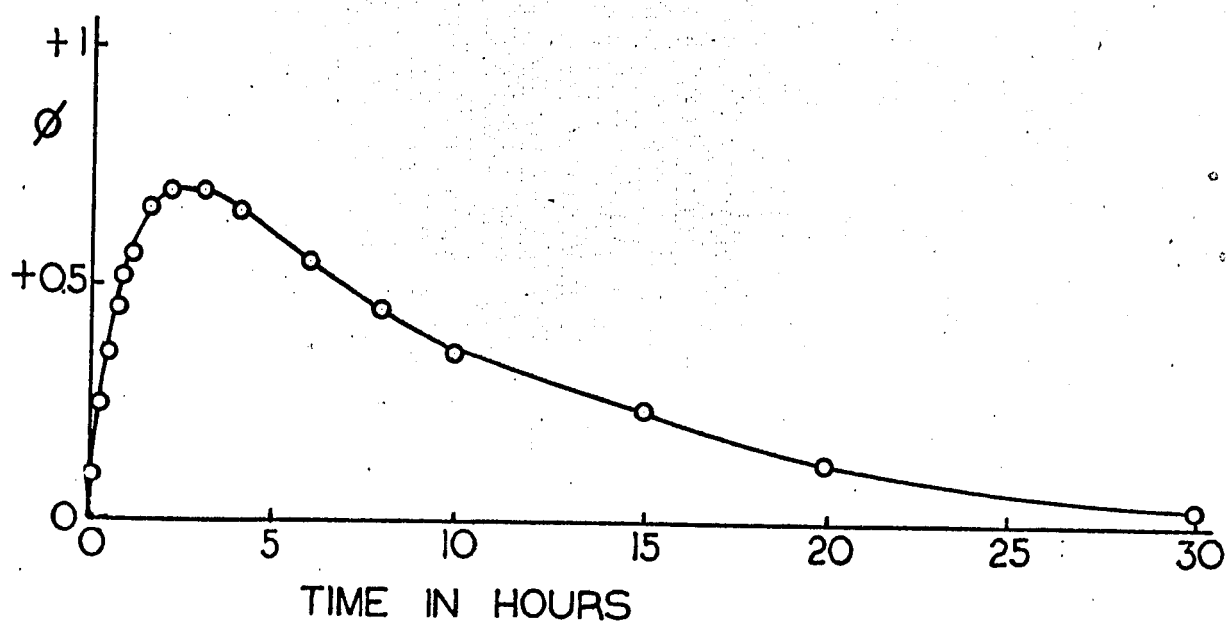


Figure 2 A Plot of $\phi = \theta_1 - \theta_2$ to illustrate the combination of two exponentials

approximation a_1 was assumed equal to a_2 and each point at various time instants was placed equal to

$$\theta_2 = \theta_1 - \phi \dots\dots\dots(49)$$

This gave a series of values, representing different points on

$$\theta_2 = a_1 e^{w_2 t} \dots\dots\dots(50)$$

A semilogarithmic plot gave a fairly straight line but the best fit was found by the least squares method. Thus w_2 was found from the slope. The value of a_2 rarely corresponded to a_1 . Since only a few points were usually available for the calculation of the second decay curve, and the slope must be positive initially, an arbitrary value of $a_2 = 0.9a_1$ was taken. The combined equation for deflection as read was

$$\phi = a_1 (e^{w_1 t} - 0.9e^{w_2 t}) \dots\dots\dots(51)$$

To determine the constant c and make the equation balance the total heat of the reaction, the formula

$$\Delta H = \int_0^t \frac{\partial H}{\partial t} dt \dots\dots\dots(52)$$

was used. Then substitution gives

$$\Delta H = \int_0^t c a_1 (e^{w_1 t} - 0.9 e^{w_2 t}) dt \dots \dots \dots (53)$$

Once c is known the equation for $\frac{\partial H}{\partial t}$ can be written as

$$\frac{\partial H}{\partial t} = c a_1 (e^{w_1 t} - 0.9 e^{w_2 t}) \dots \dots \dots (54)$$

The equation for $\frac{\partial H}{\partial t}$ was found at three different temperatures and then the combined equation was found by placing a constant value dependent on temperature in front. This constant value was found by plotting ca_1 versus temperature on semilogarithmic paper. Similarly a combined constant for $w_1 t$ was found in the same manner. The combined constant for $w_2 t$ was found by averaging since the relationship was not linear and because the second term is small compared to the first. The form of the combined equation is

$$\frac{\partial H}{\partial t} = \alpha_{1A} e^{\beta T} \left[e^{\gamma t} e^{\rho T} - 0.9 e^{ct} \right] \dots \dots \dots (55)$$

In the heat conduction equation the heat source term is $\frac{Q'}{\rho c_p}$

$$\therefore \frac{Q'}{\rho c_p} = \frac{\alpha_{1A}}{\rho c_p} e^{\beta T} \left[e^{\gamma t} e^{\rho T} - 0.9 e^{ct} \right] = f(T, t) \dots \dots \dots (55a)$$

Now if $\alpha_1 = \alpha_{1A}/\rho c_p$, then $f(T, t)$ is as follows

$$f(T, t) = \alpha_1 e^{\beta T} \left[e^{\gamma t} e^{\rho T} - 0.9 e^{ct} \right] \dots \dots \dots (56)$$

Developments

The solution of the heat conduction equation when the source is a heat pulse of duration t' hours: The differential equation of the heat flow in an infinite solid cylinder has been given by Thews (115) as

$$\kappa \left[\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right] = \frac{\partial T}{\partial t} - \frac{Q'}{\rho c_p} \dots\dots\dots(43)$$

Boundary Conditions were as follows:

$$1) T(r, 0) = T_0 \dots\dots\dots(38)$$

$$2) T(R, t) = T_1 \text{ where } t > 0 \dots\dots\dots(39)$$

$$3) \left[\frac{\partial T}{\partial r} \right]_{r=0} = 0 \dots\dots\dots(40)$$

LaPlace transforms with respect to time give

$$\kappa \left[\frac{d^2 \bar{T}}{dr^2} + \frac{d\bar{T}}{rdr} \right] = p\bar{T} - T_0 - \frac{Q'}{p\rho c_p} \left[1 - e^{-pt'} \right] \dots\dots\dots(57)$$

$$\frac{d^2 \bar{T}}{dr^2} + \frac{d\bar{T}}{rdr} - \frac{p\bar{T}}{\kappa} = -\frac{T_0}{\kappa} - \frac{Q'}{p\rho c_p \kappa} \left[1 - e^{-pt'} \right]$$

$$\text{L.H.S. } \frac{d^2 \bar{T}}{dr^2} + \frac{d\bar{T}}{rdr} - \frac{p\bar{T}}{\kappa} = 0 \dots\dots\dots(58)$$

Multiplying through by r^2 gives

$$r^2 \frac{d^2 \bar{T}}{dr^2} + r \frac{d\bar{T}}{dr} - \frac{p \bar{T} r^2}{x} = 0$$

Comparing this equation with reference (87a) gives $a=1$, $b=0$, $c=0$, $d = -\frac{p}{x}$, $s=1$.

$$p = \frac{1}{s} \sqrt{\left(\frac{1-a}{2}\right)^2 - c} = \frac{1}{1} \sqrt{\left(\frac{1-1}{2}\right)^2 - 0} = 0$$

$$\frac{\bar{d}}{s} = \sqrt{\frac{-p}{x}} = 1 \sqrt{\frac{p}{x}}$$

$$\bar{T} = A I_0 \left(\sqrt{\frac{p}{x}} r \right) + B K_0 \left(\sqrt{\frac{p}{x}} r \right) \dots\dots\dots (59)$$

Now the form of the R.H.S. is a constant and therefore $\bar{T} = D$ is a solution. Substituting this in the differential equation (57) gives

$$D = \frac{T_0}{p} + \frac{Q'}{\rho_c p^2} \left(1 - e^{-pt'} \right) \dots\dots\dots (60)$$

The total solution is

$$\bar{T} = A I_0 \left(\sqrt{\frac{p}{x}} r \right) + B K_0 \left(\sqrt{\frac{p}{x}} r \right) + \frac{T_0}{p} + \frac{Q'}{\rho_c p^2} \left(1 - e^{-pt'} \right) \dots\dots\dots (61)$$

Applying boundary condition 3) requires differentiation with respect to r

$$\frac{\partial \bar{T}}{\partial r} = A \sqrt{\frac{p}{x}} I_1 \left(\sqrt{\frac{p}{x}} r \right) - B \sqrt{\frac{p}{x}} K_1 \left(\sqrt{\frac{p}{x}} r \right) \dots\dots\dots (62)$$

$$\left(\frac{\partial \bar{T}}{\partial r} \right)_{r=0} = A \sqrt{\frac{p}{x}} I_1(0) - B \sqrt{\frac{p}{x}} K_1(0) = 0 \dots\dots\dots (62a)$$

now $I_p(x) = \frac{1}{p!2^p} x^p$ and

$$I_1(0) = \frac{1}{1!2^1} 0^1 = 0$$

also $K_n(x) = 2^{n-1}(n-1)! x^{-n}$

$$K_1(0) = 2^{1-1}(1-1)! 0^{-1} = \frac{1 \cdot 1}{0} = \infty$$

then $\left(\frac{\partial \bar{T}}{\partial r}\right)_{r=0} = A \sqrt{\frac{p}{\kappa}} \cdot 0 - B \sqrt{\frac{p}{\kappa}} \cdot \infty = 0$

therefore B must be zero

$$\bar{T} = A I_0\left(\sqrt{\frac{p}{\kappa}} r\right) + \frac{T_0}{p} + \frac{Q'}{p c_p p^2} (1 - e^{-pt'}) \dots\dots\dots (63)$$

applying boundary condition 2) gives

$$\frac{T_1}{p} = A I_0\left(\sqrt{\frac{p}{\kappa}} R\right) + \frac{T_0}{p} + \frac{Q'}{p c_p p^2} (1 - e^{-pt'})$$

and $A = \frac{(T_1 - T_0)}{p I_0\left(\sqrt{\frac{p}{\kappa}} R\right)} - \frac{Q'}{p c_p p^2} \frac{(1 - e^{-pt'})}{I_0\left(\sqrt{\frac{p}{\kappa}} R\right)} \dots\dots\dots (64)$

then $\bar{T} = \frac{(T_1 - T_0) I_0\left(\sqrt{\frac{p}{\kappa}} r\right)}{p I_0\left(\sqrt{\frac{p}{\kappa}} R\right)} - \frac{Q' (1 - e^{-pt'}) I_0\left(\sqrt{\frac{p}{\kappa}} r\right)}{p c_p p^2 I_0\left(\sqrt{\frac{p}{\kappa}} R\right)} + \frac{T_0}{p} + \frac{Q' (1 - e^{-pt'})}{p c_p p^2} \dots\dots (65)$

Some substitution $I_p(x) = i^{-p} J_p(ix)$

Let $\lambda = 1 \sqrt{\frac{p}{\kappa}}$ and then differentiating with respect to p gives

$$\frac{d\lambda}{dp} = \frac{1}{2} \frac{p^{-\frac{1}{2}}}{\sqrt{\kappa}} = \frac{1}{2 \sqrt{p\kappa}}$$

multiplying top and bottom by $p^{\frac{1}{2}}$ gives

$$\frac{d\lambda}{dp} = \frac{1 \sqrt{p}}{2 \sqrt{\kappa} p} = \frac{\lambda}{2p}$$

$$\text{also } \lambda^2 = \frac{1^2 p}{\kappa} = \frac{-p}{\kappa}$$

therefore $p = -\kappa \lambda^2$. When these values are substituted in (65)

$$\bar{T} = \frac{(T_1 - T_0) J_0(\lambda R)}{p J_0(\lambda R)} - \frac{Q'(1 - e^{-pt'})}{\rho c_p p^2 J_0(\lambda R)} + \frac{T_0}{p} + \frac{Q'(1 - e^{-pt'})}{\rho c_p p^2} \dots (66)$$

Inversion term by term gives

$$\bar{T}_1 = \frac{(T_1 - T_0) J_0(\lambda R)}{p J_0(\lambda R)} = \frac{j(p_n)}{l(p_n)} \dots (67)$$

$$p_n(t) = \frac{j(p_n)}{l'(p_n)} e^{p_n t}$$

$$l(p_n) = p J_0(\lambda R)$$

$$l'(p_n) = \frac{dl(p_n)}{dp} = J_0(\lambda R) \frac{dp}{dp} + p \frac{dl(p)}{d\lambda} \cdot \frac{d\lambda}{dp} = J_0(\lambda R) - \frac{\lambda R}{2} J_1(\lambda R)$$

There is a simple pole at $p_n = 0$

$$p_{(0)}^t = \frac{j(p_0) e^{p_n t}}{j'(p_0)} = \lim_{\lambda \rightarrow 0} \frac{(T_1 - T_0) J_0(\lambda r)}{J_0(\lambda R) - \frac{\lambda R}{2} J_1(\lambda R)} \dots\dots\dots (68)$$

$$= \frac{(T_1 - T_0) \cdot 1}{1 - 0}$$

$$= (T_1 - T_0)$$

There is a pole whenever $J_0(\lambda R) = 0$

$$p_n^t = \frac{j(p_n) e^{p_n t}}{j'(p_n)} = \lim_{J_0(\lambda R) \rightarrow 0} \frac{(T_1 - T_0) J_0(\lambda r) e^{p_n t}}{J_0(\lambda R) - \frac{\lambda R}{2} J_1(\lambda R)} = \frac{(T_1 - T_0) J_0(\lambda r) e^{-\lambda \lambda_n^2 t}}{0 - \frac{\lambda R}{2} J_1(\lambda R)} \dots\dots\dots (69)$$

$$p_n^t = (T_1 - T_0) \sum_{n=1}^{\infty} \frac{-2}{R} \frac{J_0(\lambda_n r)}{\lambda_n J_1(\lambda_n R)} e^{-\lambda \lambda_n^2 t} \dots\dots\dots (70)$$

$$T_{1A} = (T_1 - T_0) - \frac{2(T_1 - T_0)}{R} \sum_{n=1}^{\infty} e^{-\lambda \lambda_n^2 t} \frac{J_0(\lambda_n r)}{\lambda_n J_1(\lambda_n R)} \dots\dots\dots (71)$$

$$\text{Now } \bar{T}_2 = \frac{-Q'(1 - e^{-pt'})}{p c_p p^2 J_0(\lambda R)} J_0(\lambda r) \dots\dots\dots (72)$$

There is a double pole at $p_n = 0$ and also a pole whenever $J_0(\lambda R) = 0$.

For the residue at the double pole $p = 0$

$$p_n(t) = (A_1 + A_2 t) e^{p_n t} = e^{p_n t} \sum_{s=1}^{s=m} \frac{A_s t^{s-1}}{(s-1)!}$$

$$A_s = \frac{\phi_n^{m-s}(p_n)}{(m-s)!} \dots \text{where } s = 1, 2, \dots, m$$

$$\phi_n(p) = (p - p_n)^m \bar{f}(p)$$

$$\phi_n^{m-s}(p_n) = \left[\frac{d^{m-s}}{dp^{m-s}} \phi_n(p) \right]_{p_n}$$

at $m = 2, s = 1, n = 0$

$$\phi_n^{m-s}(p_n) = \left[\frac{d^{m-s}}{dp^{m-s}} \frac{(p - p_n)^2 \left(\frac{-Q'}{p c_p} \right) (1 - e^{-pt'}) J_0(\lambda r)}{p^2 J_0(\lambda R)} \right]_{p_n} \dots (73)$$

$$\frac{\phi_n^{m-s}(p_n)}{\frac{-Q'}{p c_p}} = \left[\frac{p^2 J_0(\lambda R)}{p^2 J_0(\lambda R)} \left[\begin{aligned} & (p - p_n)^2 (1 - e^{-pt'}) (-r) J_1(\lambda r) \frac{d\lambda}{dp} \\ & (p - p_n)^2 J_0(\lambda r) e^{-pt'} (-t') \frac{dp}{dp} \\ & (1 - e^{-pt'}) J_0(\lambda r) 2(p - p_n) \frac{dp}{dp} \end{aligned} \right] \dots (74) \right. \\ \left. - (p - p_n)^2 (1 - e^{-pt'}) J_0(\lambda r) \left[\frac{2p dp}{dp} J_0(\lambda R) + p^2 (-R) J_1(\lambda R) \frac{d\lambda}{dp} \right] \right]_{p_n=0} \\ \frac{p^4 J_0^2(\lambda R)}{p^4 J_0^2(\lambda R)}$$

$$\frac{\phi_n^{m-s}(p_n)}{\frac{-Q'}{p c_p}} = p^2(1) \left[p^2(1 - e^{-pt'}) (-r) J_1(\lambda r) \frac{d\lambda}{dp} + p^2(1) e^{-pt'} t' + (1 - e^{-pt'}) 2p \right] \\ - p^2(1 - e^{-pt'}) (1) \left[2p(1) + p^2(-R) J_1(\lambda R) \frac{d\lambda}{dp} \right]$$

$$p^4(1)$$

$$\phi_n^{m-s}(p_n) = \frac{p^2 e^{-pt'}}{p^2} = e^0 t' = t'$$

$$\phi_n^{m-s}(p_n) = \frac{-Q't'}{\rho c_p}$$

$$A_s = \frac{1}{(m-s)!} \phi_n^{m-s}(p_n)$$

$$A_{s=1} = \frac{1}{(2-1)!} \cdot \frac{-Q't'}{\rho c_p} = \frac{-Q't'}{\rho c_p}$$

at $m = 2, s = 2, n = 0$

$$\phi_n^{m-s}(p_n) = \left[\frac{d^{2-2}}{dp^{2-2}} \frac{(p-p_n)^2 \left(\frac{-Q'}{\rho c_p} \right) (1 - e^{-pt'}) J_0(\lambda r)}{p^2 J_0(\lambda R)} \right]_{p_n=0} \dots (75)$$

$$= \frac{(1) p^2 \frac{-Q'}{\rho c_p} (1-1) J_0(\lambda R)}{p^2 J_0(\lambda R)}$$

$$= \frac{-Q' (0) (1)}{\rho c_p (1)}$$

$$= 0$$

$$A_{s=2} = \frac{1}{(m-s)!} \phi_n^{m-s}(p_n) = \frac{1}{(2-2)!} (0) = 0$$

$$\rho_n(t) = (A_1 + A_2 t) e^{p_n t} = \left(\frac{-Q't'}{\rho c_p} + 0t \right) e^0 = \frac{-Q't'}{\rho c_p} \dots (76)$$

now to find the pole at $J_0(\lambda R) = 0$

$$p_n(t) = \frac{j(p_n)}{l'(p_n)} e^{p_n t}$$

$$\bar{f}(p) = \frac{-Q' J_0(\lambda r)}{p c_p p^2 J_0(\lambda R)} \dots \dots \dots (77)$$

$$l(p) = p^2 J_0(\lambda R)$$

$$l'(p) = 2p \frac{dp}{dp} J_0(\lambda R) + p^2 \left[\frac{d J_0(\lambda R)}{d \lambda} \cdot \frac{d \lambda}{dp} \right]$$

$$= 2p J_0(\lambda R) + p^2 \frac{d \lambda}{dp} [-R J_1(\lambda R)]$$

$$= 2p J_0(\lambda R) + p^2 \frac{\lambda}{2p} [-R J_1(\lambda R)]$$

$$= p \left[2 J_0(\lambda R) - \frac{\lambda R}{2} J_1(\lambda R) \right]$$

$$p_n(t) = \left[\frac{-Q' J_0(\lambda r) e^{-\kappa \lambda^2 t}}{p^2 J_0(\lambda R) - \frac{\lambda R}{2} J_1(\lambda R)} \right] J_0(\lambda R) = 0$$

$$= \frac{-Q' J_0(r) e^{-\kappa \lambda^2 t}}{p^2 J_0 - \frac{\lambda R}{2} J_1(\lambda R)}$$

$$= \frac{-Q' J_0(\lambda r) e^{-\kappa \lambda^2 t}}{p^2 (-\kappa \lambda^2) - \frac{\lambda R}{2} J_1(\lambda R)}$$

$$\sum p_n(t) = - \frac{2Q'}{p c_p \kappa R} \sum_{n=1}^{\infty} e^{-\kappa \lambda_n^2 t} \frac{J_0(\lambda_n r)}{\lambda_n^2 J_1(\lambda_n R)} \dots \dots \dots (78)$$

$$T_2 = - \frac{Q' t'}{p c_p} - \frac{2Q'}{p c_p \kappa R} \sum_{n=1}^{\infty} e^{-\kappa \lambda_n^2 t} \frac{J_0(\lambda_n r)}{\lambda_n^2 J_1(\lambda_n R)} \dots \dots \dots (79)$$

$$\bar{T}_3 = \frac{T_0}{p} \dots\dots\dots (80)$$

$$T_3 = T_0 \dots\dots\dots (81)$$

$$\bar{T}_4 = \frac{Q'}{\rho c_p} \frac{(1 - e^{-pt'})}{p^2} \dots\dots\dots (82)$$

$$\bar{T}_4 = \frac{Q'}{\rho c_p} \cdot \frac{1}{p^2} - \frac{Q'}{\rho c_p} \frac{e^{-pt'}}{p^2}$$

$$T_4 = \frac{Q' t}{\rho c_p} - \frac{Q'}{\rho c_p} \left[\begin{array}{l} 0 \text{ when } 0 < t < t' \\ t-t' \text{ when } t > t' \end{array} \right] \dots\dots\dots (83)$$

The full solution is

$$\begin{aligned} T = & (T_1 - T_0) - \frac{2}{R} (T_1 - T_0) \sum_1^{\infty} e^{-\kappa \lambda_n^2 t} \frac{J_0(\lambda_n r)}{\lambda_n J_1(\lambda_n R)} \\ & - \frac{Q' t'}{\rho c_p} - \frac{2Q'}{\rho c_p \kappa R} \sum_1^{\infty} \frac{(1 - e^{-\kappa \lambda_n^2 t'}) e^{-\kappa \lambda_n^2 t}}{\lambda_n^3 J_1(\lambda_n R)} \\ & + T_0 + \frac{Q' t}{\rho c_p} - \frac{Q'}{\rho c_p} \left[\begin{array}{l} 0 \text{ when } 0 < t < t' \\ t-t' \text{ when } t > t' \end{array} \right] \dots\dots\dots (84) \end{aligned}$$

where $\pm \lambda_n$, $n = 1, 2, 3, \dots$ are the roots of the equation

$$J_0(\lambda R) = 0 \dots\dots\dots (42)$$

In the past workers (26) have treated a chemical reaction as a heat source in the heat conduction equation

$$\kappa \nabla^2 T = \frac{\partial T}{\partial t} - \frac{Q'}{\rho c_p} \dots\dots\dots(34)$$

Here, the crosslinking reaction in the formation of polyurethane elastomers will be treated as a heat source and represented as a function of temperature and time. Its form has been developed previously in this work as

$$f(T,t) = \alpha_1 e^{\beta T} \left[e^{\gamma t} - 0.9 e^{ct} \right] \dots\dots\dots(56)$$

The overall equation will be solved numerically for a number of representative propellant shapes namely, the solid cylinder, an end effect on the solid cylinder, the thick walled hollow cylinder, the thin walled hollow cylinder, and the thick walled star shaped centre hollow cylinder. The Laplacian operator ∇^2 is used in cylindrical coordinates. Certain assumptions are necessary; 1) The material is solid throughout the polymerization, 2) The thermal diffusivity, thermal conductivity, density and heat capacity of the solid propellant and the viscous mixture of ingredients from which it is formed are the same, 3) The thermal diffusivity, thermal conductivity, density and heat capacity are independent of temperature in the range of interest (i.e. 77 to 200°F). The overall equation in cylindrical coordinates is

$$\kappa \left[\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial \theta^2} + \frac{\partial^2 T}{\partial z^2} \right] = \frac{\partial T}{\partial t} - \alpha_1 e^{\beta T} \left[e^{\gamma t} - 0.9 e^{ct} \right] \dots\dots(85)$$

Since an analytical solution has not yet been found for this equation it has been necessary to turn to a numerical method. Therefore, the differential equation will be converted into a finite difference equation, in this case using central differences, as given by Mickley (87c).

$$\frac{\partial^2 T}{\partial r^2} = \frac{T_{m+1,p,o,n} - 2T_{m,p,o,n} + T_{m-1,p,o,n}}{(\Delta r)^2} \dots\dots\dots(86)$$

$$\frac{\partial T}{\partial r} = \frac{T_{m+1,p,o,n} - T_{m,p,o,n}}{(\Delta r)} \dots\dots\dots(87)$$

$$\frac{\partial^2 T}{\partial \theta^2} = \frac{T_{m,p,o+1,n} - 2T_{m,p,o,n} + T_{m,p,o-1,n}}{(\Delta \theta)^2} \dots\dots\dots(88)$$

$$\frac{\partial^2 T}{\partial z^2} = \frac{T_{m,p+1,o,n} - 2T_{m,p,o,n} + T_{m,p-1,o,n}}{(\Delta z)^2} \dots\dots\dots(89)$$

$$\frac{\partial T}{\partial t} = \frac{T_{m,p,o,n+1} - T_{m,p,o,n}}{(\Delta t)} \dots\dots\dots(90)$$

$$\frac{1}{r} = \frac{1}{m(\Delta r)} \dots\dots\dots(91)$$

$$\frac{1}{r^2} = \frac{1}{m^2(\Delta r)^2} \dots\dots\dots(92)$$

$$T = T_{m,p,o,n} \dots\dots\dots(93)$$

$$t = n (\Delta t) \dots\dots\dots(94)$$

The development of equation (87) following the method in Mickley (87c). Since $T = f(r, \theta, z, t)$, the function $f(r, \theta, z, t)$ may be expanded about r , for fixed values of θ, z , and t , by using Taylor's Series

$$T(r+\Delta r, \theta, z, t) = T(r, \theta, z, t) + \Delta r \frac{\partial T}{\partial r} + \frac{(\Delta r)^2}{2} \frac{\partial^2 T}{\partial r^2} + \frac{(\Delta r)^3}{6} \frac{\partial^3 T}{\partial r^3} + \frac{(\Delta r)^4}{24} \frac{\partial^4 T}{\partial r^4} \dots (95)$$

As long as (Δr) is sufficiently small, the terms of the order of $(\Delta r)^2$ and higher, may be neglected, and a first approximation to $\frac{\partial T}{\partial r}$ is

$$\frac{\partial T}{\partial r} = \frac{T(r+\Delta r, \theta, z, t) - T(r, \theta, z, t)}{(\Delta r)} = \frac{T_{m+1, p, \theta, n} - T_{m, p, \theta, n}}{(\Delta r)}$$

similarly

$$\frac{\partial T}{\partial t} = \frac{T(r, \theta, z, t+\Delta t) - T(r, \theta, z, t)}{(\Delta t)} = \frac{T_{m, p, \theta, n+1} - T_{m, p, \theta, n}}{(\Delta t)}$$

Two series expansions are needed to obtain the first approximation to $\frac{\partial^2 T}{\partial r^2}$, these are

$$T(r+\Delta r, \theta, z, t) = T(r, \theta, z, t) + \Delta r \frac{\partial T}{\partial r} + \frac{\Delta r^2}{2} \frac{\partial^2 T}{\partial r^2} + \frac{\Delta r^3}{6} \frac{\partial^3 T}{\partial r^3} + \frac{\Delta r^4}{24} \frac{\partial^4 T}{\partial r^4} \dots$$

$$T(r-\Delta r, \theta, z, t) = T(r, \theta, z, t) - \Delta r \frac{\partial T}{\partial r} + \frac{\Delta r^2}{2} \frac{\partial^2 T}{\partial r^2} - \frac{\Delta r^3}{6} \frac{\partial^3 T}{\partial r^3} + \frac{\Delta r^4}{24} \frac{\partial^4 T}{\partial r^4} \dots$$

adding these two equations and neglecting terms of the order of Δr^4 gives the first approximation to $\frac{\partial^2 T}{\partial r^2}$. This is

$$T(r+\Delta r, \theta, z, t) + T(r-\Delta r, \theta, z, t) = 2 T(r, \theta, z, t) + \Delta r^2 \frac{\partial^2 T}{\partial r^2} \dots\dots\dots$$

$$\text{thus } \frac{\partial^2 T}{\partial r^2} = \frac{T_{m+1,p,o,n} - 2T_{m,p,o,n} + T_{m-1,p,o,n}}{(\Delta r)^2} \dots\dots\dots(86)$$

In a similar manner

$$\frac{\partial^2 T}{\partial \theta^2} = \frac{T_{m,p,o+1,n} - 2T_{m,p,o,n} + T_{m,p,o-1,n}}{(\Delta \theta)^2} \dots\dots(88)$$

$$\text{and } \frac{\partial^2 T}{\partial z^2} = \frac{T_{m,p+1,o,n} - 2T_{m,p,o,n} + T_{m,p-1,o,n}}{(\Delta z)^2} \dots\dots\dots(89)$$

The three dimensional differential equation (85) when changed to a finite difference equation is

$$\begin{aligned} & \times \left[\frac{T_{m+1,p,o,n} - 2T_{m,p,o,n} + T_{m-1,p,o,n}}{(\Delta r)^2} + \frac{1}{(\Delta r)_m} \frac{T_{m+1,p,o,n} - T_{m,p,o,n}}{(\Delta r)} + \right. \\ & \left. \frac{T_{m,p,o+1,n} - 2T_{m,p,o,n} + T_{m,p,o-1,n}}{m^2(\Delta r)^2} + \frac{T_{m,p+1,o,n} - 2T_{m,p,o,n} + T_{m,p-1,o,n}}{(\Delta \theta)^2} + \frac{T_{m,p+1,o,n} - 2T_{m,p,o,n} + T_{m,p-1,o,n}}{(\Delta z)^2} \right] \\ & = \frac{T_{m,p,o,n+1} - T_{m,p,o,n}}{(\Delta t)} - \alpha_1 e^{\beta T} \left[e^{\gamma n \Delta t} e^{e^T} - 0.9 e^{cn \Delta t} \right] \dots\dots(96) \end{aligned}$$

$$\text{Letting } M = \frac{(\Delta r)^2}{\alpha(\Delta t)} \dots\dots\dots(97)$$

$$Z = \frac{(\Delta z)^2}{\alpha(\Delta t)} \dots\dots\dots(98)$$

$$K = \frac{(\Delta \theta)^2}{\alpha(\Delta t)} \dots\dots\dots(99)$$

rearranging and collecting terms gives:

$$\begin{aligned}
 & \left[\frac{(1+1/m)}{M} T_{m+1,p,o,n} + \left[\frac{(M-2-1/m)}{M} + \frac{(-2/m^2)}{M(\Delta\theta)^2} - \frac{2}{Z} \right] T_{m,p,o,n} \right. \\
 & \quad \frac{1}{M} T_{m-1,p,o,n} + \frac{1}{m^2 M(\Delta\theta)^2} T_{m,p,o+1,n} + \frac{1}{m^2 M(\Delta\theta)^2} T_{m,p,o-1,n} \\
 & \quad \left. \frac{1}{Z} T_{m,p+1,o,n} + \frac{1}{Z} T_{m,p-1,o,n} \right] \\
 & = T_{m,p,o,n+1} - \alpha_1 \Delta t e^{\beta T} \left[\begin{array}{cc} \gamma_{nat} e^{\rho T} & \\ e & - 0.9 e^{cn\Delta t} \end{array} \right] \dots\dots\dots(100)
 \end{aligned}$$

rearranging again and letting $\alpha = \alpha_1 \Delta t$ gives

$$\begin{aligned}
 T_{m,p,o,n+1} = & \frac{(1+1/m)}{M} T_{m+1,p,o,n} + \left[\frac{(M-2-1/m)}{M} + \frac{(-2/m^2)}{M(\Delta\theta)^2} - \frac{2}{Z} \right] T_{m,p,o,n} \\
 & + \frac{1}{M} T_{m-1,p,o,n} + \frac{T_{m,p,o+1,n}}{m^2 M(\Delta\theta)^2} + \frac{T_{m,p,o-1,n}}{m^2 M(\Delta\theta)^2} \\
 & + \frac{1}{Z} T_{m,p+1,o,n} + \frac{1}{Z} T_{m,p-1,o,n} \\
 & + \alpha e^{\beta T} \left[\begin{array}{cc} \gamma_{nat} e^{\rho T} & \\ e & - 0.9 e^{cn\Delta t} \end{array} \right] \dots\dots\dots(101)
 \end{aligned}$$

Now it will be noted that when $r = 0$, $m = 0$. Thus for this case the terms $1/m$ and $1/m^2$ will become $1/0$ which is indeterminate. Therefore another equation must be found to use when $r = 0$. This is done by evaluating the term

$$\left[\frac{\partial^2 T}{\partial r^2} + \frac{\partial T}{r \partial r} + \frac{\partial^2 T}{r^2 \partial \theta^2} + \frac{\partial^2 T}{\partial z^2} \right]_{r=0} \dots\dots\dots(102)$$

noting that only the groups $\frac{\partial T}{r \partial r}$ and $\frac{\partial^2 T}{r^2 \partial \theta^2}$ give rise to trouble since

they would be $\frac{\partial T}{\partial r}$ and $\frac{\partial^2 T}{\partial \theta^2}$ at $r = 0$, the usual method is to apply

L'Hopitals Rule. The term $\frac{\partial T}{r \partial r}$ can be written $\frac{\frac{\partial T}{\partial r}}{r}$ differentiating top

and bottom gives

$$\frac{\frac{\partial^2 T}{\partial r^2}}{\frac{\partial r}{\partial r}} = \frac{\frac{\partial^2 T}{\partial r^2}}{1} = \frac{\partial^2 T}{\partial r^2} \dots\dots\dots (103)$$

This takes care of the first group. The second group $\frac{\partial^2 T}{r^2 \partial \theta^2}$ can be written $\frac{\partial^2 T}{\partial \theta^2}$ and when it is differentiated with respect to r gives

$$\frac{\frac{\partial^3 T}{\partial r \partial \theta^2}}{2r \frac{\partial r}{\partial r}} = \frac{\frac{\partial^3 T}{\partial r \partial \theta^2}}{2r} \dots\dots\dots (104)$$

which is still indeterminate at $r = 0$. Thus it must be differentiated with respect to r once more and it then gives

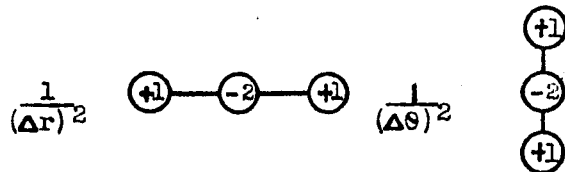
$$\frac{\frac{\partial^4 T}{\partial r^2 \partial \theta^2}}{2 \frac{\partial r}{\partial r}} = \frac{\frac{\partial^4 T}{\partial r^2 \partial \theta^2}}{2} \dots\dots\dots (105)$$

replacing these groups in equation (102) gives

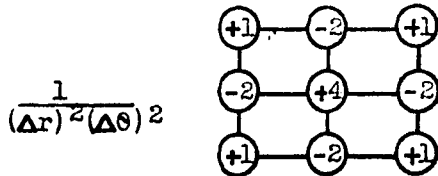
$$\left[\frac{\partial^2 T}{\partial r^2} + \frac{\partial T}{r \partial r} + \frac{\partial^2 T}{r^2 \partial \theta^2} + \frac{\partial^2 T}{\partial z^2} \right]_{r=0} = \left[\frac{2 \partial^2 T}{\partial r^2} + \frac{\partial^4 T}{2 \partial r^2 \partial \theta^2} + \frac{\partial^2 T}{\partial z^2} \right]_{r=0} \dots\dots\dots(106)$$

The next problem is to find a finite difference equivalent of $\frac{\partial^4 T}{\partial r^2 \partial \theta^2}$

using the computational molecule in Lapidus (78), who gives



now using row times column multiplication



$$\frac{\partial^4 T}{\partial r^2 \partial \theta^2} = \begin{bmatrix} T_{m+1,p,o+1,n} & -2 T_{m+1,p,o,n} & + T_{m+1,p,o-1,n} \\ -2 T_{m,p,o+1,n} & + 4 T_{m,p,o,n} & -2 T_{m,p,o-1,n} \\ + T_{m-1,p,o+1,n} & -2 T_{m-1,p,o,n} & + T_{m-1,p,o-1,n} \end{bmatrix} \frac{1}{(\Delta r)^2 (\Delta \theta)^2} \dots\dots(107)$$

Thus the finite difference equation for $r = 0$ is

$$\begin{aligned} & 2 \left[\frac{T_{m+1,p,o,n} - 2 T_{m,p,o,n} + T_{m-1,p,o,n}}{(\Delta r)^2} \right] + \frac{1}{2 (\Delta r)^2 (\Delta \theta)^2} \left[T_{m+1,p,o+1,n} \right. \\ & + T_{m+1,p,o-1,n} - 2 T_{m,p,o+1,n} + 4 T_{m,p,o,n} - 2 T_{m,p,o-1,n} + T_{m-1,p,o+1,n} \\ & \left. - 2 T_{m-1,p,o,n} + T_{m-1,p,o-1,n} \right] + \frac{T_{m,p+1,o,n} - 2 T_{m,p,o,n} + T_{m,p-1,o,n}}{(\Delta z)^2} \\ & = \frac{T_{m,p,o,n+1} - T_{m,p,o,n}}{(\Delta t)} - \alpha_1 e^{\beta T} \left[\begin{matrix} \gamma_{nat} e^{\rho T} & \\ e & - 0.9 e^{cn \Delta t} \end{matrix} \right] \dots\dots(108) \end{aligned}$$

$$\begin{aligned}
 T_{m,p,o,n+1} = & \left[\frac{2}{M} - \frac{1}{M(\Delta\theta)^2} \right] T_{m+1,p,o,n} + \left[\frac{2}{M} - \frac{1}{M(\Delta\theta)^2} \right] T_{m-1,p,o,n} \\
 & + \left[\frac{M}{M} - \frac{4}{M} + \frac{2}{M(\Delta\theta)^2} - \frac{2}{Z} \right] T_{m,p,o,n} + \frac{1}{2M(\Delta\theta)^2} \left[T_{m+1,p,o+1,n} \right. \\
 & + T_{m+1,p,o-1,n} - 2T_{m,p,o+1,n} - 2T_{m,p,o-1,n} + T_{m-1,p,o+1,n} \\
 & + T_{m-1,p,o-1,n} \left. \right] + \frac{1}{Z} T_{m,p+1,o,n} + \frac{1}{Z} T_{m,p-1,o,n} \\
 & + \alpha e^{\rho T} \left[e^{\gamma n \Delta t} e^{\rho T} - 0.9 e^{cn \Delta t} \right] \dots\dots\dots(109)
 \end{aligned}$$

Some Special Cases:

1) The solid rod of infinite length, here $\frac{\partial^2 T}{\partial z^2}$ and $\frac{\partial^2 T}{\partial \theta^2} = 0$. Thus equation (96) becomes

$$\begin{aligned}
 T_{m,n+1} = & \frac{(1+1/m)}{M} T_{m+1,n} + \frac{(M-2-1/m)}{M} T_{m,n} + \frac{1}{M} T_{m-1,n} \\
 & + \alpha e^{\rho T} \left[e^{\gamma n \Delta t} e^{\rho T} - 0.9 e^{cn \Delta t} \right] \dots\dots\dots(110)
 \end{aligned}$$

and in a similar manner the differential equation for the case $r = 0$ is

$$T_{m,n+1} = \frac{4}{M} T_{m+1,n} + \frac{(M-4)}{M} T_{m,n} + \alpha e^{\rho T} \left[e^{\gamma n \Delta t} e^{\rho T} - 0.9 e^{cn \Delta t} \right] \dots\dots(111)$$

2) The solid rod of finite length. Here $\frac{\partial^2 T}{\partial \theta^2} = 0$, and the finite difference equivalent of equation (96) is

$$T_{m,p,n+1} = \frac{(1+1/m)}{M} T_{m+1,p,n} + \left[\frac{(M-2-1/m)}{M} - \frac{2}{Z} \right] T_{m,p,n} + \frac{1}{M} T_{m-1,p,n} \\ + \frac{1}{Z} T_{m,p+1,n} + \frac{1}{Z} T_{m,p-1,n} + \alpha e^{\rho T} \left[\frac{\gamma_{n\Delta t} e^{\rho T}}{e} - 0.9 e^{cn\Delta t} \right] \dots (112)$$

and the centre equation is

$$T_{m,p,n+1} = \frac{4}{M} T_{m+1,p,n} + \left[\frac{(M-4)}{M} - \frac{2}{Z} \right] T_{m,p,n} + \frac{1}{Z} T_{m,p+1,n} + \frac{1}{Z} T_{m,p-1,n} \\ + \alpha e^{\rho T} \left[\frac{\gamma_{n\Delta t} e^{\rho T}}{e} - 0.9 e^{cn\Delta t} \right] \dots (113)$$

3) For the hollow cylinder of infinite length: Only one equation is required

$$T_{m,n+1} = \frac{(1+1/m)}{M} T_{m+1,n} + \left[\frac{(M-2-1/m)}{M} \right] T_{m,n} + \frac{1}{M} T_{m-1,n} \\ + \alpha e^{\rho T} \left[\frac{\gamma_{n\Delta t} e^{\rho T}}{e} - 0.9 e^{cn\Delta t} \right] \dots (110)$$

4) For the hollow cylinder of finite length

$$T_{m,p,n+1} = \frac{(1+1/m)}{M} T_{m+1,p,n} + \left[\frac{(M-2-1/m)}{M} - \frac{2}{Z} \right] T_{m,p,n} + \frac{1}{M} T_{m-1,p,n} \\ + \frac{1}{Z} T_{m,p+1,n} + \frac{1}{Z} T_{m,p-1,n} + \alpha e^{\rho T} \left[\frac{\gamma_{n\Delta t} e^{\rho T}}{e} - 0.9 e^{cn\Delta t} \right] \dots (114)$$

5) For the hollow cylinder of infinite length with a star shaped

hollow centre, $\frac{\partial^2 T}{\partial z^2} = 0$, then

$$\begin{aligned}
 T_{m,o,n+1} = & \frac{(1+1/m)}{M} T_{m+1,o,n} + \left[\frac{(M-2-1/m)}{M} - \frac{2/m^2}{M(\Delta\theta)^2} \right] T_{m,o,n} + \frac{1}{M} T_{m-1,o,n} \\
 & + \frac{1}{M} T_{m-1,o,n} + \frac{1}{m^2 M(\Delta\theta)^2} T_{m,o+1,n} + \frac{1}{m^2 M(\Delta\theta)^2} T_{m,o-1,n} \\
 & + \alpha e^{\beta T} \left[e^{\gamma_{n\Delta t} e^{\rho T}} - 0.9 e^{cn\Delta t} \right] \dots\dots\dots(115)
 \end{aligned}$$

6) For the solid filled hollow centre cylinder of infinite length with a star shaped mold or form in the centre: The main equation is the same as equation (115) but here a centre equation for $r = 0$ must be used, it is

$$\begin{aligned}
 T_{m,o,n+1} = & \left[\frac{2}{M} - \frac{1}{M(\Delta\theta)^2} \right] T_{m+1,o,n} + \left[\frac{2}{M} - \frac{1}{M(\Delta\theta)^2} \right] T_{m-1,o,n} + \\
 & \left[\frac{M-4}{M} + \frac{2}{M(\Delta\theta)^2} \right] T_{m,o,n} + \frac{1}{2M(\Delta\theta)^2} \left[T_{m+1,o+1,n} + T_{m+1,o-1,n} \right. \\
 & \left. - 2T_{m,o+1,n} - 2T_{m,o-1,n} + T_{m-1,o+1,n} + T_{m-1,o-1,n} \right] \\
 & + \alpha e^{\beta T} \left[e^{\gamma_{n\Delta t} e^{\rho T}} - 0.9 e^{cn\Delta t} \right] \dots\dots\dots(116)
 \end{aligned}$$

No discussion of solution of finite difference equations would be complete without a discussion of convergence and stability of the numerical methods used to approximate the solution of a partial differential equation, (Ref. 87d). Unless these criteria are fulfilled, one cannot trust the results of the calculations.

It will be recalled that convergence implies that the finite difference approximation will reduce to the exact solution when the size

of the increments is made infinitesimally small. Stability implies that errors associated with the use of increments of finite size, numerical mistakes, or round-off errors will not grow as the calculation proceeds.

Unfortunately, analytical tests for convergence and stability that are valid for a wide variety of problems that arise in practice are not available. However tests have been developed which apply to finite difference methods used to solve linear partial differential equations with constant coefficients. (Mickley 87e).

Errors due to truncation of the Taylor series may also be present.

Stability test on the equation for the solid cylinder:

The finite difference equation for the solid cylinder with the assumption of infinite length was

$$T_{m,n+1} = \left(\frac{1+1/m}{M}\right) T_{m+1,n} + \left[\frac{(M-2-1/m)}{M}\right] T_{m,n} + \frac{1}{M} T_{m-1,n} + \frac{Q' \Delta t}{c_p} \dots (110)$$

taking only the part of $T_{m,n}$ equal to the first three terms in the above equation gives

$$T_{m,n+1} = \left(\frac{1+1/m}{M}\right) T_{m+1,n} + \left[\frac{(M-2-1/m)}{M}\right] T_{m,n} + \frac{1}{M} T_{m-1,n} \dots (117)$$

Putting this in the form of equation (10-30a) in reference (87f) gives

$$T_{m+1,n} + \frac{(M-2-1/m)}{(1+1/m)} T_{m,n} + \frac{1}{(1+1/m)} T_{m-1,n} = \frac{M}{(1+1/m)} T_{m,n+1}$$

comparing this to equation (10-30a) which is

$$T_{m+1,n} - 2a T_{m,n} + b^2 T_{m-1,n} = c T_{m,n+1} + d T_{m,n-1} \dots\dots\dots(10-30a)$$

$$-2a = \frac{(M-2-1/m)}{(1+1/m)}; \quad b^2 = \frac{1}{(1+1/m)}; \quad c = \frac{M}{(1+1/m)}; \quad d = 0$$

$$\text{and then} \quad a = \frac{(-M+2+1/m)}{2(1+1/m)}; \quad b = \frac{1}{(1+1/m)}; \quad c = \frac{M}{(1+1/m)}; \quad d = 0$$

Now do the boundary conditions fit the conditions

$$T_{0,n} = h_1 T_{1,n} + u(n) \quad , \quad \text{at } m = 0$$

$$\text{and} \quad T_{L,n} = h_2 T_{L-1,n} + v(n) \quad \text{at } m = L ?$$

$$\text{at } m = 0, \quad \left(\frac{\partial T}{\partial r} \right)_r = 0$$

$$\text{then} \quad \frac{(T_{1,n} - T_{0,n})}{(\Delta r)} = 0$$

$$\text{therefore} \quad T_{0,n} = T_{1,n}$$

$$\text{this fits} \quad T_{0,n} = h_1 T_{1,n} + u(n) \quad \text{if } h_1 = 1, \text{ and } u(n) = 0$$

$$\text{at } m = L, \quad T_{L,n} = T_a$$

$$\text{when compared to } T_{L,n} = h_2 T_{L-1,n} + v(n) \quad h_2 = 0 \text{ and } v(n) = T_a$$

Do these boundary conditions satisfy the following conditions?

$$\left. \begin{array}{l} 0 \leq h_1 \leq \frac{1}{|b|} \\ 0 \leq h_2 \leq \frac{1}{|b|} \end{array} \right\} \dots\dots\dots(10-31)$$

$$|b| = +\sqrt{\frac{1}{1+1/m}} \quad \therefore \quad \frac{1}{|b|} = +\sqrt{(1+1/m)}$$

Now here m goes from 0 to 6, at $m = 0$, $\frac{1}{|b|} = \infty$
then $0 \leq 1 \leq \infty$ fits the condition.

$$\text{At } m = 6, \quad \frac{1}{|b|} = \sqrt{(1+1/6)} = \sqrt{1.16666} = 1.08$$

and $0 \leq 0 \leq 1.08$ also meets this condition.

The equation is stable (1) if the roots of the equation

$$R^2 + \frac{2(a - b \cos \alpha)}{c} R + d = 0 \quad \dots\dots\dots(10-32)$$

given in (87g), do not exceed unity in absolute value for any real value of α . (2) Neither $R = +1$, nor $R = -1$ may be a repeated root of (10-32).

$$R^2 + \frac{2/M}{(1+1/m)} \left[\frac{-M+2+1/m}{2(1+1/m)} - \sqrt{\frac{1}{(1+1/m)}} \cos \alpha \right] R + 0 = 0 \quad \dots\dots(118)$$

$$\text{Then } R = 0, \text{ and } R = \frac{2}{M} \left[\frac{M-2-1/m}{2} + \sqrt{(1+1/m)} \cos \alpha \right]$$

The root $R = 0$ satisfies the requirement $-1 \leq R \leq +1$. When applied to the second root

$$-1 \leq \frac{2}{M} \left[\frac{M-2-1/m}{2} + \sqrt{(1+1/m)} \cos \alpha \right] \leq 1 \dots\dots\dots(119)$$

taking the right hand equality

$$\frac{2}{M} \left[\frac{M-2-1/m}{2} + \sqrt{(1+1/m)} \cos \alpha \right] \leq 1$$

$$M-2-1/m + 2 \sqrt{(1+1/m)} \cos \alpha \leq M$$

here any positive value will suffice, now taking the left hand equality

$$-1 \leq \frac{2}{M} \left[\frac{M-2-1/m}{2} + \sqrt{(1+1/m)} \cos \alpha \right]$$

$$-2M \leq -2 - 1/m + 2 \sqrt{(1+1/m)} \cos \alpha$$

here the equation will start at $m = 1$, and go to $m = 6$

$$\text{at } m = 1, \quad -2M \leq -2 - 1 + 2\sqrt{2} \cos \alpha$$

$$M = 0.086 \text{ and } 2.914$$

∴ M must be 2.914 or larger.

$$\text{at } m = 6 \quad -2M = -2 - 1/6 + 2 \sqrt{(1+1/6)} \cos \alpha$$

$$M = 0.00 \text{ and } 2.1666$$

∴ M must be 2.1666 or greater.

A check on the equation to be used at $m = 0$

$$T_{m,n+1} = \frac{4}{M} T_{m+1,n} + \frac{(M-4)}{M} T_{m,n} + \frac{Q' \Delta t}{\rho c_p} \dots\dots\dots(111)$$

Here it will be noted that if M is smaller than 4 the temperature at plane m would exert a negative influence on the temperature at the same plane one time increment later, a situation which is intolerable on physical grounds. Therefore the modulus M for the case of the solid cylinder must be 4 at least. A value of 4.5687 has been chosen for actual computations.

In the problem of the star shaped centre a term of the form

$$\left[\frac{(M-2-1/m)}{M} - \frac{2}{m^2 M (\Delta \theta)^2} \right] T_{m,p,o,n}$$

arises. In accordance with the above argument the coefficient must be equal or greater than zero

$$\therefore \left[\frac{M-2-1/m}{M} - \frac{2}{m^2 M (\Delta \theta)^2} \right] \geq 0 \dots\dots\dots(120)$$

Since the smallest $m = 5$ and $\Delta \theta = \frac{\pi}{50}$

$$\left[\frac{M-2-1/m}{M} - \frac{2 (50)^2}{25M \pi^2} \right] \geq 0 \dots\dots\dots(121)$$

∴ M must be 22.464 or larger.

The actual M used in the problem was 22.5 .

In the case of the end effect on the solid cylinder there is a coefficient of the form

$$\left[\frac{M-2-1/m}{M} - \frac{2}{Z} \right]$$

If M = 4.5687, and m = 1 then

$$\left[\frac{4.5687-2-1/1}{4.5687} - \frac{2}{Z} \right] \geq 0 \dots\dots\dots(122)$$

∴ Z must be 5.82495 or larger.

at m = 6

$$\left[\frac{4.5687-2-1/6}{4.5687} - \frac{2}{Z} \right] \geq 0 \dots\dots\dots(123)$$

∴ Z must be 3.8039 or larger.

If M is 4.5687 and K is 0.008104 and Δt is 0.04689 hours, are half inch intervals of Δz possible? Putting in half an inch for Δz gives

$$Z = \frac{(\Delta z)^2}{\Delta t K} = \frac{1}{4.144 \cdot 0.008,104 \cdot 0.04689} = 4.5687$$

which is too small. Next trying one inch intervals

$$Z = \frac{(\Delta z)^2}{\Delta t K} = \frac{1}{144 \cdot 0.008,104 \cdot 0.04689} = 18.275$$

This meets the condition.

The calculation of the boundary conditions at the star: The value of the dependent variable is specified along an irregular boundary. The value of the dependent variable at a net point near the boundary is found by extrapolation. Suppose that T_s is specified and T_B is desired. Linear extrapolation gives (see Figure 10-9 in Ref. 87k)

$$\frac{T_s - T_{B+1}}{\Delta B} = \frac{T_B - T_{B+1}}{\Delta r} \dots\dots\dots(124)$$

which may be used to relate T_B to T_s and T_{B+1} . At the tip of the star it was found best to use the theta direction rather than the radial as the point in question was nearer the point to be determined. The distance ΔB was found by solving the linear equation for the straight line in polar coordinates

$$r (\sin \theta - 1.437,069 \cos \theta) = -0.239,490 \dots\dots\dots(125)$$

at the appropriate angle and subtracting.

EXPERIMENTAL

Introduction

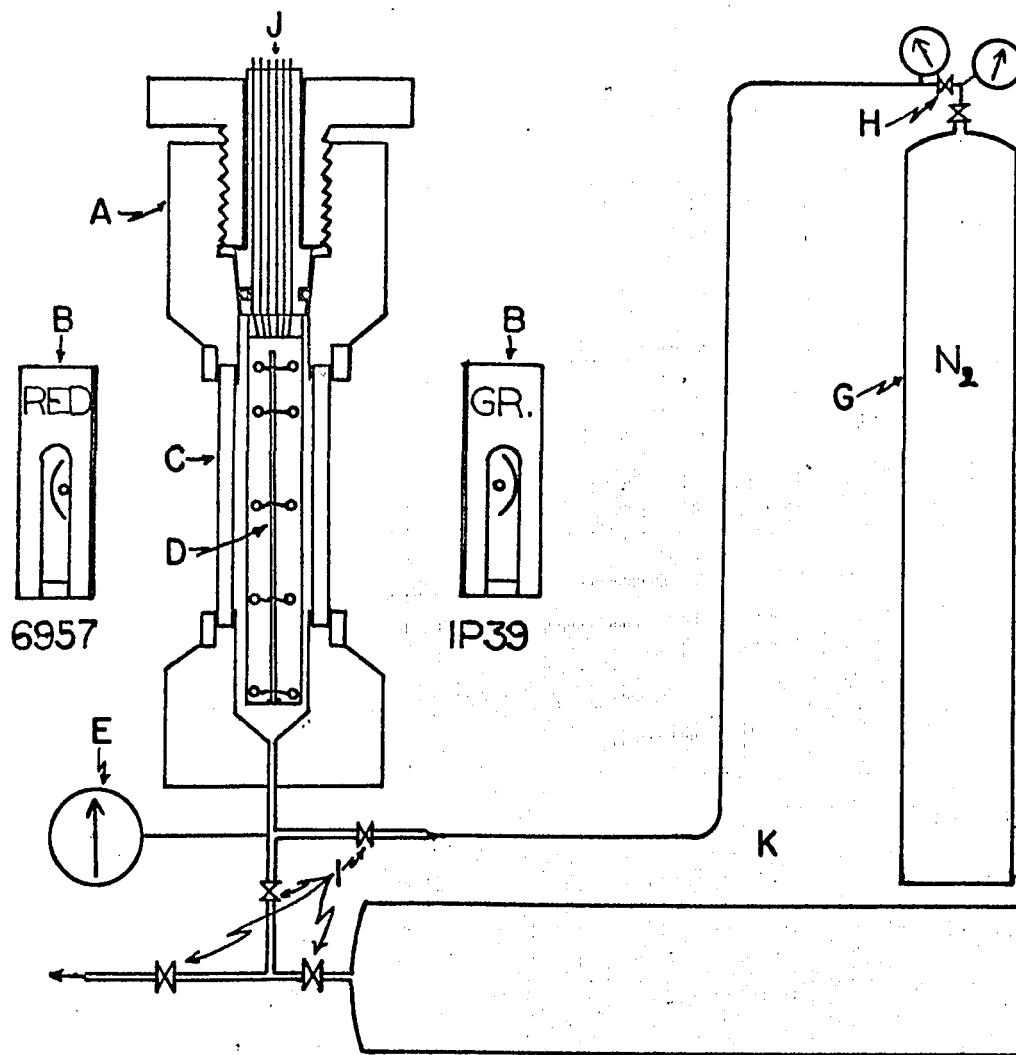
Since the objective was to see if any correlations existed between burning rate and polymerization temperature in a rocket grain, some experimental work was necessary. Burning rates were needed and temperature profiles were required. Burning rates could be measured directly, but the temperature gradients had to be obtained from the solution of a mathematical model because the facilities at hand were only extensive enough to permit the determination of the model parameters. Therefore the experimental work fell under the following headings:

1. Strand Burner
2. Polymer Production
3. Temperature Profiles
4. Measurement of Physical Properties
5. Microcalorimetry

Strand Burner

Strands, one quarter of an inch square and six inches long were cut at constant radii of 0.0, 0.5, 1.0, 1.5, 2.0, and 2.5 inches along the axial direction from a five inch diameter solid cylinder; and at constant radii of 1.5, 2.0625 and 2.625 inches from a hollow cylinder (Outer diameter equal to 5.25 inches and inner diameter equal to 3 inches) of ammonium perchlorate polyurethane propellant received from CARDE. To make the strands burn cigarette fashion they were coated on the external surface with a noninflammable material VYHH, a vinyl-chloride-

vinyl acetate copolymer. After conditioning in a room at fairly constant humidity they were placed in a jig where holes were drilled in them at intervals of 0.5, 1.0, 1.0 and 1.0 inches. Half ampere Buss lead fuse wire was threaded through and a nichrome ignition wire was placed in the hole nearest one end. The threaded strand was placed in the holder shown in Figure 6, which shows a strand burner card, front and back, in detail. The top wire on the left hand diagram is the nichrome firing wire and all the others, spaced at one inch intervals, are the lead fuse wires. The strand was held in place by tightening the tiny screw in the holder at the bottom. The right hand diagram shows the placing of the wires on the back. The card was attached to the removable head and placed in the burner as shown on Figure 3 and wires were attached to the various terminals on the top. Figure 3 is a schematic diagram of the strand burner set up but without the associated circuitry. It is essentially a pressure bomb with two armour glass windows connected to a surge tank of sufficient volume to keep the pressure constant during burning of the strand. A phototube, sensitive to red light, is situated behind a red glass filter outside the window on one side and another phototube, sensitive to green light, behind a green glass filter facing the window on the other side. A tank of nitrogen is present to supply the atmosphere for the system. Each photocell is connected to a circuit shown on Figure 5. The wires at the top were connected to the circuit shown on Figure 4 and the firing wires were connected to the circuit shown on Figure 7. A discharge pipe to vent the exhaust gases to the atmosphere outside the building is also present. The



- A - Strand bomb
- B - Photoelectric tubes
- C - Armour glass windows
- D - Strand mounted on burner card
- E - Helse Bourdon guage
- G - Nitrogen cylinder
- H - Reducing valve
- I - Valves
- J - Electrical terminals
- K - Surge tank

Figure 3 A Schematic Diagram of the Strand Burner

Figure 4 A Schematic Diagram of the Strand Burner Timing Circuits

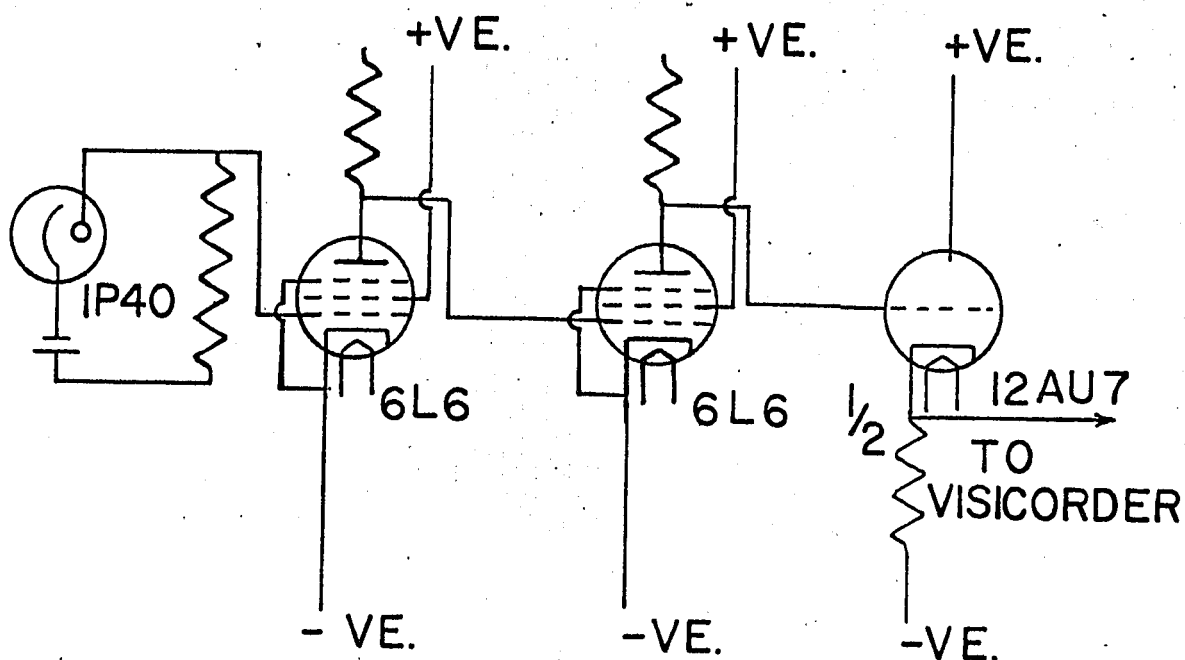
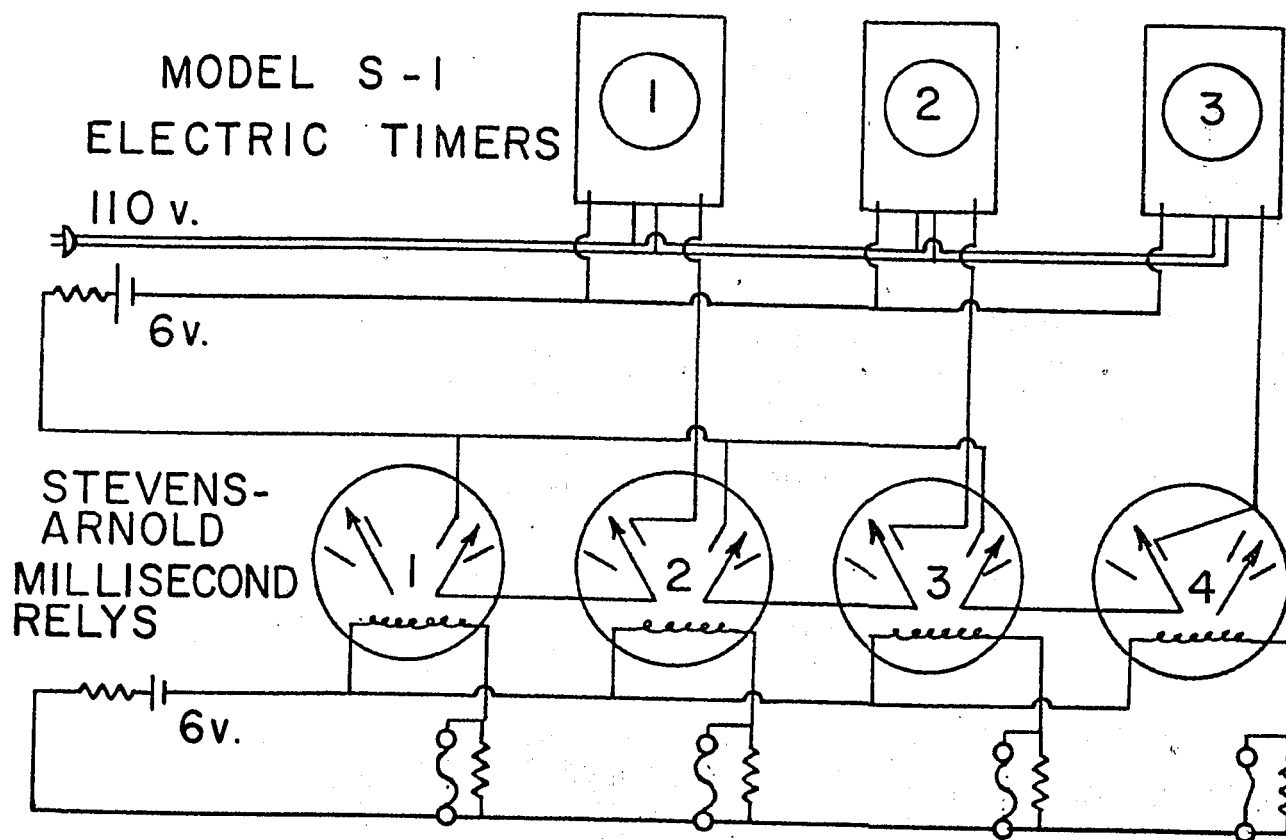


Figure 5 A Schematic Diagram of the Photoelectric Recording Circuits

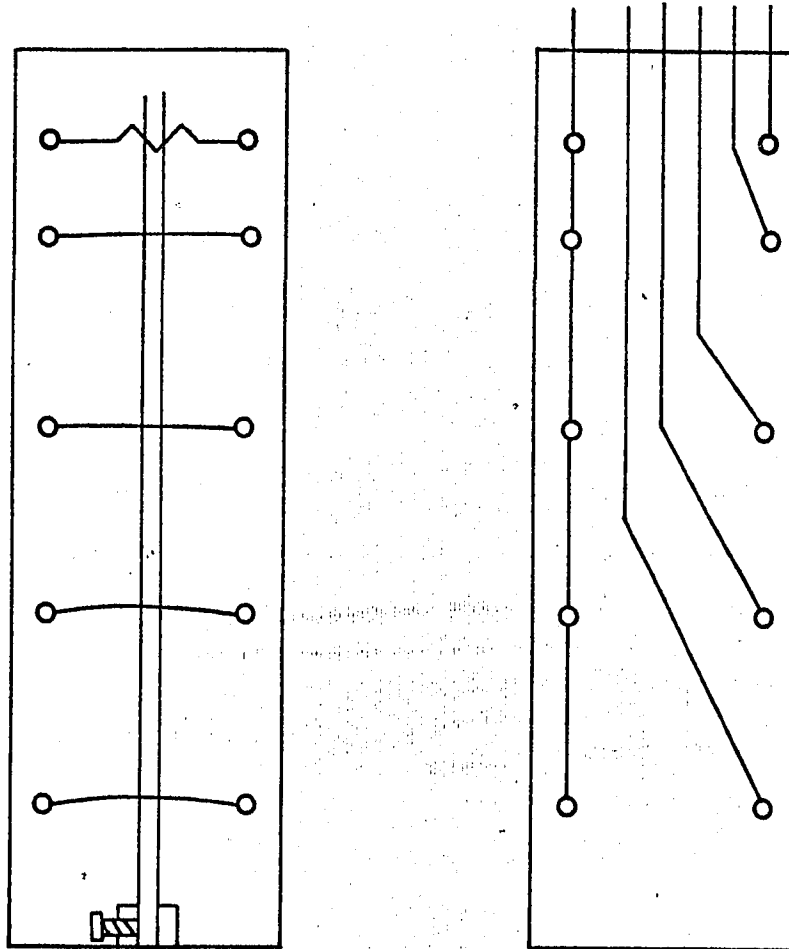
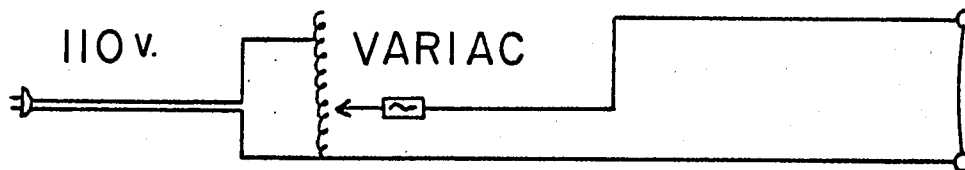


Figure 6 A Schematic Diagram of the Strand Burner Cards



THE FIRING CIRCUIT

Figure 7 A Schematic Diagram of the Strand Burner Firing Circuit

pressure in the system was read on a Heise Bourdon Gauge accurate to 0.1%.

The burner was filled with nitrogen to a pressure of about 25 psig and then the pressure was released to purge oxygen from the system. This process was repeated at least three times. Then the burner was pressurized with nitrogen to the test pressure - usually 400 psi, and allowed to stand from 15 to 30 minutes to make sure that the strand had reached the jacket temperature, previously set to the desired level, usually 25°C. The strand was fired. Flame, burning cigarette fashion, travelled down the strand. When it reached the first fuse wire, the lead melted and the circuit controlling Stevens Arnold millisecond relay #1 on Figure 4 was opened. This started Standard Electric Time Company timer, model S-1, accurate to 1/100 of a second, designated #1 on Figure 4. As the flame burned on down the strand it reached the second fuse wire and activated relay #2. Thus one set of contacts opened the circuit controlling clock #1 and it stopped while simultaneously the second set of contacts in relay #2 closed the circuit controlling clock #2 and it began to run. When the flame reached the third fuse wire, relay #3 was activated stopping clock #2 and starting clock #3. The clocks thus gave the time to burn each inch of propellant in sequence in the strand.

An additional system, consisting of two photoelectric tubes, 6957 for red light and IP39 for green light, a window in the burner and a Honeywell Visicorder, made an additional check on the burning rate possible. The length of the window and the time for the flame to pass by it were known and hence the rate could be computed. The phototube circuit is shown on Figure 5. Each phototube was connected to a pentode as shown in the figure. A second pentode was present to give the required degree of

amplification. The final stage in the circuit was a cathode follower with a low impedance output suitable for matching the galvanometers in the visicorder.

The circuit for firing the strands is shown on Figure 7. It consists of a variac connected directly to the nichrome ignition wire.

Polymer Production

An attempt to duplicate the work in Dickinson's paper (43) was crowned with considerable success. A polytetramethylene glycol of about molecular weight 2100 was produced in a sigma blade mixer, received from Dr. George Wright, of the University of Toronto. The jacket was cooled to 0°C., by circulating expanded Freon 12 from a quarter ton compressor unit, to avoid the side reaction propylene oxide to allyl alcohol. The formula for the ingredients was as follows:

1. Tetrahydrofuran	72.00 % by weight
2. Propylene Oxide	25.74 % " "
3. Butylene Glycol (starter)	1.26 % " "
4. Boron Trifluoride Etherate (catalyst)	1.00 % " "
	100.00 %

The polymerization was carried out in a 5% solution, the solvent being ethylene dichloride. The ingredients were placed in the mixer and the reaction continued for 12 hours, then it was quenched with water. This diol was then crosslinked with tolylene diisocyanate and Niax Triol

LHT 112 according to the formula:

1. Polytetramethylene Glycol	77.32 % by weight
2. Niax Triol LHT 112	9.20 % " "
3. Tolyene Diisocyanate	7.48 % " "
4. Diethylhexylazelate (plasticizer)	5.00 % " "
5. Ferric acetylacetate	1.00 % " "
	100.00 %

The elastomers produced seemed to be the same as the elastomer in CARDE's rocket powder. At this stage CARDE kindly agreed to send some of their own ingredients which obviated the need to make diol. Since CARDE's procedure and formula were different from the ones given above they are quoted below:

1. PPG + anti-oxident (polyoxypropylene glycol + Phenyl - methylamine)	76.092 % by weight
2. 2,4 - Toluene Diisocyanate	8.952 % " "
3. Cross-linker (polypropylene hexane triol)	9.904 % " "
4. Plasticizer (Diethylhexyl azelate)	4.748 % " "
5. Curing catalyst (Ferric Acetyl Acetate)	0.304 % " "
	100.000 %

The triol and the isocyanate were mixed and heated to 80°C for 2 hours then cooled to room temperature. (NOTE: here no specific temperature was used). The curing catalyst was mixed into a small amount of the PPG to make a thick paste, then slowly increasing the amount of diol to assure complete mixing. These two solutions were then combined

with mixing to give binder. Some carbon dioxide gas was evolved at this point as a result of the diisocyanate reacting with traces of water. The gas was removed by placing the mixture under vacuum until gas evolution stopped. Care was required in applying the vacuum as foaming occurred. The polymer was cured at 50°C for three to four days.

Temperature Profiles

To see if the crosslinking reaction was really exothermic some home made diol was crosslinked in an 18 mm test tube with an iron constantan thermocouple, encased in glass and with silicone fluid as a heat transfer medium, placed in the centre of the test tube through a hole in the cork. The thermocouple was connected to a cold junction (ice at 0°C) and the output wires were connected to a Phillips 12 point millivolt recorder. In all cases the temperature at the centre was higher than the ambient temperature in the bath.

Measurement of Physical Properties

Values of thermal diffusivity, thermal conductivity, heat capacity and density were required for subsequent calculations.

The density of ammonium perchlorate polyurethane propellant was measured directly. A cylinder of propellant was weighed and its dimensions were measured. This gave the density to three figures. See page 107 for a sample calculation.

Thermal conductivity was measured. Again a cylinder of

propellant was chosen and a nichrome heating wire was threaded axially down the centre. Two tiny holes were also drilled axially at r_1 and r_2 and two iron constantan thermocouples were inserted in them. The thermocouples were connected to a cold junction and the leads were connected to a 12 point Phillips millivolt recorder. The ends of the nichrome wire were clipped even with the propellant and two copper leads were attached to each end. The leads were fastened to a Heathkit battery eliminator BE 4 for DC current, an ammeter was placed in series and a voltmeter across. Both ends of the cylinder were insulated. The resistance was measured and the energy in watts at steady state was determined. At steady state the thermocouple temperatures were read and knowing r_1 and r_2 and the thermal flux, the thermal conductivity, k , could be calculated. (See page 108 for a sample calculation).

Once the thermal conductivity was known, the thermal diffusivity could be determined. A cylindrical shape was chosen again. The centre was pierced half way down axially, a drop of silicone fluid and an iron constantan thermocouple were inserted. The cylinder was warmed in a bath to about 80°C ., then removed and allowed to cool in air. The heat transfer coefficients h_c and h_r were calculated. Then the eigenvalues were calculated from the formula

$$\theta_{J_1}(\beta) = A J_0(\beta) \dots\dots\dots(126)$$

where $\pm\beta_n$, $n = 1, 2, 3 \dots\dots\dots$ are the roots of equation (126) given in Carslaw and Jaeger (20). Now writing $a\alpha_n = \beta_n$, $x t/a^2 = T$, $ah = A = a(\frac{h_c + h_r}{k})$, the thermal diffusivity could be calculated from

$$\frac{T - T_{air}}{T_1 - T_{air}} = \sum_{n=1}^{\infty} \frac{e^{-\rho_n^2 T}}{(\rho_n^2 + A^2) J_0(\rho_n)} \frac{2A J_0(r \rho_n/a)}{J_0(\rho_n)} \dots\dots\dots (127)$$

(See page 109 for a sample calculation).

The heat capacity was not measured directly but was calculated from the other values (see page 113 for a sample calculation) by the relation

$$x = \frac{k}{\rho c_p} \dots\dots\dots (128)$$

Microcalorimetry

To obtain the thermal gradient as a function of time, a Tian-Calvet (17) differential type microcalorimeter was used. This instrument gave the instantaneous heat flux throughout the reaction time

$$\Delta H = \int_0^t \frac{\partial H}{\partial t} dt \dots\dots\dots (52)$$

Figure 8 shows the electrical calibration circuit for the calorimeter. It is simply a Leeds and Northrup precision one ohm resistor (#1590907) in series with the calibrating resistor, whose value was previously measured with Tinsley Instruments Wheatstone Bridge Type 4970, in the cell. A potentiometer of the Dieselhorst pattern (Tinsley Type 3589-R) is connected to the precision resistor to read the potential and hence the current passing through the resistor, directly. A Heathkit battery eliminator, model BE 4, or a battery was used to power the circuit. A Fisher electric stopwatch accurate to a tenth of a second was required

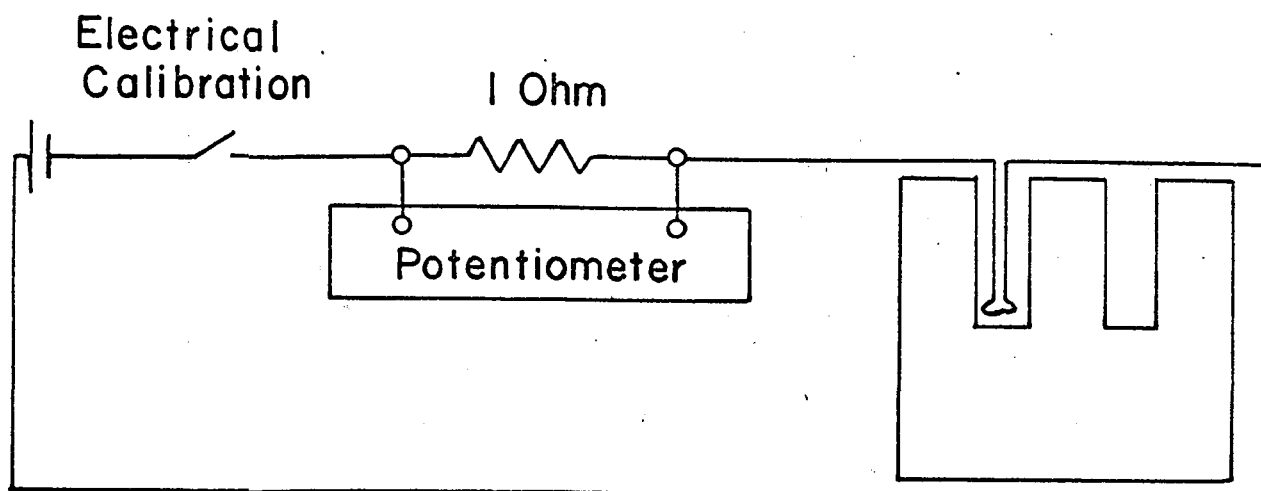


Figure 8 A Schematic Diagram of the Microcalorimeter Calibration Circuit

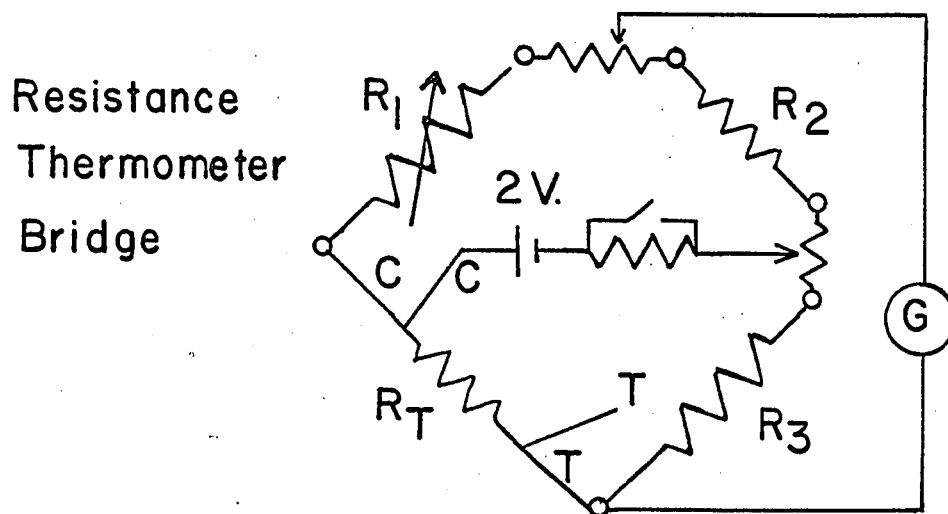


Figure 9 A Schematic Diagram of the Resistance Thermometer Bridge

to read the time. The formula for the heat in calories is

$$\text{Calories} = \frac{R I^2 t}{4.1840} \dots\dots\dots(129)$$

as given by McCurdy (32). The second circuit in Figure 9 is the Rinfret bridge (Tinsley Type J1003) for measuring the resistance of the resistance thermometer. A thermo electric free reversing switch (Tinsley Type 4092) has been added to make the interchanging of the leads easy.

The calorimeter was calibrated both chemically, using anhydrous lithium sulphate, whose heat of reaction with water is known and tabulated in Selected Values of Thermodynamic Properties (118), and electrically using a standard resistor, immersed in a bulb containing transformer oil and a cell containing water. For these experiments electrical calibration was deemed sufficient since the lithium sulphate cross check came within 2.2% and 7% of the literature values for calorimeters #1 and #2, respectively.

The time constant of a microcalorimeter is the time to reach 63.208% of the total deflection on the heat flux chart for any heat pulse, or in mathematical terms it is the constant T in the exponential growth equation

$$\phi = \phi_0 (1 - e^{-t/T}) \dots\dots\dots(130)$$

given in Calvet and Prat (17a). It can also be found from the exponential decay curve at 36.79% deflection, if the deflection has

reached a steady state before the constant heat source in the cell is cut off. In this case the mathematical equation is

$$\phi = \phi_0 e^{-t/T} \dots\dots\dots(131)$$

given in Calvet and Prat (17b). In graphical form these equations are shown on Figure 10. Basically the time constant of a calorimeter is a measure of how quickly the instrument can follow a heat pulse and determines whether the line drawn on the chart is a faithful representation of what is happening in the cell. If the production of heat is too fast the heat will not be able to flow to the aluminum block fast enough and corrections will have to be made to get the true heat flux plot. This does not mean however that the total value of the heat will be wrong, just that the rate at which it is produced will not be correctly recorded. If no corrections are to be made one must be sure that the reaction is slow enough for the results to be valid. Here, corrections were attempted for the reaction at 62°C when the rate is greatest, but no change in the curves resulted. Therefore, the curves can be taken as read.

The overall equation for the calorimeter is

$$W = P + \frac{p}{g} + \frac{M}{g} \frac{d\Delta}{dt} \dots\dots\dots(132)$$

as given by Calvet and Prat (17c). Since no Peltier heat was used, it was not necessary to know P. The quantity p/g was measured as follows:

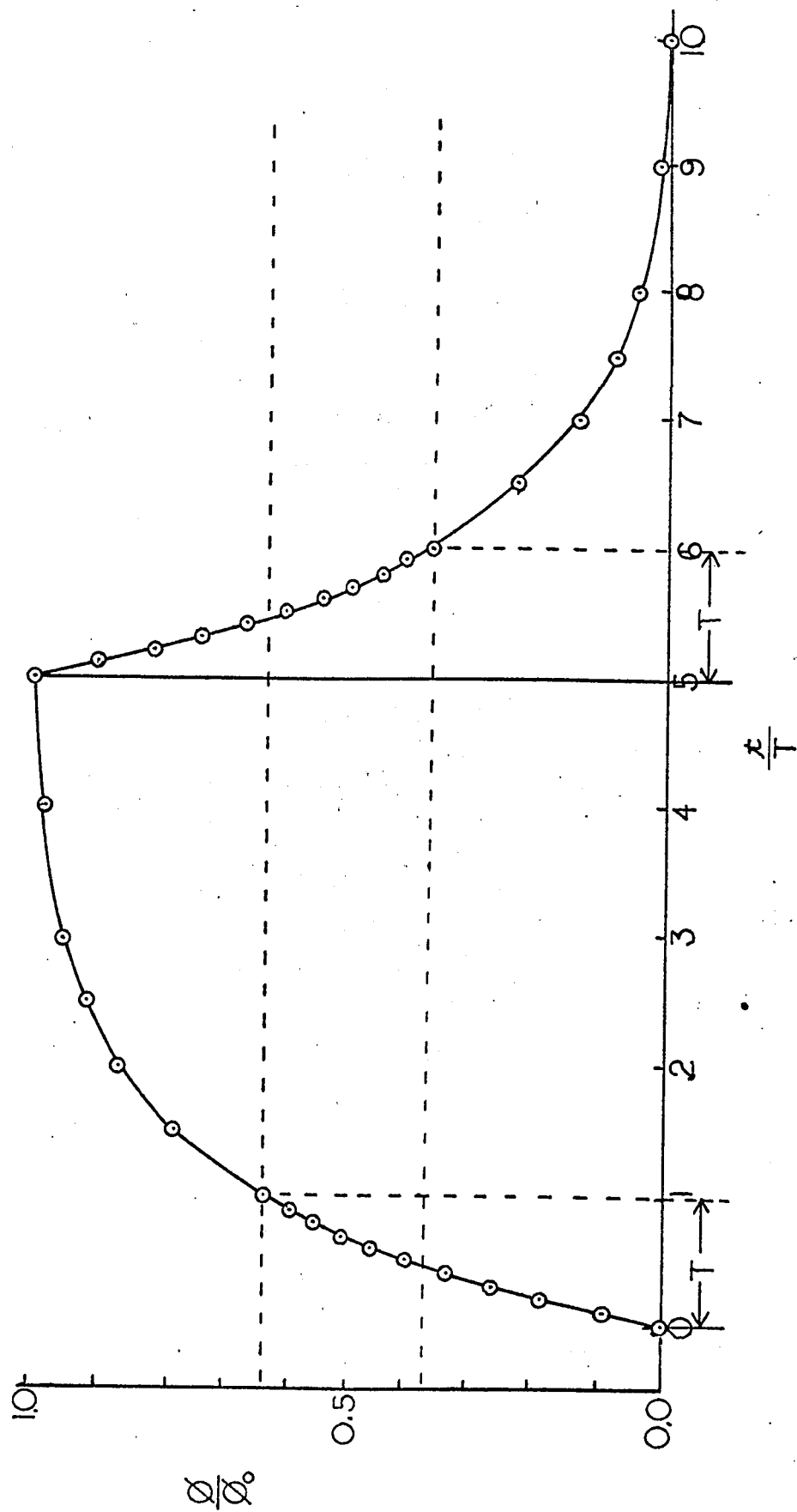


Figure 10 The Time Constants from Exponential Curves

An electrical heater was placed in the cell and a continuous, steady current was passed through it. A graph DB, as depicted in Figure 11, was obtained similar to Figure 25 in Calvet and Prat (17d). Then the current was shut off at A and the decay AC at the end was obtained. When the graph levelled out at its peak at B, $\frac{d\Delta}{dt}$ was zero and hence

$$W = 0 + \frac{p\Delta}{g} + 0$$

$$\text{or } W = \frac{p\Delta}{g} \dots\dots\dots(133)$$

W is known and Δ is also known and thus p/g can be calculated.

The constant μ/g can then be calculated from the fact that T, the time constant, equals μ/p .

$$T = \frac{\mu}{p} = \frac{(\mu/g)}{(p/g)} \dots\dots\dots(134)$$

Samples of the ingredients for the crosslinking reactions were prepared, weighed into two calorimetric cells and placed in the cabin to come to temperature. The catalyst was weighed into one of two tiny bulbs each at the end of pieces of 3 mm diameter glass tubing about 8 inches long, which were attached to the plungers. After the cells had reached temperature they were placed in the microcalorimeter and again had to stand until equilibrium was reached. The recorder base lines were adjusted to zero and both plungers were depressed. Both the instantaneous heat flux and the integrated value of the heat were recorded. The

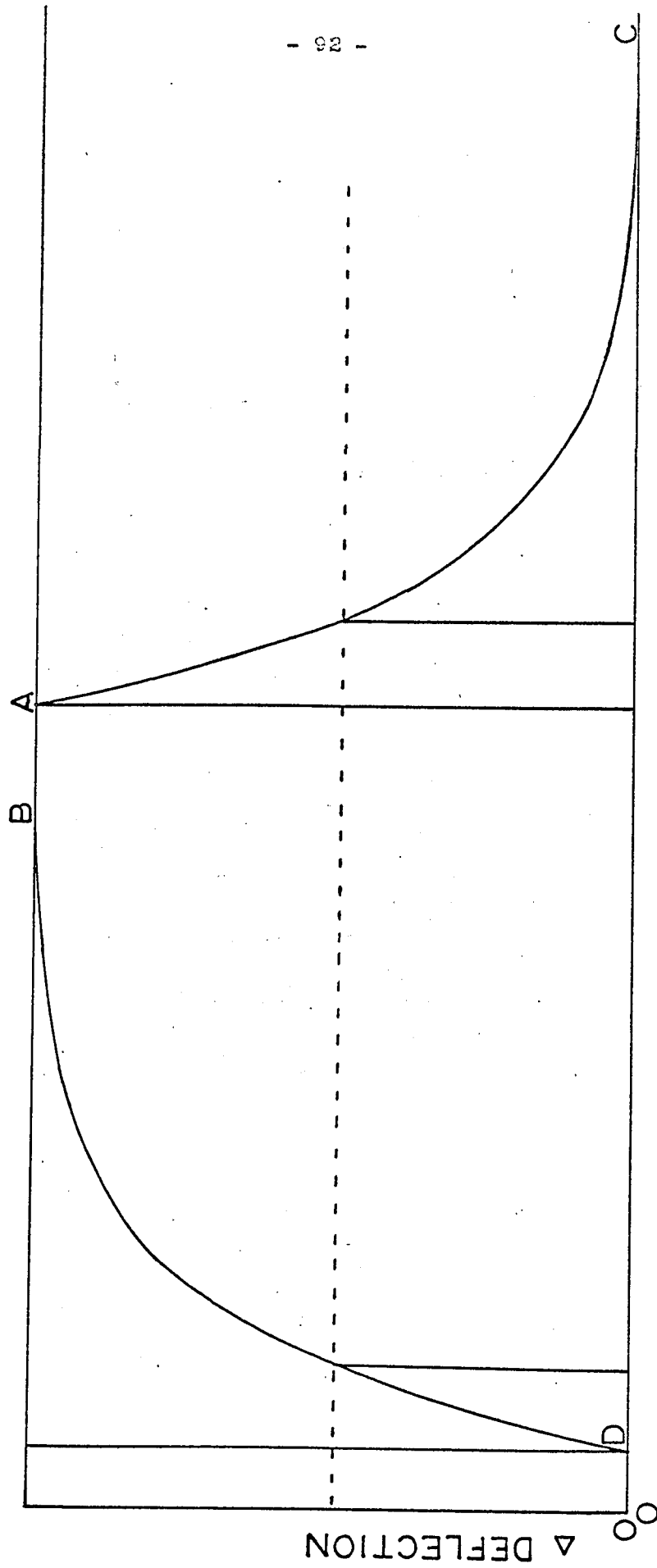


Figure 11 Curves for the Determination of the Calorimeter Constants

calibration factor was applied and the total heat of the reaction obtained as well as its temperature history.

Three ambient cabin temperatures, 25°C, 48°C and 62°C were used. The first calorimeter, #1, was used at the two lower temperatures because it has a time constant of about 20 minutes. The second calorimeter, #2, was used only at 62°C because its smaller time constant, 10 minutes, allowed it to follow a faster reaction at higher temperatures more faithfully. When a correction for the heat flux curve was attempted it was found that none was necessary even at the highest temperature.

Figure 12 is a schematic of the microcalorimeter and the associated electronic components for measuring q and ΔH .

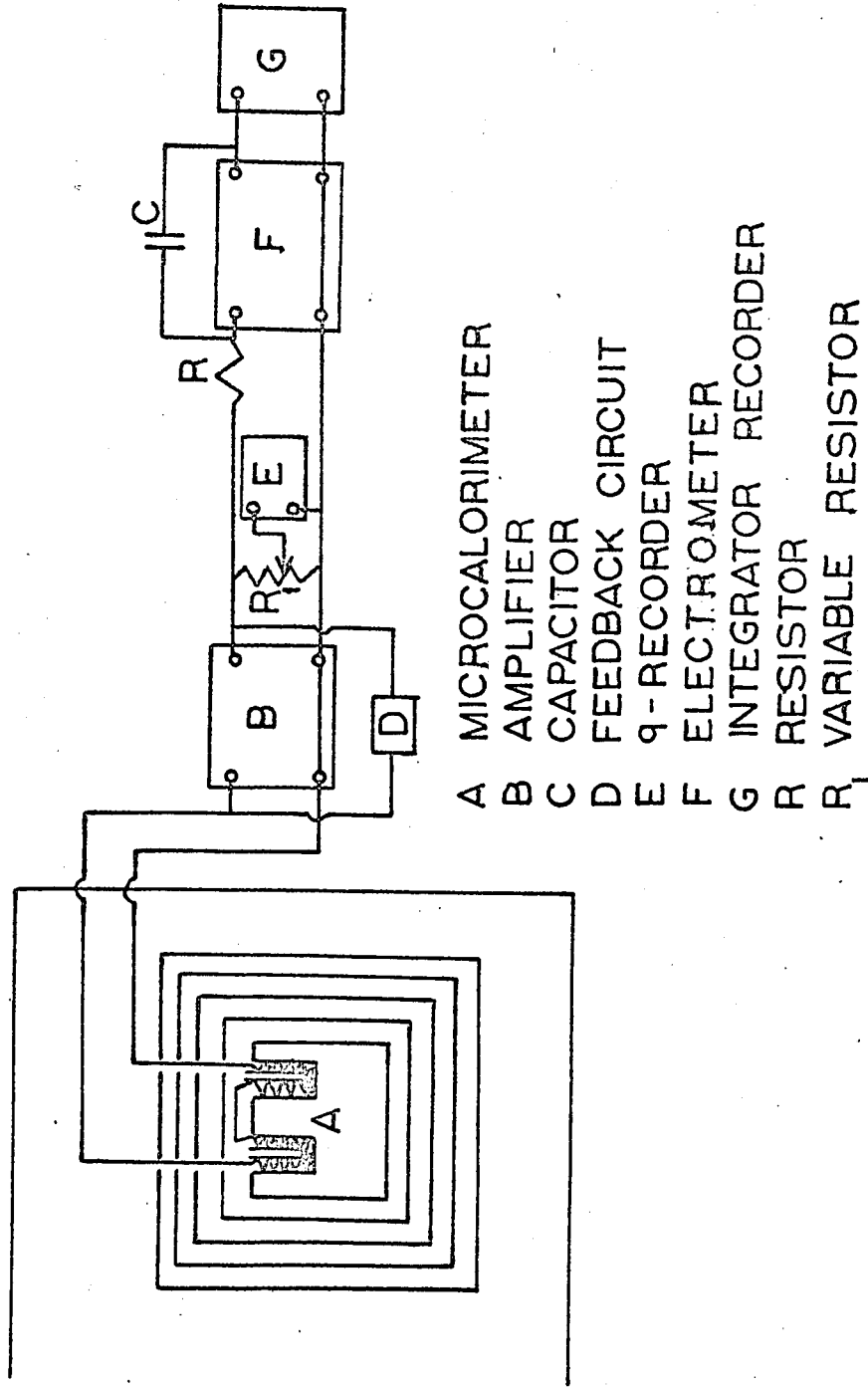


Figure 12 Schematic Diagram of the Microcalorimeter Recording Circuits

CALCULATIONS

The calculation of the function $\frac{\Delta H}{\Delta t}$ taking the sample of the recorder results, given in Table VII, on calorimeter #1 at 47.32°C as an example of the method. When the values were plotted a graph of the form shown on Figure 13 resulted, which could be represented as the difference of two exponentials

$$q = (a_1 e^{w_1 t} - a_2 e^{w_2 t}) \dots\dots\dots (135)$$

In order to find w_1 it was necessary to plot the values on semilogarithmic paper. This was done in Figure 14. Here it will be noted that the decaying portion of the graph was not a straight line but departed from linearity as time increased. This was due to the fact that the reaction was still giving off a little bit of heat. A glance at Figure 13 will show that the area under the tail is not very great and thus no great error will be made if it is partly neglected. Therefore a straight line has been drawn on the semilogarithmic plot through the points up to the time (4 hours in this case) where the tail began to depart from linearity. Once the points to be used in the calculation of the first term $a_1 e^{w_1 t}$ were known, then the best line through them is found by the method of least squares as shown in Table VII, where

$$y_1 = \ln \theta \dots\dots\dots (136)$$

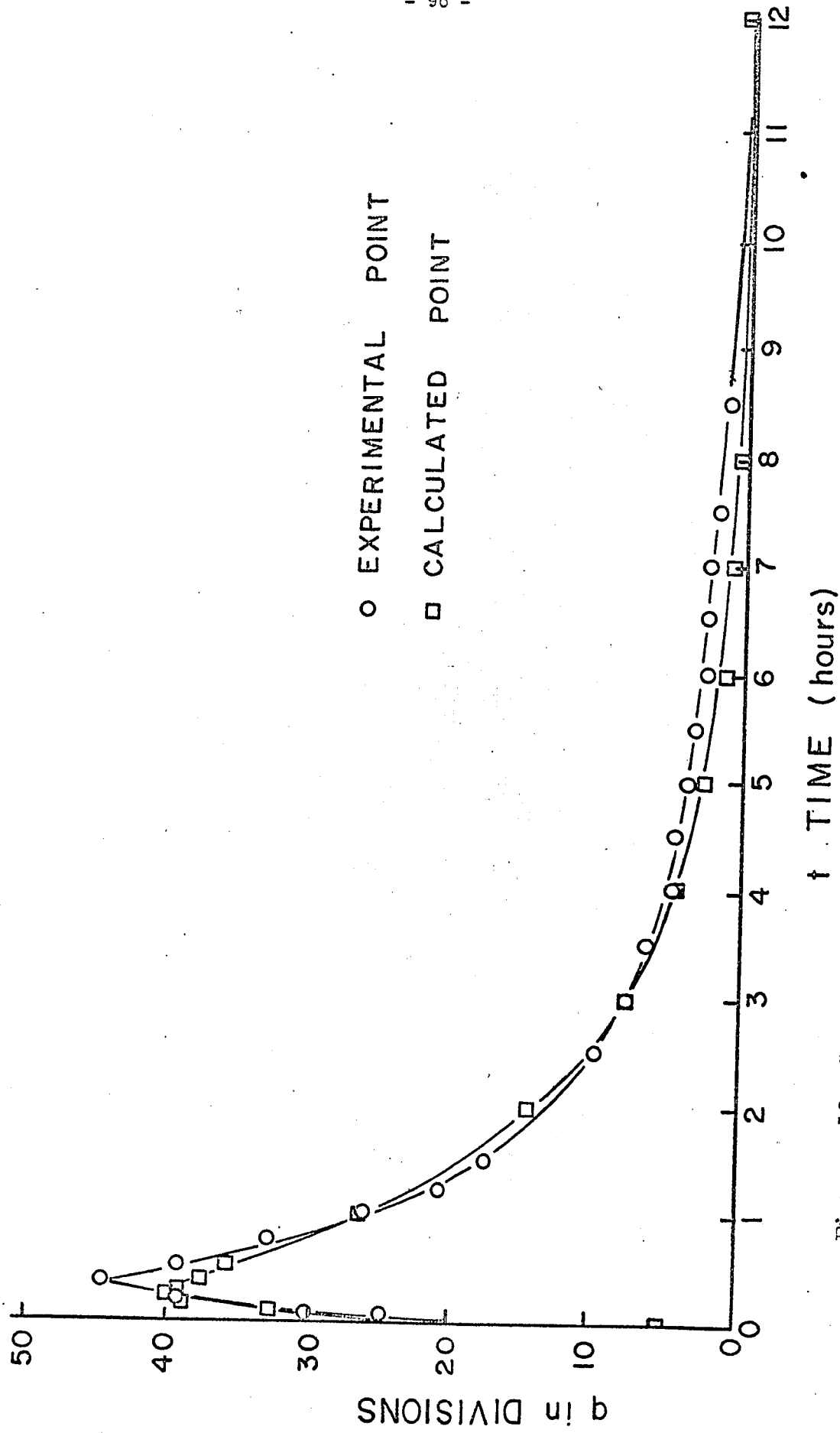
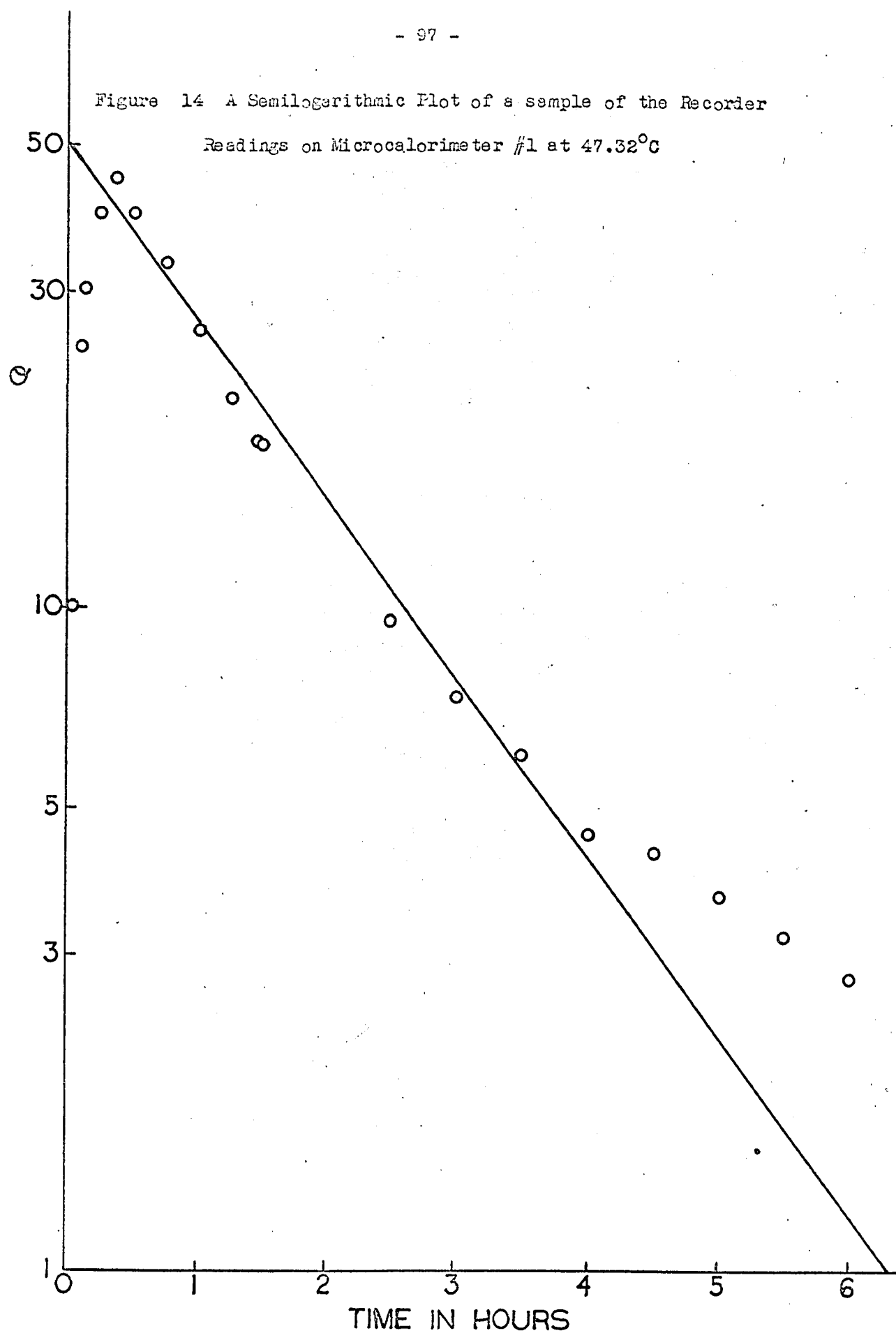


Figure 13 Comparison of the Calculated and Experimental Curves for q



and x_1 = time in hours. Therefore the first term in the equation was

$$a_1 e^{w_1 t} = 49.22 e^{-0.623,06t} \dots\dots\dots(137)$$

Now to get $a_2 e^{w_2 t}$, each point on the line was the difference between the experimental point and a point on $a_1 e^{w_1 t}$. For example at time equal to 0.05 hours the first term gave

$$\theta_1 = 49.22 e^{-0.623,06(0.05)} = 47.71 \dots\dots\dots(138)$$

The experimental point at 0.05 hours was 10.0 and thus the first point on the second exponential was the difference between the two

$$(47.71 - 10.0) = 37.71 \dots\dots\dots(139)$$

The rest of the points were tabulated in Table IX and the least squares determination of the best line through them is given in Table X. Since the first exponential had many more points than the second its value of θ_0 is much more accurate. Then for the first trial take

$$a_2 e^{w_2 t} = 49.22 e^{-11.617t} \dots\dots\dots(140)$$

and $\theta = 49.22 (e^{-0.623,06t} - e^{-11.617t}) \dots\dots\dots(141)$

Now this equation must give the right value of ΔH which in this case was

7.076, thus a constant was necessary because only a fraction of the instantaneous q is shown on the recorder. This constant was found by integration over the total time which was 12 hours in this case

$$\Delta H = \int_0^{t=12} c \cdot 49.22 (e^{w_1 t} - e^{w_2 t}) dt = 7.076 \quad \dots\dots\dots(142)$$

$$\left[\frac{e^{-7.476,72} - 1}{-0.623,06} \right] - \left[\frac{e^{-\infty} - 1}{-11.617} \right] = \frac{7.076}{c \cdot 49.22}$$

$$\therefore c = 0.094,697 \quad \dots\dots\dots(143)$$

$$\text{then } \frac{\partial H}{\partial t} = 4.661 (e^{-0.623,06t} - e^{-11.617t}) \frac{\text{cals}}{\text{gm hr}} \quad \dots\dots\dots(144)$$

Table XII contains the rest of the functions calculated in the same manner.

The calculation of ΔH overall for the sample of the recorder results:

The integrator was not on full time but for an initial period of 1.5 hours and then for another period between 7.55 and 8.5 hours. The final value was worked out by counting squares.

The number of squares in area 1 was 105.10 on Figure 15.

The number of squares total was 261.90 on Figure 15.

The number of integrator units in area 1 was 39.30 on Figure 15.

Therefore the total number of integrator units was $\frac{261.90(39.30)}{105.10} = 97.93$

The number of squares in area 2 was 7.66

The number of integrator units in area 2 was 3.78

Therefore the total number of integrator units was $\frac{261.90(3.78)}{7.66} = 129.24$

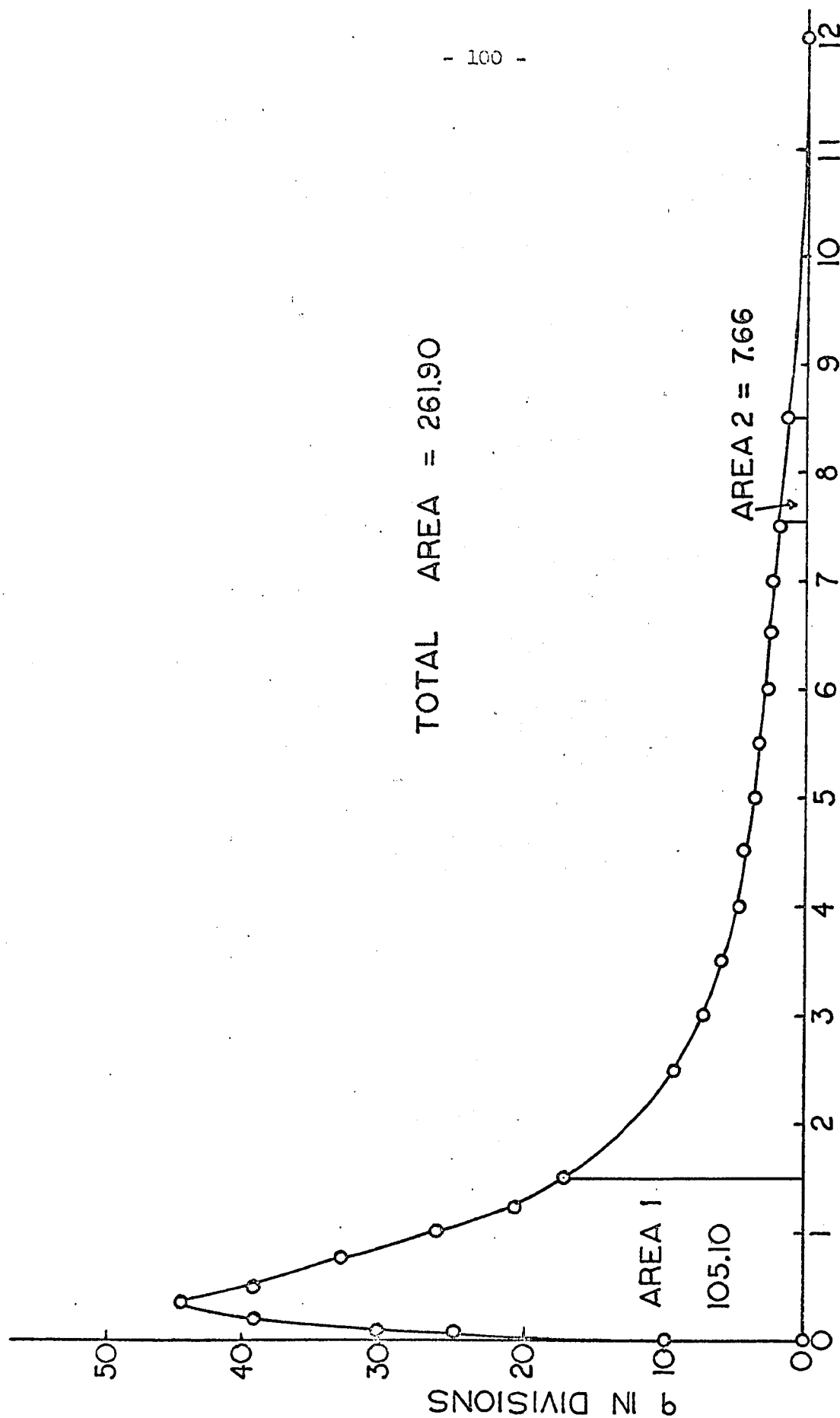


Figure 15 A Curve of q versus time to illustrate ΔH Calculation

Hence the average number of integrator units was $\frac{97.93 + 129.24}{2} = 113.58$

A calibration was carried out on this integrator using a 503.8 ohm resistor in the calorimeter through which a current of 0.013,3 amperes was passed for 24.9 seconds. The corresponding integrator reading was 7.4 units. The heat in calories given off by the resistor was given by

$$q = \frac{R I^2 t}{4.1840} = \frac{503.8 (0.013,3)^2 24.9}{4.1840}$$

The heat in calories per integrator unit was $\frac{503.8(0.013,3)^2 24.9}{4.1840(7.4)}$

The total heat given out then was $\frac{503.8(0.013,3)^2 24.9(113.58)}{4.1840(7.4)}$

In this case 1.151 grams of material were used, therefore

$$\Delta H = \frac{503.8(0.013,3)^2 (24.9) (113.58)}{4.1840 (7.4) (1.151)} = 7.076 \text{ cal/gm}$$

A check on the accuracy of the function.

$$\theta = 49.22 (e^{-0.623,06t} - e^{-11.617t}) \dots\dots\dots(141)$$

Points are calculated using the function and plotted on Figure 13 for comparison with experimental values. Here a_2 will be 0.9(49.22) to give a positive initial slope at time zero.

e.g. at time = 0.1 hours

$$\theta = 49.22 \left[e^{-0.623,06(0.1)} - e^{-11.617(0.1)} \right]$$

$$\therefore \theta = 32.53$$

The full list of values is given in Table XI.

An area check: 1) Counting squares under the experimental curve gives a number of 87.35

$$\therefore \text{area} = 87.35(2)(0.5) = 87.35$$

2) By integration of the function as given below

$$\text{area} = \int_0^{12} 49.22 \left[e^{-0.623,06t} - e^{-11.617t} \right] dt$$

$$\text{area} = 75.159$$

$$\text{The percentage deviation is} = \frac{(87.35 - 75.139)}{87.35} = 11.69\%$$

Most of this difference was in the tail and not the main part of the function.

Trials for the combined equation: 1) at 25°C

$$\Delta H_{av} = 4.243 \text{ cal/gm}$$

$$\Delta H = 4.243 = \int_0^{100} 0.264,814 C_{\text{final}} \left[e^{-0.070,52t} - e^{-2.951t} \right] dt$$

$$C_{\text{final}} = 1.159 \quad \text{and}$$

$$0.264,814 C_{\text{final}} = 0.306,8$$

Therefore at 25°C the final equation is

$$\frac{\partial H}{\partial t} = 0.306,8 \left[e^{-0.070,52t} - e^{-2.951t} \right] \text{ cal/gm/hr} \dots\dots\dots(145)$$

2) at 48°C

$$\Delta H_{av} = 6.845 \text{ cal/gm}$$

$$\Delta H = 6.845 = \int_0^{12} 5.194,5 C_f \left[e^{-0.673,6t} - e^{-10.793t} \right] dt$$

$$\therefore 5.194,5 C_f = 4.919$$

Therefore the final equation at 48°C is

$$\frac{\partial H}{\partial t} = 4.919 \left[e^{-0.673,6t} - e^{-10.793t} \right] \text{ cal/gm/hr} \dots\dots\dots(146)$$

3) at 62°C

$$\Delta H_{av} = 5.358 \text{ cal/gm}$$

$$\Delta H = 5.358 = \int_0^5 19.195 C_f \left[e^{-2.122t} - e^{-6.009t} \right] dt$$

$$\therefore 19.195 C_f = 17.58$$

Therefore the final equation at 62°C is

$$\frac{\partial H}{\partial t} = 17.58 \left[e^{-2.122t} - e^{-6.009t} \right] \text{ cal/gm/hr} \dots\dots\dots(147)$$

The constants were averaged in the $\frac{\partial H}{\partial t}$ functions at each temperature and the resultant values are given in Table XIV. The problem now is to work

out a function from these values, dependent on both temperature and time. This was done as follows: A semilogarithmic plot of ϕ versus T gave almost a straight line in Figure 16 and another semilogarithmic plot of w_1 versus T (Figure 17) also gave a nearly straight line. The method of least squares was then used to draw the best line through these two sets of values (see Table XIV). For T in degrees centigrade, the functions were

$$\phi = 0.020,65 e^{0.110,5 T} \dots\dots\dots(148)$$

$$w_1 = -0.007,216 e^{0.092,60 T} \dots\dots\dots(149)$$

and for T in degrees Fahrenheit, the functions were

$$\phi = 0.002,896 e^{0.061,408 T} \dots\dots\dots(150)$$

$$w_1 = -0.001,391 e^{0.051,447 T} \dots\dots\dots(151)$$

Since the w_2 's did not fall on a straight line on either ordinary graph paper or semilogarithmic graph paper and because they were the least accurate of all the values, they were simply averaged.

$$w_2 = \frac{-2.950 - 10.793 - 6.009}{3} = -6.584 \dots\dots\dots(152)$$

Putting all this together the master equation for the chemical reaction

Figure 16

A Semilogarithmic Plot of ϕ versus Temperature

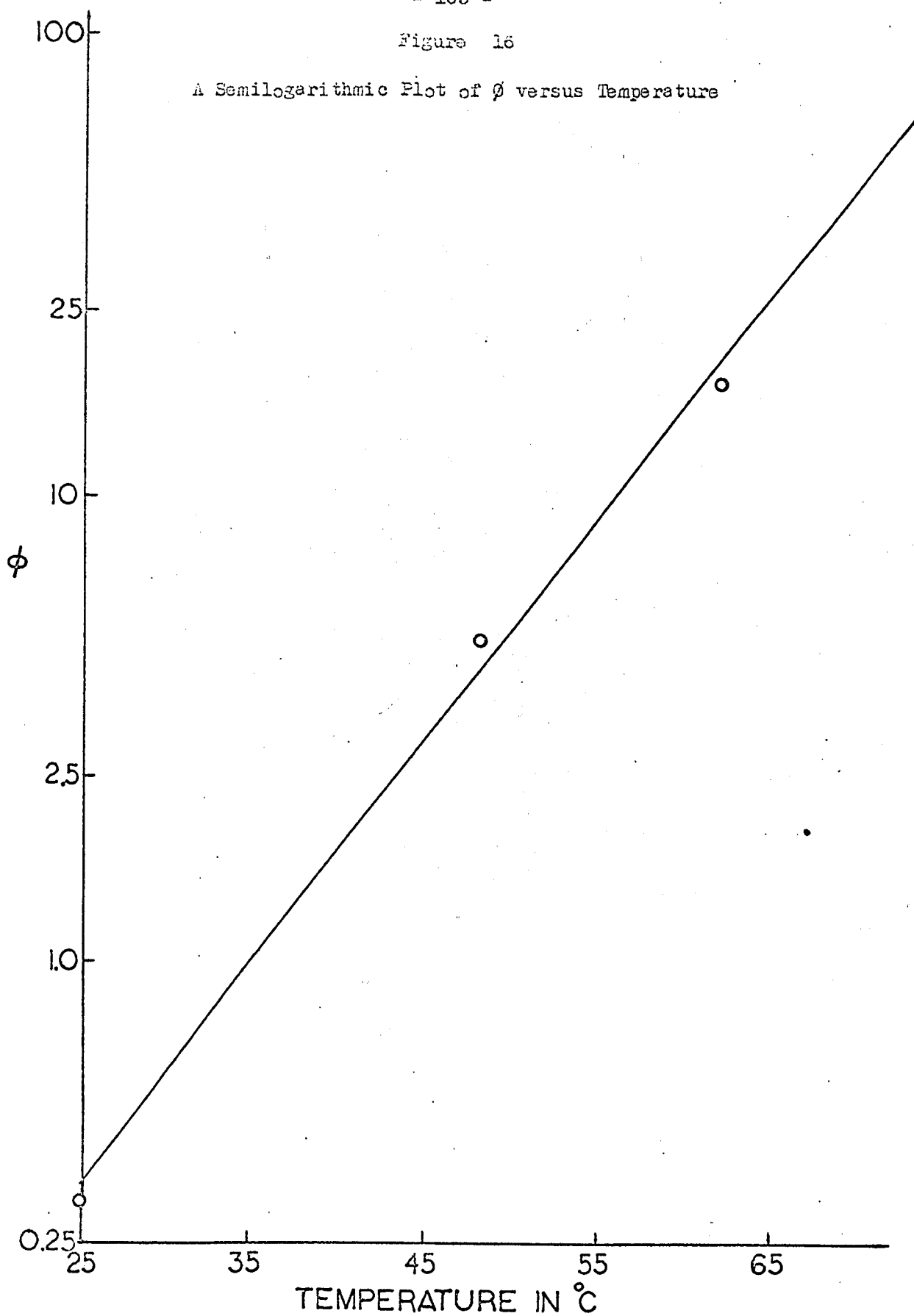
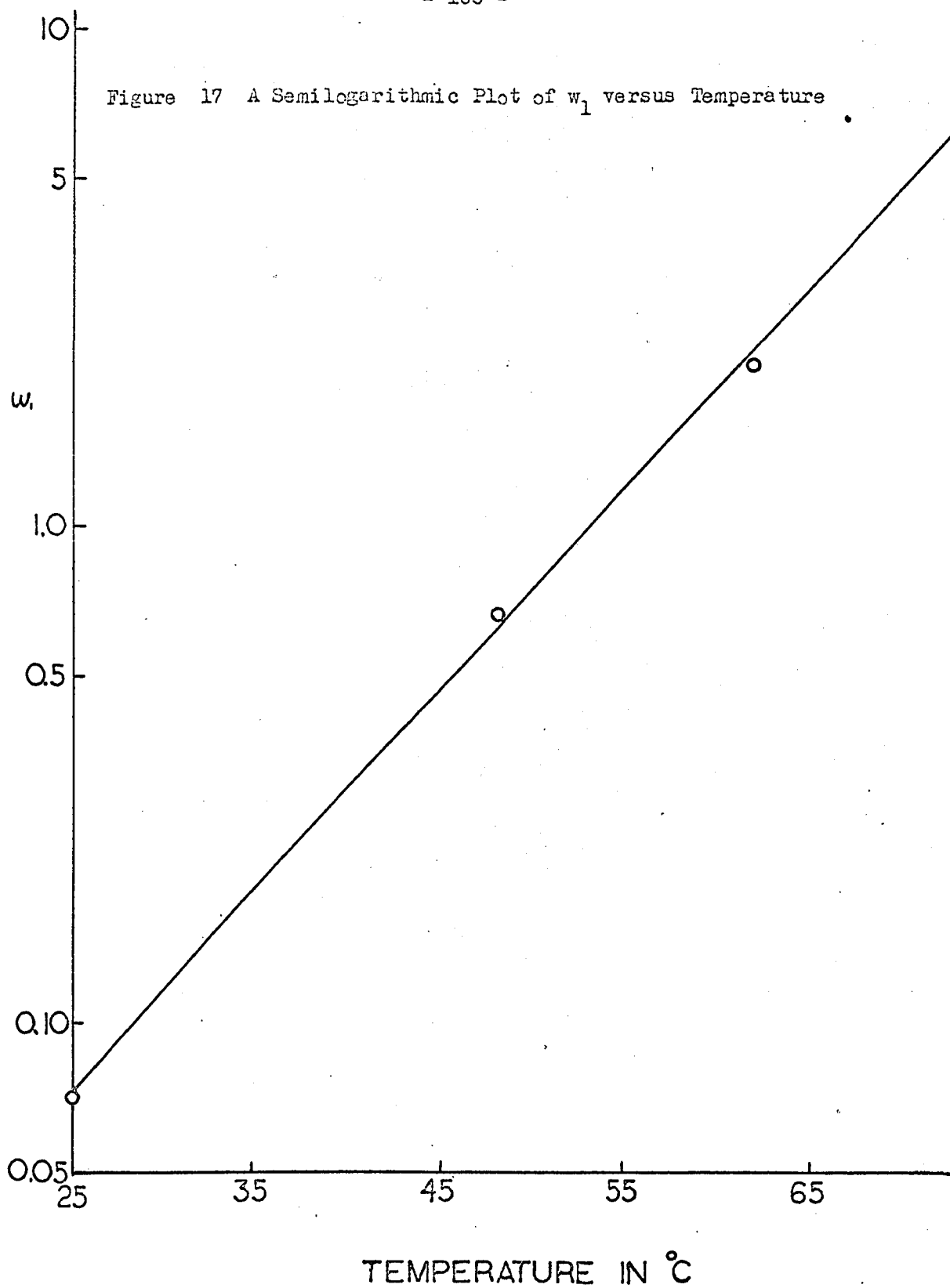


Figure 17 A Semilogarithmic Plot of w_1 versus Temperature



as a heat source, represented as a function of temperature and time was

$$\frac{\partial H}{\partial t} = 0.002,896 e^{0.061,408T} \left[e^{-0.001,391t} \left(0.051,447T - 6.584t \right) - 0.9 e^{-0.9t} \right] \frac{\text{cals}}{\text{gm hr}} \quad (153)$$

where T was in degrees Fahrenheit.

To calculate the greatest possible value of the constant α , the upper two values of ϕ were taken since the figures at the upper temperatures are more accurate. The least squares determination was given in Table XIII and the function is

$$\phi = 0.012,34 e^{0.056,59T} \quad (T = ^\circ F) \quad (154)$$

Using the highest possible value for ΔH , which was 2.6 times the average, and combining it with the value 0.012,34 the total became

$$\frac{0.012,34(2.6)}{0.002,896} = 11.079$$

Then $\frac{\partial H}{\partial t} = 11.079(0.002,896) e^{0.061,408T} \left[e^{-0.001,391t} \left(0.051,447T - 6.584t \right) - 0.9 e^{-0.9t} \right] \frac{\text{cals}}{\text{gm hr}} \quad (155)$

The calculation of the density of the propellant: A cylinder of propellant, with a conical shaped depression in one end, was weighed and

the density was calculated from the figures.

Overall height = 8.5 cms.

Height of the cone = 0.5 cms

Overall radius = $2.5/2 = 1.25$ cms

Overall diameter = 2.5 cms

Radius of the cone = 0.5 cms

Weight of the propellant = 71.6 grams

$$\text{density} = \rho = \frac{\text{weight}}{\text{volume}} = \frac{\text{weight}}{\left(\frac{\pi D^2 h}{4} - \frac{\pi r_c^2 h_c}{3} \right)} \dots\dots\dots(156)$$

$$\therefore \rho = 1.72 \text{ grams/cm}^3 \text{ or } 107.328 \text{ lbs/ft}^3$$

The calculation of the thermal conductivity of the propellant. For thermal conductivity measurements a cylinder of propellant with a piece of nichrome wire threaded through the centre in the axial direction, was used. Two other holes were drilled axially at r_1 and r_2 and iron constantan thermocouples were placed in each. The ends were sealed to heat and a known current was put through. At steady state the formula for this case, as given by Carslaw and Jaeger (20c) is

$$2\pi k (v_1 - v_2) = F_o \ln (r_2/r_1) \dots\dots\dots(157)$$

where $F_o = j I^2 R \dots\dots\dots(158)$

Volts used = 0.8 V.

Current = 0.6 A.

$r_1 = 5 \text{ mm}$

$r_2 = 10 \text{ mm}$

Watts = 0.48

Length = 85 mm

$T_1 = 76.3^\circ\text{F}$

$T_2 = 72.9^\circ\text{F}$

$$F_o = \frac{\text{Watts}}{\text{mm}} \cdot \frac{\text{kW}}{\text{Watts}} \cdot \frac{\text{BTU/hr}}{\text{kW}} \cdot \frac{\text{mm}}{\text{in}} \cdot \frac{\text{in}}{\text{ft}} = \frac{\text{BTU}}{\text{hr ft}}$$

$$2 \pi k (76.3 - 72.9) = \frac{0.48}{85} \cdot \frac{1}{1000} \cdot \frac{3,415}{1} \cdot \frac{25.4}{1} \cdot \frac{12}{1} \cdot 2.303 \log(10/5)$$

$$\therefore k = 0.191 \frac{\text{BTU}}{\text{hr ft } ^\circ\text{F}}$$

The sum of the errors is $3.75\% + 50\% + 1\% = 55\%$

Then $k = 0.191 \pm 0.105 \frac{\text{BTU}}{\text{hr ft } ^\circ\text{F}}$. It will be noted that this method of calculating errors gives a range which is probably too large.

The calculation of the thermal diffusivity. A cylinder of propellant, which has been heated uniformly to a high temperature is allowed to cool in air with an iron constantan thermocouple at its centre to record the temperature decay. The formula for this case is (Carslaw and Jaeger (201)

$$\frac{T - T_{\text{air}}}{T_o - T_{\text{air}}} = \sum_{n=1}^{\infty} e^{-\lambda_n^2 t} \frac{2C' J_o(\lambda_n r)}{R (C'^2 + \lambda_n^2) J_o(\lambda_n R)} \dots\dots\dots(159)$$

where $C' = h/k$, and $(\lambda_n R) J_1(\lambda_n R) - C J_0(\lambda_n R) = 0$ (160)

writing $R\alpha_n = \beta_n$; $\frac{xt}{R^2} = T$; $Rh = A$

$$\frac{v}{V} = \sum e^{-\beta_n^2 T} \frac{2A J_0(\beta_n R/R)}{(\beta_n^2 + A^2) J_0(\beta_n)} \dots\dots\dots(161)$$

$\pm \alpha_1; \pm \alpha_2$ negative values are included.

Now the values of the film coefficients, h_c and h_r must be found. Taking representative values of Δt and then using the average values of Δt , gives

$$\Delta t^\circ C = 63.7^\circ C \text{ or } 114.7^\circ F$$

$$\Delta t_{av} = 63.7/2$$

D'_o = diameter in inches, where $D = 22.4 \text{ mm}$

The formula given by Perry (94) is

$$h_c = 0.4 \left[\frac{\Delta t_s}{D'_o} \right]^{0.25} \dots\dots\dots(162)$$

$$\therefore h_c = 1.14 \frac{\text{BTU}}{\text{hr ft}^2 \text{ } ^\circ F}$$

Using the formula for radiation as given by Perry (94) and $T_1 = T_{av}$

$$q_r = 0.173 A \left[\left(\frac{T_1}{100} \right)^4 - \left(\frac{T_2}{100} \right)^4 \right] = h_r A (T_1 - T_2) \dots\dots(163)$$

$$\therefore h_r = 1.12 \frac{\text{BTU}}{\text{hr ft}^2 \text{ } ^\circ\text{F}}$$

$$\text{then } (h_c + h_r)_{\text{mean}} = 1.14 + 1.12 = 2.26 \frac{\text{BTU}}{\text{hr ft}^2 \text{ } ^\circ\text{F}} \quad \text{or } 2.3 \frac{\text{BTU}}{\text{hr ft}^2 \text{ } ^\circ\text{F}}$$

A check on the method using a brass cylinder (70% Cu, 30% Zn) taking the values from Table VI.

$$\text{Diameter} = 19\text{mm, then } R = 0.031,16 \text{ ft}$$

$$h = \frac{(h_c + h_r)}{k} = \frac{2.3}{74} = 0.031,08$$

$$A = hR = 0.031,08(0.031,16) = 0.000,968,4$$

$$A^2 = 0.000,000,937$$

$$\varrho_1 = 0.049,8$$

$$\varrho_2 = 3.831,7$$

$$\varrho_3 = 7.015,6$$

$$\varrho_1^2 = 0.002,48 \quad (\varrho_1^2 + A^2) = 0.002,48$$

$$\varrho_2^2 = 14.681,9 \quad (\varrho_2^2 + A^2) = 14.681,9$$

$$\varrho_3^2 = 49.218,6 \quad (\varrho_3^2 + A^2) = 49.218,6$$

$$\text{where } t = 0.375 \text{ hours} \quad \frac{T - T_A}{T_o - T_A} = \frac{45.9 - 20.3}{96.0 - 20.3} = 0.338,1$$

$$\frac{0.339,1}{4 (0.000,968,4)} = \frac{-0.002,48 T}{0.002,480,9 J_o (0.049,8)}$$

$$\therefore T = 617.177 \quad \text{and } \kappa = 1.597,8 \text{ ft}^2/\text{hr}$$

The literature value is 1.322 and the deviation from it is 20.86%.

Therefore the method is satisfactory since the literature value (45a)

for brass is nominal.

The actual calculation of thermal diffusivity of a piece of propellant taking values from Table XV.

$$R = 11.2 \text{ mm or } 0.036,7 \text{ feet}$$

$$R^2 = 0.001,346 \text{ ft}^2$$

$$T_A = 19.0^\circ\text{C}; \quad T_O = 82.7^\circ\text{C}; \quad T = 44.0^\circ\text{C at } 0.333,3 \text{ hours.}$$

$$\frac{T - T_A}{T_O - T_A} = \frac{44.0 - 19.0}{82.7 - 19.0} = 0.592,4$$

$$h = \frac{(h_c + h_r)}{k} = \frac{2.3}{0.191} = 12.04$$

$$A = hR = 12.04(0.036,7) = 0.441,868$$

$$A^2 = 0.195,2$$

$$\varrho_1 = 0.893; \quad \varrho_1^2 = 0.797,4; \quad \varrho_1^2 + A^2 = 0.992,6$$

$$\varrho_2 = 3.94; \quad \varrho_2^2 = 15.523,6; \quad \varrho_2^2 + A^2 = 15.718,8$$

Substituting these values in the formula gives

$$\frac{0.592,4}{4(0.441,8)} = \frac{e^{-0.794,4 T}}{0.992,6 J_0(0.893)} + \frac{e^{-15.523,6 T}}{15.718,8 J_0(3.94)} \dots\dots\dots (163)$$

$$\therefore T \text{ is } 2.161,7 \text{ and } x \text{ is } 0.008,727 \text{ ft}^2/\text{hr}$$

A check using the second term $e^{-1.723,7} + e^{-33.557}$ the second term is too small to make any difference and thus the value of T is satisfactory.

The values for the other cooling curves were given in Tables XVI to XXII. Similarly the values of thermal diffusivity were tabulated in Table XXIII. The effect of the variation in k and $(h_c + h_r)$ was given in Table XXIV.

The calculation of the heat capacity of the propellant is given below:

$$\alpha = \frac{k}{\rho c_p} \dots\dots\dots (128)$$

where α = thermal diffusivity in ft^2/hr

k = thermal conductivity in $\text{BTU}/\text{hr}/\text{ft}/^\circ\text{F}$

ρ = density in lbs/ft^3

c_p = heat capacity in $\text{BTU}/\text{lb}/^\circ\text{F}$

substituting in the formula

$$0.008,104 = \frac{0.191}{107.328 c_p}$$

$$\therefore c_p \text{ is } 0.219,5 \text{ BTU}/\text{lb}/^\circ\text{F}$$

The effect of the variation in the thermal diffusivity on heat capacity was given in Table XXV.

The estimation of the heat transfer constants α , k , ρ , and c_p for the 20% aluminium case was as follows: The new mixture is 20% Al., 20% polyurethane, 60% NH_4ClO_4 .

$$\alpha = 0.8(0.008,104) + 0.2(3.665)$$

$$\alpha = 0.739,5$$

$$k = 0.8(0.191) + 0.2(118) = 23.75$$

$$\rho = 0.8(107.328) + 0.2(169) = 119.7$$

$$c_p = 0.8(0.219,5) + 0.2(0.214) = 0.218,4$$

The values of these constants for aluminum, polymer alone, polyurethane propellant and propellant plus 20% aluminum were tabulated in Table XXVI.

Cross check

$$x_T = \frac{k}{\rho c_p} = \frac{23.75}{119.7(0.218,4)} = 0.908,4 \text{ ft}^2/\text{hr}$$

This is the final figure used for computation. An earlier figure of 0.476 was used in some calculations but in this range of values has negligible difference on the final figures.

The master equation converted to engineering units:

$$\frac{\text{BTU}}{\text{hr ft}^3} = \frac{\text{cals}}{\text{gm hr}} \cdot \frac{\text{BTU}}{\text{cals}} \cdot \frac{\text{grams}}{\text{cm}^3} \cdot \frac{\text{cm}^3}{\text{in}^3} \cdot \frac{\text{in}^3}{\text{ft}^3}$$

assuming that the density of the polymer is 1

$$\frac{\text{BTU}}{\text{hr ft}^3} = \frac{0.002,896(16.38)(1,728)}{252} = 0.325,2$$

Application: Now taking the finite difference equation for the infinite solid cylinder from the theoretical section, (equation 110) and using the above for the heat source term gives

$$T_{m,n+1} = \frac{(1+1/m)}{M} T_{m-1,n} + \frac{(M-2-1/m)}{M} T_{m,n} + \frac{1}{M} T_{m-1,n} + \frac{q' \Delta t}{\rho c_p} \dots\dots(110)$$

Here our heat source is only 25% of the total material so the last term must be written as

$$\frac{q'}{\rho c_p} \left[\frac{25}{100} \right] \Delta t$$

Now M has been worked out to be 4.5687

$$M = \frac{(\Delta r)^2}{\alpha \Delta t}$$

$$\text{Then } 4.5687 = \frac{(0.5)^2}{144(0.008,104) \Delta t}$$

$$\therefore \Delta t = 0.046,89 \text{ hours}$$

Then the average value of $\frac{q'}{\rho c_p} \left[\frac{25}{100} \right] \Delta t$ becomes

$$\frac{0.325,2(25)(0.046,89)}{107.328(0.219,5)100} = 0.000,161,8$$

and the top value of $\frac{q'}{\rho c_p} \left[\frac{25}{100} \right] \Delta t$ is

$$\frac{11.07(0.325,2)(0.25)(0.046,89)}{107.328(0.219,5)} = 0.001,791$$

$$q''_{av} = 0.000,161,8 e^{0.061,408T} \left[e^{-0.001,391(0.046,89)n} e^{0.051,447T} - 0.9 e^{-6.584(0.046,89)n} \right] \dots\dots(165)$$

- 116 -

$$q''_{top} = 0.001,791 e^{0.061,403T} \left[e^{-0.001,391(0.046,89)n} e^{0.051,447T} - 0.9 e^{-6.584(0.046,89)n} \right] \dots\dots\dots(166)$$

$$q'' = \text{Alfa } e^{\text{Beta}(T)} \left[e^{\text{Gama}(n)e^{\text{Ro}(T)}} - \text{CONS3T } e^{cn} \right] \text{ noting that } n\Delta t = t$$

For the low values of $\frac{Q'}{\rho c_p} \left[\frac{25}{100} \right] \Delta t$

$$M = 4.5687 = \frac{(\Delta r)^2}{\alpha \Delta t} = \frac{(0.5)^2}{144(0.006,8) \Delta t}$$

$\therefore \Delta t$ is 0.055,88 hours

$$\text{Alfa}_{av} = \frac{0.325,2(0.25)(0.055,882,7)}{107.328(0.117,8)} = 0.000,359,38_6$$

$$\text{Alfa}_{top} = 11.07(0.000,359,386) = 0.003,987,4$$

$$\text{Gama} = -0.001,391(0.055,882,7) = -0.000,077,73$$

$$\text{Ro} = 0.051,447$$

$$c = -6.584(0.055,882,7) = -0.367,95$$

For the high values of $\frac{Q'}{\rho c_p} \left[\frac{25}{100} \right] \Delta t$

$$M = 4.5687 = \frac{(\Delta r)^2}{\kappa \Delta t} = \frac{(0.5)^2}{144(0.011,413) \Delta t}$$

$\therefore \Delta t$ is 0.035,295 hours

$$\text{Alfa}_{sv} = \frac{0.325,2(0.25)(0.033,295)}{107.328(0.295)} = 0.000,085,208$$

$$\text{Alfa}_{top} = 11.07(0.000,085,208) = 0.000,943,2$$

$$\text{Gama} = -0.001,391(0.033,295) = -0.000,046,31$$

$$c = -6.584,454(0.033,295) = -0.219,229$$

For the 20% Aluminum case.

$$M = 4.5687 = \frac{(\Delta r)^2}{\kappa \Delta t} = \frac{(0.5)^2}{144(0.908,4) \Delta t}$$

$\therefore \Delta t$ is 0.000,418,3 hours

Here the heat source is only 20% of the material

$$\text{Alfa}_{top} = \frac{0.20(0.325,2)(0.000,418,3)(11.07)}{119.7(0.218,4)} = 0.000,011,51$$

$$\text{Beta} = 0.061,407,51$$

$$\text{Gama} = -0.001,391(0.000,418,3) = -0.000,000,581$$

$$R_0 = 0.051,447$$

$$c = -6.884,454(0.000,418,3) = -0.002,752$$

The computation for the Rank-Difference Method of correlation between the burning rate and the maximum temperature curve for $K = 0.008,104$ ft³/hr, 122°F boundaries, positive initial slope and top alfa was as follows:

Values of N , $\sum(u_i - v_i)$ and $\sum(u_i - v_i)^2$ were taken from Table XXVII and the formula was taken from Standard Mathematical Tables (107a)

$$P = 1 - \frac{6 \sum(u_i - v_i)^2}{n(n^2 - 1)} \dots\dots\dots(167)$$

$$P = 1 - \frac{6(14)}{6(6^2 - 1)}$$

$$P = 0.60$$

If the Rank-Difference Method is reworked according to the method given in Steel and Torrie (108c), who give the formula as

$$r_s = 1 - \frac{6 \sum(u_i - v_i)^2}{(n-1)n(n+1)} \dots\dots\dots(168)$$

where r_s is Spearman's rank correlation coefficient and n is the number of $(u_i - v_i)$ terms. The criterion

$$t = r_s \sqrt{\frac{n-2}{1-r_s^2}} \dots\dots\dots(169)$$

is distributed as Student's t with (n - 2) degrees of freedom. From previous data $\sum(u_i - v_i)^2 = 14$ and $N = 6$. If this is associated with (n - 2) degrees of freedom then

$$n - 2 = N \dots\dots\dots(170)$$

$$n - 2 = 6$$

$$n = 8$$

Now substituting $\sum(u_i - v_i)^2$ and n into the formula (181s) gives

$$r_s = 1 - \frac{6(14)}{(8-1)8(8+1)} = 0.833$$

Confidence limits on the correlation coefficients were worked out using Fisher's method given in Steel and Torrie (198b). Confidence limits cannot be placed directly on r because r is not symmetric.

Therefore the method is to calculate

$$z = f(r) = \tanh^{-1} r = 0.5 \ln \frac{(1+r)}{(1-r)} \dots\dots\dots(171)$$

which is symmetric. Compute the sample estimate of the variance in z from

$$s_z = \sqrt{\frac{1}{n-3}} \dots\dots\dots(172)$$

Place confidence limits on z , work out the high and low values, and then convert back, with the exception that r is now called ρ , a more suitable symbol for a whole population.

For $r = 0.925,2$

$$z = 0.5 \ln \frac{(1+r)}{(1-r)} = 0.5 \ln \frac{(1+0.925,2)}{(1-0.925,2)} = 1.624,3$$

$$s_z = \sqrt{\frac{1}{(n-3)}} = \sqrt{\frac{1}{(6-3)}} = 0.577,36$$

For 95% confidence limits and an infinite population a table of Student's t gives 1.96, now

$$t = \frac{\bar{z} - \bar{z}}{s_z} \dots\dots\dots(173)$$

$$\bar{z} - \bar{z} = t s_z = 1.96(0.577,36) = 1.13162$$

$$\bar{z} = \bar{z} \pm 1.132$$

$$\bar{z} = 1.624 \pm 1.132$$

or $\bar{z}$ falls between 0.492 and 2.756

The corresponding values of ρ are 0.46 and 0.98

RESULTS

Introduction

Experimental values of the burning rate, heats of polymerization, instantaneous q during polymerization, temperature profiles and physical measurements for the heat transfer constants are listed below.

The polymerizations were done at 25°C, 48°C and 62°C.

The burning rates of a solid cylinder of propellant and a thin walled hollow cylinder of propellant were measured at 400 psig.

Experiments were done to determine the density, thermal conductivity, heat capacity and thermal diffusivity of the solid propellant.

Values calculated from these figures are also included.

Calculated values of the constants in the exponential decays are given also.

Correlation of the burning rate and polymerization temperature was carried out by the Product Moment Method and by the Rank Difference Method.

Strand Burner Results

TABLE I

The Relationship between the Burning Rate and the Radius for Polyurethane

Propellant

The Five Inch Solid Cylinder

Experiment Number	Rate "r" in inches per second	Radius "r" in inches
1	0.376	0.0
2	0.370	0.0
3	0.297	0.0
4	0.835	0.0
Av.	0.469 ₅	
1	0.484	0.5
2	0.273	0.5
3	0.657	0.5
4	0.783	0.5
5	0.442	0.5
6	0.448	0.5
7	0.523	0.5
8	0.437	0.5
Av.	0.506 ₂₅	

TABLE I CONTINUED

Experiment Number	Rate "r" in inches per second	Radius "r" in inches
-------------------	----------------------------------	-------------------------

1	0.388	1.0
2	0.461	1.0
3	0.403	1.0
4	0.434	1.0
5	0.276	1.0
6	0.309	1.0
7	0.245	1.0
8	0.276	1.0
9	0.497	1.0
10	0.533	1.0
11	0.822	1.0
12	1.020	1.0
13	0.509	1.0
14	0.960	1.0
15	0.933	1.0
Av.	0.537 ₇	

1	0.539	1.5
2	0.554	1.5
3	0.494	1.5
4	0.408	1.5
5	0.722	1.5
Av.	0.505 ₄	

TABLE I CONTINUED

Experiment Number	Rate "r" in inches per second	Radius "r" in inches
1	0.189	2.0
2	0.183	2.0
3	0.200	2.0
4	0.310	2.0
5	0.303	2.0
6	0.272	2.0
7	0.394	2.0
8	0.287	2.0
9	0.288	2.0
10	0.261	2.0
11	0.275	2.0
Av.	0.269 ₃	
1	0.207	2.5
2	0.192	2.5
Av.	0.199 ₅	

TABLE II

The Relationship between the Burning Rate and the Radius for Polyurethane

Propellant

The Hollow Cylinder O.D. $5\frac{1}{4}$ ", I.D. 3"

Experiment Number	Rate "r" in inches per second	Radius "r" in inches
1	0.186	1.5
2	0.187	1.5
3	0.173	1.5
4	0.179	1.5
5	0.174	1.5
Av.	0.179 ₈	
1	0.224	2.0625
2	0.186	2.0625
3	0.184	2.0625
4	0.184	2.0625
5	0.203	2.0625
Av.	0.196 ₂	
1	0.197	2.625
2	0.226	2.625
3	0.260	2.625
4	0.208	2.625
5	0.191	2.625
Av.	0.216 ₄	

TABLE III

The Values of ΔH for the Polymerization of the Polyurethane Polymer,
obtained from the Microcalorimeter

Experiment Number	Temperature °C	ΔH in cals/gm
1	25	4.830
2	25	1.712
3	25	11.69
4	25	5.005
5	25	3.842
6	25	1.567
7	25	3.927
8	25	4.356
9	25	2.271
10	25	3.226
		Av. = 4.243
11	48	7.473
12	48	3.798
13	48	7.076
14	48	5.375
15	48	8.121
16	48	3.002
17	48	12.82
18	48	7.098
		Av. = 6.845
19	62	8.724

TABLE III CONTINUED

Experiment Number	Temperature	ΔH in
	$^{\circ}C$	cals/gm
20	62	7.608
21	62	6.396
22	62	3.017
23	62	2.583
24	62	2.459
25	62	3.434
26	62	5.282
27	62	4.406
28	62	4.171
29	62	4.074
30	62	2.841
31	62	3.786
32	62	8.110
33	62	9.313
34	62	5.503
35	62	4.410
36	62	6.671
37	62	7.709
38	62	5.362
39	62	6.567

Av. = 5.358

TABLE III CONTINUED

Experiment Number	Temperature °C	ΔH in cals/gm
-------------------	-------------------	--------------------------

Some high values not included in the main list since an O-ring was used in place of a belt on the preamplifier.

40	48	10.40
41	48	7.241
42	48	14.54
43	48	13.10

TABLE IV

Temperature History of a small sample of Polyurethane during

Polymerization - 1

Time in minutes	Millivolts	Temperature in °C
0.0	1.46	28.6
0.1	1.67	33.6
0.2	2.17	42.2
0.3	2.72	52.5
0.4	3.10	59.7
0.5	3.23	62.2
0.6	3.24	62.3
0.7	3.26	62.7
0.8	3.27	62.9
0.9	3.27	62.9
1.0	3.28	63.1

TABLE IV CONTINUED

Time in minutes	Millivolts	Temperature in °C
1.4	5.30	63.4
2.4	3.35	64.4
3.4	3.36	64.6
4.4	3.37	64.8
5.4	3.36	64.6
6.2	3.36	64.6
6.533	3.35	64.4
6.867	3.33	64.0
7.2	3.30	63.4
7.533	3.28	63.1
7.867	3.27	62.9
8.2	3.26	62.8
8.533	3.25	62.6
8.867	3.24	62.4
9.2	3.24	62.4
9.533	3.24	62.4
10.2	3.23	62.2
10.533	3.23	62.2
13.533	3.23	62.2
16.867	3.23	62.2
20.2	3.23	62.2
23.533	3.22	62.0
bath	3.22	62.0

TABLE V

Temperature History of a small sample of Polyurethane during
Polymerization - 2

Time in minutes	Millivolts	Temperature in °C
0.0	1.64	32.0
1.0	1.67	32.6
2.0	1.74	34.0
3.0	1.90	37.0
4.0	2.05	39.8
5.0	2.22	43.0
6.0	2.37	46.0
7.0	2.50	48.4
8.0	2.54	49.2
9.0	2.68	51.8
10.0	2.73	52.8
11.0	2.78	53.7
12.0	2.82	54.4
13.0	2.85	55.0
14.0	2.87	55.4
15.0	2.88	55.6
16.0	2.89	55.8
17.0	2.90	56.0
18.0	2.90	56.0
19.0	2.90	56.0
20.0	2.90	56.0
21.0	2.90	56.0
22.0	2.89	55.8

TABLE V CONTINUED

Time in minutes	Millivolts	Temperature in °C
23.0	2.88	55.6
24.0	2.88	55.6
25.0	2.875	55.5
26.0	2.87	55.4
27.0	2.87	55.4
28.0	2.86	55.2
29.0	2.86	55.2
30.0	2.85	55.2
31.0	2.85	55.2
32.0	2.84	54.8
33.0	2.84	54.8
34.0	2.83	54.6
35.0	2.83	54.6
36.0	2.81	54.2
37.0	2.78	53.7
38.0	2.77	53.5
39.0	2.76	53.3
40.0	2.74	53.0
41.0	2.73	52.8
42.0	2.72	52.6
43.0	2.71	52.4
44.0	2.70	52.2
45.0	2.70	52.2
46.0	2.69	52.0

TABLE V CONTINUED

Time in minutes	Millivolts	Temperature in °C
47.0	2.69	52.0
48.0	2.68	51.8
49.0	2.68	51.8
50.0	2.67	51.6
51.0	2.67	51.6
52.0	2.67	51.6
60.0	2.67	51.6
65.0	2.66	51.4
120.0	2.64	51.0

TABLE VI

Temperature History for a 19mm diameter Brass Cylinder cooling in air

Time in minutes	Millivolts	Temperature in °C
0.0	5.05	96.0
7.5	3.82	73.2
15.0	2.90	56.0
22.5	2.36	45.9
30.0	2.00	39.0
37.4	1.72	33.8
45.0	1.52	29.7
52.5	1.40	27.4
60.0	1.30	25.4
67.5	1.22	24.0
75.0	1.18	23.2
112.5	1.05	20.3

TABLE VII

A sample of the recorder readings taken on Calorimeter #1 at 47.32°C

Time in hours	Instantaneous q in divisions	Integrator units
0.00	0.00	0.0
0.05	10.00	
0.10	24.95	
0.125	30.17	
0.25	39.37	
0.375	44.59	
0.5	39.32	
0.75	33.09	
1.00	26.15	
1.25	20.64	
1.425	17.76	
1.50	17.58	39.30 - 0
2.50	9.43	Integrator off
3.00	7.31	
3.50	5.95	
4.00	4.54	
4.50	4.25	
5.00	3.63	
5.50	3.18	
6.00	2.76	
6.50	2.49	
7.00	2.22	

TABLE VII CONTINUED

Time in hours	Instantaneous q in divisions	Integrator units
7.50	2.02	Integrator off
7.55		0.00
8.50	1.65	3.78 - 0

TABLE VIII

Determination of the Constants a_1 and w_1 in the function $\theta = a_1 e^{w_1 t}$ by

The Method of Least Squares

n	θ	y_i	x_i	$y_i x_i$	x_i^2
1	44.59	3.798	0.375	1.424	0.1401
2	39.32	3.671	0.5	1.836	0.250
3	30.09	3.500	0.75	2.625	0.563
4	26.15	3.264	1.00	3.264	1.000
5	20.64	3.025	1.25	3.782	1.563
6	17.76	2.876	1.425	4.098	2.031
7	17.58	2.868	1.50	4.301,8	2.250
8	9.43	2.244	2.50	5.610	6.250
9	7.31	1.989	3.00	5.968	9.000
10	5.95	1.783	3.50	6.242	12.250
11	4.54	<u>1.513</u>	<u>4.00</u>	<u>6.052</u>	<u>16.000</u>
		30.531	19.800	45.200	51.298

$$w_1 = \frac{n \sum x_i y_i - \sum x_i \sum y_i}{n \sum x_i^2 - (\sum x_i)^2} = \frac{11(45.200) - 19.8(30.53)}{11(51.3) - 19.8(19.8)} = -0.623 \text{ hrs}^{-1}$$

TABLE VIII CONTINUED

$$b = \frac{\sum x_i^2 \sum y_i - \sum x_i \sum x_i y_i}{n \sum x_i^2 - (\sum x_i)^2} = \frac{51.30(30.53) - 19.8(45.20)}{11(51.30) - 19.8(19.8)} = 3.897$$

$$b = 3.897$$

$$b = \ln \theta_0; \log_{10} \theta_0 = \frac{3.897}{2.303} = 1.692,1; \therefore \theta_0 = 49.22 = a_1$$

TABLE IX

An Exponential decay, where $\theta_2 = a_2 e^{w_2 t}$

t	$\ln \theta_1$	$\log_{10} \theta_1$	θ_1	$\theta_2 = (\theta_1 - a)$	θ_2
0.00	3.897	1.692,2	49.22	49.22 - 0.00 =	49.22
0.05	3.866	1.678,6	47.71	47.71 - 10.00 =	37.71
0.1	3.835	1.665,1	46.25	46.25 - 24.75 =	21.50
0.125	3.819	1.658,3	45.53	45.53 - 29.97 =	15.56
0.25	3.741	1.624,5	42.12	42.12 - 39.71 =	2.95

TABLE X

Determination of the Constants a_2 and w_2 in the function $\theta_2 = a_2 e^{w_2 t}$ by

The Method of Least Squares

n	θ_2	y_i	x_i	$y_i x_i$	x_i^2
1	49.22	3.897	0.00	0.000,0	0.000,0
2	37.71	3.630	0.05	0.181,5	0.002,5
3	21.50	3.068	0.10	0.306,8	0.010,0
4	15.56	2.745	0.125	0.343,1	0.015,6
5	2.95	<u>1.082</u>	<u>0.25</u>	<u>0.270,5</u>	<u>0.062,5</u>
		14.422	0.525	1.101,9	0.090,6

$$b = \frac{\sum x_i^2 \sum y_i - \sum x_i \sum x_i y_i}{n \sum x_i^2 - (\sum x_i)^2} = \frac{0.090,6(14.422) - 0.525(1.101,9)}{5(0.090,6) - 0.525(0.525)}$$

$$b = 4.104$$

$$b = \ln \theta_0; \log_{10} \theta_0 = \frac{4.104}{2.303} = 1.782,0$$

$$\therefore \theta_0 = \text{antilog } 1.782,0 = 60.53 = a_2$$

$$w_2 = \frac{n \sum y_i x_i - \sum x_i \sum y_i}{n \sum x_i^2 - (\sum x_i)^2} = \frac{5(1.101,9) - 0.525(14.422)}{5(0.090,6) - 0.525(0.525)}$$

$$\therefore w_2 = -11.67 \text{ hrs}^{-1}$$

TABLE XI

Calculated values of q for Comparison with the Experimental Curve

Time in Hours	q(cal) in divisions	q(exp) in divisions
0.00	4.922	0.00
0.05		10.00
0.10	32.53	24.95
0.125		30.17
0.20	39.08	
0.25		39.37
0.2565	39.70	
0.30		39.32
0.375		44.59
0.50	35.93	39.32
0.75		33.09
1.00	26.48	26.15
1.25		20.64
1.425		17.76
1.50		17.58
2.00	14.07	
2.50		9.43
3.00	7.579	7.31
3.50		5.95
4.00	4.085	4.54
4.50		4.25

TABLE XI CONTINUED

Time in hours	q(cal) in divisions	q(exp) in divisions
5.00	2.215	3.63
5.50		3.18
6.00	1.181	2.76
6.50		2.49
7.00	0.639	2.22
7.50		2.02
8.00	0.334	
8.50		1.65
12.00	0.027,8	

TABLE XII

The Constants for the Equation $a_1 c(e^{w_1 t} - e^{w_2 t})$

No	T°C	$a_1 c$ cals/gm/hr	w_1	w_2	ΔH cals/gm/hr
1	25	0.175,8	-0.032,3	-2.246	4.83
2	25	0.165,5	-0.089,2	-1.368	1.150,5
3	25	0.264,8	-0.004,7	-2.092	11.69
4	25	0.205,4	-0.039,3	-1.816	5.005
5	25	0.600,5	-0.151,4	-4.908	3.842
6	25	0.182,6	-0.112,0	-3.141	1.567
7	25	0.251,7	-0.059,7	-3.383	3.927
8	25	0.458,0	-0.101,6	-3.742	4.356
9	25	0.132,1	-0.053,1	-3.075	4.720
10	25	<u>0.211,7</u>	<u>-0.061,9</u>	<u>-3.738</u>	3.226
		2.648,1	-0.705,2	-29.509	

$$a_{1c_{av}} = 0.264,8; w_{1av} = -0.070,52; w_{2av} = -2.950,9$$

$$\therefore \frac{\partial H}{\partial t} = 0.264,8 \left[e^{-0.070,52t} - e^{-2.950,9t} \right] \text{ cals/gm/hr}$$

1	48	4.096	-0.521,3	-11.981	7.473
2	48	1.660	-0.420,2	-12.951	3.798
3	48	4.661	-0.623,1	-11.617	7.076
4	48	4.593	-0.789,7	-10.428	5.375
5	48	6.830	-0.781,7	-11.088	8.121
6	48	1.967	-0.603,2	-7.660	3.002
7	48	11.235	-0.801,5	-9.378	12.82

TABLE XII CONTINUED

No	T°C	$a_1 c$ cal/gm/hr	w_1	w_2	ΔH cal/gm/hr
8	48	<u>6.512</u>	<u>-0.848,3</u>	<u>-11.243</u>	7.079,8
		41.554	-5.389,0	-86.346	

$$a_1 c_{av} = 5.194,2; w_{1av} = -0.673,6; w_{2av} = -10.793$$

$$\therefore \frac{\Delta H}{\Delta t} = 5.194,2 \left[e^{-0.673,6t} - e^{-10.793t} \right] \text{ cal/gm/hr}$$

1	62	7.376	-0.837	-85.745	8.724
2	62	76.858	-3.919	-6.402	7.608
3	62	14.153	-1.730	-7.292	6.396
4	62	31.37	-3.870	-6.165	3.017
5	62	9.538	-2.584	-8.605	2.583
6	62	16.16	-3.491	-7.447	2.459
7	62	7.841	-1.516	-4.506	3.434
8	62	17.27	-1.715	-3.605	5.282
9	62	11.375	-1.613	-4.296	4.406
10	62	4.399	-0.945	-9.125	4.171
11	62	12.17	-1.779	-4.397	4.074
12	62	18.29	-2.874	-5.191	2.841
13	62	8.659	-1.705	-6.697	3.786
14	62	14.28	-1.420	-7.323	8.110
15	62	19.6	-1.187	-2.720	9.313
16	62	25.94	-2.617	-5.887	5.503
17	62	30.35	-3.406	-6.742	4.410

TABLE XII CONTINUED

No	T°C	a_1 c cal/gm/hr	w_1	w_2	ΔH cal/gm/hr
18	62	18.59	-2.053	-7.793	6.671
19	62	11.79	-1.141	-4.484	7.709
20	62	12.03	-1.691	-6.858	5.362
21	62	<u>35.07</u>	<u>-2.476</u>	<u>-4.649</u>	6.567
		403.109	-44.566	-120.185	

$$a_{1c_{av}} = 19.195; w_{1av} = -2.122, 2; w_{2av} = -6.009$$

$$\therefore \frac{\partial H}{\partial t} = 19.195 \left[e^{-2.122, 2t} - e^{-6.009t} \right] \text{ cal/gm/hr}$$

TABLE XIII

Exponential Constants in the Heat Source Equation

Temperature Scale	ϕ_0	ϕ_{0max}	β	γ	ρ
°C	0.020,65		0.110,535	-0.007,216	0.092,605
°F	0.002,896	0.012,34	0.061,408	-0.001,391	0.051,447

TABLE XIV

The Constants in the ∂H Equations

Temperature	ϕ	$\frac{\partial t}{w_1}$	w_2
25°C (77°F)	0.306,8	-0.070,52	-2.950,9
48°C (118.4°F)	4.919	-0.673,6	-10.793
62°C (143.6°F)	17.58	-2.122,2	-6.009

TABLE XV

A Cooling Curve for Polyurethane Propellant in Air - 1

Time in minutes	Millivolts	Temperature in °C
0.0	4.33	82.8
1.0	4.33	
2.0	4.31	
3.0	4.24	
4.0	4.12	
5.0	3.97	
10.0	3.23	
15.0	2.63	
20.0	2.27	44.0
25.0	1.97	
30.0	1.75	
35.0	1.59	
40.0	1.47	
45.0	1.39	
50.0	1.32	
55.0	1.27	
60.0	1.24	

$T_{\text{air}} = 19.0^{\circ}\text{C}$

TABLE XVI

A Cooling Curve for Polyurethane Propellant in Air - 2

Time in minutes	Millivolts	Temperature in °C
0.0	4.33	82.8
0.5	4.38	
1.5	4.30	
2.5	4.23	
3.5	4.13	
4.5	3.98	
5.5	3.85	
10.5	3.16	
15.5	2.63	51.8
20.5	2.24	
25.5	1.96	
30.5	1.75	
35.5	1.63	
40.5	1.52	
45.5	1.44	
50.5	1.38	
55.5	1.34	
60.5	1.31	
65.5	1.28	
70.5	1.26	

$T_{\text{air}} = 24.0^{\circ}\text{C}$

TABLE XVII

A Cooling Curve for Polyurethane Propellant in Air - 3

Time in minutes	Millivolts	Temperature in °C
0.00	4.53	82.8
2.25	4.33	
5.25	3.86	
12.75	2.92	
20.25	2.26	
27.75	1.85	
35.25	1.64	32.0
42.75	1.52	
50.25	1.42	
57.75	1.35	
65.25	1.34	
72.75	1.30	25.4

TABLE XVIII

A Cooling Curve for Polyurethane Propellant in Air - 4

Time in minutes	Millivolts	Temperature in °C
0.0	4.33	82.8
3.0	4.20	
10.5	3.14	
13.0	2.33	
25.5	1.97	
33.0	1.68	
40.5	1.62	
48.0	1.42	27.8
55.5	1.34	
63.0	1.29	
70.5	1.26	
78.0	1.24	
85.5	1.23	
93.0	1.25	
100.5	1.22	24.0

TABLE XIX

A Cooling Curve for Polyurethane Propellant in Air - 5

Time in minutes	Millivolts	Temperature in °C
0.0	5.30	100.5
7.5	4.27	
15.0	3.12	
22.5	2.90	
30.0	1.96	38.2
37.5	1.69	
45.0	1.52	
52.5	1.41	
60.0	1.34	
67.5	1.30	
75.0	1.27	
82.5	1.26	
90.0	1.24	
97.5	1.24	
105.0	1.23	
157.5	1.22	24.0

TABLE 2A

A Cooling Curve for Polyurethane Propellant in Air - 6

Time in minutes	Millivolts	Temperature in °C
0.0	5.36	101.6
1.0	5.32	
3.5	3.92	
16.0	2.86	
33.5	2.21	42.8
51.0	1.83	
58.5	1.62	
46.0	1.47	
53.5	1.40	
61.0	1.33	
68.5	1.28	
76.0	1.28	
83.5	1.25	
91.0	1.24	24.3

TABLE XXI

A Cooling Curve for Polyurethane Propellant in Air - 7

Time in minutes	Millivolts	Temperature in °C
0.0	5.40	102.6
5.0	4.72	
7.0	4.30	
14.5	3.10	
22.0	2.37	46.0
29.5	1.93	
37.0	1.66	
44.5	1.50	
52.0	1.41	
59.5	1.34	
67.0	1.29	
74.5	1.25	
82.0	1.23	24.1

TABLE XXII

A Cooling Curve for Polyurethane Propellant in Air - 8

Time in minutes	Millivolts	Temperature in °C
0.0	5.26	99.8
2.0	5.17	
9.5	3.74	
17.0	2.79	
24.5	2.20	
32.0	1.82	55.4
39.5	1.60	
47.0	1.46	
54.5	1.37	
62.0	1.33	
69.5	1.28	
77.0	1.27	
84.5	1.24	24.3

TABLE XXIII

Propellant Thermal Diffusivity

Number	Thermal Diffusivity in ft^2/hr
1	0.008,727
2	0.008,966
3	0.007,569
4	0.007,039
5	0.007,490
6	0.007,270
7	0.009,318
8	0.008,403

TABLE XXIV

The Effect of the Variation in k and $(h_c + h_r)$ on Thermal Diffusivity

$(h_c + h_r)$	$\frac{\text{B.T.U.}}{\text{hr ft}^2 \text{ } ^\circ\text{F}}$	k	$\frac{\text{B.T.U.}}{\text{hr ft}^2 \text{ } ^\circ\text{F}}$	$\times \frac{\text{ft}^2}{\text{hr}}$
2.3		0.086		0.006,0
2.3		0.191		0.008,104
2.3		0.296		0.009,36
1.5		0.086		0.006,8
1.5		0.296		0.011,413

TABLE XV

The Effect of the Variation in Thermal Diffusivity on Heat Capacity

Thermal Diffusivity in ft^2/hr	c_p Heat Capacity in $\frac{\text{BTU}}{\text{lb } ^\circ\text{F}}$
0.008,0	0.133,56
0.006,8	0.117,8
0.008,104	0.219,5
0.009,36	0.294,6
0.011,413	0.241,6

TABLE XVI

The Estimation of the Heat Transfer Constants, α , k , ρ , c_p , for the

20% Aluminum Case

Material	$\alpha \frac{\text{ft}^2}{\text{hr}}$	$k \frac{\text{BTU}}{\text{hr ft } ^\circ\text{F}}$	$\rho \frac{\text{lbs}}{\text{ft}^3}$	$c_p \frac{\text{BTU}}{\text{lb } ^\circ\text{F}}$
Polyurethane Ammonium Perchlorate	0.008,104	0.191	107.328	0.219,5
Pure Aluminum	3.665	118.0	169.0	0.214
Polymer - Amm. Per. 20% Al	0.908,4	23.75	119.7	0.218,4
Polymer - alone	0.004,864	0.098,4	64.896	0.311,8

TABLE XLVII

Computation for the Rank-Difference Method of Correlation between the
Burning Rate and the Maximum Temperature Curve for $K = 0.008, 104 \text{ ft}^2/\text{hr}$,
122°F boundaries, Positive Initial Slope and Top Alfa

No	Radius "r" in inches	Rate "r" in in/sec	u_i	Temp. in °F	v_i	$(u_i - v_i)$	$(u_i - v_i)^2$
1	0.0	0.470	4	157.2	1	3	9
2	0.5	0.506	2	156.4	2	0	0
3	1.0	0.538	1	154.1	3	-2	4
4	1.5	0.503	3	149.0	4	-1	1
5	2.0	0.269	5	139.0	5	0	0
6	2.5	0.200	6	122.0	6	<u>0</u>	<u>0</u>
						0	14

$N = 6$

$\rho = 0.6$ 95% confidence limits place ρ between -0.41 and 0.95

If $n = 8$

$r_s = 0.83_3$ 95% confidence limits place ρ between 0.07 and 0.98

TABLE XXVIII

The Product Moment Method of Correlation of the Burning Rate and the
Maximum Temperature for the Top Value of Alfa ($\alpha = 0.008, 104 \text{ ft}^2/\text{hr}$)

No	Radius in inches	Rate in in/sec	r^2	$\left(\frac{r - \bar{r}}{\sigma_r}\right)$	$\left(\frac{r - \bar{r}}{\sigma_r}\right)^2$
1	0.0	0.470	0.220,900	0.427,790	0.183,004
2	0.5	0.506	0.256,036	0.704,279	0.496,009
3	1.0	0.538	0.289,444	0.950,005	0.902,509
4	1.5	0.503	0.253,009	0.681,239	0.464,086
5	2.0	0.269	0.072,361	-1.115,941	1.245,324
6	2.5	<u>0.200</u>	<u>0.040,000</u>	<u>-1.645,879</u>	<u>2.708,918</u>
		2.486	1.131,750	0.001,493	5.999,850

$$\bar{r} = \frac{\sum r}{n} = \frac{2.486}{6} = 0.4143$$

$$\sigma_r^2 = \frac{\sum r^2 - (\sum r)^2/n}{n} = \frac{1.131,750 - (2.486)^2/6}{6} = 0.016,953$$

$$\sigma_r = \sqrt{0.016,953} = 0.130,204$$

No	Radius in inches	Temp. in OF	T^2	$\left(\frac{T - \bar{T}}{\sigma_T}\right)$	$\left(\frac{T - \bar{T}}{\sigma_T}\right)^2$
1	0.0	157.2	24,711.84	0.873,968	0.763,820
2	0.5	156.4	24,460.96	0.809,823	0.655,813
3	1.0	154.1	23,746.81	0.625,408	0.391,135
4	1.5	149.1	22,230.81	0.224,505	0.050,402
5	2.0	139.0	19,321.00	-0.585,318	0.342,597
6	2.5	<u>122.0</u>	<u>14,884.00</u>	<u>-1.948,387</u>	<u>3.796,212</u>
		877.3	129,355.42	0.000,000	5.999,979

$$\bar{T} = \frac{877.3}{6} = 146.2$$

$$s_r^2 = \frac{\sum r^2 - (\sum r)^2/n}{n} = \frac{129,355.42 - (877.8)^2/6}{6} = 155.546,666$$

$$s_r = \sqrt{155.546,666} = 12.471,855$$

No	$x' = \frac{(r - \bar{r})}{s_r}$	$y' = \frac{(T - \bar{T})}{s_T}$	$x'y'$
1	0.427,790	0.873,968	0.373,875
2	0.704,279	0.809,823	0.570,341
3	0.950,005	0.625,408	0.594,141
4	0.631,239	0.224,505	0.152,942
5	-1.115,941	-0.585,518	0.653,180
6	-1.645,879	-1.948,587	<u>3.206,809</u>
			5.551,288

$$r^2 = \frac{(\sum x'y')^2}{\sum x'^2 \sum y'^2} = \frac{5.551,288^2}{6(6)}$$

$$r = \frac{5.551,288^2}{6(6)} = \frac{5.551,288}{6} = 0.925,2$$

Regression Lines:

$$x' = 0.925,2 y'$$

$$y' = 0.925,2 x'$$

TABLE XXIX

Product Moment Correlation Coefficients between Burning Rate and

Polymerization Temperature

No	α	$\times \frac{ft^2}{hr}$	T(R,O) °F	r	95% confidence limits on r
1.	0.001,792	0.008,104	122	0.925,2	0.46 to 0.98
2.	0.000,161,8	0.008,104	122	0.910,56	0.38 to 0.99
3.	0.001,792	0.008,104	77	0.918,9	0.42 to 0.99
4.	0.000,161,8	0.008,104	77	0.910,7	0.38 to 0.99
5.	0.000,943,2	0.011,413	77	0.913,7	0.40 to 0.99
6.	0.000,085,208	0.011,413	77	0.910,4	0.38 to 0.99
7.	0.000,943,2	0.011,413	122	0.917,8	0.42 to 0.99
8.	0.000,085,208	0.011,413	122	0.908,0	0.36 to 0.99
9.	0.003,97	0.006,8	77	0.921,7	0.44 to 0.99
10.	0.000,359	0.006,8	77	0.909,9	0.37 to 0.99
11.	0.003,97	0.006,8	122	0.874,0	0.22 to 0.99
12.	0.000,359	0.006,8	122	0.873,7	0.22 to 0.99

DISCUSSION

The Discussion will be given under the following headings:

1. Burning Rate
2. The Range of ΔH
3. The Duration of Polymerization
4. The Polymerization Temperature Curves for the Solid and Hollow Cylinders
5. The Polymerization Temperature Curves for the Star Perforated Cylinder
6. End Effect
7. The Role of Aluminum Additives
8. Formal Correlation of the Burning Rate and the Maximum Polymerization Temperature
9. Possible Corrective Measures
10. Implication of the high Correlation Coefficients

1. Burning Rate

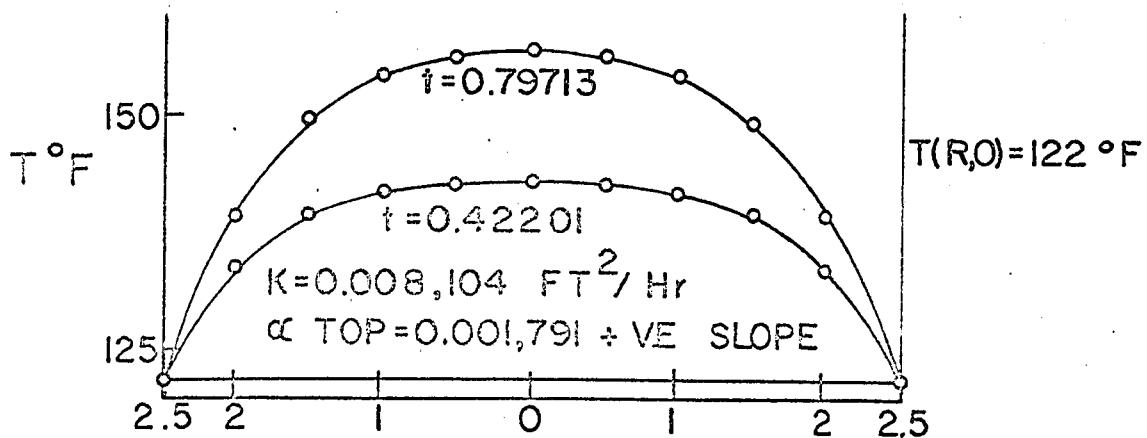
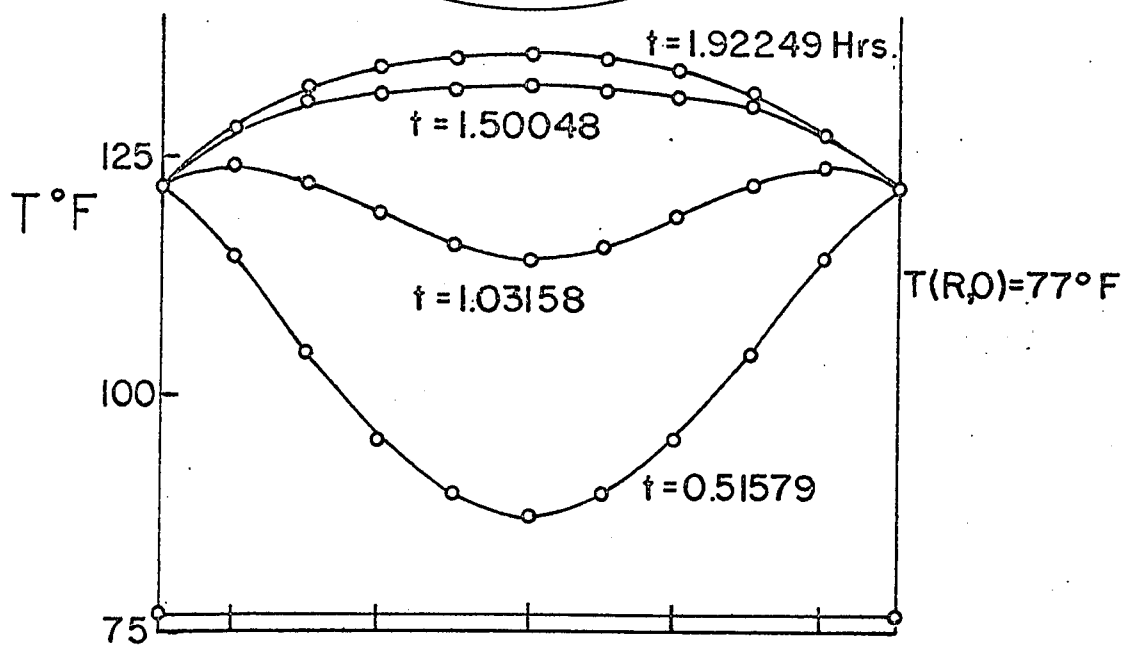
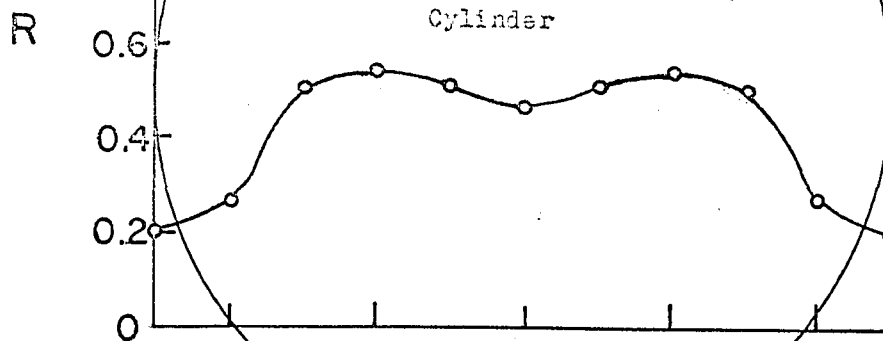
In Figure 18, the radial variation in the linear burning rate, it is easily seen that the linear burning rate across a grain (or cylinder of propellant) is not linear. As one proceeds from the outer surface towards the centre the rate rises from 0.200 inches per second at 400 psi at the surface to a peak of 0.538 inches per second at a radius of one inch then drops slightly to 0.470 inches per second at

INCH / SEC. AT 400 PS.I.

- 158 -

Figure 18

Comparison of the Burning Rate and
Temperature for the 5 inch diameter Solid
Cylinder



the centre. Although the scatter in the points making up these results is high, a statistical analysis shows that there is a significant variation between the averages and therefore the variation can not be explained on the basis of scatter.

It seems that the list of rates probably contains some values which are too high. This could be due to a piece of burning propellant dropping off the top, striking the strand further down and igniting it. Accordingly, cigarette type burning would not be maintained. Thus, the general shape of the curves could be correct but the true values are a bit lower than those shown on the graph.

Figure 18 shows the burning rate and the polymerization temperature radially across a grain of solid propellant. Only the temperature curves up to the time that maximum temperature is attained are shown. It is evident that the maximum temperature curves and the burning rate curve have the same general shape although the burning rate curve is not as smooth as the others. The early curves at 77°F initial condition show a drop in the centre and there is some hint of this in the burning rate curve. On the basis of these graphs it is fair to say that a fairly high degree of correlation is present between burning rate and temperature during polymerization.

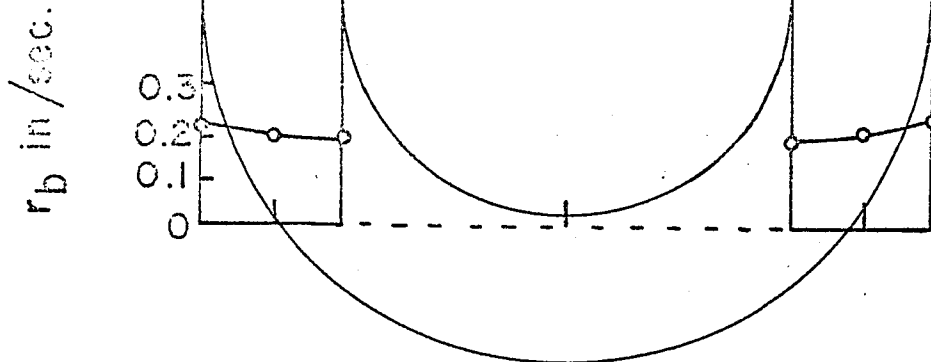
Figure 19 also shows the burning rate and polymerization temperature across a thin walled hollow cylinder of solid propellant. Here no correlation is evident probably due to the thin wall allowing heat to escape too easily.

- 130 -

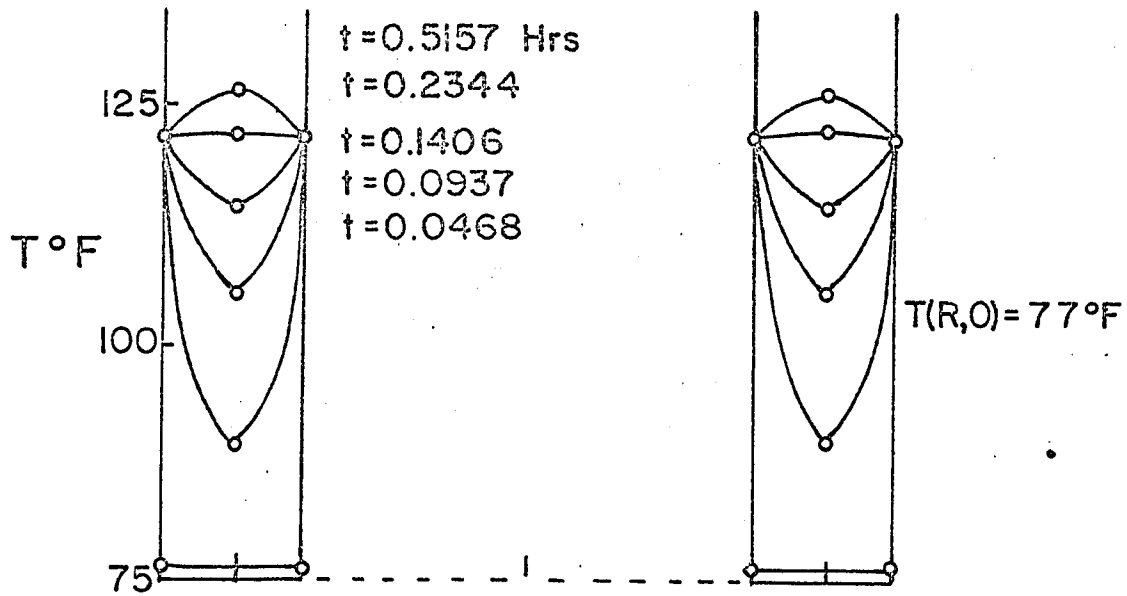
Figure 13

Comparison of the Burning Rate and
Temperature for the 5.25" O.D. and 3" I.D.
Hollow Cylinder

400 P.S.I.

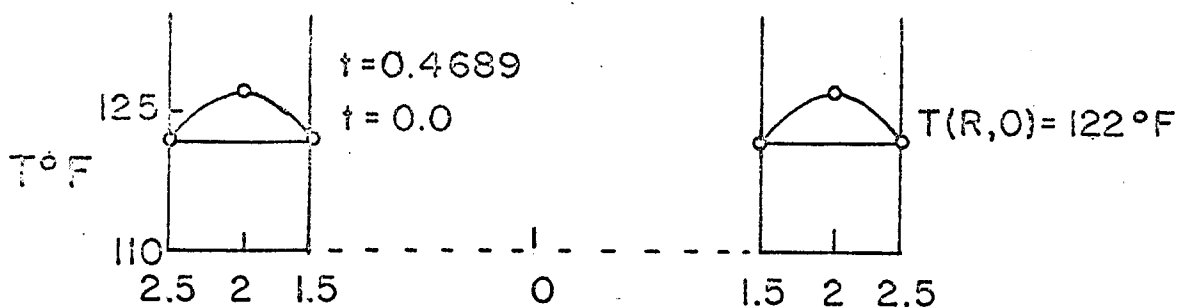


RADIUS IN INCHES



$K = 0.008,104 \text{ FT}^2/\text{HR}$

$\alpha_{\text{TOP}} = 0.001,791 \text{ + VE SLOPE}$



2. The Range of ΔH

A glance at the list of experimental values for ΔH (Table III) will show a range of about 1 to 13 calories per gram. This variation is due to a number of causes - the most important being the mixing of the ingredients in the cell. The principle on which the microcalorimeter works requires that the aluminum block and the cell contents be at equilibrium before the reaction starts. Therefore catalyst and ingredients cannot be premixed before the waiting period is over because the reaction would begin to produce heat. Since the ingredients are highly viscous any stirring would immediately produce heat and throw the reading off. The result is that the degree of mixing after the bulb containing catalyst is broken, is different in all cases. It is thought that the low results could well be caused by only partial polymerization due to the catalyst not reaching all the reactants - a conclusion confirmed by visual observation of the sample after the cell was opened. In some cases it was plainly evident that only part of the material had taken in the reaction, leading to the conclusion that the high values are the accurate ones.

Another error could have been introduced by drift in the electronics. At 25°C the reaction took at least two days to reach completion. An electronic instrument will always have some drift and if the displacement is very small it is easy for drift to become an appreciable part of the reading, especially if it has been running for some time without a resetting of the zero.

An electronic error could also be introduced by a component such as a tube changing in value over the two days run. If a tube is just starting to break down it will not be spotted immediately and will introduce some error in the reading which is not easily detectable. As the tube gets worse, it will reach a stage where its effect is unmistakable but until that point is reached, its effect may not be noticed.

The Liston Becker Breaker Amplifier has a belt driven set of contacts which should produce a square wave of four hundred cycles per second. Since the succeeding stages are deliberately designed for four hundred cycles on the superheterodyne principle, an effect will be produced if the belt should slip on the pulleys resulting in a frequency below 400. It is believed that this did happen some of the time but it is difficult to say for certain. However, it is certain that if the belt did slip the effect on the results would be considerable, resulting in lower values.

3. The Duration of Polymerization

The duration of polymerization depends upon ambient temperature. The reaction continues for 50, 12 and 3 hours at 25°C, 48°C and 62°C, respectively.

4. The Polymerization Temperature Curves for the Solid and Hollow Cylinders

The graphs (Figures 20, 21, 22, 23, 24, 25, and 26) for the temperature gradients across an infinite solid cylinder for the seventy-seven degree Fahrenheit initial condition all show the same general shape. Again only the temperature curves up to the time that maximum temperature is attained are shown. The valley, which appears initially, gradually fills and becomes a peak rising to a temperature of 137°F for the high value of ΔH and 123°F for the average value of ΔH . A range test has been conducted to find the effect of the uncertainty in the thermal conductivity on the final values. The corresponding thermal diffusivity is 0.006,8 ft²/hr on the low side and 0.011,413 ft²/hr on the high side with the centre value at 0.008,104 ft²/hr. The effect of a thermal diffusivity of 0.006,8 ft²/hr is to raise the peak to a value of 147°F while the high value, 0.011,413 ft²/hr, does not affect it at all.

If one starts with an initial condition of one hundred and twenty-two degrees Fahrenheit, an altogether different picture emerges. This time there is no valley and the temperature curves rise to a peak of 157°F, when a thermal diffusivity of 0.008,104 ft²/hr is used in the calculation. At the low end the peak is at 165°F and at the high end it is 146°F. The difference is due to the rate at which heat can flow to the outer surface. The lower the thermal diffusivity the longer it takes to escape and therefore is available to raise the temperature higher. Again if the average values of ΔH are used the peaks are at 128°F, 126°F

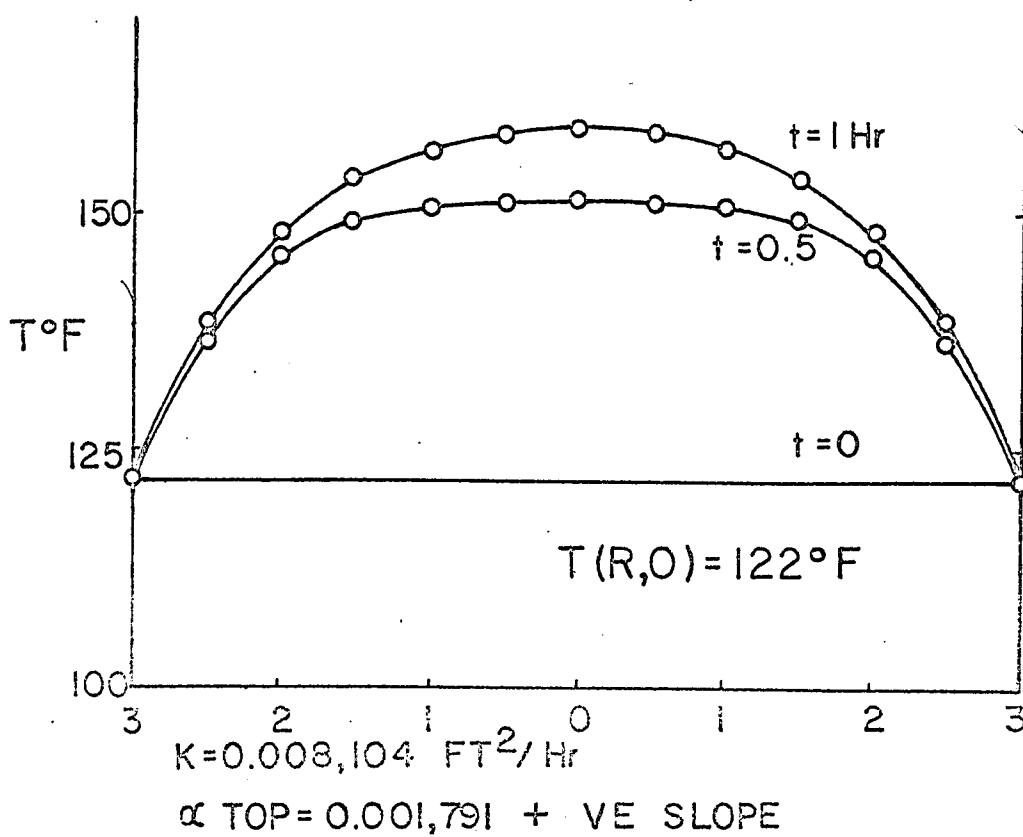
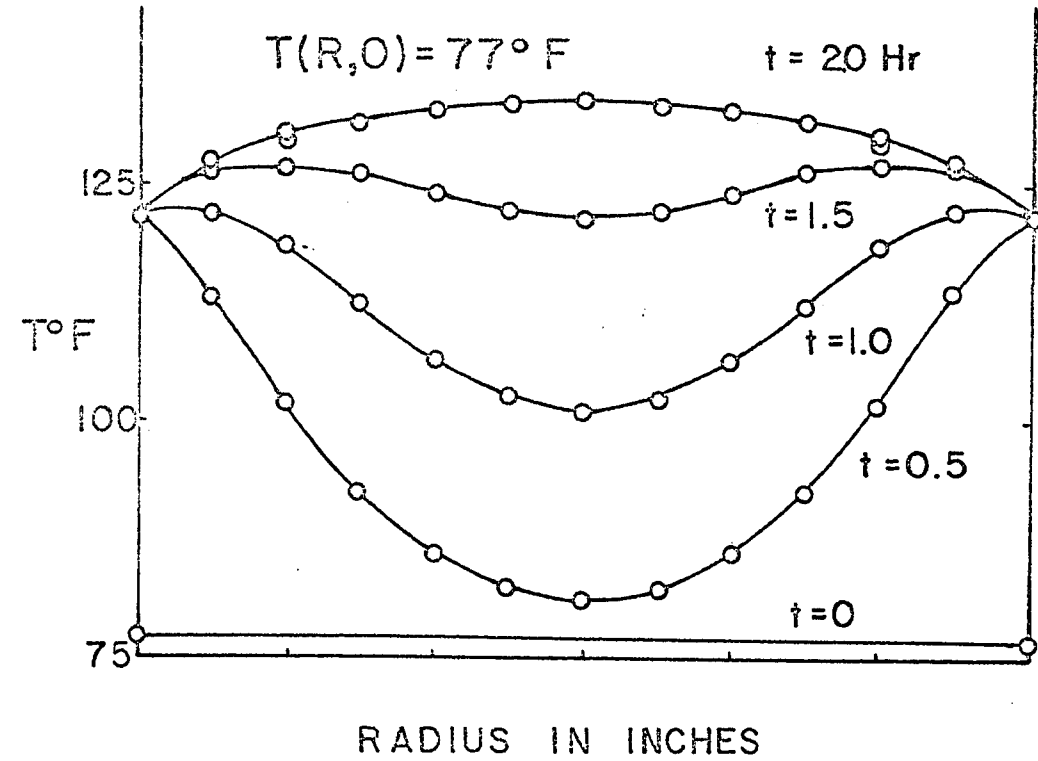


Figure 20 Temperature Gradients for the 6" diameter Solid Cylinder

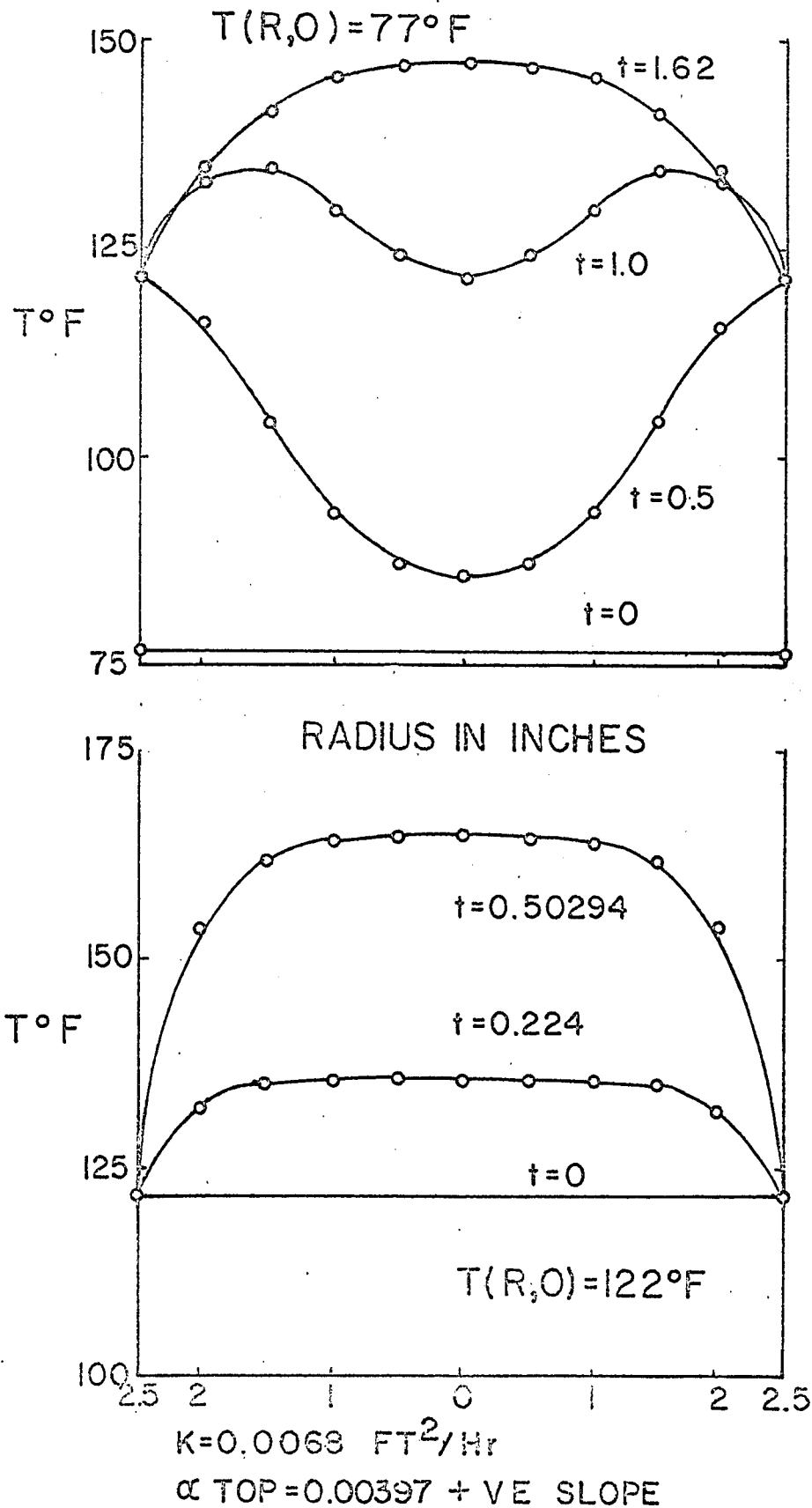


Figure 21 Temperature Gradients for the 5" diameter Solid Cylinder

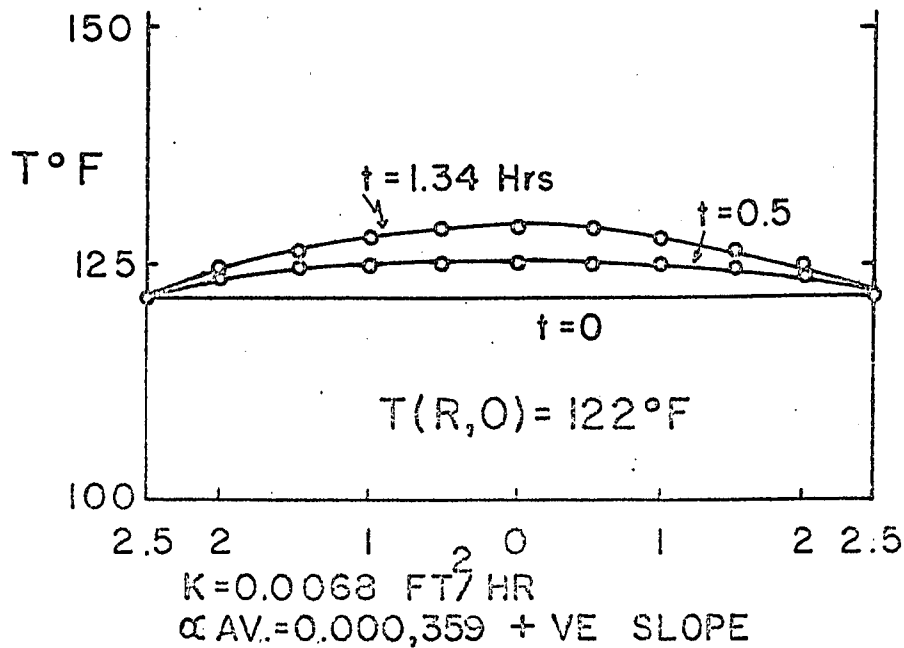
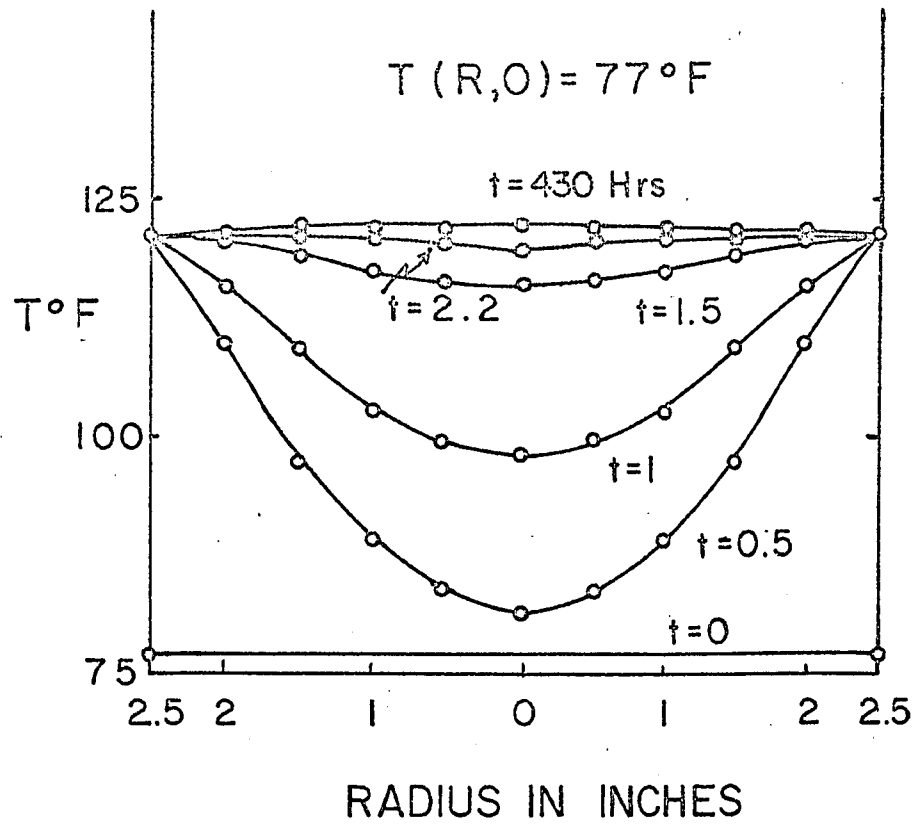


Figure 22 Temperature Gradients for the 6" diameter Solid Cylinder

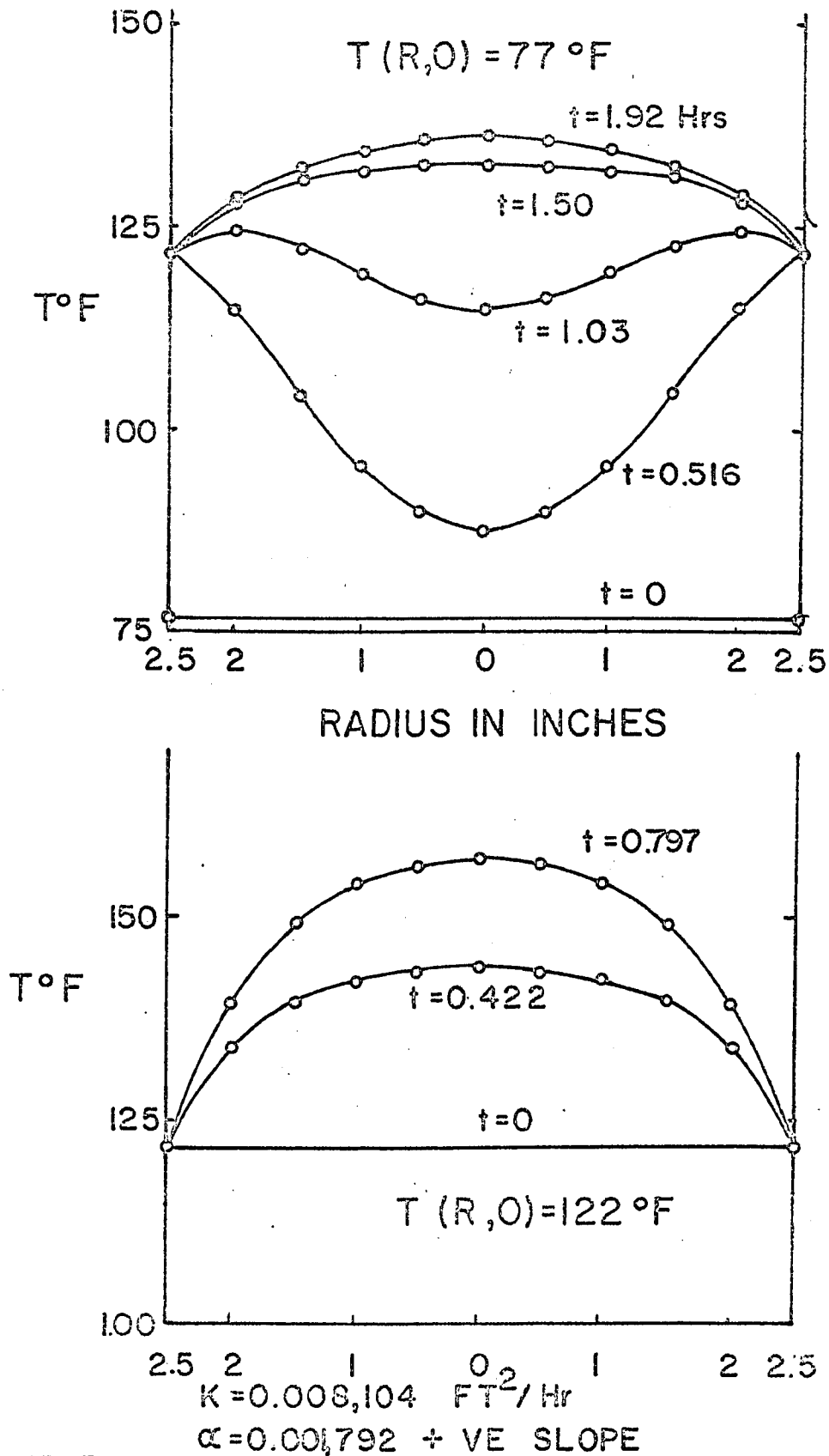


Figure 23 Temperature Gradients for the 5" diameter Solid Cylinder

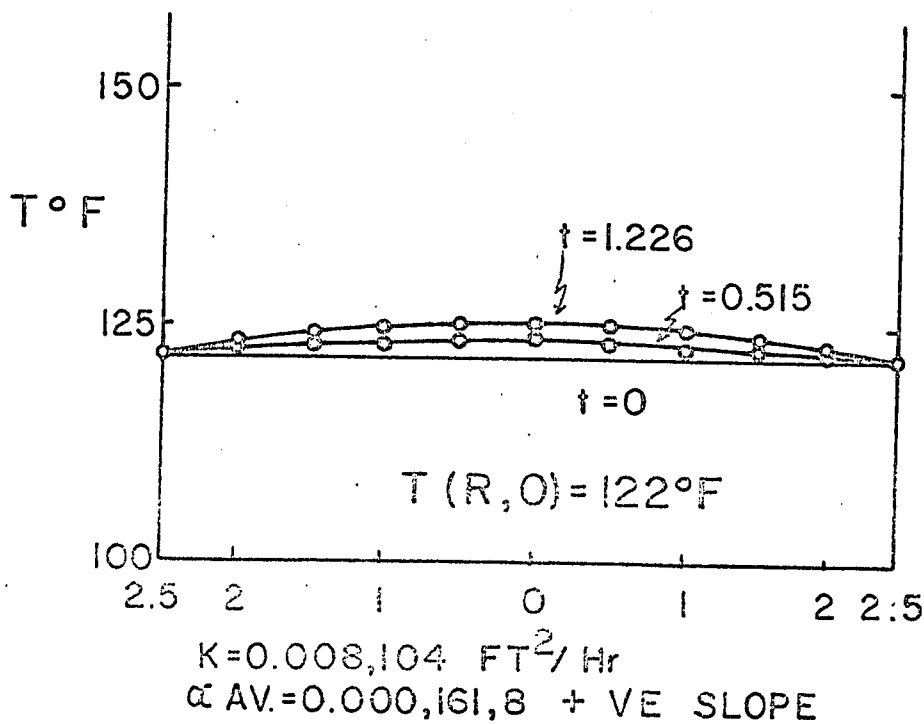
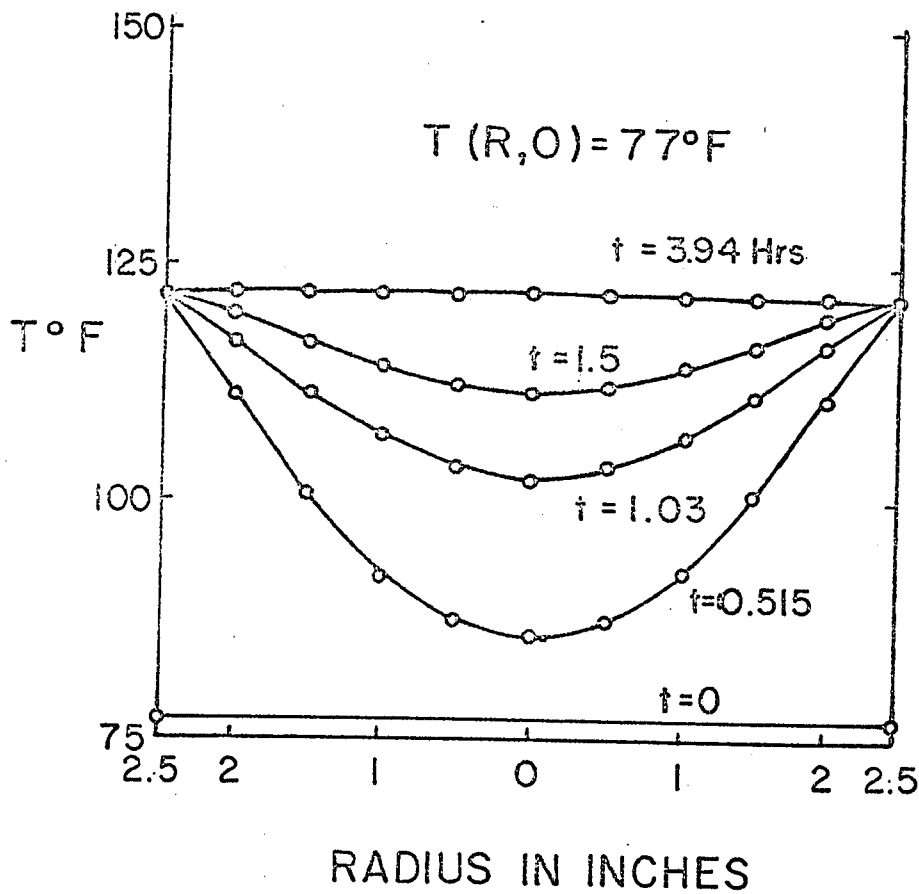


Figure 24. Temperature Gradients for the 5" diameter Solid Cylinder

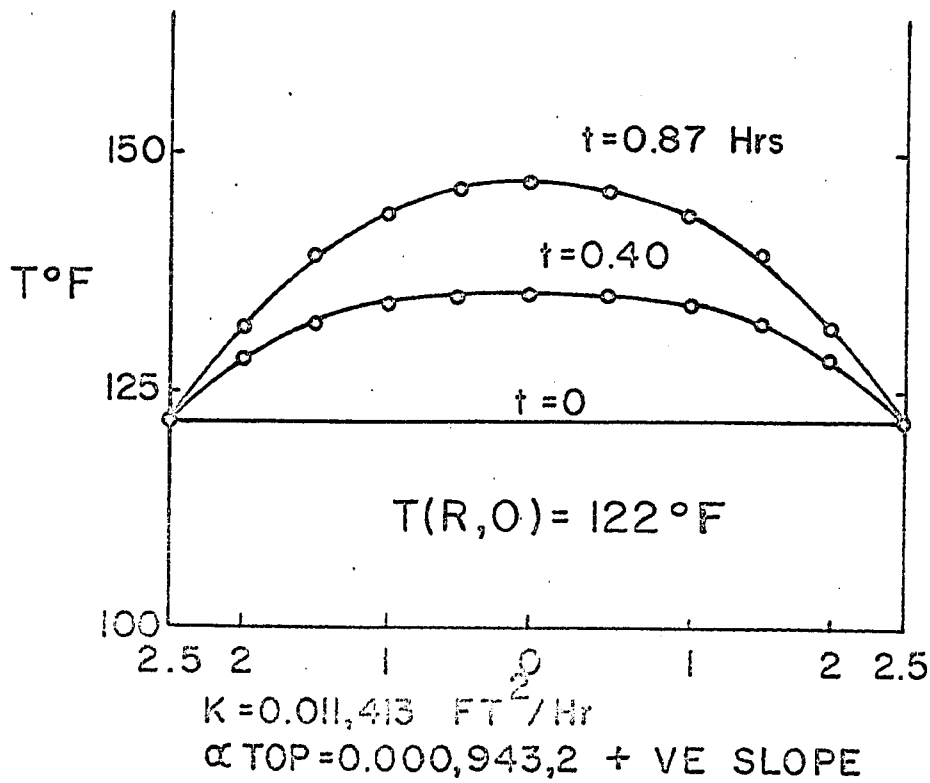
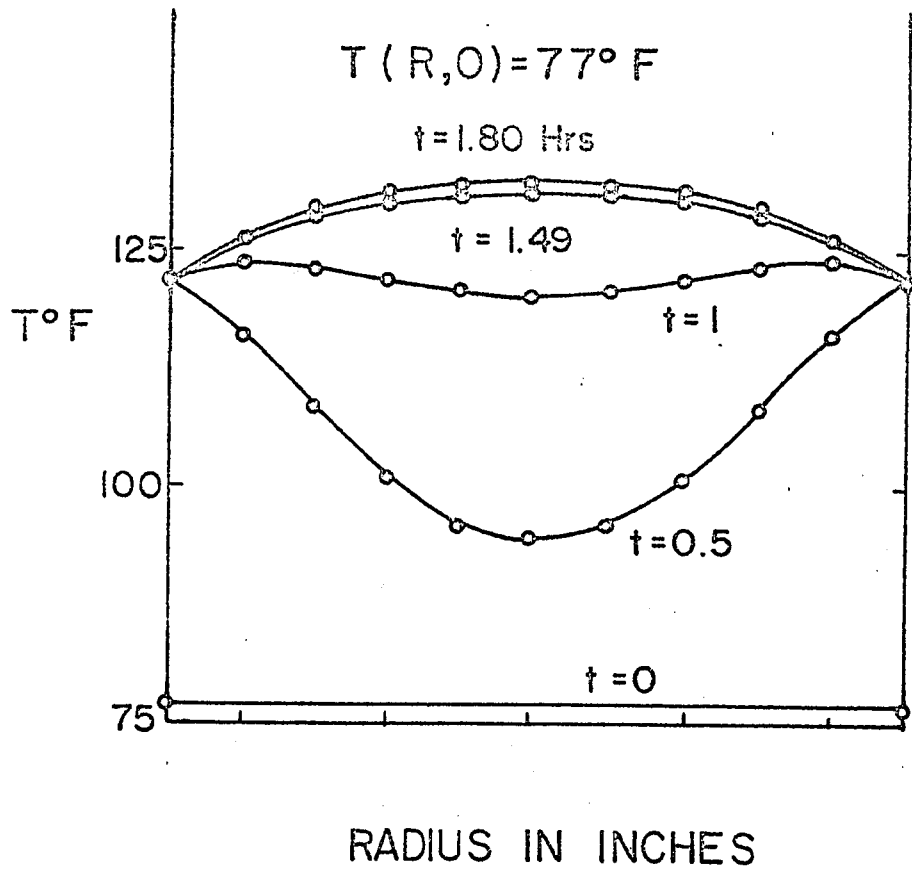


Figure 25 Temperature Gradients for the 5" diameter Solid Cylinder

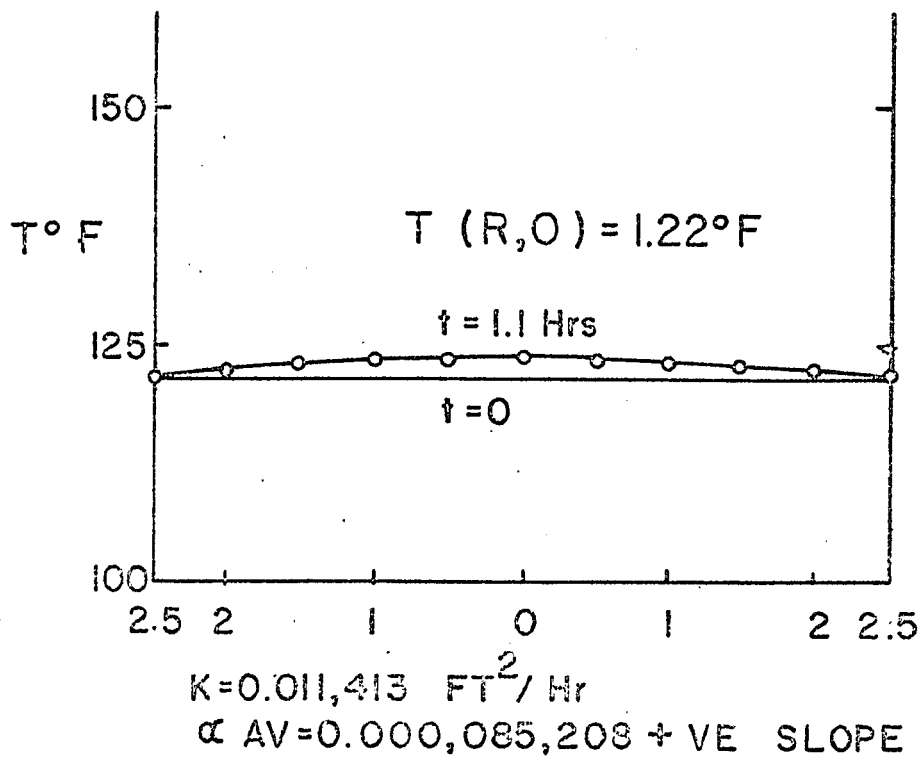
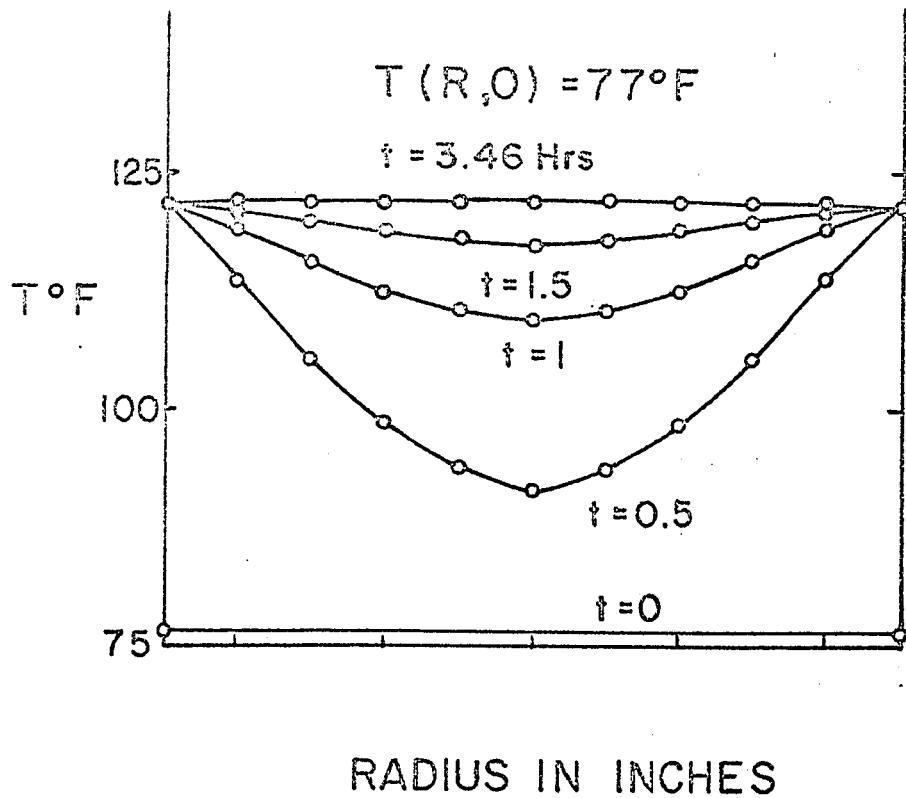


Figure 26. Temperature Gradients for the 5" diameter Solid Cylinder

and 124°F.

One six inch diameter solid cylinder has been solved for infinite length giving a 134°F peak and a 159°F peak at 77°F and 122°F initial conditions, respectively. The general shape of the curves is the same as those obtained for the five inch diameter solid cylinder.

It is thought that the true temperature gradient curves lie somewhere between the 77°F and the 122°F initial cases.

It will thus be noted that the radial temperature gradients across a piece of solid propellant, show an envelope of the same general shape as the burning rate curve (Figure 18). The envelope also rises from the surface to a maximum with a tiny dip at the centre (Figure 18). This gives rise to the possibility of an analogy between the shape of the burning rate curves and the temperature gradients during polymerization and indicates that the temperature during polymerization may be a prime factor in causing a variation in rate across the cylinder of propellant.

As the crosslinking reaction in the polymerization of the elastomer is exothermic, it is evident that although the surface of the mould may easily be kept at a constant temperature, the temperature across the radius will be higher. In this case the ammonium perchlorate polyurethane mixture is an excellent heat insulator and thus the stage is set for high temperature gradients not far from the centre of the solid.

In Figure 19, the radial variation in the linear burning rate for a thin-walled, hollow cylinder; it is seen that the variation in rate is not very great. It will be noted here that this hollow cylinder

has a difference in radii, or web, of only one inch. But even so the rate is not linear across the radius.

The corresponding temperature graphs for the thin-walled hollow cylinder (Figures 27, 28, 29, 30, 31 and 32) at an initial condition of seventy-seven degrees Fahrenheit and the top value of ΔH show a gradually filling depression which turns into a peak. The peaks are 136°F, 127°F, and 124°F for thermal diffusivities of 0.006,8, 0.008,104 and 0.011,413 ft²/hr, respectively. If the average value of ΔH is used the figures are 123°F, 122.5°F, and 122.3°F for thermal diffusivities of 0.006,8, 0.008,104 and 0.011,413 ft²/hr, respectively.

When an initial condition of one hundred and twenty-two degrees Fahrenheit is used the curves peak at 138°F, 127°F and 125°F for thermal diffusivities of 0.006,8, 0.008,104 and 0.011,413 ft²/hr, respectively, for the top value of ΔH . If the average value of ΔH is used the peaks are at 124°F, 123°F and 122.5°F for thermal diffusivities of 0.006,8, 0.008,104 and 0.011,413 ft²/hr, respectively.

It will be noted that the actual size of the thin-walled hollow cylinder used in the experiments on strand burning rates was slightly different from the size drawn here. The outer radius was 2.625 inches, one eighth of an inch larger than the outer radius used in the calculation. This is due to the fact that the computer programs were designed for a Δr of one half an inch and it was thought that this would be close enough for this case.

In the case of the thin-walled hollow cylinder it will be noted that the high temperature is fleeting and quickly disappears. Thus the

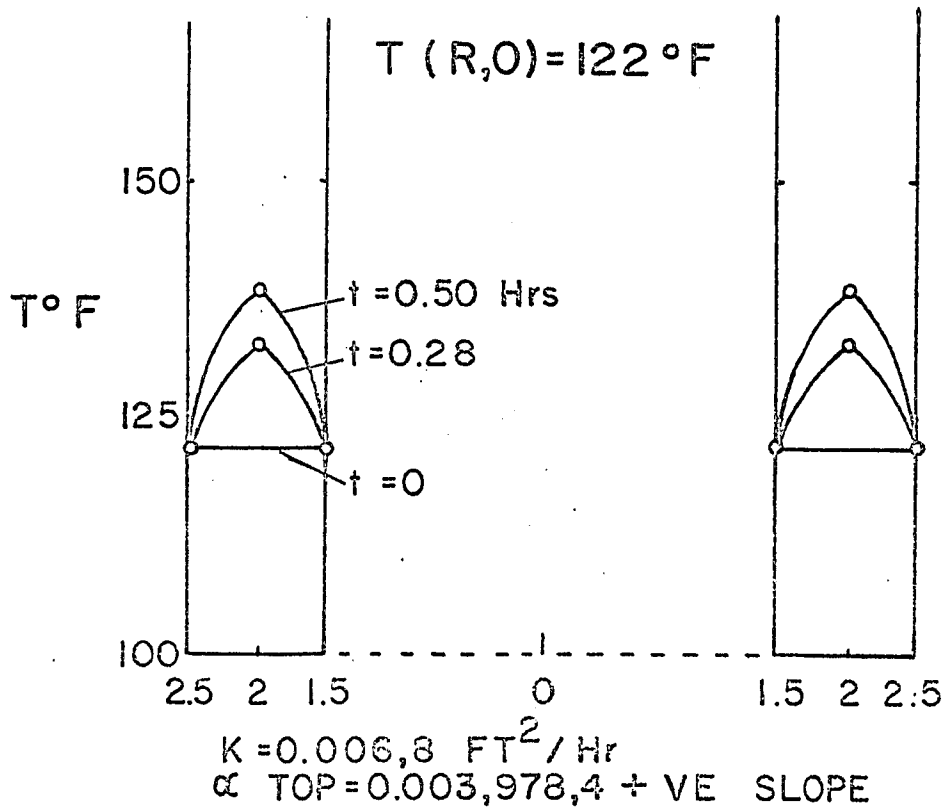
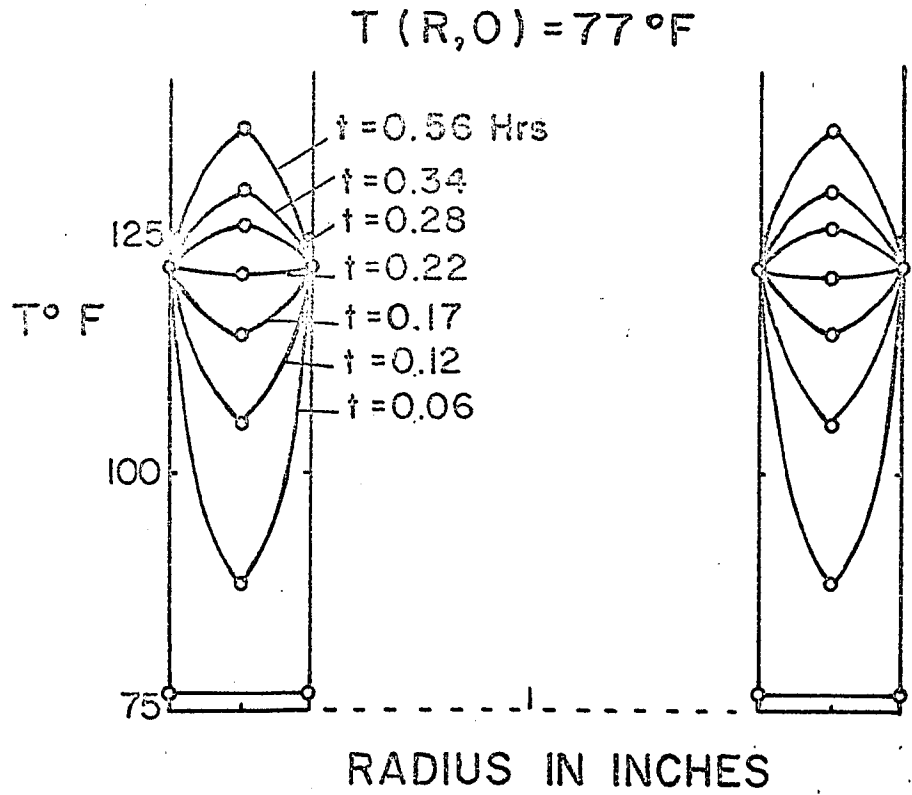


Figure 27. Temperature Gradients for the Thin Walled Hollow Cylinder

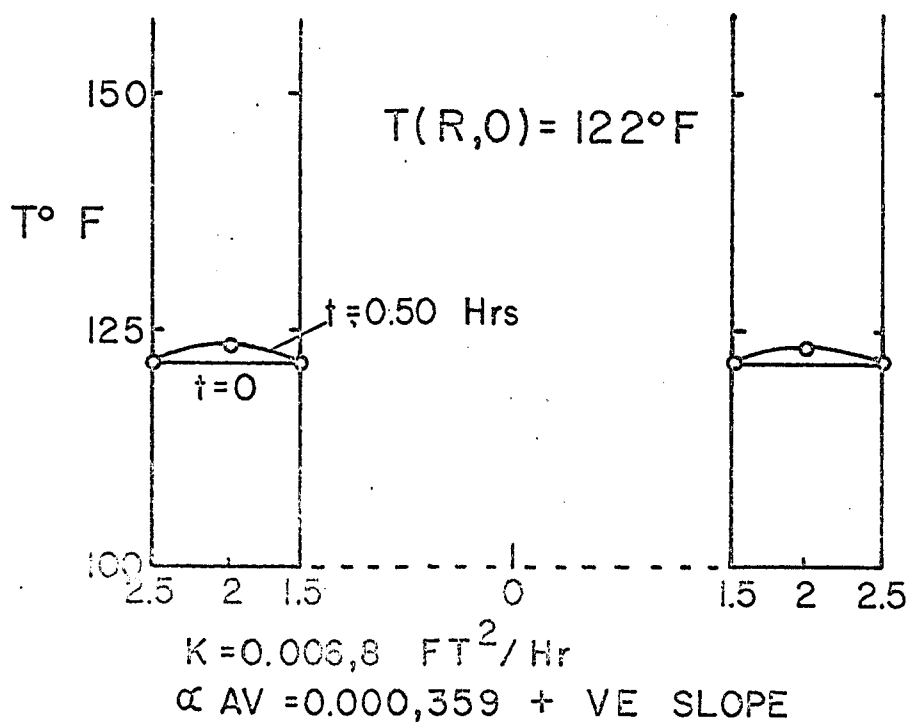
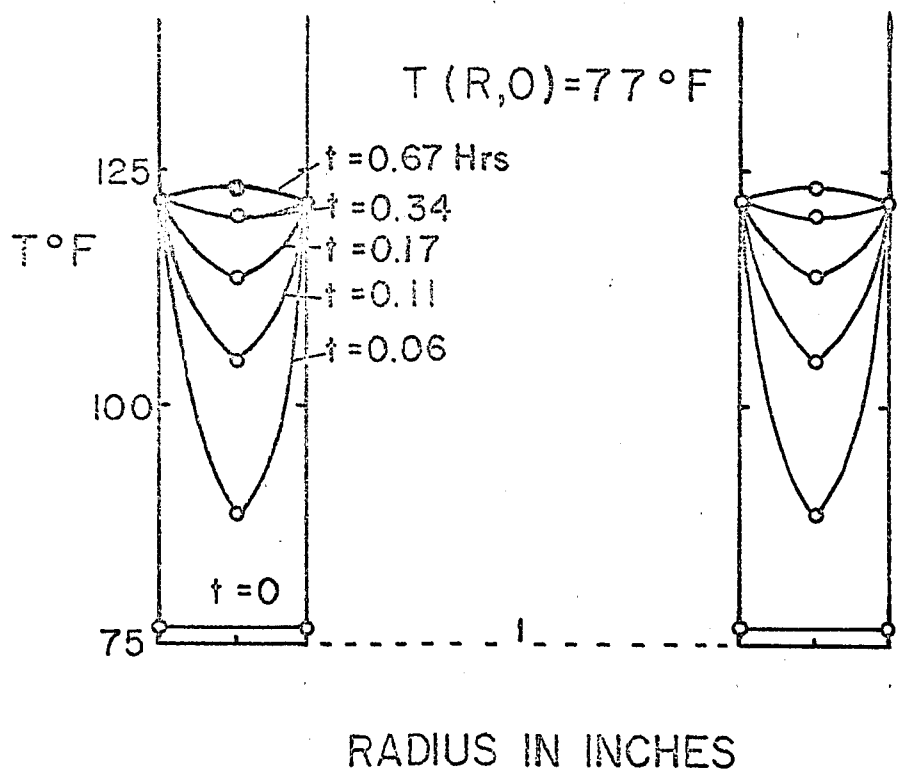


Figure 28 Temperature Gradients for the Thin Walled Hollow Cylinder

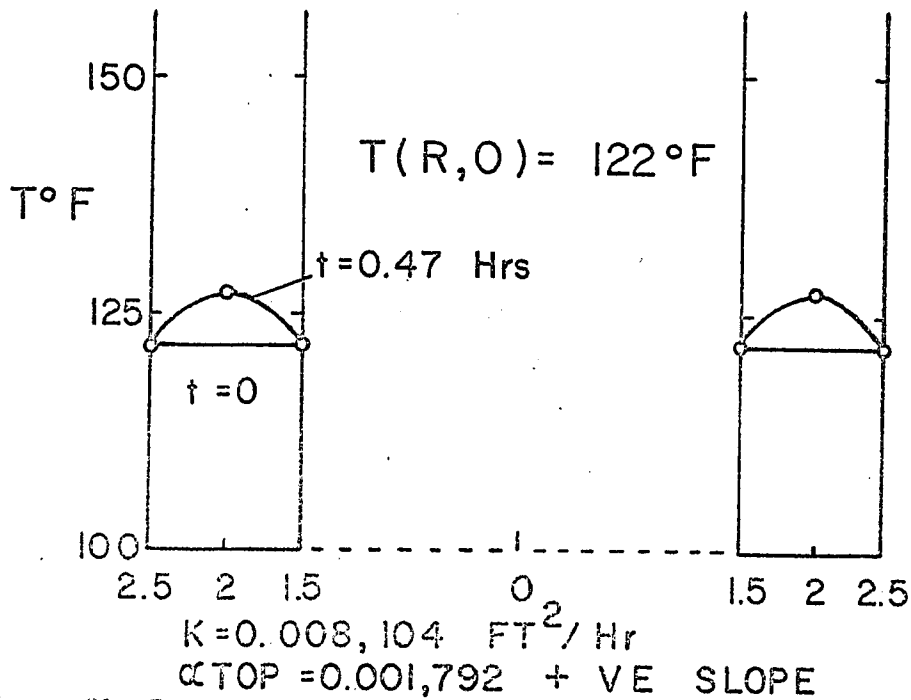
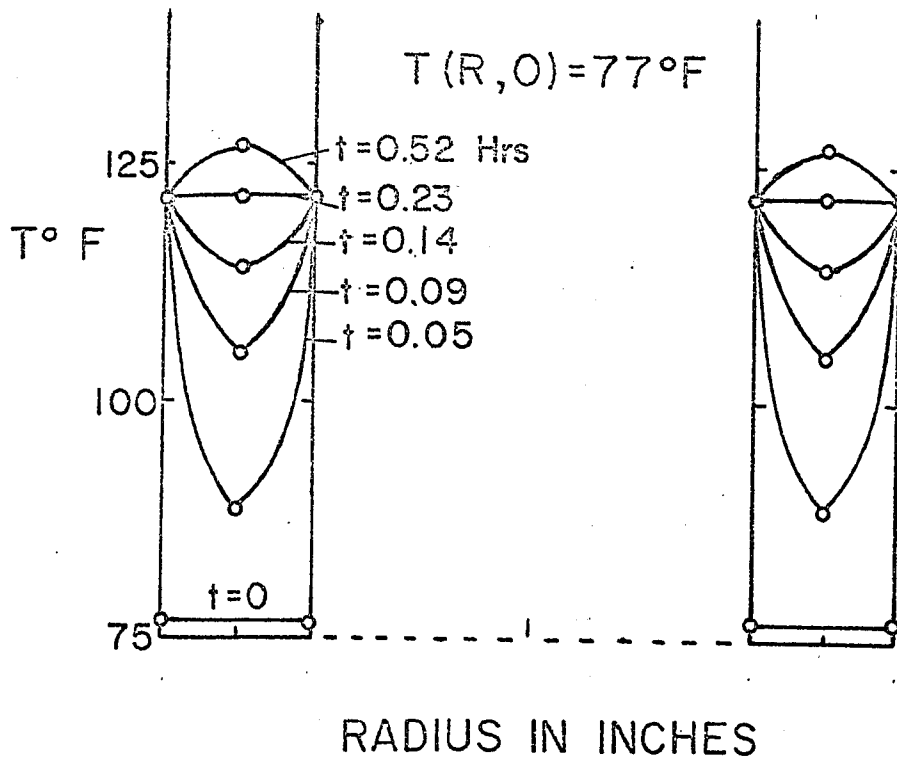


Figure 29 Temperature Gradients for the Thin Walled Hollow Cylinder

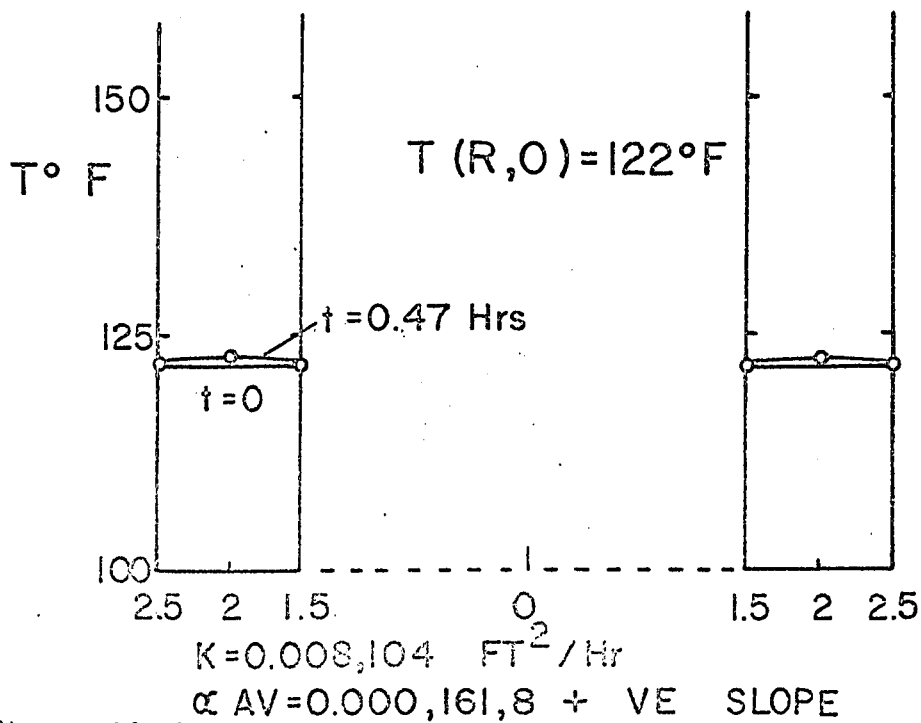
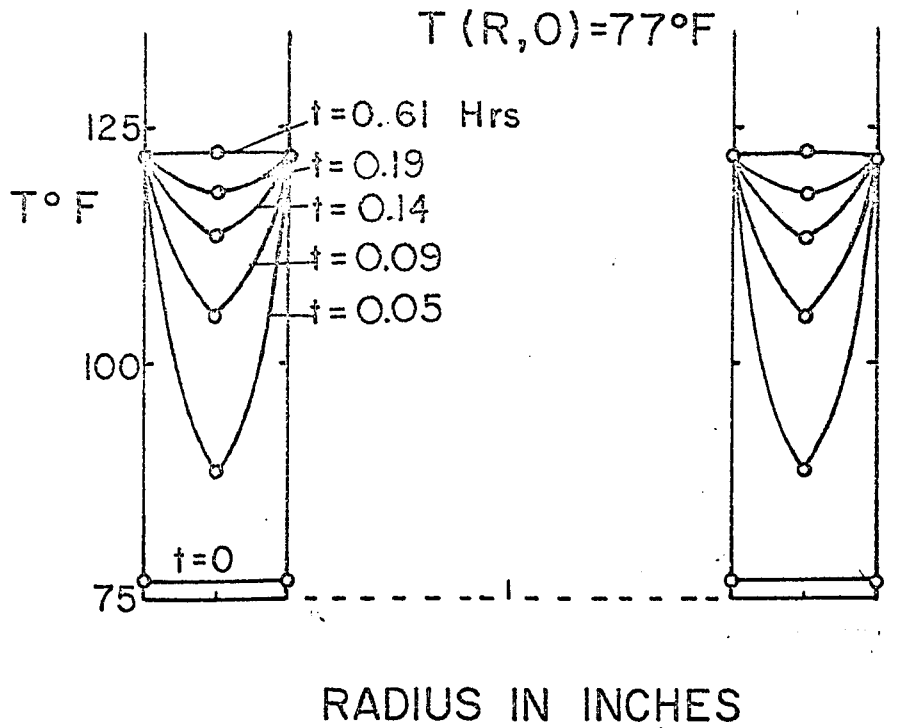


Figure 20 Temperature Gradients for the Thin Walled Hollow Cylinder

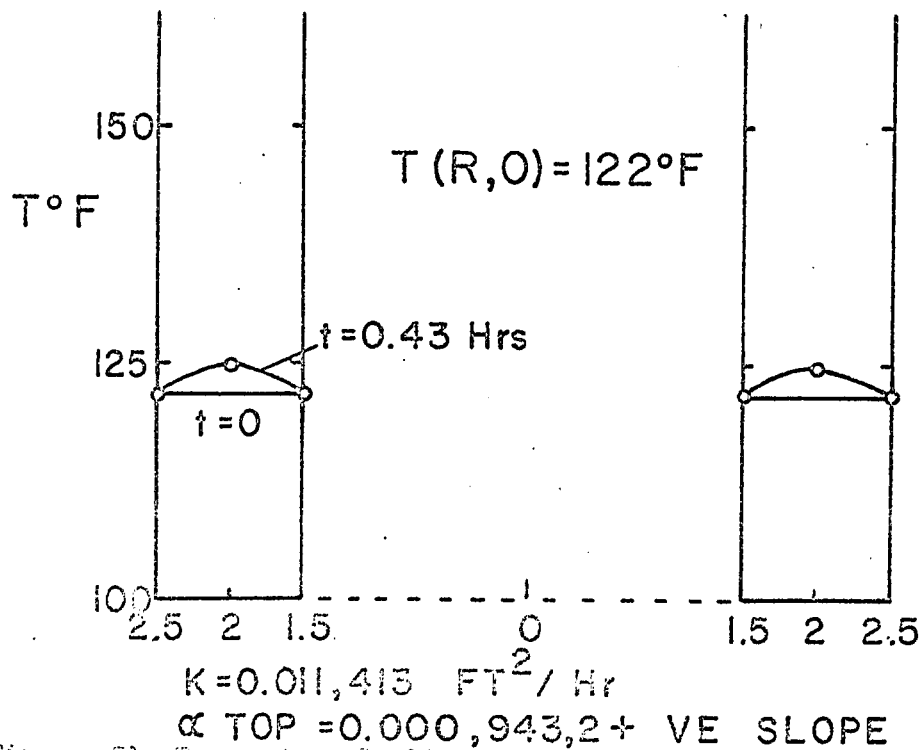
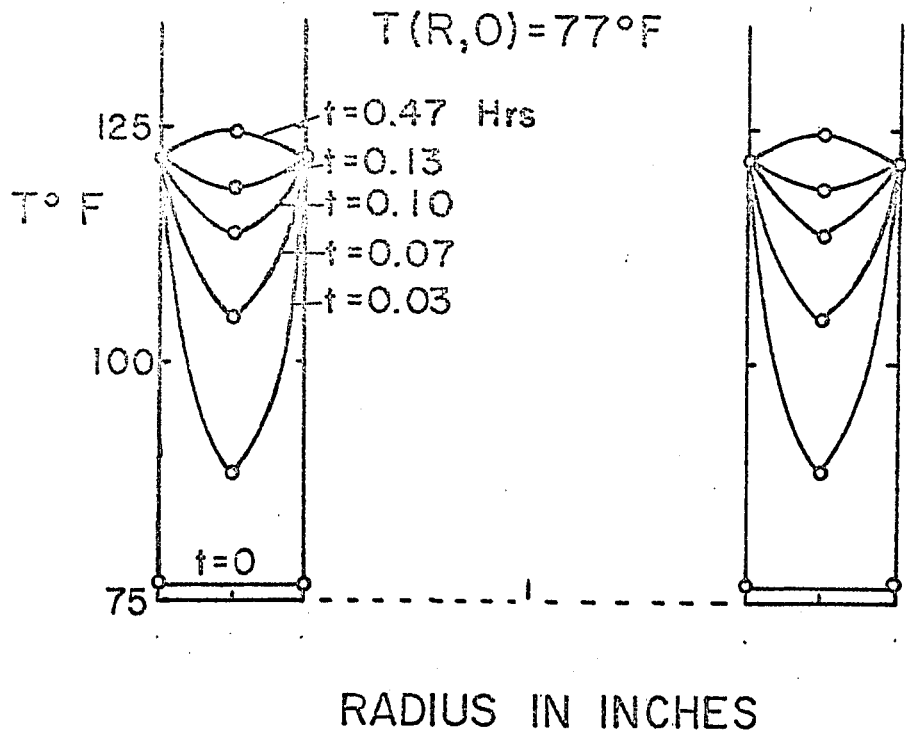
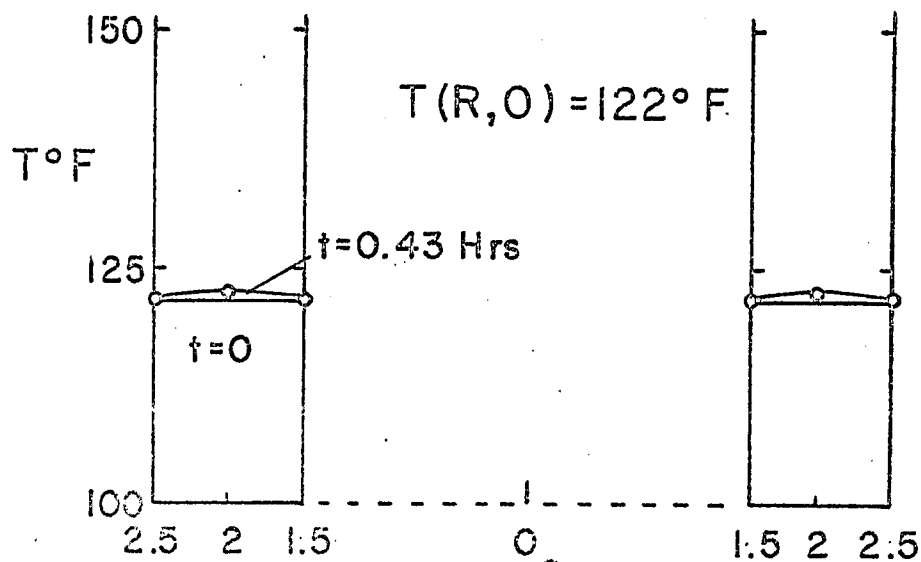
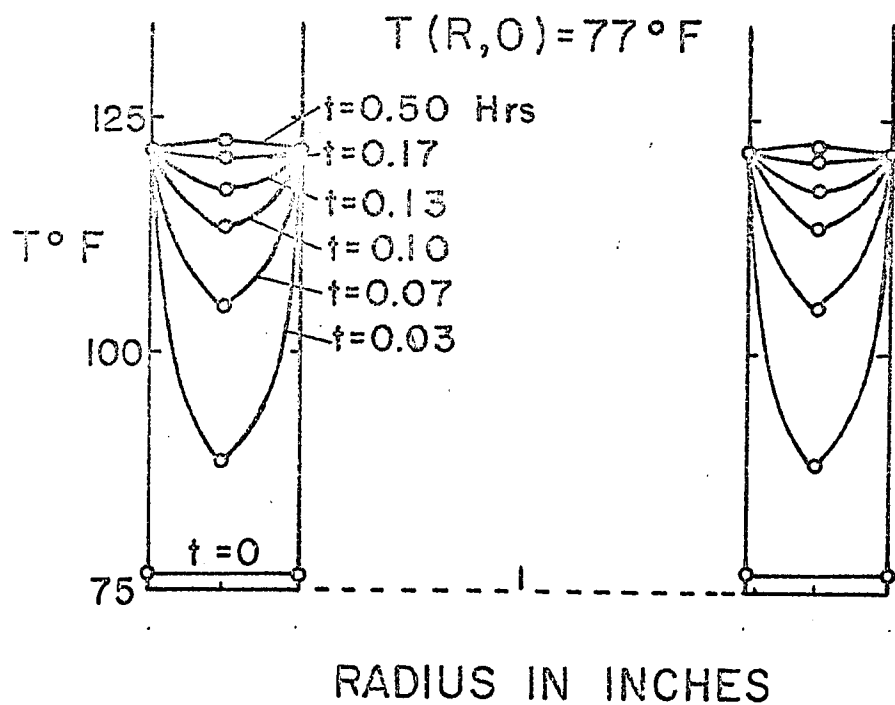


Figure 31 Temperature Gradients for the Thin Walled Hollow Cylinder



$K = 0.011, 413 \text{ FT}^2 / \text{Hr}$

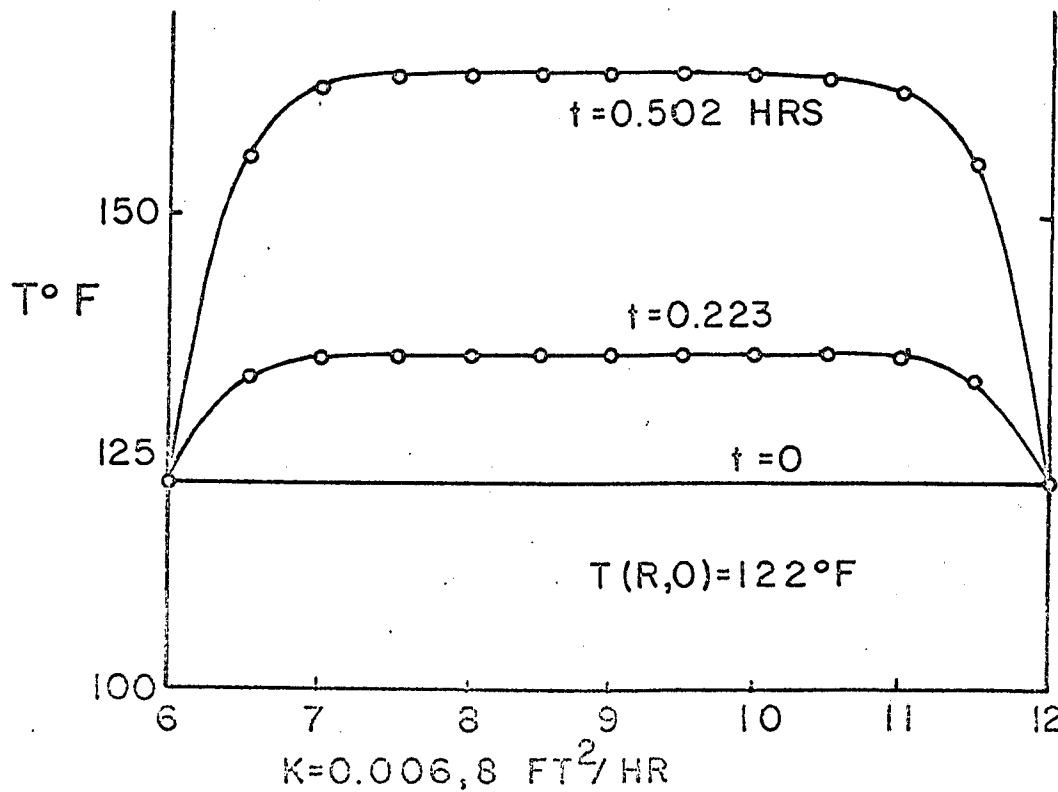
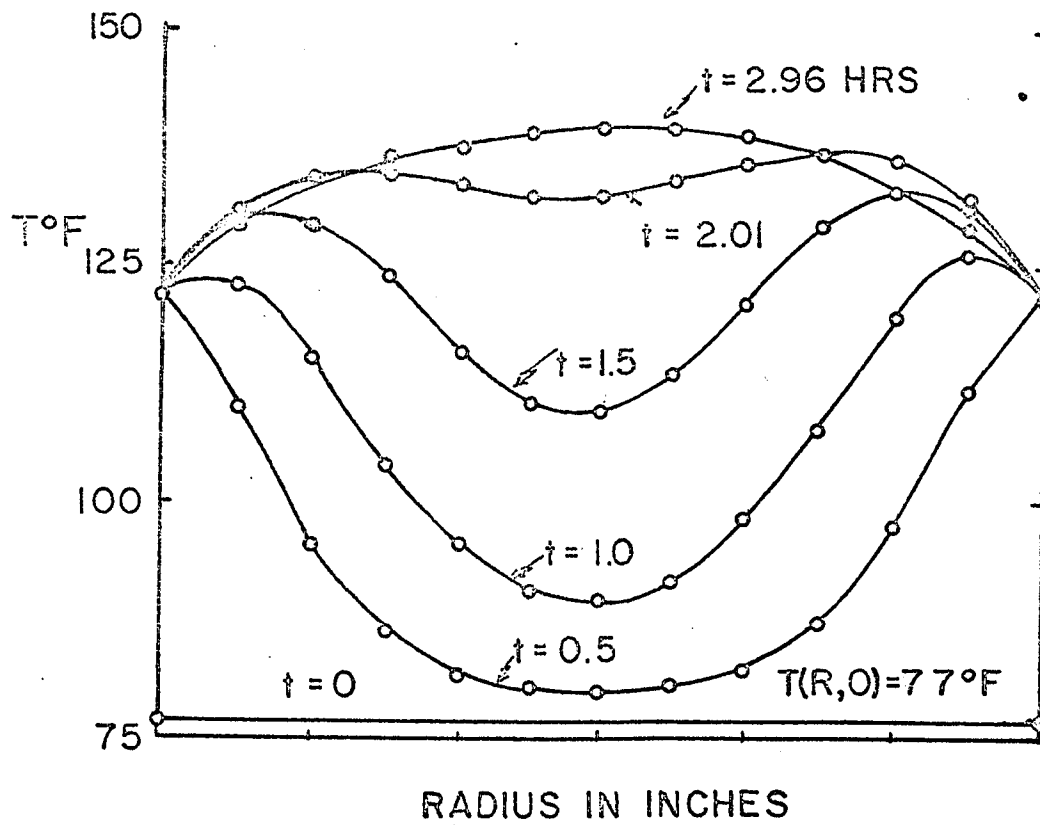
$\alpha_{AV} = 0.000, 085, 206 + \text{VE SLOPE}$

Figure 32 Temperature Gradients for the Thin Walled Hollow Cylinder

propellant does not seem to be at a high temperature long enough to alter the burning rate characteristics. But it is thought that had a larger hollow cylinder, with a bigger web been used, some variation would have appeared.

The graphs (Figures 33, 34, 35, 36, 37 and 38) for the temperature gradients across a thick walled hollow cylinder are again all of the same general shape for an initial condition of seventy-seven degrees Fahrenheit. This time the curves are not completely symmetrical as would be expected and in all cases there is a slight shift towards the outer side. Again a gradually filling depression turns into a peak at about the centre. This peak has a value of 134°F , 129°F and 127°F for thermal diffusivities of 0.006,8, 0.008,104 and 0.011,413 ft^2/hr , respectively; when the top value of alpha is taken. If the average value of alpha is used, the temperature rises to 122°F for the three values of the diffusivity.

Should a one hundred and twenty-two initial condition be used the temperature gradually rises to a peak of 165°F , 161°F and 154°F for thermal diffusivities of 0.006,8, 0.008,104 and 0.011,413 ft^2/hr , respectively; when the top value of alpha is taken. If average alphas are used then the peaks occur at 132°F , 127°F and 126°F for thermal diffusivities of 0.006,8, 0.008,104 and 0.011,413 ft^2/hr , respectively. As before the difference is due to the rate at which heat can flow to the surfaces. At lower thermal diffusivities it takes longer to escape and therefore causes a higher temperature in the centre.



$$K = 0.006, 8 \text{ FT}^2/\text{HR}$$

$$\alpha_{\text{TOP}} = 0.003, 978, 4 + \text{VE SLOPE}$$

Figure 33 Temperature Gradients for the Thick Walled Hollow Cylinder

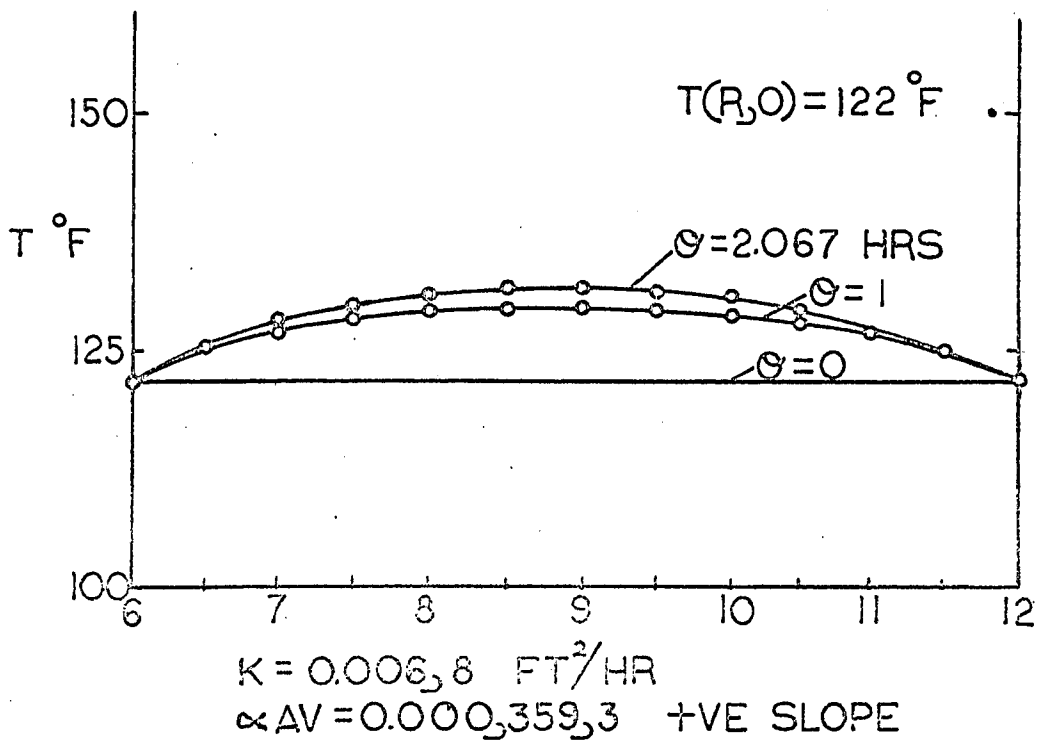
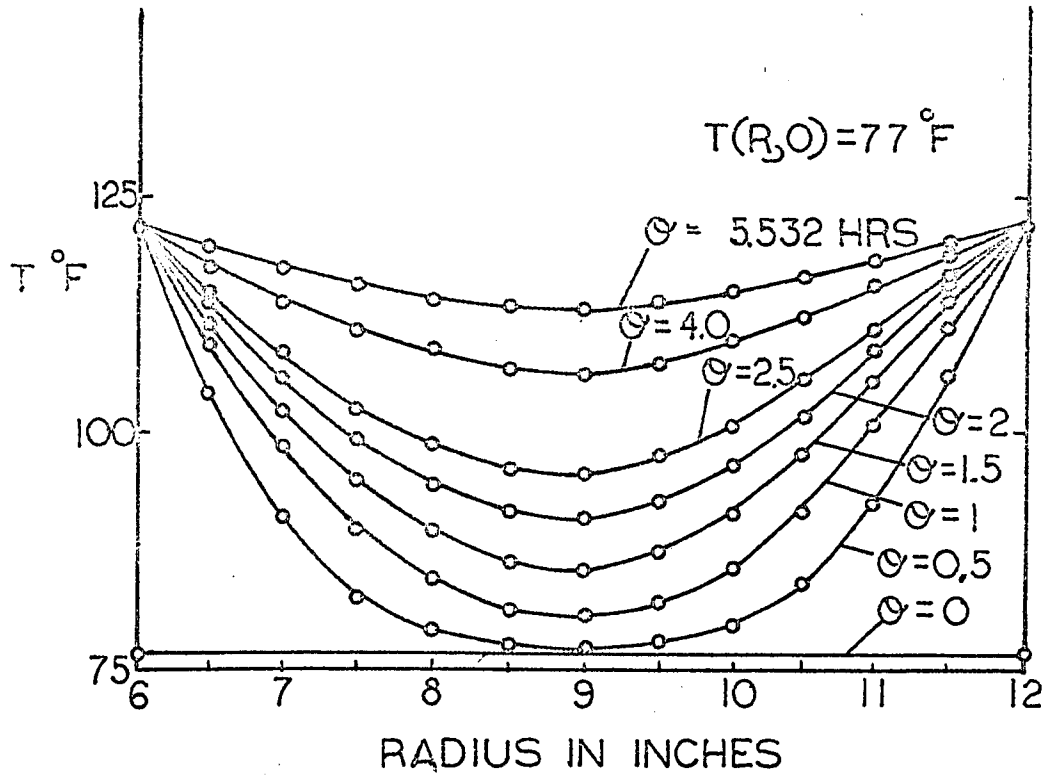


Figure 34 Temperature Gradients for the Thick Walled Hollow Cylinder

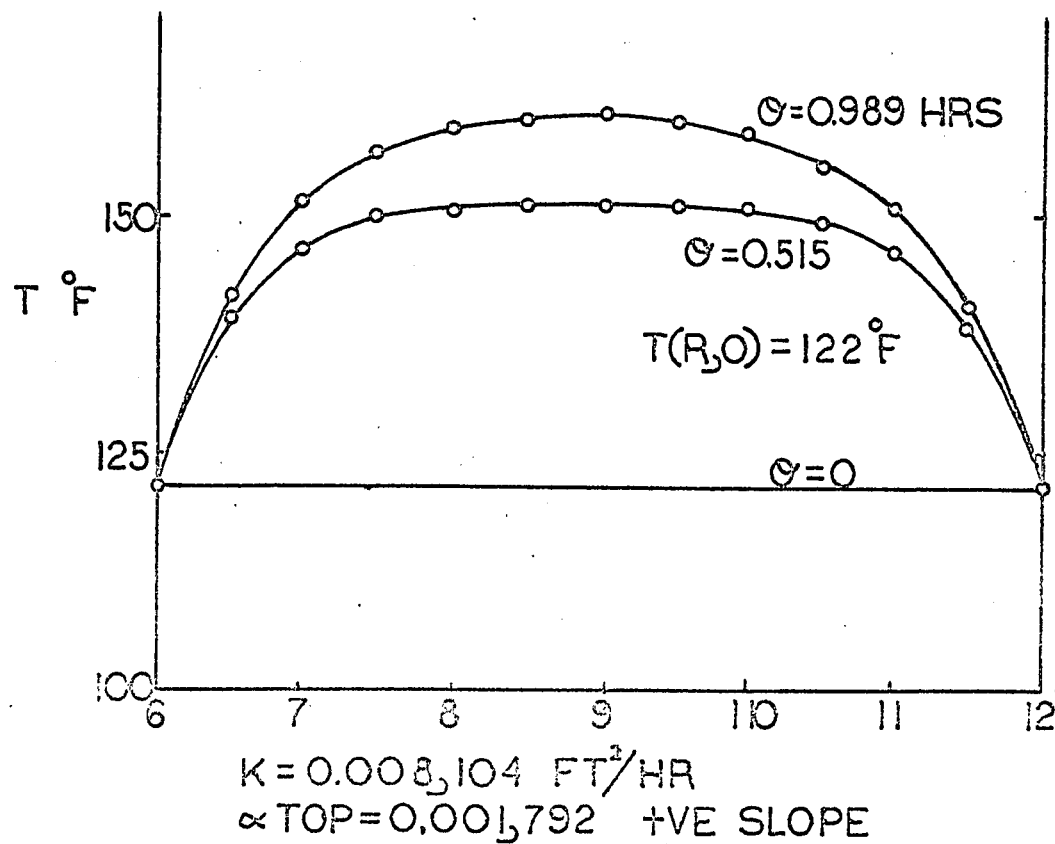
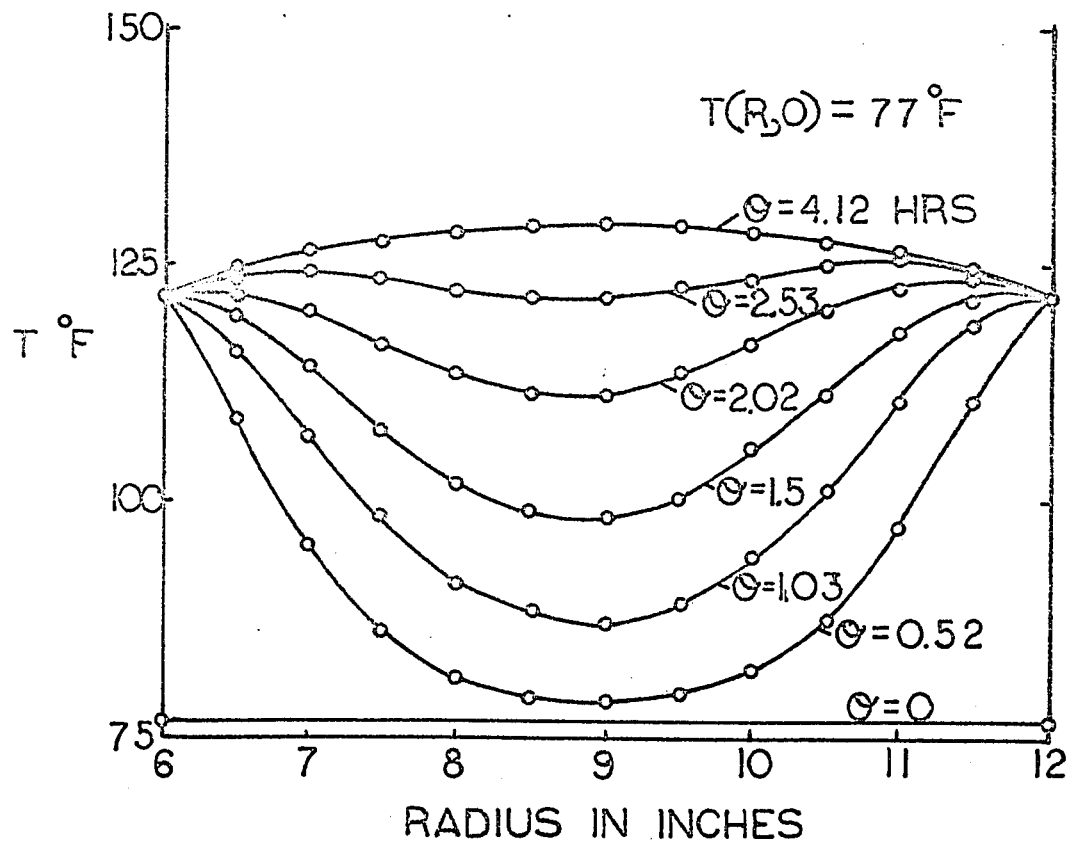


Figure 35 Temperature Gradients for the Thick Walled Hollow Cylinder

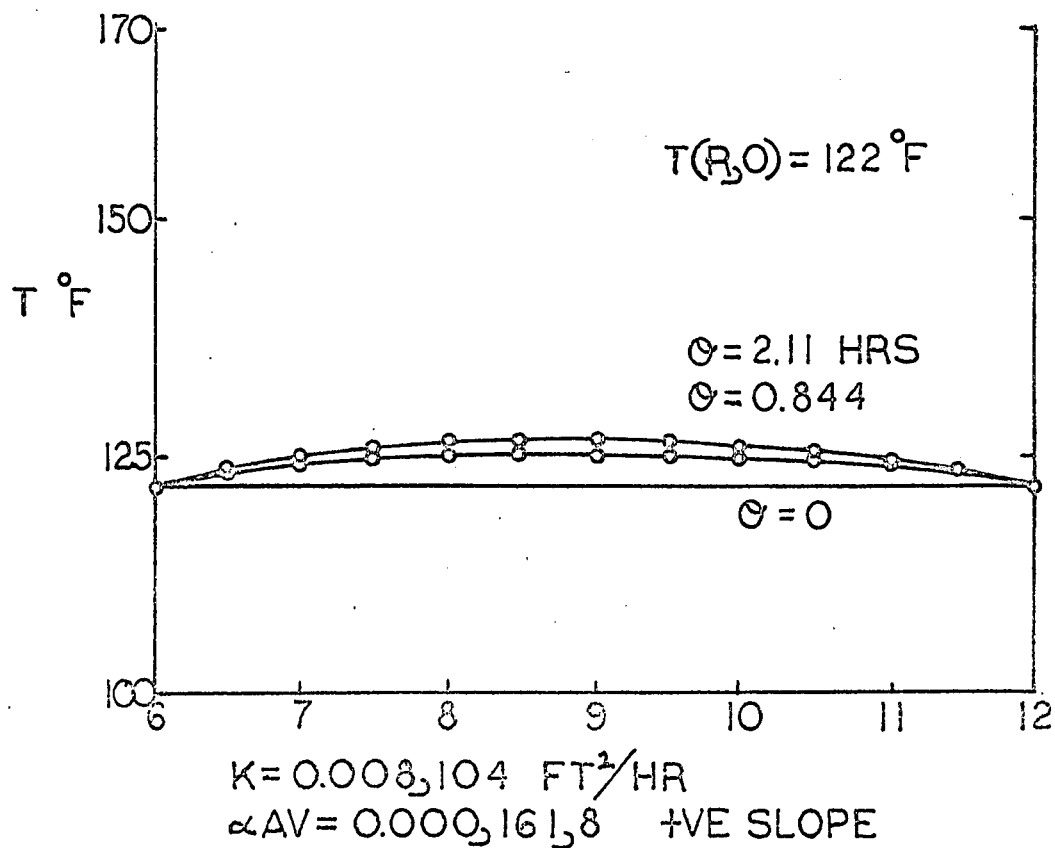
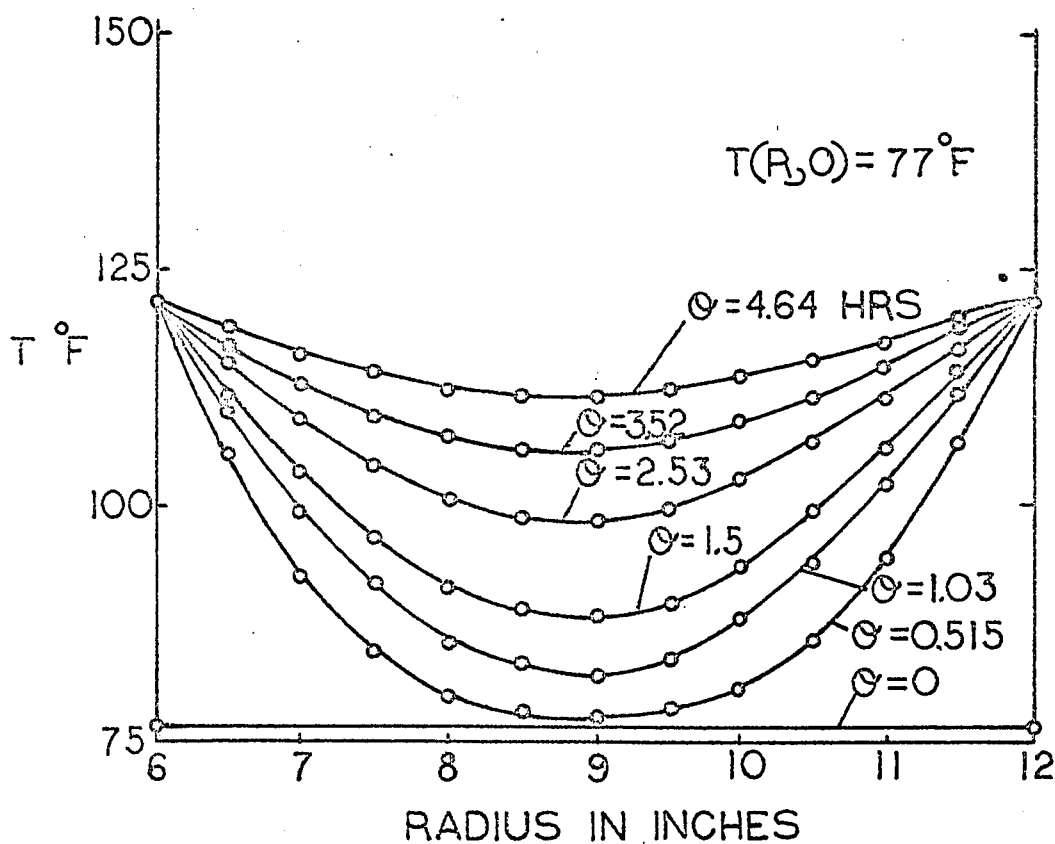


Figure 36. Temperature Gradients for the Thick Walled Hollow Cylinder

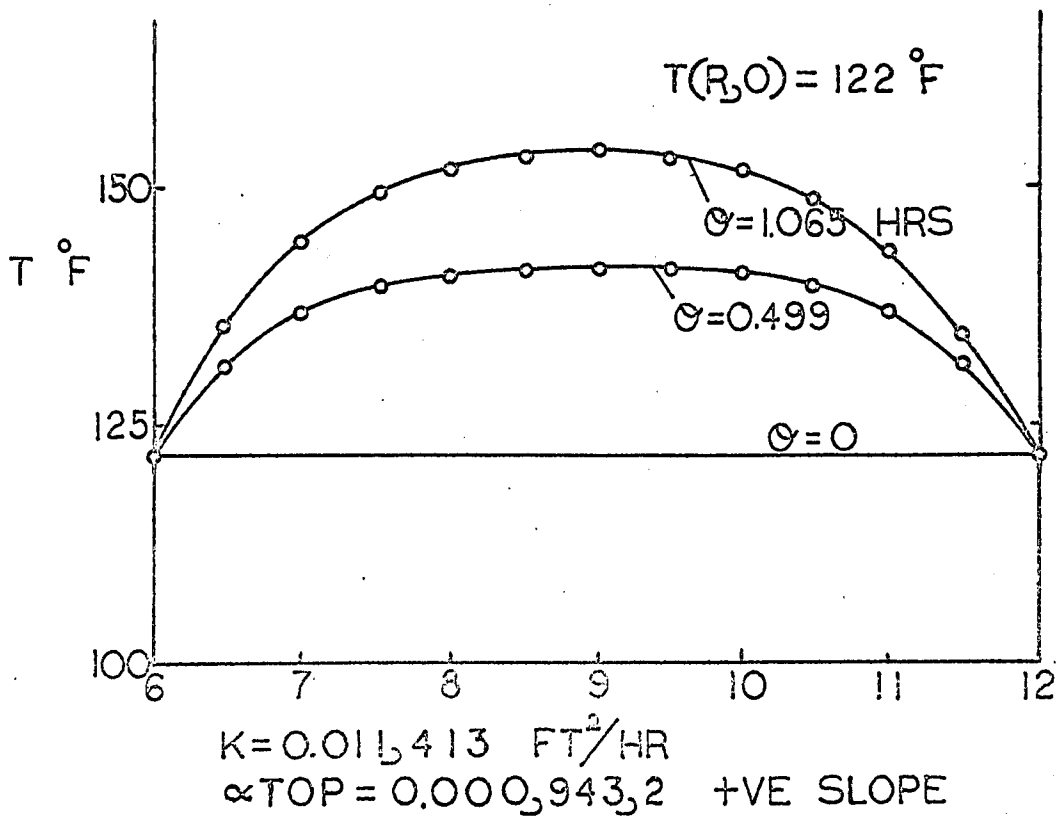
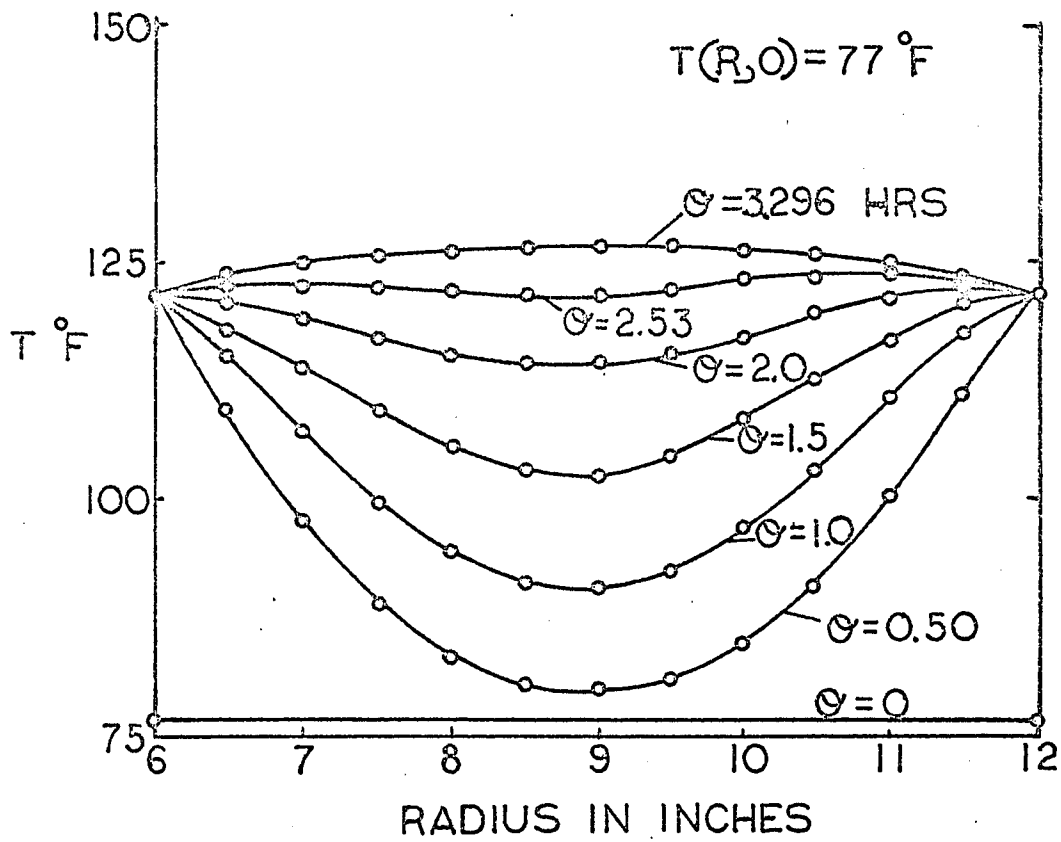
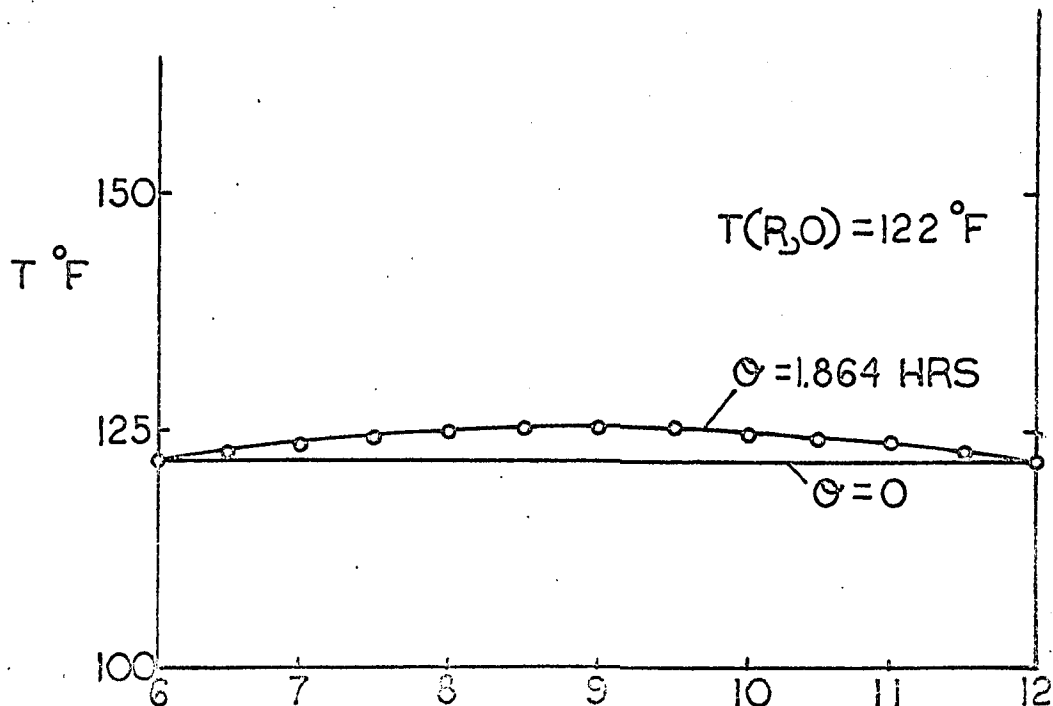
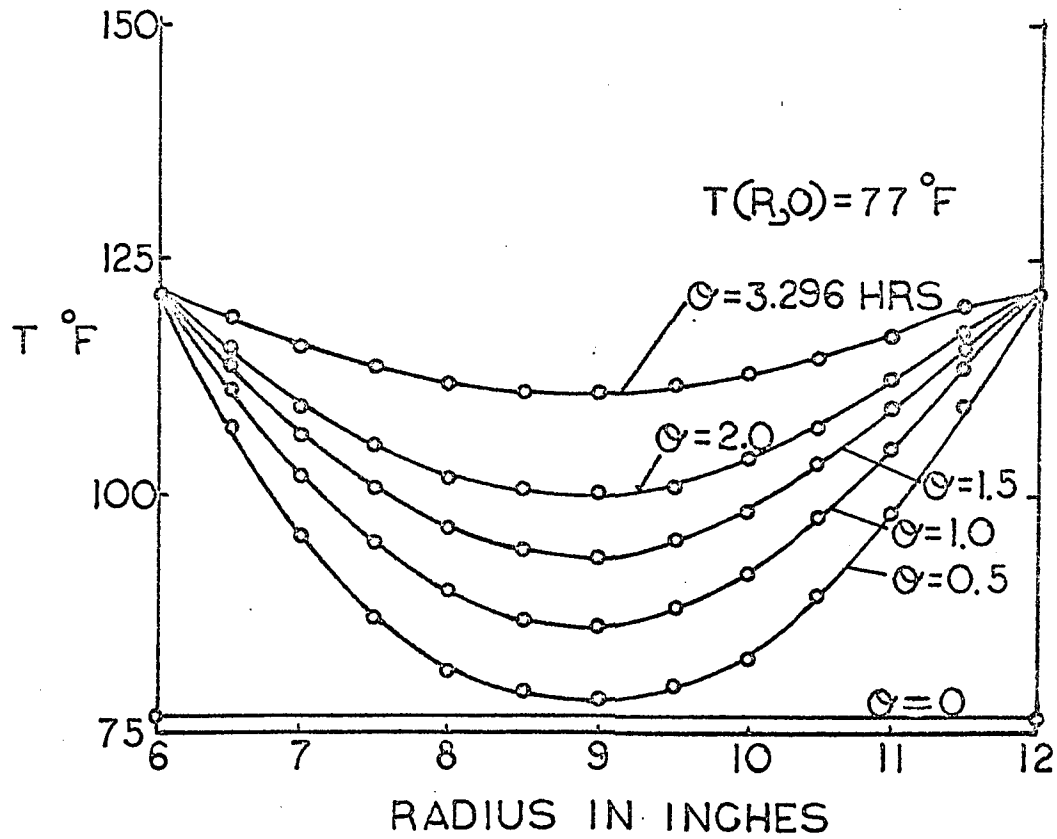


Figure 37 Temperature Gradients for the Thick Walled Hollow Cylinder



$$K = 0.011,413 \text{ FT}^2/\text{HR}$$

$$\alpha_{AV} = 0.000,085,208 \quad +\text{VE SLOPE}$$

Figure 38 Temperature Gradients for the Thick Walled Hollow Cylinder

5. Polymerization Temperature Curves for the Star Perforated Cylinder

The temperature gradients across a thick walled, star shaped centre, hollow cylinder (Figures 39 to 66) form a much more complicated pattern than any of the simpler shapes. Here a valley appears in the base of each tip where the web is thickest, if one starts out with a seventy-seven degree Fahrenheit initial condition. After one and a half hours has elapsed peaks begin to appear in each tip of the propellant and the valleys begin to fill. When two hours have passed, peaks begin to appear fairly near the wall, in the thickest part of the web. At two and a half hours the valleys are practically filled and the peaks are spreading out into regions. At three hours the valleys have all become peaks and this picture is maintained until the heat sources die out.

If an initial condition of one hundred and twenty-two degrees Fahrenheit is used, a peak forms where the web is thickest, later turns into a hot band running all the way around the cylinder and again this picture is maintained until the heat sources are no longer active.

Although samples for linear burning rate were not taken from a piece of propellant with this shape, it is thought that the burning rate curve will be similar to the shape of the temperature envelope for this configuration.

6. End Effect

Up to the present all the different propellant shapes have been solved with the assumption of infinite length and the question now

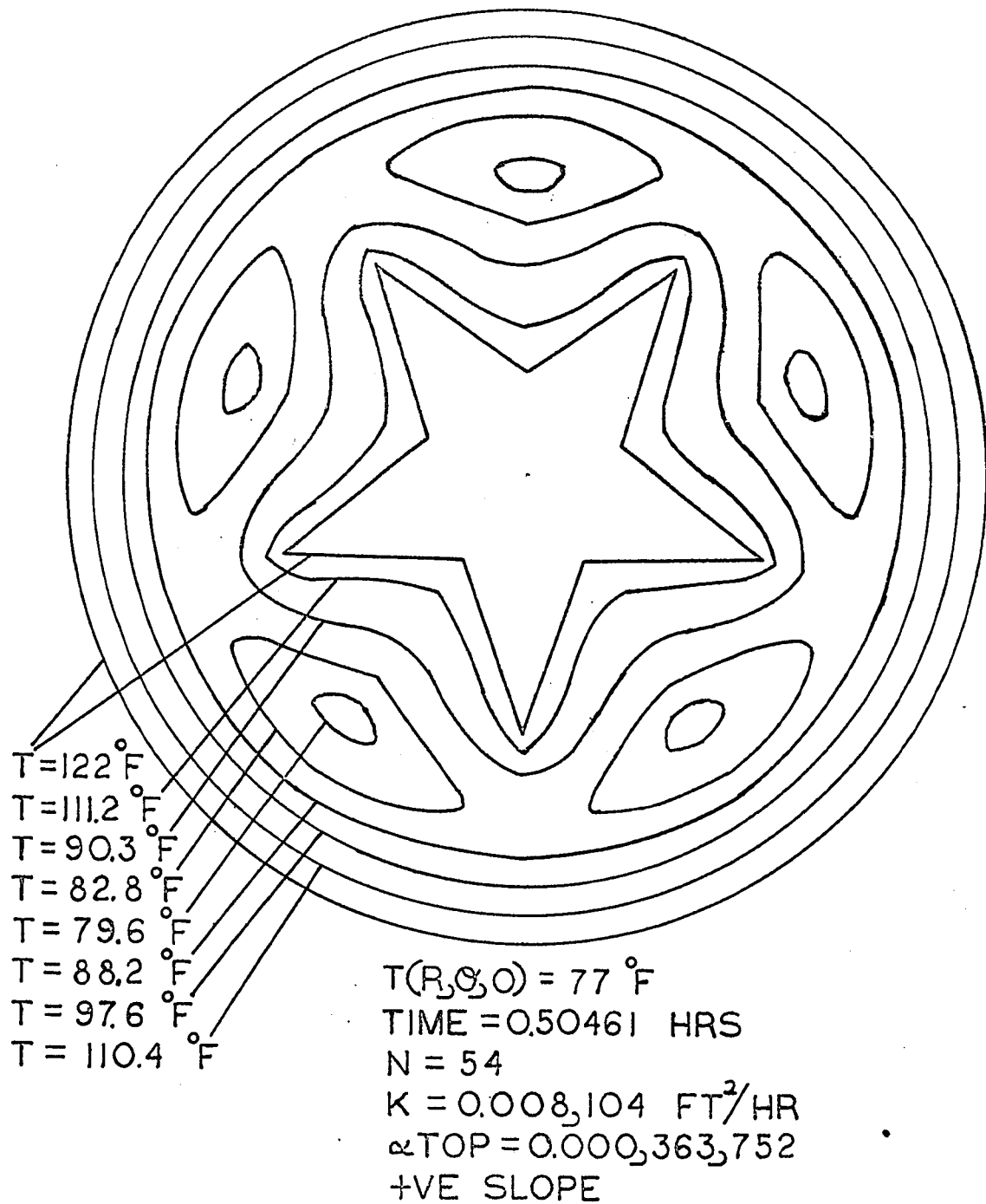


Figure 39 Isotherms for the Star Shaped Centre Hollow Cylinder

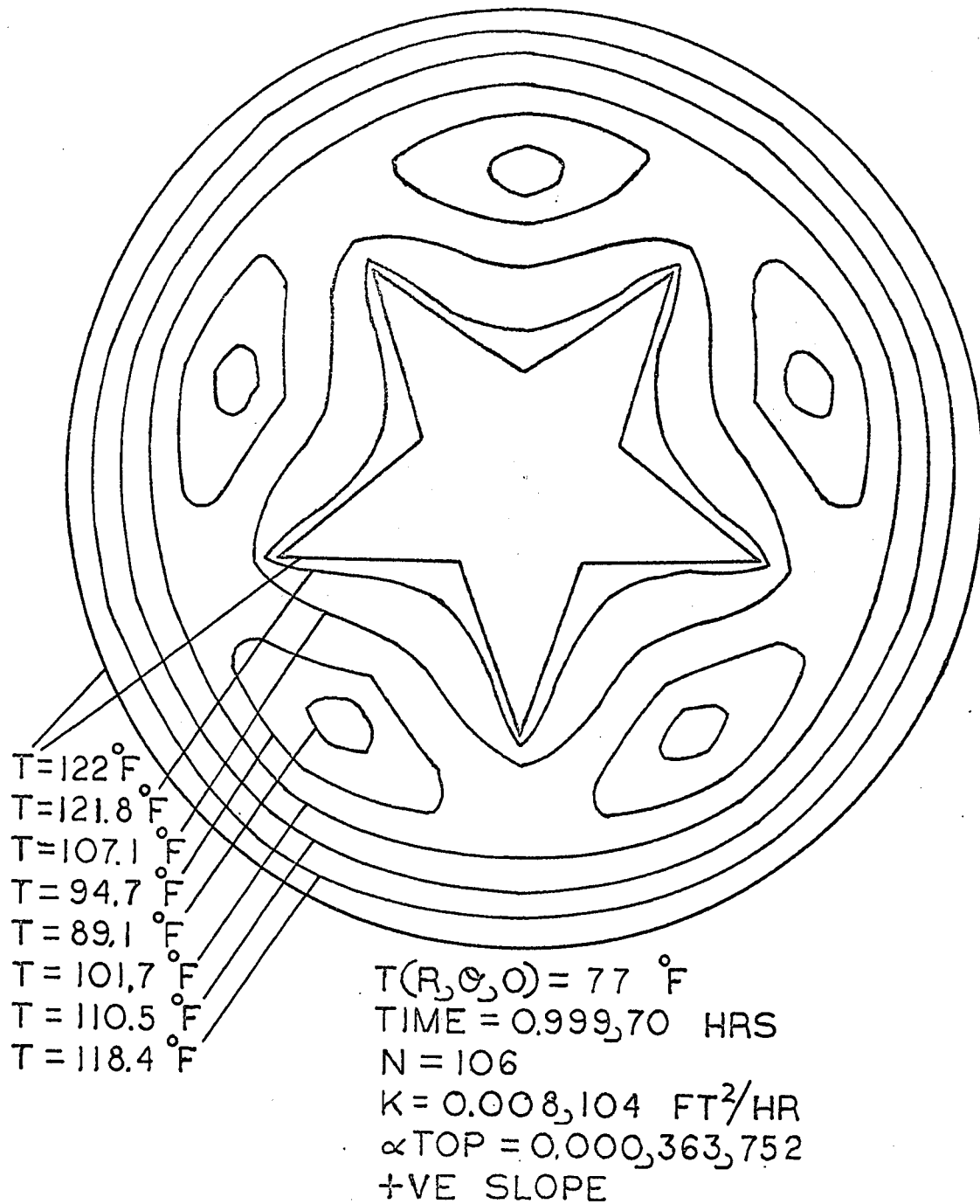


Figure 40 Isotherms for the Star Shaped Centre Hollow Cylinder

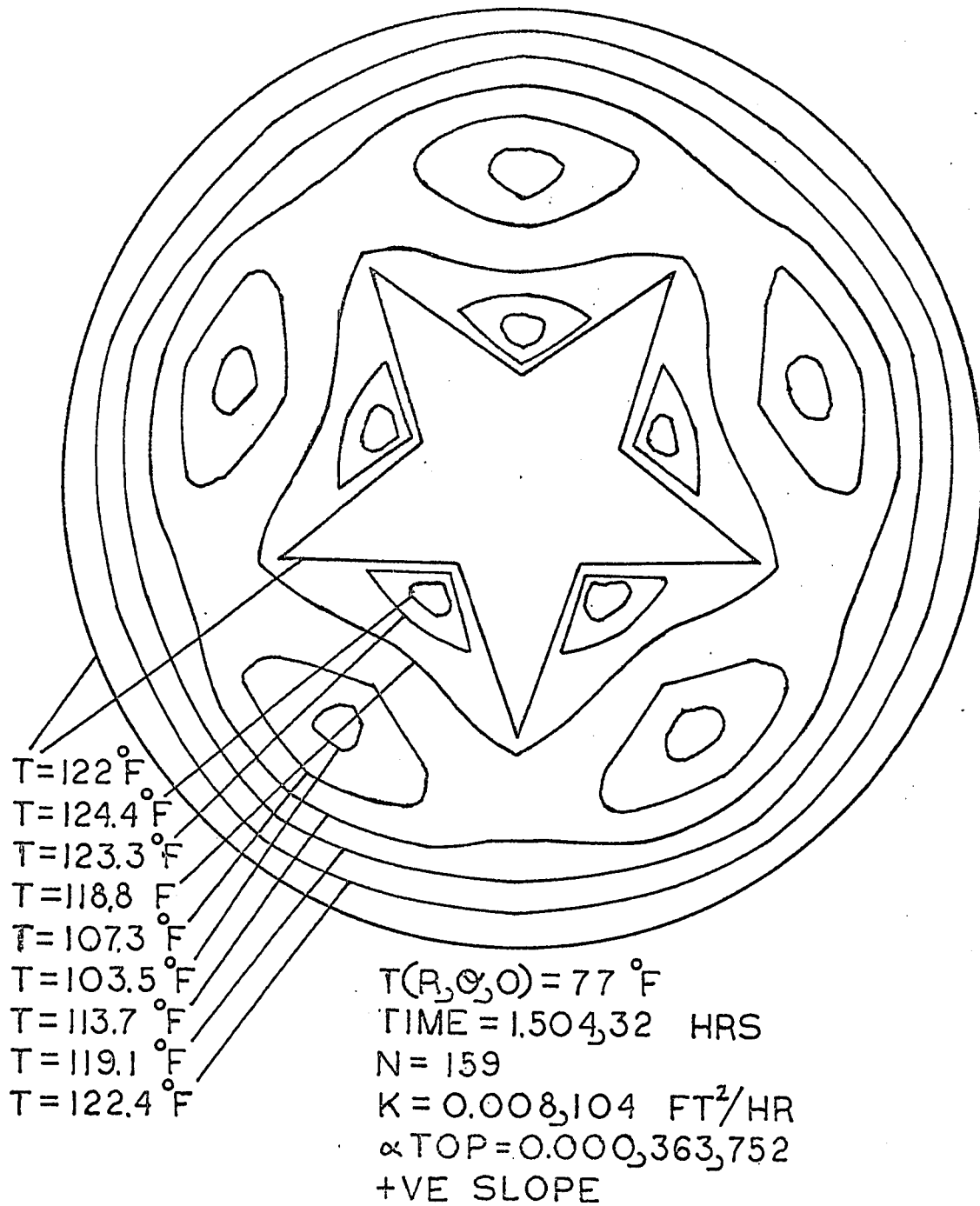


Figure 41 Isotherms for the Star Shaped Centre Hollow Cylinder

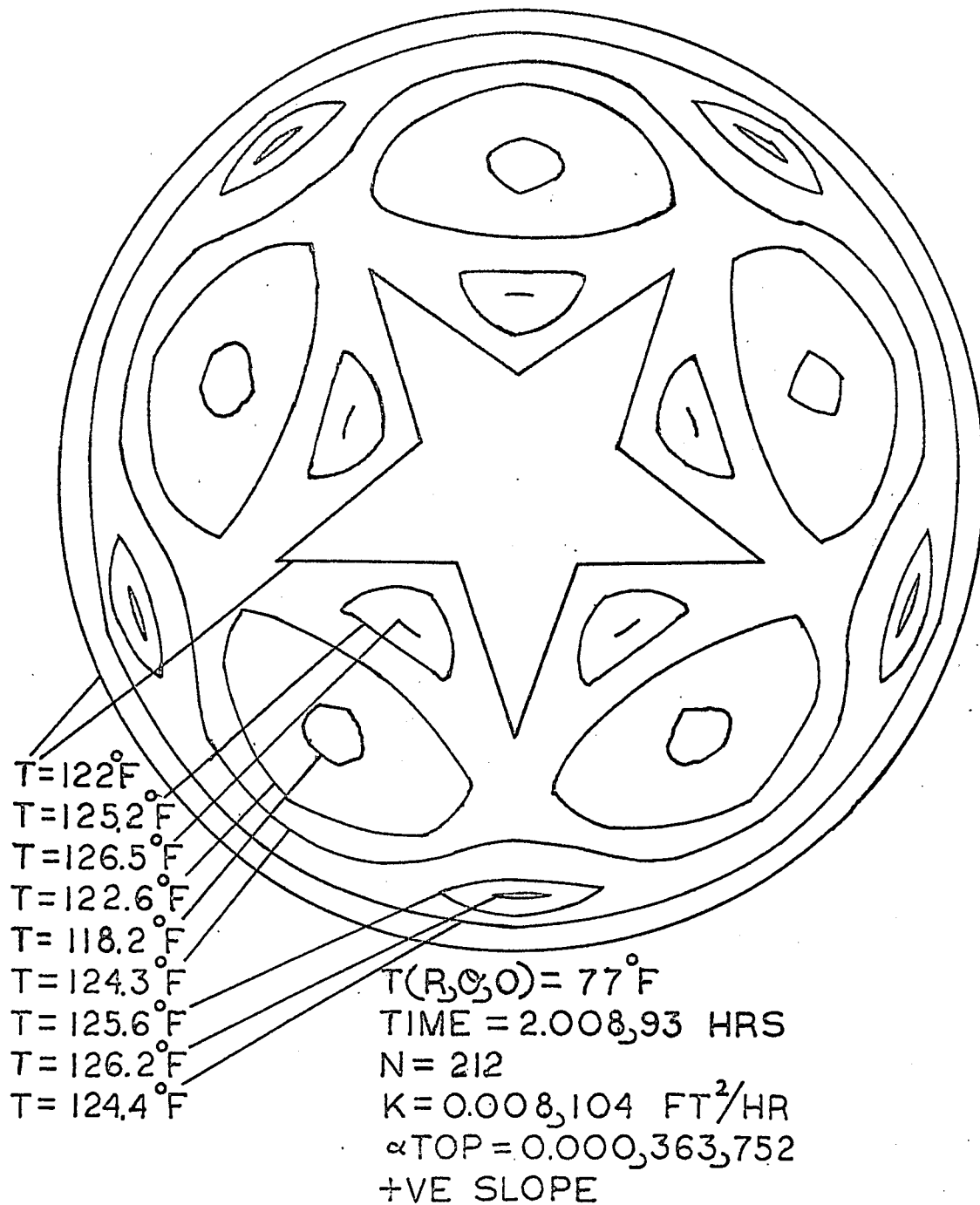


Figure 42 Isotherms for the Star Shaped Centre Hollow Cylinder

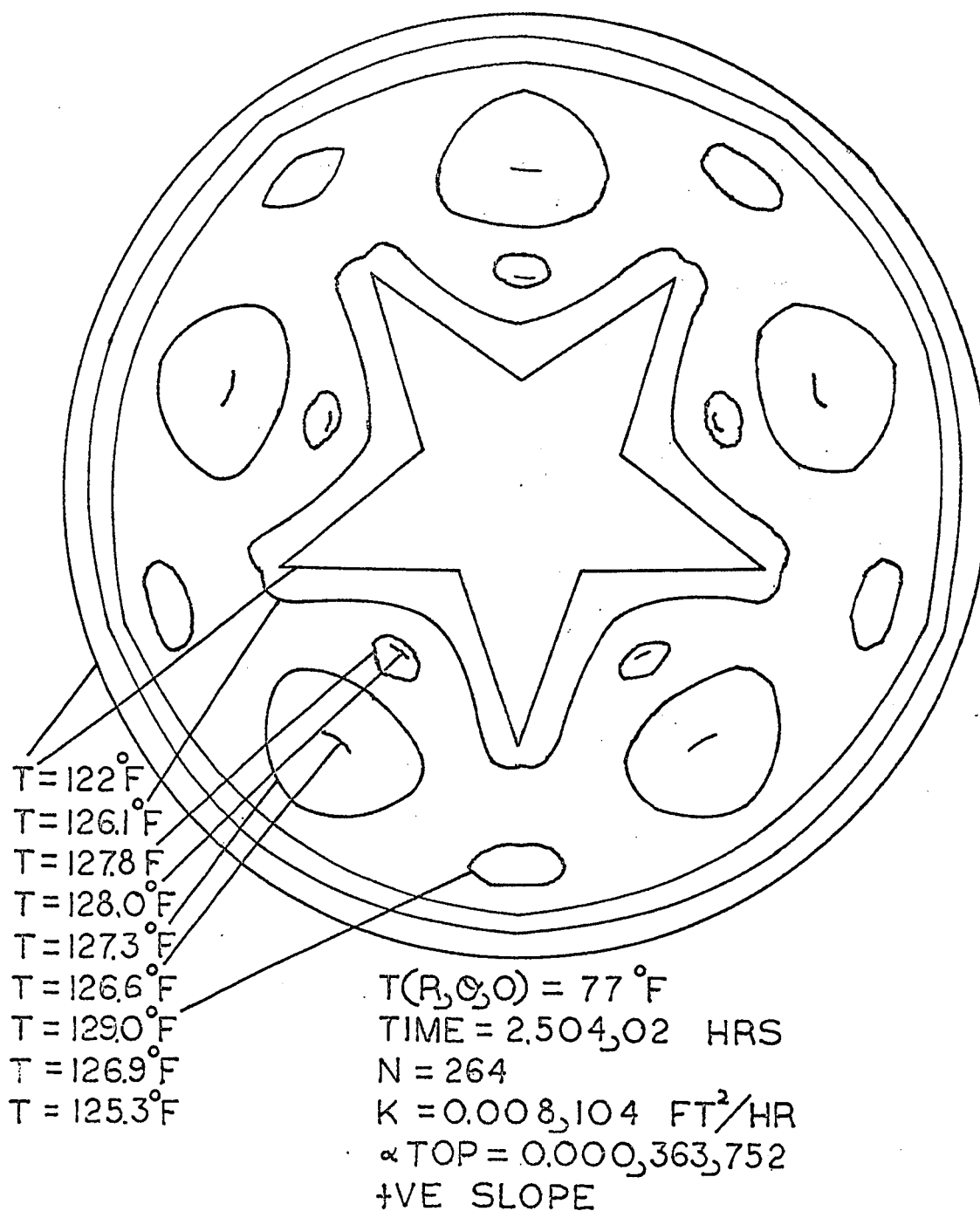


Figure 48 Isotherms for the Star Shaped Centre Hollow Cylinder

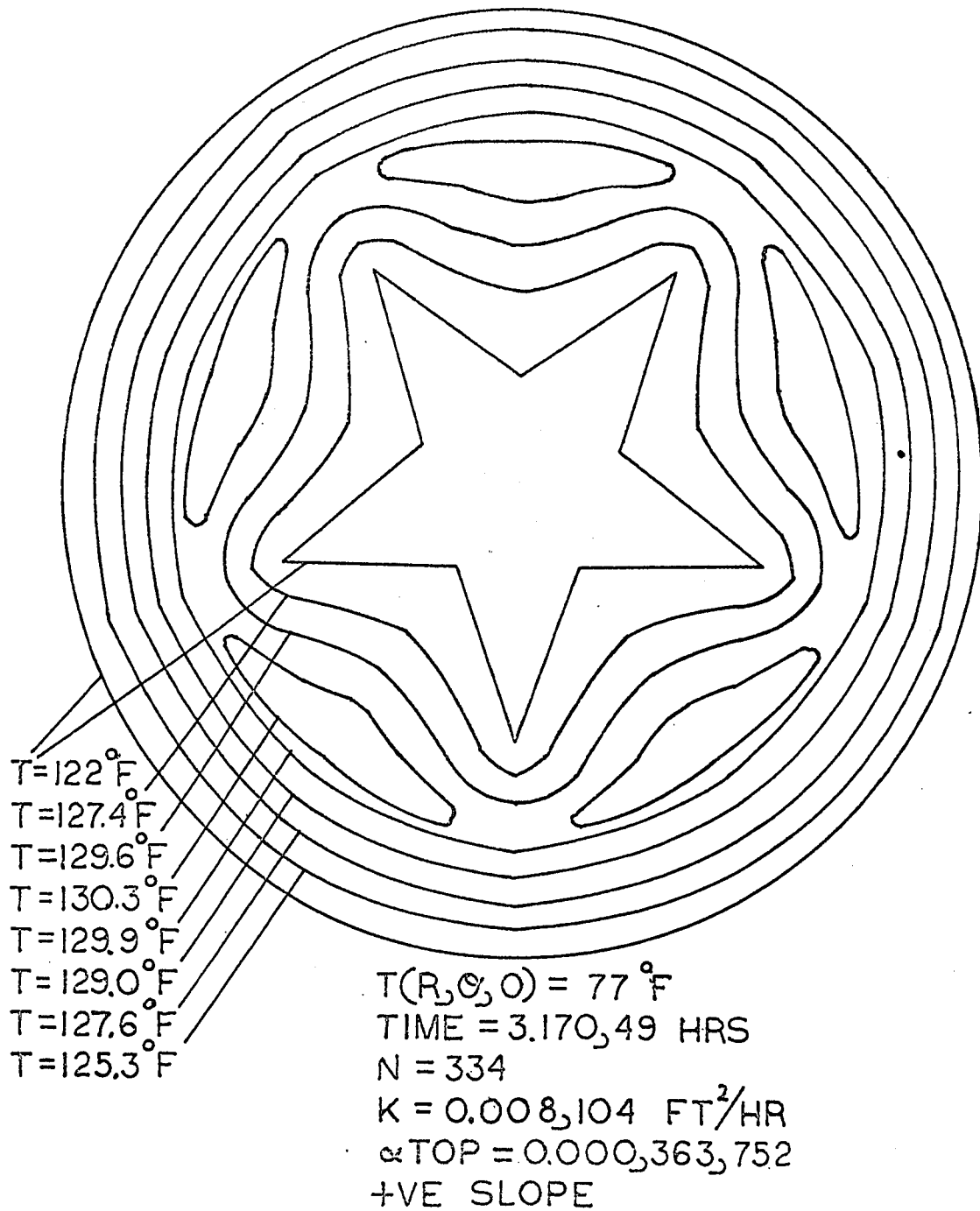


Figure 44 Isotherms for the Star Shaped Centre hollow Cylinder

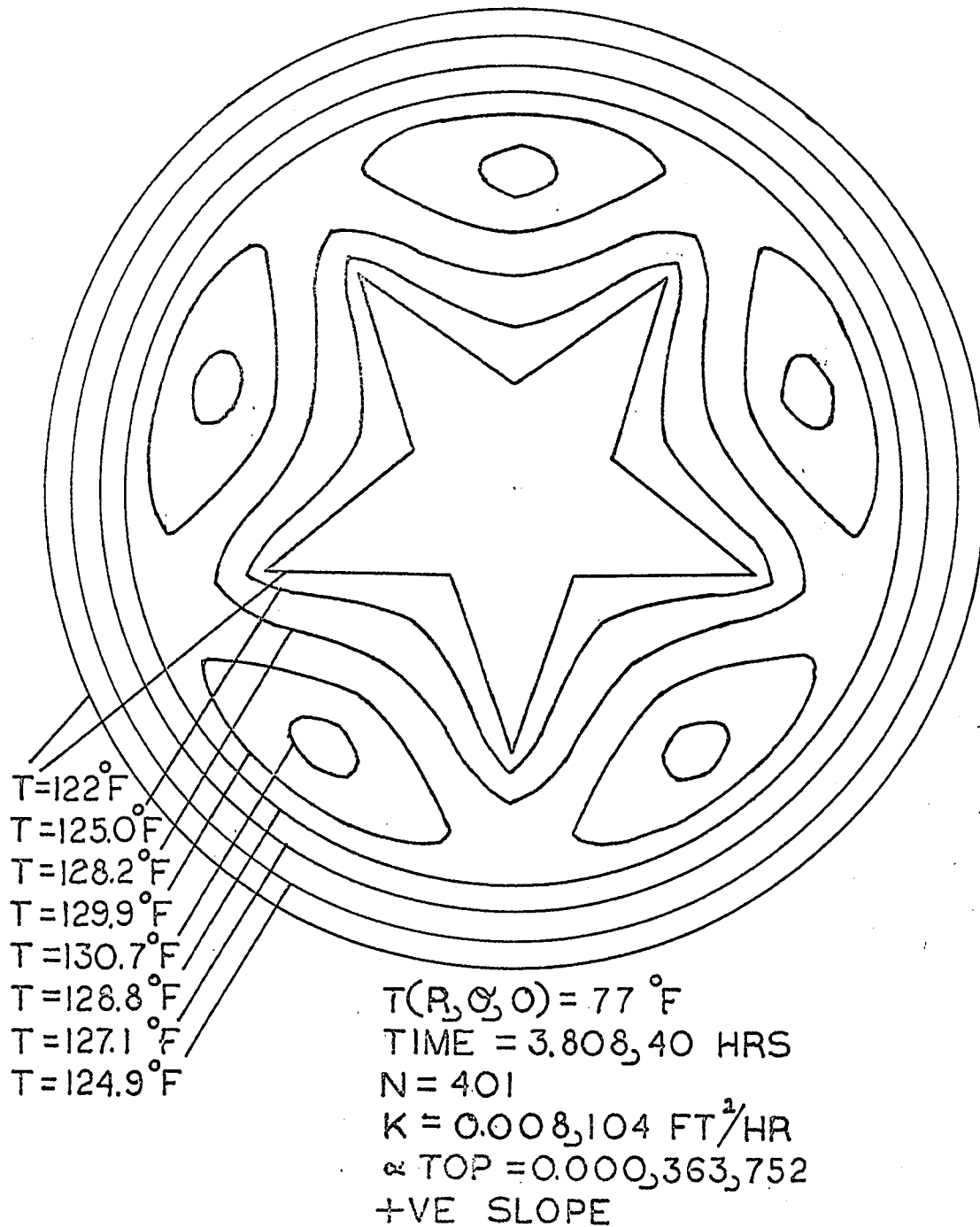


Figure 48 Isotherms for the Star Shaped Centre Hollow Cylinder

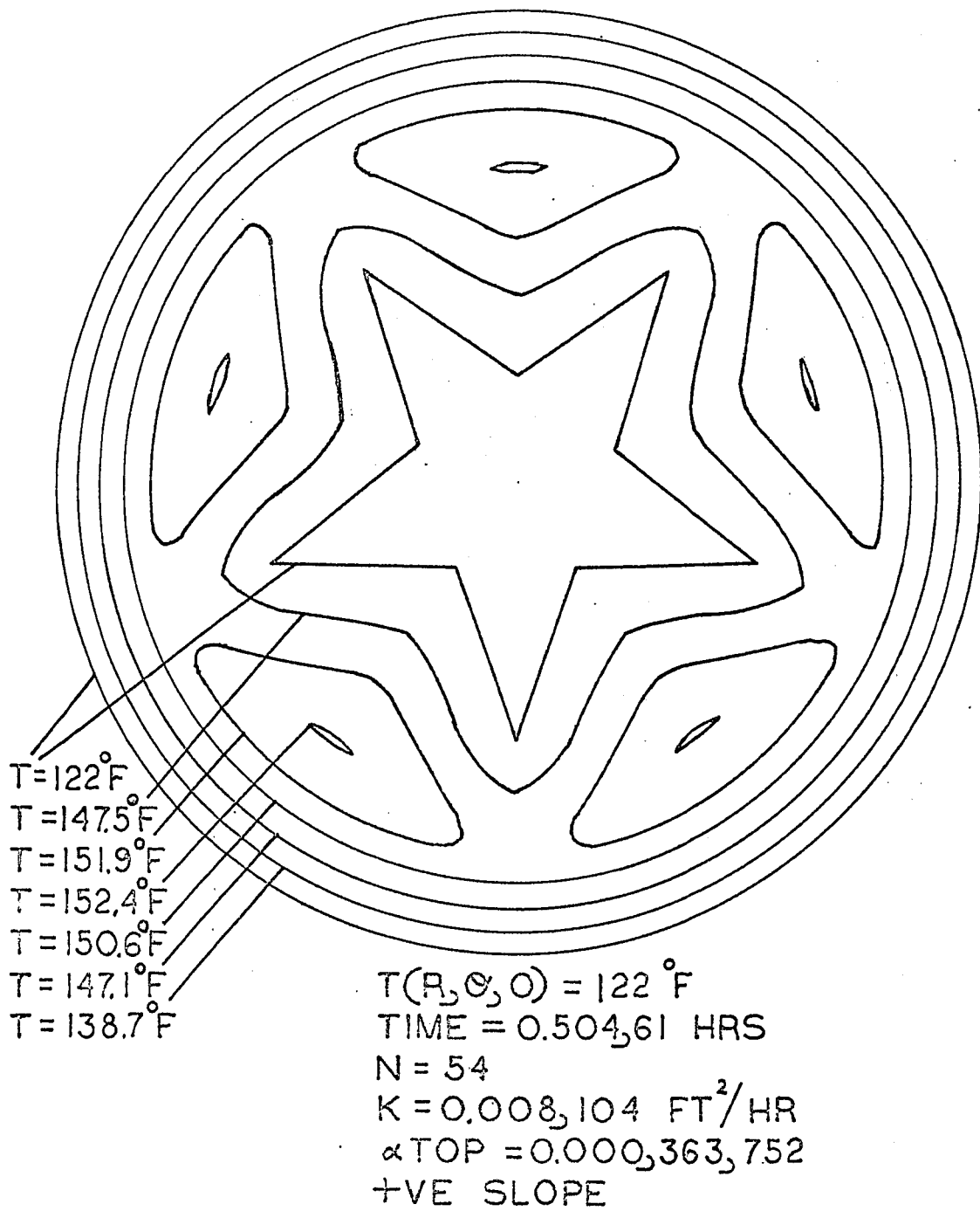


Figure 46 Isotherms for the Star Shaped Centre Hollow Cylinder

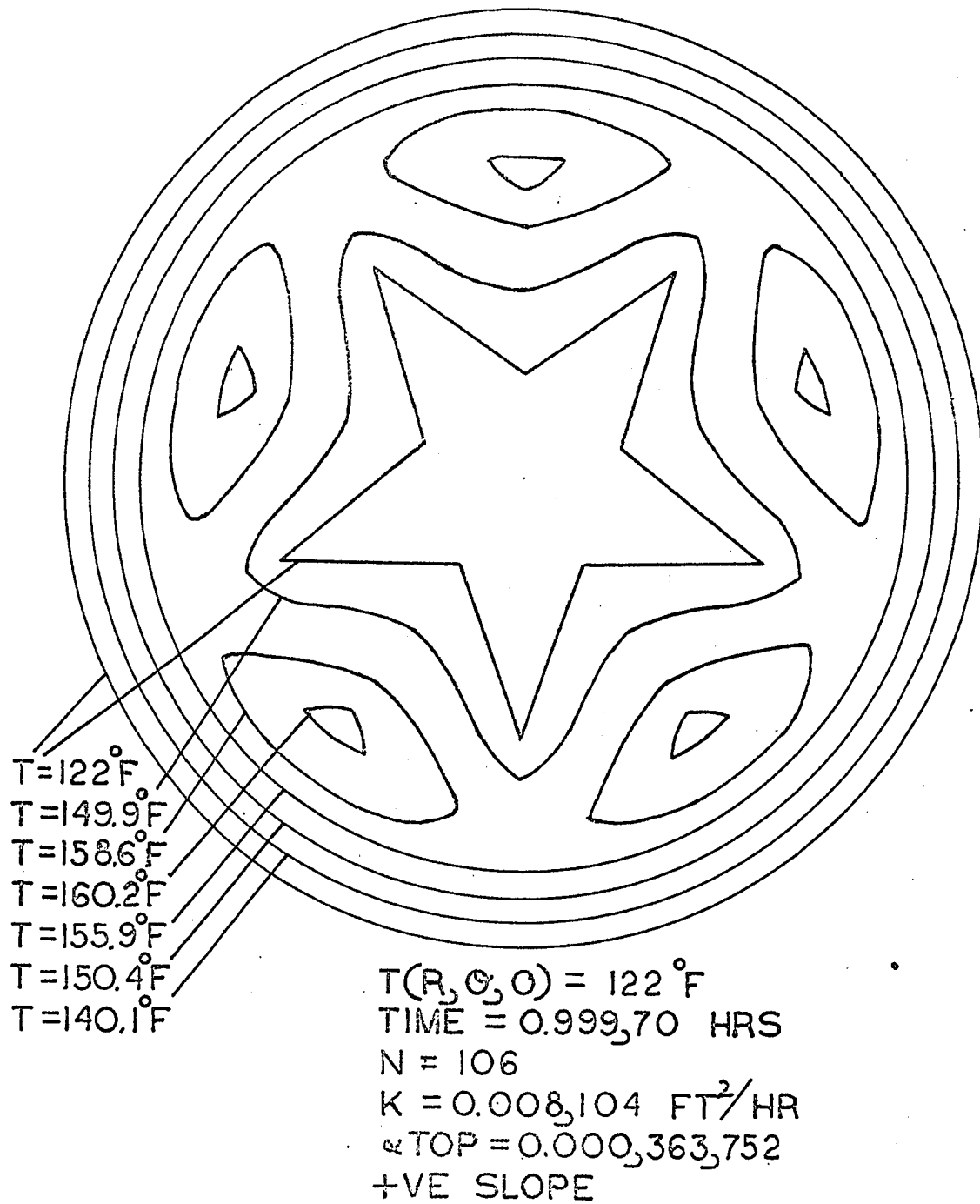


Figure 47 Isotherms for the Star Shaped Centre Hollow Cylinder

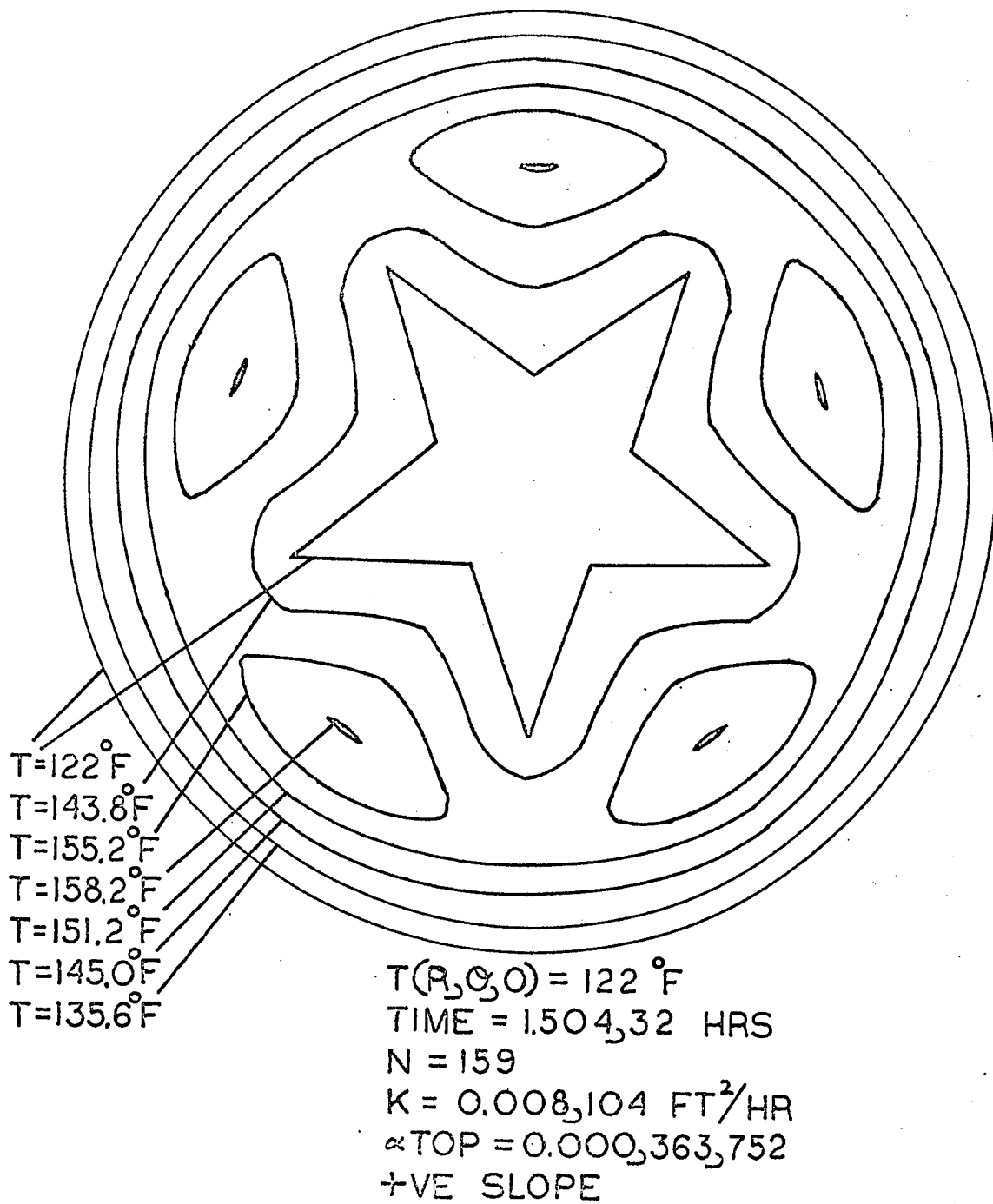


Figure 48 Isotherms for the Star Shaped Centre Hollow Cylinder

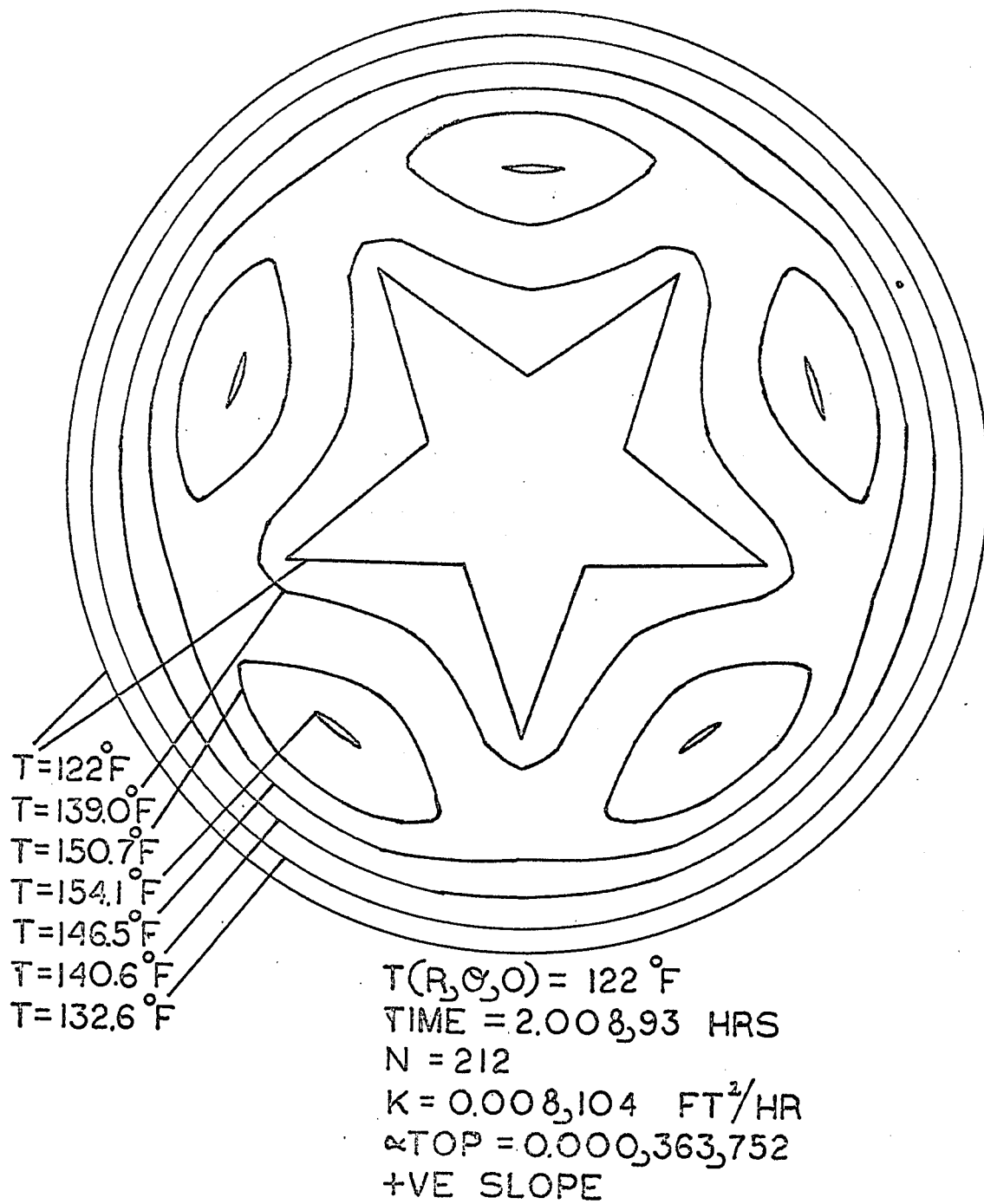


Figure 49 Isotherms for the Star Shaped Centre Hollow Cylinder

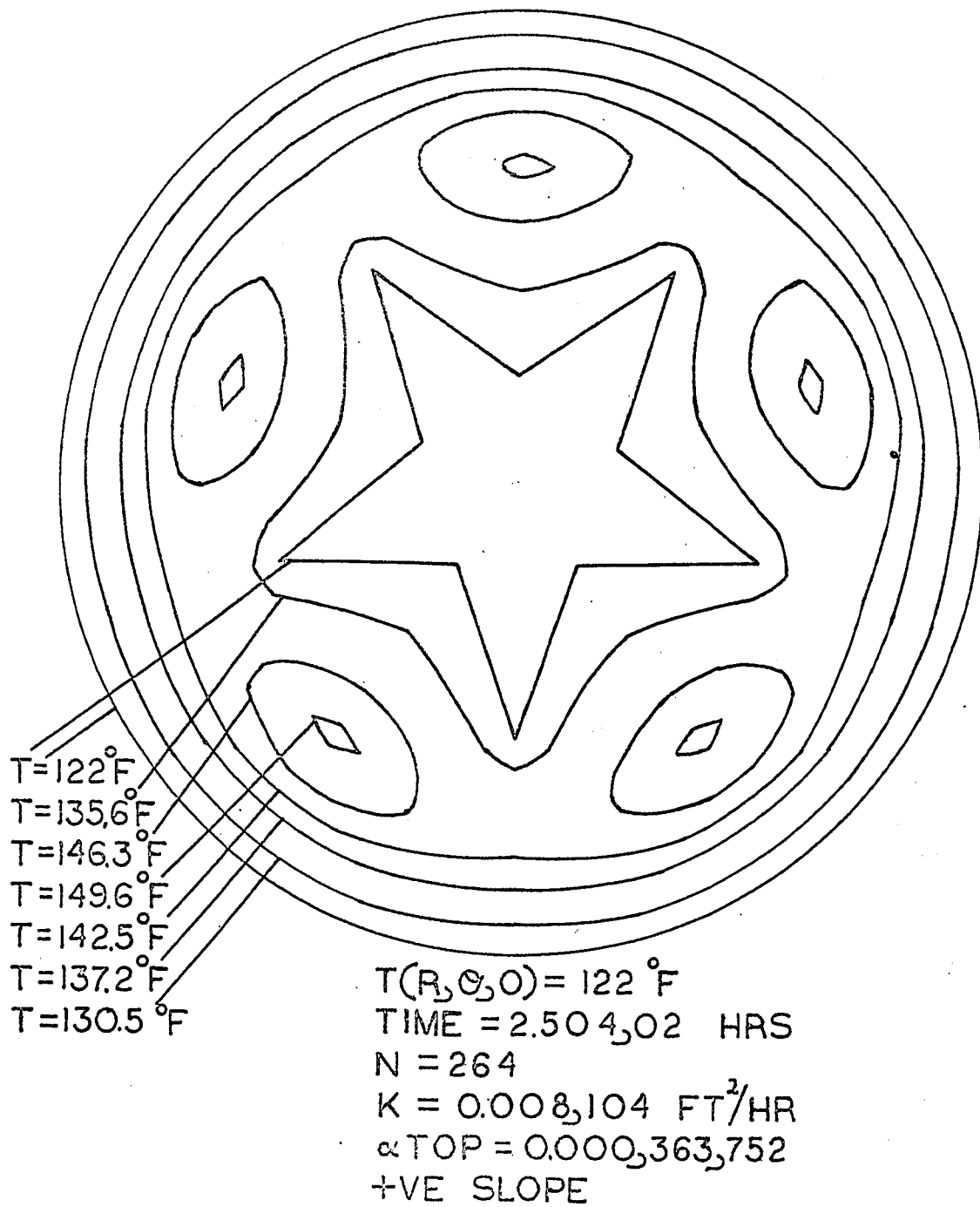


Figure 80 Isotherms for the Star Shaped Centre Hollow Cylinder

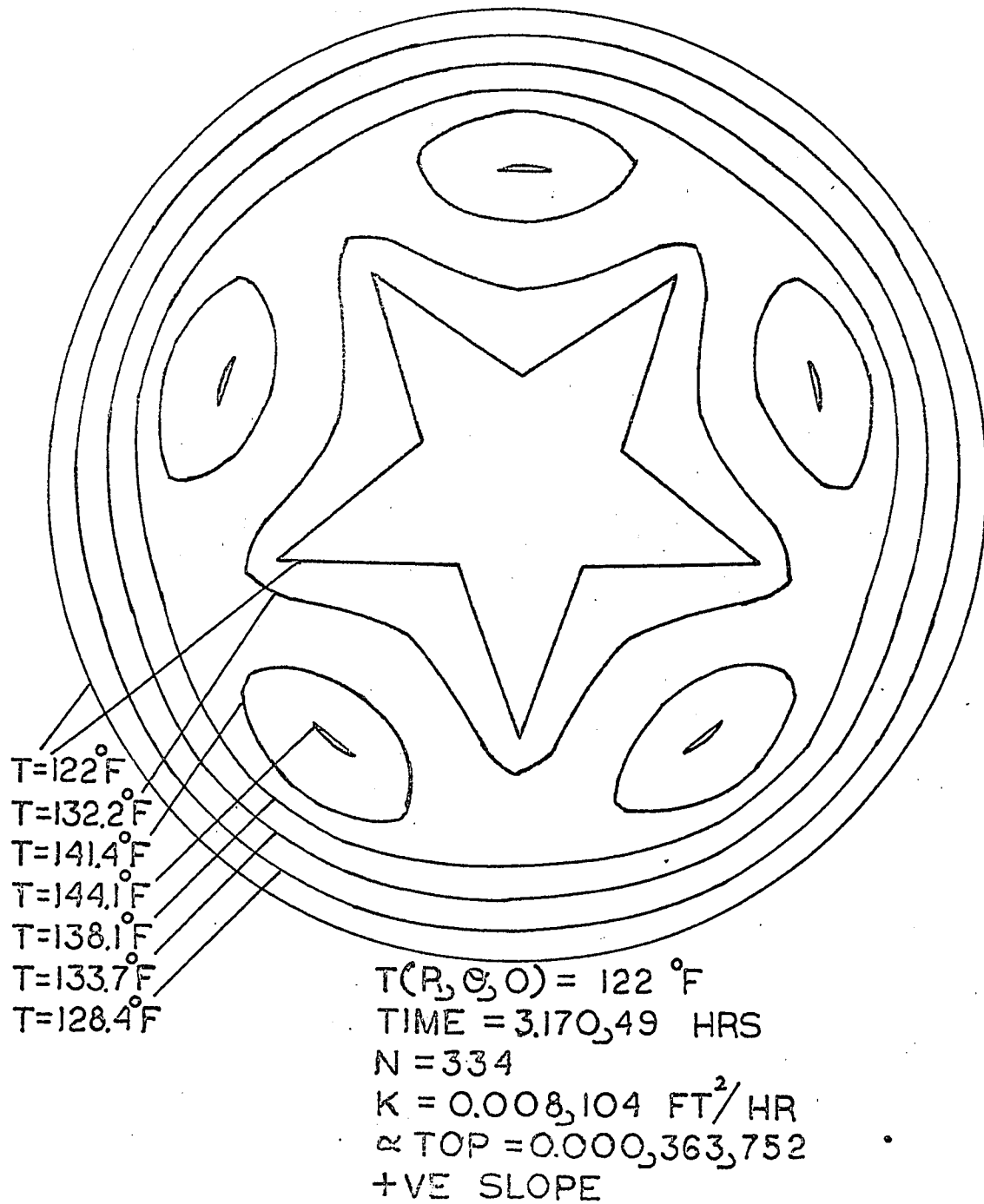


Figure 81 Isotherms for the Star Shaped Centre Hollow Cylinder

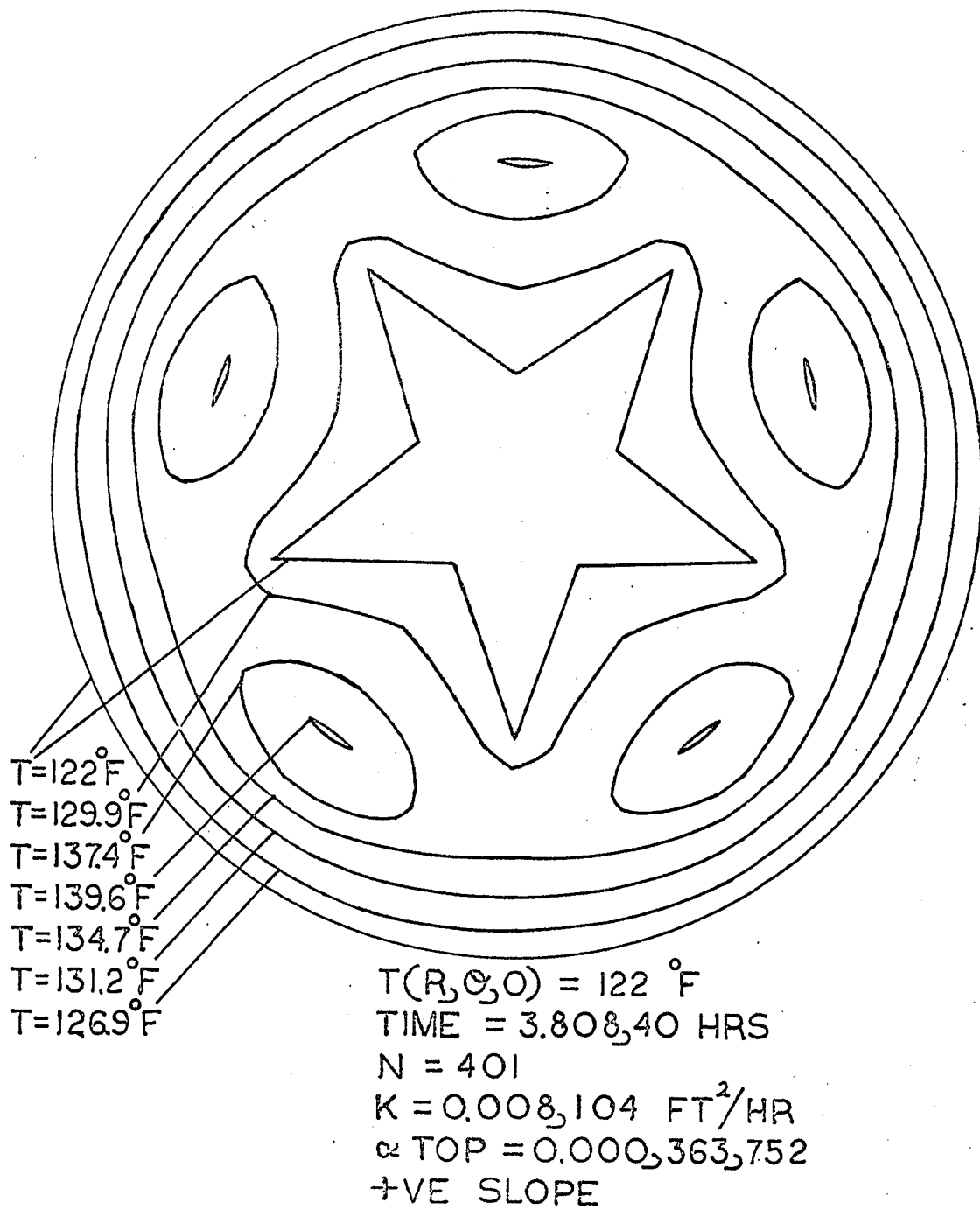


Figure 02 Isotherms For the Star Shaped Centre Hollow Cylinder

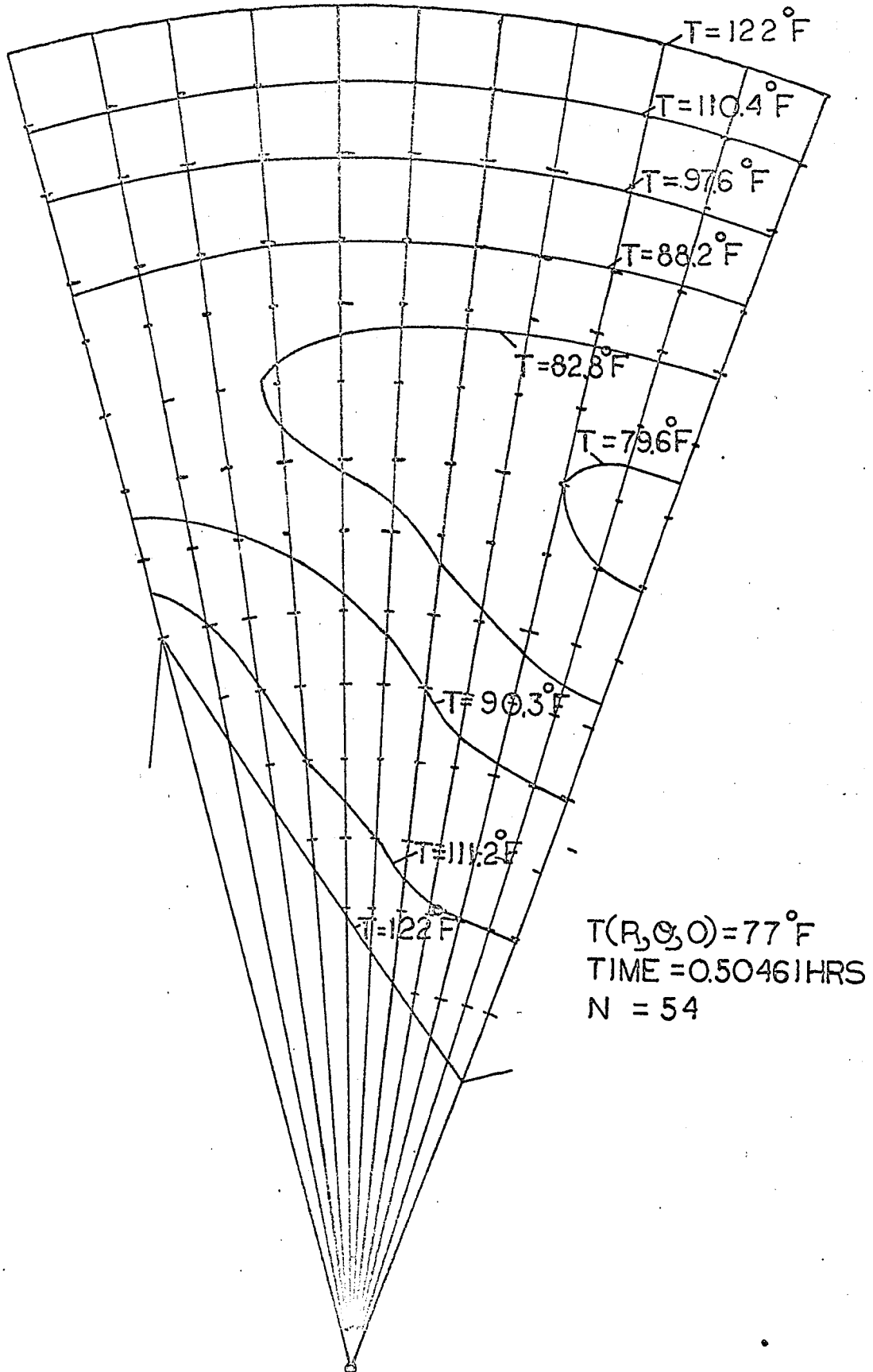


Figure 53 Sector Diagram for the Star Shaped Centre Hollow Cylinder

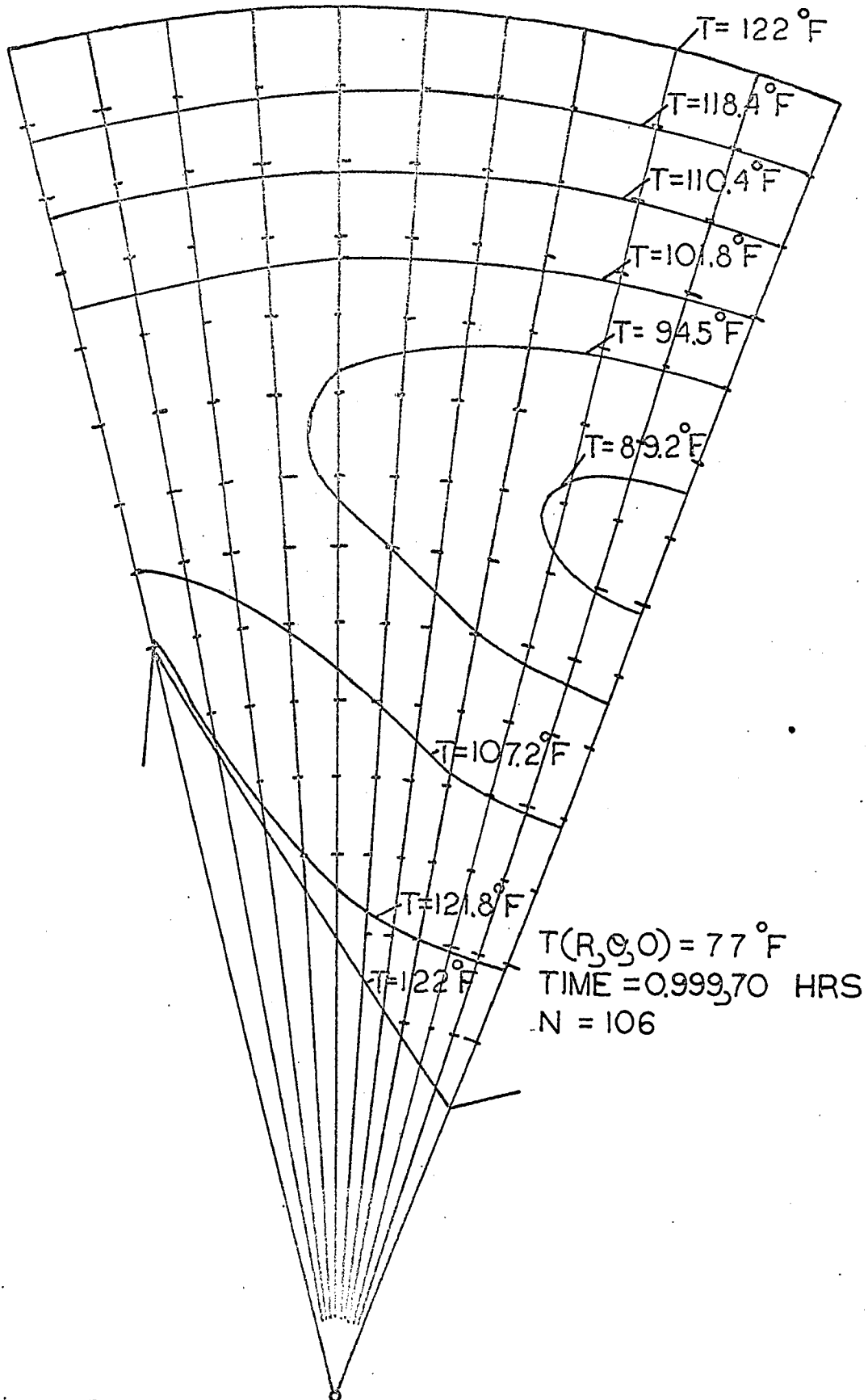


Figure 54 Sector Diagram for the Star Shaped Centre Hollow Cylinder

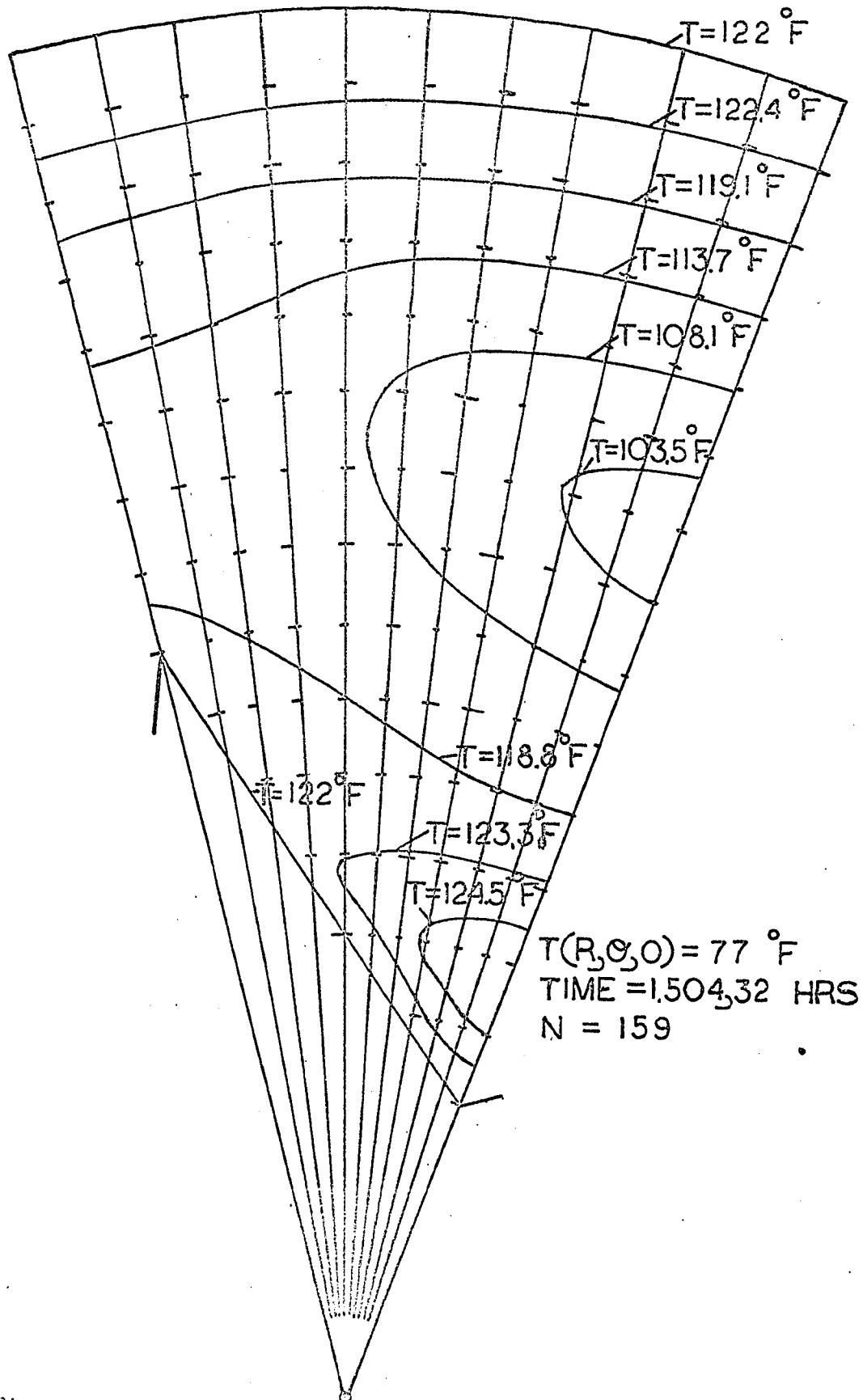


Figure 55 Sector Diagram for the Star Shaped Centre Hollow Cylinder

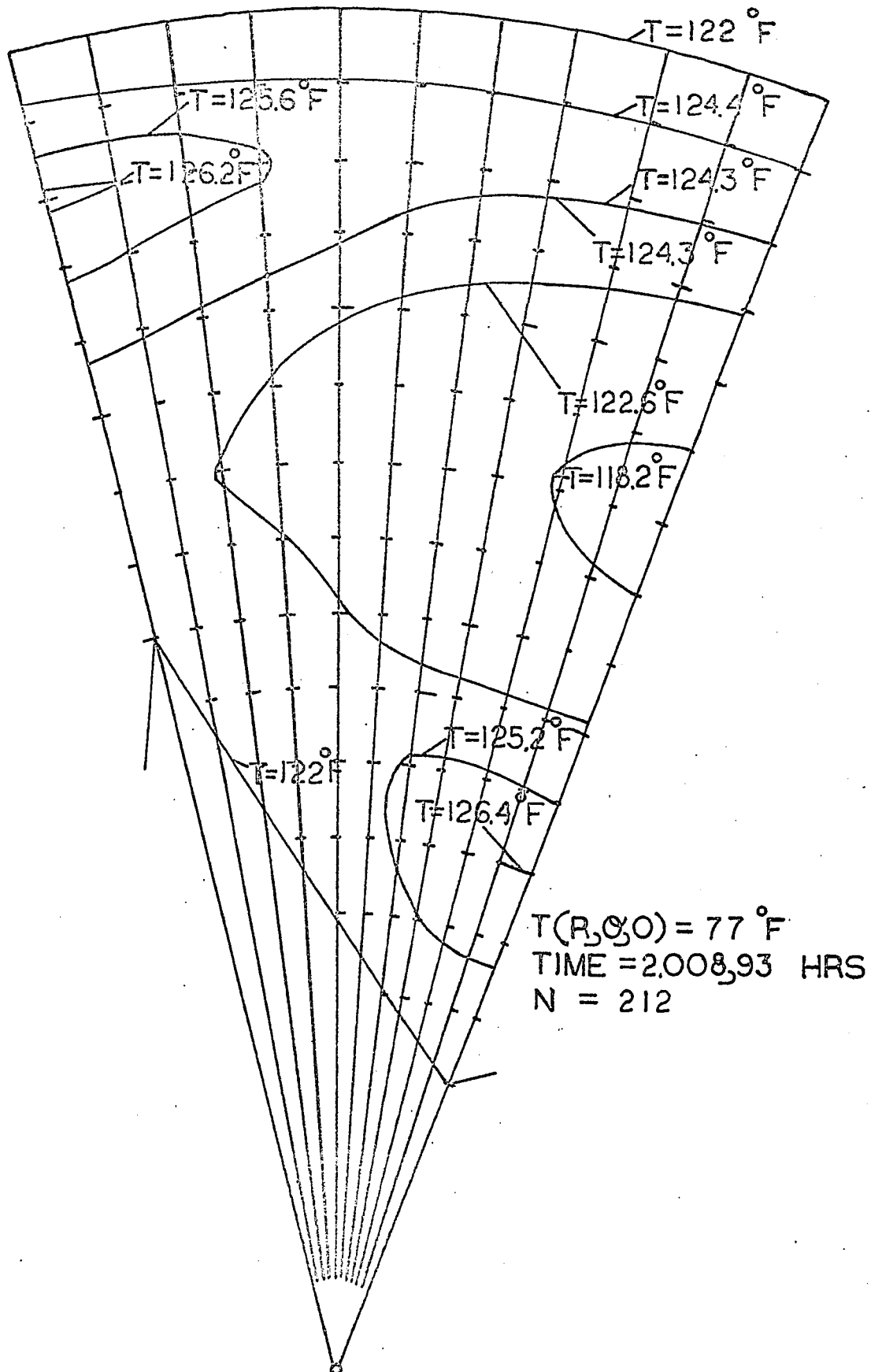


Figure 53. Sector Diagram for the Star Shaped Centre Hollow Cylinder

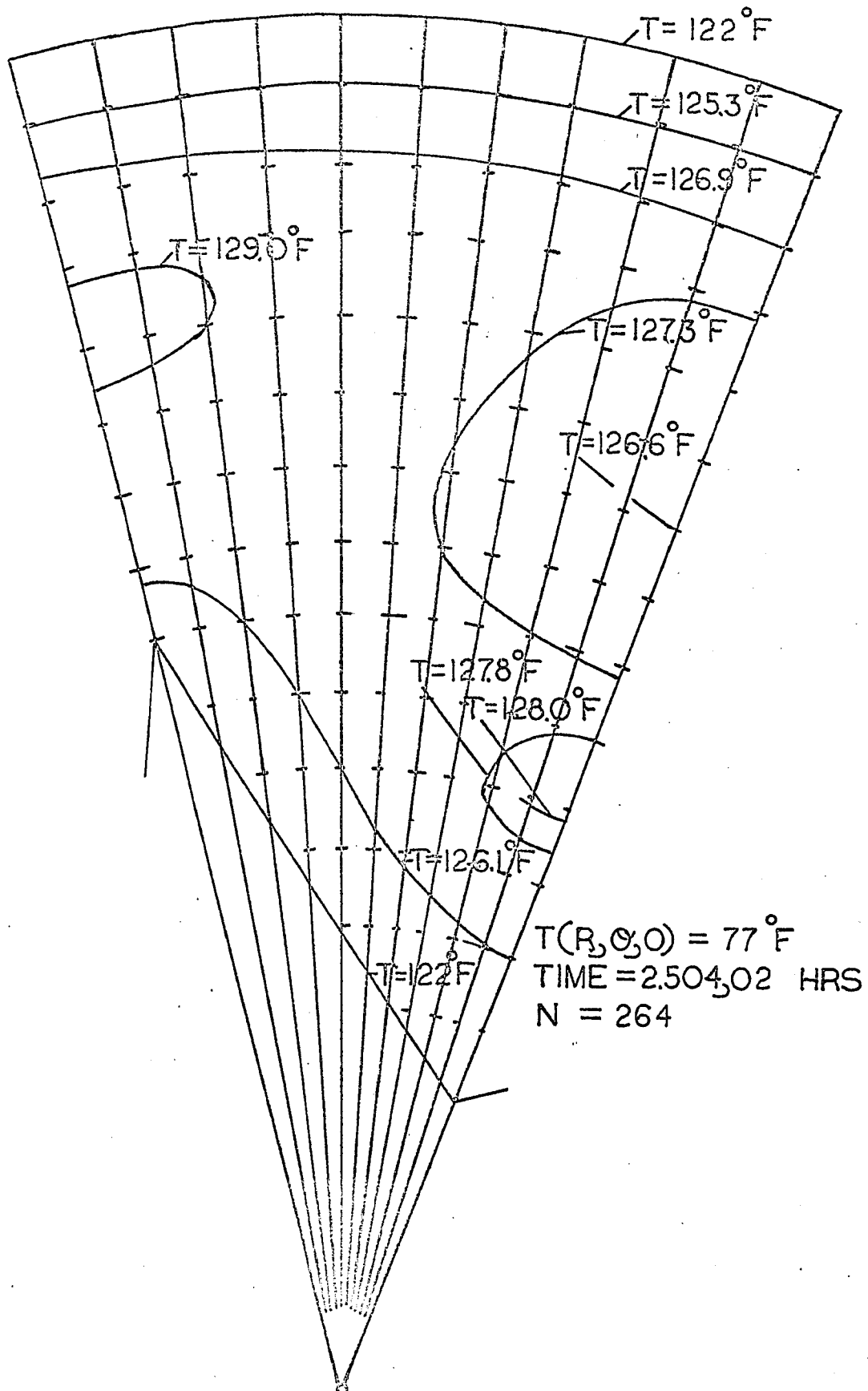


Figure 57 Sector Diagram for the Star Shaped Centre Hollow Cylinder

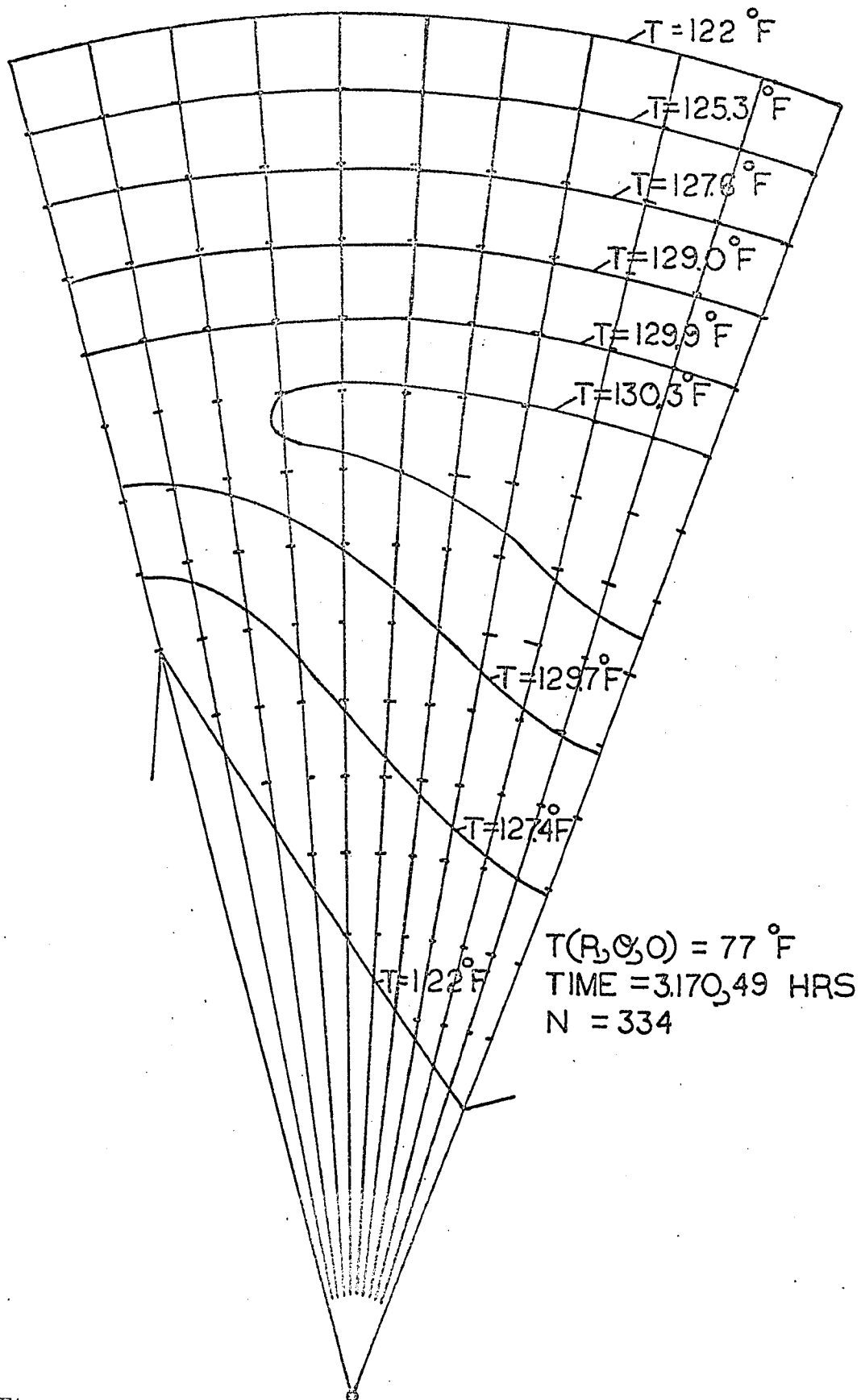


Figure 58 Sector Diagram for the Star Shaped Centre Hollow Cylinder

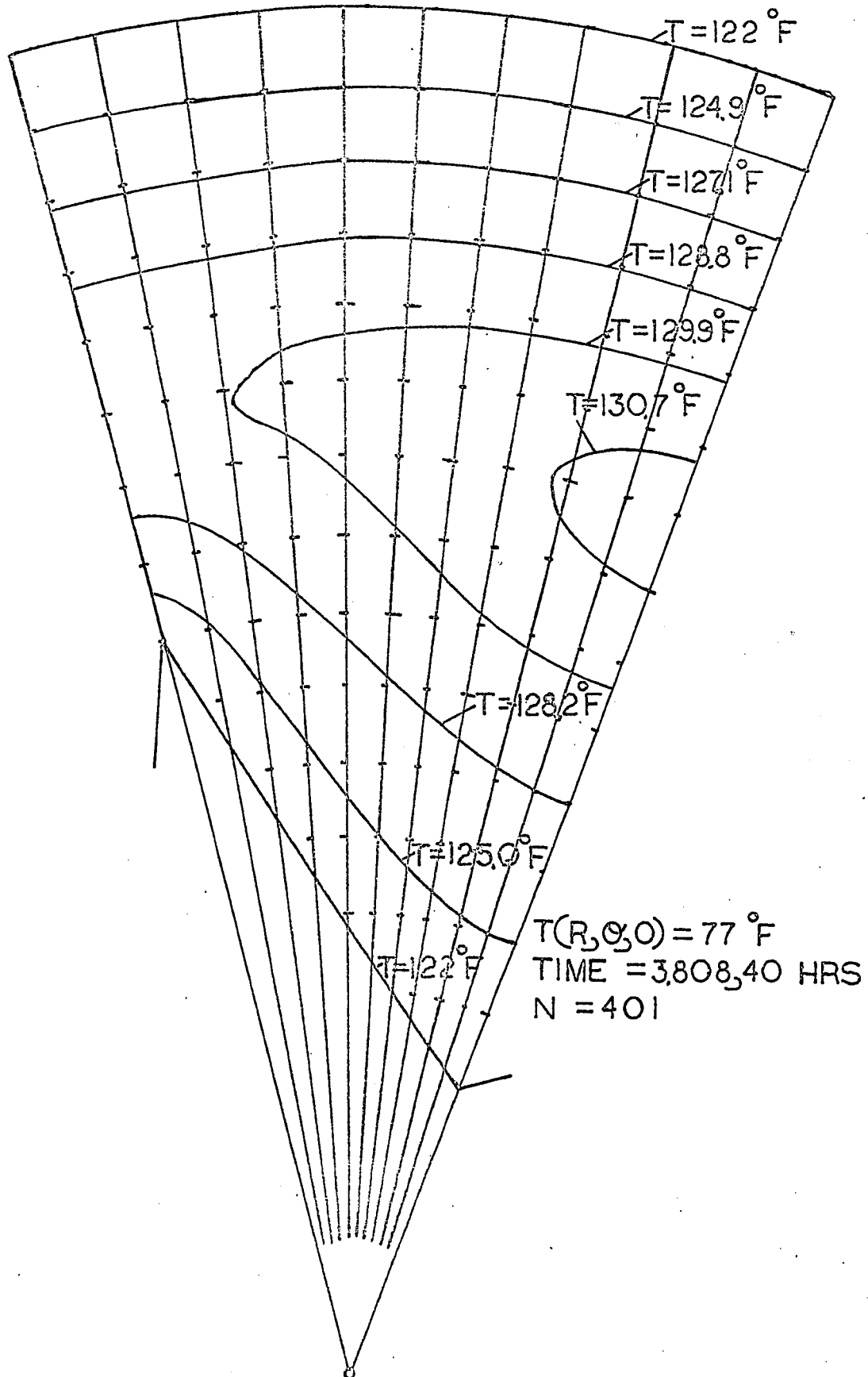


Figure 59 Sector Diagram for the Star Shaped Centre Hollow Cylinder

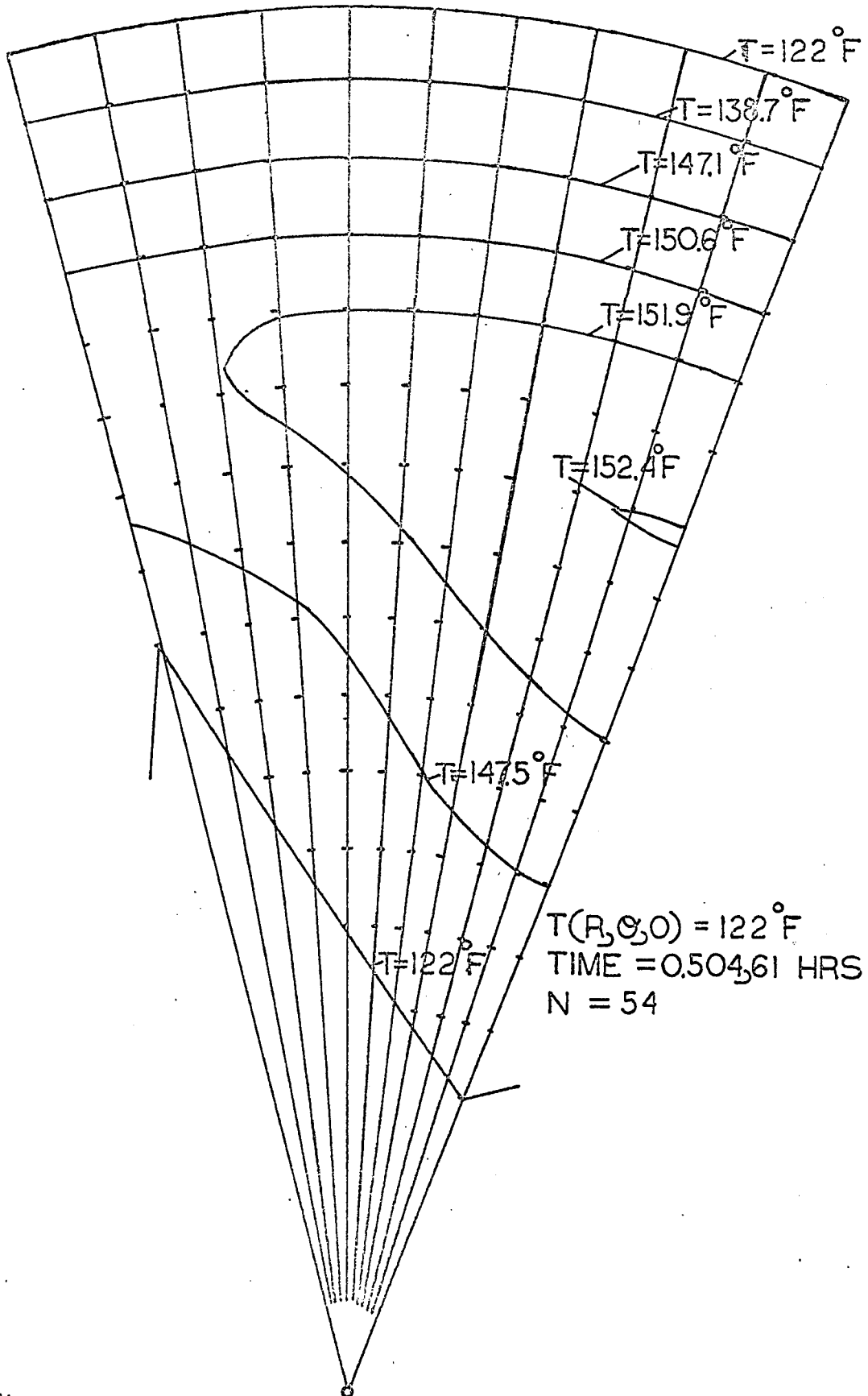


Figure 60 Sector Diagram for the Star Shaped Centre Hollow Cylinder

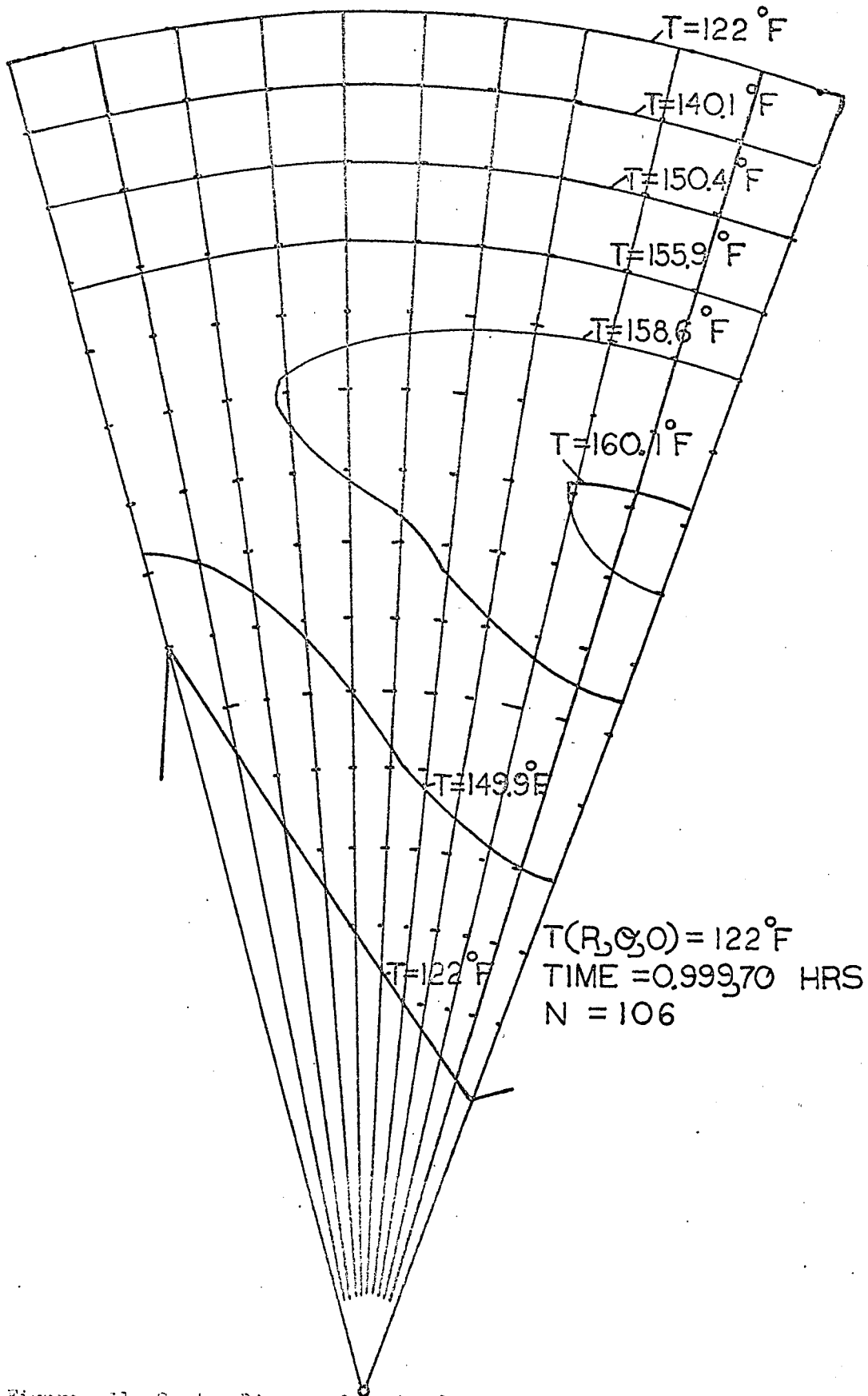


Figure 61 Sector Diagram for the Star Shaped Centre Hollow Cylinder

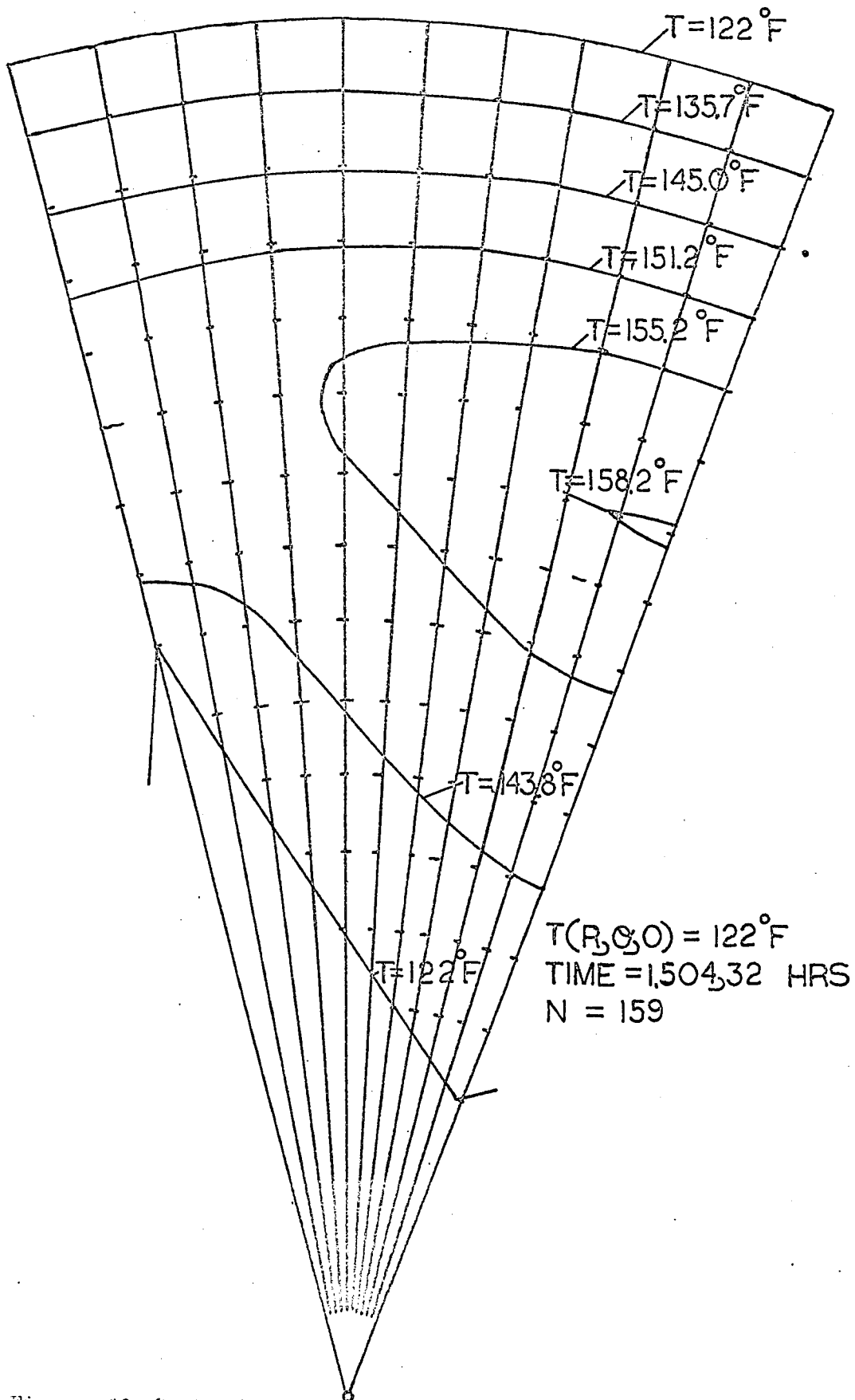


Figure 62 Sector Diagram for the Star Shaped Centre Hollow Cylinder

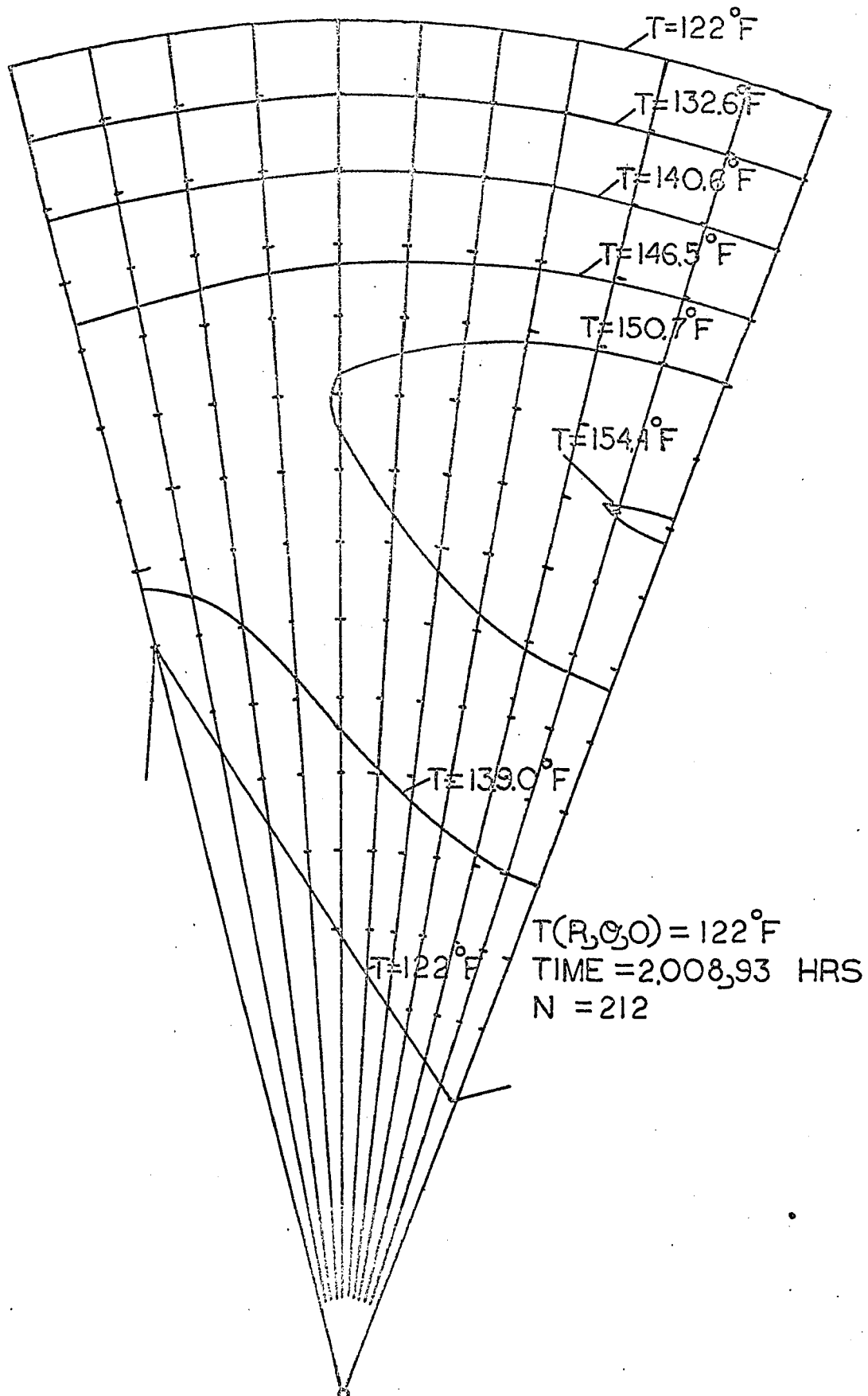


Figure 63 Sector Diagram for the Star Shaped Centre Hollow Cylinder

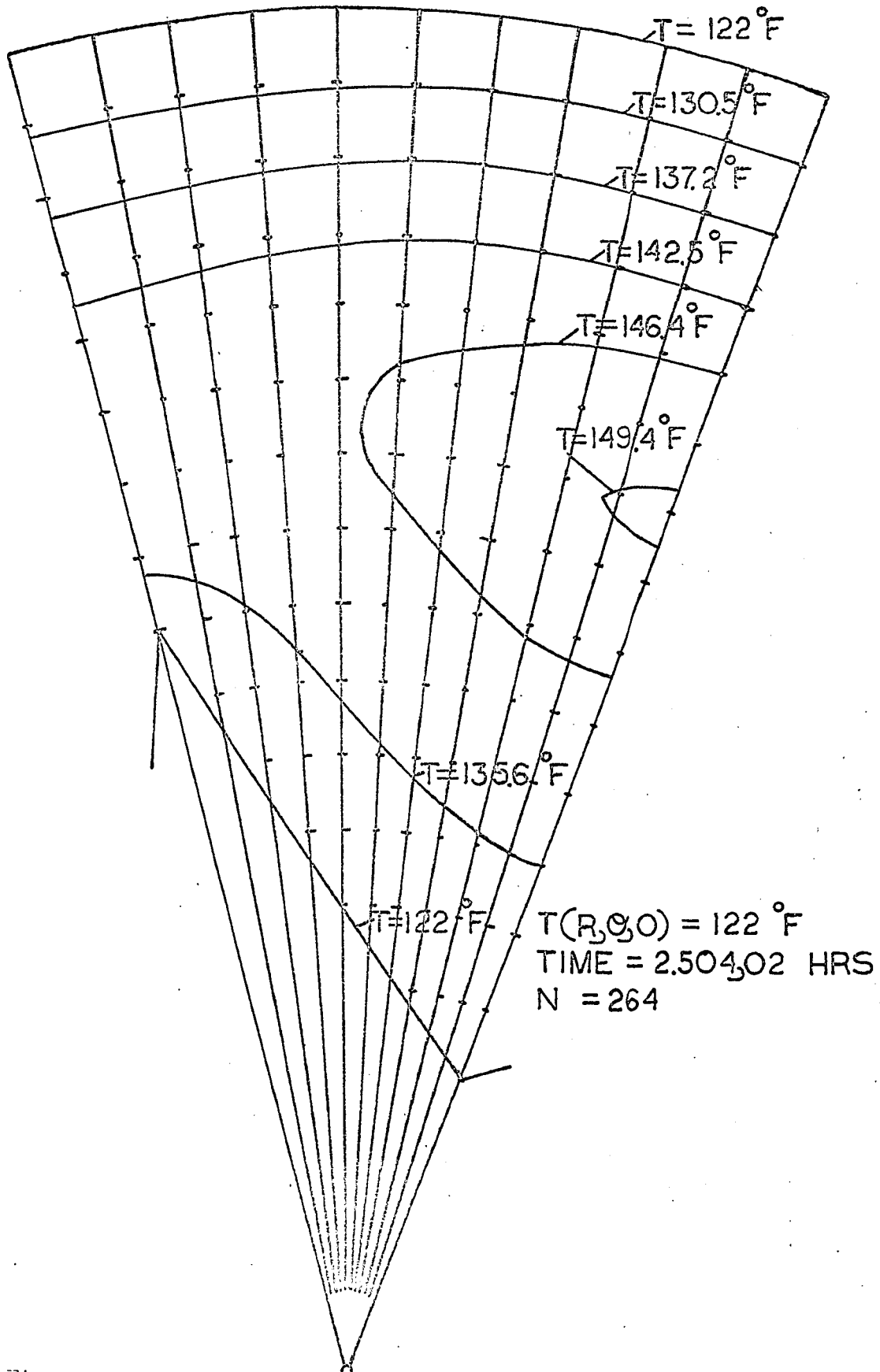


Figure 64 Sector Diagram for the Star Shaped Centre Hollow Cylinder

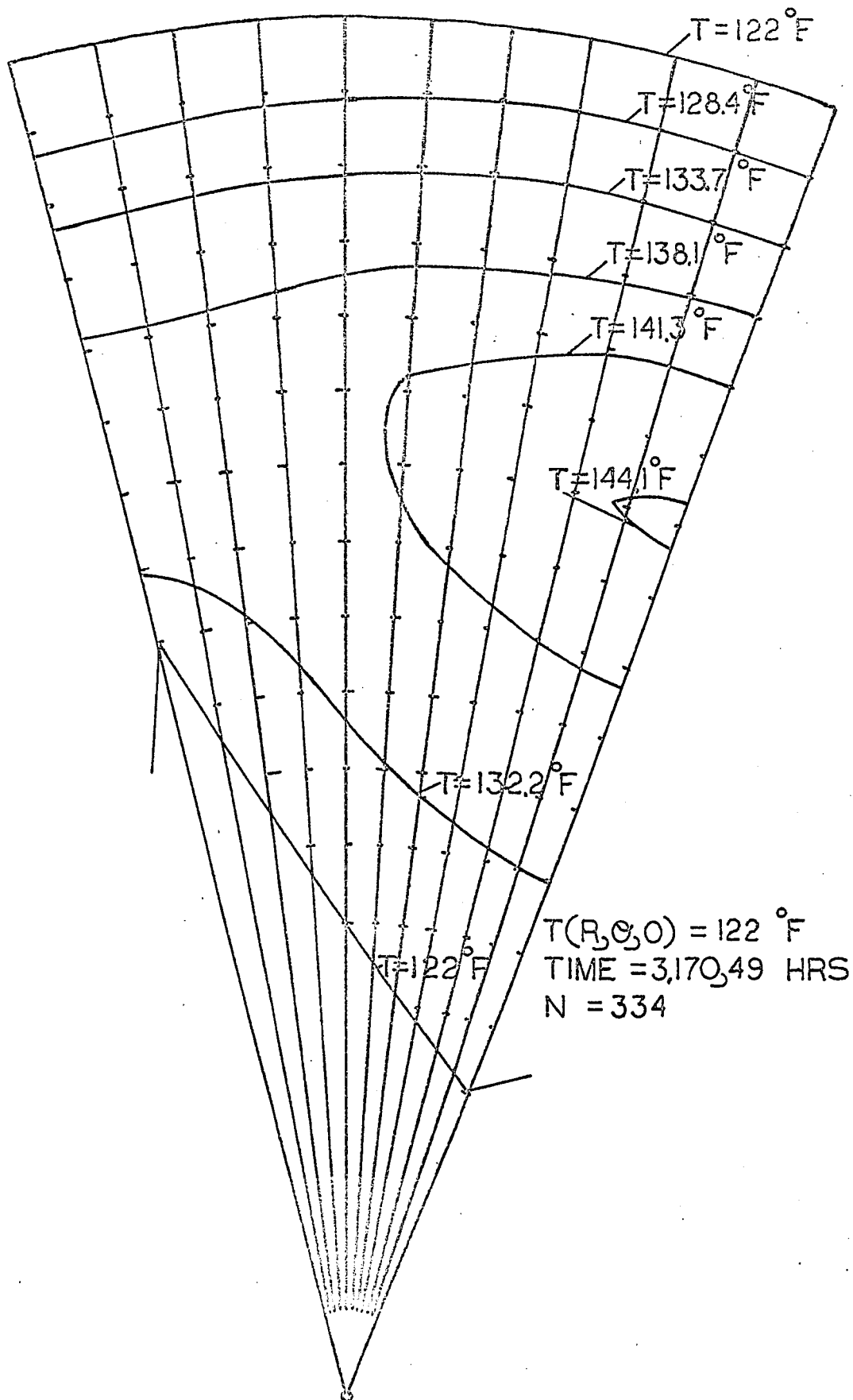


Figure 65 Sector Diagram for the Star Shaped Centre Hollow Cylinder

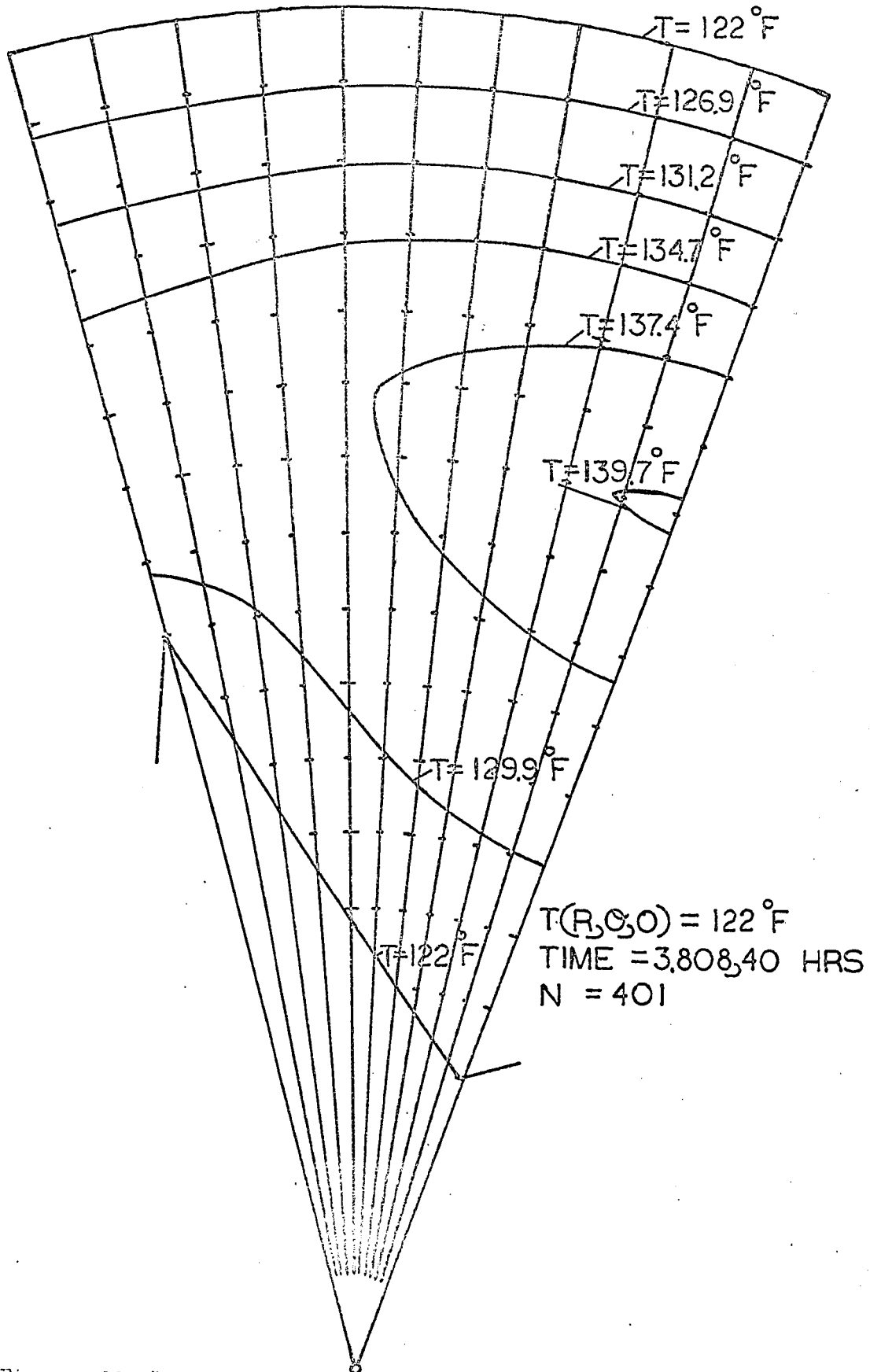


Figure 66 Sector Diagram for the Star Shaped Centre Hollow Cylinder

arises as to whether or not this assumption is really justified. To see if there is an end effect, the simplest possible shape, the solid cylinder, was solved in three dimensions - two of space, r and z , and one of time. Two sizes of cylinder - six inch diameter and five inch diameter were considered in the test and the assumption was made that the pattern at seven inches from the end was the same as the pattern for infinite length. Initially, a symmetrical pattern is assumed by the propellant when the initial condition is seventy-seven degrees Fahrenheit (Figures 67 and 68) and the outer diameter is six inches. Soon a hot doughnut shaped ring appears, at one hour past time zero, about one inch in from the end and one inch in from the outer surface. As time proceeds to one and a half hours the centre of the doughnut fills in and gives way to a hot region about one and a half inches from the end and two inches from the outer surface. Later, at two hours this region becomes compressed and moves farther in to between three and five inches from the end. At two and a half hours this region becomes much smaller, has assumed an elliptical shape, and is now centred at four and a half inches. Finally, a symmetrical pattern emerges after three hours have elapsed and this general type of pattern is maintained until the heat sources are no longer active. Then all points level out at one hundred and twenty-two degrees Fahrenheit.

If the initial condition is one hundred and twenty-two degrees Fahrenheit, (Figures 69 and 70), a symmetrical pattern appears and its general shape is maintained throughout the period in which the heat sources are active. When half an hour has gone, the centre reaches a

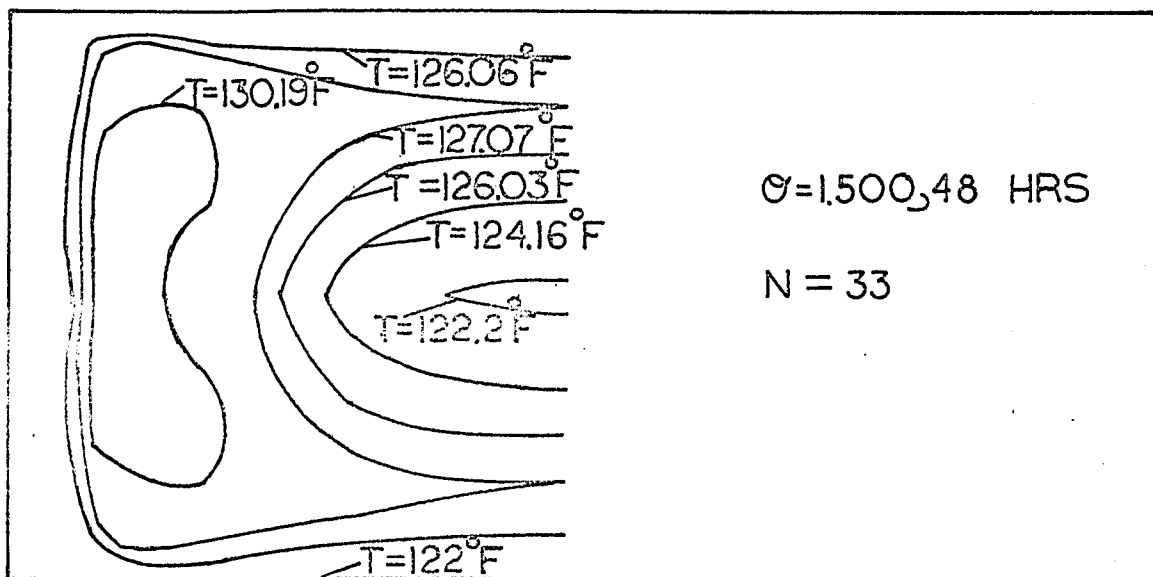
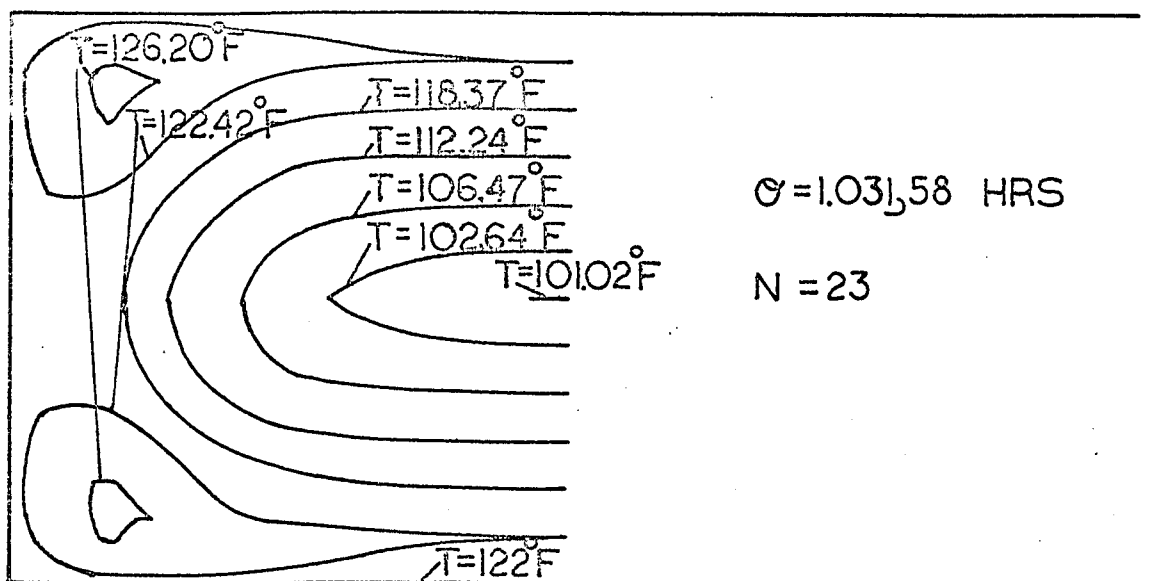
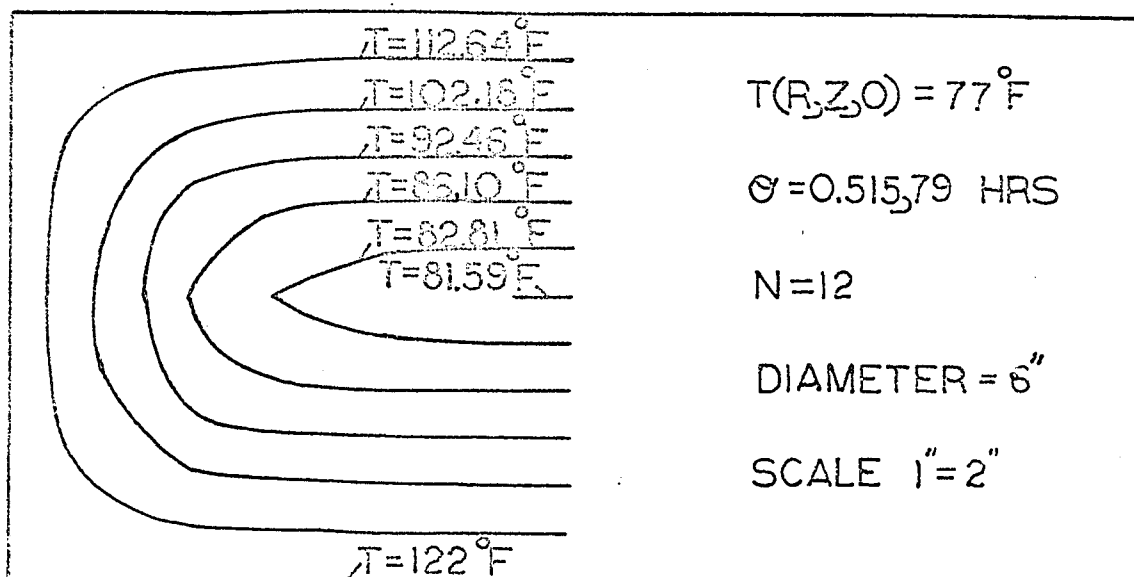


Figure 67 End Effect Diagrams for the 6" diameter Solid Cylinder

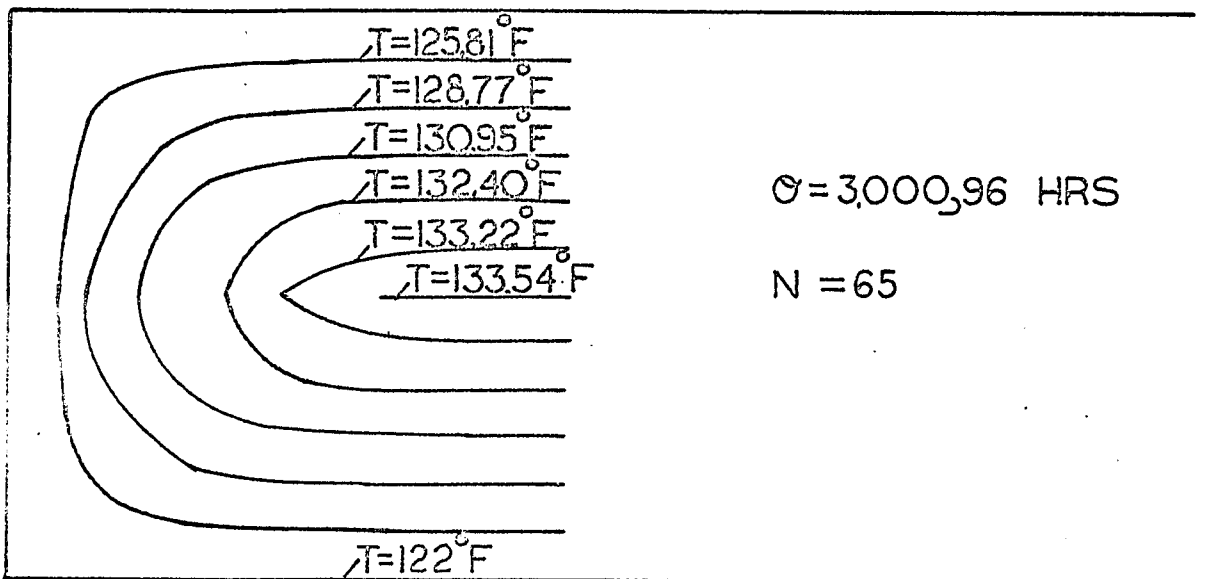
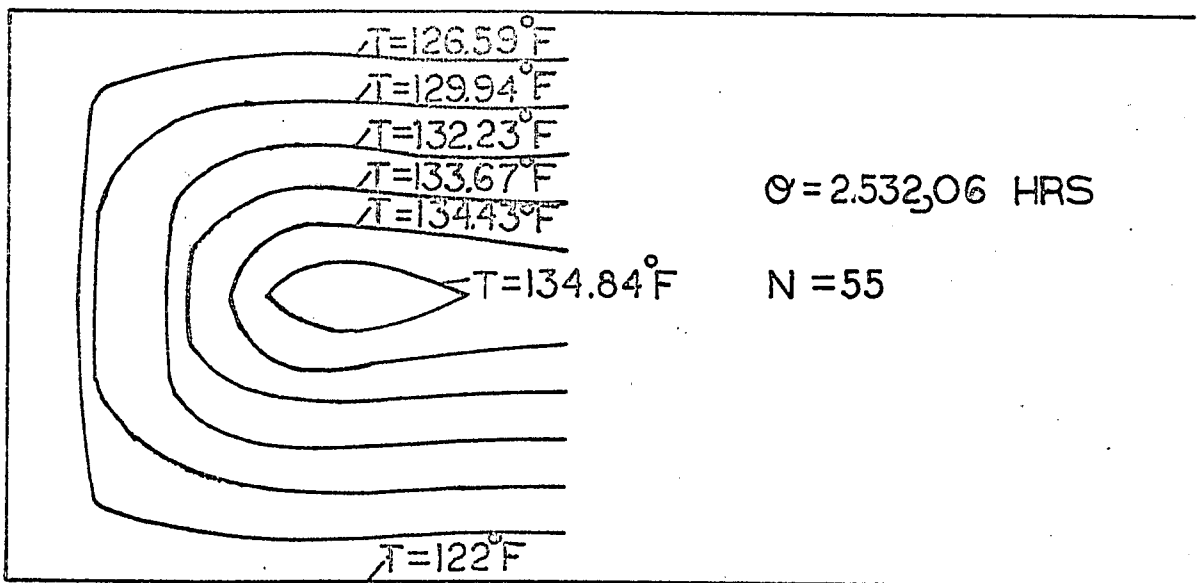
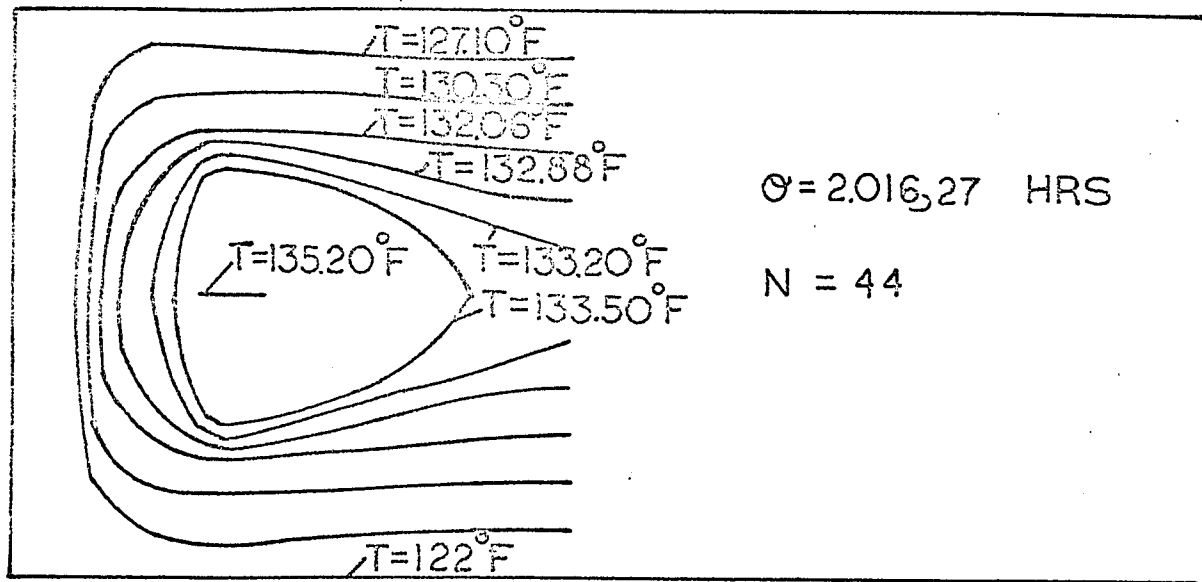


Figure 68- End Effect Diagrams for the 6" diameter Solid Cylinder

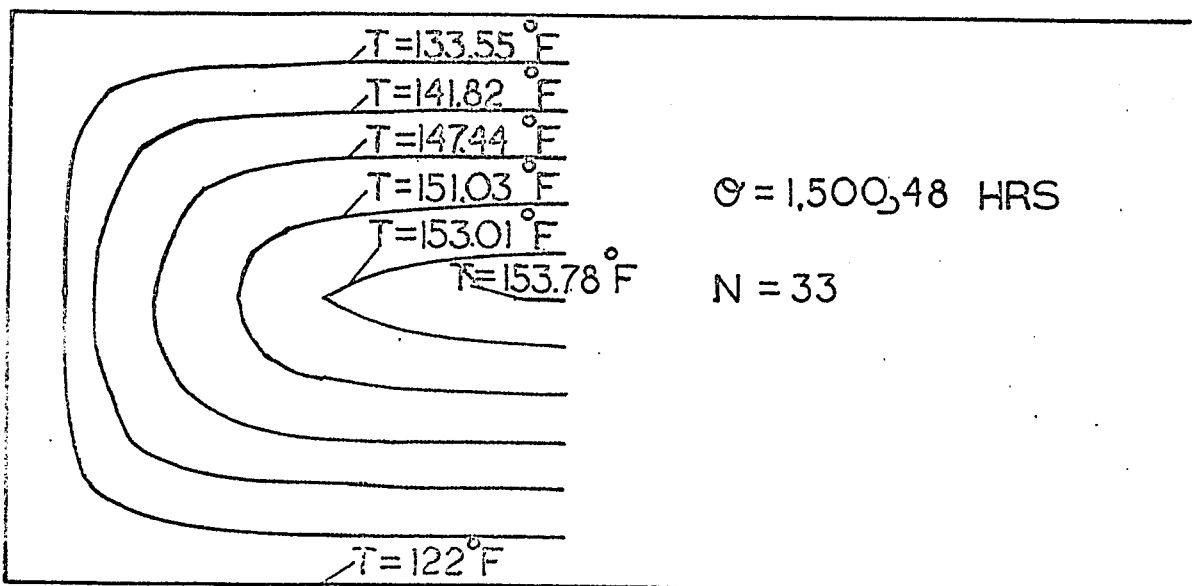
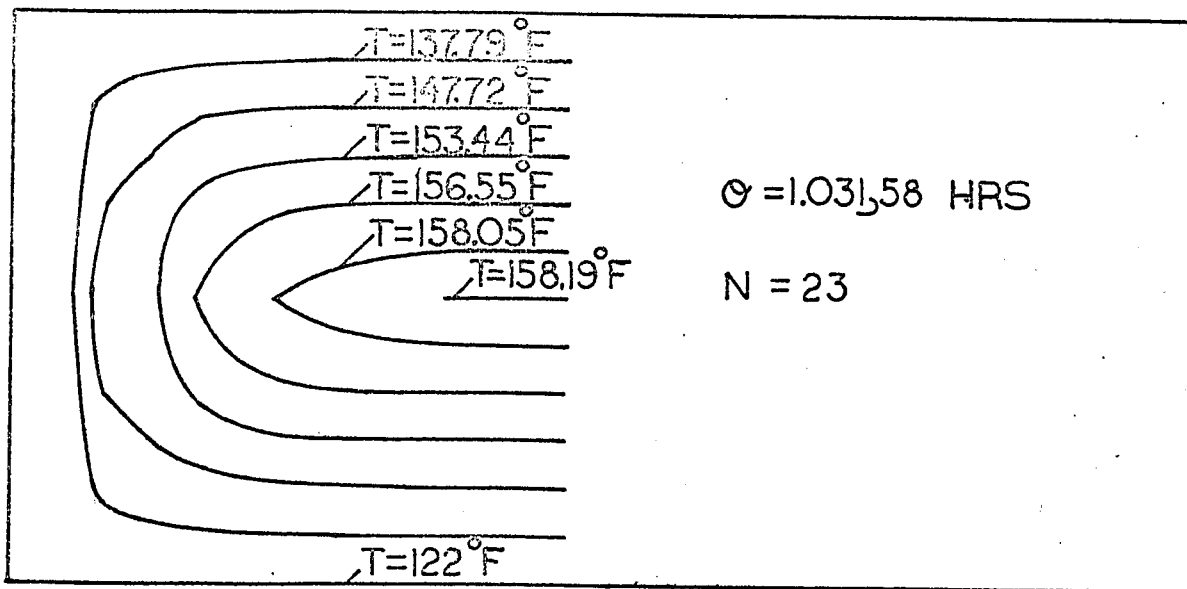
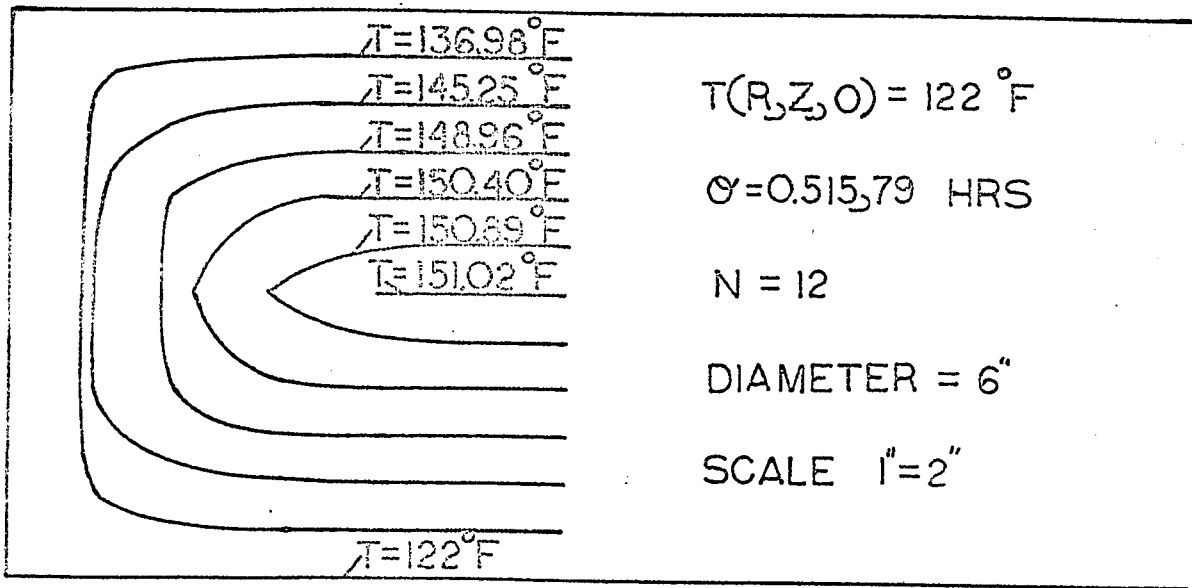


Figure 69 . End Effect Diagrams for the 6" diameter Solid Cylinder

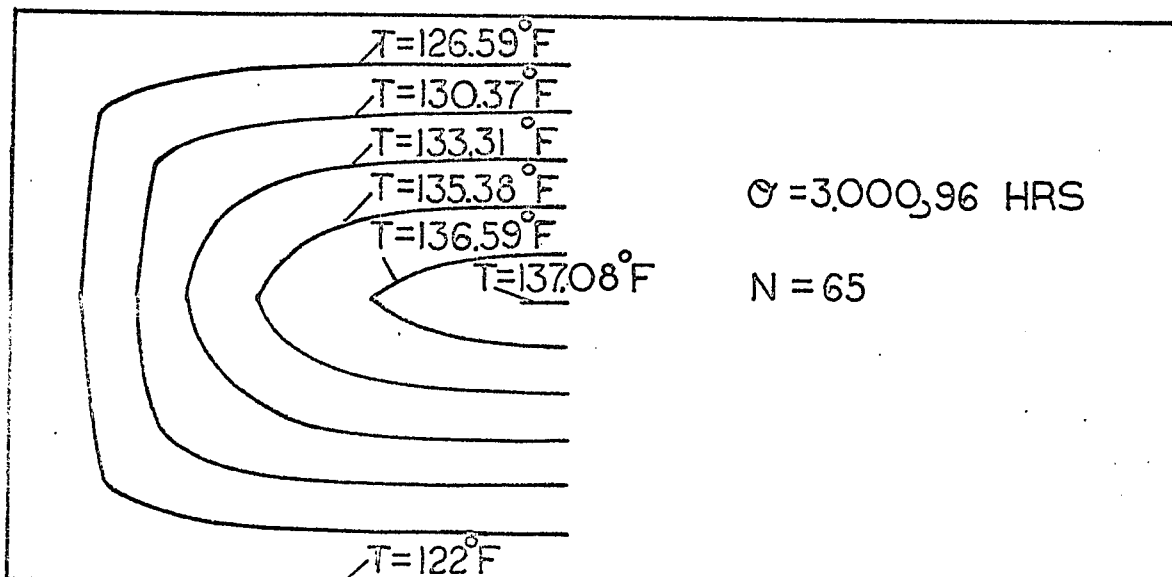
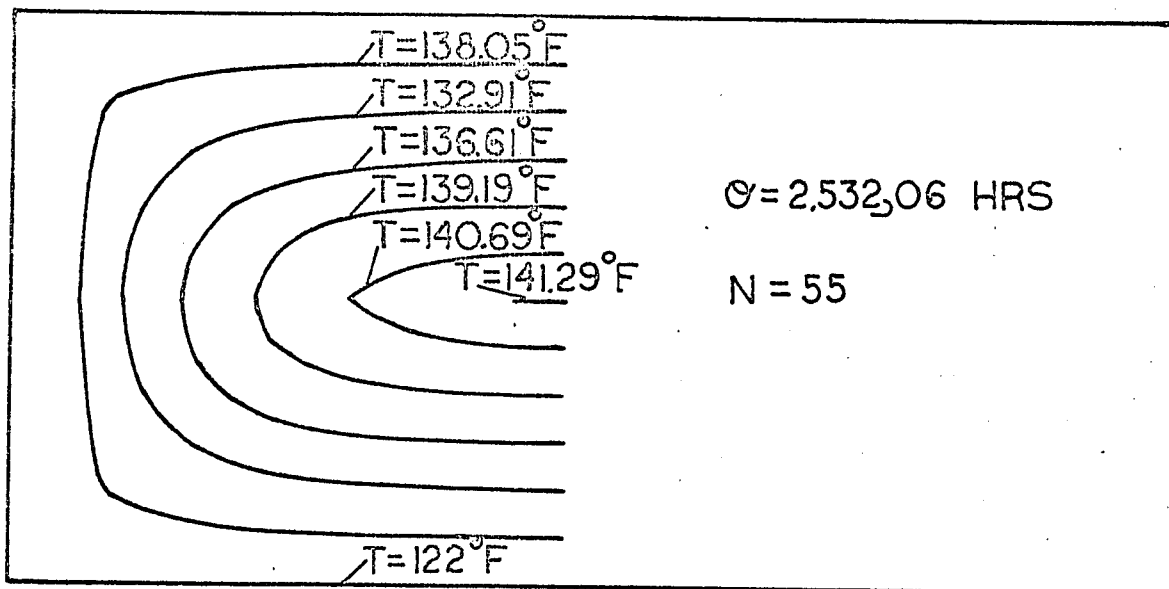
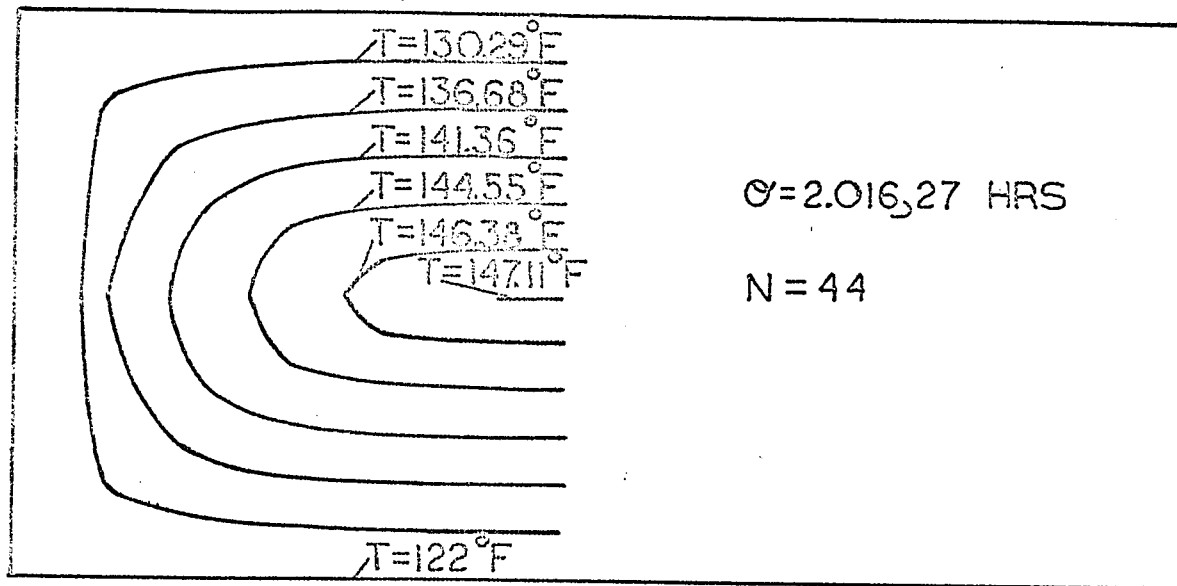


Figure 70. End Effect Diagrams for the 6" diameter Solid Cylinder

temperature of one hundred and fifty-one degrees Fahrenheit. At one hour it reaches one hundred and fifty-eight, then falls to one hundred and fifty-four at one and a half hours, falling again to one hundred and forty-seven at two hours, dips to one hundred and forty-one at two and a half hours and drops to one hundred and thirty-seven at three hours. Finally after the heat sources are no longer active the pattern levels out at one hundred and twenty-two degrees Fahrenheit.

When the test is conducted on a five inch diameter cylinder, (Figures 71 and 72), with an initial condition of seventy-seven degrees Fahrenheit, at first a symmetrical pattern appears. Then after one hour a waffle shaped hot region appears, whose shape can best be judged by looking at the diagram in Figure 71. When one and a half hours have passed the hot region has become circular in shape and has moved in to about two inches from the end, from about one inch. At two hours the pattern is almost symmetrical in shape and at two and a half hours is certainly so. This general type of pattern is maintained until the heat sources die out.

The corresponding test with an initial condition of one hundred and twenty-two degrees Fahrenheit, (Figures 73 and 74), gives a symmetrical pattern throughout the active life of the heat sources. It reaches a peak of 155°F in one hour.

Comparison of 5" and 6" diameter end effects: When the initial boundary condition is 77°F , the five and six inch diameter grains show the same general pattern but the effect is a little more pronounced and lasts a

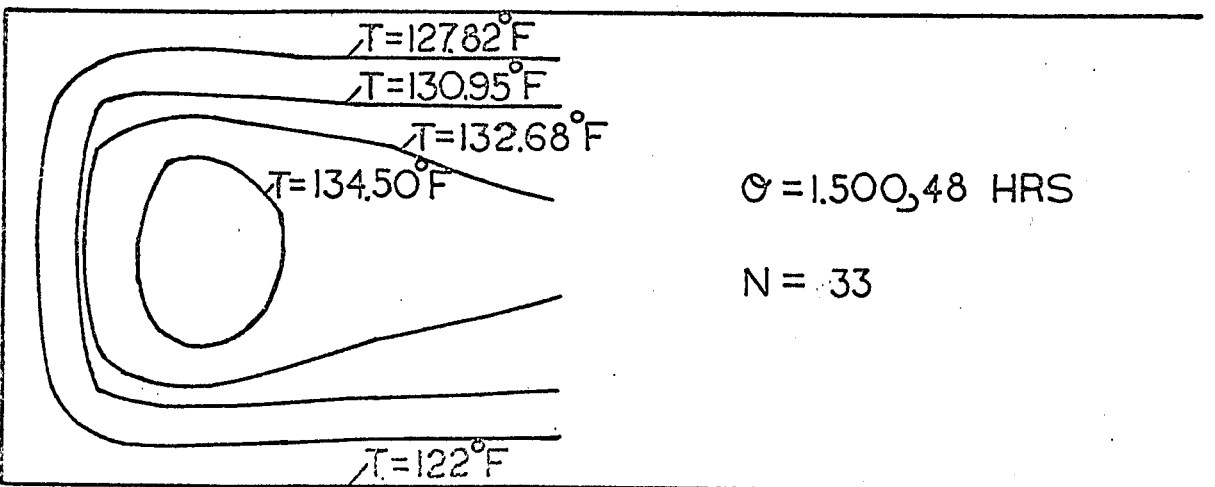
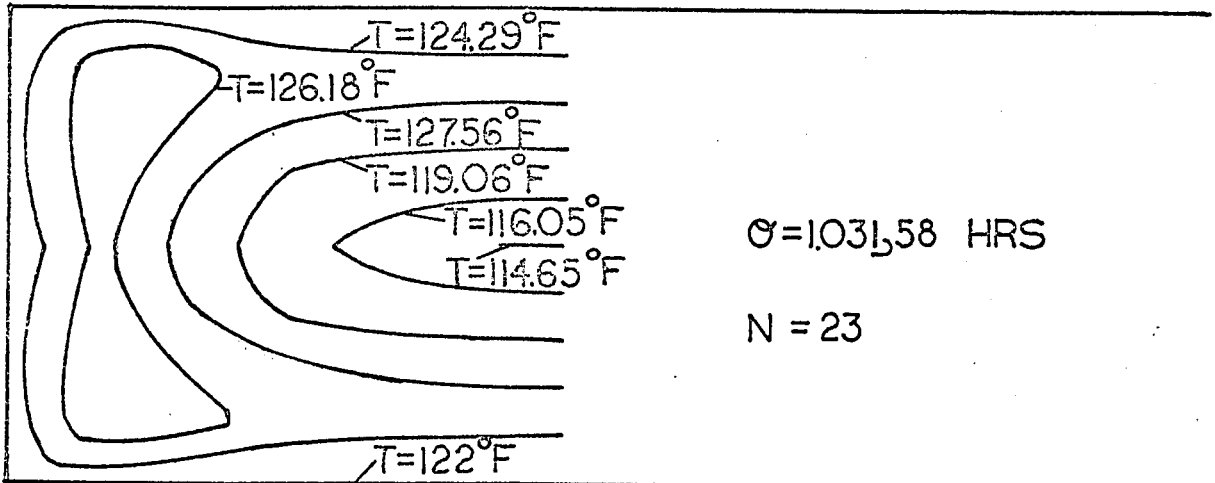
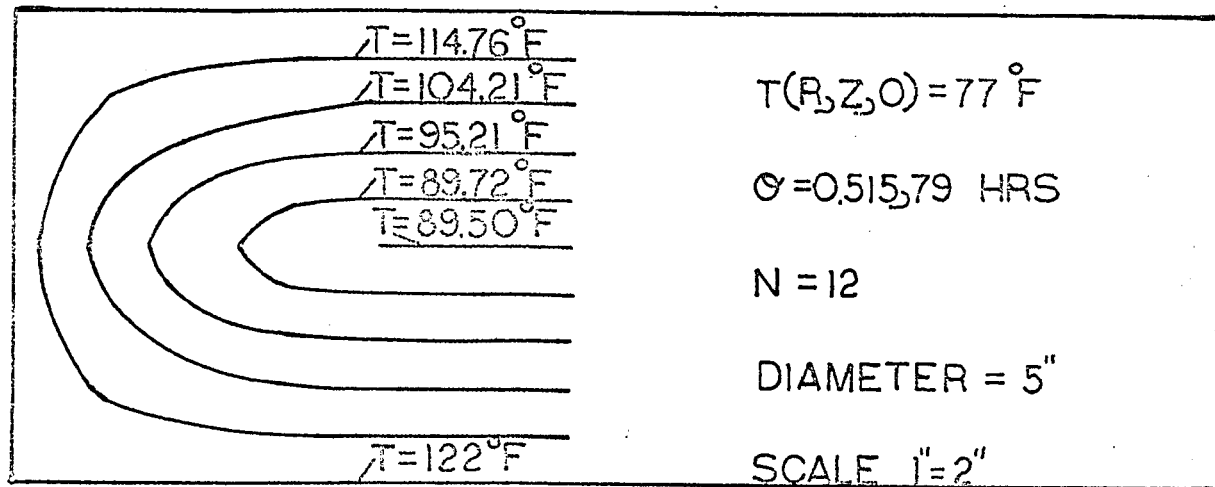


Figure 71 End Effect Diagrams for the 5" diameter Solid Cylinder

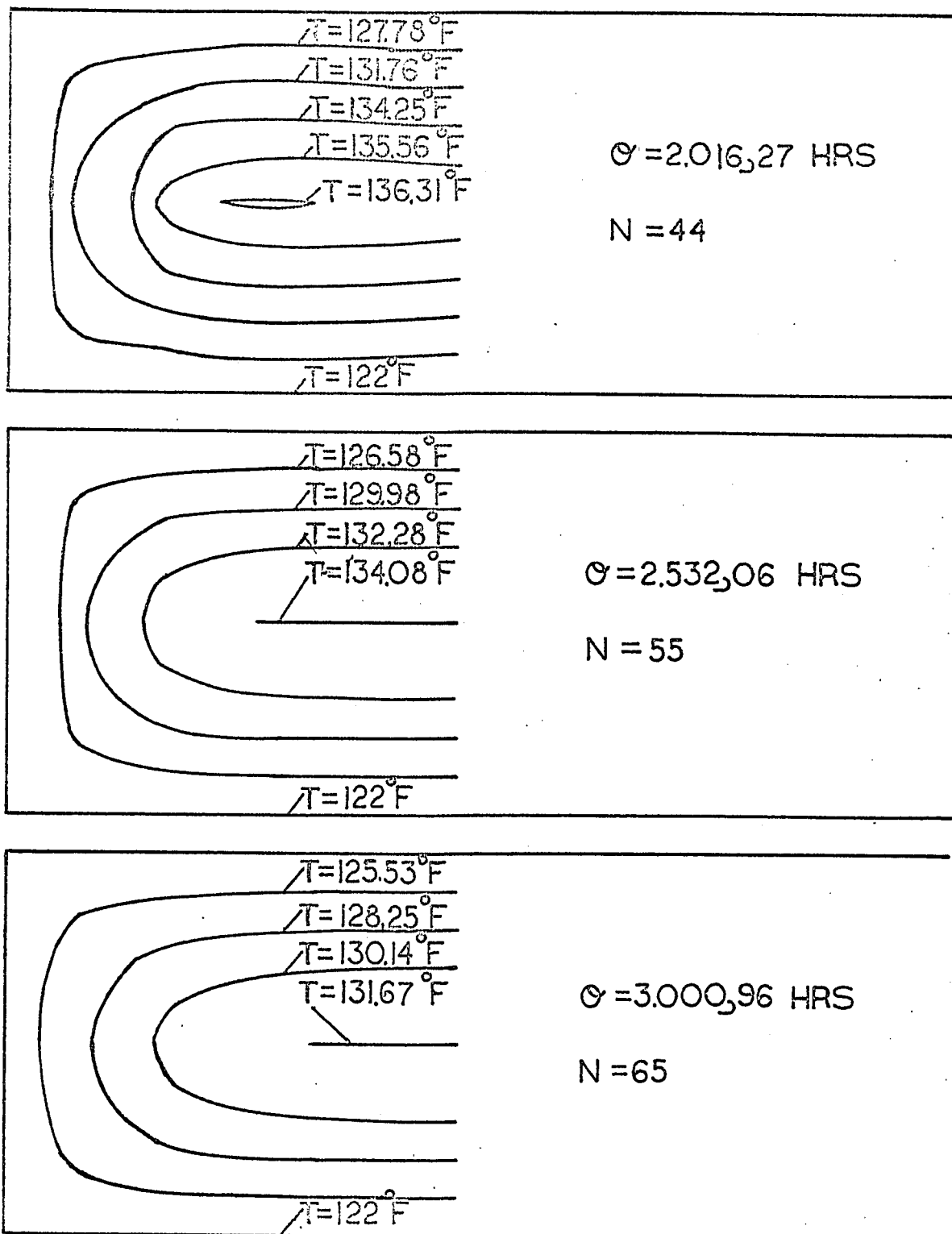


Figure 72 End Effect Diagrams for the 5" diameter Solid Cylinder

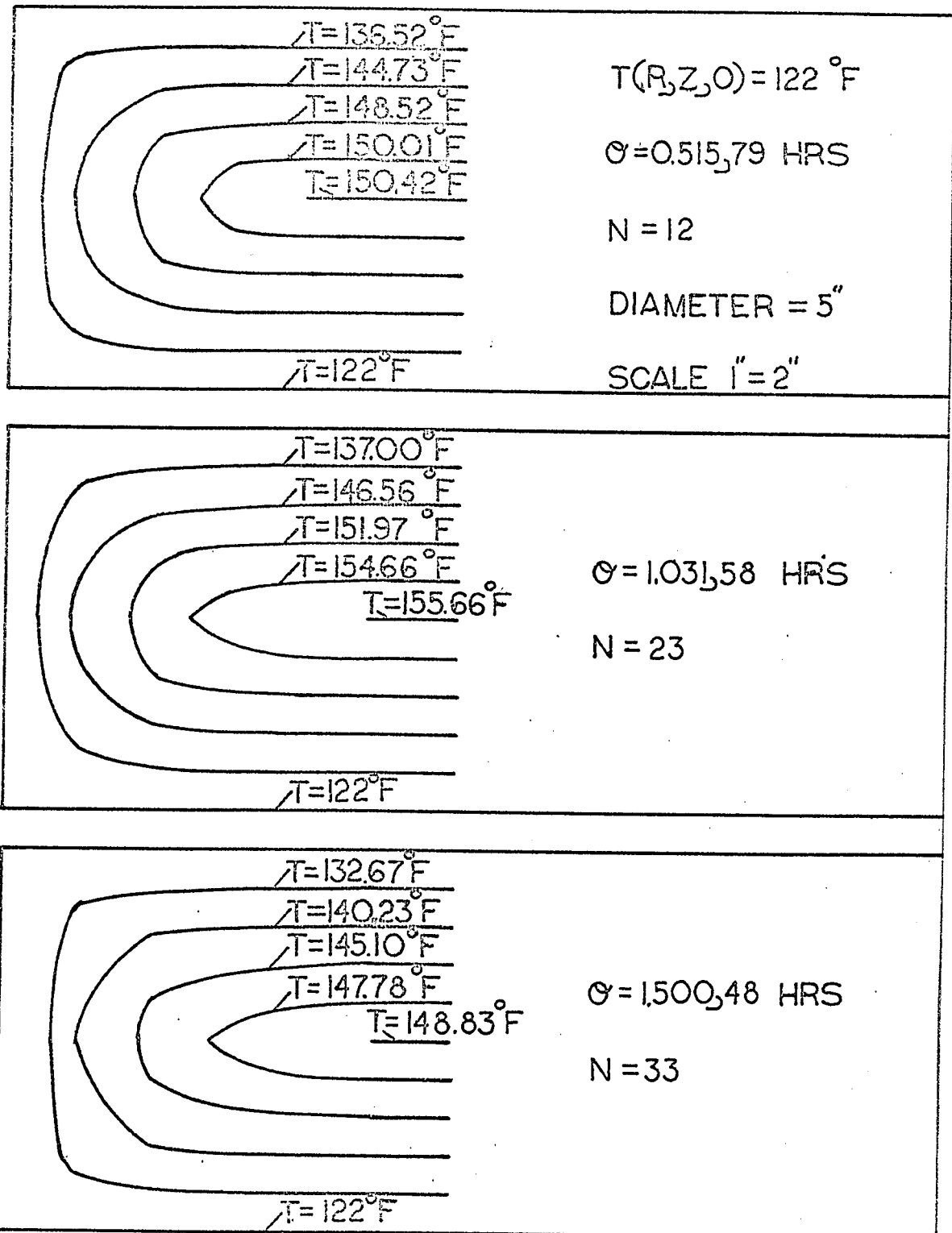


Figure 73 Isotherm Diagrams for the 5" diameter Solid Cylinder

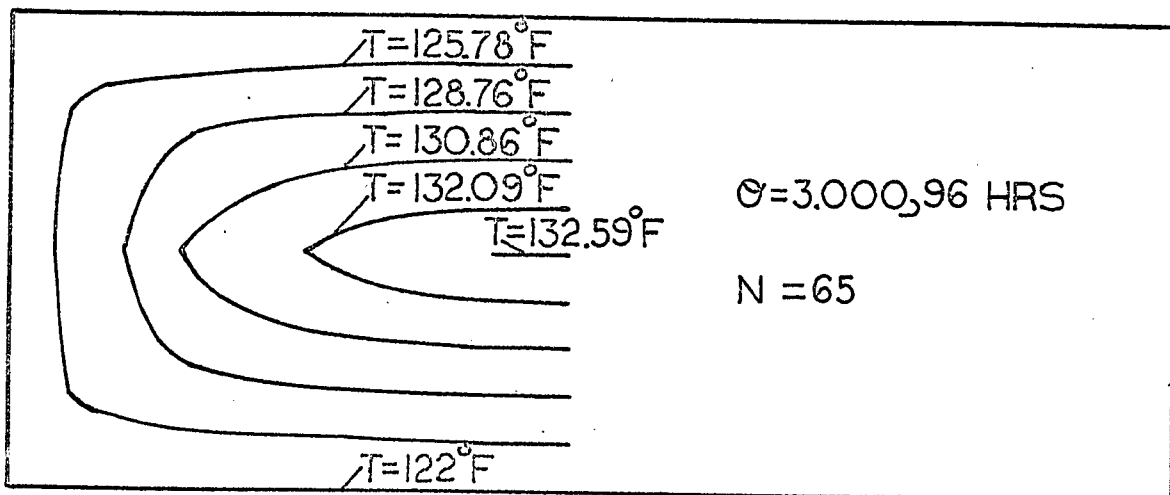
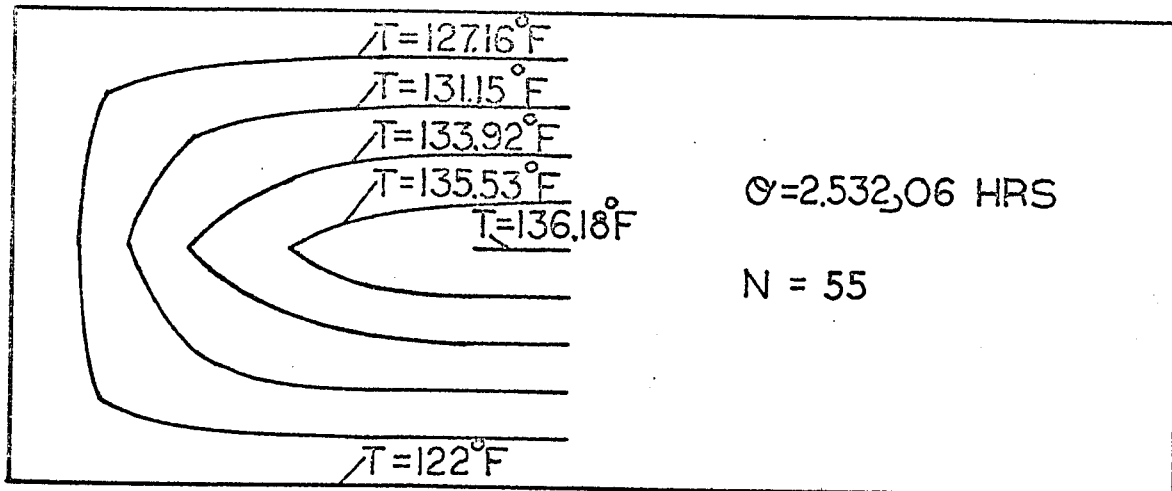
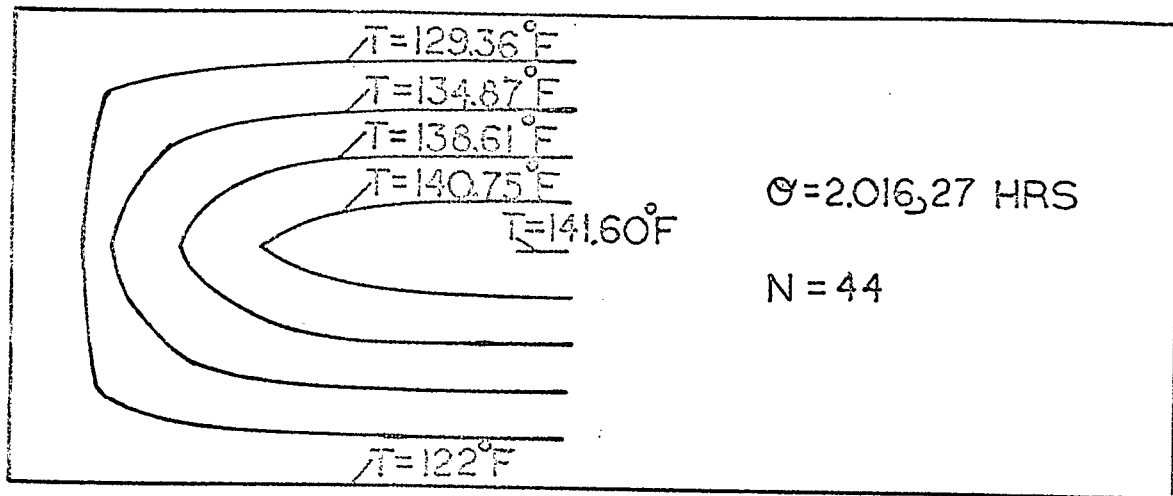


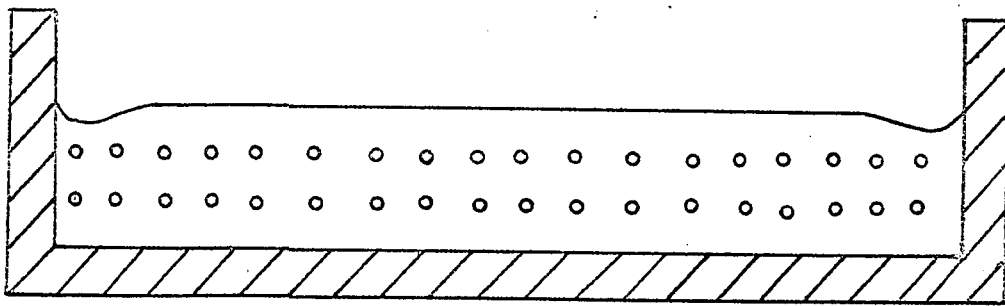
Figure 74 End Effect Diagrams for the 5" diameter Solid Cylinder

bit longer in the larger grain. In both cases a maximum temperature of 108°F is reached. If the initial boundary condition is 122°F , a symmetrical pattern appears in both grain sizes and reaches a maximum of about 158.6°F in the larger and 155.7°F for the smaller.

Hermance (61) stated that several quenched grains, burning at low and high chamber pressures, revealed an interesting general characteristic of the burning surface, as shown in Figure 75. The small dip - exaggerated in the sketch but uniform all around the grain - in the propellant surface was explained by the tendency of propellant to burn faster near a moulded surface. A "moulded surface" was that portion of a casting of solid propellant which was in contact with the surface of the casting mould. The reason for the small rise in the surface level, immediately adjacent to the inhibitor, might be explained by the complete removal of the mould release agent associated with the preparation of the cured grain for inhibiting. According to Hermance, the lack of oxidizer immediately next to the grain surface would cause a slowing of the burning rate at this surface.

But with all due respect to Hermance a glance at the diagrams of end effect immediately shows that the dip shown in Hermance's report is also exactly at the region where the early hot spots occur at the end of the grain. Therefore, it seems that these dips may be explained more satisfactorily by high temperatures during polymerization caused by heat sources made extremely active near the surface.

An end effect test on the thick walled hollow cylinder was not



QUENCHED GRAIN SURFACE

Figure 75 The Quenched Grain Surface

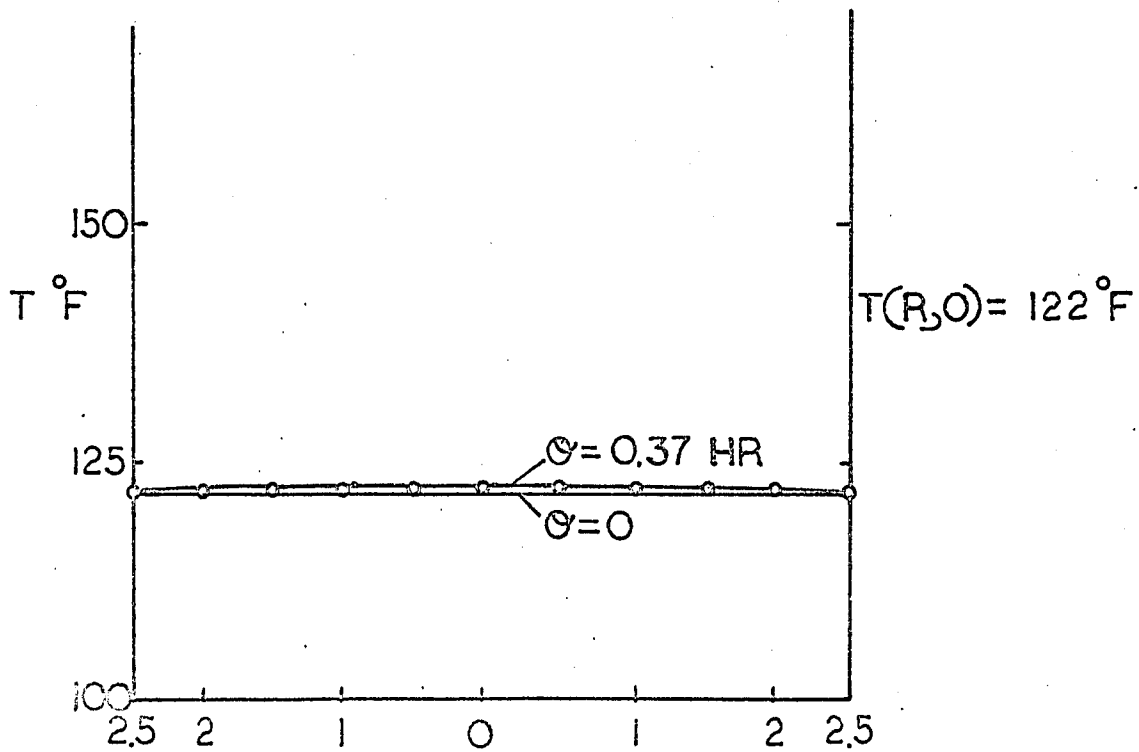
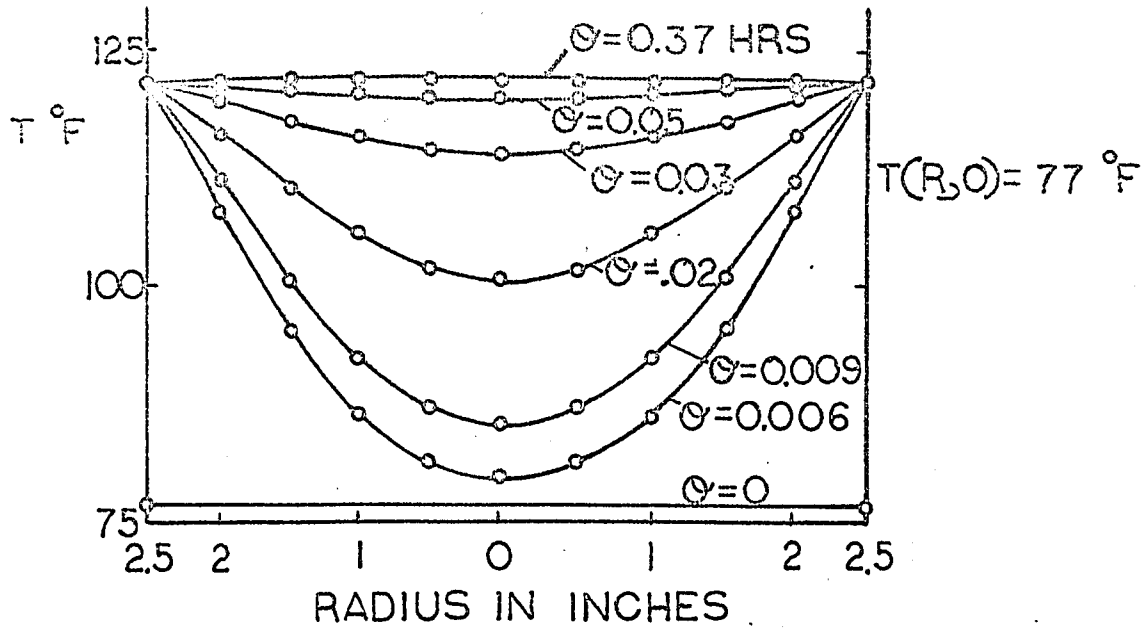
carried out but it is expected that a pattern similar to the solid cylinder with an annular ring of higher temperatures near the end, would emerge.

If an end effect test was done on a thin walled hollow cylinder, it is not believed that an unsymmetrical pattern would appear.

The end effect on the star shaped centre hollow cylinder would likely show a much more complicated picture. It is expected that a hot region near the tips of the star and another near the outer surface, would appear and come together and merge into a hot region a little farther in. Then a gradual conversion into the symmetrical shape would take place.

7. The Role of Aluminum Additives

Figures 76 and 77, the temperature gradients across a solid cylinder of ammonium perchlorate polyurethane propellant containing 20% aluminum indicates that the temperature reaches a peak just the same as it does in other cases but does it nine or ten times faster (9.333 times to be exact). The peak is not very pronounced. For average ΔH it reaches 122.03134°F and 122.03134°F for 77°F and 122°F initial conditions, respectively, as compared with 153°F and 160°F for the solid containing no aluminum and with a thermal diffusivity of 0.008,104 ft²/hr. When the top value of ΔH is used the peaks are at 122.361,74°F and 122.361,74°F for the 77°F and 122°F initial conditions as compared with 126°F and 147°F for the solid containing no aluminum. In all cases after the peak



$K = 0.476 \text{ FT}^2/\text{HR}$
 $\alpha AV = 0.000,001,172,596$
 +VE SLOPE

Figure 76 Temperature Gradients for the Solid Cylinder with 20% Aluminum

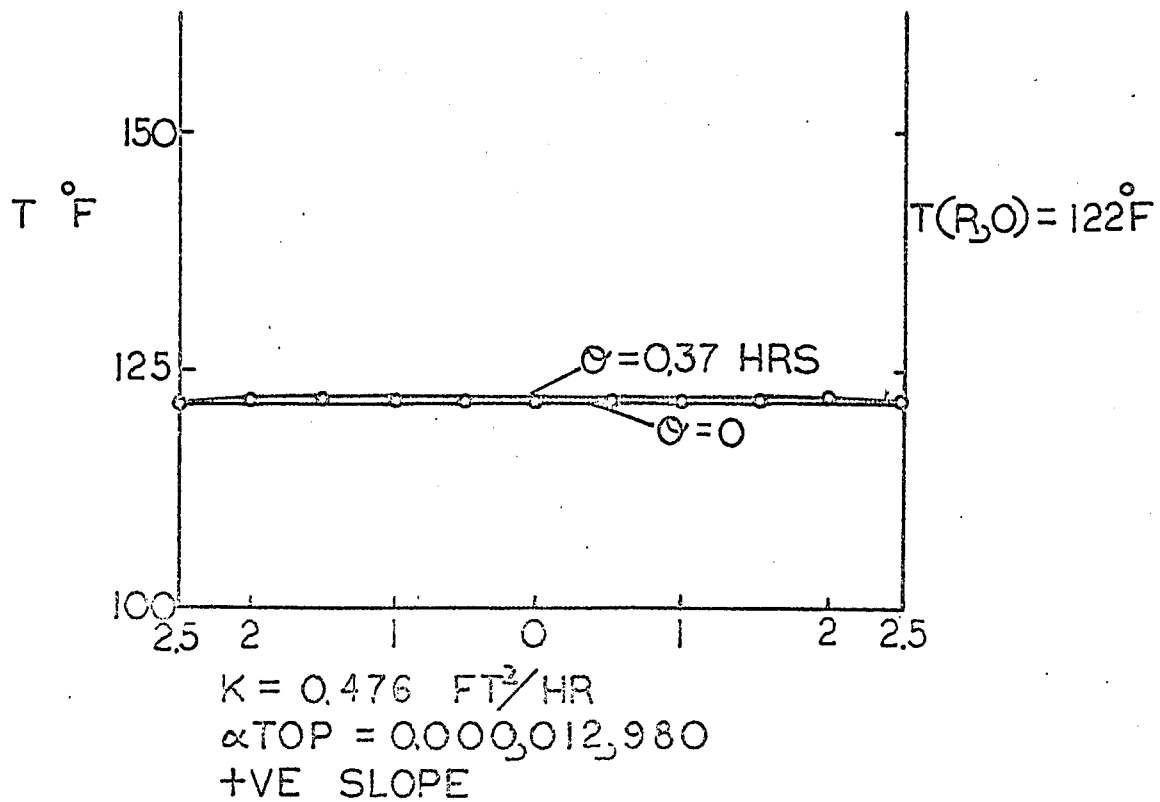
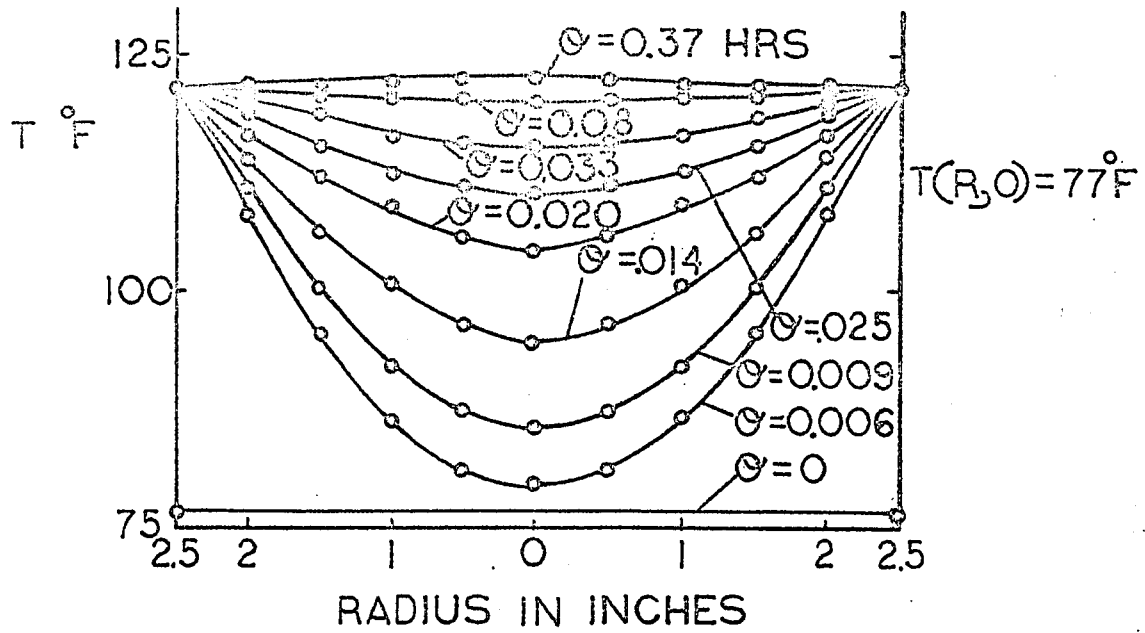


Figure 77 Temperature Gradients for the Solid Cylinder with 20% Aluminum

has been reached the temperature slowly drops back to 122°F as the heat sources die out. Therefore the burning characteristics, although altered are not as severely affected as the case where aluminum is absent. In effect one could almost say that in the aluminum case the designer has come close to achieving a steady temperature across the grain, provided one forgets about the initial period. The reason for this surprising change in the phenomenon is simply due to changes in the heat flow characteristics of the propellant and to the fact that less polymer is present. Aluminum, as is well known, is an excellent conductor of heat. Its thermal conductivity is high and its thermal diffusivity is second only to copper among the common metals. Thus, its presence, in the order of 20%, can only mean a huge increase in the heat flow characteristics. Estimated values soon show this. In effect the propellant mixture is changed from an insulator to a conductor. Heat given off by the chemical reaction raises the temperature slightly and then readily flows out of the material. The result is that the propellant is not altered as much in burning rate although the effect is not removed. Thus the addition of 20% aluminum helps to dampen the effect, but does not eliminate it. The resultant combustion instability will still reappear if the working pressure in the rocket motor is raised high enough.

3. Formal Correlation of the Burning Rate and the Maximum Temperature

A formal calculation of the correlation coefficients for the

five inch diameter solid cylinder has been done by the Product-Moment and the Rank-Difference Methods. Correlation by the Product-Moment Method of the burning rate and the maximum polymerization temperature gives correlation coefficients of 0.925,2 and 0.910,56 for the 122 degree Fahrenheit boundary condition, average thermal diffusivity of 0.008,104 ft²/hr, and top and average alfa, respectively. An example of the method of calculation has been given in Table XXVIII. The regression lines for these cases are:

$$x' = 0.925,2 y' \dots\dots\dots(174)$$

$$\text{and } y' = 0.925,2 x' \dots\dots\dots(175)$$

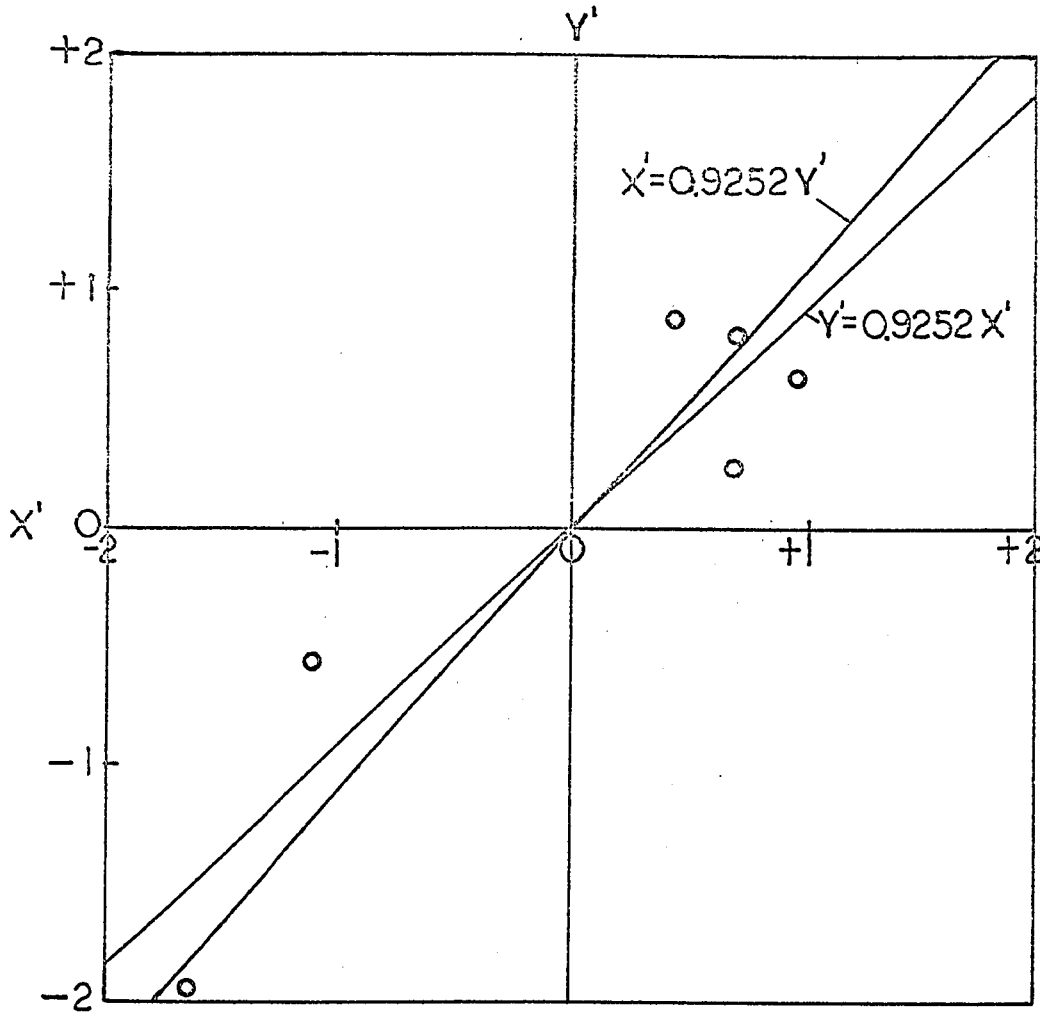
For $T(R,0) = 122^{\circ}\text{F}$, top alfa, positive slope and $K = 0.008,104 \text{ ft}^2/\text{hr}$

$$x' = 0.910,56 y' \dots\dots\dots(176)$$

$$\text{and } y' = 0.910,56 x' \dots\dots\dots(177)$$

For $T(R,0) = 122^{\circ}\text{F}$, average alfa, positive slope and $K = 0.008,104 \text{ ft}^2/\text{hr}$.

Two scatter diagrams, Figures 78 and 79, were drawn to display equations 174,175,176 and 177. In both figures the two lines are close together indicating that the degree of correlation is high. Correlation coefficients



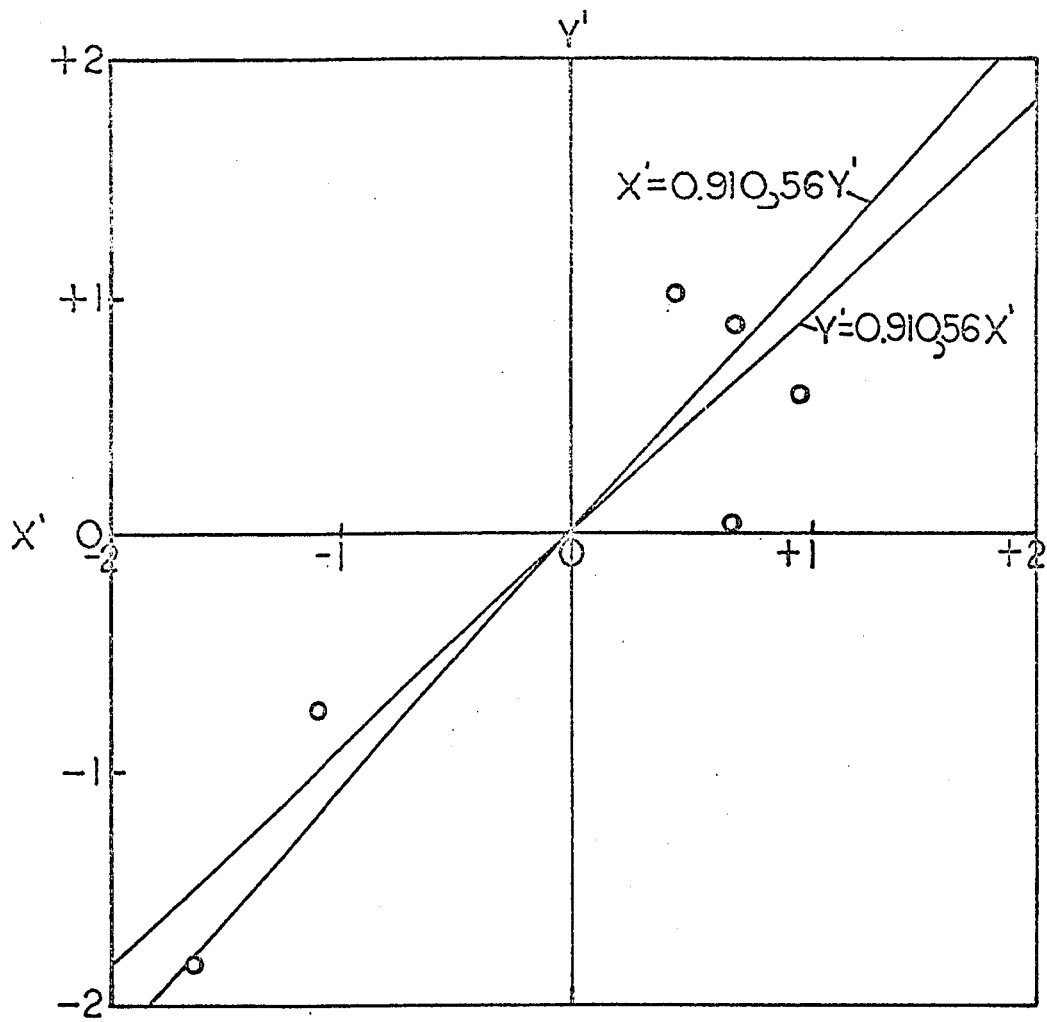
$$T(P_3, O) = 122^{\circ}\text{F}$$

+VE SLOPE

TOP ALFA

$$K = 0.008,104 \text{ FT}^2/\text{HR}$$

Figure 78 A Scatter Diagram to illustrate Correlation



$T(R_3O) = 122^{\circ} F$

+VE SLOPE

AV. ALFA

$K = 0.008,104 \text{ FT}^2/\text{HR}$

Figure 79 A Scatter Diagram to illustrate Correlation

have also been calculated for high and low initial conditions, top and average alphas and the full range of thermal diffusivities. They are tabulated in Table XXIX.

A computation of the correlation coefficient by the Rank-Difference Method for the case where $K = 0.008,104 \text{ ft}^2/\text{hr}$, top alpha, $T(R,0) = 122^\circ\text{F}$ and positive initial slope gives a value of 0.60 using the method given in Standard Mathematical Tables (107a) and a value of 0.88₃ using Spearman's method in Steel and Torrie (108c).

On the basis of these results, namely correlation coefficients of the order of 0.91 and only one chance in twenty that the value of "r" will fall outside the range 0.40 to 0.99, it is fair to say that a definite relationship exists between burning rate and temperature during polymerization for polyurethane ammonium perchlorate propellant. This relationship can only be described as strong.

9. Possible Corrective Measures

The question now arises as to how the effect of high temperature during polymerization could be reduced or eliminated. One method would certainly be to make the rocket grain in sections, each small enough to make the heat flow path as short as possible, then put them together in a composite whole. Another method might be to change the surface temperature to a lower value after the reaction has started to aid the flow of heat to the outside. For it is well known that the flow of heat

depends not only on the thermal conductivity but also on the driving force, or in other words the temperature gradient. Also the polymer might be altered to get a smaller heat of reaction in the initial period. Saunders and Frisch (104a) have stated that polyurethane propellants should not be cured above 60°C (140°F), a temperature which has been considerably exceeded in CARDE's propellant.

10. Implication of the high Correlation Coefficients

Combustion instability is a phenomenon which appears in both liquid and solid fuel rockets. In liquid fuel rockets it takes only a tiny push to start the whole thing oscillating, a push which could be initiated by a slight rise in pressure due to instantaneous better mixing, the resultant effect on the servo mechanisms controlling feed, a drop in feed rate and a resulting drop in pressure. Once the whole thing has started to oscillate it is not so easy to stop it. In solid fuel rockets a slight increase in pressure can also start the whole thing oscillating. The question is "What gives it this push?" An extensive literature exists on the subject of combustion instability. Many workers have explained it on the basis of high frequency waves, vortices and the like but all these explanations are fundamentally the result of focusing attention on what happens in the rocket after ignition. None, seem to have realized, that another factor could have had a great deal to do with the phenomenon, a factor having to do with a flaw in the preparation

of the propellant which would slip by unnoticed in all these experiments. It is believed that such a factor exists. It is the temperature of the material during polymerization. Workers have known for some time that the polymerization temperature must not become so high that decomposition would take place as this would be indicated by a burned area in the centre of the grain which would be plainly noticed provided the mixture did not blow up. But they did not realize that a polymerization temperature that did not reach these limits and gave no visible sign of its presence could easily affect the burning characteristics. Another reason that this factor was overlooked is the fact that experimental work always involves small quantities of material. No propellant manufacturer likes to have large and expensive pieces of propellant cut up for experimental tests, yet this is sometimes necessary if errors are not to slip through. The result is that a situation exists where, in spite of much good work, a phenomenon has been explained on the basis of high frequency pressure waves and vortices, while another explanation, possibly much closer to the truth than the others lay hidden out of sight. It is evident that all these other effects are present, but they are not the key to the phenomenon. The real cause of combustion instability in solid propellant rocket motors is high temperature during polymerization.

The question now arises as to the case of propellant grains that are formed by extrusion from a powder mixture. They also can show combustion instability. Here the argument still holds for it is well known that whenever a material is pressed through a die considerable heat is generated. Thus the propellant is heated during formation and

since materials like double-base powders are excellent heat insulators, with a thermal diffusivity of $0.004 \text{ ft}^2/\text{hr}$, the centre region will reach high temperatures because the heat can not escape quickly. When one considers large grains of propellant formed from small grains plus a solvent such as double-base propellant with acetone, the argument holds again for considerable heat is given off in this reaction, setting the stage for high temperatures in the centre region of the grain. It will now be evident that this factor of high temperature during the formation of solid propellants, is much more general than was first supposed. Thus the high correlation coefficient between burning rate and temperature has uncovered one of the real causes of combustion instability.

CONCLUSIONS

- 1) The burning rate across a grain of polyurethane ammonium perchlorate propellant in a radial direction is not constant as has previously been thought. A statistical analysis of the results shows that a significant difference exists at various radii, a difference which can not be explained on the basis of scatter. Therefore, it must be concluded that burning rate varies with the radius.
- 2) The link between the burning rate in a radial direction across a grain of propellant and the maximum temperature during polymerization has been established. The correlation coefficient computed by the Product-Moment Method comes to 0.92. A figure of this magnitude means that the probability of a relationship between the variables is high. On this basis it is safe to say that the real cause of uneven burning in solid propellant rocket motors is high temperature during the formation of the solid.
- 3) Aluminum affects the burning rate through the alteration of the heat transfer properties. A glance at the estimated values for propellant containing 20% aluminum soon shows the huge change in values compared to those for propellant without aluminum. In effect the material has become a heat conductor instead of a heat insulator. Even though heat sources are present the temperature gradients will be different and therefore the burning rate will differ also. It will be noted that

this effect is in addition to the other effects of aluminum reported in the literature.

- 4) It has been reported in the literature that polyurethane propellants should not be cured above 60°C (140°F). In many cases considered in this work the maximum temperature was well above 140°F , often reaching 158°F to 165°F . Thus it must be concluded that CARDE's propellant is being injured by excessive temperatures during formation.
- 5) CARDE appears to be using an excessive curing time of 50 hours at 50°C . At 50°C a 15 hour cure should be adequate whereas 50 hours would only be suitable if the reaction were carried out at 25°C .
- 6) High temperature during polymerization might be eliminated by a)
Making the rocket grain in sections, each small enough to make the heat flow path as short as possible, then putting them together in a composite whole. b) The use of different surface temperatures, e.g., high to start the reaction off, a quick drop while the reaction is going over the hump, and finally when the hump is safely past, high again to reduce the curing time. c) A higher initial propellant temperature to start the reaction off, and with a lower surface temperature to insure quick removal of heat. d) The alteration of the polymer to get a smaller heat of reaction in the initial period.

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APPENDIX - 1

STATISTICAL ANALYSIS OF THE RESULTS

NOMENCLATURE FOR STATISTICAL ANALYSIS

n	number
x	a measured quantity
$\bar{x}$	sample mean
s	sample standard deviation
s^2	sample variance
$\bar{x}$	population mean
σ^2	population variance
s^2	sample estimate of the population variance
s_m^2	estimate of the sample variance of the mean from a single set
s_m	estimate of the sample standard deviation of the mean from a single set
t	Student's "t"
P	probability
L	Neyman and Pearson's test to see if the populations represented by the samples have the same variance
s_1^2	estimated sample variance of a set
n_i	number of sets
s_e^2	estimate of within sample error variance
$\bar{x}_p$	population mean based on the sets
$s_{\bar{x},p}^2$	variance of the population means
s_p^2	second estimate of the population variance
F	ratio of s_p^2/s_e^2

TABLE XXX

The Results of the Statistical Analysis

Burning Rate of the 5" diameter Solid Cylinder

radius	No	Sample	Sample	Sample	95% confidence	"L" Test	"F" Test
"r"	n	Average	Variance	Standard	limits on $\bar{x}$		
		$\bar{x}$	σ^2	Deviation			
0.0	4	0.469,5	0.045,50	0.213,3	0.469,5 $\pm$ 0.391,9		
0.5	8	0.506,3	0.021,06	0.145,1	0.506,3 $\pm$ 0.129,7		
1.0	15	0.537,7	0.065,51	0.255,9	0.537,7 $\pm$ 0.146,7		
1.5	5	0.503,4	0.017,51	0.131,6	0.503,4 $\pm$ 0.132,6	+ ve	The Means are Different
2.0	11	0.269,3	0.003,437	0.058,63	0.269,3 $\pm$ 0.041,3		
2.5	2	0.199,5	0.000,056	0.007,483	0.199,5 $\pm$ 0.095,1		

Burning Rate of the 5.25" O.D., 3" I.D. Hollow Cylinder

1.5	5	0.179,8	0.000,034	0.005,848	0.179,8 $\pm$ 0.008,1		
2.063	5	0.196,2	0.000,244	0.015,63	0.196,2 $\pm$ 0.021,7	+ ve	The Means Differ
2.625	5	0.216,4	0.000,617	0.024,84	0.216,4 $\pm$ 0.034,5		

ΔH Results

Temp.							
25°C	10	4.243	7.515	2.741	4.243 $\pm$ 2.066		
48°C	8	6.845	8.007	2.830	6.845 $\pm$ 2.529	+ ve	The Means are the Same
62°C	21	5.358	4.174	2.043	5.358 $\pm$ 0.953		

Statistical Analysis of the Solid Cylinder Results: (Burning Rate)

$$r = 0.0 \text{ inches}$$

n	x	x ²
1	0.376	0.141,376
2	0.370	0.136,900
3	0.297	0.088,209
4	<u>0.835</u>	<u>0.697,225</u>
	1.878	1.063,710

$$\bar{x} = \frac{\sum x}{n} = \frac{1.878}{4} = 0.469,5$$

$$\bar{\sigma}^2 = \frac{\sum x^2 - (\sum x)^2/n}{n} = \frac{1.063,710 - (1.878)^2/4}{4} = 0.045,497,5$$

$$\bar{\sigma} = \sqrt{0.045,497,5} = 0.213,30$$

$$s^2 = \frac{n \bar{\sigma}^2}{n - 1} = \frac{4(0.045,497,5)}{(4 - 1)} = 0.060,663$$

$$s_m^2 = \frac{s^2}{n} = \frac{0.060,663}{4} = 0.015,165$$

$$s_m = \sqrt{0.015,165} = 0.123,15$$

For 95% confidence limits, $f = 4 - 1 = 3$

From Mickley (87h) at $f = 3$ and 0.95, $P = 3.182$

∴ 95% of the time t lies between -3.182 and +3.182

Since $t = \frac{\bar{x} - \bar{\bar{x}}}{s_m}$

$$\bar{x} - \bar{\bar{x}} = t \cdot s_m = 5.152 (0.123,15) = 0.391,86$$

therefore 95% of the time $\bar{x} - \bar{\bar{x}}$ lies between -0.391,86 and +0.391,86.

With $\bar{x} = 0.469,5$, 95% of the time $\bar{\bar{x}}$ lies between 0.077,6 and 0.861,4 inches per second at 400 lbs/in², or in only five times in 100 will the investigator be in error if he assigns $0.469,5 \pm 0.391,9$ to the result.

For $r = 0.5$ inches

n	x	x ²
1	0.484	0.234,256
2	0.273	0.074,529
3	0.657	0.431,649
4	0.786	0.617,796
5	0.442	0.195,364
6	0.448	0.200,704
7	0.523	0.273,529
8	<u>0.437</u>	<u>0.190,969</u>
	4.050	2.218,796

$$\bar{x} = \frac{\sum x}{n} = \frac{4.050}{8} = 0.506,25$$

$$s^2 = \frac{\sum x^2 - (\sum x)^2/n}{n} = \frac{2.218,796 - (4.050)^2/8}{8} = 0.021,062$$

$$q = \sqrt{0.021,062} = 0.145,15$$

$$s_b^2 = \frac{n s^2}{n - 1} = \frac{8(0.021,062)}{8 - 1} = 0.024,070$$

$$s_m^2 = \frac{s_b^2}{n} = \frac{0.024,070}{8} = 0.003,008,75$$

$$s_m = \sqrt{0.003,008,75} = 0.054,852$$

For 95% confidence limits and $f = 8 - 1 = 7$

From Mickley (37h) at $f = 7$ and 0.95, $P = 2.365$

∴ 95% of the time t lies between -2.365 and $+2.365$

$$\text{Since } t = \frac{\bar{x} - \bar{\bar{x}}}{s_m}$$

$$\bar{x} - \bar{\bar{x}} = t \cdot s_m = 2.365(0.054,852) = 0.129,72$$

Therefore 95% of the time $\bar{x} - \bar{\bar{x}}$ lies between $-0.129,72$ and $+0.129,72$.

With $\bar{x} = 0.506,25$; 95% of the time $\bar{\bar{x}}$ lies between $0.376,53$ and $0.635,97$ inches per second at 400 lbs/in^2 , or in only five times in a 100 will the investigator be in error if he assigns $0.506,25 \pm 0.129,72$ to the result.

For $r = 1.0$ inches

n	x	x^2
1	0.388	0.150,544
2	0.461	0.212,521

For r = 1.0 inches (Cont.'d.)

n	x	x ²
3	0.403	0.162,409
4	0.484	0.188,356
5	0.276	0.076,176
6	0.509	0.095,481
7	0.245	0.060,025
8	0.276	0.076,176
9	0.497	0.247,009
10	0.533	0.284,089
11	0.822	0.675,684
12	1.020	1.040,400
13	0.509	0.259,081
14	0.960	0.921,600
15	<u>0.933</u>	<u>0.870,489</u>
	8.066	5.320,040

$$\bar{x} = \frac{\sum x}{n} = \frac{8.066}{15} = \underline{0.537,7}$$

$$s_1^2 = \frac{\sum x^2 - (\sum x)^2/n}{n} = \frac{5.320,040 - (8.066)^2/15}{15} = 0.065,512,2$$

$$s_1 = \sqrt{0.065,512,2} = 0.255,95$$

$$s^2 = \frac{n s_1^2}{n - 1} = \frac{15(0.065,512)}{15 - 1} = 0.070,191,6$$

$$s = \frac{s^2}{n} = \frac{0.070,191,6}{15} = 0.004,679,4$$

$$s_m = \sqrt{0.004,679,4} = 0.068,406$$

For 95% confidence limits and $f = 15 - 1 = 14$

From Mickley (87h) at $f = 14$ and 0.95, $P = 2.145$

∴ 95% of the time t lies between -2.145 and +2.145

Since
$$t = \frac{\bar{x} - \bar{\bar{x}}}{s_m}$$

$$\bar{x} - \bar{\bar{x}} = t \cdot s_m = 2.145(0.068,406) = 0.146,73$$

Therefore 95% of the time t lies between -0.146,73 and +0.146,73. With $\bar{x} = 0.537,7$; 95% of the time $\bar{\bar{x}}$ lies between 0.391,0 and 0.684,4 inches per second at 400 lbs/in², or in only five times in 100 will the investigator be in error if he assigns $0.537,7 \pm 0.146,7$ to the result.

For $r = 1.5$ inches

n	x	x^2
1	0.339	0.114,921
2	0.554	0.306,916
3	0.494	0.244,036
4	0.408	0.166,464
5	<u>0.722</u>	<u>0.521,284</u>
	2.517	1.353,621

$$\bar{\bar{x}} = \frac{\sum x}{n} = \frac{2.517}{5} = 0.503,4$$

$$\overline{\sigma}^2 = \frac{\sum x^2 - (\sum x)^2/n}{n} = \frac{1.353,621 - (2.517)^2/5}{5} = 0.017,312$$

$$\overline{\sigma} = \sqrt{0.017,312} = 0.131,57$$

$$s^2 = \frac{n \overline{\sigma}^2}{n-1} = \frac{5(0.017,312)}{5-1} = 0.021,64$$

$$s_m^2 = \frac{s^2}{n} = \frac{0.021,64}{5} = 0.004,328$$

$$s_m = \sqrt{0.004,328} = 0.065,787$$

For 95% confidence limits and $f = 5 - 1 = 4$

From Mickley (87h) at $f = 4$ and 0.95 , $P = 2.776$

∴ 95% of the time t lies between -2.776 and $+2.776$

Since
$$t = \frac{\overline{x} - \overline{\overline{x}}}{s_m}$$

$$\overline{x} - \overline{\overline{x}} = t \cdot s_m = 2.776(0.065,787) = 0.182,62$$

Therefore 95% of the time t lies between $-0.182,6$ and $+0.182,6$. With $\overline{x} = 0.503,4$; 95% of the time $\overline{\overline{x}}$ lies between $0.320,8$ and $0.686,0$ inches per second at 400 lbs/in^2 , or in only five times in a 100 will the investigator be in error if he assigns $0.503,4 \pm 0.182,6$ to the result.

For r = 2.0 inches

n	x	x ²
1	0.189	0.035,721
2	0.183	0.033,489
3	0.200	0.040,000
4	0.310	0.096,100
5	0.303	0.091,809
6	0.272	0.073,984
7	0.594	0.352,836
8	0.237	0.056,169
9	0.288	0.082,944
10	0.261	0.068,121
11	<u>0.275</u>	<u>0.075,625</u>
	2.962	0.835,398

$$\bar{x} = \frac{\sum x}{n} = \frac{2.962}{11} = 0.269,3$$

$$s^2 = \frac{\sum x^2 - (\sum x)^2/n}{n} = \frac{0.835,398 - (2.962)^2/11}{11} = 0.003,437,4$$

$$s = \sqrt{0.003,437,4} = 0.058,629$$

$$s^2 = \frac{n s^2}{n - 1} = \frac{11(0.003,437,4)}{11 - 1} = 0.003,781,2$$

$$s_m^2 = \frac{s^2}{n} = \frac{0.003,781,2}{11} = 0.000,343,74$$

$$s_m = \sqrt{0.000,343,74} = 0.018,540$$

For 95% confidence limits and $f = 11 - 1 = 10$

from Mickley (87h) at $f = 10$ and 0.95 , $P = 2.228$

∴ 95% of the time t lies between -2.228 and $+2.228$

Since
$$t = \frac{\bar{x} - \bar{\bar{x}}}{s_m}$$

$$\bar{x} - \bar{\bar{x}} = t \cdot s_m = 2.228(0.018,540) = 0.041,307,1$$

Therefore 95% of the time $\bar{x} - \bar{\bar{x}}$ lies between $-0.041,3$ and $+0.041,3$. With $\bar{x} = 0.269,3$; 95% of the time $\bar{\bar{x}}$ lies between $0.228,0$ and $0.310,6$ inches per second at 400 lbs/in^2 , or in only five times in a 100 will the investigator be in error if he assigns $0.269,3 \pm 0.041,3$ to the result.

For $r = 2.5$ inches

n	x	x^2
1	0.207	0.042,849
2	<u>0.192</u>	<u>0.036,864</u>
	0.399	0.079,713

$$\bar{x} = \frac{\sum x}{n} = \frac{0.399}{2} = 0.199,5$$

$$\sigma^2 = \frac{\sum x^2 - (\sum x)^2/n}{n} = \frac{0.079,713 - (0.399)^2/2}{2} = 0.000,056$$

$$\sigma = \sqrt{0.000,056} = 0.007,483,3$$

$$s^2 = \frac{n \sigma^2}{n - 1} = \frac{2(0.000,056)}{2 - 1} = 0.000,112$$

$$s_m^2 = \frac{s^2}{n} = \frac{0.000,112}{2} = 0.000,056$$

$$s_m = \sqrt{0.000,056} = 0.007,483,3$$

For 95% confidence limits and $f = 2 - 1 = 1$

from Miekley (87h) at $f = 1$ and 0.95, $P = 12.706$

∴ 95% of the time t lies between -12.706 and +12.706

$$\text{Since } t = \frac{\bar{x} - \bar{\bar{x}}}{s_m}$$

$$\bar{x} - \bar{\bar{x}} = t \cdot s_m = 12.706(0.007,483,3) = 0.095,08$$

Therefore 95% of the time $\bar{x} - \bar{\bar{x}}$ lies between -0.095,1 and +0.095,1. With $\bar{x} = 0.199,5$; 95% of the time $\bar{\bar{x}}$ lies between 0.104,4 and 0.294,6 inches per second at 400 lbs/in², or in only five times in a 100 will the investigator be in error if he assigns $0.199,5 \pm 0.095,1$ to the result.

THE L TEST

The L test is applied here with the assumption that the number of readings in each sample is the same.

$$L_1 = \frac{n_i(s_1^2 s_2^2 \dots s_i^2)^{1/n_i}}{\sum_i s_i^2}$$

$$= \frac{6(0.060,663 \cdot 0.024,07 \cdot 0.070,191 \cdot 0.021,64 \cdot 0.003,718,2 \cdot 0.000,112)^{1/6}}{0.000,663 + 0.024,07 + 0.070,191 + 0.021,64 + 0.003,718,2 + 0.000,112}$$

$$\therefore L_1 = 3.28$$

Referring to Mickley (87i), and taking $n_1 = 6$ and $(n_k)_1 = 7$, the table gives about 0.6 at 5% and about 0.5 at 1%. Thus the L test is positive and it is possible to proceed to the F test.

THE F TEST

$$s_o^2 = \frac{0.181,99}{4} + \frac{0.168,493}{+8} + \frac{0.982,683}{+15} + \frac{0.086,564}{+5} + \frac{0.037,812}{+11} + \frac{0.000,112}{+2} - 6$$

$$s_o^2 = \frac{1.457,654}{45 - 6} = \frac{1.457,654}{39} = 0.037,375$$

$$\bar{x}_p = \frac{4(0.469,5)}{4} + \frac{8(0.506,25)}{+8} + \frac{15(0.537,7)}{+15} + \frac{11(0.269,3)}{+11} + \frac{2(0.199,5)}{+2} + \frac{5(0.503,4)}{+5}$$

$$\bar{x}_p = \frac{1.878,0 + 4.050,0 + 8.065,5 + 2.962,3 + 0.399,0 + 2.517,0}{45} = 0.441,595$$

$$s_{m,p}^2 = \frac{(0.469,5 - 0.441,6)^2 + (0.506,25 - 0.441,59)^2 + (0.537,7 - 0.441,6)^2 + (0.269,3 - 0.441,6)^2 + (0.199,5 - 0.441,6)^2 + (0.503,4 - 0.441,6)^2}{6 - 1}$$

$$s_{m,p}^2 = \frac{0.106,313,46}{5} = 0.021,262,692$$

$$n_o = \frac{1}{6 - 1} \left[45 - \frac{(4^2 + 8^2 + 15^2 + 11^2 + 2^2 + 5^2)}{4 + 8 + 15 + 11 + 2 + 5} \right] = 6.977,78$$

$$s_p^2 = n_o \cdot s_{m,p}^2 = 6.977,78(0.021,262,692) = 0.148,36$$

$$F = \frac{s_o^2}{s_e^2} = \frac{0.148,36}{0.037,375} = 3.969$$

now s_e^2 is associated with $45 - 6 = 39$ degrees of freedom

and s_p^2 is associated with $6 - 1 = 5$ degrees of freedom

The table in Mickley (87j) gives

$F = 2.46$ at 5% and

$F = 5.54$ at 1%

Since the calculated value of F is greater than that corresponding to the 1% level, in less than 1% of the cases could the observed difference in sample means be explained on the basis of the scatter of the observed data. It is reasonable to conclude that the sample means are different.

Statistical Analysis of the Hollow Cylinder Burning Rate Results:

For $r_i = 1.5$ inches

n	x	x^2
1	0.186	0.034,596
2	0.187	0.034,969
3	0.173	0.029,929
4	0.179	0.032,041
5	<u>0.174</u>	<u>0.030,276</u>
	0.899	0.161,811

$$\bar{x} = \frac{\sum x}{n} = \frac{0.899}{5} = 0.179,8$$

$$s^2 = \frac{\sum x^2 - (\sum x)^2/n}{n} = \frac{0.161,811 - (0.899)^2/5}{5} = 0.000,034,2$$

$$q = \sqrt{0.000,034,2} = 0.005,848,1$$

$$s^2 = \frac{nq^2}{n-1} = \frac{5(0.000,034,2)}{5-1} = 0.000,042,75$$

$$s_m^2 = \frac{s^2}{n} = \frac{0.000,042,75}{5} = 0.000,008,55$$

$$s_m = \sqrt{0.000,008,55} = 0.002,924$$

For 95% confidence limits and $f = 5 - 1 = 4$

From Mickley (87h) and $f = 4$ and 0.95, $P = 2.776$

∴ 95% of the time t lies between -2.776 and +2.776

Since
$$t = \frac{\bar{x} - \bar{\bar{x}}}{s_m}$$

$$\bar{x} - \bar{\bar{x}} = t \cdot s_m = 2.776(0.002,924) = 0.008,117$$

Therefore 95% of the time $\bar{x} - \bar{\bar{x}}$ lies between -0.008,117 and +0.008,117.

With $\bar{x} = 0.179,8$; 95% of the time $\bar{\bar{x}}$ lies between 0.171,7 and 0.187,9 inches per second at 400 lbs/in², or in only five times in a 100 will the investigator be in error if he assigns $0.179,8 \pm 0.008,1$ to the result.

$$\text{For } \frac{r_o + r_i}{2} = \underline{2.062,5 \text{ inches}}$$

n

x

x²

1

0.224

0.050,176

n	x	x ²
2	0.186	0.034,596
3	0.184	0.033,856
4	0.184	0.033,856
5	<u>0.203</u>	<u>0.041,209</u>
	0.981	0.193,693

$$\bar{x} = \frac{\sum x}{n} = \frac{0.981}{5} = 0.196,2$$

$$\sigma^2 = \frac{\sum x^2 - (\sum x)^2/n}{n} = \frac{0.193,693 - (0.981)^2/5}{5} = 0.000,244,2$$

$$\sigma = \sqrt{0.000,244,2} = 0.015,627$$

$$s^2 = \frac{n\sigma^2}{n-1} = \frac{5(0.000,244,2)}{5-1} = 0.000,305,25$$

$$s_m^2 = \frac{s^2}{n} = \frac{0.000,305,25}{5} = 0.000,061,05$$

$$s_m = \sqrt{0.000,061,05} = 0.007,813,45$$

For 95% confidence limits and $f = 5 - 1 = 4$

From Mickley (87h) at $f = 4$ and 0.95; $P = 2.776$

∴ 95% of the time t lies between -2.776 and +2.776

$$\text{Since } t = \frac{\bar{x} - \bar{X}}{s_m}$$

$$\bar{x} - \bar{X} = t \cdot s_m = 2.776(0.007,813,45) = 0.021,690$$

then 95% of the time $\bar{x} - \bar{X}$ lies between -0.021,690 and +0.021,690. With $\bar{x} = 0.196,2$ then 95% of the time $\bar{x}$ lies between 0.174,5 and 0.217,9 inches per second at 400 lbs/in², or in only five times in a 100 will the investigator be in error if he assigns $0.196,2 \pm 0.021,7$ to the result.

for $r_0 = 2.625$ inches

n	x	x ²
1	0.197	0.038,809
2	0.226	0.051,076
3	0.260	0.067,600
4	0.208	0.043,264
5	<u>0.191</u>	<u>0.036,481</u>
	1.082	0.237,230

$$\bar{x} = \frac{\sum x}{n} = \frac{1.082}{5} = 0.216,4$$

$$\sigma^2 = \frac{\sum x^2 - (\sum x)^2/n}{n} = \frac{0.237,230 - (1.082)^2/5}{5} = 0.000,617,2$$

$$\sigma = \sqrt{0.000,617,2} = 0.024,843$$

$$s^2 = \frac{n\sigma^2}{n-1} = \frac{5(0.000,617,2)}{5-1} = 0.000,771,5$$

$$s_m^2 = \frac{s^2}{n} = \frac{0.000,771,5}{5} = 0.000,154,3$$

$$s_m = \sqrt{0.000,154,3} = 0.012,421$$

For 95% confidence limits and $f = 5 - 1 = 4$

From Mickley (87h) at $f = 4$ and 0.95, $P = 2.776$

∴ 95% of the time t lies between -2.776 and $+2.776$

Since
$$t = \frac{\bar{x} - \bar{\bar{x}}}{s_m}$$

$$\bar{x} - \bar{\bar{x}} = t \cdot s_m = 2.776(0.012,421) = 0.034,480$$

Therefore 95% of the time $\bar{x} - \bar{\bar{x}}$ lies between $-0.034,48$ and $+0.034,48$.

With $\bar{x} = 0.216,4$ then 95% of the time $\bar{x}$ lies between $0.181,9$ and $0.250,9$ inches per second at 400 lbs/in^2 , or in only five times in a 100 will the investigator be in error if he assigns $0.216,4 \pm 0.034,5$ to the result.

The L test

$$L_1 = \frac{n_1(s_1^2 s_2^2 \dots s_i^2)^{1/n_i}}{\sum s_i^2}$$

$$L_1 = \frac{3(0.000,042,75 \cdot 0.000,305,25 \cdot 0.000,771,5)^{1/3}}{0.000,042,75 + 0.000,305,25 + 0.000,771,5}$$

$$L_1 = 0.578,61$$

Referring to Mickley (87i) with the number of sets equal to 3 and the number of measurements in one set equal to 5, the table gives

$L_1 = 0.575,6$ for 5% values and $L_1 = 0.429,1$ for 1% values. The calculated

value of L_1 , 0.578,61, shows that the probability of the population variances being the same is greater than 5%. It is reasonable to conclude that the population represented by the samples have the same variance.

The F test

$$s_e^2 = \frac{0.000,171 + 0.001,221 + 0.003,086}{5 + 5 + 5 - 3} = \frac{0.004,478}{12} = 0.000,373,16$$

$$\bar{x}_p = \frac{5(0.179,8) + 5(0.196,2) + 5(0.216,4)}{5 + 5 + 5} = \frac{2.962,0}{15} = 0.197,46$$

$$s_{m,p}^2 = \frac{(0.179,8 - 0.197,5)^2 + (0.196,2 - 0.197,5)^2 + (0.216,4 - 0.197,5)^2}{3 - 1}$$

$$s_{m,p}^2 = \frac{0.000,313,29 + 0.000,001,69 + 0.000,357,21}{2} = 0.000,336,095$$

$$s_p^2 = n_o s_{m,p}^2 = 5(0.000,336,095) = 0.001,680,475$$

$$F = \frac{s_p^2}{s_e^2} = \frac{0.001,680,475}{0.000,373,16} = 4.503$$

the table in Mickley (87j) gives $F = 3.88$ at the 5% level and $F = 6.93$ at the 1% level; where s_e^2 is associated with $15 - 3 = 12$ degrees of freedom and s_p^2 is associated with $3 - 1 = 2$ degrees of freedom. Since the calculated value of $F = 4.503$, falls between the 1% and the 5% level (the actual value is 4.137%) in less than 4% of the cases could the observed difference in sample means be explained on the basis of scatter in the observed data. It is reasonable to conclude that the sample

means are actually different.

Statistical Analysis of the Microcalorimeter ΔH Results:

For 25°C

n	x	x^2
1.	4.830	23.328,9
2.	1.712	2.930,944
3.	11.69	136.656,1
4.	5.005	25.050,0
5.	3.842	14.760,9
6.	1.567	2.455,4
7.	3.927	15.421,3
8.	4.356	18.974,7
9.	2.271	5.157,44
10.	<u>3.226</u>	<u>10.407,0</u>
	42.426	255.142,6

$$\bar{x} = \frac{\sum x}{n} = \frac{42.426}{10} = 4.242,6 \text{ cal/gm}$$

$$\sigma^2 = \frac{\sum x^2 - (\sum x)^2/n}{n} = \frac{255.142,6 - (42.426)^2/10}{10} = 7.514,61$$

$$\sigma = \sqrt{7.514,61} = 2.741,3$$

$$s^2 = \frac{n\sigma^2}{n-1} = \frac{10(7.514,61)}{10-1} = 8.349,56$$

$$s_m^2 = \frac{s^2}{n} = \frac{8.349,56}{10} = 0.834,956$$

$$s_m = \sqrt{0.834,956} = 0.913,76$$

For 95% confidence limits and $f = 10 - 1 = 9$

From Mickley (87h) at $f = 9$ and 0.95, $P = 2.262$

∴ 95% of the time t lies between -2.262 and +2.262

Since
$$t = \frac{\bar{x} - \bar{\bar{x}}}{s_m}$$

$$\bar{x} - \bar{\bar{x}} = t \cdot s_m = 2.262(0.913,76) = 2.066$$

Therefore 95% of the time $\bar{x} - \bar{\bar{x}}$ lies between -2.066 and +2.066. With $\bar{x} = 4.243$ then 95% of the time $\bar{\bar{x}}$ lies between 2.177 and 6.309 calories per gram, or in only five times in 100 will the investigator be in error if he assigns 4.243 ± 2.066 to the result.

For 48°C

n	x	x ²
1	7.473	55.845,729
2	3.798	14.424,804
3	7.076	50.069,776
4	5.375	28.890,625
5	8.121	65.950,641
6	3.002	9.012,004

n	x	x ²
7	12.82	164.552,400
8	<u>7.098</u>	<u>50.381,604</u>
	54.763	458.927,583

$$\bar{x} = \frac{\sum x}{n} = \frac{54.763}{8} = 6.845$$

$$\sigma^2 = \frac{\sum x^2 - (\sum x)^2/n}{n} = \frac{458.927,583 - (54.763)^2/8}{8} = 8.006,789$$

$$\sigma = \sqrt{8.006,789} = 2.829,6$$

$$s^2 = \frac{n\sigma^2}{n-1} = \frac{8(8.006,789)}{8-1} = 9.150,616$$

$$s_m^2 = \frac{s^2}{n} = \frac{9.150,616}{8} = 1.143,827$$

$$s_m = \sqrt{1.143,827} = 1.069,5$$

For 95% confidence limits $f = 8 - 1 = 7$

From Mickley (87h) at $f = 7$ and 0.95 , $P = 2.365$

∴ 95% of the time t lies between -2.365 and $+2.365$

Since
$$t = \frac{\bar{x} - \bar{\bar{x}}}{s_m}$$

$$\bar{x} - \bar{\bar{x}} = t \cdot s_m = 2.365(1.069,5) = 2.529$$

Therefore 95% of the time $\bar{x} - \bar{\bar{x}}$ lies between -2.529 and $+2.529$. With

$\bar{x} = 6.845$ then 95% of the time $\bar{x}$ lies between 4.316 and 9.374 calories per gram, or in only five times in a 100 will the investigator be in error if he assigns 6.845 ± 2.529 to the result.

<u>For 62°C</u>		
n	x	x ²
1	8.724	76.108,176
2	7.608	57.881,664
3	6.396	40.908,816
4	3.017	9.102,289
5	2.583	6.671,889
6	2.459	6.046,681
7	3.434	11.792,356
8	5.282	27.899,524
9	4.406	19.412,836
10	4.171	17.397,241
11	4.074	16.597,476
12	2.841	8.071,281
13	3.786	14.333,796
14	8.110	65.772,100
15	9.313	86.731,969
16	5.503	30.283,009
17	4.410	19.448,100
18	6.671	44.502,241
19	7.709	59.428,681

n	x	x ²
20	5.362	28.751,044
21	<u>6.567</u>	<u>43.125,489</u>
	112.526	690.610,058

$$\bar{x} = \frac{\sum x}{n} = \frac{112.526}{21} = 5.358$$

$$s^2 = \frac{\sum x^2 - (\sum x)^2 / n}{n} = \frac{690.610,058 - (112.526)^2 / 21}{21} = 4.173,946$$

$$s = \sqrt{4.173,946} = 2.043,0$$

$$s^2 = \frac{n s^2}{n - 1} = \frac{21(4.173,946)}{21 - 1} = 4.382,644$$

$$s_m^2 = \frac{s^2}{n} = \frac{4.382,644}{21} = 0.208,697$$

$$s_m = \sqrt{0.208,697} = 0.456,83$$

For 95% confidence limits and $f = 21 - 1 = 20$

From Mickley (87h) at $f = 20$ and 0.95, $P = 2.086$

∴ 95% of the time t lies between -2.086 and +2.086

$$\text{Since } t = \frac{\bar{x} - \bar{\bar{x}}}{s_m}$$

$$\bar{x} - \bar{\bar{x}} = t \cdot s_m = 2.086(0.456,83) = 0.952,9$$

Therefore 95% of the time $\bar{x} - \bar{\bar{x}}$ lies between -0.952,9 and +0.952,9.

With $\bar{x} = 5.358$ then 95% of the time $\bar{x}$ lies between 4.405 and 6.311 calories per gram, or in only five times in a 100 will the investigator be in error if he assigns 5.358 ± 0.953 to the result.

<u>Population Totals</u>			
Temperature	n	x	x ²
25°C	10	42.426	255.142,6
48°C	8	54.763	453.927,583
62°C	<u>21</u>	<u>112.526</u>	<u>690.610,058</u>
	39	209.715	1384.680,241

$$\bar{x} = \lim_{n \rightarrow \infty} \frac{\sum x}{n} = \frac{209.715}{39} = 5.377$$

$$\sigma^2 = \frac{\sum x^2 - (\sum x)^2/n}{n} = \frac{1,384.680,241 - (209.715)^2/39}{39} = 6.589,183$$

$$\sigma = \sqrt{6.589,183} = 2.566,9_4$$

$$s^2 = \frac{n \sigma^2}{n - 1} = \frac{39(6.589,183)}{39 - 1} = 6.762,583$$

$$s_m^2 = \frac{s^2}{n} = \frac{6.762,583}{39} = 0.173,399$$

$$s_m = \sqrt{0.173,399} = 0.416,412$$

For 95% confidence limits and $f = 39 - 1 = 38$

From Mickley (87h) at $f = 38$ and 0.95 , $P = 1.959$

∴ 95% of the time t lies between -1.959 and $+1.959$

Since
$$t = \frac{\bar{\bar{x}} - \bar{x}}{s_m}$$

$$\bar{\bar{x}} - \bar{x} = t \cdot s_m = 1.959(0.416,41) = 0.815,7$$

Therefore 95% of the time $\bar{\bar{x}} - \bar{x}$ lies between -0.815,7 and +0.815,7.
With $\bar{x} = 5.377$ then 95% of the time $\bar{\bar{x}}$ lies between 4.561 and 6.193
calories per gram, or in only five times in 100 will the investigator
be in error if he assigns 5.377 ± 0.816 to the result.

The L test

$$L_1 = \frac{n_1(s_1^2 s_2^2 \dots s_i^2)^{1/n_1}}{\sum s_i^2}$$

$$L_1 = \frac{3(8.349,56 \cdot 9.150 \cdot 4.382,644)^{1/3}}{8.349,56 + 9.150 + 4.382,644} = 0.952$$

Referring to Mickley (87i) and taking $n_1 = 3$ and $(n_k)_i = 15$ the table
gives $L = 0.863,2$ at the 5% level and $L = 0.797,6$ at the 1% level. Here
the "L test" is positive and hence it is possible to proceed to the
"F test".

The F test

$$s_c^2 = \frac{10(7.514,61) + 8(8.003,789) + 21(4.173,946)}{10 + 8 + 21 - 3} = 6.301$$

$$\bar{\bar{x}} = \frac{42.426 + 54.760 + 112.518}{39} = 5.377$$

$$n_o = \frac{1}{3-1} \left(10 - \frac{10^2 + 8^2 + 21^2}{10 + 8 + 21} + 8 + 21 \right) = 11.744$$

$$s_{m,p}^2 = \frac{(4.242,6 - 5.377)^2 + (6.845 - 5.377)^2 + (5.358 - 5.377)^2}{3-1} = 1.720$$

$$s_p^2 = n_o s_{m,p}^2 = 11.744(1.720) = 20.199$$

$$F = \frac{s_p^2}{s_e^2} = \frac{20.199}{6.301} = 3.205$$

Now s_e^2 is associated with $39 - 3 = 36$ degrees of freedom and s_p^2 is associated with $3 - 1 = 2$ degrees of freedom. The table in Mickley (87j) gives $F = 3.26$ at the 5% level and $F = 5.25$ at the 1% level. Since the value of F calculated is less than the 5% level, it is reasonable to conclude that the sample means are the same and that the difference is due to scatter in the results.

Now applying the F test to the most closely corresponding pair. $\bar{x}_{25} = 4.242,6$; $\bar{x}_{48} = 6.845$; $\bar{x}_{62} = 5.358$. Therefore the most closely corresponding pair are $\bar{x}_{25}$ and $\bar{x}_{62}$.

$$s_e^2 = \frac{75.146 + 87.652}{10 + 21 - 2} = \frac{162.798}{29} = 5.613,72$$

$$\bar{x}_p = \frac{42.426 + 112.518}{10 + 21} = \frac{154.944}{31} = 4.998$$

$$n_o = \frac{1}{2-1} \left(10 + 21 - \frac{10^2 + 21^2}{10 + 21} \right) = 13.549$$

$$s_{m,p}^2 = \frac{(4.242,6 - 4.998)^2 + (5.358 - 4.998)^2}{2-1} = 0.699,6$$

$$s_p^2 = n_o s_{m,p}^2 = 13.55(0.689,6) = 9.479$$

$$F = s_p^2 / s_e^2 = \frac{9.479}{5.814} = 1.633$$

Now s_e^2 is associated with $31 - 2 = 29$ degrees of freedom and s_p^2 is associated with $2 - 1 = 1$ degree of freedom. Now the table in Mickley (87j) gives $F = 4.18$ at the 5% level and $F = 7.60$ at the 1% level.

Therefore the sample means at 25°C and 62°C do not differ significantly.

Computer Programs

The five inch diameter infinite solid cylinder written in Basic Fortran IV
for the IBM360 model 40.

C 20 percent aluminium case

C top value of alfa for comparison with slightly different values

C program for finding the temperature gradients in a five inch

C diameter solid centre grain of propellant with heat sources

C active during part of the reaction time.

C heat sources columnwise deleted

C thermal diffusivity is 0.908,4 square feet per hour

C positive initial slope

C 122 degree boundaries

C final values of alfa to c were used

C delta t is 0.000,418,3 hours

C revised alfa was used here

C delta r is 0.5 inches

C G.A. Campbell February 1, 1967

C

dimension T(6,2000), MM(6), KOLUM(6)

common T, MM, KOLUM

C

C constants

C

AUT = 1989

NUT1 = NUT - 1

MIN = 1

MAX = 6

MAX1 = MAX - 1

C

CONSTM = 4.5687

CONS4M = 4./CONSTM

CONW4M = 1. - CONS4M

CONS1M = 1./CONSTM

CONS2M = CONSTM - 2.

CONS3T = .9

CONSTD = .418,3E-03

C

ALFA = .1151E-04

BETA = .6140751E-01

GAMA = -.581E-06

RO = .514469E-01

C = -.2752E-02

C

C INITIALIZE

C

DO 11 M=1,MAX

11 MM(M) = M

DO 1 M = 1,MAX1

COLUM(M) = 8888

```
1 T(M,1) = 122.
   KOLUM(6) = 8888
   T(6,1) = 122.
   DO 2 N = 2,NUT
2 T(6,N) = 122.

C
C   FILL IN THE ENTIRE TABLE
C
   DO 8 N = 1,NUT1
   N = 0
   LINES = 17
   TEST1 = 888.

C
   DO 88 NPAGES = 1,117
   WRITE(3,999) (MM(M),M = MIN,MAX)
999 FORMAT(1HL, 4H  N, 4H HRS, 4X, 6(5X11,5X) // )

C
21 DO 8 LIGNES = 1,LINES
   N = N+1
   FN1 = N - 1
   HRS = FN1*CONSTD
   EXPCN = EXP(C*FN1)
   GAMN1 = GAMA*FN1
   EXPT2N = EXP(ROXT(1,N))
   IF (N - 2) 13,888,13
```

```
13 IF(TEST1) 3, 4, 888
888 TEST1 = ALFA*EXP(BETA*T(1,N))*(EXP(GAMM1*EXPTLN)-(CONS3T*EXPCN))
      IF (TEST1) 3, 4, 4
3 TEST1 = 0.
4 T(1,N+1) = CONS4M*T(2,N) + CONM4M*T(1,N) + TEST1
```

C

```
DO 7 M = 2, MAX1
FM = M - 1
FLM = 1./FM
EXPTMN = EXP(RO*T(M,N))
IF (KOLUM(M)) 8000, 55, 8000
8000 TEST = ALFA*EXP(BETA*T(M,N))*(EXP(GAMM1*EXPTMN)-(CONS3T*EXPCN))
      IF (TEST) 5, 6, 6
5 KOLUM(M) = 0.
55 TEST = 0.
6 T(M,N 1) = (1.+FLM)/CONSTM T(M+1,N) + (CONS2M-FLM)/CONSTM*T(M,N) +
1 CONS1M*T(M-1,N) + TEST
7 CONTINUE
```

C

```
WRITE(3,9) N, HPS, (T(M,N), M = 1, MAX)
9 FORMAT(1H0, 14, F10.5, 6F11.5)
8 CONTINUE
88 CONTINUE
```

C

```
RETURN
END
```

An end effect test on the five inch diameter solid cylinder written in

Basic Fortran IV for the IBM 360 model 40

C AN END EFFECT TEST ON THE FIVE INCH DIAMETER SOLID CYLINDER

C TWO DIMENSIONS, R AND Z, ARE TAKEN INTO ACCOUNT HERE.

C THIS PROGRAM WILL BE RUN ON THE NEW IBM 360.

C T(M,L,N) CONTRACTED TO T(M,1P)

C DELTA T IS 0.046,89 HOURS

C DELTA R IS 0.5 INCHES

C DELTA Z IS 1.0 INCHES

C THE HIGH VALUE OF ALFA IS USED HERE

C THE FINAL VALUES OF THE CONSTANTS ALFA TO C WERE USED

C HEAT SOURCES ARE NOT COLUMNWISE DELETED

C 77 DEGREE BOUNDARIES

C THE THERMAL DIFFUSIVITY IS 0.008,104 SQUARE FEET PER HOUR

C POSITIVE INITIAL SLOPE

C TEMPERATURE IS IN DEGREES FAHRENHEIT

C G.A. CAMPBELL OCTOBER 24, 1966

C

DIMENSION MM(7), T(7,7), U(7,7)

COMMON MM, T, U

C

1 MAX = 40

C5812 = .001791

C73945 = .06140751

C898 = -.00006522

C56665 = .0514469

C465 = -.308745

CONS3T = .9

1R = 1

CONSTD = .04689

CM = 4.5687

C1M = 1./CM

C4M = 4./CM

Z = 18.2748

Z1 = 1./Z

Z2 = 2./Z

CMZ1 = 1. - C4M - Z2

CMZ2 = 1. - 2*C1M - Z2

CMZ11 = 1. - C4M - Z1

CMZ21 = 1. - 2.*C1M - Z1

C

DO 2 M = 1,7

2 MM(M) = M

C

C INITIAL BOUNDARY CONDITIONS

C

DO 33 1P = 1,7

DO 3 M = 1,5

T(M,1P) = 77.

T(M,1) = 100.

3 CONTINUE

T(6,IP) = 100.

T(7,IP) = 100.

33 CONTINUE

IGO = 1

GO TO 44

C

C FINAL BOUNDARY CONDITIONS

C

1000 DO 1010 IP = 1,7

T(6,IP) = 122.

T(7,IP) = 122.

DO 1010 M = 1,5

T(M,1) = 122.

1010 CONTINUE

IGO = 2

GO TO 1001

C

44 N = 0

DO 12 NPAGES = 1,MAX

WRITE(3,4) (MM(M), M = 1,7)

4 FORMAT(1H1, 2H N 2X2HIP, 7(7X11,7X) /)

DO 12 NBLOCK = 1,5

C

122 IF (N) 55, 55, 66

55 N = N+1

```
      WRITE(3,99) N, IR, ((T(M,IP), M = 1,7), IP = 1,7)
99  FORMAT( 1H, I4, I2, 2X, 7(1XE14.8) )

      WRITE(3,111)
111  FORMAT( 1H )

      66 FN = N - 1

      N = N + 1

      FN465 = FN*C465

      FN898 = FN*C898

C

      DO 8 IP = 2,7

      DO 8 M = 1,5

C

      TMP = T(M,IP)

      IP8 = IP + 1

      IF (IP8 - 8) 30, 31, 31

30  IF (M - 1) 5, 5, 6

C

      5  TPART = C4M*T(2,IP) + CMZ1*TMP + Z1*T(1,IP+1)

      GO TO 7

      6  FM = M - 1

      CMFM = CLM/FM

      6666 TPART = (CLM+CMFM)*T(M+1,IP) + (CMZ2 - CMFM)*TMP - CLM*T(M-1,IP) +
      2  Z1*T(M,IP+1)

C

      7  IP1 = IP - 1
```

```
      IF (IP1) 88, 88, 77
77  TPART = TPART + T(M,IP1)*Z1
      GO TO 88
31  IF (M - 1) 15, 15, 16
C
15  TPART = C4M*T(2,IP) + CMZ11*TMP
      GO TO 17
16  FM = M - 1
      CMFM = CLM/FM
6662 TPART = (CLM+CMFM)*T(M+1,IP) + (CMZ21 - CMFM)*TMP + CLM*T(M-1,IP)
C
17  IP1 = IP - 1
      IF (IP1) 88, 88, 177
177 TPART = TPART + T(M,IP1)*Z1
C
88  CTMP = C73945*TMP
      EXPON = FN898*EXP(C56665*TMP)
      EPART = C5812*EXP(CTMP)*((EXP(EXPON)) - (CONS3T*EXP(FN465)))
      U(M,IP) = TPART + EPART
8  CONTINUE
C
DO 10 IP = 2,7
DO 10 M = 1,5
      T(M,IP) = U(M,IP)
10 CONTINUE
```

GO TO (1000,1001), IGO

C

1001 WRITE(3,9) N, IR, ((T(M,IP), M = 1,7), IP = 1,7)

9 FORMAT(1H , 14, 12, 2X, 7(1E14.8))

WRITE(3,11)

11 FORMAT(1H)

12 CONTINUE

RETURN

END

The infinite thin-walled hollow cylinder O.D. = 5"; I.D. = 3"; written

in Fortran II for the IBM 1620

C PROGRAM FOR FINDING THE TEMPERATURE GRADIENTS IN A HOLLOW
C CYLINDER OF PROPELLANT WITH THE OUTER DIAMETER EQUAL TO
C FIVE AND A QUARTER INCHES AND THE INNER DIAMETER EQUAL TO
C THREE INCHES.
C THE WEB IS ASSUMED TO BE ONE INCH.
C THE FINAL AVERAGE VALUES WERE USED HERE
C HEAT SOURCES COLUMNWISE DELETED
C REVISED ALFA WAS USED HERE
C FINAL VALUES FOR ALFA TO C WERE USED
C DELTA T IS 0.046,89 HOURS
C DELTA R IS 0.5 INCHES
C TEMPERATURE IS IN DEGREES FAHRENHEIT
C THERMAL DIFFUSIVITY IS 0.008,104 SQUARE FEET PER HOUR

C POSITIVE INITIAL SLOPE

C C.A. CAMPBELL SEPTEMBER 28, 1966.

C

DIMENSION T(13,100), U(13), MM(13), KOL(13), V(13)

COMMON T, U, MM, KOL

C

C CONSTANTS

C

NUT = 100

NUT1 = NUT - 1

MIN = 1

MIN1 = MIN + 1

MIDDLE = 2

MAX = 3

MAX1 = MAX - 1

C

CONSTM = 4.5687

CONS4M = 4./CONSTM

CONMMM = 1. - CONS4M

CONS1M = 1./CONSTM

CONS2M = CONSTM - 2.

CONS3T = .9

CONSTD = .04689

C

ALFA = .001792

BETA = .0614075

GAMA = -.00006522

RO = .0514469

C = -.308745

C

C

INITIALIZE

C

DO 11 M = MIN, MAX

M3 = M 3

KOL(M) = M3

11 MW(M) = M3

T(MIN, 1) = 100.

T(MAX, 1) = 100.

T(MIN1, 1) = 77.

DO 2 N = 2, NUT

T(MIN, N) = 122.

2 T(MAX, N) = 122.

C

C

FILL IN THE ENTIRE TABLE

C

N = 0

NPAGES = 10

LINES = 10

LOCK = 0

C

```
DO 88 NP = 1, NPAGES
PRINT 999, (MM(M), M=MIN, MAX)
999 FORMAT(1H1, 3H N, 3X, 4H HRS, 4X, 3(3X12, 4X) )
IF (LOCK) 21, 20, 21
20 LOCK = 9999
N1 = 1
THRS1 = 0.
PRINT 9, N1, THRS1, (T(M, N1), M = MIN, MAX)
21 IF (NP - NPAGES) 2121, 2020, 888
2020 LINES = 9
```

C

```
2121 DO 8 LIGNES = 1, LINES
N = N + 1
FN = N
HRS = FN*CONSTD
FN1 = N - 1
EXPCN = EXPF(C*FN1)
GAMN1 = GAMA*FN1
```

C

```
103 M = MIN1
FM = 4.
FLM = 1./FM
EXPTM1 = EXPF(RO*T(M, N))
TEST = ALFA*EXPF(BETA*T(M, N))*(EXPF(GAMN1*EXPTM1)-(CONST*EXPCN))
V(M) = TEST
IF(TEST) 5, 66, 66
```

```
5 TEST = 0.
66 KOL(M) = 0.
6 TMN = (1.+FLM)/CONSTMT(M+1,N)+(CONSEM - FLM)/CONSTMT(M,N) +
1 CONSLM*T(M-1,N)
   TANT = TMN + TEST
   T(M,N 1) = TANT
   IF (KOL(M)) 12, 10, 12
10 U(M) = TMN
   GO TO 7
12 U(M) = TANT
C
7 N1 = N + 1
   PRINT 9, N1, HRS, (T(M,N1), M = MIN,MAX)
   PRINT 89, (U(M), M = MIN1,MAX1)
   PRINT 89, (V(M), M = MIN1,MAX1)
9 FORMAT(1H0, 13, 1X, F8.4, 1X, 3F9.3)
89 FORMAT(1H , 22X, F9.3)
8 CONTINUE
88 CONTINUE
   GO TO 99
C
388 PRINT 9999
9999 FORMAT(1H1, 26H NPAGES*NLINES = 100 - 1)
99 CALL EXIT
END
```

The infinite hollow cylinder with O.D. = 24" and I.D. = 12" written in

Basic Fortran IV for the IBM 360 model 40

C PROGRAM FOR FINDING THE TEMPERATURE GRADIENTS IN A HOLLOW CYLINDER
C OF PROPELLANT WITH THE OUTER DIAMETER EQUAL TO
C TWENTY-FOUR INCHES AND THE INNER DIAMETER EQUAL TO TWELVE INCHES.

C HEAT SOURCES COLUMNWISE DELETED

C 122 DEGREE BOUNDARIES

C FINAL VALUES OF ALFA TO C WERE USED

C DELTA T IS 0.046,89 HOURS

C DELTA R IS 0.5 INCHES

C TEMPERATURE IS IN DEGREES FAHRENHEIT

C THE THERMAL DIFFUSIVITY IS 0.008,104 SQUARE FEET PER HOUR

C POSITIVE INITIAL SLOPE

C G.A. CAMPBELL JANUARY 19, 1967

C

DIMENSION T(13,100), U(13), MM(13), KOL(13), V(13)

COMMON T, U, MM, KOL

C

C CONSTANTS

C

NUT = 100

NU1 = NUT - 1

MIN = 1

MIN 1 = MIN + 1

MIDDLE = 7

MAX = 13

MAX1 = MAX - 1

C

CONSTM = 4.5687

CONS4M = 4./CONSTM

CONS4M = 1. - CONS4M

CONS1M = 1./CONSTM

CONS2M = CONSTM - 2.

CONSTD = .04689

CONS3T = .9

C

ALFA = .1618E-03

BETA = .6140751E-01

GAMA = -.6522E-04

RO = .514469E-01

C = -.308745

C

C INITIALIZE

C

DO 11 M = MIN, MAX

M12 = M + 12

ROL(M) = M12

11 ROL(M) = M12

T(MIN,1) = 122.

T(MAX,1) = 122.

```
      DO 1 M = MIN1, MAX1
1  T(M,1) = 122.
      DO 2 N = 2, NUT
      T(MIN,N) = 122.
2  T(MAX,N) = 122.

C
C  FILL IN THE ENTIRE TABLE
C
      N = 0
      NPAGES = 10
      LINES = 10
      LOCK = 0

C
      DO 88 NP = 1, NPAGES
      WRITE(3,999) (MM(M), M = MIN, MAX)
999 FORMAT(1H1, 3H N, 1X, 13(3X12,4X) )
      IF (LOCK) 21, 20, 21
20 LOCK = 9999
      N1 = 1
      WRITE(3,9) N1, (T(M,N1), M = MIN, MAX)
21 IF (NP - NPAGES) 2121, 2020, 888
2020 LINES = 9

C
2121 DO 8 LIGNES = 1, LINES
      N = N + 1
```

FN = N

ERS = FN*CONSTD

FN1 = N - 1

EXPCN = EXP(C*FN1)

GAMN1 = GAMA*FN1

C

103 DO 7 M = MIN1,MAX1

FM = M + 11

FLM = 1./FM

EXPTMN = EXP(RO*T(M,N))

TEST = ALFA*EXP(BETA*T(M,N))*(EXP(GAMN1*EXPTMN)-(CONS3T*EXPCN))

V(M) = TEST

IF (N - 1) 55, 55, 666

55 KOL(M) = 0

666 IF (TEST) 5, 66, 6

5 TEST = 0

66 KOL(M) = 0

6 TMN = (1.+FLM)/CONSTM*T(M-1,N)+(CONS2M - FLM)/CONSTM*T(M,N) +

1 CONS1M*T(M-1,N)

TMNT = TMN + TEST

T(M,N+1) = TMNT

IF (KOL(M)) 12, 10, 12

10 U(M) = TMN

GO TO 7

12 U(M) = TMNT

```
7 CONTINUE

C

N1 = N + 1

WRITE(3,9) N1, (T(M,N1), M = MIN,MAX)

WRITE(3,89) (U(M), M = MIN1,MAX1)

WRITE(3,899) HRS, (V(M), M = MIN1,MAX1)

9 FORMAT(1H0, I3, 13F9.3)

89 FORMAT(1H , 6X, 3HHRS, 3X, 11F9.3)

899 FORMAT(1H , 3X, 12F9.3)

8 CONTINUE

88 CONTINUE

GO TO 99

888 WRITE(3,9999)

9999 FORMAT(1H1, 26H      NPAGES NLines = 100 - 1)

99 CALL EXIT

RETURN

END
```

The star shaped centre infinite hollow cylinder written in Basic Fortran IV
for the IBM 360 model 40

```
SUBROUTINE TEARPT(ATMP, IM, IIP, AT, ACLM, AC2K, ACLK, ATPART, ACMK1)

DIMENSION AT(19,11)

ATMP = AT(IM, IIP)

AFM = IM - 1

ACMIM = ACLM/AFM
```

AFM2 = AFM*AFM

AC2KFM = AC2K/AFM2

AC1KFM = AC1K/AFM2

ATPART = (AC1M+ACMFM)*AT(IM+1,IIP)+(ACMCL-ACMFM-AC2KFM)*AT(IM,IIP)+
1 AC1M*AT(IM-1,IIP)+(AC1KFM)*AT(IM,IIP+1) AC1KFM*AT(IM,IIP-1)

RETURN

END

C

SUBROUTINE FCTMP(FCTMP, FBETA, FTMP, FFN, FEPART, FALFA, FEXPON, FFN898,

1 FRO, FCONST, FFN465, FU, FTPART, JM, JIP)

DIMENSION FU(19,11)

FCTMP = FBETA*FTMP

IF (FFN) 1, 1, 2

1 FEPART = FALFA*(EXP(FCTMP))*1

GO TO 3

2 FEXPON = FFN898*EXP(FRO*FTMP)

FEPART = FALFA*EXP(FCTMP)*((EXP(FEXPON)) -(FCONST*EXP(FFN465)))

3 FU(JM,JIP) = FTPART + FEPART

RETURN

END

C

C FIRST PROGRAM ON THE NEW IEM 360

C PROGRAM FOR FINDING THE TEMPERATURE GRADIENTS IN A CYLINDER OF

C PROPELLANT WITH A HOLLOW, FIVE POINTED, STAR SHAPED CENTRE.

C THE OUTER DIAMETER IS EIGHTEEN INCHES.

C THE POINTS OF THE STAR HAVE A DIAMETER OF TEN INCHES. .
C THE VALLEYS OF THE STAR HAVE A DIAMETER OF FOUR INCHES.
C THE WEB IS FOUR INCHES.
C TWO DIMENSIONS, R AND THETA, ARE TAKEN INTO ACCOUNT HERE
C T(M,L,N) CONTRACTED TO T(M,IP)
C THE MODULUS IS 22.5
C DELTA T IS 0.009,521 HOURS
C DELTA R IS 0.5 INCHES
C DELTA THETA IS PI OVER 50 RADIAN OR 3.6 DEGREES
C THE SECTOR IS PI OVER 5 RADIAN OR 36 DEGREES
C THE HIGH VALUE OF ALFA IS USED HERE
C THE FINAL VALUES OF THE CONSTANTS ALFA TO C WERE USED
C HEAT SOURCES ARE NOT COLUMNWISE DELETED
C 122 DEGREE BOUNDARIES
C THE THERMAL DIFFUSIVITY IS 0.008,104 SQUARE FEET PER HOUR
C POSITIVE INITIAL SLOPE
C TEMPERATURE IS IN DEGREES FAHRENHEIT
C NEW VALUE FOR T(10,11)
C G.A. CAMPELL NOVEMBER 17, 1966.
C
C DIMENSION AM(19), T(19,11), U(19,11)
C
1 MAX = 100.
ALFA = .363752E-03
DELTA = .6140751E-01

GAMA = -.132437E-04

RO = .514469E-01

C = -.6269E-01

CONST = .9

IR = 1

CONSTM = 2.61818

CONSTD = .009521

CM = 22.5

CK = .0888264

CLM = 1./CK

CMK1 = 1. - 2.*CLM

CLK = 1./CK

C2K = 2./CK

C77 = 77.

C5 = .5

C115 = 11.5

C38201 = .38201

C28967 = .28967

C15633 = .15633

C28253 = .28253

C21288 = .21288

C30336 = .30536

C25755 = .25755

C225 = 22.5

DO 2 M = 5,19

2 MM(M) = M

C

C INITIAL BOUNDARY CONDITIONS

C

T(5,1) = 122.

T(5,2) = 122.

T(5,3) = 122.

T(5,4) = 122.

DO 33 IP = 1,11

DO 3 M = 6,18

T(M,IP) = 122.

3 CONTINUE

T(19,1P) = 122.

33 CONTINUE

T(6,5) = 122.

T(5,4) = 122.

T(6,6) = 122.

T(6,5) = 122.

T(7,8) = 122.

T(8,9) = 122.

T(9,10) = 122.

T(10,11) = 122.

T(7,7) = 122.

T(11,11) = 122.

GO TO 44

C

C FINAL BOUNDARY CONDITIONS

C

44 N = 0

DO 12 NPAGES = 1,MAX

WRITE(3,4)

4 FORMAT(1H1, 8H N IP , 2H 5, 6X, 2H 7, 6X, 2H 8, 6X, 2H 9, 6X,
1 2H10, 6X, 2H11, 6X, 2H12, 6X, 2H13, 6X, 2H14, 6X, 2H15, 6X, 2H16,
2 6X, 2H17, 6X, 2H18, 6X, 2H19, /)

DO 12 NBLOCK = 1,4

C

122 T(5,5) = 0

T(5,6) = 0

T(5,7) = 0

T(6,7) = 0

T(5,8) = 0

T(6,8) = 0

T(5,9) = 0

T(6,9) = 0

T(7,9) = 0

T(5,10) = 0

T(6,10) = 0

T(7,10) = 0

T(8,10) = 0

T(5,11) = 0

T(6,11) = 0

T(7,11) = 0

T(8,11) = 0

T(9,11) = 0

IF (N) 55, 55, 66

55 N = N + 1

WRITE(3,111) N

111 FORMAT(1H, 13)

WRITE(3,99) ((T(M,IP), M = 5,19), IP = 1,11)

99 FORMAT(1H, 5X, 15F8.3)

66 FN = N - 1

FN2 = N

HRS = FN2*CONSTD

N = N + 1

FN465 = FN*C

FN898 = FN*GAMA

C

IP = 1

DO 1101 MX = 6,18

M = MX

5 TMP = T(M,IP)

FM = M - 1

CMFM = CLM/FM

FM2 = FM*FM

C2KFM = C2K/FM2

```
      CLKFM = CLK/FM2
      TPART = (C1M+CMFM)*T(M+1,IP)+(CMK1-CMFM-C2KFM)*T(M,IP) +
1 C1M*T(M-1,IP)+C2KFM*T(M,IP+1)
      CALL FFCTMP(CTMP,BETA,TMP,FN,EPART,ALFA,EXPON,FN898,RO,CONST,
1 FN465, U, TPART, M, IP)
1101 CONTINUE
9004 IP = IP + 1
      GO TO (23,23,23,23,84,84,28,28,41,43,45), IP
23 DO 8000 MX = 6,18
      M = MX
      CALL TEARPT(TMP, M, IP, T, C1M, C2K, CLK, TPART, CMK1)
      CALL FFCTMP(CTMP,BETA,TMP,FN,EPART,ALFA,EXPON,FN898,RO,CONST,
1 FN465, U, TPART, M, IP)
8000 CONTINUE
      IF (IP - 12) 9004, 1001, 9643
84 DO 8006 MX = 7,18
      M = MX
      CALL TEARPT(TMP, M, IP, T, C1M, C2K, CLK, TPART, CMK1)
      CALL FFCTMP(CTMP,BETA,TMP,FN,EPART,ALFA,EXPON,FN898,RO,CONST,
1 FN465, U, TPART, M, IP)
8006 CONTINUE
      IF (IP - 12) 9004, 1001, 9643
28 DO 8001 MX = 8,18
      M = MX
      CALL TEARPT(TMP, M, IP, T, C1M, C2K, CLK, TPART, CMK1)
```

```
      CALL FFCTMP(CTMP,BETA,TMP,FN,EPART,ALFA,EXPON,FN898,RO,CONST,
1 FN465, U, TPART, M, 1P)
8001 CONTINUE
      IF (IP - 12) 9004, 1001, 9645
41 DO 8002 MX = 9,18
      M = MX
      CALL TEARPT(TMP, M, 1P, T, C1M, C2K, C1K, TPART, CMK1)
      CALL FFCTMP(CTMP,BETA,TMP,FN,EPART,ALFA,EXPON,FN898,RO,CONST,
1 FN465, U, TPART, M, 1P)
8002 CONTINUE
      IF (IP - 12) 9004, 1001, 9645
43 DO 8003 MX = 10,18
      M = MX
      CALL TEARPT(TMP, M, 1P, T, C1M, C2K, C1K, TPART, CMK1)
      CALL FFCTMP(CTMP,BETA,TMP,FN,EPART,ALFA,EXPON,FN898,RO,CONST,
1 FN465, U, TPART, M, 1P)
8003 CONTINUE
      IF (IP - 12) 9004, 1001, 9645
45 DO 8004 MX = 12,18
      M = MX
      TMP = T(M,IP)
      FM = M - 1
      CMFM = C1M/FM
      FM2 = FM*FM
      C2CFM = C2K/FM2
```

```
      CLKFM = CLK/FM2
      TPART = (CLM+CMFM)*T(M+1,IP) + (CMK1-CMFM-C2KFM)*T(M,IP) +
1 CLM*T(M-1,IP) + C2KFM*T(M,IP-1)
      CALL FFCIMP(CTMP,BETA,TMP,FN,EPART,ALFA,EXPCN,FN898,RC,CONST,
1 FN465, U, TPART, M, IP)
8004 CONTINUE
      IF (IP - 12) 9004, 1001, 9643
9643 WRITE(3,9644)
9644 FORMAT(20X,34H**HORRIBLE ERROR IN DIPROUTINED**)
C
1001 DO 7000 IP = 1,11
      GO TO (7001,7001,7001,7001,7002,7002,7003,7003,7004,7005,
1 7006), IP
7001 INIT = 6
      GO TO 7007
7002 INIT = 7
      GO TO 7007
7003 INIT = 8
      GO TO 7007
7004 INIT = 9
      GO TO 7007
7005 INIT = 10
      GO TO 7007
7006 INIT = 12
7007 DO 7008 J= INIT,18
```

7008 T(J,1P) = U(J,1P)

7000 CONTINUE

1000 T(5,1) = 122.

T(5,2) = (C5/C38201)*(122. - T(6,2)) + T(6,2)

T(5,3) = (C5/C28967)*(122. - T(6,3)) + T(6,3)

T(5,4) = (C5/C15633)*(122. - T(6,4)) + T(6,4)

DO 1010 1P = 1,11

DO 1010 M = 6,18

T(19,1P) = 122.

1010 CONTINUE

T(6,5) = 122.

T(6,6) = (C5/C28253)*(122. - T(7,6)) + T(7,6)

T(7,7) = 122.

T(7,8) = (C5/C21288)*(122. - T(8,8)) + T(8,8)

T(8,9) = (C5/C30336)*(122. - T(9,9)) + T(9,9)

T(9,10) = (C5/C25755)*(122. - T(10,10)) + T(10,10)

T(10,11) = CONSTH*(122. - T(10,10)) + T(10,10)

T(11,11) = 122.

C

1002 WRITE(3,11) N, HFS

11 FORMAT(1H, 13, 2X, F9.5)

WRITE(5,9) ((T(M,1P), M = 5,19), 1P = 1,11)

9 FORMAT(1H, 5X, 15F8.3)

12 CONTINUE

CALL EXIT

RETURN

END

APPENDIX - 3

The solution of the heat conduction equation without heat sources and
with a constant temperature boundary

$$\kappa \nabla^2 T = \frac{\partial T}{\partial t} \dots\dots\dots (35)$$

$$\text{then } \kappa \left[\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial \theta^2} + \frac{\partial^2 T}{\partial z^2} \right] = \frac{\partial T}{\partial t} \dots\dots\dots (35a)$$

Now for the solid cylinder, of infinite length

$$\frac{\partial}{\partial \theta} = \frac{\partial}{\partial z} = \frac{\partial^2}{\partial \theta^2} = \frac{\partial^2}{\partial z^2} = 0$$

$$\text{then } \kappa \left[\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right] = \frac{\partial T}{\partial t} \dots\dots\dots (37)$$

$$\text{with boundary conditions } 1) \quad T(R, 0) = T_0 \dots\dots\dots (38)$$

$$2) \quad T(R, t) = T_1 \text{ where } t > 0 \dots\dots\dots (39)$$

$$3) \quad \left(\frac{\partial T}{\partial r} \right)_{r=0} = 0 \dots\dots\dots (40)$$

Taking LaPlace Transforms with respect to time gives:

$$\kappa \left[\frac{\partial^2 \bar{T}}{\partial r^2} + \frac{1}{r} \frac{\partial \bar{T}}{\partial r} \right] = s \bar{T} - T_0$$

$$\frac{d^2 \bar{T}}{dr^2} + \frac{d\bar{T}}{rdr} - \frac{p\bar{T}}{K} = -\frac{T_0}{K}$$

Let the left hand side equal zero as this is a linear equation

$$\frac{d^2 \bar{T}}{dr^2} + \frac{d\bar{T}}{rdr} - \frac{p\bar{T}}{K} = 0$$

multiplying through by r^2 gives $\frac{r^2 d^2 \bar{T}}{dr^2} + \frac{rd\bar{T}}{dr} - \frac{p\bar{T}r^2}{K} = 0$

Comparing this equation with Bessel's Equation in Mickley (87a)

$a = 1$; $b = 0$; $c = 0$; $d = -p$; $s = 1$; then

$$p = \frac{1}{s} \sqrt{\left(\frac{1-a}{2}\right)^2 - c} = \frac{1}{1} \sqrt{\left(\frac{1-1}{2}\right)^2 - 0} = 0$$

$$\frac{\sqrt{a}}{s} = \sqrt{-\frac{p}{K}}$$

then $\bar{T} = A I_0(\sqrt{p/K} r) + B K_0(\sqrt{p/K} r) \dots\dots\dots (59)$

Since the form of Q is a constant then $\bar{T} = D$ must be a solution.

Substitution of $\bar{T} = D$ into the differential equation gives

$$0 + 0 - \frac{pD}{K} = -\frac{T_0}{K}$$

$\therefore D = T_0/p$, and the full solution is

$$\bar{T} = A I_0(\sqrt{p/K} r) + B K_0(\sqrt{p/K} r) + \frac{T_0}{p} \dots\dots\dots (173)$$

Now to find the constants in equation (178), first differentiate with respect to r

$$\left(\frac{\partial \bar{T}}{\partial r}\right) = A \sqrt{\frac{p}{\kappa}} I_1(\sqrt{p/\kappa} r) - B \sqrt{\frac{p}{\kappa}} K_1(\sqrt{p/\kappa} r)$$

applying Laplace transforms with respect to time to equation (40) gives

$$\left(\frac{\partial \bar{T}}{\partial r}\right)_{r=0} = 0$$

substituting this in the above

$$\left(\frac{\partial \bar{T}}{\partial r}\right)_{r=0} = A \sqrt{\frac{p}{\kappa}} I_1(0) - B \sqrt{\frac{p}{\kappa}} K_1(0) = 0$$

now $I_1(0) = 0$ and $K_1(0) = \infty$, and since each term must be zero, this requires that $B = 0$. Then equation (178) becomes

$$\bar{T} = A I_0(\sqrt{p/\kappa} r) + \frac{T_0}{p} \dots\dots\dots (179)$$

applying Laplace transforms with respect to time to equation (39) gives

$$\bar{T}(R, p) = \frac{T_1}{p}$$

substituting this in equation (179)

$$\frac{T_1}{p} = A I_0(\sqrt{p/\kappa} R) + \frac{T_0}{p} = \bar{T}(R, p)$$

$$\therefore A = \frac{(T_1 - T_0)}{p I_0(\sqrt{p/x} R)}$$

substituting this in equation (179) gives

$$\bar{T} = \frac{(T_1 - T_0) I_0(\sqrt{p/x} R)}{p I_0(\sqrt{p/x} R)} + \frac{T_0}{p} \dots\dots\dots (180)$$

noting that $I_p(x) = i^{-p} J_p(ix)$, equation (180) can be written

$$\bar{T} = \frac{(T_1 - T_0) J_0(i \sqrt{p/x} R)}{p J_0(i \sqrt{p/x} R)} + \frac{T_0}{p}$$

Let $\lambda = i \sqrt{\frac{p}{x}}$, then $\frac{d\lambda}{dp} = \frac{\lambda}{2p}$ and $p = -x\lambda^2$. Substituting this in gives

$$\bar{T} = \frac{(T_1 - T_0) J_0(\lambda R)}{p J_0(\lambda R)} + \frac{T_0}{p}$$

$$l(p) = p J_0(\lambda R)$$

$$l'(p) = J_0(\lambda R) \frac{dp}{dp} + p \left[\frac{d J_0(\lambda R)}{d\lambda} \right] \frac{d\lambda}{dp} = J_0(\lambda R) + p \left[-R J_1(\lambda R) \right] \frac{\lambda}{2p}$$

$$l'(p) = J_0(\lambda R) - \frac{\lambda R}{2} J_1(\lambda R)$$

The poles are at $p = 0$ and $J_0(\lambda R) = 0$. The residue at the pole $p = 0$ is

$$P_0 = \frac{l(0)}{l'(0)} = \lim_{\lambda \rightarrow 0} \frac{(T_1 - T_0) J_0(\lambda R)}{J_0(\lambda R) - \frac{\lambda R}{2} J_1(\lambda R)} = \frac{(T_1 - T_0) 1}{1 - 0} = (T_1 - T_0)$$

The residue at the poles $J_0(\lambda R) = 0$ is

$$p_n = \frac{j(p)}{l'(p)} = \lim_{J_0(\lambda_n R) \rightarrow 0} e^{p_n t} \frac{(T_1 - T_0) J_0(\lambda_n r)}{J_0(\lambda_n R) - \frac{\lambda_n R}{2} J_1(\lambda_n R)} = \frac{(T_1 - T_0) J_0(\lambda_n r)}{0 - \frac{\lambda_n R}{2} J_1(\lambda_n R)} e^{p_n t}$$

$$p_n = - \frac{2 (T_1 - T_0) J_0(\lambda_n r)}{\lambda_n R J_1(\lambda_n R)} e^{-\kappa \lambda_n^2 t}$$

Taking all values of n
$$p_n = (T_1 - T_0) - \frac{2}{R} \sum_{n=1}^{\infty} e^{-\kappa \lambda_n^2 t} \frac{J_0(\lambda_n r)}{\lambda_n J_1(\lambda_n R)}$$

The second term $\frac{T_0}{p}$ inverts to T_0 . Then the full solution is

$$T = (T_1 - T_0) - \frac{2 (T_1 - T_0)}{R} \sum_{n=1}^{\infty} e^{-\kappa \lambda_n^2 t} \frac{J_0(\lambda_n r)}{\lambda_n J_1(\lambda_n R)} + T_0$$

Rearranging

$$\frac{T - T_1}{T_1 - T_0} = - \frac{2}{R} \sum_{n=1}^{\infty} e^{-\kappa \lambda_n^2 t} \frac{J_0(\lambda_n r)}{\lambda_n J_1(\lambda_n R)}$$

where

$$J_0(\lambda_n R) = 0 \dots\dots\dots (42)$$

APPENDIX - 4

The solution of the heat conduction equation without heat sources and
with a film boundary

$$\chi \left[\frac{\partial^2 T}{\partial r^2} + \frac{\partial T}{r \partial r} \right] = \frac{\partial T}{\partial t} \dots\dots\dots (37)$$

with boundary conditions 1) $T(r, 0) = T_0 \dots\dots\dots (38)$

2) $\left(\frac{\partial T}{\partial r} \right)_{r=0} = 0 \dots\dots\dots (40)$

3) $\left(\frac{\partial T}{\partial r} \right)_{r=R} = - \frac{h}{k} (T_R - T_A) \dots\dots\dots (181)$

Taking Laplace transforms with respect to time, equation (37) becomes

$$\chi \left[\frac{d^2 \bar{T}}{dr^2} + \frac{d\bar{T}}{r dr} \right] = p \bar{T} - T_0$$

$$\frac{d^2 \bar{T}}{dr^2} + \frac{d\bar{T}}{r dr} - \frac{p \bar{T}}{\chi} = - \frac{T_0}{p}$$

Similarly to the solution in appendix 3

$$\bar{T} = A J_0(i \sqrt{p/\chi} r) + B Y_0(i \sqrt{p/\chi} r) + \frac{T_0}{p}$$

differentiating with respect to r

$$\frac{\partial \bar{T}}{\partial r} = A \left(-i\sqrt{\frac{p}{\lambda}}\right) J_1(i\sqrt{p/\lambda} r) + B \left(-i\sqrt{\frac{p}{\lambda}}\right) Y_1(i\sqrt{p/\lambda} r)$$

$$\left(\frac{\partial \bar{T}}{\partial r}\right)_{r=0} = A \left(-i\sqrt{\frac{p}{\lambda}}\right) J_1(0) + B \left(-i\sqrt{\frac{p}{\lambda}}\right) Y_1(0) = 0$$

∴ B = 0, and the equation becomes

$$\bar{T} = A J_0(i\sqrt{p/\lambda} r) + \frac{T_0}{p}$$

Let $\lambda = i\sqrt{\frac{p}{\lambda}}$, then $\frac{d\lambda}{dp} = \frac{\lambda}{2p}$ and $p = -\lambda^2$. Substituting this in gives

$$\bar{T} = A J_0(\lambda r) + \frac{T_0}{p}$$

Taking Laplace transforms with respect to time on B.C. 3)

$$\left(\frac{\partial \bar{T}}{\partial r}\right)_{r=R} = -\frac{h}{k}(\bar{T}_R - T_A/p)$$

Differentiating the main equation with respect to r gives

$$\left(\frac{\partial \bar{T}}{\partial r}\right) = -A \lambda J_1(\lambda r)$$

applying B.C. 3) gives

$$\left(\frac{\partial \bar{T}}{\partial r}\right)_{r=R} = -A \lambda J_1(\lambda R) = -h(\bar{T}_R - T_A/p)$$

$$\therefore A = \frac{h(\bar{T}_R - T_A/p)}{\lambda J_1(\lambda R)}$$

$$\text{Then } \bar{T} = \frac{h}{k} \left(\bar{T}_R - \frac{T_A}{p} \right) \frac{J_0(\lambda r)}{\lambda J_1(\lambda R)} + \frac{T_0}{p}$$

$$\text{To find } \bar{T}_R; \quad \bar{T}_R = \frac{h}{k} \left(\bar{T}_R - \frac{T_A}{p} \right) \frac{J_0(\lambda R)}{\lambda J_1(\lambda R)} + \frac{T_0}{p}$$

Rearranging and substituting back gives

$$\bar{T} = \frac{T_0 J_0(\lambda r) - T_A J_0(\lambda r) + T_0 (k/h) \lambda J_1(\lambda R) - T_0 J_0(\lambda R)}{p [(k/h) \lambda J_1(\lambda R) - J_0(\lambda R)]}$$

$$l(p) = p \left[\frac{k}{h} \lambda J_1(\lambda R) - J_0(\lambda R) \right]$$

$$l'(p) = \left[\frac{k}{h} \lambda J_1(\lambda R) - J_0(\lambda R) \right] + p \left[\frac{k}{h} \frac{d\lambda}{dp} J_1(\lambda R) - \frac{d}{d\lambda} J_0(\lambda R) \right] \frac{d\lambda}{dp}$$

$$l'(p) = \left[\frac{k}{h} \lambda J_1(\lambda R) - J_0(\lambda R) \right] + \frac{1}{2} \lambda \left[\frac{k}{h} \lambda R J_0(\lambda R) + R J_1(\lambda R) \right]$$

$$\text{The poles are at } p = 0 \text{ and } \left[\frac{k}{h} \lambda J_1(\lambda R) - J_0(\lambda R) \right] = 0$$

$$p_0 = \frac{l(p)}{l'(p)} = \lim_{\lambda \rightarrow 0} \frac{(T_0 - T_A) J_0(\lambda r) + T_0 [(k/h) \lambda J_1(\lambda R) - J_0(\lambda R)]}{\left[\frac{k}{h} \lambda J_1(\lambda R) - J_0(\lambda R) \right] + \frac{1}{2} \lambda \left[\frac{k}{h} \lambda R J_0(\lambda R) + R J_1(\lambda R) \right]}$$

$$p_0 = \frac{(T_0 - T_A)(1) + T_0(0 - 1)}{(0 - 1) + 0(0 + 0)} = T_A$$

$$p_n = e^{p_n t} \frac{(T_0 - T_A) J_0(\lambda r) + T_0(0)}{\frac{1}{2} \lambda \left[\frac{k}{h} \lambda R J_0(\lambda R) + \frac{R h}{k} J_1(\lambda R) \right]}$$

$$\text{Letting } c = \frac{hR}{k}$$

$$p_n = \frac{(T_0 - T_A) J_0(\lambda r) e^{p_n t}}{\frac{1}{2c} (\lambda^2 R^2 + c^2) J_0(\lambda R)}$$

$$\therefore \frac{T - T_A}{T_0 - T_A} = 2C \sum_{n=1}^{\infty} e^{-x \lambda_n^2 t} \cdot \frac{J_0(\lambda_n r)}{(\lambda_n^2 R^2 + c^2) J_0(\lambda_n R)} \dots\dots\dots (182)$$

where λ_n is a root of

$$\lambda R J_1(\lambda R) - \frac{hR}{k} J_0(\lambda R) = 0 \dots\dots\dots (183)$$

where $n = 1, 2, \dots\dots\dots$ etc.

if $A = \frac{hR}{k}$; $\theta_n = \lambda_n R$; $T = \frac{xR^2}{t}$; then

$$\frac{T - T_A}{T_0 - T_A} = \sum_{n=1}^{\infty} e^{-\theta_n^2 T} \cdot \frac{J_0(\frac{r\theta_n}{R})}{(\theta_n^2 + A^2) J_0(\theta_n)} \dots\dots\dots (127)$$

where $\pm \theta_n$, $n = 1, 2, \dots\dots\dots$ are the roots of

$$\theta J_1(\theta) = A J_0(\theta) \dots\dots\dots (126)$$