

APPENDIX I

Let f and g be the direct and exchange capture amplitudes. Since electrons are Fermi particles, the capture rate averaged over the spins is proportional to¹¹

$$\frac{3}{4}|f-g|^2 + \frac{1}{4}|f+g|^2 = \frac{1}{2}|f|^2 + \frac{1}{2}|g|^2 + \frac{1}{2}|f-g|^2 > \frac{1}{2}|f|^2.$$

Hence $R > \frac{1}{2}R_d$.

APPENDIX II. RESTRICTION ON THE DOMAIN OF INTEGRATION IN EVALUATION OF INTEGRAL CROSS-SECTION FOR AUGER CAPTURE

The restriction on the final states of the recoil electron is, in the notation of the text,

$$k'^2 + (1/9)K_{e.m.}^2 + \frac{2}{3}k'K_{e.m.} \cos\gamma > K_F^2, \quad (i)$$

¹¹ N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Clarendon Press, Oxford, 1950), p. 102.

where

$$\cos\gamma = \mathbf{k}' \cdot \mathbf{K}_{e.m.} / k'K_{e.m.}$$

Now $\mathbf{K}_{e.m.} = \mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_3$, where $\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}_3$ are the momenta of the three particles prior to impact; for a thermalized positron $p_3 \cong 0$. If we allow \mathbf{p}_1 and \mathbf{p}_2 to go from 0 to K_F and be oriented independently in space, then $K_{e.m.}^2 = (6/5)K_F^2$. Since, from Eq. (4), $k'^2 a^2 = \frac{4}{3} + \frac{1}{3}K_F^2 a^2 + \frac{1}{5}K_F^2 a^2$, we see on using the rms values of $K_{e.m.}$ and k' that the above condition is satisfied for all γ if the Fermi energy < 3.43 ev. For a higher Fermi energy, the momentum of the recoil electron lies in a cone of semivertical angle defined by Eq. (i). Since the differential capture cross section has no sharp maxima in the excluded region, the error involved in ignoring the above condition is approximately equal to the percentage solid angle excluded. This amounts to no more than 27% even for a high Fermi energy of 10 ev.

Effect of Impurities of Angular Correlation of Positron Annihilation Radiation*†

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Angular distribution measurements on two-quantum annihilation radiation from positrons stopping in liquid targets have been made as a function of concentration of certain impurities in the target materials. The impurities tested were Mn^{++} and Co^{++} ions (dissolved from their chloride salts) and NO_2^- and NO_3^- ions (dissolved from their sodium salts) in water, and chloroform and the free radical diphenyl-picryl-hydrazyl in benzene. The paramagnetic ions are found to produce a strong enhancement of the narrow-distribution component, ascribed to exchange conversion between triplet and singlet positronium. Conversion cross sections of a few times 10^{-19} cm² are obtained assuming a positronium velocity about 5 times thermal velocity at conversion. These are in fair agreement with recent determinations made from lifetime studies. The nitrate and nitrite ions may cause a further broadening of the broad component, which appears to be associated with the chemical binding of positrons to the ions. It is also found that positrons are chemically bound to the chloroform molecule. Some evidence is presented to show that the free radical (diphenyl-picryl-hydrazyl) may not, as previously supposed, act to convert triplet to singlet positronium, but may in fact give rise to chemical binding of positronium to the free radical.

1. INTRODUCTION

IN the past several years, considerable interest has developed in the phenomena involved in positron annihilations in matter.¹ Among other objectives, the hope has been raised that positron annihilation studies may form a useful tool with which to investigate problems in solid-state physics. Before this objective can be realized, a thorough understanding is needed of the various factors which can influence positron annihi-

lations in solids. In a previous paper² we have investigated the so-called "temperature" effect on angular distribution measurements. The present paper is devoted to a study of the effect of certain types of impurities.

Positrons entering many insulating materials, both liquid and solid, have a rather high probability of capturing an electron to form a positronium atom, either in its triplet (³S) or singlet (¹S) ground state, before annihilation finally occurs. The formation of positronium may be inferred by the appearance of a long-lifetime component (from ³S decay) in the lifetime spectrum of the annihilation radiation, and the probability of formation may be determined from the relative intensities of the short- and long-lifetime components.¹ Since the triplet state has three substates, from a purely

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† Part of the data given here was reported on at the 1958 Washington Meeting of the American Physical Society [R. L. deZafra, *Bull. Am. Phys. Soc. Ser. II*, **3**, 229 (1958)].

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¹ For review of experimental and theoretical work see, for instance, S. Berko and F. L. Hereford, *Revs. Modern Phys.* **28**, 299 (1956) and R. A. Ferrell, *Revs. Modern Phys.* **28**, 308 (1956).

² R. L. deZafra and W. T. Joyner, *Phys. Rev.* **112**, 19 (1958).

statistical basis positronium formation should result in a ratio of 3 to 1 between triplet and singlet populations in the ground state. Thus, multiplying the measured long (τ_2) lifetime intensity by $\frac{4}{3}$ should give one the fraction of entering positrons which form positronium. Experiments show that this may reach 70% in some favorable cases.³

Positronium formation may also be inferred from angular distribution measurements. If one uses the usual linear defining slits in the distribution measuring apparatus, one measures the component of the momentum of the annihilating pair in the center-of-mass system in a direction perpendicular to the long axis of the slits. Since, in general, positrons will be thermalized before annihilation, the angular distribution of positrons annihilating directly with atomic electrons will essentially be determined by the electron momenta alone. On the other hand, a much narrower distribution can arise from self-annihilation of *singlet* positronium, since only the small linear momentum of the positronium atom will be involved. (Annihilations from the triplet state cannot contribute to a narrow component, since they will involve either destruction by pick-off or 3γ emission. The latter has a very small probability of being detected by a two-slit measuring apparatus in which the slits are kept nearly collinear with the target.)

Thus, if positronium is formed, a narrow component should appear in the angular distribution, which arises from self-annihilation of 1S positronium. (Pick-off annihilation from the 1S state is unlikely because of its short lifetime.) The validity of this expectation has been shown in several experiments.⁴ In principle, one could determine the amount of positronium formed by measuring the relative intensity of the narrow component. In practice, this is very difficult however, due to the lack of a distinct separation between the narrow- and broad-component regions (except for the rather singular case of ice²). One can easily measure *changes* in the relative amount of narrow component under different conditions. It is possible that the amount of narrow component may be influenced in two distinct ways; either by alteration of the population ratio between the 3S and 1S states by a mechanism which produces conversion between the two states, or by an alteration of the over-all fraction of positrons which form positronium. (A third method, which will not be considered here, would involve prealignment of the atomic electrons before positronium formation occurs.)

2. APPARATUS

The apparatus for measuring angular distributions is similar to that used by several other investigators⁴ and has been previously described in some detail.² The

³ R. E. Green and R. E. Bell, Can. J. Phys. **35**, 398 (1957).

⁴ Page, Heinberg, Wallace, and Trout; Phys. Rev. **98**, 206 (1955); L. Page and M. Heinberg, Phys. Rev. **102**, 1545 (1956); S. D. Warshaw, Phys. Rev. **108**, 713 (1957).

width of the collimating slits was set at 1.14 milliradians as seen from the target for the measurements described here, giving a reasonable compromise between counting rate and resolution. The movable slit was so arranged that it always remained in alignment along a radius line to the target, preventing aberrations at "large" angles.

The liquid samples were held in a small tank measuring about $\frac{1}{2} \times 1 \times \frac{1}{2}$ inches, mounted on the end of a brass rod for support. The front side of the tank, facing the positron source, consisted of a nickel foil 0.00004 inch thick glued at the sides with a light coat of acrylic cement. The remaining sides of the tank were of 0.01-inch copper and were tapered to a sharp edge towards the front face. The foil passed greater than 99% of the positrons incident on it, and as the source ($\frac{1}{4}$ inch in diameter) was placed only $\sim \frac{1}{4}$ inch from the target face, virtually no positrons could reach the relatively thick tank walls without first passing through sufficient liquid to be stopped. When used with water soluble samples, the interior of the tank, except for the foil surface, was coated lightly with Neoprene cement to prevent any chemical reaction between the tank and its contents. Access for filling was provided by a small offset "chimney" at the top. The positron source consisted of about 3 millicuries of highly purified Na^{22} sealed on the end of a $\frac{1}{4}$ -inch stainless steel rod.

None of the distribution curves shown below have been corrected for the effect of finite slit width. The correction is quite small for the roughly triangular distributions found here (except perhaps at the peak itself, where the error is on the order 3%), and further we shall mainly be interested in small changes occurring in the curves under varying conditions, rather than in the absolute shape of the curves themselves. Corrections for Compton, Thomson, etc. scattering of the emerging γ radiation are negligible. Usually 3 or 4 runs of 1000 counts per point were taken on each sample (fewer on certain samples). Points were averaged and plotted on translucent paper. The distribution was then folded about the line of greatest symmetry and a curve traced through the points for a best fit to both sides simultaneously.

3. EXPERIMENTAL RESULTS

A. Paramagnetic Ions in Aqueous Solution

(i) Co^{++} .—The results of various concentrations of CoCl_2 in water are shown in Fig. 1. A progressive narrowing is apparent. The curves have been normalized to equal areas and each represents the average of two runs of 1000 counts per point. For greater clarity, a distribution taken for 4-molar CoCl_2 is not shown. It is very similar to the 2-molar shape. Figure 1(A) shows the peak height as a function of molarity. The curve in Fig. 1(A) is drawn as a best fit to the experimental points, and is given here simply to indicate the saturable nature of the effect. A meaningful relation between Co^{++}

concentration and distribution shape will be derived in the discussion below. The location of the peak heights rests on one or two points only and therefore is less certain than the location of the curves as a whole, although the statistical accuracy is still good, i.e., about $\pm 2.3\%$. (The possible error introduced through the normalization process is $\leq 0.5\%$.) All samples were prepared with distilled water and were held in the neoprene-lined tank described above.

(ii) Mn^{++} .—The results of various concentrations of $MnCl_2$ in distilled water are quite similar to those for $CoCl_2$ illustrated for Fig. 1, and will not be shown separately. The peak height for the area-normalized pure water curve falls somewhat lower, at about $77 \pm 4\%$ of the 2-molar measurements. The same general comments apply to the Mn^{++} measurements as were made above for Co^{++} .

As a check on the influence of the Cl^- ions on the distributions, a solution of 4-molar NaCl was prepared and tested. The effect on the angular distribution is shown in Fig. 2. The tendency is very slightly towards a *broader* distribution, and this can probably be ascribed to direct and pick-off annihilations occurring with the outer electrons of the Na^+ and Cl^- ions. It is evident that the effects illustrated by Fig. 1 must be due to the Co^{++} and Mn^{++} ions and not to Cl^- .

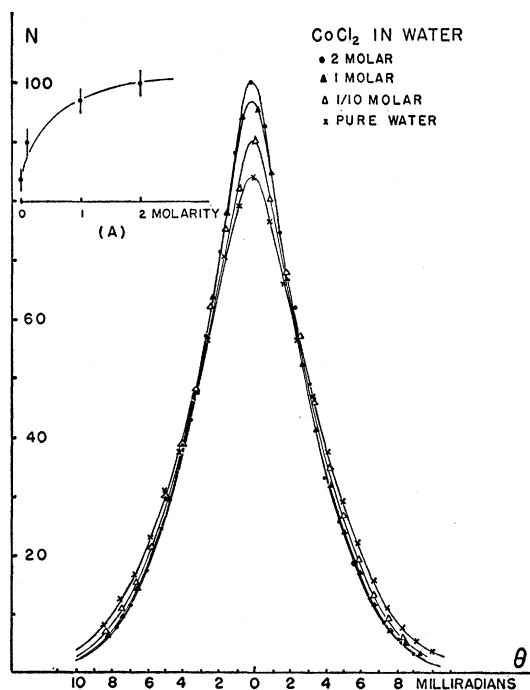


FIG. 1. Angular distribution in water as a function of $CoCl_2$ concentration. Average 2000 counts per point. Peak height vs molarity is shown in (A) where the curve is arbitrarily drawn. A 4-molar distribution very similar to the 2-molar distribution is omitted here for greater clarity. The curves are normalized to equal areas.

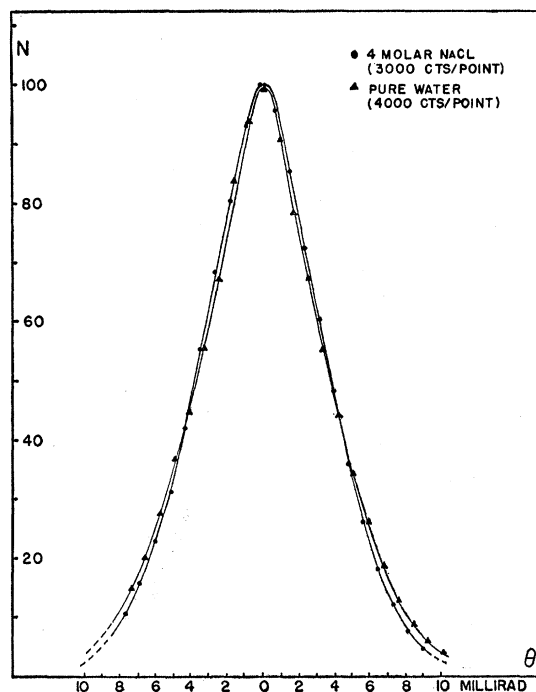


FIG. 2. Angular distribution of pure water vs a 4-molar solution of NaCl. The curves are normalized to equal areas.

B. Nitrate and Nitrite Ions in Aqueous Solution

Following the work of Green and Bell,³ the effects of $NaNO_2$ and $NaNO_3$ in distilled water were tested. Figure 3 shows the effect of various concentrations of $NaNO_3$. The effects of $NaNO_2$ were essentially identical and consequently are not shown separately here. A considerable decrease is apparent in amount of narrow component present as the concentration increases, in contrast to the effect of the paramagnetic ions. The peak height of the area normalized curves as a function of NO_3^- concentration is shown in Fig. 3(A). The saturation at higher concentrations is again evident, as it was with the paramagnetic ions. From Fig. 2, the Na^+ ions must have only a slight effect on the distribution.

C. Diphenyl-Picryl-Hydrazyl in Benzene

The stable free radical diphenyl-picryl-hydrazyl (D.P.H.) was found by Pond⁵ to decrease the 3γ decay in benzene, and the effect on lifetimes was later investigated by Berko and Zuchelli,⁶ who found a progressive quenching of the τ_2 lifetime with increasing D.P.H. concentration. It was assumed that this was an obvious case of triplet-singlet conversion by electron exchange with the unpaired electron of the free radical. An investigation of the effect on angular correlation was undertaken here with unexpected results, which suggest

⁵ T. A. Pond, Phys. Rev. **93**, 478 (1954).

⁶ S. Berko and A. J. Zuchelli, Phys. Rev. **102**, 724 (1956).

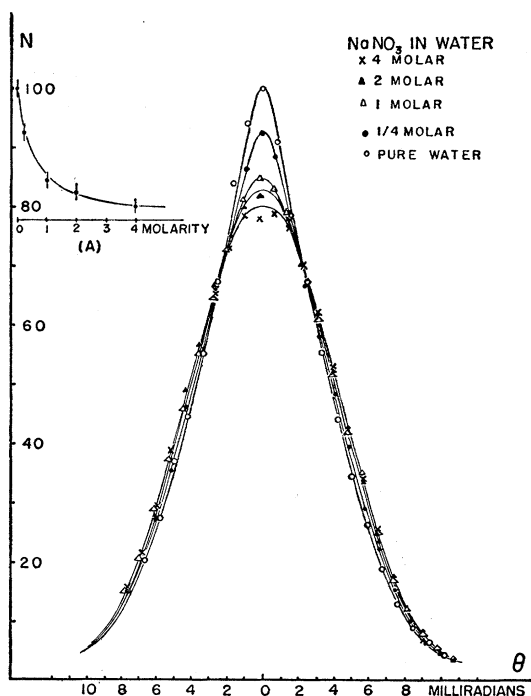


FIG. 3. Angular distribution in water as a function of NaNO_2 concentration. Average 4000 counts per point. The curves are normalized to equal areas. Peak height vs molarity is shown in (A), where the curve through the points is arbitrary.

a more complicated process than the above experiments indicate.

A quantity of D.P.H. was first prepared following the method of Goldschmidt and Renn⁷ and its effect tested in benzene. Rather than the expected narrowing, a considerable broadening was produced.⁸ A check on the effect of possible contaminants was then made, and it was found that indeed chloroform, which could have been occluded in small quantities when the D.P.H. was crystallized from the carrier solution during preparation, would produce measurable broadening in concentrations of as little as 0.5% by weight. (More will be said on this later.) In order to completely rule out contamination by chloroform, a new batch of D.P.H. was then prepared using benzene as the carrier solution throughout.

The most obvious contaminant was also tested, i.e., diphenyl-picryl-*hydrazine* which had not been converted to the free radical, or which had been converted back to the parent chemical again. The effect of a saturated

⁷ S. Goldschmidt and K. Renn, Chem. Ber. **55B**, 628 (1922), in particular p. 638. Only the rather trivial conversion of diphenyl-picryl-hydrazine to the hydrazyl free radical need be performed, thanks to the present commercial availability of the former.

⁸ Shortly afterwards the broadening effect of D.P.H. was independently discovered by S. Berko (private communication), who was also able to test the effect on lifetimes, finding that the identical sample again quenched the τ_2 lifetime as reported earlier (see reference 6).

solution of diphenyl-picryl-*hydrazine* compared to that of 5% by weight of D.P.H. in benzene is shown in Fig. 4. It is evident that although the hydrazine compound could produce most of the broadening (if indeed present in saturated quantity), the presence of the free radical seems to produce even more broadening, although the latter was present in less than saturated quantity. Unfortunately it seems difficult if not impossible to quantitatively measure the relative hydrazyl-hydrazine concentration due to the fragility of the free radical form. The free radical seems to be slightly more soluble, however, and several successive crystallizations and dissolutions, before the angular distributions (Fig. 5) were taken, may have increased the D.P.H. concentration. The solutions also were kept away from light as much as possible. D.P.H. was undoubtedly present in quantity, as shown by its distinctive exceedingly deep purple color and the presence of a strong microwave electron spin resonance signal in the sample.

As a consequence of the above mentioned uncertainties, the concentrations by weight of D.P.H. listed in Fig. 5, where the effect of increasing concentrations is illustrated, are almost certainly in excess of the true quantities. Various concentrations listed were obtained by dilution from the "5%" sample, so that the relative concentrations are correct, however.

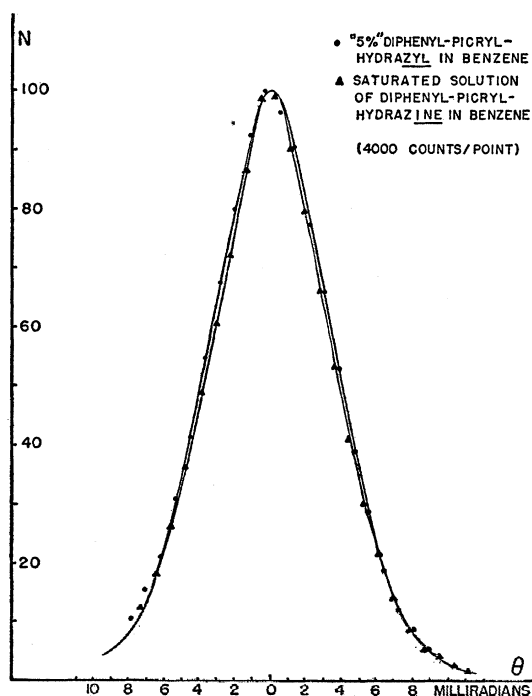


FIG. 4. Angular distribution of a saturated solution of diphenyl-picryl-hydrazine compared to a 5% solution by weight of diphenyl-picryl-hydrazyl (D.P.H.) in benzene. The true concentration of free radical in the sample is unknown. The curves are normalized to equal peak heights.

D. Chloroform in Benzene

The broadening effect of chloroform (CHCl_3) on benzene (C_6H_6) mentioned above is shown in Fig. 6. These curves (except for the pure benzene curve) are each derived from single runs of 1000 counts per point and consequently have less claim to accuracy than any of the other curves presented here. They were taken to give a qualitative indication of the effect of CHCl_3 on benzene and are presented here as such. For simplicity in preparation, the curves have been normalized to equal peak height, rather than equal areas. Their main interest lies in the fact that they show surprisingly small amounts of CHCl_3 are effective in producing broadening. A 0.5% concentration by weight represents a molecular ratio of about 1 to 100—thus the effect is quite disproportionate to the number of CHCl_3 molecules present.

4. DISCUSSION

A. The Paramagnetic Ions—Conversion of Triplet Positronium

The results of Sec. 3 show that the paramagnetic ions Mn^{++} and Co^{++} produce a strong enhancement of the narrow component, implying the presence of increased amounts of singlet positronium. Since these ions should not affect the positronium formation mecha-

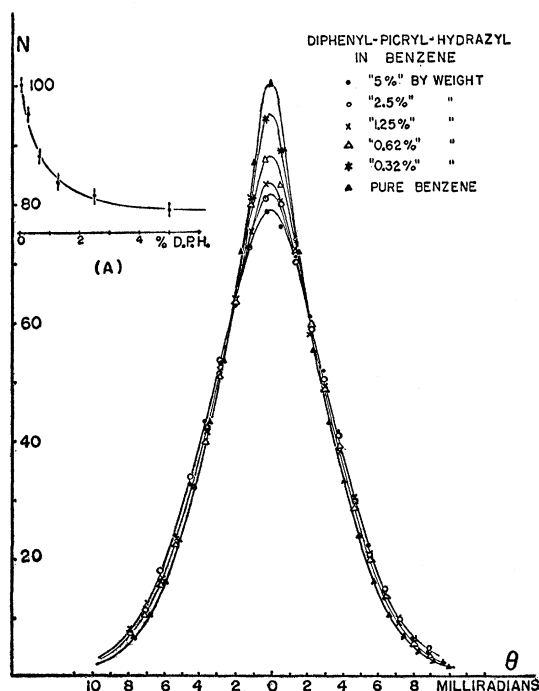


FIG. 5. Angular distribution in benzene as a function of concentration of diphenyl-picryl-hydrazyl. The true concentration of free radical is less than listed, but all solutions were made by proportionate dilution from the "5%" sample. The curves are normalized to equal areas. Peak rate vs molarity is shown in (A), where the curve is arbitrarily drawn. Average 4000 counts per point.

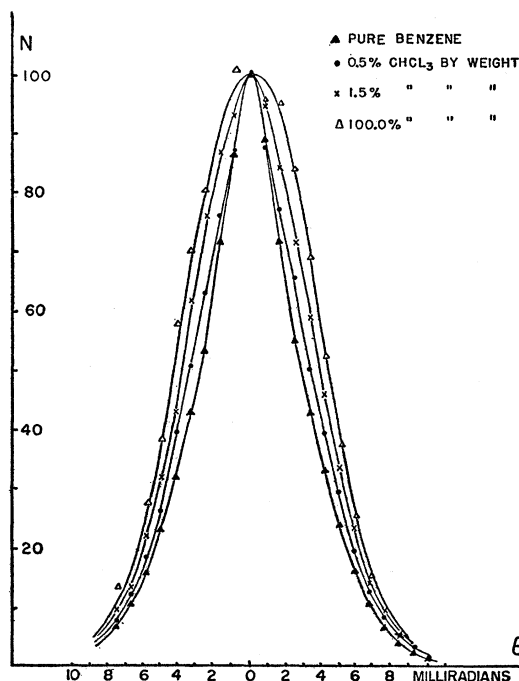


FIG. 6. Angular distribution from benzene as a function of concentration by weight of chloroform. The curves are normalized to equal peak height and were taken with 1000 counts per point.

nism, it must then be supposed that a change in the relative ^3S - ^1S population is occurring after formation, due to the presence of a conversion mechanism.

At first it might be supposed that the magnetic fields associated with the paramagnetic ions are responsible for the triplet-singlet conversion. A straightforward perturbation calculation show that this cannot be the case, however. One finds⁹ that the probability per collision that a magnetically induced triplet-singlet transition will occur is given by $(2\mu\mathcal{H}_{Av}t/\hbar)^2$, where \mathcal{H}_{Av} is the average magnetic field experienced by a positronium atom during the time t of its passage near a paramagnetic ion, and μ is the Bohr magneton. Now let the radius of the \mathcal{H}_{Av} field be r and the velocity of the positronium atom be v . Then $t \approx r/v$ and if there are N paramagnetic ions/cm³ the rate of collision is on the order of $r^2Nv \text{ sec}^{-1}$. Thus the rate of magnetic conversion, γ , is given by

$$\gamma \approx (2\mu\mathcal{H}_{Av}t/\hbar)^2 r^2 N v = (2\mu\mathcal{H}_{Av}t/\hbar)^2 N r^4 / v. \quad (4.1)$$

For the average field \mathcal{H}_{Av} we may take the approximation $\mathcal{H}_{Av} = M/4\pi r^3$, where M is the magnetic moment of the ion. We set $M = p\mu$, where μ is the Bohr magneton and p is a proportionality factor similar to the Landé g factor. Appropriate values of p for the iron group ions are listed by Kittel.¹⁰ For Mn^{++} one finds $p = 5.9$ and for Co^{++} , $p = 4.8$. For our purposes we may thus take p

⁹ M. Deutsch, in *Progress in Nuclear Physics* (Buttersworth-Springer, London, 1953), Vol. 3, p. 131.

¹⁰ C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1956), second edition, p. 219.

on the order of 5. Equation (4.1) then becomes

$$\gamma \simeq (5\mu^2/2\pi\hbar)^2 N/r^2v. \quad (4.2)$$

Taking $r \simeq 10^{-8}$ cm, $v \geq 6 \times 10^6$ cm/sec (\geq thermal velocity) and $N = 12 \times 10^{20}$ ions/cm³ for a 2-molar solution, one finally obtains $\gamma \lesssim 8.4 \times 10^4$ sec⁻¹. But this is two orders of magnitude less than the self-annihilation rate of 7×10^6 sec⁻¹ from triplet positronium: Therefore, the effect of magnetic conversion on the triplet-singlet populations may be considered negligible even in the strongest paramagnetic ion solutions obtainable. The remaining possibility is that of exchange conversion between the triplet and singlet states.

A quantitative experimental measure of the exchange conversion effect at different ion concentrations may be obtained from the angular distributions as follows. Distribution curves for various ion concentrations are area-normalized to the curve for pure water. Difference curves (having roughly a "w" shape) are then obtained by subtraction. The area of the central part of one of these w-shaped curves will represent the enhancement to the narrow component. [It is necessary to determine the lower boundary of this central region by extrapolation inward from the wings of the difference curve. The shape of this lower boundary, continuing into the wings, should have the shape of the broad component of the angular distribution (inverted), since this—i.e., the portion below the zero line of the difference curve—represents the attenuation of the broad component.] We shall denote the ratio of the area of the central portion of the difference curve to the area of the total distribution curve by α .

Assuming that the narrow and broad component shapes do not alter significantly in the presence of the paramagnetic or halide ions, the difference ratio, α , should then represent the fraction of the total number of entering positrons being affected by the paramagnetic ions. Further, making the reasonable assumption that the ions do not affect the positronium formation mechanism, but serve only to furnish a positronium conversion mechanism, α should then represent directly the increase in the number of positronium atoms annihilating from the singlet state, i.e., α should be proportional to the efficiency of the $^3S \leftrightarrow ^1S$ conversion mechanism. We shall now derive a conversion-dependent expression for this proportionality which may be tested against the experimental results.

Let P_S be the probability of finding a positronium atom, once formed, in the singlet state and P_T be the corresponding probability for finding it in the triplet state. If a conversion mechanism is present, giving a conversion rate γ between the singlet and any of the three triplet states, then the rate of change of P_T and P_S with time is given by

$$\begin{aligned} dP_S/dt &= -(3\gamma + \lambda_S + \lambda_P)P_S + \gamma P_T, \\ dP_T/dt &= 3\gamma P_S - (\gamma + \lambda_T + \lambda_P)P_T, \end{aligned} \quad (4.3)$$

where λ_S and λ_T are the singlet and triplet state self-annihilation rates, equal to 8×10^9 sec⁻¹ and 7.2×10^6 sec⁻¹, respectively,¹¹ and λ_P is the pick-off annihilation rate, which must be determined experimentally for any given material. Simultaneous solution of Eqs. (4.3) gives

$$\begin{aligned} P_S &= C_S \exp(-\lambda_1 t) + D_S \exp(-\lambda_2 t), \\ P_T &= C_T \exp(-\lambda_1 t) + D_T \exp(-\lambda_2 t), \end{aligned} \quad (4.4)$$

where

$$\begin{aligned} \lambda_{1,2} &= \delta \pm (\delta^2 - \beta^2)^{1/2}, \\ \delta &= 2\gamma + \frac{1}{2}(\lambda_S + \lambda_T) + \lambda_P, \\ \beta^2 &= (\lambda_T + \lambda_P)(3\gamma + \lambda_S + \lambda_T) + \gamma(\lambda_S + \lambda_P), \end{aligned} \quad (4.5)$$

and C_S , D_S , C_T , and D_T must be determined from the initial conditions at $t=0$. Equations (4.3), (4.4), and (4.5) are identical in form with those of Dixon and Trainor,¹² except that we have included here the effect of pick-off annihilations as well as conversion. Now the narrow component can presumably only arise from the self-decay of the singlet state. The probability P_N of a positronium atom decaying in this manner is just the probability of being in the singlet state multiplied by the singlet state annihilation rate λ_S and integrated over all time. That is,

$$P_N = \int_0^\infty \lambda_S P_S dt = \lambda_S (C_S/\lambda_1 + D_S/\lambda_2), \quad (4.6)$$

after substitution from Eq. (4.4). To determine the constants C_S and D_S , we assume the boundary conditions at $t=0$ to be $P_S = \frac{1}{4}$ and $P_T = \frac{3}{4}$ (a purely statistical distribution in the singlet and triplet states). From (4.3) and (4.4), we then obtain

$$\begin{aligned} C_S &= (\lambda_S + \lambda_P - \lambda_2)/4(\lambda_1 - \lambda_2), \\ D_S &= -(\lambda_S + \lambda_P - \lambda_1)/4(\lambda_1 - \lambda_2). \end{aligned} \quad (4.7)$$

Substituting (4.7) into (4.6) and simplifying, we obtain, finally, as the probability of decay into the narrow component

$$P_N = \lambda_S (4\gamma + \phi)/4(\gamma\theta + \Omega), \quad (4.8)$$

where

$$\begin{aligned} \phi &= \lambda_T + \lambda_P, \\ \theta &= 3\lambda_T + 4\lambda_P + \lambda_S, \\ \Omega &= (\lambda_T + \lambda_P)(\lambda_S + \lambda_P). \end{aligned}$$

Now let the actual *percentage area* of the narrow component be A_N . This represents the probability of forming positronium times the probability of decay into the narrow component. That is, $A_N = \frac{4}{3} I_2 P_N$, where I_2 is the experimentally measured intensity of the long-life (triplet) component.

The experimentally measured quantity α represents

¹¹ J. Pirenne, Arch. sci. phys. et nat. **29**, 293 (1947); R. A. Ferrell, thesis, Princeton University, 1951 (unpublished), p. 226; and J. M. Radcliffe, Phil. Mag. **42**, 1336 (1951).

¹² W. R. Dixon and L. E. H. Trainor, Phys. Rev. **97**, 733 (1955).

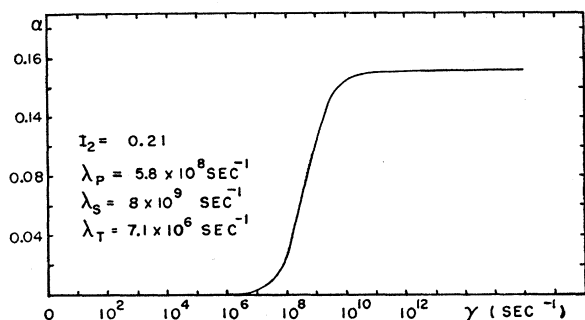


FIG. 7. Plot of percentage increase in narrow-component area, α , vs conversion rate γ , from Eq. (4.10), using experimental values appropriate for water for the quantities I_2 and λ_P .

the change in A_N . For our purposes, we shall take α equal to $[A_N$ (at molarity M) $- A_N$ (pure water)]. But A_N for pure water, i.e., for $\gamma=0$, is from Eqs. (4.8)

$$A_{N0} = \frac{4}{3} I_2 P_N = \frac{1}{3} I_2 [\lambda_S / (\lambda_S + \lambda_P)], \quad (4.9)$$

which is of course as expected. Finally, then, we have

$$\alpha = \Delta A_N = A_N - A_{N0} = \frac{1}{3} I_2 [4P_N - \lambda_S / (\lambda_S + \lambda_P)] \quad (4.10)$$

as the expression for the percentage change in the narrow component area. One sees that $d\alpha/d\gamma \rightarrow 0$ as γ approaches both zero and infinity.¹³ In Fig. 7, α vs γ has been plotted using Eq. (4.10) and the experimental values $I_2=0.21$ and $\lambda_P \approx 1/\tau_2 = 5.8 \times 10^8 \text{ sec}^{-1}$.¹⁴ The maximum value reached by α is about 0.15 although this is fairly sensitive to the value used for I_2 (e.g., $I_2=0.23$ gives $\alpha_{\text{max}} \approx 0.17$).

In Fig. 8 the experimental values for α are plotted as a function of molarity for Co^{++} . The curves through the points represent the theoretical behavior of α vs molarity,¹⁵ as determined with the aid of Fig. 7 and the relation $\gamma = N\bar{\sigma}\bar{v}$, where N = the number of ions/cm³ = molarity $\times 6.03 \times 10^{-20} \text{ cm}^{-3}$, $\bar{\sigma}$ = the average cross section (to be determined) for a conversion interaction, and \bar{v} = the average positronium velocity when conversion takes place. Similarly treating the data for Mn^{++} and using $\bar{v} = 5$ times thermal velocity, $\approx 3 \times 10^7 \text{ cm/sec}$,¹⁶ the best fits in both cases are obtained with $\bar{\sigma}$ on the order of a few times 10^{-19} cm^2 . The limiting curves in Fig. 8 are obtained by using $\bar{\sigma} = 8 \times 10^{-19}$ and $8 \times 10^{-20} \text{ cm}^2$, and the limiting curves for Mn^{++} are found to lie at about $\bar{\sigma} = 8 \times 10^{-18}$ and $2 \times 10^{-19} \text{ cm}^2$ indicating that the cross sections for Co^{++} and Mn^{++} clearly lie between these values, with the best fit for Co^{++} obtained with a somewhat smaller value for $\bar{\sigma}$

¹³ The latter is a consequence of the experimental numerical facts that $I_2 \approx 0.3$ and $\lambda_P \approx 6 \times 10^8 \text{ sec}^{-1}$.

¹⁴ R. E. Bell and R. L. Graham, Phys. Rev. **90**, 644 (1953). (Some results in this reference are superseded by those of reference 3.)

¹⁵ The asymptotic approach to the abscissa at low molarity is lost due to the scale factor.

¹⁶ We may reasonably assume this as an approximate lower value for \bar{v} on the basis of the narrow-component half-width of about 1.8 milliradians found in pure water. See further reference 2.

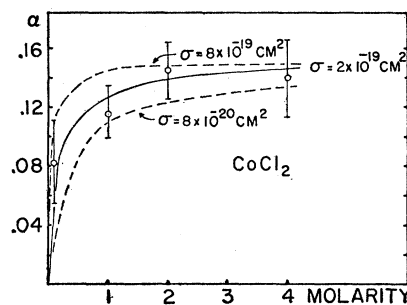


FIG. 8. α (experimental) vs Co^{++} concentration in water. The curves show the theoretical behavior for various cross sections.

than that yielded by Mn^{++} (about $2 \times 10^{-19} \text{ cm}^2$ vs $8 \times 10^{-19} \text{ cm}^2$). The validity of these cross sections depends to a great extent on what value one ought to use for \bar{v} however. If conversion should take place at somewhat higher velocities than used here, $\bar{\sigma}$ would become proportionately smaller and vice versa. It is felt that taking \bar{v} much less than that used above is not experimentally justified on the basis of the narrow-component distribution width in water, however.¹⁷

The experimental and theoretical agreement for α_{max} would seem to justify the assumption that the broad and narrow components retain their basic shapes here but only change their relative intensities. If this were not so, the experimental values for α would rise above the theoretical α_{max} at higher ion concentrations as the distribution shape became more and more distorted. (I.e., changes in distribution shape will produce non-zero values of α even though no change in the relative intensity of the broad and narrow components occurs.) This also agrees with the evidence in Fig. 2, which shows that even a 4-molar concentration of "inert" impurities has only a small effect on the distribution shapes.

In any case, $\bar{\sigma}$ would seem to be at least two or three orders of magnitude less than the geometrical cross section for an ion. This is not surprising, however, when it is remembered that the positive ions are heavily shielded by the water molecules of hydration surrounding them.¹⁸ It is perhaps remarkable that the conversion mechanism operates at all.

It would be somewhat more convenient and experimentally more accurate to derive the conversion cross section by analysis of the τ_1 and τ_2 lifetime as a function of impurity concentration. A preliminary lifetime study for Mn^{++} in water was made by Berko,¹⁹ with a tentative result of $\bar{\sigma} = 5 \times 10^{-20} \text{ cm}^2$, but this work was discontinued before full measurements were completed

¹⁷ Here we may be wrong if a part of the narrow-component width determined from the difference curves is due to a serious change in the shape of the distribution, rather than a change in intensities.

¹⁸ The hydration coordination number is probably 4; see J. D. Bernal and R. H. Fowler, J. Phys. Chem. **1**, 515 (1933).

¹⁹ S. Berko and F. L. Hereford, reference 1, in particular, p. 303.

(private communication). Recently a thorough study of the effect of various paramagnetic ions in the iron and rare earth groups in aqueous solution has been reported by Bell.²⁰ Doubly and triply ionized atoms of the iron group all were found to give cross sections of a few times 10^{-19} cm² in water. For Mn⁺⁺ and Co⁺⁺, the reported cross sections are, respectively, 2.5×10^{-19} cm² and 5.3×10^{-19} cm². In determining these cross sections, however, thermal velocity was assumed as the mean positronium velocity, rather than 5 times this, as we have used above. Although we believe that one should in fact take \bar{v} to be *larger* than thermal velocity, in any event the cross sections derived by the two methods disagree by roughly a factor of 10 when equal velocities are used.

The approximations necessarily made in deriving cross sections from the angular distribution measurements render the method more open to error than the more straightforward lifetime derivation, e.g., an error in assuming that the distribution shapes remain relatively constant, despite the arguments given above for believing this, could account for the discrepancy. The cross sections determined by Bell may thus be more nearly correct, but we believe that in any event they should be reduced, perhaps by as much as a factor of 5, to adjust for the fact that the mean positronium velocity at the time of annihilation seems to be significantly greater than thermal velocity in nonmetals.^{2,21}

B. Other Impurities: The Chemical Binding of Positrons and Positronium

(i) Nitrate and Nitrite Ions

Good evidence for the chemical binding of positrons to nitrate and nitrite ions has been obtained by Green and Bell³ on the basis of lifetime studies. They have found that NO₂⁻ and NO₃⁻ ions cause a decrease in the intensity of the τ_2 lifetime, but no shortening of the lifetime itself. From this they conclude that positrons are being removed by chemical binding from the reservoir of those which would normally form positronium.

From Fig. 4 the addition of NO₃⁻ ions (or similarly NO₂⁻ ions) results in progressive broadening of the distribution. The over-all behavior merely corroborates the findings of Green and Bell, which indicated a decrease in the amount of positronium formed. The behavior of the *broad component* in these distributions is of particular interest, however. This behavior, as determined below, is shown in Fig. 9.

From Green and Bell's measurements³ one finds that a 4-molar NaNO₃ concentration the τ_2 intensity, I_2 , is only $\approx 2.6\%$ in water. The narrow component (singlet positronium) intensity is then $\frac{1}{3}$ of this or $\approx 0.87\%$.

²⁰ R. E. Bell, invited talk at the Washington Meeting of the American Physical Society, May, 1958 [Bull. Am. Phys. Soc. Ser. II, 2, 182 (1958)]. *Note added in proof.*—This data has since been published [R. E. Bell, Can. J. Phys. 36, 1684 (1958)].

²¹ P. R. Wallace, Phys. Rev. 100, 738 (1955).

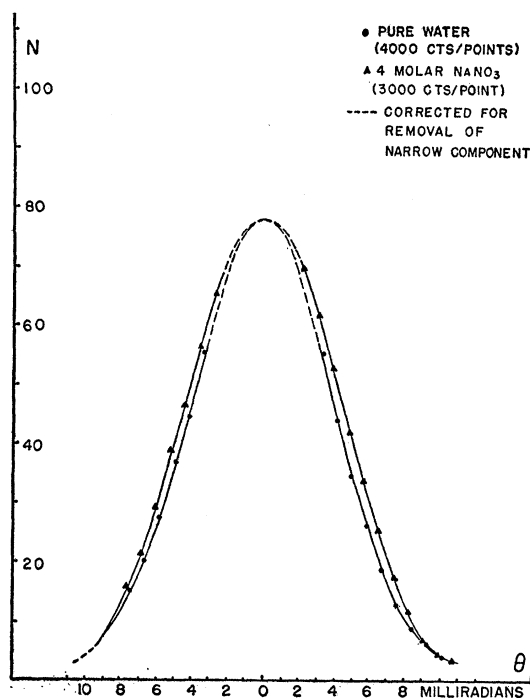


Fig. 9. Comparison of approximate broad components for pure water and 4-molar NaNO₃.

Thus shaving a mere 0.87% from the area of a 4-molar distribution near its peak should result in a very good approximation to the broad component in this concentration of NaNO₃. The broad-component distribution from pure water is more difficult to obtain. From the total pure water distribution area, we have subtracted $\frac{1}{3}$ of the I_2 intensity (i.e., $\approx 7\%$) over a region around the peak estimated from the difference curves to be that occupied by the narrow component. One might also take the broad component from ice,² which is easily separable from the narrow component. There is no assurance that this should be the same as the broad component in the liquid form, but this does not seem too unreasonable, since it comes from direct and pick-off annihilations which should be little affected momentum-wise by phase changes. One in fact finds that both methods give very nearly the same result. Thus we may assume that we have a fairly good approximation to the broad component in pure water. This, along with the broad component in 4-molar NaNO₃ is shown in Fig. 9. The two curves clearly cannot be made to coincide even allowing reasonable errors in the estimated peak shapes, the NaNO₃ distribution being significantly wider. The results from 4-molar NaCl, Fig. 2, show that at most a small amount of this comes from the Na⁺ ions.

Additional evidence that the broad component is broadened in the presence of NO₃⁻ ions is furnished by the difference-curve areas. For a 2-molar solution compared to pure water, one obtains a value of α equal to

0.107 ± 0.015 and for a 4-molar distribution, a value of $\alpha = 0.123 \pm 0.015$. Now if the difference ratio α were caused only by a loss of narrow component, its maximum value could be ~ 0.07 (from $\frac{1}{3}$ the τ_2 intensity of 21% found³ in pure water). It is thus apparent that the broad component must be getting broader to account for the larger values of α . It may be assumed that this broadening is in large part caused by the binding of positrons to the NO_3^- ions.²²

Because of this definite change in shape of the broad component which in practice is difficult to correct for, no quantitative analysis can be made of the angular distribution measurements such as was done for the paramagnetic ions. The peak height as a function of concentration, Fig. 3(A), can be used as a qualitative guide, however, as it is seen to behave in much the same manner as Green and Bell's I_2 vs molarity curve, reaching saturation at about 3-molar concentration.

(ii) D.P.H. in Benzene

In the case of D.P.H. the experimental evidence presented in the previous section indicates that little or no $^3S \leftrightarrow ^1S$ conversion is taking place. Although much of the broadening may be due to diphenyl-picrylhydrazine, the free-radical form of the molecule seems to induce still more broadening, with no indication of the formation of a superimposed narrow peak. In accordance with the findings for NO_2^- and NO_3^- this suggests that some chemical binding may be present. The situation is not the same as that for the NO_3^- ions however, since Berko and Zuchelli⁶ have found that while the lifetime changes, the τ_2 intensity stays constant within an experimental limit of error of about 10%. Ferrell²³ has pointed out that this apparently conflicting evidence may be explained by assuming capture of positronium rather than positrons, and that the lifetime data of Berko and Zuchelli may be fitted as well to a straight line (indicating a positronium binding mechanism) as to the curve representing the effect of a conversion mechanism. The failure of free positrons to be bound might, for instance, be explained by the necessity for some type of electron exchange binding in this case.

²² We should note here that it is not evident, *a priori*, that formation of a positron compound should lead to a broader broad component. Thus it might be argued that positrons annihilating by pick-off from positronium might involve momenta as large if not larger than those involved in the annihilation of chemically bound positrons. The present evidence seems to indicate the opposite conclusion, however.

²³ R. A. Ferrell, Phys. Rev. **110**, 1355 (1958).

If a chemical method were available for separating the free radical from its parent hydrazine, so that one would be sure of no contamination from the latter, the question of which process is taking place could probably be settled satisfactorily by angular distribution measurements. A remeasurement of the lifetime behavior of D.P.H. in benzene with specific attention to the τ_2 intensity would seem desirable also, since it is difficult to see why exchange conversion from 3S to 1S positronium by the free electron should not be dominant over binding if positronium is indeed being formed at a constant rate as the D.P.H. concentration increases.

(iii) Chloroform in Benzene

The effect of relatively few chloroform (CHCl_3) molecules in drastically reducing the narrow component in benzene strongly suggests the prevention of positronium formation by the chemical binding of positrons (although positronium binding would also be a possibility). Bell has recently verified that the chemical binding of positrons indeed is occurring here,²⁴ since lifetime measurements show that the τ_2 component decreases in intensity but not in lifetime upon the addition of chloroform to benzene. It is interesting to note that Deutsch²⁵ has pointed out the possibility of a positron affinity with the similar Freon (CCl_2F_2) molecule to explain certain peculiarities in the τ_2 lifetime behavior of positrons annihilating in Freon at low pressures. Sufficient data is not available on the τ_2 intensities at various impurity concentrations of chloroform to allow one to determine the shape of the broad component accurately, as could be done in the case of water and NO_3^- . Thus, unfortunately one cannot tell yet whether the broad component also becomes broader in this case of binding.

It would seem that further investigations into the phenomena of chemical binding, particularly over the large range of subtle variations available in organic compounds, might be of considerable interest in physical chemistry.

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²⁴ R. E. Bell (private communication). We are indebted to Dr. Bell for checking the behavior of chloroform in benzene from the lifetime point of view.

²⁵ M. Deutsch, Phys. Rev. **83**, 866 (1951).