THE MOBILITY OF AGED IONS IN AIR IN RELATION TO THE NATURE OF GASEOUS IONS

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Abstract

The mobility of gaseous ions in air formed by intense x-radiation has been studied by the method of Tyndall and Grindley. The mobility of ions less than 0.08 seconds of age was found to be 2.21 cm/sec per volt/cm for the negative ion and 1.59 cm/sec per volt/cm for the positive ion in agreement with values observed by Loeb and by Tyndall and Grindley. A modification of the apparatus permitted the mobility of ions which had been aged for times up to 1.5 seconds to be studied. In this case a decrease in mobility was observed to values of 2.04 and 1.46 for the negative and positive ions after 1.5 seconds aging. The ionization chamber and source of ionization were the same as those employed by Luhr in recombination measurements. From the theoretical mobility equation of Langevin, the observed decrease in mobility cannot be correlated with the probable increase in ionic mass occurring in recombination measurements under the same conditions. A much larger decrease in mobility is predicted on this basis than is observed in these experiments.

Introduction

THE properties of gaseous ions have been studied for many years with diverse methods and under a variety of conditions, but the exact nature of the ion as it exists under normal conditions of temperature, pressure, and purity can hardly be said to be known. The early stages in the life of the ion (up to ages of the order of 0.01 second) are not, however, difficult to explain. The electron is first torn off from a neutral molecule in a manner dependent upon the ionizing agent employed, thus leaving the molecule positively charged. After a period of time depending upon its kinetic energy, the number of impacts with neutral molecules, and the attachment coefficient of the gas in question, the electron may attach itself to a molecule forming a negative ion. In the case of gases in which positive and negative ions are usually studied, this time of attachment is almost instantaneous and can be completely neglected in the further history of the ion. Exactly what takes place after the formation of the positive or negative monomolecular ion in this manner is not clear. The work of Erikson[1] and others shows that an aging effect takes place in the case of the positive ion causing a lowering to the ordinary values observed in the first 0.01 second. This aging appears to take place in a single step, and while observed for positive ions in air doubtless occurs for both ions in many gases, perhaps in shorter time intervals than observed by Erikson. Further, the work of Loeb[2] on mobilities in mixtures of gases has shown, depending on the nature of gases used, that either clustering of a statistical type or definite cluster formation may take place, the na-

[1] H. A. Erikson, Phys. Rev. **28,** 372 (1926).
[2] L. B. Loeb, Phys. Rev. **32,** 81 (1928).

ture of the change observed indicating the formation of clusters of but a few molecules. It is also possible that the initially charged molecule gives up its charge to other and larger molecules of impurities present. However, whatever processes occur, the result is a single class of ions in a given gas which may be termed the normal ion in that gas within a given time interval (i.e. 0.01–0.1 seconds). Regardless of their constitution, which may be monomolecular or a group of very few molecules (2–6), their properties, as shown by their mobility, apparently change very little in the first 0.1 second.

The work of L. C. Marshall[3] and O. Luhr[4] on the coefficient of recombination of ions, however, showed that after this time, certain of the ions were undergoing marked changes. These investigators, employing methods and apparatus of considerable accuracy, studied the recombination of ions in air and other gases at normal temperatures and pressures over periods of time from 0.001 second to two seconds after ionization. They found that in the first 0.0125 sec. the value of the coefficient of recombination is not constant, but decreases sharply from a value several times greater to 1.2×10^{-6}. This high initial value, which had been observed before, was attributed by Plimpton[5] and independently by Loeb and Marshall[6] to the initial non-random distribution of ions in the gas; the positive and negative ions being formed in pairs, recombine more rapidly at first than after separation caused by the thermal agitation of the neutral molecules. This phenomenon has been treated by Loeb and Marshall,[6] who showed that it followed from the predictions of the Brownian movement equations when the ionic fields had been taken into account.

Moreover, Luhr[4] found that, after this rapid initial drop, the value of α, the coefficient of recombination, did not become constant but continued to decrease, although at a very much slower rate. When the age of the ions was made as great as two seconds, values of α as low as 0.4×10^{-6} were found. Such a decrease in α could not be accounted for by any theory of recombination which assumes an ion of constant dimensions. The only tenable interpretation seemed to be that the ions changed their character with time by picking up products formed by the intense hard x-rays to which the gas had been subjected. Evidence that this explanation was the correct one was found in the case of hydrogen in which no change in the value of the recombination coefficient with time was found. In this case no formation of impurities analogous to the formation of ozone, nitric oxides, H_2O_2, and the like, as in mixed gases, could take place. Certain impurities, e.g. water vapor, are also always unavoidably present in small amounts which could combine to form nuclei with the above chemical reaction products. On this supposition, the smaller and faster ions recombine first leaving the slower and heavier ions to recombine more slowly. The conclusions to be drawn from such a decrease in the recombination coefficient will be considered later, but it may be noted

[3] L. C. Marshall, Phys. Rev. **34,** 618 (1929).
[4] O. Luhr, Phys. Rev. **35,** 1394 (1930).
[5] S. J. Plimpton, Phil. Mag. **25,** 65 (1913).
[6] L. B. Loeb and L. C. Marshall, Jour. Frank. Inst. **207,** 371 (1929).

that α is inversely proportional to the square root of the mass of the ion; hence an increase in mass would very properly result in a lowering in the rate of recombination.

The very pronounced character of this effect in the case of ionic recombination made it obvious that the loading up occurring under these conditions must affect the mobility of ions aged over similar periods of time. Thus the existence and magnitude of a change in the mobility of ions formed under the same circumstances and in gases of the same degree of purity as those used in recombination measurements becomes of significance in gaining some insight into the nature of the gaseous ion.

It was for the purpose of studying these problems that the experiments about to be described were carried out. The first attempts were made with a modification of the simple Rutherford alternating current method[7] for mobility measurements with x-ray ionization. The construction of the apparatus, however, was such that "asymptotic feet" in the curves obtained could not be avoided, and the resolving power was, therefore, very small as is the case with all A.C. methods of this type. Hence any small change in mobility with age was undetectable.[8] In order to establish definitely the value of the mobility of ions produced in air by x-rays at normal temperature and pressure, and also to study the behavior of ions formed under such conditions as a function of their age, the apparatus was arranged so that the *absolute method* developed by Tyndall and Grindley[9] could be employed. This method is capable of yielding quite accurate and consistent results and can easily be modified to study the effects of aging. It also has the highest resolving power of any accurate method.

METHOD

The essential features of the apparatus employed are shown in Fig. 1. A Coolidge x-ray tube, run at 80 K.V. and 4 m.a. pure D.C. under conditions particularly designed for extreme constancy of voltage and current, is used as the source of ionizing radiation. The beam of x-rays passes through two meters of air and a series of defining slits before reaching the chamber; the width and position of the beam in the chamber can thus be sharply determined. Perpendicular to the beam and in its path is a heavy brass disk from which a variable sector has been cut. As this disk is rotated x-rays are intermittently cut off or permitted to pass through to the chamber. Affixed to the same axle with the disk is a commutator having a single metal segment; the angular width of the latter, as well as its position with respect to the sector cut from the disk, may be varied. Two brushes, separated by an angle slightly greater than that of the commutator segment, make contact with the commutator surface. These brushes are connected to the positive and negative terminals of a high potential battery bank, some point near the middle being grounded. As the commutator revolves, an intermittent alternating potential,

[7] Rutherford, Phil. Mag. **44,** 422 (1897).
[8] O. Luhr and N. E. Bradbury, Phys. Rev. **36,** 1394 (1930).
[9] Tyndall and Grindley, Proc. Roy. Soc. **110,** 341 (1926).

shown in Fig. 2, is applied to the lower plate of the ionization chamber. By changing the relative setting of the commutator and sector opening, the phase position of the x-ray flash in the chamber with respect to the potential on the plates may be varied. When neither of the brushes is in contact with the segment, the lower plate is maintained at zero potential by means of a half megohm resistance to ground; at such times the space between the plates is field free.

Ionization takes place between two parallel brass plates mounted on amber insulators in a heavy brass chamber with aluminum windows. The plates are approximately 10×20 cm and 7.5 cm apart. The upper plate, upon which the ions are collected, is surrounded by a guard ring and connected to ground through an electrometer. The chamber has a heavy glass top (which serves as a mounting for the upper plate) sealed on with stopcock grease. Vapor from the grease, however, is prevented from coming in contact with the gas in the

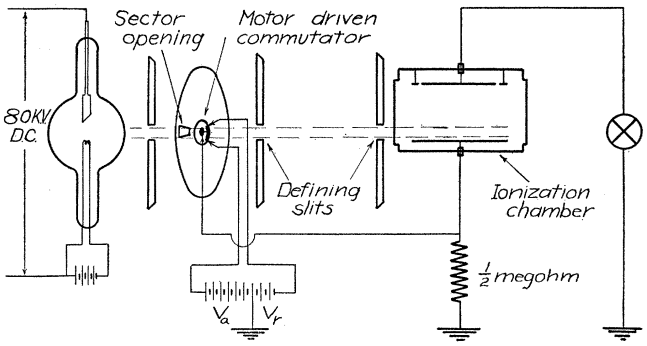

Fig. 1. Diagram of apparatus.

chamber by a special double seal and groove. A purifying system for the gases used is connected to the chamber, and the whole may be evacuated to 10^{-4} mm.

Standard technique was observed in the purification of the gases which were passed over $CaCl_2$, NaOH, and P_2O_5, and through liquid air traps. Before taking any measurements, the chamber was first pumped out as completely as possible, flushed out with purified gas, and finally refilled with pure gas to atmospheric pressure. No difficulty was experienced in obtaining gas of sufficient purity to give the usual values of mobility.

The lead defining slits outside the chamber are adjusted to give the beam a width of a centimeter or less and a position just grazing the lower plate. The commutator is set so that the x-ray flash occurs approximately in the position γT of the cycle. (Fig. 2 shows the cycle of potentials applied to the lower plate.) The values of the potentials are adjusted so that V_r, the retreating potential, is approximately equal to $1.6 V_a$, the advancing potential. This is done in order that V_r, acting during the time βT, may be sufficiently great to clear the chamber of all ions.

The operation of the cycle may now be considered in the following man-

ner: Let T be the time of one complete commutator revolution. Fractions of this period will be denoted by αT, βT, γT, and δT as in Fig. 2. During the time γT, while the x-ray flash is in the chamber, and for a time δT afterwards, the ions are acted on by the field V_r. This field acts in such a direction that those ions whose mobility is being measured are drawn towards the lower plate. Hence at the end of δT, only a thin sheath of the originally formed ions (depending upon the magnitude of $(\gamma+\delta)T$) remain in a layer just above the lower plate. A potential of the opposite sign and of magnitude V_a is then applied to the plates, and the ions being studied are drawn towards the upper plate for a time αT. Ions of opposite sign are drawn back to the lower plate and cleared from the volume. Thus *if αT is sufficiently long*, all ions not caught by the lower plate at the conclusion of αT, will be caught by the upper plate and produce a deflection of the electrometer. If, however, αT is not long enough to draw all the ions across the space between the plates, the lower

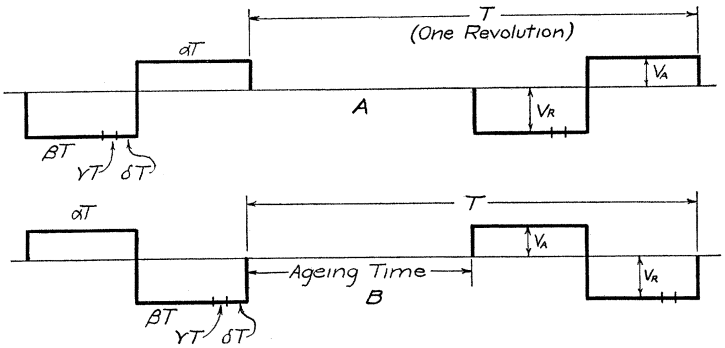

Fig. 2. Cycle of potentials applied to lower plate by the commutator. Ions are formed during γT, drawn toward lower plate during γT and δT, and drawn across volume to upper plate during αT. Volume cleared of all ions not caught at plates during βT. "A" shows cycle for *new* ions and "B" the cycle for *aged* ions.

part of the sheath, or even all of it, will escape capture at the upper plate. All ions not caught at the upper plate at the conclusion of αT are swept out of the volume by V_r acting during βT. The volume is thus prepared for the repetition of the cycle, which is repeated at each revolution of the commutator and disk.

The number of ions reaching the upper plate (and hence affecting the electrometer) during a cycle will depend upon the speed of rotation of the commutator. If the speed of rotation is too slow, δT will be sufficiently long to permit V_r to remove all the ions from the sheath before V_a can operate, and the electrometer current will be zero. On the other hand, if the commutator speed is too high, αT will not be long enough to allow V_a to draw any of the ions not caught during δT to the upper plate, and again the electrometer current will be zero. Between these limiting speeds a maximum of current to the electrometer will occur. Tyndall and Grindley[9] show that the position of this maximum is given by

$$\alpha T = D/kV_a$$

where k is the mobility of the ions, D, the distance between the plates, α the fraction of the commutator covered by the segment, T, the period of one commutator revolution at maximum current to the electrometer, and V_a the advancing field strength. It is seen that the expression is independent of the retarding voltage, V_r, the width of the beam, and the time of retardation. These facts which arise from the mathematics of the cycle, were amply verified by experiment.

Since α, β, γ, and δ are merely constant fractions, the times during which the potentials act are varied by varying T. This is accomplished by driving the commutator and disk with a D.C. motor whose speed is variable and determined by the voltage from a direct connected tachometer magneto. Speeds are thus varied and kept constant at different points with considerable ease. A lead shutter is provided which may be interposed between the x-ray tube and the brass disk. X-rays can thus be kept from the chamber while the disk and commutator are being brought to constant speed. When this shutter is removed, ionization takes place in the chamber and an electrometer deflection is observed whose rate is proportional to the number of ions caught by the upper plate during each cycle. Changing to another speed and repeating the process gives a different rate of deflection, and a series of points taken in this manner may be plotted from which the position of the maximum rate of deflection is determined. Both V_a and V_r as well as α, β, γ, and δ are kept constant while a run is being taken. The value of the speed, N, at the point of maximum current makes it possible to calculate $T\ (=1/N)$ and with this the mobility k may be determined from the other constants of the experiment.

Fig. 2 shows the two possible adjustments of the commutator system. In (A) αT follows immediately upon δT and so-called "new" ions are studied. In (B), however, the entire insulated section of the commutator is allowed to pass after δT before the ions are drawn across during αT. Ions are thus permitted to age in the gas for that length of time, after which their mobility is measured. Two types of measurement are thus possible, and a change in mobility with age should result in a shift of the position of the maximum of the curve if other conditions are kept the same.

In actual practice α was either 1/4 or 1/8 and γ and δ 0.0194. Speeds of rotation were of the order of magnitude of 15 to 300 r.p.m., and could be measured with an accuracy of 0.5 percent with the tachometer. V_a varied from 10 to 50 volts/cm depending upon the conditions of the experiment, and was read upon a 0–300 volt instrument which had been checked against the laboratory standard. In order to check upon any change of mobility in the gas during the time of measurements, runs were made in the following way: the commutator was set in the position to study *aged* ions, and sufficient readings taken to determine the position and shape of the maximum; the commutator was then shifted to the position for *new* ions and the position of the peak again determined. If this latter value did not give the standard mobility determined from a long series of experiments on new ions, the readings were rejected. This was done in order that spurious effects resulting from an impure sample of gas might be eliminated, and was very rarely necessary. When

the commutator speed was very slow, some aging took place during αT. This was taken into account in making the check runs on new ions.

Results

Measurements were carried out on both positive and negative ions under a variety of experimental conditions in an effort to determine the conditions of greatest resolving power consistent with maintaining measurable electrometer currents. Changes in any of the factors not contained in the equation

$$\alpha T = D/kV_a$$

were never observed to influence the position of the peak, but only the magnitude of the current and the slope of the curve. The average of all measurements on positive ions less than 0.08 sec. old gives 1.59 cm/sec. per volt/cm for the mobility of the positive ion in air at 20° and 760 mm. Under the same conditions the mobility of the negative ion in air is found to be 2.21 cm/sec per volt/cm. These values are in good agreement with those obtained by Loeb, and by Tyndall and Grindley[9] with absolute methods. The consistency of the values obtained is shown by the following series of values given by ten consecutive runs on different samples of gas. The mobility k was found to be for the

Negative ion		*Positive ion*	
2.21	2.18	1.56	1.61
2.20	2.21	1.58	1.56
2.20	2.21	1.56	1.58
2.19	2.21	1.61	1.58
2.22	2.22	1.61	1.60

It is seen from these values that the normal ions formed by intense hard x-radiation are apparently identical with ions formed by photoelectric and radioactive methods—a result quite to be expected.

After the value of the mobility of positive and negative ions of short age had been established, experiments were carried out on ions which had been aged for increasing intervals of time. This was done in the manner described above. Mobility curves taken under these conditions yielded quite different results. A series of curves for negative ions in air is shown in Fig. 3. It is seen that as the age of the ions is increased from 0.04 to 0.9 sec. the mobility drops from 2.22 to 2.04. This decrease, as evidenced by the shift of the point of maximum rate of electrometer deflections is accompanied by a distinct broadening of the curve at its maximum. This flattening of the curve seems to indicate the presence of a range of mobilities, although the resolving power of the apparatus is not sufficient to distinguish between two close groups. Unavoidable experimental variations in the setting of the commutator caused slight changes in the slopes of the curves, but the change itself and its approximate magnitude are very apparent. A similar series of curves was observed in the case of positive ions in air. In this case the lowest value observed was 1.46 after 1.3 sec. aging. Greater ages than this could not be studied as the very slow commutator speed and decreased electrometer currents (owing to recombination and loss of ions by diffusion) made measurements uncertain.

The possibility of attributing the observed effect to some defect in the apparatus or method has been carefully considered. The effect of space charge due to the cloud of ions of opposite sign to those measured has been shown to be negligible. During the γT and δT parts of the cycle, these ions are driven away from the lower plate and remain in the volume throughout the aging period. The resultant effect of this cloud would be to draw the ions measured away from the lower plate with a consequent decrease in effective D. Hence an apparent *increase* in mobility would be observed. However, minimizing any effect of space charge by narrowing the entering beam to 3 mm gave no change in observed mobilities. Further, a delay in the charge leaking off the lower plate through the half megohm resistance would cause αT to be longer than calculated when new ions were being measured. This would result in high values for new ions and a consequent apparent decrease in the mobility of aged ions. However, the fact that the time constant of the system was only

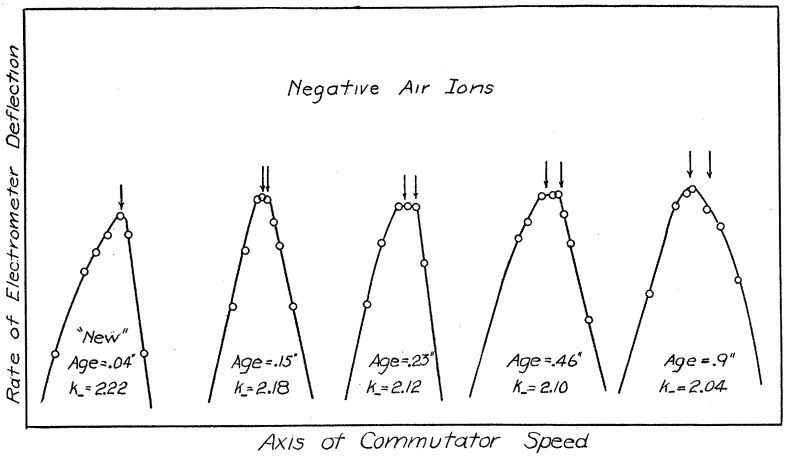

Fig. 3. Curves showing effect of aging upon negative ions in air. Right hand arrow indicates *normal* positions of peak for *new* ions. Left hand arrow indicates position of peak taken for calculation of *aged* ion mobilities.

10^{-3} seconds speaks against this possibility as does the fact that the substitution of a lower resistance did not change the values of mobility previously obtained. Furthermore, a definite gap of several degrees was left between the δT and αT phases in the case of aged ions to give the same conditions as exist in the new ion measurements.

Discussion of Results

It has been pointed out by Luhr that the only plausible explanation for the continued decrease in the value of the coefficient of recombination is one which assumes some of the ions to load up with impurities formed by the intense x-radiation. From J. J. Thomson's theory of recombination the magnitude of this increase in mass which would give the observed value for the recombination coefficient was calculated, and found to be roughly ten times

the original mass of a new ion. Such a change in ionic mass must necessarily result in a considerable increase in ionic dimensions, though the exact magnitude of this increase cannot be calculated without much more exact knowledge as to the nature of the clustering and the molecules involved. At any rate, the increase in the radius of the ion will cause a decrease in its mean free path, neglecting any effects of the charge on the ion. Moreover, this change will be more pronounced the fewer the molecules in the cluster. Now all mobility equations, with the exception of that deduced by Loeb,[10] which employs mass points as ions, contain either the mean free path directly, or a term which is closely related to it or to the ionic radius. The effect of this term in the equations is either one of proportionality or of even greater weight in the case of the rigorous Langevin equation. Hence a change in the mass of the ion which would double its radius and halve its mean free path would cause a theoretical decrease in the mobility to at least half the normal value. Yet such an increase in the radius of the ion is of the order of that predicted on recombination coefficient measurements. Such a decrease has not been observed either in these experiments, or in the less rigorous experiments of Luhr and Bradbury. It should be pointed out that, in the mobility measurements carried out by the method of Tyndall and Grindley, the majority of the positive and negative ions are not aged in each other's presence, so the selective effect of recombination in removing the smaller faster ions is not wholly operative. Hence, unless all the ions age at the same rate, a sharp effect would not be obtained. The experiments of Luhr and Bradbury, on the other hand, which employed the Rutherford alternating current method, permitted the ions to be aged together so that recombination of the faster ions could take place before the mobility measurements were made. Although this method was of insufficient resolving power to detect small changes in mobility, a change of greater than twenty percent would have been readily apparent. The negative results thus obtained, even with the advantage of selective recombination, preclude all possibility of any change in mobility with age to a degree at all comparable with that predicted by theory. Hence if the increase in ionic dimensions takes place as seems probable from recombination measurements, this discrepancy between theory and experiment in the case of ionic mobilities must point to some important and inherent defect in even the most rigorous theoretical equations which have so far been developed. The extent of the inadequacy of the mobility equations and the error in the assumptions involved will be considered in another paper.

In conclusion the author wishes to express his sincere appreciation of the interest and suggestions of Professor L. B. Loeb in the carrying out of these experiments.

[10] L. B. Loeb, Kinetic Theory of Gases, McGraw-Hill 1927, p. 468.