

Mobility of Ions in Hydrogen*

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The drift velocity of positive ions in hydrogen was measured over a range of E/p_0 (ratio of electric field strength to pressure) from 0.6–110 V per cm per mm Hg by means of a double-shutter velocity spectrometer. From these data the mobility (ratio of drift velocity to electric field) at a standard gas density of 2.69×10^{19} molecules per cm^3 could be calculated. At low electric-field strengths the observed mobility was 10.2 cm per sec per V per cm at room temperature. At an E/p_0 of 10 the mobility began to rise, passing through a maximum of 14.3 at an E/p_0 of 60. The mobility at small electric field strengths was also measured as a function of temperature from 77–470°K. Its value remained nearly constant at about 10 from 77°K to room temperature and then rose abruptly to 11.5 at 375°K. These results are compared with other recent measurements and it is suggested that H_3^+ cluster formation may be responsible for the unusual behavior of the mobility of the hydrogen ion.

INTRODUCTION

DATA on the mobility of positive hydrogen ions in H_2 gas have been available for more than thirty years. As in the case of many other gases, however, the older measurements are considered unreliable both because of the poorer techniques and because of the effects of possible contaminants which were neither adequately controlled nor understood in some cases. There have been several measurements of hydrogen ion mobilities in recent years using modern, clean, ultrahigh vacuum techniques. Rose measured the mobility as a function of E/p_0 , the ratio of electric field strength to pressure, from a value of E/p_0 of 26 to 150 V per cm per mm Hg pressure.¹ His value of the mobility, extrapolated to E/p_0 of 0, appears to be below the older values most of which cluster around a value of 12.5 $\text{cm}^2/\text{V sec}$, referred to a standard gas density of 2.69×10^{19} molecules per cm^3 . The low end of his data at $E/p_0=26$ was too high to make an accurate extrapolation to 0. Later, using a similar experimental setup, Frommhold² extended the data to values of E/p_0 of 17. The data appear to extrapolate to a value of mobility at $E/p_0=0$ of 10.9. Working in the same laboratory as Frommhold, Jaeger, and Otto³ obtained results which are similar to those of Rose. Chanin, using a modified technique, measured the mobility for values of E/p_0 down to 3. The zero-field value of mobility extrapolated from his data is 12.3, in disagreement with both Rose's and Frommhold's results.³ His data above an E/p_0 value of 30 merge with those of Rose and Jaeger and Otto within the experimental uncertainties. The data of the present experiment tend more nearly to confirm the results of Rose, of Frommhold, and of Jaeger and

Otto and are in definite disagreement with those of Chanin.

The direct product of ionization of H_2 gas is H_2^+ ions. Dissociative ionization forming H^+ also occurs but with a much smaller probability. It was natural then to label the ion whose mobility was measured in hydrogen as H_2^+ . In 1960, Varney pointed out that the secondary process $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$ would in all ordinary mobility experiments convert the H_2^+ entirely into H_3^+ .⁴ Varney's statement was based on the large cross section of the above reaction measured by Stevenson and Schissler.⁵ Barnes, Martin, and McDaniel confirmed the presence of the H_3^+ ion in mobility experiments by using a mass spectrometer, but did not take a simultaneous mobility measurement.⁶ It is now assumed that the only hydrogen ion whose mobility has ever been measured in hydrogen is the H_3^+ ion. As a convenient reference, Fig. 1 has been included giving the basic energy data on the various hydrogen ions including the calculated dissociation energy of H_3^+ .⁷

In summary then, we note that hydrogen ions present some severe contradictions as data obtained in three different laboratories, all using excellent modern techniques and all obtained in or since 1960, are not in agreement.

EXPERIMENTAL METHOD

The method used in the present experiment is the double shutter method developed by Powell, Starr, and Tyndall.⁸ It was felt that with modern electronic pulse techniques this method provided the greatest accuracy and versatility. In the original form of the apparatus used by Tyndall, sinusoidal voltages were applied to the shutters. The present square-wave technique with the

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¹ D. J. Rose, *J. Appl. Phys.* **31**, 643 (1960).

² L. Frommhold, *Z. Physik* **160**, 554 (1960); G. Jaeger and W. Otto, *ibid.* **169**, 517 (1962).

³ L. M. Chanin, *Phys. Rev.* **123**, 526 (1961).

⁴ R. N. Varney, *Phys. Rev. Letters* **5**, 559 (1960).

⁵ D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.* **29**, 282 (1958).

⁶ W. S. Barnes, D. W. Martin, and E. W. McDaniel, *Phys. Rev. Letters* **6**, 110 (1961).

⁷ R. E. Christoffersen and S. Hagstrom, *J. Chem. Phys.* **40**, 236 (1964).

⁸ A. M. Tyndall, *The Mobility of Positive Ions in Gases* (Cambridge University Press, Cambridge, England, 1938).

shutter time interval and the drift time interval separately variable considerably simplifies and improves the analysis. In the present apparatus, both narrower shutter spaces and much shorter drift space have been provided in an effort to study the ions in very short time intervals. It is interesting to note that the abrupt rise of μ found by Tyndall and his colleagues to occur in every gas somewhere between E/p_0 of 10 and 30 is in general not duplicated in the present work. It is not felt that the rise of μ in the present work occurring at E/p_0 near 10 is an equivalent phenomenon.

Figure 2 is a schematic diagram of the apparatus showing the basic electrical connections. The ions are created in a glow discharge and then drift through a 2-cm thermalizing space to the first shutter (x_2, x_3 in Fig. 2). The grid spacing of each shutter is approximately 1 mm.⁹ An electrical pulse applied to the shutter (t_0 to t_1 in Fig. 3) allows a thin slab of ions into the 1-cm drift space between the shutters. If the ions arrive

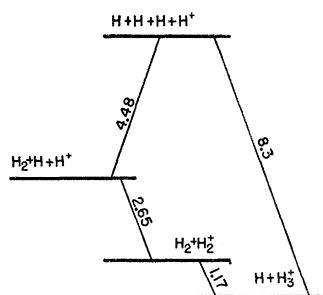


FIG. 1. Energy levels of the hydrogen ion system. Energies are in electron volts. The dissociation energies of H_2 at 4.48 eV and of H_2^+ at 2.65 eV are well established. The proton transfer energy from H_2^+ to H_2 to form H_3^+ , shown as 1.17 eV, is based on theoretical studies which contain approximations and cannot be rigidly accepted. The 1.17-eV figure is evaluated from the calculated 8.3-eV dissociation energy of H_3^+ and the sum of 2.65 and 4.48 eV and is no better than the 8.3-eV value.

at the second shutter (x_4, x_5 in Fig. 2) at the exact time that a second pulse (t_2 to t_3) "opens" the shutter, they are transmitted through to the collector electrode which is connected to an electrometer. Ions arriving at a shutter when it is "closed" are neutralized on the shutter electrodes. The potential distribution in the apparatus is shown in Figs. 3 and 4. The pulse magnitude is always adjusted so that the electrical field seen by the ions is uniform from position x_2 to x_5 . Time $t_1 - t_0$ is always equal to time $t_3 - t_2$. Holding $t_1 - t_0$ constant, time $t_2 - t_1$ is varied to find a maximum in the electrometer current. The drift velocity is then equal to:

$$v = (x_4 - x_2) / (t_2 - t_0).$$

⁹ The grids used in the two ion shutters were made of nickel "Lektromesh" manufactured by the C. O. Jelliff Corporation of Southport, Connecticut. Each consists of a square array of holes etched into 0.0015-in. nickel sheet. The holes are approximately square and 0.255 mm on an edge. There are 65 holes per inch and the open area is approximately 45%.

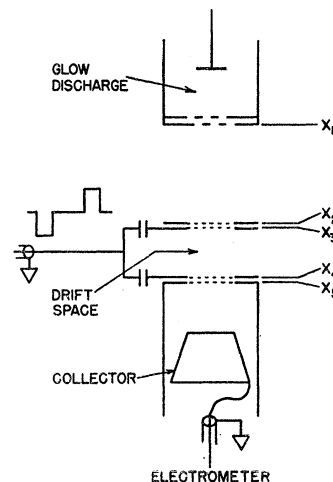


FIG. 2. Outline diagram of double shutter apparatus used in the present experiment. Pulser connection to the shutters is shown. Connection of the electrodes to the dc bias potentials is not shown.

The experimental tube was made entirely of nickel, tungsten, stainless steel, quartz, and Pyrex glass. After washing with solvents, the tube was assembled and sealed onto a glass ultrahigh vacuum system. This system was pumped with mercury diffusion pumps separated from the high-vacuum region by a liquid-nitrogen trap. After testing for leaks and pumping to a vacuum of several times 10^{-6} mm Hg, the system was baked at 400°C for at least 20 h. When brought back to room temperature, the pressure dropped below 10^{-8} mm Hg. A mercury cutoff was used to isolate the system from the vacuum pumps. With the cutoff closed, the system was required to have a rate of rise of pressure of less than 10^{-9} mm Hg per min. After the experimental gas had once been admitted, the system could no longer be pumped down to the 10^{-9} region due to the slow outgassing of the experimental gas from the wall, and the metal parts in the experimental tube. Even though this in itself represented no contamination, it did prevent making a meaningful measurement of the background pressure from day to day between data-taking runs. It is to be expected, however, that the background contamination pressure would decrease with time. This was strikingly confirmed in one case where a minor repair made it necessary to bring the system back to atmospheric pressure for about five minutes after it had been under vacuum for several months. After being pumped down and baked for about six hours, the background pressure was measured at 7×10^{-10} mm Hg and with the cutoff closed the pressure rose at a rate of 10^{-9} mm Hg per hour.

When the system was judged to have reached a

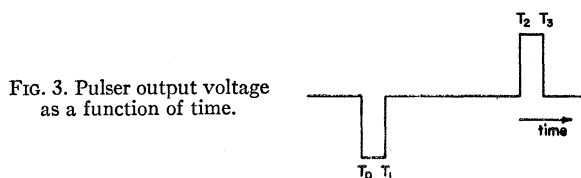


FIG. 3. Pulser output voltage as a function of time.

sufficiently good vacuum, the experimental gas was admitted by means of a bakable Alpert type valve from a flask of very pure gas supplied by the Linde Company.¹⁰ This was allowed to equilibrate for at least one hour before taking data.

Some of the data were taken with the experimental tube at temperatures as high as 200°C. To detect whether possible outgassing of the tube at these high temperatures contaminated the experimental gas, the gas was left in the tube after taking high-temperature mobility data and the tube was allowed to cool for 24 h. Room-temperature mobility data were taken on this "stale" gas and compared to room-temperature mobility data on fresh gas. The good agreement indicated the absence of important amounts of impurities due to degassing of the tube.

Measurements were taken at a variety of electric fields and gas densities. Following the usual conventions, the data were transformed to a standard state where the gas density is 2.687×10^{19} molecules per cm^3 using

$$E/p_0 = ET/273p,$$

$$\mu_0 = \frac{v}{E} \frac{p}{760} \frac{273}{T} = \frac{v}{760E/p_0},$$

where E , T , p , and v are the experimentally measured electric field, temperature, pressure, and drift velocity, respectively.

RESULTS

Figure 5 is a plot of the experimentally observed reduced mobility (μ_0) as a function of E/p_0 . This graph represents data taken under the following conditions of p_0 :

$p_0 = 1.3$ mm Hg	$E/p_0 = 20$ to 110,
$p_0 = 1.5$ mm Hg	$E/p_0 = 7.3$ to 96,
$p_0 = 2$ mm Hg	$E/p_0 = 4.8$ to 29,
$p_0 = 10$ mm Hg	$E/p_0 = 1.8$ to 6,
$p_0 = 18$ mm Hg	$E/p_0 = 0.6$ to 7.9.

As can be seen, every value of E/p_0 from 1.8 to 96 V per cm per mm Hg is covered by at least two pressures. In the region of E/p_0 below 10, where the data were

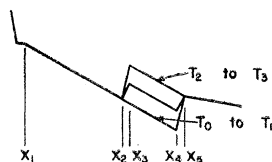


FIG. 4. Potential distribution among the electrodes labeled as in Fig. 2. The central line is the quiescent potential distribution. The potential distributions under pulse conditions are indicated.

¹⁰Linde Company, Rare Gas Department, P. O. Box 141, Tonawanda, New York.

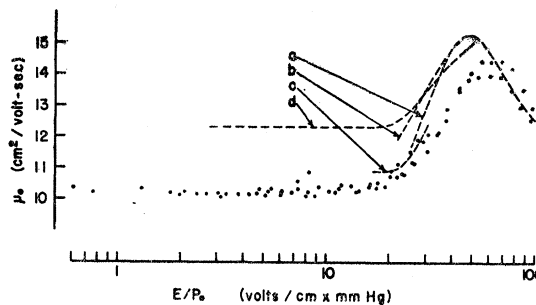


FIG. 5. Reduced mobility (μ_0) of positive ions in room-temperature hydrogen as a function of E/p_0 . Included for comparison are the following data: a—Rose, b—Jaeger and Otto, c—Frommhold, d—Chanin (Refs. 1, 2, and 3).

used to determine a value of $\mu_0(E/p_0=0)$, the data at different pressures agree and show a standard deviation from point to point of about 1%. At higher values of E/p_0 the agreement is not so good and the data disagree by as much as 5%. The value of $\mu_0(E/p_0=0)$ taken from these data is 10.2 ± 0.5 .

To make an adequate comparison of experimental mobility data with the predictions of theory, it is necessary to know the value of $\mu_0(E/p_0=0)$ as a function of temperature. In order to take measurements at an elevated temperature, electrical heating tape was wrapped around the experimental tube and a thermometer was inserted between the heating tape and tube. Several layers of insulation were then wrapped around the assembly. In this way the temperature of the tube could be raised to 200°C. Measurements were also made with the tube immersed in dry ice and in liquid nitrogen. The results are presented in Fig. 6.

One should recall that in terms of the experimentally measured quantities μ_0 is given by

$$\mu_0 = \frac{v}{E} \frac{p}{760} \frac{273}{T}.$$

If in the elevated temperature measurements heat should leak out of either end, a lower temperature in the drift space than that read on the thermometer would result. The measurement would then result in a value of μ_0 smaller than the actual value. Conversely in the case of the dry ice and liquid-nitrogen temperatures, if the drift space were at any temperature higher than that assumed for dry ice (195°K) or liquid nitrogen (77°K), the measurement would result in a value of μ_0 higher than the true value. Thus as far as errors in temperature are involved, the two points at elevated temperatures represent lower bounds and the two points at cold temperatures represent upper bounds. These limitations are of interest as they show that deviations from the results of Chanin cannot be explained by temperature discrepancies. On the contrary, errors in the temperatures, if they exist, when compensated would augment the deviations.

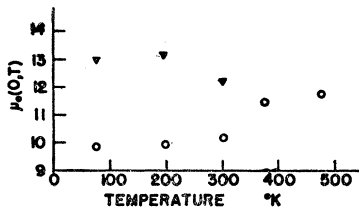


FIG. 6. The observed zero-field reduced mobility as a function of temperature. The triangles are the data of Chanin (Ref. 3). Open circles are from the present experiment.

Biondi and Chanin using a similar if not identical tube to that used by Chanin in his hydrogen experiment, have studied the mobilities of ions in the noble gases.¹¹ The apparatus used in the present experiment was used to make measurements of the mobility of the He⁺ ion in helium, and these measurements were compared to the results of Biondi and Chanin to detect any systematic differences in the two experimental setups which would account for the discrepancy in the hydrogen data. Figure 7 presents the results of these measurements and also the published results of Biondi and Chanin. There is an apparent difference of about 6%. The stated error of the Biondi and Chanin data is $\pm 5\%$ and is indicated by the error bar near $E/p_0=0$.¹² If we assume a similar error in the present data, the two sets of data agree within the stated errors. Even if the 6% difference is a real systematic error, however, it does not account for the 20% discrepancy between the two results in hydrogen.

Measurements were also made at 470°K. The result was that μ_0 at $T=470^\circ\text{K}$ was 9.0. Published measurements at this temperature could not be found for direct comparison but this value is in good agreement with the data of Chanin and Biondi if extrapolated to 470°K.¹² The data of Chanin and Biondi taken between 77 and 300°K and their errors are such that they would agree well with a value for μ_0 at 470°K anywhere between 8 and 9.5, so the comparison is not a sensitive test of this equipment. Nevertheless, the 470°K data in helium indicate a temperature effect opposite to that seen in hydrogen and thus that the temperature effect seen in hydrogen is not a purely instrumental effect.

CONCLUSION

The physical effect of increasing the drift field, that is increasing E/p_0 , is to raise the average kinetic energy acquired by the ions between collisions with the gas molecules. When the energy supplied by the electric field to the ions becomes of the order of the thermal energy it begins to alter the average energy of the collisions and can have an effect on the mobility. The data of this experiment show such an effect above an E/p_0 of 10. The average energy of collision can also be changed by changing the gas temperature. The effects

of temperature and E/p_0 on the mobility are not simply related, however, because the velocity distribution of the ions at high values of E/p_0 is not a Maxwell-Boltzmann distribution. Nevertheless, we can expect that μ_0 taken as a function of temperature and μ_0 taken as a function of E/p_0 will show qualitatively similar behavior. The data of this experiment confirm this expectation. The value of the mobility remains constant for conditions of low kinetic energy of the colliding molecules and ions, that is when E/p_0 is below about 10 and when the gas is at or below room temperature. Conversely, when E/p_0 is increased above 10 or when the gas is warmed to as little as 100°C, an abrupt increase in μ_0 results.

When E/p_0 is raised above 60, a decline in mobility occurs. It is therefore expected but not tested in the present experiment that if T should be raised above 470°K, the mobility might reverse its temperature effect and decrease with further increase of T .

As mentioned in the Introduction, there is another recent determination of $\mu_0(E/p_0=0)$ for hydrogen. It is that of Chanin. His data are included for comparison in Fig. 5. The difference between his room-temperature value (12.3) and the result of the present experiment (10.2) is well outside the assigned errors of either experiment. The close agreement between Chanin's and the present results in the case of He⁺ seems to eliminate the possibility that systematic apparatus errors are responsible for the difference, and neither observer can seriously be charged with lack of adequate gas purity control. It would thus seem that the two observers must have been measuring the mobilities of different ions.

It will be noticed on inspection of the graph of μ_0 versus temperature and μ_0 versus E/p_0 that they are not consistent with the qualitative behavior expected from the simple force laws usually considered in mobility experiments. If the ion were the H₂⁺ ion, then the charge exchange mechanism would be expected to dominate and the mobility would be a slowly decreasing function of E/p_0 and of temperature as in the case of the He⁺ ion. This is clearly not the case. If one assumes for the interaction force between an ion and a molecule an r^{-5} attractive term plus some repulsive term, then by proper choice of the repulsive term, it is possible to obtain theoretical results that show a large rise of

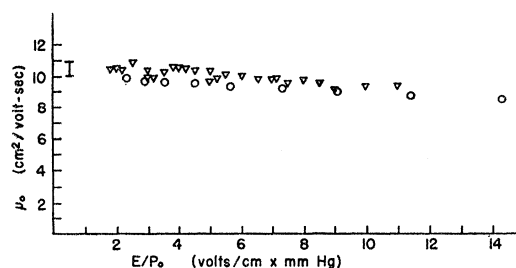


FIG. 7. Reduced mobility of He⁺ ions in helium at 300°K as a function of E/p_0 . Circles are from this experiment. Triangles and error bar are from data of Biondi and Chanin (Refs. 11 and 12).

¹¹ M. A. Biondi and L. M. Chanin, Phys. Rev. **94**, 910 (1954).

¹² L. M. Chanin and M. A. Biondi, Phys. Rev. **106**, 473 (1957).

mobility with increasing temperature. The fact that the mobility remains approximately constant below room temperature, however, leads one to consider other possible explanations.

One possibility that must be considered is that the type of ion may change with a change of E/p_0 or of temperature as is the case in some other gases.¹³ The energetic stability of the H_3^+ ion compared to the lighter hydrogen ions (Fig. 1) precludes a simple dissociation reaction either to H^+ or H_2^+ . There is an absence of heavier hydrogen ions in most mass spectrometer observations. However, Dawson and Tickner have observed the presence of H_5^+ in a beam of ions extracted from a glow discharge.¹⁴ The intensity was only about 10^{-3} that of H_3^+ . The mere fact of its existence, however, indicates that H_5^+ is stable in isolation though presumably easily dissociated by collisions with gas molecules. We have the possibility then, that at values of E/p_0 below 10, the stable ion is H_5^+ and at values of E/p_0 above 60, the stable ion is H_3^+ and for values of E/p_0 in between, there is a transition region where the ion spends part of the time as H_3^+ and part of the time as H_5^+ , thus possessing an intermediate mobility. If this is the case one is left with the problem of why Chanin obtained H_3^+ ions even at low temperatures and low values of E/p_0 . The difference in the type of source used might be cited to account for the discrepancy. The experiments of the Hornbeck type and the present experiment used relatively low-energy electron cascades or glow discharges compared to the higher energy discharge of the Chanin experiment. The present experiment used a continuous glow discharge (3 mA and 300–460 V depending on pressure). Chanin used a pulsed source obtained by applying 1000 V to his discharge electrode for 0.5 μ sec. Chanin's source might have created ions in excited states that inhibited the formation of H_5^+ .

There is also the possibility that Chanin's source created appreciable amounts of H^+ but both its existence in Chanin's experiment and its influence on his mobilities can only be matters of speculation of this point.

The H_3^+ ion presents the possibility of complicated processes of proton exchange with the neutral hydrogen gas. The spacing between its protons is given as 0.876 Å which is reasonably close to that of the hydrogen molecule (0.742 Å).⁷ In analogy with similar reactions that have been studied, the reaction $H_3^+ + H_2 \rightarrow H_2 + H_3^+$ could have a substantial cross section and a considerable influence on the behavior of the mobility. An onset of such proton exchange at a certain collision energy could account for the fairly abrupt change of μ_0 near E/p_0 of 10. The resolution of these matters must await further investigation.

¹³ F. R. Kovar, E. C. Beaty, and R. N. Varney, *Phys. Rev.* **107**, 1490 (1957).

¹⁴ P. H. Dawson and A. W. Tickner, *J. Chem. Phys.* **37**, 672 (1962).

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APPENDIX: EFFECTS OF IMPURITIES

The major cause of the many discrepancies in the values of positive ion mobilities that have appeared in the literature of the last forty years has been impurities. This is so because it is possible, as discussed below, for a very small amount of impurity to dominate a mobility measurement completely. In some cases, if the ion being measured makes one collision with an impurity molecule the charge becomes transferred to the impurity. Since the cross section for such collisions is very large, it is possible under some experimental conditions to have almost the entire charge carried by the small minority of impurity molecules. One is then in effect measuring the mobility of the impurity ions. This appendix will investigate these ion-molecule reactions and evaluate their effect on mobility measurements made in hydrogen.

A. Survey of Impurities

Those substances with vapor pressures greater than 10^{-8} mm Hg at 77°K are listed in Table I. These are the

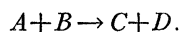
TABLE I. Substances with vapor pressures greater than 10^{-8} mm at 77°K. Second column gives the concentration as specified by Linde in parts per million.

Helium	
Neon	
Argon	1
Krypton	
Xenon	
Oxygen	1
Nitrogen	3.5
Nitrous oxide	
Carbon monoxide	1
Hydrocarbons	1
CH ₄	
C ₂ H ₄	
C ₂ H ₆	

gases that would not be condensed in a liquid-nitrogen trap. The gas used in this experiment was purchased from the Linde Company.¹⁰ It was supplied in a Pyrex flask that had been baked and evacuated to a high vacuum and filled to approximately one atmosphere with a highly purified gas whose impurities were carefully monitored with mass spectrometric and gas chromatographic techniques. The specified impurities are included in Table I.

B. Ion-Molecule Reaction Rates

A good theory of ion-molecule reaction rates can be formulated under the following assumptions: There is no activation energy, the reaction is exothermic; the probability of a collision and hence a reaction can be arrived at by calculating the orbit of an ion interacting with the induced dipole moment in a molecule. Consider N_a molecules per cm^3 of type A interacting with N_b molecules per cm^3 of type B according to the following scheme:



The rate constant (k) is defined by the following equation:

$$\dot{N} = kN_a N_b,$$

where \dot{N} is the number of interactions leading to products C and D per cm^3 per sec.

A short calculation gives as an expression for the reaction rate constant:

$$k = \frac{10^6 e}{2} \left(\frac{\alpha}{m\epsilon_0} \right)^{1/2} \text{ cm}^3/\text{sec},$$

where α is the polarizability of the gas molecules, e the electronic charge, and m the reduced mass of the gas molecules and the ions.¹⁵

TABLE II. Possible reactions of the H_3^+ ion. The reaction rate constant (k) in cm^3/sec is given in parentheses following each reaction.

$\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H} + 1.17 \text{ eV}$	(2.09×10^{-9})
$\text{H}_3^+ + \text{N}_2 \rightarrow \text{N}_2\text{H}^+ + \text{H}_2 + ?$	(1.9×10^{-9})
$\text{H}_3^+ + \text{CO} \rightarrow \text{CHO}^+ + \text{H}_2 + 2.1 \text{ eV}$	(2.0×10^{-9})
$\text{H}_3^+ + \text{CH}_4 \rightarrow \text{CH}_5^+ + \text{H}_2 + 1 \text{ eV}$	(2.4×10^{-9})
$\text{H}_3^+ + \text{O}_2 \rightarrow \text{H}_3\text{O}^+ + \text{O} + 1 \text{ eV}$	(1.8×10^{-9})

Listed in Table II are several possible exothermic reactions of H_3^+ with some of the possible contaminants listed in Table I. After each reaction is the calculated reaction rate constant (k). The nitrogen reaction is a conjecture, as the heat of formation of the N_2H^+ ion is not reported in the literature. The reaction is inferred from indirect evidence,^{16,17} and from an old mass spectrometer measurement.¹⁸ Though there are no mass-spectrometer measurements of reactions with H_3^+ reported in the literature, similar reactions with H_2^+ have been reported. These give good agreement between the calculated and measured reaction rates.^{5,15}

¹⁵ G. Gioumoussis and D. P. Stevenson, *J. Chem. Phys.* **29**, 294 (1958).

¹⁶ O. A. Schaeffer and S. O. Thompson, *Radiation Res.* **10**, 671 (1959).

¹⁷ S. C. Lind, *J. Phys. Chem.* **62**, 1601 (1958).

¹⁸ G. C. Eltenton, *Nature* **141**, 975 (1938).

As can be seen in Table II, the rate constants for all these reactions are near $2 \times 10^{-9} \text{ cm}^3/\text{sec}$. If we were to substitute a velocity-independent hard-sphere cross section in the integral expression for k , it would turn out that to get this high a reaction rate a cross section of 10^{-14} cm^2 would be required, which is very large by atomic standards. We are now in a position to do some quantitative estimates of the effects of contaminants in hydrogen mobility experiments.

C. Criticism of Experiments

If there are N_a ions and N_b impurity molecules present per cubic centimeter and if N_b is much greater than N_a , then the time constant for the disappearance of the original ion is $1/kN_b$. In the present experiment, the measurement of the ionic mobility took on the order of 10^{-5} sec . Assuming that k equals 2×10^{-9} we arrive at an upper limit on the allowable impurity pressure of about 10^{-3} mm Hg . In the case of 2-mm-pressure data this would represent an impurity concentration of 500 parts per million. Considering the quality of the vacuum obtained in the system and the specified impurities of the flask hydrogen, one can conclude that the results in this experiment were not affected by impurities.

Bradbury made measurements at atmospheric pressure with ions that were about $4 \times 10^{-2} \text{ sec}$ old.¹⁹ The required upper bound of impurity pressure in the experiment would be $4 \times 10^{-7} \text{ mm Hg}$. This would represent an impurity concentration of one part in 10^9 . The gas that Bradbury used was probably contaminated by 10^5 times this amount.

Lauer has measured the drift velocity of hydrogen ions by observing the induced current on a collector electrode with an oscilloscope.²⁰ He argues that a stable ion must be formed in $5 \mu\text{sec}$ or less. An ion-chemical reaction taking longer than this time would have had a visible effect on the oscilloscope pictures used to take his data. He made measurements over a pressure range of 50–600 mm Hg. The data least sensitive to impurities would be at 50 mm Hg. At that pressure his tolerable upper limit for impurity concentration would be 40 parts per million. This degree of purity is achievable although he does state that his nitrogen contamination was probably greater than this amount. The necessary purity for his higher pressure data could be achieved only with extreme effort.

Finally, in the experiment of Chanin,³ the gas pressures used were between 0.65 and 1.84 mm Hg. The age of the ions was about 10^{-5} sec . Thus the purity requirements would be substantially the same as in the present experiment, and with his stated techniques should have easily been met.

¹⁹ N. E. Bradbury, *Phys. Rev.* **40**, 508 (1932).

²⁰ E. J. Lauer, *J. Appl. Phys.* **23**, 300 (1952).