MAY 15, 1932 PHYSICAL REVIEW VOLUME 40

The Absolute Values of the Mobility of Gaseous Ions in Pure Gases

By Norris E. Bradbury
Physical Laboratory, University of California

(Received March 17, 1932)

The absolute method of measuring the mobilities of gaseous ions developed by Tyndall and Grindley has been employed to study the ionic mobility in gases of high purity. The method was slightly altered to improve the resolving power. An intense source of high voltage x-rays previously used in recombination measurements provided an external source of ionization for the Pyrex glass mobility chamber. Under these conditions a high degree of gas purity could be maintained in the baked out chamber, and definite knowledge concerning the existence of a velocity spectrum could be obtained from the shape of experimental curves. Careful purification and drying by liquid air was employed for all gases. At time intervals of the order of 4×10^{-2} seconds only a single class of each ion was found for the positive and negative ion in air. The mobility, 1.60 cm/sec. per volt/cm for the positive ion and 2.21 cm/sec. per volt/cm for the negative ion is in agreement with other absolute values. Oxygen prepared from $KClO_3$ gave an anomalous high mobility of 2.65 for the negative ion, due probably to the presence of chlorine oxides. Oxygen from $KMnO_4$ and from a commercial tank source carefully purified gave the values 1.58 for the positive ion and 2.18 for the negative ion. Nitrogen, as finally prepared by extreme purification of the commercial tank gas gave no negative ions and a positive ion of mobility 2.09. Hydrogen was found to give no negative ions and a predominating positive ion of mobility 8.2. Indications of a higher mobility ion at 13.1 were also found. This is in agreement with the results of Loeb on Na^+ ions in H_2. Helium gave no negative ions and a positive ion of mobility 17.0. This agrees with an approximate value observed by Tyndall and Powell for lower pressures and shorter ion ages. For pure gases and ion ages of the order of magnitude of those employed in these experiments (0.04″ to 0.07″) sharp peaks, indicative of a single class of ion, were always observed.

Introduction

SINCE the initial experiments of Rutherford and J. J. Thomson[1] in 1896 on the conductivity of air ionized by x-rays, the mobilities of the normal gaseous ions have been studied by many investigators. The results of these measurements, however, have by no means resulted in a series of accurate and absolute values of ionic mobilities for different gases. So great has been the discrepancy between different observers with different experimental procedures that, lacking a standard of comparison or interpretation, it was necessary in the compilation of the International Critical Tables[2] to include all published values of even moderate reliability. In the case of hydrogen, which is typical, this has resulted in the listing of seven different values for the mobility of the positive ion ranging from 4.96 to 6.70. Similarly discordant values are to be found for the other common gases. Under such circum-

---

[1] Thomson and Rutherford, Phil. Mag. **42,** 392 (1896).

[2] L. B. Loeb, Int. Crit. Tables, **6,** 111 (1929).

stances, it is obviously impossible to compare theory with experiment, exact values for substitution and calculation in other theoretical equations are lacking, the values obtained by one method cannot be compared with those given by another under slightly different conditions, and the whole situation is incompatible with the facilities and means for investigation of modern research. It is for these reasons that the experiments to be described were carried out to obtain a series of accurate absolute values of ionic mobilities under conditions of high gaseous purity.

A consideration of the experimental methods and techniques which have been employed in mobility measurements in the past shows that most of the causes of the discrepancies noted above may be classified under two headings. These are: (1) experimental idiosyncracies either uncontrollable or neglected; (2) the degree of gas purity maintained. Although in any given experiment it may be difficult to assign either one or both of these conditions as having been operative, yet they form a valuable means of evaluating the reliability of a proposed method.

Under (1) we have such phenomena as turbulence, which is usually unavoidable in all air blast methods, interpenetration of fields in methods employing gauzes, volumes of ionization vaguely defined and seriously affected by diffusion, and similar difficulties. In addition, conditions of low resolving power, abnormally high fields, contact potentials, and the like must be considered and guarded against.

Under (2) it is only necessary to mention the well-known effect of traces of water vapor on the mobility of the ion, and the work of Loeb,[3] on mixtures. The latter studies have shown that extremely minute traces of certain impurities can exert a marked effect on the mobility of the ion, and that furthermore such traces are frequently difficult to eliminate. The large volumes required in blast methods make adequate purification of the gas under such circumstances impossible. Radioactive materials, when employed as means of ionization, have been sources of contamination in certain gases. Metal parts that cannot be carefully cleaned are constant sources of impurities due to films of oil and grease of high vapor pressure. Hard rubbers, shellacs, stopcock greases, etc. that can come in contact with the gas to be studied are almost invariably sufficient sources of contamination to affect seriously the values of the mobility obtained.

Of the few absolute methods of mobility measurement that are relatively free from criticisms of the first type, the method of Tyndall and Grindley[4] is the only one adaptable to a large number of different gases and ions. As originally designed with α particle ionization, failing a better source, the method was not able to yield the beautiful results of which it was capable. The availability of the splendid high tension d.c. source of x-rays, built for studies on ionic recombination furnished the possibility of developing the Tyndall and Grindley method to the limit of its usefulness. With the powerful constant *external* ionizing source it became possible to measure mobilities

---

[3] L. B. Loeb, Phys. Rev. **32,** 81 (1928).

[4] Tyndall and Grindley, Proc. Roy. Soc. **A110,** 341 (1926).

by an absolute method in a baked out glass chamber with a minimum of metal parts, and so to alter the method that the mobility curves were composed of linear elements with a sharp peak and therefore had perhaps the highest resolving power of any method yet used. In addition a slight change in the cycle of potentials applied to the measuring field was made to permit the measurement of positive ion velocities in gases in which free electrons existed. The same change permitted negative ions, if any, to be observed in supposedly free electron gases. Another minor variation in the method allowed a simplification of the theory, thus permitting a clearer interpretation of the experimental curves. The results obtained with this method quite transcended expectations and will constitute the contents of this paper.

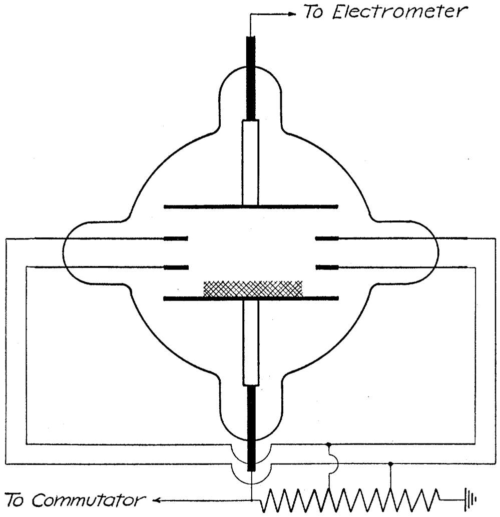


Fig. 1a. End view of ionization chamber showing sheath of ionization along the lower plate and equipotential vanes to maintain a uniform field.

APPARATUS

The source of ionization was a homogeneous beam of intense, hard x-rays from a Coolidge tube under a potential of 80 k.v. pure d.c. An elaborate control and filter system enabled the potential on the tube and the current drawn to be kept constant to within 0.3 percent. This equipment, previously used in recombination measurements, formed an invaluable source of constant ionization for these experiments.

The ionization chamber was constructed of Pyrex glass as shown in Fig. 1. The plates were 7×15 cm and 3.5 cm apart. The plates, as well as the equipotential guard rings mounted equally spaced between the plates, were kept in position and accurately parallel by a carefully made spacing block kept in place during the necessary glass blowing. When the plates were fixed in position, this spacer could be withdrawn and the remainder of the glass blowing completed. The alignment and parallelism of the plates was further checked by cathetometric measurements. All metal parts were of Monel metal save the ground shield in the front part of the chamber through which the x-rays had to pass. This was of thin aluminum. The entire plate system was surrounded by a grounded Monel metal screen to protect the measuring fields from external electrostatic disturbances. The chamber was then mounted behind an adjustable lead slit through which the ionizing x-rays could pass in a thin sheath parallel to and grazing the lower plate. Connections to the diffusion pump and gas purifying train were made as shown.

The upper plate, on which the ions were collected, was kept at ground potential and connected to the electrometer. The lower plate was connected to ground through a 30,000 ohm resistance, at the upper end of which was applied the necessary potential to produce the required field between the plates. The equipotential guard rings were then connected 10,000 ohms above ground and 20,000 ohms above ground respectively. A sensibly uniform field was thus maintained between the plates over a much larger area than otherwise. Since, however, the ions follow the lines of force, and only the ions which get across *first* (i.e., along the straightest lines or the most uniform field) are important in the measurements, these guard rings are of importance only in increasing the intensity of the observed currents.

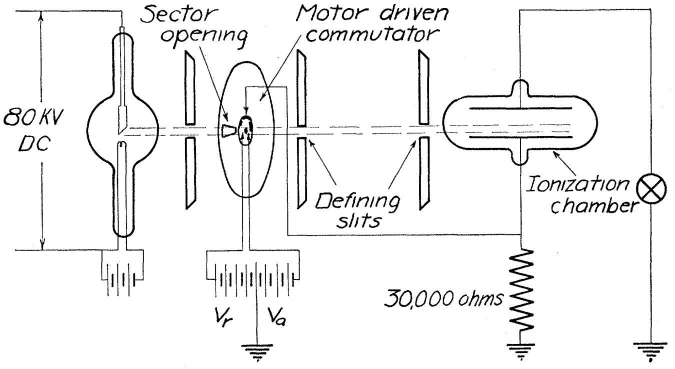


Fig. 1. Diagram of apparatus.

A lead shielded brass disk, in which two variable sector openings had been cut, was mounted in the path of the x-ray beam so that its rotation permitted a flash of x-rays to pass through at each revolution. Affixed to this disk was a commutator with suitable segments and brush system for applying the potential cycle to the plates of the ionization chamber. The position of this commutator with respect to the x-ray flash could be varied. This cummutator and disk assembly were driven by a large, variable speed d.c. motor through reduction gears. The constancy and absolute value of this speed was determined by voltage readings from an accurate magneto tachometer directly connected to the motor. The entire arrangement is similar to that employed in aging experiments on ions in air, and is shown in Fig. 1. The potential cycle applied to the plates at each revolution is shown in Fig. 2. The dotted lines represent an addition to the cycle employed when it was desired to measure positive ions in gases in which electron attachment does not occur over appreciable periods of time.

THEORY OF THE METHOD

The theory of the method has been given by Tyndall and Grindley. Inasmuch as the present experiments following a different and somewhat simpler procedure, the theory will be given as it here applies.

An individual cycle takes place as follows. A flash of x-rays in a thin sheath parallel to the lower plate occurs at the point marked γT in Fig. 2 with respect to the potential cycle. At this time the space between the plates is field free and ions accumulate in uniform layer above the lower plate. Let us suppose we are measuring positive ions. The flash of x-rays is followed by the application to the lower plate of a *negative* potential V_r which drags the positive ions *downwards* for a time δT, where T is the time of a revolution and δ a fraction. Necessarily the lower part, or even all, of the sheath may be caught by the lower plate during this phase. Those ions which are not caught at the conclusion of this phase are then drawn across the space, by an advancing potential V_a, towards the upper plate for a time αT which, if sufficiently long, will permit all the ions not caught at the end of γT to be received at the upper plate and noted as a current to the electrometer. If V_a is not great enough, or αT too short, those ions which are not caught at this time are swept out of the field by V_r acting during βT. The space between the plates is now free of ions (the negative ions having been swept out to the lower plate during αT) and the cycle may be repeated.

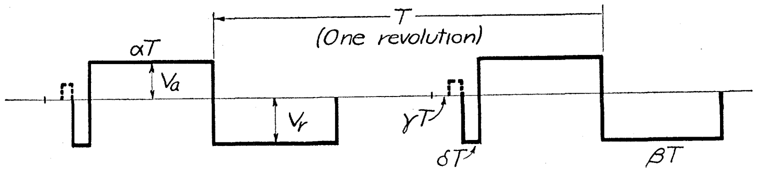


Fig. 2. Cycle of potentials applied to the lower plate. Ions are formed during γT, drawn towards the lower plate during δT, and drawn across the volume to the upper plate during αT, Volume cleared of all ions not caught during βT. Free electrons, if present, are swept out by the small potential shown in dotted lines.

In practice V_a is set at a definite value and V_r at a somewhat higher value. The speed of revolution, which directly determines the time of application of αT, βT and γT, is then varied and the relative current received at the electrometer at different frequencies noted. We can now consider the variation of the electrometer current with frequency as it is related to the mobility of the ions, the time of application and magnitude of V_a, and the distance between the plates.

Suppose the x-ray beam forms Q ions per cc per second in the sheath above the lower plate. Then during the time of application of the x-rays, γT, at A there will be formed $Q\gamma TAd$ ions in the sheath if A is its area and d its thickness. The sheath is then acted on by V_r for a time δT. If the mobility of the ions is k, the sheath will then move downwards a distance $kV_r\delta T$ and only $(d-kV_r\delta T)Q\gamma TAd$ ions remain above the plate. V_a now acts for a time αT. If V_a is great enough or αT long enough all these ions will be caught at the upper plate and the quantity received at the electrometer per cycle will be that amount. Over a series of cycles this corresponds to a current of $(d-kV_r\delta T)\,Q\gamma Ad$.

Suppose, however, we increase the frequency so that αT is no longer sufficiently long to permit all the ions to reach the upper plate. A certain fraction of the ions remaining after δT will also escape capture at the upper plate and will subsequently be swept from the field. It is easily shown that the amount now received at the electrometer in terms of current is

$$(d - kV_r\delta T - D + kV_a\alpha T)Q\gamma Ad$$

where D is the distance between the plates. We may now consider the variation of these two expressions with T, the period of one revolution. When

$$T = (D - d)/(kV_a\alpha - kV_r\delta)$$

the current will be zero and will remain so for all shorter T's. As T increases di/dT is given by $Q\gamma Ad(kV_a\alpha-kV_r\delta)$ which is positive since $\alpha/\delta > V_r/V_a$. When $D=kV_a\alpha T$, the second expression reduces to the first for which the di/dT is seen to be $Q\gamma Ad(-kV_r\delta)$. This is negative and hence the current decreases with increasing period. Obviously, there is a point of discontinuity, whose evidence is a maximum in the electrometer current-frequency curve at

$$D = kV_a\alpha T.$$

Hence if we measure the electrometer current for different periods or frequencies of the commutator, we will find a linear *increase* in i with increasing T (decreasing N where N is the frequency) until the point

$$D = kV_a\alpha T$$

is reached. At this point there will be a linear *decrease* in current until the point $d=kV_r\delta T$ is reached beyond which the current will be zero. Since we can measure D, V_a, α, and T (at the maximum) we can easily calculate k from the above equation, and this will form our method of procedure.

In the case of gases in which free electrons exist, a change in the cycle had to be made shown by the dotted lines in Fig. 2. Otherwise, during the time of application δT of the retarding phase for positive ions, the free electrons, having an approximate mobility of 10,000 cm per sec., would be entirely swept across the field to the upper plate and completely mask the following positive current. Hence it was necessary to insert a small *positive* potential (2–20 volts) *before* the application of δT. This is sufficient to sweep the electrons entirely from the field to the lower plate, causing a negligible change in the effective d of the positive ion sheath.

It is interesting to notice that k so determined is independent of V_r and d-two variables whose effects it is extremely desirable to eliminate. Moreover it can easily be shown that the same results are obtained if the beam does not exactly graze the plate but passes a short distance above it. This theory shows, then, that the mobility can be calculated from easily measured variables and it is independent of those factors whose value would be difficult to determine. Moreover, it predicts a definite type of curve for a single mobility and hence enables easy comparison with experiment. It may be mentioned here that the independence of the position of the peak with respect to V_r and d was amply verified by experiment. The resolving power of the method can be increased at will by making d as small as is compatible with the intensity of ionization and the sensitivity of the detecting system.

Purification of the Gases Used

The chamber was surrounded by a wire-wound resistance furnace enabling the chamber and metal parts to be baked out under a vacuum at a temperature of 350°C. The dimensions of the metal parts precluded their being made so as to permit outgassing with an induction furnace. By prolonged baking out, however, it was felt that most of the *adsorbed* gases on the surfaces were removed. A liquid air trap was mounted between the chamber and the remainder of the pumping and purifying system to prevent any possible diffusion of stopcock grease vapors into the chamber when filled with pure gas. This trap was kept at liquid air temperatures during the filling of the chamber and the course of a run. It was, of course, removed when baking out was in process. Under such conditions the chamber could be pumped out to better than 10^{-6} mm.

The method of purification of the gases used varied with the different gases. Liquid air was always used for drying where possible. Oxygen, which condenses at atmospheric pressure and liquid air temperatures, was dried by a freezing alcohol bath. Two or more such drying traps were always employed, in addition to the trap on the chamber itself. Even under such conditions, it was found necessary to pass the gas through the purifying train extremely slowly.

Air, upon which the first measurements were made, was purified by passing it through the usual purifying train consisting of NaOH, $CaCl_2$, and P_2O_5 followed by liquid air traps. A later series of experiments was made in which the air was purified only by passing very slowly through three liquid air traps in series. Apparently both methods were equally satisfactory.

Oxygen was first prepared by heating $KClO_3$, condensing the oxygen in a liquid air trap, and subsequently distilling through the purifying train into the chamber. In another preparation the same procedure was followed save that $KMnO_4$ was substituted for the $KClO_3$. Finally, tank oxygen was condensed by liquid air and fractionated using the middle third for filling the chamber. The latter two methods were apparently the more satisfactory, though extreme care had been taken to purify the $KClO_3$ by recrystallization and to keep out organic matter.

Nitrogen was obtained from a commercial tank. Preliminary results obtained by passing it through the usual purifying train plus a small heated tube filled with copper shot and powder showed the presence of a large number of negative ions. The value for the mobility of the positive ion was, however, higher than expected. The preparation of nitrogen was then carried out by the decomposition of sodium azide, which, after passing through liquid air traps, was led directly into the chamber. This had the gratifying result of giving only free electrons but evidences of some impurity (probably organic ammonia like compounds due to the method of preparation of the azide) were still present in a lower (though normal) positive ion mobility. Drastic purification of tank nitrogen was then attempted. A Pyrex tube one meter in length was filled with glass wool and precipitated copper powder which was thoroughly reduced by passing hydrogen through the heated tube. In addition, a tube containing metallic sodium, vaporized under vacuum, was placed in the purifying line. Liquid air traps before and after the copper tube and after the metallic sodium completed the purifying train. Under these circumstances nitrogen was obtained which gave no negative ions and every evidence of extreme purity.

Hydrogen was obtained from a commercial tank of considerable purity and passed through the usual purifying train plus a heated copper tube. With the usual liquid air drying, this hydrogen appeared to be of highly satisfactory purity.

Helium was first obtained from a small cylinder donated several years before by the U. S. Navy. Purification by the ordinary train gave a product of very doubtful purity, which was probably due to the condition of the gas employed. Another tank of the gas, stated to be of 95 percent purity, was then obtained and a specially designed purifying train constructed. Heated tubes containing precipitated copper and powdered copper oxide were put in to remove hydrogen and oxygen. In addition, the helium was sparked between magnesium electrodes to remove nitrogen and passed over heated metallic sodium. The gas, after this treatment plus absorption in two charcoal traps in liquid air, gave results indicative of high purity. Spectroscopic examination of both the hydrogen and helium showed nothing but the ordinary line spectrum.

Before filling with any gas, the chamber and purifying train were pumped out to high vacuum and the chamber was baked out. The train was then shut off from the chamber, slowly filled with gas, quickly pumped out, and slowly filled with gas again. The chamber itself was then flushed out with the purified gas, and finally filled to atmospheric pressure. Approximately two hours was required for the purification of the two liters of gas required to fill the chamber.

RESULTS

It was noted under the theory that the theoretical shape of the commutator frequency-electrometer current should be that of two straight lines intersecting in a maximum value or peak at a value of T such that

$$D = kV_a\alpha T.$$

This was deduced for ions supposedly of a single unique mobility. It has previously been shown that if there is a uniform distribution or spread of mobilities about some average value, the top of this peak will be rounded off or flattened. Naturally, it is impossible to obtain an absolutely sharp maximum with such factors as diffusion and self-repulsion, and finite separation of observed points, yet in pure gases with a single type of ions where the ionization intensity was sufficient to permit adjustment for high resolving power, very satisfactory sharp peaks could be obtained. Occasionally when it was necessary to widen the slit to too great an extent in order to secure measurable electrometer currents, the sides of the peak would drop off to zero too rapidly owing to ions of the opposite sign coming across during δT, or which were not entirely removed during αT. This resulted in an outward "bow" in the curves. Such curvature, however, was never found to influence the position of the peak, and only rendered the observed curves a little more difficult to interpret. None of the results to be reported were obtained under these conditions.

The observed values of mobility in the different gases are given below. All values have been reduced to 760 mm. The temperature of these measurements was 22°C.

Air. Typical curves for the positive and negative ions in air are shown in Fig. 3. These ions were observed at an age of 0.07 seconds and it is clear that they show a unique velocity. In general the negative curves are sharper than the positive. This is probably due to an incipient aging effect in the case of positive ions, enhanced by the products of ionization formed by the intense x-rays. The average of all values obtained for the positive ion was 1.60 cm/sec. per volt/cm and for the negative ion 2.21 cm/sec. per volt/cm. These values are in exact agreement with those obtained for "new" ions in the aging experiments previously reported and are also in good agreement with the values obtained by Loeb with photoelectric ions, and by Tyndall and Grindley with radioactive ionization. Apparently the complex chemical reaction products formed by the x-rays in a mixed gas such as air are sufficient to cause the lowered mobility in spite of the elaborate precautions taken to insure purity. These values in air are practically the same as those found with much more casual methods of purification. The value obtained by Loeb[5] of 2.16 was in air of somewhat questionable purity as was the 2.18 value of Tyndall and Grindley. Schilling[6] has worked in very pure air, but used a gauze method which gave results dependent on the auxiliary field strength.[7] Luhr and Brad-

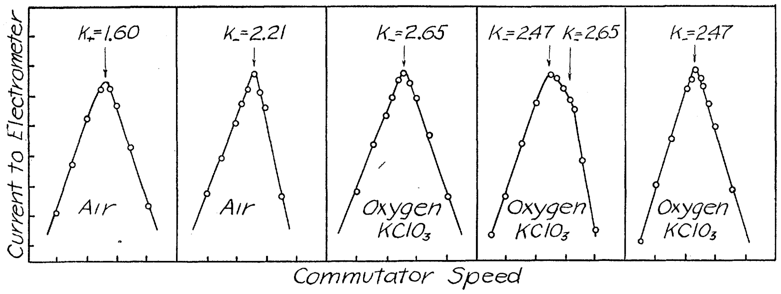


Fig. 3. Experimental curves for air and for oxygen prepared from $KClO_3$. The arrows indicate the position of the peak for calculation.

---

[5] L. B. Loeb, Journ. Frank. Inst. **196,** 537 (1923).

[6] H. Schilling, Ann. d. Physik **83,** 23 (1927).

[7] Cf. footnote, Int. Crit. Tables **6,** 112 (1929).

bury[8] with a Langevin method obtained values in agreement with those reported here. Zeleny[9] has made recent accurate studies on ions of different ages in dry and moist air in an apparatus which was not outgassed using an air blast method. His results were thus obtained under conditions which make comparison difficult. In view of the agreement of the values here obtained with the other recent values given by the absolute methods cited, *one must accept as the standard values for air the values of 1.60 and 2.21 cm/sec. per volt/cm for the positive and negative ions respectively.* These are in place of the previously accepted values of 1.36 and 1.87 obtained in 1901.[10]

Oxygen. Oxygen was first prepared, as described, by the decomposition of $KClO_3$. Under these circumstances rather remarkable values were obtained. The negative ion showed an initial high mobility—reaching values of 2.65—which subsequently decreased to 2.47 as the gas was allowed to remain in the chamber. The positive ion showed a similarly high mobility which decreased with the age of the gas from 1.71 to values approximating 1.6 with more than one type of ion present. The curves in this case are shown in Fig. 3, for the negative ion, and Fig. 4, for the positive ion. Frozen alcohol was maintained on the trap during the time the gas was in the chamber. The shift of the maximum indicates either the appearance or disappearance of some impurity. The possibility of the decomposition of the $KClO_3$ resulting in traces of chlorine oxides were any traces of foreign matter present in the salt makes the latter case seem the more probable. This method was used as it had been recommended as that method giving the purest O_2 for molecular weight determinations. It is seen that the ions are sensitive to impurities which do not affect the most accurate chemical technique. The preparation of oxygen from $KMnO_4$ was therefore carried out, in spite of the fact that Baker's C.P. chemical contained, by their analysis, 0.004 percent Cl and ClO_3. These were evidently in the form of salts which did not decompose at the low temperatures required by $KMnO_4$. In this case the average of the runs taken gave 2.19 for the negative mobility and 1.58 for the positive ion. These values did not change as the gas remained in the chamber over 24 hours, and seem much

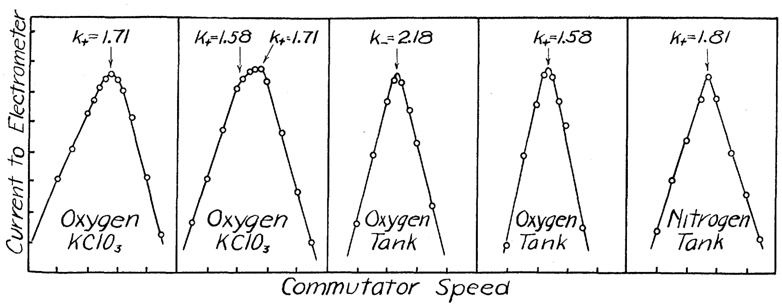


Fig. 4. Experimental curves for oxygen and an initial curve on impure nitrogen.

---

[8] Luhr and Bradbury, Phys. Rev. **36,** 1394 (1930).

[9] J. Zeleny, Phys. Rev. **34,** 310 (1929); **36,** 35 (1930); **38,** 969 (1931).

[10] J. Zeleny, Phil. Mag. **195,** 193 (1901).

more understandable than those obtained from $KClO_3$ oxygen when compared with the values obtained in air.

Finally, in spite of the practical impossibility of removing all the N_2 in the purification of liquid oxygen by fractionation, this means of preparation was attempted. The values obtained in this case were the same as those given by the $KMnO_4$ prepared gas, and lend weight to the assumption as to its purity. Typical curves obtained are shown in Fig. 4. The absolute values for the mobility of the positive and negative ion in pure oxygen at atmospheric pressure may then be taken to be 1.58 and 2.19 cm/sec. per volt/cm respectively. The only values that exist in the literature are those of Zeleny[10] (1.36 and 1.80 which may be compared with his values for air), and those of Franck[11] using his gauze modification of the Rutherford method. He obtained 1.29 and 1.79 but the gauze method makes comparison in this case futile.

Nitrogen. The first runs were made on nitrogen taken from an ordinary commercial tank and gave a positive ion of 1.82 and a rather sharp curve as shown in Fig. 4. This value was somewhat higher than that to be expected from the air and oxygen measurements, and it was rather surprising to find that there was only about 30 percent free electrons. These results are in agreement with those noted by Luhr[12] in recombination measurements whose nitrogen was purified in much the same manner. Luhr, believing his N_2 pure, ascribed his negative ions to possible attachment of electrons to atoms or molecules activated by the x-rays. These results and those to follow show in reality that the N_2 was impure and that the Cu was apparently not removing all the oxygen. Similar conditions apply to Luhr's work in argon and probably explain the results of Mario da Silva[13] who believed that attachment might take place between electrons and activated atoms of N and molecules of N_2. Since the attachment experiments of Cravath had shown that under ordinary conditions electron attachment should not take place in pure nitrogen, the existence of negative ions of a mobility 2.21 gave definite evidence that some impurity was present which could attach electrons. In consequence, the preparation of nitrogen from sodium azide was carried out. In this gas a mobility of 1.62 for the positive ion was obtained with the curve shown in Fig. 5a. No negative ions could be detected, the free electrons being removed by the application of the small auxiliary phase mentioned above.

Although the value obtained for the mobility of the positive ion in the case of the azide nitrogen seemed plausible, yet the higher value obtained in tank nitrogen and the suspected contamination of the azide by organic compounds, led to the feeling that still higher values might be obtained were purification methods more strenuous. The tank nitrogen was consequently purified as previously described with very satisfactory results. No negative ions could be detected in the gas even after standing four days in the chamber. Furthermore a mobility of the positive ion of 2.09 was found and initial curves showed an asymmetry on the high mobility side which may be com-

---

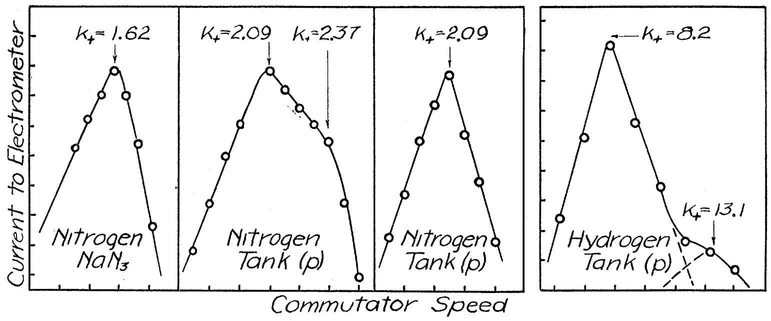
[11] Franck, Zeits. f. Physik **12**, 291 (1910).

[12] O. Luhr, Phys. Rev. **36**, 24 (1930).

[13] M. A. da Silva, Ann. d. Physik **12**, 100 (1929).

pared with the high values found by Loeb[14] for the Na ion in short time intervals in nitrogen. Fig. 5b shows the type of curve obtained and Fig. 5c that obtained after the gas had been in the chamber 36 hours, though no negative ions were detected even after three days.

The mobilities of ions in nitrogen have been measured by Franck[15] and by Yen,[16] who also used the Franck method. Their results agreed within their limits of error giving a positive mobility of about 1.3 and a negative mobility of 1.8. The impurity of the gases used and the unknown effect of the gauzes make comparison futile. Tyndall and Powell,[17] however, have measured the mobility of the positive ion in nitrogen (in which they found no negative ions) at low pressures and short time intervals. They could not determine absolute values but found a mobility for the positive ion of about 2.1 with indications of a subsidiary peak at 1.6. These investigations confirm the existence of this high mobility, however, at greater ion ages and atmospheric pressures. Loeb has measured the mobility of Na^+ ions in nitrogen and found an initial mobility of 3.75 at ages less than 5×10^{-3} seconds. Following this there is a moderately abrupt decrease to a mobility of about 3.0 and a subsequent decrease to the value 1.6 at ages of 0.01 second. The uncertain temperature correction in the experiments make his absolute values somewhat doubtful, but the appearance of the hump on the high mobility side of Fig. 5 at 2.37 is an interesting confirmation of his results. Several attempts were made to detect a higher mobility than 2.09, but were unsuccessful. Hence it may be said that the mobility of the more stable positive ion in pure nitrogen at atmospheric pressure measured within 10^{-2} seconds is 2.09 cm/sec. per volt/cm. No negative ion exists in pure nitrogen, the carriers being free electrons. It is to be noted that the 2.09 cm/sec. positive ion in nitrogen may be the unaged positive ion of mobility approximately equal to that of the negative ion observed by Erikson[18] and by Mahoney[19] in impure gases in the aging experiments.



Figs. 5 and 6. Experimental curves for nitrogen and hydrogen; the latter showing the presence of the 13.1 mobility.

---

[14] L. B. Loeb, Phys. Rev. **38,** 549 (1931).

[15] Franck, Zeits. f. Physik **12,** 613 (1910).

[16] K. L. Yen, Proc. Nat. Acad. Sci. **4,** 91 (1918).

[17] Tyndall and Powell, Proc. Roy. Soc. **A129,** 162 (1930).

[18] H. A. Erikson, Phys. Rev. **30,** 339 (1927).

[19] J. J. Mahoney, Phys. Rev. **33,** 217 (1929).

Hydrogen. The results obtained in pure hydrogen gave a curve of the shape shown in Fig. 6 for the positive ion. The peak mobility is at 8.2 and there is definite indication of a subsidiary peak at a mobility of 13.1. No negative ions could be detected in the gas under these conditions. Loeb has measured the mobility of Na^+ ions in H_2 as a function of their age[14] and found a mobility of 8.4 at ages greater than 10^{-2} seconds. He found, however, that the initial value of 17.5 at ages less than 10^{-5} seconds dropped sharply to a value of about 13.5 at 10^{-4} seconds. As mentioned above, the heating correction is somewhat doubtful, and his resultant values may not be exact. The values obtained by the method of this experiment, however, confirm the results, and furnish more accurate absolute values. The existence of the high mobility ion at 13.1 is gratifying evidence as to the purity of the gas. The detection of the 17.5 ion is beyond the limits of the experiment with the ion ages necessarily employed.

Since the values of the mobility for the hydrogen positive ion have generally been reported between 4.96 and 6.70, measurements were made on hydrogen that had been purified by merely passing through liquid air. In this case a curve was obtained with a mobility at 6.8.

Zeleny in his original measurements obtained a value of 6.70 for the mobility of the positive ion. If this is multiplied by 1.21, which is the approximate error in his standard values for air, we obtain a value of 8.1 which is in fair agreement with the results mentioned above. His hydrogen, however, maintained negative ions, and it is doubtful if the purity was sufficient for him to have observed this high value. Loeb and DuSault[20] have obtained 6.5 by the Franck method in a gas sufficiently pure so that free electrons were observed.

The negative ion mobility was measured as a matter of interest in mixture experiments for impure hydrogen. The value obtained in this case, 9.6, is in agreement with that obtained by Loeb and DuSault and by Wellisch.[21] The values for the positive ion obtained by the latter, however, are much too low. Whether this was due to field distortion or to impurities cannot be said.

In the light of these experiments and those of Loeb on Na^+ ions the mobility of the most stable positive ion in hydrogen under normal times of 10^{-2} seconds can be said to be 8.2 cm/sec. per volt/cm. In *pure* hydrogen, no negative ions are found.

Helium. The first experiments on what was evidently relatively impure helium gave the curve shown in Fig. 7 which after 24 hours in the chamber changed to one with a high mobility peak at 14.1. The main peak at 7.2 corresponds roughly to the value of 5.09 observed by Franck[22] when corrected to the new standard scale, and the 17.3 and 14.1 values are in rough agreement with results of Tyndall and Powell[17] who found the transient existence of an ion of mobility 17. They also found that, after their gas, which was of considerable purity contained in a glass chamber, had been in the apparatus for

---

[20] Loeb and duSault, Proc. Nat. Acad. Sci. **14,** 192 (1928).

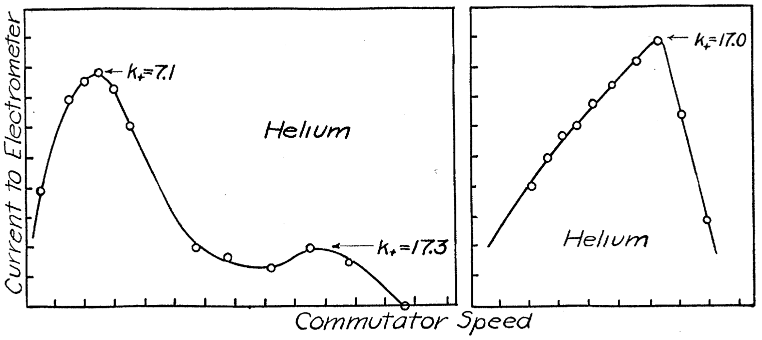
[21] E. M. Wellisch, Am. Journ. Sci. **44,** 1 (1917.)

[22] Franck, Jahrbuch der Rad. und Elek. **9,** 235 (1912).

several days, that their curves indicated the appearance of an ion of mobility approximately 7.

These results indicated that the helium was of insufficient purity, and accordingly its further purification as previously described was carried out. The results in this case gave the curve shown in Fig. 8—with a single mobility at 17.0. This value remained unchanged after the gas had been in the chamber three days. The curve lacks symmetry because of the exceptional width of the slit which was necessary with the very feeble ionization in helium. Great difficulty was experienced in obtaining measurable currents with even the highest intensity of x-rays that it was feasible to employ, without rebuilding the electrometer system for measuring currents.

Tyndall and Powell[23] have since detected an ion in helium at low pressures and ages of 10^{-5} seconds of mobility 21. No such ion could be found in these experiments where the ion ages are of the order of magnitude of 0.04 seconds and are measured at atmospheric pressures.



Figs. 7 and 8. Experimental curves for positive ions in impure and pure helium.

Discussion and Conclusion

In the setting up of the theory for the experiment it was tacitly assumed that the amount of ionization was proportional to T. This is the case provided we are sufficiently far removed from the steady state between ion production and recombination. Although this seemed certain to be the case, it was verified by taking electrometer currents for different frequencies with the commutator so arranged as to collect *all* the ions of one sign formed. No change in the electrometer current with frequency could be observed. The lack of dependence of the position of the peak on slit widths and V_r was verified by taking runs on the same sample of gas at varying values of each. The x-ray beam was necessarily slightly divergent, but since the position of the peak is independent of d, this is of no importance. Diffusion of the ions during times of the order of magnitude of these measurements is negligible. The time constant of the chamber and electrometer system and high resistance to ground was of the order of magnitude of 10^{-5} seconds and entirely negligible. The plates of the chamber were parallel and of known distance apart to 1

---

[23] Tyndall and Powell, Proc. Roy. Soc. **A134,** 125 (1931).

percent. The commutator speed could be read and kept constant to approximately 2 percent. It was checked from time to time with a revolution counter and stopwatch. The advancing voltage was measured on an instrument calibrated against the laboratory standard. It is believed that the mobilities measured in this manner are accurate to 3 percent.

In spite of the chemical purity which has been maintained in these experiments, it is extremely doubtful if any of the measurements are those for a monomolecular ion moving in its own gas and the significance of the values obtained as indicating any real characteristics of the gas other than its inherent common impurities may be questioned. The experiments of Loeb have shown that the attachment by the ion of some foreign molecule takes place with extreme rapidity. Even when the gas purity is high, the times of measurement required in these experiments are sufficient to allow many impacts of ions and impurity molecules with an estimated purity of as high as 1 part in 10^5. The measurements in the case of hydrogen, which though presenting experimental difficulties because of the low ionization, is relatively easy to prepare with high purity, show the probable limits of this method of attack. In this case the predominating ion is one which has probably attached one or two fairly bulky molecules of impurity during the course of the measurements, but sufficient ions which have possibly formed monomolecular attachments (probably to water molecules) are present in detectable quantities. In the case of nitrogen and helium, the high values obtained show that at least some impurity which has been present in the earlier experiments has been successfully eliminated. What impurities remain, and what their amounts are it is impossible to say as their limits are below those of either chemical or spectroscopic detection. This is, of course, unfortunate, as it leaves one still uncertain as to the exact character of the particular ion—that is to say, its size—at these time intervals. It is therefore impossible to make adequate comparison with theory. The value of the mobility of the positive ion in helium alone begins to approach that demanded by the complete Langevin equation, and, as indicated by the recent experiments of Tyndall and Powell, may not even then represent a true He^+ in helium. It is therefore necessary to assert

TABLE I. *Values of the absolute mobility of normal gaseous ions.*

Gas	Source	Purity	k	k
Air	—	p	2.21*	1.59*
Oxygen	$KClO_3$	i (?)	2.65	1.71
Oxygen	$KMnO_4$	p	2.18*	1.58*
Oxygen	Tank	p	2.18	1.58
Nitrogen	NaN	i	1.60	e
Nitrogen	Tank	i	1.81	2.21
Nitrogen	Tank	p	2.09* 2.37	e
Hydrogen	Tank	p	8.2* 13.1	e
Hydrogen	Tank	i	6.7	9.6
Helium	Tank	i	7.1 14.0	e
Helium	Tank	p	17.0*	e

* Values for the more stable ion.

that while values such as found in these experiments serve to give useful absolute standard values for mobilities in pure gases as usually prepared, they are of little theoretical significance. They will, however, serve in all calculations requiring a knowledge of the mobility under ordinary conditions.

The results detailed above may be presented in a condensed form in Table I which gives the absolute values of the mobility of the normal gaseous ions in the gas in question. The method of purification and probable purity is also indicated. The starred values are those for the more stable ion to be found in the gas.

In conclusion it is desired to thank Professor L. B. Loeb, under whose direction the experiments were carried out, for his continual interest and invaluable suggestions concerning all phases of the work.