curves[3–5] all showed essentially the same shape as the curve drawn by Bernardini, except that there was a systematic discrepancy along the energy axis of the type that would seem to indicate a disagreement on the stopping powers of the gases used. The present curve, plotted in Fig. 1, agrees with the later curves. If it is assumed that the lowest resonance in this curve can be described in terms of a resonance formula, such as the Breit-Wigner formula, it becomes possible to make a rough estimate of the total angular momentum of the level in C^{13} corresponding to this resonance. This level would have odd-half angular momentum, but it can be shown, for example, that a value of $J=\frac{1}{2}$ would be too small to account for the observed cross section.** From a consideration of yields and energies of the neutrons and gamma-rays observed in the decay of the C^{13}, it appears that values of J higher than 5/2 are unlikely. The total angular momentum of the observed level is therefore probably either 3/2 or 5/2.

Figures 2 and 3 show the results for magnesium and aluminum. (It should be remarked that in all three figures, the height of the zero ordinate above the abscissa represents the constant background that had to be subtracted from the data.) The statistical errors based on the number of counts are indicated for magnesium, where they were the largest. Because of the poor resolution, no resonances are readily apparent in either the magnesium or aluminum curves. The cross section given for magnesium is for the normal isotopic mixture. The (α, n) reaction in the most abundant isotope Mg^{24}, however, is too endoergic to be possible with polonium alpha-particles. Mg^{25} and Mg^{26} have abundances totaling only a little more than 20 percent, and probably both contribute to the observed (α, n) cross section. Therefore, in terms of Mg^{25} and Mg^{26} alone, the cross section is about five times as large as that given. Aluminum has only one isotope; therefore, there is no ambiguity about the assignment of the cross section.

In order to compare the values obtained for the cross sections in this article with those of previous experiments in which thick targets were used, it is convenient to convert thin-target results into thick-target yields, and these are presented in Table II.

The above table gives the number of neutrons per million polonium alpha-particles reported by a number of authors. In parentheses below the target element is given the atomic stopping power in relation to air that was used in the conversion of the thin-target results. The discrepancies that appear in the table are rather large compared with the errors that might otherwise be assigned to the individual measurements, and it is therefore not readily apparent how these discrepancies may be explained.

ACKNOWLEDGMENTS

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[4] T. Bjerge, Proc. Roy. Soc. **164A**, 243 (1938).

[5] E. Stuhlinger, Zeits, F. Physik **114**, 185 (1939).

** The author is indebted to Dr. D. C. Peaslee for pointing this out.

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The Clustering of Ions and the Mobilities in Gaseous Mixtures

ALBERT W. OVERHAUSER
Department of Physics, University of California, Berkeley, California

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It is shown by direct analysis that the deviations from Blanc's law for mobilities of ions in mixtures of gases observed when a strongly polarizable gas is mixed with one less polarizable cannot be ascribed to a statistical clustering effect as proposed by Loeb. Analysis involving the assumption that the ion undergoes labile clustering of the simplest type indicates that the observed results can be completely accounted for within the realms of simple theory. Thus assuming that the active gas can attach a single molecule to the ion and that this attachment molecule may be detached with different probabilities by collisions with the two types of gas molecules leads to an equation for the resultant mobilities which will cover practically all cases observed. The forces assumed can be dielectric but may also be secondary valence or van der Waals' forces. It is indicated how, with appropriate experimental procedures possible under modern techniques, most of the constants required for the solution of the equation can be directly determined or computed.

FOR many decades controversy raged as to whether gaseous ions were molecular clusters of large radii or charged single molecules retarded in their motion by dielectric forces with the gas. These forces were usually assumed to be attractive and of the inverse fifth power type, their effect being to increase the effective collision radius of the ion. The discussions were indecisive because little could be said about the binding forces of the proposed clusters and the conditions necessary for their formation. It was assumed that a cluster would form and be stable if $-2u_r/3kT>1$, where u_r is the potential energy of a gas molecule at a distance r from the ion equal to the sum of the radii of the molecule and the ion. If one assumes the inverse fifth power law to hold even at distances of the order of 10^{-8} cm, then $u_r=-(D-1)e^2/8\pi Lr^4$, where D is the dielectric constant of the gas and L is the Loschmidt number. This criterion is, of course, quite arbitrary, but it would appear to be correct in a qualitative way.

Investigations over the years established certain points very clearly. In many gases the ions do not attach molecules as long as the gas is pure and at room temperature. Notable examples of such behavior are the alkali ions in the inert gases. However, it was found from aging and mixture studies that ions have strong affinities for certain types of gaseous molecules and selectively attach these to form stable complex ions of relatively few atoms. These ions in some cases resemble well-known ion complexes observed in solution. The experimental observations indicated that when such clustering occured, the attachment was rapid, causing a discrete change in the mobility, and hence the size of the ion. There was no evidence of a gradual or successive change in mobility or size.

Studies of ion mobilities in mixtures of certain gases showed deviations from the behavior to be expected on simple theory. The drift velocity of an ion in a gas due to an electric field X is $v=kX$. The constant of proportionality k is called the mobility of the ion. The mobility, which depends upon the natures of the ion and the gas, is found to be inversely proportional to the density of the gas. Thus, in general, one may write $1/k=QN$, where N is the number of molecules per unit volume and Q is a constant. It is useful to define a constant K called the reduced mobility, which is the mobility if the gas is at atmospheric pressure. Thus, $1/K=QL$, where L is the Loschmidt number.

Assume a gas to be composed of N_A molecules of a gas A with a constant Q_A and N_B molecules of a gas B with a constant Q_B. Then, if mixing gases A and B does not change the nature of the ions, the mobility of an ion in the mixture will be given by $1/k_{AB}=Q_AN_A+Q_BN_B$. This result follows from the principle that for an ion of a given drift velocity, the rate of transfer of momentum to one component of the gas is independent of the presence of the other component. If we let f_A and f_B be the mole fractions of A and B molecules $(f_A=N_A/(N_A+N_B))$, then the reduced mobility in the mixed gas is given by: $1/K_{AB}=f_A/K_A+f_B/K_B$. This is Blanc's law. Since $f_A+f_B=1$, $1/K_{AB}$ is a linear function of f_A as shown in Fig. 1.

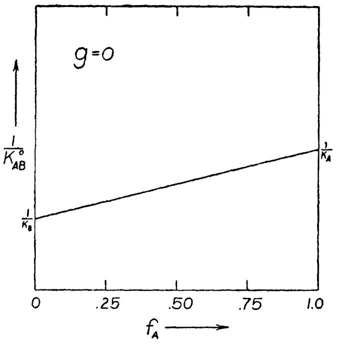

FIG. 1. Calculated reciprocal mobilities in arbitrary units against mole fraction of attaching gas. Clustering coefficient $g=0$. Blanc's law holds.

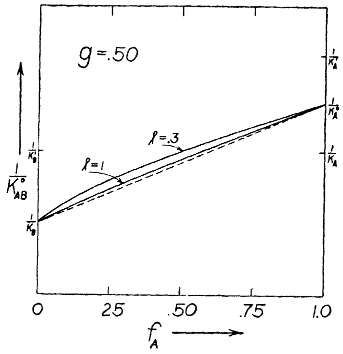

FIG. 2. Calculated reciprocal mobilities in arbitrary units against mole fraction of attaching gas. Same scale as in Fig. 1, with $g=0.5$ and two values of l. Low values of l indicate low dissociating action of neutral gas. Blanc's law is dashed curve. Note intermediate value of quasi-clustered ion in pure attaching gas.

Studies of ion mobilities in mixtures containing one constituent of high dielectric constant showed deviations from the anticipated form given by Blanc's law. The deviation from the linear curve of $1/K_{AB}$ against f_A with gases like NH_3 or HCl was convex upward as in Fig. 3, indicating that $1/K_{AB}$ increased more rapidly with f_A than the increase in concentration warranted. Since these effects were observed when gases of high dielectric constant were mixed with gases of low dielectric constant, P. Debye suggested that this action might be similar to the statistical clustering which he was then applying to ions in solutions. On this basis, E. U. Condon suggested a theory which was applied in approximate form by L. B. Loeb.[1] In what follows, however, it will be shown that statistical clustering properly accounted for cannot explain deviations from Blanc's law.

The studies of Tyndall, Powell[2,3] and their associates at Bristol on mobilities at very low temperatures and in gaseous mixtures containing polar and polarizable molecules gave results which were quite revealing. They first showed that for common gases of low dielectric

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[1] For general background see L. B. Loeb, *Fundamental Processes of Electrical Discharge in Gases* (John Wiley and Sons, Inc., New York, 1939), p. 42 ff.

[2] R. J. Munson, A. M. Tyndall, and K. Hoselitz, Proc. Roy. Soc. (London) **A172**, 28–54 (1939).

[3] H. G. David and R. J. Munson, Proc. Roy. Soc. **A177**, 192 (1941); see also reference 1, p. 65 ff.

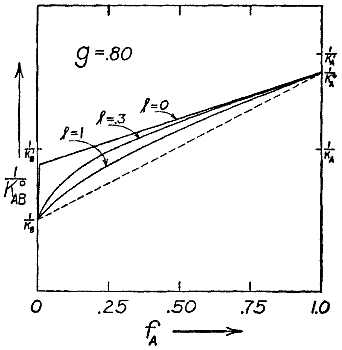

FIG. 3. Analogous to Fig. 2 with $g=0.8$ and 3 values of l. Note the progressive changes relative to Fig. 2. Blanc's law dashed.

constant clustering could occur if temperatures were sufficiently low.[2] It was further shown that if the ion were small and the gas molecule a large polarizable entity, such as Li^+ ions in Xe, clusters of one to a very few atoms could form even at room temperatures.[2] These results gave the first clear evidence of the type of attachment to be expected when $-2u_r/3kT>1$. In interpreting their results in mixtures the Bristol group concluded that the statistical clustering concept of Loeb was in error.[3] They qualitatively inclined toward another concept of the ion cluster for their interpretation of the deviations from Blanc's law. This involved the concept of a cluster which changes its size owing to association and dissociation as the ion moves, a consequence to be expected when $-2u_r/3kT\sim 1$. Such an ion can be called a labile ion cluster in contrast to the fixed and statistical clusters of history. In what follows, it will be formally proved that the statistical clustering in the gaseous phase is inapplicable and that a labile cluster theory quantitatively explains all the results on mobilities in mixtures.

In order to discuss the effect of statistical clustering in relation to Blanc's law, we may proceed as follows. The presence of the ionic charge in the gas changes the density of molecules in the neighborhood of the ion because of the force field. This change in density near the ion is given by the Boltzmann law as $\exp(\beta)$, where $\beta=-u/kT$, u being a potential of the order of magnitude of u_r. The equation for the mobility as a function of density then becomes $1/k=QN\exp(\beta)$. Thus the expression for Q is no longer $Q=1/KL$, but is:

$$Q=1/KL\exp(\beta).$$

If one now considers the mobility of a given ion in a mixture of two gases A and B, the amount of clustering of A molecules about the ion is in general different from the amount of clustering of the B molecules. The expression for the mobility in the mixture must be modified as follows: $1/k_{AB}=Q_AN_A\exp(\beta_A)+Q_BN_B\exp(\beta_B)$, where β_A and β_B are the β's appropriate to the given ion in the gases A and B. Introducing the new values of Q_A and Q_B we infer the value of K_{AB} as: $1/K_{AB}=f_A/K_A+f_B/K_B$. This is again the Blanc law. It is seen that with a proper use of the concentration factors, the statistical clustering factors drop out because they are already present in the expressions for $1/K_A$ and $1/K_B$. Although statistical clustering does occur and causes the observed mobilities to be somewhat lower than may first be expected from a solid elastic sphere model of the gas, the net effect is only to demand a renormalization of the Q's.

The formation of stable ion clusters also fails to explain deviations from Blanc's law. For example, let an ion combine with a molecule of an active gas A to form a stable cluster. Then, in mixtures with an inactive gas B, $1/K_{AB}$ is a linear function of f_A, as shown in Fig. 4, except in the neighborhood of $f_A=0$. The anomaly near $f_A=0$ is due to the fact that the ion does not attach an A molecule immediately unless there is a sufficient number of A molecules present. In the pure gas B no attachment takes place.

There remains but one alternative. One must assume that the ions involved are labile and can change their average nature continuously with concentration. In the original investigations Loeb and others used mixtures of gases like H_2 and NH_3.[4] H_2, having a low dielectric constant D_B, does not attach itself to the ion, whereas NH_3, having a large dielectric constant D_A, can associate with the ion to form a cluster. Since addition of several molecules to form an A cluster is unlikely from experimental evidence, it is best to consider a relatively simple model for study.

We will first consider the effect of labile cluster formation in a pure active gas A. We will assume that in drifting through the gas, an ion I can combine with one molecule of gas A to form a new ion $I'=I+A$. We will further assume that as the new ion I' drifts through the gas, it can dissociate as a result of molecular impacts, and become again the ion I. Thus, as the ion wanders through the gas, it spends part of its time as I and the remaining time as I'. Such actions are possible if the ratio $-2u_r/3kT\sim 1$, a condition that is not unlikely in the light of the studies of the Bristol group on temperature dependence of mobilities.[2]

The individual ions I and I' will have different mobilities, k_A and k_A', and corresponding reduced mobilities, K_A and K_A'. The observed mobility of the ion will not be equal to either of these values, but to a value k_A^0, such that $k_A'<k_A^0<k_A$. In order to determine k_A^0 as a function of k_A and k_A', one must know the fraction of the distance that the ion drifts as I or I'.

Let x be the average total distance that the ion drifts as I, and x' the average total distance that the ion drifts as I'. Then, the observed reduced mobility is given by:

$$1/K_A^0=x/(x+x')K_A+x'/(x+x')K_A'.$$

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[4] L. B. Loeb, Proc. Nat. Acad. Sci. **12**, 35, 42, 677 (1926); L. B. Loeb, and L. DuSault, Proc. Nat. Acad. Sci. **13**, 511 (1927); **14**, 192, 384 (1928); L. B. Loeb and K. Dyk, Proc. Nat. Acad. Sci., **15**, 146 (1929); L. B. Loeb, Phys. Rev. **35**, 184 (1930); A. M. Tyndall and L. R. Phillips, Proc. Roy. Soc. **A111**, 577 (1926).

Let us define a new quantity g as the clustering coefficient of ion I in gas A, given by: $g=1/(1+x/x')$. The previous expression can then be written as

$$1/K_A{}^0=(1-g)/K_A+g/K_A{}'.$$

We must now evaluate g in view of the mechanisms assumed for clustering.

Let μ_A be the probability per collision that the ion I will change to I' in collisions with the gas A. Let ν_A be the probability per collision that the ion I' will dissociate to form I as a result of impacts with the gas. The quantities μ_A and ν_A will depend upon the temperature and upon the nature of the molecules involved. We will assume for the present that they are independent of the density of the gas. Let $\bar{x}$ be the mean distance that the ion I drifts in the direction of the field X before it associates to form I', and $\bar{x}'$ the mean distance that I' drifts before it dissociates to I.

The collision frequency of I with A molecules is $Z_A=\bar{c}_A\sigma_A N_A$, where $\bar{c}_A$ is the mean relative velocity, and σ_A is the cross section for the collision. The time spent in traversing 1 cm in the field direction is: $t_A=1/kX=Q_AN_A/X$. Therefore:

$$\bar{x}=1/Z_At_A\mu_A=X/\bar{c}_A\sigma_AQ_AN_A{}^2\mu_A.$$

Similarly, with the primed symbols relating to the corresponding quantities for I', we have:

$$\bar{x}'=X/\bar{c}_A{}'\sigma_A{}'Q_A{}'N_A{}^2\nu_A.$$

Therefore,

$$p=x/x'=\bar{x}/\bar{x}'=\frac{\bar{c}_A{}'\sigma_A{}'Q_A{}'\nu_A}{\bar{c}_A\sigma_AQ_A\mu_A},$$

so that g becomes: $g=1/(1+p)$.

Since p is independent of N_A, so is g. This result implies that $1/k_A{}^0$ is proportional to N_A in active gases as well as in inactive gases. Theoretically, this conclusion follows from the assumption that μ_A and ν_A are independent of N_A. The dissociation probability ν_A is, plausibly, independent of N_A, since one would expect that the dissociation mechanism involves only simple collisions. In order for association to occur, there must be some means of carrying away the binding energy of the cluster. Such action can occur if the process of association involves a three body collision. The association probability μ_A may then depend upon the density of the gas, and in the latter case, we would have $\mu_A=\alpha N_A$. This relation implies that $1/k_A{}^0$ is not proportional to N_A. Such a non-linear dependence of mobility on density has not been reported; but the proportional law has not been under suspicion, and has never been verified for active gases. Clarification of this question appears possible only by recourse to experiment. In the discussion of mobilities in a mixture of active and inactive gases, we will treat μ_A as a constant.

In a mixture of an active gas A and an inactive gas B we assume that B forms no cluster with I, that is, $\mu_B=0$. However, collisions of $I'=I+A$ with B molecules can dissociate I' to give I. Let ν_B be the dissociation probability for impacts with B molecules. In general ν_B will be different from ν_A. Now, in the mixed gas the ions I and I' will have different mobilities: $1/k_{AB}=Q_AN_A+Q_BN_B$ and $1/k_{AB}{}'=Q_A{}'N_A+Q_B{}'N_B$.

In analogy with what has gone before, if y represent the average total distance that the ion drifts as I in the mixture, and y' the distance covered as I', then the observed mobility $k_{AB}{}^0$ in the mixture is given by:

$$1/k_{AB}{}^0=y/(y+y')k_{AB}+y'/(y+y')k_{AB}{}'.$$

For the ion I, the time to drift 1 cm in the field direction is $t=1/k_{AB}X=(Q_AN_A+Q_BN_B)/X$. The collision frequency of I with A molecules is again: $Z_A=\bar{c}_A\sigma_AN_A$. These expressions lead to the value of $\bar{y}$, the mean distance that I drifts before forming a cluster as: $\bar{y}=X/(Q_AN_A+Q_BN_B)\bar{c}_A\sigma_AN_A\mu_A$.

For the ion I' we have

$$t'=1/k_{AB}{}'X=(Q_A{}'N_A+Q_B{}'N_B)/X.$$

For collisions with gas A, $Z_A{}'=\bar{c}_A{}'\sigma_A{}'N_A$; and for collisions with gas B, $Z_B{}'=\bar{c}_B{}'\sigma_B{}'N_B$. It may be noted that $\bar{c}_A{}'$ and $\bar{c}_B{}'$ are different since these quantities are the relative velocities. Accordingly, we have for $\bar{y}'$:

$$\bar{y}'=1/(Z_A{}'\nu_A+Z_B{}'\nu_B)t'.$$

Thus, one can write:

$$\frac{y}{y'}=\frac{\bar{y}}{\bar{y}'}=\frac{(Q_A{}'N_A+Q_B{}'N_B)(\bar{c}_A{}'\sigma_A{}'N_A\nu_A+\bar{c}_B{}'\sigma_B{}'N_B\nu_B)}{(Q_AN_A+Q_BN_B)\bar{c}_A\sigma_AN_A\mu_A}.$$

From this equation and the expression for $k_{AB}{}^0$ we can find the expression for $K_{AB}{}^0$, the reduced mobility as observed in the mixed gas. Letting $N_A+N_B=L$, we obtain:

$$\frac{1}{K_{AB}{}^0}=\frac{\left(\frac{f_A}{K_A}+\frac{f_B}{K_B}\right)\left(\frac{f_A}{K_A{}'}+\frac{f_B}{K_B{}'}\right)\left[f_A+(f_A+lf_B)\frac{K_A{}'}{K_A}\left(\frac{1-g}{g}\right)\right]}{\left(\frac{f_A}{K_A}+\frac{f_B}{K_B}\right)f_A+\left(\frac{f_A}{K_A{}'}+\frac{f_B}{K_B{}'}\right)(f_A+lf_B)\frac{K_A{}'}{K_A}\left(\frac{1-g}{g}\right)}.$$

This expression is seen to be a function of the mole fractions, the reduced mobilities of the ions I and I' in gases A and B, and two characteristic constants g and l. The quantity g is the clustering coefficient of I in the pure gas A, as has already been discussed. g can have values from $g=0$ for no clustering to $g=1$, the con-

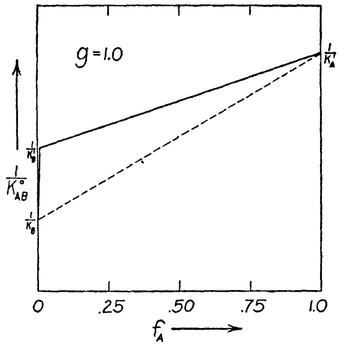

FIG. 4. Analogous to Figs. 2 and 3 with $g=1$. Note that clustering is completed at low values of mole fraction of attaching gas, and that the mobilities of both extremes refer to the ion I'. Blanc's law dashed.

dition for the formation of stable clusters. The quantity l is a dissociation parameter, and is a measure of the relative dissociation abilities of gas A and gas B. It is given by the relation $l=\sigma_B'\bar{c}_B'\nu_B/\sigma_A'\bar{c}_A'\nu_A$. l can have any positive value. In general, unless the gases have very disparate masses, or cross sections, l will be close to unity.

The curves shown in Figs. 1, 2, 3, and 4 illustrate the final result for appropriate relative values of K_A, K_A', K_B, K_B', and for several values of g and l. In Fig. 1, with $g=0$, i.e. no clustering, one has the conventional Blanc's law, as would be expected. When g is 0.5, as in Fig. 2, a slight curvature is apparent, the deviation being greater for smaller values of l. When the clustering coefficient is 0.8, Fig. 3, the bowing is quite marked.

It may be noted that when $l\sim 0$, $1/K_{AB}^0$ rises sharply at $f_A=0$, and then increases almost linearly to its maximum value $1/K_A^0$. Such a small value for the dissociation parameter means that the B molecules have little effect in the dissociation process, so that clustering is not suppressed by large concentrations of gas B. This condition may be realized when the inactive gas B is of low molecular weight, e.g. H_2; for then, the impacts delivered to the heavy clustered ions I' by the light B molecules are small, causing relatively few dissociations.

Finally, when $g=1.0$, $1/K_{AB}^0$ behaves like a Blanc's law curve for I' ions in the mixture, except for a small range of values at $f_A=0$. References to papers by Loeb, Tyndall, and Powell, and others will show the striking similarity between the observed curves and those computed, indicating that even this simple theory accounts well for the experimental results.

One might believe that with six parameters at his disposal, a theoretical curve could be found to fit almost any set of data. Five of these constants, however, can be established independently. From the complete mobility equation of Langevin,[3] the constants K_A, K_A', K_B, and K_B' can be computed. In many practical cases K_B can be measured directly, and K_A can be computed from the equation:[5]

$$K_A=0.235\left(\frac{1+M/m}{(D-1)M_0}\right)^{\frac{1}{2}}.$$

Here, M_0 is the molecular weight of gas A. The studies of Tyndall and Powell have substantiated this expression for the reduced mobility of an ion I in a gas A where the effect of dielectric attractive forces predominates over that of solid elastic collisions. However, this equation cannot be expected to hold for the clustered ions I', where the collisions will play a greater role, owing to the increased size of the ion. It was the application of this expression to K_A^0 that inclined the Bristol group to postulate multimolecular clusters, a concept at variance with the results of aging experiments.

There is a possibility that K_A and K_A' may be measured directly. If apparatus of good time resolution is applied, and mobility measurements are made over distances of the order of $\bar{x}$ and $\bar{x}'$, then a mobility spectrum will be obtained with K_A and K_A' as the upper and lower limits.

With K_A and K_A' known, measurement of K_A^0 determes g immediately:

$$g=(1/K_A^0-1/K_A)/(1/K_A'-1/K_A).$$

The remaining parameter l can then be determined by measurements in the mixed gas and subsequent comparison with computed curves. The theory is therefore open to verification. It is hoped that the concept of clustering here advanced will make possible a more complete interpretation of experimental data.

In conclusion, the author takes pleasure in acknowledging his indebtedness to Professor L. B. Loeb, whose course in discharge through gases prompted the investigation, and who was most generous with his encouragement and aid in preparing the manuscript.

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[5] See reference 1, p. 62 ff.