[16]S. Larsson, Phys. Rev. 169, 49 (1968).
[17]W. Kutzelnigg and V. H. Smith, J. Chem. Phys. 41, 896 (1964).
[18]V. H. Smith and S. Larsson in "Proceedings of the Conference on Density Matrices, Queens University, Kingston, Ontario, Canada, 1967" (unpublished).
[19]P. O. Löwdin, J. Appl. Phys. 33, 251 (1962).
[20]W. A. Goddard, Phys. Rev. 157, 93 (1967); J. Chem. Phys. 48, 450, 1008 (1968).
[21]U. Kaldor, J. Chem. Phys. 48, 835 (1968); 49, 6 (1968); Phys. Rev. 176, 19 (1968).
[22]K. M. Sando, Ph.D. dissertation, University of Wisconsin, 1968 (unpublished).
[23]S. Lunell, Phys. Rev. 173, 85 (1968), has carried out MPHF and optimized-spin-function studies on Li(^2S) which differ from the present work in that only the 2s spatial orbital was optimized. His results are qualitatively similar to those reported here.
[24]W. A. Goddard, Phys. Rev. 169, 120 (1968).
[25]D. L. Hardcastle, J. L. Gammel, and R. Keown, J. Chem. Phys. 49, 1358 (1968).
[26]A similar phenomenon was observed by C. F. Bunge, Phys. Rev. 154, 70 (1967), using orbitals of the form $\chi_i^+\alpha + \chi_i^-\beta$ for two-electron systems.
[27]F. E. Harris, Advan. Quantum Chem. 3, 61 (1967).
[28]A. W. Weiss, Astrophys. J. 138, 1262 (1963).
[29]R. K. Nesbet, in Quantum Theory of Atoms, Molecules and the Solid State, edited by P. O. Löwdin (Academic Press Inc., New York, 1966), p. 157.

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Annihilation of Positrons in Argon I. Experimental

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The annihilation of positrons in argon has been investigated as a function both of argon density and applied electric field. The direct annihilation rate decreases with increasing field as observed in earlier work. These electric field results are compared with simple theoretical models of the positron-argon atom interaction in the following paper. A small nonlinear dependence on density of the direct annihilation rate became apparent at densities larger than about 10 amagats. The linear portion of the direct rate was characterized by $Z_{\text{eff}} = 27.3 \pm 1.3$. From the density dependence of the orthopositronium lifetime, the free orthopositronium annihilation rate (λ_1) and linear quenching rate in argon (λ_q) were found to be

$$\lambda_1 = (7.53 \pm 0.18) \times 10^6 \text{ sec}^{-1},$$

$$\lambda_q = (0.24 \pm 0.02) \times 10^6 \text{ sec}^{-1} \text{ amagat}^{-1}.$$

The role that impurities play in these measurements is also discussed.

I. INTRODUCTION

Recent investigations of the lifetime of positrons in argon have shown that the free positron annihilation rate cannot be described by a single exponential.[1–4] Time spectra of the annihilation γ rays show clear evidence of a shoulder followed by an exponential decay presumed to characterize annihilation of positrons at thermal velocities. It has been shown that the shoulder is removed, and the lifetime of the exponential increased, when a moderate static electric field is applied.[5] Typically, a field of about 80 V cm^{-1} amagat^{-1} is sufficient to increase the direct lifetime by a factor of 2. These results provide the only available experimental test of the validity of models that describe the positron-argon interaction at low relative velocities. A further series of these measurements has been made with improved instrumentation offering greater experimental precision; the measurements were performed to a greater degree of statistical accuracy. The results of these measurements are used to test the validity of several empirical potentials describing the effective positron-argon interaction in paper II which follows.

While engaged in this program, several other features of the decay of positrons in argon were measured in order to facilitate comparison with the results of other workers. These measure-

ments included: the density dependence of the free positron annihilation rate (or "direct" rate) in which some departure from linearity was observed at pressures exceeding 10 atm; such impurity sensitive characteristics as the width of the "shoulder" describing the initial portion of the free positron decay rate; and the quenching rate of the orthopositronium lifetime as a function of argon density. Comparison of these measurements with the results of other workers and their relationship to the purity of the gas is discussed in Secs. IV and V.

To emphasize the density dependence of these quantities, and to eliminate the uncertainties introduced by careless use of the "atmosphere" unit for pressure, all densities are quoted in units of the amagat which is the molecular density (Loschmidts Number = 2.687×10^{19} molecules cm^{-3}) of an ideal gas at NTP.

II. METHOD OF ANALYSIS

The time spectrum of positron annihilation in argon is composed of components due to free positron annihilation, para and orthopositronium annihilation, and a random coincidence background. Over a portion of such a spectrum, the data are well fitted[1-4] by the sum of two exponentials (the free positron and orthopositronium components) and a random coincidence background. This region is evident in Fig. 1, and occurs after the "shoulder" of the time spectrum.

The analysis of the time sorter data used to extract the two lifetimes was performed using maximum likelihood theory[6] in conjunction with Poisson statistics. In order to fit the data, each spectrum was divided into two regions. The first region consisted of the sum of two exponentials plus random coincidence background expressed by

$$y_k = \int_{W_k} (I_1 e^{-t/\tau_1} + I_2 e^{-t/\tau_2} + B)\,dt, \qquad (1)$$

where I_1, I_2 are the intensities of the two exponentials that have mean lifetimes τ_1, τ_2, respectively, B is the random coincidence background per unit channel width, and W_k is the width of channel k. The small differential nonlinearities characterizing the time sorter (see Sec. III) are taken into account by suitably defining these channel widths W_k.

The second region consisted of random coincidence background events only, those occurring prior to the prompt peak. The data in this region were fitted by

$$y_k = BW_k . \qquad (2)$$

In order to obtain the best values of the five parameters I_1, I_2, τ_1, τ_2, and B, consistent with likelihood theory, the joint likelihood function, obtained by taking into account both regions, was maximized by varying all five parameters simultaneously. Details of the fitting procedure and

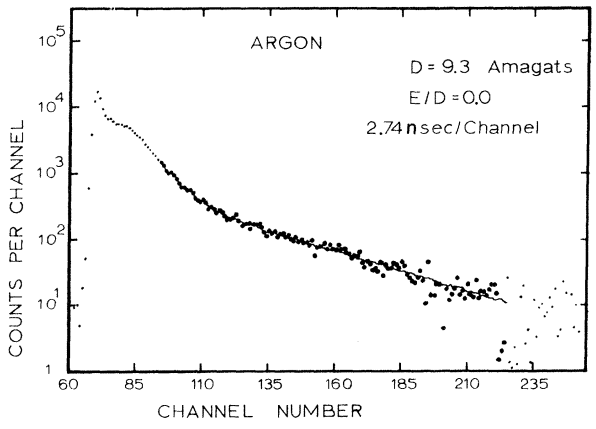

FIG. 1. Time spectrum of positrons annihilating in argon. The random coincidence background has been subtracted from the points. The heavy points indicate the range over which the maximum-likelihood fit was carried out.

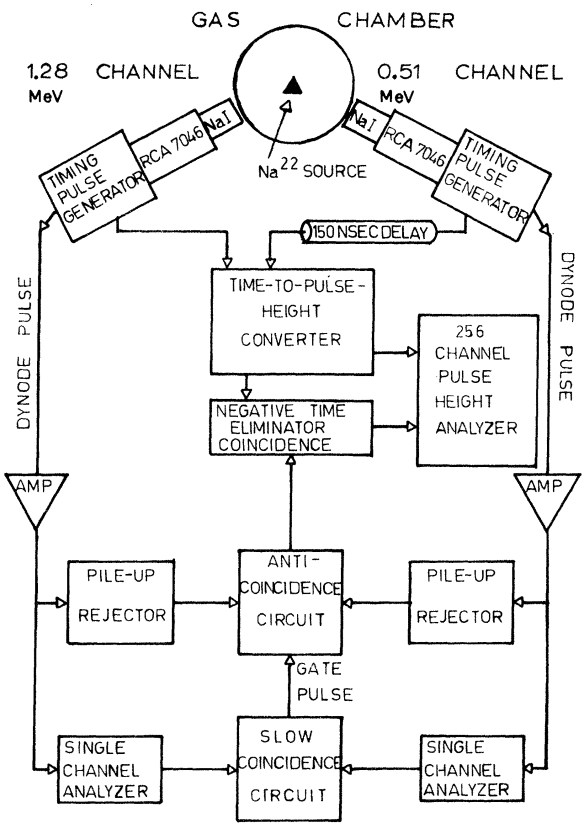

FIG. 2. Block diagram of electronic instrumentation used for recording time spectra.

computing techniques are described elsewhere.[7,6]

III. EXPERIMENTAL METHOD

A 1.0-μ Ci Na-22 source deposited on 30-μ-in. aluminum foil served as the positron source. The instrumentation for the recording of the time spectra was basically that used previously by Falk *et al.*[4,5,8] To improve reliability, the limiters and slow coincidence sections were replaced by transistorized equivalents. The limiters were simple tunnel diode discriminators,[9] the tunnel diode bias current being adjusted to obtain the optimum timing resolution for the energy interval of interest. This energy interval was selected using a single-channel analyzer (Cosmic Model 901 SCA) following a pulse amplifier (Cosmic Amplifier Model 901 A) as illustrated in Fig. 2. Inclusion of these units constituted the main modification to the original slow coincidence system.[4,5]

In order to improve the statistical accuracy of the measurements, the random coincidence background was reduced (relative to the measurements of Falk *et al.*[5]) by a factor of 10 by reducing the positron source strength. In order, however, to retain a comparable true-coincidence count rate, detectors of significantly greater efficiency and solid angle were employed. These consisted of 4-in. × 3-in. -diam NaI(Tl) crystals coupled to RCA 7046 photomultipliers. In addition, use of a 256 channel pulse-amplitude analyzer (ND101) made it possible to extend the time range of the measurements to include the whole orthopositronium decay, thus improving the accuracy of analysis.

The pressure chamber used was the same as that used previously in this laboratory.[5,10] A schematic of the chamber, showing the grid assembly used for the electric field experiments, is shown in Fig. 3. The argon gas was purified by continuous recirculation over a CaMg eutectic heated electrically to 400°C. Before use, the eutectic mixture was outgassed and conditioned by heating to 550°C under a vacuum until all the trapped gases had been removed. The eutectic, consisting of 79% Ca and 21% Mg, was operated at 400°C on the basis of the results of the work of Colli and Facchini.[11]

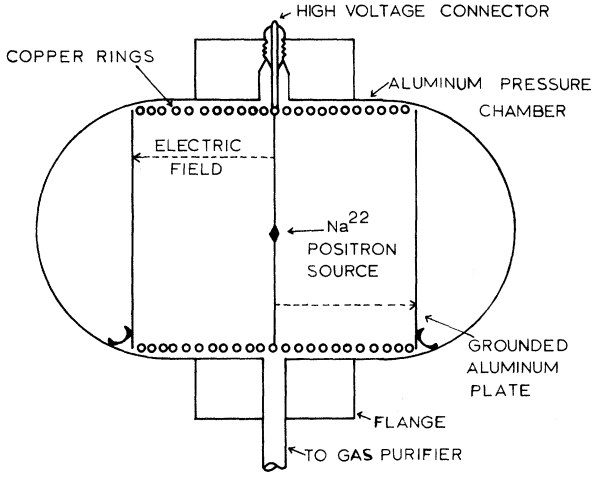

FIG. 3. Schematic diagram of high-pressure chamber.

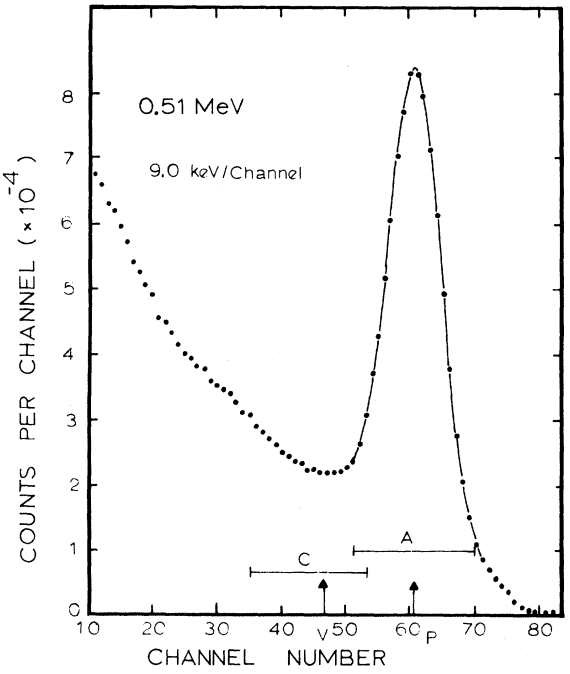

FIG. 4. Energy spectrum of 0.51-MeV annihilation radiation. *A* and *C* refer to single-channel analyzer settings. The key valley and peak positions are denoted *V* and *P*, respectively.

An analysis of the purified gas together with a general discussion of the effects of impurities on the measurements is presented in Sec. V.

A typical run extended over a period of two days in which time some 10^5 coincident events were recorded. After each run the gains of the 1.28- and 0.51-MeV phototube amplifier sections were checked as was the setting of each single-channel analyzer. The single-channel analyzer associated with the annihilation γ rays was usually set to include the full energy peak, as shown by region *A* of Fig. 4. However, many runs were also taken with the same channel width, but with the baseline set so as to include only the valley region[12] between the photopeak and the Compton edge. At this setting *C*, the ratio of three-photon to two-photon events was enhanced relative to the usual setting *A*, since the three-photon count rate in the valley region is comparable to that in the 0.51-MeV peak region,[13] while the two-photon count rate is sharply diminished. Such settings increased the relative intensity of the longer-lived orthoposi-

tronium component, thus allowing a more accurate determination of its lifetime. The over-all time resolution for either SCA setting was 2.7 kicksorter channels, or 7.4 nsec (full width at half-maximum), measured using a Na-22 source in aluminum. Results of a measurement[14] of the differential linearity of the time sorter is shown in Fig. 5. The relative channel widths so obtained were used in the analysis of the data[6] (see Sec. II). The integral linearity, also shown in Fig. 5, and from which the average time per channel was obtained, was measured using a double pulse generator with precision time separation.[8] Over a period of seven months the position of the prompt peak varied by less than 3 nsec. The integral linearity was reproduced to within 1% after this time.

A representative time spectrum for positron annihilation in 9.3 amagat of argon at room temperature is shown in Fig. 1. The peak results from the annihilation of positrons in the walls of the chamber and in the source holder, of parapositronium formed during the initial slowing-down period, and of positrons annihilating in the gas within about 7 nsec of emission from the source. The end of the shoulder is marked by a relatively short-lived exponential component, the direct component. The orthopositronium annihilations give rise to the long-lived exponential. Subtracted from the figure are the random coincidence background counts which occupy that portion of the kicksorter up to the prompt peak, counts that originate when a 0.51-MeV γ ray is detected before a 1.28-MeV γ ray. These "negative time" events were displaced to the "positive time" portion of the time calibration curve by the 150-nsec delay illustrated in Fig. 2.

IV. EXPERIMENTAL RESULTS

The data presented here represent the results of

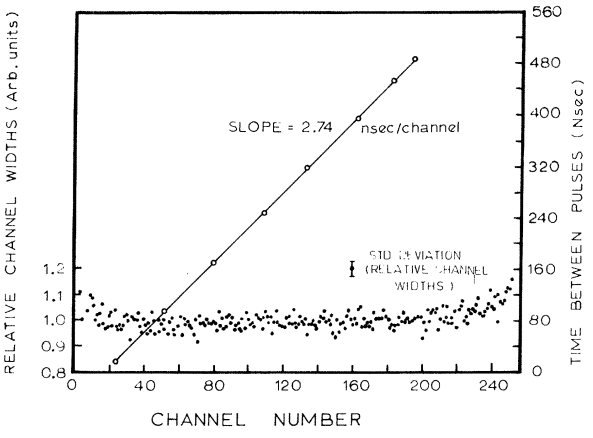

FIG. 5. Integral and differential linearity of the time sorter.

runs made with four different fillings of the chamber, the argon being from the same bottle in each case. The spectra were fitted by the sum of two exponentials and a constant random coincidence background by the maximum likelihood technique.[6] The results presented here satisfied the following conditions:

(a) Convergence was obtained varying all five parameters (see Sec. II) simultaneously in the maximum likelihood program.

(b) No high-voltage breakdowns occurred during the actual run in question. It was found that the occurrence of such breakdowns could lead to significant deviations in the results. These deviations were ascribed to the effect of contaminating gases liberated by the breakdown prior to the absorption of such contaminants by the purifier.

(c) The results of all the chi-square tests indicated that the probability of getting a worse fit was greater than 0.1 (10%).

Out of a total of 32 runs, five were rejected on the basis of criteria (a) and (b). The third criterion was used as a test of the adequacy of the assumption of two exponentials plus a constant background over the range of experimental points used in the analysis. In particular, for the few cases that the chi-square criterion indicated a poor fit, it was found that by shifting the start of the analysis a few channels further from the shoulder a satisfactory fit could be obtained.

1. Direct Annihilation Rate as a Function of Argon Density (at Zero Electric Field)

a. Results

Figure 6 shows the dependence of the direct annihilation rate without electric field on argon density. The density units indicated on the abscissa are those appropriate to argon gas at these pressures, involving deviations from direct proportionality to pressure by about 2% at the maximum pressures used.

These data were fitted by two simple polynomials in density

$$\lambda = (5.27 \pm 0.043) D, \tag{3}$$

and $$\lambda = (5.76 \pm 0.12) D - (0.041 \pm 0.010) D^2, \tag{4}$$

where the units of λ are $(\mu\text{sec})^{-1}$ and D, amagats. The confidence level (CL) for the first fit Eq. (3) was $< 10^{-4}$, whereas for Eq. (4), it is 0.015.

Clearly, inclusion of nonlinear terms in the density dependence of the annihilation rate improves the confidence level by several orders of magnitude. A further improvement in the goodness of fit would probably result using more complicated functions. Such effort was considered unjustifiable, however, in view of the lack of any theoret-

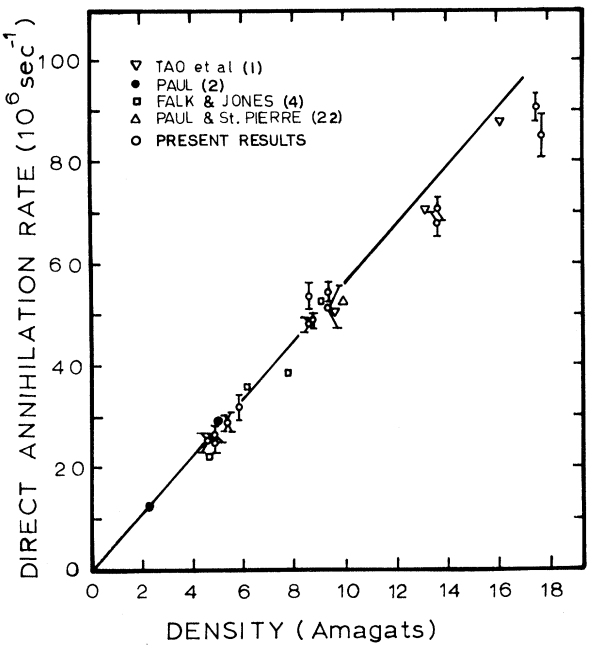

FIG. 6. Dependence of the direct annihilation rate of positrons on argon density. The solid line represents the line $\lambda_a = 5.6 \times 10^6 D$ sec^{-1}

ical guidance regarding the expected form of such a density dependence.

An accurate determination of the linear part of the dependence of λ on D will require more measurements of high statistical accuracy in the lower-density range. However, an estimate of the magnitude of the linear term can be obtained from Eqs. (3) and (4). Its value probably lies between the two values indicated, that is, between 5.25 and 5.75×10^6 sec^{-1}, thus leading to the value 27.3 ± 1.3 for the low-density limit of Z_{eff}.[15]

On the other hand, a detailed investigation of the nature and extent of the nonlinear portion of the dependence of the annihilation rate on density requires a set of accurate lifetime measurements at high density. For such measurements, instrumentation having significantly shorter time resolution than that used in these measurements would have to be employed.

The origin of such a nonlinearity at high densities could arise from the interaction of the positron with more than one argon atom at a time. The possibility of such an effect for electrons has already been raised.[16] At 15 amagat, the average interatomic distance is about 10 Å. At this distance the potential energy due to the polarization interaction of a positron with an argon atom is about 5% of the kinetic energy of the thermalized positron. It is thus possible that such interatomic distances could result in some screening of the field of the positron at the scattering atom, and thus reduce the magnitude of the very important attractive polarization potential. Clearly, this problem can only be resolved by further experiments at high pressures, and by calculations that take into account the presence of more than one scattering atom.

b. Comparison of Direct Annihilation Data with Previous Results

The magnitude of the direct annihilation rate per unit density is compared in Table I with the values obtained by other workers. The value quoted for the present work refers to the linear density term discussed in the preceding section. The error associated with this value reflects both the statistical errors and also the uncertainty in the exact nonlinear behavior of the annihilation rate. The systematic errors associated with this measurement are much smaller, of the order of 1%. There is considerable agreement between these results, a mean Z_{eff} of about 27.0 ± 0.5 encompassing most

TABLE I. Published values of the direct annihilation rate.

Z_{eff}	Direct annihilation rate per unit density (10^6 sec^{-1} amagat^{-1})	Approximate density range (amagats)	Author
25.6 ± 0.4	5.08 ± 0.08	3–6	Paul and Saint-Pierre[a]
29.3 ± 1.2	5.90 ± 0.23	10–11	Falk *et al.*[b]
26.9	5.4	10–17	Tao, Bell, and Green[c]
15.3	3.04	3.5–10	Osmon[d]
26.8	5.39	2.2–5.4	Paul[e]
26.5	5.33	5–9	Falk and Jones[f]
26.5 ± 1.1	5.34 ± 0.22	8–10	Miller *et al.*[g]
27.3 ± 1.3	5.50 ± 0.25	5–18	Present work

[a] See Ref. 24.
[b] See Ref. 5.
[c] See Ref. 1.
[d] See Ref. 3.
[e] See Ref. 2.
[f] See Ref. 4.
[g] D. B. Miller, P. H. R. Orth, and G. Jones, Phys. Letters 27A, 649 (1968).

of the individual values. The lack of agreement between Osmon[3] and the others is most likely due to the neglect by Osmon of the long-lived orthopositronium component in the lifetime analysis. The high Z_{eff} of Falk *et al.*[5] could possibly have arisen from difficulties encountered in taking into account the same orthopositronium component because of the relatively short time scale (240 nsec) available.

2. Direct Annihilation Rate as a Function of Electric Field

Figure 7 illustrates the effect of an applied electric field on the direct annihilation rate. For small E/D the annihilation rate decreases quite rapidly, reaching a fairly constant value of about 2.8×10^{6} $\text{sec}^{-1}\,\text{amagat}^{-1}$ at 90 $\text{V cm}^{-1}\,\text{amagat}^{-1}$. The current results are in excellent agreement with previous work.[10,17,18]

As observed in the earlier work, there is a tendency for the annihilation rate to increase at high E/P. Such behavior would be expected if a significant fraction of the equilibrium velocity distribution of the positrons had sufficient energy to form positronium at large fields. In this event, positronium production would contribute an extra channel through which the overall equilibrium distribution of free positrons could decay.

Such an interpretation is consistent with the measurements of the dependence of positronium production on electric field by Marder *et al.*[12] These workers found, by measuring the ratio of "valley to peak" counts in the energy spectrum of annihilation γ rays, that positronium production begins to increase at an E/D of about 50 $\text{V cm}^{-1}\,\text{amagat}^{-1}$.

As a check on the consistency of our measurements with the work of Marder *et al.*, the valley to peak ratios of the annihilation γ rays were monitored during the lifetime measurements reported here. These results are also reproduced in Fig. 7. The experimental setup employed in this work was not, however, as suitable as that of Marder *et al.* for obtaining quantitative estimates of positronium production from such measurements. In particular, the background in the region of the valley was much larger in our case due to energy degradation of the 0.51-MeV annihilation γ rays by the rather thick walls of the pressure chamber and also to the Compton tail of the 1.28-MeV γ rays emitted by the positron source (Na^{22}). When allowance was made for these effects, the results were found to be consistent with those of Marder *et al.*

In principle, the orthopositronium production could also have been determined by monitoring the intensity of the long-lived component. However, because of the amplitude selection used to enhance the detection efficiency of two-photon compared to three-photon events, the statistical uncertainty characterising orthopositronium intensity measurements was too large for such purposes in this experiment.

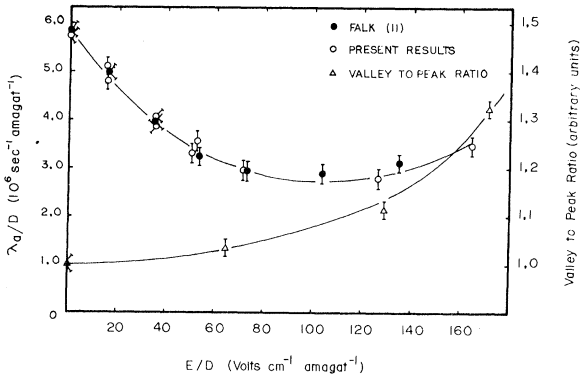

FIG. 7. Dependence of the direct annihilation rate of positrons on applied electric field for argon densities less than 10 amagat. The results of valley-to-peak ratio measurements are also shown for the same range of applied electric field.

To summarize, the rapid decrease of annihilation rate as a function of applied electric field shows that the velocity-dependent probability of annihilation of a positron with an argon atom decreases as the positron velocity increases. The explicit velocity dependence cannot be determined from the experimental data unless the velocity-dependent momentum-transfer cross section is known. However, some theoretical implications of such a dependence of annihilation rate on electric field are discussed in Paper II.

3. The Shoulder in the Annihilation Lifetime Spectra

In the case of zero applied electric field, all the time spectra displayed the usual shoulder structure[1–4] (see Fig. 1). Since the time spectrum of the direct component following the shoulder is well fitted by a single exponential, this region can be interpreted as signifying either that the positron velocity distribution has reached thermal equilibrium, or that the annihilation rate is velocity independent at low velocities. The application of a small electric field, however, reduces the annihilation rate significantly without perturbing the shoulder markedly. Since the applied field increases the average positron energy at equilibrium, the increased direct lifetime thus implies a velocity-dependent annihilation rate which decreases with increasing velocity, as suggested by earlier workers.[2,4,5] The time width of the shoulder, then, corresponds to the time taken for a positron to thermalize from an energy near that of the threshold energy for positronium formation (8.9 eV in argon).

The width-density product[1] was measured to be about 340 nsec amagat, rather larger than previous quoted results.[2,4] Since the rate of energy loss of a positron is increased when molecules having low-lying excitation levels are present, small values for the width-density product are indicative of the presence of impurities in the gas.[2,4,19] Throughout the experiment the shoulder width remained essentially constant showing that here there was no significant change in gas composition from run to run, either due to evolution of impurities from the walls, or due to the different gas samples used.

4. Orthopositronium Annihilation Rate

Figure 8 shows the dependence of the long-lived component of the annihilation rate on argon density. In order to improve the statistics for the direct lifetime measurement, the three-photon decays were in most cases discriminated against by setting the single-channel analyzer at the 0.51-MeV photopeak. For these cases, the statistical accuracy of the lifetime of the long-lived component is relatively poor.

Since other workers[20,21] have found the quenching rate to be a linear function of density, the data were fitted to a straight line given by $\lambda_1 = a_0 + a_1 D$. The solid line in Fig. 8 is the result of this fit and corresponds to the values

$$a_0 = (7.53 \pm 0.18) \times 10^6 \text{ sec}^{-1},$$

$$a_1 = (2.4 \pm 0.2) \times 10^5 \text{ sec}^{-1}\text{amagat}^{-1}.$$

As expected no dependence on E/D was found. The theoretical value for a_0, the annihilation rate of orthopositronium in a vacuum, is 7.2×10^6 sec^{-1}.[22] The quenching rate a_1, measured by Heymann *et al.*[20,21] is 2.5×10^5 sec^{-1}amagat^{-1}. These results are also in agreement with the recent measurements reported by Beers and Hughes[23]:

$$a_0 = (7.29 \pm 0.03) \times 10^6 \text{ sec}^{-1},$$

$$a_1 = (2.36 \pm 0.16) \times 10^5 \text{ sec}^{-1}\text{amagat}^{-1}.$$

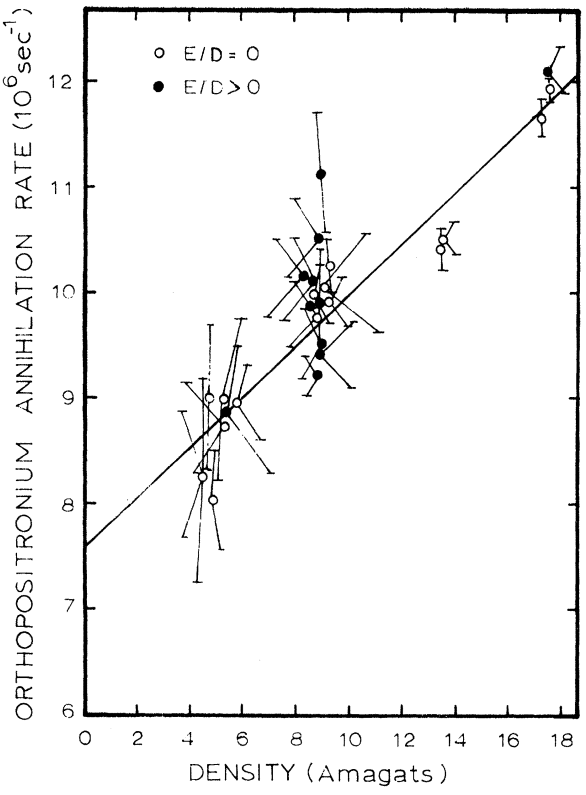

FIG. 8. Argon density dependence of the orthopositronium annihilation rate. Results obtained with and without applied electric field are shown separately. The straight line is the curve $\lambda_0 = (7.5 + 0.24D) \times 10^6$ sec^{-1}.

V. GAS PURITY: EFFECTS OF CONTAMINANTS AND RESULTING PURITY REQUIREMENTS

There is little doubt that high purity levels in the sample gas are vital in measurements of this type. For some impurities, indeed, large discrepancies can be brought about by concentrations sufficiently small that only a few collisions with a positron occur during the positron lifetime. Certain features of the lifetime spectra, however, are more sensitive to impurities than others.

1. Effects of Contaminants

a. Direct Lifetime Measurements (Zero Field)

The exponential decay characterizing the "direct" component is perhaps least sensitive to normal contaminants. In a mixture of several gases, the annihilation rate observed experimentally is the mean of the individual rates for the various components weighted according to the partial pressure of each.

For example, in the case of N_2 contamination,[10]

$$\lambda_{N_2} \approx \lambda_{Ar}$$

so the resulting λ for Ar – N_2 mixtures approximates that for pure argon.[1] The main concern, then, is to keep the partial pressure of large polyatomic impurities low. Paul and Saint-Pierre[24] found that the λ of such molecules can be more than 100 times larger than that of argon. Thus, the concentration of such contaminants must be kept well below 1%. That this has been achieved by most previous workers is indicated by the good agreement in the direct lifetime results summarized in Table I.

b. Electric Field Results

When an electric field is applied to the gas, it changes the equilibrium velocity distribution of the positron. In this case, the effect of the contaminant is to alter the average energy loss of the positron during collision. The average energy loss due to noble-gas atoms is that characterizing an elastic collision, i.e., $\Delta E \sim (m/M)E$, where E is the initial energy, M the mass of the gas atom, and m the positron mass. Thus, typical energy losses ΔE are $\sim 10^{-5}\ E$ for positrons in argon gas. Since in a collision with a polyatomic molecule many vibrational and rotational modes may be excited, ΔE can be of the order of E. Thus, in this case, impurity levels $< 1:10^5$ should be aimed for. Such effects, of course, play a similarly important role in measurements of the drift velocity of electrons in gases. In the case of electrons in argon, the drift velocity measurements were found to be significantly affected by impurity levels as small as 10 ppm.[25,26]

c. Direct Lifetime Shoulder Width

Since the shoulder width is determined by the slowing down time of the positrons, this parameter is very dependent on the presence of small amounts of impurities having large inelastic scattering cross sections. If the scattering of a positron by an argon atom is characterized by a momentum transfer cross section $\sim 10\pi a_0^2$,[5] it will suffer about 10^{12} collisions $\sec^{-1}$ at 10 amagat. In a slowing time of 30 nsec, then, the positron suffers $\sim 5\times 10^4$ collisions. Thus, an impurity concentration as low as a few parts in 10^4 could have a significant effect on the shape of the shoulder. Some of the early measurements,[1,19] in fact, had anomalously small shoulder widths because of such contamination. Subsequently, Paul[2] obtained a larger shoulder width-pressure product (190–300 nsec atm) and attributed this result to the fact that nitrogen contamination in his system was maintained below 25 ppm.

d. Orthopositronium Lifetime

For an elastic scattering cross section $\sim \pi a_0^2$ an orthopositronium atom collides with the argon atoms (at 10 amagat) at a rate $\sim 10^{11}\ \sec^{-1}$. Thus the orthopositronium atom also makes $\sim 10^4$ collisions during its lifetime. If some of these collisions involve impurity atoms with large quenching cross sections, the orthopositronium lifetime could be significantly reduced. It would thus appear that the orthopositronium annihilation rate is also sensitive to impurity concentrations of the order of a few parts in 10^4 where molecules with large quenching cross sections (such as NO, O_2) are involved. The orthopositronium lifetime is quite insensitive, however, to many other complex molecules (such as Freon) which are characterized by very small quenching cross sections.[20]

2. Quality of Argon Gas Employed

As discussed earlier, the gas used in these experiments was continuously cycled over a hot Ca-Mg eutectic to obtain the desired purity. When tested, Falk[10] found this arrangement capable of reducing the nitrogen level, for example, in an argon sample from 3000 ppm to < 200 ppm after operation for a few days. Unfortunately, the local testing facilities were limited to a minimum sensitivity ~ 200 ppm for most gases. Thus, in order to obtain a more precise estimate of the purity of the gas used in this experiment, a sample of gas was extracted from the chamber and supplied, together with a sample of the "raw" bottle gas, to Matheson Co. Inc., N. J., for analysis. The results of these analyses are shown in Table II. The rather large concentration of N_2 reported for the chamber sample is difficult to accept in view of:

(i) The pumping efficiency of the Ca-Mg eutectic for N_2 as determined by Falk.

(ii) The magnitude of the shoulder-width pressure product characterizing the measurements reported here. The measured value, ~ 340 nsec amagat was found to be reproducible from run to run and was as good as or better than previous "best" values.[2,5,10]

(iii) The orthopositronium quenching rate was in good agreement with results from previous workers.

(iv) In addition, the dependence of the direct rate on electric field (illustrated in Fig. 6) was also found to be very reproducible and in very good agreement with the previous unpublished results of Falk.[10]

For these reasons, the results quoted in Table II are interpreted as upper limits of the impurity levels only, as the contribution to these levels from outgassing of the glass vial used for shipping the argon sample (especially during flame sealing of the vial) is unfortunately unknown.

TABLE II. Gas purity analysis.

Impurity gas	Bottle gas (quoted purity: 99.98%)	Chamber gas
N_2	190 ppm	119 ppm
O_2	5 ppm	3 ppm
CO_2	4 ppm	4 ppm
H_2	23 ppm	32 ppm
He	153 ppm	100 ppm

VI. SUMMARY

The density dependence of the direct annihilation rate of positrons in argon gas has been measured at 25°C over a density range of 4.8 to 18 amagat. At the higher end of this range, a slight departure from linearity was observed. Fitting the data to a second-degree polynomial in density yielded the result

$$\lambda = (5.76 \pm 0.12)D - (0.041 \pm 0.010)D^2 ,$$

with λ in units of μsec^{-1} and D in amagats.

The dependence of the orthopositronium annihilation rate on density was measured over the same density range simultaneously. The linear fit $\lambda_1 = a_0 + a_1 D$ yielded the following results:

$$a_0 = (7.53 \pm 0.18)\,\mu\text{sec}^{-1} ,$$

$$a_1 = (0.24 \pm 0.02)\,\mu\text{sec}^{-1}\,\text{amagat}^{-1} ,$$

in agreement with previous values of the free orthopositronium annihilation rate and the quenching rate in argon, respectively.

The electric field dependence of the direct annihilation rate has also been measured up to 160 V $\text{cm}^{-1}\,\text{amagat}^{-1}$. The results confirm the previously observed decrease in annihilation rate with increasing electric field. These electric field results are used in the following paper in order to assess the usefulness of some single-particle models representing the effective positron-argon interaction.

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[1]S. J. Tao, J. Bell, and J. H. Green, Proc. Phys. Soc. (London) 83, 453 (1964).

[2]D. A. L. Paul, Proc. Phys. Soc. (London) 84, 563 (1964).

[3]P. E. Osmon, Phys. Rev. 138, B216 (1965).

[4]W. R. Falk and G. Jones, Can. J. Phys. 42, 1751 (1964).

[5]W. R. Falk, P. H. R. Orth, and G. Jones, Phys. Rev. Letters 14, 447 (1965).

[6]P. H. R. Orth, W. R. Falk, and G. Jones, Nucl. Instr. Methods 65, 301 (1968).

[7]P. H. R. Orth, Ph.D. thesis, University of British Columbia, Canada, 1967 (unpublished).

[8]G. Jones and W. R. Falk, Nucl. Instr. Methods 37, 22 (1965).

[9]G. Infante and F. Pandarese, in Proceedings of the Nuclear Electronics Conference, Belgrade, 1961 (International Atomic Energy Agency, Vienna, 1962), Vol. III, p. 29.

[10]W. R. Falk, Ph.D. thesis, University of British Columbia, Canada, 1965 (unpublished).

[11]L. Colli and U. Facchini, Rev. Sci. Instr. 23, 39 (1952).

[12]S. Marder, V. W. Hughes, C. S. Wu, and W. Bennett, Phys. Rev. 103, 1258 (1956).

[13]A. Ore and J. L. Powell, Phys. Rev. 75, 1696 (1949).

[14]W. Falk, G. Jones, and R. Orth, Nucl. Instr. Methods 33, 345 (1965).

[15]Z_{eff}, the "effective number of electrons per atom," is related to the observed annihilation rate λ by

$$Z_{\text{eff}} = \lambda(\pi r_0^2 cN)^{-1} = \lambda(2.01 \times 10^5 D)^{-1},$$

where D is in amagats.

[16]B. Kivel, Phys. Rev. 116, 926 (1959).

[17]G. Jones, W. R. Falk, and P. H. R. Orth, in Proceedings of the Fourth International Conference on the Physics of Electronic and Atomic Collisions, Quebec, 1965 (Science Bookcrafters, Inc., Hastings-on-Hudson, New York, 1965), p. 372.

[18]G. Jones and P. H. R. Orth, Positron Annihilation, edited by A. T. Stewart and L. O. Roellig (Academic Press Inc., New York, 1967), p. 401.

[19]S. J. Tao and J. Bell, Positron Annihilation, edited by A. T. Stewart and L. O. Roellig (Academic Press Inc., New York, 1967), p. 393.

[20]B. G. Duff and F. F. Heymann, Proc. Roy. Soc. (London) A270, 517 (1962).

[21]F. F. Heymann, P. E. Osmon, J. J. Veit, and W. F. Williams, Proc. Phys. Soc. (London) 78, 1038 (1961).

[22]A. I. Alekseev, Zh. Eksperim. i Teor. Fiz. 36, 1839 (1959) [English transl.: Soviet Phys. – JETP 9, 1312 (1959)].

[23]R. H. Beers and V. W. Hughes, Bull. Am. Phys. Soc. 13, 633 (1968).

[24]D. A. L. Paul and L. Saint-Pierre, Phys. Rev. Letters 11, 493 (1963).

[25]J. C. Bowe, Phys. Rev. 117, 1411 (1960).

[26]T. Nagy, L. Nagy, and S. Desi, Nucl. Instr. Methods 8, 327 (1960).