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

By Nobuji SASAKI** and Takuya HAMAMURA

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Introduction

For the kinetic study of a series of chemical reactions on the solid surface, the reaction between water vapor and a tungsten filament at high temperatures was first chosen, because the filament can readily provide an extremely clean surface by merely flashing it at a high temperature. The equilibrium study of the system of W, O_2, and H_2 has been reported by some investigaters. Chaudron[1] studied the equilibrium by starting from tungsten trioxide and hydrogen at temperatures ranging from 600 to 1100°C. Wöhler[2] and Gulbransen[3] started from water vapor and tungsten at temperatures below 1000°C. Alterthum[4] extrapolated Wöhler's results to obtain the equilibrium constant at 3000°C where vapors of tungsten oxides also must be taken into consideration and concluded that water vapor in equilibrium must almost completely be decomposed.

From these reports, however, nothing can be guessed about the reaction-kinetic behaviour of water molecules impinging upon the heated surface of tungsten.

The Principle of the Experiment

A tungsten filament is heated inside a cold glass vessel through which a reacting gas is rapidly flowing at a sufficiently low pressure. In this way some unnecessary complications can be avoided, namely, the rate of diffusion of the reacting gas has no influence on the rate of reaction, and the reaction products diffuse away to the cold wall of the reaction vessel to escape any secondary reaction in the gas phase. The collision frequency of gas molecules with the reacting surface can be calculated easily, so that the reaction probability per collision of the reacting gas molecule can be evaluated provided that the over-all rate of the reaction can be determined separately. The surface area of the filament can be determined from

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** Department of Chemistry, Faculty of Science, Kyoto University.

1) M.G. Chaudron, *Compt. Rend.*, **170**, 1056 (1920).

2) L. Wöhler and R. Gunther, *Z. Elektrochem.*, **29**, 276 (1923).

3) E.A. Gulbransen, *J. Phys. Colloid. Chem.*, **53**, 690 (1949).

4) H. Alterthum and F. Koref, *Z. Elektrochem.*, **31**, 508 (1925).

the apparent area by multiplying a certain factor correcting for the roughness[5]. The method of obtaining a high temperature for a chemical reaction by heating a filament electrically has the advantage of dispensing with a special refractory material and heating devices.

The flow method is preferred to the static one to avoid the effect of the adsorption of water vapor on the wall, which is inevitable in the static method at very low pressures.

Apparatus.—The apparatus of all soda-glass is shown schematically in Fig. 1. Reservoir 1 connected in a desired combination by means of stop cocks. To determine the composition of the permanent gasses consisting of hydrogen and possibly a small amount of oxygen, the pressure is measured with McLeod gauge M_3 and quartz fibre manometer M_2 at the same time. From the measurement the apparent molecular weight and therefore the composition of the gas can be determined. One percent oxygen added to pure hydrogen reduces by about 7 seconds the interval of time (195 seconds at 50×10^{-4} mmHg.) required for the amplitude to decrease to half value. Trap 8 cooled with dry ice is to prevent grease vapor from entering into the reaction vessel. Particular

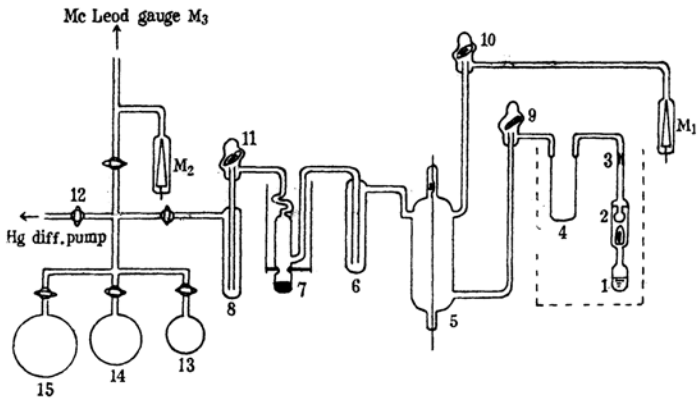


Fig. 1.

taining about 3 cc. of purified water can be connected directly to the reaction vessel by breaking a thin glass bulb 2 by means of a glass rod containing an iron core and disconnected from it by chipping constriction 3 when the experiment is finished.

Water was purified by repeating sublimation in a high vacuum, dry ice being used for condensation. Capillary tube 4 controls the flow of water vapor. The reservoir and the capillary are immersed in a thermostat. Reaction vessel 5 is 3.5 cm. in diameter and 12 cm. long, so that the pressure gradient along the vessel may be negligibly small. Manometer M_1 used to measure the pressure of condensible water vapor is a 70 mm. long hair pin of 0.3 mm. diameter quartz fibre. It was calibrated against a McLeod gauge using oxygen and hydrogen. The vapor pressure within the reaction vessel can be changed by the change of temperature of the thermostat. A tungsten filament 0.114 mm. in diameter and 120 mm. long was cleaned by dipping in the boiling 40 percent caustic soda solution for five minutes followed by wiping off aqua dag with filter paper, and then it was stretched along the axis of the vessel by means of a tungsten spring. Trap 6 cooled in liquid nitrogen freezes out undecomposed water vapor coming from the reaction vessel. Permanent gasses untrapped are compressed by mercury diffusion pump 7 into glass balloons 13, 14, 15 of different volume from 634 to 6543 cc.

5) L. Tonks, *Phys. Rev.*, **38**, 1030 (1931).

precautions have been taken to keep the filament from grease vapor contamination by using greaseless stop cock 9, 10, 11, which can be operated with a magnet.

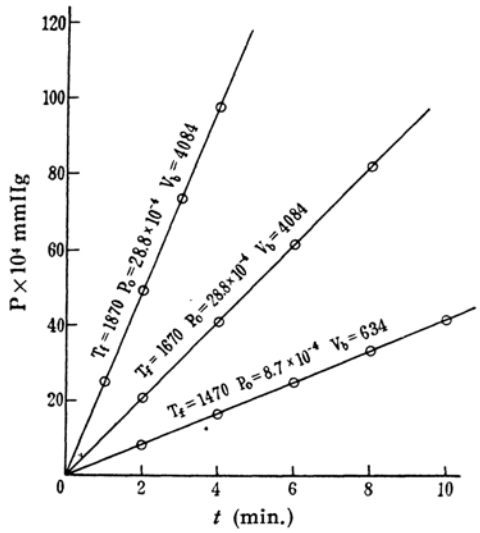
The Procedure.—Prior to the proper experiment, all the apparatus is evacuated for several days by a mercury diffusion pump with a liquid nitrogen trap before it. The reaction vessel is heated at 300°C for ten hours in an electric furnace, and the other tubes are baked out by a hand burner. After thorough evacuation of the cooled vessel the filament is heated at 2400°K for twelve hours.

After the degassing schedule is over, trap 6 is dipped into liquid nitrogen, and glass bulb 2 is broken, the thermostat being kept at a desired temperature. Water vapor flows into the reaction vessel through the capillary tube to be frozen out in trap 6. Pressure measurements with quartz fibre manometer M_1 will show the moment when the flow has become stationary. The filament is now heated, and the temperature is measured with an optical pyrometer. As the reaction proceeds the pressure in the glass balloons increases gradually and this increase is measured with McLeod gauge M_3 at suitable intervals for about eight minutes. The filament is then cooled and the balloons are evacuated through cock 12.

Experimental Result

The pressure of the balloons increases linearly with the time of heating. Some

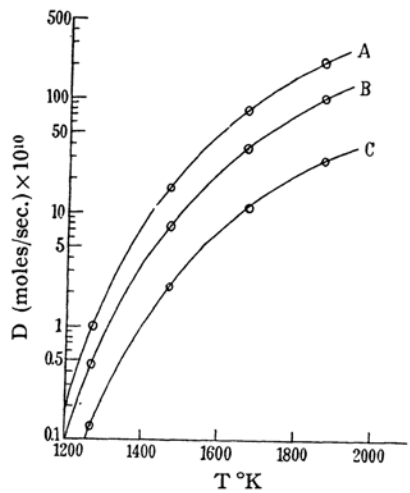
typical examples are shown in Fig. 2. The



T_b=temp. of filament (°K)
P_0=press of H_2O (mmHg)
V_b=vol of balloons (cc.)

Fig. 2. The pressure change of the glass balloons with the time of heating.

linearity can be observed for more than thirty minutes. This shows the stability both of the flow of water vapor and the surface condition of the filament. The rate of increase of the pressure gives the rate of reaction which is shown in Fig. 3 as a



A ; $P_0=64\times10^{-4}$ mmHg
B ; $P_0=28.8\times10^{-4}$ mmHg
C ; $P_0=8.7\times10^{-4}$ mmHg

Fig. 3. Rate of reaction at various filament temperature.

function of the filament temperature. The gas analysis carried out as mentioned above shows the gas produced to be pure hydrogen for varied conditions of the reaction. The temperature increase of the reaction vessel is negligibly small when the filament is heated.

Discussion

From the reaction rates thus obtained, it is possible to evaluate the probability of reaction of a water molecule with the surface of tungsten when a molecule impinges upon it. If the pressure of water vapor is low and the mean free path is comparable with the diameter of the vessel and the length of the vessel is not too long, the following conditions are satisfied.

1. The composition and the pressure of the gas are uniform throughout the vessel.
2. The temperature of water molecules inside the vessel is equal to that of the wall.
3. The flow of gas molecules through the outlet tube obeys Knudsen's law of molecular flow.

Now, if the filament is heated, and water vapor is introduced into the vessel, a part of the water molecules reacts with the filament and leaves the vessel together with the unchanged molecules which are caught in the trap. The quantity in moles of water vapor thus trapped per second is

$$\frac{8\pi r^3}{3l}\times\frac{P}{\sqrt{2\pi MRT}} \qquad (1)$$

where r and l are respectively the radius and the length of the outlet tube in cm, P the partial pressure of water vapor inside the vessel in dyne/cm², M the molecular weight of water, and R the molar gas constant.

Putting $\frac{8\pi r^3}{3l}=A$ and $\frac{1}{\sqrt{2\pi MRT}}=B$ in (1)

it becomes $$ABP. \qquad (1')$$

The quantity in moles of water vapor which reacts per second with the filament is

$$kSBP \qquad (2)$$

where k is the probability of reaction of the water molecule with the filament for a single collision, and S the surface area in cm² of the filament. The quantity of water vapor G which enters into the vessel through the inlet tube per second is equal to the sum of (1′) and (2),

thus $$G=ABP+kSBP. \qquad (3)$$

On the other hand

$$G=ABP_0 \qquad (4)$$

if P_0 is the pressure of water vapor inside the reaction vessel when the filament is cold.

The stationary state being assumed, the quantity in moles of the permanent gas produced in the vessel per second is equal to that of the gas D carried into the balloons per second by mercury pump 7 so that

$$D=kSBP \tag{5}$$

provided that one mole of hydrogen alone is produced from one mole of water. From Eqs. (3) and (5), P which is difficult to measure directly is given by

$$P=\frac{G-D}{AB}. \tag{6}$$

Eliminating P and G from Eq. (3), we get

$$k=\frac{AD}{S(ABP_0-D)}. \tag{7}$$

Thus k, the probability of reaction of the water molecule with the filament for a single collision, may be evaluated from all measurable quantities for various filament temperatures and water vapor pressures.

For the conductance A of the outlet tube the value of 0.047 cm² is used which has been obtained by actually passing carbon dioxide, (the calculated value is 0.055 cm²) and for the roughness factor of the filament the value of 1.225 is used according to the result of Tonks[5].

Results

The probabilities of reaction for a single collision of the water molecule with the heated tungsten surface thus evaluated are shown in Table I.

The conclusion therefrom is that the major part of water molecules which hit the hot surface rebound without reacting with it even at the high temperatures employed, and the reaction is of the first order with regard to the pressure of water vapor. The relation between the reaction probability and the temperature of the filament is given in Fig. 4. The mechanism of the reaction will be discussed in the succeeding paper.

6) Roughness factor of the tungsten filament.

TABLE I

Temp. of filament (°K)	Probability of reaction ($k\times1.225$[6])	Press. of water P_0 (mmHg)	Press. of water P (mmHg)
1270	4.5×10^{-5}	8.7×10^{-4}	8.7×10^{-4}
	4.8×10^{-5}	29×10^{-4}	29×10^{-4}
	4.6×10^{-5}	64×10^{-4}	64×10^{-4}
1470	7.9×10^{-4}	8.7×10^{-4}	8.7×10^{-4}
	8.2×10^{-4}	29×10^{-4}	29×10^{-4}
	8.0×10^{-4}	64×10^{-4}	64×10^{-4}
1670	4.2×10^{-3}	8.7×10^{-4}	8.4×10^{-4}
	3.9×10^{-3}	29×10^{-4}	28×10^{-4}
	3.8×10^{-3}	64×10^{-4}	62×10^{-4}
1870	1.1×10^{-2}	8.7×10^{-4}	7.9×10^{-4}
	1.2×10^{-2}	29×10^{-4}	26×10^{-4}
	1.1×10^{-2}	64×10^{-4}	58×10^{-4}

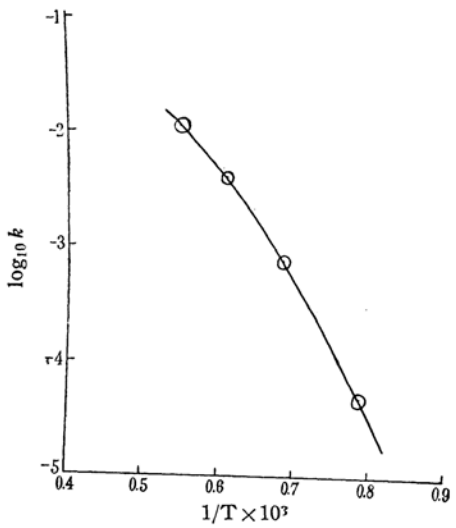


Fig. 4. Effect of the filament temperature on the reaction probability.

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Department of Chemistry, Faculty of Industrial Art, Kyoto Technical University, Kyoto