3. These measurements fail to confirm the predictions of the radiation hypothesis.
4. The absorption spectrum of nitrogen tetroxide has been determined in each of these solvents. The absorption maximum of nitrogen tetroxide showed an appreciable shift from 5.65μ in the gas phase to 5.45–5.30μ in solution.
5. Relations between molecular structure and infra-red absorption spectra have been interpreted in the light of the G. N. Lewis theory of valence, based on the electron pair.

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON AND THE FIXED NITROGEN RESEARCH LABORATORY, UNITED STATES DEPARTMENT OF AGRICULTURE]

AN X-RAY EXAMINATION OF SOME AMMONIA CATALYSTS

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RECEIVED JULY 23, 1925 PUBLISHED DECEMBER 12, 1925

Introduction

The study of a large number of heterogeneous catalytic reactions has brought to light many cases which show the extreme sensitivity of catalysts to the presence of relatively small concentrations of foreign materials. In some cases these foreign materials exert an inhibiting influence on the catalyst and are called "poisons;" in other cases, the added materials enhance the activity of the catalyst and are called "promoters."[1] The mechanism by which a promoter functions is one of the most interesting phases of catalytic action and has been the subject of much speculation. It seems highly improbable that a single explanation of promoter action, applicable to all cases, will ever be found; nevertheless, certain general suggestions have been made as to the function of promoters. These have attributed to a promoter such effects as the favorable adjustment and orientation of the adsorbed gaseous reactants, the rapid desorption of the reaction product, and the production and maintenance of a desirable physical structure.

For many catalysts, at least, the effect of the promoters on the physical structure is of primary importance. This type of effect is directly amenable to study by X-ray diffraction methods. These methods can give information regarding the atomic positions in solids, the probable limits of crystal size, and the existence of solid solutions. They can, however, yield no knowledge of the conditions existing at the surface where catalytic action undoubtedly takes place.

The extensive study of iron catalysts for ammonia synthesis at the

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[1] See Pease and Taylor, *J. Phys. Chem.*, **24**, 241 (1920), for a review of the literature.

Fixed Nitrogen Research Laboratory[2] has revealed the marked sensitivity of such catalysts to the presence of small amounts of foreign materials. Thus tin, lead and sulfur in quantities so small as to defy detection by ordinary chemical means are able to inhibit almost entirely the activity of an iron catalyst. On the other hand, small precentages of a large number of single and composite promoters increase the activity of iron. Excellent catalysts have been obtained by reducing artificial magnetite containing 2–3% of the composite promoter, potassium and aluminum oxides in the ratio of 1 K_2O to $3Al_2O_3$. These last catalysts possess an initial activity several times greater than iron reduced from pure magnetite and have a much longer life at high pressures and temperatures.

The accumulated data on the effect of this particular composite promoter have indicated that the mechanism of the promoter action is not simple but that its efficacy is due to the combination of several effects. The marked increase in activity and length of life produced on iron by this promoter, however, strongly suggests that one of its important functions is to produce a rugged physical structure in the catalyst material. It was with the hope of revealing some such influence that the present X-ray examinations of pure and promoted iron catalysts was undertaken.

With this end in view, powder photographs, prepared in the usual fashion[3] have been obtained (1) from various fused iron oxides having compositions near to Fe_3O_4 and richer in ferrous iron than Fe_3O_4, (2) from artificial magnetites containing various amounts of aluminum oxide and potassium aluminate ($K_2Al_2O_4$) as promoters, and (3) from the iron catalysts obtained by reducing these fused oxides.

The attempt to identify certain extra diffraction lines which are produced by the magnetites with an excess of ferrous iron has led to the preparation of ferrous oxide, FeO. The method of making this oxide and a determination of its crystal structure will be given in another article.[4]

Materials

All of the specimens of artificial magnetite examined for this work were prepared by the method[5] devised at the Fixed Nitrogen Research Laboratory for making ammonia catalysts. It consisted in burning Armco iron rods in pure oxygen to the average composition Fe_3O_4. The burned material was crushed and fused again in an electric fusion-pot between water-cooled electrodes. The melt, weighing about 2.3 kg. was broken up, uniform lumps were selected, crushed and screened to provide samples for

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[2] (a) Larson and Tour, *Chem. Met. Eng.*, **26**, 647 (1922). (b) Larson, *ibid.*, **26**, 683 (1922). (c) Larson, *Ind. Eng. Chem.*, **16**, 1002 (1924). (d) Other papers to appear in *Ind. Eng. Chem.* in the near future.

[3] Wyckoff, "The Structure of Crystals," Chemical Catalog Company, New York, **1924**, Chap. VI.

[4] Wyckoff and Crittenden, THIS JOURNAL, **47**, 2876 (1925).

[5] Larson and Richardson, *Ind. Eng. Chem.*, **17**, 971 (1925).

X-ray and activity tests. When it was desired to study the effect of foreign materials on the magnetite, they were mixed with the burned material before fusion.

Table I gives the percentage compositions of the materials before reduction and their relative activities for ammonia synthesis.

Table I

Analysis and Activity of Artificial Magnetites

Values in percentages

Catalyst	Total iron	Free[a] iron	Fe^{++}[a] iron	$\frac{Fe^{++}}{Fe^{+++}}$[b]	K_2O	Al_2O_3	Activity[c]
909	72.68	2.86	18.17	0.352	..	..	Medium
918	72.84	2.37	25.03	.551	..	..	Good
926	75.27	2.64	31.66	.774	..	..	Medium
928	75.24	3.34	40.49	1.276	..	..	Medium
954	65.21	0.83	24.95	0.632	..	10.12	Very good
955	67.64	.78	30.51	.890	..	7.95	Good
922	71.99	.89	24.55	.533	0.26	1.05	Excellent
435	72.2	..	...	...	.25	0.80	Excellent
421[d]	71.85	..	...	...	.43	2.07	Extra good
660	69.45	0.94	25.35	0.587	.94	3.02	Excellent
940	69.15	..	...	...	2.16	2.95	Excellent
952A	62.98	0.41	20.16	0.475	5.81	7.75	Very good

[a] Determined by method of Sims and Larsen, *Ind. Eng. Chem.*, **17,** 86 (1925).

[b] Theoretical = 0.500.

[c] For 100 atms., 450° and 5000 space velocity, the activity in percentage of NH_3 may be stated as follows: medium = 3–5%; good = 5–6%; very good = 6–10%; extra good = 10–13%; excellent = 13–15%; equilibrium = 16.43%.

[d] Contained 0.67% of zirconia, ZrO_2 as extra material.

Experimental Results

Unreduced Catalyst Materials.—It has been found that most of the oxide promoters which give high activity and long life to ammonia catalysts are by themselves difficult to reduce. This suggests that their distribution should play an important part in determining the physical structure of the reduced catalyst. An initial approach to the relation between promoter distribution and desirable physical characteristics is furnished by studying the occurrence and extent of solid solution in these promoted magnetites, since solid solution provides the best known means of obtaining a molecular distribution of one solid throughout another.

Many good promoters, such as magnesium, aluminum and manganous oxides, etc., can form spinels with either ferrous or ferric oxide. These spinels have the composition $R''R_2'''O_4$, where R'' and R''' are di- and trivalent metal atoms. They have the same cubic symmetry and type of atomic arrangement as has ferroferric oxide, Fe_3O_4, and form extensive series of solid solutions with it and with one another. At low pressures potassium oxide, K_2O, is a poison rather than a promoter for iron catalysts, but when it is heated first with an equivalent amount of aluminum oxide to make potassium aluminate, it is an excellent promoter. This potassium aluminate is also cubic in crystal structure and has a crystal habit similar to that of the spinels. The possibility of solid solution between potassium aluminate and ferroferric oxide, where two univalent atoms of potassium would replace a single divalent atom of iron, is in itself an interesting one to students of crystal structure. Several such atomic replacements involving different numbers of atoms in the solvent and solute have been reported but no such substance has been subjected to X-ray examination and few would be as simple as this one in which the crystal structures of both constituents either are known or can be established by existing diffraction methods.

In order to determine what observable effect was produced on the unreduced artificial magnetite by the addition of the promoters potassium aluminate and aluminum oxide, precision powder photographs were made and analyzed (1) from nearly pure ferroferric oxide (918), (2) from a particularly good catalyst material (940), (3) from one containing the largest quantity of potassium aluminate that it was practicable to introduce (952A), and (4) from a magnetite containing approximately 10% (excess) of ferrous oxide and an equivalent amount of aluminum oxide (954). These photographs were in all cases direct comparisons with sodium chloride as a standard with which the magnetite, ground to about 300 mesh, was intimately mixed.[3] Hygroscopic materials such as 940 and 952 Å. were sealed in glass tubes before being photographed. Results of spacing measurements on a typical film of magnetite (918) are recorded in Table II. The spacings of all the observed lines found

TABLE II

POWDER DATA FROM A FILM OF MAGNETITE (918)

Distance from central image Mm.	Sin Θ	$\sin^2 \Theta$	Ratio of $\sin^2 \Theta$	$d/n = \frac{0.710 \text{ Å.}}{2 \sin \Theta}$	Indices	a_0, Å.
98.73	0.44020	0.19378	107.68	0.806	115 (2)	8.377
90.49	.40581	.16468	91.51	.875	139 (1)	8.349
81.81	.36881	.13602	75.58	.963	133 (2)	8.396
79.68	.35959	.12930	71.85	.987	110 (6)	8.375
75.17	.34011	.11567	64.28	1.044	100 (8)	8.352
71.95	.32612	.10635	59.10	1.088	137 (1)	8.356
69.98	.31744	.10077	56.00	1.118	123 (2)	8.366
52.49	.23995	.05758	31.99	1.479_5	110 (4)	8.370
51.01	.23330	.05443	30.25	1.522	(line of FeO)	
45.34	.20777	.04317	23.99	1.709	112 (2)	8.373
36.96	.16978	.02882	16.02	2.091	100 (4)	8.364
35.76	.16433	.02700	15.00	2.160	(line of FeO)	
30.52	.14047	.01973	10.96	2.527	113 (1)	8.381
25.94	.11956	.01429	7.94	2.969	110 (2)	8.398
15.95	.07353	.00541	3.01	4.828	111 (1)	8.362
						8.371

on films of the other three oxides and calculated in the manner illustrated in Table II are shown in Table III. From these data it is immediately obvious that all these promoted catalysts give only the diffraction lines of magnetite itself. Since the structure of magnetite is already known,[6] the index assignment of Col. 6 of Table II can be made directly from the observed spacings and the length of the edge of the unit cube, a_0, can be calculated from each reflection (Col. 7). Averages of the cube-edge lengths for each of the measured films of the four oxides are recorded in Table IV. The value for ferroferric oxide (918) is higher than that for any of the promoted magnetites, but the difference in any case is scarcely more than the limit of error of the measurements (±0.15%).

TABLE III

OBSERVED SPACINGS ON TYPICAL FILMS OF MAGNETITES AND PROMOTED OXIDES

Magnetite	Observed spacings in Å.							
918	0.806	0.875	0.963	0.987	1.044	1.088_5	1.118	1.479_5
940	.806	.876	.965	...	1.045	1.089	1.117	1.479
952A	.807	.876	.963	...	1.043	1.086	1.116	1.477
954	.806	..	.963	...	1.042	1.087	1.116	1.477
918	1.522[a]	1.709	2.091	2.160[a]	2.527	2.969	4.828	
940	...	1.706	2.087	...	2.519_5	2.966	...	
952A	...	1.705	2.093	...	2.525	2.969	...	
954	...	1.702	2.091	...	2.527	2.966	...	

[a] FeO.

TABLE IV

AVERAGED VALUES OF a_0 IN Å. FOR MAGNETITE AND PROMOTED OXIDES

Film	918	940	952 Å.	954
1	8.374	8.368	8.367	8.364
2	8.371	8.373	8.366	8.372
3	8.377	8.368	8.362	8.379
4	8.376	8.374	8.366	8.362
5	8.375	...	...	...
6	8.380	...	...	...
Average a_0 =	8.375	8.371	8.365	8.369

Powder photographs of 918 and other magnetites with an excess of ferrous iron (see Table VII) contain at least two lines that cannot be assigned to magnetite. Inasmuch as these lines are not observed from the promoted magnetites, it is of vital importance to investigate both the nature of this additional phase in magnetite and the cause of its absence in promoted oxides. The four materials 918, 926, 928 and 958, contain progressively increasing amounts of an excess of ferrous iron. In their powder photographs the foreign lines previously mentioned appear with correspondingly increased intensities. Since the diffraction lines are not

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[6] Bragg, *Phil. Mag.*, **30**, 305 (1915).

those of iron itself, this fact shows that they are due to a material richer in iron than magnetite. By fusion of magnetite with increasing amounts of metallic iron a product (958) was obtained which was only slightly ferromagnetic. The principal powder lines of this oxide from which the more magnetic portion had been removed are identical with the foreign lines in 928 and the other magnetites containing an excess of ferrous iron. Chemical analysis and a determination of its crystal structure have shown 958 to be essentially ferrous oxide.

In order to gain further light on the absence of an excess of ferrous oxide, FeO, from the promoted oxide, various amounts of aluminum oxide have been added, by fusion, to a magnetite containing an excess of ferrous iron (926 + 928). After the addition of half the aluminum oxide necessary to combine with the excess of ferrous oxide to form the spinel, $FeAl_2O_4$ (955), the lines of ferrous oxide were still present in the powder photograph although much weaker than those from the original mixture of materials 926 and 928; when, in 954, the aluminum oxide content had risen to practical equivalence with the excess of ferrous oxide, the lines of the latter had vanished. The failure of new lines to appear in the photograph in place of the vanished ones of ferrous oxide indicates that the resulting ferrous aluminate ($FeAl_2O_4$) has gone into solid solution in the isomorphous ferroferric oxide. At most only a slight difference in the size of the unit cell was observed between nearly pure ferroferric oxide (918) and 954 (Table IV). This, however, is to be expected from a solid solution of 10% of ferrous aluminate in ferroferric oxide because calculation from the observed density values ($\rho = 3.91 - 3.95$) shows that a_0 from pure ferrous aluminate itself differs very little from that of magnetite (a_0 calcd. for $FeAl_2O_4 = 8.32 - 8.34$ Å.).

Several attempts were made to obtain diffraction photographs from potassium aluminate; this compound is extremely hygroscopic and every sample examined showed evidence of the presence of so much foreign material that the lines characteristic of potassium aluminate itself could not be distinguished with certainty. Since magnetites 940 and 952 Å. promoted with potassium aluminate, gave values of a_0 so near to that of ferroferric oxide itself, final knowledge of whether or not there is solid solution of the former substance in the latter must await either an accurate density determination or a measurement of the diffraction pattern of pure potassium aluminate.

Reduced Catalyst Materials.—The reduced catalysts for this investigation were obtained by heating the fused promoted oxides in hydrogen or a mixture of three molecular proportions of hydrogen to one of nitrogen at temperatures from 350° to 450°. Freshly reduced catalysts are so pyrophoric that it is necessary for photographing to have them enclosed in small glass tubes out of contact with the air.

Whereas the individual crystals of fused magnetite are very large (at least several millimeters long) the crystalline iron produced by reduction is always so fine-grained that no grinding is needed to give a perfect powder photograph. On the other hand, the iron crystals are not so small that they show with certainty the broadening of lines that is characteristic of crystals of colloidal dimensions. The data of Tables V and VI prove that the patterns obtained from catalysts reduced from both pure ferroferric oxide and from promoted oxides are those[7] of the stable α-iron.[8]

In order to find out whether the presence of a promoter in reduced catalysts alters in any observable way the position and relative intensities of the iron lines, comparison powder photographs of a pure reduced iron (918 red.) and of a good promoted catalyst (660 red.) have been made and analyzed. Data on typical films of these two preparations are reproduced in Table V; the averaged results from six films for each of these iron samples are recorded in Table VI. These measurements show that these promoters do not alter the spacings of the reduced iron by an observable amount (0.15%).

TABLE V

POWDER DATA FROM TYPICAL FILMS OF PURE IRON (918 RED.) AND A PROMOTED CATALYST (660 RED.)

Observed spacings			Values of a_0	
918 red., Å.	660 red., Å.	Indices	918 red., Å.	660 red., Å.
0.765	0.764	132 (1)	2.862	2.859
.903	.904	130 (1)	2.855	2.859
1.012	1.012	110 (2)	2.862	2.862
1.167	1.168	112 (1)	2.858	2.861
1.433	1.430	100 (2)	2.866	2.860
2.024	2.023	110 (1)	2.862	2.861
			2.861	2.860

TABLE VI

AVERAGED VALUES OF a_0 IN Å. FOR PURE IRON AND FOR REDUCED CATALYST 660

Film	1	2	3	4	5	6	
918	2.860	2.859	2.861	2.860	2.860	2.857	Av. 2.859
660	2.861	2.860	2.860	2.855	2.860	2.853	Av. 2.858

The following experiments definitely prove that the crystals of iron in such a promoted catalyst grow only at a very moderate rate under conditions which produce large crystals in a similar pure iron reduced

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[7] This similarity in structure was earlier indicated in some photographs made at the Watertown Arsenal. A photograph made there of a partly reduced, promoted catalyst (922) gave only the lines of ferroferric oxide and of iron. There thus appears to be no intermediate stage in the reduction of ferroferric oxide to iron. The writers are under obligation to H. H. Lester for his kindness in making these photographs.

[8] Hull, *Phys. Rev.*, **9,** 84 (1917), and many others subsequently.

from ferroferric oxide. A pure iron catalyst (918 red.) and a promoted one (660 red.), obtained by reduction at the same temperature, were photographed before and after being heated in hydrogen for four hours at 650° under identical conditions. The patterns resulting from 918 and 660 before they were heated were identical and perfect photographs of α-iron; *after being heated,* the promoted catalyst showed a few streaks characteristic of large crystals, but the pattern from 918 contained so many of these streaks from single crystals that the exact positions of the diffraction lines themselves could scarcely be distinguished.

Powder photographs were made from promoted catalysts 435 and 421 which had been subjected to severe tests as ammonia catalysts, during which they were heated continuously at 450–500°, and at a pressure of 100 atmospheres for four months. In view of the experiments with 918 and 660 this long heating should produce large iron crystals if no inhibiting influence were present. These photographs, however, *gave no evidence* of crystal growth.

Qualitative account of the X-ray diffraction patterns from the various materials employed in this investigation is given in Table VII.

Table VII

X-Ray Patterns of Catalyst Materials

Catalyst	Predominant patterns	Other patterns	Remarks
909	Fe_3O_4	Fe_2O_3	....
918	Fe_3O_4	FeO	....
926	Fe_3O_4	FeO	FeO stronger than 918
928	Fe_3O_4	FeO	FeO stronger than 926
958	FeO	None	....
954	Fe_3O_4	None	Al_2O_3 = excess FeO
955	Fe_3O_4	FeO	Al_2O_3 = $^1/_2$ excess FeO
940	Fe_3O_4	None	....
952 Å.	Fe_3O_4	None	....
918 red.	Fe	None	....
660 red.	Fe	None	....
922 red.	Fe	None	No large crystals
435 red.	Fe	None	No large crystals. Life tested
421 red.	Fe	None	....
918 red. heated	Fe	None	Many large crystals
660 red. heated	Fe	None	A few large crystals

Discussion of Results

Accumulated data on the activity of reduced artificial magnetites used in preparing ammonia catalysts show the advantage of using a fused iron oxide as near the composition Fe_3O_4 as possible. Since the method used in preparing these ammonia catalysts yields a magnetite containing a small excess of ferrous oxide, one advantage of using aluminum oxide and potassium aluminate is suggested by the present results. Combination of this excess of ferrous oxide with the excess of aluminum oxide from the promoter yields ferrous aluminate which then goes into solid solution in the ferroferric oxide. By this reaction the composition of the bulk of the unreduced material is adjusted towards that of a spinel and the atoms of the alumina are given a very uniform distribution throughout the magnetite. A similar effect should be shown on artificial magnetites containing an excess of hematite when promoted by magnesium oxide. This adjustment of composition of the iron oxide towards ferroferric oxide can also be obtained by adding such acidic oxides as silica and zirconia if the original material contains an excess of ferrous oxide.

The present experiments bring out one fundamental difference between pure iron and iron promoted for ammonia synthesis. Under the conditions where crystals in iron containing no promoter grow rapidly, crystals of iron in the best catalysts grow very slowly. A promoter thus maintains a large surface of iron in good catalysts by preventing or inhibiting the sintering of the reduced iron. This "guard" action would be expected to arise from a very fine-grained distribution of the promoter throughout the reduced iron.

Such a uniform distribution is best obtained if the admixture of promoter in unreduced magnetite is as intimate as possible. The extreme case of molecular homogeneity will be obtained if the promoter is in solid solution in ferroferric oxide. The preceding experiments show that magnetites promoted by aluminum oxide certainly are, and those promoted by potassium aluminate may be, such solid solutions. A good, though less perfect, distribution results when the promoter is soluble in molten ferroferric oxide and when the latter is cooled so rapidly that the promoter material which separates on solidification remains as minute crystals. The promoter compounds in unreduced magnetites promoted with silica and zirconia are probably in such a fine state of mechanical admixture. A mechanism of distribution intermediate between the two described above arises when the promoter can form solid solutions with magnetite at high temperatures, but is less soluble at room temperatures. It is conceivable that magnetites promoted by potassium aluminate may be such unmixed solid solutions.

The "guard" action of promoters postulated above is in agreement with the fact that the optimum effect on the activity of ammonia catalysts occurs within certain limits of promoter concentration. As the concentration of promoter is diminished below a lower limit, the characteristics of the reduced catalyst become more and more nearly those of pure reduced magnetite. In the region above an upper limit the number of guards becomes so large that they actually interfere with the accessibility of the iron to the reactants.

Other evidence supporting the action of promoters in preventing crystal growth is found in the inhibiting effect[9] of small amounts of thorium dioxide on the growth of tungsten crystals in non-sagging filaments.

Since the diffraction lines of iron in reduced catalysts show neither the individual streaks produced by large crystals nor the broadening charateristic of crystals of colloidal dimensions, their average length of edge (taken as cubes) may be estimated to lie in the range between 1×10^{-6} cm. and about 1×10^{-3} cm. In this wide range, differences in crystal size cannot be distinguished by any existing X-ray methods. It is, therefore, compatible with the present experimental results that large differences do exist in this range among the average crystal sizes of reduced pure iron and various reduced promoted catalysts. This may account in part for the large differences actually found in their catalytic activities.

These experiments on the physical properties of the reduced catalysts have a bearing on problems of metallurgy. After being heated in hydrogen at 650° for several hours, pure reduced iron (918 red.) is so soft and malleable that it cannot be ground; promoted iron (660 red.), on the other hand, remains comparatively hard and brittle after being heated. It has often been supposed that hardness in steels, for instance, arises from distortions in the structure of iron due to some sort of solid solution of carbon in iron crystals. In the present measurements on promoted iron catalysts, the photographs give no evidence of the diffuse broadening that would be expected from badly distorted crystals. This fact, combined with the absence of any difference in the size of the unit cells of crystals in pure and promoted iron samples, indicates that a state of persistent hardness can be produced in a metal by a small amount of finely divided material distributed between small metal crystals. These results thus show that, whether or not there actually is any solid solution of carbon in iron at room temperatures, it is unnecessary to assume such solution, or isomorphous replacement by carbon atoms, to account qualitatively for hardness in carbon steels.

In other catalysts where the physical structure or the activity is improved by promoters, it may well be that the mechanism of their action is similar to that found for ammonia catalysts. Whether or not this is true in any specific case can be determined, however, only by experiments on the particular catalysts concerned.

Summary

The length of the edge of the unit cube of magnetite is found to be $a_0 = 8.37 \pm 0.010$ Å. In magnetites containing an excess of ferrous iron this substance occurs as a separate phase. This phase disappears when an equivalent amount of the promoter aluminum oxide is added. The composition of the oxide is thus adjusted toward ferroferric oxide with the formation of ferrous aluminate which is apparently in solid solution in the magnetite. The value of a_0 for magnetite containing potassium aluminate differs so little from a_0 for pure ferroferric oxide that it is impossible to decide whether or not there is solid solution of one in the other.

[9] Smithells and others, *Trans. Faraday Soc.*, **1921**; *J. Inst. Metals*, **1922**; *Engineering*, **113**, 342 (1922).

The length of the edge of the unit cube a_0, of the α-iron obtained by reduction of magnetite is 2.859 ± 0.004 Å. The size of the unit cell of iron in the reduced material containing the promoters differs from that of pure iron by less than 0.1%. The presence of the composite promoter potassium and aluminum oxides in the reduced catalysts has been found to maintain a large surface of iron by preventing the rapid growth of the iron crystals.

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON AND THE FIXED NITROGEN RESEARCH LABORATORY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE PREPARATION AND CRYSTAL STRUCTURE OF FERROUS OXIDE

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RECEIVED JULY 23, 1925 PUBLISHED DECEMBER 12, 1925

Introduction

Numerous observations[1] on the existence of phases and phase equilibria in the system iron-oxygen are found in the literature. From them the lowest temperature at which ferrous oxide, FeO, is stable has been set at about 570°. As a result, products entirely free from ferric iron have never been prepared either by careful reduction[2] of a higher oxide or by precipitation[3] of ferrous hydroxide with subsequent removal of water. X-Ray diffraction data on oxides of iron exist only for pure ferric oxide[4] Fe_2O_3 and ferroferric oxide,[5] Fe_3O_4.

During the course of some X-ray measurements[6] on artificial magnetites, diffraction lines were found which were due to a phase richer in iron than magnetite but not due to iron itself. Efforts to establish the composition of this new phase have resulted in the preparation of a material which is essentially ferrous oxide.

The method of making this oxide and a determination of its crystal structure form the basis of this paper.

Preparation of Ferrous Oxide

An oxide of the average composition Fe_3O_4 was made by burning Armco iron in oxygen. Armco iron rods were added to this burned material in the proportion of one

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[1] See Eastman, THIS JOURNAL, **44**, 975 (1922), for a review of the evidence; also Eastman and Evans, *ibid.*, **46**, 888 (1924).

[2] Hilpert and Beyer, *Ber.*, **44**, 1608 (1911).

[3] Friend, "Textbook of Inorganic Chemistry," Griffin and Co. (London), vol. IX, part 2, p. 109. Sosman, *J. Washington Acad. Sci.*, **7**, 55 (1917). Ferguson, *Can. Chem. Met.*, **7**, 175 (1923).

[4] Pauling and Hendricks, THIS JOURNAL, **47**, 781 (1925).

[5] W. H. Bragg, *Phil. Mag.*, **30**, 305 (1915).

[6] Wyckoff and Crittenden, THIS JOURNAL, **47**, 2866 (1925).