*Work supported in part by the National Science Foundation, under Grant No. GP-9626.

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PHYSICAL REVIEW A VOLUME 6, NUMBER 4 OCTOBER 1972

Field Dependence of Gaseous-Ion Mobility: Theoretical Tests of Approximate Formulas*

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(Received 16 March 1972)

Four approximate formulas, due to Wannier, Kihara, Frost, and Patterson, for the field dependence of ion mobility are tested by comparison with special cases for which accurate theoretical results can be found. The Kihara result, an expansion in $(E/N)^2$, has only limited range. The Frost-Patterson formulas at high fields apply only to rigid-sphere cross sections. The Wannier free-flight theory yields a formula with one parameter that can be chosen once and for all to fit the zero-field Chapman-Enskog result; without further adjustable constants the formula gives reasonable results at medium and high fields (largest deviations less than 20% in the special cases tested), and is applicable to any ion-neutral mass ratio and force law, including the case of resonant charge transfer.

I. INTRODUCTION

It is well known that the drift velocity of an ion in a neutral gas depends on field strength. No general expression for the field dependence is known, although several approximate formulas have been suggested. The purpose of this paper is to test these approximate formulas by comparison with several accurate theoretical results for special cases, and to suggest a connection formula that can be used at all fields for all ion-neutral interactions. The most extensive test occurs for the case of light ions and heavy neutrals (Lorentzian mixture), for which the drift velocity can be found at all fields by numerical integration.

Dimensional arguments suffice to show that the drift velocity v_d depends on the electric field strength E and on the number density of the gas N only through the ratio E/N. At low fields, v_d is directly proportional to E/N for all ion-neutral interactions, and is given by the Chapman-Enskog kinetic theory. At high fields the nature of the ion-neutral interaction determines the dependence of v_d on E/N; for example, it is known that v_d varies directly as E/N for an r^{-4} interaction potential and as $(E/N)^{1/2}$ for a rigid-sphere interaction.[1,2]

II. APPROXIMATE FORMULAS

In this section we briefly outline four formulas which give v_d as a function of E/N.

A. Wannier Free-Flight Theory

In 1953 Wannier[2] indicated how to obtain a simple interpolation formula for v_d. Since his result has been almost universally overlooked, we indicate the line of arguments leading to it. An ion of mass m and charge e undergoes an acceleration eE/m between collisions. If the ion lost all its momentum on every collision, the drift velocity would be $(eE/m)\tau$, where τ is the mean time between collisions; but the ion loses only a fraction of its momentum on each collision. The mass dependence of the momentum loss on collision can be calculated from the equations of momentum and energy conservation; if we average this momentum loss over all collisions and ignore subtleties about the average of a product and the product of the averages, we obtain

$$v_d = \xi\,(1+m/M)(eE/m)\,\tau\ , \tag{1}$$

where M is the mass of a neutral molecule and ξ is a factor of order unity that may depend in a complicated way on the ion-neutral force law and the masses m and M. The mean free time is given by

$$\tau = 1/N\bar{v}_r\,Q\ , \tag{2}$$

where $\bar{v}_r$ is the mean relative speed of ions and neutrals and Q is the average momentum-transfer cross section. It is reasonable to take $\bar{v}_r$ as the root-mean-square speed,

$$\bar{v}_r = (\langle v^2\rangle + \langle V^2\rangle)^{1/2} \quad , \tag{3}$$

where $\langle v^2\rangle$ is the mean-square ion velocity and $\langle V^2\rangle$ the mean-square neutral velocity. For the latter quantity energy equipartition gives

$$\tfrac{1}{2}M\langle V^2\rangle = \tfrac{3}{2}kT \ . \tag{4}$$

The only remaining problem is to find $\langle v^2\rangle$, which has both thermal and field components. At low fields $\langle v^2\rangle$ is entirely thermal, but at high fields it has a negligible thermal component. Wannier[1,2] has shown that if τ is constant, then the thermal and field energies of the ions are additive, and that the field energy is exhibited partly as a drift motion and partly as a random motion,

$$\tfrac{1}{2}m\langle v^2\rangle = \tfrac{3}{2}kT + \tfrac{1}{2}mv_d^2 + \tfrac{1}{2}Mv_d^2 \quad , \tag{5}$$

where $\frac{3}{2}kT$ is the thermal energy, $\frac{1}{2}mv_d^2$ is the drift energy, and $\frac{1}{2}Mv_d^2$ is the random part of the field energy.

The foregoing formulas can be combined to yield a relation among measurable quantities by elimination of τ. It is assumed that this relation will hold even if τ itself is not a constant, at least to a useful approximation. Combining Eqs. (4) and (5), we obtain

$$\langle v^2\rangle + \langle V^2\rangle = 3kT\,(1/m + 1/M) + v_d^2(1 + M/m) \ , \tag{6}$$

and substituting back into Eqs. (1)–(3) we find

$$v_d = \xi\left(\frac{1}{m} + \frac{1}{M}\right)^{1/2} \frac{(eE/NQ)}{(3kT + Mv_d^2)^{1/2}} \quad , \tag{7}$$

which is apparently a quadratic in the variable v_d^2:

$$(v_d^2)^2 + \frac{3kT}{M}\,(v_d^2) - \frac{\xi^2}{M}\left(\frac{1}{m} + \frac{1}{M}\right)\left(\frac{eE}{NQ}\right)^2 = 0 \ . \tag{8}$$

This quadratic dependence is only apparent, however, unless Q is a constant (rigid spheres). In general, Q depends on $\bar{v}_r$ in a manner determined by the ion-neutral force law. In any case, solution of Eq. (8) gives a reasonable result for v_d at all field strengths. At low fields we have $3kT \gg Mv_d^2$ and v_d is proportional to (eE/NQ); at high fields we have $Mv_d^2 \gg 3kT$ and v_d is proportional to $(eE/NQ)^{1/2}$. At low fields the results can be compared with the accurate Chapman-Enskog kinetic-theory formula for the diffusion coefficient. All the dimensional factors in Eq. (7) are found to be correct, provided we identify the average cross section Q with a collision integral for diffusion.[3,4] The value of ξ in Eq. (7) is still at our disposal; we choose it to give agreement with the Chapman-Enskog results,

$$\xi = \frac{3}{16}\,\frac{(6\pi)^{1/2}}{1-\Delta} = \frac{0.814}{1-\Delta} \quad , \tag{9}$$

where Δ is a correction term incorporating higher Chapman-Enskog approximations and given by[3,4]

$$\Delta = \frac{M^2(6C^* - 5)^2}{30m^2 + 10M^2 + 16mMA^*} + \text{higher terms} \ , \tag{10}$$

in which A^* and C^* are dimensionless ratios of collision integrals.[4]

B. Kihara Medium-Field Expansion

Kihara[5] has shown how the kinetic-theory results based on the Boltzmann equation can be extended to higher fields by avoiding the Chapman-Enskog assumption that the ion velocity distribution function differs only slightly from the Maxwellian form. The result is an expansion for v_d in powers of the quantity $(E/N)^2$. Depending on the particular approximation procedure used to solve an infinite set of moment equations, the expansion can be written either as[6]

$$v_d = v_d(0)\,[1 + \alpha_1(E/N)^2 + \alpha_2(E/N)^4 + \cdots] \ , \tag{11}$$

or[5]

$$v_d = \frac{v_d(0)}{1 + \beta_1(E/N)^2 + \beta_2(E/N)^4 + \cdots} \quad , \tag{12}$$

where $v_d(0)$ is the low-field limit of v_d and is itself proportional to E/N. The coefficients α_i and β_i are complicated functions of the masses m and M, as well as of the ion-neutral force law. The form of the expansion obviously limits its validity to medium fields. Such an expansion in powers of $(E/N)^2$ can be obtained from Eq. (7) of the free-flight theory by expanding the denominator of Eq. (7) in powers of the small quantity $Mv_d^2/3kT$ and solving iteratively for v_d, but the values of α_1 and β_1 so obtained are not in general correct.

C. Frost-Patterson Interpolation Formulas

Knowing that v_d varies as E/N at low fields and as $(E/N)^{1/2}$ for rigid spheres at high fields, Frost[7] proposed the formula

$$v_d = A\,(E/N)\,[1 + a(E/N)]^{-1/2} \quad , \tag{13}$$

where A and a are constants that are different for every system. The form of this expression can be obtained from Eq. (7) by replacing the value of v_d^2 in the denominator of the right-hand side of Eq. (7) by its high-field value.

Patterson[8] incorporated the medium-field expansion of Kihara into a somewhat more elaborate interpolation formula,

$$v_d = A\,(E/N)\,[1 + b(E/N)^2 + c(E/N)^4]^{-1/8} \quad , \tag{14}$$

where A, b, and c are constants. This preserves the high-field variation of rigid spheres, and at medium fields it mimics the expansions of Eqs. (11) and (12) with $b = \frac{1}{8}\beta_1$.

III. SPECIAL CASES

A few accurate theoretical results are available for testing the foregoing formulas. An r^{-4} potential (Maxwell model) can be treated at all fields for all ion-neutral mass ratios. The result is that the low-field expression for v_d is valid at all fields, which is not very interesting or even physically realistic. Other known special cases are as follows.

A. High Fields

If the ions are either much heavier or much lighter than the neutrals, then v_d can be found for any ion-neutral interaction. If the ions and neutrals have equal masses, then v_d is known only for a rigid-sphere interaction. For $m \gg M$ the result is[2,9]

$$v_d = \left(\frac{eE}{MNQ^{(1)}(v_d)}\right)^{1/2} , \tag{15}$$

where the diffusion or momentum-transfer cross section $Q^{(1)}$ is evaluated at v_d. For $m \ll M$ the result is given as integrals,[10,11]

$$v_d = \tfrac{4}{3}\pi (eE/m) \int_0^\infty f^{(0)} \phi v^4 dv , \tag{16}$$

where $f^{(0)}$ is the isotropic part of the ion distribution function and ϕ is the directional part,

$$\ln f^{(0)} = \ln B - 3\left(\frac{m}{M}\right)\left(\frac{mN}{eE}\right)^2 \int [Q^{(1)}(v)]^2 v^3 dv , \tag{17}$$

$$\phi = \frac{3}{N}\left(\frac{m}{M}\right)\left(\frac{mN}{eE}\right)^2 Q^{(1)}(v) , \tag{18}$$

where B is a normalization constant. Numerical integration is required unless the velocity dependence of $Q^{(1)}(v)$ is simple. For $m = M$ the value of v_d has been calculated for rigid spheres by a method involving a trial distribution function judiciously selected to satisfy the first few moment equations; the result is[2]

$$v_d = 1.1467\left(\frac{eE}{mNQ^{(1)}}\right)^{1/2} , \tag{19}$$

where $Q^{(1)} = \pi d^2$ is a constant for rigid spheres of mutual collision diameter d.

A comparison of the foregoing accurate results with Eq. (7) of the free-flight theory is simple for the case of an inverse-power ion-neutral potential,

$$V(r) = C/r^n , \tag{20}$$

where C and n are constants. The momentum-transfer cross section for this potential is[3,4]

$$Q^{(1)}(v) = 2\pi (2nC/\mu v^2)^{2/n} A^{(1)}(n) , \tag{21}$$

where the $A^{(1)}(n)$ are pure numbers that are evaluated by numerical integration. An extensive tabulation of $A^{(1)}(n)$ has been given by Higgins and Smith.[12] To use Eq. (21) with the free-flight results, we note that the ion energy at high fields is given by

$$mv^2 = mv_d^2 + Mv_d^2 ,$$

from which it follows that

$$\mu v^2 = Mv_d^2 , \tag{22}$$

where $\mu = mM/(m+M)$ is the reduced mass. With the energy dependence of $Q^{(1)}(v)$ as given by Eq. (21), the integrals of Eqs. (16) and (17) can be evaluated to yield the result for $m \ll M$,

$$v_d = \left(\frac{4n-8}{3n}\right)^{(3n-4)/(4n-8)} \frac{\Gamma[(3n-2)/(2n-4)]}{\Gamma[3n/(4n-8)]} \times\left[\left(\frac{M}{m}\right)^{1/2}\left(\frac{eE}{MN}\right)\left(\frac{M}{2nC}\right)^{2/n} \frac{1}{2\pi A^{(1)}(n)}\right]^{n/(2n-4)} . \tag{23}$$

Similarly, the energy dependence of $Q^{(1)}(v)$ can be substituted into Eq. (15), which can then be solved to yield the result for $m \gg M$,

$$v_d = \left[\left(\frac{eE}{MN}\right)\left(\frac{M}{2nC}\right)^{2/n} \frac{1}{2\pi A^{(1)}(n)}\right]^{n/(2n-4)} . \tag{24}$$

Comparison of these values with the free-flight formula with $Q = Q^{(1)}$ shows that the latter has all the dimensional factors correct. The numerical accuracy is shown in Table I for a number of values of n. Even though ξ was chosen to fit only the low-field results, the agreement at high fields is quite reasonable, the largest deviations being less than 20%. No reasonable comparison with the other formulas can be made—the Kihara expansion breaks down at high fields; the Frost-Patterson formulas are valid only for rigid spheres, and have the wrong field dependence unless $n = \infty$.

B. Intermediate Fields

Only for $m \ll M$ is a rigorous theoretical result known for arbitrary field strengths. The ion distribution function is given by[10,11]

TABLE I. Test of the Wannier approximate free-flight equation (7) for the drift velocity at high fields for the potential $V(r) = C/r^n$.

	v_d(approx.)/v_d(accurate)		
n	$m \gg M$	$m = M$	$m \ll M$
4	0.814	0.814	0.814
6	0.857		0.902
8	0.872		0.943
10	0.879		0.966
12	0.884		0.982
25	0.894		1.022
50	0.898		1.041
∞	0.902	0.944	1.060

TABLE II. Exact drift velocity as a function of field strength for rigid spheres with $m \ll M$.

$\mathcal{E}^*$	v_d^*	$\mathcal{E}^*$	v_d^*
0.10	0.1122	1.2	0.9753
0.12	0.1342	1.5	1.134
0.15	0.1667	2.0	1.364
0.20	0.2197	2.5	1.564
0.25	0.2709	3.0	1.743
0.30	0.3203	3.5	1.906
0.35	0.3679	4.0	2.057
0.40	0.4137	4.5	2.198
0.45	0.4578	5	2.331
0.5	0.5004	6	2.576
0.6	0.5811	7	2.801
0.7	0.6566	8	3.008
0.8	0.7274	9	3.203
0.9	0.7943	10	3.386
1.0	0.8576		

$$\ln f^{(0)} = \ln B - \int \frac{mv^3 dv}{kTv^2 + \frac{1}{3}M(eE/mNQ^{(1)})^2} , \quad (25)$$

$$\phi = \frac{mv/NQ^{(1)}}{kTv^2 + \frac{1}{3}M(eE/mNQ^{(1)})^2} , \quad (26)$$

for which Eqs. (17) and (18) are the high-field limits. Given the energy dependence of $Q^{(1)}$, the integral in Eq. (25) can be evaluated, after which v_d can be found by the integration in Eq. (16). In order to test the approximate formulas, we have carried through the integrations for rigid spheres. The integration in Eq. (25) can be performed analytically, but the final integration for v_d must still be done numerically. We can consolidate the temperature and field dependence of v_d by defining the dimensionless quantities,

$$v_d^* = \left(\frac{M}{2kT}\right)^{1/2} v_d , \quad (27)$$

$$\mathcal{E}^* = \frac{3\pi^{1/2}}{16kT}\left(\frac{m+M}{m}\right)^{1/2} \frac{eE}{NQ^{(1)}} . \quad (28)$$

The equations then become, with $m \ll M$,

$$v_d^* = \frac{16}{9\pi^{1/2}} \mathcal{E}^* \frac{I_1(\gamma)}{I_2(\gamma)} , \quad (29)$$

where

$$I_1(\gamma) = \int_0^\infty x^2 (x+\gamma)^{\gamma-1} e^{-x} dx , \quad (30)$$

$$I_2(\gamma) = \int_0^\infty x^{1/2} (x+\gamma)^{\gamma} e^{-x} dx , \quad (31)$$

$$x = mv^2/2kT, \quad \gamma = 128(\mathcal{E}^*)^2/27\pi .$$

Equations (30) and (31) were evaluated by numerical integration using Simpson's rule. The results are given in Table II, and may be used as a convenient test case for any proposed theory of the dependence of v_d on E/N.

A comparison of the free-flight equation (8) and the exact equation (29) is shown in Fig. 1. In the free-flight calculations we have used the exact value[13] of $1 - \Delta = 9\pi/32$ in order to make the two results agree at low fields. The agreement is remarkably good over the whole range, the worst disagreements being about 8% at intermediate fields and about 6% at high fields (as shown in Table I). The Frost interpolation formula of Eq. (13) is also shown, the constants A and a being chosen to secure agreement at both low and high fields. The agreement with the theoretical result is comparable to that for the free-flight result, except at high fields. The Patterson interpolation formula of Eq. (14) produces very little improvement, despite the use of an additional parameter.

The medium-field expansions of Eqs. (11) and (12) are compared with the theoretical result in Fig. 2. Because of the difficulty of computing higher terms in the expansions as well as accurate values of the expansion coefficients, we have stopped with the following approximations:

$$v_d^* = \frac{32}{9\pi} \mathcal{E}^*\left(1 - \frac{11}{42}(\mathcal{E}^*)^2 + \frac{247}{1260}(\mathcal{E}^*)^4 + \cdots\right) , \quad (32)$$

$$v_d^* = \frac{32}{9\pi} \mathcal{E}^*\left(1 + \frac{1}{3}(\mathcal{E}^*)^2 - \frac{1}{18}(\mathcal{E}^*)^4 + \cdots\right)^{-1} , \quad (33)$$

which can be obtained from the results in Refs. 5 and 6. The numerical constants in these two equations are not yet mutually consistent in this order of approximation. It is clear that these expansions give a good representation only at fairly low fields, and are not to be trusted when the

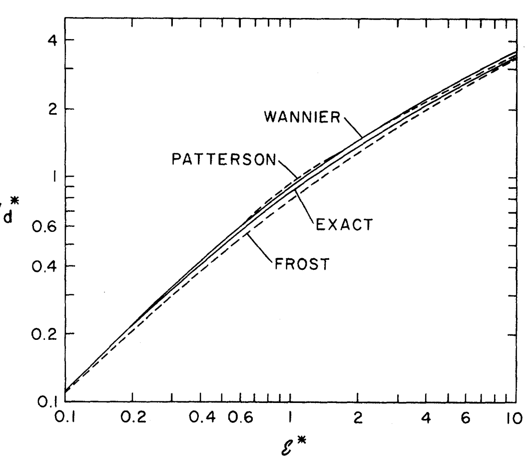

FIG. 1. Reduced drift velocity as a function of reduced field strength for rigid spheres with $m \ll M$. The two solid curves are exact numerical results (Table II) and Wannier's free-flight equation (7). The two dashed curves are Frost-Patterson empirical formulas given by Eqs. (13) and (14), respectively.

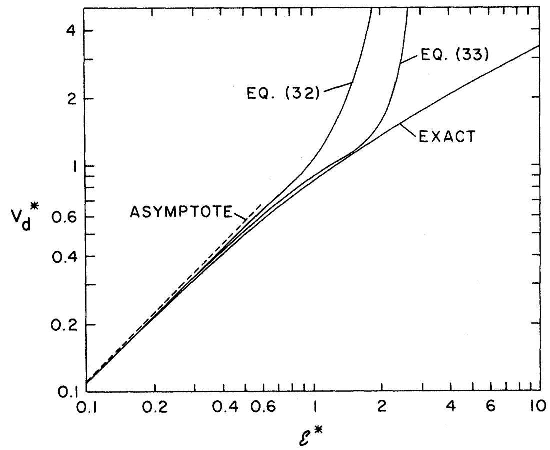

FIG. 2. Reduced drift velocity as a function of reduced field strength for rigid spheres with $m \ll M$. The exact curve represents the numerical results of Table II, and the other two curves are the Kihara expansions in powers of $(E/N)^2$ as given by Eqs. (32) and (33).

deviations from the zero-field asymptote are larger than about 10%. Equation (33) is somewhat better than Eq. (32), but the useful range of accuracy is distinctly limited for both expressions.

C. Resonant Charge Transfer

If resonant charge transfer is possible, then each collision converts a fast ion and a nearly stationary neutral into a fast neutral and a nearly stationary ion. Thus the ion may be regarded as coming essentially to rest after each collision, and the kinetic-theory problem becomes simple. Solutions have been obtained by Fahr and Müller[14] and by Smirnov.[15] If the charge-transfer cross section Q_T is independent of velocity, the low-field result is

$$v_d(0) = \frac{A'}{(mkT)^{1/2}} \frac{eE}{NQ_T} . \tag{34}$$

Fahr and Müller find $A' = 0.330$ and Smirnov finds $A' = 0.341$. At high fields both obtain

$$v_d(\infty) = \left(\frac{2}{\pi} \frac{eE}{mNQ_T} \right)^{1/2} . \tag{35}$$

It is interesting to compare these with the previous results for rigid spheres. When charge transfer is the dominant process in collisions, an accurate relation is[16,17]

$$Q^{(1)} = 2Q_T . \tag{36}$$

With this expression, Eq. (34) is the same as the Chapman-Enskog result with the constant $A' = 3\pi^{1/2}/16(1-\Delta) = 0.338$, a value in good agreement with Fahr and Müller and Smirnov. At high fields Eq. (35) may be compared with Wannier's rigid-sphere result given in Eq. (19). The form of the two results is the same; the numerical constant from Eq. (35) is $(2/\pi)^{1/2} = 0.798$, and from Eq. (19) is $1.1467/2^{1/2} = 0.811$, in good agreement.

Thus the interpolation formulas we have tested should also apply to mobility with charge transfer, provided Eq. (36) holds.

IV. CONCLUSIONS

Of the four formulas tested, the one based on the Wannier free-flight theory is the most flexible, since it can be used for all fields and all ion-neutral force laws and mass ratios. The Kihara expansion, although it might be the most accurate at fairly low fields, has only a limited range. The Frost-Patterson formulas are based on rigid-sphere interactions between ions and neutrals. They also require additional adjustable parameters, but these do not appreciably improve the agreement in the special case tested (Fig. 1). Further tests of the free-flight formula with ion-neutral interactions containing both attractive and repulsive components would be interesting, but would require extensive numerical integration.

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

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