## C. The Reaction Temperatures

The temperature data in the present paper were obtained by measurements in an aluminum block.* In spite of the good insulation of the two ends of the tubes protruding from the aluminum block with asbestos cord, the radiation from the ends of the tubes results in an around 5°C lower reading of temperature inside the tubes than the temperature of the aluminum block, as found in tests. On the other hand the catalyst temperatures are always somewhat higher than of the surrounding space because of the positive heat of the reaction, and both corrections were left out and the temperature of the block was given.

Special efforts were made during the work on the iron middle pressure synthesis to lower the reaction temperature. This seemed to be important from purely economic considerations, because on an industrial scale the synthesis whenever possible is carried out in water cooled pressure tubes and every rise in temperature here would result in a rise of the steam pressure and will necessitate a strengthening of the reaction equipment.

1. Effect of Forming

It has already been mentioned elsewhere that the temperature required for synthesis was principally dependent on the temperature of forming of the iron catalysts to be used in that synthesis. The curves in figure 9 show the limitations in the contents already discussed. The months of operation are laid out on the abscissa, the temperatures on the ordinance, and the saturation pressures of steam at these temperatures are shown. All tests were performed with a synthesis gas with the carbon monoxide and hydrogen in a proportion
* The work was done in the laboratory in pressure tubes, heated in a slanting aluminum block furnace.

Fig. 9. Effect of forming upon the synthesis temperature

Months of Operation

Atm. gauge (vapor pressure)
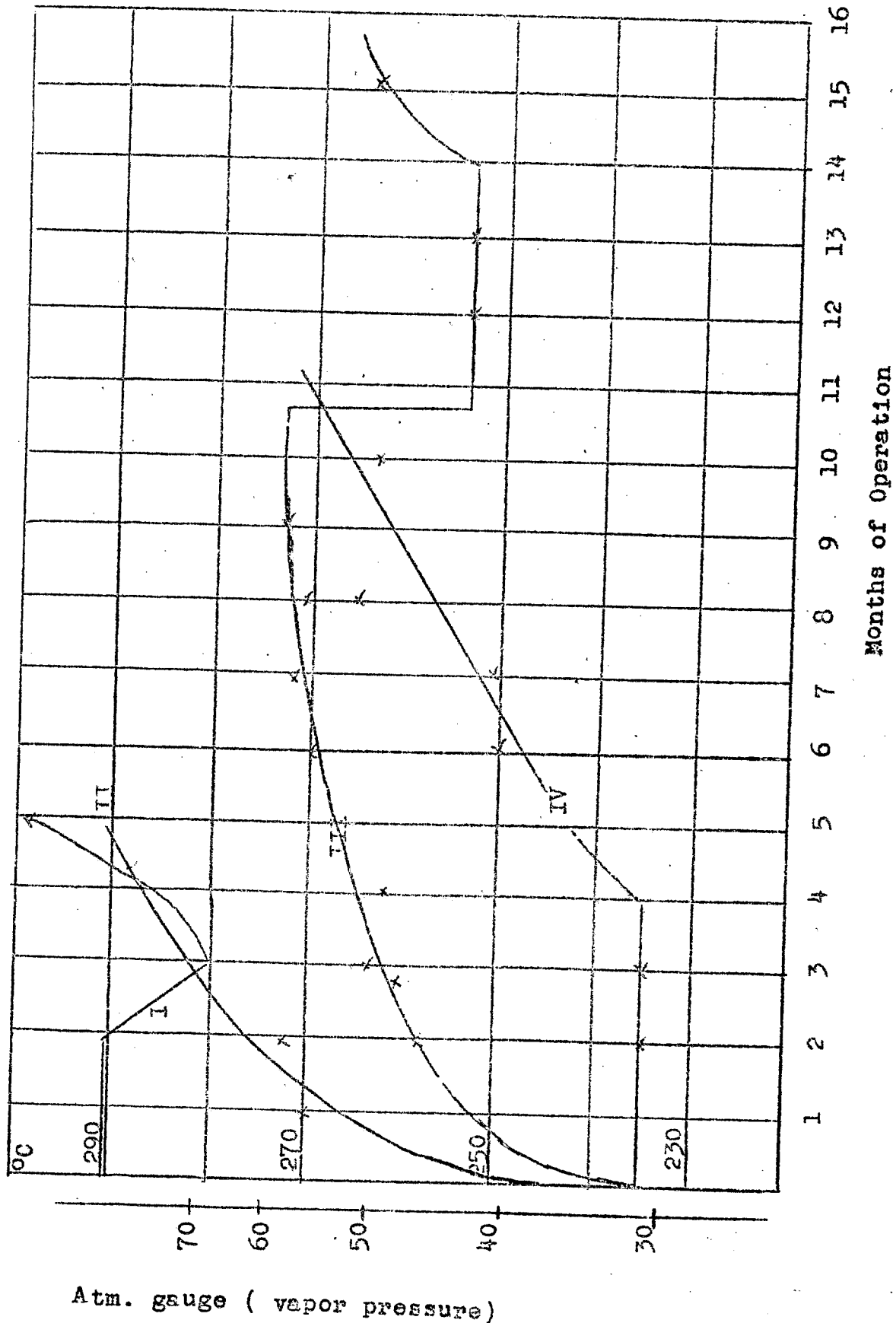
of 3 : 2 (4 li/10gFe/h).

Curve I refers to a catalyst which has been put in operation at 15 atm pressure without any previous forming. The temperature had to be raised to 290°C to produce a maximum contraction. At first the contraction amounted to 45 percent, in the course of the second month of operation the activity of the catalyst rose gradually and the contraction rose with it to around 50 percent. In further operations the temperature could be lowered without changing the conversion to 280°C. It had to be again raised during the fourth month, and by the end of the fifth month, a temperature of 300°C had been reached.

Curve II shows the temperature relationships with an iron-copper catalyst which was first operated at 1 atm and 240°C for three days with a mischgas (contraction 30 percent) and was changed over to synthesis gas at 15 atm pressure after three days. The maximum contraction of 50 - 55 percent (optimum conversion) was obtained by raising the temperature in the course of five months from 240°C to 290°C.

Curve III shows the changes in temperature in a test with a copper-free normal iron catalyst which was treated at 0.1 atm and 255°C for 25 hours with pure carbon monoxide. The maximum contraction of 50 - 55 percent was obtained by raising the temperature in the course of eight months from 235 to 272°C. At these temperatures the activity of the catalysts grew gradually and during the eleventh month the temperature could again be lowered to 254°C maintaining the contraction at 50 percent. During the fifteenth and sixteenth months the temperature had again been raised to 266°C and then lowered to 259°C. Table 16 gives the composition of some end gas obtained during this test.

Table 16

Composition of End Gases of Duration Experiment
Conducted at Different Temperatures During Sixteen
Months of Operation.

Months of Operation	Temp °C	Contr %	CO₂	Hydro-carbons Heavy	O₂	CO	H₂	Hydro-carbons	Carbon Number	N₂
1	253	50	49.6	2.2	0.1	15.0	13.3	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
14	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

(Composition of End Gas in Percent)

The table shows that as the temperature rises the
amount of gaseous hydrocarbons is increased, but the
composition of the end gas was generally very similar
when considering a variation in the composition of the
synthesis gas from the first to the sixteenth month.

Curve IV refers to a catalyst formed at 325°C
with carbon monoxide at 0.1 atm. Forming at 325°C
permitted operations at lower temperatures during the
first month. The contraction remained constant at
50 - 54 percent for four months operation at 235°C.
The temperature had then to be raised. After one year
no more advantages could be found over the iron catalyst
formed at 255°C.

The curves in this figure prove the importance
of the proper pretreatment of the catalysts for the
synthesis reactions.

2. Effect of the Composition of Gas

Table 19 shows the conversions obtained with
high-carbon monoxide and high-hydrogen synthesis gas
at a reaction temperature of 205°C (synthesis pressure
15 atm).

Table 17

Conversion of a Carbon Monoxide-Rich and a Hydrogen-Rich Synthesis Gas at a Reaction Temperature of 205°C and at 15 atm Pressure.

	CO_2	Heavy Hydro-carbons	O_2	CO	H_2	Hydro-carbons	Carbon Number	N_2	Contr. %
CO-rich Start. gas	2.2	0.0	0.2	58.9	33.9	0.2	1.0	4.6	
End gas	10.3	0.8	0.2	52.9	28.4	1.6	1.3	5.8	20
H_2-rich Start. gas	1.2	0.0	0.0	31.2	56.6	1.6	1.2	9.4	
End gas	8.3	2.1	0.2	19.5	52.3	3.9	2.0	13.7	31

Table 18 shows conversions at 225°C with gases of three different compositions.

Table 18

Conversion of Carbon Monoxide-Rich Gas, Water Gas and Hydrogen-Rich Gas with a Reaction Temperature of 225°C and a Pressure of 15 atm.

	CO_2	Heavy Hydro-carbons	O_2	CO	H_2	Hydro-carbons	Carbon Number	N_2	Contr. %
CO-rich Start. gas	2.3	0.0	0.0	58.8	33.4	0.4	1.0	5.1	
End gas	42.9	3.8	0.2	24.5	15.1	4.3	1.5	9.2	45
Water gas	1.8	0.0	0.1	46.4	43.4	0.8	1.0	7.5	
End gas	40.6	4.0	0.2	8.9	24.6	6.2	1.6	15.5	52
H_2-rich Start. gas	0.6	0.0	0.1	30.7	58.3	0.2	1.0	10.1	
End gas	22.6	1.6	0.1	0.0	43.8	13.1	1.7	18.8	46

These analyses show that operations may be
conducted at lower temperatures with low concentration
of carbon monoxide in synthesis gas, i.e. with less
carbon monoxide to be converted. At equal temperatures
and with increasing hydrogen content in the synthesis
gas the contraction values increase because of the
simultaneous formation of water (instead of carbon
dioxide), as long as the carbon monoxide is not completely
converted, as it was in the last test, table 18. The
hourly conversion of carbon monoxide in the two tests
at 205°C, table 17 was 0.66 to 0.71 li, at 225°C
according to table 18 the hourly conversion of carbon
monoxide was 1.8, 1.7 and 1.23 li. In the last test
on this table all the carbon monoxide had been converted.
As long as carbon monoxide and hydrogen are present
in sufficient amounts in the reacting gas, the amounts
of carbon monoxide remained independent from the
carbon monoxide; hydrogen ratio at temperature.

3. Operations at too Low Starting Temperatures

Tests were usually begun at 225 - 235°C
although a good conversion could be reached at a lower
temperature. Thus with hydrogen-rich synthesis gas
($CO : H_2 = 1 : 2$) a conversion of 47 percent was
measured on the second day of operation at 184°C.
The proportion of carbon monoxide to hydrogen consumed
was equal in that case to 0.7 : 1. This indicates a
tendency for the reaction to proceed according to
$CO + 2H_2 = CH_2 + H_2O$. At this low reaction temperature
the conversion drops, however, in a few days, and the
results are always less favorable when the temperature
is then increased, than in experiments where higher
temperatures were used from the start. This may be
seen in table 19. Two comparable tests were here
recorded with a carbon monoxide-rich synthesis gas
(normal iron catalysts) one of the tests starting at
235°C (test 1) the other one at 210°C (test 2).

Table 19

<u>Effect of Too Low Reaction Temperatures Upon the Activity of the Catalysts.</u>

Days of Operation	Test #1		Test #2	
	Temp $^\circ$C	Contr %	Temp $^\circ$C	Contr %
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 started at 235°C shows the constant contraction of 50 - 55 percent. The one started at 210°C produced a contraction of 42 percent after one day, 31 percent after two days, and 27 percent after three days. After the temperature was then raised only 36 percent were obtained at 235°C and even at 250°C only a contraction below 50 percent.

4. <u>Temperature and Products of Reaction</u>

It has already been mentioned (see e.g. table 16) that as the reaction temperature is raised the amount of gaseous reaction products is increased. Table 20 shows average yields with iron catalysts containing 1/4 percent potassium carbonate obtained at 235°C, 270°C and 280°C. Between 235°C and 270°C the solid paraffine yield dropped from 39 to 4 g/ncbm. The amounts of the liquid hydrocarbon, in particular of the volatile hydrocarbon, and of the gasol hydrocarbon increased simultaneously. At 280°C the paraffine yield was still smaller, and at this temperature the yields in liquid and gasol hydrocarbons were also smaller.

Table 20

The Character of the Reaction Products at Different Temperatures.

Reaction Temp. °C	Yields (g/ncbm Ideal gas)		
	Solid hydrocarbons	Liquid Hydrocarbons	Gasol
235	39	83	26
270	4	94	46
280	2	82	35

D. Effect of the Alkali Content of the Catalyst upon the Activity and upon the Nature of the Reaction Products.

We have already discussed in detail the preparation of the catalyst and the way alkalies are added. We shall show below the effect of the alkalies upon the course of the synthesis. The alkali additions shown in the table refer to percent by weight of potassium carbonate to the amount of the metallic iron. With the other alkali salts (potassium permanganate, fluoride etc,) the symbol "1 percent $KMnO_4$" mean that the amount of potassium added corresponded to that in 1 percent of K_2CO_3.

Table 21 shows first a test with a catalyst precipitated with ammonia and with no alkali addition. The activity was tested at a constant temperature of 235°C with a high-carbon monoxide synthesis gas ($CO : H_2 = 3 : 2$, with 8 - 10 percent of inert constituents) and at a pressure of 15 atm.

Table 21

The Activity of Different Alkalized Iron Catalysts.

Precipitating Agent	Alkali Addition	Days of Operation								
		1	2	5	10	20	30	40	50	100
		Percent contraction at 235°C and 15 atm.								
NH_3		0	50	50	50	50	50	49	51	51
Na_2CO_3		0	53	50	48	49				
"	1/4 % K_2CO_3	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	48	48	47		
"	2 " "	45	45	47	46	47	50			
"	5 " "	-	-	45	50	50	51	50	40	
"	10 " "	-	50	47	50	45	42			
Na_2CO_3	1 % $KMnO_4$	40	-	50	51	55	50			
"	1 " K_2F_2	-	57	53	55	48				
"	1 " K_2SiO_3	-	54	53	46	50				
"	1 " K_2HPO_4	55	46	-	46	40				

The series of the experiments shows that the alkali addition is not necessary for the preparation of active catalysts, if the character of the products obtained is left out of consideration. The ammonia precipitated catalyst, entirely free of alkali, produced contraction values after 50 days of operation which were not markedly below those with a normal iron catalyst containing 1/4 percent K_2CO_3. Tests with catalysts containing 1 percent and over of potassium carbonate show a drop of conversion sooner than with the normal iron catalyst, namely between the 30 and 50 days at 235°C. When potassium carbonate has been replaced by other alkali salts, no marked differences in the course of the reaction during the first weeks of operation were found. In these tests the catalysts with a potassium permanganate addition caused a good conversion, the catalysts with the potassium phosphate addition were less stable.

Table 22 shows the amount and nature of the reaction products obtained at 235°C and 15 atm synthesis pressure with differently alkalized catalysts. The yields in g/ncbm ideal gas varied during the first month of operation between 140 and 160 g in line with the not entirely equal contraction. The amount of alkali has a very important effect upon the reaction products. The amount of solid paraffine determined by the butanone method (referred to the total yield of solid, liquid and gasol hydrocarbon) was 12 percent in the absence of alkali, 26 percent with the addition of 14 percent potassium carbonate, 42 percent with 1 percent potassium carbonate, 43 percent with 2 percent potassium carbonate and 45 - 46 percent with 5 percent potassium carbonate. The amounts of liquid and gasol hydrocarbons were correspondingly the lower the higher the alkali content.

The table 22 shows finally that the nature of the alkali salt added to the catalyst is unimportant for the amount and character on the reaction products during the first month of operation. Tests with 1 percent potassium carbonate and the corresponding amounts of potassium permanganate, potassium silicate; potassium fluoride, and potassium phosphate show the same course of reaction inside the variations usual in such tests.

Table 22

Yields with Different Alkali Additions to Iron Catalysts

Precipitating Agent	Alkali addition	g total hydro-carbons /ncbm ideal gas	Percent Paraffin	Percent liquid hydro-carbons	Percent Gasol
NH_3	0	141	12	67	21
Na_2CO_3	0	140	13	67	28
"	1/4% K_2CO_3	148	26	56	18
Na_2CO_3	1% K_2CO_3	157	42	47	11
"	1% $KMnO_4$	155	41	45	14
"	1% K_2SiO_3	158	43	41	16
"	1% K_2F_2	163	46	42	12
"	1% K_2HPO_4	154	38	52	10
Na_2CO_3	2% K_2CO_3	143	43	44	13
"	5% "	161	45	43	12
	5% "	155	46	44	10