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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, JOHNS HOPKINS UNIVERSITY.]

**THE CATALYTIC OXIDATION OF CARBON MONOXIDE.<sup>1</sup>**

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**Introduction.**

This problem was a phase of the War Gas Investigations and was undertaken at this laboratory<sup>2</sup> early in May 1917, under the auspices of the U. S. Bureau of Mines, with the object of providing a mask ingredient which would afford protection against carbon monoxide when present in air. The desired application and the necessary specifications of such a material having been described<sup>3</sup> in detail, the present article presents, from the chemical standpoint, the most important features of the development of a suitable oxidizing catalyst.

**General Statement.**

The first work was done in making comparative tests of the materials described in the literature as capable of oxidizing carbon monoxide at room temperatures,<sup>4</sup> always with the object in view of ultimately making

<sup>1</sup> Published by permission of the Director of the Chemical Warfare Service.

<sup>2</sup> This investigation was directed by Professor J. C. W. Frazer, who is one of the authors of a recent general article, Lamb, Bray and Frazer, *J. Ind. and Eng. Chem.*, **12**, 213 (1920), concerning the treatment of this problem as a whole by various laboratories in cooperation with the Central Laboratory at Washington.

<sup>3</sup> Lamb, Bray and Frazer, Ref. 2.

<sup>4</sup> Cf. Gmelin-Kraut, "Handbuch d. anorganischen Chemie," on carbon monoxide.

the reaction catalytic. It was observed while doing this preliminary work that many of these substances when intimately mixed gave a material much more active than any one of its constituents. For example, while neither chromium trioxide,  $\text{CrO}_3$  nor yellow mercuric oxide oxidized carbon monoxide appreciably when a low concentration of this gas in air was passed through a tube containing these materials, a mixture of the oxides containing chromium trioxide, in excess of equivalent proportions was found to possess considerable oxidizing power and about 50% of the carbon monoxide was oxidized for a short period.

Again, silver oxide which oxidizes carbon monoxide only slowly at room temperatures, when mixed in various proportions with calcium hydroxide showed markedly greater activity, evidencing the increased activity of mixtures over that of single constituents. Other important factors, more or less self-evident, in the use of mixtures of two or more substances are the fineness of subdivision and intimate admixture of these substances, the resulting product being essentially a solid solution in certain cases. When a mixture of silver and calcium hydroxides was prepared by the simultaneous precipitation of the hydroxides from a water solution of the nitrates of these metals, and the precipitate washed and dried at 120–130° in a current of oxygen a material was obtained having marked activity. When dried in a current of air or oxygen the color of this mixture at times changed during the process of drying from a light brown to a slate color, a color change which indicates the decomposition of the silver oxide. On examination it was found that globules of metallic silver could be seen in the material. This decomposition was observed at 100° in the air and at 130° in oxygen, whereas the decomposition pressure of silver oxide is but 0.2 atmospheres at 130°. This notable increase in the decomposition pressure of silver oxide is being investigated further to determine whether the phenomenon is due to fineness of subdivision or to some other cause connected with the presence of calcium hydroxide, one effect of which may be to prevent the increase in size of the silver oxide particles.

The activity of these mixtures of silver oxide and calcium hydroxide was slightly increased by the addition of a small quantity of sodium hydroxide. The oxidation of the resulting material (about 80% for 20 minutes) was entirely due to the combined oxygen, as the amount of oxidation was never more than could be accounted for by the silver oxide present.

Manganese dioxide was ultimately found to be an essential constituent of the best catalysts, and here also the same general statements made above apply. Mixtures of manganese dioxide and silver or copper oxide were found to be much more active towards carbon monoxide than either of the oxides used separately. The addition of a third component, sodium hydroxide, was advantageous in the preliminary experiments on manganese dioxide. The action of these mixtures containing sodium hydroxide was

not catalytic. They functioned for only about 40 minutes under the testing conditions given below and the amount of oxidation was not greater than could be accounted for by the active oxygen contained in the material. The behavior of these mixtures is shown in Table I.

It was not until finely divided manganese dioxide was prepared, and special precautions, listed later, were used to secure the admixture therewith of other oxides, that the catalytic oxidation of carbon monoxide at room temperature was satisfactorily solved. The most satisfactory catalysts were obtained by using a mixture containing either silver oxide or copper oxide and manganese dioxide. Of these mixtures those containing silver oxide seemed to be more active than those containing copper oxide. Other oxides such as iron oxide may be tolerated in certain amounts in the final products, but such oxides seem to act more as inert diluents and decrease rather than increase the activity of the material. However, when catalysts are prepared by properly mixing manganese dioxide with both silver and copper oxides such catalysts may be quite as active as those containing either copper or silver oxide alone.

The conclusions reached from the preliminary work on manganese dioxide were, first, that the degree of subdivision was an extremely important factor in the activity of this material; and, second, that the activity is also greatly increased by properly incorporating with finely divided manganese dioxide, other metallic oxides such as copper and silver oxides.

A comparative study was then made of samples of manganese dioxide prepared by the following methods.

1. **Reduction of Potassium Permanganate by Methyl Alcohol.** (a)—When a warm solution was reduced, the manganese dioxide particles were comparatively coarse, settling rapidly, and the mixtures prepared from such materials were not very active (Table I (a)). When the reduction was brought about in a cold solution a more flocculent precipitate was obtained which settled more slowly than (a), and it will be seen by referring to Table I that the silver oxide mixtures were more active than similar mixtures made from samples (a).

The mixtures of silver oxide and manganese dioxide made from both (a) and (b) above were quite efficient in bringing about the oxidation of carbon monoxide for an hour or more and the oxygen consumed was greater than the available oxygen of the material, showing these samples to be partially catalytic. The active zone of the material at any time during the test could be immediately ascertained by the location of the warm portion of the tube. This zone moved along gradually as the efficiency of that portion dropped and finally passed to the bottom of the tube, when carbon monoxide could be detected in the effluent gas. Prior to this, however, the action was 100% efficient.

2. **The Frémy Method.**<sup>5</sup>—One hundred g. of finely ground potassium permanganate is added to 500 g. of conc. sulfuric acid in 150 cc. of water, cooled, carefully stirred, and allowed to stand, when the permanganic acid formed decomposes, giving off oxygen. Permanganic anhydride,  $Mn_2O_7$ , will sometimes separate as an oil which is extremely

<sup>5</sup> Frémy, *Compt. rend.*, **82**, 1213 (1876). We are indebted to W. A. Patrick for suggesting this method of preparation.

explosive. When all the permanganic acid is decomposed the manganese dioxide is washed in a large quantity of water by decantation until free from sulfates. At the final washing the precipitate approaches the colloidal condition and settles very slowly. The manganese dioxide still contains a small quantity of a potassium salt, which is evidently very strongly adsorbed. The oxide mixtures prepared from this grade of manganese dioxide were truly catalytic, and, when tested on dry gas, showed that a layer only about 1 cm. deep was entirely efficient in oxidizing carbon monoxide. This method of preparation of manganese dioxide was generally used in the work of development of the optimum proportions of the constituents.

**3. Electrolytic Method.**<sup>6</sup>—This consists in the electrolytic oxidation of manganese in an ammonium carbonate solution using a ferromanganese alloy as the anode. The ammonium permanganate formed decomposes with the precipitation of finely divided manganese dioxide. When a 2-component cell is used this decomposition takes place best at temperatures slightly above 40°. When a 1-compartment cell is used oxidation and reduction take place simultaneously, thus permitting lower temperatures and consequently finer manganese dioxide. The material so produced was not uniform but the best preparations were very active.

**4. Reduction of Permanganic Acid by Oxalic Acid.**—Permanganic acid, prepared from the calcium salt is diluted with a considerable quantity of water, well cooled and a cold solution of oxalic acid is added in slight excess. As carbon dioxide is the by-product, no washing is necessary. This manganese dioxide with silver oxide produced a catalytic material of unlimited life.

**5. Decomposition of Ammonium Permanganate.**—One hundred g. of calcium permanganate is dissolved in 500 cc. of water, and ammonium carbonate solution containing a little ammonia is added. Calcium carbonate is filtered off, and the ammonium permanganate, diluted to 4 liters, is reduced slowly in the cold with methyl alcohol. This method gives very finely divided manganese dioxide and yields uniformly active catalysts of unlimited life. It is probably superior to that prepared by Method 1, because ammonium salts are less strongly adsorbed than are potassium salts.

**6. Air Oxidation of Manganese Oxide.**—The probable mechanism of catalytic oxidation by manganese dioxide, *viz.*, oxidation and reduction of the oxides of manganese, indicated that a catalyst might be prepared from manganous hydroxide and its oxidation effected before use, by drying in atmospheric oxygen. Manganous and silver oxides, precipitated simultaneously from a solution of the nitrates, were dried in oxygen at 130°; a number of mixtures of moderate life were thus produced, but the product was not of uniform activity. Results using copper oxide were less encouraging.

**Preparation of Catalytic Material.**—The oxide catalysts were prepared by the following method, which was used quite generally throughout the investigation whenever the solubilities of the salts used permitted. Manganese dioxide paste of known water content (60–65%) was weighed and suspended in a large volume of cold water, care being taken to secure a uniform suspension; to this was added a standard silver nitrate solution sufficient to give the desired amount of silver oxide in the final mixture. After thorough mixing silver hydroxide was precipitated by a slight excess of sodium hydroxide solution, with constant stirring. After filtering and washing free from sodium nitrate, the mixture was dried on a water-bath and then at about 125° in air or, preferably, in dry oxygen. The drying

<sup>6</sup> This method was developed by B. F. Lovelace.

must be quite thorough, otherwise the mixture will not function catalytically.

Copper oxide cannot be incorporated with manganese dioxide by the above method and a good catalyst obtained, but by using the method of precipitating with a sodium carbonate solution as described below an excellent catalyst may be made containing only manganese dioxide and copper oxide.

An important variation of the above method consisted in the precipitation of silver (or copper) as carbonate, rather than the oxide. During the subsequent drying the carbonate hydrolyzed almost completely, so that what was essentially the oxide mixture was finally produced, similar to the above but more active, especially in the case of mixtures containing only copper oxide and manganese dioxide. When 3 component mixtures were prepared (silver oxide, manganese dioxide and cupric oxide) the nitrates of copper and silver were added to the suspension of manganese dioxide.

It has been stated that Methods 2, 4 and 5 produce the most suitable manganese dioxide for a catalytic material when mixed with other oxides. The relative activities of the different samples were better shown when the amount of silver oxide in the material was reduced (Table III). The most effective mixture prepared according to Method b contained 62.5% of silver oxide, while with that made by Methods 2, 4 and 5 the silver oxide content was successfully reduced to 37.5%, and to 28% when the silver was precipitated as carbonate. The 3-component mixtures (silver oxide, cupric oxide and manganese dioxide), described above, were developed with a practical end in view, *i. e.*, to reduce the cost of the catalyst. In this connection the precipitation as carbonates was especially valuable and, as stated above, the silver oxide could then be completely replaced by cupric oxide when using manganese dioxide prepared by the Frémy method.

Special tests on the most active 2-component catalyst (62.5% of manganese dioxide, 37.5% of silver oxide) are of interest. After a 10-hour test on 1% carbon monoxide with 100% efficiency, the material was allowed to cool and a 0.3% carbon monoxide mixture run in at the same rate (500 cc./min.). The warm area (about 0.5 cm. in length) immediately reappeared at the same place and remained stationary for 10 hours longer, no carbon monoxide at all being detected in the effluent gases at the end of this time. The "pick up" of the catalyst was excellent; as the material was found to function at even lower than room temperature, there was no initial period of low efficiency while the catalyst was warming up.

#### Effect of Humidity.

Inasmuch as these catalysts were to be used for military and naval purposes under all weather conditions with varying temperatures

and humidities, the effect of these factors was of considerable importance.

At low temperatures a poor catalyst was less active, but a good catalyst would give 100% efficiency immediately, under varying concentrations of carbon monoxide at all temperatures covered in any tests,  $-5.0^{\circ}$  being the lowest temperature used. The greater the concentration of carbon monoxide (the rate of flow being the same) the more the catalyst would automatically heat up. The most active catalysts were exposed to both high (2% to 5%) and low (0.08% to 0.1%) concentrations of carbon monoxide at temperatures ranging from  $+100^{\circ}$  to  $-5^{\circ}$  without any detectable loss of efficiency.

With water vapor the case was quite different. As has been indicated above, the deleterious effect of moisture was recognized early in the investigations while working out the best conditions of drying the first catalysts produced. Samples which were not entirely dry possessed little or no activity, while a good dry sample broke down when exposed to any appreciable quantity of water vapor. However, a catalyst which had been rendered inactive in this way could be "regenerated" by drying at  $130^{\circ}$  in a stream of dry air or oxygen. From the military point of view this effect of moisture was of great importance and efforts were made to combat it. This effect of water vapor is a necessary result of the fine structure of the catalyst, and is obviously due to condensation in the pores of the material.

The ordinary mixture is rather soft and very porous and has a low apparent density. However, if this material be put in a press while still moist and subjected to a high pressure (2819 kilograms per sq. cm.) the apparent density is greatly increased and the resultant cake when dried, is relatively hard and quite resistant to crumbling, which in itself is of great importance in the military canister. A material so treated is more resistant to moisture and will last longer than the same volume of the unpressed material against a gas mixture of a given humidity. Tests were made on both pressed and unpressed catalysts at relative humidities from 25% to 100%, the pressed material in each case having a somewhat longer life.

#### Methods of Testing and Analysis.

The standard test prescribed by the Bureau of Mines was used throughout, except in special cases. This consisted in passing the air-gas mixture at the rate of 500 cc. per sq. cm. of cross section per minute through a layer of the catalyst 10 cm. deep. This corresponds to a rate of 32 liters per minute for a canister of regulation size, and is about twice the average rate of breathing.

The standard concentration was 1.0%, regulated by mixing pure carbon monoxide and air in the proper proportion through flow meters. For the catalyst, glass tubes were used having 1 sq. cm. cross sectional area, the granular material to be tested being poured in and the tube gently tapped to cause moderate settling.

The catalyst before being tested was broken up and screened and that portion which passed through the 10-mesh sieve and was retained by the 20-mesh was used. Conditions in a canister are more favorable than those of the tube test, since in a layer of broad cross sectional area there is less channeling of the gases and the loss of heat by radiation is less.

Samples, 500 cc. in volume, of the gases issuing from the test-tubes, were taken in glass bottles by displacement of water. A sample was taken immediately after the run was started and at regular intervals (usually 10 minutes) thereafter. These samples were analyzed by the iodine pentoxide method, consisting of passing the gases over a considerable quantity of pure iodine pentoxide at 160°. The gases from the sample bottle were passed successively through standard barium hydroxide, over calcium chloride, iodine pentoxide, and finally through potassium iodide solution and then through barium hydroxide. The barium hydroxide was titrated with standard oxalic acid, and in this way the quantity of carbon monoxide oxidized by the catalyst and that oxidized by the iodine pentoxide was determined, thus furnishing a check on the analysis. This method of analysis is quite accurate and, by using a large quantity of iodine pentoxide can be made with reasonable rapidity. Frequent analyses of the gases passing effluent to the flow meters were made as a check on the flow meters.

TABLE I.  
EFFECT OF ADDITION OF SODIUM HYDROXIDE TO MnO<sub>2</sub>-Ag<sub>2</sub>O MIXTURES.  
Rate: 500 cc./min. 1.0% CO. MnO<sub>2</sub> made by Method I a.

MnO <sub>2</sub> , %.	Ag <sub>2</sub> O, %.	NaOH, %.	Percentage efficiency, Time in minutes.					
			%.	%.	%.	%.	%.	%.
27.8	69.4	2.8	100	98	88	40	10	..
27.0	67.6	5.4	100	100	92	38	22	..
26.3	65.6	7.9	100	100	99	98	63	..
25.6	64.1	10.3	100	100	100	100	88	..
25.0	62.5	12.5	100	100	100	100	100	98
25.0	62.5	12.5	100	100	100	99.5	95.6	..
25.0	62.5	12.5	100	100	98	90.1	88.5	..

TABLE II.  
RELATION OF DEGREE OF SUBDIVISION TO CATALYTIC LIFE.  
Rate: 500 cc./cm.<sup>2</sup>/min. 1.0% CO.

MnO <sub>2</sub> , %.	Ag <sub>2</sub> O, %.	Type of MnO <sub>2</sub> .	Catalytic life, % efficiency.	
			1 hr.	2 hrs.
50	50	1 a	98%	10%
50	50	1 b	97%	60%
50	50	6	Limited life	
55	45	6	100%, end of 5 hrs; limited life	
50	50	2	Catalytic; unlimited life	
50	50	5	Catalytic; unlimited life	
50	50	4	Catalytic; unlimited life	

TABLE III.  
MANGANESE DIOXIDE AND OTHER OXIDES.

Type of MnO <sub>2</sub> .	MnO <sub>2</sub> , %.	Ag <sub>2</sub> O, %.	CuO, %.	Co <sub>2</sub> O <sub>3</sub> , %.	Remarks.
2	62.5	37.5	10.0	..	Unlimited; 7 hours
4	72.0	18.0	..	..	No activity
2	50.0	40.0	10.0	..	Unlimited life
2	50.0	30.0	20.0	..	Unlimited life
2	50.0	20.0	30.0	..	Unlimited life

TABLE III (continued).

Type of MnO <sub>2</sub> .	MnO <sub>2</sub> , %.	Ag <sub>2</sub> O, %.	CuO, %.	Co <sub>2</sub> O <sub>3</sub> , %.	Remarks.
2	50.0	10.0	40.0	..	100%, 6 hours
1 a	20.0	40.0	..	40.0	94%, 80 min.
1 b	20.0	40.0	..	40.0	100%, 80 min.
2	50.0	..	..	50.0	100%, 20 min.
2	50.0	25.0	..	25.0	Unlimited life
6	72.0	18.0	..	..	Slight activity
6	62.5	..	37.5	..	No activity
6	66.6	13.4	20.0	..	100%, 5 hours

TABLE IV.

## MANGANESE DIOXIDE AND OXIDES PRECIPITATED AS CARBONATES.

Type of MnO <sub>2</sub> .	MnO <sub>2</sub> , %.	Ag <sub>2</sub> O, %.	CuO, %.	Remarks.
2	83.2	16.8	..	No activity
5	77.3	22.7	..	100%, 4 hours; limited
5	70.1	29.9	..	Catalytic; unlimited
2	70.0	30.0	..	Catalytic; unlimited
2	60.8	..	39.2	100%, 5 hours
2	80.4	..	19.6	95%, 8 hours
2	71.4	..	28.6	Catalytic
2	54.8	5.4	39.1	Catalytic
2	68.4	6.8	24.8	100%, 8 hours; limited life

## Discussion.

The present investigation relates entirely to experiments which were made for the purpose of affording protection against the poisonous action of carbon monoxide. It was done under the stress of war conditions when no opportunity was afforded to investigate the mechanism of the reactions involved. The physical structure of the oxides in the catalysts described is an essential factor in their activity; this matter is now being investigated by a careful study of their adsorption isotherms. However, certain facts were noted in the course of this work which appear to have relation to a possible chemical explanation of the reaction. The fundamental assumption of such an explanation is that the oxygen used for the oxidation of the carbon monoxide comes immediately from the oxide catalyst, and that in turn the catalyst is reoxidized by the oxygen of the air sufficiently rapidly to maintain its oxygen content and high activity. As the catalysts are mixtures of more than one oxide it is a question which of these plays the principal rôle. Since both silver oxide and manganese dioxide as prepared above will oxidize carbon monoxide at room temperature, either may be considered as the initial cause of the reaction. But both of these oxides when used alone suffer loss of oxygen, soon lose their activity and are not catalytic in their action. Copper oxide does not oxidize carbon monoxide at an appreciable rate at room temperatures. As the catalysts described above all contain manganese dioxide as an essential constituent, and as the physical condition of the manganese dioxide is of paramount importance it

is assumed on the basis of the above facts that the manganese dioxide is the initial cause of the oxidation, probably functioning by reason of the variable valence of the manganese. Manganese dioxide prepared by any method yielding relatively coarse particles has very slight activity, whereas if its particles are practically of colloidal dimensions it uniformly produces a satisfactory catalyst. Fine subdivision of the particles of the other constituents and their intimate contact with the manganese dioxide particles tend of course toward the production of the most reactive material. On the basis of this explanation of the reaction, the single oxides are not reoxidized by oxygen fast enough to maintain catalytic action; the function of the other oxide or oxides is to increase the velocity of reoxidation of the manganese dioxide, and for this purpose silver oxide appears to be more efficient than copper oxide. In support of this view is the fact that a material prepared by simultaneous precipitation of manganous and silver hydroxides can be made very reactive by air oxidation at 125°. Of course the alternative is to assume that silver or copper oxide is the immediate cause of the action and that manganese dioxide catalyses the reoxidation of the reduced oxides. In favor of this assumption is the fact that manganese dioxide is a good catalyst for the decomposition of such metallic oxides as those of silver and mercury. The present work furnishes no proof of either view, and until further observations on the behavior of these oxide mixtures are available both views are tentative.

Another fact related to the intermediate oxide theory is that a mixture which is partially catalytic, as is the case when the catalyst is not sufficiently active or when the catalyst is poisoned by water vapor, always loses "available" oxygen. The first explanation of the poisonous effect of water vapor would be that the loss of activity results from a diminution of the large internal surface, so essential in these catalysts, which is in part covered by liquid water. This, however, seems hardly to account for all the facts, since under these conditions the catalyst suffers reduction, therefore the carbon monoxide in the mixture has access to the catalyst. The loss of activity seems to result, therefore, primarily from the inability of the catalyst surface to recombine with oxygen. It is possible that this is due to a condensation of water within the pores of the catalyst which thereby separates the oxide particles and thus prevents the intimate contact of the oxides which is essential for the catalytic activity of the material. Some of these points are under investigation, and it is realized that a further discussion is premature until these results, especially those bearing on the adsorption of these catalysts, are available.

The use of these oxides as catalysts is naturally not limited to carbon monoxide, but may be applied to a number of other substances; further work along these lines is in progress, including the oxidation of ammonia. The range of applicability is quite wide, especially in the field of organic oxidations, depending of course, on the possibility of carrying out the

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.

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[CONTRIBUTION FROM THE CHEMICAL WARFARE SERVICE.<sup>1</sup>]

## THE CATALYTIC OXIDATION OF CARBON MONOXIDE AT ORDINARY TEMPERATURES.

BY DAVID R. MERRILL AND CHARLES C. SCALIONE.

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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,<sup>2</sup> 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,

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

<sup>2</sup> 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).