ON THE THERMODYNAMICS OF THE FISCHER-TROPSCH SYNTHESIS

SUMMARY

The theoretically obtainable yields at equilibrium for the synthesis of butane and octane from carbon monoxide and hydrogen were computed by standard thermodynamic methods. The effect of variations of temperature, pressure, and synthesis gas composition on the theoritical yield were investigated.

INTRODUCTION

It is inherent to the nature of chemical thermodynamics that no information is obtained concerning the time element involved in a reaction process; its chief value is to provide information regarding the state which can exist in a system, under given conditions of concentration, pressure, and temperature, and particularly the size of the maximum yield that may be expected from the reaction under those given conditions. To this end, the laws of chemical equilibrium, formulated mathematically by Waage and Guldberg in the law of mass action (1867) may be used with satisfactory accuracy.

How the theory of chemical equilibrium may be applied to the Fischer-Tropsch gasoline synthesis under normal pressure is indicated by Eucken (Chemie-Ingenieur III/1, p. 170). In his calculation of the equilibrium conditions obtained in the reduction of carbon monoxide to butane at 265°C. log K_p = -16.84 and at 349°C. log K_p = -7.73; in the determination of the composition of the equilibrium mixture, at atmospheric pressure, from the K_p values he obtained.

		At 265°C.	At 349°C.
CO	percent	5.	10.0
H_2	"	11.25	22.5
C_4H_{10}	"	16.75	13.5
H_2O	"	67.00	45.0
	Total	100.00	100.0

From these figures Eucken determined "the maximum yield based on carbon monoxide" to be 77.0% and 57.5%, respectively; in this connection, Eucken defined "the maximum yield based on carbon monoxide" as the fraction of hydrocarbon vapor in 100 volumes of hydrocarbon vapor plus unreacted carbon monoxide. In the course of this development further references to Eucken's data will be found.
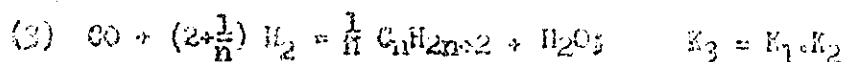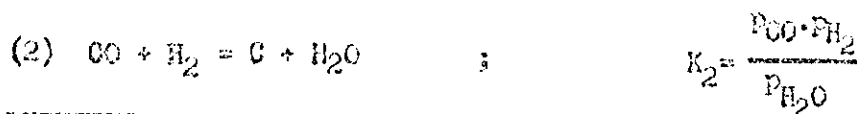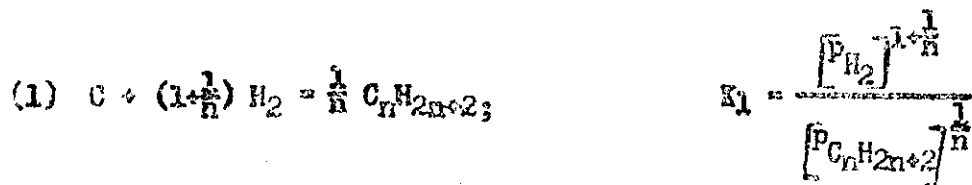
In the present paper, thermodynamic relations for the
Fischer-Tropsch synthesis are examined from the mathematical point
of view. Although the mathematical approach appears cumbersome at
first, the actual calculations offer no difficulties to the experienced
mathematician. Nevertheless, the significance of individual calcula-
tions should be considered not only for numerical value, but also for
an indication of trends, by comparison with other calculations.
Handled in this way the method rapidly attains its objective. Calcula-
tion may easily be checked for accuracy in each case by substituting
the numerical values of the equilibrium constants.

The investigation has been subdivided as follows:

      (I)   Equilibrium Constants

     (II)   Synthesis of Butane

   (III)   Synthesis of Octane

   (IV)   Discussion of Results

    (V)   Conclusion

EQUILIBRIUM CONSTANTS

The equilibrium constants for the Fischer-Tropsch synthesis
of individual hydrocarbons may be computed without difficulty, using
the values that have already been determined for the reaction between
carbon and hydrogen, and for the water gas reaction.

(1) $\quad C + \left(1+\frac{1}{n}\right) H_2 = \frac{1}{n} C_n H_{2n+2};$
$\qquad K_1 = \dfrac{\left[P_{H_2}\right]^{1+\frac{1}{n}}}{\left[P_{C_n H_{2n+2}}\right]^{\frac{1}{n}}}$

(2) $\quad CO + H_2 = C + H_2O \qquad ;$
$\qquad K_2 = \dfrac{P_{CO} \cdot P_{H_2}}{P_{H_2O}}$

(3) $\quad CO + \left(2+\frac{1}{n}\right) H_2 = \frac{1}{n} C_n H_{2n+2} + H_2O;$
$\qquad K_3 = K_1 \cdot K_2$

The equilibrium for the water-gas reaction is obtained, as we know, from the equations for the combustion of hydrogen and of carbon monoxide in oxygen. (Tables 6, 7, 8.)

Table 6

Equilibrium Constants for the Hydrocarbon Synthesis

Equilibrium Constant ($\log K_1$) =

Temp. °C	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_6H_{14}	C_8H_{18}
100	-6.37	-2.24	-0.85	-0.35	+0.55	+0.88
200	-3.97	-0.58	+0.50	+0.82	+1.53	+1.86
300	-2.39	+0.49	+1.38	+1.58	+2.26	+2.50
400	-1.29	+1.24	+2.00	+2.11	+2.75	+2.94

Table 7

Equilibrium Constants for the Water-gas Reaction

°C	100	200	300	400
$\log K_2$	-11.32	-7.35	-4.76	-2.94

Table 8

Equilibrium Constants for the Fischer-Tropsch Synthesis

Equilibrium Constant ($\log K_3 = \log K_1 + \log K_2$) =

Temp. °C	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_6H_{14}	C_8H_{18}
100	-17.69	-13.56	-12.17	-11.67	-10.77	-10.44
200	-11.32	-7.93	-6.85	-6.53	-5.77	-5.49
300	-7.15	-4.27	-3.38	-3.18	-2.50	-2.26
400	-4.23	-1.70	-0.94	-0.83	-0.19	0.

These values make it possible to establish the composition at equilibrium for a given temperature, and hence to calculate the gas yield of the synthesis, and to determine the effect of changes in composition of the synthesis gas.

The equilibrium constant for temperatures intermediate to those given in the tables is obtained by linear interpolation in a logarithmic hyperbolic coordinate system where the relation of equilibrium constant to temperature is represented by the straight line:

$$\log K_p = -\frac{A}{T} + B$$

For instance, in calculating the equilibrium constant for octane at 180°C. the values for 100°C. and 200°C. are taken from Table 3, as follows:

100°C.	$T_1 = 373°K.$	$\log K_1 = -10.44$
200°C.	$T_2 = 473°K.$	$\log K_2 = -5.49$

Substituting in the equation for $\log K_p$, we have

$$B = \frac{T_2 \log K_2 - T_1 \log K_1}{T_2 - T_1} = 12.97$$

$$A = 8732$$

$$\log K_p = -\frac{8732}{T} + 12.97$$

for 180°C. (corresponding to $T = 453°K.$) we have

$$\log K_p = -6.31 \ (180°C.) \ \text{for octane.}$$

In the same way, using the values

$$B = 12.64$$
$$A = 9067$$

we find that for butane

$$\log K_p = -\frac{9067}{T} + 12.64$$

which for 180°C. (corresponding to $T = 453°K.$) gives

$$\log K_p = -7.375 \ (180°C.) \ \text{for butane.}$$

The algebraic average of the values for 100°C. and 200°C. leads to erroneous values (-6.49 for octane, -7.56 for butane).

SYNTHESIS OF BUTANE BY THE FISCHER-TROPSCH REACTION

In studying the processes that accompany the conversion of carbon monoxide, it has been found desirable to establish a scheme of the reaction that may be applied to all cases. Since we propose to examine a series of hydrocarbons (immediate consideration being given only to the paraffins in Table 8) all reactions are based upon one gram atom of CO or one volume of CO. For example,

$$(4) \quad CO + \frac{9}{4} H_2 = \frac{1}{4} C_4H_{10} + H_2O$$

with

$$(5) \quad K_p = \frac{p_{CO} \cdot p_{H_2}^{\frac{9}{4}}}{p_{H_2O} \cdot p_{C_4H_{10}}^{\frac{1}{4}}}$$

The course of the synthesis is, therefore, presented as follows:

Reaction Scheme 1

Gas Parts by volume	I Introduced	II Reacted	III Final composition
CO	1	$-x$	$1-x$
H_2	$\frac{9}{4}$	$-\frac{9}{4}x$	$\frac{9}{4}(1-x)$
C_4H_{10}	--	$+\frac{1}{4}x$	$\frac{1}{4}x$
H_2O	--	$+x$	x
S	$\frac{13}{4}$	$-2x$	$\frac{13}{4} - \frac{8}{4}x$

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From the value of x we obtain directly the yield of hydrocarbon based on carbon monoxide, i.e., the amount of carbon monoxide converted into hydrocarbon in the course of the synthesis, divided by the amount of carbon monoxide originally introduced. This definition of the yield may be used as an experimental standard.

It now becomes necessary to express the partial pressures in the formula for equilibrium constant (5) in terms of parts by volume.

$$(6) \quad P_{CO} = \frac{(CO)}{(S)}; \quad P_{H_2} = \frac{(H_2)}{(S)}; \quad P_{C_4H_{10}} = \frac{(C_4H_{10})}{(S)}; \quad P_{H_2O} = \frac{(H_2O)}{(S)}$$

Values for the parts by volume are derived from the reaction scheme and substituted in equation 5.

$$(7) \quad K_p = \frac{(CO)(H_2)^{\frac{9}{4}}}{(C_4H_{10})^{\frac{1}{4}}(H_2O)(S)^2}$$

$$(8) \quad K_p = \frac{(1-x)\left[\frac{9}{4}(1-x)\right]^{\frac{9}{4}}}{\frac{1}{4}x\left[\frac{1}{4}(13-8x)\right]^2}$$

Therefore,

$$(9) \quad K_p^4 = \frac{2^9(1-x)^{13}}{5}x(13-8x)^8$$

A logarithmic equation can be obtained from which x may be determined by approximate methods.

(10) $4 \log K_p - 9 \log 9 = 13 \log (1-x) - 5 \log x - 8 \log (13-8x)$

Let us apply equation 10 to one of the examples cited by Eucken (see page 2). The value for the equilibrium constant given by Eucken as -7.73 for a temperature of 349°C. (622°K.) corresponds to our value of $4 \log K_p$, making the numerical value of the left-hand member of equation 10

$$4 \log K_p - 9 \log 9 = -7.73-8.59 = -16.32$$

In the right-hand member of equation 10 we now set

$$x = 0.90; \ 0.86; \ 0.82; \ 0.84$$

and in this way the calculated value for the left-hand member approaches closer and closer to the known value of the right-hand member; an accurate determination is obtained by linear interpolation between the two best values.

$-16.32 =$	$13 \log (1-x)$	$-5 \log x$	$-8 \log (13-8x)$
for $x = 0.90$	0.0000-13	+0.2290	-6.1072 = -18.88
" $x = 0.86$	1.8990-13	+0.3270	-6.2940 = -17.07
" $x = 0.82$	3.3190-13	+0.431	-6.647 = -15.72
" $x = 0.84$	2.653 -13	+0.378	-6.384 = -16.35

For $x = 0.84$ the agreement between the calculated value (-16.35) and the estimated figure (-16.32) is almost complete.

By linear interpolation between the values $x = 0.84$ and $x = 0.82$ we obtain the exact value

$$x = 0.839$$

The result of the reaction is found in reaction scheme 2:

Reaction Scheme 2

Gas Parts by volume	I Introduced	II Reacted	III Final composition
CO	1	0.839	0.161
H_2	2.25	-1.888	0.362
C_4H_{10}	--	+0.210	0.210
H_2O	--	+0.839	0.839
S	3.25	-1.678	1.572

Gas composition

	calculated (percent)	according to Eucken
CO	10.24	10
H_2	23.05	22.5
C_4H_{10}	13.34	13.5
H_2O	53.37	54.0
S	100.00	100.00

yield: $100 x = 83.9\%$

$$\left[\frac{(100)(13.5)}{10.0 + 13.5} = 57.5\%\right] \text{ according to Eucken.}$$

The yield, based on carbon monoxide, (i.e., the amount of carbon monoxide in parts by volume transformed into hydrocarbons, which is equal to 100 x percent) may, as shown above, be read directly from the reaction scheme. Eucken gives as "yield, based on carbon monoxide," the parts by volume of butane vapor present in 100 parts of carbon monoxide + butane vapor after the reaction. This definition of the yield is misleading and is of no value to the experimentalist.

Since the preceding example, taken from Eucken, has given a sufficient illustration of the mathematical process, the equilibrium of butane with carbon monoxide and hydrogen will now be studied for those temperatures at which it takes place in actual practice, i.e., for 180 - 200°C.

At 200°C.

$$\log K_p = -6.53 \quad (\text{Table } 8)$$

Equation 10, therefore, takes the following form:

$-34.71 =$	$13 \log (1-x)$	$-5 \log x$	$-8 \log (13-8x)$
for x = 0.990..	0.0000-26	-0.021	-5.647 - 31.625
0.995..	9.087 -39	-0.011	-5.619 - 35.521
0.994..	10.117 -39	-0.013	-5.624 - 34.493

By linear interpolation between 0.994 and 0.995 we obtain

$$x = 0.9942$$
$$100x = 99.42\%$$

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In other words the reaction is almost complete, the equilibrium being displaced towards the formation of the hydrocarbon from carbon monoxide and hydrogen. The composition of the reaction product is determined from reaction scheme 3.

Reaction Scheme 3

Gas Parts by volume	I Introduced	+ II Reacted	= III Final Composition	Percent
CO	1	-0.9942	0.0058	0.46
H_2	2.25	-2.2370	0.0130	1.03
C_4H_{10}	--	+0.2486	0.2486	19.71
H_2O	--	+0.9942	0.9942	78.80
S	3.25	-1.9884	1.2616	100.00

Because of the shift in equilibrium changes in the composition of the synthesis gas - with reference to the equilibrium - have only a minor effect on the yield. A decrease in the equilibrium temperature to 180°C. occasions an increase to only 99.69% as against 99.42% for 200°C.

Effect of Introducing an Inert Gas

The presence of 2 parts by volume of N_2 in 13 parts by volume of synthesis gas gives rise to the following reaction scheme:

Reaction Scheme 4

Gas Parts by volume	I Introduced	+ II Reacted	= III Final Composition
CO	1	-- x	1-x
H_2	2.25	-2.25x	2.25(1-x)
C_4H_{10}	--	+0.25x	0.25x
H_2O	--	+x	x
N_2	0.5	--	0.5
S	3.75	-2.00x	3.75-2.00x

Equation (10) now assumes the following form:

$$4 \log K_p - 9 \log 9 = 13 \log (1-x) - 5 \log x - 8 \log (15-8x)$$

at 180°C. $- 38.11 = 13 \log (1-x) - 5 \log x - 8 \log (15-8x)$

From this equation $x = 0.9961$, as against 0.9969 for the nitrogen-free gas.

Effect of Introducing Water Vapor

The effect on the yield of two and four parts by volume of water vapor, respectively, in 13 parts by volume of synthesis gas are next examined.

Reaction Scheme 5

Gas Parts by volume	I Introduced	II Reacted	III Final composition
CO	1	$-x$	$1-x$
H_2	2.25	$-2.25x$	$2.25(1-x)$
C_4H_{10}	--	$+0.25x$	$0.25x$
H_2O	0.5	$+x$	$(0.5+x)$
S	3.75	$-2.00x$	$3.75-2.00x$

Substituting in equation (8) we obtain:

$$K_p = \frac{(CO)(H_2)^{\frac{9}{4}}}{(C_4H_{10})^{\frac{1}{4}}(H_2O)(s)^2} = \frac{(1-x)\left[\frac{9}{4}(1-x)\right]^{\frac{9}{4}}}{\frac{1}{4}x^{\frac{1}{4}}(0.5+x)\left[\frac{1}{4}(15-8x)\right]^2}$$

$$K_p^4 = \frac{9^9(1-x)^{13}}{x(0.5+x)^4(15-8x)^8}$$

Equation (10) now becomes

$$4 \log K_p - 9 \log 9 = 13 \log (1-x) - \log x - 4 \log (0.5+x) - 8 \log 15-8x)$$

At 180°C.

$$-38.11 = 13 \log (1-x) - \log x - 4 \log (0.5+x) - 8 \log (15-8x)$$

from which

$$x = 0.9956$$
$$100x = 99.56\%$$

Doubling the quantity of water vapor (4 p.b.v. water vapor) in (4 p.b.v. CO + 9 p.b.v. H_2)

gives

$$- 38.11 = 13 \log (1-x) - \log x - 4 \log (1+x) - 8 \log (17-8x)$$

$$x = 0.9944$$
$$100x = 99.44\%$$

Summarizing for the synthesis of butane by the Fischer-Tropsch reaction we find that at equilibrium:

At 200°C., using pure synthesis gas	yield 99.42%
" 180°C., " " " "	" 99.69%
" 180°C., using synthesis gas + 1 p.b.v.(part by volume) N_2 per 2 p.b.v. CO	" 99.61%
" 180°C., using synthesis gas + 1 p.b.v. H_2O per 2 p.b.v. CO	" 99.56%
" 180°C., using synthesis gas + 1 p.b.v. H_2O per 1 p.b.v. CO	" 99.44%

Owing to the notable shift of equilibrium in the direction of the synthesis, differences in yield are small. Nevertheless, the specific action of additions (N_2, H_2O) is evident. Moreover, it should be observed that 4 p.b.v. CO + 9 p.b.v. H_2 + 4 p.b.v. H_2O, namely, 1 p.b.v. H_2O/1 p.b.v. CO, corresponds to a water vapor saturation of the synthesis gas at 64°C.

Although for a yield of 99.69%, the possible range of affect is small, we will now examine the effect of excess hydrogen (5.5%) on the equilibrium shift for butane at 180°C.

Reaction Scheme 6

Gas Parts by volume	I Introduced	II Reacted	III Final composition
CO	1	$-x$	$1-x$
H_2	$2.25+0.125$	$-2.25x$	$2.375-2.25x$
C_4H_{10}	--	$+0.25x$	$0.25x$
H_2O	--	$+x$	x
S	3.375	$-2x$	$3.375-2x$

(8a) $\quad K_p = \dfrac{(1-x)(2.375-2.25x)^{\frac{9}{4}}}{(0.25x)^{\frac{1}{4}}x(3.375-2x)^2}$

(9a) $\quad K_p{}^4 = \dfrac{9^9(1-x)^4(1.0556-x)^9}{x^5(13.5-8x)^8}$

(10a) $\quad 4 \log K_p - 9 \log 9 = -34.71 =$

	$4 \log (1-x)$	$+9 \log (1.0556-x)$	$-5 \log x$	$-8 \log (13.5-8x)$	
$x = 0.997$	$1.9084-12$	$+6.9111-18$	$+0.0065$	$-5.9380 =$	$-37.???$
$x = 0.999$	$0.0000-12$	$+6.7754-18$	$+0.0021$	$-5.9260 =$	$-39.???$
$x = 0.9999$	$0.0000-16$	$+6.7126-18$	$+0.0002$	$-5.9245 =$	$-33.???$
$x = 0.99995$	$2.7959-20$	$+6.7092-18$	$+0.0001$	$-5.9231 =$	-34.413
$x = 0.99996$	$2.4032-20$	$+6.7085-18$	$+0.0001$	$-5.9231 =$	$-34.???$

$$\underline{100\ x = 99.996\%}$$

The mathematical method, whose effectiveness is particularly well illustrated in this instance, therefore, shows that for a 5.5% excess of hydrogen an increase in yield from
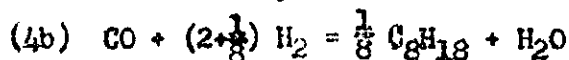
$$99.69\ \text{to}\ 99.996\%$$

is observed.

In this way a small excess of hydrogen results in a complete shift of equilibrium to the right.

Thus, calculations of the equilibrium for butane at 180°C. demonstrate the effect of various changes in composition of the synthesis gas. The actual effects remain small, since for all cases considered the equilibrium at 180°C. lies almost completely to the right. Conditions, which by their very nature, throw into sharper relief the effect on the yield of octane changes in composition of the synthesis gas will be studied in the following section.

SYNTHESIS OF OCTANE BY THE FISCHER-TROPSCH REACTION

The equilibrium for octane will now be examined according to the method already used for the butane equilibrium.

(4b) $\quad CO + (2+\frac{1}{8}) H_2 = \frac{1}{8} C_8H_{18} + H_2O$

Reaction Scheme 7

Gas Parts by volume	I Introduced	II Reacted	III Final composition
CO	1	$-x$	$1-x$
H_2	$\frac{17}{8}$	$-\frac{17}{8}x$	$\frac{17}{8}(1-x)$
C_8H_{18}	--	$+\frac{1}{8}x$	$\frac{1}{8}x$
H_2O	--	$+x$	$+x$
S	$\frac{25}{8}$	$-2x$	$\frac{25}{8} - 2x$

(7b) $\quad K_p = \dfrac{(CO)(H_2)^{\frac{17}{8}}}{(C_8H_{18})^{\frac{1}{8}}(H_2O)(S)^2}$

(8b) $\quad K_p = \dfrac{(1-x)\left[\frac{17}{8}(1-x)\right]^{\frac{17}{8}}}{(\frac{1}{8}x)^{\frac{1}{8}}\left[\frac{1}{8}(25-16x)\right]^2}$

(9b) $\quad K_p^8 = \dfrac{17^{17}(1-x)^{25}}{x(25-16x)^{16}}$

(10b) $\quad 8 \log K_p - 17 \log 17 = 25 \log (1-x) - 9 \log x - 16 \log (25-16x)$

At 200°C. log K_p = -5.49

Equation (10b) therefore takes the following form:

$$8 \log K_p - 17 \log 17 = -64.838$$

-64.838 =	25 log (1-x)	-9 log x	-16 log (25-16x)	
for x = 0.990	0.0000-50	+0.0396	-15.3904 =	-65.351
" x = 0.985	4.2900-50	+0.0594	-15.4512 =	-61.102
" x = 0.988	1.9800-50	+0.0468	-15.4144 =	-63.383

100x = 98.95%

At 180°C. log K_p = -6.31

Equation (10b) therefore takes the following form:

$$8 \log K_p - 17 \log 17 = -71.398$$

-71.398 =	25 log (1-x)	-9 log x	-16 log (25-16x)	
for x = 0.995	14.975-75	+0.0196	-15.3296 =	-75.335
" x = 0.993	21.1275-75	+0.0279	-15.3462 =	-69.391

100x = 99.37%

Comparing with butane

	Butane	Octane
200°C.	99.42%	98.95%
180°C.	99.69%	99.37%

In order to illustrate the effect of changes in composition of the synthesis gas more effectively than can be done when the yield is very high (as for butane) the octane equilibrium at 622°K. (349°C.) for which log K_p = -1.06 has been calculated

$$8 \log K_p - 17 \log 17 = -29.3978$$

-29.3978 =	25 log (1-x)	-9 log x	-16 log (25-16x)	
for x = 0.80	7.5258-25	+0.8694	-17.3824 =	-33.987
" x = 0.70	11.9275-25	+1.3941	-18.2380 =	-29.916
" x = 0.68	12.6290-25	+1.5075	-18.3973 =	-29.261

By linear interpolation

100x = 68.3%

Reaction Scheme 8 (Octane 622°K.)

Gas Parts by volume	I Introduced	II Reacted	III Final composition	Percent
CO	1	-0.6830	0.3170	18.02
H$_2$	2.125	-1.4510	0.6740	38.31
C$_8$H$_{18}$	--	+0.0854	0.0854	4.85
H$_2$O	--	+0.6830	0.6830	38.82
S	3.125	-1.3656	1.7594	100.00

Effect of Introducing Inert Gas (Octane 622°K.)

1 p.b.v. N$_2$ in 2 p.b.v. CO., corresponding to 4 p.b.v. N$_2$ in 25 p.b.v. synthesis gas.

Equation (10b) assumes the following form:

-29.3978 =	25 log (1-x)	-9 log x	-16 log (29-16x)
for x = 0.66	13.2875-25	+1.6839	-20.2522 = -30.282
" x = 0.63	14.2050-25	+1.8059	-20.4307 = -29.420

100x = 62.9%

Reaction Scheme 9 (Octane 622°K.)

(1 p.b.v. N$_2$ in 2 p.b.v. CO)

Gas Parts by volume	I Introduced	II Reacted	III Final composition	Percent
CO	1	-0.629	0.371	15.67
H$_2$	2.125	-1.3366	0.7884	33.31
C$_8$H$_{10}$	--	+0.0786	0.0786	3.32
H$_2$O	--	+0.629	0.629	26.57
N$_2$	0.50	--	0.50	21.13

<u>Effect of Introducing Water Vapor</u> (Octane 622°K.)

1 p.b.v. H₂O in 2 p.b.v. CO corresponding to 4 parts by
volume water vapor in 25 parts by volume synthesis gas.

−29.398 =	25 log (1−x)	−log x	−8 log (0.5+x)	−16 log (29−16x)	
for x = 0.63	14.2050−25	+0.2007	−0.4246	−20.4307 =	−31.450
" x = 0.58	15.5813−25	+0.2366	−0.2674	−20.7186 =	−30.405
" x = 0.55	16.3303−25	+0.2596	−0.1695	−20.8856 =	−29.465
" x = 0.54	16.5700−25	+0.2676	−0.1362	−20.9405 =	−29.2391

By linear interpolation

<u>100x = 54.7%</u>

<u>Reaction Scheme 10 (Octane 622°K.)</u>

(1 p.b.v. H₂O in 2 p.b.v. CO)

Gas Parts by volume	I Introduced	II Reacted	III Final composition	Percent
CO	1	−0.547	0.453	17.90
H₂	2.125	−1.1624	0.9626	38.03
C₈H₁₈	—	+0.0684	0.0684	2.70
H₂O	0.5	+0.547	1.047	41.37
S	3.625	−1.094	2.531	100.00

Doubling the quantity of water vapor (1 p.b.v. H₂O in 1 p.b.v.
CO corresponding to 8 parts by volume water vapor in 25 parts by volume
synthesis gas) gives

−29.398 =	25 log (1−x)	−log x	−8 log (1.0+x)	−16 log (33−16x)	
for x = 0.50	17.4743−25	+0.3010	−1.4087	−22.3670 =	−31.030
" x = 0.46	18.3100−25	+0.3372	−1.3148	−22.5427 =	−30.210
" x = 0.42	19.0858−25	+0.3767	−1.2203	−22.7141 =	−29.472
" x = 0.41	19.2713−25	+0.3872	−1.1938	−22.7614 =	−29.297

<u>100x = 41.6%</u>

Reaction Scheme 11 (Octane 622°K.)

(1 p.b.v. H$_2$O in 1 p.b.v. CO)

Gas Parts by volume	I Introduced	II Reacted	III Final composition	Percent
CO	1	−0.416	0.584	17.74
H$_2$	2.125	−0.884	1.241	37.68
C$_8$H$_{18}$	--	+0.052	0.052	1.58
H$_2$O	1.0	+0.416	1.416	43.00
S	4.125	−0.832	3.293	100.00

Effect of Excess Hydrogen

(0.125 p.b.v. H$_2$ in 1 p.b.v. CO)

Reaction Scheme 12

Gas Parts by volume	I Introduced	II Reacted	III Final composition
CO	1	−x	1−x
H$_2$	2.125+0.125	−2.125x	2.25−2.125x
C$_8$H$_{18}$	--	+0.125x	+0.125x
H$_2$O	--	+x	x
S	3.25	−2x	3.25−2x

Applying the law of mass action:

$$(7c) \quad K_p = \frac{(CO)(H_2)^{\frac{17}{8}}}{(C_8H_{18})^{\frac{1}{8}}(H_2O)(S)^2} = \frac{(1-x)(2.250-2.125x)^{\frac{17}{8}}}{(0.125x)^{\frac{1}{8}}x(3.25-2x)^2}$$

25

(9c) $K_p^8 = \dfrac{(1-x)(\frac{18}{17}-x)^{17} \cdot 17^{17}}{x^9(26-16x)^{16}}$

$K_p^8 = 17^{17} \dfrac{(1-x)^8(\frac{18}{17}-x)^{17}}{x^9(26-16x)^{16}}$

(10c) $8 \log K_p - 17 \log 17 = -29.398 =$

for	$8 \log (1-x)$	$+17 \log (1.0588-x)$	$-9 \log x$	$-16 \log (26-16x)$	
for x = 0.70	-4.1830	-7.5676	+1.3941	-18.7242 =	-29.081
" x = 0.72	-4.4227	-7.9910	+1.2840	-18.5723 =	-29.703
" x = 0.71	-4.3008	-7.7758	+1.3387	-18.6486 =	-29.387

$$100x = 71.0\%$$

Reaction Scheme 13 (Octane 622°K.)

(0.125 p.b.v. H_2 - excess in 1 p.b.v. CO)

Gas Parts by volume	I Introduced	II Reacted	III Final composition	Percent
CO	1	-0.710	0.290	15.85
H_2	2.125+0.125	-1.5088	0.7412	40.50
C_8H_{18}	--	+0.0888	0.0888	4.85
H_2O	--	+0.710	0.710	38.80
S	3.25	-1.4200	1.8300	100.00

Effect of Excess CO in the Synthesis Gas

(H_2:CO = 1.70; Octane 622°K.)

Reaction Scheme 14

Gas Parts by volume	I Introduced	+ II Reacted	= III Final composition
CO	1	$-x$	$1-x$
H_2	1.70	$-2.125x$	$1.70-2.125x$
C_8H_{18}	--	$+0.125x$	$0.125x$
H_2O	--	$+x$	x
S	2.70	$-2x$	$2.70-2x$

$$(7d) \quad K_p = \frac{(CO)(H_2)^{\frac{17}{8}}}{(C_8H_{18})^{\frac{1}{8}}(H_2O)S^2} = \frac{(1-x)(1.70-2.125x)^{\frac{17}{8}}}{(0.125x)^{\frac{1}{8}}x(2.70-2x)^2}$$

$$(9d) \quad K_p^{8} = \frac{17^{17}(1-x)^8(0.8-x)^{17}}{x^9(21.6-16x)^{16}}$$

(10d) $8 \log K_p - 17 \log 17 = -29.398 =$

	$8 \log (1-x)$	$+17 \log (0.8-x)$	$-9 \log x$	$-16 \log (21.6-16x)$
for $x = 0.60$	-3.1832	-11.7805	$+1.9962$	$-17.2672 = -30.235$
" $x = 0.57$	-2.9320	-10.8511	$+2.1969$	$-17.5393 = -29.126$
" $x = 0.58$	-3.0144	-11.1792	$+2.1494$	$-17.4500 = -29.514$

By linear interpolation

$$x = 0.577$$
$$100x = 57.7\%$$

Yield Based on Hydrogen: 72.1%

(i.e. The amount of hydrogen, in 100 parts by volume of hydrogen present in the synthesis gas, transformed by the reaction.)

Reaction Scheme 15 (Octane 622°K.)

(H$_2$:CO = 1.70)

Gas Parts by volume	I Introduced	II Reacted	III Final composition	Percent
CO	1.00	-0.577	0.423	27.36
H$_2$	1.70	-1.226	0.474	30.66
C$_8$H$_{18}$	-	+0.072	0.072	4.68
H$_2$O	-	+0.577	0.577	37.30
S	2.70	-1.154	1.546	100.00

DISCUSSION OF RESULTS

It was proposed to determine mathematically the thermodynamic properties of the Fischer-Tropsch hydrocarbon synthesis; in other words, to study the chemical equilibrium and especially to indicate how the state and composition of the synthesis gas affect the composition of the end product and influence the yield. Calculations, the general principle of which has been thoroughly discussed, were carried out for butane at 180°C. and for octane at 349°C. (622°K.). The qualitative results are the same in both cases. From a quantitative point of view, owing to the position of the equilibrium at higher temperatures, the results for octane are more striking.

Results for calculations on octane 622°K. are summarized in Table 9, which shows the effect of composition of the synthesis gas. The equilibrium was calculated for 6 cases:

(1) Pure synthesis gas with stoichiometric amounts:

1 p.b.v. CO : $\frac{17}{8}$ p.b.v. H$_2$.

(2) Synthesis gas with addition of nitrogen:
0.5 N$_2$ p.b.v. in 1 p.b.v. CO, corresponding to 13.8% N$_2$ in 100 p.b.v. synthesis gas.
(3) Synthesis gas with addition of water vapor:
0.5 p.b.v. H$_2$O in 1 p.b.v. CO, corresponding to a water vapor saturation of the synthesis gas at 59°C.
(4) Synthesis gas with addition of water vapor:
Double quantity, 1 p.b.v. H$_2$O in 1 p.b.v. CO, corresponding to a water vapor saturation of the synthesis gas at 640°C.
(5) Synthesis gas with excess hydrogen:
1 part in 17 parts H$_2$, corresponding to a 5.9% excess.
(6) Synthesis gas with excess carbon monoxide:
H$_2$:CO = 1.70, corresponding to 0.8 equivalent weight of H$_2$ per 1 equivalent CO.

Table 9 Octane 622°K.

Composition of Gas

	Stoichiometric Equivalent	13.8% N₂ Included	H₂O Vapor Saturation at 59°C. Included	H₂O Vapor Saturation at 64°C. Included	5.5% H₂ Excess Included	H₂:CO = 1.70
Synthesis Gas						
CO	1	1	1	1	1	1
H₂	2.125	2.125	2.125	2.125	2.25	1.70(2.125×0.8)
Reacted Gas						
CO	0.683	0.629	0.547	0.416	0.710	0.577
H₂	1.451	1.337	1.162	0.884	1.5088	1.226
Final Composition						
P.b.v. CO	0.317	0.371	0.453	0.584	0.290	0.423
P.b.v. H₂	0.674	0.788	0.963	1.241	0.741	0.474
P.b.v. C₈	0.0854	0.0786	0.0684	0.052	0.0888	0.072
P.b.v. H₂O	0.683	0.629	1.047	1.416	0.710	0.577
P.b.v. N₂	--	0.500	--	--	--	--
S	1.759	2.376	2.531	3.293	1.830	1.546
Percent Composition						
CO	18.0	15.7	17.9	17.7	15.8	27.4
H₂	38.3	33.3	38.0	37.7	40.5	30.6
C₈	4.9	3.3	2.7	1.6	4.9	4.7
H₂O	38.8	26.6	41.4	43.0	38.8	37.0
N₂	--	21.1	--	--	--	--
S	100.0	100.0	100.0	100.0	100.0	100.0
Yield Percent	68.3	62.9	54.7	43.6	71.0	57.7 [1] (72.3)

1/ Based on H₂.

(1) Pure synthesis gas, containing stoichimetric amounts of CO and H_2, at the high temperature of 622°K. (349°C.) gives a yield of 68.3%.

(2) The presence of inert gases in the synthesis gas (13.8% N_2) causes a decrease in yield, as evidenced by a drop from 68.3% to 62.9%.

(3) The water vapor content of the synthesis gas has a specific effect. For a water vapor saturation of the synthesis gas at 59°C., corresponding to a water vapor content in the synthesis gas of 13.8 parts in 100 parts, a diminished yield of 54.7% is observed, as against 62.9% for the same nitrogen content and 68.3% for the pure synthesis gas.

(4) When the water vapor content doubles (64°C. water vapor saturation point), the yield falls to 41.6%, almost a third of what it is in the pure synthesis gas.

(5) Even for only a slight excess of hydrogen an increase in yield is observed: 71.0% as against 68.3% for equivalent amounts.

(6) For an excess of carbon monoxide in the synthesis gas corresponding to an $H_2:CO = 1.70$ ratio, i.e., to a ratio of

1 equivalent CO to 0.8 equivalent H_2

we find, as was to be expected, that the yield based on carbon monoxide decreases. However, the yield based on hydrogen rises to 72.1% as compared with 68.3% for equivalent amounts of CO and H_2 in the synthesis gas. Nevertheless, the improvement in yield for an excess of CO is less significant than for an excess of hydrogen, which is effective even in small quantities.

The essential mathematical evidence has thus been presented.

CONCLUSION

(1) Equilibrium constants for products of the Fischer-Tropsch synthesis (paraffin hydrocarbons) are given and their dependence on temperature shown.

(2) A simple mathematical procedure for the calculation of equilibria and the evaluation of effects produced by changes in composition of the synthesis gas is developed, based on the use of reaction schemes and logarithmic equations.

(3) Equilibrium of the butane synthesis is studied at different
temperatures and the effect of changes in composition of the
synthesis gas at 180°C. is calculated (inert gases, water
vapor content, excess hydrogen, and carbon monoxide).

(4) Equilibrium of the octane synthesis is studied at various
temperatures and effect of changes in composition of the
synthesis gas at 349°C. (622°K.) is calculated (inert gases,
water vapor content, excess hydrogen, and carbon monoxide).

Experimental results are summarized and discussed.

Essen, Feb. 19, 1944.