Blanc's Law—Ion Mobilities in Helium-Neon Mixtures

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The mobilities of ions of near thermal energies are measured in helium-neon mixtures using a drift velocity apparatus. These studies permit the investigation of ion motion in gases, e.g., He^+ in Ne, under conditions where the charge transfer interaction is negligible compared to polarization attraction and short-range repulsion between ion and atom. In addition, the measurements provide a test of Blanc's empirical law, $1/\mu=f_1/\mu_1+f_2/\mu_2$, which relates the mobility μ in a binary mixture to the pure gas mobilities μ_1 and μ_2 and to the fractional gas concentrations f_1 and f_2. A theoretical treatment developed by Holstein is presented which shows that deviations from Blanc's law are limited to a few percent. The mobilities of He^+, He_2^+, and Ne_2^+ ions are found to obey accurately Blanc's law. However, the "Ne^+" ion curve deviates markedly from the law. These deviations are explained in terms of the formation of moderately stable $(He\,Ne)^+$ ions from Ne^+. Finally, the observed mobilities of He_2^+ in Ne and Ne_2^+ in He are found to agree with the predictions of polarization theory.

I. INTRODUCTION

TECHNIQUES for determining the mobilities of ions of near-thermal energy have been described in detail in previous papers.[1–3] These measurements have been extended to the study of ion mobilities in helium-neon mixtures for the purpose of investigating the mobilities of noble gas atomic ions under conditions where the charge transfer interaction is negligible compared to the interactions of polarization attraction and short-range repulsion. In addition, these studies provide a test of Blanc's law (which describes the mobilities of ions in gas mixtures in terms of their pure gas mobilities) under conditions which avoid the apparent complications, such as "clustering," of earlier studies.[4]

II. BLANC'S LAW

In 1908, Blanc[5] investigated the mobilities of ions in binary mixtures of gases, such as H_2 and CO_2. It was found that the mobility μ obeyed the simple relationship

$$\frac{1}{\mu}=\frac{f_1}{\mu_1}+\frac{f_2}{\mu_2}, \tag{1}$$

where f_1 and f_2 are the fractional concentrations of gas 1 and gas 2, respectively; i.e., $f_1+f_2=1$. The mobilities μ_1 and μ_2 are the "pure gas" mobilities for the ion in each of the gases.

Later studies[4] showed marked deviations from this simple law; however, since the measurements often applied to complicated gases, such as water vapor and air, the deviations could be ascribed to complex ion formation or to "clustering." The present measurements involve the simple gases, helium and neon, under circumstances in which clustering of ions and complex ion formation were not expected.

III. VALIDITY OF BLANC'S LAW

Let us consider the elementary "average particle" definition of mobility, i.e.,

$$\mu^{-1}=C(m/e)\langle P_{sc}\rangle_{av}, \tag{2}$$

where C is a constant, (m/e) is the mass to charge ratio of the ion, and $\langle P_{sc}\rangle_{av}$ is the average probability per unit time of scattering of the ion (obtained by averaging over the actual ion velocity distribution). In binary gas mixtures of sufficiently low density so that only *two*-body collisions involving the ion and a gas molecule need be considered, the scattering probability is simply

$$P_{sc}=f_1(P_{sc})_1+f_2(P_{sc})_2, \tag{3}$$

where $(P_{sc})_{1,2}$ are the scattering probabilities in the pure gases 1 and 2, respectively. Combining Eqs. (2) and (3), it will be seen that the empirically determined Blanc's law follows immediately.

This and other[4] elementary "proofs" of Blanc's law are based on the results of first-order mobility theory, as expressed in Eq. (2). A more rigorous approach to the investigation of the validity of Blanc's law has been made by Holstein.[6] He starts with the Boltzmann transport equation[7] for the ions:

$$\frac{\partial f}{\partial t}+\mathbf{v}\cdot\nabla f+\frac{e\mathbf{E}}{m}\cdot\nabla_{\mathbf{v}}f =\int[K(\mathbf{v}',\mathbf{v})f(\mathbf{v}')-K(\mathbf{v},\mathbf{v}')f(\mathbf{v})]d^3v', \tag{4}$$

where f is the ion distribution function, e and m the charge and reduced mass of the ion, respectively, $\mathbf{E}$ is

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[1] M. A. Biondi and L. M. Chanin, Phys. Rev. **94**, 910 (1954).

[2] L. M. Chanin and M. A. Biondi, Phys. Rev. **106**, 473 (1957).

[3] L. M. Chanin and M. A. Biondi, Phys. Rev. **107**, 1219 (1957).

[4] For a discussion, see L. B. Loeb, *Basic Processes of Gaseous Electronics* (University of California Press, Berkeley, 1955), p. 129 ff.

[5] A. Blanc, J. Phys. **7**, 825 (1908).

[6] T. Holstein, Phys. Rev. **100**, 1230(A) (1955), and private notes (unpublished).

[7] A detailed discussion of the use of the Boltzmann theory in ion mobility treatments is given by G. Wannier, Bell System Tech. J. **32**, 170 (1953).

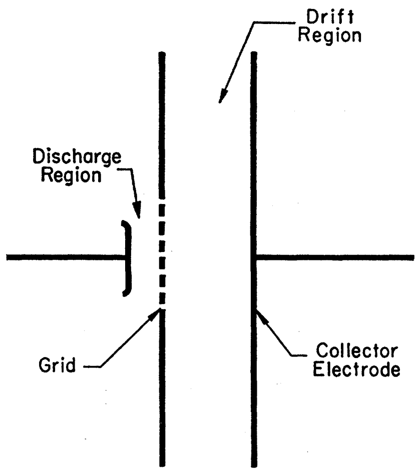

FIG. 1. Schematic arrangement of the electrodes in the ion-mobility tube.

the electric field, and $K(\mathbf{v},\mathbf{v}')d^3v'$ is the probability per unit time that an ion with velocity, $\mathbf{v}$, will have its velocity changed by a collision with an atom to the value, $\mathbf{v}'$, contained in the differential volume, (d^3v').[8] For the case of ions moving through a gas under the action of a sufficiently small electric field so that they remain essentially in thermal equilibrium with the gas, the ions' distribution function may be represented by one which is slightly displaced from a Maxwellian distribution in the electric field direction, i.e.,

$$f(\mathbf{v})=f_0(v)[1+\mathbf{v}\cdot\mathbf{E}\chi(v)],\tag{5}$$

where $f_0(v)=(m/2\pi kT)^{\frac{3}{2}}\exp(-mv^2/2kT)$ is the Maxwellian distribution.

Under steady-state conditions, Eq. (4) simplifies to

$$-(e/kT)\exp(-mv^2/2kT)=\int L(\mathbf{v},\mathbf{v}')\left[\frac{\mathbf{v}\cdot\mathbf{v}'}{v^2}\chi(v')-\chi(v)\right]d^3v',\tag{6}$$

where the new collision kernel,

$$L(\mathbf{v},\mathbf{v}')=K(\mathbf{v},\mathbf{v}')\exp(-mv^2/2kT),$$

has been introduced because of its symmetry property, $L(\mathbf{v},\mathbf{v}')=L(\mathbf{v}',\mathbf{v})$.

The drift velocity $\mathbf{v}_d$ and the associated quantity, the ion mobility, are defined by

$$\mu\mathbf{E}=\mathbf{v}_d\equiv\int\mathbf{v}f(v)d^3v.\tag{7}$$

From Eq. (5), this becomes

$$\mu=\tfrac{1}{3}\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\int v^2\exp(-mv^2/2kT)\chi(v)d^3v.\tag{8}$$

[8] For the case of near-thermal equilibrium, the principle of detailed balancing gives $K(\mathbf{v}',\mathbf{v})/K(\mathbf{v},\mathbf{v}')=\exp[-m(v'^2-v^2)/2kT]$.

In order to use a variational analysis to determine the correct mobility, one chooses the form

$$\mu=\frac{e}{3kT}\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}}\times\frac{\left[\int v^2\chi(v)\exp(-mv^2/2kT)d^3v\right]^2}{\int\int L(\mathbf{v},\mathbf{v}')[v^2\chi(v)-\mathbf{v}'\cdot\mathbf{v}\chi(v')]d^3vd^3v'},\tag{9}$$

obtained by combining Eqs. (6) and (8). For a given trial function, $\chi_T(v)$, one may prove that; (a) Eqs. (8) and (9) coincide for the correct $\chi(v)$, i.e., the $\chi(v)$ which satisfies the Boltzmann Eq. (6), and (b) a trial mobility μ_T obtained by inserting an arbitrary trial function χ_T into Eq. (9) obeys the inequality, $\mu\geqslant\mu_T$. In addition, the succession of trial mobilities obtained by using successively generalized trial χ's converges upwards toward the correct mobility, μ.

Let us now consider the application of this treatment to the derivation of Blanc's law. In a binary mixture of fractional concentrations, f_1 and f_2, the collision probability per unit time is given by

$$L(\mathbf{v}',\mathbf{v})=f_1L_1(\mathbf{v}',\mathbf{v})+f_2L_2(\mathbf{v}',\mathbf{v}),\tag{10}$$

where L_1 and L_2 are the collision probabilities for gases 1 and 2, respectively. Thus, if the correct $\chi(v)$ does not depend on the fractional concentration in the mixture, Blanc's law immediately follows from Eq. (9), i.e.,

$$\frac{1}{\mu}=\frac{f_1}{\mu_1}+\frac{f_2}{\mu_2}.\tag{11}$$

It then follows that conventional first-order mobility theory, where the distribution function is expanded to the order of Eq. (5), with $\chi(v)=$constant, independent of the nature of the gas mixture, automatically yields Blanc's law.

If the functional form of $\chi(v)$ changes with the make-up of a binary mixture (as may well be the case if the force laws describing the scattering of the ion by the two different types of atoms are of strongly different types) then deviations from Blanc's law are to be expected. From the variational analysis, Holstein shows that the deviations are in such a direction that the curve of $1/\mu$ vs f_1 has negative curvature; thus

$$\frac{1}{\mu}\geqslant\frac{f_1}{\mu_1}+\frac{f_2}{\mu_2}.\tag{12}$$

An estimate of the extent of the deviation from Blanc's law is obtained by noting that since the correct mobility is always greater than the trial mobilities,

$$\frac{1}{\mu}<\frac{1}{\mu^{(1)}}=\frac{f_1}{\mu_1^{(1)}}+\frac{f_2}{\mu_2^{(1)}},\tag{13}$$

where $\mu^{(1)}$ is the mobility given by the first-order theory [with the trial function $\chi_T(v)=\text{constant}$]. Thus, if the ion mobilities, μ_1 and μ_2, in the pure gases are accurately represented by the first-order theory values $\mu_1^{(1)}$ and $\mu_2^{(2)}$, Eqs. (12) and (13) require that the deviations from Blanc's law be small. Chapman and Enskog[9] have considered the higher order corrections to the first-order theory of mobility. In general, for various reasonable force laws, the corrections are found to be small, of the order of a few percent. Consequently, deviations from Blanc's law are limited to this order of magnitude.

IV. EXPERIMENTAL METHOD

The mobility tube used to determine the ion mobilities in helium-neon mixtures has been described in detail previously.[1] This tube, which is shown schematically in Fig. 1, consists of a shielded discharge region in which a short-duration pulse of ions is created. The ions are admitted through a grid into the drift region where their motion induces a current in a resistor in the external circuit. The resulting voltage signal is amplified and displayed on a synchronized oscilloscope. The drift velocity is determined from observation of the time required for the ions to cross the drift region.

Gas samples employed in these studies were Airco Reagent Grade. The mobility tube was mounted on an ultrahigh-vacuum system which attained pressures $<10^{-8}$ mm Hg and rates of rise of contamination pressure $<10^{-9}$ mm Hg/min.

V. MEASUREMENTS

An example of the results of our measurements is shown in Fig. 2. The mobility μ_0 of "Ne+" ions[10] moving in various mixtures of helium and neon, i.e., 38, 50, and 70% neon, is shown as a function of E/p, the ratio of drift field to gas pressure. The mobility μ_0 refers to a standard gas density of 2.69×10^{19} atoms/cc, and a temperature of 300°K, in keeping with previous usage. The short vertical lines on each curve indicate the extent of the thermal energy range. As can be seen from the figure, the experimental results extend either down into or close to this range, thereby minimizing uncertainties in the thermal values.[11]

From measurements such as shown in Fig. 2, the Blanc's law plot shown in Fig. 3 was obtained. The reciprocals of the mobilities of He^+ and "Ne+" are plotted as functions of the percent concentration of helium and neon in accordance with Eq. (1). The circled values on the ordinates indicate the values previously obtained in the pure gases.[1,2] These values serve to identify the ions in the mixture. The left-hand ordinate corresponds to the case of pure helium, the right-hand ordinate represents the case of pure neon. The total gas pressure used in these measurements was ~8 mm Hg; however, the different symbols on the Ne^+ curves indicate different runs at slightly different pressures, giving some indication of the reproducibility of the results.

The mobility of He^+ in the helium-neon mixtures is found to obey Blanc's law within the experimental error. On the other hand, the "Ne+" curve follows a reasonable straight line from 100 to ~50% neon concentration but then falls below an extension of this line. The deviation from Blanc's law is only slightly larger than the scatter in the experimental data. However, least-squares fitting of straight-line segments to the data indicates that the fit of a single straight line is considerably poorer than that obtained using two straight segments from 0–50 and 50–100% neon concentration. A discussion of possible causes of this deviation is deferred to Sec. VI.

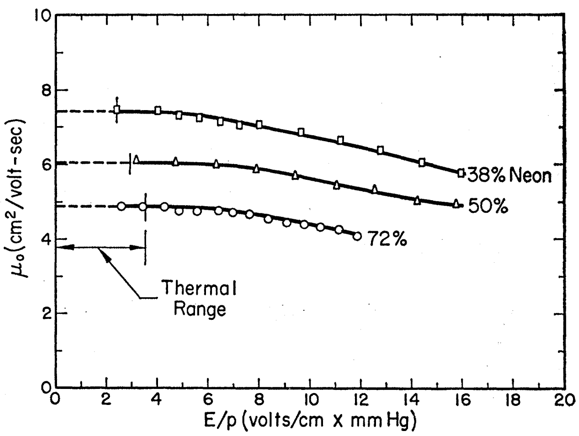

FIG. 2. Normalized mobility, μ_0, of "Ne+" ions as a function of the ratio of drift field to total gas pressure in various helium-neon mixtures at a gas temperature of 300°K. The total gas pressure was ~8 mm Hg.

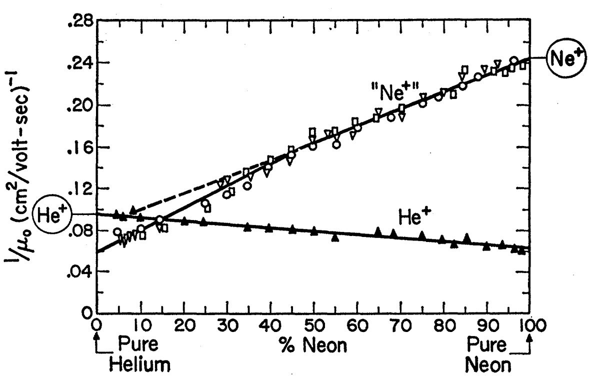

FIG. 3. Blanc's law plot for thermal "Ne+" and He^+ ions in helium-neon mixtures at 300°K and a total gas pressure of ~8 mm Hg. The circled symbols on the ordinates indicate values previously determined in single-gas studies.

[9] See, for example, S. Chapman and K. Enskog, *Mathematical Theory of Nonuniform Gases* (Cambridge University Press, London, 1939), Chap. 9. The standard mobility formulas [corresponding to a trial function of the form $\chi(v)=\text{constant}$] include a factor $1/(1-\epsilon)$ which gives the higher order corrections. For the force laws considered, ϵ is a small number.

[10] A discussion of an alternative ion identification is given in Sec. VI.

[11] Extrapolation of the mobility values to $E/p=0$ is made in such a way that the mobility becomes constant in the thermal energy range.

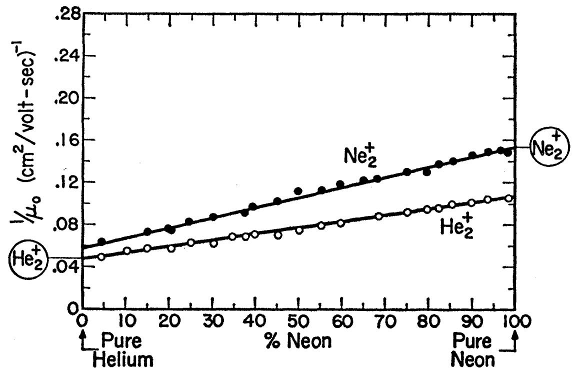

FIG. 4. Blanc's law plot for thermal Ne_2^+ and He_2^+ ions in helium-neon mixtures at 300°K and a total gas pressure of $\sim$8 mm Hg. The circled symbols indicate values previously determined in single-gas studies.

The Blanc's law plots of He_2^+ and Ne_2^+ ions are shown in Fig. 4. Once again, the pure gas mobilities previously determined for the appropriate ions are indicated on the ordinates. Here, as for He^+, Blanc's law is found to be obeyed within the limits of our experimental uncertainty.

The ion "identification" made possible by tracing the ion mobilities from their parent gas values through the various intermediate mixtures, as indicated in Figs. 3 and 4, allows us to examine the energy dependence of the mobility of ions of one gas, e.g., He^+ and He_2^+, in sufficiently high percentages of the other gas component, i.e., Ne, so that the contribution of the parent gas (He) in determining the mobility is small.

The dependence on E/p of the mobility of helium ions in neon is shown in Fig. 5. The small variation of the shape of the curves with changing neon concentration in the range 96–99% neon indicates the small effect of the helium on the mobility. Similar curves for neon ions in helium are shown in Fig. 6. As will become clear from the discussion in the next section, the "identification" of the high-mobility ion as Ne^+ is open to question.

VI. DISCUSSION

The measurements of ion mobilities in helium-neon mixtures have permitted us to test Blanc's law under simple conditions. Elementary treatments had shown that, provided the ion retained its identity over the range of gas mixtures studied, Blanc's empirical law [Eq. (1)] would be rigorously obeyed. A more sophisticated treatment by Holstein indicated that, while deviations from Blanc's law could occur, they were limited in magnitude to a few percent, and only occurred when the force laws between the ion and the two scattering gases differed considerably. Thus, the experimental confirmation of Blanc's law for He^+, He_2^+, and Ne_2^+, as indicated in Figs. 3 and 4 is consistent with theoretical conclusions. However, the deviations ($\sim$8%) from Blanc's law for "Ne^+" ions, while only moderately greater than the experimental scatter, seems to be a real effect.

Initially, the deviations were ascribed to the substantially different force laws between Ne^+ and neon (long-range charge transfer, plus a short-range repulsive interaction) and between Ne^+ and helium (polarization attraction and short-range repulsion).[12] This explanation seems unsatisfactory for two reasons; the magnitude of the deviation is greater than one calculates from theory for these types of force laws, and the case of He^+ in helium and neon involves similar force laws, yet does not exhibit detectable deviations. More recently, the existence of the ion (He Ne)$^+$ has been reported from mass spectrometer studies.[13] The fact that these ions are formed in appreciable concentrations at pressures and on time scales similar to those used in the mobility studies has very recently been confirmed in microwave afterglow studies employing mass analysis.[14] Afterglows of helium containing small amounts of neon at total pressures of several mm Hg yielded (He Ne)$^+$ ions in comparable concentrations to He^+, He_2^+, and Ne^+.

One reasonable formation and destruction reaction for (He Ne)$^+$ is the following:

$$Ne^+ + He + X \rightleftharpoons (\text{He Ne})^+ + X, \tag{14}$$

where X is a third body (either Ne or He in the present mixture studies).[15] The rates of creation and destruction are not known; however, if our measuring time scale (10–100 μsec) is long compared to the formation and destruction times, a quasi-equilibrium will exist with a given Ne^+ ion existing part of the time in an uncombined and the remainder in a "combined" state as it drifts across the tube. The mass action law gives, for the

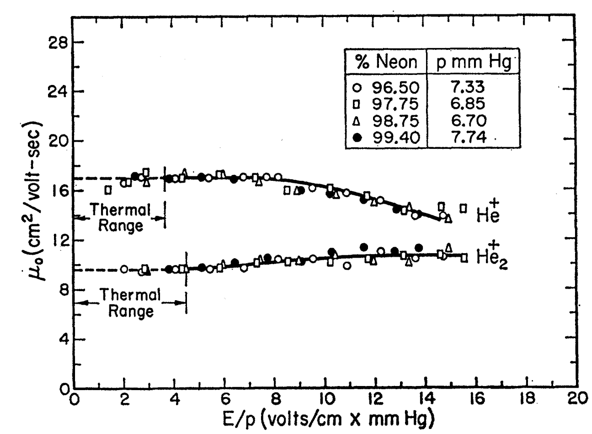

FIG. 5. The mobilities of He^+ and He_2^+ as a function of E/p at high fractional concentrations of neon and at a gas temperature of 300°K.

[12] M. A. Biondi and L. M. Chanin, Phys. Rev. **100**, 1230(A) (1955).

[13] M. Pahl and U. Weimer, Z. Naturforsch. **12a**, 926 (1957), and H. J. Oskam, thesis, University of Utrecht, 1957 (unpublished).

[14] W. A. Rogers and M. A. Biondi, Westinghouse Research Memo 403FD457-M4 (unpublished).

[15] A difficulty of the (He Ne)$^+$ hypothesis is that the analogous reaction, $He^+ + Ne + X \rightleftharpoons (\text{He Ne})^+ + X$, must be assumed to occur at a much slower rate to explain the absence of an effect on the Blanc's law curve for He^+ ions.

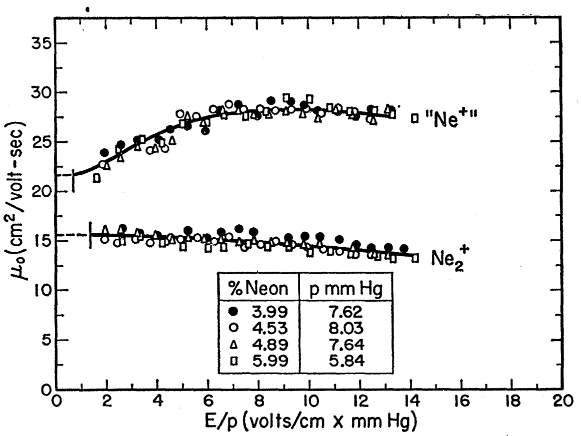

FIG. 6. The mobilities of "Ne^+" and Ne_2^+ as a function of E/p at high fractional concentrations of helium and at a gas temperature of 300°K.

fractional concentration of each type of ion:

$$\frac{N(Ne^+)N(He)}{N(He\ Ne^+)} = c\exp(-\Delta E/kT), \quad (15)$$

where c is a constant including the statistical weights of each state, ΔE is the binding energy of the $(He\ Ne)^+$ ion, and T is the common temperature of the gas atoms and of the ions. From Eq. (15), it will be seen that as the helium concentration increases, the fraction of time the ion is in the combined $(He\ Ne)^+$ state increases. Thus, at high *helium* concentrations the curve of $1/\mu_0$ vs percentage of neon is appropriate to the $(He\ Ne)^+$ ion, while at high *neon* concentrations it is appropriate to Ne^+. Since these two curves can have quite different slopes, marked deviations from a single straight line joining the end points can occur. In the intermediate concentration region, a weighted average of the two mobilities is obtained.[16]

If the rates of Eq. (14) going to the right and to the left are not fast compared to our measuring time, then the waveforms obtained in the drift tube should be distorted as a result of the fact that conversion of a Ne^+ ion to a $(He\ Ne)^+$ ion may take place anywhere along the drift path. Thus, with statistically distributed points at which conversion occurs and with a substantially different mobility for Ne^+ and $(He\ Ne)^+$ ions, the initial sharp pulse of ions becomes smeared out by the time it arrives at the collector. Although noticeable distortion of the waveforms by conversion was not observed, this point was not investigated with sufficient care since, at the time, we were unaware of the stable existence of $(He\ Ne)^+$. In this case, also, the ion "mobility," as determined from the smeared-out arrival time of the converted ions could show appreciable deviations from Blanc's law. It is hoped that future studies as functions of helium and neon pressure and of temperature will provide better evidence for one or the other of these proposed mechanisms.[17]

TABLE I. Experimental and theoretical values of positive-ion mobilities.

Ion—gas	μ_0 (exp) (cm²/volt sec)	μ_0 (pol. theory) (cm²/volt sec)
He^+—Ne	16.0	12.2
He_2^+—Ne	9.3	9.4
Ne_2^+—He	17.5	16.0

Finally, it has been possible to determine the thermal (300°K) values of the mobilities of He^+ and He_2^+ ions in neon and of Ne_2^+ in helium. The experimental values are compared with the results of mobility theory in the limiting case of a pure polarization attraction[18] in Table I.

It will be seen that rather good agreement is obtained for the cases He_2^+—Ne and Ne_2^+—He, while the simpler case He^+—Ne involves some 25% discrepancy between theory and experiment. The inclusion in the interatomic forces of the short-range repulsion between ion and atom can easily lead to an increase in the theoretical value of the mobility of this magnitude. However, in the absence of an accurate theory which includes a proper exponential repulsive potential (intermediate between the too-hard "hard-sphere" repulsion of Langevin and the too-soft $1/r^8$ repulsion of Hasse and Cook[18]), no detailed comparison of experiment and theory can be made.

ACKNOWLEDGMENT

The authors are greatly indebted to T. Holstein for many helpful discussions concerning the theoretical treatment of Blanc's law.

[16] A similar explanation has been invoked for N_2^+ and N_4^+ ions in nitrogen by R. N. Varney, Phys. Rev. **89**, 708 (1953), and J. Chem. Phys. **31**, 1314 (1959).

[17] The mobility experiment is being put back into operation for the purpose of studying the interaction between Ne^+ and He in an attempt to gain more information about the stability of $(He\ Ne)^+$.

[18] D. Langevin, Ann. Chem. Phys. **5**, 245 (1905); H. R. Hasse and W. R. Cook, Phil. Mag. **12**, 554 (1931).