The Formation of Negative Oxygen Ions in the Collisions of Positive Oxygen Ions with Gas Molecules

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Using a double mass-spectrometer a study was made of the capture of two electrons by positive atomic and molecular ions of oxygen in collisions with molecules of hydrogen, oxygen and nitrogen. The effective cross sections for these processes were measured for oxygen ions with energies between 14 and 41 kev.

INTRODUCTION

VARIOUS phenomena connected with the formation of negative ions comprise a branch of physics of elementary processes that has been only slightly investigated thus far. This fact is apparent in the monograph[1] in which the chapter devoted to a survey of various processes of formation of negative ions contains mostly a discussion of theoretical work. The most thoroughly studied processes have been the formation of negatively charged ions by means of surface ionization[2,3], by collisions of slow electrons with molecules[4,5] and by bombardment of metallic surfaces by positive ions[6,7].

The formation of negative ions can take place by collisions of fast particles with atoms or molecules accompanied by exchange of charges. Such collisions may result in exchange of one, two or a larger number of electrons, with occurence of processes of the following type:

$$A + B \rightarrow A^- + B^+; \quad (1)$$

$$A^+ + B \rightarrow A^- + B^{++}; \quad (2)$$

$$A^{++} + B \rightarrow A^- + B^{+++}. \quad (3)$$

The existence of process (2) was discovered by us during a study of collisions of protons with molecular hydrogen[8], but the processes (1) and (3) have not been studied at all. The goal of the present work is a more detailed study of process (2), i.e., the formation of negative ions by collisions of singly charged positive ions with molecular gas accompanied by capture of two electrons during each collision.

As a subject of our study we selected the collision processes of positive atomic and molecular ions of oxygen with molecules of hydrogen, oxygen and nitrogen. The above processes were selected because the electron affinity of the oxygen atom is known with sufficient accuracy and has a fairly large value (2.2 ev). In addition, it is possible to compare the previously determined effective cross sections of process (2) with the effective cross section of formation of negative ions of oxygen by collisions of slow electrons with the molecules of a series of gases.

DESCRIPTION OF THE APPARATUS AND THE METHOD OF MEASUREMENT

A schematic diagram of the apparatus used for the study of the processes of formation of negative ions of oxygen is shown in Fig. 1.

A beam of positive ions of oxygen was obtained from a high frequency ion source *1*. The ions emitted by the source were accelerated in tube *2*; they then entered a magnetic mass-monochromator *3*, where the beam was rotated by 60°. The monochromator was capable of separating from the beam the ions of O_1^+ with energy up to 50 kev. Measurement of the current of the undecomposed beam was carried out by means of a movable Faraday cylinder *6*. An electrostatic deflection system *4* was used to correct the trajectory of the beam.

The beam of positive oxygen ions selected by the mass-monochromator then entered the collision

[1] H. S. W. Massey, *Negative Ions*, 1950

[2] V. M. Dukel'skii and N. I. Ionov, J. Exper. Theoret. Phys. USSR 10, 1248 (1940)

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[8] Ia. M. Fogel', L. I. Krupnik and B. G. Safronov, J. Exper. Theoret. Phys. USSR 28, 589 (1955); Soviet Phys. 1, 415 (1955)

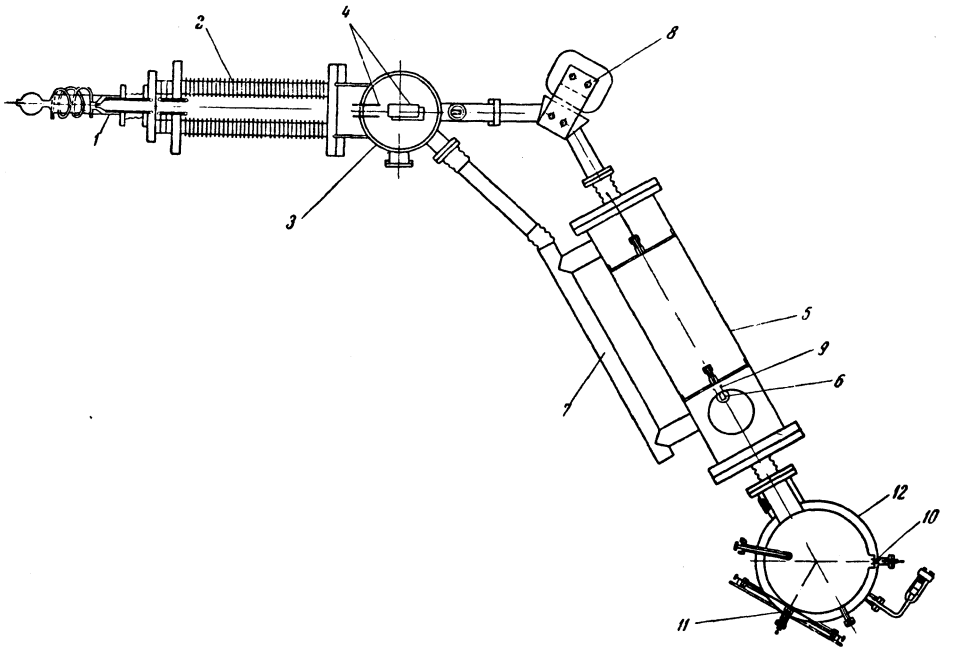

FIG. 1. Arrangement of the experimental apparatus.

chamber 5, whose cross section is drawn in larger scale in Fig. 2. At the entry to the collision chamber the beam was limited in size by a diaphragm a_1 of diameter 3 mm, and then passed through an entry tube b_1 of diameter 5 mm and length 50 mm. Having passed through the chamber, the beam again passed through a second diaphragm a_2, and then left the chamber by a second tube b_2 of the same dimensions as the entry tube. The presence of diaphragms at the entrance and exit of the collision chamber prevented the beam particles from falling on the walls of the tubes.

The evacuation of the gas admitted to the chamber and escaping through the entry and exit tubes was accomplished by means of a bypass pipe 7, flexibly connected with a branch pipe 3, which was connected to the pump MM-1000. With the above quoted dimensions of entry and exit tubes of the collision chamber a considerable pressure difference existed across these tubes, so that with a pressure of gas 10^{-3} mm inside the chamber, the pressure in the rest of the system was only 10^{-5} mm.

In the present experiments the collision chamber was filled with hydrogen, oxygen or nitrogen. Hydrogen was admitted to the chamber over a palladium filter. Oxygen, containing 1 % of impurities, was admitted through a bimetallic valve. Nitrogen, obtained by evaporation of liquid nitrogen and passed over hot copper shavings, was admitted from a glass flask through a capillary tube. The regulation of the flow of gas was done in that case by compression of rubber tubing connecting the flask with the capillary. All gases admitted into the chamber passed through a glass trap filled with liquid nitrogen. The trap was connected to a copper tube which was then soldered to an inlet valve of the chamber. In such a way all gases and vapors condensable at liquid nitrogen temperatures were eliminated from the admitted gases. The pressure of the gas in the collision chamber was measured by a McLeod gauge with a constant of 2.2×10^{-6}. The entry of mercury vapors from the gauge into the chamber was again prevented by a liquid nitrogen trap.

The current strength of the ion beam that had passed through the collision chamber was measured by a Faraday cylinder 6 with magnetic control that made possible removal and insertion of the cylinder into the beam. The secondary emission from the Faraday cylinder was suppressed by application of negative potential on the cylinder 9. The measurement of the current of the ion beam that had passed through the collision chamber was made with a mirror galvanometer of sensitivity 9×10^{-10} A/div. The current of the beam of

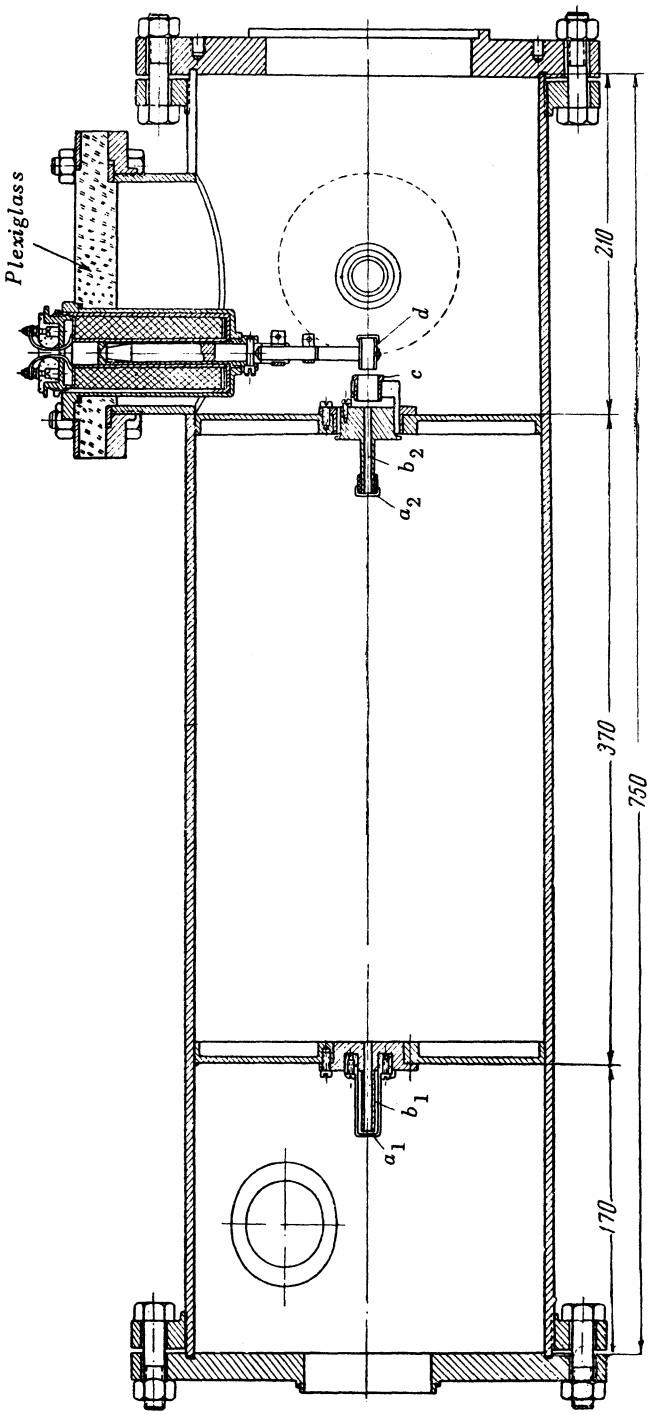

FIG. 2. Diagram of the collision chamber: a_1 and a_2 are entry and exit diaphragms, b_1 and b_2 entry and exit tubes, c is a cylinder for suppression of secondary electron emission from the Faraday cylinder, d is the Faraday cylinder with magnetic control.

ions that had passed through the chamber was usually 0.02 - 0.04 μA even though it was easily increased to 0.1 μA. The beam of particles resulting from the passage of positive oxygen ions through the collision chamber then entered a magnetic analyzer *12*, described by us previously[8].

The measurement of currents of positive and negative ions of oxygen was made by means of the Faraday cylinders *10* and *11*, connected with a string electrometer using a constant deflection scheme. Because of the non-linear characteristic of the electrometer we made use of the same resistance 3.9×10^9 ohms during measurements of the current of both positive and negative ions.

The emission and focusing potentials were measured by electrostatic voltmeters and the accelerating potential was measured by means of a system of calibrated resistances. The error of measurement of the ion energies was of the order of 3%.

The method of measurement of the effective cross section of formation of negative ions as a result of capture of two electrons by positive ions of oxygen was as follows. First, the dependence of the current of positive and negative ions of oxygen passing through the collision chamber was studied as a function of the magnetic field intensity in the analyzer chamber. Since the beam diameter, limited by the two diaphragms, was considerably smaller than the diameter of the Faraday cylinders ($\sim$ 15 mm), the curves $I = f(H)$ had a plateau of a width approximately 300 oersteds. The measurements of the current were made thereafter at the intensity of the magnetic field corresponding to the center of the plateau.

The measurements of the currents of positive and negative ions were not made simultaneously and as a result, the error in determination of the measured quantities could be considerably larger due to the fluctuations in the intensity of the ion beam that passed through the collision chamber. To minimize such effects the current strength I_0 of the beam leaving the collision chamber was measured with Faraday cylinder *6* every time the current strength of the positive ion beam I_+ or of the negative ion beam I_- was measured. The ratio of the currents I_-/I_+ was calculated in the form of a ratio of the quantities I_-/I_0 and I_+/I_0, and in that way the error of measurements connected with the fluctuations in the beam intensity was decreased considerably.

To determine the effective cross section for capture of two electrons it was necessary to obtain the dependence of the ratio of currents I_-/I_+ on pressure p of the gas in the collision chamber. These measurements had to be corrected for the fraction of the negative ions in the analyzed beam that was formed by collisions with the residual gas (other than the gas under study) in the chamber. On interruption of the flow of gas into the collision chamber, the pressure of residual gas was $2 - 3.5 \times 10^{-5}$ mm. The ratio I_-/I_+ for the beam that passed through the residual gas in the chamber was of the order of 2%, giving the background reading. It should be noted that a substantial fraction of the negative ions appearing in the beam that passed through the residual gas in the collision chamber is formed as a result of capture of electrons from molecules of condensable vapors whose pressure is not measured by the McLeod gauge. Indeed, if the pressure in the collision chamber is increased to twice the residual pressure, then the ratio I_-/I_+ increases only by 0.2 - 0.3%.

The following procedure was followed during the determination of the dependence of I_-/I_+ on the pressure of gas in the collision chamber. First, the residual pressure in the chamber p_ϕ and the ratio $(I_-/I_+)_\phi$ at that pressure were determined. Gas was admitted continuously to the chamber until pressure p was reached. Then the ratio I_-/I_+ for the pressure p was obtained. Then the flow of gas was again interrupted, and the residual pressure p_ϕ and the ratio $(I_-/I_+)_\phi$ for the residual gas were measured. By computing the average value of $(I_-/I_+)_\phi$ for the residual gas from the two measurements at the pressure p_ϕ the influence of the formation of negative ions by collisions with residual gas on the ratio I_-/I_+ at the pressure p was eliminated from the data. The pressure of the admitted gas was obtained as the difference $p - p_\phi$. A graph of $I_-/I_+ - (I_-/I_+)_\phi$ versus $p - p_\phi$ was obtained from the data. The values of I_-/I_+ both at the residual pressures and at the pressure p were computed as averages of 5 - 6 measurements.

As an example, the graph of the functional dependence for ions O_1^+ with energies 41 kev is shown in Fig. 3 for a beam passing through the collision chamber filled with oxygen. The dependence is linear for the lowest pressures, which testifies to the process of capture of two electrons by the ion O_1^+ in a single collision with a molecule O_2. Beginning with pressures of the order of 2×10^{-4} mm, the increase of the ratio I_-/I_+ with pressure becomes non-linear

because of the formation of negative ions of oxygen in two consecutive collisions of the ion 0_1^+ with molecules of oxygen ($0_1^+ \to 0_1$, $0_1 \to 0_1^-$).

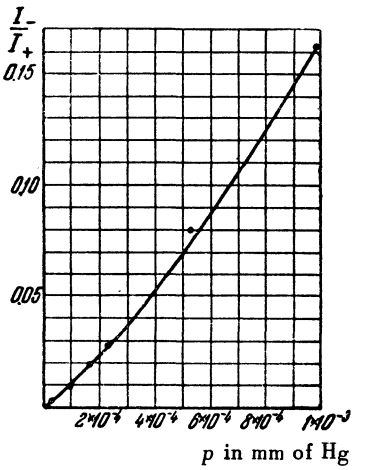

FIG. 3. Graph of dependence of $I_-/I_+ - (I_-/I_+)_\phi = f(p - p_\phi)$ for 0_1^+ ions with energy 41 kev in 0_2.

Evaluating the slope of the linear portion of the graph $I_-/I_+ - (I_-/I_+)_\phi = f(p - p_\phi)$, the effective cross section σ_{1-1} for capture of two electrons is computed according to the following formula [cf. Eq. (24) in our previous work[8]]:

$$\sigma_{1-1} = 1{,}08 \times 10^{19} \frac{T}{L} \left[\frac{d\,(I_-/I_+)}{dp}\right]_{p=0}, \qquad (4)$$

where T is the absolute temperature of the gas, L the effective length of the collision chamber, equal to 35 cm in our case, and $\left[\frac{d(I_-/I_+)}{dp}\right]_{p=0}$ is the slope of the linear section of the curve. The error of measurement of the effective cross section σ_{1-1} was of the order of 50%. A considerable part of this error was due to the small accuracy of the measurements of pressure in the linear part of the curve.

As is evident from the curve in Fig. 3, the ratio I_-/I_+ reaches 16% with an increase of pressure in the collision chamber. In individual measurements even larger values of I_-/I_+ were obtained. For example, for 14 kev 0_1^+ ions and the pressure of oxygen in the collision chamber 4.7×10^{-3} mm, the ratio I_-/I_+ was 33%. With pressure of nitrogen 2.7×10^{-3} mm the ratio was as high as 40%.

EXPERIMENTAL RESULTS

The measurements of the effective cross section for the capture of two electrons accompanied by the formation of fast negative ions were carried out both for atomic oxygen ions 0_1^+ and for the molecular ion 0_2^+, by passing the ion beam through hydrogen, oxygen and nitrogen. The process $0_1^+ \to 0_1^-$ was studied for ion beams of energy between 15 and 41 kev. The results of these measurements are shown in Table I.

Effective cross section of the process $0_2^+ \to 0_2^-$ was determined only for ions of energy 18 kev. The values obtained for the cross section are given in Table II.

Since the apparatus utilized in the present investigation of the capture of two electrons on collision of fast ions with gas molecules was considerably better than the apparatus used in our previous study[8], we have repeated the measurements of the effective cross section of the process $H_1^+ \to H_1^-$ in hydrogen with the proton energy equal to 21 kev. The effective cross section σ_{1-1} of that process turned out to be 1.5×10^{-17} cm^2, which is a much larger value than the one obtained in the previous work. Considering the improvement of the experimental conditions in the present measurements in comparison with the previous work (established effective length of the collision chamber, larger pressure drop from the collision chamber to the analyzing chamber) it is necessary to consider the data of this work to be closer to reality.

On analysis of the beam formed by the passage of the 0_1^+ ions through the collision chamber, doubly charged oxygen ions 0_1^{++} were found to be present. The appearance of these ions in the beam was due to the loss of an electron by the ion 0_1^+ by collision with a gas molecule. By an investigation of the dependence on the pressure of gas in the collision chamber of the ratio of the current strength of ions 0_1^{++} to the current strength of 0_1^+ ions, we were able to plot the curve $I_{0_1}^{++}/I_{0_1}^{+}$ versus p. From the slope of this curve the effective cross section σ_{12} for the loss of electron by the ions 0_1^+ was evaluated. Table III gives the effective cross sections σ_{12} for the ions 0_1^+ with energy 34 kev in three gases. The dependence of the effective cross section σ_{12} on the energy of the ions 0_1^+ for their passage through nitrogen is evident from the data in Table IV.

TABLE I

Process $0_1^+ \rightarrow 0_1^-$

Hydrogen		Oxygen		Nitrogen	
Energy in kev	$\sigma_{1\text{-}1} \times 10^{16}$ cm^2	Energy in kev	$\sigma_{1\text{-}1} \times 10^{16}$ cm^2	Energy in kev	$\sigma_{1\text{-}1} \times 10^{16}$ cm^2
15.0	0.9	13.7	0.7	14.0	0.5
22.6	0.7	—	—	—	—
32.6	0.8	—	—	29.0	0.7
41.4	1.3	41.0	0.9	39.4	1.1

TABLE II

Process $0_2^+ \rightarrow 0_2^-$

Gas	$\sigma_{1\text{-}1} \times 10^{18}$ cm^2
Hydrogen	4.1
Oxygen	5.1
Nitrogen	4.9

TABLE III

Process $0_1^+ \rightarrow 0_1^{++}$

Gas	$\sigma_{12} \times 10^{17}$ cm^2
Hydrogen	3.0
Oxygen	6.7
Nitrogen	5.7

TABLE IV

Process $0_1^- \rightarrow 0_1^{++}$

Energy in kev	$\sigma_{12} \times 10^{17}$ cm^2
12.5	0.3
19.2	1.3
27.0	3.1
34.0	5.7
41.0	7.5

Oxygen ions with a degree of ionization higher than two have not been observed in the beam even with the greatest sensitivity of the electrometer detection system (electrometer resistance 4.3×10^{11} ohms). We can conclude, therefore, that the cross section for loss of two or more electrons by the 0_1^+ ion is less than 10^{-19} cm^2 for the energy interval investigated in the present work. In the beam of 0_2^+ ions that passed through the collision chamber we have discovered 0_1^+ ions with energy half of the energy of the 0_2^+ ions. The presence of these ions in the beam gives evidence of dissociation of molecular ions 0_2^+ by collisions with gas molecules in the collision chamber. Having found the dependence of the ratio $I_{0_1^+}/I_{0_2^+}$ on the gas pressure in the collision chamber, we have determined the effective cross section for dissociation of 0_2^+ ions in three gases. Table V gives the values of the effective cross section for dissociation of 0_2^+ ions with energy 23 kev.

It should be added that in the beam of 0_2^+ ions that passed through the collision chamber, we have found 0_1^- ions as well. The appearance of these ions may be ascribed to one of the following processes: 1. part of the 0_2^- ions formed by the process $0_2^+ \rightarrow 0_2^-$ end in excited states and dissociate into ion 0_1^- and atom 0_1; 2. ions 0_1^+ formed by dissociation of 0_2^+ ions capture during a second collision of two electrons and form an ion 0_1^-. It is possible to determine which of the two processes takes place by a study of the dependence of $I_{0_1^-}/I_{0_2^+}$ on the pressure of gas in the collision chamber. Such dependence should be linear at low pressures if the first process takes place, while a deviation from linearity should be evident for the second process. We intend to clarify this question in the future.

TABLE V

Process $0_2^+ \rightarrow 0_1^+ + 0_1$

Gas	$\sigma_{diss} \times 10^{16}$ cm^2
Hydrogen	2.2
Oxygen	2.7
Nitrogen	3.2

A study was also undertaken to learn more about formation of negatively charged ions of oxygen by passage through thin metallic foils placed close to the entry into the magnetic analyzer. Aluminum and

silver foils of thickness about 0.01 mgm/cm^2 were used for this purpose. The preparation of these foils was described in a previous work[9] connected with a study of the formation of negatively charged ions of hydrogen by proton bombardment of such foils.

Silver foils were very rapidly attacked on exposure to the beam of 47 kev O_1^+ ions of current strength $2 - 3 \times 10^{-8}$ A. Aluminum foils were found to be more stable and withstood the ion beam under the above conditions for two hours. In the beam that passed through the aluminum foil, more negative than positive ions were found. However, the beam particles were strongly scattered, which made quantitative measurements impossible. These same foils were found to be too thick for ions O_1^+ with energy of the order of 50 kev. Our efforts to prepare thinner foils with diameter 4 - 5 mm have been unsuccessful thus far. Apparently, a study of the process $O_1^+ \rightarrow O_1^-$ in metallic foils will be possible either for ions of higher energy, or for foils with a thickness much smaller than 0.02 mgm/cm^2.

DISCUSSION OF RESULTS

Consideration of the data in Table I allows us to make several conclusions about the formation of negatively charged ions of oxygen during collisions of O_1^+ ions with molecules of hydrogen, oxygen and nitrogen. First, the magnitude of the effective cross section for capture of two electrons by O_1^+ ions during collisions with the above-mentioned gases is as high as 10^{-16} cm^2. It is of the same order of magnitude as the cross section for the capture of a single electron. Second, there is no evidence of a substantial dependence of effective cross section for capture of two electrons on the energy of O_1^+ ions, in the energy interval between 14 and 41 kev, or on the kind of gas in the collision chamber.

The data of Table II show that the effective cross section for capture of two electrons is considerably smaller for O_2^+ ions than for O_1^+ ions and is the same for all three investigated gases. It is interesting to notice that the effective cross section for formation of negative ions by capture of two electrons by positive ions is considerably larger than the effective cross section for formation of negative ions during collisions of slow electrons with molecules. For comparison it can be pointed out that the effective cross section for the process $O_2 + e \rightarrow O_1 + O_1^-$ is equal to 8×10^{-19} cm^2 and is the largest for processes of that kind[1].

Quantum mechanical calculations of the effective cross section for atomic collisions with exchange of an electron between the interacting particles were presented by Kallmann and Rosen[10]. According to these calculations the effective cross section for exchange of one electron depends on the magnitude of the resonance defect ΔE, i.e., on the change of the internal energy of the particles during their interaction. It is evident that for collisions with an exchange of a single electron the magnitude of ΔE is equal to the difference between the energy freed by neutralizing one particle and the energy necessary to ionize a second particle. It is assumed that the interacting particles are in the ground state both before and after the interaction.

The calculation[10] shows that with $\Delta E = 0$, the effective cross section is maximum (resonance charge exchange), and with $\Delta E \neq 0$ the effective cross section decreases monotonically with increasing resonance defect. This decrease is symmetric about the maximum. Experimental studies[11] have shown that in the regions of negative and small positive values of ΔE^*, the change in the effective cross section for single charge exchange as a function of the quantity ΔE agrees with the theoretical calculations. For larger positive values of ΔE we observe a considerable deviation of the experimental data from the theory.

The process of the exchange of two electrons during atomic collisions is also accompanied by a change in the internal energy and therefore may clarify the relationship between resonance defect and effective cross sections of those processes. First, it is necessary to calculate the resonance defect of the processes investigated in the present work.

We shall consider the resonance defect in the collision processes of ions O_1^+, O_2^+ and H_1^+ with a hydrogen molecule. In the first case, i.e., in the process $O_1^+ + H_2 \rightarrow O_1^- + H_1^+ + H_1^+$ the energy yielded by formation of a fast O_1^- ion is equal to

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[9] Ia. M. Fogel', B. G. Safronov and L. I. Krupnik, J. Exper. Theoret. Phys. USSR **28**, 711 (1955); Soviet Phys. **1**, 546 (1955)

* The sign of the quantity ΔE for the process $A^+ + B \rightarrow A + B^+$ is determined by the difference $V_{iA} - V_{iB}$, where V_{iA} and V_{iB} are the ionization potentials of the particles A and B.

[10] H. Kallmann and B. Rosen, Z. Phys. **61**, 61 (1930)

[11] F. Wolf, Ann. Physik **30**, 313 (1937)

$V_{i0} + S_0$, i.e., to the sum of the ionization potential and the electron affinity of the oxygen atom.

The energy lost in formation of the two slow protons, which resulted from the removal of two electrons from the hydrogen molecule, is composed of the dissociation energy of hydrogen molecule, double ionization potential of H atom and the potential energy of two protons.

In such a way the resonance defect for the above process is computed from the following equation:

$$\Delta E = V_{i0} + S_0 - (E_{diss} + 2V_{iH} + E_{pot}) \quad (5)$$

Substituting into Eq.(5) the values $V_{i0} = 13.57$ ev, $S_0 = 2.2$ ev, $E_{diss} = 4.48$ ev and $E_{pot} = 18$ ev, we obtain**

$$\Delta E = -33.8 \text{ ev}.$$

To compute the resonance defect of the processes $O_2^+ + H_2 \rightarrow O_2^- + H_1^+ + H_1^+$ and $H_1^+ + H_2 \rightarrow H_1^- + H_1^+ + H_1^+$, it is necessary to obtain first the sums $V_{i0_2} + S_{0_2}$ in the first case and $V_{iH} + S_H$ in the second case.

Substituting the values $V_{i0_2} = 12.5$ ev, $S_{0_2} = 0.7$ ev, $V_{iH} = 13.54$ ev and $S_H = 0.75$ ev into Eq. (5), we obtain***

$$(\Delta E)_{O_2^+ \rightarrow O_2^-} = -36.4 \text{ eV}$$

$$(\Delta E)_{H_1^+ \rightarrow H_1^-} = -35.3 \text{ eV}.$$

Table VI gives the resonance defects and the corresponding effective cross sections of the processes discussed above. As is evident from the Table, in the processes involving an exchange of two electrons, the resonance defect has a large negative value. The effective cross section of the process increases rapidly with the decrease in the absolute magnitude of the resonance defect (Fig. 4). No definite correlation between the magnitude of the electron affinity of a neutral particle and the magnitude of the effective cross section σ_{1-1} is observed. It may be anticipated that the same correlation will be true for the processes of the type $A \rightarrow A^-$, even though it has been shown by Dukel'skii and Zandberg[14] that it does not appear for the reverse processes $A^- \rightarrow A$.

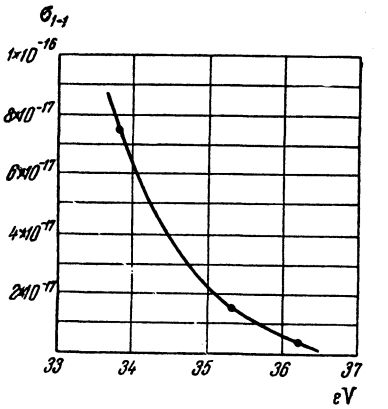

FIG. 4. The dependence of the cross section for the capture of two electrons on the absolute magnitude of the resonance defect $|\Delta E|$.

TABLE VI

Process	Gas	Energy of ions in kev	Electron affinity in ev	ΔE in ev	σ_{1-1} in cm^2
$O_1^+ \rightarrow O_1^-$	H_2	22.6	2.2	—33.8	7×10^{-17}
$H_1^+ \rightarrow H_1^-$	H_2	21.6	0.75	—35.3	1.5×10^{-17}
$O_2^+ \rightarrow O_2^-$	H_2	18.0	0.7	—36.4	0.4×10^{-17}

**The quantity $E_{pot} = e^2/R = 18$ ev, since the internuclear distance R is equal to 0.8 Å [12] for H_2 molecule in its ground state.

***The magnitude of the electron affinity of oxygen is calculated by Evans and Uri[13] from the Born-Haber cycle for the crystals KO_2, RbO_2 and CsO_2.

[12] Handb. d. Phys. **23**, part 1, p. 114 (1933)

[13] M. G. Evans and N. Uri, Trans. Farad. Soc. **45**, 224 (1949)

In the collision of fast ions with oxygen molecules, the process of exchange of two electrons may lead to the formation of various slow particles, namely: in the process $O_1^+ + O_2 \rightarrow O_1^- + O_2^{++}$ a slow, doubly charged, molecular ion of oxygen appears, while in the process $O_1^+ + O_2 \rightarrow O_1^- + O_1^+ + O_1^+$ two

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

slow, singly charged oxygen ions O_1^+ are formed. Analogous possibilities are present in collisions of fast ions with the nitrogen molecules.

It is not possible to compute the resonance defect for the latter process since the potential energy of two ions O_1^+ or N_1^+ which are formed by removal of two electrons from the oxygen or nitrogen molecules is not known. If the process takes place by means of a formation of slow O_2^{++} or N_2^{++} ions, then the calculation of the resonance defect necessitates knowledge of the second ionization potential of the molecules O_2 or N_2.

Hagstrum and Tate[5] gave the ionization potentials of ions O_2^{++} and N_2^{++} as 50 ±0.5 ev and 49.5 ±0.5 ev, respectively. Using these numbers, it is possible to compute the resonance defect for the processes involving exchange of two electrons between the ions O_1^+ and O_2^+ on the one side and the molecules O_2 and N_2 on the other.

Tables VII and VIII give the values of the resonance defect and the effective cross sections for the processes $O_1^+ \to O_1^-$ and $O_2^+ \to O_2^-$ in three gases.

On the basis of the data given in Tables V, VI and VII the following conclusions can be made:

1. The resonance defect has a large positive value in all of the investigated processes involving exchange of two electrons.

2. For processes involving capture of two electrons by various ions from the molecules of the same gas the effective cross section increases with a decrease of the absolute value of the resonance defect.

3. For processes involving the capture of two electrons by the same ion from molecules of three different gases whose resonance defects were equal within the limits of experimental error, the effective cross sections were also equal.

How general these conclusions are is difficult to judge until measurements are carried out for a large number of ion-molecule pairs with various values of resonance defect. To enlarge the range of numerical values of the resonance defect in processes involving a two electron exchange, it will be necessary to investigate not only the processes of the type $A^+ \to A^-$, for which the resonance defect will always have a sufficiently large

TABLE VII

Process	Gas	ΔE in ev	Energy of ions in kev	σ_{1-1} in cm^2
$O_1^+ \to O_1^-$	H_2	—33.8	15.0	0.9×10^{-16}
	O_2	—34.2	13.7	0.7×10^{-16}
	N_2	—33.7	14.0	0.5×10^{-16}

TABLE VIII

Process	Gas	ΔE in ev	Energy of ions in kev	σ_{1-1} in cm^2
$O_2^+ \to O_2^-$	H_2	—36.4	18	4.1×10^{-18}
	O_2	—36.8	18	5.1×10^{-18}
	N_2	—36.3	18	4.9×10^{-18}

negative value, but also processes of the type $A^{++} \to A$ (neutralization of doubly charged ions), for which the resonance defect may have small positive and negative values, or even be equal to zero.

The apparent lack of a strong dependence of the effective cross section of the process $O_1^+ \to O_1^-$ on ion energy (cf. Table I) is evidently connected with the fact that the energy interval investigated in the present work is not far from the energy for the maximum effective cross section.

As was shown previously by Hasted[15], position of the maximum on the curve giving the dependence of the effective cross section for single electron exchange on the ion energy agrees well with the

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

Massey criterion [16]

$$\frac{a|\Delta E|}{h\nu} = 1 \qquad (6)$$

where ΔE is the resonance defect, h is the Planck constant, v is the velocity of the ion and a, equal to 7×10^{-8} cm, is the separation between the colliding particles at which the interaction forces become important (effective collision radius).

From Eq. (6) follows the relationship

$$V_{max} = 3{,}04 \cdot 10^{16}\ a^2 \cdot M_0 (\Delta E)^2, \qquad (7)$$

where V_{max} is the velocity of the ion corresponding to the maximum effective cross section, expressed in volts. Here M_0 is the mass number of the ion and ΔE is the resonance defect in electron volts.

If we assume that for the process $O_1^+ \rightarrow O_1^-$ the constant a has the same value 7×10^{-8} cm as in the processes of one electron exchange, then for ions O_1^+ with energy 15 kev the quantity $a\Delta E/h\nu \approx 14 \gg 1$ and $V_{max} = 2.75$ mev.

It is well-known that the equation $a\Delta E/h\nu \gg 1$ is a condition for adiabatic atomic collision and consequently, if it were satisfied for the process $O_1^+ \rightarrow O_1^-$ there would be a ground for considering the collision of O_1^+ ions with molecules H_2, O_2 and N_2 as adiabatic in the energy range studied. However, the effective cross section for such an adiabatic collision process should increase rapidly with the increase in the ion energy. There was no such increase in our work. Thus, the value $a = 7 \times 10^{-8}$ cm used for the process $O_1^+ \rightarrow O_1^-$ must be considered too large.

If we use $a = 10^{-8}$ cm, then $V_{max} = 56$ kev, according to Eq. (7). The energy interval investigated was in a region of a flat maximum, where a comparatively slow increase of effective cross section should be observed with increase in the energy of the ions. As is evident from Table I, the effective cross section σ_{1-1} has a small tendency to increase with increases in the energy of O_1^+ ions.

If $a = 10^{-8}$ cm, we obtain from Eq. (7) $V_{max} \approx 4$ kev for the process $H_1^+ \rightarrow H_1^-$ in hydrogen. With energies of the order of several tens of kev for H_1^+ one should then observe a decrease in the effective cross section for process $H_1^+ \rightarrow H_1^-$ with an increase in the ion energy. The experimental results, given in Table 2 of the previous work [8] show that the effective cross section of the process $H_1^+ \rightarrow H_1^-$ in hydrogen, in the energy interval 13 to 31 kev, indeed decreases with increase in the H_1^+ ion energy.

The above considerations, of course, cannot be considered a conclusive proof of appropriate application of the Massey criteria for determination of the maximum effective cross section of a process involving exchange of two electrons. For a fundamental judgment on this matter it will be necessary to carry out careful measurements of the dependence of the effective cross section for processes involving two electron exchange on the ion energy in a broad interval of energies and for a large number of ion-molecule pairs.

In conclusion, we would like to express our appreciation to Professor A. K. Val'ter for his constant interest and attention to this work.

[16] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena*, Oxford, 1952

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