Mobility of Mass-Analyzed N^+, N_2^+, N_3^+, and N_4^+ Ions in Nitrogen Gas*

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Drift-velocity measurements as a function of E/p_0, the ratio of field intensity to normalized gas pressure, have been obtained for positive ions N^+, N_2^+, N_3^+, and N_4^+ in nitrogen gas using the "four-gauze" electrical shutter method of Tyndall *et al.* Extrapolation of the low-field measurements to zero field yields the values of the mobility μ_0, corrected to 0°C: 2.54±0.05, 1.70±0.05, 1.90±0.05, and 2.34±0.05 cm²/V sec for N^+, N_2^+, N_3^+, and N_4^+, respectively. The actual data were obtained at gas temperatures 28–32°C. The ions have been identified mass-spectrometrically during the process of measurement of the drift velocities. Gas pressure in the drift tube was in the 0.55–1.5 mm Hg range. Relative intensities of the four nitrogen ions were measured as functions of E/p_0. Approximate cross sections for formation of the secondary ions were also determined. The reversible reaction processes $N_2^+ + N_2 \rightarrow N_4^+$ and $N_4^+ + N_2 \rightarrow N_2^+ + 2N_2$ were observed experimentally.

I. INTRODUCTION

COMPARISON of positive nitrogen-ion mobility values reported by several authors is complicated by the fact that the ions under study had not been mass-spectrometrically identified. The drift velocity of nitrogen ions in nitrogen gas has been measured by a number of investigators[1–9] and recently, with the identification of the ions, by McAfee and Edelson[10] and by Keller *et al.*[11] The reduced mobility μ_0, which is the mobility adjusted to the standard conditions of 273°K and 760 mm Hg, has been quoted by several authors.[1,2,3,8,11] In the present experiment, the drift velocities for various nitrogen ions in nitrogen gas have been measured over the following ranges of E/p_0: $25 < E/p_0 < 160$ for N^+ and N_3^+, $35 < E/p_0 < 160$ for N_2^+, and $21 < E/p_0 < 180$ for N_4^+ where p_0 is the pressure reduced to the corresponding value for 0°C. Measurements of the drift velocities were taken at different values of gas pressure over the range $0.55 \leqslant p \leqslant 1.5$ mm Hg. Ion-molecule reactions of formation of the secondary ions have been discussed and their cross sections have been determined.

II. RESULTS AND DISCUSSION

Brief descriptions of the experimental procedures have been given in the preceding paper on mobility of hydrogen ions.

Nitrogen gas was admitted after passing the gas through a liquid nitrogen trap into the drift tube by means of a bakeable Alpert-type valve from a Pyrex flask of highly pure gas obtainable commercially (Linde). The mass spectrum obtained after baking the drift tube at 200°C shows the only ions observed to be N^+, N_2^+, N_3^+, and N_4^+. The drift velocities of the N^+ and N_2^+ ions are shown in Fig. 1 and those of the N_3^+ and N_4^+ ions in Fig. 2 plotted as functions of E/p_0. These drift velocities were calculated from the measured drift times in the 1-cm distance between shutters using the "four-gauze" electrical shutter method of Tyndall *et al.*[12,13] The data of the present experiment were obtained at temperatures 28–32°C measured directly in the drift tube with a calibrated thermocouple.

Lines of logarithmic slopes having values of one and one-half are shown in Figs. 1 and 2 in order to compare

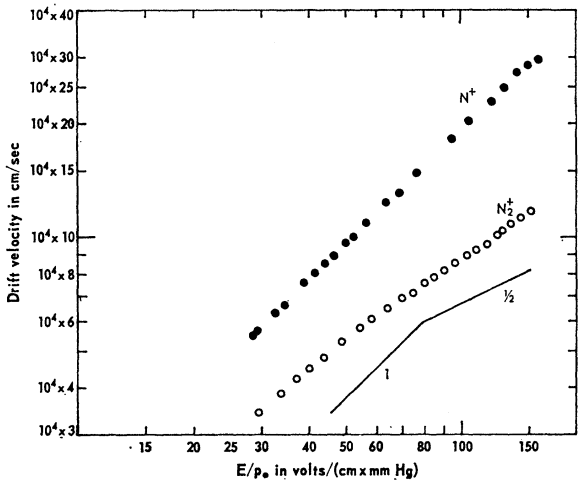

FIG. 1. Log-log plot of drift velocity of the N^+ and N_2^+ ions in nitrogen gas at 303°K versus E/p_0. Lines of logarithmic slope 1 and ½ are shown for reference.

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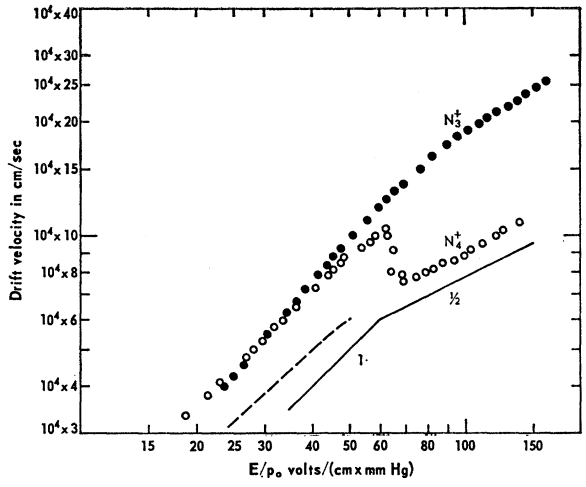

FIG. 2. Log-log plot of drift velocity of the N_3^+ and N_4^+ ions in nitrogen gas at 303°K E/p_0. Keller, Martin, and McDaniel results for the N_4^+ ions are shown (---). Lines of logarithmic slope 1 and $\frac{1}{2}$ are shown for reference.

present experimental results with Wannier's[14] theory for drift velocity as a function of E/p_0. At low field, Wannier's calculations show that the drift velocity varies directly with E/p_0 regardless of the interaction assumed. Lines through the typical data points of the drift velocity versus E/p_0 curves for N^+ and N_4^+ have a slope of unity and are approaching unity for N_2^+ and N_3^+. At high E/p_0 when the ion has an energy in excess of that of the surrounding molecules, Wannier's theory predicts that the drift velocity is proportional to $(E/p_0)^{1/2}$. With the exception of the N^+ ions, the drift velocities at high E/p_0 approach a slope of one-half on the log-log plot. For the N^+ ions, calculated energies greater than the thermal energies ($\frac{3}{2}kT$) of the nitrogen molecules are at $E/p_0 > 145$. Therefore, the drift velocity of the N^+ ions reported in this work is not in excess of thermal speeds and is proportional to E/p_0 for all values of E/p measured.

The drift velocity of the N_2^+ ions obtained in the present experiment is in good agreement with Varney's[4] for $E/p_0 \geq 80$ and with Dahlquist's[9] for practically all values measured. Dahlquist's drift velocity of the faster ions is higher by about 10% than for either N^+ or N_3^+ for $E/p_0 < 90$ in this work. Considerable disagreement exists between the present results and Keller's[11] mass-analyzed measurements of the drift velocity at low E/p_0 for the N_4^+ ions shown in Fig. 2. This is believed to be due to the fact that Keller's measurements were made at lower pressures (0.2 mm Hg) and the N_4^+ ions were formed within the space where drift measurements were made. Comparison of the other three ions shows that the N_2^+ ion drift velocity is about ten percent higher than Keller's and the N^+ and N_3^+ drift velocities agree at lower E/p_0 but disagree by a few percent at higher E/p_0 yielding different slopes which lead to different values of mobility.

The conventional zero-field mobilities of all four ions are shown in Fig. 3. The results of the zero-field mobilities of Bradbury, Mitchell and Ridler, Davies *et al.*, and Huber[15] are indicated by arrows at the left in Fig. 3. It is presumed that data were taken by Mitchell and Ridler at 20°C and their data were correspondingly reduced to 0°C by the writer. Since they used a glow-discharge ion source as in this work, higher temperature of the gas may be expected. Therefore their zero-field mobility may be lower. Bradbury's values were reduced from 22°C and Huber's from 20°C. The results of Vogel and of Frommhold are drawn. The results obtained by Keller *et al.* for the N^+, N_2^+, and N_4^+ were 2.47, 1.44, and 1.84, respectively, and are not shown in Fig. 3. Zero-field mobility of 1.85 for N_2^+ was obtained by Wobschall *et al.*[16] from measurements of the thermal energy elastic collision cross section for N_2^+ ions in N_2 gas by ion cyclotron resonance techniques. This value of mobility also is not shown in Fig. 3. The resulting values of the reduced mobility obtained in this work by extrapolation to zero value of E/p_0 are N^+: 2.54; N_2^+: 1.7; N_3^+: 1.9; and N_4^+: 2.34 in cm^2/V sec. Decline of mobility of N_3^+ for E/p_0 below 65 may be explained by the hypothesis that, at low values of E/p_0, N_3^+ ions in an encounter with N_2 molecules have a good chance

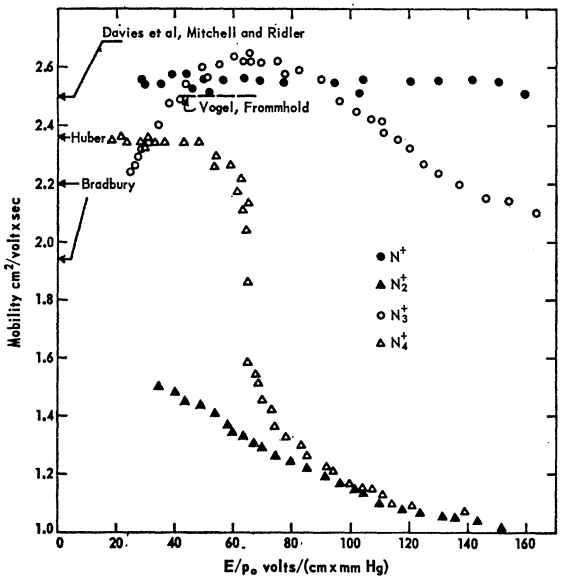

FIG. 3. Reduced mobility (μ_0) of the N^+, N_2^+, N_3^+, and N_4^+ ions in nitrogen gas at 303°K as a function of E/p_0. Low-field mobilities of Davies *et al.*, Mitchell and Ridler, Huber and Bradbury and μ_0 versus E/p_0 by Vogel and by Frommhold are also shown.

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of either clustering together to form N_5^+ ions of very low binding energy or exchanging N^+ and thereby decreasing the effective drift velocity of the N_3^+.

Figure 4 shows the composition of the ion current emerging from the drift tube. Indicated normalized ion intensities, expressed in percent, were obtained for any given ion by dividing the ionic current of that ion by the total ionic current at that E/p_0. Data were taken at 1 mm Hg gas pressure in the drift tube. The field strength was uniform from the ion source through a two-cm-long thermalizing space and the drift space including the spaces within both sets of shutters. The intensity of the secondary ions, N_3^+ and N_4^+, depends

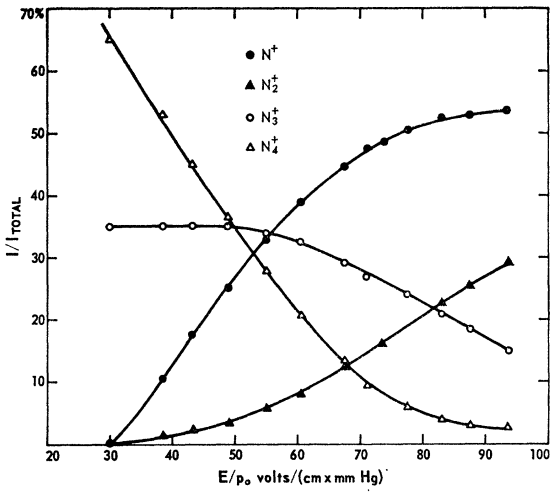

FIG. 4. Variation of normalized intensities of the N^+, N_2^+, N_3^+, and N_4^+ ions with E/p_0 in the drift tube at the pressure of 1 mm Hg.

on the pressure and the energy of the primary ions. Few secondary ions are formed in the ion source, since the field strength in the cathode fall-through, which the ions have to pass before entering the thermalizing region, is higher than 200 V/cm. The constant value of the normalized intensity of the N_3^+ ions for lower E/p_0 for a given pressure is believed to be due to the process of formation of these ions by collision of N_2^+ in the excited state with nitrogen molecules. Curran[17] found the appearance potential of N_3^+ to be 21.04±0.05 V with breaks observed at 21.8±0.1 V and at 22.2±0.2 V. Kaul and Fuchs'[18] value is 21.7±0.5 V and the author's[19] is 22.1±0.5 V. At higher values of E/p_0, not all excited N_2^+ ions react to form N_3^+ ions. This conclusion is supported by results shown in Figs. 5 and 6. Here the normalized intensities of ionic currents are shown as functions of E/p_0 in the drift space at two different constant values of electric field strength of 20 V/cm in

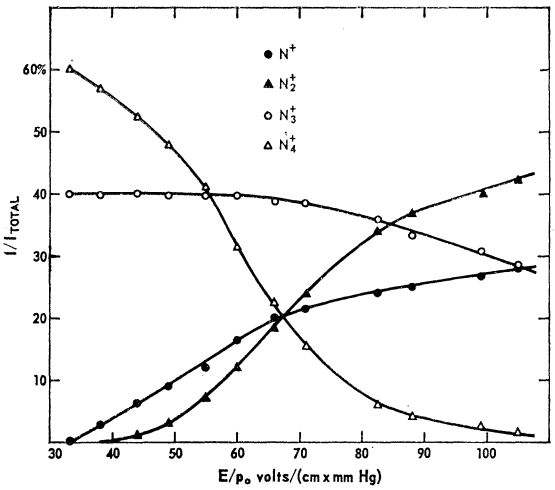

FIG. 5. Variation of normalized intensities of the N^+, N_2^+, N_3^+, and N_4^+ ions with E/p_0 in the drift space between the shutters and at constant electric field strength of 20 V/cm in 2-cm thermalizing region.

Fig. 5 and 80 V/cm in Fig. 6 in the 2-cm thermalizing region.

The normalized intensity of the N_4^+ ions decreases rapidly with increasing E/p_0. Formation and dissociation of the N_4^+ ions strongly depend on the energy of the reacting ions, much more so than in the case of the N_3^+ ions. This can be seen from Figs. 4, 5, and 6. Varney[20] evaluated the binding energy of the N_4^+ ion against dissociation into N_2^+ and N_2 obtaining a value of 0.5 eV. Figure 7 shows the energies for dissociating N_3^+ into $N_2^+ + N$ as 3.7±0.5 and into $N^+ + N_2$ as 2.6±0.5 eV, using 21.7 eV as the appearance potential

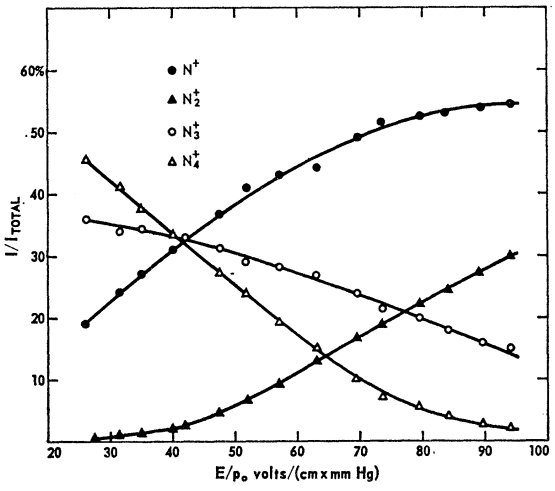

FIG. 6. Variation of normalized intensities of the N^+, N_2^+, N_3^+, and N_4^+ ions with E/p_0 in the drift space between the shutters and at constant electric field strength of 80 V/cm in 2-cm thermalizing region.

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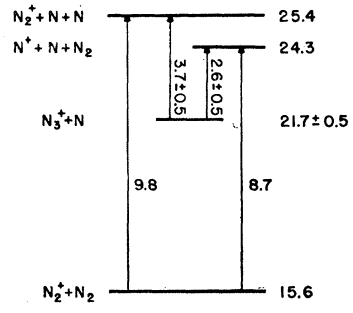

FIG. 7. Energy-level diagram of the nitrogen-ion system. Energies are in electron volts. 21.7 ±0.5-V value of the appearance potential of N_3^+ of Kaul and Fuchs is used.

of N_3^+. Franklin *et al.*[21] find the corresponding dissociation energies 3.6 and 2.56 eV.

Both secondary ions, N_3^+ and N_4^+, are formed mainly by two-body collisional processes. This can be seen from Fig. 8 where the normalized intensities of ionic currents are shown at different pressures but for a constant $E/p_0=55$ V/(cm×mm Hg). Ratio of normalized intensities of the secondary ions to the pressures are constant for all pressures. Deviations from this constant are observed for the N_3^+ ions for pressures below 0.8 mm Hg. This is due to the fact that the constant value of the normalized intensity of the N_3^+ ions at lower pressures is reached at higher value of E/p_0 than 55. Calculated values of the three-body collisions of the primary N_2^+ ions in the drift space is at least one order of magnitude lower than the number of the secondary ions at the highest pressure measured. The cross sections of formation of N_3^+ and N_4^+ ions were determined from the relation

$$e^{-n\sigma l}=1-i_s/i_p,$$

where l is the drift distance of the primary ions, n is the number of molecules per cm³, σ is the cross section, i_s is ionic current of the secondary ions, and i_p is the total ionic current measured which is assumed to be proportional to the primary N_2^+ ion current emerging from the ion source. This total current contains the N^+ ion current. It is assumed that the main contribution to the N^+ ion current takes place within the drift region due to the dissociation of some excited N_2^+ ions. This assumption is supported by the data in Figs. 5 and 6 where strong dependence of the N^+ ion current on the electric field intensity in the thermalizing region is shown. The cross sections were found within experimental error to be independent of the pressure at constant E/p_0. At $E/p_0=55$, the cross section σ for formation of the N_4^+ is $(3.00\pm0.03)\times10^{-18}$ cm² and for the N_3^+ $\sigma=(3.75\pm0.03)\times10^{-18}$ cm². The cross sections for formation of the secondary ions are strongly dependent functions of E/p_0, especially for the N_4^+ ions. Table I shows the cross sections for the N_4^+ and N_3^+ ions for various E/p_0, taken at a pressure of 1 mm Hg. The fourth column shows the calculated cross sections

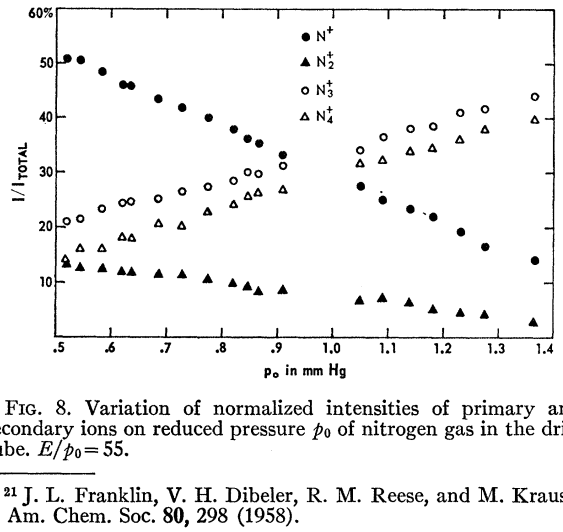

FIG. 8. Variation of normalized intensities of primary and secondary ions on reduced pressure p_0 of nitrogen gas in the drift tube. $E/p_0=55$.

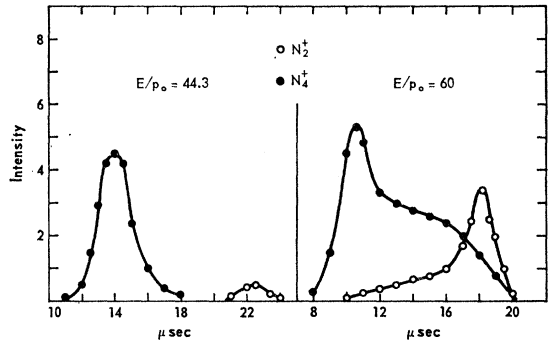

FIG. 9. Simultaneous measurement of ion transients of the N_2^+ and N_4^+ ions at E/p_0 of 44.3 and 60 V/(cm×mm Hg).

for the N_4^+ ions using the rate constant $k=5\times10^{-13}$ cm³/sec for the formation of these ions obtained by Fite *et al.*[22] The relative velocity of approach v_{12} of the primary ion and molecule was calculated from Wannier's[14] equation for the impact energy of the collision applicable at low E/p_0:

$$\tfrac{1}{2}m_{N_2^+}v_{12}^2=\tfrac{1}{2}(m_{N_2^+}+m_{N_2})v^2_{\text{drift}}+\tfrac{3}{2}kT.$$

Giese and Maier[23] studied the formation of the N_3^+ ions

TABLE I. Measured reaction cross sections for formation of the secondary ions N_3^+ and N_4^+ at various values of E/p_0 in V/(cm×mm Hg).

E/p_0	$(\sigma_{N_3^+})\times10^{18}$	$(\sigma_{N_4^+})\times10^{18}$	$(\sigma_{N_4^+})=k/\nu_{12}$
30	4.17	10.3	7.0
40	4.17	6.6	6.1
50	4.17	4.1	5.75
60	3.75	2.43	4.93
70	3.32	1.03	4.54
80	2.54	0.49	4.27
90	1.81	0.24	3.94

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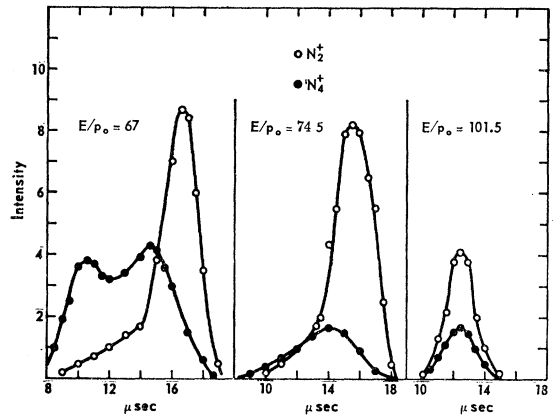

FIG. 10. Simultaneous measurement of ion transients of the N_2^+ and N_4^+ ions at E/p_0 of 67, 74.5, and 101.5 V/(cm×mm Hg). Shown intensity of the N_2^+ current is reduced ten times for E/p_0 of 101.5.

in collision of the N_2^+ in ground state with kinetic energy of 4±0.6 eV. They found the cross section for this ion equal to 20×10^{-18} cm^2.

Figures 9 and 10 show the superposed ion transients for N_2^+ and N_4^+ ions at several different values of E/p_0. The abscissa is the time during which the electrical shutters are open for the passage of the ions in the drift space and the ordinate is the ion intensities measured in the collector of the mass spectrometer focused for one type of ion at a time. In all of the measurements shown in Figs. 9 and 10, the pulse width was 2 μsec which is much longer than that used in measurements of the drift velocities. This was done in order to have higher intensities of the N_2^+ and N_4^+ ions at low and high E/p_0, respectively, for better comparison. These ion transients illustrate the reversible reaction process proposed by Varney in 1953:

$$N_2^+ + N_2 \rightarrow N_4^+, \quad (1)$$

$$N_4^+ + N_2 \rightarrow N_2^+ + 2\,N_2. \quad (2)$$

At $E/p_0=44.3$, the reaction (1) predominates. There is no dissociation of the N_4^+ ions. Most of the N_4^+ ions have formed by attachment in the thermalizing region. At $E/p_0=60$, a considerable number of the N_4^+ ions are formed in the drift space or, in terms of time, they spend a certain time drifting as N_2^+ ions. On the other hand, the N_2^+ ions drift through part of the space as N_4^+ ions which dissociate and are shown as a tail toward the shorter drift time. With the increasing E/p_0 the reaction (2) predominates and the N_4^+ ions spend a longer time and hence go a greater distance in the drift space as N_2^+ ions. Results shown in Figs. 9 and 10 explain the sharp drop in drift velocity of the N_4^+ ions at $E/p_0=65$, shown in Fig. 2. Similar ion transients have been recorded for the other two nitrogen ions, N^+ and N_3^+, in wide ranges of E/p_0 and pressures. The transients were found to be symmetrical, therefore no reversible reactions were observed. Most of these two ions were formed in the 2-cm thermalizing region.

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