reduced to a minimum by either a weakly coupled geometry or leveling of P_T. Also the neutral pressure must be low enough that collisional damping is not too large. (ii) The plasma parameters must be such that ionization effects do not occur at power levels lower than those at which nonlinear damping would be observed. Again this requires low neutral pressure.

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Mobilities and Longitudinal Diffusion Coefficients of Mass-Identified Potassium Ions and Positive and Negative Oxygen Ions in Oxygen† *

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Measurements at room temperature of the mobility and longitudinal diffusion coefficient have been made for low-energy mass-identified potassium ions and positive and negative oxygen ions in oxygen gas in a drift-tube mass spectrometer. The zero-field reduced mobilities of K^+, O_2^+, and O_4^+ in O_2 were found to be 2.68 ± 0.07, 2.24 ± 0.07, and 2.16 ± 0.08 cm^2/V sec, respectively. O^-, O_2^-, O_3^-, and O_4^- were determined to have zero-field reduced mobilities of 3.20 ± 0.09, 2.16 ± 0.07, 2.55 ± 0.08, and 2.14 ± 0.08 cm^2/V sec, respectively. The longitudinal diffusion coefficients were measured for O_2^+, K^+, O^-, and O_2^- in O_2. The longitudinal diffusion coefficients of all investigated ionic species at low E/N were at least within 16% of the values predicted from the mobilities by the Einstein relation. At higher E/N, the coefficients increased, in some cases quite rapidly, as E/N was increased.

1. INTRODUCTION

This paper presents the results of an extensive investigation of the drift and longitudinal diffusion of low-energy potassium ions and positive and negative oxygen ions in oxygen gas at room temperature. The data were obtained with a drift-tube mass spectrometer of ultra-high-vacuum construction. By an analysis described in Refs. 1 and 2, the mobilities of K^+, O_2^+, O_4^+, O^-, O_2^-, O_3^-, and O_4^- ions in oxygen gas have been determined and the longitudinal diffusion coefficients (D_L) of K^+, O_2^+, O^-, and O_2^- have been evaluated.

The *mobility* K is defined[3] as the ratio of the drift velocity v_d to the electric field strength E, and is inversely proportional to the gas number density N. To facilitate comparisons of data obtained at different gas number densities, we shall make use of the *reduced mobility* K_0, defined by the equation $K_0 = K(p/760)(273.16/T)$, where p and T are the gas pressure and temperature, in Torr and degrees Kelvin, respectively, at which the measurement of K was made. At a given temperature T, the parameter E/N determines the average energy and the transport properties of the ions. Hence, the data are presented as a function of E/N. As E/N is decreased toward zero, the reduced mobility K_0 approaches a constant value known as the *zero-field*
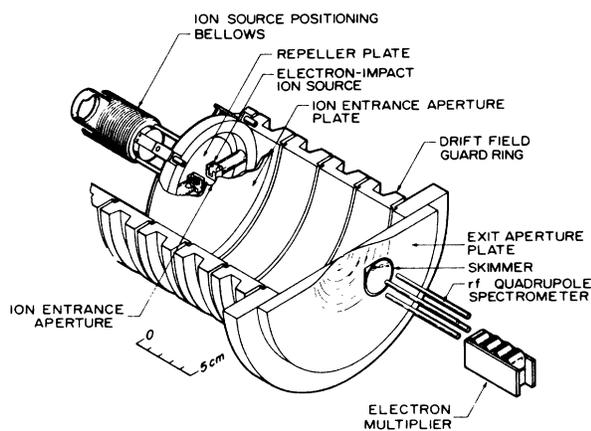
FIG. 1. Isometric view of the drift-tube ion source, and ion sampling apparatus in the Georgia Tech. drift-tube mass spectrometer.

reduced mobility. In each of the cases investigated here, the mobilities were measured to sufficiently low E/N that well-defined accurate values of the zero-field mobility could be obtained.

In accordance with the suggestion made by Huxley *et al.*,[4] the units of E/N will be denoted by the "townsend" or "Td," where 1 Td $= 10^{-17}$ V cm^2.

A detailed review of past oxygen-ion-swarm research has been made recently.[5] This review shows that many of the existing oxygen mobility data are affected by reactions of the ions with oxygen molecules or impurities, and in many of the experiments, mass spectrometric analysis of the ions was not performed. In the present research, the ions are mass analyzed, and the effects of reactions are carefully considered in the measurement and the reduction of the data.

II. APPARATUS

The drift-tube mass spectrometer apparatus employed in these measurements is essentially the same as that described by Albritton *et al.*[6] The essential internal components are shown in Fig. 1. Oxygen gas is admitted to the drift tube through a servo-controlled leak, and flows continuously from the tube through the 0.035-cm-diam exit aperture in the exit-aperture plate. The pressure in the drift tube is held constant during operation at some desired value in the range 0.02–10 Torr.

The ion source assembly shown in Fig. 1 is movable over the entire length of the drift tube, to provide 16 different values of the drift distance ranging from 1 to 44 cm. Bursts of oxygen ions are created by electron bombardment within the source, repetitively, by pulsing a beam of electrons into the ionization region from the filament assembly pictured at the left side of the source. K$^+$ ions are produced by a separate assembly mounted on the

back side of the source assembly (not shown in Fig. 1). The K$^+$ ions are emitted thermionically by a platinum-gauze filament coated with Kingman feldspar. Bursts of these ions are injected into the main part of the source by pulsing a grid arrangement, also not shown.

In the case of either K$^+$ ions or oxygen ions, a portion of the initial burst within the source assembly is gated into the drift region by a double-grid electric shutter in the ion entrance aperture, and migrates down the axis of the drift tube under the influence of a weak electric field produced by the drift-field guard rings. When the burst reaches the end of the drift tube, a sample of the ions present there is swept out through the exit aperture located on the axis. The core of the emerging jet of ions and gas molecules is cut out by the conical skimmer and allowed to pass into the rf quadrupole mass spectrometer. Ions of only one selected charge-to-mass ratio traverse the length of the spectrometer, and are then detected individually by an electron multiplier. This detector is operated as a pulse counter, and its output pulses are sorted electronically by their arrival time by a 256-channel time-of-flight analyzer. A spectrum of arrival times is built up by accumulating data from about 10^5 ion bursts for a given source position, to provide a time profile of the swarm of ions of the given species at a particular distance from the ion entrance aperture. A large number of such arrival-time spectra are obtained for different drift distances, for every ion species present in the drift tube, and for a wide range of values of E, N, and E/N.

The oxygen gas used for this work was the ultrapure grade supplied by Air Products and Chemicals, Inc., Allentown, Penn. The only impurities in this gas present to greater than 5 ppm are argon, which is present at a concentration of less than 20 ppm, and nitrogen at a concentration of less than 19 ppm. Two dry-ice and acetone traps in the gas feedline were used to remove water vapor. The gas which had gone through the traps produced no detectable impurity ions which could be attributed to impurities in the incoming gas.

III. ANALYSIS

The analysis used to reduce the data has been described in Ref. 1, and is discussed in detail in Ref. 2. For the case of an ion species formed in negligibly short bursts only in the ion source, this analysis leads to an expression describing the flux Φ of ions leaving the drift tube through the exit aperture as a function of the drift distance z and the time t:

$$\Phi(0, z, t) = \frac{Ase^{-\alpha t}}{4(\pi D_L t)^{1/2}} \left(v_d + \frac{z}{t} \right) \left[1 - \exp\left(\frac{-r_0^2}{4 D_T t}\right) \right]$$

$$\times \exp\left(\frac{-(z - v_d t)^2}{4D_L t}\right) \quad . \tag{1}$$

In Eq. (1), D_L and D_T are, respectively, the longitudinal and transverse diffusion coefficients, α is the frequency for a reaction which depletes the ion species under consideration, r_0 is the initial radius of the entering disk-shaped ion pulse, s is its initial surface density, and A is the area of the exit aperture. Comparison of the experimental arrival-time spectra with this analytical expression allows evaluation of the drift velocity and the longitudinal diffusion coefficient.

Figure 2 shows a comparison of the prediction of Eq. (1) with experimental data for nonreacting K^+ ions in oxygen. Moseley et al.[2] showed that the location of the peak is determined by the value of v_d and that the width and shape of the spectrum are determined by D_L.

As already mentioned, the analysis described here strictly applies only to the case of an ionic species that is formed only in the ion source, before the ion burst is admitted into the drift space. Of the ions investigated, only O^- and K^+ strictly obey this condition. Because of the occurrence in the drift tube of the reactions

$$O^+ + O_2 \rightarrow O_2^+ + O \quad , \tag{2}$$

$$O_2^+ + 2O_2 \rightarrow O_4^+ + O_2 \quad , \tag{3}$$

$$O_4^+ + O_2 \rightarrow O_2^+ + 2O_2 \quad , \tag{4}$$

$$O^- + O_2 \rightarrow O_2^- + O \quad , \tag{5}$$

$$O^- + 2O_2 \rightarrow O_3^- + O_2 \quad , \tag{6}$$
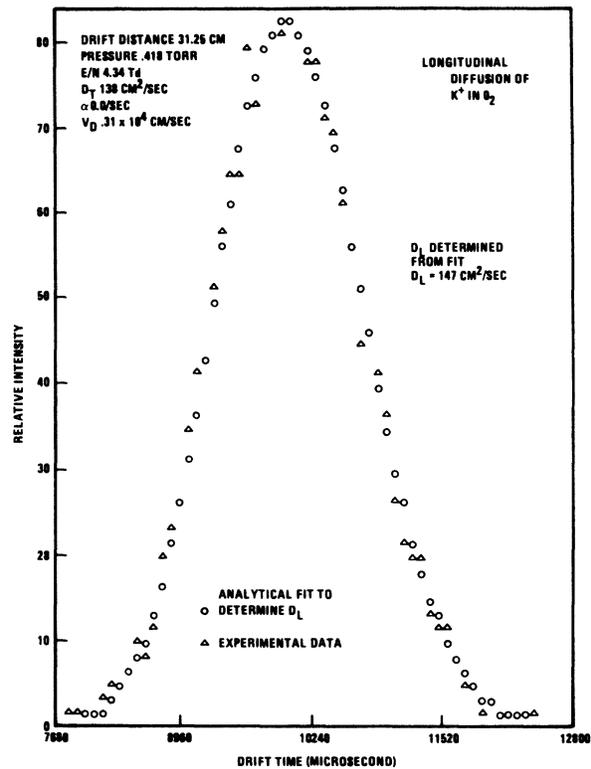
FIG. 2. Example of least-cubes fit of the analytical profile [Eq. (1)] to the experimental spectra to determine D_L.
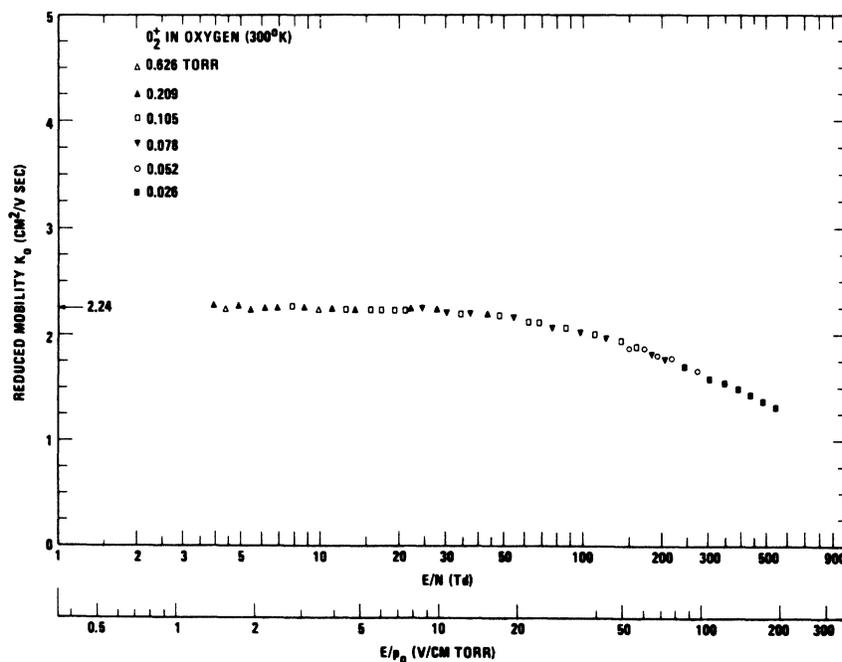
FIG. 3. Present mobility results for O_2^+ ions in oxygen at 300 °K.
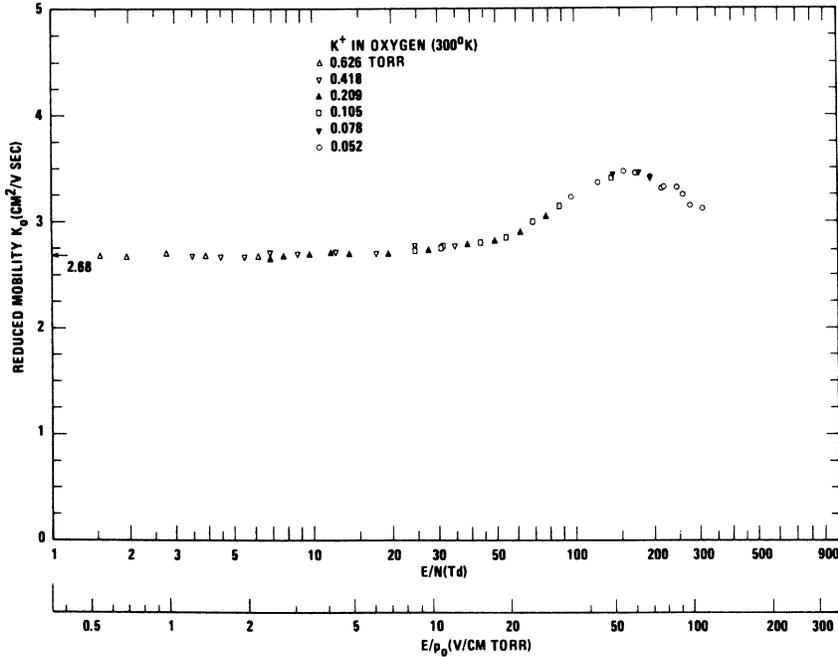
FIG. 4. Present mobility results for K^+ ions in oxygen at 300 °K.

$$O_2^- + 2O_2 \rightarrow O_4^- + O_2 \ , \tag{7}$$

$$O_3^- + CO_2 \rightarrow CO_3^- + O_2 \ , \tag{8}$$

$$O_4^- + O_2 \rightarrow O_2^- + 2O_2 \ , \tag{9}$$

$$O_4^- + CO_2 \rightarrow CO_4^- + O_2 \ , \tag{10}$$
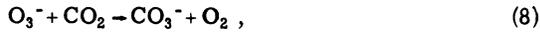
all the other investigated ions are not solely source produced. [It should be noted that reactions de-

scribed by Eqs. (8) and (10) occur because of the existence of an impurity in the drift tube. The possible source of this impurity will be discussed later.]

The relative importance of these reactions in determining the features of the arrival-time spectra is often a sensitive function of such factors as E/N, the gas number density, the drift distance, and the
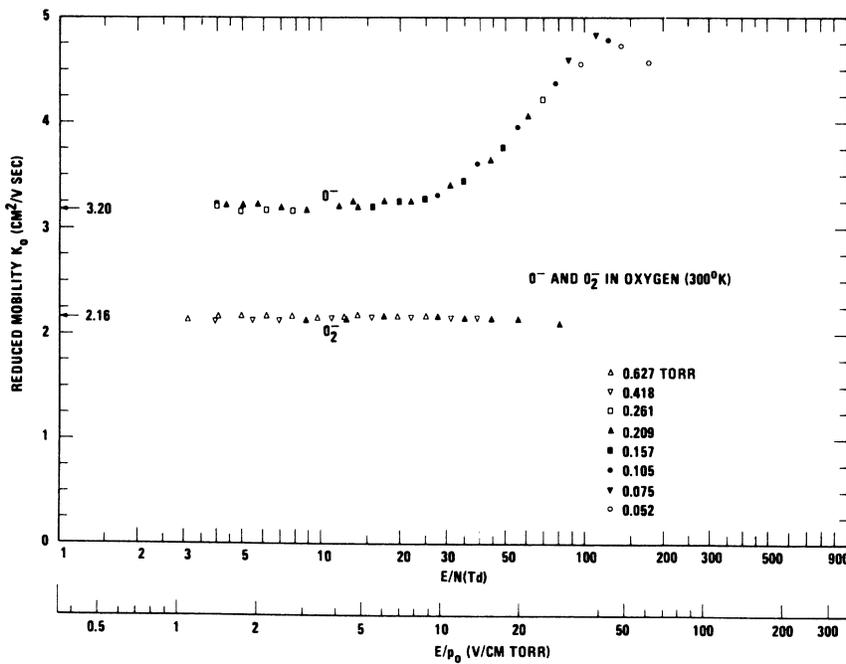
FIG. 5. Present mobility results for O^- and O_2^- ions in oxygen at 300 °K.

length of time the ion burst is "aged" in the source before it is gated into the drift space. Because these factors can be varied widely in the present experiment, it has proved possible in the case of O_2^+, O_2^-, and O_3^- to approximate closely the restriction that all of the ions of the detected species be created in the source, although sometimes over only a limited range of E/N. However, O_4^+ and O_4^- can never be considered as ions produced only in the source in the present experiment. The particulars for each ionic species are discussed in the following sections.

IV. MOBILITIES

The reduced mobilities obtained for O_2^+ and K^+ are shown in Figs. 3 and 4; those for O^-, O_2^-, and O_3^- in Figs. 5 and 6. These mobilities were determined from the mean arrival time of the ions by the method discussed in Refs. 1 and 2, using a differencing technique involving a multiplicity of ion source positions. Reference 2 showed that corrections need to be made in calculations of the drift velocity if the ion is involved in a depleting reaction. This correction can be made negligible if one can restrict the measurements to sufficiently low values of the gas pressure that the reaction frequency is small; explicit criteria discussed in Ref. 2 were satisfied in all of the measurements for these ions.

The ions O^+ and O_2^+ are the only positive oxygen ions formed by electron impact in the present experiment. Because of the large rate coefficient for reaction (2), the O^+ ion is observed in the present experiment only under conditions of high fields, low

pressures, and short drift distances. Under these conditions the ionic motion has not reached steady state, so no meaningful drift velocities can be obtained for O^+ here. O_2^+ is produced by reactions (2) and (4) as well as by electron impact in the source. In order that the O_2^+ swarm be almost entirely created in the source, all O_2^+ mobility data were taken at pressures high enough and fields low enough that reaction (2) goes to completion inside the source, and at pressures low enough and fields high enough so that extremely small amounts of O_4^+ are formed by reaction (3). Thus very little O_2^+ is formed by reaction (4).

The ions O^- and O_2^- are the only negative oxygen ions formed by electron attachment in the present experiment. O^- ions are created exclusively in the source. In order to keep the correction for the depleting reactions described by Eqs. (5) and (6) small, O^- data are obtained at low pressures. O_2^- is created by Eqs. (5) and (9) as well as in the source. The mobility measurements of O_2^- are made at low pressures so that errors due to dissociation of O_4^- should be extremely small because little O_4^- will be formed. Obtaining satisfactory O_2^- data at high E/N is made difficult by Eq. (5). This reaction results in a leading foot appearing on the O_2^- time spectra. However, deletion of the leading foot in the calculation of the mean time makes any resulting error in mobility of O_2^- small.

O_3^- ions are formed from O^- ions by the three-body reaction described by Eq. (6). By making measurements on the O_3^- ions at high pressures, it is possible to drive the reaction essentially to
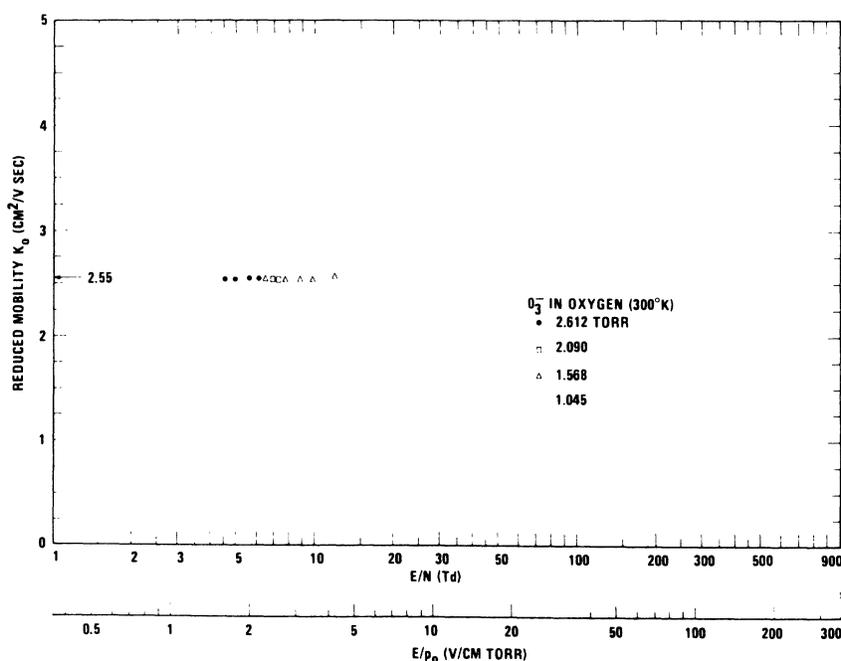
FIG. 6. Present mobility results for O_3^- ions in oxygen at 300 °K.

completion in the ion source. Thus it was possible to obtain true drift velocities for O_3^- over a restricted range of E/N, even though O_3^- ions are secondary ions formed by reactions.

O_4^+ ions are produced by the association of O_2^+ and O_2 in a three-body process described by Eq. (3). Because O_4^+ rapidly dissociates to form O_2^+ by Eq. (4), an equilibrium situation occurs which makes it impossible to consider O_4^+ as a source produced ion; thus any detected O_4^+ ion will have spent part of its drift as O_2^+. Similar remarks concerning O_4^- and O_2^- can be made in these experiments.

The mobilities of O_4^+ and O_4^- were evaluated by examining the pressure dependence of the mean arrival-time calculations. The larger the reaction frequency in Eq. (3) is in comparison to the reaction frequency in Eq. (4), the larger will be the fraction of its drift time that the detected ion has spent as O_4^+. Therefore to obtain a good value for the mobility of O_4^+, the data should be taken at as high a pressure as possible. Our upper limit on pressure for O_4^+ data is imposed by the inability of the source to produce sufficient ions to perform the experiment at pressures much above 6 Torr. Data were taken over the pressure range 3.13–6.27 Torr. The ratio of the O_4^+ detected intensity of the O_2^+ intensity was about 3/2 at 3.13 Torr and 3/1 at 6 Torr. Any pressure dependence of the mobility values is less than the scatter in the data; it is concluded that the limiting high-pressure value has therefore been reached, within the scatter of the measurements.

Similar reasoning holds for O_4^-, except that the

high-pressure limit is determined by the inability of the ion source magnetic field to prevent electrons from entering the drift region. This occurs at pressures appreciably above 4 Torr. Again the scatter in the data masks any pressure dependence of the mobility.

CO_3^- and CO_4^- are impurity ions which appear in the present experiment as the result of Eqs. (8) and (10). All mass-analyzed experiments[7-9] performed to date at pressures high enough to produce appreciable O_3^- and O_4^- have detected these impurities.

Several sources have been postulated for the CO_2 impurity involved in these reactions. The oil vapors from the diffusion pumps have been considered as a possibility, since the necessity of sampling the ions through a pinhole and of differentially pumping the analysis region might allow some oil vapors into the drift region. However, the oil vapors are not believed to be the major source of CO_2 because McKnight,[9] who uses mercury diffusion pumps, also detects these impurities. The possibility that the CO_2 is admitted with the O_2 is disallowed because the intensity of the impurities is found to be a function of the time that the gas has been left in the drift region. McKnight has been able to reduce these impurities to a negligible amount by connecting a trapped forepump directly to his drift region, so that a high gas throughout could be obtained. On the basis of this observation and similar experiences in the present investigation, it is hypothesized that the CO_2 comes from the stainless-steel walls of the vacuum system. Mobility data for CO_3^- and CO_4^- were taken at high pressures and several hours
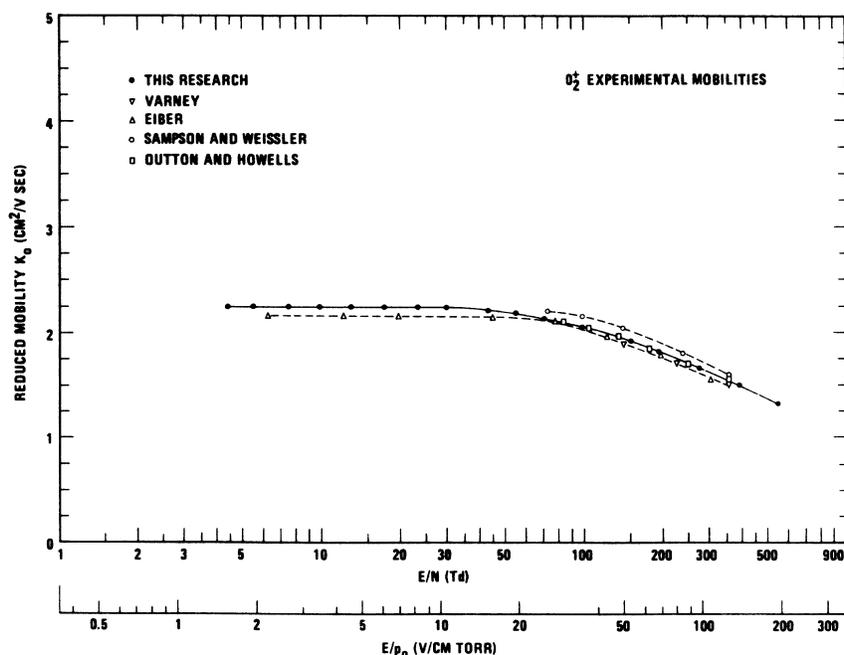
FIG. 7. Comparison of present results for mobility of O_2^+ in O_2 at 300°K with results of other experiments.
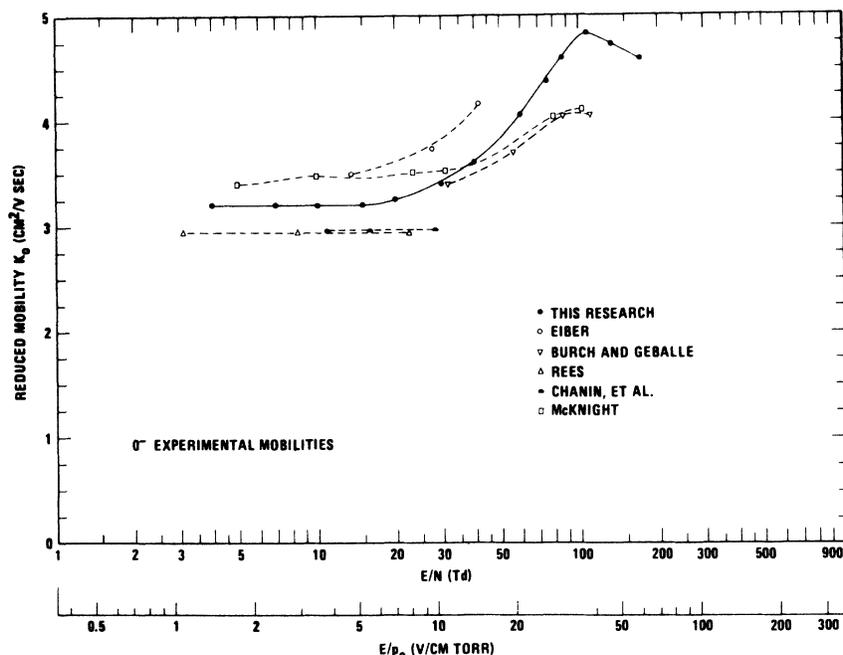
FIG. 8. Comparison of present results for mobility of O^- in O_2 at 300 °K with results of other experiments.

after the drift tube had been valved off from the pump and filled with oxygen at the desired pressure in order that the reactions described by Eqs. (8) and (10) could go to completion inside the source. These data are not plotted in this paper, but are graphed in Ref. 5.

The zero-field reduced mobilities obtained in these measurements are 2.24 cm^2/V sec for O_2^+, 3.20 for O^-, 2.16 for O_2^-, 2.55 for O_3^-, and 2.68 for K^+. The zero-field reduced mobility is found to be 2.16 cm^2/V sec for O_4^+ and 2.14 for O_4^- in O_2. Measurements made for CO_3^- and CO_4^- indicated a zero-field mobility of 2.50 cm^2/V sec for CO_3^- and 2.45 for CO_4^-. All of the zero-field mobilities quoted here are believed to be accurate to within about ±3%. A detailed error analysis is presented in Ref. 5, in which the systematic error in the pressure measurements was estimated to be ±2%. However, an improved calibration of the pressure-measuring apparatus has resulted in a reduction of this error to ±1%; the total errors quoted here are based on this revised figure.

Comparison of the data of the present experiment with the results of previous experiments in oxygen are presented in Figs. 7–10. Figure 7 gives a comparison of the O_2^+ mobility data of the present research with the results of other experiments (Varney,[10] Eiber,[11] Samson and Weissler,[12] Dutton and Howells[13]). Eiber[11] used a crude ionic mass analysis. The other investigators had no mass analysis. The agreement with all the investigators is quite good at values of E/N greater than 70 Td. The results of Samson and Weissler[12] are slightly

higher than the present data, but are well within the combined experimental errors. The present data agree well with the recent high E/N data of Fleming and Rees[14] which are not plotted here. Varney's[15] most recent results, which are also not plotted here, are about 8% above those of the present research.

At E/N less than 30 Td the present result for O_2^+ is 5% above the low E/N data of Eiber. However, Eiber's measurements were made at pressures of 10 to 340 Torr. At these pressures, a detected O_2^+ ion would have spent most of its drift time as O_4^+. Therefore, Eiber's low E/N mobility data are more appropriately assigned to O_4^+. The data of Eiber give a zero-field reduced mobility of 2.15 cm^2/V sec, which is in good agreement with the O_4^+ mobility value of the present research.

There are no mass-analyzed O_4^+ mobility data available from other experiments. Fleming and Rees[14] and Dutton and Howells[13] deduced the presence of a second positive ion species in oxygen from the pressure dependence of their drift velocities. Fleming and Rees found a value of 2.20 cm^2/V sec for the zero-field mobility of O_4^+, which was slightly above their O_2^+ result. Dutton and Howells obtained a value of 2.15 cm^2/V sec for O_4^+ which was also slightly higher than their O_2^+ result. The present data indicate that the O_4^+ mobility at low E/N (less than 7 Td) is less than the O_2^+ mobility. The present results may not be in conflict with the above experiments because the regions of E/N do not overlap.

Figure 8 shows comparisons between the present

O^- mobility data and the data of other experiments. The agreement is fair. McKnight[9] obtained results which are about 7% above the present low E/N results, but the scatter of his data overlaps the present data. His data are the only published values which were obtained with high-resolution mass analysis. The data of Eiber are about 10% above the present results. The data of Burch and Geballe[16] are in good agreement at their lowest E/N of 40 Td. However, the disagreement increases as E/N increases and is about 20% at an E/N of 100 Td. The data of Chanin et al.[17] and those of Rees[18] are about 7% below those of the present experiment, but at the pressures and the drift distances used in each of those investigations, all the O^- ions should have been converted to O_3^-. Their data may refer to an impurity.

The results of several investigators are not shown in Fig. 8, but comparisons may be made with them. Varney's[15] recently published O^- mass-analyzed data are almost 100% above those of this research. The data of Nielsen and Bradbury,[19] which were labeled O_2^-, are in fair agreement with the O^- data of this research and probably should be assigned to O^- rather than O_2^-. Shafer and Beaty[7] reported mass-analyzed mobility data for O^- which are in fair agreement with the results of this research.

The comparison of the O_2^- mobility data of the present experiment with the results of other experiments is shown in Fig. 9. Agreement is good with all investigators except Rees. The data of Rees[18] were taken at pressures high enough that the detected ions should be spending most of their time as O_4^-.

Also his data may be affected by the presence of CO_2, which converts O_4^- to CO_4^-. The results of two mass-analyzed experiments are not shown. Varney's[15] data are about 12% above those of the present research. The unpublished data of Shafer and Beaty[7] are in good agreement.

Figure 10 shows a comparison of the present O_3^- mobility data with those of other experiments. Unfortunately the present O_3^- data extend over only the E/N range 4.6–14.7 Td. Our data are in good agreement with the low E/N data of Eiber,[11] McKnight,[9] and Rees.[18] Data of Chanin et al.,[17] which were labeled O_2^-, are about 8% above the O_3^- data of the present experiment. Comparisons may also be made with the data of several investigators not shown in Fig. 10. The data of McDaniel and Crane,[20] which were labeled as O_3^-, are in fair agreement with the present O_3^- data. The results of Voshall et al.,[21] which were labeled O_2^-, are also in fair agreement. On the basis of the agreement of the present O_3^- data with the data of Doehring,[22] it can be deduced that his data could be assigned to O_3^-. The unpublished data of Shafer and Beaty[7] are in good agreement with the present results. It should be noted that the possibility of the presence of variable amounts of CO_3^- in non-mass-analyzed experiments may have caused the scatter that is observed in the mobility values in Fig. 10.

McKnight[9] and Shafer and Beaty[7] in mass-analyzed experiments found that O_4^- had a mobility very similar to O_2^-, in agreement with our conclusions. Rees[18] obtained data for an ion which had a zero-field mobility of 2.18. He labeled the ion an im-
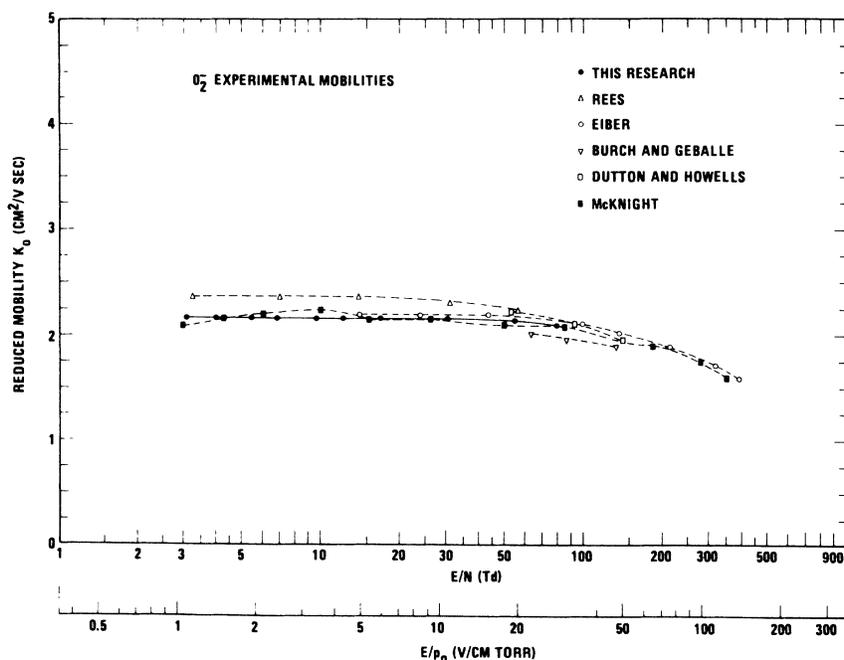
FIG. 9. Comparison of present results for mobility of O_2^- in O_2 at 300 °K with results of other experiments.
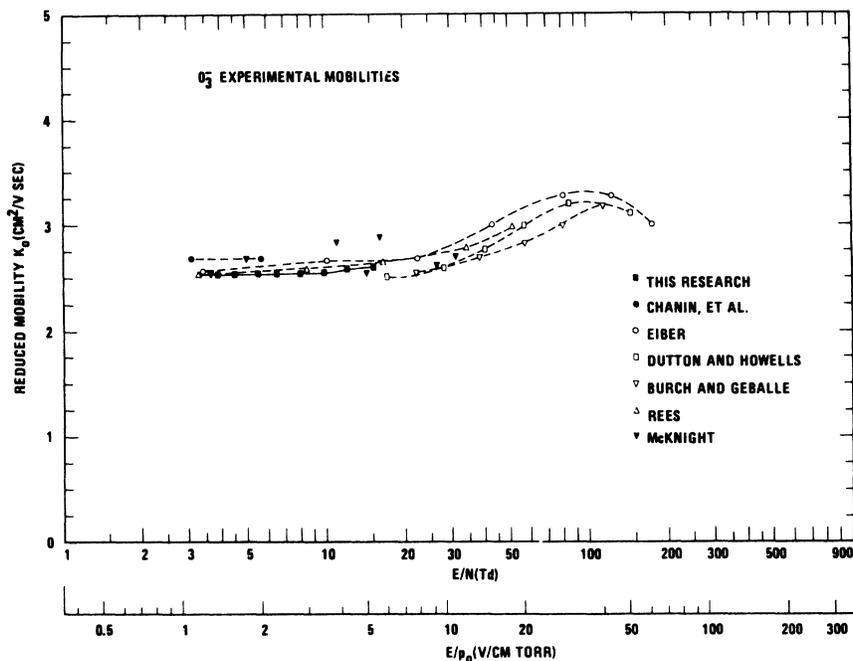
FIG. 10. Comparison of present results for mobility of O_3^- in O_2 at 300 °K with results of other experiments.

purity, but it may have been O_4^-. Eiber's O_2^- data[11] are also in agreement with the O_2^- results of the present experiment. However, this agreement is in part fortuitous, since some of his data were taken at pressures high enough that the detected ions must have spent most of their drift time as O_4^-.

V. LONGITUDINAL DIFFUSION COEFFICIENTS

Reference 2 shows that the computed shape of the

time profile of the parent species is relatively insensitive to the values used for the depleting reaction frequencies and the transverse diffusion coefficient. It was shown that the transverse diffusion coefficient could be varied from $0.01D_L$ to $10D_L$, and that the depletion reaction frequency could be varied from zero up to 10^6 sec^{-1} without distorting the shape of the computed time spectra.
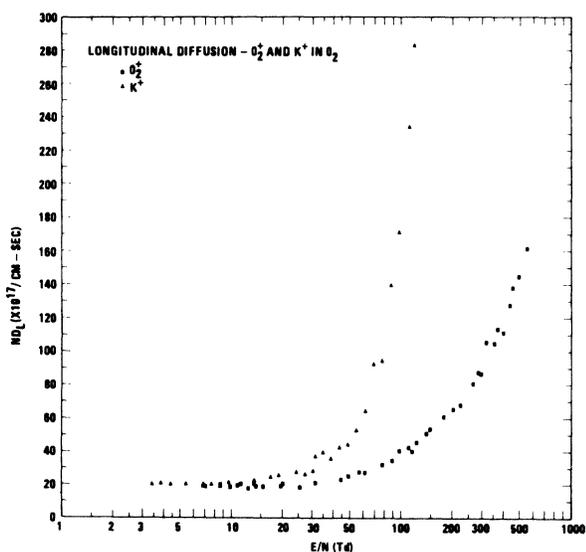
FIG. 11. Present results on longitudinal diffusion for O_2^+ and K^+ ions in oxygen at 300 °K. N is the gas number density and D_L is the longitudinal diffusion coefficient.
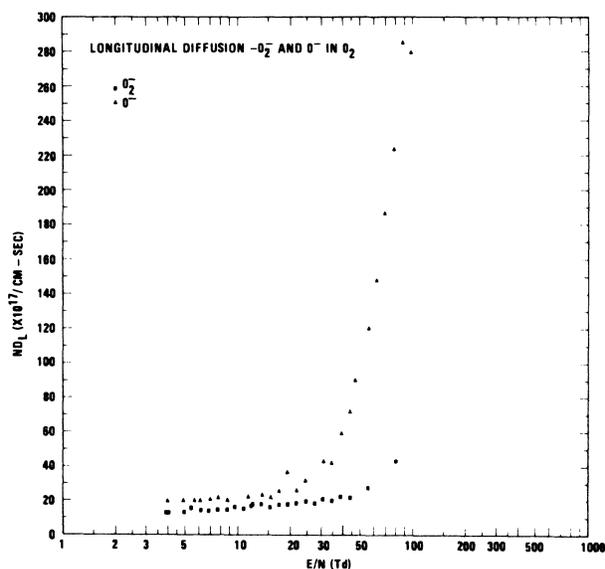
FIG. 12. Present results on longitudinal diffusion for O^- and O_2^- ions in oxygen at 300 °K. N is the gas number density and D_L is the longitudinal diffusion coefficient.

The fitting technique used to determine D_L involved an initial normalization of a theoretical spectrum generated by Eq. (1) to the experimental data, so that they agree at their peak intensity values. Because the theoretical spectrum contains no allowance for end effects (such as the time required for the ions to travel from the drift-tube exit aperture to the detector), the peak of the experimental spectrum is shifted so as to be aligned in time with the peak of the theoretical spectrum. A least-cubes fit of the theoretical spectrum to an experimental spectrum is now performed by varying D_L in Eq. (1). If the difference between the two spectra on one side of the peak is of opposite sign as compared to the difference on the other side of the peak, a shift in the spectrum should produce a better fit. The experimental spectrum is shifted one channel at a time until the differences are either of the same sign or a shift produces no improvement. In calculating the theoretical spectrum, v_d is taken to be known from the previous mobility measurements, α is taken to be zero, and D_T is calculated from v_d by the Einstein expression.

Longitudinal diffusion coefficients were determined for O_2^+, K^+, O_2^-, and O^- ions in O_2 over a wide range of drift-tube pressures, drift distances, and E/N values. The results for O_2^+ and K^+ are shown in Fig. 11. Figure 12 shows the results for O^- and O_2^- ions. Since $D_L \sim 1/N$, the results are expressed as the product ND_L versus E/N. Note that for all four ions D_L appears to approach some limiting value at low E/N, and is relatively constant below an E/N of 20 Td.

The values of ND_L predicted from the zero-field mobilities by the Einstein relation are as follows: O_2^+, 15.6×10^{17}/cm sec; K^+, 18.6; O_2^-, 14.9; O^-, 22.1. The low-field values of ND_L determined from fitting the experimental data with Eq. (1) are as follows: O_2^+, 18.6×10^{17}/cm sec; K^+, 20.3; O_2^-, 14.2; O^-, 20.2. The agreement between the low E/N ND_L values which were calculated from the mobility values and those determined by the curve-fitting technique is reasonably good. The estimated uncertainties in the longitudinal diffusion coefficient

TABLE I. Zero-field reduced mobilities of ions in O_2 at 300 °K, in cm^2/V sec.

Ion	Mobility, K_0
O_2^+	2.24 ± 0.07
O_4^+	2.16 ± 0.08
O^-	3.20 ± 0.09
O_2^-	2.16 ± 0.07
O_3^-	2.55 ± 0.08
O_4^-	2.14 ± 0.08
K^+	2.68 ± 0.07
CO_3^-	2.50 ± 0.07
CO_4^-	2.45 ± 0.07

data at low E/N are $(+12, -28)\%$ for O_2^+; $(+12, -20)\%$ for K^+; $(+17, -12)\%$ for O_2^-; and $(+20, -12)\%$ for O^-.

Examination of Figs. 11 and 12 at E/N above 30 Td shows that as E/N increases, D_L increases in each case, but it increases much more rapidly for O^- and K^+ than it does for O_2^+ and O_2^-. This weaker dependence on E/N for the O_2^+ and O_2^- values of D_L might be attributed to the fact that resonant charge transfer is an important part of the total scattering interaction for these ions in O_2. A similar relatively weak dependence of D_L on E/N has previously been observed for N_2^+ ions in N_2.[23]

No longitudinal diffusion coefficients are presented for O_3^-, O_4^-, and O_4^+. Most of the data taken for these ions severely violate the condition that all the ions be entirely source produced.

VI. CONCLUSIONS

The zero-field reduced mobilities obtained in this research are displayed in Table I. The longitudinal diffusion coefficients for O_2^+, K^+, O^-, and O_2^- were measured on the E/N range from thermal values to several hundred townsends. At low E/N, the longitudinal diffusion coefficients for all the ions investigated agreed within at least 16% with the values predicted from the zero-field mobilities by use of the Einstein expression. At higher E/N the coefficients increased, in some cases quite rapidly, as E/N was increased.

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Ion-Molecule Reactions between O⁻ and O₂ at Thermal Energies and Above [*][†]

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The rate coefficients for the reactions of O^- ions with O_2 molecules have been measured in a drift-tube mass spectrometer at 300 °K as a function of E/N, the ratio of the electric drift field to the gas number density. Two different measurement techniques were employed. One technique was based on the observation of the attenuation of the parent O^- ion species with increasing drift distance; the other involved examination of the shape of the product ion arrival-time spectra. The rate coefficient for the reaction $O^- + 2O_2 \rightarrow O_3^- + O_2$ was measured on the E/N range $6-29 \times 10^{-17}$ V cm². The rate coefficient was found to be $(1.0 \pm 0.2) \times 10^{-30}$ cm⁶/sec over the entire E/N range. The reaction $O^- + O_2 \rightarrow O_2^- + O$ was observed with a rate that increased sharply with E/N. The rate coefficient was found to increase from $(2.5 \pm 1.5) \times 10^{-14}$ cm³/sec at an E/N of 63×10^{-17} V cm² to a value of $(3.4 \pm 1.0) \times 10^{-12}$ cm³/sec at an E/N of 140×10^{-17} V/cm².

I. INTRODUCTION

The results of a study of the reactions of low-energy O^- ions in oxygen gas are presented in this paper. A drift-tube mass spectrometer was used to obtain the data. The rate coefficients for the ion-molecule reactions

$$O^- + 2O_2 \rightarrow O_3^- + O_2 \ , \tag{1}$$

$$O^- + O_2 \rightarrow O_2^- + O \tag{2}$$

have been evaluated at 300 °K as a function of E/N, the parameter which determines the energy acquired by the ions from the electric drift field E at gas number density N. In accordance with the suggestion made by Huxley *et al.*,[1] the units of E/N will be denoted by the "townsend" or "Td," where 1 Td $= 10^{-17}$ V cm². A brief historical sketch of O^- reaction research has been published recently,[2] and a detailed review has also been prepared.[3]

The drift-tube mass spectrometer apparatus employed has been described briefly in the preceding paper[4] (hereafter called I) and in detail elsewhere.[5]

It will suffice here to state that the data it provides take the form of high-resolution time profiles of ion swarms as they drift in an electric field past a fixed sampling point. The sampling involves a mass selector, so that separate profiles or "arrival-time spectra" are obtained for each distinct molecular species of ions present in the swarm. An important and unique feature of the apparatus is a movable ion source permitting the drift distance (the distance between the point at which ions are introduced and the point at which they are sampled) to be varied over the range 1–44 cm.

The positions, intensities, detailed shapes of these profiles, and the manner in which these quantities vary with the drift distance and the gas number density N, evidently depend on the mobilities and diffusion coefficients of the ions, and on the rates of ion-molecule reactions which create or destroy ions of a given species. Methods of analyzing the profile data to evaluate mobilities and diffusion coefficients have been described previously[5–7]; I presents results obtained by these methods for the mobilities