FIGURE 26.—Additional Data on Rate of Reduction of Catalyst D3001; Space Velocity of Hydrogen, 1,000 Hr.$^{-1}$.

TABLE 34.—*Magnetic characteristics of cementite, Hägg carbide, hexagonal carbide, and "FeC"*

Phase	Curie point,[1] ° C.	Saturation specific magnetization at room temperature, ergs/gm.gauss
Fe₃C	209–215	139
Hägg [2]	245–250	<139
Hägg? [3]	~250	[4] 129
Hexagonal close packed	[5] 380	>139
"FeC"	247–253	~139

[1] The Curie point is defined as the point of inflection of the thermomagnetic curve; this temperature is virtually independent of the magnetic field strength, H, and approaches closely the true Curie point for H=0. It may vary with alloying constituents.
[2] Obtained by carburization of reduced iron.
[3] Obtained by carburization of iron oxide or iron nitride.
[4] From footnote 5, p. 51.
[5] The Curie point cannot be measured accurately because of the instability of the carbide.

300° C., but it is contaminated by free carbon. The best method for preparing catalytically active cementite will be discussed in the next section.

Cementite can also be extracted from steels or prepared by the decomposition of cyanides or of the higher iron carbides.[6] Recent evidence [7-11] shows that hexagonal iron carbide (Jack refers to it as hexagonal Fe₃C) appears during the tempering of martensite and that Hägg carbide, or possibly yet another carbide with similar properties, may be formed during a later tempering stage of martensite.

SOME REACTIONS OF IRON CARBIDES

None of the iron carbides is thermodynamically stable with respect to the elements; the relative stability increases in the order hexagonal carbide, Hägg carbide, cementite. Hexagonal iron carbide is transformed to Hägg carbide at measurable rates above about 250° C., and Hägg carbide starts to decompose into cementite and free carbon above about 450° C. These rates of reaction are probably affected by the size of the crystallites, the type

[6] Work cited in footnote 1, p. 50.
[7] Heidenreich, R. D., Sturkey, L., and Woods, H. L., Decomposition of Martensitic Steel Above and Below 300°: Nature, vol. 157, 1946, p. 518.
[8] Heidenreich, R. D., Sturkey, L., and Woods, H. L., Investigation of Secondary Phases in Alloys by Electron Diffraction and the Electron Microscope: Jour. Appl. Phys., vol. 17, 1946, pp. 127-136.
[9] Work cited in footnote 4, p. 51.
[10] Crangle, J. and Sucksmith, W., Magnetic Analysis of Iron-Carbon Alloys. Tempering of Martensite and Retained Austenite: Jour. Iron Steel Inst. (London), vol. 168, 1951, pp. 141-151.
[11] Hofer, L. J. E. and Cohn, E. M., Some Reactions in the Iron-Carbon System. Application to the Tempering of Martensite: Nature, vol. 167, 1951, pp. 977-978.

and amounts of impurities and additives present, and the completeness of carburization. Thus, the rates of decomposition of cementite into its elements are known to vary widely and become measurable anywhere from about 450° to about 1,100° C., depending on the nature of the preparation.

While the mechanisms of the thermal transformations from one carbide to another are not known as yet, the modes of transition have been studied thermomagnetically, providing clues to the mechanisms as well as to the ranges of composition of two of these interstitial structures. All of the transformations are discontinuous or heterogeneous precipitations; that is, nuclei of the new phases form and grow at the expense of the parent phase. Such precipitations are characterized magnetically by the simultaneous presence of 2 Curie points, each corresponding to 1 of the phases, and the new one becoming more pronounced while the original one gradually disappears as the reaction proceeds. For the transition of hexagonal to Hägg carbide, only the Curie point of the latter can be measured after periodic heatings of the carbide.[12] As regards the transition from Hägg carbide to cementite,[13] both Curie points are conveniently accessible. The constancy of the Curie point of Hägg carbide in both instances supports the earlier observation that the range of composition of Hägg carbide is narrow.[14] The Curie point of cementite also remains constant during the Hägg carbide–cementite reaction, as it does during decomposition of cementite into iron and carbon.[15] A slight difference between the Curie points of cementite obtained by the decomposition of Hägg carbide was observed by Bernier [16] for Hägg carbide preparations carburized at 560° C. (C. p., 210° C.) and at 1,000° C. (C. p., 216° C.); small variations in composition of cementite probably caused this effect.

In the presence of iron, Hägg carbide is considerably less stable than when pure; it reacts with iron at measurable rates above about 260° C. according to the approximate equation

$$\text{Hägg-Fe}_2\text{C} + \alpha\text{—Fe} \rightarrow \text{Fe}_3\text{C}. \qquad (18)$$
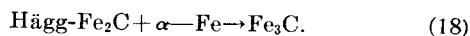
This reaction was discovered in the course of thermomagnetic studies [17] and has been used for the preparation of catalytically active cementite.[18] It requires substantially lower temperatures than any other known series of reactions by which cementite, having a high surface area and free from elemental carbon, can be made. Lack of mobility of carbidic carbon is presumably the reason why the reaction is not completed below about 450° C. Above that temperature, the rate of the approximate reaction,

$$3 \text{ Hägg-Fe}_2\text{C} \rightarrow 2 \text{ Fe}_3\text{C} + \text{C}, \qquad (19)$$

becomes appreciable. However, heating of the partly carburized iron at about 450° C. for 1 to 3 hours usually has been enough for virtual completion of the reaction.

NITRIDES AND CARBONITRIDES OF IRON

Iron nitrides are interstitial compounds similar to and, in some instances, isomorphous with iron carbides.[19-21] The low-temperature homogeneous phases found in the iron-nitrogen system are listed in table 35. They cannot be prepared by the action of molecular nitrogen on iron, but are made by treating iron with gaseous ammonia. The amount and structure of iron nitride formed depend on the temperature and time of treatment, the space velocity of the ammonia, and the ratio of ammonia to hydrogen.[22]

TABLE 35.—*Homogeneous phases in the iron-nitrogen system at temperatures below the α–γ transition of iron*

Phase	Nitrogen, weight-percent	Atom ratio, N : Fe	Arrangement of iron atoms
α	<0.2	0.008	Body-centered cubic.
γ'	5.7–6.1	0.241–0.259	Face-centered cubic.
ε	7.3–11.1	.314–.498	Close-packed hexagonal.
ζ	11.1–11.3	.498–.508	Orthorhombic.

The iron carbonitrides have been prepared by treating iron nitrides with carbon monoxide or carbide with ammonia.[23] The former treatment at 450° C. resulted in a series of carbonitrides in which nitrogen was progressively replaced by carbon; the crystal structure of the ε- and ζ-phases remained essentially unchanged until about 75 percent of the nitrogen was replaced. Further treatment with carbon monoxide yielded Hägg carbide; above 500° C.

[12] Cohn, E. M. and Hofer, L. J. E., Some Thermal Reactions of Higher Iron Carbides: Jour. Chem. Phys., vol. 21, 1953, pp. 354–359.
[13] Cohn, E. M. and Hofer, L. J. E., Mode of Transition From Hägg Iron Carbide to Cementite: Jour. Am. Chem. Soc., vol. 72, 1950, pp. 4662–4663.
[14] Work cited in footnote 5, p. 51.
[15] Honda K., Magnetic Analysis as a Means of Studying the Structure of Iron Alloys: Jour. Iron Steel Inst., vol. 98, 1918, pp. 375–419.
[16] Bernier, R., [Thermomagnetic Study of Iron and Nickel Carbides. I. Nickel Carbides. II. Nickel Nitrides. III. Cementite. IV. Iron-Nickel Carbides]: Ann. chim., vol. 6, No. 12, 1951, pp. 104–161.
[17] Hofer, L. J. E. and Cohn, E. M., Synthesis of Cementite: Jour. Chem. Phys., vol. 18, 1950, pp. 766–767.
[18] Cohn, E. M. and Hofer, L. J. E., Preparation of Iron Carbides: U. S. Patent 2,535,042, Dec. 26, 1950.
[19] Lehrer, E., [Magnetic Investigation of the System Iron-Nitrogen]: Ztschr. Elektrochem., vol. 36, 1930, pp. 460–473.
[20] Brunauer, S., Jefferson, M. E., Emmett, P. H., and Hendricks, S. B., Equilibria in the Iron-Nitrogen System: Jour. Am. Chem. Soc., vol. 53, 1931, pp. 1778–1786.
[21] Jack, K, H., Binary and Ternary Interstitial Alloys. III. Iron-Carbon System; The Characterization of a New Iron Carbide: Proc. Roy. Soc. (London), vol. A195, 1948, pp. 56–61.
[22] Work cited in footnote 20.
[23] Work cited in footnote 21.

such treatment resulted in a mixture of Hägg carbide and cementite.

Iron nitrides and carbonitrides were prepared by the Bureau of Mines using fused as well as precipitated catalysts, which were subsequently tested in the Fischer-Tropsch synthesis. Curves showing the nitrogen content of originally reduced fused catalyst D3001 as a function of time and for a range of nitriding temperatures are plotted in figure 27. They show that at low temperatures the rate of nitriding is limited by the rate of incorporation of nitrogen in the iron lattice; and the nitrogen content appears to reach a maximum near a nitrogen-to-iron atom-ratio of 0.508. At higher temperatures the rate of nitriding is apparently limited by the composition of the gas (ammonia-to-hydrogen ratio) and the limit of the nitrogen content is determined by the space velocity of ammonia. For reduced catalyst D3001 (6- to 8-mesh), at an hourly space velocity of 750, 350° C. is the optimum temperature for complete nitriding.

Before nitriding, the catalysts were generally reduced in electrolytic hydrogen at 450° or 550° C. and at an hourly space velocity of 2,500.

The reduction procedure was the same as that described on page 127. A similar procedure was used for the treatment with anhydrous ammonia, either in the special reduction unit described on page 127 and shown in figure 74 (p. 126) or with the catalyst in place in the testing unit at the end of the ammonia treatment. The catalyst was either immediately dropped from the reduction unit or the temperature of the reactor was decreased rapidly. In either method a high flow of ammonia was maintained until the catalyst had cooled below 250° C. The catalyst was not permitted to remain at temperature in an inert gas or in a slow flow of ammonia, because these conditions favor hydrogenation or decomposition of the nitride. The catalyst was then transferred and weighed. Usually, a weighted sample was removed for X-ray examination.

Tests were made with ammonia synthesis catalyst D3001 to establish the conditions necessary for the preparation of ε-phase carbonitrides of varying composition.[24] A large

[24] Hall, W. K., Dieter, W. E., Hofer, L. J. E., and Anderson, R. B., Preparation and Reactions of Carbonitrides of Iron: Jour. Am. Chem. Soc., vol. 75, 1953, pp. 1442–1447.
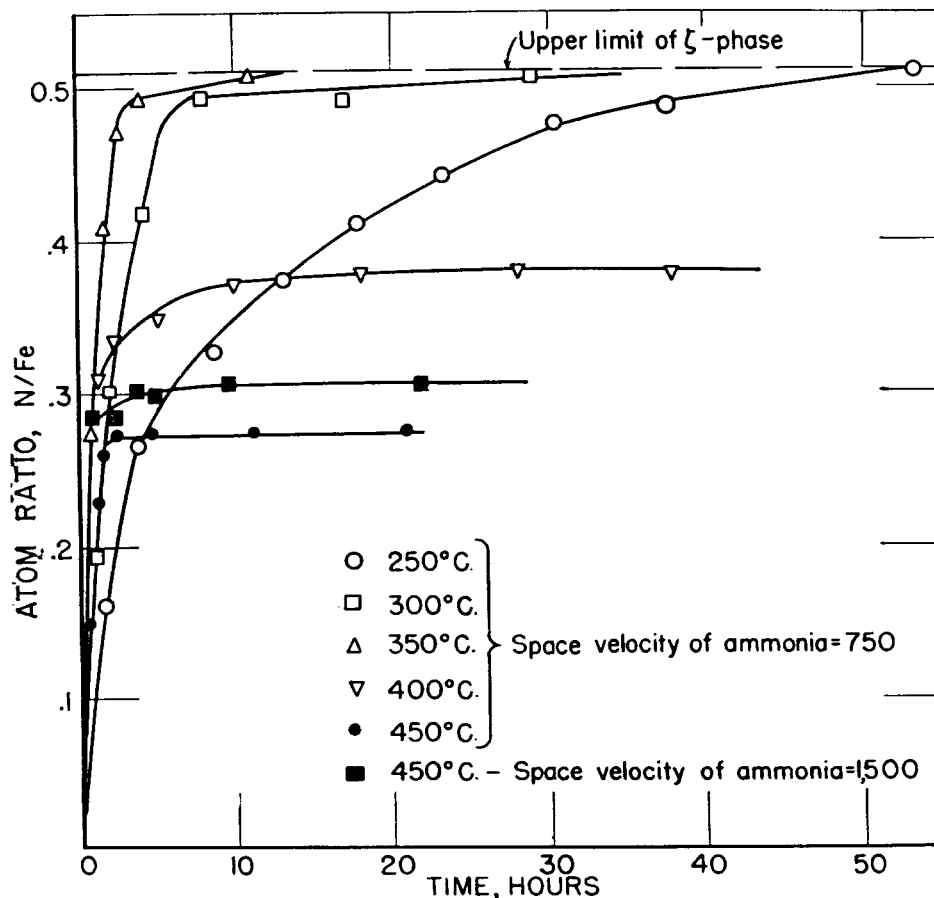

FIGURE 27.—Rate of Nitriding Catalyst D3001 in Ammonia at Various Temperatures.

standard batch of an ε-phase nitride was prepared and placed in a glass vessel in inert gas, and small samples were transferred into glass tubes and were carburized with carbon monoxide at an hourly space velocity of 80, as shown in table 36. At 350° C. and below nitrogen was neither appreciably expelled nor replaced by carbon. The removal of nitrogen increased only slightly with increased carbiding times and temperatures up to 350° C. On the other hand, the atom ratio of carbon plus nitrogen to iron increased toward a limiting value of about 0.500 to 0.508. Similar results were observed when γ'-phase nitride was carburized at 350° C.; that is, not much nitrogen was evolved or displaced, and carbidic carbon entered the lattice fairly rapidly and presumably occupied the vacant lattice positions. At 400° C. the rate of the replacement reaction was more rapid, as indicated by increases in the carbon : iron atom ratio and decreases in nitrogen : iron as the atom ratio of carbon plus nitrogen to iron approached its limit. The ζ-phase was formed during carburization for 10 hours. At 450° C. nitrogen was evolved faster than carbon was deposited. The data were somewhat erratic, indicating that the reaction may have been difficult to control at this temperature. The sample from the 10-hour carburization was largely Hägg car-

Table 36.—*Carburization of ε–iron nitride with carbon monoxide*

Temperature, °C.	Time, hours	Atom ratios to iron			Phases [1]
		Carbon	Nitrogen	$\bar{C} + \bar{N}$	
Original nitride___	0	0.00	0.46	0.46	ε.
250_____	1	.02	.47	.49	ε.
	5	.02	.46	.48	ε.
	10	.03	.45	.48	ε.
300_____	1	.02	.46	.48	ε.
	5	.04	.45	.49	ε.
	10	.04	.47	.51	ε.
350_____	1	.04	.45	.49	ε.
	5	.06	.44	.50	ε.
	10	.08	.43	.51	ε.
400_____	1	.03	.46	.49	ε.
	5	.14	.36	.50	ζ.
	10	.30	.18	.48	ζ, M.
450_____	1	.18	.20	.38	ε, M.
	5	.41	.02	.43	χ, M, α (?).
	10	.46	.01	.47	χ, α (?), M (?).

[1] ε = ε-nitride or carbonitride, ζ = ζ-carbonitride, α = α-iron, M = magnetite, and χ = Hägg carbide. Phases in order of decreasing intensities of X-ray diffraction patterns.

bide, in agreement with Jack's results.[25] Magnetite was formed, presumably due to a high carbon dioxide : carbon monoxide ratio resulting from rapid carburization reactions. The relative constancy of the sum of the atom ratios of carbon and nitrogen to iron indicates that the formation of free carbon was negligible.

[25] Work cited in footnote 5, p. 51.

STUDIES OF FISCHER-TROPSCH SYNTHESIS

In addition to a study of the physical and chemical properties of the catalysts, the synthesis was studied in the laboratory-scale reactors previously described.[26] In this way the activity and durability of the catalysts can be assayed, and the probable value of the catalyst for use in large-scale production can be judged. These tests are also used for experiments on the mechanism of the reaction and the effect of variables, such as temperature, pressure, and gas composition.

COBALT CATALYSTS

COBALT CARBIDE IN THE SYNTHESIS

The concept of metal carbide as a synthesis intermediate has been used rather loosely. Distinction must be made between bulk carbide and some sort of "surface" carbide as a possible intermediate. The idea of "surface" carbide is a particularly elusive one, as it is difficult to distinguish between a "surface"

carbide and adsorbed carbon monoxide. Early investigators [27–29] showed that both carburization and subsequent hydrogenation of cobalt-thoria- kieselguhr catalysts were much more rapid than those of pure cobalt. Studies of cobalt carbide in catalysts were undertaken with the realization that the reactions involved may be quite different from those encountered with cobalt. Figures 28 and 29 show curves of carbon content versus time for carburization in carbon monoxide and hydrogenation of catalysts 89K ($100Co:6ThO_2:12MgO:200$ kieselguhr) and 108B ($100Co:18ThO_2:100$ kieselguhr). The catalysts were initially reduced in hydrogen at 400° C., carburized in carbon monoxide at 208° C., and then hydrogenated at 208° C. Catalyst composition was determined by X-ray diffraction analysis and change in weight.

X-ray diffraction analysis showed the presence of disordered cobalt after reduction, cobalt carbide after carburization, and α-cobalt after

[26] Storch, H. H., Anderson, R. B., Hofer, L. J. E., Hawk, C. O., Anderson, H. C., and Golumbic, N., Synthetic Liquid Fuels From Hydrogenation of Carbon Monoxide, Part I: Bureau of Mines Tech. Paper 709, 1948, 213 pp.

[27] Bahr, H. A., and Jessen, V., [Dissociation of Carbon Monoxide on Cobalt]: Ber. deut. chem. Gesell., vol. 63B, 1930, pp. 2226–2237.
[28] Eidus, Y. T., and Zelenskii, N. D., [Reaction of Carbon Monoxide With Cobalt Catalysts Used in the Synthesis of Gasoline From Water Gas]: Bull. Acad. Sci. U. R. S. S., classe sci. chem., 1942, pp. 45–54.
[29] Craxford, S. R., and Rideal, E. K., Mechanism of the Synthesis of Hydrocarbons From Water Gas: Jour. Chem. Soc., 1939, pp. 1604–1614.
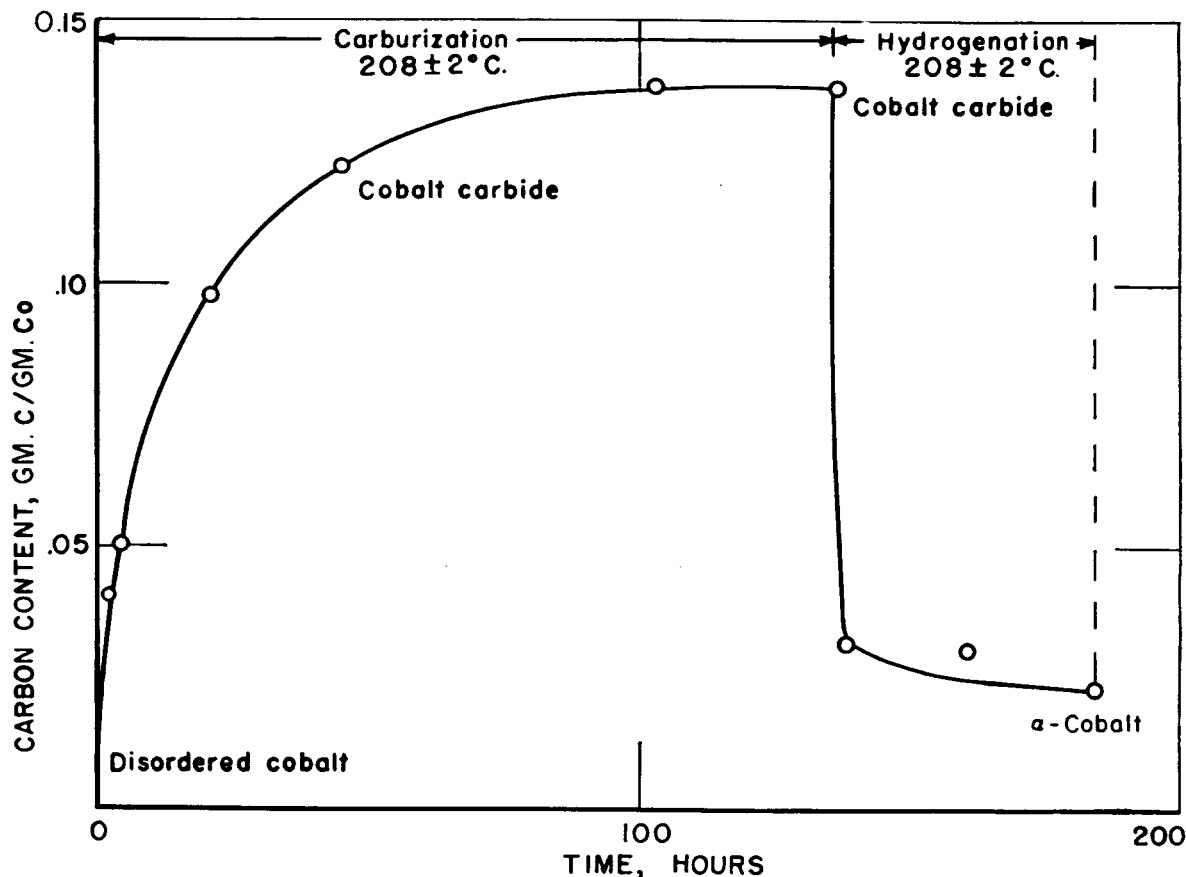
FIGURE 28.—Carburization of Cobalt-Thoria-Magnesia-Kieselguhr Catalyst 89K With Carbon Monoxide and Subsequent Hydrogenation.

rehydrogenation.[30] Schematic X-ray diffraction patterns obtained from catalyst 89K after initial reduction, after carburization, and after rehydrogenation appear in figure 30. The carbon:cobalt ratio of catalyst 108B closely approached that of Co_2C (0.1015), but this value was exceeded (0.137) for catalyst 89K. Upon hydrogenation (fig. 28), carbon equivalent to cobalt carbide was removed, the amount remaining in catalyst 89K representing (presumably) free carbon. The rate of hydrogenation of carbide was greater than its rate of formation as shown in figure 31. The cycle of carburization-hydrogenation was repeated many times without any major change in the rate or extent of carburization (fig. 32), although the amount of free carbon increased somewhat during each carburization stage. Thus, α- and disordered-cobalt react with carbon monoxide in nearly the same way.

SYNTHESIS TESTS OF CARBIDED CATALYSTS

Several tests were made to determine the activity of carbided catalysts. In one experi-

ment, catalyst 108B was reduced for 2 hours in hydrogen at 360° C., after which it was carburized in carbon monoxide for 24 hours at 200° C. This treatment should convert 80 percent of the cobalt in the catalyst to Co_2C. Synthesis in $2H_2 : 1CO$ gas at atmospheric pressure was begun at 177° C., and the temperature was quickly raised to 182° C., with the results shown in figure 33. The carburized catalyst showed low catalytic activity initially, as measured by the fractional decrease in gas volume (contraction) as the gas passed through the converter. Increasing the temperature to 190° C. increased the contraction to only 33 percent, even after one day at the higher temperature. The catalyst was then reduced in hydrogen at 210° C., a treatment that should have removed almost all of the carbide. Reexposure to synthesis gas resulted in a (normal) contraction greater than 70 percent at 180° C. Recarburizing the active catalyst 24 hours at 200° C. again reduced the activity to the low value observed after the first carburization. Rehydrogenation of the carbided sample again restored the normal activity.

In another experiment, a sample of catalyst 108B was carburized in carbon monoxide at

[30] Hofer, L. J. E. and Peebles, W. C., X-ray Diffraction Studies of the Action of Carbon Monoxide on Cobalt-Thoria-Kieselguhr Catalysts. I: Jour. Am. Chem. Soc., vol. 69, 1947, pp. 2497-2500.
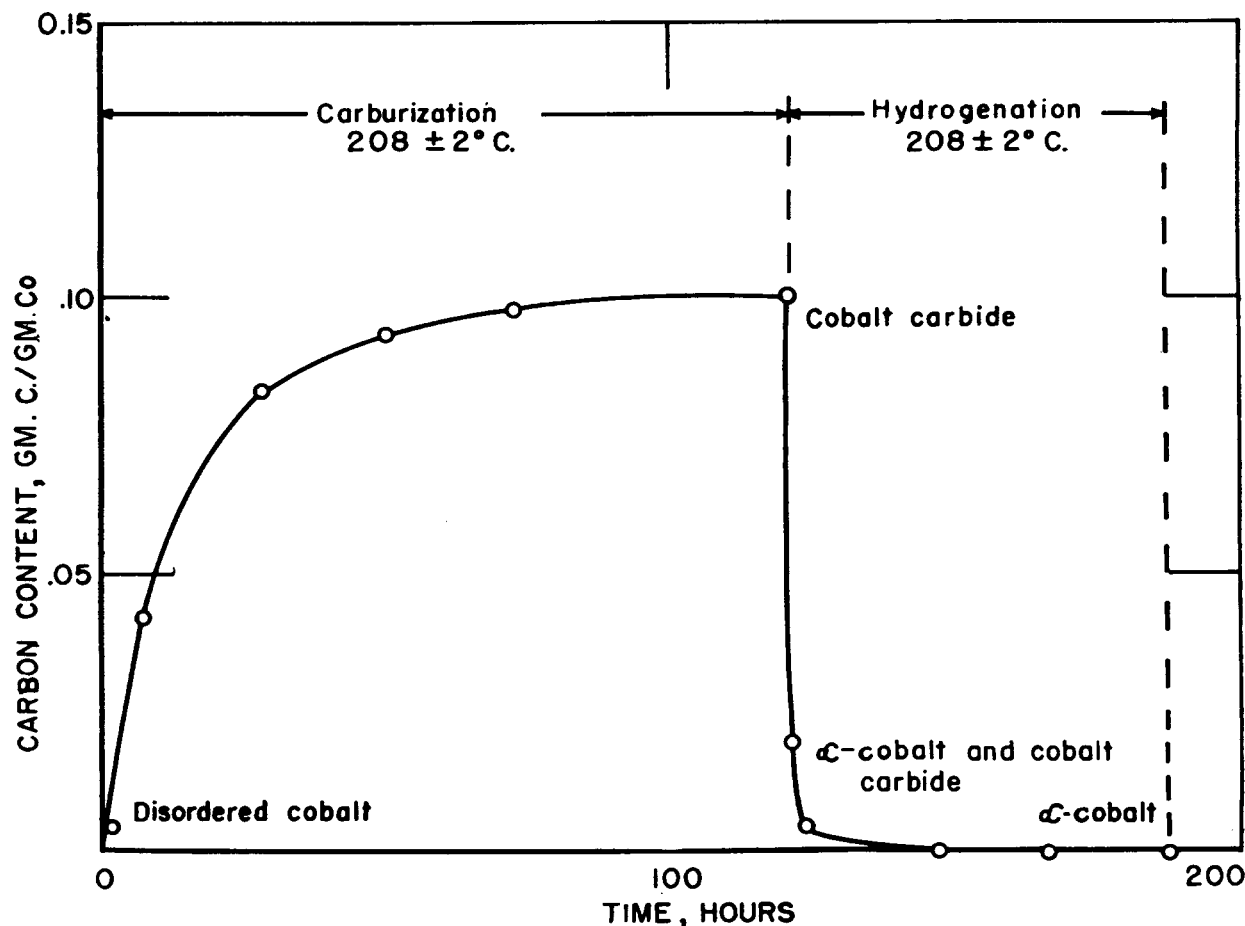
FIGURE 29.—Carburization of Cobalt-Thoria-Kieselguhr Catalyst 108B With Carbon Monoxide and Subsequent Hydrogenation.

210° C. to an extent equivalent to 110 percent Co_2C. The excess carbon monoxide may be accounted for by chemisorbed carbon monoxide or deposition of free carbon. This sample had no appreciable activity in flowing synthesis gas, while a control sample that was not carburized gave large yields of oil and water. Partial hydrogenation at 190° C. of the carburized sample removed 72 percent of the carbon that had been introduced and restored the activity to about half the normal value.

A third experiment [31] was made on a carburized sample of catalyst 108B, as shown in table 37. The sequence of carburization and hydrogenation cycles was similar to those employed in surface-area and chemisorption experiments described in table 7 (p. 16), except that catalysts for the adsorption studies were not used in the synthesis. Since the pore geometry of the catalyst seldom changes during the synthesis, the data in table 7 may be used as a basis for explaining the synthesis results. After

carburization (b) of table 37, at 208° C. the activity decreased with an increase in yield of light hydrocarbons. Conversion of the cobalt in a catalyst to cobalt carbide did not change the total surface area of the catalyst (1R and 1C of table 7); hence, the lower activity of the carburized catalyst (b of table 37) must be related to a change in the quality and not the extent of the surface. The volume of carbon monoxide chemisorbed at —195° C. on the carburized catalyst was only one-third of that chemisorbed on the original reduced catalyst. After reduction (2R of table 7), the volume of chemisorbed carbon monoxide was less than half of the chemisorption on the original reduced sample. This may be a result of poisoning by the small amount of residual carbide. Although hydrogenation at 208° C. (c) increased the activity, such a treatment did not completely counteract the inhibiting effect of previous carburization. Subsequent carburization treatments decreased the catalyst activity still further, and alternate reduction with hydrogen only partly compensated for the adverse effect of previous carburization. This effect may be

[31] Anderson, R. B., Hall, W. K., Krieg, A., and Seligman, B., Studies of the Fischer-Tropsch Synthesis. V. Activities and Surface Areas of Reduced and Carburized Cobalt Catalysts: Jour. Am. Chem. Soc., vol. 71, 1949, pp. 183-188.
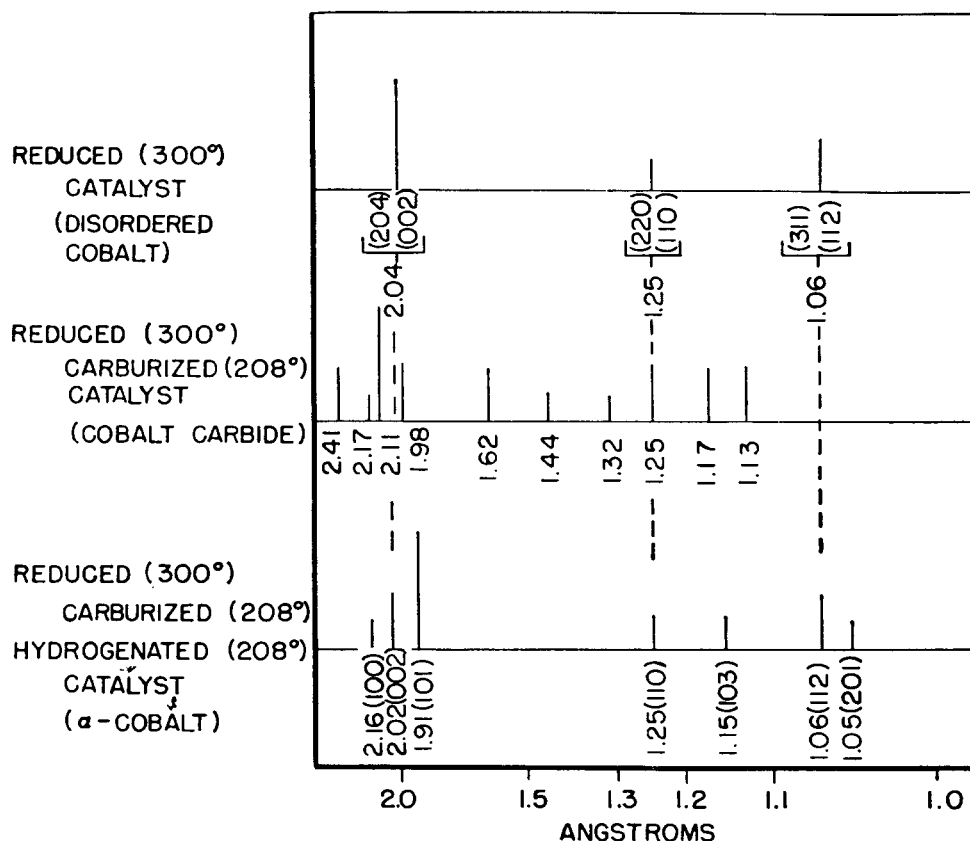
FIGURE 30.—X-Ray Diffraction Patterns of Catalyst 89K (100Co:6ThO₂:12MgO:200 Kieselguhr), Taken at Various Stages of Treatment With Carbon Monoxide and Hydrogen.

connected with the conversion of disordered cobalt to ordered h. c. p. α-cobalt. After carburization at 274° C. (i) the activity and methane formation did not differ significantly from those observed after carburization at 208° C.

An increase in the fraction of light hydrocarbons in the products accompanied the decreased activity of carburized catalysts. Free carbon, deposited from carbon monoxide at 235° C. and higher temperatures, had a smaller effect on activity; but the product distribution was

TABLE 37.—*Effect of carburization and hydrogenation on activity and product distribution of cobalt catalyst 108B*

Space velocity of synthesis gas per hour, 100; synthesis pressure, 1 atm.

| Period	Pretreatment				Synthesis		Synthesis gas reacted, percent	Products, gm./m.³ of synthesis gas reacted			
	Gas	HSV [1]	Temp., ° C.	Hours	Hours	Average temp., ° C.		CH₄	C₃+C₄	C₁—C₄	Liquids and solids
a	H₂	3,000	360	2	73	173	66. 6	21. 8	27. 2	55. 9	105. 7
b	CO	100	208	16	126	195	47. 4	41. 8	37. 8	90. 1	64. 4
c	H₂	100	208	16	149	190	63. 8	27. 7	38. 7	72. 6	106. 9
d	CO	100	208	16	149	191	32. 7	41. 6	33. 0	82. 3	
e	H₂	100	208	16	127	190	51. 7	34. 8			81. 8
f	CO	100	208	16	176	193	22. 9	84. 3			
g	H₂	100	208	16	126	190	42. 3				
h	CO	100	208	16	125	191	17. 5	122. 9	53. 7	189. 1	46. 9
i	CO	100	274	15	149	191	18. 9	106. 3	18. 5	132. 3	10. 6
j	H₂	100	208	16	119	191	56. 3	73. 5	34. 5	108. 2	15. 8

[1] Hourly space velocity.
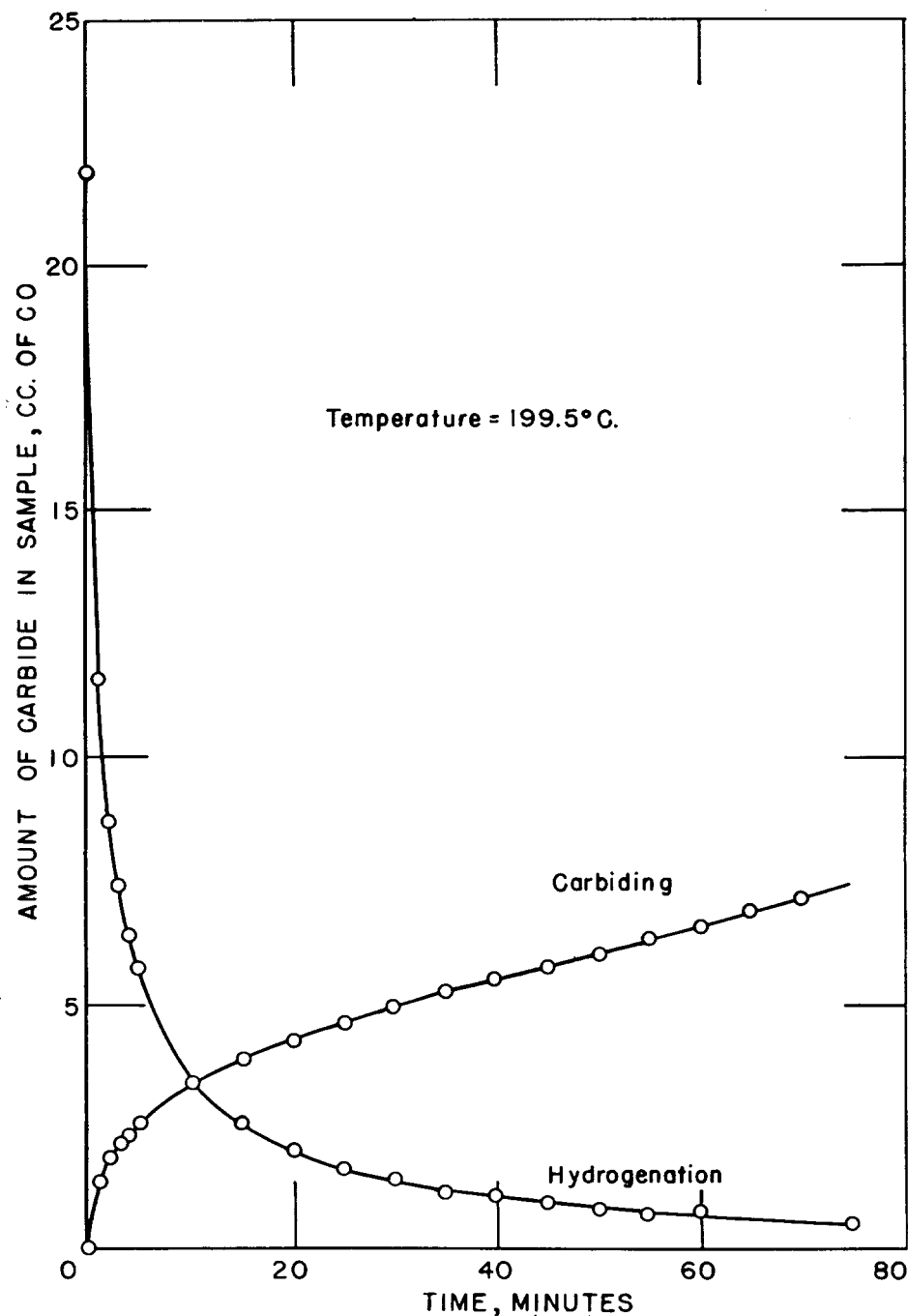
FIGURE 31.—Comparison of Rates of Formation and Hydrogenation of Carbide
in Cobalt-Thoria-Kieselguhr Catalyst 108B.

shifted more toward light hydrocarbons than for corresponding reduced or carbided catalysts without appreciable amounts of free carbon. Free carbon—or processes accompanying its formation—inhibited carbide formation from carbon monoxide at 208° C., some inhibition being observed even after the free carbon had been decreased to 2 milligrams per gram of catalyst by reduction at 360° C. (6R of table 7).

At least part of the methane and light hydrocarbons obtained from the carburized catalyst may have been formed by reducing carbide with hydrogen in the synthesis gas; concomitant with this process, the activity of the carburized catalyst increased for the first several days. The higher yields of light hydrocarbons with catalysts containing free carbon cannot be explained in this manner, because free carbon is not
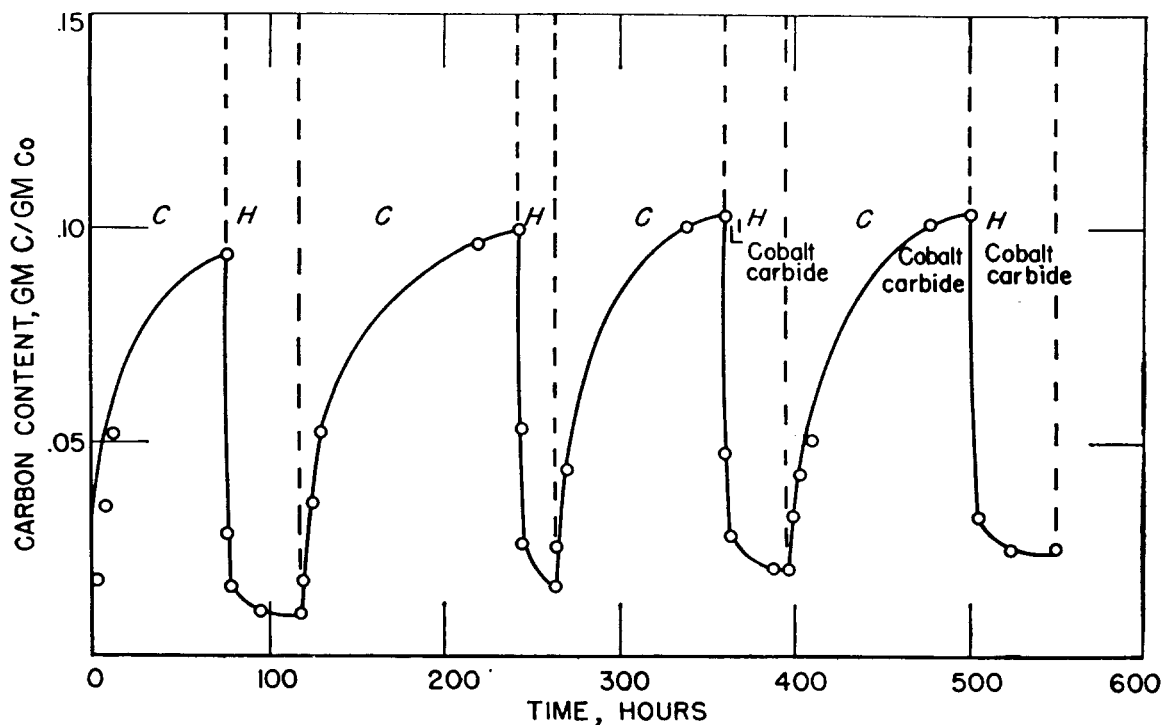
FIGURE 32.—Successive Cycles of Carburization (C) and Hydrogenation (H) of Cobalt-Thoria-Kieselguhr Catalyst 108B at $208 \pm 2°$ C.
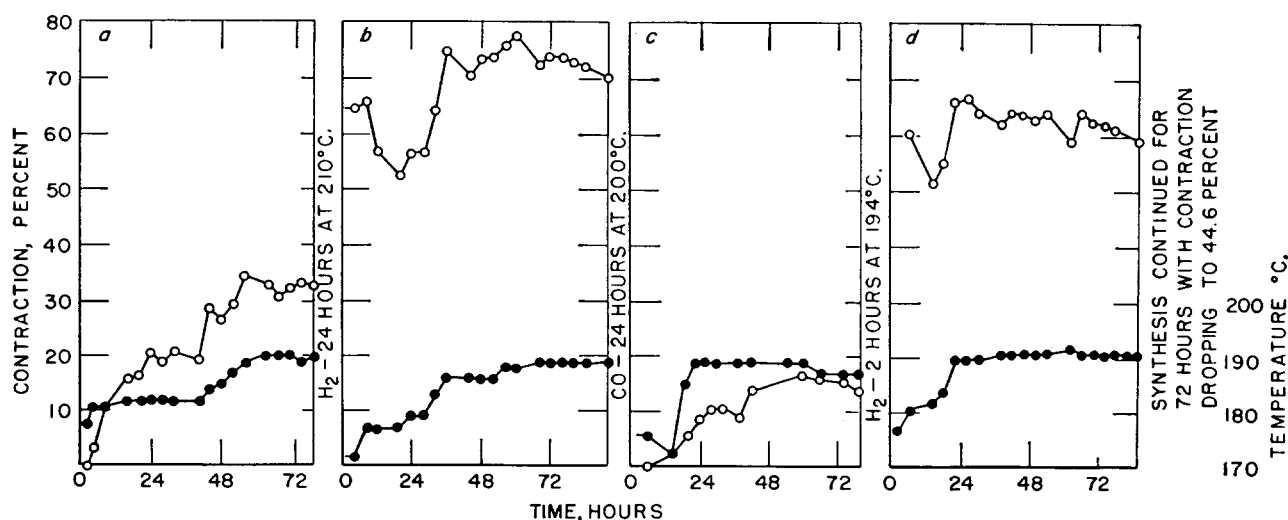

FIGURE 33.—Apparent Contraction ◯ and Temperature ● During Tests of Cobalt Catalyst 108B at Atmospheric Pressure.

hydrogenated at synthesis temperatures. Although deposition of large amounts of free carbon slightly increased the area of the cobalt surface, indicating some splitting of the cobalt lattice by carbon, this increase was relatively small. Hence, most of the free carbon was deposited at the surface and not within the crystallites of cobalt.

Corresponding results were obtained with an

89-type catalyst.[32] When catalyst 89J was reduced with hydrogen at 400° C. and carburized with carbon monoxide for 24 hours at 200° C. the volume of carbon monoxide reacted was equivalent to 70-percent conversion of the cobalt, to Co_2C. Exposure of this carburized sample to cirlatcuing synthesis gas in a glass

[32] Weller, S., Hofer, L. J. E., and Anderson, R. B., Role of Bulk Carbide in the Fischer-Tropsch Synthesis: Jour. Am. Chem. Soc., vol. 70, 1948, pp. 799–801.

reactor resulted in an over-all synthesis rate at 150° C. of 60 to 70×10^{-4} grams of carbon per gram of cobalt per hour. After removal of the carbide by hydrogenation at 150° to 194° C. and reexposure of the sample to synthesis gas, a synthesis rate of 250 to 300×10^{-4} grams of carbon per gram of cobalt per hour was observed—an increase of 400 percent.

A similar but smaller effect of carbiding was observed with catalyst 89EE. This catalyst is not entirely representative of the 89 series, being less active than other catalysts of this type. Nevertheless, carburized 89EE was less active than noncarburized samples. Figure 34 indicates that both the carburized and hydrogenated samples approached the same activity after long periods of operation.

The inhibitory effect of carburizing before use of the catalyst in the synthesis cannot be explained as a poisoning due to the deposition of free carbon during carburizing, because the catalyst is made active by hydrogenation at temperatures where free carbon is not affected.

precarburization), no carbide was found at the end of the test. In other words, bulk carbide apparently is not produced during steady-state synthesis in quantity sufficient to be detected by X-ray analysis, and carbide (already present) is not removed at an appreciable rate during steady-state synthesis.

X-ray diffraction data also indicate that appreciable quantities of bulk cobalt carbide are not present at any time in the Fischer-Tropsch synthesis. Cobalt in catalysts reduced at 400° C. exists primarily as disordered cobalt. There is a transition between hexagonal, close-packed α-cobalt and face-centered cubic β-cobalt at about 400° C.;[33] the transition is very slow, and a disordered structure is formed near the transition temperature.[34] At the temperature of the Fischer-Tropsch synthesis on cobalt catalyst (225° C. and below), disordered cobalt is thermodynamically unstable with respect to hexagonal, close-packed cobalt. Carburization of reduced samples containing disordered cobalt, followed by hydrogenation of the carbide so formed, both at 200° C., always converts the
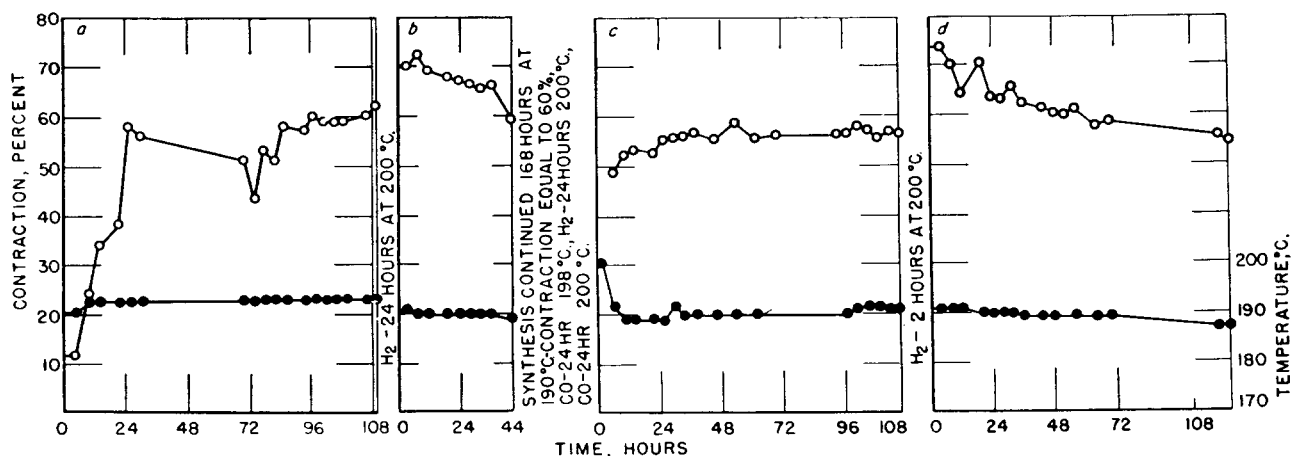

FIGURE 34.—Apparent Contraction ○ and Temperature ● During Test 79 With Cobalt Catalyst 89EE at Atmospheric Pressure.

Catalyst was reduced in hydrogen at 400° C. and carbided with carbon monoxide at 200° C. for 24 hours before test.

EVIDENCE THAT BULK COBALT CARBIDE IS NOT FORMED DURING SYNTHESIS

Further evidence that bulk carbide is not an intermediate in the synthesis is provided by X-ray analysis of used catalysts. X-ray diffraction analysis of catalysts 108B, which were partly carburized before synthesis and then used in the synthesis for several days, showed that cobalt carbide was still present in the samples. (In pure hydrogen, the carbidic carbon would have been completely removed as methane in several hours.) On the other hand, when catalyst samples were used in synthesis immediately after reduction (without

disordered cobalt to the low-temperature, stable, hexagonal form. Yet all uncarburized samples of cobalt catalyst have yielded identical X-ray diffraction patterns before and after use in the synthesis (table 9, p. 17). If any appreciable quantity (more than 5 percent) of the cobalt had passed through the carburization-hydrogenation cycle at any time during the synthesis, it would have appeared as close-packed, hexagonal cobalt rather than disordered. As this does not occur, it follows that, within the limits of the

[33] Hendricks, S. B., Jefferson, M. E., and Shultz, J. F., [The Transition Temperatures of Cobalt and Nickel. Some Observations on the Oxides of Nickel]: Ztschr. Krist., vol. 73, 1930, pp. 376–380.
[34] Edwards, O. S., and Lipson, H., An X-Ray Study of the Transformation of Cobalt: Jour. Inst. Metals, vol. 69, 1943, pp. 177–187.

X-ray method, cobalt was not converted to bulk carbide and subsequently hydrogenated during the synthesis; hence, bulk carbide is neither an intermediate in the synthesis nor a catalyst for it.

EFFECT OF OPERATING VARIABLES

Over cobalt catalysts, the Fischer-Tropsch synthesis proceeds at a rate that depends upon temperature.[35][36] operating pressure,[37] gas composition,[38-41] gas flow rate,[42][43] and the chemical and physical nature of the catalyst.[44-50]

TEMPERATURE

The rate of synthesis over cobalt catalysts is strongly dependent upon temperature. The variation of rate with the temperature of a cobalt-thoria-magnesia-kieselguhr catalyst was studied in a flow of $2H_2:1CO$ gas at atmospheric pressure.[51] The flow of gas and the temperature were varied to maintain a constant conversion, and apparent activation energies were computed from the space-time yields and the temperatures at constant conversion. For constant conversions in the range 15 to 75 percent, apparent activation energies of 25 ± 1 kcal./mol. were found. Weller[52] found similar activation energies for a cobalt-thoria-kieselguhr catalyst at atmospheric pressure with $2H_2:1CO$ at high

space velocities and low conversions (1 to 2 percent. Seligman[53] found an activation energy of 20.0 kcal./mol. for cobalt-thoria-kieselguhr catalyst at 7.8 atmospheres, using $2H_2:1CO$ gas. An activation energy of 24.3 kcal./mol. was computed from the first stage of a 2-stage test,[54] with a cobalt-thoria-kieselguhr catalyst using $2H_2:1CO$ gas at 10 atmospheres.

PRESSURE

Above atmospheric pressure the synthesis rate for kieselguhr-supported cobalt catalysts was virtually independent of total operating pressure.[55] Other cobalt catalysts, however, showed a decreased reaction rate at operating pressures greater than 1 atmosphere.[56] At pressures less than atmospheric, the rate was dependent upon total pressure. Fischer and Pichler found that at the same temperature a given contraction was attainable at 1/3 atmosphere by using 1/3 the space velocity normally used for this contraction at atmospheric pressure, suggesting that in this pressure range the synthesis rate was directly proportional to total pressure; but it had been reported previously[57] that from 0.4 to 0.9 atmosphere the rate of synthesis on a cobalt-thoria-kieselguhr catalyst varied with total pressure to the 0.45 power.

The data in table 8 (p. 17) establish that the surface of cobalt catalysts is heavily covered with hydrocarbons during operation at atmospheric pressure. A characteristic of atmospheric-pressure operation with cobalt catalysts is a high initial catalytic activity, which is followed by a lower, relatively constant rate of synthesis, continuing 2 weeks or more.[58] A rapid decline in activity eventually takes place, necessitating reactivation of the catalyst. Craxford[59] suggested that this final loss in activity is related to the time when the pores of the catalyst become completely filled with wax. This explanation is supported by the fact that, when the used catalyst is hydrogenated, large amounts of wax and other hydrocarbons are removed, and the catalyst activity is restored.

Data obtained from experiments[60] in which cobalt catalysts 89J, 89K, and 108B were used are summarized in table 38. In these experiments the space velocity of synthesis gas per hour was maintained constant, and the operating temperature was varied to maintain 70-percent contraction. These data indicate that the activities of pelleted cobalt catalysts at atmos-

[35] Weller, S., Kinetics of Carbiding and Hydrocarbon Synthesis With Cobalt Fischer-Tropsch Catalysts: Jour. Am. Chem. Soc., vol. 69, 1947, pp. 2432-2436.
[36] Anderson, R. B., Krieg, A., Seligman, B., and O'Neill, W. E., The Fischer-Tropsch Synthesis. I. Tests of Cobalt Catalysts at Atmospheric Pressure: Ind. Eng. Chem., vol. 39, 1947, pp. 1540-1554.
[37] Fischer, F. and Pichler, H., [The Influence of Pressure Upon Several Conversions of Water Gas]: Brennstoff-Chem., vol. 12, 1931, pp. 365-372.
[38] Tsuneoka, S. and Fujimura, K., Benzine Synthesis From Carbon Monoxide and Hydrogen at Ordinary Pressures. XIX. The Ratio of CO-H₂ in the Initial Gas Mixture: Jour. Soc. Chem. Ind.,(Japan), vol. 37, suppl., 1934, pp. 463-467.
[39] Fujimura, K. and Tsuneoka, S., Benzine Synthesis From Carbon Monoxide and Hydrogen Under Ordinary Pressure. XX. Composition of the Initial Gas Mixture (2): Jour. Soc. Chem. Ind. (Japan), vol. 37, suppl., 1934, pp. 704-711.
[40] Fischer, F. and Pichler, H., [The Simultaneous Effect of Carbon Monoxide and Carbon Dioxide During Hydrogenation With Particular Regard to Benzine Synthesis]: Brennstoff-Chem., vol. 14, 1933, pp. 306-310.
[41] Pichler, H., [The Reaction of Carbon Dioxide During Hydrogenation]: Brennstoff-Chem., vol. 24, 1943, pp. 39-40.
[42] Fischer, F. and Pichler, H., [The Synthesis of Paraffin From Carbon Monoxide and Hydrogen Upon Cobalt Catalysts, Medium-Pressure Synthesis]: Brennstoff-Chem., vol. 20, 1939, pp. 41-48.
[43] Erofeev, B. V., Runtso, A. P., and Volkova, A. A., [Kinetics of the Catalytic Reduction to Hydrocarbons of Carbon Monoxide by Hydrogen on a Cobalt-Thorium Catalyst]: Acta Physicochim., U. R. S. S., vol. 13, 1940, pp. 111-122.
[44] Storch, H. H., Anderson, R. B., Hofer, L. J. E., Hawk, C. O., Anderson, H. C., and Golumbic, N., Synthetic Liquid Fuels from Hydrogenation of Carbon Monoxide, Part I: Bureau of Mines Tech. Paper 709, 1948, 213 pp.
[45] Craxford, S. R., The Chemistry of the Fischer-Tropsch Synthesis: Fuel, vol. 26, 1947, pp. 119-123.
[46] Craxford, S. R., The Fischer-Tropsch Synthesis With Cobalt Catalysts: Jour. Soc. Chem. Ind., vol. 66, 1947, pp. 440-444.
[47] Craxford, S. R., Mechanism of the Fischer-Tropsch Reaction: Trans. Faraday Soc., vol. 42, 1946, pp. 576-580.
[48] Anderson, R. B., Hall, W. K., Krieg, A., and Seligman, B., Studies of the Fischer-Tropsch Synthesis. V. Activities and Surface Areas of Reduced and Carburized Cobalt Catalysts: Jour. Am. Chem. Soc., vol. 71, 1949, pp. 183-188.
[49] Craxford, S. R., The Fischer-Tropsch Synthesis of Hydrocarbons and Some Related Reactions: Trans. Faraday Soc., vol. 35, 1939, pp. 966-967.
[50] Weller, S., Hofer, L. J. E., and Anderson, R. B., Role of Bulk Carbide in the Fischer-Tropsch Synthesis: Jour. Am. Chem. Soc., vol. 70, 1948, pp. 799-801.
[51] Work cited in footnote 36, above.
[52] Work cited in footnote 35, above.
[53] Seligman, B., and Anderson R. B., Unpublished data.
[54] Fischer, F., Pichler, H., and Dienst, W. [Approach to Theoretical Possible Yields in the Fischer-Pichler Intermediate Pressure Synthesis]: Brennstoff-Chem., vol. 20, 1939, pp. 221-228.
[55] Work cited in footnote 48, above.
[56] Work cited in footnote 37, above.
[57] Work cited in footnote 44, above.
[58] Hall, C. C., and Smith, S. L., The Life of a Cobalt Catalyst for the Synthesis of Hydrocarbons at Atmospheric Pressure: Jour. Soc. Chem. Ind., vol. 65, 1946, pp. 128-136.
[59] Work cited in footnote 47, above.
[60] Work cited in footnote 48, above.

TABLE 38.—*Effect of operating pressure on cobalt catalysts*

Space velocity per hour = 100

Test No.	Operating periods	Pressure, atm. (absolute)	Average temp., ° C.[1]	Apparent contraction, percent	Products, percent			
					CH_4	C_3+C_4	C_1-C_4	Liquids plus solids [2]
Pelleted [3] cobalt–thoria–kieselguhr catalyst 108B								
29	b–q	1	185(186)	70. 9	12. 1	10. 0	24. 5	75. 5
29	i–p	7. 8	189(186)	71. 3	19. 0	10. 9	33. 5	66. 5
31	b–j	7. 8	187	71. 8	18. 6	10. 5	32. 0	68. 0
Granular [4] cobalt–thoria–magnesia–kieselguhr catalyst 89K								
17	b–k	1	186(187)	74. 4	13. 1	10. 2	25. 6	74. 4
17	v–z	7. 8	188(188)	72. 0	14. 0	8. 6	23. 2	76. 8
Pelleted [5] cobalt–thoria–magnesia kieselguhr catalyst 89J								
21	c–l	1	186(186)	72. 0	15. 6	8. 1	24. 9	75. 1
21	o–u	7. 8	191(188)	69. 5	18. 2	10. 4	28. 3	71. 7

[1] The temperatures in parentheses are those observed during the last 2 weeks at atmospheric pressure and the first 2 weeks at 7.8 atm.
[2] Liquid plus solid hydrocarbons.
[3] Cylindrical pellets, 3.2 mm. in diameter by 3.2 mm. in length.
[4] Broken filter cake.
[5] Cylindrical pellets, 3.2 mm. in diameter by 1.6 mm. in length.

pheric pressure equal, or slightly exceed the corresponding activities at 7.8 atmospheres (absolute) at which pressure greater amounts of methane and light hydrocarbons are usually produced.

In the last several weeks of operation in test 80 with cobalt catalyst 108B, the effect of alternate weeks of operation at 1 and 7.8 atmospheres was studied (table 39). After week *i*, operation was continuous, without hydrogen reactivation between operating periods. This reactivation at weekly intervals

had been used in the first part of this test. There was no change in catalyst activity with operation at 7.8 atmospheres (weeks *g*, *i*, and *k*) from that noted in the previous period of atmospheric-pressure operation (weeks *f*, *h*, and *j*). However, atmospheric-pressure operation following operation at 7.8 atmospheres required a higher operating temperature to maintain the same conversion, denoting decreased catalyst activity (see weeks *g* and *h*, *i*, and *j*, and *k* and *l*). When the catalyst was not reactivated with hydrogen, the loss in

TABLE 39.—*Alternate operation at 1 and 7.8 atm. of pelleted cobalt-thoria-kieselguhr catalyst 108B, test 80*

Operating periods of 5 and 6 days; hourly space velocity=100

Operating periods	Pressure, atm. (absolute)	Average temp., ° C.	Apparent contraction, percent	Products, percent			
				CH_4	C_3+C_4	C_1-C_4	Liquids plus solids
e [1]	1	187	72. 1	14. 9	10. 8	31. 9	68. 1
f [1]	1	186	70. 1	15. 4	16. 5	34. 0	66. 0
g [1]	7. 8	186	67. 2	21. 0	13. 0	34. 9	65. 1
h [1]	1	191	70. 3	19. 2	10. 0	36. 4	63. 6
i [1]	7. 8	188	69. 9	24. 6	13. 4	42. 5	57. 5
j	1	198	69. 1				
k [1]	7. 8	198	71. 3	41. 4	10. 3	53. 6	46. 4
l	1	207	68. 7	[2] 24. 6			

[1] Preceded by a 2-hour hydrogen reactivation at 10° C. higher than previous operating temperature.
[2] Approximate.

activity resulting from reduction of the operating pressure from 7.8 atmospheres to atmospheric pressure was larger; the yields of carbon dioxide and light hydrocarbons increased as activity of the catalyst decreased.

The general aspects of the differences in activity and selectivity may be explained by the following observations on the amount and nature of adsorbed hydrocarbons on the catalyst:

1. In the synthesis at atmospheric pressure the hydrocarbons adsorbed in the pores of the catalyst increase only slowly with time, and several weeks of synthesis are required to fill the pores completely.

2. In the synthesis at 7.8 atmospheres the pores of the catalyst become filled with hydrocarbons in a short time. The hydrocarbons deposited on the catalyst at atmospheric pressure have a higher molecular weight than those formed on the catalyst during synthesis at higher pressures.

3. In the atmospheric-pressure synthesis the bulk of the hydrocarbons are transferred out of the catalyst bed in the gas phase, which leads to selective adsorption of the high molecular weight fractions on the catalyst. In the pressure synthesis most of the hydrocarbons are liquids at synthesis condition, and the condensed hydrocarbons flow over the catalyst particles and continuously extract the high molecular weight material. On this basis the hydrocarbons in the catalyst pores are about the same as the hydrocarbons in the product oils.

4. In the atmospheric-pressure synthesis reactivation by hydrogenation or solvent extraction is very effective; however, in the medium-pressure synthesis these desirable results are not obtained. The ineffectiveness of reactivation of catalysts used at elevated pressures has never been adequately explained.

Although the pores of catalyst used in the medium-pressure synthesis are filled with waxy hydrocarbons, the solubility and rate of diffusion of synthesis gas in these liquids are great enough so that the observed rate of synthesis is about the same as in the atmospheric-pressure operation in which the pores of the catalyst are only partly filled. At 7.8 atmospheres the activity of the catalyst will remain essentially constant for periods as long as 3 months. When the operating pressure is lowered to 1 atmosphere after operation at 7.8 atmospheres, the mass transfer in the completely filled pores is too slow to maintain the synthesis rate observed at the higher pressure. In certain instances, especially when the catalyst is operated alternately at 1 and 7.8 atmospheres, the accumulation of high-molecular-weight wax during the atmospheric-pressure periods may lead to a lower activity in subsequent operation at 7.8 atmospheres.

The following observations may be made concerning the product distribution: A decrease of the accessibility of the catalyst surface, either by deposition of excessive quantities of wax (by operation at elevated pressures) or by decreasing the average pore diameter (by pelleting), causes the fraction of methane and other light hydrocarbons produced to

increase. In elevated-pressure operation the greater proportion of light hydrocarbons produced may result from the greater rate of diffusion of hydrogen, compared with that of carbon monoxide through the hydrocarbon film covering the catalyst surface,[61] so that successful operation at elevated pressure is possible with $1.5H_2 : 1CO$, whereas activity decreases rapidly with this gas at 1 atmosphere. The over-all effect of such a mechanism would be similar to operating with a hydrogen-rich synthesis gas.

COMPOSITION AND FLOW OF SYNTHESIS GAS

Seligman[62] studied the influence of gas composition on the rate of synthesis on a cobalt–thoria–kieselguhr catalyst at constant temperature and flow of synthesis gas. The conversion was maintained between 10 and 20 percent, so that only a small portion of either reactant was consumed. The volumes of hydrogen plus carbon monoxide consumed per hour were 23.6, 24.6, and 17.7 cc. (STP) per gram of catalyst at 170° C. for $3H_2 : 1CO$, $2H_2 : 1CO$, and $1H_2 : 1CO$ gases, respectively. The results of these experiments substantiate those of Craxford and Rideal,[63] who found the rate of synthesis on cobalt catalysts at constant temperature in a static system to be a maximum for $2H_2 : 1CO$ synthesis gas.

Plots of the percentage conversion of synthesis gas as functions of reciprocal space velocity for experiments with cobalt-thoria-kieselguhr at atmospheric pressure resemble those obtained for nickel catalysts.[64] Thus, in figure 35, the data of Anderson, Krieg, Friedel, and Mason[65] show that the percentage of conversion increased uniformly as the space velocity decreased for a wide variation in synthesis-gas composition. Within the accuracy of the data a considerable portion of the curves could be represented by straight lines, indicating that the rate of synthesis did not depend greatly upon the partial pressures of reactants and products. A more complete discussion of this relationship is given in the section dealing with kinetic studies with cobalt catalysts. At 200° C. and atmospheric pressure conversion over a cobalt-thoria-silica gel catalyst varied linearly with reciprocal space velocity for conversions of 25 to 45 percent.[66] This appears to be a linear portion of the type of conversion curve shown in figure 35.

[61] Work cited in footnote 45, p. 63.
[62] Work cited in footnote 53, p. 63.
[63] Work cited in footnote 26, p. 56.
[64] Storch, H. H., Golumbic, N., and Anderson, R. B., The Fischer Tropsch and Related Syntheses: John Wiley & Sons, New York, N. Y., 1951, 610 pp.
[65] Anderson, R. B., Krieg, A., Friedel, R. A., and Mason, L. S., Fischer-Tropsch Synthesis. VI. Differential Reaction Rate Studies With Cobalt Catalyst: Ind. Eng. Chem., vol. 41, 1949, pp. 2189-2197.
[66] Work cited in footnote 43, p. 63.

EFFECT OF PELLETING

In test 58 the effect of compressing cobalt catalyst 108B into large, dense (¼-inch-long by ⅛-inch-diameter) pellets is clearly demonstrated. Test 45, with ⅛- by ⅛-inch pellets, is comparable with test 58, in that reduction, induction, and operational procedures were similar. Data for these two tests are summarized in table 40. The larger pellets, with a greater density, required a higher operating temperature to maintain constant contraction at constant gas flow. This is in contrast to the behavior of granules and ¼₆- by ⅛-inch pellets of catalysts 89J and 89K, with which equal conversions were obtained at the same temperature and flow per gram of catalyst. In tests 45 and 58 and in previous experiments in which granules and small pellets were compared, the production of light hydrocarbons was higher with the denser catalyst.

KINETICS AND SELECTIVITY

Most published data on kinetics of the Fischer-Tropsch synthesis are difficult to interpret, because the reaction was usually studied under conditions yielding a high degree of conversion. Under such conditions actual partial pressures of the reactants and products throughout the catalyst bed—information important to the study of reaction kinetics—could be only vaguely estimated. Recent work in the Bureau of Mines laboratories was carried out with cobalt–thoria–magnesia–kieselguhr and cobalt–thoria–kieselguhr catalysts under carefully controlled conditions designed to minimize these difficulties.[67]

Previous studies [68] at atmospheric pressure showed that the activity of a freshly reduced catalyst decreased considerably during the first 12 hours and then remained relatively constant for 10 or more days. After hydrogen reactivation, the activity was restored to its initial value, and the cycle was repeated. The average activity remained the same over many such cycles.[69] In the Bureau of Mines special experiments [70] tests were made in this period of constant activity, using synthesis gas with H_2: CO ratios of 1, 2, and 3.

Before the special experiments under consideration, the catalyst was operated for 30 days with $2H_2$: $1CO$ gas at atmospheric pressure, with hydrogen reactivation at 200° C. every sixth day. Before the special experiment was begun, the catalyst was reactivated with hydrogen at 200° C. and operated with $2H_2:1CO$ for 3 days to insure constant activity. Pelleted catalyst 108B was used in this experiment.

⁶⁷ Work cited in footnote 65, p. 65.
⁶⁸ Work cited in footnote 58, p. 63.
⁶⁹ Work cited in footnote 36, p. 63.
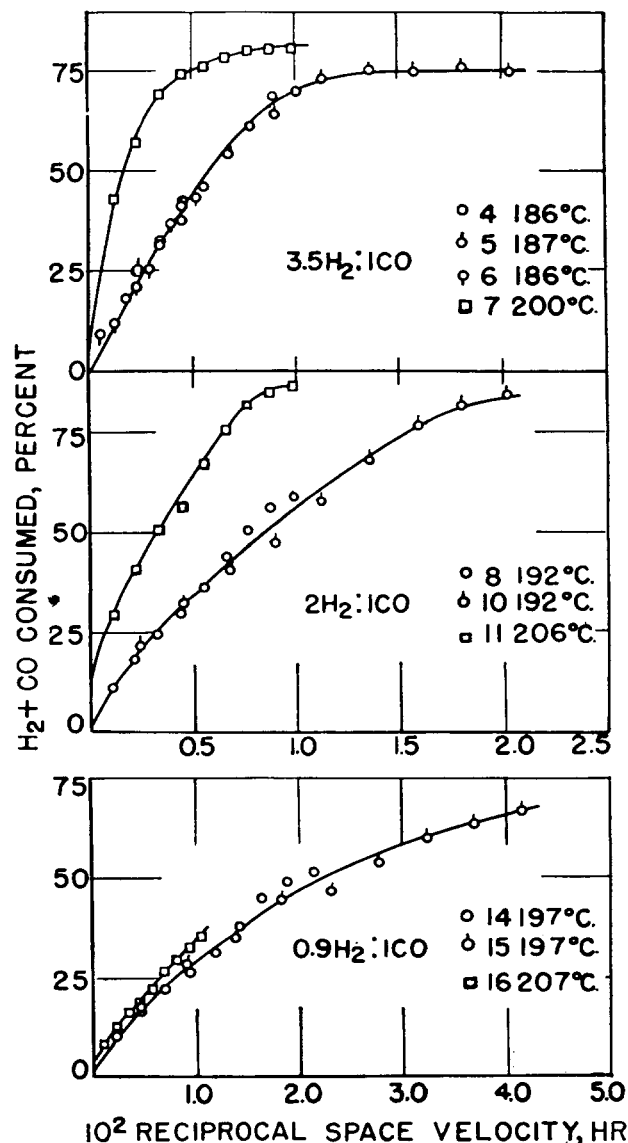⁷⁰ Work cited in footnote 65, p. 65.

FIGURE 35.—Variation of Extent of Conversion of Synthesis Gas With Reciprocal Space Velocity for Cobalt–Thoria–Kieselguhr Catalyst at Atmospheric Pressure, With Synthesis Gas Having Ratios of H_2 : CO of 3.5,2, and 0.9.

The reactor was of the type previously described [71] (see also p. 129 of Appendix). The thermocouple well, usually placed in the cross-sectional center of the catalyst tube, was replaced by a special sampling tube of the same diameter, with openings at 4-inch intervals. Gas samples could be removed from any desired opening through a close-fitting tube sliding inside the sample tube. About 5 percent of argon was added to the original synthesis gas as an inert reference component. As the argon was inert, its concentration increased with consumption of the synthesis gas. The apparent

⁷¹ Work cited in footnote 36, p. 63.

TABLE 40—*Effect of size and density of pellets on activity of cobalt catalyst 108B*

2H₂ + 1CO gas at atmospheric pressure

Test No.	Pellet size, mm.		Properties of raw catalyst		Average testing data for weeks 2–11					Activity, cc. of H₂ +CO reacted per hour per gm. catalyst at 187° C.
	Length	Diameter	Hg density, gm./cm.	Pore volume, cc./gm.	Weight of catalyst, gm.	Temp., ° C.	Yield, gm./m.³			
							CH₄	C₁–C₄	Liquid +solids	
X–45	3.2	3.2	1.13	0.56	36.8	187	25	44	82	99
X–58	6.4	3.2	1.51	.34	44.9	190	34	57	74	65

contraction, and the volume of any component at that point in the bed per unit volume of synthesis gas, can be computed from this increase in concentration of argon by means of the following equation:

$$\text{Apparent contraction} = C_x = (1 - f_o/f_x), \qquad (20)$$

where f_o and f_x equal the fractions of argon in the gas entering and at position x in the converter, respectively. The volume of gas at any point x is $V_o(1 - C_x)$. Thus the volume of component B is given by

$$V_B/V_o = (1 - C_x)f_{B_x}, \qquad (21)$$

where V_o = volume of gaseous components entering bed. As the gases were analyzed on a water-free basis and were sampled at room temperatures, water vapor and heavy hydrocarbons were not included in these volumes. The partial pressure of component B equals V_{B_x}/V_{total_x}, where V_{total_x} is the sum of the volumes of all components at position x. The volume of water

vapor was not determined directly, but was obtained from an oxygen balance

$$(V_{H_2O})_x = (V_{CO})_o - (V_{CO})_x - 2(V_{CO_2})_x. \qquad (22)$$

This is permissible, because nearly all of the oxygen in the products occurs as water and carbon dioxide. The volume of hydrocarbons other than methane was assumed to equal one-tenth of the volume of water vapor present. This assumes an average molecular weight of these hydrocarbons of C₈ to C₉; as the volume of hydrocarbon vapor was usually less than 3 percent of the total gas volume, these assumptions introduced no significant error. The total conversion from the beginning of the bed to any point is expressed as liters of hydrogen plus carbon monoxide consumed per hour, a measure of space-time yield.

Typical analyses of a set of these samples by means of the mass spectrometer are shown in table 41. The percentages of C₂ and higher hydrocarbons were too small to permit detailed treatment of their rates of formation; however,

TABLE 41.—*Gas analyses for test 10*

2H₂:1CO at 192° C.; all results in volume-percent

Sample	A	H₂	CO	CH₄	C₂	C₂= [1]	C₃	C₃=	C₄	C₄=	C₅	C₅=	CO₂
Synthesis gas	4.54	62.91	32.16	0.32									0.06
Gas port													
a	5.62	59.00	32.85	1.80	0.13	0.00	0.03		0.07	0.16	0.07	0.07	.20
b	6.31	56.97	32.67	2.89	.17	.01	.13	0.13	.10	.20		.10	.33
c	7.01	55.62	32.09	3.70	.23	−.04	.16	.10	.13	.26	.06	.13	.48
d	7.75	53.86	31.68	4.47	.33	−.02	.20	.16	.07	.36	.13	.20	.69
e	9.30	50.79	31.25	5.87	.42	.02	.26	.32	.16	.35	.10	.19	.90
f	11.37	46.24	29.98	8.07	.62	.01	.46	.42	.29	.62	.20	.29	1.34
g	14.01	40.46	28.95	10.85	.86	.01	.66	.49	.43	.73	.26	.36	1.81
h	16.36	35.61	26.96	13.48	1.10	.01	.91	.75	.52	.75	.29	.32	2.82
i	17.07	34.11	25.85	14.43	1.17	.02	1.01	.52	.62	.78	.42	.39	3.43

[1] Percentages of ethylene are calculated and represent upper limits. True contents of ethylene, if present, are probably less than 0.01 percent.
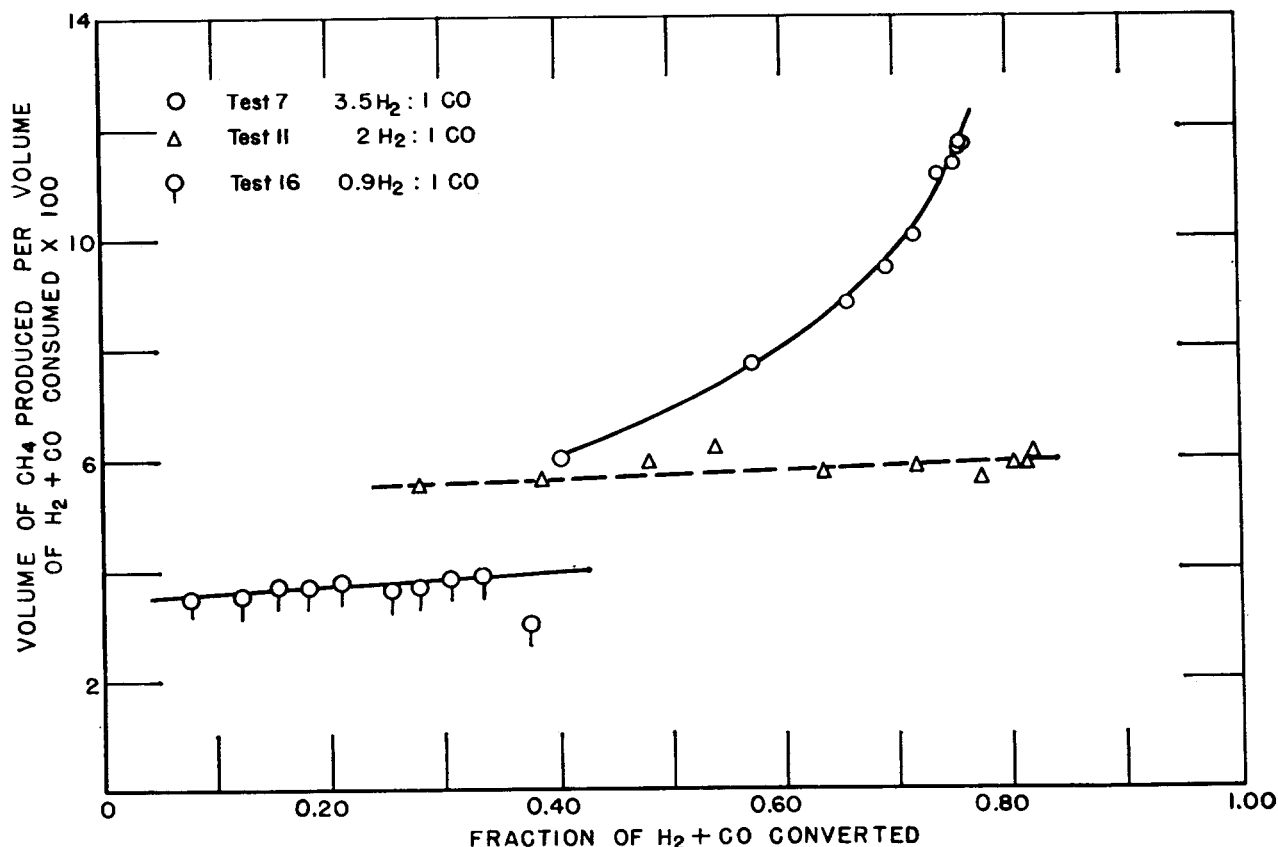
FIGURE 36.—Production of Methane on Cobalt-Thoria-Kieselguhr Catalyst at Atmospheric Pressure.

for C_2 to C_4 hydrocarbons it was possible to compare the total amount of saturated and unsaturated hydrocarbons present at any point in the bed. Figures 35 (p. 66) to 39 show the data as calculated by equations (20), (21), and (22). Figure 36 shows the effect of conversion on methane formation and figure 37 the effect of bed length (which is more or less proportional to conversion) on the ratio of saturated to unsaturated hydrocarbons. Figure 38 shows carbon dioxide formation as a function of conversion of carbon monoxide. The production of carbon dioxide is small in almost all cases, so that the usage ratio is largely unaffected.

The principal primary reaction of the synthesis on cobalt catalysts may be represented by the equation,

$$2H_2 + CO \rightarrow \frac{1}{n}(CH_2)_n + H_2O, \qquad (23)$$
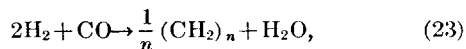
the usage ratio of H_2 to CO being about 2 $[H_2/(H_2 + CO) = 0.67]$ over a wide range of gas composition as shown in figure 39.

In the differential reactor[72] the rate of the synthesis (the slope of curves in fig. 35, p. 66) was rapid at the inlet of the bed, then decreased to a nearly constant value in the middle section,

and finally decreased again near the end of the bed or at a point where the reactants are strongly depleted. In the middle portion the rate was nearly constant, although the partial pressure of reactants and products changed considerably. The independence of the reaction rate on total pressure above 1 atmosphere[73] and the data of figure 35 suggest that the rate-controlling step is some process at the catalyst surface and not the rate of adsorption of reactants which would be strongly dependent upon the partial pressures of the reactants. A mechanism in which desorption of products is the rate-determining step predicts qualitatively many of the characteristics of the synthesis. The reaction is very complicated, because the catalyst is heavily covered with hydrocarbon products and the nature of the catalyst surface may be a function of the composition of the gas in contact with the catalyst. The synthesis rate was high for $2H_2$:1CO and $3.5H_2$:1CO gases but considerably lower for $1H_2$:1CO gas, in agreement with previous work.[74] The low activity with carbon monoxide-rich gas may result from a reversible poisoning by the high carbon monoxide concentration, possibly related to the formation of surface carbide.

[72] Work cited in footnote 65, p. 65.

[73] Work cited in footnote 48, p. 63.
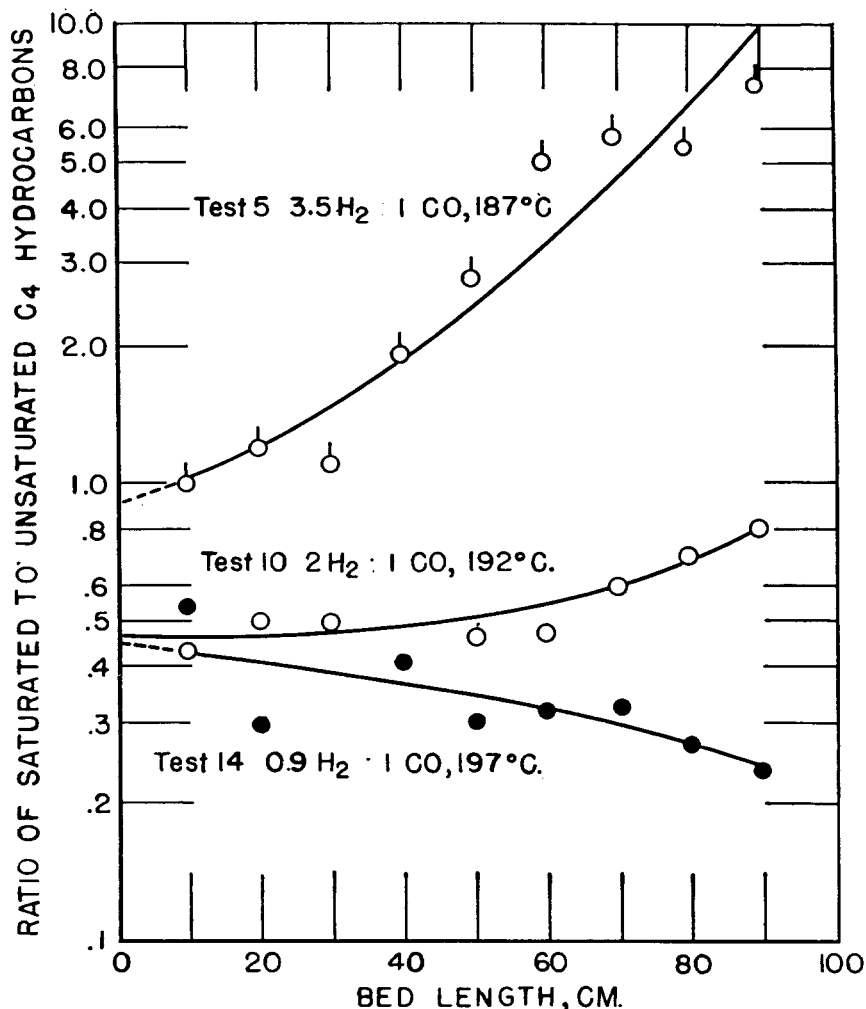[74] Work cited in footnote 45, p. 63.

FIGURE 37.—Change of Saturation of C_4 Hydrocarbons With Bed Length; Cobalt Catalyst at Atmospheric Pressure.

Some conclusions may be drawn as to the nature of the formation of methane, saturated and unsaturated hydrocarbons, and carbon dioxide. The data in figure 36 indicate that methane production was relatively constant with respect to conversion for $2H_2$:1CO and $0.9H_2$:1CO gas, but increased rapidly with $3.5H_2$:1CO. A large part of the rapid increase in methane yield with $3.5H_2$:1CO gas may be attributed to hydrocracking. The yields of methane increased with increasing operating temperature and with increasing H_2:CO ratio (fig. 36). Thus, in all tests the production of methane was favored by high H_2:CO ratios, high temperatures, and high partial pressures of hydrocarbon products in the gas stream.

The ratio of saturated to unsaturated hydrocarbons varied both with bed length and with the ratio of hydrogen to carbon monoxide at that point in the bed, as shown for the C_4 hydrocarbons in figure 37. The change with bed length indicates that the olefins may be

primary products of the reaction and that they may then be hydrogenated or undergo further reaction at the point of their formation or in later parts of the catalyst bed to form a hydrocarbon of higher molecular weight.

Carbon dioxide formation was chiefly a function of the partial pressure of water vapor and, to some extent, of the H_2:CO ratio (fig. 38). Most of the carbon dioxide appears to be formed by a secondary water-gas reaction. Even with hydrogen-rich gas, carbon dioxide was formed in sizable quantities until almost all of the carbon monoxide had been consumed. When the partial pressure of carbon monoxide decreased to less than 0.01 atmosphere, the carbon dioxide formed in the reaction was hydrogenated to methane. At the point in the bed where carbon dioxide began to be consumed, the quotient of the product of the partial pressures of carbon monoxide and water vapor divided by the product of the partial pressures of carbon dioxide and hydrogen was
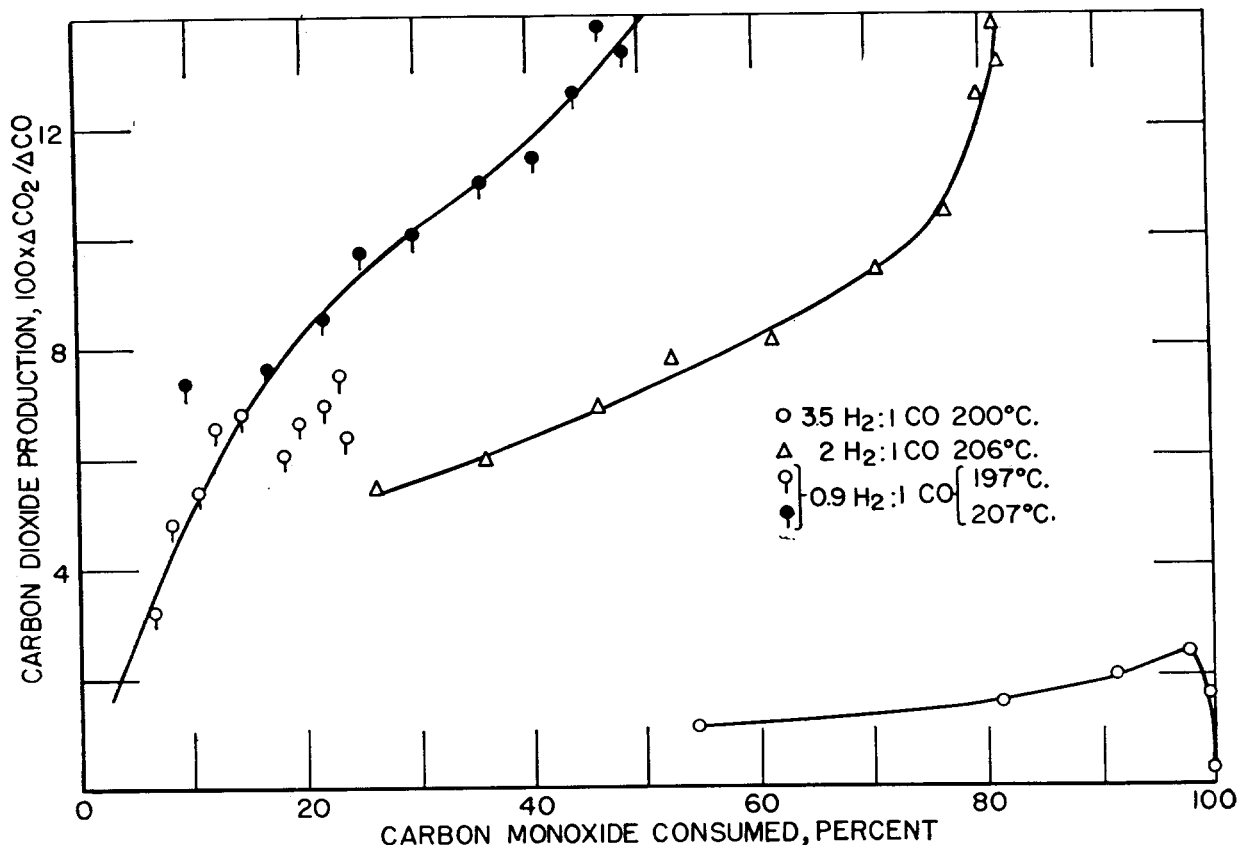
FIGURE 38.—Production of Carbon Dioxide as a Function of Conversion and Gas Composition; Cobalt-Thoria-Kieselguhr Catalyst at Atmospheric Pressure.

50 to 100 times greater than the equilibrium constant for the water-gas reaction. This indicates that carbon dioxide was consumed by direct reduction to methane and not by a reversal of the water-gas reaction. This interpretation assumes that the gases reacting at the catalyst surface have the same composition as those in the main gas stream. Apparently, carbon dioxide is not hydrogenated in the presence of carbon monoxide, in agreement with the work of Fischer and Pichler.[75][76]

Thus, the processes that form methane appear to be functions of the partial pressures of hydrogen and hydrocarbons, and processes forming carbon dioxide appear to be functions of the partial pressures of water vapor and carbon monoxide; both types of process were favored by an increase in temperature. These reactions occur to at least some extent over the entire catalyst bed. Craxford[77] reported data on the formation of methane and carbon dioxide which are similar to the above results;

he attributed the formation of these components to secondary hydrocracking of hydrocarbons and the water-gas reaction, respectively. However, he postulated that the normal synthesis occurs on parts of the surface converted to cobalt carbide, whereas the secondary reactions occur on parts of the surface covered by cobalt atoms which are not actively engaged in the synthesis. The present data[78] indicate that these reactions occurred throughout most of the catalyst bed, where normal hydrocarbon synthesis was proceeding. According to Craxford's theory, higher concentrations of carbon monoxide in the synthesis gas should favor formation of cobalt carbide and thus lower the production of carbon dioxide, rather than increase it, as is found. It has never been established that a surface carbide is the active catalyst, and it has been shown that cobalt catalysts rather completely converted to carbide are inactive in the synthesis.[79] The postulates of Craxford are, therefore, not a simple explanation of carbon dioxide and methane formation. The above data indicate that these products are formed con-

[75] Fischer, F. and Pichler, H., [The Simultaneous Effect of Carbon Monoxide and Carbon Dioxide During Hydrogenation, With Particular Regard to Benzine Synthesis]: Brennstoff-Chem., vol. 14, 1933, pp. 306–310.
[76] Pichler, H., [The Reaction of Carbon Dioxide During Hydrogenation]: Brennstoff-Chem., vol. 24, 1943, pp. 39–40.
[77] Craxford, S. R., Mechanism of the Fischer-Tropsch Reaction: Trans. Faraday Soc., vol. 42, 1946, pp. 576–580.

[78] Work cited in footnote 65, p. 65.
[79] Weller, S., Hofer, L. J. E., and Anderson, R. B., Role of Bulk Carbide in the Fischer-Tropsch Synthesis: Jour. Am. Chem. Soc., vol. 70, 1948, pp. 799–801.
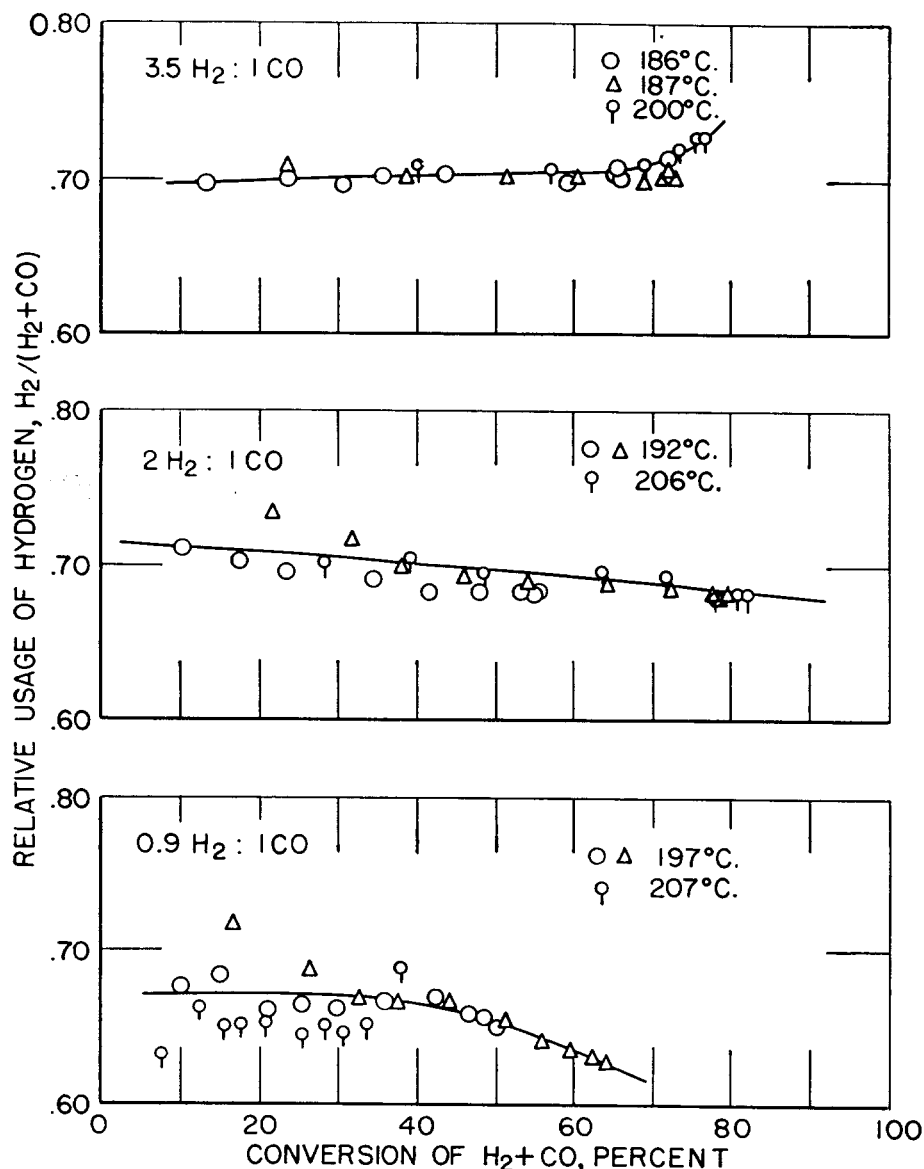
FIGURE 39.—Relative Usage of Hydrogen as a Function of Conversion for Cobalt-Thoria-Kieselguhr Catalyst at Atmospheric Pressure.

currently with the normal synthesis by secondary, and, to some extent, primary reactions and that their formation is a function of the gas composition and temperature.

ACTIVITY RELATED TO SURFACE AREA

Anderson, Hall, Seligman, and Kelly [80] [81] found that the activity of a series of cobalt-thoria-magnesia-kieselguhr catalysts varied approximately linearly with total surface area or with the area of cobalt metal as determined by the chemisorption of carbon monoxide. This linear

[80] Anderson, R. B., Hall, W. K., Seligman, B., and Kelly, R. E.: Unpublished data.
[81] Storch, H. H., Golumbic, N., and Anderson, R. B., The Fischer-Tropsch and Related Syntheses: John Wiley & Sons, New York, N. Y., 1951, 610 pp.

relationship, shown in figures 40 and 41, should be expected only if all surfaces of the catalysts are approximately equally accessible. At 185° C. only 1.93 cc. (S. T. P.) of synthesis gas was converted per hour per square meter of catalyst surface, as calculated from the slope of the curve in figure 40. The slope of the curve in figure 41 shows that 35.6 cc. (S. T. P.) of synthesis gas was converted per hour for every cc. (S. T. P.) of carbon monoxide chemisorbed (at $-195°$ C.). Thus, with a synthesis gas containing $2H_2 : 1CO$, 35.6 molecules of synthesis gas (11.9 molecules of carbon monoxide) was converted per hour per molecule of chemisorbed carbon monoxide, so that the average molecule of carbon monoxide must have remained on the
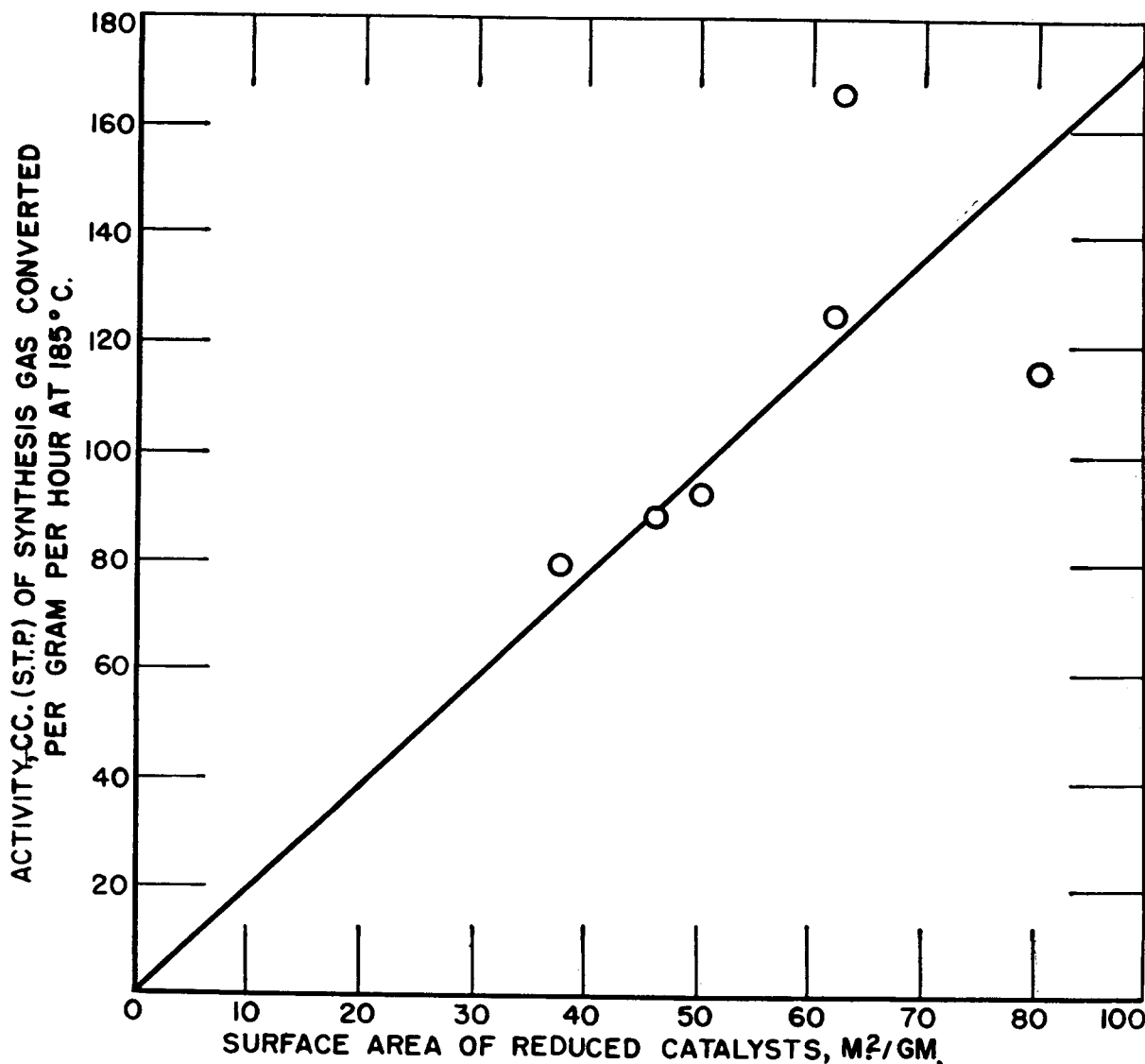
FIGURE 40.—Activity of Cobalt-Thoria-Magnesia-Kieselguhr Catalysts as a Function of Surface Area of Reduced Catalyst.

All data per gram of unreduced catalyst.

surface of the catalyst about 5 minutes $(60 \div 11.9)$ before reacting.

These data demonstrate that the Fischer-Tropsch reaction is an extremely slow catalytic process. Either only a very minute fraction of the catalyst surface is active or accessible, or an extremely slow reaction at the surface of the catalyst is rate controlling.

IRON CATALYSTS IN FISCHER-TROPSCH SYNTHESIS

The synthesis of hydrocarbons on iron catalysts differs from that on cobalt catalysts in at least three very significant characteristics. (1) Iron catalysts form carbon dioxide as the predominant oxygenated byproduct (water is

the principal byproduct obtained with cobalt catalysts); (2) the rate of reaction with iron catalysts is strongly dependent upon operating pressure (the synthesis rate is essentially independent of pressure with cobalt catalysts in the range of 1–20 atmospheres); and (3) carbides and oxides of iron are found in sizable amounts in used iron catalysts, and catalytic activity and life usually are increased by precarbiding. Carbides and oxides are not found in detectable amounts in used cobalt catalysts, and cobalt carbide in cobalt catalysts is deleterious to their use in the synthesis.

Before the discussion of synthesis tests of iron catalysts is begun, a useful method of expressing catalytic activity will be described. Kinetic experiments have shown that for most