Some time a o we published an article with the title, "The Approach of Actual
Yields to the Theoretical Yields of the Fischer-Pichler Middle-Pressure Syn-
thesis". (1) The experiments were carried out with cobalt-thorium catalysts.
The yields of solid and liquid hydrocarbons (with approximately 15 g. of gasol)
amounted to 150 g. to 170 g. maximum per normal cubic meter of ideal gas. Of
this, more than 50 percent constituted paraffins when the most favorable reac-
tion conditions were provided.

Ever since Fischer and his co-workers perfected the synthesis of hydrocarbons
from CO and H_2 by using cobalt-thorium catalysts, the desire was foremost in
our minds to use cheaper catalytic agents which would give the same or similar
products. We kept on working with iron catalysts. In 1923, Fischer and
Tropsch (2) obtained the so-called Synthol when they passed water-gas over
alkalized iron shavings at approximately 100 atm. pressure, and 350 to 450°C.
The Badische anilin- and sodafabrik (3) worked with similar pressures and
temperatures in 1913, and in 1925, they arrived at the synthesis of methanol.
Fischer and Zerbe (4) showed, in 1923, that alkalized iron shavings acting on
CO_2 and H_2 will lead to the formation of hydrocarbons. They observed that
with decreasing pressure, a tendency exists to form hydrocarbons rather than
oxygen-containing compounds. They worked in a circulating apparatus at 410°C.,
and 100-150 atm. pressure. They observed that at higher pressures, only water
soluble products were formed, but at around 7 atm., some oil was obtained which
contained approximately 40 percent of petroleum products soluble in concentrated
sulphuric acid.

In 1926, Fischer and Tropsch (5) reported that at a temperature of 300°C.,
and above, and using iron catalysts on CO and H_2, even under atmospheric pres-
sure, hydrocarbons are obtained. On the basis of these experiments and results,
we have tried repeatedly to introduce iron catalysts, and at the same time re-
duce the reaction temperature and improve the yield of liquid hydrocarbons. In
1928 (6), 30 to 40 g. of benzene and oil were obtained at atmospheric pressure
for every cubic meter of water-gas. The temperatures could be lowered down to
240-250°C. The lifetime of the catalysts amounted to several days.

Fischer and Tropsch (7) had attempted in 1927 to use water-gas at 10 to 15 at-
mospheric pressure and 250-280°C. They worked with fused iron oxide catalysts
with a small addition of copper, and they worked with water-gas directly under
pressure. Their products consisted of aqueous and oily substances in the ratio
3:2 to 1:1. At this time, the authors revealed that their results were not as
good as with atmospheric pressure. In 1934, Fischer (8), gave a lecture on the
benzene synthesis in which he reported a maximum yield of 30 to 35 g. per cubic
meter of mixed gas when using an iron catalyst under atmospheric pressure (this
corresponds to approximately 40 to 45 g. per Nm³ of CO-H_2 mixture). He also
added that the initial conversion decreased by 20 percent in the course of 3
days.

Fischer and Meyer (9) attempted in 1934-36 repeatedly to improve the yields of
liquid hydrocarbons by increasing the activity of the iron catalysts. By us-
ing iron-copper precipitated catalysts, they succeeded in getting 50 to 60
grams per normal cubic meter of gas at a maximum lifetime of the catalyst of
4 to 6 weeks.

Fischer and Ackermann (10), in 1936, obtained 55 g. of liquid hydrocarbons per normal cubic meter of mixed gas when they used certain copper-free iron catalysts produced under certain conditions. They worked at atmospheric pressure. This yield, however, started to decrease already after very few days, and in the third week, amounted to less than 40 g.

At this time, they used a synthesis gas which contained CO and H_2 in the ratio of 1:2, although they had recognized that on iron catalysts the CO conversion proceeds almost entirely according to the equation:

$$2 \times (CO) + x (H_2) = x (CH_2) + x (CO_2)$$

When they used a synthesis of $2CO + 1H_2$, the CO was used up only partly, and the activity of the catalyst decreased rapidly.

In every one of the experiments cited, the maximum yields obtained were less than half those obtained with cobalt catalysts on industrial scale. Therefore, we could not consider the use of iron on a large scale at that time. The result of the work which we are going to discuss today is to show that if we operate in a certain manner using iron catalysts at elevated pressures, the CO-H_2 mixture may be practically entirely converted into hydrocarbons. According to synthesis conditions, one gets various quantities of paraffins, benzene, and gasol hydrocarbons. The total yields of this so-called iron middle-pressure synthesis compare closely to those of the synthesis using cobalt catalysts, so that now we can consider replacing cobalt by iron.

Towards the end of 1937, Fischer reported on the favorable course of our work on the synthesis with iron catalysts. We intended, at that time, to make our results public and inform those parties which would be interested for the commercial application. Because we recognized the importance of being able to substitute iron for cobalt, since Germany has only little cobalt available, Fischer and a series of his co-workers have intensified their work in the last years.

The essential contents of the present work has been assigned to Studien and Verwertungs Gesellschaft. The assignment which goes back to the year 1937 was communicated to Ruhr-Chemie for patent purposes. In the meantime, several patents had been applied for in foreign countries.

PART I
The Catalyst

A. Precipitation of Catalyst.

At first, we were of the opinion that variation in the production methods of the iron catalysts and also that certain additions to the iron catalysts would effect the synthesis at atmospheric pressure in such a way as to improve the yields of liquid hydrocarbons. For this purpose, we produced many hundreds of different iron catalysts whereby we tested the various additions and various modes of precipitation.

In the course of our researches, we recognized soon, however, that we could only reach our aim by working at a slightly positive pressure, and the catalyst characteristics could vary considerably. When we worked with a pure iron catalyst which had been inducted with CO prior to the atmospheric synthesis, we found that we obtained satisfactory yields for many months thereafter.

1. Starting material.

A starting material for the production of the iron catalysts, we generally used iron-salt solutions. These solutions were obtained by dissolving commercial iron directly. For the sake of comparison we also used chemically pure iron. The majority of experiments were carried out with the following iron samples:

  a. Ferri nitrate (commercial)
  b. Iron nitrate solutions obtained by dissolving technical iron shavings in nitric acid. The iron was chiefly present as tervalent iron. The iron shavings were introduced in small portions into nitric acid of an initial density of 1.18, and the temperature was kept below 40 to 50°C. (Above 60 to 70°C., a decomposition of the nitrates occurs. with the formation of an insoluble precipitate).
  c. For the production of Ferro nitrate solutions, a nitric acid with a maximum density of 1.05 was allowed to act upon iron shavings at 35 to 40°C. (a higher acid concentration or a higher temperature caused a violent reaction which forms Ferri salts instead of Ferro salts).
  d. Ferro chloride (commercial).

2. Precipitation with sodium carbonate.

The concentration of the iron solutions used for precipitation generally corresponded to one kilogram of iron per 30 liters of the solution (with catalysts based on 2 and tervalent iron). The solution was pre-neutralized in the cold with the solution of sodium carbonate, and care was taken to assure enough alkalinity that no permanent precipitate remained in existence. The Ferri solutions usually were precipitated at 100°C., whereas the Ferro solutions were precipitated at a maximum of 70-75°C., in both cases a small excess of sodium carbonate was used. The sodium carbonate solutions generally contained one kilogram of soda for every 3 to 10 liters of water. After precipitation, the mixture was brought to a boil for a few minutes, filtered, and washed free of alkali with hot distilled water. The moist precipitate was repulped in distilled water, made to a uniform slurry on the water bath, and under constant stirring, the desired quantity of alkali (mostly potassium carbonate dissolved in water) was added. The chief quantity of water was evaporated off on the water bath, after this the catalyst was put into a dry oven overnight at 110°C., and thereafter was pelleted and freed of all dust. The Ferri catalysts are blackish-brown, rather solid, and mostly they show a glassy fracture. The Ferro catalysts are voluminous and earthen brown.

The Ferri catalysts precipitated with potassium carbonate generally proved to be superior to the Ferro catalysts. The Ferri catalysts obtained from technical iron over a Ferri nitrate solution were used more frequently than the Ferro catalysts, and therefore we termed the Ferri catalysts normal iron catalysts.

Two points had to be observed carefully in their preparation:

1. The pre-neutralization of the iron solution had to be carried out in the cold, because at elevated temperatures, a precipitate of insoluble salts forms which makes it difficult to get reproducible results.

2. It is important that the iron precipitate is brought to a boil before filtering. This was found to increase the activity and the lifetime of the catalyst. Table I shows that plainly. In this table, catalysts prepared under different temperature conditions are compared one with another. We used the degree of contraction occurring during the synthesis as a measure of the catalyst activity ($CO-H_2$ mixture, 3:2, 15 atm., $235^\circ C$). Thus, comparative activity data are given for various lengths of operation. The highest possible contraction amounted to 60 percent if we assumed the conversion to liquid hydrocarbons to proceed according to $2CO + H_2$ is equal to $CO_2 + CH_2$. In actual practice, the best yields are obtained at a contraction of 50 to 55 percent.

Table I.
Influence of Precipitation Temperature Upon the Activity of Iron Catalysts

Precipitating temperature, $^\circ C$	Raised to boiling after precipitation	Alkali contents, percent	Days of operation				
			1	2	5	10	20
			Contraction, percent				
20	no	1	43	–	44	43	–
60	no	1	50	–	33	20	–
20	short	1	50	–	48	51	–
20	"	1/4	–	50	43	51	50
20	1 minute	1/4	55	55	48	48	50
20	5 minutes	1/4	–	56	–	47	43
100	1 minute	1/4	50	50	50	49	56

The table shows that the catalysts which were not brought to boil did not come up to full activity or that they lost the activity rapidly. The catalysts which were boiled for a short time and those which were boiled for one minute showed equally good results. Heating longer than one minute showed no advantage. The last experiment listed in the table, where the catalyst was precipitated at boiling temperature, corresponds to a normal iron catalyst.

3. Precipitation with ammonia.

At $40^\circ C$, a stream of ammonia gas was conducted into a Ferri nitrate solution containing 100 g. of iron per liter. The flow velocity of the gaseous ammonia, in general, was regulated so that the precipitation was terminated after 20 minutes. The ammonia was absorbed quantitatively up to the end of the precipitation. An equal volume of boiling distilled water was added to the precipitate, then it was filtered and washed five times with hot distilled water. The eventual alkalization was carried out as earlier described for the catalysts precipitated with

$-\frac{6}{4}-$

sodium carbonate. The iron catalysts precipitated with ammonia are blackish-brown, solid, and show a glassy fracture.

4. The addition of kieselguhr.

From a series of experiments, we used iron-kieselguhr catalysts. These are discussed in a special chapter. The addition of the kieselguhr generally was carried out after the alkalization and during the evaporation of the water from the catalyst over the water bath. It is practicable to suspend the kieselguhr in distilled water before adding to the catalyst. By doing this, one prevents a too rapid removal of water from the catalyst mass, and hence, the formation of non-homogeneous lumps.

B. Pretreatment of the catalyst.

The freshly precipitated and dried iron precipitate is entirely inactive as a catalyst for the conversion of CO and H_2 into hydrocarbons. In this it corresponds entirely to the still unreduced cobalt catalyst which is inactive, too. In order to activate the cobalt catalyst sufficiently to serve as a good agent in the hydrocarbon synthesis, it is usually only necessary to treat the unreduced oxides with hydrogen at $360°C$. If the same treatment is given to the still inactive iron catalyst, no improvement in activity is observed and the catalyst is still not capable of performing any work. When the iron is treated with hydrogen at $300-450°C$, it is converted into a black substance which is ferromagnetic and has the composition, Fe_3C_4. This substance does not catalyze the reaction between CO and H_2. However, if the catalyst is pretreated as CO, its activity may be increased enormously, and in that form, the catalyst is well suited for the synthesis. When CO is used for pretreatment, the catalyst is more or less reduced depending on the temperatures at which the treatment is carried through, at the same time, carbides are deposited within the catalyst, which causes the granules to loosen up. The treatment with CO or CO-rich gases in general is called induction of the catalyst.

1. Induction with CO-H_2 mixture during the synthesis.

a. Mixed gas and atmospheric pressure. If the precipitated iron catalysts are induced with mixed gas (CO-H_2 is equal to 1:2), this is best done at atmospheric pressure and at $235-250°C$. Under the conditions of the normal pressure synthesis, the contraction reaches a value of 30 percent after operating for 3 or 4 days at $235°C$ and 4 liters of mixed gas per hour per 10 g. of iron. The time which is necessary to bring the activity of the catalyst up to its full strength through the action of the synthesis gas corresponds to the induction period. At atmospheric pressure, one can obtain as much as 50 g. of liquid and solid hydrocarbons per cubic meter of gas at average contraction of 30 percent, and for a length of time of 3 to 4 weeks. The CO of the mixed gas is approximately all used up, but a large excess of hydrogen remains in the end-gas. (Figure 1, curve 1, shows the observed contractions for this conversion).

b. CO-rich gas and atmospheric pressure. If the iron catalyst is allowed to work in presence of a CO-H_2 mixture of such a composition which corresponds more closely to the ratio in which the two components combine with one another at atmospheric pressure, no improvements in the degree of conversion may be observed. At $235°C$, the induction period lasted approximately 3 days. A maximum
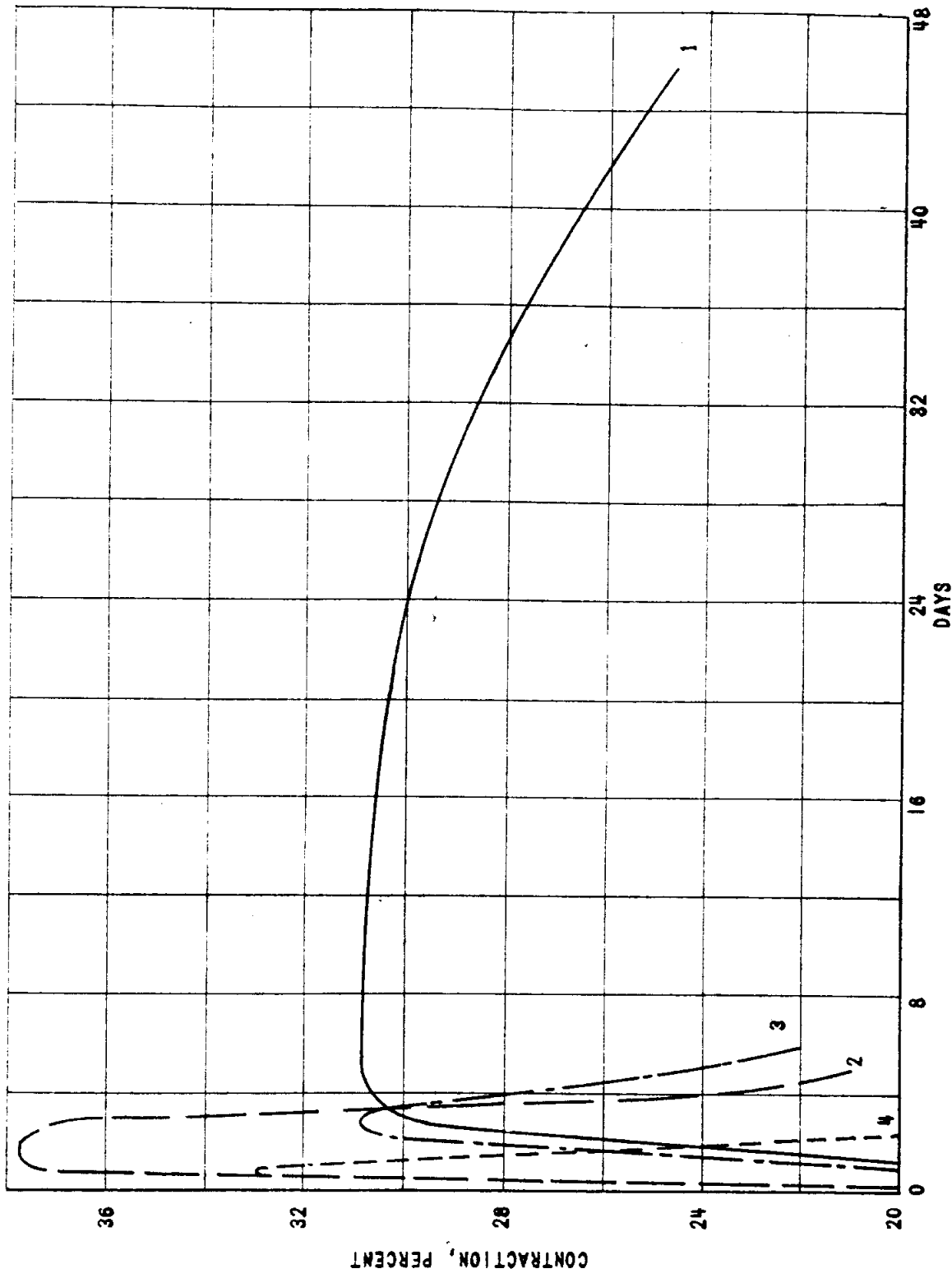
Figure 1. - Experiments at atmospheric pressure (decrease of contraction with duration of operation when various CO-H₂ mixtures are employed).

contraction of 31 percent was obtained. (Figure 1, curve 2). At 245°C., the highest contraction, namely 38 percent, was ~~already~~ reached after one day of operation (curve 3), whereas at 255°C., after one day of operation, the maximum contraction obtained was only 33 percent (curve 4). After having reached the highest contractions, the conversion decreases very rapidly again. This decrease shows that the catalyst has been damaged during the synthesis at atmospheric pressure and CO-rich gas.

c. CO-rich gas and elevated pressure. Table II shows a time-test for which a normal catalyst was allowed to work on synthesis gas at 15 atmospheric pressure. The gas had an approximate composition of $3CO + 2H_2$. Four normal liters of this gas were used for every 10 g. of iron. At 245°C., the contraction was only 4 percent after one day, after 4 days, it was 10 percent (as compared to 30 to 30 percent for the same period at one atmosphere). After the fourth day, the temperature was gradually raised, and the increase in contraction was observed through several days. On the eleventh day, 24 percent contraction was reached at 260°C. When the temperature was raised to 270°C., at first, no further increase in conversion occurred. At 275°C., 37 percent was measured, and at 280°C., 36 percent. Only when the temperature went up to 290°C., did the contraction go up to 50 percent.

Table II.- Induction and Synthesis at a Pressure of 15 Atmospheres

Days	Temp., °C.	Contraction, percent	Days	Temp., °C.	Contraction, percent
1	245	4	69	268	37
4	245	10	75	280	47
5	250	13	90	280	49
7	253	17	93	283	44
11	260	24	106	285	42
13	270	24	130	288	43
14	275	37	140	292	44
28	280	36	150	298	47
60	290	50			

Yield determination for the third month of operation at 280°C.

	CO_2	sKW	O_2	CO	H_2	KW	CZ	N_2
Starting gas	2.2	0.0	0.2	59.0	33.9	0.2	1.0	4.5
Final gas	55.5	3.4	0.2	11.5	11.7	9.3	1.7	8.4

Yield per normal cubic meter of ideal gas: 3 g. of paraffin, 93 g. of liquid hydrocarbons, 32 g. of gasol hydrocarbons.

Next we wanted to see whether this once-obtained conversion could be obtained again after lowering the temperature. At 268°C., the contraction fell back to 37 percent. At 280°C., however, a better conversion was noticed in the third month of operation than was obtained after one month. In the meantime, a slow induction of the catalyst had taken place. In order to maintain the contraction at 40 to 50 percent, the temperature had to be raised in the fourth and fifth months of operation. After five months of operation, it was 300°C.

After the third month, a yield determination for a run at 280°C., gives the results shown in Table II. Three grams of solid paraffins were obtained per normal cubic meter of ideal gas (inert-free), 93 grams of liquid hydrocarbons, and 32 grams of gasol hydrocarbons ($C_3 + C_4$).

When the catalyst was subjected to working conditions at higher pressures right from the beginning, the process of induction was inhibited and especially was the catalyst incapable of working at low temperatures. On the other hand, at a pressure of 15 atmospheres and using a CO-rich synthesis gas, the temperature of the reaction could be raised to 280-290°C., without causing a rapid decrease in catalyst activity, such as was observed at one atmosphere pressure.

These results were obtained with iron catalysts which had been prepared in very different ways (Ferro and Ferri catalysts). Some of them contained copper, others did not.

2. Induction with CO and H_2 mixtures in a process separate from that of the synthesis.

a. Induction at various pressures and synthesis at ordinary pressure. It was attempted to find out whether an increase in activity of the catalyst can be reached by carrying the induction through independent of the synthesis. We wanted to find the optimum conditions for both the induction and the synthesis as such. In order to investigate what effect the pressure has upon the synthesis at atmospheric pressure, the experiments listed in Table III were undertaken. We inducted for 20 hours at 255°C. with 4 liters of normal gas per hour per 10 g. of iron. The gas had a composition of $3CO + 2H_2$. Then we used this catalyst in a synthesis with a gas of composition $1CO + 2H_2$. Four liters per hour per 10 g. of iron were employed at atmospheric pressure. The degrees of conversion during this reaction were measured after 1-1/2 hours at 255°C.

Table III.- Influence of Induction Pressure Upon the Synthesis at Atmos. Pressure

Induction pressure, atmospheres	8.5	4.7	2.9	2.0	1.5	1	0.5	0.1
Synthesis, contraction percent	5	12	12	28	25	28	32	30

The results showed that elevated pressures impede the induction. When the induction pressures were below one atmosphere, no essential improvement could be noticed during the synthesis at atmospheric pressure.

b. Induction at ordinary pressure and synthesis at elevated pressure*. For this experiment, we worked with an iron catalyst which was precipitated with sodium carbonate and another iron catalyst precipitated with ammonia. Both catalysts were escribed earlier and contained 1/4 percent potassium carbonate.

*During the experiment, it was intended to study the influence which the induction procedure has upon the activity of the catalyst. The catalysts were examined under certain fixed synthesis conditions. The influence of the various synthesis conditions is discussed in "Synthesis".

The normal iron catalyst which was precipitated with soda was allowed to work on the CO-rich gas at a rate of 4 liters per hour per 10 g. of catalyst at one atmosphere and 245°C. The time of the experiment lasted 21-1/2 hours. This gas yielded a contraction of 33 percent at the end of the pretreatment. Then we switched over to 15 atmospheres and 235°C. Immediately the contraction went up to 50 percent, however, on the second day, it was only 33 percent, and on the third day, 30 percent. The temperature of 235°C. proved too low to assure the maintenance of the contraction of 50 percent with this catalyst. Next we pretreated the same iron catalyst with mixed gas at atmospheric pressure and 235°C. The contraction at the end of the pretreatment was 30 percent. Next we switched over to 15 atmospheres and a CO-rich gas. At 235°C., 43 percent contraction was obtained and 47 percent at 250°C. In order to maintain the contraction at 45-50 percent, the temperature ad to be raised to 257°C. within 14 days.

The iron catalyst which was precipitated with ammonia was inducted with mixed gas at atmospheric pressure and 245°C. The contraction reached 31.5 percent after 5 days of operation. Then we switched to CO-rich synthesis gas $(3CO + 2H_2)$ and operated at 15 atmospheres pressure. Table IV shows the contraction after some time of operation, and the composition of the synthesis gas and of a reaction gas obtained at 250°C. (4th day).

Table IV.- Synthesis at 15 Atmospheres with Iron Catalyst
Precipitated with Ammonia and Inducted at 1 Atm.

Days	Temp., °C.	Contraction percent
1	245	59
2	245	48
4	250	53
5	250	49
10	252	46
20	256	51
50	255	51
100	265	55

	CO_2	sKW	O_2	CO	H_2	KW	CZ	N_2
Initial Gas	2.7	0.0	0.0	55.8	37.3	0.0	--	4.2
Final Gas	53.8	3.4	0.0	11.4	16.2	6.2	2.0	9.0

This experiment gave a contraction of 59 percent on the first day of operation and and at 245°C. In order to maintain the highest possible yields and a contraction of 50 percent or above, the temperature was gradually raised. This degree of conversion could be maintained for more than 3 months. After 100 days of operation, the temperature had risen to 265°C.

(his experiment shows that the reaction temperature could be lowered by 30 to 40 degrees when the catalyst was inducted at atmospheric pressure as compared to the temperature of the reaction when the induction was carried out at 15 atmospheres. The additional increase in activity which the catalyst acquired during induction at one atmosphere remained intact for the entire duration of the experiment.

- 15 -
8

2. Induction at reduced pressure and various temperatures, synthesis at elevated pressure. Following is the description of an experiment during which normal iron catalysts were inducted with CO-rich gas ($3CO + CH_2$) at 1/10 atmosphere and various temperatures. The induction lasted for 25 hours and was carried out between 255-350°C. The activity of the catalyst was tested with the synthesis gas of composition $CO-H_2$ is equal to 3:2. The pressure during the synthesis was 15 atmos., and the temperature 235°C. Figure 2, shows the decrease of contraction with time at a constant synthesis temperature of 235°C. (6 liters of gas per 10 g. of iron per hour). When the induction was carried out at 255°C, the contraction dropped below 50 percent already on the third day of the synthesis, as the induction temperature was raised, an increase in the catalyst lifetime was observed. When the induction temperature was 315°C, the limit of 50 percent contraction was passed only after more than a month of operation. When the induction was carried out at higher temperatures, the lifetime of the iron catalyst decreased again.

Table V shows an example where a catalyst was inducted at 325°C and 1/10 atmosphere. The table gives temperatures and contractions for 200 consecutive days of operation. Besides, it also gives the initial and final gas analysis on the 10th, 100th, and 200th days of operation. The synthesis was continued at 235°C as long as the contraction did not fall below 50 percent, as soon as it did, the temperature was slowly raised and only raised enough to assure a maximum contraction. Only after operating for 2 months, did the temperature go above 240°C, and after 3 months, above 250°C.

Table V.- Results of an Iron Catalyst Inducted at 325°C, with synthesis gas
Induction: CO-rich gas, 1/10 atm., 6 liters per 10 g. or iron per hour, 25 hours.
Synthesis: CO-rich gas, 15 atm., 6 liters per 10 g. of iron per hr. Temp. 235°C up.

Days	Temp °C	Contraction percent	Days	Temp °C	Contraction percent
3	235	54	100	252	50
5	235	50	110	253	49
10	235	54	120	256	48
20	235	52	130	264	50
30	237	48	140	269	47
40	240	52	150	270	47
50	240	50	160	272	47
60	241	48	170	277	44
70	247	53	180	278	43
80	250	54	190	272	46
90	249	50	200	273	47

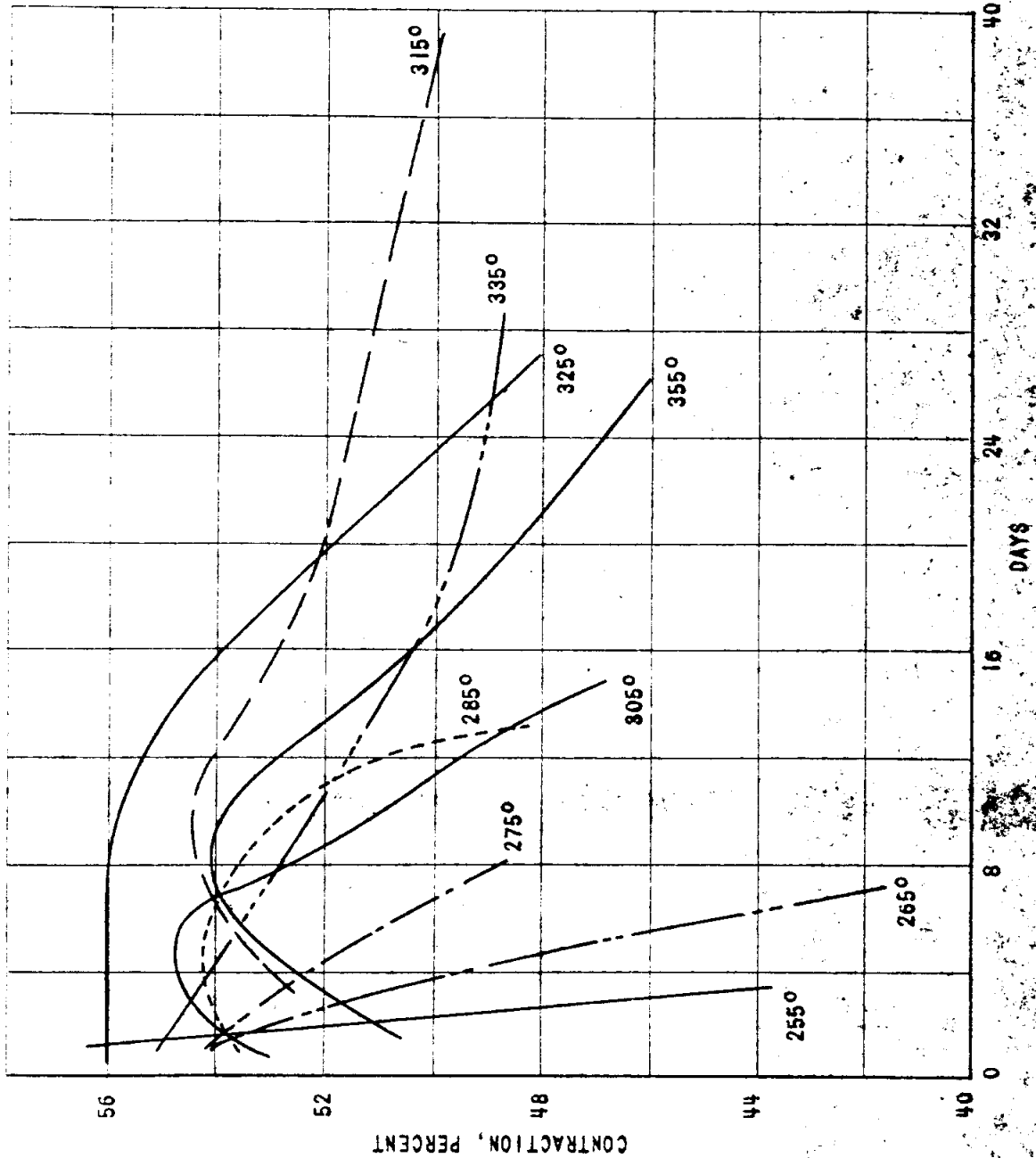|	CO_2	aKW	O_2	CO	H_2	C	CH_4	N_2
10th day								
Initial gas	2.4	0.0	0.1	58.5	37.6	0.0		6.3
Final gas	61.8	2.5	0.2	3.4	12.0	7.8	2.9	3.4
100th day								
Initial gas	2.0	0.0	0.3	53.6	37.0	0.0	1.0	5.9
Final gas	53.0	3.4	0.2	5.2	15.7	5.3	2.9	12.4
200th day								
Initial gas	2.3	0.0	0.6	57.0	31.0	0.2	1.0	7.6
Final gas	49.3	2.3	0.1	15.4	13.7	5.3	2.9	14.4

Figure 2. - Influence of induction temperatures of the catalyst upon the course of the synthesis (decrease of contraction with time of operation at 15 atmospheres and 285° C.). Induction was carried out with a CO-rich synthesis gas at 1/10 atmosphere.

The contraction decreased during the 200 days of operation from 56 to 47 percent. The composition of the final gas changed sharply during the first few days, however little only during the following longer-time operation. 140 g. of solid and liquid and gasol hydrocarbons were obtained at the end of the second week of operation. Of this, 31 g. constituted gasol hydrocarbons.

From Tables IV and II, it may be observed that a contraction of 50 percent results from a catalyst which was inducted at 1/10 atmos. and 325°C., when the reaction temperature is 235°C. When the catalyst was inducted at one atmosphere and 245°C., a 50 percent contraction resulted at 245-255°C. For a catalyst which was inducted at 15 atmospheres pressure, a temperature of 280-290°C. is required to produce a 50 percent contraction.

   d. Influence of the induction pressure upon the synthesis at elevated pressure (induction temperature, 325°C.). After we had found that for an induction pressure of 1/10 atmos., the optimum induction temperature was 325, we once more investigated the effect of pressure upon the induction at that temperature. Table VI shows these results. The induction was carried out in each case for 25 hours with a CO-rich synthesis gas, and the catalyst was tested at 235°C. with a gas of composition $3CO + 2H_2$ at 15 atmos.

Table VI.- Influence of the Induction Pressure Upon the Course of the Synthesis at 235°C. (at an induction temperature of 325°C., and the use of synthesis gas for the induction)

Pressure,	Length of Operation in Days					
atmos.	1	2	4	10	20	30
	Contraction, percent					
15	30	24	15	---	---	---
1	56	54	55	50	49	50
0.1	56	56	56	56	52	48

The table shows that the catalyst possesses only slight activity when inducted at 15 atmospheres and 325°C. Whatever little activity it had, it was lost rapidly. When the induction was carried out either at one or at 1/10 atmos. and 325°C., in both cases the same degree of conversion was obtained for the first month of the synthesis.

3. Induction with CO.

It was recognized that hydrogen alone can not be used for the induction of iron catalysts. When CO and H_2 mixtures are employed and especially is this true for temperatures of 300°C. and above, the danger exists that during the induction, products are formed which will block the active centers of the catalyst. For these reasons, we have experimented with hydrogen-free CO.

a. Influence of the induction temperature at 1/10 atmosphere pressure.
In order to find the optimum induction temperature, a series of experiments was undertaken which were analogous to that when synthesis gas was used for the induction (compare Figure 2). The induction was carried out for a length of 25 hours at 1/10 atmosphere, and different temperatures using CO. Four liters per hour of CO referred to one atmosphere pressure were used for every 10 g. of iron. The synthesis which followed the induction was carried out with a gas of composition 3CO + 2H$_2$ at a temperature of 235°C., and pressure of 15 atmos. The flow velocity of the synthesis gas was 4 liters per 10 g. of iron per hour. Figure 3 shows the behavior of the catalysts which were inducted at 255°C., 305°C., 325°C., 345°C., and 400°C., using CO. The catalyst which had been inducted at 325°C., proved to be the best one. During the first 20 days of the synthesis, the conversion gradually increased from 50 to 55 percent contraction. Up to the end of the fourth month and at 235°C., a constant conversion corresponding to a 55 percent contraction could be maintained. The catalyst which was inducted at 345°C., caused a contraction of about 50 percent for 80 days. Lower induction temperatures such as 255 and 305°C. and higher temperatures such as 400°C. showed less favorable results.

A comparison of Figures 2 and 3 shows that the catalyst which had been inducted with pure CO instead of CO and H$_2$ mixtures showed a longer lifetime. This can be said to hold for all temperatures. When the catalyst was pretreated with pure CO, the contraction decreased below 50 percent on the 12th day when the induction temperature was 255°C. When the catalyst was pretreated with synthesis gas at 305°C., the decrease in contraction below 50 percent occurred on the 12th day as compared to pure CO for which the drop below 50 percent took place after the 25th day. Similarly, for an induction temperature of 325°C., the decrease in contraction below 50 percent occurred on the 24th day when synthesis gas was used and when pure CO was employed instead, under the same conditions, the same drop occurred at the end of 120 days. When the catalyst which was inducted at 325°C., was used, the synthesis temperature had to be raised after 130 days of operation. When another catalyst inducted at 345°C, was employed, the temperature had to be increased already after 80 days. Some operating data of these experiments are presented in Tables I, VII, and VIII.

Table VII
Results of Experiments Carried Out with an Iron Catalyst Inducted at 325°C. with CO.

Induction: CO, 1/10 atm., 4 liters per 10 g. of iron per hour, 25 hours.
Synthesis: CO-rich gas, 15 atm., 4 liters per 10 g. of iron, temp. 235°C. and up

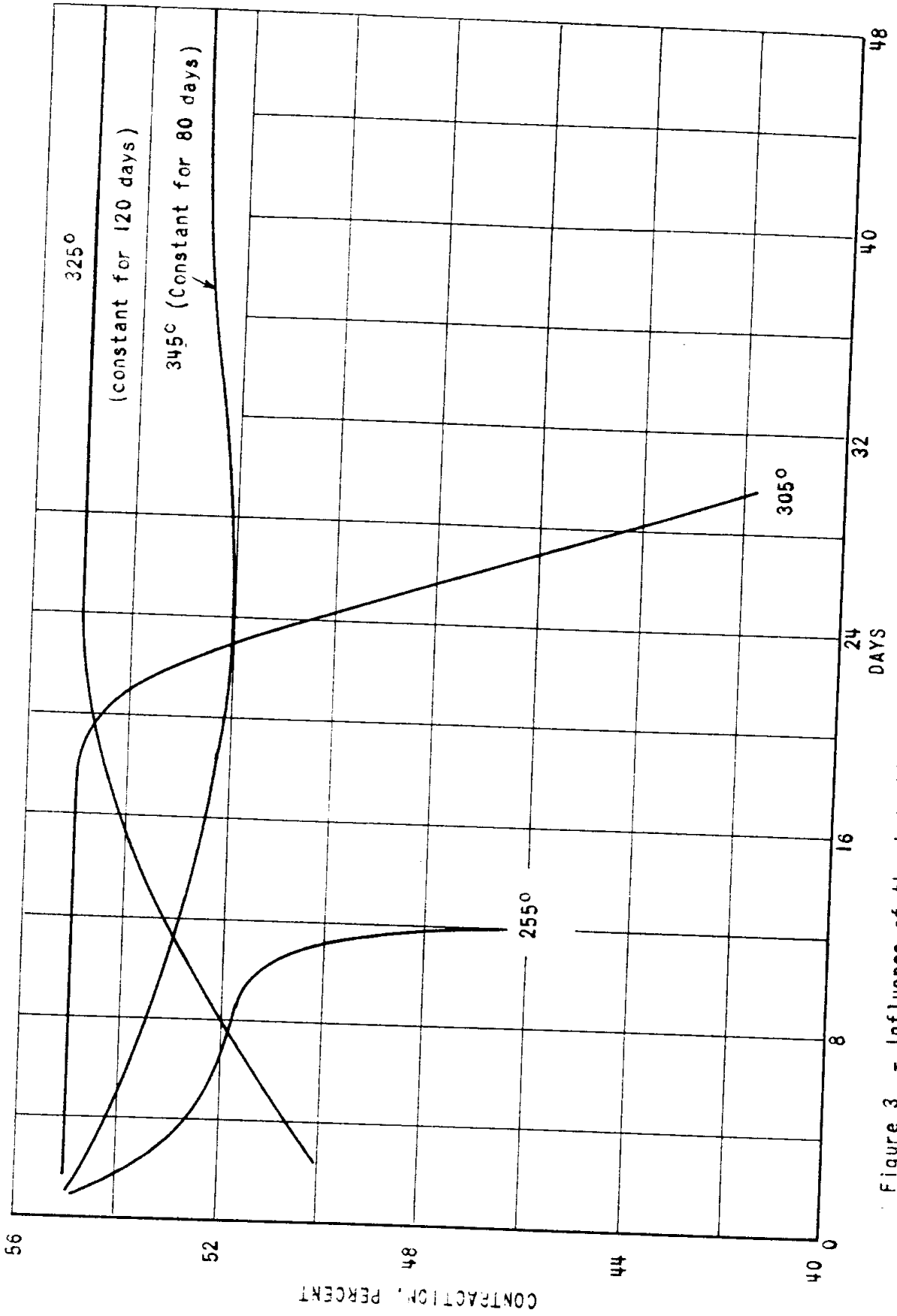| Days	Temp., °C.	Contraction percent	Days	Temp., °C.	Contraction percent
1	235	47	140	245	46
2	235	50	160	250	49
5	235	50	180	251	50
10	235	51	200	250	44
20	235	55	250	265	50
50	235	54	300	263	43
100	235	53	350	270	40
130	235	47			

Figure 3. - Influence of the induction temperature upon the course of the synthesis after an induction with CO at 1/10 atmosphere pressure.

Table VII (cont'd.)

40th day	CO_2	sKW	O_2	CO	H_2	KW	c/No.	N_2
Initial gas	2.0	0.0	0.0	53.4	39.3	0.0	--	4.8
Final gas	57.0	2.6	0.1	6.3	14.6	8.9	2.0	10.5
70th day								
Initial gas	2.5	0.0	0.2	54.7	37.9	0.2	1.0	4.5
Final gas	64.0	2.9	0.0	2.5	9.5	11.3	1.9	9.8
100th day								
Initial gas	3.5	0.0	0.0	54.4	37.1	0.2	1.0	4.8
Final gas	61.2	3.3	0.1	5.2	11.2	9.0	1.9	10.0
300th day								
Initial gas	2.0	0.0	0.2	56.6	34.3	0.2	1.0	6.2
Final gas	48.9	2.9	0.2	15.9	10.3	8.5	1.9	12.2

Yield per Nm^3 of ideal gas at the 40th day: 180 g. liquid and solid hydrocarbons, 44 g. of gasol hydrocarbons.

"   "   "   "   "   70th "   105 g. liquid and solid hydrocarbons, 45 g. of gasol hydrocarbons.

"   "   "   "   "   100th "   110 g. liquid and solid hydrocarbons, 47 g. of gasol hydrocarbons.

"   "   "   "   "   300th "   110 g. liquid and solid hydrocarbons, gasol hydrocarbons, not determined.

The experiment with the iron catalysts inducted at 325°C. lasted through one year. This catalyst gave a constant conversion for 4 months at 235°C., thereafter, for the time to follow, in order to maintain this conversion, the temperature had to be raised slowly up to 270°C. The yields remained approximately the same for the whole time of operation. They amounted to 105 to 110 g. of liquid and solid hydrocarbons and 44 to 47 g. of gasol hydrocarbons per normal cubic meter of gas.

Table VIII
Results of Experiments Conducted with an Iron Catalyst Inducted with CO at 345°C.

Induction: CO, 1/10 atm., 4 liters per 10 g. of iron per hour, 24 hours.
Synthesis: CO-rich gas, 15 atm., 4 liters per 10 g. of iron per hr. Temp. 235°C. - up

Days	Temp., °C.	Contraction, percent
1	235	55
5	235	50
10	235	51
20	235	51
40	235	53
60	235	52
80	235	49
100	248	54
115	250	49

50th day	CO_2	sKW	O_2	CO	H_2	KW	CZ	N_2
Initial gas	2.2	0.0	0.0	53.4	39.6	0.0	--	4.8
Final gas	57.7	2.8	0.2	6.2	13.8	8.9	1.9	10.5

- 14 -

12.

Up to the second month of operation and at 235°C., the catalyst which was inducted at 345°C., gave a yield of 110 g. of liquid and solid hydrocarbons and 41 g. of gasol hydrocarbons per normal cubic meter of ideal gas. Near the end of the fourth month, the temperature was 250°C., and the contraction was still approximately 50 percent.

The end-gas analyses of those instances where a catalyst was used which was inducted with CO at 1/10 atmosphere and 325-245°C., show no essential changes during many months of operation. This is in accord with the constant contractions observed.

    b. Influence of induction pressure. A series of pressure experiments was carried out with CO which was analogous to that run earlier with synthesis gas (see Table VI). Table IX shows contraction for various lengths of time of the synthesis. The induction pressures of the catalysts were 15 atmospheres, one atmosphere, and 1/10 atmosphere. The induction time again was 25 hours (4 liters per hour, the induction temperature 325°C).

During the first days of operation, all three catalysts gave good conversions. The activity of the catalyst which was inducted at 15 atmospheres, however, decreased during the fourth week, whereas, the catalyst inducted at 1/10 atmosphere remained intact through 3 months.[*]

Table IX
Influence of the Induction Pressure
(at an Induction Temperature of 325°C, and the use of CO)
Upon the Course of the Synthesis at 325°C.

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

A comparison of the results of this investigation with the results in Table VI shows that the catalyst acquires also higher activity when it is activated at elevated pressures with CO instead of with CO-H$_2$ mixtures.

    c. Induction time. During the induction at reduced pressure, approximately 100 liters of CO per 10 g. of iron were lead over the catalyst. At the required rapid rates of gas feed, only a small part was used up. The larger part of the unused gas may be used again for induction after the CO$_2$ which had formed was removed.

[*]During the induction at elevated pressure, comparatively large quantities of carbon were deposited on the catalyst. Quantitative data on this are given elsewhere.

- 15 -

/3

The induction process may be followed closely by checking up on the CO_2 formation. Curves 1 and 2, in Figure 4, represent the CO_2 quantities formed at 1/10 atmosphere and 325°C per hour for every 10 g. of iron. In the case of curve 1, the temperature of 325°C, was reached after 2-1/2 hours. In case of curve 2, this same temperature was reached after 1-1/2 hours. During this starting period the flow velocity of the CO amounted to 4 liters per hour in both cases. During the experiment represented by curve 1, this same flow velocity was maintained all through, the flow velocity of the experiment represented by curve 2 was 40 liters per hour. With 4 liters per hour of CO in the beginning, one liter of CO_2 was formed per hour. The CO_2 formation gradually decreased. Approximately, after 25 hours of operation and after a temperature of 325°C, was reached, the CO_2 formation approached a constant minimum value of 0.2 to 0.3 liters per hour. When 40 liters per hour of CO were used, the CO_2 maximum value amounted to 8 liters per hour and after operating for 2-1/2 hours, the constant amount of approximately one liter per hour was obtained. In both cases, it was necessary to pass approximately 100 liters of CO through the apparatus in order to obtain a constant minimum quantity of CO_2. During experiment 1, altogether 16 liters of CO_2 were formed, during experiment 2, only 11 liters. The CO_2 formation is caused through the reduction of CO and through the formation of combined and free carbon according to the equation

$$2\ CO = C + CO_2.$$

For the flow velocity of experiment 1, more carbon was deposited than during experiment No. 2.

Four experiments are listed in Table X. Experiment 1a and 1b belong to the CO_2 curve 1 of Figure 4, experiments 2a and 2b belong to curve 2. In the case of experiment 1a, formation lasted for 25 hours and was carried out with 4 liters per hour at 325°C. In the case of experiment 1b, the induction lasted 2-1/2 hours, for experiment 2a, 40 liters of CO per hour were used for 2-1/2 hours at 325°C. Experiment 2b lasted 20 minutes. The points at which the induction was terminated and where the synthesis was started are marked by a cross on Figure 4. The following synthesis was carried out in all cases at 15 atmospheres and 235°C. As Table X shows, after 100 liters of CO had been passed over the catalyst during experiments 1a and 2a, a good and lasting activity of the catalyst had been created. When the induction was interupted before the CO_2 formation (experiments 1b and 2b) declined catalysts were obtained which gave good initial conversion, but which lost their activity rapidly.

Table X

The Influence of Flow Velocities of CO upon the Induction Time and the Course of the Synthesis

Experiment	1a	1b	2a	2b
Liters of CO per hour	4	4	40	40
Induction time, hours	25	2.5	2.5	0.3
Total quantity of CO used	100	10	100	12
Contraction in percent for the synthesis				
1st day	47	55	53	53
2nd day	50	50	51	30
5th day	50	30	50	—
10th day	51	—	49	—
20th day	55	—	51	—
30th day	54	—	54	—

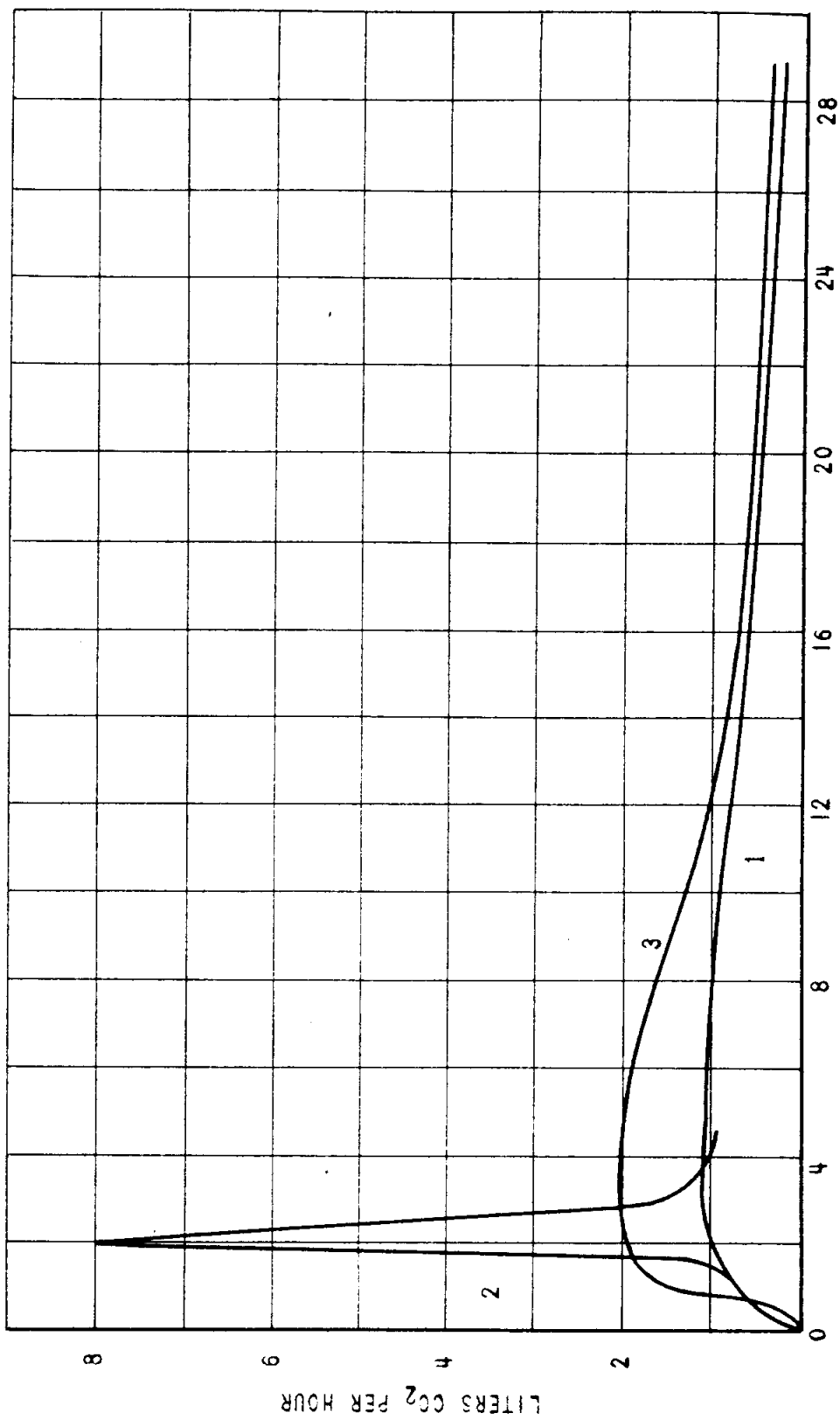DURATION OF CATALYST INDUCTION, HOURS

LITERS CO_2 PER HOUR

Figure 4. - CO_2 formation during the induction process.

In all of the experiments (1a, 1b, 2a, and 2b) the flow velocities of the gases at a pressure of 1/10 atmosphere, were sufficiently large to remove the CO_2 from the catalyst surface. The catalyst activity obtained through experiment 2a, was equal to that of 1a, in spite of that facts that the contact time between the gases and the catalyst was greatly reduced and the CO_2 formation in case of 2a was much lower than in the case of 1a (less carbon was deposited in the catalyst during experiment 2a). This constitutes an advantage.

For comparison, Figure 4 also gives the corresponding CO_2 quantities for an induction at one atmosphere, curve 3 (see also the experimental results given in Table IX). A CO flow velocity of 4 liters per hour was used (analogous curve 1).

Curve 3 shows that during the process of induction more CO_2 was formed at atmospheric pressure than at reduced pressure, this means that also more carbon was deposited.

      d. **Mixture of CO with other gases.** Mixtures of CO_2 and H_2 have been discussed already. In general they gave more unfavorable results at ordinary or elevated pressures than pure CO. This may be explained by assuming that synthesis products formed and blocked the catalyst surface.

The presence of CO_2 or water-vapor impedes the reduction process, and therefore should be avoided if possible.

The presence of small quantities of inert gases especially of nitrogen, cannot be avoided if the induction is carried out on a technical scale. Large quantities of inert gases impede the process of induction. We have found that it is favorable to work at 1/10 atmosphere pressure using CO. It is not permissable to use a gas mixture exhibiting 1/10 atmosphere partial pressure of CO and 9/10 atmosphere partial pressure of nitrogen. When an induction is carried out under those conditions over a length of time of 25 hours with 40 liters of CO-nitrogen mixtures per hour (total flow 100 liters of CO), a catalyst is produced which will give only 37% contraction at 235°C. When we worked with a CO-nitrogen mixture of a ratio 1:3, an induction carried out for 10 hours with 40 liters per hour of gas yielded an iron catalyst which gave a contraction of 50 percent through 3 weeks of operation at 235°C. and 15 atmospheres.

4. Theory of Induction Process.

It has been shown that in order to produce an active iron catalyst a pretreatment of the catalyst with CO or CO-rich gases is required at temperatures around 250-350°C. Furthermore, we have recognized that this process which we call induction has to be carried out at lower pressures than the synthesis which is to follow.

We found that induction with CO and H_2 will give a lower activity than when CO is used as such. Our explanation for this phenomena is that already during the process of induction liquid and solid hydrocarbons are forming on the catalyst surface and prevent the activating gases from coming in contact with the catalyst.

Induction with H_2 has not been found possible.