TABLE 21.—*Formation of free carbon during synthesis*

[Carburizing conditions: Temperature, 325°C.; CO pressure, 0.1 atmosphere. Synthesis conditions: Initial temperature, 235°C.; pressure, 15 atmospheres; gas composition, $3CO + 2H_2$]

Experiment No.	Operating time (weeks)	Temperature (°C.)	Contraction (percent)	Free carbon (grams/10 grams Fe)
1	0	—	—	1.75
	1	235	52	2.12
	3	235	55	2.37
2	0	—	—	1.85
	16	235	50	3.92
3	0	—	—	2.21
	78	235 to 285	55–45	7.97
4	0	—	—	1.75
	11	235	40	2.02

Table 22 shows the results of three experiments with synthesis gas of different compositions. Since conversion of carbon monoxide is more nearly complete at low temperatures with a hydrogen-rich synthesis gas than with a carbon monoxide-rich synthesis gas, an initial temperature of 190°C. was used in experiment 1. The carbon monoxide : hydrogen ratio of experiment 3 corresponded to the consumption ratio during synthesis. Consequently, it produced the maximum hydrocarbon yield in a single stage. In experiments 1 and 2 the gas had to be recycled and carbon monoxide added before each cycle.

TABLE 22.—*Formation of free carbon as a function of synthesis-gas composition*

[Pressure, 15 atmospheres]

Experiment No.	Temperature (°C.)	Operating time (days)	Synthesis-gas ratio ($CO : H_2$)	Free carbon (grams/10 grams Fe)	Contraction (percent)
1	190	0	1 : 4[b]	2.21	—
	200[a]	60		1.88	30
2	210	0	1 : 2	2.21	—
	225[a]	151		2.51	35
3	235	0	3 : 2	1.85	—
	240[a]	112		3.92	50

[a] Temperature required to maintain constant conversion.

[b] The low carbon monoxide content resulted in smaller contraction despite the high hydrogen content of the synthesis gas and low synthesis temperature, which favor the formation of water rather than carbon dioxide.

These three experiments show that undesirable carbon deposits depend largely on the composition of the synthesis gas. In experiment 1 less free carbon was present at the end of the experiment than at the beginning. This condition was similar to that found in an iron catalyst decarburized with hydrogen at 263°C., where less free carbon was found on acid decomposition after hydrogenation (see above). In experiment 3, a considerable amount of carbon was formed owing to the high carbon monoxide content.

Formation of carbon may therefore be avoided by use of hydrogen-rich synthesis gas and low reaction temperature. A series of parallel experiments showed that the composition of the catalyst is important. For instance, catalysts that were alkalized to increase the yield of solid paraffins formed more free carbon than nonalkalized catalysts.

Further study of iron catalysts used for medium-pressure synthesis showed that the disadvantages of carbon formation on promoted catalyst could be avoided by using technical water gas for the synthesis.

SUMMARY

The composition of iron catalysts used in medium-pressure synthesis was studied by means of acid decomposition. The more carbide formed during carburization, the greater was the activity of the catalysts during synthesis. Life of catalyst also increased with higher carbide content. The large amount of carbide present after pretreatment decreased during the first days of operation to 0.2–0.4 gram of carbidic carbon per 10 grams of iron in an active catalyst. There was a corresponding increase in the oxygen content to 0.1–0.2 gram per 10 grams of iron. The catalysts maintained this carbide–oxide equilibrium for months. Acid decomposition of catalysts whose activity had decreased (contraction less than 40 percent) showed at most 0.1 gram of carbidic carbon per 10 grams of iron and a correspondingly high oxygen content.

Catalysts usually produced free carbon during medium-pressure synthesis; this tendency increased with higher operating temperature and with higher carbon monoxide content of the synthesis gas. At low operating temperatures (such as may be used with especially active catalysts) and with hydrogen-rich synthesis gas, carbon formation could be eliminated in medium-pressure synthesis.

THERMOMAGNETIC ANALYSIS

DESCRIPTION OF MAGNETIC BALANCE

The question of whether a single carbide or a mixture of carbides was formed during pretreatment could not be solved chemically. No indication was found as to the presence of free metal (known to be essential in cobalt and nickel catalysts) either during pretreatment or during synthesis. The large excess of hydrogen found upon acid decomposition (table 10) was another point still to be explained. It would have been unsatisfactory to attempt to determine the amount of carbidic carbon or a carbide formula from the carburization curve and from hydrogen-reduction data. However, the ferromagnetic properties of iron, iron carbide, and magnetite offered an approach to the problem; the spacing of their magnetic transition points (Curie points) is sufficiently far apart to make identification easy. A type of magnetic balance developed by Lange[9] was found to be suitable for measurements of this kind (fig. 10).

[9] Lange, H., and Mathieu, K., work cited in footnote 98.

The magnetic field was generated by a water-cooled electromagnet which produced a field gradient of 1,750 oersteds per centimeter within the region of motion of the sample, with an operating current of 4 amperes. The force of this field gradient was sufficient to indicate the Curie point for a few milligrams of ferromagnetic substance. A small, water-cooled electric furnace with a noninductive winding was installed between the poles of

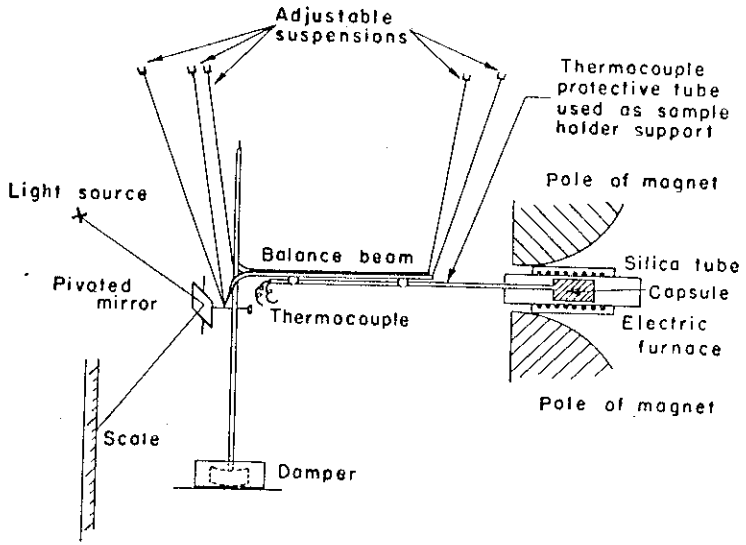

FIGURE 10.—Simplified schematic diagram of magnetic balance.

the electromagnet. Its temperature could be raised to about 900°C. by means of a resistance coil. The quartz tube of the furnace contained the thermocouple tube (sample-holder support) to which the brass sample holder was fastened. The latter had a capacity of 0.3 to 0.4 cubic centimeter of material. The sample-holder support was attached to the balance beam, which was suspended from thin copper wires that could be adjusted so that the system formed by the balance beam, thermocouple, sample holder and its support swung freely in the quartz tube of the furnace.[10] [11]

[10] Lange, H., and Mathieu, K., work cited in footnote 98.

[11] EDITOR'S NOTE.—It was thought desirable to include a fuller description of the apparatus and procedure. The following information was supplied by Dr. H. Pichler from memory, and the drawing and numerical values are approximations. Details of the assembly between the magnetic poles are shown in figure 11. The thin brass sample holder fitted tightly over the free-moving thermocouple tubing. The thermocouple junction was separated from the sample by a brass partition. The sample compartment was accessible from the end of the brass tube and could be closed with a brass cover. Numerous fine holes punctured the compartment walls to permit circulation of the nitrogen stream. The remainder of the assembly consisted of a silica tube, wound noninductively with nichrome wire, and surrounded by a layer of mica insulation and by a double-walled brass tube containing cooling water. This water-cooled heater was fitted with brass plates and fastened to the poles of the magnet.

The brass sample holder had an over-all length of about 4 cm., of which 1.5 cm. was slipped over the thermocouple tubing. The sample compartment was about 2.5 cm. in length and about 0.5 cm. in diameter. The clearance between the sample holder and the silica tube was about 2 mm.

The samples studied by Pichler and Merkel were always heated at a uniform rate from room temperature to 800°C. in about 1 hour, except where indicated otherwise. After 800°C. was reached, the furnace was turned off, and the samples were allowed to cool.

The sample was pulled into the inhomogeneous field of the electromagnet. This attraction was counteracted by the force of the balance beam and pendulum. A damper made rapid readings possible. The deflection of the balance beam was indicated by a beam of light focused on a graduated scale by a rotating mirror. The magnification of the deflection could be adjusted.

Temperature was measured by means of a platinum–platinum-rhodium thermocouple whose junction was on the bottom of the

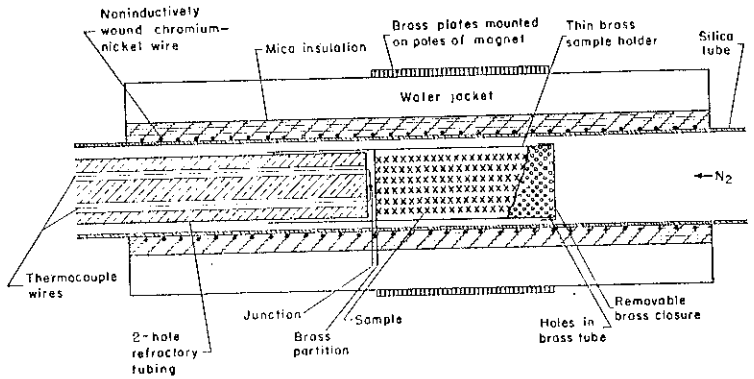

FIGURE 11.—Detail of sample holder and water-cooled furnace.

sample capsule. Since the electric furnace was water-cooled and relatively short, a marked drop in temperature was observed within the quartz tube from the center outward; this decreased the accuracy of the measurements. The temperature values were therefore considered accurate to within ±10°C.

Magnetic saturation was not determined, but the gradient of the magnetic field (in the range of movement of the sample) was determined as a function of the deflection of the beam of light. In an inhomogeneous field H, a sample of magnetic moment M experiences a force P in the direction of the gradient:

$$P = M \text{ grad } H.$$

The intensity of magnetization J (based on volume) is therefore

$$J = \frac{P}{V \text{ grad } H} \text{ Gauss.}$$

If the measurements are based on weight, the specific magnetization is

$$\sigma = \frac{J}{S} = \frac{P}{g \text{ grad } H}.$$

The gradient was determined by means of this equation with electrolytic iron (σ 218) as a standard.

Deflection of beam of light (cm.)	*Gradient (oersted/cm.)*
36.3	1,765
22	1,755
17.6	1,730
9.6	1,730

These experiments showed that the gradient was constant within the range of movement of the sample. The deflections were therefore assumed to be proportional to the force, that is, to the magnetic moment of the sample. Thus, when specific magnetization at saturation was known, the deflection was a measure of the quantity of ferromagnetic material present and accurate relative measurements could replace absolute measurements.

PRELIMINARY EXPERIMENTS

In the first experiment the sample holder was filled with precipitated ferric oxide, which was heated to 500°C. in a current of nitrogen and was then reduced in a stream of hydrogen. Figure 12 shows the magnetic moment as a function of the time

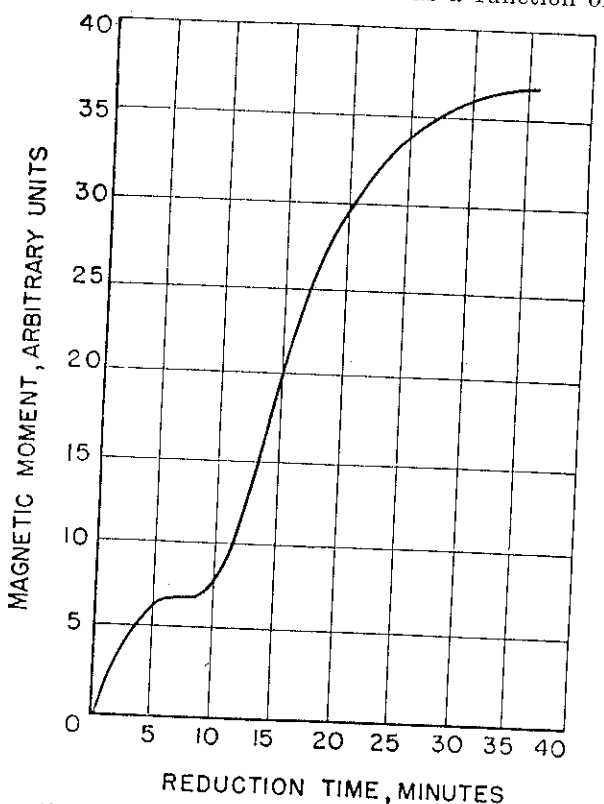

FIGURE 12.—Hydrogen reduction of Fe_2O_3 at 500° C. in magnetic balance.

during which the sample was exposed to hydrogen. At the beginning of the experiment the deflection was zero; in other words, ferric oxide showed no measurable magnetization (paramagnetic). During the first few minutes the magnetization increased sharply and then remained constant for several minutes, indicating a discontinuous reduction of ferric oxide. The first

increase in magnetization undoubtedly resulted from reduction to (ferromagnetic) magnetite. Further reduction of magnetite to metallic iron proceeded more slowly after a short induction period, and the magnetization approached a final value asymptotically.

Figure 13 shows the thermomagnetic curve for electrolytic

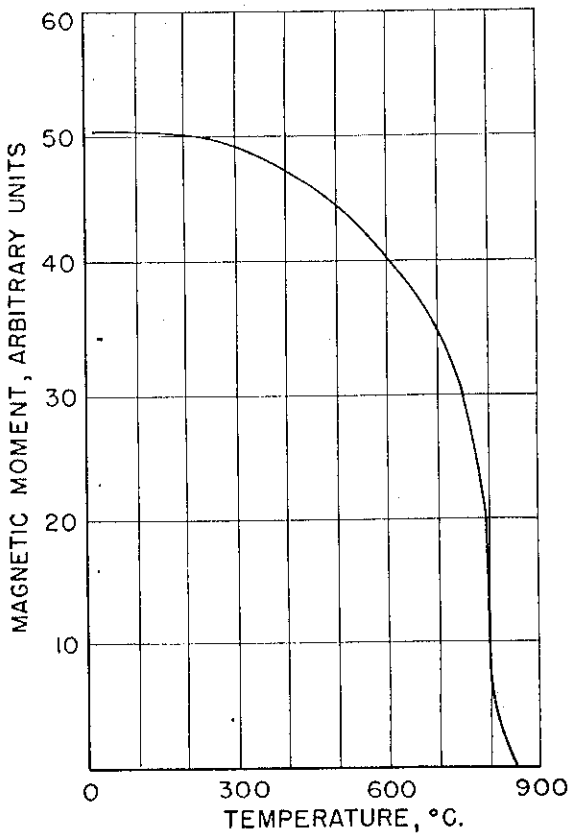

FIGURE 13.—Thermomagnetic curve of electrolytic iron.

iron, which was heated slowly to 800°C. The specific magnetization decreased slowly at first; at 600°C. the deflection had decreased from 50.5 to 40.0 divisions. Within the range of magnetic transition the decrease was very rapid. The Curie point was about 790°C.; at 800°C. the deflection was only 8 divisions.

FORMATION AND STABILITY OF HIGHER IRON CARBIDES

Preliminary experiments with the magnetic balance were followed by investigation of the formation of iron carbides by carburization of iron and iron oxide.

Since it was thought that water might affect them at higher temperatures, catalysts that had been carburized in different ways were stored under *n*-hexane, which was quite suitable because of its low boiling point and inert character. The hexane-saturated catalysts were placed in the sample holder, which was introduced into the center of the electric furnace and adjusted there in such a way as to allow it to move freely. During the entire procedure a current of oxygen-free nitrogen flowed through the quartz tube of the furnace.

An iron catalyst of the type used in medium-pressure synthesis was carburized with carbon monoxide (325°C., 0.1 atmosphere, 4 liters of carbon monoxide per hour per 10 grams of iron). Figure 14, curve I, shows the thermomagnetic curve for such a

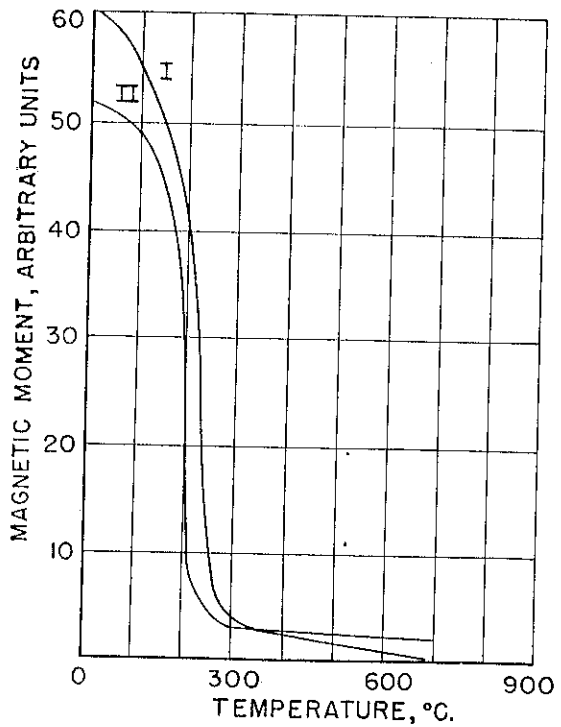

FIGURE 14.—Thermomagnetic curve of carburized, alkali-promoted iron catalyst: I, After carburization; II, after heating to 800° C. in nitrogen.

sample. The Curie point was 260°C. As will be seen from the following experiments, iron catalysts always exhibit this Curie point during carburization or synthesis, the average value of which was 265°C., as found in a large number of experiments. Comparison with the Curie points listed in table 3 shows that the ferromagnetic substance present was not identical with any known ferromagnetic iron compound and that this thermomagnetic curve probably shows a new iron carbide.

To obtain the data for curve I (fig. 14), the catalyst was heated to 800°C. in a stream of nitrogen. The effect of this treatment became apparent from a redetermination of the thermomagnetic curve (shown in curve II, fig. 14). It is clear that the ferromagnetic iron compound had undergone a change. The Curie point in the second curve was 208°C., 50°C. below that of curve I. The close agreement with the cementite Curie point (205°C., established by Mathieu on the same magnetic balance) showed that the iron carbide whose Curie point is 265°C. is unstable at higher temperatures and changes to Fe_3C. A further difference in the thermomagnetic behavior of the two iron carbides was shown by the fact that the thermomagnetic curve of

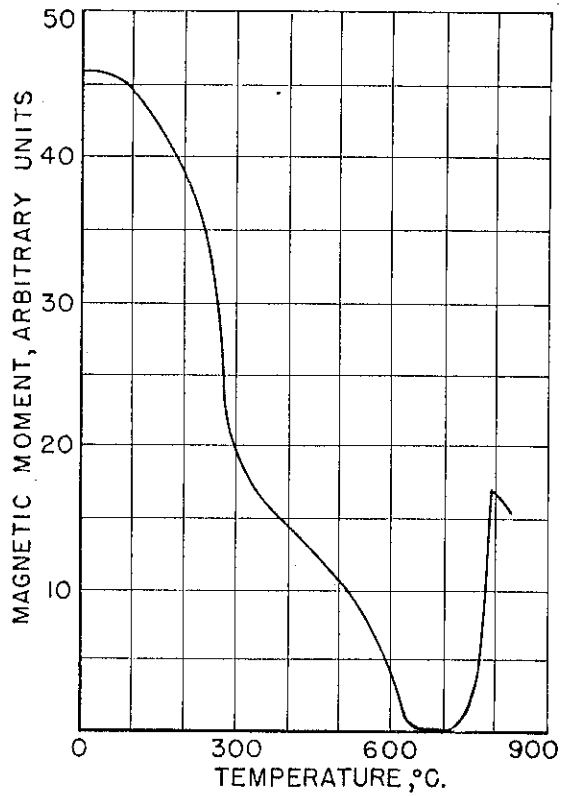

FIGURE 15.—Thermomagnetic curve of alkali-promoted (0.25 percent K_2CO_3) catalyst, reduced for 240 hours at 250°C., 1 liter H_2 per hour per 20 grams Fe; carburized for 219 hours at 220°C., 1 liter CO per hour per 20 grams Fe.

cementite (II) decreased far more slowly initially than that of the higher carbide (I).

Thermomagnetic analysis indicated formation of a homogeneous iron carbide at a carburization temperature of 325°C.; its carbide content had been determined by hydrogen reduction. Although the formula $Fe_{2.28}C$ thus derived cannot be considered definite

because of uncertainties inherent in the method, the values obtained indicated clearly that the new carbide was richer in carbon than Fe_3C, the only iron carbide whose composition is definitely known.

As observed by Bahr and Jessen, carburization (at 225°C.) of iron obtained by low-temperature reduction of Fe_2O_3 yields a carbide whose carbon content corresponds closely to the formula Fe_2C. To study this carbide, two active iron catalysts (iron–0.25 percent potassium carbonate and iron–1 percent copper–1.5 percent potassium carbonate) were reduced with hydro-

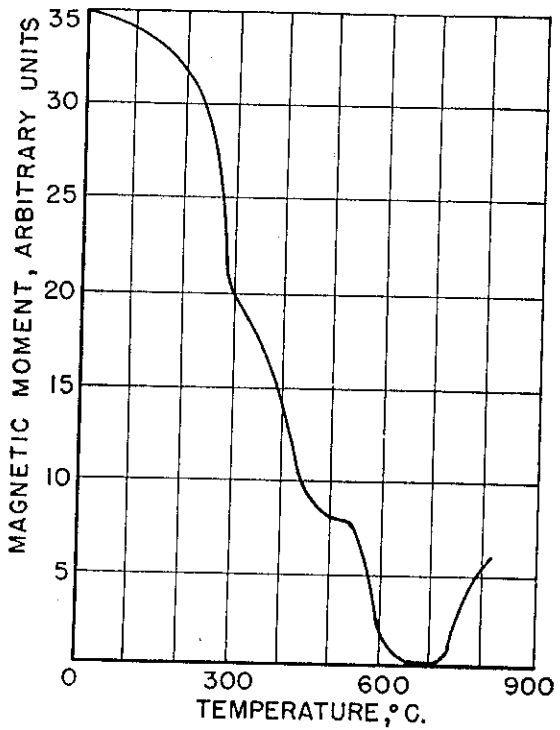

FIGURE 16.—Thermomagnetic curve of Fe, Cu, CO_3 (100 : 1 : 1.5) catalyst, reduced for 240 hours at 250°C. with 1 liter H_2 per hour per 20 grams Fe; carburized for 219 hours at 220°C. with 1 liter CO per hour per 20 grams Fe.

gen at 250°C. for 240 hours (1 liter of hydrogen per hour per 20 grams of iron) and carburized at 220°C. for 219 hours (1 liter of carbon monoxide per hour per 20 grams of iron). Figures 15 and 16 show the thermomagnetic behavior of the two carburized catalysts. The action of carbon monoxide at 220°C. led to the formation of the iron carbide whose Curie point is 265°C. However, this carbide did not form quantitatively, as it did at 325°C. Figure 15 shows a second Curie point at 600°C. The average value obtained from a large number of experiments was 595°C. A comparison with table 3 shows that this is the Curie point

of magnetite, Fe_3O_4, for which Curie points from 565° to 595°C. are reported. Reappearance of the magnetization above 700°C. pointed to the formation of free iron from the reaction between magnetite and iron carbide.

The thermomagnetic curve of the iron–1 percent copper–1.5 percent potassium carbonate catalyst was different (fig. 16). The decrease in magnetization occurred in three well-defined sections

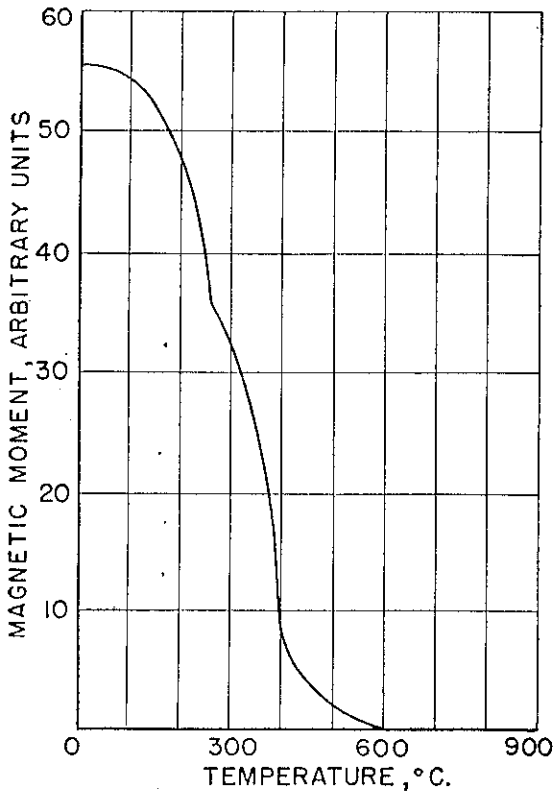

FIGURE 17.—Thermomagnetic curve of Fe, Cu, K_2CO_3 (100 : 1 : 0.25) catalyst, carburized at 205°C.

of the curve, which fused at about 300° and 500°C. The first section corresponded to the new iron carbide (Curie point, 265°C.). The second (300° to 500°C.), with a Curie point at 400°C., was new and did not correspond to any known ferromagnetic iron compound. Similar curves were obtained for a number of different catalyst samples. The carburization process was exactly that used by Gluud and Ritter[12] and by Bahr and Jessen.[13] The carbide formula (Fe_2C) derived by these authors therefore probably does not refer to a homogeneous substance.

[12] Gluud, W., Otto, K. V., and Ritter, H., work cited in footnote 87.
[13] Bahr, H. A., and Jessen, V., work cited in footnote 47.

Since the Curie point corresponding to the new compound could not be established with certainty on samples carburized above 220°C. (for instance, at 325°C.), it was assumed that low carburization temperatures are a necessary condition for its formation. Consequently another experiment was carried out with a highly active catalyst—Fe, Cu, K_2CO_3 (100 : 1 : 0.25) at an even lower carburization temperature (205°C.). The thermomagnetic curve for this experiment (fig. 17) shows that a much larger quantity of this higher iron carbide was formed under these reaction conditions. This carbide (Curie point, 380°C.) contributed the largest part of the total specific magnetization. The corresponding inflection in figure 16 was 20°C. higher. The difference between the two Curie points resulted from the fact that, in the first case, only a small amount of the carbide was formed. The change in the magnetic force was too small at first to overcome the inertia of the balance, thus shifting the Curie point toward a higher temperature. The carbide with the 265°C. Curie point was also formed in appreciable amounts, even at 205°C., as indicated by the first part of the curve of figure 17. The decrease in magnetization between 400°–600°C. was probably the result of decomposition reactions. It is interesting to note that extensive reduction and carburization of iron occurred, even at these low carburization temperatures.

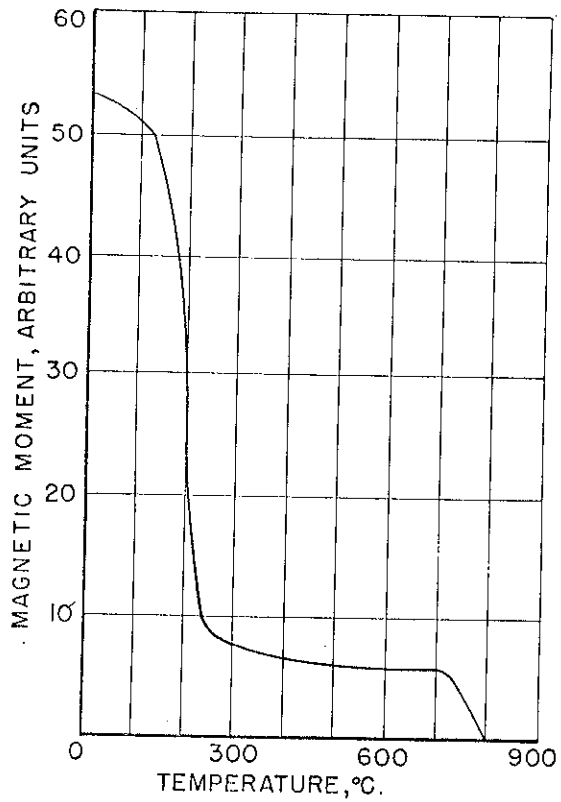

FIGURE 18.—Thermomagnetic curve of Fe, Cu, K_2CO_3 (100 : 1 : 0.25) catalyst, carburized at 205°C. and then heated to 800°C. prior to thermomagnetic analysis.

To determine the thermal stability of the 380°C. Curie-point iron carbide, the sample was heated to 800°C. in a second thermomagnetic analysis (fig. 18). After the first heating to 800°C., the 380°C. Curie-point carbide had disappeared completely and had been replaced by cementite, Fe_3C, and by some metallic iron, as shown by the decrease in magnetization above 700°C. The part of the curve corresponding to the 265°C. Curie-point carbide

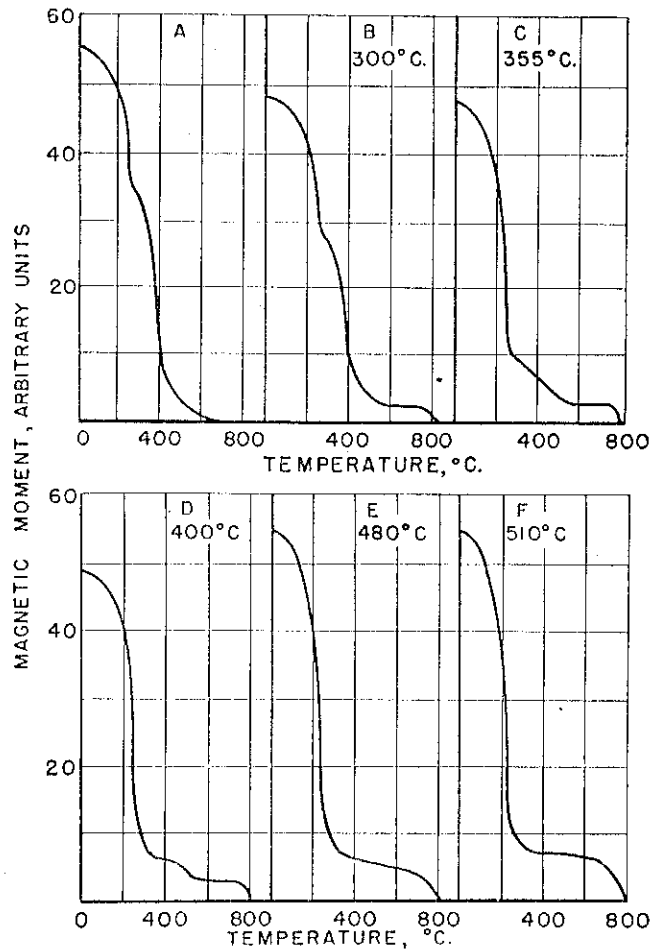

FIGURE 19.—Thermomagnetic curves showing thermal instability of higher iron carbides, obtained by carburization at 205°C. Samples *B* to *F* kept at indicated reaction temperature for 0.5 hour prior to thermomagnetic analysis as shown (100 Fe, 1 Cu, 0.25 K_2CO_3 catalyst).

was also absent, this compound was converted to cementite, as already noted in figure 14.

Figure 19 shows graphically the results of a systematic study of the thermal stability of the new iron carbides. Figure 19,*A*, represents the thermomagnetic curve of the catalyst after carburization at 205°C. The samples used for the experiments represented in figure 19, *B–F*, were heated in flowing nitrogen to 300°, 355°, 400°, 480°, and 510°C., respectively, and maintained at these temperatures for 0.5 hour. Thermal treatment at 300°C. produced little change in the carburized catalyst; however, the formation of metallic iron was perceptible (fig. 19,*B*). Treatment at 355°C. resulted in considerable decomposition of the 380°C. Curie-point carbide, whose presence was still clearly indicated by the virtually linear drop of the magnetic moment between 230° and 470°C. The unstable carbide was partly converted to the 265°C. Curie-point carbide (fig. 19,*C*.). Treatment at 400°C. left only a small quantity of the 380°C. Curie-point carbide. The 265°C. Curie-point carbide remained unchanged, as shown by the Curie point (figure 19,*D*). At 480°C., the 380°C. Curie-point carbide disappeared completely. The amount of free iron increased considerably. The 265°C. Curie-point carbide also suffered changes, as shown by the drop in the Curie point to 230°C. (fig. 19,*E*). At 510°C., the 265°C. Curie-point carbide disappeared completely. In its place appeared cementite, which is the decomposition product of both the higher carbides. The amount of free iron increased still further (fig. 19,*F*).

The effect of a current of hydrogen at ordinary pressure on the two higher iron carbides was also determined. For this purpose, iron catalysts containing both the 265°C. Curie-point and 380°C. Curie-point carbides were treated for 3 hours at 230° to 240°C. with a current of hydrogen in the sample holder of the magnetic balance. No change in magnetic moment was observed after this treatment or after displacement of hydrogen by nitrogen.

CARBURIZATION OF IRON CATALYSTS FOR MEDIUM-PRESSURE SYNTHESIS

The effect of carburization was studied on three catalysts that differed appreciably in activity and in the type of products synthesized. The procedure for preparation was the following: Iron filings were dissolved in dilute nitric acid, and the solution was neutralized and divided into three parts. The first fraction was heated to boiling and precipitated as usual with a sodium carbonate solution. It was then washed with hot water until the water was no longer alkaline and dried in an oven at 105°C. This catalyst therefore consisted essentially of iron hydroxides. The second fraction of the iron nitrate solution was precipitated and washed in the same manner. It was then alkalized with 0.25 percent of potassium carbonate, based on the iron content. This was the so-called "standard" iron catalyst that was used for the first part of this work. Copper nitrate was added to the last portion of the iron nitrate solution before precipitation. After precipitation and washing as before, it was alkalized with potassium carbonate, so that it contained 1 percent of copper and 1.5 percent of potassium carbonate, based on iron.

Unpromoted iron oxide was unsuitable as a catalyst but useful for comparison with pure iron oxides for which carburization experiments were cited in the literature survey. The "standard" catalyst containing 0.25 percent of potassium carbonate and the

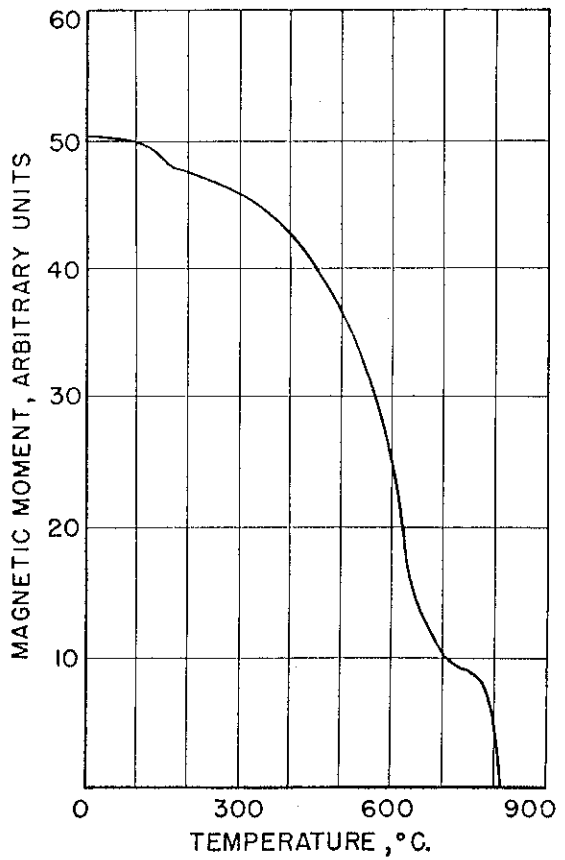

FIGURE 20.—Thermomagnetic curve of unpromoted iron oxide, after carburization for 12 hours at 325°C. and 0.1 atmosphere, 8 liters CO per hour per 10 grams Fe.

catalyst containing 1 percent of copper and 1.5 percent of potassium carbonate differed not only in activity but also in the type of products synthesized. The former was a typical gasoline catalyst yielding principally liquid and light hydrocarbons. The latter yielded a larger amount of solid paraffins because of the presence of more alkali.

CARBURIZATION OF IRON OXIDE

The iron oxide obtained by precipitation was treated in an aluminum block oven at 325°C., with a current of carbon monoxide at 0.1 atmosphere and a flow rate of 8 liters per 10 grams of iron per hour (standard carburization conditions) for different intervals. Normal hexane was introduced into the catalyst tube after cooling for protection of the carburized product. After carburization for 12 hours, the sample gave the thermomagnetic curve shown in figure 20. The major part of the magnetization was due to magnetite, and above 700°C. to metallic iron (Curie point, 770°C.). The sample showed no ferromagnetism above 850°C.

After carburization for 25 hours, the magnetic curve showed that the amount of free iron had increased appreciably at the expense of magnetite (fig. 21). The iron curve was again char-

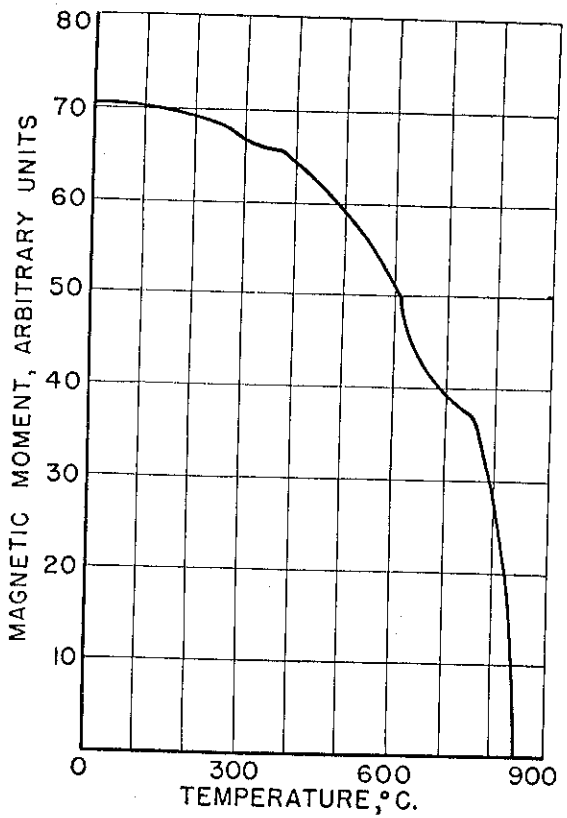

FIGURE 21.—Thermomagnetic curve of unpromoted iron oxide, after carburization for 25 hours at 325°C. and 0.1 atmosphere, 8 liters CO per hour per 10 grams Fe.

acterized by its sharp Curie point. Iron carbide had also formed, as indicated by a slight decrease in magnetization between 250°

and 300°C. Although most of the ferric oxide was reduced to free metal, the amount of carbide formed remained small, indicating that the production of free iron is not necessarily accompanied by formation of carbide. Iron can remain unchanged in an atmosphere of flowing carbon monoxide; the physical structure of the catalyst must create the conditions under which carbon (from carbon monoxide) can combine with iron to give iron carbide.

The same sample of catalyst was cooled and subjected to a second thermomagnetic analysis to determine the effect of thermal treatment (fig. 22). Comparison with figures 20 and 21 showed that the first heating caused extensive changes. This was particularly noticeable in the sharp drop of the initial magnetization from 70 divisions before heating to 27 divisions after heating. The magnetic moment (fig. 22) remained unchanged up to about

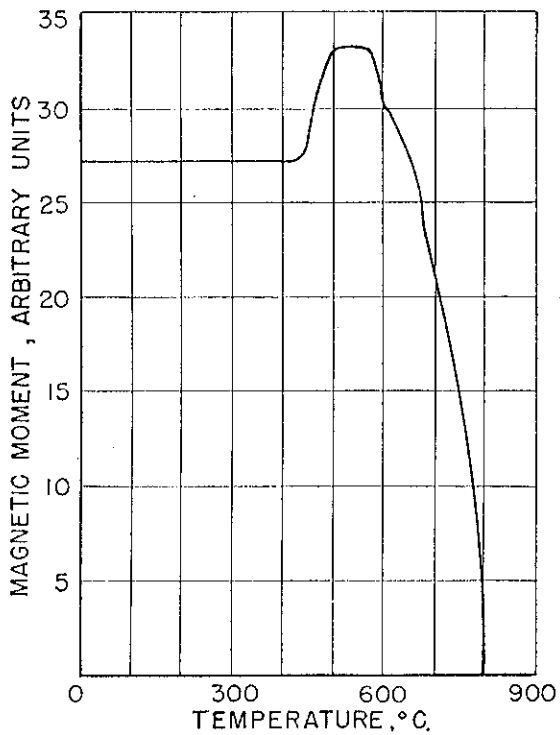

FIGURE 22.—Thermomagnetic curve, after heating to 800°C., of unpromoted iron oxide which had been carburized for 25 hours at 325°C. and 0.1 atmosphere, 8 liters of CO per hour per 10 grams of Fe.

440°C. Thereafter, it increased, then decreased in the magnetite region (Curie point, 600°C.) and finally dropped almost vertically in the region corresponding to metallic iron.

CARBURIZATION OF AN ALKALIZED IRON CATALYST

The "normal" iron catalyst containing 0.25 percent of potassium carbonate was carburized under the same conditions as the unpromoted iron catalyst. Figure 23 shows the results of carburization for 5 hours The largest part of the magnetization was due to magnetite. The course of the curve between 200° and 300°C. indicated the formation of higher carbide, although the Curie point remained rather vague. The curve shows an inflection as low as 150°C., which will be discussed later.

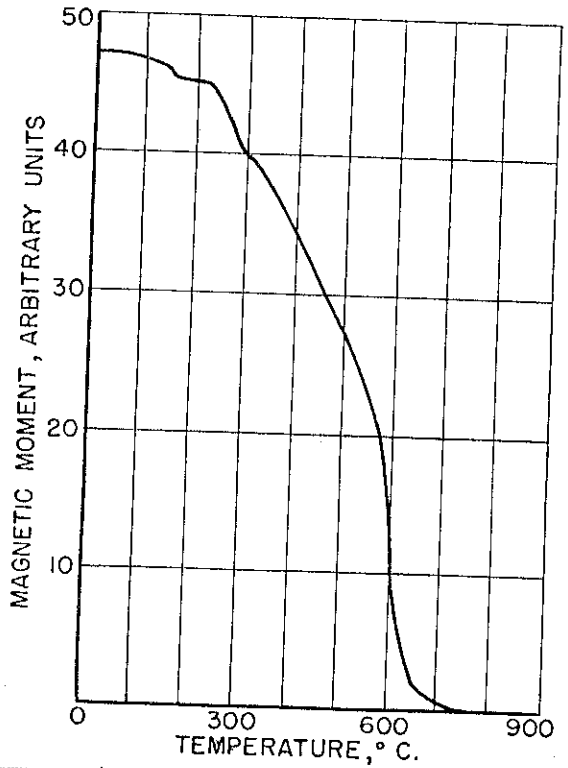

FIGURE 23.—Thermomagnetic curve of alkalized (0.25 percent K_2CO_3) iron oxide, after carburization for 5 hours at 325°C. and 0.1 atmosphere, 8 liters of CO per hour per 10 grams of Fe.

The effect of temperature on the magnetization of the catalyst after carburization for 12 hours is shown in figure 24. Formation of the 265°C. Curie-point carbide had increased to the point of accounting for almost 50 percent of the magnetization, the other 50 percent being due to magnetite. The magnetization increased again above 650°C., and the abrupt drop in the curve above 700°C. shows that metallic iron was formed.

The magnetic behavior of the catalyst after carburization for 25 hours is shown in curve I of figure 25. The proportion of iron carbide to magnetite had increased very little as compared with the previous experiment. Further reduction and carburization of this catalyst proceeded very slowly. Since the carbon dioxide content of the tail gas during pretreatment was lower than that for iron–magnetite equilibrium, this behavior must be attributed to the low reactivity of the catalyst under the carburizing conditions. Curve II (fig. 25) shows the magnetization of the same sample after it had previously been heated to 800°C. The curve coincides with the curve of the first heating at higher temperatures. Carbide and oxide had reacted to yield free iron.

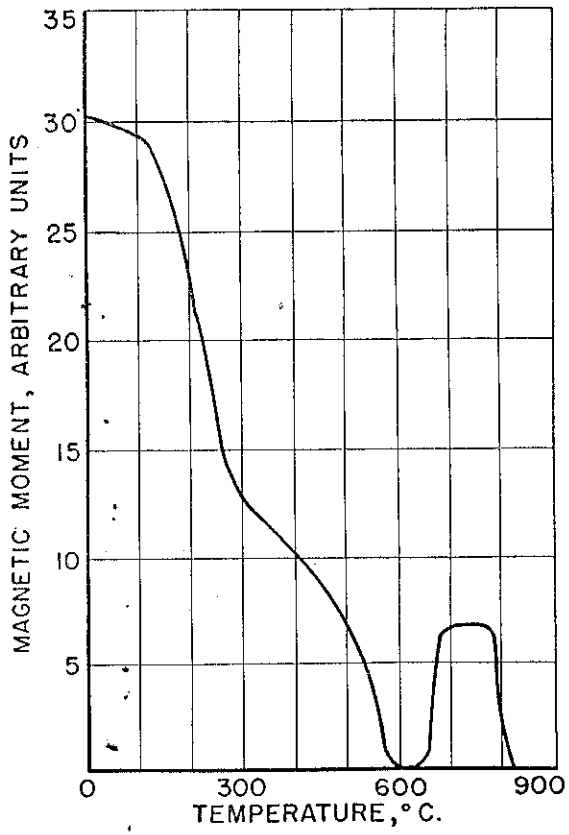

FIGURE 24.—Thermomagnetic curve of alkalized (0.25 percent K_2CO_3) iron oxide, after carburization for 12 hours at 325°C. and 0.1 atmosphere, 8 liters CO per hour per 10 grams Fe.

CARBURIZATION OF AN ALKALIZED IRON CATALYST CONTAINING COPPER

The iron–1 percent copper–1.5 percent potassium carbonate catalyst was similarly treated with carbon monoxide. Figure 26 shows the thermomagnetic curve after carburization for 0.5 hour. Comparison with figure 23 shows that carburizing the copper-

containing catalyst for 0.5 hour is equivalent to carburizing the copper-free catalyst for 12 hours. This is a proof of the extremely high reactivity of the copper-promoted catalyst during carburization. Magnetite was reduced rapidly to carbide.

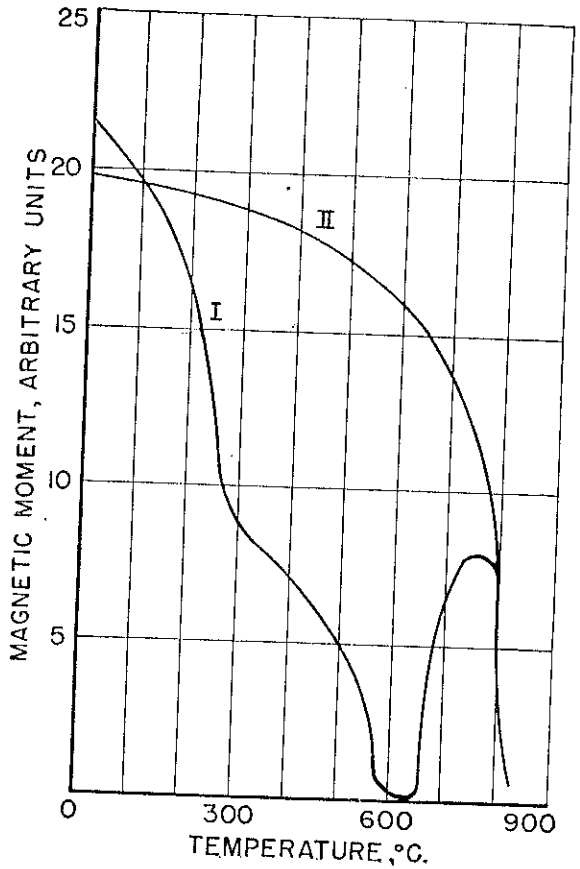

FIGURE 25.—Thermomagnetic curves of alkalized (0.25 percent K_2CO_3) iron oxide, after carburization for 25 hours at 325°C. and 0.1 atmosphere, 8 liters of CO per hour per 10 grams of Fe: I, Freshly carburized sample; II, after heating to 800°C.

Figure 27 is the thermomagnetic curve after carburization for 5 hours. Comparison with the previous experiment shows that the composition changed appreciably. The largest fraction was the 265°C. Curie-point carbide, whereas the magnetic contribution of magnetite was very small. The course of the curve between 350° and 400°C. indicates the presence of the 380°C. Curie-point carbide. This result shows the pronounced tendency of this catalyst to form carbide. After the same period of carburization, the less active iron–0.25 percent potassium carbonate catalyst consisted almost entirely of magnetite. The iron oxide preparation contained little carbide even after carburization for 25 hours.

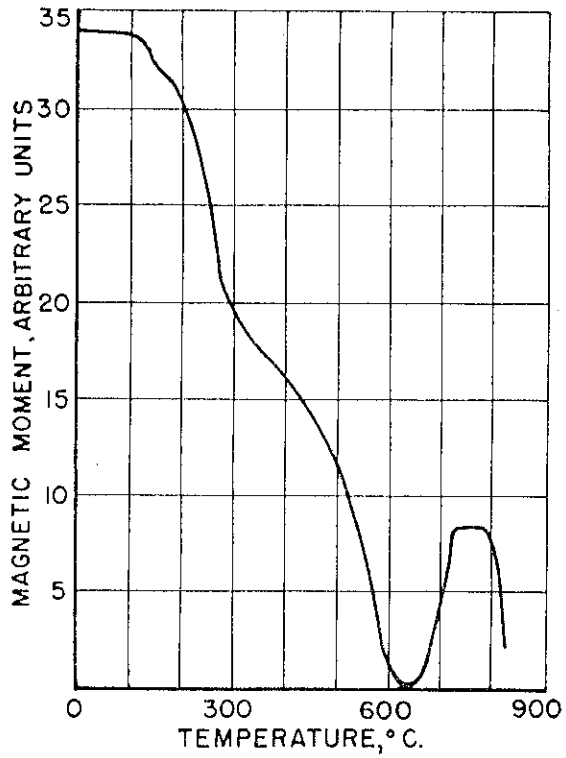

FIGURE 26.—Thermomagnetic curve of Fe, Cu, K_2CO_3 (100 : 1 : 1.5) catalyst, after carburization for 0.5 hour at 325°C. and 0.1 atmosphere, 8 liters of CO per hour per 10 grams of Fe.

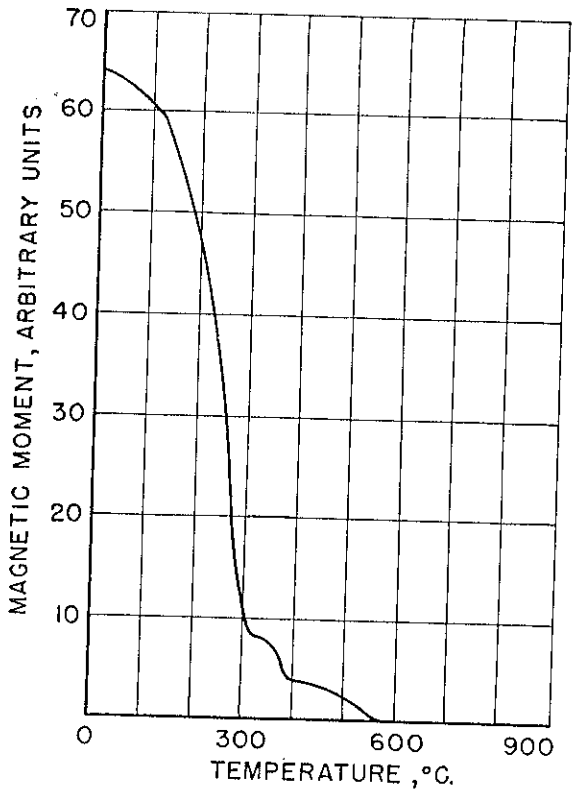

FIGURE 27.—Thermomagnetic curve of Fe, Cu, K_2CO_3 (100 : 1 : 1.5) catalyst, after carburization for 5 hours at 325°C. and 0.1 atmosphere, 8 liters of CO per hour per 10 grams of Fe.

Figure 28 is the thermomagnetic curve for the same sample after heating to 800°C. The small amount of magnetite observed previously (temperature range, 400° to 550°C., fig. 27) was absent after heating. The magnetization disappeared below 400°C.; that is, the catalyst consisted exclusively of cementite, which is paramagnetic at that temperature.

Another sample of the catalyst consisted almost entirely of the 265°C. Curie-point carbide after carburization for 12 hours (fig. 29). Magnetite was no longer detectable. The decrease in magnetization starting at about 320°C. was probably due to the 380°C. Curie-point carbide whose ferromagnetism disappears above 450°C. Carburization for 25 hours and for 62 hours produced the same results as were obtained in the preceding experiment (fig. 30, curve I). Cementite again formed as a result of the first heating (curve II). Whereas the magnetization due to cementite disappeared at 350°C., the magnetization of the original product decreased only slowly above 350°C., indicating that in this experiment, too, the 380°C. Curie-point carbide probably was

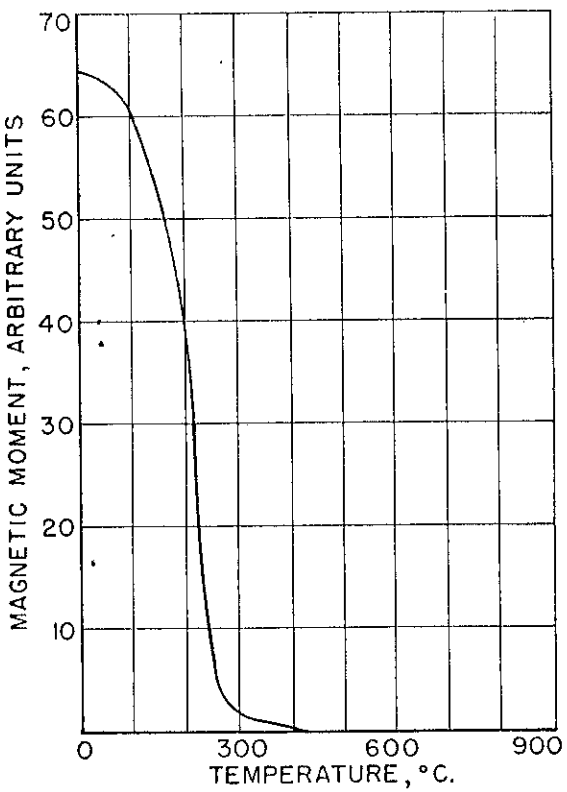

FIGURE 28.—Thermomagnetic curve, after heating to 800°C., of Fe, Cu, K_2CO_3 (100 : 1 : 1.5) catalyst which had been carburized for 5 hours at 0.1 atmosphere and 325°C., 8 liters of CO per hour per 10 grams of Fe.

present in small amounts. Both curves in figure 30 show that the values of the specific magnetization of the two carbides are nearly the same because the deflections at room temperature were almost identical.

These copper-promoted iron catalysts were exceptionally reactive, even when treated with synthesis gas (carbon monoxide : hydrogen = 1 : 2) at 100°C. Figure 31 shows the thermomagnetic analysis of an iron–1 percent copper–0.25 percent potassium carbonate catalyst, treated with synthesis gas at 100°C. for 24 hours. The fact that even at this low temperature hematite was reduced to magnetite shows that the data given in the literature for the minimum temperature at which carbon monoxide and hydrogen react with ferric oxide (180° and 280°C., respectively) are of limited value.

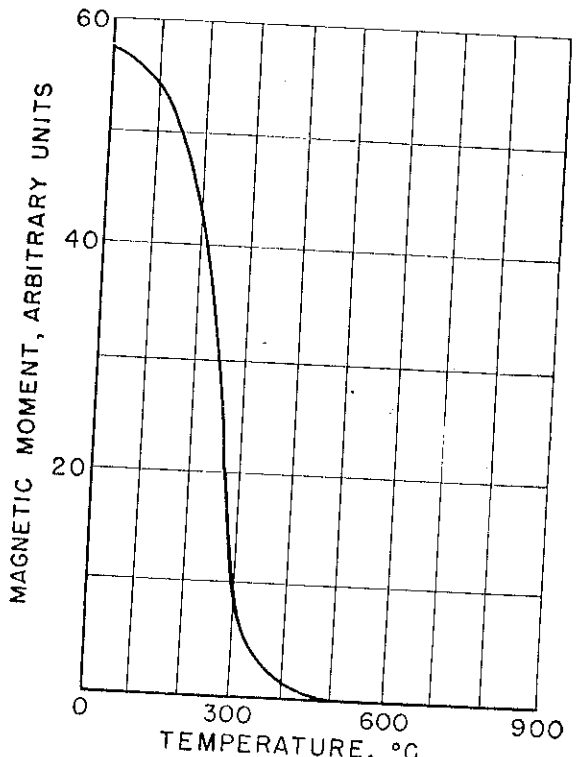

FIGURE 29.—Thermomagnetic curve of Fe, Cu, K_2CO_3 (100 : 1 : 1.5) catalyst, after carburization for 12 hours at 325°C. and 0.1 atmosphere, 8 liters of CO per hour per 10 grams of Fe.

The results obtained by carburizing the three iron preparations can be summarized as follows: The action of carbon monoxide on precipitated iron catalysts at about 325°C. always resulted in a higher-iron carbide, with a Curie point at 265°C. There are also indications that a carbide with a Curie point at 380°C. was formed. With active catalysts, carbiding occurred even when

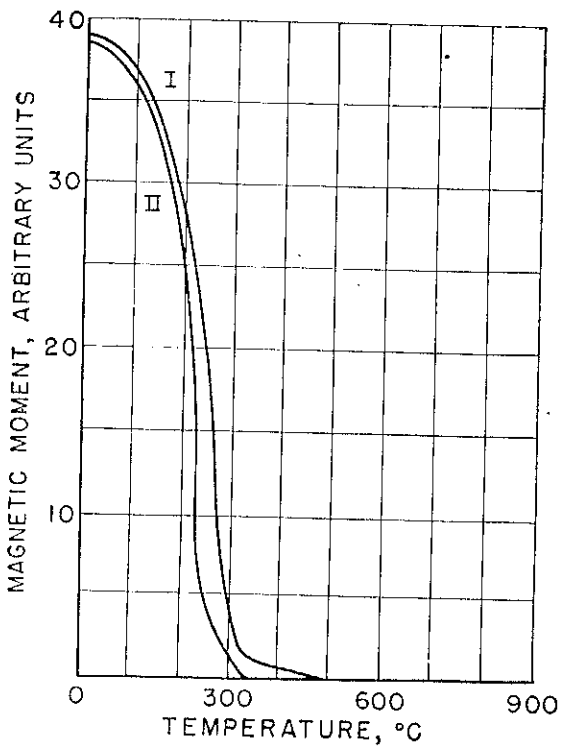

FIGURE 30.—Thermomagnetic curves of Fe, Cu, K_2CO_3 (100 : 1 : 1.5) catalyst, after carburization for 25 hours (also 62 hours) at 325°C. and 0.1 atmosphere, 8 liters of CO per hour per 10 grams of Fe: I, Freshly carburized sample; II, after heating to 800°C.