SOVIET PHYSICS JETP VOLUME 2, NUMBER 2 MARCH, 1956

Loss of Two Electrons by Negative Ions in Collisions with Atoms and Molecules

V. M. DUKEL'SKII AND N. V. FEDORENKO
Leningrad Physico-Technical Institute
(Submitted to JETP editor May 27, 1954)
J. Exper. Theoret. Phys. USSR **29**, 473-478 (October, 1955)

The appearance of positive ions was detected in simple collisions of Cl^-, Br^-, I^-, Na^-, Sb^-, Bi^- and Sb_2^- ions (at an energy of 5 to 17.5 kev) with helium and argon atoms, and also with nitrogen and hydrogen molecules. They were formed by the loss of two electrons by the positive ions. The cross section for this process is about 10^{-17} to 10^{-16} cm^2. In the case of Sb_2^- and Bi_2^- ions, dissociation was observed with the appearance of not onlynegative but also of positive atomic ions.

1. INTRODUCTION

NEGATIVE ions with energies of about 1000 ev easily lose their extra electron in collisions with the atoms of a gas[1]. Being engaged in an investigation of this phenomenon, we performed the following experiment. A beam of negative iodine ions traversed a chamber filled with argon at a pressure of 3×10^{-3} mm Hg and thereupon entered the space between the plates of a parallel plate condenser. In the field of the condenser the beam (whose emitted light it was possible to observe) was divided into two separate beams. One of them (the beam of negative ions) was deflected toward the positive plate, the other passed through the condenser without being deflected. This undeflected beam consisted of neutral iodine atoms, formed by neutralization of negative ions in collisions with argon atoms.

The appearance of a third beam was detected upon increasing the argon pressure to 1×10^{-2} mm. It was deflected toward the side lying opposite from that toward which the negative ions were deflected. Obviously, this third beam could be only a beam of positive ions. In order to explain its appearance, it was necessary to suppose that in collisions with argon atoms a portion of the negative iodine ions could lose two electrons and be converted into positive ions.

Upon decreasing the argon pressure the beam of positive ions became weaker but remained perceptible to about 10^{-3} mm. At that pressure the stripping of two electrons in two successive collisions was improbable. Therefore, one might think that the negative iodine ions had lost two electrons in a single collision with an argon atom.

[1] V. M. Dukel'skii and E. Ia. Zandberg, J. Exper. Theoret. Phys. USSR **21**, 1270 (1951)

2. APPARATUS. METHOD OF OBSERVATION

The method of the double mass spectrometer[2] is well suited to the study of the charge exchange of ions in collisions with atoms. In this apparatus a homogeneous beam of ions, prepared by a mass monochromator, is incident upon a gas cell. Ions, whose charge or mass has been changed in collisions but whose velocity has been almost fully conserved, are then analyzed by means of a second mass spectrometer (mass analyzer).

The double mass spectrometer used by us has been described in detail by Fedorenko[2]. It is shown schematically in Fig. 1. The ion source with a solid working substance was used. Sodium halide salts were used for producing sodium and halogen ions; antimony and bismuth ions were obtained from a discharge in vapors of these metals.

The experiments for the detection of positive ions, which are formed from negative ions in collisions with the atoms of a gas, were performed as follows. The apparatus was evacuated to a pressure of 10^{-5} mm Hg, and a beam of negative ions of the chosen element was emitted with a given energy into the gas cell. The magnet of the mass analyzer was then turned on and adjusted until near a certain value H_A the negative-ion beam fell onto the detector Φ_2. The gas was then admitted into the gas cell; thereupon, the current of negative ions into the detector dropped, as a portion of the ions was scattered and destroyed in the gas cell. After changing the direction of the magnetic field in the mass analyzer we found the positive ions by varying the magnetic field slowly about the value H_A In the first experiment with a beam of I^- ions (ion energy 10 kev; the gas cell

[2] N. V. Fedorenko, Zh. Tekhn. Fiz. **24**, 769 (1954)

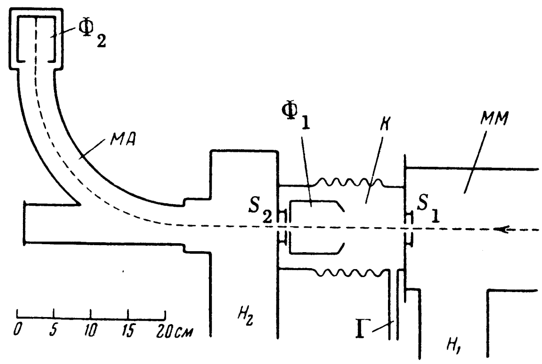

FIG. 1. Schematic drawing of the double mass spectrometer. *MM*, tube of the mass monochromator; *K*, gas cell; *MA*, mass analyzer; Φ_1, detector for measuring the current in the primary ion beam; Φ_2, detector for ions that have traversed the mass analyzer; S_1 and S_2, slits; H_1 and H_2, pipes to the vacuum pumps; Γ, gas inlet.

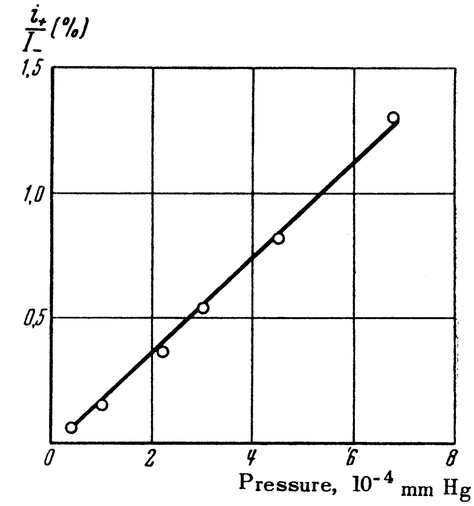

FIG. 2. Conversion of negative into positive ions as a function of gas pressure. I^- ions (10 kev; argon).

was filled with argon at 3×10^{-4} mm.) we found a sharp "line" of positive ions; it was observed at the same magnetic field intensity (within the limits of accuracy of the measurement) as the primary beam of I^- ions. We were able to interpret the observed effect as a conversion, brought about by collisions of I^- ions with argon atoms, of I^- into I^+ ions without a perceptible change of energy.

By deflecting the mass analyzer through small angles out of the null position (up to 5°), we discovered that the positive-ion beam diverged more than the negative-ion beam from which it was formed. This showed that the conversion of I^- into I^+ ions could be accompanied by a perceptible scattering of the ions coming out.

3. RESULTS OF THE MEASUREMENTS

A process of conversion, entirely like that described for the I^- ions, was detected also in all other cases investigated by us. The conversion appeared for Cl^-, Br^-, Na^-, Sb^-, Bi^- and Sb_2^- ions with the gas cell filled with argon, helium, hydrogen and nitrogen.

In the different cases the current in the primary ion beam varied from 2×10^{-10} to 2×10^{-9} amp. The magnitude of the effect depended on the kind and energy of the negative ions, and on the kind and pressure of the gas. In most cases the positive-ion current became measurable at an energy of the primary beam of about 5 kev and grew with increasing energy. The positive ion current was of the order of 10^{-12} amp at energies from 10 to 15 kev and a gas-cell pressure of 3 to 4×10^{-4} mm. The upper limit of ion energy was 17.5 kev in our experiments.

It was very important to ascertain that the appearance of positive ions did not result from a successive stripping of two electrons in two successive collisions (first of a negative ion, next of the neutral atom thus formed) with atoms of the gas. In this case the dependence of the effect upon the pressure in the gas cell was measured in a series of experiments. As an example, a curve showing this dependence for the conversion $I^- \rightarrow I^+$ in argon at 10 kev is displayed in Fig. 2. The abscissa represents the pressure of argon, and the ordinate the ratio of the current i_+ of secondary positive ions to the current I_- of the primary beam of negative ions. As is evident from the figure, the dependence upon pressure is linear in the interval from 1×10^{-4} to 7×10^{-4} mm. In the other cases investigated by us the effect of ion conversion (at gas pressures of about 10^{-4} mm) also was proportional to pressure or increased more slowly than the pressure. It was thus verified that under the conditions of our experiments the positive ions appeared as a result of single collisions of negative ions with atoms or molecules.

Having measured the current ratio i_+/I_- at a given pressure of the gas in the gas cell, we were able to effect an approximate determination of the cross sections Q for collisions accompanied by a conversion of negative into positive ions. The inaccuracy of these determinations is connected with the fact that not all the positive ions produced in the gas cell entered the detector of the mass analyzer, because of the scattering of the

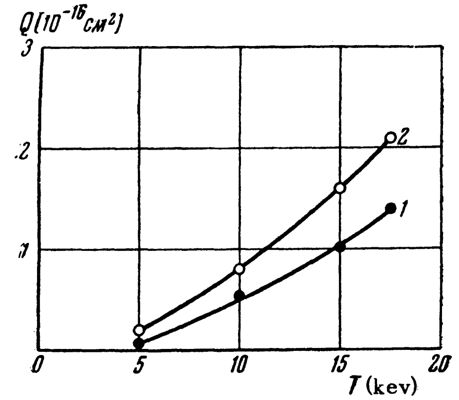

FIG. 3. Cross section for the conversion $I^- \to I^+$ as a function of ion energy. *1*, argon at 3.3×10^{-4} mm; *2*, nitrogen at 3.5×10^{-4} mm.

ions in the conversion process. Another source of error was the indefiniteness of the length l of the effective volume of gas; we took this length as equal to the distance between the slits S_1 and S_2 (Fig. 1).

The magnitude of the cross section Q was calculated by means of the approximate formula

$$Q = \frac{i_+}{I_- nlk},$$

where n is the number of atoms (molecules) per cm^3 of the gas in the gas cell, and k is the "coefficient of admission" of the mass analyzer for the primary ion beam. The quantity k (the ratio of the number of ions traversing the mass analyzer to the number of ions entering the gas cell) was measured for several primary ions at a residual pressure in the apparatus of 10^{-5} mm and was shown equal to 0.5. The values of Q calculated by this method must be less than the actual ones since the quantity k for secondary positive ions probably is considerably smaller that for the primary negative-ion beam and may depend upon the ion energy.

In Figs. 3, 4 and 5 are shown several of the curves obtained by us. They show the dependence of the cross section Q upon the ion energy T. The curves in Fig. 3 refer to the conversion $I^- \to I^+$ in collisions of I^- ions with argon atoms and molecules. At an energy of 5 kev of the I^- ions, Q is about 10^{-17} cm^2. With increasing energy Q increases and attains a value of about 10^{-16} cm^2 at 17.5 kev. Figure 4 shows curves for the conversion $Br^- \to Br^+$; the order of magnitude of Q and the character of the energy dependence in this case are similar to those for the conversion $I^- \to I^+$. The curves in Fig. 5 apply to the con-

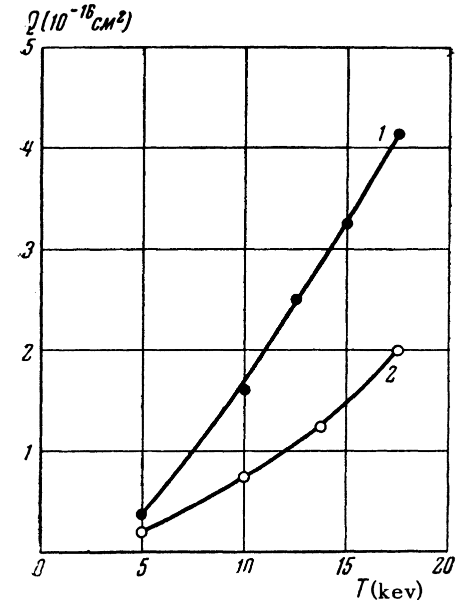

FIG. 4. Cross section for the conversion $Br^- \to Br^+$ as a function of ion energy. *1*, argon at 4.0×10^{-4} mm; *2*, nitrogen at 3.8×10^{-4} mm.

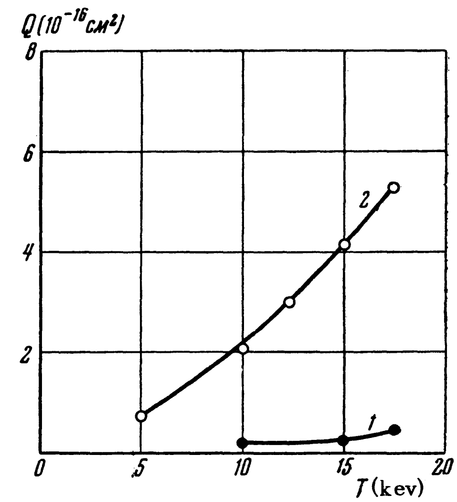

FIG. 5. Cross section for the conversion $Na^- \to Na^+$ as a function of ion energy. *1*, argon at 5.4×10^{-4} mm; *2*, nitrogen at 4.0×10^{-4} mm.

version $Na^- \to Na^+$; in this case Q for argon atoms is small (10^{-17} cm^2) and increases comparatively slowly with energy. For the conversion $Cl^- \to Cl^+$ in argon and nitrogen, Q has a value of about 10^{-16} cm^2 and in the interval 5-17.5 kev increases to several times that value. For the conversions $Sb^- \to Sb^+$ and $Bi^- \to Bi^+$ the energy dependence passed through because of insufficient intensity of the primary negative-ion beam. In both cases Q is about 10^{-16} cm^2 at 10 kev.

The conversion process was also observed for Sb_2^- ions. An Sb_2 ions can be converted into an Sb_2^+ ion in collisions with argon atoms and nitrogen molecules. In the case of argon the process is detected with difficulty because of the small cross section.

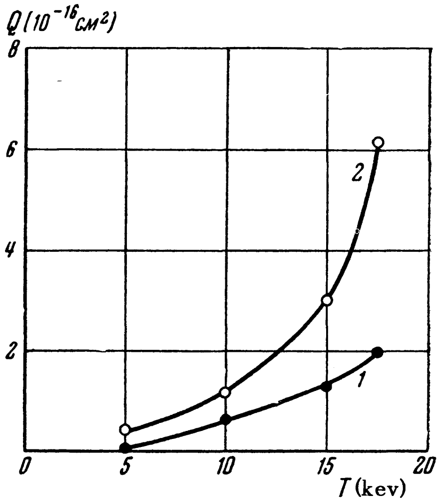

FIG. 6. Cross section for the process $Bi_2^- \rightarrow Bi^+ + Bi + 2e$ as a function of the energy of the Bi_2^- ions. *1*, argon at 2.5×10^{-4} mm; *2*, nitrogen at 2.5×10^{-4} mm.

At 10 kev we were unable to detect the conversion $Bi_2^- \rightarrow Bi_2^+$ either in nitrogen or argon.

In the case of hydrogen and helium the cross sections for conversions in most cases were smaller than in the case of argon or nitrogen, but were of the same order of magnitude (10^{-17} to 10^{-16} cm^2) and also increased with the ion energy.

Performing experiments with a beam of Sb_2^- ions we discovered two more secondary lines: one negative (Sb^-), the other positive (Sb^+), with an energy equal to half the energy of the primary Sb_2^- ions. Sb^- ions could appear as the result of a dissociation of an Sb_2^- ion into an Sb^- ion and a neutral Sb atom (in collisions with atoms of the gas). The cross section for the process $Sb_2^- \rightarrow Sb^- + Sb$ depended little on the ion energy (5-17.5 kev) and was about 10^{-17} cm^2 in argon as well as in nitrogen. The appearance of the Sb^+ ions indicated the possibility of a conversion complicated by dissociation. Evidently the Sb^+ ion appeared as the result of the loss of two electrons by the Sb_2^- ion, in which the newly formed Sb_2^+ ion disintegrated into an Sb^+ ion and an Sb atom*. The process $Sb_2^- \rightarrow Sb^+ + Sb + 2e$ appeared in argon and nitrogen. The cross section of this process increased rapidly with the primary-ion energy, attaining several units $\times 10^{-16}$ cm^2 at 17.5 kev.

In the case of Bi_2^- ions we observed the same phenomena of dissociation and of dissociation with appearance of positive ions. The curves in Fig. 6 show the dependence of the cross section Q for the process $Bi_2^- \rightarrow Bi^+ + Bi + 2e$ in argon and nitrogen upon the energy T of the primary ions. As is evident from the figure, Q increases rapidly with T.

We also observed the conversion of negative into positive iodine ions spectrographically. A beam of negative iodine ions (beam current 3×10^{-6} amp, ion energy 7.5 kev) was incident on the gas cell filled with argon at 5×10^{-3} mm. The weak light emitted by the beam was analyzed by means of a sensitive glass spectrograph. On the spectrograms we obtained the spectral lines of the iodine atom (JI), $\lambda = 5235, 5119, 4917, 4862$ Å, and others; but besides these also the lines $\lambda = 5497, 5465, 5438\text{-}5436, 5407\text{-}5405, 5338, 5161$ Å, and others belonging to the spectrum of the I^+ ion (JII). The lines JI obviously appear as the result of the stripping of the extra electron from the I^- ions in collisions with argon atoms and of simultaneous excitation of the iodine atoms being formed. The appearance of the lines JII can be explained as the result of the conversion of a portion of the negative iodine ions into positive ones with simultaneous excitation of the I^+ ions. The intensity of the observed JII lines was comparable with that of the JI lines. Upon decreasing the argon pressure to 2×10^{-3} mm and increasing it to 8×10^{-3} mm, the relative intensity of the lines JI and JII changed little. This showed that the excitation of the JII lines occurred as the result of single collisions of I^- ions with argon atoms, but not in a stepwise fashion.

---

* It seems that another process, namely, $Sb_2^- \rightarrow Sb^+ + Sb^- + e$, which could also lead to the appearance of Sb^+ ions did not take place in our experiments since the number of Sb^- ions always was considerably less than the number of Sb^+ ions.

4. CONCLUSION

The loss of two electrons by a negative ion in a single collision with an atom represents a process analogous to the two-step ionization of atoms by electrons. The ionization of atomic particles in collisions becomes possible at lower velocities than in the case of ionization by electrons, but because of the large difference between the masses of the electron and the atom it requires that the particles possess a considerably larger kinetic energy of relative motion. For stripping two electrons from a negative ion it is necessary to expend an energy equal to the sum of the energy of the electron affinity and the energy of the first ionization of the atom. This sum is always less than the energy of the two-step ionization of any neutral atom or of the more positive ion. Thus, it is explained that is is possible to observe two-step ionization of negative ions at comparatively low ion energies (beginning with 5 kev), at which practically no stripping of two electrons from neutral atoms or from positive ions takes place*.

For all ion-atom pairs investigated by us, the cross section for the conversion of negative into positive ions increased with the ion energy. The energy interval (5-17.5 kev) investigated by us was, however, too small, and the inaccuracy of the determination of the cross sections was too great to conclude anything about the form of the function $Q(T)$.

The large values of the cross sections for the conversion process--several units $\times 10^{-16}$ cm^2 at 10 to 15 kev--deserve to be noted. Since our method of measurement yielded values that are too small, the true values of the cross sections must be even larger.

As our preliminary experiments show, in the energy interval 5-17.5 kev the stripping of a single electron continues to be the fundamental process occurring in collisions of negative ions with atoms. For instance, for I^- ions with an energy of 15 kev and argon atoms the cross section for this process is about 1×10^{-15} cm^2; but the cross section for conversion into positive ions is about 1×10^{-16} cm^2.

In the region of low energies (of the order of 100 to 1000 ev) the process of stripping a single electron serves as the sole source of the appearance of slow electrons in collisions of negative ions with atoms. Therefore, by measuring the number of slow electrons it is possible to determine the cross section for this process[1,3] In applying this method in the region of energies above 5 kev, it is necessary to remember the existence of the process of conversion of negative into positive ions. At these energies the measurements with utilization of the slow electrons yield a total cross section into which the doubled cross section for the loss of two electrons enters together with the cross section for the stripping of a single electron.

---

* One of us (N.V.F.) has discovered the stripping of two electrons from Ba and A ions (at 20 kev) in collisions with argon atoms and nitrogen molecules[2].

[3] J. B. Hasted, Proc. Roy. Soc. (London) A212, 235 (1952)

Translated by J. W. Heberle
227