

reaction in the vapor phase. It has been found that the action is too energetic in some cases, but the possible variations in physical properties and in constituents present many possibilities, as is illustrated by the varying degrees of activity toward carbon monoxide observed in the various mixtures during the present investigation. Thus the degree of catalytic activity may be adapted and controlled to suit the conditions of each oxidation reaction.

Summary.

1. The decomposition temperature of silver oxide when simultaneously precipitated with calcium hydroxide is considerably lower than that of silver oxide alone.
2. A number of catalysts have been prepared which cause rapid and complete oxidation, at ordinary temperatures, of carbon monoxide in any concentration at which sufficient oxygen is present.
3. The essential constituent of this class of catalysts is specially prepared manganese dioxide, upon which is precipitated the oxide of silver or copper or both.
4. The silver or copper is best precipitated as the carbonate, and subsequently hydrolyzed to the oxide.
5. The presence of water vapor limits the life of these catalysts.
6. The application of this class of catalysts to a number of oxidation reactions is suggested.

In conclusion the authors desire to pay full tribute to Professor Frazer, to whom principally the success of this investigation is due, whose resource and pertinacity were a source of inspiration to those associated with him.

BALTIMORE, MARYLAND.

[CONTRIBUTION FROM THE CHEMICAL WARFARE SERVICE.¹]

THE CATALYTIC OXIDATION OF CARBON MONOXIDE AT ORDINARY TEMPERATURES.

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Received March 2, 1921.

The experimental work upon which this paper is based was done by the authors and their associates largely for the purpose of developing a suitable absorbent for carbon monoxide for use in gas masks,² and, because of the importance of obtaining production on a large scale without delay, it was not possible to investigate the scientific aspects of the problem as thoroughly as could be desired. An endeavor has been made in the preparation of the present paper to choose, from the large mass of data obtained,

¹ Published with the permission of General Amos A. Fries, Chief of the Chemical Warfare Service.

² An historical review of the investigations connected with the problem of the carbon monoxide mask giving due credit to the various persons concerned has been published by A. B. Lamb, W. C. Bray and J. C. W. Frazer in the *J. Ind. Eng. Chem.*, **12**, 213 (1920).

such typical data as are of scientific interest, and to present them for the use of other investigators in this field.

It is well known that, in spite of the large decrease in free energy in the oxidation of carbon monoxide by atmospheric oxygen, the rate of this reaction at room temperature is entirely negligible in the absence of catalysts. The activity of platinum and palladium blacks in catalyzing this reaction has long been recognized, but no examples of active catalysts containing only the more common metals were found in the literature at the time the present investigation was begun. The work of Wright and Luff³ on the minimum temperature of reaction of carbon monoxide with various metallic oxides had indicated the possibility of preparing oxides of sufficient activity⁴ for use as oxidizing agents in carbon monoxide masks, although these investigators did not conduct their experiments in such a way as to show whether or not the oxidation would be catalytic in the presence of excess of oxygen.

The present investigation was undertaken in an endeavor, by suitable variation of the chemical composition and physical properties of mixtures of metallic oxides, to prepare a solid substance which would oxidize dilute carbon monoxide—air mixtures with reasonable completeness at ordinary temperatures and fairly high rates of flow. These properties are of course more essential in a practical absorbent than is catalytic activity. Because of the desirability of the latter, however, the choice of materials for experimentation was based both on the suggestions obtained from the work of Wright and Luff and on the chemical theory of catalysis. According to this theory the catalyst actually takes part in the reaction, oxidizing the carbon monoxide and being itself reoxidized by the oxygen of the air. In order that this may take place it is necessary that the oxide be readily reduced and also that in its lower state of oxidation it be readily oxidized. Suitable couples of higher and lower oxide or oxide and metal are more likely to be found where more than one oxide of the metal is known than where the metal is readily oxidized to a single oxide. By the application of these ideas, it was found possible to prepare oxide mixtures (called for convenience Hopcalite or HC⁵), which catalyze the oxidation of dilute carbon monoxide—air mixtures at ordinary temperatures⁶ for

³ C. R. A. Wright and A. P. Luff, *J. Chem. Soc.*, **33**, 1, 504 (1878); cf. Fay, Sutherland and Lane, *Polytech. Eng.*, **10**, 72 (1910).

⁴ Lamb, Bray and Frazer, *Ref. 2*, p. 214.

⁵ J. C. W. Frazer and C. C. Scallione, U. S. pat. 1,345,323, June 29, 1920. *C. A.*, **14**, 2533 (1920).

⁶ Rideal and Taylor (*Analyst*, **44**, 89–94 (1919), *C. A.*, **13**, 1169 (1919)) have applied metallic oxides to the preferential oxidation of carbon monoxide in hydrogen, but their catalysts apparently are not sufficiently active to oxidize carbon monoxide at room temperature. Cf. Harger and Terrey, *Brit. Pat.* 127,609, Apr. 28, 1917. *J. Soc. Chem. Ind.*, **38**, 577A (1919).

an indefinite length of time when protected from moisture, as by a layer of calcium chloride in the canister.

General Description of the Catalysts.

An absorbent, to be suitable for use in gas-masks, must have a very high activity in proportion to its volume.⁴ Since, in heterogeneous catalysis, the amount of reaction that a catalyst is able to bring about is a function of the surface exposed, it was important to prepare the catalysts in a form exposing the maximum surface, and this was accomplished by preparing the oxide mixtures in the form of porous granules. The use of ignited oxides was not satisfactory because of their low activity at ordinary temperatures. Precipitated oxides were found to be more active, but granules prepared by simple drying and crushing of the filter cake were often lacking in mechanical strength; and no binders were found that did not materially reduce the activity of the resulting product. It was found, however, that fairly hard granules could be obtained by careful control of the conditions of precipitation, and that the hardness could be further increased by submitting the filtered precipitate to high pressure in a hydraulic press before drying.

Among the various oxides and mixtures investigated there were two mixtures which were particularly active, and it was these which were studied in most detail. The first will be referred to as the 4-component mixture (or Hopcalite I) and consisted of approximately 50% MnO_2 , 30% CuO , 15% Co_2O_3 and 5% Ag_2O . About 7,300 kg. of this mixture was produced on the large scale and used to fill about 40,000 canisters.⁷ The second mixture, referred to as the 2-component mixture, consisted ordinarily of 60% MnO_2 and 40% CuO , and, although somewhat cheaper, was developed too late for use on the large scale.

For use in gas masks, the granules were screened between 8- and 14-mesh screens, as this range of sizes gave a suitable balance between excessive pressure drops from fine granules on the one hand, and poor efficiencies due to channeling and mechanical leakage with thin layers of comparatively coarse granules on the other. The color of the granules of either mixture is a brownish black, and most samples are abraded somewhat more readily than the army soda-lime. An investigation made by G. A. Hulett of the porosity of a sample of 4-component mixture, 14-16 mesh, gave the results indicated below. The apparent density of the granules was 0.501 g. per cc. The true density of the solids was determined from the actual volume displaced, after evacuation under water to displace the air in the capillaries by water, and was found to be 5.65 g. per cc. The granules were then centrifuged to remove the excess water but leave that filling the capillaries. This latter was determined from the

⁷ Lamb, Bray and Frazer, Ref. 2, p. 220.

increase over the original dry weight, and amounted to 88 cc. per 100 g. This is equivalent to 8.8 cc. of solids, 44.2 cc. of capillary voids and 47 cc. of gross voids per 100 cc. of granules. This is a high degree of porosity⁸ and results in the catalysts being excellent absorbents for organic compounds of high molecular weight such as some of the war "gases."

Factors Influencing Activity.—The factors influencing the activity will be discussed in detail in connection with the preparation of the individual oxides, but it may be said that in general the activity of the mixtures is dependent upon the preparation of the individual oxides in a high state of oxidation and a suitable physical condition. The complexity of the problem of determining the effects of the various factors may be judged from the number of variables which must be considered. The more important of these are as follows: the choice of the constituents of mixtures of oxides and the methods of preparation of the individual oxides; the completeness of washing of the precipitates; the methods of mixing and filtration; the kneading and high-pressure filtration or other treatment of the wet cake; the conditions of drying and final moisture content; and the size of granules and method of utilization of fines. The activity is also dependent upon the conditions of test, such as the temperature, moisture content, concentration and rate of flow of the gas.

Methods Used in Testing the Catalysts.—The activity of the catalysts at room temperature was determined by the use of apparatus of the same general design as that used in testing other absorbent materials for use in gas masks. The glass tube containing the sample had a cross sectional area of about 1.5 sq. cm. and the normal depth of layer used was 5 cm. Free radiation was permitted from the tube and most of the tests were made with a room temperature of 25°. The carbon monoxide was prepared either by the action of sulfuric acid on formic acid or by the reduction of carbon dioxide by charcoal in a tube furnace. The standard rate of flow of the carbon monoxide—air mixture through the absorbent was 500 cc. per minute per sq. cm. of gross area, which, with a depth of layer of 5 cm. is equivalent to a space velocity of 6000 cc. of gas mixture per hour per cc. of catalyst. Most of the tests were made using a 1% mixture although some were made with 0.15% or 0.25% to determine whether the reaction would start properly with such dilute gas. The influent gas was analyzed occasionally and the effluent gas continuously by means of the Lamb and Larson calorimetric device⁹ which was found very convenient for the purpose. The device was calibrated frequently by comparison with analyses by the iodine pentoxide method.

⁸ For data on the porosity of charcoal, cf. H. E. Cude and G. A. Hulett, *THIS JOURNAL*, **42**, 391–401 (1920) and H. H. Lowry and G. A. Hulett, *ibid.*, **42**, 1393–1408 (1920).

⁹ A. B. Lamb and A. T. Larson, *THIS JOURNAL*, **41**, 1908 (1919).

For the tests with dry gas, the mixture was passed through two bead towers, into which conc. sulfuric acid dripped. For the tests with humidity another pair of towers was used and dil. sulfuric acid of the proper concentration to give the required vapor pressure of water. The activity specifications for the material prepared on the large scale have been already recorded.⁷

The apparent density of the granules was determined from the weight of 50 cc. measured in a special tube which permitted a standard degree of packing to be obtained. The hardness or resistance to abrasion the granules was determined by a method similar to that used for soda-lime. This consisted in shaking a weighed amount of the granules with steel balls in a pan on a Rotap machine for a definite length of time, removing the balls and weighing the granules retained on a 20-mesh screen. The percentage retained was called the hardness number. The time of shaking was chosen so as to give numbers between 50 and 80 for the majority of samples, as the results were more reproducible within this range. The values so obtained are only relative and cannot be compared directly with those for the somewhat harder army soda-lime where the standard time of shaking was longer.

Standard Methods of Preparation of the Oxides and Mixtures.—As a guide to those who may wish to prepare these catalysts for experimental purposes, the methods used in their preparation on the small scale will be given in detail. On the large scale the methods were essentially the same except in the case of the manganese dioxide. With this oxide it was difficult to reproduce small-scale conditions, and some variations were therefore necessary in adapting the process to large-scale production. The methods used in the preparation of the 4-component mixture will be described first.

Preparation of Manganese Dioxide.—One hundred and fifty g. of finely ground anhydrous manganese sulfate is mixed rapidly with 142 g. of water in a container arranged for cooling and thorough mechanical agitation. Without further delay 675 g. of 93% sulfuric acid is added with constant agitation. This produces a fine suspension of manganese sulfate in about 77% sulfuric acid. As soon as the temperature falls to 50°, 150 g. of potassium permanganate is added in small portions at a time in the form of a coarse powder. The addition should take 15 to 20 minutes and the temperature should not rise above 75°. After about 10 minutes more at 60° the reaction is practically complete and the mixture is poured in a fine stream into about 25 liters of water with thorough agitation, and washed by decantation until free of sulfates. Yield, 100 to 125 g.

On the large scale the chief difficulty experienced was in obtaining proper temperature control due to the large amount of heat given off by the reaction and the high rate at which it is given off when the reaction once

starts. This difficulty was overcome by the use of steam in the cooling coil for the first three minutes in order to give a local high temperature and insure the reaction starting before the concentration of permanganate was so high as to cause excessive temperatures and foaming when the reaction finally started. The precipitate was washed by decantation, which with a 230 kg. lot in a 38-cu. meter tank required 8 to 9 washings.

Preparation of Copper Oxide.—Ninety-five g. of copper sulfate pentahydrate is dissolved in 200 cc. of hot water and heated to the boiling point. Thirty-four g. (actual total alkalinity) of sodium hydroxide is used in the form of a lye of about 1.35 sp. gr. The hot copper sulfate solution is added to the alkali with agitation and uncontrolled increase in temperature, the final temperature being usually 60 to 70°. After thorough stirring, the mixture is diluted to a suitable volume for washing and washed by decantation until the sulfates are practically all removed. Yield, about 30 g.

Preparation of Cobaltic Oxide.—Fifty-one g. of cobalt sulfate heptahydrate is dissolved in 200 cc. of cold water. This solution is added to 25 g. of sodium hydroxide as lye of about 1.35 sp. gr., and 8.6 g. of sodium hypochlorite (actual, by titration) is then added in the form of a 10% solution with constant agitation. After stirring for about 5 minutes the mixture is diluted and washed until practically free from chlorides. Yield, about 15 g.

Mixing, and Precipitation of Silver Oxide.—After thorough washing, the manganese dioxide, copper oxide and cobaltic oxide are mixed and the silver oxide precipitated in the presence of the mixture. Two and a half g. of sodium hydroxide (free from chlorides) is dissolved in a small quantity of water and added to the suspension, and then 7.4 g. of silver nitrate dissolved in about 50 cc. of water, is added with thorough agitation. The silver nitrate is equivalent to about 5 g. of Ag_2O . After the mixed precipitate is washed practically free from dissolved salts, the subsequent treatment is essentially the same as that of the 2-component mixture, which will be described below.

Preparation of the Two-component Mixture.—The manganese dioxide for use in the 2-component mixture is prepared in the same way as that used in the 4-component mixture. The copper is precipitated as the basic carbonate rather than the hydrated oxide and the precipitation is preferably carried out in the presence of the precipitated and partially washed manganese dioxide.

Preparation of Basic Copper Carbonate.—Ninety-five g. of copper sulfate pentahydrate and 55 g. of anhydrous sodium carbonate are each dissolved in 200 cc. of hot water, the soda solution added to the suspension of manganese dioxide and the copper sulfate solution added to the mixture

with thorough agitation. After a few minutes the mixture is diluted and washed by decantation until practically free from sulfates. The copper sulfate is equivalent to about 30 g. of CuO .

Filtration and Drying of the Precipitates.—In the case of either mixture the washing is completed, wet-ground fines added if desired and the precipitate filtered in a filter press or on a Büchner funnel. The cake is kneaded, on the large scale mechanically for about 8 minutes, and submitted to a pressure of 4000 to 6000 lbs. per sq. in. between felt pads or camels'-hair cloths to permit the escape of the water. The cakes are dried at about 50° , crushed, screened and the granules redried for 4 hours at 200° , and preserved in sealed containers.

The Variation of the Activity of the Catalysts with the Method of Precipitation of the Oxides.

Since the oxides prepared by high temperature reactions, as by oxidation of metals or ignition of nitrates, were found to have a much lower activity at ordinary temperatures than those prepared by precipitation, the latter methods of preparation were those most extensively studied. It was found to be desirable in all cases to carry out the precipitations in such a way as to obtain a very finely divided precipitate; thus in precipitating metallic hydroxides concentrated solutions of the reagents were used. Reasonably complete washing is very essential, probably because of the tendency of the soluble salts to collect at the surface of the lumps by capillarity and so decrease the available surface. Of course, in the case of mixtures containing silver oxide, chlorides are particularly undesirable as silver chloride is inert as an oxidation catalyst.

The manganese dioxide is the chief component of both mixtures and hence has a very considerable influence on the activity and hardness. The preparation of it in a finely divided form with a high oxygen content, that is, with a minimum content of lower oxides, is more complicated than that of the other oxides and wider variations in quality were observed. The activity of the various samples was ordinarily tested by making them up into one of the standard mixtures with the other oxides of known activity and testing the resulting mixture with carbon monoxide at room temperature. In some cases, however, they were tested alone in an apparatus in which the temperature of the granules and gas stream could be raised and the temperature determined at which the sample oxidized a carbon monoxide—air mixture with a definite efficiency.

The oxidation of manganese sulfate suspended in sulfuric acid was the method investigated in most detail, since it appeared to lend itself best to large-scale operation, although other methods were tried with more or less success. The simple decomposition of potassium permanganate in conc. sulfuric acid gives a very active product but this procedure is not entirely unattended by risk, for dust particles or other organic matter are oxidized rather violently by the permanganic acid with evolution of

clouds of brown fumes. The product obtained by this reaction is usually darker brown than by the standard method and in the 2-component mixture it dries to a harder granule which is a little more active at low temperatures. The reduction of potassium permanganate in neutral solution by organic compounds such as methyl alcohol gives a fairly active product but at a higher cost than a process obtaining part of the manganese from manganous salts. Processes involving the oxidation of manganous sulfate by potassium permanganate in aqueous solution were uniformly unsatisfactory, the resulting material being soft and practically inactive. This is probably due to the formation of lower oxides and manganites rather than a manganese dioxide free from alkali salts.

In the standard method the reaction is complicated by the decomposition of part of the permanganic acid with evolution of oxygen. The manganese dioxide is not all present as such in the acid mixture but some is present as manganese disulfate, $\text{Mn}(\text{SO}_4)_2$, which is hydrolyzed on pouring into water. The material prepared by this method is actually a mixture of oxides and the analysis corresponds with about $\text{MnO}_{1.85}$. To a certain extent the available oxygen content is a measure of the activity, but the physical state must also be considered. Since the manganous sulfate is largely suspended in the acid rather than dissolved, it must be finely ground, as otherwise its utilization is very incomplete, only the outside of the particles being oxidized. But the utilization is never entirely complete and the reaction should therefore be carried far enough in the acid mixture to use practically all of the permanganate, to prevent the remainder from reacting on dilution to produce oxides of manganese which are soft and inactive and which seem to have some tendency to coat over and spoil otherwise good material. In the choice of the temperature for the reaction, variations in activity, hardness and yield must be considered. At high temperatures the decomposition of the permanganic acid takes precedence over the oxidation reaction with the consequence that the utilization of the manganese sulfate is very poor, and at temperatures above about 85° the available oxygen content of the product begins to fall off with corresponding decrease in activity. At temperatures below about 55° it is difficult to obtain a complete utilization of the permanganate and the product is generally very soft. The temperatures called for in the directions are those which experimentation has indicated are most suitable for preparing a hard active product. The low temperature at the beginning permits the building up of a high concentration of permanganic acid, and by proper temperature control this is kept in considerable excess throughout the course of the reaction. This is the condition which tends towards the formation of large amounts of manganese disulfate and higher oxides and reduces the formation of lower oxides to a minimum. After the permanganate is all added, the temperature is held at about 60°

until the permanganate is practically all used up, which usually requires 10 to 15 minutes. Too long a time is to be avoided as there is a tendency for the manganese sulfate on the inside of the lumps to react with the higher oxides or manganese disulfate giving lower oxides on dilution. A reaction of this type is shown by the mixture becoming thick and granular on standing and the color changing from a dark brown to a dirty purple. The method of dilution is quite important as it has a great effect on the hardness of the resulting material. In order to obtain a high degree of dispersion of the precipitate, the hydrolysis of the manganese disulfate should take place rapidly. This is accomplished by having the acid mixture enter a large amount of water in fine streams and with adequate stirring.

The methods of precipitation of copper oxide were studied largely in connection with the preparation of an absorbent for arsine although in the later work on carbon monoxide the copper oxide samples were tested by making them up into mixtures as in the case of the other oxides. More care is necessary to prepare a copper oxide that will oxidize arsine completely at room temperature than is necessary in preparing copper oxide for use in the 4-component mixture, due probably to the fact that the physical texture of the mixture is largely a composite of that of the components while with a single oxide such equalizing factors are absent. The method used in the preparation was to mix rather concentrated solutions of sodium hydroxide and copper sulfate, boil for various lengths of time, and dilute, wash and filter. In general it was found that the samples of copper oxide most active as oxidizing agents for arsine were those consisting of a rather soft porous granule. The hardness could be controlled by the conditions of acidity or alkalinity at the end of the precipitation. A precipitation with considerable excess alkali gave a precipitate which was slow in settling and hard to filter, and which dried down to a hard dense, black mass with low activity. The sodium hydroxide used contained about 4% of sodium carbonate and with insufficient amounts of alkali, carbon dioxide was evolved as the last of the copper sulfate solution was added. Under these conditions the precipitate was brownish-black with a green tinge. Such samples were active but rather soft for a satisfactory granule. The optimum conditions for an active yet fairly firm granule were found between these two extremes. By carefully controlling the amount of sodium hydroxide or by using an excess and then partially neutralizing with sulfuric acid, these conditions were realized. The correspondence between physical properties and the alkalinity of the solution is that which would be expected from the tendency of the precipitate to coagulate in acid solution and redisperse in alkaline. The low activity of the samples prepared with a large excess of alkali is probably to be attributed to a reduced porosity in the very dense granules. The catalytic oxidation of arsine affords a good example of the action of promoters, for it was

found that soaking the granules in a solution of $\frac{1}{2}$ % of their weight of silver nitrate and drying materially increased the activity of poor samples. The life of catalysts for the oxidation of arsine at low temperatures is of course limited by the deposition of metallic arsenic or oxides.

Since the hardness of the copper oxide was more readily controlled than that of the manganese dioxide, it was usual, in order to obtain the maximum hardness of the 4-component mixture consistent with high activity, to prepare a harder copper oxide than if it were to be used alone. For this reason an excess of alkali was used and the partial neutralization omitted in the standard procedure for preparing the 4-component mixture.

The precipitation of basic copper carbonate by the addition of copper sulfate solution to sodium carbonate solution results in a material which is very soft when dried and partially converted into the oxide by heating. Judging from the activity of basic copper salts in the oxidation of arsine, it was thought that an increased activity might be obtained on substituting such basic copper carbonates for the ordinary hydrated copper oxide in the 4-component mixture, but this desired effect was not realized in the experiments performed. This was probably due to the formation of silver carbonate in place of part of the silver oxide, since some preliminary experiments indicated that silver carbonate is less active than silver oxide. That the basic copper carbonate is more active than the oxide, at least in mixtures, is indicated by the fact that the 2-component mixture made up with the latter has only a slight activity in comparison with the standard 2-component mixture. This latter mixture tends to give an excessively soft granule, but this can be overcome by pressure.

The experiments of Wright and Luff had shown that cobaltic oxide is remarkably active in the oxidation of carbon monoxide at low temperatures. Hüttner¹⁰ and others had shown that cobalt oxide, prepared under certain conditions, contains more oxygen than corresponds to the formula Co_2O_3 , due to the presence in the mixture of a cobalt peroxide or dioxide. It was thought that such cobalt oxide mixtures would probably be more active than those of lower oxygen content, and this was found to be the case, properly prepared samples oxidizing carbon monoxide—air mixtures catalytically at room temperatures. Hüttner used sodium hypochlorite or alkaline solutions of iodine, and in the latter case obtained a higher ratio of oxygen to cobalt. Preliminary experiments did not indicate any advantage in the use of iodine, and most of the samples were made using hypochlorite as the oxidizing agent.

Because of the effect of cobalt oxide on hypochlorite solutions, catalyzing their decomposition with evolution of oxygen, it is necessary to use an excess of 25 to 50 % of hypochlorite to obtain a high ratio of oxygen to cobalt. The effect of temperature of precipitation on the oxygen content

¹⁰ Hüttner, *Z. anorg. Chem.*, **27**, 81 (1901).

of the precipitate is slight provided sufficient hypochlorite is used to offset the more rapid decomposition at the higher temperatures. When a sufficient excess of hypochlorite and of hydroxide was used and the precipitate thoroughly washed no difficulty was experienced in obtaining a comparatively soft, porous, active granule; in fact, the samples were frequently so soft as to be difficult to handle in the tests. The only samples which were hard and lacking in activity were those prepared with insufficient hypochlorite, and the poor activity of these samples was probably due rather to the low oxygen content than to the low adsorptive properties.

While in many cases the activity of a mixture of catalysts is merely a composite of the activities of the several components, it has often been found that mixtures of catalysts are more active than any of their components. The complete explanation of this co-activation of catalysts is still lacking, but the results of the present investigation indicate that the chemical nature of the components and the physical properties of the mixture are very important factors. The use of mixed catalysts was found to be quite essential in obtaining the requisite activity towards carbon monoxide at low temperatures. Of the common oxides tried, none acted alone as an active catalyst with the exception of cobaltic oxide. The latter, however, is itself a mixture of oxides, since, as prepared, the ratio of oxygen to cobalt is about 1.6:1.

A comparison of the activity of the 2-component mixture and its components is given in Table I. The tests were made with a 1% carbon monoxide—air mixture at a space velocity of 6000 cc. of mixture per hour per cc. of catalyst. The oxides were prepared under suitable conditions for obtaining active catalysts and were in the form of 8- to 14-mesh granules in a layer 5 cm. deep as previously described. The temperatures given are those of the entering gas, and the exterior of the catalyst tube was maintained at practically the same temperature. The efficiencies are the percentages of gas oxidized after the conditions became constant.

TABLE I.

Comparison of the activities of the 2-component mixture with Those of Some Single Oxides.

Oxide.	Dry Gas.		Humidity 14mm.	
	Temperature. °C.	Efficiency. %	Temperature. °C.	Efficiency. %
CuO	102	97	102	18
MnO ₂	100	96	100	17
Co ₂ O ₃	0	100	78	100
Fe ₂ O ₃	100	40
MnO ₂ + CuO	-10	100	76	100

The last two columns illustrate the characteristic effect of humidity which will be discussed later. The increased activity of the 2-component mixture over the activity of the copper oxide and manganese dioxide

alone is very marked. The co-activation is seen to have lowered, by more than 100° , the temperature required in the case of dry gas for 100 % efficiency. As has been stated, the 2- and 4-component mixtures were the most satisfactory from the standpoint both of activity and cost, but, of the large number of mixtures prepared, there were a few others that were fairly active. It was found that manganese dioxide and silver oxide gave an active catalyst, but not materially better than the standard 2-component mixture. A 3-component mixture consisting of 50 % manganese dioxide, 30 % cupric oxide and 20 % cobaltic oxide was found to be active towards dry carbon monoxide—air mixtures but it had much less tolerance towards humidity than the standard 4-component mixture. Some samples of nickelic oxide were prepared in the same way as the cobaltic oxide and substituted for the latter in the 4-component mixture. These mixtures did not operate catalytically towards dry gas for an indefinite length of time at room temperature. The oxidation of the carbon monoxide was accompanied by gradual reduction of the catalyst and loss of activity unless the temperature was slightly elevated. Ferric oxide was found to be even less active than nickelic oxide in these mixtures.

The Effect of Kneading and Pressure upon the Activity and Hardness of the Catalysts.

After the oxides are precipitated, washed and mixed, or preferably in many cases precipitated in the presence of each other, subsequent treatment, with the exception of drying, has more effect on the hardness than on the activity. In cases where the catalyst is used under unfavorable conditions, for instance, with some moisture in the gas—air mixture or at low temperatures (as at -15°), the oxidation of the carbon monoxide takes place to a greater or less extent at the expense of the available oxygen of the catalyst itself, and is terminated by the exhaustion of the catalyst. The life of a given volume of the catalyst under these conditions is dependent, of course, upon the amount of available oxygen present, which in turn is dependent upon the density. A high density also is advantageous in that the heat of the reaction tends to give a higher temperature within the denser granules which favors the re-oxidation of the reduced catalyst and hinders the adsorption of moisture.

The effect of kneading and high-pressure filtration upon the hardness and density of the catalysts was studied in some detail because of its importance in the utilization of fines and in preparing a satisfactory granule from the 2-component mixture. Even after filtering the mixed precipitates at a pressure of 7 kg. per sq. cm. (100 lb. per sq. in.) and blowing the excess water out of the cake by compressed air, the moisture content of the material is still about 60 %, although part of this is water of hydration of the oxides. It was found that kneading broke up the structure of the

cake so that the mass became much more fluid, and additional water could be pressed out at the same pressure if desired. Even without the second pressing, the mass on drying had a greater density and hardness, if the kneading was not excessive. This is doubtless due to a breaking down of the lamellar structure of the cake as it is formed in the filter press, permitting a closer packing of the particles. The data obtained in one series of kneading experiments are presented in Table II. A considerable amount of cake was kneaded in a Werner and Pfleiderer kneading machine and small samples removed at the times indicated. Unfortunately the hardness was not determined in this series but it was found that in general the increase in hardness was somewhat less than the increase in apparent density and the maximum was reached sooner. With the type of kneading machine used, the maximum hardness was usually reached in 6 minutes and the maximum density in 9.

TABLE II.
Effect of Kneading.

Time of kneading. Min.	Apparent density.	Volume activity.	Weight activity.
0	0.57	32	56
1	0.59	37	63
3	0.64	53	83
5	0.66	55	83
7	0.72	65	90
9	0.75	67	89
11	0.72	64	88
14	0.67	54	81

The column headed "Volume activity" gives the number of minutes that the given volume of sample operated above 85% efficiency on 1% carbon monoxide—air containing 14 mm. of water vapor. The "Weight activity" is the volume activity divided by the apparent density, these values of course being only relative. All of these samples were catalytic for an indefinite time on dry gas. The effect of kneading on activity is largely indirect, in that the increased density permits the reaction to go on for a longer time when it is taking place at the expense of the oxygen of the catalyst itself. The occurrence of maxima in the apparent density and hardness curves is probably due to the inclusion of air bubbles in the more thoroughly kneaded samples. The fact that hand kneading gave uniformly better results than machine kneading points towards the same conclusion, for in hand kneading there is less opportunity for the inclusion of air, although the superiority of hand kneading may be due in part to the packing or settling action in comparison with the rubbing action of machine kneading.

The experimentation with regard to hydraulic pressing was concerned chiefly with the utilization of fines, as with the 4-component mixture

it is possible to prepare a reasonably firm granule without the use of hydraulic pressure, except when fines are added. With the 2-component mixture, however, hydraulic pressure is necessary in order to prepare a granule of satisfactory hardness. In order to utilize the fines formed in the crushing operation, they were ground wet in a ball mill to a fine slime and added to the original precipitate and the mixture filtered. If this cake were dried immediately the product would be much too soft for use in gas masks, but by subjecting the cake, after kneading, to high pressure between felt pads to permit the escape of the water, a product is obtained of hardness similar to that of the original material or better. The density is usually somewhat higher and the activity at least as good. The action of high pressure is largely to reduce shrinkage in drying to a minimum and so eliminate shrinkage cracks as far as possible. The results of a typical series of experiments with the 2-component mixture and varying proportions of wet ball-milled fines are presented in Table III. The material was all from a single set of precipitations. The cakes were kneaded for 7 minutes and pressed between felt pads, the pressure being raised gradually and held at the final value for about 5 minutes to permit the escape of the water. At the higher pressures the cake was reduced in thickness from 25 mm. to about 10 mm.

TABLE III.
Effect of High-pressure Filtration.

Fines. %.	Pressure. lbs./sq. in.	Hardness, %.	Apparent density.	Volume activity.	Weight activity.
50	80	20	0.55	32	58
50	1000	56	0.60	52	87
50	2000	60	0.62	50	81
50	4000	56	0.68	53	78
40	80	27	0.57	48	84
40	1000	76	0.61	52	85
40	2000	65	0.64	53	83
40	4000	78	0.69	53	80
40	6000	90	0.72	63	87
30	80	32	0.56	35	63
30	1000	64	0.62	50	81
30	2000	62	0.65	54	83
30	4000	62	0.69	55	80
30	6000	62	0.73	66	80

These figures show that the apparent density and volume activity increase quite regularly with the pressure applied to the cake. The hardness figures do not show so much regularity, but this is largely due to inherent errors in the hardness determination, which are particularly evident in this series because the method had not yet been thoroughly standardized. A hardness of 70 on this scale may be interpreted as quite

sufficient for gas-mask use. It is evident that the apparent density is not a satisfactory criterion of hardness when the mixtures contain fines. The content of fines may be increased above 50 %, in fact the use of wet ball-milled fines alone gave fairly satisfactory results, when thoroughly kneaded and pressed at high pressure.

The discussion of the effect of the degree of drying on the activity of the catalysts will be postponed until after the effect of the humidity of the gas mixture has been considered.

The Effect of the Conditions of Operation on the Activity of the Catalysts.

Under the conditions of operation used in the standard tube-tests with dry carbon monoxide—air mixtures at room temperature, that is, using a 5 cm. layer of 8- to 14-mesh granules and a rate of flow of 500 cc. of 1% gas per sq. cm. per minute, good samples of either the 2- or the 4-component mixture operate at efficiencies closely approaching 100 % for an indefinite length of time. Such samples also operate at high efficiency on more dilute mixtures as shown by tests with concentrations of 0.1% or less. The theoretical temperature rise under adiabatic conditions due to the heat of the reaction is about 100° for a 1% mixture. Because of this heat effect, little difficulty is experienced in obtaining a complete oxidation at higher concentrations even with rather poor samples, although with concentrations much above 5 % the temperature rise may be sufficient to impair the activity of the catalyst after cooling. With very high concentrations the catalyst may even sinter together and be entirely inactive when cold.

The activity of the catalysts at low temperatures is of course very important when they are to be used in gas masks in exposed locations. The effect of the temperature of the carbon monoxide—air mixture on the activity is masked somewhat by the heat of the reaction, but it can be determined readily by using dilute gas mixtures so that the heat effect is small. In general for each particular sample of catalyst and gas concentration there is a minimum temperature at which the catalyst operates catalytically at 100 % efficiency. Below this temperature the efficiency gradually falls off to a more or less constant value for each temperature but returns again to 100 % when the temperature is raised. Most of the tests were made with 0.5 % carbon monoxide and the catalyst was placed in a glass tube surrounded by a freezing mixture so that there was little opportunity for it to heat up by the heat of the reaction. It was found that the 2-component mixture operated better at low temperatures than the 4-component mixture although individual samples varied somewhat, especially when there were variations in the methods of pressing and drying. The samples prepared with high pressure were much better than those

filtered at comparatively low pressures and adequate drying was found to be quite essential. A typical sample of the 2-component mixture, when tested with 1% carbon monoxide at -15° , operated initially at high efficiency, but after a few minutes the efficiency began to fall and gradually decreased to about 35% where it remained in apparent equilibrium. When the temperature of the gas and catalyst tube was allowed to rise to 0° , the efficiency gradually rose to 100%. Similar experiments on manganese dioxide and copper oxide alone at higher temperatures indicated that under proper conditions this phenomenon is accompanied by reversible reduction of the catalyst, that is, the catalyst is partially reduced at the lower temperature and reoxidized at the higher. This reduction is different from that obtained by treating the catalyst at a high temperature with carbon monoxide or other reducing agents in the absence of an excess of oxygen for in this case the reduction is more complete and is usually accompanied by a change in structure. The activity cannot then be restored by re-oxidation with air.

The general effect of water vapor in the gas mixture is to diminish the activity of the catalysts so that higher temperatures are necessary for definite efficiencies than when operating with dry gas. Somewhat the same effect is brought about by a diminution of the oxygen content of the gas. While, in gas-mask use, the oxygen requirements of the man are so high that such effects do not enter under any conditions under which a man could live, they are of importance in connection with the application of the catalysts to the removal of carbon monoxide from hydrogen by preferential combustion and in other industrial applications. It was found that for an equilibrium efficiency of 100% with 28 mm. of water vapor, reducing the oxygen content of the gas to as low as 100% excess of that theoretically required for the combustion only necessitated an increase of temperature of about 10° over the temperature required with a carbon monoxide—air mixture containing the full oxygen content. It was also found that when operating with the 2-component mixture on a mixture containing 0.5% carbon monoxide, 0.5% oxygen and 55 mm. of water vapor at a space velocity of 6000 cc. of gas per cc. of catalyst per hour, 190 hours of continuous operation at 102° and an average efficiency of 93% did not result in any appreciable deterioration of the catalyst.

The humidity of the carbon monoxide—air mixture has a very marked effect on the activities of the various oxides and mixtures. The effect is best described as reversible poisoning, to distinguish it from the type of poisoning brought about by sulfur compounds and some of the war gases. While the 2-component and 4-component mixtures act catalytically for an indefinite length of time on dry gas mixtures at ordinary temperatures, with 1% gas mixtures half saturated with water vapor at room tempera-

ture the activity falls to 85% in about an hour and rapidly decreases from then on. If the mixture is changed from wet to dry at any time before the catalyst has stopped acting, the efficiency gradually returns to the original value of about 100% in the case of active samples. The rate at which the efficiency of the catalyst decreases is a function of the temperature at which the test is made and hence indirectly of the concentration of the gas, since the heat of the reaction raises the temperature of the catalyst. At temperatures somewhat above room temperature, the catalytic oxidation proceeds indefinitely even with gas mixtures of high humidity.

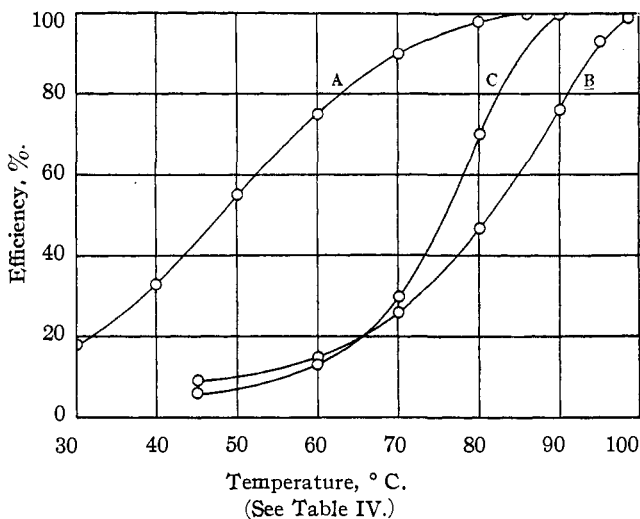


Fig. 1.

At intermediate temperatures and humidities, the activity does not fall to zero but only to a fairly definite value for any particular sample of catalyst. These efficiencies are approximately the same when approached from either side if sufficient time is allowed for conditions to become constant. The variation of these equilibrium efficiencies with the temperature is shown by the data of Table IV, which have been plotted in Fig. 1. In obtaining these results the catalyst was placed in a copper tube immersed in a water-bath which was maintained at the desired temperature, and the gas was preheated by passing through another tube immersed in the bath. The bath was held at each temperature long enough for constant efficiency to be obtained. While these results are of interest from the standpoint of the mechanism of the reaction, the equilibrium efficiencies at ordinary temperatures are so low for the usual humidity that the time necessary for the efficiency of the dried catalyst to fall to a definite value is of greater importance in connection with the application

TABLE IV.

Variation of Equilibrium Efficiencies with the Temperature.

Catalyst:	Curve A.	Curve B.	Curve C.		
Humidity.	4-component. 28 mm.	2-component. 55 mm.	2-component. 55 mm.		
Composition of gas, %.	CO 0.25 Air 99.75	CO 0.5 O ₂ 0.5 N ₂ 99.0	CO 1.0 O ₂ 1.0 N ₂ 98.0		
Temp. °C.	Effic. %.	Temp. °C.	Effic. %.	Temp. °C.	Effic. %.
40	33	45	9	45	6
50	55	60	15	60	13
60	75	70	26	70	30
70	90	80	47	80	70
80	98	90	76	90	100
87	100	95	93
..	...	98	99

of the catalysts to gas masks. It was found that this time was materially shorter at low concentrations where the heat effect of the reaction was small. This is shown in another way by the data of Table V, which represents the results of a series of experiments in which air at room temperature containing 4 mm. of water vapor was passed through a 5 cm. layer of the 2-component mixture at the rate of 500 cc. per sq. cm. per minute for a definite length of time and followed by 1% carbon monoxide also containing 4 mm. of water vapor.

TABLE V.

Time of humidification. (Min. of air flow.)	Life to 85% efficiency. (Min. of gas flow.)
0	236
30	128
45	74
60	4

Other experiments have shown that, when air of 4 mm. humidity is passed over the catalyst dried in the usual way, the moisture in the air is absorbed practically completely during the first hour. These results indicate that an absorption of water equivalent to about 3.6% of the weight of the catalyst is sufficient to reduce the efficiency to 85%. It is evident, therefore, that the dryer used in the canister must be quite effective in order to protect the catalyst from moisture.

The tests referred to hitherto were all made with the standard rate of flow of 500 cc. per sq. cm. of cross section per minute and with a depth of layer of 5 cm., that is, with a space velocity of 6000 cc. of gas per cc. of catalyst per hour. In the design of gas-mask canisters it is desirable to

reduce the resistance to the minimum consistent with efficient operation of the catalyst. The resistance is of course dependent upon the size of the granules and the area and depth of layer. As the size of granules is increased and the depth of layer decreased, there evidently must come a time when the oxidation is incomplete because the molecules of carbon monoxide do not all have an opportunity to come into contact with the catalyst. Since this effect is not due to insufficient activity of the catalyst itself, it is referred to as mechanical leakage. In order to determine approximately the conditions under which mechanical leakage begins to be appreciable, a series of experiments was performed with a constant space velocity of 7800 but with varying size of granules and depth of layer. The results of these experiments are presented in Table VI. The equilibrium efficiencies were rapidly attained and remained constant except for slight fluctuations. No mechanical leakage was encountered at this space velocity with layers 2 cm. or more thick and 10 to 14 mesh or finer.

TABLE VI.

Efficiencies with Various Sizes of Granules and Depths of Layer.

Rate of flow, cc. / sq. cm. / min.	Depth, cm.	2.	1.5.	1.
		260.	195.	130.
Mesh, 10-14		100%	99.0%	96.5%
Mesh, 14-20		100	99.8	99.7
Mesh, 20-28		100	100	99.5
Mesh, 28-35		100	100	99.8

The pressure drop at these rates of flow varied from 12 mm. of water for a 5cm. layer to about 0.2 mm. for a 1cm. layer of 10- to 14-mesh material. It is evident from these figures that the use of the catalyst in the form of granules gives a very satisfactory contact with the gas without at the same time introducing an excessive resistance to the flow.

The high degree of porosity of the catalysts and their consequent high absorptive power for many volatile substances has been mentioned. Many of these substances, particularly sulfur and halogen compounds, act as poisons and tend to prevent the catalytic oxidation of carbon monoxide. It might be thought that the sensitiveness of the catalysts to poisons would seriously interfere with their practical use in gas masks, but such is not the case for the catalyst may be protected readily from large concentrations of poisons by a layer of activated charcoal in the canister, while with small concentrations the poisoning is progressive, the first layers of the catalyst absorbing practically all of the poison leaving the rest of the catalyst available for the oxidation reaction.

The Effect of the Degree of Drying on the Activity of the Catalysts.

The usual method of drying was that indicated by preliminary experiments to give satisfactory results, namely drying the filter cake at about 120°, crushing to size and redrying at 200° for about 4 hours. Additional

experiments were made to test the effects of drying *in vacuo* or at higher temperatures. A fairly large sample of 2-component cake after hydraulic pressing was ground and bottled after thorough mixing to insure a uniform distribution of grains of slightly different moisture content. The loss of weight on drying was determined and the dried samples were tested with 1% carbon monoxide—air mixture containing 14 mm. of water vapor. The results are given in Table VII.

TABLE VII.
Effect of Degree of Drying.
Conditions of Drying.

Expt.	Temp. ° C.	Time. Hrs.	Pressure. Mm.	Loss in weight, %.	Life to 85% efficiency, Min.
16	100	3	12	37.0	41
17	400	5	12	47.3	51
20	120	15	Atm.	39.9	52
	200	5	Atm.		

The catalyst dried as in Expt. 17 did not lose more than 0.1% of water when heated to redness in a current of air in a quartz tube, and this small amount was probably absorbed from the air while the material was being placed in the tube. Analysis indicated that drying at 400° entailed a loss of available oxygen of 0.6% on the original wet weight. Allowing for this, the moisture content of the material after drying as in Expt. 20 is about 11.5%. Other experiments have shown that the moisture content may be as high as 14% without seriously decreasing the life of the catalyst on moist gas, and this is not increased much by more complete drying. These results are interesting in connection with the data of Table V, which showed that the moisture absorbed during the test with gas containing 4 mm. of water vapor was only about 3.6%, which is only a fraction of the water removed on complete drying, yet the completely dried samples have approximately the same life with moist gas as the incompletely dried ones. This indicates 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 the gas molecules and oxygen molecules, and does not re-hydrate the oxides to any considerable extent.

The properties of the 4-component mixture proved to be somewhat different, in that a sample after the usual drying at 200° contained only 4.5% of residual water. Tests with 1% gas containing 14 mm. of water vapor gave a life of 58 minutes to 85% efficiency for the sample after standard drying, but a life of only 25 minutes after complete dehydration at 400° and 12 mm. This is probably due to partial decomposition of the silver oxide under these conditions.

Application of the Catalysts.

While in the foregoing the activity of the catalysts has been discussed principally in connection with the oxidation of carbon monoxide, it has

been found that these catalysts are able to reduce materially the temperature required for the oxidation of a variety of gaseous reducing agents by atmospheric oxygen. For continued catalytic action it is necessary, however, that neither the reagents nor the products should poison the catalysts and that the temperature of operation should not be so high as to cause injury to the catalysts by sintering or loss of oxygen. Because of the possible industrial applications, some attempts were made to apply the catalysts to organic oxidations in the vapor phase, such as toluene to benzaldehyde and naphthalene to phthalic anhydride. It was found that with the 2-component mixture, the oxidations started at the comparatively low temperatures of 170° and 220° respectively, but that it was very difficult to prevent the reaction from going too far with the formation of carbon dioxide and water as the principal products. This was due largely to the difficulties inherent in controlling the temperature of operation. The heat evolved in such organic oxidations, particularly when the reaction goes to completion, is very considerable in amount and the proper dissipation of it is a serious problem. The factors such as high porosity and fineness of particles which give the catalysts their high activity are also the ones which render them poor conductors of heat and this makes temperature control by cooling the walls of the catalyst chamber very unsatisfactory. Since other methods of temperature control are inconvenient, it seems probable that the catalysts would have to be considerably modified in order to make them suitable for organic oxidations.

Summary.

A description is given of some active catalysts developed by the Chemical Warfare Service for use in gas-mask canisters as a protection against carbon monoxide. These catalysts are mixtures of metallic oxides, the two most satisfactory mixtures containing manganese dioxide and basic copper carbonate, and manganese dioxide, copper oxide, cobaltic oxide and silver oxide respectively. These mixtures oxidize carbon monoxide rapidly and completely at ordinary temperatures, and, when protected by a drying agent such as calcium chloride, are suitable for use in gas masks against the concentrations of carbon monoxide ordinarily met with except under conditions where an oxygen helmet is necessary because of the reduced oxygen content of the air. The factors influencing activity, such as the constituents of the mixtures, the conditions of precipitation, the mechanical treatment of the precipitate and the method of drying, are discussed and a description is given of the performance of the mixtures under various conditions of operation.

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