# THE IONIZATION OF HYDROGEN BY ELECTRON IMPACT AS INTERPRETED BY POSITIVE RAY ANALYSIS*

By T. R. Hogness and E. G. Lunn

## Abstract

**Ions produced in hydrogen by electron impact.**—Using an apparatus previously described in which positive ions formed by impact of electrons of definite energy $(V_1+V_2)$ are accelerated and then deflected magnetically around a semi-circle into a Faraday cylinder, the relative numbers of ions of types $H^+$, $H_2^+$ and $H_3^+$ were measured *as a function of pressure* from $<0.1\times10^{-4}$ mm to .006 mm, and also *as a function of impact energy* $(V_1+V_2)$ to 60 volts. At low pressures only $H_2^+$ ions are formed; as the pressure is increased the percentage of $H_3^+$ increases in proportion to the pressure. In the apparatus used, the percentage of $H^+$ increased with pressure but did not exceed 4 percent, while the percentage of $H_3^+$ ions reached 60. These results confirm the conclusions of Dempster and Smyth that the primary process in the ionization of hydrogen is the ionization of the molecule without dissociation. The previously measured ionization potential at 16 volts (confirmed in this work) is that for the formation of $H_2^+$. $H_3^+$ also appears at this potential, but as a result of a secondary process. It appears that the $H_2^+$ ion is readily dissociated by collision and that the $H^+$ ion formed may unite with the $H_2$ molecule collided with or with some other molecule to form $H_3^+$. The interpretation of ionization potentials reported by other observers is discussed in the light of these results.

**Ions produced in helium containing hydrogen, by electron impact.**—The percentage of $H^+$ ions found was greater even than the percentage of $H_2^+$, while no $H_3^+$ ions were observed. Evidently the primary ions $H_2^+$ are readily dissociated by impact with He atoms. Evidence was found for the ions $HeH^+$ and also for an ion with $m/e=6$, perhaps $HeH_2^+$.

IN a recently published preliminary report[1] the authors have described the apparatus employed in this investigation and have given the conclusions that could be drawn from the scanty results then available. By changing the experimental procedure and widening the range of experimental conditions employed they have since made a more detailed study of the problem. The results of this study have made untenable the conclusion formerly drawn that in the ionization of hydrogen by electron impact there are two independent primary processes

$$H_2=H_2^{+}+\epsilon \tag{1}$$

$$H_2=H^{+}+H+\epsilon \tag{2}$$

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* When this paper was first submitted the authors were informed by the editor that an article by H. D. Smyth, "Primary and Secondary Products of Ionization in Hydrogen," was already in press (Phys. Rev. **25**, 452, April 1925). Through the kindness of the editor we have had the advantage of reading proof of that article and have accordingly revised the discussion in this paper to give recognition to Smyth's work.

[1] Hogness and Lunn, Proc. Nat. Acad. Sci., **10**, 398 (1924).

and have given evidence that Eq. (1) represents the only primary process, the formation of $H^+$ and $H_3^+$ being secondary. This is the conclusion drawn by Dempster[2] in a much overlooked and neglected paper from his investigation of the ionization of hydrogen by high-voltage electrons, and also by Smyth.[3]

## Description of the Apparatus and Method

The apparatus (Fig. 1) is essentially an ionization potential tube so arranged that the products of ionization can be analyzed by Dempster's[4] positive-ray method. The preliminary report of this work gives a detailed description of the apparatus which need not be repeated here. Consideration of the equation $e/m=2V_4/H^2r^2$ by means of which

Table I

*Electrometer readings for* $H^+$, $H_2^+$ *and* $H_3^+$ *peaks, at various pressures.*

| Pressure ($10^{-4}$ mm) | Readings | | | Percent | | |
|---|---|---|---|---|---|---|
| | $H^+$ | $H_2^+$ | $H_3^+$ | $H^+$ | $H_2^+$ | $H_3^+$ |
| <0.1 | 0 | 360 | 0 | 0 | 100 | 0 |
| | 0 | 241 | 0 | 0 | 100 | 0 |
| 2.0 | 5 | 520 | 1.3 | 0.9 | 96.7 | 2.4 |
| | 3 | 434 | 0.8 | 0.7 | 97.5 | 1.8 |
| 5.4 | 17 | 850 | 35 | 1.9 | 94.2 | 3.9 |
| | 17 | 630 | 33 | 2.5 | 92.6 | 4.9 |
| | 18 | 900 | 49 | 1.9 | 93.0 | 5.1 |
| 11 | 8 | 500 | 94 | 1.3 | 83.1 | 15.6 |
| | 5 | 320 | 45 | 1.3 | 86.5 | 12.2 |
| 12 | 7 | 520 | 103 | 1.1 | 82.6 | 16.3 |
| | 10 | 512 | 115 | 1.6 | 80.1 | 18.3 |
| 15 | 15 | 530 | 110 | 2.3 | 81.0 | 16.7 |
| 22 | 1(?) | 220 | 69 | 0.3(?) | 75.9 | 23.8 |
| | 33 | 1000 | 265 | 2.5 | 77.1 | 20.4 |
| 28 | 28 | 560 | 260 | 3.3 | 66.1 | 30.6 |
| | 27 | 560 | 240 | 3.3 | 67.7 | 29.0 |
| 39 | 61 | 720 | 540 | 4.6 | 54.5 | 40.9 |
| | 27 | 520 | 360 | 3.0 | 57.3 | 39.7 |
| 56 | 40 | 470 | 690 | 3.3 | 39.2 | 57.5 |
| | 36 | 460 | 680 | 3.1 | 39.1 | 57.8 |
| He and $H_2$ | 153 | 70 | 0 | 68.6 | 31.4 | 0 |

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[2] Dempster, Phil. Mag. **31,** 438 (1916).

[3] H. D. Smyth, Phys. Rev. **25,** 452 (April 1925). See also Proc. Roy. Soc. **102A,** 283 (1922); **104A,** 121 (1923); **105A,** 116 (1924); Nature, **111,** 810 (1923); **114,** 124 (1924); Phys. Rev. **23,** 297 (1924); J. Franklin Inst. **198,** 795 (1924).

[4] Dempster, Phys. Rev. **11,** 316 (1918).

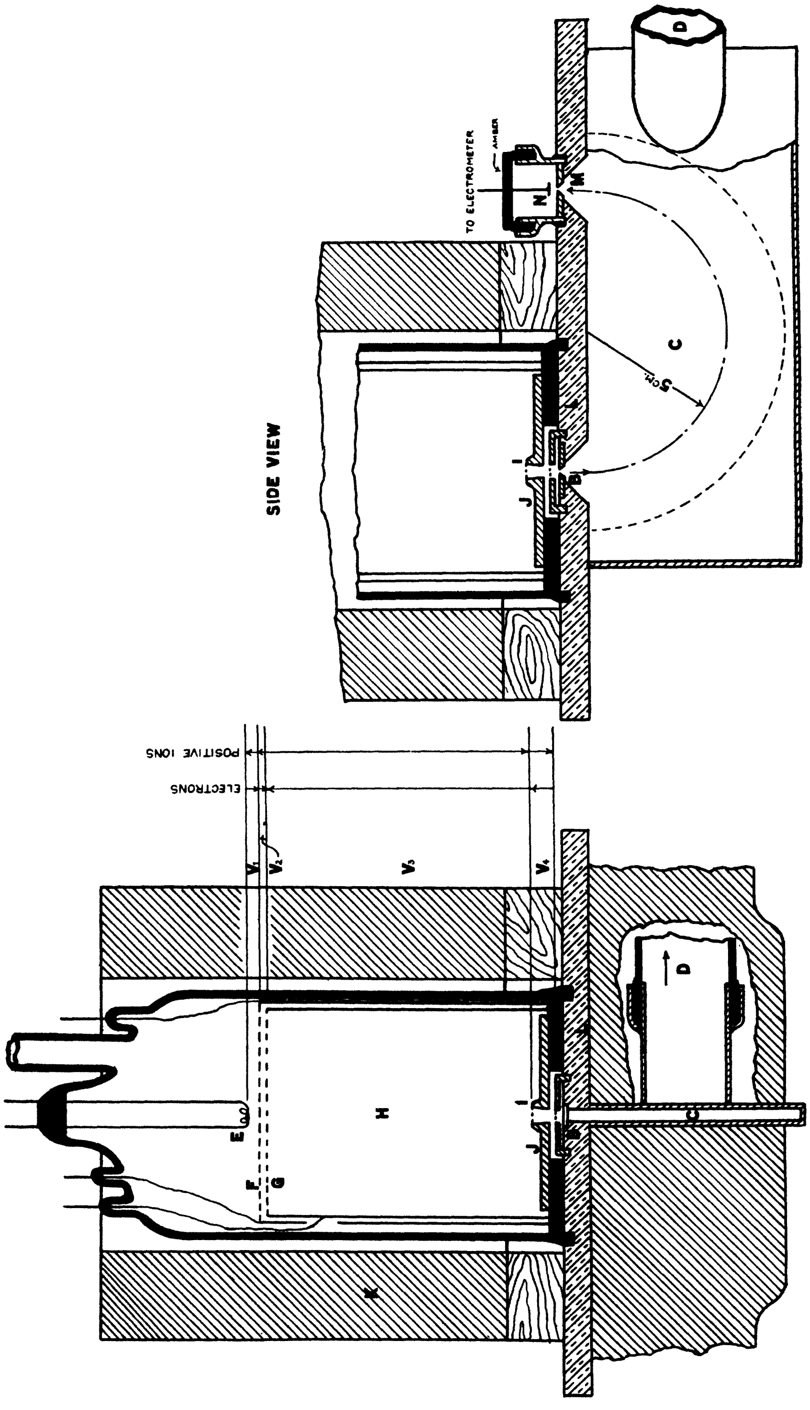

Fig. 1. Apparatus for positive ray analysis of ions.

the specific charges are determined, shows that two experimental procedures are open, (1) that of keeping the magnetic field *H* constant and focussing the ion beam by varying the accelerating potential $V_4$, and (2) that of varying the magnetic field while $V_4$ is kept constant. The former procedure was used in searching for new ions and for measuring their specific charges, the latter in measuring the ionic intensities since its use permitted constancy of electrical conditions in the tube and gave consistent and reproducible results.

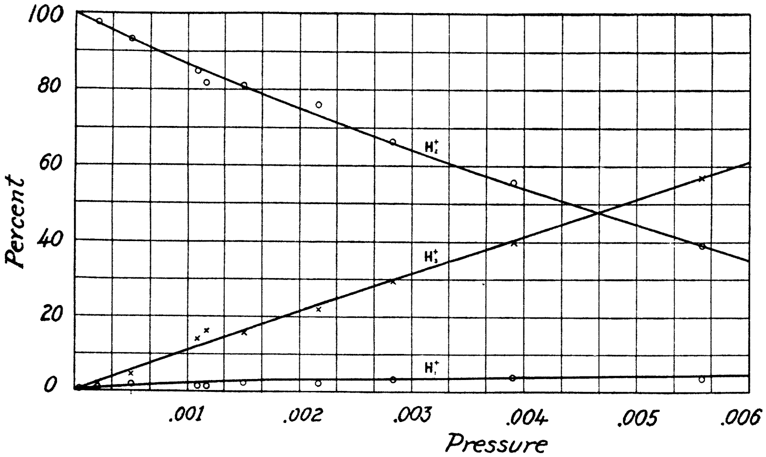

Fig. 2. Percentage of each of ionic species ($H^+$, $H_2^+$, $H_3^+$) as a function of pressure.

Of the present experiments those that seem to throw most light on the problem of interpreting the processes of ionization are the ones on the change of the relative intensities of the ions $H^+$, $H_2^+$ and $H_3^+$ with change in pressure. The data from these experiments are recorded in Table I. The electrometer deflections given were obtained with the constant deflection method. The right-hand side of Table I gives the percentage of each ionic species present as measured by the electrometer deflection ratio. The averages of the values for each pressure given in the table are plotted in Fig. 2, in which the pressures are recorded as abscissas and the percentages as ordinates.

It is evident from the table and from Fig. 2 that as the pressure is lowered the percentages of $H^+$ and $H_3^+$ decrease in a regular manner and approach zero at zero pressure. This clearly indicates that the formation of $H_2^+$ is the primary process and that $H^+$ and $H_3^+$ are formed from $H_2^+$ as the result of secondary collisions with gas molecules. $H_2^+$ is apparently metastable and is disrupted when it collides with a neutral gas molecule in one of two ways

$$H_2^+ + H_2 = H_3^+ + H \tag{3}$$

$$H_2^+ = H^+ + H \tag{4}$$

If Eq. (4) represents the sole collision reaction then the formation of $H_3^+$ would be the result of the tertiary process

$$H^+ + H_2 = H_3^+ \tag{5}$$

Now if $H_3^+$ were formed only by the reaction (5), in order to account for the fact that the intensity of $H^+$ was very small at all pressures, it would be necessary to conclude that the proton has a much smaller mean free path than would be predicted from kinetic theory considerations. Hence it seems reasonable to suppose that when $H_2^+$ ions collide with neutral molecules the reaction taking place in the majority of cases is (3), and that reaction (4) takes place less often.

When the field $V_3$ for drawing the positive ions from the ionization chamber was increased to such an extent that only those electrons in the upper portion of that chamber had ionizing energy, then the intensity of ($H^+ + H_3^+$) increased with respect to that of $H_2^+$ as might have been expected since the $H_2^+$ ions formed had greater chance of collision having had a longer average path to traverse. Moreover the ratio of the intensity of $H^+$ to that of $H_3^+$ increased considerably. This can be explained by assuming that under these conditions $H_2^+$ breaks up more often in accordance with reaction (4). This would happen if when the $H_2^+$ ion acquires sufficient energy before colliding, the $H^+$ formed by disruption were not trapped by the $H_2$ molecule to form $H_3^+$ but passed on into the resolving chamber.

There remains the possibility, however, that $H_2^+$ is stable and must acquire a definite velocity before a collision would result in disruption into $H^+$ and H. To examine this the change in the percentage of ($H_3^+ + H^+$) with small variations of $V_3$ was studied. It was found that as $V_3$ was gradually lowered from 4.5 volts to 0.1 volt, ($V_1 + V_2$) being 48 volts, the percentage of ($H_3^+ + H^+$) increased very slightly instead of decreasing as might be expected if energy were required to cause $H_2^+$ to break up. Although inconclusive, this result seems to indicate that $H_2^+$ is energetically unstable. This conclusion is in accord with the following, deduced by Sommerfeld on theoretical grounds. "The $H_2^+$ ion is *unstable energetically*; it can dissociate into H and $H^+$, giving up energy. At the same time it follows from this for the ionization of the $H_2$ molecule that if this happens in the sense of scheme [Eq. (1)] it requires a greater ionization potential than if it proceeds according to the scheme [Eq. (2)]. This conclusion is independent of any assumptions about the model of the neutral $H_2$, and also remains preserved if we pass from the $H_2^+$ molecule considered so far to a far more general molecule."[5]

In the experiments plotted in Fig. 2, 48 volts were applied to the impact electrons. The effects of slower speed electrons were investigated at one arbitrarily chosen pressure by obtaining the percentages of the several ions as a function of $(V_1+V_2)$ (Fig. 3). The increase in the percentage of $H_3^+$ as $(V_1+V_2)$ was decreased may be explained as due to the characteristics of the discharge tube. The now greater retarding potential $V_3$ decreased the velocity of those electrons that had penetrated into the lower part of the ionization chamber (*H* of Fig. 1) to such an extent that they could not ionize the gas. The $H_2^+$ ions were then formed at a greater average distance from the gauze *I*, and having had a longer average path to traverse had greater chance to collide. The curves of Fig. 3 could not be extended below 18 volts with accuracy because of the small intensity of each of the ionic species. Little significance, moreover, can be attached to the $H^+$ percentage curve at low voltages because of the inaccuracy of measurement of the small $H^+$ ion current in this region. From these observations of Fig. 3, we conclude that the processes described above are also true for impact electrons of smaller velocities.

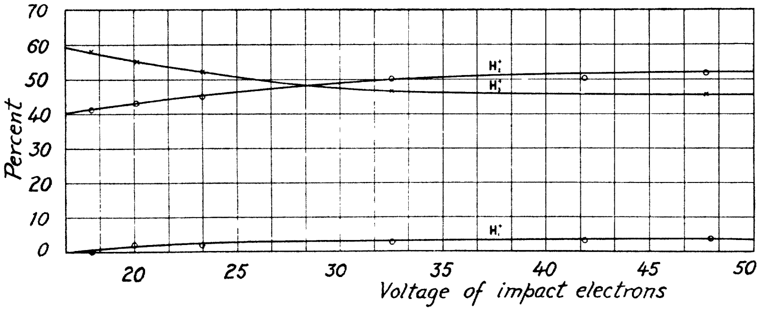

Fig. 3. Variation in relative numbers of $H^+$, $H_2^+$ and $H_3^+$ ions with energy of impact electrons.

Some experiments were made on relative ionic intensities in mixtures of helium with a relatively small amount of hydrogen. It was found that the percentage of $H^+$ was much greater than in pure hydrogen at any pressure employed (see the last line of Table I). Under these conditions the reactions designated by Eqs. (3) and (5) are much less probable and the $H_2^+$ on collision with the He atom disrupted to form $H^+$.

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[5] Sommerfeld, "Atomic Structure and Spectral Lines," 1st Eng. Ed. Appendix 14, page 605.

With mixtures of helium and hydrogen in the tube two particularly interesting intensity peaks of $m/e = 5$ and a less definite one at about $m/e = 6$ were observed repeatedly. A typical run showing these is plotted in Fig. 4. Although the small amount of these ions did not permit of a study of their origin, there is little doubt that the $m/e = 5$ ion is the ion of helium hydride, $HeH^+$, while the other may be $HeH_2^+$.

## THE IONIZATION POTENTIAL

To determine the ionization potential for the formation of $H_2^+$, $V_4$ was set to give the peak of the $H_2^+$ intensity curve and with the magnetic field, the filament current, $V_1$ and $V_3$ all held constant, the electrometer current was noted as $V_2$ was decreased in steps of 0.3 volt. When the rate of deflection of the electrometer was plotted against $V_1 + V_2$, curves like that of Fig. 5 (labelled $H_2^+$) were obtained. The point at which each curve cut the zero ordinate was taken as the approximate (uncorrected) value of the ionization potential. Then by setting $V_1$ and $V_2$ immediately above and below this, and observing the electrometer deflection over a long period of time, a more accurate value was obtained.

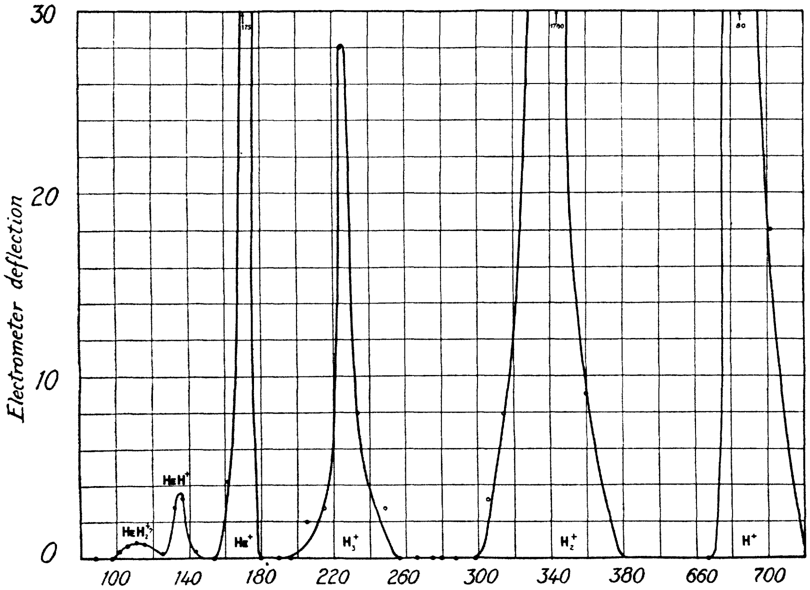

Fig. 4. Peaks obtained with mixture of He and $H_2$.

To obtain the necessary correction to be applied because of the initial velocity of the electrons, the potential drop along the filament, and contact differences of potential, and to take into account the sensitivity of the apparatus, helium was introduced into the tube and the ionization potential curve for $He^+$ obtained in a manner analogous to that described for $H_2^+$. (See Fig. 5, $He^+$.) 24.5 volts was taken as its true ionization potential. In order that the corrections thus found should have any significance it was necessary to choose the hydrogen and helium pressures such that (1) the "saturation" intensities of $He^+$ and $H_2^+$ be the same, and (2) the ionization potential curves for helium and for hydrogen be of approximately the same shape. This choice of pressures was made as follows. It was found that 50-60 volts was above the "saturation" voltage. The intensity of the $He^+$ line in the calibration run when $V_1 + V_2$ was about 60 volts was therefore noted, the helium then pumped out, and hydrogen introduced at such a pressure as gave a $H_2^+$ line of this same intensity. The smaller figure of Fig. 5 shows the appearance of the ionization potential curves for the $He^+$ and $H_2^+$ when the respective pressures were so chosen. The two curves are evidently almost superposable.

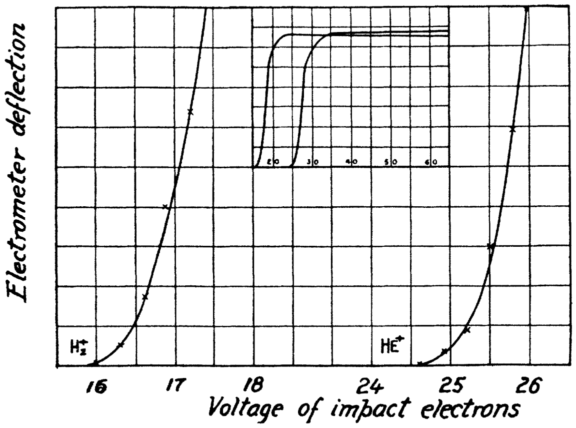

Fig. 5. Variation of intensity of peaks $H_2^+$ and $He^+$ with energy of impact electrons.

The corrected values for the ionization potential of hydrogen found in successive runs are: 16.3, 16.5, 15.7, 15.8, 16.1, 15.9, 15.8, 15.8. The average value is 16.0.

To show that $H_3^+$ and $H_2^+$ appear at the same ionization potential, the pressure was so regulated that the $H_3^+$ and $H_2^+$ lines were of equal intensity and the potentials for the formation of the two ions compared. Under these conditions the two potentials were identical, but at lower pressures where $H_2^+$ predominated, $H_3^+$ and $H^+$ were not detected at as low voltages as was $H_2^+$.

The several lines of investigation presented above unite then in giving evidence that, in the ionization of hydrogen by electron impact, the primary process of ionization is the detachment of an electron from a molecule ($H_2 = H_2^+ + \epsilon$) and that the $H_2^+$ thus formed is probably energetically unstable and can break up on collision to give $H^+$ (and H). The evidence that the formation of $H^+$ is the result of a secondary process may be briefly summarized. (1) At very low pressures no $H^+$ was found; (2) $H^+$ was never found with impact electrons having a velocity lower than the minimum necessary for the production of $H_2^+$; and (3) with mixtures of helium and hydrogen large amounts of $H^+$ were found.

The following then are the conditions for producing in a discharge tube each of the different ions of hydrogen in predominating amounts: For $H^+$, large potential difference and the addition of some inert gas such as helium; for $H_2^+$, low pressures; for $H_3^+$, higher pressure and small potential difference.

## DISCUSSION

It is of interest to note that the above results and the main conclusions derived therefrom are exactly in accord with the following conclusion of Dempster[2] who used 800 volt electrons in his experiments: ". . . . electrons ionize only by detaching a single electron from the molecule, and are not able to dissociate the molecule into atoms." Graphical analysis of his intensity ratios shows also that at zero (extrapolated) pressure no $H^+$ or $H_3^+$ would be formed. The present conclusions also agree in the main with those of Smyth,[3] differing therefrom only in detail as to the secondary process. He concludes that the formation of $H_3^+$ is a tertiary process while we believe it to be largely a secondary one (Eq. 3). Smyth's Fig. 6 shows in a striking manner the increase of $H_3^+/H^+$ with decrease of $V_3$. This we believe gives support to our view. In discussing the stability of $H_2^+$, Smyth maintains that if that ion were stable with respect to $H^+$ and H, the additional energy necessary for its disruption would have to be supplied by the impacting electron; but this energy could also be supplied by the kinetic energy of the $H_2^+$ acquired from the electrical field. The possibility may be pointed out here that, contrary to the conclusions drawn from theoretical considerations, $H_2^+$ may be stable with respect to $H^+$ and H, and yet be unstable with respect to $H_3^+$, i.e. the reaction (3) may take place with evolution of energy while that of equation (5) may not. There does not seem to be as yet sufficient experimental evidence to test this possibility.

The recently reported spectroscopic investigations of Richardson and Tanaka[6] on low voltage arcs in hydrogen lead them also to conclude that the primary process of ionization is the formation of $H_2^+$.

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[6] Richardson and Tanaka, Proc. Roy. Soc. **106A**, 663 (1924).

It may be well to discuss the bearing of the results of the positive ray studies on critical potential measurements. Table II gives the measurements of several observers on the critical potentials which they ascribe to ionization of hydrogen. All are in agreement concerning the existence of an ionization potential at about 16 volts, but all except Smyth have interpreted this potential as that at which ionization plus dissociation (Eq. 2) takes place. This interpretation is obviously no longer tenable. The 13.5 volt point observed has been ascribed to ionization of the hydrogen atom, the atomic hydrogen presumably being formed by thermal dissociation or by collision of an excited hydrogen molecule with an unexcited one (see below). The potential at about 11 volts which has been interpreted by some observers as that for the process $H_2 = H_2^+ + \epsilon$, is probably due to excitation, or, as suggested by Horton and Davies,[20] to the ionization of mercury vapor. A new interpretation must

TABLE II

*Ionization potentials of hydrogen.*

| Observers | Values in volts | | | | |
|---|---|---|---|---|---|
| Davis and Goucher[7] | 11 | | 15.8 | | |
| Bishop[8] | 11 | | 15.7 | | |
| Found[9] | | | 15.8 | | |
| Compton and Olmstead[10] | 10.8 | | 15.9 | | |
| Krüger[11] | 11.5 | | 16.4 | | 29.7 |
| Boucher[12] | | 13.6 | 15.6 | | |
| Foote and Mohler[13] | | | 16.0 | | |
| Mohler, Foote and Kurth[14] | | | 16.0 | | |
| Olmstead[15] | 11.5 | 13.6 | 16.0 | | |
| Horton and Davies[16] | | 13.5 | 15.9 | 22.8 | 29.4 |
| Mackay[17] | | | 15.8 | | |
| Olson and Glockler[18] | | | 16.7 | | |
| Olmstead and Compton[19] (2800°C) | | 13.5 | | | |
| Smyth[3] | | | 16.0 | | |
| | Mean | | 16.0 | | |

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[7] Davis and Goucher, Phys. Rev. **10**, 101 (1917).

[8] Bishop, Phys. Rev. **10**, 244 (1917).

[9] Found, Phys. Rev. **16**, 41 (1920).

[10] Compton and Olmstead, Phys. Rev. **17**, 45 (1921).

[11] Krüger, Ann. der Phys. **64**, 288 (1921).

[12] Boucher, Phys. Rev. **19**, 189 (1922).

[13] Foote and Mohler, Origin of Spectra, p. 68.

[14] Mohler, Foote and Kurth, Phys. Rev. **19**, 414 (1922).

[15] Olmstead, Phys. Rev. **20**, 613 (1922).

[16] Horton and Davies, Phil. Mag. **46**, 872 (1923).

[17] Mackay, Phil. Mag. **46**, 828 (1923); Phys. Rev. **24**, 319 (1924).

[18] Olson and Glockler, Proc. Nat. Acad. Sci. **9**, 122 (1923).

[19] Olmstead and Compton, Phys. Rev. **22**, 559 (1923).

[20] Horton and Davies, loc. cit.[16] In their helium studies they were able to detect mercury vapor spectroscopically in spite of precautions taken to prevent its entrance.

also be sought for the 22.8 volts potential of Horton and Davies, and for the 29.4 and 29.7 points of these observers and of Krüger respectively. The first was ascribed to molecular ionization, the second to molecular dissociation with ionization of both atoms, $H_2=2\ H^++2\epsilon$. If such a process as this last took place the lower curve of Fig. 3 would show an increase in the percentage of $H^+$ at about 30 volts. Olson and Glockler[18] found nine critical potentials in the interval between 14.86 and 16.68 volts, five of which, in addition to the ionization potential, are each 3.16 volts greater than a resonance potential or ionization potential of atomic hydrogen. They interpret these five critical potentials as measuring the energy necessary to dissociate the molecule and resonate one of its atoms, the 3.16 volts being then the heat of dissociation. The three remaining lines which have no apparent relation to the Lyman series they ascribe to molecular excitation not accompanied by dissociation. Hughes[21] in considering Smyth's earlier work in the light of his own experiments, concluded that excitation by electron impact is often accompanied by dissociation. If this view is accepted the interpretation of Olson and Glockler's work, with the exception of the ionization potential, remains unchanged. Von Keussler,[22] however, concluded from a study of spectral data, including his own, that dissociation is an effect secondary to molecular excitation and occurs if the excited molecule is disturbed, as by collision, before it has time to radiate. Such dissociation by collision results only if the excited molecule has energy in excess of that necessary to dissociate the molecule and produce the excited atom. In view of the present experiments and those of Smyth, it appears that von Keussler's theory is the more logical one. There can be very little difference between an ionized molecule and one in the higher stages of excitation. If dissociation does not accompany ionization it would hardly be expected to accompany excitation. If von Keussler's view is adopted, the interpretation of Olson and Glockler's work follows immediately. The 3.16 volts represents, then, the energy of the excited molecule in excess of the energy of the excited atom. If the excited molecule is energetically unstable with respect to its dissociation products and radiates energy or produces kinetic energy on dissociation, the heat of dissociation must then be less than 3.16 volts. While this excess energy of the excited molecule may not be the same for all stages of excitation, any differences that exist may be small enough to fall within the limits of error of the measurements of Olson and Glockler.

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[21] Hughes, Phil. Mag. **48,** 56 (1924).

[22] Von Keussler, Zeits. f. Physik, **14,** 19 (1923).

It may be of interest to note that the results of the experiments on mixtures of helium and hydrogen described above point toward an explanation of Merton and Nicholson's[23] experiments on the extension of the Balmer series in which they observed more lines of this series in mixtures of helium with relatively small amounts of hydrogen than could be detected in pure hydrogen.

Taking the mean of the experimental data recorded in Table II gives 16.0 volts as the ionization potential of hydrogen for the formation of $H_2^+$. As the $H_2^+$ ion is probably unstable with respect to H and $H^+$, it must give off energy when it dissociates. If ionization could take place according to the scheme in Eq. (2) the ionization potential for such a process would then be less than 16.0 volts, assuming this to be the correct value, and the heat of dissociation would then be less than $16.0 - 13.5 = 2.5$ volts, equivalent to 57,500 calories per mol. Langmuir,[24] Isnardi,[25] and Wohl,[26] by indirect methods obtained 84,000, 95,000 and 90,000 calories per mol respectively for this value. In view of the probable uncertainty of the values obtained by both these lines of investigation, we are not yet ready to assume that this discrepancy is a real one.

The several theoretical models for $H_2^+$ give values for the ionization potential of $H_2$ higher than the observed 16.0 volts. The Bohr model, considered untenable for other reasons, leads to the value 17.85 volts (2.20 Rh − 0.88 Rh), the Pauli[27] model to 23.7 volts, and the various models of Niessen[28] to values 23.5 to 28.8 volts.

Department of Chemistry,
University of California,
February 9, 1925.

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[23] Merton and Nicholson, Proc. Roy. Soc. **96A,** 112 (1919).

[24] Langmuir, J. Am. Chem. Soc. **34,** 860 (1912); Langmuir and Mackay, ibid. **36,** 1708 (1914); Langmuir, ibid. **37,** 417 (1915).

[25] Isnardi, Zeits. Elektrochem. **21,** 404 (1915).

[26] Wohl, Zeits. Elektrochem. **30,** 49 (1924).

[27] Pauli, Ann. der Physik **68,** 117 (1922).

[28] Niessen, Physica **2,** 345 (1922); Ann. der Physik **70,** 129 (1923).