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## Ion Production and Loss Processes in Helium-Nitrogen Mixtures\*

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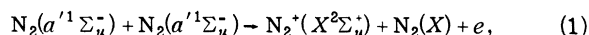
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Detailed studies of the time dependence of the number density of ions have been made during the decay period of plasmas produced in He containing various concentrations of nitrogen molecules.

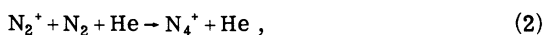
Various reaction-rate constants were obtained:  $\text{He}(2^3\text{S}) + \text{N}_2 \rightarrow \text{N}_2^+ + \text{He} + e$  [ $(6.3 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ ];  $\text{N}_2^+ + \text{N}_2 + \text{He} \rightarrow \text{N}_4^+ + \text{He}$  [ $(5.3 \pm 0.3) \times 10^{-30} \text{ cm}^6 \text{ sec}^{-1}$ ] and  $\text{N}^+ + \text{N}_2 + \text{He} \rightarrow \text{N}_3^+ + \text{He}$  [ $(4.6 \pm 0.4) \times 10^{-29} \text{ cm}^6 \text{ sec}^{-1}$ ]. Evidence for the charge-transfer process  $\text{N}_2^+ + \text{N} \rightarrow \text{N}^+ + \text{N}_2$  was obtained. The values of the ambipolar-diffusion coefficients of nitrogen ions in He were found to be  $D_a p_0(\text{N}^+) = 970 \pm 50$ ;  $D_a p_0(\text{N}_2^+) = 920 \pm 40$ , and  $D_a p_0(\text{N}_3^+) = 840 \pm 70 \text{ cm}^2 \text{ sec}^{-1} \text{ Torr}$ , while the diffusion coefficient of  $\text{He}(2^3\text{S})$  was  $D_m p_0 = 480 \pm 30 \text{ cm}^2 \text{ sec}^{-1} \text{ Torr}$ .

### I. INTRODUCTION

Recently, DeMonchy and Oskam<sup>1</sup> published studies, using mass-spectrometer techniques, of the time dependence of the  $\text{N}_2^+$  density during the decay period of a plasma produced in He containing 0.05, 0.17, and 0.5% nitrogen for total pressures varying from about 0.3 to 7 Torr. The product of the ambipolar-diffusion coefficient  $D_a$  of  $\text{N}_2^+$  and the reduced pressure  $p_0$  was found to be  $D_a p_0 = 900 \pm 50 \text{ cm}^2 \text{ sec}^{-1} \text{ Torr}$ . They confirmed the production of  $\text{N}_2^+$  during the decay period by



as postulated by Lund and Oskam<sup>2</sup> from studies in pure nitrogen. DeMonchy and Oskam, however, did not observe the conversion of  $\text{N}_2^+$  into  $\text{N}_4^+$  by the three-body process



for which Bohme *et al.*<sup>3</sup> published a rate constant  $k_2 = 1.9 \times 10^{-29} \text{ cm}^6/\text{sec}$  at a gas temperature of 280 °K.<sup>4</sup> This value was obtained by means of the flowing-afterglow method.

The authors are aware of only one other previous study of decaying plasmas produced in helium-

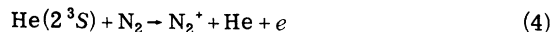
nitrogen mixtures. In 1961 Kasner *et al.*<sup>5</sup> reported a value of  $D_a p_0$  of  $\text{N}_2^+$  in He from measurements of the time dependence of the  $\text{N}_2^+$  density in He at pressures varying from 0.5 to 1.7 Torr, containing a fixed partial pressure of 0.006 Torr nitrogen. The fundamental characteristic diffusion length of their plasma container was 1.13 cm and  $D_a p_0$  was found to be approximately  $820 \text{ cm}^2 \text{ sec}^{-1} \text{ Torr}$ .

In order to resolve the difference between the results with respect to process (2) as obtained by Bohme *et al.*<sup>3</sup> and by DeMonchy and Oskam,<sup>1</sup> the present studies were performed. Moreover, it was believed that a reaction-rate constant for the process



could be obtained. Bohme *et al.*<sup>3</sup> reported  $k_3 = 8.6 \times 10^{-30} \text{ cm}^6 \text{ sec}^{-1}$  for process (3) at a gas temperature of 280 °K.

The studies were also extended to lower nitrogen concentrations so that the rate constant for the Penning ionization process



could be determined. The rate constant for process (4) has been reported by Sholette and

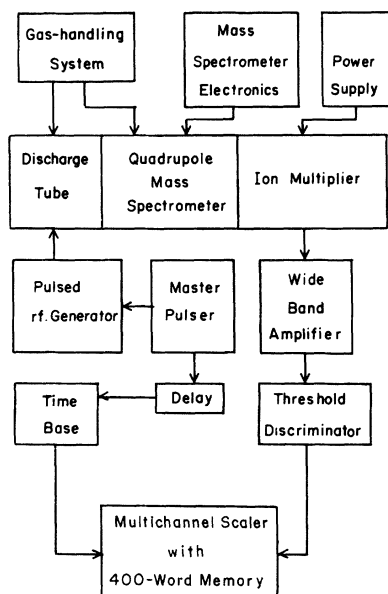


FIG. 1. Block diagram of the experimental system.

Muschlitz<sup>6</sup> as  $k_4 = 1 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$  (beam technique), by Cher and Hollingsworth<sup>7</sup> as  $k_4 = 1 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$  (flowing-afterglow technique), and by Schmeltekopf and Fehsenfeld<sup>8</sup> as  $k_4 = 0.7 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$  (flowing-afterglow technique).

## II. EXPERIMENTAL METHOD

A block diagram of the measuring system is shown in Fig. 1. The experimental tube consists of a differentially pumped mass spectrometer which samples ions diffusing to the walls of a discharge tube. The mass spectrometer used is of the electric-quadrupole type and has been described in detail elsewhere.<sup>9</sup>

The discharge region is a glass cylinder with metal endplates. One endplate is a molybdenum electrode, while the other is made of Kovar metal and contains a small hole (60  $\mu$  diam and 40  $\mu$  length) through which the ions effuse into the mass spectrometer region.

The gas-handling system is analogous to that developed by Alpert.<sup>10</sup> The ultimate pressure was less than  $10^{-9}$  Torr following a system bakeout at 350 °C for a period of about 36 h. The research-grade gases were obtained from the Air Reduction Company. Helium was further purified by means of the cataphoretic segregation method before adding nitrogen.<sup>11</sup> The final cleaning of the discharge region was achieved by covering the walls with a molybdenum layer obtained from sputtering the molybdenum electrode. This sputtering process was continued until the concentration of impurity ions was sufficiently small. The main impurity ions were  $\text{N}_2\text{H}^+$ ,  $\text{NO}^+$ , and  $\text{NH}^+$ , with the magnitude of

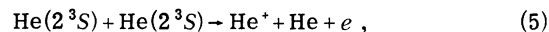
their number density generally in that order. For most experimental conditions, an impurity ion concentration less than 0.5% of that of  $\text{N}_2^+$  at 1 msec in the afterglow was sufficient for a consistent interpretation and good reproducibility of the data. The gas pressure was measured by a capacitance manometer which controlled a servo-operated valve to maintain a constant preset pressure in the discharge tube.

The discharge was produced by a pulsed 85-MHz rf generator, which was coupled to the discharge region by an external ring electrode. The ions passing through the quadrupole mass spectrometer are detected by a 14-stage ion multiplier (RCA type C1787K). The resulting anode pulses, each due to a single ion, are amplified by a wide-band amplifier and those above a minimum pulse height are selected by a discriminator in order to reduce the background count rate. The pulses from the discriminator are then fed into a multichannel scaler. The afterglow is divided into 100 to 400 equal time intervals which have a minimum duration of 25  $\mu\text{sec}$ . As the multichannel scaler advances from channel to channel, the number of pulses in the corresponding time intervals in the afterglow are recorded in the memory section. By accumulating the afterglow counts for a sufficient number of afterglow repetitions, a statistically significant number of counts can be recorded in each channel of the memory.

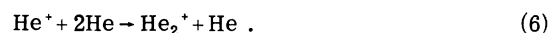
## III. RELEVANT AFTERGLOW PROCESSES AND THEORY

Several of the collision processes which have to be taken into account when discussing the properties of decaying plasmas produced in helium-nitrogen mixtures have been mentioned in Sec. I.

The presence of helium triplet metastable atoms during the plasma decay period results in the production of  $\text{N}_2^+$  ions by process (4). They can also produce  $\text{He}^+$  ions by the ionization process

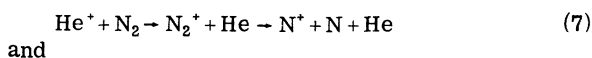


while the  $\text{He}^+$  ions are converted into  $\text{He}_2^+$  ions by the conversion process



This sequence of processes has been found to influence the properties of afterglows produced in He and He containing small concentrations of neon atoms.<sup>12-14</sup>

The  $\text{He}^+$  and  $\text{He}_2^+$  ions produced during the discharge pulse and plasma decay period produce  $\text{N}^+$  and  $\text{N}_2^+$  as a consequence of the processes



Heimerl *et al.*<sup>15</sup> published a reaction-rate constant

$k_7 = 1.0_{-0.2}^{+0.3} \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$  at 300 °K for process (7). They found that 55% of the product ions are  $\text{N}^+$  and 45%  $\text{N}_2^+$ . This is in agreement with the branching ratio reported by Warneck,<sup>16</sup> but disagrees with Schmeltekopf *et al.*<sup>17</sup> who observed 70%  $\text{N}^+$  and 30%  $\text{N}_2^+$ . Fehsenfeld *et al.*<sup>18</sup> measured  $k_8 = 0.6 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$  for process (8) at 300 °K. Because of the large rate constants for processes (7) and (8) the helium ions produced during the discharge pulse will disappear very rapidly after cessation of the discharge excitation.

In order to calculate the time dependencies of the number densities of the particles governing the decay properties of plasmas produced in helium-nitrogen mixtures, the continuity equation of each active particle [ $\text{He}(2^3\text{S})$ ,  $\text{He}^+$ ,  $\text{He}_2^+$ ,  $\text{N}_2(\alpha'^1\Sigma_u^-)$ ,  $\text{N}^+$ ,  $\text{N}_2^+$ ,  $\text{N}_3^+$ , and  $\text{N}_4^+$ ] has to be solved. The solutions of the continuity equations are rather simple functions if the experimental conditions are chosen such that the loss processes are mainly diffusion towards the walls of the plasma container and/or linear volume-loss processes.

For particles which are not produced during the decay period, the time dependence of the fundamental mode is a single exponential function. The relevant time constant is directly related to the loss processes of the particle. If the particle is also produced during the decay period, its time dependence is given by the sum of exponential functions having different time constants.<sup>19</sup> One time constant is related to the loss processes of the particle, while the other (others) describes (describe) the loss of the producing particles. The final decay of the particles will be determined by the largest time constant.

It can easily be shown that the time constant  $\tau$ , related to the loss processes of any particle, is, for the assumptions made, given by<sup>19</sup>

$$1/\tau = D/\Lambda^2 + \nu. \quad (9)$$

Here,  $D$  is the diffusion coefficient of the particle (ambipolar-diffusion coefficient  $D_a$  for charged particles),  $\Lambda$  is the fundamental characteristic diffusion length of the plasma container, and  $\nu$  is the volume-destruction frequency of the particle considered.

The ion signal measured by the mass spectrometer gives information about the time dependence of the ion density inside the plasma only if the density gradient at the plasma boundary is independent of time. This means that the density distribution of the ions has to be very close to the fundamental diffusion mode distribution. Oskam<sup>19</sup> derived requirements with respect to the time in the afterglow period as well as the decrease in the magnitude of the fundamental mode distribution after which the influence of higher diffusion modes on the measurements can be neglected for particles lost by diffusion

only. If, however, the particles disappear by a combination of diffusion loss and volume loss, the required decrease in the density of the particles involved can be shown to be considerably larger than the required decrease for loss by diffusion only. This phenomenon was observed during the present studies. It is essential, therefore, that the discharge excitation conditions are such that the spatial charged-particle distribution after cessation of the discharge excitation is close to a fundamental mode distribution.

#### IV. RESULTS AND DISCUSSION

The time dependence of the ion densities in the afterglow period was measured in plasmas produced in He containing 0.02, 0.05, 0.2, and 0.5% nitrogen for total reduced gas pressures varying from 0.4 to 8.5 Torr. The gas temperature was 300 °K and the duration of the discharge pulse was generally 1 msec applied at 25-msec time intervals. However, the pulse length was varied from 0.01 to 4 msec to determine the possible influence of the plasma excitation conditions on the data.

The dominant ion in the afterglow was, in general,  $\text{N}_2^+$ , while  $\text{N}^+$  became the major ion for low pressures and small nitrogen concentrations. The  $\text{N}_3^+$  and  $\text{N}_4^+$  ion densities were considerably smaller.  $\text{He}^+$  and  $\text{He}_2^+$  were also detected during the afterglow period, although the time dependence of their densities could be determined only at low pressures and small nitrogen concentrations. For these conditions their decay rate is determined by the production processes (5) and (6). The other ions which could be detected were impurity ions such as  $\text{N}_2\text{H}^+$ ,  $\text{NO}^+$ , and  $\text{NH}^+$ . Their concentrations during the measurements were, however, smaller than about 0.5% of the  $\text{N}_2^+$  ions.

Examples of measured decay curves are given in Figs. 2 and 3.

#### $\text{N}_2^+$

The measurements showed that the time dependence of the  $\text{N}_2^+$  density is, in general, governed by the sum of two exponential functions for low pressures. The time constant related to the later part of the afterglow period is due to production of  $\text{N}_2^+$  by process (1) and will be discussed later. The time constant determining the time dependence of the  $\text{N}_2^+$  ion density during the first part of the afterglow period is related to the loss of  $\text{N}_2^+$  by ambipolar diffusion and process (2) or by production of  $\text{N}_2^+$  by the Penning process (4). The pressure at which the time constant describing the total loss of  $\text{N}_2^+$  is larger than that related to the production of  $\text{N}_2^+$  by process (4) will decrease with increasing nitrogen concentrations for the reaction-rate constants published for processes (2) and (4).

The  $p_0/\tau$  values related to the  $\text{N}_2^+$  density during

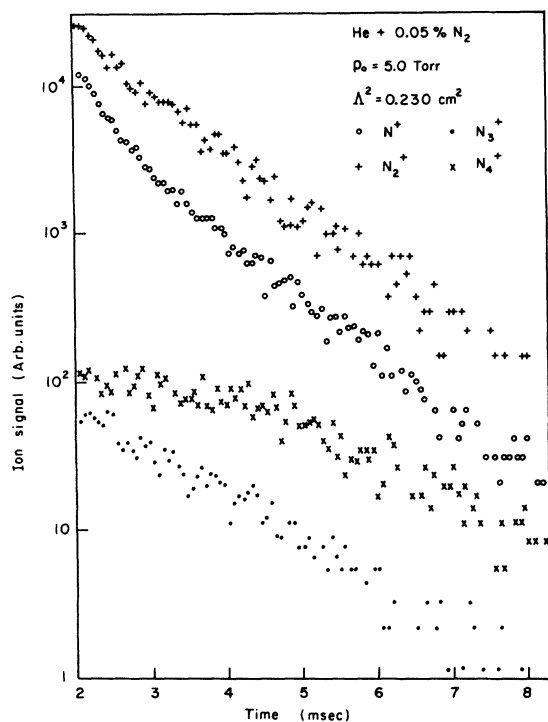


FIG. 2. Time dependence of the number density of nitrogen ions during the decay period of plasmas produced in He containing 0.05% nitrogen at a gas pressure of 5.0 Torr. The decay curves are shifted in order to avoid coincidence and crossing of the curves.

the first part of the plasma decay period for 0.02 and 0.05% nitrogen and gas pressures smaller than 2.4 Torr are given in Fig. 4 as a function of  $p_0^2$ . At low pressures the value of  $p_0/\tau$  appears to be a linear function of  $p_0^2$  and smaller than the value corresponding to loss by ambipolar diffusion. This shows that the decay rate of the  $N_2^+$  density in this pressure region is determined by the production of  $N_2^+$  by process (4), so that its time constant  $\tau$  is given by the time constant related to the loss of  $He(2^3S)$ , i. e.,

$$\frac{p_0}{\tau} = \frac{D_m p_0}{\Lambda^2} + C_4 r p_0^2, \quad (10)$$

where  $r = p_0(N_2)/p_0(\text{He})$ .

Both nitrogen concentrations give, within experimental error,  $C_4 = (2.2 \pm 0.3) \times 10^6 (\text{Torr sec})^{-1}$ , which corresponds to a rate constant for process (4) of  $k_4 = (6.3 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ . This value is in close agreement with the value published by Schmeltekopf and Fehsenfeld.<sup>8</sup> The value obtained for the diffusion coefficient of  $He(2^3S)$  in He,  $D_m p_0$  ( $480 \pm 30$ )  $\text{cm}^2 \text{ sec}^{-1} \text{ Torr}$ , is also in excellent agreement with previously published values in pure He.<sup>20</sup>

The close agreement between the values of  $k_4$  obtained from the two nitrogen concentrations, as

well as the agreement with previously published values, shows that the procedure used for obtaining the gas mixtures leads to reliable nitrogen concentrations.

The time constants of the rate of loss of  $He_2^+$  measured under these conditions were within experimental error equal to twice that of  $N_2^+$ . This confirms the occurrence of processes (5) and (6). These processes produce  $He^+$  and  $He_2^+$ , respectively, and their large influence on the time dependence of the number densities of these ions during the plasma decay period made it impossible to determine reaction-rate constants for the processes (7) and (8).

For the mixture containing 0.05% nitrogen the value of  $p_0/\tau$ , relating to the first part of the afterglow period, is independent of pressure for pressures between 1.5 and 2.4 Torr. Here, the time dependence of  $N_2^+$  is determined by the ambipolar loss process since in this case the influence of process (2) on the time constant is negligible for this small nitrogen concentration. The value of the ambipolar-diffusion coefficient of  $N_2^+$  in He following from these data is  $D_a p_0 = 920 \pm 40 \text{ cm}^2 \text{ sec}^{-1} \text{ Torr}$ , which corresponds to a reduced mobility value  $\mu_0(N_2^+) = 23.4 \pm 1.0 \text{ cm}^2/\text{V sec}$ . This value is about 10%

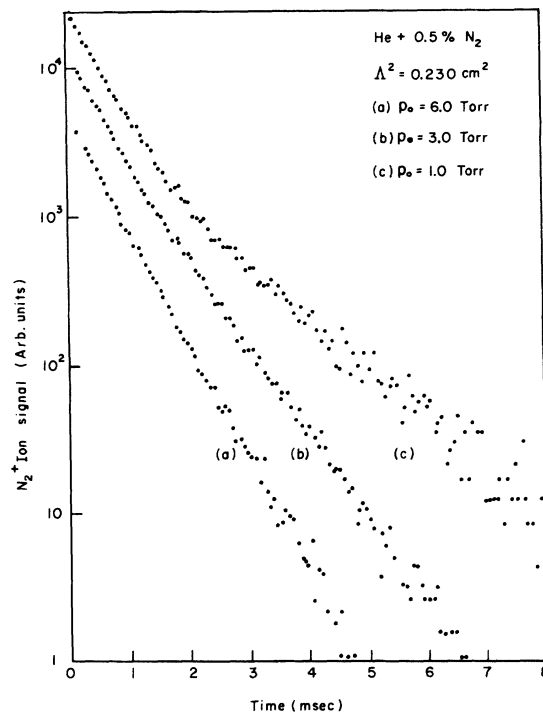


FIG. 3. Time dependence of the number density of  $N_2^+$  ion for various gas pressures during the decay period of plasmas produced in He containing 0.5% nitrogen. The decay curves are shifted in order to avoid coincidence and crossing of the curves.

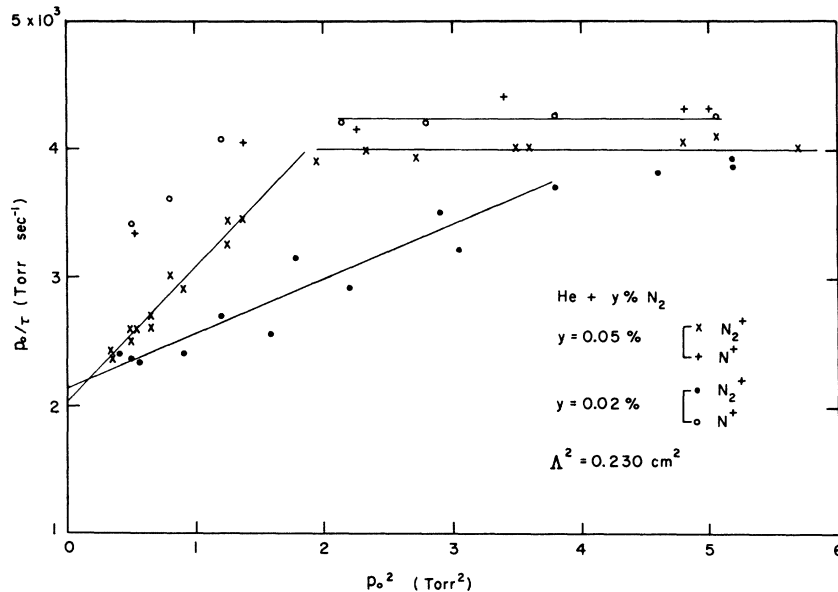


FIG. 4. Product of the inverse of the time constant  $\tau$  of the number density of  $N_2^+$  and  $N^+$  and reduced gas pressure  $p_0$  during the decay period of plasmas produced in He containing 0.02 and 0.05% nitrogen as a function of  $p_0^2$  for  $p_0$  smaller than 2.4 Torr.

larger than the values reported by Kasner *et al.*<sup>5</sup> and Johnson *et al.*<sup>21</sup>

For pressures and for nitrogen concentrations larger than those shown in Fig. 4 the  $p_0/\tau$  values related to the loss of  $N_2^+$  ions were found to depend both on the gas pressure and the nitrogen concentration. This indicates that the loss of  $N_2^+$  is due to the combination of ambipolar diffusion and conversion into  $N_4^+$  by process (2). Thus the time constant is given by

$$\frac{p_0}{\tau} = \frac{D_a p_0}{\Lambda^2} + c_2 r p_0^3. \quad (11)$$

The value of  $p_0/\tau$  was measured for four nitrogen concentrations and pressures varying from 2.0 to 8.5 Torr, corresponding to a variation in  $r p_0^3$  from

$5 \times 10^{-3}$  to  $1.2 \text{ Torr}^3$ . These values are shown in Fig. 5 as a function of  $r p_0^3$  and yield  $c_2 = (6.7 \pm 0.4) \times 10^3 \text{ sec}^{-1} \text{ Torr}^{-2}$ . This corresponds to a reaction-rate constant  $k_2 = (5.3 \pm 0.3) \times 10^{-30} \text{ cm}^6 \text{ sec}^{-1}$  for process (2), which is about a factor of 4 smaller than the value reported by Bohme *et al.*<sup>3</sup> The value of  $D_a p_0$  calculated from the intercept at  $r p_0^3 = 0$  is the same as that obtained from Fig. 4.

DeMonchy and Oskam<sup>1</sup> did not detect the conversion process (2) under analogous experimental conditions. Their measurements were performed at two different concentrations of the impurity ion  $NO^+$ , i. e., 5% and smaller than 1% of that of the dominant  $N_2^+$  ion at 1 msec in the afterglow period. The studies with about 5%  $NO^+$  ions did not show any indication of the influence of process (2) on

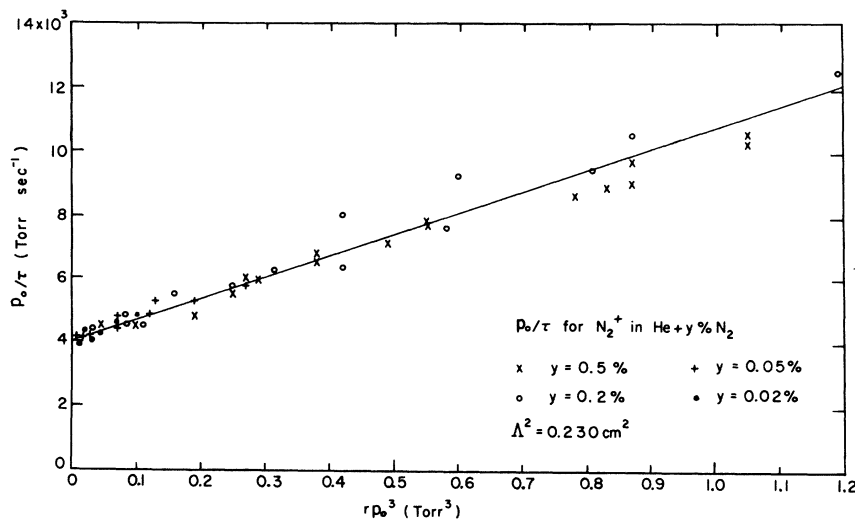


FIG. 5. Product of the inverse of the time constant  $\tau$  of the number density of  $N_2^+$  and the reduced pressure  $p_0$  during the decay period of plasmas produced in He containing various nitrogen concentrations as a function of  $r p_0^3$ , where  $r = p_0(N_2)/p_0(\text{He})$ .

the rate of loss of  $N_2^+$  (Fig. 3 of Ref. 1). The loss of  $N_2^+$  seemed to be exclusively determined by ambipolar diffusion for pressures varying from 1 to 7 Torr. The impurity ions  $NO^+$  and  $N_2H^+$  can be expected to have an ambipolar-diffusion coefficient in He close to that of  $N_2^+$ . It is, therefore, possible that, for experimental conditions during which the rate of loss of  $N_2^+$  by ambipolar diffusion and process (2) was larger than that of  $NO^+$  and  $N_2H^+$  by ambipolar diffusion, the measured final decay rate related to these ions due to the use of insufficient resolving power of the quadrupole mass spectrometer. For these conditions the conversion process (2) cannot be detected.

The data reported by DeMonchy and Oskam for conditions such that the  $NO^+$  concentration was less than about 1% of that of the  $N_2^+$  ions show deviations from  $N_2^+$  loss by ambipolar diffusion for pressures between 3 and 6 Torr. This may be due to the influence of process (2) on the measured decay rate, although the gas purity was apparently not high enough to fully reveal and measure the  $N_2^+$  conversion into  $N_4^+$  by process (2). Because of the large ion density range measured, the impurity ion concentration, determined at 1 msec in the afterglow, has to be extremely small as soon as its time constant is large with respect to that of  $N_2^+$ . An alternate method is to use high resolving power of the mass spectrometer. However, this reduces the accessible ion density range.

The present studies confirmed the production of  $N_2^+$  during the plasma decay period by process (1). The relevant time constants, measured at rather high mass resolving power, are, however, about half those reported by DeMonchy and Oskam.<sup>1</sup> No definite explanation of this difference has been found as yet. It may be due to processes occurring inside the mass spectrometer involving metastable nitrogen molecules. The influence of this possible phenomenon on the measurements is largest for low mass resolving power.<sup>22</sup>

$N^+$

The values of  $p_0/\tau$  related to the time dependence of  $N^+$  at low pressures and low nitrogen concentrations are given in Fig. 4. For these conditions it can be expected that the conversion process (3) can be neglected. The  $p_0/\tau$  values are, within experimental error, independent of pressure for  $p_0 > 1$  Torr. At lower pressure the value of  $p_0/\tau$  decreases with decreasing pressure, which is due to the electron-diffusion cooling phenomenon.

The value of the ambipolar-diffusion coefficient of  $N^+$  in He derived from the data shown in Fig. 4 is  $D_a p_0 = 970 \pm 50 \text{ cm}^2 \text{ sec}^{-1} \text{ Torr}$ , which corresponds to a reduced ion mobility  $\mu_0 = 24.8 \pm 1.3 \text{ cm}^2/\text{V sec}$ . This value is about 10% larger than the value reported by Johnson *et al.*<sup>21</sup> The influence of the  $N^+$

conversion process (3) on the data shown in Fig. 4 is about 2% for the highest pressure and nitrogen concentration shown when using the rate coefficient published by Bohme *et al.*<sup>3</sup> and about 8% when using the value determined from the present studies.

For pressures and/or nitrogen concentrations larger than those shown in Fig. 4 the  $p_0/\tau$  values related to the rate of loss of  $N^+$  ions depended on nitrogen concentration and total gas pressures, while for 0.05% nitrogen, this value depended also on the duration of the discharge excitation pulse. The  $p_0/\tau$  values measured are shown in Fig. 6 as a function of  $r p_0^3$ . For a nitrogen concentration of 0.02% the  $p_0/\tau$  values are linearly dependent on  $r p_0^3$ , while the same dependence is obtained for 0.05% nitrogen, provided the duration of the plasma excitation pulse is shorter than 0.1 msec. This indicates that these  $p_0/\tau$  values refer to loss of  $N^+$  ion by ambipolar diffusion and conversion into  $N_3^+$  by process (3), which leads to a time constant given by

$$\frac{p_0}{\tau} = \frac{D_a p_0}{\Lambda^2} + c_3 r p_0^3. \quad (12)$$

The value calculated for  $c_3$  from the slope of line (a) in Fig. 6 is  $c_3 = (5.8 \pm 0.5) \times 10^4 \text{ sec}^{-1} \text{ Torr}^{-2}$ . This results in a rate constant  $k_3 = (4.6 \pm 0.4) \times 10^{-29} \text{ cm}^6 \text{ sec}^{-1}$  for process (3), which is about a factor of 6 larger than the value reported by Bohme *et al.*<sup>3</sup> The value of  $D_a p_0$  calculated from the intercept at  $r p_0^3 = 0$  is the same as that obtained from Fig. 4.

For nitrogen concentrations of 0.2% and larger, the  $p_0/\tau$  value of  $N^+$  during the later part of the plasma decay period is closely equal to that of  $N_2^+$ . This is shown in Fig. 6, where the straight line (b) is the same as the solid line in Fig. 5. This strongly suggests the production of  $N^+$  during the decay period by



This process would also explain why, for a nitrogen concentration of 0.05%, the  $p_0/\tau$  values obtained for  $N^+$  for short excitation pulse lengths follow line (a), while for long pulse lengths they correspond with line (b). Longer plasma excitation increases the number of nitrogen atoms present during the plasma decay period.<sup>23</sup>

In order that the  $N^+$  production process (13) cause  $N^+$  to exhibit a time constant closely related to that of  $N_2^+$ , it is necessary that the rate of loss of nitrogen atoms be small compared to that of  $N_2^+$ . From studies of the time dependence of the intensity of the first positive band emissions of nitrogen, it followed that the maximum decrease in the time constant of  $N^+$  due to the time dependence of N is about 5%.<sup>23</sup>

Ferguson *et al.*<sup>24</sup> concluded from their studies

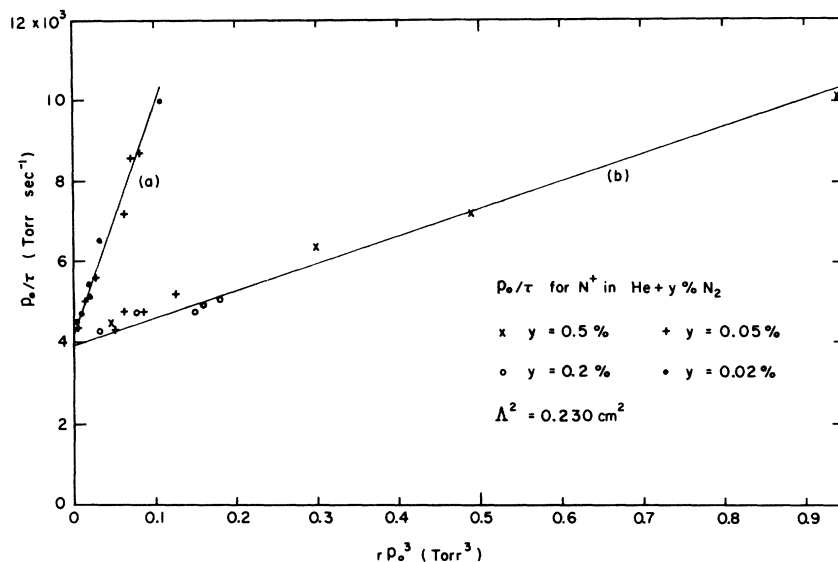


FIG. 6. Product of the inverse of the time constant  $\tau$  of  $N^+$  and the reduced gas pressure  $p_0$  during the decay period of plasmas produced in He containing various nitrogen concentrations as a function of  $rp_0^3$ , where  $r = p_0(N_2)/p_0(He)$ .

by means of the flowing-afterglow system that the reaction rate for process (13) is probably smaller than  $10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ . Our data do not allow for a determination of  $k_{13}$ , since the number density of N was not measured. However, from estimates made using the measured time constants, ion density ratios, etc., it followed that it is very unlikely that  $k_{13}$  is considerably less than  $10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ , as suggested by Briglia.<sup>25</sup>

#### $N_3^+$ and $N_4^+$

The  $N_3^+$  and  $N_4^+$  ions are produced during the plasma decay period by processes (3) and (2), respectively, while they are lost by ambipolar diffusion and recombination with electrons. It was not possible to obtain information about the loss processes of  $N_4^+$ , since the time dependence of the  $N_4^+$  ions during the measured decay periods was strongly influenced by production processes. It was, however, possible to estimate the ambipolar-diffusion coefficient of  $N_3^+$  ions in He. The value obtained was  $D_a p_0 = 840 \pm 70 \text{ cm}^2 \text{ sec}^{-1} \text{ Torr}$ , which corresponds to a value of the reduced mobility  $\mu_0 = 21.3 \pm 1.8 \text{ cm}^2/\text{V sec}$ .

#### V. CONCLUSIONS

The studies presented relate to the measurement of the time dependence of the number density of  $He^+$ ,  $He_2^+$ ,  $N^+$ ,  $N_2^+$ ,  $N_3^+$ , and  $N_4^+$  ions during the decay period of a plasma produced in He containing 0.02, 0.05, 0.2, and 0.5% nitrogen for gas pressures varying from 0.4 to 8.5 Torr.

The rate constant  $k_2$  obtained for the termolecular ion-neutral association reaction (2) is about a

factor of 4 smaller than the value reported by Bohme *et al.*,<sup>3</sup> while their rate constant  $k_3$  for re-action (3) is about a factor of 5 smaller than the value following from the present studies. From the data published by Bohme *et al.*<sup>3</sup> it follows that  $k_2 \approx 2k_3$ , while the present results yield  $k_2 \approx 10^{-1}k_3$ . This difference in the relative values of the reaction-rate constants of about a factor of 20 is difficult to explain. The value of  $k_2$  following from the present studies might have been influenced by an as yet unknown production process of  $N_2^+$ . This seems to be unlikely, however, since the rate of loss of the particles producing  $N_2^+$  should then be proportional to the He pressure as well as to the nitrogen concentration in order to explain the data shown in Fig. 5.

Moseley *et al.*,<sup>28</sup> using the ion-drift tube method, published values for the reaction-rate constants for processes (2) and (3) with  $N_2$  acting as the stabilizing third body instead of He. They obtained  $k_2 = 5.0 \times 10^{-29} \text{ cm}^6 \text{ sec}^{-1}$  and  $k_3 = 1.8 \times 10^{-29} \text{ cm}^6 \text{ sec}^{-1}$ . A comparison with the present results indicates that He is more effective at stabilizing the  $N_3^+$  complex than is  $N_2$ , while He is about a factor of 10 less effective in stabilizing the  $N_4^+$  complex than is  $N_2$ . No explanation for this apparent difference in stabilization efficiency can be given as yet.

The measured rate constant for the Penning process (4) agreed with previously published values.<sup>8</sup> The values obtained for the mobility of nitrogen ions in He are in agreement with the mass-ion mobility-dispersion curve reported by Powell and Brata<sup>27</sup> from measurements of the mobility of alkali ions in He.

The production of  $N_2^+$  ions during the plasma decay period by collisions between metastable nitrogen

molecules was confirmed.

Finally, the studies of the time dependence of  $N^+$  ions strongly indicated the importance of the charge-transfer process (13) when atomic nitrogen is present in the plasma.

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