

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

TRIATOMIC HYDROGEN. II

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Since our first paper¹ Venkataramaiah reported² the independent discovery of the active form of hydrogen, distinguished by its ability to reduce potassium permanganate solution rapidly at room temperature. He produced it first in the alternating current corona, but made the interesting observation that it is produced in measurable quantities when oxygen is exploded in an excess of hydrogen. Since all other methods of its preparation, including those reported below, are dependent on prolonged and intense ionization of the hydrogen, this preparation by explosion is of importance in determining the mechanism of its formation.

New Methods of Preparation

Siemens Ozonizer.—In view of the ready formation of the new gas by means of the electrical discharge at 10,000 to 20,000 volts and a current of 4 to 25 milli-amperes, both at atmospheric pressure and at a pressure of 4 to 8 cm. of mercury, there is little new in its successful preparation in the usual quantities of about 0.01% by means of the ordinary Siemens glass tube ozonizer, with external tin-foil electrodes. This method is simple and reliable. It is particularly effective at the temperature of boiling liquid ammonia. This method failed, however, when the ozonizer was immersed in liquid air, probably because of the increased dielectric strength of the glass walls. When metallic electrodes were inserted through the walls of the tube, the low temperature did not prevent the activation.

In this, as in all the work, the hydrogen was prepared and purified as described in the previous paper. In all cases the test for activation was the formation of hydrogen sulfide in passage of the gas over cold sulfur. In every case blank tests were made to show that the hydrogen itself, without the ionizing agent, did not attack the sulfur.

High-frequency Discharge.—A marked increase in the frequency and voltage of the electric discharge has no appreciable effect on the amount of activation of the hydrogen. This was shown by using the discharge from a Tesla coil consisting of a primary of one turn of heavy cable surrounding a secondary coil of 1680 turns of No. 28 enameled copper wire. The voltage from such a system is well up in the millions, and the frequency perhaps

¹ THIS JOURNAL, 42, 920 (1920); presented at the Philadelphia meeting, American Chemical Society, September, 1919.

² An oral communication to the Science association, Maharajah's College, Vizianagram, S. India, January 29, 1920; printed in the *Proceedings* of the Science Association July 10, 1921; *Nature*, 106, 46 (1920).

half a million cycles per second. The secondary of the Tesla coil was connected to a large Siemens ozonizer tube, and the hydrogen passed through at velocities of 25 to 150 cc. per minute. The activation was pronounced and of the same amount as in previous experiments with lower voltages.

Thermionic Emission.—All ionizing agents had now proved to be successful activators with the single exception of ultra-violet light, which is but slightly absorbed in hydrogen, and an exceedingly weak source of ionization. Even Schumann rays, which are probably absorbed, showed no activation. In order to test a remaining source of ions, though weak, hydrogen was now passed over a 0.46 mm.³ platinum wire maintained electrically at a temperature of about 800°. In spite of the relatively weak electron stream from such a wire, the hydrogen was activated readily.

The wire was 16 cm. long, and was welded at each end to 12 short lengths of 0.38mm. (No. 28) platinum wire, which were then sealed through the glass walls. This expedient was adopted in order to allow the protracted passage of a heavy current for maintaining the temperature of the wire without overheating the glass. The hydrogen entered at one end of the 20 cm. glass tube 15 mm. in diameter, and after passing over the wire left at the other end, passed through a coil which could be immersed in cold water and thence over the powdered sulfur and the lead acetate paper as usual. A heavy black sulfide test resulted in repeated runs of 30 minutes with a current of 10 to 12 amperes through the wire, and with a hydrogen flow of 60 cc. per minute.

The same sources of the hydrogen sulfide that needed to be eliminated were present here as in previous work, and in addition the possibility of a reaction by the heated ordinary hydrogen. Impurities were eliminated, as before, by the complete purifying system and a coil immersed in liquid air preceding the exposure to the hot wire. Thus all possible impurities except nitrogen and the gases of the helium group were excluded, and these latter cannot give the black sulfide test. Ions were again shown not to be present by passing the gas after activation through a sensitive radium emanation electroscope without any indication of conductivity.⁴

There remains the possibility that the hydrogen reacts because it retains a high temperature. At 200° ordinary hydrogen has an easily detectable action on sulfur. But a thermometer inserted in the side tube at the exit of the hydrogen from the hot wire tube showed a temperature of

³ No. 26 B. and S. gage.

⁴ Attention is called to an unfortunate though non-significant error in the previous paper. The sentence beginning on Line 12, p. 936, should, of course, read: "Since there are 2.7×10^{19} molecules in a cubic centimeter, 8×10^{12} molecules occupy 3×10^{-7} cc. and weigh slightly more than 3×10^{-11} g., an undetectable quantity." The same figures apply in this case, *i. e.*, even had an easily measured number of ions been present and had they been able to react with the sulfur, which is itself more than doubtful, they could have accounted for less than 0.001% of the activity actually observed.

31°, room temperature being 27°. The long coil of thin-walled glass tubing which was placed between the hot-wire tube and the sulfur tube was then immersed in an ice-water mixture at 0°. It had no effect whatever on the action of the hydrogen on the sulfur. A thermometer placed at the exit of this coil showed a temperature of 29°. Although the heat capacity of the thermometer was undoubtedly high, runs were extended to as much as 16 hours with no change in the observations, and the time thus was ample to allow the thermometer to come into thermal equilibrium with the hydrogen in which it was bathed. That the activity of the hydrogen was due to increased temperature was, therefore, also excluded, and an active form of hydrogen remains as the only possibility.

To determine what is the activating agent in this case is a problem in electronics which we cannot attempt. There seem to be three possibilities: the thermal dissociation of hydrogen into atoms, ionization by the electron stream from the wire, and disruption by positive ions from the wire.

The calculations of Langmuir⁵ show that thermal dissociation for a wire at less than 1000° is certainly inadequate, amounting to less than $5.8 \times 10^{-11}\%$. This is so small a quantity that it could not possibly account for the observed activation. The second possibility, namely, the ionization of the hydrogen by negative electrons, seems to be excluded by the work of O. W. Richardson.⁶ Not only are few, if any, negative electrons emitted at temperatures of 800–900°, but the energy of those emitted under the conditions of our experiment must be very low, since there is no accelerating potential applied. The third possibility is also unsatisfactory, but seems at present the most plausible, namely, that positive ions are emitted from the wire and cause the ionization. Richardson has shown that at low temperatures the emission of positive ions far exceeds that of negative ions, and with larger mass the energy of these ions would perhaps be sufficient to produce ionization. Richardson assumes that the positive ions emitted are ions of the alkali metals present in the platinum as impurities. Until more evidence on ionizing potentials and thermionic emission is available, this activation by the hot wires remains to be explained.

Nascent Hydrogen.—According to the theory suggested in the previous paper, the triatomic modification of hydrogen is formed by ionization because the H₂ molecule is not stable when one of its electrons has been torn off. Hence it splits into atoms which recombine to give triatomic molecules. If this suggestion is correct, the ozone form should be produced whenever atomic hydrogen is formed, and therefore nascent hydrogen

⁵ Langmuir, *Trans. Am. Electrochem. Soc.*, **20**, 225 (1911); *THIS JOURNAL*, **34**, 860 (1912); **34**, 1310 (1912); **36**, 1706 (1914); **37**, 417 (1915).

⁶ Richardson, "The Emission of Electricity from Hot Bodies," Longmans, Green and Company, 1916.

should retain a fraction of its activity after it is evolved in the gaseous form. Such an activity was, therefore, sought by three methods, but all results were negative.

First, hydrogen was produced by the solution of zinc in hydrochloric acid, using the zinc amalgam-platinum cell previously described. The hydrogen evolved was passed through glass wool to remove spray and thence over sulfur and lead acetate. No activity was detected even in runs extending for 24 hours. In this, as in the subsequent experiments, it was difficult to obtain blanks because of the hydrogen sulfide dissolved in the acid. In all cases, however, pure molecular hydrogen was bubbled through the acid for many hours, until no trace of sulfide could be detected. Then only was the nascent hydrogen produced and tested.

Since the active hydrogen is known to be very unstable, it was possible that this method of generation was too slow. A generator with heavy platinum electrodes sealed in was then used for the electrolysis of potassium hydroxide solution with a current that could be varied from 2 to 30 amperes. The tests were extended to as long as 15 hours, but in no case was any activity noted.

Finally, pure sodium amalgam was dropped into water, and the resulting hydrogen was tested as before. Again there was no activity.

The failure of these experiments does not necessarily exclude the mechanism of formation advanced. We are here between two experimental difficulties. The hydrogen must be evolved so rapidly that it reaches the sulfur within one minute, to avoid the decomposition of the active form into the ordinary. On the other hand, if evolution is made rapid, the gas carries with it large amounts of spray which are practically impossible to remove without slowing up the stream of gas more than can be allowed. The one possible means would be electrical precipitation of the droplets, but that was excluded because the electrical discharge itself would activate the hydrogen. Hence the sulfur may well have become coated with a film of moisture which prevented the access of the active hydrogen.

Catalytic Decomposition

During the course of the work it was invariably found that the active hydrogen could not be produced in copper or brass tubes and that there is a peculiar fatigue effect even when glass tubes are used. To determine the presence of catalytic decomposition such as is very common in the case of ozone itself, the hydrogen was therefore activated in the Siemens glass tube ozonizer, and was passed through a tube containing finely divided metals. No tests for activity could be obtained when the following metals were used: platinum, nickel, copper, lead, antimony and cadmium. There was, however, no destruction of the activity by silver, mercury, tin, bismuth, molybdenum, zinc or aluminum. The catalytic decomposition by

copper therefore explains the failure of brass tubes to give the active gas. The fatigue effect seems to be due to the formation of finely divided platinum on the walls of the discharge tubes by spluttering from the electrodes during the passage of the current. Whenever the tubes showed fatigue they could be restored to their original activating power by removing this film of platinum, though all other efforts, such as renewing the sulfur, had no effect. The fatigue effect was never observed when the glass ozonizer with external electrodes was used.

Contraction in Volume

The evidence for a triatomic structure of the active hydrogen molecule was summarized in the previous paper. It is difficult to establish the contraction which is to be expected from the activation by the electrical discharge if a polyatomic molecule is formed, because of the heat developed by the discharge. The device shown in Fig. 1, however, eliminated this interference and gave conclusive evidence of contraction.

A is the glass discharge tube with platinum electrodes, operated by a 20,000 volt Thordarson wireless transformer and using currents of 25 milli-amperes. It was im-

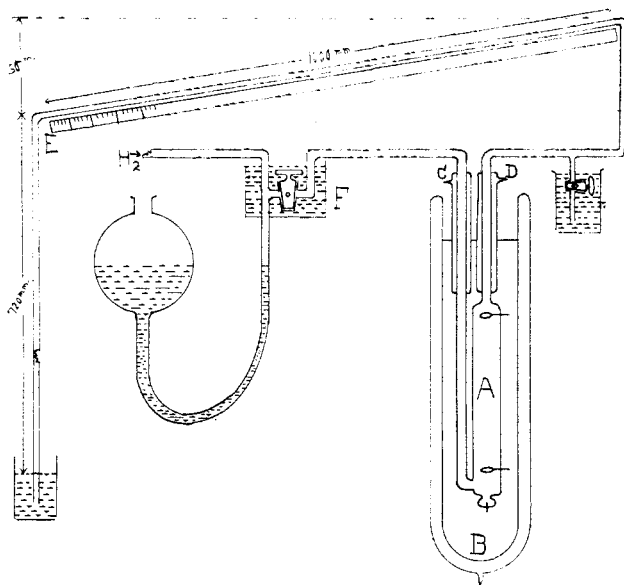


Fig. 1.

mersed in the Dewar cylinder, B, which in the various experiments contained constant temperature cooling mixtures. The tubes, C and D, cover the inlet and outlet tubes at the points where they enter the liquid. They were thoroughly evacuated before sealing and thus acted as insulators to guard against any thermal effects on the gas within from possible variation in the level of the cooling liquid in the Dewar cylinder. E is a mercury manometer the upper part of which is sloped, rising 1 cm. vertically for 20 cm. of length, in order to increase its sensitiveness. The 2 stopcocks were sealed with mercury. The

mercury level was raised above the stopcock, F, by raising the leveling bulb before the cock was closed, in order to prevent the possibility of leakage through the cock. When the tube was filled with hydrogen at 3cm. pressure and sealed, there was first an increase in pressure due to heating. Equilibrium was soon established, however, and a decrease in pressure became evident in all cases. On shutting off the current there was first a rapid, then a slower increase in pressure, until the original pressure was restored. The restoration of the original pressure proves the absence of impurities such as oxygen or nitrogen which might have reacted, and shows also the instability of the active gas. Data for typical contractions follow.

At 0° , under ice-water mixture: maximum pressure at start of contraction, 30.00 mm; successive pressures at intervals of 10 seconds, 29.6, 29.2, 28.8, 28.65, 28.30; total contraction in 50 seconds, 1.70 mm.

At -38° , under liquid ammonia: maximum pressure, 30.00 mm.; successive pressures at intervals of 3 seconds, 29.85, 29.70, 29.55, 29.40, 29.25, 29.05, 28.90; total contraction in 21 seconds, 1.10 mm.

At -85° , under carbon dioxide snow suspended in acetone: maximum pressure, 30.00 mm.; successive pressures at intervals of 5 seconds, 29.60, 29.30, 29.10, 28.95; total contraction in 20 seconds, 10.5 mm.

At -180° , under liquid oxygen: maximum pressure 24.0 mm.; successive pressures at intervals of 5 seconds, 23.70, 22.85, 22.25, 20.65, 20.10, 19.20, 17.45, 15.80; total contraction in 40 seconds, 8.20 mm.

Total contraction reduced to 40 seconds: at 0° , 1.4 mm.; at -38° , 2.10 mm.; at -85° , 2.10 mm.; at -180° , 8.20 mm.

The amount of contraction indicated that much larger amounts of the active gas were formed than had been revealed by the dynamic methods in which a stream of the gas was passed over sulfur, amounting in some cases to more than 5%. In the chemical tests a large fraction of the active gas is evidently decomposed before it has opportunity to react with sulfur. The data are not sufficiently accurate to allow a reliable calculation of the percentage of triatomic hydrogen present, nor was equilibrium reached in any case. The method can, perhaps, be extended to such measurements. It is noteworthy, too, that the contraction increases with a decrease in temperature, as would be expected for polymerization. The figures for -180° refer to the temperature of liquid oxygen, this being used in place of liquid air because of the much greater constancy of its boiling point; it was of course essential that the temperature of the tube should not change during the test. The very large contraction in this case, amounting to more than one-third the entire volume, indicates a condensation of liquid "hyzone," as is described in the next section.

The possible extraneous effects which might invalidate the observed contraction, such as leaks, heating of the surrounding liquid, insufficient cooling, and a decrease in level of the cooling liquid, all would tend to increase the pressure and are thus inoperative for such an inexact determination of the contraction as this. The one exception is the possibility that hydrogen enters the platinum electrodes under the influence of the discharge. This is practically excluded by the exact return to the original volume. Conclusive evidence that such an effect was not inter-

fering was obtained by repeating the experiment in every detail, with the same tube and electrodes, but substituting pure helium for pure hydrogen. Helium has been shown⁷ to be easily absorbed by the electrodes; indeed in spectroscopic work especial precautions must be taken to avoid this effect. In spite of this, however, helium showed absolutely no contraction in this test. The pressure in the tube remained at 24.5 mm. with perfect constancy for several tests, each extending for as long as 2 minutes. The actual contraction of the hydrogen by polymerization is therefore established.

Condensation by Liquid Air

It will be noted that the above data confirm previous observations that the active hydrogen is condensed by liquid air, for the contractions in the last column amount to more than $\frac{1}{3}$ of the entire volume present. To establish this definitely, hydrogen was now activated in the Siemens tube ozonizer immersed in liquid ammonia, which gives the greatest activation we have been able to obtain, and passed through a long coil immersed in the same 4 cooling liquids used above. The first 3 allowed the active gas to pass through unimpaired, but when liquid air was used, no trace of activity could be detected. On removal of the liquid air cylinder, however, there was an immediate and rapid evolution of the "hyzone," if so it may be called. The test paper was blackened within a few seconds. This therefore establishes definitely the condensation of this gas at a temperature of -180° . There had previously been some question as to whether its removal at that temperature was due to rapid decomposition by adsorption on the walls at the low temperature, but there is now no doubt that the hyzone has a true boiling point above that of liquid air. It was not possible, however, to collect sufficient quantities of the liquid to render it visible as such.

Spectral Evidence

The theoretical importance of the spectrum of hydrogen has led to many investigations of it. In almost all these, light emission was produced by electrical excitation. Hence in those cases the ozone form must always have been present. To select the lines due to triatomic hydrogen, we therefore planned to measure its absorption spectrum by means of a brass tube 6 meters long and 10 cm. in diameter through the axis of which passed a platinum wire attached to the high voltage transformer. At each end was a heavy plate glass mirror, one of which was fitted with 2 quartz lens windows. Light from an uncovered Nernst glower was reflected into the tube through one window, thence back and forth through the length of the tube three times and out of the other window into the slit of a Hilger quartz spectrograph. Hydrogen was passed continuously

⁷ Soddy and Mackenzie, *Proc. Roy. Soc. (London)*, **80**, 92 (1897).

through the tube at a rapid rate. The high potential discharge was turned on for a minute, and then cut off while the light from the glower passed through the tube. These alternations were repeated for many minutes. In no case was any absorption noted. This may have been due to the catalytic decomposition of the hyzone by the brass walls of the tube, though no better results were obtained when the inner wall was coated with graphite.

In another connection, however, spectral evidence was obtained. During the experiments on the contraction in volume at liquid-air temperatures, the color of the discharge went through interesting changes. Beginning with the usual lavender color, an intensification of the red first appeared. For a half-minute the color was brick red, then shifted rapidly through orange to yellow, and remained finally at a bright, greenish yellow, practically straw-color. Examination with a visual spectroscope showed the few series lines of hydrogen still present, though much weakened, and a brilliant display of the secondary line spectrum. This effect of liquid air has been observed by Lemon,⁸ though his secondary spectrum extended from the red H_{α} line only about half-way to the green line. We observed the lines, appearing much like fluted bands, well into the green. This may have been due to our use of much heavier currents, up to 25 milli-amperes. The intensification of the secondary line spectrum is usually attributed to polymerization, such as the formation of hyzone in this case. The fact that, though the hydrogen is well cooled before the discharge passes, the appearance of the secondary spectrum is a slow and progressive process, is in accord with the assumption that the heavier molecules are concerned and do not show their effect until the current has had time to produce them. If the current is shut off for a few minutes, the color on exciting the gas once more is yellow at once, as would be expected from the condensation of the hyzone at this temperature. Lemon's experimental apparatus was not so mounted that he could observe the growth of color visually.

Mechanism of Formation

Nothing has occurred since the publication of the previous paper to invalidate the explanation of the mechanism of formation of hyzone there suggested, with the exception of the failure to show a transitory active state in hydrogen collected from electrolysis or the solution of metals. This failure, however, is inconclusive in this regard.

A. L. Hughes,⁹ however, has studied the clean-up of hydrogen at pressures of 10^{-3} mm. by electrons projected from a hot filament under voltages of above 13 volts and finds, as Langmuir¹⁰ did, that the greater part of the

⁸ Lemon, *Astrophys. J.*, **35**, 109-124 (1912).

⁹ Hughes, *Phil. Mag.*, **41**, 778 (1921).

¹⁰ Langmuir, *THIS JOURNAL*, **37**, 451 (1915).

hydrogen ceases to exert pressure, being condensed on the glass walls which are immersed in liquid air. On removing the liquid air, the gas is regenerated, and thereafter only a part of it can be recondensed. This he attributes to a formation of atomic hydrogen by the electron collisions and a condensation of the atoms on the glass walls. When the temperature is raised, the atoms combine to form molecules, and only those remaining in the atomic form are recondensed. Thus ionization by electrons, at least by those with energies above 13 volts, is accompanied by atomization, as had been suggested by Franck, Knipping and Krüger¹¹ and as we assumed in the previous paper. While the condensation observed by Langmuir and by Hughes may at the low pressures used have been chiefly that of atomic hydrogen, at the higher pressures used in our experiments, where the mean free path of a molecule is much less than the diameter of the tube, the formation of hyzone is more probable, and even in the former work may have exerted a greater influence than was suspected. In any case, atomization accompanies ionization and furnishes the most probable explanation of the formation of the active modification of hydrogen. Atomization may be assumed also in Venkataramaiah's explosion method for the preparation of this gas.

The Molecular Formula

All the evidence now presented favors the view that this new gas has a larger molecule than H_2 , including its reactivity, its relative stability at atmospheric pressure, its condensation by liquid air, its catalytic decomposition by metals, its contraction on formation, and its effect on the spectrum. Positive-ray analysis indicates a triatomic molecule.

The one alternative possibility, however, has been accepted by Baly,¹² namely that it is the isotope of hydrogen suggested by Harkins¹³ as the basis of the structure of many heavier atoms. It is unfortunate that Harkins' use of the symbol H_3 for that isotope has led to some confusion. The ozone form of hydrogen may, of course, properly be designated as H_3 , which represents 3 separate hydrogen atoms combined into one molecule. The isotope, which we shall refer to as iso-hydrogen, however, is a single atom with an atomic weight of 3 units. Like hydrogen itself, it has but a single free electron, and should be similar to, if not identical with, hydrogen in all its chemical properties. Its nucleus consists of a compact of 3 ordinary hydrogen nuclei held together by two cementing electrons. Baly, then, refers to our preparation of the true H_3 as demonstrating the existence of Harkins' iso-hydrogen and thus confirming the correctness of Harkins' fascinating hypotheses of the nuclear structure of atoms.

¹¹ Franck, Knipping and Krüger, *Verh. Deut. Physik. Ges.*, **21**, 728 (1919).

¹² Baly, "Annual Reports of the Progress of Chemistry," Chemical Society, London, 1920.

¹³ Harkins, *Phys. Rev.*, **15**, 73 (1920).

To this view we cannot subscribe. More proof is needed before the actual preparation of one atomic species from another is demonstrated, especially before we can believe that a heavier nucleus has been built up from lighter ones. But *a priori* nothing should be judged impossible, and it is well to review the evidence.

There are, in fact, only two sound arguments against such an interpretation. One is the almost insuperable one that very large amounts of energy should be required to condense 3 positive nuclei and 2 negative electrons into one dense and coherent nucleus; in such gentle methods of preparation as the use of the hot wire, for instance, such amounts of energy were certainly not available. The second is that the iso-hydrogen should in the gaseous state have a diatomic molecule and hence a molecular weight of 6. But positive ray spectrographs fail to show any trace of molecules of such weight.

On the other hand, numerous facts established are wholly compatible with the assumption that iso-hydrogen is present. The high reactivity of the new gas might be thought to exclude iso-hydrogen, since isotopes have been in all cases shown to be chemically inseparable and identical. This may be true, however, for differences of a few units in an atomic weight of 208, as in the case of lead, and yet not pertain to a tripling of the atomic weight as would be the case here. Furthermore, if there were a difference, the iso-hydrogen should be more reactive than the ordinary form. Its nucleus is complex and contains two negative electrons; the net positive charge of one cannot be as concentrated as it is in hydrogen itself, and might therefore hold the planetary electron less firmly than does the single positive nucleus. The fact of increased reactivity is, therefore, not wholly incompatible with Baly's interpretation. Neither does the spectral evidence exclude the latter. The spectrum of iso-hydrogen may well be more complex than the usual one, although the marked change from the simple line spectrum to the highly complex and extended secondary spectrum observed is not to be expected. A coincidence of the spectrum of iso-hydrogen with that of the hypothetical nebular element nebulium is rather more probable. Finally, the observed contraction in volume is also no criterion, since the formation of iso-hydrogen would result in a marked contraction by the reaction $3\text{H}_2 = \text{Iso-H}_2$. The volume would thus be reduced to one-third. A quantitative study of the contraction would therefore furnish a critical test, but no technique for it has yet been developed.

There remain two facts which favor the iso-hydrogen interpretation. The first is inconclusive, namely, the fact that we were unable to obtain evidence for transitory activity in the hydrogen collected from electrolysis or the solution of metals in acid. No activity would be expected in case we have been dealing with iso-hydrogen, for the mere contact of single atoms

of nascent hydrogen would certainly not suffice to combine them into new atomic species. But, as stated above, this negative evidence is open to question. We come at last to the high boiling point of the new hydrogen. This is certainly above the boiling point of liquid oxygen, and therefore at least 70° above the boiling point of hydrogen itself. The difference in boiling points of oxygen and ozone is only 62° . On the absolute scale the boiling points of oxygen and ozone are 90° and 152° , while those of hydrogen and of hyzone are 20° and above 90° . This is an unexpectedly large difference, especially since the boiling point of hyzone may be far above 90° , though not higher than 190° . On the other hand, it would not be so strange, perhaps, if iso-hydrogen had a relatively high boiling point and low vapor pressure, since its molecule is three times as heavy as that of ordinary hydrogen.

In view of this evidence, then, it is preferable to assume the formation of triatomic molecules, and to consider atomic transmutation as yet un-effected.

Summary

1. Triatomic hydrogen has now been prepared by three new methods: the Siemens glass tube ozonizer, the high frequency Tesla discharge, and thermionic emission. Attempts to show its presence in hydrogen produced as nascent hydrogen from solutions of hydrogen ions were unsuccessful.

2. This hydrogen is catalytically decomposed by finely divided platinum, nickel, copper, lead, antimony and cadmium. It is not affected by contact with silver, mercury, tin, bismuth, molybdenum, zinc or aluminum.

3. Contraction in volume occurs when this hydrogen is produced by the electrical discharge at a pressure of 3 cm. This is particularly marked at the temperatures of liquid ammonia and of solid carbon dioxide.

4. This hydrogen is condensed to the liquid form by exposure to the temperature of liquid oxygen.

5. The spectrum of hydrogen at the temperature of liquid oxygen shows a progressive intensification of the secondary line spectrum at the expense of the primary series spectrum, which is probably due to the gradual formation of this triatomic form.

6. The effect of this work and that of others is held to confirm the mechanism of formation previously advanced.

7. The formula of the new gas is probably H_3 , and not iso- H_2 , an atomic species proposed by Harkins as a constituent of heavier atoms.

8. We gratefully acknowledge our indebtedness to the Bureau of Engineering, U. S. Navy Department for the gift of a cylinder of helium gas;

to the Director of the Ryerson Physical Laboratory of the University of Chicago for the use of indispensable apparatus and instruments; and especially to E. I. DuPont de Nemours and Co. for the establishment of a research fellowship under the tenancy of which by one of us much of this work was done.

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CLAY AS AN AMPHOLYTE

BY OLOF ARRHENIUS

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Most soil scientists know that alkali soils during filtration cause serious troubles, because the extract is grayish or turbid. Furthermore, it is a well known fact that alkali stabilizes, whereas acid peptizes the soil suspensions.

The rate of settling of soil suspensions plays a great role in mechanical soil analysis, and there has been much discussion on this subject, such as that between Rohland¹ and Maschhaupt,² in which the divergences were great and both were right. Rohland points out that the same addition of alkali or acid does not cause the same effect in suspensions of different soils and Maschhaupt finds that alkali first stabilizes and then suddenly peptizes the suspensions.

It is very probable that the actual acidity of the suspension, the hydrogen-ion concentration, plays the greatest role, rather than the amount of acid or alkali added. From this point of view it is not astonishing that the authors mentioned above and several others have not been able to find a satisfactory explanation. The conception of the soil as a buffer is a rather recent one,^{3,4} but only when one assumes this buffer action is one able to understand why some soils change their reaction markedly and others not at all when the same amount of acid is added to each.

In order to ascertain the influence of the hydrogen-ion concentration and compare it with that of the amounts of alkali and acid added, the following experiment was carried out.

Two clay soils, one used for brick-making, with a Sørensen value (P_H) of 7.5 and another, a peaty clay with a Sørensen value of 5.0, were used for making up the suspensions. Two hundred and fifty cc. portions of each suspension (100 g. of clay in 5 liters of water) were placed in glass cylinders; alkali or acid was then added and the different lots filled up to the same volume, 350 cc. The suspensions were then shaken and left

¹ Rohland, *Landw. Vers. Sta.*, 1914, 85.

² Maschhaupt, *ibid.*, 1914, 83.

³ Bjerrum, *Landbo og Veterinaerhøisk. Aarskr.*, 1917.

⁴ Arrhenius, *Soil Science*, 1922.