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Electron drift velocities in molecular-gas–rare-gas mixtures

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The drift velocity of electrons in mixtures containing a molecular gas in a rare-gas diluent has been calculated as a function of E/N (ratio of the electric field to neutral number density) and of molecular-gas concentration using a numerical solution of the Boltzmann transport equation. The results agree well with available experimental data where gas purity was strictly controlled. In argon, it is shown that very small amounts of a molecular additive can drastically alter the behavior of the electron drift velocity. The curves exhibit a local maximum with respect to E/N and an absolute maximum with respect to molecular concentration. A useful formula for the mobility has been derived, which explains the peculiar behavior of the electron drift velocity in these gas mixtures.

I. INTRODUCTION

Experimental measurements of the electron drift velocity in argon have been carried out by many authors.[1-5] Early work showed some inconsistency due to questionable gas purity. Local maxima were observed at low values of the ratio of electric field to neutral number density (E/N) which were thought to be due to the Ramsauer minimum in the momentum-transfer cross section for argon.[6] Later authors, however, were able to eliminate these peaks by taking care to remove all impurities from the gas. It is now well established that the drift velocity of electrons in pure argon is monotonic over the measured range of E/N values. The presence of small amounts of N_2, CO_2, H_2, or H_2O, however, have profound effects not only on the magnitude of the drift velocity, but also on its variation with E/N. Colli and Facchini[3] showed that by adding known amounts of nitrogen to purified argon, they could duplicate the results of earlier work in supposedly "pure" argon.

Theoretical attempts by Uman and Warfield[9] to explain these observations were only partly successful and gave little insight into the controlling physical processes. They obtained agreement with experiment in CO_2-Ar mixtures, but not in N_2-Ar. This can be explained by their assumption that the energy loss in inelastic collisions is small compared to the electron mean energy. In fact, in many molecular gases the energy lost in exciting the vibrational levels can be of the same order as the mean energy.

In this paper an iterative procedure for the solution of the Boltzmann transport equation is employed, along with the latest experimental electron-impact cross sections, to obtain the electron-energy distribution functions for various gas mixtures. These distribution functions are then integrated to obtain the drift velocity as a function of E/N and fraction of molecular gas, p. The results show good agreement with available experimental data. An expression for the drift velocity is then derived from the Boltzmann equation, which reduces to a simple form when inelastic energy losses are dominant over energy losses due to recoil. This analytic form is fitted to the numerical data with an error less than 5% over the range of E/N and p considered.

II. NUMERICAL SOLUTION

The form of the Boltzmann transport equation used was derived by Holstein[10] for electrons in a uniform electric field which undergo elastic and inelastic collisions with a cold gas. An expansion in spherical harmonics, retaining only the first two terms, was used to account for the angular distribution of electron velocities, i.e., $f(v,\theta) = f_0(v) + f_1(v)\cos\theta$. Written in terms of electron energy, the Boltzmann equation is then

$$\frac{E/N}{3u}\frac{\partial}{\partial u}(uf_1) + \sum_h Q_h f_0 = \frac{2}{u}\frac{m}{M}\frac{\partial}{\partial u}(u^2 Q_m f_0) + \sum_h Q_h(u')f_0(u')\left(\frac{u'}{u}\right), \tag{1a}$$

$$\frac{E}{N}\frac{\partial f_0}{\partial u} + \left(Q_r + \sum_h Q_h\right) f_1 = 0, \tag{1b}$$

where $u' = u + \Delta u_h$ and Δu_h is the energy loss associated with the inelastic cross section Q_h. Q_m is the sum of momentum-transfer cross sections for each gas weighted by mole fraction and the reciprocal of the molecular weight, whereas Q_r is the sum of momentum-transfer cross sections weighted simply by mole fraction. m/M is the ratio of electron to proton mass. Equation (1) may be written as a single equation for f_0 by integrating Eq. (1a) with respect to energy, substituting Eq. (1b) into Eq. (1a), and integrating again:

$$f_0(u)=\exp\left[-\frac{3}{(E/N)^2}\left(\frac{2m}{M}\int uQ_mQ_r\,du + \int\frac{Q_t}{uf_0}\int_u^{u'}Q_hf_0u\,du\,du\right)\right], \tag{2}$$

where

$$Q_t=Q_r+\sum_h Q_h .$$

This equation can be solved by iteration[11] for $f_0(u)$; substitution into Eq. (1b) then gives $f_1(u)$. The cross sections employed were those of Phelps and co-workers[12,13] and Crompton[14] obtained by fitting transport coefficients, and of Spence *et al.*[15] from beam experiments. These data are compiled and referenced for a number of gases in a report by Kieffer[16] and are plotted for N_2 and Ar in Fig. 1.

A sample of the energy distribution functions obtained by this method is presented in Fig. 2. The drift velocities are calculated using the expression

$$W=\frac{1}{3}\left(\frac{2e}{m}\right)^{1/2}\frac{\int_0^\infty f_1(u)u\,du}{\int_0^\infty f_0(u)u^{1/2}\,du}. \tag{3}$$

They are plotted in Fig. 3 for N_2-Ar along with the available experimental measurements.[3,8] The agreement is within the uncertainty in the experimental data and the cross sections used. A complete set of values is presented in Fig. 4 for N_2-Ar and in Fig. 5 for CO-Ar. The important thing to note from these curves is not only the experimentally observed maxima as E/N is increased, but also

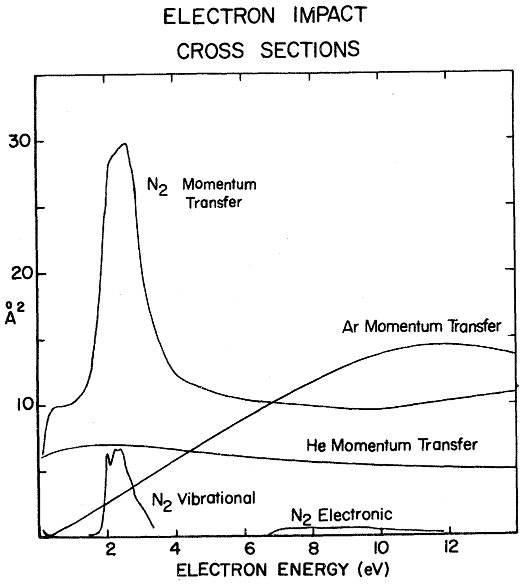

FIG. 1. Momentum-transfer cross sections for N_2, Ar, and He and inelastic cross sections in N_2.

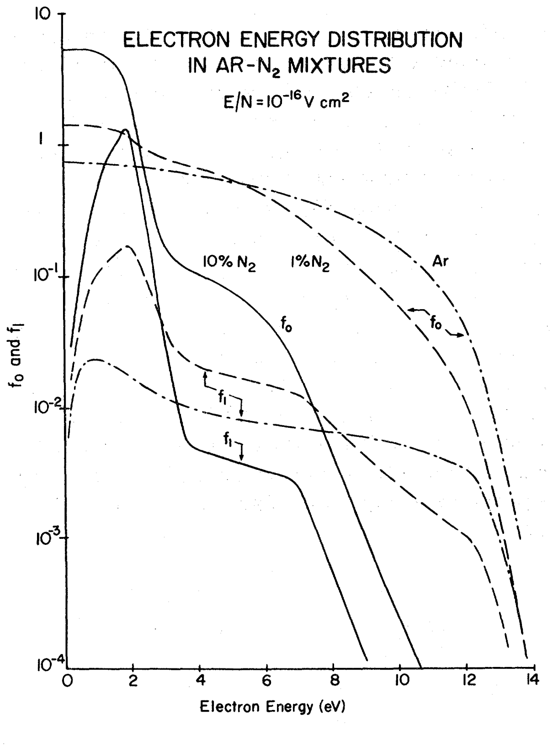

FIG. 2. Electron-energy distributions for pure Ar and for Ar with 1% and 10% N_2 at $E/N=1\times10^{-16}$ V cm².

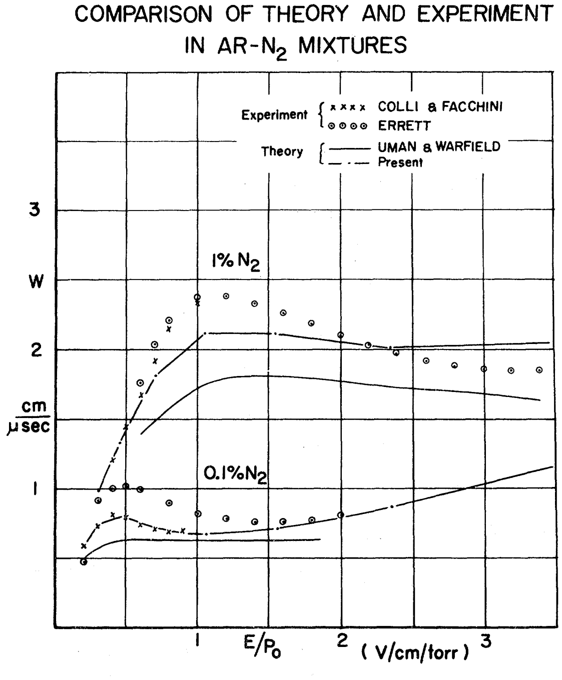

FIG. 3. Comparison of theoretical and experimental drift velocities in Ar with 0.1% and 1% N_2 added.

the variation in the drift velocity as the concentration of molecular gas is increased at each value of *E/N*. In CO-Ar the local maxima occur at lower values of *E/N* and smaller concentrations than in N_2-Ar. Results for CO_2-Ar mixtures were also in good agreement with experiment.[7,8]

The drift-velocity curves with helium as diluent, Fig. 6, do not exhibit maxima versus *E/N*, but they do go through maxima as the concentration of molecular gas is increased. This behavior in both He and Ar is an important consideration in the operation of electric-discharge lasers in gas mixtures. Both CO_2 and CO lasers typically operate in a He or Ar diluent of up to 90%. Optimum power loading in these devices can be achieved for a given electron density and *E/N* by choosing the proper ratio of molecular-gas to rare-gas diluent.

III. ANALYTIC APPROXIMATION

Expression (3) for the drift velocity is difficult to analyze directly because it involves the unknown functions f_0 and f_1. We can write this in a more readily interpretable form by integrating the denominator by parts and using Eq. (1b) to obtain

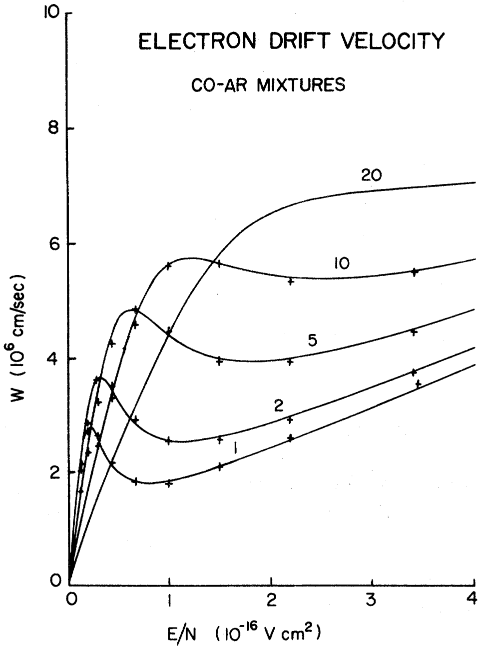

FIG. 5. Electron drift velocity in mixtures containing 1%, 2%, 5%, 10%, and 20% CO in Ar.

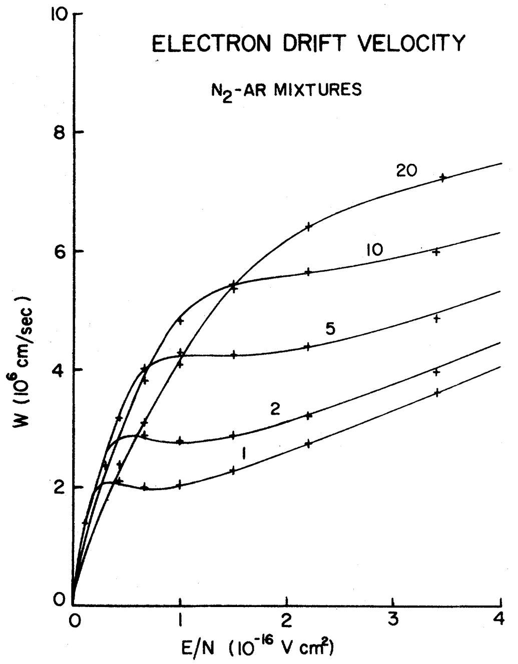

FIG. 4. Electron drift velocity in mixtures containing 1%, 2%, 5%, 10%, and 20% N_2 in Ar. The points are derived from a numerical solution of the Boltzmann transport equation. The solid curves were calculated using Eq. (8) and the data in Table I.

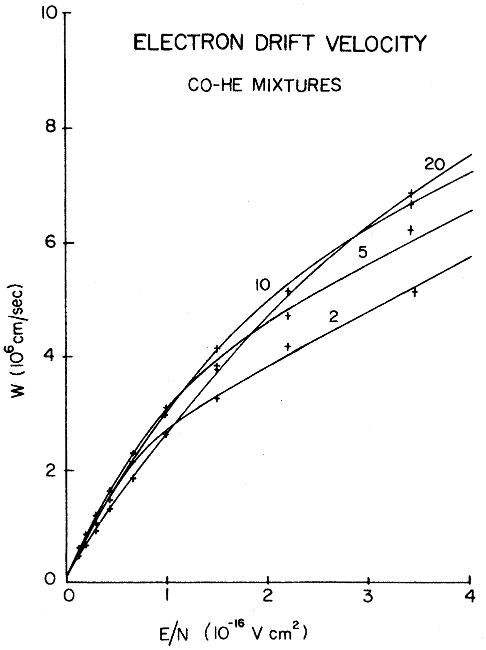

FIG. 6. Electron drift velocity in mixtures containing 2%, 5%, 10%, and 20% CO in He.

$$\int_0^\infty u^{1/2} f_0 \, du = \frac{2/3}{E/N} \int_0^\infty Q_t u^{3/2} f_1 \, du \,. \tag{4}$$

By integrating Eq. (1a) and using the resulting expression for f_1 in Eqs. (3) and (4), we arrive at the following form for the drift velocity:

$$W = \frac{1}{2}\left(\frac{2e}{m}\right)^{1/2} \frac{E}{N} \frac{\sum_h \int_0^\infty Q_h(u) f_0(u) u \Delta u_h \, du}{\sum_h \int_0^\infty Q_h(u) f_0(u) u \int_{u-\Delta u_h}^{u} u^{1/2} Q_t \, du \, du} \,. \tag{5}$$

The recoil term has been treated as another inelastic process with an energy loss equal to $(2m/M)u$. If there are only elastic collisions, with a constant collision frequency $\nu = (2e/m)^{1/2} \times u^{1/2} Q_r$, Eq. (5) reduces to $W = eE/m\nu = a/\nu$, where a is the acceleration of electrons in the electric field.

When an inelastic process is introduced, the quantity $Q_h f_0$ in Eq. (5) will have a sharp peak at an energy u_h just above threshold. Since the function

$$\frac{1}{\Delta u_h} \int_{u-\Delta u_h}^{u} u^{1/2} Q_t \, du$$

is slowly varying, it can be removed from the integral in Eq. (5) to yield the approximate form

$$W = eE/m\langle \nu \rangle \,, \tag{6a}$$

where the effective collision frequency is given by

$$\langle \nu \rangle = \left(\frac{2e}{m}\right)^{1/2} \sum_h F_h\left(\frac{E}{N}\right) \frac{N}{\Delta u_h} \int_{u_h-\Delta u_h}^{u_h} u^{1/2} Q_t \, du \,, \tag{6b}$$

and where F_h is the fraction of electrical power deposited in the hth inelastic process. It is a function of E/N and the gas mixture.

In a region where there is one dominant inelastic loss, the drift velocity will be proportional to the electric field, with slope given by $e/m\langle \nu \rangle_h$. In argon, for example, the drift velocity is nearly linear in the region above 5 Td (1 Td $= 10^{-17}$ V cm^2). The effective collision frequency is given by Eq. (6b) with $u_h = 12$ eV. Thus electronic excitation is dominant in this E/N range and determines the behavior of the drift velocity.

Let us now consider what happens when a small amount of molecular gas is added to argon. The introduction of vibrational excitation cross sections with thresholds in the vicinity of the Ramsauer minimum causes the effective collision frequency $\langle \nu \rangle$ to be reduced; hence the slope of the drift velocity curve is increased. This accounts for the linear portion of the curves in Fig. 4 at low values of E/N where vibrational excitation is the dominant process, $u_h = 2$ eV. As E/N is increased and the electrons are accelerated past the vibrational cross sections to the electronic levels, the drift-velocity curve makes a transition to the lower slope corresponding to $u_h = 7$ eV.

This transition can be described by applying Eq. (6b) to a mixture containing two inelastic processes, assuming recoil losses are unimportant; thus

$$\langle \nu \rangle = [1 - F(E/N, p)]\nu_1 + F(E/N, p)\nu_2 \,, \tag{7}$$

where F is the fraction of power expended in electronic excitation. The functions ν_1 and ν_2 are the momentum-transfer collision frequencies associated with the vibrational and electronic thresholds, respectively, and are linear functions of p, the fraction of molecular gas. Equation (7) can be compared to Blanc's law, $\langle \nu \rangle = (1-p)\nu_1 + p\nu_2$, which is valid when both gases have constant elastic collision frequencies ν_1 and ν_2.

To complete the analytic approximation for the drift velocity, we must find the functional dependence of $F(E/N, p)$ in Eq. (7). Examination of Eq. (2) indicates that $X = (E/N)p^{-1/2}$ and p are the relevant parameters when the molecular gas supplies the principal inelastic losses. All integrals involving only f_0 should be functions of these two variables. An empirical fit of Eq. (7) to the numerical data shows that $F(X, p) = A \exp(-B/X)$, where A and B are linear functions of p. This dependence is identical to that found by Townsend for the ionization and electronic excitation rates in pure gases. When used in Eq. (7) it gives an expression for the drift velocity which is accurate to 20% over the range plotted in Figs. 4 and 5. If an adjustment is made to compensate for recoil losses the agreement is improved to 5%. The final form for the drift velocity in a molecular-gas–rare-gas mixture is then

$$W = \frac{E/N}{C_1 X^a + C_2 \exp(-B/X)} \,, \tag{8}$$

where

$$C_1 = C_{11}p + C_{12}(1-p) \,, \quad C_2 = C_{21}p + C_{22}(1-p) \,,$$

$$X = (E/N)p^{-1/2} \,, \quad B = B_1 p + B_2(1-p) \,.$$

The constants in this expression are given in Table I for N_2-Ar, CO-Ar, and CO-He. This formula was used to calculate the solid curves in Figs. 4–6. It can also be used to plot the variation of drift velocity with molecular concentration, Fig. 7. Note that the maxima occur at a percentage of

TABLE I. Constants of drift-velocity equation (8). These constants will give W in cm/μsec when E/N is expressed in units of 10^{-16} V cm^2.

	C_{11}	C_{12}	C_{21}	C_{22}	B_1	B_2	a
N_2-Ar	0.633	0.0852	1.00	1.00	29.3	10.8	0.25
CO-Ar	0.81	0.0461	2.66	1.17	36.3	9.04	0.15
CO-He	0.80	0.222	1.49	0.518	50.6	15.0	0.15

CO numerically equal to the E/N value in Td.

IV. CONCLUSIONS

We have presented data for the drift velocity in molecular-gas–rare-gas mixtures which were derived from a numerical solution of the Boltzmann equation. An analytic approximation has been given which closely models the behavior of the numerical curves and the experimental observations. This formula allows the computation of drift velocity as a function of E/N and molecular concentration without the use of lengthy computer codes. It also provides a basis for explanation of the features evident in the W-vs-E/N curves.

The negative differential conductivity obtained in some mixtures is caused by a total momentum-transfer cross section which increases in the region between two resonant inelastic processes. Similar behavior is therefore expected in other rare gases which possess a Ramsauer minimum, when small amounts of a molecular gas are added. Negative conductivity may lead to plasma instabilities. Relaxation oscillations may also occur if the external circuit has a load line which intersects the current-voltage characteristic in more than one place. This will be true even though ionization is supplied by an external source.

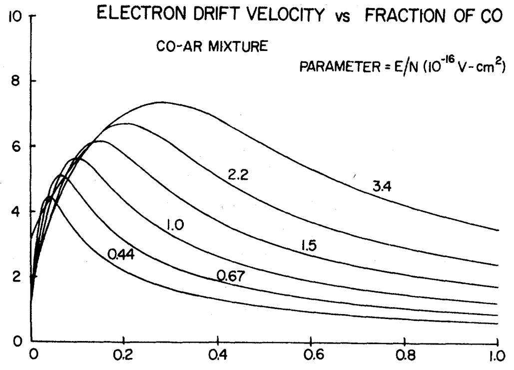

FIG. 7. Variation of drift velocity with the fraction of CO in Ar at several values of E/N.

The increase in drift velocity which occurs when a molecular gas is added to a rare gas is due to the small momentum-transfer cross section of the rare gas in the vicinity of the vibrational cross sections. The effect is reversed when the molecular gas begins to contribute significantly to momentum transfer in this region. The data shows that optimum power loading of a molecular gas can be achieved by judicious choice of the gas mixture.

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[1] R. A. Nielsen, Phys. Rev. 50, 950 (1936).

[2] E. D. Klema and J. S. Allen, Phys. Rev. 77, 661 (1950).

[3] L. Colli and U. Facchini, Rev. Sci. Instrum. 23, 39 (1952).

[4] J. M. Kirschner and D. S. Toffolo, J. Appl. Phys. 23, 594 (1952).

[5] J. C. Bowe, Phys. Rev. 117, 1411 (1960).

[6] A. A. Vorob'ev, B. A. Ivanov, A. P. Komar, and V. A Korolev, Zh. Tekh. Fiz. 29, 1252 (1959) [Sov. Phys. Tech. Phys. 4, 1148 (1960)].

[7] W. H. English and G. C. Hanna, Can. J. Phys. 31, 768 (1953).

[8] D. Errett, Ph.D. thesis (Purdue, 1951) (unpublished).

[9] M. A. Uman and G. Warfield, Phys. Rev. 120, 1542 (1960).

[10] T. Holstein, Phys. Rev. 70, 367 (1946).

[11] B. Sherman, J. Math. Anal. Appl. 1, 342 (1960).

[12] R. D. Hake, Jr. and A. V. Phelps, Phys. Rev. 158, 70 (1967).

[13] L. S. Frost and A. V. Phelps, Phys. Rev. 136, A1548 (1964).

[14] R. W. Crompton *et al.*, Aust. J. Phys. 23, 667 (1970).

[15] V. Spence, J. L. Mauer, and G. J. Schulz, J. Chem. Phys. 57, 5516 (1972).

[16] L. J. Kieffer, JILA Information Center Report No. 13 (1973) (unpublished).