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The Reactions between a Rhenium Filament and Nitric Oxide at High Temperatures and Low Pressures

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The rates of the reaction of rhenium with nitric oxide under a filament temperature of (1300—1800)°K and a nitric oxide pressure of $(3\times10^{-5}-1\times10^{-3})$Torr have been measured by a static method. The rate of the reaction increases with an increase in the temperature, and the apparent activation energy is 24 kcal/mol. The rate of the reaction is proportional to the nitric oxide pressure and independent of the nitrogen pressure. The apparent compositions of the rhenium oxide produced in the reaction have been determined from the weight change in the rhenium filament and from the amount of nitric oxide consumed in the temperature range of (1300—2100)°K. The ReO_3 and Re_2O_7 were formed at lower temperatures and at higher temperatures respectively. The Re_2O_7 was presumed to be formed by the oxidation of the ReO_3 deposited on the vessel wall with atomic oxygen evolved in a high-temperature range.

At high temperatures, some metals react with oxidizing gases to form very highly volatile metal oxides. Therefore, the reactions proceed on surfaces practically free from the accumulation of the oxide layers. Adsorption, surface reaction, and desorption are included in these processes, and kinetic studies of such systems are expected to present useful information about the gas-solid interactions. These metals can be heated resistively to a considerably high temperature and can readily provide a clean metal surface when heated at a high temperature in a vacuum. Moreover, if the reactions are carried out at very low pressures, the following advantages may be expected; the diffusion rate of gas coming to and leaving from the surface is so large that it does not limit the overall rate of the process.

Rhenium possesses some advantageous properties;[1,2] that is, many refractory transition metals can form stable carbides and nitrides, while rhenium can not,[3] and it has a high resistance to the "water cycle"[4] at high temperatures. It is of interest to investigate the interaction of nitric oxide with rhenium, since nitric oxide is an odd molecule (possessing an odd number of electrons).

Many studies of the reactions of oxygen with tungsten[5-8] and rhenium[9-11] have been reported. However, although the reaction of tungsten with nitric oxide at very low pressures has been studied by Anderson[12], no reaction of rhenium with nitric oxide has been studied.

In the present investigation, the reaction rates of the rhenium filament with nitric oxide have been measured at pressure from 3×10^{-5} Torr to 1×10^{-3} Torr and in the temperature range from 1300°K to 1800°K by a static method. The apparent compositions of the rhenium oxide have also been determined from the amount of nitric oxide consumed and from the amount of rhenium lost in the temperature range from 1300°K to 2100°K.

Apparatus

The apparatus is shown in Fig. 1. For the measurement of the rate of the reaction, a reaction vessel of 5.2 *l* (including

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[1] C. T. Sims, C. M. Craighead, R. I. Jaffé, D. N. Gideon, E. N. Wyler, F. C. Todd, D. M. Rosenbaum, E. M. Sherwood, and I. E. Campbell, "Investigations of Rhenium," Battle Memorial Institute, Wright Air Development Center Technical Report, 54—371, June (1954).

[2] C. F. Robinson, *Rev. Sci. Inst.*, **29**, 250 (1958).

[3] C. T. Sims, "Rhenium," ed. by B. W. Gonser, Elsevier, New York (1962).

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

[5] J. A. Becker, E. J. Becker, and R. G. Brands, *J. Appl. Phys.*, **32**, 411 (1961).

[6] J. B. Berkowitz-Mattuch, A. Büchler, J. L. Engelke, and S. N. Goldstein, *J. Chem. Phys.*, **39**, 2722 (1963).

[7] P. O. Schissel and O. C. Truson, *ibid.*, **43**, 737 (1965).

[8] Yu. G. Ptushinskii and B. A. Chuikov, *Surface Sci.*, **6**, 42 **7**, 90 (1967).

[9] T. Hamamura and G. Tomita, This Bulletin, **40**, 1066 (1967).

[10] D. E. Rosner and H. D. Allendorf, *J. Chem. Phys.*, **49**, 5553 (1968).

[11] R. P. H. Gasser and C. J. Massay, *Surface Sci.*, **20**, 107 (1970).

[12] H. U. Anderson, U. S. At. Energy Comm., UCRL-10135 (1962).

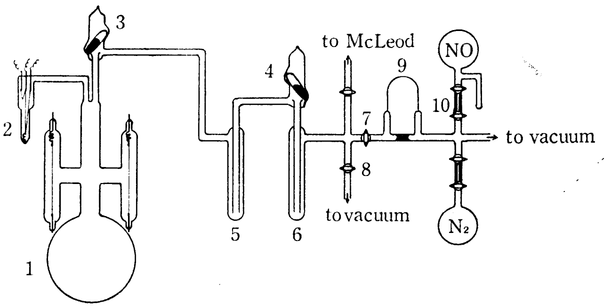

Fig. 1. The apparatus.
1: Reaction vessel, 2: Pirani gauge, 3,4: Greaseless cock, 5,6: Liquid nitrogen trap, 7,8: stop cock, 9: Capillary leak, 10: Gas pipet.

a Pirani gauge) was used. It consisted of a spherical bulb 20 cm in diameter and side tubes 3.5 cm in diameter and 15 cm long. Along the axis of each side tube, a rhenium filament, 0.152 mm in diameter and 130 mm long, was mounted, being stretched by a tungsten spring and connected to lead wires by spot welding. The lead wires were coated with glass in order to exclude any reactions that consume nitric oxide on the lead-wire surface.

For the determination of the oxide composition, the apparatus was similar to that used for the measurement of the reaction rate except that it had a reaction vessel of 98 *l*, and rhenium filaments, each 75 mm long, were mounted in it. They were clamped at both ends with platinum strips which were welded to the glass-coated lead wire so that they could be easily disconnected from the wires for weighing.

Particular care was taken to keep the filaments free from grease and mercury-vapor contamination; liquid nitrogen traps and greaseless stopcocks were used. Nitric oxide in a reservoir was supplied to the reaction vessel by a gas pipet through a capillary tube so placed as to decrease the flow rate of the gas. The pressure in the reaction vessel was measured by a Pirani gauge which was calibrated against a McLeod manometer and which had a sensitivity of 7.2×10^{-5} Torr/mV for nitrogen and nitric oxide.

The rhenium filament was heated electrically by means of a controllable DC power supply, and its temperature was measured with a micro optical pyrometer. The rhenium filament was analyzed spectroscopically (Found: Si : 0.08%, Ti : 0.001%). It was cleaned by dipping it in a boiling 40% caustic potash solution for five minutes and then wiping it off aqua-dag with filter paper; this procedure was repeated several times.

The nitric oxide and nitrogen were prepared by the methods described in the previous paper[13].

Procedure

All the apparatus was evacuated by a mercury-diffusion pump; for degassing the reaction vessel was heated at 360°C for ten hours in an electric furnace, and the filaments were heated to about 2100°K in oxygen of 1×10^{-5} Torr in order to remove any possible carbonaceous surface contamination. This heating was done until the evolution of the inactive gases from the filaments had become negligibly small.

Before each experiment, a filament was flashed at 2200 °K for 2 min in a high vacuum. Then the nitric oxide was introduced into the reaction vessel. When the nitric oxide pressure attained the desired value, the reaction vessel was separated from the evacuating system by means of the greaseless cock. The filament was then heated to the experimental temperature. As the reaction proceeded, the pressure in the vessel decreased; it was measured from time to time after the filament had been switched off and cooled down at room temperature, because the Pirani gauge could not follow the rapid change in pressure.

In the case of the determination of the composition of the rhenium oxide, each filament was weighed with a micro balance before it was mounted in the vessel. The processes of degassing the apparatus and of introducing nitric oxide into the vessel were similar to those described above. Then the filament was heated at the experimental temperature until all the nitric oxide had been consumed. Separate filaments were thus heated at the temperatures between 1300°K and 2100°K. The filaments were then taken out from the reaction vessel, removed from the lead wires, and weighed again with the micro balance in order to determine the loss of the rhenium filament.

Results and Discussion

The Rate of the Reaction. The rate of the reaction between the rhenium filament and nitric oxide was measured at temperatures from 1300°K to 1800°K and at pressures from 3×10^{-5} Torr to 1×10^{-3} Torr.

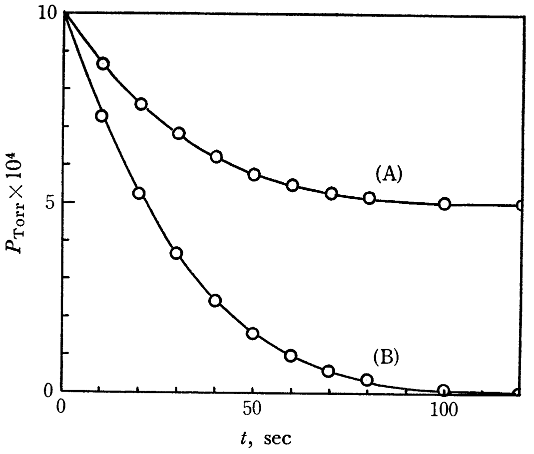

Fig. 2. Pressure *vs.* heating time of the filament. Filament temperature, 1400°K.
(A) Total pressure of nitric oxide and nitrogen.
(B) Partial pressure of nitric oxide.

A typical plot of the pressure, as measured by the Pirani gauge, against the heating time of the filament is shown by curve A in Fig. 2. Since nitrogen is formed by the reaction, the pressure indicated by curve A is the total of the pressure of nitric oxide still remaining and that of the nitrogen produced. We assume that the overall process is represented by:

$$x\mathrm{NO} + \mathrm{Re} \rightarrow (1/2)x\mathrm{N}_2 + \mathrm{ReO}_x,$$

and that nitrogen and a volatile rhenium oxide (it evaporates and sticks to the vessel wall) are produced, the intermediate steps being ignored; for every molecule of nitric oxide consumed, there is a net decrease of half molecules in the gaseous phase. It is thus possible, from measurements of the total pressure, P, at various times, to determine the partial pressure, P_{NO}, of the nitric oxide still remaining, as follows:

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[13] T. Tamura, This Bulletin, **44**, 590 (1971).

$$P_0 - P = (1/2)(P_0 - P_{NO})$$
$$P_{NO} = 2P - P_0$$

where P_0 is the initial pressure of nitric oxide. The plot of P_{NO} against the heating time is given by curve B in Fig. 2.

From the rate of consumption thus obtained, the amount of nitric oxide which reacts with the rhenium filament, D_{NO} mol/sec, can be calculated. The relation between the rate of reaction and the nitric oxide pressures at various temperatures is shown in Fig. 3.

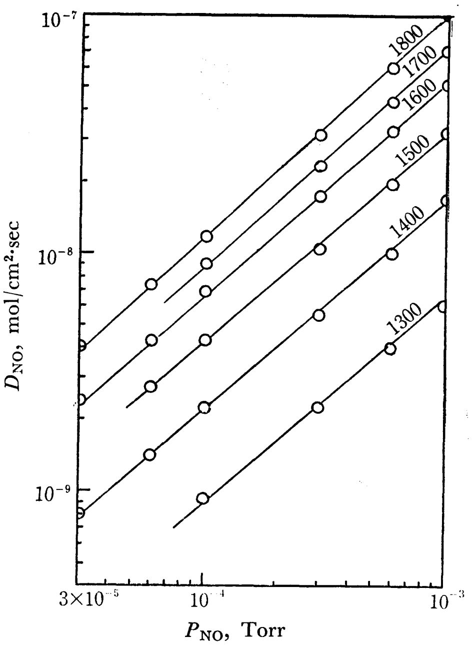

Fig. 3. Effect of nitric oxide pressure on the rate of reaction.

Under these experimental conditions, that is, when the total pressure in the reaction vessel is so low and the surface area of the filament is so small, it is assumed that the temperature of the nitric oxide molecules striking the filament is equal to that of the wall of the reaction vessel and that the pressure is uniform throughout the vessel. Therefore, the number of mols of nitric oxide that strike the filament per second can be calculated from the kinetic theory of gases as follows:

$$P_{NO}S/\sqrt{2\pi MRT}$$

where P_{NO} is the nitric oxide pressure in dyn/cm²; S, the surface area of the filament in cm²; M, the molecular weight of nitric oxide; $\boldsymbol{R}$, the gas constant, and T, the temperature of the reaction vessel. Consequently, the probability, $\boldsymbol{k}$, that a nitric oxide molecule which strikes the filament will disappear from the gaseous phase by some reaction processes can be calculated from the following equation:

$$D_{NO} = \boldsymbol{k}P_{NO}S/\sqrt{2\pi M\boldsymbol{R}T},$$

Table 1. Reaction probabilities at various temperatures at nitric oxide pressures of 6×10^{-4} torr and 1×10^{-4} torr

Filament temp. °K	$\boldsymbol{k}$	
	(6×10^{-4} Torr)	(1×10^{-4} Torr)
1300	0.011	0.015
1350	0.0168	0.024
1400	0.027	0.036
1450	0.039	0.052
1500	0.053	0.069
1550	0.070	0.094
1600	0.0875	0.11
1650	0.101	0.123
1700	0.115	0.141
1770	0.143	0.163
1800	0.161	0.190

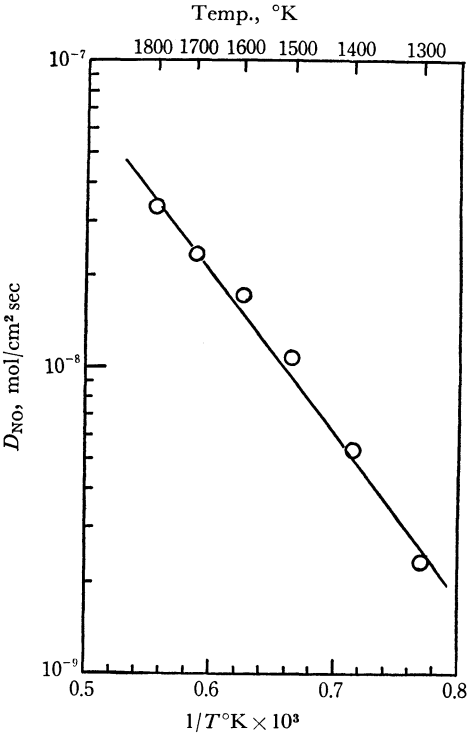

Fig. 4. Effect of filament temperature on the rate of reaction at 3×10^{-4} Torr of nitric oxide pressure.

$\boldsymbol{k}$ is the reaction probability. The reaction probabilities for various temperatures and pressures are given in Table 1. A plot of log D_{NO} *vs.* $1/T$ is given in Fig. 4. The apparent activation energy is about 24 kcal/mol. The effect of the nitrogen pressure on the rate of the consumption of nitric oxide was also investigated; the filament was heated at a constant temperature with various amounts of nitrogen added to the nitric oxide at first. As a result, the rate of consumption was found to be independent of the nitrogen pressure. This coincides with the fact that the nitrogen desorbs from the surface below 1300°K in the flash-desorption experiments.[13,14] If the filament temperature is kept constant, the rate of consumption is simply given as a function of the nitric oxide pressure alone:

$$D_{NO} = K\cdot P_{NO}^{n}$$

or: $$\log D_{NO} = \log K + n \log P_{NO}$$

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[14] T. Tamura, This Bulletin, **44**, 2116 (1971).

where K and n are constants. As can be seen from Fig. 3, the rate of consumption can be considered to be proportional to the nitric oxide pressure. If this reaction occurs with the direct impact of nitric oxide molecules from the gaseous phase to the rhenium surface, the rate of the reaction should depend on the higher-power of the pressure.

The pressure dependence of the rate of this reaction may be explained as follows. The flash-desorption experiments[13,14] have shown that nitric oxide molecules are dissociated to atomic species at high temperatures under the present experimental conditions, and that nitrogen atoms recombine and evaporate as nitrogen molecules, while oxygen atoms remain on the rhenium surface at a considerably high temperature as an adsorbed oxygen layer. Moreover, in the experiment of thermionic electron emission,[15] it was found that the surface condition for the Re-NO reaction was the same as that for the Re-O_2 reaction, the amounts of species other than oxygen atoms were extremely small on the surface, and that the surface was completely covered with oxygen atoms, whose concentration was independent of the nitric oxide pressure.

Since no rhenium oxides other than ReO_3 evaporate in the temperature range of this experiment,[16] we consider that ReO_3 is formed with oxygen atoms in an oxygen layer and incoming nitric oxide molecules. Therefore, the following steps of the reaction may be described:

$$NO_{(g)} \xrightarrow{k_1} N_{(a)} + O_{(a)} \tag{1}$$

$$N_{(a)} + N_{(a)} \xrightarrow{k_2} N_{2(g)} \tag{2}$$

$$NO_{(g)} + 2O_{(a)} + Re \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} ReO_{3(a)} + N_{(a)} \tag{3}$$

$$ReO_{3(a)} \xrightarrow{k_4} ReO_{3(g)} \tag{4}$$

In the step 1, although nitric oxide adsorbs on the rhenium surface as molecules at room temperature, it is decomposed immediately to atomic oxygen and nitrogen at elevated temperatures.[13] No nitric oxide was detected in the desorption from a mixed nitrogen-oxygen layer.[14] Moreover, in another experiment, when the rhenium filament was heated in a mixed gas of nitrogen and oxygen, nitric oxide was not detected by means of an omegatron mass spectrometer. Hence, the backward reaction of step 1 does not occur. In the step 2, hardly any nitrogen exists on the rhenium surface above 1300°K, as has been described above; k_2 in the step 2 is, therefore, very large and the rate of the backward reaction is negligibly small. In the step 3, the recombination and evaporation processes of the adsorbed nitrogen atom are the same as in the step 2; by supposing $k_3 \gg k_{-3}$ and $k_4 \gg k_3$ in such a high temperature range, the step 3 may be regarded as the rate-determining step, and nitric oxide may be regarded as consuming three molecules in one reaction. The rate equation may be written as follows:

$$-d[NO]/dt = D_{NO} = 3k_3P_{NO}.$$

The rate of the reaction between nitric oxide and rhenium is proportional to the nitric oxide pressure.

The Determination of the Composition of Rhenium Oxide. The apparent compositions of rhenium oxides were determined in the temperature range from 1300°K to 2100°K; these results are shown in Table 2, while the O/Re ratios are plotted against the temperature in Fig. 5.

Table 2. Composition of rhenium oxide

Filament temp. °K	Consumed NO mol×10^6	Loss of Re mol×10^6	Oxide ReO_x value x
1300	7.94	2.62	3.03
1400	14.25	4.89	2.92
1500	7.817	2.56	3.05
1600	7.515	2.57	2.93
1700	15.0	4.76	3.15
1800	16.02	4.98	3.22
1900	11.6	3.23	3.48
2000	7.02	2.00	3.50
2100	9.03	2.51	3.59

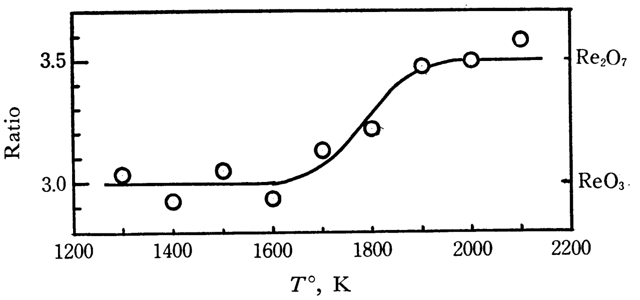

Fig. 5. The ratio, O/Re.

From these results, the ratio is seen to be close to 3.0 below 1700°K and then to increase to a steady value of close to 3.5 above 1900°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. Any ratio that lies between 3.0 and 3.5 may correspond to a mixture of the two oxides. The color of the rhenium oxide deposited on the wall of the reaction vessel depends upon the filament temperature. It is dark blue below 1600°K and colorless above 1900°K, while at intermediate temperatures its color is pale blue. Therefore, from these facts, it is considered that the ReO_3 on the wall is dark blue, that the Re_2O_7 is colorless, and that the pale blue deposit observed in the reactions at intermediate temperatures is composed of these two oxides. Although the apparent composition of Re_2O_7 is obtained at higher temperatures, the formation of Re_2O_7 on the rhenium surface and its evaporation from it at such high temperatures 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. In another

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15) will be published.

16) B. Weber, J. Fusy, and A. Cassuto, "Recent Developments in Mass Spectroscopy," Proceeding of the International Conference in Mass Spectroscopy, Kyoto, ed. by K. Ogata and T. Hayakawa, University of Tokyo Press (1969) p. 1319.

experiment using the omegatron mass spectrometer, when the filament temperature was raised above 1800 °K in nitric oxide, a considerable amount of atomic oxygen was observed. Therefore, we consider that only the ReO_3 evaporates and deposits on the vessel wall, even above 1800°K, and that the ReO_3 on the wall is oxidized succesitively to Re_2O_7 with the atomic oxygen that is evolved in this high-temperature range.

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