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The Critical Potential for the Electron Activated Mercury-Sensitized Decomposition of Hydrogen

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Introduction

The mercury-sensitized decomposition of hydrogen has been investigated by irradiating the mercury–hydrogen mixture with λ 2537,[1,2] and by passing through the mixture a stream of electrons of such energies that energy states of the mercury atoms should be excited successively as the accelerating voltage was increased.[3] It appeared necessary to postulate different mechanisms for the reactions by the two methods for the reasons which follow. The photochemical reaction is known to be due to the Hg^3P_1 atoms produced by absorption of λ 2537. These Hg^3P_1 atoms are known to be produced by impact of electrons of 4.86 e.v. minimum energy. The tubes in which the electron-initiated reaction was originally carried out were not designed for ionization or radiating potential measurements but were not designed to show pressure decrease when hydrogen began to disappear. For this reason the previously determined critical potential for disappearance of hydrogen by direct electron impact[4,5] was used to establish the voltage scale correction. The value of 11.4 volts of (4) was obtained with cupric oxide in the tube as in (3) and the value of 11.5 volts of (5) was obtained for onset of the process whereby hydrogen atoms, presumably, are produced and deposited on the tube wall of glass which is cooled in liquid air. It is possible that the processes of (4) and (5) are different but the very close agreement of the critical potentials reported would suggest that they are the same. Thomas,[6] taking 11.4 as the correct critical potential for onset of dissociation (or excitation) of hydrogen resulting in pressure decrease, found a voltage scale correction of −0.7 and fixed the critical potential for the mercury-sensitized reaction at 7.0 volts and Glockler, treating the same data,[3] fixed the critical potential of the mercury sensitized reaction at the higher value of 7.7 volts. In either case the value selected is well above the 4.86 volts where it was expected to observe the onset of pressure decrease. Failure to observe the reaction at 4.86 volts was explained by assuming relative inefficiency of the process involving Hg^3P_1 atoms compared to the one, perhaps involving metastable atoms, observed in the electron initiated reaction.

An estimate of the rate of pressure decrease in the tube to be expected from the Hg^3P_1 atom mechanism involves a knowledge of the absolute probability of excitation of the mercury atoms to the $^3P_1$ state as a function of voltage, the effective collision cross section for the presumed reaction $Hg^3P_1 + H_2 \rightarrow Hg^1S_0 + 2H$, the contribution of reabsorption or "imprisonment" of the resonance radiation to the efficiency, and the efficiency of cleanup of the presumed hydrogen atoms produced. Later work[2] has given information on the last three factors above and this combined with Seiler's[7] excitation function measurements indicates that the rate of decomposition of hydrogen through the Hg^3P_1 process should have been detectable although small compared to the rate observed. As an attempt to clarify this matter the present experiment was carried out in which it was planned to observe the light emitted as a function of voltage of the electrons along with the reaction rates in the same tube.

Experimental

The tube with oxide coated cathode, platinum grids and oxidized copper plate with Pirani gage attached is shown approximately to scale in Fig. 1. The tube differs from that used earlier,[3] by addition of the fused silica re-entrant tube and window and by addition of the outer grid which was to facilitate ionization potential measurement and which also appeared to give a desirable narrowing of the velocity distribution of the electrons over the previous design. The cathode was made of 0.004" platinum, nickel plated and coated with a barium carbonate and strontium carbonate mixture. Observation of the course of decomposition of hydrogen was carried out essentially as previously.[3] Observation of the very weak light from the window required rather elaborate detecting and measuring means. The light emitted through the window and more or less "piped" down the tube by glancing reflection was picked up through a Pyrex bubble window on the tantalum cathode of an eleven-stage electron multiplier tube made and described by Allen.[8] The current from this was led to a d. c. amplifier using the Western Electric D96475 electrometer tube in the Barth Circuit (e) as described by Penick.[9]

Observations of light intensity *vs.* accelerating voltage and of reaction rate *vs.* accelerating voltage were made in separate runs because the instrument manipulation, reading and data recording in the latter type of run fully occupy the manipulator during the short time allowable for the measurements. Results of runs of the two types are shown in Fig. 3. The observed light intensities and reaction rates are all adjusted to the same electron current by dividing by the plate current at each voltage setting. That there is a linear relation between each of the above quantities and plate current was demonstrated in a series of experiments.

The light observed by the electron multiplier tube was found to be essentially all of λ 2537 over the entire voltage range. The use of Corning filters 980 and 774 showed the light to be between λ 2000 and λ 2850 with transmission through filter 980 corresponding to λ 2537. A mercury vapor absorption cell, consisting of a short drum-shaped evacuated cell of fused silica with fused-on plane windows

(1) Cario and Franck, *Z. Physik*, **11**, 155 (1922).
(2) Thomas and Gwinn, THIS JOURNAL, **70**, 2643 (1948).
(3) Glockler and Thomas, *ibid.*, **57**, 2352 (1935).
(4) Glockler, Baxter and Dalton, *ibid.*, **59**, 58 (1937).
(5) Hughes and Skellett, *Phys. Rev.*, **30**, 11 (1927).
(6) Thomas, Ph.D. Thesis, University of Minnesota, 1935.
(7) Seiler, *Z. Physik*, **83**, 789 (1933).
(8) Allen, *Phys. Rev.*, **55**, 966 (1939).
(9) Penick, *Rev. Sci. Inst.*, **6**, 115 (1935).

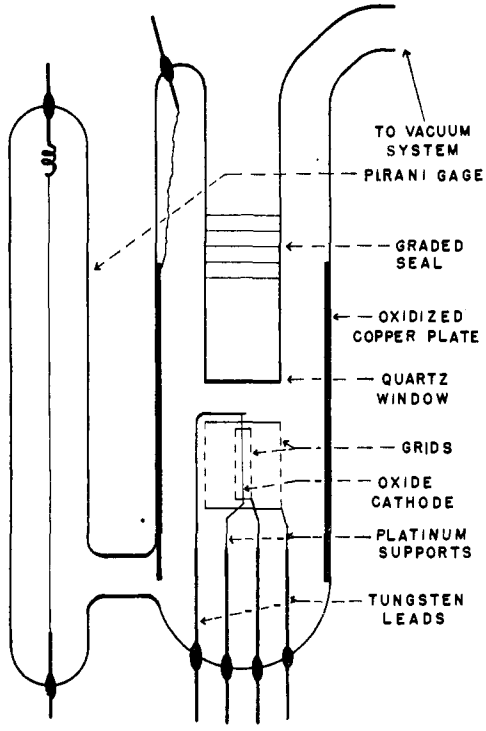

Fig. 1.—Experimental tube.

attached to a side tube with a droplet of mercury in it, was used to test the absorption of the radiation in mercury vapor and this was found at 0.001 and 0.002 mm. pressure of mercury in the cell to correspond to that expected for λ 2537. The transmission of Pyrex bubble windows was checked and found to be high for λ 2537 in the thickness used in the multiplier tube. Ionization potential measurements were made to aid in establishing the accelerating voltage correction of the apparatus. In these runs the two grids were connected together and set at the accelerating potentials and the plate was maintained at a negative potential with respect to the filament. The critical potentials for formation of H_2^+ and Hg^+ were used.

Experimental Results and Discussion

Since the work presented was done on several filaments and since even the same filament may show somewhat different voltage corrections depending on treatment, there is some uncertainty in the critical potential values reported which apparently may amount in the extreme to as much as one volt.

Figure 2.—All ordinates are in arbitrary units of the quantity concerned and abscissas are the applied accelerating voltages (except A and B) as read on the voltmeter (uncorrected). All curves of Fig. 2 were taken with the same filament. Curve C shows the rate of the mercury-sensitized decomposition of hydrogen per unit electron current and indicates onset of reaction at 8.9 volts (P of hydrogen = 0.034 mm., P of Hg = 0.0022 mm.). Sets D and E (represented by a single curve) show the intensity of light of λ 2537 observed per unit electron current and indicate onset voltage at 9.0 volts (P of hydrogen = 0.028 mm., P of Hg = 0.0022 mm.). Curves C, D and E show only the initial rise of more extended curves as in Fig. 3. Curves F and G show the Hg^+ ion current arriving at the plate with the tube elements set for ionization potential measurement with onset of ionization on a detailed plot indicated at 13.6 and 14.0 volts, respectively, from which we take 13.8 as the probable value (P of Hg = 0.0018 mm.).

Sets of points H and I (P of hydrogen = 0.037 mm.) represented by a single curve and curve J (P of H_2 = 0.026 mm.) give the H_2^+ ion current arriving at the plate. The average onset for these is chosen at 20.1 volts. The current to the plate starts several volts below the 20.1-volt value and increases approximately linearly and then breaks rather sharply upward. The slow rise may be due to photoelectric emission from the plate or perhaps minute traces of Hg or other impurity. The beginning of the break to the sharp rise is taken as the H_2^+ ion calibration point. Curves A and B show the electron current arriving at the plate in vacuum with the accelerating voltage from the filament to the grids set at 6 and 9 volts, respectively, plotted against retarding voltage between outer grid and plate. It is seen that electrons accelerated by 9 volts of applied potential are stopped by 6 volts of retarding potential, which is to be interpreted as indicating that the contact potential alone makes the platinum grids 3 volts more negative with respect to the oxide filament than with respect to the oxidized copper plate. (Data from the "International Critical Tables," Vol. VI, pp. 56 and 57 indicate that cupric oxide is negative 0.12 volt with respect to platinum.) Shown in Fig. 2 then are the onset voltages for four processes (in addition to the retarding potential curves just mentioned), one of which (C) we

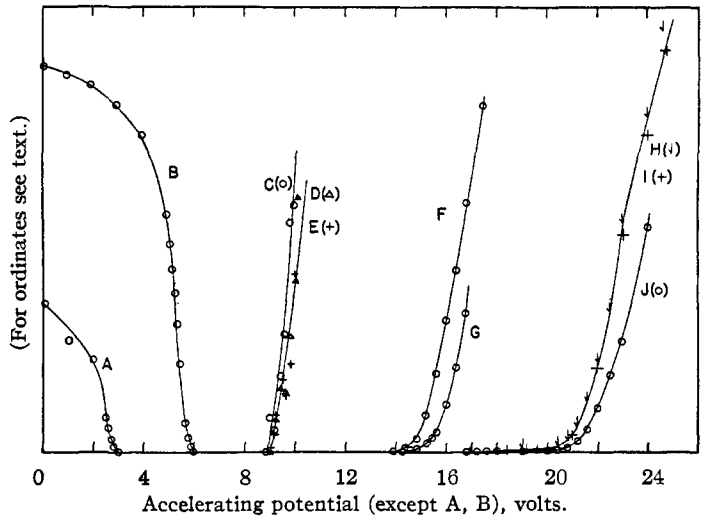

Fig. 2.

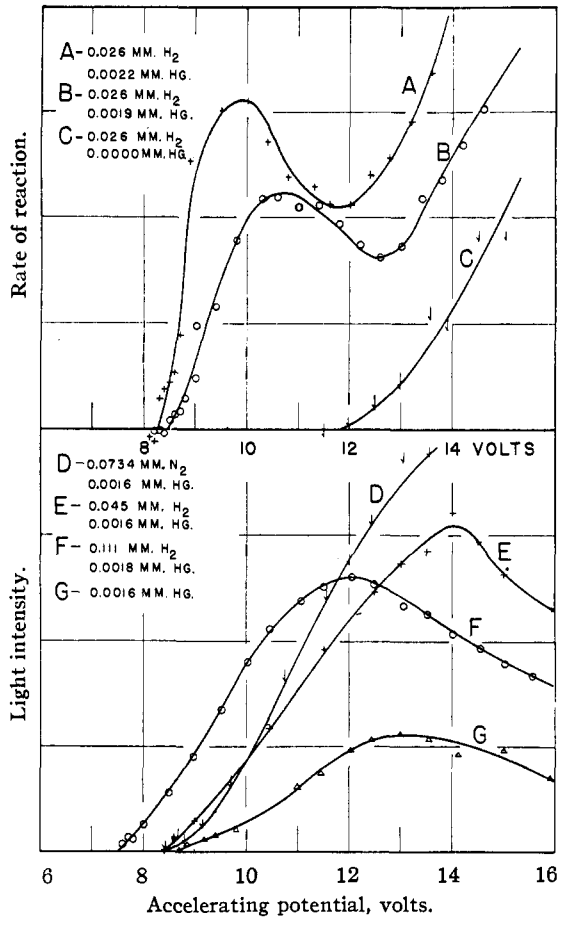

Fig. 3.

wish to establish and three of which occur at known critical potentials—D and E at 4.86 volts, F and G at 10.38 volts and H, I and J at 16.0 volts.[10] The voltage scale corrections from these curves are, respectively: 9.0 − 4.86 = 4.14 volts; 13.8 − 10.38 = 3.42 volts; and 20.13 − 16.0 = 4.13 volts. From the retarding potential curves a correction of 3.0 volts is indicated. Giving all four methods equal weight, an average correction of 3.67 volts is obtained which gives for curve (C) the corrected value 5.23 volts. Although it is hardly possible to assess objectively the validities of the respective voltage scale correction methods, the onset of radiation (λ 2537) and ionization of mercury seem less open to uncertainty. The corrections from these methods average 3.78 volts and give 5.12 volts for onset of reaction.

Figure 3.—The three upper curves show rate of disappearance of hydrogen per unit electron current and the four lower curves show the intensity of light observed per unit electron current, all plotted against the accelerating voltage. Curves A and B show the characteristic hump[3] due to the sensitized decomposition followed by a second rise predominantly due to setting in of the direct (non-sensitized) decomposition of hydrogen by electron impact. Curves A and B show onset at 8.26 and 8.45 volts, respectively. Curve C is the reaction rate for the direct decomposition of the hydrogen (no mercury present) which appears at 11.8 volts at a typical separation of 3 to 4 volts from the sensitized reaction. Curves G, E, D and F show intensity of λ 2537 per unit electron current emitted with mercury vapor alone or with hydrogen or nitrogen added as specified on Fig. 3. Onset appears at 8.7 volts on curve G and at 8.4 volts on curves E and D. Curve F was obtained with the filament operating at an exceptionally high temperature to obtain large electron currents in order to search for light emission in a voltage range below the observed onset. This curve has been discounted because the contact potential was apparently altered. A comparable temperature cannot be used on the hydrogen–mercury reaction and the curve is included here to show an extreme case of variation in the voltage correction in a tube of this type. From Fig. 3, then, it is gathered that the average onset for light emission (excluding curve F) is 8.5 volts which gives a correction 8.50 − 4.86 = 3.64 volts which, when applied to the average for onset of the sensitized reaction, gives 8.36 − 3.64 = 4.72 volts for this critical potential. Again, if curve E, because of the presence of hydrogen and its abrupt rise (similar to A and B and in contrast to G) is taken as most reliable, the correction becomes 8.40 − 4.86 = 3.54 and the average onset is located at 4.82 volts. Onset for curve C would be 11.8 − 3.64 = 8.16 volts for the direct electron decomposition of hydrogen.

We are drawn to the conclusion by the above considerations that the electron initiated, mercury-sensitized decomposition of hydrogen occurs with the direct excitation of one or more of the 6^3P states of mercury (6^3P_0 at 4.64 volts, 6^3P_1 at 4.86 volts and 6^3P_2 at 5.43 volts). Both the 6^3P_1 and 6^3P_0 states have been reported as reacting with hydrogen to produce dissociation. No experiments to our knowledge have been reported other than ref. 3 and this which might show whether or not the 6^3P_2 state is active against hydrogen. Kinetic studies from this Laboratory show definitely that at the peak reaction rate the effective mercury state or states are metastable and the 6^3P_1 state can contribute but slightly to the rate. Penney[11] has calculated approximate relative excitation probabilities of the 6^3P_0, 6^3P_1, 6^3P_2 and 6^1P_1 states as a function of voltage and cites experimental work of others in support of his calculations. On this basis the 6^1P_1 state may be dismissed as relatively ineffective against hydrogen. Penney's excitation functions of the three 6^3P states all show maxima between 7.5 and 8.5 volts with approximate relative excitation probabilities at the maxima of $6^3P_0 = 1$, $6^3P_1 = 3$,

(10) Gaydon, "Dissociation Energies," John Wiley and Sons, Inc., New York, N. Y., 1947, p. 182.

(11) Penney, *Phys. Rev.*, **39**, 467 (1932).

$6^3P_2 = 6$ and have shapes similar to the mercury-sensitized reaction rate.

Considering the above and other evidence we have found from the literature together with the present measurements it appears likely that the reaction starts with excitation of the 6^3P_0 state, is augmented by 6^3P_1 atoms excited 0.22 volt higher and then is augmented prominently by 6^3P_2 atoms beginning 0.79 volt above the first onset. The points between 8 and 9 volts of curves A and B, Fig. 3 show upward inflection following the initial rise which suggests a new highly efficient process coming in. This is also prominent in the curves of Fig. 3 of ref. 3.

It is well known that addition of hydrogen to mercury vapor exposed to λ 2537 quenches the fluorescent resonance radiation. It was therefore surprising to find that addition of hydrogen (0.0448 mm.) to the mercury vapor in the tube caused threefold augmentation of the emission per unit electron current of λ 2537 from the tube (Fig. 3, E and G). Addition of nitrogen produces the same observed effect (Fig. 3, D). This behavior appears to us to be attributable to one or both of the following effects: (a) The path length of the electrons in passing from the inner grid to the plate is increased by collision with added gas molecules and hence the electrons excite more mercury atoms to the 6^3P_1 state. (b) The mercury atoms in the metastable 6^3P_2 and 6^3P_0 states may be converted by collisions of the second kind to the radiating 6^3P_1 state, thus increasing the light emission. (Due to the sixfold higher excitation probability of the 6^3P_2 over the 6^3P_0 state and the endothermic nature of the $6^3P_0 \rightarrow 6^3P_1$ transition, the $6^3P_2 \rightarrow 6^3P_1$ transition would play the dominant role.)

An estimate of factor (a) for hydrogen and nitrogen at specified voltages and pressures may be obtained from data in the literature on the absorption coefficient for electrons[12] and on the angular distribution of electrons scattered by gas molecules.[13,14] Using data from ref. 12 a mean free path for electrons may be obtained, and from refs. 13 and 14 an experimentally determined angular distribution probability function for the electron paths following collision may be set up. To apply these to our problem a semicircle was divided with intervals proportional to the probabilities of scattering to specified angles from 0 to 180° and this together with its mirror image constituted a circle which was placed as a scale on an improvised "roulette wheel." A plot of the cross section of the tube was made to scale and a number of electron paths were constructed with the angle of scattering to right or left dictated by the region of the scale at which the wheel index stopped after random spinning. The electron path (considering three dimensions) in hydrogen at 0.0448 mm. for 10 volts was increased 2.05 times above that which holds when mercury vapor alone was in the tube and for nitrogen at 0.0734 mm.; for 10 volts the path was increased 2.8 times. From considerations mentioned in ref. 2 (Fig. 3 and top of p. 2648) we would expect the quenching of λ 2537 due to addition of 0.0448 mm. of hydrogen with 0.0016 mm. of mercury to be about 40%. The nitrogen would give only a very small quenching—about 2% at 0.0734 mm. Curve E compared to G of our Fig. 3 indicates an increase of threefold which, combined with the quenching that must take place, indicates an increase of about fivefold in the number of 6^3P_1 atoms produced with 0.0448 mm. of hydrogen added over that with only mercury in the tube. This seems higher than would be accounted for by the increase in electron path and the factor (b) above may well operate. The energy difference between the 6^3P_2 and 6^3P_1 states is 0.57 e.v. The energy of the first vibrational level of the hydrogen molecule is 0.51 e. v. and of the second vibrational level of the nitrogen molecule is 0.57 e. v. above the respective ground levels and the small energy discrepancies between these and the $6^3P_2 \rightarrow 6^3P_1$ transition would indicate good efficiency of conversion by both hydrogen and nitrogen causing increased light emission. If process (b) operates, addition of gas may augment light emission from the axial region of the cylinder (observed through the window) where electron paths are most dense by retarding diffusion of metastable atoms from this region. We hope to investigate further this effect as a possible means of obtaining information on collisions of the second kind.

(12) Normand, *Phys. Rev.*, **35**, 1217 (1930).

(13) Bullard and Massey, *Proc. Roy. Soc.* (*London*), **133**, 647 (1931).

(14) Ramsauer and Kollath, *Ann. Physik*, **12**, 529 (1932).

Summary

The onset of the mercury sensitized decomposition of hydrogen by electron impact on the mercury atoms is found, by comparison with other critical potentials, to occur in the neighborhood of five volts, indicating that the reaction starts with excitation of one of the 6^3P states of mercury. All three states are probably contributing to the reaction by the time the accelerating voltage is a volt above the first onset. The previously reported higher values (7.63 and 7.0 volts) were based on the values of the critical potential for direct decomposition of hydrogen available at the time and these appear to need revision downward about 3 volts. A marked increase of flux of λ 2537 from the tube with addition of hydrogen or nitrogen was observed which quite possibly indicates conversion by these gases of the most populous 6^3P_2 state to the 6^3P_1 state.

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