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FORMATION OF NEGATIVE HYDROGEN IONS ON AN INCANDESCENT TUNGSTEN SURFACE

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Formation of H^- ions on an incandescent tungsten surface has been observed. The temperature dependence of the ratio of the negative-ion current to the electron current in the 2600 — 2900°K range yields a value of 0.8 ± 0.1 ev for the electron affinity of the hydrogen atom.

ACCORDING to quantum-mechanical calculations, the electron-affinity energy of the hydrogen atom is 0.754 ev.[1] Using this value, it is easy to calculate from the Saha-Langmuir formula that the probability of alpha capture of an electron by a hydrogen atom, evaporated from the surface of tungsten at 2400°K, is 6×10^{-9} (assuming the work function of the tungsten to be 4.5 ev).

In the case of such small α, one must take into account, in a study of the negative surface ionization, the possibility of formation of negative ions not only on the surface of the cathode, but also under the surface, via interaction between the thermionic electrons emitted from the cathode and the gas molecules. In the case of hydrogen, the processes in the volume may be: 1) formation by impact of H^- ions from molecules H_2, and also from the H_2O molecules that are always present in the residual gas in the equipment; 2) radiative capture of slow electrons by the hydrogen atoms, produced upon dissociation of the hydrogen molecules on the surface of the incandescent tungsten.

We have shown earlier[2] that H^- ions are not produced from H_2 and H_2O molecules by collision with electrons of energy less than 5 ev. To eliminate such H^--ion production it was enough to create in the surface-ionization experiments conditions under which the electrons emitted by the cathode could not acquire an energy greater than 5 ev. Under the conditions of our experiment, the effect of radiative capture was small compared with surface ionization, and could therefore be neglected.*

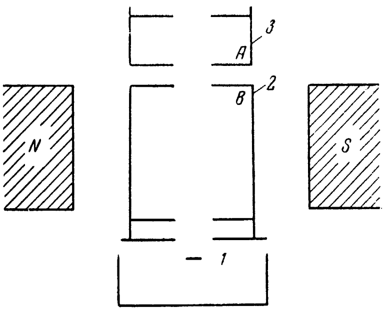

FIG. 1. Diagram of the ion source. 1 — tungsten ribbon 1.5 × 10 mm (cathode), 2 — cylinder (anode), 3 — mass-analyzer tube.

Figure 1 shows schematically the apparatus used. The cathode was an electrically-heated incandescent tungsten ribbon 1. The temperature of the central portion of the ribbon was measured with an optical pyrometer. The potential difference V used to draw out the electrons and negative ions was applied between the cathode 1 and cylinder 2. This potential difference was not more than 4 volts, to prevent the electrons that enter cylinder 2 together with the ions from producing H^- ions in this volume. The electrons were deflected by a transverse magnetic field of ~ 60 oe to the wall of cylinder 2 and were kept out of the space AB, where the negative ions (which were hardly moved by the magnetic field) were accelerated to 1000 ev before entering the mass analyzer 3. The ion current was measured with an electron multiplier connected to an electrometer amplifier.[2]

We first ascertained what occured in the apparatus with the cathode incandescent, but in the absence of hydrogen. For this purpose, after establishing maximum vacuum (1×10^{-6} mm Hg) in

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*The ratio of the H^--ion current due to radiative capture to the current due to surface ionization is approximately $4n_e\bar{Q}d/\bar{v}\alpha$, where n_e is the number of electrons emitted from 1 cm² of cathode surface per second, $\bar{Q}$ the mean value of the effective cross section for radiative capture (at an electron energy of 1 ev, $Q = 2 \times 10^{-22}$ cm² at the maximum[3]), d the length of the path on which the capture can take place, $\bar{v}$ the mean velocity of the H atoms evaporated from the cathode, and α is the degree of surface ionization. At a cathode temperature of 2700°K and d = 0.1 cm, this ratio was less than 0.02.

the equipment and adjusting the mass analyzer for H^--ion registration, we measured the ion current for various values of the drawing potential V. At a cathode temperature of 2300° K, no H^- ions could be observed for V ranging from 0.1 to 3.5 v. The H^--ion current became measurable at V = 3.7 volts and increased rapidly with increasing V. These ions were apparently due to the interaction between the electrons and the traces of water vapor in the apparatus.

When hydrogen was admitted to the instrument (pressure $\sim 10^{-4}$ mm Hg) we observed H^- ions even at drawing potentials from 0.5 to 3.5 volts. Under these conditions we observed clearly the effect of surface ionization, undistorted by the interaction of the electrons with the H_2O and H_2 molecules. We measured in this interval of V the dependence of the H^--ion current I_i at the output of the mass spectrometer on the temperature T of the cathode, within the range from 2200 to 2900° K. Simultaneously we measured the electron current I_e in cylinder 2. Figure 2 shows one of the curves obtained for the dependence of the ratio I_i/I_e on the cathode temperature. The current I_i was on the order of 10^{-16} amp; the noise level was smaller by a factor 10 − 20.

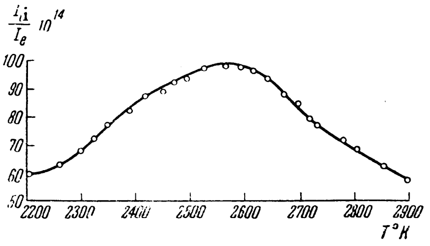

FIG. 2. Dependence of the ratio of the H^--ion current to the electron current on the cathode temperature (hydrogen pressure 2×10^{-4} mm Hg, V = 3.0 v).

It is known that observation of surface ionization with production of negative ions can be used to determine the electron affinity ϵS of an atom. At $\alpha \ll 1$, the negative-ion current density is given by

$$i_i = \varepsilon n_0 A \exp\{\varepsilon (S - \varphi^*) / kT\}, \tag{1}$$

where n_0 is the number of atoms evaporated from 1 cm^2 of cathode surface per second, and $\epsilon\varphi^*$ is the effective work function of the Saha-Langmuir formula for a polycrystalline surface. The saturation electron current density is determined from the Richardson-Dushman formula

$$i_e = BT^2 \exp(-\varepsilon\varphi_R / kT). \tag{2}$$

In the case of an inhomogeneous surface the electron emission, like the emission of negative ions, is predominantly from sections that have the low work function. This may justify setting φ^* in Eq. (1) equal to φ_R in Eq. (2). After having done this and after taking the ratio i_i/i_e, we can eliminate φ

$$\frac{i_i}{i_e} = \frac{\varepsilon n_0 A}{BT^2} \exp(\varepsilon S / kT), \tag{3}$$

hence

$$\log_{10} \frac{i_i T^2}{i_e} = \log_{10} \frac{\varepsilon n_0 A}{B} + \frac{5.04 \cdot 10^3}{T} S. \tag{4}$$

Ionov[4] confirmed experimentally the correctness of Eq. (4) in the case of formation of negative iodine ions on the surface of tungsten. Under the conditions of our experiments, the electron current was far from its saturation value (2 or 3 orders of magnitude less). It must be assumed, however, that (3) and (4) should be valid also in the absence of saturation, since the energy distributions of the ions and electrons emitted from the surface of the incandescent metal are the same.[5]

It is seen from Fig. 2 that in the interval from 2200 to 2550° K the ratio I_i/I_e increases with temperature. At these temperatures, apparently, the coefficient of dissociation of hydrogen molecules on the surface of tungsten is still less than unity and therefore n_0 depends on the temperature. To determine the energy of the electron affinity from (4), we used the temperature interval from 2600 to 2900° K, in which n_0 can be assumed constant. In this temperature interval, the points corresponding to the value of $\log_{10}(I_i T^2/I_e)$ as functions of $5.04 \times 10^3/T$ fit well a straight line. The value of the energy of electron affinity ϵS of the hydrogen atom, determined from the slope of this line, was found to be 0.8 ± 0.1 ev.

The correctness of the value obtained (in spite of its low accuracy) can be considered as a successful test of our method. In this connection, prospects are uncovered of using surface ionization to determine the electron affinities of other atoms, for which this quantity is of the same order of magnitude as for the hydrogen atom.

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Translated by J. G. Adashko
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