coefficients for a large class of states have recently been derived.[9]

RESULTS AND DISCUSSION

Some of the important results are presented in Tables I–VIII. Since the basis sets were chosen so as to identically satisfy the cusp conditions,[6] we did not include the cusp values in the tables.

We believe that the total energies computed represent the Hartree-Fock values to about five significant figures, and that the radial functions $P_{i\lambda}(r)$ represent the Hartree-Fock functions to 2–3 decimal places. Better accuracy could be obtained by extensive exponent optimizations, which would require a large amount of computer time.

A numerical SCF calculation *without* exchange on Mo^+ was published by Ridley.[10] The numerical orbitals for Mo^+ of this work disagree with those by Ridley (after normalization) mostly in the second decimal place; in the critical area of the outer loop of the $4d$ orbital they disagree even in the first decimal place. A similar disagreement exists for Cu^+, where calculations with[7,11] and without[12] exchange are available.

Since total experimental energies are not available, we can only meaningfully compare the difference of the computed energies of Mo^+ and Mo with the experimental ionization potential[13] of Mo. This is shown in Table IV.

ACKNOWLEDGMENTS

The authors appreciate the cooperation of the staff of the Computation Center at the University of Chicago, and the personnel of the IBM-7090 computing facilities at Wright-Patterson Air Force Base.

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PHYSICAL REVIEW VOLUME 133, NUMBER 5A 2 MARCH 1964

Electron-Energy Distribution Function and Electron Average Energy in Ar-CO_2 and Ar-H_2 Mixtures*

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Electron-energy distribution functions and electron average energies are calculated for low-energy electrons in Ar-CO_2 and in Ar-H_2 mixtures in the presence of a static electric field. It is shown that one part of carbon dioxide or of molecular hydrogen in 10 000 parts of argon is sufficient to alter appreciably the electron-energy distribution function and the electron average energy from the values they would have in pure argon.

I. INTRODUCTION

That small amounts of molecular gases, when added to argon, alter appreciably the value that the electron drift velocity exhibits in pure argon has been verified both experimentally[1] and theoretically.[2,3] There is, however, very little mention in the literature of the change in the electron distribution function and the electron average energy induced by the addition of molecular impurities to argon. A technique for solving the Boltzmann equation for the phase-space distribution function for electrons immersed in certain binary gas mixtures in the presence of a static electric field has been presented in a previous article.[2] In the present study, use is made of this theory to calculate the electron-energy distribution function and electron average energy as a function of the molecular-impurity concentration in argon. Carbon dioxide and molecular hydrogen have been chosen as the molecular impurities. The Ar-CO_2 mixture has been chosen because of the good agreement between experimental and theoretical electron drift velocity data for this mixture.[2] The agreement between theory and experiment lends validity to the experimental cross-section and molecular energy-absorption data used in the theoretical analysis. The Ar-H_2 mixture has been chosen for study because electron drift velocity measurements in this mixture have been used to determine the momentum transfer and inelastic cross sections for hydrogen and argon.[4]

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* This research has been supported by National Science Foundation Grant GP-800.

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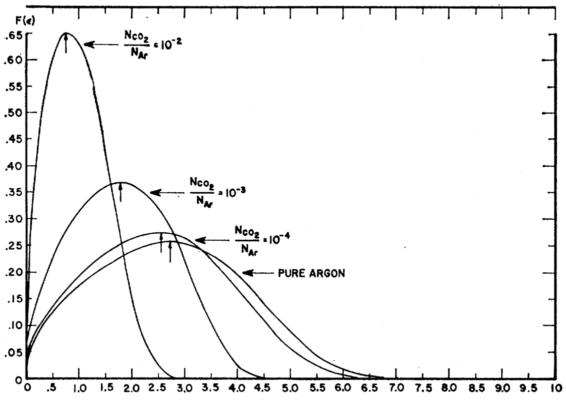

FIG. 1. Electron-energy distribution function versus electron energy for several values of carbon dioxide density to argon density ratio with $E/p=0.5$ V/cm/mm-Hg at 0°C. Vertical arrows mark maxima of curves.

II. THEORY

In an earlier paper a method for solving the Boltzmann equation for the electron phase-space distribution function for electrons in certain binary gas mixtures has been presented.[2] The calculated electron phase-space distribution function is of the form

$$f(\mathbf{u})=f_0(\epsilon)+[u_x/u]f_1(\epsilon)\,, \tag{1}$$

with

$$f_0=G\exp[-(6m/M)(N/E)^2(A\epsilon^5+B\epsilon^4+C\epsilon^3+D\epsilon^2)]\,, \tag{2}$$

$$f_1=(6m/M)(N/E)(H\epsilon^3+L\epsilon^2+J\epsilon)f_0\,. \tag{3}$$

In the above equations, m is the electron mass; M is the argon mass; N is the argon density; E is the electric field intensity; $\mathbf{u}$ is the electron velocity; ϵ is the electron energy; A, B, C, D, H, L, J are functions of the gas parameters and percentage mixture; and G is the normalization constant. The quantities A, B, C, D, H, L, J, G each assume the same number of values as there are straight-line sections in the gas parameter approximations.

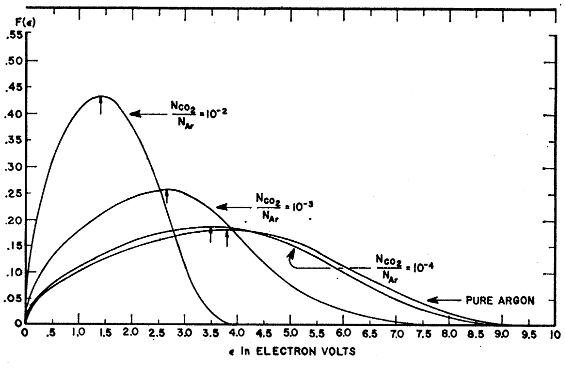

FIG. 2. Electron-energy distribution function versus electron energy for several values of carbon dioxide density to argon density ratio with $E/p=1.0$ V/cm/mm-Hg at 0°C. Vertical arrows mark maxima of curves.

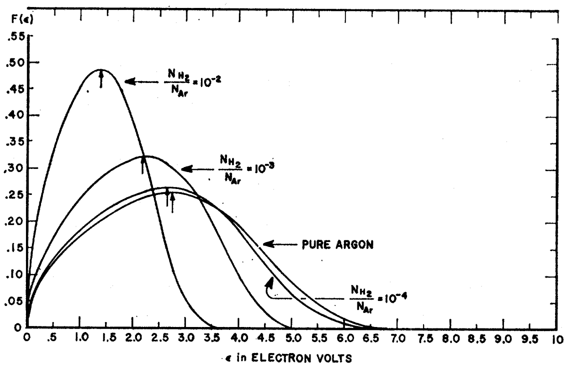

FIG. 3. Electron-energy distribution function versus electron energy for several values of molecular hydrogen density to argon density ratio with $E/p=0.5$ V/cm/mm-Hg at 0°C. Vertical arrows mark maxima of curves.

The normalized electron-energy distribution function, $F(\epsilon)$, is related to the phase-space distribution function by

$$F(\epsilon)=\epsilon^{1/2}f_0\Big/\int_0^\infty \epsilon^{1/2}f_0 d\epsilon\,. \tag{4}$$

The electron average energy is given by

$$\bar{\epsilon}=\int_0^\infty \epsilon^{3/2}f_0 d\epsilon\Big/\int_0^\infty \epsilon^{1/2}f_0 d\epsilon\,. \tag{5}$$

The straight-line approximations to the cross sections of argon, molecular hydrogen, and carbon dioxide and to the energy-absorption coefficients of molecular hydrogen and carbon dioxide have been given previously.[2,3]

III. RESULTS AND CONCLUSIONS

If Fig. 1 the electron-energy distribution function is plotted for electrons in several Ar-CO_2 mixtures with $E/p=0.5$ V/cm/mm-Hg at 0°C. In Fig. 2 the electron-energy distribution function is plotted for electrons in several Ar-CO_2 mixtures with $E/p=1.0$ V/cm/mm-Hg

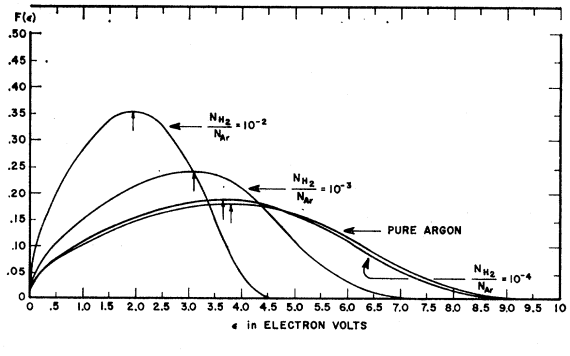

FIG. 4. Electron-energy distribution function versus electron energy for several values of molecular hydrogen density to argon density ratio with $E/p=1.0$ V/cm/mm-Hg at 0°C. Vertical arrows mark maxima of curves.

at 0°C. The electron-energy distribution functions for Ar-H_2 mixtures with $E/p=0.5$ and $E/p=1.0$ at 0°C are plotted in Figs. 3 and 4, respectively. The electron average energy as a function of the carbon dioxide density to argon density ratio for $E/p=0.5$ and $E/p=1.0$ is plotted in Fig. 5. The electron average energy as a function of the molecular hydrogen density to argon density ratio for $E/p=0.5$ and $E/p=1.0$ is plotted in Fig. 6.

The energy distribution function for electrons in pure argon at $E/p=1.0$ given in Figs. 2 and 4 is almost identical with that published by Barbiere.[5] The effect of the addition of small amounts of carbon dioxide or molecular hydrogen to the argon is to lower the electron energies. From a physical point of view, the electron energies are lowered due to the relatively large fractional energy loss per collision that an electron suffers in an inelastic collision with carbon dioxide or with hydrogen. This lowering of the electron energies is more pronounced in the Ar-CO_2 mixtures than in the Ar-H_2 mixtures because carbon dioxide can absorb a greater fraction of an electron's energy in a collision than can molecular hydrogen. It can be seen from the figures that one part of carbon dioxide or of molecular hydrogen in 10 000 parts of argon is sufficient to alter appreciably the electron-energy distribution function and the electron average energy from the values they would have in pure argon.

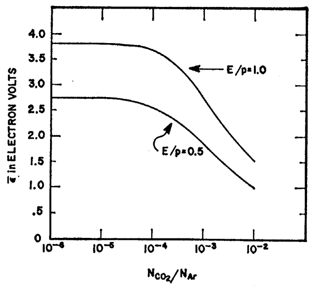

FIG. 5. Electron average energy versus ratio of carbon dioxide density to argon density for $E/p=0.5$ V/cm/mm-Hg and $E/p=1.0$ V/cm/mm-Hg at 0°C.

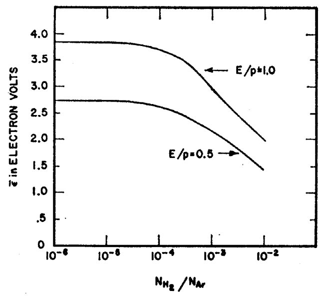

FIG. 6. Electron average energy versus ratio of molecular hydrogen density to argon density for $E/p=0.5$ V/cm/mm-Hg and $E/p=1.0$ V/cm/mm-Hg at 0°C.

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Classical Impulse Approximation for Inelastic Electron-Atom Collisions

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Analytic expressions for the ionization and excitation cross sections of atoms by electrons are derived using the classical impulse approximation, i.e., by considering only the Coulomb interaction between the incident electron and one bound electron. The results obtained are slightly simpler and more self-consistent than those obtained in an earlier calculation by Gryzinski. The cross sections are found to be roughly as good as those obtained by the Born approximation except in the high-energy limit. The apparent superiority of Gryzinski's theory to quantum approximations arises from a subsidiary approximation made in averaging the cross section over the initial angular distribution rather than from the kinematic description of the bound electrons or the nature of the impulse approximation itself. The Coulomb cross section for transfer of energy ΔE between two particles of equal mass m, charge e, initial kinetic energies E_1 and E_2, relative velocity V, with an isotropic initial angular distribution is found to be

$$V d\sigma/d(\Delta E)=2^{1/2}\pi e^4|\Delta E|^{-2}(mE_1E_2)^{-1/2}(\mathcal{E}^{1/2}+\tfrac{4}{3}\mathcal{E}^{3/2}/|\Delta E|),$$

where $\mathcal{E}$ is the smallest of the four initial and final kinetic energies. For single ionization this cross section is found to increase as the 3/2 power of the excess energy above threshold, reach a maximum at about $2\frac{1}{2}$ times the threshold energy, and decrease as E^{-1} at high energies. For hydrogenic atoms in any state the cross section goes to 5/3 the classical Thomson ionization cross section in the high-energy limit.

INTRODUCTION

UNTIL recently there has been no acceptable treatment of inelastic electron-atom collisions by the classical impulse approximation—that is, by calculating the cross sections for energy transfer in binary electron-electron collisions, neglecting the field of the nucleus and other bound electrons. Some time ago J. J. Thomson[1] treated inelastic electron-atom collisions by considering the Coulomb scattering of the

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[1] J. J. Thomson, Phil. Mag. 23, 419 (1912).