

Measurements of the Mobilities of the Negative Ions in Oxygen and in Mixtures of Oxygen with the Noble Gases, Hydrogen, Nitrogen, and Carbon Dioxide*

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The mobility constants for oxygen negative ions in He, Ne, Ar, Kr, Xe, H₂, N₂, and CO₂, each containing various partial pressures of O₂ were measured, and extrapolations to zero partial pressure of O₂ were obtained. A measurement of the mobility of the negative ion in 100% oxygen was also made. The value found for the latter was 2.46 ± 0.05 cm²/v-sec at STP. It was shown that the mobility values referred to a single species of oxygen ion, but the question as to whether it was O₂⁻ or O₃⁻ was not resolved. A time-of-flight method was used, in which the ions were made by the passage of alpha particles through the gas, and detected by a proportional counter.

INTRODUCTION

KNOWLEDGE about the mobilities and other properties of negative ions is of increasing practical importance. In ionization chambers and gas counters, negative ions play an important role in causing delayed and spurious counts, and this is of particular concern in the many new applications of counters in which it is necessary to use counter gases other than the standard ones. In high-voltage switches, Van de Graaff machines and many other kinds of high-voltage apparatus, negative ion formation plays a vital role in immobilizing the free electrons and thus quenching the incipient breakdown. There are a number of molecules, notably SF₆, SO₂, and O₂, which have extremely large cross sections for the capture of low-energy electrons. Strong effects can be caused by these molecules when they exist in small concentration in other gases. For this reason, much of the practical interest in negative ions centers in their mobilities, cross sections for formation, clustering, and other properties when they result from trace impurities or additives in other gases.

Negative ions have received far less attention, experimentally, than have positive ions, partly, perhaps, because there are relatively few negative ion-forming molecules, and partly because it is generally more difficult to contrive experiments which can be interpreted clearly.

Our interest in the subject of negative ion mobilities in foreign gases began, some years ago, as a result of trying to understand the behavior of a CO₂-filled Geiger counter. The practical object of the study was the low-level assay of C¹⁴ in the form of C¹⁴O₂ for archaeological dating. The CO₂-filled counter was sur-

rounded by a ring of anticoincidence counters for the purpose of rejecting meson counts, as is standard practice. It was found that such an arrangement could be adapted to the observation of counts caused by attached electrons, in the following way. A synchroscope was connected so that its horizontal sweep was triggered by counts in the anticoincidence ring, and the counts in the inner, CO₂ counter were displayed as vertical pips. Many of the sweeps showed a delay in the firing of the inner counter, measured from the time of firing of the anticoincidence ring, ranging up to several msec. The delayed counts could easily be identified, by an order of magnitude calculation of the drift time, as those caused by the arrival of negative ions at the counter anode. When ordinary tank CO₂ was used, about 50% of the counts were so delayed. When purified CO₂ was used, the proportion of delayed counts dropped to less than 5%. Thus there was little doubt that the negative ions were those formed from impurities in the CO₂.

The great prevalence of delayed counts in counters filled with CO₂ was at first difficult to understand. It now seems clear that the reason lies in the very low

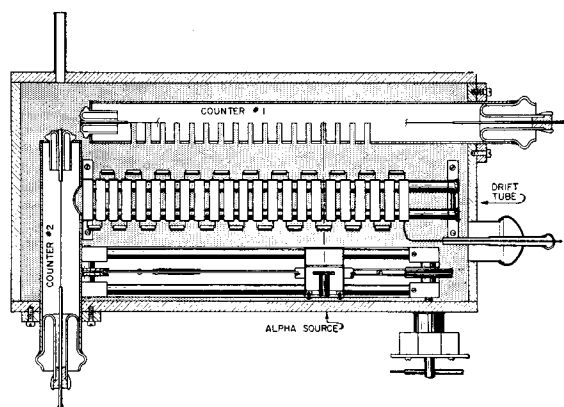


FIG. 1. Cross section through the mobility chamber, showing the ion drift tube, the alpha-particle source which is movable on a track, and the two proportional counter tubes.

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agitation energy that the electrons have in CO_2 , due to inelastic collisions. At the low agitation energy the cross section for attachment to O_2 and certain other electronegative impurities is very large. DeVries¹ has shown that one part in a million of O_2 in a CO_2 -filled counter produces an easily observable number of delayed counts. No such extreme sensitivity to impurities is found in counters filled with the noble gases. The electron agitation energy is much higher in the noble gases than it is in CO_2 , so presumably this accounts, in part at least, for the greater tolerance that noble gas counters have for electronegative impurities.

After finding that we could easily make approximate measurements of drift times using the Geiger counter arrangement just described, we undertook the separate experiment for more precise measurements of mobilities, which is to be the subject of this paper. Oxygen was chosen as the subject for study because it is believed to be the most important negative ion-forming contaminant in gas counters. By the same token, the requirements for purity were not expected to be severe because

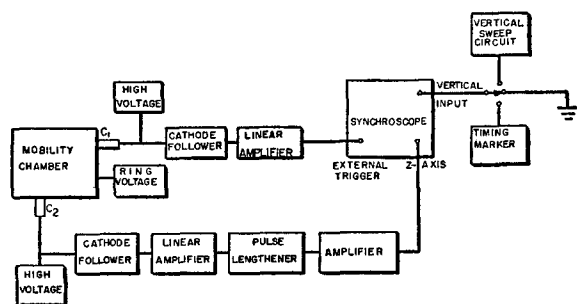


FIG. 2. Block diagram of the electronic system.

there are few other molecules that will compete with O_2 for the capture of electrons.

APPARATUS AND METHOD

A cross-sectional view of the mobility chamber is shown in Fig. 1 and a block diagram of the electronic system is shown in Fig. 2. The central feature of the mobility chamber is a drift tube consisting of a series of metal rings having a graded electric potential, which provides a long, uniform electric field. An alpha-particle source in a small box at the side, movable along a track, sends alpha particles through one of the slots formed by adjacent rings. Electrons produced in the alpha-particle track are captured by oxygen molecules to form negative ions. A proportional counter, on the other side of the drift tube, gives a signal marking the time of passage of each alpha particle and hence the starting time for each batch of negative ions formed in the drift tube. At the far end of the drift tube a proportional counter gives pulses at the arrival of the

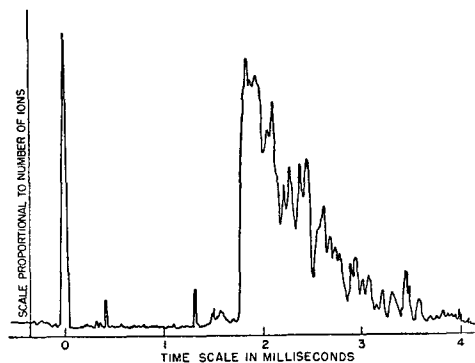


FIG. 3. A typical microphotometer trace of a drift-time spectrum. This particular one is for pure oxygen, and for a source position midway along the drift tube.

negative ions. The data are recorded by means of a synchroscope, as follows: The horizontal sweep is triggered at the instant each alpha particle crosses the drift tube. The pulses from the proportional counter at the end of the drift tube are impressed upon the grid of the cathode ray tube, so as to brighten the trace at points indicating the times of arrival of the ions at the counter. Since all the ions produced by a single alpha particle do not arrive at the counter simultaneously (because of straggling, reactions with molecules, etc.), each sweep of the synchroscope gives a line of dots having a distribution corresponding to the arrival of all the negative ions resulting from the passage of the particular alpha particle. To integrate over a large number of such traces a camera is mounted in front of the synchroscope, with shutter open throughout the run. In some cases, in order to spread the exposure vertically, the film is moved vertically at a rate of a few mm per hour. The result is that the individual dots are not resolved on the film, but a rectangular exposed area appears which resembles a spectrum from a prism spectrograph. In all of our cases a single line or edge is found. A density plot across the film is obtained by means of a microphotometer, and the position of the edge is interpreted as giving the drift time for a particular species of negative ion. Figure 3 is a typical microphotometer trace.

Details of the drift tube are visible in Fig. 1. It consists of 23 brass cylinders 1 in. i.d. by $\frac{1}{4}$ in. long, mounted axially and spaced $\frac{1}{8}$ in. apart. Each ring is supported on a brass post which is in turn fastened to a pair of glass rods near the floor of the chamber. The potential divider which gives a constant gradient along the ring system consists of 22 one-half watt carbon resistors with their Bakelite jackets removed, mounted inside the chamber near the drift tube. The range of voltage used on the divider is 600 to 3000.

The proportional counters are standard, except for the openings in their sides. No. 1 (see Fig. 1) has a series of 17 slots which correspond to, and are aligned with, the slots in the drift tube. No. 2 has a round hole

¹ Hl. deVries, Appl. Sci. Research (Netherlands) **B5**, 387 (1955).

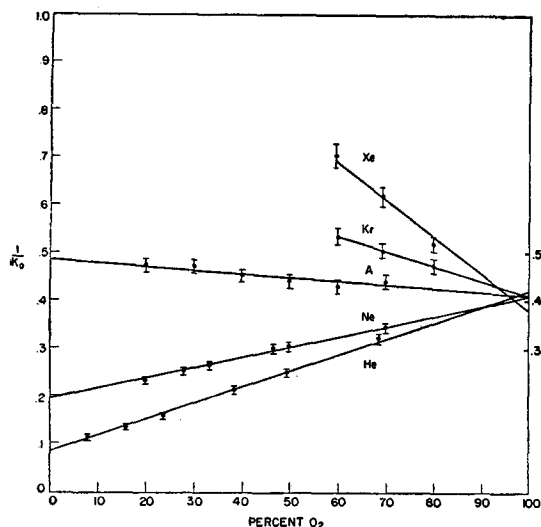


FIG. 4. Reciprocal mobilities reduced to 760 mm Hg pressure and 0°C, for the oxygen negative ion in mixtures of oxygen and each of the noble gases.

1 in. in diameter to match the end of the drift tube. The anodes are 0.004 in. tungsten and the cathodes are brass. A satisfactory plateau is found for the operation of the counters in all of the combinations of gases used in the experiments. The anode voltage is supplied by a 1000–5000 v Higinbotham² circuit.

The alpha-particle source consists of 10 μ C of polonium on a platinum disk 7 mm in diameter, covered with mica of superficial density 1 mg/cm². The disk is mounted in a cylindrical box, having defining slits which allow the alpha particles to pass through one of the slots in the drift tube without striking the edges of the rings. The source box is mounted on a block which can be moved along a pair of rods, drawn by a string and pulley system, with a crank and indicator outside the chamber. By this means the alpha particles can be sent through any one of the slots in the drift tube.

The external vacuum and gas handling system consists of a two-stage mercury diffusion pump, liquid air trap, mercury barometer, thermocouple gauge, and appropriate glass "plumbing" for attaching gas tanks or bulbs. Vacuum seals in the brass box containing the drift tube are of neoprene round gaskets and "O-rings." It was not possible to bake the apparatus during evacuation. The metal assembly was cleaned with a mixture of nitric and sulfuric acid, washed with distilled water, and pumped for several days. The gases used were the best grades commercially available in steel tanks. "Spectroscopically pure" grades were not used except as a check in the case of oxygen, as will be noted later in the paper. The CO₂ was "bone dry" grade. The range of gas pressures used in the experiments was 10 to 25 cm Hg, and the range of E/p was 0.11 to 0.79 v/mm Hg.

RESULTS

All of the data are presented in Figs. 4 and 5. The primary interest in the experiment was to obtain the mobilities of oxygen negative ions in vanishingly small concentrations in foreign gases. To accomplish this, each run was carried through a range of partial pressures of oxygen extending to the smallest concentration that would give a measurable time spectrum, and the intercept for zero concentration was obtained by extrapolation. Also, the intercept at 100% oxygen concentration was used as an important check of the various runs against one another and against the value for the mobility of the negative ions in pure oxygen which are available in the literature. The method of finding the intercepts at 0 and 100% was in all cases an extrapolation along a straight line. A straight line relationship between reciprocal mobility and percent oxygen was to be expected on the assumption that the species of carrier was the same at all concentrations. Over the range covered by the data, there appeared no indication of a departure from this linear relationship. However, the possibility of a change in carrier at vanishingly small concentration of oxygen was not ruled out by the data, so the values of the intercepts must be accepted with that qualification.

The values found for the intercepts at zero concentration of oxygen are given in Table I. They have been reduced to 760 mm Hg pressure and 0°C. In addition to the runs using mixtures, as indicated above and in Figs. 4 and 5, a number of runs were made using 100% oxygen. The value obtained for the latter, reduced to 760 mm Hg pressure and 0°C was 2.46 ± 0.05 cm²/v-sec, or a reciprocal value of 0.406 ± 0.02 . It is evident in Figs. 4 and 5 that the intercepts for 100% oxygen, given by extrapolation of the results for the mixtures, are consistent with this value.

DISCUSSION AND RESULTS

The questions we wish to consider in this section are of two kinds: those which relate to the identification of the negative ion or cluster whose mobility was measured in each run, and those which relate to the accuracy of the measurements. We shall first take up the question of identification.

TABLE I. Extrapolated mobilities of oxygen negative ions in various gases.

Foreign gas	Intercept at zero concentration of oxygen
Helium	11.8 ± 1.2 cm ² /v-sec
Neon	5.14 ± 0.5
Argon	2.06 ± 0.04
Krypton	1.39 ± 0.07
Xenon	0.88 ± 0.10
Hydrogen	11.4 ± 1
Nitrogen	2.22 ± 0.06
Carbon dioxide	1.08 ± 0.03

² W. A. Higinbotham, Rev. Sci. Instr. 22, 429 (1951).

Identification of the Negative Ion

The reasons why the actual carrier of the negative charge may not be the ion that the experimenter expects it to be may be listed briefly as follows: (1) The electron freed by the alpha particle may attach originally to an impurity molecule having a very high cross section, rather than to the molecule which is supposed to be the carrier (in this case oxygen), (2) the electron may transfer from the original carrier to an impurity molecule which has greater energy of attachment, (3) the initially formed ion may gather neutral atoms or molecules of an impurity or of the principal gas itself, so as to form either a permanent or a labile cluster, (4) the ion may enter into a dissociative or other reaction with another molecule. In this experiment, as in all others, the possibility that any one of these four phenomena occurs to a significant extent has to be assessed by indirect means, since the negative ion is not analyzed in any way at the end of its journey. We shall give the significant facts which bear upon these questions.

In respect to the possibility that the electrons were originally captured by a molecule other than oxygen, we may cite the following evidence. In the experiments with each of the gas mixtures the partial pressure of oxygen was decreased as far toward zero as possible. Assuming that oxygen was the capturing molecule, it was to be expected that as the partial pressure of oxygen was decreased the mean free path for capture of the electrons in the mixture would increase, in an inverse ratio. It was, in fact, observed that as the partial pressure became small the width of the line in the drift time spectrum increased and the intensity decreased, until at a certain partial pressure there was no longer a sharply measurable line. This point occurred at quite a high concentration in xenon and krypton and at a very low concentration in CO_2 . It occurred at intermediate values for the other gases, as is indicated by the range over which the experimental points extend in Figs. 4 and 5. The fact that the limit of measurability was encountered at different partial pressures of oxygen in the different gases can be explained fully on the basis of the differences in electron agitation energy in these gases in conjunction with the variation of the cross section for capture of electrons by oxygen with electron energy. The cross section for capture increases steeply as the electron energy decreases. The electron agitation energy is highest in the heaviest noble gas, decreasing, in order, to helium. In the other gases it is, in order, O_2 , N_2 , H_2 , and CO_2 , the last being the lowest.³

The foregoing behavior shows that the electrons were originally captured either by oxygen, or by an impurity which entered the chamber with the oxygen, in the same proportion as oxygen. The latter possibility is effectively eliminated by a comparison of the

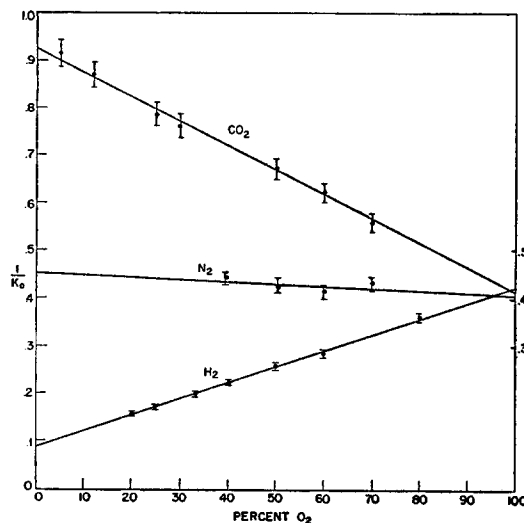


Fig. 5. Reciprocal mobilities reduced to 760 mm Hg pressure and 0°C , for the oxygen negative ion in mixtures of oxygen and each of the gases CO_2 , N_2 , and H_2 .

results obtained using oxygen from two quite different sources: a break-seal glass bulb of spectroscopically pure oxygen (Linde) and a tank of commercial welding grade oxygen. The results were identical.⁴ It is, therefore, reasonably certain that the original negative ions were those of oxygen.

In regard to clustering, charge transfer, and chemical reaction, the shape of the line in the drift-time spectrum (Fig. 3) tells a great deal but not the whole story. The tail on the right side shows that some of the ions were converted to carriers having lower mobility, by one or more of the processes mentioned above. The sharp front shows that the ion of highest mobility occurred with the highest probability. The slight amount of slope that the line edge has is consistent with the amount of straggling which is calculated for a single species of ion traveling the length of the tube, and it does not indicate that there was additional straggling due to labile clustering. These observations provide a strong indication that the ion of maximum mobility was a species which remained unchanged throughout its journey. This is not saying that it must have remained O_2^- . It may have been the product of a secondary reaction or combination of the original O_2^- with O_2 , or with some contaminant. But if it was a secondary product it must have been one which was formed very close to the point of origin of the charge, and not at a random distance down the drift tube.

It has been suggested by more than one author that O_2^- ions may react very quickly with O_2 to give O_3^- , and that the ion whose mobility is measured ordinarily under low-field conditions may be O_3^- . Recently

³ R. H. Healey and J. W. Reed, *The Behavior of Slow Electrons in Gases* (Amalgamated Wireless, Ltd., Australasia, 1941).

⁴ Extensive experiments to check this point were made by one of the authors (E.W.M.) at the Georgia Institute of Technology (O.S.R. Tech. Status Report No. 3, April 30, 1956).

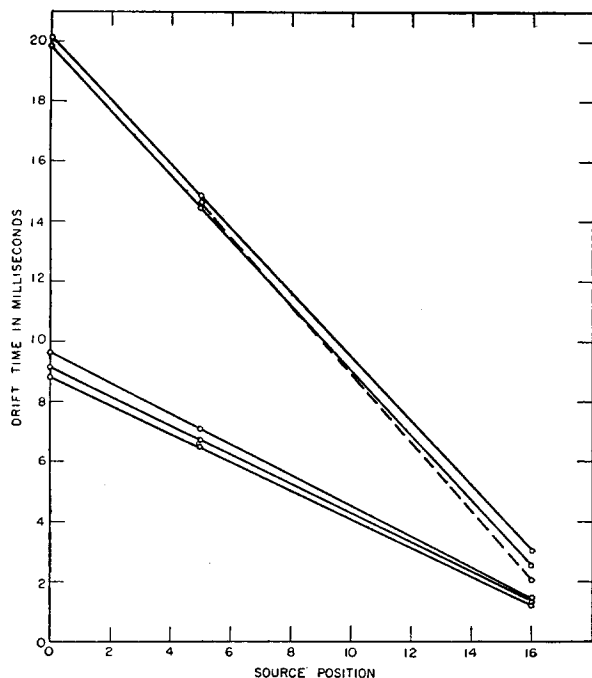


FIG. 6. Plots of drift time νs source position. Data from three runs on each of two mixtures of helium and oxygen are shown.

Burch and Geballe⁵ presented evidence for the presence of three negative ion species in oxygen. In their interpretation the species of intermediate mobility was O_3^- , and according to their analysis O_3^- is the ion which would be observed under our conditions. The question of the identity of the ions observed in our experiment cannot, however, be answered from the data we have obtained.

Accuracy of the Measurements

A brief discussion of the important factors bearing upon the precision of the measurements will now be given. First, the end effects in the drift tube. The free electrons produced by the passage of the alpha particle through the gas diffuse, and drift down the tube a short distance (a few mm) before becoming attached to form negative ions. This results in an indefiniteness in the starting point for the negative ions. At the other end of the drift tube a distortion of the electric field is produced by the proportional counter, which introduces an appreciable end effect. Both of these end effects are eliminated by plotting the drift times obtained at a series of slots along the tube and reading the drift velocity from the slope of the line. These plots are found to be straight lines to within the precision of the measurement. A typical set of plots is shown in Fig. 6.

There can be some question as to what feature of the spectrum in Fig. 3 should be used in computing the

drift time. The line is highly unsymmetrical. There are reasons for believing that it has this shape because it is composed of a narrow symmetrical line due to a single species of ion and a tail due to clusters or other types of carriers. Strong support for this interpretation is given by an experiment done subsequently by one of us (E.W.M.) at the Georgia Institute of Technology.⁶ In a direct comparison of O_2 and SF_6 the O_2 gave an unsymmetrical line like the one shown here, while the SF_6 gave a symmetrical, narrow line. This seems to eliminate any possibility that the tail is an instrumental effect. If the tail were not present the peak of the symmetrical component would be the ideal reference point to use. We used, as the best expedient, the peak of the composite line, which, as seen in the figure, must be quite close to that of the symmetrical component. When the distance of drift (slot number) was changed, the slope of the front changed in about the way which would be expected from straggling theory. This was further support for the assumption that the front was due to a single ion species. The slope changed also when different gases and pressures were used, due to the change in the distance of diffusion of the electrons before attachment, but this was an end effect which was constant throughout each measurement and which consequently had no effect upon the result.

The measurement of the gas pressure was done with a mercury barometer, and the calibration of the time axis on the oscilloscope-camera system was done in the usual way, with a standard frequency generator. The estimated probable errors in the measurements of the various quantities are: pressure, 0.5%; temperature, 0.2%, time interval, 0.5%, voltage, 1.0%, slope of the curve of drift time νs distance, 3%. The composite of these is 3.2%, and it applies to the result given for the mobility of oxygen ions in pure oxygen. In the measurements on mixtures, the determination of the intercepts at zero oxygen concentration introduced a further uncertainty. In most of the cases the latter was the predominant uncertainty, as is evident from the probable errors given in the table of values of the intercepts.

In connection with sources of error it is pertinent to ask whether the use of a proportional counter may introduce a selection such that one type of negative ion is counted while another is not. For this to be true the size of the pulse given by the counter would have to be dependent upon the type of negative ion arriving at the wire. While this may not at first sight seem likely, the possibility cannot be dismissed. We recall that in a counter the electric field increases strongly toward the wire anode (as $1/r$). As a free electron moves toward the anode, it comes to a radius at which its agitation energy is so great that it is able to ionize atoms in collisions. From this radius inward, an electron avalanche grows. Since the avalanche growth is

⁵ D. S. Burch and R. Geballe, Bull. Am. Phys. Soc. Ser. II, 1, 287 (1956); (OOR) Tech. Report No. 4, August 24 (1956); Phys. Rev. 106, 183, 188 (1957).

⁶ E. W. McDaniel, O.S.R. Tech. Status Report No. 4, July 31, 1956.

exponential, the charge delivered to the anode depends strongly upon the radius at which the growth of the avalanche begins. In our application, the electron which starts the avalanche is derived from the breakup of a negative ion in the strong field near the wire. The radius at which the breakup of the ion occurs certainly depends upon the energy of attachment, and hence upon the species of ion. The energy of attachment is generally smaller than the ionization potential of the gas by an order of magnitude. However, in a gas at a given E/p value, the free electrons may have a considerably higher average kinetic energy than the negative ions have. Consequently it cannot be assumed that because the ion breakup energy is lower than the ionization energy, ion breakup will take place at a radius greater than that at which electron avalanches start. To try to analyze the situation in detail, for the mixtures of gases used, would be beyond the scope of this paper and would be a project in itself. We can, however, see in a rather simple way the two extremes of behavior. (1) If the ion breakup occurs well outside the radius at which electron avalanches start to grow, there will be an interval between these two radii in which the electrons drift without ionizing collisions and, consequently, the radius at which an individual ion breaks up will have no correlation with the size of the resulting avalanche. (2) If the two radii overlap or blend into one another, there will be such a correlation and the counting will be selective as to type of negative ion. The larger avalanches will be produced by the negative ions which break up in the lowest E/p (largest radius) so these will be favored. The degree of selection will of course depend upon the sensitivity of the electronic circuit (discriminator level) but it will be present in any case.

We have seen, in a separate connection, evidence suggesting that behavior of the second type does occur. In operating a CO_2 -filled Geiger counter, we have found that a trace of SO_2 will reduce the efficiency at a given voltage, or make it necessary to raise the voltage in order to restore the efficiency. Practically nothing is known about these phenomena, and they offer an interesting field for experimentation.

In the use of the proportional counter in our measurements of mobility, separate evidence, as explained earlier, indicated that the ion which was counted was oxygen. In addition, the method is not one which depends upon relative intensities of lines, but only upon positions; consequently, some selectivity in the

counting would not have changed the result. It will not be possible to settle the question of selectivity before further research is done on the proportional counter itself.

COMPARISON OF RESULTS

It is possible to compare the results obtained here with all of the pertinent results obtained by other investigators, since the latter are not numerous. The only recorded measurement of the negative ion mobility in an oxygen mixture is that of Mayer⁷ in 1927. He worked with oxygen-hydrogen mixtures and obtained results in general agreement with those reported here. His value for pure oxygen was $2.05 \text{ cm}^2/\text{v-sec}$. There have been several measurements of the mobility of the negative ion in pure oxygen. The earliest is that of Zeleny⁸ in 1900. He obtained $1.8 \text{ cm}^2/\text{v-sec}$. Franck⁹ in 1910 obtained $1.79 \text{ cm}^2/\text{v-sec}$. Bradbury¹⁰ in 1932 obtained $2.19 \text{ cm}^2/\text{v-sec}$. A more recent (1937) determination by Nielsen and Bradbury¹¹ employed an improved electrical shutter method. They reported that newly formed ions, which they identified as O_2^- , had a mobility of $3.3 \text{ cm}^2/\text{v-sec}$ and that a strong aging effect was in evidence. The slowest ions observed had a mobility of 2.85. Doehring,¹² in 1952, reported the measurement of the mobility of ions he believed to be O_2^- in oxygen as $2.68 \pm 0.13 \text{ cm}^2/\text{v-sec}$. He used an electrical shutter method. A very recent study, already mentioned, by Burch and Geballe,⁵ complicates the matter of interpretation and comparison, because it introduces evidence for the presence of three negative ion species in oxygen. Their evidence, provided by measurements performed at $E/p > 8$, suggests that the one measured under conditions such as ours is O_3^- . The mobility found for this was $2.62 \text{ cm}^2/\text{v-sec}$.

It is pertinent to cite here, for comparison, the value for the mobility of the positive ion in oxygen because there is theoretical reason to believe that the mobilities of positive and negative ions of the same species are very nearly equal, provided charge exchange does not occur. Varney¹³ has made a very careful experiment on the positive ions in pure oxygen and found a value for the mobility of $2.25 \pm 0.10 \text{ cm}^2/\text{v-sec}$.

⁷ H. F. Mayer, *Physik. Z.* **28**, 637 (1927).

⁸ J. Zeleny, *Trans. Roy. Soc. (London)* **A195**, 193 (1900).

⁹ J. Franck, *Z. Physik* **12**, 291 (1910).

¹⁰ N. E. Bradbury, *Phys. Rev.* **40**, 508 (1932).

¹¹ R. A. Nielsen and N. E. Bradbury, *Phys. Rev.* **51**, 69 (1937).

¹² A. Doehring, *Z. Naturforsch.* **7a**, 253 (1952).

¹³ R. N. Varney, *Phys. Rev.* **89**, 708 (1953).