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EXCHANGE



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Manganese  
in  
The Catalytic Oxidation of Ammonia

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EXCHANGE  
JUL 24 1920

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF  
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY  
WITH THE REQUIREMENTS FOR THE DEGREE  
OF DOCTOR OF PHILOSOPHY

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BY  
CHARLES SNOWDEN PIGGOT

June, 1920

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EASTON, PA.:  
ESCHENBACH PRINTING CO.  
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#### ACKNOWLEDGMENT.

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## MANGANESE IN THE CATALYTIC OXIDATION OF AMMONIA.

### Introduction.

In the course of certain investigations undertaken in this laboratory during the war seeking to afford protection to those exposed to the danger of inhaling carbon monoxide, a number of oxide catalyts were produced some of which were very active oxygen carriers and served to completely give the protection sought.

The synthesis of ammonia having been accomplished, the production of nitric acid therefrom has come to be one of the important sources of this acid. The oxidation of ammonia to nitric acid is always accomplished by catalytic oxidation, using air and some form of platinum as the catalyst. The prospective scarcity of platinum made it desirable to find a cheaper catalyst, and the possibility of substituting some of the oxide catalyts already in hand for this reaction was a problem of considerable interest at the time. The work was begun shortly before the close of hostilities and has been continued since for the purpose of securing sufficient data to give a comparison between these oxide type of catalyts and platinum for the oxidation of ammonia. It was thought that possibly these oxide catalyts would be less influenced by the "poisonous" action of certain substances which in the case of platinum seriously interfere with the reaction and necessitate the removal of the platinum gauzes at certain intervals. At least it was thought that should these oxide catalyts show an efficiency at all comparable with that of platinum their cheapness would make their renewal a much less serious matter.

It has been shown that the oxidation of the ammonia is only one step of the reaction involved, there being the possibility that the first products of the reaction may decompose to oxygen and nitrogen in the presence of the catalyst and thus greatly lower the total efficiency of the reaction. It was anticipated that, inasmuch as the catalytic decomposition of the first products of the reaction depends largely on the structure of the catalyst, the oxide catalyts as first prepared would not be suitable for the reaction. This view was subsequently partially confirmed. At the same time, however, it was thought that the increased activity of these mixed oxides as oxygen carriers over that of the single constituents of such mixtures could be retained by making alloys of the metals in question

and then subjecting these to superficial surface oxidation in order to obtain the proper condition for their use. For this reason most of the results here recorded have been obtained by the use of alloys.

Manganese alloys were investigated because it was found that manganese dioxide was an essential constituent of all the successful oxide catalysts previously investigated and because the chemical nature of manganese made it a promising substance with which to compound a poly component catalyst.

The investigation is divided into two parts; first, the study of the oxide catalysts; and second, the study of manganese alloys.

### Oxide Catalysts.

**Manganese Dioxide.**—Ordinary manganese dioxide was found to have little catalytic effect on the oxidation of ammonia, but when in a state of fine sub-division it acted as a catalyst for this reaction.

It was prepared by adding powdered potassium permanganate to cold conc. sulfuric acid and allowing the permanganic acid thus formed to decompose spontaneously into manganese dioxide and oxygen.<sup>1</sup> It was then washed by decantation until free from sulfates, filtered and partially dried on a water-bath. When the water content had been reduced to about 50% it was subjected to a pressure of 2818 kg. per sq. cm. for 24 hours. The resulting cake was broken up and completely dried in a stream of oxygen at 130–140°. When tested<sup>2</sup> on ammonia this material showed considerable catalytic effect, as is shown in Table I following.

TABLE I.—MANGANESE DIOXIDE.

Temp. of catalyst = 800°. NH<sub>3</sub>, 300 cc./min.

Time of contact = 0.05 sec. Air, 3200 cc./min.

Time of run 50 minutes. 1.0 cm. layer.

In.	HNO <sub>3</sub> g. Out.	Eff. %	Remarks.
37.74	23.88	63.27	not pressed
37.86	24.19	63.90	not pressed
37.74	23.72	62.85	not pressed
38.23	36.52	95.44	pressed
38.63	30.64	79.31	pressed
38.85	29.46	75.84	pressed

Though functioning catalytically the oxide undergoes some change during the reaction. The color changes from black to a light yellowish-brown, the material having changed apparently from the dioxide to a lower oxide of manganese.

<sup>1</sup> Fremy, *Compt. rend.*, **82**, 1231 (1876).

<sup>2</sup> The difficulties associated with the quantitative estimation of oxidized nitrogen as described later in this article applied equally here.

**Mixture of Oxides.**—Precipitated manganese dioxide when mixed with various proportions of silver oxide or copper oxide or with both of these oxides produces a catalyst which is quite active in the oxidation of ammonia.

The manganese dioxide used for these mixtures was prepared by treating a concentrated solution of potassium permanganate at 80° with methyl alcohol, filtering on a Büchner funnel, washing and drying to about 50% water content, this latter being determined by analysis. A weighed quantity of this paste was made into a fine suspension in water and the proper amount of silver added in the form of silver nitrate solution. Silver oxide was then precipitated on the manganese dioxide by means of a slight excess of strong sodium hydroxide solution. The two oxides quickly settle out as a single precipitate. When silver and copper were used together they were added in the form of their nitrate solutions as above. When copper alone was added it was usually added as the sulfate and precipitated by sodium carbonate. In any case the precipitates were washed by decantation until free from alkali or sulfates, filtered with suction and dried in a current of oxygen at 130–140°. The dry cake was broken up, screened to convenient size and used for testing.

Catalysts so made have proved to have considerable activity, are very porous, thus offering a very large surface, and are quite resistant to the high temperatures of the reaction, *i. e.*, they show no tendency to sinter together even when the temperature is raised to 1000° or more. The activity can be more or less closely controlled by the method of preparing the catalytic mixture; mixtures containing the constituents in a very fine state of subdivision and in intimate contact being much more active than those in which the reverse is true.

The disadvantages of such catalysts are softness, tendency to crumble and produce fines which clog the gas passages, their tendency to take up moisture due to their extreme porosity, the fact that in contact with a liquid they disintegrate, and that liquid nitric acid will dissolve out the silver or copper oxides. Tables II, III and IV show the results of the tests on these oxide mixtures.

Manganese dioxide when prepared by the Fremy method and mixed with silver oxide, copper oxide, or mixtures of both, produces materials which are such vigorous oxidizing catalysts that the ammonia is largely converted into nitrogen and water, with a consequent low efficiency for nitric acid.

TABLE II.—MIXTURES OF OXIDES.

Composition: MnO<sub>2</sub> (Fremy), 71.43%; CuO, 21.43%; Ag<sub>2</sub>O, 7.14%; dried at 135°. Time of contact, 0.11 sec. NH<sub>3</sub>, 300 cc./min. Air, 3200 cc./min. Temp. of cat., 800°. Time of run, 50 min. 1.8 cm. layer.

In.	HNO <sub>3</sub>		Efficiency %
	g.	Out.	
38.63	18.85		48.77
38.77	21.10		54.41

Manganese dioxide prepared by treating hot (100° approx.) potassium permanganate solution with methyl alcohol is relatively coarse in structure and consequently not so active. This type was used in preparing mixtures of which the following is a fair example. Though not so active an oxidizing catalyst it gave greater efficiencies based on the nitric acid yield.

TABLE III.—MIXTURES OF OXIDES CONTAINING COARSER MANGANESE DIOXIDE.

Composition: MnO<sub>2</sub>, 60%; CuO, 40%; dried at 140°. 4 cm. layer. Time of contact, 0.2 sec. NH<sub>3</sub>, 300 cc./min. Air, 3500 cc./min. Temp. of cat., 800°. Copper precipitated as carbonate.

	In.	HNO <sub>3</sub> g. Out.	Eff. %
	38.10	33.80	88.96
	38.60	37.74	97.71
	38.62	33.79	87.50
	38.62	38.29	96.57
	38.23	36.69	95.98

Manganese dioxide was prepared as for the MnO<sub>2</sub>-CuO mixture described above and mixed with silver oxide, the latter being precipitated on the former from the nitrate solution by sodium hydroxide. The efficiency, not high at first, rapidly decreased. The time of exposure of each charge was 6 hours.

TABLE IV.—OXIDES OF MANGANESE AND SILVER.

Composition: MnO<sub>2</sub>, 62.5%; Ag<sub>2</sub>O, 37.50%. 1 cm. layer.

Time of contact. Sec.	NH <sub>3</sub> cc./min.	Air cc./min.	HNO <sub>3</sub> .		Temp. cat. °C.	Eff. %	
			In.	Out.			
0.082	400	4200	50.67	29.37	650	57.9	
0.082	400	4200	50.67	29.86	650	58.8	
0.082	400	4200	51.36	37.42	790	72.86	
0.082	400	4200	51.50	34.65	820	67.20	
0.057	300	3000	38.52	24.69	800	64.11	NH <sub>3</sub> pass- ing
New Charge 2 cm. layer.							
0.13	200	2600	25.49	21.55	700	84.52	
0.13	200	2600	25.42	20.04	700	81.04	
0.13	200	2600	25.42	20.60	800	79.00	
0.13	200	2600	25.42	19.34	800	76.09	NH <sub>3</sub> pass- ing
0.057	300	3100	38.23	22.62	800	57.16	"

## II. Manganese Alloys.

The variable valence of manganese together with its other chemical properties, recommended it as a good catalytic agent if brought into intimate contact with suitable promoters. It was thought that this intimate contact might well be obtained in an alloy. The advantages of an easily workable metallic catalyst are many; as for instance the possibility of making connections and reaction chambers of it and the weaving of gauzes for the actual contact material.

S. F. Zhemchuzhnii and V. K. Petrashevich<sup>5</sup> state that they have been able to cold draw a manganese alloy of the composition 1.1% Fe, 3.53% Cu, 0.50% Al, 0.12% Si and 94.75% Mn, to a wire 1 to 1.5mm. diameter without annealing between passes. None of the alloys used in this investigation, though more or less ductile, exhibited such ductility as indicated by the above.

Some 6 months of the investigation were devoted to the problem of obtaining a manganese alloy relatively free from impurities (Fe, C, Si). This proved very difficult, and has not been entirely solved up to the present time.

Crucibles of carbon, silicon, or porcelain were of course out of the question, and the usual magnesite crucibles proved to be too porous and frail for melting satisfactorily 200- to 400-g. charges of material.

Alundum crucibles tended to adsorb large quantities of the molten manganese, forming a slag coating which was extremely hard. This difficulty was only partially overcome by lining the crucibles with magnesium oxychloride. The most satisfactory crucibles so far tried were made from a magnesite—iron oxide mixture of about the same composition as that used in making the ordinary magnesite brick for iron smelting purposes.

When using a molybdenum-wound "hydrogen" furnace, the hydrogen formed many "blow holes" in the ingots, the small magnesite crucibles being too frail to permit pouring.

With an electric-resistance vacuum furnace the volatilization of the manganese was excessive even when the furnace was filled with hydrogen under slightly reduced pressure.

The best results have been obtained by using the magnesium oxide—iron oxide crucible as stated above, and a Seger gas furnace. The melt was covered with fused sodium borate as a flux, and the charge was protected as much as possible from contact with the furnace gases by enclosing the crucible in a fire-clay muffle. The best obtainable thermit-process manganese, and electrolytic copper and silver were used. A comparatively large charge was melted and the best of the metal poured into a steel mould coated with graphite, giving a rod 12 mm. in diameter by 15cm. long, which required about half the metal of the melt. This rod was then turned on a lathe and the turnings after oxidizing were used as catalysts.

Considerable time was devoted to various methods of oxidizing metallic surfaces so as to give a firm and adherent coating as well as one of maximum activity. Various gauzes, especially those containing manganese were investigated with this end in view, the final result being the method of electrolytic oxidation described below.

The preliminary oxidation of the catalysts was done electrolytically, the turnings being placed in a porous cup and made the anode by thrusting a platinum wire into the mass. The electrolyte used was 0.1 N sodium hydroxide solution. A current of 0.5 to 1.0 ampere was passed for from 3 to 4 hours, the potential across the electrodes being 10.0 to 15.0 volts.

This treatment caused the material to be thoroughly oxidized super-

<sup>5</sup> Zhemchuzhnii and Petrashevich, *Bull. acad. sci.*, 1917, 863-76.

ficially, with a very adherent dark brown coating. After being washed and dried it was ready for testing.

It was found in the course of the investigation that it was not essential to oxidize the alloys before using, for like the platinum gauzes they could be "activated" by exposure at 600–700° to the ammonia-air mixture, for several hours. However, the electrolytic method was more rapid and satisfactory, and was the usual method employed.

#### Analytical Difficulties.

A very troublesome problem was the devising of a suitable testing and analytical method, and the building of a satisfactory apparatus to put the same into operation. The chief difficulty was to prevent as much as possible the decomposition of the nitric oxide once formed and to bring about its *complete* oxidation to nitrogen dioxide or the higher oxides and to insure their absorption. This was accomplished by using oxidation towers of large volume, water vapor in the form of saturated steam, and vigorous agitation by means of high-speed stirring.

Nitrogen oxides are very difficult to absorb, as is also ammonium nitrate, the latter especially so when in the condition of a colloidal "smoke." Efforts were first directed toward absorbing the oxides of nitrogen in towers of various types. Soda-lime, sodium hydroxide, water, hydrogen peroxide, potassium permanganate solution, conc. sulfuric acid, etc., were tried separately and in conjunction.

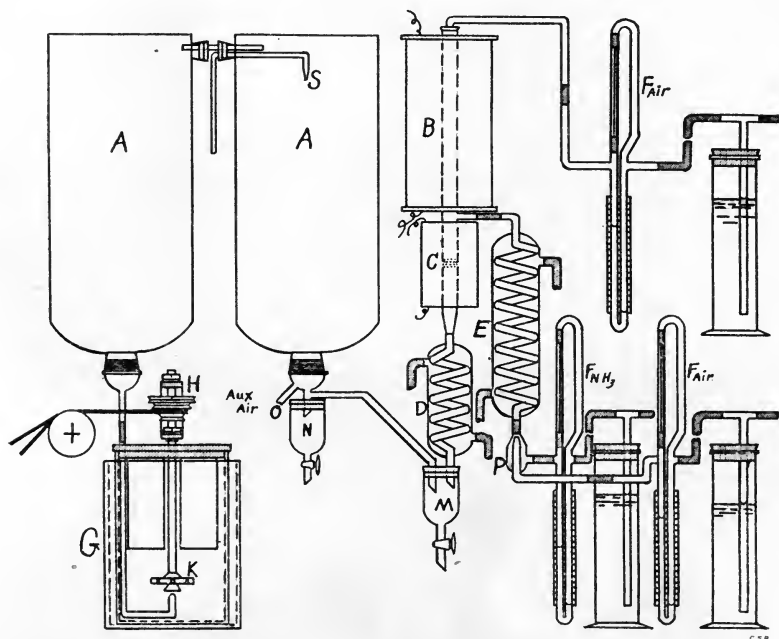
The efficiency was to be calculated on the basis of the oxygen used up. This involved accurate measurement of flows of affluent and effluent gases and absolute oxidation and absorption of the nitrogen oxides. All such methods proved unavailing. Various types of flow-meters were made and tried but none could be devised which would measure accurately the varying concentrations of the various oxides of nitrogen which passed through it, without being affected thereby.

Conc. sulfuric acid may absorb oxides of nitrogen quantitatively, as stated by Nernst, in small quantities and on long exposure; but it was found entirely inadequate under the conditions of this investigation.

#### Apparatus.

The apparatus used in the investigation is shown diagrammatically in the accompanying drawing. *A, A* are two 10-liter aspirating bottles which serve to give volume, and allow time for the oxidation of nitric oxide to nitrogen dioxide or the higher oxides. A jet of low-pressure steam is passed in at *S* which furnishes water for the formation of nitric acid which is drawn off at *N*. *B* is a Hoskins electric furnace and *C* the catalyst, supported on a Witt plate, the whole being surrounded by an auxiliary heating unit which serves to start the reaction and to maintain it at the proper temperature. The clay combustion tube which contains the catalyst passes through the two heating units and is provided in one side with a porcelain tube through which the mixed gases enter. It is connected below with a water-cooled condenser *D* which serves to cool the products of the reaction quickly. The catalyst bed is provided with a small quartz bulb in which is a thermocouple whose wires lead to a Leeds and Northrup compensating potentiometer. *E* is a coil condenser, which serves as a preheater of the mixed gases, through the jacket of which steam is passed at from 140 to 210 g. per sq. cm. pressure. *P* is a mixing chamber for the ammonia and air, while  $F_{\text{NH}_3}$ ,  $F_{\text{air}}$  are flow-meters for the measurement of these gases respectively. *G* is the absorption apparatus consisting of two battery jars with cold water circulating in the annular space between. The inner jar contains sodium hydroxide solution which is

kept stirred by the stirring mechanism *H* which revolves at a speed of 10,000–20,000 r. p. m., the stirring head *K* being heavily gold plated. This stirring head is so constructed that the entering gases and vapors are sucked up at the center and thrown out through the radial holes, which at the speed of operation brings about an emulsoid condition which insures a very thorough mixing and accomplishes complete absorption of the vapors of nitric acid and the oxides of nitrogen. Baffle plates are provided to prevent a circular motion of the liquid and to prevent the latter from being thrown out of the container. It was found necessary to cool the solution, as otherwise the heat produced by the rapid stirring during a run was sufficient to bring the solution almost to its boiling temperature. The water (usually slightly acid) produced by the oxidation of the ammonia is collected and drawn off at *M*. If desired, an auxiliary stream of air could be passed in at *O*, but this was seldom used.



The flow-meters were carefully calibrated at average room temperature, 25°, and were used only on the gas with which they had been previously calibrated.

### Methods of Testing.

In making a run the following procedure was usually adopted. 1000 cc. of *N* sodium hydroxide solution was placed in the adsorption apparatus *G*; and the catalyst, placed at *C*, heated externally to about 600°. The furnace *B* was heated to its maximum temperature (950–1000°) and steam passed in at *S* and through *E*. Ammonia from a steel cylinder, and air, measured by their respective flow-meters, were passed into the mixing chamber *P*. The quantity of air mixed with the ammonia at this point was usually only sufficient to furnish a volume of oxygen equal

to that of the ammonia; the remaining air for the completion of the reaction being passed through the other air flow-meter and down through the hot furnace *B*, meeting the ammonia-air mixture just before contact with the catalyst. This air was heated by the furnace *B* to about 300° to 400°, while the mixture passing through the preheater *E* was heated not above 90–100°, thus ensuring no decomposition of the ammonia. The liquids which collect at *M* and *N* were drawn off from time to time and added to the sodium hydroxide solution at the end of the run. At first runs of 100 minutes were made, but later 50-minute runs were used and this time was maintained throughout the remainder of the investigation.

The gases issuing from the second reaction chamber were by-passed and allowed to escape for some time until the run became stabilized and everything was working properly before a test was begun.

The ammonia entering the apparatus was calculated as g. of nitric acid,  $\text{HNO}_3$ , due correction being made for temperature at the flow-meter. At the end of the run the solution in *G* was measured and its normality determined by titrating a 10.00cc. sample with *N* hydrochloric acid using phenolphthalein as indicator. From this the g. of nitric acid produced was obtained and the percentage efficiency calculated.

To the 10.00cc. sample of solution from *G*, taken above, when just neutralized, was added an additional 10.00 cc. of *N* sodium hydroxide solution, any ammonia thus liberated was boiled off and the solution back titrated with *N* hydrochloric acid. In this way the quantity of ammonia which passed the catalyst unoxidized was determined and could be corrected for. This procedure however was not always necessary as even a slight trace of ammonia passing the catalyst would fill the reaction chambers with a dense white cloud of ammonium nitrate and thus indicate its presence.

A number of preliminary test runs were made to determine the effect of glass, quartz, porcelain, and other materials on the decomposition of ammonia and the oxides of nitrogen when formed. All those materials

Rate of $\text{NH}_3$ , 80 cc./min.		
Temp. of cat. C.	Material.	Eff. %
900	Quartz	33.40
830		34.10
800		40.48
650	Pyrex	39.91
630		35.50
700		44.10
800		59.10
845	Clay	70.70
850		75.60
900		73.60



were found to favor the decomposition to a greater or less extent, quartz being the most active catalyst for this decomposition.

A clay combustion tube was found to give the least decomposition. Condensed results of this investigation are shown briefly in the following tabulation. The same catalyst was used throughout.

After the clay tube was adopted an idea of the effect of heat and time of heating, on the decomposition of ammonia, was obtained by locating the catalyst bed at various points up and down in the electric furnace.

Temp. of cat. ° C.	Rate of NH <sub>3</sub> , 80 cc./min.	
	Eff. %	Position of catalyst bed.
830	51.91	5 cm. from lower end
835	57.52	7.5 cm.
845	70.70	Center of furnace
850	68.62	
900	77.50	5 cm. from upper end
750	74.10	
850	81.12	

These results led to the adoption of the arrangement shown in the drawing of the apparatus, whereby all the ammonia and about  $\frac{1}{2}$  of the air, after being warmed to about 80° enter the reaction tube just above the catalyst bed and are quickly swept down over the latter by the remaining air which, having passed through the furnace, was heated to about 300°.

When a very reactive catalyst was being tested no heat at all was necessary in the larger furnace; in fact it was sometimes necessary to take precautions to prevent the catalyst from melting.

### Experimental.

As has been indicated, a number of manganese alloys were made. The results of the tests of those which were examined are shown in the tables below.

TABLE V.  
ALLOY No. 1.

Composition: Mn, 48.78%; Cu, 37.25%; Ag, 12.70%; Fe, 0.85%; SiO<sub>2</sub>, 0.50%.  
Run, 50 min. 0.5 cm. layer. Temp. of cat., 800°.

Time of contact. Sec.	NH <sub>3</sub> . Cc./min.	Air. Cc./min.	HNO <sub>3</sub> .		Eff. %
			In.	Out.	
0.043	200	2000	25.58	15.88	62.08
0.043	200	2000	25.58	16.06	62.60
0.028	300	3000	38.52	23.18	60.20
0.028	300	3000	38.63	24.00	62.10
0.028	300	3000	38.63	24.82	64.25
0.022	400	4000	50.98	31.63	62.04
0.022	400	4000	51.36	32.50	63.20

An alloy containing a somewhat higher percentage of manganese with consequent lower percentages of copper and silver gave better yields of

nitric acid. The impurities of iron and silicon were also higher. Results of test of this alloy (No. 2) are shown in Table VI.

TABLE VI.  
ALLOY No. 2.

Composition: Mn, 59.60%; Cu, 27.40%; Ag, 8.55%; Fe, 3.25%; SiO<sub>2</sub>, 1.25%.

Time of contact. Sec.	NH <sub>3</sub> . Cc./min.	Run, 50 min. 0.5 cm. layer.			Temp. of cat. ° C.	Eff. %.
		Air. Cc./min.	In.	Out.		
0.107	80	800	10.48	8.09	838	77.25
0.107	80	800	10.48	8.38	842	79.95
0.107	80	800	10.13	7.66	848	75.60
0.045	100	2100	12.92	9.64	800	74.70
0.045	100	2100	12.84	11.71	800	91.05
0.045	100	2100	12.79	7.12	800	56.00
0.045	100	2100	12.84	8.32	800	64.70
0.051	160	1600	20.88	18.12	856	86.80
0.043	200	2000	25.68	20.66	800	80.40
0.043	200	2000	26.01	23.31	855	89.60
0.043	200	2000	26.01	23.97	857	92.10
0.022	400	4000	52.03	43.72	800	84.03
0.022	400	4000	51.88	39.62	800	76.50
0.022	400	4000	52.02	44.20	800	85.13
0.022	400	4000	51.88	40.20	800	77.68
0.022	400	4000	51.50	40.88	800	79.30
0.022	450	4000	51.40	39.50	800	76.80
0.019	400	4600	58.15	44.10	800	75.80
0.019	450	4600	57.90	44.10	800	76.16
0.019	450	4600	57.76	43.66	800	75.60
0.017	500	5000	64.37	46.00	800	71.00
0.017	500	5000	61.60	46.43	800	71.90

An alloy high in manganese was made and tested to determine the limiting proportion of manganese. This alloy was not analyzed but it is believed that its composition closely approximates the proportions of the constituents which were weighed into the melt: *i. e.*, Mn, 80%; Cu, 10%; Ag, 10%.

TABLE VII.  
ALLOY No. 3.

Composition: Mn, 80%; Cu, 10%; Ag, 10%. Run, 50 min. 0.5 cm. layer. Temp. of cat., 800°.

Time of contact. Sec.	NH <sub>3</sub> . Cc./min.	Air. Cc./min.	In.	HNO <sub>3</sub> .		Eff. %.
				In.	Out.	
0.032	200	2800	25.58	13.48	52.85	
0.032	200	2800	25.49	13.45	52.80	
0.027	300	3200	38.23	22.80	59.65	
0.022	400	4800	50.80	23.56	46.38	

It is evident from the above that the maximum manganese content lies well below 80%.

Alloy No. 4 of the following composition: Mn, 54.79%; Cu, 43.77%;

Fe, 1.22%; Si, 0.09%, containing no silver at all, showed less than 25% efficiency.

Alloy No. 5 was made with the idea of duplicating No. 2. Analysis showed that it contained Mn, 56.07%; Cu, 32.81%; Ag, 9.96%; Fe, 1.23%; Si, 0.07%.

TABLE VIII.

## ALLOY No. 5.

Time of contact. Sec.	NH <sub>3</sub> . Cc./min.	Air. Cc./min.	Run, 50 min. 0.5 cm. layer.		Temp. of cat. ° C.	Eff. %.
			HNO <sub>3</sub> .			
			In.	Out.		
0.036	200	2400	25.58	14.91	700	58.27
0.027	300	3200	38.37	20.34	700	53.06
0.027	300	3200	38.62	18.67	700	48.34
0.027	300	3200	38.52	19.79	800	51.38
0.027	300	3200	38.37	18.27	800	47.60
0.027	300	3200	38.52	20.10	800	52.18
0.027	300	3200	38.52	20.85	850	54.13

## Discussion.

As stated in the literature, manganese dioxide was found to have some effect as a catalyst for the oxidation of ammonia.

Early in this investigation it was shown that this effect can be greatly increased by the method of preparing the oxide. The physical structure of the material is of great importance, extremely fine subdivision giving a large adsorbing surface with very small pores being conducive to greater activity.

It was also shown that suitable promoters have a great influence on the catalytic activity of the material. Manganese dioxide is apparently reduced, in the course of the reaction, to some lower oxide of manganese, and the promoter serves to aid the oxygen to reoxidize it back to the dioxide. This is indicated by the fact that when used alone, after several hours, the greater part of the manganese dioxide is reduced to the lower reddish colored oxide. That part of the material which remains black (MnO<sub>2</sub>) is always a thin layer on the top of the catalyst bed, being that portion which first comes into contact with the air and is consequently more readily re-oxidized. When a promoter is mixed with the manganese dioxide very little of the material shows reduction after several hours' use; in this case the reduced area (if any) is always at the bottom of the catalyst bed and is never very great.

Manganese dioxide produced by the action of methyl alcohol on potassium permanganate and, consequently consisting of comparatively coarse particles, was always less completely re-oxidized by the promoter than that prepared by the Fremy method, thus indicating qualitatively the relation of subdivision to reactivity.

When silver and copper were used together as promoters with manganese dioxide prepared by the Fremy method (Table II) there was no indication whatever of permanent reduction of the latter. This would indicate that these two materials tend to act as very efficient carriers of oxygen to the manganese.

On the other hand, however, the temperature and oxygen pressure at which the material was used was far above the dissociation temperature of silver oxide, which would lead to the conclusion that finely divided silver alone is as effective a promoter as silver oxide. This agrees with the conclusion of Lanning<sup>6</sup> drawn from his work on the carbon monoxide catalyst, in this laboratory.

The low yields of nitric acid obtained from the 3-component mixtures as shown in Table II coupled with the fact that no ammonia was detectable in the effluent gases indicates that this material (the catalyst used for carbon monoxide oxidation) is very active and that a very small time of contact is sufficient for it also to favor the decomposition of the nitric oxide once formed. This is analogous to the behavior of platinum black when used alone for this reaction. Some mixture should be possible which would be just active enough to favor the formation of nitric oxide while preventing the liberation of elementary nitrogen. Such a mixture seems to be approximated by that shown in Table III.

It was shown that alloys of manganese exist which possess considerable catalytic activity for this reaction and the data point toward an alloy of rather restricted composition which gives promise of high efficiency. Such an alloy should exist within the following limits of composition: Mn, 55-65%; Cu, 25-35%; Ag, 5-15%; Fe, 1-5%; Si, 0-3%.

Small changes of composition apparently have great influence on the catalytic activity and efficiency and it is believed that further investigations in this more restricted field will develop a catalyst which will yield an efficiency of 90 or 95%, or even greater.

### Summary.

Due to mechanical difficulties encountered during this investigation the above experimental data are not as extensive or complete as would be desired. It is believed, however, that the way has been cleared for a more comprehensive and exhaustive study of this subject and that in the future, such can be carried out without great difficulty.

Mixtures of especially prepared manganese dioxide containing promoters of copper and silver oxides have been made which possess great catalytic activity for the oxidation of ammonia by air.

Attention is called to the mixture of manganese dioxide and cupric oxide shown in Table III. This mixture apparently possesses as great efficiency

<sup>6</sup> Lanning, *Dissertation, Johns Hopkins Univ.*, June, 1920.

as platinum and during the tests showed no appreciable deterioration after 6 hours continuous run.

A method is indicated for the preparation of manganese alloys relatively free from impurities. Alloys of manganese with silver and copper have been made which serve as catalysts for the oxidation of ammonia, and the approximate composition of an alloy is indicated which should give a high efficiency for this reaction.

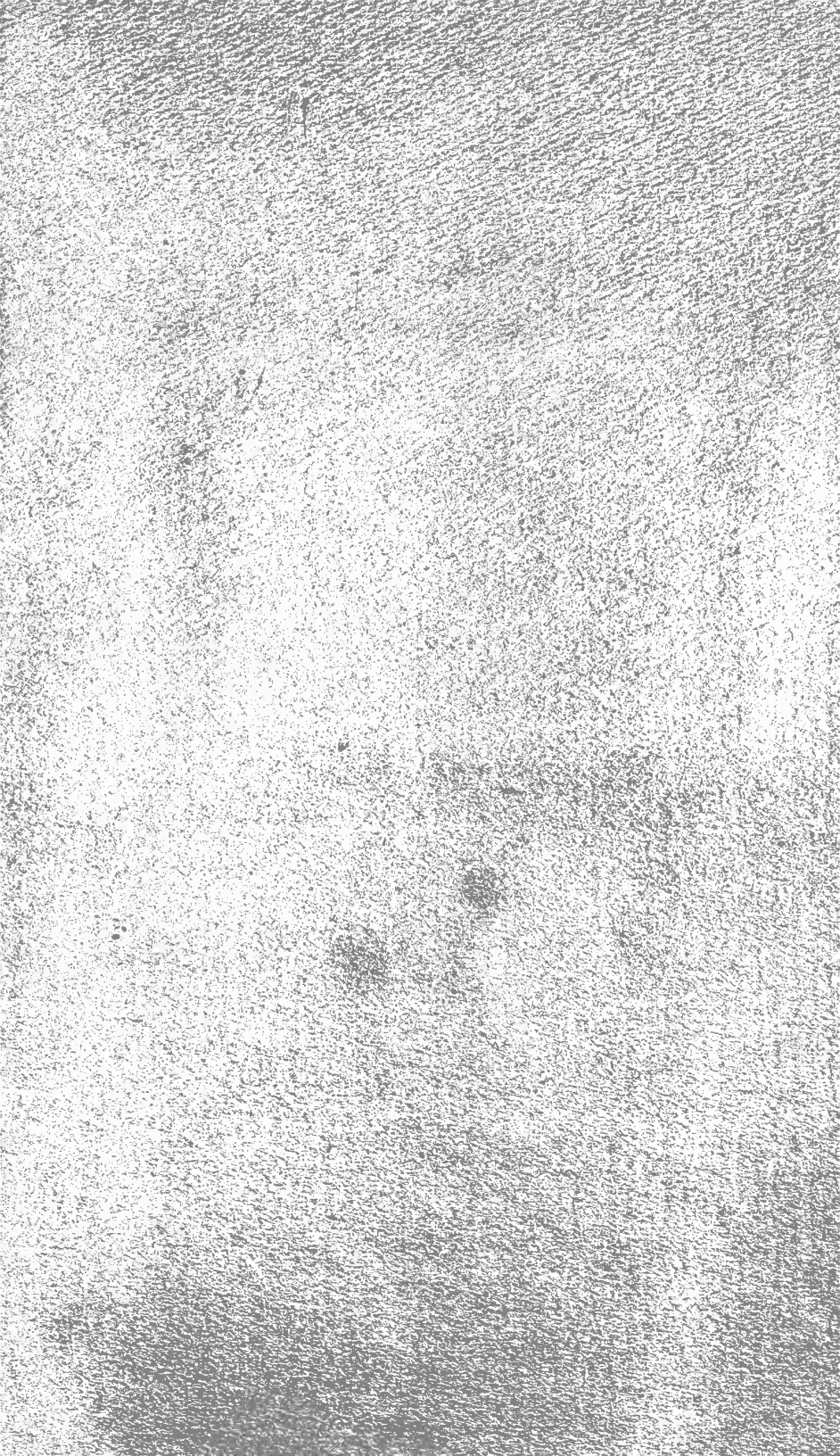
### BIOGRAPHY.

Charles Snowden Piggot was born in 1892 at Swanee, Tennessee. His early education was received at the Swanee Military Academy and the Boy's Latin School of Baltimore, Md. He entered the University of the South in 1911, graduating with the degree of B.A. in 1914. The school years of 1914-15 and 1915-16 were spent in post graduate work in Chemistry at the University of Pennsylvania where he held the University and Harrison Scholarships. He entered Johns Hopkins University in 1916 taking Chemistry, Physical Chemistry and Mineralogy as his major and subordinate subjects respectively. The years 1917-1918 were spent in the United States Army and on research work in war gases. The year 1919-20 he held the DuPont Research Fellowship in Chemistry.









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