Ionic Drift Velocities and Electron Attachment Coefficients in Oxygen*

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Transient ion currents following an initiating electron pulse have been studied in oxygen over a range of pd from 7 to 26 cm mm Hg and of E/p from 9 to 50 volts/cm mm. Analysis of oscillographic records yields information regarding ionic drift velocities and the electron attachment coefficient. Three distinct and pressure-independent velocities are found consistent with zero field mobilities of 3.4, 2.6, and 1.95 cm²/v sec. The multiplicity of velocities is ascribed to clustering reactions through which a single initially formed species of negative ion is converted into two slower species, although initially formed O_2^+ ions retain their identity. It is then possible to compute the attachment coefficient from measured ion transient areas. The attachment coefficient thus obtained varies gently in the region $10 \leq E/p \leq 25$ and joins at each end with curves previously reported. Consideration of the mobilities of the ions as well as other evidence leads to the identification of the initial ion as O^-, while the clustered species appear to be O_3^- and O_2^- corresponding, respectively, to the above mobilities. No difference is detected between the mobilities of O_2^+ and O_2^- ions.

I. INTRODUCTION

THE functional variation of the electron attachment coefficient η/p, where η represents the number of attachments per cm of directed motion and p is the pressure in mm of Hg, with the field parameter E/p, the ratio of electric field strength to pressure, has been studied for oxygen by a number of workers[1–5] using a variety of methods. The results of these investigations have been summarized by Harrison and Geballe[5] (hereinafter referred to as HG) in Fig. 7 of their paper. A serious discrepancy was found between their result at $E/p \sim 25$ v/cm mm, the lower limit of applicability of their method, and measurements reported by those who had worked in lower ranges of E/p which extended up to this value. HG suggested that the source of the discrepancy might be due to neglect by previous authors of electron multiplication from collisions of electrons with molecules. They proposed that the complete curve might include a relatively smooth portion of magnitude approximately 0.1 cm^{-1} from E/p about 10 to 25. To test this hypothesis the present authors undertook an experiment of the pulsed Townsend discharge type.

II. EXPERIMENTAL DETAILS AND DATA

The experimental equipment was similar to that described by Hornbeck.[6] The electrodes were 40.0 mm in diameter, could be separated from 0 to 3 cm, and were housed in a Pyrex cylinder of diameter 3 in. The molybdenum cathode was coated with BaO-SrO which was activated during outgassing. The vacuum system was capable of evacuating the tube to 10^{-7} mm Hg when it was well baked and the electrodes were outgassed by induction heating. Oxygen gas was obtained from commercial Airco flasks or, alternatively, generated from $KMnO_4$ with precautions to insure purity. Mass spectrometric analysis of the generated gas indicated its fractional impurity content to be less than 4×10^{-5}. Pressure of gas admitted to the discharge vessel was read to $\sim$0.05 mm Hg on an oil manometer. The associated electronic equipment had a gain of 90 db at 10 Mc/sec band width. The series resistor of the discharge circuit was 10 kilo-ohms giving a circuit time constant two orders of magnitude smaller than the time required for an ion to cross the discharge gap and about three times larger than the reciprocal of the amplifier bandwidth. Data were taken in the form of photographs of the ion transient current displayed on a Tektronix 514AD oscilloscope fitted with a Polaroid Land camera.

Figure 1 shows an example of one of the transients. The shapes and other characteristics of such photographs change with E/p, p, and d, the electrode separation, so Fig. 1 cannot be said to be typical of all observed. Quantities which may be measured on the photographs are: (1) the transit times of the various kinds of ions present, (2) the area under the ionic part of the transient, and (3) by extrapolation, the initial height of the ionic part of the transient.

It is convenient to discuss the first of these in terms of the reduced mobility constant defined by the ex-

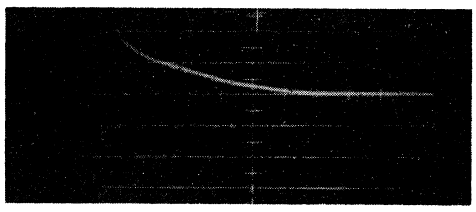

FIG. 1. Characteristic ion transient. Data: $d=1.07$ cm, $p_0=23.1$ mm, applied potential=845 volts, sweep speed=3 μsec/div. Breaks at approximately 4.5 and 7.0 divisions correspond to mobilities of 3.0 and 1.95 cm²/v sec, and are attributed to triatomic and diatomic ions, respectively.

* Supported in part by the Office of Ordnance Research, U. S. Army.
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[1] N. Bradbury, Phys. Rev. 44, 883 (1933).
[2] R. H. Healey and J. W. Reed, *The Behavior of Slow Electrons in Gases* (Amalgamated Wireless, Sydney, 1944), p. 94.
[3] A. Doehring, Z. Naturforsch. **7a**, 253 (1952).
[4] P. Herreng, Cahiers phys. **38**, 7 (1952).
[5] M. A. Harrison and R. Geballe, Phys. Rev. **91**, 1 (1953).
[6] J. A. Hornbeck, Phys. Rev. **80**, 297 (1950).

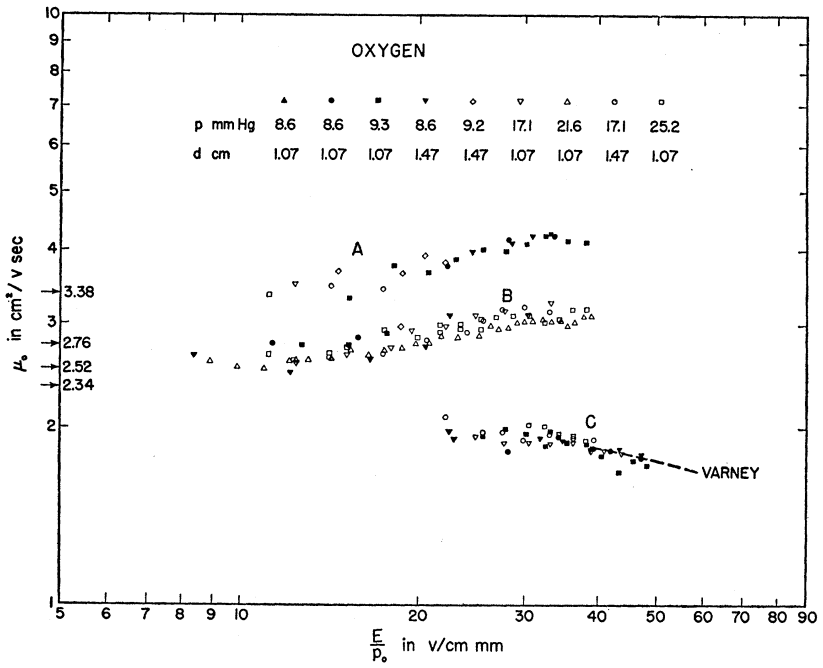

FIG. 2. Reduced ion mobilities *vs* E/p_0. Arrows along the ordinate axis refer to Langevin mobilities for O, O_2, O_3, and O_4 ions, respectively, starting from above. The dashed curve is taken from reference 7.

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$$\mu_0=(pd/760E\tau)(T/273), \qquad (1)$$

where τ is the measured ionic transit time and T is the absolute temperature. Figure 2 presents the experimental values of μ_0 as a function of E/p_0, where p_0 is the gas pressure reduced to 0°C. Three distinct curves resulted. It will be noted that points on the curves are independent of pressure and electrode separation within the experimental error, although it was found that transit times giving rise to the upper two curves are measurable only in some ranges of pressure and E/p_0; seemingly ions responsible for these curves are not present outside certain limits of these parameters. Above $E/p_0\sim 40$ no transit times associated with the upper two curves could be measured. Ions with the lowest mobility gave rise to observable current only when E/p_0 exceeded 25 and were present at all higher values studied here. The two lower curves appear to level off as E/p_0 is decreased, tending toward values of 1.95 and 2.6 cm²/v sec at zero field. The mobility of the fastest ion does not seem to have assumed its limiting zero-field value. We point out that its course is similar to that of the intermediate curve. This suggests that the zero-field mobility is close to 3.4 cm²/v sec. Hereinafter the ions associated with the three mobility curves will be designated by the symbols A, B, and C in the order of decreasing mobility. In the region of E/p_0 from 40 to 50, the curve for C overlaps the data of Varney,[7] which he interpreted as due to O_2^+.

Figure 3 shows the result of measurements of ionic transient area as a function of E/p_0 for one particular combination of pressure and electrode separation. Areas were obtained by using Simpson's rule on $8\frac{1}{2}\times 11$ in. enlargements of the oscilloscope photographs. The first few microseconds of each transient are obscured by a spike of current due to the initiating electron burst which requires that the ionic part be extrapolated from ~ 2 μsec back to the start of the trace. This extrapolation is the only significant source of error in the area measurements and causes an uncertainty estimated to be no more than 10%. The initial height H_0 obtained by extrapolation is subject to much greater uncertainty and may be in error by as much as 40%. In general a curve of H_0 *vs* E/p rises monotonically and more smoothly than does the corresponding area curve.

III. CLUSTERING HYPOTHESIS

Electrons reacting with oxygen have been reported to generate negative ions by three distinct processes.[8]

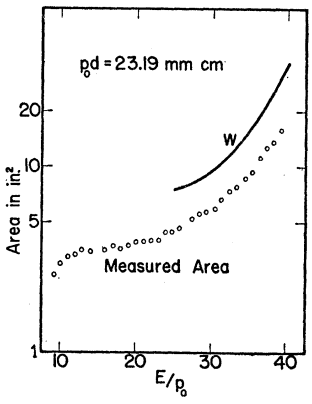

FIG. 3. Measured areas from a sequence of transients at $p_0d=23.19$ mm cm compared with the function w of Eq. (2). Normalizing the area curve to w permits extrapolation of the latter to lower E/p. The normalization constant can be used to estimate that there are 10^6 electrons per pulse.

[7] R. N. Varney, Phys. Rev. **89**, 708 (1953).

[8] For a review, see H. S. W. Massey, *Negative Ions* (Cambridge University Press, Cambridge, 1950), second edition.

The first of these, direct attachment to form O_2^-, is believed to occur for energies of less than one ev with a cross section that decreases rapidly with increasing electron energy. Another, dissociative attachment to give O^-+O, is a resonance process with a large cross section and requires about 3.6 ev of electron energy. The third is a reaction that requires 17 ev and produces O^++O^-. Under the conditions of this experiment, only the second can be a significant source of negative ions.

On similar grounds one may rule out all positive-ion-forming reactions except simple ionization giving O_2^++2e, which requires 12.2 ev.

If the reasoning which leads to the above conclusions is correct, the experimental observations (Fig. 2) require that some ions be formed by processes other than electron collision. We are then led to invoke ionic reactions which will, in effect, alter the mass of a charge carrier during its transit across the discharge gap. The discreteness and pressure independence of the mobilities of Fig. 2 show that any altered ions maintain their new identity thereafter. Reactions of this kind will be called "stable clustering" in contrast to "labile clustering" which has been discussed occasionally in the literature.[9] The experiment does not give an immediate association of any particular ion with a given curve of Fig. 2, nor does it provide direct identification of the clustered species. Such identification could be inferred at this point, but it is more convenient to discuss the determination of the attachment coefficient first so that this information can be used to aid in the identification.

IV. ATTACHMENT COEFFICIENT

Anticipating that ions would be formed only during transit of the initiating electrons, we intended to analyze the transient shapes in terms of appropriate equations. Had we been able to fulfill this intention, absolute values of the ionization and attachment coefficients would have been obtained. The observation that there were at least three kinds of ions in the discharge required that this plan be abandoned. A substitute analysis is based on invariance of the total ionic transient area under clustering; i.e., the area depends only on the number of ions initially produced and their initial spatial distribution. We define a quantity w given by

$$w=A/m=(\exp y-1)(z-1)/y+1, \tag{2}$$

where A = area under transient, m = a constant containing the number of initial electrons, the electronic charge, the sweep speed of the oscilloscope, and the current sensitivity of the amplifiers, $z=\alpha d$ where α is the first Townsend coefficient, and $y=(\alpha-\eta)d$. This relation is derived from Eqs. (2), (3), and (4) given in HG by introducing a drifting delta function for the electron density in the source terms. Figure 3 exhibits a plot of w in the range of E/p common to this experiment and that of HG based on their values of α/p and η/p. The similarity of the curve of w and that of a portion of the measured areas suggests a manner in which the latter may be used to determine η/p in the region below $E/p=25$. By normalizing the area curve to that for w over the range of E/p common to both, we can obtain values of w for $E/p<25$. Then, if α/p can be determined for the region below $E/p=25$, Eq. (2) can be used to calculate η/p.

On examining the algebraic expression for w, we have found that its slope will be small, i.e., insensitive to the behavior of α/p, only where η/p is at least a few times greater. The measurements of HG indicate that this condition on the coefficients is met at $E/p=25$, and the flatness of the experimental area curve is evidence for its continued validity down to $E/p\sim12$. Accordingly, values of α/p satisfactory for use in Eq. (2) can be taken from an extrapolation of the data given by HG.

The experiment provides an alternative method which does not require normalization. The initial height of the transient, H_0, depends on instrumental sensitivity and the total initially liberated electron charge through exactly the same factors as does the transient area A. The quotient of these two quantities is

$$\frac{A}{H_0}=\frac{d}{S}\frac{(\exp y-1)(z-y-1)+y\exp y}{(\exp y-1)[z(v_+ +v_-)-yv_-]}, \tag{3}$$

where S is the reciprocal oscilloscope sweep speed and v_+ and v_- are the drift velocities of the ions created by the initiating electrons. All elements of this expression save α and η are determinable from the experiment. In a region of E/p where $\alpha/p\ll\eta/p$, the latter quantity can be calculated from Eq. (3) provided that the proper velocities can be selected from those of Fig. 2. From a practical standpoint this method is subject to considerable error because H_0 cannot be measured accurately and because Eq. (3) is a slowly varying function of η/p under the conditions of the experiment.

Figure 4 presents a composite curve for η/p, open points having been determined by the area normalization method and solid points from Eq. (3). In computation of the latter the assumption was made that $\alpha/p\ll\eta/p$ in the neighborhood of $E/p=10$. In accordance with the aforementioned conclusion that O^- is the only negative ion produced by the initiating electrons, and consistent with the interpretation of Fig. 2 to be given in the following section, the uppermost curve in this figure was used for the calculation of negative ion drift velocities for use in Eq. (3).

The hypothesis stated at the beginning of this paper is verified by the results as displayed in Fig. 4: η/p varies gently and is approximately 0.1 cm^{-1} in the region of E/p from 10 to 25. Of the earlier measurements at the lower extreme of this range, only the most recent and presumably most reliable, those of Doehring[3] and Herreng,[4] are shown on Fig. 4. The present data fit more smoothly into those of Herreng. His curve is, in

[9] L. B. Loeb, *Basic Processes of Gaseous Electronics* (University of California Press, Berkeley, 1955), Chap. 1.

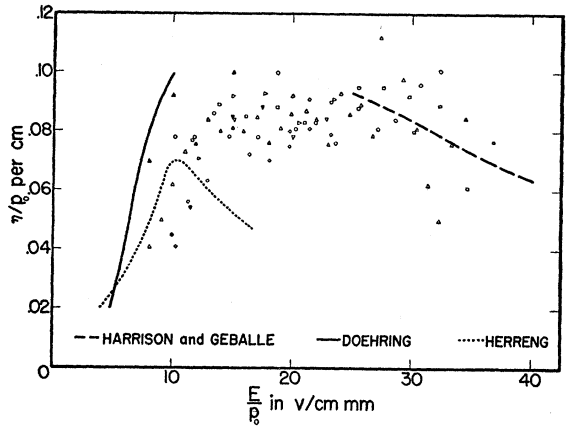

FIG. 4. Attachment coefficient as a function of E/p_0. The code for experimental points is the same as for Fig. 2. Solid points result from Eq. (3); open ones from area normalization and Eq. (2).

fact, the lowest of all those previously published in the region $E/p\sim10$. Were one to use the results of any author other than Herreng for normalization at $E/p\sim10$, the data of the present experiment would rise above the curve of HG in the neighborhood of $E/p\sim25$. A discrepancy at this latter E/p would thereby be introduced which is opposite to that mentioned in the Introduction. Points obtained from the measured quotient A/H_0 and Eq. (3), in spite of their large uncertainty, lend credence to the results of the area normalization method.

V. IONIC MOBILITIES

Classically, zero-field mobilities are most completely described by a theory originally formulated by Langevin.[10] This theory is based on the assumptions of an attractive polarization force and a hard-sphere repulsion between ions and neutral gas molecules. In the case of an ion in its parent gas, quantum mechanical effects due to symmetry and charge exchange must also be taken into consideration. Experimental observations have shown that in such cases mobilities are substantially smaller than the Langevin theory predicts.[11–15] Where quantum mechanical calculations have been made, there is satisfactory agreement with observation.[16,17] It is possible to include the symmetry effect as a contribution to the hard-sphere repulsion of the Langevin formulation if a means can be found for estimating its equivalent cross section.

Experience has shown that for cases where symmetry plays no role, the polarization force is overwhelmingly predominant so that satisfactory agreement is obtained by neglecting the gas kinetic repulsion.[13] Table I presents zero field mobilities for four oxygen ions in oxygen gas calculated from the Langevin equation with no hard-sphere repulsion and with the polarizability of O_2 taken from the Landolt-Bornstein tables.[18] A comparison of Table I with the curves of Fig. 2 shows that the low-field mobility of ion A is consistent with the Langevin value for an atomic ion. The observed low-field mobility of ion C is less than that of any ion of Table I and, in fact, corresponds to an ion of unreasonably large mass. This comparison suggests that symmetry effects are responsible for the low value and that ion C is diatomic, consistent with Varney's interpretation of his observations.[7] It appears most unlikely that the zero-field mobility of ion B will lie below 2.5 cm²/volt sec; therefore this ion is considered to be triatomic.

VI. ION IDENTIFICATION

Mobility theory is as yet inadequate for more than the tentative identifications suggested in the preceding paragraph. We therefore call on other aspects of the present observations to provide corroborative evidence. Table II shows the approximate regions of pd and E/p in which the various ions are observed to be predominant in the discharge. Discussion of this table begins with the region of low E/p. It follows from the preceding section on attachment and ionization coefficients that the initiating electrons generate only negative ions in this region. It has been shown previously that energy considerations leave only a single process, dissociative attachment, to create negative ions. Therefore, only one of A and B has been formed by the initiating electrons. The other must result from a clustering reaction, and also, therefore, carries a negative charge. The extent to which this clustering reaction takes place should increase with increasing chance of collision of the parent ion while in transit. Since ion A is observed at low pd when the chance is relatively small and B appears as this parameter increases, we conclude that A is the parent ion and B a clustered species.[19]

TABLE I. Calculated zero-field mobilities for oxygen ions.

Ion	μ_0 (cm²/volt sec)
$O^{\pm}$	3.38
$O_2^{\pm}$	2.76
$O_3^{\pm}$	2.52
$O_4^{\pm}$	2.34

[10] P. Langevin, Ann. chim. et phys. **5**, 245 (1905).
[11] J. A. Hornbeck and G. H. Wannier, Phys. Rev. **82**, 458 (1951).
[12] R. N. Varney, Phys. Rev. **88**, 362 (1952); **89**, 708 (1953).
[13] A. M. Tyndall, *The Mobility of Positive Ions in Gases* (Cambridge University Press, Cambridge, 1938).
[14] R. J. Munson and A. M. Tyndall, Proc. Roy. Soc. (London) **A177**, 187 (1941).
[15] L. M. Chanin and M. A. Biondi, Phys. Rev. **94**, 910 (1954).
[16] H. S. W. Massey and C. B. Mohr, Proc. Roy. Soc. (London) **A144**, 188 (1931).
[17] T. Holstein, Phys. Rev. **82**, 567 (1951).
[18] Landolt-Bornstein, *Zahlenwerte und Funktionen* (Springer-Verlag, Berlin, 1953), Vol. III, p. 514.
[19] R. A. Nielson and N. E. Bradbury [Phys. Rev. **51**, 69 (1937)] have reported an oxygen ion of mobility 3.3 cm²/v sec which changed into one of mobility 2.65 cm²/v sec. Doehring (reference 3) searched for this process but observed only the lower

The evidence and arguments pertinent to the nature of A are summarized as follows: (1) it is a primary negative ion; (2) there is but one primary negative ion; (3) O^- may be expected on the basis of energy considerations; (4) A has a zero-field mobility consistent with the Langevin value for O^-. We conclude that A is O^-.

We next discuss ion C. Its mobility curve joins that found by Varney[7] using the same experimental method in the range of E/p from 40 to 1000. Because he observed only one mobility curve, and because it extended to such high values of E/p, Varney concluded that he was observing O_2^+ with a mobility reduced by charge exchange interactions. A theory of Wannier[20] provided means for computing from high-field mobilities an effective hard-sphere cross section to represent this interaction. Using this cross section in the Langevin formula, Varney obtained the low-field mobility 2.78 cm^2/v sec. To compare with this, we have an extrapolated mobility from the present work of 1.95 cm^2/v sec, somewhat lower than the value 2.2 cm^2/v sec which Varney obtained from his data by extrapolating from a higher E/p. Disagreement between the computed and extrapolated mobilities is considerable, but not much confidence should be placed in the former because of the approximation involved in this combination of classical and quantum mechanical ideas. In view of all of the above considerations, we concur with Varney in concluding that this ion is diatomic.

TABLE II. Experimental conditions for observations of particular oxygen ions.

pd in mm Hg cm	E/p in v/cm mm Hg: Low (8–20)	Intermediate (20–35)	35	High (>35)
Low (8–14)	A	A, C	A, C	C
High (>17)	B	B, C	B, C	C

A positive diatomic ion is expected as a result of the ionization process discussed in Sec. 3. Certain of the transients did not yield to such a simple interpretation of the nature of ion C. In particular, at $E/p=35$, where the results of HG indicate $\alpha/p=\eta/p$, it can be shown that the calculated contributions of positive and negative ions to the transient area are equal; and moreover an ion which does not cluster contributes a linearly decaying current. Figure 5 is a drawing of a transient observed with $E/p=35$. If the terminal, nearly straight, portion, which because of its mobility must be due to ion C, be extrapolated back to zero time, the contribution in area of this presumably positive ion is found to be substantially larger than half of the total. There are two possibilities for explaining this anomaly: either a contribution from negative charges has been lost, or some type-C ions must be negative. The first possibility cannot be correct because no suitable mechanism for loss of negative ion area exists under the conditions of this experiment. Moreover it can be argued from the variation of area with E/p that no loss occurs. We conclude that negative diatomic ions are present, having been formed in a clustering reaction. The absence of ion B in the upper row of Table II is evidence that O^- is the direct parent of O_2^-. The mobilities of O_2^+ and O_2^- appear to be equal within the 10% accuracy of the experimental method, although theoretical work of Holstein[21] indicates that this result is not necessarily to be expected.

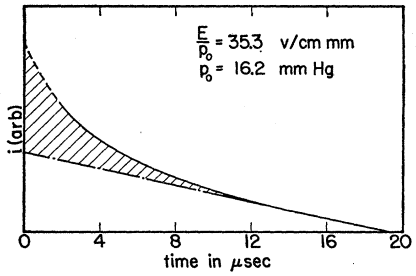

FIG. 5. Drawing made from a transient at $E/p_0=35$. The shaded area represents the contribution of negative ions based on the assumption that the slow ions all are positive. At $E/p_0=35$, however, the contributions of positive and negative ions to the area should be equal. Thus some slow ions must be negative.

The ion B remains to be identified. It is a clustered species found in conjunction with A. If the reasoning in the above sections is correct, it cannot be O^- or O_2^-. Its mobility is close to that of the Langevin prediction for a triatomic ion and is inconsistent with that of an O_4 ion. In the following paper[22] we point out that a reaction producing O_3^- is not excluded energetically. We are not aware of previous observation of O_3^- but present considerations, albeit indirect, point to its existence and stability.

mobility. Since the lowest value of pd employed by Doehring was ~60 cm mm, the results of the present work explain his failure to observe the higher mobility under these conditions.

[20] G. H. Wannier, Phys. Rev. **83**, 281 (1951); **87**, 795 (1952).

[21] T. Holstein, J. Phys. Chem. **56**, 832 (1952).

[22] D. S. Burch and R. Geballe, following paper [Phys. Rev. **106**, 188 (1957)].

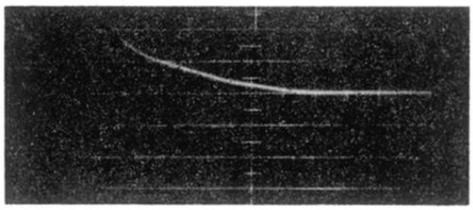

FIG. 1. Characteristic ion transient. Data: $d=1.07$ cm, $p_0=23.1$ mm, applied potential=845 volts, sweep speed=3 μsec/div. Breaks at approximately 4.5 and 7.0 divisions correspond to mobilities of 3.0 and 1.95 cm^2/v sec, and are attributed to triatomic and diatomic ions, respectively.