point; therefore, no correction has to be applied for a necessary excess of acid. In the titration of 0.1 *N* solutions the Sörensen value (*P*H) at the end-point is about 5.0.

Dimethylyellow, methyl orange and indicators with similar range of Sörensen values for their intervals may also be used.

I wish to thank Professor Schoorl for his great interest shown in the course of this investigation.

Summary

1. An application is made of the reaction: $6H^+ + IO_3^- + 5I^- \rightleftarrows 3I_2 + 3H_2O$ for the standardization of strong acids with pure potassium iodate in the presence of a slight excess of thiosulfate.

2. When the right conditions are employed, sodium carbonate, borax and potassium iodate as standard substances give the same respective titers for 0.1 *N* and 0.5 *N* hydrochloric acid solutions.

3. As sodium carbonate is hygroscopic, and the color change of dimethylyellow at the end-point can be observed accurately only when the excess of carbon dioxide is removed, this salt cannot be recommended as a standard substance.

4. The most favorable standard substance for acids is *borax.* It has a high equivalent weight, and the color change with indicators such as methyl red and dimethylyellow can be observed very accurately.

5. From the determination of the water content of borax and from the results of the titrations we find good confirmation of the internationally accepted atomic weight of boron (10.82).

UTRECHT, HOLLAND

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

THE CATALYTIC OXIDATION OF CARBON MONOXIDE. II. THE ADSORPTION OF CARBON DIOXIDE, CARBON MONOXIDE, AND OXYGEN BY THE CATALYSTS, MANGANESE DIOXIDE, CUPRIC OXIDE, AND MIXTURES OF THESE OXIDES

BY W. M. HOSKINS AND WILLIAM C. BRAY

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In the present paper are presented the results of experiments, completed in 1922, on the adsorption of carbon dioxide, oxygen and carbon monoxide by the catalysts, investigated by Almquist and Bray,[1] the compositions of which with respect to cupric oxide, MnO_x (where x is less than 2), water and carbon monoxide are given in the first paper. The results of Almquist and Bray (see the last column of Table I below) showed that in three related series of catalysts, in which the composition varied between

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[1] Almquist and Bray, THIS JOURNAL, **45**, 2305 (1923). This article contains references to earlier work on the catalytic oxidation of carbon monoxide.

MnO_x and CuO, all the mixtures are much more active catalytically than either of the components.

Our problem was to investigate adsorption in relation to this "mixture effect." We have determined both adsorption isotherms and rates of adsorption. Throughout, adsorption is used in the sense of total adsorption. The possibility of distinguishing between rapid and slow processes was practically excluded in the determination of adsorption isotherms, since this involved the addition of successive portions of gas to an adsorbent, and a long wait after each addition.

Benton[2] in his recent articles in the same field, has restricted the use of the term "adsorption" to rapid processes, and here has been able to differentiate between "primary and secondary adsorption." Subsequent slow processes are considered to be due to solution or to chemical reaction. The latter was marked in the case of carbon monoxide, and at higher temperatures was usually rapid enough to interfere with his "adsorption" determinations. He stresses the parallelism between this "chemical reaction" and the high "primary adsorption" which he found for carbon monoxide at low temperatures.

The preparation of the catalysts in the form of porous granules has been described.[1] The stock material had already been dried at about 75° for 72 hours, but further dehydration was necessary to bring the catalysts into the active condition. A fresh portion of stock material was taken for each measurement, and it was heated in a vacuum at 138° for four hours. As this treatment seems more severe than that employed by Almquist and Bray (one-half hour at 175° and $^1/_3$ atmosphere), the water and carbon dioxide contents were probably somewhat smaller than given by their analyses. However, there is no reason to believe that dehydration was carried beyond the region of maximum catalytic activity. Indeed, one mixture, Series 2, No. 2, after the adsorption measurements with carbon dioxide, gave almost the same efficiency-temperature curve as that previously determined.

The carbon dioxide used was made by dropping concd. sulfuric acid on sodium bicarbonate; carbon monoxide was made by dropping hot, concd. sulfuric acid on sodium formate; and the oxygen was prepared by adding distilled water to sodium peroxide. All the gases were dried by passing through long tubes containing calcium chloride near the entrance and phosphorus pentoxide near the exit end.

Apparatus and Operation

The absorption apparatus, partly shown in Fig. 1, consisted essentially of an adsorption vessel F of Pyrex glass, a measuring vessel A, and generators for the gases (not shown).

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[2] Benton, THIS JOURNAL, **45**, 887, 900 (1923).

The temperature of the adsorbent in F was controlled either by placing water (at 20°) in the large Pyrex tube K, or by boiling a liquid in K to give a vapor-bath of known temperature. In the latter case a water-cooled condenser inside and near the top of K served to condense the vapors. The gas, after being measured in A, was introduced into the vessel E, which was connected with F by the gound-glass joint J, provided with a mercury seal. The vertical tubes S, S′ and T were connected above with the vacuum line. T was used in evacuating the adsorption vessel. S and S′ were provided with scales so that the pressures in the vessels A and F could be read directly when the mercury was brought to the marks M and M′ by means of the leveling bulbs L and L′. The junctions of S and S′ with the rest of the apparatus were so constructed that any air that leaked in through or along the rubber tubing passed up through S and S′ and did not enter the vessels A and E.

In the actual set-up the measuring vessel A was joined to six vessels like E and F set in parallel. This arrangement enabled the adsorption measurements for all six members of a series to be run simultaneously and, therefore, under exactly similar conditions. The volumes of the six adsorption vessels (to the mark M′) varied slightly, but were close to 120 cc. No correction was made for the volume of the adsorbent because the true volume was small in comparison with 120 cc.—probably less than 1 cc. for the 5 g. of adsorbent used.

The stopcock G was inserted in the line in order that the gas from E might be admitted to the adsorbent at any desired time. This enabled measurements of the rate of adsorption to be made by following the change in pressure as shown on scale S′.

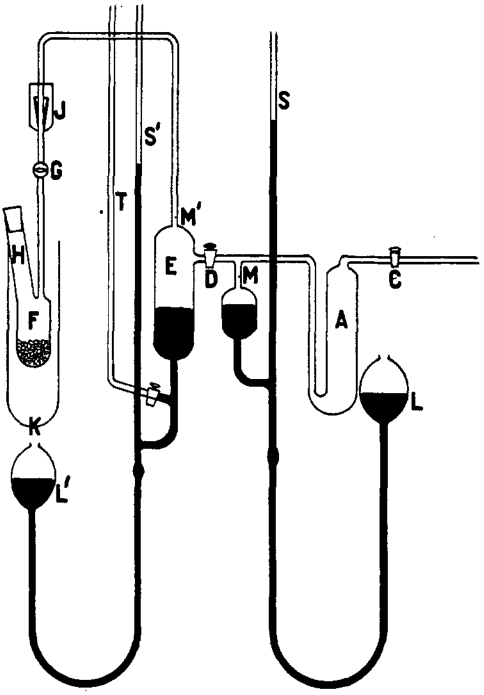

Fig. 1.—Apparatus.

A high vacuum was obtained by the use of a mercury diffusion pump backed up by a rotary oil pump. A McLeod gage was used to read the pressure in the main vacuum line.

The method of operation was as follows. A 5g. sample of the adsorbent was introduced through the side arm H, and this was closed with a rubber stopper sealed over with de Khotinsky cement. The system was evacuated and allowed to stand overnight, during which time considerable gas was evolved by the adsorbent. Evacuation was continued for four hours while the adsorption vessel and its contents were heated to 138° by means of a xylene vapor bath. The final pressure at 20° was always in the neighborhood of 0.005 mm. of mercury, which was mainly due to water vapor from the still partially hydrated absorbent.

The adsorbent was then washed[3] by introducing carbon dioxide and, after several hours, evacuating for one hour at 138°. In several cases tested (using a Toepler pump at 138°) the entire amount of carbon dioxide was recovered, readily from the mixture catalysts, but with more difficulty from the pure oxides, especially the manganese dioxide. Evidence that the preliminary treatment with carbon dioxide did not interfere with the adsorption determination in the case of oxygen will be mentioned later.

The adsorption measurements were begun immediately after the preliminary washing. One of the three gases studied was introduced into the measuring vessel A, and its pressure and temperature noted. A portion was carefully admitted through D into E and F, and its amount measured by the decrease in pressure in A. At intervals the pressure in the adsorption vessel was measured, the amount of unadsorbed gas calculated, and the amount adsorbed determined by difference. No corrections were applied for deviation from the gas laws. The pressure was read with the temperature of the adsorbent at or close to 20°.

When the pressure did not change during a period of from 12 to 24 hours, equilibrium was assumed to have been reached, a second portion of the gas was introduced, and the equilibrium pressure determined as before. In this way from five to ten measurements were made, the pressure ranging from about 1 cm. of mercury to an atmosphere.

The time necessary to reach equilibrium varied with the adsorbent and with the gas used, but four days was the longest time ever required. In general, carbon dioxide came to equilibrium most rapidly, carbon monoxide more slowly, and oxygen most slowly of all. With all three gases the pure oxides required a longer time than the mixed oxides.

The *adsorption isotherms* for the members of Series 2 are shown as typical examples in Figs. 2, 3 and 4, the abscissas being the equilibrium pressures, and the ordinates the volume of gas (cc. at standard condition) absorbed by 1 g. of adsorbent.

Evidence demonstrating the reproducibility of the results was obtained by repeating some of the measurements with each of the three gases. Also in a few cases with carbon dioxide, some points on or near the same curves were obtained when the equilibrium was approached from the other side.

The Adsorption Data

By means of the smooth curves drawn through all the experimentally

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[3] This preliminary washing with carbon dioxide was essential for obtaining reproducible results. It seems probable that the treatment removed a film of adsorbed material, presumably water. The recent results of Lamb and Vail (Ref. 15, p. 131) support the idea that the water film may be regenerated within 24 hours by the transfer of water from the interior to the surface of the hydrated oxides. The formation of such a film would account for the delay in attaining the catalytic steady state observed by Almquist and Bray.

determined points, the amounts of each gas adsorbed at equilibrium pressures of 5, 15, 30 and 50 cm. of mercury were determined. These data are shown in Table I. In the last column is given for reference the temperature at which each catalyst operated at 50% efficiency.[1]

TABLE I

ADSORPTION DATA AT 20° FOR MnO_x (No. 1), CuO (No. 6) AND THEIR MIXTURES (Nos. 2–5)

Amount of gas, cc. at standard conditions adsorbed by 1 g. of absorbent at various equilibrium pressures, cm. of mercury.

	CO_2 Equil. press.				O_2 Equil. press.				CO Equil. press.				Temp. for 50% efficiency as a catalyst
No.	5	15	30	50	5	15	30	50	5	15	30	50	
Series 2													
1	1.5	3.4	5.5	7.6	0.37	0.54	0.64	0.69	1.9	3.2	3.9	4.3	138°
2	1.3	2.9	4.4	5.8	.11	.25	.42	.58	8.0	17.7	25.2	29.4	31
3	1.9	3.5	5.0	6.3	.12	.20	.29	.40	7.2	15.2	22.4	26.2	25
4	1.5	3.0	4.4	5.6	.13	.21	.30	.31	14.0	20.2	22.0	22.8	40
5	1.8	3.0	4.3	5.2	.04	.10	.14	.18	16.0	18.8	20.8	22.0	46
6	1.8	2.9	3.9	4.7	.04	.13	.19	.21	14.4	16.8	19.0	21.7	99
Series 3													
1	1.8	4.1	6.4	7.9	0.18	0.39	0.58	0.71	1.9	4.4	6.2	7.7	155
2	1.8	4.0	6.1	7.8	.05	.165	.29	.42	2.7	7.2	12.3	17.0	29
3	1.5	3.3	4.8	5.9	.03	.09	.18	.28	2.4	7.2	13.4	18.8	36
6[b]	0.5	0.9	1.4	1.9	.02	.05	.06	.07	5.1	6.2	6.5	6.8	181
Washington samples													
1	8.0	11.7	15.0	(18.0)[a]	1.29	1.5	1.65	1.8	2.6	3.1	3.6	4.0	120
3	1.7	4.1	6.2	8.0	0.06	0.16	0.25	0.32	7.3	12.7	19.0	(26.0)[a]	−2
6	2.7	5.3	8.1	10.7	.07	.16	.24	.30	5.8	7.0	8.0	8.8	100
Series 1b washed with water													
1	2.7	4.9	6.5	8.0	0.14	0.30	0.43	0.60	3.0	5.0	6.4	7.7	...
3	2.1	4.1	5.7	6.9	.05	.10	.22	.33	4.4	7.8	10.8	13.5	...
6	0.9	2.0	3.1	4.2	.05	.12	.15	.15	6.9	8.4	9.6	10.4	...
Series 1a unwashed													
1	0.4	0.9	1.3	1.4	..	..	..	..	..	..	..	..	182
2	1.8	3.6	5.2	6.3	..	..	..	..	..	..	..	..	68
3	2.2	3.8	5.0	5.9	..	..	..	..	..	..	..	..	47
4	1.9	3.2	4.3	5.3	..	..	..	..	..	..	..	..	54
5	1.8	3.1	4.2	5.3	..	..	..	..	..	..	..	..	54
6	1.5	2.8	4.0	5.1	..	..	..	..	..	..	..	..	125

[a] Obtained by extrapolation.

[b] Carbonate.

Carbon Dioxide Adsorption.—An examination of Fig. 2 for Series 2 and of the additional data in Table I shows that in general the various adsorbents do not differ greatly in their adsorptive capacities for carbon dioxide; and that in a related series the order of increasing adsorptive capacity is from copper oxide (No. 6) to manganese dioxide (No. 1), at least at high pressures. At low pressures there is a distinct tendency toward lower adsorption in the case of the samples rich in manganese dioxide, and the curves for Nos. 1 and 2 cross some of the other curves at pressures below 20 cm. of mercury.

The few apparent exceptions are easily accounted for. The unusually high adsorption by No. 1 of the Washington samples, manganese dioxide, may be attributed to its physical properties; it was made up of exceedingly small particles and, therefore, had a relatively large surface. The smaller adsorptive capacity of the Washington mixture, No. 3, as compared with the Washington samples Nos. 1 and 6 is not significant, since the single catalysts, Nos. 1 and 6, were not related to the mixture. No. 6 of Series 3 was a carbonate, and adsorbed much less carbon dioxide than any of the three samples of copper oxide. Nos. 4 and 5 of this series, which were not measured, would probably also have given relatively low results.

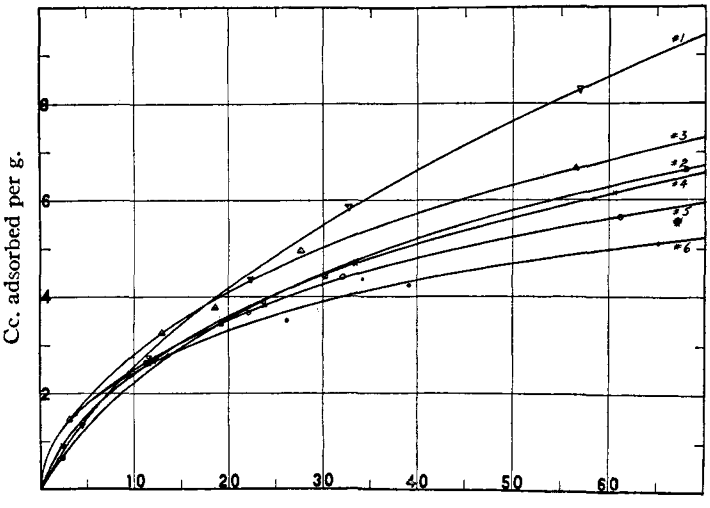

Fig. 2.—Series 2 with carbon dioxide.

The low adsorptive capacity of No. 1 of Series 1 seemed to be connected with the presence of impurities. Draper had found over 4% of soluble salts in each member of Series 1, and besides had noted that No. 1 reacted vigorously with water and changed its appearance. He had, therefore, washed samples of Series 1 until the wash-water contained no sulfate.

In order to investigate the effects of the presence of the soluble salts in the members of Series 1, three of the washed samples, Nos. 1, 3 and 6, were tested. The results are given in Table I as Series 1b. The adsorptive capacity of the manganese dioxide, No. 1, was increased no less than five-fold;[4]

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[4] An incidental result with the Washington catalysts may be mentioned. Samples which had been allowed to stand for several months in the laboratory side by side in open vessels were tested in the usual manner: the adsorptive capacity of the manganese dioxide had been lowered nearly three-fold, that of the copper oxide had been lowered about 25%, while that of the mixture had been practically unchanged. This seems to be an example of a covering effect, or poisoning, due to the adsorption of laboratory

that of the mixture, No. 3, was increased slightly; and that of the copper oxide was slightly decreased.

The data for carbon dioxide were shown to agree with the well-known "exponential" adsorption formula, except in the case of the Washington manganese dioxide where the adsorption was exceptionally great and the measurements had been made only at comparatively low pressures. The values of the exponent $1/n$ in the equation were between 0.49 and 0.6 for all the members of Series 3 (except manganese dioxide), Nos. 2, 3 and 4 of Series 2, Nos. 1 and 2 of Series 1a, and Washington samples Nos. 3 and 6. Higher values were shown by three samples of manganese dioxide, 0.63 in Series 3, 0.69 in Series 2, and approximately 0.7 in the case of the Washington sample; and lower values, 0.37–0.47, by the remaining samples.

Oxygen Adsorption.—In addition to the measurements summarized in Table I, a number of runs were made in which oxygen, instead of carbon dioxide, was used in the preliminary treatment. In all cases the results agreed closely with those already obtained, showing that both carbon dioxide and oxygen were competely removed by the evacuation for 1 hour at 138°.

Additional evidence that the oxygen adsorption is reversible was afforded by a number of quantitative experiments made in connection with the preliminary washing of fresh samples with oxygen. A measured quantity was allowed to remain in contact with the adsorbent for several hours, the evacuation was done with a Toepler pump, mainly at 138°, and the gas obtained was analyzed for oxygen with phosphorus. In every case, except possibly with manganese dioxide, the same quantity of oxygen was regained as had been introduced. The time required to pump off all the oxygen was least for the mixtures and greatest for manganese dioxide, just as with carbon dioxide.

While the amount of oxygen adsorbed (see Table I and Fig. 3) is small compared with carbon dioxide, the two sets of results are definitely parallel. Thus, with oxygen as with carbon dioxide, the usual order of increasing amount is from copper oxide to manganese dioxide; the values for the Washington manganese dioxide are abnormally high, and those for the copper carbonate are low in comparison with the copper oxides.

Accordingly, the ratios of the amounts of carbon dioxide and oxygen adsorbed at the same pressure were calculated and compared. At the higher

gases. The effect was "temporary" in the case of the mixture, and "permanent" for the single oxides, especially the manganese dioxide. There is an obvious analogy between this and the difficulty of removing adsorbed carbon dioxide (or oxygen), which increased rapidly in the order, mixtures, copper oxide, manganese dioxide. It is possible that a water film (Footnote 3) was responsible, and that the single preliminary washing with carbon dioxide was not sufficient to remove all the adsorbed water in the case of the copper and manganese oxides.

pressures the results were quite regular. At 50 mm. of mercury pressure the ratios for the 4 samples each of Nos. 1, 3 and 6, were: No. 1, 10.0–13.3, average 11.4; No. 3, 15.8–25.0, average 20.6; and No. 6, 22.4–35.7, average 28.4; showing a definite increase in the order, manganese dioxide, mixtures and copper oxide (or carbonate). This trend is more pronounced than Benton[5] found for rapid adsorption; his ratios at 0° and 1 atmosphere were 25, 25 and 35, respectively. At low pressures our ratios, while less regular, varying from 4.1 to 19 for manganese dioxide and from 16 to 50 for the mixtures and copper oxide, showed the same general trend as at higher pressures. It is evident that manganese dioxide in comparison with copper oxide adsorbs either somewhat more oxygen, or less carbon dioxide. We may, therefore, conclude either that there is a specific adsorption of oxygen by manganese dioxide; or that the less acidic oxide, copper oxide, adsorbed relatively more carbon dioxide. The latter alternative was favored by Benton.[5]

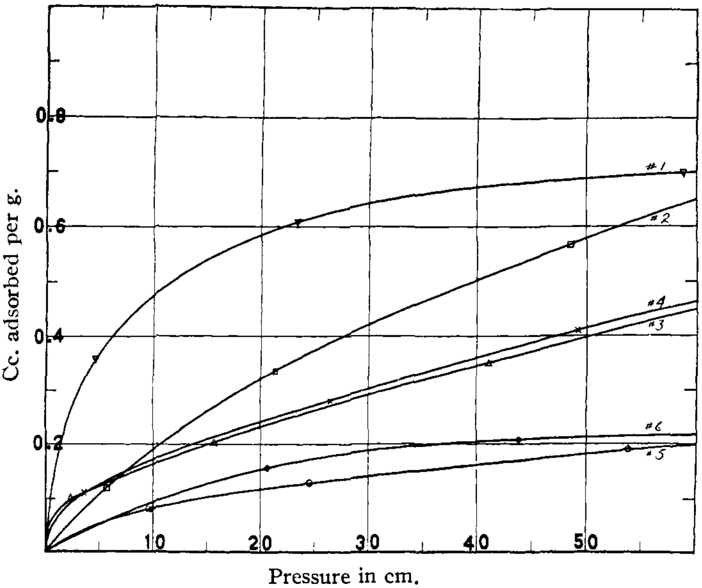

Fig. 3.—Series 2 with oxygen.

The oxygen data showed fairly good agreement with the adsorption formula except in the case of three samples, No. 6 of Series 1b, 2 and 3 (copper oxide or carbonate). The values of the exponent, however, were much more divergent than those for carbon dioxide. Thus, with manganese dioxide the range was from 0.16 for the Washington sample to 0.60 for No. 1 of Series 1b; and with mixture No. 3 from about 0.5 in Series 2 to over 0.9 in Series 3. With the Washington copper oxide the exponent was

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[5] Ref. 2, p. 894.

0.62 over the whole range, while with the other No. 6 samples referred to above it was small at high pressures and large at low pressures.

Carbon Monoxide Adsorption.—The striking feature of the carbon monoxide results in Table I is the high adsorption by all the catalysts. When values of the ratio of the amounts of carbon monoxide and dioxide adsorbed are compared, the results fall into three classes:[6] (a) manganese dioxide, for which the ratio (CO/CO_2) is in the neighborhood of unity and tends to decrease with increasing pressure; (b) mixtures Nos. 3 and 2, for which the ratio is high (from 2- to 6-fold) and sometimes increases with increasing pressure; and (c) copper oxide (or carbonate) and mixtures rich in copper oxide, for which the ratio is very high (from 8- to 10-fold) at low pressures and decreases rapidly with increasing pressure.

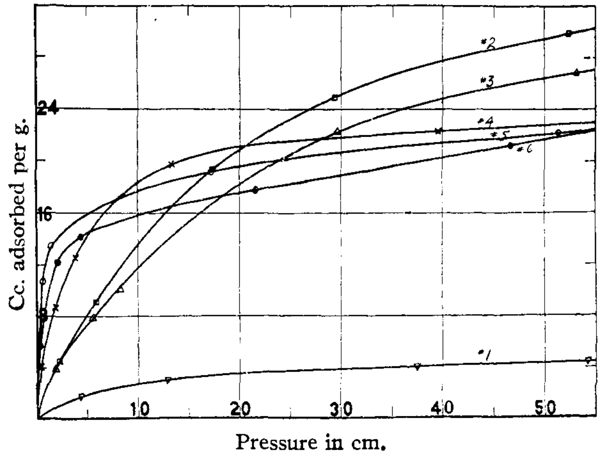

Fig. 4.—Series 2 with carbon monoxide.

Fig. 4, for Series 2, shows a typical set of curves, the position and shape of which illustrate the three types of results just mentioned.

The carbon monoxide adsorption cannot be completely reversible with respect to carbon monoxide, since the formation of carbon dioxide at the expense of the oxygen of the catalyst must be taking place continuously. If this reaction were complete, we should expect to find approximately the same total adsorption with carbon monoxide as with the dioxide; for Benton[7] has shown that "the quantity of carbon dioxide adsorbed was substantially unaffected by partial reduction." This is the result attained with manganese dioxide; it follows that in this case the formation of

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[6] There are only two exceptions, the Washington manganese dioxide with an average ratio of 0.25, and the Washington copper oxide with a ratio decreasing from 2 to less than unity. These low results are believed to have been due to a difference in the condition of the samples in the carbon monoxide and dioxide experiments (compare Footnotes 3 and 4).

[7] Ref. 2, p. 898.

carbon dioxide is probably nearly complete in the long time necessary in the experiments. In the other cases, however, the high values of the CO/CO_2 ratio show that the reaction is far from complete at 20°, and that a large amount of adsorbed carbon monoxide must be held firmly, especially by copper oxide. Additional evidence on these questions is furnished by the rate measurements described below.

The agreement with the adsorption formula was rather unsatisfactory, but this alone would not have been sufficient to prove that the carbon monoxide results should not be treated as adsorption data. The values of the exponent ranged from about 0.17 for the copper oxide samples, to 0.9 for Nos. 2 and 3 of Series 2 at low pressure; but a similar wide range was shown in the case of oxygen. The exponent $1/n$ decreased with increasing pressure in several cases, namely, some of the mixtures, and the manganese dioxide and copper carbonate of Series 3.

Total Adsorption and the Mixture Effect in Catalysis

It is evident that there is no difference in adsorption between mixtures and components that corresponds in any way to the marked difference in catalytic activity, that is, the "mixture effect." Instead, there is in general in a related series a fairly regular change in adsorptive capacity in passing from manganese dioxide through the mixtures to copper oxide or carbonate; this change is a decrease in adsorptive capacity in the case of carbon dioxide and oxygen, and an increase in the case of carbon monoxide.

Attempts were also made to find some relation between adsorption and catalytic activity for catalysts of the same composition, such as the various samples of manganese dioxide; but they failed completely. A certain adsorptive power for the reacting substances is doubtless a prerequisite for contact catalysis; but, for the reaction here considered, the distinction between high and low catalytic activity bears no relation to total adsorptive capacity. This conclusion is in conformity with that of other investigators for various reactions.

Rate Measurements

The rate of adsorption of the first portion of *carbon dioxide* added after the preliminary washing was determined for many of the samples. This rate was very great in the first minute, but after about five minutes became relatively small and nearly constant. The amount of gas adsorbed in the first few minutes could be calculated from the observed drop in pressure, or more accurately by using Benton's method[2] of extrapolating back to zero time. Comparison of the results obtained when approximately the same quantity of gas was added to various samples led to the following conclusions. The amount of carbon dioxide taken up in the first few minutes was considerably greater for each of the Washington samples than for any corresponding member of our three series. In each related series, the amount thus rapidly adsorbed, and probably also the rate of adsorption in the first minute, increased from manganese dioxide to copper oxide (which is in the opposite order from that of total adsorption). In this case, also, there is no difference between mixtures and components corresponding to the mixture effect manifested in catalytic activity.

In a few incidental experiments with *oxygen* in small amount, the drop in pressure in the first few minutes was too small to yield definite results. However, since Benton[2] had no difficulty in measuring the rapid adsorption at a constant pressure of one atmosphere, we may conclude that the pressure-time curves with large amounts of oxygen would have been similar in shape to those for carbon dioxide.

In the case of *carbon monoxide* the pressure-time curves did not show an abrupt change in slope within five minutes (except in the case of manganese dioxide), which agrees with the fact that Benton did not attempt to measure rapid adsorption above 0°. Also there was a marked difference in the behavior of mixtures and single oxides at 20°. To investigate this, special experiments were carried out at 20° and 76°, and provision was made for withdrawing and analyzing the gas.

Rate Experiments with Carbon Monoxide at 20° and 76°.—The catalysts chosen were Nos. 1, 3 and 6 of Series 2, and the Washington mixture. The first three had been prepared from the same samples of manganese dioxide and copper oxide. The composition of the two mixtures corresponded to that of two-component "Hopcalite." As catalysts,[1] the efficiency of the Washington mixture at 20° and of both mixtures at 76° was 100%, and that of the No. 3 mixture at 20° was about 35%. On the other hand, the manganese dioxide (No. 1) was still inactive as a catalyst at 76°, and the efficiency of the copper oxide at this temperature did not exceed 5%.

Each sample was subjected to the usual preliminary treatment, a 44- to 62cc. portion of carbon monoxide (at a temperature of 20° and accurately measured) was introduced, and the pressure measurements were continued for five hours. The initial pressures at each temperature were calculated and were between 35 and 54 cm. of mercury. The detailed results are presented later in Table II. In Fig. 5 the drop in pressure is plotted against time.

In the case of the mixtures there is a large and rapid initial drop in pressure, and the pressure remains nearly constant after one hour. This proves that at both temperatures a large amount of carbon monoxide is taken up rapidly and held by the mixture.

At 20° the behavior of the single oxides is very different from that of the mixtures. The initial drop in pressure is slow for copper oxide, and small (though rapid) for manganese dioxide, while the pressure continues to decrease slowly for two or three days. These results, together with the fact that but little carbon dioxide is present after five hours (see below), prove that the rate of adsorption of carbon monoxide is very slow for the single oxides at 20°.

At 76° the initial behavior of copper oxide is similar to that of the mixtures at 20° and 76°. For manganese dioxide the initial drop in pressure is also greater at 76° than at 20°. It is evident that the rate of adsorption of carbon monoxide by these substances increases with the temperature.

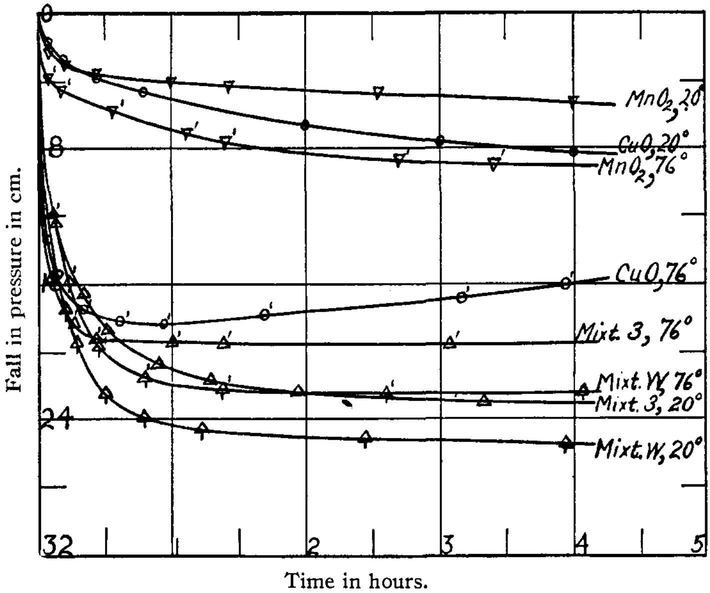

Fig. 5.—Pressure-time curves with carbon monoxide at 20° and 76°.

There is a parallelism at 20° between the rapid adsorption of *carbon monoxide* by the mixtures and their great catalytic activity, as compared with the single oxides, but the result with copper oxide at 76° shows that a catalyst may take up carbon monoxide rapidly at a temperature below that at which it operates at high efficiency as a catalyst. The first observation corresponds with Benton's general result that there is a parallelism between the catalytic activity of various oxides (in the carbon monoxide-oxygen reaction) and their adsorption of carbon monoxide; the idea is the same whether the process is called "specific adsorption" or "chemical reaction." The second observation shows that rapid interaction with carbon monoxide is not the sole criterion for an efficient catalyst in the reaction considered.

The curve for copper oxide at 76° reaches a minimum in about one hour and then rises gradually for the remaining four hours. This result was confirmed by a second experiment. A re-examination of the adsorption data at 20° led to the detection of a slight rise in pressure after several days in some of the experiments with copper oxide, but in no other cases. Since the rise in pressure must have been due to the formation of carbon dioxide gas, the important conclusion may be drawn that in the case of copper oxide at both temperatures the formation of carbon dioxide gas is slow compared with the adsorption of carbon monoxide. The interaction between copper oxide and carbon monoxide thus takes place in two stages, namely, one involving the disappearance of carbon monoxide, and a later one leading to the formation of carbon dioxide. The second is slower than the first, but both are very slow at 20°.

At the end of each five-hour run the sample was evacuated without altering the temperature, using a Toepler pump, until a very low pressure was reached and maintained. The recovered gas was analyzed for carbon monoxide and dioxide as described in the next section, with the results shown in Table II. Since the amount of gas withdrawn from the catalyst itself during the evacuation (Line 7, Table II) is small in comparison with the total amount of gas recovered (Lines 5 and 6, Table II), the analysis shows approximately the composition of the gas phase in contact with the catalyst at the end of the five-hour run.

In the experiments with the mixtures it is seen that large amounts of carbon dioxide are formed at both temperatures. With the single oxides comparatively little carbon dioxide is present after five hours at 20°, and even at 76° the amount is smaller than for the mixtures. These results complete the proof that the taking up of carbon monoxide by the single oxides is a slow process at 20°, and indicate that a portion of the carbon monoxide is rapidly transformed into carbon dioxide by the mixtures at both temperatures.

Since in the cases of manganese dioxide and the mixtures no final rise of pressure was detected, it is clear that carbon dioxide gas was given off at the same time that carbon monoxide was being taken up. In other words, there is no evidence of a second rate-determining step such as was demonstrated for copper oxide. Hence, with the mixtures, where the first stage was rapid, large amounts of carbon dioxide should be present in the gas phase early in the run. To check this conclusion, the experiments at 20° were repeated with fresh samples of the two mixtures, and six minutes after the carbon monoxide had been introduced 46.5 and 51% of carbon dioxide were found with No. 3 and W, respectively. When the results of the adsorption experiments are recalled, it is evident that this rapid conversion to carbon dioxide by the mixed oxides is effective for only a part of the carbon monoxide.

Successive Treatments with Carbon Monoxide and Oxygen.—Immediately after the treatment with carbon monoxide just described, an accurately measured 43- to 62cc. portion of oxygen at a temperature of

20° was added to each sample, and pressure readings were taken for about five hours. The drop in pressure (from the calculated initial pressure) is plotted against time in Fig. 6. After each run the gas was pumped out with a Toepler pump, first at the temperature of the run (20° or 76°), and then at 138° to ensure complete removal of the adsorbed oxygen.

The samples of gas collected after the carbon monoxide and oxygen treatments were analyzed for carbon dioxide, oxygen, and carbon monoxide by the methods of Burrell and Seibert;[8] using potassium hydroxide solution, phosphorus and ammoniacal cuprous chloride, respectively.

The experimental results are summarized in Lines 1 to 12 of Table II. All volumes are expressed in cubic centimeters, measured at 20° and one atmosphere. The pressures in Lines 2 and 3 are expressed in centimeters of mercury at the temperature of the experiment.

TABLE II

EXPERIMENTAL RESULTS IN THE SUCCESSIVE FIVE-HOUR TREATMENTS WITH CARBON MONOXIDE AND OXYGEN

	Sample (5 g.)	$MnO_{1.83}$		CuO		Mixture 3		Mixture W	
	Temp., °C.	20	76	20	76	20	76	20	76
1	Initial vol. of CO	59.4	49.4	45.4	44.2	56.2	55.3	57.5	61.9
2	Initial pres. (calcd.)	45.4	43.2	34.8	39.6	43.0	48.3	43.9	54.0
3	Final pres.	39.9	34.1	24.2	24.5	20.2	28.8	18.6	31.7
4	Corr. vol. (calcd. from 3)	52.1	39.1	31.6	28.1	26.4	33.0	24.2	36.3
5	CO recovered	47.9	16.0	35.4	10.5	6.0	4.9	4.9	6.1
6	CO_2 recovered	7.6	25.5	1.0	23.9	23.9	31.5	24.0	34.8
7	Adsorbed gas removed by evac. (calcd. from 5, 6 and 4)	3.4	2.4	4.8	6.3	3.5	3.4	4.7	4.6
8	Initial volume of O_2	54.7	43.2	46.5	45.4	59.2	60.3	61.9	61.3
9	O_2 recovered	53.5	39.0	46.1	43.7	52.6	49.2	58.9	53.8
10	CO recovered	1.1	1.1	0.9	0	0	0	0	0
11	CO_2 recovered	0.4	2.2	1.1	2.0	0.6	2.5	1.8	3.6
12	CO not recovered, cc. (calcd. from 1, 5, 6, 10 and 11)	2.4	4.6	7.0	7.8	25.7	16.4	26.7	17.4
13	CO not recovered, % (calcd. from 1 and 12)	4.0	9.3	15.4	17.4	45.7	29.6	46.7	28.2

In each run some carbon monoxide was not recovered (see Lines 12 and 13); the amount was largest for the mixtures, over 45% at 20°, and smallest for manganese dioxide, 4% at 20°. The carbon monoxide thus held did not react rapidly with oxygen as is shown by the comparatively small amounts of carbon dioxide formed in the oxygen treatment (see Line 11). At 20° the ratio between the amount of carbon monoxide held (Line 12) and the amount of carbon dioxide formed in the first stage (Line 6) is 7.0 for copper oxide, 1.1 for the mixtures, and only 0.3 for manganese dioxide. By reference to the adsorption data, Table I, it is evident that

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[8] Burrell and Seibert, *Bur. Mines Bull.*, **42**, 39 (1913).

the amount of carbon monoxide firmly held by copper oxide continues to increase after five hours, and finally exceeds that held by the mixtures.

In the case of the manganese dioxide at 20°, 12.8% of the carbon monoxide was converted into dioxide in five hours, and it may be seen from Fig. 5 that the rate of decrease in pressure remained constant after the first half-hour. We may conclude that, in the three or four days required for each measurement in the adsorption experiments, the reaction was nearly complete. A small amount undoubtedly remained as firmly held material (see Line 13 and preceding paragraph).

Carbon monoxide was recovered in the final evacuation (at 138°) only in the experiments with copper oxide at 20° and with manganese dioxide at 20° and 76° (see Line 10). These are also the cases in which the largest proportion of the carbon monoxide was recovered in the first stage (see Line 5), and in which the rate of interaction with carbon monoxide was the smallest. It follows that this gas is taken up less readily and given off more readily by the single oxides than by the mixtures. Or we may say that at ordinary temperatures carbon monoxide adsorption is more nearly a reversible process with the single oxides than with the mixtures.[9]

In Table III are shown the *changes in oxygen content* of the samples themselves as calculated from the data in Table II. The amount of oxygen lost in the carbon monoxide treatment (Line 1) is derived from the amount of carbon dioxide formed (Line 6, Table II) by means of the factor 0.665 mg. of oxygen per cc. of carbon dioxide. The number of milligrams of oxygen regained in the oxygen treatment (Line 2) is equal to 1.33 times the

TABLE III

CHANGES IN OXYGEN CONTENT OF THE SAMPLES IN THE SUCCESSIVE TREATMENTS WITH CARBON MONOXIDE AND OXYGEN

Sample	$MnO_{1.83}$		CuO		Mixture 3		Mixture W	
Temp., °C.	20	76	20	76	20	76	20	76
Oxygen lost in Stage I, mg....	5.0	17.0	0.7	15.9	15.9	21.0	16.0	23.2
Oxygen regained in Stage II, mg......................	1.3	4.1	.0	0.9	8.4	13.2	2.8	7.6
Net loss of oxygen, mg.......	3.7	12.9	.7	15.0	7.5	7.8	13.2	15.6
Oxygen regained in Stage II, %	26	24	0	6	53	63	18	31

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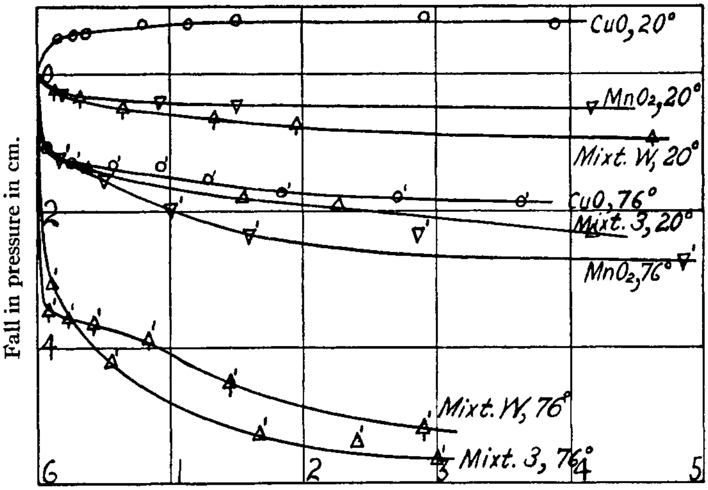
[9] Additional evidence in support of this conclusion is supplied by the data in Line 7. In the case of copper oxide at 20°, of the 4.8 cc. (Line 7) at least 3.8 cc. must have been carbon monoxide, since only 1.0 cc. of carbon dioxide was recovered (Line 6). In the three remaining cases the quantity of carbon dioxide that would have been adsorbed in the absence of carbon monoxide was calculated from the adsorption data of Table I and the partial pressure of carbon dioxide in the gas phase. Even when it was assumed that the gas listed in Line 7 was pure carbon dioxide the calculated results were relatively high, especially for the mixtures; thus the figures were 6.5 cc. for manganese dioxide and 17.5 and 20 cc. for mixtures 3 and W, as compared with 3.4, 3.5 and 4.7, respectively, in Line 7. It is clear that little or no carbon monoxide was recovered from the mixtures by evacuation at 20°.

volume of oxygen used up (Lines 8 and 9, Table II) diminished by an amount corresponding to the carbon dioxide formed in this stage (Line 11, Table II).

The relative position of the curves in Fig. 6 after three hours agrees fairly well with the relative magnitude of the numbers in Line 2 of Table III. Perfect agreement is not to be expected, since some oxygen is used up in forming carbon dioxide which divides itself between the gas phase and the surface of the sample.



Time in hours.

Fig. 6.—Pressure-time curves with oxygen at 20° and 76° after previous treatment with carbon monoxide.

Only in the experiment with copper oxide at 20° was there no reoxidation of the solid, and the pressure rose gradually to a nearly constant value due to the formation of carbon dioxide (and possibly carbon monoxide) gas. In the other experiments the pressure decreased from the beginning, the initial drop being least rapid for manganese dioxide at 20°. (A reexamination of the experimental data showed that this curve might have been 0.1 cm. higher than shown in the figure.) For each substance the initial drop in pressure is greater at 76° than at 20°; and at each temperature the initial decrease is greater for the mixtures than for the single oxides. Here, again, there is a relation to the mixture effect in catalysis.

When, however, the total amount of oxygen regained is considered, instead of the initial rate, the manganese dioxide seems to be closely related to the mixtures. This is more evident when the oxygen regained is expressed as per cent. of the amount of oxygen lost in the carbon monoxide treatment, as in Line 4 of Table III. The mixtures and manganese dioxide are reoxidized to a considerable extent at both temperatures, and the copper oxide not at all at 20° and only slightly at 76°. Of the two mixtures the Washington catalyst regains much less oxygen. A similar result was reported by Almquist and Bray.[10] They also noted the ready reoxidation of manganese dioxide at a higher temperature, 150–160°.

Discussion

The adsorption of carbon monoxide by various oxide catalysts has been shown by Benton[2] to be a reversible process at the very low temperature of —79°. In the temperature range, 20–76°, we have found that the adsorption is still reversible to some extent with copper oxide and with manganese dioxide alone, but not with their mixtures. This difference appears to be due to the increased speed, in the case of the mixtures, of certain reactions which we shall now consider.

In the oxidation of carbon monoxide to dioxide by copper oxide (in the absence of oxygen) in the temperature range just below that in which it is capable of acting as a catalyst, there are two rate-determining steps, the second of which is slower than the first. The possible consecutive steps, (*a*) direct addition, (*b*) electronic rearrangement, and (*c*) splitting off of carbon dioxide, have been discussed by Benton.[11] In agreement with him, we shall assume that (*a*) is a rapid process, and that (*b*) is the first rate-determining step in the reaction. It follows from our rate results that at 20° a small amount of carbon monoxide is sufficient to saturate the surface, and that more is taken up only as (*b*) proceeds. The second and slower rate-determining step is probably (*c*), which involves the breaking of the bonds between an oxygen atom and the neighboring copper atoms. Some idea of the nature of Steps *b* and *c* may be obtained from the following considerations. In crystalline cupric oxide the arrangement is a distortion of that of sodium chloride.[12] The atoms are really ions, the bivalent oxide ion with 8 valence electrons and the cupric ion with none. Within a crystal each oxide ion is surrounded by 6 copper ions, and *vice versa;* but in the surface of the catalyst each oxide ion is associated with from 1 to 5 copper ions. When an oxygen atom is removed from the copper oxide surface, 2 of its 8 electrons must remain in the surface. They may be considered to convert one copper ion to an atom of metallic copper, but this atom remains associated with oxygen ions. Moreover, copper oxide is probably a metallic conductor; and, if this is so, the electrons may move to other positions.

Carbon monoxide and dioxide contain 10 and 16 valence electrons, respectively. In any arrangements that may be assumed on the basis of the Lewis theory, the carbon atom of the dioxide shares its electrons with the two oxygen atoms, while the carbon of the monoxide has at least one

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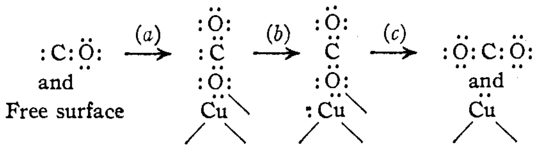
[10] Ref. 1, pp. 2319–2320.

[11] Ref. 2, p. 903.

[12] Wyckoff's summary, *J. Franklin Inst.*, **195**, 205 (1923).

lone pair of electrons. It is suggested that the electronic rearrangement in (*b*) is the transfer of a pair of electrons from the carbon atom toward the surface. One way, though not the only one, of representing (*a*), (*b*), and (*c*) is shown below; for simplicity only one atom each of oxygen and copper is shown in the surface:



(*a*) is rapid and reversible, (*b*) is slow and may be reversible to a slight extent, and (*c*) is irreversible and very slow at 76° or below. The material formed in (*b*) has been termed "firmly held carbon monoxide," but it is evidently closely related to carbon dioxide. The incomplete conversion of carbon monoxide into dioxide and the storing of large amounts of firmly held material are characteristic of copper oxide at ordinary temperatures.

In the reaction of carbon monoxide with manganese dioxide at 20° and 76°, the amount taken up in the rapid step (*a*) is greater than with copper oxide, but is still small. There is only one rate-determining step. This is concluded to correspond to (*b*) rather than to (*c*); since, otherwise, there would be opportunity for carbon monoxide and any transformation product to accumulate in large quantity on the surface. This does not occur; and it would seem unreasonable to assume either that there is no such transformation product or that the adsorptive capacity of manganese dioxide for such a substance is negligibly small compared with that of copper oxide. Also it is not improbable that an oxygen atom can be more easily removed from manganese dioxide than from copper oxide. Our results show that complete conversion of carbon monoxide into dioxide is characteristic of manganese dioxide.

This conclusion has already been demonstrated by Whitesell and Frazer[13] on the basis of their experiments with more active samples of manganese dioxide. Oxides prepared by various methods were rendered active by treatment with nitric acid, whereby the amounts of impurities, as potassium oxide, and of manganous oxide, were greatly lessened. The resulting highly porous materials oxidized carbon monoxide rapidly, catalytically when oxygen gas was present, or by direct action in its absence. The electronic rearrangement, the rate-determining step (*b*), thus is rapid in the case of these active samples. Whitesell and Frazer suggest that the low content of potassium oxide is the significant factor. It may be unfortunate that we did not analyze our samples for potassium,

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[13] (a) Whitesell and Frazer, THIS JOURNAL, **45**, 2848 (1923). (b) See also Frazer and Greider, *J. Phys. Chem.*, **29**, 1099 (1925).

but it would have been in the form of sulfate, and we assumed that washing the hydrated material until the wash water gave no test for sulfate would remove nearly all the soluble salts. Moreover, it is difficult to imagine how the presence of a small amount of potassium sulfate can lower by nearly 200° the temperature at which MnO_x can act as an efficient catalyst. It seems more probable that the high oxygen-manganese ratio of the active samples and the correspondingly low content of manganous oxide are the important factors. The presence of manganous oxide, which Whitesell and Frazer state to be present in solid solution, seems likely to have a great influence on the speed of electronic rearrangement. If this is so, then its effect is in the opposite direction to that of copper oxide in the heterogeneous mixture.

There is another difference between the active and inactive manganese dioxide which may be attributed to the effect of the presence of manganous oxide in the latter: after it has been adsorbed, carbon dioxide is given off much more readily and completely from the active samples. Indeed, this explanation was mentioned by Whitesell and Frazer[14] to account for their observation that, after considerable reduction of an active oxide by carbon monoxide, the carbon dioxide comes off more slowly. More recently Frazer and Greider[13b] have found that in this reaction 17 to 20% of the carbon monoxide was not recovered as carbon dioxide, and have assumed that it was retained as manganous carbonate. Since both the active and inactive manganese dioxides thus behave alike (in retaining some carbon monoxide), it seems certain that the firmly held material in our inactive samples cannot be responsible as a protective film for the slow reaction with carbon monoxide. We had already concluded that this was unlikely, since the amount held is small, and since the results of Lamb and Vail[15] show that about 2% of water is necessary to lower the efficiency of Hopcalite from 90 to 20%.

In the case of the mixtures at 20° and 76° it seems certain that the component oxides have retained their characteristic properties, the manganese dioxide being responsible for the oxidation of part of the carbon monoxide to dioxide, and the copper oxide for the firm retention of nearly all the remainder. However, the oxidation of carbon monoxide by the manganese dioxide is now very rapid. Also, the copper oxide takes up carbon monoxide more rapidly when in the mixture than when alone. In each case the speed of electronic rearrangement, which we have concluded is the determining factor, is greatly increased merely by bringing discrete particles of the two oxides into intimate contact.

We are unable to suggest a theoretical reason for the change in speed of the electronic rearrangements. But it must not be forgotten that we are

[14] Ref. 13 a, p. 2846.

[15] Lamb and Vail, This Journal, **47**, 135 (1925).

dealing with very complex systems. An active binary catalyst, for example, contains copper oxide and basic copper carbonate,[16] manganese dioxide with manganous oxide in solid solution, water and appreciable amounts of impurities.[17] The material is very porous; and the surface contains, in addition to the substances just named, much firmly held carbon monoxide, some oxygen and the carbon dioxide which is being formed. Also, the two component oxides are probably metallic conductors, and a rapid rearrangement of electrons within the catalyst is then possible.

The slow desorption of carbon dioxide formed from the monoxide has not the general significance suggested by Almquist and Bray,[1] though it is the limiting factor in the reaction with copper oxide. Nor is it necessary to assume in all cases a film of such material to account for the rapid decrease in speed when the oxides are treated with carbon monoxide at temperatures at which they are efficient catalysts. It is sufficient to assume that only a small part of the oxygen in the surface is able to react rapidly. Such lack of uniformity in the surface of a catalyst was illustrated in our discussion of the structure of copper oxide, and has been emphasized by H. S. Taylor in recent articles.[18]

After partial reduction by carbon monoxide the initial rate of reoxidation is more rapid for the mixtures than for the single oxides, thus showing a parallelism with catalytic activity. When it is considered that the mixtures are less efficient catalysts after partial reduction, as Almquist and Bray[1] have shown, it is clear that this accords with the theory that reoxidation by oxygen during catalysis, and before the reduction is appreciable, is sufficiently rapid to enable the process to continue without reduction of the catalyst. All investigators of the carbon monoxide–oxygen reaction have accepted this chemical theory of the catalysis. It has often been called "alternate" reduction and oxidation, but the term "simultaneous" might be used equally well. The reactions are alternate only when a portion of the surface of molecular dimensions is considered.

Summary

Adsorption isotherms of carbon dioxide, oxygen and carbon monoxide at 20° have been determined for the various members of three related series of manganese-dioxide–copper-oxide catalysts and for three other samples, for which the catalytic efficiency in the carbon monoxide–oxygen reaction had been measured by Almquist and Bray.

The mixture effect in the catalysis is not related to total adsorption,

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[16] Merrill and Scalione [(a) THIS JOURNAL, **43**, 1991 (1921)] state that mixtures made from the carbonate are better catalysts than those made from the oxide. Lamb, Scalione and Edgar [(b) THIS JOURNAL, **44**, 745 (1922)] have shown that prolonged heating at 240° fails to remove completely the carbon dioxide of constitution.

[17] Ref. 15, p. 130.

[18] Taylor, *Proc. Roy. Soc.*, **108A**, 105 (1925); *J. Phys. Chem.*, **30**, 145 (1926).

of any of the three gases studied, nor to the rate of adsorption of carbon dioxide.

The rate of interaction of carbon monoxide with four representative catalysts at 20° and 76° has been investigated by measuring the decrease in pressure, and analyzing the gases after removal by evacuation at the end of a five-hour period. The rate of reoxidation by oxygen of the partly reduced materials was then determined in a similar manner.

Both the rate of interaction with carbon monoxide and the initial rate of reoxidation are greater for the mixtures than for the single oxides.

The behavior of copper oxide toward carbon monoxide differs greatly from that of manganese dioxide. In the latter case there is only one rate-determining step, the conversion to carbon dioxide is ultimately nearly complete, and the total adsorption coincides closely with that of carbon dioxide. In the case of copper oxide there are two rate-determining steps, the second of which is slower than the first. The result is that at 20° a large amount of carbon monoxide is held firmly by copper oxide, and the total adsorption is finally much greater than with carbon dioxide. The first step in this reaction and the single step in that with manganese dioxide are believed to be electronic rearrangements after rapid adsorption of small amounts of carbon monoxide.

In the reaction of the mixtures with carbon monoxide the component oxides appear to retain their characteristic properties, except that in each case the speed of the electronic rearrangement is increased.

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A STUDY OF THE CRYSTALLIZATION OF SOME METAL LACTATES

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Introduction

The preparation of barium lactate as a reagent for the preparation of ethyl lactate led to observation of the fact that this salt did not crystallize except in alkaline solutions. Very limited investigations seemed to indicate that neutral or slightly acid solutions would give a thick sirup, whereas, similar preparations of the salt containing a very marked excess of the base, barium hydroxide, would first form a sirupy mass and upon continued dehydration, would solidify with the formation of crystals of the salt. This peculiarity was considered of sufficient interest to justify further study.

Very little literature could be found on the salts of lactic acid, with the exception of those salts of the metals used in the purification of the acid