MATERIAL AGING SEMINAR

I. THERMAL AGING - ARRHENIUS OR ERRONEOUS?

II. HUMIDITY AGING - DEVELOPMENT OF METHODOLOGY

III. RADIATION AGING - IMPORTANCE AND IMPLICATIONS OF DOSE RATE EFFECTS

IV. AGING OF PVC AND PE - DISCOVERY AND INTERPRETATION OF STRONG SYNERGISM OF RADIATION AND TEMPERATURE

V. FIRE RETARDANT AGING

ACCELERATED AGING

PRIMARY GOAL - PREDICT MATERIAL (COMPONENT) LIFETIME UNDER USE CONDITIONS

SECONDARY GOAL- SCREEN FOR BEST MATERIALS

FIRST STEP - KNOWLEDGE OF

1. FAILURE MODES - FROM EXPERIENCE AND FAILURE MODE TESTS
2. IMPORTANT STRESSES - FROM LITERATURE, FAILURE MODE TESTS, COMPATIBILITY TESTS

SECOND STEP - USE ABOVE TO DETERMINE

1. SUSPECT MATERIAL(S)
2. ENVIRONMENTS DAMAGING TO EACH MATERIAL
3. QUANTITATIVE DAMAGE PARAMETER(S) TO FOLLOW DEGRADATION

CONCENTRATE ON THERMAL AGING AT CONSTANT TEMPERATURE - STILL HAVE TYPICALLY TWO ENVIRONMENTAL VARIABLES.

eg. (TEMP, OXYGEN CONCENTRATION), (TEMP, H_2O)

...MER SCIENCE Polymer Chemistry Edition VOL. 15, 799-813 (1977)

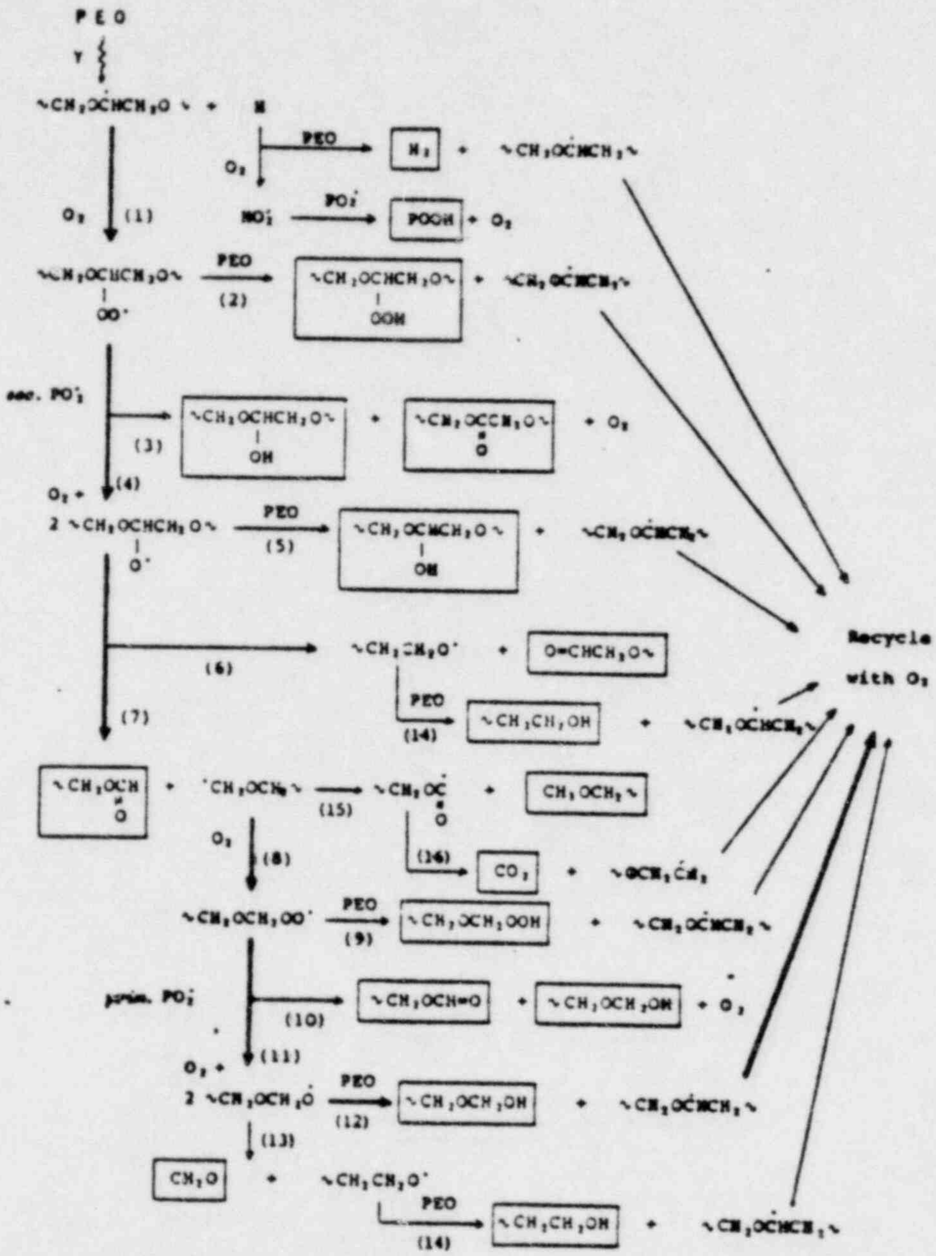


Fig. 1. Scheme for γ-oxidation of poly(ethylene oxide). Final products are in boxes; important routes are marked by heavy arrows. In reactions (10) and (11), cross-interactions of primary and secondary peroxy radicals are also possible:

prim PO· + sec PO· + O...

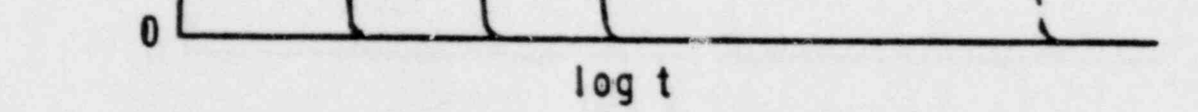
AGING OF A FILLED POLYMER

Let C_A, C_B, C_C, ... be concentrations of chemical species (chemical groups being destroyed or formed, cross-link density, plasticizer).

Parameter D used to follow degradation under use and accelerated conditions. Assumed

$$D = \mathcal{D}\,(C_A, C_B, C_C, \ldots)$$

PRESCRIPTION FOR ACCELERATED AGING - Raise environmental stresses (eg. temperature) to accelerate equally all PERTINENT reactions which change C's



Shapes superimposable by horizontal shifts- evidence that all relevant reactions accelerated equally

SHIFT FACTOR $A_T(T)$ - DETERMINE, RATIONALIZE, EXTRAPOLATE

HELPFUL SIMPLIFICATIONS

1. D INSENSITIVE TO CHANGES IN SOME SPECIES
2. ONE KINETIC TERM OF MOLECULARITY ≤ 2 USUALLY DOMINANT OVER A REASONABLE TEMPERATURE RANGE

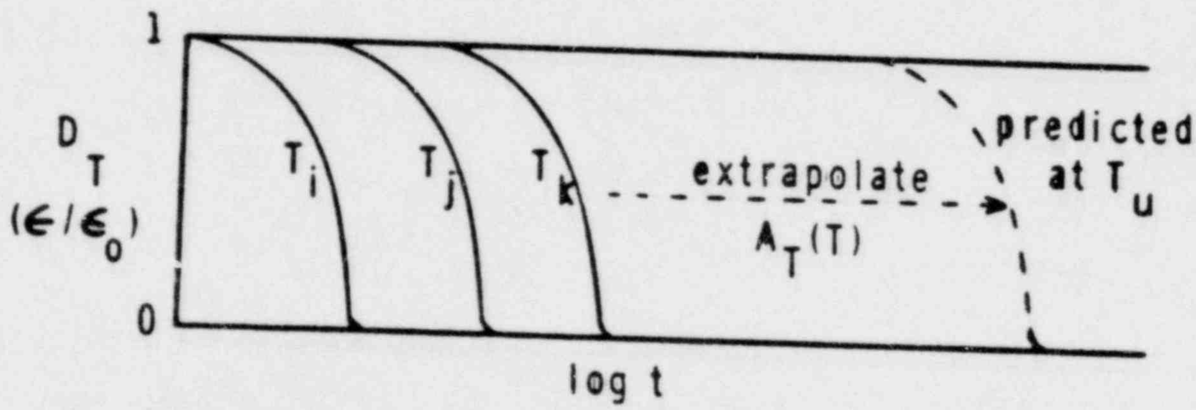
ie. suppose

$$\frac{dC_A}{dt} = k_1(T)\ C_A^{a}\ C_B^{b}$$

where $B = O_2$ or H_2O and $C_B \sim$ constant during reaction

shift factor $A_T(T)$ from temperature dependence of degradation,

$k_1(T) \propto \exp(-E_a/RT)$



GOOD EXPERIMENTAL PROCEDURE

1. RANGE OF STRESSES AS LARGE AS POSSIBLE TO CHECK FOR EVIDENCE OF CHANGE IN MECHANISM (CHANGE IN SHAPE OR $A_T(T)$)
2. KEEP EXTRAPOLATIONS TO A MINIMUM
3. DON'T EXTRAPOLATE THROUGH A TRANSITION

SAFETY CABLE AGING

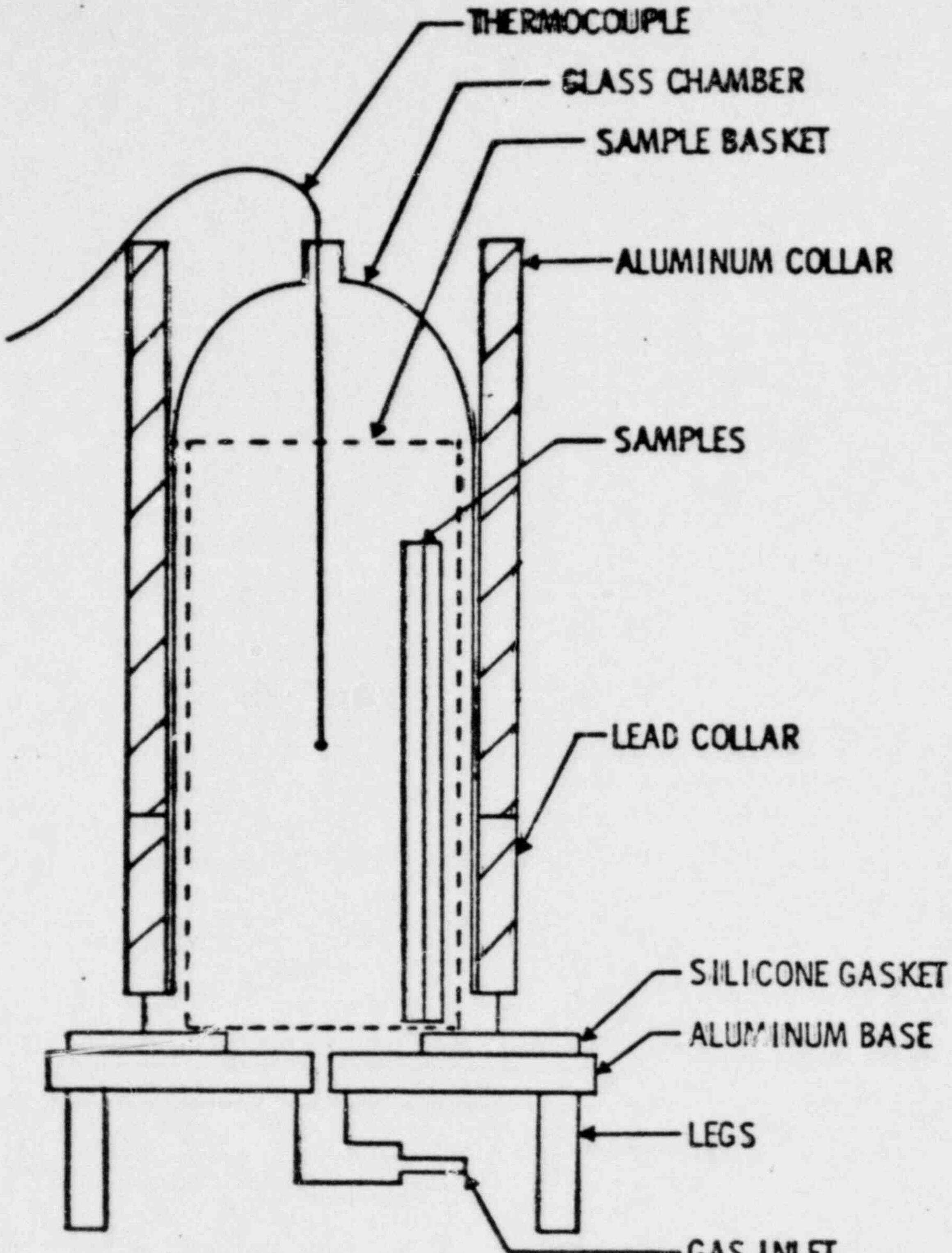
FAILURE MODE - EMBRITTLEMENT OF INSULATION

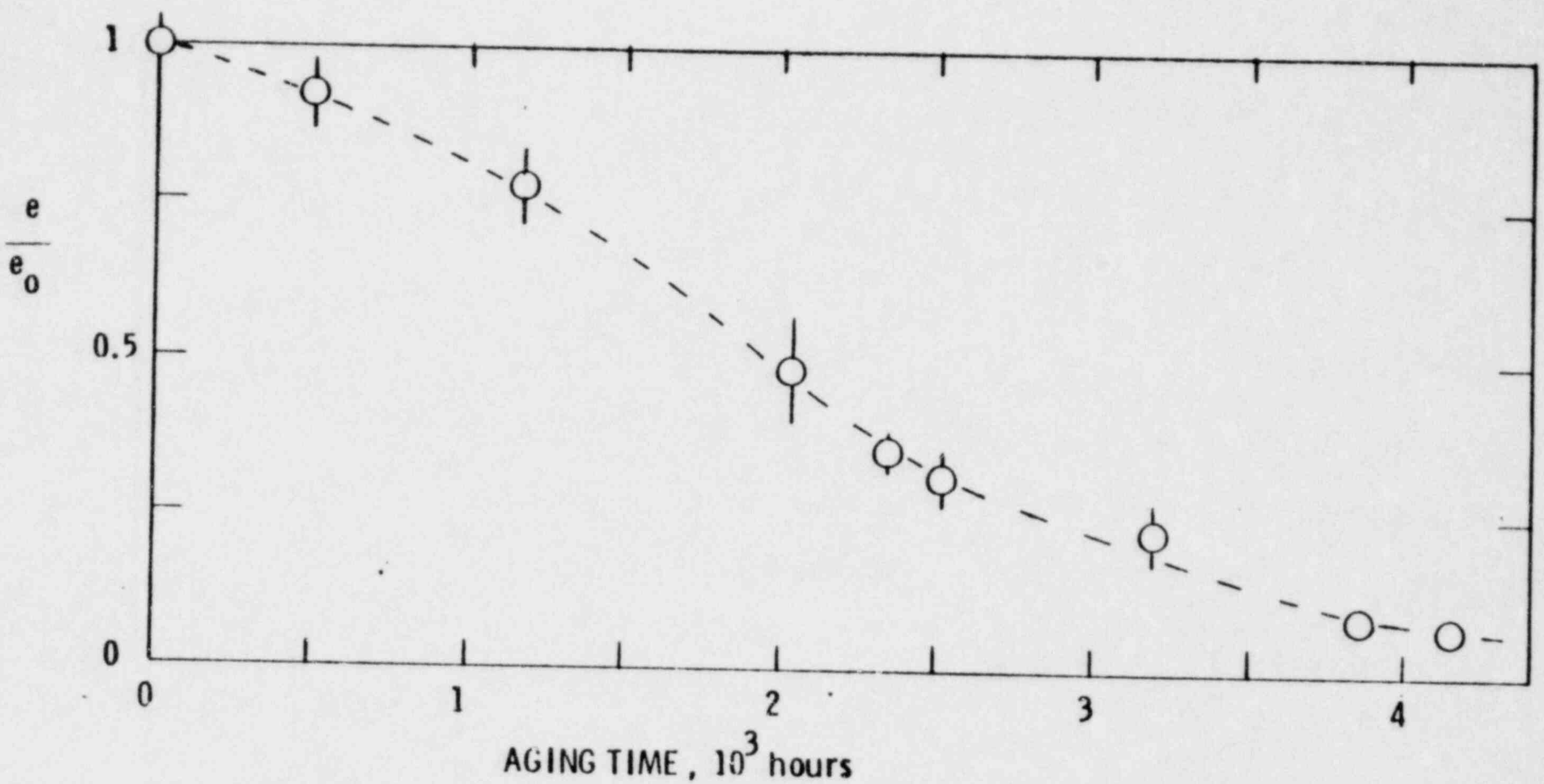
ENVIRONMENT - THERMOOXIDATIVE

DAMAGE PARAMETER - REDUCED ULTIMATE TENSILE ELONGATION

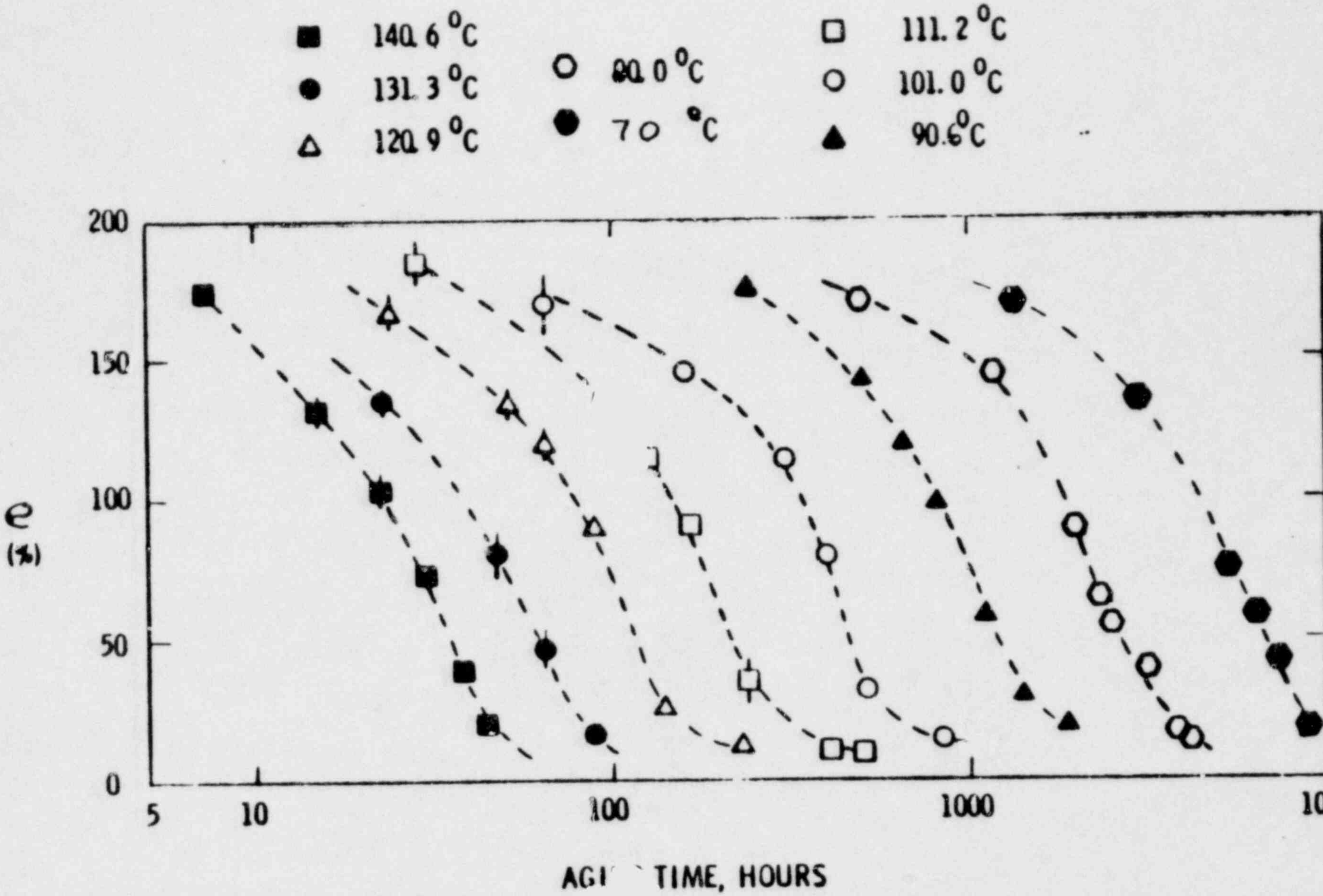
THREE EXAMPLES

1. NEOPRENE - SUCCESSFUL
2. CROSSLINKED POLYOLEFIN - SUCCESSFUL THROUGH TRANSITION (CRYSTALLINE MELTING POINT)
3. ETHYLENE-PROPYLENE RUBBER - DOMINANT REACTION CHANGES

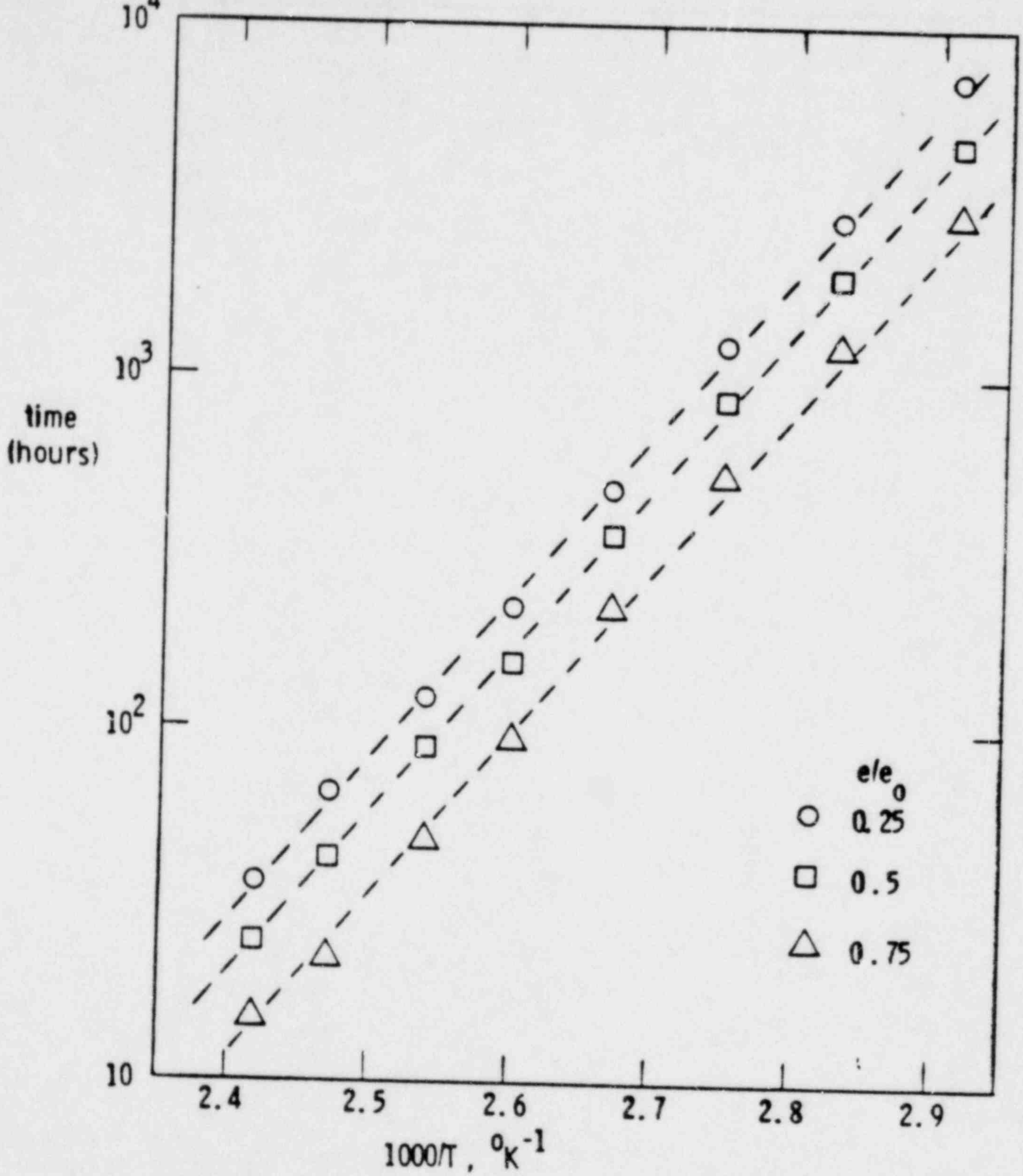

THERMOCOUPLE
GLASS CHAMBER
SAMPLE BASKET
ALUMINUM COLLAR
SAMPLES
LEAD COLLAR
SILICONE GASKET
ALUMINUM BASE
LEGS
GAS INLET



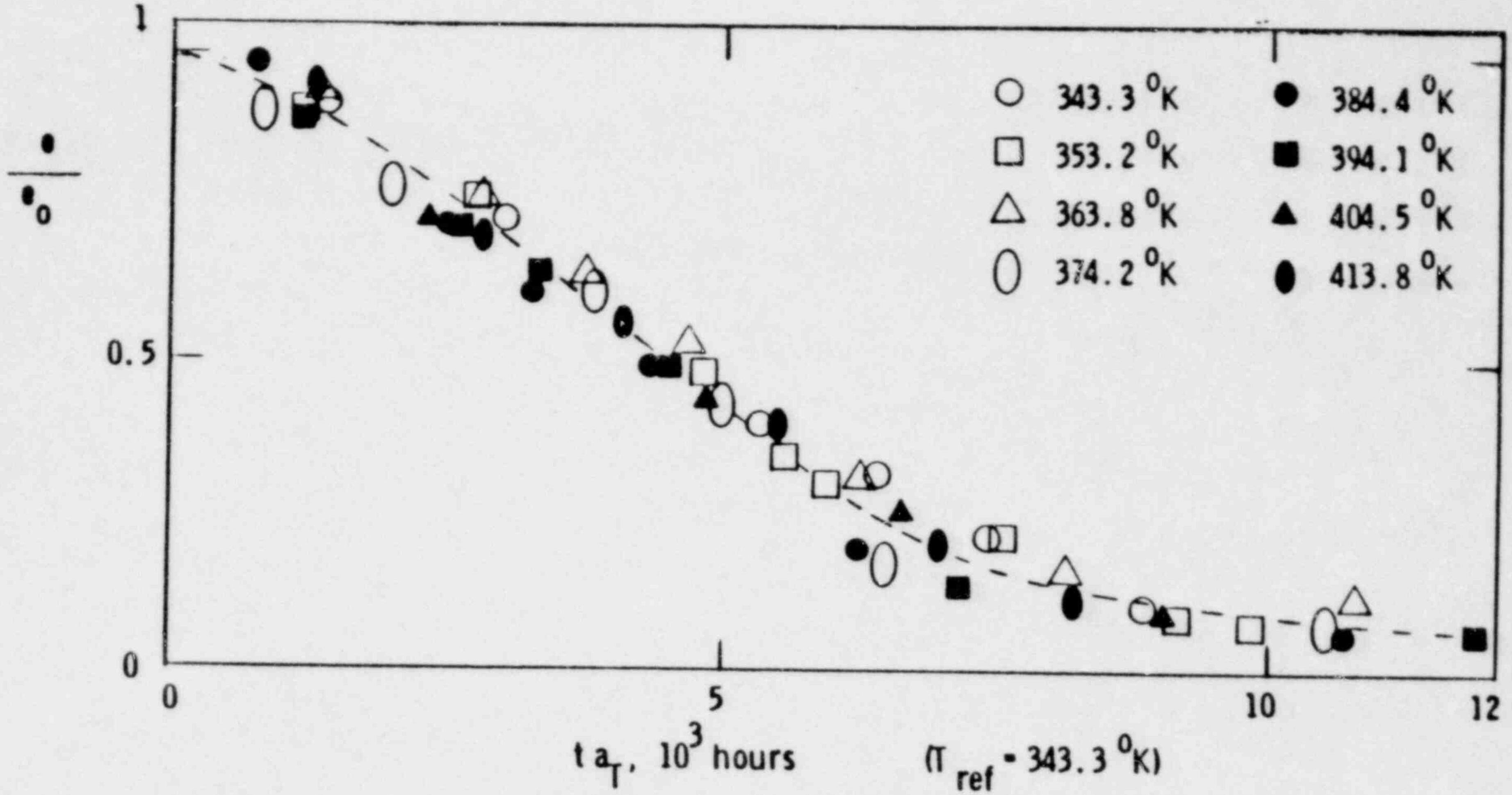
1
e/e0
0.5
0
0
1
2
3
4
AGING TIME, 10^3 hours



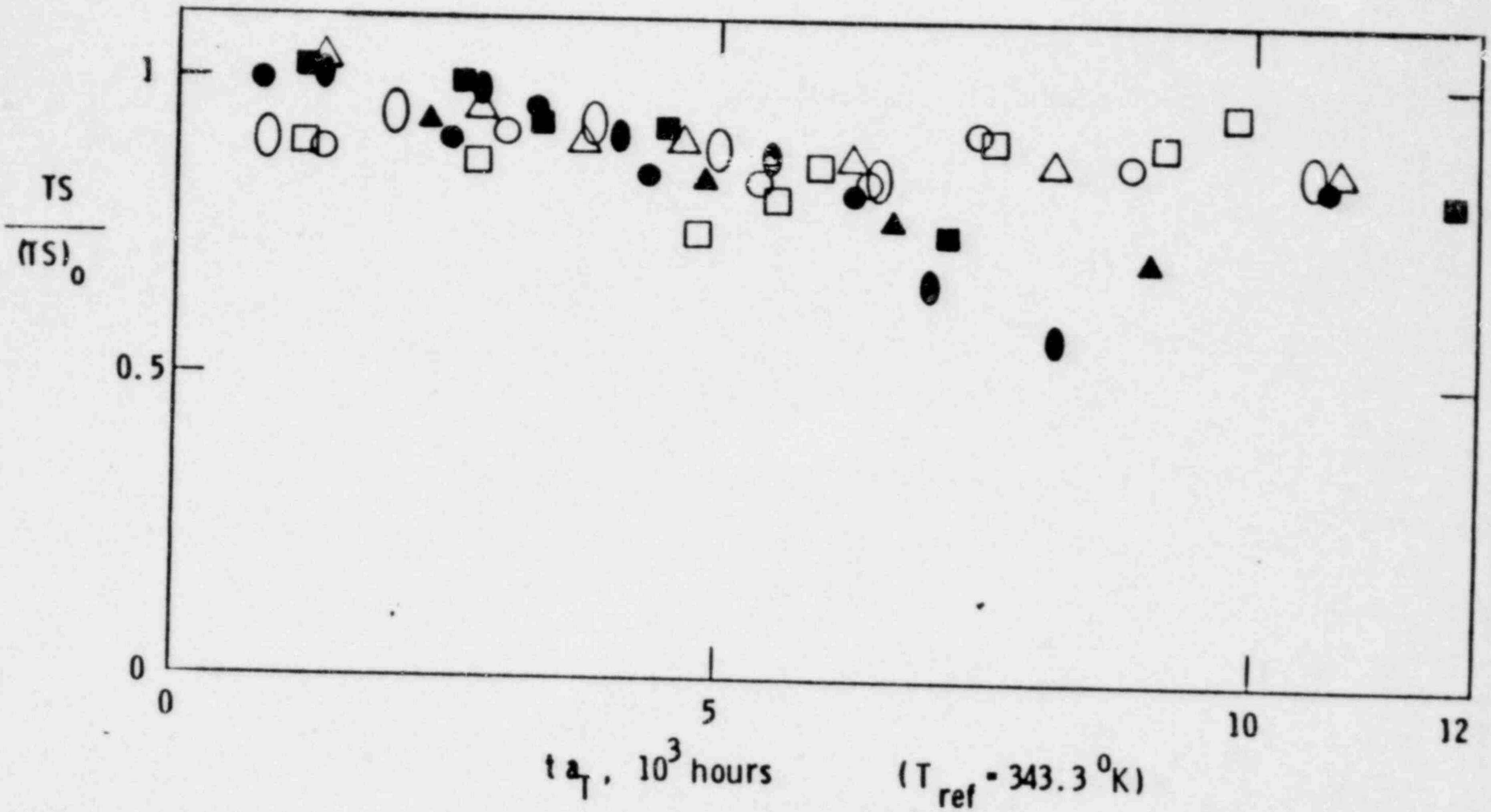
Ultimate tensile elongation (e) vs. aging time for chloroprene material at the indicated temperatures.

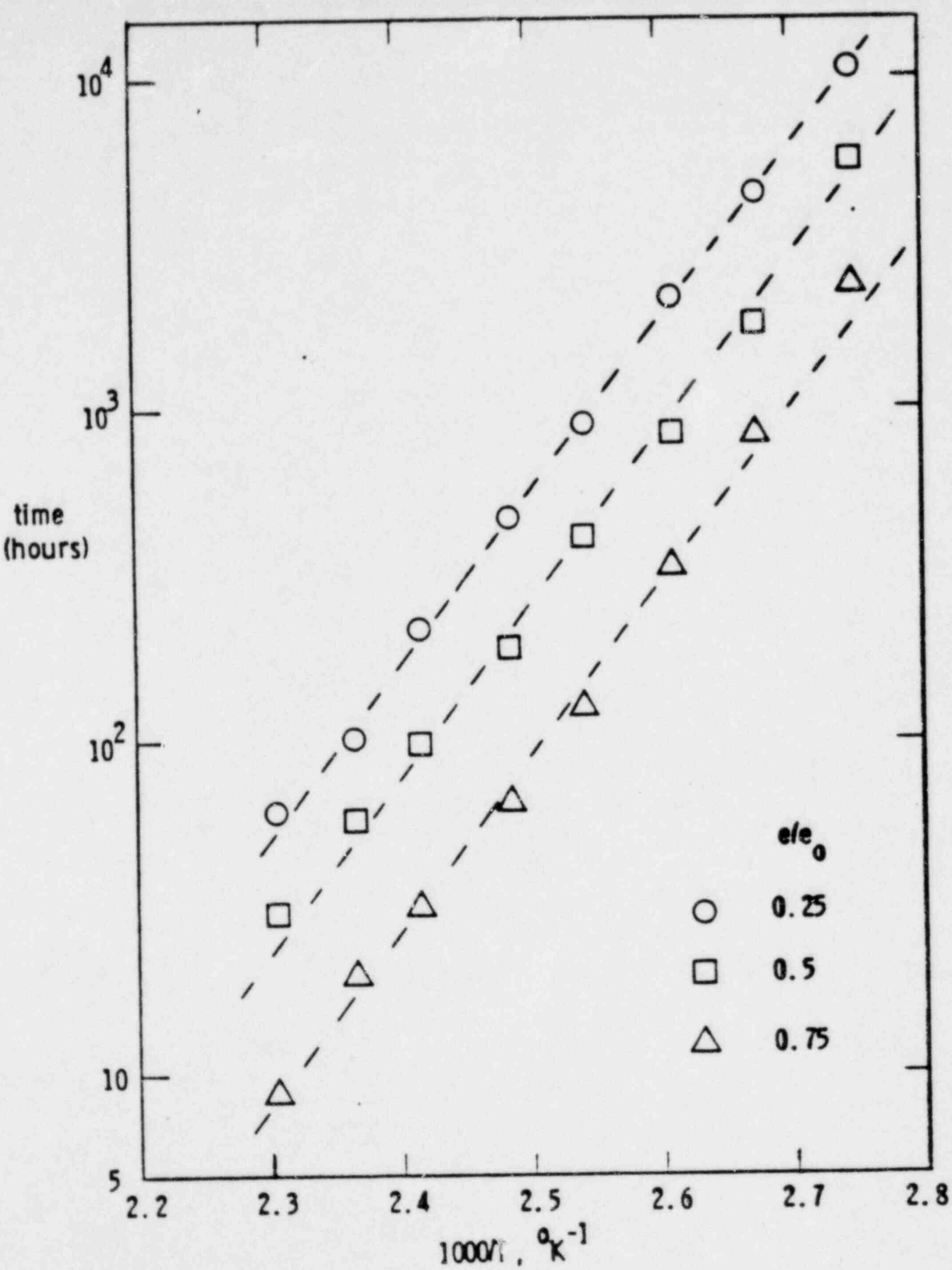


10^4
10^3
10^2
10
time (hours)
2.4
2.5
2.6
2.7
2.8
2.9
1000/T, °K^-1
e/e_o
0.25
0.5
0.75

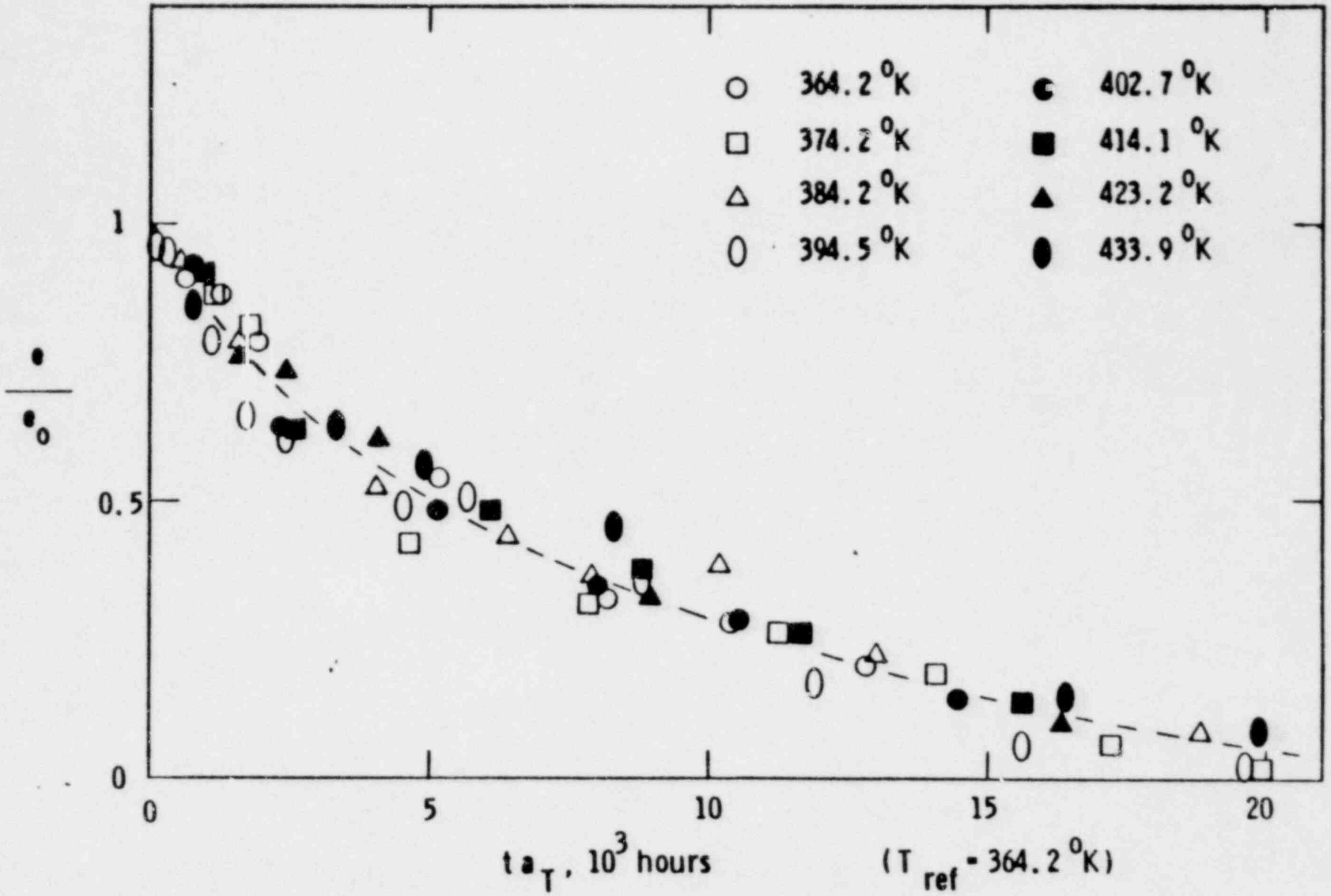


e/e_0
1
0.5
0
0
5
10
12
$t\,a_T$, 10^3 hours
(T_{ref} = 343.3 °K)
343.3 °K
353.2 °K
363.8 °K
374.2 °K
384.4 °K
394.1 °K
404.5 °K
413.8 °K

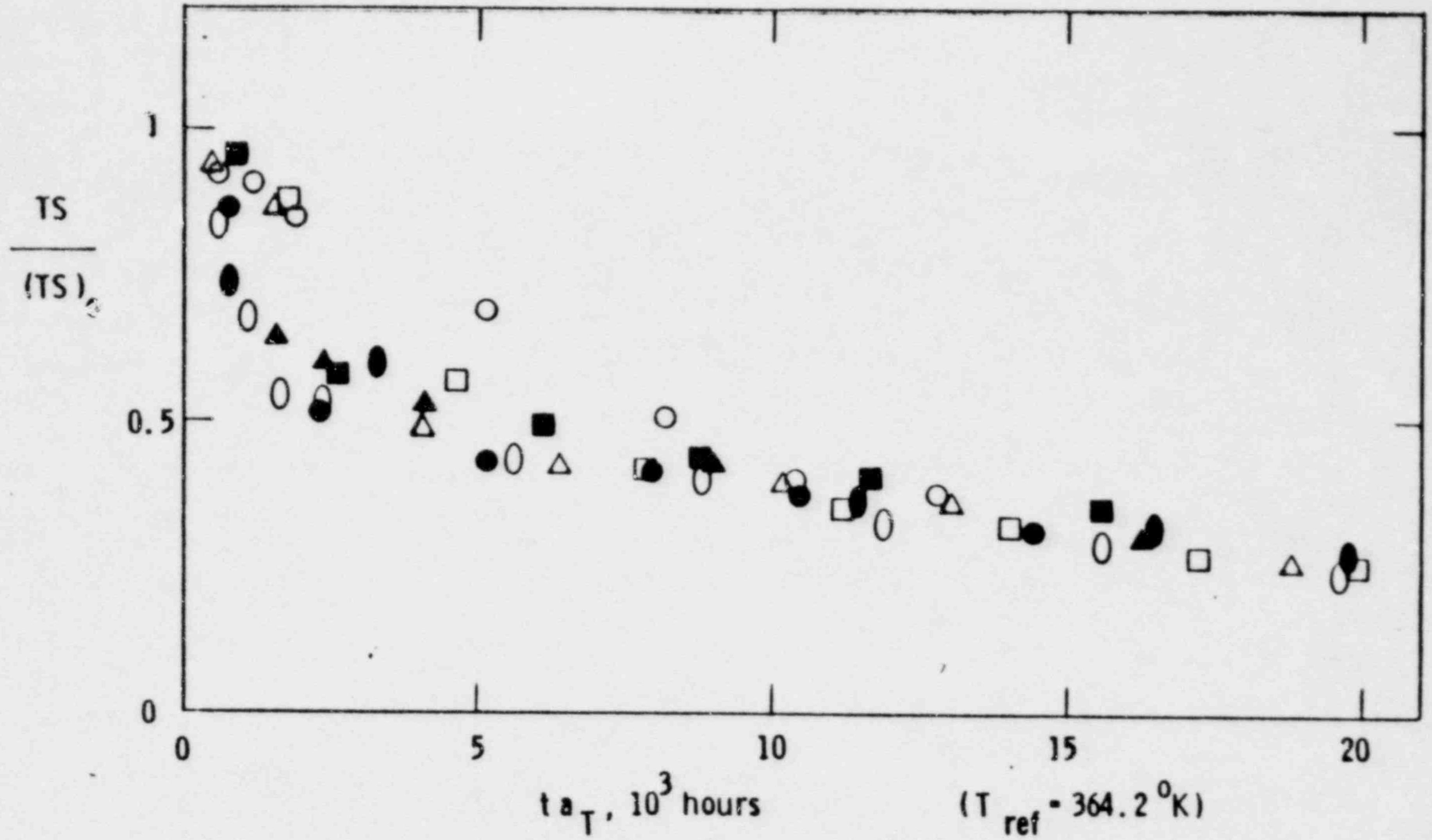

1
0.5
0
TS
(TS)o
0
5
10
12
t aT , 10³ hours
(T ref = 343.3 °K)



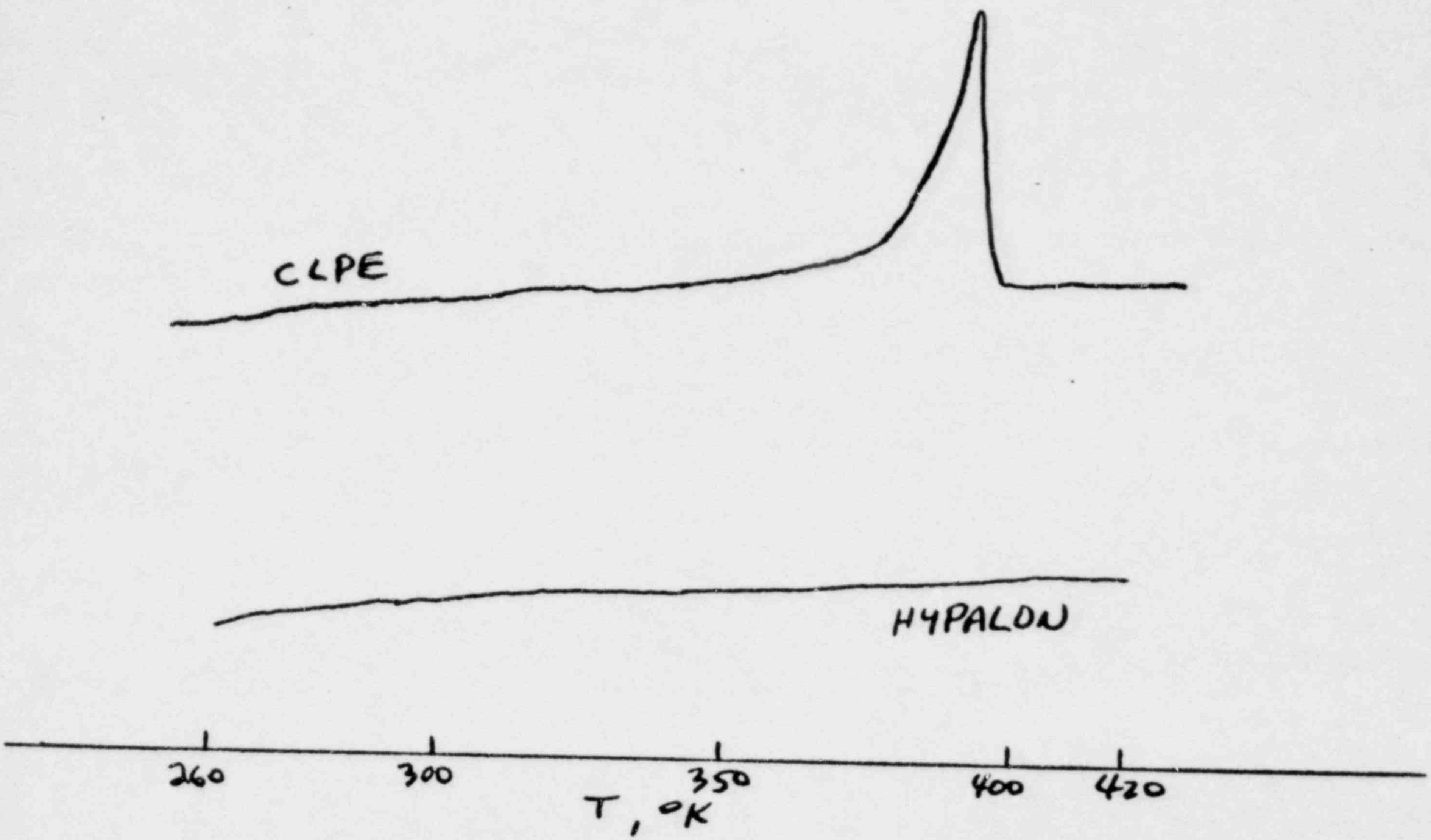
10^4
10^3
10^2
10
5
time
(hours)
e/e_o
0.25
0.5
0.75
2.2
2.3
2.4
2.5
2.6
2.7
2.8
1000/T, °K^-1

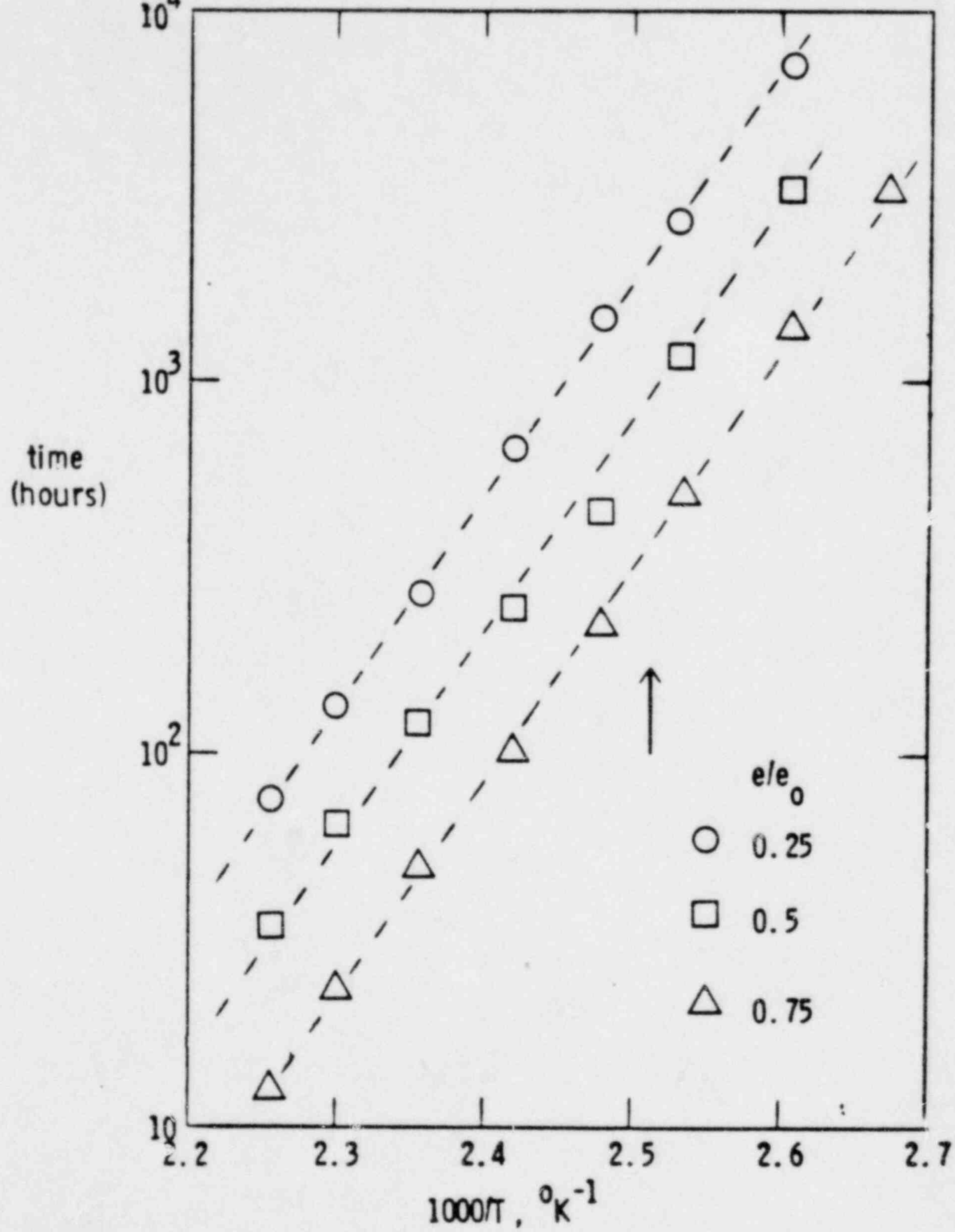


364.2 °K
374.2 °K
384.2 °K
394.5 °K
402.7 °K
414.1 °K
423.2 °K
433.9 °K
e / e_o
1
0.5
0
0
5
10
15
20
t a_T, 10^3 hours
(T_ref = 364.2 °K)

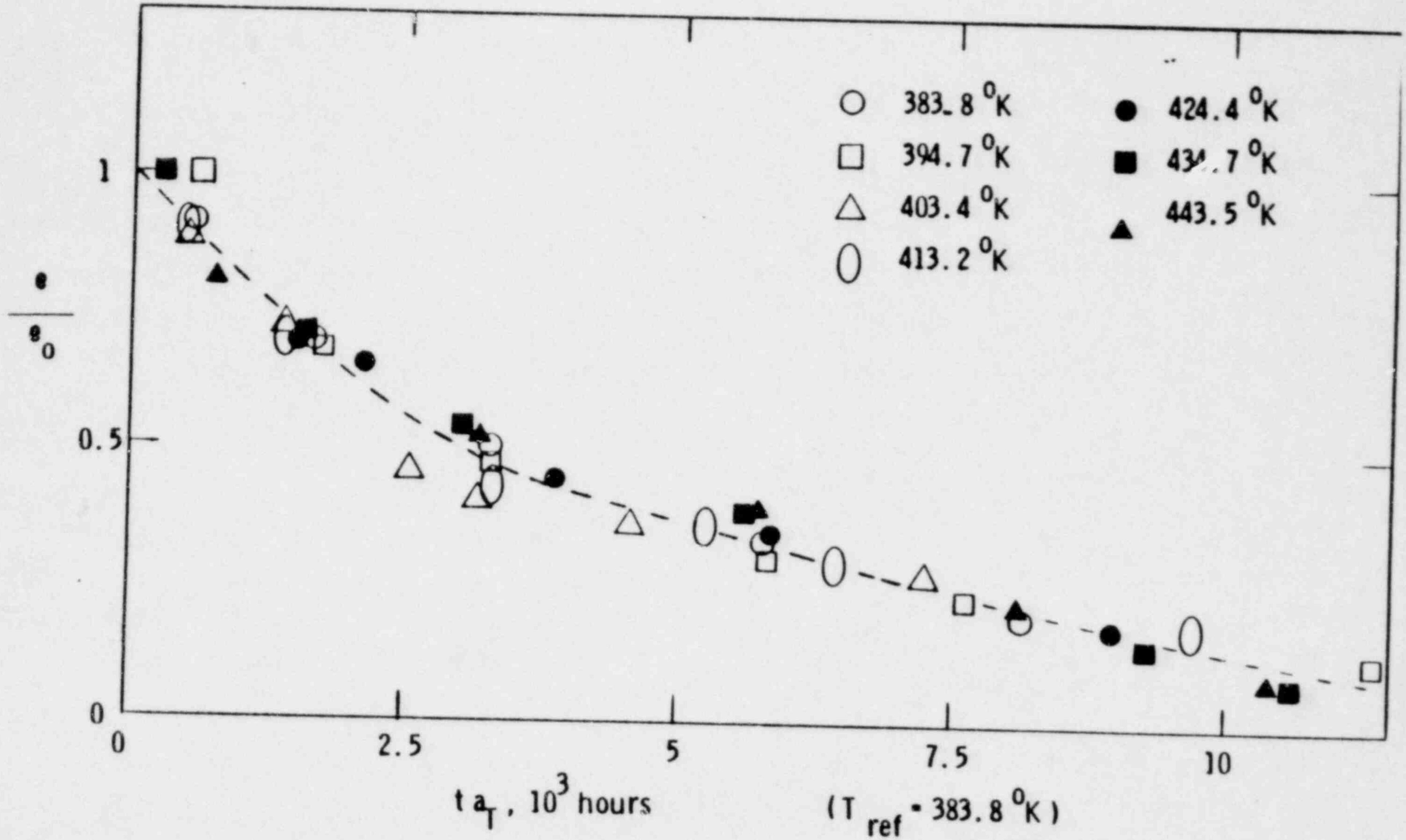

TS
(TS)₀
1
0.5
0
0
5
10
15
20
t a_T, 10^3 hours
(T_ref = 364.2 °K)

DSC SCANS

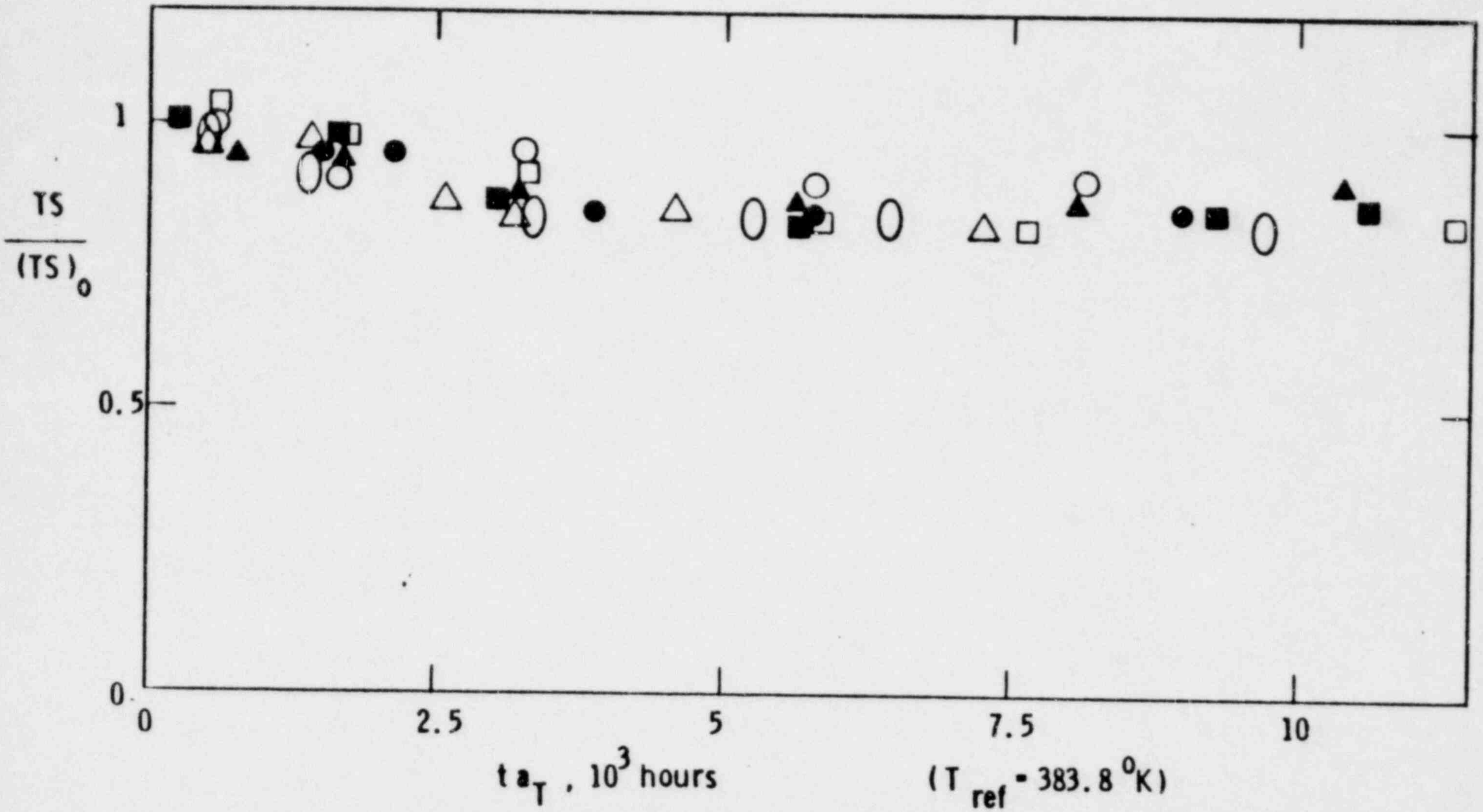


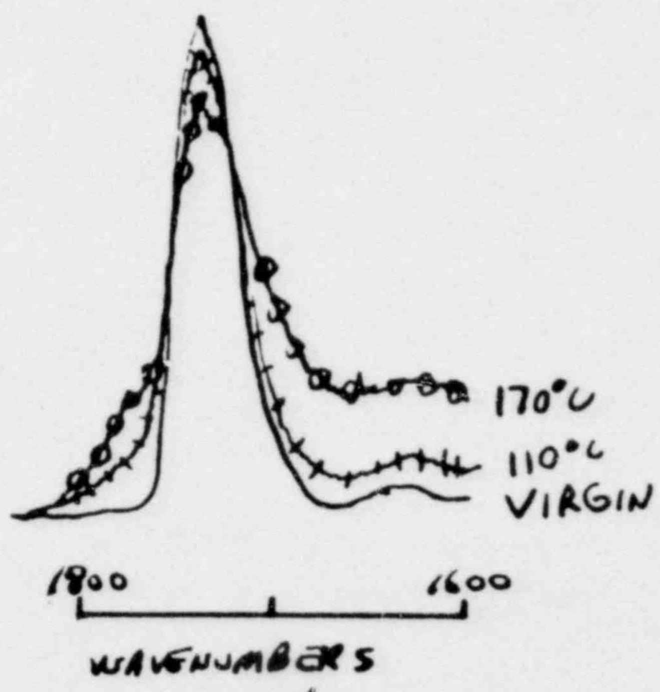


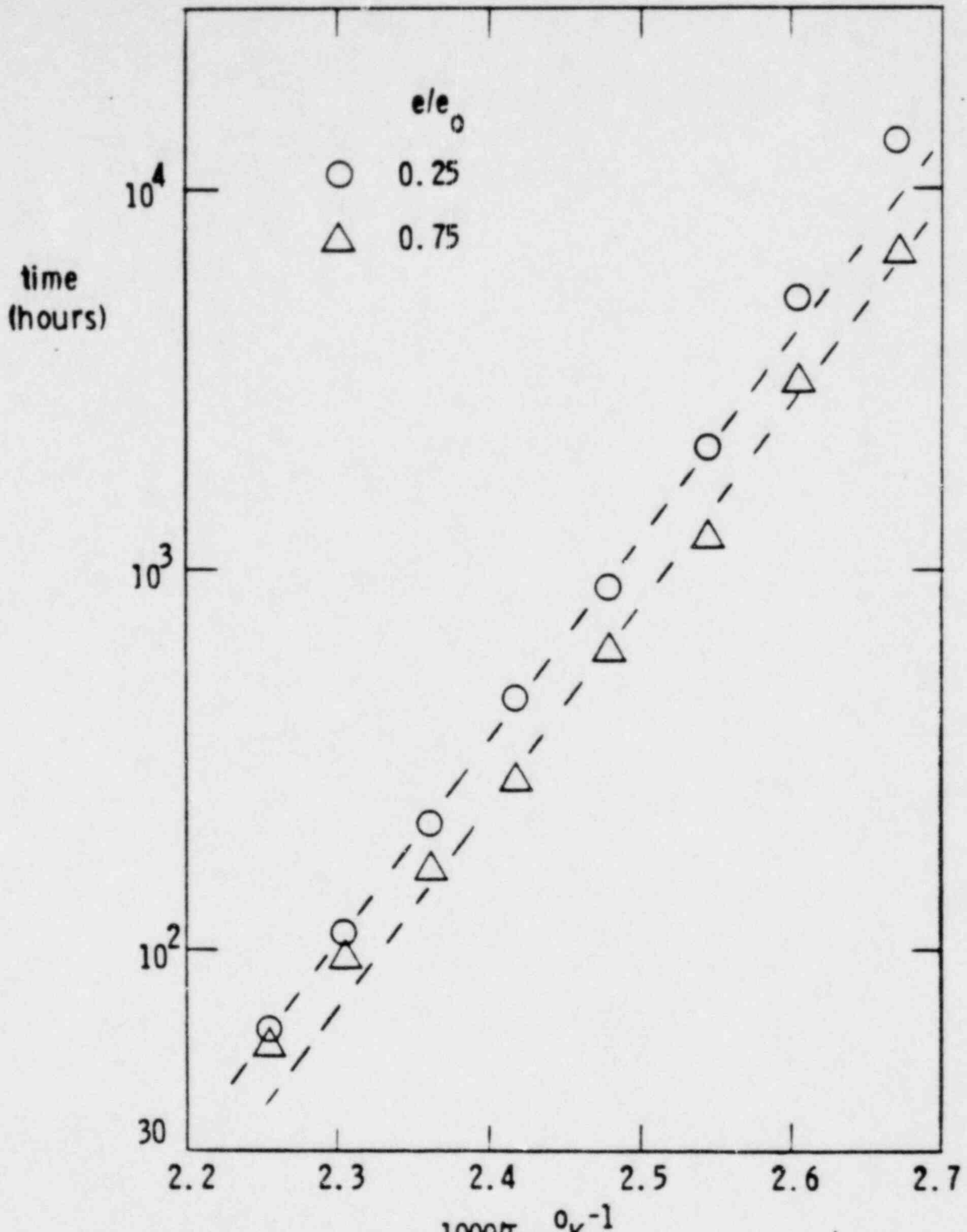
time
(hours)
10
10²
10³
10⁴
2.2
2.3
2.4
2.5
2.6
2.7
1000/T, °K⁻¹
e/e₀
0.25
0.5
0.75

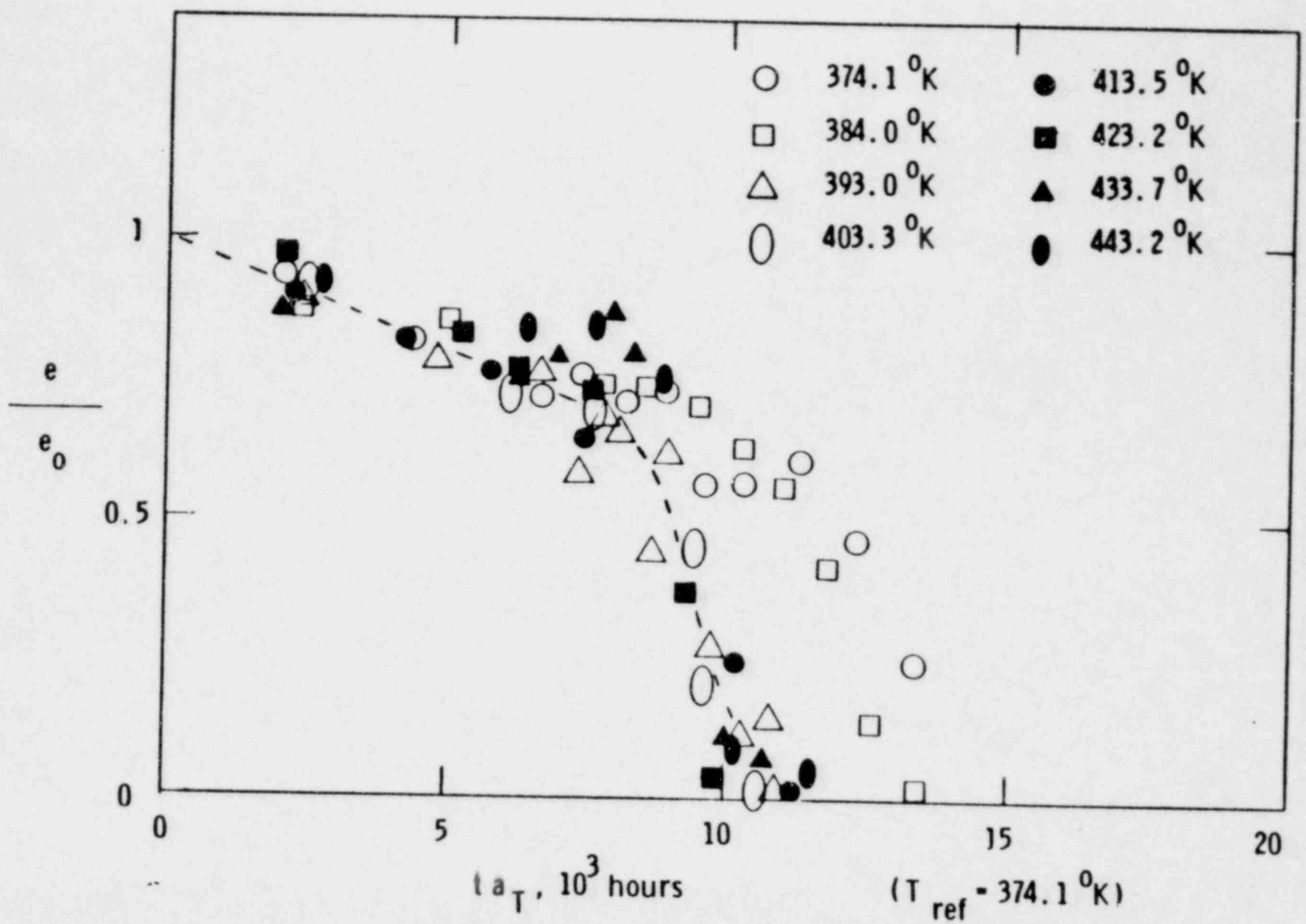


383.8 °K
394.7 °K
403.4 °K
413.2 °K
424.4 °K
434.7 °K
443.5 °K
1
0.5
0
2.5
5
7.5
10
t a_T , 10^3 hours
(T_ref = 383.8 °K)


TS
(TS)0
1
0.5
0
0
2.5
5
7.5
10
t aT , 10^3 hours
(T ref = 383.8 °K)

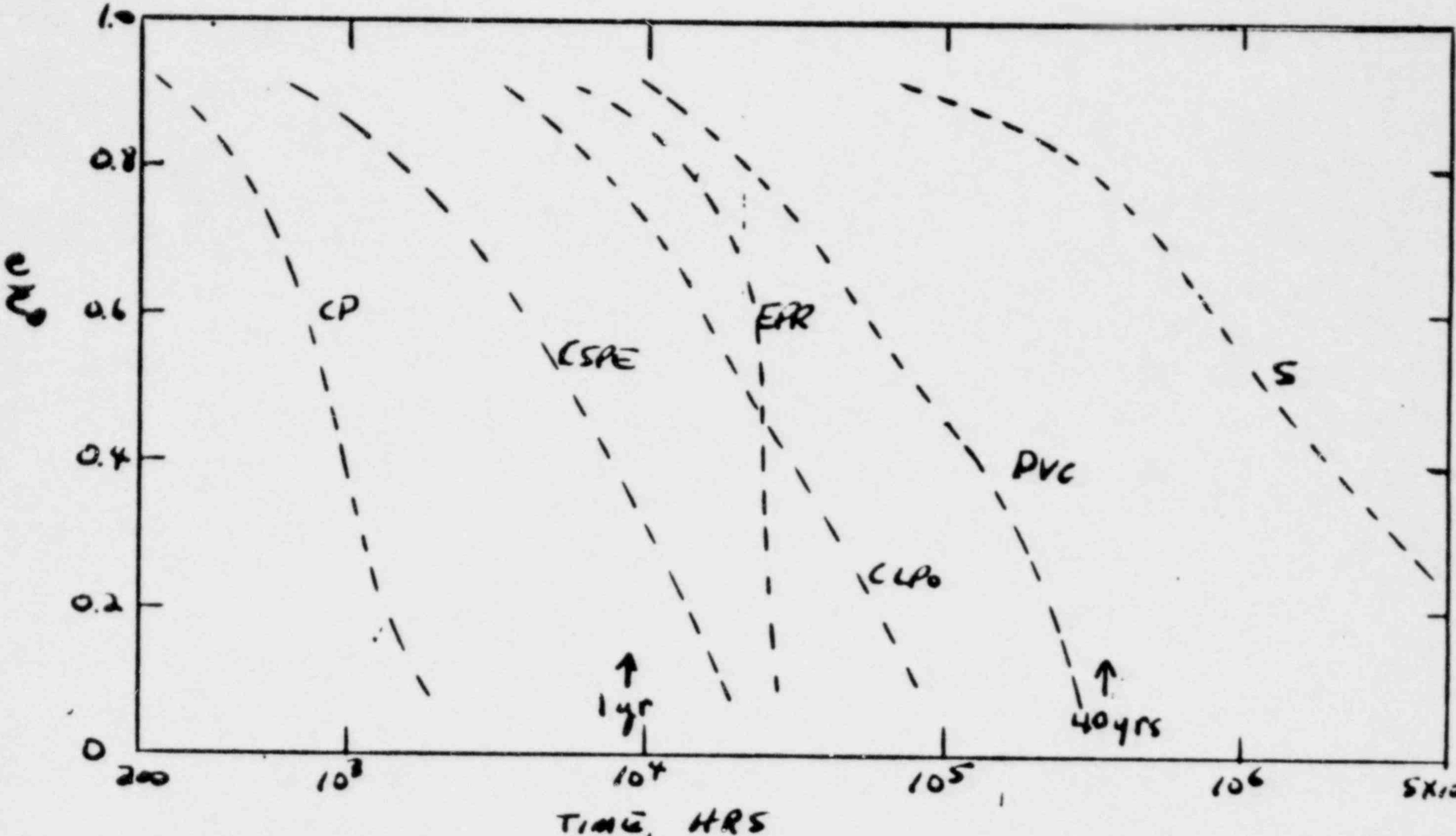

170°C
110°C
VIRGIN
1800
1600
WAVENUMBERS
cm⁻¹


e/e$_o$
0.25
0.75
time
(hours)
10^4
10^3
10^2
30
2.2
2.3
2.4
2.5
2.6
2.7
1000/T , $^oK^{-1}$



374.1 °K
384.0 °K
393.0 °K
403.3 °K
413.5 °K
423.2 °K
433.7 °K
443.2 °K
e / e0
1
0.5
0
0
5
10
15
20
t aT , 10^3 hours
(T ref - 374.1 °K)

EXTRAPOLATED OR INTERPOLATED RESULTS AT 90°C



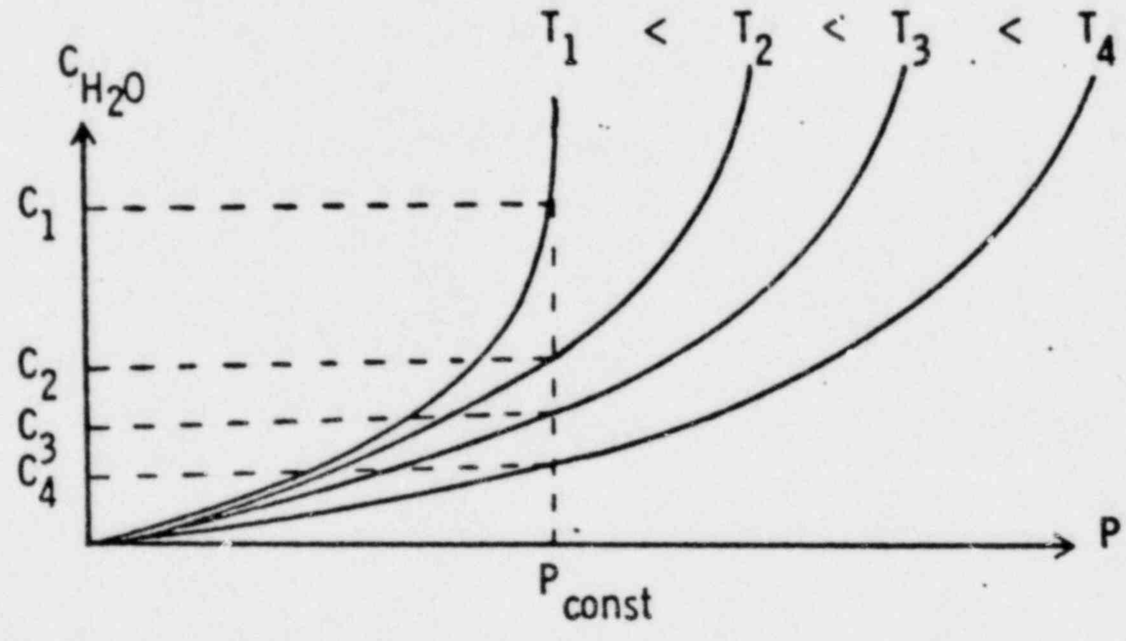
HUMIDITY AGING

TYPICAL KINETIC EXPRESSION

$$Rate = k(T)\, C_A^a\, C_{H_2O}(T)$$

$$C_{H_2O} = \sigma(P)\; P$$

solubility coeff. ↑ partial pressure



At P_{const}, Rate is non-Arrhenius with temperature

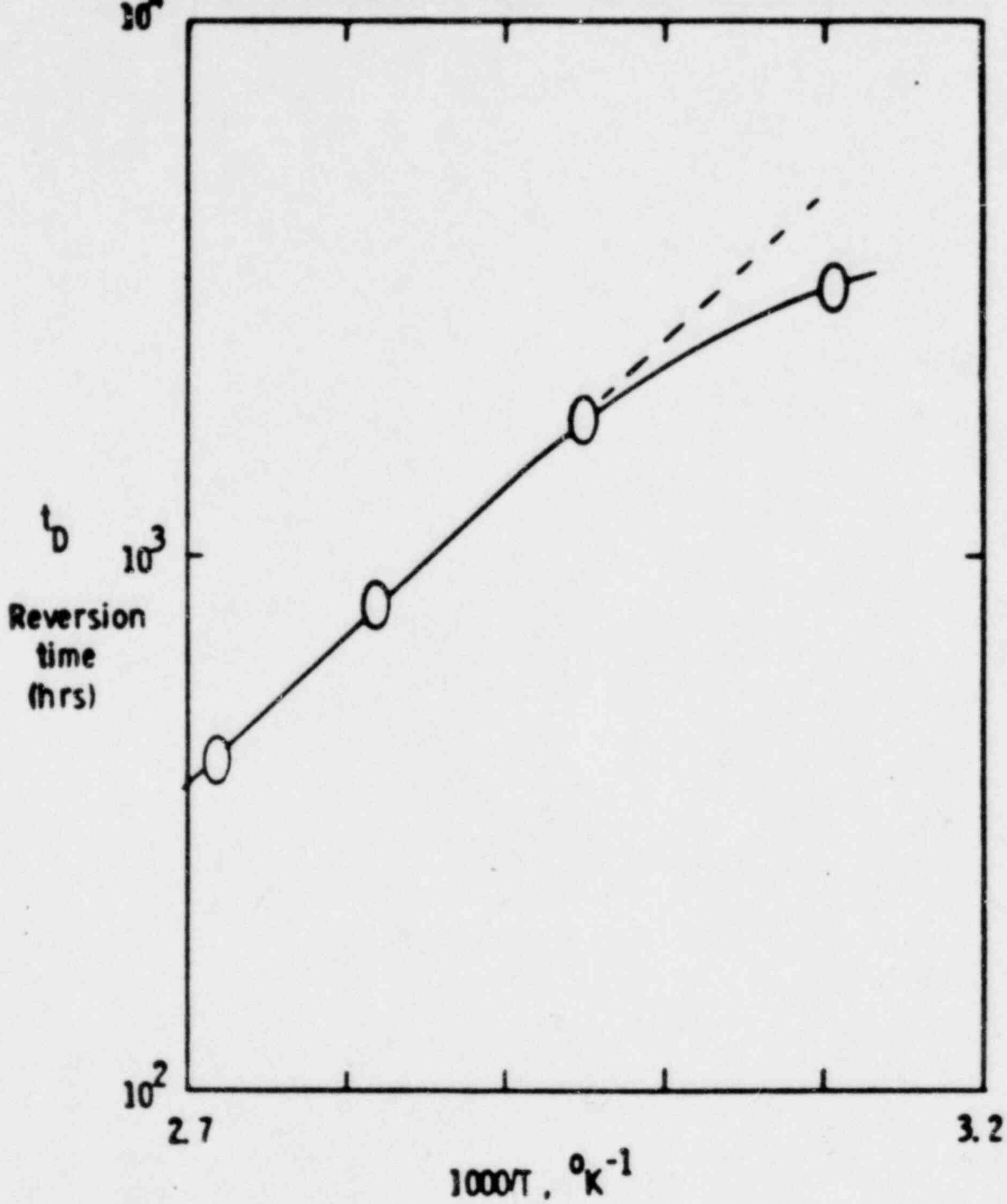
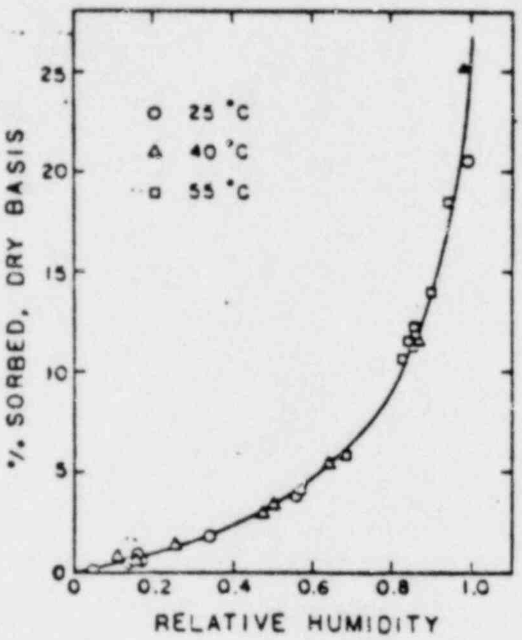


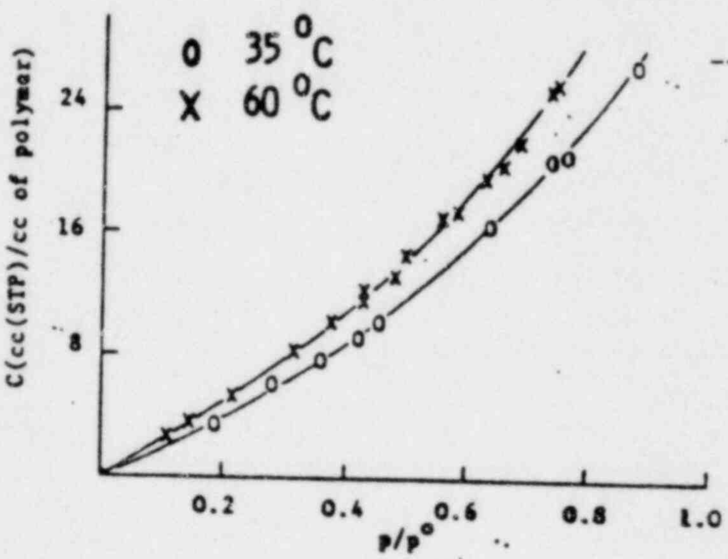
FIGURE 2

HUMIDITY ISOTHERMS VS. P/P_0 (RELATIVE HUMIDITY)

Ref. 3



Ref. 4



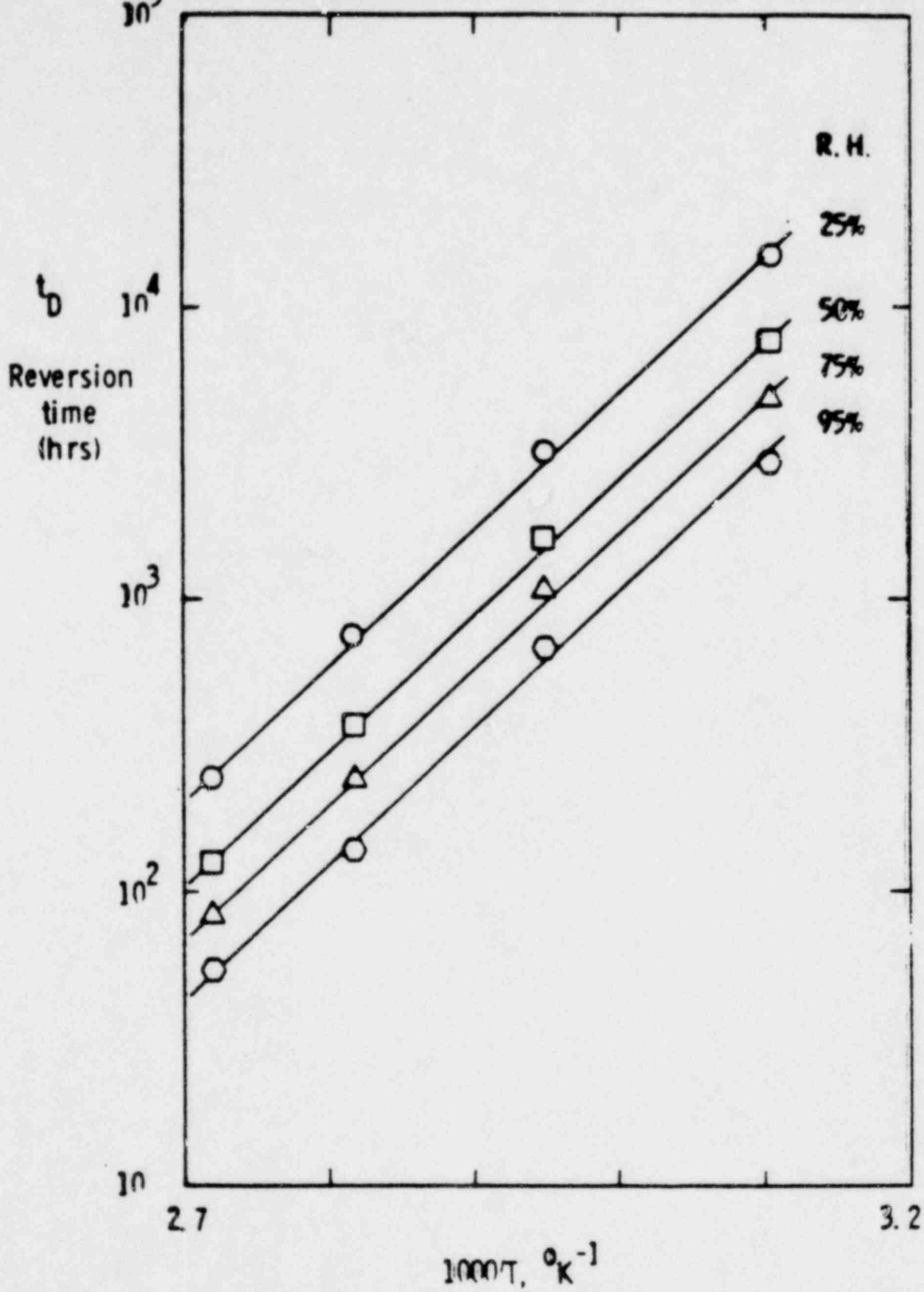
$$\sigma(RH) = \sigma_0(RH) \exp(-\Delta H(RH)/RT)$$

$\Delta H(RH)$ typically small

DO ACCELERATED AGING AT CONSTANT RH

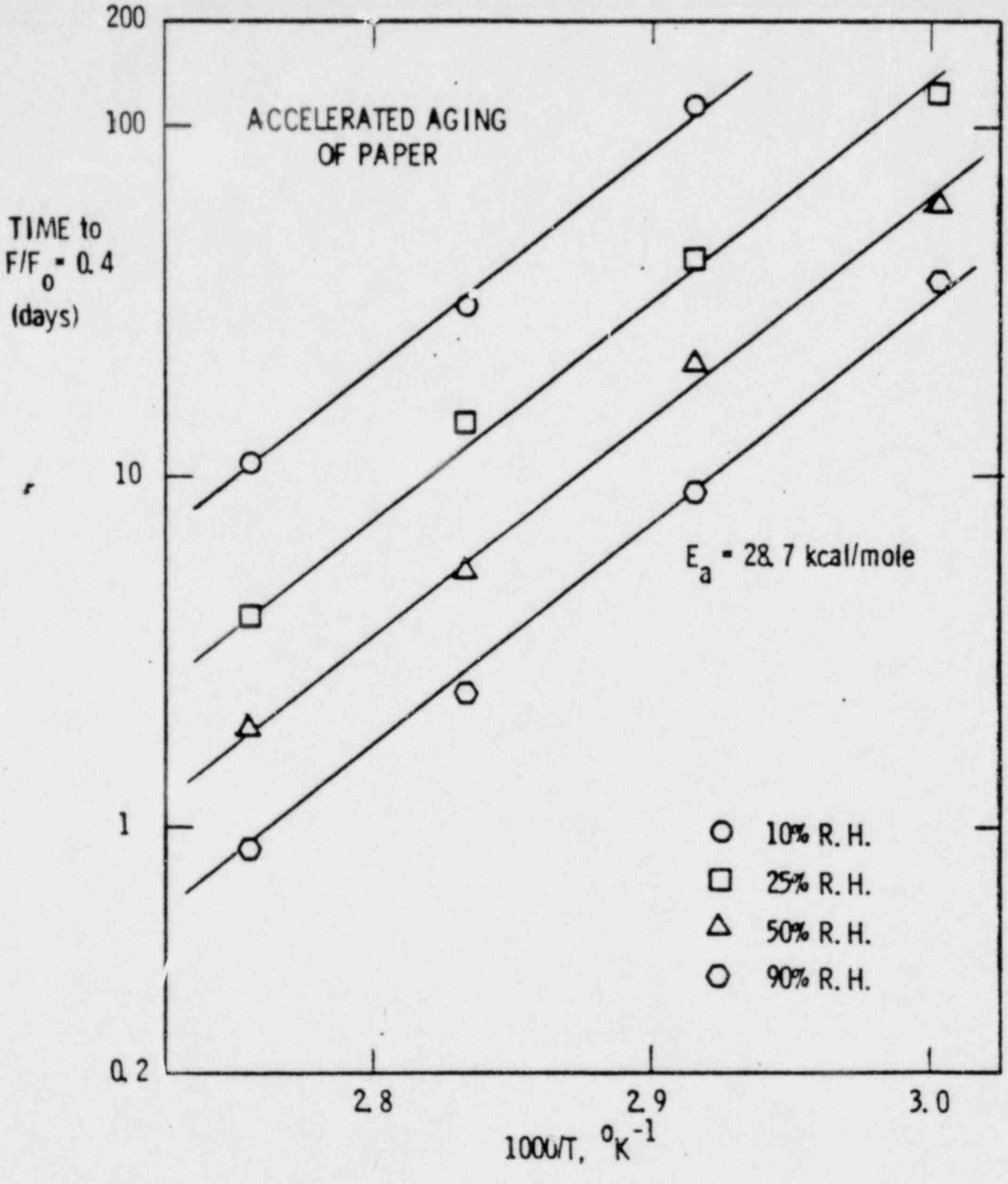
$$k_{eff} = k\, C_{H_2O}^{b} \propto \exp(-E_a/RT) \exp[-b\, \Delta H(RH)/RT]$$

$$E_{eff} = E_a + b\, \Delta H(RH)$$



R.H.
25%
50%
75%
95%
t_D
Reversion time (hrs)
10^5
10^4
10^3
10^2
10
2.7
3.2
1000/T, $^oK^{-1}$

FIGURE 5

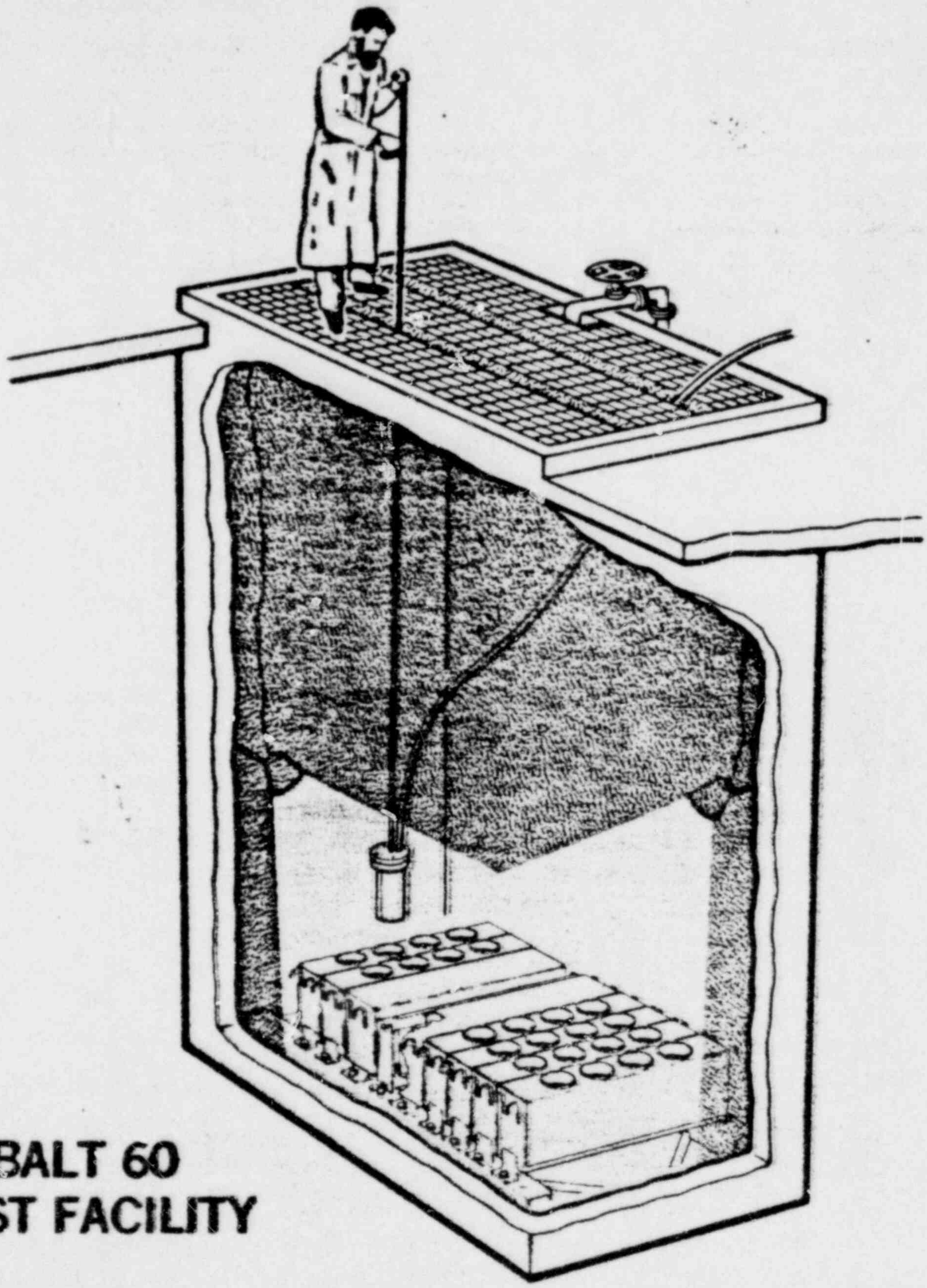

ACCELERATED AGING OF PAPER
TIME to F/F_o = 0.4 (days)
200
100
10
1
0.2
2.8
2.9
3.0
1000/T, $^oK^{-1}$
E_a = 28.7 kcal/mole
10% R. H.
25% R. H.
50% R. H.
90% R. H.

SUMMARY

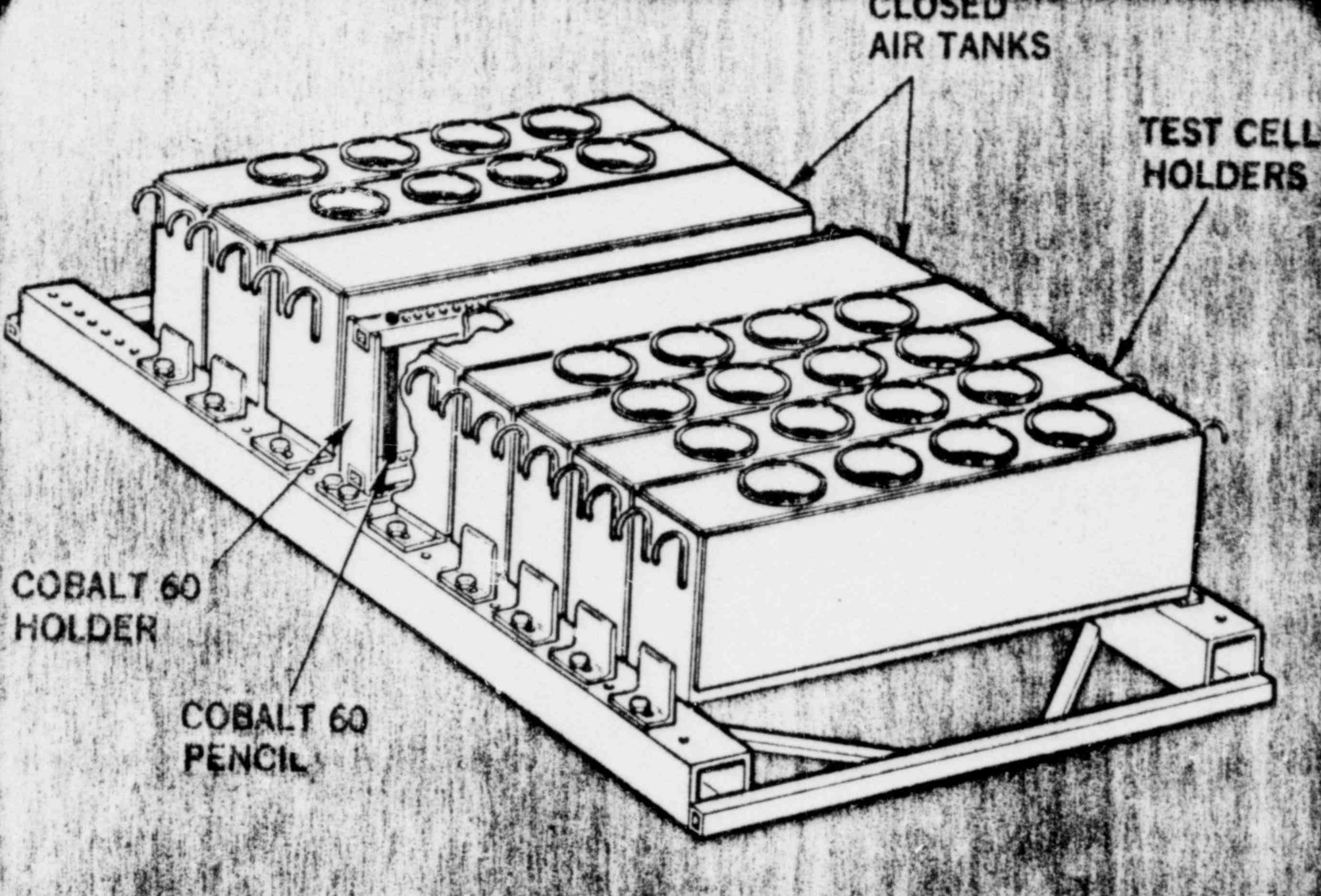
1. DETERMINE FAILURE MODES, IMPORTANT STRESSES, APPROPRIATE MATERIAL DAMAGE PARAMETERS

2. CHECK FOR SUPERPOSITION, THEN DETERMINE AND RATIONALIZE $A_T(T)$
   a. USE LARGE RANGE OF STRESS LEVELS
   b. KEEP EXTRAPOLATIONS TO A MINIMUM
   c. DON'T EXTRAPOLATE THROUGH A TRANSITION

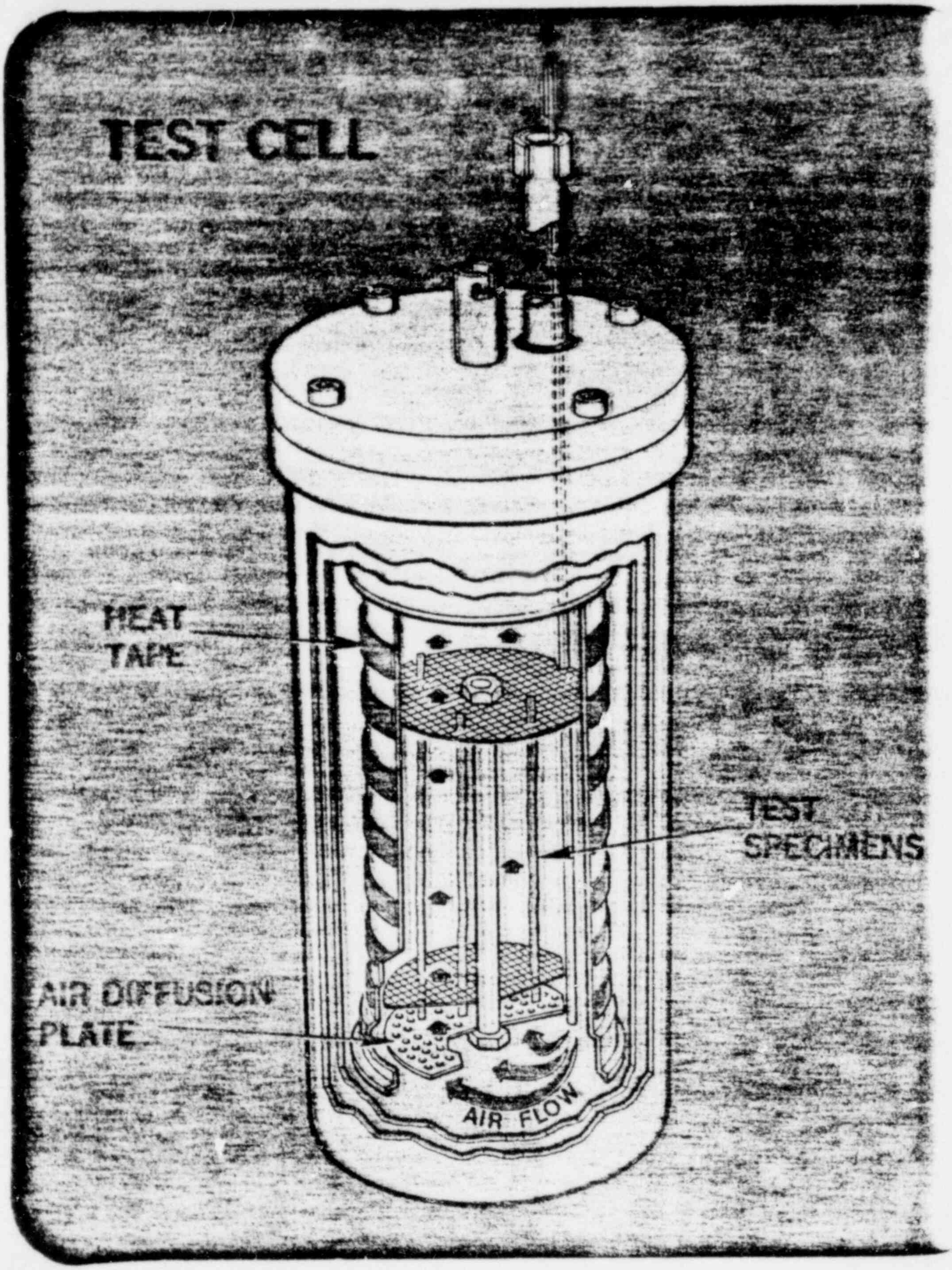
3. FOR HUMIDITY AGING, ANALYZE AT CONSTANT REL. HUM.

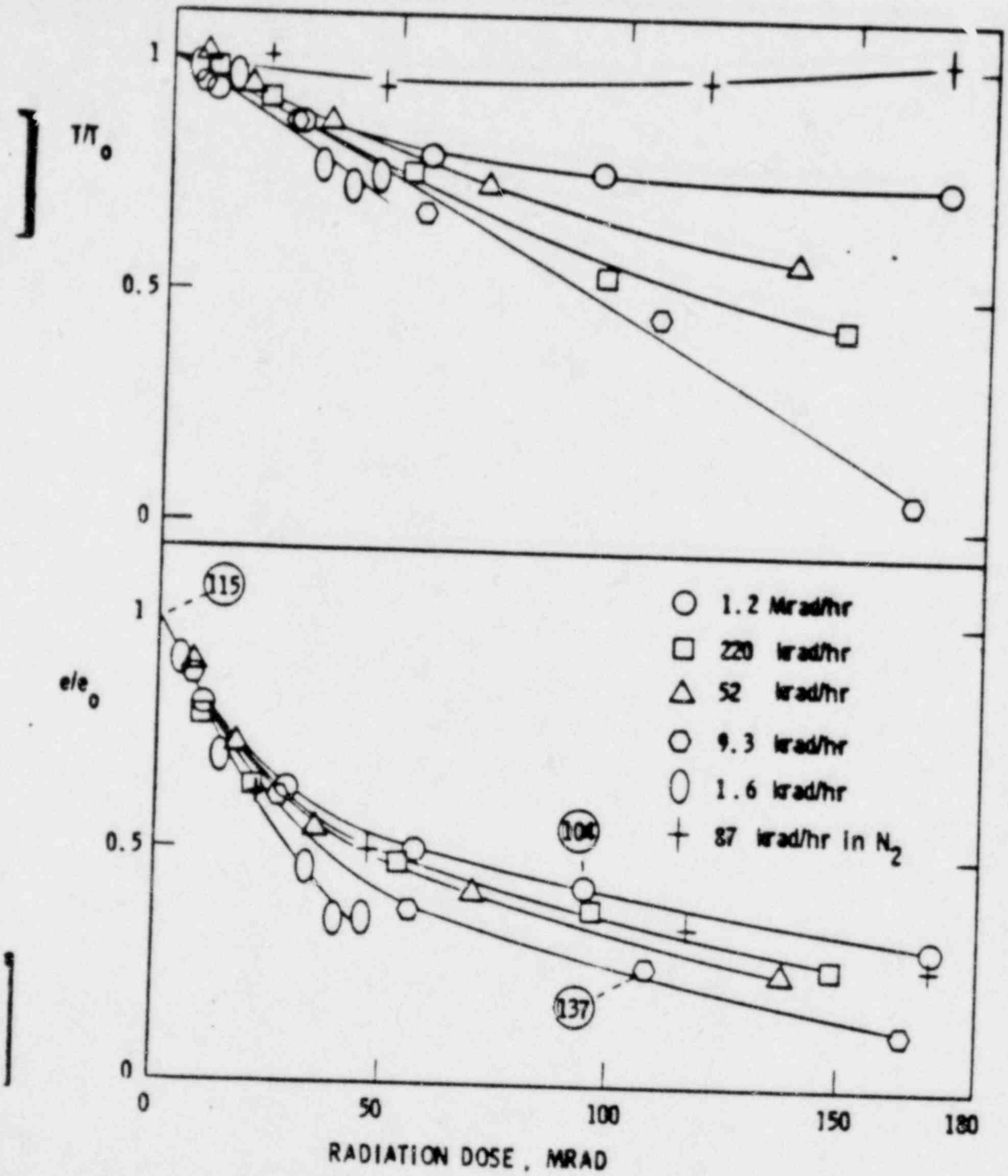


COBALT 60
TEST FACILITY

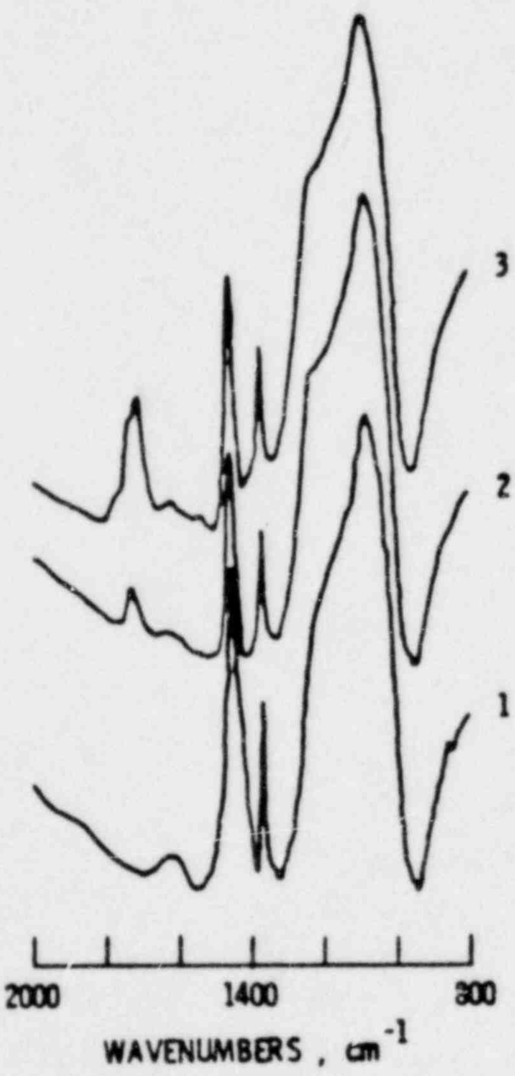


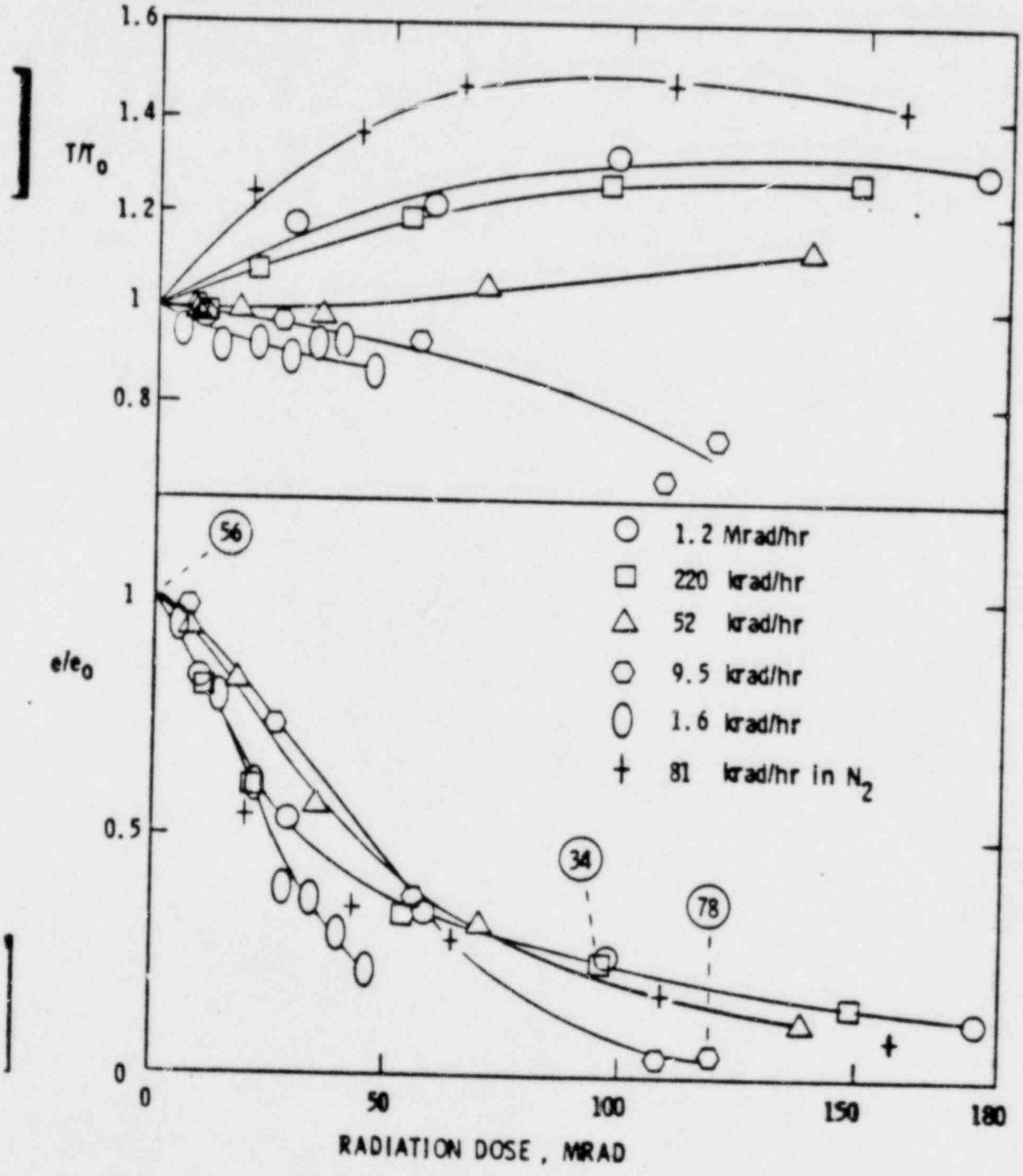
LINEAR ARRAY RADIATION SOURCE


TEST CELL
HEAT TAPE
TEST SPECIMENS
AIR DIFFUSION PLATE
AIR FLOW

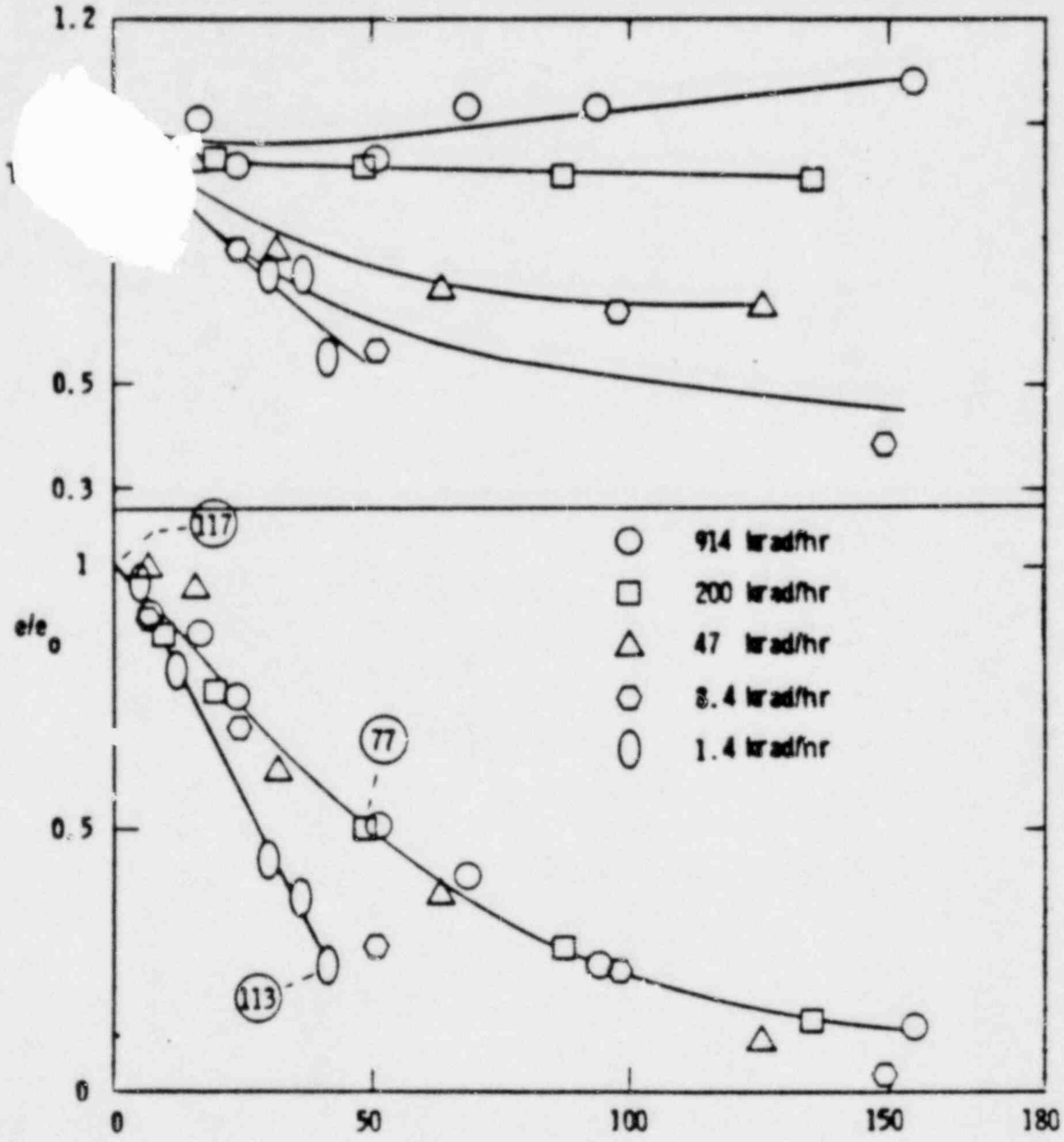


T/T$_0$
1
0.5
0
e/e$_0$
1
0.5
0
115
100
137
1.2 Mrad/hr
220 krad/hr
52 krad/hr
9.3 krad/hr
1.6 krad/hr
87 krad/hr in N_2
0
50
100
150
180
RADIATION DOSE, MRAD


3
2
1
2000
1400
800
WAVENUMBERS , cm-1

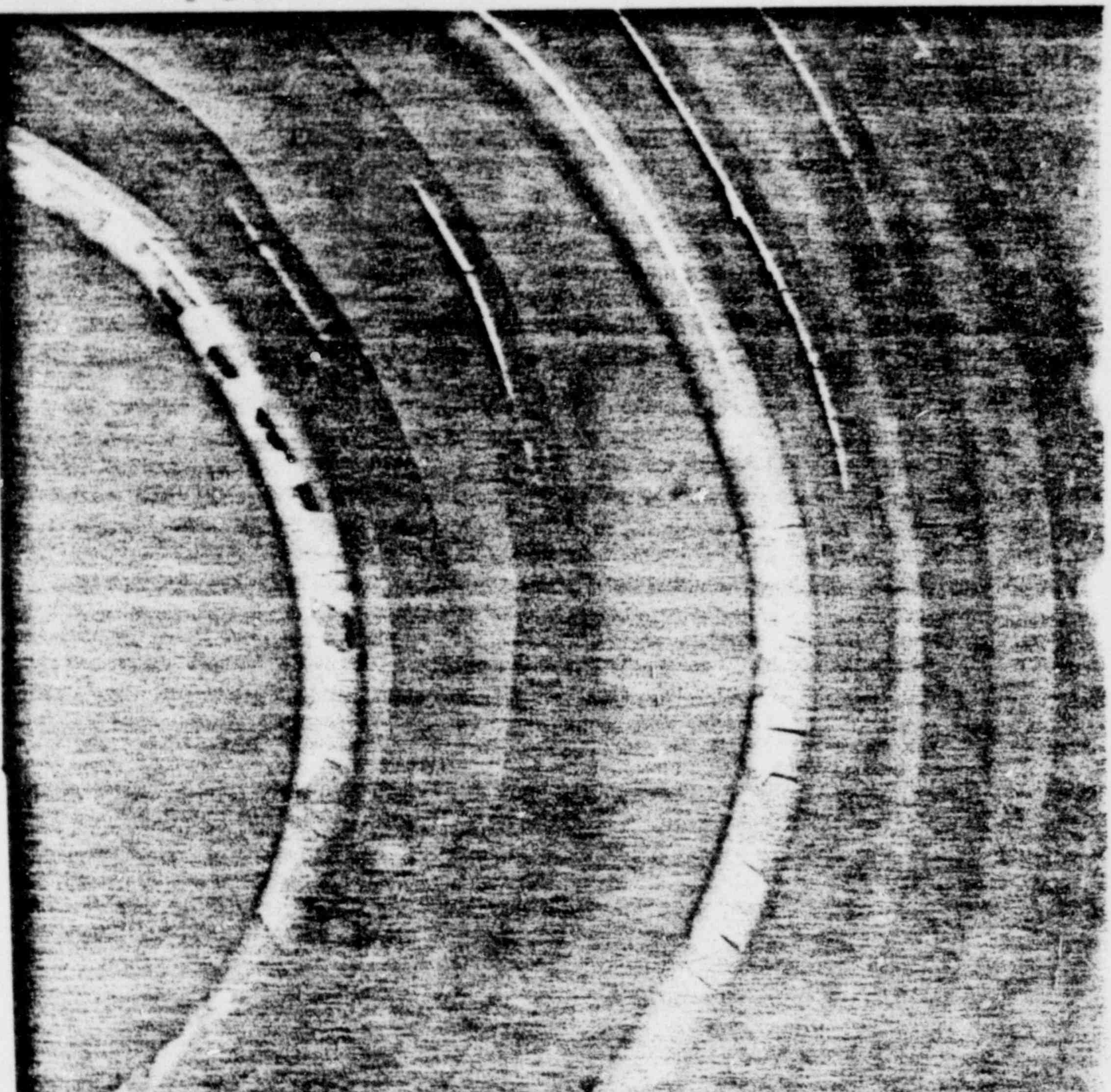


1.6
1.4
T/T_0
1.2
1
0.8
56
1
e/e_0
0.5
0
34
78
1.2 Mrad/hr
220 krad/hr
52 krad/hr
9.5 krad/hr
1.6 krad/hr
81 krad/hr in N_2
0
50
100
150
180
RADIATION DOSE, MRAD



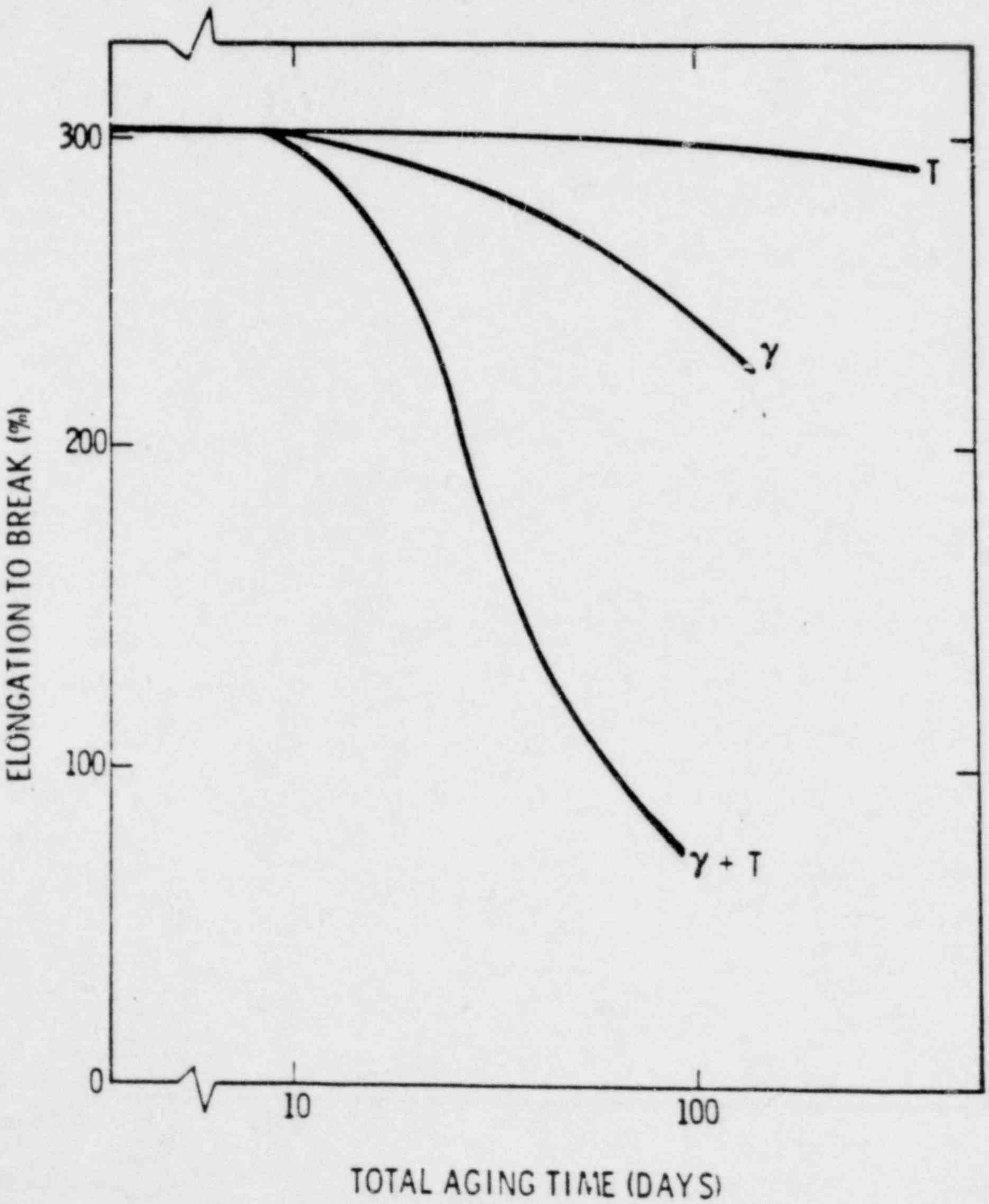
1.2
1
0.5
0.3
1
0.5
0
e/e₀
117
77
113
914 krad/hr
200 krad/hr
47 krad/hr
8.4 krad/hr
1.4 krad/hr
0
50
100
150
180
RADIATION DOSE , MRAD

80 142



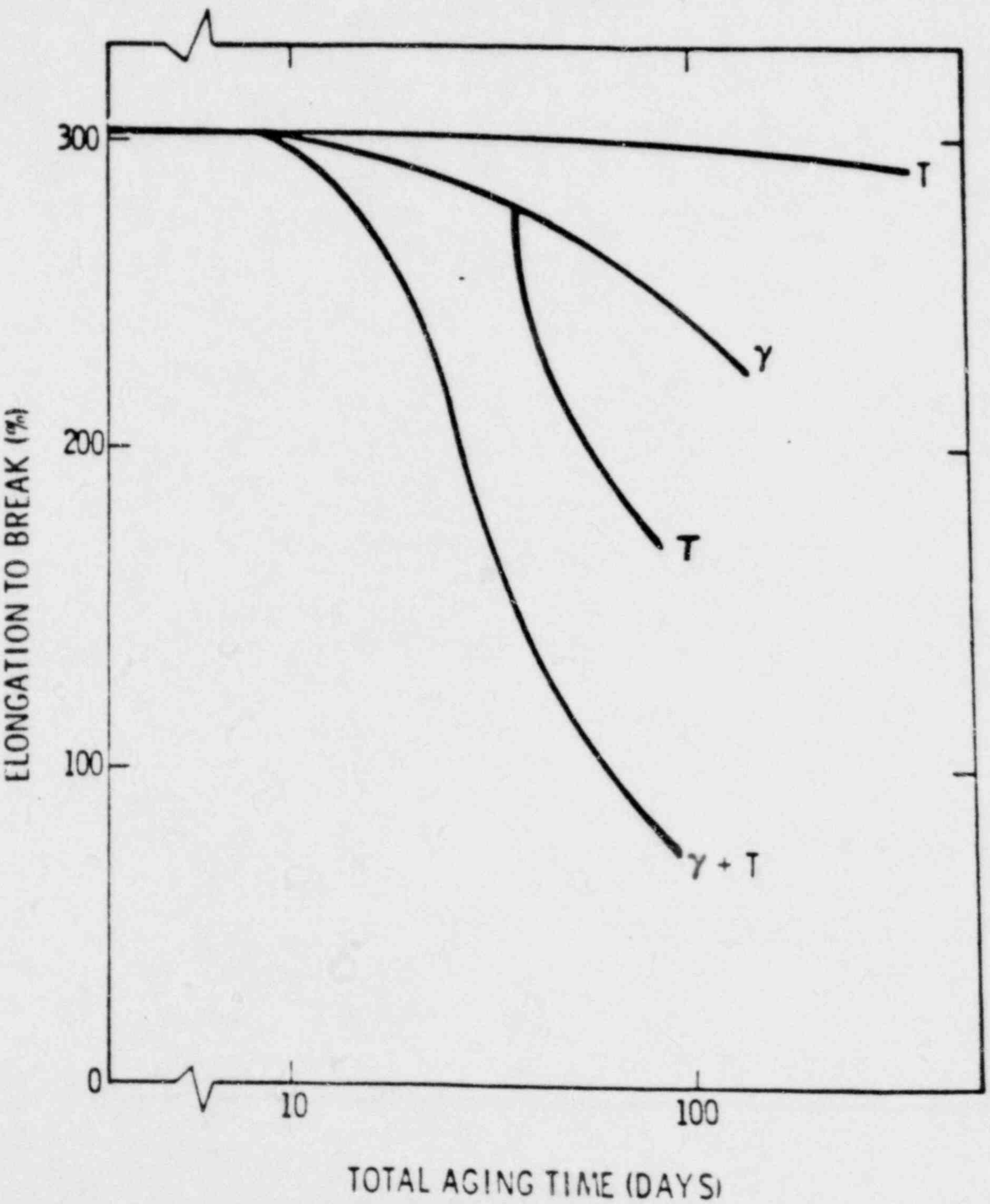
POLYVINYL CHLORIDE DEGRADATION

γ: .1 MRAD/DAY   T: 80°C



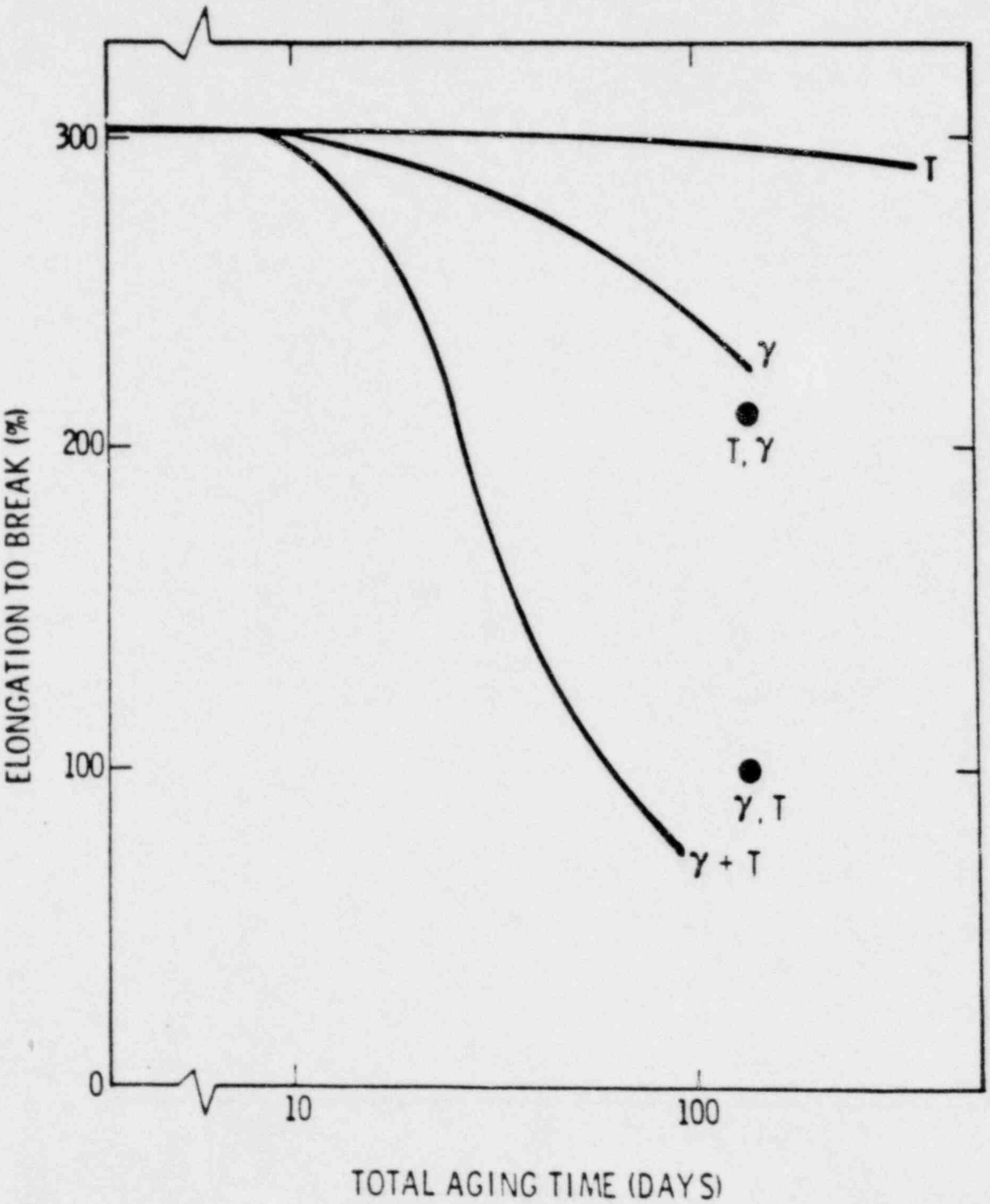
POLYVINYL CHLORIDE DEGRADATION

γ: .1 MRAD/DAY T: 80°C

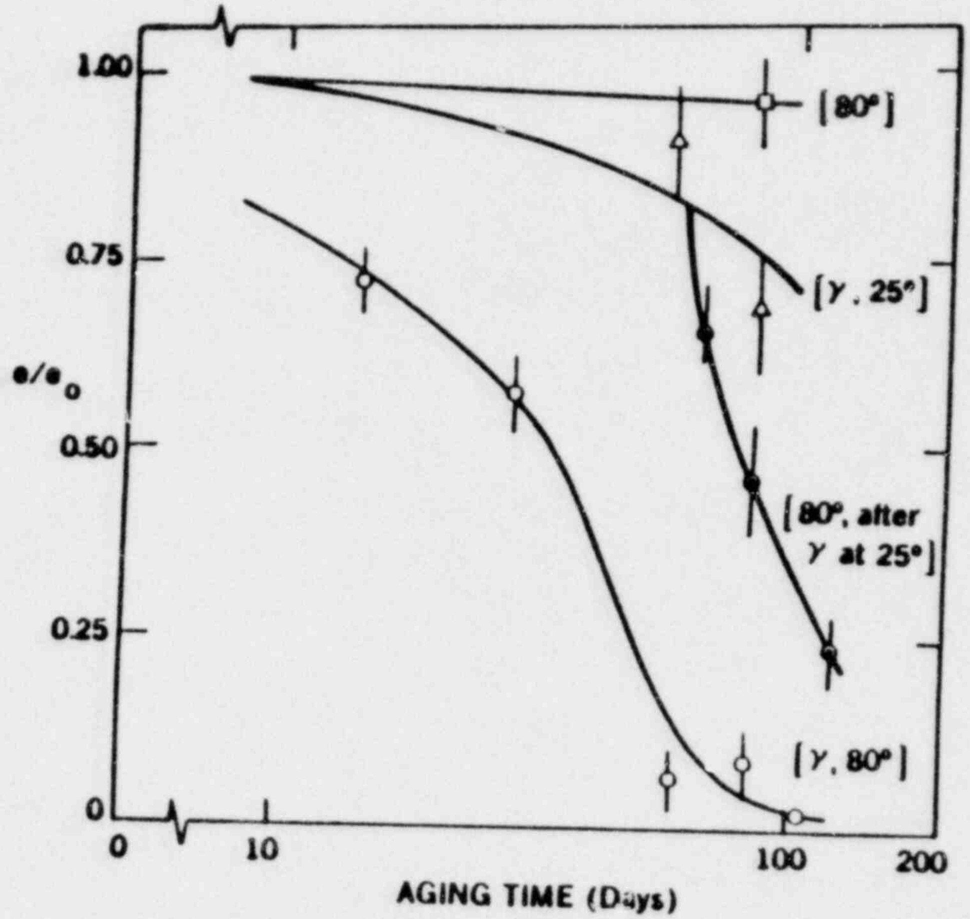


POLYVINYL CHLORIDE DEGRADATION

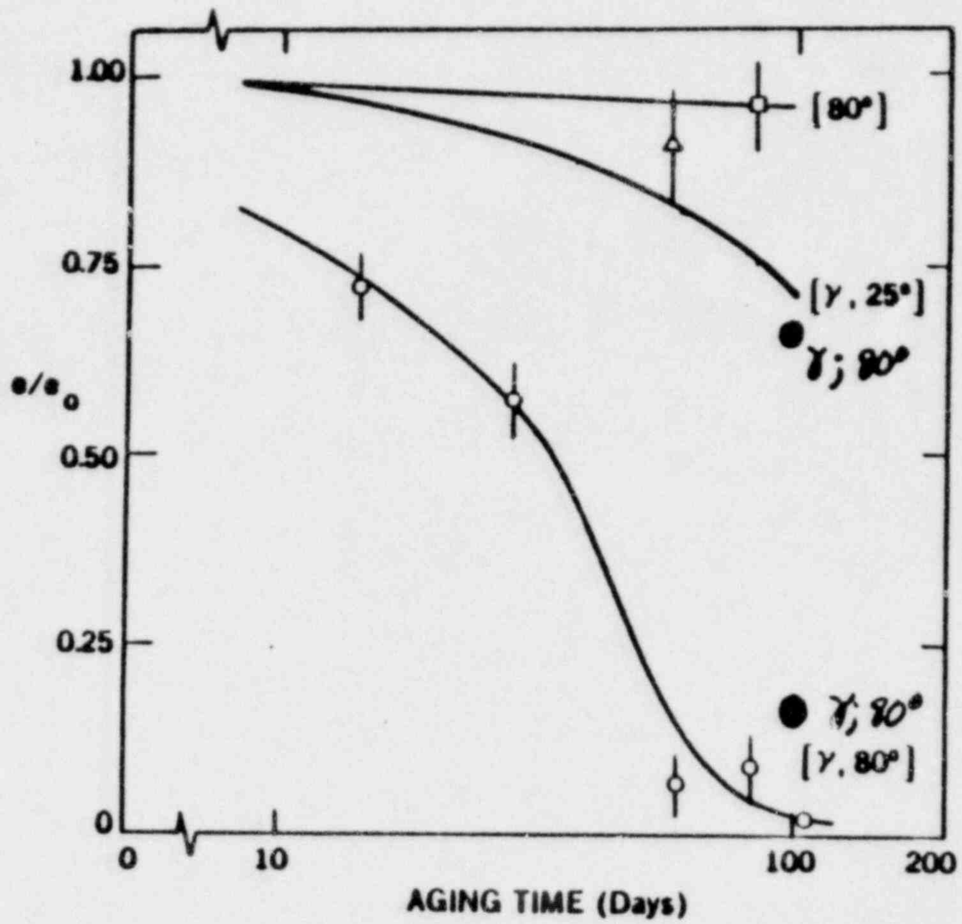
γ: .1 MRAD/DAY   T: 80°C

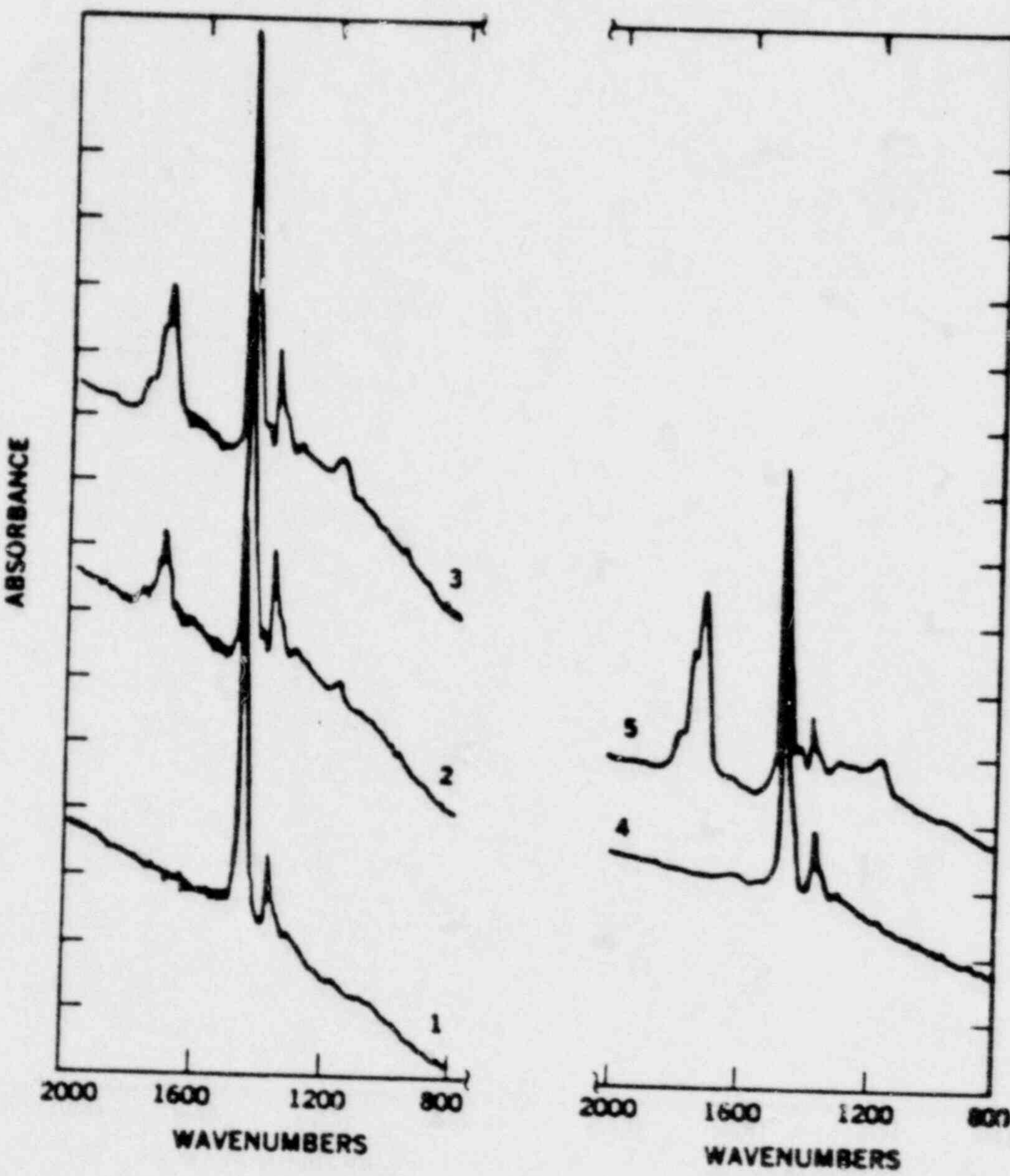


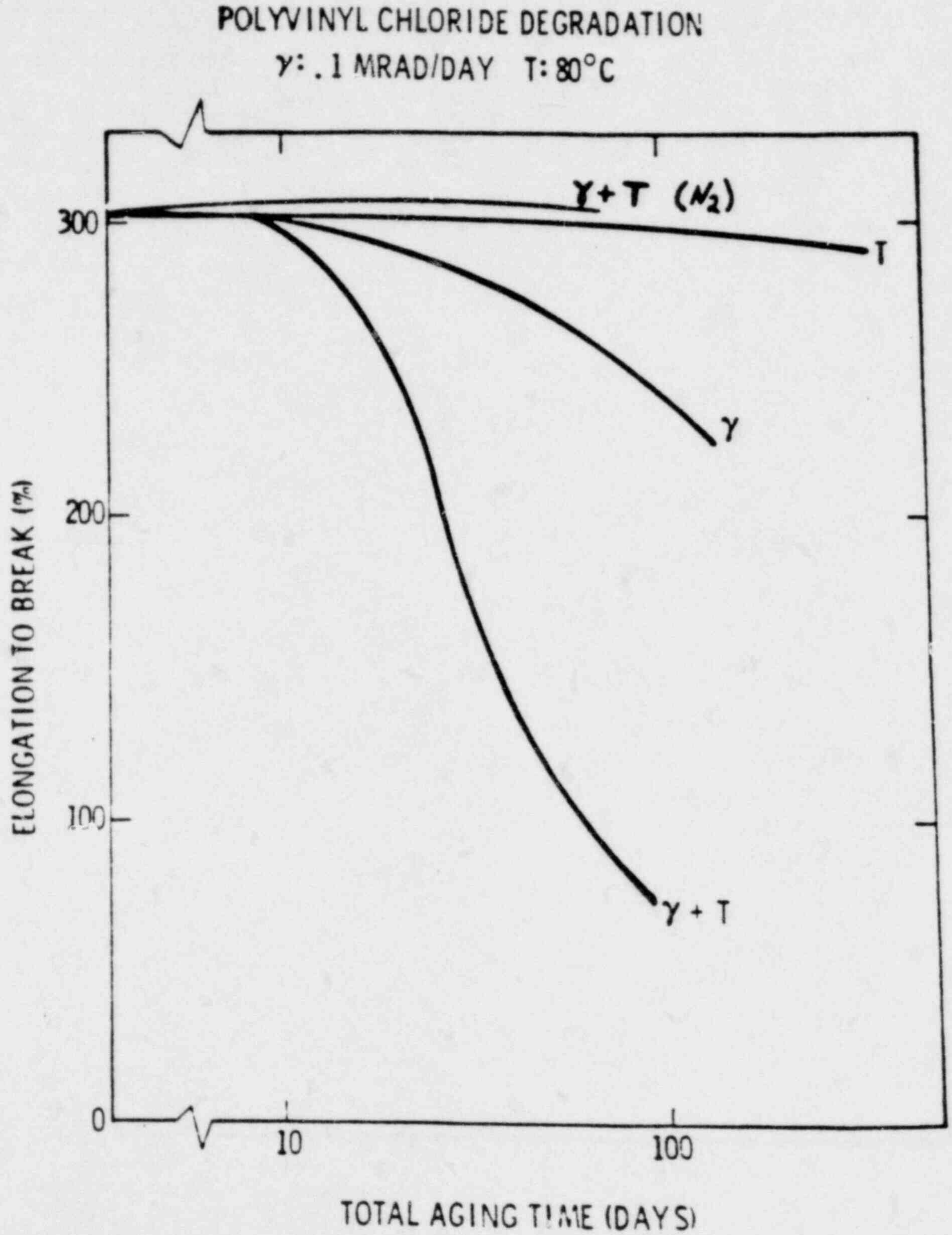
POLYETHYLENE DEGRADATION



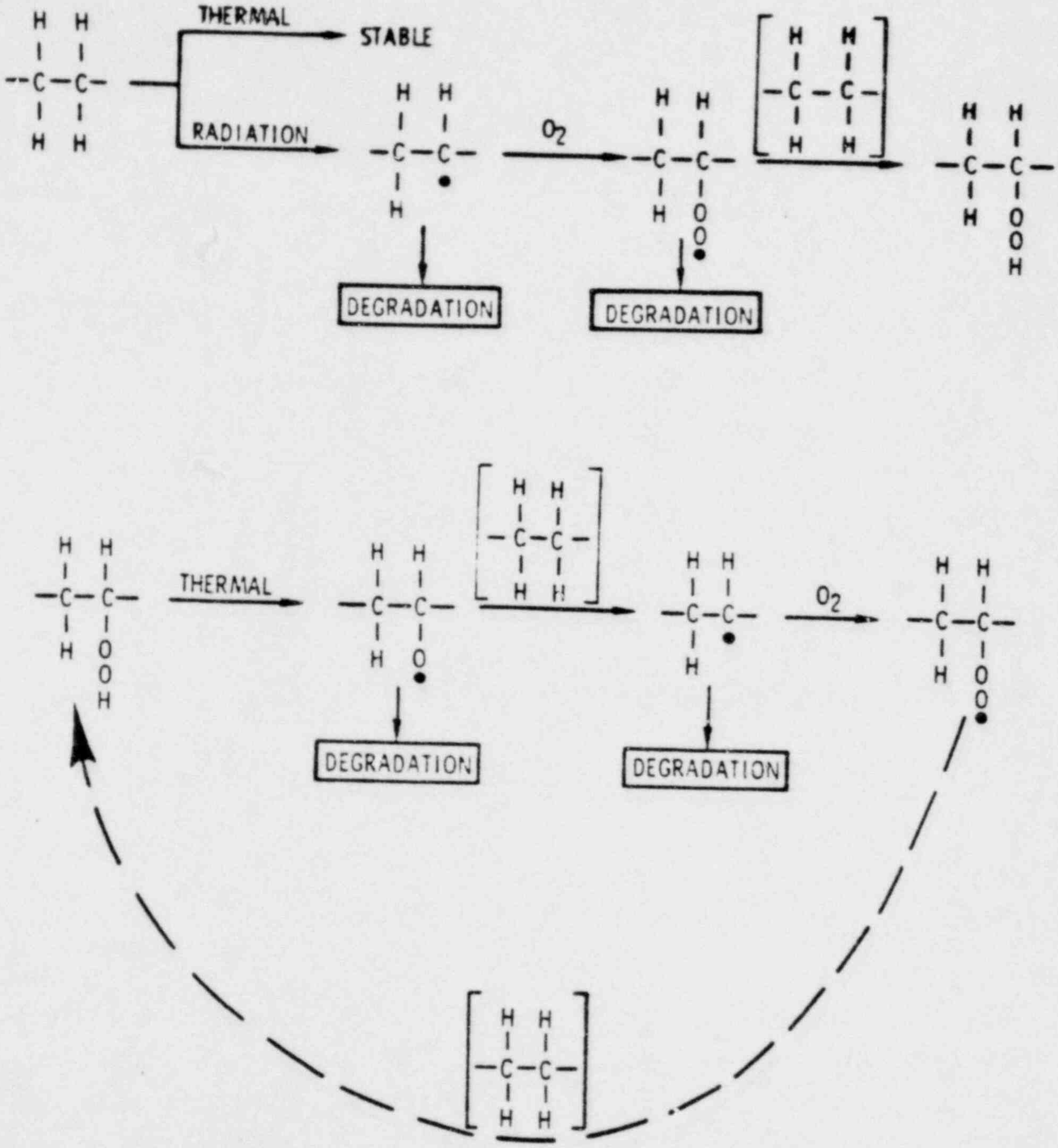
POLYETHYLENE DEGRADATION



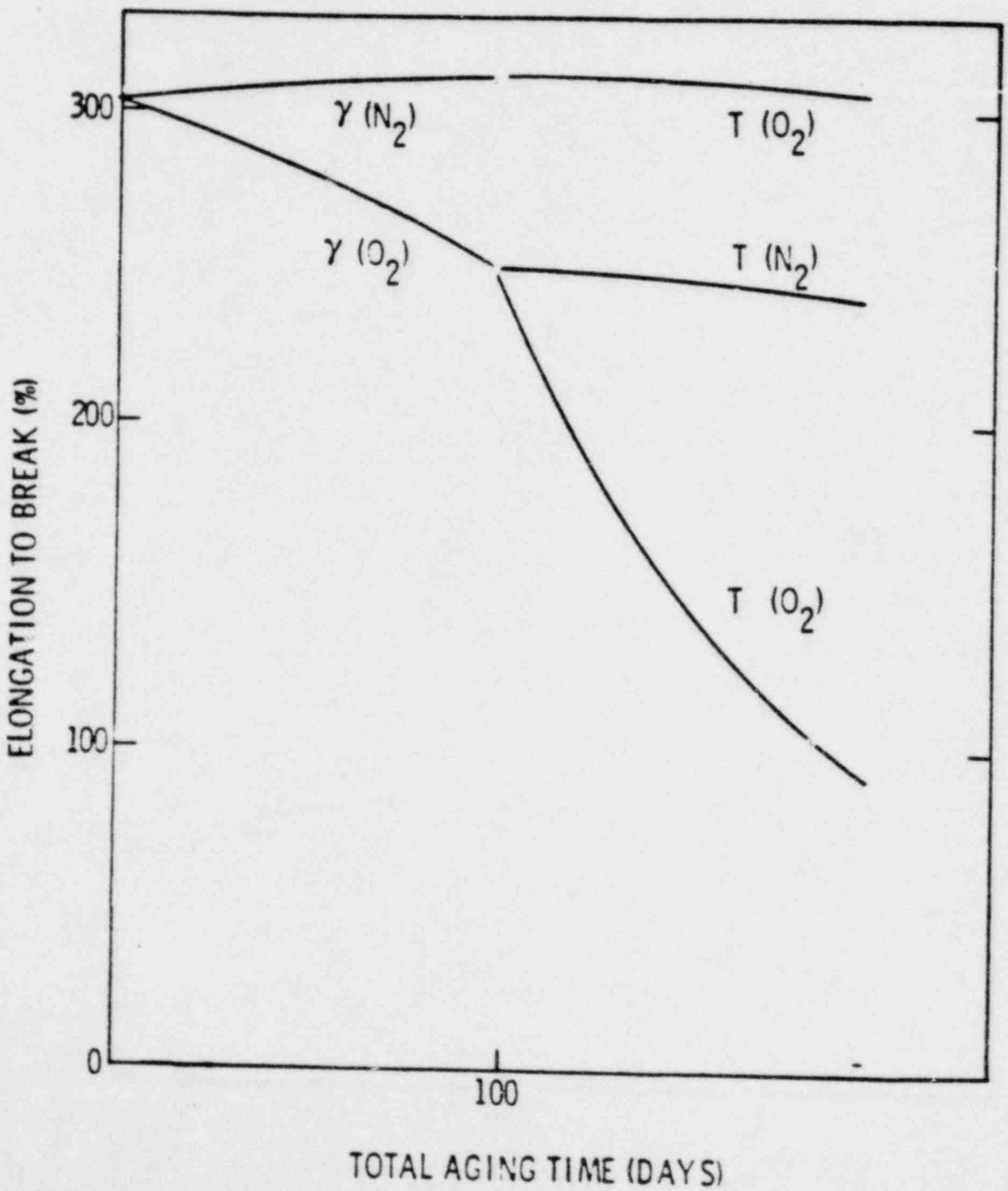

ABSORBANCE
3
2
1
2000
1600
1200
800
WAVENUMBERS
5
4
2000
1600
1200
800
WAVENUMBERS

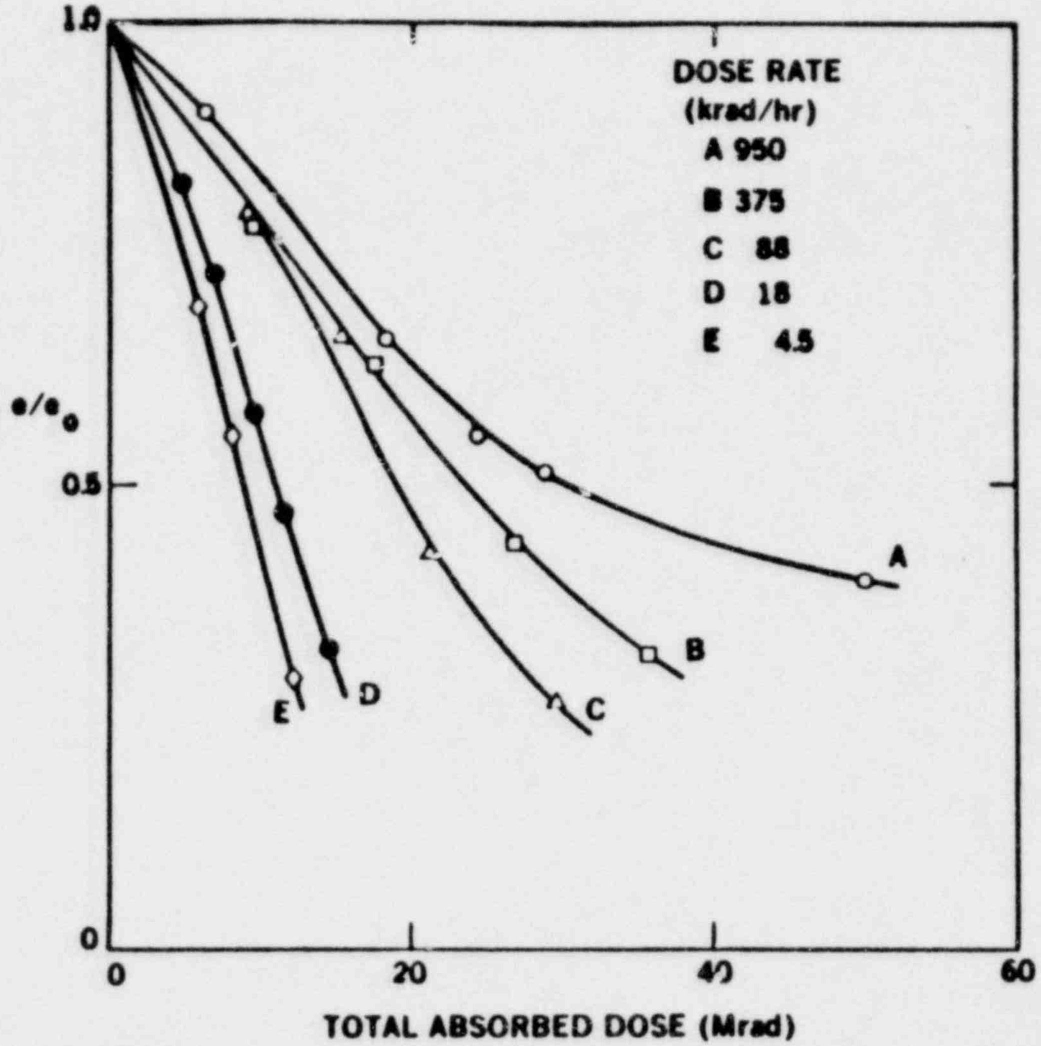


POLYVINYL CHLORIDE DEGRADATION
γ: .1 MRAD/DAY T: 80°C
ELONGATION TO BREAK (%)
TOTAL AGING TIME (DAYS)
300
200
100
0
10
100
γ + T (N2)
T
γ
γ + T


THERMAL
STABLE
RADIATION
O_2
DEGRADATION
DEGRADATION
THERMAL
DEGRADATION
O_2
DEGRADATION

SEQUENTIAL (γ FOLLOWED BY T) EXPERIMENTS, USING N_2, IMPLICATE O_2 INVOLVEMENT IN BOTH RADIATION AND THERMAL STEPS OF THE DEGRADATION




DOSE RATE
(krad/hr)
A 950
B 375
C 88
D 18
E 4.5
e/e₀
1.0
0.5
0
0
20
40
60
TOTAL ABSORBED DOSE (Mrad)
A
B
C
D
E

POOR ORIGINAL

Table III.3

Radiation stability of organic materials at temperatures above 25°C

Material	Temp. °C	Max. dose (electrical) rad	Max. dose (mechanical) rad
THERMOPLASTICS			
Casein	125-140		2.5×10^7
Polychlorotrifluoroethylene	200	5×10^8	5×10^6
Polyamide	100	5×10^8	2.5×10^8
Polyethylene	85	5×10^9	2.5×10^8
Polystrene	75	5×10^9	5×10^8
Polytetrafluoroethylene	250	2.5×10^9	2.5×10^6
Polyvinlacetate	130	5×10^8	2.5×10^8
Polyvinylcarbazole	150	5×10^9	5×10^8
Polyvinylchloride	85	10^9	5×10^7
Polyvinylformal	130	10^9	5×10^8
THERMOSETTINGS			
Epoxy	130	5×10^9	2×10^9
Furan	120-160	-	3.3×10^9
Melamine formaldehyde:			
cellulose filler	110	-	1×10^8
glass-fibre filler	120	-	1×10^8
Phenol formaldehyde:			
no filler	120	-	1.1×10^7
cellulose filler	120	-	2.6×10^7
mineral filler	175-190	-	3.9×10^9
Polyester:			
no filler	100	-	8.7×10^5
mineral filler	110	-	3.9×10^9
Silicones	150	5×10^9	2.5×10^8
ELASTOMERS			
Butyl	85	5×10^8	5×10^7
Natural rubber	85	8×10^8	10^8
Neoprene	100	1.5×10^9	5×10^8
Polyisobutylene	85	5×10^8	5×10^7
Silicones	125	2×10^9	5×10^7

750MR!

50MR!

500MR

50MR

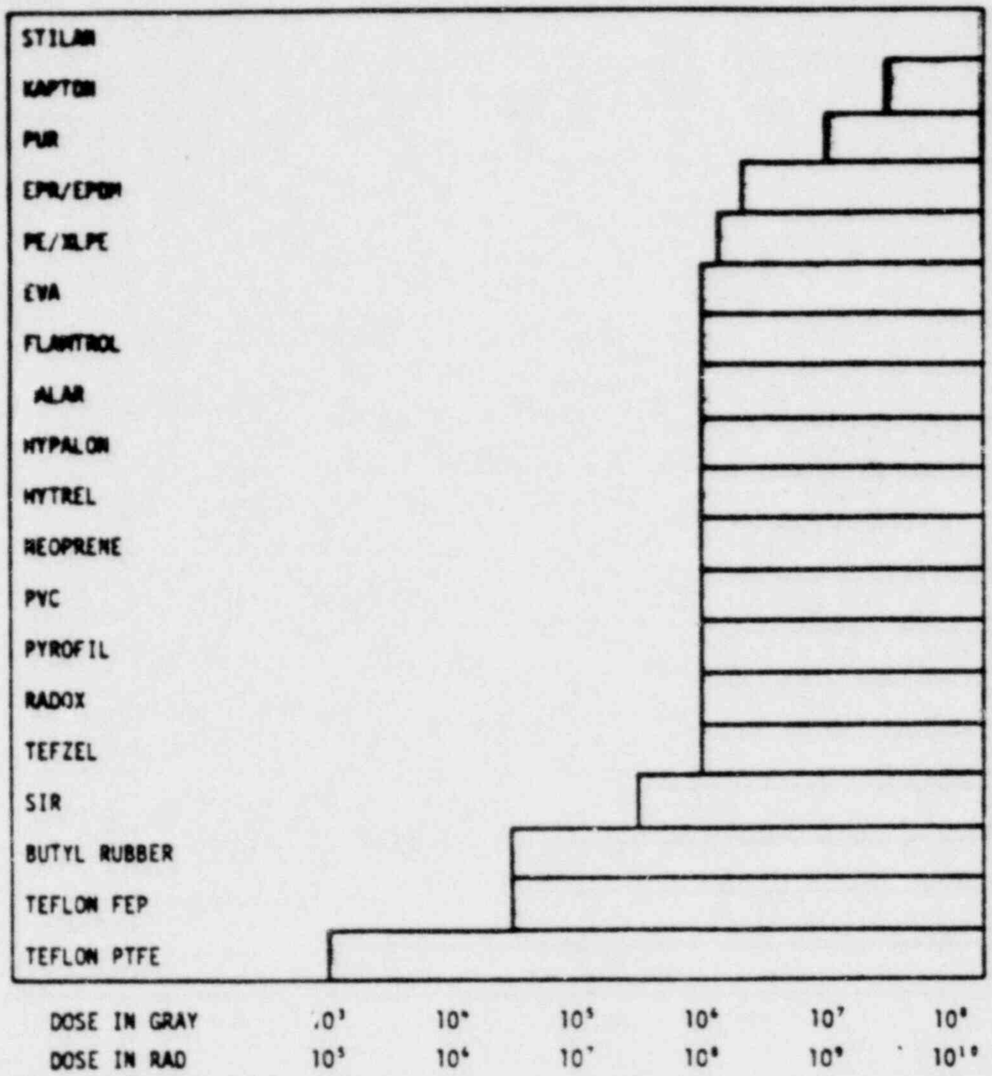
if 50 mrad dose, must be high dose rate!!

Elastomers Gamma dose rate ~ 10^1 Gy/hr = 10^3 rad/hr

P4 CFLN 79-04

Table 2

Classification of materials according to their radiation resistance



USE NOT RECOMMENDED

FIRE RETARDANT AGING

OBJECTIVE : DETERMINE EFFECT OF AGING (γ AND T) ON FLAME RETARDANT PROPERTIES OF POLYMERS

EPR, HYPALON FORMULATIONS
(WITH CHLORINATED HYDROCARBON + Sb_2O_3)

WE FOLLOW : 1) LOSS OF RETARDANTS BY CHEM ANALYSIS
2) FLAMMABILITY PARAMETERS (BY COMBUSTION TESTS)

RESULTS : SUBSTANTIAL LOSS OF BOTH Cl AND Sb

THERMAL IS A MAJOR FACTOR

RCl ↑

$$RCl \longrightarrow HCl$$
$$HCl + Sb_2O_3 \longrightarrow SbOCl \ (SbCl_3)\uparrow$$

FLAMMABILITY CHANGES NOT LARGE (OXYGEN INDEX)

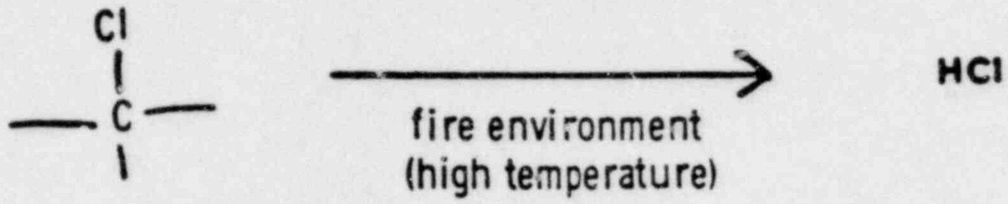
FLAMMABILITY CAN INCREASE OR DECREASE

INCREASE - LOSS OF RETARDANTS
DECREASE - LOSS OF VOLATILE COMPONENTS
(SEEN BY TGA)

FIRE RETARDANT SYSTEMS FOR THE CABLES:

Sb_2O_3 + chlorocarbon

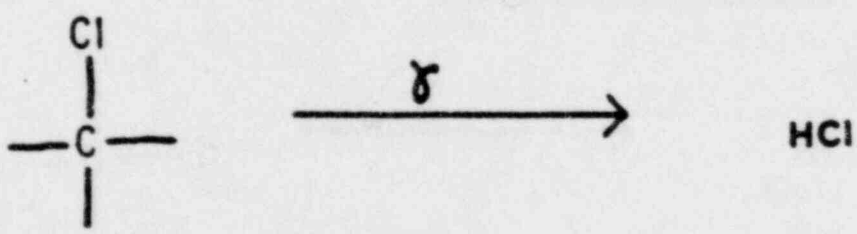
MODE OF ACTION:



$HCl + Sb_2O_3 \longrightarrow SbCl_3$ and/or $SbOCl$

(volatile)

Radiation Environment:



$HCl + Sb_2O_3 \longrightarrow$?

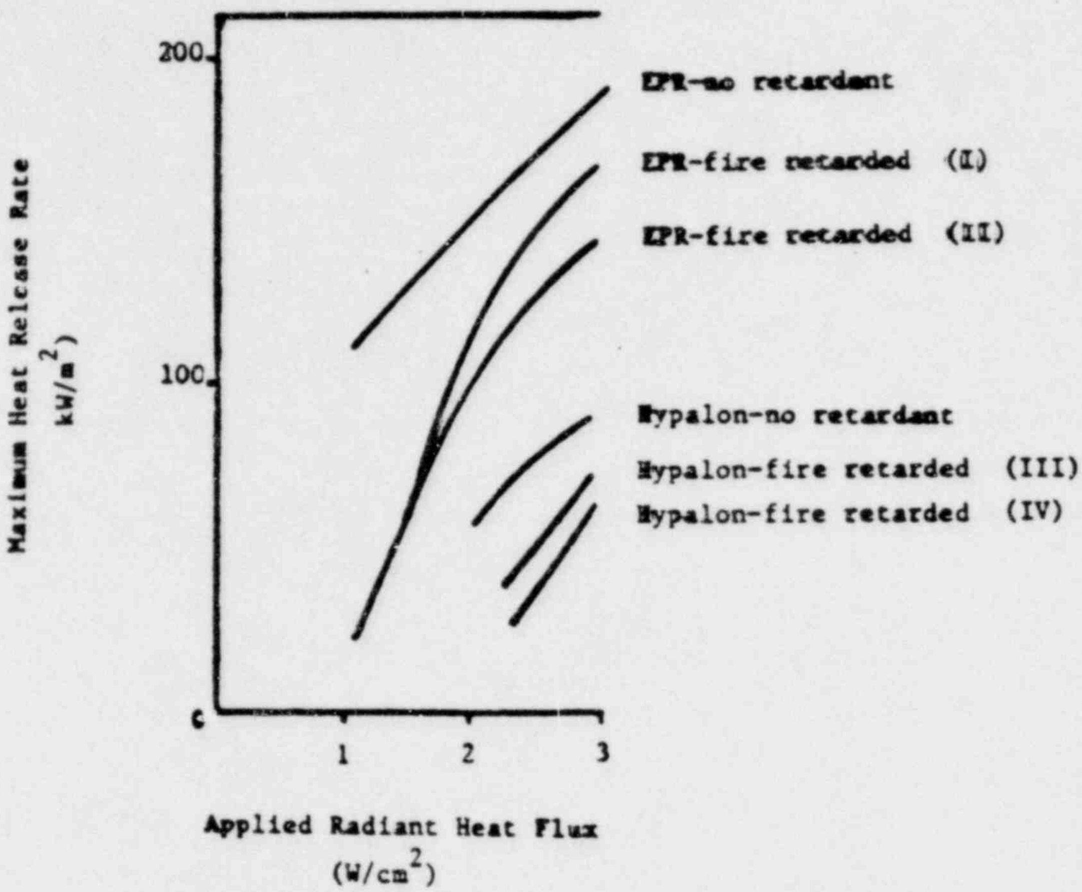
$$\text{O.I.} = \frac{[O_2]}{[O_2] + [N_2]}$$

TABLE I
OXYGEN INDEX RESULTS ON VIRGIN AND HEAT-AGED POLYMER SAMPLES

SAMPLE	OXYGEN INDEX VIRGIN MATERIAL	OXYGEN INDEX HEAT-AGED MATERIAL
1. EPR no fire retardant	22.5	24.0
2. EPR with Sb_2O_3 + chlorinated component type I	27.5	27.0
3. EPR with Sb_2O_3 + chlorinated component type II	30.0	29.0
4. HYPALON no fire retardant	37.5	51.0
5. HYPALON with Sb_2O_3 + chlorinated component type III	47.0	47.0
6. HYPALON with Sb_2O_3 + chlorinated component type IV	41.0	48.0

EPR Fire Retardant Aging

	Cl	Sb
Virgin	4.4 ± .3	3.0 ± .3
110°, 4.5 Mo	3.5 ± .3	1.0 ± .3
110°, 6 Mo	3.2 ± .3	.7 ± .3


200
100
C
1
2
3
Maximum Heat Release Rate
kW/m2)
Applied Radiant Heat Flux
(W/cm2)
EPR-no retardant
EPR-fire retarded (I)
EPR-fire retarded (II)
Hypalon-no retardant
Hypalon-fire retarded (III)
Hypalon-fire retarded (IV)

NUREG/CR-1466
SAND79-1561

PREDICTING LIFE EXPECTANCY AND SIMULATING AGE OF COMPLEX EQUIPMENT USING ACCELERATED AGING TECHNIQUES*

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ABSTRACT

This document outlines some of the types of experiments which can be used to improve reliability, simulate age, and predict life expectancy of complex equipment. Brief discussion is given of failure mode tests and compatibility tests, which often give useful qualitative aging information. A detailed discussion is presented on accelerated aging methods, emphasizing an approach based on kinetic rate expressions. This kinetic approach offers a convenient framework for describing the importance of competing reaction pathways, transitions in a material, diffusion effects, and sorption effects. It is concluded that, when properly conceived and carried out, accelerated aging studies of materials and simple components offer the best opportunity for making quantitative age simulations and lifetime predictions of equipment.

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*This work was support ...)
under Contract #DE-AC ...
Testing Evaluation (Q ...
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**A U. S. DOE facility.

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