

Under these conditions, a rather high plasma density and temperature are required to achieve an observable counting rate using existing laser technology. For example, using an amplified giant pulse ruby laser, it is possible to obtain $n_1=n_2=10^{16}$ photons in an interaction volume $V^0=10^{-1}$ cm³ with $k_1=10^5$ cm⁻¹, $\omega_0=3 \times 10^{15}$ sec⁻¹. To achieve a counting rate of 10^{14} photons per second or 10^6 photons in a 10^{-8} second laser pulse requires [with $(M/m)^{1/2}=10^2$] (T in °K)

$$n^2/T^{1/2} \gtrsim 10^{30}. \quad (4.19)$$

This restriction as well as those listed above can be met for the minimum values $n \simeq 3 \times 10^{17}$ cm⁻³ and $T \simeq 2$

$\times 10^5$ °K = 20 eV. Such plasmas are probably obtainable in various magnetic pinch machines.¹⁰

ACKNOWLEDGMENTS

The authors wish to thank Dr. W. Wagner and Dr. R. W. Hellwarth for several helpful discussions.

¹⁰ The main restriction involved in the above estimate is the requirement $k_1 \ll k_D$ which requires $n/T < 10^{12}$ if $k_1 = 10^5$ cm⁻¹. However, if the experiment could be performed at extremely small scattering angles θ then we have $k = k_1 \theta$ and we can relax the condition $k_1 \ll k_D$. In this case the principal limitations are $\alpha(k/k_D) \gg \lambda \ln \lambda^{-1}$ and the requirement (4.19) on the counting rate. These conditions can be satisfied for the minimal values $n \sim 10^{16}$ cm⁻³ and $T \sim 3$ eV. For forward angles, however, the problems of background discrimination would become more difficult.

Mobility of Positive Ions in Liquefied Argon and Nitrogen*

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Drift velocities of positive ions in liquid argon and liquid nitrogen have been measured for applied electric fields in the range from 0 to 4300 V/cm. These data were taken at pressures of 1 atm and at temperatures corresponding to the respective liquids' boiling points at this pressure. A time-of-flight spectrometer, consisting of an ion source, an electronic shutter, and a final drift space, was used. The ions were produced by the technique of field ionization. This was accomplished by immersing a tungsten point (etched down to a radius of less than 1000 Å) in the respective liquefied gases and applying a high potential to it. The times of flight of the ions across the final drift space were determined by amplifying the ion current and displaying it on an oscilloscope. It was found that step-like changes in the curves of ion mobility versus E occurred in both liquid argon and liquid nitrogen. Five such constant-mobility regions were found in liquid argon and four in liquid nitrogen. These constant mobilities were found to be 6.0×10^{-4} , 9.75×10^{-4} , 8.50×10^{-4} , 7.75×10^{-4} , and 7.25×10^{-4} cm²/V-sec in liquid argon, and 2.50×10^{-3} , 1.80×10^{-3} , 1.54×10^{-3} , and 1.36×10^{-3} cm²/V-sec in liquid nitrogen. It is suggested that these mobilities may correspond to ionic clusters.

I. INTRODUCTION

PARTICULARLY during the past 12 years, the measurement of mobility of ions in gases has been developed as a powerful tool for the identification of the ions. Enough cross comparisons with mass spectrographic data have been made to establish the validity of mobility measurements for such identification. The existence of several types of ion in one gas, for example, He⁺ and He₂⁺ in helium,¹ and the change of one ion to another with changing field strength to pressure ratio, E/p , as for example, N₂⁺ changing to N₄⁺,² are illustrations of the successes of mobility measurements in accomplishing ion-type identification.

In gases, the cross section for ion-molecule collisions regulating the mobility is a momentum transfer cross section. There are at least three different atomic phenomena now well known which contribute to this cross section. The first and most obvious is the hard-sphere

cross section. While the actual form of interaction is probably an inverse ninth power repulsive force, a hard-sphere model is a good approximation. The second critical atomic characteristic influencing momentum transfer cross sections is the inverse fifth power attractive polarization force acting on ions in the vicinity of atoms or molecules. (In this work, only nonpolar substances are contemplated so that atomic or molecular polarizations must be induced by the field of the ions in the near proximity.) The combination of these two forces was assembled into a single theory of mobilities by Langevin³ in 1905 in a monumental work both in point of effort and importance. In it, by laborious numerical integrations, he deduced equivalent momentum transfer cross sections. Quantum-mechanical modernizations by Hassé and Cook⁴ in the period 1926 to 1931 have improved but only slightly altered Langevin's results.

The third atomic phenomenon of key influence on

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¹ J. A. Hornbeck, Phys. Rev. **83**, 374 (1951); **84**, 615 (1952).

² R. N. Varney, Phys. Rev. **89**, 708 (1953).

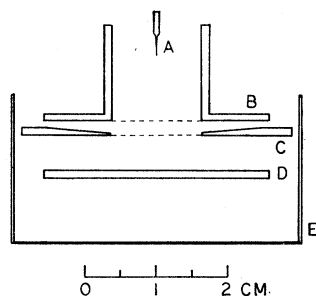
³ P. Langevin, Ann. Chim. et Phys. **8**, 245 (1905).

⁴ H. R. Hassé and W. R. Cook, Phil. Mag. **12**, 554 (1931).

momentum transfer and mobilities is the exchange of charge occurring at relatively large cross sections when the ions are the exact daughter ions of the parent gas atoms or molecules, for example, He^+ in He or N_2^+ in N_2 . Charge transfer has an influence on mobilities which can be introduced mathematically as a hard-sphere cross section. When charge exchange does occur, its influence over-rides the first two effects and causes the daughter ions of a parent gas to have the lowest mobility observed in the gas, obviously excluding such special ions as charged dust particles, etc.

All of the factors described as influencing motions of ions in gases may also be active in the case of liquids. However, because of the higher densities of liquids, it would seem that momentum transfer is not the basic mechanism of drag on ions in liquids. Such drag is more likely to be the actual retarding force of polarization attractions, but polarization forces are active in determining the finally observed mobility. In liquids, a considerable array of additional possibilities influencing the mobility present themselves, the two most outstanding being (1) the likelihood of existence of ionic

FIG. 1. Schematic diagram of the grid structures forming the time-of-flight spectrometer.



clusters, altering the mass but primarily the effective size of the ions, and (2) the possible existence of a liquid structure, causing the ionic mobility to be a form of motion from one trapping center to another. The present findings make the ionic cluster picture seem to be highly suitable as a description of the ionic motions.

II. APPARATUS

Figure 1 is a schematic diagram of the time-of-flight spectrometer. The various regions and electrodes may be described as: AB, the ionic source region, BC, the ionic shutter region, CD the drift region. These regions and the cryogenics are next described in more detail.

A. The Ion Source

In some mobility studies in gases, there is no difficulty in duplicating results from one measuring method to another or from one laboratory to another. Positive-ion mobilities in gaseous oxygen are characteristically easily reproduced. On the other hand, mobilities in nitrogen are remarkably difficult to reproduce, and it has become clear that the ion source is a seat of trouble,

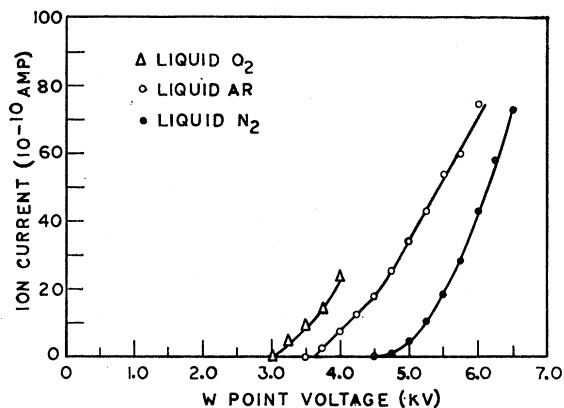


FIG. 2. Graphs of ion currents from a sharp tungsten point submerged in liquid O_2 , Ar, and N_2 , respectively, as a function of voltage applied to the point. The values of the field strengths at the point may be calculated by Müller's empirical formula, $F = V/(5r)$, where r is the radius of the point. Using this equation and further data on field ionization due to Müller, the radius of the point has been established to be 670 \AA .

each different source seemingly producing a different kind of ion with a different mobility.

It accordingly seemed desirable to develop an ion source for liquids which would be variable over a considerable range of currents for convenience in control and in the process possibly variable also in the type of ion produced. For this purpose, the field ionization ion source due to Müller⁵ was selected, and it proved to live up to the hopes. A tungsten wire of 5 mil diam was etched electrochemically following the procedures described in Ref. 6. It was mounted in the source and is A in the schematic diagram of Fig. 1. A voltage up to 10 000 V could be applied between A and B. The entire arrangement of the schematic, including the sharp point, was submerged in the liquid. The point was at the positive potential to make it form and repel positive ions.

Figure 2 shows the ion current as a function of the voltage on the point in each liquid. If Müller's data⁷ for current in the corresponding gases versus field strength

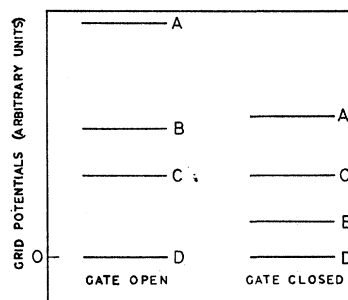


FIG. 3. Diagram of the grid potentials during the "open" and "closed" cycles.

⁵ E. W. Müller, *Ergeb. Exakt. Naturw.* **27**, 290 (1953).

⁶ E. W. Müller, in *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press Inc., New York, 1960), Vol. XIII, p. 129.

⁷ E. W. Müller and K. Bahadur, *Phys. Rev.* **102**, 624 (1956).

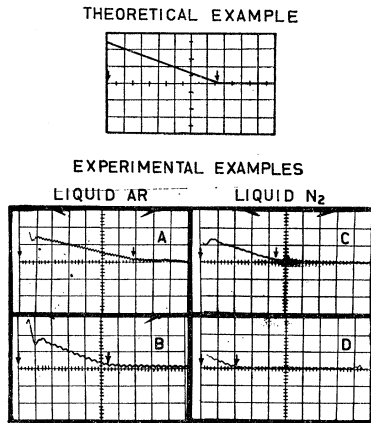


FIG. 4. Comparison of theoretical and actual oscillograms which represent the decay of collector current versus time. A time scale = 0.1 sec/cm; B time scale = 0.05 sec/cm; C time scale = 0.05 sec/cm; D time scale = 0.05 sec/cm.

are extrapolated to lower fields, onset field strengths for ionization may be estimated to be the values shown in Table I. If in addition, Müller's formula for the maxi-

TABLE I. Computation of point radius from minimum voltage for ionization.

Substances	Field strength for onset of field ionization (MV/cm)	Computed point radius (Å)
O ₂	90	668
Ar	110	665
N ₂	135	674

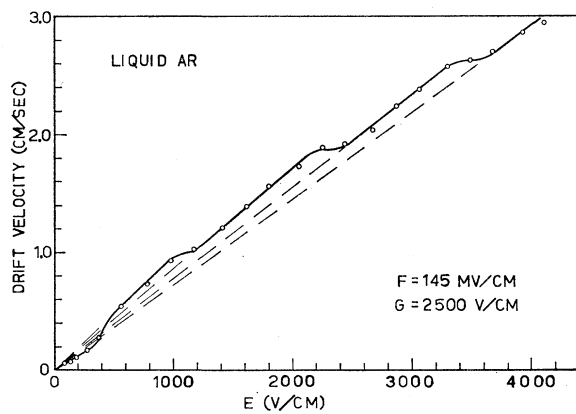


FIG. 5. Experimental data in liquid argon presented as ion drift velocity versus applied field with $F=145$ MV/cm and $G=2500$ V/cm.

mum field strength F near a point at positive potential V and having radius r is used, $F=V/5r$, in combination, with the onset values of V of Fig. 2 and the onset field strengths of Table I, the radius of the point may be determined as shown in the last column of Table I. The agreement is encouragingly good.

It will appear in the subsequent discussion of findings that the voltage on the point also influenced the mobility observed. This source seems clearly to offer interesting improvements over an alpha-particle device for generation of ions.

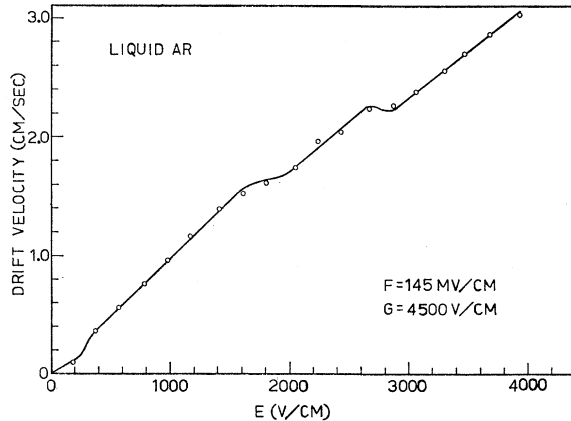


FIG. 6. Experimental data in liquid argon presented as ion drift velocity versus applied field with $F=145$ MV/cm and $G=4500$ V/cm.

B. Shutter

The application of a square-wave voltage to a pair of parallel grids as a means of admitting pulses of ions to a region is well known. The only items of significance to note here are the following:

(1) The grids were C. O. Jelliff Company "Lektromesh" 5 mil thick, made of Cu-Ni alloy, with square holes 5 mil on a side and with 100 holes per inch. This combination gives 25% open area. At the same time, the holes are small enough in relation to the drift space d , which is 5 mm, to make field penetration through the grid negligible.

(2) The square-wave voltage was generated by a HP-202A function generator and then amplified to high

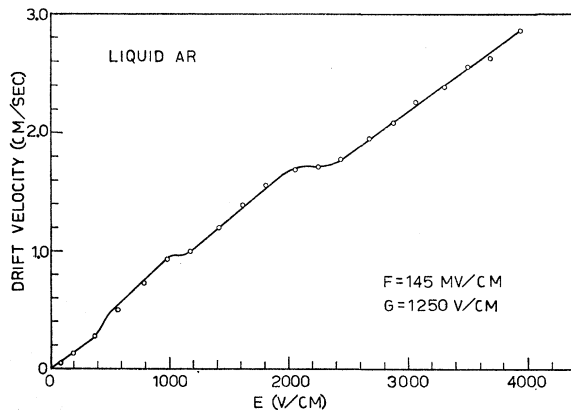


FIG. 7. Experimental data in liquid argon presented as ion drift velocity versus applied field with $F=145$ MV/cm and $G=1250$ V/cm.

voltages. Since drift speeds are in the range from 0.05 to 6.0 cm/sec in the present experiment, relatively long shutter intervals are needed compared with those for gaseous experiments where speeds range from 10^4 to 10^6 cm/sec. The electric field strength in the shutter space is designated G in the ensuing pages.

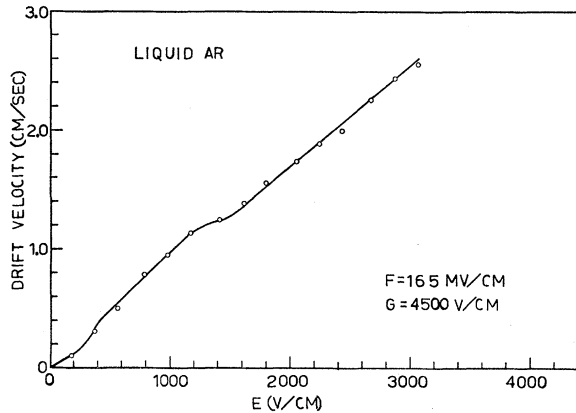


FIG. 8. Experimental data in liquid argon presented as ion drift velocity versus applied field with $F=165$ MV/cm and $G=4500$ V/cm.

(3) Figure 3 shows a schematic diagram of the grid potentials during operation. It should be noted that the source field strength and the drift field strengths do not change as the shutter voltage oscillates.

C. Drift Space and Detection

Once ions emerge through shutter grid C, they find themselves in a region of uniform field strength E . They drift at constant speed in this field and are finally collected on electrode D. The distance CD, designated d , is 5 mm and has been verified to retain this value to $\pm 0.5\%$ whether the grid structures are at room temperature or are at boiling liquid argon or nitrogen temperatures.

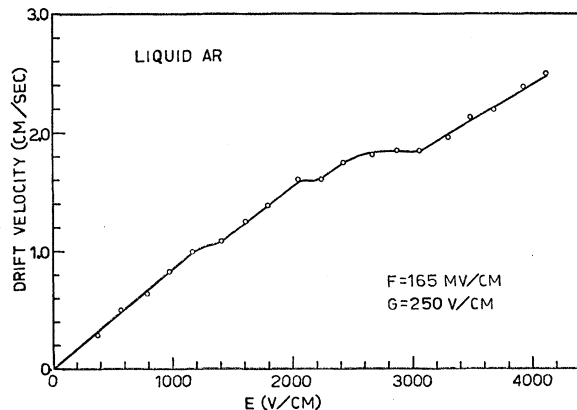


FIG. 9. Experimental data in liquid argon presented as ion drift velocity versus applied field with $F=165$ MV/cm and $G=250$ V/cm.

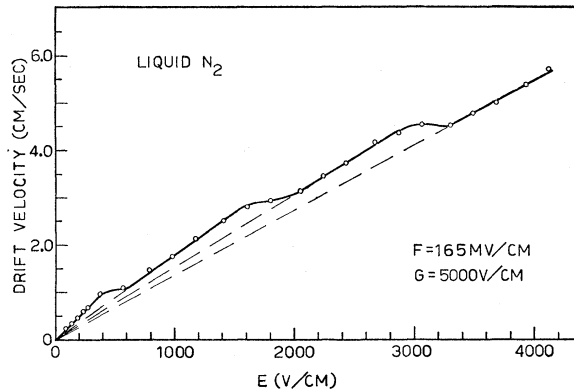


FIG. 10. Experimental data in liquid nitrogen presented as ion drift velocity versus applied field with $F=165$ MV/cm and $G=5000$ V/cm.

The drift field potential was provided by a pack of batteries. Values from 0 to 2100 V were used.

The ion current from D passes to a General Radio Company dc amplifier, type 1230-A and is displayed on a Tektronix type-531 oscilloscope. Currents of magnitude 10^{-10} - 10^{-12} A are measured, and the circuit time constants are shorter than 5 msec. The currents in the drift space were never space-charge limited.

D. Technique of Measurements

The method of determining the drift velocity of the ions is as follows:

(1) The gate BC is opened for a time which is much longer than the time for the ions to travel from grid B to the collector D. Hence, a constant current is established in the collector circuit.

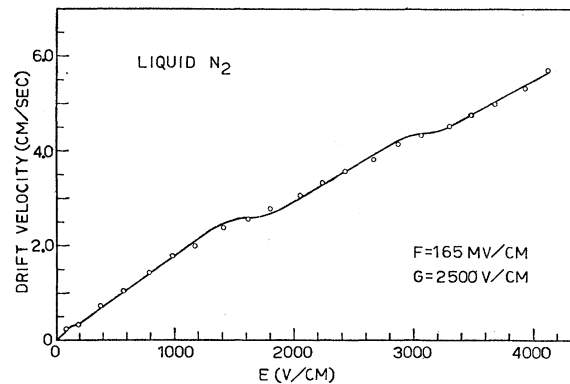


FIG. 11. Experimental data in liquid nitrogen presented as ion drift velocity versus applied field with $F=165$ MV/cm and $G=2500$ V/cm.

(2) The gate is then closed, and no more ions enter the drift space. The time required for all of the remaining ions to drift across the drift space and be collected is the time of flight of the ions. The distance d divided by the measured time of flight gives the drift velocity v .

Figure 4 shows some sample oscillograms of decay of

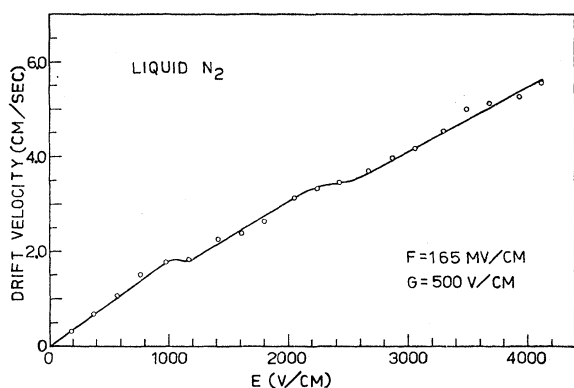


FIG. 12. Experimental data in liquid nitrogen presented as ion drift velocity versus applied field with $F=165$ MV/cm and $G=500$ V/cm.

current versus time compared with a theoretical one. The arrows indicate starting and stopping times for measurements. The difficulty of reading these oscillograms is the primary source of statistical error in the data. This uncertainty is always less than $\pm 4\%$ and for velocities below 4.0 cm/sec it is decreased by at least a factor of 2.

Figures 5-13 inclusive show sample curves of drift velocity as a function of drift field strength E . Figures 14 and 15 show values of the mobility $\mu = v/E$ for sample cases. The nature and significance of the results are discussed in Sec. III.

E. Cryogenics

The grid structures shown in Fig. 2 were placed inside a Dewar vessel which was sealed vacuum tight so that it could be evacuated through a system of valves. After evacuation, liquid nitrogen or liquid argon was transferred from a storage container into this Dewar vessel through an insulated transfer tube sealed through the top by double O rings. By this method of transfer, no impurities were introduced into the liquids.

The inner closed vessel system was surrounded by an outer Dewar vessel which was filled with liquid nitrogen. This prevented the liquid in the inner container from boiling and thus affecting the measurements.

Liquid nitrogen was obtained in LS-110 storage containers from Hill Equipment Company, St. Louis, Missouri, who claimed it to have 30 ppm impurities. High-purity gaseous argon was obtained from Sanders Welding, Inc., St. Louis, Missouri, and was liquefied using liquid nitrogen as a refrigerant. The liquid argon was stored in a Linde Liquefied Gas Container, type LD-25. The impurity content of the gaseous argon was stated to be 1 ppm. Since the liquid argon was stored under pressure in the LD-25 container with a valve to allow the evaporating gases to escape, the liquid was probably not contaminated by air components.

Vapor pressures were measured using a mercury manometer, and the temperatures of the liquids were

monitored using a copper-constantan thermocouple. The temperatures of the liquids were constant as measured within the accuracy limits of the thermocouple, which was about 0.1°K . The pressures were constant at 760 Torr to within a few tenths of a percent.

III. FINDINGS

The following features of the results shown in Figs. 5-15 inclusive are pointed out.

(1) The mobilities in both nitrogen and argon are constant over a range of values of drift field E and then change rather abruptly, in a stepwise fashion, to a new constant value.

(2) These steps are similar to those reported by Careri *et al.*⁸ in liquid helium II. In the present case, the stepping values of E are higher than Careri's, by a factor of about 10.

(3) Zero-field mobilities are 6.0×10^{-4} in argon and 2.50×10^{-3} in nitrogen. Ions in nitrogen are thus faster than in argon by a factor of about 4.17 at low fields.

(4) All mobility steps are downward with increasing E except the first one in argon which is upward.

(5) The location, as to E value, of the steps changes if the source field F or the shutter field G is changed. The only rule deduced about these changes is that the steps usually occur at higher E value if the F or G field strength is higher. Correspondingly, if G is lowered far enough, the E field strength at the mobility step may drop so low that the first step may vanish.

(6) All velocity versus E curves pass through the origin. This observation is construed to mean that there is no serious penetration of fields through grids and that there is no persistence-of-velocity effect for the ions corresponding to that in superfluid helium reported by Rayfield and Reif.⁹

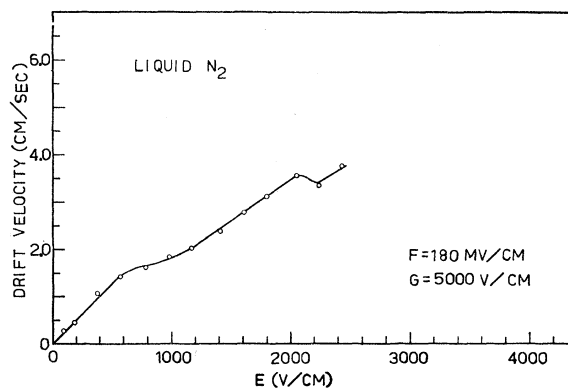


FIG. 13. Experimental data in liquid nitrogen presented as ion drift velocity versus applied field with $F=180$ MV/cm and $G=5000$ V/cm.

⁸ G. Careri, S. Cunsolo, and P. Mazzoldi, Phys. Rev. Letters 7, 151 (1961).

⁹ G. W. Rayfield and F. Reif, Phys. Rev. Letters 11, 305 (1963).

IV. ANALYSIS OF FINDINGS

The mobility constant μ_0 , defined as $\mu(\rho/\rho_0)$, where ρ is the density at which mobility μ is measured and ρ_0 is the gas density at NTP, is constant over an enormous range of densities. This fact has been verified over a range of values of ρ/ρ_0 from 10^{-3} to 10^{+2} . Comparison of liquid mobilities at zero-field strength with gaseous values by application of this density factor is therefore possible. Since at low fields and high densities the gaseous ions are believed to be Ar_2^+ and N_4^+ respectively, the gaseous mobilities for these ions are used. The comparison appears in Table II.

It is seen at once that the measured mobilities are low relative to gas values by a factor of 4 in argon and 1.5 in nitrogen.

The finding in argon compares favorably with that of Davis, Rice, and Meyer.¹⁰ The present value is 6.0×10^{-4} compared with their value of 6.5×10^{-4} .

The result of Williams¹¹ in argon at field strengths of 24 to 187 kV/cm is approximately 2.8×10^{-3} . It is higher than present findings by a factor of approximately 4 or 5 placing it in better agreement with density corrected gaseous data.

V. COMPARISON WITH THEORY

The theoretically predicted mobility for gaseous ions¹² with an effective collision cross section $\pi\sigma^2$ is

$$\mu = \frac{e}{\frac{1}{3} 8N\sigma^2 [2\pi M_i M_a kT / (M_i + M_a)]^{1/2}} \quad (1)$$

In this equation, σ is $(\sigma_{\text{ion}} + \sigma_{\text{atom}})/2$ where all σ 's refer to diameters of the particles indicated in the subscripts.

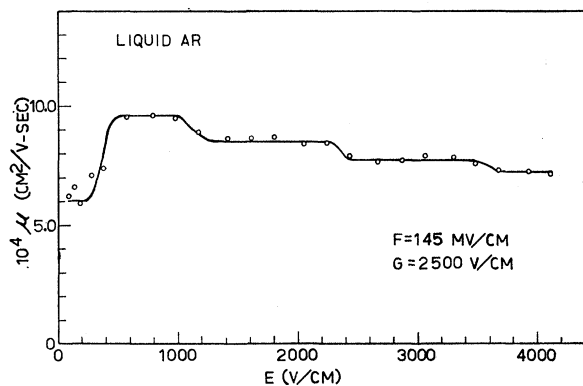


FIG. 14. Experimental data in liquid argon, presented as ion mobility versus applied field, with $F=145$ MV/cm and $G=2500$ V/cm. The reproducibility of the results is near to the limit of readability of the oscillograms. In general, probable errors may be estimated at less than 5%. The near-zero-field mobilities show a greater scatter. It is believed that the scatter represents a genuine fluctuation in the mobility.

¹⁰ H. T. Davis, S. A. Rice, and L. Meyer, *J. Chem. Phys.* **37**, 947 (1962).

¹¹ R. L. Williams, *Can. J. Phys.* **35**, 134 (1957).

¹² H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, New York, 1952), p. 367.

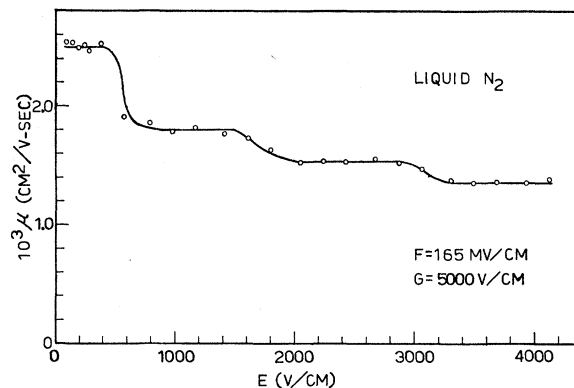


FIG. 15. Experimental data in liquid nitrogen presented as ion mobility versus applied field with $F=165$ MV/cm and $G=5000$ V/cm.

Only a small increase over the gaseous ion diameter σ_{ion} is necessary to account for the lower-than-predicted liquid mobility. In the case of Ar, a completed, one layer cluster around a central ion increases σ_{ion} by a factor of 3, increases σ by a factor of 2 and decreases μ by a factor of $\frac{1}{4}$, in agreement with the experiment. The mass correction factor is small.

The hypothesis is advanced here that the stepwise change in mobility is the result of changes in the cluster size. It is necessary to postulate that a threshold collision energy for cluster formation exists in order to account for mobility decline with increasing field. The existence of an activation energy threshold for cluster formation has been observed in gases, particularly in the case when the cluster is a crystallite, subject to orientation and to preferential attachment along certain directions.¹³ It was first suggested by Atkins¹⁴ in the case of helium that a solid cluster formed around an ion, and the near proximity of the freezing temperature of argon to the normal boiling temperature makes the same argument applicable to argon. Hence, an enlarging cluster with increasing field strength is not beyond reason.

The high value of μ obtained by Williams in strong fields suggests that the mobility must step up again at very high fields. This effect is not observed, but the highest field used in the present work is 4.3 kV/cm as compared with Williams' lowest field of 24 kV/cm. The unobserved range between 4.3 and 24 kV/cm may well contain the stepping up phenomenon.

In qualitative support of the cluster hypothesis is the work by Bloom and Margenau¹⁵ showing theoretically the growth of cluster size in certain cases with decline in temperature. While present results have not been obtained at variable temperatures but only at the normal boiling points of the liquids, Davis, Rice, and Meyer have noted a strong, in fact near to an exponential rise in mobility with rising temperature. The finding

¹³ L. B. Loeb, *Basic Processes of Gaseous Electronics* (University of California Press, Berkeley and Los Angeles, 1955), p. 176.

¹⁴ K. R. Atkins, *Phys. Rev.* **116**, 1339 (1959).

¹⁵ S. Bloom and H. Margenau, *Phys. Rev.* **85**, 670 (1952).

TABLE II. Predicted ion mobility in liquids using known gas mobility constant.

Gas	Gas density at NTP (g/cm ³)	Liquid density at NBP (g/cm ³)	Suspected or known ion	Gaseous mobility constant (cm ² /V-sec)	Predicted liquid mobility (cm ² /V-sec)	Measured liquid mobility (cm ² /V-sec)
N ₂	1.25×10 ⁻³	0.808	N ₄ ⁺	2.4 ^a	3.72×10 ⁻³	2.5×10 ⁻³
Ar	1.79×10 ⁻³	1.39	Ar ₂ ⁺	1.83 ^b	2.32×10 ⁻³	6.0×10 ⁻⁴

^a D. W. Martin, W. S. Barnes, G. E. Keller, D. S. Harmer, and E. W. McDaniel, in *Sixth International Conference on Ionization Phenomena in Gases* (Paris, 1963), Vol. 1, p. 295.

^b E. C. Beatty in *Proceeding of the Fifth International Conference on Ionization Phenomena in Gases, Munich, 1961* (North-Holland Publishing Company, Amsterdam, 1962), Vol. 1, p. 187.

seems correlated with Bloom and Margenau's decline in cluster size with increasing temperature.

No serious attempt to account for the initial step up in mobility in argon with increasing field is offered here. Nor is any quantitative attempt to compute and justify cluster sizes offered. A reasonable size of cluster, for example, a single layer of atoms or molecules around an ion seems the most that is needed.

It is pointed out that no explanation for stepwise changes in mobility appears in any theoretical analysis except insofar as the cluster size may change by an atomic unit at a time.

The observation that the ion appears to remember its past history in fields F and G does not seem to be explicable by a simple assumption that cluster size is associated with field strength and persists for a time after the ion passes into a new field. All observations are contradictory to such a picture as may be seen from an example.

If field G is high, the mobility should be low as the ion enters field E . Yet (in nitrogen) the ion in field E persists in traveling with high mobility in weak E up to a fairly strong E . Lowering G , which suggests increased mobility from curves like Fig. 10, leads to lower mobility in the E field or at least to earlier step-down of mobility.

Rayfield and Reif, studying helium in the range from 0.3 to 0.6°K, introduced an explanation of the carry-over of past history of ions without the use of actual translational kinetic energy based on the formation of vortex rings. Under the conditions prevailing in boiling argon or nitrogen, this sort of explanation seems inapplicable because of viscosity considerations.

An alternative hypothesis seems more attractive. Since the ions in our work seem to be properly presumed to be molecule ions, Ar₂⁺ and N₄⁺, the possibility of excitation of vibrations in the source region may be considered. The lifetime of a vibrationally excited state is progressively longer as the difference between the vibrational energy and the thermal translational energy per molecule grows. Thus at temperatures below 100°K, in the liquid phase, this life time may well exceed one second. Landau and Teller¹⁶ first studied this matter theoretically. A set of experimental papers by White and Millikan¹⁷ at General Electric Research Laboratories supports the theory in several sample cases. The life of vibrational states fits an equation of the form

$$\tau = (c_1/\rho)e^{c_2T^{-1/3}}, \quad (2)$$

c_1 and c_2 are constants, ρ is the density, T is the absolute temperature, and τ is the half-life. To fit the observed mobility behavior, the state of excitation would have to influence the cluster formation.

Further data are being sought covering a greater range of field strength E and extending to other gases, most notably helium.

ACKNOWLEDGMENT

This work was done under the direction of Professor Robert N. Varney whose assistance is gratefully acknowledged.

¹⁶ L. Landau and E. Teller, *Physik. Z. Sowjetunion* **10**, 34 (1936).

¹⁷ See, for example, D. R. White and R. C. Millikan, *J. Chem. Phys.* **39**, 1803 (1963).