

ELECTRON CONDUCTIVITY IN RAMSAUER GASES AND GAS MIXTURES

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INTRODUCTION

In applications such as plasma switches, particle counters and plasma deposition reactors, various gas mixtures are used. This paper presents the results of calculations of the electron drift velocity (W_D) for rare gas-molecular gas mixtures and pure methane, silane and silane plasma reactor mixtures over a wide range of the ratio of the electric field to the total number density (E/N).

CALCULATIONS AND RESULTS

The calculations use an iterative numerical solution of the collisional Boltzmann transport equation and incorporate the latest experimental electron impact cross-sections to derive the electron energy distribution function (EEDF). The form of the Boltzmann transport equation used was derived by Holstein¹ for electrons in a uniform electric field undergoing elastic and inelastic collisions in a cold gas. An expansion in spherical harmonics retaining the first two terms is used to account for the angular distribution of electron velocities. The analysis indicates that addition of small amounts of a molecular gas (e.g., nitrogen, carbon monoxide) to a rare gas diluent exhibiting a Ramsauer minimum in the momentum transfer cross-section (argon, krypton, xenon) dramatically influences the electron drift velocity. The cross-sections for the rare gases were taken from the compilation of Kieffer²; and for the molecular gases, N_2 and CO, from Phelps et al³ and from Spence et al⁴, respectively. Over a range of concentrations of the molecular gas, drift velocity increases of several hundred percent are obtained. In addition, differential negative conductivity (DNC) occurs over a substantial range of E/N for some gas mixtures. These results show good agreement with experimental data⁵ and other calculations⁶ where comparisons are available.

The drift velocity thus calculated in argon-nitrogen mixtures is shown in Figure 1. The conductivity of the mixture is higher than that of either component. The sensitivity of the drift velocity to the concentration of the molecular gas means that, if the shape and threshold of the inelastic cross-section at low energy is known, the absolute magnitude can be determined by the measurement of the drift velocity. The latter can be determined quite accurately, and so a macroscopic measurement can be used to calibrate a microscopic quantity. Further, if the gas concentrations are measured accurately, the comparison between experiment and the theory, iterating on a cross-section value, is made over a three dimensional surface. This checks the uniqueness of the cross-sections better than the single line result given by drift tube measurements in pure gases.

Figure 2 displays the electron drift velocity in krypton-carbon monoxide mixtures. The DNC occurs over a range up to 25% addition of CO. For selected E/N , drift velocity enhancements greater than 300% occur. Figure 3 displays similar results for xenon-carbon monoxide mixtures. The enhancement for the 10% CO mixture at $E/N = 20$ Townsends actually approaches 600%. Thus this mixture should be a very sensitive test of the amplitude of the CO vibrational

cross-sections. Figure 4 shows the calculated drift velocity of argon-carbon monoxide mixtures. The effects are somewhat larger with CO as the added molecular gas in argon as compared to N₂.

Results also have been obtained (not shown) for helium and neon as the diluent. There is only a modest enhancement of the drift velocity and no evidence of DNC with N₂ or CO as the added molecular gas.

Drift-tube measurements with methane and silane⁷ have shown that the electron drift velocity in these gases is very high and that DNC occurs. The polyatomic gas methane has been shown to have a Ramsauer minimum, and it has been suggested that an analogous minimum occurs in silane. The saturated bonds cause the gases to behave like a closed shell rare gas with regard to momentum transfer; however, the gas has inherent vibrational inelastic losses at low energy. Thus, to some extent, these individual gases resemble the gas mixtures discussed earlier. We have used these data to derive the transport properties of gas mixtures containing these polyatomic gases.

The transport properties of silane mixtures are important in semiconductor processing using a plasma reactor. The calculations used the momentum transfer cross-sections derived by Pollock⁷ from his drift-tube measurements, the ionization thresholds of Franklin and Field⁸ and an extrapolation of methane data for excitation losses. The vibrational cross-section was assumed to be associated with the lowest energy Raman mode. Various results are shown in Figure 5. The drift velocity in silane is very high and displays DNC. When additional gases are added, the conductivity decreases. The DNC is predicted to still remain even with large helium dilution. The drift velocity for a typical "reactor mix," SiH₄ 1.6%/N₂ 20%/remainder argon, is also shown. While there is an inflexion in the drift velocity vs E/N, the DNC is predicted not to occur.

CONCLUSION

Our physical interpretation of the Ramsauer gas results is that, for selected conditions and a fixed E/N, the addition of the molecular gas reduces the electron mean energy to a region where the characteristic electron, although traveling slower, experiences fewer momentum changing collisions. It therefore travels farther in the direction of the field and the ensemble of electrons has a higher drift velocity than in the diluent alone. If E/N is increased, the average momentum transfer collision frequency $\langle v \rangle$ increases.

If the latter is sufficiently rapid, as $W_D = \frac{eN(E/N)}{m\langle v \rangle}$, the conductivity actu-

ally can decrease and DNC occurs. It is possible to derive simplified criteria for the DNC to occur. The necessary conditions are that there should be an increasing momentum transfer collision frequency with energy and that the fractional energy into a particular inelastic process also should be changing rapidly.

With respect to the plasma reactor studies, we note that the conductivity of the reactor is a sensitive function of the concentration of silane. In contrast to other molecular gases, when silane is diluted with a rare gas, the electron drift velocity decreases. However, the effects are generally significant only below 40 Td. The conductivity at the higher E/N, characteristic of the reaction zone, is less sensitive to the gas mixture. The conductivity near the sample deposition, if the field is lower, may be influenced by the phenomena illustrated.

Since radio frequency reactors are usually run at high E/N values where significant dissociation and ionization occur, reactor modelling must include plasma chemistry analysis. Studies are continuing to describe the various kinetic processes under these higher field conditions.

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DRIFT VELOCITY IN ARGON - NITROGEN

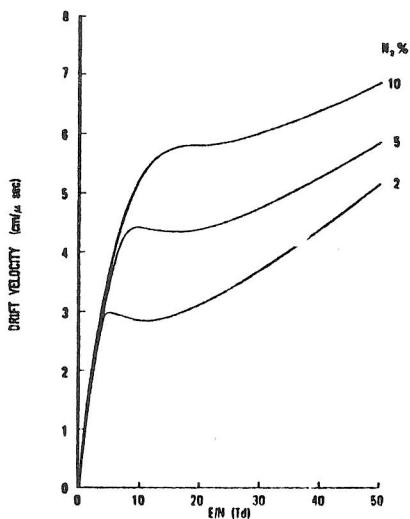


FIGURE 1
DRIFT VELOCITY IN ARGON-NITROGEN

DRIFT VELOCITY IN KRYPTON - CARBON MONOXIDE

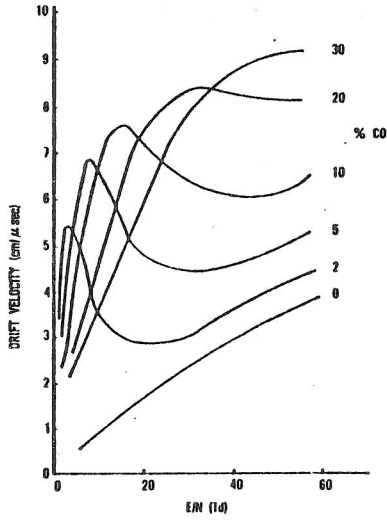


FIGURE 2
DRIFT VELOCITY IN KRYPTON-
CARBON MONOXIDE

DRIFT VELOCITY IN XENON - CARBON MONOXIDE

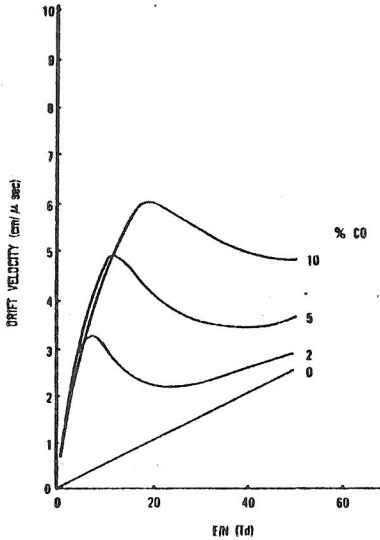


FIGURE 3
DRIFT VELOCITY IN XENON-
CARBON MONOXIDE

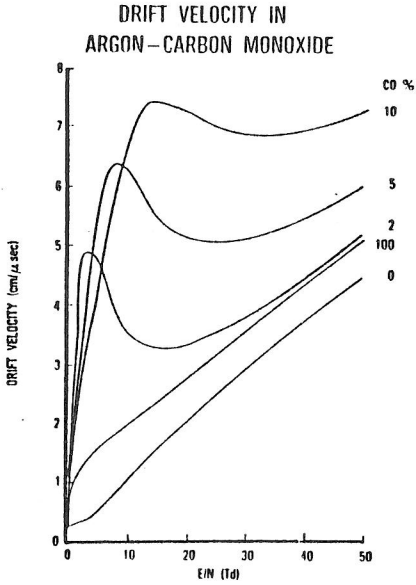


FIGURE 4
DRIFT VELOCITY IN ARGON-
CARBON MONOXIDE

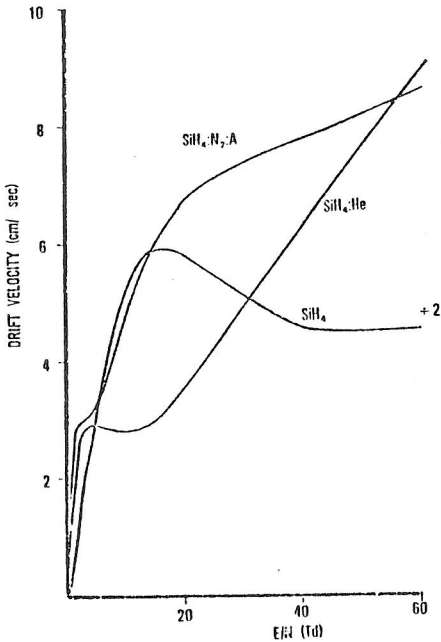


FIGURE 5
ELECTRON DRIFT VELOCITIES IN
SILANE MIXTURES;
100% SiH₄, 5% SiH₄/95% He,
1.6% SiH₄/20.0% N₂/78.4% Ar.