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The Reactions between a Rhenium Filament and Oxygen at High Temperatures and Low Pressures*[1]

Takuya HAMAMURA and Genzo TOMITA

Department of Chemistry, Faculty of Industrial Arts, Kyoto Technical University, Matsugasaki, Sakyo-ku, Kyoto

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The rate of the reaction of oxygen with a rhenium filament under a filament temperature of (1500—2100)°K and an oxygen pressure of $(2\times10^{-4}—4\times10^{-6})$mmHg have been measured with a flow method. The reaction rate increases with an increase in the temperature, reaches a maximum at about 1800°K, and then decreases with a further increase in the temperature. The reaction rate is proportional to the 0.9th power of the oxygen pressure below 1700°K, whereas it is proportional to the 1.8th power above 1900°K. The apparent compositions of the rhenium oxides produced in the reaction have been determined from the weight change of the filament, and the oxides in the formulas of Re_2O_7 and ReO_3 have been found. For purposes of comparison, the reaction rates of oxygen with a tungsten filament have also been measured by the same method.

Rhenium is a refractory metal with a melting point of 3180°C, which is second only to tungsten among metals. It possesses many advantageous properties for use as a filament material in an electron tube[1-3]; it has a high tensile strength and a high resistance to the "water cycle"*[2] at high temperatures; it maintains its h. c. p. structure up to the melting point and does not form carbide. However, it has a poor resistance to oxidation at elevated temperatures and reacts with oxygen to form volatile oxide, just as tungsten and molybdenum do. Although the oxidation of rhenium in air has been studied by several investigators,[4-6] no study of the reaction rate with oxygen at low pressures has been reported.

We have studied the reactions of the high-temperature rhenium filament with oxygen at low pressures and have obtained the reaction rates by a flow method. The apparent composition of the oxides produced in the high-temperature range have also been determined from the amounts of oxygen consumed and of rhenium lost.

For purposes of comparison, the reaction rates of tungsten with oxygen have been measured by the same method. Tungsten was chosen because studies of tungsten-oxygen reactions under conditions of temperature and pressure similar to those of the present investigation have been reported by several investigators.[7-11]

Principle of the Experiment

When a rhenium filament is heated electrically at a high temperature in oxygen flowing through a reaction chamber at a low pressure, a part of the oxygen is consumed by the filament, thus forming a deposit of rhenium oxide on the wall of the reaction chamber. If the flow rate of the oxygen is measured at the outlet of the reaction chamber, it should change according to the change in the rate of the consumption of oxygen in the reaction chamber. Therefore, the rate of the consumption of oxygen can be determined from the flow rates as follows: Let G(mol/sec) be the flow rate with the filament at room temperature, and H, the flow rate with the filament at an experimental temperature; then the rate of the consumption of oxygen D (mol/sec) is given by:

$$D = (G - H) \tag{1}$$

From the rate of consumption thus obtained, it

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*[2] "Water cycle" is a cyclic process of an oxidation reduction reaction of the hot filament with the residual water vapor in the vacuum tube, which causes the failure of the filament.

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is possible to calculate the probability that an oxygen molecule which strikes the filament will disappear from the gaseous phase by some reaction mechanism. The oxygen pressure in the reaction chamber is so low, and the surface area of the filament is so small, that the temperature of the oxygen molecules striking the filament is assumed to be equal to that of the wall of the chamber. Therefore, the number of moles of oxygen that strike the filament per second can be calculated from the kinetic theory of gases as follows;

$$\frac{PS}{\sqrt{2\pi M\boldsymbol{R}T}} \tag{2}$$

where P is the oxygen pressure (dyn/cm^2); S, the surface area of the filament (cm^2); M, the molecular weight of oxygen; $\boldsymbol{R}$, the gas constant, and T, the temperature of the reaction chamber. Since the number of moles of oxygen that disappear from the gaseous phase per second is given by Eq. (1), the reaction probability, k, can be expressed by the following equation:

$$k = \frac{D\sqrt{2\pi M\boldsymbol{R}T}}{PS} \tag{3}$$

The rate of consumption is then given by;

$$D = \frac{kPS}{\sqrt{2\pi M\boldsymbol{R}T}} \tag{4}$$

and if the filament temperature is kept constant, the rate of consumption is given as a function of the oxygen pressure;

$$D = KP^n \tag{5}$$

where K and n are constants. Therefore, from Eqs. (3) and (5),

$$k = \frac{KP^{n-1}\sqrt{2\pi M\boldsymbol{R}T}}{S} \tag{6}$$

or

$$\log k = (n-1)\log P + \log (K\sqrt{2\pi M\boldsymbol{R}T}/S) \tag{7}$$

If $\log k$ is plotted against $\log P$, $(n-1)$ is given as a slope of the curve and the reaction order, n, is readily obtainable.

Since the moles of the oxygen that is consumed by the formation of rhenium oxides in t seconds is given by $(G-H)\cdot t$, and since the gram atoms of the rhenium lost can be determined from the weight loss of the filament, the apparent composition of the oxide product can be determined by comparing these two quantities, and expressed in an empirical formula of ReO_x.

Apparatus

The apparatus is shown schematically in Fig. 1. Oxygen in the primary reservoir (1) was continuously introduced through a capillary leak (3) into the reaction chamber (4) of 1.4 l, and was then pumped out with a mercury diffusion pump (7) to be accumulated in secondary reservoirs, (9), (10), (11), of known volumes. A steady flow of oxygen into the reaction chamber at a desired pressure could be obtained by adjusting the oxygen pressure of the primary reservoir. The primary reservoir, about 12 l in capacity was large enough to keep a steady flow in the reaction chamber for several hous.

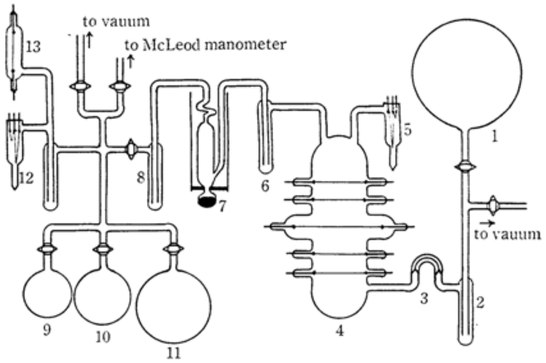

Fig. 1. The apparatus.

Oxygen pressures in the reaction chamber and the secondary reservoirs were measured with Pirani gauges, (5) and (12), which had been calibrated against a McLeod manometer. The McLeod manometer was also used for the pressure measurement in the secondary reservoirs. The traps, (2), (6), (8), were immersed in liquid nitrogen to prevent grease vapor and mercury vapor from entering the reaction system.

A reaction tube (13) was used for the determination of the oxide composition by a static method, and was also used for the determination of the purity of the oxygen. In the latter case, a tungsten filament was stretched in the tube and heated in the oxygen to be analysed while the pressure was being measured. The oxygen would be consumed by the heated filament, and the inactive gases, such as carbon monoxide or nitrogen, would remain; thus the purity of the oxygen could be determined from the initial and final pressures. Because the cold traps were contained in the system, only non-condensable gases could be detected by this method, however,

The rhenium filament used for the measurement of the reaction rate was 128 mm long and 0.125 mm in diameter. It was connected to Fernico wires with platinum connectors and mounted in the reaction chamber. The wires were coated with glass in order to exclude any reactions that consume oxygen at the wire surface.

For the measurement of the weight loss, filaments 73 mm long were used; they were weighed with a micro balance before and after the experiment. They were clamped at both ends with platinum strips which were welded to the glass-coated

Fernico wires, so that they could be easily disconnected from the wires by unfastening the platinum strips.

The filaments were heated electrically, and their temperatures were measured with a micro optical pyrometer.

The rhenium filament was analyzed spectroscopically. (Found: Fe, 0.05; Si, 0.03; Al, 0.01; Ca, 0.01; Mg, 0.01%) The filament was cleaned by dipping it in a boiling solution of 40% caustic soda and rinsed by distilled water prior to being stretched in the reaction chamber. Oxygen was prepared by the thermal decomposition of potassium permanganate; its purity (99.95%) was determined by the method previously described.

Procedure

All the apparatus was evacuated, and the reaction system was baked out and degassed at 320°C for more than eight hours. Then the filaments were heated at 2300°K in an oxygen flow at a pressure of 10^{-5} mmHg in order to remove carbon and gases from the filaments.[8,9] This heating was continued until the evolution of the inactive gases from the filaments became negligibly small. The experiments were carried out after these pretreatments were over.

For the measurement of the reaction rate, oxygen was allowed to flow through the reaction chamber at a pressure in the range of 6×10^{-4}—1×10^{-5} mmHg, with the filament at room temperature; the flow rate was obtained by measuring the rate of pressure increase in the secondary reservoirs with the Pirani gauge. Then the filament was heated at a temperature in the range of 1500—2100°K and the flow rate was measured in the same way. The oxygen pressure in the reaction chamber was obtained by calculating it from the conductance of the path from the reaction chamber to the diffusion pump; the conductance ($4.8\times\times10^{-6}$ mol/sec mmHg) had previously been determined experimentally. Thus the reaction rates under varying conditions of filament temperature and oyxgen pressure were measured.

In the case of the weight-change and oxygen-consumption measurements, each filament was weighed and stretched in the reaction chamber, and then the degassing and baking process was carried out in the manner described before. The loss in weight of the filaments, that had risen during the pretreatment, had previously been determined in an auxiliary experiment.

With the filaments at room temperature, oxygen was allowed to flow through the system for 30 min; the flow rate was measured with the McLeod manometer. Then one of the filaments was heated at an experimental temperature for 300 min, after which the amount of oxygen that had been accumulated in the 7.46 l reservoir was measured. After these measurements at various temperatures above 1600°K had been carried out, the filaments were taken out of the apparatus and weighed again. In this method, the lower limit of the oxygen pressure in the reaction chamber was about 3×10^{-5} mmHg, and that of the filament temperature was 1600°K, because the rates of reaction at the lower pressures or at the lower temperatures were very slow and it was difficult to keep a steady flow of oxygen for a very long time.

For the measurements at the lower temperatures, the static method was used. After a filament of a known weight was stretched in the reaction tube, the system was evacuated. Some oxygen was then admitted into it and that amount was measured with the McLeod manometer. Then the filament was heated at an experimental temperature until all the oxygen had been consumed.

Results and Discussion

The reaction probabilities of oxygen with the rhenium filament, as calculated from the rates of consumption using Eq. (3), are plotted in Fig. 2 in relation to the oxygen pressure. As can be seen from this figure, the reaction probability at a fixed temperature varies with the oxygen pressure; it increases slightly as the pressure decreases below 1700°K, whereas it decreases as the pressure decreases at higher temperatures. The reaction order, n, obtained from this figure is 0.9 below 1700°K independently of the oxygen pressure, but above 1800°K it increases as the pressure decreases and reaches 1.8 as its highest value, except for the pressure range immediately above 2100°K, where it begins to decrease. The reaction probability at a fixed pressure increases with a rise in the temperature, reaches a maximum, and then decreases with a further increase in the temperature. The filament temperature, at which the maximum reaction probability occurs, lowers with a decrease in the oxygen pressure; it is 1900° at 1×10^{-4}, 1800° at 2×10^{-5}, and 1700°K at 5×10^{-6} mmHg.

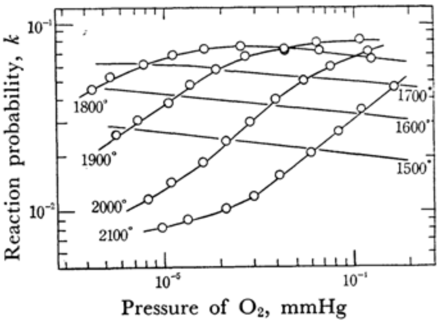

Fig. 2. Effect of oxygen pressure on the reaction probability of oxygen with rhenium.

Such a pressure and temperature dependence of the reaction probability may be explained as follows. Oxygen is adsorbed on the filament surface as atoms. In the higher pressure range, the surface is completely covered with a monolayer of oxygen atoms whose concentration is independent of the pressure. Hence, if ReO_3 is formed from an oxygen atom in the adsorbed layer and an oxygen molecule striking the filament, the reaction probability is independent of the pressure. The rate of the formation of ReO_3 is thus proportional to the oxygen pressure. In the lower pressure range, the adsorbed layer becomes incomplete, and the concentration of oxygen atoms on the surface decreases with a decrease in the pressure. Accordingly, the reaction probability decreases corresponding to the decrease in pressure. The pressure at which the adsorbed layer becomes incomplete shifts to a lower value with a decrease in the filament temperature; hence, the temperature at which the maximum reaction probability occurs lowers as the pressure decreases, as can be seen in Fig. 2.

In the extremely low pressure range, the concentration of oxygen atoms on the surface is proportional to the square root of the oxygen pressure, and the rate of the formation of ReO_3 is proportional to the 1.5th power of the pressure.

The same dependence can be derived from the assumptions that oxygen atoms are adsorbed to form the first and second layers, and that ReO_3 is formed from oxygen atoms in the first layer in the extremely low pressure range and is formed from atoms in the first and second layers in the higher pressure range.

The reaction probabilities of oxygen with a tungsten filament were also measured in the present investigation for the sake of comparison; they are shown in Fig. 3. The reaction order obtained from this figure is 1.25 above 2000°K; this value agrees well with that found by Anderson.[11)]

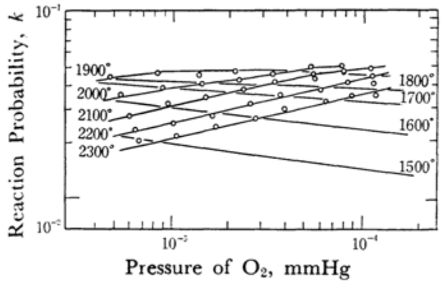

Fig. 3. Effect of oxygen pressure on the reaction probability of oxygen with tungsten.

The reaction probabilities of oxygen with the rhenium filament and with the tungsten filament at the oxygen pressure of 3×10^{-5} mmHg are plotted on the log*k* *vs.* $1/T$ curves in Fig. 4. The figure shows that the reaction probability of O_2-Re is higher than that of O_2-W below 1900°K, While at the higher temperatures that of O_2-Re declines so markedly with a rise in the temperature that it becomes lower than that of O_2-W.

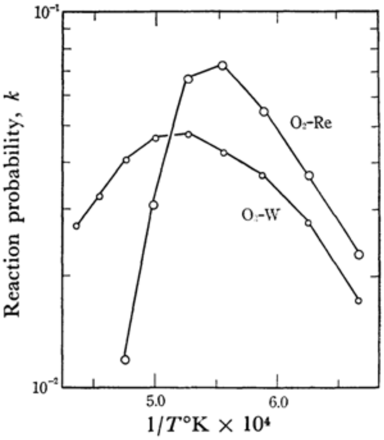

Fig. 4. Effect of filament temperature on the reaction probability, at 3×10^{-5} mmHg of oxygen pressure.

The rate of rhenium loss can be calculated from the reaction rate of oxygen with the filament and from the reaction ratio of oxygen to rhenium, which will be presented below. The rates of rhenium loss (g·atom/cm²·sec) thus obtained at the oxygen pressure of 3×10^{-5} mmHg are shown, together with those of tungsten, in Fig. 5. The rate of rhenium loss is about 1.4 times that of tungsten below 1800°K, but at 2100°K the former is only one-fourth of the latter.

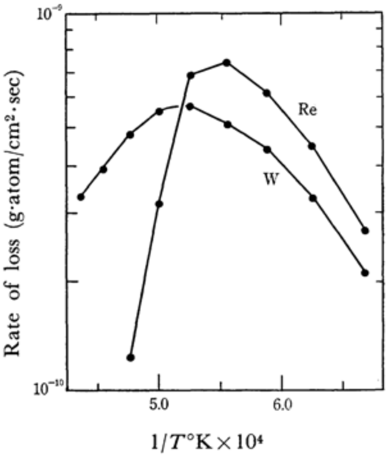

Fig. 5. Effect of filament temperature on the rates of loss of rhenium and tungsten, at 3×10^{-5} mmHg of oxygen pressure.

The apparent compositions of rhenium oxides determined at various temperatures are shown in Table 1, while the O/Re ratios are plotted against

TABLE 1. COMPOSITION OF THE RHENIUM OXIDE

Filament temp. °K	Pressure of O_2 mmHg	Consumed O_2 mol × 10^6	Loss of Re mol × 10^6	Oxide ReO_x value x
2100	7.8×10^{-5}	7.29	4.10	3.55
2000	4.6×10^{-5}	7.68	4.36	3.52
1900	8.3×10^{-5}	8.37	4.85	3.60
1800	3.1×10^{-5}	10.98	6.27	3.50
1700	8.7×10^{-5}	12.60	7.82	3.22
1600	4.2×10^{-5}	9.22	6.06	3.03
1600	15.2×10^{-3}	10.37	6.67	3.11*
1580	1.06×10^{-3}	10.13	6.70	3.02*
1413	1.01×10^{-3}	9.65	6.37	3.02*
1233	1.03×10^{-3}	5.15	3.24	3.18*
1100	15.1×10^{-3}	10.37	6.04	3.44*

* Obtained with the static method and the pressure is the initial pressure.

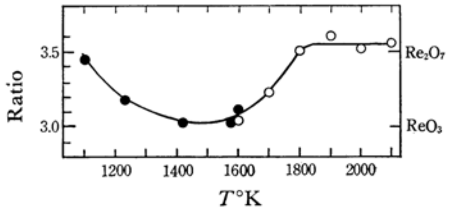

Fig. 6. The ratios, O/Re.
○: determined by the flow method
●: by the static method

TABLE 2. TUNGSTEN OXIDE, WO_x

Filament temp, °K	2200	2000	1800	1600
Value x	3.25	3.06	2.95	3.01

the temperature in Fig. 6. The figure shows that the ratio is 3.44 at 1100°K. With an increase in the temperature, it passes through a minimum value of 3.0 at about 1500°K and then increases to be a steady value of close to 3.5 above 1800°K. These ratios of 3.0 and 3.5 correspond to the admitted oxides of rhenium trioxide, ReO_3, and rhenium heptoxide, Re_2O_7, respectively. The ratio that lies between 3.0 and 3.5 may correspond to a mixture of the two oxides. The apparent composition of tungsten oxide can be regarded as tungsten trioxide, WO_3, as can be seen in Table 2. The color of the rhenium oxide deposited on the wall of the reaction vessel depended upon the filament temperature at which the deposit was produced. It was pale blue at 1100°K, and became dark blue with a rise in the temperature to 1500°K, but it faded again to pale blue at 1700°K and finally became colorless above 1800°K.

On the basis of the apparent compositions of the oxides and their colors, it may be concluded that ReO_3 on the wall is dark blue and Re_2O_7, colorless, and that, consequently, the pale blue deposits observed in the reactions at 1100° and 1700°K are composed of these two oxides.

Although the apparent composition of Re_2O_7 is obtained above 1800°K, the formation of Re_2O_7 on the filament surface and its evaporation from it in this high-temperature range are thermodynamically unfavorable because the heat of the formation of Re_2O_7 is larger than that of ReO_3, and because the ReO_3 is found at lower temperatures. A probable explanation is that, above 1800°K, ReO_3 evaporates from the filament surface and deposits on the wall of the reaction chamber; there it is oxidized to Re_2O_7 with the atomic and/or molecular oxygen that would be evaporated from the filament surface in this high-temperature range.[12] In order to prove this assumption, an additional experiment was attempted.

A rhenium filament, which was stretched down the center of a reaction tube 18 mm in diameter, was heated in oxygen at 1600°K unitl a blue deposit was observable on the wall of the reaction tube. On the subsequent addition of a second supply of oxygen, the temperature was elevated to 2100°K. Then it was observed that the blue deposit gradually faded in color.

From these experimental results, the following may be concluded: In the pressure range of this experiment, the oxide that evaporates from the rhenium filament at a low temperature is Re_2O_7, as is established for the higher pressures[4,5]; at about 1100°K, ReO_3 begins to exvaporate and its concentration increases with an increase in the temperature. Above about 1400°K, only ReO_3 evaporates and deposits on the wall. Above about 1700°K, only ReO_3 evaporates and the deposit on the wall is oxidized succesively to Re_2O_7 with the atomic and/or molecular oxygen that is evolved in this high-temperature range.

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