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THE VELOCITY SPECTRUM OF NORMAL GASEOUS IONS IN AIR AND THE PROBLEM OF IONIC STRUCTURE

By Leonard B. Loeb and Norris E. Bradbury
Department of Physics, University of California

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Abstract

A consideration of the evidence as to the existence of the so called spectra of ion mobilities recently reported by various observers combined with experimental results of the writers indicate that while ions at ages of from 0.5 to 2.0 seconds show marked ranges of mobilities this is not necessarily the case for the normal ions studied over shorter time intervals. It is shown from the recent work of Loeb and the more recent results of Luhr that ions probably consist of one or two molecular addition products of an active type of molecule which pick up the original charged carrier as a result of electrochemical forces depending on the molecular constitution and the sign of the charge. Such products may be present in traces as impurities or may be produced in air by the ionizing agent. The rate of formation of the velocity spectrum therefore will depend on the relative stability of the various ion addition products and the relative and absolute concentrations of the active molecules. Hence the appearance of such a spectrum will vary with the age of the ions and the experimental conditions. It is believed that the greater portion of the lowering of the mobility of the ions below the theoretical value deduced by the assumption that the neutral molecules are not attracted by the ions is due to the usually assumed force of dielectric polarization as utilized in the complete Langevin equation. While the law utilized is not accurate for close approach of ion and molecule (i.e. to one or two atomic radii) it suffices at greater distances. The effect of the electrochemical combinations mentioned above are superposed on this general attraction and lead to an explanation of the differences of positive and negative mobilities and to the three fold lowering of the recombination coefficient on long aging without a very significant (10 percent) change in the ionic mobility recently observed by Luhr and Bradbury.

Introduction

In A recent article one of the writers (Loeb)[1*] pointed out the necessity for a decision on the question of the reality of the existence of what might be termed a spectrum of mobility among the normal positive and negative gaseous ions. In recent years there have been many papers which on various grounds indicated the possibility that the gaseous ions usually measured had instead of a unique mobility a sort of distribution curve of mobilities confined between narrow limits and centered about some more probable value.[2,10] The *critical* study of the problem has however been confined to but a few observers.[11,12] The diverse results obtained and conclusions drawn, (extending from the notion of a large number of separately resolved mobilities[3,5] through the notion of a continuous band or spectrum of mobilities[6,7,8,10,11,12,18] down to that of a unique mobility,[1] have indicated the existence of a lack of

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[*] Numbered references appear in bibliography on page 1728.

critical control in some cases. They have further indicated a rather wide range of experimental conditions sometimes offering obstacles to any careful critical investigation and at other times causing such a real difference in physical conditions as to make a comparison of conclusions impossible.

In view of the fact that the experimental work of the writers' appeared at least in part to be in conflict with the very careful work of Zeleny[11] and of Fontell[12] a critique of the writers' work was undertaken with results which will constitute a portion of this paper. The conclusions reached from this analysis together with other recent results including those of Luhr[14] make possible a general interpretation of the nature of gaseous ions which serves to clarify a number of hitherto obscure points. It is the purpose of this paper to present these results and conclusions.

THE EXISTENCE OF A MOBILITY SPECTRUM

A. Previous investigations

The first notion as to the existence of mobility spectra among the ions doubtless arose in the study of the slow or Langevin ions whose heterogeneous nature led to the observation of such spectra.[2,3,4] The application of this concept to the case of normal ions in air doubtless began as a result of more recent modifications of the air blast methods to normal ions,[2,3,17,18] although as early as 1915 Haines[13] reported to have observed separate groups of normal ions in H_2. The air blast methods utilized what was assumed to be a narrow slab of ionized air and this when caught on a collector of narrow but finite extent as a result of a transverse electrical field led at once to current-potential, or current-down stream distance curves of such shape and width that the assumption of a spectrum of mobilities was inevitable. No critical study of these curves, however, was made and little significance was placed on such curves until the experiments of La Porte[6] using a sort of Fizeau toothed wheel method. This study which was a pioneer investigation in which a critique of the various sources of error was made gave a continuous spectrum of a wide scope of mobilities in air for both ions. In the method ions generated by alpha particles from an intense polonium source were driven through a region between two plates with constant field and received at the other end by an ion collector. The entrance of the ions into the measuring field and their reception at the collector after the lapse of a given time was regulated by a rotating disk in the apparatus having slits which passed the slits in the entrance and exit ends of the constant field. The variation of ion current to the collector as a function of speed of rotation, or as a function of the constant field, gave curves starting at zero rising to a maximum and falling again to zero. The method in itself was bound to give curves of this sort. The extent of the velocity, and hence mobility, range of ions studied was however such as to indicate that there was a real range of mobilities present. In view of the fact that the range observed by La Porte was markedly greater than that observed by the later observers[11,12] using methods in which the control of disturbing variables is simpler; in view of the impurities present due to large quantities of ebonite and the circulating action of the rotating shutters on the gas; finally owing to what appears to have been an inadequate correction for diffusion it is doubtful whether too much reliance can be placed on this apparent spread as evidence of a spectrum, although the results appear to point significantly towards the existence of such a spectrum.

Following La Porte's work there have been published two further papers utilizing what is essentially a Fizeau method. In these cases, however, the shutters were electrical instead of mechanical. These are the experiments of R. I. Van de Graaf[19] and of Tyndall, Starr and Powell.[8] Both groups of workers admitted the ions to the constant field and from it to the collecting chamber by means of properly timed alternating potentials, actuated by commutators or transformers. Unfortunately in both these experiments the sharpness of the boundaries of the ionized groups of gases entering the field were limited by the fact that the auxiliary alternating fields used interacted with the fixed driving field through gauzes. Despite certain criticisms leveled at the explanation[21] it is an experimental fact that two fields of opposing sign so interpentrate through the meshes of a gauze, (in ion mobility work large mesh gauzes are generally used because of the high absorption coefficient of finer gauzes for the ions), that the equipotential surfaces may well bulge considerably in one sense or the other through the gauzes. Hence at the zero of time when the ions start moving they do not start at the same level but may have a distribution extending a mm or two ahead of or behind the gauze, depending on whether auxiliary or driving field is the greater. The ions are only able to reach to the equipotential surface during the retarding field and are allowed to accumulate there during that period except for diffusion. Such nonplanar distributions of ions act materially to distort and enlarge the extent of the velocity spectra observed. This difficulty was unquestionably recognized by Tyndall, Starr and Powell, who did not attempt to ascribe too much significance to the width of their ion spectrum.

More recently Fontell[12] in his doctor's dissertation has made a most careful study of the reality of the existence of a mobility spectrum among the ions in air. His work was exceedingly carefully controlled and in principle constitutes a method which is perhaps one of the most sensitive used. In this method a thin beam of x-rays ionizes the air near one plate of a condenser system for a short time interval, the ions being in a field. Thereafter the ionized air is driven by the field to a collecting electrode where the current due to the ions is measured as a function of the time by an amplifying system and galvanometer devised for other purposes by Wassastjerna. Under these conditions the ion group is spread apart by the field in transit so that at first only the fastest ions reach the collector but gradually the slower ones and some faster ones liberated later in the cycle reach the collector. From the record of the galvanometer deflection as a function of time by means of a complicated reduction system, Fontell obtains the actual mobility spectrum of the ions caught. The work carefully corrects for diffusion, self repulsion, width of x-ray beam and similar effects. It covers ages of ions ranging from 0.3 to 4.0 seconds and in this sense coincides well with the ionic age range involved in Zeleny's work.

Another most careful and critical of the recent investigations is that of John Zeleny,[11] using ions in air from the room with water vapor present, an age range of the order of 1 second and an air blast method. In this investigation most sources of error have been critically analyzed with the possible exception of the action of the moving air stream in aspirating more ions (and perhaps a larger spatial extent of ionization) into his chamber than is evident from the measurements. When the spectrum obtained using mobilities is compared to that due to the geometrical considerations and corrections are made for diffusion there is in these ions an unexplained spectral width indicating ions existing in air with mobilities spread from 1.03 to 1.48 for the positive and 1.68 to 2.18 for the negative ions. In view of the fact that the corrections are as great as the observed differences perhaps too much emphasis cannot be placed on the *exact* values of the spread of the spectrum. That there definitely appears to be a spectrum is, however, most significant and it coincides in general extent and for the same ion age with that inferred by Fontell from his data.

B. Investigations of the writers

One of the writers (Loeb) has in the past been one of those who have remained somewhat skeptical of the reality of a mobility spectrum. The recent results of this writer[22] on the change of the mobilities of Na^+ ions with time and certain results in this laboratory to be mentioned have led to a more critical analysis of all the evidence at hand, with the result that this article has been written. The reason for the skepticism lay in the observations of Loeb[23] on mobilities of photoelectrically generated negative ions using the original Rutherford A.C. method under carefully controlled conditions. In this method if ions of a unique mobility k exist the ratio of the A.C. ion current i to the half saturation current i_0 can be deduced by theory to be given by $i/i_0=(V-V_0)/V$, where V is the potential applied to the condenser and $V_0=D/kT$, where T is the half period of the square wave and D is the plate distance. The actual i/i_0 curves obtained experimentally on ordinary dried air in 0.1 second or less, under these conditions agreed so closely with theory that the possibility of the existence of more than a single mobility seemed rather remote. The recent work of Fontell and Zeleny led, however, to an investigation of the resolving power of this method with the following results.

One can assume that ions are generated with mobilities ranging from k_1 to k_2 distributed equally over this range of mobilities. An alternating potential of amplitude V is placed across the plane parallel plates separated by D cm. Ultraviolet light is liberating ions continuously from the one plate at a rate of i_0 ions of all sorts per second. The field driving the ions across D is on for a time T, after which ions liberated too late in the phase, or of mobility too low to reach D are swept out of the space by a strong reverse field. It is now necessary to see how many ions the upper collecting plate will collect as a function of V, T and D. The current i relative to the saturation current i_0 in this case compared with that given for a single class of ions will then give an idea of the resolving power of the method. To make such a comparison one may reason as follows.

If ions are uniformly distributed in a band between k_1 and k_2 (an assumption probably contrary to fact but producing negligible errors as far as this question is concerned) the i_0dt ions emitted in dt seconds will in a time t be distributed over an area $V(k_1-k_2)\ t\ dt$ in the x, t diagram of Fig. 1. Here V is the field strength across the plate S. The fast ions k_1 will be at $x_1=Vk_1t$ and the slowest ions at $x_2=Vk_2t$. The density ρ of ions in this strip dt wide will then be $\rho=i_0dt/V(k_1-k_2)t\ dt$. In the ensuing intervals dt beginning at $t=t$ and going back to $t=0$ the successive areas containing the ions in the $x-t$ plane will present the appearance of the shaded triangle AOB indicated in the Fig. 1. From $x_1=Vk_1t$ to $x_2=Vk_2t$ the ions will be contained in a triangular element. ABC. Within this element the number of ions reaching a certain distance D will be given by the area of the triangle intercepted between $x_1=Vk_1T$ and $D=x=k_1Vt$. Hence the *initial* increase of charge received by a plate at a point D will be parabolic beginning at a mobility k_1. At a time such that $D=Vk_2T$ all the ions in ABC will have reached D. From then on the number of ions is distributed in the space time diagram inside the triangle bounded by OBC. At any value of x below $x_2=Vk_2T$ the number of ions is constant and equal to i_0. The curve for the quantity reaching D as a function of t between $D=Vk_1T$ and $D=Vk_2T$ is then given by the integral

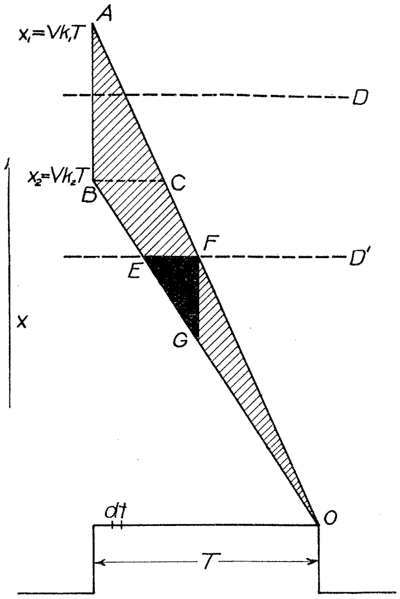

Fig. 1.

$$Q=\int_{D/Vk_1}^{T}\frac{i_0(Vk_1t-D)dt}{V(k_1-k_2)t}$$

which includes the density of ions as a function of t.

$$Q=\frac{i_0}{V(k_1-k_2)}\left[(Vk_1T-D)-D\log\frac{k_1VT}{D}\right].$$

As $Q/T=i$ and calling $k=D/VT$ between limits $k_1>k>k_2$ we have

$$i/i_0 = \frac{1}{k_1 - k_2}\left[k_1 - k\left\{1 + \log\frac{k_1}{k_2}\right\}\right] \tag{1}$$

This gives i/i_0 as a function of the variable k between the limits k_1 and k_2. Here k can be espressed as a f (D, V or T) and for each k the i/i_0 can be expressed as a f (V) by calculating the value of k corresponding to each V for D and T constant. Beyond time intervals for which ions of mobility k_1 and k_2 reach D we can express the quantity Q in terms of the area $ABEF$ represented by the smaller distance D' in the figure. This area is the area of the whole triangle ABO less the area of triangle OEF, or better the area of triangle ABO less the area of triangles OFG and GEF. Hence we can write that for a plate D' the quantity is given by

Area $ABO = i_0T$

Area $OFG = i_0(D'/k_1V)$

Area $EFG = \int_{D'/Vk_1}^{D'/k_2V} \frac{i_0(D' - Vk_2t)dt}{V(k_1 - k_2)t} = \frac{i_0}{V(k_1 - k_2)}\left(D\log\frac{k_1}{k_2} - D - D\frac{k_2}{k_1}\right).$

Whence the quantity Q received by D' under these conditions is

$$\begin{aligned} Q &= i_0T - \frac{i_0D}{k_1V} - \frac{i_0}{V(k_1 - k_2)}\left(D\log\frac{k_1}{k_2} - D - D\frac{k_2}{k_1}\right) \\ &= i_0T - \frac{i_0D}{V(k_1 - k_2)}\log\frac{k_1}{k_2}, \text{ whence } i = Q/T, \\ i &= i_0\left(1 - \frac{D}{VT(k_1 - k_2)}\log\frac{k_1}{k_2}\right). \end{aligned} \tag{2}$$

Putting $k=D/VT$ between the limits $k_2>k>0$ we get for the current ratio after the slower ions begin to cross the relation

$$i/i_0 = 1 - \frac{k}{k_1 - k_2}\log\frac{k_1}{k_2}\cdot$$

At $k=k_2$ the Eqs. (1) and (2) are the same. As k_1 approaches k_2 the Eq. (2) becomes $i/i_0=1-D/kTV$ which is the simple equation $i/i_0=(V-V_0)/V$ given above for a unique mobility.

An idea of the resolving power of this Rutherford A.C. method as applied to the case of ions with mobilities lying between $k_1=2.2$ and $k_2=1.6$, as observed by Fontell for negative ions is shown in Fig. 2. There i/i_0 as computed from the above is compared with the curve i/i_0 computed for ions of a single $k=1.9$, the average value. It is seen that the difference is not very marked and the resolving power is small. In Fig. 3 is a typical result, previously published[23] obtained by Loeb for nearly identical conditions for dry air $T=0.0275$ at atmospheric pressure. D was 1.41 cm. in this case and negative ions from a plane photoelectric source were used. The observed curve in this case shows no asymptotic foot within the limits of accuracy of the method.

As Zeleny[11] correctly points out, these results should have been corrected for diffusion. However, the correction becomes small in time intervals of 0.02 seconds and in any case the presence of notable diffusion would have yielded asymptotic feet. This may in part account for such feet at longer times of passage as observed.

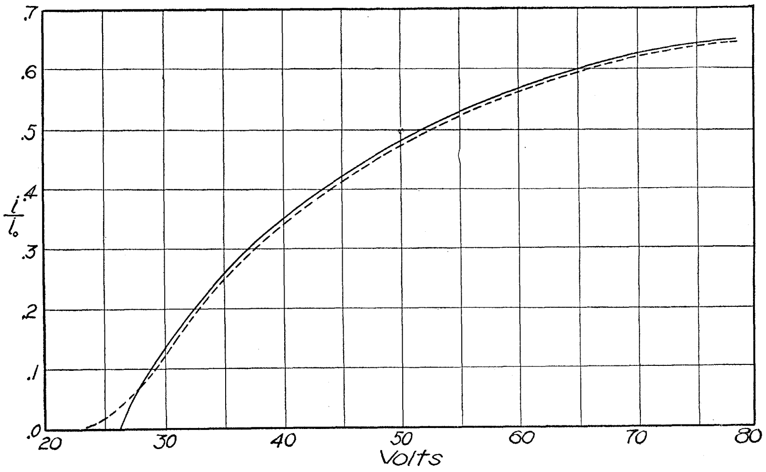

Fig. 2.

It appears from the above that the method as used is a highly insensitive one for indicating the existence of mobilities spread over a more limited range of values. Perhaps the best conclusion that can be drawn on the basis of this work is that with *dry air*, *photoelectric ions* (no great amount of chemical products e.g., ozone and nitric oxides are formed by the ionizing agent) and in *shorter time intervals* the spread of the mobility spectrum is even without

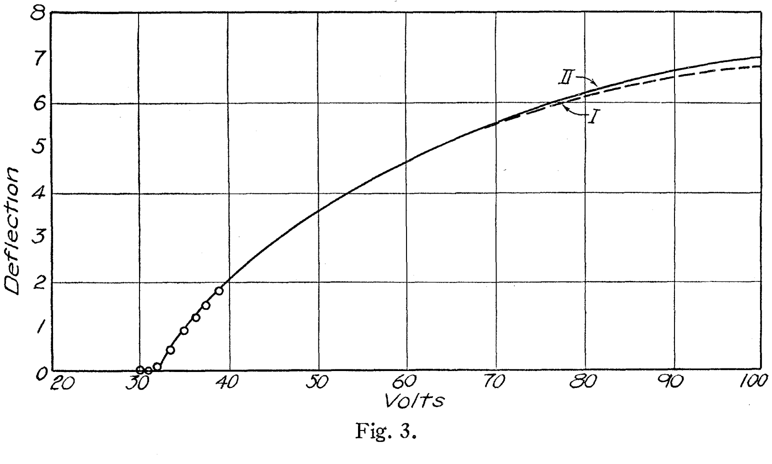

Fig. 3.

corrections for diffusion distinctly less than that observed by Zeleny and Fontell at *longer* intervals of time and under different conditions.

There is a chance that by using a differential method, i.e., measuring the *current at each instant* during the cycle instead of the *integrated current*, as was done by Fontell, a much more significant result might be obtained. This is, however, at present experimentally impossible. A better result than the one above could be obtained by using an ionizing flash of ultraviolet light which is short in duration compared to T. Such a curve could be analyzed to get the form of the distribution if with very sensitive measurements the derivative of the curves obtained in this fashion were determined graphically. Such an experiment is to be undertaken in the near future.

An almost exact analogue of this proposed method has been carried out by J. L. Hamshere[10] in an admirable investigation. Hamshere used ions generated by polonium and driven into the measuring field by means of an auxiliary gauze and plate in the generating chamber. The apparatus was so arranged that the auxiliary field as used in the Franck modification of the Rutherford A.C. method was put on so that just at the beginning of the phase driving the ions from the origin towards the collecting plate this auxiliary field was put on for but a short time. This gave a burst of ions through the gauze into the measuring field which then was spread into a velocity spectrum by the field. The current reaching the upper plate then depends on the distance D, the duration T of the positive or driving field acting on the ions before the field reversed, and the field V applied. The process is then repeated. This method except for the use of polonium as an ionizing agent and the gauze, instead of a photoelectric source is the one suggested above. However, in spite of Hamshere's use of the high auxiliary field, as had been suggested by the writer,[23] to avoid the effects of the initial displacement of the ions due to interpenetration, (his gauzes had wide meshes of 1 mm) it is most probable that much scattering of the origin of the ions at the beginning of T must have resulted from this procedure. Further the intense polonium ionization as we shall see produces ideal conditions for formation of products which are active on the ions. Again no attempt at correction for diffusion was made. Finally one of the writers in all his work with methods of this type never observed the type of intercepts obtained by Hamshere on the high mobility side of his curves which are neither intercepts of the abrupt type to be expected from unique mobilities, nor intercepts of a truly asymptotic character which would be expected. It appears as if some spurious effect must have subvened to cause these curves. Perhaps this was due to accumulations of ions at the equipotential barriers in the meshes while the reverse field was on. The curves obtained by Hamshere were then graphically differentiated to give the mobility spectrum. In general they agree with the type of curves of Zeleny and Fontell. They appertain, however, to ions of much shorter life than the ions of the latter observers. In view of the conditions mentioned and in view of Bradbury's results to be discussed it appears to the writers that while Hamshere has devised an ideal method in principle, the work should be carried out with the photoelectric method before too much credence can be placed in an interpretation of these curves as representing a true velocity spectrum of ions over short time intervals.

While the results of Loeb on the absence of a broad mobility spectrum over short time intervals are not entirely convincing, even admitting the possible sources of difficulty in Hamshere's work, the conclusions arrived at are substantially borne out by recent work of Bradburg[16] using the method of Tyndall and Grindley.[24]

The mobility of gaseous ions in dry air of considerable purity and also of normal purity has recently been investigated by one of the authors (Bradbury). In these experiments the alternating current method devised by Tyndall and Grindley[24] with intense x-ray ionization was employed. This is a "peak" method, and the mobility is calculated from the position of the maximum in the ion current curve as the time of alternation of the field is varied. The mathematical theory of this method has been developed by Tyndall and Grindley. It appears from the integrals relating the ion current to the time of one complete cycle that the sides of the peak should be straight lines, intersecting at a point, by the position of which a mobility is uniquely determined. In practice this is not always the case. Even when new ions are studied, the sharp peak will be slightly rounded off by diffusion, self-repulsion, and other factors arising from the measuring instruments themselves. In addition to this if the time, the time $(\delta-\gamma)T$, of retardation of the ions being measured towards the lower plate is too great, or the position of ionized band between the plates is too near the upper plate, at the higher and lower frequencies of alternation, ions of the opposite sign will begin to reach the upper plate. This causes the measured current to decrease more rapidly than

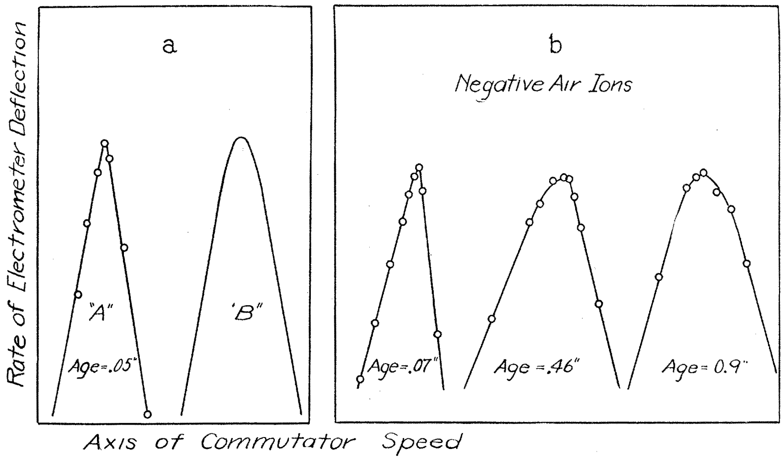

Fig. 4. (a) Curve A is a typical curve for positive ions of age equal to 0.05″ giving a value for the mobility of 1.60. Curve B is the theoretical curve to be expected if the mobilities were distributed over a ten percent range on either side of the accepted value. (b) A series of typical curves for negative air ions of increasing age, showing the change to a type of curve corresponding to B in Fig. 1 and giving evidence of a spread of mobilities.

that predicted by the simple Tyndall and Grindley equations and an outward curvature of the sides of the peak results. Since the curving was never found to influence the position of the maximum, no great care was taken to avoid this condition in the effort to obtain ion currents of measurable intensity. However, by varying the conditions of δT, V_r, and the slit width (width of ionized beam) the sides of the curve could be made quite satisfactorily straight as seen in Fig. 4. It seems in view of such curves of interest to consider the resultant shape of the Tyndall-Grindley curve should there be a distribution of mobilities between certain limits. In other words, it is important to see what the effect of a continuous distribution of mobilities will be on these curves. This can be accomplished by testing the effect of a range of mobilities on the curve shape; a result which can most easily be accomplished, in view of the integrals involved, by a graphical method which sums the ordinates of a series of individual curves over the range of mobilities involved. When this is done we obtain a curve of the shape shown in Fig. 4 a curve B. Curve A is an experimental curve recently obtained in pure air with x-ray ionization for positive ions of age equal to 0.05 seconds. By combining a series of curves of this shape distributed uniformly over a range ten percent greater and ten percent less than the accepted value (a smaller range than was found by Zeleny) curve B was obtained. With sides of the same slope, the rounded top is very apparent. Fig. 4b shows a series of experimental curves for negative ions in less pure gas taken on ions of increasing age, as shown. Comparing these curves with that of Fig. 4a it seems very apparent that ions of age less than 0.08 do not have a spread of mobilities as great as that chosen.

The curves shown indicate quite strikingly two facts. First the ions of shorter life in pure air *do not appear to show any certain indications of a velocity spectrum of any great extent,* (certainly the range is smaller than 10 percent. Secondly at ages greater than 0.1 second the appearance of a range of velocities is quite definite and becomes more pronounced as time goes on. Again as in all methods the resolving power is too small to indicate the nature of the changes occurring but it is clear that such a real spectrum exists. These results strikingly confirm the conclusions to be drawn from the photoelectric method for newer ions and the results of Fontell and Zeleny on older ions. They disagree definitely with those of Hamshere and the results at shorter time intervals of LaPorte.*

THEORETICAL CONCLUSIONS

That this confirmation should occur is not surprising in view of certain theoretical considerations concerning ions together with recent results obtained by Luhr[14] in this laboratory. Luhr has been studying the ions produced in air, O_2, N_2, and SO_2 and other gases by a Geissler discharge after sorting the somewhat aged ions by means of the method of molecular beams and a positive ray analyzer of the Dempster type. While he has as yet not achieved a

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* In a recent paper Zeleny (Phys. Rev. **38,** 969 (1931)) has confirmed the absence of a mobility spectrum in air over the shorter time intervals using an air blast method.

study of the really older ions the facts found in air with *high concentrations of the ionization products of discharge* indicate that as the pressure of the gas increases, especially in air, the ions are predominantly of a higher molecular weight than those at low pressures which consist of O^+, O_2^+ and N_2^+ and O^{3+}, etc. These older ions have molecular weights ranging up to 200. They are not in a continuous group of all masses, but *largely consist of single charged molecules of the reaction products of the discharge*, i.e., oxides of nitrogen, nitric acid and where SO_2 is present even H_2SO_4.

It is clear that in any ionized complex gas such as air all sorts of chemical products must be formed in quantities depending on the nature of the ionizing process. Depending on their electrochemical affinity as shown from studies of mixtures[34] certain of these molecules are strongly attracted to ions of one sign or the other. These compounds or attached molecular ions are formed not by the inverse fifth power law attractions but forces between the charged portions of single molecules due to structural characteristics as worked out by researches analogous to those of H. A. Stuart,[25] C. P. Smyth,[26] C. T. Zahn[27] and others. For example the O atom in ethyl ether is highly negative and should strongly attract and attach positive ions, or the positive atom or molecule can combine with an NH_3 molecule to give an ammonium like ion, while the strongly positive H in the OH group attracts negative ions. Now there must be formed a number of such ion complexes *with not more than one or two molecules attached*, in any gas ionized by x-rays or α-rays, in the measure that active molecules are present, and that probability of reaction and number of impacts of ions with these lead to formation of such complexes. The lower the concentrations of these substances the longer times of sojourn in the gas must transpire for such attachments. In gases as ordinarily studied there will even be competition among various molecules for the ions of a given sign. At first a less strongly attracted but more frequent impurity will win, but with age the more strongly attracted but rarer substances will get a large share of the remaining charged atoms. This action is beautifully illustrated in the aging effects observed by one of the writers' for Na^+ ions in N_2 and H_2, and by the aging effects observed by Erikson[17,31] and the action of water vapor, alcohol and ozone on ions in air as observed by Tyndall[24,28] and his collaborators, Mahoney,[30] Valasek,[29], Hamshere[10] and others.

Thus it is to be expected that while the earlier ions are more uniform in structure, and thus of uniform mobility, aging particularly in gases with many chemical products will lead to the predominance of a greater diversity of the ion structures present, with a consequent spread of mobilities. Hence it is not surprising that in gases like those used by Fontell, Zeleny and one of us over long time intervals with the selective action of recombination in some cases removing the lighter complexes, to find quite a velocity spectrum among the ions. With greater resolving powers of our measuring equipment of course the separation of the ion groups should appear, if the spectrum has not too many components, as in Luhr's apparatus. It is also clear that the distribution of mobilities in such a group must be rather more like that found by Zeleny and others than the uniform velocity band utilized in calculations in this paper.

THE DIFFERENCE BETWEEN POSITIVE AND NEGATIVE MOBILITIES

This assumption of the nature of ions at once clarifies many heretofore disturbing phenomena which have been very hard to understand. To utilize this concept let us first restate the situation. It must, and will be maintained throughout, that the *ions are essentially simple in structure* one charged molecule O_2, N_2, O_3, etc., attached to possibly one and perhaps two, but not more, other molecules of appropriate structure. More than one or two attached molecules would so weaken the bonds, with the space limitations imposed by the attached molecules that they would cease to be effective. These attachments must be considered in the nature of loose chemical combinations caused by structural effects, and *not primarily caused by the inverse fifth power law attractions.* In some active organic molecules of high molecular weight, i.e., with large inactive chains of CH_2 groups the effect of this attachment alone will cause marked diminution of the mobility owing to great increase in ion radius. This has been observed by Tyndall[28] and his collaborators with the alcohols and by Loeb and Dyk[32] with the amines.

In the main, however, the very great lowering of the mobilities, to one-fifth the simple kinetic theory value,[35] are due not to this compound formation but to the *apparent increase of the ionic radius due to the attractive forces of the ionic charges on neutral gas molecules.* The main lowering will therefore be ascribable to dielectric attractive forces of the inverse fifth power law type which must hold fairly well at distances of 10^{-7} cm and greater. For closer approach doubtless the dielectric forces are less and this with our understanding of repulsive forces show why the influence of the actual kinetic theory radius as it appears in Langevin's equation may not be as critical as it appears.[1] That these dielectric forces must be the main factor in reducing ionic mobilities to the observed low values is definitely attested by the fact that this Langevin law alone or even the Loeb-Thomson modification and the Wellisch equation as modified by Loeb,[33] give the correct order of magnitude and nearly correct values for the mobilities of the ordinary ions. Hence the mobilities observed are produced by (1) the dielectric attractions which have superposed on them and (2) the increases in mass and actual physical diameter caused by the one or two electrochemically bound molecules.

Granted this postulate we can at once see that the effect of the sign of the charge on mobilities is not in any way to be ascribed to a difference in the dielectric constant for positive and negative ionic force fields.[36] It must be ascribed to the specific electrochemical combinations which result by reaction of positive and negative ions with molecules present in some gases, the negative ion adding the larger molecule in some gases in others the positive ion doing so. If this is true the whole question of the difference of positive and negative mobilities is simplified and may be even extended to the C. T. R. Wilson cloud chamber experiments. The fact that negatively charged droplets condense to visible size much more readily than do the positively charged drops may not need to be ascribed to more intense dielectric forces on the water droplets in the intense radial fields of the small negative drops than on small positive drops. They can now be ascribed to the fact that the droplet that has picked up a negative ion has also picked up from the negative ion a more hygroscopic addition product than there exist about the positive ions. Thus a droplet such as Thomson postulates, containing 1000 water molecules, that cannot grow at a given supersaturation because of surface tension forces, in picking up a negative $O_2^-(2\ SO_2)$ ion has besides the compensating charge the vapor tension of 20 N H_2SO_3 solution. This may cause more ready condensation on the negative ion than on the positive ion which has no such addition product.

THE RECOMBINATION COEFFICIENT

Another problem which is clarified by this viewpoint is the apparent difficulty in the different effects of aging on mobilities and recombination coefficients as observed by Luhr[15] and Bradbury.[16] In the intense x-ray ionization reactive substances are formed in the gas in progressively greater amounts on aging. The faster ions owing to lighter mass recombine quickly and leave the slower ions. Now since those reaction products picked up by ions in air are, as Luhr[14] has observed, atoms not of atomic and molecular weights 16 and 32, but some molecules of molecular weights as high as 200, we can see how the value of the recombination coefficient which is inversely proportional to the square root of the mass of the ion can be reduced without materially changing the mobility of the ions. Thus the reduction of the recombination coefficient with time is not due to the formation of a very large cluster ion which is incompatible with a 10–20 percent mobility decrease, but is due to the attachment of a molecule of greater mass without a very much greater radius: Thus the increase in radius of an O_2^+ ion to that of an $(HNO_3)_2O_2^+$ ion is not as drastic an increase in radius as would be that due to an addition of 8 to 12 O_2 molecules in a monomolecular cluster which are loosely bound by dielectric forces.

It is therefore seen that the recent studies of the velocity spectrum of ions together with other recent work leads to a comparatively simple picture of ionic structure and behavior which from its nature and its simplicity cannot be far from true. It is hoped that the clarification due to this analysis will guide future workers to a means of more quickly and completely establishing the obvious conclusions here made.

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