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PREPARATION OF FORMALDEHYDE.[1]

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The preparation of formaldehyde was first accomplished by Hofmann[2] by passing air laden with methyl alcohol vapor over a heated platinum wire. The process was greatly improved later by Tollens[3] and Loew,[4] who substituted a roll of copper gauze for the platinum catalyst. In 1908 O. Blank[5] recommended silver, precipitated on asbestos, as a much more efficient contact agent than copper. Finally Jobbling, in his monograph on catalysis, has made the statement that gold is the best catalyst of all for this purpose.

Two systematic investigations bearing on this subject have been published. Orlaff[6] studied the effect of variations in the following factors: (*a*) the amount of alcohol vapor in the air; (*b*) the speed of the gas; (*c*) the nature and dimensions of the catalyst; (*d*) the purity of the alcohol. As catalysts, copper in various forms was tried as well as platinum, mantle

[1] From a dissertation submitted to the University of Oxford, February, 1919, in partial fulfilment of the requirements for the Degree of Bachelor of Science.

[2] Hofmann, *Ann.*, **145**, 357 (1868); *Ber.*, 2, 152 (1869); 11, 1686 (1878).

[3] Tollens, *Ber.*, **15**, 1629 (1882); **16**, 917 (1883); **19**, 2134 (1886).

[4] Loew, *J. prakt. Chem.*, [2] **33**, 324 (1886).

[5] O. Blank, *D. R. P.*, 228697.

[6] Orlaff: "Formaldehyde," translation by Kietaibl, 1909; *Centr.*, **1908**, I, 114 and 155; **1908**, II, 1499.

oxides, vanadium oxide, and iron. The best results were obtained with rolls of copper gauze, when the reaction mixture contained from 0.37 to 0.6 g. of oxygen per g. of alcohol. A roll of 30 mm. diameter gave a maximum yield of 54.5% while a 15 mm. copper roll yielded 49%. The best speed of the gas past the catalyst was found to lie within the limits 140–160 liters per hour. 2% of acetone in the alcohol caused a hotter reaction and an appreciable lowering of the yield, while traces of substances containing chlorine in the alcohol poisoned the catalyst.

Le Blanc and Plaschke[1] have investigated the action of a roll of silver gauze with great thoroughness. The conditions of the experiment were rigidly controlled, and it was shown that silver was a better catalyst than copper. Some of the results are plotted on the curves for comparison with the results of the present investigation. Attempts were made to measure the temperature of the catalyst, but it is evident from the work below that these attempts did not succeed.

The following investigation was undertaken at the suggestion of Professor W. H. Perkin to supply more information concerning the process of making formaldehyde. The results are particularly interesting bebecause the corresponding yields of formaldehyde are considerably higher than the yields recorded by either Orlaff or Le Blanc, though the work of these two investigators is in general confirmed.

The arrangement of the apparatus was not essentially different from that used by Tollens. Air was drawn through a loosely packed sodalime tube into a gas meter. Then it was dried in 2 sulfuric acid bottles and led to a battery of 3 flasks immersed in a thermostat regulated to $\pm 0.05°$. These flasks were joined together by well-insulated connections and both the intake and exit tubes were provided with glass taps; also each flask carried a dropping funnel. About 100 cc. of methyl alcohol was placed in each vessel and the battery was accurately weighed before and after each experiment. It was possible to secure complete saturation of the gas at all the speeds employed, with this system. The air-alcohol vapor mixture was now warmed to 100° by passing it through a coil heated with boiling water, and then led directly to the reaction chamber containing the catalyst. A hard glass tube served as a reaction chamber for the first 3 series of experiments, but it proved unsatisfactory because it could not stand the strain of the high temperatures without breaking on cooling. For the last series, an opaque silica tube was used In all experiments the wire gauze was well wrapped in prepared asbestos in order to force all the gas to go through the roll.

The reaction chamber communicated with a large air-cooled flask in which a solution condensed containing from 33 to 50% formaldehyde and from 5 to 20% alcohol. After this flask was placed a condenser and an-

[1] Le Blanc and Plaschke, *Z. Elektrochem.*, 17, 45 (1911).

other receiver; then 2 or 3 weighed wash-bottles and a sulfuric acid bottle. Only traces of alcohol and aldehyde reached the drying agent. There was now provided a gas sampling pipet containing mercury. The tap of this pipett was opened at the beginning of the experiment as soon as the air had been swept out of the apparatus, and the sample was allowed to leak in slowly throughout the entire run. Finally the apparatus led to another gas meter (provided with a manometer); then through a control tap and a large stabilizing bottle, to the pump.

At the commencement of an experiment, the catalyst was warmed to about 400°, but as soon as the stream of air was started, this external heating was discontinued. The speed of the gas could be adjusted quickly and sufficiently closely by regulating the pump and the last control tap. A run was allowed to proceed for from 15 to 90 minutes, according to the conditions. At the end the distillates and wash waters were carefully weighed and analyzed. The formaldehyde in the distillates was determined by the "sodium hydroxide-hydrogen peroxide" method[1] but the wash waters were analyzed by Romijn's iodine method.[2] The alcohol was found by oxidizing with chromic acid[3] and making allowance for the formaldehyde present. The gas sample was analyzed in an Orsat apparatus.

It was thus possible to control each experiment in 3 different ways:

(1) Amount of alcohol taken = alcohol accounted for in products as unchanged alcohol, formaldehyde, carbon monoxide and carbon dioxide.

(2) Volume of nitrogen in air = volume of gaseous products less volume of carbon monoxide, carbon dioxide, hydrogen and oxygen.

(3) Volume of hydrogen in products was compared with the theoretical amount according to the equations below. All of these comparisons showed good concordance in most of the runs.

Four series of experiments are here recorded with 4 different catalysts.

(1) A copper spiral: Length 74 mm.; diameter 14 mm.
Weight 30.5 g.; mesh 61 (per inch).

(2) A silver spiral: Length 75 mm.; diameter 10 mm.
Weight 13.5 g.; mesh 53.
(This gauze had been used for halogen combustions.)

(3) A new silver spiral: Length 102 mm.; diameter 13 mm.
Weight 40.75 g.; mesh 61.

(4) A gold-plated copper spiral: Length 100 mm.; diameter 14 mm.
Weight of copper 31.35 g.
Weight of gold 2.40 g.; mesh 35.

The effects of varying the following factors was sought: the proportion of air to alcohol vapor; the speed of gas; the length of the catalyst; and the purity of the alcohol. Curves have been drawn to illustrate the results. A serious difficulty arises when one seeks to depict graphically

[1] Haywood and Smith, THIS JOURNAL, 27, 1188 (1905).

[2] Williams, *ibid.*, 27, 596 (1905).

[3] Blank and Finkenbeiner, *Ber.*, 39, 1326 (1906).

the influence on the yield, of changing the composition of the reaction mixture, because the heating effect increases as the proportion of oxygen in the gas increases; and also as the speed is raised. Le Blanc and Plaschke used constant temperature of the catalyst as the basis of this comparison, thus ignoring the effect of large differences of speed. (Also it is altogether probable that their temperatures were not constant at all.) In the curves below, constant speed of the air has been chosen for this comparison. This is equivalent to saying that the oxygen supply to the catalyst was held constant; therefore the heat of the reaction was nearly constant, though the temperature actually generated depended on the dilution with alcohol.

The alcohol used was carefully fractionated with a 5-piece Young's column. It boiled constantly at 65.0° (758 mm.), and contained 0.02% of acetone.

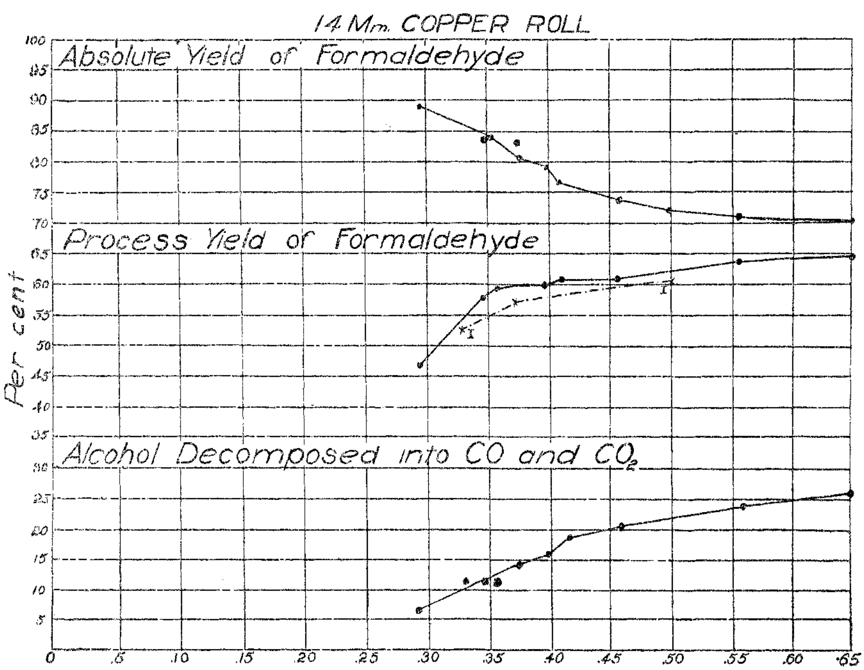
It was noted in the experiments with silver that the quantity of alcohol carried off at constant temperature, by the same amount of air, varied appreciably from day to day, as well as with different speeds of the air. These variations were shown by the gas law to be due to differences in the total pressure in the vaporizers. Accordingly, in the last series of experiments, a manometer was put into communication with the last vaporizing flask through the dropping funnel, and the pressure was adjusted by means of the tap on the intake tube of the first flask. Good concordance in the quantity of alcohol vaporized at constant temperature was thus obtained. It is remarkable that Le Blanc and Plaschke should have had such excellent concordance in this factor without regulating the pressure.

Various attempts were made to determine the temperature of the catalyst, which ranged from a dull glow, visible only in the dark, to a bright red heat. That part of the roll nearest the entrance end of the reaction tube was always the hottest. When a thermocouple, protected by a thin-walled hard glass tube, was embedded here, it registered temperatures from 350 to 565° in both the third and fourth series of experiments. This was the range that Le Blanc and Plaschke had observed also. But it seemed probable that the incoming gases exercised a cooling influence because the temperatures indicated were frequently anomalous. Therefore, when the last series was finished, a piece of gold gauze was rolled on a small, thin walled quartz tube, closed at one end, and the whole was placed in a large, silica tube, so that the open end of the smaller tube communicated with the outside. A copper-constantan couple was prepared and standardized with sulfur (444°); phosphorus pentasulfide (515°); potassium iodide (m. p. 623°); and potassium chloride (740°). This could be introduced into the center of the roll and the place of maximum temperature easily found.

The conditions which had obtained in each experiment of the series in turn were now accurately duplicated. A range from 530° to above 900° was thus found, indicating that the values previously found were quite worthless.

Experiments with Copper.

The roll of copper gauze was quite new and had the dimensions recorded above. It was well packed into a hard glass tube with Gooch asbestos. When this packing was loose the yield of formaldehyde was appreciably lower than when it was tight. The series is not complete, but enough results are given to serve as a basis for comparing copper as a catalyst with gold and silver. The optimum speed of the air was about 130 liters per hour and this speed was used throughout this series. The temperature of the catalyst was not measured. The yield of formaldehyde was calculated in 2 ways. The "process yield" is the percentage of the total alcohol taken that was converted into formaldehyde; and the "absolute yield" is the percentage of alcohol affected by the reaction which was found as formaldehyde. From a commercial point of view the second



Grams O_2 per gram alcohol.

Fig. 1.

Speed of air: 115–140 liters per hour.

Curve I.—Illustrates the influence of imperfectly packing the roll of gauze into the tube.

TABLE I.—14 MM. COPPER GAUZE.

No.	Temp. of thermostat. ° C.	G. O_2 per g. of alcohol.	Speed of air. L. per hr.	Alcohol accounted for in products as: HCHO. %.	Unchanged alcohol. %.	$CO + CO_2$. %.	Total. %.	Yield HCHO % alcohol changed.	Gas products. CO_2. %.	CO. %.	H_2. %.	H_2 (calc.). %.	Total acc. for %.
1	45.0	0.287	123	47.8	45.0	6.88	99.68	87.5	5.37	..	..	..	...
2	43.6	0.329	129	53.7	34.25	11.7	99.65	82.2	7.23	Nil	14.7	15.0	101.3[a]
3	42.9	0.345	140	58.2	31.2	10.75	100.17	83.3	6.27	Nil	..	..	...
4	42.7	0.357	126	59.6	29.45	11.0	100.05	84.5	6.53	0.22	11.9?	13.2	101.5
5	41.7	0.368	114.5	59.25	27.7	11.4	98.35	83.9	6.5	Nil	..	..	...
6	41.5	0.375	125	57.25	27.9	13.53	98.68	81.0	7.4	0.13	13.7	13.25	100.0[a]
7	41.6	0.374	132	59.15	26.32	14.13	99.6	80.7	7.43	0.23	14.05	14.4	102
8	41.6	0.372	142.5	59.5	24.4	15.7	99.6	79.1	7.95	0.48	15.6	17.4	101
9	40.7	0.391	124	59.9	24.75	15.4	100.05	79.5	7.75	1.0	15.0	15.7	101.5
10	39.6	0.412	129	60.25	21.5	17.95	99.7	77.0	8.69	0.23	14.5	15.0	101.5
11	38.6	0.465	135	61.3	17.55	20.75	99.6	74.6	9.0	0.34	13.8	14.3	99.3
12	37.6	0.496	127	60.2	17.3	22.05	99.55	73.1	9.07	0.25	12.0	11.3	99.6[a]
13	35.7	0.562	132	63.6	12.55	24.8	100.95	72.0	8.63	0.94	8.5	8.7	101
14	31.9	0.658	128.5	63.6	9.15	26.55	99.3	70.5	7.83	1.4	Lost	..	...

[a] The roll was loosely packed into the tube.

yield is the more important because the unchanged alcohol can be recovered by fractionation.

The curve representing the "process yield" is unique by comparison with the curves for the other catalysts, because it rises so rapidly at first as the proportion of air to alcohol is increased; then it breaks sharply and continues rising much more slowly. Also the maximum yield occurs when the oxygen content of the gas is higher than with the other metals. (See Fig. 1.) Likewise the curves representing the "absolute yields" and "total destruction" have a different form as compared with the corresponding curves for the other metals.

Experiments with Silver.

I. An old silver spiral which had been used for halogen combustions was next tried after heating it long and carefully in a flame. The first experiments gave yields that were both low and erratic. But the fifth run employed a high proportion of oxygen to alcohol and was, therefore, attended by a rather high-temperature reaction. When the preceding runs were now duplicated a regular curve was obtained. After a second strong heating, the curve was pitched still higher with respect to the yield of formaldehyde, but the series had to be discontinued because of the extremely fragile condition of the roll. This series shows clearly the harmful effects of traces of impurities, probably halogens, on the silver. But at the end of this series, the silver roll seemed to be operating in a manner almost identical with that of the new silver gauze described below, so that these impurities can be removed by heating.

II. A much more complete series of experiments than either of the preceding was now performed with a roll of new silver gauze in a hard glass tube (Table II). The reaction tube broke after the fifteenth run and the roll was damaged in shifting it to another tube. But on repeating the first experiment concordant results were obtained, showing that the damaging of the roll had a negligible effect on the process. (Table II, Nos. 11 and 12.)

It is remarkable that variations in the speed, when the composition of the reaction mixture was held constant had such a small effect on the results in spite of large temperature differences on the catalyst, which were obvious from the appearance of the metal. This series is characterized by extremely low "total destruction" of the alcohol (*i. e.*, alcohol decomposed into carbon monoxide and dioxide); combined with high "process yields" of formaldehyde (Fig. 2). The highest "process yields" were obtained when the gas mixture contained about 0.45 g. of oxygen per g. of alcohol. But the best absolute yields required less than 0.3 g. of oxygen per g. of alcohol. (Fig. 2). It was possible to obtain an absolute yield of 95.0% and a process yield of 55.5% when this ratio was 0.25 g. of oxygen per g. of alcohol.

Table II.—13 Mm. Silver Spiral.

No.	Temp. of thermostat. ° C.	G. O_2 per g. of alcohol.	Speed of air L. per hr.	Apparent temp. of catalyst. ° C.	Alcohol accounted for in products as: HCHO. %.	CH_3OH. %.	$CO + CO_2$. %.	Total. %.	Yield HCHO % alcohol changed.	Gas products. CO_2. %.	CO. %.	H_2. %.	H (calc.). %.	Total acc. for. %.
1	53.6	0.157	196	363	32.4	65.55	1.76	99.71	95.0	2.48	0.05	9.63	9.35	102.5
2	50.6	0.184	180	380	40.3	57.5	2.20	100.0	94.9	2.64	Nil	12.12	12.7	101.8
3	48.6	0.228	228	405	49.4	47.5	2.69	99.59	94.9	2.65	Nil	12.97	12.2	99.4
4	48.6	0.218	177	400	47.1	50.0	2.82	99.92	94.5	2.78	0.05	12.42	12.8	102.0
5	46.6	0.256	230	423	55.5	40.9	3.96	100.09	93.7	2.95	0.18	13.1	13.8	102.0
6	46.6	0.253	196	422	55.6	41.2	3.58	100.38	93.9	3.02	Nil	13.5	13.5	102.0
7	46.6	0.257	157	420	53.75	42.4	3.45	99.6	94.0	2.93	0.06	12.3	11.7	100.0
8	46.6	0.253	129.4	414	52.8	43.6	3.96	100.36	93.0	3.46	0.05	12.18	12.5	101.5
9	44.6	0.294	123	423	60.0	35.15	5.30	100.45	92.0	3.75	0.12	13.2	12.8	101.2
10	43.6	0.325	185	444	63.7	29.4	6.57	99.67	90.5	4.23	0.20	12.3	12.9	100.5
11	42.6	0.345	124	440	62.7	31.1	6.66	100.47	90.3	4.2	0.16	Lost	9.75	...[a]
12	42.9	0.346	125	440	64.3	28.05	6.86	99.21	90.6	4.11	0.27	10.6	10.1	100.0[b]
13	42.6	0.354	90	403	63.2	29.0	7.77	99.97	89.0	4.88	Nil	10.6	10.55	100.7
14	39.6	0.418	163	500	71.4	17.75	10.58	99.73	86.9	4.86	0.64	11.65	10.1	101.0[c]
15	39.6	0.422	121	460	72.75	16.85	10.7	100.3	87.2	5.21	0.32	11.5	11.0	100.8
16	39.5	0.426	92	423	70.7	18.45	10.6	99.75	86.9	5.42	0.05	10.23	9.25	101.5
17	37.4	0.480	163	565	71.35	11.33	18.3	100.98	79.5	5.65	2.55	11.3	11.35	99.7[d]
18	37.4	0.487	125	503	73.5	12.73	13.95	100.18	84.0	5.67	0.78	8.1	8.1	101.0
19	37.47	0.463	95	...	73.1	11.32	13.8	99.25	84.2	5.54	0.99	9.9	97.5	101.0
20	37.2	0.511	94.6	445	72.7	11.65	15.45	99.8	82.5	5.83	0.52	6.7	5.7	101.2
21	37.45	0.479	62.5	...	69.9	17.4	13.65	100.95	83.75	5.9	0.43	8.8	7.1	101.5
22	35.1	0.583	126	565	68.75	7.1	24.3	100.15	73.8	7.05	2.10	8.85	8.1	99.5
					Length 80 mm. (in two pieces).									
23	39.6	0.432	125	460	71.6	15.0	12.0	98.6	85.5	5.14	0.67	11.15	11.1	102.0[e]
					Length 60 mm.									
24	39.8	0.423	128	460	71.6	18.35	9.4	99.35	88.3	4.67	0.27	11.5(?)	8.0	98.7

[a] The first expt. of this series.

[b] One of the final expts. Catalyst 97 mm. long.

[c] All the preceding expts. except No. 12 were done before the tube broke the first time.

[d] The catalyst was crushed to a length of 96–98 mm.

[e] The shorter piece of the roll was extremely compact. This experiment does not seem comparable with the others, therefore.

It will be noted that the general form and direction of the curves are almost identical with those found by Le Blanc and Plaschke, but the yields of formaldehyde are about 10 to 15% higher and the "total destruction" about 5% lower. The reason for this variation was not determined

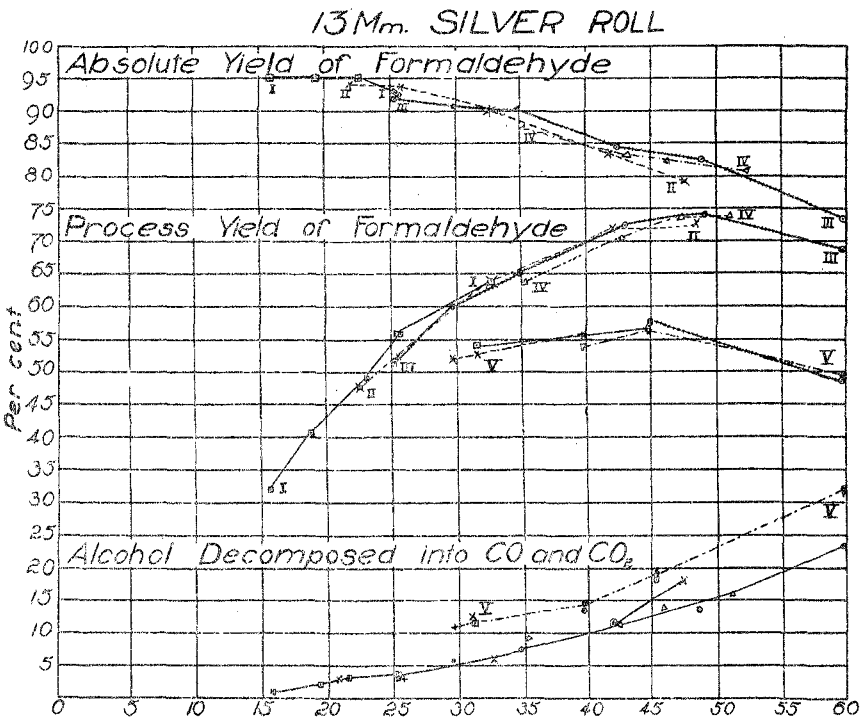


Fig. 2.

Curves I—Speed of air: 180–230 liters per hour.
Curves II—Speed of air: 160–180 liters per hour.
Curves III—Speed of air: 120–130 liters per hour.
Curves IV—Speed of air: 90–100 liters per hour.
Curves V—Characteristic results from Le Blanc and Plaschke.

Diameter of silver roll, 30 mm. Speed of air about same as indicated by notation above.

but the conditions attending the 2 sets of experiments differed in the following details: Le Blanc and Plashke used a roll of gauze 30 mm. in diameter and worked at pressures of 770–800 mm. in the reaction chamber, whereas in this investigation the roll was 13 mm. in diameter and the pressure in the reaction chamber 715–750 mm.

Experiments with Gold.

A piece of copper gauze was electroplated with pure gold. The coating of metal was made thick and coherent by frequent scratch-brushing.

TABLE III.—GOLD PLATED SPIRAL, LENGTH 10 CM., DIAMETER, 14 MM.

No.	Temp. of thermostat. ° C.	Pressure in vaporizer. Cm.	G. O_2 per g. of alcohol.	Speed of air. L. per hr.	Max. temp. of catalyst. ° C.	Alcohol accounted for as: HCHO. %.	CH₃OH. %.	CO + CO₂. %.	Total. %.	Yield HCHO % alcohol changed.	Gas products. CO₂. %.	CO. %.	H₂. %.	H₂ (calc.). %.	Total acc. for %.
1	48.9	72.0	0.194	200	520	40.2	54.2	3.85	98.25	91.2	4.18	0.22	14.9	14.8	98
2	45.5	70.7	0.245	202	580	49.7	45.0	5.85	100.55	90.4	4.8	0.20	15.25	15.45	100.5
3	43.2	71.2	0.291	194	640	56.4	36.1	7.55	100.5	88.2	5.17	0.20	16.1	15.0	100
4	43.2	71.25	0.286	150	620	52.9	39.3	8.0	100.2	87.3	5.65	0.22	15.23	14.5	100
5	39.9	71.85	0.374	203	770	59.8	29.3	10.9	100.0	84.5	5.05	1.1	12.3	9.0	98.6
6	39.9	71.85	0.378	152	720	60.8	27.3	10.15	98.25	85.7	5.7	0.22	11.3	10.2	100.0[a]
7	39.9	71.85	0.369	149	720	62.2	26.2	10.75	99.15	85.2	6.15	0.10	13.9	12.5	99.3[b]
8	39.9	71.85	0.378	100	660	54.55	32.7	13.1	100.35	80.6	7.52	Nil	13.0	10.7	97.4
9	39.9	71.65	0.377	58	585	38.3	44.6	17.7	100.6	69.0	10.15	Nil	11.4	10.3	97.0
10	37.9	71.5	0.427	195	...	57.5	22.7	17.8	98.0	76.3	4.7	4.25	10.8	9.0	99.2
11	37.9	71.5	0.425	152.5	Ca 850	65.0	21.1	12.65	98.75	83.6	6.25	0.40	11.7	10.0	98
12	37.9	71.5	0.422	106	735	60.6	23.65	15.2	99.45	80.0	7.58	0.22	12.9	11.4	98
13	37.9	71.5	0.432	65	605	48.5	27.6	23.3	99.4	67.3	10.9	0.05	15.75	16.25	101.7
14	35.1	72.5	0.515	156	Above 850	63.6	18.0	17.6	99.2	78.0	5.0	2.97	6.1	4.0	99.2
15	35.15	72.5	0.516	97	790	63.0	15.0	21.4	99.5	74.4	8.4	0.55	9.95	10.1	99.3
16	32.6	72.0	0.605	150	...	55.0	11.3	33.0	99.3	62.5	6.35	5.3	6.95	6.75	101
17	32.6	72.0	0.608	101	Ca 850	60.2	10.3	28.1	98.6	68.2	9.2	0.70	7.45	7.65	101

							Length 6 cm.								
18	48.9	72.0	0.194	183	520	41.4	54.6	4.35	100.35	90.6	4.45	0.30	15.6	16.97	...
19	39.9	71.95	0.370	194	770	63.2	24.1	11.9	99.2	84.2	5.6	1.15	14.2	13.5	100
20	39.9	71.85	0.367	149	720	62.25	27.4	10.4	100.05	85.8	5.38	0.88	11.32	11.9	99.5
21	39.9	71.9	0.363	97.5	650	57.35	27.9	14.1	99.35	80.4	7.55	0.33	16.6	15.9	99.4
							Length 4 cm.								
22	39.9	71.85	0.368	150	720	60.0	30.2	9.7	99.9	85.9	5.35	0.60	10.1	9.75	99.5
23	39.9	71.9	0.368	106	665	59.0	29.0	12.0	100.0	83.1	6.55	0.50	12.6	12.55	99.0
							Length 2 cm.								
24	39.9	71.85	0.365	147	720	63.0	25.55	11.5	100.05	84.5	5.5	1.35	Lost	10.6	...
25	39.9	71.95	0.369	102	660	60.0	27.7	13.0	100.7	82.6	6.55	1.05	13.35	14.05	97.5
			Influence of impurities in the Alcohol: Water and Acetone. Length of Roll 6 Cm.												
26	39.9	71.9	0.366	151.5	...	63.25	26.9	9.0	99.15	87.5	5.2	0.20	11.6	10.4	100 [c]
27	39.9	71.95	0.365	151	...	61.5	27.5	10.25	99.25	85.6	5.75	0.30	12.6	11.5	100.3 [d]
28	39.9	71.8	0.368	152	...	63.3	25.75	10.95	100.0	85.2	6.0	0.45	12.8	13.3	98.7 [e]

[a] The first expt. of this series.
[b] The last expt. The catalyst had changed only slightly.
[c] 5% H_2O added.
[d] 10% H_2O added
[e] 1.7% acetone added

The experience gained in the foregoing work was used to make this series as complete and uniform as possible. An opaque silica tube was used as the reaction chamber and it withstood all the experiments without breaking. The thermostat was enlarged, to make it easier to regulate at the beginning of a run, so that it was possible to avoid a fluctuation of more than 0.05° at this time. Finally a manometer was attached to the last vaporizing flask as described above.

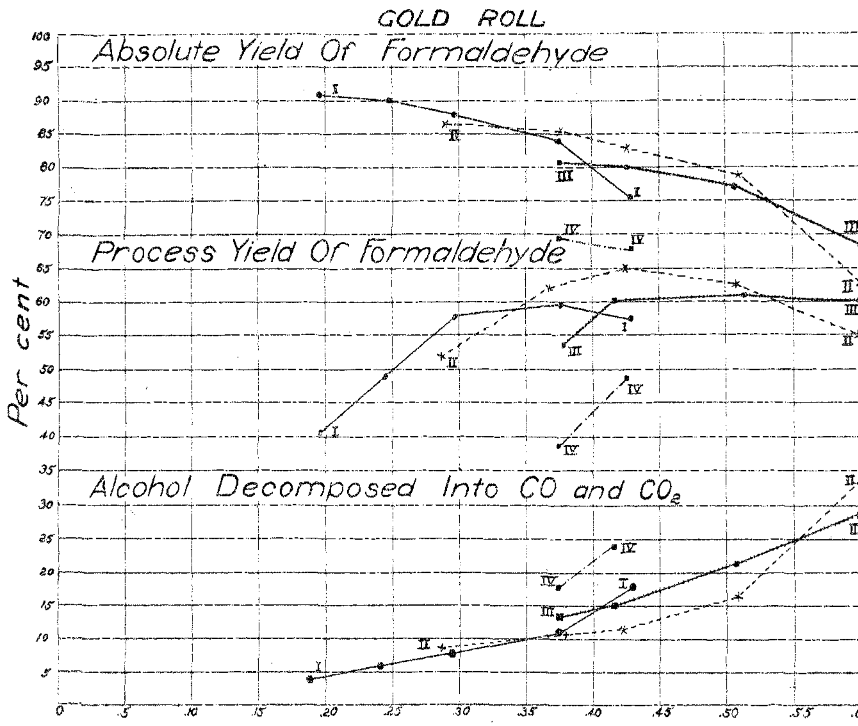
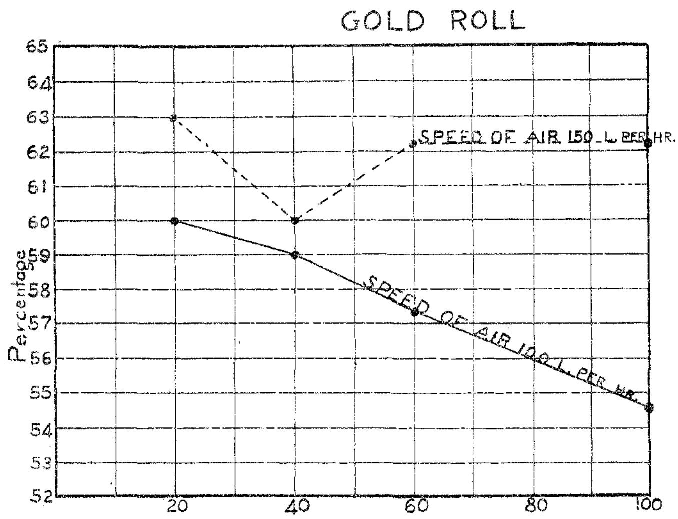


Fig. 3.

Curve I—Speed of air: 200 liters per hour.
Curve II—Speed of air: 150 liters per hour.
Curve III—Speed of air: 100 liters per hour.
Curve IV—Speed of air: 60 liters per hour.

Only 4 different speeds of the air were used throughout. It will be observed that speed had a tremendous influence on the process at constant composition of the gas mixture. Gold has a much greater tendency to decompose formaldehyde than silver. This also is shown by the curves illustrating the "total destruction" of alcohol (Fig. 3). With silver, speed has no influence on "total destruction;" with gold this value increases directly with the speed. When the length of the roll was cut down, the yields of formaldehyde increased slightly and it is evident that the reaction was practically completed in the first 2 centimeters of the roll (Fig. 4). The maximum process yield (65%) was obtained when the reaction mixture contained 0.425 g. of oxygen per g. of alcohol. When this ratio was 0.245 : 1 the process yield was 49.7% and the absolute yield 90.4% (Fig. 3).

Three experiments were performed (Table III: Nos. 26, 27, 28) in which water and acetone were added to the reacting mixture by allowing the liquid to flow from a buret into the preheating coil, at a controlled rate of speed. When the ratio of weight of alcohol to water was 9 to 1, the process



Length of roll mm.

Fig. 4.

Influence of length of the roll on the "process yield" of formaldehyde.

was only slightly affected. The addition of 1.7% acetone to the alcohol caused a somewhat hotter reaction, but did not change the yield appreciably.

In Fig. 5, the total amounts of alcohol affected by the catalyst, (*i. e.*, alcohol converted into formaldehyde, carbon monoxide and dioxide), have been plotted against the composition of the reaction mixture, at constant speed of the air. One curve is given for each of the 3 metals. The values for the gold were found by interpolating from higher and lower speeds of air. Silver is thus seen to be more active than copper, which in turn is slightly more active than gold. And since silver is less active than the other 2 in decomposing formaldehyde it is undoubtedly to be preferred to copper or gold as a catalyst in this reaction.

Theoretical.

The fundamental reactions of this process are no doubt the following dehydrogenations:

$$CH_3OH \longrightarrow HCHO + H_2$$
$$HCHO \longrightarrow CO + H_2$$

These are then followed by partial oxidation of the hydrogen and carbon monoxide until all the oxygen is used up.

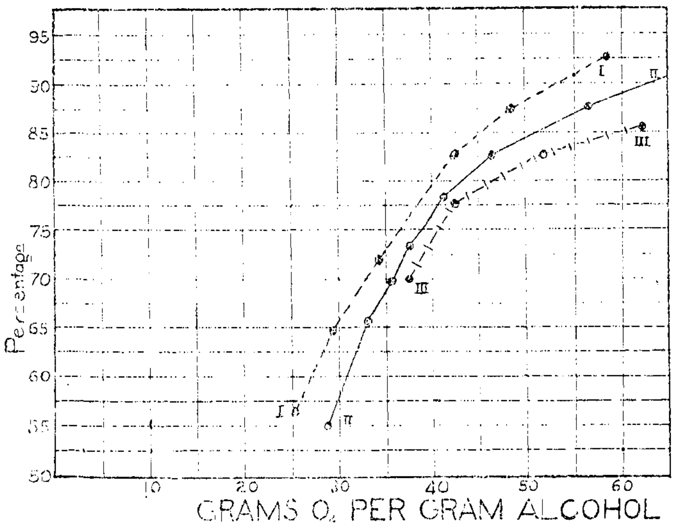


Fig. 5.

Alcohol converted into HCHO, CO and CO_2 by silver, copper and gold.
Curve I—13 mm. silver roll.
Curve II—14 mm. copper roll.
Curve III—14 mm. gold roll.
Speed of air: 125 liters per hour.

The theoretical excess of hydrogen is readily calculated from these equations by means of the formula:

$$[(\text{Wt. of HCHO } 22.4/30) + 2(\text{vol. CO} + CO_2)] - [2 \text{ vol. } O_2 - {}^1/_2 \text{ vol. } CO_2.]$$

This result is then divided by the volume of the gas products to give the percentage of hydrogen. From the tables it will be seen that this value agrees quite closely in most cases with the percentage of hydrogen actually found.

It should be noted also that Le Blanc and Plashke[1] were able to get a 27% yield of formaldehyde by passing alcohol vapor free from air over a copper spiral heated to 600 to 700°. It was observed, however, that this yield fell off gradually to 4% as the experiment was repeated, but the activity of the metal could be restored by oxidizing and reducing it.

[1] *Loc. cit.*

Accordingly the function of the oxygen seems to be, aside from maintaining the necessary temperature, to keep the catalyst active by oxidizing and removing any "poisons" and also by keeping the surface of the metal in the proper physical condition.

The amount of carbon monoxide in the gaseous products offers some interesting data for consideration. It will be seen from the experiments with gold, that the quantity of this constituent in the gas increases, (1) when the speed of the gas is increased, the composition of the reaction mixture and the dimensions of the catalysts being unchanged; (2) when the proportion of oxygen to alcohol is raised, the other 2 factors just mentioned being constant; and (3), when the length of the roll of gauze is decreased, the other conditions being unchanged. The first 2 factors involve an increase in the temperature of the reaction and in general a corresponding increase in the quantity of alcohol "completely destroyed." But in the first case the quantity of alcohol completely destroyed is usually influenced more by the length of time of contact of the gases with the catalyst than by the temperature of the reaction and, therefore, it is not so much the quantity of total decomposition that influences the carbon monoxide content of the gas. The reaction

$$CO_2 + H_2 = H_2O + CO$$

suggests itself as a possible explanation, but this equilibrium is so slow that it could not play an important part in this phenomenon. The following table, taken from the data of the gold roll, and the work of Hahn[1] on this reaction, indicates that though the equilibrium is in every case far from complete, it is always less complete when according to the theory one would expect it to be more complete:

TABLE IV.

Grams O_2 per gram alcohol.	Approximate maximum temperature catalyst. ° C.	Length of catalyst. Cm.	Liters of air per hour.	CO. %.	$K = \frac{CO.H_2O}{CO_2.H_2}$ (found).	K. Calc.
0.369	720	10	149	0.10	0.02	0.64
0.367	720	6	149	0.88	0.17	0.64
0.368	720	4	150	0.60	0.105	0.64
0.365	720	2	147	1.35	0.24	0.64
0.427	950	10	195	4.25	0.69	1.4
0.425	850	10	152	0.40	0.056	1.08
0.422	735	10	106	0.22	0.025	0.69
0.422	605	10	65	0.05	0.0035	0.30
0.374	770	10	203	1.10	0.24	0.82
0.516	790	10	97	0.55	0.086	0.85

The data are insufficient to permit drawing any definite conclusion in regard to the matter, but it seems probable that the reaction is not always completed on the catalyst when the speed and the "total destruction"

[1] Hahn, *Z. phys. Chem.*, **42**, 705 (1903); **44**, 513 (1903); **48**, 735 (1904).

are high. Under these circumstances the carbon monoxide, which is ordinarily burned completely to dioxide on the catalyst, in spite of the large excess of hydrogen, is only partially oxidized on the metal, and when the gases containing some free oxygen are swept past the catalyst the oxygen is used up by the hydrogen instead of by the carbon monoxide. No steps were taken to test this theory, however.

Summary.

The results of this investigation may be summarized as follows:

1. Silver is more active as a catalyst than either gold or copper in inducing the dehydrogenation of methyl alcohol. At the same time it causes less decomposition of formaldehyde so that the yield of this product is greater with silver than with copper or gold.

2. With silver, an absolute yield of 95.0% and a process yield of 55.6% was obtained when the reaction mixture contained 0.25 g. of oxygen per g. of alcohol. Under similar conditions with gold the absolute yield was 90.5% and the process yield 50.5%. These values for copper, found by extrapolating the curves, would be about 88.5 and 40%, respectively.

3. The best process yields were obtained with silver and gold when the reaction mixture contained 0.4 to 0.5 g. of oxygen per g. of alcohol. With copper, this value was higher: 0.55–0.65 g. of oxygen per g. of alcohol.

4. The optimum speed of the air for all 3 catalysts was 125–150 liters per hour.

5. The length of the roll of gauze did not exert a very marked influence on the process.

6. The temperature of the reaction was measured for the gold roll and was found to vary from 520° to above 900° according to the conditions. The temperatures of the silver roll were probably about the same.

7. One and seven-tenths % acetone or 10% water in the alcohol did not the influence process appreciably (gold roll).

8. An old silver roll which had been used for halogen combustions gave very low and erratic yields until it had been purified by several very high temperature reactions. The "poisoning" substances seem to have been retained with great tenacity.

9. Evidence is given to indicate that the essential reactions are dehydrogenations followed by the oxidation of hydrogen and carbon monoxide.

The author acknowledges his indebtedness to Professor W. H. Perkin, under whose supervision this work was carried out, for encouragement and many helpful suggestions.

LOGAN, UTAH.