THE RECOMBINATION OF IONS IN AIR AND OXYGEN IN RELATION TO THE NATURE OF GASEOUS IONS

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ABSTRACT

Coefficient of recombination of ions produced by x-rays as a function of the age and initial concentration of the ions. Measurement of the coefficient of recombination of ions in air and oxygen has been continued, with an improved form of the apparatus previously described by L. C. Marshall. Marshall's results in air have been checked, showing a sharp initial drop in the coefficient α for short time intervals ascribed to initial non-random distribution of the ions. Further measurements at longer time intervals have been made, using a new system of calculation whereby α is found as a function of τ, the age of the ions, rather than t, the total time of recombination. In this case α does not drop to a constant value of about 0.8 to 0.9×10^{-6} as indicated by Marshall's results, but continues to drop off to values of 0.5 to 0.6×10^{-6} after the ions have aged for one second, and 0.3 to 0.4×10^{-6} after two seconds. This is for a high initial concentration of ions of about 3.5×10^6 ions per cm^3. With an initial concentration of 1.55×10^6 ions per cm^3, α drops only to 1.15×10^{-6} after a time of one second. In pure oxygen the values of α are in general higher than the corresponding ones for air, although they become equal at low inital concentrations.

Interpretation of results and the absolute value of the coefficient in air. The results may be explained by assuming that heavy slow-moving ions are formed in increasing amounts as time goes on by reaction with impurities present. The faster ions are constantly being removed at a high rate by recombination, leaving the slow ions behind with a resulting increasingly low coefficient of recombination. It is possible that the ionizing agent produces nitric oxides, O_3 or H_2O_2, which load up the ions. It is impossible to set accurately an absolute value of α in air, due to two disturbing factors: initial non-random distribution producing abnormally high values of α at short time intervals, and the loading up of the ions with impurities producing abnormally low values of α at long time intervals. At a time where these two factors have a minimum effect α has the value $1.4 \pm 0.1 \times 10^{-6}$, which is set as the closest approximation to an absolute value.

INTRODUCTION

R ECENTLY in this laboratory L. C. Marshall[1] measured the coefficient of recombination of ions in air and argon using a new direct method with x-rays as a source of ionization. His results showed that the coefficient α given by the equation $dn/dt = -\alpha n^2$ is not a constant as has generally been supposed with a value about 1.6×10^{-6} for air but is a function of three factors: (1) the time of x-ray exposure t'; (2) the initial ion concentration n_0; (3) the time of recombination t. He found that α dropped from a value of 4.0×10^{-6} at short times of recombination to an apparent nearly constant value of about 0.8 or 0.9×10^{-6} at time intervals of about one second. Also, the value of α was in general higher for short times of x-ray exposure and small

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

initial concentrations of ions. The high values at short time intervals were shown by experiment and also by the theory of Loeb and Marshall[2,3] to be due to the initial non-random distribution of the ions which results from their formation in pairs along a β-ray track. The theory indicates that after a time interval of about 2.25×10^{-3} seconds, the value of α should become constant since by that time the ions would attain random distribution due to their heat motions.

The work has been continued by the writer in air and oxygen with essentially the same apparatus as that used by Marshall, although with important improvements in some details and particularly using a new method of measurement and calculation. These results show that the value of α does not become constant after a short time as indicated by Marshall's results but continues to fall off quite rapidly as the ions become older. This leads to important conclusions concerning the nature of gaseous ions.
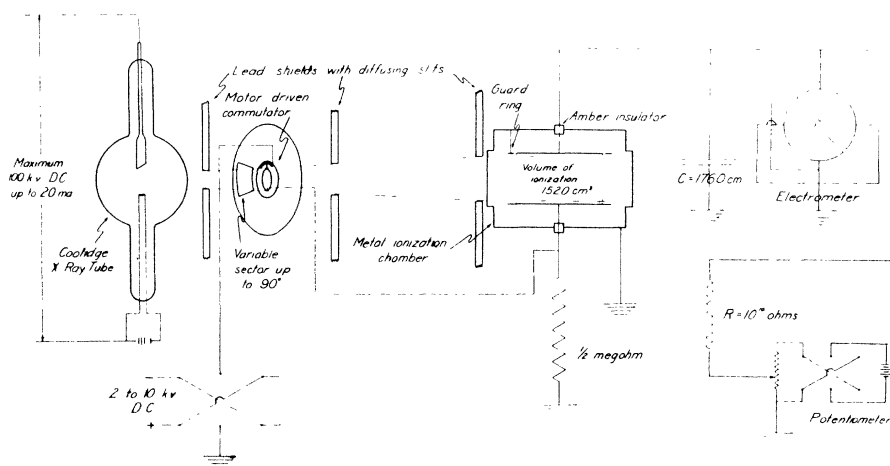

Fig. 1. Diagram of apparatus.

METHOD OF MEASUREMENT

The apparatus and system of measurement has previously been described by Marshall.[1] The essential features are shown in Fig. 1. D.C. potential is applied to the Coolidge x-ray tube by means of a transformer, kenotrons and filter system not shown in the diagram. The x-rays pass through a solid brass rotating disk which has a variable sector from 0° to 90° cut in it, thus producing a flash in the metal ionization chamber. The beam of x-rays is defined by three lead slits and passes through almost two meters of air and an aluminum window before reaching the chamber. The beam is thus sharply defined and nearly homogeneous. The shaft carrying the sector also carries an adjustable commutator by which potentials of 1000 to 10,000 volts may

[2] L. B. Loeb and L. C. Marshall, Jour. Franklin Inst. **207**, 371 (1929).
[3] L. B. Loeb, Trans. Am. Electrochem Soc. **LV**, 131 (1929).

be applied to the lower plate of the chamber. The high field almost instantly sweeps all the ions of one sign to the upper plate at any desired time after the x-ray beam has been cut off by the brass disk. The lower plate is also connected to ground through a one-half megohm resistance so that its potential becomes zero immediately after the brush breaks contact with the commutator segment.

Since the upper plate must also be kept at zero potential during the flash time and time of recombination, a neutralizing mechanism is used to prevent a charge from building up on the plate and electrometer system as a result of the repeated flashes of x-rays. For this the alternate system described by Marshall is used. A current of opposite sign to that collected on the upper plate of the chamber is forced through the high resistance leak R by means of a voltage applied from a potentiometer. Thus, when the electrometer deflection is zero, the two currents are neutralizing each other and the voltage
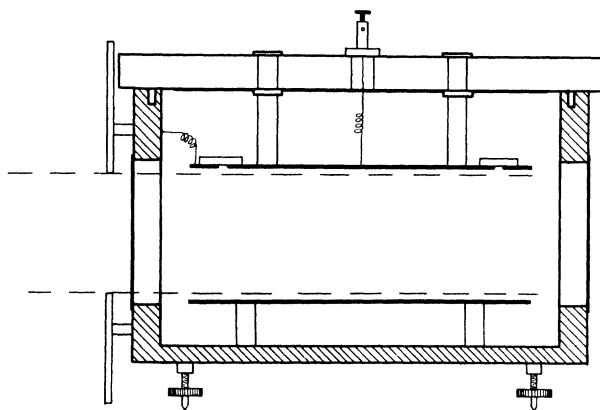

Fig. 2. Ionization chamber.

read directly from the potentiometer will be proportional to the ionic current.

It may be noted that difficulty was encountered in constructing a high resistance leak of the order of 10^{10} ohms which would remain constant over a period of several hours. Experiment showed that an India ink line drawn on typing paper and enclosed in an airtight vessel containing a small amount of P_2O_5 to remove the moisture, was satisfactory. Such a leak exhibits no polarization and stays constant well within 0.5 percent.

The only major change made in the apparatus used by Marshall was the substitution of a new ionization chamber allowing much greater volume of ionization (See Fig. 2). It consists of rectangular brass plates in a heavy brass box fitted with aluminum windows through which the x-ray beam passes. An important feature of the chamber is the plate glass cover to which the upper plate and guard ring are attached by means of amber insulators. The cover is sealed on by means of stopcock grease, a double seal with a groove between being employed to prevent the diffusion of stopcock grease vapor

into the chamber. The stopcock grease is employed only in the outer seal, all excess grease being forced either outside or into the groove. The total volume of ionization is 1520 cm^3 compared to 63 cm^3 in Marshall's apparatus. The advantages of this large volume are: (1) the ionic currents are much larger and can be measured more accurately; (2) the volume can be determined more accurately and diffusion plays a smaller though still appreciable role. In this connection it may be noted that the x-ray beam extends well beyond the sides of the plates; so that only diffusion toward the plates must be considered; not that toward the sides or ends.

The air and oxygen used in the ionization chamber were purified according to standard technique, all dust, moisture, CO_2 and organic vapors being removed by passage through glass wool, $CaCl_2$, sodium calcium hydrate, P_2O_5, and two liquid air traps. Special care was taken to remove organic substances by cleaning the metal chamber thoroughly with cleaning solution.

In calculating α the integrated form of the well-known equation,

$$\frac{dn}{dt} = -\alpha n^2 \tag{1}$$

is used, where n is the number of ions of either sign per cm^3. Integration gives:

$$\alpha = \frac{1}{t}\left(\frac{1}{n} - \frac{1}{n_0}\right) \tag{2}$$

where t is the time of recombination, n_0 is the number of ions per cm^3 at $t = 0$ and n is the number of ions left after time t. Inserting the experimental constants Eq. (2) becomes:

$$\alpha = \frac{1.59 \times 10^{-19}RNV}{\epsilon} \frac{1}{t}\left(\frac{1}{r} - \frac{1}{r_0}\right) \tag{3}$$

where R is the value of the high resistance leak in ohms, N is the number of revolutions per second of the commutator, V is the volume of ionization, ϵ is the e.m.f. of the neutralizing potentiometer battery in volts, and r and r_0 are the direct potentiometer readings at the time $t = t$ and $t = 0$ respectively.

In the method of calculation one important change is made from that used by Marshall who measured n_0 the number of ions at the instant the x-ray flash was cut off, then n the number left after varying time intervals t. α was calculated between these two limits thus giving an average value over the whole time of recombination. In the present work values of n_0, n_1, n_2, $\cdots$ are measured at short intervals of time 0, t_1, t_2, $\cdots$. Then α may be calculated between any two of these intervals. That is, Eq. (2) becomes of the form:

$$\alpha = \frac{1}{t_p - t_q}\left(\frac{1}{n_p} - \frac{1}{n_q}\right). \tag{4}$$

This allows α to be studied as a function of the age of the ions rather than as a function of the time of recombination after the x-rays are cut off. Setting τ as the average age of the ions over any period of recombination $t_p - t_q$ and assuming $\tau = 0$ at $t = 0$ we have:

$$\tau = t_q + \frac{t_p - t_q}{2}.$$ (5)

If $t_p - t_q$ is a short time interval compared to the maximum time allowable at any particular commutator speed, τ is a fairly accurate measure of the age of the ions and the variation of α with τ can be studied.

Results

The first series of runs were taken as a check on Marshall's work and show results similar to his, α being plotted as a function of t the time of recombination (see Fig. 3). Each succeeding run was taken with the commutator speed one-half that of the previous run. These show the sharp initial drop due to the non random distribution of the ions with the apparent flattening out of
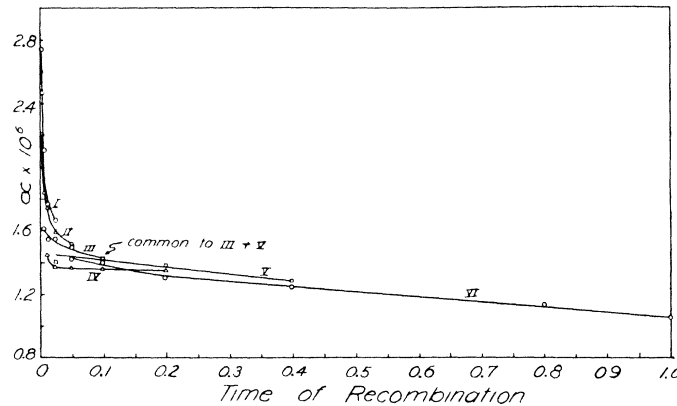

Fig. 3. First six runs corrected for diffusion.

the curves at longer time intervals. The final value at one second is about 1.03×10^{-6} compared to Marshall's value of 0.9×10^{-6}. This is due to a very short time of exposure (0.01562 seconds which was kept constant throughout the series of runs by narrowing the sector) and a resulting low initial concentration of the ions. The matter of initial concentration is important even at long time intervals as will be seen later.

All later runs were taken by measuring n at short intervals of time thus making it possible to calculate α as a function of τ the age of the ions, as well as a function of t the time of recombination. All the curves (Fig. 5) show without exception a continued drop in α up to a time of two seconds, the maximum time which could be studied. At the end of these long time intervals α still shows no indication of becoming constant although the slope of the curves gradually decreases.

Fig. 4 shows a comparison for one particular run of the two methods of calculating α. In the upper curve, α is plotted as a function of the time of recombination, in the lower curve as a function of τ the age of the ions. In the lower curve α drops more sharply than in the upper. In other words, Marshall's results gave an average high value of α rather than the true value at any particular time. However, on the magnified scale of Fig. 4, α still drops quite sharply even with Marshall's method of calculating, while it appeared to be nearly constant on the scale used in Fig. 3.

Values of α calculated as a function of τ do not lie as close to a smooth curve as those calculated as a function of t. (See Fig. 4). This is because α is obtained for comparatively small differences in the potentiometer readings, especially at the later time intervals when the concentration of ions
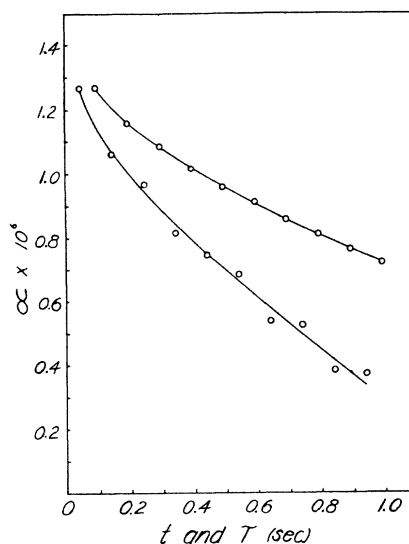

Fig. 4. Comparison of two methods of calculating α.

Чas become small and very little recombination takes place. Thus small errors in the potentiometer readings may result in large errors in the calculated values of α. However, the points show a definite trend in every case. This is more important than the absolute values since a final definite value of α does not seem to exist.

Fig. 5 shows the complete results for all the runs taken over the longer time intervals in air and oxygen. α is plotted against τ, the age of the ions, and the curves are all averages of values taken from two or more runs which may vary by considerable amounts due to an overcorrection for diffusion at the longer time intervals which will be discussed later. The dotted lines show the results in oxygen and the full lines those for air.

Curve I is a run taken with the commutator revolving at the rate of two revolutions per second; curve II, one revolution per second; curve III 0.5 revolutions per second; curve IV 0.25 revolutions per second; all at rather

high intial ion concentrations varying from 2.5 to 3.5×10^6 ions per cm^3. Curve V is taken in air at 0.5 revolutions per second corresponding to curve III, only in this case the initial concentration was reduced to 1.55×10^6 ions per cm^3 compared to 3.5×10^6 for curve III. As can be seen, the values of α for the low concentration are much higher than those for high concentration although the slope of the curve is approximately the same in each case.

Curves VI, VII and VIII are those for pure oxygen; VI corresponding to III for air, VII corresponding to V and VIII corresponding to IV. Curve VI is much higher than the corresponding curve III for air at the same initial concentration. For low concentrations the oxygen and air curves (V and VII) are approximately the same although the points do not fall on a smooth curve due to the extreme difficulty of measuring the coefficient accurately at these low concentrations. The trend is very definite however,
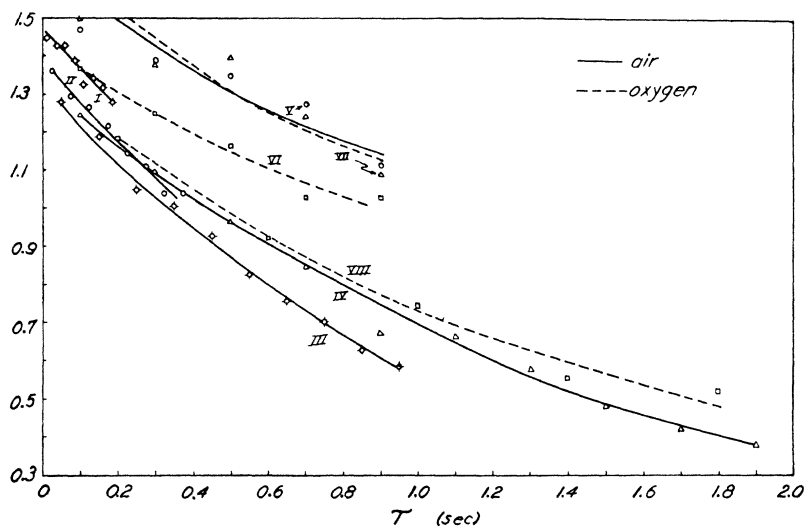

Fig. 5. Complete results for all runs taken over the longer time interval in air and oxygen.

and shows the slope to be about the same as for the curves taken at higher concentrations. Curve VIII for the longest time intervals in oxygen is only slightly higher than the corresponding curve IV for air although there is a distinct difference.

One question which must be considered in connection with these results is the correction for diffusion. Two types of runs were made: one with the beam of x-rays grazing though not touching the plates; so that the whole volume between the plates was ionized; and another with the beam about one centimeter from the plates. In general if no diffusion correction is made, the values of α obtained in each case are nearly the same. If, however, correction is made for diffusion, the values are higher when the beam is one centimeter from the plates, especially at the longer time intervals. This results from the fact that the correction is in the opposite direction in the two cases.

For the case when the beam grazes the plates, a certain number of ions diffuse to the plates during the time of recombination and are thereby lost. This loss is in addition to the loss due to recombination. The number lost by diffusion may be calculated, and this number then added to the measured value n_p at the time t_p to give the true value due to recombination alone. The number diffusing to the plates in time $t_p - t_q$ is given by

$$2n_pA[(\overline{\Delta x})_p - (\overline{\Delta x})_q] \text{ where } (\overline{\Delta x})_p = \left(\frac{4Dt_p}{\pi}\right)^{1/2} \text{ and } (\overline{\Delta x})_q = \left(\frac{4Dt_q}{\pi}\right)^{1/2}$$

n is the number of ions per cm^3 of either sign, A is the area of each plate, $\overline{\Delta x}$ is the average distance an ion diffuses in the time t derived from the Brownian movement equation,[2] and D is the coefficient of diffusion having a value about 0.047. The number

$$2n_pA\left[\left(\frac{4Dt_p}{\pi}\right)^{1/2} - \left(\frac{4Dt_q}{\pi}\right)^{1/2}\right]$$

being added to the measured value of n_p serves to reduce the uncorrected value of α by as much as ten percent.

Marshall has derived a rather complicated equation for the case when the beam is some distance from the plates but this is not readily applicable when α is calculated as a function of τ rather than t. In this paper therefore, a correction is made assuming a swelling of the volume of ionization due to diffusion which gives approximately the same results as Marshall's equation. In calculating α at any time τ the volume is assumed to be:

$$V = V_0 + 2A(\overline{\Delta x})_\tau = V_0 + 4A\left(\frac{D\tau}{\pi}\right)^{1/2}.$$

Since V occurs in the numerator of Eq. (3) this increases the value of α over that calculated without the diffusion correction.

From the fact that the diffusion correction throws the values of α as much as twenty percent apart at the longest time intervals there is apparently an overcorrection for this effect in the equations and values used. This would follow if the coefficient of diffusion becomes less for the ions remaining after long time intervals. Other factors may further reduce the actual rate of diffusion, but from a kinetic theory standpoint a correction like that indicated is necessary. As it does not seem justifiable to omit the correction, all the results are calculated in this manner and the average of the two types of runs is taken in plotting the curves in Fig. 5. The absolute value of α in the curves may be too high or too low by several percent especially for large values of τ since the correction for the case when the beam is one centimeter from the plates is greater than for the case when the beam is grazing the plates. However, the important fact remains that in every case, no matter whether a diffusion correction is made or not, the value of α still drops off continuously with the aging of the ions.

Summary of Results and Conclusions

From the curves in Fig. 5 the behavior of α may be summed up as follows:

(1) α is not a constant as has always been supposed, but beyond the sharp initial drop due to the non-random distribution of the ions, the curves continue to drop indefinitely as the ions age. At the end of one second the value of α is 0.5 to 0.6×10^{-6}; at the end of two seconds, 0.3 to 0.4×10^{-6}.

(2) The lower the initial concentration of ions, the higher the value of α after random distribution has been attained. The value for an initial concentration of 1.55×10^6 ions per cm^3 drops to about 1.15×10^{-6} at the end of a second compared to about 0.6×10^{-6} when the initial concentration is 3.5×10^6 ions per cm^3. However, the slope of the curves is about the same in each case.

(3) The values of α in pure oxygen are in general higher than the corresponding ones in air although they become equal when the initial concentration of the ions is small. The slope of the curves is still the same indicating that the same type of aging effect is taking place.

At first glance it would seem impossible to explain these results by any reasonable assumption. *However, the whole situation becomes clear at once if it is supposed that as time goes on some of the ions form clusters with the impurities present.*

Although special care was taken to remove organic vapors such as ether, alcohol, stopcock grease, etc., which are known to affect the nature of the ion, the number of these heavy molecules present was probably comparable to the number of ions. In addition, water vapor may be present coming from the walls of the metal chamber and there is the possibility that the intense hard x-rays form small quantities of nitric oxides, O_3 or H_2O_2. Any of these impurities might form large ion clusters in increasing quantity during the time of measurement. The method is particularly sensitive to impurities as the small, fast moving ions are removed first by recombination leaving the heavier ions as time goes on. Hence α drops continuously.

The supposition that impurities formed by the x-rays form clusters is in agreement with the work of Tyndall, Grindley and Sheppard,[4] also that of Erikson.[5] Erikson showed definitely that the presence of β-rays from radium emanation tubes formed impurities which hastened the aging of the ions so that clusters formed in about 0.001 second. Passage of the gas through a metal ionization chamber which had not been thoroughly cleaned also hastened the aging although to a lesser degree. If neither the β-rays or metal ionization chamber were present there was no appreciable aging effect up to 0.1 second.

Since measurements of the coefficient of recombination in pure oxygen give in general higher values than in air, it would seem that the extremely low values in air are due in part to nitric oxides. The fact that low initial ion concentrations give higher values of α than high initial concentrations is

[4] Tyndall, Grindley and Sheppard, Proc. Roy. Soc. **A121**, 125 (1928).

[5] H. A. Erikson, Phys. Rev. **34**, 635 (1929).

further evidence that clusters of some sort are forming and that the more intense the ionizing agent the more impurities there are present to retard recombination.

It has always been a moot question as to the true nature of ions in gases of normal purity such as are used in this experiment. Practically the only evidence on this subject is from mobility measurements. Erikson's well-known aging of the positive ions gives an indication of clustering and Loeb's measurements in mixtures show definitely that clustering occurs in some gases. Apparently in other gases the ions may consist of single molecules or at any rate small aggregates. However, the evidence from mobility measurements is incomplete in two respects: first because the measurements are generally made within a time interval of less than one tenth of a second after the ions are formed, and second because the mass factor is an unimportant one in mobility; i.e., the mobility is decreased very little by a considerable increase of mass.

The coefficient of recombination measurements are more reliable since in this case the ions can be studied up to time intervals of two seconds after they have had a chance to collide with all kinds of impurities and the faster ions have been weeded out by recombination. In addition, the mass factor is much more important than in mobility or diffusion. On J. J. Thomson's[6] theory of recombination which Loeb and Marshall[2] have shown to be a correct approach to the problem, α is proportional to the velocity of thermal agitation of the ions. The velocity of thermal agitation is in turn inversely proportional to the square root of the mass. The better of two equations as given by Loeb and Marshall after inserting the various constants turns out to be:

$$\alpha = 1.9 \times 10^{-5}\left(\frac{273}{T}\right)^{3/2}\left(\frac{1}{M}\right)^{1/2}\epsilon$$

where T is the absolute temperature, M is the molecular weight of the ions, and ϵ is the probability that recombination will occur if the ions approach each other within a defined distance d. For the case of air or oxygen at room temperature and 760 mm pressure the theory gives ϵ a value of about 0.9 which, however, may be too high. T is about 295° so that the equation reduces to:

$$\alpha = 1.51 \times 10^{-5}\left(\frac{1}{M}\right)^{1/2}.$$

If α has a value of 0.4×10^{-6} which is the lowest observed in this work, it turns out that M the molecular weight of the ions is about 1400. This seems unreasonably high but is not inconceivable if there were a large cluster of heavy molecules. The equation, however, is correct only to the roughest approximation and probably gives high values of α. As a result, the mass, which varies inversely as the square of α may be much less than 1400.

[6] J. J. Thomson, Conduction of Electricity through Gases, III Edition, Cambridge 1928.

The only conclusion which can safely be drawn is that little is actually known concerning the nature of gaseous ions, but that in gases of normal purity that are ordinarily used in gas ion work, clusters of large mass are formed, due probably to the effect of the ionizing agent. The process of cluster formation and weeding out of the faster ions by recombination continues for at least two seconds after the ions are formed. The exact nature and true mass of these clusters cannot be accurately determined owing to the lack of a completely satisfactory theory.

The absolute value of α in air. It appears to be of considerable interest to know the absolute value of α in air for use in numerous calculations. It is evident from the results in this paper that there are two factors which make it impossible to set an accurate absolute value. The first factor is the initial non-random distribution of the ions which produces very high apparent values of α at short time intervals and the second is the loading up of the ions with impurities and selective recombination which produces abnormally low values of α at long time intervals. Probably the closest approach to an absolute value is at a time when the ions have nearly attained random distribution but clustering and elimination of the faster ions has not yet played a major role. In other words, a point must be chosen on the curves in Fig. 3 where the sharp drop in α ends and the more gradual steady drop due to clustering begins. Such a point appears to lie between 0.05 and 0.1 seconds where the value of α is $1.4 \pm 0.1 \times 10^{-6}$. This is not much different from the commonly accepted value of 1.5 or 1.6×10^{-6} which has been determined by earlier investigators under conditions where, in general, these important disturbing factors have not been detected, or at any rate not clearly differentiated. The value of 1.4×10^{-6} for air may then be used with some degree of confidence under conditions where the ions have attained random distribution but have not aged more than one-tenth of a second.

In conclusion, the writer wishes to express his appreciation to Dr. Marshall who designed and constructed the fundamental parts of the apparatus; to Mr. G. P. Kraus of the shop who accomplished a difficult piece of work in building the ionization chamber; and to Mr. N. E. Bradbury who assisted in taking some of the later readings. Particularly, the writer wishes to thank Professor Loeb for his unfailing interest in the work and for his suggested explanation of the experimental results.

At present, the measurements are being continued in other gases, particularly argon and hydrogen.