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Ion Drift Velocities in Gaseous Mixtures at Arbitrary Field Strengths*

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A momentum-transfer theory is used to obtain an expression for the drift velocity of an ion in a multicomponent gas mixture. This is combined with an approximate calculation of the partition of the ion energy in the mixture to yield a formula for the drift velocity in terms of the drift velocities in the pure component gases. Positive deviations from Blanc's law at high fields are predicted, of magnitudes that should be easily measured experimentally.

I. INTRODUCTION

The purpose of this paper is to find an expression for the drift velocity of an ion in a gas mixture, in terms of the drift velocities in the pure component gases. Despite its obvious practicality, the problem has apparently been little studied, except at very low electric fields where the drift velocity is directly proportional to the field strength. In this regime Blanc's law[1,2] holds,

$$1/K_{\mathrm{mix}}=\sum_j x_j/K_j\ , \qquad (1)$$

where the x_j are mole fractions and the K_j are the mobilities in the pure component gases at the same total number density as the mixture. If the ion retains its identity in the mixture, deviations from Blanc's law are usually small.[3] The behavior at higher field strengths does not seem to be known.

Deviations from Blanc's law might be expected for high fields, where the drift velocity itself becomes approximately proportional to the square root of the field strength.[4]

Since we consider only the binary collision limit and seek only a composition dependence, any theory that counts collisions correctly should suffice. We therefore use a simple momentum-transfer theory rather than the elaborate Chapman-Enskog kinetic theory. Difficulty arises only when we need to know how the mean ion energy is partitioned among thermal energy, drift energy, and random-field energy. An approximate answer to the energy partitioning problem is obtained by an extension of Wannier's[5,6] high-field theory to mixtures; this suffices to produce the desired final result. Unfortunately, no suitable experimental results exist for comparison with the theory, but sample calculations on K^+ ions in $H_2 + N_2$ mixtures show positive deviations from Blanc's law at high fields of about 20%, which should be easily detectable experimentally.

II. MOMENTUM-TRANSFER THEORY

By Newton's second law, the electric field transfers momentum to the ions, but since the ions are not accelerated on the average, the momentum must be transferred by collisions to the gas molecules. It is easy to show that in one collision the momentum transferred to a gas molecule by an ion has a component parallel to their relative velocity $\vec{v}_r$ of[7]

$$\delta\vec{p}_{\parallel} = \mu\vec{v}_r(1-\cos\theta) , \tag{2}$$

where μ is the reduced mass of the colliding pair, and θ is the deflection angle in relative coordinates. If we average over many collisions, we expect all the random components of $\vec{v}_r$ to average to zero and only the nonrandom drift velocity to contribute. The average momentum communicated to the gas per collision is therefore proportional to $\mu v_d \times (1-\cos\theta)$, where v_d is the drift velocity. The average number of collisions an ion makes per unit time per unit volume with impact parameter in the range db is $N\bar{v}_r(2\pi b\, db)$, where N is the number density of gas molecules and $\bar{v}_r$ is the mean relative ion-molecule speed. The total momentum transferred per ion to the gas is therefore proportional to

$$\mu v_d N\bar{v}_r \int_0^\infty (1-\cos\theta) 2\pi b\, db \ . \tag{3}$$

For ions of charge e in a field of strength E we must then have

$$\xi\mu v_d N\bar{v}_r \int_0^\infty (1-\cos\theta) 2\pi b\, db = eE \ , \tag{4}$$

where ξ is a proportionality constant of order unity.

The total momentum transferred per ion to a gas mixture is just the sum of the momenta transferred to each species in the mixture, provided that only binary collisions are considered. The generalization of Eq. (4) to a mixture is therefore

$$\xi v_d \sum_j \mu_j N_j \bar{v}_{rj} Q_j = eE \ , \tag{5}$$

where we have defined a momentum-transfer or diffusion cross section as

$$Q_j = 2\pi\int_0^\infty (1-\cos\theta_j) b\, db \ . \tag{6}$$

We now make the approximation that the mean relative speed is proportional to the rms relative velocity,

$$\bar{v}_{rj} \propto \langle v_{rj}^2 \rangle^{1/2} \ . \tag{7}$$

The constant of proportionality can be absorbed into the parameter ξ, and will remain constant as long as the velocity distribution functions do not change. But the ion distribution function does change as the field strength is changed, and so (7) is only an approximation, although probably a good one. It is easy to show that

$$\langle v_{rj}^2 \rangle = \langle v^2 \rangle + \langle V_j^2 \rangle \ , \tag{8}$$

where $\langle v^2 \rangle$ is the mean square ion velocity and $\langle V_j^2 \rangle$ is the mean square velocity of molecular species j. The only condition on the validity of Eq. (8) is that the velocity distribution function of the molecules be isotropic.

Combining the foregoing results, we obtain

$$\xi v_d \sum_j [mM_j/(m+M_j)](\langle v^2 \rangle + \langle V_j^2 \rangle)^{1/2} N_j Q_j = eE \ , \tag{9}$$

where m is the ionic mass and M_j the molecular mass. The only remaining problem is to find $\langle V_j^2 \rangle$, which has both thermal and drift components. At low fields $\langle v^2 \rangle$ is entirely thermal, and energy equipartition gives

$$\langle v^2 \rangle + \langle V_j^2 \rangle = 3kT(1/m + 1/M_j) , \tag{10}$$

from which we obtain

$$\xi v_d(0) \sum_j [mM_j/(m+M_j)]^{1/2} (3kT)^{1/2} N_j Q_j = eE \ . \tag{11}$$

The drift velocity in pure gas j of density N equal to the total density of the mixture is given by one term in this sum,

$$\xi v_{d_j}(0) [mM_j/(m+M_j)]^{1/2} (3kT)^{1/2} N Q_j = eE \ . \tag{12}$$

Combining Eqs. (11) and (12) we obtain

$$v_d(0) \sum_j [x_j / v_{d_j}(0)] = 1 \ , \tag{13}$$

where $x_j = N_j/N$ is the mole fraction of species j in the mixture. This expression is equivalent to Eq. (1), Blanc's law.

For high fields $\langle v^2 \rangle$ has a negligible thermal component, but it would not be correct to take $\langle v^2 \rangle = v_d^2$, because collisions randomize part of the ion energy, which on the average then consists of a part visible as drift motion plus a random part. For a model of constant mean free time between collisions and angular scattering pattern independent of speed, Wannier[5,6] has shown that in a single gas the ion energy is

$$m\,\langle v^2\rangle = mv_d^2 + Mv_d^2\,, \tag{14}$$

the last term being the random part of the field energy. Moreover, at intermediate fields the thermal and field energies are simply additive.[5,6] As an indication of the general applicability of the approximations embodied in Eqs. (7) and (14), we note that their substitution in Eq. (9) for a single gas leads to an explicit formula for the field dependence of the drift velocity which is remarkably successful in its predictions of dependence on physical parameters, and even predicts absolute magnitudes with fair accuracy.[5,6]

Thus the problem is now reduced to finding the generalization of Eq. (14) for mixtures, which is done in Sec. III. But we can always write the result formally as

$$m\,\langle v^2\rangle = mv_d^2 + \overline{M}v_d^2\,, \tag{15}$$

where $\overline{M}$ is some sort of average mass of the gas mixture. Then Eq. (9) becomes, for high fields,

$$\xi\,[v_d(\infty)]^2 \sum_j \left(\frac{mM_j}{m+M_j}\right)\left(\frac{m+\overline{M}}{m}\right)^{1/2} N_j Q_j = eE\,, \tag{16}$$

which leads to the mixture rule,

$$\left(\frac{1}{v_d(\infty)}\right)^2 = \sum_j x_j\left(\frac{m+\overline{M}}{m+M_j}\right)^{1/2}\left(\frac{1}{v_{d_j}(\infty)}\right)^2 . \tag{17}$$

This result is quite unlike Blanc's law in appearance. Here the reciprocals of the *squares* of drift velocities are added with respect to a peculiar sort of mass fraction.

For intermediate fields we assume that thermal and field energies are additive,

$$\langle v^2\rangle + \langle V_j^2\rangle = 3kT\left(\frac{1}{m}+\frac{1}{M_j}\right) + v_d^2\left(\frac{m+\overline{M}}{m}\right). \tag{18}$$

From this plus Eq. (9) we readily obtain the result

$$\left(\frac{1}{v_d(E)}\right)^2 = \sum_j x_j\left(\frac{1}{v_{d_j}(E)}\right)^2\left[\frac{m+\overline{M}}{m+M_j} + \frac{3kT}{M_j v_d^2(E)}\right]^{1/2} \times\left[1+\frac{3kT}{M_j v_{d_j}^2(E)}\right]^{-1/2}, \tag{19}$$

which reduces to Blanc's law for low fields and to Eq. (17) for high fields.

III. PARTITION OF ION ENERGY

To find $\overline{M}$ we use the moment equations derived for high fields from the Boltzmann equation by Wannier. For ions in a single gas these are[5,6]

$$(2\nu+1)\left\langle\frac{1-I_{s,\nu}(\theta)}{(eE/m)\tau}\,v^s P_\nu(\cos\vartheta)\right\rangle = \nu(\nu+s+1)\langle v^{s-1}P_{\nu-1}(\cos\vartheta)\rangle + (\nu+1)(s-\nu)\langle v^{s-1}P_{\nu+1}(\cos\vartheta)\rangle\,, \tag{20}$$

where the pointed brackets represent averages over the distribution function, ν and s are integers, τ is the mean time between collisions for ions, ϑ is the angle measured from the electric field direction, the $P_\nu(\cos\vartheta)$ are Legendre polynomials, and

$$I_{s,\nu}(\theta) = (v/v')^s P_\nu(\cos\kappa)\,, \tag{21}$$

in which $\vec{v}\,'$ is the ion velocity after collision and κ is the angle between $\vec{v}$ and $\vec{v}\,'$. These equations are quite general, subject to the condition of high field and to some temporary cutoff procedure to prevent divergences for interaction potentials that nominally extend to infinity. It is a simple matter to trace the derivation of Eq. (20) from the Boltzmann equation for a mixture; the only change is that the left-hand side becomes a summation,

$$(2\nu+1)\sum_j x_j\left\langle\frac{1-I_{s,\nu}(\theta_j)}{(eE/m)\tau_j}\right\rangle v^s P_\nu(\cos\vartheta)\,, \tag{22}$$

where τ_j is the mean time between ion collisions in pure gas j at the same total density as the mixture. For ion collisions with species j the factors of $I_{s,\nu}(\theta_j)$ are given by[5,6]

$$v/v' = (m^2+M_j^2+2mM_j\cos\theta_j)^{1/2}/(m+M_j)\,, \tag{23}$$

$$\cos\kappa = (m+M_j\cos\theta_j)/(m^2+M_j^2+2mM_j\cos\theta_j)^{1/2}\,. \tag{24}$$

The moment equations from which we find the ion energy correspond to $s=1$, $\nu=1$ and $s=2$, $\nu=0$:

$$\sum_j \frac{x_jM_j}{m+M_j}\left\langle\frac{(1-\cos\theta_j)}{(eE/m)\tau_j}\,(v\cos\vartheta)\right\rangle = 1\,, \tag{25}$$

$$\sum_j \frac{x_j mM_j}{(m+M_j)^2}\left\langle\frac{(1-\cos\theta_j)}{(eE/m)\tau_j}\,v^2\right\rangle = \langle v\cos\vartheta\rangle\,. \tag{26}$$

In order to evaluate the averages in Eqs. (25) and (26) we invoke the special properties of a model—we assume that both $(1-\cos\theta_j)$ and τ_j are independent of v, whereby the averages of products split into products of averages. Alternatively, we can consider the splitting of averages of products into products of averages as a reasonable approximation for any ion-molecule interaction, and that this approximation happens to be exact for a special model. In either case the two equations can be combined to yield

$$\sum_j \frac{x_j mM_j}{(m+M_j)^2}\,Q_j\,\langle v^2\rangle = \sum_j \frac{x_jM_j}{(m+M_j)}\,Q_j\,\langle v\cos\vartheta\rangle^2\,. \tag{27}$$

The momentum-transfer cross sections Q_j arise from the averages $\langle(1-\cos\theta_j)/\tau_j\rangle$. Noting that $\langle v\cos\vartheta\rangle = v_d$, we see that Eq. (27) reduces to Eq. (14) in the case of a single gas.

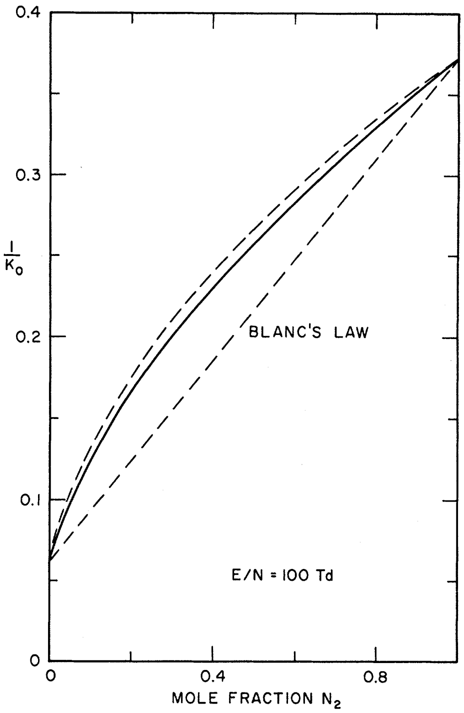

FIG. 1. Predicted deviations from Blanc's law for K^+ ions in H_2+N_2 mixtures at $E/N=100$ Td and 300°K. The solid curve is that given by Eq. (19), and the upper dashed curve is the result obtained from the same equation with thermal energy neglected.

Comparing Eq. (27) with Eq. (15), we see that $\overline{M}$ can be identified as the following average:

$$\overline{M} = \sum_j \omega_j M_j / \sum \omega_j \,, \tag{28}$$

where the weight factors ω_j are

$$\omega_j = x_j M_j Q_j / (m+M_j)^2 \,. \tag{29}$$

This result holds at all field strengths if the thermal and field energies are additive. It is more convenient to express the Q_j in terms of drift velocities via Eqs. (9) and (18) written for a single gas. The ω_j can then be put in the useful form

$$\omega_j = \frac{x_j}{v_{d_j}^2}\left(\frac{m}{m+M_j}\right)^{3/2}\left(1+\frac{3kT}{M_j v_{d_j}^2}\right)^{-1/2} \,. \tag{30}$$

IV. RESULTS

The mixture rule we propose for all fields consists of Eq. (19), with $\overline{M}$ given by Eqs. (28) and (30). Although Eq. (19) is simple to use for either low or high fields, it must be handled for intermediate fields by numerical methods or expansion techniques. Nevertheless, the information needed consists only of the temperature, the composition of the gas mixture and the molecular weights of its components, and the drift velocities in the pure components at the same temperature, density, and field strength as the mixture.

Although no data exist at present for testing our results, it is interesting to examine the effects predicted. We present two examples, based on existing measurements in pure gases: K^+ in H_2+N_2 mixtures[8,9] and in N_2+O_2 mixtures.[10,11] The results for H_2+N_2 mixtures are shown in Fig. 1, reported as mobilities at standard gas density, where mobility is defined by $v_d = KE$. Although Blanc's law is followed at low fields, deviations up to about 20% are predicted for $E/N = 100$ Td (1 Td = 10^{-17} V cm^2). At 100 Td the thermal energy is not yet negligible, as shown by the upper dashed curve, and Eq. (19) was solved by iteration. For N_2+O_2 mixtures, the deviations from Blanc's law are quite small even at $E/N = 300$ Td, as might be expected for a mixture of two such similar gases. The maximum deviation from Blanc's law at 300 Td is predicted to be less than 0.05%.

These examples show that easily detectable deviations from Blanc's law are to be expected at high fields, when the species in the gas mixture are sufficiently different. It is hoped that the present results will serve to stimulate experimental work on ion mobilities in gas mixtures at high electric fields.

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