

## Low-Energy (1- to 100-eV) Charge-Transfer Cross-Section Measurements for Noble-Gas-Ion Collisions with Gases

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(Received 21 August 1967; revised manuscript received 5 January 1968)

Cross sections for charge transfer between positive ions and atoms and molecules have been measured in the low-energy range (1 to 100 eV), using direct-current techniques for slow-product-ion detection. The electrode configuration adopted is designed to discriminate against elastically scattered primary particles. Resonant symmetric systems such as  $\text{He}^+ + \text{He}$  and  $\text{Ar}^+ + \text{Ar}$  and near-resonant pairs like  $\text{He}^+ + \text{N}_2$  and  $\text{He}^+ + \text{O}_2$ , respectively, have been investigated. Cross-section functions for the symmetric cases conform to an expression of the form  $\sigma^{1/2} = a - b \ln E$ . Other reactions studied include  $\text{Ar}^+$  in  $\text{N}_2$  and  $\text{H}_2$  and the inverse reactions  $\text{Ar}^+ + \text{He}$  and  $\text{He}^+ + \text{Ar}$ , respectively. Results are compared with existing literature values.

### I. INTRODUCTION

**E**XPERIMENTAL investigation of interactions between ions and atoms or molecules at low translational energies of the ions becomes generally difficult because of such effects as space-charge spreading of the beam due to mutual repulsion of particles, influence of stray magnetic and electrostatic fields, and, above all, low ion-current densities.<sup>1</sup>

In this paper we show that the method usually adopted for the study of low-energy ion impact on surfaces can be usefully adopted for the investigation of gas-phase collisions as well, and ion currents available at energies of the order of few eV are large enough to warrant the use of conventional direct-current techniques for these studies.

The results of several charge-transfer cross-section measurements made in the ion-energy range 1 eV to 100 eV for ion-atom and ion-molecule collisions are presented. These measurements have been made with a relatively smaller spread in the kinetic energy of the interacting ion beam than generally available for such studies. The systems investigated include symmetric resonant reactions, accidentally resonant collisions, and cases where the intrinsic energy balance for the reaction is either negative or positive.

The ions are produced in an electron bombardment ion source,<sup>2</sup> extracted, accelerated to 200-eV energy, mass selected, and then collimated to enter an equipotential interaction region. The required interaction energy is set by keeping the entire interaction chamber at a suitable potential above ground. The difference in potential between the plasma in which the ions are produced in the ion source and the floating potential of the interaction chamber gives the ion energy. The full width

of the ion energy distribution, at half maximum, measured with a parallel plate analyzer,<sup>3</sup> is 0.4 eV.

### II. APPARATUS

#### Electrode Structure

A schematic diagram of the electrode structure is given in Fig. 1. This is a modification of the arrangement used by Bailey and Mahadevan<sup>4</sup> to measure charge-transfer and electron-detachment cross sections for negative ions colliding with neutral gases. The interactions take place in an equipotential region enclosed by the grid  $G_1$ , collector  $C$ , and the entrance aperture assembly 5, all maintained at the bias potential of the collision chamber.

Following a 2-mm entrance aperture 1, a set of apertures on parallel plates 2, 3, and 4 collimate the ion beam. The aperture 5 defining the beam entrance into the collision region is also 2 mm in diameter. Electrode 1

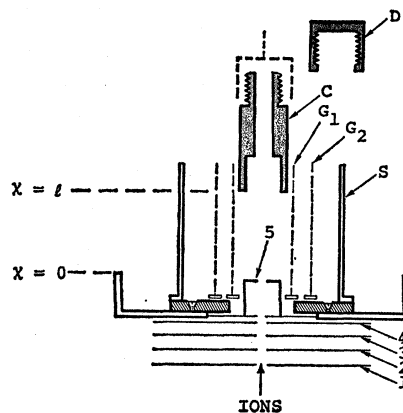


FIG. 1. Schematic of the electrode structure.

<sup>1</sup> W. L. Fite, R. T. Brackmann, and W. R. Snow, *Phys. Rev.* **112**, 1161 (1958).

<sup>2</sup> G. D. Magnuson, C. E. Carlston, P. Mahadevan, and A. R. Comeaux, *Rev. Sci. Instr.* **37**, 866 (1966).

<sup>3</sup> G. D. Yarnold and H. C. Bolton, *J. Sci. Instr.* **26**, 38 (1949).

<sup>4</sup> T. L. Bailey and P. Mahadevan, in 13th Gaseous Electronics Conference, Monterey, California, 1960 (unpublished).

was always maintained at ground potential and 5 at bias potential. At low ion energies, it was useful to keep the plates 2, 3, and 4 at various potentials different from 1 or 5. The aperture sizes, spacings, or potentials on these electrodes, however, were not critical.

An extraction potential, negative with respect to the bias, is applied on grid  $G_2$  to draw out the slow ions formed by charge transfer in the collision path interval  $0 \leq x \leq l$  essentially at right angles to the primary ion direction, and any primary ions elastically scattered at large angles. The length  $l$  is taken as the effective scattering length for all processes which give slow positive ions. If now, the outer cylinder  $S$  is maintained suitably positive with respect to bias, the slow charge-transfer ions would be repelled back to  $G_2$  by  $S$ , while the more energetic elastically scattered ions would still be collected on  $S$ . Secondary electrons released from  $G_2$  by the slow ions would be collected on  $G_1$  since the potential gradient between  $G_2$  and  $G_1$  is much larger than that between  $G_2$  and  $S$ . It should be possible to draw out all scattered particles (elastic and inelastic collisions products) to the outer cylinder  $S$  by making it sufficiently negative. However, since the purpose of this electrode design was simply to separate slow charge-transfer ions from elastically scattered primary particles, total scattering cross sections were not measured. Also, the angular resolution of the apparatus was made deliberately poor to miss most of the elastic scattering events.

#### Derivation of a Collision Cross Section from Current Measurements

The following brief analysis explains our method of reducing the measured values of current to the various electrodes to a collision cross section for charge transfer.

With reference to Fig. 1, let  $\Delta I^+ = I_0^+ - I_l^+$  = total attenuation of primary ion current due to charge transfer and elastic scattering in the collision interval  $0 \leq x \leq l$ , where  $I_0^+$  and  $I_l^+$  are the respective primary ion currents at  $x=0$  and  $x=l$ . (Processes such as ionization and electron stripping are unlikely at the low ion kinetic energy range under investigation here.) Then

$$\Delta I^+ = \delta I_{el}^+ + I_{slow}^+, \quad (1)$$

where  $\delta I_{el}^+$  = current loss from the primary ion beam due to elastic scattering through angles large enough to miss the collector  $C$ , and  $I_{slow}^+$  = total slow ion production by charge transfer in the interval  $x=0$  to  $l$ .

If the geometrical opacities of the grids  $G_1$  and  $G_2$  are  $f_1$  and  $f_2$ , respectively,

$$I_{G1}^+ = f_1 [I_{slow}^+ + \delta I_{el}^+] - I_e^-, \quad (2)$$

where  $I_e^-$  = secondary electron current from  $G_2$  due to positive ions intercepted by  $G_2$ :

$$I_{G2}^+ = I_{slow}^+ (1 - f_1) + f_2 \delta I_{el}^+ + I_e^- \quad (3)$$

Adding Eqs. (2) and (3) we obtain

$$I_{G2}^+ + I_{G1}^+ = I_{slow}^+ + (f_2 + f_1) \delta I_{el}^+. \quad (4)$$

Even at the highest operating pressure in the target gas chamber  $I_{G1}^+$  was observed to be negligibly small, less than 1% of  $I_{G2}^+$  for all ion energies and potential configurations. It therefore seems justified to neglect  $I_{G1}^+$  and Eq. (4) becomes simply

$$I_{G2}^+ = I_{slow}^+ + (f_2 + f_1) \delta I_{el}^+. \quad (5)$$

The geometrical opacities  $f_1$  and  $f_2$  were 2.8% and 1.7%, respectively. The elastically scattered primary ion current  $I_s^+ = \delta I_{el}^+ (1 - f_1 - f_2) = 0.955 \delta I_{el}^+$  arriving at  $S$  was observed to be never more than 5% of the total slow ion current collected on  $G_2$  and quite often was immeasurably small. Thus, since  $I_s^+ < 0.05 I_{slow}^+$ , the second term on the right hand side of Eq. (5) is less than  $0.00236 I_{G2}^+$ , and can quite safely be neglected. Therefore, we may take as the slow ion current produced by charge transfer the measured grid current  $I_{G2}^+$ .

Using the standard derivation for the cross section,

$$\sigma = \frac{1}{nl} \ln \left( \frac{I_0^+}{I_0^+ - I_{slow}^+} \right), \quad (6)$$

where  $n$  is the number density of the gas in the charge-transfer chamber and  $l$  is the path length (see Fig. 1). Since  $I_0^+ = I_l^+ + I_{slow}^+ + \delta I_{el}^+$ ,

$$\sigma = \frac{1}{nl} \ln \left( 1 + \frac{I_{slow}^+}{I_l^+ + \delta I_{el}^+} \right), \quad (7)$$

or, using the measured values of the currents,

$$\sigma = \frac{1}{nl} \ln \left[ 1 + \frac{I_{G2}^+}{I_l^+ + I_s^+ / 0.955} \right]. \quad (8)$$

As mentioned before,  $I_s^+$  was observed to be small and represents only a small correction to the measured ion current  $I_l^+$ .

In view of the fact that the current to  $G_1$  was always negligibly small, an alternative configuration with the grids  $G_1$  and  $G_2$  tied together electrically was tried. Currents arriving at this combination were measured, with  $S$  maintained suitably positive in potential with respect to bias. Cross checks of several data points were made with this modification. This arrangement is very similar to that adopted by Cramer and Simons<sup>5</sup> except for the angular resolution, which is designed to be poor here.

The primary ion collector  $CD$  was designed to be an effective secondary electron suppressor. Electrode  $C$  consisted of a  $\frac{5}{8}$ -in.-diam cylinder with a  $\frac{1}{8}$ -in.-diam hole of length 1 in. See Fig. 1. With a cap  $D$  as shown in

<sup>5</sup> W. H. Cramer and J. H. Simons, J. Chem. Phys. **26**, 1272 (1957).

Fig. 1, insulated from  $C$ , about 90% of the primary ion current was collected on the cap and the remainder on  $C$ . In order to investigate the loss, if any, of secondary electrons due to primary ions arriving at the electrodes, the currents to the cap  $D$  and to  $C$  were measured as a function of suppressing voltage (positive) on the cap. The results are shown in Fig. 2. The total current to the cap and  $C$  was found to be independent of the suppression voltage on the cap. This indicates efficient trapping of secondary electrons by the collector assembly. The cap was, therefore, screwed directly on  $C$  for the current measurements.

The current collection characteristics of the grids  $G_1$  and  $G_2$  are shown for two systems and ion kinetic energies in Fig. 3. The current-saturation curves have been obtained for both modes of operation of the electrode geometry, namely (1) with a draw out potential on  $G_2$  with  $G_1$  maintained at bias voltage and (2) with  $G_1$  and  $G_2$  tied together at bias potential. Cross checks of the experimental data have also been made using these two modes of operation for the various systems studied.

The excellent agreement between data obtained under the two modes of operation, confirms our assumption that secondary current effects on  $G_2$  and  $G_1$  are negligible.

Target gas pressure was measured by a Veeco RG-75 ionization gauge, operated normally. The following values of sensitivity were used to get the absolute target particle density from the ionization gauge readings.<sup>6-8</sup>

He	Ar	N <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub>
0.157	1.21	1.00	1.13	0.298

The cross sections, as presented in this paper, are

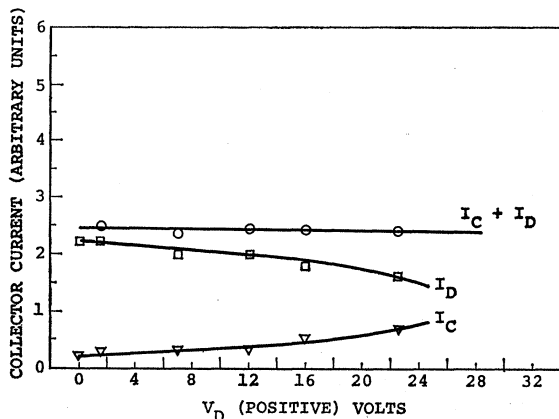
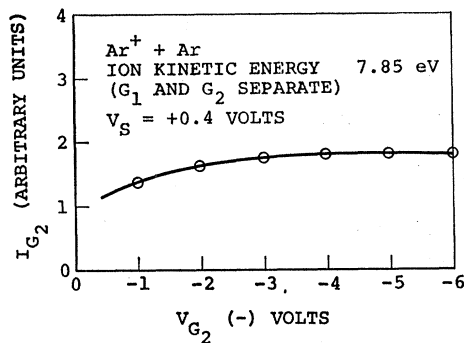


Fig. 2. Secondary electron suppression characteristics of the ion-collector assembly, CD.

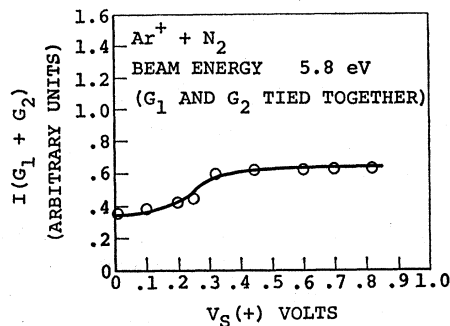
<sup>6</sup> J. W. McGowan and L. Kerwin, Can. J. Phys. 39, 373 (1961).

<sup>7</sup> S. N. Ghosh and B. N. Srivastava, Can. J. Phys. 39, 373 (1961).

<sup>8</sup> N. G. Utterback and T. Griffith, Jr., Rev. Sci. Instr. 37, 866 (1966).



(a)



(b)

Fig. 3. (a) Ion current collection on  $G_2$  as a function of draw-out potential on  $G_2$ ; (b) current saturation properties of the two grids  $G_1$  and  $G_2$ , electrically tied together, with a repelling voltage on  $S$ .

believed to have a  $\pm 20\%$  uncertainty due mainly to variation of the total primary ion current during the measurement.

All electrode surfaces between the analyzing magnet and the interaction chamber were painted with a colloidal suspension of graphite in alcohol to provide a highly conducting surface and thus minimize beam instability due to stray charge build up.

The kinetic energy of the ions was determined by a retarding potential analysis of the current reaching the collector assembly CD. The potential difference between the ion source and the ion collector at which the ion current is reduced to half its original value is taken as the ion energy. All voltage measurements were made with a vacuum tube voltmeter.

### III. RESULTS

#### Symmetric Resonant Reactions, He<sup>+</sup>+He and Ar<sup>+</sup>+Ar

These two systems were investigated primarily for comparison with other experimental data at higher ion energies and to extend the existing data to lower energies. Our earlier data<sup>9</sup> for He<sup>+</sup>+He<sup>9</sup> was rechecked again to detect any possible contribution to the measured cross section from elastic scattering of the prim-

<sup>9</sup> P. Mahadevan, C. E. Carlston, and G. D. Magnuson, Bull. Am. Phys. Soc. 11, 505 (1966).

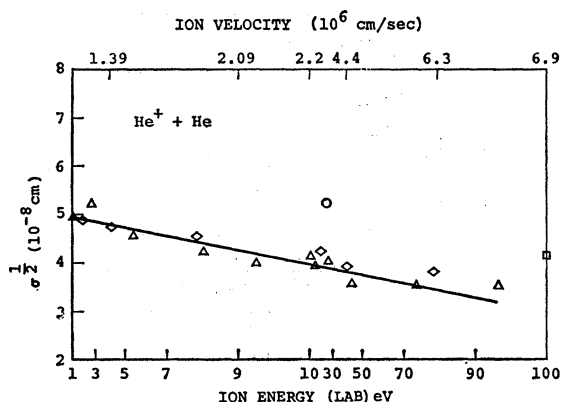


FIG. 4. Square root ( $\sigma^{1/2}$ ) of charge-transfer cross sections for  $\text{He}^+ + \text{He}$  versus ion energy and ion velocity.  $\diamond$  Cramer and Simons, Ref. 5;  $\circ$  Moisewitch, Ref. 13;  $\square$  Gilbody and Hasted, Ref. 29;  $\nabla$  Potter, Ref. 12;  $\triangle$  present results. A cross-section measured at 0.55 eV energy ( $\sigma^{1/2} = 5.8 \text{ Cm}$ ) is consistent with the slope of the curve shown here.

ary ions. This became necessary in the light of Aberth and Lorentz's<sup>10</sup> measurement of differential elastic scattering for this system.

Using a parallel plate collection system, the smallest half angle subtended by the slow ion collector electrode on the beam axis was varied from  $4.5^\circ$  to  $62.5^\circ$ . The measured cross section at a given ion energy appeared to decrease as the collection angle increased almost to an angle of  $40^\circ$ , thus confirming our suspicion that the earlier measurements gave too large values for the charge-transfer cross section. This electrode arrangement, however, could not be used in practice since the signal became too small a fraction of the total slow ion production. The electrode setup, described earlier in this paper, was, therefore, adopted to get the benefits of

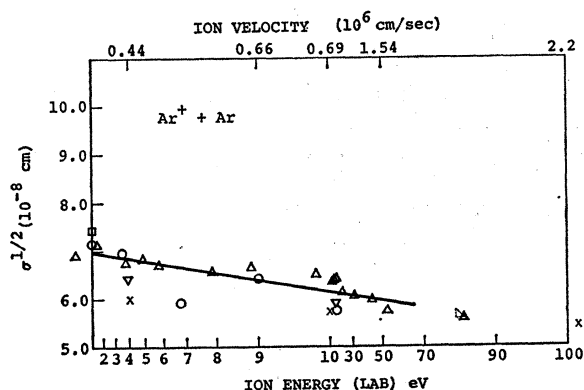


FIG. 5. Square root ( $\sigma^{1/2}$ ) of charge-transfer cross sections for  $\text{Ar}^+ + \text{Ar}$  versus ion energy, ion velocity.  $\circ$  Nichols and Witteborn, Ref. 14;  $\nabla$  Rapp and Francis, Ref. 11;  $\square$  B. Zeigler, *z. Physik* **136**, 108 (1953); L. J. A. Dillon *et al.*, *J. Chem. Phys.* **23**, 776 (1955);  $\triangle$  present results;  $\times$  R. H. Neynaber *et al.*, *Phys. Rev.* **157**, 101 (1967). One cross section measurement at 0.98 eV energy is shown on the left of the axis.

<sup>10</sup> D. C. Lorentz and W. Aberth, *Phys. Rev.* **139**, 1017 (1965).

long collection path length and discrimination against spurious currents.

The results are shown in Figs. 4 and 5. The data conform to the form

$$\sigma^{1/2} = a - b \ln E,$$

where  $\sigma$  = cross section in units of  $10^{-16} \text{ cm}^2$ ,  $E$  = kinetic energy of the ions in eV, and  $a$  and  $b$  are constants. The cross-section function for He could be represented by the expression  $\sigma^{1/2} = 5.5 - 0.58 \ln E$ . The agreement is better than 10% over the energy range 75 eV to 1 eV. The corresponding expression for Ar is given as  $\sigma^{1/2} = 6.9 - 0.25 \ln E$ . The agreement is better than 3% over the energy range 50 to 2.5 eV.

Our data for He are in almost exact agreement with the calculated values of Rapp and Francis<sup>11</sup> and are reasonably close to the experimental values of Cramer and Simons<sup>5</sup> and Potter.<sup>12</sup> The largest discrepancy exists between our values and those of Moisewitch.<sup>13</sup>

In the case of argon, the more recent measurement made by Nichols and Witteborn<sup>14</sup> gives values that agree closely with us at energies below about 5 eV. Their cross-section function tends to drop off much faster than ours at higher energies.

#### $\text{He}^+ + \text{N}_2$

The total cross section for electron capture by  $\text{He}^+$  in collision with  $\text{N}_2$  has been measured over the energy range 1 to 150 eV. The results are shown in Fig. 6. The present results, especially at the higher ion velocities, are lower than the earlier values. With the previous electrode arrangement, we were collecting a small frac-

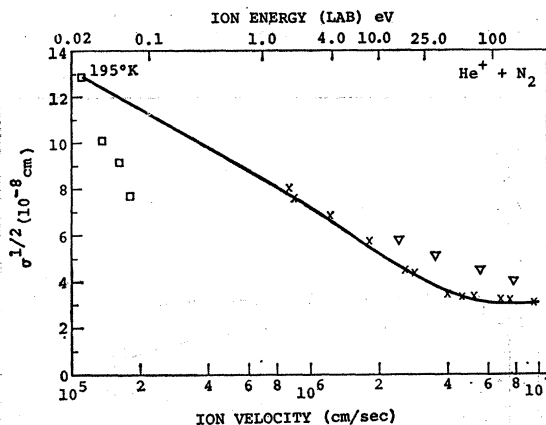


FIG. 6. Square root ( $\sigma^{1/2}$ ) of cross sections for charge neutralization of  $\text{He}^+$  in  $\text{N}_2$  versus ion velocity.  $\times$  present results;  $\triangle$  Stebbings *et al.*, Ref. (20);  $\square$  Sayers and Smith, Ref. 15. The data points correspond to temperatures 195, 293, 408, and 503°K, respectively.

<sup>11</sup> D. Rapp and W. E. Francis, *J. Chem. Phys.* **37**, 2631 (1962).

<sup>12</sup> R. F. Potter, *J. Chem. Phys.* **22**, 974 (1954).

<sup>13</sup> B. L. Moisewitch, *Proc. Roy. Soc. (London)* **A69**, b53 (1956).

<sup>14</sup> B. J. Nichols and F. C. Witteborn, Report No. NASA TN D-3265, 1966 (unpublished).

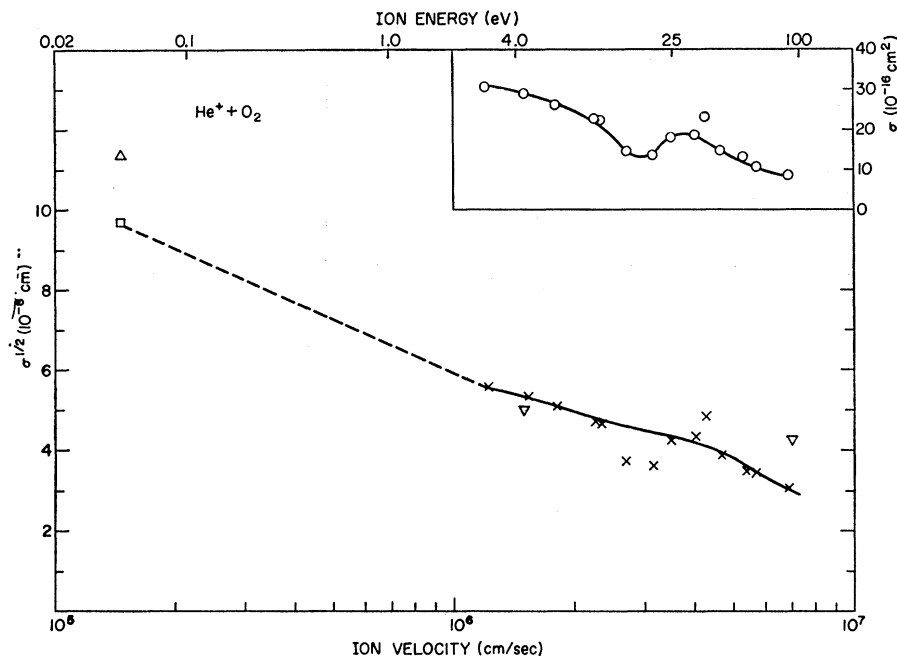


Fig. 7. Square root ( $\sigma^{1/2}$ ) of total charge-transfer cross sections for  $\text{He}^+$  in  $\text{O}_2$  versus ion velocity.  $\times$  present results;  $\Delta$  Stebbings *et al.*, Ref. 20;  $\square$  Sayers and Smith, Ref. 15 temp of 420°K; Fehsenfeld *et al.*, Ref. 17. Insert shows the variation of the cross section ( $10^{-16} \text{ cm}^2$ ) with ion velocity, indicating an apparent maximum at a lab energy of about 30 eV.

tion of elastically scattered primary ions also with the slow ion signal. The smaller cross sections now being reported are, therefore, to be expected since the new electrode geometry discriminates against elastically scattered primary ions. However, since the electrode geometry discriminates against product ions that have acquired kinetic energy, our results might be too low at these higher energies.

Interpolation to Sayers's and Smith's<sup>15</sup> value at 196°K appears justified. The higher temperature data from afterglow measurements by Sayers and Smith tend to drop off much faster than the interpolation shown here.

With the present experimental setup, it is not possible for us to mass analyze the productions. However, in the light of recent results of Inn<sup>16</sup> and others, it seems reasonable to conclude that the major reaction is an accidental near-resonant charge-transfer process, followed by predissociation to yield atomic ions of nitrogen. There appears to be linear dependence of  $\sigma^{1/2}$  on  $\ln v$ , at lower velocities, which is characteristic of accidental resonance charge transfer.<sup>17</sup>

#### $\text{He}^+ + \text{O}_2$

Figure 7 shows the variation of  $\sigma^{1/2}$  with velocity for the system  $\text{He}^+$  and  $\text{O}_2$ . Some ion-energy values are given at the top of the graph. The insert is a plot of  $\sigma$  (note the scale at the right) versus velocity and is shown to point out an apparent maximum occurring at about 30-eV ion energy. The variation in absolute values of the cross section, around the observed maximum, is larger

<sup>15</sup> J. Sayers and D. Smith, *Discussions Faraday Soc.* **37**, 167 (1964).

<sup>16</sup> E. C. Y. Inn, *Planet. Space Sci.* **15**, 19 (1967).

<sup>17</sup> W. L. Fite *et al.*, *Proc. Roy. Soc. (London)* **A268**, 527 (1962).

than the scatter in the data. The absence of such structure in other measurements is not enough reason to disbelieve our data since we have measured these cross sections at much smaller energy intervals than others. An energy defect of order 0.2 eV could account for the observed maximum on the basis of the adiabatic theory. However, we are unable to postulate a specific mechanism for the same at present.

Interpolation to Sayers's and Smith's<sup>15</sup> value at 420°K seems justified.

Fehsenfeld *et al.*<sup>18</sup> obtain a larger value, even for the partial cross section for the production of  $\text{O}^+$  ions. This is due possibly to the fact that they make no correction for the production of  $\text{O}^+$  ions by Penning ionization of  $\text{O}_2$  by He metastable atoms. The relative ratio of production of  $\text{O}_2^+$  and  $\text{O}^+$  by thermal energy  $\text{He}^M$  impact on  $\text{O}_2$  is given as 3:1 by Muschlitz and Weiss.<sup>19</sup>

Since the product ions are not mass analyzed, it is not possible to say whether an intermediate complex ion  $(\text{HeO})^+$  is formed in the reaction, as suggested by Moran and Friedman.<sup>20</sup> The discrepancy between our data at higher energies and those of Stebbings's<sup>21</sup> persists as for the system  $\text{He}^+ + \text{N}_2$ .

#### $\text{He}^+ + \text{Ar}$

This reaction was studied down to a low-energy limit of order 25 eV only. The measured cross sections tend to

<sup>18</sup> F. C. Fehsenfeld *et al.*, *J. Chem. Phys.* **44**, 4087 (1966).

<sup>19</sup> E. E. Muschlitz, Jr. and M. J. Weiss, in *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland Publishing Co., Amsterdam, 1964), p. 1073.

<sup>20</sup> T. F. Moran and L. Friedman, *J. Geophys. Res.* **70**, 4992 (1965).

<sup>21</sup> R. F. Stebbings, J. A. Rutherford and B. R. Turner, *Planet. Space Sci.* **13**, 1125 (1965).

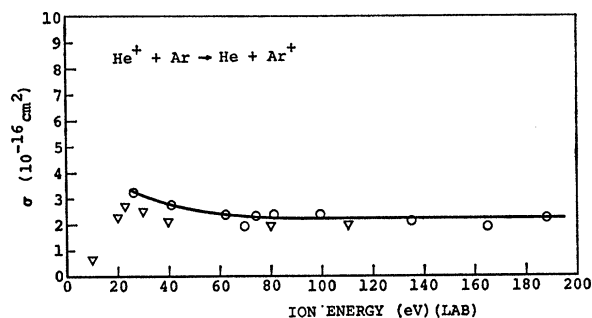


Fig. 8.  $\text{He}^+ + \text{Ar}$ .  $\circ$  present results;  $\nabla$  optical excitation data (200–1200 Å) of Lipeles, *et al.*, Ref. 21.

increase slightly towards lower energies as shown in Fig. 8. On comparison with the optical-excitation studies of Lipeles *et al.*,<sup>22</sup> we find almost one to one correspondence between our values for charge-transfer and the apparent cross section for photon emission in the wavelength range 200–1200 Å.

The similarity suggests the possibility that the processes studied in the two cases are the same, namely the production of excited slow ions in an endothermic process.

If Lipeles's cross-section curve is extrapolated down to threshold, we get a kinetic energy minimum for optical excitation of approximately 5 eV in the laboratory system. In the center-of-mass system, this is equivalent to 4.54 eV. This should equal the intrinsic energy defect at threshold. The optical transition in the Ar II spectrum could possibly be  $\text{Ar}^+ (3s^2 3p^6 - 2S_{1/2}) \rightarrow \text{Ar}^+ (3s^2 3p^6) + h\nu$  (919 Å). The net energy defect for this transition = 4.63 eV, reasonably close to the estimated value from threshold. Lipeles *et al.* were unable to resolve the emission lines in the ultraviolet region.

It should be pointed out that Van Eck, De Heer, and Kistemaker<sup>23</sup> have been able to resolve the 919 Å line in the optical emission spectrum and observe the same general shape for the cross-section function. The cross-section maximum, however, is observed at an ion kinetic

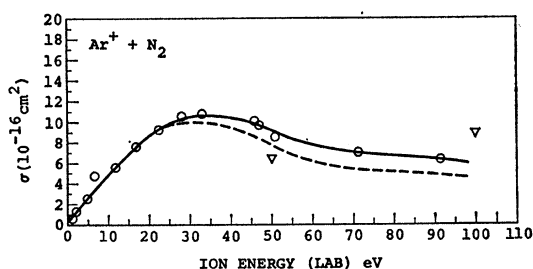


Fig. 9.  $\text{Ar}^+ + \text{N}_2$ .  $\circ$  present results; dashed line: cross section for the production of  $\text{N}_2^+$  only, obtained by subtraction Ref. 23;  $\nabla$  R. C. Amme and H. C. Haydon, *J. Chem. Phys.* **42**, 2011 (1965).

<sup>22</sup> M. Lipeles, R. Novick, and N. Tolk, *Phys. Rev. Letters* **15**, 815 (1965).

<sup>23</sup> J. Van Eck, F. J. De Heer, and J. Kistemaker, *Phys. Rev.* **130**, 656 (1963).

energy of 9 keV, and this maximum could be accounted for on the basis of the adiabatic criterion.

### $\text{Ar}^+ + \text{N}_2$

The results for the system  $\text{Ar}^+ + \text{N}_2$  are shown in Fig. 9. Approximately half the number of data points on the curve have been obtained on a recheck of the system and the data show good reproducibility. A broad maximum for the cross section is observed at an ion energy of about 30 eV (lab). The maximum looks even more pronounced if the partial cross section for production of  $\text{N}^+$  (obtained from an estimate by Shahin<sup>24</sup>) is subtracted from the total measured values.

The increasing cross-section function (as the ion energy increased from 2.2 to about 30 eV) conforms approximately to the form<sup>25</sup>

$$\sigma \propto \exp[-K/E^{1/2}],$$

where  $K$  is a function of an atomic parameter  $a$ , the energy defect  $\Delta E$ , and  $m^{1/2}$ , where  $m$  = mass of the pro-

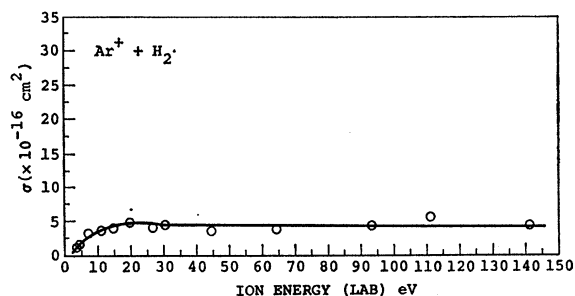
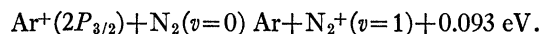


Fig. 10.  $\text{Ar}^+ + \text{H}_2$ . This curve apparently gives the cross section for slow ion production only.

jectile. The observed maximum could also be accounted for approximately on the basis of the adiabatic theory if the reaction is predominantly the following:



This is likely to be the mechanism in the light of McGowan's<sup>26</sup> observation that the cross section for electron capture to the  $2P_{3/2}$  state of  $\text{Ar}^+$  is much larger than to the  $2P_{1/2}$  state.

Danilov's<sup>27</sup> estimate of a reaction constant of order  $10^{-11} \text{ cm}^3 \text{ sec}^{-1}$  for this reaction at near-thermal energies is about ten times as large as the value obtained by extrapolation of our data. Reference also should be made to two recent experimental measurements made by Shahin<sup>24</sup> and Warneck,<sup>28</sup> respectively. From a glow discharge in a mixture of Ar and  $\text{N}_2$ , the former observes

<sup>24</sup> M. M. Shahin, *Advan. Chem. Ser.* **58**, 315 (1966).

<sup>25</sup> J. B. Hasted, *Advan. Electron. Electron Phys.* **13**, 36 (1960).

<sup>26</sup> J. W. McGowan, P. Marmet and L. Kerwin, in *Proceedings of the Third Conference on Atomic Collisions* (John Wiley & Sons, Inc., New York, 1964), p. 854.

<sup>27</sup> A. D. Danilov *et al.*, *Usp. Fiz. Nauk* **85**, 259 (1965) [English transl.: *Soviet Phys.—Usp.* **8**, 92 (1965)].

<sup>28</sup> P. Warneck, *J. Chem. Phys.* **46**, 513 (1967).

that the production rate of  $N_2^+$  in the discharge remains almost unchanged down to about 20-eV ion energy. The drop in the cross-section function at low energy is thus not to be expected from his results. Using a photo-ionization mass spectrometer technique, the latter obtains a cross section of  $7.3 \times 10^{-16} \text{ cm}^2$  at near-thermal energies for the same reaction. These measurements obviously contradict our results.

### $Ar^+ + H_2$

The measured cross sections (Fig. 10) apparently correspond to the simple exothermic charge transfer reaction leading to the formation of  $H_2^+$ . The cross section appears to be independent of translational energy over a

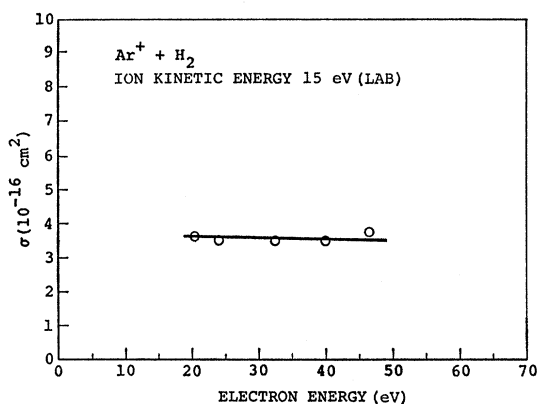
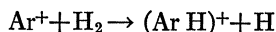


FIG. 11. Dependence of the cross section for the system  $Ar^+ + H_2$  on the energy of the ionizing electrons in the ion source.

large fraction of the ion energy range investigated here.<sup>29</sup> The complex ion  $(Ar H)^+$  formed in the hydrogen atom transfer reaction



is unlikely to be detected with our experimental arrangement, since the ion would retain a considerable fraction of the primary energy after collision and would not be counted as a collision product due to poor angular resolution. The cross sections for  $(Ar H)^+$  formation, measured by Stevenson and Schissler<sup>30</sup> at low kinetic

<sup>29</sup> J. H. Futrek and F. P. Abramson *Advan. Chem. Ser.* **58**, 119 (1966).

<sup>30</sup> D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.* **23**, 1353 (1955)

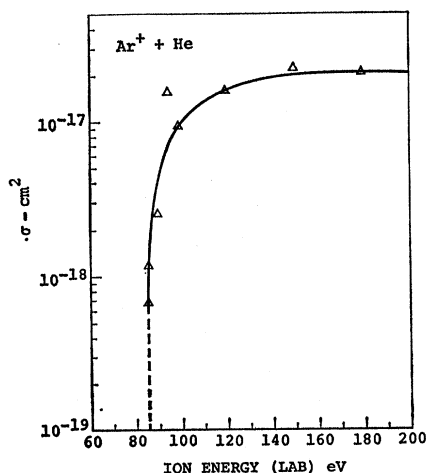


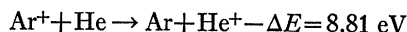
FIG. 12.  $Ar^+ + He$ . Dashed line: extrapolation of the cross-section function to threshold ion energy gives a value approximately 85 eV.

energies, are about two orders of magnitude larger than our values.

The dependence of the cross section on the energy of the bombarding electrons in the ion source was investigated at constant ion energy (15 eV). The results, shown in Fig. 11, indicate that the electron energy in the source has no significant influence on the cross sections over the electron energy range 20 eV to about 50 eV.

### $Ar^+ + He$

This highly endothermic reaction for charge transfer between ground states was investigated for threshold effects.<sup>31</sup> The cross section for the system



should decrease to a threshold laboratory kinetic energy given by

$$E_{lab} = E_{cm} \times \frac{\text{total mass of particles}}{\text{target mass of particles}} = 96.9 \text{ eV.}$$

As expected (Fig. 12), the cross section decreases with ion energy by almost two orders of magnitude in the primary energy range 150 to 87 eV. A threshold of approximately 85 eV is obtained by extrapolation.

<sup>31</sup> H. B. Gilbody and J. B. Hasted, *Proc. Roy. Soc. (London)* **A238**, 334 (1956).