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Electron Attachment and Negative Ion Formation in Oxygen and Oxygen Mixtures

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A direct method is employed to determine the probability of electron capture in oxygen and oxygen mixtures. The principle of the method lies in the analysis of a mixed current stream at two points along its path by means of wire grids which permit only the ionic fraction of the current to pass when a high frequency field is applied between adjacent grid wires. A means of measuring the mobility of the electrons is also possible. The probability of attachment has been determined for oxygen, air, and mixtures of oxygen with the rare gases. The probability of attachment is a marked function of the electronic energy, decreasing with increase in electronic energy. In oxygen and in all mixtures of oxygen, however, there is an *increase* in the probability of attachment occurring at approximately 1.6 volts electronic energy. This can be definitely explained as being due to the appearance of *low energy* electrons following inelastic impacts with O_2 molecules. The energy at which these inelastic impacts begin is well correlated with the first excited level of the O_2 molecules which is 1.62 volts above the ground state.

It is well known that certain molecules and atoms have the property of forming stable negative ions by the capture of an additional electron. Thus it is impossible to have a purely electronic current through such a gas, and the entirely different properties of negative ions and electrons as current carriers make the attachment process of great importance in determining the conduction characteristics of the gas.

The work of Loeb,[1] Wahlin,[2] Bailey[3] and Cravath[4] has shown that the attachment process is a random one and only a fraction of the computed number of kinetic theory collisions made by an electron result in capture. This fraction is of the order of magnitude of 10^{-3} to 10^{-8} and is a characteristic of the gas, varying in addition with the electronic energy. The early assumption of Wellish[5] that an electron must have a certain minimum energy before attachment can occur has been shown to be untenable by the work of the above investigators, and his recent reassertion of it[6] is quite incompatible with other experimental evidence. J. J. Thomson[7] first deduced an expression for the rate of disappearance of free electrons moving through a gas if a constant number of impacts, n, were, on the average, required before capture took place. The predicted exponential decrease in number of electrons with distance traversed has been shown to be in agreement with experiment. Furthermore, negative ions, once formed, are permanent and lose their excess electron only under the most extreme conditions.

Experimental determinations of the quantity n or its reciprocal h, the probability of electron capture at a collision,[8] have been attended by considerable difficulty and measurements by different observers apparently have not agreed.[9] It is the purpose of this paper to present the initial results of a series of measurements of the probability of electron capture as a function of electronic energy in different gases and gas mixtures. A direct method is employed which permits all the necessary quantities for calculation to be simultaneously determined.

THEORY OF THE EXPERIMENT

If the capture of electrons by molecules is a random phenomenon, and the cross section for such a capture be denoted by σ_c, then the loss of free electronic current, dI, in going a distance dx

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* National Research Fellow.

[1] L. B. Loeb, Phys. Rev. **17**, 89 (1921).

[2] H. B. Wahlin, Phys. Rev. **19**, 173 (1922).

[3] V. A. Bailey, Phil. Mag. **50**, 825 (1925).

[4] A. M. Cravath, Phys. Rev. **33**, 605 (1929).

[5] E. M. Wellish, Phil. Mag. **34**, 55 (1917).

[6] E. M. Wellish, Proc. Roy. Soc. **A134**, 427 (1931).

[7] J. J. Thomson, Phil. Mag. **30**, 321 (1915).

[8] L. B. Loeb, *Kinetic Theory of Gases*, McGraw-Hill, 1927, p. 511.

[9] V. A. Bailey, Phil. Mag. **6**, 1073 (1928).

under the influence of an external field is given by

$$dI = -IN\sigma_c(c/W)\, dx, \tag{1}$$

in which I is the current at x, and c/W the ratio of the random velocity of the electron to its drift velocity in the direction of the field (i.e., this ratio is the total distance actually traversed by the electron in drifting one centimeter in the direction of the field). This expression may be put into another form which is more common in the literature in which the probability of capture, h, at a single Ramsauer collision is employed. In such a form Eq. (1) becomes at once, since $\sigma_c/\sigma_R = h$ and $\lambda = 1/N\sigma_R$

$$dI = -(Ihc/\lambda kX)\, dx. \tag{2}$$

In this expression λ is the mean free path of the electrons in the gas; k, their mobility in cm/sec. per volt/cm; and X, the field strength in volts/cm. This expression may be integrated between two points x_1 and x_2 a distance x apart to give

$$\ln I_2/I_1 = -hcx/\lambda kX, \tag{3}$$

in which I_1 and I_2 are the free electron currents at x_1 and x_2. It has been customary to employ the mobility equation to evaluate c and λ for Eq. (3). This equation is of the form

$$k = 0.75e\lambda/mc,$$

where e and m refer to the charge and mass of the electron. This equation substituted in (2) gives for h

$$h = (300mk^2X/0.75ex)\ln(I_1/I_2). \tag{4}$$

Either the quantity h, the probability of capture, or σ_c, the capture cross section, may be used in discussing the phenomenon. The former is more common in the literature, and the latter more interesting in theoretical significance.[10] For purposes of comparison both types of reference will be employed in this paper.

It is apparent that either a knowledge of the electron mobility or the ratio of the average random velocity of the electron to its drift velocity in the direction of the field is required for the evaluation of the total number of electronic impacts. Since the existing data on electronic mobilities are not altogether certain, and even nonexistent for gaseous mixtures, it is imperative to have some method of simultaneously determining the electronic mobility. The means for accomplishing this in the present work lies in an equation given by J. J. Thomson[11] relating the photoelectric current between parallel plate electrodes to the mobility of the electrons and their initial energy. This equation is of the form

$$i/I_0 = (6\pi)^{\frac{1}{2}}kX/(c_0 + (6\pi)^{\frac{1}{2}}kX), \tag{5}$$

in which c_0 is the mean initial velocity of the photoelectrons leaving the cathode; X, the field strength in volts/cm; i is the current reaching the anode, and I_0 the total current of electrons given off by the cathode, part of which returns to it by diffusion. A recent paper[12] by the author showed this to be a feasible, if not direct, method of determining electronic mobilities providing the initial energy of the electrons from the photoelectric source was known. In the present experiment this quantity could be determined. While so simple an equation probably does not entirely adequately represent the facts and certain theoretical objections can be adduced, nevertheless, the agreement between mobilities obtained in this manner with those determined by entirely independent methods makes it extremely useful. This is particularly the case for arbitrary mixtures of gases where no other data exist for the electronic mobility.

APPARATUS

The essential features of the apparatus are shown schematically in Fig. 1. A polished zinc plate, A, serves as a source of photoelectrons when the narrow image of a quartz mercury arc is focussed along its center. The guard rings, B, D, C and E, maintain a uniform field from V_F, and the photoelectrons emitted from A pass through the gas towards the collecting electrode, P. In their passage through the gas the electrons are captured by neutral molecules.

The guard rings D and E are movable and are divided into identical halves, one-half of each guard ring carrying a grid of fine platinum wires,

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[10] L. A. Young and N. E. Bradbury, Phys. Rev. **43**, 1054 (1933).

[11] J. J. Thomson, *Conduction of Electricity through Gases*, University Press, Cambridge, 1928, p. 466.

[12] N. E. Bradbury, Phys. Rev. **40**, 980 (1932).

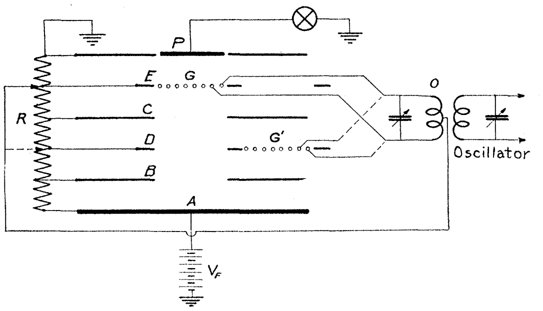

FIG. 1. Schematic diagram of apparatus. Alternate wires in grids G and G' are connected together and either grid may be moved into or out of the uniform field space.

G and G'. Between alternate wires of each of these grids a high frequency alternating field may be produced by means of the oscillating circuit O which is coupled to a short wave oscillator (20–70 meters). Such a grid served to separate electrons from a mixed current of negative ions and electrons and was proposed by Loeb and employed by Cravath.[4] Electrons reaching the grid as they move through the space between A and P are swept out to the grid wires during one-half cycle of the alternating field, but negative ions, whose mobility may be 1000 times less, do not have time to reach a grid wire in a single half cycle, and the continual reversal of the grid field permits the driving field V_F to carry them beyond the influence of the grid. The grids are maintained at a mean potential equal to that of the guard ring in which they are placed and consequently do not distort the main field for more than a negligible distance on either side. The voltage between the grid wires could be varied between 0 and 200 volts.

In actual practice conditions are not as ideal as described above, since some electrons may escape and some ions may be caught by the grids. It is to avoid this difficulty, that *two* grids, G and G', are employed, either one of which may be removed and an identical guard ring substituted when measurements are being carried out with the other. The whole assembly is mounted in a Pyrex tube and the grids carried in an out of position by an externally operated magnetic device. In Fig. 1, the grid G is shown in position and the grid G' withdrawn to one side with its corresponding guard ring D in place. A side view of the apparatus, without the grids drawn in, is shown in Fig. 2.

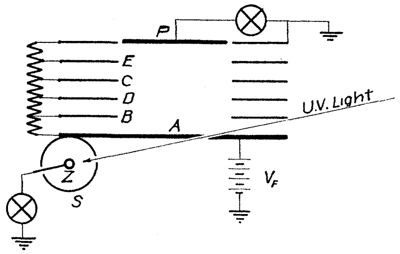

FIG. 2. Side view of apparatus (grids not shown).

It is thus possible to study the electronic composition of the current stream at two points, D and E. The distance between these grids, measured by means of a cathetometer, was 2.40 cm and is the value of x in Eq. (2). The actual measurements were carried out by measuring the total current of ions plus electrons with one of the grids in place. The high frequency voltage was then applied to the grid causing a reduction of the current corresponding to that part of it carried by the electrons, the measured remainder being the part carried by the negative ions. Having determined the current passing through one grid as a function of V_g, the voltage between grid wires, this grid could be moved to the side and the other grid moved into place to make similar measurements. Denoting the values obtained with and without V_g by I_0 and i, respectively, it is immediately apparent that

$$\ln (I_1/I_2) = \ln ((I_0 - i_1)/(I_0 - i_2)).$$

The value of I_0 measured will not be the true value of I_0, owing to loss of electrons by ordinary diffusion to the grid wires. Since, however, the effect is practically the same at both grids, the effect on the ratio is negligible. Furthermore, since the fraction of ions inevitably caught by a grid will increase slightly with increasing voltage between the wires of the grid, i is not constant for all values of grid voltage, but decreases slightly as higher grid voltages are reached, as will be seen later in Fig. 3. Calculations, however, may be made with any values of i_1 and i_2 which correspond to the *same* grid voltage.

To determine the mobility of the electrons, *both* grids were moved out of the main field which then became the uniform field between parallel

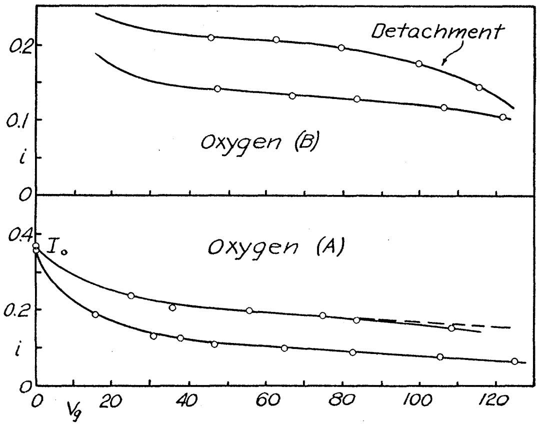

FIG. 3. Curves showing variation of negative ion current to collector with voltage between grid wires, V_g. (A) shows the normal behavior with slopes nearly parallel and a slight trace of detachment at high V_g. (B) is a typical curve at a lower pressure showing marked detachment.

plate electrodes required by Eq. (5). The ratio of the saturation current (the current with no gas between the electrodes) received by P to the current received by P with various gas pressures and field strengths could then be determined. Eq. (5) requires further a knowledge of the average initial velocity of the emitted photoelectrons. This was obtained in the following manner. A small hole (see Fig. 2) is cut through the lower zinc plate such that a small part of the image of the mercury arc falls upon a small zinc sphere, Z, which is at the center of another large copper sphere, S. This zinc sphere was polished and cleaned in exactly the same manner as the photoelectric surface at A and both were assembled without touching the active surface. The energy distribution of the electrons from Z could then be determined in the classical manner of retarding potentials. While such a procedure does not guarantee that the two surfaces will be identical, yet it seems entirely reasonable to assume that they will be adequately so since each is subjected to the same baking out, gas conditions, and light treatment. Furthermore, preliminary experiments in a separate tube[13] showed that great changes in the mean energy were not to be expected under ordinary treatment.

The distance between the plates was 7.00 cm, and the area of the collecting electrode 10 cm^2. The whole apparatus was contained within a large Pyrex tube provided with a graded quartz-Pyrex seal and plane quartz window for admission of the ultraviolet light. No wax seals or joints were employed and a liquid air trap placed immediately before the tube kept out mercury vapor and any vapors from stopcock greases employed in the gas purifying system. The tube was baked out prior to use at 200° (the zinc softening at higher temperatures) and could be pumped out to better than 10^{-6} mm.

In practice, because the formation of ozone was feared, the light from the quartz mercury arc was passed through a filter 12 cm long containing Cl_2 at 15 cm pressure. This cuts off the wavelengths shorter than 2537Å and experiments of Dickinson and Sherrill[14] have shown that ozone is not produced in pure oxygen by this wavelength unless mercury vapor is present.

The methods of gas purification employed were similar to those employed in measurements of the mobility of gaseous ions where the highest purity has been shown to be necessary.[15] To guard further against any change in the character of the gases being studied by the ultraviolet light, all measurements in air and oxygen were carried on while fresh gas was being continually circulated through the tube at the rate of 5–10 cc per second, though other experiments showed this to be an unnecessary refinement. No difficulty was experienced in obtaining repeatable results.

EXPERIMENTAL RESULTS

Typical experimental results for the determination of the electron mobility will be considered first. The character of the observed i/I_0 curves plotted against field strength for different pressures is the same as that previously published and will not be reproduced here. The determination of the average energy of the emitted photoelectrons was carried out in the usual manner by taking the derivative of the observed current to the outer collecting sphere plotted as a function of the retarding potential between the two spheres. The exact theory of this method has been re-

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[13] N. E. Bradbury, Phys. Rev. **43**, 502 (1933).

[14] R. G. Dickinson and M. S. Sherrill, Proc. Nat. Acad. Sci. **12**, 175 (1926).

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

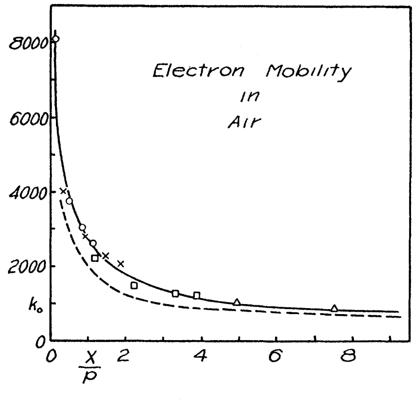

FIG. 4

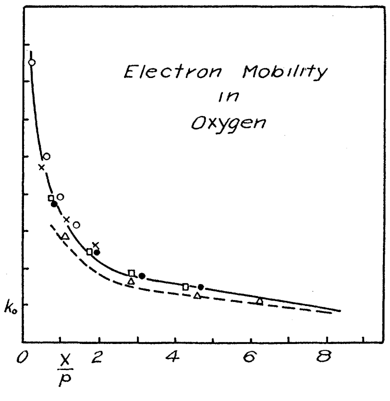

FIG. 5

FIG. 4. Electron mobility in air as a function of X/p. The dotted line is the variation reported by Townsend.

FIG. 5. Electron mobility in oxygen as a function of X/p. The dotted line is Townsend's curve.

cently set forth by DuBridge,[16] but for the purposes of this experiment, this procedure is sufficient. The most probable energy comes out to be of the order of 0.7 volt. This value will vary somewhat from time to time depending on the character of the surface and must be redetermined for each i/I_0 run. Converting values so obtained into the corresponding values of c for Eq. (5), we may calculate values of k_0 corresponding to various values of X/p, where p is the pressure in mm of Hg.

Such mobility curves as a function of X/p are shown in Figs. 4 and 5 for air and oxygen. With each are plotted dotted curves corresponding to the values given by Townsend determined by his magnetic method.[17] The agreement is within the limits of error of both types of observation. The different points indicate data taken at different pressures between 12 and 95 mm of Hg.

The determination of the probability of attachment was carried out as described in the preceding section. Fig. 3 shows typical curves obtained for the *negative ion* current passing through the grids at the two points in the current stream. It is seen that this current decreases slightly as the voltage between the grid wires is increased owing to the larger number of negative ions which are caught by the grid. In the case shown the main field strength, X, was 41.6 volts/cm, and the pressure 15 mm. In general the slope of

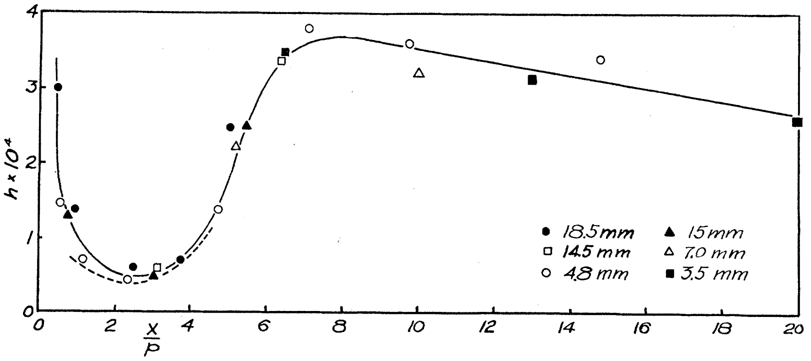

FIG. 6. Probability of electron attachment in oxygen as a function of X/p. The points indicate data taken at different pressures as shown. The dotted line is the curve given by Cravath.

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[16] L. A. DuBridge, Phys. Rev. **43**, 727 (1933).

[17] J. S. Townsend, J. Frank. Inst. **200**, 563 (1925).

the curves decreased with increasing pressure. Fig. 3B shows a type of behavior observed in oxygen at lower pressures in which the negative ion current, instead of having a constant small slope, decreases very rapidly with increasing values of the grid potential beyond certain amounts. This phenomenon, which has been observed by Cravath, is ascribed to a "detachment" of the excess electron from the negative ion owing to the extremely high fields in the neighborhood of the closely spread wires. The effect was only in evidence at low pressures when the values of X/p in the vicinity of the wires became extremely high. This phenomenon will be discussed in more detail at another point.

The calculation of h was carried out with values of k taken from appropriate data with the use of Eq. (4). The points chosen for the calculation of i_1 and i_2 were those points at which the slope of these quantities where V_g first became constant since these more nearly approximated the ideal values desired.

Fig. 6 is a summary of all the data taken in oxygen at the different pressures indicated. The probability of attachment is plotted as a function of X/p. The range of data obtained by Cravath is shown by a dotted line. Fig. 7 is a similar curve for air. Fig. 8 shows the types of curves obtained for mixtures of equal parts of oxygen with nitrogen, argon and helium. The significance of these curves will be discussed in the next section.

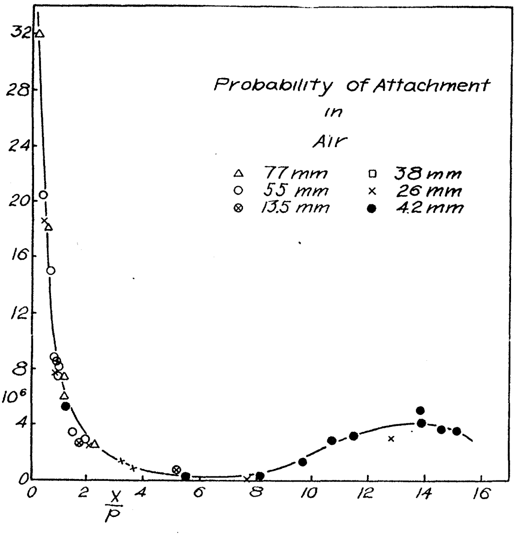

FIG. 7. Probability of electron attachment in air plotted as a function of X/p. The data were taken at different pressures as indicated.

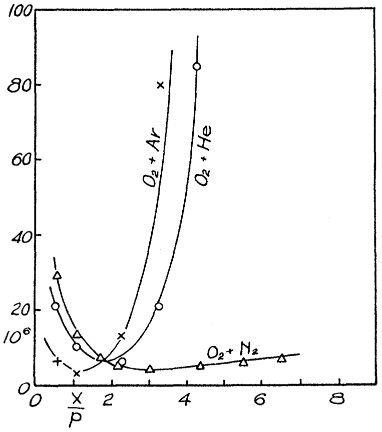

FIG. 8. Probability of electron attachment in oxygen-rare gas mixture as a function of X/p. The gases in each case are in 1 : 1 ratio.

DISCUSSION OF RESULTS

The above data show that the probability of attachment of an electron to an oxygen molecule is markedly dependent upon the value of X/p, i.e., upon the average *energy* of the electrons which are being captured. According to Compton[18] the terminal energy of an electron moving through a gas subject to elastic impacts and under the influence of an electric field is given by the relation

$$U_T=(1/2.31)(\lambda X(M/m)^{\frac{1}{2}}), \qquad (6)$$

which can be put into the form

$$U_T=(1/2.31)(760\lambda/p)(X(M/m)^{\frac{1}{2}})\sim 4.5X/p.$$

In these expressions m is the mass of the electron M that of the gas molecule, and λ the mean free path of an electron at 760 mm. At a value of $X/p=2$ this corresponds to a terminal energy of the order of 9 volts. This, however, is much too large and it has long been known that electronic impacts in oxygen were probably more inelastic than in other gases.

The only experimental measurements of this important quantity, the *random energy* of the electrons as a function of X/p, are those of Townsend and his students. While taken by an

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[18] K. T. Compton, Rev. Mod. Phys. 2, 221 (1930).

indirect method, their measurements of the lateral rate of diffusion of a beam of electrons passing through the gas should give results correct, at least, in order of magnitude. The values obtained do not agree with the simple theory given above. It is probable that the too simple assumptions of constant cross section, uniform angular scattering, and energy losses resulting only from momentum transfers at impacts upon which Eq. (6) is based are responsible for the deviation.

Assuming the approximate correctness of Townsend's values for the terminal energy of electrons in air and oxygen, it is interesting to plot the data of Figs. 6 and 7 upon an *electron energy* (E_c) scale rather than as a function of X/p. When this is done in Fig. 9, the apparent discrepancy between the air and oxygen curve vanishes. Since it is known that the nitrogen molecule does not attach electrons, all attachment in air must be due to the oxygen present, and it would be surprising to find the attachment a very different function of the electronic energy in the two cases. Within the limits of error the two curves show the same behavior and differ only in magnitude.

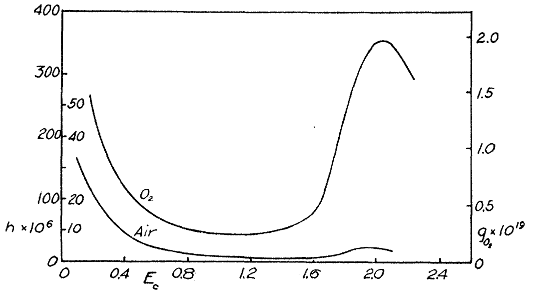

FIG. 9. Probability of electron capture and electron capture cross section plotted as a function of average electronic energy. The smaller scale on the left refers to the lower curve which is for air. The upper curve is for oxygen.

Two questions remain: What is the cause of the rapid rise in probability of capture after the electrons reach approximately 1.6 volts energy? and second, what is the relation between the magnitudes of the two curves? Theoretical considerations recently published[10] make it seem probable that the electron capture cross section, in some cases at least, varies roughly as the inverse square root of the electronic energy. This theory is compatible with the portion of the curves before 1.6 volts. *The explanation for the rise beyond this point must lie in the fact that at this energy, electrons begin to make inelastic impacts with oxygen molecules.* According to Birge,[19] the first level above the ground state of the oxygen molecule occurs at 1.62 volts.

Electrons which make such an inelastic impact have their velocity reduced to zero, and must gain their terminal energy anew. While this is going on, their probability of attachment is that for electrons of *extremely low velocity*, and hence the sudden appearance of large numbers of negative ions at and a little above this energy. This, of course, does not go on indefinitely. Theoretical and intuitive considerations make it seem apparent that, as the energy of an electron increases, the probability of attachment must ultimately decrease, and this appears to be the case in the present experiments. It was not possible to trace the entire right-hand portion of the curve as the low pressures and high field strengths required caused breakdown in other parts of the tube.

That this explanation of the phenomenon is the correct one is supported by measurements made in mixtures of O_2 with argon and helium. No energy scale exists for these mixed gases, but from elementary considerations the rate of gain of energy in the two must be roughly proportional to X/p at low X/p and electrons should gain energy faster in argon than in helium. Hence the order of reaching the critical potential of 1.62 volts should be argon, helium, nitrogen. Fig. 8 shows this to be the case. Further, the rise is extremely rapid beyond the minimum corresponding more nearly to the uniform energy scale graph of Fig. 9. The difference in the appearance of the N_2+O_2 curve is due to the fact that an X/p scale rather than electron energy has been used. It seems certain that the probability of attachment is a steadily decreasing function of the electronic energy and that the observed rise is due to inelastic impacts.

Since the attachment in air is due only to the oxygen present, it might seem that the value of h should be 1/5 that of oxygen. Actually the calculation is not so simple, for we must compute the relative number of impacts with the two types of molecules, which will in turn be a func-

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[19] R. T. Birge, *Molecular Spectra in Gases*, Bull. Nat. Research Council, 1926, p. 244.

tion of the mean free path and the mol fraction of the respective gases. Such an expression turns out to be

$$h_{O_2}=h_{\text{air}}(1+f_1\lambda_2/f_2\lambda_1),$$

where f_1 and f_2 are the mol fractions of the respective gases and λ_1 and λ_2 the mean free paths of an electron in them. This latter quantity is difficult to ascertain correctly. At 0.8 volt electronic energy Townsend gives the ratio λ_2/λ_1 for H_2 and O_2 as approximately 2. Ramsauer cross sections are vague in this region. Assuming a value of 2, we see that the value of h for air should be 1/9 that for O_2. Experimentally in the region 0–1.0 volts electronic energy the ratio is of the order 10 to 13 which is well within the uncertainty of the calculations. At 1.8 volts electronic energy, the probability of attachment in O_2 becomes more than 50 times that for air. Although in this region the Ramsauer cross sections for N_2 show values 3–4 times those for O_2, it is doubtful if this will explain the discrepancy. It seems much more probable that an electron having suffered an inelastic collision starts out with practically zero velocity. During its next impacts it is continually gaining energy from the field, but it will not reattain its terminal energy until after many collisions. If these subsequent *low energy* collisions are with molecules of O_2, there is great probability of capture. If, however, in the interval between collisions with oxygen molecules an electron has gained energy corresponding to several collisions with inert nitrogen molecules, its chance of attachment to the next oxygen with which it collides is far less than had the intervening collisions been with capturing atoms. With such high capture probabilities at low electron energies, such a phenomena will readily account for the discrepancy between the values of h. Quantitative calculations are not feasible because of the inadequacy of collision data.

No variation with pressure was observed, in agreement with the results of Bailey, though the values obtained here are somewhat higher than his. Cravath observed a variation of h with pressure for air, but his values at higher pressures are compatible, in their range, with these. The directness and consistency of this method, however, lend weight to these results.

The phenomenon of detachment is of sufficient interest to deserve mention. It is observed in low pressure measurements in oxygen with comparatively high potentials between the wires of the grid. Fig. 3B shows the type of observation. In this case detachment appears to set in at $V_g=60$ volts and the value of X/p between the grid wires is of the order of magnitude of 110. Under such circumstances the gain in energy of a negative ion in one free path might be of the order of 0.6 volt. This behavior of negative ions should be further investigated, for, from the energy necessary to remove the excess electron, we may obtain direct measurements of that interesting quantity, the electron affinity of the molecule. Measurements have been attempted by Oldenburg[20] to determine this quantity for the iodine atom by spectroscopic observations but without success.

In connection with the mechanism postulated here of increased attachment following inelastic impacts, it is of interest to note the qualitative experiments of Mohler.[21] With a beam of electrons of controlled energy passing into a gas at low pressure, he observed the formation of negative ions as a function of electron energy. In several cases an increase in the number of negative ions formed was found at a point corresponding to a known critical potential of the molecules involved. He, however, did not investigate oxygen.

CONCLUSION

It will be of interest to investigate other gases for the appearance of the phenomenon of increased attachment following an inelastic impact. Gases such as NH_3 and NO_2 have been found by Bailey[22] to give an increasing number of negative ions as the electron energy is increased. This may be another type of attachment cross section or the result of an inelastic impact. Experiments with very low electronic energies should settle such a question.

In conclusion, the author desires to express his indebtedness to Mr. Howard Tatel for the construction of the high frequency oscillator and to Mr. J. E. Ryan, departmental glass blower, for his skill and assistance in the assembly of the complicated tube.

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[20] O. Oldenburg, Phys. Rev. **43**, 543 (1933).

[21] F. A. Mohler, Phys. Rev. **26**, 614 (1925).

[22] V. A. Bailey, Phil. Mag. **95**, 993 (1932).