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The Modifications of the Carbide, Fe_2C; Their Properties and Identification

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In addition to the well-known carbides of iron, cementite and martensite, and the less-well-known iron acetylide, carbides of the formula Fe_2C have been reported. Recent X-ray diffraction studies by Halle and Herbst[3] indicate the existence of a carbide in which the iron atoms are arranged in hexagonal structure. X-Ray diffraction studies also were made by Hägg[4] and later by Jack[5] on a more complex iron carbide whose structure has not yet been worked out. Pichler and Merkel[6] have recently made thermomagnetic studies of iron carbides, and they conclude that there are two ferromagnetic iron carbides with the formula Fe_2C and with Curie points at 265° and 380°, respectively. Unfortunately, no X-ray diffraction experiments were made by Pichler and Merkel; and similarly Hägg, Jack, and Halle and Herbst made no thermomagnetic measurements. It is therefore impossible to interpret the thermomagnetic studies in terms of the X-ray diffraction studies and *vice versa*.

The chief purpose of this paper is to determine the relationship between the Fe_2C carbides which were reported in thermomagnetic studies and those reported in X-ray diffraction studies. In addition, the results obtained with iron catalysts in this paper have made possible a general unification of data presented in the literature.

Experimental

Thermomagnetic Analysis.—This method of analysis is based on the observation that every ferromagnetic phase loses its ferromagnetism at a temperature characteristic of the phase, known as the Curie point. The method has been described by many authors (see, for example, Lange and Mathieu[7]).

The magnetic balance used has been previously described.[8,9] The balance suspension assembly is shown in Fig. 1. A strong torsion wire (about 0.1° twist per gram-centimeter torque) was used. The sample holders used for the iron synthetic ammonia catalyst consisted of 6 mm. i. d. graded vitreous silica to Pyrex seals which were closed at the silica end and provided with a standard taper joint at the Pyrex end. (This sample holder is particularly useful for determining Curie points at high temperatures but was not essential to the experiments here described.) The sample holders used for the copper-promoted, precipitated iron catalysts were 7-mm. o. d. Pyrex tubes, closed at one end and also provided with a standard taper at the other. The samples were held in position at the bottom of the sample holders by means of Pyrex glass wool plugs. A coin-silver cap (i. d. 8.8 mm., o. d. 13.9 mm., length 38.4 mm., bottom thickness 2.5 mm.), provided with a groove on the inside for a thermocouple and its porcelain protective tube, was slipped over the end of the sample holders. This cap assured a uniform temperature distribution throughout the sample and also the identity of the temperature of the thermocouple with that of the sample. The junction of the thermocouple was placed as near the sample as possible. Two non-ferromagnetic thermocouples were used, platinum–platinum + 10% rhodium, or Chromel–constantan. To insure unrestricted motion of the suspension assembly, the ends of the thermocouple dipped into two mercury pools from which two wires, identical with those of the thermocouple, led to an ice-bath cold junction. The furnace consisted of an Alundum thimble about 0.9 cm. long and 1.5 cm. i. d., wound non-inductively with asbestos-covered 24-gage Nichrome wire, and insulated on the outside with a layer of asbestos paper. It was supported between the poles of the magnet by a brass holder and was adjusted so that it made no contact with the suspension assembly.

Normally, a thermomagnetic analysis is made by heating the unknown sample sufficiently slowly in the magnetic balance so that the magnetic moment can be measured at suitable intervals. The magnet is operated at a field strength of 2160 gauss. When a predetermined temperature has been reached, the heating is stopped, and the sample is allowed to cool slowly so that the magnetic moment can again be measured at suitable intervals. The whole process takes about one to two hours. Due to the excellent thermal characteristics of this system, the curves obtained on heating and cooling can be very nearly superimposed in every case where the sample has undergone no change during heating.

The thermocouples were calibrated in the following boiling baths, using proper pressure corrections: water, naphthalene, benzophenone and sulfur.

X-Ray Diffraction Analysis.—The X-ray diffraction studies were carried out with a simple Debye–Scherrer powder camera of 71.62 mm. inside diameter. Radiation, as obtained from a sealed-off iron target X-ray tube equipped with beryllium windows and manganese dioxide filters, was used. The tube was operated at 40 p.k.v. and 7.0 milliamperes. The samples were preserved under petroleum ether. They were ground to a fine paste while still wet with petroleum ether, mixed with collodion, and partly extruded from a short section of 19-gauge, 0.7-mm. i. d. stainless steel tubing. This procedure was effective in preventing oxidation of the samples, which otherwise were quite pyrophoric. The diameters of the diffracted rings on the films from which the d/n values were obtained were determined by measuring to the outside of the ring and subtracting the sample diameter (0.7 mm.).

Preparation of Carbide in Synthetic Ammonia Catalyst.—The synthetic ammonia catalyst used was a commercial preparation obtained from the Hercules Powder Company. Its chemical analysis is as follows: Iron as Fe_3O_4, 92.6%; magnesium as MgO, 4.2%; silicon as SiO_2, 0.7%; and chromium as Cr_2O_3, 0.4%. This catalyst has been tried in the Fischer–Tropsch testing units previously described,[10] and yields of 70 g. of solid and liquid hydrocarbons were obtained per cubic meter of synthesis gas (one part carbon monoxide and one part hydrogen) per single pass over 50 cc. of catalyst at 255°.

The reduction and carburization of the catalyst were

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[3] Group Leader Conference Ludwigshafen, T.O.M. Reel 26, Bag 2463. Report Dr. Wenzel, T.O.M. Reel 134, Item II/10.

[4] G. Hägg, *Z. Krist.*, **89**, 92 (1934).

[5] K. H. Jack, *Nature*, **158**, 60 (1946).

[6] H. Pichler and H. Merkel, Ph.D. thesis describing work carried on at the Kaiser Wilhelm Institut für Kohlenforschung. A translation of this document will be published in a Bureau of Mines Technical Paper.

[7] H. Lange and K. Mathieu, *Mitt. Kaiser-Wilhelm Inst. Eisenforsch. Düsseldorf*, **20**, 239 (1938).

[8] L. J. E. Hofer, W. C. Peebles and W. E. Dieter, THIS JOURNAL, **68**, 1953 (1946).

[9] R. Buehl and J. Wulf, *Rev. Sci. Instruments*, **9**, 224 (1938).

[10] R. B. Anderson, A. Krieg, B. Seligman and W. E. O'Neill, *Ind. Eng. Chem.*, **39**, 1548 (1947).

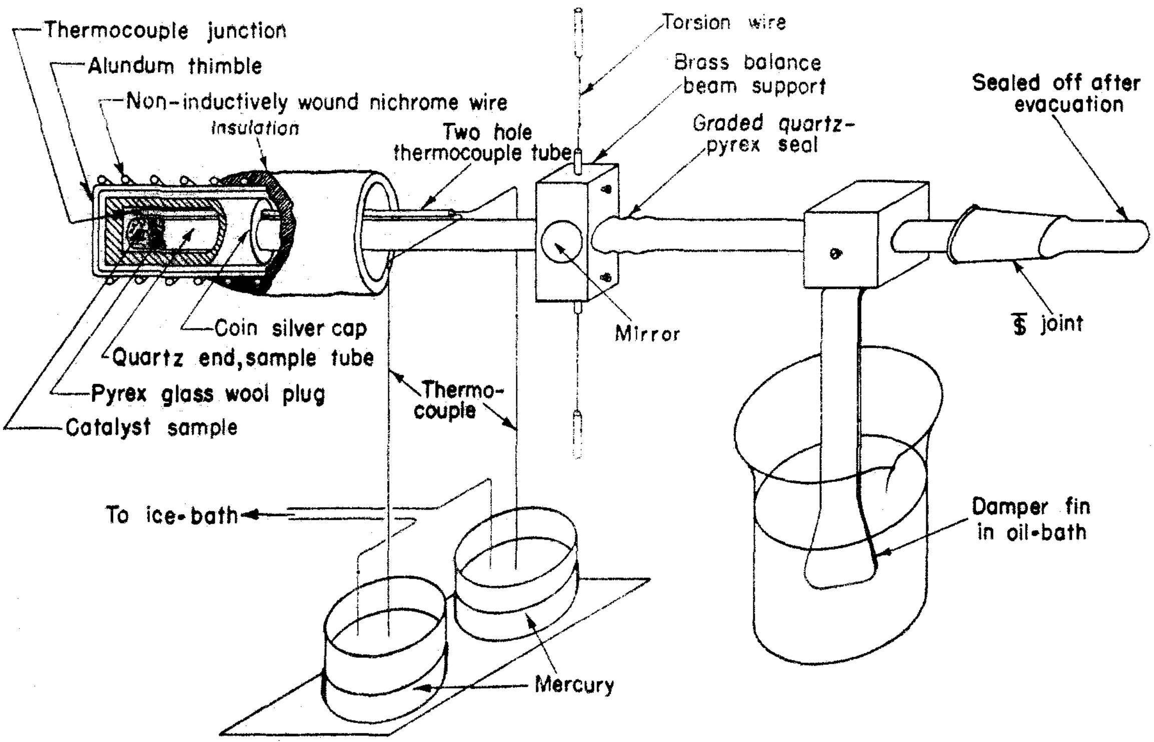

Fig. 1.—Schematic diagram of suspension assembly with quartz-Pyrex sample tube. The direction of the field and the field gradient is perpendicular to the plane of the paper.

carried out in an apparatus similar to that previously described.[11] Samples of about 5 g. each were weighed into four reaction vessels, which were placed side by side in the aluminum block furnace. A stream of electrolytic hydrogen (flowing at 0.75 liter per hour and purified by passage over palladized asbestos at 360°, soda lime, Ascarite and anhydrous magnesium perchlorate) was admitted to the reaction vessels. The temperature was maintained at 450°. During this time the reaction vessels were periodically disconnected and weighed. After eighty-two hours, the change in weight was less than 0.05 mg. per hour per sample.

At this point carburization was started. The carbon monoxide used in the carburization was made from formic acid and orthophosphoric acid at 150–200°. It was purified over sodium hydroxide, copper at red heat, soda lime and anhydrous magnesium perchlorate. The carburization was carried out at 240° for 539 hours. During this time the reaction vessels were periodically disconnected and weighed. (The samples were heated and cooled in an atmosphere of nitrogen to prevent carbonyl formation.) The weight increase observed is due almost entirely to the deposition of carbon rather than of oxygen. This was demonstrated by the fact that the products of hydrogenation of similar carburized catalysts are not absorbed in anhydrous magnesium perchlorate. The results of the carburization are summarized in Fig. 2. The final, average carbon:iron ratio (for 3 tubes) was 0.1164 (theoretical for Fe_2C is 0.1076).

The reaction vessel was opened in a carbon dioxide atmosphere to prevent oxidation.

Preparation of Carbide in Iron–Copper–Potassium Oxide (100:10:0.32) Catalyst.—This catalyst is analogous to those used at the Kaiser Wilhelm Institut für Kohlenforschung.

Ferric nitrate nonahydrate (41.35 lb.) and copper nitrate trihydrate (2.17 lb.) were dissolved in 22.5 gallons of distilled water. A sodium carbonate solution (18.10 lb. in 20 gallons of distilled water) was made. Sixteen gallons of this solution were added to the nitrate solution at room temperature. The mixture was then heated to 70°, and the remaining carbonate solution (at room temperature) was added to form the precipitate. The mixture was then heated rapidly to boiling and held there for several minutes, after which it was filtered in a filter press and washed with 400 gallons of hot distilled water until the filtrate was free of nitrate ion. The filter cake was then dropped from the press and mixed into a smooth paste with a solution of 13 g. of potassium carbonate dissolved in 2 liters of distilled water. The catalyst was then dried at 105–110° for forty-eight hours.

The activity of this catalyst, when tried in the Fischer-Tropsch testing units, gave yields of 103 g. of liquid and solid hydrocarbons per cubic meter of synthesis gas (one part carbon monoxide and one part hydrogen) per pass over 50 cc. of catalyst at 236°.

The reduction and carburization were carried out with the same apparatus and using a procedure similar to that described above for the iron-synthetic ammonia catalyst. After reduction with hydrogen for 327 hours at 220°, the 7-g. samples did not vary more than 0.05 mg. per hour. The carburization (as shown in Fig. 2) was carried out at 188° for 211 hours when the carbon:iron ratio (average for 3 reaction tubes) had reached 0.1072. In a similar experiment a catalyst carburized at 205° for 239 hours to a carbon:iron ratio of 0.1068 lost all but 18% of the carbon as methane when heated with hydrogen at 250°. Thus the carbon in this catalyst was held largely as carbidic carbon.

The reaction vessel was opened in an atmosphere of carbon dioxide to prevent oxidation. The samples for the magnetic balance were transferred to sample holders in a carbon dioxide atmosphere, connected to a high-vacuum system, evacuated for two hours, and then sealed off.

Results

Carburized Iron Synthetic Ammonia Catalyst.—The X-ray diffraction powder pattern of this

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[11] L. J. E. Hofer and W. C. Peebles, This Journal, **69**, 893 (1947).

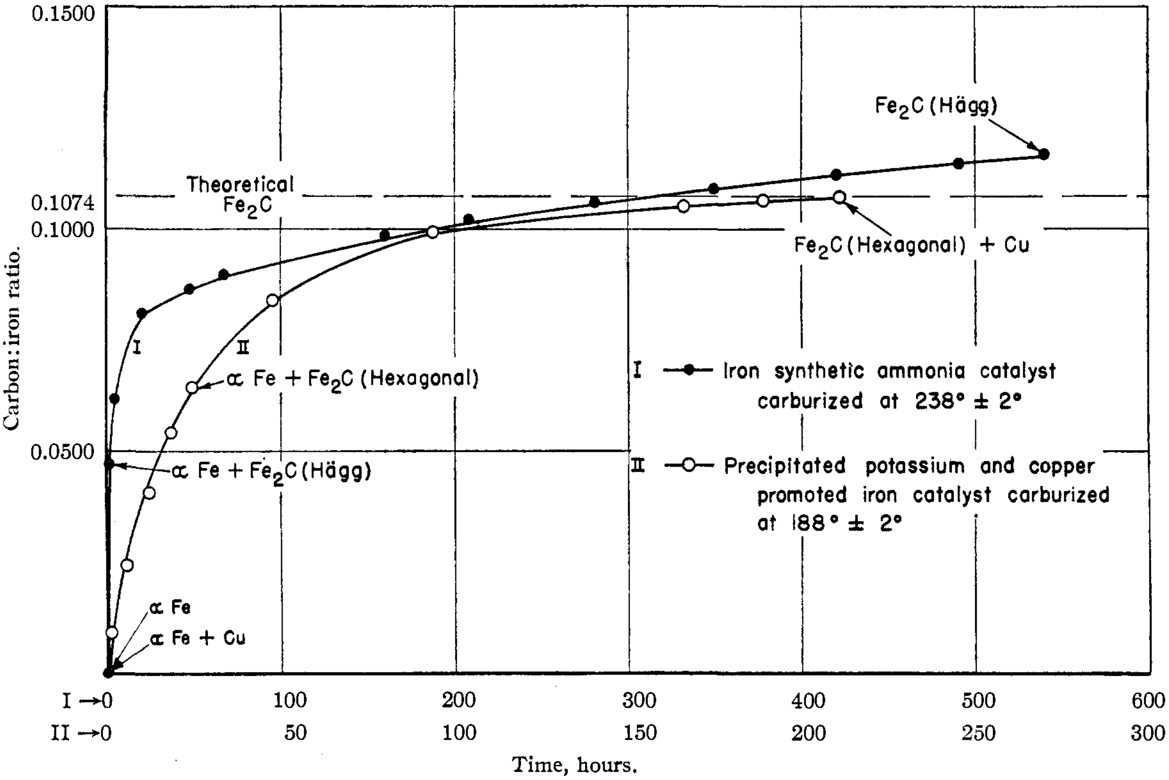

Fig. 2.—Carburization of two types of iron Fischer–Tropsch catalysts.

product was that of the Hägg[4] carbide. The d/n values obtained are compared with those reported by Hägg in Table I, column 2. The diffraction pattern was diffuse, and some of the weaker lines reported by Hägg are missing; nevertheless, the match is good. Comparison of the pattern of Hägg carbide with that of cementite (column 1) reveals some similarities, but both patterns have enough characteristic lines to make identification positive.

TABLE I

COMPARATIVE X-RAY DIFFRACTION DATA FOR CEMENTITE, HÄGG CARBIDE AND THE HEXAGONAL CARBIDE

(1) Cementite data Westgren (calcd.)	d/n	hkl	Sample 7-68 I	d/n	(2) Hägg carbide data Hägg I	d/n	Sample 7-255 I	d/n	(3) Hexagonal iron carbide data hkl	Sample 8-20 I	d/n
					w−	2.64	vw	2.62			
					w	2.49	w	2.48			
1800	2.38	112			w+	2.41	w	2.39			
1900	2.37	021	M	2.37					100	w	2.38
1600	2.26	200	w	2.25	M	2.27	M	2.26			
					vw	2.24					
1400	2.18	120	w	2.18	M	2.20	M	2.18			
					w	2.18					
									200	M	2.16
3800	2.10	121	w	2.10	w+	2.10					
3800	2.06	210	M	2.06	S	2.07	vS	2.06	101	vS	2.08
3500	2.02	022			S	2.04	vS	2.03			
6300	2.01	103	vS	2.01	w	2.01					
					w	2.00					
3700	1.97	211	M	1.97	w	1.97	w(br)	1.98			
					w+	1.91	M	1.91			
3400	1.87	113	M	1.87							
4200	1.85	122	M	1.85							
					M	1.81	S	1.80			
					w	1.76	vw	1.76			
					w(br)	1.72	vw	1.72			

Table I (*Continued*)

(1) Cementite data					(2) Hägg carbide data				(3) Hexagonal iron carbide data		
Westgren			Sample 7-68		Hägg		Sample 7-255			Sample 8-20	
I	(calcd.) *d/n*	*hkl*	*I*	*d/n*	*I*	*d/n*	*I*	*d/n*	*hkl*	*I*	*d/n*
430	1.68	004									
1100	1.68	023	w	1.68	w(br)	1.68	vw	1.67			
					vw(br)	1.625					
					vw	1.623	vw	1.62			
									102	M	1.60
1600	1.58	130	w	1.58	M	1.57	S	1.57			
950	1.51	222									
240	1.51	114	w	1.51	w	1.51	vw	1.50			
					w	1.47					
					w	1.41					
510	1.401	024	vw	1.403							
					w	1.38	vw	1.37	110	M	1.37
					w	1.33	vw	1.34			
6200	1.324	312	M	1.322	w	1.32	vw	1.32			
					w(br)	1.27	w	1.27			
					w	1.25	w	1.25	103	M	1.24
3200	1.219	140	M	1.222							
400	1.211	313	M	1.214							
					S	1.21	M	1.21			
580	1.200	141			w	1.20					
280	1.190	224	M	1.189	w(br)	1.19	w	1.17			
4800	1.157	233	S	1.159	w(br)	1.16	w	1.16	112	M	1.16
190	1.152	134							201		
540	1.148	125									
170	1.146	142	M	1.149	M	1.15	w	1.14			
750	1.127	400									
3500	1.126	215									
4600	1.122	330									
2300	1.121	006	S	1.124	S	1.12	M	1.13			
4800	1.102	043	S	1.104	w(br)	1.10	w(br)	1.11			
2000	1.094	314	vw	1.096							
					w(br)	1.08	w(br)	1.09			
1800	1.085	411	vw	1.087							
2000	1.050	225									
1100	1.045	412	w	1.052							
1400	1.017	421	vw	1.002							
1500	1.003	206	w	0.992							
6800	0.991	243	M(br)	0.986							

vS = very Strong, S = Strong, M = Medium, w = weak, vw = very weak, + = slightly more intense, — = slightly less intense, br = broad.

The thermomagnetic curve for this product is given in Fig. 3, curve I. The temperature was not raised above 300° so as not to decompose the sample. The values obtained during the first heating (circles) correspond very closely to those obtained during the first cooling (X's), showing that the sample remained unchanged. Furthermore, a second heating and cooling (not shown) gave the same results. As an additional check on the thermal stability of the sample at temperatures up to 300°, another sample (with which a thermomagnetic curve similar to Fig. 3, curve I, had been obtained) was removed for X-ray diffraction analysis and found to consist of Hägg carbide. Thus the average Curie point at 247° is undoubtedly characteristic of the Hägg carbide. The uncertainty in this value as determined by thermomagnetic curves on different samples of this and similar products is ±3°. It will be noted that the magnetic moment at 300° is not zero. This is probably due either to some residual iron which was not converted to carbide, or to some magnetite formed during the carburization. The observed magnetic moment above the Curie point of the Hägg carbide can be accounted for by not more than 2% metallic iron or 6% magnetite.

The above-described sample was then heated at 580° for two hours and the thermomagnetic curve shown in Fig. 3, curve II, was obtained. This curve has a Curie point at 208°, considerably lower than that of curve I. After curve II was obtained, the sample was removed for X-ray diffraction analysis which proved that the sample contained cementite. The diffraction pattern was very sharp, and in Table I, column 1, the measured *d/n* values for the sample are compared with the

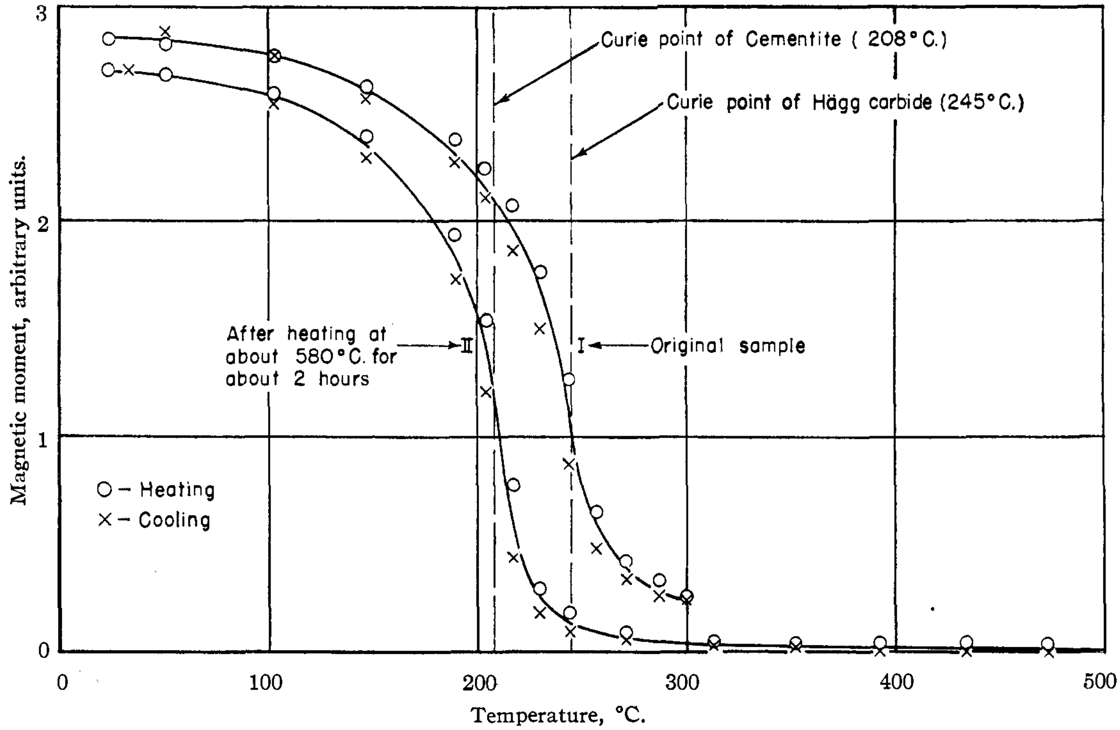

Fig. 3.—Thermomagnetic curves showing: I, presence of Hägg carbide in iron synthetic ammonia catalyst; II, same catalyst decomposed into cementite.

reported values for cementite as determined by Westgren.[12] (Only that part of Westgren's data is shown for which his calculated intensities are greater than 500 of his arbitrary units.) The agreement is very good. The Curie point, 208°, also checks the Curie points given for cementite in the literature, which range from 205° to 220°. (This wide range is due in part to experimental difficulties and in part to a certain arbitrariness in the definition of the term "Curie point." In the present paper, it has been defined as the point of inflection in the thermomagnetic curve.) Thus the Hägg carbide, with its characteristic diffraction pattern and its 247° Curie point, reacts at a sufficiently high temperature to form cementite with a different diffraction pattern and a different Curie point, according to the reaction

$$\underset{\text{Hägg Carbide}}{3Fe_2C} \longrightarrow \underset{\text{Cementite}}{2Fe_3C} + \underset{\text{Free Carbon}}{C}$$

As can be seen from the curves in Fig. 3, the magnetic moment due to the Hägg carbide is roughly the same as that of an equivalent amount of cementite, since both curves were made on the same sample and with the balance at the same adjustment. Furthermore, the equivalent amounts of cementite and Hägg carbide are nearly equal in weight. As a result, the specific magnetizations of cementite and Hägg carbide must be about the same, or about 139 c. g. s. units per gram, according to Lange and Mathieu.[1]

Carburized Iron–Copper–Potassium Oxide (100:10:0.32) Catalyst.—The X-ray diffraction pattern contained faint lines due to the 200, 220, 311 and 222 reflections of face-centered copper metal. In addition, the relatively strong lines presented in Table I, column 3, were present. (One of the lines of the hexagonal iron carbide as observed in the diffraction pattern, the 2.08 Å., 101 line of the hexagonal carbide, coincides with the 111 line of copper. However, since this line is by far the strongest line of the pattern and since the copper lines are relatively weak due to the low percentage of copper, the high intensity of this line must be due to the hexagonal carbide.) No other lines were observed in the pattern.

Thermomagnetic analysis gave the curves shown in Fig. 4. During the first heating two Curie points were found, one at 247° and one at 380°, indicating the presence of two different ferromagnetic phases. As has been demonstrated, the first Curie point can be identified with the Hägg carbide. The occurrence of this phase is somewhat surprising because no lines from the X-ray diffraction pattern of the Hägg carbide could be detected. The other phase with the Curie point at 380° is unstable and decomposes below 435°, for upon cooling from 435° the curve (X's) does not coincide with the first heating curve (circles) but instead is the curve of a typical Hägg carbide. Similar experiments with other samples of this same preparation show that the 380° Curie point carbide decomposes appreciably in the range

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[12] A. Westgren, *Jernkontorets Ann.*, **114**, 457 (1932).

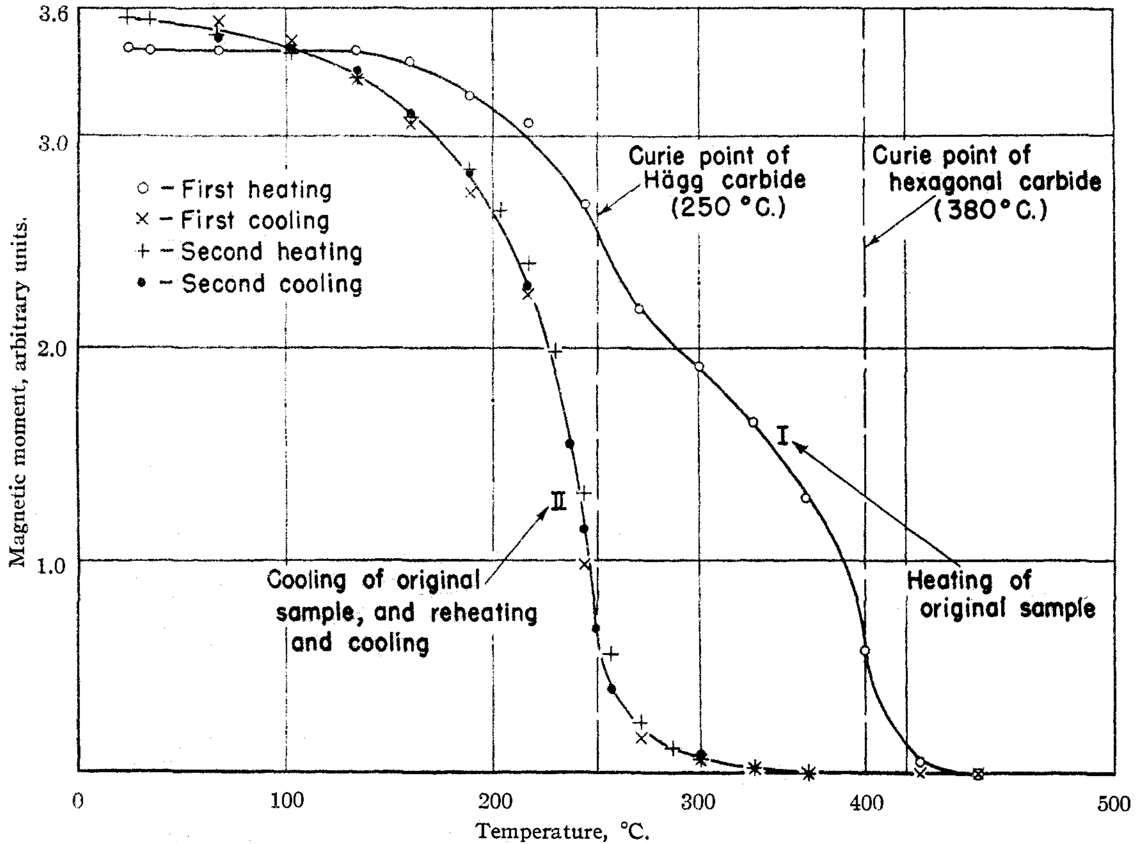

Fig. 4.—Thermomagnetic curves showing the presence of the Hägg and hexagonal iron carbides in copper-promoted Fischer–Tropsch catalyst, and the reversibility of the Hägg carbide curve.

300–380°. If the thermomagnetic measurements are made sufficiently rapidly, the point of inflection of the curve is invariant at 380° showing that it is a real transition temperature. The magnetic moment at 435° is very nearly zero, showing that no measurable amount of metallic iron or magnetite was present at that point. A second heating curve (crosses) and a second cooling curve(heavy dots) again coincided with the curve for Hägg carbide, showing the stability of the carbide under the conditions. This sample, when removed from the magnetic balance for X-ray diffraction analysis, was found to contain only Hägg carbide and copper. From these experiments one must conclude that the unstable carbide (Curie point 380°) is none other than the hexagonal close-packed iron carbide.

Since the formula of the Hägg carbide is nearly Fe_2C, as determined by both Hägg[4] and Jack,[5] and since the gross formula of this preparation is also Fe_2C, the formula of the hexagonal carbide must be Fe_2C. This formula can also be based on the similarity of structure between the hexagonal carbide and Fe_2N, which had been studied by Hägg.[13]

The over-all magnetic moment of the original sample is nearly the same as that of the Hägg carbide formed from it. Since the formulas of the two carbides are the same, one must conclude that the specific magnetization of the two carbides is the same, namely, about 140 c. g. s. units. Since the specific magnetization of both the Hägg carbide and the hexagonal carbide is known and since both carbides have the same formula, one can estimate the fraction of each carbide present from the shape of the thermomagnetic curve (Fig. 4, curve I). Calculated in this way, the Hägg carbide in the carburized catalyst is 10–30% of the total carbide.

Using the method previously described[14] and using the lattice parameter of face-centered cubic copper as 3.608kX, the lattice parameters of the hexagonal carbide were determined as a_0 = 2.749kX, c_0 = 4.340kX, and a_0/c_0 = 1.579.

In other experiments, the thermal stability of Hägg carbide was shown to be about the same in this catalyst as in the iron synthetic ammonia catalyst.

Discussion

The 247° Curie point carbide or Hägg carbide is readily identified as the 265° Curie point carbide of Pichler and Merkel, since it was produced under similar conditions and behaved similarly. The

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[13] G. Hägg, *Z. physik. Chem.*, **B8**, 455 (1930).

[14] L. J. E. Hofer and W. C. Peebles, This Journal, **69**, 2497 (1947).

Curie points are sufficiently close together to support this identification. This carbide can also be identified with the so-called "cubic ferric sesquioxide saturated with potassium oxide" of Lefebvre and LeClerc.[15] This phase develops in iron Fischer–Tropsch catalysts during synthesis in the same way as the 265° Curie point carbide of Pichler and Merkel. Claims are made by both Lefebvre and LeClerc and by Pichler and Merkel that the phase improves the characteristics of the catalyst. Lefebvre and LeClerc place the Curie point at 250°, which is very close to that found in the present paper. On the other hand, Lefebvre and LeClerc present no positive evidence, such as X-ray diffraction data, that the phase with the 250° Curie point is really the cubic ferric sesquioxide (γ Fe_2O_3) saturated with potassium oxide, which has been described in the literature. This *bona fide* cubic ferric sesquioxide saturated with potassium oxide does not have a Curie point at 250° but does have one at 630°.[16] From fragmentary data[17] it appears that the Hägg carbide (Curie point found about 250°) was also formed in Rheinpreussen (Moers, Ruhr Valley) catalysts during synthesis, although the distinctly different carbide was not recognized as such but was termed "unstable cementite."

The 380° Curie point carbide or hexagonal carbide is evidently the same as Pichler and Merkel's 380° Curie point carbide. Pichler and Merkel emphasized the importance of copper in promoting the formation of this carbide.

TABLE II

COMPARATIVE *d/n* VALUES OF THE HEXAGONAL CLOSE-PACKED CARBIDE WITH THOSE OF THE CARBIDES OF TUTIYA, HOFMANN AND GROLL, AND BRILL AND MARK

vS = very Strong, S = Strong, M = Medium, w = weak, vw = very weak.

Hexagonal Close-Packed Carbide		Tutiya	Hofmann and Groll		Brill and Mark
d/n	*I*	*d/n*	*d/n*	*I*	*d/n*
2.38	w	2.32	2.263	M	2.28
2.16	M	2.20	2.172	M	...
2.08	vS	2.065	2.050	S	2.12
		1.815	1.802	w	1.826
		1.706	...		1.716
		...	1.543	M	...
		...	1.465	w	1.491
1.37	M	1.377	1.372	w	1.367
1.24	M	1.251	1.244	vw	...
		1.212	1.212	M	1.206
1.16	M	1.165	1.167	M	1.148

This carbide may possibly be identified with the carbides of Tutiya,[18] Hofmann and Groll,[19] and Brill and Mark.[20] For purposes of comparison the X-ray diffraction data of all three groups of investigators are compared with those for the hexagonal iron carbide in Table II. With the exception of a few extra lines contained in the data of Tutiya, and Hofmann and Groll, the data of these authors agree very well with those for the hexagonal carbide. The data of Brill and Mark, however, bear little resemblance to those for the hexagonal carbide.

The hexagonal carbide forms the carbon-rich extreme of the series of hexagonal close-packed ϵ-phase carbonitrides studied by Jack.[3]

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Summary

1. The existence of two carbides of iron with formula Fe_2C and having Curie points at 247° and 380° has been confirmed. (Pichler and Merkel reported the Curie points at 265° and 380°, respectively.)

2. A hexagonal close-packed carbide of iron has been prepared; this carbide has properties similar to those of the carbide described by Halle and Herbst.

3. The identity of the 380° Curie point carbide of Pichler and Merkel with the hexagonal carbide has been established.

4. The identity of the 247° (265° according to Pichler and Merkel) Curie point carbide with the Hägg carbide has been established.

5. The carbides reported by Hofmann and Groll and by Tutiya seem to be the hexagonal carbide.

6. The hexagonal carbide decomposes above about 300° to Hägg carbide which in turn decomposes at about 550° in one hour to cementite and free carbon.

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[15] H. Lefebvre and G. LeClerc, *Compt. rend.*, **203**, 1378 (1936); H. Lefebvre and G. LeClerc, *Congres. chim. ind. Compt. rend.*, 98th Congr. Nancy, France, Sept.–Oct., 1938, 725; G. LeClerc, *Compt. rend.*, **207**, 1099 (1938).

[16] A. Michel, *Ann. chim.*, **8**, 317 (1937).

[17] FIAT Reel 116, frames 1673–1683.

[18] H. Tutiya, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **10** 556 (1931).

[19] U. Hofmann and E. Groll, *Z. anorg. allgem. Chem.*, **191**, 414 (1930).

[20] R. Brill and H. Mark, *Z. physik. Chem.*, **133**, 443 (1928).