equal to 0.44369, while Baxter[1] obtained 0.44367, for the same ratio. Combining the average of these two ratios, 0.44368, with the value here obtained for bromine we get 79.3066 × 0.44368 = 35.186(7) for the hydrogen chlorine ratio. The value obtained by Noyes and Weber was 35.184. Dixon and Edgar obtained 35.195[2] and Edgar in the second series obtained 35.193.[3]

Taking the atomic weight of hydrogen as 1.00779[4] the value for bromine on the oxygen basis becomes 79.924 as against the value 79.920 given by the International Commission for 1912.

WASHINGTON, D. C.

A CHEMICALLY ACTIVE MODIFICATION OF HYDROGEN.[5]

BY IRVING LANGMUIR.

Received August 8, 1912.

During the life of a tungsten lamp the vacuum gradually improves.[6] This "clean-up" of gas is often of electrical nature and depends, to a very marked degree, on the voltage across the terminals of the filament, as well as on the temperature of the latter. In making a careful study of the nature of this clean-up with various gases, some points have been observed that seem to be of sufficient general interest to warrant their publication.

The present paper will deal with some observations made in experiments on the clean-up of hydrogen.

"Clean-up" of Hydrogen.

When a tungsten wire is heated to a temperature between 1300° K and 2500° K in hydrogen at very low pressure (0.001 to 0.01 mm.) the hydrogen slowly disappears. The rate of disappearance depends on many factors and varies widely according to conditions, ranging from 0.002 to 0.20 cu. mm. of hydrogen (at 1 atm.) per minute per micron (0.001 mm.) of initial pressure.

Apparatus.—The apparatus used in the experiments which furnished the following data consisted essentially of a Töpler pump, McLeod gage, and U-tube dipping in liquid air separating the pump and gage from the lamp being exhausted. The apparatus was so designed that the gases delivered by the pump could be collected over mercury and mixed with either oxygen or hydrogen and brought in contact with a glowing platinum wire and returned to the vacuum system without coming into contact

---

[1] Richards, *Atomgewichte*, p. 825 (1909).

[2] *Phil. Trans.*, **205A**, 169 (1905).

[3] *Proc. Roy. Soc.*, **81A**, 216 (1908).

[4] Clarke, "Recalculation of Atomic Weights," p. 41 (1910).

[5] Paper read at the Washington meeting of the American Chemical Society, December, 1911. Abstract appeared in *Science*, **35**, 428 (1912).

[6] W. R. Whitney, *Proc. Am. Inst. Elec. Eng.*, **31**, 921 (1912).

with any stopcocks or any substance other than glass, mercury or platinum. With this apparatus we are able to make quantitative analyses of amounts of gas as small as 1 cu. mm., determining the following constituents: H_2O, CO_2, CO, H_2, O_2 and N_2 (the latter by difference). The errors of the analyses are less than 5% with 1 cu. mm. of gas and much less when larger quantities are used. Each lamp experimented with was exhausted and then heated for an hour or more to a temperature from 360 to 500° C., in order to drive out as much as possible of the moisture from the surface of the glass.

Effect of Temperature of the Wire.—As a general rule, the clean-up was the more rapid the higher the temperature of the wire, but the temperature coefficient was very much less than that of an ordinary chemical reaction. The effect was often quite marked when the wire was at a temperature as low as 1300° K. This is in strong contrast to the effects observed in nitrogen, for with this gas the "clean-up" does not begin to appear until the temperature is 2200° K or above, and then increases extremely rapidly with the temperature, or more especially with the voltage. As an example of the way the rate of clean-up of hydrogen depends on the temperature, the results given in Table I may be of interest.

TABLE I.—RELATION BETWEEN TEMPERATURE OF WIRE AND RATE OF "CLEAN-UP."

Approx. temp.	Duration of run, Min.	Initial pressure, microns.	Average rate of "clean-up" cu. mm. per min.
1300°	15	16.1	0.21
1500	10	14.3	0.29
1800	10	12.3	0.37
2300	10	18.9	0.78
2400	10	14.2	0.36
2600	10	12.0	0.34
2400	10	15.8	0.35
2300	10	20.5	0.31
1800	10	11.3	0.08
1500	10	16.5	0.04
1300	10	16.2	0.01

Fatigue Effect.—The rate of clean-up gradually becomes less and less. This is clearly illustrated in Table I, where the rates with the descending temperatures are seen to be much lower than at the same temperature ascending. In other cases a long continued treatment of the wire in hydrogen has brought the clean-up practically to a standstill.

This fatigue effect is not due to any change in the wire. If, for example, two sections of wire be placed in a lamp and furnished with separate electrical connections, and one of these sections be heated until the clean-up has ceased, then it is found that changing over to the other section of filament never restores the effect.

Effect of Voltage and Polarity.—At any given temperature of the wire the voltage taken by the filaments seems to be without influence on the rate of clean-up. This is very different from the effects observed with nitrogen at 2200° or above. The direction of the current is also without influence.

Temperature of Bulb.—The bulb temperature was varied between —193° C. (liquid air) and +360°, but no very marked effect on the rate of clean-up was observed. There is some evidence that the clean-up is slightly more rapid when the bulb is hot than when it is cold. These tests were made only while liquid air surrounded the U-tube between the lamp and the pump.

Clean-up of Methane.—When a tungsten filament is heated in methane at low pressure the carbon is taken up by the wire, as proved by the increase in the resistance and the decrease in the temperature coefficient of the resistance. In some cases the pressure increases to nearly double its original value, as is to be expected from the equation

$$CH_4 = C + 2H_2.$$

But under other conditions the volume actually decreases. This is due to the clean-up of hydrogen as observed with pure hydrogen.

Attempts to Recover the Hydrogen.—By pumping out what hydrogen remains and heating the filament at a very low or a very high temperature, no hydrogen is recovered. In one case, after about 35 cu. mm. of hydrogen had been made to disappear, 4 cu. mm. were recovered by heating the bulb to 115° and simultaneously heating the filament.

Other phenomena observed in connection with the clean-up of hydrogen throw a great deal of light upon the fate of the cleaned up gas. These will now be described.

Non-recondensable Gas.

"NR Gas."

If, after a considerable quantity of hydrogen has been made to disappear, the wire is allowed to cool and the liquid air is removed from the U-tube, a certain amount of gas (1–7 cu. mm.) will be set free. If, now, the liquid air be replaced little, if any, of this gas will be recondensed. Gas obtained in this way and having these properties we have called NR gas. Carbon dioxide, which is given off in small amount from the surface of the glass when first heated, is condensed by liquid air completely and is liberated almost instantly when the liquid air is removed, but of course it condenses again when the U-tube is dipped in liquid air. This makes it impossible to mistake NR gas for carbon dioxide. The formation of NR gas has never been observed except after heating a wire for a considerable time in a gas containing hydrogen.

In attempting to analyze this NR gas some remarkable phenomena were observed. The usual method of analysis of gases was as follows: The gas was pumped over into a small bulb of about 1 cc. capacity, which contained a short piece (2 mm.) of very fine platinum wire. This wire was then brought to a dull red heat for a couple of minutes and the gas was then allowed to return to the system and readings were taken on the McLeod gage to determin if there had been any contraction. Such contraction would denote the presence of oxygen together with carbon monoxide or hydrogen. The carbon dioxide or water vapor produced by such a combination would be condensed by the liquid air. Then a measured excess of pure oxygen was admitted and the reading again taken on the gage. In any ordinary analysis the amount of gas calculated from the increase in pressure indicated by the gage would agree closely with the measurement of the volume of oxygen made before admitting it to the system. The mixture of oxygen with the sample of gas was now again pumped over into the small ignition bulb and the wire brought to a red heat. After allowing the gas to again return to the system and permitting the liquid air to condense the carbon dioxide or water vapor formed, the gage was again read. Two-thirds of the contraction gave the amount of hydrogen plus carbon monoxide. By replacing the liquid air by solid carbon dioxide in acetone, the carbon dioxide in the system was liberated, while the water vapor was held back. From this increase in pressure the amount of carbon dioxide could be calculated and from this was found the carbon monoxide originally present. As the sum of the hydrogen and carbon monoxide was known, the amount of hydrogen could now be calculated.

This method of analysis had proved extremely reliable and satisfactory for all gases liberated within the bulbs of lamps *except* after the filament had been heated in the bulb for a long time in *presence of a gas containing hydrogen.* Our first real difficulty arose when we attempted to analyze some NR gas. The following is a typical example of what then happened.

In one experiment, after a long extended series of treatments of the filament in methane, water vapor, hydrogen and vacuum, a very large quantity of NR gas was obtained when the liquid air was removed and then replaced. The actual quantity was 7.3 cu. mm. Only a very slight contraction took place when this gas was brought into contact with the glowing wire in the ignition bulb. A measured volume of 9.6 cu. mm. of oxygen was then admitted to the system. This should have given a total volume of $7.3 + 9.6 = 16.9$ cu. mm. of gas in the system, but actually only 9.6 cu. mm. was found. Thus there had been a disappearance of 7.3 cu. mm. of gas. A fresh portion of 11.4 cu. mm. of oxygen was admitted, but this only caused an increase in the amount of gas from 9.6 to 9.7 cu. mm. A third addition of 25.3 cu. mm. of oxygen finally increased the volume to 32.7 cu. mm., only 2.5 cu. mm. less than if no further contraction had taken place. Thus the total amount of oxygen which had been added was 46.3 cu. mm., but this caused an increase of volume of only 25.4. In other words, 20.9 cu. mm. of gas, presumably oxygen, had disappeared, although the whole system was at room temperature (except the liquid air tube). It must be emphasized that nearly two years' experience in working with this apparatus has shown that nothing of this sort ever occurs except after the wire has been heated for some time in gases containing hydrogen.

The gas mixture which now undoubtedly contained an excess of oxygen was pumped over into the ignition bulb and ignited. Upon allowing it to return, the contraction was found to be 20.5 cu. mm. Two-thirds of this (13.7 cu. mm.) gives the hydrogen present in the mixture, no carbon dioxide being found by substituting solid carbon dioxide for the liquid air. It will be noted that the amount of hydrogen found is nearly double the amount of NR gas originally present.

Disappearance of Oxygen.

It was found that this disappearance of oxygen was not caused by the NR gas, for if the latter were pumped out before the oxygen was admitted the same phenomenon would be observed. In this case, after enough oxygen had been added so that it ceased disappearing, an analysis showed the presence of several cu. mm. of hydrogen; that is, the oxygen not only disappeared but was partially replaced by hydrogen.

In order to make sure that the disappearance of oxygen was not caused by the oxidation of very finely divided tungsten on the bulb, the following experiments were made: The filament of a lamp was heated to a temperature of about 3000° K. in a good vacuum until the bulb was nearly black. After cooling the filament oxygen was admitted, but no contraction could be observed. Another time the bulb was blackened in a similar way in a good vacuum and a mixture of oxygen and hydrogen was then admitted, but here too no contraction could be detected, showing that the tungsten deposit did not act catalytically on the reaction between oxygen and hydrogen.

In some experiments the lamp and liquid air tube were sealed off by a mercury seal from the rest of the system, just before admitting oxygen to the latter. Little or no contraction occurred in these cases, but on opening the seal and allowing the mixture to enter the lamp the contraction took place.

The presence of liquid air around the U-tube was not necessary for the production of these phenomena. In one case no liquid air was used on any part of the system, and yet the heated filament caused a disappearance of hydrogen and subsequently, on admitting oxygen, after cooling the filament, the disappearance of a large part of the oxygen was observed.

If, after hydrogen has been made to clean up by heating the filament, the latter is allowed to cool and nitrogen (or hydrogen) be admitted, no contraction in volume occurs like that observed with oxygen.

In some cases, while liquid air still remained on the lamp, oxygen was admitted to a lamp which had been immersed in liquid air during the treatment in hydrogen. The oxygen disappeared extremely slowly under these circumstances, but on *removing the liquid air a rapid contraction* took place.

Probable Explanation of the Phenomena.

The following tentative theory seems to offer a satisfactory explanation of the observed phenomena:

The hydrogen dissolves slightly in the heated tungsten wire and as is usually the case for gases dissolved in metals, it will probably be in the atomic condition. The concentration of the dissolved hydrogen would be proportional to the square root of the pressure, so that the relative solubility at low pressures would be much greater than at atmospheric pressure.

The hydrogen atoms, in diffusing out of the metal, find little opportunity to combine together to form molecules, because of the extremely low pressure. The author has shown[1] that hydrogen at very high temperatures is largely dissociated into atoms. From the formula given the degree of dissociation is calculated to be:

Temperature. ° K.	Per cent dissociation	
	at 760 mm.	at 0.001 mm.
1500	0.00045	0.39
2000	0.13	69.0

Thus over the range of temperature and at the pressures in which the clean-up of hydrogen is observed, the degree of dissociation of hydrogen is quite appreciable. This would indicate that a part of the hydrogen which diffuses out of the metal is in the form of atoms, even after leaving the surface of the metal. At ordinary pressures these atoms would combine in pairs to form hydrogen molecules, but at the pressures with which we are here dealing the normal free path of the molecules is several times the diameter of the lamp bulb, and hence the atoms fly directly from the surface of the wire to the surface of the glass, without having any opportunity to combine. Some of these atoms of hydrogen are held on the surface of the glass by adsorption. Perhaps the unsaturated chemical affinity of the atomic hydrogen gives it unusual tendencies to be adsorbed on surfaces, or possibly it actually forms some unstable chemical compounds with some of the constituents of the glass. Or, again, perhaps some electrical phenomena are involved in the adsorption of the hydrogen. But in any case the experiments indicate that the active substance deposits on the

---

[1] This Journal, 34, 860 (1912).

glass as if by adsorption. Another portion of the hydrogen atoms diffuse out of the lamp bulb into other parts of the system. In the tube cooled by liquid air the adsorption is greater than in the parts of the system at room temperature, so that when the liquid air is removed part of the atomic hydrogen is liberated and immediately forms ordinary molecular hydrogen, which constitutes the NR gas.

The fatigue effect is also readily accounted for by this hypothesis. For example, if after a certain number of hydrogen atoms are adsorbed by the bulb the supply of atomic hydrogen continues, the effect will be that the fresh atoms will combine with ones on the glass and set free ordinary hydrogen. In other words, the glass will be capable of retaining only a very small amount of this atomic hydrogen.

A priori a fatigue effect of this kind might be supposed to be due to a kind of balance between the rate of leakage of hydrogen off the bulb and the rate of deposition on it. In this case one would expect that the hydrogen would leak off the bulb when the current is turned off, at about the same rate as it would be deposited on the fresh bulb. But this is far from being the case. Only in rare instances, after very prolonged treatment, was any evolution of gas from the bulb observed on turning off the current. This fact receives a simple unforced explanation by the above hypothesis.

The atomic hydrogen on the bulb and in the liquid air tube must retain all of the chemical activity that it possessed when dissolved in the metal. In fact, its free energy must be much greater than when dissolved in a metal. It is therefore quite natural that it should be capable of combining directly with oxygen at room temperature, just as it would do if it were dissolved in platinum black. In this way the hypothesis accounts fully for the disappearance of oxygen observed in the experiments.

This theory of the disappearance of oxygen would also account for the observed fact that introducing oxygen into the bulb removes the fatigue effect observed in the clean-up of hydrogen.

The fact that the solubility of hydrogen in metals decreases at high temperatures would furnish a reason for the rate of disappearance of hydrogen not increasing as rapidly with the temperature of the wire as is the case in ordinary chemical reactions.

The observed excess of hydrogen found by analysis after an excess of oxygen had been added would indicate that although the oxygen combines with a part of the active hydrogen on the bulb, it liberates another part of the hydrogen in the molecular form. It may be supposed that the hydrogen atoms are held only very short distances apart on the bulb and that even very slight disturbances will bring them into combination.

Test of the Theory.

In order to test the validity of the above theory and to obtain these effects on a larger scale, several changes were made in the conditions of the experiments.

Effect of Cooling the Bulb by Liquid Air.—It was thought that by cutting down the distance from the heated wire to the cooled glass surface the amount of clean-up and of NR gas would be increased. A lamp was made in tubular form (Exp. 183), so that it could be completely immersed in liquid air while running. The liquid air U-tube was also retained. The effect of the liquid air was to greatly facilitate the production of NR gas. Without liquid air the average amount of NR gas produced after short treatments in hydrogen was 0.4–0.8 cu. mm. But with liquid air around the bulb the quantities under similar conditions were 1.7–2.0 cu. mm.

Platinum Wire Filament (*Exp. 186*).—Presumably the solubility of hydrogen in platinum is greater than in tungsten and it was therefore expected that with filaments of this material, the production of NR gas would be more rapid. As before, a tubular bulb immersed in liquid air was used.

With the wire at 1700° K. the rate of clean-up was only slightly greater than with tungsten, but the rate at which NR gas could be produced was about double that obtained with the tungsten filament under similar conditions. In other respects the phenomena with the platinum wire were exactly like those with the tungsten.

Palladium Wire Filament (*Exp. 188*).—A palladium wire lamp was made similar to the platinum wire lamp, and tested in like manner, with the wire at about 1400–1500° K. The average rate of disappearance of hydrogen was about 3 times that with a tungsten wire and the rate of production of NR gas was about 10 times as great as with tungsten. With this lamp the largest amount of NR gas ever produced was obtained, namely 9.4 cu. mm. The treatment in hydrogen preceding this evolution of NR gas lasted only 20 minutes, whereas with tungsten lamps only in one case was more than 2 cu. mm. of NR gas ever obtained. In this exceptional case, 7.3 cu. mm. were produced, but only after treatment in methane, water vapor, and hydrogen extending over many days.

With palladium it was expected that the absorption of hydrogen by the metal and its catalytic effect on the reaction between oxygen and hydrogen would be very marked, but this was not found to be the case. In the early part of the experiment the filament had been heated to about 1550° K. for a short time and this had caused a considerable amount of palladium to volatilize and deposit on the bulb, producing very distinct blackening. Yet even with this very large surface of palladium exposed, the absorption of hydrogen and disappearance of oxygen without previous heating of the filament were not nearly so marked as with the ordinary heated tungsten filament. In order to try to produce effects similar to those observed with tungsten lamps, but without heating the filament, the following experiments were made with the palladium lamp:

The lamp which contained a good vacuum was heated in the oven to about 350° to expel any gases that might have been absorbed by the bulb during previous work. Only a very little gas was evolved during this heating. The lamp was then cooled to 220° and exhausted to a good vacuum, after which, and while the bulb was still at 220°, hydrogen at *atmospheric pressure* was admitted. The lamp was next cooled to room temperature and then immersed in liquid air. Liquid air was also on the condensing tube underneath the lamp during the entire experiment. With the bulb cooled by liquid air, the hydrogen was then all pumped out.

The liquid air was then removed from the bulb of the lamp, with the expectation of a consequent evolution of hydrogen (NR gas). The evolution took place, but very slowly, amounting in about 30 minutes to 1.25 cu. mm. By the following morning it had increased to about 6 cu. mm. This was mixed with oxygen and ignited and the resulting contraction indicated it to be almost entirely hydrogen, but it was also NR gas, for when it was first produced by removing the liquid air from the lamp bulb, there still remained liquid air on the condensing tube, and yet the gas would not recondense.

Moreover, liquid air was replaced upon the lamp bulb about 7 minutes after its removal and this not only failed to cause a contraction, but did not even stop the evolution, and after a few minutes it was again removed, the gas continuing to come off during the night as already stated.

After the ignition test had been made, the liquid air was removed from the condensing tube, but no additional evolution resulted.

There was a considerable disappearance of the oxygen which was admitted, when mixed with the gas, and before the ignition took place, but no accurate measurement of this was made. After pumping out the residual gases, however, careful tests for additional disappearance of oxygen admitted to the exhausted lamp were made. With liquid air on the bulb, the disappearance was slight, about 1.5%, but with no liquid air on the bulb it amounted to 12%.

The disappearance was slow, only one-half taking place in the first 37 minutes. In a second trial for the production of NR gas without treating the filament and following the method already described, the amount of NR gas evolved upon removing the liquid air from the bulb was 6.6 cu. mm.

After pumping out this gas, 8.8 cu. mm. of oxygen was admitted to

TABLE II.

I. Experiment.	II. Treatment in H_2, min.	III. Disappearance of H_2, cu. mm.	IV. NR gas, cu. mm.	V. Apparent disappearance of O_2, cu. mm.	VI. H_2 by analysis, cu. mm.	VII. Calc. recovery of H_2, cu. mm.	VIII. Per cent recovery.	Remarks.
160	several days	greater than 45	7.3	20.9	13.7	68.0	?	Bulb at 20° C.
183	89	5.5	1.77	0.71	2.13	4.27	78.0	Bulb in liquid air
	49	8.0	1.75	0.84	2.03	4.27	53.0	
	54	7.3	2.02	0.49	2.33	3.93	54.0	
	51	4.1	1.61	0.74	1.72	3.42	83.0	
	74	5.0	1.91	1.07	2.77	6.6	120.0	
186	94	5.7	2.23	0.62	2.27	3.59	63.0	Platinum filament; bulb in liquid air
188	20	10.2	9.4	2.46	7.8	?	?	Palladium filament; bulb in liquid air
	25	8.0	6.7	2.13	7.6	13.4	168.0	

the system with liquid air on the lamp bulb. In 11 minutes, the volume was 8.5 cu. mm., showing a disappearance of only 0.3 cu. mm. of the oxygen.

Upon removing the liquid air from the lamp bulb the volume shrank to 7.5 cu. mm. in 23 minutes. After 19½ hours more the volume had contracted to 6.6 cu. mm. and after remaining for an additional 44 hours there were only 4.7 cu. mm. of gas remaining, or a total disappearance of 4.1 cu. mm. after removing the liquid air from the lamp bulb.

Direct tests were made to determin whether the palladium deposit on the bulb would cause the combination of a mixture of hydrogen and oxygen at a few microns pressure. The results showed that with the bulb at room temperature the rate of reaction was so slow that it could not be measured with certainty. And with the bulb cooled in liquid air there was no indication of such a combination occurring.

These experiments demonstrate conclusively that the ordinary effects observed when heating the filament in hydrogen are in no way connected with any metallic deposit on the bulb.

A summary of a few of the results of Experiments 160, 183, 186, and 188 is given in Table II. Column 2 gives the time of treatment in hydrogen; Column 3 gives the amount of hydrogen which disappeared.

Recovery of the Hydrogen.—According to our theory the hydrogen which disappears during contact with the hot filament is driven to the bulb. Part of this escapes as NR gas, part combines with the oxygen and part is liberated as ordinary hydrogen during the disappearance of the oxygen. The question how nearly these portions add up to the original amount of hydrogen which disappeared is answered by columns 7 and 8 of Table II.

The amount of hydrogen liberated from the glass during the disappearance of oxygen is equal to the difference between the amount of hydrogen found by analysis and the amount of NR gas. Call this difference x and call the apparent disappearance of oxygen y. Then the true "disappearance of oxygen" is equal to $x + y$. The amount of hydrogen on the bulb which combines with the oxygen is then $2\ (x + y)$. The total amount of hydrogen accounted for is therefore the NR gas $+\ 2(x + y) + x$. This "calculated recovery" has been tabulated in column 7, Table II. In column 8 is given the ratio between this and the "disappearance of hydrogen." It will be seen that it is nearly always less than 100%, but is of the same order of magnitude. We can therefore conclude that it is only a small portion of the hydrogen that cannot be recovered by the action of oxygen. The experiments have shown oxygen to be much more effective in liberating the hydrogen than heat applied to the bulb. Even by heating the bulb to 360° C. only a very small part of the hydrogen can be recovered.

The water vapor produced by the action of oxygen on the active hydrogen on the bulb is in much too small quantity to be detected, or to have any appreciably effect on the vacuum. It simply remains adsorbed by the glass or condenses in the liquid-air tube.

Effect of Pressure.—Several attempts were made to increase the yield of NR gas by using higher pressures of hydrogen. At a pressure of 104 mm. of mercury no perceptible clean-up could be observed. After a 15-minute run at this pressure with the bulb immersed in liquid air the hydrogen was pumped out and the liquid air removed from the bulb for a time and then replaced. Only 0.6 cu. mm. of NR gas was obtained.

A series of experiments was made at lower pressure than usual, with the following results:

TABLE III.

Time of treatment.	Initial pressure, microns.	Clean-up	
		from cu. mm.	to cu. mm.
5	0.40	1.14	0.15
5	0.35	0.95	0.39
13	0.45	1.30	0.42
17	0.86	2.48	1.34
12	0.49	1.42	0.92
	NR gas obtained	0.89 cu. mm.	

The results indicate that the best pressure for the observation of these various effects is from 1 to 20 microns and that nothing is to be gained by using higher pressures. This again is in agreement with the theory, for higher pressures would not only decrease the mean free path and so make it difficult for the atomic hydrogen to reach the bulb without recombination, but would also decrease the relative amount of dissociation of the gas diffusing out of the filament.

Experiments with Phosphine.

In September, 1910, we made some experiments to determin the effect of introducing phosphine into a lamp bulb while the filament is heated. The results were in many ways remarkable and seemed at that time inexplicable. At present, however, the results then obtained seem to fit in so well with our more recent experience with active hydrogen that they demonstrate the usefulness of the present theory. As they are also of interest on their own account a description of these experiments will now be given.

The experiment of most interest (Exp. 120) was made with a lamp containing three sections of tungsten wire, 0.0012 inch diameter, each section being 19.9 cm. long. This was sealed onto a system consisting of Töpler pump, McLeod gage and "appendix" separated from the system by a mercury seal. This appendix could be immersed in liquid air and served for the removal of moisture and carbon dioxide. For experimental work we find this much more convenient and simple than phosphorus pentoxide. As we wish to measure gas volumes we avoid the use of charcoal or anything that might cause adsorption of gases. Even at liquid air temperatures the adsorption of nitrogen, oxygen and such gases by dry glass is negligibly small.

In the above vacuum system there was also a U-tube directly below the lamp which separated the lamp from the rest of the apparatus and which, during most of the experiment, was kept immersed in liquid air. The total volume of the system was about 800 cc., so the amount of gas in cu. mm. is numerically very nearly equal to the pressure in microns.

The lamp was exhausted at 360° C. for 90 minutes to about 0.1 micron. The filament was heated 5 seconds to 1770° K., which caused the evolution of 3.3 cu. mm. of gas, mostly carbon monoxide. All but 0.4 cu. mm. of this compound was pumped out. All three sections were then run in series for 15 minutes at 2300° K. The quantity of gas in the system decreased from 0.4 to 0.05 cu. mm., this being the ordinary (apparently) electrical clean-up usually observed with the filament at very high temperatures. After allowing the filament to cool, a quantity of 2 or 3 cc. of phosphine was admitted to the system. The liquid air under the lamp condensed this and the impurities were pumped out. The pressure soon reached a constant value of 3.4 microns, or more accurately, on different days, different pressures, ranging from 2.5 to 3.5 microns, were obtained, according to the freshness of the liquid air. The true vapor pressure must be less than this, in the ratio of the square roots of the absolute temperatures of liquid air and the McLeod gage. Hence at —185° C. the vapor tension of PH_3 is 1.9 microns.

The above mentioned rule that the pressure in various parts of any vacuum system (with pressure less than 5 or 10 microns) is proportional to the square roots of the absolute temperatures of the various parts, was discovered in this laboratory in September, 1909, and has since received ample verification. Knudson[1] has fully described this phenomenon and given the explanation of it, but apparently it is not yet as well known as it should be.

During the remainder of this entire experiment the phosphine remained condensed in the U-tube and continued to give a constant pressure of about 3.4 microns of PH_3.

Section A was first heated to 1240° K. There was a steady evolution of gas, so that in 13 minutes the quantity of gas had increased from 3 to 78 cu. mm. This is exactly what was expected. It is well known that PH_3 is easily decomposed by heat (above 400° C.) producing hydrogen and phosphorus vapor. Since PH_3 is a distinctly exothermic compound (molecular heat of formation, 11,600 g.-calories) the degree of dissociation would constantly increase with rising temperature, so that,

---

[1] *Ann. Phys.*, 31, 205 (1910).

as the dissociation is apparently complete at 400° C., we should never expect this substance to form at higher temperatures, especially at low pressures. We should then expect the filament at 1240° K. to dissociate the gas into its elements; the phosphorus condenses on the bulb, and the hydrogen accumulates and causes the observed increase in pressure.

This hydrogen was pumped out and section B was heated to 2020° K. for 19 minutes. During this time the amount of gas increased more slowly than before for the first 4 minutes, and then remained constant during the next 15 minutes. The total increase in volume was only from 3 to 17 cu. mm.

A third run with the filament C at 2670° gave a result similar to the last, except that increase in volume was only 3 to 12.

These results seemed remarkable, for it seemed thermodynamically necessary that the dissociation of PH_3 should occur at the higher temperatures at least as well as at lower temperatures. Yet the experiment indicated that the action was incomplete and seemed to reach some sort of equilibrium. To test this out, Section A was next run at 1240° again, with exactly the same result as before; that is, a continuous and rapid evolution of gas. Then instead of pumping this gas out, Section B was lighted to 2020° K. in it. The result was very striking. The amount of gas decreased in 9 minutes from 76 to 31 cu. mm. and then remained practically constant. Section A was now lighted to 1240 and the volume steadily increased in 16 minutes from 31 to 96 cu. mm. Upon raising the temperature to 2020° the gas immediately began to decrease and in 10 minutes dropped from 96 to 39 cu. mm.

We have here very clear evidence of a disappearance of very large quantities of hydrogen, and the natural assumption is that it recombines with the phosphorus to form PH_3, which then condenses again in the U-tube. But at the time the experiments were made, no satisfactory explanation of this probable synthesis of PH_3 was thought of.

We tried the effect of heating the bulb to 160° C. The only effect was to prevent the disappearance of such large quantities of gas. For example, with the bulb cold and the filament at 2020°, the amount of gas decreased from 96 to 39, while under similar conditions, with the bulb at 160° C., the gas decreased only from 95 to 61. But the *rate* of disappearance, while it lasted, was very closely the same in the two cases.

During these experiments the tungsten filament was not perceptibly altered in any way. The phosphorus was not absorbed, as was proved by the resistance of the wire remaining constant. No difference could be observed between the action of different sections of filament. No fatigue effect, such as would have been found with ordinary hydrogen, could be detected in these experiments.

At present all these facts seem to receive a simple explanation in the light of our theory of the atomic hydrogen. In outline the explanation is as follows:

At 1240° the PH_3 decomposes practically as rapidly as it comes in contact with the filament, the hydrogen accumulates indefinitely, while the phosphorus deposits on the bulb as yellow phosphorus (it could easily be seen).

When a filament at higher temperature, say 2020°, is heated in PH_3, the gas is dissociated, as before, by coming into contact with the filament. The hydrogen formed, however, is very largely dissociated into atoms. These leave the filament and come in contact either with the phosphorus on the bulb or with phosphorus vapor in the space around the filament. In either case the hydrogen atoms, because of their much greater free energy than ordinary hydrogen, combine at once with the phosphorus to reproduce the PH_3. If we start out with a large excess of hydrogen the latter will rapidly disappear, whereas if we start at a low pressure, hydrogen will rapidly accumulate until it disappears at the same rate at which it is produced.

By raising the temperature of the bulb to 160° C. the phosphorus vapor rapidly diffuses out of the lamp bulb into the cooled U-tube and hence not enough remains in the lamp to combine with all the hydrogen present. But as long as the phosphorus does last, it allows the hydrogen to disappear at the same rate, as if the temperature of the bulb were lower. The rate in either case would be determined simply by the rate of dissociation of the hydrogen.

The reason for the lack of any fatigue effect is also clear from this theory, for the phosphorus combines with the active hydrogen as fast as it is formed and it ceases to be a question as to the capacity of the bulb to retain it. For the same reason, the amounts of hydrogen which disappear in this experiment are very much greater than is ever observed with hydrogen alone.

As far as I have been able to determin, the above experiments are the first which have led to a direct synthesis of PH_3 from its elements.

Miscellaneous Observations.

Mixtures of hydrogen and nitrogen were tried, with the idea that perhaps the active hydrogen would combine with the nitrogen to form ammonia. But in every case the hydrogen would disappear and leave the nitrogen without change.

The active hydrogen seems to be able to remain on glass several days without losing its activity.

On the other hand, after a very long treatment of the filament in gases containing hydrogen the U-tube dipped in liquid air becomes so saturated that it gradually gives it up spontaneously. This is apparent if the attempt is made to exhaust the system to a very high vacuum. Great difficulty is experienced and there appears to be a slight leak, but if the liquid air is removed and shortly afterwards replaced, this difficulty at once disappears and the system can then be exhausted to a very high vacuum with ease.

Summary.

1. When a tungsten wire is heated to a temperature between 1300° and 2500° K. in hydrogen at very low pressure (0.001–0.020 mm.) the H_2 slowly disappears.
2. With N_2 or CO such disappearance never occurs below about 2200° K. and seems to be an electrical effect, while with H_2 it seems purely thermal.
3. There is a distinct fatigue effect, but the substitution of a new section of wire does not restore the action.
4. The H_2 is not absorbed by the wire, but is deposited on the glass, especially where the latter is cooled by liquid air. If the wire is allowed to cool and the liquid air is then removed, ordinary H_2 is set free which will not recondense when the liquid air is replaced.
5. If this gas is pumped out and oxygen is admitted, the oxygen will disappear and in its place a small quantity of hydrogen will appear.
6. With platinum and especially with palladium wires these effects are much more marked.
7. These effects are not due to the presence of finely divided metal on the surface of the glass.
8. When phosphorus is present on the bulb and H_2 is introduced and the wire heated, the H_2 disappears and PH_3 is formed (apparently the first direct synthesis of PH_3).
9. These effects are accounted for by the theory that the H_2 dissolves in the material of the wire in the atomic condition and that some of these atoms, leaving the wire, do not meet other atoms (because of the low pressure), but diffuse into the tube cooled by liquid air or become adsorbed by the glass, and thus remain in the atomic condition, retaining all of the chemical activity of the atoms.

The author wishes to express his appreciation of the careful work of Mr. S. P. Sweetser, who has carried out most of the experimental part of this investigation.

Research Laboratory, General Electric Company,
July 27, 1912.

RESEARCHES UPON THE COMPLEXITY OF TELLURIUM.

By William R. Flint.

Received August 21, 1912.

In continuation of the research upon the tellurium problem,[1] the following experiments have been carried out:

---

[1] *Am. J. Sci.*, **28,** 112, 347; **30,** 209.