

THE RECOMBINATION OF IONS IN ARGON,
NITROGEN AND HYDROGEN

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ABSTRACT

Since free electrons are known to exist in ionized A, N₂ and H₂ these gases are employed in an effort to measure directly the coefficient of recombination for positive ions and electrons. At the same time the coefficient is determined for positive and negative ions in H₂ which would be expected theoretically to differ from other gases. The method is one using x-rays as the ionizing agent and has already been described by L. C. Marshall and the writer. Previous indirect methods and theory indicate that α , the coefficient of recombination for ions and electrons is of the order of 10^{-10} compared to 10^{-6} for positive and negative ions. In the present work results similar to those in air are obtained in the pure gases, and only a slight change in α is observed when sufficient O₂ is added to cause immediate attachment of the free electrons. Further direct tests in pure A, N₂ and H₂ indicate that negative ions are present in large quantities at all times, although a constant number of free electrons is also present. Hence it is probable that recombination was taking place between positive and negative ions rather than positive ions and electrons. It is assumed that as a result of the action of the ionizing agent negative ions are formed by attachment to excited metastable molecules in the case of A and N₂ and by attachment to atoms or triatomic molecules in the case of H₂.

In accordance with the criterion established in a previous paper for air, "absolute values" of α are set as follows:

<i>Gas</i>	<i>Coefficient of Recombination</i>
Air	$1.4 \pm 0.1 \times 10^{-6}$
O ₂	$1.5 \pm 0.1 \times 10^{-6}$
A	$1.2 \pm 0.1 \times 10^{-6}$
N ₂	$1.2 \pm 0.1 \times 10^{-6}$
H ₂	$0.32 \pm 0.05 \times 10^{-6}$

The results in H₂ show a constant value of $0.32 \pm 0.05 \times 10^{-6}$ which is much lower than in the other gases contrary to the prediction of the J. J. Thomson theory of recombination. However, the theory is deficient in certain respects which may explain this discrepancy.

INTRODUCTION

THE present work on the recombination of ions produced by x-rays is a continuation of previous investigations by L. C. Marshall¹ and the writer.² This second part was undertaken in an effort to measure directly the coefficient of recombination of positive ions and electrons, and at the same time to determine the coefficient of recombination in H₂ which would be expected to differ from other gases. Gases were used in which free electrons

¹ L. C. Marshall, Phys. Rev. **34**, 618 (1929).

² O. Luhr, Phys. Rev. **35**, 1394 (1930).

are known to exist for considerable periods of time. Thus in A, N₂ and H₂ free electrons will not attach to the normal molecules, but may attach to excited molecules or to molecules of impurity which may be present.

Theoretically it is to be expected that recombination between electrons and positive ions would proceed very slowly compared to that between negative and positive ions.³ This has in general been born out by numerous indirect spectroscopic methods of measurement⁴ and in one case by the direct measurements of Atkinson⁵ whose results, however, were inconclusive. Kenty,⁶ using spectroscopic methods and the Langmuir probe estimated the coefficient in very pure A to be of the order of 10⁻¹⁰ compared to 10⁻⁶ for positive and negative ions. Marshall,¹ with practically the same apparatus as that used by the writer believed he had found evidence of a low coefficient of recombination in pure A since the value was only about half that obtained when one cm partial pressure of O₂ had been added to the pure gas. The one cm of O₂ was sufficient to cause immediate attachment of all the free electrons present. Marshall used a metal ionization chamber where it is impossible to obtain the best conditions of purity, and he believed that the recombination in pure A was taking place principally between positive ions and negative ions formed by attachment of electrons to molecules of impurity.

In the present work it was found that Marshall's results were partially in error due to an unshielded lead (from the commutator to the ionization chamber) which caused a small statically induced charge to remain on the lower plate of the ionization chamber. No such effect was to be expected since the lead and lower plate were grounded through a half megohm resistance. However, because of the very high potentials in the room from the x-ray equipment, there was actually sufficient field to draw out most of the free electrons in 0.15 seconds, though there was no appreciable effect on the ions. Marshall attributed this loss of electrons to diffusion, but very little loss was observed in the present work even after a second, when the lead was shielded by enclosing it in a grounded metal tube. Also, the coefficient of recombination remained approximately the same when sufficient partial pressure of O₂ was added to any of the gases to obtain immediate attachment of the free electrons. This might indicate that the coefficient of recombination for positive ions and free electrons is nearly the same as for positive and negative ions, but it is believed that actually a considerable number of free electrons were attaching, possibly to impurities, but more likely to metastable excited molecules produced by the ionizing agent.

METHOD OF MEASUREMENT AND PRELIMINARY EXPERIMENTS

The apparatus has already been described by Marshall¹ and the writer,² and was used in exactly the same form in the present work. It consists of a rotating shutter and commutator mechanism which furnishes a means of

³ L. B. Loeb, *Trans. Am. Electrochem. Soc.* **LV**, 131 (1929).

⁴ R. Seeliger, *Phys. Zeits.* **30**, 329 (1929).

⁵ R. d'E. Atkinson, *Zeits. f. Physik* **51**, 188 (1928).

⁶ C. Kenty, *Phys. Rev.* **32**, 624 (1929).

ionizing the gas in the ionization chamber by a flash of x-rays, then measuring the charge remaining at any time afterward by a suitable adjustment of the commutator and brushes. A sufficiently high field is applied to the lower plate of the ionization chamber through the commutator to produce a saturation current, thus sweeping all the ions of one sign to the upper plate almost instantly at any desired time. A neutralizing current is forced through a high resistance carbon line leak by means of a potentiometer, thus keeping the upper plate and electrometer system always at zero potential during the flash time and time of recombination.

The method of calculation is also the same as before, all values of α , the coefficient of recombination—obtained from the equation $\alpha = 1/t(1/n - 1/n_0)$ —being determined as a function of τ the age of the ions rather than t the total time of recombination.² In some cases this produced rather irregular results due to the very small differences in the potentiometer readings when the time of recombination was of the order of a few thousandths or a hundredth of a second. Thus very small errors in taking the potentiometer readings, due principally to fluctuations in intensity of the x-rays caused large errors in the values of α , and the plotted points do not always lie as close to a smooth curve as would be desired. However, since this method of calculation gives the only true picture of what is happening at any particular time, it was thought best to use it throughout.

Two small though important changes were made in the method of measurement. Instead of making use of the total volume of the ionization chamber ($10 \times 20 \times 7.5$ cm), the defining slit at the front of the chamber was narrowed down so that a beam of x-rays about 2.5 cm instead of 7.5 cm high passed between the plates. The volume of ionization was thus kept about 2.5 cm from each plate so that the possibility of diffusion of electrons to the plates with a resulting spuriously high coefficient of recombination would be at a minimum. On a kinetic theory basis it may be estimated that an electron would, on the average, diffuse a distance of two or three cm in as little as one-tenth of a second. However, this is extremely unlikely in the present case since the space charge produced by the positive ions remaining in the volume of ionization would prevent the electrons from diffusing to any great extent. Nevertheless, it was actually found in tests on A that the coefficient of recombination dropped off about fifteen percent as the distance of the x-ray beam from the plates was increased to a maximum.

The other change in the method of measurement consisted in having the sector opening the same for every run regardless of the commutator speed. This was necessary to produce sufficient ionization for convenient measurement. The sector opening was only 18° for A due to the intense ionization and 90° for air, N_2 and H_2 . Thus effectively older ions and more random distribution occurred at faster commutator speeds. Hence, α dropped more rapidly with time though the initial and final values remained the same as before, as shown by a comparison of the results in air obtained with the two methods. The situation was further aggravated by the high intensities of x-radiation which were necessary to produce sufficient ionization in H_2 and

N₂. As a result it is more difficult to set an "absolute value" for the coefficient of recombination as was done for air,² since the point at the end of the sharp drop due to nonrandom distribution is not clearly defined.

As in the previous work on air and O₂, all values of α are corrected for diffusion by assuming a swelling of the volume of ionization given by,

$$V = V_0 + 2A(\overline{\Delta x})_\tau$$

where V_0 is the initial volume, A is the area of the upper plate of the ionization chamber and $(\overline{\Delta x})_\tau$ is the average distance an ion will diffuse in time τ given by $(\overline{\Delta x})_\tau = (4D\tau/\pi)^{1/2}$ from the Brownian movement equation.⁷ D is the coefficient of diffusion given by $D = 0.0236k$ where k is the mobility of the ions. For air, A and N₂ the average mobility is about 2 cm per second per volt per cm, or D is 0.047. The mobility in H₂ is of the order of 6 cm per second giving D as 0.142. Owing to the use of a relatively small volume of ionization (though it was still 448 cm³ or seven times as large as that used by Marshall) the diffusion corrections were of the order of twenty percent at the longest time intervals but this correction gave results apparently consistent with the previous ones in air using larger volumes.

One extraneous effect observed in pure A, N₂ and H₂ is worthy of note. While Marshall was continually losing free electrons until there were very few left after 0.15 seconds, in the present work the negative readings were in general about three percent higher than the positive. This effect was evidently due to the presence of free electrons since the positive and negative readings became equal if sufficient O₂ was added to produce attachment. It was apparently not caused by a residual field as in Marshall's case since it was purely a percentage effect not varying with time. This possibility was further investigated by allowing x-rays to pass into the chamber with no field present to sweep out the ions. No appreciable charge was built up on the upper plate as long as the shielded lead was employed, but if the unshielded one used by Marshall was inserted a large positive charge accumulated indicating the loss of electrons to the lower plate. It was thought that possibly scattered radiation from the x-ray beam was in some way producing an excess of negative charges by photoelectric action on the metal surfaces, but photographs of the beam emerging from the ionization chamber showed it to be very sharply defined with no indication of any scattered radiation. The explanation may lie either in the presence of contact potentials or in a slight distortion of the field producing weak curved lines of force outside the volume of ionization which would sweep electrons of high mobility but not negative ions to the upper plate. The effect was not considered to be serious, however, since the positive readings were always used in calculating the coefficient of recombination. The negative readings would in general have given slightly higher values of α indicating a very small loss of electrons by diffusion from between the plates.

In regard to the purity of the gases, extreme care was taken so that the possibility of attachment of free electrons to molecules of impurity was

⁷ L. B. Loeb and L. C. Marshall, *Jour. Frank. Inst.* **207**, 371 (1929).

reduced to a minimum. The ionization chamber was thoroughly cleaned with cleaning solution to remove any organic materials. The A, N₂ and H₂ were first passed over copper heated to 400°C to remove the oxygen. They were then subjected to the same treatment as the air by passage through glass wool, sodium calcium hydrate, CaCl₂, P₂O₅ and two liquid air traps. The A, which was the purest obtainable in large quantities contained considerable N₂ as indicated by the presence of N₂ bands in the spectrum. Otherwise the gases were spectroscopically pure showing no evidence of organic compounds or oxygen when the discharge was observed with a large direct vision spectroscope.

Direct tests for the presence of free electrons. In view of the unexpectedly high values of α obtained in pure A, N₂ and H₂ it was thought desirable to test further for the presence of free electrons. In order to accomplish this a second brush was added to the commutator system so that an alternating potential could be applied to the lower plate of the ionization chamber. Thus by keeping the volume of ionization close to the lower plate and varying the driving and retarding potentials, the apparatus could be used to measure mobilities by the simple Rutherford alternating current method.⁸ Although the measurements were somewhat complicated by the presence of positive ions, the results in every case indicated two facts: (1) Only a part of the negative carriers were free electrons (probably twenty to forty percent) when the age of the ions was about 0.01 seconds, the newest that could be studied; (2) The total number of electrons remained approximately the same as the ions aged to 0.5 seconds or more, although a considerable portion of the negative carriers had disappeared by recombination. Thus negative ions and free electrons were probably both present in large quantities during the period of recombination, but there was no gradual attachment of free electrons taking place as would be expected if impurities were present. This can only lead to the conclusion that most of the attachment occurred within a few thousandths of a second after the formation of the ions, which would result if the effect were due to metastable excited molecules produced by the ionizing agent. This question will be considered further in the discussion of the results.

EXPERIMENTAL RESULTS

Values of the coefficient of recombination obtained in pure argon are shown in Fig. 1. The different curves correspond to commutator speeds varying from 16 to 1/2 revolutions per second. The initial concentration of the ions varied from about 2.5×10^6 ions per cm³ at 16 revolutions per second to 1.1×10^7 ions per cm³ at 1/2 revolution per second. The initial value of α at a time of 0.002 seconds is about 1.6×10^{-6} , and the value then drops off in a manner similar to that in air to about 0.55×10^{-6} at 0.75 seconds. A similar series of runs was next taken with the addition of 2 cm partial pressure of O₂ added to the A. This was sufficient to cause almost instant attachment of the

⁸ J. J. Thomson, *Conduction of Electricity Through Gases*, p. 102, III Edition, Cambridge 1928.

free electrons as indicated by the equality of the positive and negative readings. The results, however, (which are not shown in the diagrams)

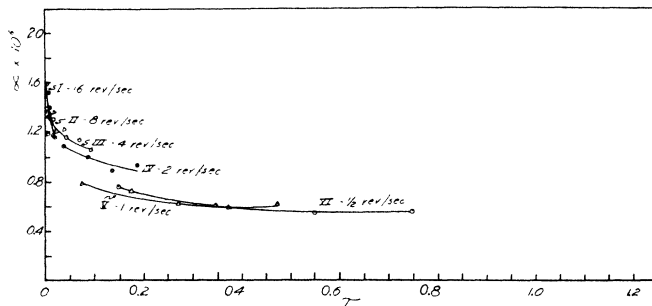


Fig. 1. Coefficient of recombination for pure argon.

were exactly the same as for pure A within the limits of experimental error except at the very shortest time interval (0.002 seconds) where $\alpha = 1.7 \times 10^{-6}$

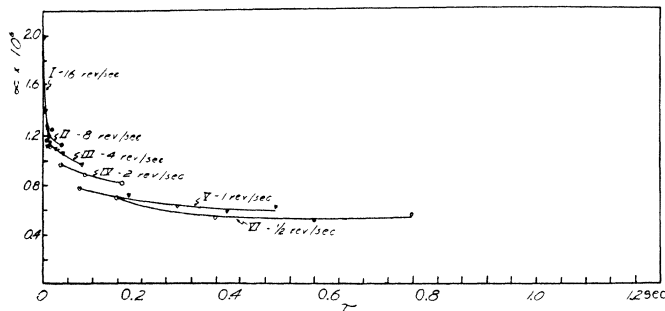


Fig. 2. Coefficient of recombination for argon with 15 cm partial pressure of O_2 .

instead of 1.6×10^{-6} . With the possibility that insufficient O_2 had been added, another series of runs was taken with 15 cm partial pressure of O_2 correspond-

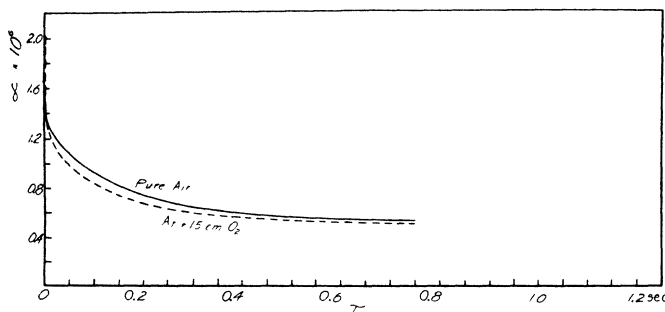


Fig. 3. Comparison of results in pure argon and argon with 15 cm partial pressure of O_2 .

ing to the N_2-O_2 mixture in air. The results shown in Fig. 2 were again almost the same as in pure A except at the very shortest time when $\alpha = 2.0$

$\times 10^{-6}$. A comparison of the results obtained with pure A and A+15 cm O_2 are shown in Fig. 3. Average values of α for any particular age τ are plotted against τ . The A+ O_2 curve starts higher, crosses the pure A curve at about 0.005 seconds and continues on slightly lower for the remainder of the time.

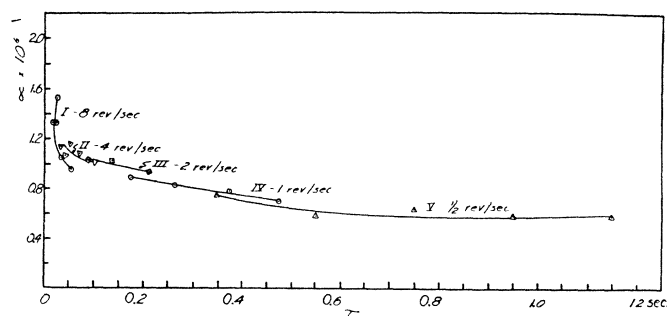


Fig. 4. Coefficient of recombination for pure nitrogen.

Fig. 4 shows the results for pure N_2 which are not far different from the corresponding values for A. It was impossible to obtain accurate results at the fastest commutator speed (16 revolutions per second) owing to the lack of sufficient concentration of ions. Even at 8 revolutions per second (time of

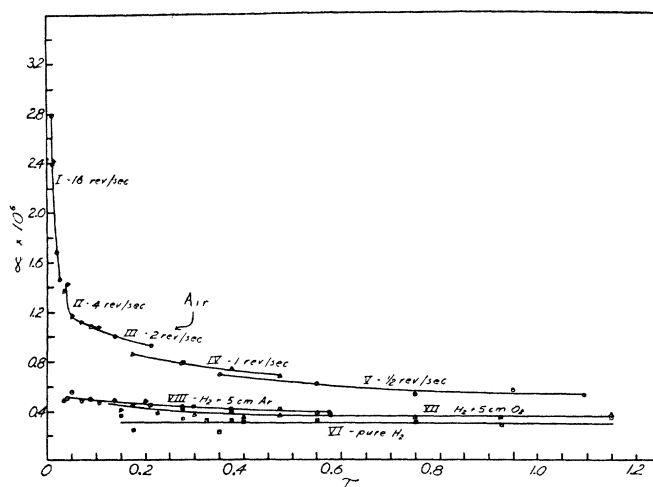


Fig. 5. Results for air and hydrogen.

exposure to x-rays 0.0156 seconds) the concentration was only 0.91×10^6 ions per cm^3 which gave rather inaccurate values of α .

Fig. 5 gives the results for air and H_2 . Curves I to V were taken in air for varying commutator speeds under the conditions corresponding to those for A and N_2 ; i.e. with constant sector opening of 90° and as high initial concentration as possible. The initial concentration varied from 0.79×10^6 ions per cm^3 at 16 revolutions per second to 4.8×10^6 at 1/2 revolution per

second. The value of α varies from 2.8×10^{-6} at $\tau = 0.008$ seconds to 0.55×10^{-6} at $\tau = 1.15$ seconds.

Curve VI, Fig. 5 gives the results for pure H_2 , showing a constant value of 0.32×10^{-6} for α between 0.15 and 1.15 seconds. Owing to the extreme difficulty of obtaining sufficient concentration of ions, no runs at commutator speeds faster than one revolution per second could be taken. Even at one revolution per second (time of exposure to x-rays 0.25 seconds) only 0.46×10^6 ions per cm^3 were obtained. At 1/2 revolution per second the initial concentration was 0.90×10^6 ions per cm^3 . Argon in varying quantities was then added to the H_2 to obtain greater concentration of ions, but made no appreciable difference in the value of α up to 5 cm partial pressure. The results for 5 cm partial pressure of A with H_2 are shown in Curve VIII, Fig. 5. The values of α are only slightly higher than for pure H_2 , starting at about 0.50×10^{-6} at $\tau = 0.03$ seconds (commutator speed 4 revolutions per

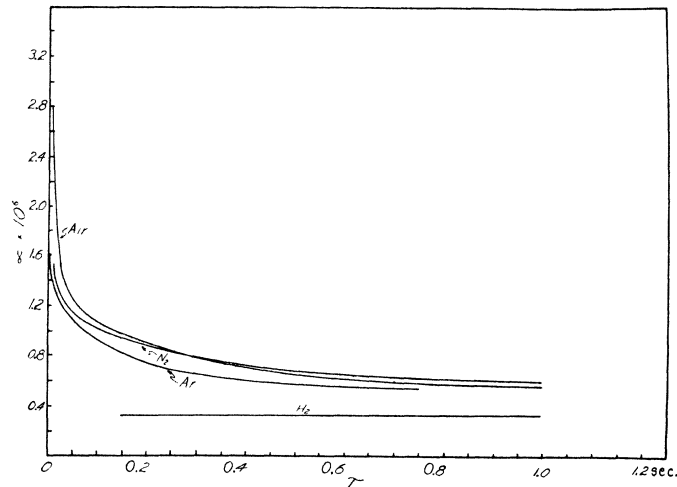


Fig. 6. Comparison of results for pure gases.

second) and dropping to 0.40×10^{-6} at $\tau = 0.6$ seconds. Runs at commutator speeds of 1 and 1/2 revolutions per second were next taken with 5 cm partial pressure of O_2 added to pure H_2 to obtain attachment of the free electrons. The results (Curve VII, Fig. 5) again show only a small change from those in pure H_2 , α dropping from 0.45×10^{-6} at 0.15 seconds to 0.35×10^{-6} at 1.15 seconds. A final series of runs was taken with 5 cm partial pressure of A and 5 cm of O_2 added to pure H_2 but gave results identical with those for 5 cm partial pressure of A (Curve VIII).

A comparison of the results for air, pure A, pure N_2 and pure H_2 are given in Fig. 6. As in Fig. 3 average values of α are plotted against τ the age of the ions. Except at the shorter time intervals the results show a marked similarity for air, N_2 and A despite the fact that free electrons in large quantities were undoubtedly present in the N_2 and A. The values of α for H_2 are strikingly lower than those for the other three gases.

DISCUSSION OF RESULTS

From the results in the preceding section four facts stand out clearly:

(1) The coefficient of recombination for pure A and N_2 where free electrons should be present is only slightly lower than for air except at very short time intervals (probably 0.05 seconds or less) when random distribution of the ions has not been attained.

(2) The coefficient of recombination in pure H_2 is much lower than in the other three gases having approximately a constant value of 0.32×10^{-6} .

(3) The addition of sufficient O_2 to cause instant attachment of free electrons in A, N_2 and H_2 increases the value of α at the very shortest time intervals.

(4) In A and N_2 the addition of O_2 apparently results in a slight lowering of the values of α after random distribution has been attained.

Regardless of the question of recombination between positive ions and free electrons, one definite conclusion may be drawn from these facts. When free electrons are present, the value of α is lower at the very short time intervals indicating that random distribution is attained more rapidly. This is of course to be expected since electrons would diffuse evenly throughout the volume much more quickly than negative ions and the so-called initial recombination would not occur to as great an extent.

Interpretation of results in A and N_2 . In regard to the question of recombination between positive ions and electrons the results are inconclusive. If theory and previous spectroscopic results are to be relied on, α should be so small (of the order of 10^{-10}) that no recombination could be observed in the present work where the concentration of ions is of the order of 10^6 per cm^3 . Either, then, the spectroscopic results (obtained at low pressures and generally in the presence of rather high fields) are not applicable here, or else recombination was occurring in the present case only between positive and negative ions. If α for positive ions and electrons is very low, and attachment were taking place gradually, the curves would be expected to start at a low value of α for short times, then increase as time goes on until all the free electrons had attached. However, no such low value of α at short time intervals was observed, the values actually increasing rapidly down to 0.002 seconds. Finally, then, one of two conclusions may be drawn: either recombination between positive ions and free electrons is as rapid as that between positive and negative ions, or else a large portion of the free electrons had attached in less than 0.001 seconds. The second view is strongly supported by the evidence obtained in the tests for the presence of free electrons which have already been described.

In view of the precautions taken to obtain pure gases, and the results of the tests for free electrons which indicated that a definite number of electrons were present at all times, it does not seem likely that many electrons had attached to molecules of impurity in 10^{-3} seconds. Nevertheless, such a conclusion might conceivably be in error. As already mentioned there is however another mechanism by means of which attachment might have

taken place in A and N_2 . The intense hard x-rays and fast β -particles produced by them undoubtedly excite a large number of molecules. If these excited molecules remain in metastable states for a considerable period of time (as in the case of active N_2) impacts between the excited molecules and free electrons could give a means of dissipating the electron energy and allow attachment to form negative ions. An effect of this kind has been observed by da Silva⁹ who found some attachment in N_2 and H_2 which had been ionized by α particles. A similar process might occur in A which also has metastable states. On the other hand Loeb¹⁰ and Cravath¹¹ observed no attachment in these gases where the electrons had been produced by ultra-violet light and hot filaments.

Interpretation of results in H_2 . Hydrogen presents a different problem from A and N_2 since metastable excited states do not exist. However, attachment may still take place to atoms or triatomic molecules as indicated by the results of da Silva. Observations in H_2 by Langevin,¹² Townsend¹³ and McClung¹⁴ indicated that the coefficient of recombination was slightly lower than in air (1.4×10^{-6} compared to 1.6×10^{-6}) while in the present work α was found to be 0.32×10^{-6} for H_2 compared to 1.4×10^{-6} for air. The present results may be assumed more reliable owing to the improvements in technique now possible. On the other hand, J. J. Thomson's theory of recombination as modified by Loeb and Marshall⁷ gives much higher values of α for H_2 than for air, even assuming the molecular weight of the ions to be 32 (since the negative ion is ordinarily a molecule of impurity such as O_2). In this case it turns out that α is 2.34×10^{-6} compared to 1.62×10^{-6} for air. If the molecular weight is taken as 2.016, α is 9.50×10^{-6} . Since in pure H_2 , α is observed experimentally to be much lower than in air, this might be taken as an indication of the presence of a preponderance of free electrons which would recombine slowly. However, the addition of sufficient O_2 to produce attachment of the electrons should then bring the value of α up at least as high as for air, probably higher. As shown in Fig. 5 very little change was observed. The theory, however, is based on the assumption that if both ions suffer a single impact when they are within a defined distance d of each other they will lose all the excess kinetic energy gained as a result of their mutual attractions since the last impact. This single impact is assumed a sufficient condition for recombination. Since the mass of the ions is probably large compared to that of the molecules, a single impact may not suffice to remove the excess energy and the ions may drift apart without recombining. In other words, several impacts are probably required to reduce the excess energy, which fact cannot be taken into consideration by the theory as it stands. In this way α could be less for H_2 than for air in agreement with the experimental results.

⁹ M. A. da Silva, *Ann. de Physique* **12**, 100 (1929).

¹⁰ L. B. Loeb, *Kinetic Theory of Gases*, p. 507, New York, 1927.

¹¹ A. M. Cravath, *Phys. Rev.* **33**, 605 (1929).

¹² P. Langevin, *Ann. de Chim. et de Phys.* **28**, 433 (1903).

¹³ J. S. Townsend, *Phil. Trans. Roy. Soc.* **A193**, 157 (1900).

¹⁴ R. McClung, *Phil. Mag.* **3**, 383 (1902).

Thus, in view of the experimental facts it is probable that the recombination observed in this work was taking place between positive and negative ions rather than positive ions and free electrons. The negative ions may have been formed by attachment of electrons to impurities but the evidence points strongly to the supposition that the attachment was to metastable excited molecules in the case of A and N₂, and to atoms or triatomic molecules in the case of H₂.

Values of the recombination coefficient in various gases. As indicated earlier it is more difficult to set an "absolute value" of α in this work than in the previous work on air owing to unfavorable experimental conditions. However, if the value of α for air is taken as $1.4 \pm 0.1 \times 10^{-6}$ at the point where the sharp drop due to non-random distribution ends, and the more gradual drop due to aging begins, comparison of the curves in Fig. 6 indicates a value of $1.2 \pm 0.1 \times 10^{-6}$ for A and N₂. The value for H₂ may be more definitely set as $0.32 \pm 0.05 \times 10^{-6}$ since in this case there is no appreciable change with time.

A list of values for the coefficient of recombination determined by the above criterion for all the gases studied may then be given as follows:

<i>Gas</i>	<i>Coefficient of Recombination</i>
Air	$1.4 \pm 0.1 \times 10^{-6}$
O ₂	$1.5 \pm 0.1 \times 10^{-6}$
N ₂	$1.2 \pm 0.1 \times 10^{-6}$
A	$1.2 \pm 0.1 \times 10^{-6}$
H ₂	$0.32 \pm 0.05 \times 10^{-6}$

In conclusion the writer wishes to express his sincere thanks to Mr. N. E. Bradbury for assisting in taking the readings and to Professor Loeb for his inspiring guidance throughout the course of these experiments.