The determination of electron collision cross sections from swarm data

A. V. Phelps
Joint Institute for Laboratory Astrophysics
National Bureau of Standards and University of Colorado
Boulder, Colorado 80309 U.S.A.

1. Introduction
Electron collision cross sections have been determined from swarm data, such as mobility and diffusion coefficients, ever since the early studies of Townsend and coworkers.\(^1\) Work through the 1940's provided a) still useful measurements of electron transport coefficients and approximate momentum transfer cross sections in a wide variety of gases\(^2\); b) the recognition of the unique ability of swarm measurements to provide cross sections for very low energy processes such as rotational excitation\(^3\); and c) rigorously formulated, lowest order solutions to the Boltzmann equation for electrons in gases in a uniform electric field.\(^4,5\) The application of high speed computers\(^6,7\) and the development of techniques for precision measurement of electron transport coefficients\(^8-10\) in the 1960's made possible the serious determination of electron collision cross sections from swarm data. With the recognition\(^11\) of the usefulness and accuracy of this approach has come more precise formulations of the relationship between the experiments and the Boltzmann equation used to calculate the measured quantities from electron collision cross sections.\(^12-18\) The determination of cross sections at energies for which inelastic collisions are important requires that the analysis include comparisons with rate coefficients for electron attachment, ionization and excitation.

Swarm experiment data have been used for the determination of electron collision cross sections for the rare gases,\(^19-22\) some metal vapors\(^23-25\) and several molecular gases.\(^26-32\) In Sec. 2 we will review the methods of data analysis. In Secs. 3 and 4 we summarize results obtained for atomic and molecular gases, respectively. We will not consider cross section and rate coefficient data related to free-free and free-bound recombination, dissociative recombination or other electron-ion collision processes.

2. Data Analysis
The process of determining electron collision cross sections from swarm data is that of an unfolding of the cross section or a weighted cross section from the electric field and gas temperature dependence of electron transport and rate coefficients. The only essential difference between this
process and the unfolding of cross sections from scattering and excitation data obtained using electron beams is that in the swarm analysis the electron energy distribution function varies with the electric field and gas temperature and is very difficult to determine experimentally. Thus, in the more precise analyses\textsuperscript{6, 9, 19-21, 26} the electron energy distribution function is calculated from a trial set of cross sections using numerical solutions of the Boltzmann equation. The appropriately weighted cross sections are then folded into the electron energy distribution to obtain transport and rate coefficients. The difference between calculated and measured transport and rate coefficients is then used to adjust the trial cross section set. Except for one case,\textsuperscript{19a} this iterative loop has been closed by human judgement.

In the older treatments\textsuperscript{1, 2} and in recent approximate analyses the Boltzmann equation for the electron energy distribution is often replaced by energy and momentum balances using the properties of a typical electron or using a functional form for the electron energy distribution, e.g., generalized Druyvesteyn. Although these and other\textsuperscript{33} simplified procedures greatly reduce the expense of data analyses, provide initial trial cross sections, and often lead to analytical expressions for the derived energy dependent cross sections,\textsuperscript{34} these procedures occasionally lead to very misleading results.\textsuperscript{35} The uncertainties in electron attachment cross sections determined from swarm data can be reduced by making measurements of attachment coefficients in a mixture of a well characterized gas, e.g., He or \textsubscript{N}2, and vanishingly small concentrations of the attaching gas.\textsuperscript{32} One still has the problem of calculating the electron energy distribution for the pure main gas.

In the absence of mathematically based and justified iteration procedures there have arisen different philosophies regarding the best use of transport and rate coefficients calculated from trial cross section sets. The common procedure is to compare directly calculated and measured drift velocities \(w\) and ratios of diffusion to mobility coefficients \(D/\mu\) at various values of the gas temperature \(T\) and of the ratio of the electric field to gas density \(E/N\). A number of authors have worked with effective cross sections\textsuperscript{1, 2} or rate coefficients,\textsuperscript{6} which are directly derivable from experimental data and which separate the effects of momentum changing (mostly elastic) and energy changing (mostly inelastic) collisions of electrons with the atoms or molecules. This separation works particularly well in gases, such as hydrogen, where the energy exchange rate is small compared to the momentum exchange rate. These rate coefficients are shown in Fig. 1, where the momentum transfer collision frequency per molecule, \(v_{\text{m}}/N = e/(\sqrt{2}mN)\), and the energy exchange frequency per molecule, \(v_{\text{e}}/N = e\ln(E/N)/(eD/\mu - kT)\) for \textsubscript{H}2.
Fig. 1. Momentum transfer and energy exchange frequencies versus characteristic energy for H₂. Also shown are the contributions of various excitation processes to the energy exchange frequency.

are plotted against the characteristic energy, $\varepsilon_k = eD/\mu$. Also shown are the contributions of various processes to the energy exchange frequency. One notes that the range of electron energies over which any one inelastic process dominates is rather limited, e.g., from 0.02 to 0.3 eV for rotational excitation and 0.5 to 1.5 eV for vibrational excitation. In gases with relatively large energy exchange frequencies (N₂, CO, CH₄) or with a Ramsauer minimum (CO₂) in the momentum transfer cross section the separation is not complete, e.g., factor of two changes in assumed inelastic cross sections can cause changes in the calculated $\nu_m/N$ versus $\varepsilon_k$ curve (up to 5% in CO₂ and N₂).

Because of the relatively low and fixed fractional energy resolution of swarm experiments the analyses of swarm data can be expected to yield the energy dependence of inelastic collision cross sections in only a few cases. Examples in which the near threshold portion of excitation cross sections have been determined are rotational and vibrational excitation of H₂ and vibrational excitation of N₂ and CO. Unfortunately, for each of the vibrational excitation determinations made thus far there are unresolved discrepancies between the results of swarm analyses and of electron beam experiments. The optimum situation for the application of swarm analysis is when the energy dependence of the excitation cross section is known from electron beam experiments or from theory and when cascade contributions from higher levels are small, e.g., the excitation of the C₃Π₂ state of N₂. In less favorable cases the electronic excitation rate coefficient is controlled by
cascading from higher levels, e.g., the \( ^3\Sigma_u^+ \) state of \( \text{N}_2 \) and the \( ^1\Sigma_g^+ \) state of \( \text{O}_2 \).

Finally, it should be pointed out that, despite contrary claims, essentially all of the publications in which calculated electron-transport coefficients are compared with experiment are in fact participating in the determination of electron collision cross sections from swarm data. This situation results from the fact that the published electron collision cross section data are either based on swarm analysis or are sufficiently divergent so that the authors must make choices which lead to realistic transport and rate coefficients.

3. Summary of Results - Atomic Gases

In this section we will briefly summarize the results of determinations of electron collision cross sections for the more thoroughly studied atomic gases. Since elastic scattering of electrons determines the electron transport coefficients in rare gases over a wide range of electron energies, the momentum transfer cross section can be determined from analysis of measured values of either drift velocity or \( D/\mu \) values versus \( E/N \) and \( T \).

A. Helium. The momentum transfer cross section for electrons in helium at energies below 12 eV obtained by analysis of drift velocities\(^{19a,b}\) appears to be the most accurately known of any electron-atom or electron-molecule cross section. At higher electron energies the momentum transfer cross section obtained from drift velocity data is much less certain.\(^{19c}\) Inelastic cross sections have not been obtained from swarm data.

B. Neon. The techniques developed for helium have been applied to the measurement and analysis of electron drift velocities in neon and yield momentum transfer cross sections for energies below 7 eV.\(^{20}\)

C. Argon. Through careful attention to the problems of impurities and of electron energy equilibrium, electron drift velocities and \( D/\mu \) values accurate to better than \( \pm 3\% \) have been obtained and used to derive momentum transfer cross sections for energies below 4 eV.\(^{21a}\) Concern as to the effect of the Ramsauer minimum in the momentum transfer cross section has led to verification of the validity of the two-term spherical harmonic solution of the Boltzmann equation for electrons in argon.\(^{21b}\) In my opinion the results of the analyses of electron drift velocity and \( D/\mu \) data must be preferred to the results of less thoroughly tested methods.\(^{21e}\) Analyses of ionization coefficients have been used to obtain high energy momentum transfer cross sections\(^{21d}\) or total excitation cross sections.\(^{21e}\)

D. Krypton. Momentum transfer cross sections for electrons in krypton derived from electron drift velocities\(^{22a}\) and from microwave conductivity
measurements\textsuperscript{22b, c} show a great deal of spread (±50%). Total excitation cross sections derived from ionization coefficients data agree well with data from electron scattering experiments.\textsuperscript{21e}

E. Xenon. The fractional differences among the momentum transfer cross sections for electrons in xenon derived from drift velocity data\textsuperscript{22a} and from microwave conductivity data\textsuperscript{22b, c} are qualitatively similar but smaller in magnitude than for krypton.

F. Alkali Atoms. Analyses of electron drift velocity data in cesium have led to momentum transfer cross sections which are reasonably consistent with the rather uncertain experiments.\textsuperscript{23a} Analysis of drift velocities in Cs–Ar mixtures yielded\textsuperscript{23b} the initial slope of the excitation cross section for the resonance state of Cs, while analysis of ionization in the positive column of electrical discharges yields the initial slope of the cross section for ionization of Cs atoms in the resonance state.\textsuperscript{23c} Momentum transfer cross sections determinations have also been made using measured electron drift velocities in sodium\textsuperscript{23d} and using plasma conductivities in potassium.\textsuperscript{23e}

G. Mercury, Thallium and Cadmium. A rather complete determination of momentum transfer and inelastic cross sections for electrons in mercury from available drift velocity and D/µ data\textsuperscript{24a} has been followed by new measurements of drift velocities and accompanying determinations of momentum transfer cross sections for energies below about 4 eV.\textsuperscript{23d, 24b} The same approach has been used for thallium.\textsuperscript{23d} Effective cross sections for metastable production and further excitation of cadmium have been obtained from measurements of excitation rate coefficients in discharges.\textsuperscript{24c}

H. Other Atoms. Average momentum transfer cross sections for a few atoms (H, C, O) have been obtained from the electrical conductivity in arcs\textsuperscript{25a, b} and shock tubes.\textsuperscript{25c} Measurements of excitation rate coefficients for O atoms have yielded excitation cross sections data.\textsuperscript{25d}

4. Summary of Results - Molecular Gases

Because of the possibility for rotational, vibrational, and dissociative excitation and for dissociative attachment and ionization the analyses of swarm data for molecules must make use of all of the available data, i.e., the results of transport and rate coefficient experiments, electron beam experiments, and theory. It should be kept in mind that any measurement of excitation rate coefficient must be based on a thorough understanding of the kinetics of the excited state and an accurate accounting of the excitation and relaxation of vibrational levels of the excited state.
A. Hydrogen. As suggested by Fig. 1, molecular hydrogen is attractive for the application of swarm analyses because of the well separated regions in which rotational and vibrational excitation each dominate the energy loss. This feature, along with the availability of precision electron drift velocities and $D/\mu$ values, has led to accurate determinations of momentum transfer, rotational excitation and vibrational excitation cross sections for energies below about 2 eV. $^{26a,b}$ At higher energies ionization, uv continuum and dissociative excitation rate coefficients have been used to obtain momentum transfer and electronic excitation cross sections. $^{26b}$

B. Nitrogen ($N_2$). As in the case of $H_2$, the recent analyses $^{27a,b}$ of electron transport and rate coefficients at electron energies below about 1.5 eV use very accurate measurements. At higher mean electron energies the analyses make use of the energy dependences of cross sections from electron beam experiments, but adjust their magnitudes to fit swarm data. Our recent results for five experimental rate coefficients, i.e., momentum and energy transfer, $A^3\Sigma$ and $C^3\Pi$ state excitation and ionization, are shown in Fig. 2. Calculations $^{27c}$ for $N_2$ have established useful relationships among excitation and ionization cross sections and the respective rate coefficients similar to those cited for argon. $^{21d,e}$ Improved solutions of the electron Boltzmann equation are being used. $^{27d}$

C. Oxygen ($O_2$). Attempts to obtain momentum transfer, effective three-body attachment dissociative attachment and electronic excitation cross sections consistent with measured transport and rate coefficients have

![Diagram showing momentum transfer, total energy exchange, $A^3\Sigma$ and $C^3\Pi$ excitation and ionization rate coefficient versus $N/E$ for $N_2$. The dashed lines are for vibrational excitation cross sections chosen to fit the energy exchange data, while the solid curves are for vibrational excitation chosen to fit $A^3\Sigma$ excitation data in each case the magnitude of electronic excitation cross sections are adjusted to fit ionization data.](image-url)
revealed several unresolved questions. These problems may arise from the difficulties of making and interpreting electron transport and rate coefficient measurements in the presence of large rate coefficients for electron attachment. Unanswered questions at very low energies are a) whether the extremely high energy resolution claimed can be obtained by other workers and b) the origin of unexpected variations of observed low energy attachment rate coefficients with density and mean energy in O2-N2 mixtures. The experimental data and calculated curves in Fig. 3 illustrate the spread in three-body attachment coefficients and absence of data at low E/N.

D. Carbon Monoxide (CO). Momentum transfer and inelastic cross sections for electrons at energies below about 4 eV have been reevaluated using new measurements of the electron drift velocity. In addition cross sections have been derived from Monte Carlo analyses at very high E/N.

E. Carbon Dioxide (CO2). Determinations of electron collision cross sections from swarm data for CO2 range from the studies emphasizing low energy electrons and vibrational excitation through analyses of electron attachment and ionization data and high E/N transport data.

F. Methane (CH4). Very recent theoretical analyses of electron transport data for methane have shown that it is essential to take into account the fact that the vibrational excitation cross sections are comparable with the elastic scattering cross sections in the vicinity of the Ramsauer minimum at 0.4 eV. No attempt appears to have been made to analyze the higher energy data.

G. Water Vapor (H2O). Only the cross sections from very preliminary analyses of electron drift velocity, D/μ, attachment and ionization data appear to have been used in published works. One reason for this situation has been the large spread and small amount of D/μ data and the concerns as to the applicability of the two-term spherical harmonic expansion solution of the Boltzmann equation for electrons in water vapor.

![Fig. 3. Three-body attachment coefficients versus E/N for O2. Our curve (-----) and that of Ref. 27c (- - -) are calculated for the low O2 density limit, i.e., three-body collisions only.](image-url)
Other Molecules. There are too many investigations of complex molecules for us to attempt to summarize them. References to some of them have been compiled. Good examples of the determination of cross sections from swarm data are the studies of electron attachment using the beam-swarm technique.

References


