Rev. Letters 21, 970 (1968).

[16]R. A. Gerber and M. A. Gusinow, Phys. Rev. A 4, 2027 (1971).

[17]E. P. Gray and D. E. Kerr, Ann. Phys. (N. Y.) 17, 276 (1962); L. Frommhold and M. A. Biondi, ibid. 48, 407 (1968).

[18]M. A. Biondi, Phys. Rev. 82, 453 (1951).

[19]J.-F. Delpech and J. Boulmer, Internal Report No. 72/21, Institut L'Electronique Fondamentale (Orsay, France) (unpublished).

[20]J. A. Ingraham and S. C. Brown, Phys. Rev. 138, A1015 (1965).

[21]J. B. Gerardo (private communication).

[22]C. Sol, J. Boulmer, and J.-F. Delpech (unpublished).

[23]A. Wayne Johnson and J. B. Gerardo, Phys. Rev. Letters 27, 835 (1971); Phys. Rev. A 5, 1410 (1972); Phys. Rev. Letters 28, 1096 (1972).

[24]P. A. Miller, J. T. Verdeyen, and B. E. Cherrington, Phys. Rev. A 4, 692 (1971).

[25]C. Vauge and J. L. Whitten, Chem. Phys. Letters 13, 541 (1972).

[26]P. L. Patterson, J. Chem. Phys. 48, 3625 (1968).

[27]C. P. de Vries and H. J. Oskam, Phys. Letters 29A, 299 (1969).

Composition Dependence of Ion Diffusion Coefficients in Gas Mixtures at Arbitrary Field Strengths*

J. H. Whealton and E. A. Mason

Brown University, Providence, Rhode Island 02912

(Received 1 May 1972)

Expressions for the diffusion coefficient of ions in gas mixtures are obtained from momentum-transfer theory, and are given in terms of the diffusion coefficients and drift velocities of the ions in the pure component gases. Blanc's law holds exactly at all field strengths if the mean free time between collisions is independent of velocity (Maxwell model), but otherwise there may be either positive or negative deviations from Blanc's law at high fields. Such deviations are of comparable magnitude for the diffusion coefficients and the mobility, but are not identical. Specific cases of inverse-power potentials are treated in further detail, and some numerical examples are given for rigid-sphere interactions.

I. INTRODUCTION

The diffusion coefficients of ions in gases are proportional to their mobilities at low electric field strengths, but at high fields the proportionality breaks down and the diffusion coefficients usually increase more rapidly than the mobilities.[1] Moreover, the diffusion coefficient becomes anisotropic at high fields, the rates of diffusion parallel and perpendicular to the field direction being different. The purpose of this paper is to find an expression for the composition dependence of ion diffusion coefficients in gas mixtures at arbitrary field strengths in terms of the diffusion coefficients in the pure component gases. Although no data at present exist, measurements in mixtures introduce no new experimental difficulties, and the present work predicts interesting effects.

Since we seek only a composition dependence, we can use a simple momentum-transfer method used previously for finding the composition dependence of the ion mobility.[2] As a side result we make explicit a hidden assumption in the previous work, namely that the dependence of the momentum-transfer cross section on the drift velocity itself could be ignored. This has a distinct effect on the deviations from Blanc's law predicted for high fields.

At low fields, the analog of Blanc's law for ion mobilities holds to first order in the Chapman-Enskog approximation,

$$1/D = \sum_j (x_j/D_j) , \tag{1}$$

where D is the diffusion coefficient of the ion in the mixture, the x_j are mole fractions, and the D_j are the diffusion coefficients of the ion in the pure component gases at a number density the same as the total number density of the mixture. Higher Chapman-Enskog approximations yield only positive deviations from Blanc's law, but these are usually small.[3] For high fields we find that appreciable deviations from this linear rule can occur, and that the deviations are sensitive to the form of the ion-neutral interaction.

II. MOMENTUM-TRANSFER THEORY

The basic idea in a momentum-transfer calculation is that the momentum given to the ions by external forces must be balanced by the momentum the ions transfer to the neutral molecules by collisions, since the ions are not accelerated on the average. For mobility, the external force is obviously supplied by the electric field. For diffusion, the external force is regarded as coming from the gradient of partial pressure of the diffusing species.[4]

Wannier[5,6] has shown that the drift and diffusive motions are separable, in the sense that the diffusion is simply superposed on the net drift velocity. Thus the momentum transferred per unit volume in the field direction (along the z axis) for ions in a single gas is[2,4]

$$n\xi\mu\bar{v}_z\left\langle Nv_r\int_0^\infty (1-\cos\theta)2\pi b\,db\right\rangle_z = neE - \frac{\partial p_i}{\partial z} , \qquad (2)$$

and perpendicular to the field direction is

$$n\xi\mu\bar{v}_x\left\langle Nv_r\int_0^\infty (1-\cos\theta)2\pi b\,db\right\rangle_x = -\frac{\partial p_i}{\partial x} , \qquad (3)$$

where n is the number density of ions, ξ is a proportionality constant of order unity, μ is the reduced mass of an ion-neutral pair, $\bar{v}_z$ and $\bar{v}_x$ are the average ion velocity components, N is the number density of neutrals (it is assumed that $N \gg n$), v_r is the relative speed on an ion-neutral pair colliding with impact parameter b and deflection angle θ, e is the ionic charge, E the electric field strength, and p_i the partial pressure of ions. The pointed brackets indicate averages over relative speeds. The average ion velocities are related to the drift velocity v_d and to the diffusive fluxes J_x and J_z by the expressions

$$\bar{v}_z = v_d + (J_z/n), \quad \bar{v}_x = J_x/n , \qquad (4)$$

and the diffusion coefficients parallel and perpendicular to the field direction are defined by the equations

$$J_z = -\frac{D_\|}{kT}\frac{\partial p_i}{\partial z} , \quad J_x = -\frac{D_\perp}{kT}\frac{\partial p_i}{\partial x} . \qquad (5)$$

Comparison of Eqs. (2)–(5) identifies $D_\|$ and $D_\perp$ in terms of the average momentum-transfer cross sections.

For mixtures, the left-hand sides of Eqs. (2) and (3) become summations over the species in the mixtures. The results for both $D_\|$ and $D_\perp$ then become

$$D\sum_j \mu_j N_j \langle v_{rj} Q(v_{rj})\rangle = kT/\xi , \qquad (6)$$

where $Q(v_{rj})$ is the momentum-transfer or diffusion cross section

$$Q(v_{rj}) = 2\pi \int_0^\infty (1-\cos\theta_j)b\,db , \qquad (7)$$

in which θ_j signifies $\theta(v_{rj})$. The diffusion coefficients in pure gas j of density $N = \sum N_j$ are given by one term in these sums,

$$D_j\mu_j N \langle v_{rj} Q(v_{rj})\rangle_j = kT/\xi , \qquad (8)$$

where now the average $\langle\ \rangle_j$ is *not* the same as the corresponding average in Eq. (6), because the ion velocity distributions are different in the pure gas and in the mixture. From here on the notation $\langle\ \rangle_j$ means an average taken in the pure gas j, whereas $\langle\ \rangle$ means an average taken in the mixture. Com-

bining Eqs. (6) and (8), we obtain

$$\frac{1}{D} = \sum_j \frac{x_j}{D_j} \frac{\langle v_{rj}Q(v_{rj})\rangle}{\langle v_{rj}Q(v_{rj})\rangle_j} . \qquad (9)$$

An analogous treatment of v_d yields an expression of similar form:

$$\frac{1}{v_d} = \sum_j \frac{x_j}{v_{dj}} \frac{\langle v_{rj}Q(v_{rj})\rangle}{\langle v_{rj}Q(v_{rj})\rangle_j} . \qquad (10)$$

However, this does not necessarily mean that the D's have the same composition dependence as does v_d, because the averages in general depend on v_d unless the field is very weak.

The problem is now reduced to finding the ratio of the averages, $\langle v_{rj}Q_j\rangle/\langle v_{rj}Q_j\rangle_j$. In general this will require further approximations, but two especially simple cases can be distinguished at once. First, if the field is weak the relative velocities are essentially all thermal, the ion distribution functions are the same in the pure gases and in the mixtures, and the ratios of the averages are all unity. Second, if Q_j is inversely proportional to v_{rj} (the Maxwell model), the products $v_{rj}Q_j$ are all constants and the ratios are again unity. Thus Blanc's law holds for both these special cases.

III. EVALUATION OF AVERAGES

To evaluate the ratios of averages appearing in Eqs. (9) and (10), we make three approximations. We first assume that the averages can be decomposed,

$$\langle v_{rj}Q(v_{rj})\rangle_j \approx \langle v_{rj}\rangle_j Q(\langle v_{rj}\rangle_j) , \qquad (11)$$

and second we assume that

$$\langle v_{rj}\rangle_j \propto \langle v_{rj}^2\rangle_j^{1/2} . \qquad (12)$$

It is easy to show that

$$\langle v_{rj}^2\rangle_j = \langle v^2\rangle_j + \langle V_j^2\rangle_j , \qquad (13)$$

where $\langle v^2\rangle_j$ is the mean-square ion velocity and $\langle v_j^2\rangle_j$ is the mean-square velocity of neutral species j. The latter is always entirely thermal and equal to $3kT/M_j$, where M_j is the neutral mass, but $\langle v^2\rangle_j$ contains both thermal and field components, and the field component is partitioned between a part visible as drift motion and a random part. Thus the first two assumptions reduce the problem to the determination of the partitioning of the ion energy, for which an approximate result is already known.[2,6] For ions in a single gas, Wannier[6] has shown that the energy partitioning is approximately

$$\langle v^2\rangle_j + \langle V_j^2\rangle_j = 3kT(1/m + 1/M_j)$$
$$+ v_{dj}^2[(m + M_j)/m] , \qquad (14)$$

where m is the ion mass. This result is exact for the Maxwell model, and is thought to be a reasonable approximation for other ion-neutral interactions. The generalization to mixtures yields[2]

$$\langle v^2 \rangle + \langle V_j^2 \rangle = 3kT(1/m + 1/M_j) + v_d{}^2[(m + \bar{M})/m],$$
(15)

where the mean mass of the gas mixture is

$$\bar{M} = \sum_j \omega_j M_j / \sum_j \omega_j,$$
(16)

$$\omega_j = x_j M_j Q(\langle v_{rj} \rangle) / (m + M_j)^2.$$
(17)

Equations (15) and (16) can always be considered correct in a formal sense, so the third approximation is embodied in Eq. (17).

Combining the foregoing approximations, we obtain

$$\frac{\langle v_{rj} Q(v_{rj}) \rangle}{\langle v_{rj} Q(v_{rj}) \rangle_j} \approx \frac{v_d Q(\langle v_{rj} \rangle)}{v_{dj} Q(\langle v_{rj} \rangle_j)} \left[\frac{m + \bar{M}}{m + M_j} + \frac{3kT}{M_j v_d{}^2} \right]^{1/2}$$

$$\times \left[1 + \frac{3kT}{M_j v_{dj}{}^2} \right]^{-1/2}. \quad (18)$$

Substitution of this expression back into Eqs. (9) and (10) yields the final formulas for the composition dependences of $D_{||}$, $D_{\perp}$, and v_d. The previous result[2] for v_d implicitly assumed that the ratios of the Q's in Eq. (18) were all unity, an assumption valid only for rigid spheres. The velocity dependences of the Q's must be known before numerical results can be calculated; although the same Q's appear in both numerator and denominator in Eq. (18), they are to be evaluated at different mean velocities corresponding to averages in the pure components and in the mixtures.

IV. EXAMPLES

Here we present a few illustrations of the foregoing results. If the ion-neutral interaction potentials V_j vary inversely as some power of the separation r_j,

$$V_j = C_j / r_j{}^{n_j},$$
(19)

where C_j and n_j are constants, then the cross sections vary as $v_{rj}{}^{-4/n_j}$,

$$Q(v_{rj}) = 2\pi A^{(1)}(n_j) \left(\frac{2n_j C_j}{v_{rj}{}^2} \right)^{2/n_j} \left(\frac{1}{m} + \frac{1}{M_j} \right)^{2/n_j}, \quad (20)$$

where the $A^{(1)}(n_j)$ are pure numbers that have been evaluated by numerical integration.[7,8] The averages in Eqs. (9) and (10) can then be readily found. Thus Eq. (9) becomes

$$\frac{1}{D} = \sum_j \frac{x_j}{D_j} \left(\frac{v_d}{v_{dj}} \right)^{1 - 4/n_j} \left(\frac{m + \bar{M}}{m + M_j} + \frac{3kT}{M_j v_d{}^2} \right)^{1/2 - 2/n_j}$$

$$\times \left[1 + \frac{3kT}{M_j v_{dj}{}^2} \right]^{-1/2 + 2/n_j}, \quad (21)$$

and a similar expression for v_d follows from Eq. (10). The weight factors ω_j of Eq. (17) for finding $\bar{M}$ can now be written

$$\omega_j = \frac{x_j M_j A^{(1)}(n_j)}{(m + M_j)^2} \left(\frac{2n_j C_j}{M_j v_d{}^2} \right)^{2/n_j}$$

$$\times \left(\frac{m + \bar{M}}{m + M_j} + \frac{3kT}{M_j v_d{}^2} \right)^{-2/n_j}. \quad (22)$$

Since Eq. (22) itself contains $\bar{M}$, the actual computation of $\bar{M}$ may require iteration.

For a numerical example we consider rigid spheres at high fields, for which Eq. (21) can be put in the form

$$\frac{1}{D/v_d} = \sum_j \frac{x_j}{D_j/v_{dj}} \left(\frac{v_d}{v_{dj}} \right)^2 \left(\frac{m + \bar{M}}{m + M_j} \right)^{1/2}. \quad (23)$$

For a binary gas mixture the fractional deviation of D from Blanc's law can be written in terms of three dimensionless ratios,

$$\frac{D_{\text{Blanc}}}{D} = \frac{D^{-1} - D_{\text{Blanc}}{}^{-1}}{D_{\text{Blanc}}{}^{-1}} + 1$$

$$= \frac{x_1 + x_2 D^* (v^*)^2 (m^*)^{1/2}}{(x_1 + x_2 D^* v^*)[x_1 + x_2 (v^*)^2 (m^*)^{1/2}]^{1/2}}$$

$$\times \left(\frac{x_1 + x_2 (v^*)^2 (m^*)^{1/2}}{x_1 + x_2 (v^*)^2 (m^*)^{3/2}} \right)^{1/4}, \quad (24)$$

where

$$D^* = (D_1/v_{d1})/(D_2/v_{d2}),$$
(25)

$$v^* = v_{d1}/v_{d2},$$
(26)

$$m^* = (m + M_1)/(m + M_2).$$
(27)

If we choose x_1 and D^*, then deviations from Blanc's law can be shown as contours in a v^*-m^* plane. Such a diagram is shown in Fig. 1, with $x_1 = \frac{1}{2} = x_2$ and $D^* = 1$. The latter choice means that the deviations from the Einstein relation are the same in the two pure components; as a consequence, the diagram represents the deviations from Blanc's law for v_d as well as D. Two points on the diagram refer to K^+ in $H_2 + N_2$ and to He^+ in $He + Ne$. The deviations for the latter case are predicted to be small, in agreement with experiment.[9] Unfortunate-
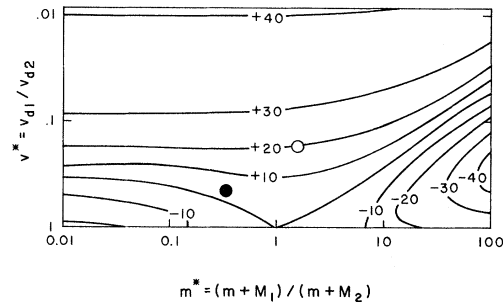

FIG. 1. Percentage deviations from Blanc's law, $100 \times [D^{-1} - D_{\text{Blanc}}{}^{-1}]/D_{\text{Blanc}}{}^{-1}$, at high fields for an equimolar rigid-sphere binary gas mixture, as contours in a v^*-m^* plane with $D^* = 1$. The dimensionless variables are defined in Eqs. (25)–(27). The same contours hold for v_d as for D when $D^* = 1$. The open circle refers to K^+ in $H_2 + N_2$, and the filled circle to He^+ in $He + Ne$.

ly there are no measurements for the case with large predicted deviations. Both positive and negative deviations are seen to be possible.

V. CONCLUSIONS

The present results predict that deviations from Blanc's law for both mobility and diffusion coefficients can be of either sign at high fields, and can be of a magnitude that should be detectable experimentally. The deviations depend explicitly on the nature of the ion-neutral interaction through the averages $\langle v_{rj}Q_j\rangle$ and $\langle v_{rj}Q_j\rangle_j$, and are zero for the Maxwell model in which Q_j is inversely proportional to v_{rj} and the mean free time between collisions is

the same at all velocities. This behavior is reminiscent of the behavior of thermal diffusion in neutral gases, which has been used as a sensitive probe of intermolecular forces, [10] and indeed the same sort of averages occur in the momentum-transfer theory of gaseous thermal diffusion. [11] This suggests that deviations from Blanc's law at high fields might be a useful probe of ion-neutral forces. Physically, the present theory ascribes the deviations from Blanc's law to the difference in the ion energy partitioning in the gas mixture and in the pure components. Only the particular velocity dependence of the cross section given by the Maxwell model is just right to compensate for this effect.

---

*Work supported in part by the National Aeronautics and Space Administration under Grant No. NGL-40-002-059.

[1]E. W. McDaniel and J. T. Moseley, Phys. Rev. A 3, 1040 (1971).

[2]E. A. Mason and H. Hahn, Phys. Rev. A 5, 438 (1972).

[3]S. I. Sandler and E. A. Mason, J. Chem. Phys. 48, 2873 (1968).

[4]R. D. Present, Kinetic Theory of Gases (McGraw-Hill, New York, 1958), Secs. 4-2 and 8-3.

[5]G. H. Wannier, Phys. Rev. 87, 795 (1952).

[6]G. H. Wannier, Bell System Tech. J. 32, 170 (1953).

[7]J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids (Wiley, New York, 1964), Chap. 8.

[8]L. D. Higgins and F. J. Smith, Mol. Phys. 14, 399 (1968).

[9]G. E. Courville and M. A. Biondi, J. Chem. Phys. 37, 616 (1962).

[10]E. A. Mason, R. J. Munn, and F. J. Smith, Advan. At. Mol. Phys. 2, 33 (1966).

[11]Reference 4, Sec. 7-1.

Ground State of Two-Dimensional Liquid Helium*

Michael D. Miller and Chia-Wei Woo[†]

Department of Physics, Northwestern University, Evanston, Illinois 60201

and

Charles E. Campbell

Institute of Theoretical Physics, Department of Physics, Stanford University, Stanford, California 94305

(Received 28 April 1972)

In the interest of understanding the nature and properties of physically adsorbed helium monolayers in the mobile limit, we study the ground state of a two-dimensional helium liquid, using integral-equation techniques which have been thoroughly tested in connection with bulk helium. Our results are compared to those of computer experiments by Hyman and by Campbell and Schick, and to actual experimental data obtained by Dash and co-workers.

As a model for adsorbed helium monolayers, we consider N helium atoms adsorbed on a uniform homogeneous substrate of surface area A. Recent studies[1] of single helium atoms interacting with structured substrates such as graphite indicate that ignoring the structure of the adsorbing surface may be quite realistic for the calculation of some properties of the adsorbate Specifically, the bands are very broad and overlapping. The resulting high mobility makes it reasonable to expect that the ground-state and low-excited-state properties of interacting helium atoms will not be

significantly modified by the structure of the substrate. The submonolayer heat capacities measured by Bretz and Dash[2] for He^4 adsorbed on graphite provide strong experimental evidence for this point of view in the low-density regime. It should be noted, however, that densities which are in registry with adsorption sites provided by the substrate may show a tendency to take advantage of the weak substrate potential at the expense of their mobility, as evidenced by the order-disorder transitions observed in the aforementioned experiments at commensurate densities.[3] In that case,