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Drift velocity of electrons in liquid argon, and the influence of molecular impurities

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Abstract. The drift velocity of electrons has been measured in liquid argon and in liquid argon containing nitrogen, oxygen and hydrogen as impurities. It has been found that with nitrogen and hydrogen in solution the drift velocity increases, but that, because of strong electron attachment, insufficient oxygen could be added to produce an observable effect. The results support the view that the behaviour of electrons in liquid argon can be understood by treatment of the liquid argon as a high pressure gas.

1. Introduction

The problems encountered in deriving a quantitative description of the motion of charge carriers in liquids are complicated by the inadequacies in the theory of the liquid state, and by uncertainties concerning the nature of the ions. Because of their simple structure liquefied gases are attractive systems for investigation, both theoretically and experimentally, and considerable effort has been devoted to the study of ion motion in these liquids. Rice and Allnatt (1961) have developed a theoretical explanation of ionic movement in simple condensed fluids, and the results have been applied to ions in helium, argon, krypton and xenon. Leaving aside helium liquid, which possesses strange properties as a result of quantum effects, the most widely investigated inert gas in the liquid phase is argon. However, even for this fluid there is some uncertainty as to the nature of the ions, particularly the negative charge carrier; and a short discussion of the available evidence is given here in an attempt to clarify the situation.

A number of investigators found that the mobility of the negative carrier in liquid argon was very high (~ 10 cm^2 v^{-1} sec^{-1}), and it was assumed that these ions were, in fact, free electrons (Malkin and Schultz 1951, Williams 1957, Swan 1962). These results were obtained with field strengths in excess of about 5 kv cm^{-1} and with electrode spacings of approximately 1 mm or less. There have been very few investigations with electrode spacings in the centimetre range, and only one of these has been concerned directly with the mobility of the ions (Davis, Rice and Meyer 1962). Contrary to all other published data these authors reported that they were able to observe only ions of low mobility ($\sim 10^{-4}$ cm^2 v^{-1} sec^{-1}), which they attributed to the formation of negative ions by collision of electrons with impurity molecules. It was suggested that these impurities were most probably oxygen or nitrogen, and some recent measurements of electron attachment coefficients for oxygen dissolved in argon liquid support this hypothesis (Swan 1963). Figure 1 shows the attachment coefficients for oxygen in argon at 90 °K as a function of electric field strength. The coefficients η were determined

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experimentally in the electric field range 15–60 kv cm^{-1} for various electrode spacings and oxygen concentrations P_o, but the ratio η/P_o was found to be independent of P_o. Extrapolating these results to a field strength of 250 v cm^{-1}, which corresponds to the experimental conditions of Davis, Rice and Meyer (1962), gives $\eta/P_o = 7{\cdot}3 \times 10^7$ cm^{-1}. An oxygen concentration of 1 part per million with these conditions would give a mean capture distance of $1{\cdot}37 \times 10^{-2}$ cm, and it is not surprising that with electrode spacings of centimetre size no free electrons are observed. It is realized that the extrapolation involved is considerable, but even if in error by a factor of 10 no pulses due to free electrons would be observed with such low field strengths. For a mean capture free path of 1 cm in a field of 250 v cm^{-1} the argon must contain less than 0·02 parts per million of oxygen, a condition which is unlikely to be fulfilled with the most vigorous purification techniques normally employed.

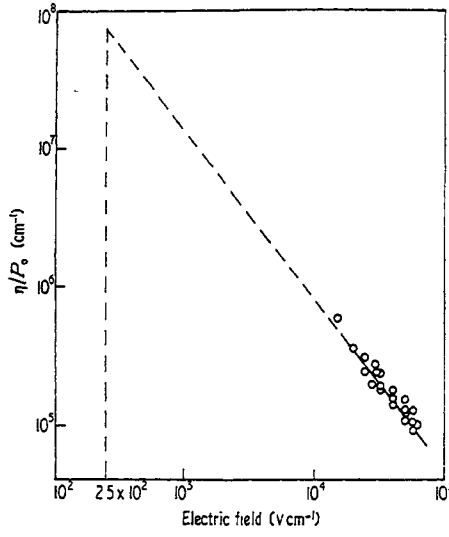

Figure 1. Attachment coefficients for oxygen in solution in liquid argon.

An investigation of the behaviour of liquid argon as a radiation detector (Marshall 1954) was carried out using electrode spacings up to 2 cm, but with field strengths as high as 30 kv cm^{-1}. From the gap dependence of pulse height the attachment coefficients were estimated, and comparing these values with those of Swan (1963) it would appear that Marshall's argon contained approximately 1 part per million of oxygen. Marshall also points out the importance of careful degassing of the system prior to the introduction of the argon since he observed that a residual air pressure of 6×10^{-3} mmHg resulted in a measurable loss of pulse height. However, from the rise time of the pulses produced by the ionizing radiations it is clear that the negative charges were moving with very high velocity. Thus all the available evidence is consistent with the conjecture that in pure liquid argon the negative ions are free electrons.

The present investigation was undertaken in an attempt to verify an interpretation of electron drift velocity measurements in liquid argon which had been put forward earlier (Marshall 1954, Swan 1960). This interpretation was based on the fact that in gaseous argon a small percentage of molecular gaseous impurity greatly increases the drift velocity of electrons (English and Hanna 1953). It was postulated that the variance

in the observed electron mobilities in liquid argon as reported by different investigators was due to a similar influence, with nitrogen the most likely impurity.

2. Experimental details

The test cell and electrode arrangement have been described in an earlier publication (Swan 1963). However, the electronic requirements for this investigation were different from those necessary for the attachment coefficient measurements. The ions were produced by α particles emitted from a 0·02 μc deposit of ^{239}Pu on the surface of one electrode. The electrode spacing was set at a fixed value which was in all cases much greater than the α-particle range in the liquid. All the ions were produced essentially at the surface of the radioactive electrode. By making the active electrode the cathode, negative ions which escaped recombination within the ionized column were transported by the applied field across the gap. The current resulting from the motion of these ions generated a voltage across a resistance in series with the test cell. This voltage pulse was recorded oscillographically. It has been shown (Swan 1963, equation (4)) that if the time constant of the series resistance R in parallel with the total capacitance C of the electrodes and the input circuit of the preamplifier is much greater than the ion transit time τ, then the temporal growth of voltage $V(t)$ across the resistance is given by

$$V(t) = \frac{eNt}{C\tau} \tag{1}$$

where e is the electron charge and N is the number of ions escaping from an α-particle track. This equation assumes that the number of carriers does not change as the charges cross the gap, and thus is invalid where attachment is occurring.

The bandwidth of the amplifier system was adjusted to be 8 Mc/s, with a low frequency cut-off at 100 kc/s. These values were selected so that any positive or negative ions formed by attachment would not contribute to the current. The input stage of the preamplifier was a 6AK5-6J6 cascode. The pulses were observed on a Tektronix 517A oscilloscope and each pulse was recorded photographically. In estimating the pulse rise time correction was made for the rise time of the amplifying system (Elmore and Sands 1949).

Commercial grade argon was used as supplied by British Oxygen Gases. This was stated to be 99·995% argon, with nitrogen the major impurity. No further purification was normally undertaken. Liquid mixtures were produced by letting a known volume of impurity gas into the evacuated system, and then condensing a predetermined volume of liquid argon. The impurity concentrations given in the text have been computed on the assumption that all the molecular gas went into solution, and thus only give an estimate of relative percentage impurities.

3. Experimental results

3.1. *Argon liquid*

According to equation (1) the voltage across the resistance increases linearly with time until $t = \tau$, after which it decays with the time constant RC. The linear portion was extrapolated to zero and maximum voltage and the transit time determined by the interval between these intercepts. Figure 2 shows the measured drift velocity of electrons in commercial grade argon at 90 °K for field strengths up to 100 kv cm^{-1}, and shows also

the results obtained by Williams (1957) and by Malkin and Schultz (1951). Electron drift velocities in pure argon gas corrected to the density of liquid argon are also given. It is apparent from a comparision of these data that some factor other than minor experimental differences was responsible for the large variance between measurements as recorded by individual investigators, since the technique of obtaining the data was essentially the same in every case. It was speculated that impurities were responsible, and subsequent measurements supported this view. Passing the argon gas through a

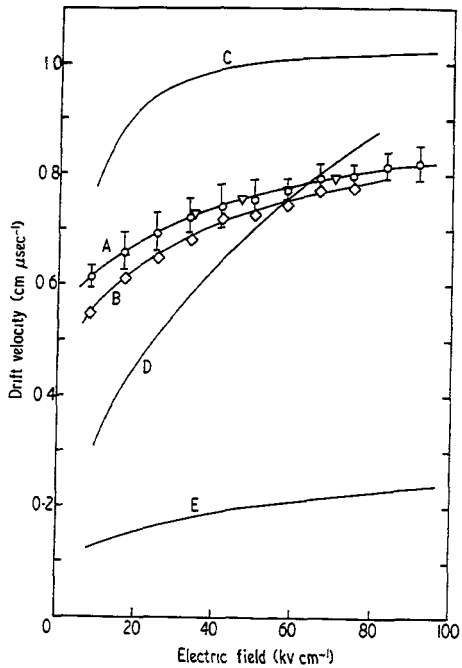

Figure 2. Electron drift velocity in liquid argon. A, commercial grade argon: ○, d = 0·1203 cm; △, d = 0·172 cm. B, commercial grade argon after passage through a cold trap: ◇, d = 0·1203 cm. C, Williams 1957. D, Malkin and Schultz 1951. E, pure gaseous argon.

cold-trap at liquid oxygen temperature resulted in a slight reduction in velocity which was more pronounced at the lower stresses. This would indicate that the trap was effective in removing some impurities. The measured velocity at a particular field strength was independent of electrode spacing (see figure 2).

3.2. *Argon–nitrogen mixtures*

The pulses observed in argon–nitrogen mixtures were generally of the same form as for argon, except that for low fields and high nitrogen concentrations attachment could be significant. As will be discussed in § 3.3 a linear extrapolation to zero and maximum voltages was not valid and the transit time was determined from the point of discontinuity in the voltage which occurs at the time the electrons reach the anode. The transients at the greater field strengths were not influenced by this process. Loss in pulse height due

to enhanced columnar recombination with low fields also limited the range of investigation. Figure 3 shows the electron drift velocity for argon and a number of argon–nitrogen mixtures. Continued addition of nitrogen increases the drift velocity in the concentration range employed here.

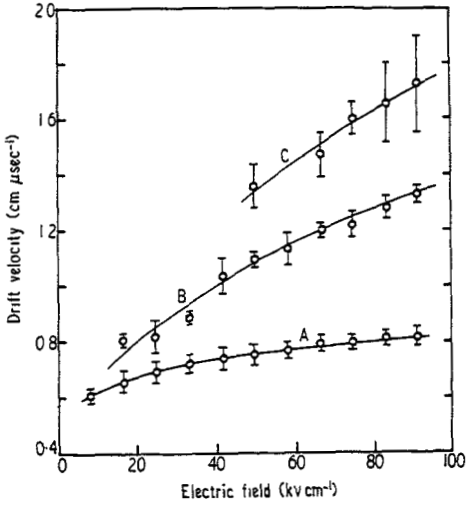

Figure 3. Electron drift velocity in argon–nitrogen mixtures. A, argon. B, argon + 0·07% N_2. C, argon +0·4% N_2.

3·3. *Argon–oxygen mixtures*

If the impurity present in the argon reduces the number of free electrons by attachment as the charges traverse the gap, the wave form observed on the oscilloscope will not be of the form of equation (1). It has been shown (Swan 1963, equation (5)) that the voltage across the resistance in conditions where attachment is occurring is given by

$$V(t) = \frac{eN}{C\eta d}\left[1 - \exp\left(-\frac{\eta dt}{\tau}\right)\right]. \qquad (2)$$

Here η is the probability of an electron becoming attached to an impurity molecule per unit length of drift. The final voltage attained ($t = \tau$) is less than in argon because of the influence of η; and in addition the value of N is reduced also by increased columnar recombination. The attachment coefficient for oxygen in argon is large, and thus the quantity of oxygen that can be added without excessive loss of pulse height is very limited. Because of the loss of electrons to oxygen molecules the rate of increase of voltage across the resistance R becomes progressively smaller as the electron pulse crosses the gap. Extrapolation of the linear portion to maximum and minimum voltage is not valid in this case, and would give erroneously high velocities. Because of the severe curvature it becomes difficult to determine the point at which the electrons reach the anode, and for this reason no extensive measurements could be made. For concentrations up to 0·02% there was no measurable change in drift velocity.

3.4. *Argon–hydrogen mixtures*

Figure 4 shows the influence on electron drift velocity of hydrogen in solution in argon. Difficulty was experienced with this system in that if the test cell were isolated and allowed to come into equilibrium at 90 °K most of the hydrogen came out of solution.

This was particularly noticeable as bubbles forming between the electrodes. Curve A of figure 4 shows the velocity of electrons as measured for a hydrogen–argon mixture 60 minutes after condensation was completed and the system isolated. There is no significant difference between these results and those obtained for argon alone.

It was normal procedure during condensation to maintain an argon pressure of 10 lb in^{-2} gauge within the test cell, and with this pressure applied a significant quantity

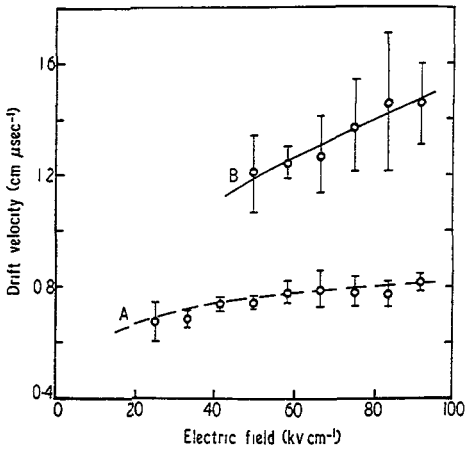

Figure 4. Electron drift velocity in argon–hydrogen mixtures. A, argon +0·04% H_2 in equilibrium; broken line is measured velocity in liquid argon. B, argon + 0·24% H_2 (during condensation of argon).

of hydrogen would dissolve. Curve B of figure 4 shows the electron velocities measured in a hydrogen–argon mixture with 10 lb in^{-2} argon pressure applied. There is no tendency for bubbles to form under these conditions. It was verified that the hydrogen was responsible for the observed velocity increase by applying the same pressure to liquid argon alone, there being no increase of mobility in this case.

4. Discussion

The results presented in this paper show that a small percentage of molecular impurity in liquid argon causes an increase in the drift velocity of electrons. From the magnitude of the mobility of these carriers there would seem to be little doubt that they are free electrons. Much of the difference in drift velocity as recorded by different investigators (figure 2) can be attributed to variations in the purity of the argon employed. Since the carriers are free electrons having drift velocities of comparable magnitude with electrons in argon gas, it has been suggested that gaseous kinetic theory might be applicable to electronic motion in liquid argon (Malkin and Schultz 1951, Williams 1957). However, gas kinetic theory has been developed on the assumption that energy is interchanged between molecules and ions during collisions, and that the collisions occupy only a very small part of the life of the ion. This implies that only binary encounters are important, and that the time between collisions should be very much larger than the collision time. In a dense fluid, however, intermolecular forces arising from the proximity of neighbouring atoms generally invalidate these assumptions. The motion of an individual molecule which is subjected to essentially continuous interaction with its neighbours has been

investigated theoretically (Kirkwood 1946), but because of its negligible dimension in comparison with the surrounding atoms a free electron in a dense medium may behave in a very different way to an ion of molecular size. In particular, it is feasible that the influence of the surrounding medium may be allowed for by a modification of the gaseous momentum transfer cross section, and that in other respects the electron–atom interaction may be considered as a binary kinetic collision.

Stacey (1959) has proposed a mechanism of electronic motion in liquid argon which assumes that the collision time is much greater than the time between collisions. He considered that the electron was trapped within the argon atom and then activated from this trap to move as a free electron, but this model does not seem applicable for reasons which have been discussed earlier (Swan 1960).

Direct application of drift velocity equations as derived from kinetic theory indicates that the cross section for argon in the liquid phase must be 100 times smaller than the cross section in the gaseous phase, and that the mean electron energy in the liquid should be between 10 and 20 ev. It was suggested by Marshall (1954) and by Swan (1960) that as far as electronic motion is concerned liquid argon might be considered as a compressed gas if impurities were taken into account, since it is a well established fact that the electron drift velocity in argon gas is increased greatly by small quantities of molecular impurity gases (English and Hanna 1953). The difference between the electron mobilities in gaseous and liquid argon might then be attributed to the impurities existing in the argon prior to condensation.

The impurity effect in gaseous argon is a result of the energy dependence of the momentum transfer cross section, which increases rapidly with energy in the range 1–10 ev (Ramsauer cross section). For energies less than the first-excitation potential of argon there are no inelastic collisions, but if a molecular impurity is present vibrational and rotational collisions are introduced at energies of approximately 1 ev. Clearly, such an impurity will reduce the equilibrium mean energy of the electron swarm in its path across the gap, and because of the unusual momentum transfer cross section such a reduction of energy also reduces the cross section for electron–argon collisions. According to kinetic theory the electron drift velocity is proportional to the reciprocal of the momentum transfer cross section and to the reciprocal of the square root of the mean energy. Since both cross section and energy are reduced by the impurity, the velocity increases. This argument is valid as long as the concentration of impurity is sufficiently small so that most of the collisions are between electrons and argon atoms.

The observed behaviour of electrons in liquid argon is identical with that in the gas with respect to the influence of molecular impurities, and it is natural to interpret the data in the same way. However, such an interpretation suggests that there is little interaction between neighbouring atoms of the liquid. The Ramsauer cross section is considered to be due to a quantum effect, and has been explained theoretically by introducing an additional polarization potential to the usual Hartree scattering atomic potential (Massey and Burhop 1952). The Hartree field for argon is very small at a radius of 2 Å, while Holtsmark's polarization correction extends to well over 4 Å from the atom. In liquid argon the nearest neighbour to any atom can approach to within 3·05 Å, while the mean separation between atoms is 3·86 Å (Henshaw 1957). Thus there would be considerable overlap and distortion of the scattering field as a result of the proximity of the neighbouring atoms. The polarization correction is essentially a long range effect, and without this term added to the Hartree scattering potential it is not possible to give a theoretical description of the Ramsauer cross section. Thus, it is surprising that in the liquid phase, where very considerable distortion of the scattering field would be expected, the electron drift velocity data suggest that the energy dependence of the momentum transfer

cross section is of a similar form for the gaseous and liquid states. Absolute magnitudes of the cross sections may be different, but further experiment using carefully purified argon is necessary in order to check this.

It is possible that an alternative explanation can be given for the results presented here, but the simplest interpretation is that the electrons in argon liquid behave as in a gaseous medium. If this is accepted it is difficult to see how the usual polarization correction to the Hartree scattering field can be valid.

5. Conclusions

The strong dependence of electron drift velocity in liquid argon on the presence of molecular impurity gases in solution can be interpreted if it is assumed that the electrons in the liquid move freely as in a gaseous medium, and that kinetic theory can be applied. The results suggest that interaction between neighbouring atoms is very weak, a concept which is difficult to reconcile with the usual scattering potential assumed for the argon atom and with the small interatomatic distances in the liquid state.

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