Drift Velocity of Ions in Oxygen, Nitrogen, and Carbon Monoxide

ROBERT N. VARNEY*

Bell Telephone Laboratories, Murray Hill, New Jersey

(Received October 17, 1952)

The drift velocities of ions of the parent gas in oxygen, nitrogen, and carbon monoxide have been measured as a function of field strength to pressure ratio by techniques previously reported. Oxygen gave results similar to those in the rare gases reported previously. A log-log plot of drift velocity against E/p_0 in volts/ (cm×mm Hg) starts with a slope near unity which gradually decreases to one-half at high values of E/p_0. The mobility, extrapolated to zero field and atmospheric pressure is 2.25 cm²/volt-sec. Nitrogen and carbon monoxide both show a novel characteristic; the drift velocity first rises with E/p_0 but reaches a maximum and actually decreases, then finally resumes a more normal rise with E/p_0 as described for oxygen. It is believed that at high E/p_0 the drift velocity is characteristic of N_2^+ ions and CO^+ ions, respectively. At low fields the ion in nitrogen is believed to be N_4^+. In CO the ion at low fields is believed to be CO^+, with $(CO)_2^+$ being formed at intermediate fields. The results are complicated by an additional ion which appears in the range of E/p_0 from 95 to 250 and which has a higher speed than the other ion. It is suspected of being C^+.

INTRODUCTION

THE apparatus for the present work has been described in detail in reference 1 and has been used previously to measure drift velocities of ions in the rare gases.[1,2] Briefly summarized, a field is applied between parallel-plate electrodes, and a pulse of electrons is released from the cathode by the radiation from an external spark of short duration. A typical Townsend avalanche results, and an exponential distribution of positive ions is left between the plates. The time needed (2 to 20 microseconds) to sweep out these ions is measured. The result, combined with the measured plate separation, yields the drift velocity.

The tube is thoroughly degassed until residual pressure readings are below 5×10^{-9} mm Hg, and highly purified gas from commercially available flasks (Airco) is then admitted. Liquid nitrogen cooling is continu-ously maintained on a connected trap. Pressures are read on a calibrated McLeod gauge.

The drift velocity is then plotted against E/p_0, the ratio of field strength to pressure, in a log-log form. The symbol p_0 is used to indicate that pressure readings are reduced to the corresponding value for 0°C. Also plotted is a graph of the mobility, defined as

$$\mu = (v \times p_0)/(760 \times E),$$

as a function of E/p_0. At each value of E/p_0, readings of the velocity are taken with several values of p_0 spread over a range of a factor of 2, and with several values of X, the plate separation, spread over a range of a factor of 3. No significant changes in velocity are observed except as a function of E/p_0.

RESULTS

Figure 1 is the drift velocity plot for pure oxygen. It is seen to approach a slope of one-half at high E/p_0 and unity at low E/p_0 in accordance with the theory given by Wannier.[3] The slope of one-half is characteristic of a repulsive force field of fixed radius surrounding the gas molecules, hence frequently described as hard-sphere repulsion. The slope of unity at low E/p_0 leads
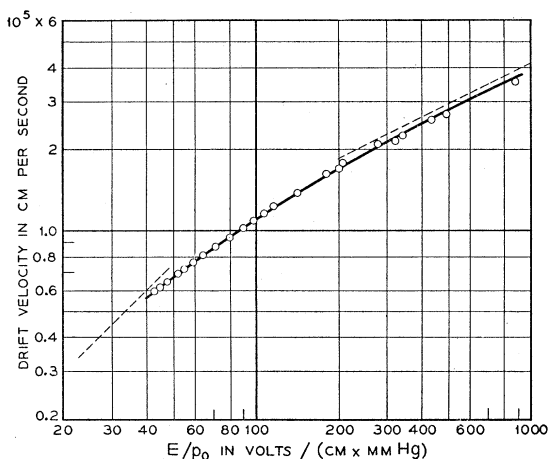

FIG. 1. Log-log plot of drift velocity of ions in oxygen vs E/p_0. The dashed lines are drawn at slopes of one-half and one, respectively.
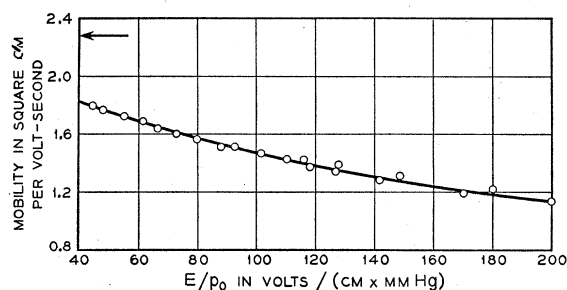

FIG. 2. Mobility of ions in oxygen plotted against E/p_0. The arrow at the left indicates an approximate extrapolated value for E/p_0 of zero. The arrow is at $\mu = 2.30$ cm²/volt-sec, although any value between 2.15 and 2.35 is reasonably suitable.

* Now at Washington University, St. Louis, Missouri.
[1] J. A. Hornbeck, Phys. Rev. 83, 374 (1951); 84, 615 (1952).
[2] R. N. Varney, Phys. Rev. 88, 362 (1952).
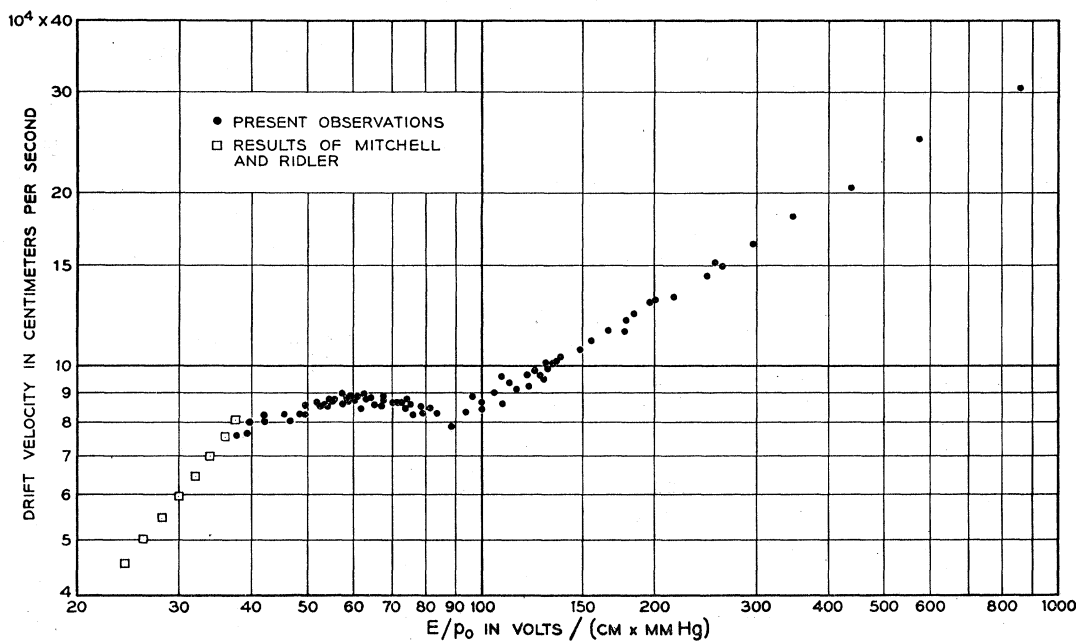
[3] G. H. Wannier, Phys. Rev. 83, 281 (1951).

FIG. 3. Log-log plot of drift velocity of ions in nitrogen vs E/p_0. Actual points are shown to indicate the precision of observations. Mitchell and Ridler's results at low E/p_0, adjusted by the writer from 20°C to 0°C, are shown. It is proposed that at low E/p_0 the ions are largely N_4^+, at high E/p_0 they are N_2^+, and in the intermediate region each ion changes many times from N_2^+ to N_4^+ and back.

to the constant mobility characteristic of all ions in this range. Figure 2 shows the mobility vs E/p_0 for oxygen. The extrapolated mobility for E/p_0 of zero is estimated at 2.25±0.1 cm²/volt-sec. Both Figs. 1 and 2 are similar to typical results in the rare gases.

The drift velocities of ions in nitrogen and in carbon monoxide are shown in Figs. 3 and 4, plotted logarithmically as before against E/p_0. Both graphs differ notably from the oxygen result in that after a preliminary rise in drift velocity with E/p_0, the velocity drops by several percent as E/p_0 grows. Finally, after an appreciable further increase in E/p_0, the drift velocity resumes a more uniform growth with E/p_0 at a rate approaching a slope of one-half on the log-log plot. The anomalous region of decreasing velocity with increasing E/p_0 ranges from E/p_0 of 60 to 88 in nitrogen and 100 to 150 in carbon monoxide. In nitrogen, however,the lower bound of abnormal behavior might be set as low as E/p_0 of 38 upon consideration of the mobility vs E/p_0 plot in Fig. 5. The limits in carbon monoxide may be regarded as extending from E/p_0 of 90 to 170 if the criterion for abnormal behavior is that the log velocity vs logE/p_0 curve has a slope of less than one-half.

In carbon monoxide, an additional ion appears in the range of E/p_0 from approximately 95 to 250. The pattern on the oscilloscope characteristic of this second and faster ion is considerably less sharp in form. Hence it is likely that this type of ion is not formed by the initial electron avalanche within the very short time interval of its duration, but rather is formed as a by-

product of the other ions as they are swept out by the applied field. The drift velocity is correspondingly less clearly readable, and the scatter of points in Fig. 4 for the fast ion is a consequence. No similar ion is found in nitrogen.

The mobility vs E/p_0 curves for nitrogen and carbon monoxide are shown in Figs. 5 and 6. The curve for nitrogen is seen to join with that of Mitchell and Ridler.[4] (Mitchell and Ridler's results are presumed to refer to a temperature of 20°C and their pressures have been adjusted to 0°C both in E/p and μ.) The curve
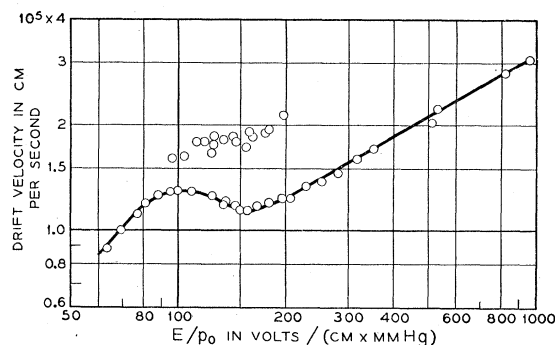

FIG. 4. Log-log plot of drift velocity of ions in carbon monoxide vs E/p_0. A second ion with higher velocity appears at values of E/p_0 between 95 and 250 volts/(cm×mm Hg). Since its oscilloscope pattern is less sharp, this drift velocity is less certain. Judgment errors in the case of the faster ion probably tend to give too low a velocity reading.

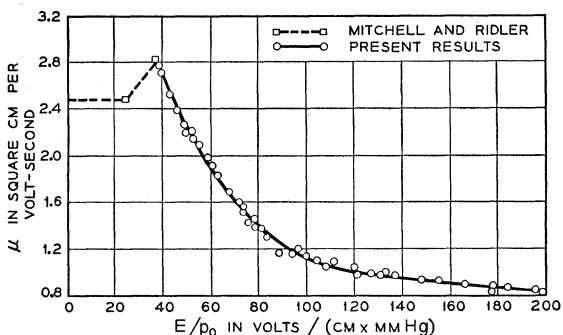[4] J. H. Mitchell and K. E. W. Ridler, Proc. Roy. Soc. (London) 146, 911 (1934).

FIG. 5. Mobility of ions in nitrogen as a function of E/p_0. The present results join suitably with the older observations of Mitchell and Ridler at low E/p_0. Their results have been adjusted from 20°C to 0°C for this plot.

for carbon monoxide suggests a very much lower mobility at E/p_0 of zero for ions in this gas than for ions in nitrogen. The significance of this observation is discussed at a later point.

ANALYSIS OF RESULTS

By use of a previously established equation derived by Hornbeck and Wannier,[5] the molecular cross sections for the ions at high E/p_0 values are obtained shown in Table I. The low value for oxygen indicates that charge exchange occurs less readily in this gas than in N_2, CO, or A (from reference 1), a result that is not altogether surprising for oxygen because of its known electron affinity. The values for N_2 and CO are more nearly comparable with values for Ne and A.

The Langevin formula may be applied to predict zero field mobilities in these gases if several assumptions are made. The first assumption concerns the chemical formula of the ion; the second concerns the nature of the ion-molecule force interaction. In this paper, only two force laws will be considered. On the one hand, only attractive polarization forces may be used if the hard sphere repulsion is assumed to be negligible. On the other hand, the repulsive forces may be included by using the hard sphere radius obtained from Table I. The results are shown in Table II. (It was pointed out in references 2 and 5 that the repulsive forces treated in this way include the action of charge exchange.)

Examination of Table II and of the various drift velocity and mobility curves suggests certain possible explanations for the present results.

In oxygen, it is difficult to believe that any ion other than O_2^+ is present despite the poor agreement in mobility values shown in the table. The appearance potential[6] for O^+ in O_2 demands that electrons have 6 to 8 ev more energy to produce this ion than to give O_2^+. Such ions as O_3^+ and O_4^+ have been omitted from the table since they were not observed in the mass spectroscope by Luhr[7] with basic experimental conditions equivalent to the present ones.

Consider next the results obtained with nitrogen. The drift velocity curve (see Fig. 3) may be divided into three parts which will be referred to here as regions of high, intermediate, and low E/p_0. The two extremes are each reasonably similar, as far as they go, to curves obtained for single types of ions in the rare gases, but since the two sections are only connected by the decidedly unusual intermediate section which has a negative slope, it may be judged that a different ion exists at high fields than at low fields. In the intermediate region, a transition from one type of ion to the other must be occurring.

If the high field and the low field sections of the curve are each extended as might be guessed from comparison with rare gas curves, the high field section is seen to lie at lower velocity values than the low field section. This gives a first clue to the nature of the ions since it is reasonably well established that the slowest ion in a gas is the one which will exchange charge most readily with the gas molecules. Charge exchange always occurs with maximum cross section in any gas for the ion which becomes the normal gas molecule after exchange, in this case N_2^+;[8] in fact at the low energies involved, charge exchange occurs only for this case. Hence the ion at high E/p_0 is believed to be N_2^+.

The ion at low E/p_0 values is not likely to be N^+ since considerably more energy is needed to produce N^+ from N_2 than to give N_2^+. It is more probable that it is N_4^+, produced by attachment of N_2 gas molecules to the N_2^+ ions formed in the initial electron avalanche. Such attachment has been observed by Luhr[7] and the ions identified in the mass spectrograph.

It remains to explain the presence of only one observed velocity, especially through the transition region. The mechanism invoked is the reversible reaction system
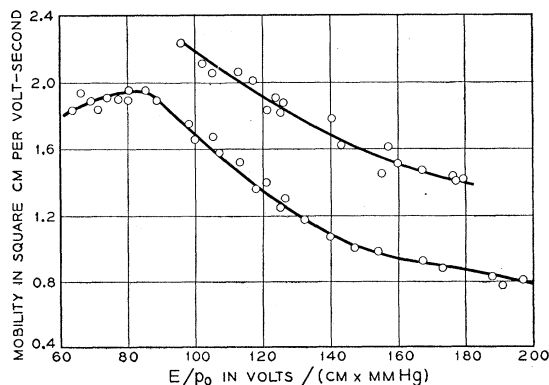
$$N_2^+ + N_2 \rightarrow N_4^+, \quad N_4^+ + N_2 \rightarrow N_2^+ + 2N_2.$$

FIG. 6. Mobility of ions in carbon monoxide as a function of E/p_0. The mobility fails to show the very great increase with decreasing E/p_0 seen in Fig. 5 in nitrogen. The behavior of CO may thus be compared with that of N_2 only in the high field regime. The upper curve is for the faster ions suspected of being C^+ and observed only in a limited range of E/p_0 values.

[5] J. A. Hornbeck and G. H. Wannier, Phys. Rev. **82**, 458 (1951).
[6] H. D. Hagstrum, Revs. Modern Phys. **23**, 185 (1951).
[7] O. Luhr, Phys. Rev. **44**, 459 (1933).

[8] See, for example, H. Kallmann and B. Rosen, Z. Physik **61**, 332 (1930).

At low E/p_0, the reaction proceeds in the direction of the first equation by attachment, and detachment is much slower. At high E/p_0, N_4^+ might not even form, but any N_4^+ ions so formed break up rapidly by collision according to the second equation, which is now dominant. The necessary and sufficient condition that only one drift velocity be observed is that the mean free path for at least one of the above reactions be much less than the drift space. That is, at low E/p_0, the free path for the reaction $N_2^+ \rightarrow N_4^+$ is short, and at high E/p_0, the free path $N_4^+ \rightarrow N_2^+$ is short. In the intermediate region, each ion undergoes a long series of attachments and detachments giving, as a result, the average single observed velocity. If the interchanges were too infrequent, a measurable spread in drift velocity would be observed, because of the arrival of ions at the cathode with various histories. There are in fact some 10^4 collision free paths between the electrodes, so that if the attachment or detachment occurred only in one collision out of every 100 to 500, the spread in arrival times would be less than about 10 percent, and hence unobservable (a slight spread amounting to 10 percent is always present because of diffusion and pulse width).

TABLE I. Molecular cross sections of O_2, N_2, and CO at high E/p_0.

Molecule	Cross section
O_2	0.79×10^{-14} cm^2
N_2	1.23
CO	1.45

In carbon monoxide, a similar analysis is applicable. At high fields, the ion is probably CO^+ since in CO gas this ion should have the largest charge exchange cross section and the smallest drift velocity. It may be noted that at high E/p_0 the CO and the N_2 drift velocity curves are nearly superposable. Since CO and N_2 bear many chemical and electronic resemblances to one another, it may be assumed that the nearly corresponding drift velocity curves indicate corresponding ions. Hence, the assumptions of N_2^+ ions and CO^+ ions at high E/p_0 mutually support one another.

At low E/p_0 the drift velocity curve in CO falls appreciably below the curve in nitrogen; in fact it may even be possible that the low E/p_0 region coincides with an extrapolation of the observed curve at high E/p_0. Finally, the low mobility in CO at low E/p_0 and the agreement of the zero field mobility seen in Table II combine to suggest that CO^+ is also the ion present in the low E/p_0 regime.

The transition region in CO, if it is to bear any relationship to the experimentally similar one in nitrogen, must then be governed by the attachment-

TABLE II. Calculated and experimental zero-field mobilities of ions in O_2, N_2, and CO.

Gas	Assumed ion	Mobility without repulsive force	Mobility with repulsive force	Experimental mobility at zero field
O_2	O^+	3.37	...	
O_2	O_2^+	2.75	2.78	2.25[a]
N_2	N^+	3.42	...	
N_2	N_2^+	2.80	2.17	
N_2	N_3^+	2.55	...	2.49[b]
N_2	N_4^+	2.42	...	
CO	CO^+	2.19	1.58	
	$(CO)_2^+$	1.89	...	
	CO_2^+	1.93	...	1.6[a]
	C^+	2.82	...	

[a] Extrapolated from present data.
[b] From Mitchell and Ridler (reference 4).

detachment reactions

$$CO^+ + CO \rightarrow (CO)_2^+, \quad (CO)_2^+ + CO \rightarrow CO^+ + 2CO,$$
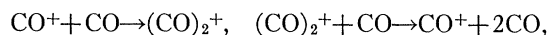
with the added provision that the first reaction occurs most favorably at an E/p_0 value above zero with the reverse reaction favored by a still higher E/p_0 value. Finally, since still another ion is observed but only in the intermediate E/p_0 band where this presence of $(CO)_2^+$ ions is likely, an irreversible disruption of this ion following the equation

$$(CO)_2^+ \rightarrow C^+ + CO_2$$
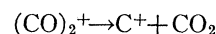
is suggested. There is evidence of deposition of carbon on the cathode and of accumulation of CO_2 in the liquid nitrogen trap. It must be emphasized that the scope of possibilities in carbon monoxide is considerably greater than in nitrogen rendering the present hypothesis notably more speculative.

CONCLUSION

The drift velocity curves in nitrogen and carbon monoxide have disclosed a definitely new and unexpected behavior of ions in these gases. The observations may have far reaching influence on the analysis of other observations, covering glow phenomena, afterglow, and catalysis. The hypotheses advanced to explain the observations must await further mass spectrographic studies for their confirmation but seem at the moment to offer the only reasonable ones.