

FAST COINCIDENCE STUDIES OF POSITRON ANNIHILATION  
IN ORGANIC LIQUIDS CONTAINING HALOGENS

by

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## ABSTRACT

Two fast coincidence circuits have been constructed; one a conventional delayed coincidence circuit (resolving time -  $2 \times 10^{-9}$  seconds); the other using time to pulse height conversion and simultaneous recording of the whole time spectrum on a hundred channel pulse height analyzer, (resolving time -  $1.2 \times 10^{-9}$  seconds). These circuits have been used to study the decay of positrons in organic liquids containing halogens. A semi-empirical equation is derived which predicts the intensity ( $I_2$ ) of the long-lived component in the benzene halides and the propyl halides. For the organic halides mentioned, the intensity ( $I_2$ ) is given by

$$\left(100 - \frac{4}{3} I_2\right) = AN_1 + 2.4N_2$$

where A is the "annihilation factor" for the parent molecule and  $N_1$  and  $N_2$  are the percent volumes of the parent and halide respectively.

The variation of  $I_2$  for different concentrations of carbon tetrachloride in benzene has been measured. The results fit the equation

$$I_2 = \frac{36}{1 + .5P}$$

where P is the percent volume occupied by the carbon tetrachloride in the solution.

## CHAPTER I

### POSITRONS AND POSITRONIUM

#### 1) Early Experiments

Positrons were first discovered by Anderson in 1932, and in 1951 Deutsch (De-51) experimentally verified the existence of positronium, a bound state of a positron and an electron similar to a hydrogen atom. The lifetime of a positronium atom or a positron in matter is very short; the calculated lifetime for the positronium atom's singlet state (anti-parallel spins)  $\tau_1 = 1.25 \times 10^{-10}$  seconds (Pi-47) and for the triplet state (parallel spins)  $\tau_3 = 1.4 \times 10^{-7}$  seconds (O-49a). The lifetime for free positrons is, of course, dependent on the media involved, but is still very short. The experiment of Deutsch was to measure the delayed emission of annihilation radiation after the positron had entered a gaseous medium, the lifetimes observed being of the order of  $2 \times 10^{-7}$  seconds.

Bell and Graham (B-53) postulated the formation of positronium in various liquids and solids to explain their experimental results. The observed long lifetimes were of the order of  $10^{-9}$  seconds. They showed that this lifetime decayed almost exclusively by 2 quantum annihilation, i.e. from the singlet state, since the triplet state decays with 3 quanta (to first order). They suggested that this longer-lived <sup>( $\tau_2$ )</sup> component was due to positrons that initially formed <sub>positronium</sub> in the triplet state and through collision with the atoms in the sample were converted to the short-lived singlet state. This mode of decay was first

suggested by Ore and Powell (O-49a).

Since these initial experiments, the decay of positrons has been studied in many different materials. A comprehensive list of these experiments has been compiled by Paul (P-58).

## 2) Formation of Positronium

Consider a positron from  $\text{Na}^{22}$  entering some medium. The energy of the particle may be as great as 0.54 MeV. Bethe (Be-35) has shown that the chance of annihilation of fast positrons is small, the annihilation of free positrons occurring at or near thermal energies. By a series of inelastic collisions, the positron slows down to an energy below the lowest excitation

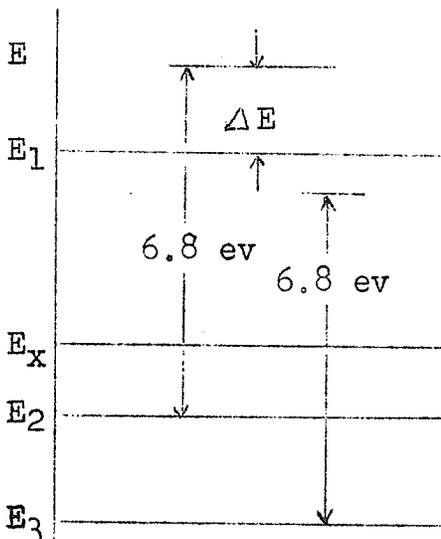


Diagram #1

potential ( $E_x$ ) of the molecules in the medium. Once below  $E_x$ , the positron can lose energy only by elastic collisions - a relatively slow process. This is the region most favorable to positronium formation, immediately below the lowest excitation potential and well above thermal energies, for the positron must be travelling with a velocity comparable to the orbital electrons for positronium

formation. Consider a positron of energy  $E_2$  just below  $E_x$ , the lowest excitation potential of the material. Should it become bound to an electron (the binding energy of positronium is  $\sim 6.8$  ev) it can leave the atom with an energy of  $\Delta E$ , the excess energy of the system above the ionizing potential of the atom  $E_1$ . If a positron of energy  $E_3$  becomes bound to an electron, it does not

have sufficient energy to escape the atom. Hence, a relatively narrow region exists in which positronium can form, extending from  $E_x$  down to  $E_1 - 6.8$  ev. This is termed the Ore gap. (0-49).

A positronium atom can be formed from a positron of energy greater than  $E_x$  but the probability is small because it is losing energy relatively quickly due to inelastic collisions, thus remaining for a very short time in any given energy band. A positronium atom formed well above the Ore gap will have a net positive energy and be unstable.

The theoretical work of Ore was with respect to the formation of positronium in gases and its applicability to liquids is questionable. Consider, for example, n-Propyl chloride, one of the samples studied in the present work. When excited, organic liquids tend to dissociate rather than assume an electronically excited configuration. Thus one may assign the dissociation energy as the lowest excitation potential in determining the Ore gap - in this case  $\sim 3$  ev. (If lower excited states exist, they would only tend to make the argument stronger.) The ionization potential of this molecule is 10.7 ev; consequently, no Ore gap exists. However, n-Propyl chloride displays a pronounced  $\tau_2$  component, proving that positronium is formed.

### 3) Annihilation of Positrons and Positronium.

As previously stated, the positronium atom can annihilate from the triplet or the singlet state. Three quantum annihilation in condensed media is rare compared to two quantum

annihilation, the ratio being  $1/370$  (O-49a). A positron in a positronium atom can also decay with an external electron. This is most probable during a collision ("pick-off"), (G-53) or if the positronium atom forms a compound with some other atom. Simons (Si-53) has shown that positronium chloride is dynamically stable in free space. Paul (P-58) has postulated the formation of positronium helide and positronium argide and performed a novel experiment which appears to verify their existence.

The primary mechanism by which the lifetime of the long-lived ( $\tau_2$ ) component is decreased from the mean life of the triplet state might be either "pick-off", as stated above, or conversion - in which a positronium atom in the triplet state collides with an atom and exchanges electrons, leaving the collision in the short-lived singlet state. This is of no consequence in the present work; the fact that some such mechanism exists is sufficient.

Another process which decreases  $\tau_2$ , quite apart from the above mentioned mechanisms, is "magnetic conversion". An applied magnetic field tends to decrease the value of  $\tau_2$  by mixing the  $m = 0$  substate of triplet positronium and the singlet state ( $m = 0$ ). Due to the much shorter lifetime of the singlet state, the triplet ( $m = 0$ ) substate is depopulated. This effect has been studied (He-57) with angular correlation apparatus; the applied field causing an enhancement of the narrow component which is due to thermalized positronium two quantum decay.

The presence of small amounts of oxygen in liquid

nitrogen and liquid argon decreases  $\tau_2$ , an effect possibly due to the high magnetic susceptibility of oxygen. However, some form of chemical association with the positronium atom would also explain the experimental results.

#### 4) Solids.

Lee Whiting (L-55) has calculated that positrons thermalize in metals in  $3 \times 10^{-12}$  seconds. Since the mean life of positrons in metals is approximately  $2 \times 10^{-10}$  seconds, decay occurs after thermalization. This conclusion is experimentally substantiated by angular correlation experiments, the resultant momentum distribution being that of the electrons in the Fermi sea. No long lifetime has been observed in metals or crystalline substances (except by Gerholm in aluminum - a result that has not been observed in further investigations). If the positronium wave function is confined in a sphere less than  $1.8 \text{ \AA}$ , the lowest energy it can have will be positive (DeB-50). Hence, the lack of a  $\tau_2$  component is not surprising when the close packing of atoms in crystals is considered. The abundance of conduction electrons in metals will also tend to hasten the decay. Amorphous solids - teflon, polystyrene and certain types of glass, exhibit an appreciable  $\tau_2$  component.

#### 5) Liquids.

The formation of positronium in liquids is not surprising. In a crystal lattice, the interatomic spacings are small and if a positronium atom is formed, it is probable that it would be squeezed to annihilation or dissociation unless a lattice

<sup>1</sup>lattice exhibits a  $\tau_2$  of  $1.2 \times 10^{-9}$  sec. (B-53)

defect is convenient. Liquids present a more favorable environment. The concept of "holes" (small volumes of vacuum, not volumes of the liquid vapour) moving about in a liquid (Fr-46) would afford a freshly formed positronium atom ample room to exist in a bound state. (An attempt to fit experimental data to the mean radius of these "holes" failed, possibly due to the uncertainty in their radius). This concept probably isn't even necessary, for the intermolecular distances in most liquids would allow room for the positronium atom to form.

Liquids exhibit a  $\tau_2 \sim 2 \times 10^{-9}$  seconds with an intensity of up to 40%. A few liquids have no  $\tau_2$  component, such as carbon-tetrachloride and dichlorobenzene (Ha-58a).

Two interesting effects are worth noting. First, the addition of molecular iodine to heptane decreases the value of  $\tau_2$  without varying  $I_2$ , the relative number of positrons forming triplet positronium. (Ha-58). Actually,  $I_2$  did vary in a random fashion, but the authors stated that this was probably due to the interpretation of the curves. The effect is analagous to the addition of oxygen to nitrogen or argon, but the magnetic susceptibility of iodine is a few orders of magnitude less than oxygen. This would seem to indicate that an effect different than "magnetic conversion" could explain both results. As yet, no satisfactory explanation exists. Secondly, the addition of  $\text{NaNO}_3$  to water depresses  $I_2$ , but leaves  $\tau_2$  unchanged (Gr-57). This has been explained by the formation of positron nitrate  $e^+\text{NO}_3^-$ ; the positrons captured by the nitrate ions decaying with a lifetime comparable to the singlet state.

6) Summary.

Gases display three resolvable lifetimes: one of about  $10^{-10}$  seconds due to singlet state decay; one of about  $10^{-7}$  seconds due to positrons that formed <sup>positronium</sup> in the triplet state; and a pressure dependent intermediate lifetime due to the annihilation of free positrons.

Experimental limitations do not allow the separation of the singlet state decay and the free positron decay in condensed media. The free positrons decay with a mean life of the order of  $10^{-10}$  seconds, approximately the same lifetime as the singlet state. Present techniques can measure time intervals of the order of  $10^{-10}$  seconds only by centroid shifts.

Crystalline solids and metals exhibit one decay component only of the order of  $10^{-10}$  seconds.

Liquids in general display two lifetimes; one of about  $10^{-10}$  seconds due to the decay of singlet positronium and free positrons, and the other of the order of  $2 \times 10^{-9}$  seconds due to positrons that initially formed <sup>positronium</sup> in the triplet state.

## CHAPTER II

### SOURCES

The positron source throughout the experiment was  $\text{Na}^{22}$  in the form of  $\text{NaCl}$  in aqueous solution with a specific activity of  $57 \mu\text{c}/\text{cc}$  obtained from Abbott Laboratories in Chicago, Illinois. For positron decay in copper, ordinary  $3/8$ " copper tubing was flattened and soldered at one end. The required activity was pipetted in, allowed to evaporate and then the rest of the tube flattened and the open end soldered. The aluminum source was obtained from A.E.C.L. For positron decay in water, a test tube was partially filled with distilled water and  $4 \mu\text{c}$  of  $\text{Na}^{22}$  dissolved in it.

Many sources were made for positron decay in organic liquids, none of which were altogether satisfactory. Mica "sandwich sources" -  $\text{Na}^{22}$  evaporated onto a sheet of mica (usually  $2-3 \text{ mg}/\text{cm}^2$ ) and a similar piece of mica glued on top with an epoxy resin - were unsuitable because the organic liquids attacked the resin and opened the source. For these sources, the positron absorption in the mica was determined by a comparison of  $I_2$  for distilled water, first with the sandwich source in distilled water and then with the activated  $\text{NaCl}$  solution mentioned above.

$\text{Na}^{22}$  was not soluble in the liquids studied, and an open source was finally used. A sheet of mica -  $3 \text{ mg}/\text{cm}^2$  - was roughened on one side and  $3 \mu\text{c}$  of  $\text{Na}^{22}$  evaporated onto it.

This was immersed in a test tube of the liquid under study.  
The activity in the liquid after removal of the source was negligible.

## CHAPTER III

### APPARATUS - MARK I

#### 1) Operation.

A 1.28 MeV  $\gamma$  ray is emitted essentially in coincidence with a positron in the decay of  $\text{Na}^{22}$ , as shown in Fig. 2. (En-54). The positron eventually annihilates, emitting two 0.511 MeV rays, correlated at  $180^\circ$ . (A small fraction annihilate by other modes, but can be ignored in this discussion). One can think of the 'timer' as being turned on by the 1.28 MeV  $\gamma$  ray and turned off by the .511 MeV  $\gamma$  ray. Actually, the number of .511 MeV  $\gamma$  rays occurring at a certain time delay with respect to their 1.28 MeV  $\gamma$  rays are counted, and a 'resolution curve' - the number of counts plotted against time delay - is obtained. The delay is determined from measured lengths of RG7U coaxial cable inserted from the detector to the fact coincidence.

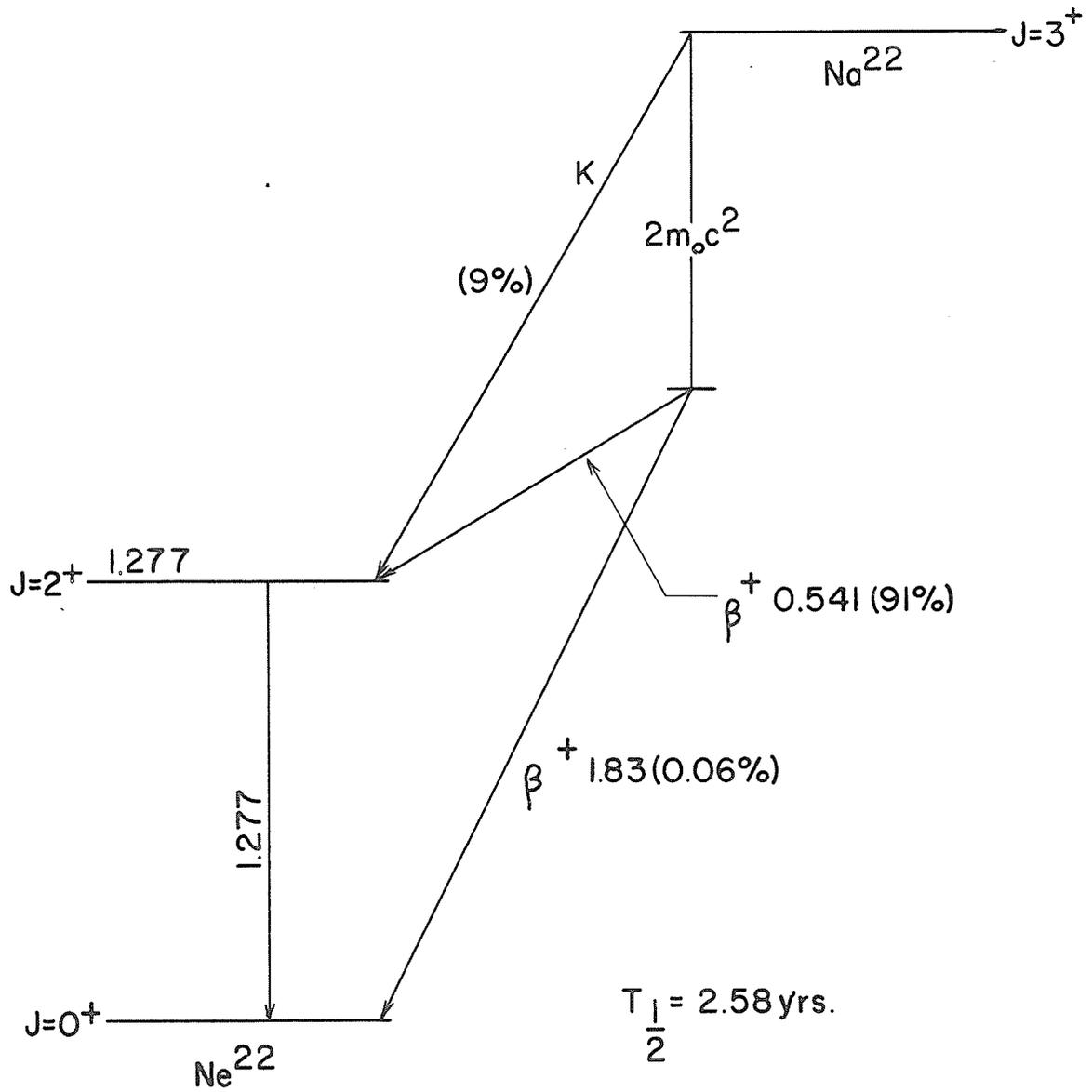
The block diagram of the apparatus is shown in Fig. 6. For a delayed coincidence count to register on scaler 1, three events must occur within two micro-seconds:

- 1) There must be a 'fast coincidence' between the limited pulses.
- 2) The 1.28 MeV side channel must register a pulse in excess of .52 MeV.
- 3) The .511 MeV side channel must register a pulse in the energy range .2 MeV to .5 MeV.

This is accomplished by the two cascaded 'slow coincidence' circuits, which are equivalent to a triple coincidence. The .511 MeV side channel will register counts from the Compton distribution of the 1.28 MeV  $\gamma$  rays, but the 1.28 MeV side

FIG. 2

DECAY OF  $\text{Na}^{22}$



channel cannot register the annihilation radiation because of the discriminator setting.

The pulses that operate the side channels were taken from the ninth dynode of the photomultipliers and all subsequent circuitry is of standard design.

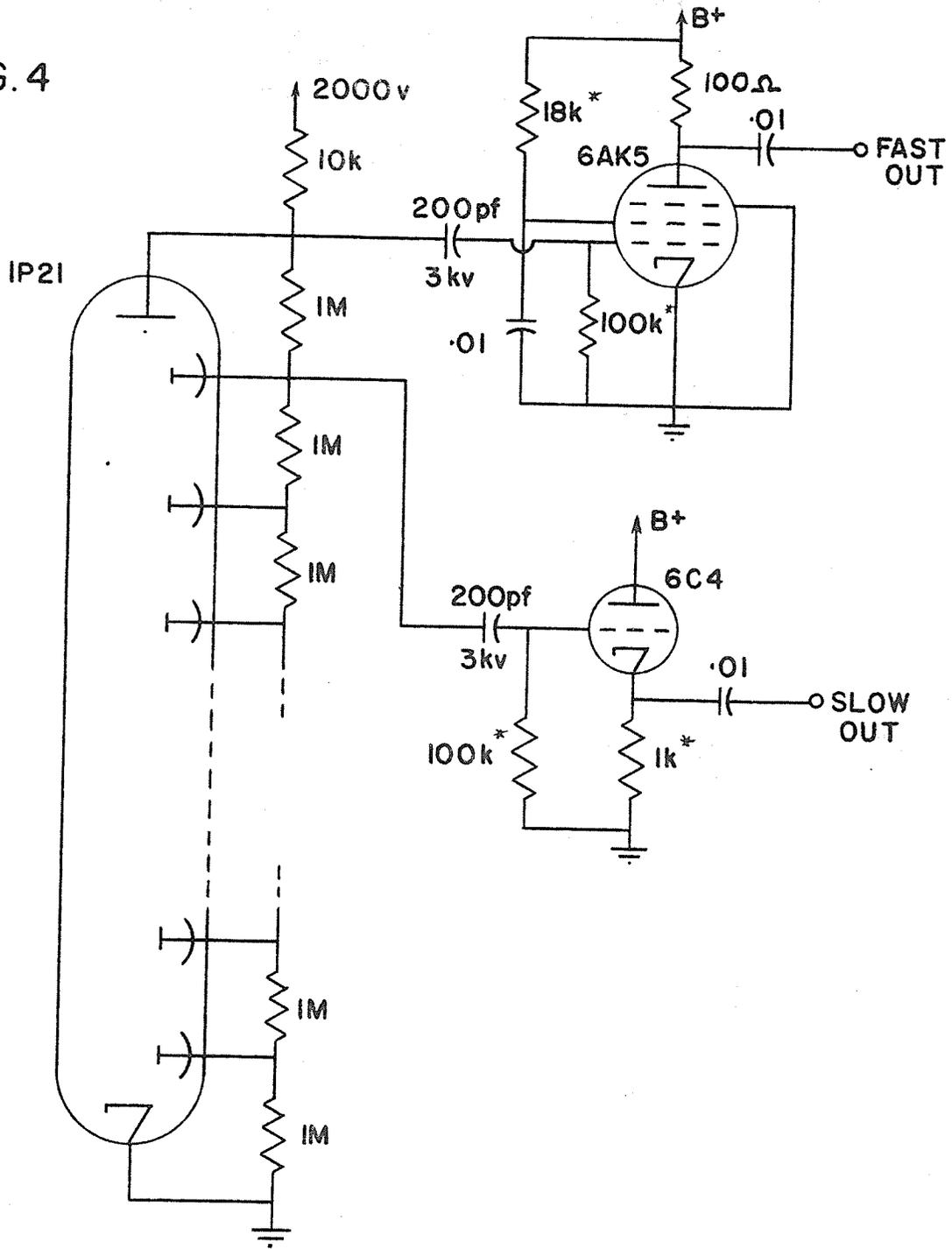
## 2) Fast Coincidence.

Stilbene crystals were used to detect the  $\gamma$  rays. One of the factors limiting the resolving time in such a fast coincidence circuit is the uncertainty in the time with which the first photo-electron strikes the photo-cathode after the  $\gamma$  ray has entered the crystal. Stilbene is one of the best phosphors in this respect but has the disadvantage of low counting efficiency and poor energy resolution.

R.C.A. 1P21 photomultipliers were used because of the close geometry of the dynodes. They were operated in excess of 2000 v to yield a high gain and ensure short transit time spreads. At this voltage, the number of noise pulses may become excessive, and the best two tubes out of six available were chosen.

The fast coincidence <sup>circuit</sup> is the conventional circuit described by Bell, Graham and Petch (B-52). A  $\gamma$  ray detected by one of the crystals produces a large (10-20 volts) fast-rising negative pulse at the grid of the 6 AK5 pentode limiter, cutting off the quiescent plate current of 15 m.a. (See Fig.4). The A.C. plate load is the 100 $\Omega$  resistor in parallel with the 100 $\Omega$  cable; hence a fast-rising flat-topped pulse of approximately .75 volts is transmitted down the cable. We shall

FIG. 4



## DETECTOR BOXES

$B^+ = 180\text{ v}$

All resistors  $\frac{1}{2}$  w carbon deposit unless followed by a star

assume the pulse to have a vertical leading edge in the following discussion. The  $50\Omega$  shorted stub negatively reflects the pulses, this reflection being delayed by a time  $2p$  with respect to the common point of the three coaxial cables.

' $p$ ' is the time length of the  $50\Omega$  stub. (See Fig. 5). The limiter ends of the  $100\Omega$  cable are terminated with the cable's characteristic impedance and no secondary reflections occur.

Hence, each detected  $\gamma$  ray gives rise to a rectangular pulse at the anode of the diode of width  $2p$  and amplitude  $0.38$  volts. The diode is biased off just beyond this amplitude so that very little current is passed by a "single" pulse. If, however, pulses should come down both of the  $100\Omega$  cables so that the rectangular pulses partially overlap, the diode bias is overcome and a voltage will develop across the  $10K$  diode load. This is a fast coincidence.

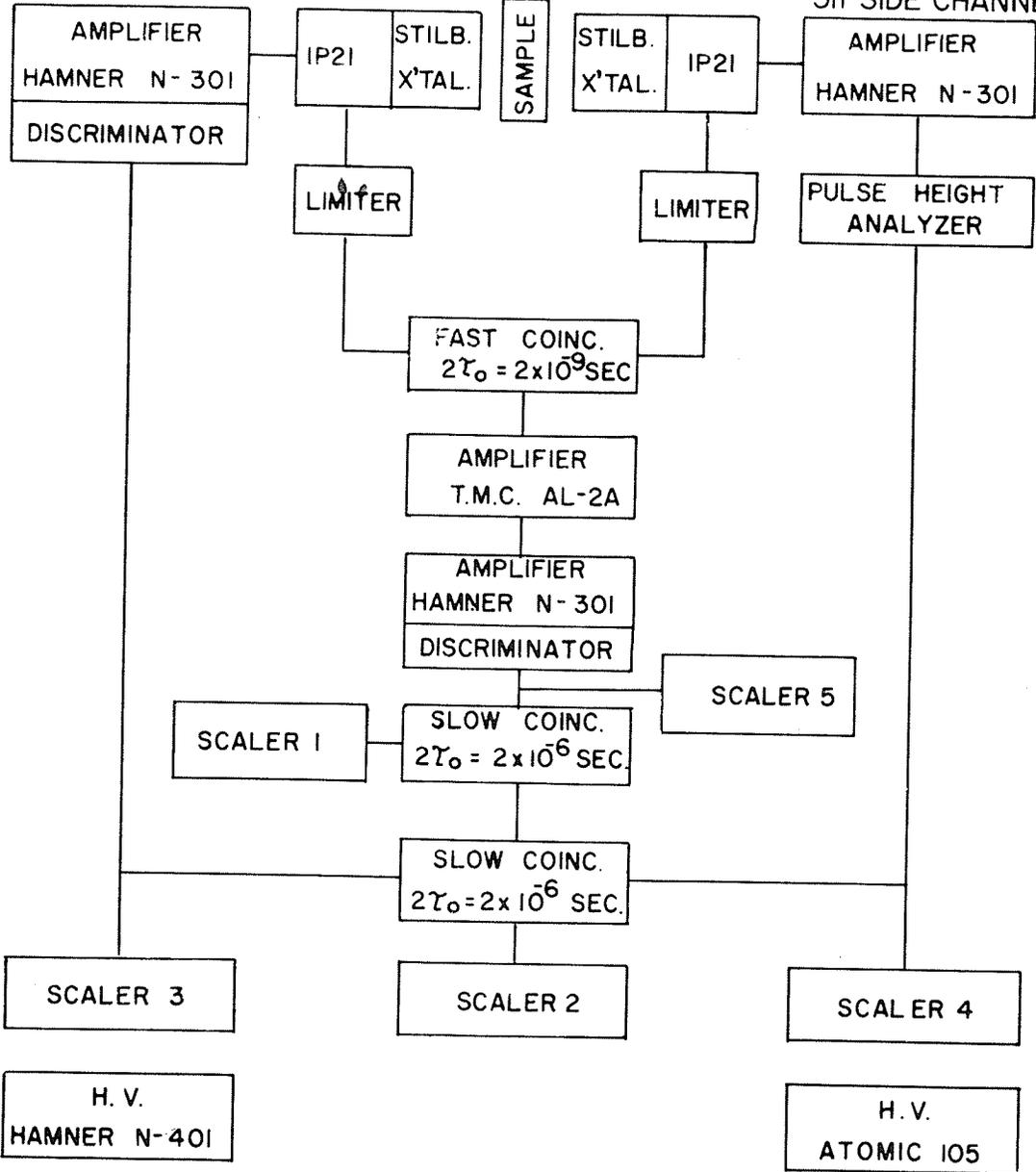
The resolving time ( $2\tau_0$  - the full width at half height of the prompt coincidence curve) of such a circuit under ideal conditions is easily seen to be  $4p$ . However, due to the finite rise time of the limited pulses, the clipped pulse tends to be more triangular than rectangular. The amplitude of the clipped pulse is therefore no longer constant, but dependent on the slope of the leading edge of the limited pulse. The singles to doubles amplitude ratio is also not a constant, but a function of the degree of overlap of the pulses, and the resolving time of the apparatus will vary with the temperature of the diode.

This variation was minimized by surrounding the diode

FIG. 6

128 SIDE CHANNEL

511 SIDE CHANNEL



ALL SCALERS T.M.C. SG-3A

BLOCK DIAGRAM OF APPARATUS

with a small block of polystyrene foam and enclosing the whole fast coincidence chassis with a 2" foam box. The room temperature was maintained as constant as possible.

Fig. 6 shows the electronic apparatus in block form used in the Mark I arrangement. The B<sup>+</sup> power supplies for the limiters and slow coincidence circuits were constructed at the University of Manitoba and are of standard design. A.C. power for the equipment came from a Sorenson Model 2000S voltage regulator.

### 3) Prompt Coincidence Curves.

A prompt resolution curve is the response of the circuit to events that occur in exact coincidence or separated by a time interval much less than the resolving time of the apparatus. Theoretically, this curve should be flat-topped, of width  $4p$  and with vertical sides. Actually, the curve has a rounded top and sides that fall with a finite slope. This departure is due to the uncertainty in the time of emission of the first photo-electron, transit time spreads in the photo-multipliers, electronic shifts and the variation in shape of the clipped pulses. The first and last reasons cited probably make the greatest contribution to this departure.

Fig. 7 shows two resolution curves. The open-circle curve was determined by pulsing the grids of the limiters simultaneously with a 60 cycle pulse generator, thus eliminating the uncertainty in the time of emission from the crystals and shaping the clipped pulses identically. The second curve was obtained by a method described by Gerholm (Ge-56). The

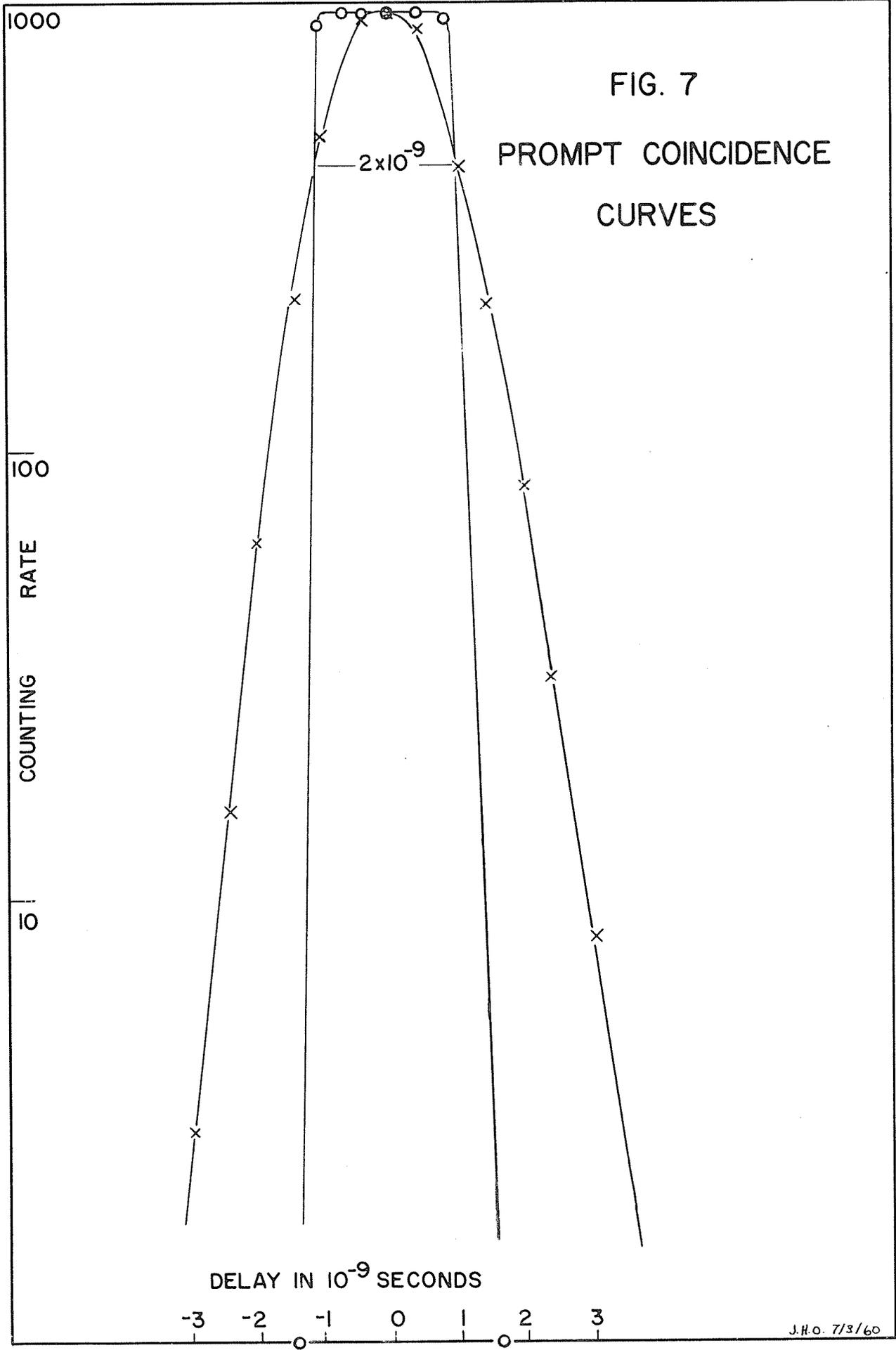


FIG. 7  
 PROMPT COINCIDENCE  
 CURVES

DELAY IN  $10^{-9}$  SECONDS

-3 -2 -1 0 1 2 3

two photomultipliers viewed a single crystal from opposite sides and both received a portion of the emitted light from each incident  $\gamma$  ray.  $\text{Co}^{60}$  was chosen as the source because it has two  $\gamma$  rays which are more than twice the discriminator setting of the 1.28 MeV side channel.

The two curves have been normalized to the same peak counting rate and the centroids adjusted to coincide. The consequence of the above mentioned effects is quite evident in the figure.

#### 4) Curve Analysis.

The decay of positrons in n-Propyl chloride as determined with the Mark I apparatus is shown in Fig. 8. An identical analysis was used with the curves obtained from Mark II. The curve was plotted on semi-logarithmic paper and the position of the break between the prompt and the  $\gamma_2$  portions determined. The points on the tail, i.e. at delays beyond the break, were fitted by least squares, using the formula:

$$\tau_2 = \frac{\log e \left( \sum x_i^2 - \frac{1}{n} (\sum x_i)^2 \right)}{\frac{1}{n} \sum x_i \sum y_i - \sum x_i y_i}$$

where

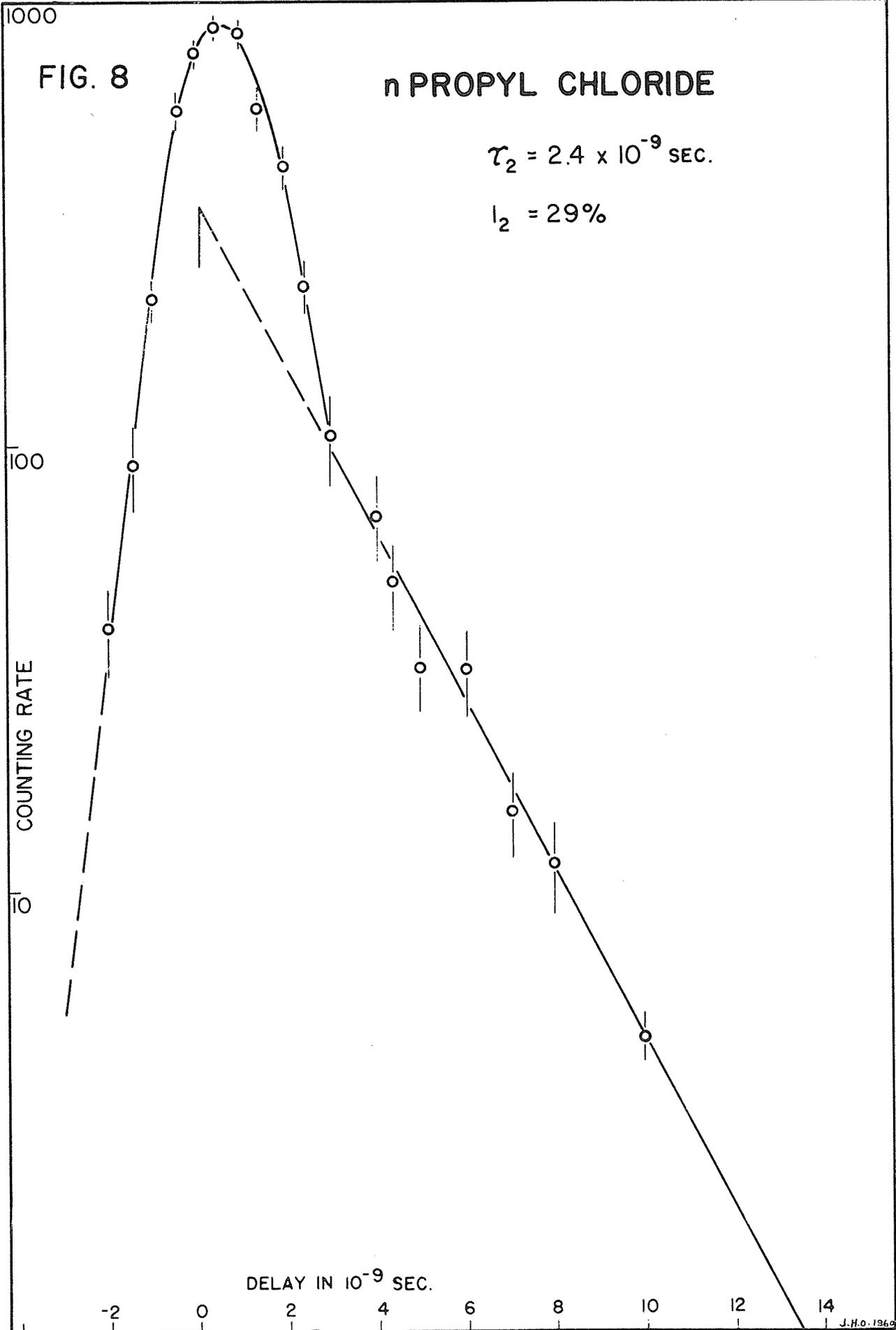
$\tau_2$  = mean life.

$x_i$  = time delay of the  $i^{\text{th}}$  point.

$y_i$  = logarithm (base 10) of the number of counts of the  $i^{\text{th}}$  point.

$n$  = number of points used in the analysis.

The rest of the curve was fitted by eye.



The intensity of the long-lived component was determined by a method described by Green and Bell (Gr-57). The tail was projected back to the position of zero delay. This point was determined by using the centroid of an aluminum curve and the known lifetime of positrons in aluminum,  $2.8 \times 10^{-10}$  seconds. (Ge-56). The intensity of the  $\gamma_2$  component then equals the ratio of the area under this line to the area under the whole curve, with a small correction for source absorption. These areas were determined by numerical integration. Although this method of determining  $I_2$  is not exact, it gives a very good value for comparison, the error introduced being systematic. The correction for source absorption is given by:<sup>1</sup>

$$I_2 = I_2(\text{EXP}) (1 - a)^{-1} \quad (\text{Gr-57})$$

where 'a' is the fraction of positrons absorbed in the source. For the sandwich sources, 'a'  $\sim$  0.1 and for the open source 'a' was estimated to be 0.05. No correction was made for positron annihilation in the epoxy resin; the percentage was probably less than 1%.

<sup>1</sup> Since mica has no long component the positrons decaying in the mica will add counts to the 'prompt' portion of the curve.

## CHAPTER IV

### APPARATUS - MARK II

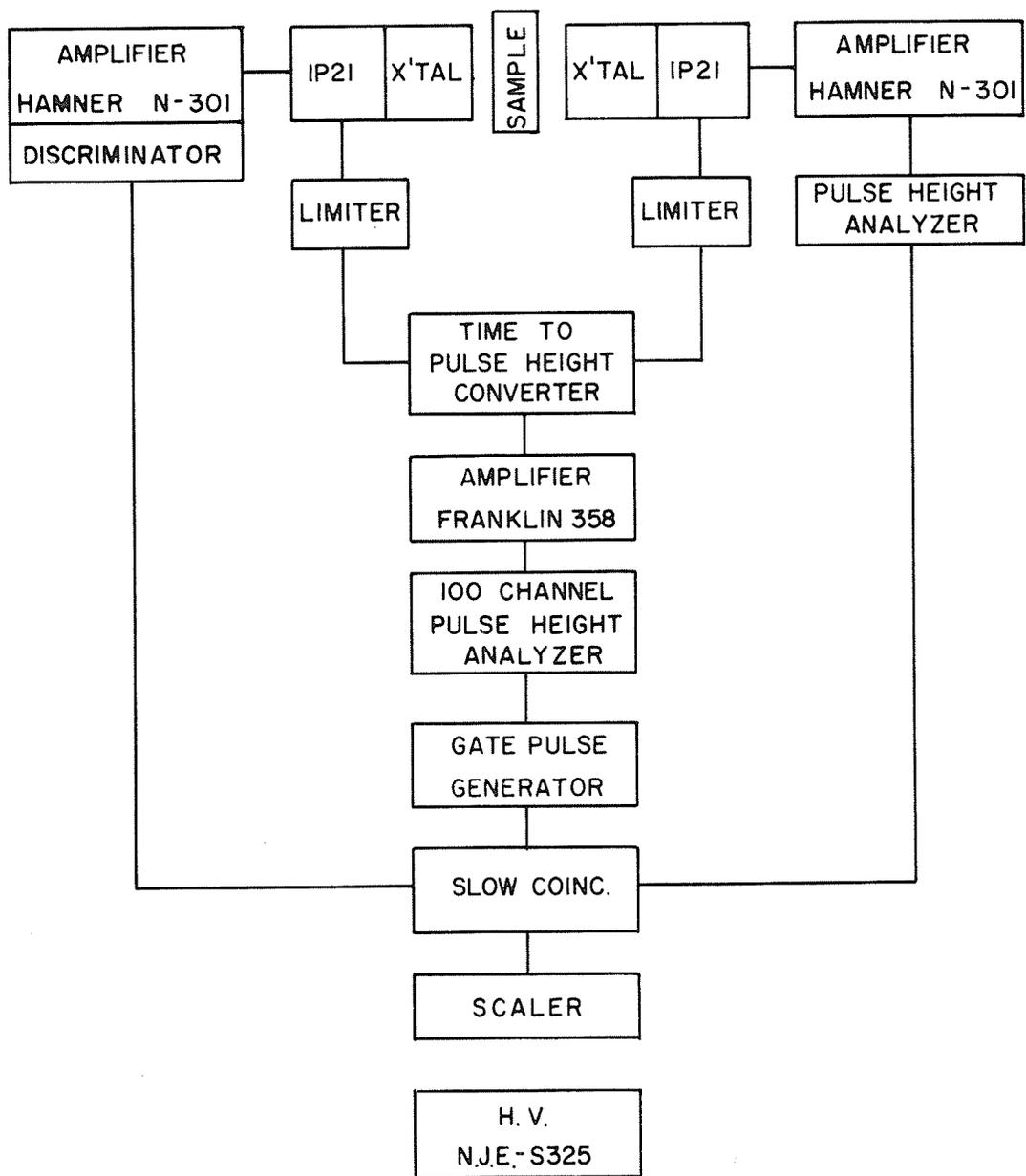
#### 1) Operation.

The operation of this circuit is fully described by Jones (J-60) and the principle of operation only will be outlined below:

Pulses from the two detectors are limited and shaped as described previously, their length now being 15  $\mu$ s instead of 1  $\mu$ s. The pulses are added and a biased diode switch passes only the overlapping portion. This overlap is integrated and amplified, the magnitude of the output pulse being proportional to the degree of overlap. Thus, one achieves time to pulse height conversion. The resultant output is gated to a 100 channel pulse height analyzer by the slow coincidence in the side channels. In this way, a whole resolution curve can be accumulated at once.

The transformation to Mark II was effected with a minimum of changes from the original arrangement. A larger amplitude was required in the limited pulses. This was achieved simply by increasing the  $B^+$  to the limiters, which unfortunately required the tubes to operate slightly above their rated plate dissipation. The limiter circuitry employed by Jones is to be preferred and will be incorporated in the present circuit upon the arrival of the components. The  $B^+$  supply used in the original arrangement had exceptional regulation and was quite adequate for the new circuit.

FIG. 9



BLOCK DIAGRAM OF APPARATUS

MARK 2

The gating pulse was obtained from a modification in the double slow coincidence circuit. (Fig. 3) The plate load of the second 6AK5 in the univibrator was increased to 5.6 k and the stub on the grid increased in length to give a 3  $\mu$ s pulse. This output was fed directly to the cable driver (modified White cathode follower). The 100 channel pulse height analyzer was Model CDC-W410/BC made by Computing Devices of Canada Limited.

The apparatus is shown in block form in Fig. 9. Not shown in the diagram are two count rate meters which were eventually incorporated to monitor the side channels. The count rate meters operated Esterline Angus pen recorders.

## 2) Circuit Performance.

The time resolution and linearity of the apparatus, although quite adequate for the present experiment, were not as good as that of the circuit of Jones. This is most likely due to the limiters. The rise time of the limited pulses could not be determined, (the fastest oscilloscope available - Tektronix Model 517 - had a minimum rise time of 7  $\mu$ s) but an amplitude variation was noticeable within 15  $\mu$ s of the beginning of the pulse. While this would have no effect on the original arrangement, (the Bell, Graham and Petch circuit), it would be of consequence here.

The resolving time of the apparatus, the full width at half height of a prompt curve, was determined using  $\text{Co}^{60}$  as a source yielding  $2\tau_0 = 1.2 \times 10^{-9}$  seconds.

The time to pulse height linearity of the circuit is

shown in Fig. 10, where the centroid of "copper" curves (positron decay in copper) as a function of inserted delay is plotted against channel number. Only the counts in the channels on the linear portion of the curve were used in the analysis of complex decays.

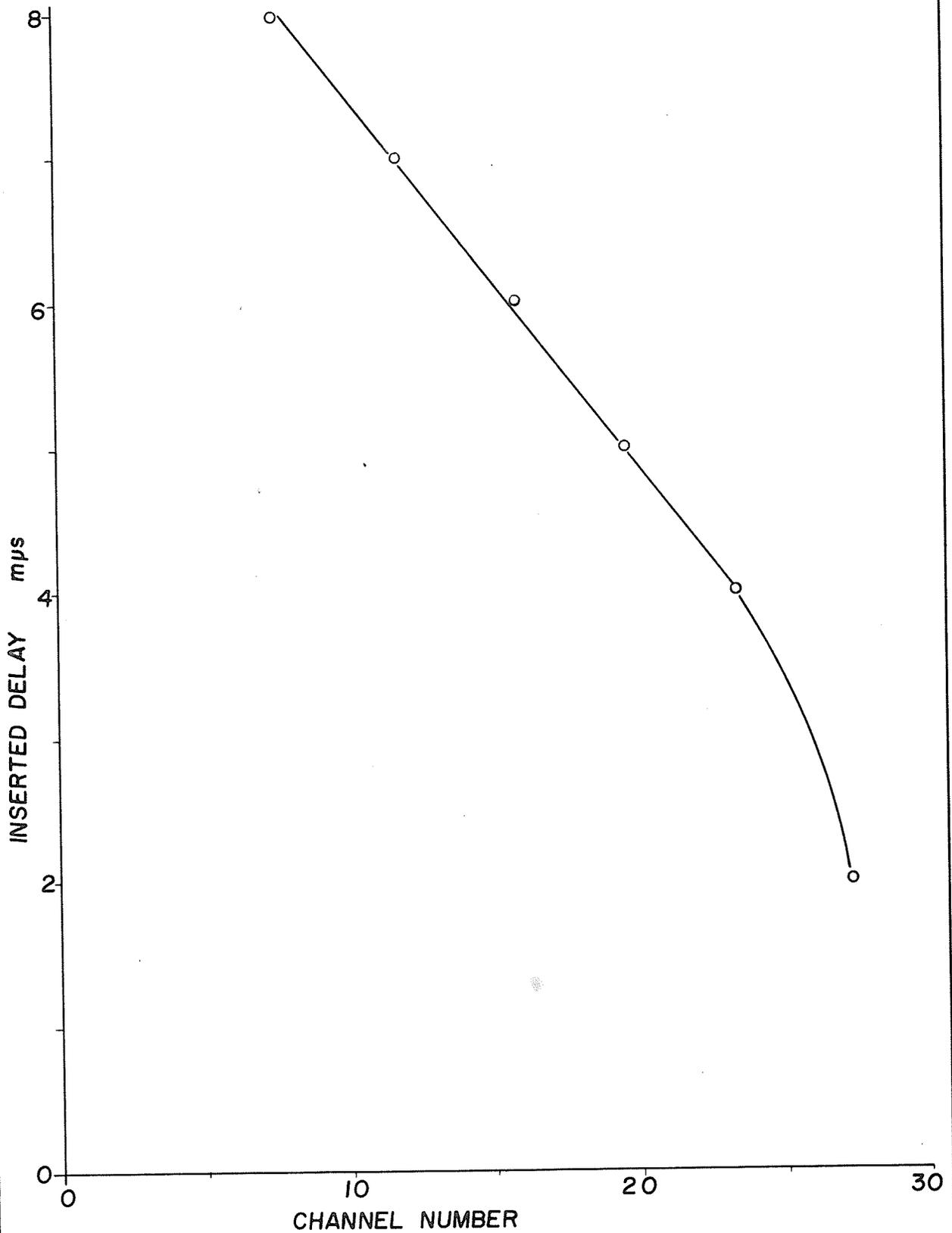
The shape of the curve might suggest that the capacitor in the Miller integrator was approaching saturation. This was not the case since the width at half height of the copper curves was relatively independent of inserted delay. One would expect these curves to narrow considerably at or near saturation. Also, a larger integrating capacitor did not affect the non-linearity.

When using an inserted delay that would permit the front of a resolution curve to register on the hundred channel analyzer, less than two mean lives of the  $\tau_2$  component could register on the linear portion. To obtain a statistically better value for  $\tau_2$ , a delay was inserted that permitted at least two mean lives to register.

The background counting rate was determined by running a copper curve at the delay used in measuring  $\tau_2$ . The source was adjusted to give the same side channel counting rates as registered in studying the organic liquids. The total number of chance counts thus registered was converted to an average correction per channel of 0.24 counts per 1000 slow coincidence counts. Actually, the background decreased for increasing channels (larger delays). Only the chance coincidence counts under the tail would be of consequence in the analysis since

FIG. 10

TIME TO PULSE HEIGHT CONVERSION



J.H.O. 21/3/60

the chance counts in any given channel under the peak were much less than 1%. The error introduced by assuming the background constant under the tail would tend to make  $\tau_2$  less than its actual value.

Two sample curves obtained while testing the apparatus are shown in Fig. 11. The curve showing the decay of positrons in copper has been normalized to the same peak counting rate as the water curve. The accepted values (Gr-57) for the decay of positrons in water are:

$$\begin{aligned}\tau_2 &= 1.8 (\pm 1) \times 10^{-9} \text{ seconds} \\ I_2 &= 21 (\pm 5)\%\end{aligned}$$

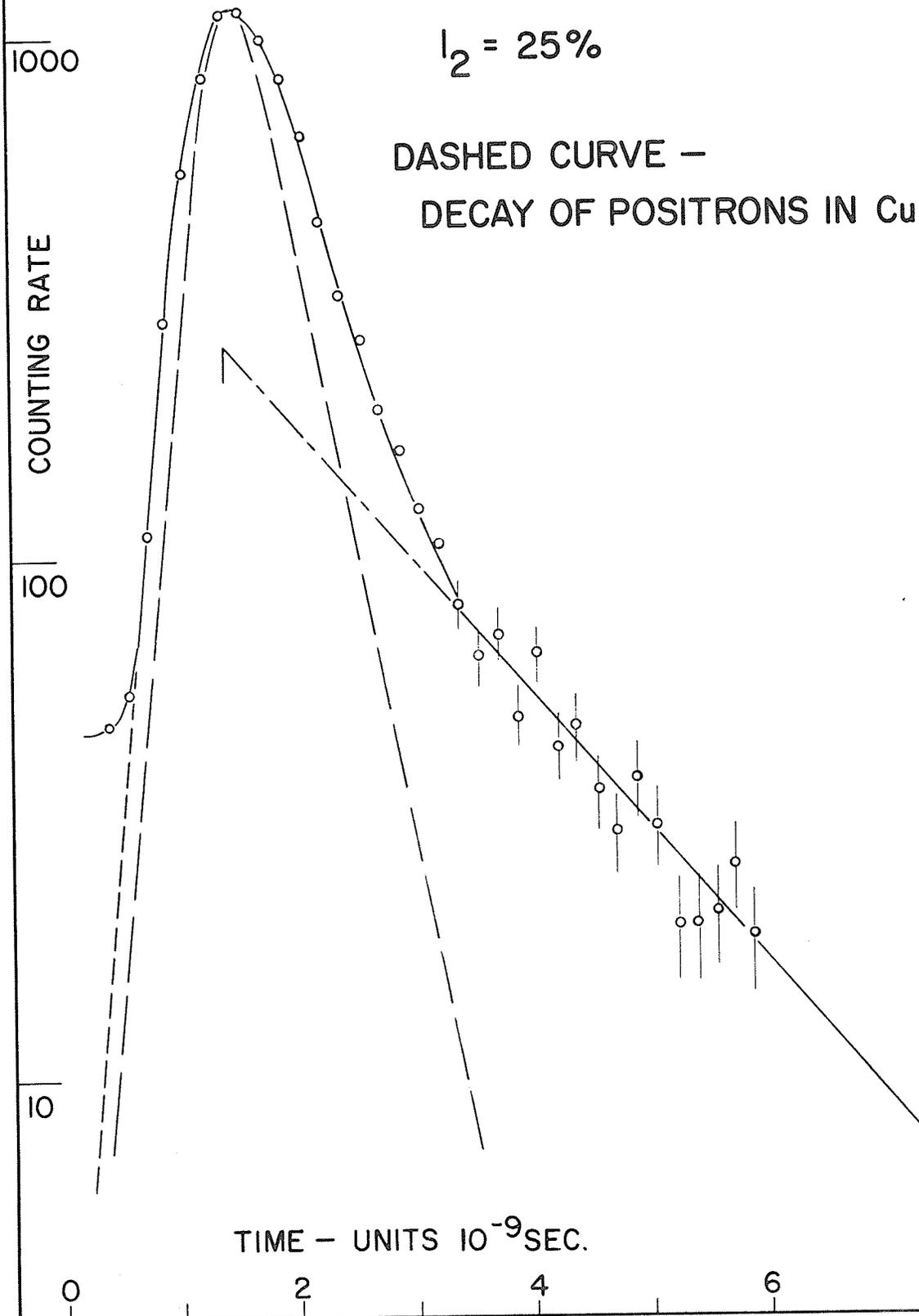
The front of the water curve does not fall as expected but curls over to a plateau. This effect was apparent in all curves and is a characteristic of the circuit. Several causes contribute to this, photomultiplier pulses of too small an amplitude to be limited probably being the greatest factor.

FIG. II DECAY OF POSITRONS IN WATER

$$\tau_2 = 18 \times 10^{-10} \text{ SEC.}$$

$$I_2 = 25\%$$

DASHED CURVE -  
DECAY OF POSITRONS IN Cu



## CHAPTER V

### EXPERIMENTAL RESULTS AND DISCUSSION OF POSITRON DECAY IN HALIDE COMPOUNDS

#### 1) Experimental Results.

The first experiment, the decay of positrons in the Propyl-halides, was performed to determine whether the intensity of positrons forming in the triplet state ( $I_2$ ) varied in a manner similar to the variations observed in the benzene halides (Na-58a); that is,  $I_2$  decreasing as the atomic number of the halogen increased. The Propyl-halides were studied with both the Mark I apparatus and the Mark II. The values of  $\tau_2$  measured on Mark I are high because no background was subtracted; the relative values of  $I_2$ , however, would not be greatly affected by this systematic error. The results are also subject to errors introduced by electronic shifts since a statistically significant curve required a total counting time of about 10 hours.

The curves were obtained by counting over the time spectrum several times, letting a preset number of counts register at each point, thus reducing the errors due to electronic shifts. Taking the same number of counts at each point on the tail ( $\tau_2$  portion) also has the advantage of giving each point the same statistical weight in the least squares fit. A sample curve is shown in Fig. 8. The results are tabulated in Table 1.

The Propyl-halides were not studied in detail with the

Mark II apparatus because the intensities were in agreement with the previous results. Also, propane and fluoro-propane could not be tested with the existing experimental arrangement because they are both gases. The results of the Propyl-halides (Mark II) are listed in Table Ia. The Mark II apparatus had just been assembled when these samples were tested, and large errors have been assigned because of the initial instability of the apparatus.

TABLE I

POSITRON DECAY IN PROPYL HALIDES (MARK I)

SAMPLE	NO. OF RUNS	$\tau_2(10^{-10} \text{ Sec.})$	$I_2 (\%)$
n-Propyl Chloride	4	26 (?)	26 ( $\pm 3$ )
2-Propyl bromide	3	23 (?)	15 ( $\pm 3$ )
2-Propyl iodide	4	24 (?)	12 ( $\pm 3$ )

(Errors quoted are for comparison purposes only.)

TABLE Ia

POSITRON DECAY IN PROPYL HALIDES (MARK II)

SAMPLE	NO. OF RUNS	$\tau_2(10^{-10} \text{ Sec.})$	$I_2 (\%)$
n-Propyl chloride	1	15 ( $\pm 3$ )	23 ( $\pm 4$ )
2-Propyl bromide	1	16 ( $\pm 3$ )	16 ( $\pm 4$ )
2-Propyl iodide	1	16 ( $\pm 3$ )	12 ( $\pm 4$ )

(Errors quoted are for comparison purposes only.)

Whereas the intensities of the two sets of results are in reasonable agreement, the rate of decay as determined with

the Mark I apparatus was, as expected, much slower. Hence, the values of  $\gamma_2$  in Table Ia are probably more accurate.

## 2) Volume Effect.<sup>1</sup>

The following discussion describes the formulation of a semi-empirical relationship which predicts  $I_2$  for liquid halide compounds.

$I_2$  is the relative number of positrons entering a given material that form positronium in the triplet state. The relative number of positrons that form positronium is then  $\frac{4}{3} I_2$ , since the triplet state has three substates ( $m = 0, \pm 1$ ) while the singlet state has but one ( $m = 0$ ). Hence, their relative formation is 3 : 1. As mentioned previously, the positrons that form singlet positronium appear in the "prompt" portion of the curve. We shall be concerned with the percentage of positrons that do not form positronium,  $100 - \frac{4}{3} I_2$ .

Consider a liquid such as benzene halide. The benzene portion of the compound occupies a certain % volume  $N_1$  in the liquid and the halide a % volume  $N_2$  ( $N_1 + N_2 = 100\%$ )  $N_1$  is considered an effective volume which includes the inter-molecular voids. An "annihilation factor", A, is assigned to benzene and a similar factor, B, to the halide. Then

$$(100 - \frac{4}{3} I_2) = AN_1 + BN_2 \quad \dots\dots\dots 1$$

The equation simply states that the number of positrons annihilating is dependent on the environment and the time spent in that environment; the times being proportional to the relative volumes of the molecules (atoms, ions) of the compound.

<sup>1</sup> Further comments in App. C 22

The fact that a constant annihilation factor B can be assigned to the halogens as a group is not so remarkable for all have identical outer electronic shells and annihilation occurs predominantly with outer electrons.

The annihilation cross-section for the halide portion is easily determined from the product  $BN_2$  by equating it to  $N\sigma\bar{v}T$  where

- N - number of halide atoms per cc
- $\sigma$  - annihilation cross-section in  $cm^2$
- $\bar{v}$  - average relative velocity of the positron  
and halide
- T - time of decision for positronium formation

Similarly, the annihilation cross-section for the benzene portion can be obtained from the product  $AN_1$

No problem is involved if the sum  $AN_1 + BN_2$  should be greater than 100%; the compound simply annihilates positrons at a greater rate than required to completely quench the  $\tau_2$  component.

The relative volumes were determined as follows: For a given compound, the effective volume of the molecule is given by

$$V_M = \frac{A}{dN_0}$$

where A - molecular weight

d - density

$N_0$  - Avogadro's number -  $6.02 \times 10^{23}$

The volume of a halide ion,  $V_H = \frac{4}{3}\pi R^3$  where R was deter-

mined by Pauling (H-57) on the basis of wave mechanics. It follows immediately that

$$N_2 = \frac{V_H}{V_M} \times 100\%$$

$$N_1 = 100 - N_2$$

A and B were determined from the experimental data of (Ha-58a);

A = 0.53 from benzene alone ( $N_2 = 0$ ) and B = 2.4 to best fit the results.

The agreement between the calculated and experimental values is shown in Table II.

TABLE II  
EXPERIMENTAL AND CALCULATED VALUES OF  $(100 - \frac{4}{3} I_2)$  FOR BENZENE HALIDES

Sample	%Vol. of Benzene ( $N_1$ )	% Vol. of Halide ( $N_2$ )	$I_2$ Observed (Ha-58a)	$100 - \frac{4}{3} I_2$ Exp.	$\frac{4}{3} I_2$ Calc.
Benzene	100	0	35 $\pm 2$	53	53
Fluoro-benzene	93.3	6.7	24 $\pm 2$	68	66
Chloro-benzene	85	15	14 $\pm 2$	81	82
Bromo-benzene	82	18	6 $\pm 2$	92	88
Iodo-benzene	77	23	4 $\pm 2$	95	97
Dichloro-benzene	75.6	24.4	0	100	100
Carbon-tetrachloride	-	~100	0	100	100

As stated previously, propane could not be examined with the existing experimental arrangement and an average value of A' was determined to fit the experimental results. The halide annihilation factor determined above (2.4) was left unchanged.

Table III lists the experimental and calculated values of  $(100 - \frac{4}{3} I_2)$  for the Propyl halides studied. The calculated values were determined from the equation

$$(100 - \frac{4}{3} I_2) = .36N_1' + 2.4N_2$$

where  $N_1'$  is the relative volume of the Propyl group and all other symbols are as previously defined.

TABLE III  
EXPERIMENTAL AND CALCULATED VALUES OF  $(100 - \frac{4}{3} I_2)$  FOR THE  
PROPYL HALIDES

Sample	%Vol. of Propane( $N_1'$ )	%Vol. of Halide( $N_2$ )	$I_2$ Observed	$100 - \frac{4}{3} I_2$ Calc.	$100 - \frac{4}{3} I_2$ Expt'l
n-Propyl chloride	83	17	23	71	69
2-Propyl bromide	80	20	16	77	79
2-Propyl iodide	75	25	12	87	84

$I_2$  has been measured (Gr-57) for a 5M solution of HCl in water. The value predicted by the above equation is 12%, whereas the experimental value is 16%. The discrepancy was first attributed to the hydration of the  $Cl^-$  ion, the water molecules shielding the ion from the positron. However, in view of the results of the second experiment, it is quite possible that the equation does not apply to ionized halide ~~ions~~ <sup>atoms</sup>.

In the formulation of the equation, nothing is assumed as to the fate of the positron save that it annihilates without forming positronium. Three possibilities present themselves:

1) Free annihilation and positronium formation are directly competing processes and the majority of free annihilations occur in the energy band where positronium is formed.

2) The presence of the halide inhibits positronium formation and the positrons pass through the energy band where positronium can be formed down to near thermal energies, where they can only annihilate as free positrons.

3) Some form of chemical association exists whereby the positron is bound in an electronic environment with an electron density of appropriate spin to allow singlet decay.

The first possibility can be eliminated as a predominant factor in view of the results of angular correlation experiments. The angular distribution shows that positrons annihilate well below the energy range generally accepted as the region of positronium formation.

Which of the other two phenomena occur remains a matter of conjecture. Many authors (Ha-58a, De-53) have proposed the formation of positronium compounds from molecular structures. How such a transition might occur remains obscure. The simple mechanism of a positron rupturing a molecular bond and then having a favorable orientation to permit chemical combination is highly speculative. Possibly the positron need not ionize the molecule, the rupture occurring after some form of combination has been established. In any event, further investigations are required to determine the exact nature of the positron's fate.

## CHAPTER VI

### EXPERIMENTAL RESULTS AND DISCUSSION OF POSITRON DECAY IN SOLUTIONS OF BENZENE AND CARBON TETRACHLORIDE

As a further test of the applicability of the volume effect, a second experiment was performed decaying positrons in solutions of benzene and varying concentrations of carbon tetrachloride. The results, however, differed greatly from that predicted by the volume effect; the quenching of the  $\tau_2$  intensity being much greater than expected.

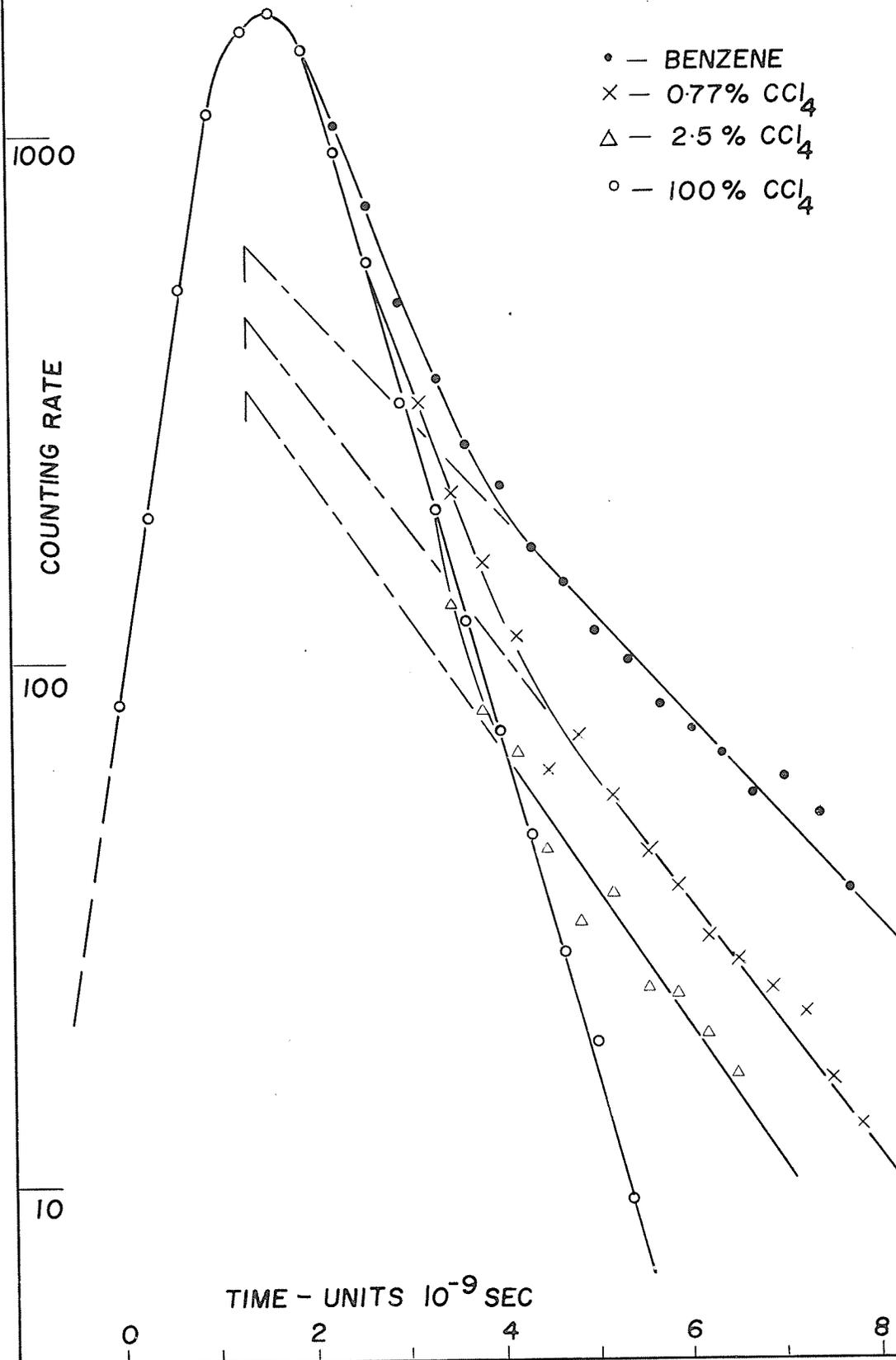
Fig. 12 shows four of the experimental curves normalized with respect to peak counting rate. The results are listed in Table IV. For those concentrations which included several runs, an average of the results is given.

TABLE IV  
DECAY OF POSITRONS IN SOLUTIONS OF BENZENE AND CARBON TETRACHLORIDE

%Volume of $\text{CCl}_4$	No. of Runs	$\tau_2$ ( $10^{-10}$ sec.) $I_2$ (%)	
		$\pm 2$	$\pm 3$
0	5	23.0	36
0.5	1	17.7	29
0.77	2	17.5	26
1.06	1	16.5	24
2.50	3	17.7	16
4.45	2	17.9	11
6.50	1	18.0	8
100	1	-	0

(Errors quoted are for comparison purposes only)

FIG. 12 DECAY OF POSITRONS  
IN BENZENE- $\text{CCl}_4$  SOLUTIONS



The errors quoted are a measure of the variations observed in tests with samples of the same concentration of  $\text{CCl}_4$ .

The initial series of tests including a 2.5% and a 4.45%  $\text{CCl}_4$  concentration was run with one sample of benzene and the  $\text{CCl}_4$  added for successive runs. It was noted that the quenching of  $\text{I}_2$  was much greater than expected and a second series of tests was started. 80 ml of benzene was measured into a container and 0.4 ml  $\text{CCl}_4$  was added. 6 ml of the solution was removed for the 0.5% concentration measurements. Succeeding samples for higher concentration runs were obtained by adding quantities of  $\text{CCl}_4$  to the remaining solution and removing 6 ml for each run. The pure benzene runs were interspersed throughout the experiment. The total number of counts registered varied from curve to curve, the average being ~50,000 counts.

The decay of positrons in pure benzene and pure carbon tetrachloride has been studied previously (Ha-58a); the results are in agreement with the present experiment.

## 2) Variation of $\text{I}_2$ .

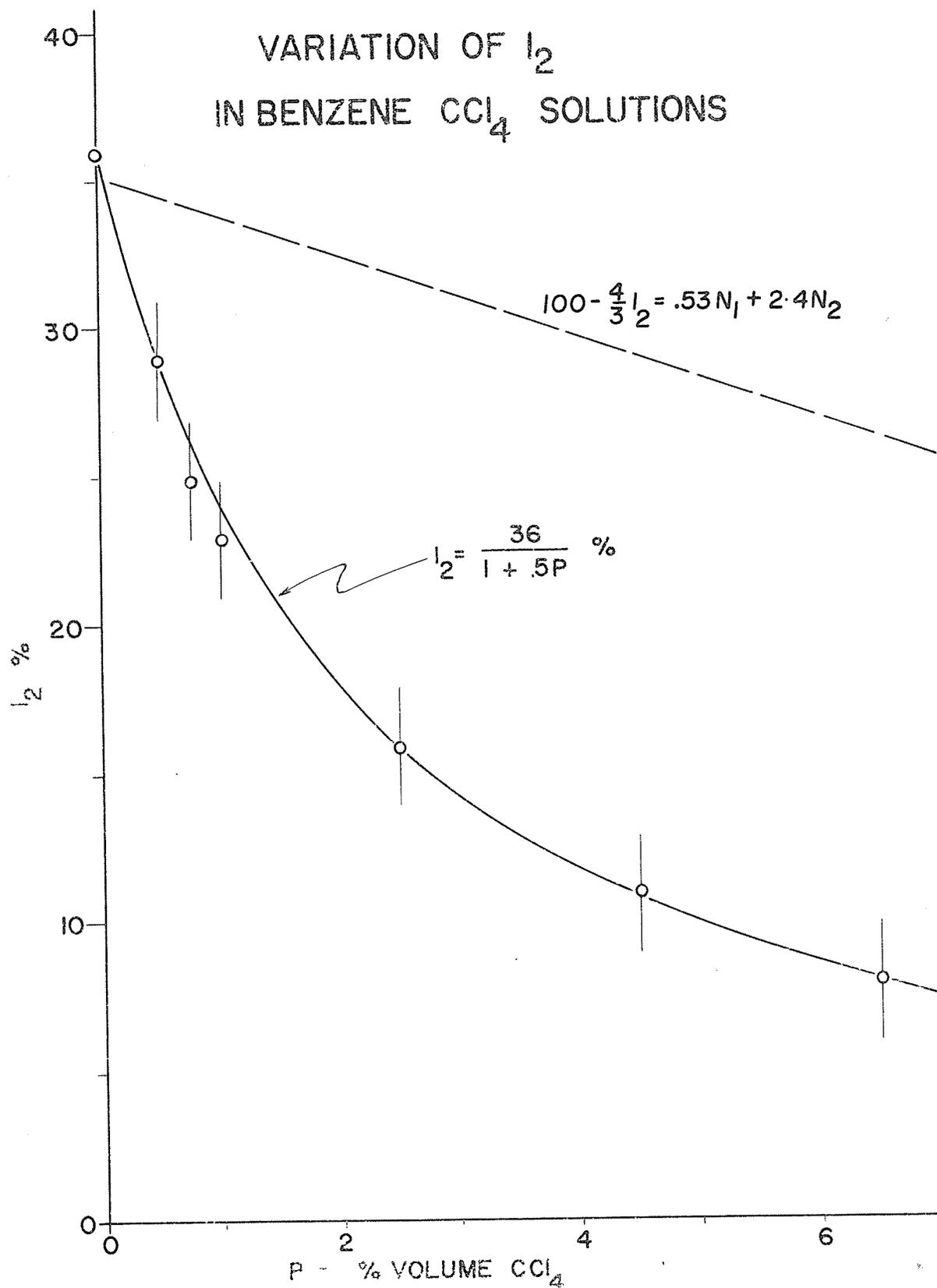
The results of the benzene-carbon tetrachloride dilution experiments do not show the volume effect characteristic of the halide compounds. They do, however, fit the following equation:

$$\text{I}_2 = \frac{36}{1 + .5 P} \% \quad \dots \quad (2)$$

where P is the percent volume occupied by the carbon tetra-

FIG. 13

VARIATION OF  $I_2$   
IN BENZENE  $CCl_4$  SOLUTIONS



J.H.O. MARCH/60

chloride. This is shown graphically in Fig. 13. The dashed curve represents what one would expect on the basis of the volume effect (Equation 1), while the experimental points are seen to lie on the solid line which represents Equation 2.

It is clear that either two distinct processes occur, (comparing the dilution experiment with results of the halide compounds), or, if it is a single process, it is inhibited when the halide is bound to the benzene ring. For example, the experimentally determined value of  $I_2$  for chloro-benzene is 14% (Table II) while the value predicted by equation 2 is only 4%.

The form of equation 2 is the same as that which predicts  $I_2$  for different concentrations of nitrate ions in water (Gr-57).

$$I_2 = \frac{21}{1 + N\sigma\bar{v}T} \% = \frac{21}{1 + kM} \dots\dots\dots (3)$$

- where
- 21% -  $I_2$  for pure water
  - N - concentration of nitrate ions
  - $\bar{v}$  - relative velocity of the positron and the nitrate ion
  - T - time of decision for the positron to form positronium or not
  - $\sigma$  - mean capture cross-section for the formation of positron-nitrate
  - M - molarity

Green and Bell have interpreted their results on the basis of an  $e^+NO_3^-$  compound being formed, with the positron's

lifetime comparable to that of the singlet state. It would require great boldness to apply this mechanism to the halogen bound to the carbon tetrachloride molecule.

The values of  $\bar{v}$  and T can only be roughly estimated and the value of  $\sigma$  determined from equation 3 has little meaning. A more significant value is the product  $\sigma \bar{v} T = K$ . K has the dimensions of a volume. The results on nitrate ions in water yield a  $K = 6.8 \times 10^{-21} \text{ cm}^3$ . The results on carbon tetrachloride molecules in benzene yield a  $K = 7.9 \times 10^{-21} \text{ cms}$ . For two such chemically dissimilar systems, the agreement is striking. The possible fates of the positron cited in the conclusion of Chapter V are also applicable here.

No definite conclusion has been reached in either experiment as to the nature of the mechanism causing the variation of  $I_2$ . Several alternate or competing processes have been suggested. In Appendix A, forthcoming experiments are listed which might give further evidence of the formation of positron compounds and cast some light on whether the mechanism is of a chemical nature.

## APPENDIX A

The following three experiments are to be attempted in the near future:

1) Decay of positrons in the Hexyl-halides. This experiment will be a further test of the volume effect. Hexane is a liquid; hence the annihilation factor for the parent molecule can be determined.

2) Variation of  $\tau_2$  in low concentrations of  $\text{CCl}_4$  in benzene. The salient feature of the  $\tau_2$  variation in the second experiment is that it decreased markedly from that of pure benzene for a concentration of 0.5%  $\text{CCl}_4$  and remained relatively constant for all benzene- $\text{CCl}_4$  solutions. (See Table IV) The benzene-halides display a similar variation. (Ha-58a); benzene  $\tau_2 = 21 \times 10^{-10}$  seconds; fluoro-benzene,  $18 \times 10^{-10}$  seconds; and the other three benzene halides  $16 \times 10^{-10}$  seconds. The variations suggest that some process exists having a large cross-section for triplet to singlet conversion. However, the conversion rate soon reaches a constant value.

This could be explained by the existence of chlorine molecules in small concentrations in the liquid. Deutsch (De-53) and Hatcher (Ha-58) have noticed an increase in conversion rate in various substances with increasing concentrations of halogen molecules. In the benzene- $\text{CCl}_4$  experiment, the conversion rate would become constant when the solution had been completely saturated with  $\text{Cl}_2$ .

The present apparatus is not suitable for measuring small variations in  $\tau_2$  since the nonlinearity in the time scale

permits only two mean lives of the decay to register. Modifications in progress will improve this.

3) Ultra-violet irradiation experiment. An experiment that might give evidence to support the hypothesis of the formation of positron-halides is the decay of positrons in an organic halide compound being irradiated with ultra-violet light. If positron halides are formed, the quenching should be greater during the irradiation when free halogens are present, providing the time for reassociation is long enough.

## APPENDIX B

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## APPENDIX C

### FURTHER COMMENTS ON THE VOLUME EFFECT

The equation for the volume effect evolved from a consideration of the variation of  $I_2$  in the benzene halides as a function of different parameters such as density, atomic cross-section ( $R^2$ ), atomic number of the halogen, halogen electron density, ionization potential, and as a function of the relative volumes of the benzene and halide.

The best fit for the data was given by the volume effect where the volume of the halide was computed using the ionic radius. Subsequently, it has been suggested (G. E. Dunn-private communication) that the covalent radii of the halogens would be more appropriate since the compounds are covalently bound. However, the experimental results do not fit the values of  $I_2$  calculated with the covalent radii using a constant halogen annihilation factor.

The exact radii that should be used in calculating the halogen volumes remains undetermined. The edge of the electron cloud is of a diffuse nature, and the problem is to define an 'effective sphere of influence' for each halogen. The radius of this sphere would be greater than the covalent radius since this radius is near the maximum electron density. Consider the positronium atom itself. The positron and the electron are approximately one Angstrom apart, yet annihilation occurs from the bound state since their wave functions still overlap.

It would be difficult to estimate the exact correction to apply to the covalent radii. The choice that gives the best fit to the data are the ionic radii which equal the covalent radii plus 0.8 Angstrom.