for both $Q_1$ and $Q_2$ at a number of different electron energies. Relative-cross-section measurements, normalized to these absolute values, were used to complete the experimental curves shown in Fig. 1. This figure also presents the theoretical curve for $Q_1$ as calculated by Seaton.[5]

Several comments in regard to our measurements are appropriate. First, relative-cross-section measurements of $Q_T$ confirm the shape of Tate and Smith's curve and disagree with the more recent measurements of Craggs, Thorburn, and Tozer.[6] Second, the ratio of atomic ions to molecular ions formed in collisions of electrons with oxygen molecules increases rapidly from zero at a threshold energy of 18.5 ev, reaches a maximum at about 150 ev, and decreases slightly to a value which remains constant at higher energies. Third, at energies in excess of about 100 ev, only about two-thirds of the ions formed in electron collisions with oxygen molecules appear to be $O_2^+$ ions. Fourth, the cross section for ionization of the atom near threshold increases linearly with the excess energy of the incident electron. Fifth, the agreement between the measured and calculated cross sections for ionization of the atom appears quite satisfactory.

[5] M. J. Seaton, preceding paper [Phys. Rev. **113**, 814 (1959)].
[6] Craggs, Thorburn, and Tozer, Proc. Roy. Soc. (London) **A240**, 473 (1957).

PHYSICAL REVIEW VOLUME 113, NUMBER 3 FEBRUARY 1, 1959

# Formation of $H^-$ Ions by Electron Impact on $H_2$

G. J. SCHULZ
*Westinghouse Research Laboratories, Beulah Road, Churchill Borough, Pittsburgh, Pennsylvania*
(Received August 25, 1958)

The cross section for production of $H^-$ ions by electron impact in hydrogen gas is studied. The cross section exhibits a plateau around 10 ev with a value of $1.2\times10^{-20}$ cm$^2$. A sharp peak with a cross section of $3.5\times10^{-20}$ cm$^2$ is observed at $14.2\pm0.1$ ev. The first plateau is associated with the reaction $H_2+e\rightarrow H^-+H$ and the sharp peak with the production of hydrogen atoms in the first excited state, $H_2+e\rightarrow H^*+H^-$.

## I. INTRODUCTION

THE formation of negative $H^-$ ions by electron impact was first reported by Lozier.[1] He found peaks in the negative-ion current at an electron energy of 6.6 and 8.8 ev with hydrogen in the apparatus. Because the observed peaks were small, Lozier attributed these to an impurity. When water vapor was admitted to the apparatus, the peaks appeared at the same energy and were more pronounced. The conclusion that the 6.6-ev peak observed by Lozier is due to $H^-$ formation from $H_2O$ was recently confirmed in a mass spectrometer experiment by Khvostenko and Dukel'skii.[2] With either hydrogen or water vapor in the system, they observed a peak in $H^-$ current at 7.2 ev.[3] In addition, Khvostenko and Dukel'skii observed $H^-$ currents resulting from electron impact on $H_2$ up to 38 ev, with a peak at 14.5 ev, but were able to determine the cross section only approximately.

In the present work, the production of $H^-$ is studied using ultrahigh vacuum techniques. The electron energy scale is established by using the retarding potential difference method,[4] and correcting for contact potentials from the onset of the $H_2^+$ ions. The collection efficiency for negative ions is higher than in either of the two previous experiments so that cross sections can be determined.

## II. EXPERIMENT

A diagram of the tube is shown in Fig. 1. Electrons from the tungsten filament $F$ pass through the electron gun ($P_1$ $P_2$ $P_3$) and are collected, after passage through the collision chamber $C$, by the electron collector $E$. A magnetic field of about 200 gauss prevents electron spreading. The collision chamber, formed by grid $G_1$ is surrounded by a cylindrical grid $G_2$ (90% transparent) and the cylindrical ion collector $M$. The ion collector is mounted on long glass supports so that electrical leakage currents are minimized. The electron gun, using the retarding potential difference method, and its dimensions have been described previously.[5] Electrons are retarded at $P_2$ to zero energy and therefore the potential $V_A$ (see Fig. 1) is the true electron energy except for a small correction for the contact potential between $P_2$ and $G_1$. To reduce contact potentials, all parts of the tube are gold plated. The ion collector is operated a few volts positive with respect to $G_1$ to collect most of the

[1] W. W. Lozier, Phys. Rev. **36**, 1417 (1930).
[2] V. I. Khvostenko and V. M. Dukel'skii, J. Exptl. Theoret. Phys. (U.S.S.R.) **33**, 851 (1957) [translation: Soviet Phys. JETP **6**, 657 (1958)].
[3] The peaks observed at 6.6 and 7.2 ev in the two experiments could be due to the same phenomenon. Uncertainty in the electron energy scale may have caused the discrepancy of 0.6 ev.
[4] Fox, Hickam, Grove, and Kjeldaas, Rev. Sci. Instr. **26**, 1101 (1955).
[5] G. J. Schulz and R. E. Fox, Phys. Rev. **106**, 1179 (1957).

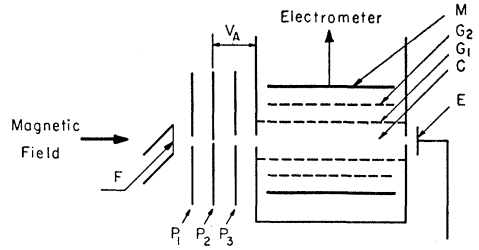


FIG. 1. $F$ is the filament, $P_1$, $P_2$, $P_3$ are the three electrodes constituting the electron gun, $C$ is the collision chamber, $G_1$ and $G_2$ are two concentric cylindrical grids, $M$ is the gold-plated cylindrical ion collector, and $E$ is the collector for electrons in the electron beam.

negative ions produced in the tube. $G_2$ and $G_1$ are at the same potential.

A vacuum system using a copper trap[6] is used. The whole system is baked at 400°C. Although background pressures of $2\times10^{-10}$ mm Hg are obtained without refrigeration, it is necessary to use a liquid air trap in order to reduce the concentration of water vapor produced by the presence of hydrogen and the hot filament in the tube. The liquid air trap refrigerates the manifold of the vacuum system and the pumping arm of the tube so that water vapor produced in the tube is removed efficiently.

## III. RESULTS

The cross section for $H^-$ formation as a function of electron energy is shown in Fig. 2. The solid curve is obtained using liquid air on the trap and is associated with electron collisions in $H_2$. The dashed peak at 6.8 ev is observed with no liquid air and results most probably from water vapor.[7] The apparent cross section at the peak of the dashed curve (with no liquid air) varies with the purity of the hydrogen gas admitted to the system. The magnitude shown in Fig. 2 by the dashed line corresponds to reagent grade hydrogen being introduced directly. When the gas is admitted through a heated nickel leak without refrigeration, the magnitude of the peak at 6.8 ev increases tenfold, and therefore use of the nickel leak was given up. It is possible that the heated nickel leak gives off small amounts of oxygen which form water vapor.

The curve shown in Fig. 2 agrees, in its gross structure, with the curve obtained by Khvostenko and Dukel'skii for production of $H^-$ in a mass spectrometer,[2] and the dashed curve agrees essentially with the shape of the mass spectrometer curve for the production of $H^-$ from $H_2O$.[8]

[6] D. Alpert, J. Appl. Phys. **24**, 860 (1953).

[7] The magnitude of the 6.8-ev peak decreases to its equilibrium value ($7\times10^{-22}$ cm²) within seconds after the trap is filled with liquid air.

[8] The sharper peaks observed in the present experiment result from the small energy spread of the electron beam in the present experiment (0.2 volts). The present value of the water vapor peak, 6.8 ev, compares with 6.6 ev observed by Lozier and 7.2 ev observed by Khvostenko and Dukel'skii.

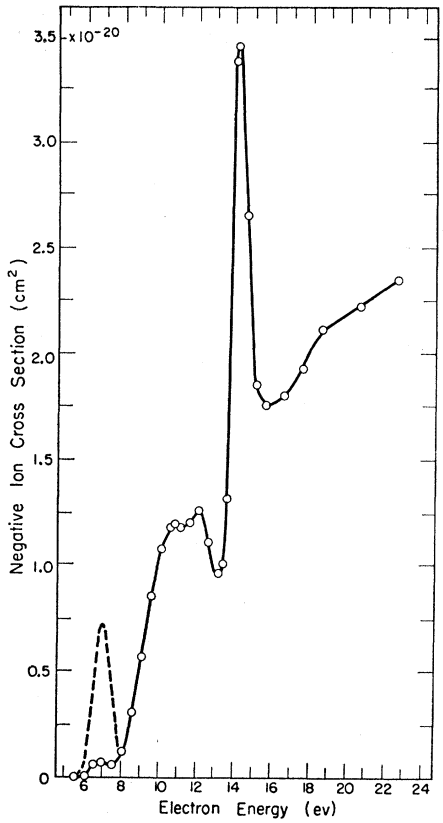


FIG. 2. Negative-ion cross section against electron energy in hydrogen. The solid curve is associated with the reaction $H_2+e\rightarrow H^-+H$ below 13.6 ev and the reaction $H_2+e\rightarrow H^-+H^*$ above 13.6 ev. The simultaneous production of $H^-$ and $H^+$ can occur above 17.2 ev. The formation of negative ions indicated by the dashed curve is obtained when the reagent grade hydrogen is introduced with no liquid air on the trap and is interpreted as the production of $H^-$ from water vapor.

The energy scale is obtained from the onset of the positive ions of hydrogen at 15.56 volts. The correction to the accelerating voltage $V_A$ is 0.2–0.3 volts, and is attributed to contact potentials between the retarding plate $P_2$ and the collision chamber. A retarding experiment on the electron beam confirms the above correction.[9]

[9] Retarding experiments in tubes of the type shown in Fig. 1 must be performed by retarding the electron beam before it enters the collision chamber (by varying $V_A$ around 0 volts) and keeping a fixed electron collection potential of about +2 volts between the electron collector $E$ and the collision chamber electrode. Experimentally it is found that serious errors in the retarding curves result when the electron collector is kept at the potential of the collision chamber electrodes or when the retarding on the beam is performed at the electron collector $E$. Presumably, these limitations are not encountered at high magnetic fields (3000 gauss) as shown by H. Shelton [Phys. Rev. **107**, 1553 (1957)]. Even with the precautions described above, retarding curves are not considered reliable in all cases for determining the contact potential unless checked by a known positive ion threshold. The contact potential measured in a retarding curve is that between plate $P_2$ and the entrance hole to the collision chamber whereas the contact potential desired is that between $P_2$ and the inside walls of the collision chamber ($G_1$). In many cases, the two values are not identical.

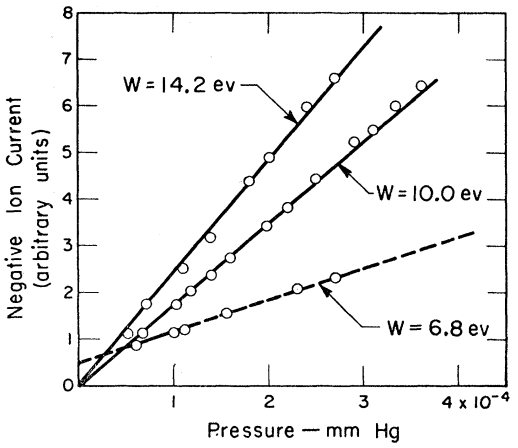


FIG. 3. Negative-ion current against pressure. The electron energy, $W$, for the three curves is indicated. The data for $W=6.8$ ev are taken with no liquid air on the trap.

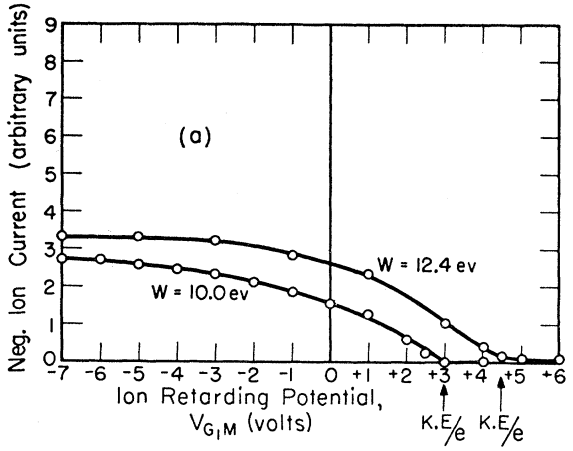


FIG. 5. Retarding curves for negative ions at two values of electron energy, $W$. The intercept of the curves with the abscissa is the kinetic energy of the ions and is indicated by the arrows.

The absolute values of the cross section $Q$ given in Fig. 2 are obtained in two ways; (A) from the experimental ratio of $H_2^+$ and $H^-$ currents at particular electron energies and using Tate and Smith's[10] value for the cross section of $H_2^+$; and (B) from the equation $Q=i_-/(i_eNl)$ where $i_-$ is the negative ion current, $i_e$ is the electron current, $N$ is the gas density, and $l$ is the length of the collision chamber. The two determinations differ by 20%. The cross sections given in Fig. 2 are the mean of the two determinations and the errors afflicting the measurement are estimated at $\pm 30\%$.

Plots of the negative-ion current against pressure (as measured on a calibrated Bayard-Alpert ionization gauge[11]) and electron beam current are shown on Fig. 3 and Fig. 4. The anomalous behavior of the pressure dependence of the 6.8-volt peak should be noted. It indicates that a portion of the 6.8-volt negative-ion peak in the absence of refrigeration (dashed line in Fig. 2) is due to residual gases and a portion due to the formation of water vapor by hydrogen. The formation of other compounds beside water vapor by hydrogen cannot be excluded.[12] Whatever the compound, it is condensed by liquid air. The pressure and current dependence of the $H^-$ current at 10 and 14.2 volts are linear.

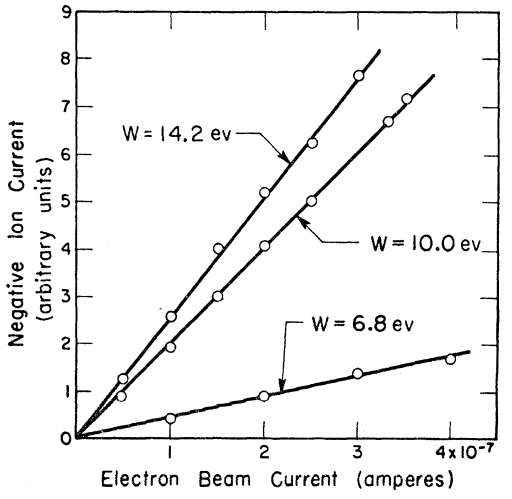


FIG. 4. Negative-ion current against electron beam current. The electron energy, $W$, is indicated.

Figure 5 shows a plot of ion current as a function of the potential between $G_1$ and $M$ for two values of accelerating voltages. The intercept of these retarding curves with the abscissa is marked by the arrows and indicates the kinetic energy of the ions. The kinetic energy, K.E., of the $H^-$ ions resulting from the reaction $H_2+e\rightarrow H+H^-$ is given by[13] $\text{K.E.}=\frac{1}{2}(W-D+A)$, where $W$ is the energy of the incident electrons, $D$ is the dissociation energy, and $A$ is the electron affinity of H. The factor $\frac{1}{2}$ results from the equal division of kinetic energy between the dissociated products, H and $H^-$. Figure 6 shows a plot of K.E. against $W$. The solid line is drawn with a slope of $\frac{1}{2}$ through the point $W=3.7$ ev [for hydrogen, we have $D=4.46$ ev and $A=0.75$ ev, so that $(D-A)=3.7$ ev]. The circles in Fig. 6 are experimental and are obtained from Fig. 5 and similar curves not shown. The experimental points lie on the theoretical line.

## IV. DISCUSSION

We can attribute the portion of the curve of Fig. 2 below about 13.6 volts to transitions from the ground state of $H_2$ to the repulsive part of the $H_2^-$ molecule with dissociation into $H^-$ and H. Transitions to the "bound" state of the $H_2^-$ molecule in the Franck-

[10] J. T. Tate and P. T. Smith, Phys. Rev. 39, 270 (1932).
[11] G. J. Schulz, J. Appl. Phys. 28, 1149 (1957). The emission current of the Bayard-Alpert gauge was reduced to 1 microampere in order to reduce pumping by the gauge.
[12] T. W. Hickmott, Bull. Am. Phys. Soc. Ser. II, 3, 259 (1958).
[13] J. T. Tate and W. W. Lozier, Phys. Rev. 39, 254 (1932).

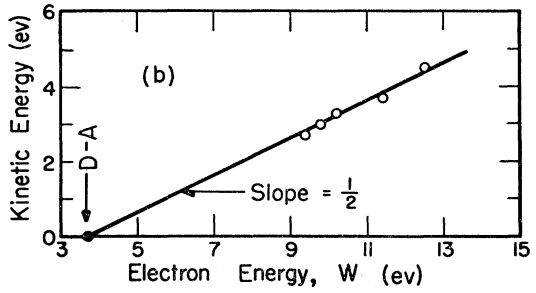


FIG. 6. Ion kinetic energy *vs* electron energy. The open circles are experimental and the closed circle is the value of the difference between the dissociation energy, $D$, and the electron affinity, $A$; $(D-A)=3.7$ ev. The solid curve is drawn through this point with a slope of $\frac{1}{2}$.

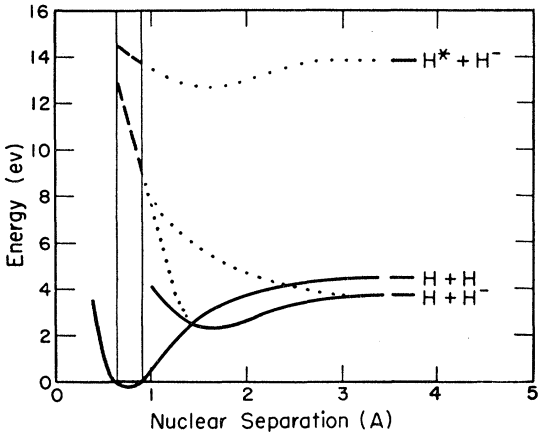


FIG. 7. Potential energy diagram of the $H_2^-$ molecule and its excited state. The curves marked H+H and H+H⁻ are taken from reference 14. The dashed curves are an interpretation of the data in Fig. 2. The dotted curves are speculative extrapolations.

Condon region result in the formation of H+H⁻ since the potential minimum is shifted from the minimum of the ground state.[14] The small plateau of the solid curve at 6.8 ev, of the order of $7\times10^{-22}$ cm², may be due to an impurity, possibly oxygen. An impurity content of 0.03% of oxygen could account for the residual cross section at 6.8 ev.[15]

Above 13.6 volts, a new process for production of negative ions is indicated by the sharp rise of the cross section. The curve peaks at 14.2±0.1 volts. The electron capture process leading to an excited hydrogen atom seems to be involved. The onset of this process, from Fig. 2, occurs about 0.6 ev below the maximum. However, about 0.2 ev tailing must be subtracted from this value, so that the capture process seems to set in at 0.4±0.1 ev below 14.2±0.1 ev, or 13.80±0.2 ev. Energetically, the reaction $H_2+e\rightarrow H^*+H^-$ requires a minimum energy of 13.80 ev, [using the value $(D-A)=3.7$ ev] in agreement with the experiment.

The preceding interpretation of the experimental results is illustrated by the potential energy diagram shown in Fig. 7. Here, the theoretical potential energy curves for $H_2$ and $H_2^-$ are plotted against internuclear separation. The Franck-Condon region is indicated by the vertical lines. The dashed curves intersect the vertical lines at that energy at which the cross section for negative ion production (Fig. 2) drops to $1/e$ of its peak value. The dotted lines indicate some possible shapes of the potential curves and are purely speculative.

The kinetic energy of the H⁻ ion produced in the reaction $H_2+e\rightarrow H^*+H^-$ should be of the order of 0–0.8 ev. Retarding curves on the H⁻ ions show an abrupt change in shape above 13.8 ev, consistent with the expected shape for zero energy ions but a determination of the kinetic energy of these ions was not possible in this energy range because of secondary electron emission from the ion collector due to incident photons.

Above 17.2 ev, the simultaneous production of $H^+$ and H⁻ can occur. This process causes a rising cross section at the highest energies used in this experiment. Khvostenko and Dukel'skii[2] find a linearly rising cross section between 17.2 and 38 volts.

## ACKNOWLEDGMENTS

The author wishes to acknowledge the suggestions offered by A. V. Phelps and T. Kjeldaas during the course of this work.

[14] Eyring, Hirschfelder, and Taylor, J. Chem. Phys. 4, 479 (1936). See also H. S. W. Massey, *Negative Ions* (Cambridge University Press, Cambridge, 1950), p. 27.

[15] Craggs, Thornburn, and Tozer [Proc. Roy. Soc. (London) **240**, 473 (1957)] find a peak in the cross section for production of $O^-$ from $O_2$ at 6.7 ev. Their value for the cross section at this energy is $2.25\times10^{-18}$ cm².