

3. An equation for change in temperature coefficient with frequency has been derived and successfully used in interpreting existing data.
4. The causes for apparent deviations from Einstein's law of photochemical equivalence have been discussed.
5. Experimental work in this Laboratory is now in progress for further testing the ideas presented in this article.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

THE ADSORPTION OF GASES BY COPPER

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During a recent investigation of the combination of ethylene and hydrogen in the presence of metallic copper,² a considerable amount of data on the adsorption isotherms of hydrogen, ethylene, ethane and carbon monoxide on copper was accumulated. As these results show many points of special interest, it has seemed worth while to devote a separate paper to them.

The apparatus, procedure and method of preparation of the copper and the gases have already been described² and need not be repeated here in detail. Suffice it to say that adsorptions at a series of pressures between 0 and 760 mm. were determined by admitting the gases in small quantities to an evacuated bulb containing the copper and measuring the pressure after equilibrium had been established. The dead space in the bulb and connecting tubes was determined by the use of helium, which was assumed not to be adsorbed.

The absorbent consisted of about 100 g. of copper granules prepared by reduction of copper oxide by hydrogen at 200° in its original position.

Adsorption Isotherms on Active Copper at 0°

The adsorption isotherms at 0° in the presence of active copper are shown graphically in Fig. 1. Ethane was not actually run on this sample but its comparative behavior is known from two other series on similar samples of copper. An isotherm has been sketched in for completeness. Nitrogen was also run on this sample but the variability of the results indicated the presence of varying but small quantities (less than 0.5%) of some strongly adsorbed impurity. The nitrogen was prepared from ammonium chloride and sodium nitrite and was purified by passage through sulfuric acid, phosphorus pentoxide and a tube cooled in a mixture of solid carbon dioxide

¹ The work represented by this paper was performed while the author was National Research Fellow at Princeton University.

² Pease, *THIS JOURNAL*, **45**, 1196 (1923).

and alcohol. A curve corresponding to the least adsorption noted for nitrogen has been sketched in. From the form of this particular curve, it would appear that this particular sample of nitrogen contained negligible amounts of impurity.

The marked specificity of the adsorption is conclusively demonstrated by the results of these measurements; for the order of adsorption not only bears no simple relation to the order of boiling points (that is, condensa-

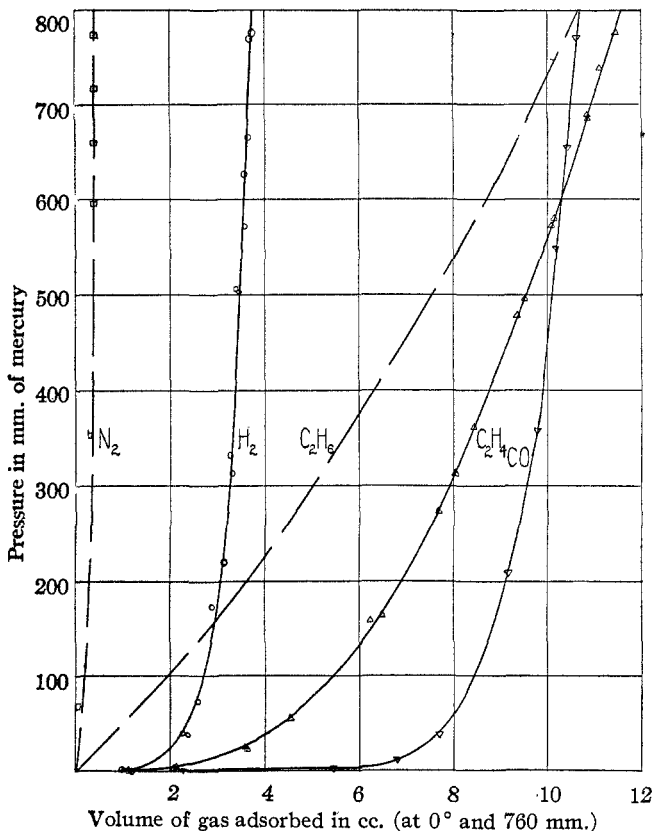


Fig. 1.—Adsorptions of N₂, H₂, C₂H₆, C₂H₄ and CO on active copper at 0°. Weight of copper catalyst: 117.0 g. Volume of dead space: 58.50 cc.

bility) but in addition depends upon the pressure at which comparison is made. Thus, at 10 mm. pressure the order of adsorptions is N₂, C₂H₆, H₂, C₂H₄, CO; while at 760 mm., the order is N₂, H₂, C₂H₆, CO, C₂H₄; and from the slopes of the curves it is evident that at still higher pressures the order will be N₂, H₂, CO, C₂H₄, C₂H₆. The order of boiling points is H₂, N₂, CO, C₂H₄, C₂H₆. The marked difference in the behavior of nitrogen and carbon monoxide toward copper is especially to be emphasized in view of the similarity in many physical properties of these two gases.

Leaving nitrogen out of account for the moment, certain interesting relationships among the adsorptions are clear. It is plain that the curves for hydrogen, carbon monoxide and ethylene are similar in form.³ There is a portion representing adsorption at a pressure of less than 0.2 mm. which amounts to about 1 cc. for hydrogen, 2 cc. for ethylene and 4 cc. for carbon monoxide, a second portion pronouncedly concave to the pressure axis and a third portion which is nearly rectilinear. The curve for ethane differs from the above in showing no marked low-pressure adsorption and being slightly concave to the pressure axis over the whole range. It is of interest that the slopes of the curves at 1 atm. for the four gases stand in the order of boiling points, that of hydrogen (expressed in cc. per 10 mm.) being 0.010, of carbon monoxide 0.020, of ethylene 0.065 and of ethane 0.092. If it were not for the fact that the slope of the nitrogen curve is certainly much less than that of hydrogen, one might be inclined to say that the adsorption at the higher pressures was due to the "physical" forces of capillarity. There would still be the difficulty that this implied the liquefaction of the gases in the capillaries of the copper at temperatures which for hydrogen and carbon monoxide are much higher than the critical, though not for ethylene and ethane ($t_c = 9.5^\circ$ and 32.1° , respectively).

Much time was spent in attempting to fit the data to various adsorption equations to be found in the literature, but it was found that none reproduced satisfactorily the values for the concave portions of the curves, that is the adsorptions up to about 0.5 atm. The best fit was obtained with a modification of Langmuir's equation⁴ for adsorption on a single type of elementary space. The simple equation may be written, $V_{ads.} = [ap/(1 + ap)]V_{sat.}$, in which a and $V_{sat.}$ are constants.

According to this equation, when ap is large compared to unity, $V_{ads.} = V_{sat.} = a$ constant, and when ap is small compared to unity, $V_{ads.} = ap$, $V_{sat.} = \text{const.} \times p$. The coefficient, a , may be taken as a measure of the strength of the adsorption. It is probable that with an adsorbent such as the copper granules used in the work, elementary spaces or active adsorbing centers of all degrees of activity are scattered over the surface and that before Langmuir's equation can be properly applied, the "distribution curve" for activity must be known.⁴ We may assume, however, that over the range of pressure considered these activities may be grouped around three average values corresponding to (1) a high activity and large value of a (for which $V_{ads.} = V_{sat.}$); (2) a medium activity and medium value of a (for which $V_{ads.} = [ap/(1 + ap)]V_{sat.}$) and a low activity and low value of a (for which $V_{ads.} = apV_{sat.}$). We may then write $V_{ads.} =$

³ Adsorption curves for CO on copper like those here reported had been previously obtained by H. A. Jones and H. S. Taylor in the Laboratory of Princeton University.

⁴ Langmuir, *THIS JOURNAL*, **40**, 1361 (1918).

$V_1 + V_2 + V_3 = V_{1sat.} + \frac{a_2 p}{1 + a_2 p} V_{2sat.} + a_3 V_{3sat.} p$. This equation can be made to fit the experimental values for hydrogen, carbon monoxide and ethylene within the experimental error. Considering that it is a four-constant equation, which may be written $V_{ads.} = A + \frac{Bp}{1 + Bp} \cdot C + Dp$, this is not strange. As it may be considered to have some theoretical basis, this equation has been preferred to others, however. It may be noted that the three terms correspond in a way to the three portions of the characteristic adsorption isotherms. The best values of the four constants for hydrogen, carbon monoxide and ethylene are given in Table I.

TABLE I
VALUES OF CONSTANTS IN ADSORPTION EQUATION

	$V_{1sat.}$	$V_{2sat.}$	a_2	$a_3 V_{3sat.}$
H ₂	0.95	2.21	0.037	0.000855
C ₂ H ₄	1.95	4.34	.0173	.00658
CO.....	4.95	4.74	.0419	.00191

The Effect of Poisoning the Copper with Mercury

Since previous experiments had demonstrated that mercury was a very powerful catalyst poison in the ethylene-hydrogen combination and that adsorption runs approximately parallel to catalytic activity, it was of interest to investigate further the influence of poisoning on the latter property. Accordingly, with the sample of copper used in the experiments just described, the influence of mercury on the adsorptions of hydrogen, ethylene and carbon monoxide at 0° was determined.

A small quantity of mercury, estimated at 0.015 cc., was forced into the adsorption bulb with hydrogen, after which the bulb was evacuated and heated to 200°. During the heating a few small globules of mercury condensed out on the cool portions of the connecting tube but the bulk of the mercury remained in the bulb. After heating, the mercury was found to have completely disappeared and there was no visual evidence of a change in the copper. Adsorption measurements revealed a marked decrease in activity, however.

The character of the effect of mercury poisoning is made clear by an examination of the curves in Fig. 2. (Broken curves, before poisoning; solid curves, after poisoning). It will be noted that the curves have been moved nearly parallel to themselves toward the pressure axis, corresponding to decreases of different magnitudes mainly in the strong (low pressure) adsorption. The amounts of these decreases in adsorption at 1 atmosphere are 4.85 for carbon monoxide, 3.40 for hydrogen and 1.60 for ethylene; at 100 mm. the decreases are 5.00, 2.70 and 1.90, respectively.

It is not clear why these decreases should vary so much among themselves, if the effect of mercury is to saturate permanently a certain number of elementary spaces. In particular, the result seems to be at odds with

a conclusion arrived at in another paper.² There it was shown that when a mixture of ethylene and hydrogen was let into the bulb containing copper catalyst, the initial pressure (obtained by extrapolation) was what would be expected if the total amount of gas adsorbed were equal to the amount of ethylene alone which would have been adsorbed if it alone were present. This did not necessarily mean that no hydrogen was adsorbed under these conditions. In fact, quite the opposite was indicated by the results of

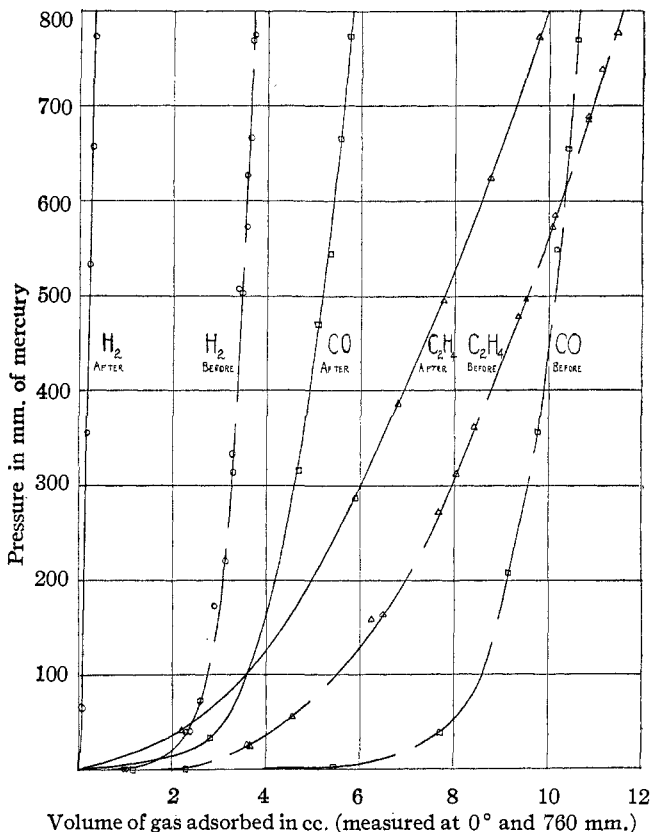


Fig. 2.—Adsorptions of H₂, C₂H₄ and CO on copper before and after poisoning with mercury. Broken curves: before poisoning. Solid curves: after poisoning. Weight of copper catalyst: 117.0 g. Volume of dead space: 58.50 cc.

the research as a whole. Rather the result was interpreted to mean that those active centers on the catalyst surface which could hold hydrogen molecules were also among those which could hold ethylene molecules, so that any hydrogen adsorbed from a mixture of the two simply displaced an equivalent amount of ethylene from the surface, one molecule of hydrogen replacing one of ethylene. The writer would have been inclined

to predict from this that the mercury would have decreased the adsorptions of the two gases by like amounts, whereas it actually decreases that of hydrogen about twice as much as that of ethylene. It would seem that de-activation of the active centers could proceed in steps, so that while a given active center was completely prevented from adsorbing molecules of hydrogen, it could still adsorb ethylene strongly. Carbon monoxide, which is the most strongly adsorbed of the three, is also most affected by the mercury, its adsorption being decreased about three times as much as that of ethylene. The fact that the decrease for ethylene is both absolutely and relatively the least of the three may be connected with its relative ease of condensation.

It may be mentioned that the decreases in adsorptive capacity were accompanied by a decrease in catalytic activity toward ethylene-hydrogen combination in the ratio of more than 200:1. It is only at very low pressures that the decreases in adsorption approach this ratio. This would seem to be conclusive evidence that the strongest adsorbing centers are responsible for the main part of the catalytic activity of the preparation.

Effect of De-activation by Heat Treatment

In the course of the experiments on the catalytic combination of ethylene and hydrogen, the effect on both catalytic activity and adsorptive capacity of partially de-activating a copper catalyst by heating it to 450° in a vacuum was determined.⁵ As this gave results which differ somewhat from those obtained by de-activation with mercury, they are also included.

The results of measurements of adsorption of ethylene and hydrogen before and after heating the copper adsorbent to 450° are shown graphically in Fig. 3. It will be seen that the effect of de-activating this sample of copper by heating was in a general way similar to the effect of de-activating the other sample by poisoning it with mercury. The curves have been moved over toward the pressure axis to nearly parallel positions, at the higher pressures at least. The heating has, however, decreased the hy-

⁵ Interesting results on the effects of heating active copper to successively higher temperatures have been obtained in the course of this investigation. In the present instance, the catalyst had been prepared at 200°, and heated to 300° after reduction. It had not thereafter been taken above 200°. After the experiments on the active material so obtained had been carried out, the catalyst was heated first to 350° for an hour and then to 400° for 1/2 hour without a marked change in activity resulting. It was then heated to 450° for one hour after which it was found to have decreased in activity as will be shown. Further heating at 450° for 1/2 hour was without noticeable effect, however. Similar results were obtained with another catalyst which was eventually heated to 550° to produce a very inactive material. For each rise in temperature a noticeable decrease in activity occurred but further heating at the same temperature was without marked effect. There seems, therefore, to be a stable condition of the surface corresponding to the highest temperature to which it has been heated. All the heatings described above were carried out in a vacuum.

drogen adsorption relatively less than the poisoning and the ethylene adsorption relatively more. Thus, at one atmosphere the decrease in hydrogen adsorption amounts to 70%, while the decrease in ethylene adsorption amounts to 22%. These are to be compared with decreases of

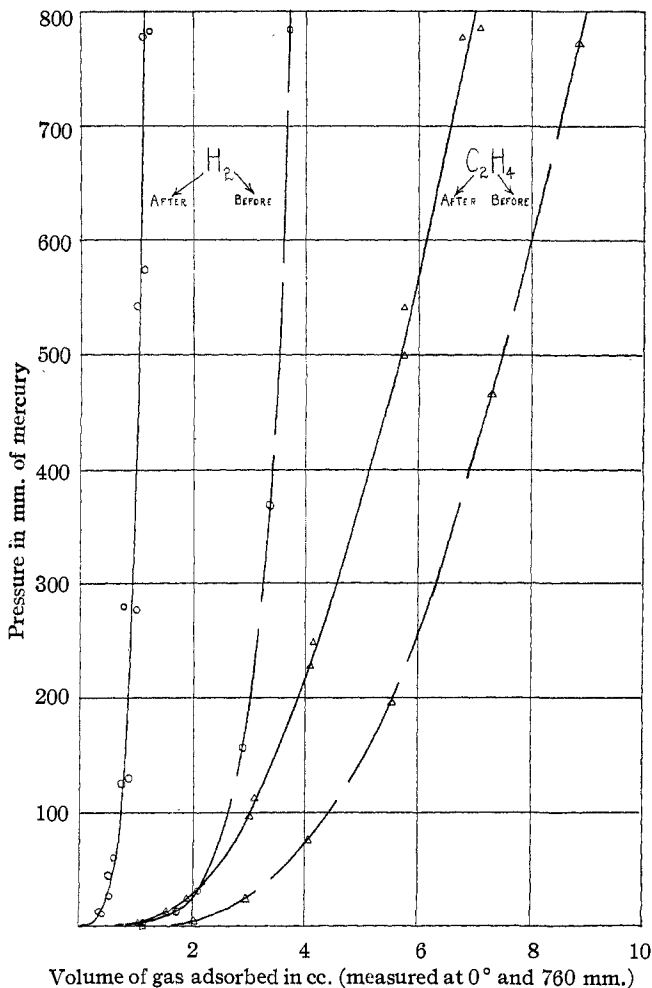


Fig. 3.—Adsorptions of H₂ and C₂H₄ on copper at 0° before and after de-activation by heating to 450° in a vacuum. Broken curves: before heating. Solid curves: after heating. Weight of copper catalyst: 94.9 g. Volume of dead space: 47.05 cc.

92% for hydrogen and 14% for ethylene caused by mercury poisoning. The absolute decreases at one atmosphere are 2.60 for hydrogen and 1.95 for ethylene. It will be seen that these figures are much more nearly of the same order than in the case of copper poisoned with mercury.

The decrease in catalytic activity in the ethylene-hydrogen combination accompanying these decreases in adsorption amounted to 85%. Just as in the case of the poisoning by mercury, one must go to very low pressures to find a corresponding decrease in adsorption, indicating again that it is the strong (low-pressure) adsorption which is mainly responsible for catalytic activity.

Seat of the Adsorptive Action of Active Copper

It is clear from the relative adsorptions of the different gases by active copper that we may at once conclude that ordinary condensation in capillaries is not a sufficient explanation of the results, although it may account for the adsorption of ethane and partially for that of ethylene. The action seems rather to be a specific one between the copper surface and the particular gas. It seems probable, however, that *any* copper surface will not do but that the surface must be in a special condition.⁶ From the evidence here presented, taken in conjunction with previous experience in the Princeton Laboratories, it would seem that an active copper surface is one which has scattered over it regions containing atoms whose fields are highly unsaturated. This follows from the fact that heating active copper to temperatures as low as 450° caused appreciable sintering besides decreasing the surface activity. Sintering at so low temperatures points to the pre-existence on the surface of atoms of high mobility and therefore in a state of unsaturation. The process of sintering is the process of saturation of these atoms and since the agency which causes the sintering also decreases the surface activity, it is reasonable to look upon these unsaturated atoms as the cause of this activity. One would look for atoms of this character in surfaces of high degree of curvature—in “peaks,” that is to say, on the copper surface—rather than in the “valleys,” or capillaries.

It seems probable that each of these “peaks” can attach more than one molecule of adsorbed gas. Otherwise it is difficult to see how combination of ethylene and hydrogen, for example, can take place as a result of adsorption. As already pointed out, since each hydrogen molecule that is adsorbed apparently displaces an ethylene molecule, the same point on the copper surface cannot hold a molecule of both. The two must, however, be in close juxtaposition if combination is to occur. This can be true only if a given peak possesses more than one possible point of attachment. The activity is, therefore, not due to isolated active atoms scattered over the surface but to groups of these atoms.

It has sometimes been assumed that catalysts owe their activity to the presence of an allotropic form. While this cannot be rated very highly as an explanation, still it appeared to be of interest to find whether active

⁶ See Taylor and Burns [THIS JOURNAL, 43, 1273 (1921)], Gauger and Taylor [*ibid.*, 45, 920 (1923)] and Benton, [*ibid.*, 45, 887, 900 (1923)] on the effect of method of preparation and of heat treatment on adsorptive capacity.

copper had the same crystalline structure as inactive. Accordingly, at the suggestion of Dr. A. W. Hull, the General Electric Research Laboratory was requested to make an X-ray analysis of a sample of active copper and very kindly consented to do so.⁷ The analysis proved that active copper has the same arrangement and spacing of atoms as ordinary massive copper, thus disposing of the assumption of a different allotropic form. This result also indicates that amorphous metal does not exist in any quantity on the surface. The discovery by Scheerer⁸ that metals preserve their characteristic crystalline arrangement and spacing of atoms even when in the colloidal state would render the existence of amorphous copper in the material used still more doubtful.

The peculiar appearance of active copper (it usually has a dull, reddish-brown surface) may be laid to its fine state of subdivision rather than to the presence of another form. Platinum black and precipitated silver behave similarly. Wood⁹ has suggested that the phenomenon is probably due to the "trapping" of the incident light in the pores of the substance by multiple reflection and consequent abnormally large adsorption.¹⁰

Apparent Density of the Copper Adsorbent

As a check on the determination of the dead space with helium on one sample of copper, determinations were also carried out by filling the exhausted bulb with water after the experiments were concluded. The value obtained with helium was 47.05 and with water was 47.13 after correction had been made for the volumes of the connecting tubes. The volume of the empty bulb was also determined and was found to be 58.00 cc., after applying the above correction. From these data the apparent density of the copper can be calculated. The average of the two values for the dead space, 47.09 cc., will be used.

	Vol. cc.	
Empty bulb.....	58.00	Wt. of copper = 94.925 g.
Dead space.....	$\frac{47.09}{10.91}$	Dens. of copper = $\frac{\text{wt.}}{\text{vol.}} = \frac{94.93}{10.91} = 8.70$
Copper.....	10.91	Dens. of massive copper ¹¹ = 8.935

⁷ This request was made by Dr. Arthur F. Benton who prepared the sample and sent it in for investigation.

⁸ Scheerer, Appendix to Zsigmondy's "Kolloidchemie," 4th Edition, 1922, p. 387.

⁹ Wood, "Physical Optics," Macmillan Co., 1921, p. 449.

¹⁰ A sample of active copper recently prepared in the writer's laboratory has the characteristic appearance of ordinary copper and yet possesses high activity both as a catalyst and as an adsorbent with this exception, namely, that the adsorption of ethylene is almost the same as that of hydrogen instead of being two or three times as great. Accepting Wood's explanation, the appearance of this sample indicates that it is non-porous. The absence of large adsorption of ethylene at higher pressures is a strong indication that such adsorption is due to capillary condensation.

¹¹ Landolt-Börnstein "Tabellen," Julius Springer, 1905, p. 226.

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-

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).