ELECTRON MOBILITY IN LIQUID ARGON*

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Experiments of Williams (1957) showed that the drift velocity of electrons in liquid argon to which an electric field F is applied is essentially independent of F. If the electrons remain free then their motion can be described by kinetic theory, from which it appears that electron mobility is proportional to $F^{-\frac{1}{2}}$ and drift velocity to $F^{\frac{1}{2}}$. This is the dependence reported by Malkin and Schultz (1951), but it is evident that the recent, more exhaustive work of Williams (1957) is correct on this point and therefore that kinetic theory is not applicable to the problem. This theory could in principle be extended to explain a field-independent velocity, by supposing a special dependence upon electron energy of the scattering cross section for the collision of electrons with argon atoms, but this is very artificial and unnecessary in view of the alternative explanation suggested here ; in any case it leaves further serious objections, which will also be discussed briefly.

Williams (1957) calculated the scattering cross section needed to explain his electron mobility results by kinetic theory, observing that at high fields this gave electron kinetic energies up to 20 eV, several electron-volts in excess of the

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first ionization energy of argon. This he concluded to be in agreement with observations of ionization currents in liquid argon (Williams and Stacey 1957), suggesting that some electron multiplication occurred at the highest fields. It has since been shown (Stacey 1958) that no electron multiplication is needed to explain the ionization current measurements and, further, that the maximum energy of electrons in columns of ionization formed by α-particles in liquid argon is of the order 7 eV, less than half the first ionization energy.

One of the reasons for experimenting with liquid argon as a conduction counter medium was that argon was considered to have no electron affinity, and the high electron mobility is in qualitative agreement with this supposition. However, the constant electron velocity is strongly suggestive of an attachment process, whereby heavy negative ions of very short lifetime are formed. This suggestion is now examined quantitatively.

If the cross section for the capture of electrons by neutral argon atoms is Q and the mean velocity of an electron between successive captures is v, then the probability that a free electron will be captured in a time $\mathrm{d}t$ is

$$NQv\mathrm{d}t,$$

N being the atomic density. The probability that a particular captive electron will escape in the same interval of time is

$$C\mathrm{e}^{-E/kT}\mathrm{d}t,$$

where E is the attachment energy, k is Boltzmann's constant, and T the absolute temperature. C is a frequency factor of the order kT/h, h being Planck's constant. The ratio of the times which an electron spends in the free and captive states is thus

$$(C/NQv)\mathrm{e}^{-E/kT},$$

and the observed electron velocity is

$$v' = v \cdot \frac{C\mathrm{e}^{-E/kT}}{NQv + C\mathrm{e}^{-E/kT}}, \qquad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

neglecting any contribution due to motion of the heavy negative ions during their lifetimes.

The mean free velocity v is a function of F, and if it is assumed that between successive captures an electron starts from rest and accelerates freely in the field, v is given by

$$v = \left(\frac{e}{m} \cdot \frac{F}{2QN}\right)^{\frac{1}{2}}, \qquad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

e/m being the electronic charge-to-mass ratio. If v' is independent of F (as is observed) it is evidently independent of v, a condition which is satisfied by equation (**1**) if

$$NQv \gg C\mathrm{e}^{-E/kT}, \qquad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

i.e. an electron is captive most of the time, so that equation (**1**) reduces to

$$v' = (C/NQ)\mathrm{e}^{-E/kT}. \qquad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Numerical values of the interesting quantities, Q and E, cannot be obtained from equations (2) and (4), in which v is unknown. A proper experimental determination of Q and E would require the measurement of electron mobility over a range of temperatures, but as liquid argon at atmospheric pressure only exists over a very small temperature range, this would be a difficult undertaking. However, we can impose limits on the values of Q and E by simple physical arguments. The following three conditions must apply :

(i) The lifetime of the heavy negative ion is long by comparison with that of the free electron. This condition is expressed in equation (3).

(ii) The motion of the heavy ions does not contribute significantly to the measured electron velocities, since the negative ion mobility would only be of the same order as that for positive ions. Thus the ratio of the free electron to heavy ion lifetimes must be greater than the ratio of the positive ion mobility, μ_+, to the observed electron mobility, μ_e. This condition may be written

$$(C/NQv)\mathrm{e}^{-E/kT} \gg \mu_+/\mu_e. \qquad (5)$$

Since electron velocity is roughly constant over a wide range of fields, μ_e is not a quantity with much physical significance. However, the results of Williams (1957) indicate $\mu_e/\mu_+ \sim 4\times10^3$ at $F=10^5$ V/cm.

(iii) To be consistent with the theory of ionization of liquid argon by α-particles (Stacey 1958), the maximum electron energy should not exceed 7 eV, and therefore the mean kinetic energy of electrons in the free state should be less than 2 eV. This is expressed

$$\tfrac{1}{2}mv^2 = eF/4QN < 2 \text{ eV}. \qquad (6)$$

Conditions (i) and (ii) (equations (3) and (5)) may be written together as

$$(NQv/C)\mathrm{e}^{+E/kT} = f, \qquad (7)$$

where

$$1 \ll f \ll 4\times10^3,$$

so that the value of f may be taken as 60 within a factor of about 10. Thus from equations (4) and (7)

$$v = fv'. \qquad (8)$$

Combining equations (2) and (8) we obtain

$$Q = \frac{e}{m}\,\frac{F}{2N}\left(\frac{1}{v'f}\right)^2, \qquad (9)$$

so that equation (4) then gives

$$E = kT \ln (C/NQv'). \qquad (10)$$

The following numerical values may be used to estimate the magnitudes of Q and E from equations (9) and (10): $F=10^5$ V/cm$=333$ e.s.u., $e/m=5\cdot3\times10^{17}$ e.s.u./g, $m=9\cdot1\times10^{-28}$ g, $N=2\cdot1\times10^{22}$ per cm^3, $v'=10^6$ cm/sec

(Williams 1957), $k=8\cdot6\times10^{-5}$ eV °C^{-1}, $T=90$ °K, $h=6\cdot6\times10^{-27}$ erg sec. We then obtain

$$Q=1\cdot7\times10^{-18}\ \mathrm{cm}^2,$$
$$E=3\cdot7kT=2\cdot9\times10^{-2}\ \mathrm{eV}.$$

Owing to its logarithmic dependence upon the uncertain values, E has been estimated more accurately than Q, for which it is suggested only that the above result is correct within a factor 10.

To test whether the above estimates are reasonable, condition (iii) can be applied. Using the same numerical values we find

$$\tfrac{1}{2}mv^2=1\ \mathrm{eV},$$

which shows that the above values are consistent with this condition.

Williams (1957) suggested that the electron mobility in liquid argon agreed with Eyring's (1936) theory of ionic mobility and related phenomena in liquids. It must be noted that Eyring's theory refers only to heavy ions, the potential wells responsible for trapping them being physical holes and not electrical potential wells. Eyring's theory has no application to electron mobility. Williams himself showed that this theory could not be successfully applied even to positive ions in argon, whose mobility gives much better agreement with Stokes's formula for spheres in a viscous fluid. It must be concluded that the trapping centres for the electrons are the neutral argon atoms; any trapping centres due to impurities would give heavy ion lifetimes far too long. The lifetime of the heavy negative ion in liquid argon (at 90 °K) can be estimated as $1/Ce^{E/kT}\sim3\times10^{-11}$ sec, which is sufficient explanation why such ions are not normally observed.

If the energy E of attachment of electrons to neutral atoms is comparable in liquid helium it can be seen immediately that at the lower temperature of helium the heavy negative ions will have very long lifetimes, and therefore that the observed negative ion mobility will be comparable with that of positive ions. This was found to be the case (Williams 1957), but in helium the detailed problem is rather more complex and an analysis will not be attempted here.

In conclusion it may be stated that the measured velocity of electrons in liquid argon is consistent with the formation of heavy negative ions having lifetimes of the order 3×10^{-11} sec, resulting from an electron affinity of neutral argon atoms, which gives an attachment energy of the order $0\cdot03$ eV. The calculated capture cross section is of the order 10^{-18} cm^2. This picture is consistent with the theory of α-particle ionization of liquid argon (Stacey 1958) and indicates that no electron multiplication occurs.

References

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