The nitrogen was generated from ammonium hydroxide and bromine water.[14] It was purified by standing over sodium hydroxide solution, passing through a trap cooled with liquid air, then over phosphorus and finally over phosphorus pentoxide. Three different samples were used, generated at different times. The third sample was further purified by a fractional distillation, but the vapor pressures agree very satisfactorily with the first two samples, showing that this method gives very pure nitrogen.

Table I gives the results, which are found to be fairly well represented by the equation $\log_{10} P = -302.34/T + 3.94127 - 0.000274T + 1.116 \times 10^{-6} (T - 100.5)^3$, in which the pressure is expressed in normal atmospheres. When extrapolated to low pressures this equation agrees fairly well with the data of von Siemens.

Table I

Vapor Pressures of Nitrogen

Temp., °K.	90.12	92.73	95.44	96.00	98.64	104.46
$P_{\text{obs.}}$, atm.	3.631	4.520	5.583	5.820	7.056	10.440
$P_{\text{obs.}} - P_{\text{calcd.}}$	—0.003	—0.003	0.000	—0.005	—0.006	—0.007

Temp., °K.	106.97	108.76	113.60	116.18	118.94	121.47
$P_{\text{obs.}}$, atm.	12.193	13.594	17.85	20.47	23.57	26.75
$P_{\text{obs.}} - P_{\text{calcd.}}$	—0.009	0.035	—0.05	0.00	—0.06	—0.05

Summary

The vapor pressure of nitrogen has been determined in the range from 90.12°K. (3.631 atm.) to 121.47°K. (26.75 atm.). The results are represented fairly well by the equation $\log_{10} P = -302.34/T + 3.94127 - 0.00274T + 1.116 \times 10^{-6} (T - 100.5)^3$.

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[Contribution from the Chemical Laboratory of the University of California]

THE CATALYTIC OXIDATION OF CARBON MONOXIDE
III. CATALYTIC EFFICIENCY OF MIXTURES OF DRY MANGANESE DIOXIDE AND CUPRIC OXIDE

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The mixtures of manganese dioxide and copper oxide considered in the first papers of this series[1] were prepared by kneading together measured quantities of the wet hydrated oxides. A "related series of catalysts" consisted of four mixtures and samples of the single oxides from which these mixtures had been made, all of which had been slowly dried and partially dehydrated, and were in the form of porous granules. In the dis-

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[14] Waran, *Phil. Mag.*, [6] **42**, 246 (1921).

[1] (a) Almquist and Bray, This Journal, **45**, 235 (1923) (on p. 2317, three lines from the bottom of the page, for "Catalyst 2" read "Catalyst 3"). (b) Hoskins and Bray, *ibid.*, **48**, 1454 (1926). References to the work of Frazer and his associates, and of other investigators, are given in these papers.

cussion of the "mixture effect" in the catalytic oxidation of carbon monoxide, it was assumed that the two oxides in such mixtures were present as distinct particles in intimate contact with each other. In support of this assumption we are now presenting the results of experiments, completed in 1923, which demonstrate that a mixture prepared by grinding together certain samples of the dry, powdered oxides is much more efficient as a catalyst than either of the constituent oxides.[2]

The catalysts tested were derived from three members of Series 2 of Almquist and Bray: Nos. 1, 6 and 2 which were, respectively, manganese dioxide, $MnO_{1.83}$, copper oxide, and the mixture containing MnO_x and CuO in the proportion of 72 to 28. These were in granular form, and the filter cake from which the granules were made had been dried at 75° for 72 hours. The two single oxides and the mixture are designated Mn°, Cu° and M°.

Mn, Cu and M were powdered samples of these three catalysts. The grinding in an agate mortar was continued for 30 minutes and each powder felt free from gritty material when rubbed between the fingers; 10.5 cc. of M° granules yielded 12.5 cc. of M powder.

Mn′, Cu′ and M′ were powdered samples of the three catalysts which had been heated for 2.5 hours at red heat before being ground to powder.

The four possible mixtures were prepared from the two sets of powdered single oxides by mixing them intimately in the proportion of 72 to 28: MnCu, MnCu′, Mn′Cu and Mn′Cu′.

The method of testing the catalysts was similar to that described by Almquist and Bray,[1a] and the carbon monoxide analyzing device had the modifications recommended by Larson and White.[3] The gas was 0.18 to 0.2% by volume of carbon monoxide in air. The temperature recorded was that of the influent gas, and not that of the catalyst as in the measurements of Almquist and Bray. The difference was found in our first measurements with M° to be 5°, or 6° when 5 cc. of the catalyst was operating at 90% efficiency with 0.2% gas and a space velocity of 5400 (liters per hour per liter of catalyst); which is only 1° greater than the difference reported by Almquist and Bray. This heating effect, of course, would be smaller at lower efficiency or lower space velocity.

In order to make sure that we could obtain reproducible efficiency-temperature curves, several runs were made with 5 cc. of the granular

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[2] Attention must be called to the fact that the mixture effect in this catalysis has been demonstrated only when inactive manganese dioxide has been used in preparing the mixtures, and that Whitesell and Frazer [This Journal, **45**, 2841 (1923); see also Ref. 1 b, p. 1471] have prepared very active samples of manganese dioxide. However, it seems important to record the result that a relatively active catalyst can be produced merely by bringing particles of copper oxide and inactive manganese dioxide into intimate contact with each other.

[3] Larson and White, This Journal, **44, 21** (1922).

mixture M°, in a tube of 1 sq. cm. cross section, at a space velocity of 5400. It was found that reproducible results could be obtained rapidly only when the catalyst had been brought into an active condition either by letting it operate at high efficiency or by heating it in a current of dry air, whereby, presumably, a water film was removed from the surface.[4] Accordingly, in the later work, each catalyst was first heated for an hour in a current of dry air. This heat treatment was at 150° when the catalyst operated at 100% efficiency at a lower temperature, and at a higher temperature in other cases. Points on the efficiency-temperature curve were then determined in the order of decreasing temperatures, the temperature being held constant for 30 minutes for a single measurement.

The results with M° at 5400 space velocity were reproducible to 1°. The data given in the first line of Table I were read from a smooth curve. Comparison with the corresponding curve of Almquist and Bray shows that at the same efficiencies our points are 4° or 5° lower (even after allowance is made for the difference in temperature between the gas and the catalyst). The discrepancy is not large, and is probably due to the fact that in this instance the measurements of Almquist and Bray were made in the order of increasing temperatures and were not repeated after the catalyst had operated at 100% efficiency.

TABLE I

CATALYTIC EFFICIENCY OF THE GRANULAR MIXTURE OF TWO-SPACE VELOCITIES. TEMPERATURE AT VARIOUS EFFICIENCIES

Efficiency, %	50	60	70	80	90	100
Space velocity 5400	22°	26°	30°	34°	40°	50°
Space velocity 2700	16°	20°	24°	29°	34°	45°

Two runs with M° were also made at a lower space velocity, 2700, with catalyst volumes of 5 and 10 cc., respectively, in the tube of 1 sq. cm. cross section. The seven points determined in the first case and the three in the second were on the same curve, thus illustrating the well-known fact that the efficiency at a given temperature depends mainly on the space velocity. Some of the experimental points are shown in curve M° in Fig. 1, and the data in the second line of Table I were read from the curve. The results in Table I show that at a given efficiency the temperature of operation is lowered by 5° to 6° when the space velocity is halved.

The powdered catalysts were tested at a space velocity of 2700 in a tube 0.57 sq. cm. in cross section. A 2.5cc. portion of catalyst was used in each run, the powder and glass wool being placed in the tube in alternate layers, each about 1 cm. in depth. The experimental results are plotted in Fig. 1, and summarized in Table II.

The curve for the powdered mixture M coincides with that for the

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[4] See Ref. 1 a, p. 2312 and Ref. 2, Footnote 3.

TABLE II

CATALYTIC EFFICIENCY OF THE CATALYSTS AT 2700 SPACE VELOCITY. TEMPERATURE AT VARIOUS EFFICIENCIES

Efficiency	20%	50%	80%
M°, granular mixture	...	16°	29°
M, powdered mixture	...	16°	29°
M′, powdered after heating M°	111°	165°	230°
[Mn° granular $MnO_{1.83}$ (A. and B. at 5400 s. v.)	118°	138°	156°]
Mn, powdered $MnO_{1.83}$	209°	273°	...
Mn′, powdered after heating Mn°	265°	(330°)	...
[Cu°, granular CuO (A. and B. at 5400 s. v.)	88°	99°	110°]
Cu, powdered CuO	158°	211°	270°
Cu′, powdered after heating Cu°	250°	(310°)	...
MnCu, mixture of Mn and Cu	32°	51°	60°
MnCu′, mixture of Mn and Cu′	(29°)	49°	60°
Mn′Cu, mixture of Mn′ and Cu	45°	67°	97°
Mn′Cu′, mixture of Mn′ and Cu′	98°	128°	160°

granular catalyst M°; showing that in this case there was no change in efficiency when the granules were powdered.

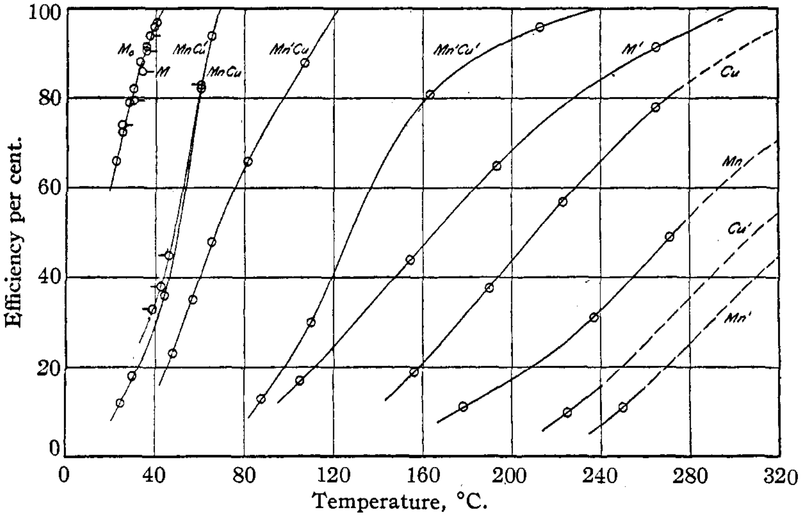

Fig. 1.—Efficiency-temperature curves for powdered catalysts at 2700 space velocity.

This, however, was not true in the case of the single oxides; the powders were found to be much less efficient than the granules. (The latter were not tested at 2700 s. v., but the results of Almquist and Bray at 5400 s. v. are included in Table II.) This marked difference in the effect of powdering the mixtures and the single oxides may be related to the fact that in the latter case the granules are relatively very soft. The grinding may have changed materially the structure of the particles of the single oxides, or the fine, soft powder may have packed in such a way that adequate contact with the gas was not possible.

That the efficiency of these porous, partially hydrated catalysts is greatly lessened by heating has long been known, and is illustrated by our results with powders prepared from strongly heated granules. Thus the temperature at which the catalyst acts at 50% efficiency is increased from 16° to 165° in the case of the mixture (M′), and is over 300° in the case of the single oxides after heating (Mn′ and Cu′). The oxides are dehydrated by the heating, and the structure of the fine particles is altered.

There remains to be considered the behavior of the catalysts prepared by mixing the dry, powdered single oxides. The most striking result is the high efficiency of the two mixtures, MnCu and MnCu′, of which the unheated manganese dioxide powder is the principal constituent. The two curves are nearly coincident, and the temperature at 50% efficiency is 50° ± 1°. Comparison with the curves for the component oxides shows that there is a very great "mixture effect" and, therefore, that this effect depends primarily upon the intimate contact of particles of the two oxides. It is not surprising that the curve for the original mixture, M, is 31° to 34° lower than the curve for these mixtures, since the wet mixing and the drying bring about more intimate contact of the particles.[5]

The third mixture, Mn′Cu, is almost as good a catalyst as either of the preceding mixtures. The fourth, Mn′Cu′, made from the heated oxides, is much less efficient; but it is a somewhat better catalyst than the heated mixture M′. Both show large mixture effects with reference to the constituent oxides.

Summary

Catalysts prepared by grinding together certain samples of the dry powdered oxides, manganese dioxide and copper oxide, have been shown to be much more efficient in the carbon monoxide-oxygen reaction than the constituent oxides.

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[5] See Ref. 1 a, p. 2321, Footnote 16.