AUGUST 15, 1929 *PHYSICAL REVIEW* *VOLUME 34*

THE RECOMBINATION OF IONS AND OF IONS AND ELECTRONS IN GASES

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(Received May 16, 1929)

Abstract

Coefficient of recombination of ions, produced by x-rays, as function of x-ray exposure time, initial ion concentration and time of recombination.—The present work constitutes a study of the recombination of ions and of ions and electrons in gases, by means of a new direct method, using constant radiation from a Coolidge x-ray tube as the ionizing agent, together with a rotating commutator shutter. This method permits wide limits of independent variation of: (1) x-ray exposure (t'); (2) initial ion concentration (n_0); (3) time of recombination (t). Results in air show that α, previously assumed constant and equal to 1.6×10^{-6} actually varies as a function of t' and of t. It is high, 4×10^{-6} or more, for small values of the above quantities and drops rapidly to nearly a constant value. α is also found to be a function of n_0. These facts can only be explained on the assumption that the ions are not initially uniformly distributed, but are in pairs along the paths of the x-rays. This leads to fictitiously high calculated values of α corresponding to low apparent values of n_0 and n, erroneously computed on the assumption of random distribution. As t', and with it n_0 and also t, increase, α approaches a constant value between 0.8 and 0.9×10^{-6}, which is probably nearly the true value. This result lends strong support to the theory of Thomson that the process of diffusion plays the major role in the initial stages of the mechanism of recombination; i.e. in bringing ions together.

Coefficient of recombination in argon: mechanism of recombination, formation of negative ions by electron attachment to impurities.—In argon, where electrons remain free for appreciable intervals, α is nearly constant. For the same time intervals it has only about half the value found in argon-oxygen mixtures, where the electrons attach rapidly, or the value found in dry air. On the basis of the kinetic theory α would be expected to be the same in argon as in air. The constancy of α with t and t' is due to the rapid achievement of random distribution when free electrons are present. The value of α indicates that the coefficient of recombination for electrons and positive ions is less than for positive and negative ions. This conclusion is in agreement with the results of Kenty on recombination between electrons and positive ions in argon. Consequently α, as observed in pure argon, is not a true measure of the recombination of positive and negative ions, but serves as an indication of the rate of negative ion formation through the attachment of electrons to impurities present.

Introduction

Attempts at formulating an adequate theory of recombination of positive and negative ions, in gases near atmospheric pressure, and of ions and free electrons in these gases under similar conditions, have in recent years met with considerable difficulty owing to inadequate information on the following points:

1. Whether the fundamental mechanism of ion recombination may be ascribed: (a) to the attractive forces between the ions according to the

treatment of Langevin;[1] or (b) to the random heat motions as provided in the more recently published theory of J. J. Thomson.[2]

2. Whether one may state with assurance that the coefficient of recombination, designated henceforth as α, is constant with time as *assumed* in previous investigations, or if it does vary, why it does so.

3. The unknown role of free electrons in recombination; for electrons have, in the last ten years, been shown to remain free for appreciable periods of time in many gases, even at high pressure.

It seemed essential, therefore, to undertake measurements which might help to clarify these questions especially in relation to the third point, evience for which had been claimed by Rümelin as a result of a study of the recombination of ions within short time intervals after ionization. A direct method of study of recombination, following ionization by x-rays, was suggested to the writer by Professor L. B. Loeb. This seemed capable of greater flexibility and control than the previous methods used, due to the development of modern x-ray technique. After two years' time the elaborate equipment required to carry on measurements under satisfactory conditions was assembled and the results obtained this year appear to have entirely fulfilled the expectations. It is the purpose of this paper to describe the method and the preliminary results obtained.

Method of Measurement

Reference to the accompanying diagram (Fig. 1) will make the following description more clear. The development of the Coolidge x-ray tube, supplied with a constant high-potential direct current, has made the production of constant x-radiation possible for long intervals of time. The intensity may be determined, over a wide range, by the variation of either current through the tube or applied voltage, or both. Provision is made to vary the duration of the ionizing flash of x-rays, in a chamber, by means of a sector, variable from 0° to 90°, cut out of a solid brass disk, rotating at any desired speed. The same shaft carries a commutating mechanism, which may be adjusted relative to the sector. Thus the ions may be swept from the ionized volume at any time after the x-ray flash has ceased. The x-rays are limited by means of a series of square slits of large aperture, and directed in a nearly parallel beam into the ionization chamber, through a thin aluminum window. Here a volume of gas is ionized, between two parallel horizontal plates, and the beam is allowed to pass out through another window in the rear of the chamber. The plates are so placed, with relation to the path of the x-rays, that no appreciable diffusion of the ions, to them, may take place in the range of time intervals over which measurements are made. Also care is taken, in the design and placing of the slits, that practically no scattered radiation shall be incident upon the plates. The lower plate is connected alternately, by the commutating mechanism, to the high voltage for sweeping out the ions,

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[1] P. Langevin, Ann. de Chimie et Physique **28,** 403 (1903).

[2] J. J. Thomson. Phil. Mag. **47,** 337 (1924).

and to ground through a high resistance. Thus the plate is at zero potential during the x-ray exposure and the period of recombination. A relay grounds the electrode permanently when the final measurement of charge is made. The upper collecting electrode is surrounded by a grounded guard ring and connected to the quadrant electrometer. Thus the ions are swept from a sharply defined volume of ionization of about 63 cm^3. The process is cyclic, the exposure to x-rays, the lapse of time for recombination after cutting off of the x-rays, and the sweeping out of the ions being repeated in succession during each complete rotation of the commutating shaft. The control of each of these functions is completely independent of the others over a wide range, determined by the relative settings of the variable sector and commutating mechanism, and the speed of rotation. The chamber and electrometer are shunted by a large capacity and a single measurement is allowed to extend over sufficient time (30 seconds to 4 minutes) to build up a conveniently measureable charge on this system. This charge is neutralized, as it grows, by a hand-operated potentiometer, with one of the two methods indicated in the diagram. Thus the effective potential, on the upper plate, is kept very near to zero at all times. The ions are formed and permitted to recombine free from the influence of stray fields.

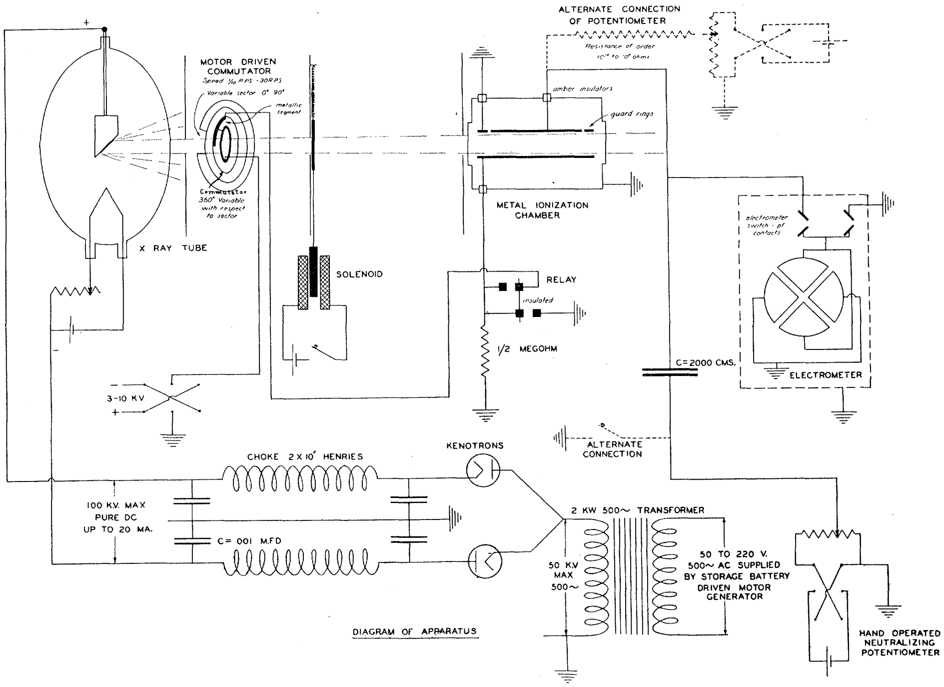

Fig. 1.

The method of neutralization indicated by the solid lines in the diagram is the least accurate. This was the first developed and used in the measurements on air, which are described later. The upper plate may be kept as close to zero potential as the amount of charge collected in a single cycle. Due to sluggishness of the electrometer, however, the variance may be much greater. Moreover, it becomes necessary to time the period over which the reading is taken by means of the sliding shutter. This method is, therefore, not practical for measurement in gases in which free electrons are present, because of their high velocities, even in very small fields. For measurements in air and in mixtures where electrons are not free for appreciable intervals, it suffices. α may then be calculated from the relation

$$\alpha=\frac{300eVNT}{C\epsilon R}\,\frac{1}{t}\left(\frac{1}{r}-\frac{1}{r_0}\right)$$

where e is the electronic charge, V the volume ionized, N the speed of commutator in r.p.s., T the time of observation, C the capacity of the electrometer system, ϵ the voltage of the potentiometer battery. R is a multiplying factor, entering because the capacity, to the lower plate of which the potentiometer is connected, does not comprise the total capacity of the system. The time t is the recombination time as determined by setting of the commutator. r_0 is the potentiometer reading corresponding to $t=0$, and r the potentiometer reading corresponding to $t=t$.

With the second method, indicated by the broken lines in the diagram, the variation of the collecting electrode from ground may never exceed the potential built up in a single revolution of the commutator. Naturally this may be made very small by properly increasing the shunt capacity in the electrometer system. If, moreover, the proper value of high resistance is chosen, the variation may be made well within the limit set above. As before, the values of r_0 and r are read directly from the potentiometer, in volts, when equilibrium is reached. α is now given by the relation

$$\alpha=\frac{1.59\times 10^{-19}RNV}{\epsilon}\cdot\frac{1}{t}\left(\frac{1}{r}-\frac{1}{r_0}\right)$$

where R is the value of the high resistance in ohms, N the speed of the commutator in r. p. s., V the volume ionized, ϵ the voltage of the potentiometer battery, t the recombination time, r_0 the potentiometer reading corresponding to $t=0$, r the potentiometer reading corresponding to $t=t$.

In both systems a series of measurements was made with the same exposure to x-rays, t', and the same commutator speed. Different relative settings of commutator with respect to sector are used to determine first r_0 and then corresponding values of r for different values of t. Such a series of observations is designated as a run. In all cases, readings for both positive and negative charge are taken.

The voltage induced on the electrometer by the high field used for sweeping out ions is very small. This is because the inter-electrode capacity of the plates in the ionization chamber is very small compared to the total capacity of the electrometer system, and the two capacities are in series with each other and the high potential during the application of the field. In taking readings with the first method, the field is first applied. The electrometer deflects slightly to a new position which is taken as the zero during the measurement. The shutter is then opened and the measurement proceeds. Actually the system is at true ground potential except when the field is applied. The constant deflection here is then due to the sluggishness of the electrometer. When sufficient charge has been collected the shutter is closed and the lower plate of the chamber is permanently grounded by means of of the relay. Final neutralization with the potentiometer is made by adjusting to the original zero point. With the second method of measurement, the presence of the shunting leak resistance together with the high total capacity of the system and the sluggishness of the electrometer, renders the inductive effect of the field so small that it cannot be observed.

Gases were purified[3] with procedure along the lines of standard technique. Air was filtered and dried thoroughly. The argon was obtained from the General Electric lamp works. Its purification was not carried beyond the removal of all substances having high electron affinity, and drying. Consequently a small amount of nitrogen was present in the samples of argon on which measurement was made.

RESULTS

1. *Air.* All measurements in air were taken with the first method described. A sequence of runs was made, starting with short x-ray exposures t', small values of recombination time, t, and extending to longer intervals. The variation of these two quantities was systematic, the value of t' and the range of variation of t being doubled in each successive run. This was accomplished merely by halving the commutator speed in each case. The x-ray intensity was held constant with respect to current and voltage on the tube for a complete series of runs. In this manner, results were obtained for values of t' beginning with 0.0156 seconds and ending with 0.5 seconds. This range made possible the production of ions of various ages over a wide range of concentrations. At the longer intervals of 0.25 and 0.5 seconds, equilibrium between the rate of formation and of recombination during the flash was reached. The equality of total numbers of ions produced in the two cases stood as proof. The above procedure provided a series of overlapping ranges of t between the limits 0.0015 sec. and 1.2 sec., the range covered in each run being 24 fold. Variation of t within a run was also systematic, each successive value being made double the preceding one. The values of α and n_0 were calculated from the readings thus obtained, in the manner previously described. These results were also pictured graphically by plotting α as a $f(t)$ for each run. The initial concentration, n_0 was also plottd on the same diagram as a $f(t')$. The result is shown in Figures 2 and 3. Figure 3 is a magnification of Fig. 2 shown in order to facilitate comparison of the results for short time intervals. For this reason, only the first two points on curve V and the first one on curve VI appear on Fig.3. The points on the

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[3] L. B. Loeb, Phys. Rev. **19**, 24 (1922); Phil. Mag. **43**, 230 (1922).

curve labeled n_0, give a picture of the range of variation of n_0 and t' and the shape of the curve clearly illustrates the approach to equilibrium. A glance at the curves showing α as $f(t)$ brings out some very interesting features, as follows:

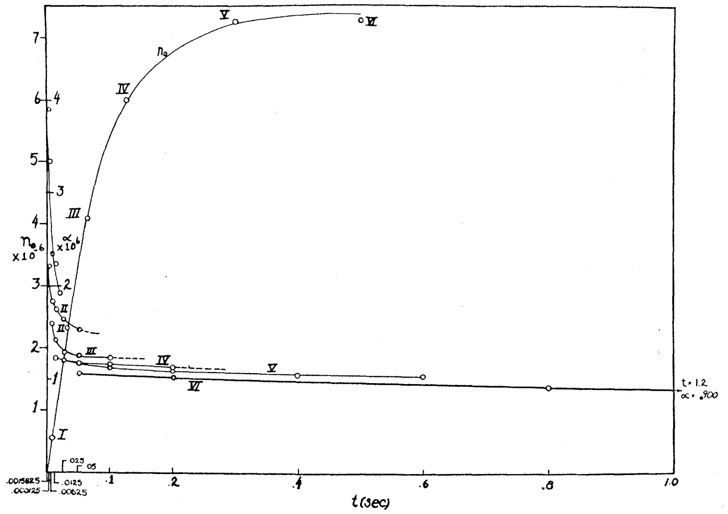

Fig. 2.

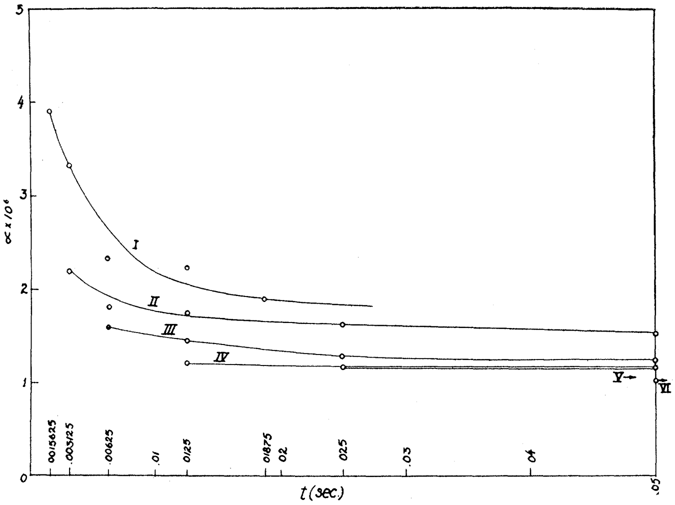

Fig. 3.

1. *α is by no means a constant with time* as apparently observed previously by the majority of experimenters. On the contrary α starts at a high value, about 4×10^{-6}, for $t' = 0.0156$ and $t = 0.00156$, and drops off very rapidly during the run.

2. As t' and t are increased the drop becomes less sharp and at the longer time intervals the curves become nearly straight, showing only a gradual, but nevertheless definite, falling off in the value of α.

3. If the calculations for these longer time intervals are carried out as indicated previously, the dropping off of α is more rapid than that shown by the curves given. This was found to be due to the effects of diffusion. Since the edges of the beam are far from the plates, diffusion to the latter will not occur. The process of diffusion, as time goes on, will, however, increase the volume, V, in which the ions are contained. This quantity falls in the numerator of the expression used in calculation. If, therefore, we use the original uncorrected volume in determining α, an apparent value is obtained, for longer intervals, t, which is too low, and the variation due to this cause must be corrected for.

Since $dn/dt = -\alpha n^2$ and $n = N/V$, where N is the total number of ions in the volume V, $dn = dN/V - N dV/V^2$. The last term is very small, compared to the first, and may be neglected so that $dn = dN/V$. Now $V = lx^2$, where l is the length of the ionized volume and x its width. Because of diffusion, x varies with time. The quantity l remains practically constant; for it is to be remembered that this dimension is determined by the guard ring and that the gas in either direction along the length of the ionized region is also uniformly ionized. Therefore the chance of ions diffusing in or out of the volume from either end is equal. Thus we need only concern ourselves with the change in V due to increase in x. If we let x_0 be the original width of the ionized volume, then $x = x_0 + \overline{2\Delta x}$. Now $\overline{\Delta x} = [(2/\pi)\overline{\Delta x^2}]^{1/2}$ and $\overline{\Delta x^2} = 2Dt$, so $\overline{\Delta x} = (4Dt/\pi)^{1/2}$. In this we are only considering diffusion along the x direction. The general three dimensional case gives $\overline{\Delta S^2} = 6Dt$. Now D, the coefficient of diffusion of the gas, is given by $D = 0.0236K$, where K is the ionic mobility in centimeters per second per volt per centimeter. Then, if we let V_0 be the originally ionized volume, and remember that $V_0 = lx_0^2$, we find that $V = V_0 + bt^{1/2}$. b is a constant involving the coefficient of diffusion and the dimensions of the ionized volume, i.e. $b = 4.512\ x_0 D = 4.512 V_0 D/x_0$. The differential equation then reads

$$\frac{dN}{N^2} = \frac{-\alpha\, dt}{V_0 + bt^{\frac{1}{2}}}$$

which on integration yields

$$\alpha = -\frac{10.18lD}{4.512(Dt)^{1/2}/x_0 - \log\cdot(1 + 4.512(Dt)^{1/2}/x_0}\left(\frac{1}{N} - \frac{1}{N_0}\right)$$

or, in terms of potentiometer readings, by the first method of neutralization

$$\alpha = -\frac{300eNT}{C\epsilon R}\cdot\frac{10.18lD}{4.512(Dt)^{1/2}/x_0 - \log\cdot(1 + 4.512(Dt)^{1/2})/x_0}\left(\frac{1}{r} - \frac{1}{r_0}\right).$$

In the runs for which t' was large, an initial correction was also made in x_0, for the diffusion which took place during the exposure. The equation above affects the value of α very little for small values of t, but renders the falling off more gradual for the longer times. The curves, as shown, in Figs. 2 and 3 are corrected in this way.

In as much as some photo and longer range recoil electrons are lost from the volume, during the process of ionization, before they could attach to form ions, the positive and negative readings differed at the start, i.e. $r_{0-} \neq r_{0+}$. Moreover the rate of decrease was not quite the same. This latter effect was attributed to the fact that the positive and negative ions present have different rates of diffusion, due to the different mobilities, the positive rate being less than the negative. The accuracy of these first measurements did not warrant very great refinement in calculation. Therefore, a coefficient of diffusion was used determined from the average value of the two mobilities. This is $D=0.0236\times 2=0.047$, which is as close as D is really known.

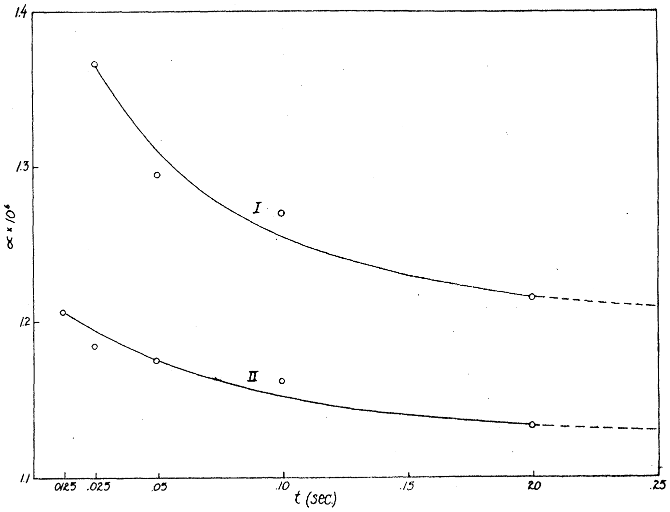

Fig. 4.

α, as determined from the positive and from the negative readings, is not quite the same. Owing to the use of a common value for D, the average value of α was used in plotting and maybe safely assumed to represent the true condition of affairs within the limits of error.

The systematic variation of t', carried out at constant x-ray intensity, produces not only an ageing effect in the ions from run to run, but also a marked change in the number produced. Some measurements were therefore made, using the same values of t' and t, but with different x-ray intensities The intensity was varied by means of the electron current through the tube keeping the applied voltage constant. Thus the ions in each case might be said to have been formed in the same manner, since the x-rays are of equal hardness. The only difference, then, in the conduct of two runs with corresponding intervals, t' and t, lay in the number of ions formed initially. A comparison of two such runs is shown in Figure 4. These curves correspond to curve IV in Figure 3, and are seen to be of the same general type. *α is however consistently much smaller here on curve II than on curve I. Also the lower curve does not show such a sharp rise in α for smaller values of t.* It is important to state that the values of this curve were taken with a higher initial density of ions than was the case on curve I.

The same effect was noted in measurements, taken in argon to which 1 centimeter partial pressure of oxygen in the form of air had been added. The result is shown by the curves, in Fig. 5, which correspond to curve III in Fig. 3. The runs were taken for $t' = 0.0139$ sec and t from 0.00625 sec to 0.15 sec. A ratio of initial ion densities of about 3:1 was obtained. The drop in α, with increase in density, is seen here to be much more pronounced than in the previously discussed case. As before, the lower curve, (curve II), corresponding to higher concentration, does not rise as sharply for small values of t. The significance of these results in relation to others obtained, will be discussed later.

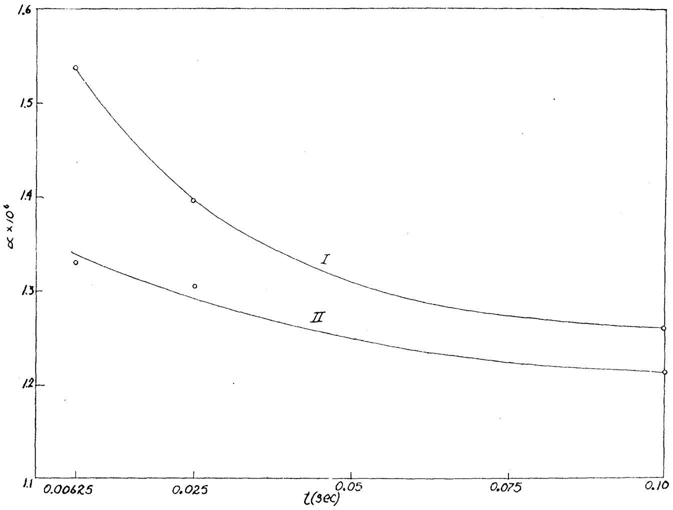

Fig. 5.

Although the accuracy of the readings obtained by this method is well within ± 2 percent, the accuracy of determination of α cannot be so great. In the first place, the value of α depends on the difference, $(1/r)-(1/r_0)$, and a variation of ± 2 percent, in r or r_0, introduces a variation in α which may be much greater and depends on the relative values of r and r_0. In addition, as pointed out, the value of D is not known with certainty, and this introduces an unknown error in this correction. Finally the present measurements were undertaken only as a preliminary survey of the field, with the new method, for the purpose of determining the real conditions existing. Although the method is absolute, no attempt was made to secure high accuracy in this regard, because of lack of time after significant results were obtained. More accurate results can be obtained when certain portions of the equipment are changed to meet the unforeseen difficulties encountered in these measurements. Work is at present under way with a view to extending the field. So far as the relative values of α are concerned the accuracy may be claimed to be fairly high. The absolute values may be said with confidence to hold within a range of ± 10 percent.

2. *Argon.* Thus far the results obtained have apparently had very little bearing on the originally stated goal of this experiment, i.e. the determination of the role of the free electron in recombination. Results obtained by Loeb,[4] on attachment of electrons to molecules, make it possible to estimate that in air any free electrons present will attach to molecules, chiefly of oxygen within 10^{-5} sec after separation from the parent molecule. Consequently it is safe to state that in the measurements thus far described we have been concerned only with recombinations between positive and negative ions. It seemed highly desirable to obtain a series of observations in a gas in which electrons do remain free for an appreciable time. Such gases are hydrogen, nitrogen and argon. Argon was chosen because of the extremely high degree of ionization obtainable with moderate x-ray intensities. A series of runs was made, as before, over ranges of t' from 0.0139 sec to 0.0556 sec, and t, between the limits 0.00625 sec and 0.15 sec. Since the velocity of electrons in a unit field is of the order 10^3 times that for ions, the rate of diffusion must be high. Therefore the first method of measurement described proved impractical. The second method was consequently resorted to and gave satisfactory preliminary results. The negative as well as the positive readings were carefully taken. Free electrons were present in profusion, as evidenced by the behavior of the negative readings as compared with the positive. Even during the short exposure time of 0.0139 sec, enough electrons diffused from the volume to make the intital negative readings far smaller than the positive. As t increased, the rate of decrease of the negative charge was much greater than that of the positive. In the time intervals used, the positive charges could diffuse only a very short distance so that their rate of disappearance was taken to indicate the trend of recombination. The original differential equation, $dn/dt = -\alpha n^2$, assumes equal numbers of positive and negative ions present during the process, and therefore cannot apply here. Consequently the method of calculation of α must also be changed. The modification is as follows:

Let n_+ be the number of positive ions per cc, n_- the number of electrons per cc, α the coefficient of recombination, t the time of recombination, n_0 the number of negative charges initially present (at $t=0$), n' the number of positive ions initially present and n the number of positive ions present after a time t.

Then we write

$$dn/dt = -\alpha\, n_+\, n_-.$$

The disappearance of the negative charges may be ascribed to two causes, namely: recombination and diffusion from the region between the plates.

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[4] L. B. Loeb, Proc. Nat. Acad. Sci. **7,** 5 (1921); Phys. Rev. **17,** 89 (1921); J. Franklin Inst. **197,** 45 (1924); Phil. Mag. **46,** 1088 (1923).

This change is shown, as a function of t, in the negative readings. It was assumed that n_- might be expressed as a function of t as follows:

$$n_- = a/(1+bt).$$

Then at $t=0$, $a=n_0$, and we may write

$$n_- = n_0/(1+bt).$$

When this expression is substituted for n_- in the above equation, integration yields the following expression for α

$$\alpha = \frac{b}{n_0}\,\frac{\log n'/n}{\log(1+bt)} = \frac{b}{n_0}\,\frac{\log r'/r}{\log(1+bt)}\,.$$

Values of n_0, r' and r were measured and calculated as described in the second method. It remained to determine the proper value of b. The values of n_- were plotted as a function of t, yielding curve I in Fig. 6. Then, using n_0 and another point on the curve, b was computed from the relation $b=(n_0-n_-)/n_-t$. Proper choice of b gave a calculated series of values represented by the curve II in Fig. 6. This fit was considered to be sufficiently close to give values of $\varkappa$ well within the limits of error.

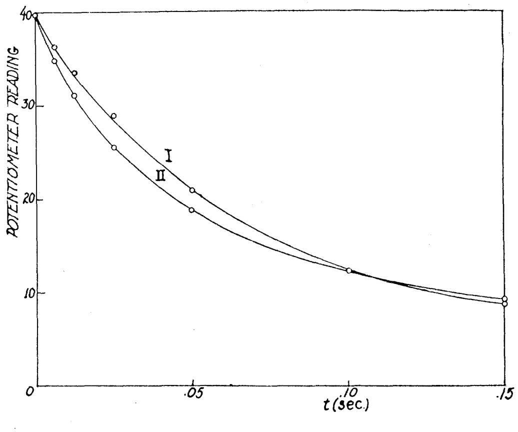

Fig. 6.

The results obtained are shown by the curves in Fig. 7. Curve I corresponds to curve III in Fig. 3. Curve III in Fig. 7 represents a run taken with a longer interval t' and corresponds to curve V in Fig. 3. The curves marked n' and n_0 show the change in these quantities with t'. All these curves are plotted in the same manner as in Fig. 3. The difference in the rate of increase of n' and n_0 is most striking. During the exposure times used, n' does not even approach equilibrium, while n_0 very quickly reaches a maximum. The latter effect may be ascribed to the rapid diffusion of the electrons so that the rate of loss very soon approaches the rate of generation. Most striking, however, is the shape of the curves showing α as a $f(t)$ and the *low values of* α

obtained. These are, in general, about half the corresponding values in air. On the basis of the kinetic theory, α, for argon, would be expected to be about equal to α for air. The sharp drop in the value of the coefficient, which was observed in air for these conditions, is here absent. The significance of these facts will be discussed later.

Two errors enter the above determinations which make the value of α uncertain. The first is introduced by the loss of electrons from the volume ionized. The plates in the chamber were circular, and not designed for this type of measurement, so that electrons may travel several centimeters to the side before passing from the region between the plates. It is therefore possible for the electrons to leave the volume of ionization, and in which the positive ions stay, and still be collected when the charge is swept to the upper plate. This will lead to the measurement of a spuriously high value of n_0 or n_-, corresponding to given values of n' or n. Such an effect would tend to produce a calculated value of α lower than the actual one. On the other hand, electrons diffusing upwards to the collecting plate will tend to increase the measured values of n_0 and n_- and decrease those of n' and n. This is an effect in the opposite direction. Obviously diffusion in and out of the ends will be equal. Electrons lost to the lower plate will not affect the reading, inasmuch as this electrode is grounded except when the ions are being swept out. It is estimated that the two effects will about compensate each other and that the value of α obtained is true within the limits ± 10 percent. Naturally a series of experiments with a chamber designed to eliminate these effects would be most desirable. Such measurements are now being undertaken in this laboratory.

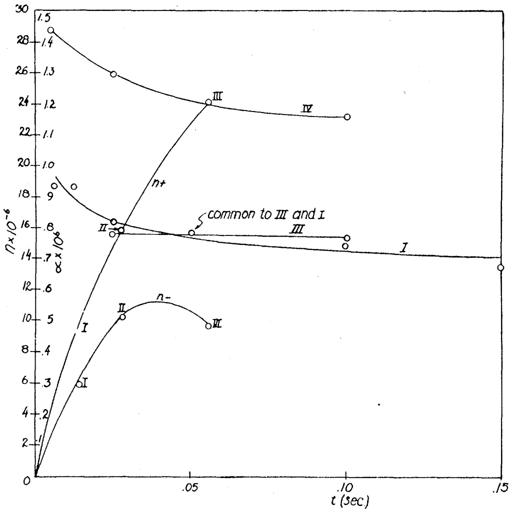

Fig. 7.

3. *Argon mixed with air.* The measurements in argon, to which 1 cm partial pressure of O_2 in the form of air was added, afford interest when compared

with these just described. Curve IV in Fig. 7 corresponds to curve I and is identical with curve I in Fig. 5 and represents the value of α in the mixture. The runs are identical, with the exception of a slight difference in the x-ray intensities used. *The values of α are seen to have risen to the corresponding ones for air.* (curve III, Fig. 3). There was no sign of the presence of free electrons and the positive and negative readings were nearly equal. In calculating and plotting α the same system of averaging was employed as described in the work with air.

PREVIOUS INVESTIGATIONS

The earliest direct[5] measurements were made by Townsend[6] Rutherford,[7] and McClung, [8] who used either air-blast methods or methods in which a gas was ionized by a flash of x-rays and the number of ions remaining after a time t was measured relative to the initial ions present. The coefficient of recombination α is then calculated from the solution of the well-known differential equation

$$dn = -\alpha n^2 dt,$$

which reads

$$\alpha = \frac{1}{t}\left(\frac{1}{n_t} - \frac{1}{n_0}\right)$$

where n_t and n_0 are the number of ions per cm^3 after a time t, and the initial number at $t=0$ respectively. The values of n_t and n_0 are computed from the numbers of ions observed, divided by the volume ionized. These earlier observers found that the value of α so observed was constant and equal to about 1.6×10^{-6} for air. Inasmuch as these results were obtained at a time when the control of experimental conditions was much inferior to that possible later and did not eliminate the effects of diffusion, the conclusions drawn from them, which have been only too generally accepted, must be regarded with caution. More recently Rümelin[9] and Plimpton[10] have carried the measurements further. The work of both these men was excellent, but the conditions under which they worked did not allow of the independent control of the variables, ionization flash period, t', recombination time, t, and ion concentration, n_0, now possible. Both these observers found that, for very short

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[5] Other measurements have been made by many workers including Langevin (reference 1); Bragg and Kleeman, Phil. Mag. **11,** 466 (1906); Kleeman, Phil. Mag. **12,** 273 (1906); Hendren, Phys. Rev. **21,** 314 (1905); Erikson, Phil. Mag. **18,** 328 (1909); Thirkill, Proc. Roy. Soc. **A88,** 488 (1913); Phillips, Proc. Roy. Soc. **A83,** 246 (1909); and Retchinsky, Ann. d. Physik **17,** 518 (1905). The methods employed by these workers were more or less "indirect" so that they did not permit independent control of the important variables t', t and n_0 and thus the effects which are here under discussion were masked.

[6] J. S. Townsend, Phil. Trans. Roy. Soc. **193,** 157 (1900).

[7] E. Rutherford, Phil. Mag. **44,** 422 (1897).

[8] A. McClung, Phil. Mag. **3,** 283 (1902).

[9] Rümelin, Ann. d. Physik **43,** 821 (1914).

[10] S. J. Plimpton, Phil. Mag. **25,** 65 (1913).

time intervals, t' and t, α was high and not constant, dropping rapidly to lower values as the time intervals t' and t increased. Rümelin interpreted his high values as being due to an initial rapid recombination of free electrons and positive ions, an erroneous interpretation as the present results show. Plimpton correctly ascribed his results to an initial non-random distribution of ions due to the mechanism of ionization, a distribution which became more nearly random through diffusion of the ions as time progressed This interpretation, it will be seen, is in good accord with the results herein described. The non-random nature of the initial ionization in the meantime had been discussed theoretically by Jaffe,[11] particularly for the case of α-particle ionization where the columnar effects are much more pronounced than for ionization by x-rays. Finally while the present work was in progress Schemel[12] carried out measurements on α-ray ionization by a direct method of measurement. His results are excellent and are made the basis for discussion in a theoretical paper by Jaffe.[13] While they deal with a more troublesome mode of ionization the conclusions are in good accord with the conclusions of Plimpton and those independently arrived at from the present work before the paper of Schemel's came into the writer's hands. The complications due to α-particle ionization, however, have made the absolute evaluation of α in the work difficult, as pointed out by Jaffe, so that the results of the present investigation may serve to throw some light on this subject.

Discussion of Results

The first feature to excite interest is the unusual variation of the coefficient of recombination as evidenced by the results obtained in air. Except in the measurements of Rümelin and Plimpton and very recently Schemel the sharp increase of α, for short time intervals, t, has not been observed before. Recent investigations have led to a rather clear picture of the mechanism of x-ray ionization.[14] It is now fairly certain that the ions are formed, initially, in pairs. In most of these the ions are separated by relatively small distances. Especially is this true in gases and mixtures such as air, where the electrons attach quite rapidly to form negative ions. It is fairly safe to assume that in air the average initial distance between the ions in a pair is of the order 10^{-3} cm or less. This would correspond to a concentration of 10^9 ions/cc, with uniform distribution throughout the volume and only 10^{-3} cm between any two ions of a pair. Now an initial concentration of the order 10^6 ions/cc, such as calculated for small values of t from the observed readings and assumed volume, corresponds to a distance between ions of 10^{-2} cm at uniform distribution. These facts lead to a clear picture of the conditions existing as the x-rays are cut off following a *short* exposure. The ions must be scattered in pairs rather irregularly throughout the volume,

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[11] G. Jaffé, Ann. d. Physik **43**, 249 (1914); **75**, 391 (1924).

[12] J. Schemel, Ann. d. Physik **85**, 137 (1928).

[13] G. Jaffé, Ann. d. Physik **1**, 977 (1929).

[14] A. H. Compton, X-Rays and Electrons, pp. 227–314.

along the paths of the x-rays and photo and recoil electrons. Due to the fact that some diffusion has taken place between ions formed at the beginning of the x-ray flash, we shall have distances within pairs ranging from less than 10^{-3} cm to somewhat over this amount. Consequently, though there be but 10^6 ions in each cm^3 of gas, the effective concentration may amount to $10^7/\text{cm}^3$ or more. In order to see the effect of such a condition on the results, it is well to consider the simple expression for α.

$$\alpha=\frac{1}{t}\left(\frac{1}{n}-\frac{1}{n_0}\right)=\frac{1}{nt}\left(\frac{n_0-n}{n_0}\right)=\frac{1}{nt}\left(1-\frac{n}{n_0}\right).$$

Now calculation gives $n=N/V$ and $n_0=N_0/V_0$ where N and N_0 represent the total measured numbers of ions in volumes V and V_0 respectively. Then we may write

$$\alpha=\frac{1}{Nt/V}\left(1-\frac{NV_0}{N_0V}\right)$$

The value of α depends on the quantities n_0 and n, which are computed from the ratios N_0/V_0 and N/V. N_0 and N are found by measurement. The values of V and V_0 used are the *total volumes over which the ionization is distributed.* These are consequently much higher, for small values of t' and t, than the effective volumes, which are determined by the distribution in pairs just described. That is to say n, as we determine it is much smaller than the effective n which is influencing recombination, and which, for a given measured N, corresponds to a much smaller effective value of V. Consequently, for a given calculaton, since our evaluation of n and n_0 is much too small, the apparent value of α will be correspondingly high. For a given run, i.e. a given exposure time, t', the error in n_0 will be constant. However, as t increases the ions begin to diffuse apart. The effective value of V is closer to the assumed one and the determination of n is less in error. Consequently the apparent value of α, though still high, will drop off, the drop becoming more gradual as t increases. In other words, we have measured the total number of ions present as a function of t and from this have computed erroneous values of n_0, and of n as a function of t, obtaining a value of α which varies as shown in the curves. The effective value of n_0 and the actual variation of the effective values of n with t, is determined by the initial distribution and the processes of diffusion which ensue. This time varitaion may or may not be such as to make the true value of α constant.

As we increase t' from run to run two things occur. First, the ions are older, when measurement is started, and consequently have had more time to diffuse apart. Second, the total concentration is greater due to the increased exposure to x-rays. Therefore the effective and computed values of n_0 become more nearly the same, and the ions need not diffuse so far before the effective and apparent values of n become equal. The value of α, thus calculated, is lower and drops less sharply with t. Finally at the longer values of t', distribution is nearly uniform before observation of recombination is begun. The apparent and true values of α coincide and are very nearly constant at least for the longer intervals t. As mentioned before, lack of quantitative knowledge concerning the initial conditions of distribution prevents our determining definitely whether the true value of α is constant for the smaller values of t. The experimental evidence however, indicates quite strongly that it is,and that the predominating effect,causing the observed falling off of α, is that described above. The strongest proof of this conclusion lies in the drop observed in the values of α for identical runs, when only the concentrations were increased. This is also in accord with the observed drop, at the beginning of successive runs, for the same values of t. A comparison of the curves, in Fig. 3, with each other, and with the corresponding ones in Figs. 4 and 5 will make the matter strikingly clear.

It is to be noted that the final value of 0.8 to 0.9×10^{-6} toward which α tends in these experiments, is only about half the previously accepted one. It is believed that the value here given is more nearly correct in view of the fact that this result was obtained by a *direct* method, in which the sources of error could be foreseen and avoided, and which made use of the high degree of development of modern experimental technique.

These results also distinguish definitely between the two opposing viewpoints, i.e. of Langevin and J. J. Thomson, mentioned in the introduction, concerning the fundamental process of recombination. If, as assumed by Langevin, the bringing of the ions together be due to the mutual effect of their electric fields, we should expect a very high and practically constant value of α. This would be especially so, inasmuch as the ions are known to be formed so close together initially. The field, if the dominating factor, would also prevent diffusion apart and there should be no marked apparent decrease of the coefficient with time. The contrary is seen to be true. Hence the results obtained seem to be thoroughly in accord with the fundamental assumption of Thomson, i.e. that the ions are brought into the immediate neighborhood of each other by their heat motions and the role of the electrical forces is secondary.

The next feature which claims the attention is the behavior of the coefficient in argon. As stated, we now know that electrons do not attach to atoms of argon to form negative ions. The results set forth here would then indicate that the rate of recombination of electrons with positive ions in argon is very slow compared to the recombination in argon contaminated with oxygen, where electrons are no longer free. This conclusion is borne out by the recent results of Kenty,[15] concerning the recombination of positive ions with electrons following electrical discharges in very pure argon. It is found that the apparent coefficient of recombination between electrons and positive ions in argon is of the order 10^{-10}.

The observed recombination in pure argon must then take place between positive ions and negative carriers of a nature other than electronic. Undoubtedly the electrons must attach to molecules of impurity present in the

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[15] C. Kenty, Phys. Rev. **32**, 624 (1928).

sample of gas used, thus forming negative ions. That sufficient impurity was present to permit such a process to take place is very likely to be the case inasmuch as a metal ionization chamber was used. In such chambers spectroscopically pure gas can still contain impurity enough to cause fairly rapid attachment. The gas was, however, sufficiently pure to make the rate of attachment relatively slow, as shown by the numbers of free electrons observed. The measurements obtained, therefore, are not to be regarded as a true indication of the rate of recombination between electrons and positive ions, but rather as the rate of attachment of electrons to molecules of impurity. This view is nicely substantiated by the effect of adding small quantities of O_2. The percentage of impurity was then sufficiently great to allow rapid attachment, probably within 10^{-3} to 10^{-4} seconds. All evidence of free electrons disappeared, and the recombination rose to the same rapid rate as previously observed in air.

It was also pointed out that the sharp drop in α at short time intervals was absent in pure argon, as evidenced by the flatness of the curves in Fig. 7. The rate of electron diffusion is so rapid in argon that even at the short times involved the distribution of charge was probably completely uniform.

The experiments are now being continued by Mr. Overton Luhr, to whom the writer wishes to extend sincere thanks for his assistance and suggestions in the carrying out of the work in the last stages of this complicated method. Most of all it is desired to thank Professor Loeb, at whose behest the problem was undertaken, for his unfailing interest and kind assistance, rendered both by advice and suggestion, throughout the course of the experiments.