

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

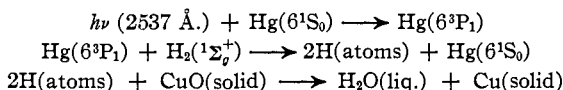
## The Sensitized Decomposition of Hydrogen with Electrons of Controlled Energy

BY GEORGE GLOCKLER AND LLOYD B. THOMAS<sup>1</sup>

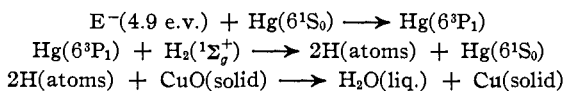
### I. Introduction

The use of electrons of known energy as activating agents for chemical reactions has been studied by one of us<sup>2,3</sup> in the case of hydrogen and oxygen. In this paper we wish to report further experiments on the decomposition of hydrogen in the presence of mercury using electrons of controlled speed as activating agents. This reaction is the analog of the Cario and Franck<sup>4</sup> experiment substituting for the incident radiation ( $\lambda = 2537 \text{ \AA.}$ ) electrons of definite voltage. The general basis of studying such electron activated reactions is to elucidate mechanisms for such reactions as are produced in electric fields (ozonizers) and by alpha particles<sup>5</sup> and to compare reactions activated by various agents.

The photosensitized decomposition of hydrogen can be described best by the steps



The last reaction simply serves as a means of removing hydrogen atoms so that the whole process may be followed by a pressure decrease. From this photochemical reaction one would predict that the corresponding electron-activated reaction should be



Electrons of 4.9 e. v. energy should dissociate hydrogen molecules in the presence of mercury vapor. Since it is known that electrons in the absence of mercury atoms must have 11.7 e. v. energy<sup>2,6</sup> before they can dissociate molecular hydrogen, it should be easy to detect the effect of mercury atoms on the decomposition of hydrogen when induced by electrons. The pressure decrease should happen at 4.9 instead of 11.4 volts.

(1) This article is based upon a thesis presented to the Faculty of the Graduate School of the University of Minnesota by Lloyd B. Thomas in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Glockler, Baxter and Dalton, *THIS JOURNAL*, **49**, 58 (1927).

(3) Glockler and Wilson, *ibid.*, **54**, 4544 (1932).

(4) Cario and Franck, *Z. Physik*, **11**, 161 (1922).

(5) S. C. Lind, "The Chemical Effects of Alpha Particles and Electrons," Chemical Catalog Co., New York City, 1928, second edition.

(6) Hughes and Skellett, *Phys. Rev.*, **30**, 11 (1927).

The results of the experiments described in this paper are not in accordance with this prediction. We find that at low pressures ( $\text{H}_2$  at 0.02 mm. and Hg at 0.002 mm.) decomposition starts at 7.7 volts. The reasons for this difference will be given below.

### II. Experimental Procedure and Results

The apparatus used is shown in Fig. 1. The experimental tube used is the sixth one developed in this work. The earlier ones were discarded for various reasons. They are described in detail elsewhere.<sup>1</sup> It is important in this work to produce a copious stream of electrons from a filament of as low a temperature as can be attained. The filament must not heat up the copper oxide surface. A hot copper oxide surface would readily be reduced by molecular hydrogen, entailing a large background of pressure drop, which would be very undesirable. The filament was made of nickel, oxide covered (9 mm. long, 0.5 mm. wide and about 0.1 mm. thick) and required only 1.5 amperes heating current. The filament drop was less than 0.4 volt so that less than 0.6 watt was consumed. Since only the central portion of the filament was hot enough to emit electrons, it delivered electrons of nearly uniform velocity. The electron current to the plate was of the order of 50 microamperes depending on the accelerating voltage. Since very little heat is evolved by a filament of this kind no large background of pressure drop was observed and the Pirani gage showed very little zero drift, *i. e.*, pressure drop at "zero" accelerating voltage. The wire of the Pirani gage was a tungsten filament 5 cm. long and 0.025 mm. thick. The glass tube carrying this wire concentrically was of 8 mm. inside diameter. A six-volt storage battery connected in series with a milliammeter and a dial resistance box (10,000 ohms) heated the gage to a dull red heat. The fall of potential over the Pirani wire is balanced by the potentiometer using a moderately sensitive galvanometer ( $5.68 \times 10^4$  cm. divisions per volt) with telescope and scale. The rate of pressure change is measured by the rate of drift of the galvanometer. The potentiometer is not read but is used as a convenient means of bringing the galvanometer to the desired position on the scale. If the tungsten wire is allowed to cool or to run a long time without heating strongly its resistance drops markedly so that it cools below red temperature. As adsorbed gases are driven from the filament the wire will assume its original condition. After baking the tube out and setting the apparatus in operation, it required at least two days to reach steady conditions. Even during the calibration measurements some adsorption of gas is noted for the ascending and descending portions of the curves for hydrogen (Fig. 1) do not coincide, but the difference is noted to be very small. A mixture of krypton and hydrogen was also studied and it is seen that the slope of the curve is the same in pure hydrogen or in mixtures containing various amounts of krypton. Kryp-

ton was more convenient to use than mercury as foreign gas. Dividing the slope of the pressure *versus* voltage curve by that of the deflection *vs.* voltage curve gives the pressure change per scale division. The former value for hydrogen is 0.480 mm. Hg/volt and the latter is  $5.68 \times 10^4$  cm./volt so that the sensitivity of the Pirani gage is  $8.45 \times 10^{-6}$  mm. pressure change per cm. scale deflection. In order to determine the validity of this calibration it was checked by an entirely different method. A certain pressure of krypton was led into the apparatus and its volume was reduced by allowing a mercury column to rise in one of the cut-off tubes. The galvanometer deflection was observed for the two positions of the mercury column. The agreement was very good with the deflection predicted from the compression, the slope of the curve (Kr) and the galvanometer sensitivity.

It was found that a well baked out tube would adsorb the water formed during the reaction so that liquid air was not necessary for the removal of the reaction product, although it was used in some of the runs. Hydrogen was introduced through a palladium tube in the usual manner. The applied voltage was read on a "Jewel" precision voltmeter. The volume of the reaction tube to the mercury cut-off was 77.9 cc. The plate galvanometer had a current sensitivity of  $3.81 \times 10^{-8}$  amp./cm. on shunt 1.0 and one-tenth and one-hundredth of this value on shunts 0.1 and 0.01.

It is desired to determine the number of hydrogen molecules decomposed per electron passing between the filament and plate as a function of the energy of the electrons. This relationship may be calculated from the following four readings taken at a series of accelerating potentials: the accelerating voltage as registered by the precision voltmeter, the drift of the galvanometer in the Pirani circuit, the time over which the drift is measured and the current which reaches the plate. From the pressure decrease, the volume of the tube (77.9 cc.) and the temperature (298°), the number of hydrogen molecules disappearing per minute may be calculated.

The detailed calculations and data can be found in another place.<sup>1</sup> The results are shown in Fig. 3 and Table I. The experimental values of the electron energies needed to cause the decomposition of hydrogen with and without mercury atoms as sensitizers are found to be 7.77 and 11.86 e. volts. These values must be corrected for the initial velocity of the electrons.

**Initial Velocity Correction.**—A variety of methods was tried to determine the initial velocity of the electrons as they leave the filament. The most satisfactory results are obtained by the use of the excitation potential or term value of the  $^3\Sigma_g^+$  state of hydrogen. This value is known

from spectroscopic studies<sup>7-9</sup> to be 11.72 e. volts. On this basis then the correction is 0.14 e. v. and the non-sensitized decomposition happens at  $11.72 \pm 0.22$  e. v. This value is higher than the earlier results<sup>2,6</sup> by 0.28 e. v. Since the spectroscopic term is more accurate than the values based on any current-potential experiment, the present figure is greatly to be preferred. It is well known that the matter of obtaining velocity corrections in an unambiguous manner is difficult. We have studied five different methods of

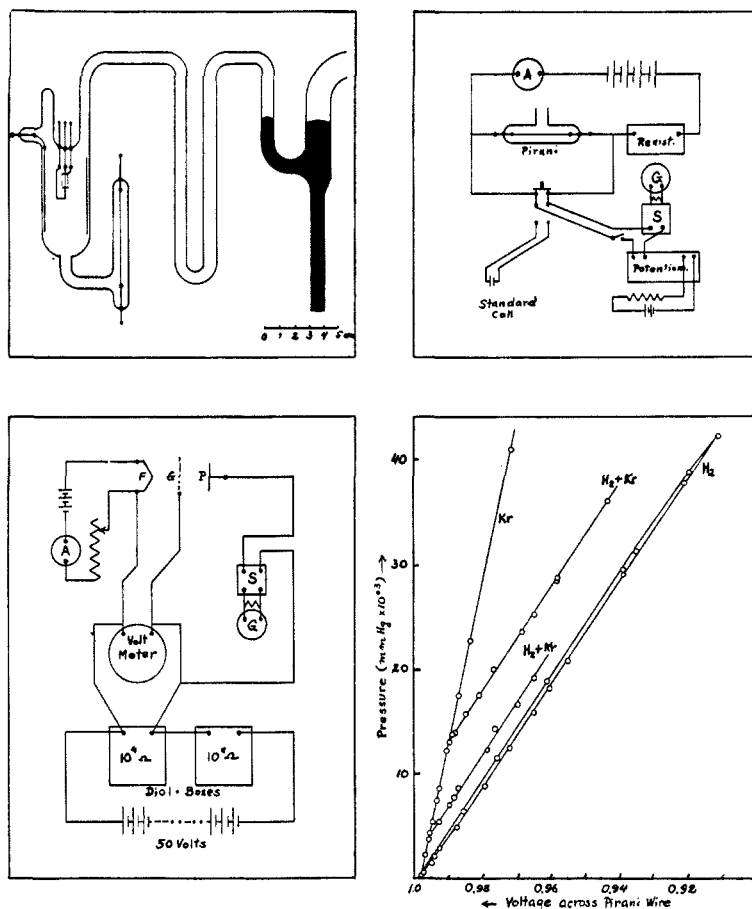


Fig. 1.—Apparatus: reaction tube; Pirani gage; electrical connections for reaction system and Pirani gage calibration curves.

obtaining the initial velocity correction. They gave values which would lower the result (11.86 e. v.) by 0.4 to 1.0 e. volt. However, every method has its drawbacks. Either a foreign gas or a gas mixture ( $H_2$  and He or  $H_2$  and Hg) has to be employed or the method depends on some complicated use of current-potential relations. After an extended and time-consuming study of the situation, we came to the conclusion that the use of the spectroscopic term value of  $^3\Sigma_g^+$  of hydrogen was the most satisfactory way of eliminating the initial velocity correction of the electrons.

(7) O. W. Richardson, "Molecular Hydrogen and Its Spectrum," Yale University Press, New Haven, Conn., 1934, p. 327.

(8) W. Jevons, "Band Spectra of Diatomic Molecules," The University Press, Cambridge, England, 1932, p. 268.

(9) R. S. Mulliken, "Interpretation of Band Spectra," Part III, *Review of Modern Physics*, 4, 1 (1932).

TABLE I  
SUMMARY OF EXPERIMENTAL RESULTS: NON-SENSITIZED  
AND MERCURY SENSITIZED DECOMPOSITION OF HYDROGEN

Run	Pressure, mm. Hg $\times 10^3$ H <sub>2</sub>		Beginning of pressure drop, volts (uncorr.)
1	4.6		12.12
2	11.3		12.08
3	10.4		12.02
4	11.2		11.69
5	12.7		11.65
6	27.8		11.58
			<hr/>
			11.86 = 0.22
7	2.1	1.85	8.24
8	5.9	1.85	7.46
9	10.3	1.90	7.70
10	15.4	2.00	7.44
11	25.2	2.30	7.44
12	47.3	2.20	7.68
13	6.2	1.70	7.86
14	11.7	1.85	7.76
15	17.3	1.60	7.84
16	34.3	1.60	8.24
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			7.77 = 0.23

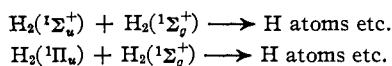
### III. Discussion of Results

**The Non-Sensitized Reaction.**—The higher energy states of hydrogen molecules which need to be considered in the interpretation of these experiments are given in Table II and Fig. 2.

TABLE II  
ENERGY STATES OF HYDROGEN MOLECULE

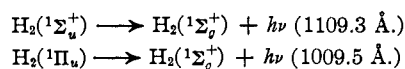
State	Term-values (zero vibration)	Excitation potential (Franck- Condon)	Possible transition
(1s <sup>2</sup> ) <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	Zero		
(2p) <sup>3</sup> Σ <sub>u</sub> <sup>+</sup>	Repulsive	8.5–10.4	Two H atoms
(2p) <sup>1</sup> Σ <sub>u</sub> <sup>+</sup>	11.12 e. v.	11.4–12.6	Radiation
(2p) <sup>3</sup> Π <sub>u</sub>	11.72 e. v.	11.7–13.0	Metastable H <sub>2</sub>
(2s) <sup>3</sup> Σ <sub>g</sub> <sup>+</sup>	11.73 e. v.	11.6–12.4	Continuum + 2H
(2p) <sup>1</sup> Π <sub>u</sub>	12.22 e. v.	12.2–13.6	Radiation
(2s) <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	12.25 e. v.	12.0–13.4	Metastable H <sub>2</sub>

Electrons can transfer normal hydrogen molecules into the various excited states shown above.<sup>10</sup> If the excited state is an odd singlet state then the excited molecule can return to normal with emission of radiation. Such transitions will lead to chemical action with only low probability for it would mean that the excited molecule during its short life will either have to make an impact with another normal molecule or the wall in order that decomposition occurs. The chance for reactions of the type



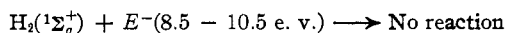
(10) Condon and Smyth, *Proc. Nat. Acad. Sci.*, **14**, 871 (1928).

most likely is much smaller than the return to the normal state with radiation



If the life of an excited hydrogen molecule is of the order of 10<sup>-7</sup> seconds it can readily be calculated that it will make only very few collisions (0.01) during its life. At 0.01 mm. pressure, its collision diameter would have to be many times the kinetic theory diameter of the normal molecule in order that these states would be involved in the reaction. It can also readily be shown that the average excited molecule cannot reach the wall of the reaction tube during its life. It would appear then that the excited states <sup>1</sup>Σ<sub>u</sub><sup>+</sup> and <sup>1</sup>Π<sub>u</sub> do not contribute to the chemical reaction.

The repulsive state <sup>3</sup>Σ<sub>u</sub><sup>+</sup> could be reached by impact with electrons having 8.5 or 10.5 e. v. energy or any value between these limits (Franck-Condon principle). However no such transfer is observed and we conclude that this step is of very low probability



The last excited state mentioned in Table II, (2s)<sup>1</sup>Σ<sub>g</sub><sup>+</sup> with a term value and excitation potential of 12.25 e. v. is higher than two other states which appear to contribute to reaction. The state appears to have the desired property of a long life, for it cannot combine with any lower triplet nor singlet state and hence is metastable. It should contribute to reaction when the impinging electrons reach the appropriate energy.

The most likely states which are responsible for the initial pressure decrease in our reaction are the states (2p)<sup>3</sup>Π<sub>u</sub> and (2s)<sup>3</sup>Σ<sub>g</sub><sup>+</sup>. Being triplet states they cannot combine with the normal state which is a singlet state and hence they cannot radiate and return to normal. Nor can the state <sup>3</sup>Π<sub>u</sub> interact with the repulsive triplet state <sup>3</sup>Σ<sub>u</sub><sup>+</sup> on account of the "odd-even" selection rule. Hence this state ((2p)<sup>3</sup>Π<sub>u</sub>) is metastable. Hydrogen molecules in this state should readily reach the wall and there react with the copper oxide, reducing it. But the <sup>3</sup>Σ<sub>g</sub><sup>+</sup> state also should be involved in the chemical reaction. While it can radiate the continuum<sup>11,12</sup> when the molecule goes to the repulsive state it also produces two hydrogen atoms of high kinetic energy which should readily reduce copper oxide producing a

(11) Winans and Stueckelberg, *ibid.*, **14**, 867 (1928).

(12) Finkelburg and Weizel, *Z. Physik*, **66**, 577 (1931).

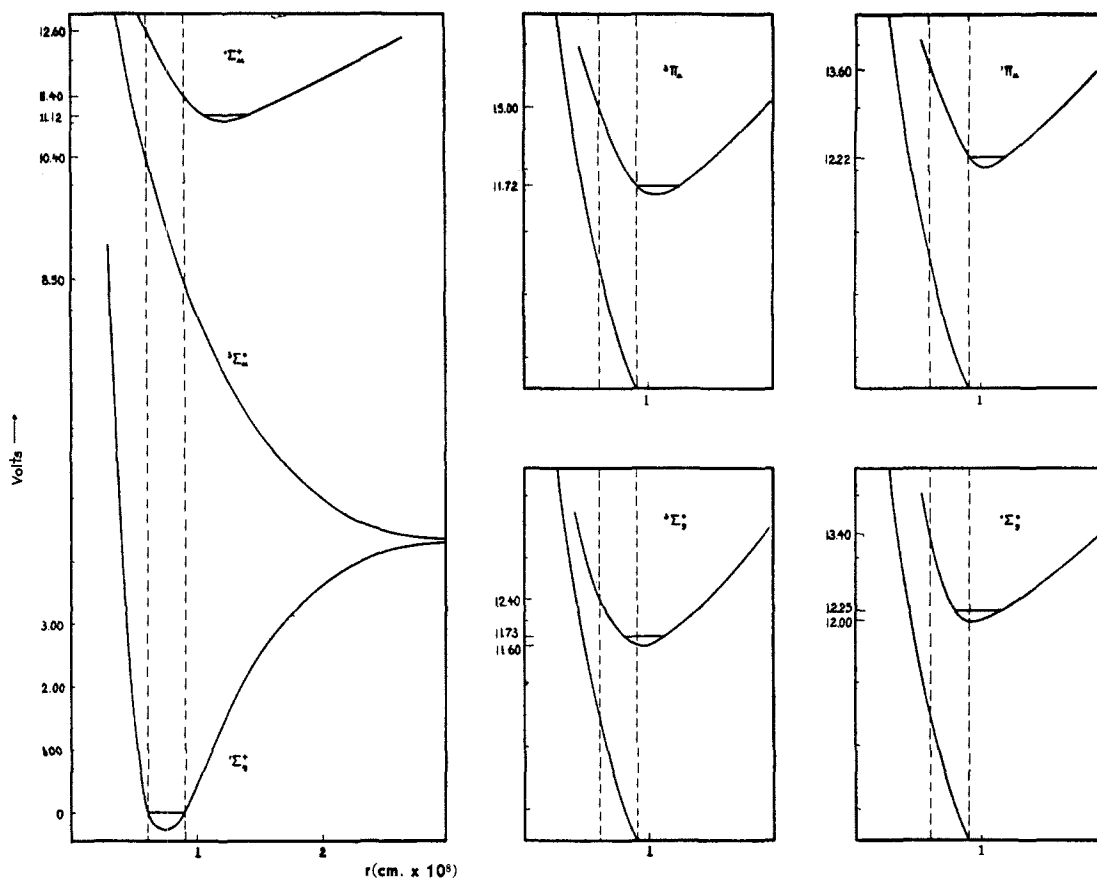
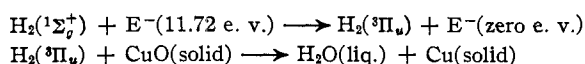
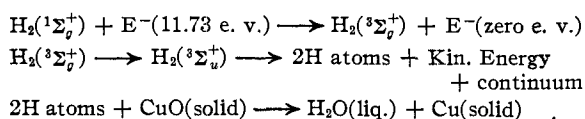


Fig. 2.—The one and two quantum states of hydrogen molecule.

pressure drop under our experimental conditions. The reactions taking place are



and



No choice is possible between these two reaction mechanisms. Both should happen. They have nearly the same electron energy and their excitation potentials are nearly the same. Hence it appears reasonable to consider 11.72 e. v. to be the voltage for onset of pressure drop. We calculate the initial velocity correction to be  $11.86 - 11.72 = 0.14$  e. v. as was noted above.

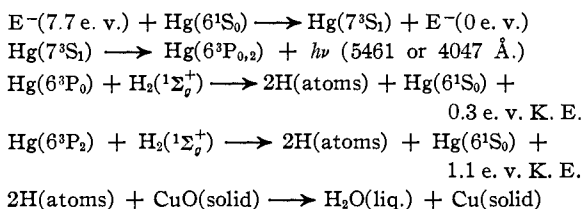
A change in slope in the curves ( $M/E$  vs. electron speed) is noticeable at about 15.5 e. v. Ionization is known to set in at this voltage. The slope decreases, showing lessened probability for reaction. When ions are produced their recom-

bination is necessarily involved in the reaction mechanism. At the low pressures used such recombination between hydrogen mole ions and electrons would be very infrequent and reaction of the cluster type<sup>5</sup> would not happen readily. The reaction observed is most likely due to excited states which are still produced with some probability even at voltages somewhat higher than their term values. Hydrogen mole ions might be thought of as ionic catalysts. However, they would not be expected to attract greatly hydrogen molecules of small polarizability nor would these molecules be greatly distorted in the field of the ion. Hence at low pressures of hydrogen ionization does not produce increased chemical action.

**The Mercury Sensitized Reaction.**—From Table I it is seen that the presence of mercury lowers the voltage at which reaction sets in from 11.86 to 7.77 e. v. (uncorr.). Applying the correction just determined we find that the mercury-sensitized reaction occurs at  $7.77 - 0.14 = 7.63$  e. v. and not at 4.86 e. v. as might be predicted

from the photosensitized reaction. It must mean that at low pressures the  $6^3P$  (4.9 e. v.) state of mercury is inefficient in producing reaction. The energy states of the mercury atom which must be considered in the interpretation of the experimental results are the following:  $6^3P_0$ (4.64),  $6^3P_1$ (4.86),  $6^3P_2$ (5.43),  $6^1P_1$ (6.67),  $7^3S_1$ (7.69) and  $7^1S_0$ (7.86) e. v.

Since the metastable states of mercury  $6^3P_0$  and  $6^3P_2$  do not assist the reaction, we must suppose that the efficiency of their direct production by electron impact is small. If they are produced then mercury atoms in these metastable states should be able to transfer energy to hydrogen molecules by collisions of the second kind with consequent dissociation. That these two metastable states are indeed much less readily produced by electron impact can be seen from current-potential curves obtained by Franck and Einsporn<sup>13</sup> and Foard.<sup>14</sup> The  $6^3P_1$ (4.9 e. v.) state, however, is not metastable and hence can return to normal with emission of 2537 Å. Hence this state will only be efficient if the excited mercury atoms during their short life can make a sufficient number of impacts with hydrogen molecules. At low enough hydrogen and mercury pressures an insufficient number of mercury atoms may be created and not enough impacts may happen to produce a measurable pressure change. We believe that these conditions are maintained in our experiments. Similarly therefore the states  $6^1P_1$ (6.67 e. v.) and  $7^1S_0$ (7.86 e. v.) are inefficient. The only remaining state is the term  $7^3S_1$ (7.69 e. v.). While it also will radiate to the three  $^3P$  states, only two of these are metastable and will have a sufficiently long life to interact with hydrogen molecules in accordance with the following reaction mechanism.

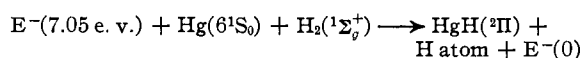


It is seen that the term value (7.69 e. v.) of the  $7^3S_1$  state of mercury is closer to our experimental onset voltage (7.63 e. v.) than any other possible term value and the above mechanism affords a reasonable picture of the steps leading to reaction.

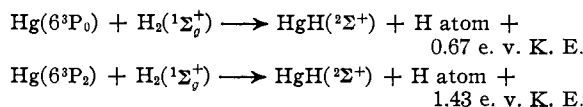
(13) Franck and Einsporn, *Z. Physik*, **2**, 18 (1920).

(14) Foard, *Phys. Rev.*, **35**, 1186 (1930).

There have been mentioned in the literature<sup>13,15</sup> some energy states of the mercury atom which do not fit into the spectroscopic set of term values. These states were found by critical potential methods. The values of interest here are 7.1 and 7.45 e. v. We have not involved these states in our considerations of a reaction mechanism for the sensitized reaction because we feel that they are not close enough to our experimental value for the beginning of the reaction. Similarly we have excluded the possible formation of mercury hydride in a triple collision which might happen at 7.05 e. v.<sup>9</sup>

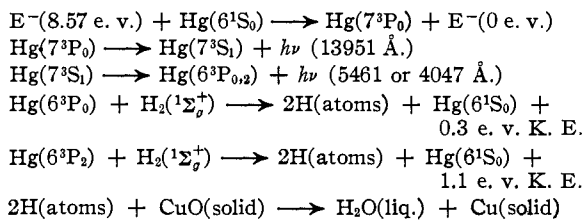


However the formation of mercury hydride may be involved in the reaction



We see that greater amounts of kinetic energy are liberated when mercury hydride molecules are involved. On the well-known principle that collisions of the second kind happen with greatest probability when the amount of energy going to kinetic energy is smallest, it is seen that the  $^3P_0$  state is more likely to lead to reaction.

**The  $7^3P$  States of Mercury.**—From Fig. 3 we can see that there is a change in slope at about 8.5 e. v. in the curve ( $M/E$  vs. voltage). This kink would indicate a new process becoming of importance. Indeed we notice that the  $7^3P$  states of mercury atom have the term values 8.57, 8.61 and 8.78 e. v. We therefore interpret the reaction in the following way.



The mercury atoms reach the metastable states by two radiative transitions. We have not looked for the radiations involved for the presence of the filament makes the discovery of a faint radiation a matter of great difficulty.

However, we have been able to explain the reactions studied on the basis of the energy level

(15) Messenger, *ibid.*, **28**, 962 (1926).

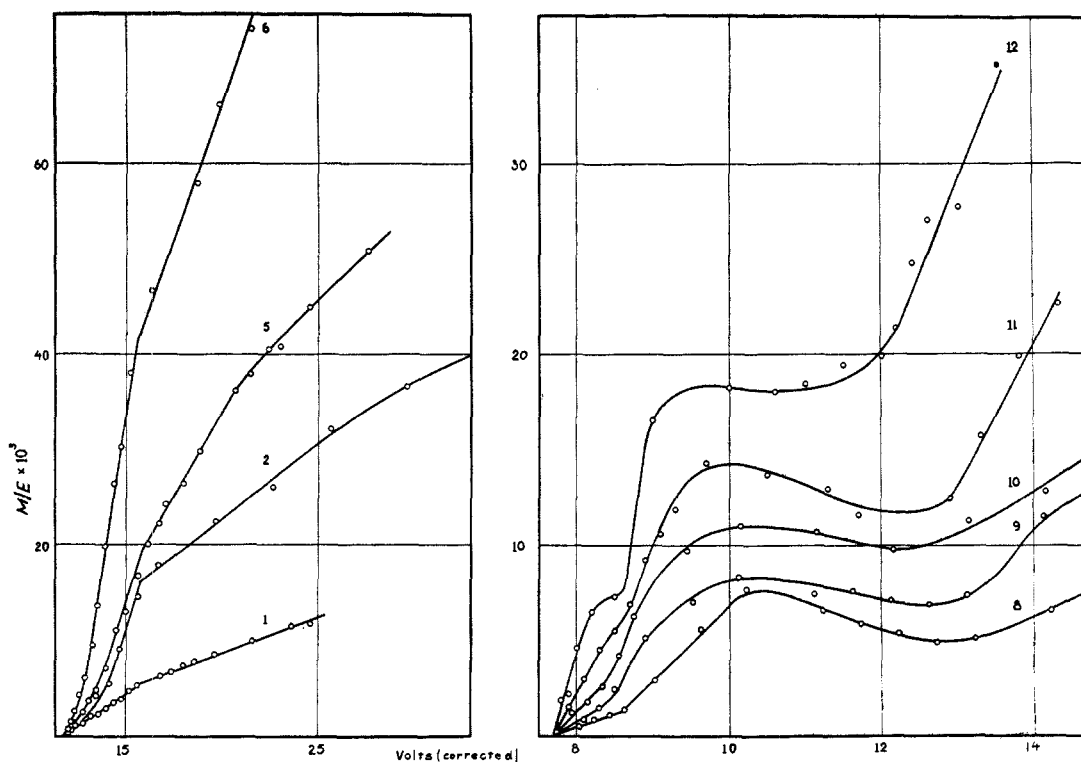


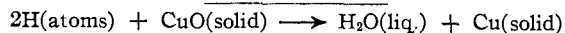
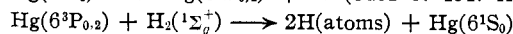
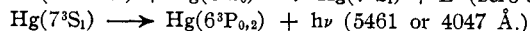
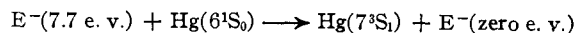
Fig. 3.—Molecules of hydrogen reacting per electron as a function of electron speed; non-sensitized and sensitized by mercury atoms.

diagrams of the substances involved. While we hope to deal with more complicated cases later, we expect to study next the effects of increasing pressure for the case reported here. At higher mercury and hydrogen pressures onset of reaction should appear at 4.9 e. v., corresponding to the original Cario-Franck experiment.

#### Abstract

Hydrogen molecules have been dissociated by electrons of known speed using mercury atoms as a sensitizing agent. These reactions are analogous to the photochemical decomposition of hydrogen using  $\lambda = 2537 \text{ \AA.}$  and mercury (Cario and Franck experiment). From the photochemical case one would predict that 4.9 e. v.

electrons should initiate the mercury-sensitized reaction; while without a sensitizer electrons must possess 11.7 e. v. energy. In the present experiment it is found that at low pressures ( $\text{H}_2$  at 0.02 mm. and Hg at 0.002 mm.) the short-lived radiative states of mercury (4.9 and 6.7 e. v.) and the well-known metastable states ( $6^3\text{P}_{0,2}$ ) are not efficient or are too short-lived to cause reaction. However, electrons of 7.7 e. v. energy can cause dissociation of hydrogen in the presence of mercury. The sequence of reaction is



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RECEIVED AUGUST 20, 1935