The active copper is seen to have an apparent density lower by about 2.5% than that of massive copper. Since the X-ray analysis of a sample of active copper just mentioned showed that the copper had the normal arrangement and spacing of atoms, it is evident that the low density is probably due to the presence of cavities within the mass into which neither helium nor water penetrated.

Summary

1. The adsorption isotherms of hydrogen, ethylene, ethane, carbon-monoxide and nitrogen at 0° and up to one atmosphere have been measured. The results are discussed and the specific nature of the adsorption emphasized.

2. The effect of poisoning the copper with mercury on the adsorptions of hydrogen, ethylene and carbon monoxide and the effect of partially deactivating copper by heating on the adsorptions of hydrogen and ethylene have been determined. In both cases it has been found that the strong adsorption at low pressures has been markedly decreased while the additional adsorption at higher pressures has suffered little or not at all.

3. From these results and certain incidental observations it has been concluded that the adsorption is due to specific adsorbing centers on the copper surface rather than to the surface as a whole. These centers, it seems most reasonable to suppose, are regions of high curvature or "peaks" on the surface.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE CATALYTIC OXIDATION OF CARBON MONOXIDE. I. EFFICIENCY OF THE CATALYSTS, MANGANESE DIOXIDE, CUPRIC OXIDE AND MIXTURES OF THESE OXIDES

BY J. A. ALMQUIST AND WILLIAM C. BRAY

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In connection with the work of the Defense Research Section, C. W. S., it was discovered[1,2,3,4] that specially prepared mixtures of certain oxides catalyzed the combustion of carbon monoxide at low concentration in air. The catalyst composed of 60% of manganese dioxide and 40% of copper oxide furnished a striking example of the "mixture effect"[5] in contact ca-

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[1] Lamb, Bray and Frazer, *J. Ind. Eng. Chem.*, **12**, 213 (1920).

[2] Rogers, Piggott, Bahlke and Jennings, THIS JOURNAL, **43**, 1973 (1921).

[3] Merrill and Scalione, *ibid.*, **43**, 1982 (1921).

[4] Lamb, Scalione and Edgar, *ibid.*, **44**, 738 (1922).

[5] The mixture effect is probably closely related to promoter action. For a discussion of a number of examples, see Pease and Taylor, *J. Phys. Chem.*, **24**, 241 (1920).

talysis, since with dry gas it had been made to operate at high efficiency at a temperature as low as 0°, although each of its components was active only at a much higher temperature.

In 1920, an investigation of the mixture effect was begun in this Laboratory, and the manganese dioxide-copper oxide catalysts for the combustion of carbon monoxide were chosen for study. It was planned to obtain as complete data as possible for several series of catalysts, varying in composition from pure manganese dioxide to pure copper oxide, rather than to attempt to prepare especially active catalysts. In order that the results for each series might give comparable data on the mixture effect, all of the catalysts of one series were prepared from the same moist samples of the individual oxides, and were dried under similar conditions. The program included the study of catalytic activity, adsorption and desorption of the gases involved, and the pore volume of the catalysts.

Since the completion of our work the results of a related investigation by Benton[6] have been published, in which special attention was paid to the adsorption of gases by several oxide catalysts, including manganese dioxide, cupric oxide, and one mixture of these oxides. The experimental details differ greatly in these two independent investigations, and each will be a useful supplement to the other.

The present paper deals primarily with the activity of the catalysts. A satisfactory measure of activity, as has been pointed out in earlier papers[2,4], is the efficiency of the catalyst at a given temperature, or is the temperature corresponding to a given efficiency, when a "steady state" has been attained. It was found that a definite efficiency could be obtained for each catalyst provided that certain experimental conditions, as the temperature and volume of the catalyst, the rate of flow of the gas, and the partial pressure of water vapor, were kept constant. The results of the measurements, under controlled conditions, and in general with dry gas, are given in the form of efficiency-temperature curves, the efficiency being expressed as the percentage of the carbon monoxide oxidized in passing through the catalyst. The curves do not intersect, and their positions with reference to the temperature axis give a convenient measure of the relative activities of the catalysts.

In general, a very low concentration of carbon monoxide in air, approximately 0.2%, was used in these tests. Higher concentrations would have introduced a complication due to the greater heat of combustion in the mass of the catalyst. However, the precaution of measuring the temperature within the catalyst, when operating under constant conditions, prevented any error due to this heating effect. In fact, it was proved for one catalyst that the same efficiency-temperature curve was obtained when the carbon monoxide concentration was varied between 0.1% and 0.6%.

[6] Benton, This Journal, **45**, 887, 900 (1923).

Preparation of the Catalysts

The *manganese dioxide* and *copper oxide* were prepared according to the directions of Merrill and Scalione[7] except that larger quantities were used. However, we believe that products of this type made by different investigators or at different times may vary greatly in properties.

In the preparation of the *basic copper carbonate,* the directions of Merrill and Scalione[8] were followed except that it was not precipitated on the manganese dioxide. The product was a fine, green precipitate and settled rapidly.

Three series of catalysts were prepared. Each consisted of six members, the pure components, and four mixtures of the following approximate compositions: 80% MnO_2, 20% CuO; 60% MnO_2, 40% CuO; 40% MnO_2, 60% CuO; 20% MnO_2, 80% CuO. The catalysts of each series will be referred to later by numbers from 1 to 6, in the order of decreasing manganese dioxide content.

In each series the moist constituents were mixed in the desired proportions, drained on a filter, and the six samples in the form of filter cakes dried slowly at about 75° for 72 hours in an electric oven. In each case the resulting material was broken up, and granules which passed a 10-mesh screen and were retained on a 20-mesh screen were collected and stored in well-stoppered bottles. Before these granules were tested or analyzed, they were given a final drying for half an hour at 175° under a pressure of about $^1/_3$ atmosphere.

The catalysts of Series 1 were later found to contain soluble sulfates, and in some cases seemed not to have been well mixed. Accordingly, in the two later series the constituents were washed more carefully during their preparation, and the mixing was done by grinding the moist oxides in a large mortar until a uniform paste resulted. The basic copper carbonate (No 6, Series 3) had a tendency to pulverize on drying and did not give satisfactory granules. No. 5 in the same series gave very soft granules.

Three catalysts prepared by the Washington investigators were also tested: manganese dioxide, a 60% (MnO_2) mixture, and copper oxide. Portions of the original samples were given the usual half-hour heat treatment under diminished pressure at 175° before being tested. These catalysts are numbered W1, W3, and W6 respectively, but do not constitute a related series. The methods of preparation of the two oxides, W1 and W6, were similar to those used by us; but the mixture, W3, is not directly comparable with any of our mixtures. It is probably closely related to or identical with that used by Lamb, Scalione and Edgar.[9] Its properties, which will be presented later, indicate that its constituents differed from those of the other mixtures, but may be partly accounted for by the pressure treatment to which the moist filter cake was subjected.

[7] Ref. 3, p. 1986.

[8] Ref. 3, p. 1987.

[9] Ref. 4, p. 740, Footnote 6.

Apparatus and Experimental Method

The general method of testing consisted in passing a mixture of carbon monoxide and air of known composition through the catalysts at a definite constant rate and determining the percentage of the carbon monoxide oxidized by analyzing the effluent gas. Since it was desirable to make analyses continuously, use was made of a calorimetric device developed by Lamb and Larson,[10] with a modification essentially like that described by Larson and White[11] for the prevention of premature combustion on the thermocouple leads.

The flowmeter, A, gave a head of 35.8 cm. of water for a rate of flow of $^5/_{12}$ liters per minute. This corresponds to the space velocity of 5000 for 5 cc. of catalyst which was used in these tests.

E is a bead tower through which concd. sulfuric acid dripped and G is a tower containing solid sodium hydroxide for removing acid spray.

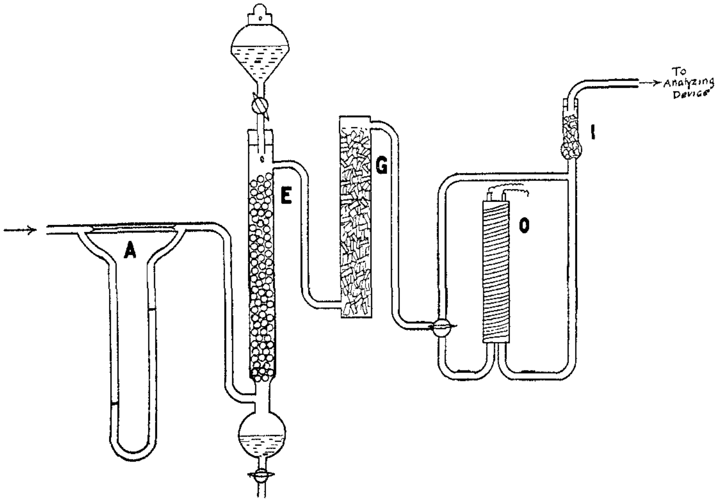

Fig. 1

The catalyst to be tested was placed in a tube at O. The testing tube was of 1 cm. cross section and the catalyst was placed therein on a perforated plate, to a depth of 5 cm. The gas passed up inside of the outer jacket and down through the catalyst contained in the inner tube. For tests above room temperature, heating was accomplished by a coil of resistance wire wound on asbestos paper around the outer tube, and the temperature was controlled by means of a lamp bank and a rheostat. The temperature within the catalyst and that just above it was measured by means of two copper-constantan thermocouples. Readings were made on a commercial potentiometer indicator to within 1°. When the catalyst was operating at 100% efficiency with 0.2% carbon monoxide air mixture, its temperature was 4° or 5° higher than that of the entering gas; but at 20% or lower efficiency the difference was not measurable. For tests below room

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[10] Lamb and Larson, THIS JOURNAL, **41**, 1908 (1919); compare Figs. 3 and 4, p. 1914.

[11] Larson and White, *ibid.*, **44**, 20 (1922).

temperature the entering gas was precooled before reaching the catalyst by passing through a copper tube, closely wound around the glass jacket. The apparatus was immersed in a Dewar tube containing a suitable cooling mixture and the temperature of the catalyst was measured as before.

In Fig. 1, I represents a calcium chloride drying tube, placed beyond the catalyst, which was used in all our work. It is probable that the drying of the gas at this point was unnecessary, since there is no evidence that water vapor interferes with the performance of the analyzing device.

The mixture of carbon monoxide and air used for testing was kept in a 500-liter gasometer, built of tin-plated copper and equipped with an electric fan for stirring. The carbon monoxide was prepared by the action of concd. sulfuric acid on sodium formate.

Analytical Methods

Carbon Monoxide.—The iodine pentoxide method for the determination of carbon monoxide was employed to determine the composition of the gas used for testing. The procedure followed was essentially the same as that developed by Larson, Jayson and White, Defense Research Section, C. W. S.[12] When small corrections were made by means of blanks, an accuracy of 1 to 2% was obtained for samples containing about 0.2% of carbon monoxide.

The composition of the catalysts, as determined by the following analytical methods, is shown in Tables I–IV, which are placed in the following section near the efficiency-temperature diagrams, Figs. 2–6.

Water and Carbon Dioxide in the Catalysts.—A current of air, previously dried by passing over solid potassium hydroxide and phosphoric anhydride, was aspirated slowly through a Pyrex tube containing a weighed sample of the catalyst, and then through weighed U-tubes containing phosphorus pentoxide and potassium hydroxide. The tube containing the catalyst was heated almost to redness and allowed to cool in position. The amounts of water and carbon dioxide were determined by weighing the absorption U-tubes. It is interesting to note that even the manganese dioxide (before its use as a catalyst) contained some carbon dioxide although no carbonate was used in its preparation. The only explanation is that it was absorbed from the air.

In Tables I–IV the results of these analyses are expressed as the number of grams of water or carbon monoxide per 100 g. of the water-free sample. The calculations were made by subtracting the weight of water found from the weight of the original sample. In Series 1 (Table I) the carbon dioxide content was very small and was neglected.

Available Oxygen.—The oxidizing power of the catalysts was determined by their ability to liberate iodine from a solution of potassium iodide, which was slightly acid with sulfuric acid. The oxidizing power thus determined includes the reduction of the manganese dioxide to manganese oxide and of the cupric to cuprous oxide. The liberation of iodine was

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[12] Compare Teague, *J. Ind. Eng. Chem.*, **12**, 964 (1920).

slow, especially with copper present, and was not complete in some cases in less than two or three days. To prevent the oxidation of the iodide by the air during this period the solutions were kept in glass-stoppered flasks from which air had been displaced by carbon dioxide. The iodine set free was titrated with 0.1 *N* sodium thiosulfate solution. After titration the solution was allowed to stand for 24 hours and if no color developed, the reaction was regarded as complete.

In Tables I–IV the available oxygen is shown in the fifth column as the number of grams of oxygen per 100 g. of the anhydrous sample (that is, the original material minus the water content).

An attempt was made to check the method described above by comparison with a gravimetric one. A sample of the oxide was treated as described under the determination of water, and the catalyst was weighed after the heating. The weight lost by the oxide minus the weight of water and carbon dioxide was taken as the amount of oxygen lost on heating. The available oxygen content of the same oxide before and after heating was determined by the potassium iodide method and the difference between these should also be equal to the oxygen lost. In almost every case, the oxygen loss as determined by the latter method was slightly greater than that found by the direct weighing. The discrepancy was mainly due to the fact that the oxide after being heated was extremely hygroscopic and gained some weight before it could be weighed. It was found that a momentary exposure to the air produced an appreciable increase in weight, and that the discrepancy became less as precautions to prevent exposure were increased. It was concluded, therefore, that the iodide method was the better and could be relied upon to give satisfactory results on the relative available oxygen contents of the catalysts used.

Copper Oxide.—The mixed catalyst was treated with dil. sulfuric acid and solid sodium sulfite, in excess of that required for the reduction of the manganese dioxide, was added. The oxides dissolved rapidly and the solution was evaporated until fumes of sulfuric acid appeared, in order to expel the excess of sulfur dioxide. The acid concentration was reduced to about 0.2 *N* by addition of water, and excess of potassium iodide was added. The liberated iodine was treated with 0.1 *N* sodium thiosulfate solution in the usual manner.

In Tables I–IV the results of these copper determinations are shown in the third from the last column as percentage of cupric oxide in the anhydrous sample.

Manganese Oxides.—After correction had been made for the water content, 100 g. of the anhydrous sample contained known amounts of carbon dioxide and cupric oxide and the remainder was assumed to be manganese oxides, MnO_x, (except in Series 1, where the impurities were not negligible); x was calculated from the available oxygen content, after the amount corresponding to the cupric oxide present had been subtracted. The values of x, given in the last column of the Tables, are always less than 2, and are not constant within a single series. While they are evidently not very accurate, they serve to show approximately the state of oxidation of the manganese oxide. Another method of representing the composition of MnO_x is shown in the tables, namely, as a mixture of manganese dioxide and monoxide; the fourth from the last column shows the amount of dioxide corresponding to the available oxygen in MnO_x, and the remainder is given in the next to the last.

The presence of impurities in the catalysts of Series 1 interfered with the determination of the MnO_x content and of x. The impurity was 4.5% in the copper oxide; and it was probably as large in the manganese oxide, No. 1, as was shown by its behavior towards water (in experiments by Draper which will be described in a later article). The value of x for this sample (No. 1) is 1.65 when the impurity is assumed to be zero, and 1.69 for 4.5% impurity. The latter value was arbitrarily assumed, and the 4.5% correction for impurities was made on all the members of Series 1.

The composition of the catalysts with respect to MnO_x and cupric oxide is shown in the second and third columns of Tables I–IV.

Results of Standard Efficiency Tests with Dry Gas

In making a run, air was passed through the line until the galvanometer deflection remained constant at or near the zero point. This indicated that the two thermocouple junctions in the analyzing device were in temperature equilibrium. The dilute mixture of carbon monoxide and air was then drawn through at a rate of $^5/_{12}$ liters per minute directly to the analyzer and a constant deflection was obtained in a few minutes. By changing the resistance in the galvanometer circuit this constant deflection was made to occur at a position between 20 and 25 cm. on the scale. The gas was then turned through the catalyst tube by means of a stopcock; the reading then varied between the above maximum and zero, depending on the efficiency of the catalyst. For this analyzing device Lamb and Larson found that the calibration curve, relating deflections to carbon monoxide concentrations, was a straight line up to 0.4% of carbon monoxide. From this it follows that at these low concentrations the percentage decrease in the deflection is equal to the percentage of carbon monoxide oxidized in the catalyst tube. This gives the efficiency of the catalyst under the given conditions directly, provided that sufficient time has been allowed for a steady state to be realized.

In a given run, after the steady state had once been attained, giving one point on the efficiency-temperature curve, the determination of the other points could be made comparatively rapidly. When the temperature of the catalyst was then maintained constant for half an hour the efficiency remained constant for the last 15 minutes of this period. However, on starting a run, either with a fresh catalyst or with a sample which had been tested on the previous day, there was some delay in attaining the steady state, and the efficiency gradually increased at constant temperature. This was especially marked when the catalyst was operating at low efficiency. Accordingly, the most satisfactory procedure was first to operate at or above the temperature corresponding to 90–100% efficiency. Each of the points marked on Figs. 3, 4 and 5 was obtained at constant temperature and the efficiency remained constant for 10 minutes. The points were shown to be reproducible whether the catalyst had previously been operating at higher or lower efficiencies.

In making the tests on Series 1 the less satisfactory method was adopted of beginning the measurements at the lower temperature, and taking a large number of readings without definitely proving that the efficiency remained constant at a given temperature. The smooth curves drawn through these points are shown in Fig. 2, but it is possible that the efficiency may be slightly low in some cases. However, when a second run was made with Catalyst 3 by the regular method, the steady-state points fell on or very close to the curve previously obtained.

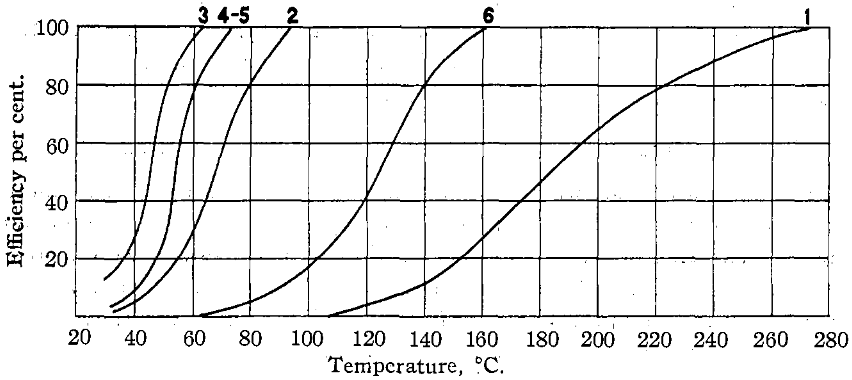

Fig. 2.—Efficiency data for Series I; compare Table I

The results in Fig. 2 show that the four mixtures were 100% efficient at temperatures below 90°, while the copper oxide, No. 6, and the manganese

TABLE I

COMPOSITION OF CATALYSTS, SERIES 1. COMPARE FIG. 2

			Composition referred to 100 g. of anhydrous sample					
No.	MnO_x	CuO	H_2O	Available oxygen	MnO_2	CuO	Remainder MnO + salts	x
1	100	0	7.5	12.8	70.0	0.0	30.0	(1.69)
2	70	30	6.4	12.6	53.0	28.8	18.2	1.75
3	55	45	7.5	12.2	43.0	43.2	13.8	1.78
4	42	58	7.0	11.1	29.8	56.0	14.2	1.70
5	21	79	4.1	10.5	15.9	75.7	8.4	1.75
6	0	100	3.5	9.6	0.0	96.0	4.0	

TABLE II

COMPOSITION OF CATALYSTS, SERIES 2. COMPARE FIG. 3

			Composition referred to 100 g. of anhydrous sample						
No.	MnO_x	CuO	H_2O	Available oxygen	CO_2	MnO_2	CuO	Remainder MnO	x
1	100.0	0.0	4.0	15.7	0.9	85.0	0.0	14.1	1.83
2	71.8	28.2	4.0	14.8	.7	65.2	28.0	6.1	1.89
3	54.9	45.1	3.7	13.1	.7	46.8	44.8	7.7	1.82
4	38.1	61.9	4.4	12.6	.7	34.8	61.5	3.0	1.90
5	20.2	79.8	3.0	11.4	.4	18.0	79.5	2.1	1.87
6	0.0	100.0	2.8	9.9	.4	0.0	99.6	0.0	..

TABLE III

COMPOSITION OF CATALYSTS, SERIES 3. COMPARE FIG. 4

			Composition referred to 100 g. of anhydrous sample						
No.	MnO_x	CuO	H_2O	Available oxygen	CO_2	MnO_2	CuO	Remainder MnO	x
1	100.0	0.0	3.8	16.2	trace	88.3	0.0	11.7	1.85
2	66.0	34.0	5.8	13.6	4.1	56.3	32.6	7.0	1.86
3	43.7	56.3	7.8	11.1	6.7	31.8	52.5	9.0	1.74
4	36.7	63.3	8.2	10.2	6.0	23.0	59.5	11.5	1.62
5	28.5	71.5	9.8	10.1	9.8	19.5	64.5	6.2	1.72
6	0.0	100.0	9.5	9.3	7.0	0.0	93.0	0.0	..

dioxide, No. 1, did not reach this efficiency until the temperature was raised to 160° and 280°, respectively.

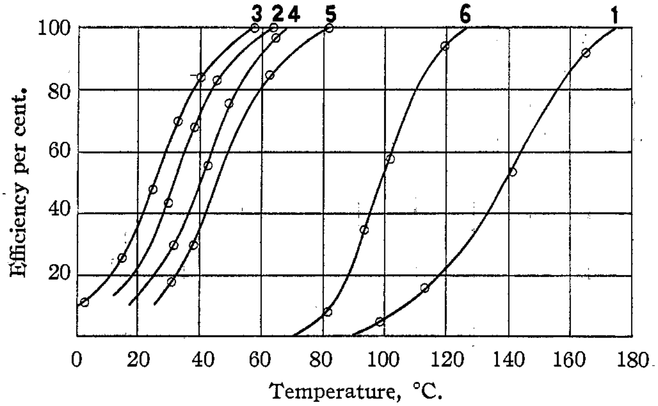

Fig. 3.—Efficiency data for Series 2; compare Table II

A comparison of Figs. 2 and 3 shows a distinct improvement in efficiency for the catalysts of Series 2, over the corresponding ones of Series 1. This is probably due to the fact that the oxides of Series 2 were washed free from soluble salts.

In Fig. 4 the results for Series 3, except for the poor efficiency of the basic copper carbonate, No. 6, are seen to be in close agreement with those for Series 2, Fig. 3. It is remarkable that the relatively high carbon dioxide content (see Table III) of the mixtures has so little effect. The water content is also higher than in Series 2, but there is no reason to suspect that the catalysts were not operating in the region of maximum efficiency (compare the following section). In this series, as in the two earlier ones, the catalyst whose composition is closest to 60% of MnO_x and 40% of cupric oxide (No. 2 in this case) is the most active; but the difference between it and the other mixtures in the series is not great.

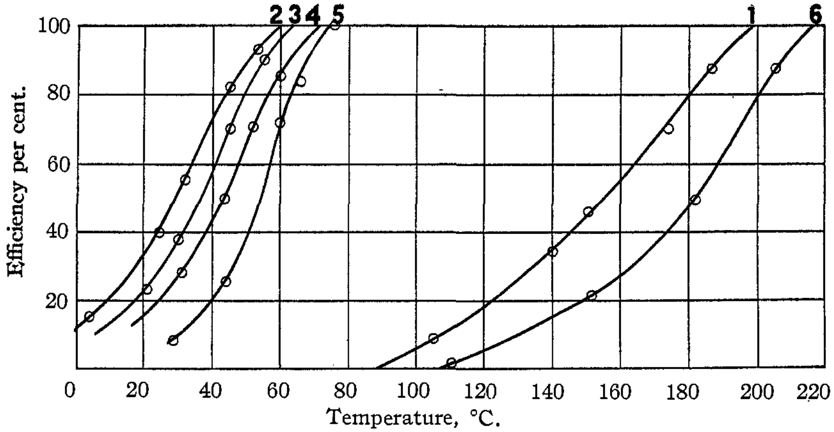

Fig. 4.—Efficiency data for Series 3; compare Table III

The efficiency-temperature curves for the Washington catalysts, Nos. 1 and 6, Fig. 5, correspond closely with those for Nos. 1 and 6 of Series 2, Fig. 3, for which the methods of preparation were similar. But the mixture, W3 (Curve 3), is a far more active catalyst than any of our mixtures; it operated at 100% efficiency below 20°, while no other did so below 55°. The analytical data in Table IV show that this catalyst is remarkable for the high content of oxygen in its MnO_x; the value of x, 1.95, is higher than in any other sample. Its carbon dioxide content is relatively low (compare

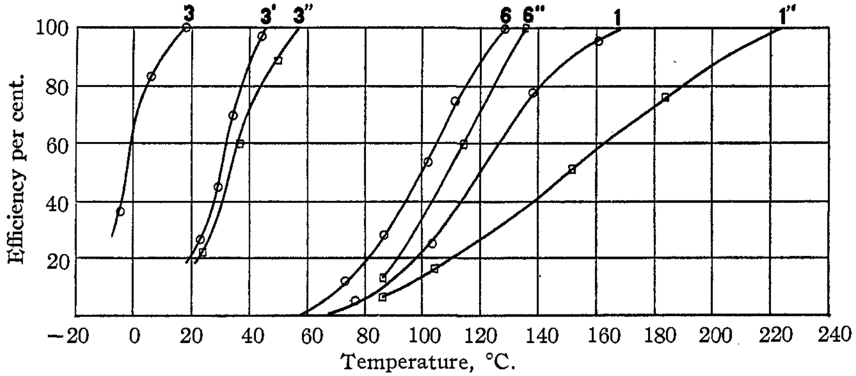

Fig. 5.—Efficiency data for Washington catalysts; compare Table IV

Nos. 2 and 3, Table III). These facts suggest that there was some unknown but essential difference in the methods of preparing the constituents of this catalyst, but we do not know whether its high activity is to be attributed to such an explanation, or to the fact that the moist mixture of the constituents was subjected to high pressure. The data of Merrill and Scalione[13] on the effect of pressure on the "life" of the catalyst in moist air probably do not throw any light on this question.

Table IV

Composition of Washington Catalysts. Compare Fig. 5

			Composition referred to 100 g. of anhydrous sample						
				Available		Remainder			
No.	MnO_x	CuO	H_2O	oxygen	CO_2	MnO_2	CuO	MnO	x
1	100	0.0	15.2	15.6	trace	85.0	0.0	15.0	1.82
3	52.8	47.2	6.2	13.6	3.6	48.9	45.5	2.0	1.95
6	0.0	100.0	2.9	10.0	trace	0.0	100.0	0.0	..
1′	100.0	0.0	10.5	14.6	trace	..	..	..	..
1″	100.0	0.0	2.4	13.4	trace	..	..	..	..
3′	52.8	47.2	12.4	13.6	3.9	..	..	..	..
3″	52.8	47.2	4.3	12.8	trace	..	..	..	..
6′	0.0	100.0	3.7	10.0	trace	..	..	..	..
6″	0.0	100.0	2.2	10.1	trace	..	..	..	..

Variation of the Water and Oxygen Contents of the Catalysts

Other investigators have found that partial dehydration of the oxide catalysts is necessary in order to make them appreciably active. A rapid increase in activity is caused by the initial removal of water. This rate of increase, however, does not continue indefinitely, for a region is reached such that further slow dehydration causes a comparatively slight change in the activity. For example, in the case of Catalyst 3, Series 1 (approximately 60% of manganese dioxide and 40% of cupric oxide) a decrease in the water content from 12% to 7.5% (referred to the water-free material) reduced the temperature required for 50% efficiency only from 49° to 45°. The removal of water up to this point did not cause an appreciable decrease in the oxygen content of the catalyst.

Reference to the tables of the preceding section shows that the water content of the mixed catalysts did not differ greatly within a given series, and was for each catalyst probably in the region where the change of activity with dehydration was slight. Since all were submitted to a similar drying process, the variation of the water content indicates the relative ease with which each lost water. In Series 1 and 2 the manganese dioxide was the more hydrated and the water content of the mixtures decreased with the manganese dioxide content. In Series 3 there was a trend in the opposite direction because the basic copper carbonate contained the more water.

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[13] Ref. 3, p. 1995, Table III.

It was found that continued drying of the catalyst, beyond the region referred to above, resulted in decreased activity, and loss of oxygen except in the case of copper oxide. A sample of the Washington mixture, No. 3″ Table IV and Fig. 5, was dried over a moving flame for a short time. Comparison with No. 3 shows a great lowering of activity when the water content had been changed from 6.2 to 4.3 and the oxygen content lowered from 13.6 to 12.8. Another example of the loss of a small amount of oxygen in drying is furnished by the results for No. 3, Series 1 in Table V below. Data for the Washington samples of copper oxide and manganese dioxide are given in Table IV and Fig. 5. The efficiency of a sample of copper oxide, No. 6′, which contained 3.7% of water was found to be coincident with Curve 6 (2.9% of water); but the activity was ultimately reduced by further drying at a higher temperature (compare No. 6″). The oxygen content was unchanged. In the case of the manganese dioxide loss of oxygen occurred before the decrease in activity. Thus, No. 1′, which had been dried under suction for two hours at 200° and contained 10.5% of water, showed an efficiency corresponding to Curve 1 (15.2% of water), although its oxygen content had been changed from 15.6 to 14.6. Continued drying at higher temperature reduced the efficiency to that represented by Curve 1″, and lowered the oxygen content to 13.4. It seems probable from these results that the decrease in activity finally obtained is due to a change of structure. The active mixed catalyst is sensitive to loss of oxygen, while the much less active manganese dioxide is not.

The high oxygen content of the most active catalyst, W3, has already been referred to and, as implied in the preceding paragraph, it is possible that there is a relation between the content of available oxygen of a mixed catalyst and its activity. However, even if this should prove to be true, oxygen comparisons would have to be restricted to samples of the same catalyst which had been subjected to various treatments. From our data for Series 1 to 3 we have found no relation between the values of x, Tables I to III, and the relative activities of the various catalysts.

Merrill and Scalione considered that the oxygen content of a catalyst is one of the variables at the steady state, and reported[14] that the catalyst, when operating at low efficiency with either dry or wet gas, lost oxygen which was restored by operation at higher efficiency. We, however, have been unable to check this result. In each of the four sets of experiments in Table V, the oxygen content is seen to be practically the same whether the catalyst was operated at low or high efficiency. In each experiment the catalyst was operated for from one hour to two hours with dry gas at the efficiency stated before a sample was taken for analysis. These results are not conclusive, since the amount of oxygen that could be removed in one hour from a catalyst operating at low efficiency with 0.2% to 0.4% of

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[14] Ref. 3, pp. 1993 and 1997.

carbon monoxide does not exceed the possible limit of error in the analysis. But our failure to detect an increase of the oxygen content in any sample of a catalyst operating at high efficiency, and the result given in a later section that the speed of reduction is slower than the speed of catalysis, make it probable that there is no appreciable change in the oxygen content of the catalyst.

TABLE V

OXYGEN CONTENT OF CATALYSTS

Catalyst	CO %	Last operated at Temp.	Last operated at Efficiency %	Available oxygen
3; Series 1; undried	0.17	62	93	12.24
		41	32	12.18
			25	12.22
3; Series 1; dried at 100° for one hour	.20	64	100	11.92
		41	33	12.04
3; Series 1; dried at 200° for one hour	.23	70	100	11.70
		30	4	11.69
3; Series 2; dried at 200° for 1/2 hour	.38	60	100	12.82
		30	40	12.90

Tests with Moist Gas

The effect of moisture on the operation of these catalysts has been studied extensively by the earlier investigators. For example, Merrill and Scalione[15] gave efficiency-temperature curves for gas of varying humidity, which show that the water vapor causes a decided decrease in activity. From these and other results, they concluded that the moisture absorbed from the gas remains for the most part as a film on the surface of the catalyst, hindering the adsorption of carbon monoxide and oxygen, and does not re-hydrate the oxides to any considerable extent. This film was removed by operation with dry gas at higher temperatures and the catalyst gradually regained its former activity.

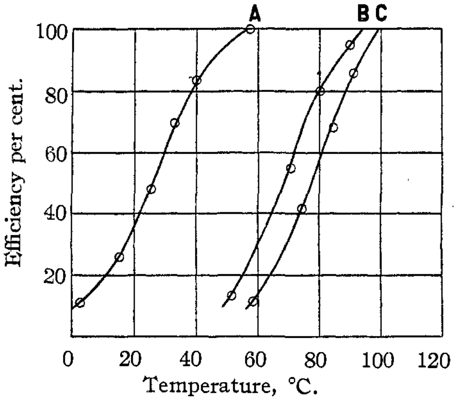

Fig. 6.—Efficiency-temperature curves for dry and moist gas

In order to check these observations and to obtain comparable efficiency-temperature curves for dry and moist gas, some tests were made on Catalyst 2 of Series 2. Vapor pressures of 11.5 mm. and 5.1 mm. were obtained by allowing 44% and 58% sulfuric acid solutions to drip through the bead tower. The steady-state points were obtained as in the dry gas tests

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[15] Ref. 3, p. 1998.

and were found to be quite reproducible whether approached from higher or lower efficiencies. Contrary to the results of Merrill and Scalione, no decrease in the oxygen content was detected for samples which had been operating at low efficiencies. In Fig. 6, A represents the efficiency for dry gas, B for water-vapor pressure of 5.1 mm. and C for vapor pressure of 11.5 mm.

The fact that water vapor is strongly adsorbed and tends to form a film on the surface of the catalyst, indicates that this equilibrium film is the retarding factor which accounts for the decreased efficiency of the catalyst with moist gas. The similar form of the curves for moist gas and dry gas suggested the presence of a strongly adsorbed film, when operating with dry gas also, which might be the limiting factor in the catalysis. It seemed likely that carbon dioxide would be the more strongly adsorbed, of the gases concerned and would, therefore, be more apt to exert such a covering action. It was thought that the addition of carbon dioxide to the testing gas might cause a decrease in efficiency, if the catalyst had a tendency to take on such a film of carbon dioxide. However, the results of some experiments on Catalyst 3 of Series 2, with a partial pressure of carbon dioxide of $^1/_3$ atmosphere, indicated that there was no marked effect. Since in the absence of added carbon dioxide the partial pressure of carbon dioxide in the gas leaving a catalyst operating at 100% efficiency would be only 0.002 atmosphere, it follows that an increase in the carbon dioxide pressure of 167 fold (or more when the catalyst is operating at lower efficiency) has little or no effect. This result does not prove that there is no protective film of carbon dioxide, but simply that such a film, if it exists, is not in equilibrium with the surrounding gas. In other words, this is a question of rate and not of equilibrium, and it is possible that the carbon dioxide is given off so slowly by a catalyst operating at low efficiency that a film is built up at the steady state. Definite evidence in favor of this mechanism will be presented in a later paper.

The Reduction of the Catalyst by Carbon Monoxide

The probability that the oxygen content of a catalyst remains practically constant has already been mentioned. In order to obtain data on the ease of reduction of the catalysts some runs were made with a mixture of about 1% of carbon monoxide in nitrogen. Oxygen was removed by means of yellow phosphorus, and the mixture was passed through the catalyst at the rate of 300 cc. per minute. Air was admitted to the gas stream after passing the catalyst in order that the analyzing device might be used to measure the change in the carbon monoxide content of the gas; the rate of flow of air was maintained constant at about 420 cc. per minute by means of another flowmeter. Before an experiment was begun nitrogen was passed through the system for half an hour to sweep out oxygen.

The behavior of Catalyst 3 of Series 2 was typical for all experiments started at a temperature close to that at which the catalyst operated at 99–100% efficiency with carbon monoxide in air, and will be described in detail. The experiment was begun with the catalyst at a temperature of 56° (compare Fig. 3), and its behavior is shown graphically in Fig. 7.

The initial reading of 23.0 corresponds to the concentration of carbon monoxide in the nitrogen mixture, which was 0.86% as determined by the iodine pentoxide method. When the gas was turned through the catalyst (fourth minute) the drop in the reading indicated a very rapid reaction and the temperature of the catalyst rose from 56° to 63° during the first 9 minutes. As shown by the curve the rate of carbon monoxide oxidation then became progressively slower and seemed to be practically constant between the times 40 and 65 minutes. The catalyst temperature had now returned to 58°. Between the times 65 and 85 minutes the temperature of the catalyst was raised to 86° and the decreasing deflections showed that carbon monoxide was then being oxidized, at the expense of the catalyst, more rapidly at the higher temperatures. While the rate of this reaction and the temperature were still increasing the input of heat was decreased; this corresponded to the gradual rise of the curve, indicating at the end of the experiment 22% oxidation at a temperature of 84°.

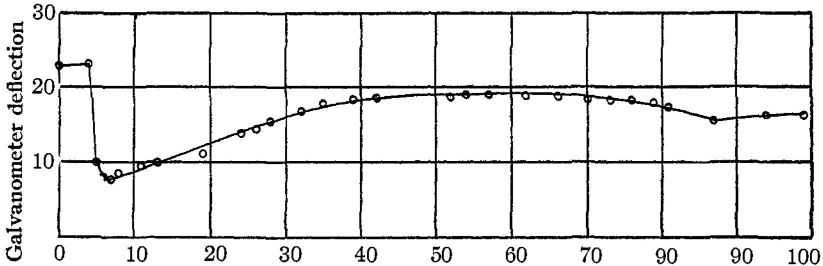

Fig. 7.—Reduction of catalyst by carbon monoxide

A sample of the catalyst taken immediately after the run showed a loss of 16.3 mg. of oxygen per gram of the anhydrous sample, which corresponds to about 10% of the available oxygen originally present. From the amount of carbon monoxide oxidized during the run, and the weight of the sample, 1.38 g., an approximate calculation of the oxygen loss was made, which agreed fairly well with the above figure, thus showing that the gas mixture was practically free from oxygen. It was found that, unless extreme precautions were taken to remove all the oxygen, the carbon monoxide combined with this oxygen in preference to reducing the catalyst.

The partially reduced catalyst was then treated with the usual mixture of carbon monoxide and air for two hours. It then showed an efficiency of but 10% at 55° and of 80% at 82°, while the same catalyst before reduction was 100% efficient at 60°. Analysis of the sample showed that over half of the lost oxygen had been restored by this air treatment. The failure of the catalyst to return to its former state of activity, in spite of the partial restoration of oxygen, suggests that it had suffered a change of structure. The efficiency of the more active mixed Washington catalyst was also found to be permanently impaired by similar reduction (at 30–38°) with carbon monoxide, but in this case there was little evidence to indicate that any of the lost oxygen was regained in the subsequent operation of the catalyst with carbon monoxide in air. These results support the suggestion made in a previous section that the oxygen contents of samples of a given mixed catalyst may indicate the relative activity.

A similar experiment at a higher temperature (150–166°) with the manganese dioxide of Series 2 showed that its efficiency was not permanently lessened by reduction to the extent of 7% of its available oxygen. It returned to its former activity when treated with carbon monoxide and air, and analysis showed that most of the lost oxygen had been restored. It has already been pointed out above that the active manganese dioxide catalyst is not very sensitive with respect to a change in the oxygen content. Whether this fact and the restoration of the oxygen lost in reduction are due simply to the high temperature necessary for operation as a catalyst, or can be taken as evidence that the mixed catalysts possess a structure different from that of the one-component catalysts, we are unable to decide.

In the reduction experiment begun at a temperature at which the catalyst could act with 99 to 100% efficiency as a catalyst, there action was very fast only for the first few minutes, after which its speed decreased fairly rapidly. It follows that there is only a small supply of "active" oxygen at the surface of the catalyst, and that the removal of oxygen from the catalyst becomes increasingly difficult as the reaction proceeds. The speed of the latter slow reaction increases rapidly with the temperature, and hence must be negligible at low efficiency. Similarly, the initial reaction is slow when the experiment is started at these lower temperatures. The simplest explanation of the decrease of the rate as the reaction proceeds and as the temperature is lowered is that the solid surface is protected by a film which is then held more firmly.

Our results show that at a given temperature the catalytic process cannot be replaced by a series of alternate treatments with carbon monoxide and air, at least unless the duration of each single treatment is made very short. The simultaneous reaction of the catalyst with carbon monoxide and oxygen takes place more rapidly than the reaction with carbon monoxide alone at the same temperature.

Discussion of the Mixture Effect

The relation of the compositions of the catalysts to their activity is best shown by the temperature-composition diagram, Fig. 8. Here the ordinate represents the temperature corresponding to 50% efficiency and the abscissa gives the percentage of MnO_x in the anhydrous mixture. The values of MnO_x were given in Tables I to III and the temperatures of 50% efficiency were read from Figs. 2 to 4. The numbers 1, 2 and 3 at the right-hand side of the figure refer to the three different series.

The striking result is the rapid increase, in all cases, of the activity of the one-component catalyst on the addition of small amounts of the second component. Evidence is therefore lacking of any fundamental difference between this example of co-activation of catalysts, and the promoter action of an inert substance on a catalyst. Our results also indicate that the mixture of 60% of MnO_x and 40% of cupric oxide is but slightly more active than other mixtures, and that basic copper carbonate as a component has little, if any, advantage over copper hydroxide.

The following theory of the mixture effect in this case, which was developed early in the investigation, proved useful throughout our work, and will be discussed in connection with additional evidence in a later paper.

By the action of carbon monoxide and oxygen a protective film is formed on the catalyst which interferes with further action, unless it can be rapidly desorbed as carbon dioxide. The film builds up to a lesser extent for mixtures than for the one-component catalysts at the same temperature. The slow limiting reaction may be the rate of desorption of carbon dioxide or the rate of a transformation within the film. We could stop with the statement that this is a question of the structure of the catalyst, but it seemed worth while to seek an interpretation in terms of valence theory.

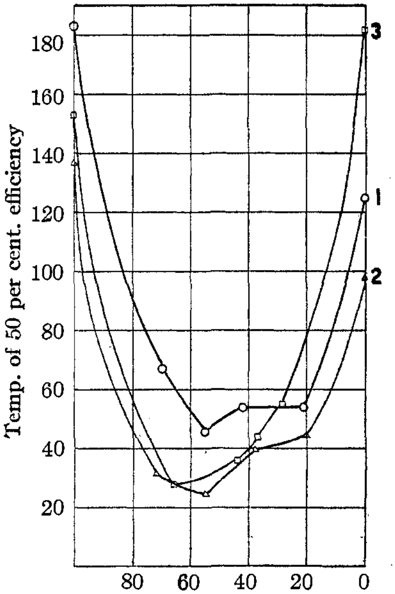

Fig. 8

The porous granules are believed to consist of a network of chains of atoms held together by valence forces.[16] The forces that come into play

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[16] Compare Langmuir, This Journal, **38**, 2285 (1916).

The formation of the firm porous granule from the hydrated oxide or oxides may be thought of as follows. Each hydrated oxide is precipitated in the form of minute particles, the size of which is determined by the method of precipitation, but is greater than molecular dimensions. The filter cake, before it is dried consists of particles surrounded by films of water, which enable the relative positions of the particles to be easily changed for example, in a kneading process. In the preliminary drying as the water is slowly expelled, the particles are gradually drawn together, and in many places contact is suffiat or in the film are also valence forces. When the catalyst contains the two oxides, they will tend to neutralize each other's valence forces, since they differ in basicity or polarity, and the strength of the valence forces at the film may be expected to be less than for a one-component catalyst. In other words, an increase in the rate of desorption, or increase in the rate of a reaction within the film, is attributed to what may be considered a partial chemical reaction between the two oxides.

Summary

Temperature-efficiency curves have been obtained for three series of partially hydrated, porous catalysts of manganese dioxide and cupric oxide. Pronounced improvement in activity is caused by the addition of a small amount of either oxide to the other.

Partial dehydration is necessary to bring a catalyst to the region of maximum activity, but the water content may then be lowered to a relatively small value by slow dehydration with but little change in the efficiency. Continued dehydration, however, finally lowers the efficiency, and causes loss of oxygen (except in the case of copper oxide).

The efficiency of a catalyst is independent of the carbon monoxide concentration between 0.1 and 0.6%, and is practically unchanged by the presence at high concentration of carbon dioxide, the product of the reaction.

Water vapor has a marked poisoning effect, which is reversible.

It is probable that under steady-state conditions the oxygen content of a catalyst is practically constant whether the catalyst is operating at low or high efficiency.

A catalyst is reduced when treated with carbon monoxide in the absence of oxygen at a temperature at which it would act as a catalyst. The activity of a mixed catalyst is permanently impaired by this reduction, even when much of the lost oxygen is restored on subsequent operation as a catalyst.

A theory for the mixture effect in this case has been suggested.

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ciently close to allow valence forces to come into play between the molecules of different particles. The plastic material has now been transformed into a solid. Finally, as the water of hydration is gradually expelled, the body becomes porous.