The Kinetic Study of Surface-chemical Reactions at Extremely Low Pressures. IV. The Thermal Reaction between Water Vapor and a Tungsten Filament. Part IV

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Tungsten compound formed by the reaction of water vapor with tungsten at high temperatures has been studied by some investigators. Smithells[1] has studied the reaction by using a gas-filled electric bulb and reported that tungsten was removed from the hotter part of the filament as WO_2 and deposited as W on the colder part. Alterthum[2] assumed the formation of WO_2 in their estimation of equilibrium constants of the system W–H_2O at high temperatures, and Dushman[3] showed thermodynamically that water vapor could oxidize W to WO_2 or W_2O_5. In the previous experiments[4-6] concerning the heating of a tungsten filament in water vapor at low pressures, however, it was found that a blue deposit was formed on the wall of the reaction vessel as the reaction proceeded.

Since WO_2 is brown, this deposit seemed to correspond to another compound. This difference may come from the fact that other authors' results are those at the equilibrium state and not applicable to the present case. It is the aim of the present work to identify the blue deposit and to explain the process of its formation.

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[1] C. J. Smithells, "Tungsten", Chapman & Hall, Ltd., London (1952), p. 141.

[2] H. Alterthum and F. Koref, *Z. Elektrochem.*, **31**, 508 (1925).

[3] S. Dushman, "Vacuum Technique", John Wiley & Sons, Inc., New York (1949), p. 822.

[4] N. Sasaki and T. Hamamura, This Bulletin, **29**, 365 (1956).

[5] T. Hamamura, ibid., **32**, 845 (1959).

[6] T. Hamamura, ibid., **32**, 848 (1959).

Experimental

The tungsten compound formed by the reaction vaporizes from the filament at high temperatures to produce the deposit on the wall of the vessel. The composition of deposit was determined by means of an electron diffraction method and an indirect method mentioned below.

Electron Diffraction Method. — A film of formval attached on a sheet mesh was placed in the reaction vessel to deposit the product on it; and after the reaction ended, it was taken out of the vessel and a diffraction pattern was taken with a micro-diffraction apparatus.

Indirect Method. — Composition of the deposit was determined from the weight loss of the filament and the amount of hydrogen produced. Since no layer of the product was formed on the filament above 1200°K and the evaporation of tungsten was negligible below 2400°K, the weight loss of filament gave the weight of tungsten converted to the product. On the other hand, if one molecule of hydrogen was assumed to be formed from one molecule of water vapor, the quantity in moles of hydrogen was equal to twice that of oxygen combined with tungsten. Therefore, the mean apparent composition was determined from the weight loss of filament and the amount of hydrogen produced.

Apparatus. — The experimental apparatus was the same as that described in the previous papers, except that the filaments were made removable from the lead wires for weighing, i. e., they were clamped at both ends by nickel strips welded to the leads. The filaments used were taken from the same spool as that used in the previous experiments and pretreated in a similar manner. Six filaments, 0.114 mm. in diameter and 75 mm. long each, were mounted perpendicular to the axis of the reaction vessel at a distance of 5 cm. from each other. One of them was used for a standard to compensate all the weight changes that were not caused by the reaction itself; for example, the change caused by the oxidation and adsorption during the weighing process and the evaporation during the degassing process and so on. The filament was degassed in a similar manner as the others, but not heated in water vapor. The other five filaments were used for the determination of the composition. A glass balloon of 10.278 l. was used to introduce hydrogen into it and the pressure was measured with a McLeod manometer.

Procedure.—Prior to the mounting, each filament was weighed with a micro-balance and mounted in the vessel in a manner such as that mentioned above. The procedures of evacuating the apparatus, degassing the filaments and introducing water vapor into the vessel were similar to those of the previous experiments, except that the filaments were degassed at 2200°K for 6 hr. When the flow of water vapor became stationary, one of the filaments was heated at a definite temperature and the hydrogen liberated was carried by the diffusion pump into the balloon. After a certain interval of time, the filament was cooled and the pressure of the balloon was measured to obtain the amount of hydrogen. Thus, five filaments were heated one by one under different filament temperatures and pressures of water vapor. After five filaments had been heated, all the filaments were heated again in high vacuum at 2000°K for twenty minutes. Then the filaments were taken out of the vessel, removed from the leads and weighed again with a micro-balance. The net weight loss was obtained as a difference of weight loss of the respective filament and the weight change of the standard filament.

The experiments were made at temperatures from 1480 to 1950°K and initial pressures of water vapor from 63×10^{-5} to 200×10^{-5} mmHg. The hydrogen pressure in the vessel was controlled whenever it was necessary. The temperature of the vessel remained at room temperature throughout the experiments.

The hydrogen in the balloon was compressed by a diffusion pump into a sampling bulb of one liter up to about 0.1 mmHg and analyzed with a Consolidated Electrodynamics Corporation mass-spectrometer model 21-401.

Results and Discussion

Electron Diffraction Method. — All the diffraction patterns obtained consisted of diffused lines, presumably because the deposits were too fine crystalline or amorphous. Therefore, this method was not used for identification of the products.

Indirect Method. — Results obtained are given in Table IV*, representing the composition in form of WO_x. It is evident from this table that the compositions are about $WO_{2.80}$ independent of filament temperatures, pressures of water vapor and hydrogen pressures. The colors of all the deposits were blue by transmitted light.

From the color and composition the deposits seem to be composed of some of the following oxides(7,8) or hydroxides(9-11) of tungsten, e. g., β-($WO_{2.9}$) and γ-($WO_{2.72}$) for oxide and $H_{0.1}WO_3$, $H_{0.33}WO_3$ and $H_{0.5}\cdot WO_3$ for hydroxide. These are blue or violet, respectively, and have compositions close to those of the blue deposits, (hydroxide has the apparent composition of $WO_{2.95}$, $WO_{2.83}$ and $WO_{2.75}$ respectively, if determined by means of the indirect

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* Tables, figures and equations in the present paper are numbered after those of the previous papers.

7) O. Glemser and H. Sauer, *Z. anorg. u. allgem. Chem.*, **252**, 144 (1943).

8) A. J. Hegedüs, T. Millner, J. Neugebauer and U. Sasvari, ibid., **281**, 64 (1955).

9) O. Glemser and C. Neuman, ibid., **265**, 288 (1951).

10) O. Glemser, U. Hauschild and G. Lutz, ibid., **269**, 93 (1952).

11) F. Ebert and H. Flasch, ibid., **226**, 65 (1935).

TABLE IV

Temp. of filament K°	Initial press. of H_2O mmHg×10^5	Press. of H_2 in vessel mmHg×10^5	Net weight loss of filament mol.×10^6	Amount of H_2 produced mol.×10^5	Composition	Gas. product mass No. %
1480	176	2	3.96	1.11	$WO_{2.81}$	
1580	63	2	4.04	1.12	$WO_{2.78}$	
1580	179	5	4.22	1.19	$WO_{2.82}$	
1700	63	6	4.59	1.28	$WO_{2.79}$	
1700	200	16	4.86	1.35	$WO_{2.77}$	28 0.4% 32 ——
1730	103	8	3.89	1.09	$WO_{2.80}$	
1730	103	9	5.17	1.46	$WO_{2.83}$	
1730	103	127	5.56	1.55	$WO_{2.79}$	
1800	103	11	5.07	1.43	$WO_{2.82}$	
1900	103	16.5	7.00	1.97	$WO_{2.82}$	
1950	103	24	3.88	1.09	$WO_{2.81}$	
1950	103	24	7.94	2.20	$WO_{2.78}$	

method). It is known that these oxides are formed by reduction of WO_3 with hydrogen and the hydroxides by reduction of WO_3 with atomic hydrogen.

The following two processes may be considered for the production of the blue deposit:

1) the product vaporizes from the filament as a blue compound to make a blue deposit on the wall.

2) the product vaporizes from the filament as trioxide and its colorless deposit is secondarily reduced on the wall to form a blue deposit.

The process, by which the deposit was, produced was studied by vaporizing γ-oxide from the filament in high vacuum. When a tungsten filament was heated at 700°C in about 0.01 mmHg pressure of oxygen, a dark violet layer of γ-oxide[12] was formed on the filament. After forming a certain thickness of the layer, excess oxygen was evacuated and the filament was heated above 1500°K. Then the oxide layer vaporized from the filament and made a deposit on the wall of the vessel. The experiments were carried out at various thicknesses of deposit up to about 1000 Å and vaporizing temperatures up to about 2200°K. It was found that the deposits produced were always colorless regardless of the thickness of the deposit and the vaporizing temperature and the blue deposit was not formed at all. The thickness was estimated from the amount of oxygen combined with the filament to make γ-oxide. It was found experimentally that deposit of about 100 Å thick was detectable as a blue film when it was formed by the reaction of water vapor with tungsten. Blackburn[13] has found that WO_2 decomposed completely to W and WO_3 above 1300°K and made WO_3 deposit on the wall. γ-Oxide and probably β-oxide, too, would behave similarly. Hydroxides are not likely to vaporize from the filament as they are. $H_{0.5}WO_3$ is known[9] to decompose into $WO_{2.9}$, hydrogen and water vapor above 60°C. Other hydroxides seem to behave in a similar manner, although their thermal stability is not known. As a result, it is probable that the blue deposit was formed not primarily by the deposition of blue compounds, but secondarily by the reduction of a colorless deposit of WO_3 with hydrogen on the wall.

As for the reduction, the following facts are known in the present stage of research. It is evident that the reduction was not carried out with hydrogen in gas phase, because the composition of the deposit and the reaction rate[6] were independent of the hydrogen pressure in the vessel. Accordingly, the reduction should be carried out with hydrogen liberated by the reaction of water vapor with tungsten. The hydrogen would contain the molecules excited in the electronic or the vibrational energy and even the atoms, if generated. These will be discussed in a subsequent paper.

The independence of the composition $WO_{2.80}$ of deposit upon the filament temperatures and others mentioned above may be due to the fact that the reduction rate becomes smaller at the lower oxidation state. The reduction rate was studied by means of a static method by heating

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12) H. Hashimoto, K. Tanaka and E. Yoda, *J. Electron-Microscopy*, **6**, 8 (1958).

13) P. E. Blackburn, M. Hoch and H. L. Johnston, *J. Phys. Chem.*, **62**, 769 (1958).

a tungsten filament in hydrogen within a reaction vessel whose wall had been covered with WO_3 deposit formed by heating the filament in a definite amount of oxygen. The hydrogen pressure was measured as a function of the heating time of the filament and the extent of reduction was determined from the pressure decrease of hydrogen. Two examples are shown in Fig. 10, where the filament temperature was 1740°K and the thickness of WO_3 was about 50 and 100 Å, respectively, and the initial pressure of hydrogen was 50×10^{-4} and 100×10^{-4} mmHg each. It is evident from the figure that the reduction proceeds swiftly down to about $WO_{2.80}$ but the rate slows down appreciably at the lower oxidation state. It is obvious in these experiments that the reduction is carried out mainly with atomic hydrogen formed from the molecules by the dissociation in contact with the filament, and not with hydrogen molecules which rebound from the filament, because the mean temperature of rebounding molecules is about 280°C (for the filament temperature of 1740°K) which is too low to reduce WO_3, since the accomodation coefficient of hydrogen on tungsten surface is 0.19[14].

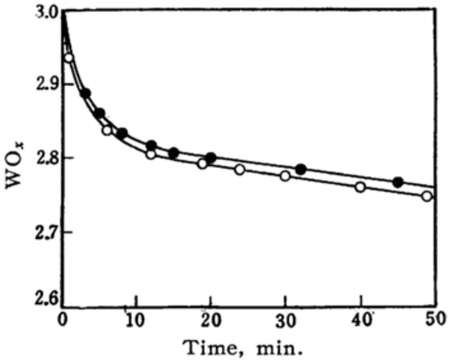

Fig. 10. Reduction of WO_3 with atomic hydrogen.
● 100 Å, 100×10^{-4} mmHg
○ 50 Å, 50×10^{-4} mmHg

Result of analysis of hydrogen is shown in Table IV. Only a small amount of gas of mass number 28, presumably carbon monoxide formed from carbon in the filament and water vapor, is contained. The fact that oxygen was not detected in hydrogen suggests that WO_3 was formed by a direct reaction of water vapor with tungsten and not by the reactions through the thermal decomposition of water vapor

$$2H_2O \rightarrow 2H_2 + O_2$$
$$W + 3/2O_2 \rightarrow WO_3$$

If oxygen was liberated, a part of it would leave the vessel without reacting with the filament and be introduced into the balloon, and a part would react with the filament to form WO_3 deposit. The ratio of the former oxygen to the latter can be evaluated by the kinetic theory of gases as follows; the quantity in moles of oxygen which leaves the vessel per second is given similar to Eq. 12 by

$$A'\bar{B}''P'' \qquad (13)$$

where $A'\bar{B}''$ is a constant determined experimentally and P'' the partial pressure of oxygen in the vessel. While the quantity which reacts with the filament per second is given similar to Eq. 2 by

$$k''SB''P'' \qquad (14)$$

where k'' is the reaction probability of oxygen with tungsten. From these formulae, the ratio is calculated as a function of filament temperature as shown in Table V, where values of k'' are determined experimentally by using a filament taken from the same spool. It is evident that if WO_3 was formed by a reaction of gaseous oxygen with tungsten at 1700°K, oxygen had to be detected by the mass spectrometer which was able to detect 0.1% oxygen in hydrogen.

TABLE V

Temp. of filament °K,	1600	1700	1800	1900
Ratio	1.7	1.1	0.64	0.51

Summary

1) Reaction product vaporizes from the filament as tungsten trioxide and its colorless deposit is reduced with hydrogen liberated by the reaction. Consequently, the blue deposit having the mean apparent composition of $WO_{2.80}$ can be obtained.

2) The WO_3 deposit is reduced readily with atomic hydrogen down to $WO_{2.80}$, but the reduction rate becomes appreciably slower at the lower oxidation state.

3) Oxygen is not contained in hydrogen. This suggests that WO_3 is not formed by a reaction of tungsten with gaseous oxygen liberated by thermal decomposition of water vapor, but is formed directly by a reaction of tungsten with water vapor.

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[14] I. Langmuir, *J. Am. Chem. Soc.*, 38, 1145 (1916).

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