certain extent by the fact that it gives a value for titanium (49) which is close to the values for titanium (48) found by direct comparisons with oxygen and carbon. The values for iron 54 and 56 deduced by different methods are close together as are also the values for zinc.

In Table II mass comparisons are given between atoms for which neither mass is known accurately at the present time. As soon as further observations give a value for one of the masses, the comparison may be used to deduce the other. The values are also of immediate interest in connection with the packing fraction curve. Theoretical curves may be tested and a probable curve drawn in which the masses agree with all the comparisons in Table II as well as with the values in Table I. A discussion of this curve will be given in a later paper.

The author is indebted to Dr. A. E. Shaw for assistance in preparing the electrodes, and to Mrs. G. S. Monk for carrying out most of the computations.

JANUARY 1, 1938 PHYSICAL REVIEW VOLUME 53

The Recombination of Ions in Pure Oxygen as a Function of Pressure and Temperature

Milton E. Gardner
Department of Physics, University of California, Berkeley, California

(Received October 25, 1937)

All previous investigations of the coefficient of recombination in pure gases have employed the older technique which did not allow the use of an outgassed chamber and made no corrections for initial recombination, diffusion, etc. This work was undertaken in pure oxygen in order to compare the results with existing theories. Aside from the initial drop in the curves of the recombination coefficient plotted against time due to preferential and initial recombination, the value of the coefficient of recombination in oxygen was found to be constant at a given pressure over extended intervals of time. It was, accordingly, possible to obtain a definite and probably correct value for the coefficient of recombination in pure oxygen at 76 cm pressure and 25°C. This value is $\alpha=(2.08\pm0.05)\times10^{-6}$. Comparison of the variation with pressure in the range 10 cm to 76 cm pressure was approximately in good agreement with the theory of J. J. Thomson assuming the ion to have a mass of $M=64$ and a mean free path of that given by mobility measurements. The temperature variation between the limits of -78°C to $+105$°C verified the Thomson equation quite accurately using the same data concerning the ion. At the lowest temperature a deviation was observed, indicating a possible increase of ionic mass to 96. While these results are a good confirmation of the Thomson theory they cannot be reconciled with the Langevin theory, although the Langevin theory probably holds beyond 10 atmospheres. Loeb has indicated the character of the transition between the two theories. The outstanding difficulty introduced by the change in the coefficient with time, due presumably to initial recombination, which is impossible of analysis in the less pure gases of the previous workers, is now somewhat more amenable to treatment. It is shown that if one includes the retarded diffusion of the ions created within ten times the radius of the sphere of active attraction, the time intervals involved in the x-ray flash periods, and the gradual formation of ions of mass $M=64$ from the initially ionized particles which may be accelerated by x-ray irradiation, the rough theory of initial recombination given by Loeb will account for the behavior.

Introduction

When equal numbers of positive and negative ions in a gas are left in a field free space far from the walls of a container they recombine at the rate,

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

where n is the density of ions of either sign and α is the coefficient of recombination.[1] Now experiments evaluating α have shown that under varying conditions ranging from 100 atmospheres of pressure to pressures in discharge tubes the processes giving rise to an α are of diverse types.[2]

---

[1] L. B. Loeb, *Kinetic Theory of Gases*, second edition, pp. 583–600. J. J. Thomson, *Conduction of Electricity through Gases*, third edition, Vol. 1, pp. 20–57.

[2] W. R. Harper, Proc. Camb. Phil. Soc. **28**, (Part II) 219 (1932); I. S. Bowen and E. F. Cox, Phys. Rev. **51**, 232 (1937).

In recent years it has therefore become desirable to classify recombination processes into one of several categories in which the value of α and the mechanisms involved may be very different. In order properly to present the scope of this investigation the recombination processes will be classified as follows:

1. Electron recombination; free electrons with + ions, a relatively improbable radiative process for which $\alpha \sim 10^{-10}$. It does not occur appreciably in gases ionized by x-rays due to low ion densities but may occur in discharge tubes plasma.

2. Normal or volume recombination; + and − ions randomly distributed in space, $\alpha \sim 10^{-6}$, which is the process concerned in this investigation. It predominates with ion densities of intermediate magnitudes shortly but not immediately after ionization, at pressures of one atmosphere and below. It is governed by the theory of J. J. Thomson.

3. Initial recombination occurring where x-ray or β-ray processes result in electron attachment and negative ion formation near the + ion of the initially ionized molecule. The ions are distributed in pairs which gives a fictitiously high value of the coefficient. It is important for time intervals less than 0.1 sec. after ionization in O_2 and is quite pronounced at lower pressures and lower ion densities. It disappears as an important factor with increase in time after ionization due to diffusion. This process will be discussed in this work.

4. Columnar ionization takes place chiefly with α-particle or proton ionization in gases, where high densities of ions occur in columns. This has theoretically been analyzed successfully by Jaffé[3] and the validity of the equation has been checked.[4] It does not concern this study.

5. Preferential recombination where the electrons attach to form a − ion within the sphere of active attraction d of the parent + ion. Here d is given by $d = e^2/[(\frac{3}{2})kT]$. It occurs at higher pressures, 10 atmospheres and up in O_2 and air, and follows according to Langevin's theory. At low pressures it is unimportant except for very low ion densities. It is of great importance in cosmic-ray studies and can be avoided by use of inert gases.

Two theoretical equations for α based upon entirely different assumptions have been derived. The theoretical value of α as developed by Langevin[5] assuming the motion of the ions to be largely governed by their electrical attractions gives,

$$\alpha = 4\pi e(k_+ + k_-)\epsilon, \tag{2}$$

where e is the electronic charge, k_+ and k_- are the ionic mobilities of the positive and negative ions respectively, and ϵ is a correction factor less than unity at atmospheric pressure but approaching unity at high pressures, which cannot be theoretically computed on this theory. The Langevin theory makes α depend upon the mobility k of the ions which varies inversely with the pressure, is nearly independent of the temperature at constant density and depends largely upon the mean free path L and relatively little on the mass of the ion. The factor ϵ being unknown served merely as a correction factor to make the experimental values conform to theory and could be evaluated experimentally from Langevin's method of measurement.

The theoretical value of α as derived by J. J. Thomson[6] assumes that recombination is largely governed by the random heat motions of the ions and molecules, and gives

$$\alpha = 2^{\frac{1}{2}}\pi d^2 C\epsilon. \tag{3}$$

Here C is the root-mean-square thermal velocity of the ions and $d = e^2/[(\frac{3}{2})kT]$ is the distance where the potential energy of one ion in the field of the other is equal to the kinetic energy of thermal agitation of the ions and molecules of the gas. The probability ϵ that recombination will occur after the ions have approached to within a critical distance d where active attraction sets in was derived by Thomson as

$$\epsilon = 2w - w^2, \tag{4}$$

where
$$w = 1 - 2[1 - e^{-x}(x+1)]/x^2, \tag{5}$$

$x = 2d/L$, and L is the mean free path of the ions.

---

[3] G. Jaffé, Ann. d. Physik **42**, 303 (1913).

[4] J. Schemel, Physik. Zeits. **1**, 977 (1929); **30**, 849 (1929); **85**, 137 (1928).

[5] L. B. Loeb, *Kinetic Theory of Gases*, first edition, pp. 479–483. P. Langevin, Ann. de Chim. et Phys. **28**, 433 (1903).

[6] L. B. Loeb, *Kinetic Theory of Gases*, second edition, pp. 592–598. J. J. Thomson, *Conduction of Electricity through Gases*, third edition, Vol. 1, pp. 40–47.

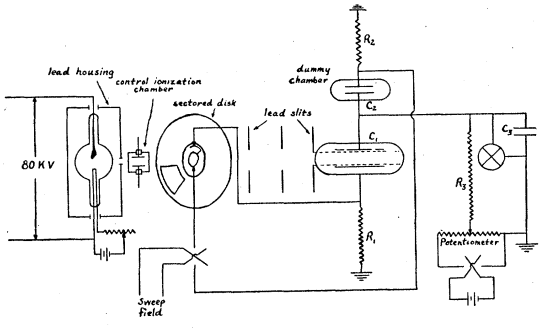

FIG. 1. Arrangement of apparatus.

The value of α as derived by Thomson depends not only upon the pressure and temperature at constant density but it is also primarily a function of the mass M of the ion. The equation as derived by Thomson, after inserting known constants, becomes,

$$\alpha = 1.90 \times 10^{-5}(273/T)^{\frac{3}{2}}(1/M)^{\frac{1}{2}}\epsilon, \tag{6}$$

where ϵ is a function of x and

$$x = 0.810(273/T)^2(P/760)(La/L) \tag{7}$$

the factor La/L being the ratio of the mean free path of molecules in air at N.T.P. (about 1×10^{-5} cm) to the mean free path of the ions in the gas at N.T.P. This ϵ is not logically applicable to the Langevin theory although Richardson derived it for that purpose.

Several measurements in the past have been made of the recombination of ions as a function of pressure and temperature for different gases, but there is a considerable amount of discrepancy in the results obtained by the different investigators.[7] This discrepancy can be attributed to the fact that the experiments were not performed under comparable conditions. The investigators did not all work in the same region of ion age, they used different types of ionizing agents, the gases employed were far from pure, they neglected diffusion and in experiments employing air blasts there was a great deal of turbulence. Heretofore no measurements of α as a function of pressure and temperature have been made employing the modern technique of thoroughly outgassing the ionization chamber prior to the introduction of carefully purified gases of a single molecular specie in which ion formation is insured before measurements begin, and where initial recombination is eliminated.

APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus and procedure were essentially the same as those employed by Marshall[8] and Luhr[9] except for some important modifications. The essential features of the apparatus are shown in Fig. 1. First among the modifications was an ionization chamber which was placed in the beam of x-rays so that the radiation could be observed and maintained constant. To compensate for the charge induced on the electrometer system by the sweep field, a dummy chamber was employed so that a potential of opposite sign could be applied to the lower plate of this chamber. By adjusting $R_2/R_1 = C_1/C_2$ the induced charges canceled. Instead of having all metal chambers as in the earlier work, the recombination chambers were made of glass.

Two recombination chambers were used, one having an ionized volume of 190 cm^3 and one an ionized volume of 700 cm^3. The chambers consisted of rectangular monel metal electrodes sealed inside of Pyrex glass tubes. The lower plate was connected through a resistance R_1 to ground and to a brush in contact with the commutator. The upper electrode was connected to a capacity and a Compton electrometer. Surrounding the upper electrode was a wide guard ring directly connected to ground. Mid-potential vanes, not shown in the figure, were also installed to maintain the lines of force straight from the lower plate to the collecting electrode, and were connected to appropriate points along R. The course of the fields involved was tested electrolytically on cross-sectional models. Electrostatic shielding was accomplished by surrounding the metal electrodes with a cylindrical screen made of monel metal which fitted closely to the glass inside the tube. In the smaller chamber the ends of the screen were

---

[7] P. Langevin, Comptes rendus **87**, 177 (1902); R. J. McClung, Phil. Mag. **3**, 283 (1902); L. L. Hendren, Phys. Rev. **21**, 314 (1905); H. Thirkill, Proc. Roy. Soc. **A88**, 590 (1913); H. A. Erickson, Phys. Rev. **27**, 473 (1908); H. A. Erickson, Phil. Mag. **18**, 328 (1909); H. A. Erickson, Phil. Mag. **23**, 747 (1912); H. Philips, Proc. Roy. Soc. **A83**, 246 (1910).

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

[9] O. Luhr, Phys. Rev. **35**, 1394 (1930); O. Luhr, Phys. Rev. **36**, 24 (1930); O. Luhr and N. E. Bradbury, Phys. Rev. **37**, 998 (1931).

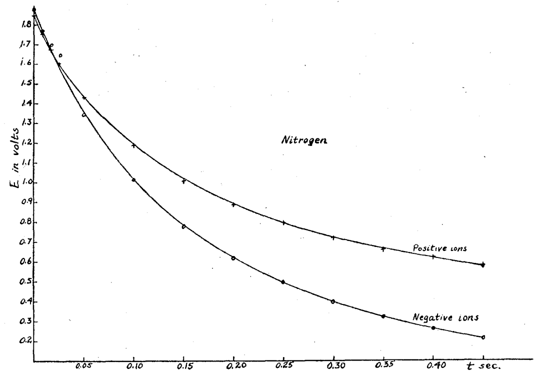

FIG. 2. Relative number of ions in the ionization chamber after a time t.

closed with thin sheet aluminum. In the later chamber the contact potentials present in the first chamber were reduced by making the electrostatic shield entirely of monel metal screen. Since the chambers were made of Pyrex glass it was possible to thoroughly outgas them at 400°C for several hours prior to the introduction of the carefully purified gas.

The oxygen employed was commercial tank oxygen which was purified in a manner similar to that used by Bradbury.[10] The oxygen which was slowly admitted to the purifying train first passed through a liquid-air trap than through a tube of heated copper oxide, then through tubes of $CaCl_2$, KOH, P_2O_5 and finally to a second liquid-air trap. At half an atmosphere of pressure liquid oxygen collected in the liquid-air traps. After pumping off the first fraction of the gas, the gas was permitted to enter the ionization chamber after passing through another liquid-air trap which separated the chamber from contamination by mercury vapor and stopcock grease from the rest of the system. The liquid oxygen was thus fractionally distilled into the recombination chamber insuring a high degree of purity. In order to make a run at atmospheric pressure, the liquid-air flask on the last trap was replaced by a flask of frozen alcohol and the oxygen allowed to distill into the tube. Below half an atmosphere pressure, a liquid-air flask could be used on the trap.

In taking measurements, the charge collected on the electrometer system was measured as a function of the age of the ions in the same manner employed by Marshall[8] and Luhr.[9] Integration of Eq. (1) gives

$$\alpha = 1/t(1/n - 1/n_0), \tag{8}$$

where t is the time during which the ions recombined after the termination of the x-ray flash, n_0 the ionic density at $t=0$ and n the ionic density after a time t.[11] Inserting the experimental constants in Eq. (8) gives,

$$\alpha = 1.59 \times 10^{-19}(RfV/t)(1/E - 1/E_0), \tag{9}$$

where R is the value of the high resistance, R_3, in ohms between the potentiometer and the electrometer, f the frequency of rotation of the sectored disk, V the volume of ionization and E and E_0 the potential in volts read from the potentiometer at the time $t=t$ and $t=0$, respectively.

EXPERIMENTAL RESULTS

Measurements were first made on purified nitrogen in which electrons do not attach to form negative ions but remain free.[10] The measurements were made in an attempt to determine the rate of electron recombination mentioned as process 1. With carefully purified nitrogen introduced into the outgassed glass chamber of 190 cm^3 ionized volume, electrons were found to be in profusion as evidenced by the high diffusion rate of the negative ions. A typical result obtained is shown in Fig. 2. The ordinates are the potentiometer readings in volts which are proportional to the number of ions in the chamber. The curves therefore show the proportional numbers of ions remaining in the tube after a time t. The negative ions fall off more rapidly with time than do the positive ions. Thus due to the extremely high diffusion rate of electrons, they diffused out of the space, leaving a positive space charge. The positive space charge in turn increases the rate of diffusion of the positive ions out of the chamber. Since this loss by diffusion may be comparable or even greater than the loss by recombination, this makes a calculation of α impossible. Analogous conditions obtain in

---

[10] N. E. Bradbury, Phys. Rev. **40**, 508 (1932).

[11] Since α is nearly constant with time in the region where data are to be used in this work this equation was used in place of the more accurate equation of Luhr, reference 9, $\alpha_t = (1/t_2 - t_1)(1/n_2 - 1/n_1)$. It gave more accurate values because of the larger differences in potentiometer readings.

the positive column of glow discharge tubes. Consequently further investigations in nitrogen were abandoned as electron recombination was obviously orders of magnitude less than diffusion losses. Attention was then turned to an accurate evaluation of α as a function of temperature and pressure in a pure molecular gas where electrons attach to form ions rapidly and where complications due to aging were a minimum, in order to test the Thomson theory.

The gas chosen was pure O_2 as Luhr[12] and Bradbury[13] have shown that the ions are relatively simple and attachment is rapid. In most of the runs with oxygen, readings were taken of both positive and negative ions and the values obtained averaged. Fig. 3 shows a series of values taken at atmospheric pressure and room temperature with the chamber of 190 cm^3 ionized volume, with the sectored disk rotating at different speeds. For short time intervals there is a sharp decline in α as was observed by Marshall[8] and Luhr.[9] This is due to the nonrandom distribution of the ions shortly after being formed. This initial recombination takes place in short time intervals while the ions are diffusing to a random distribution. Since the sharp decline in α at short time intervals is due to nonrandom distribution of the ions this effect should be more pronounced at lower pressures where the ionic densities are correspondingly decreased. Fig. 4 shows a set of runs taken at half an atmosphere with the small chamber. The ionization in this case is just half that obtained at atmospheric pressure, and the sharp decline in α with short time intervals is much more pronounced. In addition it will be noted that the curves taken with the sectored disk rotating at different speeds are now more widely separated, except for the curves taken at 1 and 0.5 r.p.s.

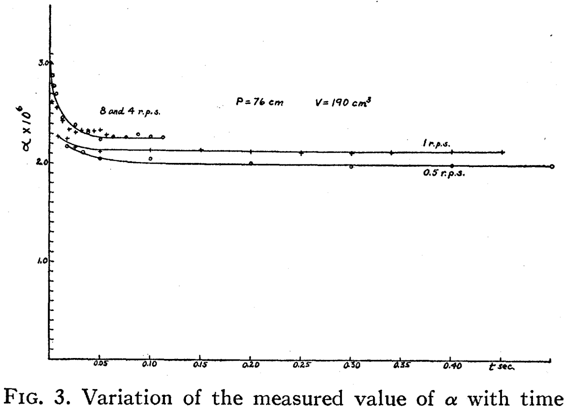

FIG. 3. Variation of the measured value of α with time. Press. 76 cm. Ion density about 10^6 ions/cm^3.

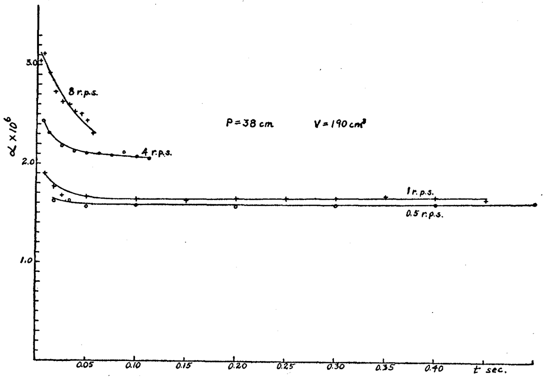

FIG. 4. Variation of the measured value of α with time. Press. 38 cm.

For the longer time intervals in the small chamber the value of α gradually increased with time instead of decreasing as observed by Marshall and Luhr. This small increase was probably due to loss of ions by contact potentials existing in the chamber. If this were true, then at lower pressures where the mobility and diffusion of ions has increased, this increase in α with longer time intervals should be more pronounced, which was just what was observed. With the larger chamber, constructed so as to eliminate these errors as much as possible, no such effects were observed. Instead, a very slight and continual decline of α with time was observed, which may or may not be entirely due to observational errors.

The values of α taken for the pressure variation were taken at an aging time $t=0.15$ sec. where it can be seen from the curves that the decline in α due to initial recombination has ceased and during this time the loss by diffusion to the electrodes is negligible. Fig. 5 shows the values of α as a function of pressure. The readings were all taken at room temperature which varied between 20°C and 30°C, and which for many reasons could not be maintained constant during the eight hour runs. Several readings were taken at each pressure with the small chamber and are represented by the crosses. The spread of values

---

[12] O. Luhr, Phys. Rev. **38**, 1730 (1931); O. Luhr, Phys. Rev. **44**, 459 (1933).

[13] N. E. Bradbury, Phys. Rev. **44**, 883 (1933).

shows the degree of reproducibility of the readings. The full line curves are the theoretical values of α calculated from the Thomson theoretical equation for the two temperatures shown. At 10 cm pressure the value of α is some three times what it should be according to the Thomson theory. Assuming that this high value was entirely due to loss of ions by contact potentials, calculations were made to determine what magnitude these potentials would have to be to account for this loss. This turned out to be of the order of one to two volts. Consequently the new and larger chamber was constructed to decrease this loss as much as possible. The points indicated by circles are the values obtained with the chamber of 700 cm^3 ionized volume. It will be noted that the value of 10 cm pressure with the larger chamber gave a value of about half that obtained with the smaller chamber. The value of α is still 50 percent higher than the theoretical value, and the curve of α with time shows a continual decline as may be seen from Fig. 6. The values taken at 10 cm pressure with the sectored disk rotating at 4, 2, 1, and 0.5 r.p.s. are shown in Fig. 6. Here it will be noted that the decline of α with time has become much more pronounced relative to those at higher pressures (compare Figs. 3 and 4). Also the effect of ionic density on the value of α is much more pronounced, giving a value at 4 r.p.s. twice that at 2 r.p.s. Hence it was clear that at 10 cm the value at 1 r.p.s. is no longer satisfactory and since the curve at 0.5 r.p.s. is lower and the decline in α with time at 0.5 r.p.s. is practically negligible, the value of α for 0.5 r.p.s. at 10 cm should be used. From Fig. 5 it can be seen that the value of α at 10 cm pressure as taken from the values at 0.5 r.p.s. lies nearly on the Thomson theoretical curve. At 5 cm pressure, the value of α as obtained with the large chamber is some 5 times the theoretical value even at 0.5 r.p.s. However at 5 cm pressure a large proportion of the negative ions are temporarily free electrons so that loss by diffusion probably accounts for the abnormally high values. Hence free electrons again preclude a study of recombination at lower pressures.

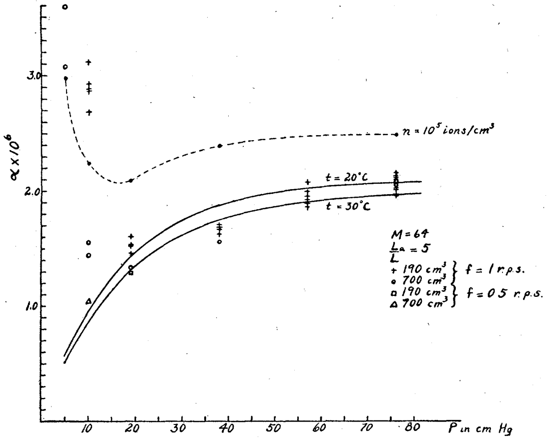

FIG. 5. Variation of α with pressure. Full lines show theoretical values of α calculated from Thomson's equation. Points about theoretical curves are for $n=10^6$ ions per cm^3.

Figures 3, 4, and 6, show that α is greatly influenced by the ionic density as pointed out by Marshall[8] and Luhr.[9] To study this, the value of α as a function of pressure was measured with the ionic density reduced to the value obtained at 5 cm pressure by filtering the x-rays through copper sheets. The value of α so obtained is given by the dotted line in Fig. 5 and is seen to be markedly increased. The effect of ionic density on the value of α will be discussed later.

The measurements of α as a function of temperature were all taken at atmospheric pressure, and with the sectored disk rotating at 1 r.p.s. In these measurements the difficulties encountered in the pressure measurements due to marked changes in ionic density as well as to the mobility and diffusion of the ions and electrons were absent. The results of the measurements of α as a function of temperature are shown in Fig. 7. The curve represents the

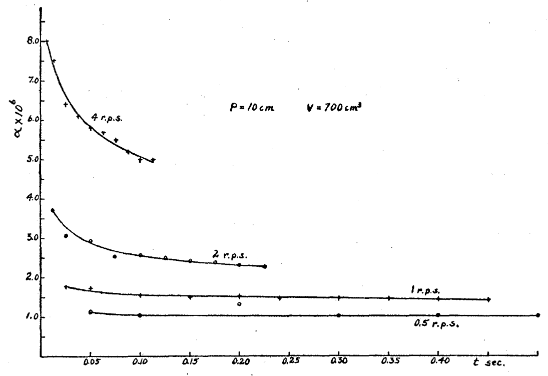

FIG. 6. Variation of α with time at different sector speeds. $P=10$ cm. Vol. $=700$ cc.

theoretical values as calculated from the Thomson equation.

The influence of impurities in the gas on α is shown by the values obtained when the tube had a slow leak of 10 microns in 12 hours when evacuated. The readings taken under these conditions are shown by the triangular points in Fig. 7. The striking change due to the minute traces of CO_2 or C_2H_5OH which diffuse into the tube filled with O_2 at atmospheric pressure for most of the time through the minute hole is obvious. These impurities also destroyed the constancy of α with time characteristic of a pure gas and the curves showed a continual decline with time. This is in beautiful accord with the observations of Marshall[8] and Luhr[9] who used metal chambers and who found that α was not a constant but continually decreased with time. On the basis of theory, α, after the initial decline, should be a constant in a pure gas. Thus the explanation of the continual decrease in α with time on the basis of impurities in Marshall's and Luhr's experiments which now appears to be confirmed.

In the present investigation the use of a glass chamber which could be thoroughly outgassed and the use of carefully purified gas showed α to be practically constant after the period of initial recombination as is seen in the curves of Figs. 3, 4, and 6. The new constant value of α found was much higher than that obtained by Luhr. It was $\alpha = (2.08 \pm 0.05) \times 10^{-6}$ while Luhr[14] found $\alpha = 1.32 \times 10^{-6}$. In view of the effect of impurities the character of the present curves indicates that the present value is more probably the correct value for O_2.

Discussion and Conclusion

That the Thomson theory is theoretically and experimentally the correct approach to the problem at atmospheric pressure has been shown by Loeb and Marshall[15] and later by Harper.[16] No measurements of α as a function of pressure and temperature for pressures below two atmospheres by investigators[7] of the past can be logically explained by Langevin's theory. Furthermore, the sharp decline of α at short time intervals at ordinary pressures as observed by Rümelin,[17] Plimpton,[18] Marshall,[8] and Luhr[9] can only be explained on the basis of the Thomson theory since it definitely indicates a diffusion to a more random distribution. Yet in spite of this evidence, the Langevin theory generally has been quoted as the accepted theory in texts. In a recent article by Mächler[19] and Kraus,[20] based upon high pressure measurements, ordinary atmospheric recombination is again ascribed to the Langevin process.

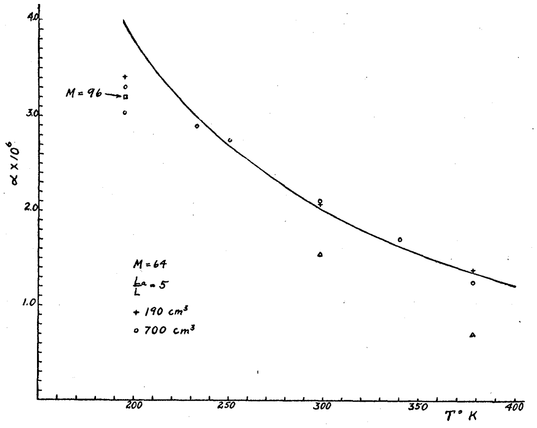

FIG. 7. Variation of α with temperature.

The theoretical curves based on Thomson's equation which are compared with the experiments reported here were calculated from Eq. (6). As can be seen, the Thomson equation has two somewhat adjustable constants, the mass M and the mean free path L of the ion. Experiments on the mobilities of ions have shown that there is, on the average, a fivefold lowering of the mean free path of the ion in comparison to the uncharged molecule due to the action of the dielectric attractive forces.[21] Thus $La/L = 5$ should be used in the Thomson equation. Furthermore, mass spectrograph investigations of ion formation by Luhr[13] have shown that the mass of the ion is greater than a single molecule for high

---

[14] O. Luhr and N. E. Bradbury, Phys. Rev. **37**, 998 (1931).

[15] L. B. Loeb and L. C. Marshall, J. Frank. Inst. **208**, 371 (1929); L. B. Loeb, *Kinetic Theory of Gases*, second edition, pp. 587–591.

[16] W. R. Harper, Proc. Camb. Phil. Soc. **28** (Part II), 219 (1932).

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

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

[19] W. Mächler, Zeits. f. Physik **104**, 1 (1936).

[20] P. Kraus, Ann. d. Physik **29**, 449 (1937).

[21] L. B. Loeb, *Kinetic Theory of Gases*, second edition, pp. 567–568.

pressures. It was therefore assumed that the ionic mass M is 64, that is, that the O_2^+ ion after 10^{-2} sec. consisted of two molecules. This is consistent with aging experiments. The curves of Figs. 5 and 7 were calculated using these values. Other combinations of M and L were tried but none gave as good agreement with experimental results as the values given above. It is seen that the agreement obtained for the experimental and computed values is quite good. Better agreement with the variation in pressure could not be expected due to the changes in ionic density and the mobility of the ions with decrease in pressure. The temperature variation is in excellent accord with the theory except at the lowest temperature where the deviation is greater than can be attributed to experimental error. Since at this lower temperature oxygen is not far from its critical temperature it is possible that polymers are being formed. The theoretical value of α was therefore calculated for this temperature on the assumption that the mass of the ion $M=96$, that is, the ion then consists of a group of three molecules. The point marked by the square, Fig. 7, shows the result of this calculation. Thus it is possible that the mass of the ion is increasing at these lower temperatures.

The measurement of α made in pure oxygen as a function of pressure and temperature reported here are a good confirmation of the Thomson theory and are absolutely incompatible with the Langevin theory. The numerical and experimental agreement leaves no doubt as to the applicability of the Thomson theory for O_2 in this region of measurements. The assumptions and approximations made in the deduction of the theory permit of no closer agreement than observed.

That the Langevin equation might be valid for the high pressure was already recognized by Thomson.[22] On the Thomson theory the ions will in general diffuse through the gas until they approach to within a distance d where active electrical attraction tends to bring the ions together. But if the ions are initially formed closely enough to each other (within a distance d), as they will be at high pressure by rapid electron attachment, the electrical attractions of the ions will largely govern their motion, i.e. preferential recombination will occur. Thus for high pressures the assumptions underlying the Langevin theory become valid. Loeb[23] has shown that the transition from low pressures to high pressures can be given by an equation of the form

$$\alpha=\alpha_T f+\alpha_L(1-f), \tag{10}$$

where α_T is the Thomson value and α_L is the Langevin value of the recombination coefficient, and f is the fraction of negative ions formed within a distance d of the positive ion. The fraction f can be calculated from the rate of attachment of the liberated electrons to form negative ions and the rate of diffusion of the electrons from the parent atom before attachment takes place. This coefficient of diffusion demanded by theory as applied to experiments is surprisingly low.

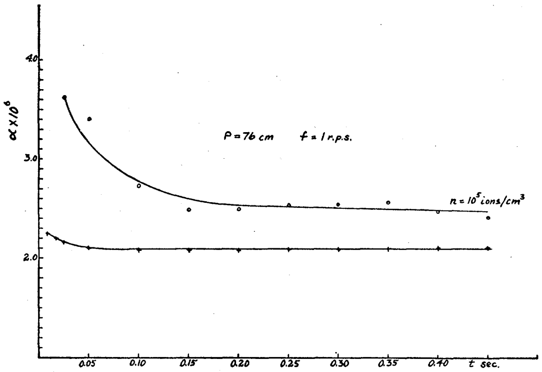

Fig. 8. Variation of α with time. Lower curve for ion density ten times that for upper curve.

The effect of ionic density on the value of α is shown in Figs. 3, 4, 5, and 6. Fig. 8 shows the apparently higher value of α obtained at atmospheric pressure when the ionic density was reduced to approximately one-tenth the value of that previously obtained at atmospheric pressure as represented by the lower curve. Curves of α as a function of time taken with shorter x-ray exposures and lower pressures, show that longer values of t are required for α to reach an apparent constant value, but in addition these same conditions appear to produce a higher value of the constant portion of the curves. This seems to indicate an apparent increase in the average

---

[22] J. J. Thomson, *Conduction of Electricity through Gases*, third edition, Vol. 1, pp. 47–48.

[23] L. B. Loeb, Phys. Rev. **51**, 1110 (1937).

value of α after the initial phase of recombination has ceased. Except at the longest time intervals the apparent constancy of the curves of short exposure time, low pressure, and ionic density is illusory. Loeb[24] has shown that if the ions are initially formed at a distance Δr_0 apart and diffuse to a distance Δr where random distribution of the ions is obtained, then during initial recombination the value of α as measured becomes

$$\alpha = \alpha' \left\{ \frac{\Delta r}{\Delta r_0 + (12Dt/\pi)^{\frac{1}{2}}} \right\}^3 \tag{11}$$

where α' is the true coefficient, and D is the coefficient of diffusion. For practical purposes the value of Δr can roughly be taken as

$$\Delta r = (1/n)^{\frac{1}{3}} \tag{12}$$

where $n =$ the ionic density. This equation when calculated to take into consideration the aging of ions during the x-ray flash period, gives rise to curves following fairly closely the general shape and trend of the observed curves. It predicts, however, that, if the normal coefficient of diffusion is used, the curves would drop to a constant value in intervals of time 0.01 of those observed. This would indicate that as far as achieving random distribution is concerned, the coefficient of diffusion is apparently 0.01 as great as that for normal ions. This is not entirely unreasonable since the diffusion from the sphere of active attraction is strongly retarded at distances from d to 10 d. The equation further predicts that the point where α has a certain definite value relative to the true value α' should vary inversely with ionic density. The data taken with the x-rays filtered through copper sheets to give a tenfold reduction in n show that corresponding points are shifted in time by 50-fold, Fig. 8, while the theory predicts a shift of 4.7 without correction for the x-ray flash period.

Finally, since the concentration of ions is proportional to pressure while the coefficient of diffusion is inversely proportional to pressure it would be expected that corresponding values of the ratios α/α' in initial recombination would vary in time directly as the cube root of the pressure. This is contrary to observation, for the theory would predict an increase in t with increase in pressure for corresponding values of α/α' but Figs. 3, 4, and 6 show a decrease in t with increase in pressure. There is, however, another factor which cannot be neglected. Immediately after ionization, the ionized molecules undergo further changes in forming the stable ions existing at longer time intervals. This is the well-known aging effect observed in mobility experiments and in Luhr's[12] investigations of ion formation with the mass spectrograph. Consequently the mass of the ion in oxygen is probably undergoing changes up to some 0.01 second so that the average value of α will decrease gradually with time. Hence, part of the high values and gradual decrease of the observed α with time for the lower concentrations and pressures may be ascribed to newer and less massive ions. It is possible that in addition the products of x-ray ionization and excitation in oxygen may facilitate the rate of formation of these complexes, i.e. that aging is facilitated by dense ionization and a high concentration of ionization products. These phenomena are not included in the rough Eq. (11) of Loeb so that too much cannot be expected from this equation as regards verification of these experiments. It can be concluded, however, that making the assumptions of a decreased rate of diffusion to random distribution, taking into account the finite time of ionization, and recognizing the existence of aging effects in pure oxygen the type of curves obtained for α at shorter time intervals and lower ionic concentrations can be satisfactorily explained in a general way.

In conclusion, the writer wishes to thank Professor Loeb under whose direction the investigations were made and whose helpful criticisms made the culmination of the difficult measurements possible.

---

[24] L. B. Loeb, Lecture notes, "Conduction of Electricity in Gases," mimeographed edition, 1937.