known, and may give relatively large errors in the calculations.

We have not worried about this problem in our work, but have concentrated upon other parameters. If we could trust the BG method, we could say something about the potentials. If we could trust a potential, we could tell more about the BG method. At the moment, it seems that we neither know the correct potential nor are we sure about the method. But some qualitative results and conclusions should be generally valid, independent of the specific potential which is used in the calculations.

The main conclusion is that our calculations give approximately the same results for the two-body potential energy and the single-particle energy spectrum as the calculations of Brueckner and Gammel[1] and others.[17–19] The binding energy with only two-body terms included is approximately $-1°$K/particle or more likely only $-\frac{1}{2}°$K/particle. In a future paper we shall see if we can get some additional binding energy from three-body correlations.

ACKNOWLEDGMENTS

The author would like to thank Professor G. E. Brown for helpful suggestions and stimulating discussions. He is also grateful for the support and kind hospitality of NORDITA in Copenhagen, where this work was begun.

PHYSICAL REVIEW VOLUME 170, NUMBER 1 5 JUNE 1968

Positive-Ion Mobilities in Dry Air*

G. Sinnott, D. E. Golden, and R. N. Varney
Lockheed Palo Alto Research Laboratory, Palo Alto, California

(Received 15 January 1968)

Drift velocities of mass-identified positive ions in air have been measured to about ±5% as a function of E/N for $2\times10^{-16}\lesssim E/N\lesssim 2\times10^{-14}$ V cm^2 and for $1.8\times10^{15}\lesssim N\lesssim 7\times10^{15}$ cm^{-3}. These measurements lead to values of the zero-field mobilities of 1.6, 3.5, and 2.5 cm^2/V sec for N_2^+, NO^+, and O_2^+, respectively, in air. The high-E/N data yield momentum-transfer cross sections of 110, 21, and 30 Å^2 for N_2^+, NO^+, and O_2^+, respectively. The rapid disappearance of N^+ and O^+ due to ion-molecule reactions prevented good drift-velocity measurements for them, but partial results indicate that O^+ is about 5% faster, and N^+ about 10% faster, than NO^+ in air. N_2^+ is shown to disappear rapidly by charge transfer with O_2. Thus, although the classical value of 1.6 is obtained for the mobility of N_2^+ in air, N_2^+ cannot be present long enough at pressures close to atmospheric to account for the classical observations.

I. INTRODUCTION

This paper reports measurements of the drift velocities and hence the mobilities of mass-identified positive ions in air. It results from an investigation of both the ion-molecule reactions and drift velocities of ions in dry air carried out in a drift tube. Details of the reactions studied will be presented elsewhere.[1]

Among the several methods of measuring the mobilities of ions in gases, the double-shutter, drift-velocity spectrometer of Tyndall, Starr, and Powell[2] operated with square-wave voltage is the most direct and versatile. The device can be connected in tandem with a mass spectrometer to provide both mass analysis and drift-velocity analysis of the same ions. The resulting data can be easily interpreted even in the presence of complicated ion-molecule reactions; in fact, the same apparatus can be used to measure many ion-molecule reaction rates. The ability to make meaningful measurements on complicated gas-ion systems accounts for the increase in popularity of the method in recent years.[3]

The present work has been carried out in dry air at pressures below 0.2 Torr. The findings are thus pertinent to the ionosphere, where the altitude and the temperature combine to produce similar or lower pressures and low humidity. The disagreements with the older measurements on positive ions in air, while failing to identify the ions studied by Bradbury[4] and others, do eliminate some surmises concerning the ions in the older experiments.

---

* Work supported by Lockheed Independent Research Funds.

[1] D. E. Golden and G. Sinnott (unpublished).

[2] A. M. Tyndall, L. H. Starr, and C. F. Powell, Proc. Roy. Soc. (London) **121**, 172 (1928).

[3] For some other apparatus incorporating tandem drift-velocity mass analysis, see E. W. McDaniel, D. W. Martin, and W. S. Barnes, Rev. Sci. Instr. **33**, 2 (1962); K. B. McAfee and D. Edelson, in *Proceedings of the Sixth International Conference on Ionization Phenomena in Gases, Paris, 1963* (SERMA, Paris, 1964), Vol. I, p. 299; M. Saporoschenko, Phys. Rev. **139**, A349 (1965); Y. Kaneko, L. R. Megill, and J. B. Hasted, J. Chem. Phys. **45**, 3741 (1966); P. Warneck, *ibid.* **46**, 502 (1967); J. Heimerl, R. Johnsen, and M. A. Biondi, Abstracts of the Twentieth Annual Gaseous Electronics Conference, San Francisco, 1967 (unpublished).

[4] N. E. Bradbury, Phys. Rev. **40**, 508 (1932).

II. APPARATUS AND PROCEDURE

Figure 1 is a schematic diagram of the drift-tube mass-spectrometer combination used in the present measurements of positive-ion drift velocities. When the tube was used for drift-velocity measurements, the potential on electrode 8 (V8) was equal to that of V7 +80 V. The thoria-coated iridium filament (F) was connected to electrode 7. Electrons from F (typically 10 μA) oscillated about and were collected by electrode 8, which was an 85% open grid. Positive ions created between electrodes 7 and 8 were in an electric field that drove them down the drift tube. Grids were placed on electrodes 1, 5, and 6. Electrodes 1–5 defined the drift region. A dc potential with suitable dropping resistors created a uniform field throughout this region. The system of electrodes 1–5 was coupled to a programmed pulser circuit capable of driving the system several volts positive or negative. The electric fields between 6 and 5 and between 1 and S were normally reversed by about 4 V, closing these shutters to the drifting ions. Driving electrodes 1–5 by more than 4 V negative opened the first shutter (electrodes 6, 5) and driving electrodes 1–5 by more than 4 V positive opened the second shutter (1,S). Figure 2 shows the potential distribution down the tube at various times. The distance between electrode 5 and S was 3.4 cm. The correct programming of these pulse sequences made it possible to discriminate against ionization created along the drift tube by ultraviolet radiation, neutral metastables, and stray secondary electrons.[5]

The delay time (t) between the negative and positive gating pulses was varied, and the mass-analyzed positive-ion current was recorded as a function of t. This was done for a variety of values of E/N and N, where E is the electric field and N is the number of gas molecules per cm^3. In practice, it was necessary to make recordings, scanning t in both directions, to compensate for the slight shift in the drift spectrum caused by the integrating time constant used to filter noise in the ion-current amplifier. The value of t for which the ion current was maximum was used in calculating the drift velocity. A 0.75-mm-diam hole in S allowed a sample of the ions reaching S to enter a quadrupole mass spectrometer.[6] An expanded 4-in. oil-diffusion pump with a Zeolite trap pumped the mass-spectrometer-multiplier region. The differential pumping ratio between the drift space and the pump was about 1000. The ultimate pressure was about 4×10^{-8} Torr. A 10-stage electron multiplier operated at a gain of 10^4 was used at the output of the mass spectrometer. The multiplier–lock-in-amplifier combination allowed ion currents down to 4×10^{-18} A to be measured. The pressure of air in the drift space was varied in the experiment from 0.05 to 0.20 Torr and was measured by a McLeod gauge connected to the drift tube through a liquid-nitrogen trap. Matheson dry air was used, which was admitted to the drift tube through another liquid-nitrogen trap.

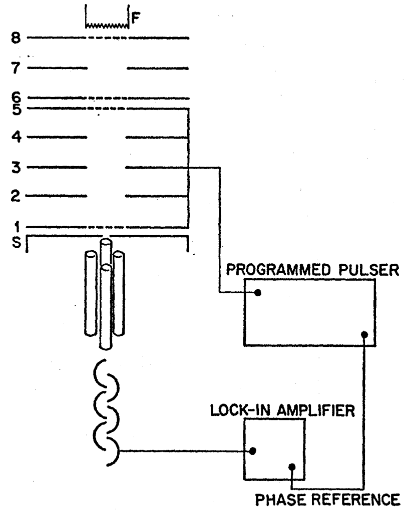

FIG. 1. Schematic diagram of the drift-tube mass-spectrometer combination.

As a check on possible systematic errors, we measured the mobility of He$^+$ ions in helium. The result agreed with the data reported by Hornbeck to within 5%.[7]

III. RESULTS

Electron collisions with N_2 and O_2 molecules in the source created N$^+$, O$^+$, N_2^+, and O_2^+ ions. Of these, the first three disappeared rapidly with increasing numbers of ion-molecule collisions (attainable by increasing the gas pressure or decreasing the drift speed). In the process, NO$^+$ ions appeared and the current of O_2^+ ions increased. Drift-velocity measurements could be made on O_2^+ and NO$^+$ ions, and at speeds over 5×10^4 cm/sec

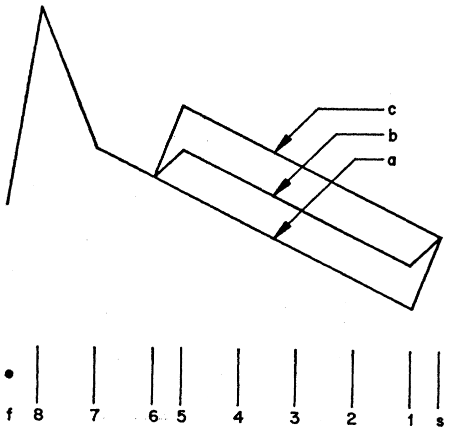

FIG. 2. Potential distribution along the drift tube (a) during negative gating pulse, (b) with both gates closed, (c) during positive gating pulse.

---

[5] G. Sinnott, D. E. Golden, and R. N. Varney (to be published).

[6] The quadrupole ion-mass spectrometer used is Varian Model No. 974-0002.

[7] J. A. Hornbeck, Phys. Rev. 84, 615 (1951).

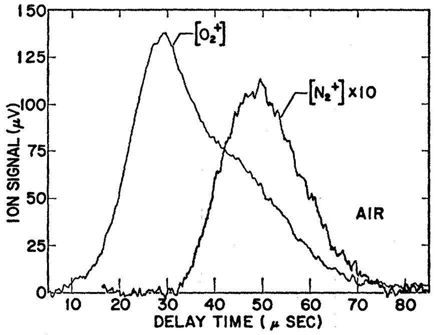

FIG. 3. O_2^+ and N_2^+ signals as a function of delay time for $E/N = 1.66\times10^{-15}$ V cm^2, $N = 2.38\times10^{15}$ cm^{-3}.

on N_2^+ ions (i.e., before they disappeared). Only an estimate could be made concerning the drift speeds of the atomic ions: O^+ ions traveled some 5% faster than NO^+, and N^+ ions were about 10% faster than NO^+.

The decrease in N_2^+ current at a fixed value of E/N but increasing N (or pressure) corresponded closely to the increase in O_2^+ current, indicating that the primary reaction of the N_2^+ was the charge exchange

$$N_2^+ + O_2 \rightarrow N_2 + O_2^+. \qquad (1)$$

This was substantiated by the fact that the shape of the ion-current curves as a function of the delay time t between the operation of the two shutters actually exhibited the transition in flight of the slower N_2^+ ions into the faster O_2^+ ions. Figure 3 shows a recorder tracing of the O_2^+ and N_2^+ ion signals, $[O_2^+]$ and $[N_2^+]$, respectively, as a function of delay time t for $E/N = 1.66\times10^{-15}$ V cm^2 and $N = 2.38\times10^{15}$ cm^{-3}. Under these conditions, $[O_2^+]_{\text{max}} \simeq 12[N_2^+]_{\text{max}}$. The shape of the $[N_2^+]$ curve is roughly symmetrical, and its width is determined by diffusion; that of $[O_2^+]$ is skewed toward longer times, which is the result of reaction (1) occurring in the drift tube. The line shapes may be used to determine rough values of both the diffusion constant and the ion-molecule reaction-rate constant, though this analysis is not included in the present paper.

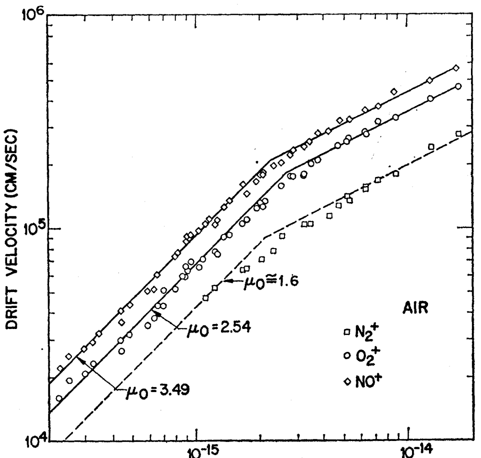

FIG. 4. Drift velocities in air as a function of E/N. Lines are drawn with the slopes of 1 and 0.5 to exhibit the fit of the data to such variations. The poor fit for N_2^+ ions makes the mobility value only approximate.

The measured drift velocities for N_2^+, O_2^+, and NO^+ are presented in Fig. 4 as a function of E/N. When the gas density is sufficiently low, so that only two-body interactions are important, kinetic theory demonstrates that averages over the ion-velocity distribution such as drift velocity and average energy are a function of E and N only through the ratio E/N. For values of drift velocity of the order of, or less than, thermal velocity, kinetic theory predicts that the drift velocity is proportional to E/N. Following the usual convention, we express this in terms of the mobility constant μ_0:

$$v_d = 2.687\times10^{19}\ \text{cm}^{-3}\times\mu_0\times E/N. \qquad (2)$$

In Fig. 4, lines of slope unity have been superimposed on the lower ranges of the data. For NO^+ and for O_2^+, the agreement is excellent; for N_2^+, there are not enough readings to permit comparison.

The linear relationship between drift velocity and E/N is maintained for values of the drift velocity much higher than thermal only for the particular force law $1/R^5$, and not for more general types of interaction. It may be shown, however, that for a scattering cross section that is independent of velocity, such as the hard-sphere or the charge-exchange type, the drift velocity is proportional to $(E/N)^{1/2}$ for drift velocities considerably greater than thermal velocity.[8] O_2^+ and NO^+ ions showed this type of behavior, as is indicated by the good fit of the data to lines of slope 0.5 superimposed on the higher-velocity points.

TABLE I. Mobilities and momentum-transfer cross sections for several positive ions in dry air.

	μ_0 (cm^2 V^{-1} sec^{-1}) (theory)	μ_0 (cm^2 V^{-1} sec^{-1}) (expt)	σ_D (Å^2) (expt)
N_2^+	2.82	~1.6	~110
NO^+	2.77	3.49	21.2
O_2^+	2.73	2.54	30.4

Calculations of the transport phenomena of diffusion and mobility involve the so-called momentum-transfer or diffusion cross section σ_D, which is defined as

$$\sigma_D = \int (1-\cos\theta)\sigma(\Omega)d\Omega,$$

where $\sigma(\Omega)$ is the differential cross section for scattering into the solid angle $d\Omega$ at a scattering angle θ. For a differential cross section that is isotropic, σ_D is equal to σ_{tot}. Charge exchange of ions in their parent gases is equivalent to collisions whose scattering cross section is

---

[8] G. H. Wannier, Phys. Rev. **83**, 281 (1951); **87**, 795 (1952); **96**, 831 (1954). See also Bell System Tech. J. **32**, 170 (1953).

strongly peaked backward ($\cos\theta = -1$), so that for such collisions $\sigma_D = 2\sigma_{\text{tot}}$. The higher values of drift velocity can be used to calculate a momentum-transfer cross section, using an equation given by Wannier[8]:

$$v_d = 1.147(eE/mN\sigma_D)^{1/2}, \tag{3}$$

where m is the mass of the ion. The values of μ_0 and of σ_D calculated from the observed values of v_d are given in Table I. The values for N_2^+ must be recognized to be approximate.

Table I also shows the μ_0 values predicted by the polarization limit of the Langevin theory. The value of μ_0 for N_2^+ extrapolated from this work is lower than this prediction (43%), again because of the well-known charge-exchange process with N_2. The value of μ_0 found in this work for O_2^+ is slightly lower than the prediction of the polarization limit (~7%). The value of μ_0 found in this work for NO^+ is larger than the prediction of the polarization limit (~25%). One would thus expect that the study of the mobility of NO^+ in N_2, O_2 mixtures as a function of the gas temperature at various lower temperatures would lead to information concerning the repulsive part of the interaction of NO^+ with N_2 and O_2.[9]

Varney[10] found a value of σ_D for N_2^+ in N_2 of 120 Å^2 from mobility studies. Similarly, he found a value of 78 Å^2 for O_2^+ in O_2. The results of the present experiment give a value of σ_D of 21 Å^2 for NO^+ in air, which we may take as the typical hard-sphere cross section for molecular ions in air, that is, for collisions not involving charge exchange. Using this value for the N_2^+-O_2 and O_2^+-N_2 cross sections and Varney's values for the N_2^+-N_2 and O_2^+-O_2 cross sections, we can arrive at weighted-average cross sections for N_2^+ and O_2^+ ions in air. This results in a value of the momentum-transfer cross section in air of 100 Å^2 for N_2^+ and 32 Å^2 for O_2^+. These values are within 10% of the values measured for these quantities in the present experiment.

There are several previous mobility results for unidentified positive ions in dry air, obtained at higher pressures (up to 650 Torr) than those used in this work.[11–13] All of these previous results give values of mobility in rough agreement with the present value for O_2^+. Young *et al.*[14] found a value of μ_0 for NO^+ in N_2 of 3.1 which is somewhat lower than the present result for NO^+ in air.

The value of μ_0 for positive ions in dry air of atmospheric pressure reported by Bradbury[4] in 1932 and confirmed by various observers is 1.6. The agreement of the present result for μ_0 of N_2^+ in air with this value must be regarded as fortuitous. N_2^+ ions could not survive at atmospheric pressure because of the charge-transfer reaction with O_2.[1]

The work of Shahin[15] on humid air indicates that hydrated ions of the form $H^+(H_2O)_n$ are preponderant and these ions may be responsible for the classical value of μ_0 of 1.6 in air. Water, however, seems questionable as a contaminant in the work of Bradbury[4] because of his purification procedures, in particular, the use of multiple liquid-air traps. Sinnott[16] has estimated what degree of purity Bradbury would have had to attain under certain assumed conditions of ion-reaction rates to obtain "pure-gas" results; the findings showed that contaminant pressures would have had to be below the pressure range of 10^{-6}–10^{-7} Torr. The vapor pressure of water at −185°C is reported as 10^{-16} Torr, so the older mobility values are apparently not to be explained on this basis.

The present work gives, for the first time, mobilities of mass-identified positive ions in dry air, which are unquestionably applicable to high-altitude observations.

---

[9] E. A. Mason and H. W. Schamp, Ann. Phys. (N. Y.) **4**, 233 (1958).

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

[11] L. Frommhold, Z. Physik **160**, 554 (1960).

[12] H. Ryzko, Proc. Phys. Soc. (London) **85**, 1283 (1965).

[13] D. T. A. Blair, J. McNaull, D. J. Tedford, and F. M. Bruce, in *Proceedings of the Fifth International Conference on Ionization Phenomena in Gases, Munich, 1961* (North-Holland Publishing Co., Amsterdam, 1962), p. 162.

[14] R. A. Young, C. R. Gatz, R. L. Sharpless, and C. M. Ablow, Phys. Rev. **138**, A359 (1965).

[15] M. M. Shahin, in *Ion-Molecule Reactions in the Gas Phase* (American Chemical Society, Washington, D. C., 1966), p. 329.

[16] G. Sinnott, Phys. Rev. **136**, A370 (1964).