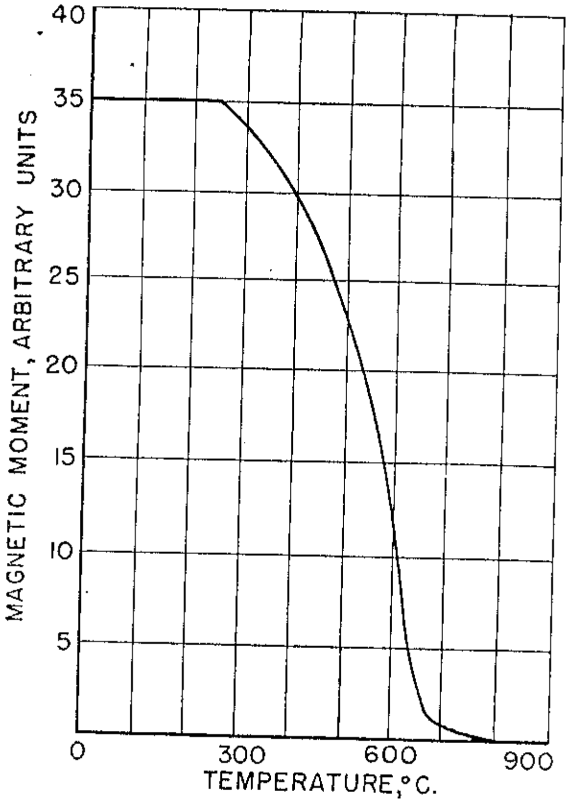

FIGURE 31.- Thermomagnetic curve of Fe, Cu, K_2CO_3 (100 : 1 : 0.25) catalyst, treated for 24 hours at 100°C. with synthesis gas (1 CO + 2 H_2 mixture).

only 100 liters of carbon monoxide per 10 grams of iron was used because of the relatively high carburization temperature and the low pressure.

Above their region of thermal stability, both higher iron carbides (Curie point, 265°C., and Curie point, 380°C.) were converted to cementite. In no instance was there any evidence that cementite had been formed directly as a result of carburization. Hofmann,[14] however, observed that cementite lines were always present in the X-ray pattern obtained from pure iron carburized within the same temperature range.

Thermomagnetic analysis clearly showed the effect of reactivity of catalysts on their carburization and final composition. A comparison of figures 20 (iron oxide without promoter, carburized 12 hours with carbon monoxide), 24 (iron catalyst with 0.25 percent K_2CO_3, carburized 12 hours with carbon monoxide), and 29 (iron–1 percent copper–1.5 percent K_2CO_3 carburized 12 hours with carbon monoxide) shows that iron oxide without promoter produced no detectable amounts of carbide, that alkali-promoted catalyst produced considerable amounts of carbide in the same period, and that the catalyst promoted with copper and alkali was converted to carbide almost quantitatively. In 25 hours of carburization of the pure iron oxide (fig. 21) only traces of carbide could be detected, while the catalyst promoted with copper and alkali was about half converted to carbide in 0.5 hour of carburization (fig. 26).

Copper-containing catalysts are characterized by a tendency to form a higher carbide which is virtually the exclusive carburization product. The high activity of these catalysts in the Fischer-Tropsch synthesis is apparently related to the process of carburization. This necessary pretreatment for medium-pressure synthesis converts the iron catalysts more or less completely to the 265°C. Curie-point carbide.

BEHAVIOR OF IRON CATALYSTS DURING HYDROCARBON SYNTHESIS

MEDIUM-PRESSURE SYNTHESIS

An iron catalyst containing a small quantity of copper was carburized for 24 hours at 325°C. and 0.1 atmosphere with carbon monoxide (8 liters of carbon monoxide per hour per 20 grams of iron). It will be seen from figure 32 that the 265°C. Curie-point carbide was virtually the only ferromagnetic component. The catalyst was then used for synthesis at 235°C. and 11 atmospheres. Samples for thermomagnetic analysis were taken at intervals from the inlet side of the converters in a nitrogen-flushed sample collector while the synthesis gas was flowing to prevent contact with air. Since each removal diminished the original 10 grams of iron by about 1 gram and since the throughput of synthesis gas was kept constant, the residual catalyst was increasingly overloaded.

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[14] Hofmann, U., work cited in footnote 90.
Hofmann, U., and Groll, E., work cited in footnote 91.

After operating for 2.5 hours (contraction 46 percent, fig. 33), and even after 6.5 hours of operation (fig. 34), the catalyst remained essentially unchanged. After 18½ hours of operation, gas conversion corresponded to a contraction of 51.5 percent.

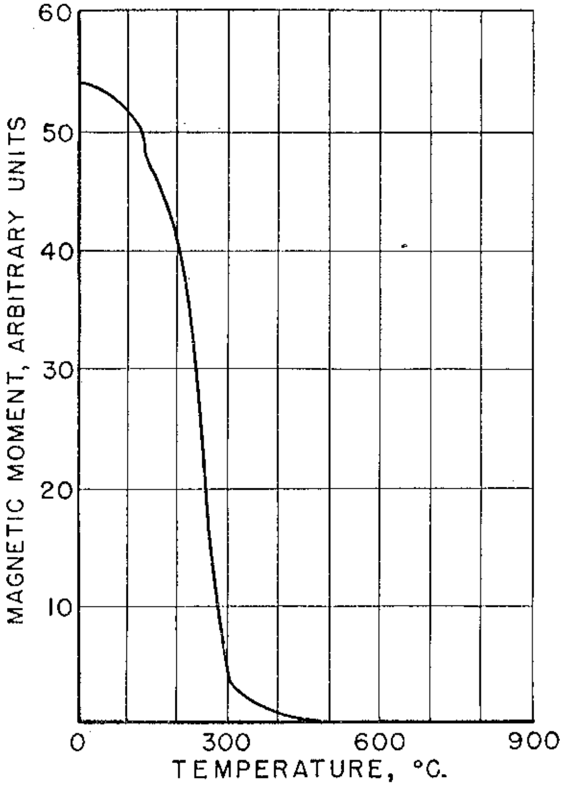

FIGURE 32.—Thermomagnetic curve of Cu- and alkali-promoted iron catalyst, carburized for 24 hours at 325°C. and 0.1 atmosphere, 8 liters of CO per hour per 20 grams of Fe.

The thermomagnetic curve shows that the catalyst was composed entirely of the 265°C. Curie-point carbide at this high activity (fig. 35). The absence of magnetite indicates that it is not essential for gasoline synthesis. On the contrary, subsequent experiments showed that its presence hinders synthesis. Figures 33 to 35 show that no free iron is formed during medium-pressure synthesis. The presence of the free metal for the synthesis is thus unnecessary.

Figure 36 shows the thermomagnetic behavior after 40 hours of operation. The contraction was 50 percent. The decrease in magnetization above 500°C. shows that magnetite was present. After 62 hours of operation the amount of magnetite increased considerably (fig. 37). The oxidation of the catalyst resulted in reducing the contraction from 50 to 40 percent, the synthesis

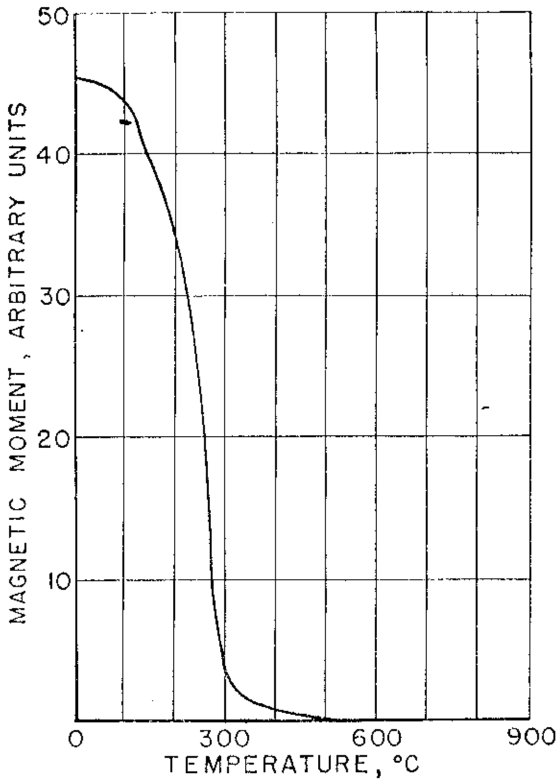

FIGURE 33.—Thermomagnetic curve of Cu- and alkali-promoted iron catalyst, carburized for 24 hours at 325°C. and 0.1 atmosphere, 8 liters of CO per hour per 20 grams of Fe and used for synthesis for 2.5 hours at 235°C. and 11 atmospheres.

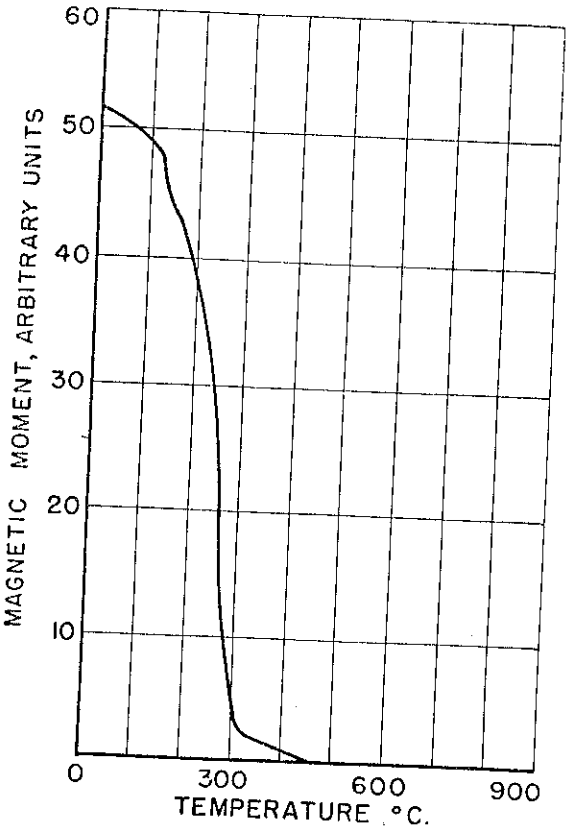

FIGURE 34.—Thermomagnetic curve of Cu- and alkali-promoted iron catalyst, carburized for 24 hours at 325°C. and 0.1 atmosphere, 8 liters of CO per hour per 20 grams of Fe, and used for synthesis for 6.5 hours at 235°C. and 11 atmospheres.

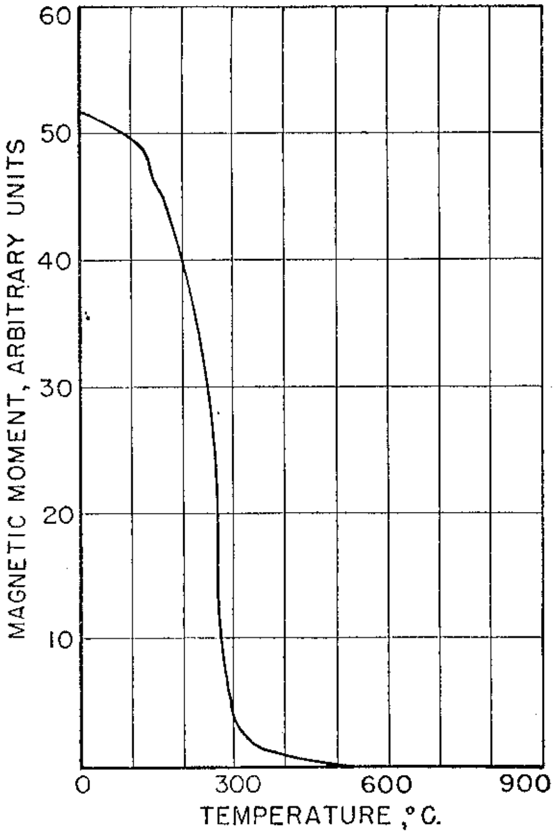

FIGURE 35.—Thermomagnetic curve of Cu- and alkali-promoted iron catalyst, carburized for 24 hours at 325°C. and 0.1 atmosphere, 8 liters of CO per hour per 20 grams of Fe and used for synthesis for 18.5 hours at 235°C. and 11 atmospheres.

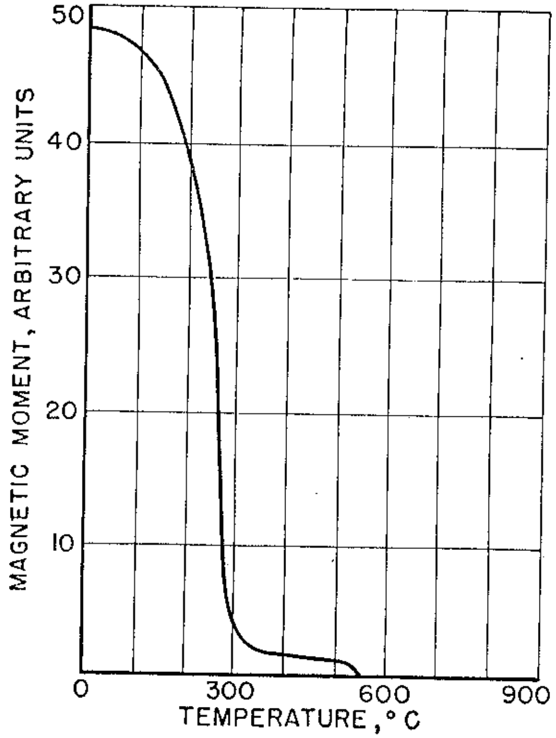

FIGURE 36.—Thermomagnetic curve of Cu- and alkali-promoted iron catalyst, carburized for 24 hours at 325°C. and 0.1 atmosphere, 8 liters of CO per hour per 20 grams of Fe and used for synthesis for 40 hours at 235°C. and 11 atmospheres.

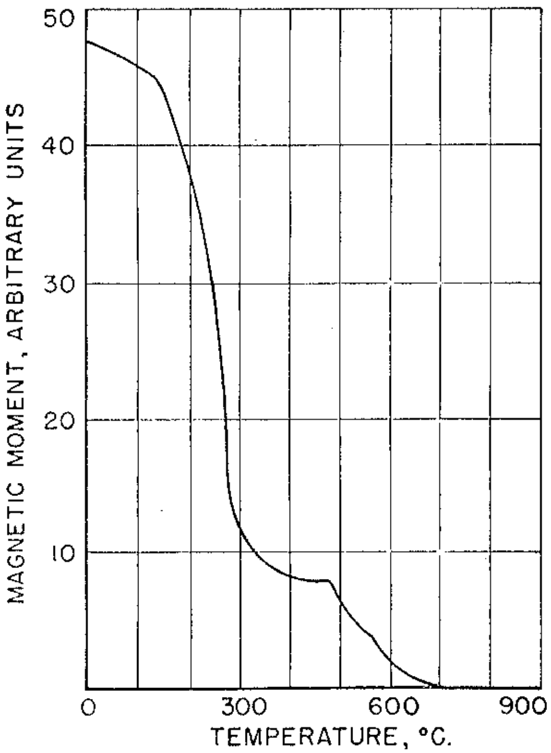

FIGURE 37.—Thermomagnetic curve of Cu- and alkali-promoted iron catalyst, carburized for 24 hours at 325°C. and 0.1 atmosphere, 8 liters of CO per hour per 20 grams of Fe and used for synthesis for 62 hours at 235°C. and 11 atmospheres.

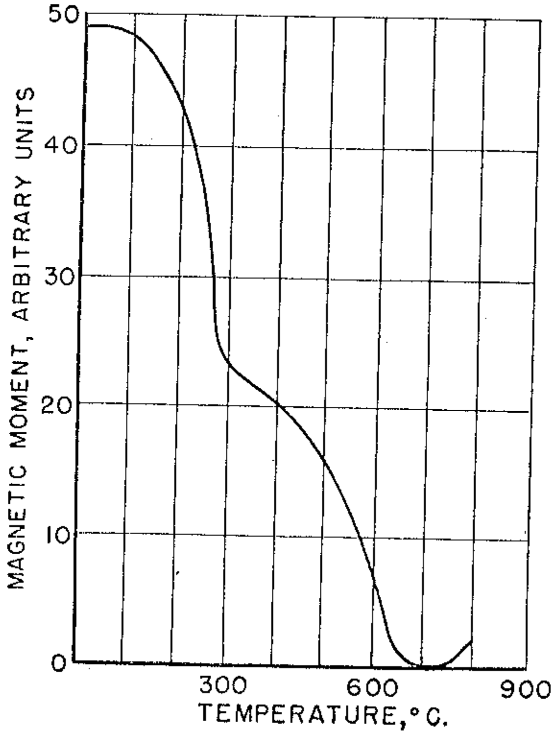

FIGURE 38.—Thermomagnetic curve of Cu- and alkali-promoted iron catalyst, carburized for 24 hours at 325°C. and 0.1 atmosphere, 8 liters of CO per hour per 20 grams of Fe and used for synthesis for 100 hours at 235°C. and 11 atmospheres.

temperature having been kept constant. After 109 hours the amount of magnetite increased considerably at the expense of the carbide as shown in figure 38. Oxidation probably was caused by the carbon dioxide formed during the reaction. The carbon dioxide of the tail gas increased to 40 percent during the first part of the experiment and then decreased with diminishing conversion.

This series of experiments also demonstrates the approximately linear relationship in medium-pressure synthesis between the activity of the catalyst and the amount of 265°C. Curie-point iron carbide present. There was no positive evidence of the presence of the 380°C. Curie-point carbide.

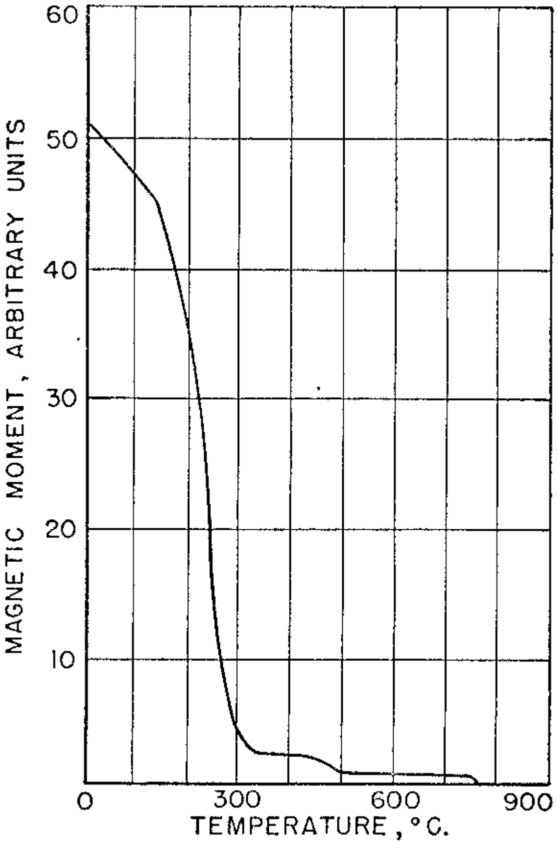

FIGURE 39.—Thermomagnetic curve of Cu- and alkali-promoted iron catalyst, carburized for 25 hours at 325°C. and 0.1 atmosphere, 8 liters of water gas per hour per 40 cc. of catalyst, and used for synthesis for 54 hours at 215°C. and 12 atmospheres.

Thermomagnetic analysis showed that by extending the operating time the magnetite content was increased. However, the gradual increase in space velocity over the remaining portion of the catalyst made it impossible to evaluate the later results in terms of the usual synthesis conditions.

In the following series of experiments comparable operating conditions were maintained by using equal portions of a catalyst (which had been carburized identically) in several converters.

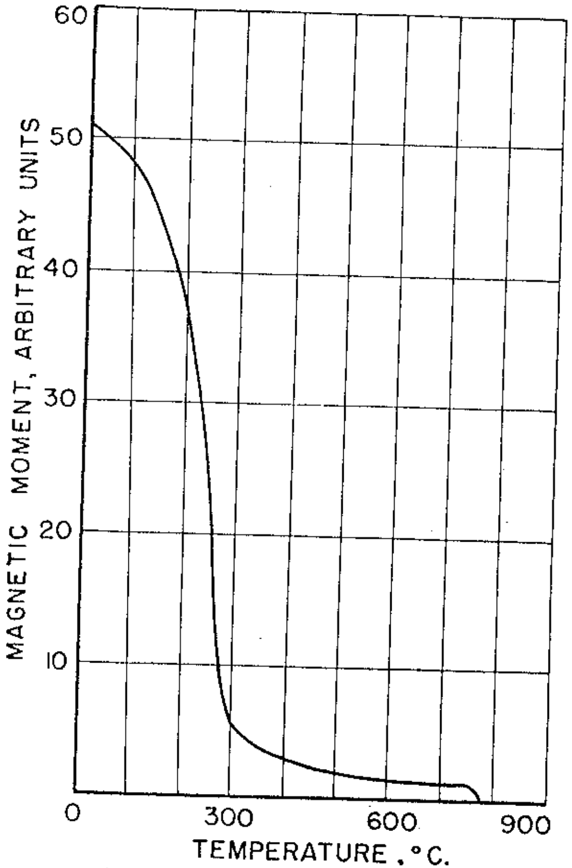

FIGURE 40.—Thermomagnetic curve of Cu- and alkali-promoted iron catalyst, carburized for 25 hours at 325°C. and 0.1 atmosphere, 8 liters of water gas per hour per 40 cc. of catalyst and used for synthesis for 410 hours at 215°C. and 12 atmospheres.

The experiments were interrupted at intervals and the ferromagnetic components of the catalyst determined. This method eliminated the disturbances due to changes in pressure and temperature which accompany the study of a single sample.

Batches of 40 cubic centimeters of catalyst were pretreated with water gas for 25 hours (325°C., 0.1 atmosphere). The rate of flow was 8 liters per hour, making the total volume of carbon monoxide passed over the catalyst 100 liters. The carburized catalysts were placed in operation at 215°C. and 12 atmospheres. After 54 hours of operation, contraction for one sample amounted to 49 percent. Here too, the synthesis gas had little effect on the magnetic behavior of the catalyst (fig. 39).

In a second experiment (fig. 40) the catalyst was operated for 410 hours under the same conditions as before. At the end of this time contraction had attained an approximately constant value of 40 to 41 percent. The curve corresponds to a catalyst containing chiefly the 265°C. Curie-point carbide.

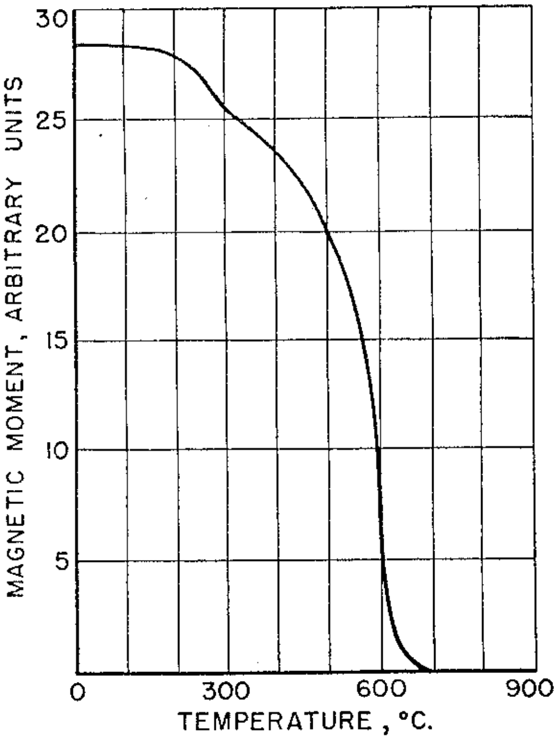

FIGURE 41.—Thermomagnetic curve of Fe, Cu, K_2CO_3 (100 : 20 : 1.5) catalyst heated in synthesis gas at 1 atmosphere until an exothermic reaction occurred.

It will be seen from figures 23, 26, and 32 to 35 that a new Curie point appeared between 125° and 150°C. This phenomenon might be explained by the formation of potassium ferrite which has a Curie point of 150°C., according to Hilpert.

Although no definite conclusions can be drawn from the data, it does appear now that the opinion of Lefebvre and LeClerc[15] is incorrect; according to them, catalytic activity during synthesis is to be attributed to cubic iron oxide which is stabilized by ferrite formation. The thermomagnetic curve these authors ascribed to potassium ferrite is undoubtedly characteristic of carbide.

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[15] Lefebvre, H., and LeClerc, G., work cited in footnote 12, p. 3.

ATMOSPHERIC PRESSURE SYNTHESIS

The production of especially active iron catalysts makes it possible to obtain good conversion of the synthesis gas even at atmospheric pressure, so that the carbon monoxide in water gas is converted almost quantitatively at 220°C. By adjusting the composition of the synthesis gas and the alkalization of the catalyst, this method can yield gasoline and oil having the desired boiling range, and white, high-molecular-weight paraffin wax.

In atmospheric pressure synthesis, active iron catalysts form paraffins a few minutes after being put into operation. In order to study the state of a catalyst (Fe, Cu, K_2CO_3 = 100 : 20 : 1.5) just before synthesis starts a thermocouple was introduced into the center of the catalyst, which was heated in a flow of synthesis gas. The gas was shut off when the thermocouple indicated an exothermic reaction. The catalyst was blackened on the gas-inlet side, whereas it still showed the brown color characteristic of ferric oxide on the outlet side. As will be seen from the thermomagnetic analysis (fig. 41), the sudden reduction of ferric oxide to magnetite was accompanied by carbide formation, thus demonstrating the rapid carburization of active catalysts by synthesis gas at 225°C.

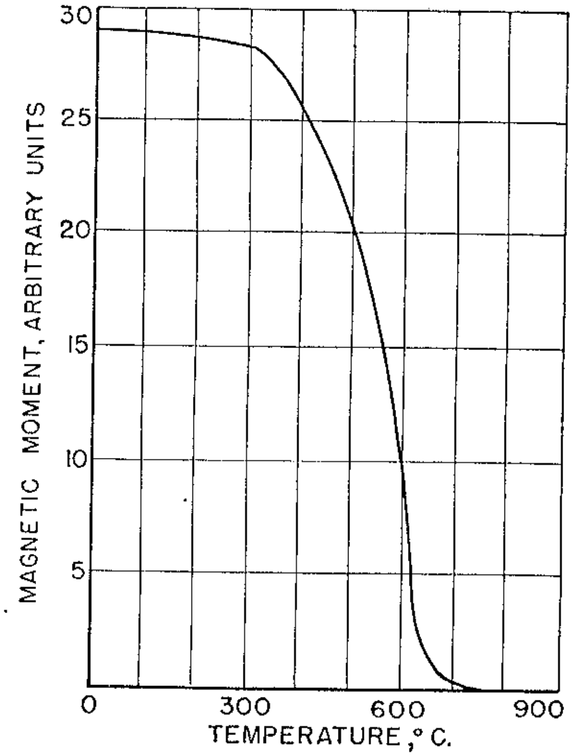

FIGURE 42.—Thermomagnetic curve of Cu- and alkali-promoted (0.25 percent Cu) iron catalyst after heating to 235°C. in synthesis gas at 1 atmosphere (time, 90 minutes).

Three types of iron catalyst were studied in various stages of carburization and synthesis at atmospheric pressure with synthesis gas ($2H_2 + 1CO$). An alkalized catalyst containing 0.25 percent of copper was used for the first group of experiments. This catalyst was not very active and was therefore carburized and simultaneously operated at 235°C. It produced little paraffin. The data on time, temperature of aluminum block oven, rate of flow of exit gas, contraction, and carbon dioxide content of the tail gas are tabulated in table 23 for the first 6 days of operation. Contraction rose sharply during the first hour and, after reaching a maximum value of 54 percent, decreased to 2.6 percent; the carbon dioxide content of the end gas was approximately proportional to the contraction. This first reaction was a reduction of the original oxide to magnetite. A second rise in the contraction (and parallel carbon dioxide increase) followed and

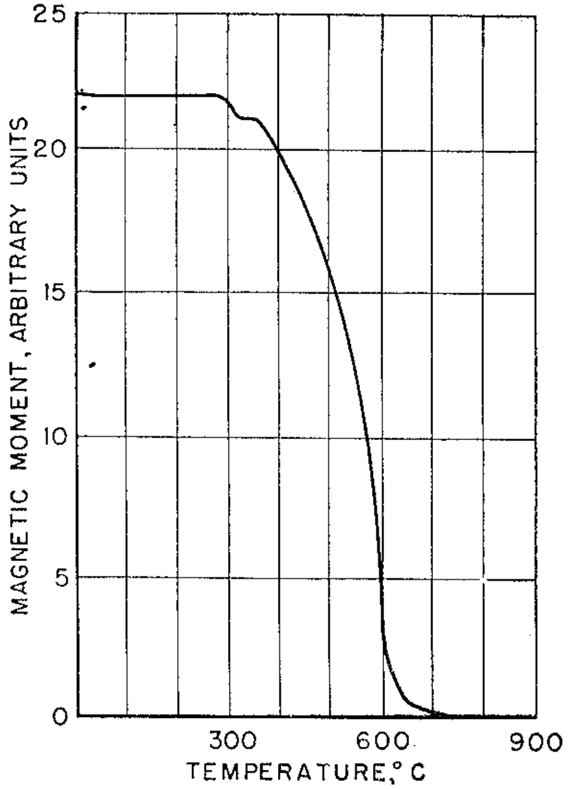

FIGURE 43.—Thermomagnetic curve of Cu- and alkali-promoted (0.25 percent Cu) iron catalyst, heated to 235°C. in synthesis gas at 1 atmosphere and kept at that temperature (total time, 4 hours and 40 minutes).

reached a final value of 34 percent after several days. This was due to the reduction of magnetite, to carburization (decomposition of carbon monoxide and carbide formation), and to hydrocarbon synthesis. Samples for thermomagnetic analysis were collected periodically as before in a current of synthesis gas, in samplers which were flushed with nitrogen.

Figure 42 shows the thermomagnetic curve of the catalyst at the conclusion of 1.5 hours of operation. At this point contraction had reached its lowest value (2.6 percent). The catalyst evidently consisted of magnetite. The thermomagnetic curve after a total of 4 hours and 40 minutes is shown in figure 43, magnetite was still the principal component, but the higher iron carbide became perceptible at 330°C. Contraction had risen to 16.1 percent. The catalyst reached its maximum contraction after 49 hours of operation. Figure 44 shows that the amount of 265°C. Curie-point carbide had increased considerably. Figure 45 is the thermomagnetic curve of the catalyst after operation for 120 hours. The contraction remained unchanged, but the amount of higher carbide increased still more at the expense of magnetite. The horizontal portions (figs. 44 and 45) at the lower temperatures and around 400°C. are unusual.

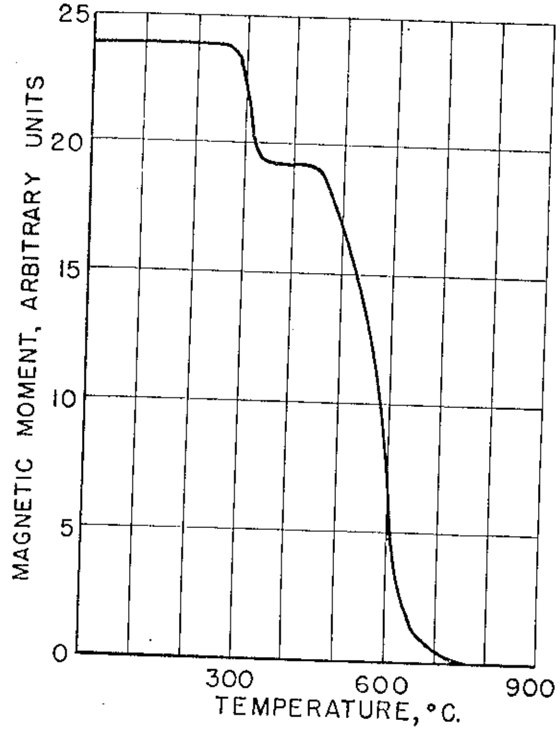

FIGURE 44.—Thermomagnetic curve of Cu- and alkali-promoted (0.25 percent Cu) iron catalyst, heated to 235°C. in synthesis gas at 1 atmosphere and kept at that temperature (total time, 49 hours).

Thus, the first effect of synthesis gas at atmospheric pressure was to reduce and carburize the iron catalyst. As carbide formation increased, the contraction and the amount of carbon dioxide also increased and reached their maximum value when carbiding was complete. The first stage in atmospheric-pressure synthesis corresponds therefore to carburization in medium-pressure synthesis, although no free carbon is formed. Because carburization is a separate, preliminary operation in medium-pressure synthesis, correlation between activity and carbide content of the two processes becomes possible only after carbide formation in the atmospheric pressure synthesis is complete.

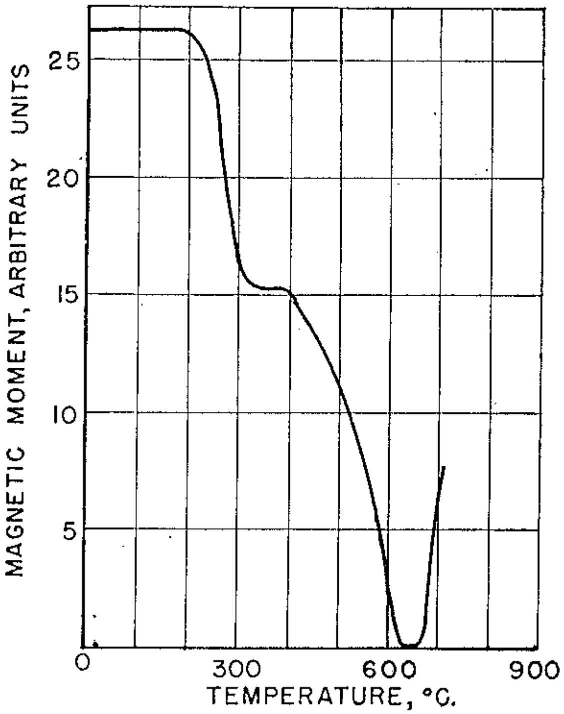

FIGURE 45.—Thermomagnetic curve of Cu- and alkali-promoted (0.25 percent Cu) iron catalyst, heated to 235°C. in synthesis gas at 1 atmosphere and kept at that temperature (total time, 120 hours).

In the second group of experiments with synthesis gas at normal pressure, an iron catalyst (Fe, Cu, K_2CO_3 = 100 : 20 : 0.25) was used at 235°C. This was more active than the preceding one. Several converters were operated simultaneously under the same conditions for different periods and samples were withdrawn and analyzed thermomagnetically.

A contraction of 14 percent was attained after 17 hours of operation. At this point the thermomagnetic curve (fig. 46) clearly indicated the presence of higher carbide. However, the

TABLE 23.—*Operation of a copper-containing iron catalyst at normal pressure*

Date, November	Time	Oven temperature (°C.)	Tail gas (liters per hour)	Contraction (percent)	Carbon dioxide in tail gas (percent)
23	*a.m.*				
	8:55	30	4.0	--	--
	9:00	56	3.9	—	--
	9:05	75	4.0	--	—
	9:10	91	4.0	--	—
	9:15	115	3.9	--	—
	9:20	128	3.81	—	—
	9:25	140	3.72	7.0	—
	9:30	162	3.48	13.0	4.2
	9:40	192	2.40	40.0	39.8
	9:50	214	1.95	51.3	—
	9:55	230	1.83	54.2	45.0
	10:05	232	3.55	11.3	10.8
	10:10	227	3.80	5.0	--
	10:25	231	3.89	2.6	5.4
	10:45	235	3.81	4.7	—
	11:00	231	3.78	5.5	6.0
	11:20	237	3.78	5.5	—
	11:40	236	3.72	7.0	6.7
	p.m.				
	1:15	236	3.31	17.1	—
	1:35	236	3.36	16.1	11.2
	2:30	237	3.36	16.1	10.4
	3:05	237	3.36	16.1	—
	3:45	237	3.36	16.1	—
	4:30	236	3.31	17.1	—
24	*a.m.*				
	8:00	237	2.82	29.6	17.1
	9:00	233	2.76	31.0	--
	10:30	233	2.76	31.0	17.4
	p.m.				
	2:00	234	2.64	34.0	—
	a.m.				
25	10:00	230	2.61	34.0	19.6
27	8:40	230	2.61	34.0	17.7
28	8:30	230	2.61	31.5	—

catalyst still consisted mainly of magnetite. After 47.5 hours of operation (contraction, 26.5 percent) the thermomagnetic curve clearly showed the 265°C. Curie-point carbide (fig. 47). After 121 hours of operation the catalyst reached its maximum contraction, amounting to 30 to 31 percent. As shown in figure 48, there was only a slight change in the relative amounts of carbide and magnetite. However, the formation of the 380°C. Curie-point carbide in this experiment was evident from the Curie point at about 390°C.

The relationship between activity and carbide content is clear from this group of experiments. Increased formation of carbide was associated with increased contraction. The appearance of the 380°C. Curie-point carbide in the last experiment was accompanied by a rise in contraction from 26.5 to 31 percent.

In the third group of experiments an iron catalyst (Fe, Cu, K_2CO_3 = 100 : 20 : 1.5) was used (at 225°C.) which was considered to be the best catalyst for the Fischer-Tropsch process at atmospheric pressure. Since the catalyst was alkalized with 1.5 percent of potassium carbonate, large quantities of solid paraffin blocked the surface, and periodic extraction with Diesel oil was necessary. Extraction resulted in an immediate rise in the carbon dioxide content, showing the reaction was resumed at

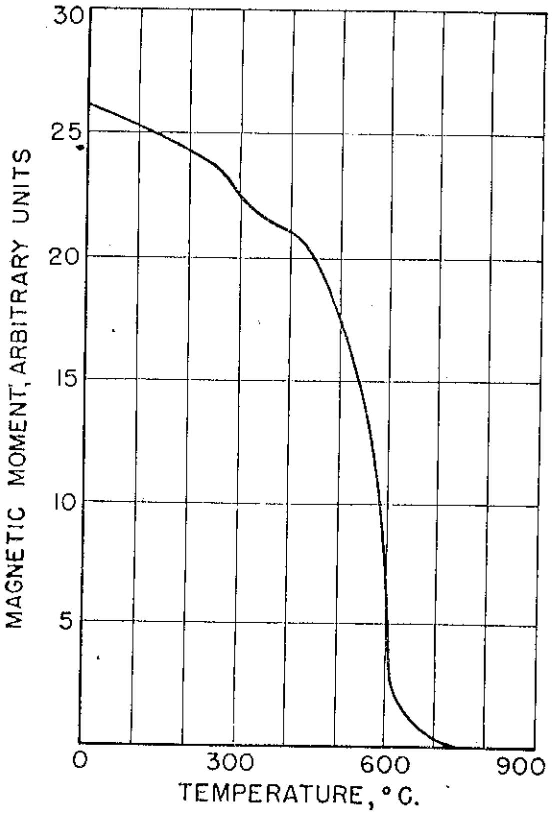

FIGURE 46.—Thermomagnetic curve of Fe, Cu, K_2CO_3 (100 : 20 : 0.25) catalyst, heated in synthesis gas at 1 atmosphere to 235°C., and kept at that temperature (time, 17 hours).

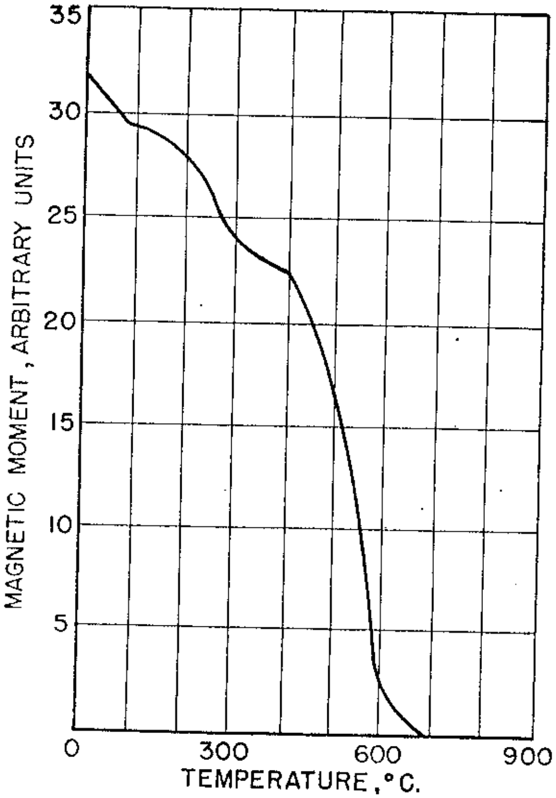

FIGURE 47.—Thermomagnetic curve of Fe, Cu, K_2CO_3 (100 : 20 : 0.25) catalyst, heated to 235°C. in synthesis gas at 1 atmosphere and kept at that temperature (time, 47.5 hours).

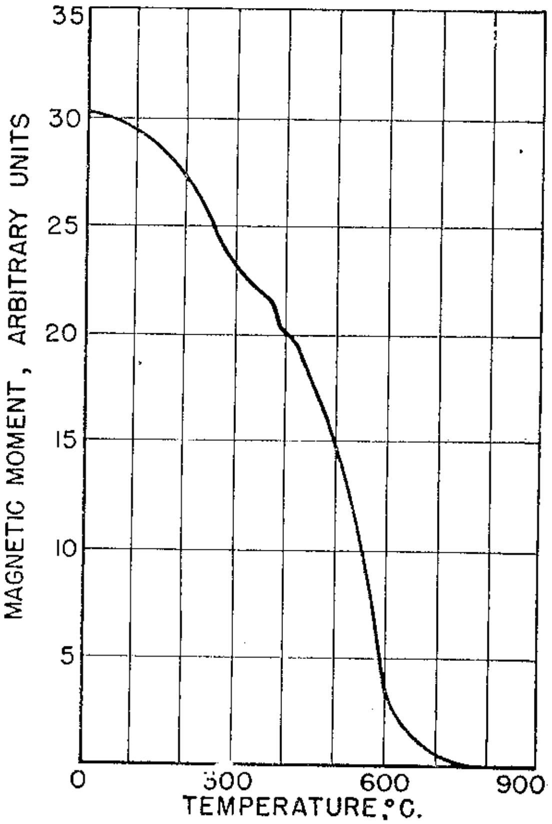

FIGURE 48.—Thermomagnetic curve of Fe, Cu, K_2CO_3 (100 : 20 : 0.25) catalyst, heated to 235°C. in synthesis gas at 1 atmosphere and kept at that temperature (time, 121 hours).

once. Samples were collected at various intervals for thermomagnetic examination.

Figure 49 shows the thermomagnetic behavior of the catalyst after treatment for 24 hours with synthesis gas at 225°C. The gas throughput was 20 liters per hour per 40 cubic centimeters of catalyst. An appreciable amount of paraffin and oil had been formed. The graph clearly shows the composition of the catalyst. The 265°C. Curie-point carbide was already formed at this time. It is interesting to note that, after elimination of the magnetization due to this carbide, the curve proceeded horizontally from 290° to 340°C.; that is, magnetization was independent of the temperature. The second drop in magnetization shows a Curie point at 395°C., which was the result of the formation of the 380°C. Curie-point carbide, as the following experiments demonstrate more clearly. The next well-defined inflection at 430° to 440°C. was probably due to the formation of copper ferrite whose Curie point, according to Chaudron, is 455°C. The remaining drop in magnetization was due partly to magnetite and above 600°C. to iron.

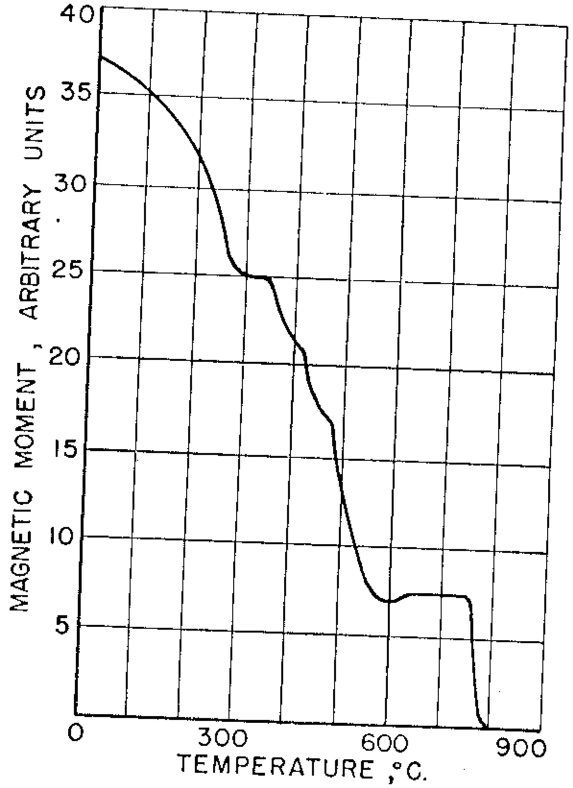

FIGURE 49.—Thermomagnetic curve of Fe, Cu, K_2CO_3 (100 : 20 : 1.5) catalyst, treated for 24 hours at 225°C. with synthesis gas (20 liters 1 CO + $2H_2$ gas mixture per hour per 40 cc. catalyst).

Figure 50 shows the effect of a 3-day treatment with synthesis gas. The catalyst was extracted with Diesel oil before the end of the experiment. It is interesting to note that the amount of 265°C. Curie-point carbide remained virtually unchanged, as compared with the 24-hour experiment in this group. The Curie point at 380°C. was more clearly defined, showing that the 380°C. Curie-point carbide content had increased. This probably explains the absence in figure 50 of the first horizontal section that appears in figure 49; the magnetization in this region was more temperature-dependent now. As a result of increased carbide formation, the quantity of free iron was also considerably greater than in the preceding experiment. After 6 days, during which time the catalyst was extracted twice with Diesel oil, the thermomagnetic curve shown in figure 51 was obtained. Here, too, the Curie point at 380°C. is well-defined. The formation of free iron began below 500°C. (flat portion of the curve). The carbide content of the catalyst shows virtually no change, as compared with the preceding experiment (fig. 50).

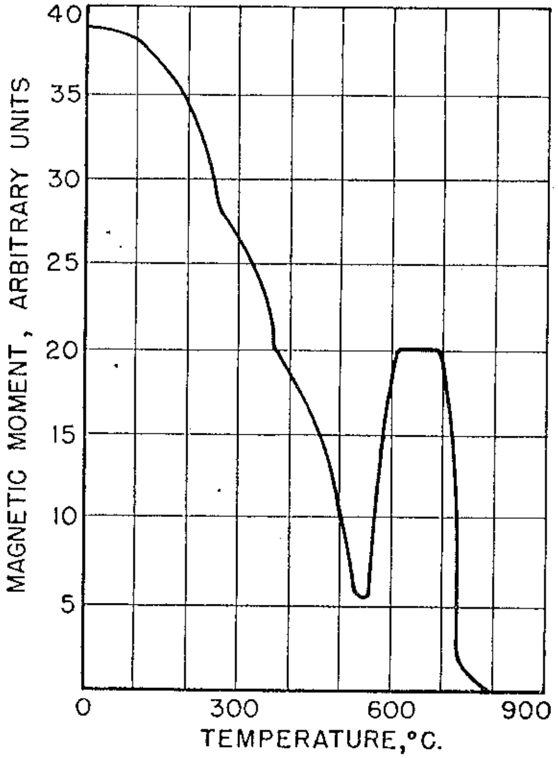

FIGURE 50.—Thermomagnetic curve of Fe, Cu, K_2CO_3 (100 : 20 : 1.5) catalyst, treated for 3 days at 225°C. with synthesis gas (20 liters 1 CO + 2 H_2 gas mixture per hour per 40 cc. catalyst).

In another experiment in this series, a catalyst was operated for 4 days with synthesis gas (20 liters per hour per 40 cubic centimeters of catalyst at 225°C. and 1 atmosphere) and was then operated with water gas (4 liters of water gas per hour per 40 cubic centimeters of catalyst at 220°C. and 1 atmosphere). Following the third extraction, the carbon dioxide content of the tail gas was over 30 percent, corresponding to about 36 percent contraction. After 2 days of operation with water gas, the catalyst gave the thermomagnetic picture shown in figure 52. It will be seen that the 265°C. Curie-point and 380°C. Curie-point carbides were equally prominent. The amount of 380°C. Curie-point carbide had increased during the synthesis with water gas over that formed during operation with synthesis gas.

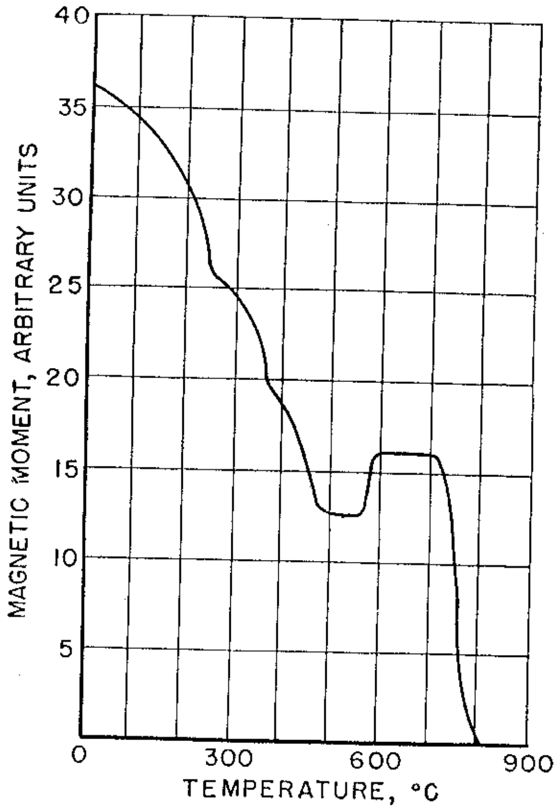

FIGURE 51.—Thermomagnetic curve of Fe, Cu, K_2CO_3 (100 : 20 : 1.5) catalyst, treated for 6 days at 225°C. with synthesis gas (20 liters 1 CO + 2 H_2 gas mixture per hour per 40 cc. catalyst).

Comparison of the three series of experiments on the effect of pretreatment with synthesis gas ($1CO + 2H_2$) on iron catalysts at atmospheric pressure shows the following: The catalyst used in the first series contained mainly magnetite, but also some higher carbide (Curie point, 265°C.). There was no evidence of the formation of the 380°C. Curie-point carbide. An operating temperature of 235°C. was necessary in this case to obtain satisfactory conversion. The carbon dioxide value on the fifth day amounted to 17.7 percent, showing that the catalyst was not very active.

In the second series of experiments, the higher activity of the catalyst containing 20 percent copper was apparent from the 31 percent contraction obtained at the same operating temperature. Figure 48 shows that the 380°C. Curie-point carbide was formed in addition to the 265°C. Curie-point carbide.

The third series of experiments was characterized by low operating temperature (220°C.), by high contraction, and by high content of 380°C. Curie-point carbide (fig. 52). Under these conditions the catalyst converted the carbon monoxide in water gas quantitatively. The gas ratio was approximately 100 parts of carbon monoxide to 60 parts of hydrogen, and contraction amounted to 36 percent.

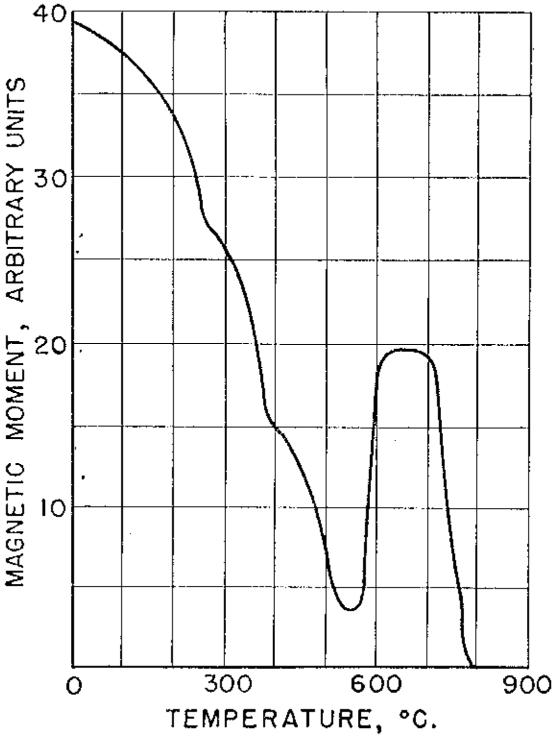

FIGURE 52.—Thermomagnetic curve of Fe, Cu, K_2CO_3 (100 : 20 : 1.5) catalyst, treated for 4 days at 225°C. and 1 atmosphere of synthesis gas (20 liters 1 CO + 2 H_2 gas mixture per hour per 40 cc. of catalyst) and then 2 days at 220°C. and 1 atmosphere of water gas (4 liters gas per hour per 40 cc. of catalyst).

With an iron catalyst of this type, pretreated as usual with synthesis gas (220° to 225°C., 1 atmosphere, 20 liters per hour) and operated at medium pressure (that is, 10 to 20 atmospheres) instead of atmospheric pressure, the optimum synthesis temperature dropped from 220°C. to 205°C., for the same conversion. This increased activity (as compared with iron catalysts pretreated at 325°C. with carbon monoxide, which require operating temperatures between 220° and 230°C. for the same pressures) was probably caused by the 380°C. Curie-point carbide, to which the characteristic properties of synthesis at atmospheric pressure are due. As already stated, there were only minor indications of the presence of the 380°C. Curie-point carbide in copper-free iron catalysts pretreated at 325°C. In this case, the synthesis proceeded through the 265°C. Curie-point carbide, which required a higher synthesis temperature. The oxide content of catalysts was appreciably higher in atmospheric-pressure synthesis than in medium-pressure synthesis (for the same activity). Thus, the oxide content alone is no measure of the activity of an iron catalyst.

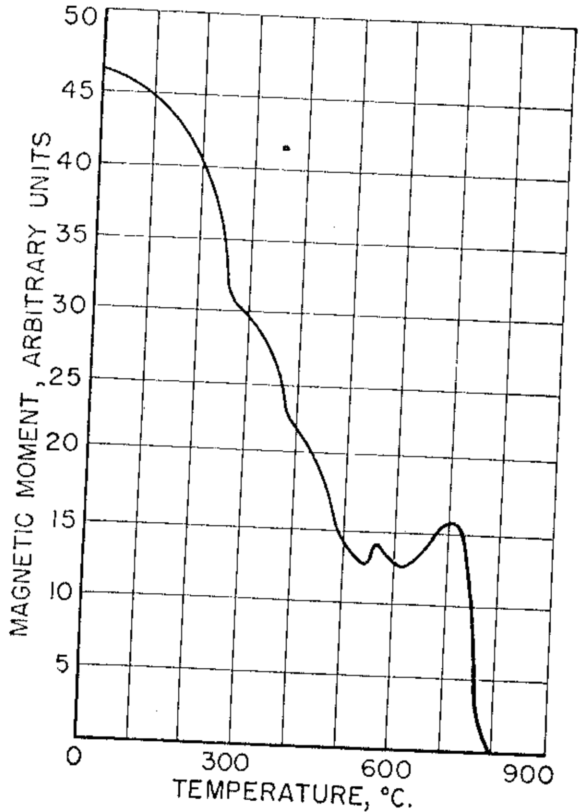

FIGURE 53.—Thermomagnetic curve of an active catalyst used for synthesis at atmospheric pressure and poisoned by extraction with sulfur-containing Diesel oil.

Even a catalyst containing the carbide needed for satisfactory activity may prove inactive in the gasoline synthesis. Figure 53 shows the thermomagnetic curve of an iron catalyst in an experiment in which the carbon monoxide of the synthesis gas was converted almost quantitatively at normal pressure; it became almost completely inactive after extraction with Diesel oil containing sulfur. Chemical analysis showed that the catalyst had a high sulfur content. As a result, the active centers were rendered inoperative due to sulfide formation, though the structure remained unchanged. While the thermomagnetic curve offered no explanation of this behavior, the catalyst had already shown atypical behavior in the course of thermomagnetic measurement, when large quantities of oil vapor were evolved above 220°C. Figure 53 is unusual because the drop at 550°C. (corresponding to magnetite) is followed by a slight peak. Subsequently, there is a second rise followed by a drop with a point of inflection at 760°C. (Curie point of α-iron).

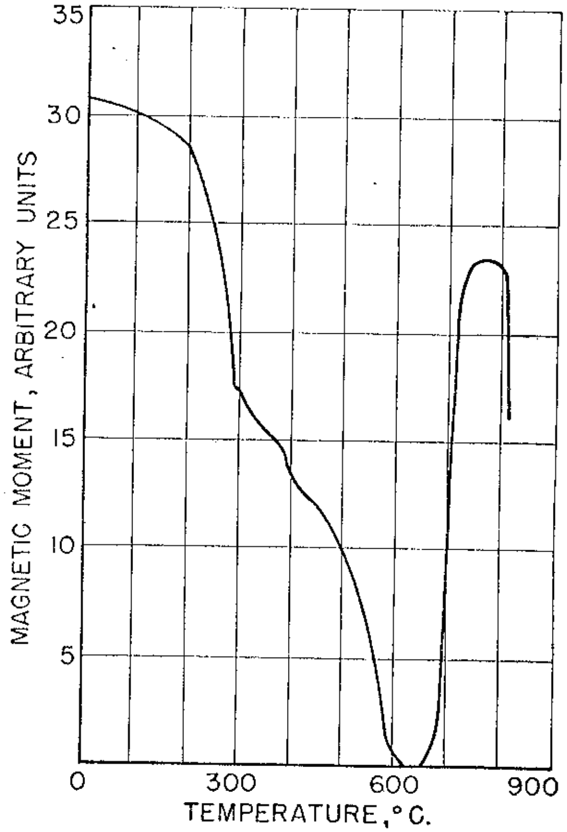

FIGURE 54.—Thermomagnetic curve of Fe, Cu, K_2CO_3 (100 : 20 : 0.25) catalyst at high activity.

EFFECT OF CARBIDE CONTENT ON CATALYST ACTIVITY

Figure 54 is a thermomagnetic curve obtained with a highly active catalyst (Fe, Cu, K_2CO_3 = 100 : 20 : 0.25) which attained a contraction of 40 percent at atmospheric pressure and 235°C. Figure 55 is the thermomagnetic curve of the same catalyst after its activity had dropped to a contraction of 2 percent after prolonged operation. Figure 54 shows that high activity at normal pressure and 235°C. was characterized by large amounts of 265°C. Curie-point carbide and some 380°C. Curie-point carbide. Magnetite was present in large amounts, as indicated by the Curie point at 590°C. The amount of iron carbide in the inactivated catalyst was extremely small. The catalyst consisted chiefly of magnetite, which was formed by oxidation of the carbides.

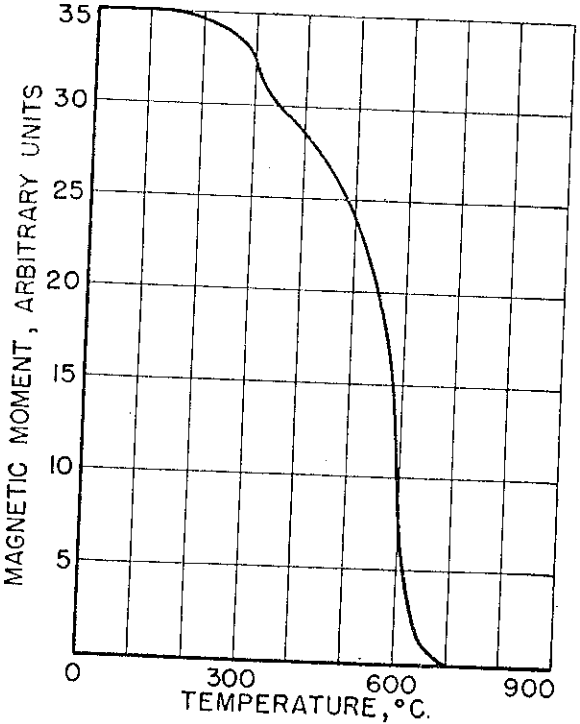

FIGURE 55.—Thermomagnetic curve of Fe, Cu, K_2CO_3 (100 : 20 : 0.25) catalyst at low activity.

The following experiment again illustrates the need of iron carbide for the synthesis. An iron catalyst that gave a 30-percent contraction when operated at atmospheric pressure was reduced with hydrogen at 400°C. Synthesis gas was then passed over the reduced catalyst, which reached a contraction of 10 to 12 percent in the course of several days. It is apparent from the thermomagnetic curve that the catalyst consisted of metallic iron (fig. 56). The catalyst was almost completely inactive for the gasoline synthesis in this state. Metallic iron is not capable of catalyzing the formation of hydrocarbons from carbon monoxide and hydrogen, and the iron formed by reduction at 400°C. could not be carbided at the prevailing synthesis temperature. It should be mentioned that iron catalysts that were reduced to the free metal by hydrogen at 250°C. reacted almost completely with carbon monoxide at 205°C. to yield higher-iron carbides.

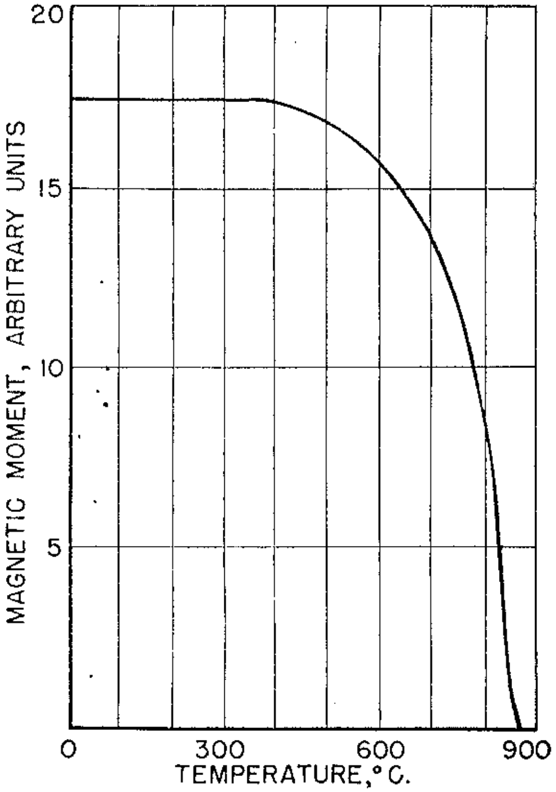

FIGURE 56.—Thermomagnetic curve of an active iron catalyst after reduction with H_2 at 400°C.

SUMMARY

The outstanding characteristic of atmospheric pressure synthesis was that the catalysts formed both the higher-iron carbides in approximately equal amounts with synthesis gas at 220° to 230°C. (assuming that the specific magnetization of the two carbides is of the same order of magnitude). The formation of the 380°C. Curie-point carbide was favored by the low reaction temperature and by the high copper content of the catalyst, as shown in earlier experiments on the formation of this carbide.

After operation for several days, the catalysts still contained appreciable amounts of magnetite, although free iron and iron carbide are stable in the presence of the synthesis gas used. This