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Charge Transfer for Protons in H_2†

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A precise measurement of the electron capture cross section for protons in H_2 is reported for proton energies between 2.4 and 60 kev. The method involves collection of the residual ions by a sequence of identical condensers. The same scattering chamber is also used for the measurement of σ_{01} and $(\sigma_{01}+\sigma_{10})$. The recent measurements of Stier and Barnett are in close agreement with our results.

INTRODUCTION

In this paper is reported a measurement of the electron capture cross section for protons in molecular hydrogen for proton energies between 2.4 and 60 kev. The method used is precise and the cross sections obtained show much less scatter than any previously reported. Except on a narrow range of energy near 10 kev near the peak of the cross section, they agree closely with those recently measured by Stier and Barnett.[1] A feature of the measuring apparatus was that it could also be used without modification for measurement of other charge transfer cross sections, such as the electron loss cross section and the sum of the capture and loss cross sections by entirely different techniques. Thus two independent measurements of σ_{10}, the capture cross section, by vastly different methods employing the same apparatus can be made.

When a monoenergetic beam of ions and neutral particles of a single species passes through a gas whose density is n, the neutral beam current as a function of distance is

$$I_0(x)=I_0(\infty)+[I_0(0)-I_0(\infty)]\times\exp[-n(\sigma_{10}+\sigma_{01})x], \qquad (1)$$

provided single electron capture and loss are the only important charge transfer processes. In the notation σ_{if}, i denotes the initial charge state and f the final charge state of a beam particle. The equilibrium neutral current $I_0(\infty)$ is given by

$$I_0(\infty)=I\sigma_{10}/(\sigma_{01}+\sigma_{10}), \qquad (2)$$

where I is the total particle current.

Measurements of charge transfer cross sections usually are based on the use of the appropriate high-pressure or low-pressure approximation to Eq. (1). In equilibrium methods the pressure is so high that the equilibrium mixture of ions and neutrals is achieved. The various charge components of the beam are separated and measured and a cross section ratio such as that in Eq. (2) deduced.[1–5] Individual cross sections can then be given by measurement of the composition of the beam before equilibrium is reached for varying path lengths or pressures.[6–14] Or they may be obtained if the charged component is removed as it is formed by means of electric or magnetic fields and an absorption experiment performed on the residual neutral component.[1–4,15] Alternatively a chosen charge component of the beam may be deflected by a field into a well-defined path which particles thrown into other charge states cannot follow, and the charge transfer cross section for the selected component measured in an attenuation experiment.[1,2,4]

At low gas pressures a more direct method of measuring σ_{10} or $\sigma_{0,-1}$ involves the collection of the slow ions left behind after charge transfer along the beam path.[16–26] This method has been modified and adapted

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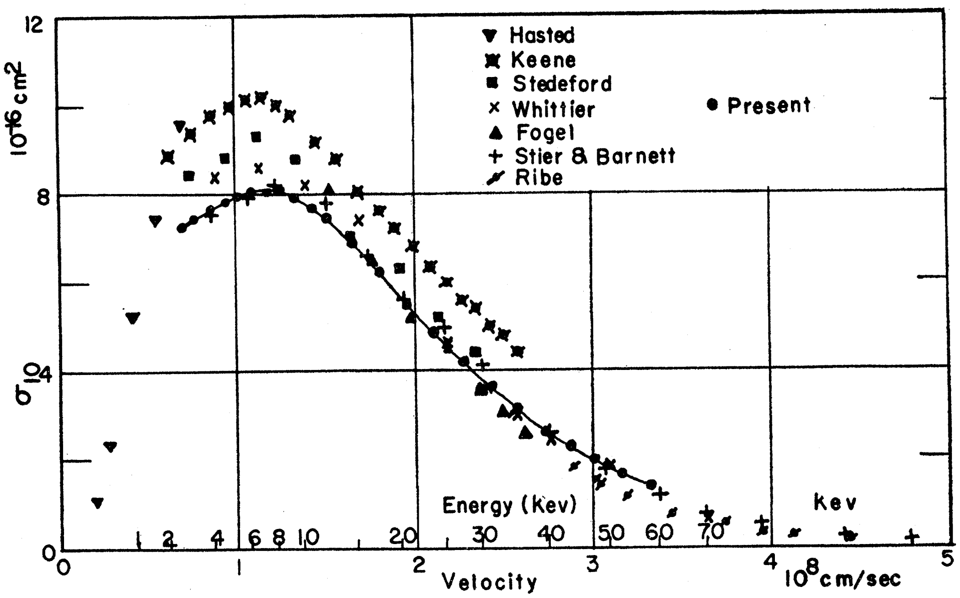

FIG. 1. Measurements of electron capture cross sections σ_{10} for protons in H_2. All results are shown in units of cross section per molecule. In some cases we have applied to the published results a correction factor of 300/273.[19,20,22]

recently to the measurement of electron capture cross sections in cases for which there are several important charge transfer processes.[27]

For electron capture by protons in H_2, measurements based on these methods have led to the results plotted in Fig. 1. Agreement is very rough and there is considerable scatter. The theoretical situation has been even less satisfactory, for until very recently there has been no calculation available for the cross section actually measured. Instead comparisons have been made with twice the cross section for capture by protons from atomic hydrogen. Recent calculations by Tuan and Gerjuoy[28] indicate that molecular effects are large enough to make agreement between observed cross sections for molecular hydrogen and those computed for atomic hydrogen largely fortuitous.

We have undertaken an experiment designed to reduce uncertainties in the measurement of these cross sections, particularly with regard to the effective volume of the scattering region, in the hope of making a measurement of precision. The experiment was designed in such a way that measurements of both types, equilibrium and direct, could be carried out in the same apparatus under conditions as nearly identical as possible. In what follows, we present a general discussion of our procedure together with the results and save the finer experimental details for publication elsewhere.

MEASUREMENT OF σ_{10}

The principal feature of the experiment was the use of a linear array of nine identical condensers in the scattering chamber to collect the slow ions in the one type of measurement, or to remove the charge component in the beam in the other. A sketch of the apparatus is presented in Fig. 2. Protons from an rf ion source, accelerated in a simple two-electrode lens system, were deflected through 90° and focused on the entrance slit of the scattering chamber by a magnetic field produced between pole tips of a special design. The energy of the protons was determined by the magnetic field. After passing through a fore chamber which could be pressurized for the production of a large neutral component, and between two electrodes which could be used to remove the charged component, and after collimation, the beam proceeded into the main scattering chamber past the series of nine condensers and into a Faraday cup.

In the measurement of σ_{10} by the direct method, no gas was admitted to the beam preparation chamber so that the beams contained protons only. Low voltage was applied to all of the nine condensers and an electrometer connected as in Fig. 3. Any number of condensers could be switched to the electrometer circuit which then measured, aside from leakage current, the rate of production of slow ions by charge transfer in the region from which these condensers collected current. The circuit arrangement obviously compensates for ion pair currents and secondary electron currents. Since the collecting voltages and the dimensions of the condensers were carefully adjusted to uniformity, the addition of each condenser to the measuring circuit adds a constant volume of interaction between the beam and the gas in the chamber.

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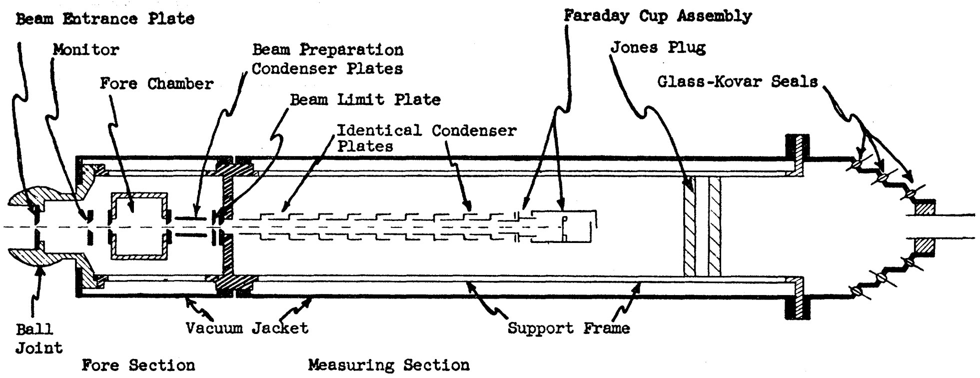

FIG. 2. Horizontal cross sectional sketch of collision chamber.

From Eqs. (1) and (2) it follows that at low gas pressure the positive-ion beam current as a function of distance from the place where the neutral current is zero is

$$I_+(x)\cong I(1-\sigma_{10}nx), \tag{3}$$

where $I=I_+(0)$. If the distance x is divided into m equal segments of length x_c plus an end correction x_0, Eq. (3) may be written

$$I_+(m)\cong I_+(0)[1-(\sigma_{10}n+\sigma_{10}'n')(mx_c+x_0)], \tag{4}$$

where $(\sigma_{10}'n')^{-1}$ is the mean free path in whatever impurities are present. When these m segments represent m successive condensers collecting residual charge transfer ions, the current to these condensers is the decrement in Eq. (4) over the distance mx_c+x_0, or

$$J(m)\cong I_+(0)(\sigma_{10}n+\sigma_{10}'n')(mx_c+x_0). \tag{5}$$

From the slope of $J(m)/I_+(0)$ as a function of mx_c combined with a pressure and temperature measurement, σ_{10} may be derived.[29] Or, preferably, $(\sigma_{10}n+\sigma_{10}'n')$ obtained as a function of n may be plotted against n and σ_{10} read from the slope.

To avoid the need to make repeatedly accurate pressure measurements, the cross sections relative to that at a standard energy (20.29 kev) were measured.

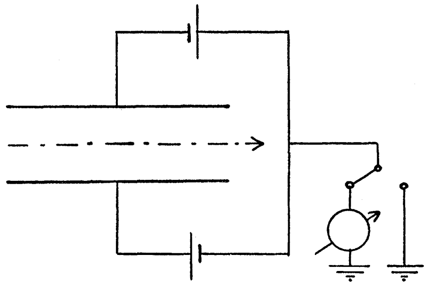

FIG. 3. Electrometer circuit for slow-ion collection.

The procedure used at first was to permit hydrogen at relatively high pressure to come to equilibrium in the scattering chamber. Then, while the pressure remained fixed, the slow ion current, $J(m)$, was measured as successive condensers were switched into the measuring circuit and again as they were switched out of it. $I_+(0)$ was obtained by reading the current to all condensers, the Faraday cup and its associated guard rings at the beginning and end of each run. The proton beam was deflected away from the chamber and the leakage current read for each switch position. This procedure was repeated, the pressure still remaining constant, for several successively higher proton energies including always the standard. For each energy $J(m)/I_+(0)$ after correction for leakage current was plotted against m (Fig. 4). $(\sigma_{10}n+\sigma_{10}'n')$ was thus obtained for all energies at a value of n which was unknown but was presumed the same for each energy. This procedure was followed repeatedly at 6 to 10 successively lower pressures. The values of $(\sigma_{10}n+\sigma_{10}'n')$ for each energy were then plotted against the corresponding $(\sigma_{10}n+\sigma_{10}'n')_s$ for the standard energy and σ_{10}/σ_{10s} read from the slope of the straight line drawn through these points (Fig. 5).

The absolute cross section at the standard energy as well as at several other energies was measured by following the above procedure (for a single energy setting) with accompanying pressure and temperature measurements. $\sigma_{10}n+\sigma_{10}'n'$ was then plotted against n and the cross section obtained from the slope of the resulting straight line (Fig. 6).

The use of this method yielded a curve for the cross section as function of proton energy which was very smooth, and which agreed with other measurements at the standard energy but disagreed with them as well as our own absolute measurements at other energies.[30] It was decided finally that the assumption of constant pressure during runs through several energies was a poor one. Thereafter the reading of a sensitive ionization gauge was recorded for each energy setting and $(\sigma_{10}n+\sigma_{10}'n')$ plotted for each energy against the gauge

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[29] If $I_0(0)\neq 0$, what is measured is

$$\sigma_{10}\left(1-\frac{I_0(0)}{I_+(0)}\frac{\sigma_{01}}{\sigma_{10}}\right),$$

where n is assumed constant from $x=0$ on and $\sigma_{1,\,-1}$ is neglected.

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reading. The result, illustrated in Fig. 7, was a family of straight lines radiating from a common intercept on the ion gauge axis. The slopes relative to the slope of the standard were taken as the relative cross sections.

RESULTS AND DISCUSSION FOR σ_{10}

The result is a curve (Fig. 1 and Fig. 8), again smooth, which agrees well with the checks made on the absolute cross section (Table I) and also agrees with the results of Stier and Barnett.[1] Judging by the scatter in the points of Stier and Barnett, it would appear that their results nowhere disagree with ours even though the smooth curve they draw through their points does not everywhere coincide with ours. The most notable difference is at the peak value where we obtain a σ_{10} of 8.04×10^{-16} cm^2 per molecule at a proton velocity of 1.12×10^8 cm/sec, compared to their 8.14×10^{-16} cm^2 per molecule at 1.24×10^8 cm/sec.

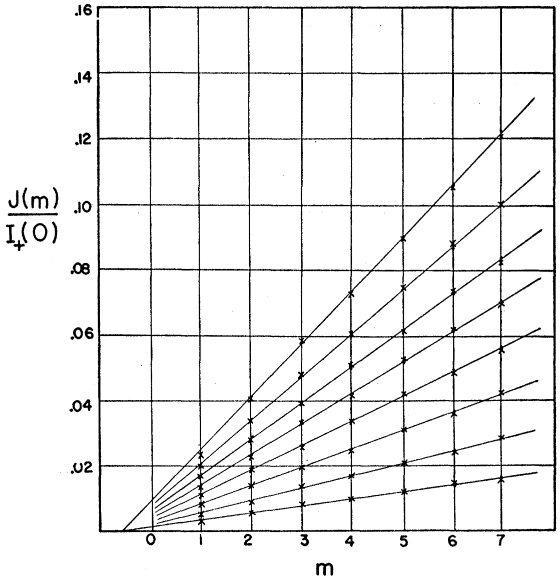

FIG. 4. Ratio of slow ion to total current as a function of the number of collecting condensers for protons at 20.3 kev. The parameter is H_2 pressure.

From Fig. 1 it can be seen that our agreement with the results of other workers is really good throughout the entire energy range only in the case of Stier and Barnett, despite the use of a method which differs greatly from theirs and most closely resembles that of Stedeford and Keene. In Fig. 1 and Fig. 8 we have presented all experimental results in terms of the cross section per gas molecule. It should be noted that similar comparisons between different experimental results or between experiment and theory have in several cases been confusing because of a failure consistently to use units per atom or per molecule for the cross section.[4,22,23,31]

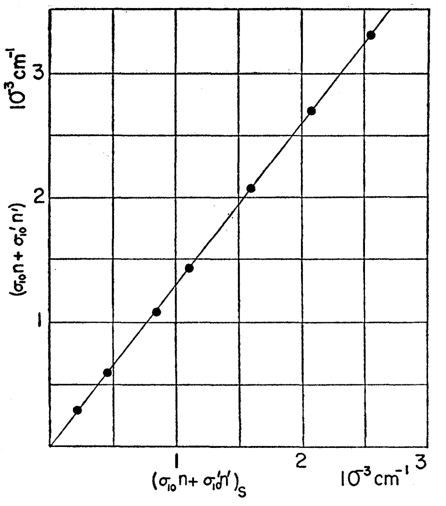

FIG. 5. Slope of $J(m)/I_+(0)$ *vs* m curves at 9.49 kev plotted against slopes for corresponding pressures at 20.3 kev.

The precision of the results we have obtained for absolute and relative cross sections has been estimated. The greatest uncertainty in the absolute measurement comes from the pressure measurement with a McLeod gauge. Taking into account the performance of the electrometer, and the contribution of electron loss by the neutral component in the beam to the condenser currents, we estimate the accuracy of the relative capture cross sections at $\pm2\%$ for energies greater than 3 kev and $\pm3\%$ for energies less than 3 kev. The accuracy of the absolute measurements was estimated to be $+6\%$, -4%.

These results are based on the assumption that double electron capture does not occur. $\sigma_{1,-1}$ has, however, been measured recently over the energy range from 9 to 30 kev.[11,23] The fact that the variation of this cross section with energy is similar to that of σ_{10} means that the effect on the relative cross-section curve should be slight. It is difficult to assess the effect on the absolute

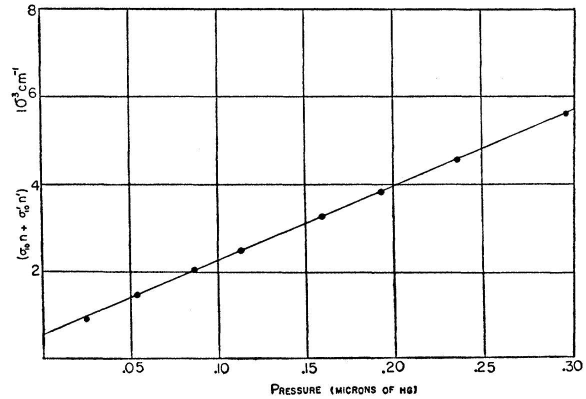

FIG. 6. Slope of $J(m)/I_+(0)$ *vs* mx_c curves at 20.3 kev plotted against gas density. The slope of the straight line drawn gives σ_{10} as 5.54×10^{-16} cm^2/molecule.

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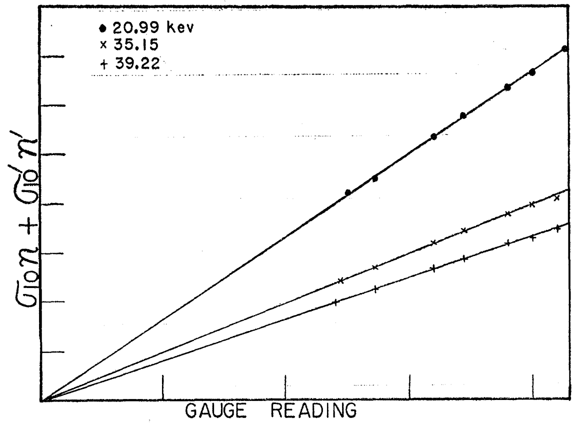

FIG. 7. Slope of $J(m)/I_+(0)$ *vs* m plotted against ionization gauge reading at three energies.

value because of poor agreement in the values of $\sigma_{1,-1}$ so far published. If account is taken of the fact that this process contributes a double measure of collected current the value of σ_{10} computed would appear to be too large by from 1 to 2%. This is smaller than the experimental errors.

MEASUREMENT OF σ_{01}

The same instrument can be used to measure σ_{01} if the scattering chamber is filled with gas to a moderately high pressure (of the order of 2 microns) and a large neutral component provided in the incident beam by the beam preparation chamber. The first few condenser lengths of the chamber may equally well serve as a region of build up for the neutral ratio. Inside the Faraday cup and connected to it electrically is a thin-foil thermocouple detector which responds to the total particle current. This detector is calibrated in a preliminary experiment at each energy with an evacuated chamber, a pure proton beam, and the help of the Faraday cup. When there is applied to the last m condensers in the array a voltage so high that all positive ions are removed from the beam as quickly as they are formed, the total particle current reaching the detector is the neutral current at the end of the last condenser:

$$I_0(m)=I_0(0)\exp[-(\sigma_{01}n+\sigma_{01}'n')(mx_c+x_0')], \quad (6)$$

where the zero is taken at the beginning of the first of the m condensers. Now if the voltage is removed from the last condenser, the detected current is given by Eq. (6) with m reduced by one; if it is removed from the last two, with m reduced by two; and so on. The experimental procedure of obtaining relative and absolute cross section σ_{01} from Eq. (6) is then just the same as that used to determine σ_{10}.

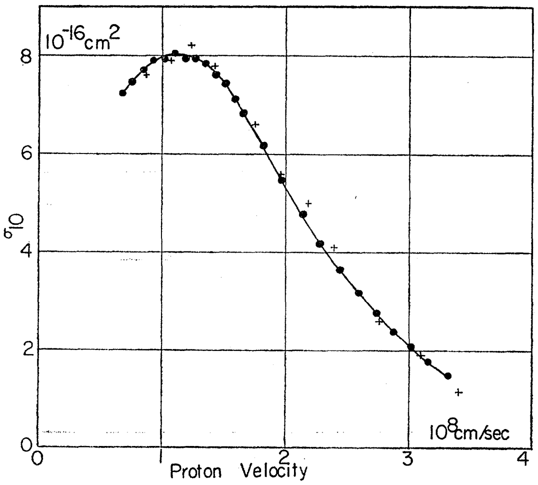

FIG. 8. Present results (circles and solid line) for σ_{10} compared to results of Stier and Barnett (crosses).

TABLE I. Comparison of absolute and relative σ_{10} measurements.

Energy (kev)	No. of measurements	Absolute σ_{10} (cm^2)	From σ_{10} relative to σ_{10} at 20.3 kev (cm^2)
9.49	5	7.90×10^{-16}	7.84×10^{-16}
20.3	5	5.48×10^{-16}	(Standard)
31.1	5	3.67×10^{-16}	3.63×10^{-16}
43.5	6	2.18×10^{-16}	2.38×10^{-16}

TABLE II. Comparison of cross sections obtained by equilibrium and direct methods (in units of 10^{-16} cm^2 per molecule of H_2).

Energy (kev)	$\sigma_{10}+\sigma_{01}$	$\sigma_{01}+\sigma_{0,-1}$	$\sigma_{10}-\sigma_{0,-1}$ deduced	σ_{10} direct method
9.49	7.44±2.32	0.72±0.07	6.72±2.40	7.84
20.29	7.22±0.80	1.32±0.13	5.90±0.93	5.48
29.22	6.00±0.46	1.44±0.14	4.56±0.60	3.90

MEASUREMENT OF $(\sigma_{10}+\sigma_{01})$

A further high-pressure experiment making use of the thermal detector is capable of measuring $\sigma_{01}+\sigma_{10}$. This is obtained from Eq. (1) by a measurement of the fraction of the total current neutral at the end of the mth condenser:

$$\begin{aligned}F_0(m)=I_0(m)/I=F_0(\infty)+[F_0(0)-F_0(\infty)]\\ \times\exp\{-[(\sigma_{01}+\sigma_{10})n+(\sigma_{01}+\sigma_{10}')n']mx_c\}\\ \times\exp\{-[(\sigma_{01}+\sigma_{10})n+(\sigma_{01}'+\sigma_{10}')n']\Delta\}, \quad (7)\end{aligned}$$

where Δ is an end correction. This may be condensed to read

$$F_0(m)=A+B\exp[-(\gamma n+\gamma' n')mx_c]. \quad (8)$$

This fraction is measured by taking a detector reading with no voltage applied to the condensers for I and then applying high voltage to the $(m+1)$st condenser. What is then actually obtained is

$$\begin{aligned}F_0(m)\exp[-\sigma_{01}(x_c+\delta)]\\ =C+D\exp[-(\gamma n+\gamma' n')mx_c]. \quad (9)\end{aligned}$$

Equation (9) is somewhat difficult to deal with in practice. If, for example, differences are taken between values for successive values of m to eliminate C the differences are small compared to $F_0(m)$. Best success and speediest processing of data has been afforded by securing the best fit of the data to an equation of type of Eq. (9) with the help of an IBM 650 computer. The computer program also fits $(\gamma n+\gamma' n')$ for different values of n to a straight line and gives $\sigma_{01}+\sigma_{10}$ together with the probable error.

The results for two energies are given in Table II. In the treatment of this problem we have ignored the presence of negative ions in the beam. Actually what was measured, instead of σ_{01}, was $\sigma_{01}+\sigma_{0,-1}$. The effect of a negative component on the measurement of $\sigma_{10}+\sigma_{01}$ is to make the sum arrived at too large by no more than 1.5% up to 40 kev.

ACKNOWLEDGMENTS

Many of the data for this paper and in fact almost all of those so far taken for σ_{01} and $(\sigma_{10}+\sigma_{01})$ have been contributed by Mr. James Nolan. The help of Mr. William Folger also has been most welcome.

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Chemical Reactions of Positronium in Aqueous Solutions*

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An attempt to a preliminary but systematic study of the chemical properties of the element positronium is described. It is verified (in agreement with Green and Bell) that positrons react with nitrates; it is believed that this reaction is an oxidation process. It is found that positronium is not so readily attacked by the ions Cl^- and SO_4^{--}. In chloride and sulfate solutions positronium more effectively replaces the metals which are lowest in the electrochemical series: this result opens the possibility of determining the position of positronium in the electrochemical scale.

INTRODUCTION

Numerous workers have found evidence for the existence of a bound state of positronium in water. Measurements of lifetime show a long-lived component[1]; studies of angular correlation of two-photon annihilation radiation show a narrow component[2]; and determinations of the three-photon annihilation rate indicate that this is greater in water than in metals.[3] All of these results can be explained by assuming that triplet positronium exists for a short time in water before it is destroyed by conversion to singlet and subsequent annihilation.

The existence of this "atom" of positronium in water suggests the possibility of observing chemical reactions in which the atom takes part. If a chemical is dissolved into the water, a reaction between this chemical and the positronium would tend to destroy or reduce the magnitude of the effects mentioned above. Experiments along these lines have been conducted by Green and Bell[4] and by de Zafra.[2] Lifetime measurements by Green and Bell showed that the long-lived components tended to disappear when increasing concentrations of nitrate were added to the water, but when certain chlorides and sulfates were added there was only a small variation in the long lifetime.

The angular correlation measurements by de Zafra confirmed some of the results of Green and Bell and also showed that certain paramagnetic salts caused the narrow angular distribution to broaden, indicating some effect on the positronium atom.

It appears from these observations that a more systematic study of the behavior of positronium in solution was desirable. The present work was started for the purpose of determining the position of the element positronium (Ps) in the electrochemical scale. The method is obvious; it consists in studying which metallic ions are "replaced" by positronium in solution.

EXPERIMENTAL PROCEDURE AND RESULTS

The equipment used to reveal triplet positronium was similar to that described by Siegel.[5] The three-quantum annihilation rates were measured in the various solutions and compared to those found in water. All comparisons were made by replacing the salt solutions with water several times during each run. Our positron source consisted of ten microcuries of Na^{22} sealed in a narrow, thin-walled glass tube (1 mm diameter and

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† Submitted by J. McGervey in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology.

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