The fact that the latter 3 analyses show a progressive increase in the value of the atomic weight suggests the possibility that the degree of purity of the 3 preparations might have progressively changed. Nevertheless, since from the method of crystallization they should have been essentially alike, the appearance of a march in the figures is probably fortuitous. In any case no claim can be made for great accuracy in the result, because the amount of crude material was not sufficient for work of the highest precision. In spite of this lack, the outcome serves its purpose, for it shows that the atomic weight of this lead from a Japanese radioactive spring is not far from that of ordinary lead. Probably it is chiefly ordinary lead, with perhaps not over 5 % of isotope of lower atomic weight. The result coincides well with the fact, reported by Hayakawa and Nakano,[1] that the lead chloride shows but little if any radioactivity. The quantity of the metallic lead obtained was too small to determine a trustworthy value for its density.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

TRIATOMIC HYDROGEN.

BY GERALD L. WENDT AND ROBERT S. LANDAUER.

Received March 2, 1920.

Many years ago Osann[2] published a series of papers on a reactive variety of hydrogen produced by the electrolysis of dil. sulfuric acid. To this he gave the name of "*Ozonwasserstoff*" on account of its analogy to Schönbein's ozone which had just been discovered, but without knowledge of its molecular formula. After protracted arguments Löwenthal[3] seems to have proved that the reducing action of Osann's gas was due to sulfur dioxide produced from the sulfuric acid. In any case, Osann's work has never been confirmed, though G. Magnus[4] made persistent efforts to do so. All other known forms of active hydrogen are undoubtedly monatomic, including the ordinary nascent hydrogen and Langmuir's modification[5] which is produced when a metallic filament is heated in hydrogen at very low pressures.

In 1913, however, Sir J. J. Thomson[6] published photographs of the

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[1] *Loc. cit.*

[2] *J. prakt. Chem.*, **58**, 385 (1853); **61**, 500 (1854); **69**, 1 (1856); **71**, 355 (1857); Verh. Würzburger phys.-med. Ges., Bd. VI; *J. prakt. Chem.*, **66**, 102 (1855); **78**, 93 (1859); **81**, 20 (1860); **92**, 210 (1864); *Pogg. Ann.*, **95**, 315 (1855); **95**, 311 (1855); **97**, 327 (1856); **98**, 181 (1858); **106**, 326 (1859).

[3] *J. prakt. Chem.*, **73**, 116 (1858).

[4] *Pogg. Ann.*, **104**, 555, Par., 98–110 (1858).

[5] THIS JOURNAL, **34**, 1310 (1912); **36**, 1708 (1914); **37**, 417 (1915).

[6] *Proc. Roy. Soc. A.*, **89**, 1 (1913); "Rays of Positive Electricity," Longmans, Green & Co., 1913.

parabolic traces obtained on a sensitized plate upon which the positively charged particles present in a high vacuum discharge tube had been allowed to impinge after simultaneous electrostatic and magnetic deflection. The position and form of the parabolas revealed the presence of particles having an atomic weight of 3, presumably triatomic molecules of hydrogen. This was later confirmed by Dempster,[1] using the electrical method. Duane and Wendt[2] showed, in 1917, that when hydrogen is exposed to bombardment of α-particles from radium emanation a contraction in volume ensues, a fact which had been incidentally observed by Usher and which has been recently confirmed by Lind.[3] These indications that hydrogen may exist in the ozone form deserve careful study not only because a reactive variety of hydrogen might be of great value when applied to hydrogenation and other reducing reactions, but also because the existence of such a form is not compatible with the older theories of valence. If hydrogen has an indivisible valence of one, no triatomic molecule can be formed. The present conceptions of atomic structure, on the other hand, do permit such a molecule, as Bohr[4] has recently shown.

In the present research this form of hydrogen has been prepared in several ways, all dependent on gaseous ionization, and has been shown to be chemically very active. Although formed in relatively small quantities by present methods, it is a much stronger reducing agent than ordinary hydrogen, and, as would be expected, it rapidly decomposes into the ordinary variety.

The Preparation of Pure Hydrogen.

The hydrogen was prepared in the familiar zinc amalgam-platinum cell with 8% hydrochloric acid as the electrolyte This type of cell has been found to deliver very pure hydrogen in numerous atomic weight determinations in the laboratories of T. W. Richards.

In order to prevent contamination of the hydrogen by organic materials, we avoided the use of stopcock grease throughout. The stoppers of the generator and of the purifying towers were surrounded by short lengths of wide rubber tubing, which permitted the entire stopper to be covered with mercury. This arrangement proved to be sufficiently gas-tight. In place of stopcocks, we substituted U-tubes filled with mercury, which could be opened by applying suction through a side tube to withdraw the mercury from the U.

The hydrogen from the generator passed first through 3 Emmerling towers filled with lumps of potassium hydroxide which had been fused with

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[1] *Phil. Mag.*, 31, 438 (1916).

[2] *Phys. Rev.*, 10, 116 (1917).

[3] THIS JOURNAL, 41, 545 (1919).

[4] *Medd. K. Vetenskapsakad. Nobelinst.*, 5, No. 28, 1 (1919).

a little potassium permanganate to remove organic matter. This freed the gas from the acid spray, chlorine, carbon dioxide, and a large part of its water vapor. Air, which had been dissolved in the acid solution, was next removed by passing the hydrogen through a hard glass tube filled with clean asbestos fibers which had been soaked in chloroplatinic acid solution and ignited to impregnate them with platinum black. The tube was wound with Nichrome ribbon covered with asbestos and was maintained at a red heat by an electric current. The joints between the hard glass and the soft glass of the rest of the system were ground to a close fit and were surrounded by a jacket of glass filled with mercury. This again gave a gas-tight joint without the use of grease. The gas was again dried in 3 towers of potassium hydroxide lumps and passed finally through a U-tube about 45 cm. in length and filled with phosphorus pentoxide, which removed the remaining water vapor.

The hydrogen, after this treatment, could have been contaminated only with nitrogen and the rare gases which might have been dissolved in the acid of the generator. To remove even these as far as possible, we exhausted the whole system by means of a water aspirator to very close to the vapor pressure of the acid solution. Hydrogen was then generated until the pressure reached atmospheric value. After 3 repetitions of this exhaustion, the entire system was swept out by its own hydrogen for 40 hours before the commencement of the actual experiment.

As a further precaution against some unknown impurity in this hydrogen, we made a few experiments with hydrogen derived from the electrolysis of a weak solution of potassium hydroxide containing a little barium hydroxide to remove carbonate. The solution was in a cylindrical vessel and a wide ring of heavy platinum wire formed the anode. Within this hung a smaller glass cylinder tapering at the top and sealed to a glass tube which, in turn, was sealed to the U-tube in place of the previous generator. A strip of platinum gauze sealed into the inner cylinder formed the cathode. The cylinder extended 25 cm. below the level of the cathode and anode in order to prevent contamination by the oxygen liberated at the anode. This hydrogen was purified exactly as in the first case, except that the system could not be exhausted.

The effects observed were obtained with both varieties of hydrogen and equally well with compressed electrolytic hydrogen purchased in tanks and purified in the above purifying system. Most of the later work was done with such hydrogen. The impurities present, with the exception of oxygen, seem to have little effect on the preparation of an active gas. In several experiments the hydrogen was passed through a long coil immersed in liquid air with no change in the observed results.

Activation by Alpha Rays.

One of us, using moderate quantities of radium emanation, presented for the purpose by Dr. William Duane, of the Harvard University Cancer Commission, has shown[1] that when α-rays from radium emanation are allowed to ionize pure hydrogen gas, an active form of hydrogen results, which is able to reduce sulfur to hydrogen sulfide, the latter being detected by its blackening lead acetate paper. Similarly, phosphorus was reduced to phosphine, arsenic to arsine, permanganate to manganese dioxide in neutral solution, and to a manganous salt in acid solution. The chemical activity is not due to ions, since an electrostatic field does not remove it. Liquid air, however, condenses or removes the active form. The test papers in Fig. 1 show typical results, the first and third being normal results, while the second was obtained by interposing a coil immersed in liquid air between the exposure of the hydrogen to α-rays and its reaction with the sulfur. The active form of hydrogen thus obtained is unstable, since little or no test for it is obtained if more than a minute is allowed to elapse between its activation and its reaction.

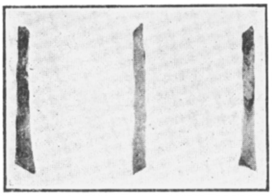

Fig. 1.

Two questions of fundamental interest remain unanswered by this work—the molecular formula of the active gas and the mechanism of its formation. Is it formed by direct bombardment, that is, by the energetic projection of one molecule or atom into another molecule by the α-rays, or is the activity due to the molecular fragments themselves, or, finally is the active molecule polyatomic and a secondary result of the ionization of the hydrogen? The subsequent work all points to the third of these possibilities.

Activation by the Electrical Discharge in Vacuum.

Assuming that the active variety is an ozone form, the high potential electric discharge in vacuum seemed to offer a feasible method of activation, inasmuch as ozone is readily formed in such a discharge, and R. J. Strutt has recently shown[2] that nitrogen also is activated on passing through it. Activation by this method would indicate, of course, that no direct bombardment is needed, and that the activity is due either to molecular fragments, to ions, or to secondary products of ionization.

The apparatus we used is shown diagrammatically in Fig. 2. F is the discharge tube, made of Pyrex glass, about 10 cm. in length and 2 cm. in diameter, with ring electrodes of aluminum, platinum, or tungsten. These latter were attached either to the secondary terminals of a large induction coil or to the terminals of a 2,200 volt alternating current trans-

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[1] *Phys. Rev.*, **10**, 116 (1917).

[2] *J. Chem. Soc.*, **113**, 200 (1918).

former, operated on a 220-volt lighting circuit. The hydrogen entered from the purifying system through the stopcock A and the long, capillary tube B. By this means the speed of the hydrogen stream could be delicately regulated to maintain any desired pressure in the discharge tube. The entire system beyond this point was under reduced pressure produced by a rotary oil pump. The pressure was varied between 2 and 8 cm. in the various experiments. After passing through the discharge in a continuous stream the hydrogen passed through a glass coil at G, through a plug of glass wool in H, then over coarsely ground, crystallized sulfur, I, held in place by loosely packed glass wool, and finally through the tube J, in which was suspended a small strip of filter paper, the lower end of which was dipped in 10% lead acetate solution. The hydrogen was not allowed to pass directly through the solution because of the splashing caused by the rapid stream, but the paper needed to be constantly moistened because the hydrogen had been so thoroughly dried. The gas then passed on through the pump.

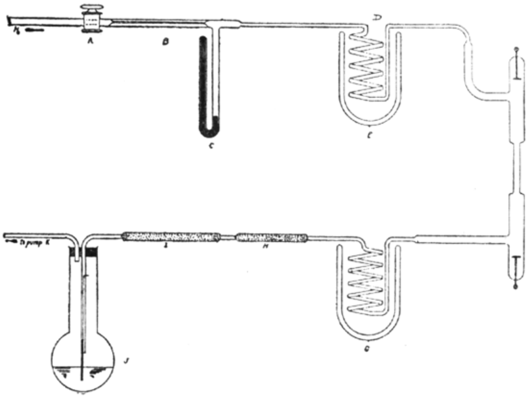

Fig. 2.

Hydrogen was first passed through this apparatus for one hour without the application of the discharge. No blackening of the test paper resulted. Many similar blank runs were made in the course of the work, but in no case was there any indication of sulfide formation when the discharge was not passing. As soon as the discharge was applied, however, sulfide was formed. In many experiments as much sulfide was formed in one minute as had been produced in a run of 8 hours with the α-ray tube. The papers shown in Fig. 3 were typical tests obtained within 3 minutes. Longer runs gave heavy brown precipitates in the lead acetate solution. A blank run was usually made between 2 positive experiments. There is no doubt whatever that the discharge is responsible for the action on the sulfur.

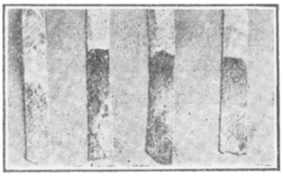

Fig. 3.

In order to exclude the possibility that the action on the sulfur had been due to a slight warming of the latter by the heat of the discharge, either by conduction along the walls or by the hot hydrogen, the coil at G, was immersed successively in boiling water, an ice-water mixture, calcium chloride-ice mixture (about —20°) and liquid air. There was no apparent difference in the amount of sulfur recorded in any case except the last. As in the experiments with the α-ray tube, liquid air seems to condense out the active gas and there is no action on the sulfur. That the effect is not due to a condensible impurity was shown by interposing a long coil cooled with liquid air at E before the hydrogen entered the discharge tube, an expedient which had no effect on the results obtained. The actual quantity of active gas was always so small, however, that no evidence of its collection in the cooled coil has yet been obtained.

It is not certain that positively or negatively charged molecules or atoms of hydrogen would attack the sulfur, but it was important to show that these were not present. This was first done by interposing between the discharge tube and the sulfur a glass tube one cm. in diameter which had been silvered longitudinally in 2 quarter cylinders. These were connected to the 2 terminals of an 800-volt battery of small dry cells, and should thus have removed the ions completely. This tube had no effect on the activity of the hydrogen. The hydrogen went through the tube rapidly, however, and it was possible that ions were still passing. In order to obtain positive evidence, therefore, a very sensitive electroscope, such as is used for the determination of small quantities of radium emanation, was interposed at that point, represented by F in Fig. 4. To test its sensitiveness a glass tube containing 2 mg. of radium bromide was placed at C and shielded from the rest of the system by the lead blocks D. The "natural leak" of the electroscope was 75 minutes per scale division. With the radium in place and the hydrogen passing, but with no discharge, the leaf G fell through one division in 19 minutes. The radium was then removed, the hydrogen was passed at the same rate and pressure as before, but with the discharge passing. The leaf fell through a division in 75 minutes—a leak identical with the natural leak of the instrument, indicating that no ions were passing through. The discharge thus seems to remove all the ions it produces. Indeed, the rate of fall was no greater when the radium was left in place and the discharge passed. The discharge removed the ions produced by

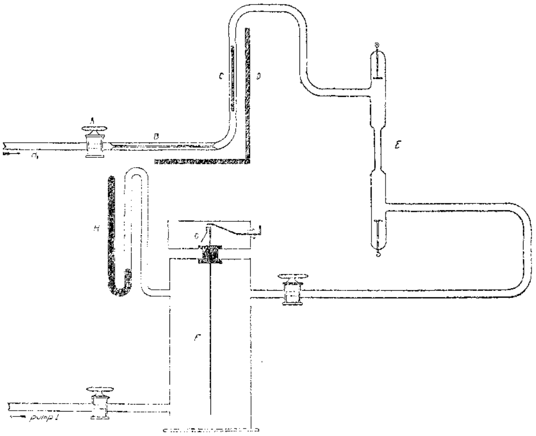

Fig. 4.

the radium. This is hardly surprising, however, since these form only a minute fraction of the ions present in the discharge itself. These experiments are conclusive evidence that the activity of the hydrogen is not due to ions, for good sulfide tests were obtained in every case.

The number of ions produced in air by the β-rays from one g. of radium is 9×10^{14} and by the γ-rays is at most 13×10^{14}, the sum being 2.2×10^{15}. Only 2 mg. was used, which thus could give 4.4×10^{12}. Since, however, the rays passed through not more than one mm. of hydrogen, 1% of this would far exceed the number of ions actually produced. This is 4.4×10^{10}. If every ion produced a molecule of hydrogen sulfide there should have been 4.4×10^{10} molecules of hydrogen sulfide formed per second, or 8×10^{12} in a run of 3 minutes. Since there are 10^{23} molecules in a cubic centimeter, this is less than 10^{-10} and less than 10^{-13} g., an undetectable quantity. Hence, even had the number of ions detectable by the electroscope been present, they would have been entirely inadequate to give the observed quantity of hydrogen sulfide.

It was important to determine this quantity. A solution of sodium sulfide containing the equivalent of 0.0386 g. of hydrogen sulfide per liter was prepared, and various amounts of it were placed in a small round-bottomed flask inserted in the system in place of the sulfur tube. Dil. hydrochloric acid was added through a dropping funnel while the stream of hydrogen was passing as usual. The solution was boiled to expel all the hydrogen sulfide formed. It was found that one cc. of the sulfide solution was sufficient to give a typical test with the acetate paper. Similar tests were obtained in the actual experiments when hydrogen passed for 3 minutes at the rate of 133 cc. per minute. Hence, 400 cc., *i. e.*, 0.035 g., of hydrogen contained 0.0000386 g. of hydrogen sulfide or 0.0000022 g. of combined hydrogen. If we assume the active form to be utilized completely in sulfide formation, as for instance by the reaction $2H_3 + 3S = 3H_2S$, the minimum percentage is 0.0000022/0.035 or 0.006%. Though this determination is not exact, it is evident that the percentage is of the order of 0.01%.

This percentage is confirmed by experiments on the reaction of active hydrogen with nitrogen at atmospheric pressure, which will be described in the next section of this paper.

Activation by the Corona.

Since the activation of hydrogen by α-radiation shows that the active form of this gas is fairly stable at pressures as high as atmospheric, and since the activation by the electric discharge shows that ionization by an electron stream is sufficient to cause the activation, it should be possible to produce the active gas by passing it through a corona tube or through an ordinary ozonizer. This proved to be the case.

Fig. 5 shows diagrammatically the apparatus used. This was devised by Mr. A. C. Grubb, in this laboratory, and was used by him in the activation of nitrogen, as will be described in a paper soon to be published. We are indebted to Mr. Grubb for much of the work on hydrogen at atmospheric pressure. A platinum wire, 0.625 mm. in diameter, was mounted in the axis of the inner tube of an ordinary glass condenser by passing its ends through holes drilled through glass plates and supported by cement. The condenser tube was made of Pyrex glass in order to prevent the electrical puncturing to which soft glass is subject. The condenser jacket was filled with a dilute solution of sulfuric acid which was kept circulating in order to prevent heating. The acid served as the earthed terminal of the secondary circuit of a high voltage transformer. The latter was constructed by the Thordarson Electric Mfg. Co., of Chicago, and furnished 20,000 volts from a primary current of 110 volts, alternating at 60 cycles per second. The primary current was varied from one to 11 amperes by means of a water resistance. The corona produced by this apparatus was even and continuous. The hydrogen passed through it and thence over sulfur and a lead acetate paper as before.

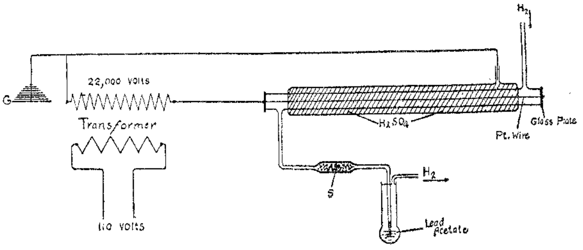

Fig. 5.

Hydrogen sulfide was produced. The quantities recorded were, however, smaller than in the case of the vacuum discharge. This may well have been due to the slow rate of passage of the hydrogen in the experiments at atmospheric pressure. The active gas is undoubtedly unstable and reverts to the diatomic modification with such rapidity that not more than a minute must elapse between activation and contact with the sulfur. At reduced pressures, when the hydrogen is being rapidly pumped through the system, the time interval is so small that a large portion of the hydrogen is able to react with the sulfur. The effect at atmospheric pressure is only about $^1/_4$ as great, due largely to the greater time interval. That this interpretation is correct is shown by testing the effect of varying the velocity of the hydrogen stream.

This is particularly evident in quantitative experiments on the reaction of the active hydrogen with pure nitrogen to form ammonia. Evidence of the formation of ammonia has previously been obtained when a mixture of the component gases was passed through a corona. When pure hydrogen is activated by this method, however, and is then mixed with nitrogen, there is ready formation of ammonia. Nitrogen was prepared by the usual method of decomposition of ammonium nitrite formed from sodium nitrite and ammonium chloride. It was purified by passage through a long tube of pure reduced copper kept at low red heat and dried by passage over lumps of previously fused potassium hydroxide and a tube of phosphorus pentoxide powder. The chemically prepared nitrogen was later replaced by compressed atmospheric nitrogen obtained from the fractional distillation of liquid air, with no change in the results obtained. The nitrogen was passed at a constant rate of about 5 liters per hour. The hydrogen from the corona tube was mixed with it and the mixed gases were immediately passed through a small absorption apparatus designed especially for the maximum absorption of a small constituent in a minimum quantity of reagent. This absorption tube is shown in Fig. 6. It contained about 5 cc. of dil. hydrochloric acid solution, which was later rinsed into a Nessler tube and the quantity of ammonia was determined by the usual method of comparison of the color produced in Nessler's reagent with that produced by standard quantities of ammonium chloride solution.

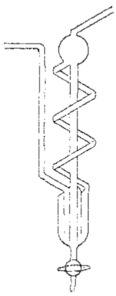
Fig. 6.

The gases were passed through for 10 minutes with the corona passing through the hydrogen. The effect of varying the velocity of the hydrogen stream is shown in the following table:

Velocity of H_2 liters per hour.	Cc. of standard NH_4Cl solution.	% hydrogen combined.
0	0	0
3.6	0.85	0.0034
6.0	8.0	0.0192
7.6	5.0	0.0095

The standard ammonium chloride solution contained 0.00001 g. of nitrogen. The percentages are calculated on the assumption that the reaction is $N_2 + 2H_3 = 2NH_3$, which may, of course, not be accurate. The percentage activation is of the same order as was observed for the reaction with sulfur in the vacuum experiments. The brief "life" of the active form is shown by the marked increase at higher velocities. In the experiment at zero velocity the corona was passed for 10 minutes through static hydrogen and this was then rapidly swept out and mixed with nitrogen. Decomposition was complete before the nitrogen could react. The highest velocity used was more than the optimum. Since the volume of the corona tube was 80 cc. and this velocity is 8 liters per hour, it seems that the equilibrium concentration of the active gas is not reached in this corona tube in less than one minute. The amount of activation in the corona is of the same order of magnitude as in the vacuum discharge, and at the optimum velocity is somewhat higher. Another point worthy of note is that little and perhaps no water vapor is needed for the ammonia reaction, as both gases were well, though not perfectly, dried before use. Less thorough drying did not affect the results.

Activation by Schumann Light.

Although hydrogen is extremely transparent to light even in the extreme ultra-violet, Lyman[1] has found some evidence that at wave lengths of 1300 Å and 1600 Å there is absorption, which may, however, be due to impurities. If hydrogen does absorb in this region, the ionization produced should give rise to the active variety of hydrogen. Conversely, the formation of active hydrogen by Schumann light would be definite evidence that one or both of the absorption bands observed by Lyman are due to hydrogen itself, and not to impurities. All attempts to activate hydrogen by this means, however, were unsuccessful.

The source of the light was the hydrogen spectrum produced at a gas pressure of about 7 cm. in a tube of fused quartz by an electrical discharge from a 2200-volt alternating current transformer. The tube was provided at one end with a thin window of clear transparent fluorite. Some specimens of this material are transparent to waves as short as λ 1230 Å. The window appeared perfectly clear and colorless, but its absorption was not measured. The entire tube was immersed in cold water to prevent heating, which accentuates the visible line spectrum of hydrogen at the expense of the shorter wave lengths. The spectrum tube was not sealed off, but was kept connected to the hydrogen supply and to a vacuum pump, so that the pressure could be maintained constant and independent of the heating effect of the current.

A glass tube 3 mm. in diameter was attached by means of a ground joint to the end of the spectrum tube holding the window in such a manner that its axis and that of the spectrum tube formed one straight line. Hydrogen at atmospheric pressure passed through this tube for a distance of 10 cm. and then, after passing a right angle bend, encountered the sulfur as in all other experiments. Continuous runs extending over 8 hours showed no trace of sulfide formation. This indicates that the fluorite was not sufficiently transparent or that the hydrogen does not absorb the Schumann light or that being absorbed, no active hydrogen is formed. If the last is true it is important evidence on the mechanism of the formation of the active molecule. Further work is in progress to evaluate these possibilities.

The Molecular Formula.

Ions.—While there is no reason at present for supposing that gaseous ions may not have some chemical activity and that the reactions observed may, therefore, be due to a reaction of the charged atoms or molecules, the

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[1] "Spectroscopy of the Extreme Ultra-violet," Longmans, Green & Co., 1914, p. 70.

experimental evidence is conclusive that no ions are present in the reacting gas. A heavy plug of glass wool, which is ordinarily very effective in removing ions, does not reduce the chemical action. Neither does passage of the gas through an electrostatic field of several hundred volts per centimeter. Finally, the absence of any effect on a sensitive gold leaf electroscope by the strongly reducing gas eliminates all possibility of ionic action.

Atomic Hydrogen.—If, then, the active form of hydrogen is an uncharged molecule, it must be either monatomic or polyatomic. All its properties point to the latter. It is well known that nascent hydrogen, which is probably monatomic, exists only momentarily, while this gas persists for minutes. The ability to pass without sensible weakening through a plug of glass wool is hardly to be expected of atomic hydrogen. The fact that several easily reducible organic dyes are not affected by this gas also argues against a monatomic formula. Finally, Langmuir's active modification is almost certainly monatomic, and is quite distinct from the present gas in many of its properties.

Langmuir's active hydrogen[1] is produced when the diatomic molecule is dissociated into atoms by contact with a metallic filament heated above 1300° K or by evaporation of the atoms dissolved in the metal when that temperature is reached. From calculations of the heat loss of the wires Langmuir calculates the degree of dissociation of hydrogen into atoms as 0.0033 at 2000° K. and 0.34 at a temperature of 3500° K. This hydrogen is very reactive, and is destroyed at room temperatures by oxygen or by phosphorus vapor. It reduces rapidly the layers of tungsten and of platinum oxides which occur within electric lighting bulbs. It persists for hours when the pressure is below 0.02 mm. of mercury, but recombines with great speed in the presence of excess hydrogen. It is not detectable at higher pressure. Perhaps the most marked characteristic of this form is its strong adsorption by glass surfaces, especially by glass wool. Freeman[2] has shown that while it will diffuse through side tubes sealed on the filament bulb, it cannot be found in the side tube if a plug of glass wool is placed at the joint. Hence, the relative stability at atmospheric pressure and the ready passage through glass wool distinguish the new form from this one.

Contraction in Volume.—Positive evidence for a polyatomic molecule is furnished by the contraction in volume now observed by many experimenters when hydrogen is ionized. In the work with α-rays it was shown that a contraction of 3 mm. in 760 was obtained when pure hydrogen was bombarded by α-rays. In a bulb of 5 cc. this meant a contraction of 0.02 cc., a quantity far larger than the volume of niton used. This ex-

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[1] *Trans. Am. Electrochem. Soc.*, **20**, 225 (1911); THIS JOURNAL, **34**, 860 (1912); **34**, 1310 (1912); **36**, 1706 (1914); **37**, 417 (1915).

[2] THIS JOURNAL, **35**, 927 (1913).

cluded the supposition that the α-rays had driven hydrogen into the walls of the bulb, for it would have been necessary for each α-particle thus to drive many thousands of hydrogen atoms. There remained the possibility that the active hydrogen was reacting with the mercury in the manometer tube, though this was a $^1/_2$ mm. capillary about 15 cm. long (X, Fig. 7). This improbable hypothesis was excluded by the fact that the original volume of hydrogen was reformed when the niton was withdrawn from the α-ray bulb K, into the bulb N, and reformed at a rate which corresponded with the decay of the powerful α-radiator, radium C, which had, of course, been deposited in the bulb K, by the niton. Lind[1] has recently confirmed this decrease of pressure in hydrogen under the action of α-rays as well as the attack of the active hydrogen on the mercury to form a hydride which is readily decomposed on heating. In his work, however, much mercury was exposed to a mixture of hydrogen with niton, and chemical action on the mercury alone may account for the contraction.

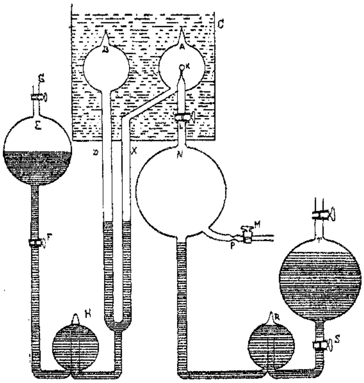

Fig. 7.

Usher[2] attempted to synthesize ammonia by exposing a mixture of nitrogen and hydrogen to the action of α-rays from niton mixed with the 2 gases. Using, in one experiment, 1.602 cc., he observed a contraction of 0.24 cc., but only 0.006 cc. of ammonia had been formed. Analysis showed that the nitrogen was still present intact, but that nearly a quarter of a cubic centimeter of hydrogen had "ceased to exert any pressure." Since it could not have been projected through the heavy glass walls, he pulverized and heated the latter, but regained thus only 0.06 cc. He left the problem in this stage with the remark that it "is probably much more complicated than it at first sight appears." It is now evident that the observed contraction was due to the formation either of larger molecules of hydrogen or of mercury hydride.

We have repeated Usher's work with the modification that the niton was contained in a small α-ray bulb within the reaction bulb, and that mercury was removed so far as possible by exposing only a very small surface of it in a very fine capillary about 15 cm. distant from the mass of hydrogen and removed from the direct action of α-rays, as shown in Fig 7. Forty cc. suffered a contraction of 0.2 cc., but less than 0.013 cc. of ammonia was found. It is noteworthy that though the possibility of reac-

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[1] THIS JOURNAL, 41, 545 (1919).

[2] *J. Chem. Soc.*, 97, 400 (1909).

tion with mercury was reduced to a very small fraction of Usher's value, the order of contraction is about the same, indicating a real contraction of the hydrogen.

Collie and Patterson[1] have obtained a similar effect in sparking hydrogen under reduced pressure. In one experiment 3.6 cc. out of 4.6 cc. "apparently disappeared" when sparked for 6 hours in a tube with copper or aluminum electrodes at less than one mm. pressure. Here a reaction of the hydrogen with the electrodes is not excluded, although the general tendency under such conditions is for the electrodes to lose any gases they contain. Volume measurements were made by withdrawing the hydrogen from the tube.

Chattock and Tyndall[2] have also noted a definite contraction when pure hydrogen is sparked between a fine platinum point and a metallic plate, the contraction corresponding to about one molecule per ion. This they interpreted to mean that the ion or single electrified atom of hydrogen is absorbed by the metallic electrode on which it is discharged. This interpretation is by no means certain in view of the present work. The quantitative relation between the ionization and the contraction is in striking accord with the simple relation stated by Lind[3] for the chemical action of α-rays. In a large number of such reactions the ratio of the number of ions produced and the number of molecules reacting is very close to unity. If such a reaction as $3H_2 = 2H_3$ is responsible for Chattock and Tyndall's observation, the fact that a single ion produces such a reaction is of vital importance in determining the mechanism of the reaction, as will be discussed later.

The volume change in the electrical discharge tube is being further studied in this laboratory, to confirm the work of Collie and Patterson and of Chattock and Tyndall. The heat of the discharge causes so great and so irregular an expansion that no results can yet be announced.

Positive Ray Analysis.—Definite evidence of the existence of relatively large quantities of triatomic molecules is furnished, however, by the method of the positive ray analysis. By this method both Sir J. J. Thomson[4] and A. J. Dempster[5] have shown that H_3 exists in the vacuum discharge. According to Dempster higher pressures favor the formation of H_3 at the expense of H_2 and H, as would be expected, and in some cases H_3 is actually the major constituent. While positive ray analysis is remote from ordinary chemical technique, it is an admirable method of molecular weight determination. Aston's failure to separate neon into

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[1] *Proc. Chem. Soc.*, **29**, 22, 217 (1913).

[2] *Phil. Mag.*, **16**, 24 (1908).

[3] *J. Phys. Chem.*, **16**, 564 (1912); *Le Radium*, **8**, 289. (1911).

[4] *Proc. Roy Soc.*, **89A**, 1 (1913); "Rays of Positive Electricity," Longmans, Green & Co., 1913.

[5] *Phil. Mag.*, **31**, 438 (1916).

2 constituents by diffusion,[1] following Thomson's discovery of 2 neon lines on the positive ray photograph has cast some doubt on this method, which is now removed by W. D. Harkins[2] separation of chlorine into two isotopes by diffusion simultaneously with Aston's report of 2 chlorine lines in the positive ray "spectrum."[3]

Chemical Properties.—Finally, the properties of the new gas are precisely those to be expected of an ozone form. It is much more reactive than ordinary hydrogen, yet not as active as nascent hydrogen. Its boiling point is much higher than that of ordinary hydrogen. And it is unstable, for it cannot be detected if more than about a minute is allowed to elapse between the time of its formation and its reaction with a reducible substance.

All the evidence obtained, then, points to the formation of triatomic hydrogen, perhaps properly called "hyzone," whenever hydrogen is ionized.

The Structure of the Molecule.

The chief theoretical interest of this work lies in the fact that no hydrogen molecule larger than H_2 is possible on the older conception of valence. Heretofore there has been no evidence that demanded more than a unit valence for hydrogen, and our valence system is based on this unit valence. Yet no triatomic ring can be constructed from unit valence bonds. Increasing the valence of hydrogen to 2 is not possible because this valence is so uniformly connected with one Faraday's equivalent. Nor does the centering of 3 unit valence bonds from 3 hydrogen atoms on a central point solve the question, since such an indefinite subdivision of valence is still a subdivision, and is not to be countenanced if valence is a matter of unit quantities.

Of the numerous electronic valence hypotheses which have recently come to the assistance of the theory of valence, only one, that of J. Stark,[4] can picture the triatomic molecule of hydrogen. According to this a valence bond consists of an electron held in position, between the two atoms which it binds, by numerous lines of force extending to the two atoms, and an ordinary single bond really has two such electrons, one arising from each atom. A triatomic ring of monovalent atoms thus requires simply the alternation of atom with electron in a 6 membered ring. The picture is not convicing, both on physical and on chemical considerations.

There remain the modern fundamental reconstructions of our conceptions of atomic structure, in particular the Rutherford atom on the basis

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[1] Private communication, May 5, 1919.

[2] *Science,* **51,** 289 (Mar. 19, 1920).

[3] *Nature,* **104,** 393 (1919).

[4] *Jahr. Radioakt. Elektronik.,* **9,** 15 (1912).

of which both Bohr[1] and Crehore[2] have predicted the possibility of the existence of a fairly stable triatomic molecule of hydrogen. Recently Bohr[3] has discussed the structure of this molecule, which he gives as a system of 3 electrons rotating at equal angular intervals in a circular orbit, the 3 nuclei being placed, respectively, at the center of the orbit and at 2 points on the axis equidistant from the center. Such a structure is consistent with all that is known on atomic structure and on valence.

Triatomic hydrogen furnishes definite chemical evidence, if not of this structure, then at least of the need for considering valence on the basis of the new knowledge of subatomic phenomena. If it is not a confirmation of present atomic structures, it does demonstrate the inadequacy of past analysis and nomenclature.

The Mechanism of Formation.

Lind[4] accounted for the fomation of ozone from oxygen by the decomposition of cluster ions. He found that each ion produced by α-rays causes the formation of one molecule of ozone. Chattock and Tyndall made a similar observation for hydrogen in the electric spark. Lind found, indeed, that practically all the known gaseous reactions caused by α-rays follow this law closely. It is difficult to picture the mechanism by which a single ion causes a complex reaction such as $3H_2 = 2H_3$. Lind supposes that a large "cluster ion" is at once formed by the adhesion of neutral molecules to the original ion and that this breaks down when the charge is neutralized into diatomic molecules and one triatomic molecule, presupposing thus a general loosening of the valence bonds in the cluster ion.

While this explanation accounts for the observed facts, recent evidence seems to prove that cluster ions do not exist. The cluster ion hypothesis was devised originally to account for the extremely low mobility of gaseous ions in traveling through gases. This mobility is now accounted for, however, by the retardation of the ion in its path through the gas by virtue of its attraction for other molecules and the increased number of collisions it therefore suffers without actually attaching itself to the molecules. The work of Loeb[5] and of Wellisch[6] shows that if cluster ions exist they do not break up even when traveling under electrical potentials that merge into the potentials necessary for ionization by collision. It is impossible to attribute to them a greater stability than that of ordinary neutral molecules, however, and it thus seems clear that gaseous ions remain very small.

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[1] *Phil. Mag.*, 26, 857 (1913).

[2] *Ibid.*, 30, 613 (1915).

[3] *Medd. K. Vetenskapsakad. Nobelinst.*, 5, No. 28, 1 (1919).

[4] *Am. Chem. J.*, 47, 397 (1912).

[5] *Phys. Rev.* 8, 633 (1916); *J. Franklin Inst.*, 184, 775 (1917).

[6] *Am. J. Sci.*, 39, 583 (1915).

Hence, the explanation of the reaction is to be based rather on the calculations of Bohr,[1] who showed that the usual molecule of hydrogen, consisting of 2 nuclei with 2 electrons rotating in an orbit perpendicular to the line joining the nuclei and equidistant from them, must break up when one of these electrons is removed by any cause. Thus the ionization of hydrogen by any agent inevitably forms 2 free atoms of hydrogen as an intrinsic part of the process of ionization. Since neutral molecules are present in great excess over the free atoms, these latter at once attach themselves to the molecules and form molecules of H_3 with a structure as described in the previous section. This very simple picture accounts for the seemingly complex reaction $3H_2 = 2H_3$, and is in accord with the generalization of Lind. Since the same relation holds experimentally for oxygen as for hydrogen, it follows that the O_2 molecule is similarly unstable and dissociates into atoms whenever it is ionized, with the consequent formation of ozone.

This interpretation is ventured as a rational deduction from the Rutherford theory of the atom, and is by no means free from criticism. It will bear much study, and in particular data are needed for the examination of other reactions on this basis. Fuller consideration of the subject must be delayed until a later time.

Summary.

1. A reactive modification of hydrogen has been produced by several methods, all dependent on gaseous ionization—by the α-rays from radium emanation, by the electrical discharge under reduced pressure, and by the high potential corona at atmospheric pressure. Attempts to produce activation by Schumann light rays failed.

2. This active hydrogen reduces sulfur, arsenic, phosphorus, mercury, nitrogen, and both acid and neutral permaganate. It is condensed or destroyed by liquid air temperatures. It is unstable and reverts to the ordinary form in about a minute. It passes readily through glass wool. It is not less stable at atmospheric pressure than at low pressures.

3. The activity is not due to gaseous ions, and the properties of the active gas are quite different from those of Langmuir's atomic hydrogen. The formation of a polyatomic molecule is indicated by the contraction of the hydrogen when ionized. Positive ray analysis at very low pressures shows a large proportion of triatomic molecules which are undoubtedly the ones responsible for the chemical activity. All the properties of the gas point to its being an ozone form, perhaps properly called "hyzone."

4. The existence of H_3 is applied to the explanation of several previously observed phenomena. The calculations of Bohr on the basis of Rutherford's atom furnish the only valence hypothesis which satisfactorily accounts for its existence.

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[1] *Phil. Mag.*, **26**, 857 (1913).

5. The mechanism of the formation of triatomic molecules is considered on the basis of the Bohr atom. Stable molecules of hydrogen are perhaps dissociated into free atoms when an electron is removed in the process of ionization, and these atoms attach themselves to neighboring neutral molecules to form triatomic systems.

6. We desire cordially to acknowledge our gratitude for much assistance in this work: to the Director of the Ryerson Physical Laboratory of the University of Chicago for the use of indispensable alternating current and the privileges of that laboratory; to the Research Grant of the American Association for the Advancement of Science for the funds for the construction of the quartz spectrum tube for the Schumann ray investigation; to Professor Stuart Weller, of the University of Chicago, for the gift of an excellent crystal of clear transparent fluorite for the Schumann ray investigation, and to Mr. A. C. Grubb for much of the work on the corona discharge.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

THE ADSORPTION OF SULFUR DIOXIDE BY THE GEL OF SILICIC ACID.

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Introduction.

Many investigations of the adsorption of vapors by porous bodies have been made without a satisfactory explanation of the phenomenon being found. The fact that the adsorbing material is not chemically definite but has adsorbent properties dependent upon its method of preparation is not the least of the reasons for apparent lack of agreement both in experimental results and theoretical conclusions. Again, the possibility, and in many cases, the great probability of chemical reaction occurring during the process bring in another factor which is hard to control.

In the investigations carried on in this laboratory during the war it was found necessary to test many types of adsorbents, both as to their specific action against poisonous war gases as well as to their susceptibility towards other vapors and gases. It was realized in the beginning that porous bodies—mere mechanical condensers so to speak—were going to play an important part. Charcoal was brought into use and its protective ability greatly increased by improved methods of preparation. This laboratory focused a good part of its attention upon colloidal substances and gels. The gel of silicic acid, having been previously shown to possess adsorptive properties, received first attention. The main difficulty was its large scale preparation. Up to this time the method