Summary

The choice of a standard form of copper for use in potential measurements was discussed.

The standard potential of copper amalgam and the activity coefficients of copper sulfate over a limited range were determined.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 42]

THE CATALYTIC SYNTHESIS OF WATER VAPOR IN CONTACT WITH METALLIC GOLD[1]

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Introduction

In a previous communication[3] evidence was presented to show that the mechanism of water formation over a reduced silver catalyst involves collisions of gaseous hydrogen with adsorbed oxygen on that fraction of the surface not covered by adsorbed water. In this case the reaction kinetics proved to be relatively simple.

Metallic gold like metallic silver does not form definite compounds by direct combination at ordinary pressures with either hydrogen or oxygen.[4] Their similarity in chemical properties would lead one to expect that the reactions in contact with the two metals would exhibit similar kinetics and mechanism. The present investigation shows that this is not the case, although the adsorption phenomena for the two metals are similar.

Bone and Wheeler[5] have studied the hydrogen-oxygen combination in contact with gold gauze at 250° by a circulatory method. They state that the results for gold and silver were analogous; namely, that the rate of reaction was roughly proportional to the pressure of hydrogen, but independent of the pressure of oxygen, and that the activity of the catalyst was greatly stimulated by previous heating in hydrogen but not in oxygen. This latter effect was further investigated by Chapman, Ramsbottom and Trotman.[6]

The experimental method and the conclusions of Bone and Wheeler have been discussed and criticized in other places.[3] The difficulties

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[1] Presented before the Division of Physical and Inorganic Chemistry at the meeting of the American Chemical Society held at Richmond, Virginia, April 11–16, 1927.

[2] Du Pont Fellow in Chemistry during the period covered by this investigation.

[3] Benton and Elgin, THIS JOURNAL, **48,** 3027 (1926).

[4] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans and Co., London, **1923,** Vol. III, pp. 525–526, 577.

[5] Bone and Wheeler, *Phil. Trans.*, **206A,** 1 (1906).

[6] Chapman, Ramsbottom and Trotman, *Proc. Roy. Soc.* (*London*), **107A,** 29 (1925).

inherent in the manometric method of measuring contact catalytic reactions were avoided in the present study by use of the flow method', which allowed the attainment of a "steady state" under each set of conditions. The kinetics of the reaction have been accurately determined, the adsorptions of hydrogen and oxygen by the gold catalyst measured and an attempt made to deduce a mechanism for the catalytic reaction.

Experimental Method

Apparatus.—The apparatus was the same as that employed in the investigation of the reaction in contact with metallic silver. Suitably purified gas mixtures were passed over the catalyst maintained at constant temperature in an electric furnace, and the progress of the reaction was followed by weighing the water absorbed in a calcium chloride tube from the exit gases during time intervals of five minutes.

Preparation of the Catalyst.—A 6% solution of C. P. gold chloride was heated to 80° and a slight excess of a 6% solution of sodium carbonate added with constant stirring. The mixture was then heated to boiling for thirty minutes. The precipitated gold hydroxide was washed repeatedly by decantation, then filtered off and the washing continued until no chloride could be detected in the wash water. The layer next to the filter paper was discarded, and the remainder dried in an oven at 100°.

The hydroxide was reduced in a current of dried hydrogen. The reduction was started at about 5°, but the temperature increased slowly as reaction proceeded. The temperature was maintained at 35° for fifteen hours, after which it was slowly raised to 100° and maintained until no water could be detected in the exit gas.

The reduced gold thus obtained was placed in the catalyst furnace and heated in a stream of dry oxygen at 200° for two hours. This sample of gold was used throughout the experiments, and gave detectable conversion at 100°. It was 2.1 cm. in diameter and approximately 2 cm. high, giving an apparent volume of 7 cc. Its weight was 8.78 g.

Procedure.—The procedure used with silver was followed. The uniform preliminary treatment of the catalyst with hydrogen for an hour previous to each run was made at 130°. The total rate of flow was maintained constant at 50.0 cc. (0°, 760 mm.) per minute throughout the experiments.

Check runs were made alternately throughout the investigation. During the first ten runs no material change in catalyst activity was noted. The small changes which occurred in the later runs were corrected for by adding to or subtracting from the yield in each run the percentage amount per run necessary to make the checks agree.

Experimental Results on Reaction Kinetics

One hundred thirty degrees proved to be a convenient temperature at which to investigate the reaction kinetics. The results of typical catalytic runs are shown in Fig. 1, in which the yield of water per five minute interval is plotted as a function of time.

With oxygen in excess the initial course of the reaction could not be followed due to the time required to sweep from the furnace the hydrogen used in the preliminary treatment. Here attainment of the "steady state" required a much longer time than when hydrogen was present in excess. In the previous work with silver, the "steady state" was always reached within an hour of the start of a run, irrespective of which gas was present in excess.

When hydrogen was used in excess, determinations of the oxygen present in the exit gas showed that the rate at which oxygen disappeared was equivalent to the rate of water formation. This fact indicates that oxygen was not continuously taken up and retained by the catalyst in any considerable amount. From experiments with oxygen in excess, a similar conclusion was drawn in regard to hydrogen.

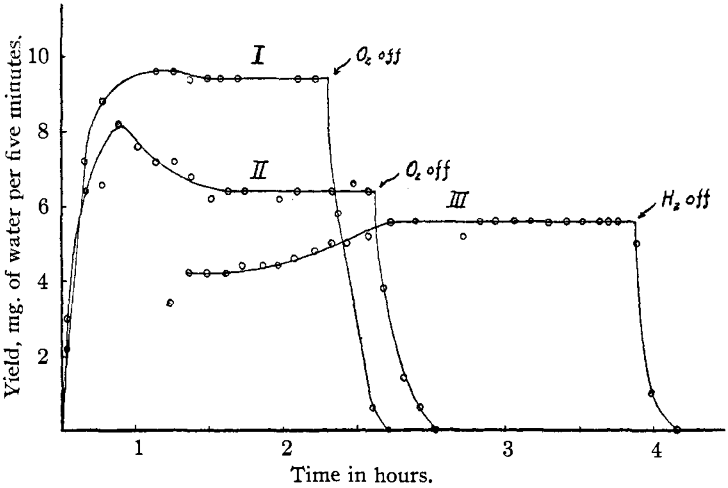

Fig. 1.—Variation of yield with time in typical runs. Curves I (Run 7) and II (Run 6) are with excess hydrogen, and oxygen equivalent to 40.4 and 20.2 mg. of water per five minutes, respectively. Curve III (Run 12) is with excess oxygen, and hydrogen equivalent to 40.4 mg. of water per five minutes.

With constant total flow rate the influence on the yield of oxygen pressure, hydrogen pressure and temperature, as well as the effect of water vapor and of preliminary treatment of the catalyst with oxygen, have been studied.

Effect of Oxygen Pressure.—To determine the effect of oxygen pressure on the rate, experiments were made at 130° with excess hydrogen and with amounts of oxygen equivalent to from 10 to 100 milligrams of water per five minutes. The average partial pressures corresponding to these quantities may be seen in Table I. In order to keep the flow constant and at the same time vary the oxygen pressure, the flow of hydrogen was suitably adjusted to allow for variations in the volume of oxygen introduced. The average hydrogen pressures, therefore, vary slightly, but due to the excess of hydrogen this does not exert a marked influence upon the yield, as will be shown below. The variation is taken care of quantitatively in the final equation summarizing the kinetic results.

TABLE I

EFFECT OF OXYGEN PRESSURE ON THE YIELD

Total flow rate, 50 cc. per minute. Temperature, 130°

Run no.	Oxygen, cc. per min.	Barometer, mm.	Av. hydrogen press., mm.	Av. oxygen press., mm.	Yield, mg. of water per five minutes	
					Calcd.	Obs.
5	5.02	745.7	661.6	66.7	40.4	9.2
6	2.51	749.9	706.0	31.7	20.2	6.4
7	5.02	749.0	664.2	66.8	40.4	9.4
8	1.25	750.1	727.0	15.8	10.1	4.6
9	5.02	756.0	670.5	67.1	40.4	9.3
10	12.55	757.0	551.9	180.1	101.0	13.0

These experiments show that the rate of the reaction in contact with gold, unlike the case of silver, is a function of the oxygen pressure. Although the yield appears to be approximately proportional to the square root of the oxygen pressure under these conditions, the true relation can be found only by taking into consideration the effect on the yield of the varying quantities of water vapor produced. This effect forms the subject of a later section.

Effect of Hydrogen Pressure.—The influence of hydrogen pressure was next investigated, using small hydrogen concentrations in excess oxygen. Quantities of hydrogen equivalent to 10 to 100 milligrams of water per five minutes were used. The alternate check runs showed a gradual change in activity during the series. Run 16 was chosen as the standard since this seemed best to represent the state of activity existing in the series with excess hydrogen. The yields of the present runs have been corrected to this standard by adding or subtracting the required amounts in the manner previously indicated. Run 19 was used in relating the results of Tables I and II. The corrected yields of runs 5

TABLE II

EFFECT OF HYDROGEN PRESSURE ON THE YIELD

Total flow rate, 50 cc. per minute. Temperature, 130°

Run no.	Hydrogen, cc. per min.	Barometer, mm.	Av. oxygen press., mm.	Av. hydrogen press., mm.	Yield, mg. of water per five minutes		
					Calcd.	Obs.	Corr.
12	10.04	743.7	593.8	139.4	40.4	5.6	5.0
13	5.02	746.6	671.7	69.7	20.2	2.8	2.6
14	10.04	744.6	594.6	140.3	40.4	5.2	5.0
15	2.51	744.0	706.8	34.7	10.1	1.4	1.4
16	10.04	746.7	595.6	141.8	40.4	5.0	5.0
17	25.09	746.6	364.8	360.2	101.0	9.2	9.8
18	10.04	751.8	...	...	40.4	4.4	5.0
19[a]	44.98	748.8	66.9	667.1	40.4	8.6	9.2

[a] Excess hydrogen.

to 19 are thus based, as closely as possible, on the same state of catalyst activity. The data obtained for the effect of hydrogen pressure are given in Table II.

From these experiments it is seen that when oxygen is present in large excess the rate of water formation is markedly dependent upon the hydrogen pressure. The apparent proportionality to the first power of the pressure of this gas must be corrected, as in the case of oxygen, for the variations in the pressure of water vapor. Incidentally it may be mentioned that the largest conversion obtained was with an approximately stoichiometric mixture.

Effect of Water Vapor.—A series of five runs was made to determine the effect on the yield of water vapor initially present in the entering gas. The desired concentration of water vapor was added by passing the entering gas through a saturating train containing distilled water at the required temperature. Table III gives the data obtained.

TABLE III

EFFECT OF WATER VAPOR ON THE YIELD

Excess hydrogen. Temperature, 130°. Total flow, including entering water vapor, 50 cc. per minute.

Run no.	Barometer, mm.	Oxygen cc. per min.	Mg. water per 5 min. in entering gas	Mg. water per 5 min. in exit gas	Yield, mg. of water per five minutes	
					Obs.	Corr.
23	743.4	5.02	0.0	9.6	9.6	8.6
24	740.4	5.02	5.6	9.2	3.6	3.4
25	739.9	5.02	0.0	8.6	8.6	8.6
26	743.0	5.02	1.6	10.2	8.6	7.2
27	743.7	5.02	0.0	11.4	11.4	8.6

Water vapor initially present in the reacting gases markedly decreases the rate of water formation. The effect is greater when larger amounts of water are present. However, the retardation in these experiments is not nearly so marked as that observed with silver. This undoubtedly is to be attributed to the higher temperature used in the present instance. The retarding influence exhibited by water vapor can be ascribed to the adsorption of water vapor on the gold surface, which largely prevents contact with the reacting gases.

Temperature Coefficient.—To ascertain the variation of yield with temperature, the run with excess hydrogen and an oxygen concentration equivalent to 40.4 milligrams of water per five minutes was made at several temperatures. Due to increased yield at higher temperatures, the average pressures of hydrogen and oxygen varied somewhat through the series. The yields have, therefore, been corrected to a hydrogen pressure of 660 mm. and an oxygen pressure of 67 mm., using the data previously obtained for the effect of the pressures of these gases. Due to the large excess of hydrogen, the corrections for variation in its average pressure are practically negligible. The results are recorded in Table IV.

TABLE IV

EFFECT OF TEMPERATURE ON THE YIELD

An excess of hydrogen was used. Total flow rate, 50 cc. per min.

Run no.	Temp., °C.	Av. hydrogen press., mm.	Av. oxygen press., mm.	Yield, mg. of water per 5 min. Obs.	Corr. for activity	Corr. for activ. and gas press.
19	130	664.6	67.8	8.6	8.6	8.6
20	145	651.2	58.1	19.2	19.2	20.9
21	130	662.3	67.5	8.6	8.6	8.6
22	151	637.9	48.5	29.1	25.7	31.2
23	130	658.8	66.4	9.6	8.6	8.6

If the logarithms of the corrected yields are plotted against the reciprocals of the absolute temperatures a straight line is obtained. The slope of this line when multiplied by —4.58 gives a value of 20,800 calories for the apparent heat of activation (E). This is about 8000 calories larger than the value obtained with a silver catalyst. The actual temperature coefficient for a 10 degree rise is 1.95 for the interval 130–140° and 1.88 for the interval 145–155°. The average temperature coefficient with silver was 1.6.

Effect of Preliminary Heating of the Catalyst in Oxygen.—In the runs made to determine the effect of preliminary treatment of the catalyst with each reacting gas all other conditions were identical. The results are shown in Table V.

TABLE V

EFFECT OF PRELIMINARY TREATMENT OF THE CATALYST

Temp., 130°. Excess hydrogen. Flow rate, 50 cc. per min. Calcd. yield, 40.4 mg.

Run no.	Preliminary heating at 130° In hydrogen, hours	In oxygen, hours	Obs. yield, mg. of water per 5 min. Time from start, hours One quarter	One	Two	Three
27	1	...	..	11.4	11.4	11.4
28	...	1	26.2	16.0	13.2	...
29	1	...	11.6	12.0	12.8	13.0
30	...	6.5	31.0	23.8	18.6	17.8
31	1	...	16.4	15.2	15.2	...
32	9	...	10.4	11.6	12.8	13.8

These experiments show that the gold is a more active catalyst after preliminary heating in oxygen. The stimulating effect was not lasting, a maximum yield being obtained at first, followed by a gradual decrease toward a normal one after several hours' time. Preliminary treatment with oxygen for six and one-half hours is more effective and enduring than treatment for one hour.

Sieverts[7] found that gold *ab*sorbs neither hydrogen nor oxygen under any conditions examined, and the measurements described below show that under the prevailing conditions oxygen but not hydrogen is appreciably *ad*sorbed. The effect observed is, therefore, presumably to be con-

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[7] Sieverts, *Z. physik. Chem.*, **60**, 179 (1907).

sidered as an increase in yield due to oxygen treatment rather than a decrease due to hydrogen.

The difference between the total quantity of water obtained in a run following treatment with oxygen and that which would be obtained over the same period in a normal run, in which the catalyst was previously heated in hydrogen, was many times greater than the amount equivalent to the volume of oxygen which the subsequent adsorption experiments showed was taken up by the catalyst. The increased yield is not, therefore, simply the conversion of the oxygen adsorbed during the preliminary treatment. The presence of oxygen initially on the surface produces some distinctive influence on the rate of the reaction which gradually disappears as the reaction proceeds.

A proposed explanation of the observed phenomena will be considered in the discussion.

Adsorption Measurements

Apparatus and Procedure.—The adsorption measurements were made by the usual static method. The essential features of the apparatus were a bulb containing the gold connected by 3-way stopcocks to a mercury manometer, a Töpler pump, a gas buret with mercury as retaining liquid and generating and purifying lines for the gases employed.

The adsorptions at each pressure were determined in separate experiments. The bulb was evacuated at the desired temperature (generally 130°) and the gas admitted up to a definite pressure. The pressure change was followed at frequent intervals until it became very small. Occasional readings were then taken until successive ones over about six hours' time were identical, when equilibrium was assumed to have been reached. The volume adsorbed at each pressure was determined by subtracting from the total volume admitted the volume of gas in the free space. The latter was measured with nitrogen, which was assumed not to be measurably adsorbed.

The bulb was evacuated at 130° immediately following an experiment, and the gas pumped off measured. Adsorbed oxygen could not be pumped from the surface at this temperature and it was therefore necessary to burn it off with hydrogen after each measurement. The hydrogen recovered after this process was measured. The amount disappearing was closely equivalent to the volume of oxygen which was found to remain on the surface after an oxygen run,

The sample of gold used in the catalytic experiments was employed. Some of it was lost in transferring to the adsorption bulb so that its weight was reduced to 7,94 g.

Results.—The oxygen adsorption isotherm for 130° is shown in Fig. 2. The results of the measurements are summarized in Table VI.

Attempts were made to measure hydrogen adsorption at 25° on the gold surface covered with adsorbed oxygen, but no adsorption could be detected under such conditions.

The measurements show that considerable quantities of oxygen are adsorbed, but a scarcely measurable amount of hydrogen. Although the hydrogen was quantitatively recoverable, only a few tenths of a cubic centimeter of oxygen could be pumped off at 130° after an experiment with this gas. It is evident that the adsorption of oxygen at equilibrium is very nearly independent of the pressure.

TABLE VI

ADSORPTIONS BY 7.94 G. OF GOLD

Gas	Temp., °C.	Vol. introduced, cc.	Vol. in free space, cc.	Final press., mm.	Vol. adsorbed, cc.
H_2	130	28.27	28.17	739.2	0.10
O_2	130	3.57	0.0	0.0	3.57
O_2	130	6.95	2.78	74.7	4.17
O_2	130	20.35	15.75	416.0	4.60
O_2	130	29.48	24.70	646.2	4.78
O_2	130	29.46	24.65	650.2	4.81
O_2	98	32.15	28.58	676.6	3.57
O_2	157	28.78	23.05	646.0	5.73
O_2	157	29.46	23.70	657.7	5.76

In the range of the measurements the oxygen adsorption at apparent equilibrium increases with increasing temperature. At about 650 mm. pressure the gold took up 3.57 cc. at 98°, 4.78 cc. at 130° and 5.73 cc. at 157°. At first glance these results would seem to indicate a negative heat of adsorption. This conclusion would, however, be justifiable only in case true equilibrium is attained at each temperature. To test this point further, the oxygen adsorption at 130° and 650 mm. pressure was repeated, the measurement being continued for forty-eight hours after apparent equilibrium had been reached. Without removing the oxygen, the temperature was raised to 157° and the system allowed to come to equilibrium. The adsorptions so determined were in agreement with those found in the previous experiments. The temperature was then lowered to 130°. Although this temperature was maintained for eighty hours no decrease occurred in the amount of gas adsorbed. Hence we must conclude that, in spite of the apparent constancy of the pressure, true equilibrium was not attained in the first part of the experiment.

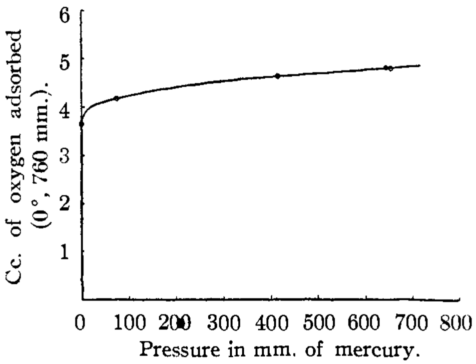

Fig. 2.—Oxygen adsorption isotherm at 130°.

Rate of Oxygen Adsorption.—Typical curves showing the rate of oxygen adsorption at different temperatures and pressures are shown in Fig. 3, in which manometer readings are plotted against the square root of the time, this function being chosen merely for convenience. It will be noted that the rate decreases markedly with decreasing temperature.

Thus at 130° approximately twenty-four hours were required for apparent equilibrium to be established, one hundred and eight hours at 98°, while at 25° only 4 mm. pressure drop, corresponding to an adsorption of 0.1 cc. of gas, occurred in seven hours. Curves III and IV of Fig. 3 show that the rate of adsorption is nearly independent of the gas pressure. During the first minute the rate is slightly higher at the higher pressures, but thereafter no appreciable difference was observed. Experiments at intermediate pressures, not shown in Fig. 3, confirm these results.

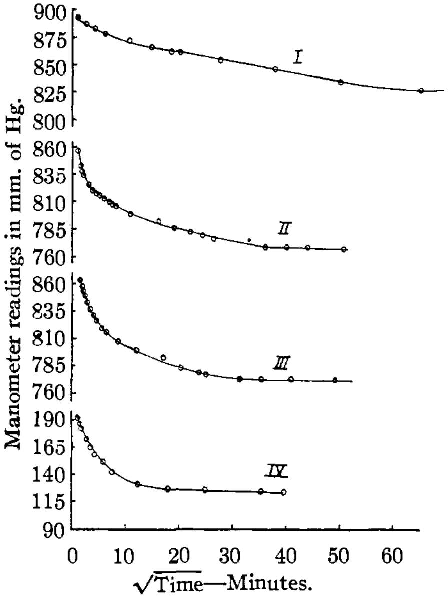

Fig. 3.—Decrease of pressure with time in the adsorption of oxygen. Curve I is for 98° and 752 mm. and Curve II for 157° and 735 mm. pressure. Curves III and IV are for 130° and 776 and 94 mm. initial pressures, respectively.

In the previous work with silver. slow rates of oxygen adsorption were also encountered, but to a less pronounced degree than in the present experiments with gold. The slow rate of adsorption cannot be attributed to oxidation of the gold in the ordinary sense since it is well established that this metal is not oxidized by oxygen under any conditions. The possibility that the slow disappearance of oxygen is due to solution appears improbable in view of Sieverts' measurements,[7] which indicate that massive gold does not dissolve this gas in appreciable quantities at any temperature. It seems necessary to conclude that at least that part of the gas taken up at low pressures, which is the major portion, is in the *ad*sorbed state.

Discussion

Kinetics.—The treatment of the kinetics in flow systems is much simplified by expressing the yield as a function of the average pressures of the various gases instead of employing the more accurate method of integration. We have previously shown[8] that this approximation is justifiable unless the conversion approaches completion.

Since water vapor markedly retards the reaction, presumably because of extensive adsorption on the catalyst surface, the effect of changes in the pressure of this gas must be included in the consideration of the kinetics.

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[8] Benton, *Ind. Eng. Chem.*, 19, 494 (1927).

It has been shown by Langmuir[9] that the fraction of a surface not covered by adsorbed gas is given by the expression $1/(1 + ap)$, where p is the gas pressure and a is a constant at a given temperature. For large adsorptions this reduces to $1/ap$. We may, therefore, write for the yield in the reaction under consideration

$$Y = kp_h^m \cdot p_o^n/ap_w$$

where p_h, p_o and p_w are the averages of the inlet and exit pressures of hydrogen, oxygen and water, respectively, k is the reaction-rate constant and m and n are constants to be determined by comparison with experiment. In the present work the rate of flow was maintained constant, and, therefore, p_w is proportional to Y. Hence,

$$Y^2 = k \cdot p_h^m \cdot p_o^n$$

This expression shows that the exponents of the pressures of the hydrogen and oxygen should be twice as great as those which are obtained when the retarding effect of the water vapor is neglected. Since the results of Tables I and II indicate that the apparent exponents are unity and 0.5, respectively, before correcting for the effect of the water, the true kinetic equation evidently should be

$$Y = k \cdot p_h^2 \cdot p_o/(1 + ap_w)$$

This may be put in the form

$$\frac{p_h^2 \cdot p_o}{Y} = \frac{1}{k}(1 + ap_w) = \frac{1}{k} + k'Y$$

If this relation satisfies the data, the points obtained by plotting $p_h^2 \cdot p_o/Y$ against Y at constant temperature should fall on a straight line. Fig. 4 shows that this is the case for the results of Tables I and II considered separately. It is possible that the failure of the points obtained with excess oxygen and with excess hydrogen, respectively, to fall on the same curve is due to a real difference in kinetics in the two cases, but in view of the uncertainty in the correction of the separate series to the same state of catalyst activity, it is felt that no stress should be laid on this point.

Reaction Mechanism.—It has been shown previously that an active silver catalyst adsorbs oxygen to an extent nearly independent of the pressure, but does not adsorb hydrogen. It would appear reasonably certain, therefore, that during catalysis the active parts of the silver surface are largely covered with adsorbed oxygen under all conditions. In agreement with this result the rate of water formation was found to be independent of oxygen pressure and directly proportional to the pressure of hydrogen. Since a gold catalyst adsorbs the gases in question in a similar manner, it would appear that the kinetics with gold should be similar to those with silver. With gold, however, the yield is proportional to the

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[9] Langmuir, This Journal, **40**, 1370 (1918).

square of the hydrogen pressure and to the first power of the oxygen. Since in both cases the oxygen adsorptions at equilibrium are nearly independent of the pressure, the only basis upon which to explain this difference in reaction kinetics appears to lie in the fact that the *rate* of oxygen adsorption on gold is considerably slower than on silver. More than half of the equilibrium adsorption on silver occurs instantaneously, while less than a quarter occurs thus with gold. Nevertheless, it is evident that this explanation alone is inadequate to account for all the facts, since the rate of adsorption of oxygen by gold is almost entirely independent of the pressure.

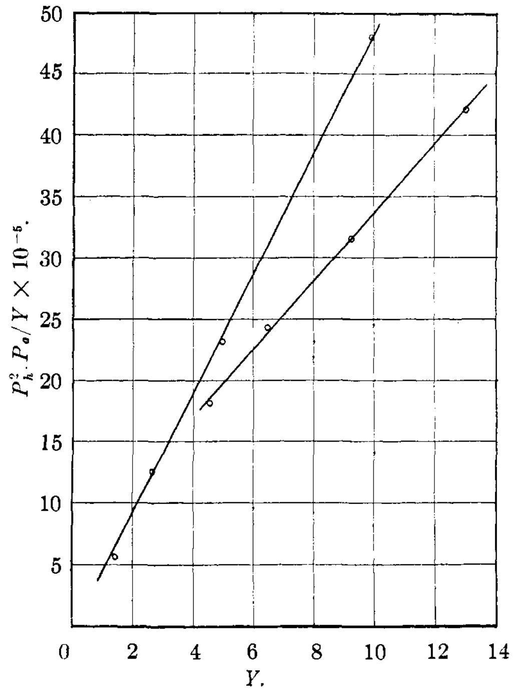

Fig. 4.—The combined effect on the yield of hydrogen, oxygen and water-vapor pressures at constant temperature. Upper curve, Runs 12–18, Table II (with excess oxygen); lower curve, Runs 5–10, Table I (with excess hydrogen).

The possibility exists that the rate of adsorption which is of importance in the catalysis may differ from the rates here measured. This could be true if the oxygen which is active catalytically forms only a small fraction of the total oxygen which is adsorbed. It is not improbable that the catalytically active centers are to be identified with the fraction of the surface which exhibits an intermediate adsorptive activity, as suggested by Beebe.[10] This point should be capable of experimental proof by a study of the adsorptions and kinetics over a catalyst poisoned under carefully controlled conditions.

In view of the much slower rate of adsorption and the shorter time of preliminary treatment of the gold, it is probable that this metal did not become so nearly covered with oxygen during preliminary treatment with this gas as did the silver. This consideration, combined with the hypothesis that only oxygen adsorbed next to a bare space on the surface is readily capable of reaction with hydrogen, would explain the difference in the effect produced on silver and gold by previous oxygen treatment. In one experiment with silver before which it was heated in oxygen for a

[10] Beebe, *J. Phys. Chem.*, **30**, 1538 (1926).

shorter time and at a lower temperature, the yield was increased in the same manner that was found in the case of gold.

It does not seem possible to deduce a reaction mechanism from the present experiments which will offer a satisfactory explanation for the dependence of the yield upon the square of the hydrogen pressure. A mechanism based on the interaction of adsorbed oxygen with two hydrogens adsorbed on adjacent spaces on the catalyst surface will not account for the observed kinetics, since it may readily be shown that with the relative adsorptions found for the two gases this assumption requires the velocity of reaction to be proportional to the square of the hydrogen pressure, but *inversely* proportional to the oxygen. It seems necessary to conclude that the essential mechanism is the collision of gaseous hydrogen with adsorbed oxygen. If it is required that two gaseous hydrogen molecules strike adsorbed oxygen simultaneously for reaction to occur, dependence on the square of the hydrogen pressure necessarily follows. This offers a possible explanation, but one which is rather unsatisfactory for a heterogeneous reaction of this type, especially in view of the probability that the adsorbed oxygen is at least partially dissociated into atoms.

It is probable that an explanation of the result of Bone and Wheeler that the kinetics were independent of oxygen pressure is to be sought in the higher temperature used by them. At increased temperatures the rate of oxygen adsorption would be greatly increased, so that the catalytically active centers would be largely covered with oxygen under all conditions. This could also explain their result that previous oxygen treatment decreased the rate of combination.

Summary

A study has been made of the catalytic formation of water vapor from hydrogen and oxygen in the presence of a reduced gold catalyst in the temperature range 130–150°, including measurements of the reaction kinetics by the flow method and determinations of the adsorptions of the two gases. The principal results are as follows.

1. The rate of reaction varies as the square of the hydrogen pressure and the first power of the oxygen pressure, and is approximately inversely proportional to the pressure of water vapor. Preliminary treatment of the catalyst with oxygen produces a large but transitory increase in yield. The average temperature coefficient is 1.92.

2. Under the conditions of the catalysis hydrogen is adsorbed by gold in scarcely measurable amount. Oxygen, on the other hand, is strongly adsorbed, the quantity taken up increasing with increasing temperature, but being practically independent of the pressure. The rate of its adsorption is very slow; it is practically independent of the gas pressure and increases with increasing temperature.

In spite of the similarity in chemical properties of gold and silver, the kinetics of the hydrogen-oxygen combination over the two metals show little in common. It appears that no simple mechanism for the reaction in contact with gold is adequate to account for the observed results.

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[COMMUNICATION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

STUDIES IN PHOTOSENSITIZATION. I

BY JOHN R. BATES AND HUGH S. TAYLOR

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The field of photosensitization by mercury vapor has been extended during the past year to processes which do not involve hydrogen. Dickinson and Sherrill[1] showed that ozone was formed from the collision of excited mercury atoms and oxygen. Since the energy of the quantum corresponding to the 2536.7 Å. line is insufficient to decompose an oxygen molecule, they assumed that the reaction occurred through the collision of an excited and normal oxygen molecule.

Olson and Meyers,[2] investigating in more detail the reaction between hydrogen and ethylene reported by Marshall and Taylor, have shown that the reaction does not go smoothly to form ethane. Ethylene itself is polymerized, there being at the beginning of the reaction an increase in pressure which falls off again as the polymerization proceeds. They also found that the rate of the hydrogen-ethylene reaction was proportional to the square root of the hydrogen concentration.

Senftleben[3] has found that the excited mercury atoms will decompose water vapor. Measuring the change in heat conductivity of water vapor when mixed with varying amounts of hydrogen and oxygen, he found that the change which occurred when water vapor and mercury were illuminated indicated that hydrogen was the sole product in the vapor phase. He, therefore, postulated the formation of hydrogen peroxide which condensed out.

The work here presented has as its object an attempt to broaden the field still further by the development of improvements in light sources for use in photosensitized processes and for general photochemical purposes, and by a study of a number of photosensitized and photochemical reactions. Those investigated are the hydrogenation and polymerization of ethylene and acetylene, the reaction of hydrogen and oxygen to form hydrogen peroxide and the decomposition of water, ammonia, ethylene, ethyl and methyl alcohols, acetone, formic acid, hexane, benzene and

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[1] Dickinson and Sherrill, *Proc. Nat. Acad. Sci.*, **12**, 175 (1926).

[2] Olson and Meyers, THIS JOURNAL, **48**, 389 (1926).

[3] Senftleben, *Z. Physik*, **37**, 529, 539 (1926).