The Energy of Formation of Negative Ions in O_2

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This paper reports the results of an attempt to evaluate the energy of attachment of electrons to molecules in O_2, by determining at what energy the electron is detached from the O_2 ion in impact with molecules. A value of 0.34 volt is found. In this investigation the complicated phenomena reported by Cravath and Bradbury as a function of the potentials of the high frequency fields employed in the Loeb electron filter, are investigated and explained. At the proper frequencies and with uniform fields electrons can effectively be filtered out without material ion capture. At higher fields the negative ions break up leading to an increased capture of carriers. If many free electrons are present at about the first radiating potential in O_2 (8 volts of energy) at high frequencies photoelectrons liberated at the wires and escaping capture may cause an increase in the current through the filter, especially at higher pressures ("hump effect" of Cravath). Finally at very high fields and especially at higher pressures the electrons ionize by impact producing an increase in current followed by a rapid decline due to capture. Shortly thereafter an arc breaks. At the highest pressures studied (20–60 mm) reattachment of electrons masks all the phenomena and a spark breaks very shortly after a rise of current is observed. The ions have been shown to break up in an X/p (field strength in volts/cm, pressure in mm of Hg) of 90. This corresponds to an ion energy of between 0.136 and 0.68 volt with the higher value the more likely. Of this only about half is available for electron detachment so that one can set 0.34 volt as the probable upper limit of the attachment energy which might correspond to a wavelength of 36,000A.

EVER since it has been clearly recognized that free electrons attached themselves to molecules to form negative ions it has been the goal of investigators to learn something of the nature of this process. The early experiments of Franck,[1] and of Wellisch,[9] the theory of J. J. Thomson[2] and the later researches of Loeb,[3] Wahlin,[4] Bailey[5] and his collaborators, Cravath,[7] and finally the beautiful papers of Bradbury[6,8] have given some indication as to the molecular and atomic types attaching electrons and as to the probability of attachment as a function of electron energy. Of the gases investigated by Bradbury *apparently* only two gases attach electrons with the emission of radiation,* to wit, O_2 and SO_2. All other processes are of a nature where the energy of attachment can be removed by a third body. As to the heat of formation of these ions nothing is known. The observation of even atomic recombination spectra is so difficult that all too little is known of these processes. All attempts to observe the so-called "electron affinity spectrum"[10] of *atoms* or molecules have thus far proved futile. It is in fact quite unlikely that any progress can be made in this line of attack in the near future for the radiation in O_2 if emitted will be in the infrared and conditions for intense radiation from ion formations require high electron densities in a gas at considerable pressure with very low electron energies, a set of conditions which are more or less mutually exclusive.

Both Cravath and Bradbury, who investigated attachment probabilities using Loeb's electron filter, observed at high alternating field strengths between the grid wires of their filters, a decrease in the transmitted current as the applied alternating field increased. Since *ions* are not captured by the grids at the frequency used, the interpretation made by them was that in such fields the negative ions were accelerated to energies sufficiently great to enable them to knock off their electron in impacts with molecules. The electrons were then captured by the grid wires. Bradbury estimated the energy as about 0.6

* Bradbury and F. Bloch have been investigating this question wave mechanically and though results are not complete the work up to the present makes a radiative process seem unlikely.

[1] J. Franck, Verh. Deutsch, Phys. Ges. **12**, 291, 613 (1910); Pohl, ibid. **9**, 194 (1907).
[2] J. J. Thomson, Phil. Mag. **30**, 321 (1915).
[3] L. B. Loeb, Phys. Rev. **17**, 89 (1921); Phil. Mag. **8**, 98 (1929); **43**, 230 (1912); J. Frank. Inst. **197**, 45 (1922).
[4] H. B. Wahlin, Phys. Rev. **19**, 173 (1922).
[5] V. A. Bailey, Phil. Mag. **50**, 825 (1925).
[6] N. E. Bradbury, J. Chem. Phys. **2**, 829, 835, 840 (1935).
[7] A. M. Cravath, Phys. Rev. **33**, 605 (1929).
[8] N. E. Bradbury, Phys. Rev. **44**, 883 (1933).
[9] E. M. Wellisch, Phil. Mag. **31**, 180 (1916); **34**, 33 (1917); Am. J. Sci. **44**, 1 (1917).
[10] O. Oldenburg, Phys. Rev. **43**, 534 (1933).

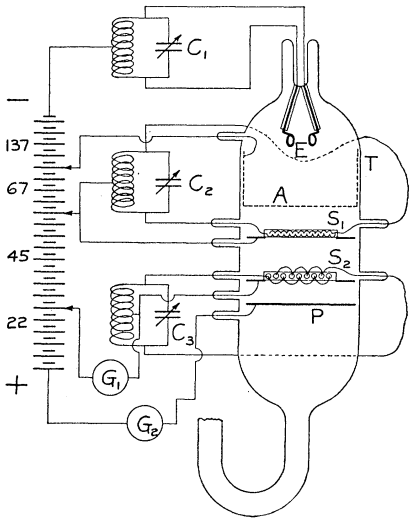

FIG. 1.

volt in O_2. Inasmuch as in neither Cravath's[7] nor Bradbury's[8] measurements uniform fields obtained, an attempt was made to study the phenomenon under better conditions. The apparatus is as indicated in Fig. 1. Inside the tube T a high frequency arc of 10^5 cycles at from 1000 to 5000 volts was operated by resonance from the condenser and coil C_1, across the platinum ring electrodes E. The electrons and ions were driven by a potential of 137 volts across a 5 cm gap through the gauze A. Between A and the filter S_1, 3 cm away, 67 volts drove the ions and electrons to and through the filter. This consisted of alternate 0.2 mm wires 2 mm apart connected to the tuned oscillator C_2. The frequencies used varied from 1×10^6 cycles to 3×10^6 cycles and the potential across the wires was varied by varying the coupling between primary oscillator and C_2. It could be read on a quadrant electrometer used as voltmeter. Three cm below S_1 at S_2 there was a second system of insulated parallel wires denoted as the "smasher." The copper wires were 0.317 cm in diameter with 0.3 cm between the adjacent surfaces (i.e., axes 0.617 cm apart). These were alternately connected to two sides of the oscillator C_3 which was 45 volts positive to S_1. Frequencies of 10^6, 3×10^6 and 10^7 cycles were used here. The smasher potential was varied by coupling as before and the potential was again read on an electrometer. A galvanometer G_1 could be inserted between C_3 and the batteries. At 2 cm below S_1 was a collector plate P at 22.5 volts above S_2 and connected to the positive end of the battery through the galvanometer G_2. The gas used was tank oxygen which had been passed through a purifying train and had been stored in contact with P_2O_5. The purity of the O_2 within the limits assured by that treatment appeared to make little or no difference in the results. The pressures found to be of interest ranged from 2 to 20 mm of Hg and were read on a specially constructed McLeod gauge.

The mixture of ions and electrons generated by the arc was driven by the fields to the filter S_1. Here a transverse high frequency alternating potential between the parallel wires of about 60 to 70 volts swept out the greater portion of the electrons of high mobility, letting the ions through. In the field of the smasher of which the high frequency alternating potential could be run from 10 up to 1000 volts by varying the coupling, and the power output from a push pull neutralized amplifier, the ions could be accelerated to speeds at which they would shed their electrons. While the field between the grid wires was not uniform it was sufficiently uniform compared to those of Bradbury and Cravath to enable some conclusions to be drawn. At the surface of the smasher wires the field X was 1.318 V/d (V potential, d wire spacing), in the center of the field it was 0.879 V/d, by calculation. Measurements on an electrolytic model gave 1.33 V/d and 0.835 V/d, respectively, with a field of 1.2 V/d about 0.1 d from the surface of the grid. The current of ions escaping smashing or capture at the smasher were received by plate P and registered as a current through the galvanometer G_2. The galvanometer G_1 gave the current captured by the smasher. A decrease in the current through G_2 with an increase through G_1 indicated capture by the smasher of ions or electrons. An increase in both currents denoted production of negative ions in the smasher field. Measurements of the current through G_2 were made for pressures from 2 mm to 60 mm as a function of the potential across S_2 for frequencies of 10^6, 3×10^6 and 10^7 cycles.

The highly complicated curves are shown in Figs. 2, 3 and 4 at three characteristic pressures

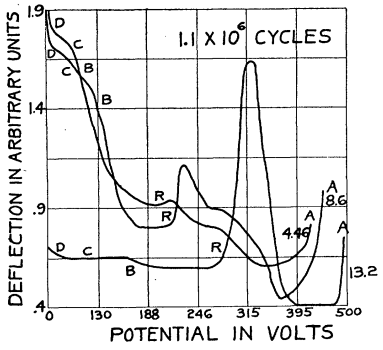

FIG. 2.

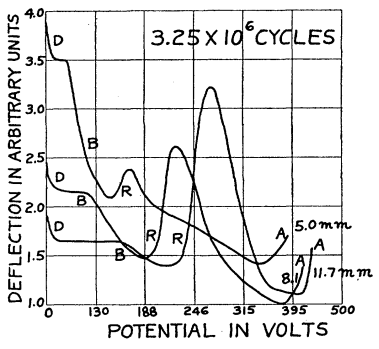

FIG. 3.

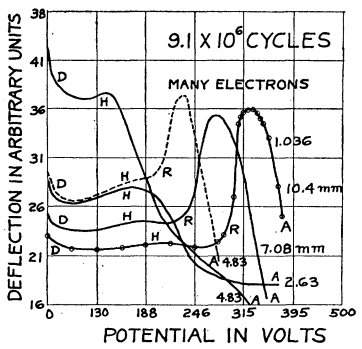

FIG. 4.

expressed in mm of Hg and for the three frequencies. The galvanometer deflections are in arbitrary units and the scales are not the same for the curves at different pressures. It is to be noted that the origin of ordinates in these curves in no case indicates zero current. At best the deflections at ion break-up never dropped much below about half the initial current due to secondary ionization at high fields, as will be seen. The abscissae are in volts as indicated, the scale being uneven since for these curves it sufficed to plot the potential in terms of electrometer readings which have been converted to volts from calibration curves. There are certain important features of the curves designated by letters; *viz.* *A*, arc breaks; *R*, sharp rise in current; *H* (in high frequency curves only), designating a "hump effect" of Cravath, *B* (in lower frequency curves only) indicating ion breakup, *C* (in lowest frequency curves only), indicating *ion* capture by grid, and *D*, decline of the curves due to capture of some free electrons not removed by the filter. In Fig. 5 are plotted the early parts of the curves for G_1 (dashed) and G_2 (full) for 3×10^6 and 10^7 cycles at the pressures indicated. They show the true character of events indicated by *B* and by *H* as will be seen.

The interpretation of the events indicated by the letters will now be given.

A represents the breaking of an arc or glow discharge between the smasher wires as was evidenced not only by large changes in current but by visual observation. At times, careful increase in smasher potential led to step-like increases in the current through G_2 accompanied by one pair, two pairs and three pairs of the wires exhibiting arcs or glow discharges between them. The plots of arcing potential *versus* pressure for the curves at 10^7 and 3×10^6 cycles are given by the observed points *AH* and *AL* in Fig. 6. Why the arcing potentials were always lower for the high frequency *AH* as well as being more uniform is not clear, except that at the higher frequency there were always plenty of free electrons which had not been captured by the electrodes so that the potentials were not capricious due to time lags as at lower frequencies *AL*.

The rise *R* common to all curves can unquestionably be attributed to a very intense ionization by electron impact due to energy gained in the smasher field. It was always greater the less the chance for capture of free electrons by the grid, i.e., at higher pressures. The value of the potential at *R* as a function of the pressure is shown in the two curves *RH* and *RL* of Fig. 6 for high and low frequencies, respectively. The high frequency potentials are higher for this phenomenon than the low frequency since presumably the electrons could no longer get their full terminal energy in one half-cycle at 10^7 cycles and hence the rate of gain of energy to cause *R* demanded higher fields. It may appear strange that any increase should be observed in the curves since electron capture by the electrodes is occurring at these fields. It does tend to disappear below 4 mm. However, the electron mobility varies inversely with the average electron energy and thus as the electrons approach 14 volts energy in the field before ionizing the chance of capture by the grid is not increased proportionally to the

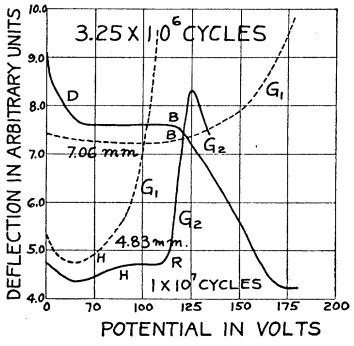

FIG. 5.

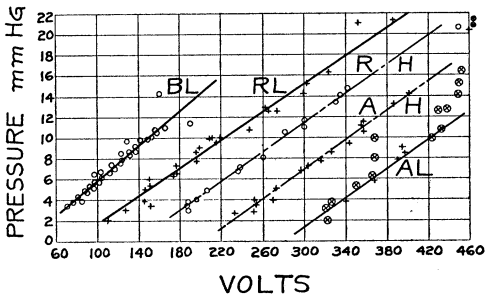

FIG. 6.

field. Thus the rate of gain of current by ionization by collision may outweigh the rate of capture. When all electrons get the ionizing energy in one half-cycle and produce new electrons, thus having their average energies reduced by inelastic impacts, their mobilities go up and an increased capture occurs. This causes the decline, which, however, never reaches zero and is converted to a current increase again as an arc breaks. There are in fact indications of other critical potentials in the declines of many of the curves.

In the high frequency curves the sharp rise is preceded by a small rise and a subsequent decline. It is observed chiefly at the higher frequency and is particularly prominent with inadequate filtering, i.e., with many free electrons reaching the grid. It is the "hump effect" observed by Cravath and as the curves for the currents through G_1 and G_2 of Fig. 5 show, it is clearly an *increase of current due to an increase* in *electrons created at* S_2. It is quite possible that it is due to liberation of photoelectrons at the smasher wires which can escape capture at high frequencies. They come from radiation due to the free electrons present receiving energy enough to excite the first radiating potentials of O_2. The hump is not prominent at higher pressures, and disappears at all lower frequencies where electron capture by the grids is effective.

The curves at 3×10^6 cycles all show a sharp break B, which is shown also at 1×10^6 cycles as a sharp increase in slope. This is masked by the "hump effect" at 1×10^7 cycles. It is also probable that at 1×10^7 cycles at these pressures the chance of an ion making an impact with a neutral molecule in one half-cycle becomes small so that the efficiency of break-up is diminished. A graph of this break-up to larger scale in the upper curves of Fig. 5 shows that at B the current through G_2 decreases while that through G_1 increases. The percentage changes do not appear to be equal as the galvanometer sensitivities are not the same and as the current through G_1 is initially greater than that through G_2. This means that we are observing a sudden increased capture of ions at S_2. This can only be due to an ion break-up in the smasher field, with subsequent capture of free electrons knocked off from the negative ions. The values of the potentials at B taken from the break points on the curves at 3×10^6 and 1×10^6 cycles when plotted against pressure give the line BL in Fig. 6. It is seen that they lie on a fairly smooth straight line.

At the lowest frequencies the initial drops due to D are followed by a continual decline C which appears more marked at lower pressures. Actually the rate of decline is probably the same and appears more prominent only due to the much larger currents observed at the lower pressures. This decline is undoubtedly due to a *capture* of some of the *ions* at the lower frequencies by the grid, and mobility studies bear this out. Calculation shows that capture of ions is probably negligible at 3×10^6 cycles while it begins to be important at 1×10^6 cycles, for if mobilities are normal the ions will move 0.08 of the distance between wires in one half-cycle.

The initial decline of all curves D is marked at the lower pressures and is undoubtedly due to the capture of some electrons by the lower potentials at S_2 which had escaped capture due

to the weaker fields at S_1. They are of no significance. At pressures much lower than 2 mm all curves show an almost monotonous decline at different rates for different frequencies due to the efficient capture of electrons by the grid. Collisions of electrons with the molecules in the space between wires begin to be so infrequent as to permit the escape from attachment to form ions of newly created electrons which produced the effects observed above. At pressures above 20 mm the electrons produced by processes below the ionization potential in most cases attach to molecules and thus the currents observed are nearly constant or increase slightly until the point R is reached. As with increasing pressure at these distances the arcing field strength is lowered we usually get an arc before the current increases much beyond R.

Since the potentials at which the various features A, R and B of these measurements occur vary linearly with pressure even though they do not pass accurately through the origin in the ranges studied the values of the field strengths and ratios of field strengths to pressure may be calculated to a sufficient degree of approximation for any one point of the line conveniently chosen in the region of reliable measurement and are characteristic of the process involved. At $p=7.6$ mm the values of the potential at which the phenomena are observed may be tabulated as in Table I. The quantity V/d is the field strength for a uniform field. $(X)_{0.1}$ is the field at 0.03 cm from a wire of S_2 where we can expect the phenomena to begin to be important, here $(X)_{0.1}=1.2\ V/d$. $(X)_{0.1\,\max.}$ is the *peak* value of the field and these quantities divided by $p=7.6$, the pressure in mm, gives the parameter of interest. Max. k is the factor k by which the electron energy exceeds that of thermal agitation at 0°C in a given potential field. The data of

TABLE I.

Event	V	V/d	$(X)_{0.1}$	$(X)_{0.1\,\max.}$	$\frac{(X)_{0.1}}{p}$	$\frac{(X)_{0.1\,\max.}}{p}$	max. k
B	120	400	480	680	63	89.5	200
RL	183	610	732	1035	96.5	137	—
RH	245	815	980	1380	128	181	—
AH	310	1033	1250	1770	165	233	—
AL	385	1283	1540	2180	203	287	—

Brose[11] on O_2 permit us to obtain an extrapolated value at $(X/p)_{0.1\,\max.}$ of about 220 in the case of B. This means that the *electron* energy is about 7.8 volts in the fields where the break-up of negative *ions* begins. While it is not safe to extrapolate Brose's curves for electron energy too far one can say that as the curve for k as a function of X/p is nearly linear at high fields, the electron energy at $(X/p)_{0.1\,\max.}=137$ (where the electrons ionize), allows us to place k at R as of the order of 300. This represents an electron energy of about 10 volts. This value is of the order of magnitude of the energy required to ionize the O_2 molecule (14 volts). It may further be added that the electron energy at the beginning of the hump in the "hump effect" is again of the order of 8 volts which is near that of the first radiating potential of O_2. Thus at high frequencies where electron capture is inefficient the "hump effect" may be caused by a photoelectric liberation of electrons from the grid wires of S_2.

As regards the *actual energy* of the *negative ions* when the ion begins to lose its electron probably little more definite can be said than that this phenomenon occurs closely in the neighborhood of an $X/p=90$. While the general break-up will occur when the root-mean-square field reaches the break-up value, the *beginning* of the break in the curve which is here recorded will occur when ions as far away as the distance of travel in one half-cycle from a grid wire *begins* to break up. Hence $(X/p)_{0.1\,\max.}$ is the value selected as leading to an evaluation of the energy of attachment. It is unfortunate that one cannot estimate the average energy of a *negative ion* in a field of this value. Because of persistence of velocity the ion will gain its energy over several free paths and thus the energy cannot be calculated. Its large gain will, however, be in the first free path and at best will be of the order of twice that in one path. Furthermore the free path of an ion is not known when X/p is high. The *normal ion* in O_2 has a free path of the order of 0.2×10^{-5} cm at N.T.P. It is conceivable that at an $X/p=90$ the path could nearly be that of an O_2 *molecule* as the attractive forces between ions and molecules here may become inappreciable.

[11] H. L. Brose, Phil. Mag. 1, 536 (1925).

Evidence for such increases in the case of ions of high energy is given by Mitchel and Ridler[12] and by Ramsauer and Beeck.[13] Hence one can, assuming that the energy is gained in one free path, set the energy of the ion as about $X\lambda$, i.e., the potential existing across an ionic free path in the direction of the field. This yields 0.68 volt for $\lambda=1\times10^{-5}$ cm and 0.136 volt for $\lambda=0.2\times10^{-5}$ cm. Considering persistence of velocity and the probability that λ has begun to increase in this region the upper figure seems the more probable. Again it must be remembered that in ion impact with a molecule the total energy above is not all available for detachment for some must go to conserve momentum, which in this case means that only half of the 0.68 volt is available for detachment. Hence we can conclude that the *electron when it attaches to an O_2 molecule in general does not liberate much more than 0.34 electron volt of energy.* Thus the red limit of a continuous attachment spectrum would lie at 0.34 volt and since Bradbury has shown that attachment becomes small for electrons of 0.4-volt energy it is clear that a continuous electron affinity spectrum must be looked for between 36,300A and 15,800A, and it might possibly be in still longer wave-lengths. As at present there seems to be no way of accurately fixing the energy of an ion in O_2 in a field where $X/p=90$ these limits must for the present suffice.

In conclusion the writer desires to express his thanks to Mr. Fred Ludecke who was sent to him by S.E.R.A. to help in this work, and without whose assistance some of the data could not have been taken, to Dr. A. M. Cravath for his calculations of the value of the smasher field, to Professors N. E. Bradbury and O. Luhr for their valuable discussions in connection with this work and to Dr. L. C. Marshall for the design of the oscillators used.

[12] Mitchel and Ridler, Proc. Roy. Soc. **A146**, 911 (1934).
[13] Ramsauer and Beeck, Ann. d. Physik **87**, 1 (1928).

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On the Mechanism of Unimolecular Electron Capture

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The formation of negative ions by electron capture in gases in which a dissociation process does not occur is explained by a unimolecular process involving the excitation of molecular vibrational levels and subsequent loss of energy by collision or resonance. In order to obtain a proper order of magnitude to agree with experimental observations, one must assume a change of only one vibrational quantum number. This sets an upper limit on the electron affinity. For the case of O_2, this limit is 0.17 volt consistent with other observations. The theory also yields a dependence of the phenomenon on the average energy of the electrons which is in agreement with experiment.

1. INTRODUCTION

IT is an experimental fact that if a current of free electrons be sent into certain gases, a more or less rapid change in the character of the carriers of negative electricity occurs. This change is one from a high mobility and high random velocity of agitation to drift velocities a thousand-fold smaller. Such a change must be associated with a change from electronic carriers to carriers of at least molecular dimensions. There occurs, therefore, a capture process in gases wherein initially free electrons become attached to neutral molecules forming stable negative ions. The experimental aspects of this process of electron capture and negative ion formation have been studied in some detail,[1, 2] and some of the important characteristics of the phenomena may be briefly summarized.

If the capture process is a random one as the electrons drift through the gas, then a *capture*

[1] N. E. Bradbury, Phys. Rev. **44**, 883 (1933); J. Chem. Phys. **2**, 827 (1934).
[2] V. A. Bailey, Phil. Mag. **10**, 145 (1930).