# CCXLII.—*Reactions of Incandescent Tungsten with Nitrogen and with Water Vapour.*

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(Communication from the Research Staff of the General Electric Company, Ltd., Wembley.)

## 1. *Reaction with Nitrogen.*

The temperature at which a tungsten filament can be operated in a vacuum is in practice limited by the rate of evaporation of the metal, which forms a black deposit on the bulb, thereby reducing the candle power of the lamp. By surrounding the filament with an atmosphere of inert gas, the loss of metal by evaporation is reduced, and the filament can be operated at a higher temperature, and therefore at a higher efficiency, for an equal life (Brit. Pat., 10,918, 1913). In lamps of small wattage, it is customary to use as the inert gas a mixture of argon and nitrogen containing 10—20% of the latter, but lamps of 500 watts and upwards are frequently filled with pure nitrogen on grounds of economy. The filaments operate at a temperature of about 2850° K. It is found that a dark brown deposit is slowly formed on the inside of the bulb during the life of such lamps; but it forms much more slowly if an argon–nitrogen mixture is used. The cause of this coloration has now been investigated.

Very little information exists as to the formation, composition, or properties of the nitrides of tungsten. Henderson and Galletly (*J. Soc. Chem. Ind.*, 1908, **27**, 387) heated tungsten powder to 860° in a current of ammonia, but the product contained only a trace of nitrogen. By heating "tungsten nitramide," $W_3N_6H_4$, in ammonia, Uhrlaub ("Die Verbindungen einiger Metalle mit Stickstoff," Göttingen, 1859) obtained a substance to which he assigned the formula $W_3N_2$. By heating tungsten hexachloride in ammonia, Rideal (J., 1889, **55**, 41) obtained a black, metallic-looking powder, the composition of which was represented as $W_2N_3$.

Langmuir (*J. Amer. Chem. Soc.*, 1913, **35**, 931) has studied the rate at which nitrogen is absorbed in a tungsten-filament vacuum lamp. He found that this was dependent on the rate of evaporation of the filament, and that one molecule of nitrogen disappeared for each atom of tungsten evaporated. He therefore assumed that nitrogen did not react with solid tungsten at temperatures in the neighbourhood of 2200° K., but that when an atom of tungsten struck a molecule of nitrogen they combined to form $WN_2$, which was deposited on the bulb. This nitride is described as a brown compound, readily decomposed by water to form ammonia and tungstic oxide, $WO_3$. No direct analyses were made.

It appeared probable that the coloration of the lamps under consideration might be due to the formation of such a nitride. Alternatively, it was possible that the deposit was evaporated tungsten from the filament, or nickel or molybdenum from the supporting and leading-in wires. The presence of traces of oxidising gases might also give rise to oxides of any of these metals. The total weight of the deposit on the inside of the largest lamps, which have a capacity of about 4 litres, is only 5—10 mg. after the lamp has been operated for 1000 hours. Special methods of analysis had, therefore, to be developed.

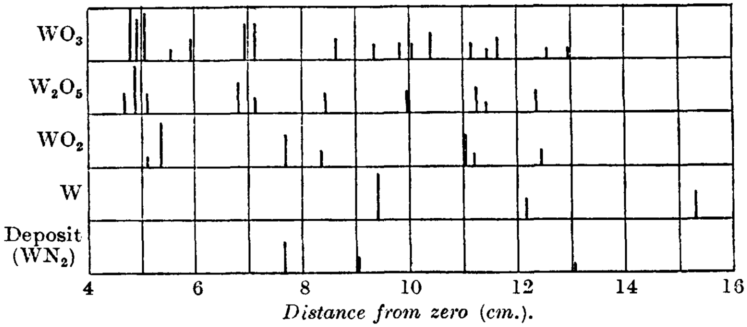
*Preliminary Examination.*—On opening the lamp a distinct odour is observed, which resembles ammonia, but is difficult to identify. The deposit can easily be rubbed off with the finger, or scraped together with a knife. After being exposed to the air for an hour, it becomes slightly sticky, more difficult to remove, and somewhat lighter in colour. After two or three days' exposure, it is again quite dry and easily rubbed off. A small quantity was ignited in air and gave a greenish-yellow residue, which resembled tungstic oxide and yielded its characteristic *X*-ray pattern, thus proving that the original material was definitely tungsten or one of its compounds.

X-*Ray Examination.*—Tungsten forms three oxides, which are readily distinguished by their colour: $WO_3$, yellow; $W_2O_5$, deep blue; and $WO_2$, chocolate-brown. Pure specimens of each of these oxides were prepared, and the characteristic *X*-ray diffraction patterns obtained, together with that of the metal. These are shown in Fig. 1, where the height of the lines represents their relative intensities on the film. A little of the deposit was then smeared on a piece of tissue paper, and exposed to the *X*-ray beam. Three strongly marked but somewhat diffuse lines appeared in the pattern. Although they were sufficiently clear for purposes of identification, it was not easy to measure their position accurately. The diffuseness was due to the extremely fine state of division of the deposit. By heating another sample at 600° in a current of pure, dry argon for 2 hours, the particles became coarser, and the lines in the diffraction pattern appeared much sharper. Their position, however, was unchanged. This pattern is also shown in Fig. 1. On comparing the positions of the lines with those in the patterns of the metal and its oxides, it is clear there is no correspondence and that the deposit must be some other compound.

*Spectroscopic Examination.*—The fact that the material burnt readily in air to tungstic oxide suggested a simple way of proving whether it was a nitride, for nitrogen should be formed when such a compound is oxidised.

FIG. 1.

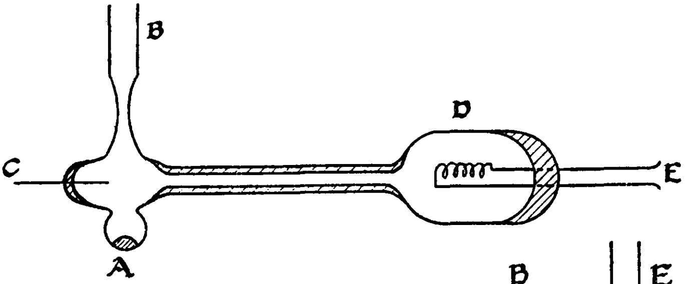
*X-Ray diffraction patterns of tungsten compounds.*



A small hard-glass spectrum tube was made as shown in Fig. 2. This had a bulb, A, into which a mixture of the deposit with a little potassium permanganate was introduced through B. A plain molybdenum electrode, C, was arranged at this end, whilst at the other end of the tube a thick tungsten spiral filament, D, acted as the second electrode for the discharge. The electrodes were thoroughly freed from gas before the mixture was introduced, after which the tube was evacuated and sealed off. The whole volume of the apparatus was less than 1 c.c., and since a pressure of about 1 cm. was sufficient to obtain a satisfactory discharge, only 0·0003 g. of material was necessary.

On heating the bulb, A, a vigorous reaction occurred between the material and the permanganate. On passing a discharge, the spectrum of both nitrogen and oxygen appeared. The excess oxygen, derived from the permanganate, was then removed by heating the tungsten filament, and finally the tube contained nearly pure nitrogen. The material was therefore most probably a nitride of tungsten having the formula $WN_x$.

FIG. 2.
*Discharge tube.*



*Composition of the Nitride.*—The value of $x$ was determined by measuring ($a$) the volume of oxygen required to burn a small weight of the material, and ($b$) the volume of nitrogen evolved. From the equation

$$2WN_x + 3O_2 = 2WO_3 + xN_2,$$

it is seen that the value of $x$ is determined from the ratio of the volumes of oxygen and nitrogen. It is not necessary to know the weight of the nitride, but, as a further check on the analysis, the material was weighed before the combustion was carried out. A special form of combustion apparatus was made (Fig. 3) which consisted of a hard-glass tube, A (volume about 3 c.c.), attached to a tap, B, and to a piece of barometer tubing, C (volume 1·5 c.c.). The lower end of the barometer tube was connected by a flexible rubber tube to a second piece of barometer tubing, D. The volume of the apparatus was carefully calibrated and a scale was attached to the tube C.

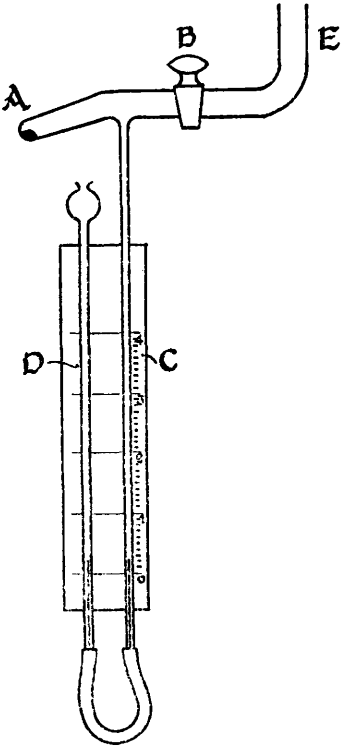


FIG. 3.
*Combustion apparatus.*

A weighed quantity (2—3 mg.) of the nitride was introduced into the limb A. The barometer **U** was filled with mercury up to about the scale zero, and the tap closed. The whole apparatus was carefully protected from draughts and allowed to attain a steady temperature, which was read on an attached thermometer. The pressure was adjusted and the scale reading gave the volume of air in the apparatus. The nitride was then heated to about 650° by means of a blow pipe; it burnt readily to the yellow oxide, $WO_3$, and nitrogen was liberated. The apparatus was allowed to cool to room temperature during 5—10 hours, the pressure was adjusted, and the new volume read off. The difference between this reading and the previous one, after correction for any change of temperature, gave the volume of oxygen absorbed minus the volume of nitrogen evolved.

The external limb, E, was now filled with an alkaline solution of pyrogallol and the apparatus tilted so that when the liquid was drawn into the wide limb it would not enter the barometer tube. By lowering or raising the tube D, the solution was alternately drawn into the apparatus and expelled. The walls of the tube A were thus repeatedly wetted with fresh liquid until the remaining oxygen was absorbed. After allowing the apparatus to attain a steady temperature, a new reading of the volume was taken. This represented the known volume of nitrogen originally in the apparatus plus the nitrogen evolved.

The apparatus had been originally filled with atmospheric air, the humidity of which was determined from wet and dry bulb thermometer readings. It was found that the water-vapour pressure was, within the limits of accuracy attainable in the experiments, the same as that of the 40% caustic soda solution used for the absorption. No correction for the vapour pressure of the liquid was therefore required.

Although the formation of oxides of nitrogen during the combustion did not seem probable, caustic potash was introduced into the apparatus before the pyrogallol solution in one experiment. No absorption occurred, thus indicating that no oxides higher than nitrous oxide were present. It was thought justifiable to neglect the possibility of the presence of the latter.

From the equation we have

$$x/3 = \text{Vol. of } N_2 \text{ evolved/Vol. of } O_2 \text{ absorbed.}$$

Let $c$ be the volume of nitrogen evolved and $b$ the contraction on burning. Then

$$b = \text{Vol. of oxygen} - c,$$

and

$$x = 3c/(b + c).$$

After a number of preliminary trials to test the apparatus, two accurate determinations were made with weighed quantities of materials from two different lamps. The results are given in Table I.

TABLE I.

| Expt. | Weight of material (g.). | $b$ (c.c.). | $c$ (c.c.). | $x$. |
|---|---|---|---|---|
| 1 | 0·0026 | 0·10 | 0·19 | 1·96 |
| 2 | 0·0036 | 0·15 | 0·27 | 1·93 |

These values show very good agreement and indicate that the nitride has the formula $WN_2$. Assuming this to be correct, it is possible to check the values obtained for $c$ from the weight of material used. In both cases, the experimental value is about 70% of the theoretical value for the volume of the combined nitrogen. The difference is probably accounted for by the presence in the material of small fragments of glass and mica, with which it becomes unavoidably contaminated when the lamp is broken open.

These results confirm the conclusion reached by Langmuir as to the composition of the nitride, by an entirely different method. The formulæ assigned by earlier workers are probably in error owing to the difficulty of separating the nitride from the metal powder, and to the inherent difficulties of gravimetric methods when dealing with oxides and nitrides of tungsten, the molecular weights of which are so nearly the same.

The approximate density of the nitride was determined by weighing samples of 5—10 mg. in air and in benzene. A small pellet of the material was pressed in a steel die, and weighed in a pan made from aluminium foil which weighed only 8 mg. The pan holding the pellet was immersed in benzene in an evacuated vessel, in order to remove any occluded air, and its weight in the liquid then determined. The method was checked by determining the density of a pellet made from a thin film of tungstic oxide condensed on a glass surface; this gave a value of 6·3 g. per c.c., the density of fused crystalline tungstic oxide being 7·2 g. per c.c. Two determinations of the density of the nitride gave a mean value of 5 g. per c.c., with a maximum error of $\pm 0{\cdot}5$ unit.

## 2. *Reaction with Water Vapour.*

The action of water vapour on an incandescent tungsten filament has been described previously by one of us (Smithells, *Trans. Faraday Soc.*, 1921, **17**, 485). It was shown that a reversible reaction took place in which tungsten was oxidised at the hotter parts of the filament, and the oxide reduced to metal at lower temperatures and deposited on the cooler parts of the filament: $W + 2H_2O \leftrightarrows WO_2 + 2H_2$. The reaction is accompanied by a gradual blackening of the bulb, and it would be expected that this is due to a certain amount of both metal and oxide being carried by convection in the gas. Langmuir (*Gen. Electric Rev.*, 1926, **29**, 153) has shown, however, that atomic hydrogen, which is formed when molecular hydrogen comes in contact with incandescent tungsten, will reduce tungsten oxides at room temperature. It therefore appeared of interest to determine the nature of the deposit, which is nearly black and easily distinguishable from the nitride just described. The $X$-ray diffraction pattern was found to be identical with that obtained from pure tungsten powder, no trace of oxide being present. This can only be explained by assuming that atomic hydrogen formed during the reaction, and in contact with the incandescent filament, arrives at the surface of the glass and reduces any oxide deposited. That oxide molecules do reach the glass walls is almost certain, since the cyclic action can hardly be so complete as to prevent their escape entirely. The fact that they are subsequently reduced explains why even very minute quantities of water vapour have such a deleterious effect in gas-filled lamps. Water vapour present in the filling gas to the extent of 1 part in 10,000 parts will cause the filament to burn out in less than an hour.

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