

2. The sensitivity of the reaction with respect to molybdenum was also found in the case where no interfering substances were present, the sensitivity being about one part of molybdenum per million parts of solution. Many substances such as mercuric chloride, phosphoric acid and organic compounds were found to decrease the sensitivity.

3. The ratio between the molybdenum and the sulfur in the thiocyanate radical, when the compound was dissolved in ether, was found to be such as to correspond to the formula,  $\text{Mo}(\text{SCN})_3$ .

MADISON, WISCONSIN

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## THE CATALYTIC SYNTHESIS OF WATER VAPOR IN CONTACT WITH METALLIC SILVER

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### Introduction

One type of contact catalysis having a relatively simple mechanism consists in the interaction of two gases in contact with a solid under such conditions that no compounds are formed involving the catalyst and only one of the gases is measurably adsorbed. The formation of water vapor from hydrogen and oxygen in contact with metallic silver appears to be an example of this kind.

The reaction has been studied by Bone and Wheeler<sup>2</sup> who used a number of different catalysts, including silver foil and gauze. Their method consisted in continuously circulating the gas mixture over the catalyst held at constant temperature (usually 400°), condensing the water thus formed and measuring the rate of steam formation by the pressure decrease in the system. The results indicated that with silver foil the rate of reaction was roughly proportional to the pressure of the hydrogen but independent of the oxygen pressure; with silver gauze the results appeared to be less simple. It was also found that the activity of the catalyst was greatly stimulated by previous heating in hydrogen, but not in oxygen. Bone and Wheeler interpreted these results to mean that the hydrogen becomes activated by association with the silver surface, probably by forming an unstable hydride which reacts with oxygen to form water and regenerate the catalyst. As evidence for this view they state that an active silver surface was found to absorb hydrogen both at 400° and at dull red heat.

The conclusions of Bone and Wheeler have been criticised in another

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<sup>2</sup> Bone and Wheeler, *Phil. Trans.*, 206A, 1 (1906).

place.<sup>3</sup> If reaction should occur when gaseous oxygen molecules strike adsorbed hydrogen, the rate would be proportional to, rather than independent of, the oxygen pressure; whether or not the hydrogen pressure would affect the rate would depend on the shape of the adsorption isotherm for hydrogen at the temperature in question. Since with all the metallic catalysts investigated by Bone and Wheeler the reaction rate was mainly determined by the hydrogen pressure and independent of the oxygen pressure, it seems necessary to conclude that it is the oxygen which is adsorbed and thus activated, rather than the hydrogen.

This conclusion is not in conflict with Bone and Wheeler's absorption measurements in which hydrogen was found to be taken up, because the silver employed undoubtedly held a film of adsorbed oxygen, and the hydrogen apparently absorbed was merely that which reacted with this oxygen. Sieverts<sup>4</sup> found that the amount of hydrogen absorbed by silver at the temperatures in question was scarcely measurable.

Chapman, Ramsbottom and Trotman<sup>5</sup> have recently confirmed the stimulating effect of previous treatment of the silver with hydrogen, as compared with oxygen, and show that this is probably due to a retarding influence of a film of oxygen, which is merely burned off by the hydrogen.

The kinetic measurements of Bone and Wheeler did not yield sufficiently definite results with silver to form the basis for a reaction mechanism. This is partly due to the small number of experiments but mainly, we believe, to the method employed. The manometric method of measuring the velocity of contact catalytic reactions, which these investigators used, gives results that are capable of a simple interpretation only when the velocity of the separate step which determines the rate of the whole process is very slow in comparison with any other steps that may occur. Where adsorption is involved, for example, the equilibrium in this process must be rapidly established in order that the amount of gas actually on the surface at any given instant may be the same that would be present if no reaction were occurring. When the adsorption is large, and particularly when it is "preferential," this condition may not be fulfilled. The measurements discussed below show that it is not fulfilled in the case of the reaction under consideration. Although it has the advantage of greater speed, the manometric method is open to other objections. Thus it is difficult to distinguish between a change in reaction kinetics and a mere change in the activity of the catalyst. This is especially troublesome in cases where preliminary heating in one or other of the reactants produces effects which persist for relatively long periods.

Most of these difficulties may be avoided by use of the ordinary flow

<sup>3</sup> Benton and Emmett, *THIS JOURNAL*, **48**, 632 (1926); **46**, 2735 (1924).

<sup>4</sup> Sieverts, *Z. physik. Chem.*, **60**, 179 (1907).

<sup>5</sup> Chapman, Ramsbottom and Trotman, *Proc. Roy. Soc.*, **107A**, 92 (1925).

method, in which a "steady state" is reached under each set of conditions. This method has, therefore, been used in the present work. In addition to an accurate determination of the kinetics of the reaction, the adsorptions of hydrogen and oxygen have been measured, and a definite mechanism has been deduced for the reaction.

### Experimental Method

**Apparatus.**—In its main features the apparatus was similar to that employed by Pease and Taylor<sup>6</sup> in their study of copper and copper oxide as catalysts for this reaction. Hydrogen and oxygen, generated electrolytically in separate generators and purified in the usual way, were passed in suitable proportions over the catalyst maintained at a constant temperature, the latter being read on a thermometer whose bulb was imbedded in the catalyst. The progress of the reaction was followed by means of frequent determinations of the increase in weight of a calcium chloride tube through which the exit gases passed. The amount of oxygen (or hydrogen) which had escaped conversion to water was also determined, by use of an arrangement similar to that described by Larson and Smith.<sup>7</sup>

**Preparation of Catalyst.**—An 8% solution of twice recrystallized silver nitrate was heated to 70° and an exactly equivalent amount of saturated barium hydroxide solution slowly added from a buret during constant stirring. The precipitated silver oxide was washed repeatedly by decantation and filtered off. After the part next to the filter paper had been discarded, the remainder was dried in a current of air at 100°, and finally in a stream of oxygen for about 100 hours at 160°. The entire preparation of the oxide was carried out in the absence of carbon dioxide.

The oxide sample was then placed in the catalyst furnace and reduction carried out *in situ* in a current of dry hydrogen. The temperature at the start was about 25°, but this increased gradually as reduction proceeded. After eight hours the furnace was slowly heated, 100° being reached in four more hours. This temperature was then maintained until water could no longer be detected in the exit hydrogen.

The same sample of silver was used in all of the velocity experiments. It was 2.1 cm. in diameter and approximately 2.5 cm. in height, giving an apparent volume of 8.7 cc. The weight was 11.72 g.

**Procedure.**—To avoid any uncertainty due to the previous history of the catalyst, the latter was given a uniform preliminary treatment before each run, consisting in heating in a current of hydrogen for about an hour at the highest temperature which had been previously used in any experiment. This temperature was 100° in the earlier runs and 130° in the later (after Run 58). The temperature was then lowered to a point

<sup>6</sup> Pease and Taylor, *THIS JOURNAL*, **43**, 2179 (1921); **44**, 1637 (1922).

<sup>7</sup> Larson and Smith, *ibid.*, **47**, 346 (1925).

somewhat below that desired in the experiment and oxygen admitted to the hydrogen stream at a suitable rate. The heat of reaction raised the temperature somewhat, and it was then brought as quickly as possible to the desired value and maintained constant thereafter within a few tenths of a degree. The extent of reaction was then determined at frequent intervals by weighing the water absorbed by the calcium chloride tube during five minutes' passage of the exit gases from the furnace. At less frequent intervals determinations were made of the amount of oxygen (or hydrogen) which had escaped conversion. Each run was continued for two or three hours after a steady state was reached. The oxygen was then cut off and hydrogen alone was passed over the catalyst until water was no longer formed.

In the first 32 runs, in which an excess of hydrogen was used, the desired quantity of oxygen was added in the form of electrolytic gas; in all succeeding experiments oxygen alone was added. It is convenient in all cases to express the quantity of the gas present in smaller amount in terms of the number of milligrams of water which would be obtained in each five minutes if conversion were complete. Thus, for example, an electrolyzing current of 0.720 amp. generates 2.51 cc. per minute ( $0^\circ$ , 760 mm.) of oxygen and 5.02 cc. per minute of hydrogen, each of which is capable of furnishing 20.2 mg. of water per five minutes when completely converted in an excess of the other gas. In nearly all the experiments the calculated yield was an exact multiple of 10.1 mg. of water per five-minute interval. Gas volumes have been reduced to  $0^\circ$  and 760 mm. throughout.

### Treatment of Results

**Changing Activity of Catalyst.**—Checks made during the course of the first 15 runs showed only a very slight decrease in activity of the catalyst. Later, at temperatures near the maximum to which the catalyst had been previously heated, a more pronounced decrease was observed. It is believed that the falling off in activity is not largely due to poisoning, but rather to a gradual sintering produced by long heating.

In order to obtain accurate determinations of the reaction kinetics, it was necessary to apply corrections for the changing activity. In doing so the investigation was divided into a number of separate series, in each of which the effect of a single variable was studied. The results of each series have been corrected, but it has not been necessary to compare the separate series with one another. In most series check runs under a standard set of conditions were made alternately with the other runs. If an exact check was not obtained, the change in activity was assumed to be proportional to the number of runs intervening, and the yield in each was corrected by the percentage amount per run necessary to bring the check runs into agreement. This correction seldom amounted to more than a

few per cent. in any one series. Owing to the large number of readings, the steady-state yield could generally be determined to 0.1–0.2 mg., but in most of the series the uncertainty is made considerably greater by the changing activity.

### Experimental Results on Reaction Kinetics

The results obtained in a typical run (Run 10) when hydrogen was used in excess are shown in Fig. 1. The lower curve gives the yield as a function of the time from the start of the run. It will be observed that the rate of water formation rises rapidly to a maximum and finally reaches a steady state after about 40 minutes. On cutting off the oxygen the yield dropped

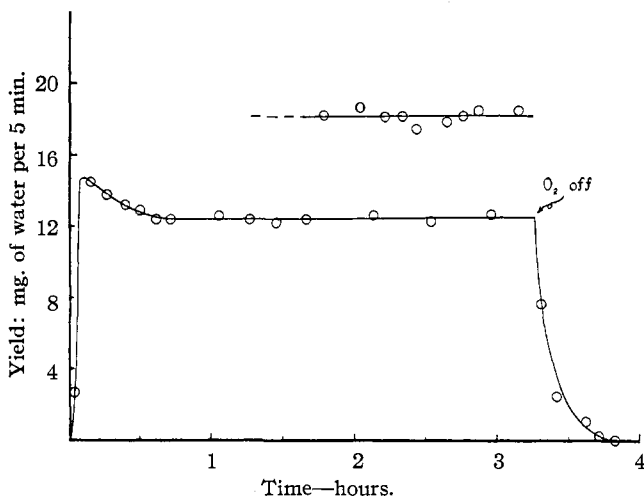


Fig. 1.—Variation of yield with time in a typical run (Run 10). The lower curve shows the conversion over the catalyst; the upper curve gives the water obtained from the oxygen which escaped conversion over the catalyst.

rapidly to zero, usually within 15 to 30 minutes. The upper curve gives the amounts of water corresponding to the oxygen unconverted in the furnace. Since in all cases the sum of the amounts of oxygen unconverted and those converted to water was equal within the experimental error to the total oxygen introduced, it is evident that oxygen was not continuously taken up and retained by the catalyst. Small quantities could, however, have been adsorbed at the start of a run. Later experiments showed this to be the case. With these points established, the measurements of the unconverted oxygen were continued throughout the work, to serve as a check on the accuracy of the results.

When oxygen was used in excess, the initial stages of the approach to the steady state could not be followed, owing to the time required to sweep out of the furnace the hydrogen used in the preliminary treatment. In

general, the steady state was reached sooner than when hydrogen was present in excess. By measuring the unconverted hydrogen at intervals, it was found that this gas was not continuously taken up by the catalyst. This was confirmed by the rapid drop in yield obtained when the hydrogen was cut off at the conclusion of a run.

The separate variables investigated are the oxygen pressure, hydrogen pressure, rate of flow and temperature. The effects produced by water vapor and by preliminary treatment of the catalyst with hydrogen or oxygen have also been studied.

It may be mentioned here that a test for hydrogen peroxide in the reaction products was made during a run, but no trace of this substance was detected.

**Effect of Oxygen Pressure.**—In determining the influence of the oxygen on the rate of conversion, experiments were made at several temperatures with hydrogen in large excess and with amounts of oxygen equivalent to from 10 to 40 mg. of water per five minutes. A constant current of hydrogen was generated, 50.0 cc. per minute, and electrolytic gas was added to this in suitable proportion. As a result, the total rate of flow was not constant but varied only between the limits 52.5 and 60.0 cc. per minute.<sup>8</sup> In order to estimate the necessary correction for this difference, a few experiments were made at two widely differing rates, approximately 30 and 100 cc. per minute. By plotting a curve for each temperature giving the relation between the yield (corrected for changing activity) and the total rate of flow, and interpolating over the short distances necessary, the yields observed in all of the experiments were corrected to the nearest of the three standard rates of flow, 30, 60 and 100 cc. per minute. This correction is so small in most cases that the conclusions to be drawn from the experiments would not be materially affected by neglecting it.

During these early experiments check runs were not made as frequently as could be desired, only seven of the first 33 being repetitions of earlier runs. These showed that the activity decreased on the average by about 1% per run. Accordingly, Run 20 was taken as standard and all the others were corrected to this by adding to or subtracting from the observed yields 1% for every run separating the run in question from Run 20. While not entirely free from uncertainty, nevertheless this correction is sufficiently small in all cases so that the error involved is probably not great. Runs in which conversion was nearly complete obviously cannot be corrected in this manner.

The results of Runs 4–33 are presented in Table I. The average hydrogen pressure is not strictly constant throughout this set of experiments, the values varying from 628 mm. (Run 28) to 735 mm. (Run 16). At any given temperature and flow rate, however, the extreme variation

<sup>8</sup> Rates of flow are expressed throughout as cc. per min. (0°, 760 mm.) of gas entering the catalyst.

never exceeds 46 mm. The results in the next section will show that the change in yield due to this maximum difference is only about 3%.

The constancy of the final corrected values given in Table I for the yield obtained under given conditions of temperature, rate of flow and hydrogen pressure shows that under all conditions tried the yield is independent of the oxygen pressure. There is evidence, however, that at very low oxygen pressures the rate of reaction becomes smaller, since in runs where the conversion would otherwise have been complete, such as 4, 5 and 23, a small amount of oxygen escaped unchanged.

TABLE I  
EFFECT OF OXYGEN PRESSURE ON THE YIELD  
(a) Total flow rate corrected to 60.0 cc. per min.

Run	Temp., °C.	Total flow, cc. per min.	Oxygen in, cc. per min.	Baro- meter, mm.	Average oxygen press., mm.	Yield: mg. of water per 5 min.			
						Calcd.	Obs.	Corr. for activity	Corr. for activity and flow
24	60	51.9	0.63	745.7	6.2	5.0	3.2	3.3	3.7
6	60	53.8	1.25	756.7	13.9	10.1	4.4	3.8	4.1
12	60	53.8	1.25	755.2	14.2	10.1	4.0	3.7	4.0
7	60	57.5	2.51	755.0	29.6	20.2	4.2	3.7	3.8
9	60	61.3	3.76	743.3	42.7	30.3	4.1	3.7	3.7
11	60	61.3	3.76	753.1	43.2	30.3	4.2	3.8	3.8
15	60	61.3	3.76	754.6	43.3	30.3	4.2	4.0	4.0
14	60	65.0	5.02	749.8	55.2	40.4	4.0	3.8	3.7
4	80	53.8	1.25	747.4	9.4	10.1	9.3	..	..
5	80	53.8	1.25	750.7	9.2	10.1	9.6	..	..
23	80	53.8	1.25	751.1	9.5	10.1	9.2	..	..
8	80	57.5	2.51	745.1	22.7	20.2	12.4	11.0	11.2
10	80	61.3	3.76	748.4	36.9	30.3	12.4	11.2	11.1
32	80	61.3	3.76	747.1	39.2	30.3	9.3	10.7	10.6
13	80	65.0	5.02	749.1	49.4	40.4	12.4	11.5	11.1
19	90	61.3	3.76	746.3	32.9	30.3	17.5	17.3	17.1
33	90	61.3	3.76	754.4	35.3	30.3	14.9	17.4	17.2
20	90	65.0	5.02	748.0	45.7	40.4	17.6	17.6	16.9
27	100	57.5	2.51	749.6	16.5	20.2	20.0	..	..
25	100	60.5	3.51	745.2	23.6	28.2	25.8	27.3	27.3
21	100	61.3	3.76	749.0	25.4	30.3	27.3	27.6	27.3
22	100	65.0	5.02	748.7	38.0	40.4	28.3	28.9	27.5

(b) Total flow rate corrected to 30.0 cc. per min.

26A	60	28.8	1.25	746.0	29.2	10.1	2.2	2.3	2.3
26	60	36.3	3.76	746.0	74.7	30.3	2.3	2.4	2.1
29	90	36.3	3.76	747.2	62.9	30.3	12.2	13.5	12.3
28	100	40.0	5.02	749.7	72.2	40.4	20.0	21.9	18.8

(c) Total flow rate corrected to 100 cc. per min.

16	60	103.8	1.25	747.0	6.6	10.1	5.4	5.2	5.1
18	60	111.3	3.76	740.2	23.0	30.3	5.0	4.9	4.7
17	60	115.0	5.02	738.7	30.2	40.4	5.2	5.1	4.8
31	90	111.3	3.76	745.4	16.1	30.3	22.0	25.0	23.7
30	100	115.0	5.02	746.7	17.3	40.4	37.9	(42.6)	38.8

**Effect of Hydrogen Pressure.**—The first series of runs to determine the influence of the hydrogen pressure was carried out by passing a constant current of 50 cc. per min. of oxygen, to which were added quantities of hydrogen (not electrolytic gas as in the earlier experiments) equivalent to 10, 20, 30, 40 and 100 mg. of water per five minutes. The temperature was 100° in all cases, and the observed yields were corrected for the slight change in the activity and for the variations (from 60 cc. per minute) in the rate of flow, by the methods already indicated. Since the conversion is independent of the oxygen pressure, the slight variations of the latter in these experiments are without influence on the results. The data for this series are given in Table II.

TABLE II  
EFFECT OF HYDROGEN PRESSURE ON THE YIELD. FIRST SERIES  
Temperature, 100°

Run	Total flow, cc. per min.	Hydrogen in, cc. per min.	Barometer, mm.	Average hydrogen press. mm.	Yield: mg. of water per 5 min.			
					Calcd.	Obs.	Corr. for activity	Corr. for activity and flow
35	52.5	2.51	750.2	27.8	10.1	4.6	4.6	5.0
40	55.0	5.02	748.4	55.5	20.2	7.6	7.3	7.8
39	57.5	7.53	750.9	82.6	30.3	10.0	9.8	10.1
34	60.0	10.04	748.6	107.9	40.4	11.5	11.5	11.5
37	60.0	10.04	752.6	108.5	40.4	11.5	11.5	11.5
43	60.0	10.04	748.6	105.4	40.4	12.3	11.5	11.5
42	75.0	25.09	743.2	223.1	101.0	22.9	21.6	18.6

When the logarithms of the average hydrogen pressures ( $P_H$ ) are plotted against the logarithms of the corrected yields ( $Y$ ), the points lie on a straight line within experimental error. The equation representing this line, with units as given in Table II, is  $Y = 0.62 P_H^{0.63}$ .

In view of the uncertainties in this series due to variations in activity and rate of flow, another series of runs was carried out in which the total flow was kept constant at 50 cc. per min. and check runs under standard condi-

TABLE III  
EFFECT OF HYDROGEN PRESSURE ON YIELD. SECOND SERIES  
Temperature, 110°. Total flow, 50 cc. per min.

Run	Hydrogen in, cc. per min.	Barometer, mm.	Average hydrogen pressure, mm.	Yield: mg. of water per 5 min.		
				Calcd.	Obs.	Corr. for activity
64	10.04	744.6	132.0	40.4	10.1	10.2
65	2.51	759.7	29.7	10.1	4.5	4.5
66	10.04	755.7	133.9	40.4	10.2	10.2
67	5.02	741.6	62.4	20.2	6.7	6.7
68	10.04	758.0	134.4	40.4	10.1	10.2
69	7.53	755.1	98.8	30.3	8.3	8.5
70	10.04	751.9	133.9	40.4	9.8	10.2
71	25.09	741.4	349.5	101.0	15.5	16.1
72	10.04	738.0	130.9	40.4	9.8	10.2



tions were made alternately. The temperature was  $110^{\circ}$ . The results are given in Table III.

The points obtained by plotting  $\log P_H$  against  $\log Y$  again lie on a straight line, giving the relation  $Y = 0.78 P_H^{0.52}$ . The significance of these equations will be considered in the Discussion. It should be noted here, however, that they disregard the effect of the variations in the pressure of water vapor which necessarily accompany the variations in yield.

**Effect of Water Vapor.**—To determine the effect of water vapor in the entering gases, a pair of experiments was made under conditions which were the same in all other respects (temperature,  $110^{\circ}$ ; total flow, including the water vapor added, 50.0 cc. per min., of which 10.04 cc. per min. was hydrogen). In Run 95 the gases entered dry; in Run 96 they were passed through a saturating train containing distilled water at  $24.6^{\circ}$ , giving a concentration of water vapor equivalent to 5.1 mg. per five minutes. In the former case the observed yield was 5.4 mg. of water per five minutes; in the latter run the exit gases contained 5.6 mg. per five minutes, giving a yield of only 0.5 mg.

These results show that water vapor initially present very greatly represses the activity of the catalyst at  $110^{\circ}$ . This effect is almost certainly due to adsorption of the water by the silver, thus preventing free access of the reacting gases to a large part of the surface. It is evident, therefore, that when water is initially absent, conversion must take place largely in the upper part of the sample, where the dry incoming gases keep the catalyst relatively free from water. This would account for the great decrease in yield produced by the added water in Run 96, in spite of the fact that the average pressure of water vapor was only about twice as great as in Run 95.

**Effect of Rate of Flow.**—The results given in Table I show that an increase in flow rate materially increases the yield. Thus in Runs 29, 31 and 33, in which all the conditions were roughly the same except the oxygen pressure, which is without influence, and the rate of flow, it will be seen that a threefold increase in flow approximately doubled the yield. A similar result was obtained from the experiments at  $60^{\circ}$  and at  $100^{\circ}$ . In all three cases the points obtained by plotting the logarithm of the rate of flow ( $F$ ) against  $\log Y$  lie on lines which are nearly straight. These may be represented by an equation of the form  $Y = kF^n$ , where  $n$  has values varying from 0.55 to 0.7.

Owing to the fact that this comparison requires the use of runs made at widely separated intervals and hence involving comparatively large activity corrections, it was thought desirable to check the results obtained by two further series in which runs under standard conditions were made more frequently. The first of these series (Table IV) was carried out at  $100^{\circ}$ , using oxygen in excess. The quantity of hydrogen was adjusted

so that its partial pressure in the entering gases was constant in the various runs except for insignificant differences in atmospheric pressure. It so happened that the average hydrogen pressure also was nearly constant.

TABLE IV  
EFFECT OF RATE OF FLOW ON YIELD. FIRST SERIES  
Temperature, 100°. An excess of oxygen was present.

Run	Total flow, cc. per min.	Hydrogen in, cc. per min.	Average hydrogen press., mm.	Yield: mg. of water per 5 min.		
				Calcd.	Obs.	Corr. for activity
43	60.0	10.04	105.4	40.4	12.3	11.9
44	60.0	10.04	106.4	40.4	12.2	11.9
45	40.8	6.78	104.1	27.4	9.3	9.3
46	24.0	3.98	101.7	16.2	6.1	6.2
47	60.0	10.04	109.3	40.4	11.4	11.9

The second series was carried out at 80°, using hydrogen in excess and keeping the concentration of the entering gases identical in each run. As before, the average pressures of both gases were practically constant. The results are given in Table V.

TABLE V  
EFFECT OF RATE OF FLOW ON YIELD. SECOND SERIES  
Temperature, 80°. An excess of hydrogen was used.

Run	Total flow, cc. per min.	Oxygen in, cc. per min.	Average hydrogen press., mm.	Yield: mg. of water per 5 min.		
				Calcd.	Obs.	Corr. for activity
52	55.0	5.02	677	40.4	6.8	6.8
53	27.5	2.51	675	20.2	4.7	4.7
54	55.0	5.02	671	40.4	6.8	6.8
55	110.0	10.04	672	80.8	8.6	9.1
56	55.0	5.02	669	40.4	6.0	6.8
57	82.5	7.53	672	60.6	6.7	8.2
58	55.0	5.02	671	40.4	4.9	6.8

The logarithmic plots of the results of these two series are nearly straight lines, but are slightly convex toward the yield axis in both cases. The values in Table IV may be represented approximately by the equation  $Y = 0.55F^{0.71}$ . For the second series (Table V),  $Y = 0.85F^{0.50}$ . These relations are suitable for purposes of interpolation, but the bend in the curves shows that at high rates of flow the yield would increase less rapidly than the equations indicate. It appears that as the flow is increased the yield tends toward a constant maximum value. The curves are of the same general type, therefore, as those obtained in technical practice giving the relation between space-time-yield and space-velocity.

Aside from a slight mixing effect which might possibly result from increased turbulence of flow, the number of collisions of gas molecules with the surface in unit time is independent of the rate of flow, since the linear velocity of the gas is always small in comparison with the molecular

velocity. Probably the only significant effect of an increased rate of flow is the lowering of the partial pressure exerted by a given quantity of water vapor in the exit gases. At lower partial pressures less water would be adsorbed and hence more of the catalyst surface would be available for reaction. It will be shown in the Discussion that the observed results on the effect of rate of flow are satisfactorily accounted for on this basis.

**Temperature Coefficient.**—In addition to the experiments listed in Table I on the effect of temperature on the yield at each of three different rates of flow, two further series of runs were made to determine the temperature coefficient. The results of these two series are given in Table VI. Here oxygen was present in excess and a constant hydrogen concentration equivalent to 40.4 mg. of water per five minutes was used. Since the flow rate was maintained constant at 60 cc. per minute, and the barometric pressure was practically the same throughout, the partial pressure of hydrogen in the entering gases remained constant. Owing to the increased yields at the higher temperatures, however, the average hydrogen pressures varied considerably. On the basis of the previous data on the effect of hydrogen pressure, the yields have all been corrected to a pressure of 110 mm. by using the relation,  $Y = k P_H^{0.6}$ . Before Run 59 the catalyst was heated at 130° for six hours.

TABLE VI  
EFFECT OF TEMPERATURE ON YIELD  
An excess of oxygen was used. The total flow rate was 60.0 cc. per min.

Run	Temp., °C.	Average hydrogen press., mm.	Yield: mg. of water per 5 min.		
			Obs.	Corr. for activity	Corr. for activity and hydrogen press.
FIRST SERIES					
47	100	109.3	11.4	11.2	11.2
48	80	120.8	4.2	4.1	3.9
49	100	109.8	11.2	11.2	11.2
50	120	92.0	22.4	24.1	26.8
51	100	113.8	8.6 <sup>a</sup>	11.2	11.2
SECOND SERIES					
59	110	110.2	9.8	10.0	10.0
60	90	119.5	4.2	4.2	4.0
61	110	110.3	10.0	10.0	10.0
62	130	92.4	21.6	21.2	23.5
63	110	108.8	10.6	10.0	10.0

<sup>a</sup> Catalyst accidentally heated to 130° for several minutes before Run 51.

As may be seen from Fig. 2, on plotting the logarithms of the corrected yields against the reciprocals of the absolute temperatures, the points in each case lie on a straight line within experimental error. By multiplying the slopes of these lines by  $-4.58$ , the so-called heat of activation ( $Q$ ) is obtained. These values for the various series are as follows: For the

experiments in Table I(a) (flow, 60 cc. per minute),  $Q = 12,120$  cal.; Table I(b) (flow, 30 cc. per minute), 12,300; Table I(c) (flow, 100 cc. per minute), 12,850; Table VI, First Series, 12,980; Table VI, Second Series, 12,970. It will be seen that the temperature coefficients are substantially identical for different rates of flow and for different concentrations of the reacting gases. The actual temperature coefficient for a  $10^\circ$  rise decreases somewhat with increasing temperature, being about 1.75 for the interval  $60-70^\circ$  and 1.50 for the interval  $120-130^\circ$ . The significance of these values will be considered in the Discussion.

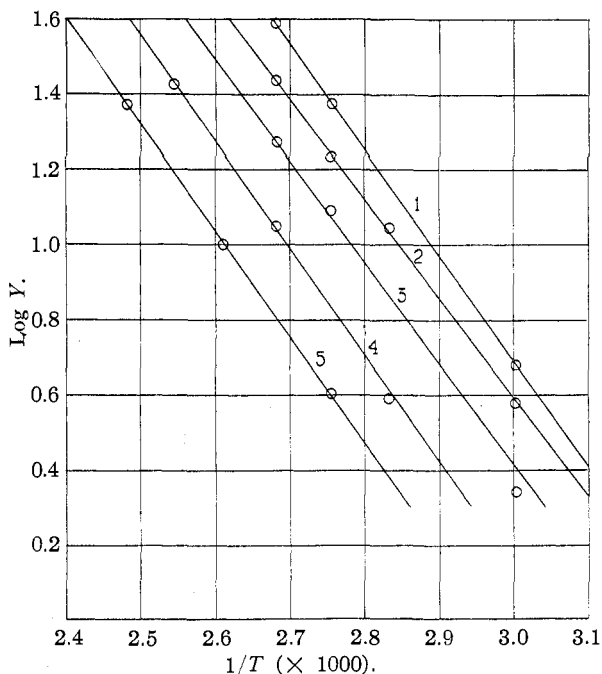


Fig. 2.—The effect of temperature on yield. Curves 1, 2 and 3 are from the data of Table I, for flow rates of 100, 60 and 30 cc. per minute, respectively; Curve 4 is from Table VI, First Series; Curve 5 is from Table VI, Second Series.

**Effect of Preliminary Heating of Catalyst in Oxygen.**—A series of experiments was carried out in which all the conditions were the same except the preliminary treatment of the catalyst. Before the first, third and fifth runs of the series it was heated for one hour in a current of hydrogen at  $110^\circ$ ; before the second and fourth runs it was heated in a current of oxygen at  $110^\circ$  for one and three-tenths and thirty hours, respectively. The latter period was chosen because it was found that silver required about this length of time to reach adsorption equilibrium with oxygen at  $110^\circ$ . The results are given in Table VII.

TABLE VII  
EFFECT OF PRELIMINARY TREATMENT OF CATALYST

Temperature, 110°. Flow rate, 50 cc. per min. Calculated yield, 40.4 (excess of oxygen).

Run	Preliminary heating at 110° in		Obs. yield:
	Hydrogen,	Oxygen,	mg. of water per 5 min.
	hr.	hr.	
91	1	..	5.2
92	...	1.3	3.9
93	1	..	5.2
94	...	30	3.1
95	1	..	5.4

Since the measurements described below show that oxygen, but not hydrogen, is adsorbed by silver under these conditions, these results point to a decrease in yield due to the oxygen treatment rather than an increase due to hydrogen. Heating in oxygen for 30 hours was evidently somewhat more effective than heating for one hour. An unexpected feature of the runs following oxygen treatment was the absence of any gradual reversion to the normal yield. Thus in Run 94 the steady state was maintained within  $\pm 0.1$  mg. per five minutes for the four hours' duration of the run.

It should be mentioned that in an earlier experiment previous treatment with oxygen produced a slight increase in yield. This occurred in Run 36 in which the conditions were the same as in Run 35 except that in the former case the catalyst was heated for one hour in oxygen at 100° instead of in hydrogen. The yields were 4.6 mg. in Run 35 and 5.2 mg. in Run 36, and no correction was required for changing activity since Run 37 checked Run 34 exactly. It is probable that in an hour at 100° the surface did not become so nearly covered with oxygen as it did in the experiments at 110°. If this is correct, the reaction mechanism discussed below is in harmony with the results observed.

#### Preliminary Adsorption Measurements

Measurements of the adsorption of oxygen and hydrogen (Runs 73-90) were carried out on the same sample of silver used in the velocity experiments. The procedure consisted in heating the catalyst at 110° for a definite length of time in either hydrogen or oxygen, sweeping out with a rapid current of nitrogen, and finally collecting and weighing any water formed on passing the other gas. The results, of course, show only the amount of gas adsorbed at zero pressure. Neither at 110° nor at room temperature was any measurable quantity of hydrogen retained, even when the nitrogen was passed for only five minutes. Oxygen, on the other hand, was retained in considerable amount. After three hours in this gas at 110° and five to fifteen minutes' sweeping out with nitrogen, an average of 3.3 mg. of water was obtained on passage of hydrogen; one run in which the catalyst was heated for nine hours in oxygen at 110°

gave 3.5 mg. of water. This is equivalent to 2.2 cc. of oxygen ( $0^\circ$ , 760 mm.) for the 11.72g. sample, or 0.19 cc. per g.

### Final Adsorption Experiments

**Apparatus and Procedure.**—In order to determine the adsorptions on silver at higher gas pressures, a series of measurements was made by the usual static method. The apparatus consisted essentially of a bulb containing the silver connected by 3-way stopcocks to a mercury manometer, a Töpler pump, a gas buret containing mercury, and the generating and purifying lines for the various gases employed.

After evacuation at  $110^\circ$  (boiling toluene), the silver was brought to the desired temperature and a suitable amount of gas admitted from the buret. The pressure produced was read at frequent intervals until the values began to approach constancy. Further quantities of gas were then introduced and the process repeated. The volume adsorbed at each pressure was obtained by subtracting from the total volume admitted the volume of gas in the free space. The latter was determined with nitrogen which was assumed not to be measurably adsorbed.

At the end of an experiment the gas was pumped off at  $110^\circ$  and measured. It was found that adsorbed oxygen could not be removed at this temperature and, therefore, it was necessary to burn this gas off with hydrogen at  $110^\circ$ . The preliminary experiments had already shown that no hydrogen is retained at  $110^\circ$ .

The new sample of silver used in these experiments was obtained by reduction of another portion of the same silver oxide previously employed. Reduction was conducted for 60 hours at room temperature and completed at  $100^\circ$ . The weight of silver was 48.16 g.

**Results.**—The results of the measurements are summarized in Table VIII. It will be observed that hydrogen is not measurably adsorbed either at  $26^\circ$  or  $110^\circ$ . A considerable quantity of oxygen, however, is adsorbed at both temperatures.

TABLE VIII  
ADSORPTIONS BY 48.16 GRAMS OF SILVER

Gas	Temp., $^\circ\text{C.}$	Volume introduced, cc.	Final press., mm.	Volume in free space, cc.	Volume adsorbed, cc.
H <sub>2</sub>	26	31.96	736.7	31.97	0.0
H <sub>2</sub>	110	25.59	747.6	25.56	0.0
O <sub>2</sub>	26	41.37	739	32.08	9.29
O <sub>2</sub>	110	35.31	658	22.49	12.82
O <sub>2</sub>	110	36.29	726	24.82	11.47
O <sub>2</sub>	110	33.86	556	19.02	14.84

While the hydrogen could be quantitatively recovered after a measurement with this gas, the oxygen adsorptions were found to be almost completely irreversible, both at  $26^\circ$  and at  $110^\circ$ . Thus, for example, at the

end of the fourth experiment in Table VIII, 23.3 cc. of gas was recovered by exhaustion at  $110^{\circ}$ , leaving 12.0 cc. on the silver. Therefore, of the 12.8 cc. adsorbed in this run, only 0.8 cc. was recoverable by evacuation. A rough check on the amount of oxygen remaining in vacuum was obtained by comparison with the volume of hydrogen required to remove it. In the present case, 23.5 cc. of hydrogen disappeared in this way; the equivalent quantity of oxygen, 11.8 cc., is in fair agreement with the 12.0 cc. found above. In the other runs with oxygen still less of the adsorbed gas was recoverable. In conformity with these results it was found that in a second measurement with oxygen, without an intervening treatment with hydrogen, only a few tenths of a cubic centimeter was adsorbed in addition to that remaining in the vacuum from the first experiment.

In the third and fifth experiments in Table VIII the oxygen was introduced in stages for the purpose of establishing the course of the adsorption isotherms. In both cases the first 6 or 7 cc. was rapidly adsorbed at zero pressure but after the introduction of each additional quantity a gradual and long-continued decrease in pressure occurred. No satisfactory method was found of extrapolating the readings to equilibrium. At  $110^{\circ}$  a measured adsorption of 9.0 cc. was obtained, however, at a pressure of 10 mm., and only 2.5 cc. more was taken up on gradually increasing the pressure to atmospheric during the next five hours. In conjunction with the results given in the previous paragraph, these figures indicate that at equilibrium the adsorption of oxygen must be nearly independent of the pressure except at very low pressures. It is probably also nearly independent of temperature, at least over the range of these measurements.

The slowness with which equilibrium is approached in these experiments cannot be attributed to progressive oxidation in the ordinary sense or to solubility of oxygen in silver, since it is apparently well established that this metal is not oxidized by oxygen at any temperature, and Sieverts<sup>4</sup> has shown that it does not dissolve oxygen in appreciable quantities below  $400^{\circ}$ . In this connection it may be noted that the last experiment recorded in Table VIII was continued for 30 hours, a constant value being reached in about 24 hours.<sup>9</sup> The final volume taken up, 14.8 cc. on 48.16 g., or 0.307 cc. per g., is of the order of magnitude to be expected for an adsorption rather than for ordinary compound formation.<sup>10</sup> The oxygen presumably reacts with the exposed silver atoms (most readily with those which are most active), forming a surface chemical compound. If such cases are to be classified as adsorption, it is evident that the customary

<sup>9</sup> The smaller values given in Table VIII for the other experiments with oxygen are attributable to the fact that equilibrium was not reached in the much shorter times of observation used in these cases.

<sup>10</sup> The fact that considerably smaller adsorptions per gram were obtained in the flow measurements is attributable to the decrease in surface area which doubtless accompanied the decrease in activity of the first silver sample during its use as catalyst.

postulate of a rapid attainment of adsorption equilibrium must be revised.

### Discussion

Before taking up a detailed consideration of the reaction mechanism, it is desirable to coördinate the kinetic results obtained. Since it has been shown that water vapor markedly retards the reaction, it is obvious that the empirical equations given above for the effect on the yield produced by changes in the hydrogen pressure must be corrected for the differences in the pressure of water vapor. This may be done as follows. Assuming for the adsorption of water vapor on silver an isotherm of the form<sup>11</sup>  $s = S \times aP/(1 + aP)$ , where  $s$  and  $S$  are the surface areas covered (and are proportional to the volumes adsorbed) at pressure  $p$  and at infinite pressure, respectively, and  $a$  is a constant for a given temperature (but which decreases with increasing temperature), the surface area free from water is  $S - s = S/(1 + aP_{\text{H}_2\text{O}})$ . According to the kinetic theory the rate at which gas molecules strike unit surface is given by the relation  $R$  (moles per sq. cm. per sec.) =  $43.74 \times 10^{-6} (P/\sqrt{MT})$ , when  $P$  is expressed in bars. Putting in the value of the molecular weight ( $M$ ) for hydrogen, changing pressures to millimeters of mercury and  $R$  to the number of milligrams of water equivalent to the amount of hydrogen striking unit surface per five minutes, we obtain

$$R \text{ (mg. of water per 5 min.)} = 2.22 \times 10^5 (P_{\text{H}}/\sqrt{T}) \quad (1)$$

The rate at which hydrogen strikes that part of the silver surface which is free from adsorbed water is then  $R'$  (mg. of water per 5 min.) =  $2.22 \times 10^5 (P_{\text{H}}/\sqrt{T}) \times S/(1 + aP_{\text{H}_2\text{O}})$ . If the reaction mechanism is such that at a given temperature a certain fraction ( $f$ ) of these collisions results in the formation of water, then the yield will be

$$Y = fR' = 2.22 \times 10^5 \frac{fP_{\text{H}}}{\sqrt{T}} \cdot \frac{S}{1 + aP_{\text{H}_2\text{O}}}$$

Strictly, this equation should be written in differential form and integrated between the pressure limits at the top and bottom of the catalyst. However, the use of average pressures is justifiable as an approximation.

Since the pressure of water vapor in the entering gas is zero, the average pressure of water is half the exit pressure. The latter, if fluctuations in barometric pressure are neglected, is proportional to the mole fraction of water in the exit gas. Neglecting also the small decrease in volume due to reaction (which rarely exceeded 4%), the mole fraction is proportional to the ratio of yield to flow rate, or  $Y/F$ . As a fair approximation, therefore, the average pressure of water,  $P_{\text{H}_2\text{O}}$ , is given by the relation  $P_{\text{H}_2\text{O}} = c.Y/F$ , where  $c$  is a constant. Substituting in the last equation, and putting  $ac = k$ , we finally obtain the expression

<sup>11</sup> Compare Langmuir, THIS JOURNAL, 40, 1370 (1918).



$$Y = \frac{2.22 \times 10^5}{\sqrt{T}} \cdot fP_H \cdot \frac{S}{1 + kY/F} \quad (2)$$

This equation indicates that when  $kY/F$  is small in comparison with unity, the yield should be proportional to the average hydrogen pressure. This would be the case at high temperatures (small  $k$ ) and high rates of flow—conditions unfavorable for the adsorption of the reaction product. Such conditions were not encountered in this investigation. When, on the other hand,  $kY/F$  is large in comparison with unity, the equation assumes the form

$$Y^2 = \frac{2.22 \times 10^5}{\sqrt{T}} \cdot \frac{fS}{k} \cdot P_H F$$

and the yield is proportional to the square root of the hydrogen pressure and the square root of the rate of flow. Judging by the empirical equations previously given, these conditions were presumably fulfilled approximately in the present measurements.

Equation 2 may be rewritten in the form

$$\frac{2.22 \times 10^5}{\sqrt{T}} \cdot fS \cdot \frac{P_H}{Y} = k \cdot \frac{Y}{F} + 1$$

If this satisfies the data, the points obtained by plotting corresponding values of  $P_H/Y$  and  $Y/F$ , for a given temperature, should fall on a straight line. It will be seen from Fig. 3 that this is approximately the case for the results given in Tables III and V. Owing to the uncertainty of the activity correction, the various other series in which check runs were not made alternately are not included, especially since this method of plotting greatly magnifies experimental errors. The lower curve in Fig. 3 represents a series of runs (64–72) in which the flow rate remained constant and the hydrogen pressure was varied. The upper curve gives the results for a series (Runs 52–58) in which the hydrogen pressure remained constant and the rate of flow was changed. The fact that both curves are nearly straight lines<sup>12</sup> shows that the reaction kinetics are satisfactorily summarized by Equation 2.

**Reaction Mechanism.**—A consideration of the probable reaction mechanism is greatly simplified by the fact that under the conditions of the catalysis silver does not form a new phase of oxide or hydride. The adsorption measurements show that hydrogen is not measurably taken up, even when present alone, so that in mixture with oxygen, which is strongly adsorbed, the hydrogen adsorption must be infinitesimally small. Although the measurements with oxygen show that the last few cubic centimeters of this gas were taken up very slowly, yet much more than half of the total amount was adsorbed practically instantaneously. Since this rapid adsorption presumably occurs at those centers on the surface which

<sup>12</sup> A slight curvature in the direction shown is to be expected, owing to the neglect of the volume change in the reaction.

are also most active catalytically, it would appear reasonably certain that during the catalysis the active parts of the surface are very largely covered with adsorbed oxygen under all conditions. This would account for the fact that the oxygen pressure exerts no influence on the yield of water obtained.

As already indicated, the observed kinetics are satisfactorily accounted for on the assumption that at each temperature a definite fraction of all

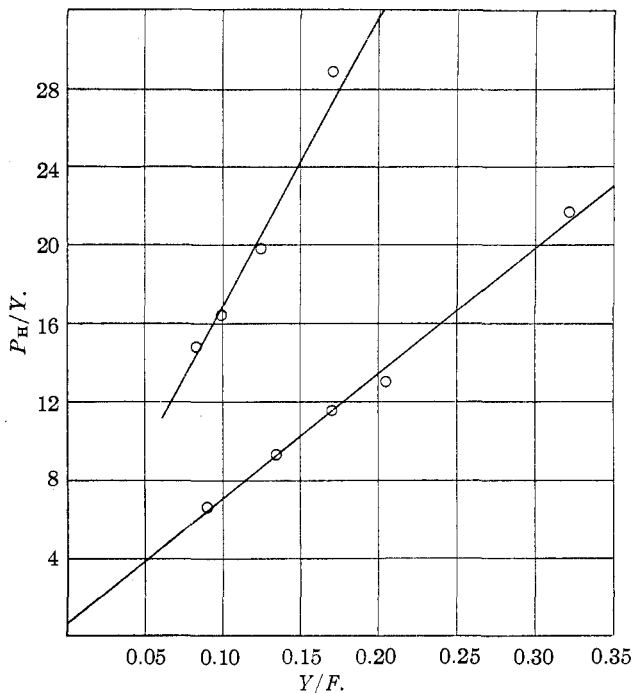


Fig. 3.—The combined effect on the yield of variables other than temperature. Lower curve, Runs 64-72 at 110°, Table III; upper curve, Runs 52-58 at 80°, Table V. (In plotting the latter curve the ordinates have been divided by 5.)

the collisions of gaseous hydrogen on that part of the surface not covered by adsorbed water, leads to reaction. This fraction may be calculated from the data as follows. On the assumption that each silver atom in the surface adsorbs one *atom* of oxygen, it follows that the 14.86 cc. of this gas adsorbed by 48.16 g. of silver represent a surface containing  $8.0 \times 10^{20}$  silver atoms.<sup>13</sup> Since the molecular volume of silver is 10.3 cc., the volume occupied by each silver atom is  $1.70 \times 10^{-23}$  cc., and the area assignable to each atom in the surface is  $(1.70 \times 10^{-23})^{2/3}$ , or  $6.6 \times 10^{-16}$  sq. cm.

<sup>13</sup> Even if the surface is not completely covered with oxygen, this calculation gives the area of the part which is so covered and, hence, active in the catalysis.

Hence, the surface area of the silver was  $8.0 \times 10^{20} \times 6.6 \times 10^{-16} \div 48.16$ , or  $1.1 \times 10^4$  sq. cm. per g.; for the 11.72g. sample used as catalyst, the corresponding area would be  $1.3 \times 10^5$  sq. cm. Taking Run 64, Table III ( $T = 383^\circ\text{K}.$ ;  $P_{\text{H}} = 132.0$  mm.) as an example, we can calculate from Equation 1 that if every collision of hydrogen with this surface resulted in the formation of water, the yield would be  $1.9 \times 10^{11}$  mg. per five minutes. Since the observed yield was only 10.1 mg., it follows that one impact in  $1.9 \times 10^{10}$  was effective. In order to determine to what extent this low efficiency is due to the presence of water adsorbed on the surface, the constants ( $fS$ ) and  $k$  in Equation 2 must be evaluated. Thus, for the series of Runs 64-72 (Fig. 3, lower curve), the value of  $f$  obtained from the intercept on the axis of ordinates is one in  $1.0 \times 10^9$ , indicating that about 5% of the surface was free from adsorbed water in Run 64.<sup>14</sup> It is evident, therefore, that certain hydrogen molecules or certain adsorbed oxygen atoms, or both, must be more active than the average.

The average temperature coefficient for the reaction was found to be about 1.6. Apart from the insignificant change in the rate of collision, this coefficient represents the combined effect of increased collision efficiency and decreased adsorption of water. When corrected for this last effect, the calculated "heat of activation" of roughly 13,000 cal. would certainly be considerably reduced.<sup>15</sup> It seems very doubtful that energy quantities of this magnitude would be capable of activating gaseous hydrogen molecules.

The effects of preliminary treatment of the catalyst with oxygen show definitely that hydrogen cannot react with equal ease with every adsorbed oxygen atom. If this were the case, it would be difficult to account for the fact that preliminary heating in oxygen for one hour and for 30 hours decreased the activity by about 25 and 40%, respectively. A possible explanation of the observations might be that only those oxygen atoms are capable of reacting readily which are situated next to bare spaces on the catalyst surface. Since the decomposition of silver oxide is an autocatalytic reaction<sup>16</sup> which proceeds only at the interface between metal and oxide, it is conceivable that a unimolecular film of adsorbed oxygen atoms might show a similar behavior.

### Summary

A study has been made of the catalytic formation of water vapor from hydrogen and oxygen in contact with reduced silver, including precise

<sup>14</sup> It is immaterial whether the presence of water prevents hydrogen from reaching the adsorbed oxygen or whether it interferes with the adsorption of oxygen itself.

<sup>15</sup> The necessary correction cannot be determined accurately from the present measurements because the lack of experiments at high flow rates makes difficult the estimation of the intercepts on the axis of ordinates in Fig. 3.

<sup>16</sup> Lewis, *Z. physik. Chem.*, **52**, 310 (1905).

measurements on the reaction kinetics by the flow method, and a determination of the adsorptions of the reacting gases. The principal results are as follows.

1. A quantitative method is developed for treating the results of kinetic measurements by the flow method.

2. The rate of the reaction is proportional to the pressure of hydrogen and independent of the oxygen pressure. The reaction is greatly retarded by the water formed. It is somewhat retarded by subjecting the catalyst to preliminary heating in oxygen. The average temperature coefficient is about 1.6.

3. The increase in the yield with increasing rate of passage of the gas mixture is satisfactorily accounted for by the lowering of the partial pressure of water vapor in the exit gases.

4. Hydrogen is not measurably adsorbed by active silver under the conditions obtaining in the catalysis. Oxygen, on the other hand, is strongly adsorbed, the amount taken up being nearly independent of pressure and temperature over the range in question.

5. The mechanism of the reaction is shown to depend on collisions of gaseous hydrogen molecules with adsorbed oxygen atoms which are free from adsorbed water. However, since under the conditions employed only about one such collision in a billion is effective, it is suggested that only those oxygen atoms react readily which are adjacent to bare spaces on the surface of the catalyst.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE  
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## DECOMPOSITION OF DIACETONE ALCOHOL IN ALKALI HYDROXIDE-ALKALI SALT SOLUTIONS

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### Introduction

It has been shown in a number of investigations<sup>1</sup> that the velocity of reaction of compounds subject to catalytic decomposition in acid-salt solutions is nearly always directly parallel to the activity of the hydrogen

<sup>1</sup> (a) Harned, *THIS JOURNAL*, **40**, 1461 (1918). (b) Åkerlöf, *Medd. Vetenskaps-akad., Nobelinst.*, **4**, 13 (1921); *Z. physik. Chem.*, **98**, 260 (1921). (c) Jones and Lewis, *J. Chem. Soc.*, **117**, 1120 (1920). (d) Harned and Pfanstiel, *THIS JOURNAL*, **44**, 2193 (1922). (e) Harned and Seltz, *ibid.*, **44**, 1475 (1922). (f) Scatchard, *ibid.*, **43**, 2387 (1921); **45**, 1580 (1923). (g) Moran and Lewis, *J. Chem. Soc.*, **121**, 1613 (1922). (h) Fales and Morrell, *THIS JOURNAL*, **44**, 2071 (1922). (i) Livingston and Bray, *ibid.*, **45**, 2048 (1923). Compare further the theoretical studies of (j) Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); **115**, 337 (1925). (k) Bjerrum, *ibid.*, **108**, 82 (1924); **118**, 251 (1925). (l) Christiansen, *ibid.*, **113**, 35 (1924).