3. Forming with Carbon Monoxide

Hydrogen does not assist in the forming of an iron catalyst, and there is danger that products may be produced during forming which will coat the active spots of the catalyst, especially at forming temperatures of 300°C and above when carbon monoxide-hydrogen mixtures are used, and for that reason tests were run with hydrogen-free carbon monoxide.

a. Effect of the Forming Temperature at .1 atm Forming Pressure.

The optimum forming temperature was determined in a series of experiments analogous to those for forming with synthesis gas (v. figure 2). The forming was done for 25 hours with carbon monoxide at 0.1 atm and at different temperatures. The rate of supply of carbon monoxide was 4 l1/10gFe/h (referred to 1 atm). The syntheses carried out for the testing of the catalysts were performed at 235°C with a high-carbon monoxide synthesis gas ($3CO : 2H_2$) at a pressure of 15 atm and a rate of flow of 4 l1/10gFe/h. Figure 3 shows the behavior of the catalysts formed with carbon monoxide at 255, 305, 325, 345, and 400°C. The iron catalysts formed at 325°C acted best. During the first twenty hours of the synthesis the conversion rose gradually from 50 to 55 percent contraction. Up to the end of the four months the conversion remained constant at 235°C with a contraction of 55 percent. An iron catalyst formed at 345°C produced a contraction in excess of 50 percent for 80 days. Lower forming temperatures, e.g. 255 and 305°C, as well as higher, e.g. as 400°C, gave poorer results.

A comparison of figure 2 and 3 shows that at all forming temperatures the iron catalysts formed with pure carbon monoxide had a longer life than when treated with carbon monoxide-hydrogen mixtures. At 255°C the contraction dropped on the 12th day below 50 percent with a catalyst treated with carbon monoxide, while after pretreatment with synthesis gas it dropped on the third day; with a forming temperature of 305°C the corresponding drop occured on the 25th. and 12th days respectively, and at 325°C after 120 days against 24 days. With a catalyst forming at 325°C the temperature was raised after 130 days of operation, and with the catalyst formed at 345°C after eight days. A few operating data of these tests are shown in tables 7 and 8.

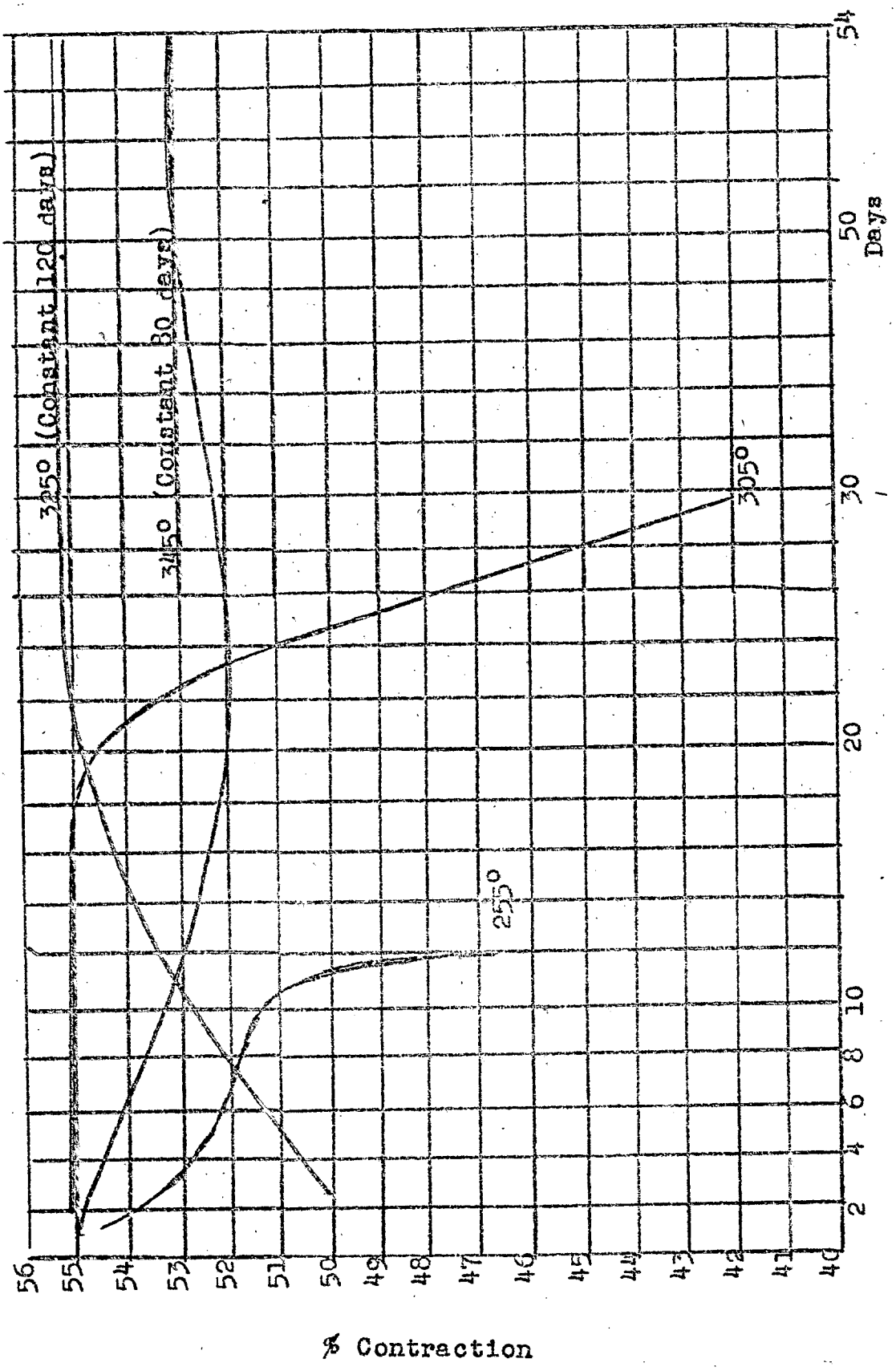

Fig. 3 Effect of the temperature of forming on the course of synthesis after forming with CO at 1/10 atm.

Table 7

Results with an Iron Catalyst Formed with Carbon Monoxide at 325°C

Forming: Carbon monoxide, .1 atm 4 l1/10gFe/h, 25 hours
Synthesis: CO in rich gas, 15 atm 4 li/10gFe/h, temperatures rising from 235°C

Day	Temp. °C	Contr. percent	Day	Temp °C	Contr. percent
1	235	47	140	245	48
2	"	50	160	250	49
5	"	50	180	251	50
10	"	51	200	250	44
20	"	55	250	265	50
50	"	54	300	263	43
100	"	53	350	270	40
130	"	47			

40th day	CO_2	Hydro-carbons	O_2	CO	H_2	Hydro-carbons	carbon number	N_2
Starting gas:	2.0	0.0	0.0	53.4	39.8	0.0	-	4.8
End gas:	57.0	2.6	0.1	6.3	14.6	8.9	2.0	10.5
70th day								
Starting gas:	2.5	0.0	0.2	54.7	37.9	0.2	1.0	4.5
End gas:	64.0	2.9	0.0	2.5	9.5	11.3	1.9	9.8
100th day								
Starting gas:	3.5	0.0	0.0	54.4	37.1	0.2	1.0	4.8
End gas:	61.2	3.3	0.1	5.2	11.2	9.0	1.9	10.0
300th day								
Starting gas:	2.0	0.0	0.2	56.6	34.8	0.2	1.0	6.2
End gas:	48.9	2.9	0.2	15.9	10.8	8.5	1.9	12.2

Yield/ncbm ideal gas, 40th day: 108 g liq. + sol. hydroc. 44 g gasol.
Yield/ncbm ideal gas, 70th day: 105 g liq. + sol. hydroc. 45 g gasol.
Yield/ncbm ideal gas 100th day: 110 g liq. + sol. hydroc. 47 g gasol.
Yield/ncbm ideal gas 300th day: 110 g liq. + sol. gasol hydroc. not determined

The tests with the iron catalysts formed at 325°C were carried on for one year. After being kept for four months at 235°C with a constant conversion, the temperatures had to be raised to 270°C to maintain the same conversion. The yields remained approximately the same during the whole time of operation. They amounted to 105 - 110 g liquid and solid hydrocarbon and 40 - 47 g gasol hydrocarbon/ncbm ideal gas.

Table 8

Results with an Iron Catalyst Formed with Carbon Monoxide at 345°C

Forming: Carbon Monoxide, .1 atm, 4 l1/10gFe/h, 25 hours
Synthesis: CO - rich gas, 15 atm, 4 l1/10gFe/h, temperature rising from 235°C.

Day	Temp °C	Contr.	Day	Temp °C	Contr
1	235	55	60	235	52
5	"	50	80	"	49
10	"	51	100	248	54
20	"	51	115	250	49
40	"	53			

	CO_2	Hydro-carbons Heavy	O_2	CO	H_2	Hydro-carbons	Carbon number	N_2
50 Day								
Starting gas	2.2	0.0	0.0	53.4	39.6	0.0	-	4.8
End gas	57.7	2.8	0.2	6.1	13.8	8.9	1.9	10.5

The yield with catalysts formed at 345°C at the end of the second month of operation at 235°C amounted to 110 g solids and liquids and 41 g gasol hydrocarbon/ncbm ideal gas. The temperature at the end of the second month was 250°C with a contraction still approximately 50 percent. The analysis of the end gas of the synthesis after forming with carbon monoxide at .1 atm and 325 - 345°C (cf table 7), corresponding to constant values of the contraction, remained without any important changes during many months of operation.

b. Effect of Forming Pressures

A series of tests were run with carbon monoxide, analogous to those for forming with synthesis gas

(cf table 6). Table 9 shows contractions after different lengths of synthesis with forming at 15 atm, 1 atm and .1 atm. The length of forming was again 25 hours (4 li/h) the forming temperature was 325°C. During the first days of operation the conversion was good with all three catalysts. However, it dropped during the fourth week with the catalysts formed at 15 atm, while with the catalysts formed at 0.1 atm, the conversion remained constant after three months.*

Table 9

Effect of the Forming Pressure(with a Forming Temperature of 325°C, with Carbon Monoxide used in Forming)upon the Course of Synthesis at 235°C

	Days of Operation					
Pressure	1	10	20	25	30	60
	Contraction in percent					
15	58	52	48	40	-	-
1	58	57	53			
0.1	-	51	55	54	56	54

A comparison of the results of the different series of tests with those shown in table 6 tells us that forming at higher pressures with pure carbon monoxide gives better results than forming with carbon monoxide-hydrogen mixtures.

c. Rate of forming

When forming at reduced pressures, about 100 li of carbon monoxide were led over 10 g of Fe of the catalysts. The flow was relatively rapid, and only a small part of the gas was used up, and after eliminating the carbon dioxide the gas could be used again for the pretreatment of the iron catalysts.

We may judge the process of forming by the determination of the carbon dioxide formed during the process. Curves I and II on figure 4 show the amounts of carbon dioxide formed at .1 atm and 325°C/10 g Fe/h. The

* Relatively much carbon was deposited upon the catalysts when formed at higher pressures. Quantitative results on it are reported elsewhere.

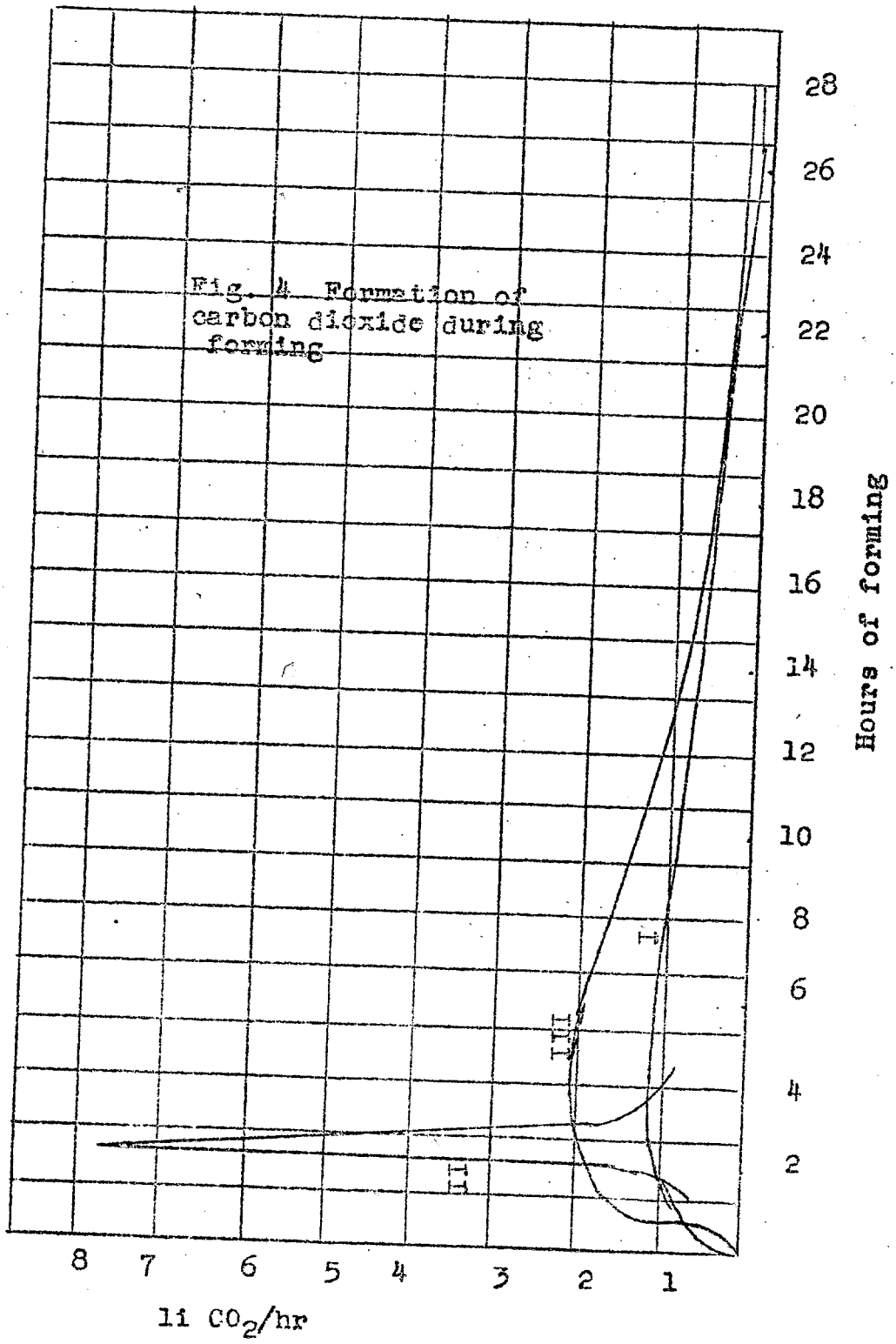

Fig. 4 Formation of carbon dioxide during forming

temperature of 325°C was reached in 2 1/2 hours in curve I, while 1 1/2 hours were required for curve II. During this preheating time the rate of flow of the carbon monoxide was 4 li/h. In the test curve I, the work was continued at the same rate of flow of gas, while in curve II it was increased to 40 li/h. With 4 li carbon monoxide/h at first more than 1 li of carbon dioxide/h was formed. The rate of formation of carbon monoxide gradually dropped. 25 hours after reaching the temperature of 325°C the carbon dioxide formation reached a certain minimum value 0.2 - 0.3 li/h. With 40 li/h the maximum carbon dioxide value amounted to 8 li/h, and became constant and equal to about 1 li/h after 2 1/2 hours. In both cases about 10 li of carbon monoxide were led over the catalysts before reaching the constant minimum value. The total amount of carbon dioxide formed in tests 1 up to this time was 16 li, in test 2 - 11 li. The forming with carbon dioxide represents a reduction process as well as the formation of the combined and free carbon according to the equation $2\ CO = C + CO_2$. Larger amounts of carbon were incorporated during the slow passage of gas in the test 1, than in test 2.

Table 10 summarizes 4 tests. Tests 1a and 1b correspond to the carbon dioxide formation of curve I, figure 4, tests 2a and 2b belong to the curve II.

The forming in test 1a lasted 25 hours with 4 li/h at 325°C, in the test 1b 2 1/2 hours, in the test 2a 2 1/2 hours with 40 li of carbon monoxide/h at 325°C, and in test 2b only 20 minutes. The time when forming was interrupted and the reaction with the synthesis gas was begun are shown with crosses on the curves of figure 4. The subsequent synthesis was carried out in all gases with a pressure of 15 atm and with a temperature of 235°C. Table 10 shows that in tests 1a and 2a, after passing 100 li of carbon monoxide, a good and permanent activity of the catalysts has been reached. Interruption of the forming before the dying down of the "carbon dioxide curve" (tests 1b and 2b) produced catalysts with good conversion at the beginning but which dropped off very rapidly.

process and must therefore be avoided as much as possible during forming.

The presence of some amounts of inert gas, primarily nitrogen, cannot be avoided in industrial operations. Larger amounts of inert gases interfere with forming. Results obtained with 0.1 atm pressure cannot be duplicated by working at atmospheric pressure with 0.1 atm partial pressure of carbon monoxide and 0.9 atm partial pressure of nitrogen. 25 hours forming under these conditions with 40 li carbon monoxide-nitrogen/h (total thruput again 100 li carbon monoxide), produced a catalyst which gave only 37 percent contraction at 235°C. A 1 : 3 carbon monoxide - nitrogen mixture with a 10 hour forming with 40 li/h, produced an iron catalyst which gave 50 percent contraction for three weeks at 235°C and 15 atm.

4. Theory of Forming

We have shown that a pretreatment with carbon monoxide or with gases containing carbon monoxide at 250 - 350°C is necessary for the production of active iron catalysts, and furthermore that forming has to be carried out at pressures lower than those used in the synthesis.

The activity of the catalysts formed with carbon monoxide - hydrogen mixtures is somewhat lower than when formed with carbon monoxide alone, which was explained by the interaction of carbon monoxide with hydrogen during the first stages of forming, with formation of compounds which have a tendency to block more or less the surface of the catalysts.

No forming with hydrogen has been found possible.

The fundamental difference in the action of carbon monoxide and hydrogen may be based on the fundamental differences in the reduction processes of iron oxide, secondly in the loosening up of the iron structure by the carbon intercalated during the reaction with carbon monoxide, and in the third place by the formation of carbides during the treatment with carbon monoxide.

The reduction with hydrogen is more rapid than with carbon monoxide, if we disregard the diffusion, sintering and the deposition of carbon, as is well known from data in literature. When operations are run under conditions

under which these above mentioned points must be considered, the reduction with carbon monoxide may proceed more readily because of the loosening up caused by the intercalation of carbon 11/.

The original process of the reduction is the formation of the ferromagnetic Fe_3O_4. It is formed during the reduction with carbon monoxide as well as with hydrogen, and can be obtained by a precipitation of a mixture of ferrous and ferric salts with alkalies, followed by dehydration; it possesses, however, no catalytic properties for the middle pressure synthesis.

We may refer to the equilibrium conditions of the iron-carbon-oxygen system in our subsequent discussion of the course of the action of carbon monoxide. This equilibrium depends on the temperature, the gas pressure, and the proportion of carbon monoxide to carbon dioxide in the gas. Figure 5a refers to atmospheric pressure. It represents the results of investigations of R. Schenck 12/. The broken curves were obtained by U. Hoffmann and E. Growl 13/ by computation. Figure 5b reproduces the equilibrium relationships at the pressure of 0.1 atm. The Fe_3O_4-Fe_2C curve was calculated taking into consideration the relationship between pressure and equilibrium values, the other curves from results of Schenck in the work quoted above.

We may draw the conclusion from figure 5 that at temperatures below 550 - 560°C, FeO is unstable (according to Schenck, because it already contains Fe_3O_4 called by him "Wüstite"). The reduction of Fe_3O_4 proceeds therefore without passing through the FeC phase.

The metallic phase, which according to Schenck consists an oxygen-containing oxo-ferrite and the oxygen and carbides-containing oxoaustenite, and is in stable equilibrium only at temperatures above 550 - 600°C. At lower temperatures the carbide may therefore form by a direct interaction of carbon monoxide and Fe_3O_4 or by way of formation of unstable lower - oxygen intermediate substances. U. Hoffmann and E. Growl have subjected to X-ray analysis the substances formed by passing carbon monoxide over iron and found only a very slight amount of free iron at temperatures below 655°C.

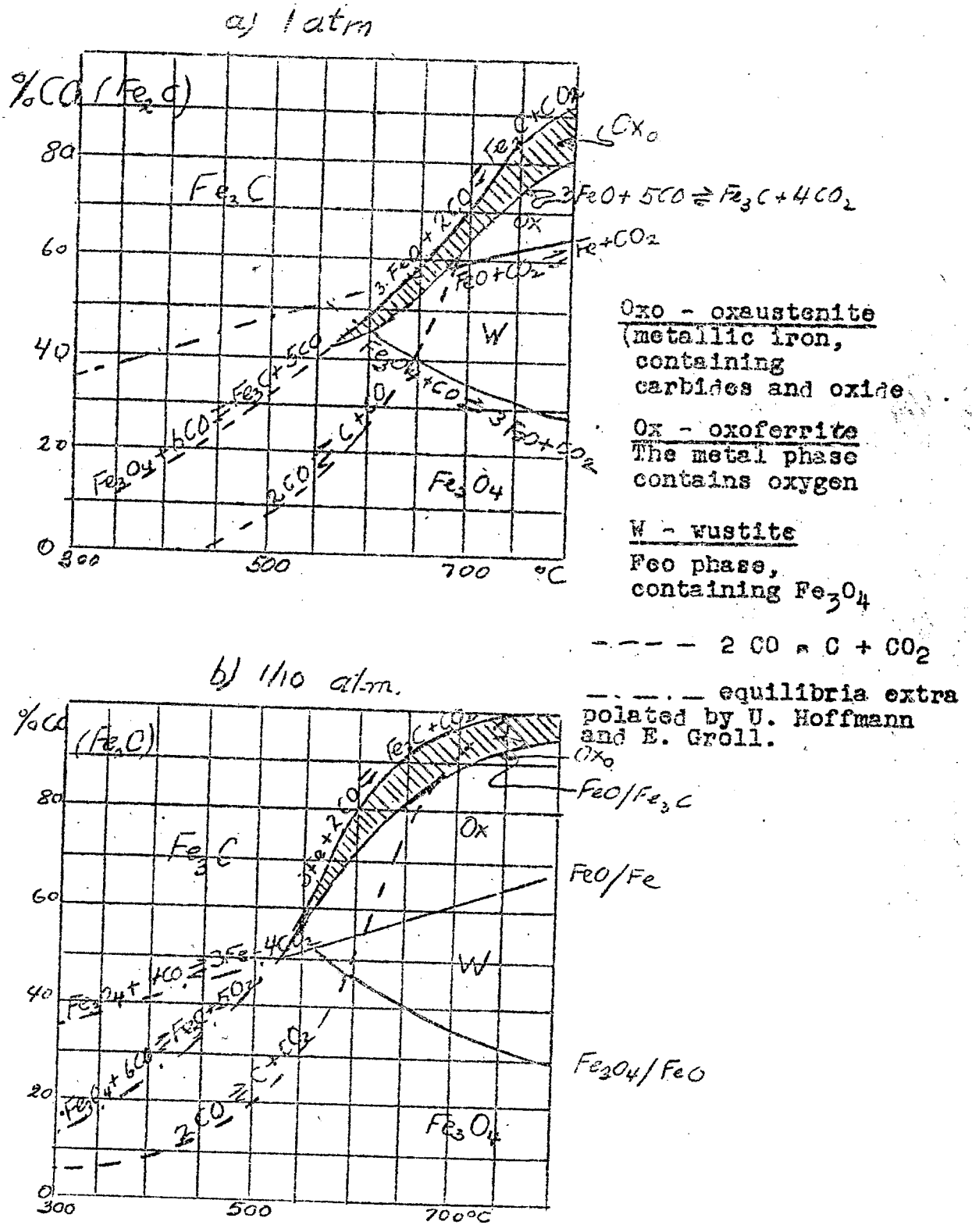

Fig. 5 Equilibrium conditions in the Fe-C-O system.

The reduction of the higher oxides to the lower oxides or to metallic iron does not depend on the pressure, and therefore only on the proportion of carbon dioxide: carbon monoxide, and from the temperature; we may see, however, from the figure 5b that the conversions during the formation of either the carbide or of carbon monoxide are displaced by lowering the pressure towards the carbon monoxide side. Raising the pressure will therefore favor the formation of carbides and of carbon.

When operations are conducted with a 100 percent carbon monoxide, as may be done when the carbon monoxide is conducted in a very rapid stream over the substance, only iron carbide is stable during equilibrium at 1 atm as well as 0.1 atm.

Should equilibrium become established during the action of pure carbon monoxide upon metallic iron, the carbide would form first, while the carbon dioxide formed acts as an oxidizing agent upon the metallic iron. This explains the fact that the forming of an iron catalyst is favored by lower pressures and the higher rates of carbon monoxide, because the process is a reduction process, and both these factors reduce the partial pressure of carbon dioxide and provide the rapid removal of the adsorbed carbon dioxide from the reacting surface.

In both diagrams the carbide is assumed to exist as cementite Fe_3C, and not as some higher carbide. Hilpert 14/ was the first to assume its existence in 1915. Franz Fischer and his collaborators have repeatedly referred to the formation of higher carbides as intermediate products of the gasoline synthesis. Franz Fischer and H. Bahr 15/ have even described such a carbide of iron. Gluud and his collaborators, 16/ have assigned the formula Fe_2C to this carbide. U. Hoffmann and E. Groll have reported in their work, cited above, on the interaction of carbon monoxide upon iron at below 400°C, the proof of the existence of such carbides from interferences in their X-ray investigations, and established that at temperatures over 400°C this carbide disappears with a simultaneous increased deposition of carbon. It is assumed that during this deposition cementite and free carbon are formed.

Only little can be said at present about equilibrium conditions of this particular carbide or any possible higher carbides. The range of its existence could not

therefore be indicated in the figure 5 by curves or areas of it. It appears, however, definitely established that lower temperatures and high carbon monoxide concentrations are necessary for its formation. These requirements represent the optimum forming requirements for the iron catalyst. It becomes therefore very probable that the existence of these compounds is of significance for the degree of forming of the catalysts and therefore for the course of the subsequent synthesis.

These carbides should necessarily not only be formed prior to the synthesis, during some suitable pretreatment, but they must not break down in a short while if the synthesis is not to die down, or else they should not be decomposed at lower rate than re-formed, if they are formed as intermediate compounds. This might be indicated by an observation made during synthesis. The synthesis may proceed satisfactorily with a good conversion immediately after forming at some low temperatures (e.g. below 220°C). However, the conversion becomes gradually lower and may be uncapable of becoming increased at higher temperatures (e.g. at 230 - 240°C) at which it would proceed if the initial operations were conducted at that temperature (at lower temperatures the carbide may be more rapidly decomposed by hydrogen than re-formed by the interaction with the carbon monoxide).

It may further be pointed out that the extraordinarily large initial activity of the iron catalyst can be explained by its structure, as well as by the results of some unfinished experiments which are still in process. Very little oxygen is found in the substance after forming with high concentration of carbon monoxide to the production of equilibrium, but a gas is formed during synthesis containing 50 - 60 percent carbon dioxide, which may bring about a partial oxidation of the substance by the equilibrium conditions and this will result in a reduction of activity. The "best formed" catalysts are nevertheless superior to those less thoroughly formed, and their performance must be connected with structure changes in the catalysts during forming.

We may finally assume that the high-carbon carbide acts catalytically in the formation of carbon. The present investigations are intended to explain

to what extent this undesired break-down of the carbon monoxide is interferred with by the simultaneous presence of hydrogen. It has, however, been already proven that the formation of carbon during forming is strongly repressed by lowering the pressure and by increasing the rate of flow of carbon monoxide.