

# Electron Attachment Processes in Liquid Argon containing Oxygen or Nitrogen Impurity

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**Abstract.** The formation of negative ions of oxygen and nitrogen has been investigated by measurement of the attachment coefficients for electrons in dilute solutions of these impurity gases in liquid argon. Pulses of electrons were injected into the liquid by  $\alpha$ -particle ionization, and the attachment coefficients were obtained by two methods involving changes of the magnitude of the pulses and of the average ionization current when the electrode spacing and impurity concentration were varied. The attachment cross section for oxygen is appreciably greater than that observed in oxygen gas for low energy electrons ( $\sim 10^{-17}$  cm<sup>2</sup>), while for nitrogen the cross section is as small as  $3 \times 10^{-20}$  cm<sup>2</sup>. The field variation of the cross sections suggests that the attachment is a three-body process in both cases. Uncertainty in the exact composition of the liquids, particularly in the case of argon-nitrogen mixtures, makes detailed interpretation of these results difficult.

## § 1. INTRODUCTION

THE behaviour of electrons in liquid argon has been studied previously by measurement of the mobility of these charges, and by observing that a trapping process to impurity molecules also occurs (Williams 1957, Swan 1962, Davidson and Larsh 1950). These impurity ions have a very low mobility ( $\sim 10^{-4}$  cm<sup>2</sup> v<sup>-1</sup> sec<sup>-1</sup>), being similar in magnitude to that of the positive charges (Davis, Rice and Mayer 1962). The more recent breakdown studies for dielectric liquid systems have revealed that the formation of low mobility negative ions can give rise to a very pronounced anode effect; in some cases it is so pronounced that it masks any effect of the cathode surface (Swan and Lewis 1961). It is believed that this anode influence arises as a result of a local space charge near the anode surface, and that this space charge is formed because the negative charges concerned can not be neutralized instantly. No previous measurements have been reported for the attachment coefficients of electrons moving in a liquid medium, and the present investigation was undertaken in an effort to obtain a better understanding of some of the fundamental phenomena associated with the breakdown mechanism. Liquid argon was employed as the liquid dielectric, since electrons do not become attached to the atoms of this simple fluid, and oxygen and nitrogen were added as electron trapping impurities.

## § 2. THEORETICAL CONSIDERATIONS

As in earlier investigations, the ions were produced by  $\alpha$  particles emitted from an active electrode. The length of the  $\alpha$ -particle track in liquid argon has been estimated

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to be about  $5 \times 10^{-3}$  cm, and by using electrode spacings very much larger than this, it is possible to assume that the ions are produced at the active electrode surface. By making the active electrode the cathode, negative charge is transported across the gap, and because of the very high electron mobility in liquid argon the positive ions and any negative ions ultimately formed by attachment processes to impurity molecules during the electron transit may be considered as stationary. Thus, the only charge contributing to the current flow is that of the free electrons.

Let the number of ions escaping recombination in an  $\alpha$ -particle track be  $N$ , then this is the number of electrons leaving the cathode at time  $t = 0$ . The value of  $N$  will be field dependent, and will also be influenced by the angle of emission of the  $\alpha$  particle and by the impurities in the argon. As the electrons move across the electrode spacing they will become attached to impurity molecules, and the number of free electrons remaining at time  $t$  is given by

$$n(t) = N \exp(-\eta vt) \quad (1)$$

where  $v$  is the electron drift velocity and  $\eta$  is the attachment coefficient. By definition, this coefficient is the probability of attachment for an electron per centimetre path of drift. Figure 1 shows a diagrammatic arrangement of the electrical system used in the

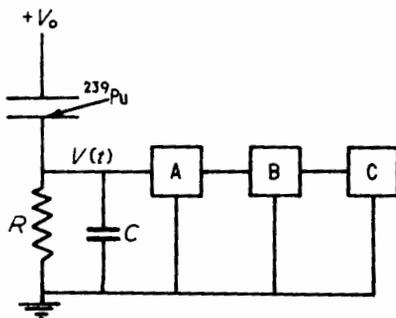


Figure 1. Diagrammatic arrangement of electrical measuring system.

A, preamplifier; B, delay-line pulse shaping amplifier; C, 70 channel pulse height analyser.

pulse analysis. The capacitance  $C$  is the total capacitance of the electrodes and of the input circuit of the preamplifier. The differential equation for the voltage  $V(t)$  developed across  $R$  by a current  $i(t)$  is  $dV(t)/dt + V(t)/RC = i(t)/C$ , which has the general solution

$$V(t) = \frac{1}{C} \exp\left(-\frac{t}{RC}\right) \left[ \int_0^t i(\theta) \exp\left(\frac{\theta}{RC}\right) d\theta + CV(0) \right]. \quad (2)$$

For an electron density given by equation (1) the current in the circuit is

$$i(\theta) = en(\theta)/\tau = (eN/\tau) \exp(-\eta v\theta),$$

$\tau$  being the electron transit time  $d/v$ .

Inserting  $i(\theta)$  into (2) and integrating gives

$$V(t) = \frac{eNR}{\tau[1 + RC\eta d/\tau]} \left[ \exp\left(-\frac{\eta dt}{\tau}\right) - \exp\left(-\frac{t}{RC}\right) \right]. \quad (3)$$

The value of  $R$  was chosen so that the time constant  $RC$  was very much greater

than the electron transit time, and if  $\eta = 0$ , as for pure argon liquid, then (3) reduces to

$$V(t) = \frac{eNt}{C\tau}. \quad (4)$$

Thus for  $0 \leq t \leq \tau$ ,  $V(t)$  increases linearly with time, while after  $t = \tau$ ,  $V(t)$  decays with the time constant  $RC$ . The  $\alpha$ -emitter strength was chosen so that there was only a small probability of two electron bursts being in the gap at the same time. The low frequency cut-off of the amplifier system was adjusted so that the full pulse height was obtained without introducing a clipping correction, and so that one pulse had completely decayed before another appeared. This latter precaution precludes the possibility of an erroneous pulse height being recorded as a result of the superposition of one pulse on the tail of the preceding pulse.

With an impurity present in sufficient quantity to give a measurable reduction in pulse height, the term  $RC\eta d/\tau$  is much greater than unity, and equation (3) reduces to

$$V(t) = \frac{eN}{C\eta d} \left[ 1 - \exp\left(-\frac{\eta dt}{\tau}\right) \right]. \quad (5)$$

From equations (4) and (5), therefore, the pulse heights in liquid argon  $V_A$  and in liquid argon containing an electron attaching impurity  $V_C$  are

$$V_A = \frac{eN_A}{C} \quad (6)$$

and

$$V_C = \frac{eN_C}{C\eta d} [1 - \exp(-\eta d)]. \quad (7)$$

The values of  $N$  for the two cases are not the same, since the presence of the impurity modifies the recombination rate in the ionized  $\alpha$  track.

From equation (7) it is possible to obtain  $\eta$  by measuring  $V_C$  at two different electrode spacings ( $d_1$  and  $d_2$ ) for the same liquid, in which case the equations reduce to

$$\frac{V_{C1}}{V_{C2}} = \frac{[1 - \exp(-\eta d_1)]d_2 C_2}{[1 - \exp(-\eta d_2)]d_1 C_1}. \quad (8)$$

$C_1$  and  $C_2$  will differ slightly because of the change in electrode spacing.

Since the system employed for the experiments reported here did not permit the electrode spacing to be changed without dismantling the test cell, this method of evaluating  $\eta$  depended very strongly on the ability to reproduce a particular liquid mixture. To overcome this, an alternative technique was developed which permitted the attachment coefficient to be obtained from a single liquid mixture and one value of electrode separation, and which did not require a measurement of the capacitance  $C$ . From equations (6) and (7) the ratio of pulse heights in the mixture to those in pure liquid argon with a given electrode spacing is

$$\frac{V_C}{V_A} = \frac{N_C [1 - \exp(-\eta d)]}{N_A \eta d}. \quad (9)$$

The values of  $N_C$  and  $N_A$  are the numbers of electrons leaving an ionized column at  $t = 0$  for the mixture and for liquid argon alone. Now, if the pulses were all of equal magnitude, the average currents  $I$  measured with an electrometer would be proportional

to  $N_C$  and  $N_A$ , and the ratio of the currents  $I_C/I_A$  would be equal to the ratio  $N_C/N_A$ , since the formation of low mobility ions would have no influence on a direct stress conduction measurement. The value of  $N$  for each particle will depend on the angle of emission with respect to the field direction, since the recombination loss is different at different angles. Pulses at all angles contribute to the current, but since the emission is isotropic, the majority of pulses are emitted parallel to or nearly parallel to the electrode surface. It is the same pulses which are least affected by recombination, since the distance travelled by the ions of each sign before complete separation is a minimum; thus little error is introduced by assuming that there is a direct relationship between the pulses of maximum magnitude and the currents measured by an electrometer. The current in liquid argon will thus be of the form  $I_A = KN_A$ , where  $K$  is related to the rate of  $\alpha$ -particle disintegrations; and similarly for a mixture  $I_C = KN_C$ . Thus the ratio  $N_C/N_A$  may be determined from the ratio of the average currents for the mixture and for argon.

Returning to equation (9) and substituting for  $N_C/N_A$  we obtain

$$\frac{V_C/V_A}{I_C/I_A} = \frac{[1 - \exp(-\eta d)]}{\eta d} \quad (10)$$

Thus for one electrode spacing measurement of the variation of pulse heights and average currents in liquid argon and in any mixture allows the attachment coefficients to be obtained directly without having to reproduce exactly the same liquid mixture a second time.

In principle, the attachment coefficient may also be determined oscillographically from observation of the growth of voltage during the electron transit time. Differentiation of (5) gives

$$\frac{dV(t)}{dt} = \frac{eN}{C\tau} \exp\left(-\frac{\eta dt}{\tau}\right) = G(t)$$

therefore

$$G(0) = \frac{eN}{C\tau} \quad \text{and} \quad G(\tau) = \frac{eN}{C\tau} \exp(-\eta d).$$

By dividing and rearranging we obtain

$$\eta = \frac{1}{d} \ln \left[ \frac{G(0)}{G(\tau)} \right]. \quad (11)$$

Thus from the gradient of the voltage-time curve at  $t = 0$  and  $t = \tau$ ,  $\eta$  may be obtained.

This technique has limited application for liquids, since the addition of impurity leading to a measurable  $\eta$  also causes loss of pulse height due to enhanced columnar recombination, but for gaseous systems such a method could be used.

### § 3. EXPERIMENTAL DETAILS

Figure 2 shows the arrangement of the electrode assembly and the glass test cell. The latter was constructed from a ten inch length of one inch diameter glass tubing, and was attached to the main vacuum system by a demountable copper gasket seal. The stabilized high voltage lead was brought in through a tungsten seal at the bottom of the cell. An oil diffusion pump, with a water cooled baffle and a liquid nitrogen trap, was used to evacuate the system to better than  $10^{-6}$  mmHg. The liquid to be investigated

was condensed by surrounding the cell with a Dewar flask containing liquid oxygen boiling at reduced pressure, but before measurements were made the system was allowed to come to equilibrium with the oxygen boiling at atmospheric pressure. Thus all data were recorded at 90 °K.

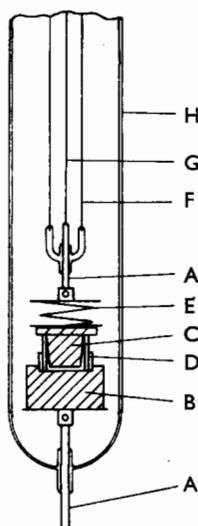


Figure 2. Electrode assembly and glass test cell.

A, tungsten seal; B, bottom brass electrode; C, radioactive electrode; D, quartz spacer; E, compression spring; F, stainless steel tube, shielding signal lead; G, signal lead; H, glass test cell.

A quantity of  $^{239}\text{Pu}$  was deposited on the centre of the upper brass electrode (C figure 2), which was held apart from the second electrode B by a quartz spacer D. The electrode separation was changed by using spacers of different lengths. Correction was made for the temperature change. A light compression spring E made contact between the upper electrode and the lead to the amplifier system or the electrometer. Care was necessary in design to minimize the capacitance of the input circuit of the pulse amplifier in order to obtain maximum pulse height. The first stage of the pre-amplifier (A, figure 1) was a 6AK5-6J6 cascode, and the bandwidth of the complete pulse preamplifier was 7 kc/s to 3.2 Mc/s. A delay line pulse shaping amplifier B was incorporated, which delivered rectangular pulses of 1.5  $\mu\text{sec}$  duration. These were sorted and counted on a 70 channel pulse height analyser C.

The strength of the plutonium source was 1  $\mu\text{c}$ , and this gave an average current of approximately  $10^{-11}$  A, which was measured with a vibrating reed electrometer.

The argon was supplied by British Oxygen Gases and was stated to be 99.995% pure, with nitrogen the principal impurity. No further purification was undertaken. Oxygen and oxygen-free nitrogen were added as impurities. Liquid mixtures were produced by letting a known volume of impurity gas into the evacuated system, and then condensing a known quantity of argon liquid. It has not been possible to calculate exactly the relative percentages of impurity in the liquid and in the vapour phase, but for the small concentrations involved it has been assumed that all the impurity went into solution. The liquid system was allowed to come to equilibrium over about one hour.

## § 4. EXPERIMENTAL RESULTS

## 4.1. Argon-Oxygen Mixtures

Figure 3 shows average currents for liquid argon and for liquid argon and oxygen mixtures for field strengths up to  $90 \text{ kv cm}^{-1}$ . As mentioned earlier the impurity concentration additions were computed on the assumption that all the impurity was

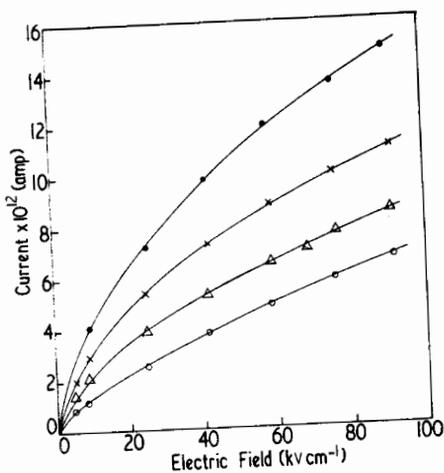


Figure 3. Average ionization currents in liquid argon and liquid argon-oxygen mixture.

●, liquid argon; ×, liquid argon with  $P_0 = 2.6 \times 10^2 \text{ mmHg}$ ; Δ, liquid argon with  $P_0 = 1.8 \times 10^3 \text{ mmHg}$ ; ○, liquid argon with  $P_0 = 1.8 \times 10^4 \text{ mmHg}$ .

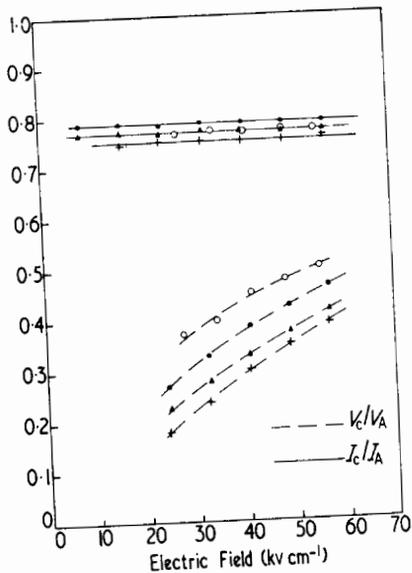


Figure 4. Average ionization currents and maximum pulse sizes for liquid argon-oxygen mixtures as a fraction of the average current and pulse size in liquid argon.

●,  $P_0 = 46 \text{ mmHg}$ ,  $d = 0.123 \text{ cm}$ ;  
○,  $P_0 = 69 \text{ mmHg}$ ,  $d = 0.0726 \text{ cm}$ ;  
▲,  $P_0 = 67 \text{ mmHg}$ ,  $d = 0.123 \text{ cm}$ ;  
+,  $P_0 = 84 \text{ mmHg}$ ,  $d = 0.123 \text{ cm}$ .

in solution, and are expressed as equivalent pressures  $P_0$  at  $15^\circ \text{C}$ . The reduction in current with increasing addition of oxygen is due to stronger recombination in the  $\alpha$ -particle column. The range of impurity concentration for which attachment can be measured is limited by the very large cross section for this process. Thus in order to realize sufficient pulse height for reliable measurements the maximum concentration of oxygen used was about  $0.01\%$ . The accuracy of pressure measurement set a lower limit of approximately  $0.005\%$ .

The ratio  $I_C/I_A$  was found to be independent of field over the range investigated, while the ratio of maximum pulse heights  $V_C/V_A$  increased with field as shown in figure 4.

The values of  $\eta$  deduced from equation (10) are shown in figure 5. The electric field is expressed in terms of an electron energy by a procedure outlined in the following section and the attachment coefficient as  $\eta/P_0$ .

As a further check of the present results, some measurements were taken using different values of electrode spacing for the same liquid mixture. The coefficients deduced in this way from equation (8) are also shown in figure 5.

The voltage waveform due to a single pulse was recorded oscillographically for liquid argon-oxygen mixtures. It was verified that equation (11) gave essentially identical results for the attachment coefficients and for the more accurate methods described.

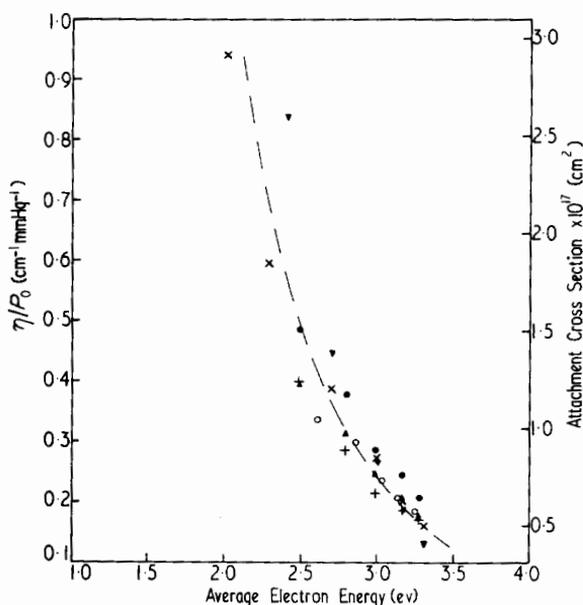


Figure 5. Attachment coefficients for oxygen in liquid argon. Using equation (10): ●,  $P_0 = 46$  mmHg,  $d = 0.123$  cm; ○,  $P_0 = 69$  mmHg,  $d = 0.0726$  cm; ▲,  $P_0 = 67$  mmHg,  $d = 0.123$  cm; +,  $P_0 = 84$  mmHg,  $d = 0.123$  cm. Using equation (8): ×,  $P_0 = 31$  mmHg. ▼,  $P_0 = 69$  mmHg,  $d_1 = 0.0666$  cm,  $d_2 = 0.117$  cm.

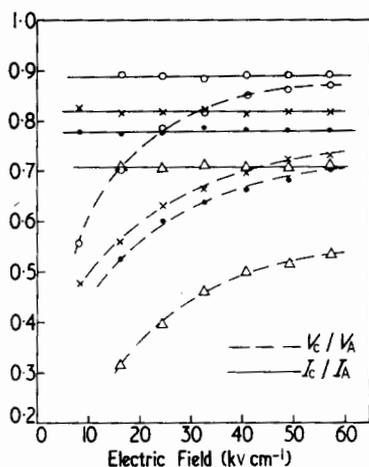


Figure 6. Average ionization currents and maximum pulse sizes for liquid argon-nitrogen mixtures as a fraction of the average current and pulse size in liquid argon.

$d = 0.123$  cm: ○,  $P_N = 5.31 \times 10^2$  mmHg;  
 ×,  $P_N = 1.36 \times 10^3$  mmHg;  
 ●,  $P_N = 2.23 \times 10^3$  mmHg;  
 △,  $P_N = 3.13 \times 10^3$  mmHg.

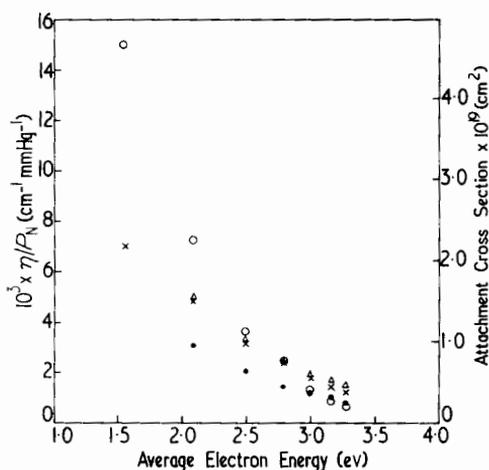


Figure 7. Attachment coefficients for nitrogen in liquid argon.

○,  $P_N = 5.31 \times 10^2$  mmHg;  
 ×,  $P_N = 1.36 \times 10^3$  mmHg;  
 ●,  $P_N = 2.23 \times 10^3$  mmHg;  
 △,  $P_N = 3.13 \times 10^3$  mmHg.

## 4.2. Argon-Nitrogen Mixtures

The attachment occurring with nitrogen as the impurity was found to be very much less than with an equivalent concentration of oxygen. This agrees with earlier observations of pulse magnitudes in these liquid mixtures (Davidson and Larsh 1950). As a consequence it was possible to add considerably more nitrogen without reducing the pulse height excessively. Figure 6 shows the ratios  $I_C/I_A$  and  $V_C/V_A$  for various nitrogen concentrations; and the values of  $\eta$  calculated from equation (10) are presented in figure 7. As before, the results are expressed in the form  $\eta/P_N$ , where  $P_N$  is the equivalent nitrogen pressure at 15 °C.

## § 5. DISCUSSION

Figure 8 shows the attachment coefficients determined for oxygen and nitrogen as a function of electron energy. A single representative series of measurements is shown in each case to avoid confusion. The electron energy has been calculated on the assumption that the collision of electrons with the atoms of the liquid can be described by

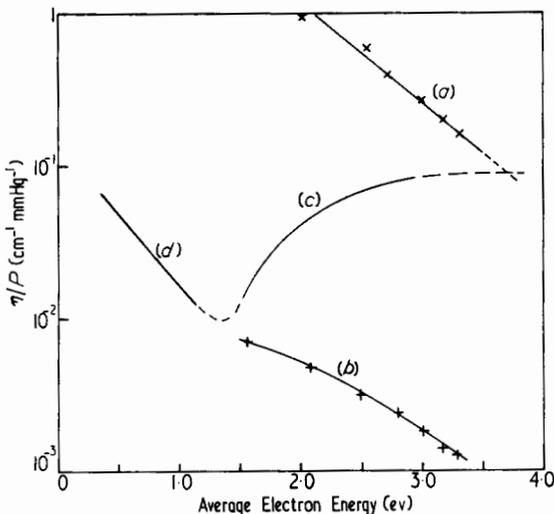
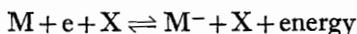


Figure 8. Attachment coefficients for nitrogen and oxygen in liquid argon, and for oxygen gas.

- (a) oxygen in liquid argon,  $P_0 = 31$  mmHg; (b) nitrogen in liquid argon,  $P_N = 1.36 \times 10^3$  mmHg; (c) three-body process in oxygen gas,  $P_0 = 44$  mmHg; (d) two-body process in oxygen gas,  $P_0 = 44$  mmHg.

gaseous kinetic theory. Measurements of electron drift velocity in argon suggest that this may be close to the truth (Swan 1962). Knowing the ratio of the diffusion coefficient  $D$  to the mobility  $\mu$  for electrons in argon gas, a mean electron energy may be expressed as  $3D/2\mu$  (Chanin, Phelps and Biondi 1962), and the values shown in figure 8 were taken from reported data for argon at 77 °K (Warren and Parker 1962). It is assumed that the mean energy is not disturbed by the impurities; for oxygen at very low concentrations this is probably valid. However, for nitrogen the inelastic loss due to vibrational and rotational collisions appears to be significant with the concentrations used in the present experiments (Swan 1962), and the mean energy is actually reduced by the impurity. Also shown are some recent data for electron attachment in pure gaseous oxygen.

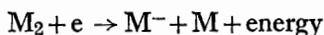
From comparison of the field variation of the coefficients in gaseous oxygen and in the liquid mixtures, it may be inferred that the attachment mechanism is a three-body process. Such a mechanism involves the collision of an electron and a molecule to which it can become attached, forming a negative molecular ion in an excited vibrational state. The excess energy must then be removed by a 'third body' before autodetachment of the electron occurs. The process is summarized by the equation



where M is the attaching molecule, e is the electron and X is the 'third body'. In pure oxygen gas where the third body is another oxygen molecule the vibration excitation energy of the ion is transferred by a resonant process to the other molecule. However, it is not necessary that M and X should be identical, since other atoms or molecules can stabilize the ion.

The values of  $\eta/P_0$  measured in the liquid mixtures are seen to be very much larger than the corresponding coefficients for the gas. This may be due to any of the following. Firstly, the value of  $P_0$  used may be in error, since it is almost certainly not true that all of the impurity is in solution; but if less were dissolved the deduced values of  $\eta/P_0$  would be greater than those shown in figure 8, not less. Secondly, the electron energy calculated by analogy with argon gas might be considerably in error, but interpretation of electron drift velocity data suggests that the energies computed are of the correct magnitude. It has been shown that the behaviour of the electron drift velocity in liquid argon containing nitrogen in solution is, at least qualitatively, analogous to the corresponding phenomenon in gaseous mixtures of the same components (Swan 1962). The explanation of the extraordinary dependence of drift velocity on impurity concentration is based on the Ramsauer elastic collision cross section for argon, which increases rapidly with energy for energies in excess of about 1 ev. Thus the drift velocity data suggest that electrons are present with energies of the magnitude estimated above. Thirdly, it is possible that mechanisms for stabilizing the ion other than a second impurity molecule may be important. In liquid argon it is well known that there is considerable local order about any one atom (Henshaw 1957), and as such there will be a range of vibrational frequencies associated with the close packing of the atoms. Thus an ion  $M^-$  which is loosely embedded in the 'lattice' of the surrounding liquid may be able to dissipate the excess energy for stabilization into the vibrational motion of its neighbours. If the probability of stabilization by this means is large, then considerably greater attachment would be measured in the liquid than in gaseous mixtures or in pure oxygen gas. Also, if the 'third body' density were greatly in excess of that of the attaching molecule,  $\eta/P_M$  would be independent of the pressure  $P_M$ . Results presented in figures 5 and 7 show that this is essentially true over the range of impurity concentrations investigated.

There is a further possible reason why  $\eta/P_M$  is independent of impurity pressure. A two-body process of negative ion formation which involves dissociation of the attaching molecule into an atomic ion may be represented by the equation



and values of  $\eta/P_M$  resulting from such a process would be independent of pressure. However, the magnitude of the two-body coefficient increases with increasing electron energy (curve (c) of figure 8) while the observed values decrease, and it may be necessary to measure attachment at greater field strengths in order to bring the two-body process to a significant level. The onset of dissociative capture in oxygen is at 4.5 ev, but a

significant fraction of the electron swarm may attain this value when the mean energy is well below this level. Extrapolation of the values of  $\eta/P_0$  for gaseous oxygen and for oxygen in liquid argon (figure 8) suggests that the transition would occur at about 3.7 eV, which corresponds to a field strength of  $110 \text{ kv cm}^{-1}$  in liquid argon. It is important that the attachment processes should be investigated at electric stresses nearer to breakdown, since, if the transition from a three-body to a two-body process could be observed, this would be very strong evidence in favour of the hypothesis that electrons in liquid argon can reach average energies of about 4 eV in transit across the gap, and that those in the high energy tail of the distribution could reach ionizing energies. The occurrence of ionizing collisions has been postulated in the explanation of the breakdown of liquid dielectrics, but very little direct reliable evidence is available to support this. Such experiments would be of great value in obtaining a better understanding of the breakdown mechanism.

If the mean free path for attachment is put equal to  $1/\eta$ , then the attachment cross section may be evaluated from the relationship  $Q = \eta/N$ , where  $N$  is the number density of the attaching molecule. These cross sections are also shown in figures 5 and 7. It is noticeable that the cross section for nitrogen is only about one hundredth that of oxygen at the same  $E/P$ . The measured values of  $\eta$  in nitrogen-argon mixtures were found to be very sensitive to residual contamination in the system, and it was necessary to evacuate the system to better than  $10^{-6}$  mmHg and to flush with argon prior to filling, in order to obtain reproducible results. In view of this, the very small cross section for attachment in nitrogen might be due to impurities in the nitrogen itself.

Davidson and Larsh (1950) found that twenty times more nitrogen than oxygen was required to reduce the pulse heights in argon to any given level. However, in the present series of measurements, it was found that over fifty times more nitrogen than oxygen had to be admitted to the system to produce the same pulse magnitude, and it is possible that the difference was due to impurities in the nitrogen added.

## § 6. CONCLUSIONS

The attachment of electrons to oxygen and to nitrogen in liquid argon appears to be due to a three-body process in which the excess energy of the ion is dissipated by the surrounding structure of the liquid argon. Such a mechanism can explain why the measured attachment coefficients for oxygen are very much larger when measured in the liquid mixtures than in pure oxygen gas, and also why, for a three-body process, the coefficient  $\eta/P_0$  should be independent of oxygen concentration. A very much smaller attachment coefficient is observed with nitrogen, the cross section being only about one per cent that of oxygen. It is thought that impurities in the nitrogen could be responsible for this attachment, but further experiments should be carried out using carefully purified nitrogen as an additive to argon.

## ACKNOWLEDGMENTS

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