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Composition dependence of ion-transport coefficients in gas mixtures*

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Simple momentum-transfer theory for the composition dependence of ion mobilities and diffusion coefficients in gas mixtures at arbitrary field strengths is corrected and extended, and compared with a similar theory based on momentum and energy transfer, and with results based on direct solution of the Boltzmann equation by Kihara's method. Final equations are recommended for predicting composition dependences, given only results on ion mobilities and diffusion coefficients in the pure component gases.

Simple momentum-transfer theory has recently been used to predict the composition dependence of ion mobilities[1] and diffusion coefficients[2] in gas mixtures at arbitrary field strengths. The purpose of this paper is threefold: to extend the range of validity of the results of Ref. 2 to higher fields by allowing the ion temperature to be anisotropic and to differ from the gas temperature; to correct an error in the expression used for the ion energy that affects the final results of Refs. 1 and 2; and to point out the relation of these results to a similar theory developed by Milloy and Robson,[3] and to recent work based on direct solution of the Boltzmann equation.[4]

By equating the momentum transferred to ions of charge e by an electric field $\vec{E}$ to the momentum transferred by the ions to the neutrals through collisions,[1] and by taking into account the pressure forces that arise if the ions are not distributed uniformly in space,[2] one obtains the following momentum-balance equation for the mean ion velocity $\langle\vec{v}\rangle$:

$$\xi n\langle\vec{v}\rangle \sum_j \mu_j N_j \langle v_{rj} Q(v_{rj})\rangle = ne\vec{E} - \vec{\nabla}\cdot\vec{p}_i , \tag{1}$$

where ξ is a proportionality constant of order unity, n is the number density of ions, μ_j is the reduced mass of an ion-neutral pair, N_j is the number density of neutral species j, v_{rj} is the relative speed of a colliding ion-neutral pair, $Q(v_{rj})$ is their momentum-transfer or diffusion cross section, and p_i is the partial-pressure tensor for the ions. Angular brackets indicate an average over relative speeds. In a coordinate system in which $\vec{E}$ is directed along the z axis, $\vec{p}_i$ is a diagonal tensor with components $p_{xx}=p_{yy}=p_\perp$ and $p_{zz}=p_\parallel$. Assuming that the ions obey the ideal-gas equation of state, we introduce

$$p_\parallel = nkT_\parallel , \quad p_\perp = nkT_\perp , \tag{2}$$

where the temperatures parallel and perpendicular to the field are defined by

$$kT_\parallel = m(\langle v_z^2\rangle - \langle v_z\rangle^2), \quad kT_\perp = m\langle v_x^2\rangle , \tag{3}$$

where m is the ion mass. Then $\vec{\nabla}\cdot\vec{p}_i = k\vec{T}_i\cdot\vec{\nabla}n$.

We focus attention first on the mobility by considering spatially uniform conditions, for which $\langle\vec{v}\rangle = v_d \equiv KE$, where v_d is the drift velocity and K is the mobility. From Eq. (1) we [redacted]write K in terms of the mobilities K_j in the[redacted]components

$$\frac{1}{K} = \sum_j \frac{x_j}{K_j}\frac{\langle v_{rj}Q(v_{rj})\rangle}{\langle v_{rj}Q(v_{rj})\rangle_j} , \tag{4}$$

where the x_j are mole fractions, and $\langle\ \rangle_j$ means an average in pure gas j, as distinguished from an average in the mixture $\langle\ \rangle$. The evaluation of the ratios $\langle v_{rj}Q_j\rangle/\langle v_{rj}Q_j\rangle_j$ proceeds as in Ref. 2, and involves three approximations. First, the average of the product $\langle v_{rj}Q(v_{rj})\rangle$ is decomposed into the product of the averages $\langle v_{rj}\rangle Q(\langle v_{rj}\rangle)$. Second, the average $\langle v_{rj}\rangle$ is replaced by the rms average $\langle v_{rj}^2\rangle^{1/2}$, which is then evaluated from the partitioning of the ion energy among thermal energy, drift energy, and random field energy. The third approximation enters through the expression for the energy partitioning

$$\langle v_{rj}^2\rangle = \langle v^2\rangle + \langle V_j^2\rangle = 3kT/\mu_j + \langle v_z\rangle^2[1+\langle M\rangle_{\mathrm{av}}/m] , \tag{5}$$

where V_j is the neutral species velocity, M_j is its mass, T is the gas temperature, and $\langle M\rangle_{\mathrm{av}}$ is a mean mass of the gas mixture, defined as

$$\langle M\rangle_{\mathrm{av}} \equiv \sum_j \omega_j M_j \Big/ \sum_j \omega_j , \tag{6}$$

$$\omega_j \equiv x_j M_j \langle v_{rj}Q(v_{rj})\rangle/(m+M_j)^2 . \tag{7}$$

The energy partitioning can be calculated by Wannier's method, as was done in Ref. 1, or equivalently by an energy-balance equation, as was done in Ref. 3. Unfortunately, there is an error in the expression for the energy partitioning in Ref. 1—in Eqs. (27) and (29) the Q_j should be replaced by $\langle v_{rj} Q_j \rangle$ to give the correct weight factors ω_j as in Eq. (7). The numerical example in Ref. 1 is therefore incorrect in detail because of the incorrect ω_j used. However, at high fields the relative speed is the same as the ion speed, and there is then no mistake in the ω_j.

The theory of Milloy and Robson[3] for the mobility is essentially the same as the foregoing treatment up to this point, but makes further approximations in order to express the deviations from Blanc's law entirely in terms of the behavior of the ions in the pure neutral components, without explicit reference to the mixture itself. Thus, the mixture averages are expanded in series

$$\langle v_{rj} Q(v_{rj}) \rangle = \langle v_{rj} Q(v_{rj}) \rangle_j + [\langle v_{rj}^2 \rangle - \langle v_{rj}^2 \rangle_j] \times \frac{d\langle v_{rj} Q(v_{rj}) \rangle_j}{d\langle v_{rj}^2 \rangle_j} + \cdots . \tag{8}$$

From Eq. (5) we find

$$\langle v_{rj}^2 \rangle - \langle v_{rj}^2 \rangle_j = v_d^2 [1 + \langle M \rangle_{\text{av}} / m] - v_{dj}^2 (1 + M_j / m) . \tag{9}$$

Since this expression appears as a correction term in Eq. (8), it need be evaluated only in lowest order, corresponding to $\langle v_{rj} Q_j \rangle \approx \langle v_{rj} Q_j \rangle_j$, which yields

$$m[\langle v_{rj}^2 \rangle - \langle v_{rj}^2 \rangle_j] \approx \left(\sum_j \frac{x_j}{v_{dj}} \right)^{-1} \left(\sum_j \frac{x_j}{v_{dj}(m + M_j)} \right)^{-1} - (m + M_j) v_{dj}^2 . \tag{10}$$

The derivative in Eq. (8) is obtained by differentiation of Eq. (1) written for a single pure component having the same total number density as the mixture $(N_j = N)$, and is found to be

$$\frac{d \ln \langle v_{rj} Q(v_{rj}) \rangle_j}{d\langle v_{rj}^2 \rangle_j} = \frac{1}{2 v_{dj}^2} \left(\frac{m}{m + M_j} \right) \left(\frac{d \ln v_{dj}}{d \ln(E/N)} \right)^{-1} \left(1 - \frac{d \ln v_{dj}}{d \ln(E/N)} \right) \approx - \frac{1}{2 v_{dj}^2} \left(\frac{m}{m + M_j} \right) \frac{d \ln K_j}{d \ln(E/N)} . \tag{11}$$

Substituting these results back into Eq. (4), we obtain

$$\frac{1}{K} - \sum_j \frac{x_j}{K_j} \approx \frac{1}{2} \sum_j \frac{x_j}{K_j} \frac{d \ln K_j}{d \ln(E/N)} (1 - \Delta_j) , \tag{12}$$

$$\Delta_j^{-1} = (m + M_j) K_j^2 \left(\sum_i \frac{x_i}{K_i} \right) \left(\sum_i \frac{x_i}{(m + M_i) K_i} \right) , \tag{13}$$

which is the result of Milloy and Robson. This expression is remarkably similar to one obtained from a direct solution of the Boltzmann equation by Kihara's method.[4] The main difference is that the Δ_j in Eq. (12) is multiplied by a complicated factor G_j that happens to be numerically close to unity. Thus, Eq. (12) can be recommended as an excellent estimate for deviations of the mobility from Blanc's law.

The preceding calculations can obviously also be applied to the longitudinal $(D_{\parallel})$ and transverse $(D_{\perp})$ diffusion coefficients, but an additional feature must enter. It is clear from Eq. (1) that spatial inhomogeneity affects $\langle \vec{v} \rangle$. Since Eq. (5) shows that $\langle v_{rj} \rangle$ is related to the mean ion speed, spatial inhomogeneity must also affect $\langle v_{rj} \rangle$. Thus we must allow *both* $\langle \vec{v} \rangle$ and $\langle v_{rj} \rangle$ to have small contributions from spatial inhomogeneity, but we may consider these as perturbations and linearize with respect to them. Denoting the spatially homogeneous case with a superscript, we expand the average $\langle v_{rj} Q(v_{rj}) \rangle$ in a series similar to Eq. (8),

$$\langle v_{rj} Q(v_{rj}) \rangle = \langle v_{rj} Q(v_{rj}) \rangle^o + [\langle v_{rj}^2 \rangle - \langle v_{rj}^2 \rangle^o] \frac{d\langle v_{rj} Q(v_{rj}) \rangle^o}{d\langle v_{rj}^2 \rangle^o} + \cdots . \tag{14}$$

From Eq. (5) we find, on setting $\langle v_z \rangle^o = v_d$,

$$\langle v_{rj}^2 \rangle - \langle v_{rj}^2 \rangle^o = (\langle v_z \rangle^2 - v_d^2)(1 + \langle M \rangle_{\text{av}} / m) , \\ \approx - 2 v_d \left(1 + \frac{\langle M \rangle_{\text{av}}}{m} \right) \frac{v_d k T_{\parallel}}{neE} \frac{\partial n}{\partial z} , \tag{15}$$

the last step following by substitution for $\langle v_z \rangle - v_d$ from Eq. (1). Since this last result is independent of j, we can multiply Eq. (14) by $\mu_j N_j$ and sum over j; the derivative term is then obtained by differentiation of Eq. (1), yielding a result similar to Eq. (11),

$$d \ln \sum_j \mu_j N_j \langle v_{rj} Q(v_{rj}) \rangle^o / d\langle v_{rj}^2 \rangle^o \approx - \frac{1}{2 v_d^2} \left(\frac{m}{m + \langle M \rangle_{\text{av}}} \right) \frac{d \ln K}{d \ln(E/N)} . \tag{16}$$

Substituting these results back into Eq. (1) and linearizing with respect to derivatives of n, we identify the transport coefficients and observe the following relations among them:

$$\frac{eD_\parallel}{K} \approx kT_\parallel \left(1 + \frac{d\ln K}{d\ln(E/N)}\right), \tag{17}$$

$$\frac{eD_\perp}{K} \approx kT_\perp . \tag{18}$$

Equations (17) and (18) have been derived previously by phenomenological arguments,[5,6] and have been shown to give good qualitative agreement with numerical solutions of the Boltzmann equation.[6] A more elaborate treatment according to kinetic theory gives[4]

$$\frac{eD_{\parallel,\perp}}{K} = kT_{\parallel,\perp} \left(1 + \gamma_{\parallel,\perp}\frac{d\ln K}{d\ln(E/N)} + \cdots\right), \tag{19}$$

where $\gamma_\parallel = 1$ and $\gamma_\perp \leqslant 0$, which is valid to order $(E/N)^4$.

The ion temperatures are obtained from Eq. (3) by an energy-partitioning calculation, either by Wannier's method applied to mixtures,[1] or from a first-order solution to the Boltzmann equation.[7] In either case, the result for the mixture is

$$kT_\parallel = kT + \left(\frac{5m\langle M\rangle_{\text{av}} - (2m - \langle M\rangle_{\text{av}})\langle MA^*\rangle_{\text{av}}}{5m + 3\langle MA^*\rangle_{\text{av}}}\right) v_d^2, \tag{20}$$

$$kT_\perp = kT + \left(\frac{(m + \langle M\rangle_{\text{av}})\langle MA^*\rangle_{\text{av}}}{5m + 3\langle MA^*\rangle_{\text{av}}}\right) v_d^2, \tag{21}$$

where $\langle M\rangle_{\text{av}}$ is given by Eq. (6) and

$$\langle MA^*\rangle_{\text{av}} \equiv \sum_j \omega_j M_j A_j^* \Big/ \sum_j \omega_j , \tag{22}$$

in which A^* is a ratio of cross sections of order unity.

To find the composition dependence of the diffusion coefficients we substitute Eq. (19), which applies to both mixtures and pure gases, back into Eq. (4),

$$\frac{T_{\parallel,\perp}}{D_{\parallel,\perp}} = \sum_j x_j \frac{(T_{\parallel,\perp})_j}{(D_{\parallel,\perp})_j} \frac{\langle v_{rj} Q(v_{rj})\rangle^o}{\langle v_{rj} Q(v_{rj})\rangle_j{}^o} \times \left(1 + \gamma_{\parallel,\perp}\frac{d\ln K_j}{d\ln(E/N)}\right)\left(1 + \gamma_{\parallel,\perp}\frac{d\ln K}{d\ln(E/N)}\right)^{-1} \tag{23}$$

The important new feature is the appearance of the ion temperatures in Eq. (23). The temperatures in the mixture and in the pure components are not the same at the same value of E/N because the partitioning of the ion energy among drift and random field components depends on the nature of the ion-neutral collisions. One immediate consequence of this is the recognition that the diffusion coefficients will deviate from Blanc's law at high fields even for the Maxwell model of constant collision frequency, for which the ratios $\langle v_{rj}Q_j\rangle^o / \langle v_{rj}Q_j\rangle_j{}^o$ are all unity and all derivatives of mobility with respect to E/N are zero. Numerical calculations of deviations from Blanc's law for the Maxwell model have been performed and the results are shown in Fig. 1.

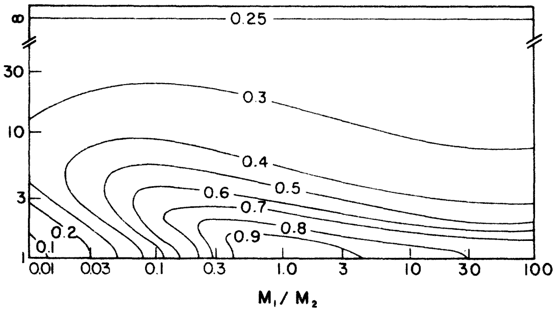

FIG. 1. Ratio of $D_\parallel$ (Blanc) to $D_\parallel$ (mix) at high fields for an equimolar Maxwell-model binary-gas mixture, as contours in a K_1/K_2 vs M_1/M_2 plane. We have taken $m = M_2$. Note that the deviations from Blanc's law are always negative. The corresponding ratio for mixture mobility is always unity for the Maxwell model.

The ratios $\langle v_{rj}Q_j\rangle^o/\langle v_{rj}Q_j\rangle_j{}^o$ in Eq. (23) can obviously be evaluated by the same methods used for the mobility. Substituting these results into

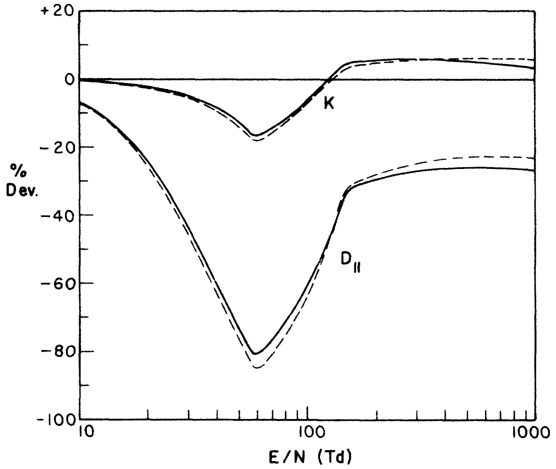

FIG. 2. Percentage deviations from Blanc's law for mobility, $100[K^{-1} - K^{-1}_{\text{Blanc}}]/K^{-1}_{\text{Blanc}}$, and for $D_\parallel$ as a function of field strength, as calculated for K^+ ions in an equimolar He + Ar mixture at 300°K. The solid curves are the results from the Boltzmann equation according to Ref. 4, and the dashed curves are the present momentum-transfer results of Eqs. (12) and (26). The abscissa unit Td is the townsend (1 Td = 10^{-17} V cm^2).

Eq. (23) and linearizing with respect to the derivatives of mobility, in order to be consistent with the truncations in Eqs. (8) and (14), we obtain an expression that still contains a mixture quantity on the right-hand side, namely, the derivative $d\ln K/d\ln(E/N)$ from the last factor of Eq. (23). In order to evaluate this quantity in terms of pure component properties, we differentiate Eq. (12), which leaves us with *second* derivatives of K_j with respect to E/N. These second derivatives can be approximated by appeal to the following symmetry argument.[8] Since the gas is isotropic K must be an even function of E/N; expansion in series must therefore involve only even powers of E/N,

$$K = K(0)[1 + \alpha_1(E/N)^2 + \alpha_2(E/N)^4 + \cdots] . \tag{24}$$

Differentiating twice and comparing results, we find

$$\frac{d^2 \ln K}{d(\ln E/N)^2} \approx 2\frac{d\ln K}{d\ln(E/N)} + [\text{terms of order } (E/N)^4] . \tag{25}$$

This expression holds for both mixtures and pure gases. Substitution of this expression then yields the final result for the composition dependence of the diffusion coefficients,

$$\frac{1}{D_{\parallel,\perp}} - \sum_j \frac{x_j}{(D_{\parallel,\perp})_j} \approx \sum_j \frac{x_j}{(D_{\parallel,\perp})_j} \left(\frac{(T_{\parallel,\perp})_j - T_{\parallel,\perp}}{T_{\parallel,\perp}} \right) + \frac{e}{2kT_{\parallel,\perp}} \sum_j \frac{x_j}{K_j} \frac{d\ln K_j}{d\ln(E/N)} (1-\Delta_j)(1+2\gamma_{\parallel,\perp}) . \tag{26}$$

The ion temperatures in this expression are to be evaluated from Eqs. (20)–(21), but with the average masses calculated with weight factors ω_j approximated by making expansions as in Eq. (8),

$$\omega_j \approx \frac{x_j}{(m+M_j)K_j} \left(1 + \tfrac{1}{2} \sum_i \frac{x_i}{K_i} \frac{d\ln K_i}{d\ln(E/N)} (1-\Delta_i) \right) . \tag{27}$$

These results are nearly the same as those obtained by solution of the Boltzmann equation. The differences are relatively minor: the Δ_j is missing the G_j factors as in the mobility expression of Eq. (12), the value of $\gamma_\perp$ may be slightly different, and the Boltzmann expression does not include the small derivative term in the expression for the ω_j.

As an excellent estimate for deviations of the diffusion coefficients from Blanc's law we recommend the following procedure: use Eq. (26) with Δ_j given by Eq. (13), with $\gamma_\parallel$ and $\gamma_\perp$ given their kinetic-theory values, and with the ω_j given by just the leading term of Eq. (27).

As a numerical example we consider K^+ ions in an equimolar mixture of He + Ar at 300°K, using as input data the measurements on K^+ in He[3] and K^+ in Ar.[9] Deviations from Blanc's law for K and for $D_\parallel$ are shown as a function of field strength in Fig. 2, as calculated from the Boltzmann equation and from Eqs. (12) and (26). The shapes and magnitudes of these curves have been discussed elsewhere[4]; the important point here is the closeness of the agreement for the two calculation methods.

In summary, the various theories for the composition dependence of ion mobilities and diffusion coefficients in gas mixtures have been shown to be consistent. Equations (12) and (26) (modified as suggested above) are recommended for predicting deviations from Blanc' s law as a function of field strength.

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