01 Dec 1969

Charge-transfer Cross Sections For Negative Ions On Atomic And Molecular Targets

W. (William) R. Snow

R. D. Rundel

R. Geballe

*Work supported by the U. S. Atomic Energy Commission.

[1] For a general review, cf. E. Merzbacher and H. W. Lewis, Encyclopedia of Physics, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 34, p. 166.

[2] W. Brandt, R. Laubert, and I. Sellin, Phys. Rev. 151, 56 (1966).

[3] J. M. Khan, D. L. Potter, and R. D. Worely, Phys. Rev. 139, A1735 (1965).

[4] J. H. Ormrod, J. R. MacDonald, and H. E. Duckworth, Can. J. Phys. 43, 280 (1965).

[5] R. D. Moorhead, J. Appl. Phys. 36, 394 (1965).

[6] W. White and R. M. Mueller, J. Appl. Phys. 38, 3660 (1967).

[7] R. Laubert and W. Brandt, Bull. Am. Phys. Soc. 12, 1074 (1967).

[8] R. W. Fink, R. C. Jopson, Hans Mark, and C. D. Swift, Rev. Mod. Phys. 38, 513 (1966).

[9] T. Huus, J. Bjerregaard, and B. Elbek, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. 30, No. 17 (1956).

[10] J. Bang and J. M. Hansteen, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. 31, No. 13 (1959).

[11] Handbook of Mathematical Functions, edited by M. Abramowitz and I. A. Stegun, National Bureau of Standards (U. S. Government Printing Office, Washington, D. C. 1964), Appl. Math. Ser. 55, Chap. 5, p. 245 ff.

Charge-Transfer Cross Sections for Negative Ions on Atomic and Molecular Targets*†

W. R. Snow,† R. D. Rundel,§ and R. Geballe
Department of Physics, University of Washington, Seattle, Washington 98105
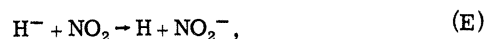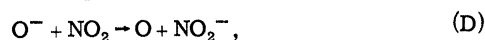(Received 23 September 1968)

Charge-transfer cross sections for H^- on O, O_2, and NO_2; O^- on H, O, H_2, O_2, and NO_2; and C^- on H and O have been measured over an energy range of 0.5 to 4 keV using a modulated crossed-beam apparatus. The experimental cross sections are compared with theories of resonant and nonresonant charge transfer based on a two-state approximation. For the reactions $H^- + O \rightleftharpoons O^- + H$, the cross sections are found to be consistent with detailed balancing. The effect of electron detachment on charge-transfer cross sections is discussed.
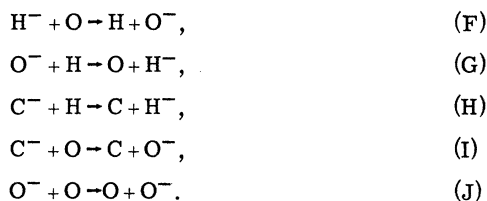
INTRODUCTION

Charge-transfer collision phenomena involving negative ions have not generally been investigated as extensively as those involving positive ions. Measurements of charge-transfer cross sections for atmospheric negative ions have been made in the range of a few electron volts to a few hundred electron volts by Bailey,[1] Rutherford and Turner,[2] and Paulson.[3] In the energy range of a few hundred to a few thousand electron volts, which is covered by the present work, Hummer,[4] *et al.*, have made an absolute measurement of the $H^- + H$ resonant charge-transfer cross section, and Bydin[5] has measured charge-transfer cross sections for negative ions of some of the alkali metals.

This paper contributes experimental data which, it is hoped, will further the understanding of negative ions in general and the charge-transfer process in particular, and discusses these data in terms of current theoretical approaches to charge transfer for both negative and positive ions.[6-11]

Measurements have been made over an energy range of 0.5 to 4 keV, for the following reactions:

$$O^- + O_2 \rightarrow O + O_2^- , \tag{A}$$

$$H^- + O_2 \rightarrow H + O_2^- , \tag{B}$$

$$O^- + H_2 \rightarrow O + H + H^- , \tag{C}$$

$$O^- + NO_2 \rightarrow O + NO_2^- , \tag{D}$$

$$H^- + NO_2 \rightarrow H + NO_2^- , \tag{E}$$

$$H^- + O \rightarrow H + O^-, \tag{F}$$

$$O^- + H \rightarrow O + H^-, \tag{G}$$

$$C^- + H \rightarrow C + H^-, \tag{H}$$

$$C^- + O \rightarrow C + O^-, \tag{I}$$

$$O^- + O \rightarrow O + O^-. \tag{J}$$

APPARATUS

The cross sections were measured using the modulated crossed-beam technique which was developed originally for experiments involving chemically unstable species.[12] Figures 1 and 2 are cross-sectional diagrams of the apparatus through the ion and neutral beams.

Negative ions were extracted from a hot cathode arc source[13] that operated typically with an arc current of 0.5 A and a pressure of 50 to 200 μ. The energy spread of the ions as determined by a retarding potential measurement was less than 20-eV full width at half-maximum. The ion beam was mass analyzed by a 60° sector magnet with a resolution of 1 part in 50 and focused so as to pass through the collision chamber and on to the collector in a nearly parallel beam. Ion-beam currents at the collector were of the order of 10^{-9} A for O^- and H^- and 10^{-11} A for C^-.

Slow negative ions formed in charge-transfer collisions of primary ions with the thermal-energy particles of the neutral beam were extracted from the collision region into the product-ion mass analyzer by an electric field (2 V/cm) too weak to disturb the primary-ion beam significantly. An electrostatic quadrupole lens[14] was used in the product-ion analyzer because of its ability to focus a large area source to a line image. A large exit slit, used in the product ion mass analyzer to increase its transmission, limited the resolution to about 1 part in 10.

The product-ion current was detected with a Bendix resistance-strip electron multiplier. The output of this multiplier was amplified by a phase sensitive, narrow-band (lock-in) amplifier and recorded, along with the primary-ion current, on
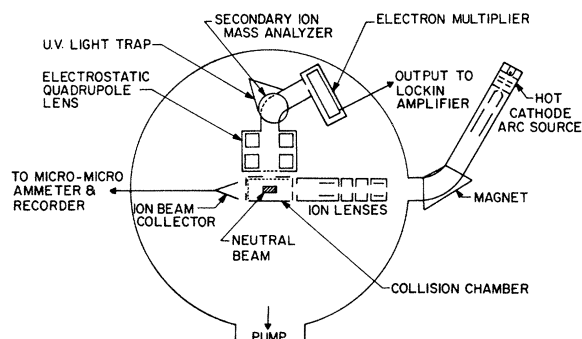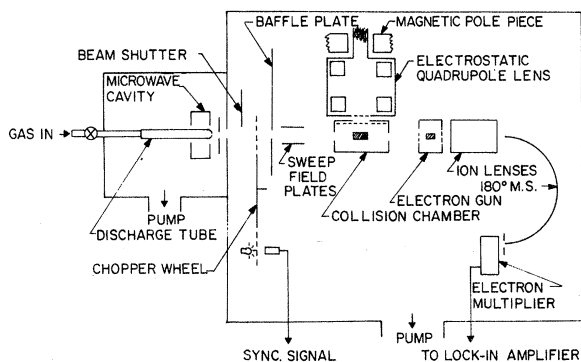

FIG. 2. Cross section of apparatus through neutral beam.

a two-channel chart recorder.

Beams of O and H atoms were formed by dissociating the molecular gas in a microwave discharge, shown in Fig. 2. Gas was admitted to a Vycor discharge tube with a 0.030-in. hole in the end. The dissociating discharge was produced by a cavity driven by a 10 W, 2450 MHz (diathermy) magnetron oscillator. With a single stage of differential pumping it was possible to maintain pressures in the experimental chamber of the order of 5×10^{-6} Torr. Beams used for the measurement of molecular cross sections were formed by admitting the gas through a hypodermic needle.

The neutral beam was modulated at 1440 Hz by a rotating, toothed wheel, which also provided a synchronizing signal for phase discrimination by interrupting a light beam. Ions and electrons traveling with the neutral beam were removed by a sweep field of about 1200 V/cm.

An ionizer and a 180° magnetic mass spectrometer were provided to measure the ratio of the density of atoms to that of molecules in the neutral beam. The ratio of atomic to molecular ion currents produced by electron bombardment of the neutral beam was measured, and the density ratio derived from published cross sections for ionization and dissociative ionization.[12, 15, 16]

The presence of unknown concentrations of metastable ions or neutrals often creates an uncertainty in beam experiments. However, there is no evidence for the existence of metastable excited states of any atomic negative ion. The primary metastable state of the hydrogen atom is the 2s state. Sellin[17] and Jaecks, et al.,[18] have shown that an electric field of 100 V/cm reduces the lifetime of this state to about 10^{-8} sec. In the present apparatus the H atom beam passed through a field of about 1200 V/cm so that all 2s atoms were quenched before reaching the collision region. No direct evidence was obtained to show that metastable oxygen atoms were absent from the beam; however, in a recent investigation of a similar O atom source, Brink[20] was unable to detect any metastable atoms.

FIG. 1. Cross section of apparatus through negative-ion beam.

SNOW, RUNDEL, AND GEBALLE

Signals were shown to be linear with respect to variations in intensity of each of the two beams.

RESULTS

Cross sections for reactions A, B, and C are shown in Fig. 3. Also shown are the results of Bailey[1,19] for reactions A and B, and the results of Rutherford and Turner[2] for reaction A. The present relative measurements for reactions A to E were normalized to the absolute results of Bailey for reaction A in the energy region common to the three sets of measurements for reaction A (150 to 300 eV). The shape of the present cross section fits the data of Bailey significantly better than those of Rutherford and Turner. These authors put forth two possible reasons for the disagreement between themselves and Bailey. One is that since Bailey did not mass analyze his collision products, he may have included elastically scattered primary O^- ions, or O^- from the dissociative charge-transfer reaction $O^- + O_2 \rightarrow O + O^- + O$, whereas Rutherford and Turner used secondary mass analysis, and detected only O_2^-. The second possibility is that, due to increasing kinetic energy transfer to the collision products at lower primary energies, the collection efficiency of collision products in the Rutherford and Turner experiment fell off with decreasing energy, giving too low a cross section. The present measurement seems to favor the latter explanation, since the shape of the present results fits better onto Bailey's cross section, and since mass analysis of the collision products showed no indication of O^- formation even at the lowest primary energy. However, the region of energy overlap is not sufficient to draw more definite conclusions.
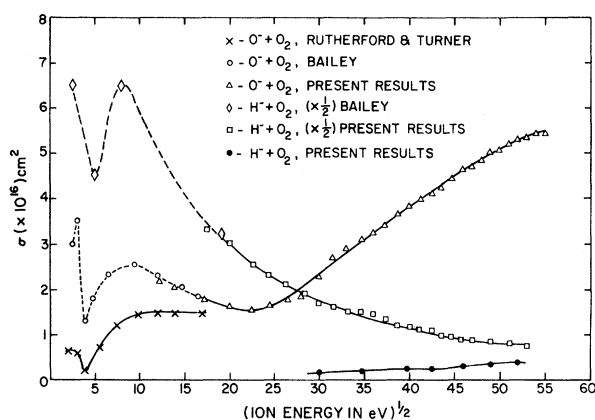
As mentioned above, the reaction products were mass analyzed in all cases except for O^- on H_2, for which the signals were too small to be detected after mass analysis. It is assumed that this collision proceeds by dissociative charge transfer since the formation of the weakly bound H_2^- molecular ion ($D \simeq 0.15$ eV), whose equilibrium internuclear separation is much larger than that of H_2, is unlikely in a two-body collision. No evidence was found for dissociative charge transfer in any of the other reactions studied.

The cross sections for reactions D and E are shown in Fig. 4, along with the results of Rutherford and Turner for reaction D. These cross sections decrease monotonically over the energy range covered in the present measurements.

The nonresonant charge-transfer cross sections involving atomic targets which have not previously been studied are shown in Figs. 5 and 6. These cross sections, and that for the resonant case, $O^- + O$, displayed in Fig. 7, are normalized to the measured cross section of Hummer, et al.,[4] for $H^- + H \rightarrow H + H^-$. The cross sections are plotted as $\sigma^{1/2}$ versus $\ln(v)$ to facilitate comparison with theory.

The possible systematic error in the measurement of all the cross sections except those involving NO_2 is estimated to be $\pm 30\%$. Difficulties in pressure gauge calibration for the chemically active NO_2 lead to an estimated error of $\pm 50\%$ for reactions D and E. The rms deviations of the data for typical points are indicated by the error bars.

DISCUSSION

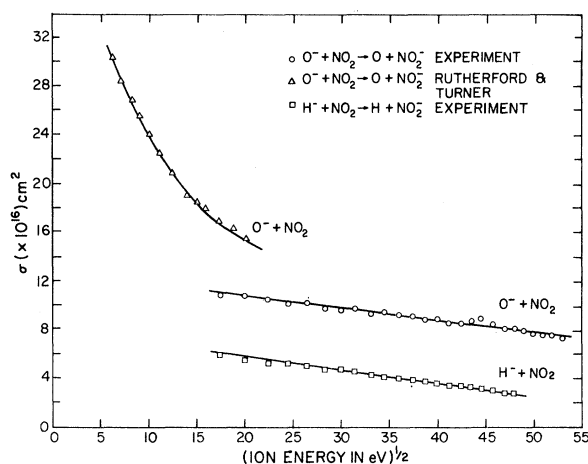### A. Detailed Balancing

The reaction

$$H^-(^1S) + O(^3P) \rightleftarrows H(^2S) + O^-(^2P)$$

FIG. 3. Experimental charge-transfer cross sections for $O^- + O_2$ ($\triangle$), $H^- + O_2$ ($\square$), and $O^- + H_2$ ($\bullet$). These data are normalized to Bailey's[1] $O^- + O_2$ ($\bigcirc$) cross section at 300 eV. $O^- + O_2$ (X) of Rutherford and Turner[2] and $H^- + O_2$ ($\Diamond$) of Bailey[19] are also plotted. Note that $H^- + O_2$ cross sections are multiplied by $\frac{1}{2}$.
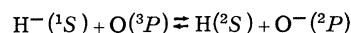
FIG. 4. Experimental charge-transfer cross sections for $O^- + NO_2$ ($\bigcirc$) and $H^- + NO_2$ ($\square$). $O^- + NO_2$ ($\triangle$) of Rutherford and Turner[2] is shown for comparison.

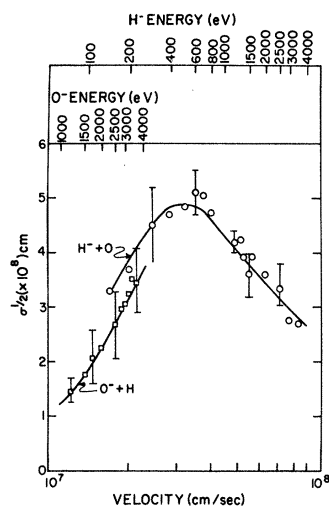FIG. 5. Experimental charge-transfer cross sections for $O^- + H$ (□) and $H^- + O$ (○). Error bars represent rms deviations of data.
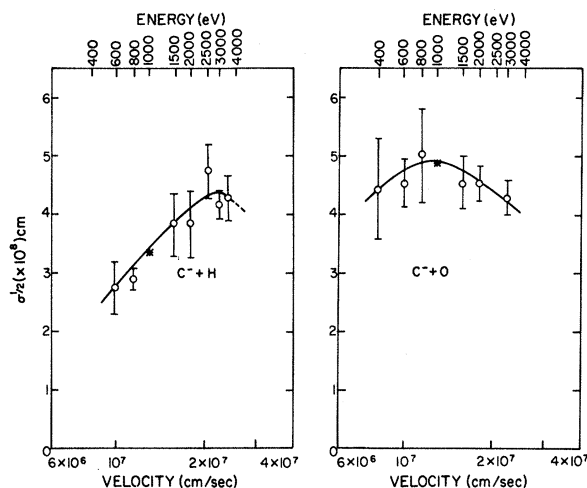

FIG. 6. Experimental charge-transfer cross sections for $C^- + H$ (A) and $C^- + O$ (B). Error bars represent rms deviations of data.

affords an opportunity to apply detailed balancing to a charge-transfer collision. The principle of detailed balancing states that the transition probability for a reaction is the same in both the forward and reverse directions.
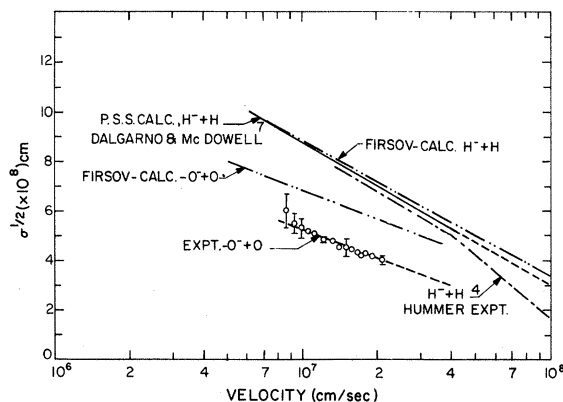

FIG. 7. Experimental charge-transfer cross section for the resonant reaction $O^- + O$ (○). Also shown are the theoretical cross sections of Firsov for this reaction and of Firsov[8] and Dalgarno and McDowell[7] for $H^- + H$. The experimental results of Hummer[4] for $H^- + H$ are also shown.

The ratio of the two cross sections can be computed readily if we assume (following Ref. 10, for example) that the collision can be treated in terms of a transition between two electronic states of the quasimolecule AB^+ having the two asymptotic states $(A^+ + B)$ and $(A + B^+)$. When A^+ and B collide, a number of states of AB^+ are formed and populated statistically, but only those states with identical symmetry to $A + B^+$ can produce charge transfer. The ratio of the cross sections in the forward (1) and backward (2) directions is equal to the inverse ratio of the number of possible final states, leading to reaction:

$$\sigma_1/\sigma_2 = f_2/f_1 .$$

The above reaction is well suited to test against the principle because the negative ions are expected to have no bound excited states, and the atoms are expected to be predominantly in the ground state. Following the Wigner-Witmer rules[21] it is possible to form two $^3\Pi$ states and one $^3\Sigma$ state from $H^-(^1S) + O(^3P)$ and two $^3\Pi$, two $^1\Pi$, one $^3\Sigma$, and one $^1\Sigma$ states from $O^-(^2P) + H(^2S)$. The ratio of final states is then, $f_2/f_1 = \frac{12}{9}$, so that

$$\sigma_1(H^- + O)/\sigma_2(O^- + H) = \frac{4}{3} .$$

In the region of overlap of the two curves (Fig. 5) the ratio of the experimental cross sections at equal velocities is 1.4 ± 0.4. This agreement lends experimental weight to the above assumptions about the states of the particles and the nature of the reaction.

B. Resonant Charge Transfer

In this section we make use of analyses which have been published earlier, but we present them in a way which emphasizes the limitations imposed by the approximations used in them.

The perturbed stationary-state approximation,[6] which describes the collision in terms of an expansion in the eigenfunctions of the quasimolecule formed during the collision, has been found useful in calculating charge-transfer cross sections. For the special case of resonant charge transfer ($\Delta E = 0$) the expansion can be limited to a single pair of gerade and ungerade eigenfunctions, making computations much simpler.

Ignoring the change in translational motion of the active electron, the probability of transfer in "slow" collisions is proportional to $\sin^2\xi(\rho)$ where

$$\xi(\rho) = \frac{1}{\hbar v} \int_\rho^\infty \frac{R[E^+(R) - E^-(R)]dr}{(R^2 - \rho^2)^{1/2}}, \tag{1}$$

and R is the internuclear separation, ρ is the impact parameter, and $E^+(R)$ and $E^-(R)$ are the potential energies of the gerade and ungerade states. The charge-transfer cross section is

$$\sigma = 2\pi \int_0^\infty \rho \sin^2\xi(\rho) d\rho . \tag{2}$$

The factor $\sin^2\xi(\rho)$ oscillates rapidly for small ρ and may be replaced by the average value of $\frac{1}{2}$. If ρ^* is the largest value of ρ for which $\sin^2\xi(\rho)$ equals $\frac{1}{2}$, then[6]

$$\sigma = \frac{1}{2}\pi(\rho^*)^2 + 2\pi \int_{\rho^*}^\infty \rho \sin^2\xi(\rho) d\rho . \tag{3}$$

A few relatively simple resonant charge-transfer collisions have been treated by this approximation using accurate (or exact) eigenergies in Eq. (1). The H⁻ + H calculation of Dalgarno and McDowell,[7] shown in Fig. 7, is one of these.

A number of more complicated resonance charge-transfer processes involving both positive and negative ions have been treated less accurately but with moderate success,[6] through the use of nodeless, spherically symmetric atomic orbitals to approximate the molecular wave functions.[8-11] The additional approximation

$$E^+(R) - E(R)^- = (2k/R)e^{-kR}, \tag{4}$$

where $k = (2I)^{1/2}$ and I is the binding energy of the electron, has also been used for s states. In this analysis the assumption is made that k is independent of ρ and that $k\rho$ is large. The resulting cross section is[7]

$$\sigma = \frac{1}{2}(\rho^*)^2[1 + \pi^2/8k\rho^* + O(1/k\rho^*)^2 + \cdots] . \tag{5}$$

However, the assumption $k\rho^* \gg 1$ was used in the expansion, so that in comparing theory and experiment at the present time one may use simply

$$\sigma = \frac{1}{2}\pi(\rho^*)^2 . \tag{6}$$

The condition $\sin^2\xi(\rho^*) = \frac{1}{2}$ which determines ρ^* becomes[8]

$$k\rho^* + \frac{1}{2}\ln(k\rho^*) + 1/8k\rho^* = \ln[(2\pi^3)^{1/2}k]/\hbar v. \tag{7}$$

The restriction that $k\rho^* \gg 1$ can be translated via this equation into an upper bound on the projectile velocity for which the theory is valid. When $k\rho^*$ is of the order of 1, the velocity, $v_{\lim}$ is of order $k/\hbar$;

$$v_{\lim} \simeq k/\hbar = (I)^{1/2}/13.6 \text{ a.u.} = 6\times10^7 \ I^{1/2} \text{ cm/sec}, \tag{8}$$

where I is the electron binding energy in electron volts. Since electron affinities are in general much smaller than ionization potentials, $v_{\lim}$ will be appreciably lower for negative ions than for positive ions. The limiting velocity for H⁻ + H by this criterion is about 5×10^7 cm/sec and for O⁻ + O about 9×10^7 cm/sec. The former limit is substantiated by the observation that the experimental cross section of Hummer et al. (see Fig. 7) begins to deviate from the calculated cross section of Dalgarno and McDowell in the neighborhood of 5×10^7 cm/sec. The velocity range for the measurements of O⁻ + O in this experiment is well below the estimated limiting velocity.

Utilizing Eqs. (6) and (7), the formula for the cross section may be written in a form

$$\sigma^{1/2} = A - B\ln v \tag{9}$$

which has long been used to extrapolate charge-transfer cross sections to high velocities. The slope, B, is equal to k^{-1} [from Eq. (7)], and therefore depends only on the ionization potential of the ion.

The O⁻ + O charge-transfer cross section measured in the present work is compared in Fig. 7 to that calculated from Firsov's theory. The slope of the experimental curve agrees well with this theory, but the magnitude is considerably lower. The comparison between theory and experiment for this case is complicated by the circumstance that the theory assumes spherically symmetric wave functions, whereas the ground states of O⁻ and O are both p states, which may contribute to the difference in magnitude between the theoretical and experimental cross sections. Nevertheless, the good agreement of the slope of $\sigma^{1/2}$ indicates that this feature of the theory is not very sensitive to details of the approximations used.

C. Nonresonant Charge Transfer

The two-state approximation used by Rapp and Francis[10] in calculating nonresonant charge-

transfer cross sections for positive ions gives reasonable agreement with experimental data. The assumptions are such that the theory should give best results when all particles are in s states and when ΔE is small. This latter condition is fulfilled better in negative-ion reactions than in most positive-ion reactions. Direct application of the theory to negative-ion reactions, however, gives cross sections which are about five times larger than the experimental data of Figs. 5 and 6.

These data are replotted in Fig. 8 with appropriate account taken of the statistical weight factors[10] as follows:

(a) $H^-(^1S)+O(^3P) \rightarrow H(^2S)+O^-(^2P)$, $f=\frac{2}{3}$;
(b) $O^-(^2P)+H(^2S) \rightarrow O(^3P)+H^-(^1S)$, $f=\frac{1}{2}$;
(c) $C^-(^4S)+H(^2S) \rightarrow C(^3P)+H^-(^1S)$, $f=\frac{3}{8}$;
(d) $C^-(^4S)+O(^3P) \rightarrow C(^3P)+O^-(^2P)$, $f=\frac{1}{2}$.

The cross sections for reactions a and b are coincident when each is multiplied by its statistical weight factor as we have seen earlier. It will be
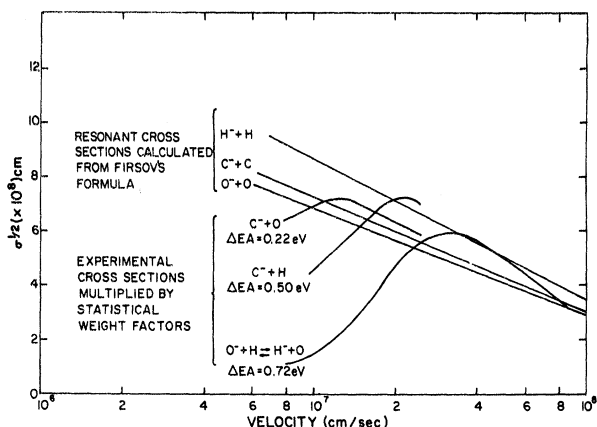

FIG. 8. Comparison of measured nonresonant charge-transfer cross sections with calculated values. The experimental values have been multiplied by statistical weight ratios given in the text.

seen from Fig. 8 that the general shape of the curves tends to follow the Rapp and Francis pre-computed by using an average (whose nature is not clearly specified) of the two ionization potentials involved. In Fig. 8 the three pertinent resonant curves, calculated by Firsov's formula, have been plotted with the experimental results. The "resonant curve" appropriate to the C^-+O reaction should fall somewhere between the O^-+O and C^-+C curves, and similarly for the other two reactions.

dictions: i.e., the nonresonant curves rise with increasing velocity, join a certain "resonant curve" at a velocity characteristic of ΔE for the reaction, and fall off at higher velocities along the "resonant curve." According to Rapp and Francis[10] the appropriate "resonant curve" is one

D. Detachment

The above discussion of charge transfer has neglected the possibility that the electron can become detached into the continuum during the collision. This channel for the reaction tends to be more significant for small binding energies of the electron and so should be an important consideration for the theory of negative-ion charge transfer.

Firsov,[8] and Smirnov and Firsov,[11] have calculated the detachment cross section by methods similar to those used for the charge-transfer calculations and find the cross section to be of the order of $1/(k\rho^*)$.[2] Since the charge-transfer theory outlined above neglects terms of this order, the result of Smirnov and Firsov suggests that detachment, although not correctly allowed for in the present theory of charge transfer, will be negligible compared to resonant charge transfer at velocities less than v_{lim}. The detachment cross section has been measured[4] for H^-+H and is indeed negligible compared to the charge-transfer cross section below v_{lim}. Therefore the theoretical results presented in Fig. 7 for O^-+O probably do not need an appreciable correction for detachment.

[1]T. L. Bailey, in Proceedings of the Second International Conference of the Physics of Electronic and Atomic Collisions (University of Colorado, Press, Boulder, Colo., 1961), p. 54.

[2]J. A. Rutherford and B. R. Turner, Symposium on the Physics and Chemistry of the Lower Atmosphere (Joint Institute for Laboratory Astrophysics, University of Colorado, Boulder, Colo., 1966), p. 16; J. Geophys. Res. 72, 3795 (1967).

[3]J. F. Paulson, Symposium on the Physics and Chemistry of the Lower Atmosphere (Joint Institute for Laboratory

Astrophysics, University of Colorado, Boulder, Colo.,
1966), p. 18.

[4]D. G. Hummer, R. F. Stebbings, W. L. Fite, and
L. M. Branscomb, Phys. Rev. 119, 668, (1960).

[5]Yu F. Bydin, Zh. Eksperim. i Teor. Fiz. 46, 1612
(1964) [English transl.: Soviet Physics — JETP 19,
1091 (1964)].

[6]D. R. Bates, Atomic and Molecular Processes
(Academic Press, Inc., New York, 1962).

[7]A. Dalgarno, and M. R. C. McDowell, Proc. Phys.
Soc. (London) A69, 615, (1956).

[8]O. B. Firsov, Soviet Physics — JETP 21, 1001 (1951).
See also Ref. 6, p. 708.

[9]E. F. Gurnee and J. L. Magee, J. Chem. Phys. 26,
1237 (1957).

[10]D. Rapp and W. E. Francis, J. Chem. Phys. 33, 1230
(1960).

[11]B. M. Smirnov, and O. B. Firsov, Zh. Eksperim. i
Teor. Fiz. 47, 232 (1965), [English transl.: Soviet
Physics — JETP 20, 156 (1965)].

[12]W. L. Fite and R. T. Brackmann, Phys. Rev. 112,
1141–1151 (1958).

[13]L. M. Branscomb, Advances in Electronics and
Electron Physics (Academic Press, Inc., New York,
1957), Vol. 9, p. 51.

[14]C. F. Giese, Rev. Sci. Instr. 30, 260 (1959).

[15]J. T. Tate and P. T. Smith, Phys. Rev. 39, 270
(1932).

[16]W. L. Fite and R. T. Brackman, Phys. Rev. 113,
815 (1959).

[17]I. A. Sellin, Phys. Rev. 136, A1245 (1964).

[18]D. H. Jaecks, B. Van Zyl, and R. Geballe, Phys.
Rev. 137, A340 (1965).

[19]T. L. Bailey, in Proceedings of the New Orleans 1962
Conference on Mass Spectrometry, p. 333. Bailey has
published only the points of the H⁻ + O₂ cross section
shown in Fig. 3. The dashed curve has been drawn
through these points according to Bailey's description of
the behavior of the cross section.

[20]G. O. Brink, Symposium on Physics and Chemistry of
the Lower Atmosphere Joint Institute for Laboratory
Astrophysics, Boulder, Colo., 1966.

[21]G. Herzberg, Spectra of Diatomic Molecules (D. Van
Nostrand Co., Inc., Princeton, New Jersey, 1950),
2nd ed.

Measurement of Transport Properties of Ions in Gases; Results for K⁺ Ions in N₂[†][‡]

J. T. Moseley,[*] I. R. Gatland, D. W. Martin, and E. W. McDaniel
School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332
(Received 2 October 1968)

A solution is developed to the transport equation describing the drift, diffusion, and reaction
of an ion swarm moving under the influence of a uniform electric field E in a gas of uniform
number density N. An easily applied analytical expression is obtained for a particular type
of source input of the ions under the assumption that the only reaction occurring is one which
results in the depletion of the ion species under consideration. Data obtained with a drift-
tube mass spectrometer on K⁺ ions in N₂ at low E/N, where the parameters in the solution
can be determined from other considerations, are presented to show that the solution does
closely describe the drifting ion swarm. The solution is then applied to K⁺ data obtained at
higher E/N to determine the mobility, the longitudinal diffusion coefficient and the transverse
diffusion coefficient for K⁺ in N₂, up to an E/N of 350×10^{-17} V cm². The zero-field reduced
mobility of K⁺ in N₂ is determined to be 2.55 cm²/V sec, in excellent agreement with the non-
mass analyzed data of other experiments and with the Langevin polarization limit prediction
of 2.60 cm²/V sec. Both diffusion coefficients are found to be in agreement with the value
predicted from the Einstein relation at low E/N, and to increase as E/N is increased.

I. INTRODUCTION

It has been stated for many years that drift-tube
experiments can provide information about the drift
velocities, diffusion coefficients, and ion-molecule
reaction rates of ions in gases. However, the vast
majority of such experiments to date have yielded
only drift-velocity results. Except for measure-
ments reported by this laboratory,[1] there apparent-
ly exist no determinations of the coefficient for
diffusion parallel to the applied electric field (the
longitudinal diffusion coefficient) and only a few
measurements[2-4] of the coefficient for diffusion
perpendicular to the applied electric field (the
transverse coefficient). Approximately 16 mea-
surements of reaction rates have been reported[5]