APRIL, 1929 *PHYSICAL REVIEW* *VOLUME 33*

THE RATE OF FORMATION OF NEGATIVE IONS BY ELECTRON ATTACHMENT

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ABSTRACT

By a new method, the fraction h of the collisions between electrons and molecules which result in the attachment of the electron to form a negative ion has been measured in air and oxygen as a function of the average electron energy, the gas pressure, and the moisture content. In oxygen h had a minimum at 0.9 volts average electron energy, and increased with either increase or decrease of the energy from this value. In air h increased as the average electron energy was reduced below 0.9 volts. The absolute value was about 0.4 of that predicted from the value in O_2 assuming simple additivity, but this difference is possibly within the limits of error. The variation with electron energy and the order of magnitude of h are in agreement with Bailey's results for air. On the other hand, a rapid increase in h with increase in pressure at constant electron energy was found at low energy, while Bailey's results, which seem more reliable, show no variation with pressure. In H_2O h is of the same order of magnitude as in O_2, but in mixtures of H_2O and O_2 h is much larger than in either alone, showing that here at least the attachment process is complex.

Permanence of ions.—Evidence of the detachment of electrons from negative ions in oxygen at very high fields was found.

1. INTRODUCTION

THE work of Loeb,[1] Wahlin[2], and Bailey[3] has shown that, in many cases at least, the formation of negative ions from free electrons is a slow process, the electron making many collisions with gas molecules before finally becoming attached. The rate of ion formation is conveniently measured by the fraction of the collisions which result in attachment. We shall call this fraction the attachment coefficient and denote it by h. It is also the reciprocal of the average number of collisions made by an electron before becoming attached.

For a number of gases Loeb and Wahlin obtained approximate values of h. They range all the way from 0 for H_2 and N_2 to more than 10^{-3} (beyond the range of measurement) for Cl_2 and HCl. Their method was to measure the current between two plane parallel electrodes, one of which emitted photoelectrons, when a square wave, alternating voltage just insufficient to drive ions across in half a cycle was applied. This current obviously is a measure of how far the electrons go before attachment. From the latter and the electron mobility, h could be calculated. In some cases the mobility was measured in the same apparatus by the Rutherford alternating current method, and in some cases it was estimated.

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[1] L. B. Loeb, Kinetic Theory of Gases, McGraw Hill, New York, 1927, p. 507; J. Frank. Inst. **197**, 45 (1924); Phil. Mag. **43**, 229 (1922).

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

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

The quantity h has been measured as a function of the average electron energy by Bailey[3] in air and by Bailey and McGee[4] in NH_3. Bailey's method is to pass a mixed current of ions and electrons through a succession of slits in plane electrodes perpendicular to a uniform electric field. The fraction of the current passing one slit which also passes through the next is a measure of the rate of lateral diffusion and this in turn depends on the fraction of the current which is electronic, the electrons diffusing much more rapidly than the ions. The loss of electrons by attachment between one electrode and the next, together with the electron mobility, which is taken from the data of Townsend and Tizard[5] for air, gives h.

The present work is a study of the attachment coefficient h as a function of electron energy, gas pressure, and moisture content in air and oxygen. A new method is used. The results seem to be sufficiently new and interesting to warrant publication although their consistency and reliability leave much to be desired.

2. Principles of the Present Method

In Fig. 1, F is an oxide coated platinum filament emitting electrons which are driven downward by a uniform electric field. The gas pressure is higher than 6 mm. Hence the electrons on their way downward make many collisions with gas molecules and some attach to form ions. S is a plane electrode with a slit for the filament at its center. G is a grid of fine parallel

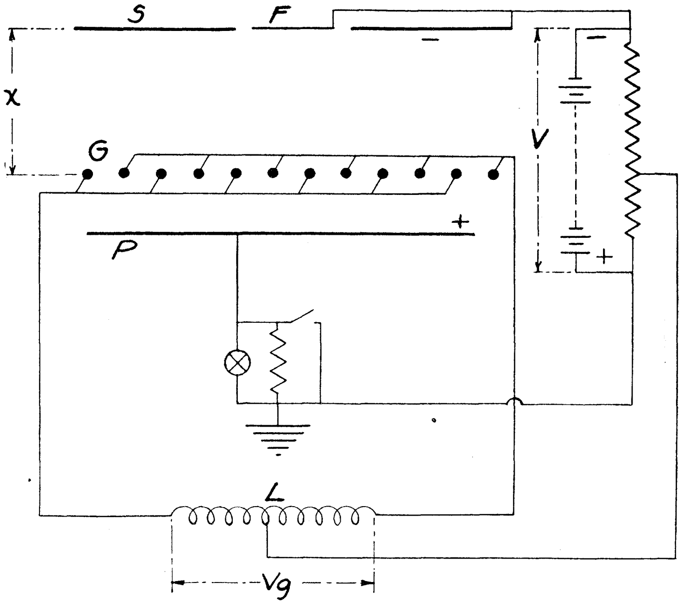

Fig. 1. Essentials of apparatus.

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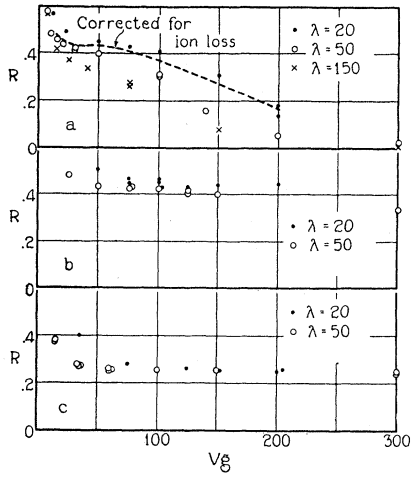
[4] Bailey and McGee, Phil. Mag. **6**, 1073 (1928).

[5] Townsend and Tizard, Proc. Roy. Soc. **A88**, 336 (1913); J. S. Townsend, J. Frank. Inst. **200**, 563 (1925).

wires (0.0080 cm diameter, spaced 0.1 cm apart). Alternate wires are connected to opposite ends of the coil L in which a high frequency voltage V_g can be induced. P is the collecting plate connected to the electrometer. With $V_g = 0$, the fields above and below G are equal, the fine grid wires disturb the field but little, and both ions and electrons pass through the grid to P. When a sufficient alternating voltage is applied, the transverse field between adjacent wires removes the electrons, which have a high mobility, but does not affect the ions, which are too slow to move an appreciable distance before the field reverses. In practice, of course, some ions will be caught by the alternating field and some electrons will escape. When R, the ratio [(current received by the plate with a given V_g)/(current when $V_g = 0$)],[4] is plotted as a function of V_g (Figs. 2a, 2b, and 2c) the curves drop rapidly as V_g rises to the value at which nearly all electrons are captured, and then straighten out to a small slope caused by the capture of an increasing number of ions by the larger alternating fields. The ordinate at the point where the curve becomes straight, after a small correction for ion capture, gives R_i, the fraction of the electrons which have attached before reaching G. The ion loss correction is calculated from curves at high pressure where no electrons are present.



Figs. 2*a*, 2*b*, and 2*c*. Experimental curves of R against V_g. (λ = wavelength of high frequency V_g in meters.)

	Fig. 2*a* O_2	2*b* Air	2*c* $1.3\% O_2$ $98.7\% N_2$
p	15 mm	60	100
X/p	1.05	0.89	0.12
R_i	0.42	0.42	0.26

Note improvement in curves with increasing pressure.

Let l be the mean free path of the electrons, v their average random speed W their average velocity in the direction of the electric field (drift velocity), x the distance from the source of electrons, measured parallel to the electric field, and I the current of *free electrons* at the distance x. The number of collisions an electron makes in going the distance dx in the direction of the field is $(v/lW)dx$. Hence the chance that an electron will attach in going the distance dx is $(hv/lW)dx$ and

$$dI/I = -(hv/lW)dx \quad \text{or} \quad ln(I/I_0) = -hvx/lW$$

$I/I_o=(1-R_i)$ is found experimentally. To eliminate v/l the mobility equation is used. It is

$$k=W/X=[83/(4\times 300)](el/mv)$$

where X is the field in volts per cm, e the electronic charge in e. s. u., and m the mass of the electron. The result is

$$h=-\frac{lW}{vx}ln(1-R_i)=\frac{4\times 300mW^2}{3Xex}ln(1-R_i)=\frac{4\times 300mk^2X}{3ex}ln(1-R_i).$$

Thus if the electronic mobility k, or its equivalent the velocity W in the direction of the electric field is known, h can be calculated. The values used for this calculation in the present work are those obtained by Townsend and Tizard[5] for air and by Brose[6] for O_2. For values of X/p below 0.5 in air (p = pressure in mm) W was extrapolated by Compton's mobility equation.[7]

It should be pointed out that values of the attachment coefficient obtained by all methods are subject to a good deal of uncertainty because of the unreliability of the electron mobility data. For instance, Bailey found a considerable discrepancy between his values of the electron energy in air as a function of X/p and those of Townsend and Tizard. This of course throws doubt on the values of W which were obtained at the same time as the energy values.

3. APPARATUS AND PROCEDURE

The chamber containing the electrodes was of brass and had a ground joint made tight with dry shellac and sealing wax applied on the outside. Guard rings were used to secure uniform fields. In the first apparatus the electrodes were brass and copper, and the distance x from filament to grid was 5.51 cm. In the last apparatus the electrode surfaces were platinum and x was 2.80 cm. Before filling, the chamber was evacuated through a liquid air trap by a mercury vapor pump until after standing an hour or so with the pump off no discharge could be obtained in a discharge tube connected to a one inch spark coil. The last apparatus was heated to 115°C while being evacuated, which greatly hastened the liberation of water vapor from the large metal surface.

Air and oxygen were purified by passing slowly over hot copper oxide, sodium hydroxide, calcium chloride, and P_2O_5, each in 60 cm tubes, and finally through two liquid air traps. For N_2, the copper oxide was replaced by hot copper. The oxygen and nitrogen were obtained from ordinary commerical tanks. The system was clean enough so that no formation of negative ions was observable in nitrogen, even at 300 mm pressure, though an attachment coefficient 1/100 of that in air could have been measured.

4. SOURCES OF ERROR

a. Uncertain electron mobility. This has already been pointed out.

b. Excess attachment near filament. The assumption that attachment takes place at a uniform rate throughout the paths of the electrons from

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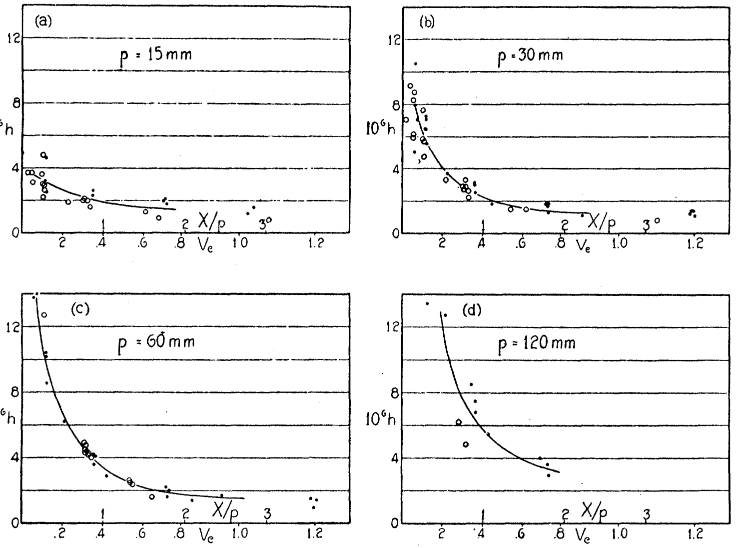
[6] H. L. Brose, Phil. Mag. **50,** 536 (1925).

[7] K. T. Compton, Phys. Rev. **22,** 333 (1923); L. B. Loeb, Kinetic Theory of Gases, p. 503.

filament to grid can not of course be exactly true, for the electrons acquire their terminal energy only after travelling a certain distance in the field. However, at 15 mm pressure 90 percent of the terminal energy would be acquired within about 1/2 cm from the filament if the collisions between electrons and molecules were perfectly elastic, and since the energy loss is actually much more rapid, the steady state is reached much more quickly. For the experimental evidence see section 5a.

c. Diffusion of electrons to grid wires. In the absence of the alternating field the observed current is too small because some of the electrons diffuse to the grid wires instead of following the lines of force. This makes the observed value of h too large. A calculation of the error in h so introduced, using the usual mobility and diffusion laws, gives $+100$ percent at a pressure of 11 mm and electron energies from 0.3 to 0.8 volts. This is too high, probably by a factor of at least 2, because at this pressure the electronic mean free path is about equal to the radius of the grid wires and hence the ordinary diffusion law no longer holds in the neighborhood of the wire (it gives infinite current density for an infinitesimal wire). The error is further reduced by the fact that nearly all measurements were made at pressures higher than 11 mm, and the error drops rapidly with increasing pressure.



Figs. *3a*, *3b*, *3c*, and *3d*. Attachment coefficient, h, in air. Circles and dots are experimental values with $x=5.51$ cm and 2.80 cm respectively. (x is distance from filament to grid.) V_e = average electron energy in volts; X = field in volts per cm; p = pressure in mm.

d. Effect of change in current magnitude. In air and oxygen, change in the magnitude of the electron current caused by changing the filament current had no effect on R. In the mixture of 1.3 percent $O_2+98.7$ percent N_2 and in H_2O, an increase in current caused a decrease in R for which no explanation could be found. Hence no calculations can be based on the latter measurements.

e. The "hump effect." With low main field and rapid attachment, the curves of R against V_g showed an anomalous rise to a maximum at V_g from 50 to 150. The most reasonable explanation seems to be that some fault in the apparatus caused an alternating field at the filament which increased the electron current. The effect prevented measurements in weak fields, but is not believed to be an important source of error in the results presented.

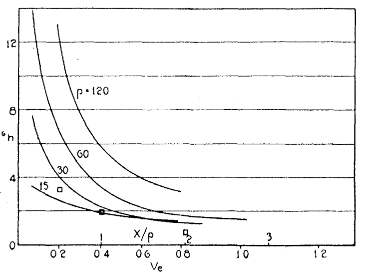
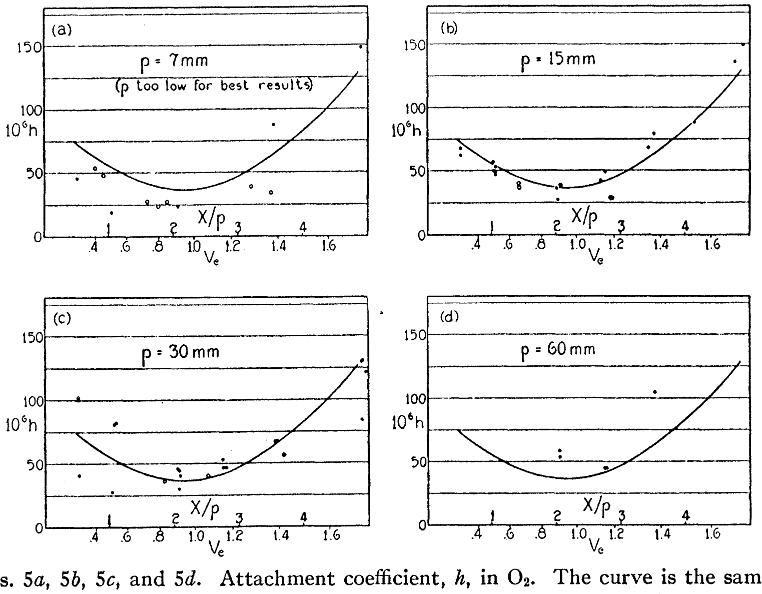


Fig. 4. Curves of Figs. *3a* to *3d* and results of Bailey, shown by squares, collected for comparison. V_e = average electron energy in volts; X = field in volts per cm; p = pressure in mm.

f. Non-reproducibility. The discrepancies between measurements with different fillings of the same gas are sometimes large, particularly at weak fields (see Figs. 3a to 5d). They show no correlation with the rate of filling, length of time the chamber was heated and pumped before filling, or any other known factors. With few exceptions, the results with a given filling did not change appreciably on standing up to 7 days. A mixture of roughly 1 part oxygen and 4 parts nitrogen gave about the same result as air.

5. Results

Figs. 3a to 5d give the results of all determinations in air and oxygen. Points shown by circles were obtained with the older apparatus where the distance x from filament to grid was 5.51 cm. The solid points were obtained with the last apparatus in which x



Figs. *5a*, *5b*, *5c*, and *5d*. Attachment coefficient, h, in O_2. The curve is the same in all figures. Circles and dots are experimental values with x = 5.51 cm and 2.80 cm respectively. (x is distance from filament to grid.) V_e = average electron energy in volts. X = field in volts per cm. p = pressure in mm.

was 2.80 cm, about half the previous value. The results for H_2O and for mixtures will be given only as rough comparisons of the attachment per cm of travel in the direction of the field, for h could not be calculated because of lack of knowledge of W or the electron mobility, and the measurements were too few in number to make exact quantitative figures of any significance.

a. Region in which attachment occurs. Permanence of ions. If the attachment took place primarily near the filament, or if a steady state were reached in which attachment were balanced by detachment, the two distances x would have given about the same values of R_i (R_i=fraction of electrons attaching before reaching grid), at the same values of p and X/p. Hence the values of h calculated for the larger distance x (shown by circles in Figs. 3a to 5d) would have been only about half as large as the values calculated for the smaller x. The fact that h is the same within the limits of experimental error, except at the lowest pressures where the electrons travel the largest distances before attaining their final energies, shows that attachment is a process taking place throughout the lives of the electrons as assumed, and that detachment is inappreciable in the main field.

b. Detachment of electrons from negative ions in high fields (violent collisions). The much stronger alternating field, on the other hand, seems to be able to cause detachment. The R curves in oxygen (e.g., Fig. 2a) fall off more and more steeply after V_g rises above about 50 volts. This must be due either to an abnormally high ion mobility, caused for instance by the breaking up of a cluster ion, or to detachment. If it were due to high ion mobility, it should be exaggerated by low frequency which increases the capture of ions, and curves taken at $\lambda = 150$ should fall about three times as fast as curves taken at $\lambda = 50$. This does not occur. (The principal reason that the curve for $\lambda = 20$ appears so much higher than the curve for $\lambda = 50$ is that the voltmeter reads about 20 percent too high at this high frequency, and the uncorrected readings are plotted. There is also a little "hump effect"). A certain amount of difference between the curves at different frequency is to be expected even in the case of detachment, for the lower frequency moves more ions into the region of strong field near the grid wires. Hence it appears that detachment rather than an increase of mobility which still remains of molecular order is taking place. When $V_g = 200$, the fields at the surface of a grid wire and half way between two wires are respectively 9000 and 1200 volts per cm. At a pressure of 15 mm the corresponding values of X/p are 600 and 80, giving 3.6 and 0.5 volts drop along one molecular mean free path. It is therefore not surprising to find detachment in the alternating field although none was found in the far weaker main direct field.

The air curves also show the abnormal drop in R at high V_g, but to a smaller extent as would be expected, for the higher total pressure reduces X/p, i.e., reduces the energy gain per free path. In H_2O detachment occurred less readily if at all. However, an addition of 4 percent H_2O to O_2, which was sufficient to double the attachment, did not greatly decrease the detachment.

c. Variation of h with average electron energy. In both air and oxygen h falls as X/p increases up to about 2, corresponding to 0.9 volts average electron energy. Bailey[3] found the same variation, his results being shown in Fig. 4. In oxygen h has a minimum at this value and then increases more and more rapidly as X/p rises. In air the results are not reliable at such high electron energies, because R_i was too small, but there may well be such a minimum. In ammonia Bailey and McGee[4] found an increase in h with increase in X/p. The variation with X/p indicates that in oxygen there are *two* processes of ion formation: one, dominant at low X/p, which gives out energy and so becomes less probable as the energy rises, and another, dominant at high X/p, which requires energy, and so becomes more probable as the number of electrons having the requisite energy increases with increasing X/p.

d. Variation of h with pressure. The values of h in air at low X/p are seen to rise rapidly with increase in pressure at constant X/p. The variation with pressure decreases as X/p increases. In oxygen the results disagree badly at low X/p, but there is some indication of the same variation as in air. Above $X/p=2$, which gives the minimum value of h, there is practically no variation with pressure. The variation with pressure is contrary to the results of Bailey who found that h was independent of pressure at constant X/p. To be sure he assumed this to start with, but he checked his assumptions by the agreement of the different values of h and of the electron energy (which is also given by his method) calculated from different pairs of pressures. An attempt to recalculate his results assuming a variation with pressure such as here observed shows that his method would really be quite sensitive in detecting such a variation. It is hard to find a reasonable cause for the difference between the present results and those of Bailey. Although all the sources of error in the present work which occur to the writer (diffusion of electrons to grid wires, detachment, excess attachment near filament, and impurities) would apparently produce a variation with pressure in the opposite direction to that observed, the greater consistency of Bailey's data and the simpler conditions in his apparatus justify greater confidence in his results. A variation of h with pressure at constant X/p is of course contrary to the hypothesis that attachment is a simple one stage process in which an electron strikes a single molecule and sticks to it permanently.

e. Comparison of h in air and oxygen. On the assumption that attachment consists simply in an electron striking a single molecule and sticking to it permanently, h depends only on the kind of molecule and the electronic energy, and the relative values of h in air and oxygen may be calculated as follows.

$$h_{\text{air}}=\frac{\text{number of attachments}}{\text{number of collisions}}.$$

Since $h_{N_2}=0$,

$$h_{\text{air}}=\frac{h_{O_2}\,(\text{number of collisions with } O_2)}{\text{number of collisions with } O_2+\text{number of collisions with } N_2}$$

$$=\frac{h_{O_2}vnp/L_{O_2}}{vnp/L_{O_2}+v(1-n)p/L_{N_2}}$$

where $n=0.2$ is the mol fraction of O_2 in air, p is the total pressure in mm, and L_{O_2} is the electronic mean free path in O_2 at 1 mm pressure. This gives

$$h_{O_2}=h_{\text{air}}(1+4L_{O_2}/L_{N_2}).$$

The results of this comparison, using values of L_{O_2} and L_{N_2} calculated from the mobility and electron energy, are shown in the table, the values of h_{O_2} so calculated from the measurements in air being given beside those actually measured in O_2. The former are less than half the latter. The combined errors in W, L, and the electronic energy coupled with the errors of the present work may well be responsible for the discrepancy. If a disagreement really exists, it shows that attachment is not the simple process assumed in this calculation. If results at the same total pressure instead of at the same partial pressure of oxygen had been compared, the discrepancy would have been more than 5 to 1.

TABLE I. *Relative values of h_{O_2} from measurements in air and oxygen at same electron energy V_e, and same partial pressure of oxygen, p_{O_2}.*

V_e volts	p_{O_2}	L_{O_2}	L_{N_2}	$10^6\,h_{O_2}$ from: air	oxygen
0.4	7	0.064	0.037	20	65
0.5	15	.064	.035	27	55
0.65	15	.062	.033	21	45
0.76	7	.061	.032	13	40
0.9	15	.059	.031	16	35

f. H_2O and mixtures containing H_2O. Definite evidence of the complexity of the attachment process, in some cases at least, is furnished by a few experiments in H_2O and mixtures of H_2O and O_2. H_2O alone gave roughly the same attachment per cm of travel in the direction of the field as O_2, but 4 percent H_2O added to O_2 doubled the attachment per cm, and 30 percent H_2O removed all trace of free electrons, which means that the attachment per cm was increased at least five fold. *Hence H_2O and O_2 cooperate in a complex attachment process which is much more efficient than the processes involving either alone.* On the other hand, 20 percent H_2O added to N_2 gave about the same attachment as 20 percent O_2 added to N_2.

The experimental work and most of the calculation was done at the Physical Laboratory of the University of California. The writer wishes to express his thanks to Professor Leonard B. Loeb, at whose suggestion this problem was undertaken, for his kind advice and criticism.

PRINCETON UNIVERSITY,
January, 1929.