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IONIZATION OF GASES BY NEGATIVE IONS

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The total cross sections for positive-ion formation in collisions of H^- ions (10 to 50 kev) with the atoms He, Ne, Ar, Kr and Xe and the molecules H_2, N_2 and O_2 have been measured; the same cross sections have been measured for O^- ions with the same energy in collisions with inert gas atoms and H_2 and O_2. The ionization cross sections for H^- and H^+ are compared.

INTRODUCTION

BECAUSE of the great amount of work[1-16] carried out in recent years, chiefly by N. V. Fedorenko and his co-workers, a number of the characteristic features of the ionization of gases by positive ions have been established. One of the results of this work is an understanding of the differences in the ionization of gases by positive ions and by electrons. It is also of interest to compare ionization processes in gases when ionization is caused by ions of the same type with opposite charge.

A comparison of this kind can be useful in establishing the role of the sign of the charge of heavy particles with the same mass and atomic number. In H^+ and H^- there is a sharp difference in the structure of the electron shell: one is a bare nucleus while the other has a closed shell, similar to that in helium. Another important difference in ionization caused by positive and negative ions should be kept in mind. Ionization by positive ions is accompanied by a competing process, capture of a single electron (single-electron charge exchange). Ionization by negative ions is not accompanied by this process. The chief competing process in this case is the one in which a single electron is detached from the negative ion.

It follows that a comparison of the ionization of gases by positive and by negative ions should furnish certain data concerning ionization of gases by heavy particles. However, such a comparison is not possible because of the complete lack of experimental data on the ionization of gases by negative ions. The present work has been undertaken in order to obtain these data and to compare them with data on ionization cross sections for positive ions. For a number of reasons, ionization of gases by H^- is of greatest interest. To clarify the role of ion mass, we have also measured ionization cross sections for D^-. In addition, to determine the effect of the atomic number and electron-shell structure of the ion, we have measured ionization cross sections for O^- ions.

METHOD OF MEASUREMENT

When negative ions move through a gas the following inelastic processes can occur:

I. $A^- + B \to A^- + B^*$ — excitation
II. $A^- + B \to A^- + B^{k+} + ke$ — ionization $(1 < k < Z_B)$;
III. $A^- + B \to A^{(k-1)+} + ke + B$ — stripping $(1 < k < Z_A + 1)$;
IV. $A^- + B \to A + B^-$ — charge exchange

(the last process is possible if particle B has a positive electron affinity).

If the gas is molecular the molecules can dissociate into positive and negative ions. In an atomic gas traversed by a beam of negative ions, slow positive ions are formed only by ionization. Thus, the total cross section for positive-ion formation, σ_i^+, can be measured by a potential method; the method used here is essentially that described in references 1, 3, and 6.

A magnetic field parallel to the plane of the measurement electrode is used to suppress secondary electron emission from this electrode; this method has also been used earlier.[6]

The cross section σ_i^+ is computed for single collisions from the formula

$$\sigma_i^+ = i_H^+ / I_0^- nL, \tag{1}$$

where i_H^+ is the positive current at the measurement electrode with the magnetic field on, I_0^- is the current of the primary beam, n is the number of gas particles per cm^3, and L is the length of the measurement electrode.

The total cross section for the formation of electrons and slow negative ions, σ^-, is determined from the formula

$$\sigma^- = i^-/I_0^- nL, \tag{2}$$

where i^- is the negative current at the measurement electrode in the absence of the magnetic field. The value of σ^- computed from Eq. (2) is somewhat high because of the secondary emission from the negatively charged plate of the measurement capacitor. If the secondary emission coefficient for this plate is small, the following relation holds:

$$\sigma^- = \sigma_i^+ + \sum_{k=0}^{Z_A} (k+1)\,\sigma_{-1k} + \sigma_i^-, \tag{3}$$

where σ_{-1k} is the cross section for the detachment of $k+1$ electrons from the negative ion and σ_i^- is the cross section for the formation of slow negative ions.

If

$$\sigma_i^- \ll \sigma_i^+ + \sum_{k=0}^{Z_A} (k+1)\,\sigma_{-1k}$$

we have

$$\sigma^- = \sigma_i^+ + \sum_{k=0}^{Z_A} (k+1)\,\sigma_{-1k}. \tag{4}$$

The cross section σ_i^- is determined from the expression

$$\sigma_i^- = i_H^-/I_0^- nL, \tag{5}$$

where i_H^- is the negative current at the measurement electrode in the presence of the magnetic field.

The following remarks should be made with regard to σ_i^+. Actually, σ_i^+ represents the sum $\sum_{k=1}^{Z_A} k\sigma_i^{k^+}$ where $\sigma_i^{k^+}$ is the cross section for ionization with detachment of k electrons from the gas particle. $\sigma_i^{k^+}$ can be determined from the relative intensity of the peaks in the charge spectrum characteristic of the slow positive ions as obtained by an auxiliary mass spectrometer. In turn, each $\sigma_i^{k^+}$ represents the sum of the cross sections for ionization without change of charge of the negative ion and with detachment of one, two, or more electrons from the negative ion.

APPARATUS

A diagram of the apparatus used for measuring the cross sections for ionization of gases by negative ions is shown in Fig. 1.

The negative-ion source is the negative-ion injector of the charge-exchange electrostatic accelerator being built at the Physico-Technical Institue, Academy of Sciences, Ukrainian S.S.R. The design of this injector and its characteristics have been described by us in detail earlier[17] and will not be considered further in the present paper.

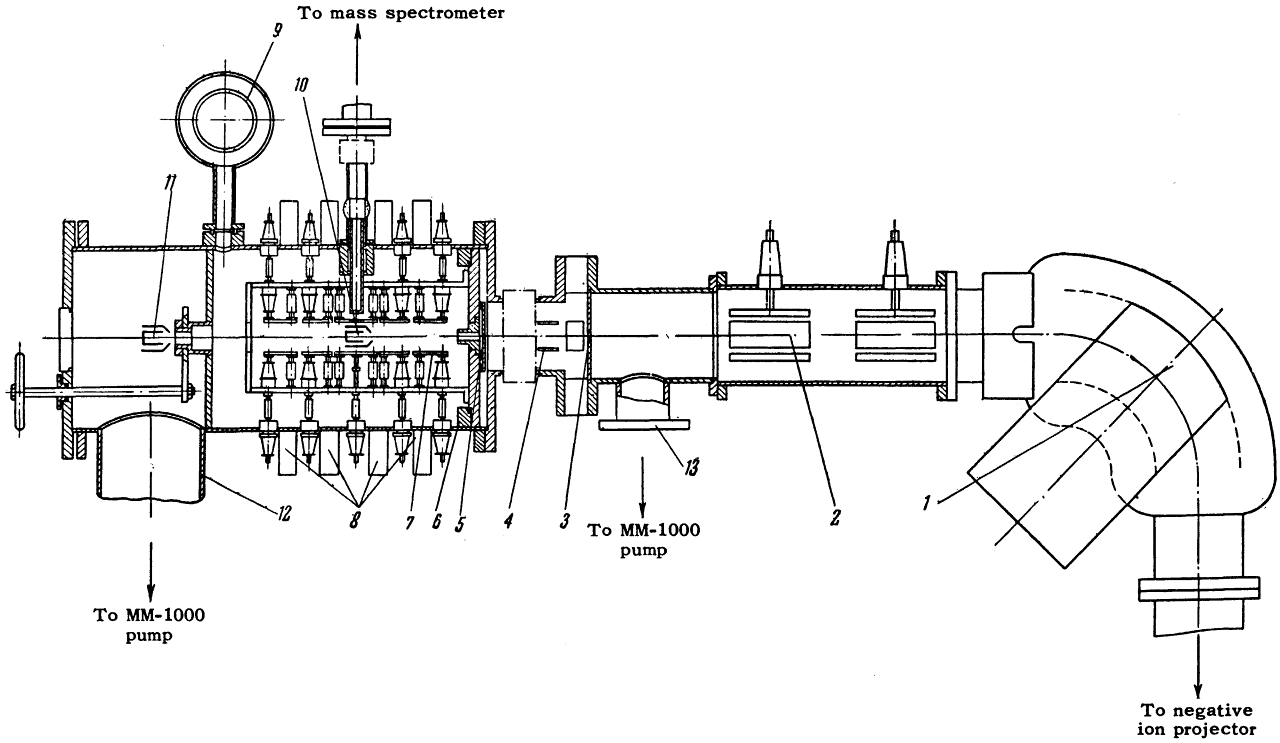

FIG. 1. Diagram of the apparatus.

A monoenergetic beam of negative ions of a given kind is selected by the magnetic mass monochromator 1 and focused by the electrostatic quadrupole lens 2 on the slit (2×4 mm). The beam is then deflected through an angle of 10° by the electric field of the plane capacitor 4 and strikes the input slit 5 of the collision chamber 6. The axis of the collision chamber is inclined with respect to the beam axis in front of the capacitor 4 by an angle of 10° (not shown in the sketch). By means of the deflection capacitor it is possible to select neutral atoms and positive ions produced by collisions of ions of the beam with molecules of the residual gas in the space between the magnetic analyzer and the collision chamber.

The primary beam enters the collision chamber through an input slit (0.5×1 mm), traverses the input channel (4×6 mm and 25 mm long) and leaves through an exit channel (5.5×8.5 mm and 15 mm long). In order to supress secondary electron emission from its edges, the input slit is insulated from the frame of the collision chamber and is maintained at a positive potential of 300 v. The measurement volume is formed by the five plane capacitors 7 consisting of electrodes with an area of 50×50 mm which are spaced every 30 mm. The four coils 8 wound directly on the frame are used to produce a longitudinal magnetic field in the chamber. The gas pressure in the collision chamber is measured with a Knudsen gauge. When the trap 9 is filled with liquid air the pressure of the residual gas in the chamber is 7 or 8×10^{-6} mm Hg.

The current in the primary beam is measured with a Faraday cylinder 11. The beam transmission through the collision chamber is monitored by a Faraday cylinder 10. Both Faraday cylinders are furnished with magnetic control. At the residual gas pressure indicated above the chamber transmission is 100%; at a pressure of 1×10^{-4} mm Hg the transmission is reduced to 85 or 90%.

The primary beam current is measured with a mirror galvanometer with a sensitivity of 1×10^{-10} amp per division. The primary beam current varies from 1.5×10^{-7} to 1×10^{-8} amp. The current at the measurement electrode (plate of the fourth capacitor) is measured with a string electrometer with a sensitivity of 1×10^{-12} amp per division. The currents I_0^- and i_H^+ are measured simultaneously in order to avoid errors due to random fluctuations in the primary beam current.

An auxiliary mass spectrometer is connected to the collision chamber; this instrument is used to make mass spectrometer analyses of the slow ions formed in the gas by passage of the negative ions.

Differential pumping for the collision chamber is realized by means of an MM-1000 diffusion pump which pumps through two ports, 12 and 13. Liquid-air traps are used to prevent vapors of the organic materials in the pump from reaching the apparatus.

The energy of the negative ions is determined from the potential difference traversed by these ions. In the case of H^- resulting from $H_2^+ \rightarrow H^-$, the energy is computed from the formula $E = e[\frac{1}{2}V_{ext} + V_{acc}]$; for H^- and O^- resulting from $H^+ \rightarrow H^-$ and $O^+ \rightarrow O^-$ the energy is computed from the formula $E = e[V_{ext} + V_{acc}]$. The extraction and acceleration potentials V_{ext} and V_{acc} are measured with S-96 electrostatic voltmeters. The random error in the measurements, as estimated from the spread in the results, is ±10%; the error in the energy measurements is ±3%.

RESULTS OF THE MEASUREMENTS

Before the measurements were made, a number of $i_H^+/I_0^- = f(H)$ and $i_H^+/I_0^- = F(V)$ characteristic curves were obtained to determine the magnetic field H required for suppression of secondary emission from the measurement electrode and the electrode potential V required for obtaining a saturation current. Subsequently all measurements were made at $H = 140$ oe and $V = 100$ v. In order to find the conditions required for obtaining single collisions, the dependence of i_H^+/I_0^- on gas pressure p in the collision chamber is determined. The cross sections σ_i^+ and σ^- are determined from the slope of the linear portion of this curve.

To check the accuracy of the overall method, the total cross sections for the positive-ion formation by protons in hydrogen and argon were measured. The cross sections obtained this way agree, within the error limits of the measurements, with the data available in the literature.[6,14,15]

In addition, measurements were made to determine the total cross sections for free-electron formation in hydrogen and argon by H^- ions. The relation $\sigma^- = \sigma_{-10} + 2\sigma_{-11} + \sigma_i^+$ should hold for H^- ions [cf. Eq. (4)]. This relation was found to hold fairly well, as can be seen from Fig. 2, where we show the dependence of σ^- and $\sigma_{-10} + 2\sigma_{-11} + \sigma_i^+$ on v. The values of σ_{-10} for argon and hydrogen were taken from the work of Stedeford and Hasted[18] and Stier and Barnett[19] respectively; the value of σ_{-11} was taken from reference 20. For hydrogen

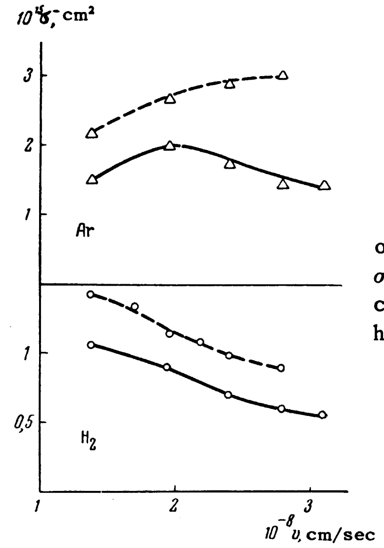

FIG. 2. The dependence of σ^- (solid curve) and $\sigma_{-10} + 2\sigma_{-11} + \sigma_i^+$ (dashed curve) on v for argon and hydrogen.

the quantities σ^- and $\sigma_{-10} + 2\sigma_{-11} + \sigma_i^+$ are in agreement, within the experimental errors; in argon, however, at velocities greater than 2×10^8 cm/sec, the second quantity is somewhat greater than the first.

The results of measurements of σ_i^+ for H^- ions with energies from 10 to 50 kev for five inert gases and three molecular gases are shown by the $\sigma_i^+(v)$ curves in Fig. 3.

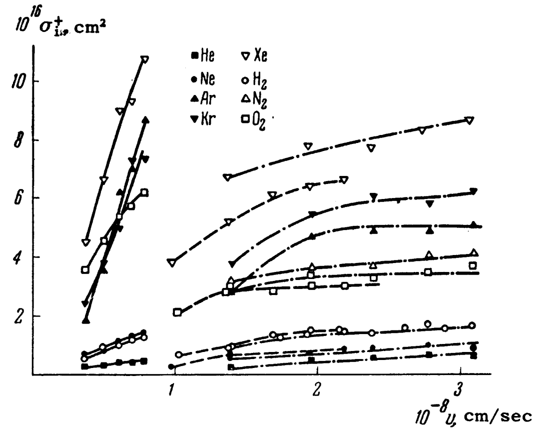

FIG. 3. The function $\sigma_i^+(v)$ for H^- (dot-dashed curves), D_1^- (dashed curves) and O_1^- (solid curves) for five inert gases and three molecular gases.

The dependence of σ_i^+ on ion velocity is the same for all gases: initially σ_i^+ increases as the velocity increases; then the $\sigma_i^+(v)$ curve reaches a plateau which extends up to the end of the velocity range which has been studied. σ_i^+ varies somewhat from one gas to another. In inert gases it increases with the atomic number of the gas while in molecular gases it increases in the order H_2, O_2, N_2.

To determine the effect of ion mass on σ_i^+ (all other conditions remaining the same) we have measured this cross section for D^- ions with energies from 10 to 50 kev in hydrogen, oxygen, neon, and xenon. The $\sigma_i^+(v)$ curves for H^- and D^- are compared in Fig. 3. As is apparent from the figure, σ_i^+ is the same for H^- and D^-, within the limits of the experimental errors, for the velocity range investigated; thus, the ion mass does not affect σ_i^+.

As has been indicated above, it is of interest to compare ionization caused by protons and by negative hydrogen ions. It is obvious that σ_i^+ for H^- must be compared with σ^-, the total cross section for the formation of free electrons by H^+. In Fig. 4 this comparison is made for inert gases. The data for argon are taken from reference 15 while the data for the other gases have been kindly furnished to us by N. V. Fedorenko from his publications. It is apparent from Fig. 4 that $\sigma_i^+(v)$ and $\sigma^-(v)$ vary in the same way and that the absolute values of the cross sections are approximately the same. However, the ionization cross section curves for heavy particles and electrons differ markedly. The reasons for this difference have been discussed many times in papers published by Fedorenko and his co-workers and will not be considered here. A similar situation obtains for the molecular gases. Thus, H^+, H^- and D^- yield ionization cross sections which are approximately the same, in spite of the differences in the sign of the charge, mass, and electron-shell structure. In order to clarify the effect of the nuclear charge it would seem desirable in the future to compare σ_i^+ in H^-, He, and Li^+.

We have already indicated that in collisions of H^- with gas molecules ionization of the gas particle and detachment of electrons from the ion (stripping) are competing processes. The stripping probability for the H^- depends on the sum $\sigma_{-10} + \sigma_{-11}$, the sum of the cross section for stripping of one and two electrons from the fast ion. The total probability for transition of electrons into the continuum of the system comprised of the two colliding atomic particles is given by the sum $\sigma_{-10} + \sigma_{-11} + \sigma_i^+$. In Fig. 4 we compare the functions $\sigma_i^+(v)$, $\sigma_{-10} + \sigma_{-11} = f(v)$ and $\sigma_{-10} + \sigma_{-11} + \sigma_i^+ = F(v)$ for inert gases. The values of σ_{-10} are taken from reference 18 while the values of σ_{-11} are taken from reference 20.

The following conclusions follow from an analysis of the curves in Fig. 4: 1) the cross section σ_i^+ is much smaller than the sum of the cross sections $\sigma_{-10} + \sigma_{-11}$ (20 — 25% of this sum for xenon, krypton, and argon and approximately 12% for neon and helium); 2) the quantities σ_i^+, $\sigma_{-10} + \sigma_{-11}$ and $\sigma_{-10} + \sigma_{-11} + \sigma_i^+$ increase monotonically with the atomic number of the gas; 3) the behavior of the

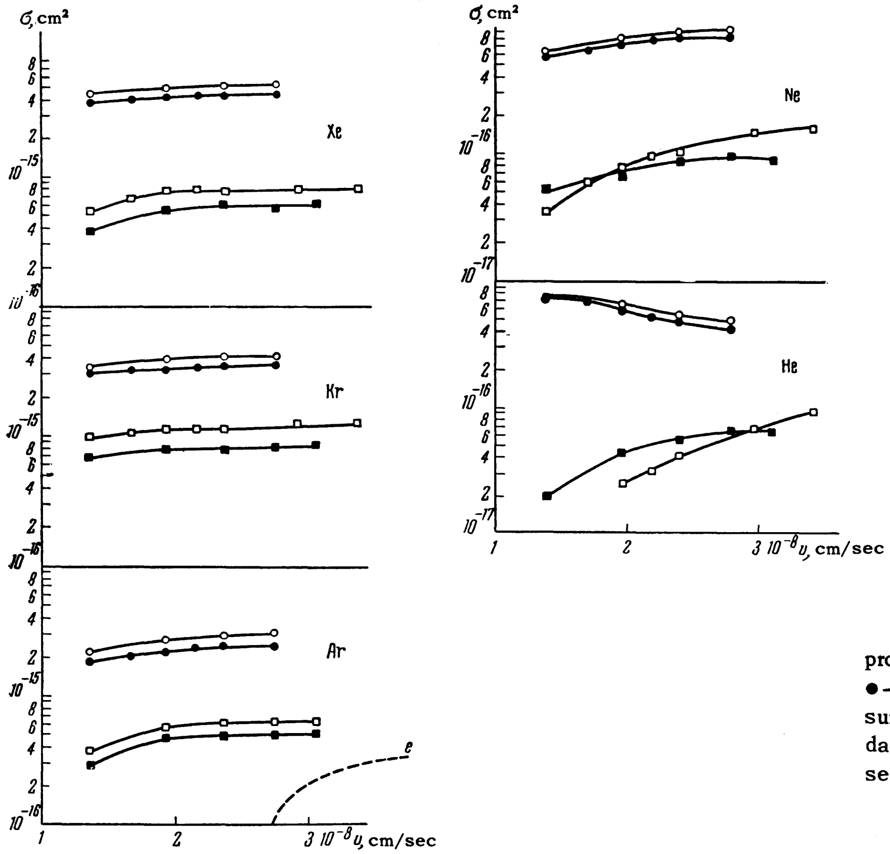

FIG. 4. □ – cross section for ionization by protons, ■ – cross section for ionization by H_1^-, ● – sum of the cross sections $\sigma_{-10} + \sigma_{-11}$, ○ – sum of the cross sections $\sigma_{-10} + \sigma_{-11} + \sigma_i^+$, the dashed curve is the electron ionization cross section.

functions $\sigma_i^+(v)$, $\sigma_{-10} + \sigma_{-11} = f(v)$ and $\sigma_{-10} + \sigma_{-11} + \sigma_i^+ = F(v)$ is the same for all gases except helium. These conclusions would seem to be incompatible with the notion of competition between ionization and stripping in atomic collisions; according to this interpretation, $\sigma_{-10} + \sigma_{-11} + \sigma_i^+$ should be a weak function of the atomic number of the gas while the σ_i^+ and $\sigma_{-10} + \sigma_{-11}$ should vary in opposite directions as the atomic number of the gas varies. These quantities should also vary in opposite directions as the ion velocity varies. Actually, both vary in the same direction as the atomic number of the gas and the velocity of the ion; moreover, $\sigma_{-10} + \sigma_{-11} + \sigma_i^+$ increases appreciably with the atomic number of the gas. This last finding would seem to indicate that the total probability for transition of electrons from bound states in the colliding atomic particles into states in the continuum depends on the number of electrons in the electron shell of the colliding particles and increases as this number increases.

The data obtained in measurements of the cross sections σ_i^+ for O^- ions with energies from 10 to 50 kev in five inert gases and in hydrogen and oxygen are shown in Fig. 3 in the form of $\sigma_i^+(v)$ curves.

A characteristic feature of the $\sigma_i^+(v)$ curves for O^- is the rapid increase in σ_i^+ with ion velocity; in this feature these curves differ essentially from the corresponding curves for H^-. This difference is due to the fact that in the energy range which has been investigated the O^- velocities are much smaller than the H^- velocities. The increase in the derivative of the $\sigma_i^+(v)$ curve with a reduction in ion velocity is also observed for positive ions (cf. Fig. 11 of reference 7). Although the velocity ranges investigated for H^- and O^- do not overlap, from the behavior of the $\sigma_i^+(v)$ curves for these ions we may conclude that at the same velocity the total cross section for positive-ion formation by O^- is greater than for H^-. This result is in agreement with the suggestion that the cross section for transition of electrons into a state in the continuum increases as the number of electrons in the electron shells of the colliding particles increases. A more detailed analysis of the results presented in the present paper will be made after completion of the second stage of this work, which will consist of an investigation of the slow-ion charge spectrum and the determination of the cross sections for ionization with detachment of one, two, or more electrons.

In conclusion, we wish to take this opportunity to express our gratitude to Professor A. K. Val'ter for his continued interest in this work, to L. P. Rekova and A. F. Khodyachikh who participated in the measurements, and to Technician P. A. Chudnyĭ for construction of the collision chamber.

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