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Report on the Middle-Pressure Synthesis With Iron Catalysts  
The Kaiser Wilhelm Institute for Coal Research

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The Kaiser-Wilhelm Institute for Coal Research

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The Middle-Pressure Synthesis With Iron Catalysts

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## INTRODUCTION

Some time ago we published an article with the title, "The Approach of Actual Yields to the Theoretical Yields of the Fischer-Pihler Middle-Pressure Synthesis". (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 reaction conditions were provided.

Ever since Fischer and his co-workers perfected the synthesis of hydrocarbons from CO and H<sub>2</sub> 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 alkaliized 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 alkaliized iron shavings acting on CO<sub>2</sub> and H<sub>2</sub> 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.

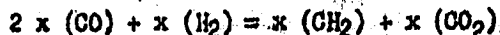
In 1926, Fischer and Tropsch (5) reported that at a temperature of 300°C., and above, and using iron catalysts on CO and H<sub>2</sub>, even under atmospheric pressure, hydrocarbons are obtained. On the basis of these experiments and results, we have tried repeatedly to introduce iron catalysts, and at the same time reduce 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 atmospheric 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 Nm<sup>3</sup> of CO-H<sub>2</sub> mixture). He also added that the initial conversion decreased by 20 percent in the course of 8 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 using 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<sub>2</sub> in the ratio of 1:2, although they had recognized that on iron catalysts the CO conversion proceeds almost entirely according to the equation:



When they used a synthesis of 2CO + 1H<sub>2</sub>, 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<sub>2</sub> 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 und 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 trivalent iron. The iron shavings were introduced in small portions into nitric acid of an initial density of 1.10, and the temperature was kept below 40 to 50°C. (Above 60 to 70°C., a decomposition of the nitrates occurs. 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 trivalent 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 8 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<sub>2</sub> mixture, 3:2, 15 atm., 235°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<sub>2</sub> is equal to CO<sub>2</sub> + CH<sub>4</sub>. 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, °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	50	48	51	50
20	1 minute	1/4	55	55	48	48	50
20	5 minutes	1/4	-	56	-	47	48
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 60°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

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

#### h. 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<sub>2</sub> 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<sub>3</sub>O<sub>4</sub>. This substance does not catalyze the reaction between CO and H<sub>2</sub>. 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<sub>2</sub> mixture during the synthesis.

a. Mixed gas and atmospheric pressure. If the precipitated iron catalysts are inducted with mixed gas (CO-H<sub>2</sub> 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<sub>2</sub> 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



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	98	283	44
11	260	24	106	285	43
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 <sub>2</sub>	SK%	O <sub>2</sub>	CO	H <sub>2</sub>	KW	CZ	N <sub>2</sub>
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 described 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 had 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.

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

Initial Gas	CO <sub>2</sub>	SKW	O <sub>2</sub>	CO	H <sub>2</sub>	KW	CZ	N <sub>2</sub>
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 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.

This 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.

c. 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 ( $3CO + 2H_2$ ) at 1/10 atmosphere and various temperatures. The induction lasted for 25 hours and was carried out between 255-355°C. The activity of the catalyst was tested with the synthesis gas of composition CO-H<sub>2</sub> 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. (4 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., 4 liters per 10 g. of iron per hour, 25 hours.  
 Synthesis: CO-rich gas, 15 atm., 4 liters per 10 g. of iron per hr. Temp. 235°- up.

Days	Temp., °C.	Contraction percent	Days	Temp., °C.	Contraction percent
1	235	56	100	252	52
5	235	56	110	243	48
10	235	56	120	256	48
20	235	52	130	264	56
30	237	48	140	269	47
40	240	52	150	270	43
50	240	50	160	270	47
60	241	48	170	277	44
70	247	53	180	278	43
80	250	54	190	272	46
90	249	53	200	273	47

	CO <sub>2</sub>	SKW	O <sub>2</sub>	CO	H <sub>2</sub>	K <sub>2</sub>	CZ	N <sub>2</sub>
<u>10th day</u>								
Initial gas	2.4	0.0	0.2	52.5	37.6	0.0	—	6.3
Final gas	61.8	2.8	0.0	1.6	12.2	7.2	1.9	14.4
<u>100th day</u>								
Initial gas	2.0	0.0	0.2	53.6	37.0	0.3	1.0	5.9
Final gas	53.0	2.4	0.1	8.1	15.9	8.3	1.9	12.2
<u>200th day</u>								
Initial gas	2.3	0.0	0.2	57.0	31.3	0.2	1.0	7.6
Final gas	48.3	2.8	0.1	15.4	13.4	5.6	1.9	14.4

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<sub>2</sub> 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, atmos.	Length of Operation in Days					
	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<sub>2</sub> 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  $3\text{CO} + 2\text{H}_2$  at a temperature of  $235^\circ\text{C}$ ., 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  $255^\circ\text{C}$ .,  $305^\circ\text{C}$ .,  $325^\circ\text{C}$ .,  $245^\circ\text{C}$ ., and  $400^\circ\text{C}$ ., using CO. The catalyst which had been inducted at  $325^\circ\text{C}$ ., 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  $235^\circ\text{C}$ ., a constant conversion corresponding to a 55 percent contraction could be maintained. The catalyst which was inducted at  $345^\circ\text{C}$ ., caused a contraction of about 50 percent for 80 days. Lower induction temperatures such as 255 and  $305^\circ\text{C}$ . and higher temperatures such as  $400^\circ\text{C}$ . 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  $\text{H}_2$  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  $255^\circ\text{C}$ .. When the catalyst was pretreated with synthesis gas at  $305^\circ\text{C}$ ., 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  $325^\circ\text{C}$ ., 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  $325^\circ\text{C}$ ., was used, the synthesis temperature had to be raised after 130 days of operation. When another catalyst inducted at  $345^\circ\text{C}$ . 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  $325^\circ\text{C}$ . 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.  $235^\circ\text{C}$ . and up

Days	Temp., $^\circ\text{C}$ .	Contraction percent	Days	Temp., $^\circ\text{C}$ .	Contraction percent
1	235	47	140	245	48
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			

Table VII (cont'd.)

	CO <sub>2</sub>	SKW	O <sub>2</sub>	CO	H <sub>2</sub>	KW	CZ	N <sub>2</sub>
<u>40th day</u>								
Initial gas	2.0	0.0	0.0	53.4	39.8	0.0	--	4.8
Final gas	57.0	2.6	0.1	6.3	14.6	0.9	2.0	10.5
<u>70th day</u>								
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
<u>100th day</u>								
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
<u>300th day</u>								
Initial gas	2.0	0.0	0.2	56.6	34.8	0.2	1.0	6.2
Final gas	48.9	2.9	0.2	15.9	10.8	8.5	1.9	12.2

Yield per Nm<sup>3</sup> 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

	CO <sub>2</sub>	SKW	O <sub>2</sub>	CO	H <sub>2</sub>	KW	CZ	N <sub>2</sub>
<u>50th day</u>								
Initial gas	2.2	0.0	0.0	53.4	39.6	0.0	--	4.8
Final gas	57.7	2.8	0.2	6.1	13.8	8.9	1.9	10.5

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 Tabel 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	10	20	25	30	60
	Contraction, percent					
15	58	52	48	40	--	--
1	58	57	53	--	--	--
0.1	--	51	55	54	56	54

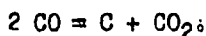
A comparison of the results of this investigation with the results in Table VI shows that the catalyst acquires also higher activity when it is activated at elevated pressures with CO instead of with CO-H<sub>2</sub> mixtures.

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<sub>2</sub> 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.



The induction process may be followed closely by checking up on the CO<sub>2</sub> formation. Curves 1 and 2, in Figure 4, represent the CO<sub>2</sub> 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<sub>2</sub> was formed per hour. The CO<sub>2</sub> formation gradually decreased. Approximately, after 25 hours of operation and after a temperature of 325°C. was reached, the CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>. During experiment 1, altogether 16 liters of CO<sub>2</sub> were formed, during experiment 2, only 11 liters. The CO<sub>2</sub> formation is caused through the reduction of CO and through the formation of combined and free carbon according to the equation



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<sub>2</sub> 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, 4 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 interrupted before the CO<sub>2</sub> 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	—

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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> and H<sub>2</sub> 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<sub>2</sub> 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 permissible 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.

#### 4a. 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<sub>2</sub> 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<sub>2</sub> has not been found possible.

The action of CO upon the iron catalyst is fundamentally different from the action of  $H_2$ . First of all, the reduction into iron oxides proceeds differently than it does with  $H_2$ ; secondly, by using CO, the catalyst structure is loosened because carbon is deposited within the lattice; and thirdly, carbides are formed when CO is used.

If one disregards diffusion, sintering, and carbon deposition, it is known from the literature that the reduction is accomplished faster with hydrogen than with CO. If one works with CO, however, the catalyst lattice is loosened up to such a degree that reduction processes can take place rapidly with CO.

The primary process during the reduction is the formation of ferromagnetic  $Fe_3O_4$ . It was formed during the reduction with CO as well as with  $H_2$ , and it may also be obtained by precipitating a mixture of ferri and ferro salts with alkalis and following dehydrogenation. However, it possesses no catalytic action in so far as the middle-pressure synthesis is concerned.

Next let us discuss the equilibrium conditions for the system iron, carbon, and oxygen. It depends on temperature, gas pressure, and the ratio of CO to  $CO_2$  contained in the gas. Figure 5a refers to atmospheric pressure. This corresponds to results of investigations by R. Schenck (12). The dotted curves were obtained by U. Hofmann and E. Groll (13) through calculations. Figure 5 shows the equilibrium conditions for 1/10 atmosphere. The  $Fe_3O_4$ - $Fe_3C$  curve was calculated by taking into consideration the pressure as a variable. The other curves were compiled through data by Schenck.

One can see from Figure 5 that at temperatures of below 550-560°C., no FeO is stable (Schenck termed this wuestit, because it always contains  $Fe_3O_4$ ). At low temperatures therefore, the reduction of  $Fe_3O_4$  may be accomplished without going through the FeO phase.

The metallic phase is only stable above temperatures of 550-600°C. (according to Schenck, it decomposes into oxoferrit containing oxygen and oxo-austenit containing oxygen and carbides). It is assumed therefore that at lower temperatures, the carbide is formed by the direct action of CO upon  $Fe_3O_4$ . This is believed to take place over unstable oxygen deficient in the immediate compounds. Hofmann and Groll made X-ray analyses of the bodies which one obtains from CO and iron. Below 655°C., they were only able to detect small quantities of free iron. We have found that the reduction of the higher to the lower oxides of iron is independent of pressure. It only depends on the ratio of CO to  $CO_2$  and the temperature. Raising the pressure favors the formation of carbides and carbon. In presence of 100 percent CO, as it may actually occur in some instances with high flow velocity, at one and at 1/10 atmospheres, only iron carbide is stable in the equilibrium.

If it is desired to come to equilibrium for the inter-action of pure CO upon metallic iron, first of all carbide has to be formed. At the same time, the  $CO_2$  obtained exerts oxidizing influence upon the iron. It seems plausible that for the induction of an iron catalyst, low pressures and high CO velocities are advantageous, since these factors lower the  $CO_2$  partial pressure and effect a rapid removal of the  $CO_2$  from the catalyst.

In both figures the cementite ( $Fe_3C$ ) has been recorded as carbides only, not however any higher carbides. Its existence was first assumed by Hilpert in 1915 (14). Fischer and his co-workers have repeatedly mentioned the formation of higher carbides as intermediate products during the benzine synthesis. Fischer and Bahr (15) also described such an iron carbide. Glud and his co-workers (16) gave the formula  $Fe_2C$  to this iron carbide. The X-ray analysis of Hofmann and Grott have ascertained that at temperatures of over  $400^{\circ}C.$ , this carbide becomes unstable because it splits off carbon. It is assumed that this decomposition occurs under the formation of cementite and free carbon.

~~Little can be said about equilibrium conditions of this or the higher carbides. Figure 5 therefore does not represent curves or areas referring to the existence of this carbide. It seems probable, however, that for their formation low temperatures and high CO concentrations are required. These conditions correspond to the optimum induction conditions for the iron synthesis. Therefore it appears very likely that the presence of these compounds in the catalyst is very essential for the degree of induction obtained and for the course of the synthesis to follow.~~

It is desirable of course that this carbide must be formed through a proper pretreatment before the synthesis is undertaken. Furthermore, in order to keep the synthesis going, this carbide should not be used up. Immediately after the induction the synthesis reaction proceeds satisfactorily even at low temperatures (for instance, below  $220^{\circ}C.$ ).

However, the conversion gradually decreases and may not even be maintained when the temperature is raised, for example at  $230-240^{\circ}C.$  If the temperature would have been  $230-240^{\circ}C.$  from the beginning, the catalyst would have continued to work at this temperature. It is believed that at the low temperatures the carbide was decomposed more rapidly by the hydrogen than it was re-formed by the action of the CO.

So far as the formation of free carbon is concerned, it may be assumed that this may be catalytically accelerated by the carbon-rich carbide. How far this undesirable decomposition of CO in presence of hydrogen may be prevented is still the subject of present investigations. However, it is definitely recognized that the formation of carbon may be suppressed by lowering the pressure and raising and increasing the flow velocity of the CO.

## PART II

### The Synthesis

#### A. The Synthesis Gas

The optimum synthesis gas composition corresponds to the ratio in which the reaction components CO and  $H_2$  are used up. The only limitation is that the catalyst used for such theoretical mixture possesses a sufficiently high lifetime. The conversion on iron proceeds according to the general equation:



as a wide reaction water is formed according to:



Figure 6 shows the formation of the reaction water (also contains water soluble organic compounds) at various pressures when a synthesis gas of composition  $1\text{CO} + 2\text{H}_2$  is used at a temperature of  $235^\circ\text{C}$ . Between 0 and 20 atmospheres, the amount of reaction water increases from 14 to 60 per normal cubic meter of ideal gas.

Figure 7a and 7b show for 0 and 15 atmospheres, the portion of CO-O which at various synthesis gas compositions was converted to water and  $\text{CO}_2$ . At an initial content of 30 percent of CO in the starting gas and at atmospheric pressure, 7 percent of the CO-O are converted to water, whereas at 15 atmospheres 25 percent of CO-O are converted to water. With 60 percent of CO in the starting gas under atmospheric conditions, the process practically proceeds according to equation (1), whereas at 15 atmospheres, still 4 percent of the CO-O are used up for water formation. In addition to elevated pressures, an increase in the  $\text{H}_2$  contents in the synthesis gas favors the water formation also.

Figures 8a and 8b show the influence of the synthesis gas composition upon the yields of solid and liquid and gasol hydrocarbons. The dotted straight lines show the calculated yields by assuming the reaction to proceed according to equation (1) over  $\text{CO}_2$  formation. The dotted pointed curves show the corresponding results according to equation (2) with concurrent water formation. The solid curves show an actually obtained yield (4-weeks average). Theoretically it should be possible to obtain 208 g. of hydrocarbons with or without water formation for every normal cubic meter of synthesis gas. For atmospheric pressure and taking into consideration only the formation of  $\text{CO}_2$  and still the theoretically best gas composition should be according to  $2\text{CO}-1\text{H}_2$ , for 15 atmospheres, it should be  $1.85 \text{CO} - 1 \text{H}_2$  (apparently an error).

Fundamental differences exist between the synthesis carried out at atmospheric pressure and at 15 atmospheres. One cannot work at atmospheric pressure with the theoretical CO mixture because at these conditions, the activity of the catalyst decreased too rapidly. This is not the case for the middle-pressure synthesis. At one atmosphere synthesis pressure, a gas of composition  $1\text{CO} + 2\text{H}_2$  behaves best. For the first 4 weeks of operation, it gave an average of 60 g. of solid and liquid and gasol hydrocarbons. These yields decrease rapidly during the fifth and sixth weeks.

It is possible to work well for many months with the theoretical gas mixture and obtain complete conversions. For the lower saturated homologues or methane, more hydrogen is required than equations (1) and (2) demand. Since the formation of methane is not entirely suppressed, CO and  $\text{H}_2$  are not used up in the ratio of 1.85-1 but rather in the ratio of 1.6-1.8:1. Finally, it appears to be advantageous as regards the lifetime of the catalyst as the end-gas of the synthesis still contains a small excess of hydrogen. The ideal synthesis gas therefore contains 60 percent CO and 40 percent  $\text{H}_2$  ( $\text{CO}-\text{H}_2 = 1.5:1$ ). With such a gas mixture, it is possible to obtain 150-160 g. of solids, liquids, and gasol per normal cubic meter for many months when iron catalysts are used.

Table XI gives the ratio of CO and H<sub>2</sub> for a series of various synthesis conditions. It gives the ratio of the 2 components for the initial gas and also the usage ratio in which both components are used up during the synthesis.

During all the experiments slightly more CO was used than would correspond to the initial ratio of CO and H<sub>2</sub> in the starting gas. For experiments 1 and 2, the starting gas contained CO and H<sub>2</sub> in the ratios of 1.4:1 respectively 1.5:1. Both gases were used up in the ratio 0.54 to respectively 1.58:1.

Table XI  
Ratio in which CO and H<sub>2</sub> are Used Up During the Synthesis for Various Conditions

Exp. No.	Catalyst type	Pres- sure, atm.	Temp., °C.	Days of opera- tion	Percent Con- traction	Ratio of CO and H <sub>2</sub> initial gas	Ratio of CO and H <sub>2</sub> used up
1	Fe-Normal catalyst	15	235	30	56	1.41:1	1.54:1
2	" " "	15	270	325	47	1.51:1	1.58:1
3	Fe-NH <sub>3</sub> precipitated 1/4% K <sub>2</sub> CO <sub>3</sub>	15	255	24	51	1.5 : 1	1.7 : 1
4	Fe-NH <sub>2</sub> CO <sub>3</sub> precipitated 1% K <sub>2</sub> CO <sub>3</sub>	15	234	7	49	1.5 : 1	1.59:1
5	" " "	15	237	14	50	1.64:1	1.78:1
6	Fe-Normal catalyst	5	270	9	37	1.45:1	1.77:1
7	" " "	60	254	6	52	1.46:1	1.67:1
8	" " "	15	230	5	45	0.53:1	0.87:1
9	" " "	15	240	4	50	1.76:1	1.96:1
10	Fe-Na <sub>2</sub> CO <sub>3</sub> precipitated 1% K <sub>2</sub> CO <sub>3</sub>	15	235	16	50	1.75:1	2.1 : 1
11	Fe-Na <sub>2</sub> CO <sub>3</sub> precipitated 5% K <sub>2</sub> CO <sub>3</sub>	15	238	7	49	1.76:1	2.08:1

With other experiments the difference was greater (experiment 3, 6, and 7). Experiments 4, 5, and 10 were carried out with a catalyst containing one percent K<sub>2</sub>CO<sub>3</sub>. For experiments 4 and 5, the CO-H<sub>2</sub> ratio was 1.5 respectively 1.64:1 for the initial gas. For the same experiments, the end-gas contained 1.59 respectively 1.78 CO to 1H<sub>2</sub>. For experiment 10, the initial gas contains too much CO. The experiment points toward a carbon formation. The catalyst of this experiment only had about half as long a lifetime as the catalysts of experiments 4 and 5. The situation is similar for experiments 9 and 11. Experiment 8 was carried out with mixed gas (CO-H<sub>2</sub>, 1.3-5.36:1). Hereto the ratio in which the components were used up was higher than the original and amounted to 0.87:1.

In order to get maximum yields, it is necessary to work with an initial gas containing both components in approximately the ratio in which they were used up. Initial gases which contain less CO than is required for the optimum conditions (1.4-1.6:1) are not capable of yielding maximum yields. This is because the end-gas contains an excess of H<sub>2</sub>. Initial gases with too high a percent of CO increase the danger of carbon formation and shorten the lifetime of the catalyst. It is well to remember here that with increasing CO contents of the synthesis gas the reaction temperature has to be higher for maximum yield.

## B. The Synthesis Pressure

In the paragraph on synthesis gas, the reasons have already been explained why it is not practicable to work at atmospheric pressure when using iron catalysts.

Following are a few series of experiments carried out with catalysts having undergone different processes of induction. The experiments are designed to show the influence of the synthesis pressure upon the conversion.

First Series of Experiments. The catalyst used contained iron and copper in the ratio of 5:1. It was obtained from the solutions of ferrous chloride and copper chloride by precipitation with sodium carbonate. It had been alkalized by adding 1/8 percent  $K_2CO_3$ . This catalyst was subjected to an induction process at atmospheric pressure for 4 days at a temperature of  $245^\circ C$ . (4 liters of mixed gas per 10 g. of iron per hour). After switching over to 15 atmospheres pressure, we carried out the synthesis by using 4 liters of synthesis gas ( $CO + H_2 = 3:2$ ) per 10 g. of iron per hour. Table XII gives the results of this series of experiments. Contractions are recorded for 5, 15, 30, and 80 atmospheres and the necessary working temperatures. (The temperatures of this series of experiments, in general, were high as compared to the induction of the catalyst.)

Table XII  
Reaction Temperature and Contraction at Various Pressures  
Fe-Cu Catalyst Inducted with Mixed Gas at  $245^\circ C$ . and One Atmosphere

Days of operation	5 atmospheres		15 atmospheres		30 atmospheres		80 atmospheres	
	Temp., $^\circ C$ .	Contraction percent	Temp., $^\circ C$ .	Contraction percent	Temp., $^\circ C$ .	Contraction percent	Temp., $^\circ C$ .	Contraction percent
10	257	44	257	42	263	50	270	38
20	265	45	265	50	275	50	286	49
30	270	42	270	53	280	48	300	48
40	272	45	274	53	287	52	302	50
50	275	45	275	55	289	52	-	-
60	285	48	272	52	290	49	-	-
90	278	50	281	51	-	-	-	-
120	-	-	285	49	-	-	-	-
150	-	-	290	47	-	-	-	-

For 5 atmospheres, the contractions obtained during 3 months of operation were between 45 to 50 percent. At 15 atmospheres and otherwise equal conditions, 50 to 55 percent contraction was obtained. Correspondingly at 15 atmospheres the yields of liquid and solid and gasol hydrocarbons were approximately 10 degrees higher than at 5 atmospheres. At 30 atmospheres, contractions of 50 to 52 percent could be reached too. However, at temperatures which were 10 to 15 degrees higher, and after the second month were 20 degrees higher than the temperatures required at 15 atmospheres pressure. When operating at 80 atmospheres, it was necessary to increase the temperature by 10 to 20 degrees over that at 30 atmospheres in order to obtain the same degree of conversion.

Table XIII shows the end-gas analyses obtained for a contraction of 50 percent at 5, 15, 30, and 80 atmospheres. The corresponding initial gas analyses of the runs carried out at 5 and 15 atmospheres contained 56 percent CO and 36.1 percent H<sub>2</sub>; those carried out at 30 and 80 atmospheres, 55.5 CO and 39.5 H<sub>2</sub>.

Table XIII

Reaction Gases at Various Pressures and Constant Contraction at 50 percent.

Pressure, Days of atmos. operation	Temp., °C.	CO <sub>2</sub>	sKW	O <sub>2</sub>	CO	H <sub>2</sub>	KW	CZ	N <sub>2</sub>	
5	6	257	53.8	3.4	0.2	12.3	13.3	7.0	1.9	10.0
15	3	252	55.5	3.8	0.2	11.5	11.6	8.0	1.8	9.4
15	23	267	51.4	3.8 ?	0.3	11.2	16.4	9.9	1.6	7.5
30	10	263	51.1	2.3	0.6	11.3	18.0	7.7	1.8	9.0
80	23	297	51.1	1.4	0.1	13.6	11.0	14.3	1.9	8.5

The end-gas analyses show that in spite of the various pressures and the correspondingly different temperatures, the course of the conversions does not change fundamentally. It had already been pointed out that at elevated pressures, the formation of reaction water increases at the expense of the formation of CO<sub>2</sub>. Furthermore, it may be seen from the analyses, that at higher pressures, the quantities of unsaturated hydrocarbons decreases, and that the quantities of the saturated hydrocarbons increases correspondingly to the necessary higher reaction temperature. The increased consumption of H<sub>2</sub> is well expressed in the ratio in which CO and H<sub>2</sub> are used up. This usage ratio for the various pressures is as follows: For 5 atm., 1.7:1; 15 atm. 1.66:1; 30 atm. 1.6:1; 80 atm. 1.44:1.

With respect to the lifetime of the catalyst at various working pressures, it should be pointed out that working temperatures above 290°C. should be avoided on account of the danger of carbon formation. The experiment carried out at 15 atmospheres showed that the catalyst had the longest lifetime. With the catalyst\* used for this series of experiments, a temperature of 290°C. was required for 5 months operation and working at 15 atmospheres; the same temperature was required after 2 months when working under 30 atmospheres, and already during the first month when working under 80 atmospheres.

Second Series of Experiments. For this series of experiments, a copper-free so-called normal iron catalyst was used which had been inducted for 24 hours at 1/10 atmosphere and 325°C. with a CO-rich synthesis gas. Table XIV shows the results of experiments carried through at various pressures such as 1, 5, 10, 30, and 60 atmospheres. All the experiments were initially started at 235°C.

\*The iron-copper catalyst used for this series really had a low activity if compared to the catalysts known at the present time. The influence of the pressure and the existence of an optimum pressure between 5 and 30 atmospheres, however, may even be observed from this catalyst.



Table XIV

Reaction Temperature and Contraction at Various Pressures  
(Normal Iron Catalyst Inducted with CO-rich Gas at 325°C. and 1/10 Atmosphere)

Days of Operation	5 atmospheres		10 atmospheres		30 atmospheres		60 atmospheres	
	Temp., °C.	Contraction percent	Temp., °C.	Contraction percent	Temp., °C.	Contraction percent	Temp., °C.	Contraction percent
1	235	30	233	42	235	53	235	50
2	-	-	234	42	235	56	238	42
3	235	25?	235	48	234	57	235	40
6	250	38	238	50	-	-	254	52
9	270	37	239	50	-	-	-	-
12	-	-	237	50	-	-	-	-

This catalyst did not give a conversion at atmospheric pressure and 235°C., neither did it give a conversion on the second day at 250°C. (When we switched to 15 atmospheres and 235°C., this catalyst immediately gave a contraction over 53 percent.) At 5 atmospheres, the contractions lie somewhere between 30 and 40 percent. Hence the conversion was still incomplete. This did not improve even when the temperature was raised to 270°C. at the ninth day of operation. (When we went back to 15 atmospheres and 235°C., 50 percent conversion was obtained even then). At 10 atmospheres and 235°C., a contraction of 50 percent was reached. This was the case also at pressures of 30 and 60 atmospheres. However, in the case of the 30 atmosphere run, the conversion fell off sharply on the third day and for the 60 atmosphere run, it decreased rapidly already during the first day of operation. At 60 atmospheres, a contraction of 52 percent could only be reached on the sixth day of operation when the temperature was raised to 254°C.

Here too, we found that an optimum pressure of somewhere between 10-30 atmospheres exists giving the highest yields and longest catalyst lifetime. (A comparison with experiments recorded in Table V for the same catalyst at 15 atmospheres shows that the optimum pressure is somewhere above 10 atmospheres)

Third Series of Experiments. A catalyst was used which was copper-free and had been precipitated with soda. One percent potassium carbonate was added, and the induction was carried out with CO at 1/10 atmosphere. The catalyst was prepared by a so-called inverted precipitation, that is, by running the iron solution (60°C.) into a boiling soda solution. We wanted to find out how long at 15, 20, 30, and 60 atmospheres at a reaction temperature of approximately 235°C. a contraction of more than 50 percent could be maintained. Table XV shows that for 15 atmospheres this time was 20 days, at 20 atmospheres, it was 9 days-operation at 30 atmospheres, 5 days; and at 60 atmospheres, a contraction of more than 50 percent could be maintained only for one day.

Tablo XV

The Influence of the Synthesis Pressure Upon the Length of Time of Operation (Length of Time for Which a Contraction of 50% was Possible at 235°C., When Using an Iron Catalyst Alkalinized with 1%  $K_2CO_3$ )

Days of operation	15 atmospheres		20 atmospheres		30 atmospheres		60 atmospheres	
	Temp., °C.	Contraction percent	Temp., °C.	Contraction percent	Temp., °C.	Contraction percent	Temp., °C.	Contraction percent
1	235	40	235	52	234	54	235	56
2	239	45	234	51	236	50	235	40
3	237	52	234	55	234	55	235	35
6	239	54	235	55	234	40	-	-
9	238	54	235	49	-	-	-	-
12	238	52	-	-	-	-	-	-
20	234	50	-	-	-	-	-	-
28	235	40	-	-	-	-	-	-

Results of Experiments Carried Out at Various Pressures

The optimum pressure of the middle-pressure synthesis for an iron catalyst lies somewhere between 10 and 20 atmospheres. (For most catalysts, the optimum pressure is most probably near 15 atmospheres). At lower or higher pressures, the conversion during the synthesis and the lifetime of the catalyst decreases.

C. The Reaction Temperature.

The temperature of the following work refers to the temperature recorded in the aluminum block.\* Since both ends of the reaction tube stick out of the aluminum block inspite of good insulation with asbestos rope, heat is conducted towards the outside. As a consequence of that, the temperature in the interior of the tube is somewhat lower. Calibrations have shown that the temperature in the interior is approximately lower by 5 degrees. However, no temperature correction was taken into consideration, and the temperature of the block was taken as that of the synthesis.

We paid special attention to the temperature problem. We endeavored to keep the temperature for the iron middle-pressure synthesis as low as possible. This was necessary for economic reasons. On the large scale, the reactor is intended to be cooled with water and a small elevation in temperature would cause a considerable increase in steam pressure, and therefore increase the weight of the equipment.

\*In the laboratory, we worked with pressure tubes which were embedded in a slanted position in the aluminum block furnace.

## 1. Influence of Induction.

It has been pointed out at another place that the induction temperature of the catalyst exerts an important influence upon the following synthesis. The curves shown in Figure 9, supplement the material already presented. The abscissas give the length of operation in months, the ordinates give the operating temperatures, and the steam pressure corresponding to these temperatures. All the experiments were carried out with a synthesis gas containing CO and H<sub>2</sub> in the ratio 3:2 (4 liters per 10 g. of iron per hour).

Curve 1 refers to a catalyst not previously inducted but taken into operation at 15 atmospheres immediately. In order to get maximum contraction, the temperature had to be raised to 290°C. The initial contraction was 45 percent, in the course of the second month of operation, the activity of the catalyst increased gradually so that a contraction of 50 percent was obtained. The temperature then could be lowered down to 280°C. without impairing the yield. During the fourth month of operation, however, it had to be raised again, and at the end of the fifth month it had reached 300°C.

Curve 2 shows the temperature relationships for an iron-copper catalyst which had acted upon a mixed gas for 3 days at 1 atmosphere and 240°C. (contraction 30 percent). Then it was switched to 15 atmospheres using the same synthesis gas. In order to get a maximum contraction of 50 to 55 percent (optimum conversion), the temperature had to be raised from 240 to 290°C. over the course of 5 months.

Curve 3 represents the temperature conditions for an experiment with a copper-free normal iron catalyst, which prior to the synthesis had been inducted at 1/10 atmosphere and 255°C. for 25 hours with pure CO. In order to get maximum contraction of 50 to 55 percent, the temperature had to be raised to 235-272°C. in the course of 8 months. The activity of the catalyst increased slowly at this temperature so that in the eleventh month, the temperature could be lowered again to 254°C. and still a contraction of 50 percent could be obtained. For the 15th and 16th months, the temperature was raised again to 265°C., and then lowered again to 259°C. Table XVI presents some end-gas analyses for this experiment.

End-gas Analyses of a Time-Test at Different Temperatures  
During 16 Months of Operation

Months of operation	Temp., °C.	Contraction percent	End-gas composition in percent							
			CO <sub>2</sub>	sKW	O <sub>2</sub>	CO	H <sub>2</sub>	KW	CZ	N <sub>2</sub>
1	253	50	49.6	2.2	0.1	15.0	13.2	8.8	1.9	11.0
9	272	52	54.5	3.3	0.0	8.1	7.4	11.2	1.8	15.5
11	254	50	50.1	2.8	0.2	14.9	11.9	7.3	1.7	12.8
16	266	48	53.5	3.1	0.1	8.2	10.6	11.9	1.9	12.6
16	259	48	51.2	3.2	0.2	9.9	12.6	10.4	1.8	12.5

The table shows that by increasing the temperature, the quantity of gaseous hydrocarbons formed increases. On the whole, the end-gas analyses obtained from the synthesis gas do not differ too much for the 16 months of operation.

Curve 4 refers to a catalyst inducted at 325°C. with CO and 1/10 atmosphere. The induction at 325°C., facilitated operating at low temperatures for the first few months. The contraction remained constant at 50 to 54 percent through the course of 4 months at 235°C. After that, the temperature had to be raised. After one year, this iron catalyst did not show any advantages any longer as compared to a catalyst inducted at 255°C.

~~The curves of the figure bring out of what significance the pretreatment of the iron catalyst is to the synthesis temperature.~~

## 2. Influence of Gas Composition.

In Table XVII, comparative results are given for conversions of CO-rich and H<sub>2</sub>-rich synthesis gases at a reaction temperature of 205°C. (synthesis pressure 15 atmospheres).

Table XVII  
Conversion of CO-rich and H<sub>2</sub>-rich Synthesis Gas at 205°C., and 15 Atmospheres

	CO <sub>2</sub>	SKW	O <sub>2</sub>	CO	H <sub>2</sub>	KW	CZ	N <sub>2</sub>	Contraction percent
CO-rich starting gas	2.2	0.0	0.2	58.9	33.9	0.2	1.0	4.6	20
end-gas	10.3	0.8	0.2	52.9	28.4	1.6	1.3	5.8	
H <sub>2</sub> -rich starting gas	1.2	0.0	0.0	1.2	56.6	1.6	1.2	9.4	31
end-gas	0.3	2.1	0.2	19.5	52.3	3.9	2.0	13.7	

Table XVIII shows the conversion of 3 different gases at 225.

Table XVIII  
Conversion of CO-rich Gas, of water-gas, and of H<sub>2</sub>-rich Gas at 225°C., and at a pressure of 15 atmos.

	CO <sub>2</sub>	SKW	O <sub>2</sub>	CO	H <sub>2</sub>	KW	CZ	N <sub>2</sub>	Contraction percent
CO-rich starting gas	2.3	0.0	0.0	58.8	33.4	0.4	1.0	5.1	45
end-gas	42.9	3.8	0.2	4.5	15.1	4.3	1.5	9.2	
Water-gas, starting	1.8	0.0	0.1	46.4	43.4	0.8	1.0	7.5	52
end-gas	40.6	4.0	0.2	8.9	24.6	6.2	1.6	15.5	
H <sub>2</sub> -rich starting gas	0.6	0.0	0.1	0.7	58.3	0.2	1.0	10.1	46
end-gas	22.6	1.6	0.1	0.0	43.8	13.1	1.7	18.8	

The analyses show that the reaction temperature can be lower if less CO is contained in the synthesis gas, that is, the less CO is converted. For the same temperature an increase in H<sub>2</sub> contents in the synthesis gas, the percent contraction increases, (as long as the CO is not converted entirely as shown by the last experiment of Table XVIII). 0.66 respectively 0.71 liter of CO is converted per hour at 205°C. (according to both experiments of Table XVII). According to Table XVIII, 1.8, 1.7, and 1.23 liters per hour of CO were consumed at 225°C. In the last experiment of this table, all of the CO was converted. As long as CO and H<sub>2</sub> were present in the gas in sufficient quantity to react for the same temperatures and for the same length of time, the converted quantities of CO and CO-H<sub>2</sub> ratio remained independent,

### 3. Effect of Too Low Starting Temperature.

In general, the experiments were started at 225°C. to 235°C., although good conversion could have been obtained at lower temperatures immediately after the induction. Thus, with an experiment conducted with H<sub>2</sub>-rich synthesis gas (CO-H<sub>2</sub> = 1:2), a contraction of 47 percent was still obtained at a temperature of 184°C. after the second day of operation. The ratio in which CO and H<sub>2</sub> were used up amounted to 0.7:1. This points to a reaction proceeding according to  $CO + 2H_2 = CH_4 + H_2O$ . At such low reaction temperatures, the amount of conversion decreases after a few days and then the results are more unfavorable even after the temperature raised again, as compared to the results one would obtain if operation would have been commenced at the higher temperatures from the start. Table XIX brings this out too. This table contains the results of two comparative experiments using CO-rich synthesis gas and a normal iron catalyst. Experiment one is conducted at 235°C., experiment 2, at first, at 210°C.

Table XIX  
Influence of Too Low a Reaction Temperature Upon the Stability of the Catalyst

Days of operation	Experiment 1		Experiment 2	
	Temp., °C.	Contraction percent	Temp., °C.	Contraction percent
1	235	56	210	42
2	"	52	"	31
3	"	51	"	27
4	"	51	-	-
5	"	52	220	21
6	"	55	235	36
7	"	55	250	45
8	"	55		
9	"	55		
10	"	57		
15	"	55		

The catalyst taken into operation at 235°C. gives constant contractions of 50 to 55 percent. The catalyst which was started at 210°C. gives contraction of 42 percent after one day of operation, after 2 days, it gave 31 percent, and after 3 days only 27 percent. When the temperature was then raised, the catalyst gave only 36 percent conversion at 235°C. and even at 250°C., 50 percent contraction could not be reached.

### 4. Temperature and Reaction Products.

It has been pointed out previously (for example, see Table XVI) that with raised temperatures the formation of the gaseous products increases. Table XX shows average yields obtained on an iron catalyst containing 1/4 percent potassium carbonate, temperatures were 235, 270, and 280°C. When the temperature was raised from 235 to 270°C., the yields of solid paraffin dropped from 39 to 4 g. per normal cubic meter. The quantity of liquid and especially the volatile

liquid hydrocarbons and the gasol hydrocarbons increased at the same time. At 280°C. the paraffin yields were still lower, however, at this temperature, the yields of liquid and gasol hydrocarbons decreased also.

Table XX

Reaction temperature, °C.	Yields (g./Nm <sup>3</sup> ) of Ideal Gas		
	Solid Paraffin	Liquid hydrocarbons	Gasol hydrocarbons
235	39	83	26
270	4	94	46
280	2	82	35

D. The Influence of Alkali Contents of an Iron Catalyst Upon Its Activity and Upon the Nature of the Reaction Products.

The preparation of the catalysts and the nature of the addition of alkali has been discussed earlier. In the following, an analysis is presented to show the influence of the alkali upon the course of the synthesis. The alkali additions indicated in the tables refer to potassium carbonate expressed as percent potassium carbonate referred to metallic iron. In the case of the other alkali salts (permanganate, fluoride, etc.) the notation "1 percent KMnO<sub>4</sub>" is to signify that as much potassium was used in the formation of this salt as would correspond to one percent K<sub>2</sub>CO<sub>3</sub>. Table XXI, to start with, brings an experiment the catalyst of which was precipitated with ammonia and which did not contain any alkali. The testing of this catalyst was carried out at constant temperature (235°C.) with a CO-rich synthesis gas (CO-H<sub>2</sub> = 3:2, containing 8 to 10 percent inert ingredients). The pressure was 15 atmospheres.

Table XXI

Activity of Various Alkalized Iron Catalysts

Alkali addition	Days of operation									
	1	2	5	10	20	30	40	50	100	
0	50	50	50	50	50	49	51	51		
0	53	50	48	49						
1/4% K <sub>2</sub> CO <sub>3</sub>	47	50	50	51	55	56	54	54	53	
1/2% "	54	-	54	47	-	45				
1% "	40	-	54	53	50					
1% "	45	45	45	52	43	48	47			
2% "	45	45	47	46	47	50				
5% "	-	-	45	50	50	51	50	40		
10% "	-	50	47	50	45	42				
1% KMnO <sub>4</sub>	40	-	50	51	55	50				
1% K <sub>2</sub> F <sub>2</sub>	-	57	53	55	48					
1% K <sub>2</sub> SiO <sub>3</sub>	-	54	53	46	50					
1% K <sub>2</sub> HPO <sub>4</sub>	55	46	-	46	40					

The series of experiments shows that alkali addition to the catalyst is not required if one disregards the nature of the formed hydrocarbons. The catalyst

which was precipitated with ammonia and was entirely free of alkali was tested for 50 days and gave values of contraction which were not essentially below those obtained with a normal iron catalyst containing 1/4 percent  $K_2CO_3$ . We found that catalysts which contained up to one percent or more potassium carbonate showed a decrease in activity earlier than normal iron catalysts, namely, at  $235^\circ C.$ , the decrease occurred between the 30th and 50th days. When we continued to operate and used catalysts which had been alkalinized by salts other than potassium carbonate, no worth-while variations in the course of the synthesis could be observed during the first few weeks. However, the catalyst containing potassium permanganate showed very good conversion, whereas the one containing potassium phosphate was less stable.

Table XXII shows the quantity and the nature of the reaction products which were obtained with the various alkalinized catalysts at  $235^\circ C.$  and 15 atmospheres synthesis pressure. The yields expressed in grams per normal cubic meter of ideal gas vary to some extent all through the first month of operation, corresponding to the not entirely uniform contraction obtained. Thus, we obtained between 150 to 160 grams per normal cubic meter of ideal gas. The alkali content of the catalyst exerts a very essential influence upon the nature of the reaction products. When no alkali was present only 12 percent of solid paraffin (referred to the total yields of solid, liquid, and gasol hydrocarbons) were obtained according to the Butanon method. When 1/4 percent potassium carbonate was added to the catalyst, this increased to 26 percent, for one percent potassium carbonate to 42 percent, for 2 percent to 43 percent, and at 5 percent potassium carbonate contents 45 to 46 percent of solid paraffins were obtained referred to the total yields. The quantity of liquid and gasol hydrocarbons correspondingly falls off as the alkali contents increases.

Table XXII finally brings out that it was unimportant what alkali salts had been added to the catalyst so far as the quantity and nature of the reaction products were concerned. The experiments conducted with a catalyst containing one percent potassium carbonate and the corresponding quantities of potassium manganate, potassium silicate, potassium fluoride, and potassium phosphate showed the same course of the reaction within limits of experimental error.

Table XXII  
Yields With an Iron Catalyst Containing Various Amounts of Alkali Additions

Precipitating agent	Alkali addition	Solid, liquid, and gasol hydrocarbons g./Nm <sup>3</sup> of ideal gas		Liquid hydrocarbons Gasol	
		ideal gas	Paraffin percent	percent	percent
NH <sub>3</sub>	0	111	12	67	21
Na <sub>2</sub> CO <sub>3</sub>	1/4% K <sub>2</sub> CO <sub>3</sub>	118	26	56	18
	0	110	13	67	28
Na <sub>2</sub> CO <sub>3</sub>	1% K <sub>2</sub> CO <sub>3</sub>	157	42	47	11
	1% KMnO <sub>4</sub>	155	41	45	14
	1% K <sub>2</sub> SiO <sub>3</sub>	158	43	41	16
	1% K <sub>2</sub> F <sub>2</sub>	163	46	42	12
	1% K <sub>2</sub> HPO <sub>4</sub>	154	38	52	10
Na <sub>2</sub> CO <sub>3</sub>	2% K <sub>2</sub> CO <sub>3</sub>	143	43	44	13
	5% " "	161	45	43	12
	5% " "	155	46	44	10

## E. Treatment with Hydrogen Before and After the Synthesis.

### 1. Pretreatment with Hydrogen.

The normal iron catalyst instead of having been treated with CO was inducted with 6 liters per hour of  $H_2$  at 1/10 atmosphere,  $325^\circ C$ . for 2-1/2 hours. When we switched over to CO-rich synthesis gas and operated at 15 atmospheres and  $235^\circ C$ ., an end-gas analysis made after 1-1/4 hours showed 2 to 3 percent contraction, and another gas analysis made after 3-1/4 hours disclosed 4 percent contraction. The catalyst behaved in the same way as a non-inducted catalyst would have behaved. Nevertheless the catalyst after having been removed from the reaction tube was faintly pyrophoric and ferromagnetic. A comparative experiment which was run with a catalyst having been inducted with CO instead of  $H_2$  prior to the synthesis gave a contraction of 54 percent from the very beginning.

In a further experiment we worked with a catalyst of somewhat lower activity, and we wanted to see whether a pretreatment with  $H_2$  prior to the induction would result in an improvement. For this purpose, we worked for 6 hours passing 8 liters of  $H_2$  per hour over the catalyst at  $325^\circ C$ . and 1/10 atmosphere. Then we passed 4 liters of CO per hour over the catalyst for 20 hours at 1/10 atmosphere and  $325^\circ C$ . Then we started to operate with CO-rich synthesis gas at 15 atmospheres. The contraction amounted to 42 percent on the second day at a temperature of  $234^\circ C$ ., 45 percent on the sixth day, and  $236^\circ C$ ., 47 percent on the eighth day and  $238^\circ C$ ., and again 47 percent on the tenth day at  $238^\circ C$ . Comparing this data with the experiment conducted with a catalyst which was not pretreated with hydrogen, 42 percent contraction was obtained on the second day at  $234^\circ C$ ., and 46 percent on the eighth day at  $238^\circ C$ . The hydrogen treatment prior to induction therefore was without influence upon the conversion.

### 2. Hydrogen Treatment Between Induction and Synthesis.

To start with, we passed 40 liters of CO for 2-1/2 hours at  $325^\circ C$ . and 1/10 atmosphere over the catalyst. Thereafter, we passed 6 liters of  $H_2$  per hour over the catalyst at  $325^\circ C$ . Then we switched over to CO-rich synthesis gas at 15 atmospheres, and the activity was tested at  $210^\circ C$ . The contraction went up to 42 percent immediately. After one day, it was 43 percent. For a comparative experiment in which the  $H_2$  pretreatment was omitted, the contraction after one day was 42 percent. The intermittent  $H_2$  treatment was therefore of no influence upon the catalyst activity. (This result is surprising because one would expect that the  $H_2$  would reduce the carbides having formed during the induction with CO).

### 3. Hydrogen Treatment During the Synthesis.

A catalyst which ordinarily should have been taken into operation at a somewhat higher temperature was tested at  $235^\circ C$ . and 15 atmospheres with 4 liters per hour of CO-rich gas. It gave 52 percent contraction on the first and second days (see Figure 10), 50 percent contraction after 2 days, and 47 percent contraction after 3 days. The dotted curve shows that the contraction should have arrived at 40 percent if the experiment could have been continued for one week at  $235^\circ C$ . However, after 3 days, a  $H_2$  treatment was undertaken for 15 hours, using 8 liters per hour of  $H_2$  at one atmosphere and  $325^\circ C$ . After this  $H_2$  treatment, the contraction in the following synthesis amounted to 55 percent. It



slowly decreased thereafter but remained at 51 percent for 12 days. Here again, another  $H_2$  treatment was undertaken at the same conditions as outlined earlier. The contraction held up again to 57 percent and slowly decreased down to 50 percent at the 19th day. After the third  $H_2$  treatment had been carried out, at first a contraction of 55 percent was obtained, after 3 days the value of 51 percent, and after 4 days, 52 percent contraction was measured. Then for 2 months of operation the contraction remained constant between 50 to 53 percent at  $235^\circ C$ .

Figure 10 shows that the  $H_2$  treatment undertaken between syntheses causes an increase in catalyst activity. This increase was especially pronounced during the first hours after the  $H_2$  treatment, and it also resulted in a lasting improvement of the catalyst. When these peaks of activity were obtained immediately after the  $H_2$  treatment, the ratio  $CO-H_2$  were used up (at 50 to 52 percent contraction) and was the same as under normal circumstances. In both cases,  $CO$  and  $H_2$  were used in the ratio of 1.67 to 1.70:1.

Iron catalysts which had worked already for a great length of time or which had experienced an essential decrease in activity could not be improved by such  $H_2$  treatment. As a matter of fact, an activity improvement will not even result if another induction is carried through with  $CO$ . If it is planned to give an  $H_2$  treatment, it is important that it should be given before the activity of the catalyst has decreased below 45 to 50 percent.

#### F. Catalysts Based on Ferrous Salts.

In the initial description of the preparation of catalysts having ferrous salts as their base, it was pointed out that these iron catalysts have the form of voluminous brown powder. The catalysts built on ferric salts are almost black and show glassy fracture. A fundamental distinction may therefore be made between the two catalysts from their appearance.

When the ferro catalyst was employed without previous induction ( $CO$ -rich gas at 15 atmospheres) the results were equally unfavorable as those with the other catalysts. Thus, on the first day of operation at  $244^\circ C$ , 8 percent contraction was obtained, and 45 percent on the ninth day at  $265^\circ C$ . The ferro catalyst under these conditions thus could be brought to its highest working capacity to yield 50 percent contraction at  $280-290^\circ C$ .

After an induction with mixed gas at one atmosphere and  $254^\circ C$ , a synthesis was undertaken with  $CO$ -rich gas at 15 atmospheres and  $245^\circ C$ . 43 percent contraction was obtained at  $245^\circ C$ , 44 percent contraction at  $255^\circ C$ , and 47 percent contraction at  $265^\circ C$  on the 10th day. When the catalysts prepared from ferro chloride and ferro nitrate and inducted with  $CO$  at 1/10 atmosphere and  $235^\circ C$  were used in a synthesis at 15 atmospheres and a  $CO$ -rich synthesis gas, they showed an initial activity which, however, decreased rapidly already after one to two days. Table XXIII shows this for 3 experiments.

Table XXIII  
Experiment With Ferro Catalysts

Catalyst preparation by	FeCl <sub>2</sub>		FeCl <sub>2</sub>		Fe(NO <sub>3</sub> ) <sub>2</sub>	
	Days of operation	Temp., °C., Contraction percent	Temp., °C., Contraction percent	Temp., °C., Contraction percent	Temp., °C., Contraction percent	
1	235	57	235	56	235	56
2	235	57	225	56	235	57
3	235	34	225	49	235	40
4	235	30	215	38		
5			225	35		
6			225	29		

The contraction for the first experiment decreased from 57 to 34 percent on the third day when the operating temperature was 235°C. For the second experiment (after a contraction of 56 percent was obtained initially) the temperature was lowered on the first day, in order to minimize any possible damage to the catalyst activity which could have occurred due to the high temperature. At the lower temperature, however, the contraction decreased as well. A third experiment carried out with a catalyst derived from ferro nitrate behaved similarly.

Under the previously adhered to test conditions for the other normal catalysts (prepared from ferri salts), the ferro catalysts showed essentially more unfavorable behavior.

For the experiments in Table XII, iron-copper catalysts built on ferro chloride-copper chloride were employed. They were inducted with mixed gas at atmospheric pressure. The table shows that these ferro catalysts give full conversion for several months. However, it should be pointed out that the temperature has to be 260°C. and up, corresponding to the induction conditions.

#### G. The Influence of the Addition of Copper.

The experiments of Fischer, Ackermann, and Meyer (17) have shown that the synthesis carried out at atmospheric pressure with copper-free catalysts is inferior to the synthesis carried out with copper-containing iron catalysts. The following table brings the best results with both catalysts at atmospheric pressure. The reaction temperature was 230-235°C. Four liters of mixed gas per 10 g. per hour of iron were used for the synthesis.

Table XXIV. The Influence of the Addition of Copper Upon the Normal Pressure Synthesis

Catalyst: Induction time:	Fe:Cu = 5:1 2 days		Fe (without Cu) 4 - 7 days	
	Days of operation	Contraction percent	Liquid products grams per cu. m.	Contraction percent
1	30	56	32	55
5	30	56	31	50
10	30	55	30	48
20	30	56	27	38
30	29	50	26	34
40	27	46		

The copper containing catalysts required a shorter induction time in order to reach the maximum contractions of approximately 30 percent. The maximum yields at the beginning of the synthesis in both cases were approximately the same, however, the copper-containing catalysts retained their activity somewhat longer than the copper-free catalysts.

When the catalysts were employed at 15 atmospheres pressure (without previous induction at lower pressures), those catalysts containing copper (5Fe + 1Cu) as well as copper-free catalysts gave contractions of 40 to 44 percent after the reaction temperature had gone up to 260-270°C. Copper-free catalysts under these conditions and at 280-290°C. gave a contraction of 50 percent for several months. In comparison to that, the copper-containing catalysts deteriorated rapidly.

Table XXV shows 2 experiments the catalysts of which were produced from ferri salts and were inducted at 325°C. and 1/10 atmosphere by using CO. Then the synthesis was carried out at 15 atmospheres with CO-rich gas. Results are compared for temperatures of 235 and 225°C. for catalysts containing copper and copper-free catalysts.

Table XXV

The Effect of the Addition of Copper Upon the Activity of Iron Catalysts

Synthesis temperature Days of operation	235°		225°	
	Fe without Cu	5Fe:1Cu	Fe without Cu	5Fe:1Cu
1	55	54	52	55
2	53	56	-	54
3	53	-	50	50
4	55	50	-	-
5	55	50	45	50
10	54	52		

The experiments show that the addition of copper to iron catalysts for use in the middle-pressure synthesis at 235°C. is of no advantage.

H. The Effect of the Addition of Kieselguhr.

In the synthesis of hydrocarbons with cobalt catalysts, kieselguhr plays an important part as a carrier used in the catalyst. Satisfactory yields of liquid and solid hydrocarbons may only be obtained with catalysts containing kieselguhr.

When iron catalysts were used in the normal-pressure synthesis, it was found that the catalysts not containing a carrier were more effective than those having kieselguhr as a carrier. In some cases yields of 50 to 55 g. of liquid hydrocarbons per cubic meter of gas were obtained, but the lifetime of such catalysts lasted only a few days. Recently we have carried out experiments using iron catalysts containing kieselguhr for the middle-pressure synthesis. The purpose of this investigation was not so much to improve the yields of the synthesis as it was to operate with catalysts of lower density in vertical reaction tubes. Operation with catalysts containing no kieselguhr in vertical tubes results in much shorter life than when kieselguhr is present (see part IV of this paper).

The kieselguhr was added at various stages of the catalyst preparation. The following experiments were carried out: Experiment 1, 4 g. of kieselguhr per 10 grams of iron were added to the iron solution prior to precipitation; Experiment 2, 4 grams of kieselguhr per 10 grams of iron were added to the soda solution prior to precipitation; Experiment 3, 4 grams of kieselguhr per 10 grams of iron were added to the moist catalyst slurry after alkalization (see Part I, "Catalyst Preparation"); Experiment 4, the possibility of adding dry kieselguhr to the finished catalyst has to be dismissed if one desires to produce a solid granular catalyst.

The results of experiments 1 to 3 are given in Table XXVI. Experiment 3a refers to a synthesis temperature of 235°C., 3b refers to 225°C. The various contractions obtained after various times of operations are recorded in the table. In all cases, the catalyst was induced for 24 hours using 4 liters per hour of CO per 10 g. of iron. The induction pressure was 1/10 atmosphere, and the temperature, 325°C. After this, the synthesis was carried out with a CO-rich gas ( $3CO + 2H_2$ ) at 15 atmospheres.

Table XXVI  
The Effect of the Addition of Kieselguhr to the Catalyst

Days of operation	Experiment 1		Experiment 2		Experiment 3a		Experiment 3b	
	Temp. °C.	Contraction percent	Temp. °C.	Contraction percent	Temp. °C.	Contraction percent	Temp. °C.	Contraction percent
1	235	53	234	55	235	54		
2	235	50	234	53	235	54	225	56
3			234	51			225	56
4			234	50			225	56
5			235	49	235	54	225	54
6	234	45	236	50	235	54	225	54
8			235	49	235	56	225	54
9			234	40	235	55	225	50
10					235	54	225	46
20					235	54		
30					235	52		
40					235	52		
50					235	50		
60					235	50		

Table XXVI shows that experiment 3a gives the best results. In this case, the kieselguhr was added to the catalyst after alkalization. The contraction remained above 50 percent for 2 months of operation (without regeneration). For 225°C. (experiment 3b), the contraction fell below 50 percent after 10 days of operation.

Table XXVII gives a composition of the reaction gas at a contraction of 53 to 54 percent. Experiment 3a gives the maximum amounts of gaseous hydrocarbons. The catalysts for which the kieselguhr had an opportunity to be saturated with alkali during the process of precipitation (experiments 1 and 2), as well as experiments 3b carried out at 225°C. yielded essentially less saturated gaseous hydrocarbons for the same contraction. (A normal iron catalyst under analogous conditions gave a reaction gas containing 6 to 8 percent gaseous hydrocarbons.)

Table XXVII  
Analyses of the Reaction Gases  
From the Kieselguhr Catalysts at a Contraction of 53-54 Percent

	CO <sub>2</sub>	sKW	O <sub>2</sub>	CO	H <sub>2</sub>	KW	CZ	N <sub>2</sub>
Experiment 1	59.1	3.5	0.2	6.3	12.9	4.7	1.8	13.3
Experiment 2	59.2	4.4	0.1	5.4	11.1	6.1	1.7	12.7
Experiment 3a	64.9	3.0	0.1	1.3	6.0	11.4	1.9	13.4
Experiment 3b	55.9	2.6	0.2	8.8	9.9	7.7	2.1	14.2

A yield determination made for experiment 3a disclosed 87 g. of solid and liquid hydrocarbons and 36 g. of gasol hydrocarbons per normal cubic meter of ideal gas.

At the beginning, the liquid hydrocarbons contained 3 percent solid paraffin, 12 percent after 4 weeks, and 24 percent after 6 weeks. (This catalyst was alkalinized with one percent potassium carbonate, the formation of paraffin consequently is essentially smaller than in the case of the corresponding kieselguhr-free iron catalysts.)

The products were colorless. The composition will be disclosed at another place.

A catalyst corresponding to that used in experiment 3b was charged into a vertical apparatus composed of 18 tubes (18 catalyst charges, 10 g. of iron par tube). After the catalyst was inducted with CO at 1/10 atmosphere and 325°C., it was switched over to the synthesis at 15 atmospheres and 225°C. using a CO-rich gas. Within 6 days, the contraction decreased from 54 to 50 percent. After this, the catalyst was treated with H<sub>2</sub> at the same temperature. On the eighth day, the contraction was 52 percent, on the tenth day, it was 47 percent. After a second H<sub>2</sub> treatment, the synthesis was carried out at 230°C. and then at 232°C. On the 17th day, the contraction had decreased to 48 percent again. After another H<sub>2</sub> treatment, the experiment was conducted for another week at 236°C., etc. (see Figure 11).

When the results of the experiments carried out in horizontal respectively slightly inclined tubes (experiment 3b, Table XXVI) were compared with experiments carried out in a vertical apparatus, it was observed that the latter showed a less uniform course. Anyhow, it was possible to maintain a contraction of approximately 50 percent by treating several times with H<sub>2</sub>. (Details on the apparatus used in these experiments are contained in Part IV).

### Part III The Reaction Products

In the middle-pressure synthesis with iron catalysts, paraffin and olefin hydrocarbons are formed showing great variation in molecular size. They vary from methane and low gaseous hydrocarbons up to high molecular solid paraffins. In Table XXVIII the yields of solid paraffins, liquid products, and gasol hydrocarbons of some experiments carried out under different conditions are summarized.

Table XXVIII  
Solid, Liquid, and Gasol Hydrocarbons at Various Reaction Conditions

Catalyst	K <sub>2</sub> CO <sub>3</sub> percent	Synthesis	Paraffin percent	Liquid hydrocarbons percent	Gasol percent
		Temp., °C.			
Fe(Na <sub>2</sub> CO <sub>3</sub> prec.)	1/4	270	3	65	32
Fe - Cu	1/8	260	4	76	20
Fe-Kieselguhr	1	235	8	63	29
Fe (NH <sub>3</sub> prec.)	0	235	12	67	21
Fe-Normal catalyst	1/4	235	26	56	18
Fe(Na <sub>2</sub> CO <sub>3</sub> prec.)	1	235	42	47	11
Fe " "	5	235	46	44	10

As the table shows, the amount of paraffins formed varies between 3 to 46 percent (referred to total yield). If this is referred to liquid and solid products alone, it corresponds to 5 to 51 percent. The portion of liquid hydrocarbons produced varied between 44 and 76 percent of the total reaction products. Between 10 and 32 percent of gasol referred to total yield was obtained. The catalysts which were precipitated with soda and those precipitated with ammonia gave the best results. When the synthesis temperature was 235°C, it can generally be observed that lowering the reaction temperature and increasing the alkali contents causes a high molecular weight hydrocarbon to be formed. The iron-kieselguhr catalyst forms an exception.

The liquid products obtained not only showed a different boiling range for the various reaction conditions, but also contained a different percentage of unsaturated hydrocarbons.

As a byproduct, the synthesis furnishes an exceedingly high melting paraffin. Furthermore, oxygen containing organic compounds similar to those of Fischer's Synthol (18) were formed.

Finally, the iron catalysts may be used under certain conditions for the production of city gas,

The middle-pressure synthesis carried out with iron catalysts offers a possibility to control the formation of the products of reaction by imposing specific conditions upon the course of the reaction. In the discussion of the reaction products, only approximate limits about the formation of the various hydrocarbons can be set. This is on account of the many different variables which can occur in the synthesis.

#### A. Liquid Hydrocarbons.

The crude liquid total product generally is not colorless but is somewhat yellowish. After distillation, one obtains water-clear colorless benzine. The small quantities of yellow oil remain as a residue. The benzine is stable, it remains colorless after months of storage. The percentage of liquid hydrocarbons boiling off below 180°C. is greatly dependent in the experimental conditions

and can vary between wide limits. Thus, \_\_\_\_\_ percent boiled off below 180°C. from liquid hydrocarbons produced with a normal catalyst containing 1/4 percent  $K_2CO_3$  and a reaction temperature of 235°C. When a catalyst containing one percent  $K_2CO_3$  was used (at 235°C.), \_\_\_\_\_ percent boiled off below 180°C. When a catalyst was used which was precipitated with ammonia, and contained 1/4 percent  $K_2CO_3$  at 250°C., 55 percent distilled over below 180°C. When an iron-copper catalyst was used at a reaction temperature of 260°C., 80 percent came over below 180°C.

Figure 12, shows a boiling point curve of the products obtained with the normal iron catalyst at 235°C.

Figure 13, shows an Enxler-Distillation curve for a benzene synthesis at a reaction temperature of 250°C. and boiling up to 180°C. 50 percent of this benzene boiled below 88°C.; 60 percent below 100°C. The boiling point characteristics of the benzene can be changed drastically by changing the working conditions during the synthesis. Thus, at 235°C., and used the normal iron catalyst, the benzene was produced boiling up to 180°C. Of this 50 percent boiled below \_\_\_\_\_ °C. For another iron catalyst and a working temperature of 260°C., a benzene boiling below 180°C. was produced of which 50 percent could be driven over below 73°C. Table XXIX shows the density, olefin contents, boiling point characteristics, and octane number of some benzenes produced with the iron catalyst.

Table XXIX  
Properties of Benzenes Produced with Iron Catalysts

No.	Washed with NaOH	$d_{15}$	Olefin	Boiling Point Analyses				P37.8°	OZ
				Starting	10%	50%	90%		
1	Yes	0.696	64	30°	46°	88°	145°	0.54	61
2	Yes	0.678	65	30°	38°	73°	145°		62
3	No	0.698	38					0.48	63

Test No. 1, in Table XXIX, refers to a catalyst precipitated with ammonia, that of test No. 2, refers to an iron-copper catalyst, and test No. 3, to an iron-kieselguhr catalyst.

The density of the benzenes boiling below 180°C. was somewhat lower than 0.7. With phosphorous pentoxide-sulphuric acid, 64 respectively 65 respectively 38 volume percent of olefins could be taken out. The octane number of the 3 stabilized benzenes was found to be 61-63 according to the motor method. Possibilities of improving the anti-knock properties of the benzene are discussed in another section dealing with the development of the primary products.

If one compares the portions which have been removed from the benzene by phosphorous pentoxide-sulphuric acid with the octane numbers, then one can observe that these do not depend exclusively on the olefin contents.

The synthol products contained in the reaction products from the iron middle-pressure synthesis are of importance. The quantity and nature of these compounds obtained varies considerably with the working conditions also. Table XXX shows acid-ester-saponification-and hydroxyl numbers of some of the synthesis products.

Table XXX  
Oxygen-Containing Constituents of the Liquid Hydrocarbons

Catalyst	Boiling range °C.	Acid number	Ester number	Saponification number	Hydroxyl group number
Fe 1/4% K <sub>2</sub> CO <sub>3</sub>	30 - 180				
Fe " "	under 180	0.2	0.2	0.5	2.3
Fe 1% K <sub>2</sub> CO <sub>3</sub>	under 180	1.8	8.1	9.9	7.0
Fe-Kieselguhr 1% K <sub>2</sub> CO <sub>3</sub>	30 - 180	1.4	15.0	16.4	
Fe-Kieselguhr 1% K <sub>2</sub> CO <sub>3</sub>	under 180	0.1	2.0	2.1	

The table shows that the synthesis in addition to small quantities of acid, produces larger quantities of esters and alcohols. These compounds are not only lower weight constituents, but they also contain higher molecular weight components (water and alcohols). The formation of these products is greatly favored by the alkalization of the iron catalysts.

When the products obtained from the iron-kieselguhr catalyst were washed with a 30 percent calcium chloride solution, 2.5 percent was extracted. When another washing was carried out with sodium hydroxide, another .8 percent went into the aqueous solution.

Table XXXI shows results of an elementary analysis of the reaction products, boiling below 180°C., obtained from the three different iron catalysts. The numbers refer to unwashed products. They show that the lowest boiling benzenes have a higher oxygen content than the total products.

Table XXXI  
Elementary Analysis of the Synthesis Products

	Total product			Benzene		
	C	H	O	C	H	O
Fe-Normal Catalyst						
Fe - Cu	84.60	15.16	0.24	83.94	14.97	1.09
Fe-Kieselguhr						

### B. Paraffin

The solid and liquid reaction products contain (according to the Dutanon-method) approximately 5 to 50 percent paraffins. When a H<sub>2</sub>-rich synthesis gas and an alkali-deficient catalyst is used, the paraffin obtained is white to slightly yellowish. When a CO-rich gas is used and catalysts with one or more percent potassium carbonate, the paraffins are yellow to yellowish-brown. The coloring substances are believed due to iron respectively iron salts. Generally however, small quantities of higher boiling oils are responsible for the discoloration. These oils may be extracted or may be made colorless by hydrogenation.



The melting points of the paraffins extend over the entire known melting point region of the known paraffins. The total product especially contains high melting constituents, so that it melts to a clear liquid at comparatively high temperatures. Meniscus formation was observed in the melting point tubes at 80°C. for a paraffin freed of liquid hydrocarbons by the Eutanon method produced through a catalyst with 1/4 percent  $K_2CO_3$ . When a catalyst containing one percent  $K_2CO_3$  was used, the meniscus formation was observed at 104°C. When an iron catalyst was used, which contained one percent  $K_2CO_3$ , a paraffin was obtained which was 50 percent soluble in boiling ether. The product re-precipitated from this solution with methyl alcohol showed a final melting point of 66 to 70 percent. 41 percent was insoluble in ether (24 hours extraction in the Soxhlet). It was, however, soluble in boiling hexane. They had a final melting point between 90 to 104°C. The rest (9 percent) which was insoluble in hexane had a melting point of 122°C.

When the iron catalyst was extracted, a so-called paraffin was obtained which after fractional extraction was insoluble in boiling benzol, but soluble in boiling toluol. It contained constituents melting at about 126°C.

### 3. Gasol.

From Table XXVIII, it may be seen that 10 to 30 percent of the reaction products of the synthesis consist of gasol hydrocarbons ( $C_3 + C_4$ ). In addition to that, the iron middle pressure synthesis yields ethylene too. Figures 14 and 15 show the results of some low temperature distillations carried out at the Institute by F. Weinrotter. In order to obtain the gaseous reaction products, the whole end-gas of an experiment (Fe with 1 percent  $K_2CO_3$ ) was conducted through a cooler cooled with liquid air. All of the gaseous hydrocarbons and lower benzenes with the exception of the methane were retained in the receiver. The  $C_2$  to  $C_4$  fraction of a partial aliquot of the gases distilled over, up to room temperature corresponds to Figure 14 (Distillation 1). The benzene remaining back in the receiver still contained considerable quantities of  $C_4$  hydrocarbons. They are removed by distillation. Figure 15 (Distillation 2) refers to the  $C_4$  fraction. The presence of iso-butylene was not proven in both distillations.

Table XXXII brings a summary of the results of the low temperature distillations. The figures referring to the first distillation are calculated on the basis of the gasol quantities referring to the second distillation. The portion of unsaturated hydrocarbons of the various fractions was determined with mercury nitrate.

Table XXXII  
 $C_2$  to  $C_4$  Hydrocarbons Formed During the Synthesis

	First distillation ccm	Second distillation ccm	Weight percent of $C_2 +$ gasol- fraction
Ethylene	2360		15.8
Ethane	1830		13.1
Propylene	3480		34.9
Propane	1130		11.9
Butylene	1010	333	17.9
Butane	370	87	6.4

The C<sub>2</sub> fraction contained 55 weight percent of ethylene, 74 percent of the total gasol fraction consisted of unsaturated hydrocarbons. For this experiment, 5.2 grams per normal cubic meter of ethylene, 11.1 of propylene, and 6.0 g. per normal cubic meter of butylene were obtained.

Quantity and composition of the gaseous hydrocarbons depends on the nature of the catalyst and the reaction temperature. Table XXXIII shows yields of gasol hydrocarbons with their respective contents of unsaturated constituents for various synthesis conditions. All the experiments refer to a synthesis gas composed of 3CO + 2H<sub>2</sub> and synthesis pressure of 15 atmospheres.

~~Table XXXIII~~  
Yields of Gasol Hydrocarbons With Different Catalysts

Catalyst	Temp., °C.	Grams of gasol per normal cubic meter of ideal gas	Percent of gasol unsaturated hydrocarbons
Fe, NH <sub>3</sub> precipitated, 0% K <sub>2</sub> CO <sub>3</sub>	235	30	70
Fe, Na <sub>2</sub> CO <sub>3</sub> precipitated 0% K <sub>2</sub> CO <sub>3</sub>	235	28	80
Fe, " " 1/4% "	235	26	76
Fe, " " 1% "	235	17	80
Fe, " " 1/4% "	270	46	47
Fe-Kieselguhr 1% K <sub>2</sub> CO <sub>3</sub>	235	36	35

For the iron catalysts which were precipitated with ammonia or soda, and for a synthesis temperature of 235°C., 20 to 30 g. per normal cubic meter of ideal gas of gasol hydrocarbons were obtained, which were 70 to 80 percent unsaturated. At higher reaction temperature, the quantity of gasol hydrocarbons formed increased. The hydrogenation of the hydrocarbons increased at the higher reaction temperature also with a result that at 270°C., reaction temperature, approximately 20 g. of unsaturated hydrocarbons were formed. The gasol hydrocarbons produced with iron-kieselguhr catalysts vary considerably from those produced with the kieselguhr-free catalyst in so far as the amount is concerned. Just as in the case of the benzene, here too, the kieselguhr catalyst produces a gasol which contains less unsaturated hydrocarbons.

#### D. Oxygen-containing Products.

##### 1. The Reaction Water.

With the iron-kieselguhr catalyst and the reaction temperature 235°C. (CO-rich gas, 15 atm.), approximately 13 g. per normal cubic meter of aqueous products were formed. They contained acids, aldehydes, and esters as well as alcohols. (Test for formic acid was negative, that for acetic acid, positive. Test with fuchsin sulphurous acid, positive. The presence of ester was demonstrated by saponification. Little methyl alcohol was found, ethyl alcohol was recognized but its boiling points, and the iodoform reaction.) The reaction water was subjected to a distillation through a micro column. Figure 16 shows the boiling point analysis of the constituents boiling below 90°C. (28 percent of the total reaction water).

\*The quantity of the gasol hydrocarbons produced during the synthesis may be increased. Research being conducted at present is concerned with that problem.

The boiling curve shows very distinctly the ethyl alcohol fraction. It corresponds to 7.5 percent of the total reaction water.

## 2. The Hydrocarbons.

Table XXI has shown that the reaction products boiling above as well as those boiling below 180°C. contain more or less synthol, depending on the working conditions. In addition to organic acids, esters and alcohols were detected. Investigations are in progress designed to disclose the nature of the higher alcohols and esters. The results of these investigations will be published separately.

In the following, a description is given of the products which can be extracted with a 30 percent calcium chloride solution from a benzene boiling up to 180°C. (5.5 percent of the benzene). Figure 17 gives the results of a distillation (corresponding to Figure 16) of the aqueous solution distilled off up to 95°C.

## E. City Gas.

The question has been asked repeatedly whether it is possible to use coke for the production of city gas. Since water-gas has too low a heating value, it would be necessary to increase this heating value by partially converting the water-gas into hydrocarbons. With the aid of nickel or cobalt catalysts, this is possible without any difficulties. It was investigated whether the production of such a gas could also be accomplished over the iron middle-pressure synthesis. With a normal pressure synthesis and using iron catalysts, the gas which was produced did not possess the desired heating value.

A usable city gas should fulfill the following requirements and possess the following properties:

### I. Combustion properties.

1. Heating value (higher heating value) is equal to 4,200 to 4,600 kilogram calories per normal cubic meter.
2. Density is equal to 0.4 to 0.5 as referred to air = 1.
3. Gas pressure, higher than 60 mm.
4. Flash-point, 60 to 100.

### II. Purity.

1. Oxygen less than 0.5 percent.
2. Hydrogen-sulfide less than 2 g. per 100 m<sup>3</sup>
3. Ammonia, less than 0.3 g. per 100 m<sup>3</sup>
4. Naphthalene  $\frac{5 \text{ to } 10}{p}$  g. per 100 m<sup>3</sup>
5. Organic sulfur, less than 25 g. per 100 m<sup>3</sup>, hydrogen cyanide less than 15 g. per 100 m<sup>3</sup>, nitrogen oxides, 0.2 cc. per m<sup>3</sup>.
6. Practically free of tar.

### III. Final purification.

By keeping the hydrogen contents low by a rigorous process of purification, the corrosive properties of the gas can be materially decreased.

Aspects I to III are no standard requirements. However, they merely are general requirements which should be fulfilled from the viewpoint of the public interest. These directions no longer contain the earlier limits of the contents of inert gases.

Brückner and Weissbach (20) have proposed to mix propane into the water-gas. They have shown that propane-water-gas mixtures with a propane content of between 6 to 7-1/2 percent have the desired heating value of between 4,200 to 4,500 kilogram calories per normal cubic meter. Such a gas, however, has too high a density (0.61 to 0.63) and too low a flashpoint (40 to 46).

If one mixes all the gaseous hydrocarbons with the CO<sub>2</sub>-free tail-gas from the Fischer synthesis, however, the resulting gas then consists chiefly of C<sub>1</sub> to C<sub>4</sub> hydrocarbons with additional water-gas, and a city gas may be produced which comes close to the requirements for such a gas.

A city gas may also be produced from a CO-H<sub>2</sub> mixture (1:3) when one uses an iron catalyst at pressures of around 10 atmospheres.

In order to avoid the formation of higher hydrocarbons, an iron catalyst was used which was precipitated with ammonia and was alkali-free. Induction and gas rate corresponded to the usual conditions. The temperature at the beginning of the synthesis was 235°C., after one month, it was 250°C., after 2 months, 265°C., and after 3 months, 270°C. For the whole time of operation, a gas of constant composition was obtained. Table XXXIV gives data on the usual and final gas of this synthesis.

Table XXXIV

Production of a Gas With the Properties Required by a City Gas

Catalyst: Alkali-free iron catalyst.  
Synthesis Gas: CO to H<sub>2</sub> is equal to 1:3.  
Pressure: 10 atmospheres  
Temperature: 235 to 270°C.

	CO <sub>2</sub>	sKW	O <sub>2</sub>	CO	H <sub>2</sub>	KW	CZ	N <sub>2</sub>
Initial gas	0.0	0.0	0.0	23.5	73.5	0.0	-	3.0
Final gas	10.9	0.2	0.1	1.0	69.8	13.1	1.8	4.9

This reaction gas has a heating value of 4154 kilogram calories per normal cubic meter (Junkers-Kalorimeter), a density of 0.4 to 5, and a flashpoint of 70 to 71. When a more N<sub>2</sub>-deficient gas is used, the heating value may be increased by 100 kilogram calories.

The gas, therefore, corresponds to all requirements.

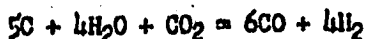
According to our experiences, the iron-kieselguhr catalyst is best suited for the production of a city gas.

Part IV  
General Problems

A. Synthesis Gas Production.

We found that a synthesis gas which contains CO and H<sub>2</sub> in the ratio, 3:2, gives the best results during the middle-pressure synthesis on iron catalysts.

For our experiment, we generated such a gas in a normal water-gas generator (21) which we had here at the Institute. We passed a mixture of steam and CO<sub>2</sub> over burning coke. Such a procedure we believe could also be recommended for the technical scale, since during the synthesis with the iron catalyst, much more CO<sub>2</sub> is formed than is required for the production of the synthesis gas. Use of one m<sup>3</sup> of synthesis gas of composition 3CO + 2H<sub>2</sub>, gives approximately 250 liters of CO<sub>2</sub> at normal conversion. This occurs according to the equation:



According to this equation, only 100 liters of CO<sub>2</sub> are required per cubic meter of CO-rich gas. Therefore, it would only be necessary to wash the CO<sub>2</sub> out of the end-gas partially, and lead the end-gas back into the gas generator.

The separation of the CO<sub>2</sub> may also be accomplished by activated charcoal. Herbert and Huping (22) have recorded recently on such a procedure, namely for the separation of CO<sub>2</sub> from gasol. When a cobalt catalyst is used in the Fischer-synthesis, practically no CO<sub>2</sub> is produced. However, if one uses a synthesis gas which was obtained from water-gas by partial conversion, this synthesis gas is rich in CO<sub>2</sub>. In this case, one obtains approximately 35 to 45 percent CO<sub>2</sub>. If the activated charcoal is subjected to a steaming operation, the various gases are driven off separately, and it is possible to separate methane and CO<sub>2</sub> very well from the C<sub>3</sub> and C<sub>4</sub> hydrocarbons.

If one would charge the whole end-gas from the synthesis into the gas generator (CO<sub>2</sub>, methane, unreacted CO, and H<sub>2</sub>, etc.), one would approximate the theoretical yield of 208 g. of hydrocarbons per normal cubic meter of ideal gas.

In the following, the reactions which occur in the water-gas production, mixed gas production (CO-H<sub>2</sub> = 1:2), and CO-rich gas (CO-H<sub>2</sub> = 3:2) production are compared one with another.

1. Water gas.  $C + H_2O = CO + H_2$  for every cubic meter of water-gas; 267 g. of carbon, and 500 liters of steam are used. 650 kilogram calories are required.

2. H<sub>2</sub>-rich mixed gas.  $3C + 4H_2O = 2CO + 4H_2 + CO_2$ . The equation represents the overall reaction for the primary production of water-gas and a partial conversion of this to CO<sub>2</sub> and H<sub>2</sub>. Theoretically, one requires 269 g. of carbon per cubic meter of gas, 670 liters of steam, and 570 kilogram calories.

3. CO-rich synthesis gas.  $5C + 4H_2O + CO_2 = 6CO + 4H_2$ . For producing one cubic meter of such a gas, 268 g. of carbon, 400 liters of steam, 100 liters of CO<sub>2</sub>, and 690 kilogram calories are required. For the production of all of these three gases, one requires the same amount of carbon per cubic meter of gas.

When a Dellwig-Fleischer-Generator is used, one requires 550 g. of coke per cubic meter of water-gas, that is, twice as much as is theoretically necessary. The temperature and heat requirements for the production of the CO-rich gases are approximately the same as that for the water-gas production.

We were able to produce 100 m<sup>3</sup> of CO-rich gas per hour in our water-gas generator for several years without interruptions. The composition of the synthesis gas, for example, was as follows: 2% CO<sub>2</sub>, 55% CO, 37% H<sub>2</sub>, and 6% N<sub>2</sub>. In several instances, in order to determine the expressed contraction more accurately, a little more nitrogen than given above was added to the synthesis gas.

The purification of the gases was carried out in the same manner as with H<sub>2</sub>-rich gas.

Another way for producing the desired synthesis gas, consists in the gasification of coke or coal with the addition of oxygen. It is not necessary to discuss this here.

#### B. Space-time Yields and Apparatus Details.

For most of the experiments in the laboratory, we used reaction tubes of 12 to 13 mm. I.D. The catalyst was distributed evenly over a length of 30 m<sup>3</sup> within the tube. A normal catalyst charge contained 10 g. of iron. This corresponds to 15 to 16 m<sup>3</sup> of freshly-prepared normal catalyst. The free space in the tube amounted to 35 m<sup>3</sup> (in the reaction zone). Consequently, the catalyst filled approximately half of the reaction space. The upper half of the tube remained empty: Drawing 1 in Figure 19 shows the relationships schematically.

If various synthesis gas quantities are thus passed over the catalyst under the conditions of the synthesis, the reaction temperature has to be kept higher if it is desired to convert more gas per unit of time. According to Figure 20, contractions of around 50 percent were obtained at an hourly gas rate of 1.7 liters (referred to one atmosphere pressure) at a temperature of 220°C. When 4.1 liters per hour of gas were used, the temperature was 233°C. At 8 liters per hour, it was 250°C., and it was 275°C. for 16 liters per hour of gas. In another experiment, 4 liters per hour of gas were passed over at 235°C., and a contraction of 15 percent was obtained, at 280°C. and 20 liters per hour, the same contraction was reached.

With respect to the lifetime of the catalyst, the magnitude of the yields of higher hydrocarbons and for other technical reasons, it is advantageous to carry the synthesis through at as low a temperature as possible for as long a time as possible. With respect to the space-time yields, however, it appears more favorable to work at higher temperatures and higher gas rates. We found that at gas rates between 10 and 20 liters per hour per 10 g. of iron, serious difficulties arise when the reaction is carried out on the large scale. The difficulties encountered are chiefly due to the fact that the heat of reaction cannot be carried away fast enough. This causes the catalyst to overheat and free carbon is formed which rapidly causes a decrease in the catalyst activity. For this reason we chose to work at a flow velocity of 4 liters of synthesis gas per hour per 10 g. of iron. Drawing 1 in Figure 19 shows the arrangement of the catalyst in the tubes, and it is to be observed that it was possible to operate for one to 2 years with the same catalyst without regeneration, and a satisfactory degree of conversion was always obtained.

For the iron middle-pressure synthesis, we have discovered also that with increased pressure, the gas rate per unit weight of catalyst may not be increased. We have found that processes occurring on the surface of the catalyst are controlling the reaction velocity (transportation of the reaction products away from the catalyst, respectively carrying the reactants to the catalyst surface). These processes are not accelerated by increasing the pressure.

If the reaction tube is arranged at a vertical position (Figure 19, Schematic Drawing #2), the catalyst layer length only amounts to 10 to 15 cm., instead of 30 cm. as compared to a horizontal arrangement. The contact time of the gases going through the catalyst is much shorter therefore when the tube is arranged in a vertical position. The empty space through which the gas flows is approximately 4 times as large in the case of a horizontal tube than it is in a vertical tube. By taking into consideration the relationship between rate of gas flow and temperature (shown in Figure 20), it may be understood that the same favorable results are not obtained when the work is carried out with an apparatus arranged according to Drawing #2. In addition to that, we found that the catalyst takes up considerable quantities of the reaction products and large quantities of carbon are deposited on the catalyst. This causes the percentage voids in the catalyst to decrease with a consequent shortening of the contact time between the gas and the catalyst.

Since on the large scale, one would be chiefly interested in working with vertical reaction tubes, we have attempted to find a solution to the problem according to the Schematic Drawings #3 and #4. The dotted lines represent perforated plates. In case 3, a perforated plate divides the reaction tube into two equal sections. In case 4, a perforated reaction tube is concentrically arranged within the larger reaction tube. The catalyst is distributed in the annulus between the two tubes. In both cases, the catalyst layer length and the percentage free-space correspond to the conditions of case 1. The results were similar for case 1, also. The perforated plates did not cause a noticeable decrease in conversions (the induction of the catalyst had been carried out in a separate apparatus, and the catalyst was transferred in an atmosphere of  $\text{CO}_2$ ). After several weeks of operation, the experiments carried out according to cases 3 and 4 showed a decline in the conversion as compared to the procedure of Drawing #1. The reason for this, we believe, might be that the catalyst in case 1 had the possibility to expand during the synthesis, whereas in cases 3 and 4, this expansion occurred mainly at the expense of the internal voids between the catalyst particles.

The Schematic Drawing 5 of Figure 9, shows the arrangement when a catalyst was used the structure of which was loosened up by the addition of kieselguhr. When the normal quantity of iron, namely 10 g., is diluted with 4 g. of kieselguhr, then this iron-kieselguhr catalyst fills a 12 to 13 mm. I.D. reaction tube up to a length of 30 cm. The percentage free-space is smaller than in case 1, in amount approximately equal to the quantities of kieselguhr used, on the other hand, the loosening of the catalyst by the kieselguhr causes a considerable improvement in its activity. A small percentage expansion of the iron on account of the deposition of carbon does not produce as unfavorable a result in case 5, as it has caused in cases 2 to 4. An experiment which has been under investigation for several weeks gives a satisfactory conversion (Figure 11).

We want to mention here that the disturbing influence of the volume increase of the catalyst observed in experiments 2 to 4 was not observed in all cases. Thus a catalyst which was precipitated by ammonia and inducted with mixed gas at one atmosphere yielded good conversions for three months in vertical position at temperatures of between 240 and 260°C. Experiments to clarify the situation are still in progress.

It can be mentioned here that the space-time yields observed with the iron-kieselguhr catalysts approximately correspond to that of the cobalt catalysts. If the iron-kieselguhr catalysts should be used on an industrial scale, similar pieces of apparatus as are used in the case of cobalt should be satisfactory for the iron-kieselguhr catalysts. In the laboratory, we worked with water-cooled tubes. The steam pressures of course are higher corresponding to the increased reaction temperatures. They vary between 30 to 50 atmospheres, all according to the duration of the test.

### C. Pelleting of the Catalyst.

The catalyst described earlier and produced from ferric nitrate solutions with sodium carbonate as well as the iron catalysts which were precipitated with ammonia (also ferri catalysts) were solid after having been dried and broke with a glassy fracture. Their rigidity should be sufficient for industrial application.

Nevertheless experiments were carried out the object of which was to grind the iron catalysts and put them into shape of pellets. The blackish-brown color of the granular original catalyst changes over to reddish-brown when it is ground. The pellets which are formed from the powder retain this brown color. We have discovered that the pellets not always retain the original activity of the catalyst. It might be that the cause for this activity decrease has something to do with the overheating through which the catalyst goes when it is pressed into pellets.

We were in a position to produce iron catalyst pellets of very good activity and high lifetime when we mixed paraffin to the catalyst powder prior to pelleting. For this we used synthetic paraffin which had been made into fine scales.

Table XXXV, Experiment 1, gives the results of an experiment conducted with pellets. They contained 25 percent paraffin as referred to the iron. Experiment 2 brings a comparative experiment where no paraffin was added. The paraffin does influence the process of induction and may be regained practically all. The pellets retained their shape even after a long time of the synthesis.

At the beginning of the reaction period, the conversion obtained was practically the same in both cases (this is also brought out in the table with the respective gas analyses). After several weeks of operation, however, the temperature had to be raised more rapidly for case 2 where no paraffin had been used in the preparation of the catalyst. The activity of the catalyst of Experiment 1, after 50 days of operation corresponds to the activity of the catalyst of Experiment 2 after 25 days of operation.

Even with the addition of only 5 to 10 percent of paraffin, a favorable result upon the activity of the pelleted catalyst was observed.



Table XXXV  
Experiments with a Catalyst Which was Pelleted

Days of operation	Experiment 1		Experiment 2	
	Temp., °C.	Contraction percent	Temp., °C.	Contraction percent
1	235	53	234	55
2	235	54	235	56
10	235	51	236	54
16	234	53	236	50
20	235	52	235	49
25	235	47	240	48
31	235	46	246	47
47	240	49		
60	240	45		

	CO <sub>2</sub>	sKW	O <sub>2</sub>	CO	H <sub>2</sub>	KW	CZ	N <sub>2</sub>
Experiment 1-Initial Gas:	2.1	0.0	0.2	53.8	35.7	0.2	1.0	8.0
Experiment 1-Final Gas:	59.7	3.9	0.1	1.1	10.2	7.6	1.9	17.4
Experiment 2-Initial Gas:	2.1	0.0	0.1	53.7	38.0	0.4	1.0	5.7
Experiment 2-Final Gas:	61.5	3.5	0.0	1.8	13.2	7.2	1.8	13.0

D. Some Details on the Further Processing of the Primary Products.

In the middle-pressure synthesis with iron catalysts, various types of reaction products are obtained as will be shown in another chapter. They may be utilized in a similar manner as the products obtained during the synthesis with cobalt catalysts. It is superfluous here to mention the various usages of these products. In some points, however, there are some fundamental differences between the products of the iron synthesis, and the cobalt synthesis. First, there is the appearance of synthol-like byproducts as for instance various alcohols, and secondly, there is also the appearance of more unsaturated hydrocarbons. The oxygen-containing as well as the unsaturated compounds give the iron benzene higher anti-knock properties. These compounds have no tendency toward resin formation. The benzene which is produced with iron catalysts remains entirely colorless and water-clear after months of storage.

The middle-pressure synthesis with the iron catalyst gives a greater amount of unsaturated gasol hydrocarbons. These may be polymerized and form liquid hydrocarbons of high octane numbers. Therefore, the synthesis with iron catalysts seems to be especially adapted for the production of high quality benzene.

The catalytic polymerization of olefin hydrocarbons has been investigated by Ipatieff and co-workers (23) of the Universal Oil Products Co. We carried out some similar investigations which had to do with synthesis and polymerization taking place concurrently.

The catalyst which we used consisted of  $\text{Cd}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{PO}_4$ . As a carrier we used cadmium phosphate  $\text{Cd}_3(\text{PO}_4)_2$  which was produced from cadmium nitrate solutions with a calculated quantity of  $\text{Na}_2\text{HPO}_4$  and  $\text{NaOH}$ . The precipitation was carried out at the boiling point. It was washed with hot water and 98 percent phosphoric acid was added, evaporated, dried, and pelleted.

When gasol containing 35 to 40 percent of unsaturated hydrocarbons was passed over this catalyst, (one liter of gaseous gasol per hour per 10 g. of catalyst) at a pressure of 7 atmospheres and 140°C., 40 percent of the unsaturated hydrocarbons were converted, at 160°C., 60 percent, and at 180°C., 70-80 percent was converted. A polymerized benzene was obtained which split off 10 to 20 percent of the compounds boiling above 180-200°C. The residue was hydrogenated and had an octane number of 97 to 99. Next we carried out a series of experiments where we passed the total reaction gas from the iron middle-pressure synthesis at the synthesis pressure over the phosphoric acid catalyst (after precipitation of the condensable products at room temperature). Approximately the same catalyst volumes were used both in the synthesis and the polymerization. The synthesis was in progress already for two months before we started polymerizing. We used an iron catalyst precipitated with ammonia and containing 1/4 percent  $K_2CO_3$ . It had been inducted with mixed gas at atmospheric pressure. The yields of solid, liquid, and gasol hydrocarbons amounted to 140 g. per normal cubic meter of ideal gas. Table XXXVI shows some analyses of the reaction gases after the synthesis (a). Under (b) analyses of the reaction gases after the polymerization are given. The series of experiments was carried out at 15 atmospheres. The temperature and the syntheses were near 250°C., and for the polymerization near 200-220°C.

**Table XXXVI**  
Composition of Reaction Gases After Synthesis and Polymerization

	CO <sub>2</sub>	SKW	O <sub>2</sub>	CO	H <sub>2</sub>	KW	CZ	N <sub>2</sub>
a	58.3	3.7	0.2	8.7	12.8	6.7	1.6	9.6
b	59.8	1.1	0.2	9.1	13.0	6.2	1.7	10.6
a	62.9	3.7	0.2	7.0	10.1	7.7	1.8	8.4
b	64.8	1.2	0.3	7.1	10.0	7.6	1.8	9.0
a	58.4	4.2	0.0	10.9	5.1	6.4	1.7	15.0
b	60.6	1.2	0.4	10.8	5.0	6.0	1.8	16.0

The analyses show that 2/3 to 3/4 of the volume of the hydrocarbons disappeared during the polymerization.

Table XXXVII shows the quantities expressed as g. per cubic meter of ideal gas of solid, liquid, and gasol hydrocarbons formed during the synthesis with, and during the synthesis without polymerization. The first values correspond to approximately 3 weeks of operation. The latter correspond approximately to an additional week of operation, for which the polymerization step was omitted. The activated-carbon-benzene was only recovered once at the end of the conversion (that is, in between the synthesis and polymerization).

**Table XXXVII**  
Coupling of Synthesis and Polymerization

Polymerization	Yields, g./Normal cu. meter		Weight Percent of Liquid Hydrocarbons		
	Liquid hydrocarbons including paraffin	Gasol	Behind synthesis	Behind polymerisation	After activated-carbon-benzene
with	125	14	70	20	10
without	105	30	85	0	15

During the first period, 139 g. of liquid hydrocarbons (including paraffins) and gasol hydrocarbons were produced by the synthesis. During the second period (without polymerization) 135 g. per normal cubic meter were produced. The synthesis, therefore, furnished approximately 3 percent more products during the first period, the amount of liquid hydrocarbons formed, however, was 19 percent greater, mostly at the expense of the gasol converted by the polymerization. In the case of the polymerization experiment, 70 percent of the liquid products after the synthesis apparatus precipitated in the receivers working at room temperature. 20 percent of the products obtained therein originated from the polymerization apparatus and 10 percent consisted of activated-carbon-benzene. Some of the activated-carbon-benzene was not condensed in the first receiver and it was carried over the phosphoric acid catalyst. Consequently part of this activated-carbon-benzene polymerized and formed unsaturated benzene hydrocarbons. The gasol hydrocarbons during the polymerization decreased from 30 to 14 g. per normal cubic meter, the quantity of the activated-carbon-benzene only decreased from 16 to 13 g. per normal cubic meter. This may be explained by the fact that the  $C_4$  hydrocarbons polymerize most readily. Whereas, molecules having either more or less carbon atoms polymerize more slowly. Therefore, over the phosphoric acid, esters chiefly only the dimers of the olefins are obtained.

It is advantageous to remove the synthetic benzene from the reaction gas before the polymerization step. Therefore, it is possible to further process the reaction gas obtained through the middle-pressure synthesis with iron catalysts and obtain polymer benzene. This may be done in one step. It has to be found out in actual practice whether it is more economical to proceed in such a manner or whether it is better to carry out a separate polymerization of the various constituents.

Experiments which have used acid iron phosphate instead of cadmium phosphate have shown similar results.

The benzenes reported in Table XXXVII were stabilized and washed with sodium hydroxide and tested for the octane number in a motor. Approximately 2/3 of the total liquid products of this experiment boiled in a range of 30-180°C.

Table XXXVIII shows the properties of a benzene without following polymerization, of a benzene boiling up to 180°C. which was produced by a synthesis and polymerization, and of a benzene which boiled up to 150°C. with following polymerization. Of all three products, Table XXXVIII shows the density, the olefin content, the boiling point characteristics, and the vapor pressure at 37.8°C. as well as the octane number.

Table XXXVIII  
Influence of an Additional Polymerization Upon the  
Properties of Benzene Obtained in the Middle-Pressure Synthesis with Iron Catalysts

No.	$d_{15}^4$	Boiling Point Characteristics						
		Olefin percent	Beginning °C.	10% °C.	50% °C.	90% °C.	$p_{37.8^\circ}$	OZ
1	0.696	64	30	46	88	145	0.54	61
2	0.705	65	32	53	100	150	0.48	67
3	0.700	65	34	60	95	130	0.55	71

With the additional polymerization of the olefins (Table XXXVIII No. 1) an octane number of 61 was obtained, with polymerization, the octane number was 67 (No. 2). When the benzene was cut off at 150°C. (No. 3), then it had an octane number of 71.

When 0.7 cc. of lead tetra-ethyl was added to each liter of benzene (No. 2), the octane number could be raised to 79, when the same amount of lead tetra-ethyl was added to the benzene (No. 3), the octane number was 80.

### Conclusion

A survey was made of the work carried out on the middle-pressure synthesis with iron catalysts. First we discussed the precipitation, alkalization, and induction of the catalyst. Secondly, we were concerned with finding the most favorable synthesis conditions (gas composition, pressure, temperature, additions, regeneration, etc.). Thirdly, we discussed the reaction products and lastly, we discussed the general problem of synthesis gas production, apparatus constructions, pelleting of the catalyst, and further processing of the primary products.

The most important results of all the investigations are as follows:

1. Precipitation of the Iron Catalyst. Generally, the catalysts were precipitated by treating ferric nitrate solutions with sodium carbonate or ammonia. The ferric nitrate solutions were separated by dissolving technical iron in dilute nitric acid. The catalysts which were prepared from ferric solutions were superior to those prepared from ferrous solutions.

2. Alkalization of the Catalysts. The presence of alkali is not required for the synthesis, and is of no importance to the yield. The addition of alkali in increased quantities, however, causes the formation of higher molecular weight hydrocarbons. In the production of paraffins, therefore, the addition of alkali is important. In general, we used potassium carbonate. However, other alkali salts produced the same effects.

3. Induction of the Catalyst. In order to produce an active catalyst it is necessary to carry out an induction with CO-rich gases or better still with pure CO. The induction is carried out at pressures which are below those of the synthesis, as for example, atmospheric pressure. It was found, however, that reduced pressures are still more favorable.

The gas used for the induction, in order to get the best results, should be conducted over the catalyst surface at a high velocity and at temperatures of over 250°C., preferably between 300 and 350°C. This should be continued up to a point where the formed CO<sub>2</sub> reaches a more or less constant minimum value.

4. The Synthesis. The optimum ratio of CO-H<sub>2</sub> in the synthesis gas was found to be 3:2. The optimum synthesis pressure was found to be between 10 to 20 atmospheres. The optimum synthesis temperatures were found to be between 230 and 240°C. The catalysts are able to convert the synthesis gas at considerably

lower temperatures already from the very beginning. However, this is unfavorable for the lifetime of the catalyst. Neither are temperatures above 280°C. recommended for the beginning (on account of carbon formation).

The addition of kieselguhr (after alkalization) causes a considerable increase in catalyst activity.

Hydrogen treatment of the catalyst prior to the synthesis shows no advantages. However, a hydrogen treatment given repeatedly between syntheses causes a regeneration and reactivation of the iron catalyst.

5. Optimum Yields. The best solid, liquid, and gasol hydrocarbons were found to be somewhere near 150 g. per normal cubic meter of ideal gas. The longest lifetime was found with a catalyst which still gave 140 g. per normal cubic meter after 1-1/2 years of operation at a temperature of 260°C. without any kind of regeneration.

6. Reaction Products. The nature of the reaction product can be varied within wide limits according to the working conditions.

Five to 50 percent of the total solid and liquid hydrocarbons consisted of paraffins. Not only low-melting paraffins are obtained, but especially high-melting ones with a melting point above 125°C. were discovered.

The liquid reaction products differ from those of the cobalt catalysts in that they contain a greater percentage of unsaturated hydrocarbons as well as a greater quantity of synthol-like products. These, for example, contain alcohols and esters of various size molecular weight.

The octane number of the stabilized benzene cut off at 180°C. is 60 to 63. When the synthesis is coupled with the following polymerization, the unsaturated gasol hydrocarbons may be polymerized and the octane number may be raised by 10 points, and by the addition of 0.7 cc. of lead tetra-ethyl per liter of benzene, an additional increase of 10 points can be obtained.

Ten to 30 percent of the solid, liquid, and gasol hydrocarbons consist of gasol. Its contents of olefins amounts up to 80 percent. Increase in temperature or catalyst activity causes an increase in total gasol yield, also a lowering in their olefin content, however.

Furthermore, we found that the iron catalysts are capable of producing an acceptable city gas at 10 atmospheres working pressure.

7. Synthesis Gas Production. The production of a synthesis gas containing CO and H<sub>2</sub> in the ratio of 3:2 may be accomplished by the interaction of CO<sub>2</sub> and steam in the water-gas generator. The necessary CO<sub>2</sub> is furnished by the synthesis itself. Furthermore, it is possible to produce a useful synthesis gas by gasification of coke or coal with oxygen.

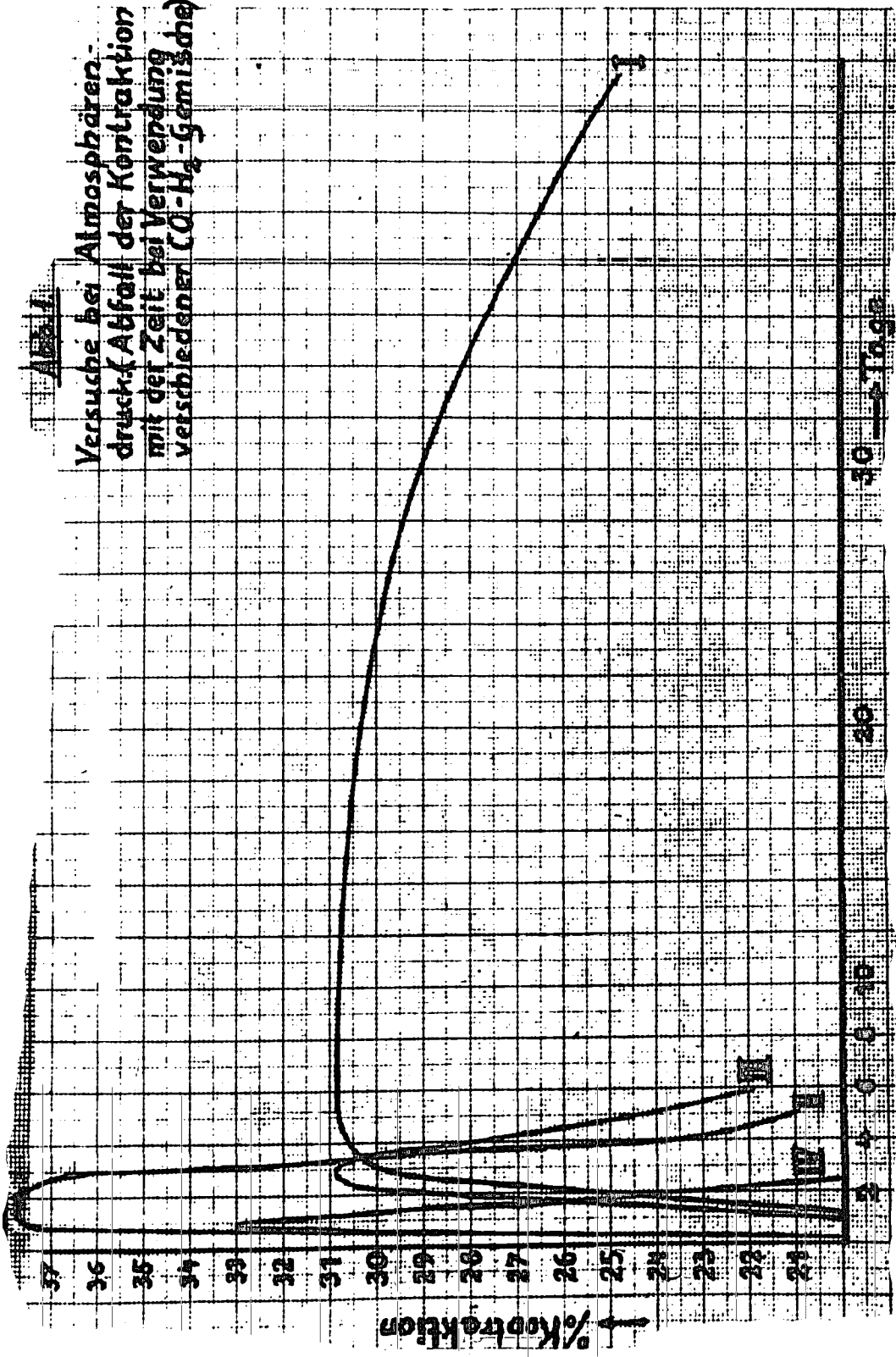
8. Apparatus Details. We discussed the relationships between apparatus details and the lifetime and effectiveness of the catalyst. The best results are obtained in horizontal respectively slightly inclined reaction tubes. If it is desired to cool the reaction vessels with water, they have to be strong enough to withstand a steam pressure of 30 to 50 atmospheres.

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Abb. 1

Versuche bei Atmosphären-  
druck. Abfall der Kontraktion  
mit der Zeit bei Verwendung  
verschiedener  $O_2-H_2$ -Gemische







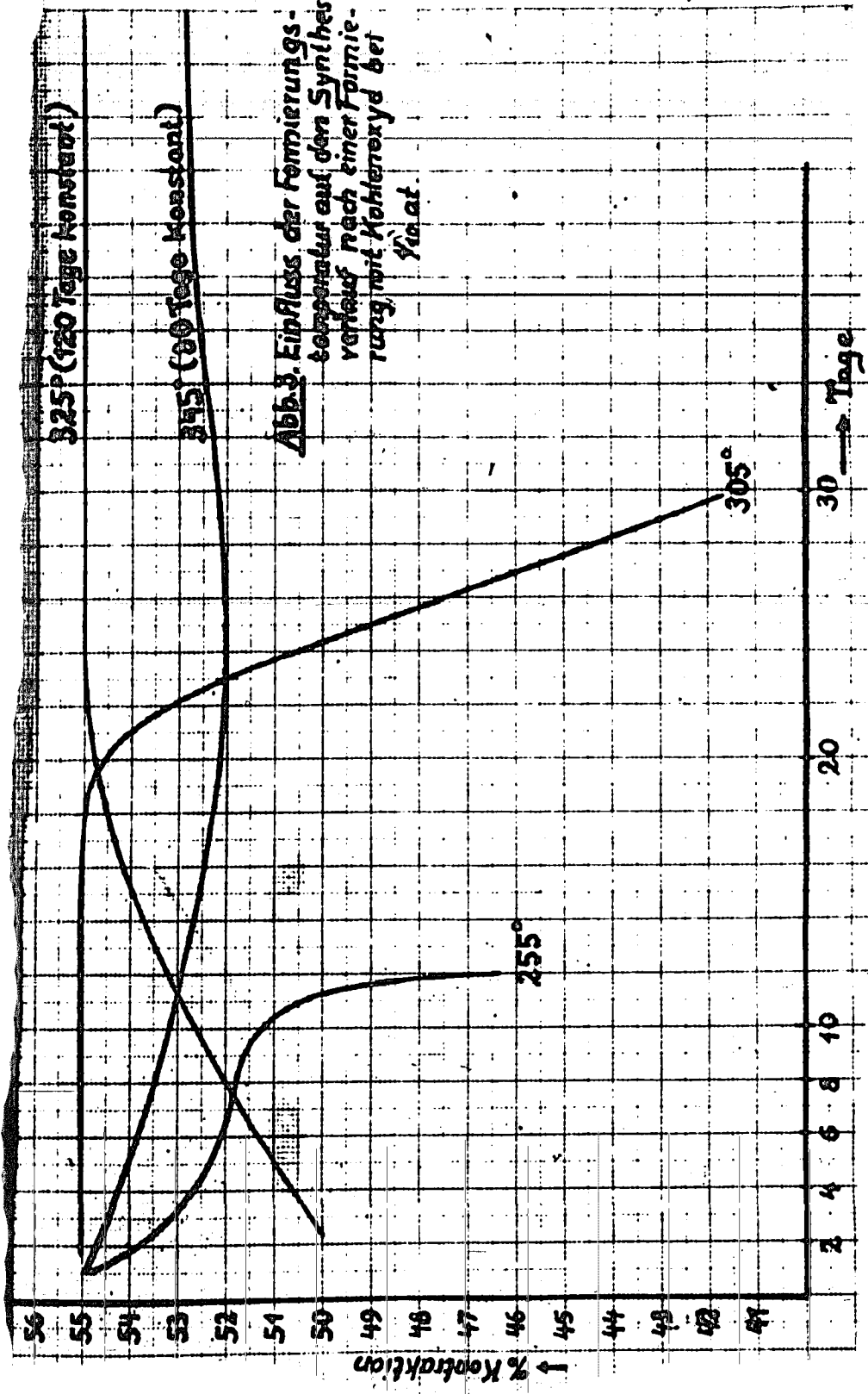
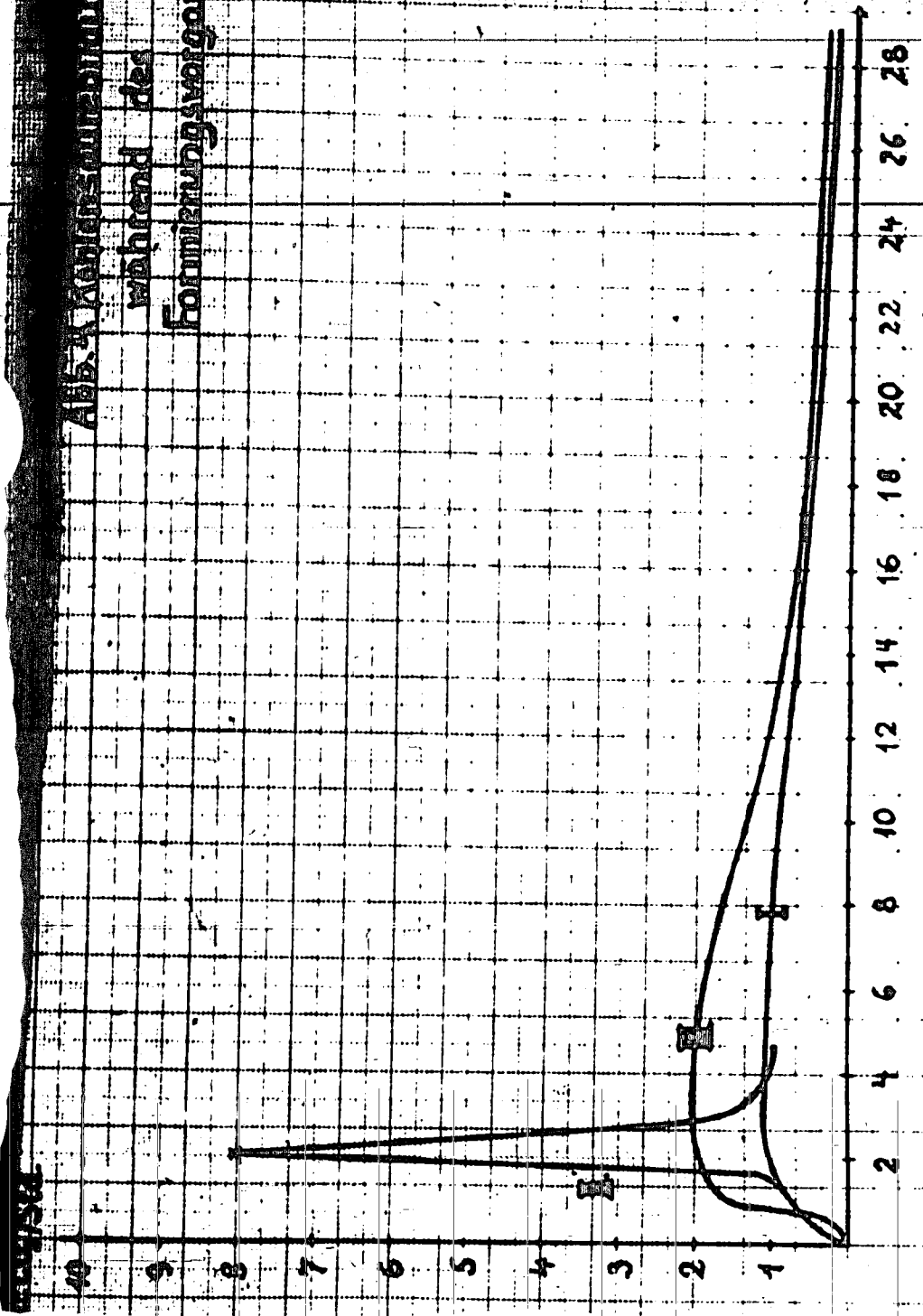


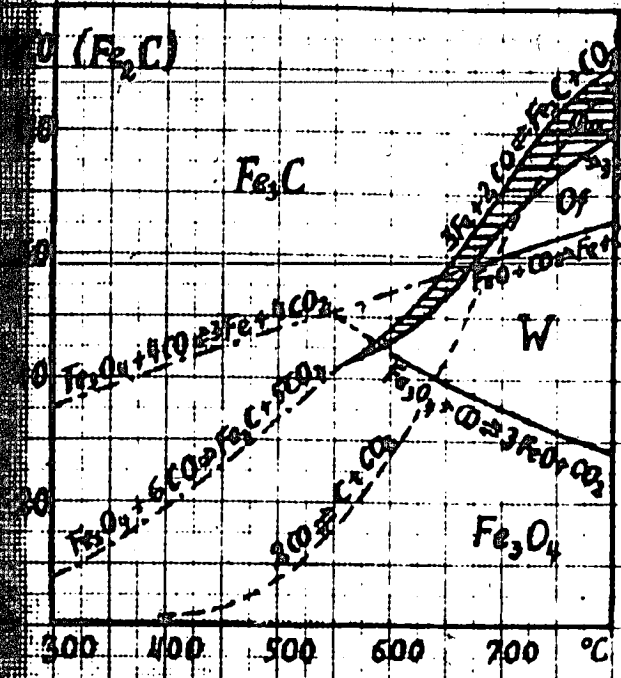
Abb. 3. Einfluss der Förmierungs-  
temperatur auf den Synthese-  
verlauf nach einer Förmie-  
rung mit Kohlenoxyd bei  
Vicat.

# ABSTÄNDSPREISEN Während der Formierungszeit



→ 5td. Formierungsdauer

a) 1at



**O<sub>a</sub> = Oxo-austenit**  
 (Oxyd u. Carbid enthaltendes  
 metallisches Fe)  
 $3FeO + 3CO \rightleftharpoons Fe_3C + 4CO_2$

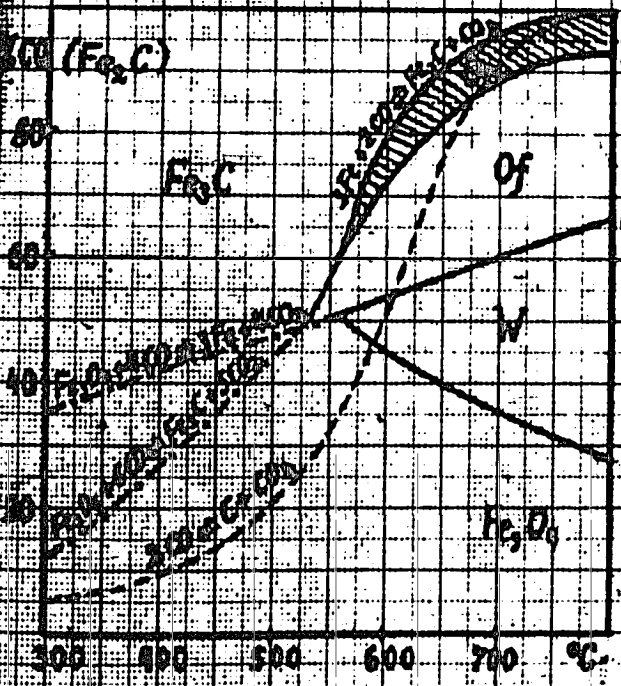
**O<sub>f</sub> = Oxoferrit**  
 (O-enthaltende = metall-Phase)

**W = Wüstit**  
 (Fe<sub>3</sub>O<sub>4</sub>-haltige FeO-Phase)

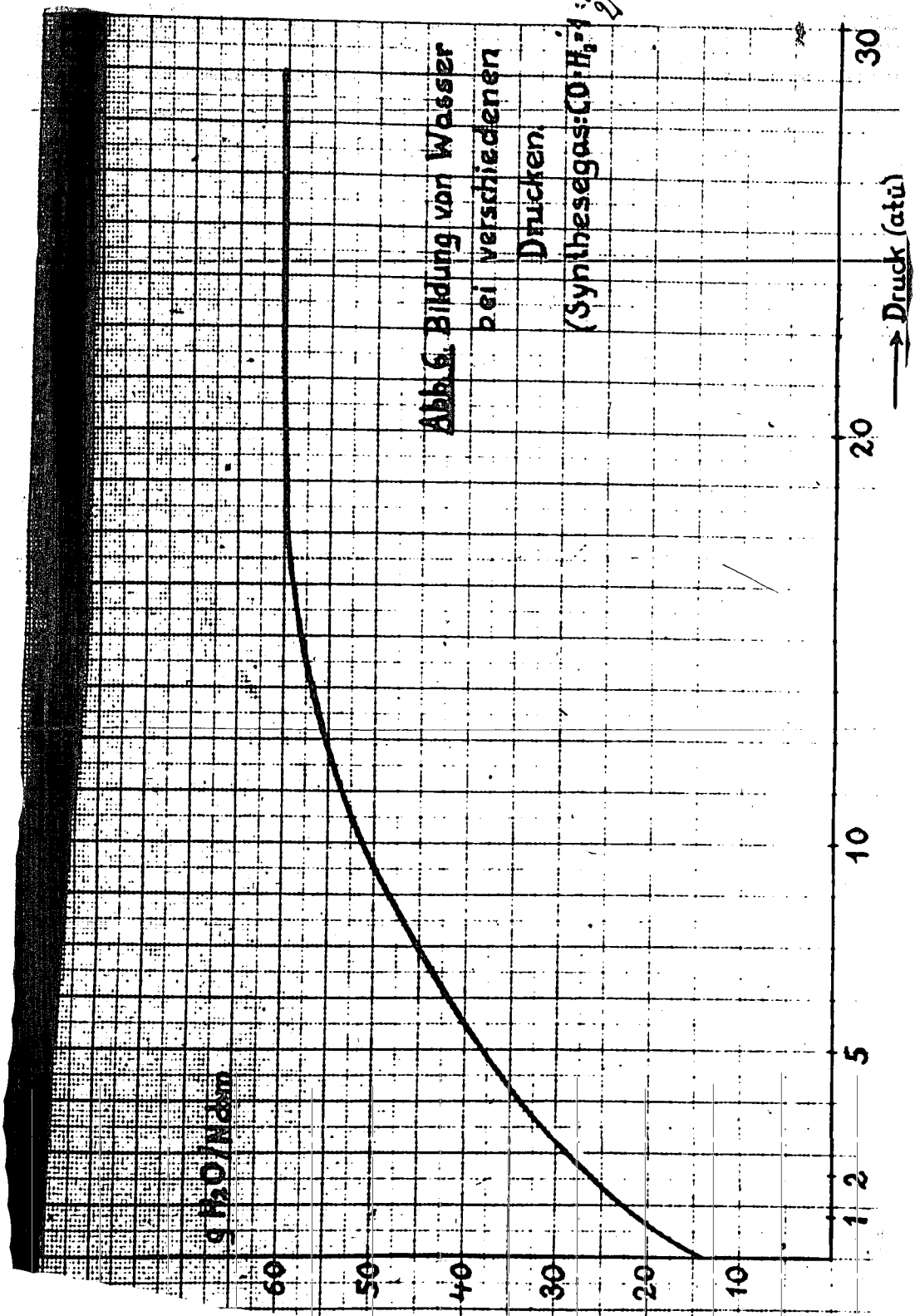
---  $2CO \rightleftharpoons C + CO_2$

--- von U. Hofmann  
 und E. Groll extrapolierte  
 Gleichgewichte.

b) 1/10 at



Gleichgewichtsverhältnisse im System Fe-C-O.



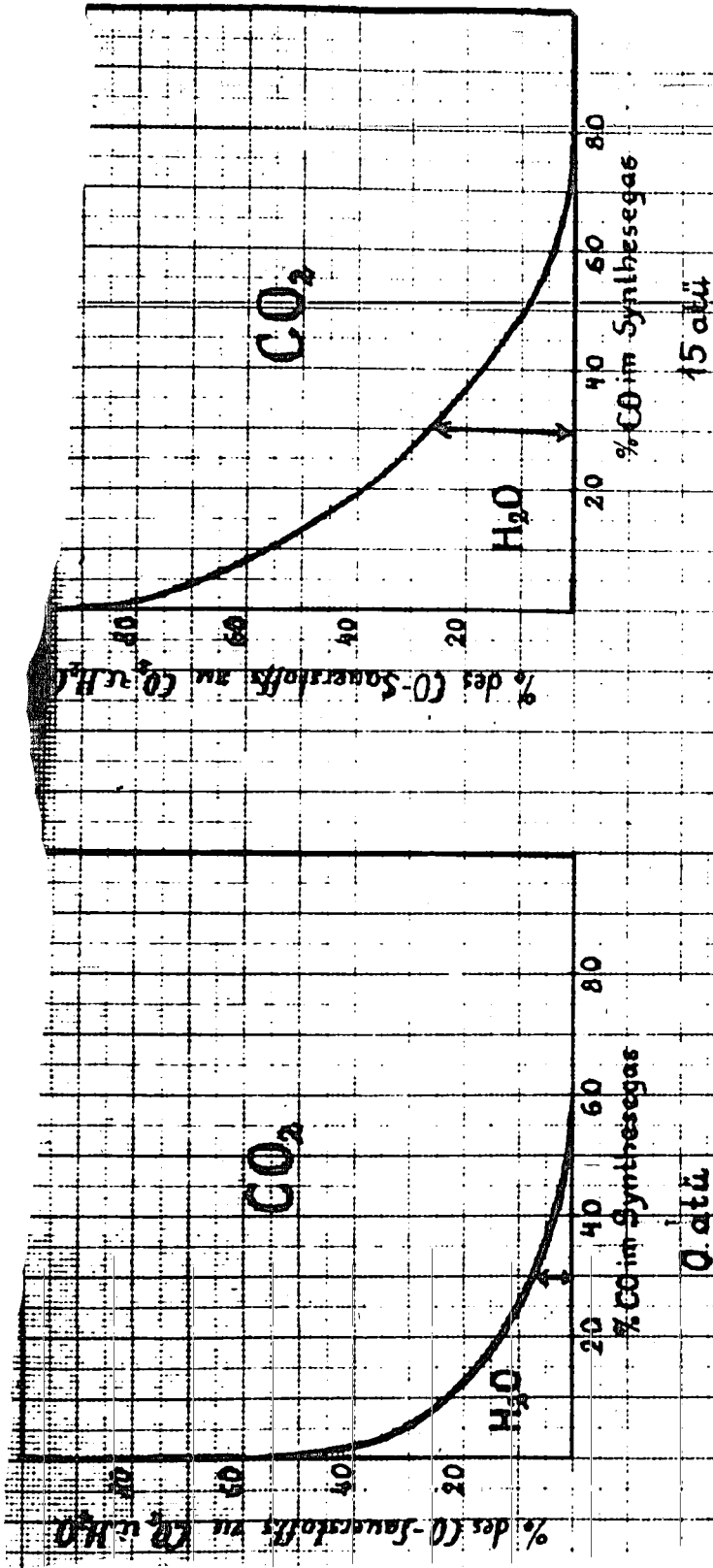


Abb. 7. Umsetzung des Kohlenoxydsauerstoffs zu CO<sub>2</sub> bzw. H<sub>2</sub>O bei verschiedener Synthesegaszusammensetzung bei 0 u. 15 atm.

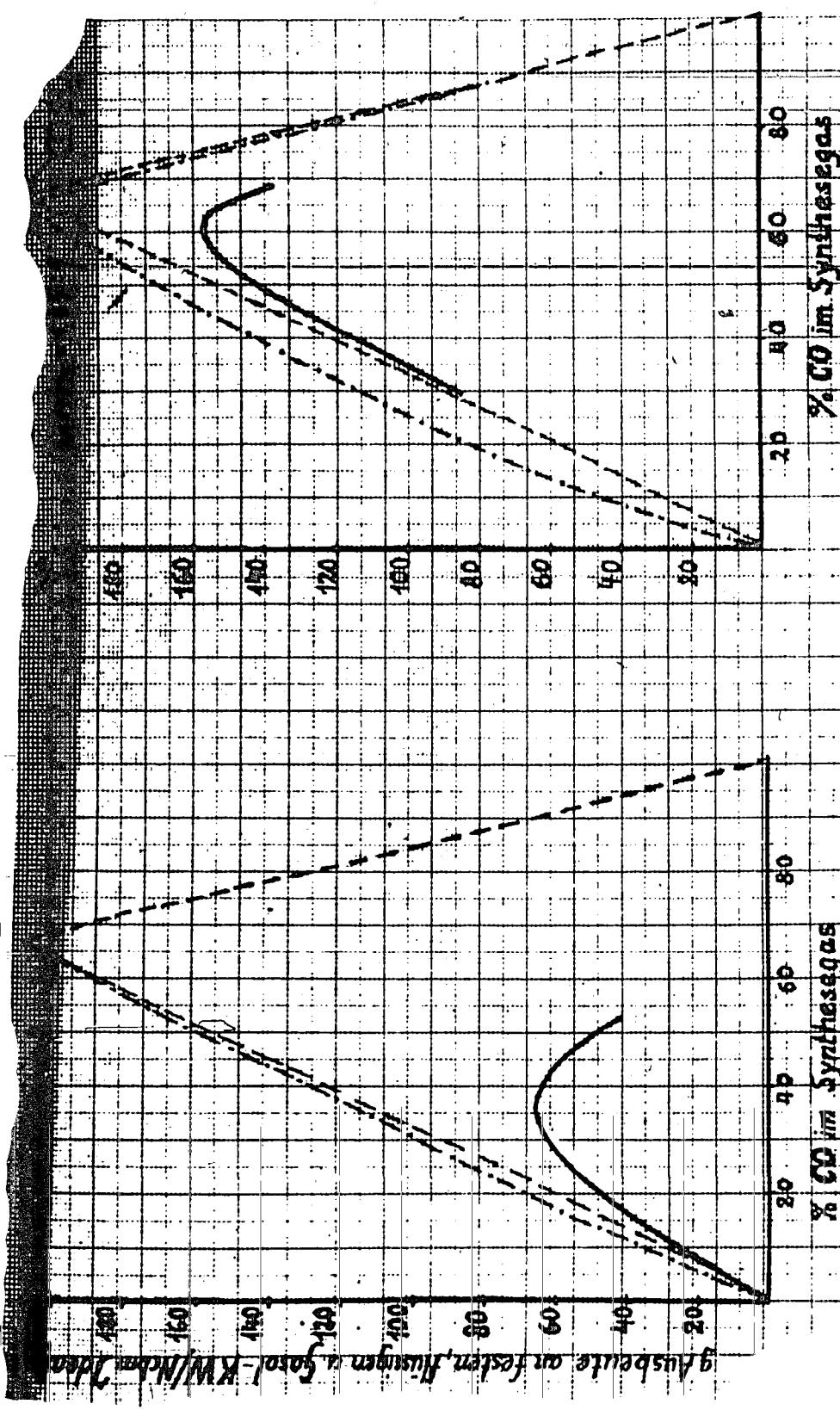
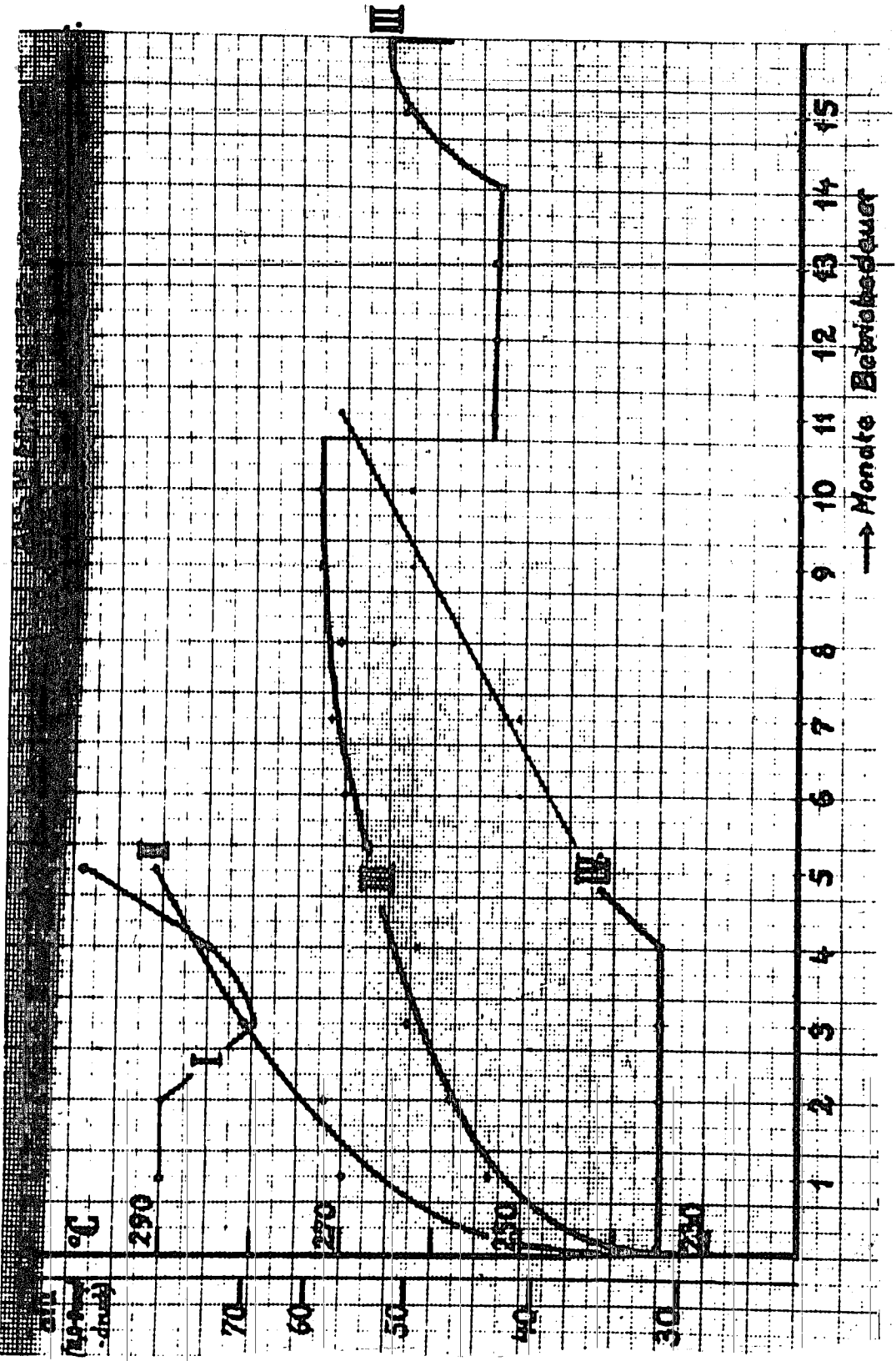


Abb. 8. Einfluss der Zusammensetzung des Synthesegases auf die Ausbeuten.



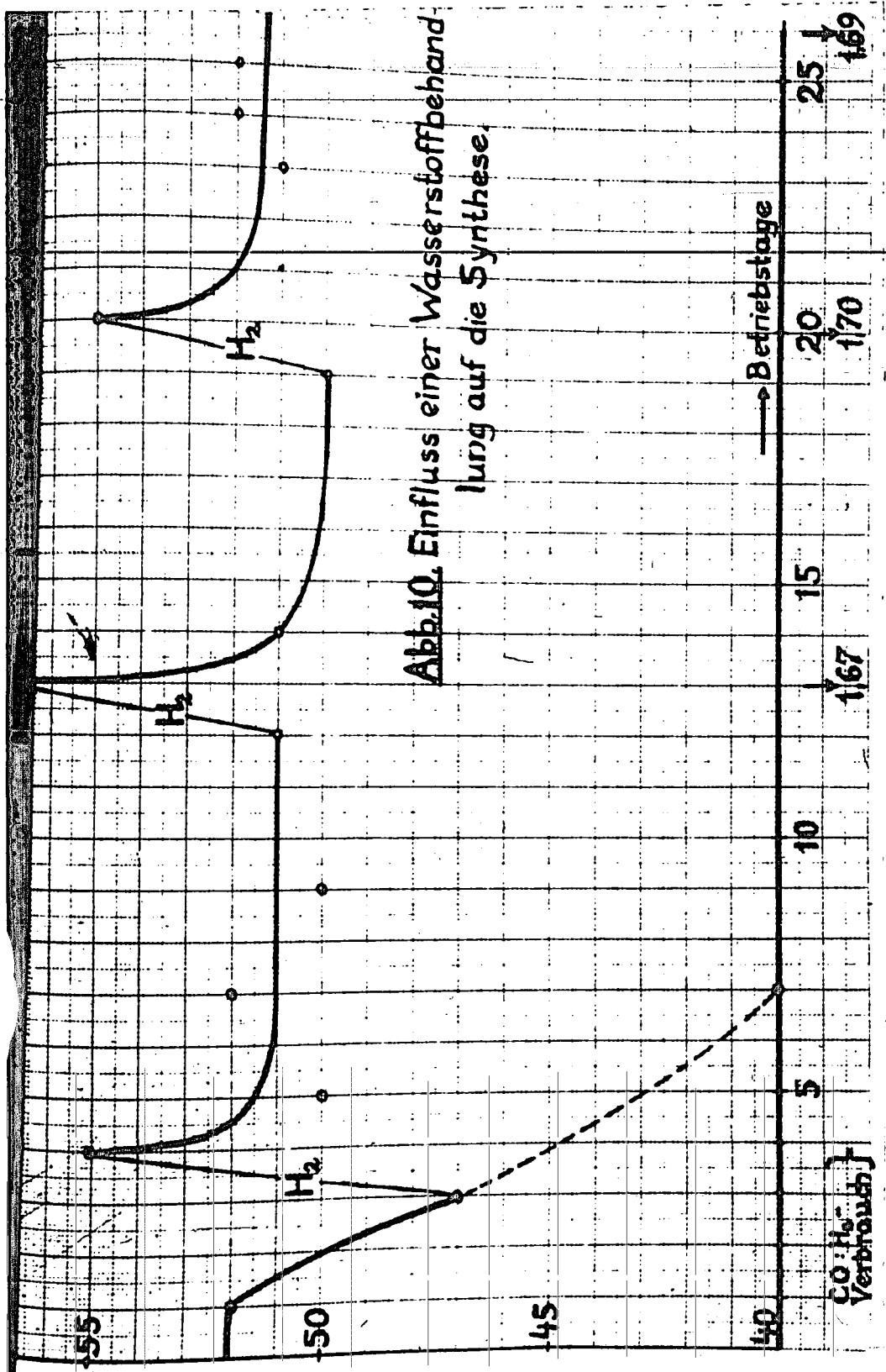


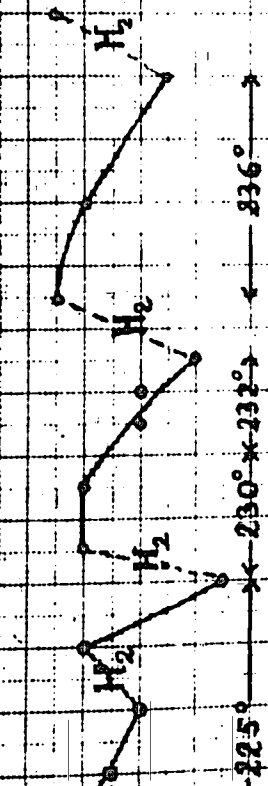
Abb. 10. Einfluss einer Wasserstoffbehandlung auf die Synthese.



INSTRUMENTELLE AUSWERTUNG

20.08.2020

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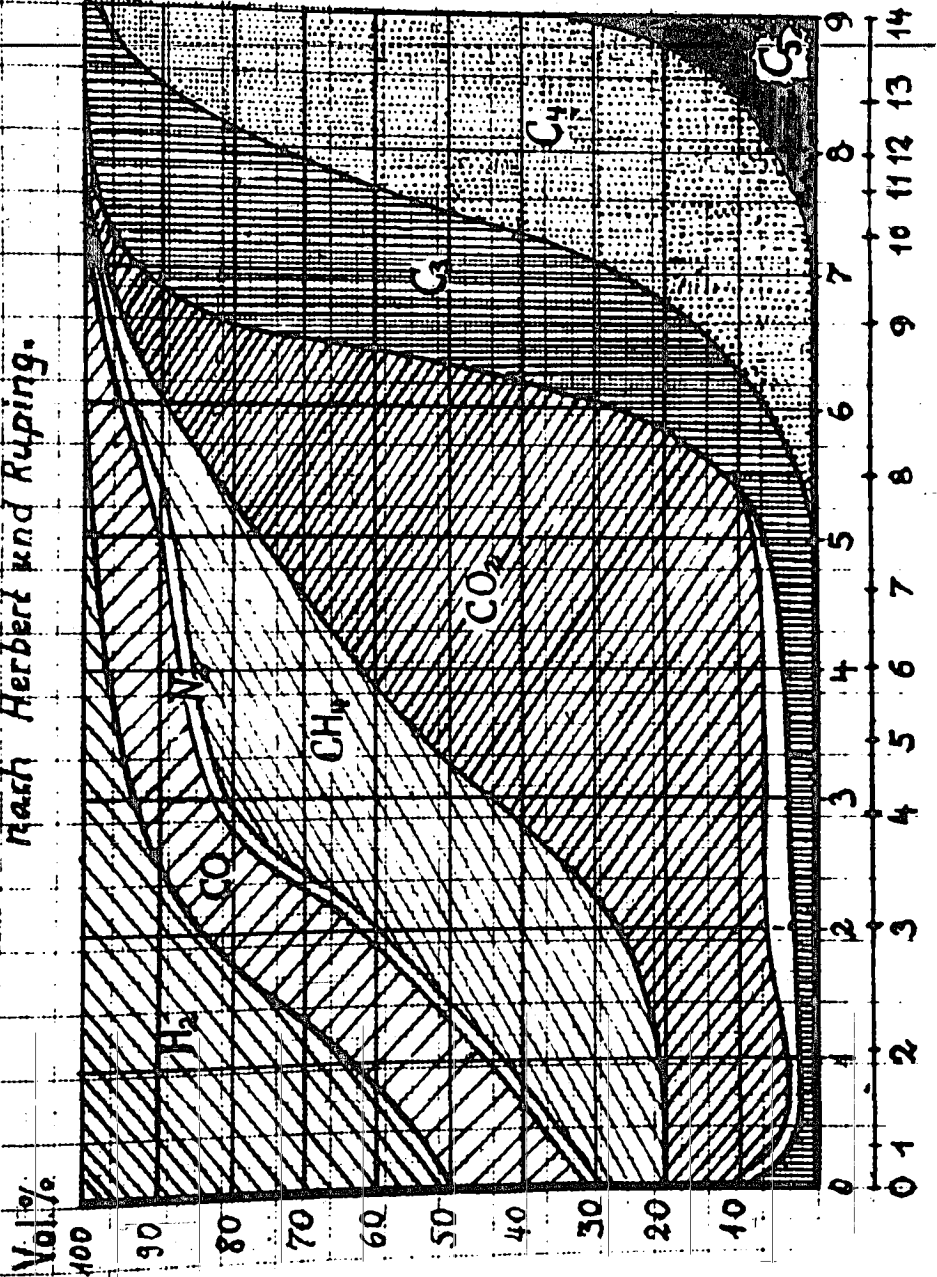
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30

→ Betriebsstage

beladener Supersorbon-Aktivkohle beim Ausdampfen  
 mit Wasserdampf (Momentanwerte nach 1, 2, 3 usw. min.)  
 nach Herbert und Ruping.



Minuten  
 Gasanfall  
 m<sup>3</sup>/to A-Kohle

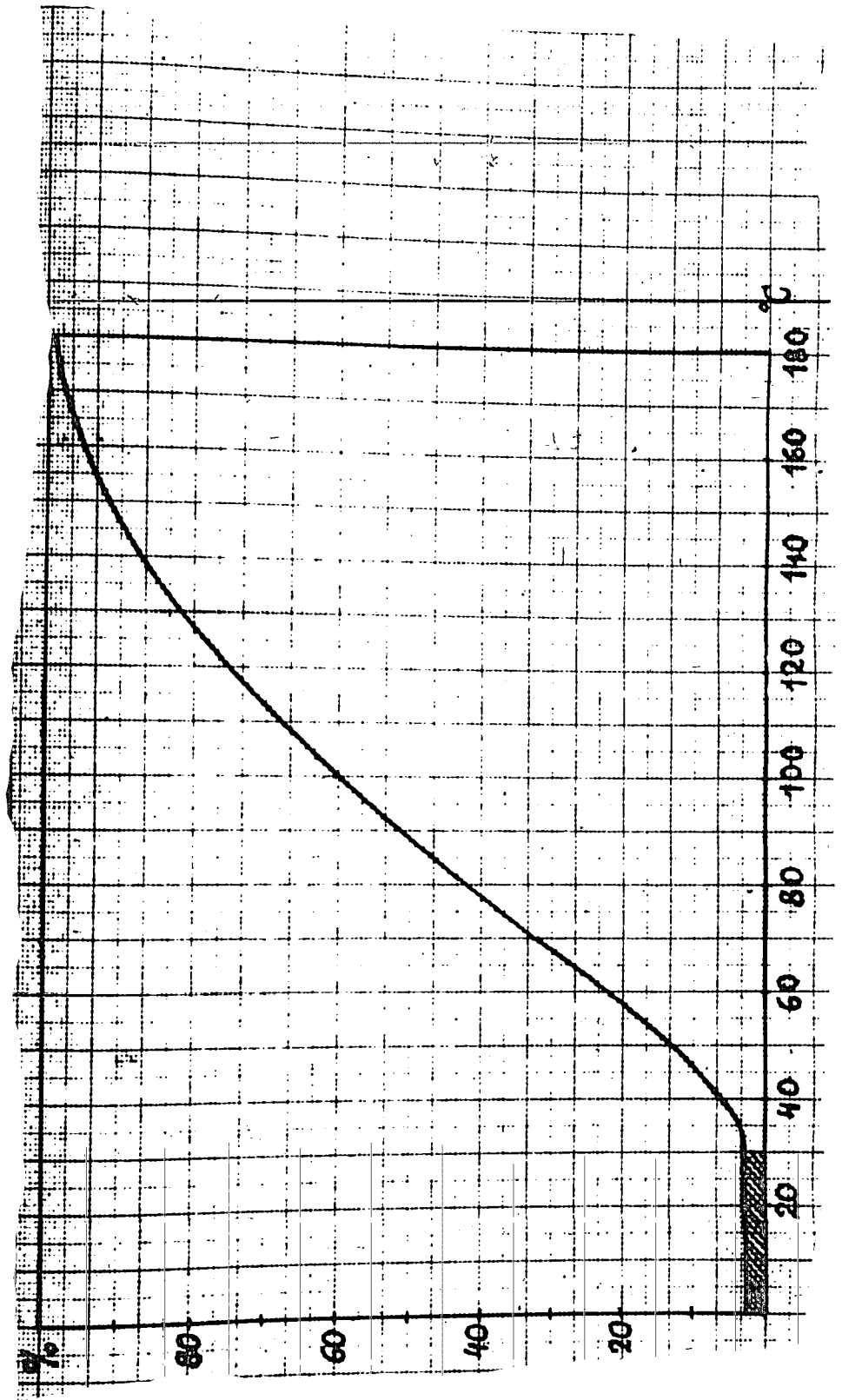


Abb. 14 Destillation gasförmiger Kohlenwasserstoffe.

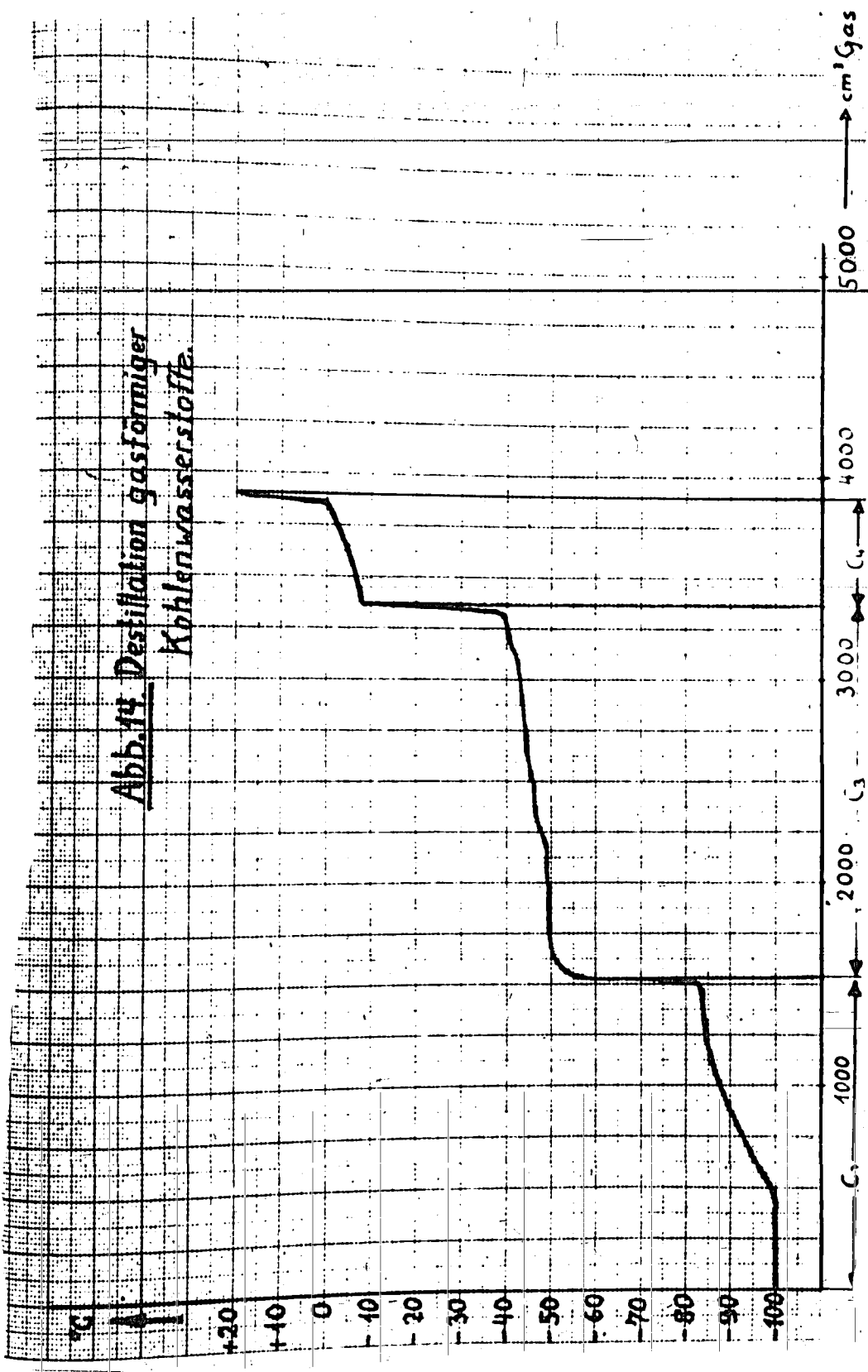
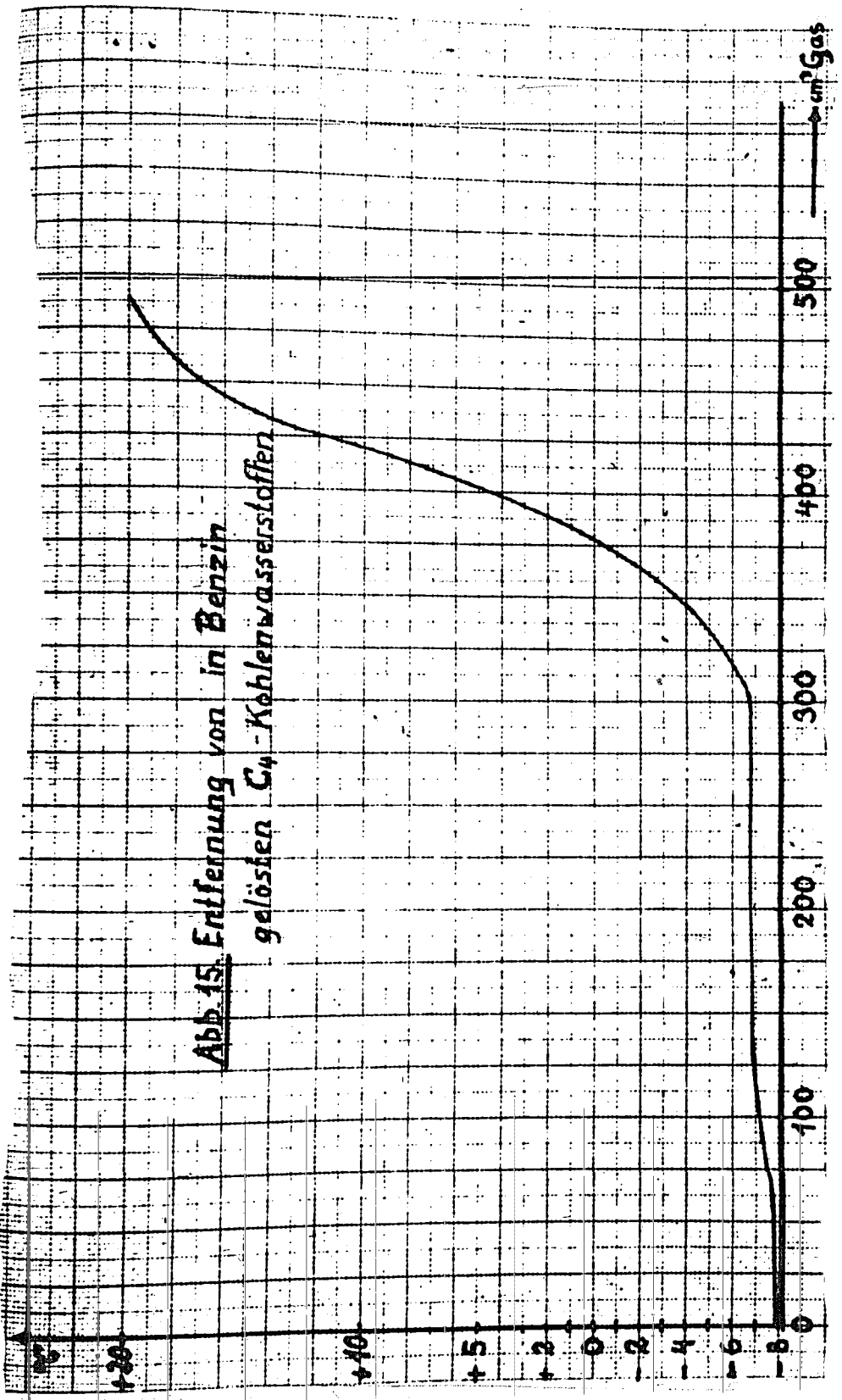


Abb. 15. Entfernung von in Benzin  
gelösten C<sub>4</sub>-Kohlenwasserstoffen



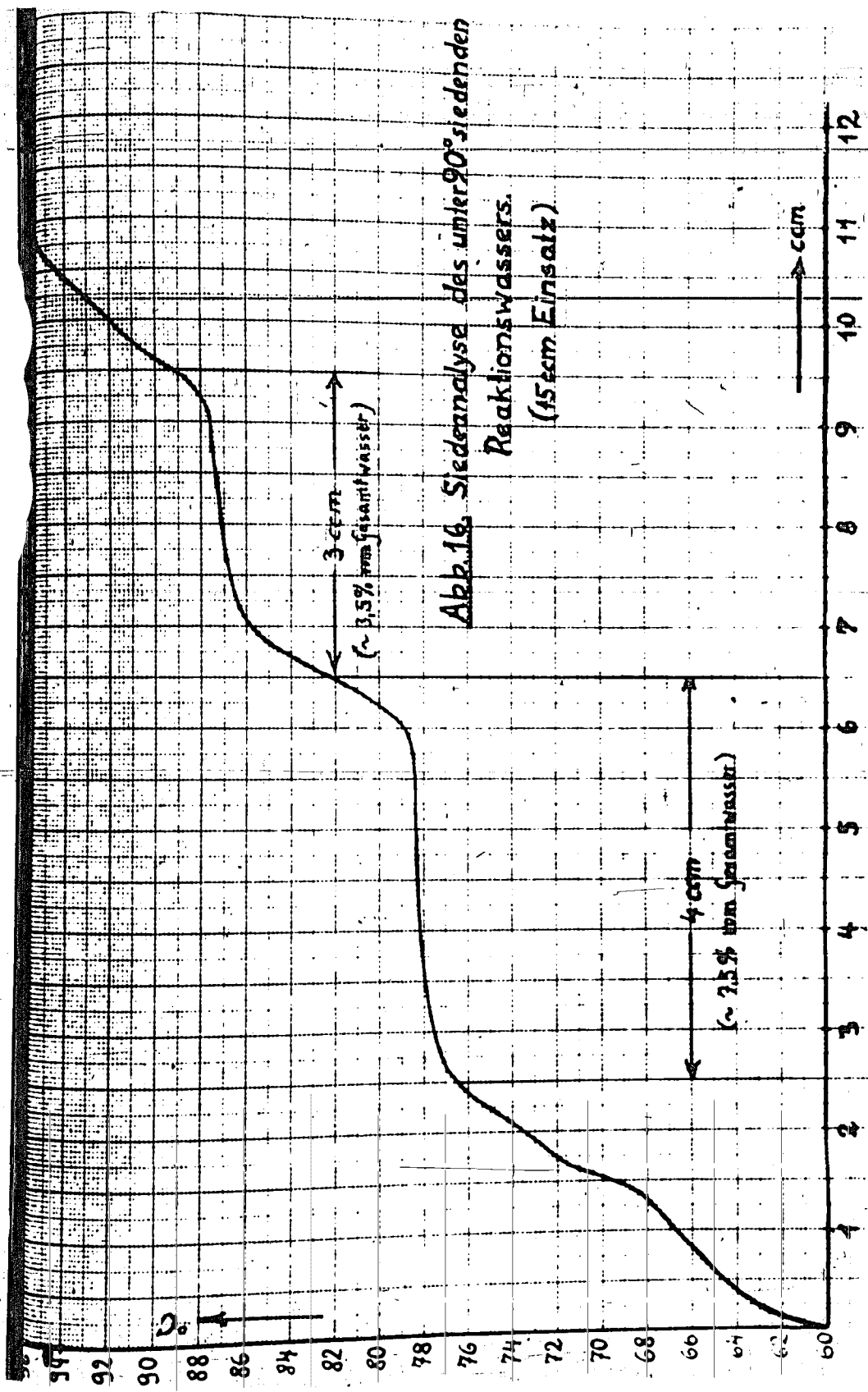
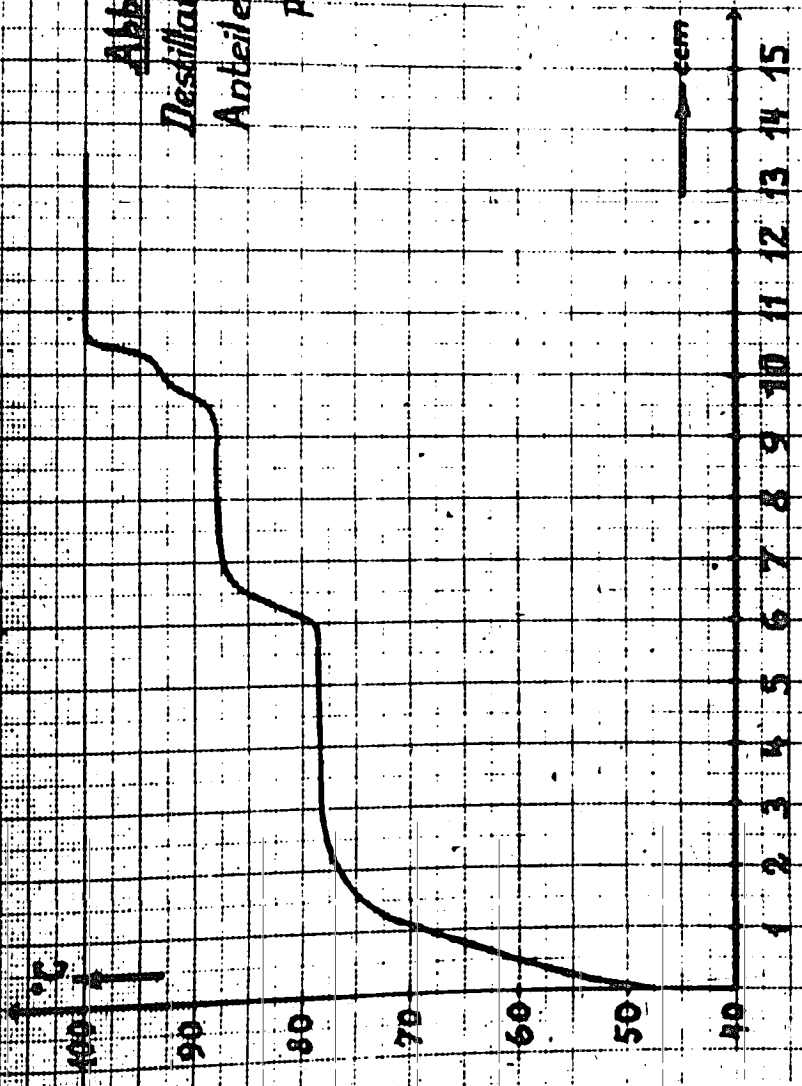


Abb. 16 Siedeanalyse des umher 90° siedenden  
 Reaktionswassers.  
 (15cm Einsatz)

Abb. 17.

Destillation von wasserlöslichen  
Anteilen der flüssigen Reaktions-  
produkte (Einsatz: 15cm).



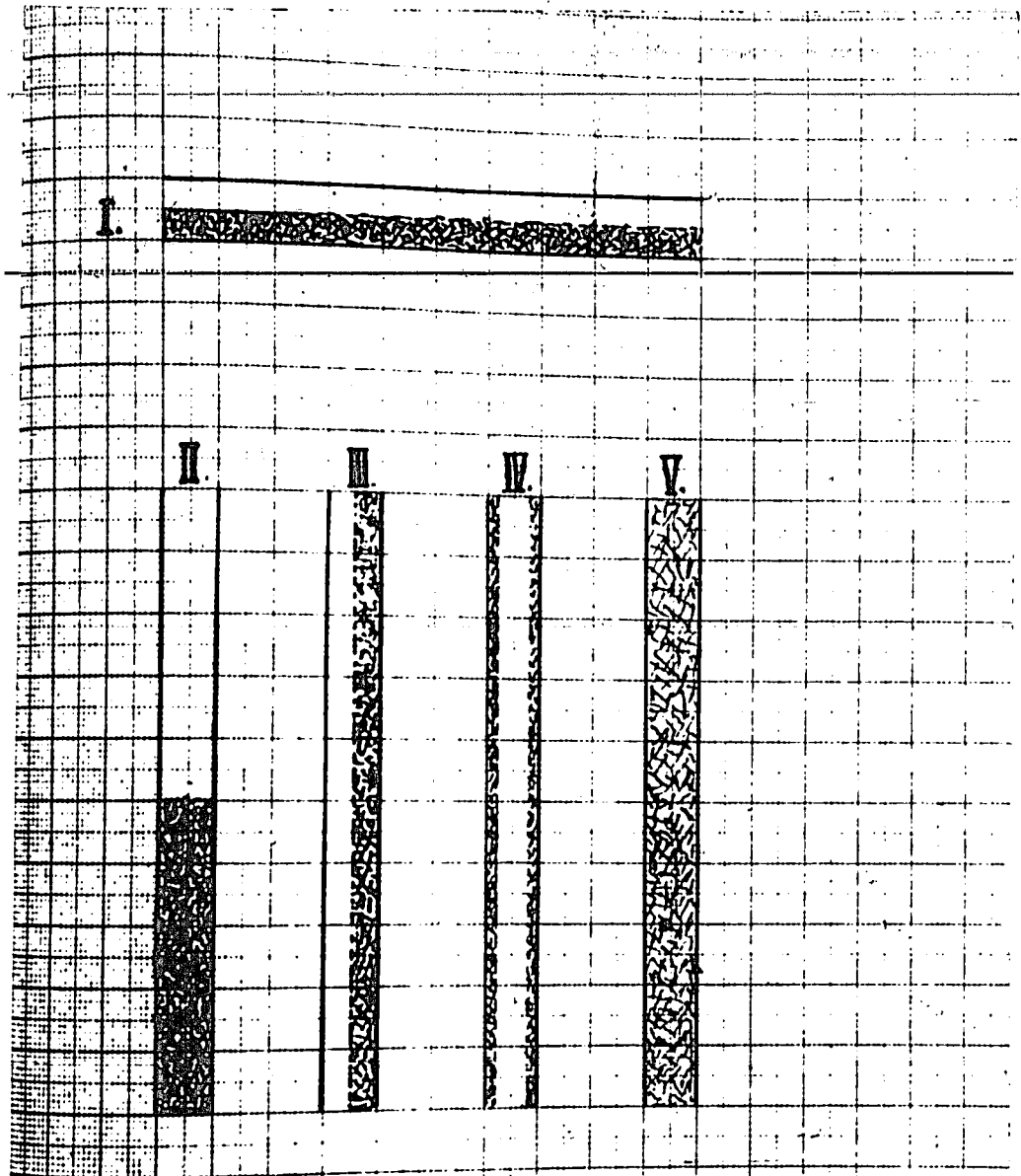


Abb. 19. Schematische Darstellung verschieden gefüllter Kontaktrohre.



Temperatur  
 konstant  
 (Gleichbleibend)

Umsatz: 50% Kontraktion

Temperatur bei Volle  
 ca. 50% Kontraktion

