PRIMARY AND SECONDARY PRODUCTS OF IONIZATION IN HYDROGEN

By H. D. Smyth*

Abstract

Previous results obtained by the magnetic deflection method of analysis have been extended, using a new but similar apparatus in which ions produced by accelerated electrons are accelerated through a slit into a chamber where a magnetic field bends them around a semi-circle whose radius depends on the speed, field and ratio of mass to charge. Those going into a Faraday cylinder are measured by means of an electrometer. The conclusion that ions produced at 16 volts are diatomic is confirmed, but no evidence of simultaneous ionization and dissociation, which was previously thought to occur for voltages above 20.2, is obtained. However, atomic ions H^+ are readily produced by secondary dissociation of molecular ions H_2^+ even when the maximum electron energy is just above 16 volts. Triatomic ions H_3^+ also appear in large numbers as secondary products, for any voltage above 16. A mathematical theory of the dependence of the relative numbers of H_2^+ and H^+ ions on pressure, gives curves in general agreement with experiment and leads to the conclusions that the probability of dissociation of H_2^+ is about 15 times the probability of a collision with a molecule according to the ordinary kinetic theory, and that the probability of the formation of H^+ by dissociation is greater for H_2^+ than for H_3^+. The processes involved in ionization followed by dissociation are discussed, and it is shown that the apparent discrepancy between the heat of dissociation computed from the ionization potentials and Langmuir's result for the heat of thermal dissociation may perhaps be explained by the energy radiated, which is at present unknown.

Introduction

In a series of papers,[1] the writer has described experiments designed to study the products of ionization by impact of slow electrons in various gases. The ratio of mass to charge of the ions produced in an ionization tube was measured by the method of positive ray analysis and the relative numbers of different types of ion produced under different conditions were compared. In all the polyatomic gases studied it was found that the first ionizing potential corresponds to ionization of the molecule without dissociation. In particular, results in hydrogen indicate that ionization of molecules by sixteen volt electrons is not accompanied by dissociation but that dissociation of the diatomic ions may follow as

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[1] H. D. Smyth, Proc. Roy. Soc. A **102,** 283-293 (1922); **104,** 121-134 (1923); **105,** 116-128 (1924); Nature **111,** 810 (1923) and **114,** 124 (1924); Jour. Frank. Inst. **198,** 795-811 (Dec. 1924)

a secondary effect. Since this conclusion was contradictory to the prevailing notions of the ionization processes in hydrogen, further investigation was undertaken.

The confirmation and extension of the earlier results has been reported briefly in Nature[1] and will be discussed in detail in the present paper. Moreover, certain theoretical considerations regarding the effect of varying conditions in the ionization tube will be developed. Therefore, although the method used is almost identical with that described elsewhere, it is desirable to recall it in some detail.

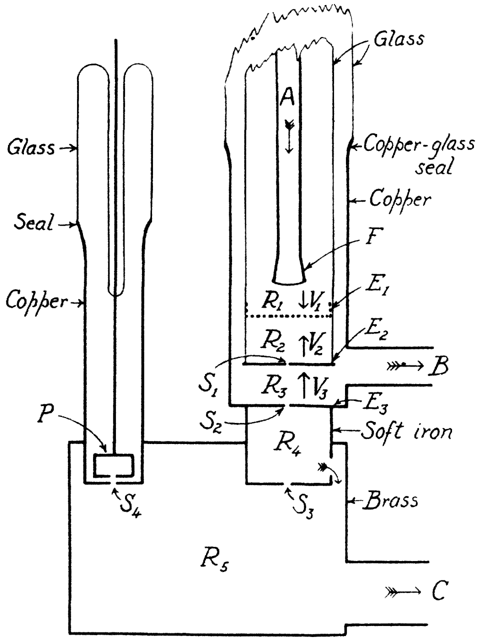

Fig. 1. Apparatus.

APPARATUS AND METHOD

The diagram in Fig. 1 is a schematic representation of the experimental tube. It is drawn approximately to scale except that the distances F to E_1 to E_2 to E_3 have been exaggerated. The electrodes and slit system divide the tube into five different regions which have been designated R_1, R_2, . . . R_5 for convenience in discussion. The filament F is of tungsten or oxide coated platinum, while the electrodes E_1, E_2 and E_3 are platinum, copper and soft iron respectively. E_2 is sealed to the inner glass tube so that the only communication between R_2 and R_3 is through S_1, a slit of .1 mm width. The slits S_2, S_3, and S_4 are .2, 2.0 and 2.0 mm in width. The cylinder enclosing R_4 is of soft iron so that this region is shielded from the magnetic field in R_5, which is between the poles of a powerful electromagnet. The regions R_1, R_2 and R_3 are also carefully shielded from this field.

As shown by the feathered arrows, gas flows down the inner tube, diffuses through the slits and is pumped out at B and C, each of which is connected to a diffusion pump through liquid air traps, etc. A McLeod gauge is connected to the tube by which the gas enters and should measure very nearly the pressure in the regions R_1 and R_2. Hydrogen was generated by electrolysis of barium hydroxide, and stored over phosphorous pentoxide. It was admitted to the apparatus through a fine capillary leak, passing on the way over more phosphorous pentoxide and through a U-tube immersed in liquid air. By the use of copper-to-glass seals de Khotinsky cement is eliminated except on two ground glass joints which allow the removal of the entire inner tube or of the filament stem and which never become warm. So far, no attempt has been made to "bake out" the tube.

Let us turn now to the electrical arrangement and consider the ionization phenomena which occur. The arrows indicating the electrical fields due to the potential differences V_1, V_2 and V_3 are drawn in the direction in which an electron moves. If V_1 is sufficiently great, electrons from the filament will make ionizing collisions with gas molecules in the regions R_1 and R_2 and in general a few may get through into R_3, but in the cases with which we are concerned the magnitudes of V_1, V_2 and V_3 are such that ionization in R_3 may be neglected. Further, any positive ions that are formed in R_1 will go to the filament and therefore do not interest us. Consider, however, positive ions formed in the region R_2. Some of these will pass through the slits S_1, S_2 and S_3 and then enter the region R_5 with energies between eV_3 and $e(V_2+V_3)$ or velocities v between $\sqrt{2V_3e/m}$ and $\sqrt{2(V_2+V_3)e/m}$ if e is the charge and m the mass of each ion. In R_5 they are subjected to the action of the magnetic field H and will be bent in semicircular paths of radii given by the relation $\rho = mv/eH$. For a constant field and radius, the value of e/m for an ion must be $>2V_3/H^2\rho^2$ and $<2(V_3+V_2)/H^2\rho^2$ or the accelerating voltage must be $\frac{1}{2}H^2\rho^2(e/m)$ in order that it may travel in such a path that it passes through S_4 to the Faraday cylinder, bringing a positive charge to the electrometer. If, therefore, a number of different kinds of ion are produced in R_2 then corresponding to the value of m/e for each there will appear a maximum in the current to the electrometer observed as a function of V_3, with other conditions constant. The results of such an experiment are plotted in

Fig. 2 where the abscissas are $m/e \propto 1/(V_2+V_3)$ and the ordinates current to the electrometer.

The shape and the exact position of each peak will be determined by conditions in R_2. Since the electrons will lose their ability to ionize as soon as they have been retarded by a fraction of V_2 given by $xV_2 = V_1 - V_0$ where V_0 is the ionizing potential, clearly the width of a peak is proportional to $xV_2/(V_2+V_3)$. Also, since the greatest number of collisions is near E_1 and the probability of ionization at a collision is proportional to $(V-V_0)/V$ the greatest number of ions will be produced near E_1, so that the peak will not be symmetrical but will fall off more gradually for higher values of V_3. This consideration may be modified somewhat by the greater chance of ions produced near E_2 getting through the S_1. If the greatest number of ions come from some point between E_1 and E_2 the $1/(V_2+V_3)$ scale will give too small a value of m/e and the error will be the greater, the greater V_2/V_3. These effects may be observed in the curve in Fig. 2 and to a varying extent in the later figures.

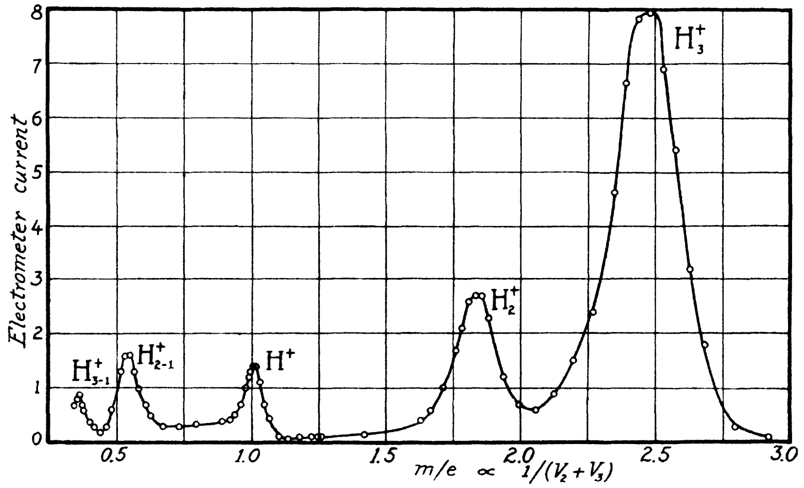

Fig. 2. Run No. 74. $V_1 = 25$ volts; $V_2 = 5$ volts; $i = 150$-160 microamp.; $p = .043$-$.039$mm

Now let us consider secondary effects such as might be caused by production or modification of ions by collision with other ions or molecules. Suppose that the ions formed by the primary electrons are X_2^+ but that they may each be converted at any point along their path into $X^+ + X$ by collision with another molecule. If this occurs anywhere in R_2 a peak will result at a value of $1/(V_2+V_3)$ appropriate to ions of $m/e = \frac{1}{2}X_2^+$ and this peak will be nearly as sharp as if the X^+ ions were a primary product, but should be slightly shifted toward larger values of V_3. The same remarks apply to any new ions produced by these secondary collisions. For conversions of X_2^+ to X^+ occurring in R_3 or for new ions produced there, the V_3 required to give the new ions the necessary radius of curvature in the magnetic field will vary rapidly and continuously so their effect will be merely to increase stray current between peaks. For collisions in R_4, on the other hand, the case is different; the X_2^+ ions have now fallen through the entire electric field but do not enter the magnetic field until they pass S_3. If they are to enter at S_2 as X_2^+ and emerge at S_3 as X^+ and yet be bent around to the Faraday cylinder P, they must have fallen through a potential drop (V_2+V_3) four times as great as would be necessary for ions which remained X_2^+ throughout, since for the same radius of curvature their velocity must be twice as great. Moreover, since a conversion anywhere in R_4 would have the same effect a peak might be expected corresponding to an m/e value $\frac{1}{4}$ that for X_2^+. Similarly reasoning may be applied to conversions of different primary ions and may include secondary associations as well as dissociations.

It may seem absurd to suppose that ions can be disrupted by collision in R_4 and yet retain their speed and direction sufficiently to get through S_3 and around to the Faraday cylinder, P. A much more natural supposition is that any collision in this region merely scatters the ion out of the beam so that it never reaches P at all no mater what its velocity is when passing S_2. This was the position taken by the writer in his early work but it is untenable in the light of the peaks appearing in hydrogen at $m/e=\frac{1}{2}$ and $\frac{1}{3}$, examples of which are shown in Fig. 2. The evidence that these are effects of the type just described will be discussed presently.

In the last few paragraphs we have described various possible ionization processes which may occur in our apparatus with reference to the general character of the curves to be expected. No mention has been made of relative intensities. It is obvious that these will depend on the pressure and electric fields but these questions may be studied more profitably in connection with the new experimental evidence.

RESULTS ON THE EFFECT OF PRESSURE

Previous experiments indicated that the only primary product of ionization in hydrogen is H_2^+, a positively charged diatomic ion. This conclusion is entirely confirmed by the present work in which curves of the type of A Fig. 3 were obtained at low pressures. At the lowest pressure used, .00032 mm, H_3^+ had entirely disappeared though a trace of H^+ still persisted. However, the relative intensities of H^+ and the secondary $\overset{+}{H}_{2-1}$ peaks in curve A Fig. 3 suggest that even at these low pressures the H^+ is due to the break up of H_2^+, which appears to be very unstable. It is also plain that the production of H_3^+ ions is a secondary effect.

Curve B in Fig. 3 taken at $p = .053$ mm shows the H_2^+ peak almost suppressed but H_3^+ and H^+ strong. This is in harmony with the earlier work though then no attempt was made to study H_3^+ at high pressures so that the conclusions were incomplete. In Fig. 4 the intensities of H_3^+, H_2^+ and H^+ are plotted against pressure, all other conditions remaining the same. The two solid line curves are computed theoretically for H_2^+ and H^+. In the case of H_2^+ the agreement with experiment is so good that no additional curve was drawn; the results are indicated merely by circles. For H^+ and H_3^+ the experimental points are joined by dotted lines and in the case of H_3^+ no theoretical curve was calculated. Before proceeding to the analysis which leads to the theoretical curves given, further qualitative evidence on the dissociation of the H_2^+ and H_3^+ ions will be considered.

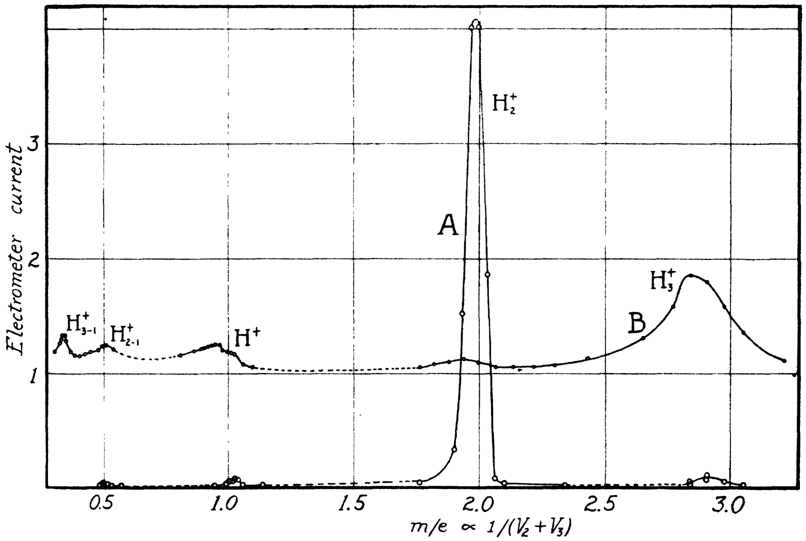

Fig. 3.

Curve A, Run No. 54. $V_1 = 25$ volts; $V_2 = 9$ volts; $i = 130\text{-}140$ microamp.; $p = .0007$ mm.
Curve B, Run No. 45. $V_1 = 25$ volts; $V_2 = 9$ volts; $i = 130$ microamp.; $p = .0542\text{-}.0515$mm.

As has already been mentioned the peaks at $m/e = \frac{1}{2}$ and $m/e = \frac{1}{3}$ are attributed to H^+ ions resulting from H_2^+ and H_3^+ ions that have broken up in R_4 after passing through the electric field. Therefore, they may be conveniently designated H_{2-1}^+ and H_{3-1}^+. If this idea is correct, the intensity of these peaks relative to the H_2^+ and H_3^+ should be greater if the pressure in R_4 could be increased without altering other conditions.

This was actually done in run 28 by stopping the pump that operates through C. As is shown in Table I, columns 3 and 4, there was a marked increase in the intensities of $H_2{}^{+}_{-1}$ and $H_3{}^{+}_{-1}$ relative to $H_2{}^+$ and $H_3{}^+$ compared to runs 26 and 29 taken under conditions otherwise identical. Further, with all pumps going, at higher pressures, their relative inintensities were much greater. This may be seen from columns 3 and 4, Table I. Finally, the variation of their absolute intensities was always parallel to that for $H_2{}^+$ and $H_3{}^+$. The conclusion is, therefore, that these peaks are due to the break up of $H_2{}^+$ and $H_3{}^+$ ions in R_4. But it is obvious that they represent only a small fraction of the disruptions that take place since usually the ions produced by such disruptions will not keep on through S_3. Thus, if N be the number of ions entering S_2, l_1 be the distance S_2 to S_3, l_2 the length of the semi-circular path S_3 to S_4 and p, the average pressure in R_4 and R_5, then

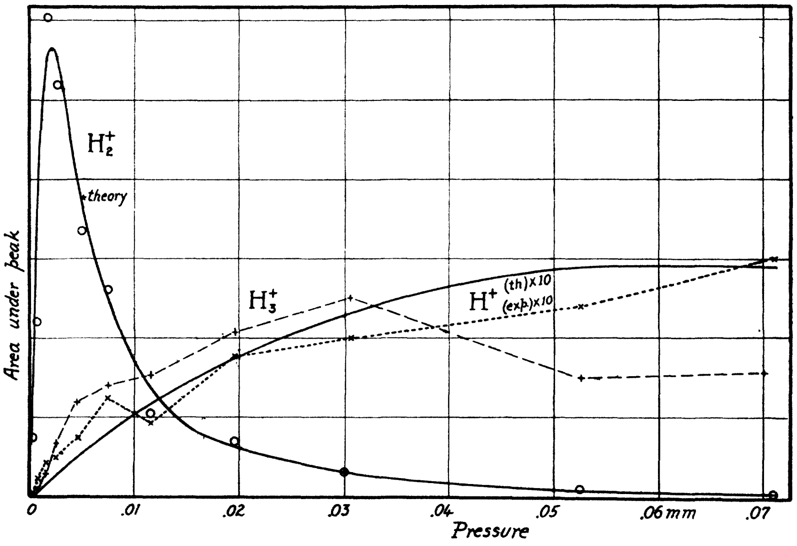

Fig. 4. $V_1=25$ volts; $V_2=9$ volts; $i=120$–150 microamp.

$$A(H_2{}^+) \propto N\epsilon^{-p(l_1+l_2)n_2}$$

$$A(H_2{}^+{}_{-1}) \propto N(1-\epsilon^{-pn_2l_1})$$

if we neglect the possibility of H^+ being removed by collisions in R_5 and use n_2 to denote the number of disrupting collisions suffered by an $H_2{}^+$ ion per unit path at unit pressure. The difficulty of estimating p makes it hardly worth while to go into the calculations. Suffice it to say that if p be taken as one tenth the pressure in R_2 and $1/n_2$ be taken as the molecular free path, about one tenth of the disruptions in R_4 must give atomic ions which get through to the electrometer, whereas if $n_2=1100$, a value suggested by the following analysis, the fraction is about 3×10^{-10}. The latter appears to be a much more reasonable value.

The results summarized in Table I also serve to indicate the relative stability of H_3^+ and H_2^+. Again the uncertainty concerning the pressure in R_4 and R_5 make calculations unreliable but if the same assumption is made as in the last paragraph, n_3 is found to be about 1050. If the pressure is taken as one hundredth that in R_2, n_3 is found to be about 440. It must be remembered that here n_3 refers to collisions resulting in the production of H^+. Apparently these are less probable for H_3^+ than for H_2^+.

Besides secondary peaks corresponding to dissociation of H_3^+ and H_2^+ into H^+, peaks due to $H_3^+\rightarrow H_2^+$ or to associations might be expected. No definite evidence of such effects was observed.

TABLE I

Run No.	Pressure	Ratios of heights of peaks		
		$H_3^+/H_3^+{}_{-1}=r_{31}$	$H_2^+/H_2^+{}_{-1}=r_{21}$	r_{31}/r_{21}
14	.0111 mm		30.	
15	.0236		5.	
16	.0835		0.1	
26	.0334	29.	7.0	4.1
28*	.0278	7.3	1.0	7.3
29	.0264	26.6	8.0	3.3
43	.1110	1.2		
44	.0710	2.25		
45	.0530	2.74	.5c	5.5c
46	.0306	13.	3.1	4.2
47	.0195	26.	7.3	3.6
48	.0117	24.	18.	1.3
49	.0075	65.	39.	1.7
50	.0039	70.c	80.c	1.0c
51	.0039	70.c	60.c	
73	.0445	3.0	.85	3.5
74	.0404	10.	1.9	5.3
75	.0375	6.7	2.16	3.1

* During this run the pump exhausting R_4 and R_5 through C was not operating.

Theoretical Analysis

Intensity of H_2^+ *peak as a function of pressure.* Starting from the assumptions that an H_2^+ ion is created by the impact of an electron and a molecule of hydrogen, and that it may be destroyed by a collision with another molecule, we wish to derive an expression for the relation between the number of H_2^+ ions reaching E_2 and the pressure in R_1 and R_2. We must make the further assumptions, (1) that the electric fields are uniform and given by V_1/d_1 and V_2/d_2; (2) that the electrons at a collision lose their ability to ionize at a subsequent collision.

Let d_1 = the distance from F to E_1;
d_2 = the distance from E_1 to E_2;
n_0 = number of collisions at 1mm pressure per cm advance along the x-axis by an electron;
n_1 = the same for an H^+ ion;
n_2 = the same for an H_2^+ ion;
n_3 = the same for an H_3^+ ion;
p = pressure in millimeters of mercury.

Then, if N is the number of electrons leaving the filament, the number passing into R_2 with the ability to ionize is proportional to

$$N\epsilon^{-pn_0d_1}.$$

Now consider any layer in R_2 of width dx and distant x from E_1. Since the speed of the electrons will be $V_1-(V_2/d_2)x$ the number of ions formed in this layer will be

$$d\nu \propto N\epsilon^{-pn_0(x+d_1)}\left[V-V_0-(V_2/d_2)x\right]pn_0dx \tag{1}$$

where the probability of ionization at a collision has been taken as proportional to $V-V_0$ because the more exact expression $(V-V_0)/V$ gives an equation which cannot be integrated, and, in the range of voltages with which we are concerned, the simpler expression is sufficiently accurate.

If, now, $d\nu$ be multiplied by the probability of an ion reading E_1 without collision and the product be integrated, we have for the total number of ions formed in R_2 and reaching E_2 without collision

$$M=A\epsilon^{-p[n_0d_1+n_2(2d_2-a)]}\Bigg\{(V-V_0)\left(\epsilon^{p(n_2-n_0)a}-1\right) -(V_2/d_2)\left[\frac{\epsilon^{p(n_2-n_0)a}(p(n_2-n_0)a-1)+1}{(n_2-n_0)p}\right]\Bigg\} \tag{2}$$

where $a=(V-V_0)d_2/V_2$ and A is a factor of proportionality. Finally, putting in $\alpha=n_0d_1+n_2(2d_2-a)$, $\beta=n_2-n_0$, $\gamma=a\beta$, $K_1=V_1-V_0$ and $K_2=V_2/d_2$, we have

$$M=A\epsilon^{-\alpha p}\left\{K_1(\epsilon^{\gamma p}-1)-K_2\left[\frac{\epsilon^{\gamma p}(\gamma p-1)+1}{\beta p}\right]\right\} \tag{3}$$

where A is independent of pressure and voltage, and K_1, K_2, α, β, and γ are independent of pressure but dependent on voltage and the dimensions of the apparatus.

Let us next apply this formula to the series of runs which give the points for H_2^+ in Fig. 4. Here, of course, what is measured is the number of ions getting through the slit system but this is proportional to M or to $M\epsilon^{-kp}$ so that the above formula may be applied if α is extended to contain k, an unknown constant.

The voltages and dimensions used in this series of runs were

$$V_1=25;\ V_2=9;\ d_1=.2\ cm;\ d_2=.8\ cm.$$

Take $V_0=16$ volts. Then $K_1=V_1-V_0=9$; $K_2=V_2/d_2=9/.8$; $a=.8$.

Since we have no knowledge of what the proper value of n_2 is let us consider α and γ as unknown and see whether our equation can be made to fit the experimental results. We have then

$$A(H_2^+)=A'\epsilon^{-\alpha p}(\epsilon^{\gamma p}-\gamma p-1)/\gamma p \tag{4}$$

where $A(H_2^+)$ is the area under the H_2^+ peak and measures the number of H_2^+ ions reaching P. The solid curve in Fig. 4 is computed from this formula with $\alpha=900$, $\gamma=870$ and $A'=40$. The agreement of the curve with the observed points is as good as their agreement with each other. Putting these values in the definitions of α and γ we have

$$n_2-n_0=1090;\ .2n_0+.8n_2+k=900.$$

But $1/n_0$ may be taken as approximately equal to $4\sqrt{2}$ times the molecular free path, which gives $n_0=12{\cdot}7$. Therefore n_2 must be 1100, i.e., the distance an H_2^+ ion travels on an average before being dissociated by the proximity of another molecule is about 1/15 the ordinary molecular free path. This gives a value of 20 for k, the constant which was introduced to allow for collisions in R_3, R_4 and R_5. The path through these regions is about 12 cm. Therefore if p' is the pressure, $k=n_2\times 12\times p'/p$; hence $p'=.0015p$, even lower than expected.

Intensity of H^+ *peak.* In order to extend this type of analysis to the intensity of H^+ as a function of pressure, two new quantities must be introduced. Let the number of collisions of H_2^+ (per cm advance toward E_2 at 1 mm pressure) which result in the production of an H^+ ion, be $n'_2=\kappa n_2$ where $\kappa\leqq 1$ and let the number of collisions (per cm advance at 1 mm pressure) by H^+ ions which result in the elimination of these ions be n_1.

From Eqs. (1) and (2) integrating from 0 to x instead of 0 to a we have for the number of H_2^+ ions reaching a plane at x from E_1

$$\nu_x\propto m\epsilon^{-pn_2x}\Big\{K_1(\epsilon^{p(n_2-n_0)x}-1) \\ -\big[K_2/p(n_2-n_0)\big]\big[\epsilon^{p(n_2-n_0)x}(p(n_2-n_0)x-1)+1\big]\Big\}. \tag{5}$$

Therefore, the number of H^+ ions produced between x and $x+dx$ and reaching E_2 without collision is

$$d\nu(\mathrm{H})^+ = pn_2'\epsilon^{-pn_1(d_2-x)}\nu_x dx \tag{6}$$

and the total number reaching E_2 is

$$\nu(\mathrm{H})^+ = pn_2'\int_0^{d_2}\epsilon^{-pn_1(d_2-x)}\nu_x dx. \tag{7}$$

The integrated expression is considerably simplified if $K_1 = K_2 d_2$, i.e., if $V_1 - V_0 = V_2$, and since this is the experimental fact, the more general case will not be discussed. With this simplifying assumption, then, we have for the number of H^+ ions passing through the slit in E_2 and finally reaching the electrometer

$$\nu(\mathrm{H})^+ = B\epsilon^{-(n_0 d_1 + n_1 d_2 + c)p}\left\{\left[d_2 + \frac{1}{(n_2-n_0)p}\right]\left[\frac{\epsilon^{p(n_1-n_0)d}-1}{n_1-n_0} - \frac{\epsilon^{p(n_1-n_2)d_2}-1}{n_1-n_2}\right] - \frac{\epsilon^{p(n_1-n_0)d_2}[p(n_1-n_0)d_2-1]+1}{n_1-n_0}\right\} \tag{8}$$

where all the constants have been determined except n_1, c, and B.

When numerical values are substituted in this equation, it becomes evident immediately that n_1 must be of the order of magnitude of n_0 rather than of n_2 as in the latter case a negative value is obtained. The theoretical values shown by the solid curve in Fig. 4 were computed from $n_1 = 17$, $c = 0$ and $B = 38$. The agreement with experiment is seen to be only fair. However, as may be seen in Figs. 2 and 3, it is difficult to determine the area of H^+ peak accurately. Also the contribution to H^+ from the break up of H_3^+ has been neglected. Moreover, as will be discussed later, n_1 is probably a function of speed though it might be expected to be of the same order of magnitude as n_0 rather than n_2 since an H^+ ion is simply a proton with no electronic satellites. Therefore, we may conclude that the agreement between theory and experiment is as good as could be hoped for and that our assumptions as to the process of formation of H^+ are supported.

Formation of H_3^+. Simultaneously with the production of H^+ ions, there will be an equal production of neutral hydrogen atoms. There are thus three conceivable ways in which H_3^+ might be formed, which may be represented symbolically by the equations

$$H_2^+ + H \rightarrow H_3^+ \tag{a}$$

$$H_2 + H^+ \rightarrow H_3^+ \tag{b}$$

$$\left.\begin{array}{l} H_2 + H \rightarrow H_3 \text{ followed by} \\ H_3 + W(\mathrm{H}_3) \rightarrow H_3^+ + e^- \end{array}\right\} (c)$$

where, as usual in such equations, W denotes the ionizing potential. The last process appears very unlikely but the relative probability of (a) and (b) must depend both on the a priori probability of the processes and on the concentrations of the reactants. Neither of these factors can be gauged with any degree of certainty. Obviously an analysis such as has been used for H_2^+ and H^+ becomes too complicated and uncertain to be of any value. In general the number of H_3^+ ions would fall off with decreasing pressure in agreement with the experimental results.

The relative intensities of H_3^+ and H^+ in Figs. 2 and 5 are seen to be very different although the only condition varied was V_2. It was found that H^+ was always relatively much stronger at higher values of V_2 as may be seen from the curve in Fig. 6 which shows the results of a group of runs made to test this point. Both processes (a) and (b) suggested above depend on the association of ions with neutral molecules and the probability of such an association might be expected to decrease with increasing speed of the ion. Thus, as V_2 is increased, the favorable region for such associations becomes narrower, crowding more closely against E_1. That is to say conditions become less propitious for the formation of H_3^+. On the other hand, the probability of H_3^+ or H_2^+ dissociating to form H^+ might be expected to remain constant or even increase with speed. Further, as V_2 is increased, the electrons lose their power of ionizing at shorter and shorter distances from E_1, so that the average distance the ions must travel to reach E_2 becomes longer and

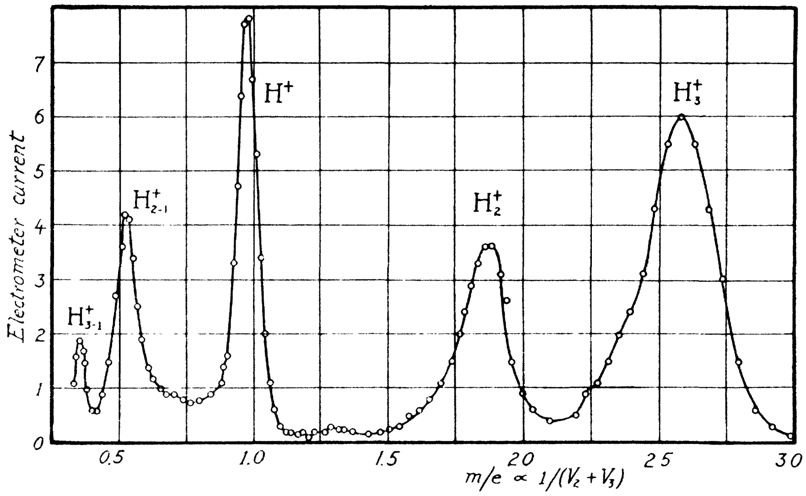

Fig. 5. $V_1=25$ volts; $V_2=25$ volts; $i=150$–160 microamp.; $p=.047$–$.042$ mm.

longer. Since n_2 and, as we have seen, n_3 are large compared to n_1, this will favor dissociation much more strongly than association. On these grounds, then, the ratio of the areas under the peaks, $A(H_3^+)/A(H^+)$ should decrease with increasing V_2, a conclusion in agreement with the observations.

Hughes,[2] in a recent paper, has pointed out that his earlier results on dissociation by electron impact are compatible with the writer's results if we assume that an electron of 12·9 volts speed may cause dissociation accompanied by excitation even though the ionization at 15·9 volts is not accompanied by dissociation. This appears a perfectly tenable suggestion, and might make the process (c) important in the formation of H_3^+. But it would also favor the production of H^+ at 13·5 volts and since our curves show no trace of such an effect, there is no evidence in favor of Hughes' idea.

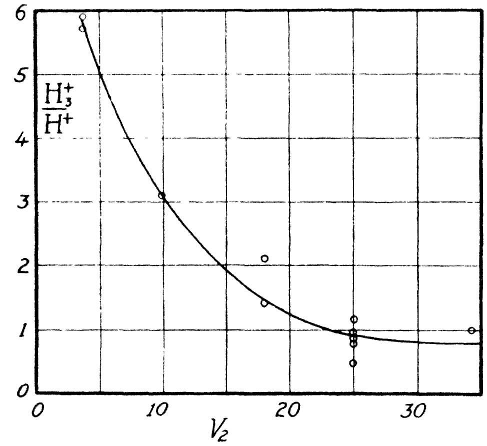

Fig. 6. $V_1=25$ volts. Various pressures and thermionic currents.

RESULTS ON CRITICAL POTENTIALS

Up to this point the various probable primary and secondary processes of ionization have been discussed without considering the energy changes involved and the experimental material presented has all been from runs where $V_1=25$ volts so that electrons reached E_1 with velocities well above the ionizing velocity. We will now consider the effect of varying V_1.

The conclusion previously published was that an impact between an electron and a hydrogen molecule caused simultaneous ionization and dissociation very rarely and not at all unless the electron had a velocity

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[2] Hughes, Phil. Mag. **48**, 81-89 (1924)

greater than 20·2 volts. Reconsideration of the evidence in the light of the present work forces the conclusion that the range of pressures in the previous experiments was insufficient to prove this value a true critical potential independent of the conditions in the ionization tube. In fact, the results summarized in Table II from curves of which those in Fig. 7 are typical, show no evidence for any critical potential at a fixed interval from the ordinary ionizing potential of about 16 volts.

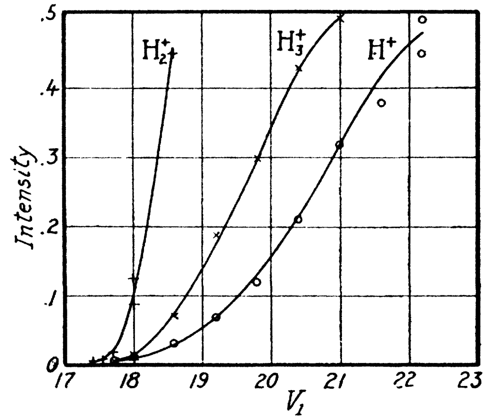

Fig. 7. Series 11. $V_2 = V_1$; $i = 240\text{–}260$ microamp.; $p = .011$ mm.

The voltages relative to $V(H_2^+)$ at which H_3^+ and H_2^+ first appear in measurable quantities seem to depend entirely on the values of p and V_2. Thus in series S4 at low pressure we know that H_2^+ is strong compared to H_3^+ and H^+, the secondary products and further, since V_2 is small, that H_3^+ is relatively stronger than H^+. This is reflected in the appearance voltages, $V(H_2^+) = 15{\cdot}4$, $V(H_3^+) = 15{\cdot}9$, $V(H^+) = 18{\cdot}9$. Again in series S11, V_2 is large so that H^+ is as strong or stronger than H_3^+ and further

TABLE II

Results on appearance potentials

Series	p (mm)	i (microamp.)	$V(H^+)$	$V(H_2^+)$	$V(H_3^+)$	Remarks
S 1	.0181	75	19.8 ± .5	17.8 ± .5	17.7 ± .5	V_2 small
S 3	.0100	500	19.0 ± .3	17.0 ± .6	17.1 ± .5	
S 4	.0042	120	18.9 ± .3	15.4 ± .5	15.9 ± .4	
S 5	.0165	200		16.0 ± .3	16.0 ± .3	
S 6	.0140	350		16.0 ± .3	16.0 ± .3	
S 7	.0125	190	18.5 ± 2.0	15.0 ± .5	15.1 ± .3	
S 8	.0135	145	18.4 ± .5	17.0 ± .7	17.0 ± .7	$V_2 = V_1$
S 9	.0330	150	18.0 ± .5	18.0 ± .5	18.0 ± .5	
S 11	.0125	250	17.6 ± .3	17.3 ± .3	17.6 ± .3	
S 12	.0097	40	18.0 ± .5		18.0 ± .5	
S 13	.0095	200	18.3 ± .5		18.6 ± .3	

the pressure is larger, correspondingly we find $V(H_2^+) = 17{\cdot}3$, $V(H_3^+) = V(H^+) = 17{\cdot}6$. A particular search was also made for a change in the slope of the curves in the neighborhood of 23 volts which has been reported as a critical potential by Horton and Davies and others. In a few curves such a break may have been present but it was not reproducible. The conclusion is, then, that H_3^+ and H^+ may appear as secondary products as soon as H_2^+ is formed, and that there is no evidence for higher critical potentials corresponding to their formation as primary products or to a sharp increase in the probability of their formation from H_2^+.

It may be well at this point to discuss a recent paper by Hogness and Lunn.[3] The general principles of their method were laid down by the writer[4] in an early paper to which Hogness and Lunn neglect to refer, and their apparatus and procedure are almost identical with those described in the present paper and previously. They present one curve with relative intensities of H_3^+ to H_2^+ roughly like Fig. 2 and of H_3^+ to H^+ like Fig. 5. It is stated that at lower pressures the ratio of H_3^+ to H^+ becomes smaller but no indication is given of what range of pressures was studied. From five series all taken at $p = .003$ mm and presumably with the same arrangement of fields, they conclude that $V(H_2^+) = 15{\cdot}7$, $V(H^+) = V(H_3^+) = 16{\cdot}6$. Incidentally, these absolute values are obtained by using a method of correction for initial velocity of electrons which needs to be very much modified to apply to such an apparatus. But this question has been settled long since[5] and need not be discussed here. The results given in Table II and of the previous work show that an apparent critical potential for H^+ or H_3^+ may be observed anywhere between 16 and 21 volts if conditions are properly chosen and not varied. Yet, Hogness and Lunn state "These results show conclusively that there are two distinct processes taking place:

$$(1)\ H_2 = H + H^+ + E^-;\ 16{\cdot}6 \text{ volts}$$

$$(2)\ H_2 = H_2^+ + E^-;\ 15{\cdot}7 \text{ volts}$$

and one secondary process,

$$H^+ + H_2 = H^+_3."$$

The writer makes so bold as to differ with what is new in this statement and ventures to suggest that the results obtained by Hogness and Lunn, excellent as far as they go, are in perfect accord with the ideas he has

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[3] Hogness and Lunn, Proc. Nat. Acad. Sci. **10,** 398-405 (Sept. 1924)

[4] Smyth, Proc. Roy. Soc. A **102,** pp. 283-293, (1922)

[5] See Compton and Mohler, Bulletin of Nat. Res. Coun. on Critical Potentials, p. 49. Also, Smyth, Phys. Rev. **14,** 409, (1919)

suggested elsewhere and developed fully in this paper. The reasons for this opinion should be clear from the evidence already presented, but there remains one point which might be thought to favor the existence of two critical potentials about one volt apart. This will now be discussed.

THE HEAT OF DISSOCIATION OF HYDROGEN

Out of the confusion of many discordant observations on critical potentials in hydrogen there emerge a few facts apparently well established. The data are summarized and discussed fully in the recent Bulletin by Compton and Mohler,[5] but it may be recalled that the explanation of several critical potentials is satisfactory only if the work of dissociation be taken as $D = 2{\cdot}4$ volts, where D means the net difference in energy between H_2 and 2H. In particular the old theory that ionization at 15·9 volts was accompanied by dissociation required a value of 2·4 volts since the ionizing potential of atomic hydrogen is 13·5 volts. The new interpretation requires either that $D \leqq 2{\cdot}4$ volts or that the molecular ions formed just at 15·9 volts cannot dissociate without gaining more energy. The latter assumption would mean that no secondary H^+ ions would appear until the impacting electrons began to transfer at least $15{\cdot}9 + (D - 2{\cdot}4)$ volts to the molecules. The experimental evidence has been shown unfavorable to this assumption. There remains the problem of reconciling the value 2·4 volts with that of 3·5 volts determined experimentally by Langmuir.[6] Consider exactly what the processes are with which we are concerned. They may be represented symbolically as follows:

$$\left.\begin{aligned} H_2 + W_2 &\to H_2^+ + R_1 + E^- \\ H_2^+ &\to H^+ + H + R_1' \end{aligned}\right\} \quad (1)$$

$$\left.\begin{aligned} H_2 + D' &\to H + H + R_2 \\ H + W_1 &\to H^+ + E^- + R_2' \end{aligned}\right\} \quad (2)$$

if we consider the most general possible process where R_1 and R_1' and R_2 and R'_2 represent energy dissipated as radiation, and W_1 and W_2 the atomic and molecular ionizing potentials.

Now if R_1, R_1', R_2 and R_2' are all equal to zero, we must have $W_2 - W_1 = D'$. But is there any evidence that this is the case? From what is known about ionization in monatomic gases, R_2' may fairly be expected to be zero, but there seems to be no criterion which can be applied to the other three cases. Certainly Langmuir's experiments will give the value of D', not of $D = D' - R_2$, the net gain in energy. Therefore, the relation which has to be satisfied is

$$W_2 - R_1 - R_1' = W_1 + D' - R_2 - R_2'.$$

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[6] Langmuir, J. Am. Chem. Soc. **36**, 1708, (1914); **37**, 417 (1915)

Assuming that R_2' is zero, we must have

$$W_2 - W_1 = D' - R_2 + R_1 + R_1'$$

or

$$2{\cdot}4 = 3{\cdot}5 - R_2 + R_1 + R_1'$$

in order to have agreement between the ionization results and Langmuir's experiments. Nothing is known of the magnitude of R_2, R_1 and R_1'. Moreover, W_2 cannot be exactly determined experimentally since it depends on the initial and final states of vibration and rotation, a point that should be remembered in dealing with polyatomic gases. There is, therefore, really no proved discrepancy between Langmuir's work and that on ionization.

The writer is very much indebted to Mr. H. A. Barton for assistance in setting up the apparatus and taking readings. He is also much obliged to the Department of Physics at Princeton for extending the privileges of the laboratory to him while he was still National Research Fellow.

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