CONCLUSIONS

On the basis of the experimental investigations reported here we propose the following:

1. From the example of positive Cs ions with Ni atoms for the case $V_i < \varphi$, $m_1 < m_2$ it has been shown that (a) there is virtually no secondary ion-electron emission from a pure cold (300° K) nickel surface or a heated (1350° K) nickel surface; (b) within the accuracy of these experiments the secondary ion emission contains no scattered Cs ions. At high temperatures the secondary ion emission from a pure nickel target consists only of evaporated ions which appear at the surface after diffusion.

2. From the example of positive Ba ions with Mo atoms for the case $V_i > \varphi$ and $m_1 < m_2$ it has been shown that (a) within an accuracy of about 1 percent there is no secondary ion-electron emission from a pure cold (300° K) molybdenum surface or a heated (1300° K) molybdenum surface; (b) within the accuracy of the experiments there is no secondary ion emission of any kind.

3. A qualitative examination of the results leads to the conclusion that secondary ion emission results from multiple individual scattering of ions which penetrate deep into the target and interact with target atoms.

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FORMATION OF NEGATIVE H^- IONS IN COLLISIONS OF ELECTRONS WITH HYDROGEN MOLECULES

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The formation of H^- ions has been observed when electrons collide with H_2 molecules. In the curve of H^- ion yield as a function of electron energy there is a sharp maximum at 14.5 ev, attributed to the resonance capture of electrons by the H_2 molecules. The formation of H^- ions at higher electron energies apparently results from the dissociation of H_2 molecules into positive and negative ions.

WHILE studying the ionization of hydrogen molecules by electron bombardment, Lozier[1] found negative ions present in his apparatus; these were formed in a narrow range of electron energy, with maxima occurring at 6.6 and 8.8 ev. Mass-spectrometric analyses carried out by Bleakney showed that they were atomic ions, H^-.

The number of ions so formed was extremely small, and Lozier suspected that they came, not from H_2 molecules, but from molecules of H_2O which might have entered the apparatus as an impurity in the

hydrogen. And, in fact, when water vapor was added to the hydrogen these same negative ions were formed in much larger numbers. This established the fact that interactions between electrons and water vapor could give rise to H^- ions; but the possibility that these ions could also be formed by electrons colliding with H_2 atoms remained unexplored.

The aim of the present work was to study this second possibility under conditions where the masking effect of water vapor was removed as completely as possible, using a highly sensitive method of detecting the negative ions.

The experiments were conducted in glass apparatus (a mass spectrometer) with no stopcocks or massive metal parts. The ions were obtained by electron bombardment in an ion source of the usual type. The cathode was made of thoriated tungsten, and was kept below temperatures at which hydrogen could dissociate on its surface. The electron beam entered the ionization chamber through a 1×6 mm slit, and was kept from spreading by a magnetic field of about 150 gauss.

In order to make full use of the ions produced in the source, the ionization chamber slit and the entrance slit to the mass analyzer were both made 3 mm wide. The slit in front of the collector had a width of 3.5 mm. With this arrangement, the resolving power of the mass spectrometer was still sufficient to distinguish between ions of mass 16 and mass 18.

To measure ion currents at the exit of the mass spectrometer, an electron multiplier was used, with a multiplication factor of approximately 1000 for H^- ions with energies of 1000 ev. The output of the electron multiplier was connected to an electrometer amplifier with a sensitivity of 10^{-15} amp/mm. With this arrangement it was therefore possible to measure ion currents as low as 10^{-17} amp.

Special attention was paid to the purification of the hydrogen introduced into the ion source. Gaseous hydrogen was obtained from the liquid phase, filtered through a heated palladium tube, and then passed through a glass helix cooled with liquid nitrogen before entering the apparatus.

Mercury pumps were used to evacuate the apparatus, the mercury vapor being condensed in traps cooled with liquid nitrogen. Before the measurements, the entire apparatus was baked out at a temperature of 400°C for several hours.

A series of preliminary experiments was carried out in order to explain the presence of a "background" of H^- ions in the apparatus. After being pumped down to the limiting vacuum (but with no baking-out) the apparatus produced H^- ions when the electron accelerating potential in the ion source was between 6 and 13 volts. Upon baking out the apparatus, the number of H^- ions (arising, apparently, from the presence of traces of water in the apparatus) decreased to an unobservable value.

After removal of the residual H^- ions by prolonged baking of the apparatus, hydrogen was admitted into the ionization chamber. Its pressure could not be measured within the chamber itself; but a thermionic gauge sealed into the hydrogen inlet tube indicated a hydrogen pressure of a few times 10^{-4} mm Hg.

When hydrogen was admitted into the ionization chamber, H^- ions appeared in the apparatus in larger numbers and over a wider range of electron energies than in the case of the preliminary "background" experiments.

At a constant value of hydrogen pressure (on the order of 10^{-4} mm Hg) we measured the negative H^- ion currents at the mass spectrometer collector for electron accelerating voltages in the ion source of 2 to 40 volts. Simultaneously, for each value of accelerating voltage we measured the electron current in the ionization chamber. We calibrated the zero of the electron energy scale by measuring the yield curve for negative O^- ions from the collision of electrons with O_2 molecules. Using Thorburn's data[2] for the appearance potential of negative O^- ions from O_2, we determined the correction to be applied to the accelerating potential difference. This correction was found to be -0.5 volts. We used the same value of the correction over the entire interval of electron energies studied.

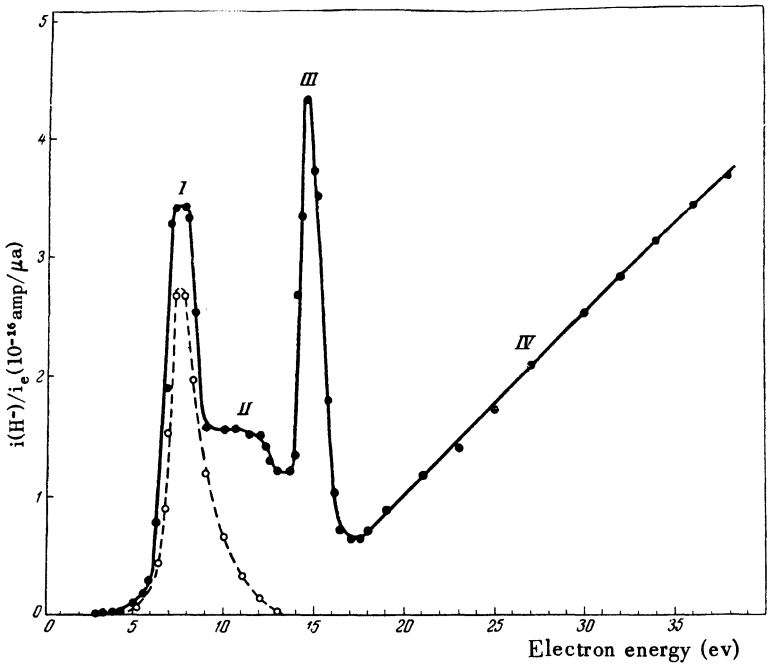
The figure shows the curve of H^- ion yield obtained from our studies on hydrogen. Electron energy is plotted along the horizontal axis, in electron volts, including the zero-point correction. The ordinate is the ratio of H^- ion current $i(H^-)$, at the mass spectrometer collector, to the electron current i_e in the ion source.

In the region of electron energy investigated, the yield curve for H^- ions shows three maxima, marked I, II, and III on the figure, and a steadily rising portion on the right-hand side, labelled IV. In all these regions of the curve we have measured the dependence of the ion current $i(H^-)$ on the hydrogen pressure. At maximum III, and for a series of points in region IV, the H^- ion current varies linearly with the hydrogen pressure between 1×10^{-5} and 2×10^{-4} mm Hg. The height of maximum I was not

proportional to the pressure. When the hydrogen was pumped out of the apparatus, maximum III and region IV completely disappeared at once. Maximum I (and, to a lesser extent, maximum II) could be observed for some time, even after the hydrogen had been removed from the apparatus.

Tests were made of the dependence of H^- ion current on the electron current density j_e in the ionization chamber. When j_e was between 0.15 and 3 $\mu a/mm^2$, this dependence was linear.

On the basis of the above observations, the curve in the accompanying figure can be explained in the following way. Maximum I is apparently not connected with the ionization of hydrogen molecules. The location of this maximum on the electron energy scale (7.2 ev) coincides with the location of the maximum in the curve for the formation of H^- ions by the interaction of electrons and H_2O molecules.[3] Apparently maximum I owes its existence to traces of water which we were unable to remove completely from the apparatus. This assumption is supported by the fact that when hydrogen is introduced into a previously baked-out apparatus, H_2O^+ ions appear in the spectrum of positive ions. For a conclusive test, an experiment was made with water vapor in the apparatus. An intense group of H^- ions appeared, whose maximum coincided in shape and location with the one found in hydrogen. The yield curve of the H^- ions obtained from water vapor in the apparatus is shown as a dashed line in the figure.



Yield curve for H^- ions obtained by introducing hydrogen into the ion source of a mass spectrometer. Hydrogen pressure less than 2×10^{-4} mm Hg; electron current density 1.5×10^{-6} amp/mm^2. The absolute values of the current $i(H^-)$ are only approximate. The dashed line is the yield curve for H^- ions obtained with water vapor. The ordinates of this curve are reduced by an arbitrary factor; the scale on the ordinate axis does not refer to it.

All the facts enumerated above force one to conclude that maximum I of the hydrogen curve is to be attributed to H^- ions formed from H_2O molecules. The appearance of these ions when using hydrogen which has been subjected to elaborate purification could be explained by the formation of water molecules within the apparatus itself, as a result of the hydrogen reacting with oxide films on the metal parts of the ion source.

Maximum III and the portion IV of the curve in the figure are therfore to be attributed to H^- ions formed by the collision of electrons with H_2 molecules. Evidence for this conclusion is provided by the direct proportionality between the number of ions and the hydrogen pressure, their disappearance when hydrogen is removed from the apparatus, and also the absence of H^- ions when water vapor is bombarded with electrons in this energy range. It seems very unlikely that these ions could be formed from some other impurity in the hydrogen.

Maximum III is similar in shape to the maxima obtained when other negative atomic ions are formed by resonance capture of electrons by diatomic molecules. It is therefore natural to assume that maximum III is due to the process

$$H_2 + e \rightarrow (H_2^-) \rightarrow H^- + H. \qquad (1)$$

The difference in energy between the system H_2 + e and the system H^- + H can be found from the difference between the dissociation energy of a hydrogen molecule into atoms (4.4 ev) and the electron affinity of a hydrogen atom (0.75 ev), and is equal to 3.7 ev. The fact that maximum III lies at a considerably higher electron energy than this (14.5 ev) points to one of two possibilities: (1) either the H^- ion and the H atom carry away some kinetic energy (about 5 ev at the most) or (2) the H atom is formed in an excited state.

In a paper by Eyring, Hirschfelder and Taylor[4] the potential curve is calculated for the system H + H^-

(i.e., the H_2^- ion). The minimum in this curve lies at a considerably higher internuclear distance (about 1.8 A) than the minimum in the potential curve for the H_2 molecule (0.76 A). The internuclear separation corresponding to the fundamental vibrational level of the H_2 molecule must correspond to the steeply rising portion of the potential curve for the H_2^- ion. But if this is so, then the process of resonance capture of electrons by a hydrogen molecule requires the expenditure of a considerably greater amount of energy than the dissociation energy of the H_2^- ion, and leads to the appearance of an H^- ion with considerable kinetic energy.

The right-hand portion of the curve in the figure, denoted by the number IV, has a shape reminiscent of the yield curves of negative ions in the dissociation of a diatomic molecule into positive and negative ions. Hence we may assume that, for electron energies corresponding to region IV, the process which takes place is

$$H_2 + e \rightarrow (H_2)^* + e \rightarrow H^+ + H^- + e. \quad (2)$$

The H_2 molecule in its ground state appears to be an atomic molecule, and dissociates into atoms upon electron bombardment. However, a series of excited states exists, as well as the ionized state.[5] If the transition to such a state is accompanied by the transfer of sufficient energy to dissociate the molecule, process (2) would be able to take place.

The dissociation energy of an H_2 molecule into H^+ and H^- ions is equal to 17.2 ev. Therefore process (2) cannot go for electron energies less than this value. In the curve shown in the figure, maximum III and the slope region IV apparently overlap. The location of the minimum between them (17 ev) is not in contradiction with this value for the energy threshold of process (2).

The curve shows still another maximum, labelled II, less pronounced than maxima I and III. Not enough data is available for us to be able to interpret this.

The apparatus used in this work did not permit the determination of an effective cross-section for the process of ion formation by the collision of electrons with gas molecules. However, comparing the yield of H^- ions with the yield of H^+ ions, and using the data of Tate and Smith[6] for the effective cross-section for ionization of H_2 molecules by electron impact, we can estimate in a very crude way the effective cross-section for process (1). At the 14.5 ev maximum, the cross-section comes out to be of the order of 10^{-21} cm^2.

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