

cm² degree². The values of work function ϕ_0 corresponding to the above values of b_0 are 0.75 volt and 0.905 volt.

A great deal of the work in connection with these measurements was performed by Mr. T. T. Eaton, and to him should go the

credit for first noticing the very high efficiencies here reported.

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September 24, 1930.

Negative Ions in Hydrogen and Water Vapor

In the course of the writer's¹ investigation of the positive ions produced in hydrogen by electron impact the presence of negative ions was observed. These were indicated by the appearance of two sharp peaks when the negative ion current was studied as a function of the electron velocity. They were suspected of being H⁻ ions and Bleakney upon re-examining hydrogen in his mass spectrograph² observed the ions and found them to have the e/m value of H⁻. The maxima of the peaks, corresponding to the maxima for the efficiency of their production occurred at electron velocities of 6.6 and 8.8 volts. These negative ions were found to possess kinetic energy, presumably acquired in the dissociation process which accompanies their formation. The velocity of the ions of the 6.6-volt group was about 1.5 volts while that of the 8.8-volt group could not be accurately determined because there were so few of them.

The negative ions were so few in number that it was thought they might be due to an impurity in the hydrogen—most probably water vapor. They persisted, however, after all reasonable precautions were taken to eliminate possible sources of the vapor. On the other hand when water vapor was admitted to the tube and the hydrogen removed the same H⁻ ions appeared in much greater abundance, and a determination of their velocities could be made.

A preliminary study of their kinetic energies showed that the velocity of the 6.6-volt group was about 1.5 volts while that of the 8.8-volt group was about 3.2 volts. This would mean that if they are formed by dissociation of H₂O⁻ the energy of the dissociated system is in the first case 5.1 volts above the normal H₂O state and in the second case 5.6 volts.

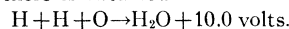
Bleakney has informed me that he has obtained H⁺ ions from H₂O at a minimum electron velocity of 19.2 volts. If we assume that these ions result from the dissociation of H₂O⁺ into H⁺+OH, we find, by adding an electron to the H⁺ that the energy of the system H+OH is 5.7 volts above the normal H₂O state.

Less than this by the electron affinity of the H atom would be the energy of the system H⁻+OH. Assuming that this is the system which results from the 6.6-volt electron impact we find the value 0.6 volts for the electron affinity of the hydrogen atom. It is interesting to note that Hylleraas³ gives 0.7 volts for this quantity.

The second group of H⁻ ions appearing at 8.8 volts may possibly result from the dissociation of H₂O⁻ into H⁻, excited, and OH. The energy of this system would be expected to lie above the energy of H⁻+OH by the amount of the excitation potential of H⁻ which would be in the neighborhood of 0.6 volts. (H⁻ would be expected to resemble He with an excitation potential near its ionization potential.) Actually its energy is 0.5 volts above the energy of the system resulting from the 6.6 volt impacts.

On the other hand if it be true that the H⁻ ions are formed by dissociation of H₂⁻ the energy of the system resulting from the 6.6-volt impacts would lie 3.6 volts above the normal state of the H₂ molecule and that resulting from the 8.8-volt impacts 2.4 volts above. The former might be regarded as the heat of dissociation of H₂ less the electron affinity which would give 0.8 volts for the affinity. There is no reasonable explanation of the energy of the state resulting from the 8.8-volt impacts.

Upon combining with thermochemical data the known heats of dissociation of H₂ and O₂ there is obtained



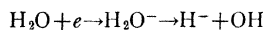
From the above consideration that H+OH lies 5.7 volts above the normal state of H₂O we see that the heat of dissociation of the OH molecule would be 4.3 volts. The writer has been unable to find any data concerning this.

¹ See paper in this issue.

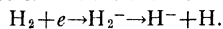
² W. Bleakney, Phys. Rev. **34**, 157 (1929); and Phys. Rev. **35**, 139 (1930).

³ E. A. Hylleraas, Zeits. f. Physik **63**, 291 (1930).

In conclusion I believe in the reality of the transition



but am not certain of the transition



It is hoped that more precise measurements in the future will throw additional light on the matter.

One interesting feature of the phenomena is the extremely narrow range of electron

velocities which are capable of producing these negative ions. The range is but little wider than the normal velocity distribution in the electron beam, as though the electrons, to produce a negative ion of a given type, were compelled to have a perfectly precise velocity.

W. WALLACE LOZIER

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October 6, 1930

Wave Mechanics of Deflected Electrons

In a letter¹ appearing in the September 1 number of the Physical Review, Carl Eckart makes the assertion that the major conclusion of my paper² on the above subject is incorrect, and that the difference between $(e/m)_{\text{defl}}$ and $(e/m)_{\text{sp}}$ cannot be explained as a difference between wave and classical mechanics. He attributes the alleged error in my conclusion to the interpolation method of calculating the mean radius of curvature, admitting that the rest of the analysis is correct.

I had not neglected to verify the interpolation formula in question by direct calculation of the mean radius of curvature for the states $k=0$ and $k=1$. Shortly after seeing Dr. Eckart's letter, however, I noticed that the method of interpolation which I had employed is unnecessary, since the mean radius of curvature may be calculated rigorously from Eq. (43) of my paper. This equation does not lead to an infinite series even when p is fractional since k is a positive integer. For the mean radius of curvature it gives

$$\begin{aligned} \bar{\rho} = & \frac{(\pi/2)^{1/2}}{s!} \left[\left(s - \frac{1}{2} \right)! \left(2s + \frac{1}{2} - k \right) \right. \\ & + \frac{(s-3/2)!k(2s-\frac{1}{2}-k)}{2^2[1!]^2} \\ & + \frac{(s-5/2)!k(k-1)(10s-3/2-9k)}{2^4[2!]^2} \\ & \left. + \dots \right]. \end{aligned}$$

For the first order correction we need only the first two terms. Using S and K as defined in my paper

¹ Carl Eckart, Phys. Rev. **36**, 1014 (1930).

² Leigh Page, Phys. Rev. **36**, 444 (1930).

$$\bar{\rho} = \left(\frac{\pi}{2} \right)^{1/2} \frac{(s - \frac{1}{2})!}{s!} S \left[1 - \frac{K+1}{4S} \right],$$

and applying Stirling's formula

$$\bar{\rho} = S^{1/2} \left[1 - \frac{K-1}{4S} \right],$$

which is (except for the negligible -1 in the numerator of the second term) the same formula as obtained by interpolation. Therefore it is clear that Dr. Eckart was mistaken in his assertion that I had been led to incorrect results by the method of interpolation used.

Dr. Eckart bases his criticism of my work on a supposed disagreement between my conclusions and those obtained by Kennard³ in an earlier paper. Working with the transformation theory of Dirac and Jordan, Kennard obtains the coordinates of the center of a wave packet moving in a magnetic field in terms of initial coordinates and momenta and notices that he is led to a formula identical with that given by classical electrodynamics. He does not, however, obtain the radius of curvature in terms of the energy, which is the significant relation from the experimental point of view. Therefore there does not seem to be any necessary conflict between Kennard's conclusions and mine.

LEIGH PAGE

Yale University
New Haven, Conn.
October 3, 1930

³ E. H. Kennard, Zeits. f. Physik **44**, 347 (1927).