HOPCALITE CATALYSTS

SUMMARY

A brief description is given of an adiabatic twin calorimeter having the calorimeter covers in thermal contact with the liquids in the calorimeters. The results of thirty-nine runs on relatively dilute sodium chloride solutions at 25°C. are given. Compared with the first work from this laboratory, some improvement in precision of measurement seems to have been attained, but the results are somewhat higher than those obtained earlier.

The experimental part of this work was carried out under the supervision of Dr. Arthur A. Sunier; the final calculations and the preparation of this brief report are due to him. Grateful acknowledgment of these facts is here made.

REFERENCES

- DANIELS: Mathematical Preparation for Physical Chemistry, pp. 235-7. McGraw-Hill Book Company, Inc., New York (1928).
- (2) GUCKER AND SCHMINKE: J. Am. Chem. Soc. 54, 1358 (1932).
- (3) HESS: Thesis, University of Rochester Library, 1935.
- (4) HESS AND GRAMKEE: J. Phys. Chem. 44, 483 (1940).
- (5) WHITE: J. Am. Chem. Soc. 58, 1615 (1936).
- (6) WHITE: J. Phys. Chem. 44, 494 (1940).

THE PHYSICAL CHEMISTRY OF HOPCALITE CATALYSTS¹

E. C. PITZER² AND J. C. W. FRAZER

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland

Received May 20, 1940

I. INTRODUCTION

The catalytic oxidation of carbon monoxide has been the subject of numerous publications from this Laboratory. Two types of catalysts have been extensively investigated,—the higher oxides of the metals of the first transition group (2, 5, 11, 13, 21) and the chromites of certain bivalent metals (9). The higher oxides of manganese, cobalt, and nickel, when scrupulously pure, are catalysts for this reaction at temperatures as low as -20° C., whereas the chromites are appreciably active only above 100° C.

The purpose of the present investigation was to determine whether a high degree of purity and a fine state of subdivision are the only requisites

¹ An abstract of the dissertation which was presented by E. C. Pitzer to the Faculty of The Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May, 1939.

² Present address: Standard Oil Company of Indiana, Whiting, Indiana.

for a satisfactory catalyst, or whether a definite submicroscopic structure is necessary. Manganese dioxide of various degrees of purity was prepared by the following methods, which yielded products varying from almost impalpable powders to coarse, crystalline aggregates:

Method 1: Decomposition of a manganous salt the anion of which is capable of oxidizing manganous ion to manganese dioxide.

Method 2: Oxidation of manganous ion in highly acid solution, on the assumption that the adsorption of undesirable substances is at a minimum in the presence of a high hydrogen-ion concentration.

Method 3: Precipitation of the hydrated dioxide from solutions buffered by bases other than the alkali and alkaline-earth hydroxides.

Method 4: Activation of impure manganese dioxide by the adsorption of promoting oxides.

II. METHOD OF TESTING CATALYSTS

The method of testing these catalysts has been adequately discussed in previous papers (2, 21). It was soon found that the retentivity for moisture varied from one sample to another. A drying temperature of 130° C., for example, is sufficient to activate hopcalite, but many catalysts prepared during this investigation were found to retain excessive moisture even at 200°C. A uniform drying procedure was adopted, which consisted in passing dry air for 2 hr. over the catalyst heated to 280°C. The catalyst was then cooled to the desired testing temperature. A gaseous mixture composed of 99 per cent of air and 1 per cent of carbon monoxide was dried over soda lime and calcium chloride, and was passed over the catalyst at the rate of 100 cc. per minute.

In this experiment an arbitrary standard was established, in that a catalyst was considered 100 per cent efficient at a given testing temperature if no carbon monoxide was detected in the exhaust gases after operating at 25°, 0°, and -20° C. for 4, 3, and 2 hr., respectively.

III. PREPARATION OF CATALYSTS

Method 1: Comparatively few salts of manganese decompose to yield the dioxide. In order for this reaction to be thermodynamically possible, the anion of the salt must be a stronger oxidant than manganese dioxide under conditions experimentally obtainable. For example, a molar solution of manganous nitrate at room temperature is quite stable. Upon raising the temperature, however, decomposition takes place, and Whitesell (26) succeeded in preparing a very active catalyst by this reaction. If the solution is allowed to evaporate rapidly, the reaction becomes too vigorous, and the residue sinters to a dense, non-catalytic mass.

Further inspection of thermodynamic data revealed that chlorate and bromate ions are more energetic oxidants than nitrate ion. Thus,

$$Mn^{++} + 2ClO_3^- \rightarrow MnO_2 + 2ClO_2 \qquad \Delta F_{298}^0 = +3400 \text{ cal.}$$

from which it follows that the partial pressure of chlorine dioxide above a molar solution of manganous chlorate is 43 mm. at 25°C. It was found by Wächter (25) that complete decomposition of a manganous chlorate solution takes place during evaporation at 50°C.

A catalyst was accordingly prepared by reacting equimolar solutions of barium chlorate and manganous sulfate in aqueous solution, filtering the supernatant liquid free from barium sulfate, and evaporating at 50°C. After digestion in concentrated nitric acid and thorough removal of acid by washing, the residue was found to be completely active at -20° C.

Method 2: As an oxidant for manganous ion in acid solution, chlorate ion was again found to be the most convenient. Manganous carbonate was dissolved in concentrated nitric acid, and sodium chlorate was added a few crystals at a time until complete oxidation had apparently taken place. The precipitate was allowed to settle; then the entire mass was poured into a large volume of water and filtered. The residue was completely catalytic at -20° C.

Method 3: The dependence of the Mn^{++}/MnO_2 electrode potential on the hydroxide-ion concentration permits the oxidation of manganous ion in basic solutions by the halogens or oxygen:

$$Mn^{++} + 4OH^{-} \rightarrow MnO_2 + 2H_2O + 2e \qquad \Delta F_{298}^0 = -17,340 \text{ cal.}$$

From the solubility product,

$$K_s = 7.1 \times 10^{-15}$$

it follows that in a saturated solution of manganous hydroxide the redox free energy is

$$\Delta F_{298} = \Delta F_{298}^0 - 1364 \log (7.1 \times 10^{-15}) = +2360 \text{ cal.}$$

From the half-cell values

$$\begin{aligned} \text{Cl}_2 + 2e &\to 2\text{Cl}^- & \Delta F_{298}^0 = -62,660 \text{ cal.} \\ \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e &\to 2\text{OH}^- & \Delta F_{298}^0 = -18,480 \text{ cal.} \end{aligned}$$

it is evident that the oxidation of manganous ion by these reagents should be complete in alkaline solution.

Among the basic substances available, exclusive of the alkali and alkalineearth hydroxides, are ammonia, organic bases, anions of weak acids, and ammines of certain heavy metals. Each type of base was tried as a buffer.

In the presence of ammonia, both chlorine and oxygen failed to produce an active catalyst. In the case of chlorine, difficulties were experienced in ridding the precipitate of admixed manganous salts. With oxygen, complete oxidation to manganese dioxide was not obtained, in agreement with the observations of Meyer and Nerlich (16).

As an example of an organic base, pyridine was chosen. Chlorine, in

hot solution, yielded a voluminous, black precipitate, completely active at -20° C. A current of oxygen failed to produce manganese dioxide.

Manganous carbonate was selected as the source of an anion of a weak acid. It was found that aqueous chlorine oxidizes manganous carbonate to manganese dioxide at room temperature. Unreacted manganous carbonate was entrained, however, and the product was found to be a poor catalyst.

In contrast to chlorine water, bromine water reacts with manganous carbonate to form a clear yellow solution at room temperature. Upon heating the solution to boiling, manganese dioxide separates, presumably because of the increased rate of hydrolysis of bromine to bromide ion and bromate ion in the hot buffered solution. The precipitate was tested for catalytic activity and found to be completely active at -20° C.

The sluggishness of molecular oxygen, in spite of the favorable energy balance, presented an interesting problem. Meyer and Nerlich (16) obtained complete oxidation to manganese dioxide only in strong alkali, but precipitates contaminated with fixed alkali have been found to be noncatalytic (2). The need is clearly indicated for a strong base that does not poison the product and for an oxidation catalyst that increases the rate of reaction between molecular oxygen and bivalent manganese.

Both of these needs were found to be satisfied by cupric ammonia hydroxide. It is not only a fairly strong base, but also an oxidizing agent, the reduction product of which, cuprous ammonia hydroxide, rapidly absorbs oxygen, being thereby restored to the original compound. Cupric ammonia ion, in the presence of an excess of ammonia, was found to precipitate hydrated manganese dioxide, along with varying amounts of cupric oxide:

 $Mn(OH)_2 + 2Cu(NH_3)_4^{++} + 2OH^- \rightarrow MnO_2 +$

 $2Cu(NH_3)_2^+ + 4NH_3 + 2H_2O$

A solution was made up containing manganous and cupric sulfates in the molar ratio 1:2. Ammonia was added in slight excess, and the solution was aerated for 18 hr. The solid was washed free from the blue complex, and, after drying, was found to be completely active at -20° C.

In view of the fact that the cobaltic hexammine complex is a stronger base than the cupric tetrammine and is also a better oxidizing agent, it was considered desirable to compare the two bases as precipitants for manganese dioxide. One-tenth of a mole of cobaltous chloride was dissolved in 300 cc. of water, an excess of ammonia was added, and a current of air was bubbled through the solution for 18 hr., after which the solution was heated to boiling and manganous sulfate was added slowly during vigorous aeration. The aeration was continued for 24 hr., and the precipitate was dried to lustrous black granules. This product was completely active at -20° C. The composition of a thoroughly dried sample was as follows: Co₂O₃, 47.5 per cent; MnO₂, 52.5 per cent.

Method 4: A certain measure of success having been obtained with manganese dioxide freshly precipitated in the absence of poisons, attention was next directed to the activation of relatively inert preparations of manganese dioxide.

One of the simplest methods for preparing impure manganese dioxide is the procedure of Guyard (8), who attempted to determine manganese oxidimetrically with potassium permanganate. Subsequent work by Volhard (24) and by Morse (17) revealed that bivalent manganese, as well as potassium ion, is coprecipitated by Guyard's method, and these investigators developed methods by which the coprecipitation of lower oxides of manganese is inhibited by the addition of zinc compounds. Later, Sarkar and Dhar (22) found that cupric and certain other salts could be substituted for zinc salts.

Inasmuch as the nature of the cupric oxide-manganese dioxide mixture in hopcalite has been the subject of a considerable amount of speculation, it seemed that some light might be thrown on the function of the promoting oxide by determining the catalytic properties of a number of precipitates obtained by the Guyard method and by suitable variations of it. The following experiments were of special interest:

(a) A hot solution of manganous sulfate was oxidized with potassium permanganate. The product was tested as a catalyst and was found worthless, even at room temperature. Partial reduction of the solid took place, as was attested by the evolution of carbon dioxide at the beginning of the test.

(b) A hot solution containing equal molalities of zinc and manganous solutions was oxidized with potassium permanganate. The product was completely active at 25° C., but not at 0° C.

(c) A hot solution containing cupric and manganous sulfates in the molar ratio 3:2 was treated with potassium permanganate. The product was completely active not only at 25° and 0° C., but also at -20° C.

(d) A hot solution of manganous sulfate, containing sufficient freshly precipitated cupric carbonate to produce a final product equivalent in composition to hopcalite, was treated with permanganate. The precipitate was worthless as a catalyst.

On the basis of analytical work of Morse (17), Volhard (24) and Sarkar and Dhar (22), it was concluded (a) that the low activity of the Guyard precipitate was due to coprecipitated lower oxides of manganese as well as alkali, (b) that zinc oxide is not a promoter for alkali-poisoned manganese dioxide, (c) that the high activity of the third sample is due to freedom from lower oxides of manganese as well as to the promoting action of cupric oxide, and (d) that cupric oxide does not promote magnanese dioxide contaminated with substantial amounts of manganous oxide.

IV. TECHNICAL APPLICATIONS

A practicable method for the activation of commercial manganese dioxide would be of considerable economic and military significance. For example, the removal of traces of carbon monoxide from hydrogen is imperative in the synthesis of ammonia. A cheap, rapid method for the manufacture of canister fillers containing activated manganese dioxide will be necessary if carbon monoxide is used extensively as a combat gas (10). At the present time, the only commercially successful catalyst for this purpose is made from potassium permanganate.

The equilibria between various oxidation states of manganese and copper suggested a series of experiments by which pyrolusite might be advantageously used as the source of manganese. Metallic copper was dissolved in dilute nitric acid in the presence of an excess of pyrolusite that had been previously washed in nitric acid. A slight excess of ammonia was added, and the suspension was aerated for 24 hr. The product was thoroughly washed, dried, and tested, and found to be completely active at -20° C.

The expedient next adopted was the etching of the surface of the granules by dissolving an amount of copper sufficient to generate only the amount of nitric oxide necessary to dissolve one-tenth of a given amount of pyrolusite. The mixed oxides were redeposited upon the etched surface by ammoniacal aeration, by which means a poor catalyst was obtained.

Upon substituting cobalt for copper in the etching and redeposition experiment, a catalyst was obtained which was completely active at -20° C.

Inasmuch as the nature of the reducing agent should have no effect upon the structure of the etched surface, sulfurous acid was substituted for the combination of metal and nitric acid. To 5 moles of pyrolusite was added 1 mole of sulfurous acid, which dissolved 0.5 mole of manganese dioxide:

$$MnO_2 + 2H_2SO_3 \rightarrow Mn^{++} + S_2O_6^{--} + 2H_2O$$

Half a mole of cobaltous nitrate was added, and the solution was heated to boiling, made ammoniacal, and aerated for 24 hr. The catalyst obtained upon drying the residue was completely active at -20° C.

This series of experiments was conducted at the standard rate of 100 cc. of air containing 1 per cent of carbon monoxide per minute over 10 cc. of catalyst. A thorough technical investigation would, of course, involve a detailed study of the catalysts at various temperatures and space velocities.

HOPCALITE CATALYSTS

V. THEORETICAL CONSIDERATIONS

A. Microstructure of catalysts

The most obvious physical characteristic of these oxides is their fineness of subdivision. Except for the surface-activated pyrolusite, all were precipitated and dried under conditions that are assumed to retard crystal growth. It was a matter of considerable interest to obtain at least a qualitative estimate of the size of the crystallites composing these catalysts, in order to determine whether they are to be considered as amorphous or crystalline. The Bureau of Mines Station at College Park, Maryland, kindly offered the facilities of its x-ray department for this phase of the problem, and as a result a number of diffraction patterns were obtained.³

A comparison of figures 1 to 4 reveals the following information:

(1) A pattern of hopcalite (figure 1, A) is contrasted with a pattern (figure 1, B) of a poor catalyst of identical composition but prepared by the addition of cupric oxide to the Guyard precipitate (see page 765). It is evident that both of the materials are almost devoid of regular structure; hence catalytic activity is not uniquely determined by fineness of subdivision.

(2) In only one case,—that of the product of the decomposition of manganous chlorate,—was a pattern characteristic of manganese dioxide observed (figure 2, A; figure 4, A). Even in this case, the most prominent interplanar distance, 3.11 Å., was missing. In the pattern of pyrolusite (figure 2, B), taken under identical conditions, the 3.11 Å. line is very strong. The conclusion to be drawn from the breadth of the lines is that the particles of the manganese dioxide catalysts are very small, perhaps no more than ten unit cells across.

(3) In two other catalysts, lines of cupric oxide and of cobaltoso-cobaltic oxide, respectively, are very prominent (figure 3, B; figure 4, B). Here again, the lines are broad, indicating very poor development of crystal planes or very small crystallites.

B. Proposed mechanism for reaction

The most prominent chemical characteristic common to these catalytic oxides is their instability with respect to decomposition into free oxygen

³ The x-ray tube was of the thermionic type, with a sealed-in molybdenum target. The radius of the camera was 8.897 cm. In order to decrease the time of exposure, no filter was used; hence an occasional β -line, readily identified, will be found. This work was done with the permission of Dr. A. C. Fieldner of the Bureau of Mines. The operator was Dr. Howard F. Carl.

In spite of the diffusences of most of these patterns, an attempt was made to interpret the negatives by means of the densitometer and charts at the Burðau of Mines Station at College Park, Maryland. The results are tabulated in columns, parallel with appropriate data from the literature (see tables 1, 2, and 3).



	INTERPLANA	R DISTANCES	
MnO ₂ from Mn(NO ₃) ₂ , HNO ₃ , and NaClO ₃ (figure 4,A)	MnO ₂ from Mn(ClO ₃) ₂ (figure 2,A)	Pyrolusite (figure 2,B)	MnO ₂ (in tables*)
Å.	Å.	Å.	Å.
		3.14	3.11
2.40	2.40	2.42	2.40
			2.21
2.10	2.11	2.12	2.12
			1.98
1.61	1.62	1.63	1.62
		1.56	1.56
			1.44
		1.31	1.30
		1.06	1.05
		1.00	1.001
1	Faint lines, not predi	cted (probably β -lines)
2.70	2.71	2.72	
1.82	1.83	1.84	
1.375	1.385		

TABLE 1 Interpretation of x-ray diffraction patterns

* HANAWALT, J. D., RINN, H. W., AND FREVEL, L. K.: Ind. Eng. Chem., Anal. Ed. 10, 457 (1938).

TABLE 2

1	Interpretation	of x-ray di	ffraction pa	atterns (cont	inued)	
Mixture of cupr	ic oxide and n	anganese d	ioxide prep	pared from p	yrolusite (figure 3, B)

,			
Measured	Nearest CuO line*	Nearest MnU: lines*	Nearest MnaO4 line*
Å.	Å.	Å.	Å.
2.94			
2.83			2.87
2.45	2.51	2.40	2.48
2.32	2.31	2.21	2.36
2.08		2.12	2.03
1.86	1.85		
1.79			1.79
1.70	1.70		
1.59	1.57	1.62	1.57
1.50	1.50		1.54
1.46		1.44	1.466
1.41	1.408	1.39	1.438
1.37	1.370		
1.31	1.298	1.303 .	1.300
1.265	1.258)	1.277
1.165	1.159		1.123
1.080	1.080	1.051	

* HANAWALT, J. D., RINN, H. W., AND FREVEL, L. K.: Ind. Eng. Chem., Anal. Ed. 10, 457 (1938).

and a lower oxide of the metal. Thus Morse (18) showed that manganese dioxide prepared by the reduction of potassium permanganate is unstable in the absence of an excess of this oxidant. This observation might lead to the hasty conclusion that oxygen is evolved in an activated or "nascent" form (cf. 20) and that this active modification reacts more readily with carbon monoxide. Unpublished results from this laboratory show that no such activation is responsible for the catalytic activity. Experiments with an ozonizer (11) show that the production of activated oxygen in the gas phase is not the critical factor in this reaction. Experiments by Frazer and Greider (5) demonstrated the reduction of manganese dioxide by carbon monoxide, and pointed to a mechanism actually involving the

Interpretation of x-	-ray diffraction	patterns	(concluded)
MnO_2 -"Co	₂ O ₃ '' mixture	(figure 4,	B)

INTERPLANAR DISTANCES					
Measured	Nearest CorO4 line*	Nearest MnO ₂ line*	Nearest Mn:O4 line*		
Å.	Å.	Å.	Å.		
2.76	2.86				
2.44	2.43	2.40	2.48		
2.01	2.02		2.03		
1.76			1.79		
1.55	1.56		1.54		
1.42	1.432	1.44	1.438		
1.228	1.235)		
1.050	1.084	1.05			
1.010	1.012				
.930	0.931		1		
.848	0.850				

* HANAWALT, J. D., RINN, H. W., AND FREVEL, L. K.: Ind. Eng. Chem., Anal. Ed. 10, 457 (1938).

molecules of the solid. The reaction must accordingly involve some kind of bond formation between the catalyst and carbon monoxide, followed by a splitting out of carbon dioxide. The activated adsorption of oxygen on the unsaturated manganese atoms would then regenerate the catalyst.

The poisoning effects of water and alkali must of necessity be explained by any proposed mechanism for the reaction. The amphoteric nature of the catalytic oxides offers a possible clue, in that the formation of a salt, such as a manganite or cobaltite, certainly leads to a superficial layer in which the manganese or cobalt atom is more completely coördinated than in manganese dioxide. The acid reaction (6) of aqueous suspensions of manganese dioxide is considered indicative of the existence of manganese acid, the structure of which must differ considerably from that of manganese



Fig. 3. A, cupro precipitate of Guyard; B, cupric oxide and manganese dioxide mixture from aeration of ammoniacal solution.

FIG. 4. A, manganese dioxide from manganous nitrate + nitric acid + sodium chlorate; B, manganese dioxide and cobaltoso-cobaltic oxide (?) from aeration of ammoniacal solution of manganous and cobaltous dioxide. This more complete coördination results in a smaller reactivity between the solid and gaseous phases, that is, the catalytic surface is poisoned. Poisoning by moisture is thus temporary and may be relieved

OXIDE	DISTANCE	REMARKS				
	°A.	1				
SiO ₂	1.59	β -Quartz				
BeO	1.64					
Nd_2O_3	1.66					
\Pr_2O_3	1.67					
Ce ₂ O ₃	1.68					
La_2O_3	1.70					
Co ₃ O ₄	1.75					
GeO ₂	1.80	Goldschmidt (1932)				
MnO ₂	1.84					
Ni ₂ O ₃	1.84	Sum of atomic radii [†]				
Co ₂ O ₃	1.85	Sum of atomic radiit				
CuO	1.87	a-Axis				
TiO ₂	1.91	Anatase				
Al ₂ O ₈	1.93					
ZnO	1.94					
TiO ₂	1.95	Brookite				
${ m TiO}_2$	2.01	Rutile				
Ga ₂ O ₃	2.0					
Fe_2O_3	2.06					
SnO ₂ ,	2.07					
NiO	2.09					
Cr_2O_3	2.1					
V ₂ O ₃	2.1					
CoO	2.13					
FeO	2.14					
PbO ₂	2.16					
ZrO ₂	2.20					
CeO ₂	2.34					
ThO ₂	2.41					

		TAB.	LE 4			
Interatomic	or	interior	nic di	stances	in c	xides
(From Strukt	urb	ericht*	unles	s other	wise	noted)

* EWALD, P. P., AND HERMANN, C.: Strukturbericht. Akademische Verlagsgesellschaft, Leipzig (1931).

[†] Atomic radii from data in N. V. Sidgwick's *The Covalent Link in Chemistry*, Cornell University Press, Ithaca, New York (1933) and from M. C. Neuberger (Z. Krist. **93**, 1 (1936)).

by thorough drying, whereas alkali poisoning is permanent, except insofar as the alkali may be removed by electrodialysis, as in the researches of Bennett (2), or counteracted by the addition of a promoter, such as cupric oxide. Accepting provisionally the hypothesis that the oxide catalyst undergoes alternate reduction and reoxidation, only those oxides should be catalytic for which the reaction

$$MO_x + CO \rightarrow MO_{x-1} + CO_2$$

proceeds with a diminution in free energy. Thus:

$2\mathrm{MnO}_2 + \mathrm{CO} \rightarrow \mathrm{Mn}_2\mathrm{O}_3 + \mathrm{CO}_2$	(15)	$\Delta F^0_{298} =$	-63,620 cal.
$3\mathrm{Fe_2O_3} + \mathrm{CO} \rightarrow 2\mathrm{Fe_3O_4} + \mathrm{CO_2}$	(19)	=	-20,840
$2\mathrm{CuO} + \mathrm{CO} \rightarrow \mathrm{Cu}_2\mathrm{O} + \mathrm{CO}_2$		=	-35,790
$HgO + CO \rightarrow Hg + CO_2$		=	-47,500

Since, however, the number of oxides obeying this criterion exceeds by far the number of oxides found to be catalytic, the fact that an oxide is thermodynamically unstable in the presence of carbon monoxide is not a sufficient condition for catalytic activity.

The emphasis recently placed upon catalyst geometry (14, 1, 7) makes it desirable to consider the interatomic distances in the various oxides as a possible criterion of catalytic activity. In table 4 the nearest metal-tooxygen distances have been compiled for a number of oxides, most of which have been investigated for catalytic activity. Except where otherwise noted, the data are from *Strukturbericht*.

It is immediately apparent that among the extremely active catalysts, manganese dioxide, nickelic oxide, cobaltic oxide, and cobaltoso-cobaltic oxide, the smallest metal-to-oxygen distance lies in the narrow range between 1.75 Å. and 1.85 Å. No known catalysts active at room temperature for this reaction lie outside this range. One oxide, germanium dioxide, lies within these limits.⁴ The conduct of germanium dioxide is unknown, but from the free energy of formation estimated by Latimer, -142,000 cal., it is not possible to reduce germanium dioxide to germanium metal at room temperature by the reaction:

$$\text{GeO}_2 + 2\text{CO} \rightarrow \text{Ge} + 2\text{CO}_2$$

$$\Delta F_{298}^0 = +19,120 \text{ cal.}$$

No data are available for a similar calculation involving germanium dioxide and germanium monoxide, but, according to Dennis (3), the reaction

$$GeO_2 + CO \rightarrow GeO + CO_2$$

does not begin below 785°C. It is unlikely, therefore, that germanium dioxide is a catalyst for the oxidation of carbon monoxide at low tem-

.

⁴A more recent determination of the Ge \rightarrow O distance is 1.89 Å. (Pauling, L.: *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York (1939)). Thus the apparent exception to this classification is removed.

peratures. It is of interest to note that cupric oxide, which begins to manifest catalytic activity at 70°C., has a minimum metal-to-atom distance of 1.87 Å.

The pertinent data that must be of value in deducing a mechanism for the action of manganese dioxide may now be summarized and restated: (1) Activated adsorption of carbon monoxide takes place on oxides other than MnO₂, Co₂O₃, and Ni₂O₃, yet only these three oxides are catalytic at 0°C.; (2) carbon monoxide is oxidized by poisoned manganese dioxide, but not catalytically; (3) increased coördination around the manganese atom occurs simultaneously with poisoning of the catalyst; (4) the oxides known to be catalytic have an interatomic distance of 1.75 to 1.85 Å.

In representing the adsorption of carbon monoxide diagrammatically, three configurations are conceivable: (1) Adsorption of the carbon end of the molecule on an oxygen atom of the oxide. (2) Adsorption of the oxygen atom on the metal atom of the oxide. (3) Simultaneous adsorption of both ends of the molecule, with a resulting shifting of the electron configuration so that the correct bond formation takes place.

Representing a fragment of infinite surface by a single O Mn O configuration (not necessarily linear), these cases may be illustrated as follows:

	\mathbf{C}	
	0	C 0
O Mn O·CO	O Mn O	O Mn O
Case 1	Case 2	Case 3

It is evident that case 1 or case 3 is geometrically compatible with the splitting off of a carbon dioxide molecule, and that case 2 does not permit such a decomposition. Since the experimental results show that such a reaction takes place, case 2 is at once ruled out. A choice is therefore to be made between cases 1 and 3.

It is likewise evident that, if case 1 be correct, the mechanism should hold true even in the presence of moisture or alkali, as there would still be unsaturated oxygen atoms (attached to manganese atoms) upon which carbon monoxide could be absorbed. On the other hand, if case 3 be a correct diagrammatic representation of the actual mechanism, it is at once apparent why the increased coördination around the metal atom as a result of poisoning should inhibit the reaction. The almost identical value of the $M \rightarrow O$ bond distance in active catalysts would be of minor importance for case 1, but would lend a considerable amount of support to a mechanism involving case 3.

The objection might be raised that this type of adsorption would require

the stretching of the carbon monoxide bond from 1.15 to 1.8 Å. The energy involved in this process cannot be determined from available data, but the calculation would be strictly comparable to that of Sherman and Eyring (24), who discussed the adsorption of hydrogen on carbon atoms 3.6 Å. apart.

SUMMARY

1. X-ray data show the active catalysts, with one exception, to consist of crystallites so small that in classical language they would be called amorphous. Samples of catalysts of identical compositions and diffraction patterns are not necessarily identical in catalytic behavior.

2. The catalytic oxides, and no others, satisfy the criteria of favorable free-energy change for the reduction of the oxide by carbon monoxide and of an interatomic distance of 1.75 to 1.85 Å.

3. The results of experiments on poisoning and a consideration of catalyst geometry suggest that the catalytic reaction involves adsorption of each molecule of carbon monoxide on two points of the catalyst.

The junior author was the recipient of the H. A. B. Dunning Fellowship for the State of Maryland during the academic years 1936–39, and of an award from the Hynson, Westcott, and Dunning Research Fund in 1939, which he gratefully acknowledges.

REFERENCES

- (1) BALANDIN, A. A.: Z. physik. Chem. B2, 289 (1929).
- (2) BENNETT, O. G.: Dissertation, The Johns Hopkins University, 1930.
- (3) DENNIS, L. M.: Z. anorg. Chem. 174, 107 (1928).
- (4) FRAZER, J. C. W.: J. Phys. Chem. 35, 405 (1931).
- (5) FRAZER, J. C. W., AND GREIDER, C. E.: J. Phys. Chem. 24, 1099 (1925).
- (6) GORGEU, M. A.: Bull. soc. chim. [3] 4, 16 (1890).
- (7) GRIFFITH, R. H.: The Mechanism of Contact Catalysis, p. 136 ff. Oxford University Press, London (1936).
- (8) GUYARD, A.: Bull. soc. chim. 6, 38 (1863).
- (9) HEARD, LLEWELLYN: J. Phys. Chem. 42, 855 (1938).
- (10) HOGENUK HANSEATISCHE APPARATEBAU GES.: German patent 672,845 (March 10, 1939).
- (11) LAMB, A. B., BRAY, C. W., AND FRAZER, J. C. W.: Ind. Eng. Chem. 12, 213 (1920).
- (12) LATIMER, W. M.: Oxidation Potentials. Prentice-Hall, New York (1938). All calculations, unless otherwise acknowledged, have been based upon data in this monograph.
- (13) LOANE, C. M.: J. Phys. Chem. 37, 615 (1933).
- (14) LONG, J. H., OTT, E., AND FRAZER, J. C. W.: J. Am. Chem. Soc. 56, 1101 (1934).
- (15) MAIER, C. G.: U. S. Bur. Mines Bull., Information Circular 6769 was the source of the following standard free energies of formation: $MnCO_3$, $\Delta F_{298}^0 = -200,880$ cal.; Mn_2O_3 , $\Delta F_{298}^0 = -198,330$ cal.

- (16) MEYER, J., AND NERLICH, R.: Z. anorg. Chem. 116, 117 (1921).
- (17) MORSE, H. N.: Exercises in Quantitative Chemistry, p. 468. Ginn and Company, New York (1905).
- (18) MORSE, H. N.: Am. Chem. J. 18, 401 (1896).
- (19) PARKS, G. S., AND KELLEY, K. K.: J. Phys. Chem. 30, 47 (1926).
- (20) POURBAIX, M.: Rev. universelle mines 11, 367 (1935).
- (21) ROGERS, T. H., PIGGOT, C. S., BAHLKE, W. H., AND JENNINGS, J. M.: J. Am. Chem. Soc. 43, 1973 (1921).
- (22) SARKAR, P. B., AND DHAR, N. R.: Z. anorg. Chem. 121, 135 (1922).
- (23) SHERMAN, A., AND EYRING, H.: J. Am. Chem. Soc. 54, 2661 (1932).
- (24) VOLHARD, M. J.: Bull. soc. chim. [2] 34, 714 (1880).
- (25) WÄCHTER, A.: J. prakt. Chem. 30, 326 (1843).
- (26) WHITESELL, W. A., AND FRAZER, J. C. W.: J. Am. Chem. Soc. 45, 2841 (1923).

THE STARCH MOLECULE

G. V. CAESAR AND M. L. CUSHING

Research Laboratory, Stein Hall & Co., New York, New York

Received September 6, 1940

INTRODUCTION

The structure, size, and spatial configuration of the starch molecule have long been bones of contention. Polysaccharides such as starch, cellulose, glycogen, all yield *d*-glucose on complete hydrolysis. It is generally agreed that *d*-glucose forms the principal building block or basic unit of these higher complexes. But how *d*-glucose is combined in the amyloses, whether or not there may in part be present derivatives of *d*glucose, the number of units in a single amylose chain (molecular weight), the question of a "second" or associative dimension, the spatial configuration of the molecule,—these and other problems have proved exceedingly difficult and controversial.

One of the purposes of this paper has been to review these questions critically, and another to submit original work of our own, bearing upon the rather understressed but exceedingly important problem of molecular spatial configuration.

STRUCTURE OF THE AMYLOSE MOLECULE

A structure of the maltose type is at present accepted, although Hudson and coworkers have recently demurred (31). The contention of the British school of chemists,—Haworth, Hirst, and coworkers (1, 24, 21, 13, 25, 23, 26, 15, 18, 14, 22, 19, 20, 16, 17, 29, 30),—that amylose is a polymer of glucopyranose units in the maltose (α) linkage, appears to be well founded