VOL. XXXV. AUGUST, 1913. No. 8

THE JOURNAL

OF THE

American Chemical Society

THE ABSORPTION OF ACTIVE HYDROGEN BY PLATINUM.

BY A. E. FREEMAN.

Received May 5, 1913.

The purpose of this paper is to describe an experiment which seems to give additional support to the conclusion drawn by Dr. Langmuir of this laboratory, that there is present in incandescent lamps hydrogen in the atomic condition.[1] It is a well-known fact that some water vapor is always present even in the best exhausted lamps. This water vapor is decomposed by the hot filament and thus is the source of hydrogen in the lamp.

Several phenomena have occurred while using a Hale-Pirani vacuum manometer,[2] the explanation of which seemed difficult. As described in Dr. Hale's paper, this manometer consists of platinum wire, 1.1 mils in diameter, mounted on glass supports and sealed in a thin-walled, glass bulb. When in use, a constant currrent of about 0.00925 amp., taken from a special storage battery, is sent through the wire, heating it to about 125°. The principle of the manometer is based on the fact that at low pressures the equilibrium temperature of the wire, and therefore its resistance, is a function of the gas pressure.

To calibrate the manometer, the resistance of the wire is taken at various pressures, which pressures are measured by a sensitive, accurate McLeod manometer. Readings are taken at as low a pressure as 0.00002 mm. mercury. Thus a curve (the calibration curve) is obtained giving resistance of the platinum wire in terms of the pressure. This curve is a straight line below 0.0005 mm. By extrapolation, the resistance which the manometer would have at zero pressure can be determined. The difference

[1] THIS JOURNAL, 34, 1310 (1912).

[2] *Trans. Am. Electrochem. Soc.*, 21, 243.

in the conductivities of the various gases would have no effect on this point. This point will be referred to several times later as the zero-pressure resistance. Some minor changes in the construction of the manometer have been made since the publication of Dr. Hale's paper. The wire in each of the manometers used in the following experiments was of one piece and mounted directly on the glass supports. These supports were about 0.5 mm. in diameter. The wires were fastened to the supports by means of carbon paste such as is used in fastening carbon filaments in electric incandescent lamps. This arrangement was tried for long periods of time and found to be satisfactory in every way.

This manometer has been used to measure the pressure in electric incandescent lamps during their lives. As was already known,[1] the Hale-Pirani manometer showed that the pressure in a lamp became less as the lamp was burned.

After burning the lamp, to which a manometer was attached, for about 50 hours, the Hale-Pirani manometer in a number of cases showed a resistance *greater* than the zero-pressure resistance mentioned above. Since the presence of gas *decreases* the resistance, the gage in this case may be said to indicate a negative pressure, sometimes of as much as one-half micron. In spite of the obvious impossibility of negative gas pressures it will be convenient to refer to these abnormal readings of the gage as indicating "negative pressure." In attempting to find the explanation of these negative pressures, all possible external causes, such as loose contacts, etc., were investigated and in every case the effect was due to the filament of the manometer itself. Furthermore, when the manometer was detached from the lamp, thus admitting air, then resealed to the calibrating system and recalibrated, the resistance readings for a particular pressure were the same as the original resistance readings. From this we first thought that the specific resistance of the platinum wire had not changed.

The problem was now to find a source of heat which would raise the temperature of the platinum wire and would thus account for the increase of resistance. As a possible explanation, it was suggested that ions or electrons produced by the glowing filament might diffuse over into the manometer and there be taken up by the platinum wire. As Richardson and others have shown, such absorption of electrons is accompanied by an evolution of heat, so that a heating of the platinum wire might be accounted for. A strong objection to the hypothesis is the improbability that electrons or ions at pressures as low as 0.0001 mm. can diffuse through a length of glass tubing of 20–30 cm. when there are no potential gradients great enough to cause ionization by collision. At such low pressures the normal free paths of molecules and ions would be much greater than the

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

diameter of the connecting tubes, and hence ions would presumably have to make many collisions with the glass in traveling from the lamp to the manometer.

However, to test out this hypothesis a lamp and manometer were connected through a tube containing two parallel aluminum plates maintained at a difference of potential of about 250 volts. This should entirely prevent ions from passing into the manometer, yet it was found that this had no effect on the occurrence of negative pressure. It may, therefore, safely be concluded that the negative pressures are not due to the passage of ions from the lamp to the manometer.

About this time Dr. I. Langmuir suggested his theory concerning the active modification of hydrogen in incandescent lamps, formed from the decomposition of traces of water vapor by the filament. Assuming that there is atomic hydrogen present, it is reasonable to believe that the atoms reaching the platinum filament would recombine there, the heat of recombination being the source of heat causing the abnormal action in the manometer. A few rough calculations showed that there might easily be a sufficient supply of hydrogen in the lamps to account for the phenomena. Dr. Langmuir found that the active modification of hydrogen tended to be adsorbed on the walls of glass tubes, especially at liquid-air temperatures.[1] In view of this it was decided to try the effect of cooling, by liquid-air, a tube connecting an incandescent lamp and a Hale-Pirani manometer. A glass tube between the lamp and manometer was bent into the form of a U and this was immersed in liquid air. The experiments showed that if the U tube connecting the manometer and lamp was at liquid air temperatures before the lamp was lighted, and kept so constantly during the time when the lamp was burning, no "negative pressures" were observed.

In another experiment two manometers were connected to the same lamp, the one through a U tube immersed in liquid air, the other directly. After the lamp had run a day or so, the manometer connected directly to the lamp indicated a "negative pressure," while the one connected through the U tube continually showed a slight positive pressure.

If a plug of glass wool was placed between the manometer and the lamp, we found no "negative pressures." The strong tendency of glass to adsorb active hydrogen would make it probable that a plug of glass wool would prevent the entrance of this substance into the manometer.

It looked, therefore, as if it were the active hydrogen which caused the "negative pressures." There were two phenomena, however, which did not seem to fit in with the hypothesis that the increase in the resistance of the wire was due to the heat liberated by the recombination of hydrogen atoms. The first was that these abnormally high resistances, or "negative

[1] THIS JOURNAL, 34, 1310 (1912).

pressures," would persist for periods of 50 hours after the source of supply of atomic hydrogen was cut off by turning the current off the lamp. The pressure would gradually rise, but we knew from other experiments that gas is given off from the glass when the filament is not glowing. It did not seem likely that a sufficient quantity of active hydrogen could be stored up within the bulb to supply the amount that would be needed to heat the filament for such a time as 50 hours. The second objection to this hypothesis was found in connection with the experiments in which the U tube was cooled by liquid air. If the lamp was allowed to burn for about 50 hours, and the manometer gave negative pressures, then immersing the U tube in liquid air did not cause the pressures to return to the normal. Although liquid air on the U tube would prevent the pressure from becoming "negative," it would not cause a change in a pressure which had already become negative.

In other words, the active hydrogen seemed to produce a permanent effect, presumably by changing the specific resistance of the wire. Yet, as we have already seen, letting air into the apparatus caused the specific resistance to return to its normal value.

These phenomena, together with the others already noted, then led to the theory that the active hydrogen was absorbed by the platinum, and caused an increase in resistance. This hydrogen, being in the atomic condition, oxidized on coming in contact with the oxygen of the air. Thus the platinum would return to its original specific resistance.

As the change was now supposed to be in the specific resistance, some measurements were made to prove this. The temperature of the wire was so greatly affected by even very small currents that it was found impracticable to measure its resistance at the temperature of the thermostat containing the manometer.

According to Delinger[1] the presence of small amounts of impurities in pure metals lowers the temperature coefficient of the resistance in the same ratio as it increases the specific resistance, or, in other words, an impurity increases the resistance at different temperatures by the same amounts.

The temperature coefficient of resistance of the alloy should therefore be smaller than that of the original platinum. The relative variation in resistance would be greater the lower the temperature of the wire in the manometer. In interpreting this change in terms of pressure, it would be still further magnified at lower temperatures, since a change of resistance of 0.1 ohm at high temperatures (140°) would correspond to a change of pressure of 0.00025 mm., while at low temperatures (40°) it would indicate a change in pressure of about 0.001 mm.

In one experiment two resistance readings were taken on the same

[1] *Bull. Bur. Standards*, **7**, 72 (1911).

manometer, one shortly after the other. One reading was taken at a low wire temperature and the other at a higher wire temperature. The manometer had previously been calibrated at both of these temperatures. The pressure corresponding to the resistance at the higher temperature was 0.00078 mm., according to the calibration curve. That corresponding to the resistance at the lower temperature was "negative" and equal to —0.002 mm. These two readings showed that there was an increase of resistance of about 0.12 ohms more than the zero-pressure resistance and that the temperature coefficient of resistance was lower than the temperature coefficient of the wire when calibrated. The hypothesis that the active hydrogen is absorbed by the platinum therefore seems justified.

Although the experimental evidence is hardly conclusive, we feel that the abnormalities observed when a Hale-Pirani manometer is used with a tungsten lamp can best be explained by assuming that atomic hydrogen is produced in the burning lamp and that this hydrogen alloys with the platinum of the manometer, increasing its resistance. The writer hopes to be able to conclusively prove this point at a later date.

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CHEMICAL REACTIONS AT VERY LOW PRESSURES. II. THE CHEMICAL CLEAN-UP OF NITROGEN IN A TUNGSTEN LAMP.[1]

BY IRVING LANGMUIR.

Received June 6, 1913.

It has been previously shown[2] that small amounts of hydrogen introduced into a tungsten lamp with heated filament will slowly disappear. Subsequently, a careful study was made of the kinetics of the reaction between a hot tungsten wire and oxygen at low pressure.[3]

The object of the present paper is to record some observations made during a detailed study of the behavior of nitrogen in tungsten lamps.

In the manufacture of tungsten filaments it was long the common practice to thoroughly sinter the filament by electrically heating it to a very high temperature in an atmosphere consisting largely of hydrogen. Originally pure hydrogen was used; subsequently, to avoid dangerous explosions and to reduce cost, mixtures of nitrogen and hydrogen were employed. Both of these gases appeared to be completely inert towards the metallic tungsten, even at temperatures close to the melting point of the filament.

The power required to maintain a tungsten wire at high temperatures in nitrogen at atmospheric pressure was determined, and it was thus

[1] Paper read before the New York Section of the American Chemical Society, Nov. 8, 1912.

[2] THIS JOURNAL, **34**, 1310 (1912).

[3] *Ibid.*, **35**, 105 (1913).