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RECENT LIGHT ON THE NATURE OF GASEOUS IONS

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ABSTRACT

The nature of gaseous ions from a study of mobilities in mixtures. After a general survey of the previous status of the question of the nature of the gaseous ion, it is concluded that for pure gases the dielectric attraction of the molecules by the charged ion can account for the order of magnitude of the mobility nearly equally well on either cluster or small ion theory. Such calculations are therefore indecisive. The measurements of mobilities in mixtures use Blanc's law as a criterion for the absence of the change of the cluster ion. The results show that Blanc's law holds in some cases and not in others. The observed nature of the mobility curves in mixtures shows three types of effects. These may be interpreted as indicating absence of clustering, labile clustering, stable clustering. The nature of the deviations in different gases indicates that where marked stable clustering occurs it is a specific effect depending on the chemical nature of the gas and sign of charge on the ion. Such effects are superimposed on the dielectric attractions mentioned above. Erikson's results on aging are discussed in their bearing on this work.

INTRODUCTION

IN THEIR initial paper on the electrical conductivity produced in air by x-rays, published in 1896, Rutherford[1] and J. J. Thomson stated that the observed mobility of the carriers studied was so much lower than the kinetic theory value for a charged molecule whose charge did not influence its motion through the gas by changing the paths of the molecules, that these carriers or ions were most probably composed of groups or clusters of molecules. Later measurements seemed to confirm this belief, which was generally accepted. In 1909 Sutherland[2] and Wellisch[3] independently stated that the shortening of the free paths necessary to explain the low observed mobility of gaseous ions could just as simply be imputed to the curvature of the paths of the ions and molecules as a result of the electrical forces between ions and molecules. These papers initiated a controversy which has continued with varying intensity up to the present. As is usual the discussion was carried on most violently by the extremists of both viewpoints and experimental evidence gained largely from the study of pure gases never seemed to be decisive. In recent times new evidence from the quantitative study of two previously neglected fields, that of the mobilities in mixtures and that of the mobilities as functions of the age of the ions, has given some very definite answers to the questions raised.

As is usually the case in such controversies, neither side was absolutely right nor completely wrong. Ions form clusters under some conditions ann probably do not form them under other conditions. Both types of actioy exist and exist together—hence the confusion. Although the results are faird

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

[2] W. Sutherland, Phil. Mag. **18,** 341 (1909).

[3] E. M. Wellisch, Phil. Trans. Roy. Soc. A**209,** 249 (1909).

convincing, many points yet remain to be cleared up and it may not be amiss to reformulate anew the gas ion problem in terms of what is known today, with the hope that this discussion will not only clarify the situation and therefore direct research in fruitful channels, but will also give rise to investigations of some of the phenomena yet obscure.

THE STRICT CLUSTER THEORY

Shortly after the fundamental researches of Rutherford and Thomson and the careful experiments of Zeleny[4] on mobilities, attempts were made to deduce equations for the mobilities on the kinetic theory, using various lines of approach. Among those may be mentioned the theories of J. J. Thomson,[5] Riecke,[6] Lenard,[7] and Langevin.[8] These theories are based on an assumed cluster and leave the mass and the radius of the cluster undefined. As the mass factor for the ion plays a relatively unimportant role (the mass of the gas molecules present on the contrary being very important), the chief burden falls on the radius of the ion in these theories. It accordingly became the custom to assume that an undefined cluster existed and, by taking the observed value of the mobility together with the other factors, all of which were known, to compute a plausible radius of the ion which would satisfy this theory. Such a procedure is legitimate if the ion is a cluster and its radius as given by the theory is its real radius, that is to say, is not a radius that is in part due to attractive forces which alter its free path. Beyond this, however, the above method of approach is sterile, for it does not decide the question and leads to no further researches. It is, however, the point of view which has been taken by those strongly insistent on the strict cluster theory.

THE NATURE OF THE FORCES DETERMINING IONIC MOBILITIES

The more stimulating approach to this question is the one which asks whether it is possible, with known forces and properties of ions and molecules, to predict what will happen to a charged molecule moving among neutral molecules of dielectric constant D. Will, under such circumstances, the ion surround itself with a group of neutral molecules, or will it have its path merely altered in consequence of such forces? Finally do such forces suffice to give the approximate observed five-fold general decrease of the mobility of the ion below that of the theoretically computed mobility based on the equations cited above, if one assume a single charged molecule? Many such calculations have been made, although they have not been recently summarized.

In his recent book[9] on the kinetic theory the writer reviews the old idea that, with the inverse 5th power law of force which holds for dielectric

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[4] J. Zeleny, Phil. Trans. Roy. Soc. **A195**, 193 (1900).

[5] J. J. Thomson, Proc. Camb. Phil. Soc. **15**, 375 (1910).

[6] Riecke, Wied. Ann. **66**, 376 (1898).

[7] P. Lenard, Ann. d. Physik **3**, 313 (1900); **60**, 329 (1919); **61**, 665 (1920).

[8] P. Langevin, Ann. de Chim. et de Phys. **28**, 317 (1903).

[9] L. B. Loeb, Kinetic Theory of Gases, McGraw-Hill, New York, 1927, p. 455.

molecules attracted by a charge, the condition for stability of an ion cluster is that the ratio of the potential energy W to the kinetic energy $K.E.$ given by

$$W/K.E. = (D-1)e^2/12\pi p\sigma^4,$$

is equal to or greater than unity. If the usual values of the quantities are chosen for the case of air, $W/K.E.$ is found equal to about three. This indicates the possibility of a cluster formation. Nevertheless the value of $W/K.E.$ is so critically dependent on the unknown distance σ between the charge of the charged molecule and the molecules attracted in the cluster, and the laws of force on dielectric molecules are so little known at distances comparable with molecular radii, that we cannot with certainty assert that a cluster will form in any given case.* We may conclude from this that cluster formation is possible in air and may even be probable in HCl, but that in any case a cluster formed on the basis of this law is probably limited to a monomolecular layer of molecules surrounding the charged molecule. That is, the ion is limited to about thirteen molecules all told and possibly less, because twelve spherical molecules are all that can surround a single spherical molecule of like radius, and the radius required for a second monomolecular layer makes the cluster consisting of two molecular layers surrounding the molecule improbable.

Some workers[11] have attempted to superimpose on these electrical forces the van der Waals attractive forces of cohesion and thus obtained much larger clusters. While this is possible the writer agrees with Professor J. Franck in a recent discussion of the subject, that after all the electrical forces cannot be superimposed on the van der Waals forces, inasmuch as both are of the same nature (i.e., electrical) and it is probable that the van der Waals forces will be replaced by electrical forces, of a different nature produced by the ionic charge.

It must also be borne in mind that if a cluster forms under this law of force, the ion so formed will still act on neutral molecules beyond the confines of its own cluster with electrical forces in such a way as materially to change their free paths. Thus even a cluster of the electrical nature outlined above must in part act like a small ion.

One more conclusion may be drawn from this theory. It has been shown by Langevin that in the recombination of two ions[12] attracting each other according to a law of force in which $W/K.E. = 2e^2/mv^2r$ and in which the forces are many times larger than above, the ions do not recombine whenever they collide, but that there is a large chance that they will again separate even at atmospheric pressure. This follows from the dynamics of the process of recombination. It is therefore to be expected that the chance that a molecule which is attracted to an ion by a vastly smaller force will have a

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* In spite of the question above concerning the validity of the dielectric laws of attraction in the intense radial fields of ions at molecular distances, Debye[10] has shown that the law appears to hold surprisingly closely.

[10] Debye and Hückel, Phys. Zeits. **24,** 205 (1923).

[11] A. P. Alexeievsky, Phys. Rev. **27,** 811 (1925).

[12] L. B. Loeb, Kinetic Theory of Gases, p. 483.

much smaller chance of attaching to the ion to form a cluster. This low probability of attachment is naturally counterbalanced by the very much greater number of impacts which the charged molecule has with neutral molecules. It must however be recognized that this situation may lead to a relatively slow formation of the ion, such that it might be conceivable that the ion cluster would require periods of the order of a thousandth of a second in a gas at atmospheric pressure to form itself by attachment of molecules.

It may well be asked whether the same forces, do they not cause a clustering, could give the proper order of magnitude to the mobility on the basis of a small ion concept, i.e., a single charged molecule. This question can be answered in the affirmative by citing a small ion theory first developed by Wellisch in 1909[3] and later modified by the writer,[13] or a theory independently developed by the writer[14] which he later found to be a special case of the more complete theory of Langevin.[15] The theory of Wellisch which was the first theory which from known physical quantities without arbitrary assumptions as to the size of a cluster gave mobilities of the observed order of magnitude, is based on the decrease of the free path caused by the attractions between ions and molecules, using the law of dielectric attraction cited above. The values from this theory as modified by the writer are quite successful, both in general magnitude and the order in which the various gases follow.

More interesting in a sense than the theory of Wellisch, though a theory which is definitely in error, is the theory of the writer based on a rigorous calculation of the changes of path resulting from an analysis of J. J. Thomson,[16] using the dielectric law of force. In this theory the ion is considered as a *point* charge moving in a gas of dielectric constant D and molecular weight M_0. The mobility is given by

$$K=\frac{0.104[(M+m)/m]^{1/2}}{(\rho/\rho_0)[(D-1)_0 M_0]^{1/2}},$$

where m is the mass of the ion, M the mass of the molecule, while ρ is the density and ρ_0 is the density for N.T.P. The constant term is questionable, because of the process of averaging, and m is unknown. The factor containing m changes the mobility by 40 percent for infinite mass so that it is not important. This equation again gives the mobility in order of magnitude for all gases fairly successfully, deviations by a factor of two at most being present. It is also interesting insofar as the theoretical mobility varies as nearly as the results warrant, according to the observed experimental data, being independent of temperature, the mass of the ionized molecule, and depending largely on D and M_0. The mobility in this equation is independent of the charge in contradistinction to the case of a particulate ion, such as one would have in the case of a Millikan oil drop. The theory therefore is interesting, as it furnishes an extreme type of theory of ionic behavior. This leads

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[13] L. B. Loeb, Kinetic Theory of Gases, p. 456 ff.

[14] L. B. Loeb, Kinetic Theory of Gases, p. 460 ff.

[15] P. Langevin, Ann de Chim. et de Phys. **5**, 245 (1905).

[16] J. J. Thomson, Phil. Mag. **47**, 337 (1924).

one to see that as the radius of the ion is less and less dependent on the charge, the mobility varies more nearly in proportion to the value of the charge. As stated the theory however is definitely wrong in neglecting the molecular radius, but it serves to show how insensitive the mobility is to the radius of the ion in the presence of electrical forces. In this respect the theory is analogous to the Debye theory of ionic mobility in solution.

THE MORE COMPLETE ELECTRICAL THEORY

The closest approach to the mathematical solution of the ion problem today extant is the one due to Langevin[15] in 1905, who using the above law of force calculated from rigorous kinetic theory the mobility of an ion of radius σ. This theory was assailed by Mayer[17] on the ground that it neglected the velocity of the ion in the direction of the field on a single free path. According to Mayer, had Langevin taken account of the velocity in the direction of the field, he would have obtained a mass factor in his theory which agrees with the mass factor noted by Lenard[7] on a strict cluster basis. Inasmuch as most measurements are carried out under conditions fulfilling Langevin's assumption, it seems hardly worth while to alter the theory, since the change in mass factor alters the mobility far less than many other factors. One may therefore accept the complete equation of Langevin as later developed by Hassé,[18] as being the most complete theory to date. It unfortunately leaves one with an undetermined radius and consequently makes it another arbitrary equation.

CONCLUSIONS FROM THE THEORETICAL CONSIDERATIONS

The conclusions to be drawn from these considerations are as follows:

(1) The inverse 5th power law of dielectric attraction suffices for the calculation of mobilities of ions of the correct order of magnitude for ions either of the small ion type or of the cluster type.

(2) The laws so deduced agree as far as we can determine from the experiments equally well with either theory if pure gases are used, though such a comparison between the two points of view is difficult, as the ionic radius chosen in the case of the cluster theory is more or less arbitrary.*

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[17] H. F. Mayer, Ann. d. Physik **62,** 358 (1920).

[18] Hassé, Phil. Mag. **1,** 139 (1926).

* This is not quite true in such extreme cases as the forceless cluster or the point charge. For the former the mobility is inversely proportional to the square root of the absolute temperature if the cluster size is not a function of temperature. For the latter the mobility is independent of temperature. It is probable that some other law for the variation of mobility with temperature, such as that of Sutherland[2] holds. Experiments on this point differ so widely that no conclusion can be reached. Phillips[19] claims to have established the Sutherland equation as does Schilling.[20] The equation as applied to a cluster ion exerting forces at constant density reads:

$$k_T = K_0\left(\frac{273}{T}\right)^{1/2}\frac{A}{1+C/T}$$

where K_0 is the mobility at N.T.P., T the absolute temperature, and A and C are constants. The work of Phillips is in disagreement with that of Kovarik,[21] done under the same conditions; and both are in disagreement with the careful work of Erikson.[22] The results of Schilling

(3) Doubtless both types of action occur and in some cases simultaneously. In this case the theory which is most nearly correct is that of Langevin. It is also likely that in some cases the cluster action predominates and in others the small ion action predominates. Thus *in order of magnitude ordinary forces of the dielectric type suffice to account for the mobilities, the nature of the ion and its mobility being undetermined* as far as crucial experiments in pure simple gases can ascertain. We must therefore turn to investigations in other fields to determine the nature of the ion.

Work on Mobilities in Mixtures of Gases

The first of the fields to be discussed, that of the mobilities in mixtures, presents because of the rather more complete control of experimental conditions, possibly the best line of approach. The study of the mobilities in mixtures began with Blanc[23] in 1908 for mixtures of gases H_2, CO_2, and air. He found that for these gases the law of mixtures to be developed below held quite well. To deduce the mobilities of the gases in the mixtures, it must be remembered that in analogy to the electrical conductivities, electrical gas ion mobilities in mixtures cannot be added. The reciprocals of both of these, that is the resistances to the current or to the motion of the ions, have however the additive property. Since the resistances are directly additive and the mobilities are inversely proportional to the densities of the gases, i.e., to the number of molecules present, the product of the reciprocal of the mobility in a given gas by its mol fraction can be added to the similar products for the other gases present and will equal the resultant resistance for the mixture. Thus dealing with binary mixtures at atmospheric pressure, consisting of c atmospheres of the gas a whose mobility is k_a and resistance $R_a=1/k_a$, and $(1-c)$ atmospheres of a gas b of mobility k_b and resistance $R_b=1/k_b$, we can at once write the resistance $R_c=1/k_c=R_ac+R_b(1-c)$. This leads to the mobility in the mixture expressed by the relation

$$k_c=\frac{k_ak_b}{(1-c)k_a+ck_b},$$

which is Blanc's law. The law applies within the limits of experimental error to an early measurement made by Wellisch[24] on a mixture of C_2H_5I and H_2 in 1909. These constituted all the complete, accurate measurements until more recent years.

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cover but a small range and as satisfactorily fit one theory as another, so that we cannot judge by these. If the Sutherland law should hold, the action is one based on a small ion type of action, since Sutherland's theory is based on the effect of the temperature on the free path of particles attracting each other according to some law of force. Erikson's work, which seems to be the most careful and covers a large range of mobilities, indicates independence of mobility on temperature, except near the liquid air temperature where the mobility is slightly decreased.

[19] P. Phillips, Proc. Roy. Soc. **A73,** 167 (1906).

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

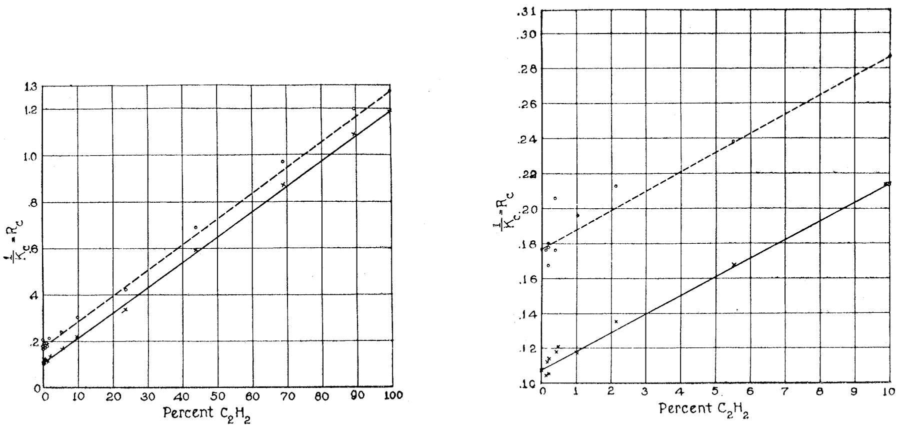
[21] A. F. Kovarik, Phys. Rev. **30,** 443 (1910).

[22] H. A. Erikson, Phys. Rev. **3,** 151 (1914); and **6,** 349 (1915).

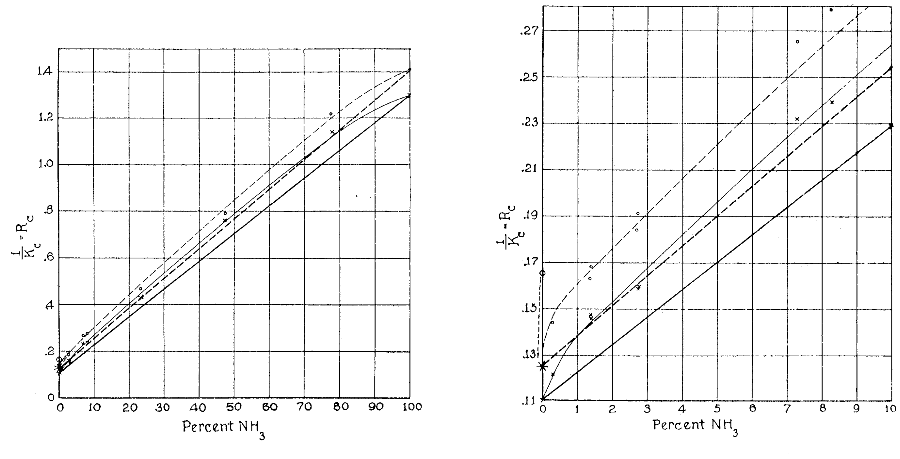
[23] A. Blanc, Jour. d. Physique, **7,** 825 (1908).

[24] E. M. Wellisch, Proc. Roy. Soc. **A82,** 500 (1909).

Although it had been repeatedly asserted that traces of water vapor and Cl_2 abnormally decreased the value of k for negative ions in air, to the writer's knowledge no careful quantitative studies of the mobilities over any considerable range were made until about 1924. Since that time the writer,[25,26] Tyndall and Phillips,[27] and H. Mayer[28,29] have extended the



Figs. 1 and 1a. Mobility of ions in C_2H_2-H_2 mixtures. Reciprocal of mobility is plotted against percent of C_2H_2.



Figs. 2 and 2a. Mobility of ions in NH_3-H_2 mixtures. Reciprocal of mobility is plotted against percent of NH_3.

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[25] Loeb and Ashley, Proc. Nat. Acad. Sci. **10,** 351 (1924); and Loeb, Proc. Nat. Acad. Sci. **12,** 35 and 42 (1926); ibid. **12,** 617 and 677 (1926).

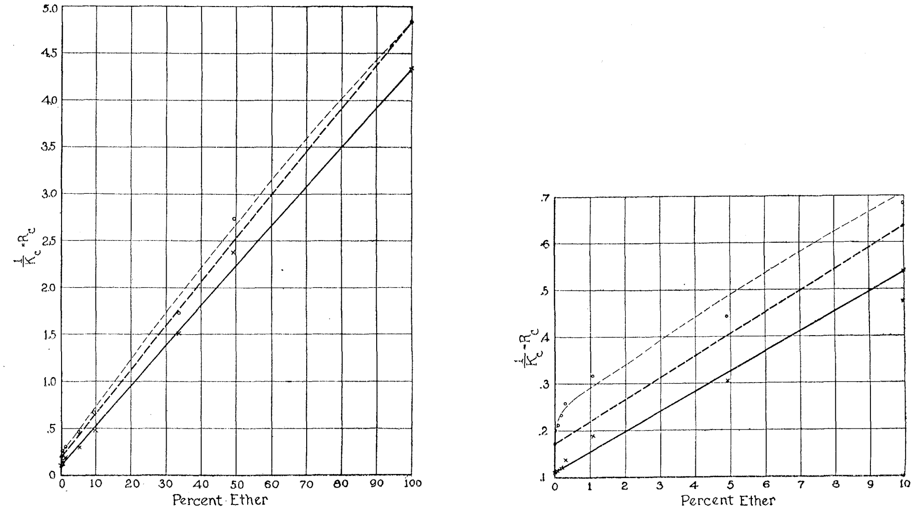
[26] Loeb and DuSault, Proc. Nat. Acad. Sci. **13,** 510 (1927); **14,** 193 (1928); and **14,** (1928) (in press).

[27] Tyndall and Phillips, Proc. Roy. Soc. **A111,** 577 (1926).

[28] Herbert Mayer, Phys. Zeits. **27,** 513 (1926); **28,** 637 (1927).

[29] Herbert Mayer, Bulletin Faculty of Sciences, Cernauti, Roumania, Vol. II, No. 1, p. 65.

literature to a large number of mixed gases. The results of these investigations may be summarized in three types of curves. Typical curves representing these types taken from experiment are shown in Figs. 1, 2, 3, 4, 1a, 2a, and 3a. For purposes of comparison it is simpler to plot the curves for



Figs. 3 and 3a. Mobility of ions in ether-air mixtures. Reciprocal of mobility is plotted against percent of ether.

the mixtures in terms of the resistance, as these in the case of Blanc's law give a straight line, and deviations from a straight line very clearly indicate deviation from Blanc's law. In Figs. 1 and 1a the results for a C_2H_2-H_2 mixture of the writer's for positive and negative ions are given, showing the linear form characteristic of the strict Blanc's law in mixtures. In Figs. 2 and 2a the results for NH_3-H_2 mixtures are shown, the straight lines being the theoretical curves for Blanc's law following from the observed mobilities in pure hydrogen and NH_3 and the star representing the beginning of the positive ion curve in NH_3, indicating the observed mobilities in almost pure hydrogen after a trace of NH_3 had been admitted to the chamber. The third and fourth figures give the results for ether-air mixtures and for HCl-air mixtures, the solid line curve in each case referring to the negative ion, the other curve referring to the positive ion. In each case the calculated linear Blanc's law expression is included in the figure.

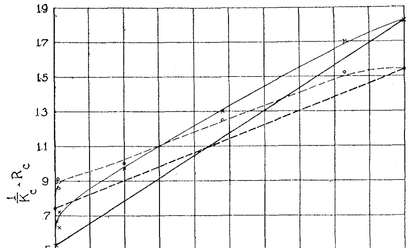


Fig. 4. Mobility of ions in HCl-air mixtures. Reciprocal of mobility is plotted against percent of HCl.

PREDICTIONS FROM THEORY AS TO MIXTURE CURVES TO BE EXPECTED

Before interpreting these results it seems advisable to study the two theories to foresee if possible what is to be expected.

(1) On the small ion theory since the mobility is inversely proportional to the density and the forces are exerted on the gas molecules as the ion encounters them, Blanc's law would be expected to hold and should characterize, where strictly obeyed, a small ion type of behavior. It seems that the Blanc law is probably as nearly definite a test of the small ion type of activity as possible, provided the ion does not in any way change the concentration of molecules about it.

(2) It is possible that with either cluster or small ion the forces on certain of the more actively attracted gas molecules resulting from high dielectric constant might change the concentration of the molecules in the neighborhood of the ion. It was shown by Condon[30] on the basis of the law of equipartition of energy, that such a local change in density of HCl in air was to be expected. In how much such a change of density can alter the mobility it is impossible to say, inasmuch as the change, no matter how reckoned, introduces only a partial increase in the drag on the ion by interaction with such molecules, since the molecules near the ion are already moving more or less in the same direction as the ion. An empirical relation only partially satisfied was found by Loeb[25] and Mayer[28] in certain mixtures. This equation

$$k_c = \frac{k_a k_b}{[(1-c)k_a^2 + c k_b^2]^{1/2}}$$

in the resistance form indicates an effect of such a nature as pointed out by Debye.[25] It is conceivable, however, that this relation may be explained in other ways.

(3) On the strict cluster concept in which the forces around the charged molecule vary greatly in their action on the two constituent molecules of the mixture, Blanc's law would hardly be expected to hold. Immediately a trace of the more active gas were admitted to the mixture this would selectively go to the ion to change its constitution; and *if the mobility depends on the size of such an ion*, the mobility should change abruptly to lower values which might be expected for a cluster of the more active gas. This means that low concentrations of the more strongly attracted gas should cause the mobility to drop and the resistances to the ions to jump upward very sharply, a marked deviation from the linear relationship being observed for low concentrations of the active gas. It is of course conceivable that the time consumed in the reconstitution of the ion might be fairly long, such that if the ion were measured in such cases very shortly after the ionizing act, the lowering effect to be expected would not have had time to occur and the mobility would appear to be unaffected by this gas.

(4) On a less rigid interpretation of the cluster theory, which one might expect on the basis of the electrical forces between ions and molecules, in

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[30] L. B. Loeb, Kinetic Theory of Gases, p. 472.

which important forces are exerted beyond the immediate region of the cluster and where the cluster is more or less statistical in nature, it is to be expected that the cluster would adapt itself more or less readily to the average mixture. On this assumption it is probable that a more or less close approximation to the Blanc law would occur. If, however, there is some definite clustering it seems unlikely that the Blanc law would be obeyed with any accuracy and the same sort of deviation described under Paragraph 2 and illustrated by the curve of Fig. 2 might be expected.

Conclusion from the Mixture Experiments

These three types of behavior are illustrated by the schematic curves drawn in Fig. 5, the Curve (1) representing the resistance law, Curve (2) the deviation from the resistance law to be expected on either an increase of concentration effect for a small ion or for a labile ion, and (3) a typical curve indicating a marked cluster formation. Comparison of Fig. 5 with Figs. 1, 2, 3, 4, 1a, 2a, and 3a at once indicates that all types of action have been observed in only four mixtures mentioned. The mixture work may be summed up in terms of these factors as follows.

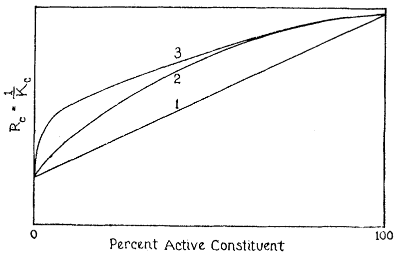

Fig. 5. Variation, anticipated from different ion theories, of mobility with concentration of the active constituent in a mixture.

(1) In mixtures of C_2H_2-H_2, CO_2-H_2, O_2-CO_2, C_2H_5I-H_2 and negative ions in ether-H_2 mixtures, Blanc's law is followed. In these one may properly assume no apparent clustering. If, as is likely, the final positive ion in air, CO_2 and H_2 is already a bimolecular cluster, as indicated by Erikson, this clustering is inherent in one or both of the gases and is not changed by the mixture. This could also be true for the negative ion, though it is less likely in view of the aging effect (see later). If in one gas, however, the positive ion clustering suggested by Erikson is replaced by another complex, we would see the abrupt change in mobility resulting.

(2) In mixtures of NH_3-H_2, NH_3-air, SO_2-H_2, the part of the HCl-air curves for *higher* concentrations of HCl, and in Cl_2-O_2 mixtures for positive ions, deviations from the Blanc law of the indeterminate nature mentioned in Classes 2 and 4 and illustrated in Fig. 2 and Curve (2), Fig. 5, occur. This will be due to a statistical labile cluster or to some concentration effect mentioned above, which amounts to the same thing.

(3) All other gases examined, negative ions in Cl_2-H_2 and Cl_2-O_2, Br_2-H_2, HOH and ROH-air mixtures, positive ions in ether-H_2 mixtures, and positive and negative ions in HCl-air and H_2S-H_2 show the definite clustering behavior unmistakably, HCl showing it over and above the concentration effect prominent at higher pressures of HCl.

There can therefore be no doubt concerning the cluster formation in some gases, while in others it is quite unlikely that clusters form. Probably the most striking proof in this direction are the cases of ether, SO_2, and NH_3 in H_2 gas. The positive ion in ether shows indubitable clustering, while the negative ion shows no deviation from the Blanc law within experimental error. In NH_3-H_2 and SO_2-H_2 the NH_3 or SO_2 first admitted *increases* the mobility of the positive ion to nearly the value of the negative ion, after which both ions behave according to a law of an indeterminate type indicating a labile cluster or changes in concentration. In SO_2-H_2 mixtures[26] the positive ion shows this effect even more pronouncedly. One experiment on a mixture of ether, NH_3 and H_2 indicates that ether acts more strongly on the positive ion than NH_3, where present in equal quantities, so that the ether cluster or addition product is the more stable.

One more interesting fact is brought out by Tyndall and Phillips[27] in a study of the mobilities of positive and negative ions in a homologous series of alcohols ROH mixed with air. Here starting with water the deviations from the resistance law at very low concentrations of the vapors progressively decrease k more and more effectively. Since in general properties (i.e., the dielectric constant, vapor pressure, etc.) these vapors are more or less similar, the difference must be attributed to the size of the R group or chain of the alcohol added. This effect is not surprising inasmuch as the large size of the R group even if one molecule only were added would materially change the radius of the ion, and thus the sudden lowering will be the more effective, the greater the molecule attached. The mobilities at atmospheric pressure for these ions are all more or less nearly the same. We must therefore add to the consideration of the clustering the importance of the size of the molecules attached, in discussing the influence on the mobility for low concentrations.

EVIDENCE FROM AGING EFFECTS

The second line of evidence comes from the pioneer work of Erikson.[31,32] In spite of objections to these experiments to be mentioned, there are certain facts which cannot be neglected and which point to conclusions similar to those drawn from the mixture work. Erikson uses an air blast method which enables him to measure velocities at atmospheric pressure for ions very soon after the ionizing process takes place. He observed that independently of the age in all gases examined the negative ion retained a nearly constant k to within 0.002 seconds after formation. The positive ions at the shorter time interval have a k equal to that of the negative ions, but change to the lower values usually observed for positive ions in time intervals less than 0.03 seconds. The change is evidenced, on varying the age, by two definite peaks, the area under which varies relatively as the ions grow older. This occurs in such a manner that at the shorter time interval the one curve having the same mobility as the negative ion is all that is observed, but as the age of the ions is increased the second curve corresponding to the slower ion develops in area at the expense of the first curve and eventually, after 0.03 seconds,

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[31] H. A. Erikson, Phys. Rev. **20,** 117 (1922); **24,** 502 and 622 (1924).

[32] H. A. Erikson, Phys. Rev. **26,** 465, 625, and 629 (1925); **28,** 372 (1926); **30,** 339 (1927).

comprises all the positive ions observed under its single peak. The age is varied by introducing the ionizing source in the gas at various distances from the measuring field. The existence of two independent peaks comprising all the ions has only one interpretation: the initial positive and negative ions are characterized by nearly the same value of k, while a slower type of stable positive ion develops after some time in the gas. There are therefore two distinct types of positive ions with no intermediate forms of any marked stability existing between them. The change of the mobility of the positive ion must therefore be regarded as a single step process. The simplest interpretation is that given by Erikson, who believes the negative ions to be monomolecular, as are the initial positive ions, while the aged positive ions have added another molecule to form a bimolecular ion. It could also be that the initial negative and positive ion are polymolecular and that the positive ion changes to a still more complex polymolecular form in a single process after a sufficient lapse of time.

While these results are fairly definitely established it must be stated that they have not been unquestionably verified experimentally either by another observer* or by using different methods. H. B. Wahlin[33] believed he had verified the effect using an alternating current method. The results of Wahlin were questioned by the writer[34] on a theoretical basis, and neither the writer nor Mr. Cravath, working in the writer's laboratory, was able to confirm the effect, although they seriously tried to find it with their methods. Tyndall and Grindley[35] also claimed to have verified the phenomenon of aging, using a modified A.C. method. They did not simultaneously observe the two types of positive ions and the experimental data reported are so meager as to be unconvincing.

Erikson has also observed many other curious effects, some of which are in agreement with observations of the writer in mixtures, while others appear to be exceedingly difficult to explain in any manner. The observations with ammonia in air confirm the experiments of the writer. The observations in which Cl_2 and H_2O added to the main body of the gas failed to produce the lowering of the negative ion mobility observed by other workers on older ions, could be explained on the hypothesis that the time spent in these gases in the high fields is too short to permit the negative cluster formation. The mobilities of high value observed for the radioactive recoil atoms of radium A, actinium A and thorium A, which apparently show no aging effect, are very difficult to explain. The high value of the positive mobility cannot possibly be explained by a double positive charge, but would require a triple or quadruple charge on the ion. Such a charge might be possible after disruption of the nucleus by an effect such as observed by Auger in the case of photoelectrically ionized atoms from short wave-length x-rays.[36]

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* Since this paper was written J. J. Mahoney in the writer's laboratory has completely confirmed Erikson's results in air. (May 27, 1928.)

[33] H. B. Wahlin, Phys. Rev. **20,** 267 (1922); Proc. Nat. Acad. Sci. **10,** 475 (1924).

[34] L. B. Loeb, Proc. Nat. Acad. Sci. **11,** 428 (1925).

[35] Tyndall and Grindley, Proc. Roy. Soc. **A110,** 358 (1926).

[36] L. B. Loeb, Science **67,** 468 1928.

The most difficult of the observations to explain is the effect of C_2H_2 mixed with the ionized air in changing the mobility of the aged positive ion in air to the unaged positive ion in C_2H_2. The explanation on the basis of a cluster formation which has a higher mobility than the positive ion in air is completely negatived by the writer's experiments in C_2H_2-H_2 mixtures.[26] Erikson's explanation on the basis of the transfer of the charge from O_2 to C_2H_2, which might be expected in the light of the work of Franck and Cario, is not entirely satisfactory. It would force one to assume that the charged C_2H_2 molecule is incapable of forming an addition product or bimolecular cluster with foreign molecules, while the positively charged oxygen molecule can do so. As far as evidence goes, the nucleus has little influence on the cluster while the charge and the surrounding gas molecules are very important.

Another effect observed by Erikson in H_2 and in C_2H_2 in which the initial positive mobility was slightly less than the initial negative mobility, can receive a simple explanation suggested by the writer[26] on the basis of the fact that Erikson measures his mobilities so soon after ionization in gases like H_2 and C_2H_2, where the electron does not attach except to impurities, that it is probable that the high values are due to the initial presence of electronic carriers in these gases. This is confirmed as a result of the writer's own studies on the existence of free electrons in both H_2 and C_2H_2, even though slightly impure, when the mobilities are measured within short time intervals.

These more complicated results have not been discussed in as much detail as they possibly warrant, inasmuch as the writer feels that in its present state the Erikson method has sufficient uncertainties as not to give one the utmost confidence in the more unusual results. The chief uncertainties apparent to the writer may be summed up under the four heads below.

(1) The air-blast method as used *does not permit of much control of the purity of the gas*. This the writer's work on mixtures has shown to be of the greatest importance.

(2) The effects of the high fields on the values of the mobility are unknown. While this fact does not influence the important results of Erikson quoted above, inasmuch as they depend for aging on processes independent of the field and on relative mobilities, it is still important that these effects be understood and controlled.

(3) An air blast method is distinctly unsuited for the measurement of true absolute mobilities, and it is a natural tendency to standardize such an apparatus in terms of the mobilities in air and assume that this standardization is applicable in the case of other gases. *It is essential that the absolute values of the mobilities, as nearly as it is possible to get them, should be determined directly in almost every set of measurements.* An instance of the importance of such standardization may be cited by the hypothetical case to be detailed. In the presence of water vapor where the negative mobility is depressed relative to the positive mobility, an apparent relative change in the positions of the aged positive peak and the negative peak might seriously confuse the conclusions to be drawn. Doubtless in Erikson's experiments precautions

of this type were always taken, but their importance cannot be overemphasized.

The criticisms not withstanding, the results of Erikson all in all indicate a type of cluster formation which is in general agreement with the conclusions drawn from the results on mixtures. They are cogent in that they indicate the *unitary* nature of the change of mobility of the positive ion and emphasize the *time element* in the process.

THE DIFFERENCE IN POSITIVE AND NEGATIVE MOBILITIES AND FINAL CONCLUSIONS

It is now essential to go one step further and investigate the difference of positive and negative ion mobilities, a difference not to be expected on the simple assumption of dielectric forces of attraction. This difference of the action of positive and negative forces in regard to dielectric attractions is similar to one occurring in the preferential condensation of water or alcohol vapor on negatively charged droplets, in comparison with the positively charged droplets in the C. T. R. Wilson cloud method. While there are suggestions to account for the differences in the mobility, such as made by Hassé,[18] who assumes that the negative cluster consists of a group of molecules surrounding an electron, while the positive ion is a similar group of molecules surrounding a positive molecule, these will not suffice. The latter suggestion is particularly unsuccessful as the relation of electrons to molecules assumed is not in accord with modern views as to the relation of the electrons to the molecules, and as it is incapable of accounting for the lower negative mobility in some gases.

To account for these effects one may call upon a limited clustering or a difference in forces of positive and negative ions on molecules. In any case there must be a difference in these forces and one may well inquire into the cause for this, inasmuch as the quantity D as usually used is independent of the sign of the charge.

All forces between ions and molecules and between molecules themselves are largely electrical in nature. Two neutral molecules attract each other according to kinetic theory estimates with forces of the form a/r^5 (the van der Waals forces of cohesion) and repel each other with forces of the form b/r^n, where $n=9$ to $n=11$, which are the repulsive forces defining atomic radii. If one of the attracting molecules is charged the forces are again an attractive one a'/r^5 and a repulsive one $b'/r^{n'}$, which may be different, a' being distinctly larger than a, while b' and n' may be changed in various ways. In one recent theory[11] of ionic mobilities the van der Waals forces have been superposed on the dielectric forces of attraction without any modification. This leads to a prediction of ionic nature and ionic size markedly different from any theory proposed. It is highly questionable whether the two forces may be superposed independently as the van der Waals forces will obviously be altered by the charge on the ion. Were it not for this the theory proposed would have to receive serious consideration.

The outer portions of the molecules are predominatingly negative and for intermolecular distances of the order of a molecular diameter or two, these negative shells are nearer to the positive and negative charges of an ion by an important amount relative to the distances to the positively charged portions of the atoms. The repulsion or attraction of these shells by the positive and negative charges of an ion will not be equal. Hence it is to be expected that a', b' and n' will be different by small amounts for positive and negative ions.

The negative ion will therefore attract most molecules slightly less than the positive ion. Such a difference would account for the fact that the negative ion in general has a higher mobility than the positive ion. This explanation is in essence one first suggested by Yen in a slightly different form.[37] For gases where the positive mobility is greater than the negative mobility, Condon[38] suggests an explanation which may be presented in a slightly more generalized form. In molecules where dipole moments occur which are fairly symmetrically placed relative to the center of the molecules, i.e., relative to the outer shells of electrons, the explanation suggested by Yen should hold and the negative mobility should exceed the positive mobility. For molecules where the dipoles are so placed that the positive constituent is relatively nearer the outer shells of electrons in the molecule, the positive charge will be oriented toward the negative ion and away from the positive ion. The action of this sort will be such as to decrease the effect of the repulsion between the outer shell of the molecule on the negative ion, and where the effect is pronounced it may make the positive mobility greater than the negative mobility. The unsymmetry of the dipole is most pronounced in the case of the halogen acids and here we actually find the greatest decrease of the negative mobility relative to the positive mobility. For other strongly polar compounds like SO_2, H_2O, ROH and H_2S, the effect is present but not in so marked a fashion. The gases which as yet have not been definitely studied in regard to this effect and may invalidate this explanation are the halogens, Cl_2 and Br_2, which are not exceptionally polar. In small concentrations Cl_2 and Br_2 depress the mobility of the negative ions in mixtures well below that of the positive ions. It is however not known whether in pure gases at atmospheric pressure, the positive mobility is greater than the negative mobility or not. Were the former the case the explanation given above would become invalid. Care must, however, be used in these experiments to eliminate HCl, which is usually present with Cl_2 in most methods of preparation, before any conclusions can be drawn.

CONCLUSIONS

The explanation given above of the difference in the forces brings still another important feature into the consideration of ionic mobilities. It shows the importance of specific molecular structure in all these considerations. The importance of such structure is also borne out by the effects of traces of

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[37] K. L. Yen, Proc. Nat. Acad. Sci. **4,** 106 (1918).

[38] L. B. Loeb, Kinetic Theory of Gases, p. 478.

NH_3, H_2O, ether, Cl_2 and SO_2, which exert very marked specific effects on one ion in a gaseous mixture, leaving the other ion relatively unaffected. All the above facts lead us pretty well to one conclusion, namely, *the mobilities of gaseous ions are controlled as regards order of magnitude and general variation by the dielectric attraction* according to the $(D-1)e^2/2\pi Nr^5$ law, similarly in this respect to the situation in aqueous solutions where it makes little or no difference except in name whether we speak of a cluster or not. In addition there are *secondary effects influencing mobilities, such as changes in concentration of more active molecules about the ion.* These occur and may or may not be of importance. In a sense such effects may as well be described in terms of a statistical clustering effect as in terms of a concentration effect, the terminology having no importance as their action is understood. In part *the above effects may both be influenced by deviations in the intense radial fields surrounding ions*, which cause deviations from the $(D-1)$ law, these deviations depending on the particular electro-chemical structure of the molecules and ions. Finally there is no doubt *that actual clustering of a much more permanent and stable sort* comes into play, which causes abrupt changes in mobility, both in mixtures and on aging. It now appears as if *these effects* (because of their magnitude and nature) *probably involve very few molecules*, possibly only one or two. They are *definitely dependent on the electro-chemical structure of molecules and ions and approach in their stability and nature definite chemical combinations*, possibly somewhat of the type of NH_4^+ ions in solution.

We are thus led to conclude that the problem of gaseous ions is not a simple one fitting one theory or the other exclusively, but that probably all types of action assumed occur under appropriate circumstances for normal gas ions. While the picture so drawn seems to be in the main justified by facts, it is far from completely proven and the purpose of this article has been to sum up the newer facts and to state the problem in its present status, with the hope that the presentation so given will lead to further investigations and thus further clarify the situation.

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