QUENCHING OF TRIPLET POSITRONIUM BY IONS IN AQUEOUS SOLUTIONS

by

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ABSTRACT

Measurements of positron lifetimes in liquids and solids have been performed using a fast coincidence time-to-amplitude converter with a resolution of $\sim 10^{-9}$ sec.

The lifetime, τ_2 , of the triplet positronium component of the complex decay observed in water, decreases when paramagnetic salts are added. This quenching of the τ_2 lifetime is attributed to the unpaired electrons in the structure of the paramagnetic atoms, which cause triplet $\leftrightarrow$ singlet conversion and so enable the positronium to decay mainly from the shortlived singlet state. The experimental evidence favours a simple "pickoff theory" and cross sections based on this theory have been calculated. They range from 4.0×10^{-20} cm² for NdCl₃ to 3.8×10^{-18} for FeCl₃. A different type of quenching was observed for nitrates and nitrites, where the addition of these salts to water decreased the amount of positronium formed.

Lifetime measurements in non-quenchers show that the amount of positronium formed in these substances is not constant as previously suggested. Positron lifetime measurements in Mg, Al, and Si give some evidence for positronium formation in these elements but it is not certain that the observed effects are not instrumental. Measurements of the lifetimes in crystalline LiF, NaCl and NaI are also described.

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I. INTRODUCTION

1. Theory of Positron Annihilation

The comparatively rare positive electron or positron appears to have exactly the same mass as the negative electron. In a vacuum it is stable, but in the presence of matter in any form, it readily combines with an ordinary negative electron, and the result is the complete disappearance of the mass of the pair and the emission of gamma rays of equivalent energy. This process is called annihilation and the radiation emitted is annihilation radiation.

The emission of one photon is theoretically possible but can occur only in the presence of a very strong external field or very near a nucleus⁸. Otherwise the total momentum for the process could not be conserved. One photon annihilation therefore is so rare an event that it will not be considered in this work.

The two-quantum process is by far the most probable mode of decay for the positron-electron pair. It is the "allowed" process for the singlet S-state of the pair, i.e. the state with zero orbital angular momentum and with the electron and positron spins "antiparallel". (This applies equally well to unbound states and to any bound state which may exist) (see Section 2). In order that momentum and energy be conserved in this process, the two photons are emitted in exactly opposite directions in the center of mass coordinate system, each with energy equal to $mc^2 = 511$ kev. In the laboratory coordinate system, the departure from antiparallelism for the emitted photons is due to the momentum possessed by the pair before annihilation. Angular correlation experiments^{1,2,3,4} have shown that in solids, at least, the annihilating pair has low relative momentum and that the departure from antiparallelism can be attributed entirely to the

momentum of the electron before annihilation. This is in agreement with the theoretical predictions^{5,6,28} that when a positron enters a solid medium it is quickly "thermalized" by ionization and inelastic collisions. The thermalization time in metals has been estimated²⁸ as $\sim 10^{-12}$ sec., i.e. much less than the lifetime of the positron. The cross section (for two photon annihilation) averaged over all possible electron spin orientations and neglecting Coulomb interaction, was calculated by Dirac⁷, and is given by:

$$\sigma = \frac{\pi r_0^2}{\gamma+1} \left[\frac{(\gamma^2 + 4\gamma + 1)}{\gamma^2 - 1} \ln (\gamma + \sqrt{\gamma^2 - 1}) - \frac{\gamma + 3}{\sqrt{\gamma^2 - 1}} \right] \quad (1)$$

where γmc^2 is the positron energy and r_0 is the classical electron radius. For the singlet state only, this becomes $\sigma_s = 4\sigma$ since only 1/4 of all collisions will give singlet state annihilation. For low relative velocities ($v \ll c$), σ becomes

$$\sigma = \pi r_0^2 (c/v) \quad (2)$$

The rate of annihilation is given by

$$R = \sigma v |\psi(o)|^2 = \pi r_0^2 c |\psi(o)|^2 \quad (3)$$

where $|\psi(o)|^2$ represents the density of electrons at the position of the positron.

Since the low energy positron will be repelled by the nucleus, its wave function will overlap the wave function of only the electrons near the periphery of the atom. Hence the annihilations will take place mainly with the valence and conduction electrons. The work of Stewart⁴ has shown this to be true. Hence $|\psi(o)|^2$ should be replaced by the number of valence or conduction electrons per cc. For the alkali metals where there is one conduction electron per atom this would give a minimum value for R of,

$$R_{MIN} = \pi r_0^2 c N_A = \pi r_0^2 \frac{c N_A}{A} = \frac{1}{\tau_{MAX}} \quad (4)$$

where N_A is the number of atoms per cc., N is Avogadro's number, ρ is the density and A the atomic weight.

In the above expression (4) no allowance is made for the attractive Coulomb interaction between the electron and positron and for low energy positrons this correction becomes important. The more correct expression can be obtained by including the interaction in the expression for $|\psi(o)|^2$. This then becomes

$$|\psi(o)|^2 = \frac{N_e 2\pi \epsilon}{1 - e^{-2\pi \epsilon}} \quad (5)$$

where N_e is the number of electrons per cc. available for annihilation and $\epsilon = \alpha/\beta = (\frac{e}{v})(\frac{1}{137})$. Since the positrons are rapidly slowed to thermal energies, the relative velocity v must be of the order of orbital electron velocities, i.e. $\beta \sim \alpha$ and $|\psi(o)|^2$ becomes $\sim 2\pi N_e$. For metals, however, $|\psi(o)|^2$ must be averaged over the velocities of the conduction electrons. For the alkali metals the expression for the maximum value of R is then⁹,

$$R_{MAX} = \frac{3\pi mc}{137 P_{MAX}} \pi r_o^2 c N_A = \frac{1}{\tau_{MIN}} \quad (6)$$

where P_{MAX} is the momentum corresponding to an electron with Fermi energy E_F .

Two-quantum annihilation is completely forbidden by quantum selection rules^{10,11} for the triplet spin state of the electron-positron pair, i.e. the state with the spins "parallel". The mode of decay here is the emission of three quanta. This process is less probable than the two-quantum one and the ratio of triplet and singlet cross-sections is¹²,

$$\frac{\sigma_t}{\sigma_s} = \frac{4}{9\pi} (\pi^2 - 9) \alpha \sim \frac{1}{1115} = \frac{\tau_s}{\tau_t} \quad (7)$$

To conserve momentum the three quanta must be emitted in the same plane and not all in the same half plane. The energy spectrum, however, is continuous extending from zero to a maximum of mc^2 . Since there will be three

times as many collisions in the triplet state as in the singlet state, the ratio of the number of three quantum events to two quantum events will be three times (7) or $1/372$, i.e. the ratio of the spin averaged cross-sections for free collisions.

2. Lifetime Measurements and the Existence of Positronium

The main features of the annihilation theory outlined above can be observed by making measurements of the lifetimes of positrons in gases, liquids and solids. In particular, the work on gases by Deutsch and Shearer^{13,14,15} definitely confirmed the formation of the bound system of electron and positron first suggested by Mohorovicic¹⁶ and called positronium by Ruark¹⁷. This system is similar in its gross features to the proton-electron system of hydrogen except for the difference in mass of the proton and positron. This mass difference causes all energy levels to be reduced by a factor of 2 so that the ionization energy is now 6.8 ev ¹⁸. The electron wave functions are the same as those for hydrogen except that the positron-electron separation distance is twice the electron-proton distance.

The lifetimes of the two states of positronium can be calculated using (2) and (7).

$$1/\tau_s = \lambda_s = 4\pi r_o^2 c |\psi(o)|^2 \quad (8)$$

where the factor 4 arises from the fact that theoretically only $1/4$ of the annihilations will be from the singlet state. $\psi(o)$ is now the ground state wave function and $|\psi(o)|^2$ is given by¹⁸

$$|\psi(o)|^2 = \frac{1}{\pi(2a_o)^3} \quad (9)$$

where a_o is the Bohr radius of the hydrogen atom. The lifetime for singlet annihilation is then

$$\tau_s = \frac{2a_0^3}{r_0^2 c} = 1.25 \times 10^{-10} \text{ sec.} \quad (10)$$

The triplet lifetime is 1115 times this and is given by

$$\tau_t = 1.4 \times 10^{-7} \text{ sec.} \quad (11)$$

In CCl_2F_2 (Freon), Deutsch observed a lifetime which decreased only slightly with pressure (the decrease being due to an increased number of free collision annihilation events) and which when extrapolated to zero gas pressure gave good agreement with (11) thus proving the formation of positronium. The short singlet lifetime could not be measured because of the poor resolution of the apparatus.

In liquids, and amorphous solids, positron lifetime measurements by Bell and Graham¹⁹ have shown that there are two definite lifetime components in these materials; one called τ_1 , being a few times 10^{-10} sec., and the other τ_2 , ranging from 0.45×10^{-9} to 3.5×10^{-9} sec. depending on the substance. The amount of the τ_1 component was $\sim 2/3$ and the τ_2 component $\sim 1/3$, roughly the same for all substances tried. This again is evidence for positronium formation. Attributing the τ_2 component to the formation of triplet positronium, and keeping in mind the statistical weights of the triplet and singlet states their figures of $2/3$ and $1/3$ for the amounts of the τ_1 , τ_2 components are consistent with $\sim 50\%$ of all the positrons forming positronium.

A study made by Bell and Graham of the properties of the τ_2 radiation, showed it to be almost entirely due to two-quantum annihilation. Since the triplet state cannot decay by two-quantum annihilation then the τ_2 component must be due to one of two things:

- (a) the conversion of triplet positronium to singlet by exchange collisions with electrons of the medium followed by rapid annihilation from the singlet state ($\tau_s = 1.25 \times 10^{-10}$ sec.)

The observed τ_2 lifetime is then a sort of "conversion" lifetime.

- (b) Annihilation, directly from the triplet state, of the positron with an electron, (from a neighbouring atom) which has the proper spin orientation. This is the so-called "pick-off" annihilation first suggested by Garwin⁶.

If positronium is really formed in these condensed materials the number of three-quantum events should be greater than in a medium where no positronium is formed, e.g. metals (see below). The extra three-photon events will be due to annihilation from the triplet state before either "conversion" or "pick-off" annihilation takes place. This enhancement of the number of 3-photon events has been found experimentally^{20,21}, and also its variation with the τ_2 lifetime²⁰. These facts prove rather conclusively the formation of positronium in liquids and amorphous solids.

In metals and crystalline solids however, the situation is less clear. The measurements of lifetimes in these materials^{19,22} showed within the resolution of the apparatus only a single component with values from $(1.5 - 2.5) \times 10^{-10}$ sec. The values for all the metals (1.5×10^{-10} sec.), were the same within the experimental accuracy. The constancy of these results is puzzling. If positronium is not formed in a metal, the lifetimes should vary for these as predicted by (4) and (6) since N_A and P_{MAX} are different for different metals[†]. On the other hand, if positronium is formed in these substances, the measured lifetimes agree favourably with

* For Li, K, Cs, e.g. the τ_{MAX} , τ_{MIN} values⁹ are: (in units of 10^{-10} sec.)

	LI	K	Cs
τ_{MAX}	29	102	160
τ_{MIN}	1.7	4.2	5.6

The experimental results do not show any such variation.

the singlet lifetime of positronium viz. 1.25×10^{-10} sec. The fact that thermal positrons were not observed²³ diffusing from the surface of metals has been interpreted as evidence that positronium is formed in a metal. But Garwin⁶ has shown that if positronium is formed the lifetime which should be observed, even with infinite conversion between the singlet and triplet states, is $4 \times \tau_s$ since the positronium will spend $3/4$ of its time in the triplet state.

However, recent more accurate work²⁹ on the absolute measurement of $\frac{\sigma(2\gamma)}{\sigma(3\gamma)}$ giving 402 ± 50 in a metal gives excellent agreement with the theory for free collision annihilation and suggests that little if any positronium is formed in a metal. Also theoretical estimates of the "enhancement" of the number of electrons at the position of the positron due to polarization by the positron, are reducing the discrepancy between observed and calculated metal lifetimes. Hence it now seems unlikely that any positronium (at least very little) is formed in a metal.

3. Quenching of triplet positronium

The quenching of triplet positronium in gases has been observed by Deutsch and Dulit²⁴ and Pond and Dicke²⁵. The application of a magnetic field causes a mixing of the $m = 0$ substate of the triplet state with the singlet state and the short lifetime of the singlet state results in the quenching of this part of the triplet positronium. The quenching is measured by noting the decrease in the number of three-photon annihilations with increasing field.

The addition of small quantities of NO to a gas exhibiting the triplet positronium lifetime will completely quench this lifetime. The mechanism is a rapid conversion from the triplet to the singlet state caused by the unpaired electron of the NO, the energy required to "flip" its spin being very small.

Small quantities of diphenylpicrylhydrazyl (DPH), which is a free radical with one unpaired electron, added to pure benzene will rapidly quench^{21,26} the triplet positronium contribution to the lifetime. Using a theoretical treatment of Dixon and Trainor²⁷, where the pure benzene is considered a sufficient converter to give the τ_2 lifetime and the DPH is considered an extra converter, Berko and Zuchelli²⁶ arrive at a cross-section for conversion from triplet to singlet positronium of $1.18 \times 10^{-17} \text{ cm}^2$ for DPH, in agreement with Pond²¹. This cross-section agrees within an order of magnitude with that initially observed by Deutsch for NO in a gas and so suggests that the conversion mechanism is similar in both these cases.

4. Purpose of this work

The purpose of the present work was to study the lifetimes of positrons in liquids and solids and in particular to look for substances which would quench out the long lived component (τ_2) of the positron decay curve in the liquids. The study of the quenching of the long lived component in water by making aqueous solutions of various chemical compounds was considered a logical approach and the study of the transition group elements including the iron group and the rare earths, was undertaken since these substances exhibit paramagnetism due to the presence in their electron structure of unpaired electrons. It was hoped that the presence of these unpaired electrons would cause a fairly large quenching effect similar to that observed in benzene with the addition of DPH and in gases with NO present.

It was also thought that a search for evidence of positronium formation in metals might be worthwhile. Since the structure of the medium through which the positron passes governs the mode of its annihilation, a study of

this kind should perhaps bring to light some details of the internal structure of various atoms. It has been suggested many times that the study of positron annihilation in matter could have many applications in the field of solid state physics as well as being an interesting study on its own.

During this work many quenchers have been found and the quenching has been correlated to the presence of unpaired electrons in the material studied. The cross-sections for the conversion process have been evaluated for all quenchers and some evidence has been found for favouring the "pick-off" process over the conversion process to explain the unquenched τ_2 lifetime.

The lifetime measurements in the few metals studied have not proven completely the presence of positronium in these materials but upper limits can be placed upon the percentage, if any, formed. Lifetime measurements of positrons in halide crystals give disagreement with a very recent theoretical estimate³⁶ of the variations expected for these crystalline materials.

Nearly all the measurements in this work have been made using a slightly different type of fast coincidence circuit which turns out to have much improved counting efficiency, the major change from the standard type circuit being the replacing of the delay line by a time-to-amplitude converter and the use of a multichannel pulse height analyzer to perform the pulse amplitude analysis. This new circuit was found to experience no loss in resolution from the standard delay line type circuit³¹ previously used for this type of experiment.

II. EXPERIMENTAL

1. The Delayed Coincidence Method:

In order to measure the lifetimes of positrons in solids or liquids, fast coincidence techniques are necessary since the lifetimes will range from a few times 10^{-10} sec. to a few times 10^{-9} sec. Coincidence circuits operating in this region have been in use for several years and the theory of operation of such circuits is well established.* It has been shown³⁰, that the limit of resolution possible with the scintillation phosphors and phototube detectors available today is determined by the speed of the phosphor, i.e. its decay time. These theoretical predictions were verified by Bell, Graham and Petch³¹, and their coincidence setup is in common use today for the very shortest lifetime measurements, both of positrons and γ -ray excited states.

The usual method of measurement is the differential delayed coincidence method³². In this arrangement pulses from the detectors are kept fixed in length but the pulses from one detector, A say, are delayed by a known time x before being impressed upon the coincidence circuit. Thus, the pulses detected from counter B are those which occur later in time than those in A by an amount x . The range of delays near x where coincidences are detected is given by the resolving time, $2\tau_0$ of the circuit. (For the Bell-Graham-Petch circuit $2\tau_0 \sim 2 \times 10^{-9}$ sec.) The curve of the coincidence counting rate plotted against inserted delay x is then of the form $e^{-(x/\tau)}$ which gives the lifetime τ of the events being recorded in detector B.

* R.E. Bell³² has written an excellent review article on the various types of fast coincidence circuits in use today.

In the early part of this work, the circuit of Bell, Graham and Petch was used in almost exactly its original form. However, most of the final measurements were made with a modified Bell-Graham-Petch circuit where now a time-to-amplitude converter was incorporated and the resulting amplitude spectrum analyzed using the McGill 28-channel kicksorter. This modification of the original circuit introduced no apparent loss of resolution and greatly increased the counting efficiency of the system. The time-to-amplitude converter will be discussed in detail below.

2. Source:

The most convenient source for the study of positron lifetimes is the radioactive isotope Na^{22} . First, the half-life of the positron activity is relatively long (~ 2.5 years) so that the decay of the source is unimportant during the time required for any particular program of lifetime measurements. In addition, almost 100% of the positron decay to Ne^{22} leaves the Ne^{22} in an excited state, 1.28 Mev. above the ground state. The lifetime of this state is known to be very short, recent estimates giving it as $\sim 10^{-11}$ sec³³. This means that the 1.28 Mev. γ -ray is emitted essentially simultaneously with the positron and announces its birth. The characteristic annihilation radiation of the positron announces its death and the time between these two events is the positron lifetime.

The Na^{22} used in these experiments was produced in the McGill synchrocyclotron by bombarding "specpure" aluminum at a proton energy of 55 Mev. The reaction is

the cross section being 45 mbarns at 50 Mev. A long bombardment (50-60 hrs) was obtained which produced ~ 140 μ curies of Na^{22} . The Na^{22} was separated

from the Al by ion exchange, the yield being ~ 130 μ curies. The separation^{*} was a clean one, the activity being present as NaCl, with a specific activity of 0.1 μ curies/ μ gm.

For a given source to be used in the experiments, about 10 μ curies of the activity was sandwiched between two thin mica discs of ~ 1.8 mgm/cm² areal density and $1\frac{1}{2}$ " in diameter. The mica discs were mounted on tantalum rings (tantalum being acid resistant) and the edges of the mica were cemented with Apiezon black wax to ensure that the source was waterproof. The source was then placed in a Lucite cell containing the liquid being studied, the size of the cell being such that all the positrons emerging from the source were stopped in the liquid before reaching the cell walls.

3. Detector and Limiter:

For the actual lifetime measurements, the cell containing the sample and source was placed between two RCA 6342 photomultiplier tubes fitted with $1" \times 1" \times \frac{1}{2}"$ diphenylacetylene crystals. In the early part of the work trans-stilbene crystals and RCA 1P21 phototubes were used. Operating the 1P21 phototubes at 2200 volts anode voltage, it was possible to get sufficient gain to cut off the 6AK5 limiter tubes with the first photoelectron from the photocathode. Using the 6342 type phototubes with their much better light collection and photocathode efficiency, it was found that equally good results could be obtained even though it required ~ 25 photoelectrons to cut off the limiter tube. The anode voltage required for these tubes, however, was still large, 2150 volts. Running at these high voltages caused several tubes to fail, the failure being characterized by a large

^{*} The separation was kindly performed by Mrs. Hollbach, in the Radiochemistry Laboratory of McGill University.

increase in the number of noise pulses and the disappearance of the true signals^{*}. This effect was due to a current instability in the bleeder chain, initiated by the high anode voltages used, and was cured by stabilizing the last two dynode voltages with neon tubes.

The diphenylacetylene crystal was preferred to the trans-stilbene since its decay time τ_c was about a factor of 2 less than that for stilbene and its light output, although less than stilbene, was still sufficient so that on the whole, better results were obtained with it. The criterion of the speed of the fast coincidence circuit is given by Post and Schiff³⁰. The mean time $\bar{t}$ between the entrance of a photon into the crystal and the appearance of the Q^{th} photoelectron is

$$\bar{t} = \frac{Q\tau_c}{R} \left[1 + \frac{(Q+1)}{2R} \right] \text{ for } R \gg 1 \quad (12)$$

where R is the total number of photoelectrons produced during the pulse. For best results then, the figure of merit (R/τ_c) should be as large as possible for a given crystal.

The limiter circuit consists of a 6AK5 pentode that normally runs with zero grid bias and 16 mamp. plate current. The fast pulse from the anode of the phototube cuts off this tube rapidly since 3 volts is sufficient to completely cut off the tube while the anode pulses of interest are (20-30) volts. Thus, all the anode pulses that correspond to events to be studied give the same size output pulses from the plates of the 6AK5. Thus, the only difference between pulses from detectors A and B is the fact that they occur at different times. The circuit of the detector and limiter is shown in Fig. 1. The slow outputs shown are fed to the pulse height selection circuits shown in schematic form in Fig. 2, which is a block diagram of the

* This effect was also noticed by Stump and Talley³⁴.

FIG. I - DETECTOR AND LIMITER

FIG. 2-BLOCK DIAGRAM OF THE APPARATUS

complete apparatus used for the lifetime measurements. The operation of the pulse height selection circuits and the other components of the apparatus will be described below.

4. Pulse Height Selection:

In a particular coincidence experiment, both detectors will be capable of counting both the 1.28 Mev nuclear gamma rays as well as the annihilation radiation. It is therefore necessary to perform pulse height selection in both slow circuits so that effectively one detector is observing annihilation events and the other the nuclear gamma rays. The pulse height selection was done in the following manner.

The slow outputs (shown in Fig. 1) take pulses off the eighth dynode of the phototube. Let us call the detector which will effectively observe only annihilation radiation the "0.51 Mev detector" and the other the "1.28 Mev detector". Positive pulses from the dynode of the 0.51 Mev detector were fed to a single channel pulse height analyzer, consisting of a linear amplifier, a pair of discriminators and an anticoincidence circuit, the overall circuit having a resolving time of $\sim 2 \mu\text{sec}$. A pulse height analysis was made of the incoming pulses and a typical pulse height spectrum is shown in Fig. 3. The Compton distributions for both the 0.51 Mev and 1.28 Mev γ -rays are clearly resolved. No full energy peaks are observed since the photoelectric cross section for the organic crystals is very small and also it is unlikely that the γ -ray will lose all its energy in the relatively thin $1/2$ " crystals. The thin crystals are used to reduce any extra time delays which might arise as a result of events occurring in various parts of the crystals and hence at different distances from the photocathode. The pulse height analyzer gate is then set, as shown in

FIG. 3 - DIFFERENTIAL PULSE HEIGHT SPECTRUM

the diagram, on the upper edge of the Compton distribution for the 0.51 Mev γ -ray, so that only events giving rise to pulses lying within this gate can be recorded. Of course it is clear from the diagram that some 1.28 Mev events ($\leq 15\%$ of the total) will be accepted by the pulse height analyzer gate; but these can never give true coincidences with 0.51 Mev events in the 1.28 Mev slow circuit since as described below the latter circuit has its discriminator set above the maximum of the 0.51 Mev Compton distribution.

The pulses from the slow output of the 1.28 Mev detector are fed to a linear amplifier and discriminator circuit having a resolving time of ~ 2 μ secs. The discriminator in this circuit is set so that only pulses arising from 1.28 Mev events are accepted.

5. Time-to-Amplitude Converter:^{*}

In the original Bell-Graham-Petch circuit, the delays to be inserted in series with the fast pulses were supplied by a helical delay line. A fast coincidence diode circuit moved along the delay line in discrete steps and so delay was introduced into one side of the circuit and taken out of the other simultaneously. The coincidence rate was then measured at each delay position separately.

The present method, however, consists of a time-to-amplitude converter so that coincidences for all delays can be recorded during the same counting interval. The operation of this circuit is based on the characteristics of the 6BN6 gated beam tube³⁵ operated at low electrode voltages. A set of such characteristics is shown in Fig. 4. The 6BN6 has two separate control grids G_1 , G_3 and it can be seen from the graph that with a plate supply of 20 volts and a screen supply of 10 volts it is possible to bias each grid

^{*} The design of this circuitry is due to Dr. R.E. Bell of this Laboratory.

FIG. 4 - 6BN6 CHARACTERISTICS

separately so that effectively no current flows in the plate circuit and yet produce full plate current saturation with positive pulses of less than 1 volt simultaneously impressed on the two grids. Of course a signal on either grid alone produces no plate current. With 16 mamp. plate current in the 6AK5 limiter tube and using 125Ω cables throughout the circuit, pulses of 1 volt are available without further amplification, thus the full speed of these pulses is preserved. At the converter tube, then, the shaped and limited pulses from the two detectors are applied to separate grids (the 1.28 Mev pulse to G_1 and the 0.51 Mev pulse to G_3) and plate current flows only during the overlap in time of these pulses. The integrated plate current or total charge transferred to a condenser in the plate circuit then varies linearly with the time delay between the two pulses.

Fig. 5 shows a schematic diagram of the arrangement of the 125Ω cables and the fast components of the circuit. The detectors have been labelled the 0.51 Mev. and 1.28 Mev. detectors, corresponding to the pulse height selection being performed in their slow output circuits. (Section 4.) In this diagram the two detectors are quite separate physically. In the performance of an actual lifetime experiment, however, this is not the case, for the cell containing the source and sample under study is then sandwiched between these two detectors as mentioned earlier.

Let us first ignore that part of the circuit labelled fast coincidence circuit. Then, the positive pulses from the limiters are each clipped by 400 cm. of short-circuited 125Ω cable to a length of $32\mu\text{sec}$. The $32\mu\text{sec}$ is the time required for the pulse to travel up and down this 400 cm. of cable, the speed of the pulses in this type of cable being 84 percent of the speed of light. The 1.28 Mev. pulse is given a delay of $30\mu\text{sec}$. before being impressed on the converter grid G_1 , while the 0.51 Mev pulse is

FIG. 5 — FAST PULSE CABLE SETUP

delayed by only 6 μ secs. The result at the converter for a prompt annihilation event is a pair of 32 μ sec. pulses overlapping by 8 μ sec., the sense being such that any further delay in the 0.51 Mev pulse tends to increase this overlap. In practice, however, it was found that the particular arrangement shown gave an overlap of only about 3 μ secs. The difference is due to the fact that the grids G_1 , G_3 are separated physically in the 6BN6 by perhaps several millimeters, G_3 being nearer to the anode. This means that there will be a transit time delay introduced between these two pulses which will delay the 1.28 Mev pulse by an amount which is equal to the time required for the electrons to travel from G_1 to G_3 inside the tube. For the particular electrode voltages used this delay is of the order of several μ secs. and so explains the observed overlap.

Returning to the fast coincidence circuit portion of the diagram, the 1.28 Mev pulse is still 32 μ sec. long but the 0.51 Mev pulse is only 3 μ sec. long, being clipped by only 37 cm. of the cable. A coincidence signal from this circuit shows that the pair of pulses entering the converter lies in the desired range of delays.

Fig. 6 shows the time sequence of the fast pulses. The open pulses represent a prompt annihilation event, the shaded 0.51 Mev pulses represent an event where this pulse is delayed by 5 μ sec. with respect to the 1.28 Mev pulse, e.g. a positron lifetime of 5 μ sec. The overlap of the converter pulses increases as the 0.51 Mev pulse is delayed until the pulses are in full coincidence. Any further delay in the 0.51 Mev pulse will cause a smaller overlap at the converter. At this point, however, there ceases to be any overlap at the fast coincidence circuit and so no fast coincidence output pulse is produced.

FIG. 6 — TIME DISTRIBUTION OF FAST PULSES

The anode current flowing in the 6BN6 during the overlap of the pulses is integrated, as shown in the circuit of Fig. 7, amplified and passed through a gate circuit shown in Fig. 8, which is actuated by the output of a triple coincidence circuit whose inputs are;

(1) the output of the pulse height analyzer selecting the 0.51 Mev annihilation radiation,

(2) the output of the discriminator circuit that selects the 1.28 Mev events to be observed, and

(3) the output of the fast coincidence circuit which consists mainly of a diode biased to accept only coincidence events, i.e. when the 3 μ sec. 0.51 Mev pulse and the 32 μ sec. 1.28 Mev pulse overlap as shown in Fig. 6. The pulses at the fast coincidence diode are taken off through 500 Ω resistors to limit cross-coupling between the two delay cables connected to the 6BN6 grids. There will be a small reflection from this point on the delay cables but it has never given any noticeable distortion at the converter. The fast coincidence output pulses are sent first to a fast preamplifier, then to another linear amplifier with a discriminator circuit. In practice, this discriminator may be set to accept only pulses arising from coincidence events. The output of this circuit will be the "unselected coincidences", consisting of all possible coincidence events, chance and true, occurring between the two detectors. The fast coincidence diode and preamplifier circuit is shown in Fig. 9.

The triple coincidence unit will give an output pulse if all three input pulses lie within its resolving time, $\sim 3 \mu$ sec. The output of this circuit is the "selected coincidences". Since the setting of the discriminator recording the unselected coincidences determines the number of selected coincidences and hence the number of gate pulses, an "integral bias" curve

FIG. 8- GATE CIRCUIT

was taken to determine the correct discriminator setting to give the optimum number of selected coincidences. Such a curve is shown in Fig. 10 where the selected coincidence counting rate is plotted against the discriminator setting of the amplifier recording the unselected coincidences. The presence of the plateau signifies a rather narrow grouping of the selected coincidences about a fixed size which means that the pulses being accepted are well equalized in height. The shape of this integral bias curve is an excellent monitor of the operation of the fast coincidence circuit. The discriminator was usually set near the upper end of the plateau so that $\sim 90\%$ of the coincidences were accepted. The increase in counting rate at low settings in Fig. 10 is due to "singles" pulses being transmitted through the capacity of the diode, which will produce unwanted triple coincidences.

The selected coincidences were used to activate the converter gate circuit. Therefore an output pulse from the converter means that

(1) the 1.28 Mev detector has observed a nuclear gamma ray announcing the birth of a positron,

(2) the 0.51 Mev detector has observed an annihilation gamma ray announcing the death of the positron, and

(3) the delay between these events lies within the range set by the fast coincidence circuit.

The converter output pulses are next fed to the 28-channel kicksorter for amplitude analysis. In order to interpret the results observed on the kicksorter in terms of time it is necessary to calibrate this instrument. This was done by using a prompt annihilation source and inserting known delays into the 0.51 Mev side of the circuit, i.e. changing the length of the cable marked 151 cm. in Fig. 5. The result of inserting delay in this way is to move the prompt resolution curve up the scale of the kicksorter.

FIG.10 - INTEGRAL BIAS CURVE

The results of a typical calibration experiment are shown in Fig. 11. In this diagram the position of the centroid of the prompt resolution curve is plotted against the length in cm. of the 0.51 Mev cable, where 100 cm. of cable is equivalent to 4 μ sec. The slope of this curve gives the time-to-amplitude calibration in terms of sec. per channel. In the particular example shown here, the calibration gave 6.62×10^{-10} sec. per channel. This is suitable for lifetime measurements of $(1-4) \times 10^{-9}$ sec. For lifetimes $< 10^{-9}$ sec. a mere factor of two increase in the gain of the amplifier gives the calibration as 3.31×10^{-10} sec. per channel. The dotted portion of the curve of Fig. 11 was not observed in this particular experiment, but has been for similar cable arrangements. It is obvious from this diagram that the curve is double-valued in the delay as mentioned earlier. However, the operation of the fast coincidence circuit (see Fig. 6) is such that no output from this circuit occurs for delays corresponding to the right hand side of the triangle in Fig. 11. Therefore the gate circuit is not actuated for these long delays and so no "doubling-back" is ever observed experimentally. The calibration curve is linear over a large region except at the extreme left hand side of the curve, but here the curvature is what is expected from the finite rise time of the pulses. The prompt source used for the calibration was Na^{22} imbedded in aluminum, a piece of the original target bombarded in the cyclotron to produce the Na^{22} source. This aluminum was wrapped in more aluminum foil so that all positron annihilations were in the metal. The lifetime of positrons in aluminum was measured by Bell and Graham and the result was a single lifetime equal to 1.5×10^{-10} sec. This source can then be considered prompt for the purpose of calibration.

In order to measure the instrumental resolution, a prompt Co^{60} source was used. This source emits two gamma rays of 1.17 Mev and 1.33 Mev in

cascade, and in coincidence to $\sim 10^{-11}$ sec.³⁸ A resolution curve obtained using this source is a direct measure of the instrument's resolution. Fig. 12 shows the resolution curve obtained with this source. The pulse height selection here was similar to that used for a Na^{22} source when measuring positron lifetimes, and so this result is the limit of the instrument for all the lifetime measurements made. The result of this experiment was a resolution, taken as the width at half maximum, of

$$2\tau_0 = 8.5 \times 10^{-10} \text{ sec.} \quad (13)$$

The slope of the tail of this curve gave an instrumental half life of

$$T_{1/2} \sim 1.4 \times 10^{-10} \text{ sec.} \quad (14)$$

This means that the shortest lifetime that can be measured with this instrument by measuring the slope of the tail is

$$\tau_{\text{MIN}} = \frac{T_{1/2}}{\ln 2} \sim 2.1 \times 10^{-10} \text{ sec.} \quad (15)$$

Nearly all the measurements in this work have been made using the "slope method"³⁷. Some pulses appear in the low channels of the kicksorter in Fig. 12. These may be due to noise pulses in the linear amplifier preceding the kicksorter or some spuriously gated pulses. However, since these do not appear on the right hand side of the resolution curve where all the lifetimes are measured no great attempt has been made to trace them.

The resolving time given in (13) cannot be compared with that of the Bell-Graham-Petch circuit³¹ since the coincidence measurement mechanism is different for the two circuits. In the present circuit, the time distribution of the coincidence events being studied is divided into narrow time channels by the converter and the events lying in these channels are counted separately but at the same time. The counting rate summed over all channels is equal to the total rate of occurrence of coincidences, prompt and delayed. In the

delay line type circuit however, the time distribution was scanned in discrete steps with a much wider gate, $\sim 2 \times 10^{-9}$ sec. wide determined by the lengths of the clipped fast pulses, each $\sim 1 \times 10^{-9}$ sec. Here then, the resolving time was set by the width of the gate, and although this time is longer than the width of the Co^{60} time distribution of Fig. 12, the capabilities of the two methods for lifetime measurements are similar.

The present circuit has two major advantages over the original delay line type circuit. First of all, the counting efficiency is greatly increased since now coincidences for all delays are counted during the same time interval, whereas in the original setup counts had to be taken for each delay position separately. The counting efficiency for this system is at least a factor of 10 higher than the original system. Secondly, the present circuit is more reliable in its operation. Great stability was required in the previous arrangement since any change in gain or sensitivity of one of the counting elements would cause a variation in the coincidence rate. It was necessary for the circuits to remain stable for all the delay line positions since they were being counted separately and any changes in coincidence rate would cause errors in the resolution function obtained. In this present circuit however, any counting rate changes affect all delays the same way and since all the delays are being counted together the stability is not nearly so critical here as in the delay line type apparatus.

6. Measurement Technique:

The 28-channel kicksorter used in this work has provisions in its recording circuits for displaying the spectrum being observed on a cathode ray oscilloscope screen, even while the counting is in progress. In this

way it is possible to watch the coincidence resolution curve growing on the CRO screen as the spectrum is being counted. Each separate channel also has a set of two high quality condensers in its integrating circuit, one corresponding to 1000 counts full scale, the other 10,000 counts full scale. Their low leakage properties ensured negligible loss over many hours running time. The typical procedure for a lifetime measurement was as follows.

With the sample under study in position between the counters, the spectrum was observed using the small condensers (1000 counts full scale). The shape of the resolution curve at this point determined which was the correct gain setting to be used, $\sim 3.5 \times 10^{-10}$ sec. per channel or $\sim 7.0 \times 10^{-10}$ sec. per channel. Once this had been decided a calibration curve was taken, using the aluminum with Na^{22} source imbedded to determine the accurate time calibration for each channel. The 151 cm. cable shown in Fig. 5 was used for normal running since it gave a peak position near the lower end of the kicksorter scale - the long tail due to the lifetime could then extend to the upper channels of the kicksorter. Once the calibration was performed, another quick run was taken on the small condensers. All channels above 10% of full scale were switched to the larger condensers, and then the run began. When the peak of this curve reached full scale the counting was stopped, the time noted and the spectrum recorded by the kicksorter slow sampling switch, the result appearing on an Esterline-Angus recorder chart. Then, without cancelling the counts already accumulated, the run was continued and at a time equal to three times the first counting period, the spectrum was again recorded. The channels reading $>33\%$ on the initial spectrum of course were now beyond full scale. After recording, the spectrum was allowed to count again, this time until the total counting time was ten times the initial time required for the filling of the peak channels. This meant that by normalizing

all channels to the total elapsed time the complete resolution curve could be obtained and the number of counts in the peak of this curve was ~ 100000 . This gave enough of a variation in counting rate so that the decay curve could be followed through four decades on a semilog plot of coincidences versus channel number. There were then enough points on the tail of the curve so that a fairly accurate lifetime value could be obtained. Of course, in order for the normalization to be legitimate, the counting rates in the pulse height selector circuits and the unselected coincidence circuit must be constant. These were continuously monitored with counting rate meters and Esterline-Angus recorders and if one of these rates varied during a run, the run was repeated. Gain shifts in the apparatus were also important and these were monitored by quickly looking at the position of the peak of the resolution curve, using the small condensers, before and after each run. If an appreciable shift of the peak was noticed, the run was discarded. The calibration procedure outlined above was repeated every day before and after each series of runs. The apparatus was very stable, the calibration usually varying by less than 2% from day to day. The time required for a complete lifetime measurement was a little over an hour for the larger time channels ($\sim 7 \times 10^{-10}$ sec) and twice this time for the higher gain setting where the channels were only half as wide in time ($\sim 3.5 \times 10^{-10}$ sec.)

After the run was completed the normalized coincidence counts were plotted against channel number after the appropriate number of chance counts was subtracted. The number of chance coincidences was assumed equal to the number of counts in the channels of the kicksorter corresponding to delays so long that the number of true coincidences becomes vanishingly small. This chance subtraction was always checked by calculating the chance rate using the expression

$$N_c = 2 \tau N_1 N_2 T \quad (16)$$

where N_c is the number of chance coincidences, N_1 , N_2 are the rates of the 0.51 Mev, 1.28 Mev pulse height selector counters, 2τ is the time width of a channel and T is the total elapsed time of a run. The experimental chance was not very accurate since the number of counts was small but it was always in fair agreement with the calculated value. The number of chance counts is very small compared to the number of counts in the peak of the curve, being (20 - 30) for 100,000 in the peak. This gives a true to chance ratio of ~ 5000. On the tail of the curve, however, the number of chance counts is comparable to the number of true counts and so the statistics naturally become poorer for the longer delays. Once the chance has been subtracted, the slope of the semilog plot gives the mean life in terms of a certain number of channels. Using the calibration factor, the lifetime is obtained absolutely.

7. Search for Quenchers:

In the search for quenchers, fairly strong solutions of about 1M or stronger were tried at first. One run established whether the solution was a quencher or not. If so, then a series of solutions was prepared by dilution and they were studied in turn. Most of the solutions were standardized using standard techniques of quantitative chemical analysis. In the next section the results of the measurements are presented.

III. EXPERIMENTAL MEASUREMENTS AND DISCUSSION OF RESULTS

1. The Quenchers:

(a) Iron Group:

The first substances studied in this work were aqueous solutions of the iron group elements. These elements were chosen since they exhibit a strong paramagnetism due to the presence of unpaired electrons in their electronic structure. The unpaired electrons arise from the filling of the 3d sub-shell of these atoms. The 3d electrons do not pair off until they are forced, i.e. until 6 electrons are added, so that as many as five unpaired electrons can be present. It was thought that these unpaired electrons would quench out the τ_2 lifetime observed for positrons in water by causing a rapid conversion between the two states of positronium, as has been observed for NO in gases¹⁴ and DPH in benzene²⁶.

The salts studied were chlorides. They were chosen since no quenching had been observed¹⁹ when the lifetime was measured in a strong NaCl solution. This suggested that both the chloride and sodium ions were non-converters and so any quenching observed in the chlorides could be attributed to the cation. The non-quenching nature of NaCl is reasonable since the Na^+ ion has a stable neon structure and the Cl^- ion has a stable argon structure, neither of which is likely to cause conversion. Nitrates were first tried but since NaNO_3 exhibited a different quenching action which was attributed to NO_3^- , the chlorides were used. (The quenching by NO_3^- and NO_2^- will be discussed in more detail below.) Also the fairly large solubility of most chlorides made these salts convenient since it was almost always possible to make the solutions concentrated enough to observe complete quenching.

The results of a series of lifetime measurements made in FeCl_3 solutions of various concentrations are shown in Fig. 13, where the zero of time is

arbitrary. The complex nature of the decay is evident, and the variation of the τ_2 lifetime with FeCl_3 concentration is quite definite. Other concentrations of FeCl_3 have been tried, but for the sake of clarity are not shown on this diagram. The 0.001M solution is essentially a non-converter since the τ_2 lifetime is the same as that observed with a distilled water sample, i.e. $\tau_2 = 1.80 \times 10^{-9}$ sec. The shortest lifetime observed with FeCl_3 was $\sim 4 \times 10^{-10}$ sec., the particular one shown here being 4.1×10^{-10} sec. This is not an instrumental limit but rather one set by the conversion mechanism. This is clear from the fact that there is a distinct difference between this curve and the aluminum curve also shown in Fig. 13. Also the Co^{60} prompt resolution curve of Fig. 12 shows a rather shorter lifetime than the 1.0M FeCl_3 curve. The slight "tail" on the aluminum curve will be discussed later. The results indicate then, that τ_2 varies with concentration between the limits 4.0×10^{-10} sec. for concentrated solutions and 1.80×10^{-9} for pure water. The measured variation of τ_2 as a function of concentration is shown for FeCl_3 in Fig. 14. The errors assigned to the observed values of τ_2 are $\pm 1.0 \times 10^{-10}$ sec. for values obtained using the wide time channels ($\sim 7 \times 10^{-10}$ sec.) and $\pm 0.5 \times 10^{-10}$ for those obtained with the narrow time channels ($\sim 3.5 \times 10^{-10}$). This means that the same relative error in terms of kicksorter channels has been assigned.

In Fig. 14 two theoretical curves are shown. One of these, labelled conversion theory, is calculated on the basis of water as a weak converter giving $\tau_2 = 1.80 \times 10^{-9}$ sec. and the FeCl_3 as a separate converter. The other, labelled pickoff theory, is calculated assuming pickoff annihilation directly from the triplet state to explain the water lifetime and the FeCl_3 as a converter to account for the quenching. The equations by which these curves have been calculated have been written down by Dixon and Trainor²⁷, and their

FIG. 14 — LIFETIME vs. CONCENTRATION

calculations, for the complete conversion assumption, give the lower limit for the lifetime as four times the free space singlet lifetime, i.e.

5.0×10^{-10} sec. The pickoff theory however, predicts a lower limit of 3.9×10^{-10} sec. A brief outline of the method of calculation of these theoretical curves will now be given.

Using the notation of Dixon and Trainor²⁷, let us assume that P_s is the probability of finding a positronium atom, once formed, in the singlet state and P_t is the corresponding probability for the triplet state. Then the rate of change of these probabilities is given by,

$$\frac{dP_s}{dt} = -(3\gamma + \lambda_s) P_s + \gamma P_t \quad (17)$$

$$\frac{dP_t}{dt} = 3\gamma P_s - (\gamma + \lambda_t) P_t \quad (18)$$

where γ is the conversion rate between the singlet and any one of the triplet states, λ_s is the two quantum annihilation rate for the singlet state and λ_t is the three quantum annihilation rate for the triplet state. The decay of positronium will then exhibit two lifetimes τ_1, τ_2 given by,

$$1/\tau_1 = \lambda_1 = \alpha + \sqrt{\alpha^2 - \beta^2} \quad (19)$$

$$1/\tau_2 = \lambda_2 = \alpha - \sqrt{\alpha^2 - \beta^2} \quad (20)$$

where $2\alpha = 4\gamma + \lambda_s + \lambda_t$
and $\beta^2 = \gamma(\lambda_s + \lambda_t) + \lambda_s\lambda_t$

Let us consider the τ_2 component only. Using the free space values of λ_s, λ_t the variation of τ_2 with γ can be evaluated using (20). This variation is shown in Fig. 15. If it is now assumed that water is a sufficient converter to give the observed τ_2 lifetime of 1.80×10^{-9} sec., the partial conversion rate γ_1 for water is $7.0 \times 10^8 \text{ sec}^{-1}$. For a particular quenching experiment

λ_2 (sec⁻¹)

FIG. 15

with a given τ_2 value, the total conversion rate γ can be obtained from Fig. 15. The partial conversion rate for the added substance then becomes the total rate γ minus the value for water γ_1 . The curve shown in Fig. 16, and labelled conversion, is a plot of γ_2 vs. τ_2 . The lower lifetime limit which this curve tends to is four times the singlet lifetime viz., 5×10^{-10} sec. This factor of 4 arises from the fact that, at a given time, 1/4 of the positronium is in the singlet state while 3/4 is in the triplet state, so that for rapid conversion the positronium atom spends 3/4 of its time in the triplet state.

To obtain the pickoff curve of Fig. 16 it is assumed that the observed τ_2 lifetime of water is due to the fact that the triplet positronium decays mainly by the pickoff mechanism. This means that the positron annihilates by two photon annihilation directly from the triplet state by picking off an electron, which has the proper spin orientation, from a neighbouring water molecule. (The remainder of the triplet positronium of course decays by the less probable three photon annihilation process.) The λ_2 value corresponding to the observed τ_2 for water is then given by

$$\lambda_2 (\text{H}_2\text{O}) = \lambda_p + \lambda_t \quad (21)$$

where λ_p is the pickoff annihilation rate in water. The λ_t term in equations (17) to (20) must then be replaced by this term given in (21). The λ_s term in these equations must also be replaced by $\lambda_s + \lambda_p$ since pickoff can also occur for the singlet state. Using these values for λ_s and λ_t in (17) to (20), the variation of τ_2 with γ is obtained. Since there is now no γ_1 term, $\gamma = \gamma_2$ and this is plotted as a function of τ_2 in Fig. 16. The limit for this curve is given by

$$\lambda_2 (\text{MAX}) = \frac{(\lambda_s + \lambda_p) + 3 (\lambda_t + \lambda_p)}{4} \quad (22)$$

This gives $\tau_2 (\text{MIN}) = 3.9 \times 10^{-10}$ sec.

FIG. 16

The curves shown in Fig. 14 have been normalized to the experimental points at the lifetime value $\tau_2 = 1.0 \times 10^{-9}$ sec., a region where the variation is fairly linear. Neither of these theoretical curves gives an exact fit to the experimental points for FeCl_3 but the variation is of the same form and so there seems to be little doubt but that the quenching is due to a conversion process^{*}. Owing to the chemical complexity of the solutions, it is not surprising that the curve calculated on such simple grounds fails to give an exact fit. A better fit was found for the FeCl_2 results but this was the exception rather than rule.

There is one further theoretical treatment which should be mentioned. The complete conversion theory can be made to fit the experimental results at high concentrations (i.e. $\tau_2 = 4 \times 10^{-10}$ sec.) by assuming that positronium has values of λ_s and λ_t in liquids that are different from the λ_s and λ_t values for positronium in free space. This variation would be due to a distortion of the wave function as a result of the positronium atom being confined in the liquid. This would result in an enhancement of the probability of finding an electron at the position of the positron and so shorten the lifetime. It seems unlikely that this would be a large enough effect to produce the required change ($\sim 20\%$) in λ_s and λ_t because of the very small mass of the positronium atom and hence its great manoeuvrability as well as the fact that its structure suggests great flexibility in motion.

The pickoff plus conversion theory on the other hand seems a more reasonable one. The observed τ_2 lifetimes for non-quenchers are in order of magnitude agreement with those that would be predicted using the Dirac

^{*} Of course when a quenching agent is added to water the λ_p value will be altered due to pickoff annihilations with the added material. For most solutions used here this will not be a big effect but might explain some of the disagreement observed, especially at large concentrations.

cross-section for this process. Also physically, it is quite possible for an electron with the proper spin orientation to approach the neutral triplet positronium atom and annihilate with the positron which cannot easily annihilate with its own atomic electron due to its unfavourable spin orientation. In addition, more evidence will be given later for favouring the pickoff theory and so it will be assumed to be correct in this work. If one accepts this pickoff theory, the fact that it correctly predicts the lower limit for the lifetime using the free space values of λ_s and λ_t proves that these values are not much changed in the liquids. This view will be accepted here.

The results of similar experiments with other iron group elements are shown in Figs. 17, 18, 19. The FeCl_3 results are shown again as comparison with the other salts. The solid lines shown are those drawn to fit the experimental points and do not represent any particular theoretical curve. It is seen that FeCl_3 is by far the strongest converter of all the substances studied.

(b) The Rare Earth Group..

The paramagnetism exhibited by the rare earth elements suggested that a study of this group might be interesting. The paramagnetism here is due to the presence of unpaired electrons in the unfilled 4f subshell of these atoms. Only two of the rare earths have been studied to date, one of these being diamagnetic lanthanum, the first member of the group, which is not a converter, since it has no 4f electrons. The other substance investigated was neodymium which is paramagnetic, having three unpaired 4f electrons. The results for the NdCl_3 are shown in Fig. 20. It was not possible to make the NdCl_3 solution strong enough to follow the complete variation of τ_2 with concentration. However, the results obtained show it to be a converter but much weaker than the elements in the iron group.

FIG. 17.

FIG. 18

MOLARITY OF SOLUTION

FIG. 19

MOLARITY OF SOLUTION

FIG. 20

The reason for the much weaker conversion by the NdCl_3 is fairly apparent when the electron configuration of the atom is considered. The 4f subshell lies deep in the structure of the atom, being surrounded by the 5s and 5p subshells. (The 5d and 6s valence electrons are assumed to be removed by the ionization of NdCl_3 or occupied in the chemical combination with the chlorine.) The iron group elements however have their 3d electrons on the outside of the atom once the valence electrons are taken away. Hence the unpaired electrons of the 3d subshell of the iron group are in easy reach of the positronium atom while the 4f electrons of the rare earths are protected by the outlying subshells. This explains why conversion is more marked for the iron group elements than for the rare earths, even though the paramagnetic susceptibilities of the two groups are comparable.

(c) Antimony, NO_3^- and NO_2^-

While making a study of several different chlorides an unexpected converter was discovered. This was SbCl_3 , the conversion of course being due to the antimony. The electronic configuration of antimony does not show any obvious abnormality which would explain the observed effects. The ion Sb^{+++} at first sight appears to consist of a closed 5s subshell within which lie a vacant 4f subshell and filled 4d, 4p and 4s subshells. On this arrangement of electrons no conversion would be expected.

One possible explanation might be the following. If it is assumed that the antimony exists as Sb^{+++} , then when the 5p valence electrons are taken away perhaps one or both 5s electrons fall back into the vacant 4f shell; then both would be unpaired, and capable of producing the observed effects. This sort of behaviour is thought to occur for non-trivalent rare earth ions³⁹. For example, the normal trivalent rare earths Eu^{+++} and Gd^{+++} have six and seven 4f electrons respectively, and exhibit different paramagnetic suscept-

ibilities. The divalent Eu^{++} ion however gives an almost identical paramagnetic susceptibility to the Gd^{+++} ion and this suggests that the 5d electron of the Eu^{++} ion has dropped back into the 4f subshell to give a structure identical to Gd^{+++} . This might also occur for the 5s electrons in antimony.

The other explanation is that perhaps the antimony is not present in the solution as the Sb^{+++} ion but rather as an ion in a different valence state, which might leave the antimony with one or more unpaired electrons in its structure. (Sidgwick⁴⁵ says that an SbCl_3 solution consists mainly of the complex ion SbCl_4^+ , suggesting that the situation is more complex than would be expected from a simple interpretation.)

In order to keep the antimony in solution it was necessary to use strong ($\sim 5\text{M}$) HCl as the solvent and the dilution of the solutions was performed using $\sim 3\text{M}$ HCl . A lifetime experiment using 5M HCl showed the same τ_2 as water so that using the HCl as the diluting agent was not thought to interfere with the conversion by the antimony. The results for SbCl_3 are also shown in Fig. 20.

In the investigation of the NO_3^- and NO_2^- ions a different type of quenching was observed. This new effect is best illustrated by Fig. 21 which shows lifetime measurements for NaNO_3 . It is clearly seen from this diagram that the presence of the NaNO_3 in water decreases the intensity of the τ_2 component quite markedly without altering the τ_2 lifetime appreciably. A water run is shown as a comparison. Similar effects have been observed for NaNO_2 and HNO_3 , proving that the NO_3^- and NO_2^- ions are responsible for the observed effects. The amount of the τ_2 component is difficult to evaluate due to the statistical inaccuracy of the low points on the resolution curves, but it seems that I_2

FIG. 21—QUENCHING BY NaNO_3

decreases rapidly for the addition of a small amount of the salt and that the further addition of NaNO_3 causes I_2 to approach a limit of about 2% of the total number of observed coincidences. The I_2 value for water is 20% (See section 3). The action of these ions is perhaps analogous to similar observations made in gases by Deutsch et al⁴⁴, where the addition of small amounts of a polyatomic gas altered the amount of triplet positronium formed.

2. Measurements of Cross Sections:

For all the quenchers (or converters^{*}) discovered, and shown in the preceding diagrams, cross sections for the triplet $\leftrightarrow$ singlet conversion have been calculated. This has been done assuming that all the atoms of the quenching agent are able to cause conversion. If the solutions are 100% ionized this would be correct, and even if this is not true, little difference is expected for an unionized molecule since the valence electrons will be occupied in the formation of the compound and should not interfere with the conversion produced by the unpaired electrons. Assuming this then, the cross sections were calculated in the following manner.

From Fig. 16 was obtained the value of γ_2 corresponding to the lifetime $\tau_2 = 1.0 \times 10^{-9}$ sec. From the experimental curves of τ_2 vs. molar concentration the molarity corresponding to $\tau_2 = 1.0 \times 10^{-9}$ sec. was read off. The number of atoms per cc. was obtained from the molarity and the cross section σ was calculated using

$$\gamma_2 = N_A \sigma \bar{v} \quad (23)$$

* Throughout this discussion quenching and conversion have been used, albeit rather loosely to mean the same thing, i.e. a change of τ_2 .

where N_A is the number of atoms per cc. and $\bar{v}$ is the average velocity of the positronium atom assuming thermal equilibrium. $\bar{v}$ is given by

$$\bar{v} = \sqrt{\frac{8 kT}{\pi m}} \quad (24)$$

where m is twice the electronic mass, k is Boltzmann's constant and T is the absolute temperature. For $T = 295^\circ\text{K}$ $\bar{v}$ becomes

$$\bar{v} = 7.55 \times 10^6 \text{ cm/sec.}$$

The number of atoms per cc. for an M molar solution is given by

$$N_A = \frac{M N}{1000} = 6.02 \times 10^{20} M \quad (25)$$

where N is Avogadro's number.

The cross section for triplet $\leftrightarrow$ singlet positronium conversion finally becomes

$$\sigma = \frac{\gamma_2}{6.02 \times 10^{20} M \times 7.55 \times 10^6} = 2.20 \times 10^{-28} \frac{\gamma_2}{M} \text{ cm}^2 \quad (26)$$

For the pickoff plus conversion process, Fig. 16 gives γ_2 at $\tau_2 = 1.0 \times 10^{-9}$ sec. as $5.5 \times 10^8 \text{ sec}^{-1}$. Thus the cross section is

$$\frac{1.21 \times 10^{-19}}{M_0} \text{ cm}^2 \quad (27)$$

where M_0 is the molarity of a particular solution required to give the

$\tau_2 = 1.0 \times 10^{-9}$ sec. lifetime. (For the complete conversion mechanism Fig. 16 gives $\gamma_2 = 1.06 \times 10^9 \text{ sec}^{-1}$, and

$$\sigma = \frac{2.34 \times 10^{-19}}{M_0} \text{ cm}^2 \quad (28)$$

From (27) and (28) it is seen that if the complete conversion mechanism had been assumed to explain the τ_2 observed in water, the cross sections evaluated for the various triplet $\leftrightarrow$ singlet converters would have been about doubled.)

Table I shows a list of all the quenchers found in this work and their quenching cross sections, calculated using (27). Apart from assumptions in the mechanisms involved, the standard error in the cross sections is about 10%.

TABLE I

Ion	Compound	σ (cm ²)	No. of Unpaired Electrons
Cr ⁺⁺⁺	CrCl ₃	6.3 x 10 ⁻¹⁹	3
Mn ⁺⁺	(a) MnCl ₂	2.5 x 10 ⁻¹⁹	5
	(b) MnSO ₄	1.8 x 10 ⁻¹⁹	
Fe ⁺⁺⁺	FeCl ₃	3.8 x 10 ⁻¹⁸	5
Fe ⁺⁺	FeCl ₂	4.8 x 10 ⁻¹⁹	4
Co ⁺⁺	CoCl ₂	5.3 x 10 ⁻¹⁹	3
Ni ⁺⁺	NiCl ₂	5.6 x 10 ⁻¹⁹	2
Cu ⁺⁺	CuCl ₂	1.1 x 10 ⁻¹⁸	1
Nd ⁺⁺⁺	NdCl ₃	4.0 x 10 ⁻²⁰	3
Sb ⁺⁺⁺	SbCl ₃	3.7 x 10 ⁻¹⁹	?

The NdCl₃ cross section was calculated by fitting, to the few points obtained for this substance, a curve of the same form as was observed for the other quenchers. No attempt was made to get a cross section for the NO₃⁻ and NO₂⁻ ions since it was very difficult to get accurate values of τ_2 when the intensity of this component became very small.

The results of Table I show large variations for the ions studied. It can be said for the iron group that the quenching is definitely associated with the presence of unpaired electrons in the electronic structure of these atoms. This becomes evident when it is seen that a ZnCl₂ solution of ~4M exhibited no quenching but showed a τ_2 lifetime almost identical to that of pure water. This is to be expected since the Zn⁺⁺ ion, at the end of the iron group has a filled 3d shell, hence no unpaired electrons (see Section 4).

There seems to be little relation between the number of unpaired electrons and the observed cross sections; for example Cu^{++} with only one unpaired electron is next to Fe^{+++} in quenching power, and better than other ions with 2, 3, 4, and 5 unpaired electrons. Again, the difference between the Mn^{++} cross sections for the two different salts MnCl_2 and MnSO_4 is puzzling since the only ion contributing to the quenching in both cases is Mn^{++} . (Both NaCl and Na_2SO_4 are non-quenchers suggesting that the Cl^- and SO_4^{--} ions do not contribute to the quenching.) The fact that very little correlation exists between the number of electrons and the observed cross sections may be due to the following facts.

(1) The assumption that all the atoms contribute equally is not a good one and that only the ions do any quenching. The variation of the degree of ionization for the various solutions would then perhaps explain some of the observed differences, e.g. the difference between MnCl_2 and MnSO_4 . However the modern theory of complete ionization for strong electrolytes (such as the iron group elements) would tend to make all the solutions comparable in their degree of ionization and bring back the old disagreement.

(2) The chemical composition of the solutions is very complex. The formation of complex and hydrated ions in these solutions is well known and their presence is likely to inhibit the conversion process. Experiments on paramagnetic spin resonance⁴⁰ have shown that the presence of complex ions in solutions tends to reduce the paramagnetic resonance signals. This is a good reason for assuming that similar effects can be expected in the quenching of triplet positronium since both processes depend on the availability of unpaired electrons. These chemical effects, which are very difficult to evaluate, make it impossible to correlate the observations with any reasonable theory.

The cross section obtained here for the Fe^{+++} ion is about $1/3$ that found by Berko and Zuchelli for DPH in benzene. Since these authors calculated the DPH cross section using the complete conversion theory, the agreement of the two values is actually much better than this $1/3$ factor, being more closely $2/3$. This suggests strongly that the quenching mechanism is the same in both cases, i.e. triplet $\longleftrightarrow$ singlet conversion.

The result obtained here for NdCl_3 is understandable if one assumes that the subshells outside the $4f$ shell are protecting the latter so that it is more difficult for the positronium atom to encounter the unpaired electrons. The quenching observed here can also be attributed to the three unpaired electrons of the $4f$ shell of the Nd^{+++} ion, since a saturated solution of LaCl_3 showed no quenching, consistent with the fact that the trivalent ion of La, the first member of the rare earth group, has no $4f$ electrons, hence no unpaired electrons.

The results for SbCl_3 are difficult to explain but it appears that the chemical properties of the solution are influencing the type of compound formed and so the quenching action.

3. Non-Quenchers

In the search for quenchers, many substances were tried which showed no large change in the τ_2 value from that observed in water, even for fairly concentrated solutions. These substances were termed non-quenchers and a list of such substances is shown in Table 2 with their τ_2 lifetime values, concentrations and the intensity I_2 , of the τ_2 component.

TABLE II

Compound	Concentration	τ_2 Lifetime (10^{-9} sec. units)	I_2 (%)
H ₂ O	pure	1.80 ± 0.10	20 ± 4
NaC ₂ H ₃ O ₂	7.6 M	1.91 ± 0.10	18 ± 4
K ₂ CO ₃	5.8 M	1.57 ± 0.10	14 ± 3
NaOH	10 M	1.49 ± 0.10	20 ± 4
BaCl ₂	1.7 M	1.72 ± 0.10	16 ± 3
HCl	5.0 M	1.83 ± 0.10	15 ± 3
LaCl ₃	saturated solution	1.80 ± 0.10	17 ± 3.5
KCl	3.9 M	1.68 ± 0.10	16 ± 3
AlCl ₃	3.9 M	1.71 ± 0.10	19 ± 4
Na ₂ CO ₃	1.3 M	1.77 ± 0.10	19 ± 4
ZnCl ₂	6.3 M	1.82 ± 0.10	15 ± 3
NaCl	5.2 M	1.76 ± 0.10	14 ± 3
NH ₄ Cl	5.2 M	1.72 ± 0.10	13 ± 2.5
Na ₂ SO ₄	3.3 M	1.75 ± 0.10	15 ± 3
p-dioxane	pure	2.67 ± 0.10	34 ± 7

The computation of I_2 is performed by a technique best illustrated by the diagram of Fig. 22 which shows a typical water run. The area under the τ_2 component is found by extrapolating the line defining the τ_2 decay back to a point 3×10^{-10} sec. to the left of the center of the short lifetime part of the complex decay curve. The value 3×10^{-10} sec. was chosen since previous work¹⁹ had shown that the short lifetime τ_1 observed for such substances was $\sim 3 \times 10^{-10}$ sec. This means that extrapolating back to this point brings the τ_2 decay curve back to the zero of time. The extrapolation

FIG. 22

point A then is hoped to be the center of a prompt resolution curve if such a curve could have been observed here. The coincidence rate at this point A and the measured value of the τ_2 lifetime give the area under the τ_2 component of the resolution curve. I_2 is then this area expressed as a percentage of the total area under the complete resolution curve of Fig. 22. I_2 must be corrected for two things.

(1) The finite width of the resolution curve. The measured area must be multiplied by

$$(\tau_0 / \tau_2) / \sinh(\tau_0 / \tau_2)$$

where τ_0 is the usual half width at half maximum for the short lifetime part of the resolution curve. For the results of Table 2 this factor is about 0.95.

(2) The self absorption of the source and the mica sheets between which the source is sandwiched. The source is only 100 μgm total weight and so absorption here can be considered negligible. The positrons lost in the mica will contribute to the area of the short lifetime portion of the curve at the expense of the tail since positron lifetime measurements in mica¹⁹ have shown it to have only a single component τ_1 , i.e. it exhibits a behaviour similar to metals. (This was one of the reasons for using it as a source mounting, the other being its chemical inertness). In order to get some idea as to the number of positrons being lost in mica, a water run was performed by dissolving Na^{22} activity directly in the water, the latter contained in a thin-walled Pb cell. The I_2 values for the mica source in water and the Pb cell source were within agreement within experimental accuracy and since the loss in the Pb cell walls was calculated as $\sim 5\%$ then the loss in the mica must be of the same order. Calculations based on the absorption and back-scattering data of Rosenfeld et al⁴¹ also give a value of $\sim 5\%$ for the mica loss.

Using these corrections then the results of Table 2 were obtained. The errors are given as $\pm 20\%$ and this is because of the uncertainty of the extrapolation, since the value of 3×10^{-10} sec. for τ_1 is only an average value and might be in error by $\pm 10^{-10}$ sec.

The interesting point about the I_2 values in Table 2 is their disagreement with the constant value of $\sim 30\%$ given by Bell and Graham¹⁹ for all the substances, which showed a complex decay, studied by these authors. Other results to be given later show even more strikingly that I_2 is far from being a constant for different substances. The values of I_2 in Table 2 vary from 13% to 20% for aqueous solutions, but for p-dioxane, an organic liquid with a structure very similar to benzene the value of I_2 is 34% in good agreement with the value reported for benzene. (The p-dioxane lifetime is also equal to that found in benzene viz. $\tau_2 = 2.67 \times 10^{-9}$ sec.)

Most of the lifetimes of the non-quenchers are the same as that for pure water within experimental accuracy. A very few do show a slightly different lifetime (e.g. 10 M NaOH has $\tau_2 = 1.49 \times 10^{-9}$ sec.) from that observed in water. This effect has not been interpreted as quenching and is perhaps due to the very large concentration of the added material which will tend to increase the pickoff annihilation rate and so decrease the lifetime.

4. Lifetime Measurements in Al, Mg and Si.

The purpose of these measurements was to search for evidence of positronium formation in the metals Al, Mg and the semiconductor Si. To do this properly it is essential that no positrons annihilate in source or backing materials where positronium might be formed since this would mask the effect sought. For this reason only Al, Mg and Si were studied here and the positron sources were ideal ones for the activated elements were themselves the positron

sources. These ideal sources were prepared by bombarding Al, Mg and Si in the synchrocyclotron at the appropriate proton energies to produce Na^{22} directly in these samples. The reactions for these processes are

After bombardment, the samples were stored until all the short lived activities had decayed and only the Na^{22} activity remained in measurable amount. The samples were then wrapped in more material of the same kind and of sufficient thickness so that no positrons could annihilate in material other than that being studied. Lifetime measurements were then made using these sources. The results are shown in Fig. 23 for the Al, Mg and Si samples. In these runs the gate on the pulse height analyzer selection circuit was narrowed in order to improve the resolution.

The small tails observed for these runs do suggest that a few percent of the positrons entering a metal form positronium. However it is not possible to say definitely that the observed tails are not due to instrumental effects. Although no such tail was observed for the Co^{60} prompt resolution curve with similar pulse height selection it is not fair to say that the observed effects are real since the radiation spectrum from the Co^{60} source is unlike that for a Na^{22} source. This could perhaps cause a difference in the resolution of the instrument. If however one assumes that the observations are proof of positronium formation the amounts formed are $\sim 4\%$ for Al, $\sim 8\%$ for Mg, $\sim 5\%$ for Si.

Basson²⁹ has shown that the ratio of the intensities of two quantum and three quantum annihilation events in aluminum is in agreement with the theory¹², assuming no positronium formation. However the accuracy of his measurement is such that the result would still be consistent if only a few percent of the positrons formed positronium, as observed here.

It seems logical that some positronium should be formed in metals due to the interaction of the positrons with core electrons; the formation by capture of free Fermi electrons will be a radiative process and so less probable. The amount of positronium will be expected to be small since the core electrons are bound with tens of volts energy and so only positrons with at least this energy, less the binding energy of positronium, can capture these electrons.

Once formed, positronium should be about as stable as in amorphous solids since in order to cause dissociation a Fermi electron will need greater than 6.8 volts energy and the two resulting electrons will therefore each be left with a small energy. The most favourable case is the one where an electron at the top of the Fermi distribution dissociates the positronium atom. The energy balance for this event is

$$E_F - 6.8 = e_1^- + e_2^- + e^+ \quad (29)$$

where E_F is the Fermi energy, e_1^- , e_2^- are the kinetic energies of the two resulting electrons, and e^+ is the kinetic energy of the positron. The maximum energy of an electron is realized when the other electron and the positron both have zero kinetic energy. This maximum energy is

$$e_{MAX}^- = E_F - 6.8 \text{ volts} \quad (30)$$

It is obvious from (29) and (30) that such a process of dissociation will leave the two electrons with energies corresponding to low lying levels in the energy distribution. These levels are normally filled and so this process does not occur.

Also triplet $\longleftrightarrow$ singlet conversion by Fermi electrons is unlikely since the electron, after the conversion, will have the opposite spin and this process can only occur for electrons at the very top of the Fermi distribution where vacant spin states exist. Hence this process is unlikely.

If positronium is formed, then it should be fairly stable and it would be expected that a small tail should occur for metals. The τ_2 value may well be smaller than for amorphous solids and liquids since there is increased probability of annihilation, by pickoff, with the free electrons.

To sum up then, some evidence has been found for positronium in Al, Mg and Si and the behaviour observed is in fair agreement with some simple assumptions outlined above for metals. However, since the measurements were made near the ultimate resolution of the instrument, it is not known whether the observed effects are real or only instrumental. Gerholm³³ has recently reported evidence for a τ_2 component of about 6% in Al corresponding to 8% positronium formation.

5. Amorphous Solids

A piece of fused quartz known commercially as "Vitreosil" ($>99.8\% \text{ SiO}_2$) was bombarded in the cyclotron at a proton energy of 75 Mev. After short lived activities had decayed the specimen was enclosed in a container made of more fused quartz of sufficient thickness to stop those few positrons which might emerge from the specimen. (Few are expected to emerge since the activated quartz was 1/8" thick). The resulting source was an ideal one for measuring the lifetime of positrons in the fused quartz sample. The result of such a measurement is shown in Fig. 24.

The τ_2 component is very much in evidence here and the decay is followed over a factor of 1000 with no variance from the exponential shape.

It is also evident from this graph that the intensity of the τ_2 component, I_2 , is large, much larger than that observed for the aqueous solutions. On measuring this intensity in the manner already described for the aqueous solutions (the point A on Fig. 24 is the zero of time) the result is a value of I_2 equal to 53% for the Vitreosil. This is much larger than has been observed previously, the fused quartz value of Bell and Graham being $\sim 29\%$.

On the same graph are shown two other curves for high-silica glasses, one for "Vycor" which is 96% SiO_2 and the other for ordinary Pyrex glassware which is $\sim 80\%$ SiO_2 . The Vycor and Pyrex runs were done using the 10 μc mica source, previously described, sandwiched between slabs of the material being studied. These runs were shorter than the Vitreosil run, the number of coincidences at the peak of the curve being 10,000 instead of the usual 100,000. For this reason larger errors are placed on the I_2 values. These runs are also corrected for mica loss which in this case is 10% for these solids⁴¹.

The results of these experiments show clearly that I_2 varies markedly with the composition of the fused quartz sample. The Vycor sample shows an I_2 value not far from the Bell and Graham value for fused quartz, which suggests that this was the type of fused quartz used by these workers. The Pyrex sample also shows a different τ_2 lifetime than either of the other fused quartz samples.

In addition to the amorphous solids shown in Fig. 24 other such substances were studied. The results for these are given in Table III along with the results shown in Fig. 24.

TABLE III

Substance	$\tau_2(10^{-9} \text{ sec. units})$	$I_2 (\%)$	% Positronium Formed
Vitreosil	1.53 ± 0.1	53 ± 8	71 ± 11
Vycor	1.7 ± 0.2	30 ± 6	40 ± 8
Pyrex	1.2 ± 0.2	33 ± 7	44 ± 9
Homosil [*]	1.5 ± 0.2	47 ± 9	64 ± 12
Ultrasil ^{**}	1.5 ± 0.2	47 ± 9	64 ± 12
Paraffin Wax	3.1 ± 0.2	24 ± 5	32 ± 7
Lucite	2.0 ± 0.2	22 ± 5	29 ± 7
Polythene	2.5 ± 0.2	25 ± 5	33 ± 7
Teflon	3.3 ± 0.2	23 ± 5	31 ± 7

* Optical Grade Fused Quartz

** Stated to be the best available fused quartz from the point of view of ultraviolet transparency.

The results above show variations in the value of I_2 and hence in the amount of positronium formed in the various substances. The result for Vitreosil obtained here gives another bit of evidence to favour the pickoff process as the major mode of decay for triplet positronium in matter. This arises in the following way.

In angular correlation experiments in fused quartz on the departure from antiparallelism of the two annihilation quanta, Page et al⁴² have observed a narrow component which is not present in crystalline quartz. This narrow component is due to annihilation of the positron-electron pair with low relative momentum. This can be attributed to the annihilation of singlet positronium which will have thermal energy at the time of annihilation. The amount of this narrow component was given as 18%. If pickoff annihilation

occurs, the "picked-off" electrons will have energies much greater than thermal and so this mode of annihilation will not contribute to the narrow component observed in the angular correlation experiment. If then the 18% narrow component observed by Page et al is attributed solely to singlet positronium annihilation, the amount of triplet positronium present should be 54% in excellent agreement with the I_2 value found here for Vitreosil. If the τ_2 lifetime were due to conversion rather than pickoff, essentially all the positronium would decay from the singlet state and Page's curve would have shown a narrow component of about 72%.

6. Crystalline Alkali Halides

In a recent report R.A. Ferrell³⁶ suggests that the lifetimes of positrons in the alkali halides should increase by about a factor of four in going from fluoride to iodide and be independent of the particular alkali. The reason he gives for this variation is that the positrons will be attracted to and combine with the negative ions and then annihilate with an electron of the ion. Since the size of the ion increases in going from fluoride to iodide then the density of outer electrons at the position of the positron decreases and hence the lifetime should increase. If this is so, and the lifetime in the fluoride is two or three times 10^{-10} sec. (as observed for other crystals by Bell and Graham¹⁹) then the iodide lifetime should be about $(8-12) \times 10^{-10}$ sec., a lifetime easily measured with the apparatus used here.

For this reason it was decided to measure the lifetimes in these halides. The results of these experiments are shown in Fig. 25 where curves are given for LiF, NaCl and NaI, with an aluminum curve for comparison. The aluminum curve was used as the time reference and the lifetimes were measured by the

FIG. 25 — POSITRON LIFETIMES IN ALKALI HALIDES

shift of centroid method⁴³ since no lifetime occurred which could be accurately measured by the slope method. The difference between the centroid of the aluminum curve and any particular halide curve gives the difference in lifetime between those two substances. Using the known lifetime¹⁹ in Al (1.5×10^{-10} sec.) the halide lifetime can then be calculated. The centroid shift method was thought to be legitimate here since the radiations seen by the counters was the same for all specimens, the measurements being made with the mica source sandwiched between slabs of these materials. The lifetimes observed in this way were

$$\text{LiF} \quad \tau = (2.1 \pm 0.5) \times 10^{-10} \text{ sec.}$$

$$\text{NaCl} \quad \tau = (2.9 \pm 0.5) \times 10^{-10} \text{ sec.}$$

$$\text{NaI} \quad \tau = (2.5 \pm 0.5) \times 10^{-10} \text{ sec.}$$

The errors assigned are considered generous, the main contribution to the error being due to the uncertainty in the lifetime of positrons in Al. These results clearly contradict Ferrell's predictions.

IV. CONCLUSIONS

The work described here has been mainly concerned with the measurement of the lifetimes of positrons in aqueous solutions and in addition some experiments with Al, Mg and Si, crystalline salts and amorphous solids.

The complex decay exhibited by positrons annihilating in aqueous solutions has been studied in detail and the quenching of the long lived component of this decay, which is considered due to the presence of triplet positronium in the solution, has been observed. Many substances have exhibited the ability to quench out the long lived component and in almost every case this quenching has been attributed to the presence of unpaired electrons in the electronic structure of the atom. These unpaired electrons are capable of causing triplet $\longleftrightarrow$ singlet conversion of the positronium by electron exchange and so the long τ_2 component is shortened. The conversion process permits most of the triplet positronium to become singlet positronium and so it can decay rather rapidly from this state.

Two alternative theories to explain the observed variation of τ_2 with quencher concentration have been presented. The first assumes that water itself is a sufficient triplet $\longleftrightarrow$ singlet converter to account for the observed τ_2 in water. Adding the quenching agent increases the conversion rate and so decreases the τ_2 lifetime. The other theory assumes that the τ_2 lifetime for water can be explained by assuming that the triplet state decays by a two photon pickoff annihilation process. The added quencher then decreases the lifetime by promoting the triplet $\longleftrightarrow$ singlet conversion process. The experimental results appear to fit better to the pickoff theory especially at the low lifetime limit. This latter theory has thus been accepted as the more correct one.

Quenching (or conversion) cross sections have been measured for all the quenchers discovered. Little correlation of the observed cross sections

with the number of unpaired electrons present in the atom has been found and it must be assumed that chemical effects are responsible for this. The quenching by SbCl_3 is still unexplained but a plausible rearrangement of the electron structure could account for the observed effects.

A different type of quenching was discovered for NO_3^- and NO_2^- . The main effect observed when salts containing these ions are added to water is a marked decrease in the intensity of the τ_2 component. This is not clearly understood but may be similar to the effects recently observed in gases by Deutsch et al⁴⁴ when polyatomic molecules are added.

The lifetimes in several non-quenchers have been measured. These lifetimes are similar to that of water. The relatively small variation in τ_2 observed for a couple of these substances has been attributed to the variations in the pickoff annihilation rates due to the differences in the densities of electrons for these solutions. Measurements of the intensities I_2 of the τ_2 components in the non-quenchers have shown that this intensity is not constant as was previously suggested¹⁹ but varies from 13% to 20% for the aqueous solutions studied. An I_2 value of 34% was found for the organic liquid p-dioxane.

Further study of the τ_2 intensities in amorphous solids confirmed the fact that this quantity is not a constant. The work in quartz shows that I_2 varies appreciably depending on the composition and hence structure of the specimen. More evidence for the pickoff annihilation process was obtained when the results for fused quartz were compared with angular correlation experiments performed using this substance.

The measurements of positron lifetimes in Al, Mg and Si have shown some evidence for positronium formation in these materials. The results

are not conclusive however since the observations were made at the very limit of the resolution of the instrument. Further work with improved instrumental resolution is necessary to decide this point definitely. Upper limits of a few percent however have been given for the amount of positronium formed in Al, Mg and Si.

Measurements on crystals of the alkali halides showed that there were no very great differences in the positron lifetimes in these crystalline salts, contradicting recent theoretical estimates.

REFERENCES

1. S. DeBenedetti, C.E. Cowan, W.R. Konneker, H. Primakoff, Phys. Rev. 77, 205, (1950)
2. P.E. Argyle, J.B. Warren, Can. J. Phys. 29, 32 (1951)
3. R.E. Green, A.T. Stewart, Phys. Rev. 98, 486 (1955)
4. A.T. Stewart, Roy. Soc. of Canada Meeting - June 1956
5. W. Heitler, The Quantum Theory of Radiation, Oxford Press (1936)
6. R.L. Garwin, Phys. Rev. 91, 1571 (1953)
7. P.A.M. Dirac, Proc. Camb. Phil. Soc. 26, 361 (1930)
8. H.A. Bethe, Proc. Roy. Soc. A, 150, 129 (1935)
9. S. DeBenedetti, H.C. Corben, Annual Review of Nuclear Science 4, 191 (1954)
10. C.N. Yang, Phys. Rev. 77, 242 (1950)
11. D. Peaslee, Helv. Phys. Acta, 23, 845 (1950)
12. A. Ore, J.L. Powell, Phys. Rev. 75, 1696 (1949)
13. J.W. Shearer, M. Deutsch, Phys. Rev. 76, 462 (1949)
14. M. Deutsch, Phys. Rev. 82, 455 (1951)
15. M. Deutsch, Phys. Rev. 83, 866 (1951)
16. S. Mohorovićić, Astron. Nacht., 253, 94 (1934)
17. A.E. Ruark, Phys. Rev. 68, 278 (1945)
18. J.A. Wheeler, Ann. N.Y. Acad. Sci. 48, 219 (1946)
19. R.E. Bell, R.L. Graham, Phys. Rev. 90, 644 (1953)
20. R.L. Graham, A.T. Stewart, Can. J. Phys. 32, 678 (1954)
21. T.A. Pond, Phys. Rev. 93, 478 (1954)
22. S. DeBenedetti, H.J. Richings, Phys. Rev. 85, 377 (1952)
23. E. Madansky, F. Rasetti, Phys. Rev. 75, 397 (1950)
24. M. Deutsch, E. Dulit, Phys. Rev. 84, 601 (1951)
25. T.A. Pond, R.H. Dicke, Phys. Rev. 85, 439 (1952)
26. S. Berko, A.J. Zuchelli, Phys. Rev. 102, 724 (1956)
27. W.R. Dixon, L.E.H. Trainor, Phys. Rev. 97, 733, (1955)

28. G.L. Lee-Whiting, Phys. Rev. 97, 1557 (1955)
29. J.K. Basson, Phys. Rev. 96, 691 (1954)
30. R.F. Post, L.I. Schiff, Phys. Rev. 80, 1113 (1950)
31. R.E. Bell, R.L. Graham, H.E. Petch, Can. J. Phys. 30, 35 (1952)
32. R.E. Bell, "Beta and Gamma-Ray Spectroscopy", Chap. 18 (1) (p. 494)
Edited by K. Siegbahn, North Holland Publishing Company, Amsterdam (1955)
33. T.R. Gerholm, Arkiv. For Physik, 10, 523 (1956)
34. R. Stump, H.E. Talley, Rev. Sci, Inst. 25, 1132 (1954)
35. J. Fischer, J. Marshall, Rev. Sci, Inst., 23, 417 (1952)
36. R.A. Ferrell, Revs. Mod. Phys. (To be published in July 1956)
37. T.D. Newton, Phys. Rev. 78, 490 (1950)
38. Z. Bay, V.P. Henri, F. McLernon, Phys. Rev. 97, 561 (1955)
39. P.W. Selwood, "Magnetochemistry", Interscience Publishers, New York (1943)
40. B.M. Kozyrev, Discussions of the Faraday Society No. 19, 135 (1955)
41. A.H. Rosenfeld, R.A. Swanson, S.D. Warshaw, Phys. Rev. 103, 43 (1956)
42. L.A. Page, M. Heinberg, J. Wallace, T. Trout, Phys. Rev. 98, 206 (1955)
43. Z. Bay, Phys. Rev. 77, 419 (1951)
44. E. Dulit, B. Gittelman, M. Deutsch, Bull. Amer. Phys. Soc., Series II,
Vol. I, 69 (1956)
45. N.V. Sidgwick, "Chemical Elements and their Compounds", Vol. I, p. 793,
Oxford Press (1950).