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

By Takuya HAMAMURA

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It has been shown previously[1] by a hot filament method that the major part of water molecules impinging on the hot surface of tungsten filament rebound without reaction even at high temperatures. These results, however, were not free from the end effect of the filament, since it was kept cooler at the both ends, where it was joined with leads which were much thicker than the filament and hence practically not heated at all by an electric current; the reaction probability* determined directly from the observed rate of reaction is, in consequence, an average one being smaller than that at the middle portion. The present paper is concerned with the elimination of the effect of the above-mentioned end losses.

Several devices[2] have been reported for the elimination of end losses, e. g., to heat the leads with auxiliary heaters attached to them or to heat the filament from outside of the vessel by an electric furnace, but the former is complicated in structure and the latter is not suitable for the present purpose. The use of a long filament often employed for this purpose is not appropriate to the flow method, since the pressure difference along the filament becomes too large at a high rate of reaction.

Two-filament Method. — In the present work, two filaments differing in length are used and the end effect of the longer filament is compensated with that of the shorter one. Two filaments, one longer (main) and the other shorter (compensating), of the same diameter and material are mounted in the vessel and heated one by one with the same current to obtain the reaction probabilities separately. Then, the reaction probability free from the end effect is obtained as follows. Let L_m and L_c denote the lengths of the two filaments ($L_m > L_c$) and k_m and k_c the respective reaction probabilities. Dividing the main filament into two end portions $L_c/2$ in length each and the middle portion $L_m - L_c$ in length, the reaction probability k_m can be expressed as a weighted mean of the probability k'_c at the end portions and k' at the middle portion. Then, k' is given by

$$k' = (k_m L_m - k'_c L_c)/(L_m - L_c) \qquad (8)^{**}$$

When the two filaments are heated with the same current, the end portions of the longer one will attain the same distribution of temperature as that along the compensating filament, and the middle portion at a uniform temperature provided that the filaments are long enough. Therefore, k'_c is equal to k_c if the reaction probability is independent of the pressure of water vapor, and is equal to k_c at the same partial pressure of water vapor as that under which k_m is obtained if the probability depends upon the pressure. Therefore, if k_c is obtained at various pressures P of water vapor and plotted against P, k'_c is obtained graphically, and hence k', the reaction probability free from the end losses, can be evaluated by Eq. 8. Although the two filaments are heated under the same initial pressure, the partial pressure while the respective filament is being heated is not the same, owing to the difference in the reacting areas of the filaments.

Experimental

Apparatus. — The apparatus was essentially the same as that of the previous paper. Only the changed points will be described below.

A reaction vessel was 7.0 cm. in diameter and 30 cm. in length. In it two tungsten filaments each 0.114 mm. in diameter and 128 mm. and 81 mm. long, respectively, were mounted perpendicular to the axis of the vessel at a distance of 5 cm. from each other. The distributions of

1) N. Sasaki and T. Hamamura, This Bulletin, **29**, 365 (1956).
2) L. B. Thomas and R. E. Brown, *J. Chem. Phys.*, **18**, 1367 (1950).
* The probability of reaction of water molecule with the filament for a single collision.

** Eqs., Figs. and Tables are numbered following consecutively those of the previous paper (Ref. 1).

temperature along the filaments were previously determined by the method of Langmuir and others[3]. The tungsten filaments used were taken from the same spool as that used in the previous experiments and pretreated in a similar manner. A Pirani gauge having a sensitivity of 1.42×10^{-5} mmHg for hydrogen was attached to the glass balloons in place of McLeod manometer M_3. The wall in front of the filaments was protected from the blue deposit of reaction product by a glass tube containing an iron rod which was hung in the vessel with a thin wire and shifted by a solenoid only when the temperature was measured by an optical pyrometer.

Procedure.—Procedures of evacuating the apparatus, degassing the filaments and introducing water vapor into the vessel have been described previously[1]. When the flow of water vapor became stationary, the main filament was heated and the temperature was measured with an optical pyrometer. As the reaction proceeded the pressure in the glass balloons increased gradually and this increase was measured with the Pirani gauge, every two minutes for sixteen minutes. The filament was then cooled and the balloons were evacuated. After this treatment, the compensating filament was heated with the same current and the pressure increase was measured similarly for the same time. The pressure increase gave the rate of reaction, and hence k_m[4] and k_c were evaluated by Eq. 7 and P by Eq. 6. Variations of k_m and k_c with P at a definite temperature were determined by a series of the experiments carried out by heating the filaments with a fixed current under various initial pressures of water vapor.

The temperature of the vessel remained at room temperature throughout the experiments, the effect of the heated filament being negligible at its highest temperature.

Results and Discussion

The experiments were carried out at temperatures from 1430 to 1940°K and initial pressures of water vapor from 12×10^{-5} to 125×10^{-5} mmHg. Values of k_m and k_c obtained were plotted against P in a log—log plot, respectively. Some of them are shown in Fig. 5.

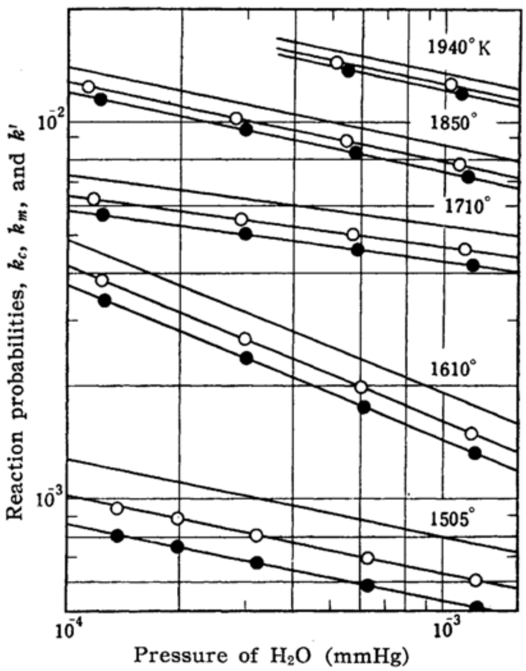

Fig. 5. Effect of pressure of water vapor on the reaction probabilities, k', k_m and k_c.
—— k', —○— k_m, —●— k_c

TABLE II. REACTION PROBABILITIES AT 60×10^{-5} mmHg PRESSURE OF WATER VAPOR

Temp. of filament (°K)	k_m	k_c	k'
1430	$3.3_4\times10^{-4}$	$2.6_3\times10^{-4}$	$4.5_7\times10^{-4}$
1470	$5.1_6\times10^{-4}$	$4.2_0\times10^{-4}$	$6.8_2\times10^{-4}$
1505	$7.0_2\times10^{-4}$	$5.9_1\times10^{-4}$	$8.8_4\times10^{-4}$
1560	$1.2_2\times10^{-3}$	$1.0_6\times10^{-3}$	$1.4_9\times10^{-3}$
1610	$1.9_8\times10^{-3}$	$1.7_6\times10^{-3}$	$2.3_4\times10^{-3}$
1675	$4.0_8\times10^{-3}$	$3.6_7\times10^{-3}$	$4.7_9\times10^{-3}$
1710	$4.9_8\times10^{-3}$	$4.5_7\times10^{-3}$	$5.7_0\times10^{-3}$
1760	$5.3_2\times10^{-3}$	$4.9_4\times10^{-3}$	$5.9_8\times10^{-3}$
1850	$8.7_3\times10^{-3}$	$8.2_5\times10^{-3}$	$9.5_6\times10^{-3}$
1940	$1.4_0\times10^{-2}$	$1.3_5\times10^{-2}$	$1.4_8\times10^{-2}$

From these plots, values of k_m and k'_c at a definite pressure were obtained, and the probability k' free from the end losses was evaluated by Eq. 8. Values of k_m, k'_c and k' at 60×10^{-5} mmHg pressure of water vapor thus obtained are given in Table II. Plots of $\log k'$ vs. $1/T\times10^3$ at 30×10^{-5} and 60×10^{-5} mmHg of water vapor are given in Fig. 6. Humps observed in the curves in the vicinity of 1700°K were not observed in the previous experiments, perhaps because of insufficient points of observation. No hysteresis was observed in the whole range of temperatures. The apparent heat of activation at 60×10^{-5} mmHg of water vapor is plotted against the filament temperature in Fig. 7.

Plots of $\log k'$ vs. $\log P$ at various temperatures are also shown in Fig. 5. It is evident that the elimination of end losses is significant especially at lower temperatures. It was found from this figure that the reaction probability decreased with increase of the pressure of water vapor. Although this decrease seemed to be

3) I. Langmuir, S. MacLane and K. Blodgett, *Phys. Rev.*, 35, 478 (1930).
4) The roughness factor of 1.225 was used according to Tonks. L. Tonks, *Phys. Rev.*, 38, 1030 (1931).

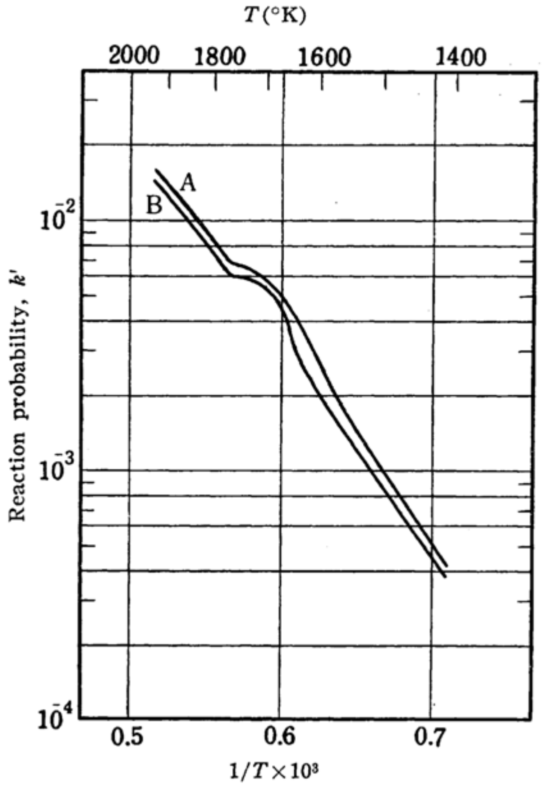

Fig. 6. Effect of filament temperature on the reaction probability k' at 30×10^{-5} and 60×10^{-5} mmHg of water vapor. A—30×10^{-5} mmHg, B—60×10^{-5} mmHg.

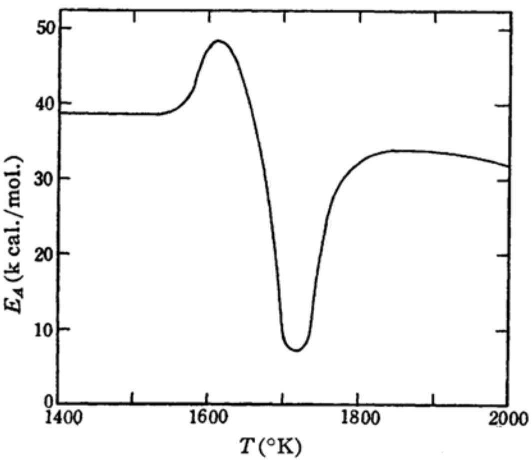

Fig. 7. Apparent heat of activation at 60×10^{-5} mmHg of water vapor.

caused by cooling of the filament by water vapor or by decrease of the reaction probability itself, the lowering of the temperature was not observed by either the optical pyrometer or the resistance of filament.

At filament-temperatures and pressures of water vapor plotted in Fig. 5, the reaction rates were independent of hydrogen pressures. Effect of hydrogen pressure on the reaction rate will be described in the following paper.

From the plot of log k' vs. log P the order n of reaction with respect to water vapor can be determined. As described in the previous paper, the rate of reaction D is given by

$$D=k'SBP \qquad (5)$$

The reaction rate depends only upon the pressure of water vapor, when the filament temperature is fixed, as

$$D=KP^{n} \qquad (9)$$

where K and n are constants. Eliminating D from Eqs. 5 and 9, k' is given by

$$k'=K/SB\times P^{n-1} \qquad (10)$$

or

$$\log k'=\log(K/SB)+(n-1)\log P \qquad (11)$$

The value of $n-1$ is thus given as the slope of the curve of log k' plotted against log P as in Fig. 5. The order of reaction thus obtained are tabulated in Table III. The reaction is nearly the first order.

Table III. Order of reaction

Temp. of filament (°K)	1505	1610	1710	1850	1940
Order of reaction, n	0.8_0	0.6_0	0.8_6	0.8_0	0.8_0

Summary

1) The end effect of filament upon the reaction probability was eliminated by means of the two-filament method. Its principle and procedure were described.

2) Reaction probabilities were determined at temperatures from 1430 to 1940°K and pressures of water vapor from 12×10^{-5} to 125×10^{-5} mmHg.

3) The reaction probability increased remarkably with the increase of temperature, but the rate of increase became smaller in the vicinity of 1700°K.

4) The order of reaction with respect to water vapor was found to lie between 0.6_0 and 0.8_6.

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