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THE ACTIVATION OF MOLECULAR HYDROGEN BY ELECTRON IMPACT

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Introduction

In this research we have undertaken to study the activation of hydrogen molecules by electron impact under conditions in which we know the energies of the impinging electrons. The experiments of Cario and Franck[1] show that hydrogen molecules can be activated by excited mercury atoms by collisions of the second kind and that copper oxide and tungstic oxide can then be reduced. In their experiments the mercury atoms receive energy of 4.9 volts from the light source, which is sufficient to dissociate hydrogen molecules, the heat of dissociation of hydrogen being 3 to 4 volts. Furthermore, it has been known for some time that in a discharge tube hydrogen will disappear when a discharge is passed.[2] Hughes,[3] in particular, has investigated the electrical clean-up of hydrogen and nitrogen, and finds a definite decrease in the hydrogen pressure at 13.3 volts and higher. He adopts Langmuir's conclusion[4] that hydrogen is dissociated under these conditions, and that the decrease in pressure is due to the freezing out of atomic hydrogen on surfaces cooled by liquid air. His results will be referred to later in connection with our own experiments. In Hughes' investigations no copper oxide was present, and the minimum electron energy at which hydrogen disappears was not accurately determined. A number of experimenters[5] also have investigated the chemical reactivity of hydrogen activated by an electric discharge, but the energies of the impinging electrons were not known.

We shall discuss four possible mechanisms by which electrons may be expected to activate hydrogen molecules.

First, it might be that an electron having kinetic energy of 3 to 4 volts could transfer its energy to the hydrogen molecule and cause its dissociation into atoms. These in turn could then react with other substances. However, it is known that no kink occurs in current-potential curves of hydrogen near 4 volts, and it seems, therefore, that electrons having kinetic energy equal to the dissociation energy of hydrogen molecules

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[1] Cario and Franck, *Z. Physik*, **11**, 161 (1922).

[2] An excellent discussion of these phenomena may be found in Dushman "High Vacuum," Gen. Electric Rev., **1922**.

[3] Hughes, *Phil. Mag.*, **41**, 778 (1921).

[4] Langmuir, THIS JOURNAL, **34**, 1310 (1912): **37**, 417 (1915).

[5] Wendt and Landauer, *ibid.*, **42**, 930 (1920); **44**, 510 (1922). Bonhoeffer, *Z. physik. Chem.*, **113**, 199 (1924); and others.

cannot transfer their energy to these molecules. We then should expect to find no evidence of reaction when hydrogen is bombarded with 4-volt electrons, and our experiments actually do give no indication of reaction. This is in agreement with the commonly held idea that the dissociation of molecules does not occur as the direct result of electron impact.

Second, electrons may have to possess sufficient energy to resonate the molecule, which may then dissociate if its heat of dissociation is less than its resonance potential. The hydrogen molecule has, according to the latest results of spectroscopy,[6] a resonance potential at 11.6 volts. Electrons of this energy can raise hydrogen molecules into an upper quantum state. These activated molecules would ordinarily return to the normal state after a short time. However, they may either dissociate into atoms upon impact with other molecules and the atoms thus react, or the resonated molecules may act directly on any oxide or other substance on which they impinge.

A third mechanism of causing activation by electron impact might be that where the impinging electron transfers enough energy to the hydrogen molecule to cause its dissociation and resonance of one of the atoms. This process may be expected at 13 to 14 volts, which is the sum of the heat of dissociation and the resonance potential of the hydrogen atom. This is the mechanism postulated by Hughes.[3]

A fourth possibility may be considered. It may be necessary that an electron ionize a hydrogen molecule before the latter can be made to react. It was found by Anderson[7] and Storch and Olson[8] that nitrogen and hydrogen reacted to form ammonia when bombarded by 17-volt electrons. This voltage is near the ionization potentials of these molecules.

We may state at once the results of our experiments. *Electrons of 11.4 volts' energy can activate hydrogen molecules*, for we find that there is a definite pressure decrease when the accelerating voltage applied to our tube has this value. At the same voltage we also obtain a kink in the current-potential curves, using the Franck method.

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Experimental Procedure

The experimental arrangement is shown in Fig. 1.

The filament F was made of platinum foil coated with calcium oxide. This was surrounded with a platinum can having in the end a circular grid G_1, 0.5 cm. in diameter made from platinum gauze of 52 mesh. The next electrode consisted of a copper cylinder B, 4.5 cm. in diameter with a platinum grid G_2, also of 52 mesh at the end. One millimeter behind this second grid was a platinum plate P. The distance between the

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[6] Witmer, *Proc. Nat. Acad. Sci.*, **12**, 238 (1926).

[7] Anderson, *Z. Physik*, **10**, 54 (1922).

[8] Storch and Olson, THIS JOURNAL, **45**, 1605 (1923).

filament and first grid was 1 mm., and between the two grids 4 cm. A copper cooling coil C, through which tap water could be circulated, was introduced into the tube by means of copper disk seals, and made good electrical and thermal contact with the copper cylinder. The copper cylinder and cooling coil were surface oxidized in a Bunsen flame before being placed in the tube, thus providing a large surface of copper oxide.

With the tube first used, which had no cooling coil, it was found that with the filament lighted, but with no accelerating field on, there was a noticeable rate of decrease of pressure. Since this effect may have been due to reduction by the hydrogen of the copper oxide heated by conduction from the hot filament, the cooling coil described above was introduced into the tube, with the result that there was no longer any decrease in pressure, but instead a smaller rate of pressure increase. This increasing pressure may possibly be due to slow evolution of gas from the heated filament or from the metal surfaces bombarded by electrons. It was too large to be accounted for by leaks, which were carefully tested for. These zero rates, however, caused no difficulty in determining the voltage at which reaction did begin.

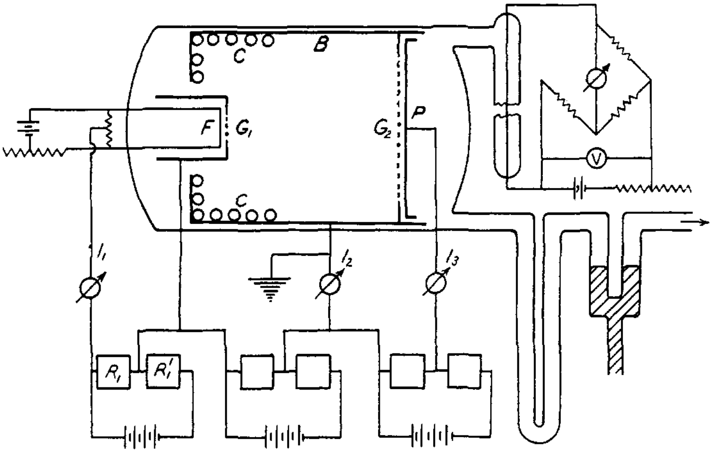

Fig. 1.—Experimental tube and wiring diagram.

The electrical connections are as shown. The total current, henceforth designated by I_1, and the current to the second can, I_2, were measured on the same galvanometer with a scale 1 meter long and 3 meters away. On the most sensitive shunt 8.16×10^{-9} amperes gave a deflection of 1 cm. Another galvanometer, giving a deflection of 1 cm. for 1.09×10^{-11} amperes on its most sensitive shunt, was used to measure the plate current I_3. The voltage applied between the filament and grid G_1 was calculated from the equation

$$E_1 = \frac{R_1}{R_1 + R_2} [E - I_1R_2]$$

E is the voltage across the potentiometer, and R_1 and R_2 are the respective readings of the two resistance boxes (the sum of whose resistances was kept at 10,000 ohms). The term I_1R_2 is introduced because of the electron current flowing from the filament to the other electrodes, hence through R_2 and back to the filament, and is relatively important at the emissions used (0.1 to 1 milliampere).

One side tube led to a liquid-air trap and mercury cut-off, thence to a palladium tube for admitting hydrogen, a McLeod gage, another mercury cut-off, and pumps. Another side tube led to a Pirani resistance gage which consisted of a thin tungsten wire

9 cm. long enclosed in a narrow glass tube. It was used according to the method described by Campbell,[9] and shown in the figure. By putting the gage in one arm of a Wheatstone bridge, the other three resistances of which were fixed and each one-third greater than the Pirani resistance at room temperature, any change in pressure could be followed by means of the voltage necessary to obtain a balance. The voltage was calibrated against the McLeod gage for a series of pressures of hydrogen up to 0.3 mm. of mercury. The Pirani gage was shielded from drafts, but no attempt was made to thermostat it. In order to follow small pressure changes, a more sensitive galvanometer was thrown across the bridge after a balance had been obtained, and readings were made with a telescope and scale 80 cm. away. With this set-up 1 cm. change in the scale reading corresponded to approximately 4×10^{-5} mm. in a total pressure of hydrogen of 0.2 mm. The volume of the tube up to the mercury cut-off was about 320 cc.

It will be seen that with this apparatus the following objectives can be attained. (a) Electrons emitted from the heated filament can be accelerated to a known velocity by the first grid and activate hydrogen molecules, which may then react with the copper oxide. (b) The water formed can be frozen out in the liquid-air trap with a resulting decrease in pressure. (c) The rate of decrease of pressure can be followed by means of the Pirani gage. (d) Mercury vapor is frozen out by the liquid air; thus, resonated mercury atoms cannot excite hydrogen molecules and cause reaction. (e) Current-potential curves can be taken by either the Franck or Lenard methods in the usual manner.[10]

The procedure adopted was as follows. After pumping out to 10^{-5} mm., hydrogen was admitted by heating the palladium tube in a gas flame, and readings were taken on the McLeod gage and on the voltmeter of the Pirani gage after liquid air had been placed about the liquid-air trap. The filament was then lighted and its temperature adjusted to give the emission desired at a definite accelerating voltage. After conditions had become steady, the mercury cut-off was closed and a series of readings with no accelerating field was taken on the rate of deflection of the sensitive galvanometer in the Pirani set-up. These readings constituted a set of "zero rates" for that particular run. Then the electrons were accelerated with a definite potential, and a similar set of rate measurements was taken. From time to time the mercury cut-off was opened and closed, allowing the hydrogen to come up to its original pressure. The voltage was increased in steps of 0.4–0.5 v. This process was repeated until rates had been obtained covering the voltage range desired. At the same time readings were taken of the total current I_1, and of I_2 and I_3. No field was applied between the two grids, but a retarding potential of 0.5 v. was maintained between the second grid and plate. In these runs either the total current I_1 or the sum of the currents $I_2 + I_3$ was kept constant by adjusting the filament temperature.

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[9] Campbell, *Proc. Phys. Soc. London*, **33**, 287 (1921).

[10] These methods are fully described in "Critical Potentials," Compton and Mohler, *Bull. Nat. Res. Council*, **1924**, and elsewhere.

Experimental Results

Reaction Measurements.—Careful investigation failed to give any evidence of reaction between 0 and 10 volts' accelerating potential. It was found, however, that reaction does begin around 11.4 volts. From 11.4 volts on, the rate of pressure decrease rises rapidly with the applied voltage until the ionization potential is just passed and the glow discharge sets in. Above ionization it was found in most of the runs that the rates increase only slowly with the voltage, but depend primarily on the number of electrons passing through the first grid.

Since electrons are not emitted from a heated platinum-calcium oxide surface until a certain accelerating voltage is applied, a corresponding correction must be applied to the voltage scale. This initial velocity correction was determined as follows. For a constant heating current, the accelerating voltage was increased in small steps from 0 to 5 v., and the total current I_1 read. The foot of the curve so obtained corresponds to the voltage at which the fastest electrons will just escape from the filament and gives the correction to be subtracted from the observed voltage at which reaction begins. Four determinations for different heating currents gave 1.12, 1.19, 1.20 and 1.21, average 1.2 v.

In Table I are given the voltages (from which the correction of 1.2 v. has been subtracted) at which reaction is found to begin. The average of these values is 11.4 v. The table contains all our experiments.

TABLE I

VOLTAGE (CORRECTED) AT WHICH REACTION STARTS

Expt.	Pressure of H_2, mm. of Hg	Volts	Expt.	Pressure of H_2, mm. of Hg	Volts
1	0.262	11.8	7	0.203	10.9
2	.249	11.9	8	.244	11.2
3	.168	11.8	9	.175	12.0
4	.124	11.4	14	.162	10.9
5	.103	11.9	15	.193	10.4
6	.158	11.5	18	.185	11.5

Resonance Potential of Hydrogen.—In order to determine the significance of the value 11.4 v., Franck current-potential curves were taken in hydrogen and in hydrogen-helium[11] mixtures of the composition 0.1 mm. of hydrogen and 1.1 mm. of helium. In making these runs, I_1 was kept constant and readings taken of I_3. A retarding potential of 0.5 v. was applied between the plate and second grid, while the accelerating potential was increased in small steps. Prominent kinks occurred in the I_3 curves taken in pure hydrogen around 13.5 and 19 v. uncorrected. In the curves for the hydrogen-helium mixtures similar kinks were found,

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[11] The helium used was that prepared previously. Glockler, *Phys. Rev.*, **27**, 423 (1926).

as also a new one at 22 volts, due to the first resonance potential of helium. By plotting the differences of successive I_3 readings the kinks were brought out very strongly. The voltages at which the kinks occurred were obtained from the maxima in these difference curves, which give the point at which the rate of change of slope is the greatest, thus corresponding to the middle of the electron velocity distribution. Two determinations by the Franck method gave the helium kink at 21.88 and 21.75 v., and a Lenard run, 21.90. From spectroscopy the value of the resonance potential of helium is 19.77 v., which has also been obtained by the method of electron impact. Therefore, by subtracting 19.77 from the above values the initial velocity correction can be obtained. This comes out 2.11, 1.98 and 2.13, average 2.08 v. Table II summarizes the values found for the first kink in hydrogen after the correction of —2.08 v. has been applied.

It is seen that the two methods used to determine the initial velocity correction give identical results for the voltage at which reaction starts and for the resonance potential of hydrogen.

TABLE II

RESONANCE POTENTIAL OF HYDROGEN

Expt. No.	10	11	12	13	14	15	16	17
H_2 pressure in mm.	0.128	0.28	0.16	0.162	0.162	0.175	0.1[a]	0.1[a]
Volts, corrected	11.28	10.93	11.27	12.09	11.58	11.73	10.83	11.33
Volts, averaged	11.38							

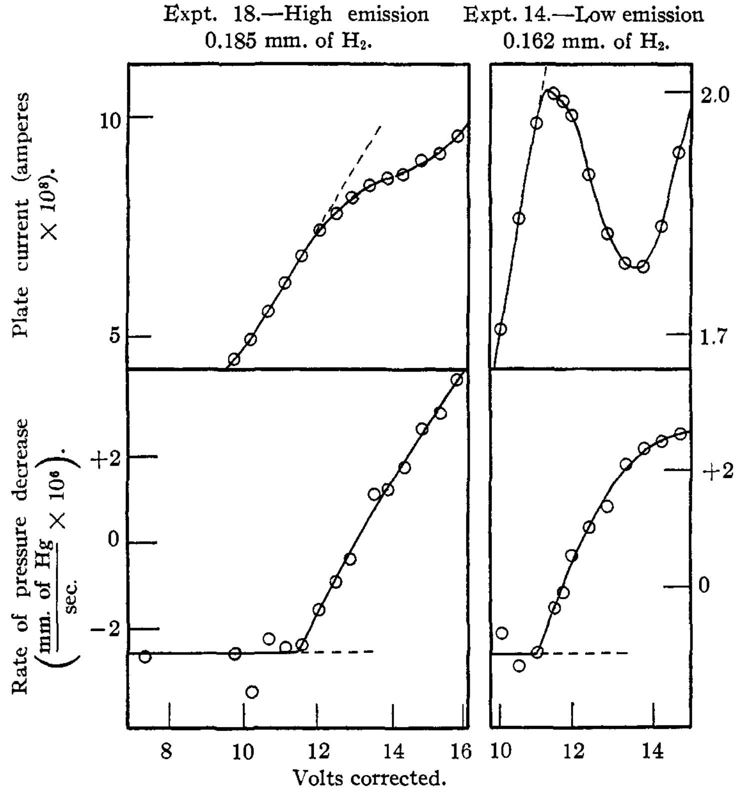
[a] Plus 1.1 mm. of He.

This experimental value of 11.4 v. agrees well with the value 11.6 derived by Witmer[6] from spectroscopic data for the first resonance potential of the hydrogen molecule. It is also seen to coincide with the voltage at which hydrogen begins to disappear and we may therefore conclude that the first step in the reaction at these voltages is the formation of resonated hydrogen molecules by collision with 11.4 electrons. The resonated hydrogen molecule may then react directly with the copper oxide or be dissociated by collision with other molecules and subsequently react. Of course, after the first resonance potential is passed, the process of activation may include higher energy levels, and when ionization is reached the mechanism of reaction may be considerably altered. Further work on these points is to be continued; we wish only to record here the fact that reaction does set in when the first resonance potential of the hydrogen molecule is reached.

In order to identify still further the beginning of reaction with the resonance potential, several runs were made in which both rates and Franck current-potential curves were taken. Fig. 2 illustrates two of these runs. *In each case, it was observed that the break in the Franck curve begins at the same point as that at which the hydrogen pressure starts to drop.*

Identification of the Reaction Product

In order to determine the nature of the final reaction product, one of the runs was continued until all of the hydrogen had reacted (pressure about 10^{-4} mm.). On removing the liquid air the pressure rapidly rose. After 30 minutes the liquid air was replaced. The pressure immediately fell to its original value. This is the opposite of the results of Hughes[3] (in the absence of copper oxide) for he found that on removing the liquid air and replacing it the pressure did not fall to its original value due to the presence of a non-recondensable gas. The non-recondensable gas he assumes, with Langmuir,[4] to be molecular hydrogen formed by the recombination of atomic hydrogen that had previously been frozen out on the walls at liquid-air temperature. To determine whether or not water was formed in our experiment the liquid air was again removed, the mercury cut-out opened, and the pressure read on the McLeod gage. The two



Expt. 18.—High emission 0.185 mm. of H_2.

Expt. 14.—Low emission 0.162 mm. of H_2.

Fig. 2.—Two runs illustrating the relation between the beginning of the break in the Franck current-potential curve and the voltage at which reaction starts.

columns maintained a nearly constant difference of height except near the closed end of the capillary. After correcting for the small pressure of uncondensable gases, the difference of height was found to be 2.6 cm. The vapor pressure of water at the same temperature is 2.65 cm.

Summary

Hydrogen molecules have been activated by collisions with electrons of known energy and made to react with copper oxide. It is found that reaction begins at 11.4 volts. At the same time Franck current-potential curves show a resonance point at 11.4 volts. This agrees with the recent value of 11.6 volts for the first resonance potential of the hydrogen molecule as obtained from spectroscopy. It is concluded, therefore, that the first step in the activation process at low voltages is the formation of a resonated hydrogen molecule.

No evidence is found that 3- to 5-volt electrons dissociate hydrogen molecules.

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[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY]

THE CONCENTRATION OF WATER VAPOR IN COMPRESSED HYDROGEN, NITROGEN AND A MIXTURE OF THESE GASES IN THE PRESENCE OF CONDENSED WATER

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Recently developed commercial processes involving the use of gases under pressures of several hundred atmospheres have aroused keen interest in the physical properties of compressed gases. Not only does engineering design depend upon these properties, but accurate data concerning them must be available for a complete scientific understanding of the process itself.

In the synthetic preparation of ammonia from hydrogen and nitrogen the efficiency and life of the catalyst as well as the purity of the product depend upon the purity of the gases. Of possible impurities, water vapor is always present. It has been customary to calculate the water vapor content of "indifferent" gases in contact with a liquid by assuming the application of the perfect gas law both to gas and vapor, and the constancy of the vapor pressure of a liquid with temperature, but neglecting the effect of pressure. The volume per cent. of water vapor at temperature T in any indifferent gas and at any pressure is thus expressed

$$(\text{Volume \% of water vapor})_T = (100p)/(760P)_T \qquad (1)$$

where p is the vapor pressure of water at T in millimeters of mercury and P is the total pressure in atmospheres. If a portion of the compressed gas in equilibrium with condensed water be removed from contact with