

Active Hydrogen

A. C. Grubb and A. B. Van Cleave

Citation: [The Journal of Chemical Physics](#) **3**, 139 (1935); doi: 10.1063/1.1749620

View online: <http://dx.doi.org/10.1063/1.1749620>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/3/3?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Activation of erbium films for hydrogen storage](#)

J. Appl. Phys. **109**, 114911 (2011); 10.1063/1.3590335

[Hydrogen passivation of electrically active defects in diamond](#)

Appl. Phys. Lett. **55**, 1391 (1989); 10.1063/1.101604

[Sorption of Activated Hydrogen on Vycor Glass](#)

J. Vac. Sci. Technol. **3**, 324 (1966); 10.1116/1.1492496

[Reactions of Sodium with Active Hydrogen](#)

J. Chem. Phys. **36**, 2239 (1962); 10.1063/1.1732871

[Active Hydrogen](#)

J. Chem. Phys. **3**, 317 (1935); 10.1063/1.1749662



Active Hydrogen

A. C. GRUBB AND A. B. VAN CLEAVE,¹ *University of Saskatchewan*

(Received November 9, 1934)

Dry hydrogen can be activated in an electric discharge if the pressure and voltage are carefully regulated. Active hydrogen reduces metallic sulphides whose heat of formation is 22,000 cal. or less. The active gas is decomposed by 3 cm of well packed glass wool. A quantitative method is given for the determination of active hydrogen. Less of the active gas is formed in a tube coated with stearic acid or phosphoric acid than when no coating is employed. The decay reaction was found to follow the expression for a

unimolecular reaction. The rate of decay appears to be independent of the wall surface. The period of half-life at room temperature and 40 mm pressure is 0.2 sec. approximately. The energy of formation of active hydrogen is approximately 18,000 cal. The energy of activation for the decay of the active constituent is approximately 17,800 cal. The properties of active hydrogen are considered in relation to the properties predicted for H_3 .

SINCE the pioneer work of Sir J. J. Thomson² who showed by positive ray analysis that the group H_3^+ existed, and the investigations of I. Langmuir³ and R. W. Wood⁴ who found that a special chemical activity shown by hydrogen was due to atoms, many investigators⁵⁻¹³ have studied the properties of active hydrogen. During the early work, the idea prevailed that neutral H_3 could be formed in discharge tubes of different design from the Wood's tube which produced atomic hydrogen from wet gas. Attempts to confirm some of the work on triatomic hydrogen led investigators¹⁴ to consider that the contamination of the discharge tube had influenced the positive results. Up to this time no concise information had been given in regard to the exact quantitative conditions under which triatomic

hydrogen could be formed. No quantitative method had been developed so that consistent results could be obtained for consecutive determinations as had been accomplished for ozone.

Through their investigations, mathematical physicists had concluded that any triatomic hydrogen formed in discharge tubes by the collision of an atom with a molecule of hydrogen could exist for only a very short time. The life of H_3 was estimated to be of the order of 10^{-8} seconds.¹⁵ This time was too short for triatomic hydrogen to leave the discharge and manifest the properties claimed for it. This led many workers to consider that the only activity manifested by hydrogen was due to atoms.

The first consistent quantitative work reported for active hydrogen formed under conditions not favorable to the production of hydrogen atoms is that of Binder, Filby and Grubb.¹⁶

The present study is largely the presentation of new evidence for the existence of an active form of hydrogen which differs markedly in its properties from atomic hydrogen.

EXPERIMENTAL METHOD

Apparatus

The arrangement of apparatus is shown in Fig. 1. A high pressure tank of electrolytic gas was used as a source of hydrogen. The gas was purified by passing it through a strong solution of sodium hydroxide, a soda lime tower, an electric

¹ This communication is based on a thesis submitted by A. B. Van Cleave in 1933 in partial fulfilment of requirements for the degree of Master of Science in Chemistry at the University of Saskatchewan, Saskatoon, Canada. Mr. Van Cleave was the holder of a Bursary under the National Research Council of Canada.

² Sir J. J. Thomson, *Proc. Roy. Soc. A* **89**, 20 (1911).

³ I. Langmuir, *J. Am. Chem. Soc.* **34**, 1310 (1912).

⁴ R. W. Wood, *Phil. Mag.* **42**, 729 (1921).

⁵ Wm. Duane and G. L. Wendt, *Phys. Rev.* **7**, 689 (1916).

⁶ Y. Venkataramaih, *Nature* **106**, 46 (1920).

⁷ G. L. Wendt and R. S. Landauer, *J. Am. Chem. Soc.* **42**, 930 (1920); **44**, 510 (1922).

⁸ P. Anderson, *J. Chem. Soc.* **121**, 1153 (1922).

⁹ A. E. Mitchell and A. L. Marshall, *J. Chem. Soc.* **123**, 2448 (1923).

¹⁰ K. F. Bonhoeffer, *Zeits. f. physik. Chemie* **113**, 199 (1924).

¹¹ A. Bach, *Ber.* **B58**, 1388 (1925).

¹² M. Scanavy-Grigoriowa, *Zeits. f. anorg. allgem. Chemie* **159**, 55 (1926).

¹³ F. Paneth, E. Klever and K. Peters, *Zeits. f. Elektrochemie* **33**, 102 (1927).

¹⁴ H. M. Smallwood and H. C. Urey, *J. Am. Chem. Soc.* **50**, 620 (1928).

¹⁵ Conrad, *Zeits. f. Physik* **75**, 504 (1932).

¹⁶ Binder, Filby and Grubb, *Can. J. Research* **4**, 330 (1931).

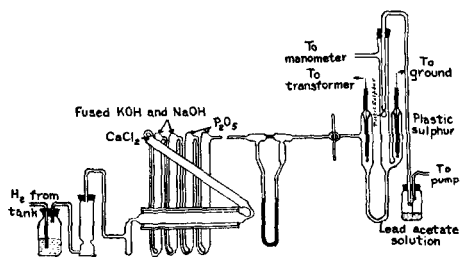


FIG. 1.

furnace containing platinized asbestos heated to 550°C, two towers containing fused potassium and sodium hydroxide and finally two towers of phosphorus pentoxide. The rate of flow of hydrogen was measured by a calibrated flowmeter of the type used by Benton.¹⁷ A fine capillary tube and a stopcock were placed between the flowmeter and discharge tube to facilitate in the adjustment of pressure which was maintained by a Cenco Hyvac pump and measured by an open mercury manometer.

The vacuum discharge tube was made from ordinary glass tubing 6 mm inside diameter and shaped in the form of a U-tube to permit immersion in an ice-water bath or freezing mixture. Two 14 mm tubes were sealed to the ends of the U-tube. Electrodes of No. 15 (B. and S.) platinum wire were sealed into 6 mm tubes which were connected to the 14 mm tubes by inner seals as shown in Fig. 1. The distance between the electrodes varied from 20 to 30 cm. The reagent on which the action of the active hydrogen was tested was placed at any desired distance from the discharge in the wide reaction chamber on the ground electrode side. Unless otherwise stated, the inner surface of all tubes was coated with stearic acid. All results reported were taken with the tube immersed in an ice-water bath.

The electrical energy was obtained from a rotary converter which supplied an alternating current through a water rheostat to the primary of a Thordarson 25,000 volts, 1 kva, type R transformer. The primary wattage, voltage and amperage were measured with standard Weston instruments.

¹⁷ Benton, *J. Ind. and Eng. Chem.*, **11**, 623 (1919).

1. Blanks and tests for atomic hydrogen

In a previous investigation¹⁶ it was found that plastic sulphur could be used as a testing agent for active hydrogen without contaminating the discharge with sulphur blown back into the discharge tube. But to eliminate all sources of contamination careful blanks were run. In this work a perfect blank consisted in running the hydrogen from the purifying system through the tube with the discharge off and over plastic sulphur, for two hours at 3 liters per hour without producing a trace of lead sulphide, as shown by a blank test paper. The plastic sulphur was then removed from the reaction chamber, the discharge turned on and the gas under the same conditions directed against lead acetate paper producing no lead sulphide.

The first part of the blank showed that the gas was free from hydrogen sulphide, that it contained no constituent which reacted with sulphur, and that the sulphur contained no volatile sulphides. The second part of the blank showed that the hydrogen contained no sulphur compound capable of forming hydrogen sulphide in the discharge, that the tube was free from contaminations, and that the escaping gas contained no silicon hydride as advocated by Hiedemann.¹⁸ These tests were tried repeatedly all through the course of this work and in no case was any evidence for silicon hydride found.

Some authors considered that our former results were due to atomic hydrogen. Very extensive tests were made for atomic hydrogen. A fragment of tungsten wire was mounted in place of the plastic sulphur and placed 3, 2, 1 cm, respectively, from the discharge and finally into the discharge. For each of the positions for the tungsten, the pressure was varied from 40 mm down to 0.5 mm and as viewed in the dark there was no trace of a glow on the tungsten. At 0.5 mm pressure and with the wire in the discharge, had atoms been present, the tungsten should have been incandescent. These results confirm those of R. W. Wood,¹⁹ who found that dry hydrogen from a discharge brought in contact with a small tungsten wire produced no glow.

¹⁸ E. Hiedemann, *Zeits. f. physik. Chemie* **A153**, 210 (1931).

¹⁹ R. W. Wood, *Phil. Mag.* **44**, 538 (1922).

2. The critical potential-pressure relation for activity

During an attempt to substitute a 20,000 volt Thordarson transformer for the 25,000 volt instrument that had been used, it was observed that the two transformers operated at the same primary wattage did not produce the same results. No sulphide was produced when the lower voltage instrument was used. Further investigation showed that the energy input of this instrument had to be increased considerably to give positive results. With a pressure of 40 mm in the tube and the plastic sulphur 20 cm from the discharge, the original transformer, using 90 volts in the primary, produced a discharge that gave good sulphide tests. These results could not be duplicated with the lower voltage instrument operated with 110 volts in the primary.

The primary potential-pressure relation for two tubes, using the 25,000 volt transformer, is shown in Fig. 2. Tube No. 1 was constructed with reaction chamber 12 mm in diameter and with 22 cm between electrodes while tube No. 2 had a reaction chamber 16 mm in diameter and electrodes 26 cm apart. In obtaining the data represented by points on these curves, first a

run was made below the critical voltage and then the primary voltage raised in subsequent runs in steps of $2\frac{1}{2}$ volts until at the end of a half hour run only a faint trace of sulphide appeared on the test paper. If the potential is raised a few volts above the minimum value for any pressure, the amount of sulphide formed is greatly increased. Perfect blanks may be obtained at will by lowering the potential a few volts below the minimum. Preliminary experiments showed that tube No. 1 could be operated with plastic sulphur mounted 20 cm from the discharge except in the pressure range 70 to 80 mm. No sulphide was obtained in this region at any voltage up to 110.

3. Reduction of sulphides

Bonhoeffer¹⁰ studied the energy associated with atomic hydrogen by using it to reduce various compounds including sulphides. In our investigation pure sulphides were prepared by standard methods²⁰ and mounted 4 cm from the discharge in tube No. 2. Careful blank runs were made just before the sulphide was introduced into the reaction chamber and also after it was removed. Both silver sulphide and cuprous sul-

TABLE I. Reaction of sulphides to active hydrogen.

Sulphide	Heat of formation Int. Crit. Tab.	Reaction to active hydrogen
Ag ₂ S	5.02 kg cal.	Reduced (markedly)
Cu ₂ S	18.97 kg cal.	"
NiS	20.78 kg cal.	Reduced slightly 1 cm from discharge
Tl ₂ S	21.98 kg cal.	Reduced (slightly)
FeS	23.06 kg cal.	Not reduced

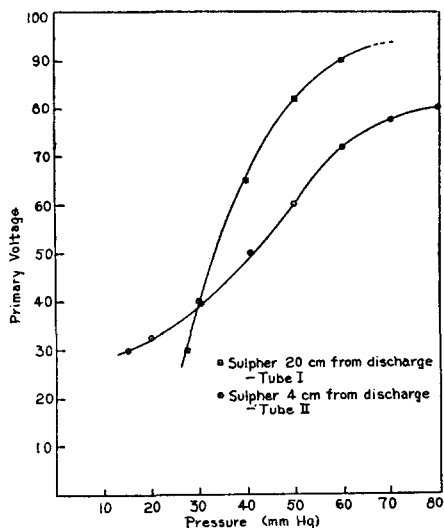


FIG. 2. Variation of critical voltage with pressure.

phides were very greatly reduced during a half hour run while thallous sulphide showed only a slight reduction. Nickel sulphide was reduced slightly 1 cm from the discharge but iron sulphide was not reduced.

4. Effect of glass wool upon the stability of active hydrogen

In some investigations the hydrogen from the discharge has been passed through glass wool before coming in contact with sulphur. The amount of wool used by different investigators has varied from 1 to 10 cm. In the present study

²⁰ Keyes and Felsing, J. Am. Chem. Soc. **42**, 246 (1920).

no glass wool was used except in this special test. The plastic sulphur was mounted 4.5 cm from the discharge in a special tube into which glass wool could be packed. A run, at 85 volts and 40 mm pressure, made for 30 min. without any glass wool present gave a good sulphide test. Runs at the same potential and pressure were then made using increasing quantities of glass wool between the discharge and the sulphur, but it required a column 2.5 cm in length weighing 0.2535 g to decompose completely the active hydrogen. The perfect blank tests also showed the tube was not contaminated with sulphur.

5. Quantitative estimate and the rate of decay of active hydrogen

Since molecular hydrogen has a small amount of reducing action upon potassium permanganate solution¹⁶ the use of this reagent to absorb hydrogen sulphide quantitatively from excess hydrogen is not entirely satisfactory. It necessitates the use of carefully determined blanks.

Other methods were tried but the following procedure was found to be most satisfactory. The sulphide was absorbed in 25 cc of 0.5N sodium hydroxide solution. After the run the base was neutralized with standard sulphuric acid, the correct amount having been previously determined using methyl red as indicator. The hydrogen sulphide was titrated with N/400 iodine solution using starch as an indicator. It was found that 0.4 cc of the iodine solution was required with starch to give a visible color to the neutralized reagents. This blank was subtracted from each titration. The results obtained by this method were quite consistent. The following is an example of the results for runs made under duplicate conditions. The values were 2.85 cc, 2.75 cc, 3.00 cc, 2.85 cc of N/400 iodine solution. The behavior of tubes in respect to the distance the sulphur was located from the discharge in the study of the critical voltage-pressure relation and the destruction of the activity by glass wool seemed to indicate that the active hydrogen had a very rapid rate of decay. By maintaining a constant rate of flow, pressure and voltage with the sulphur testing agent located at varying distances from the discharge it was possible to obtain results that were an indication of the order of the decay reaction. If the rate of flow

of hydrogen, the pressure, the diameter of the reaction tube in which the testing agent is mounted are known, then by the method of refills the time taken for the hydrogen to travel a definite distance may be calculated.

A new tube of similar design was constructed having a reaction chamber whose diameter was 14.6 mm. The walls of this tube were left uncoated since it was planned to make a study of the wall effect upon the formation and decay of the active constituent. For the initial determination the plastic sulphur was mounted 2 cm from the discharge. Subsequent determinations were made at distances of 3, 4, 5, 6, 7 and 8 cm from the discharge. Runs were made with the sulphur mounted at greater distances but the amount of sulphide formed was too small to be titrated by the quantitative method used. However, preliminary runs with lead acetate paper as a testing agent had shown a range of 15 cm for the active hydrogen. This result shows that an extremely small concentration of hydrogen sulphide may be detected by a lead acetate test paper. After completing the results for the tube uncoated, it was taken down and both discharge tube and reaction chamber coated with a thin layer of very pure stearic acid. The tube was then replaced and operated under identical conditions as before and results secured for the coated tube. The stearic acid was removed and the tube coated with syrupy phosphoric acid. Runs were again made under duplicate conditions although not so many points were obtained as before. The only variable factor in these data is the wall coating. The same tube was used throughout and the runs were made under

TABLE II. Values obtained for the titration of sulphide formed by active hydrogen.

Duration of runs—2 hr. Pressure—42 mm.
Hydrogen flow—3 liters per hr. Primary e.m.f.—85 volts

Distance of plastic sulphur from discharge in cm	Cc. of N/400 iodine solution		
	Tube uncoated	Stearic acid coating	Phosphoric acid coating
2	5.70	4.45	—
3	3.90	—	—
4	2.85	1.95	1.85
5	1.85	—	—
6	1.10	.85	—
7	.45	—	.35
8	.00	—	—

identical velocity, pressure and voltage conditions. The titration values are the average of several determinations as illustrated above. The results obtained for the tube operated under the conditions described above are given in Table II.

Calculations were made of the time required for the hydrogen to travel from the initial position of the sulphur to each subsequent position. The amount of iodine used in each titration is directly proportional to the concentration of active hydrogen. The logarithms of these titration values plotted against the time are shown in Fig. 3. The straight line indicates that the decay of active hydrogen is a reaction of the first order and appears to be unimolecular at the pressure studied.

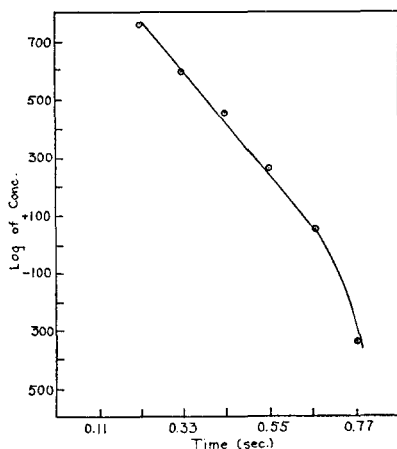


FIG. 3. Plot of $\log C$ against time.

Calculations

For a unimolecular reaction the specific reaction rate k is given by the equation

$$k = 2.303 / (t_2 - t_1) \log a / (a - x).$$

As applied, a is the initial concentration of active hydrogen at time t_1 and $a - x$ is the concentration at time t_2 . Since the amount of iodine used to titrate the hydrogen sulphide absorbed is proportional to the concentration of active hydrogen, these titration values have been substituted in the above expression to calculate the reaction rate constant k . The k values agree very well

TABLE III. Specific decomposition rate of active hydrogen for different tubes calculated from data in Table II. Temp. 298T. Values of k (sec.⁻¹).

Glass walls	Stearic acid walls	Phosphoric acid walls
3.4	—	—
3.2	—	—
3.4	3.7	—
3.7	3.7	—
4.6	—	5.0

except the last value for the tube uncoated, and the k value for the tube coated with phosphoric acid. These decay constants represent the rate of decay over the last centimeter of the range where the concentration or partial pressure of the active hydrogen is extremely low. There is probably more error in the determination of this k value than in the preceding ones. However, Hirst and Rideal²¹ found that the decay constant for nitrogen pentoxide tended to increase at very low pressures.

The decay reaction for active hydrogen appears to occur independently of the surface of the container and may be considered as a homogeneous gas reaction of the first order.

DISCUSSION OF RESULTS

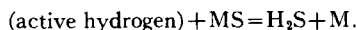
The evidence presented in the experimental work just described shows that active hydrogen has properties not previously reported by other workers. The reports of former investigations have included but brief statements of the design of tubes and the types of electrical equipment used. Apparently it was not recognized that any special control of the electrical conditions needed to be considered if the results were to be consistent. Also in the design of the discharge tube, the distance between electrodes, the diameter of the reaction chamber and the distance of the plastic sulphur from the discharge are factors to be considered if the investigators' results are to be confirmed. No doubt many of the negative or sporadic results recorded in the literature may be due to the use of potentials that were below the minimum for the pressure or to the fact that the sulphur was mounted beyond the range for the active gas. Preliminary experiments showed

²¹ Hirst and Rideal, Proc. Roy. Soc. **A109**, 526 (1925).

that with other conditions identical, the range of the active constituent varied inversely with the diameter of the reaction chamber. This would also indicate a negligible wall effect.

There are two energy relations to be considered on the basis of the data given—the energy of activation of the hydrogen in the discharge, and the energy of activation for the decay of the active constituent.

The amount of energy absorbed from the discharge by one mole of hydrogen in changing from the inactive to the active state is the energy of activation. In a collision between active hydrogen and a metallic sulphide which results in the reduction of the sulphide and the formation of hydrogen sulphide, the reaction may be indicated as follows:



If the energy evolved in the formation of MS is 23,000 cal. and that evolved in the formation of H₂S is 5260 cal., then the amount of energy required to activate the hydrogen will be approximately 18,000 cal. There was a noticeable decrease in the amount of metallic sulphide reduced in testing various sulphides as the heat of formation for the sulphide increased. Thallium sulphide was only slightly reduced 4 cm from the discharge, nickel sulphide slightly reduced at 1 cm from the discharge, and iron sulphide was not reduced. Therefore it is concluded that the energy acquired by the hydrogen as it leaves the discharge is at least 18,000 cal.

In determining the energy of activation for the decay reaction, the usual method involves the determination of k 's at two temperatures, and the calculation of E , using the integrated form of the Arrhenius equation:

$$\log k_2/k_1 = -E(T_2 - T_1)/2.303RT_2T_1. \quad (1)$$

The very high rate of decay for this reaction makes it extremely difficult to bring the system to temperature equilibrium for the determination of k at some other temperature. Therefore, a suggestion has been taken from the paper by H. Eyring and F. Daniels.²²

They state, "The value of E can be calculated more accurately with the equation

$$k = se^{-E/RT}, \quad (2)$$

or

$$\log k = -E/2.303R \times 1/T + \log s, \quad (3)$$

from k at one temperature on the assumption that s is about 5×10^{13} than it can be calculated in the usual way from the k 's at two temperatures in Eq. (1). The accuracy of such a calculation depends upon the constancy of s . This relation has been discussed by several investigators^{22, 23, 24} who consider that for unimolecular reactions, s may be considered a constant within certain limits. The rate constant for the decay

TABLE IV. Calculated energy of activation for the decay reaction using the rate constants of Table III and $s = 5 \times 10^{13}$.

Tube glass walls	Tube stearic acid walls	Tube phosphoric acid walls
17.8 kg cal.		
17.9 kg cal.		
17.8 kg cal.	17.8 kg cal.	
17.8 kg cal.	17.8 kg cal.	
17.7 kg cal.		17.6 kg cal.

reaction in the tube coated with phosphoric acid is 1.3 times greater than the average, yet the value for the energy of activation is but 200 cal. less than the average. The period of half-life at 25°C may be calculated by the equation: $t_{1/2} = 0.6932/k$. If the average k for the decay reaction in the tube with glass walls is used, $t_{1/2}$ is equal to 0.188 sec. For the tube coated with stearic acid, $t_{1/2}$ is equal to 0.185 sec. If we use the average of the first four constants found for the glass tube, $t_{1/2} = 0.20$ sec.

The question of the identity of active hydrogen may be somewhat involved but the new experimental evidence presented tends to eliminate some ideas and to support others. Some investigators²⁵ consider that any activity manifest by hydrogen is due to atoms. A tube of the Wood's type, using moist hydrogen or coated with phosphoric acid, is usually employed for producing hydrogen atoms. The atoms will reduce metallic

²² Christiansen and Kramers, *Zeits. f. physik. Chemie* **104**, 451 (1923).

²³ C. N. Hinshelwood, *Chemical Reviews* **3**, 227 (1926).

²⁴ G. R. Schultz, *J. Phys. Chem.* **35**, 3186 (1931).

²⁵ H. Eyring and F. Daniels, *J. Am. Chem. Soc.* **52**, 1482 (1930).

sulphides of much higher heat of formation than 23,000 cal. per mole since the energy available by their recombination is of the order of 100,000 cal. per mole.

The recombination of hydrogen atoms is considered to be a trimolecular gas reaction influenced by the walls of the vessel.^{26, 27, 28}

The discharge tube used in this investigation is of different design and is operated under different conditions from that usually employed for the production of hydrogen atoms.

The same tube coated with stearic acid or phosphoric acid and operated under identical conditions produced one-third less active hydrogen than when used with glass walls. This is the opposite of what one would expect if atoms were present. However, this is in agreement with the work of H. G. Thode and A. C. Grubb²⁹ who found less ozone produced in a discharge tube whose walls were coated with stearic acid or paraffin than was produced in the same tube with the wall surface of glass.

The specific reaction rate constant for the decay of active hydrogen is practically constant under the conditions described, and the decay appears to be a homogeneous reaction. The logarithms of the concentration plotted against the time gives a straight line which is in agreement with the conditions for a unimolecular reaction.

All the evidence points to the formation and decay of a complex molecule. Unimolecular reactions are found chiefly among complex molecules.

Triatomic hydrogen, once accepted and later held in disrepute by mathematical physicists, is now granted a "sticky" existence by Eyring.^{30, 31} These authors calculate the minimum energy of activation on the basis of the collision of three hydrogen atoms on a straight line. Their result for this type of a collision is 13 kg cal. A higher

energy of activation is found for collisions not on a straight line. Experimentally one might expect the majority of collisions to be at an angle, and the statistically averaged energy of activation for the formation of H_3 to be greater than the minimum of 13 kg cal.

For the unimolecular decomposition of H_3 the minimum energy of activation predicted by Eyring is 1.6 kg cal. This quantity of energy as represented on the contours "is the depth of the potential energy basin measured from the bottom to the lowest point in the rim of the basin through which the ball can escape to the outside." This would limit the escape to a particular point on the rim for those molecules having just the minimum energy of activation. But for those molecules having an excess of E over the minimum the region of escape would cover a larger fraction of the rim. The statistically averaged value for the energy of activation would be higher than 1.6 kg cal. and lower than 24 kg cal. required for an H_3 molecule stable at room temperature. The value of 17.8 kg cal. for the energy of activation for the decomposition of active hydrogen is within the limits of Eyring's predicted result for H_3 .

Sir J. J. Thomson³² has shown that a fleeting neutral type of H_3 exists and that it can be obtained from normal hydrogen. He considers that the group is composed of three atoms of hydrogen of mass one. (Private communication.)

Since other complexes³³ possibly involving the isotope exist in a discharge through hydrogen, a disagreement between experimental and theoretical physics does not obviate the possibility that some other complex may be involved in the activity manifest in this study. However, H_3 would be the simplest complex to undergo unimolecular decomposition. It is trusted that future investigation will elucidate this point.

Thanks and appreciation are expressed to the National Research Council of Canada for financial assistance during the course of this investigation.

²⁶ H. Smallwood, J. Am. Chem. Soc. **51**, 1985 (1929).

²⁷ Steiner and Wicke, Zeits. f. physik. Chemie, Bodenstein-Band, 817 (1931).

²⁸ H. Smallwood, J. Am. Chem. Soc. **56**, 1542 (1934).

²⁹ H. G. Thode and A. C. Grubb, Trans. Electrochem. Soc. **63**, 297 (1933).

³⁰ Henry Eyring, Chem. Rev. **10**, 111 (1932).

³¹ Eyring and Polanyi, Zeits. f. physik. Chemie **B12**, 279 (1931).

³² Sir J. J. Thomson, Phil. Mag. **17**, 1025 (1934).

³³ P. Zeeman and J. De Gier, Proc. K. Akad. Wetensch Amsterdam **36**, 717 (1933).