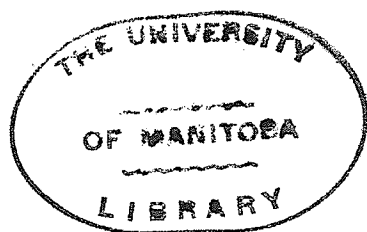A STUDY OF THE TIME SPECTRA OF POSITRONS ANNIHILATING IN

SOME ORGANIC MATERIALS AS A FUNCTION OF STATE AND TEMPERATURE

by

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A thesis submitted in partial

fulfilment of the requirements

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LIST OF FIGURES

ACKNOWLEDGMENTS

ABSTRACT

The mean life (τ_2) of the long lived component in positron decay has been measured as a function of temperature for benzene, napthalene, phenol, and cyclohexane. The measurements were taken over a temperature range including the liquid-solid transition.

τ_2 was found to vary linearly with the temperature and to change in the region of the melting point to an extent dependent on the magnitude of the volume change effected by the transition.

Evidence was found for a solid-solid phase transition in cyclohexane at approximately $-100\ ^{\circ}C$. This is consistent with X-ray diffraction experiments which reveal that a phase transition from cubic to monoclinic occurs between $-80\ ^{\circ}C$ and $-196^{\circ}C$.

Chapter I

INTRODUCTION

Theoretical considerations[1] show that it is
possible for a positron, on entering a medium, to combine with
an atomic electron thereby forming the atom (e^+e^-) known as
positronium. According to quantum mechanics, this atom can
exist in either of two S-states: (a) The singlet or 1-S state
of zero angular momentum (antiparallel spins) or (b) one of
the three triplet or 3-S states of unit angular momentum
(parallel spins). Also, the atom will be unstable against
annihilation, and if formed in the singlet state will annihilate
with a lifetime of the order of 10^{-10} seconds via two photons,
whereas if formed in the triplet state it will annihilate with
a lifetime of the order of 10^{-7} seconds via three photons,
provided that it remains in this state until annihilation.

In recent years, experimenters have measured
the lifetime of positrons in a large variety of media. In
many cases they find two lifetimes against two quanta annihi-
lation; one of the order of 10^{-10} seconds and another of the
order of 10^{-9} seconds. The longer lifetime is attributed
to[2,3] the annihilation of the positron of the positronium
atom in the triplet state with an external antiparallel
electron.

Bell and Graham[2], in 1953, reported a temperature dependence of the longer lifetime (τ_2) for teflon, water, and polystyrene. The results for teflon showed a pronounced effect; the value of τ_2 decreasing from the value 3.5×10^{-9} seconds at $20^{\circ}C$, to 2.5×10^{-9} seconds at $-78^{\circ}C$, to 1.6×10^{-9} seconds at $-196^{\circ}C$. The intensity (I_2) of the component remained constant at about 33 percent. In the case of water, the value of τ_2 was observed to drop from 1.7×10^{-9} seconds at room temperature to 1.2×10^{-9} seconds for ice at $-7^{\circ}C$, and further to 0.35×10^{-9} seconds for ice at $-196^{\circ}C$. The intensity appeared to remain constant. Polystyrene showed a somewhat weaker dependence than teflon with τ_2 decreasing from 2.3×10^{-9} seconds at $20^{\circ}C$ to 1.5×10^{-9} seconds at $-196^{\circ}C$. The intensity, again, was found to be roughly independent of temperature. Results for fused quartz showed little change in either the value of τ_2 or I_2 between $20^{\circ}C$ and $-196^{\circ}C$.

Berko and Landes[4] have since verified the result for teflon. They observed, in addition, that the τ_2 vs. temperature curve levels off between liquid nitrogen and liquid helium temperatures.

Bell and Graham noted that a connection seemed to exist between the shortening of the lifetime and the increasing regularity of structure as the sample is cooled.

It has been suggested[5,6] that the positronium atom moves adiabatically in response to the thermal agitation of the atoms of the sample. That is, the positronium atoms tend to concentrate in regions of low electron density formed by thermal agitation.

To further investigate the order-disorder dependence, mentioned above, Landes, Berko, and Zuchelli[7] measured the values of τ_2 and I_2 as a function of temperature for the molecular crystal napthalene. The value of τ_2 was found to remain constant at 1.14×10^{-9} seconds up to a few degrees below melting and then to increase, reaching the value of 2.68×10^{-9} seconds at and above the melting point. The value of I_2 was found to remain independent of temperature at 9 percent to within $0.2^{\circ}C$ of the melting point and then to increase, sharply, to 29 percent at and above the melting point.

More recently, Brandt, Berko, and Walker[8] have derived the dependence of τ_2 on lattice parameters and compared their results with experimental data obtained for

polytetrafluoroethylene ($-CF_2-$), glycerol, and the exisiting
results for napthalene. They conclude that the temperature
and phase dependence of γ_2 is, primarily, a ''free volume''
effect. This is, the overlap of the wave function of the
positronium atom and that of the lattice decreases with
increasing lattice spacing. However, an anomaly arises in
the case of the ice-water transition where γ_2 increases with
decrease in volume.

Chapter II

APPARATUS

On the emission of a positron by the Na^{22} nucleus, Ne^{22} is formed in an excited state. The excitation energy is immediately released in the form of a 1.28 Mev gamma ray. With respect to the resolving time of the apparatus, this gamma ray is emitted in coincidence with the positron. The annihilation of the positron with an electron in the sample results in the appearance of two 0.511 Mev gamma rays correlated at 180°. The lifetime of the positron in the sample is then determined by measuring the time between the appearance of the 1.28 Mev gamma ray and the appearance of one of the 0.511 Mev gamma rays.

ELECTRONICS

A block diagram of the electronic apparatus is shown in Fig. 1. On detection of a gamma ray by either scintillator a negative pulse of the order of 10 volts in amplitude is delivered to the limiter from the photo-multiplier. The output pulse from the limiter is a flat-topped positive pulse of about 2 microseconds duration having a rise time of the order of 1 millimicrosecond

FIGURE 1

BLOCK DIAGRAM OF THE
ELECTRONIC APPARATUS
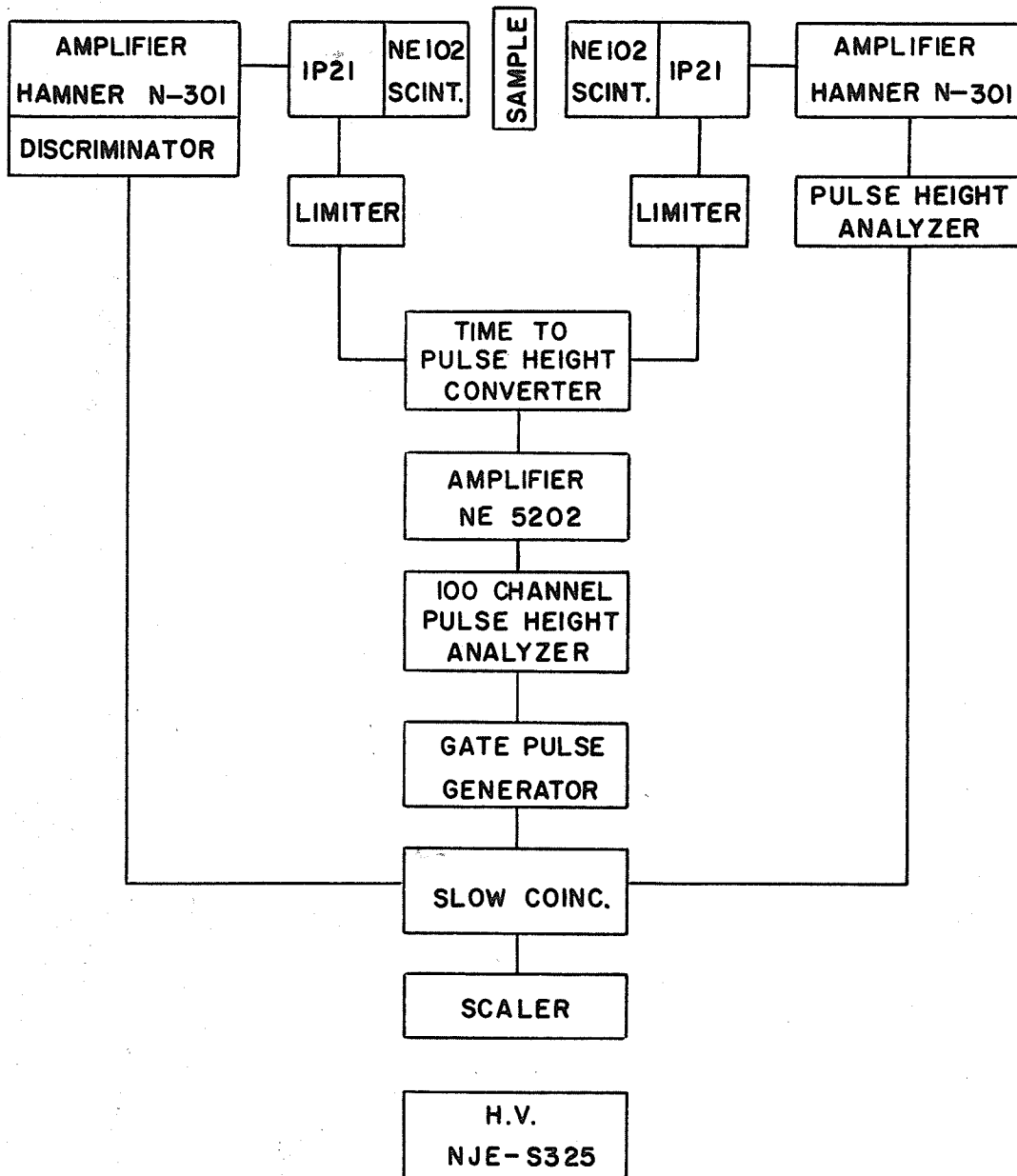
(hereafter written mμs). The output cable from the limiter is connected to both the time-to-pulse height converter and a shorting stub by means of a T-connector. On arriving at the junction of the T the pulse from the limiter is reflected by the stub. The reflection is opposite in sign and delayed by about 32 mμs with respect to the original pulse. The result is that the input pulse to the time-to-pulse height converter is closely rectangular in shape with a duration of about 32 mμs. The time to pulse height converter produces an output pulse of amplitude proportional to the degree of overlap of the two input pulses. This pulse is amplified and passed to the 100 channel pulse height analyzer, provided that the analyzer is gated to receive it. Gating is achieved in the following manner. The level of the discriminator in one channel is set at 0.511 Mev and this channel passes pulses corresponding to the Compton distribution from the 1.28 Mev gamma rays. The lower level of the pulse height analyzer of the other channel is set at 0.2 Mev and the gate set to a width of 0.3 Mev so that this channel passes pulses corresponding to the Compton distribution from the 0.511 Mev gamma rays. The slow-coincidence unit delivers a gating pulse to the 100 channel analyzer provided that the pulses from the two channels arrive within 0.5 microseconds of one another.

The principle of operation of the time-to-pulse height converter is as follows. The pulses from the limiters of the 1.28 and the 0.511 Mev channels are applied to separate control grids of a 6BN6 gated beam tube. This tube is operated so as to conduct only when both grids have a positive potential with respect to the cathode. The plate of the 6BN6 is coupled to the control grid of a 5842 tube, in a cathode follower arrangement, by way of an RC circuit. The amplitude of the pulse applied to the grid of the 5842 and accordingly the output pulse from the cathode is proportional to the duration of conduction of the 6BN6. This time, however, is proportional to the time that both grids of the 6BN6 are held positive, that is, to the degree of overlap of the two pulses from the limiters. Thus, the amplitude of the output pulse from the 5842 is proportional to the degree of overlap of the two limited pulses.

HIGH TEMPERATURE APPARATUS

The measurements at temperatures above room temperature were made by the use of the arrangement shown in Fig. 2. A glass test tube containing the sample was inserted into an electrically heated brass sleeve

FIGURE 2

ELECTRIC FURNACE

TO CONDENSER

ASBESTOS
HEATER WINDING
BRASS
TEST TUBE

THERMOCOUPLE
SOURCE
SAMPLE

IP 21

IP 21
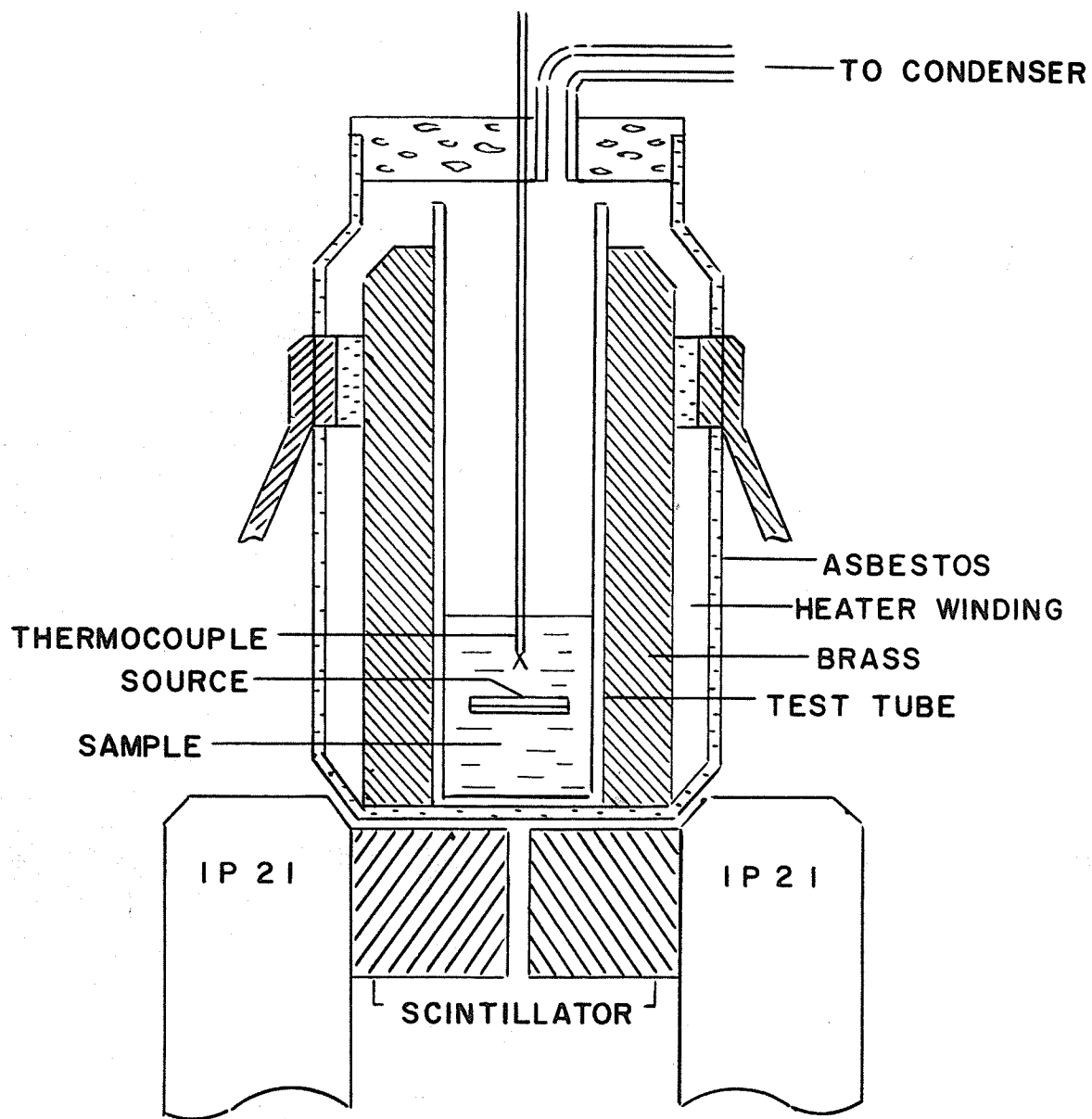
SCINTILLATOR

(I.D. 3/4''; O.D. 1-1/2''; Height 4-1/2''), mounted verti-
cally above the scintillators. The assembly was thermally
insulated by an outer asbestos wall. The temperature was
measured by inserting a thermocouple directly into the
sample. Heater power was obtained from the a.c. line by
way of a constant voltage transformer. Vapors from the
sample were removed by allowing them to pass through a water
cooled condenser.

The source used here was made up by evaporating
about 5 μc of $Na^{22}Cl$ from an aqueous solution (specific
activity 57 μc/cc) onto a thin mica disk. A similar disk
was placed over the first forming a sandwich which was sealed
around the edge with R313 bonding agent. This source was
sealed inside the crystal, by heating and recrystallizing,
in the position shown in the diagram. At temperatures above
the melting point of the sample it was held in place by a
fine-wire support. Open and sandwich sources were compared
using a benzene sample. The introduction of the R313 bonding
agent in the sandwich source presented no noticeable effect.

LOW TEMPERATURE APPARATUS

Figure 3 shows the arrangement for measurements
below room temperature. Two test tubes, each containing about

FIGURE 3

DEWAR ARRANGEMENT

TEMP. BATH

SOURCE
SAMPLE

SCINTILLATORS

IP21
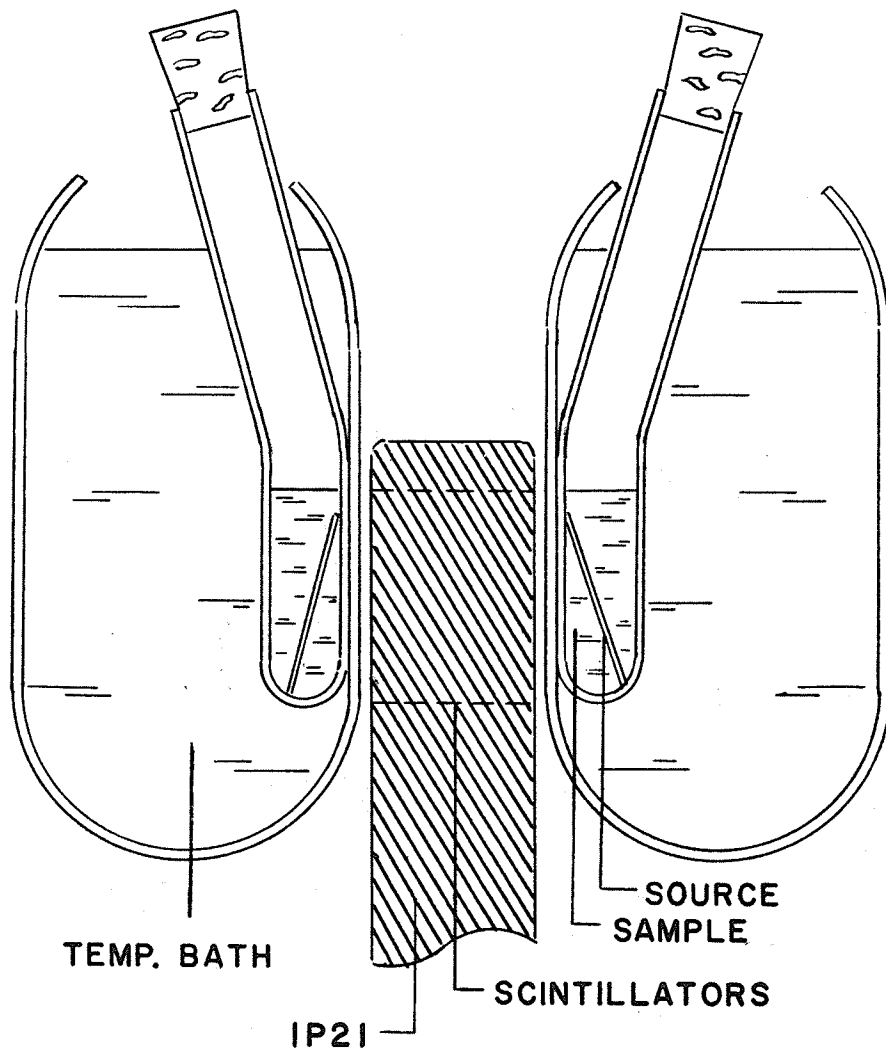
4 cc of the sample, were held inside dewars; one on either side of the scintillators. In this way measurements were made with the sample in temperature baths of ice-water (0°C) dry-ice and acetone (-78°C) and liquid nitrogen (-196°C). Open sources were used here. These were made up by evaporating $Na^{22}Cl$ from an aqueous solution onto one side of thin mica strips roughened for greater adhesion. The location inside the sample is shown in the diagram.

The cryostat used for measurements at low temperatures other than -78°C and -196°C is shown in Fig. 4. A narrow jet installed in the bottom of the reservior provided a steady stream of liquid nitrogen. The flow could be directed into the sample dewar or diverted from it by operating a valve consisting of a metal strip mounted on the shaft of an electric motor. The temperature of the sample was adjusted automatically by means of the circuit shown in Fig. 5. Microswitches S1 and S2 are operated by a cam arrangement on the motor shaft. The photo-resistor is attached to the scale of the galvanometer of the temperature measuring circuit. The principle of operation is as follows. When the light-beam indicator of the galvanometer is in the null position the valve is closed so that the nitrogen flow

FIGURE 4

CRYOSTAT ASSEMBLY

NITROGEN
RESERVOIR—
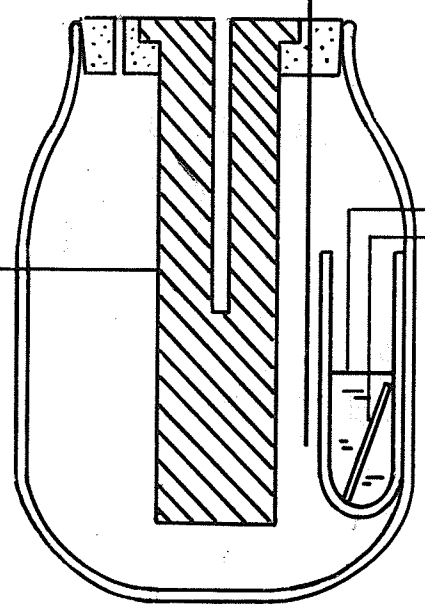
VALVE ———

THERMOCOUPLE

BRASS
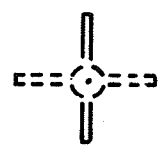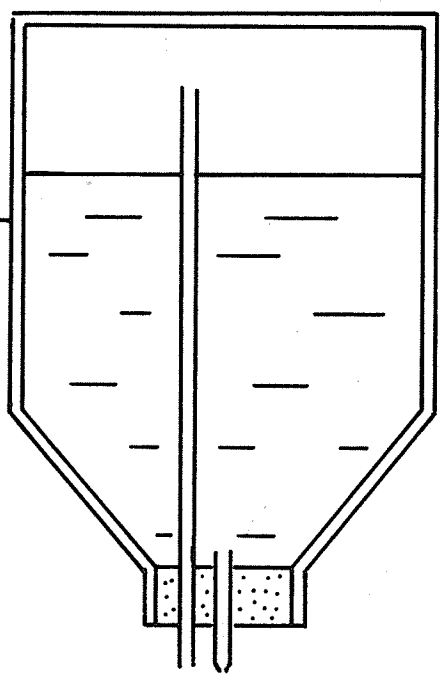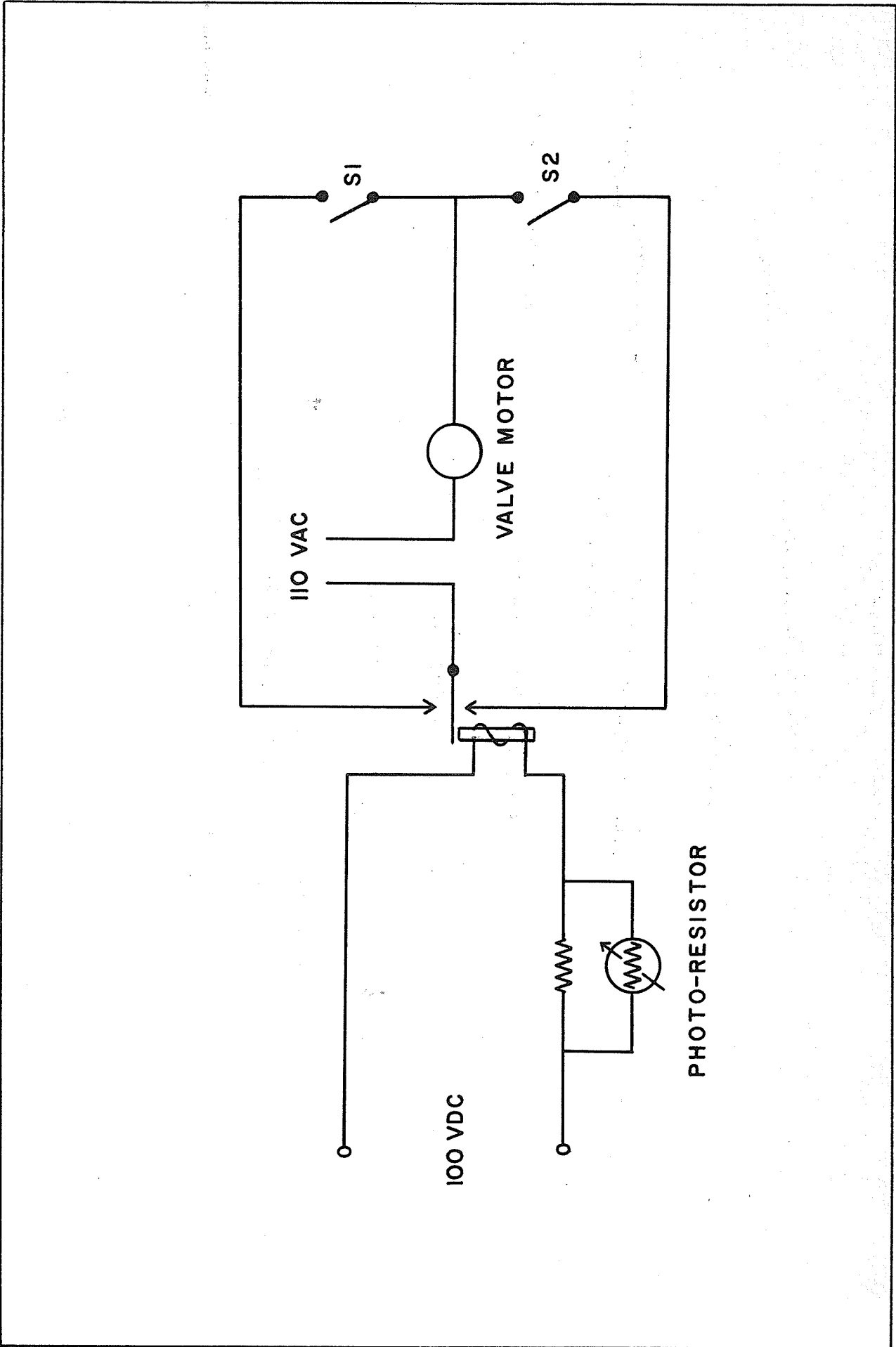CYLINDER

SAMPLE
SOURCE

DETECTORS
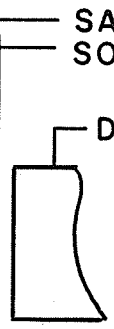
FIGURE 5

CRYOSTAT CONTROL

is diverted from the sample dewar. A small rise in temperature causes the light beam to drift from the null position onto the photo-resistor. The motor is activated and rotates the valve to the open position so that nitrogen is permitted to flow into the dewar until the temperature is restored to its original value.

Using this apparatus the temperature of the sample could be held constant to within $\pm$ $1^{\circ}C$. The above system was found to be the most reliable of several methods conceived for this purpose. An attempt was made to control the liquid nitrogen flow by means of a valve installed in the outlet of the reservior. This system was found difficult to control due to freezing of water vapor which frequently stopped or retarded the action of the valve. In another attempt air was pumped into a partially filled reservior of liquid nitrogen in order to obtain a stream of cold air and nitrogen gas from a jet mounted in the top. It was found that the air could not be sufficiently dried so as to ensure a steady flow.

Chapter III

PROCEDURE

CALIBRATION

A calibration curve for the electronic apparatus is shown in Fig. 6. Co^{60} was used as a source of prompt coincidences. The amount of overlap of the pulses from the 0.511 and the 1.28 Mev limiters was varied by inserting different known delays in the 0.511 Mev channel, between the limiter and the time-to-pulse height coverter. The variable delay was achieved by changing the length of RG/7U cable between the limiter and the converter. Since the speed of pulse transmission in this cable is 0.84c, a cable of length 25 cm presents a delay of 1 mμs. A prompt resolution curve was obtained for each value of the inserted delay. The positions of the centroids of these curves were plotted as a function of the time delay. In this manner points were obtained for delays from 3 to 14 mμs in 1 mμs steps.

The resolution characteristic of the apparatus obtained using a Co^{60} source is shown in Fig. 7. The resolution was calculated by multiplying the width (in channels) at half height by the time sensitivity (in mμs per channel) determined as described above.

+ See page 16(a)

The pulse corresponding to 1.28 Mev is delayed by a fixed delay-line so that on arrival at the time-to-pulse height converter it partially overlaps the pulse corresponding to 0.511 Mev when the variable delay in the 0.511 Mev channel is set at 4 mµs. This amount of overlap is taken as the zero time-delay reference.

As the variable delay in the 0.511 Mev channel is increased the amount of overlap of the two pulses and also the amplitude of the output pulse from the time-to-pulse height converter increases.

FIGURE 6

TIME-TO-PULSE HEIGHT
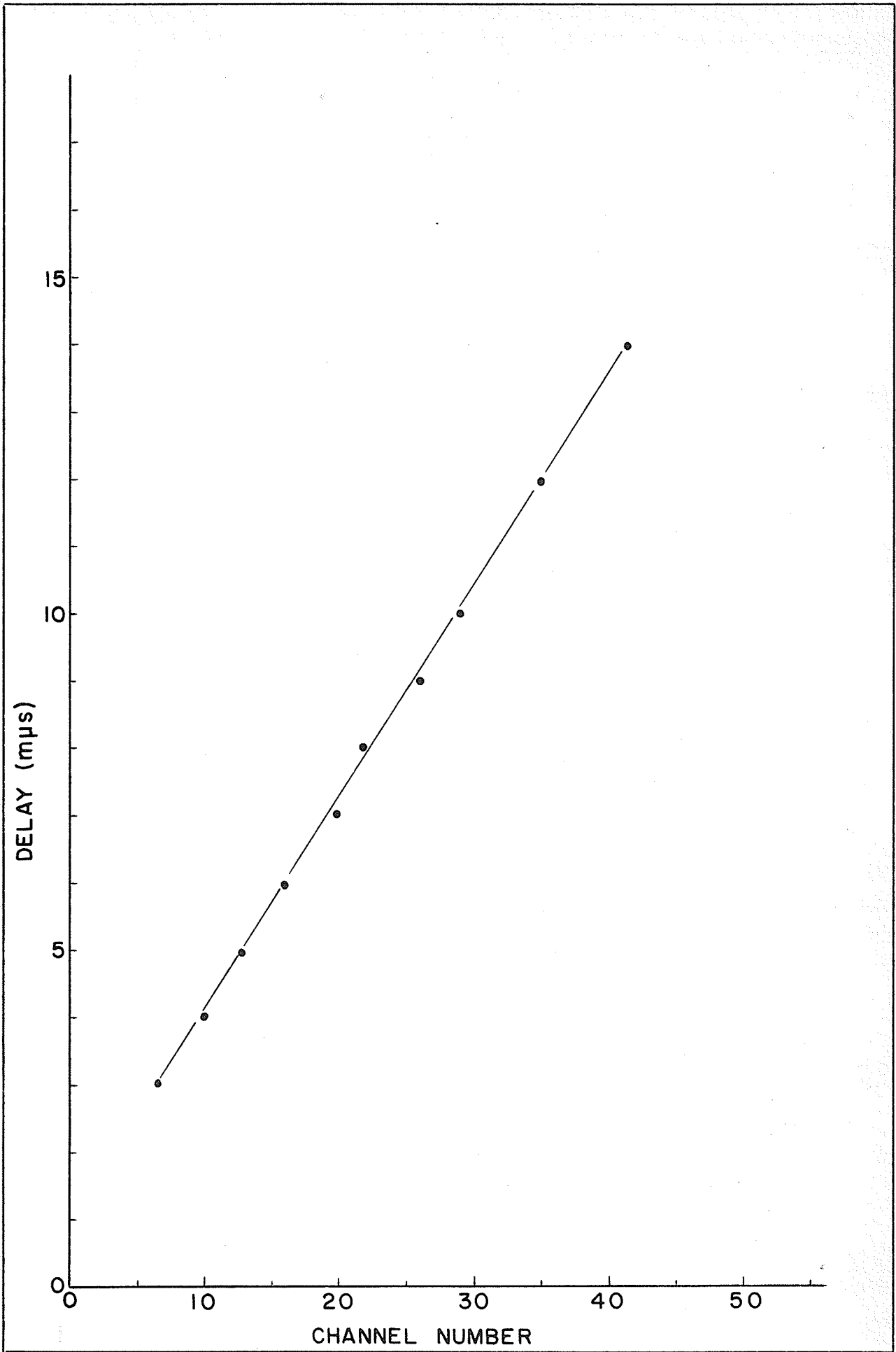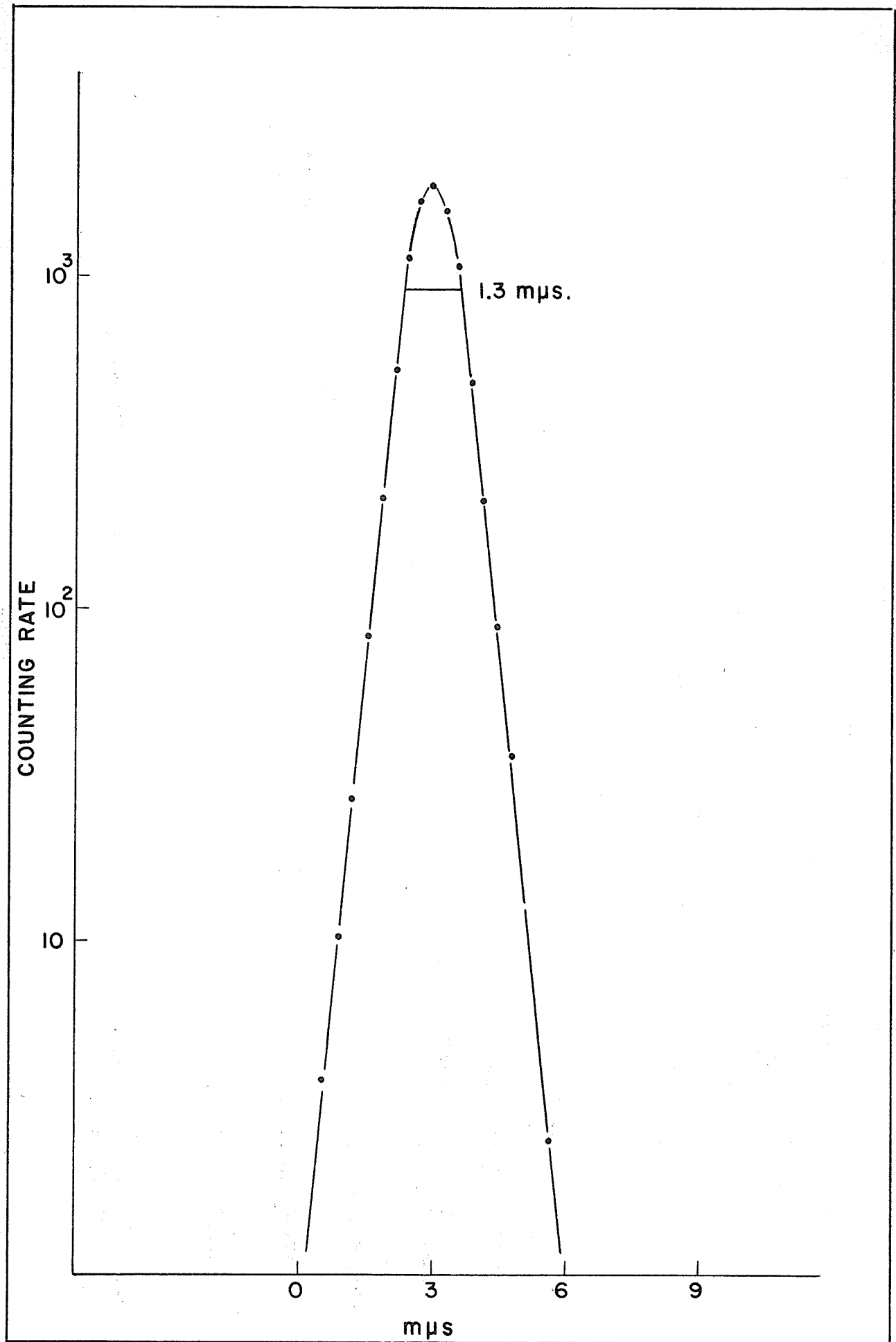### CALIBRATION CURVE

FIGURE 7

RESOLUTION CHARACTERISTIC

The 0.511 and the 1.28 Mev channels of the gating circuit were calibrated using a Cs^{137} source which emits a gamma ray with an energy of 0.662 Mev. The gate of the pulse height analyzer in the 0.511 Mev channel was fully opened and the lower level raised until the counting rate from this channel was reduced to about one count per second. This was determined by connecting a scalar directly to the output of the pulse height analyzer. Using this value of the lower level, and assuming linear energy response, the settings of the lower level and gate width such as to pass pulses corresponding to energies in the range from 0.2 Mev to 0.5 Mev were calculated. Similarly, the level of the discriminator in the 1.28 Mev channel was set to pass pulses corresponding to energies of 0.5 Mev and over.

The time spectra for a benzene sample was determined and the values obtained, $\gamma_2 = (2.3 \pm .1) 10^{-9}$ sec; $I_2 = (32 \pm 2)\%$ agree, within experimental error, with those of Kerr[9].

EXPERIMENTAL

The duration of the runs ranged from 12 to 24 hours, depending on the counting rate obtainable. The time sensitivity as determined from the slope of the time

-to-pulse height conversion curve was checked before and
after each run.

The complete time spectrum could, in all cases,
be recorded in the first 50 channels of the 100 channel
analyzer. The background counting rate was determined by
taking the mean rate obtained for the range of 50 to 69 channels
and subtracted from the time spectrum. The resulting time
spectrum (counting rate vs. time delay) was then plotted on
semi-logarithmic paper. The value of ℓ_2 was determined[10] from
the slope of the straight line drawn through the points on the
tail of the curve.

$$\tau_2 = \frac{.434}{\text{slope}}$$

In some cases this line could easily be fitted by eye, whereas
in other cases it was calculated by the method of least
squares, in which case,

$$\tau_2 = .434 \frac{\left[\sum x_i^2 - \frac{1}{n} (\sum x_i)^2 \right]}{\frac{1}{n} \sum x_i \sum y_i - \sum x_i y_i}$$

where x_i = the time delay of the ith point.

y_i = logarithm (to base 10) of the number of counts in
the ith point.

n = the number of points used in the analysis.

The intensity of the long lived component was determined from the ratio of the area under the straight line (extra-polated back to zero time delay, taken as the position of the centroid of an aluminium spectrum) to the area under the total spectrum.

Chapter IV

RESULTS AND DISCUSSION

Figures 8, 9, 10, and 11 show the experimental time spectra. The set of curves obtained by varying the temperature of a particular sample are shown in a single diagram. The prompt peaks are normalized in order to illustrate the manner in which the slope and position of the tail vary with the temperature. Graphs of τ_2 plotted as a function of temperature are shown in Figs. 12, 13, 14, and 15.

BENZENE

The experimental results are shown in Figs. 8 and 12. This chemical is of particular interest in view of the ''free volume'' idea described earlier, since it undergoes a large decrease in volume on freezing ($\Delta V = 131.7 \ cm^3/kg$)[11]. As shown in Fig. 12, a marked change in the value of τ_2 was observed over the 20 degree range within which the transition from the liquid to the solid state occurs. The measurements for the liquid, taken at $20^\circ C$, and for the solid, taken at $0^\circ C$, show a decrease in τ_2 of about 35%. As the temperature of the sample is further reduced, values taken at $-78^\circ C$ and $-196^\circ C$ indicate that τ_2 continues to decrease with temperature, though relatively more slowly, and that the

relationship is linear for the solid.

NAPTHALENE

Figures 9 and 13 show the experimental results for napthalene. This substance also undergoes a large change in volume as it changes state ($\triangle V$ = 145.8 cm^3/kg)[11]. As in the case of benzene, the large change in volume is observed to be accompanied by a pronounced change in $\tilde{\mathcal{C}}_2$. Measurements for the liquid state, taken at 90°C show an increase in $\tilde{\mathcal{C}}_2$ of about 90% as compared with the value obtained for the solid at 60°C. Within experimental error, the value of $\tilde{\mathcal{C}}_2$ was observed to remain constant for a particular state of the sample over the temperature ranges investigated.

PHENOL

On the basis of the suggestion that the variation in $\tilde{\mathcal{C}}_2$ with temperature is primarily a ''free volume'' effect, phenol, which undergoes a much smaller volume change on changing state ($\triangle V$ = 56.7cm^3/kg)[11], would be expected to exhibit a smaller variation in $\tilde{\mathcal{C}}_2$ than either of the substances discussed above. In fact, as shown in Fig. 14, no discontinuity in the variation of $\tilde{\mathcal{C}}_2$ with temperature or change in slope of the $\tilde{\mathcal{C}}_2$ vs. temperature curve is detected in the region of the melting point. The time spectrum for phenol is shown in Fig. 10.

CYCLOHEXANE

As another example of a substance for which the change in volume associated with the change of state is small, cyclohexane ($\triangle V = 62$ cm^3/kg)[12] was investigated. The results are shown in Figs. 11 and 15. As in the case of phenol, the $\dot{\gamma}_2$ vs. temperature curve appears to be continuous at the melting point and to maintain the same slope for both the liquid and solid state in that region.

As shown in Fig. 15, $\dot{\gamma}_2$ was observed to vary linearly with temperature as the solid is cooled. However, in the region of -110°C the curve changes slope and thereafter the relationship again appears to be linear. From X-ray studies of the crystal structure of solid cyclohexane,[13,14,15] it has been established that as the sample is cooled a solid-solid phase transition occurs in the region between -80°C and -196°C; the structure changing from cubic to monoclinic.

FIGURE 8

POSITRON TIME-SPECTRUM
FOR BENZENE

BENZENE

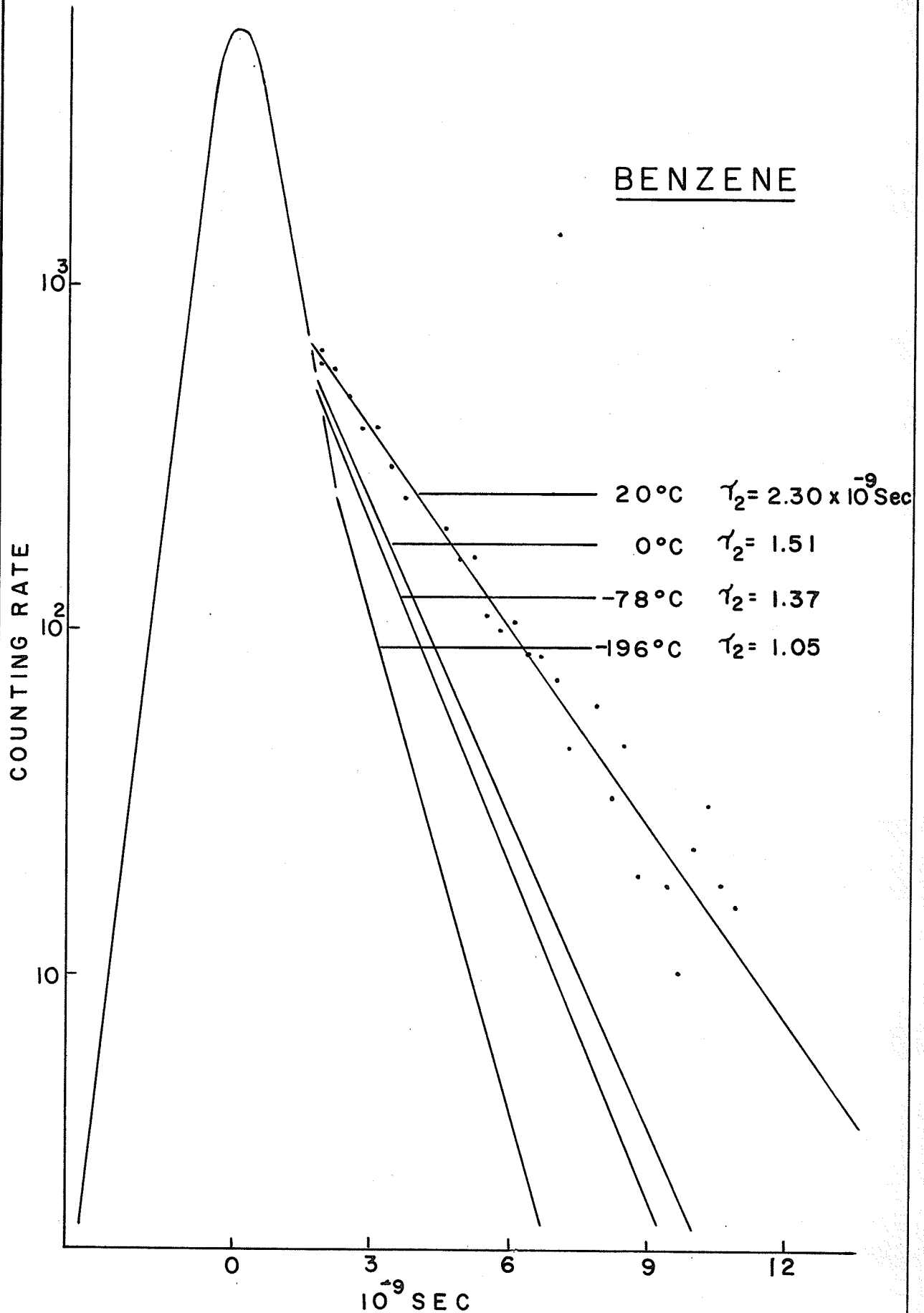20°C $\gamma_2 = 2.30 \times 10^{-9}$ Sec
0°C $\gamma_2 = 1.51$
-78°C $\gamma_2 = 1.37$
-196°C $\gamma_2 = 1.05$

COUNTING RATE

10^3
10^2
10

0   3   6   9   12

10^{-9} SEC

-25-

FIGURE 9

POSITRON TIME SPECTRUM
FOR NAPTHALENE

NAPTHALENE

$\tau_2 = 1.11 \times 10^{-9}$ Sec. (LIQUID)

$\tau_2 = 2.28 \times 10^{-9}$ Sec. (SOLID)

COUNTING RATE
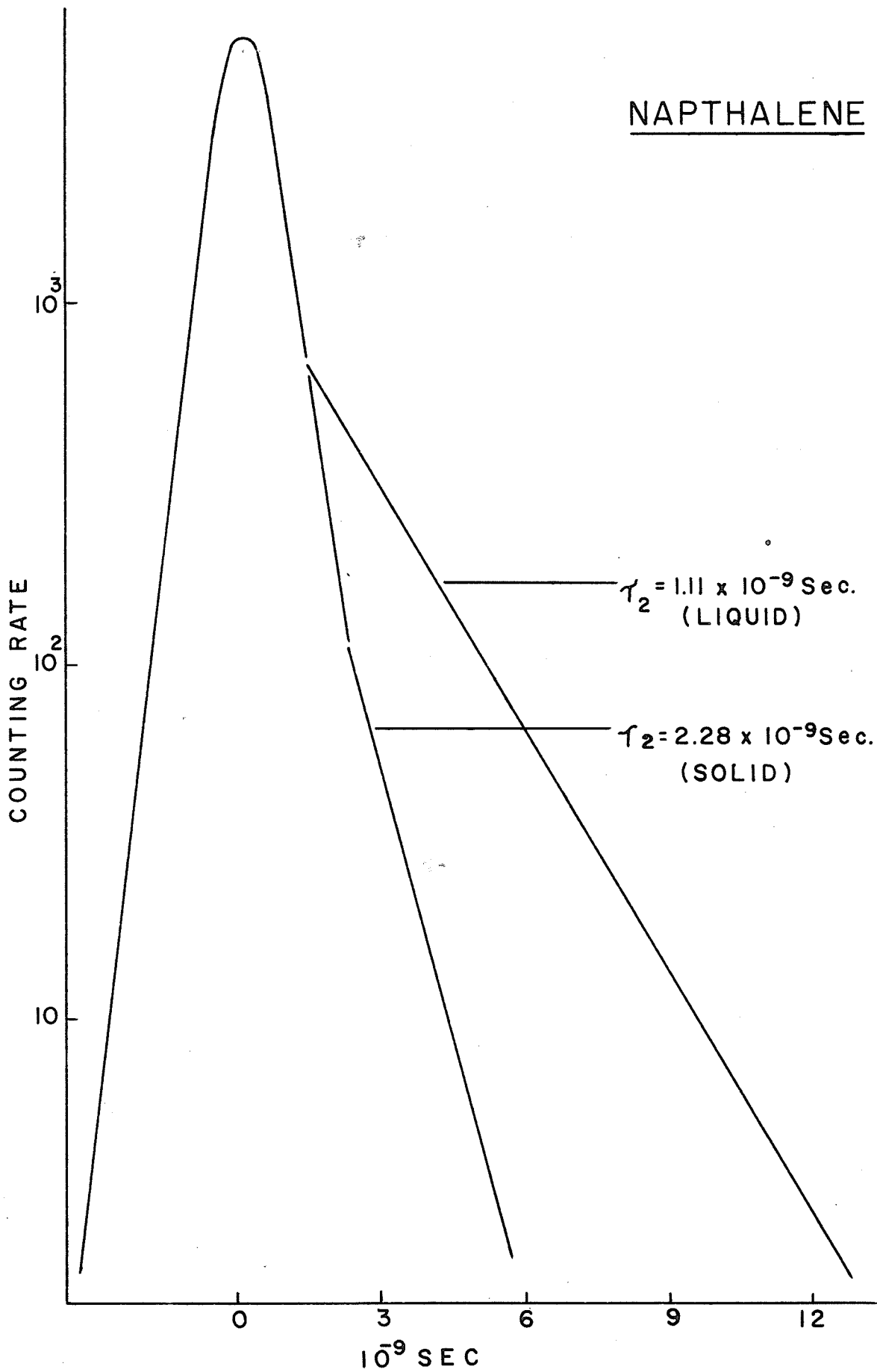
10^{-9} SEC

FIGURE 10

POSITRON TIME-SPECTRUM
FOR PHENOL

PHENOL

80 °C $\tau_2 = 2.1 \times 10^{-9}$ Sec.

50 °C $\tau_2 = 1.9$

40 °C $\tau_2 = 1.7$

20 °C $\tau_2 = 1.6$

COUNTING RATE
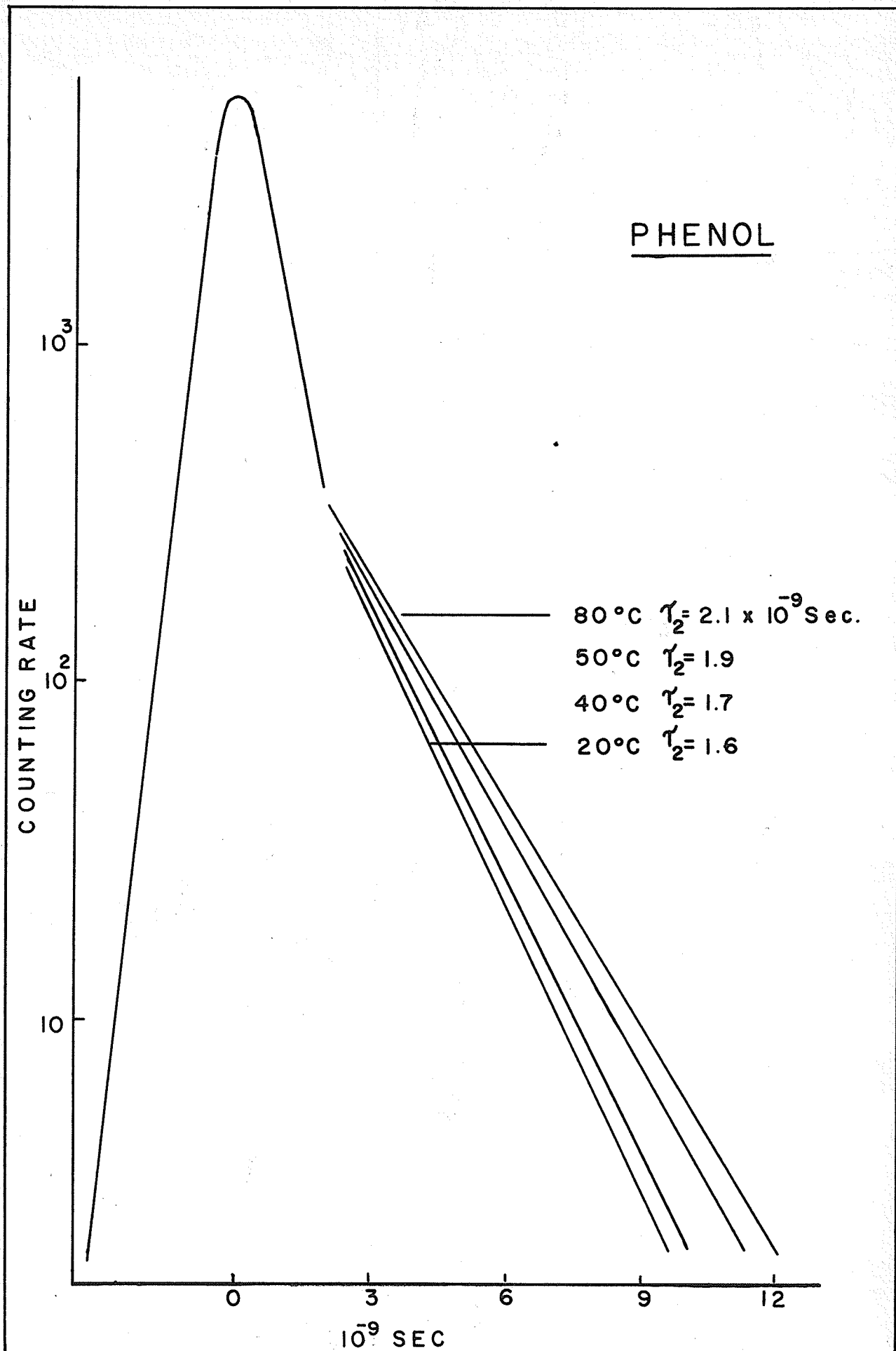
10^{-9} SEC

FIGURE 11

POSITRON TIME-SPECTRUM
FOR CYCLOHEXANE

CYCLOHEXANE

40°C.	$\tau_2 = 2.44 \times 10^{-9}$ Sec.
20	2.36
0	2.36
−78	2.00
−100	1.90
−110	1.81
−150	1.50
−196	1.12

10^{-9} SEC.

FIGURE 12

VARIATION OF ζ_2 WITH TEMPERATURE
FOR
BENZENE

BENZENE
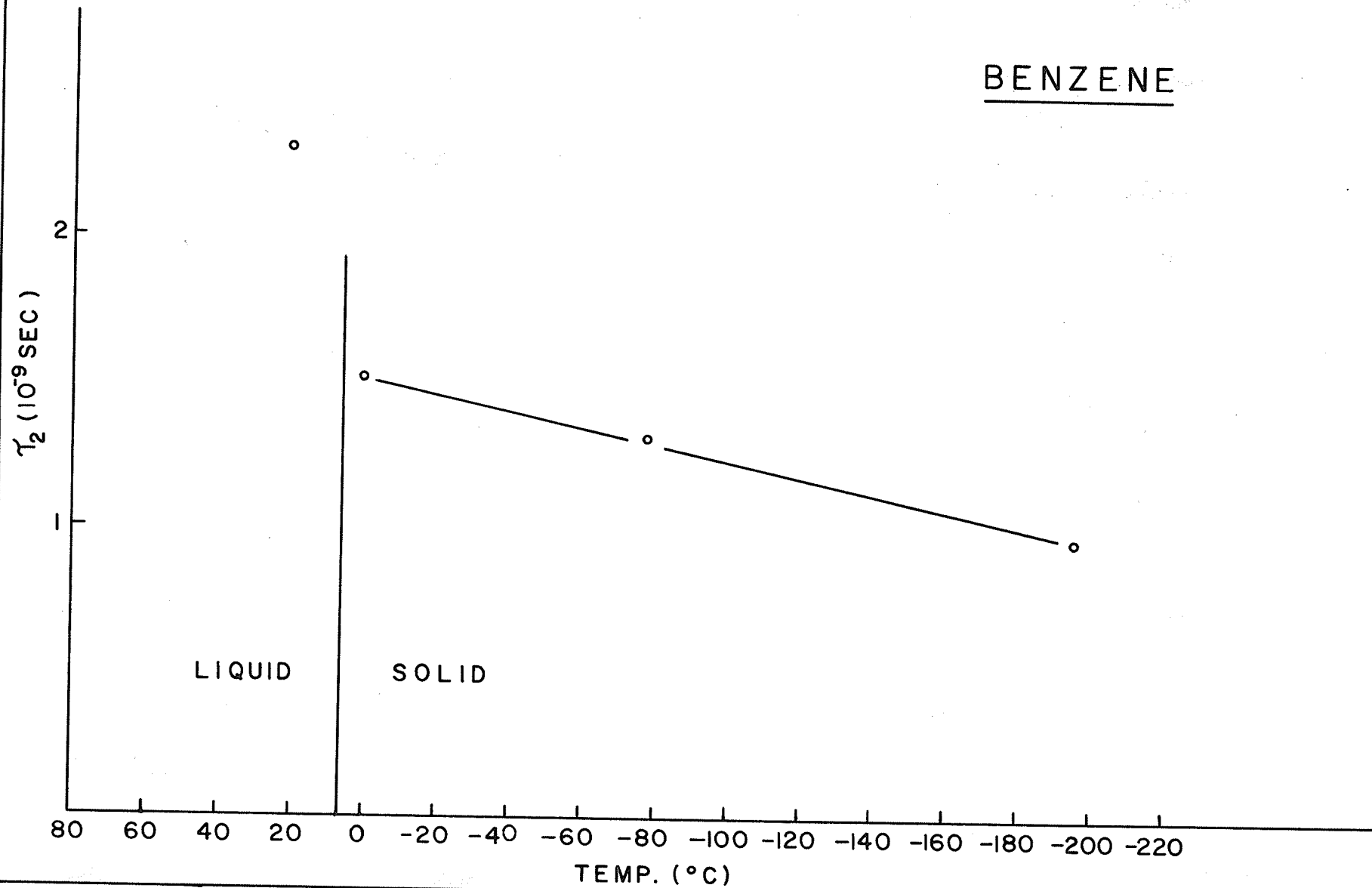
FIGURE 13

VARIATION OF τ_2 WITH TEMPERATURE

FOR

NAPTHALENE

NAPTHALENE
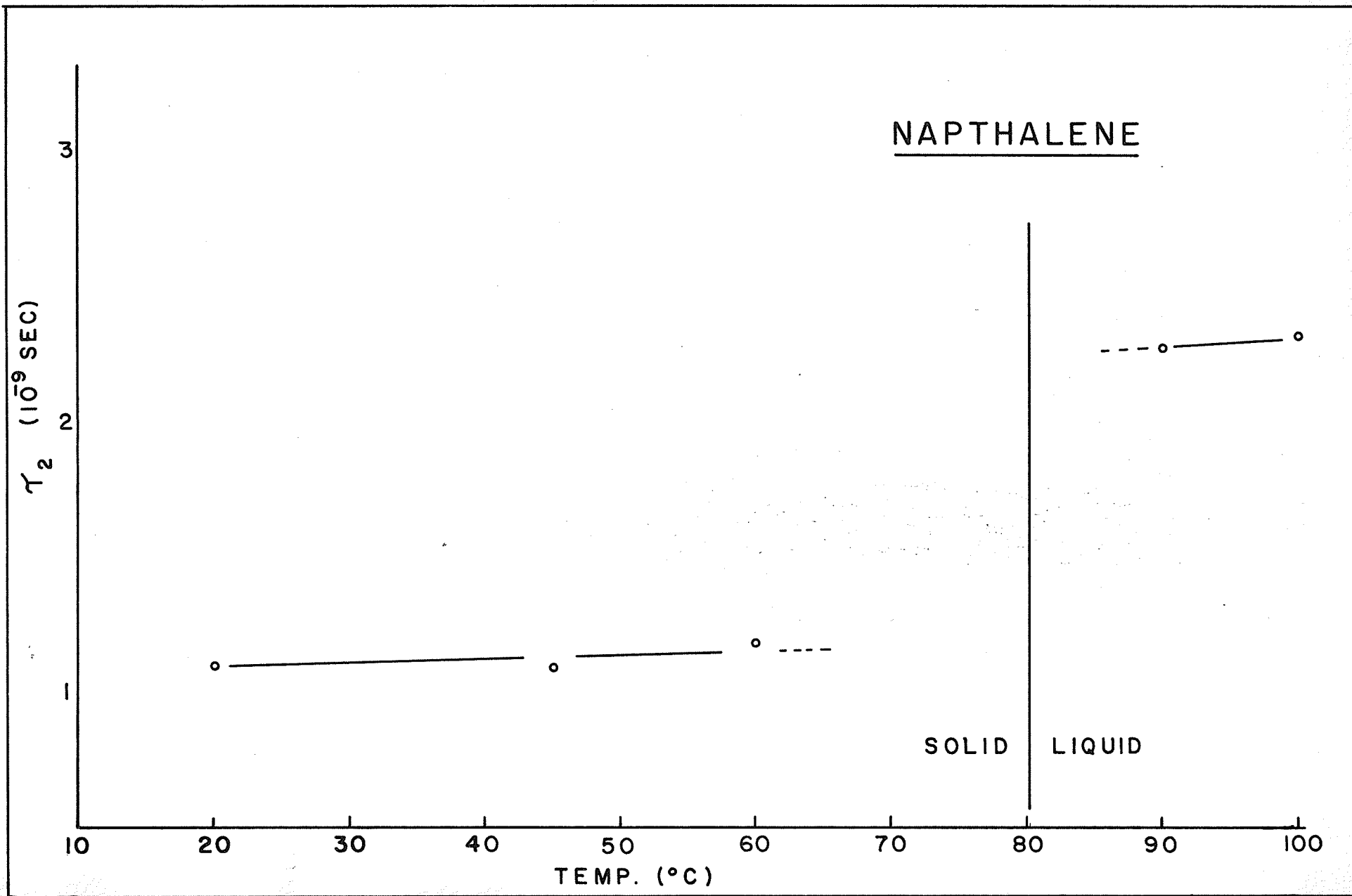
FIGURE 14

VARIATION IN τ_2 WITH TEMPERATURE
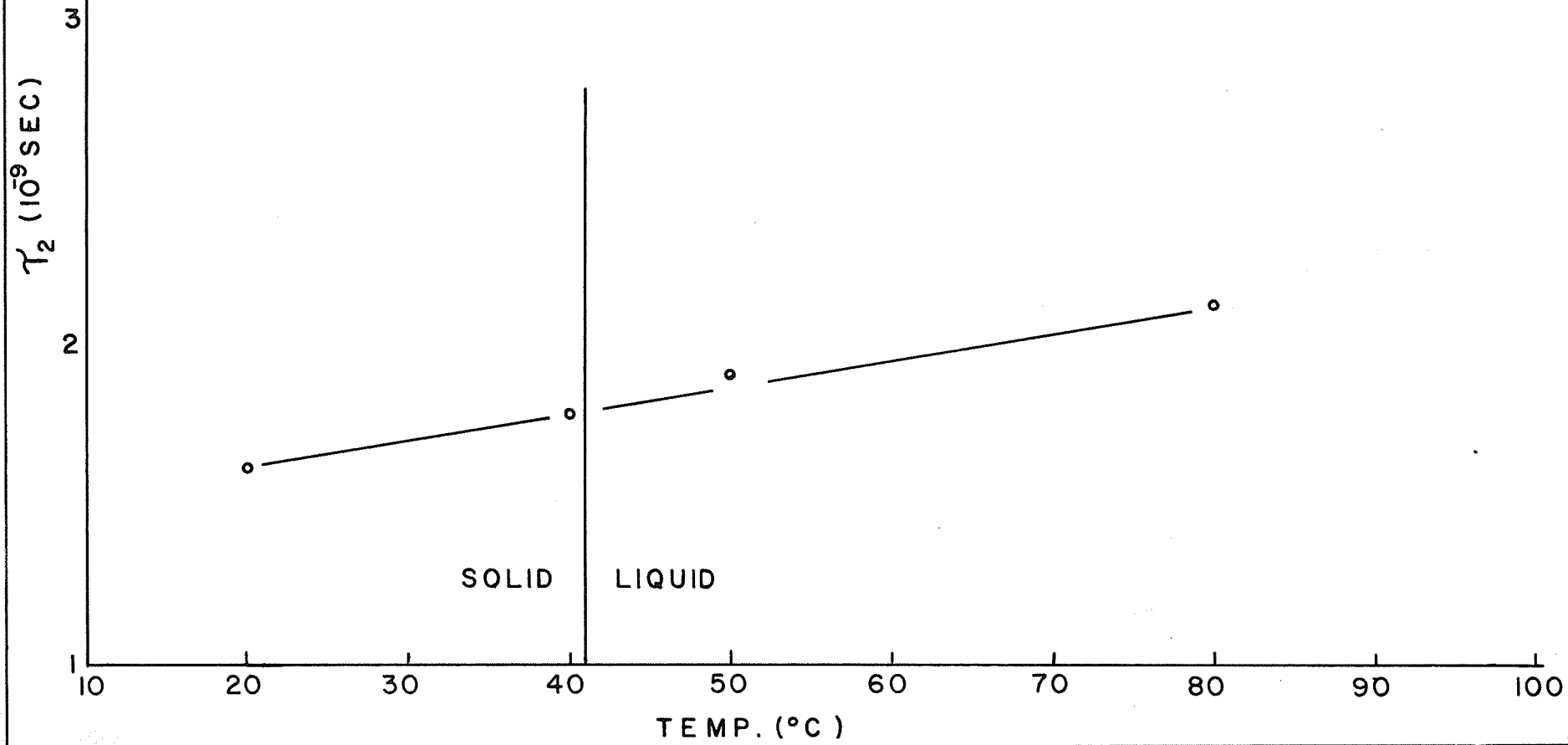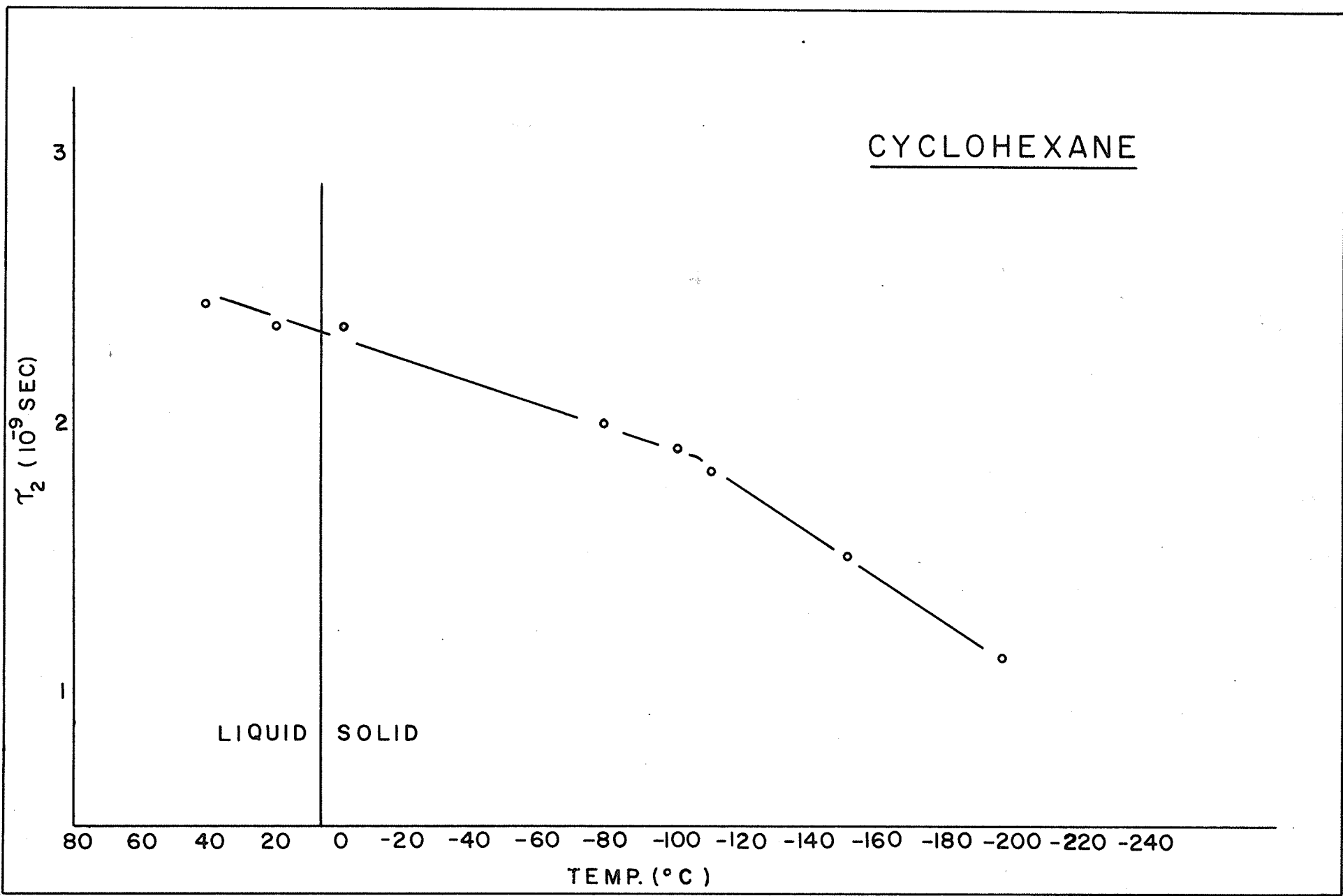FOR
PHENOL

PHENOL

SOLID   LIQUID

FIGURE 15

VARIATION IN τ_2 WITH TEMPERATURE
FOR
CYCLOHEXANE

CYCLOHEXANE

CONCLUSIONS

From the results of these experiments, it appears that a change in the long lived component of positron decay is associated with a change of state of the sample and is dependent upon the magnitude of the change in volume effected by the transition. Moreover there seems to be a critical volume change below which no detectable change in τ_2 occurs. These experiments would place the critical volume change in excess of 60 cm^3/kg for the organic crystals tested.

It also appears that for a particular crystal structure, τ_2 varies linearly with the temperature; decreasing as the temperature is decreased.

The most reasonable interpretation of the change is slope of the τ_2 vs. temperature curve for solid cyclohexane in the region of -110°C is that it is a result of the solid-solid phase transition.

FURTHER REMARKS

In view of the foregoing conclusions it is conceivable that positronium may be used as a probe in investigating the structure of crystals. The information obtained in this way would complement the data obtained from X-ray measurements. The method would be unique in that the positronium probes the crystal in regions of low electron density, whereas in X-ray experiments regions of high electron density are examined.

TABLE I

SUMMARY OF RESULTS

Sample	°C	$\tau_2(m\mu s)$	$I_2(\%)$
Benzene	20	$2.30 \pm .07$	32 ± 5
	0	$1.51 \pm .07$	$32 \pm 2.$
	-78	$1.37 \pm .07$	$25. \pm 4$
	-196	$1.05 \pm .09$	$27. \pm 6$
Cyclohexane	41	$2.44 \pm .08$	$18. \pm 5$
	20	$2.36 \pm .06$	20 ± 5
	0	$2.36 \pm .08$	$23. \pm 1$
	-78	$2.00 \pm .04$	21 ± 2
	-100	$1.90 \pm .05$	22 ± 5
	-110	$1.81 \pm .05$	20 ± 5
	-150	$1.50 \pm .05$	20 ± 5
	-196	$1.12 \pm .04$	$18. \pm 3$
Napthalene	20	$1.1 \pm .04$	$23. \pm 5$
	45	$1.07 \pm .04$	$22. \pm 5$
	60	$1.17 \pm .05$	$17. \pm 5$
	90	$2.25 \pm .08$	$31. \pm 5$
	100	$2.30 \pm .08$	32 ± 5

Table I - continued

Sample	$^{\circ}C$	$\tau_2(\text{m}\mu\text{s})$		$I_2(\%)$	
Phenol	20	1.6	$\pm$ .17	20	$\pm$ 3
	40	1.7	$\pm$ .1	22	$\pm$ 5
	50	1.9	$\pm$ .1	18	$\pm$ 5
	80	2.1	$\pm$ .1	19	$\pm$ 5

Errors quoted are not absolute but are for comparison purposes. Experimental error is of the order of $\pm$ 10%.

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