[Eq. (37), reference 16] which obeys the boundary conditions at $t=0$, $t=\infty$ can define the correlation tensor of a possible stationary process. If from such a solution we calculate the space-time Fourier transform of the scalar $Q_{ii}(r,t)$, defined by Eq. (3), reference 16, we must find that the transform is not everywhere non-negative as required by Cramér's theorem.

The discussion of (4.9) in the text indicates that the cited difficulties remain for $\nu\neq 0$. Equations (4.13) and (4.14) perhaps provide a significant measure of their physical importance.

The incompatibility of the differential equation with physical requirements may be partly responsible for the fact that Chandrasekhar was actually unable to find a nonsingular solution obeying the boundary conditions and, instead, had to piece together solutions in two regions in such fashion that the resulting function had discontinuities in its second and higher derivatives across a line in the r, t plane. It would be surprising, one may note, if the space-time Fourier transform of this nonanalytic "solution" did not exhibit oscillations in sign.

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Drift Velocities of Ions in Nitrogen at Various Temperatures*

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Drift velocities of nitrogen ions in nitrogen gas as a function of field over pressure have been studied by a pulsed Townsend discharge method at temperatures of 77°K, 300°K, and 450°K. Results support the theory that N_2^+ ions are responsible for drift velocities at high E/p_0 values, N_4^+ ions are responsible for drift velocities at low E/p_0 values, while the drift velocity at intermediate E/p_0 values is an average velocity determined by the relative lifetimes in transit of the N_4^+ and N_2^+ ions. Present results further substantiate the existence of N_4^+ at low E/p_0 and N_2^+ at high E/p_0 by showing opposite temperature effects on the mobility of the two ions. The binding energy of the N_4^+ ion has been estimated at 0.14 ev.

INTRODUCTION

THE apparatus constructed by Beaty[1] for the study of drift velocities of ions in gases at various temperatures has now been used with minor modifications to examine ions in nitrogen. Earlier results by Varney[2] showed that the drift velocity of ions in nitrogen at room temperature, plotted on a log-log scale against E/p_0 (where E is the electric field strength and p_0 is the pressure corrected for temperature to the value it would have for the same density of gas at 0°C), behaved abnormally in the middle range of E/p_0. Here the velocity stayed constant and even decreased with increasing E/p_0. The graph at low and high values of E/p_0 was fundamentally similar to that for a gas like argon; however, in the intermediate region the curves at high and low E/p_0 joined together in a smooth transition and only one drift velocity was observed for a given value of E/p_0. The suggestion was made at the time that ions believed to be N_4^+ were stable at low values of E/p_0, that N_2^+ ions were probably responsible for the observations at high E/p_0, and that in the intermediate region, the ion changed its character in flight leading to a velocity between the two extremes and determined by the relative times the ions in flight existed as N_4^+ or N_2^+, respectively. The arguments leading to the assignment of the various ions to the various E/p_0 ranges are not reproduced here; readers are referred to reference 2.

If the conception of ions dissociating in flight to an increasing degree with increasing collision energies (E/p_0) is valid, then a similar effect should occur with increasing temperature, for in this case too, impacts should occur with greater energy. The present work has been done to test this possibility, and it has indeed served to confirm the views expressed.

PROCEDURE

The pulsed Townsend discharge tube described by Hornbeck,[3] as modified by Beaty[1] to permit submersion in a controlled temperature bath, was used with little modification. Nitrogen from Air Reduction Company in sealed Pyrex bulbs was the gas used, the analyses furnished indicating that impurities were not above the 0.01% level. Intensive pumping, baking, and degassing techniques were utilized to reduce possible errors from foreign gases. In order to give readable currents below $E/p_0=100$ volts/(cm×mm Hg), nitro-

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[1] E. C. Beaty, Phys. Rev. **104**, 17 (1956).

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

[3] J. A. Hornbeck, Phys. Rev. **83**, 374 (1951).

gen required a more copious supply of electrons than the rare gases so nickel electrodes, coated with $BaCO_3$, and activated as described by Hornbeck, were used because of their greater electron emission rather than molybdenum electrodes.

The experimental tube could be entirely surrounded by a 6-inch diameter Dewar jar with Styrofoam cover. For low-temperature work, the Dewar was filled with boiling nitrogen yielding a temperature of 77.4°K. For high-temperature work, a bath of molten Ceresin at a temperature of 450°K was used. (The Styrofoam lid then needed a layer of Masonite as protection against softening and decomposition at the elevated temperature.)

The gas pressure, ranging from 0.1 mm to 32 mm Hg, was read by means of a McLeod gauge. Since the gauge was of necessity external to the temperature bath surrounding the tube, considerable concern was felt lest the tube fail to be in thermal equilibrium with the bath. A minimum of six hours of heating or cooling was observed to be adequate to assure that no pressure drifts occurred. Since complete sets of data necessary for plotting the results required readings at the full range of pressures, each experimental run was duplicated, first in steps of increasing pressures by admission of additional gas into the tube, and then in steps of decreasing pressure by pumping it out in small amounts at a time. Finally, the criterion advanced by Beaty[1] that at very high E/p_0 all drift velocities should be the same regardless of temperature was noted to be met. No significant errors are thus believed to be present due to errors in temperature uniformity or in p_0.

All oscillographic observations were photographed on 35-mm film, and the times of travel of ions for crossing the fixed 1-cm gap were read from the oscillograms with the aid of a microfilm reader. Only single-sweep oscillograms were used as the brightness of the trace and the film speed were adequate. It may be remarked that, as previously noted by Varney,[2] the oscillograms never disclosed more than a single "break" in nitrogen so that the presence of two different ions at once, so characteristic of the rare gases, was not found to be a feature of nitrogen.

RESULTS

The measured drift velocities are plotted as a function of E/p_0, on a log-log scale, all points at the same temperature being connected by a smooth curve. The plot is shown in Fig. 1. The results of the present work above, below, and at room temperature are shown together with older results of Varney[2] and of Mitchell and Ridler[4] at room temperature. All results are essentially in agreement.

The first notable feature of the results is that a drastic change of drift velocity with temperature occurs in the transition region of E/p_0 values. Next, this change is in the direction such that higher temperatures cause onset of the transition region at lower E/p_0 values. The change is in accordance with the belief that as impacts between ions and gas molecules grow more energetic, the N_4^+ ions should dissociate and travel at the slower speed characteristic of N_2^+ ions.

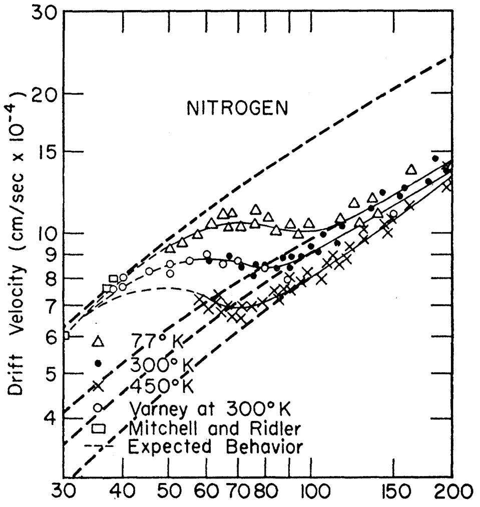

FIG. 1. Drift velocities of ions in nitrogen at various temperatures, including extrapolations of velocities to high and low values of E/p_0.

The drift velocity, which is nearly constant in the transition region, is higher the lower the gas temperature is made. This result again reflects the fact that the dissociation of the N_4^+ ions is associated with the energy of impact, that the energy of impact is influenced by both temperature and E/p_0, and finally that the drift velocity of the undissociated ion is only influenced by E/p_0. A drop in temperature necessitates an increase in E/p_0 to bring on dissociation; the higher E/p_0 causes faster drift at the onset of dissociation.

Figure 1 further shows extrapolations of the velocity curves which prevail at the low and high E/p_0 ranges beyond their natural ranges. A rough attempt has been made to evaluate the energy of binding of the N_4^+ ions against dissociation into N_2^+ and N_2. The degree of dissociation of N_4^+ ions at any value of E/p_0 may be read from the extrapolated speeds of N_4^+ and N_2^+ ions at the chosen value of E/p_0 and the actually measured speed. Then the change of E/p_0 which is necessary to compensate for a change of temperature in order to cause the same degree of dissociation provides a rough estimate of collision energies in terms of E/p_0. The results suggest roughly that at E/p_0 of 70 volts/(cm ×mm Hg) ions acquire approximately 0.11 ev of energy from the field as compared with kT at room temperature of approximately 0.026 ev. At room temperature and E/p_0 of 70, Fig. 1 indicates approximately 50% dissociation of N_4^+ ions to N_2^+. Making the overly simple

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[4] J. H. Mitchell and K. E. W. Ridler, Proc. Roy. Soc. (London) **A146**, 911 (1934).

assumption that 50% dissociation should occur for impact energies approximately equal to binding energies, the binding energy is indicated to be the sum of the field and thermal energies or about 0.14 ev. Pending a more rigorous analysis, this value may serve as a starting point for further studies of the N_4^+ ions. It is noteworthy that it is appreciably smaller than the binding energy of He_2^+, Ne_2^+, and A_2^+ reported by Hornbeck and Molnar[5] which in some respects are ions comparable with N_4^+.

An interesting feature of the extrapolation mentioned above is that the velocity curves for ions believed to be N_2^+, when extended toward E/p_0 of zero, show a temperature effect indicating that the highest extrapolated velocity is obtained at low temperatures. By contrast, Tyndall and Pearce[6] who studied drift velocities in nitrogen at very low E/p_0 and hence presumably were observing the N_4^+ ions discussed in the present paper, found that low temperatures gave lower drift velocities. The difference is highly significant and supports the belief that the N_4^+ ions are correctly to be associated with low values of E/p_0 and N_2^+ with high values. The N_2^+ ions on passing through N_2 gas do so with frequent charge exchange in accordance with the direct observations of Kallman and Rosen.[7] The drift velocity is largely determined by this mechanism, and since charge exchange is little influenced by ionic speed in the present range of interest the thermal effects on drift velocity are concentrated in the inverse molecular velocity factor of the early Langevin theory.[8] The N_4^+ ions by contrast are less subject, if at all, to charge exchange, and their drift velocity at lowest E/p_0 values is dominated by the growing influence of the inverse fifth power polarization attraction as the temperature drops. The drift velocities, in the light of these views, may be expected to rise with falling temperature for N_2^+ and drop for N_4^+, as observed. It is believed that this series of observations of a complete and strong reversal of temperature effect on drift velocity with change of the collision mechanism is the most striking one in existence.

CONCLUSION

The picture of N_4^+ as the dominant ion in nitrogen at low E/p_0 is more strongly established by two independent features of the influence of temperature on drift velocity. The dissociation of N_4^+ at lower values of E/p_0 with rising temperature is strongly evident. The reversed effect of temperature on drift velocity of N_4^+ and of N_2^+ (extrapolated) at low E/p_0 also seems clear and in support of the over-all views. A rough estimate of the binding energy of N_4^+ is set at 0.14 ev. Extension of the work to CO, which has shown similar behavior to N_2, and theoretical analysis leading to more precise establishment of the N_4^+ binding energy are in progress.

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[5] J. A. Hornbeck and J. Molnar, Phys. Rev. **84**, 621 (1951).

[6] A. M. Tyndall and A. F. Pearce, Proc. Roy. Soc. (London) **A149**, 434 (1935); A. F. Pearce, Proc. Roy. Soc. (London) **A155**, 490 (1936).

[7] H. Kallman and B. Rosen, Z. Physik **61**, 332 (1930).

[8] L. B. Loeb, *Fundamental Processes of Gaseous Electronics* (University of California Press, Berkeley and Los Angeles, 1955), p. 42.