Translations of German Documents on Mathematical Expressions

for Thermodynamic Relationships and the Calculation

of Yields in the Fischer-Tropsch Synthesis

By

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FOREWORD

This report is one of a series in the process of compilation at the Office of Synthetic Liquid Fuels, United States Bureau of Mines, Pittsburgh, Pennsylvania. Translations of seized German scientific documents are being prepared and grouped in reports according to subject. Two groups of translations concerning Fischer-Tropsch iron catalysts have been issued. These are: "Translations of German Documents on the Development of Iron Catalysts for the Fischer-Tropsch Synthesis - Part I" which includes the following documents:

    TOM Reel 101, Document PG-21559-NID

    TOM Reel 101, Document PG-21574-NID

    TOM Reel 101, Document PG-21581-NID

    TOM Reel 101, Document PG-21577-NID

"Translations of German Documents on the Development of Iron ysts for the Fischer-Tropsch Synthesis - Part II", which includes llowing documents:

    TOM Reel 101, Document PG-21576-NID

    TOM Reel 101, Document PG-21578-NID

    TOM Reel 101, Document PG-21579-NID

    TOM Reel 134, Navy 5811, Item Ib-23 (First Half)

    TOM Reel 86, Bag 3979, Item 78.

The present report includes information on thermodynamic relationships and the calculation of yields from gas consumption

data in the Fischer-Tropsch Synthesis, described in the following documents:

TOM Reel 134, Navy 5811, Item Ib-1

TOM Reel 134, Navy 5811, Item Ib-2

TOM Reel 134, Navy 5811, Item Ib-3

TOM Reel 134, Navy 5811, Item Ib-4.

TOM REEL NO. 134, NAVY 5831, ITEM Ib-1

THERMODYNAMIC EXPRESSIONS FOR THE FORMATION AND

STABILITY OF HYDROCARBONS

SUMMARY

The temperature range for which the formation from $CO + H_2$ of various hydrocarbons (saturated and unsaturated) is possible is determined from consideration of the free energies of formation of the reactants and products. Calculations are carried over a range of pressures between 1 and 100 atmospheres. The conditions of thermodynamic stability are applied to consideration of condensation and decomposition reactions.

THEORETICAL CONSIDERATIONS

The expressions are derived from the free energies of formation as represented in graphs 1 to 7 (these free energy values are taken from Parks and Huffman, Free Energies of Some Organic Compounds, New York, 1932). The difference in energies of formation indicates whether a reaction is possible. When the difference is equal to zero, the reaction is at equilibrium (equilibrium constant = 1).

In order to represent conditions at higher pressures, the standard method of referring free energy to atmospheric pressure has been extended to include the "free energy at 100 atmospheres" in addition to the usual expression, "free energy at 1 atmosphere". When the "free energy at 100 atmospheres" equals zero, the corresponding equilibrium constant, $100 K_p$, equals 1. This means that 100 atmospheres are to be taken as unit pressure.

For example

Methane,	at 25 atmospheres	$P_{CH_4} = 0.25$
H_2O vapor,	at 25 atmospheres	$P_{H_2O} = 0.25$
Carbon monoxide,	at 50 atmospheres	$P_{CO} = 0.50$
Hydrogen,	at 50 atmospheres	$P_{H_2} = 0.50$

$$100 K_p = \frac{(0.25)(0.25)}{(0.5)(0.5)^3} = 1 \text{ (free energy at 100 atmospheres = 0)}$$

Thus, the zero value of "free energy at 100 atmospheres", indicates average conversion for pressures of less than 100 atmospheres.

Figure 1 gives the energy for formation $\left(\frac{F_{form}}{n}\right)$ at 1 atmosphere of several paraffin hydrocarbons and of ethylene (based on one C-atom).

$$n(c) + m H_2 = C_nH_{2m}; \quad F_{form.}$$
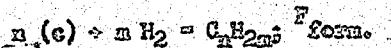
Curves A and B are used in calculating the formation of these hydrocarbons from the CO-H_2 mixture.

$$A. \quad (C) + H_2O = CO + H_2; \quad F_A$$
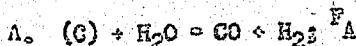
The free energy of synthesis of a hydrocarbon formed from CO + H_2 is equal to the difference between curve A and the hydrocarbon curve. Formation of the hydrocarbon is possible as long as its curve remains below the A curve.

$$(C) + \frac{1}{n} H_2 = \frac{1}{n} C_nH_{2m}; \quad \frac{F_{form}}{n} \qquad \text{(hydrocarbon curve)}$$

Subtract $\quad (C) + H_2O = CO + H_2; \quad F_A \qquad \text{(curve A)}$

$$CO + \frac{m+n}{n} H_2 = \frac{1}{n} C_nH_{2m} + H_2O; \quad \frac{F_{form}}{n} - F_A$$

$$n\,CO + (m+n)\, H_2 = C_nH_{2m} + nH_2O$$
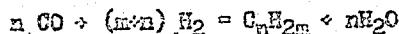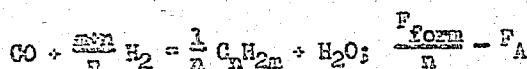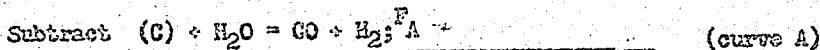
The synthesis formula in this case is based on one atom of carbon. The formula based on 1 molecule reads as follows:

$$n\,CO + (m+n)\, H_2 = C_nH_{2m} + nH_2O.$$
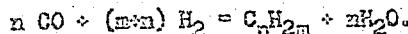
The oxygen fraction of CO is present here as water. It could also be present as CO_2. The free energy of the latter reaction is given by the difference from the B curve, corresponding to reaction B:

$$B. \quad (C) + CO_2 = 2CO; \qquad F_B$$

$$(C) + \frac{n}{n} H_2 = \frac{1}{n} C_nH_{2m}; \quad \frac{F_{form}}{n}$$

Subtract $\quad (C) + CO_2 = 2CO; \qquad F_B$

$$2CO + \frac{n}{n} H_2 = \frac{1}{n} C_nH_{2m} + CO_2; \quad \frac{F_{form}}{n} - F_B$$

$$2n\,CO + m\, H_2 = C_nH_{2m} + n\,CO_2.$$
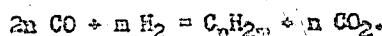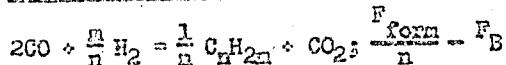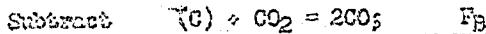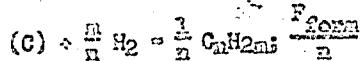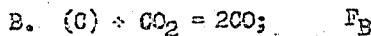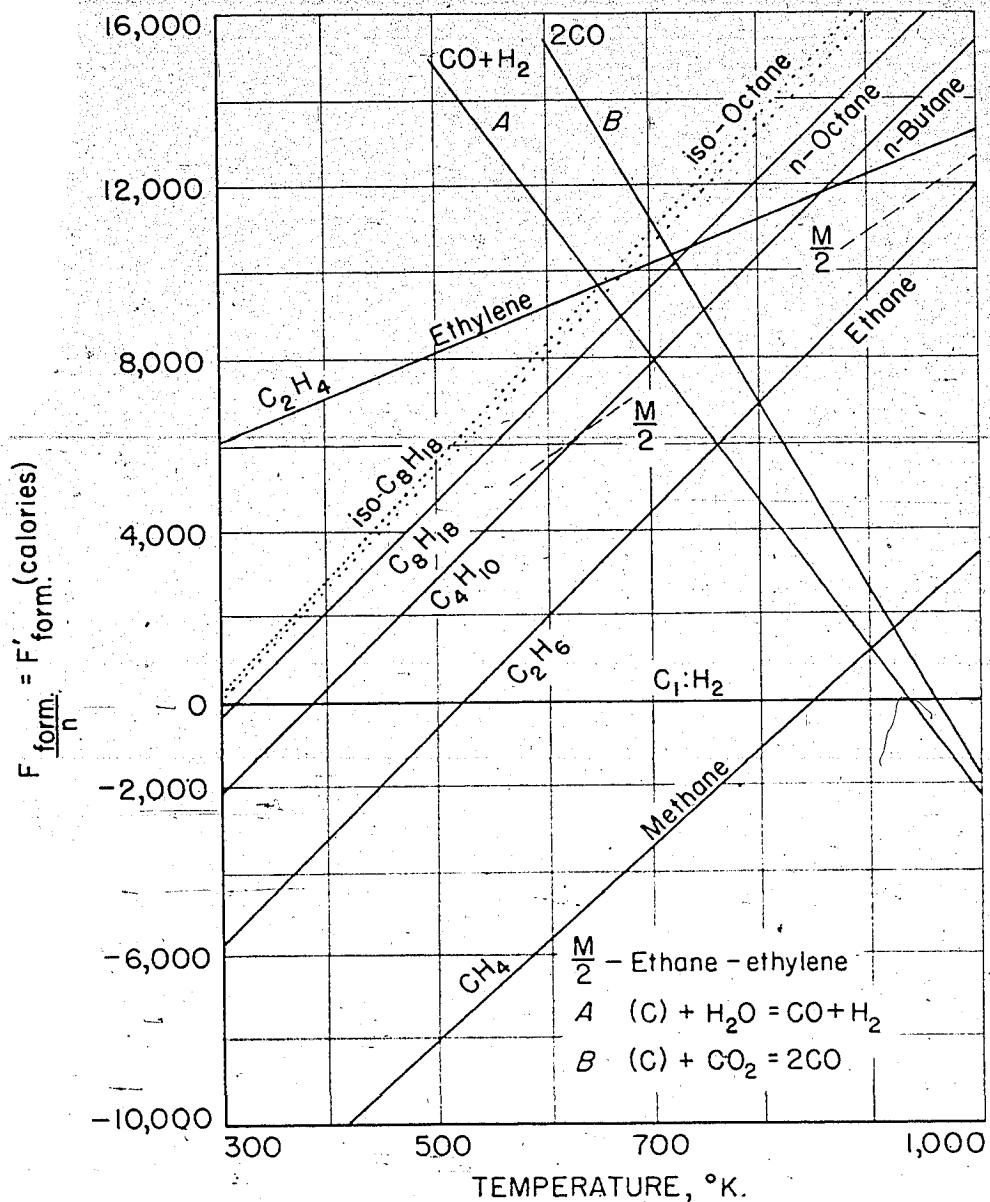
Figure I.— Free energy of formation of several paraffin hydrocarbons
at I atmosphere.

APPLICATIONS

Inspection of figure 1 shows that all hydrocarbons may be formed from CO + H_2, below certain temperatures. The limiting temperatures for several hydrocarbons, for which the free energy becomes equal to zero, are shown in Table 1.

Table 1

Limiting Temperatures for Hydrocarbon Synthesis from CO + H_2
(Free Energy at 1 Atmosphere Equals Zero)

Hydrocarbon	Temperature for Reaction to HC* + H_2O		Temperature for Reaction to HC* + CO_2	
	°K	°C	°K	°C
n-octane	675	400	725	450
methane	900	625	920	645
ethylene	655	380	220	445

*HC = hydrocarbon.

The intersection of the ethylene curve with the ethane curve shows that the zero point for the dehydrogenation of ethane according to the equation,

$$C_2H_6 = C_2H_4 + H_2$$
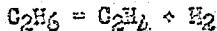
is at 1030°K. = 805°C. for 1 atmosphere.

Figure 2 gives the free energies of formation for the same hydrocarbons at 100 atmospheres. Compared with figure 1, the displacement of the curves in calories is given by the equation

$$F_{100\ atm.} - F_{1\ atm.} = \Delta\gamma\ RT \ln 100 = (\Delta\gamma)(T)(4.573)(2)$$

where $\Delta\gamma$ is the change in number of molecules in the gas.

For paraffin hydrocarbons $\Delta\gamma$ equals 1, since

$$(C) + \frac{n+1}{n} H_2 = \frac{1}{n} C_n H_{2n+2}; \quad \Delta\gamma = 1$$

For ethylene $\Delta\gamma$ equals 1/2.

For olefins and naphthenes in general $\Delta\gamma = \frac{n-1}{n}$

For benzene $\Delta\gamma = 1/3$.

For curves A and B $\Delta\gamma = -1$.

3
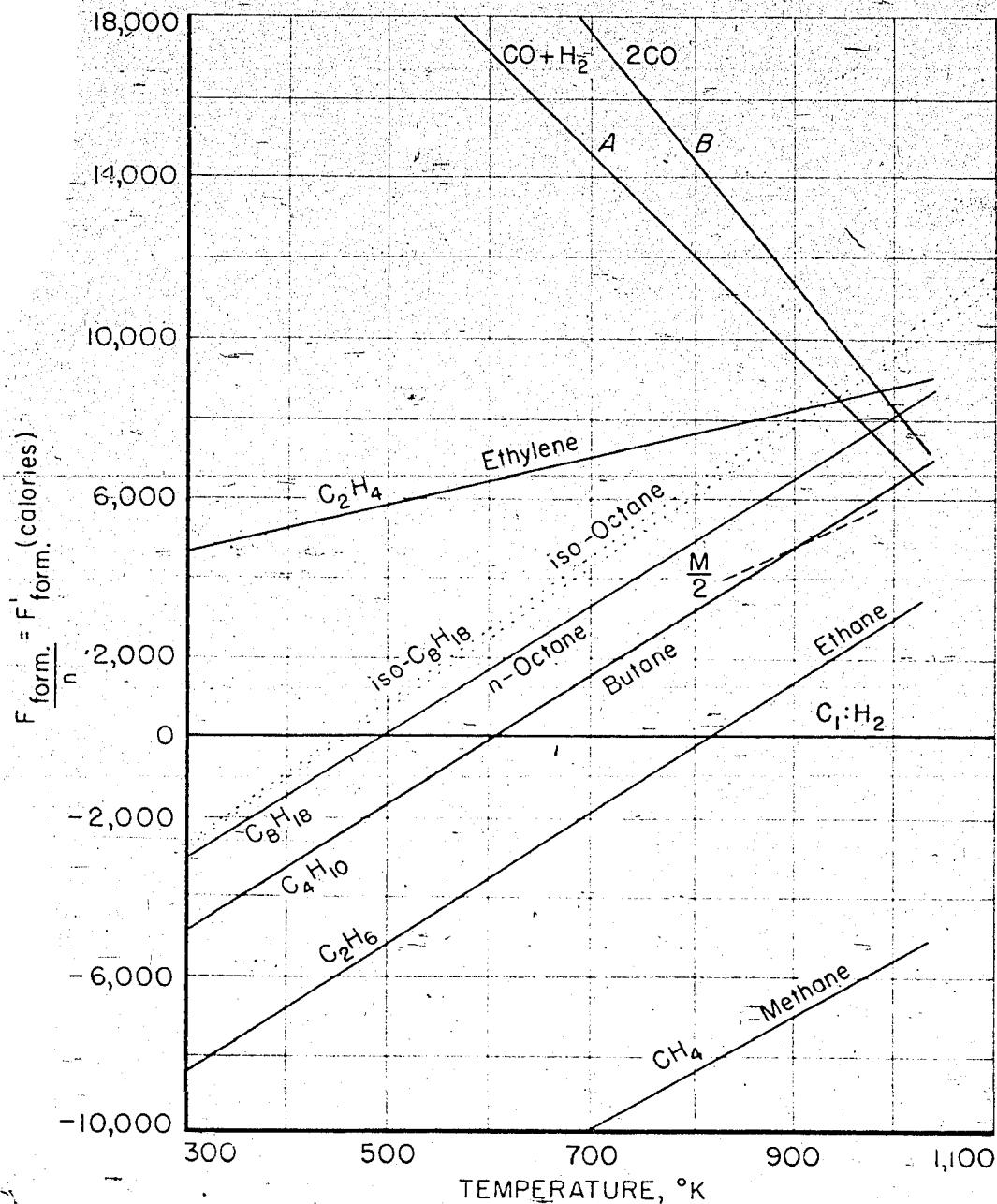
Figure 2.- Free energy of formation of several paraffin hydrocarbons at 100 atmospheres.

The increase in pressure immediately results in an increase in the stability of the hydrocarbons towards C and H_2. That the tendency towards hydrocarbon formation from $CO + H_2$ is increased is shown by the fact that the A and B curves are displaced in the opposite direction. Consequently, the limiting temperatures are higher at 100 atmospheres, as shown in Table 2.

Table 2

Limiting Temperatures for Hydrocarbon Synthesis from $CO + H_2$

(Free Energy at 100 Atmospheres Equals Zero)

Hydrocarbon	Temperature for Reaction to $HC^* + H_2O$		Temperature for Reaction to $HC^* + CO_2$	
	°K	°C	°K	°C
n-octane	975	700	1000	725
methane	about 1300	about 1000	about 1300	about 1000
ethylene	945	670	965	710

*HC = hydrocarbon.

Figures 3 and 4 give the free energy of formation for benzene and for cyclohexane at 1 and 100 atmospheres, respectively. Tables 3 and 4 summarize the data.

Table 3

Limiting Temperatures for Hydrocarbon Synthesis from $CO + H_2$

(Free Energy at 1 Atmosphere Equals Zero)

Hydrocarbon	Temperatures for Reaction to $HC^* + H_2O$		Reaction to $HC^* + CO_2$		Hydrogenation or Dehydrogenation	
	°K	°C	°K	°C	°K	°C
benzene	710	435	770	495	545	270
cyclohexane	660	385	715	440		

*HC = hydrocarbon.

Table 4

Limiting Temperatures for Hydrocarbon Synthesis from $CO + H_2$

(Free Energy at 100 Atmospheres Equals Zero)

Hydrocarbon	Temperatures for Reaction to $HC^* + H_2O$		Reaction to $HC^* + CO_2$		Hydrogenation or Dehydrogenation	
	°K	°C	°K	°C	°K	°C
benzene	1005	730	1040	765	760	485
cyclohexane	935	660	970	695		

*HC = hydrocarbon.
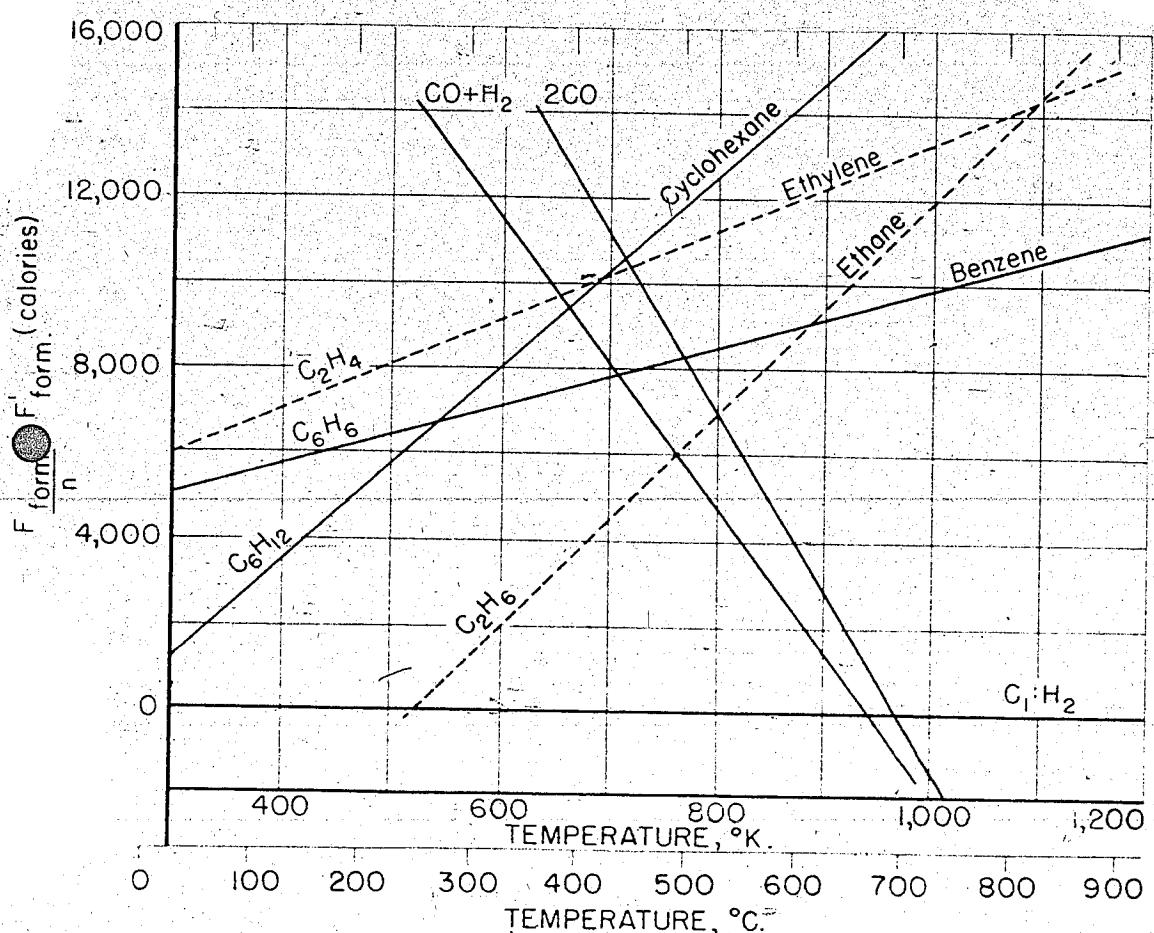
Figure 3.— Free energy of formation of benzene and cyclohexane at 1 atmosphere
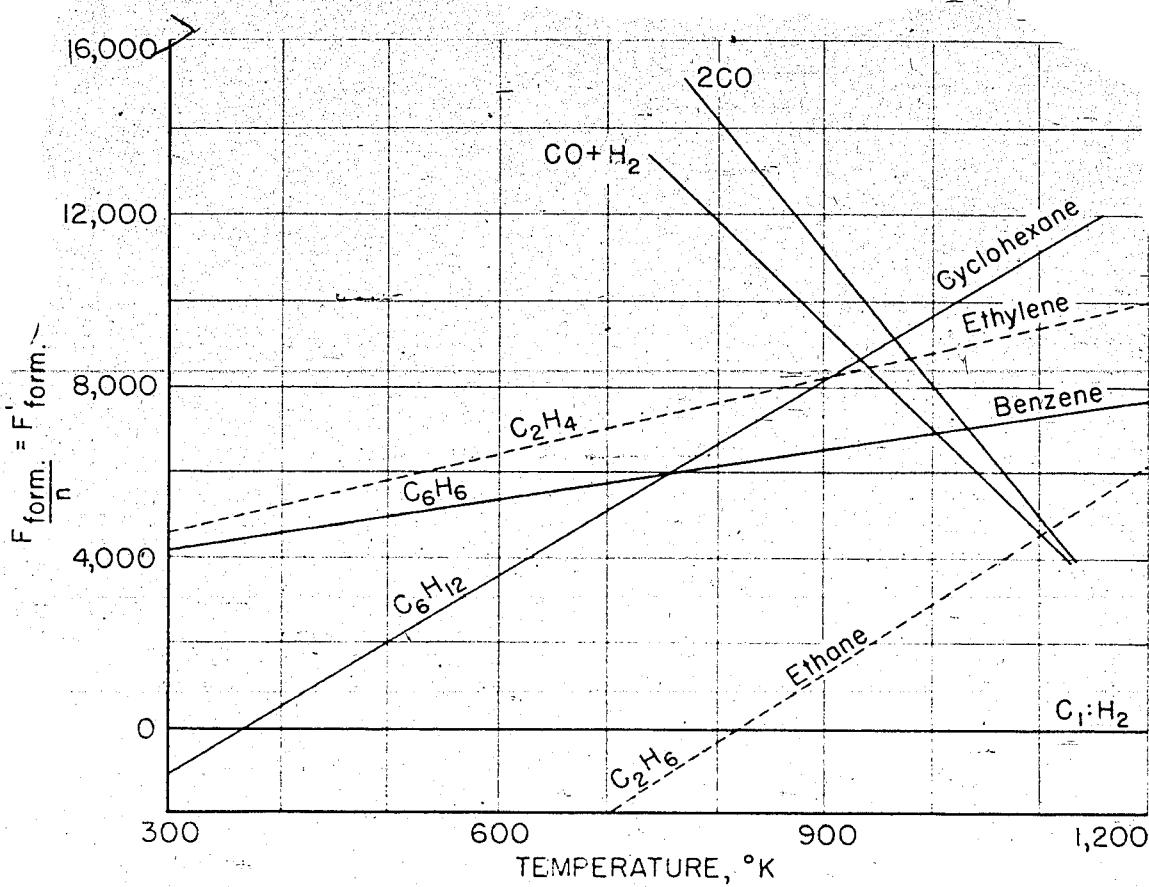
Figure 4 — Free energy of formation of benzene and cyclohexane at 100 atmospheres.

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In consequence, the formation of benzene and of cyclohexane from CO-H$_2$ is possible, thermodynamically speaking, up to 400°C. at 1 atmosphere and up to 700°C. at 100 atmospheres.

The intersection of the benzene and cyclohexane curves shows the zero point of free energy for the hydrogenation – dehydrogenation equilibrium.

Examples of the benzene-cyclohexane equilibrium,

Benzene + 3H$_2$ = Cyclohexane
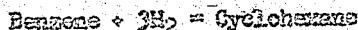
are shown in Table 5.

Table 5

Examples of Benzene-Cyclohexane Equilibrium

		1 atmosphere		100 atmospheres	
Temperature at which free energy equals zero, °C.		270		485	
examples		1	2	3	4
partial)	benzene	1	0.8	100	80
pressure)	cyclohexane	1	0.4	100	40
atmospheres)	hydrogen	1	0.8	100	80
total pressure, atmospheres		3	2	300	200

Free energies of formation for a few olefins are given in figures 5 and 6. The olefin curves intersect (in closely grouped points) at 415°C. (for 1 atmosphere). In other words, below this temperature we may expect polymerisation, and above it, dissociation. At higher pressures, the points of intersection (free energy of polymerisation equals zero) are displaced towards higher temperatures, as for example, 740 to 780°C. at 100 atmospheres.

Comparison with saturated hydrocarbons having the same number of carbon atoms shows the olefin curves to be flatter and situated higher in the usual temperature range, so that, for higher temperatures, the free energy of dehydrogenation equals zero. In other words, above this temperature dehydrogenation of paraffins to olefins becomes possible.

Examples	Limiting temperatures at which free energy at 1 atmosphere equals zero, °C.
ethane to ethylene	805
butane to butylene	725
octane to octylene	550
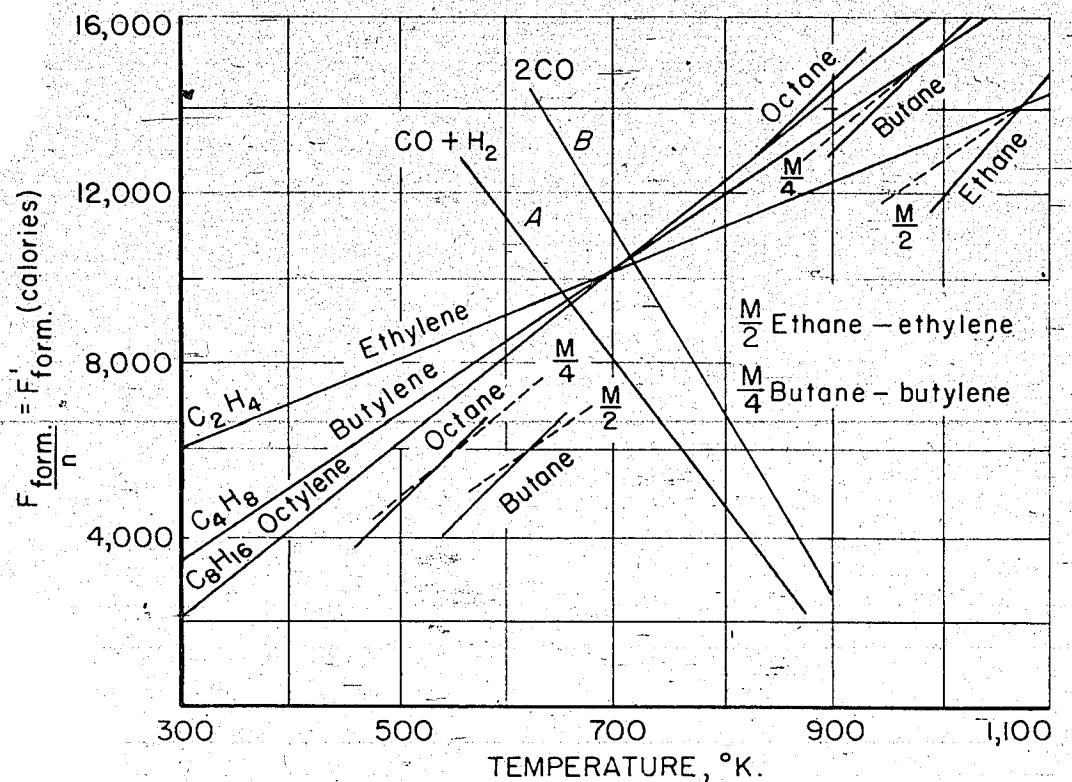
Figure 5.— Free energy of formation of several olefins at 1 atmosphere.

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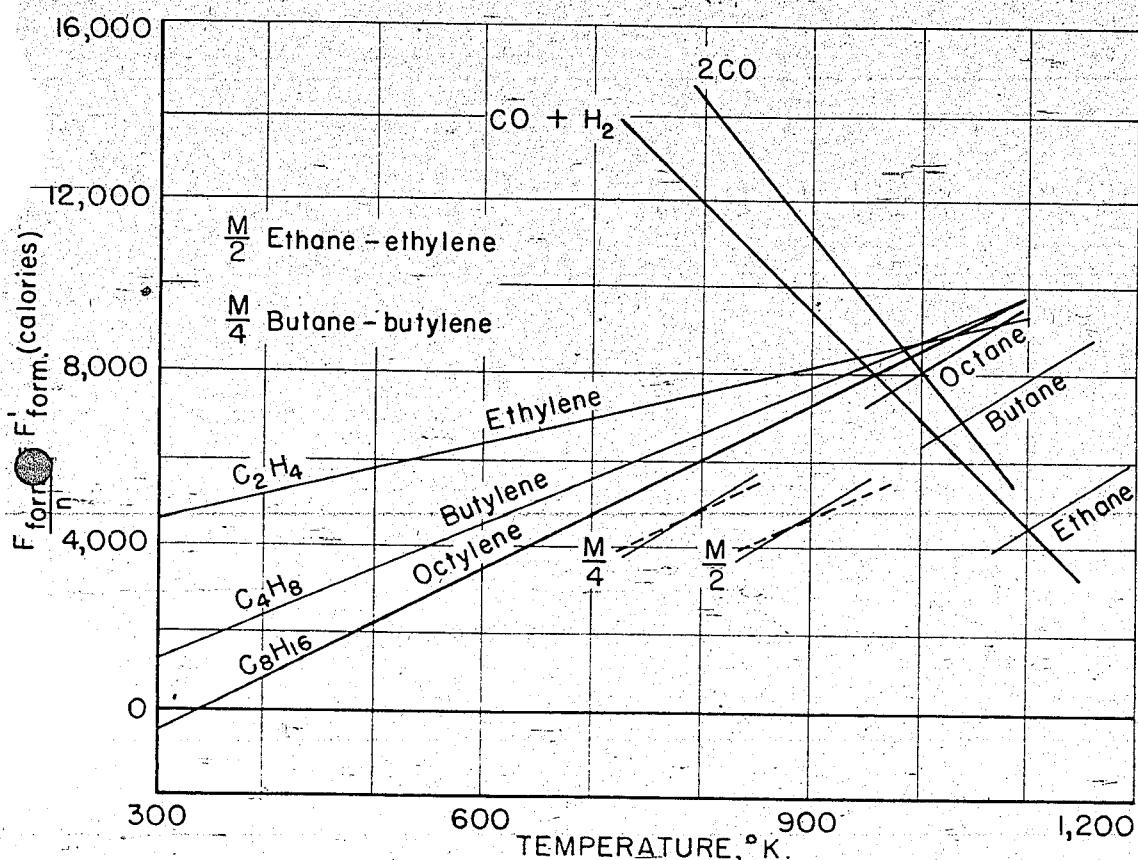
Figure 6.- Free energy of formation of several olefins at 100 atmospheres.

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It will be seen from the examples of octane, that from C_8 upward the dehydrogenation temperature for paraffins lies within the region of cracking temperatures. The presence of hydrogen under pressure* (figure 6) increases the dehydrogenation temperature considerably. For octane it rises to 800°C. and it is still higher for the lower paraffins. Consequently, under hydrogen pressure paraffins are completely stable towards dehydrogenation.

Olefins may be obtained from the $CO-H_2$ mixture, at 1 atmosphere, at temperatures below 320°C. (hydrocarbon + H_2O reaction) and 440°C. (hydrocarbon + CO_2 reaction). At 100 atmospheres the temperature range lies as high as 700°C.

EXPRESSIONS FOR CRACKING AND CONDENSATION

Hydrogen Present

The parallel course of the paraffin curves in figures 1 and 2 indicates that the cracking of a paraffin into lower paraffins is accompanied by a loss in free energy at all temperatures and pressures. This may be expressed as follows:

$$C_{(m+n)}H_{2(m+n)+2} + H_2 = C_mH_{2m+2} + C_nH_{2n+2}$$
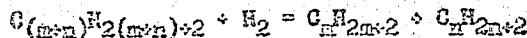
F is always negative.

For ethylene, whose curve lies above that of methane at ordinary temperatures, the relatively flat course of the curve indicates that the tendency to cracking at ordinary temperatures, according to the equation:

$$C_2H_4 + 2H_2 = 2CH_4$$
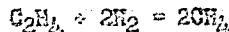
gives way to a tendency on the part of methane to condense to form ethylene at about 1500°C.

The same is true of the benzene curve, whose course is still flatter and lies somewhat below that of ethylene. Condensation of methane to benzene is possible above 1100°C.; condensation of ethane to benzene may occur above 600°C. (figure 5).

The condensation of ethylene to benzene is possible at all temperatures at 1 atmosphere, as well as for 100 atmospheres since the ethylene curve always lies above that of benzene.

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*Hydrogen is always present as these considerations are based on energies of formation from C and H_2.

Hydrogen Absent

The general case to be considered here is that of the cracking of paraffin into olefin + paraffin.

$$C_{(m+n)}H_{2(m+n)+2} = C_mH_{2m} + C_nH_{2n+2}$$
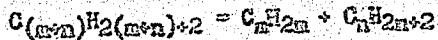
Since hydrogen is neither formed nor consumed, its presence is not a factor and the free energies may be derived from the curves for the energy of formation. In this connection, it should be observed that the free energy given in the curves is based on 1 C-atom, $\frac{F_{form.}}{n}$, where n = 1.

$$F'_{form.} = \frac{F_{form.}}{n} \text{ (n = number of C-atoms per molecule)}$$

The free energy of cracking, $F_{cracking}$, based on one molecule of paraffin, may be expressed as follows:

$$F_{cracking} = F_{form., C_m \text{ olefin}} + F_{form., C_n \text{ paraffin}} - F_{form., C_{(m+n)} \text{ paraffin}}$$

Introducing the average value based on 1 atom of carbon.

$$F_{cracking} = \frac{m\, F_{form.\ C_m \text{ olefin}} + n\, F_{form.\ C_n \text{ paraffin}}}{m+n} - F'_{form., C_{(m+n)} \text{ paraff}}$$

Example 1. — Decomposition and Synthesis of Butane

$$C_4H_{10} = C_2H_4 + C_2H_6$$
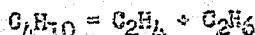
The mean curve $\frac{M}{2}$ (figures 1, 2, and 3) gives the behavior of the decomposition products. Since it intersects the butane curve at 345°C., we may expect decomposition above 345°C. and synthesis (alkylation) below 345°C. at 1 atmosphere. At a pressure of 100 atmospheres the limiting temperature is 620°C.

Example 2. — Decomposition and Synthesis of Octane

$$C_8H_{18} = C_4H_8 + C_4H_{10}$$
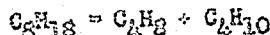
The means curve for butane + butylene is given by $\frac{M}{2}$ (figures 5 and 6). At 1 atmosphere the curve intersects the octane curve at 250°C. Thus, decomposition occurs above 250°C., and synthesis (alkylation) below. At 100 atmospheres the point of intersection lies at 510°C.

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These two examples show that at least the lower paraffins are quite stable towards central cleavage of the molecule. At temperatures of 200 to 300°C., the synthesis from paraffin + olefin (alkylation) is by far the more likely reaction.

Example 9. — Decomposition of n-octane to Give Olefin + Paraffin (figure 7)

The various fractions obtained from n-octane by cleavage at different points are shown in figure 7. The greatest decrease in free energy occurs for cleavages giving heptylene + methane or hexylene + ethane. This cleavage is possible even at 160°C. Cleavage of the molecule to give a higher order paraffin and an olefin of correspondingly lower order is accompanied by little increase in free energy. However, the differences are not considerable.*

Hydrogen Eliminated

There are some reactions in which elimination of hydrogen occurs. We may cite, for example, the condensation of ethane with ethylene to give benzene. Another example is the cracking of n-octane to form ethylene, according to the equation,

$$C_8H_{18} = 4 \ C_2H_4 + H_2$$
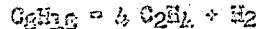
The curves for ethylene and n-octane are shown in figure 1. The cracking reaction is possible at temperatures above 460°C., at 1 atmosphere.

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*Translator's note: Interpretation of the last two sentences in this paragraph is not clear.
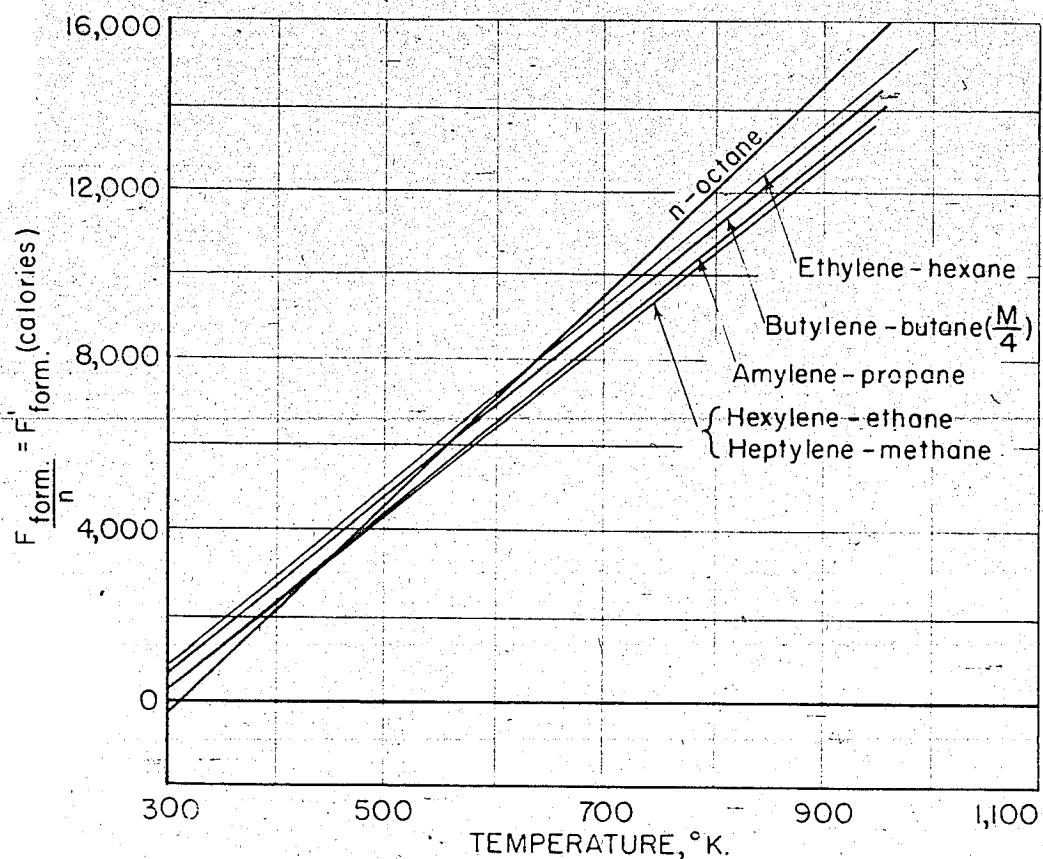
Figure 7.- Free energy of formation of n-octane and cleavage at 1 atmosphere.

TOM REEL 134, NAVY 5811, ITEM Ib-2

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 Fisher-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 calculations 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. Calculation 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) $C + (1 + \frac{1}{n}) H_2 = \frac{1}{n} C_n H_{2n+2};$ $\quad K_1 = \dfrac{[P_{H_2}]^{1 + \frac{1}{n}}}{[P_{C_n H_{2n+2}}]^{\frac{1}{n}}}$

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

(3) $CO + (2 + \frac{1}{n}) H_2 = \frac{1}{n} C_n H_{2n+2} + H_2O;$ $\quad K_3 = K_1 \cdot K_2$
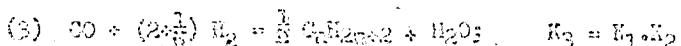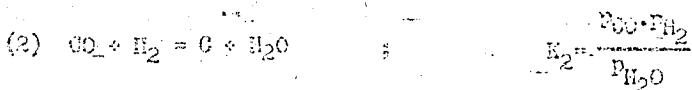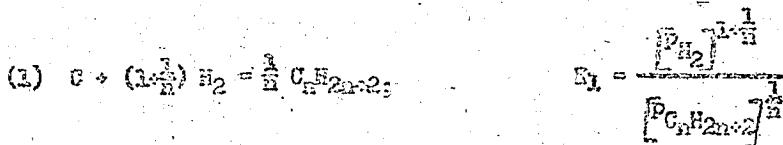
The equilibrium for the water-gas reaction is obtained, as we know, from the equations for the combustion of hydrogen and of carbon monoxide in oxygen. (Tables 6, 7, 8.)

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	+0.85
200	-3.97	-0.58	+0.50	+0.82	+1.58	+3.66
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	-10.14
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

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

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

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,

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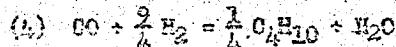
with

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

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 constants (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.

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

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

Therefore,

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

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

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

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

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

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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	+0.376	-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: $100 x = 83.9\%$

$$\boxed{\frac{(100)(13.5)}{10.0 + 13.5} = 57.5\%}$$ 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.

$$\log K_p = -6.53 \quad (\text{Table } 3)$$

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..	9.037 -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	−2.00.x	3.75−2.00.x

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:

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

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

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) H_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 (H_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 effect is small, we will now examine the effect of excess hydrogen (5.5%) on the equilibrium shift for butane at 180°C.

Effect of Excess of Hydrogen (5.5 %)

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	$-2x$	$3.375-2x$

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

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

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

	$4 \log (1-x)$	$+9 \log (1.0556-x)$	$-5 \log x$	$-8 \log (13.5-8x)$	
$x = 0.997$	1.9084-12	+6.9111-18	+0.0055	-5.9360 =	-27.112
$x = 0.999$	0.0000-12	+6.7754-18	+0.0021	-5.9280 =	-29.142
$x = 0.9999$	0.0000-16	+6.7126-18	+0.0002	-5.9243 =	-32.211
$x = 0.99995$	2.7959-20	+6.7092-18	+0.0001	-5.9231 =	-34.418
$x = 0.99996$	2.4082-20	+6.7085-18	+0.0001	-5.9231 =	-34.806

$$100 \; x = 99.996$$

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

$$99.69 \; to \; 99.996$$

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) $\quad CO + (2\tfrac{1}{8}) H_2 = \tfrac{1}{8} C_8H_{18} + H_2O$
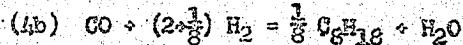
Reaction Scheme 7

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

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

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

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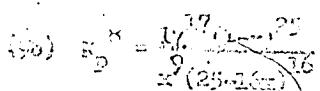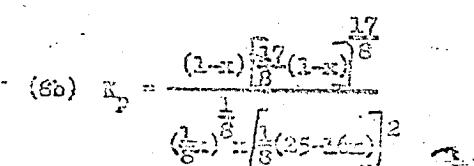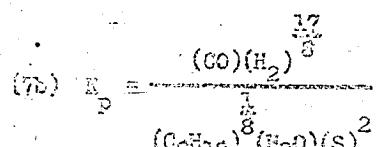
At 200°C. log $K_p = -5.49$

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
" $x = 0.988$	1.9600-50	+0.0468	-15.4144 =	-63.388

$$100x = 98.95\%$$

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	-15.3752 =	-69.191

$$100x = 99.37\%$$

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 $K_p = -1.09$ 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_8H_{18}	—	+0.0854	0.0854	4.85
H_2O	—	+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:

$$-29.3978 = 25 \log (1-x) \quad -9 \log x \quad -16 \log (29-16x)$$

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_8H_{10}	—	+0.0786	0.0786	3.32
H_2O	—	+0.629	0.629	26.57
N_2	0.50	—	0.50	21.13

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Effect of Introducing Water Vapor (Octane 622°K.)

1 p.b.v. H_2O 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

$$100x = 54.7\%$$

Reaction Scheme 10 (Octane 622°K.)

(1 p.b.v. H_2O in 2 p.b.v. CO)

Gas	I	+ II	= III	
Parts by volume	Introduced	Reacted	Final composition	Percent
CO	1	−0.547	0.453	17.90
H_2	2.125	−1.1624	0.9626	38.03
C_8H_{18}	—	+0.0684	0.0684	2.70
H_2O	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. H_2O 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	−1.4037	−22.3670 = −31.000
" 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 = −29.471
" x =	0.41	19.2713−25	+0.3872	−1.1938	−22.7614 = −29.297

$$100x = 41.6\%$$

Reaction Scheme 11 (Octane 622°K.)

(1 p.b.v. H₂O 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	-0.684	1.241	37.68
C_8H_{18}	-	+0.052	0.052	1.58
H_2O	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. H₂ 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_8H_{18}	-	+0.125x	+0.125x
H_2O	-	+x	x
S	3.25	-2x	3.25-2x

Applying the law of mass action:

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

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

	$8 \log (1-x)$	$+17 \log (1.0588-x)$	$-9 \log x$	$-16 \log (26-16x)$	
for $x = 0.70$	-4.1830	-7.5676	$+1.3941$	-18.7242 ^{b}	-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) $\quad K_p = \dfrac{(CO)(H_2)^{\frac{17}{8}}}{(C_8H_{18})^{\frac{1}{8}}(H_2O)S^2} = \dfrac{(1-x)(1.70-2.125x)^{\frac{17}{8}}}{(0.125x)^{\frac{1}{8}}x(2.70-2x)^2}$

(9d) $\quad K_p^6 = \dfrac{17^{\frac{17}{9}}(1-x)^8(0.8-x)^{17}}{x^9(21.6-16x)^{16}}$

(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	$+1.9942$	$-17.2672 =$	-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_8H_{18}	—	+0.072	0.072	4.68
H_2O	—	+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_2O 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_2O 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% N$_2$ Included	H$_2$O Vapor Saturation at 59°C. Included	H$_2$O Vapor Saturation at 64°C. Included	5.5% N$_2$ Excess Included	H$_2$:CO = 1.70
Synthesis Gas						
CO	1	1	1	1	1	1
H$_2$	2.125	2.125	2.125	2.125	2.25	1.70(2.125x0.8)
Reacted Gas						
CO	0.683	0.629	0.547	0.416	0.710	0.577
H$_2$	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. H$_2$	0.674	0.788	0.953	1.241	0.741	0.474
P.b.v. C$_8$	0.0854	0.0785	0.0684	0.052	0.0888	0.072
P.b.v. H$_2$O	0.683	0.629	1.047	1.416	0.710	0.577
P.b.v. N$_2$	–	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
H$_2$	38.3	33.3	38.0	37.7	40.5	30.6
C$_8$	4.9	3.3	2.7	1.6	4.9	4.7
H$_2$O	38.8	26.6	41.4	43.0	38.8	37.0
N$_2$	–	21.1	–	–	–	–
S	100.0	100.0	100.0	100.0	100.0	100.0
Yield Percent	68.3	62.9	54.7	41.6	71.0	57.7 [1] (72.1)

[1] Based on H$_2$.

(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.

TOM REEL NO. 134, NAVY 5531, ITEM 1b-3

CALCULATION OF GAS CONSUMPTION AND SYNTHESIS

COURSE IN THE HYDROGENATION OF CARBON MONOXIDE

BY DR. OTTO ROELEN

SUMMARY

The characteristic properties of a mixture of synthesis
gas and reaction products, which describe the course of the synthesis,
are discussed and an appropriate nomenclature is suggested. On the
basis of simple stoichiometry, a variety of relationships among these
properties is derived. A numerical method for calculation of the
yield and related properties from gas analysis data is devised.
Methods for testing the accuracy of calculations of the experimental
data are developed.

INTRODUCTION

Introduction to the Mathematical Procedure

For several decades, gas analysis data derived from the
hydrogenation of carbon monoxide have been used to predict the course
of the synthesis and the yield. Such calculations are made daily in
many places. The current procedure is the same cumbersome one used
twenty years ago in the early work on the gasoline synthesis, in which
each individual calculation necessitates a more or less complete
general derivation. The great advantages offered by a strictly
mathematical approach and the introduction of suitable symbols have
not as yet been utilized.

In the present paper, we shall attempt to develop the prin-
ciples of a mathematical treatment of gas consumption in the hydrogena-
tion of carbon monoxide. Starting from the fundamental quantative
relationships between reactants and products, equations whose manipula-
tion offers no difficulty are easily derived.

The use of these formulas eliminates errors of calculation,
reduces the number of mathematical operations, and enables untrained
workers to carry out rapid, reliable gas analyses and to check the
values obtained. Uniform application of such formulas would facilitate
comparison of synthesis data from various sources.

Further, new quantitative relations between the components of the reaction have been brought to light, which could neither have been observed nor applied, without the aid of mathematical analysis. Finally, we now have a better perception of the degree of accuracy that may be expected with such calculations, as well as of the sources of error and the effect of such errors.

Discussion of the Notation[*]

Progressive development over a period of years is responsible for the lack of uniformity in the use of symbols, and no agreement concerning the choice of nomenclature is in prospect. In consequence, it has seemed desirable to present a detailed explanation of the terms used.

The Residual Volume, R

The quantity, "contraction", dates from the early days of experimental research. At that time, contraction was a characteristic property whose determination was particularly simple for small scale experiments in vacuo. In cobalt contact catalysis, for instance, the conversion is essentially proportional to the contraction. Although contraction is evident, its numerical value must be calculated. In calculating the conversion, the numerical value of the residual volume, which is determined experimentally, is used. Since in the course of calculation it would be necessary to calculate the contraction from the residual volume, and since both values are complementary, it is simpler and more efficient to use only the residual volume.

The quantity, contraction, and its numerical values may, therefore, be ignored in estimating the course of a synthesis used simply as a means of expressing the idea of a decrease in volume. The term, contraction, may be preferred to that of residual volume, which implies a quantitative idea. In the present work, only the quantity, residual volume, indicated by the symbol R is used. No symbol for contraction is given.

Description of Characteristic Variables

Of all the numerical values which characterize the course of a synthesis, the most essential are those used in calculating the yields. Consequently, the calculation of gas consumption during the course of a synthesis has as its ultimate object either the determination of the yield to be expected, or an explanation of the reasons why the maximum yield was not obtained.

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[*] A list of formulas for the utilization of Fischer-Tropsch gas analyses in calculation of yields and study of synthesis course appears on page 69, table 15.

If we next consider the factors which affect the maximum yield, we find them to be as follows:

1. Incomplete conversion.
2. Formation of methane instead of higher hydrocarbons.
3. Consumption of CO and H_2 in a different ratio from that expected.
4. Deposition of carbon.

No other stoichiometric changes affecting the consumption of gas are known. Since either the formation of carbon is negligible, or else the catalyst is rapidly inactivated, the fourth factor need not be considered here. The determination of factors 1 to 3 must be sufficient for a complete characterization of the course of the synthesis.

Moreover, when conversion, methane formation, and usage ratio are known, the theoretical yield can always be calculated. In consequence, the present development will be limited to the calculation of the following four characteristic variables:

Conversion, U
Methane formation, M
Usage ratio, X
Yield, A

Characteristic Variables for CO + H_2 Conversion

A graphic representation of the characteristic variables is shown in figure 6.

When the synthesis is accompanied largely by the formation of water, as is the case on nickel and cobalt catalysts, the ratio of the yield of higher hydrocarbons to the amount of carbon monoxide reacted is a simple one, 1 CO:1 CH_2. For this reason it has become general practice to base calculations such as those for the conversion or the yield on the amount of carbon monoxide reacted. It is always desirable to determine the residue of unreacted gas as carbon and here again calculations are based on carbon monoxide.

Where carbon dioxide is the chief by-product, as occurs on iron catalysts, a simple and clear relation is obtained with the CO+H_2 conversion. An advantage of this procedure, as against that based on the CO conversion, lies in the fact that CO+H_2 conversion may be compared directly for synthesis conducted under widely varying conditions.
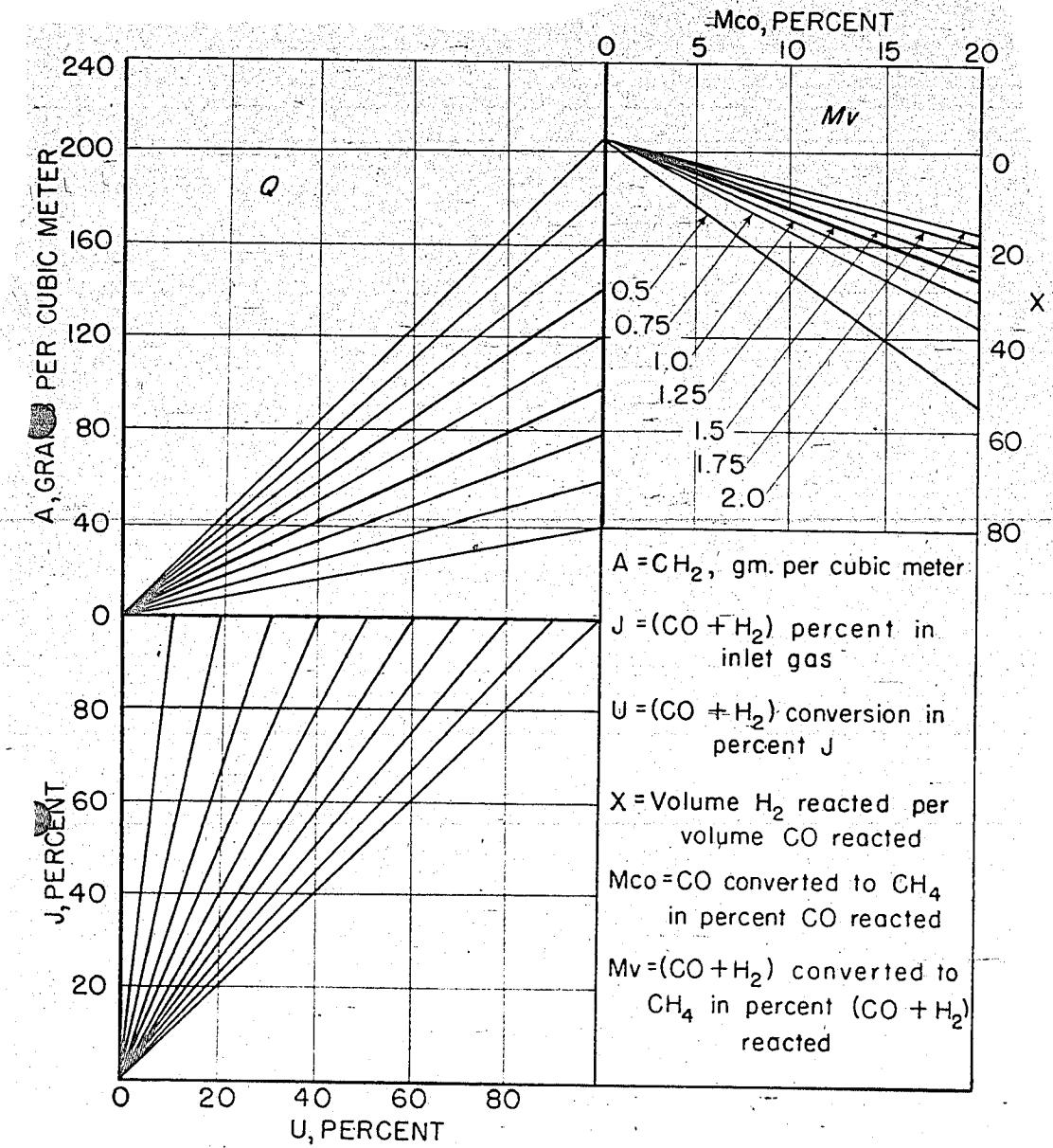
Figure 8. Graphic representation of characteristic variables.
(for n = 2.0)

I. $Q = 208\left(1 - \dfrac{Mco}{25(1+X)}\right)10^{-4}$

II. $Q = 208(100 - Mv)10^{-6}$

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In the following discussion the term conversion refers exclusively to the CO+H₂ conversion and is represented by the symbol, U. Values for the CO conversion, as well as for the H₂ conversion, may be omitted as these are evident from the H₂:CO usage ratio. The symbol Uco for the CO conversion may be used as intermediate value in certain calculations.

What has been said of conversion is also true for the amount of methane formed. In the following pages, the formation of methane designated as Mv is indicated solely by the CO+H₂ consumption. These Mv values are always susceptible to direct comparison no matter how widely the syntheses and catalysts differ.

Explanation of Selection of Symbols

In all, symbols for some ninety different quantities are needed. Some of the symbols are identical with those already in use; however, this is not the case for most of them. In selecting symbols the following rules were observed.

(a) When possible symbols already in use are maintained.

(b) When possible a correspondence between the symbol and its significance is sought.

(c) When several similar symbols occur, the simplest form is assigned to the most frequent case.

(d) All symbols must be easily distinguished and be reproducible on a standard typewriter.

(e) No symbols are given for concepts still in current use, but which became obsolete in the light of the present study, for example, the degree of liquefaction, the H₂ conversion, etc.

For typographical reasons when no confusion is likely between an index letter and an independent symbol, the index is written on the same line rather than as a subscript, for example, Uco instead of U_{co}.

The yield may be expressed in a number of different ways depending on the gas composition and the conversion used as reference. The products considered, and method chosen in calculating these values are as follows:

1. Gases

    (a) Synthesis gas.
    (b) Total $CO+H_2$ content.
    (c) The $CO+H_2$ fraction used for a given usage ratio.

2. Conversion

    (a) The conversion actually achieved.
    (b) The conversion that may be attained in practice, for example, 90%.
    (c) Complete conversion, 100%.

3. Products

    (a) All hydrocarbons formed, including methane.
    (b) Hydrocarbons formed, except methane.
    (c) Hydrocarbons formed, except methane, ethane and ethylene.
    (d) (a) - (c), with inclusion of oxygenated products or of oxygenated groups.

Allowing for the various combinations of the different individual cases enumerated, the possible methods of expressing the yield become numerous. In general, these different expressions are easily converted from one to another. The choice, therefore, does not depend on mathematical derivation, but is a matter of convention, and as such, does not properly lie within the scope of the present discussion. For our purpose, all calculations of yield are limited to a simple case, namely, the weight in grams of higher hydrocarbons (excluding methane) per cubic meter of synthesis gas. Where necessary, oxygenated groups are included.

CALCULATIONS FOR THE HYDROCARBON SYNTHESIS FROM GAS ANALYSIS DATA

Three Fundamental Rules for all Gas Analysis Calculations

When the gas analysis calculations are reduced to their essential factors three fundamental rules appear:

First rule (for all substances participating in the reaction):

The sum of all substances entering the converter is equal to the sum of all substances issuing from the converter, whether reacted or unreacted.

Second rule (for each individual gas fraction):

The amount of any gas present is equal to the sum of the amount reacting (or formed) plus the unreacted fraction.

Third rule (for nitrogen only):

The quantity of nitrogen present in the inlet gas is neither increased nor reduced during the reaction.

These three rules form the basis, not only for the mathematical derivation, but also for a check of the accuracy of the numerical results.

Algebraic Interpretation of the Three Rules

The Two Fundamental Stoichiometric Equations and Their Solution

According to the first rule, for a given amount of substance introduced into the reaction system an equal amount of substance must be withdrawn from the system. In this connection, the high-melting paraffin that separates out in the reactor may be neglected since they play no part in the gas analysis, and since the calculations are made on a synthesis operating continuously at the steady state. All hydrocarbons may be classified by the general term, CH_n. In consequence, the initial quantities may be equated to the final quantities as follow:

$$a\ CO + b\ H_2 = c_m\ CH_{n_m} + d\ CO_2 + e\ H_2O \qquad (1)$$
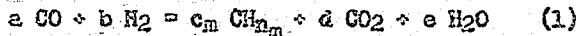
This equation will be known as the "first fundamental stoichiometric equation". The values, a, b, c, d, and e, represent the volumes of carbon monoxide and hydrogen reacted and the volumes of hydrocarbons, carbon dioxide, and water formed, and will be referred to as the "intermediate variables".

Equation (1) gives rise to a series of stoichiometric reactions derived by means of temporary summation equations for the three elements carbon, oxygen, and hydrogen, as follows:

Summation equation for carbon: $a = c_m + d$
Summation equation for oxygen: $a = 2d + e$
Summation equation for hydrogen: $2b = n_m\ c_m + 2e$

From these three equations general solutions of equation (1) are derived by simple algebra.

The term c_m CH_{2m} includes all hydrocarbons formed. However, since methane may be determined separately in the gas analysis, this term may be resolved into two parts: the volume of higher hydrocarbons formed (exclusive of methane) c^+ CH_n and the volume of methane formed c CH_4. Substituting in equation (1) we obtain:

$$a\ CO + b\ H_2 = c^+\ CH_n + c\ CH_4 + d\ CO_2 + e\ H_2O \qquad (2)$$

This equation is known as the "second fundamental stoichiometric equation".

From equation (2) the following summation equations are obtained for the three elements:

Summation equation for carbon: $a = c^+ + c + d$
Summation equation for oxygen: $a = 2d + e$
Summation equation for hydrogen: $2b = nc^+ + 4c + 2e$

From these three equations the general solutions of equation (2) are obtained algebraically.

These solutions show how the volume c^+ of higher hydrocarbons depends on the values a, b, c, and d, obtained by gas analysis, as well as on n. In this way, these equations constitute the basis for the calculation of the yield.

Calculation of the Intermediate Variables

The second rule states that for gaseous substances taking part in the reaction, the amount initially introduced equals the sum of the reacted plus the unreacted fractions. For carbon monoxide this may be expressed as follows:

Inlet CO = reacted + unreacted CO

The amount of unreacted CO is determined by analysis and the amount of residual gas is given by $R.CO'$. Thus:

$$CO = a + R.CO' \qquad or \qquad a = CO - R.CO' \qquad (3)$$

The three other intermediate variables are determined in the same way:

$$b = H_2 - R.H_2' \qquad (4)$$

$$c = R.CH_4 - CH_4 \qquad (5)$$

$$d = R.CO_2 - CO_2 \qquad (6)$$

Whereas the algebraic interpretation of the first rule gives the mathematical relations among the four values a, b, c, and d, and n, the second rule leads to the correlation of the four intermediate variables with the gas analysis data on the one hand and with the residual volume on the other. With the exception of the rather uncertain nitrogen content, which will be discussed later, all other possibilities of establishing fundamental relations by the sole means of gas analysis have, herewith, been exhausted. All further calculations are based on the algebraic interpretation of the first and second rules given above.

Calculation of the Residual Volume from the Nitrogen Content

The third rule states that the amount of nitrogen present in the inlet gas is not affected by the reaction and, therefore, appears unchanged in the outlet gas. It is upon this observation that calculation of the residual volume from the nitrogen content first used in the early days of the gasoline synthesis is based.

The amount of inlet gas is assumed equal to 1, the residual volume is then calculated as follows:

$$\frac{\text{Inlet gas}}{\text{Amount of nitrogen}} = \frac{1}{\text{Amount of nitrogen}} = \frac{100}{N_2}$$

$$\frac{\text{Outlet gas}}{\text{Amount of nitrogen}} = \frac{R}{\text{Amount of nitrogen}} = \frac{100}{N_2^*}$$

$$R_3 = \frac{N_2}{N_2^*} \qquad (7)$$

Thus, the third rule leads to yet another fundamental relation. Its practical value, however, is slight, for R values determined in this way are erroneous, owing to the fact that the analytical values for nitrogen are not obtained by a direct nitrogen determination, but are given as the difference between 100 and the sum of the other determinations. In this way the accumulated errors in all the other determinations affect the value for the relatively small volume of nitrogen. Moreover, it is known that errors are very apt to occur when R is calculated from two N_2 determinations that were not carried out simultaneously and under exactly the same conditions.

The n-R Equation

The following equation was obtained from equation (2) by solving for d:

$$d = \frac{n(a-c) + 2(a-b) + 4c}{n+4}$$

Substituting the terms for the intermediate variables derived from the second rule and transposing, we obtain:

$$R = \frac{2(2CO_2 + CO) - (H_2 + 2CH_4) + n(CO + CH_4 + CO_2)}{2(2CO_2' + CO') - (H_2' + 2CH_4') + n(CO' + CH_4' + CO_2')}$$

Let:

$$p = (CO_2 + CO + CH_4) \qquad q = 2\left[(2CO_2 + CO)) - H_2 + 2CH_4\right]$$

$$p' = (CO_2' + CO' + CH_4') \qquad q' = 2\left[(2CO_2' + CO') - (H_2' + 2CH_4')\right]$$

Using these abbreviations, the preceding equation may be written in two ways, for n and R, respectively.

$$n = \frac{q' R - q}{p - p' R} \qquad R_6 \text{ or } R_7 = \frac{p n + q}{p' n + q'} \qquad (8)$$

These two identical equations will be known as the "n-R equation" (8). Aside from n and R, it contains only gas analysis data obtained from the composition of the inlet and outlet gas. Thus, for every set of gas analysis values, equation (8) establishes a numerical relation between n and R.

Since equation (8) was derived without calling upon any additional hypotheses, it satisfies the first and second rules completely.

In the same way, an "n_m-R equation" may be derived from equation (1). This equation applies to cases where methane is not treated separately, but included with the other hydrocarbons in the calculations. This is indicated by an m subscript on all the abbreviations. Thus:

$$P_m = CO_2 + CO \qquad q_m = 2(2CO_2 + CO - H_2)$$

$$p'_m = CO'_2 + CO' \qquad q'_m = 2(2CO'_2 + CO' - H'_2)$$
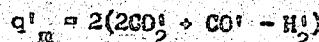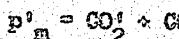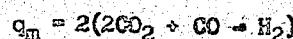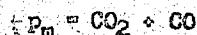
$$n_m = \frac{q'_m R - c_m}{p_m - p'_m R} \qquad R = \frac{c_m + p_m n_m}{q'_m + p'_m n_m}$$

Conversion from n to n_m, or the reverse, proceeds as follows:

Summation equation for hydrogen: $c_m n_m = c^+ n + 4c$

Summation equation for carbon: $\quad c_m = c^+ + c$

This gives:

$$n_m = \frac{c^+ n + 4c}{c^+ + c}$$

or:

$$n_m = n + c \frac{4 - n}{a - d} = \frac{2(b + 2d) - a}{a - d}$$

Application and Validity of the Correlation

Between Characteristic and Intermediate Variables

In calculating the actual characteristic variables, as will be shown below in more detail, numerical values of a, b, c, and d are needed. These values could easily be obtained from equations (3), (4), (5), and (6), if some simple means for accurate determination of the residual volume were available. Unfortunately, this is not the case. Herein lies the essential difficulty of all calculations based on gas analyses.

It has been shown that determination of the residual volume by the nitrogen method does not offer sufficient accuracy. The same is true of direct measurement of the residual volume especially when synthesis takes place at high pressure.

The third, and at present, only other means of determining R is offered by equation (8). For this purpose, we need the numerical value of n. However, when both R and n are unknown, we have no way of determining them solely from gas analysis data and without some deviation from the first and second rules. Another method of determination makes use of the analysis of the products formed, as a means of determining n. Substituting this value for n in equation (8) we obtain the quantity R_6.

If now we take a series of approximate values for n and substitute them in equation (8), we obtain a series of useful approximate values for R (R_5, R_7), based exclusively on gas analysis data, that satisfy the first and second rules. This means that values of the characteristic variables calculated from these values of R are really valid for hydrocarbons of formula CH_n. This is by no means the general case when the values for R are calculated from direct measurement (R_1, R_2) or by the nitrogen method (R_3, R_4). Here we find, for instance, that the values of the characteristic variables obtained hold for the formation of hydrocarbons whose H:C ratio shows considerable deviation from the correct average composition, for example, $CH_{0.5}$ or CH_7.

The chief advantage in calculating R from equation (8) lies in the agreement of the relation between the characteristic variables obtained, and the known average composition of the hydrocarbons formed, CH_n.

As regards the character of the n-R equation, the following may be added. Graphic representation of pairs of values for R and n obtained from various sets of gas analyses give a series of curves which start at the origin. The shape of the curve is such as to give the impression that the coordinates of the maximum are the n and R values for the corresponding gas analysis. However, neither by differentiation nor by graphical analysis can such a critical point be determined. That no critical points exist is apparent from the following discussion.

All relations between intermediate values and characteristic variables calculated from n and R take the analytical form of a straight or almost straight line. This, however, can only be the case if equation (8) holds not only for a given operation but for any number of such operations.

If, for instance, we take an n-R equation obtained for any run and substitute the integers 1 to 9 for n, solving for the values of R, we obtain nine pairs of values for n and R. Each of these pairs gives the correct characteristic variables for a corresponding synthesis. From a purely stoichiometric point of view, nothing prevents us from carrying out each of these nine syntheses. This is the case, not only for the integral values assigned here to n, but for all fractional values of n, therefore, for any values of n, and for all n-R pairs.

This means that a set of gas analysis values obtained for an inlet and an outlet gas need not be derived from any one particular synthesis, but will hold for any number of different syntheses, a given n-R pair corresponding to each synthesis.

Table 10 illustrates the range for which equation (8) is valid. If the inlet gas is water gas the same final composition would be obtained for the following different conditions:

(1) For a residual volume of 47.3% and a yield of 121.1 g/m^3, provided that aside from methane only acetylene or benzene (C:H=1) formed.

(2) For a residual volume of 61.7% and a yield of 85.7 g/m^3, provided that aside from methane only pure olefin hydrocarbons (1C:2H) form.

(3) For a residual volume of 68.9% and a yield of 68.4 g/m^3, provided that aside from methane only ethane (C$_2$H$_6$) forms.

(4) For a residual volume of 73.0%, provided that aside from the methane formed in the other cases, a further yield of 58.2 g/m^3 of methane forms and that no other hydrocarbons form.

(5) For a residual volume of 81.5% and a yield of 37.6 g/m^3, provided that aside from methane only hydrocarbons of the hypothetical composition CH$_9$ form.

Table 10

Range of Validity of the n-R Equation for a

Set of Gas Analyses

1. Gas Analyses

	CO_2	CO	H_2	CH_4
Inlet, volume percent	6.0	38.3	50.0	0
Outlet, volume percent	28.0	3.9	42.0	7.6

2. The n-R Equation

$$p = 44.3 \qquad p' = 49.5 \qquad q = 0.6 \qquad q^0 = 45.4$$

$$R = \frac{44.3n + 0.6}{49.5n + 45.4}$$

3. Intermediate Variables

n =	1	2	3	4	5	7	9
R =	0.473	0.617	0.689	0.730	0.758	0.790	0.815
a =	36.5	35.9	35.6	35.4	35.3	35.2	35.1
b =	30.1	24.1	21.1	19.3	18.2	16.8	15.8
c =	3.6	4.7	5.2	5.5	5.8	6.0	6.2
d_1 =	12.0	17.4	20.1	21.7	22.8	24.0	24.9
d_2 =	12	17.4	20.1	21.7	22.8	24.0	24.9

4. Characteristic Variables

U =	75.4	68.0	64.3	61.0	60.6	58.9	57.6
M_W =	21.6	31.5	36.6	40.2	43.4	46.2	48.7
X =	0.85	0.67	0.595	0.545	0.516	0.475	0.450
A_1 =	121.1	85.7	68.2	58.2	51.3	43.1	37.6
A_2 =	121.1	85.7	68.2	58.2	51.3	43.1	37.6
A_3 =	121.1	85.7	68.2	–	51.3	43.1	37.6
A_4 =	121.1	85.7	68.2	58.2	51.3	43.1	37.6
A_5 =	121.1	85.7	68.2	58.2	51.3	43.1	37.6
A_6 =	121.1	85.7	68.2	58.2	51.3	43.1	37.6

5. Notes

(a) It is assumed in all cases that none of the hydrocarbons on
which the yield is based remains behind in the residual gas.

(b) The values for A check only when sufficient decimal places are
retained (calculating machine).

(c) For $n = 4$, $A_3 = 0$.

From the data in Table 10 it will be seen how greatly the value
of the yield varies with n. This is also shown in the following data,
which lists values for n and A, for the same example, as they occur most
frequently in the current synthesis of higher hydrocarbons:

n = 2.0	2.1	2.2	2.3	2.4	2.5
A = 85.7	83.2	80.6	78.9	77.2	75.4

A change of 0.1 in n is sufficient to change the yield by as much as 2.5 g.

Under present conditions to determine n with an accuracy of 0.1
is no easy matter. One of the most important problems in this connection
is the development of a more accurate, simple method of obtaining n, as
well as the determination of approximate values which may be applied to
different individual synthesis. For the cobalt normal pressure synthesis,
according to our present information, n should lie between 2.15 and 2.20.

It is useless in calculating the yield to strive for a greater accuracy than that with which the hydrogen-carbon ratio is determined either for the hydrocarbons formed or for the residual volume.

Moreover, since our lack of information concerning the molar volume of most higher hydrocarbons contributes additional uncertainty in calculating the yield, it is appropriate for the present to round off the yield values to whole numbers, thus avoiding an impression of accuracy that would be misleading.

The agreement in the yields occurs only when corresponding n and R values are used. When this is not the case, the differences in the yields obtained by means of the various formulas increase as R differs increasingly from the value which corresponds to the given n value. The geometrical locus of all yields calculated from one and the same formula for a given n may be considered a family of straight lines (figure 9). All these yield lines intersect at a point for which n and R satisfy the conditions of equation (8) for that particular set of gas analyses.

Calculation of Characteristic Variables

Conversion and Usage Ratio

Once the residual volume is determined, values of the intermediate variables a, b, c, and d, are easily obtained from equations (3), (4), (5), and (6). When numerical values for a and b are known, conversion and usage ratios are calculated directly from the following formulas:

$$U = \frac{a + b}{J} \cdot 10^2 \quad (10) \qquad \Sigma = \frac{b}{a} \quad (11)$$

As indicated, U gives the amount of carbon monoxide and hydrogen reacted per hundred parts of $CO + H_2$ mixture present in the inlet gas.

Formation of Methane

Calculation of the Pure Methane in the Outlet Gas

Gas analysis data contribute two values for the calculation of conditions attending the formation of methane. First, the volumes of methane + any higher paraffin hydrocarbons (designated as CH_4 and CH_4') and second, the average carbon number of this hydrocarbon mixture (designated as Z). The conventions for the application of Z are not well established.
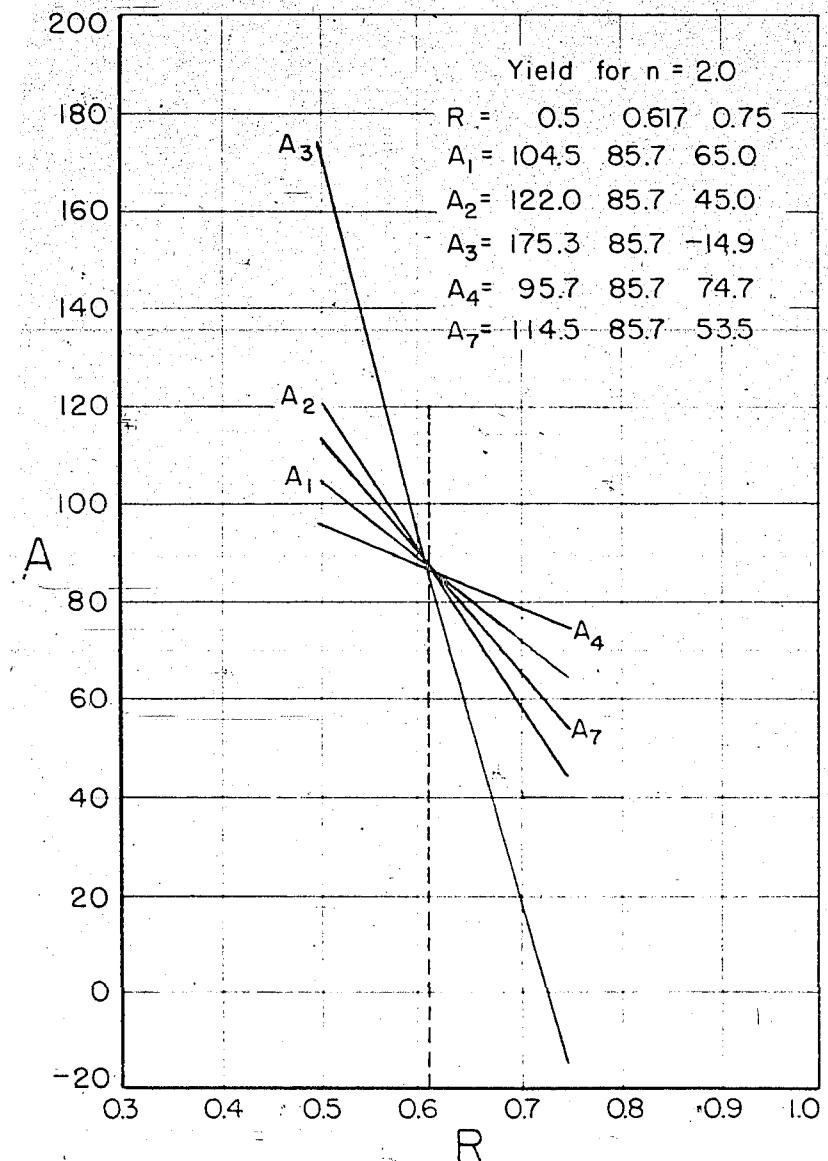
Figure 9.-The yields as functions of the residual volume.

	CO_2	CO	H_2	CH_4
Inlet gas	6.0	38.3	50.0	0.0
Outlet gas	38.0	3.9	42.0	7.6

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For industrial purposes it may be convenient to multiply CH_4^0 by Z. This gives the total volume of carbon contained as "methane" hydrocarbons and may be used to check on the calculation of residual substances.

The use of the term Z is necessary if the pure methane content is to be determined accurately. It can be shown that when gas analysis data alone are used this determination is only approximate.

Let m = pure methane content in CH_4^0

Kw = higher hydrocarbon content in CH_4^0

Then:

$$CH_4^0 = m + Kw \qquad (12)$$

If s is the average carbon number for the higher hydrocarbons in CH_4^0, then we have the following summation equation for carbon:

$$Z(CH_4^0) = 1 \cdot m + s \cdot Kw \qquad (13)$$

$$(Kw = \text{hydrocarbons})$$

Combining (12) and (13) we obtain:

$$m = CH_4^0 \frac{Z - s}{1 - s} \qquad (14)$$

Let $m = \beta (CH_4^0)$ and multiply numerator and denominator by -1. Since s is always greater than Z and greater than 1, the β-factor may be expressed as follows:

$$\beta = \frac{s - Z}{s - 1} \qquad (15)$$

From equation (15) it is apparent that in order to calculate the pure methane content of CH_4^0 exactly, s and Z must be known. Gas analysis data, however, is of no help in calculating s, which must be determined experimentally by means of condensation analysis.

However, it has been suggested that a value might be determined for the pure methane content solely from gas analysis by dividing Z into CH_4^0. If this method is to give correct results, we must be able to write:

$$\frac{1}{Z} = \beta \text{ or } \frac{1}{Z} = \frac{s - Z}{s - 1}$$

Transforming, we obtain:

$$z = \frac{1 - z^2}{1 - Z} \cdot \frac{(1 - Z)(1 + Z)}{1 - Z}, \text{ or } z = 1 + Z \qquad (16)$$

It is evident that calculation of the pure methane content, using division by the carbon number Z, gives accurate results only for the special case where z is greater than Z by exactly 1. It will be remembered that z is the carbon number for the hydrocarbons higher than methane. The value of Z, the carbon number for all the hydrocarbons, is obtained from combustion experiments. It is not to be expected that equation (16) will in general be satisfied, nor can we ever say with certainty that it is satisfied. In certain cases, as for instance when Z is large (around 1.6) the results obtained by division are completely unacceptable. Consequently, division by the carbon number Z does not constitute a practical method.

Approximate Values for the β factor

By substituting numerical values for z and Z in equation (15), the value of β for any given case may be calculated in advance. Table 11 and figure 10 show the values obtained.

As regards the hydrocarbons associated with methane, a distinction must be made between the outlet gas before and after removal of the condensable hydrocarbons, for instance, by activated charcoal. Before the removal of these hydrocarbons, relatively little C_2 is present as against C_3, C_4, and higher hydrocarbons. The average carbon number Z is 1.5 – 1.7.

Removal of condensable hydrocarbons by a simple adsorption on activated charcoal leaves, for all practical purposes, besides methane, only ethane and a little propane with Z between 1.0 and 1.2. If, after adsorption, the values obtained for Z are greater than 1.2, it is best to discard the samples and eliminate the cause of error.

In this way, the instances for which β can be determined are limited to two well-defined cases. It may be more or less correctly assumed that after removal of condensable hydrocarbons, for Z between 1.0 – 1.2, only ethane is present. The following values for β may then be obtained from the table or from the graph:

For Z = 1.1   β = 0.9   For Z = 1.2   β = 0.8
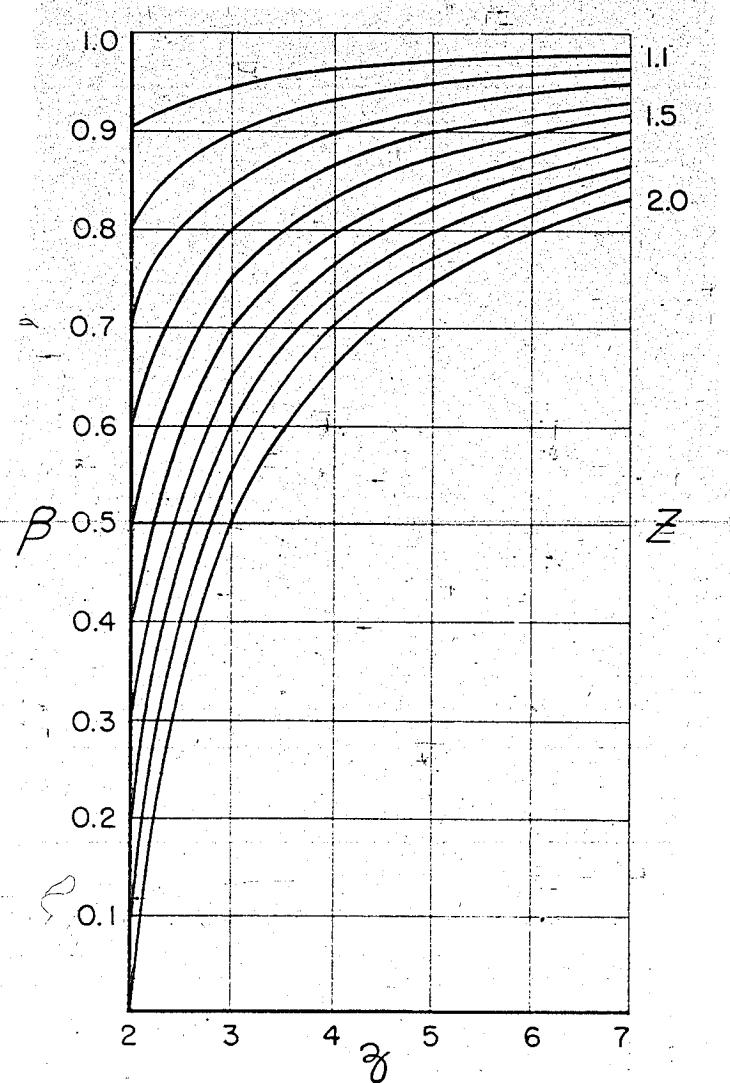
Figure 10. — The β factor for the calculation of pure methane.
(as a function of the two C-numbers, γ and Z)

As for the other case, that of gas samples taken before adsorption, we know from industrial practice that the "methane" content determined by combustion is generally about 2% higher before than after adsorption. For an average "methane" content of 15% before adsorption, we obtain $\beta = 0.857$. Since the corresponding carbon number Z generally lies between 1.5 and 1.7 the value of z as determined from figure 2 must be about 5. For want of more reliable data, we may let z equal 5 for gas samples before removal of condensable hydrocarbons. The following approximate values may then be calculated for methane:

| | Gas Sample | | |
	Before Hydro- carbon Condensation	After Hydro- carbon Condensation	$\frac{z}{Z}$
		5	
Z	5	2	—
1.0 – 1.05	—	1.0	—
1.1	—	0.9	0.91
1.2	—	0.8	0.834
1.5	0.87	—	0.666
1.6	0.85	—	0.625
1.7	0.82	—	0.589

For comparison, values obtained for β from division by the carbon number Z are listed in the last column. It will be seen that the differences are negligible for small values of Z, but become important for larger values.

Examination of the approximate values obtained shows that β always seems to be between 1.0 and about 0.8. The range for which errors may occur, therefore, does not exceed 20% of the "methane" value obtained by combustion.

The effect of an error in evaluating β on the calculated yield may be seen from the following calculations:

Gas composition:	CO	H_2	CH_4	Z	N_2
Inlet, volume percent	37.8	49.1	0.2	—	6.1
Outlet, volume percent	30.1	29.3	5.1	—	12.0

Characteristic variables: U = 65.5%   Mv = 16.75%   A = 98.4 g/m³

Changes in Mv and A with β:

β	Mv	Diff.	A	Diff.
1.00	16.75		98.4	
		0.92		1.1
0.95	15.83		99.5	
		0.92		1.1
0.90	14.92		100.6	
		0.91		1.2
0.85	14.00		101.8	
		0.90		1.0
0.80	13.10		102.8	

For the example chosen, a change of 0.05 in β results in a change of not more than about 1%, although methane formation is relatively high (about 17%).

Summarizing the results obtained above, approximate rules may be set down for the calculation of pure methane as follows:

(a) For Z = 1.0 - 1.05   β = 1.0
     For Z = 1.05 - 1.15   β = 0.9

(b) For Z > 1.15   β = 0.85

(c) Gas samples where Z values is greater than 1.2 after adsorption are discarded.

If these rules are observed, the values obtained for β probably do not differ from the true ones by more than 0.05%. Consequently, the error in the calculated yield probably does not exceed 1%. The rule applies when higher hydrocarbons are removed either by activated charcoal or by condensation at low temperatures. The use of scrubbing oil would lead to different results.

Ritter, Fischer, and Stoek (Krupp-Treibstoff-Werke) determine the pure methane content before adsorption in such a way that a so-called artificial residual gas results. This gas, prepared for analytical purposes, is obtained by treating part of the effluent gas with activated charcoal under certain specified conditions. With the exception of methane, it contains only the total ethane and has a carbon number that lies consistently between 1.05 - 1.06. In this case, β is about 0.99.

It has been indicated that the pure methane content is always a factor in calculating values of the characteristic variables. In other words, according to the rule given above, when Z is greater than 1.05, CH_4 must be multiplied by β. In order to simplify, β does not appear in the formulas, for example, CH_4 should always be replaced mentally by $CH_4^! \beta$.

Calculation of Methane Formation

Mv represents that percent of the total $CO + H_2$ gas mixture converted which enters into the formation of methane. From equation (1) as solved for $e = \frac{1}{4}(a + b)$ or $(a + b) = 4e$ we obtain $a_g = 4e$.

Consequently, the formation of methane requires a quadruple volume of $CO + H_2$ gas mixture. From the preceding definition, we have:

$$\frac{Mv}{100} = \frac{4e}{a + b} \qquad Mv = \frac{4e \cdot 10^2}{a + b} \qquad (17)$$

For Mco we may write:

$$Mco = \frac{g}{a} 10^2 \qquad (18)$$

The relation between the two characteristic variables may be written as follows:

$$Mv = Mco \frac{4}{q} \cdot \frac{a}{X} \qquad (19)$$

Yield of Higher Hydrocarbons

Equation (2) gave use to four equations by means of which c^* was calculated in four different ways, using any three of the four intermediate variables a, b, c, and d. However, c^* represents the volume of higher hydrocarbons formed and as such also gives the yield. Since the yield is usually expressed in grams, c^* must be expressed units of weight, for which purpose it is multiplied by the fraction $\frac{(12 + n)}{\text{molar volume}}$.

Our next problem is what value to substitute for the molar volume of higher hydrocarbons. Molar volumes have been determined experimentally only for the lower members up to octane. For pentane and lower members, values of less than 22.41 were obtained. For heptane and octane, the values exceed 22.41. This is probably also the case for still higher members. However, we are not in a position to suggest approximate values. The average molar volume of the hydrocarbons formed must, therefore, remain undetermined for the present. It may be smaller than 22.41 (for ideal gases), but it may be larger.

Moreover, when we consider that the molar volumes for carbon monoxide and hydrogen also differ from the ideal values (CO 22.40, H_2 22.43) it appears advisable to take 22.4 as an approximate value. In any case it should be understood that this constitutes another unavoidable source of error and is a further factor in limiting the accuracy of the calculations.

The yield, in units of weight, is therefore given as the product $c^2 \left[\frac{12 + n}{22.4}\right]$. Since the yield is based on one cubic meter of inlet gas, this value must be multiplied by 10. Four formulas for calculating the yield are then obtained.

$$A_1 = \left[\frac{12 + n}{22.4}\right]\left[\frac{2}{n + 4}\right](a + b - 4c)\,10 = h_1\,(a + b - 4c) \quad (20)$$

$$A_2 = \left[\frac{12 + n}{22.4}\right](a - c - d)\,10 = h_2\,(a - c - d) \quad (21)$$

$$A_3 = \left[\frac{12 + n}{22.4}\right]\left[\frac{2}{4 - n}\right](3a - b - 4d)\,10 = h_3\,(3a - b - 4d) \quad (22)$$

$$A_4 = \left[\frac{12 + n}{22.4}\right]\left[\frac{2}{n + 2}\right](b + d - 3c)\,10 = h_4\,(b + d - 3c) \quad (23)$$

The fractional terms, being functions only of n, are independent of any given gas analysis data and recur for all calculations. These terms may therefore be multiplied by 10 and expressed as h_1, h_2, h_3, and h_4, thus giving the four right-hand equations for the yield.

In equation (20) the methane term (- 4c) may also be expressed by either of the two characteristic variables for methane formation, Mv or Mco. In the same way, the term (a + b) may be replaced by the conversion, U, and by the ideal gas content of the inlet gas, J. This gives:

$$A_5 = h_1\,(a + b)(100 - Mv)\,10^{-2} = h_1\,JU(100 - Mv)\,10^{-2} \quad (24)$$

$$A_6 = h_1\,(a + b)(1 - \frac{Mco}{25(1 + X)})\,10^{-2} = h_1\,JU(1 - \frac{Mco}{25(1 + X)})\,10^{-2} \quad (25)$$

In the same way, still other transformations of equation (20) and its analogs are possible. The six formulas derived for A are equivalent and give the same numerical values for accurate calculations.

In calculating the maximum theoretical yield, we must know that fraction of carbon monoxide and hydrogen, present in the inlet gas, is capable of complete transformation for a given usage ratio X. This fraction J_X is obtained as follows:

When the hydrogen content of the inlet gas exceeds that of J_X,

$$J_X = CO \ (1 + X) \qquad (26)$$

When the carbon monoxide content of the inlet gas exceeds that of J_X,

$$J_X = H_2 \ \frac{1 + X}{X} \qquad (27)$$

The maximum theoretical yield is generally not given for the entire conversion but only for a small part. For $U = 90\%$ the calculation is as follows:

$$A_{max90} = h_1 \ J_X \ 90(100 - h_V) \ 10^{-4}$$

The equations derived above for the yield always contain n as one of the terms. Using equation (6), n may be expressed in terms of R and the gas analysis data. Substituting $\frac{a \cdot R - g}{p - p' \cdot R}$ for n, in any equations (20-49), we obtain for all four equations an identical new expression for A, in which n no longer appears but is replaced by the four intermediate variables a, b, c, and d.

$$A_7 = 0.892 \ [5a + b - 4 \ (2c + d)] \qquad (28)$$

This equation appears to be the most convenient for practical purposes when sufficient decimal places are retained (calculating machine). Numerical values are obtained which are identical with those for $A_1 - A_4$.

The preceding formulas for the yield give the quantities of higher hydrocarbons, exclusive of methane. Formulas for the total hydrocarbon content, including methane, may be obtained in two ways. Formulas may be derived from equation (1) in the same manner as from equation (2), or the methane term (c) may be set equal to zero in the equations for A_1 to A_7. As already stated in discussing the n-R equation, the inclusion of methane with the other hydrocarbons in our calculations is always indicated by the index n after all abbreviations. Thus:

$$A_{1m} = \frac{20(12 + n_m)}{22.4(4 + n_m)} (a + b) \qquad = h_1 (a + b)$$

$$A_{2m} = \frac{10(12 + n_m)}{22.4} (a - d) \qquad = h_2 (a - d)$$

$$A_{4m} = \frac{20(12 + n_m)}{22.4(2 + n_m)} (b + d) \qquad = h_4 (b + d)$$

$$A_{7m} = \frac{20}{22.4} (5a + b - 4d) \qquad = 0.893 (5a + b - 4d)$$

Factors h_1, h_2, and h_4 have the same numerical values as in equations (20)-(23).

DETERMINATION OF HYDROGEN-CARBON RATIO AND OF

UNSATURATED COMPOUNDS IN THE PRODUCTS

Reasons for Extending the Evaluations

Equation (9) offers one means of calculating the relation between n and E. However, when gas analysis data alone are used, there exists no reliable methods for deciding which of a given number of n-E pairs applies to the particular synthesis run under consideration.

A satisfactory determination of the residual values, either by direct measurement or from the nitrogen determination, is difficult. However, R must be redetermined for each synthesis and for every individual gas analysis, thus giving values that may vary considerably and precluding the possibility of using approximate average values determined in advance.

The considerations for n are completely different. Each type of synthesis has a characteristic value for n, which remains more or less constant during the whole run. Moreover, the variations in numerical values are limited, so that when such values have once been accurately determined they may be used more or less consistently as approximately average values. For practical purposes approximate values for n may be obtained by analysis of the products formed.

The quantitative analysis of the products formed has us still another means for determining of the total yield. The formulas derived above normally would apply only to the formation of pure hydrocarbons, but do not take into account the possible formation of oxygenated groups. The yields calculated by A_1 to A_7 are, therefore, too low—

by the amount of such groups as the hydroxyl or the carboxyl that
may be present in the products. We will next examine to what extent
the oxygenated groups may be determined by purely mathematical methods
from gas analysis data.

Calculation of Oxygenated Groups from Gas Analysis Data

We know from experience, that the oxygenated by-products
of the synthesis are composed largely of saturated alcohols.
Therefore, it would seem possible to determine their amount from
gas analysis data in such a way that a term similar to that for
methane could be introduced into equation (2) and the equation
solved for this term, for example, CH_2O, CH_2O, etc. However, no
valid algebraic expression has been obtained in this way. Both
sides of the equation cancel out or the expression is equal to zero.
In consequence, the idea of calculating oxygenated groups by this
method must be discarded.

The reason for this is plain. From a purely stoichiometric
point of view, it may be assumed that alcohols are composed of one
olefin molecule and one water molecule. Without enlisting additional
experimental evidence there is no means of distinguishing between the
water which leaves the reactor as such and that which enters into
chemical combination.

In the case of methane, it is possible to divide the group
of substances by introducing a special term into the fundamental
stoichiometric equation, because methane may be treated as a separate
individual for the purpose of gas analysis. Water cannot be deter-
mined by gas analysis and only with difficulty by other methods.

Chemical Investigation of the Products Formed

Combustion

The elementary analysis of the liquid products by combus-
tion analysis offers a means of determining the H:C ratio, and con-
sequently n, directly. At the same time it gives an indication of
the possible oxygen content. Unfortunately, not enough is known at
present on this subject. Experiments are in progress.

The general procedure for such a combustion is well known.
We will simply note here that the boiling range of the fractions to be
examined must be considered in choosing the conditions of combustion.
Combustion of heavy oils and of solid paraffins may be effected
in boats with addition of kieselguhr when necessary. For the volatile
portion, the procedure described by Dennstedt[*] is recommended.

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[*] Meyer, H., Analyse und Konstitutionsermittlung, 1938, p. 118.

Precise Fractional Distillation and Chemical Analysis

The oxygenated groups and the H:O ratio may also be determined by precise fractional distillation of the products, followed by quantitative and qualitative analysis of the fractions obtained. The procedure is tedious, but gives a good insight into the composition of the products.

The evaluation of the results entails extensive mathematical operations. The procedure may be considerably simplified by preliminary tabulation of quantities that occur frequently, and by use of suitable work sheets. Examples of such work sheets are shown in tables 11 and 12.

These stoichiometric representations are possible for the oxygenated compounds:

Hydrocarbon residue + oxygen
Hydrocarbon residue + carbon dioxide
Hydrocarbon residue + water

The first case is not directly accessible to calculation since it cannot be reduced to equations (1) and (5). The second case cannot be used in calculations as it stands. Simple calculations for this case show that other yield formulas would have to be derived, taking into account any chemically bound carbon dioxide. The third formula may be used directly since the term for water (w) was always carried in deriving the formulas for yields. Consequently, we are free to consider whatever portion is chemically bound.

The following will illustrate the use of the work sheets reproduced in tables 11 and 12.

To calculate a given the products, the amounts which make up each individual fraction are multiplied by the corresponding n and the sum of all the values thus obtained is divided by the total weight of the product. Nothing is neglected, according to the definition of n. This process (directly or indirectly in all the formulas for the yields down to 4) . Since the definition of these formulas is such that they express only the yield in hydrocarbons, it becomes necessary, when determining the oxygenated compounds in each in the products, to deduct one molecule of water for each molecule of oxygen. The molecule of water, therefore, is deducted for molecule of alcohol, aldehyde, or ketone, and two molecules for each molecule of acid or ester. The hydrocarbon residue (n) thus in calculation may then be expressed as follows:

For alcohols:

$$(OH)_a = C_nH_{2n+2}O - H_2O = C_nH_{2n}$$

For esters:

$$(OH)_e = C_nH_{2n}O_2 - 2H_2O = C_nH_{2n-4}$$

For acids:

$$(OH)_s = C_nH_{2n}O_2 - 2H_2O = C_nH_{2n-4}$$

For aldehydes and ketones:

$$(OH)_{ald} = C_nH_{2n}O - H_2O = C_nH_{2n-2}$$

For olefins:

$$(Olef.) = C_nH_{2n}$$

For paraffins:

$$(Par.) = C_nH_{2n+2}$$

These hydrocarbons residues are now multiplied by the appropriate n value:

For olefins: $\quad \dfrac{2n}{n} = 2$

For paraffin: $\quad \dfrac{2n + 2}{n} = n_p$

For alcohols: $\quad \dfrac{2n}{n} = 2$

For esters: $\quad \dfrac{2n - 4}{n} = n_e$

For acids: $\quad \dfrac{2n - 4}{n} = n_s$

For aldehydes and ketones: $\quad \dfrac{2n - 2}{n} = n_{ald}$

The formula for n therefore reads:

$$n = \frac{2\left[\sum(\text{Olef.})\right] + \sum\left[n_p(\text{Par.})\right] + 2\left[\sum(\text{CH})_a\right] + \sum\left[n_o(\text{CH})_o\right] + \sum\left[n_s(\text{CH})_s\right] + \sum\left[n_{ald.}(\text{CH})_{ald.}\right]}{\sum(\text{Olef.}) + \sum(\text{Par.}) + \sum(\text{CH})_a + \sum(\text{CH})_o + \sum(\text{CH})_s + \sum(\text{CH})_{ald.}} \quad (29)$$

The chemically bonded water (w^a) as well as the (CH) portion of the oxygenated compound is calculated in the following manner. Since the procedure is essentially the same for all oxygenated products a simple example will suffice.

Let a fraction of the total product to be examined equal g grams and let its ester number be (EZ). This fraction then contains $\frac{g(EZ)}{\text{Theor.}(EZ)} = \frac{g(EZ)M_o}{56000}$ grams of ester. (M_o = molecular weight of the ester.) For each mole of ester two moles of water are deducted. The water content of $\frac{g(EZ)M_o}{56000}$ grams of ester is therefore:

$$w_o^a = \frac{36.032 \, g \, EZ \, M_o}{M_o \, 56000} = g(EZ)(0.6434)(10^{-3}) \text{ grams} \quad (30)$$

For the (CH) portion of this weight of ester we then have:

$$\text{Grams ester} - w_o^a = \frac{g(EZ)M_o}{56000} - \frac{g(EZ)36.032}{56000} = g(EZ)\frac{M_o - 36.032}{56000} \quad (31)$$

The fractional term is designated as K_o and calculated in advance for all fractions as well as for all other oxygenated compounds. Thus, the formula for the (CH) portion of the ester becomes $(\text{CH})_o = g(EZ)K_o$.

The amount of paraffin in each fraction is obtained by subtracting the olefins as well as all other (CH) portions and all (w^a) portions of this fraction from g. Thus:

$$(\text{Par.}) = g - \left[\sum(\text{Olef.}) + \sum(\text{CH}) + \sum(w^a)\right] . \quad (32)$$

To obtain the total yield, the amount of chemically bound water must be added to the (CH) yield calculated from A_1 to A_7. This amount (Y) is the sum of all the w^a values divided by the amount of synthesis gas introduced during the time of measurement (reduced to normal conditions). Thus:

$$Y = \frac{\sum(w^a)}{n^a} \quad (33)$$

APPLICATION OF THE FORMULAS DERIVED

Evaluation of Gas Analysis and Synthesis Data

General Course of Calculations

Evaluation of gas analyses by means of the formulas derived may follow one of several different courses according to the nature of the experimental evidence available. An attempt may be made, for instance, to establish practical values for the residual volume by direct measurement or by calculations based on the so-called nitrogen content. The value for R, obtained thus, may be checked by substitution in the n-R equation calculated for the corresponding set of gas analysis data. If R is correct, n must have a value approaching that which has been determined experimentally; for example, for the standard hydrocarbon synthesis under the conditions currently in use, n lies between 2.0 and 2.5. If this is not the case there must be an error either in the experimental data or in the calculations.

Assuming that the source of error lies in the gas analysis data, the calculation will have to be continued with values of the characteristic variables known to be incorrect, or be abandoned. If we assume that the error lies in the residual volume approximately accurate values of the characteristic variables may be obtained for the corresponding gas analysis, by substituting the experimental value for n in equation (8) and solving for R.

Determination of the residual volume by measurement, or from the nitrogen values, and checking of the result obtained, involves more extensive mathematical operations than calculating its value from an assumed value of n known to be approximately correct. Moreover, even if these calculations are correct, the results obtained are equivalent or nearly so, and the method does not guarantee greater accuracy. This last remark is also true of the nitrogen determination. It is therefore possible, under certain conditions, to eliminate R_1, R_2 (direct measurement) and R_3, R_4 (from N_2) completely from the calculations, except as a means of checking the experimental data. This has the advantage of simplifying the laboratory procedure by eliminating the nitrogen determination.

Where sufficient data are available from analysis of the products formed, they may be used in determining n and then calculating R_5. Although the procedure is cumbersome, n must always be determined from the products when values of the characteristic variables are to be calculated with the greatest possible accuracy for a new synthesis whose course is still unknown.

Once R has been determined, evaluation of the intermediate variables a, b, c, and d, and subsequently of the characteristic variables U, W, X, and A, offers no further difficulty. In calculating the yields A_1 to A_5 corresponding values for n and R must be used.

Checking the Results

Check on the Experimental Data

The newly established relations offer a rather simple means of judging the accuracy of the experimental data. For this purpose values for R and n, obtained by different methods, are compared. The examples shown in table 13 will serve as illustrations.

Examples 1 and 2 show what degree of accuracy may be obtained in actual practice for the experimental data. However, particular care is necessary here. Examples 3 and 4 involve less accurate data containing one or more errors. The question is, how shall such errors be estimated.

A series of careful pilot stage experiments (Reichhardtsversuche Schwarzheide) involving a variety of completely different synthetic procedures, consistently gave values for n ranging between 2.0 and 2.3. For the present, $n = 2.15 \pm 0.15$ may, therefore, be considered a reliable approximate value. If the calculated n values (using R values obtained by measurement or from N_2) differ appreciably from the approximate values determined above, corresponding inaccuracies must be sought in the experimental data.

It seems probable that sufficient numerical material will eventually be available to enable us to determine more exactly the sources of discrepancy in the R and n values, as for instance, in measuring the amounts of gas, or in one or another step of the gas analysis.

Table 13

Examples of Calculations of Syntheses Runs

No. Source Catalyst Pressure	1 Lab. Cobalt Normal		2 R.-A.-Res. [1] Iron 10 Atmos.			3 Lab. Cobalt Normal		4 Industry Cobalt Normal	
Gas Analyses									
CO_2	5.2	31.2	0.0	12.2	11.22 [2]	5.0	30.0	14.4	41.9
Olefins	0	0	0.0	1.0	1.0	0.0	2.6	–	0.5
CO	23.6	5.2	39.2	26.8	27.1	28.1	2.7	26.8	12.4
H_2	59.0	21.7	48.4	37.7	38.13	59.8	20.1	53.6	18.6
CH_4	0.2	12.9	3.7	7.9	7.99	0.2	18.9	0.4	11.9
C_2	–	–		1.14		–	1.77	–	1.06
N_2	6.9	28.8	8.6	14.4	14.56	6.9	25.6	4.9	14.6
Residual Volumes R_1	0.231					0.205			
R_2				0.603	0.603				
R_3	0.239			0.598	0.591	0.269		0.336	
R_7	0.221			0.605	0.642	0.222		0.364	
N from R_1	2.22					2.03			
N from R_2				2.145	1.914				
N from R_3	2.27			2.115	1.854	2.47		1.79	
N for R_7	2.15			2.150	2.150	2.15		2.150	
Cal. from R_1 d_1	2.01					1.15			
Cal. from R_1 d_2	2.02					1.15			
Cal. from R_2 d_1				7.36	6.77				
Cal. from R_2 d_2				7.26	6.77				
Cal. from R_2 d_2				–0.01	–0.595				
Cal. from R_3 d_1	2.27			7.30	6.63	3.07		–0.32	
Cal. from R_3 d_2	2.26			7.30	6.65	3.07		–0.32	
Cal. from R_3 d_2	+0.45			–0.087	–0.782	+1.04		–1.16	
Cal. from R_7 d_1	1.70			7.38	7.20	1.66		0.85	
Cal. from R_7 d_2	1.70			7.38	7.20	1.65		0.85	

[1] Government Research.
[2] This value correct, 1% less than corresponding value in preceding column.

Table 13 (Continued)

Examples of Calculations of Syntheses Runs

Yield	A_7					
Cal. with	R_1	143.5	-	-	146.5	-
" "	R_2	-	95.2	96.0	-	-
" "	R_3	141.4	96.2	98.9	130.3	120.6
" "	R_7	145.9	94.8	86.4	142.3	113.0
Conversion U						
Cal. with	R_1	92.90	-	-	94.7	-
" "	R_2	-	55.6	55.1	-	-
" "	R_3	92.70	56.0	56.0	93.1	86.90
" "	R_7	93.20	55.5	52.3	94.3	85.95
Methane formation, Mv						
Cal. with	R_1	13.69	-	-	14.84	-
" "	R_2	-	4.85	5.31	-	-
" "	R_3	14.25	4.48	4.49	20.30	18.33
" "	R_7	12.99	4.94	8.05	16.30	20.50

As long as such a detailed check is not possible, we are free to consider any one part of the data as reliable as the rest. For instance, the measurement of the amounts of gas may be considered as accurate as, or more accurate than, the gas analysis, or vice versa. However, in no case may we neglect the fact that where significant divergences exist between the values for R and the values for n, values of the characteristic variables and the yields calculated from such data offer only a limited degree of accuracy.

Nor should we be misled by the following fact. Using R_1 to R_4 on the one hand and A_7 on the other, it is possible to calculate yields without the term n appearing explicitly in any calculation. At first glance, this procedure would seem to avoid the difficulties which arise from the relation of the yield to the H:C ratio in the products obtained. However, the derivation of A_7 proves beyond doubt that this is not the case.

Check on the Formation of Carbon Dioxide

The amount of carbon dioxide formed may be expressed by two different formulas:

$$d_1 = RCO_2^0 - CO_2 \qquad (34)$$

$$d_2 = \frac{n(a - c) + 2(a - b) + 4e}{n + 4} \qquad (35)$$

When corresponding values, obtained from equation (8), are used for R and n, the values d_1 and d_2 are always in such exact agreement that this offers a means of checking the calculations.

On the other hand, d_2 and the intermediate variables a, b, c, and d, may be calculated from values of R determined experimentally (R_1-R_4). If then, we substitute in equation (35) an approximate n value known to be correct for the hydrocarbon synthesis, for example, 2.15, we find that d_1 is greater or smaller than d_2, according to whether the quantity of carbon dioxide present in the outlet gas is greater or smaller than the amount to be expected for the formation of hydrocarbons whose composition is $CH_{2.15}$. Let d'' be the difference determined in this way.

When no error exists in the experimental data, d'' = $d_1 - d_2$ (calculated from $R_1 - R_4$ and for n = 2.15 ± 0.15) for a standard hydrocarbon synthesis is zero. When carbon dioxide is formed or taken up in any process other than the formation of $CH_{2.15}$ hydrocarbon (including conversion) d'' may be negative or positive.

An error in gas analysis may easily make the carbon dioxide content of the outlet gas appear high or low. The water seal, for instance, may absorb or release carbon dioxide. An example will show what effect this can have on the numerical results.

Example 2, table 13, offers almost perfect experimental data and consequently d'' is very small (- 0.02). The third column of this example shows that changes occur when the carbon dioxide content of the outlet gas is reduced by 1%, for example, 12.2% to 11.2%, and the analysis recalculated on the basis of 100%. If we assume that this decrease in the carbon dioxide content occurs when the gas sample is taken, the measured residual volume R_2 remains unchanged whereas the residual volume R_2 determined from the nitrogen content decreases. In both cases, n decreases considerably and d'' becomes negative. At the same time, the value d'' = 0.782 for R_3, is of the same order of magnitude as the decrease of carbon dioxide in the gas analysis (- 1.0%).

Checking the carbon dioxide formation by calculation of d" offers a means of evaluating the data underlying the calculations, in that it shows to what extent and in what way the amount of carbon dioxide obtained differs from that determined theoretically for the hydrocarbon formation. However, it should be noted that this statement presupposes that the source of error really lies with the carbon dioxide and that the analytical results for the other three gas fractions are correct.

The method used in checking the formation of carbon dioxide could also be applied to the three other intermediate variables a, b, and c. However, there are certain distinctions. New fundamental relations cannot be established since only the equation already used for d₂ is available as a term of comparison. Moreover, for carbon monoxide, hydrogen, and methane the formation or breaking of chemical bonds cannot be assumed as readily as for carbon dioxide.

Calculation of d" makes it possible not only to find sources of error, but to trace other processes that affect the carbon dioxide content of the outlet gas, such as the liberation or absorption of carbon dioxide by the catalyst. This phenomenon may be observed when catalysts, saturated by carbon dioxide, are used.

Compensation of Errors

Assuming that an error in the gas analysis occurs only for carbon dioxide, the calculation of d" gives the difference between the erroneous value obtained and the correct value. Knowing the magnitude and sign of this difference, the corresponding correction for the error may be made.

Knowing d", the correct composition of the outlet gas, may be determined and values of the characteristic variables calculated in the usual manner. If, however, only the yield is desired, it may be calculated directly from the inaccurate analytical values for the outlet gas, by substituting (d - d") in the yield formulas in place d₁ and letting n = 2.15.

In this way, the yield obtained from the inaccurate analysis of example 2 is in excellent agreement with that obtained from the correct analysis (96.3 - 96.5 g. as against 96.5 g. for the correct analysis). If no correction for error is made, the yield for the corresponding n is 99 g. and for n = 2.15 it is 93.8 - 117.5 g.

The procedure is essentially the same for carbon monoxide, hydrogen, and methane, as for carbon dioxide. It must, however, always be stipulated that the error affects only one of these gases and that we know which one of them it is. However, in general this is not the case. In consequence, this type of error compensation cannot at present be applied in every instance. Research on this point is still in progress.

Location of Errors in the Calculations

As already indicated, within the limits of error, we may always write $d_1 = d_2$. This identity may be used in locating errors in the calculation.

Moreover, the value for n in

$$n = 2\frac{(b + 2d) - (a + 2e)}{a - (c + d)} \qquad (36)$$

must be the same as the value of n obtained from equation (8) for the R value used in calculating a, b, c, and d.

Errors in calculation may further be located by using a number of different formulas to calculate the yield. Here, too, accurate calculations (calculating machine) should give complete agreement for the results. The extent to which d_1 and d_2, as well as the various values for A, are in agreement, may be seen from the numerical example given above for the range of validity of equation (8) where this agreement is shown for values of n from 1 to 9.

Finally, when n = 2.0, it is possible to establish the composition of the outlet gas by reversing the order of calculation and starting with the formulae for CO_2, CO, H_2, and CH_4.

Use of Work Sheets

For the actual process of calculation, the use of work sheets has been found convenient. Such a work sheet is shown in table 14. A short list of formulas, showing only those formulas needed in actual practice is given in table 15.

Experience has shown that the use of these work sheets makes it possible for non-technical personnel to calculate values of the four characteristic variables for a gas analysis in about five minutes.

Calculations for the Prediction of the Course of a Synthesis

The formulas derived above would be of considerable help in predicting the course of a synthesis, as for instance, when planning a new installation. However, since no specific problem presents itself for consideration here, this indication must suffice.

An accompanying diagram gives a graphic representation of the relations between the characteristic variables for the simple case where n = 2.0. When three of the four numbers are known, the fourth one may be read directly from the graph.

Uniform Use of Symbols

Notwithstanding the intensive research on the hydrogenation of carbon monoxide and despite the extensive exchange of experimental data from numerous sources, there is still no uniformity in definitions, abbreviations, and symbols used in calculating gas consumption. The numerous advantages offered by a uniform procedure make agreement on the following points highly desirable.

(1) Choice and accurate definition of symbols.

(2) Specification of abbreviations used.

(3) Exchange of most reliable values obtained for n and β, as well as, agreement as to average values.

(4) Agreement with respect to inclusion of oxygenated products in the yield, working procedures, and methods of calculation.

(5) Establishment of a general procedure for compensation of errors.

Formulas were derived and the charts developed with assistance of Eugen Jacob.

Table 11

Sample Worksheet II

Characteristic Variables

Yields per m^3

$U = \quad \%$

$M_v = \quad \%$

$X =$

A_1	
$A_{11} \dfrac{G}{E}$	
$A_{11} A_2 + Y$	
$2\left(\text{Olef.}\right) =$	g $\sum(\text{O}$
$\sum(n_p \cdot \text{Par.}) =$	g $\sum(\text{P}$
$2\sum(CH_a) =$	g $\sum(CH$
$\sum[n_e(CH)]_e =$	g $\sum(CH$
$\sum[n_1(CH)]_4 =$	g $\sum(CH$
$\sum[n_e(CH)]\text{ald} =$	g $\sum(CH$
numerator	g
denominator	

	E	A(')
CO_2		
Unsaturates		
O_2		
CO		
H_2		
J		
CH_4		
2		
N_2		
N_2-P		

$\beta =$ $\beta - CH_4' =$

$p =$ $q =$

$p' =$ $g' =$

Date / Time

Amount Sy.-Gas m^3 Amount outlet gas m^3

	R	n		
			a.	
1			b.	
2			a + b.	
3			c.	
4			$d_1 =$	
6			$d_2 =$	
7			$d_{11} =$	

Main Worksheet Table

Tot. Prod. Amount in G.	Olefins		Paraffins			Alcohols				Esters				
C–Z Fract. •g	Percent	Amount in G. g-[Olef. +CH+Wⁿ]	n_p	n_p-Par.	OH-Z	W_a^n g-OH-Z 3.217·10⁻⁴	$K_a \cdot 10^3$	$(CH)_e$ g-OH-Z-K_a	E-Z	W_e^n g-E-Z 6.434·10⁻⁴	$K_e \cdot 10^3$	$(CH)_e$ g-EZ-K_e	N_e	$N_e(CH)$
1			4.000				0.250				0.679		0.667	
2			3.000				0.500				0.929		1.000	
3			2.667				0.751				1.179		1.200	
4			2.500				1.001				1.430		1.333	
5			2.400				1.251				1.680		1.429	
6			2.333				1.627				1.930		1.500	
7			2.286				2.127				2.431		1.600	
8			2.250				2.628				2.931		1.667	
9			2.222				3.003				3.432		1.714	
10			2.200				3.379				3.682		1.733	
11/12			2.174				4.255				4.683		1.790	
13/14			2.148				6.257				7.437		1.867	
15/16			2.129				0.500				0.000		0.000	
17/18			2.114											
19/27			2.087											
>27			2.057											
$\sum = C =$	$\sum(\text{Olef})$		$\sum(n_p \cdot \text{Par})$			$\sum(W_a^n)$		$\sum(CH)_a$		$\sum(W_e^n)$		$\sum(CH)_e$		$\sum(n_e \cdot CH) =$

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Table 12

Sample Worksheet II

Characteristic Variables	Yields per m³	Actual Conversion	% Conversion	Without Methane		With Methane	
		Syn. Gas	CO + H₂	Syn. Gas	CO + H₂	Syn. Gas	CO + H₂

$U = \ldots \%$

$M_v = \ldots \%$

$X = \ldots$

A_z

$A = \dfrac{G}{E}$

$A_{11} = A_z' + Y$

$2 \ (Olef.) = \ldots \ldots g$

$n_p \cdot Par = \ldots \ldots g$

$2 \ (CH)_a = \ldots \ldots g$

$n_e \cdot (CH)_e = \ldots \ldots g$

$n_1 \cdot (CH)_4 = \ldots \ldots g$

$n_{ald} \cdot (CH)_{ald} = \ldots \ldots g$

numerator $\ldots \ldots g$

denominator $\ldots \ldots g$

$W_a'' = \ldots \ldots g$

$W_e'' = \ldots \ldots g$

$W_s'' = \ldots \ldots g$

$W_{ald}'' = \ldots \ldots g$

$W'' = \ldots \ldots g$

$Y = \dfrac{W''}{E} = \ldots \ldots g/m^3$

$n = \dfrac{numerator}{denominator}$

$n_m = \dfrac{numerator + 4(CH_4)}{denominator}$

ESTERS

W_e in G. $\dfrac{g \times E-Z}{6.434} \times 10^{-4}$	$K_e \times 10^3$	$(CH)_e$ $g \times EZ \times Ke$	N_e	$\eta_e \times (CH)_e$	N-Z
	0.679		0.667		
	0.929		1.000		
	1.179		1.200		
	1.430		1.333		
	1.680		1.429		
	1.930		1.500		
	2.431		1.600		
	2.931		1.667		
	3.432		1.714		
	3.682		1.733		
	4.683		1.790		
	7.437		1.867		
	0.000		0.000		
$\sum(W_e'')=$	$\sum(CH)_e$		$\sum[\eta_e(CH)_e]$		

ACIDS

W_a' in G. $\dfrac{g \times NZ}{6.434} \times 10^{-4}$	$Ka \times 10^{-3}$	$(CH)_s$ $g \ N2 \ Ka$	N_s
	-		-
	-		-
	0.179		-2.000
	0.429		0.000
	0.679		0.667
	1.305		1.111
	1.661		1.333
	2.181		1.500
	2.681		1.600
	3.183		1.687
	4.685		1.778
	7.687		1.862
	0.000		0.000
$\sum(W_s'')=$	$\sum(CH)_s=$		

ALDEHYDES AND KETONES

W_{ald}'' in G. $\dfrac{g \ CO-2}{6.434} \times 10$	$K_{ald} 10^3$	$(CH)_{ald}$ $g \ CO-2 \cdot K_{ald}$	n_{ald}	$n_{ald}(CH)_{ald}$
	1.179		1.200	
	1.931		1.500	
	2.431		1.600	
	2.931		1.667	
	3.432		1.714	
	3.932		1.750	
	4.689		1.790	
	5.936		1.833	
	6.936		1.857	
	7.936		1.875	
	11.439		1.913	
	17.950		1.944	
	0.000		0.000	
$\sum(W_{ald}'')$	$\sum(CH)_{ald}$		n_{ald} $\sum[(CH)_{ald}]=$	

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Table 14

Sample Worksheet III

Date	Time			Exper. No.		Temp.			
		E	A₁/A		Reqd. volume from			R	n	R.CO $= CO_2$
Time				Measurement		1			d_1
CO_2				Standard state		2			d_2
Olefina				N_2		3			n
O_2				H_2 Micro-determination		4			U = %
CO				Calculated for n = 2.0		5	2.0		Mr = %
H_2				Calculated N_2 from Prod. A		6			X =
I				Calculated for Theoret. A		7			A = R/ ob. m.
CH_4				p =					
C-No.				p¹ =					
N_2				q =					
N_2R				q³ =					
				CH_4 β =					

Right-side symbols: CO = R.C — a; H_2 = B·H_2 — b; a+b; R.CH_4 = CH_4 — c

Table 15

List of Formulas for the Evaluation of Gas Analysis Data from
the Hydrogenation of Carbon Monoxide

R_1, R_2 (as measured) R_3, $R_4 = \dfrac{N_2}{N_2'}$

$$R = \frac{2CO + 3CO_2 - (H_2 + CH_4)}{2CO' + 3CO_2 - (H_2 + CH_4 \cdot B)}$$
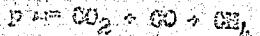
$p = CO_2 + CO + CH_4$

$p' = CO_2' + CO' + CH_4' \cdot B$

$q = 2\left[(2CO_2 + CO) - (H_2 + 2CH_4)\right]$

$q' = 2\left[(2CO_2' + CO') - (H_2' + 2CH_4' \cdot B)\right]$

R_5, $R_7 = \dfrac{p \cdot R + q}{p' \cdot R + q'}$ $n = \dfrac{q' \cdot R - q}{p - p' \cdot R}$

$a = CO - R \cdot CO'$ $e = R \cdot CH_4' \cdot B - CH_4$

$b = H_2 - R \cdot H_2'$ $d_1 = R \cdot CO_2' - CO_2$

$$d = \frac{n(a - n) + 2(e - b) + 4c}{n + 4}$$

R	B
1.0 – 1.05	1.0
1.05 – 1.25	0.9
Über 1.25	0.85

$U = \dfrac{a + b}{2} \cdot 10^2$ $x = \dfrac{b}{2}$

$W = \dfrac{4c}{a + b} \cdot 10^2$

$A_7 = 0.893\left[5x + b - 4(2c + d)\right]$

$n = 2 \cdot \dfrac{(b + 2d) - (c + 2e)}{b - (c + d)}$

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CALCULATION OF YIELD FOR HIGHER HYDROCARBONS

BASED ON RECENT METHODS

BY DR. OTTO ROELEN

SUMMARY

The methods for the calculation of the yield and related properties, discussed in the preceding paper (Ib-3), are developed further and compared by RARW (Reichsamtversuchen Angewandte Rechenweise. Trans., Methods of calculation employed in experimental work carried out under the direction of the Reich).

INTRODUCTION AND EXPLANATION OF SYMBOLS

Experiments undertaken under the auspices of the Reich at Schwarzheide have led to a new method for calculating the yield obtained in the synthesis of higher hydrocarbons. Examples of this procedure have already been given (see preceding paper, Ib-3), but to date there has been no description of the method detailed enough to enable an outsider to use it without additional instructions. Experience has shown that an agreement on this subject presents certain difficulties. In order to compare the method used in government research (RARW = Reichsamtversuchen angewante Rechenweise) with the formulas that have been derived more recently. A description of RARW is given below.

To facilitate comparison between the two methods, RARW has expressed the abbreviated terms which were introduced in our own procedure. An explanation of the abbreviations used is given in the preceding paper (Ib-3). In addition, the following new symbols have been included:

o   (1) as a coefficient: volumes of oxygen formed ($\frac{1}{2} O_2$) present in chemical combination in the oxygenated products.

    (2) as a superscript: indicates the value after deduction of oxygen.

n^o Average value for H:C ratio in the CH-portion of the products (not including methane) after deduction of oxygen from the oxygenated compounds.

n^o_m As above, but with methane included in the products.

A^o_{co} Yield according to the fundamental molar calculation designated as "CO yield".

A^o_2 Yield according to the calculation of the limiting yield for an ideal gas, designated as "ideal gas yield".

THE CO YIELD

1. 100 - contraction = residual volume, R.

2. The final amounts of carbon monoxide and dioxide are given as the product of the residual volume times the content (percent) in the exit gas:

$$R(CO'), \quad R(CO_2')$$

3. The amounts formed or reacted are given as the difference between the amounts in the product and the initial amounts:

$$a = CO - R(CO') \qquad d = R(CO_2') - CO_2$$

4. The volume of reacted carbon monoxide minus the volume of carbon dioxide formed gives the volume of hydrocarbons formed CH^o_n (incl. methane):

$$c_m = a - d$$

5. Multiplication by the "molecular weight:22.4" gives the volumes of CH-products in grams. The molecular weight of CH^o_n is known as the fundamental molar constant:

$$A^c_o = \frac{\text{fundamental molar constant}}{22.4} (a-d) = \frac{12 + n^o_m}{22.4} (a-d)$$

IDEAL GAS YIELD

1. Reacted carbon monoxide and hydrogen are determined as described in previous section, Nos. 1-3:

$$a = CO - R(CO') \qquad b = H_2 - RH'_2.$$

2. Dividing, we obtain the usage ratio:

$$u = \frac{b}{a}$$

3. For a given usage ratio the amount of CO + H2 gas present in an ideal inlet gas that would undergo complete conversion is calculated, thus:

$$J_X = CO \, (1+x), \text{ for an excess of } H_2 \text{ over the H in } J_X.$$

4. The limiting yield is the possible yield, given complete conversion, for a m^3 of ideal gas measured under normal conditions. This yield is calculated from the analysis for fluid products (liquid and gas), each class of substance contributing to the total sum.

5. The CO conversion is obtained by dividing the reacted carbon monoxide by the carbon monoxide initially present:

$$U_{CO} = \frac{a}{CO}$$

6. The yield in hydrocarbons $CH_{2n}O$ may then be written:

$$Ai^o = \text{limiting yield x amount of ideal gas x CO conversion}$$
$$= \text{limiting yield} \left[CO(1+\frac{b}{a})\right]\frac{a}{CO}$$
$$= \text{limiting yield} \, (a+b)$$

LIMITING YIELD AND FUNDAMENTAL MOLAR CONSTANT

The following considerations may be useful in clarifying the concept of "limiting yield". The yield formula, which contains the limiting yield, reads as follows:

$$Ai^o = \text{limiting yield} \, (a+b)$$

This yield must be the same as the yield obtained from the third fundamental stoichiometric equation (see appendix).

Therefore:

Limiting yield $(a+b) = h_1 (a+b+o)$

From which:

Limiting yield $= \frac{a+b+o}{a+b} (h_1)(100).$

When hydrocarbons above are formed, o equals zero and the limiting yield equals h_1.

Sample calculations lead to the same result. The formation of ethanol, for example, may be expressed in two ways:

$$2\ CO + 4\ H_2 = C_2H_6O + H_2O$$

or

$$3\ CO + 3\ H_2 = C_2H_6O + CO_2$$
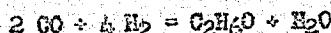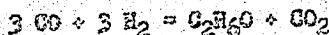
In both cases 6 volumes $(CO + H_2)$ give one volume C_2H_6 as ethanol. When ethane forms, however, 1 volume C_2H_6 requires 7 volumes $(CO + H_2)$:

$$2\ CO + 5\ H_2 = C_2H_6 + 2\ H_2O$$

or

$$4\ CO + 3\ H_2 = C_2H_6 + 2\ CO_2$$
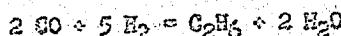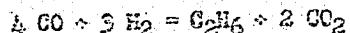
The limiting yield for $1\ m^3$ $CO + H_2$ under standard conditions is therefore:

Formation of ethanol and deduction of oxygen: 223 g C_2H_6

Formation of ethane: 192 g C_2H_6

For ethanol, after deduction of oxygen, the H:C ratio is given by $n^0 = 3.0$. It follows that:

$$h_1 = \frac{20(12+n^0)}{22.4(4+n^0)} = 1.92$$

Thus, when hydrocarbons alone form, the limiting yield is equal to h_1. When oxygenated compounds form, the limiting yield is in inverse proportion to the amount of $CO + H_2$ that reacts.

$$\text{Limiting yield} = \frac{(CO + H_2) - \text{Amount reacting to give CH as hydrocarbons}}{(CO + H_2) - \text{Amount reacting to give oxygenated compounds}}\ h_1$$

For the example of ethanol:

$$\text{Limiting yield} = \frac{7}{6}\ h_1 = \frac{7}{6}\ .192 = .223\ g$$

The fundamental molar constant is given by $12 + n_n^0$ and for ethanol equals $12 + 3.0$ or 15.0.

THE FUNDAMENTAL STOICHIOMETRIC RELATIONS

According to RAHN, the total yield is composed of Aco or Ai calculated for the CH-fraction and of the oxygen contained in the products.

Consequently, this oxygen must also appear in the fundamental stoichiometric relation, if this relation is to give a true picture of the total reaction. When oxygen is deducted, the second fundamental stoichiometric equation must, therefore, be extended to include the term cO. The following equation, known as the third stoichiometric equation, is then obtained:

$$a\ CO + b\ H_2 = c^+\ CH_nO + c\ CH_4 + d\ CO_2 + e\ H_2O + o\ O.$$
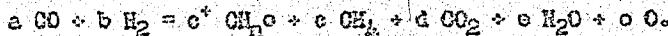
This equation is the basis for RARW. Its algebraic interpretation will be found in the appendix.

It can be shown that the RARW calculations for the CO and ideal gas yields call upon the same formulae as those derived from the above fundamental stoichiometric equation for A_2^o or A_1^o. A purely formal difference is occasioned by the introduction of the limiting yield which takes the oxygen term out of the expression in parentheses and places it in the limiting yield:

RARW	Third Fundamental Stoichiometric Equation
$A_{CO}^o = \dfrac{12 + n_m^o}{22.4}\ (a-d)$	$A_2^o = \dfrac{12 + n_m^o}{22.4}\ (a-d)$
	$= h_2\ (a-d)$
$A_i^o = \text{limiting yield}\ (a+b)$	$A_1^o = h_1\ (a+b+o)$
$= \dfrac{a+b+o}{a+b}\ h_1\ (a+b)$	

THE ANALYSIS CONTRACTION

The yields calculated by RARW for A_{CO}^o and A_i^o do not in general agree. It was observed that the two yields are brought into agreement when another contraction is substituted in the calculation. However, such an agreement exists for only one specific contraction. This contraction is known as the "analysis contraction" and must be determined empirically. For this purpose, the amounts of inlet and outlet gas obtained by measurement are altered in such a way that the ensuing calculation gives the same value for both yields. This value is then taken as the correct one.

As will be seen from the derivation of our new formulas, the n-R equation constitutes the basis for this empirical method of calculation. Both the yield formulas used by RARW:

$$A_{CO}^o = \frac{\text{fundamental molar constant}}{22.4}\ (a-d) \qquad A_i^o = \text{limiting yield}\ (a+b)$$

implicitly contain the n or n_m^o value, and consequently the value for R. The difference between the two yields increases, as R differs from the value which, according to the n-R equation, corresponds to the given n_m^o. When n and R satisfy the n-R equation for a given set of gas analyses, the two yields coincide.

These relations hold not only for the two yield calculations already used by RAHN, but also for three other different yield formulae (A_3, A_4, A_7). Two of these formulas (A_4 and A_7) show an even greater discrepancy than the yields already obtained by RAHN. If the problem were still in the experimental stage it would, therefore, be advisable to consider these two new formulas. However, this is not the case.

Given n, the n-R equation offers a means of determining the appropriate residual volume (R_6, R_7) for every set of gas analyses and thus of calculating the analysis contraction. Therefore:

Analysis contraction = $100 - R_6$ (or R_7).

SEPARATION OF OXYGENATED COMPOUNDS INTO THE CH-RADICAL AND WATER OR OXYGEN

For the purpose of calculation, RAHN has chosen to break down the oxygenated compounds by elimination of oxygen as such, rather than as water. The reason for this, as explained by Dr. Pichler, is that the CH yield then contains all the hydrogen, which is not the case when water is eliminated. Except for this rather theoretical advantage, the other method, which proceeds by eliminating water, is the more convenient.

When oxygen is eliminated, the yield is expressed as A_{co}^o, and, by means of the limiting yield, as A_L, without necessitating the introduction of an explicit term for oxygen. However, as far as we now know, the method offers no other advantages. All other expressions, derived from the third fundamental stoichiometric equation, contain the cO term. Hence, they cannot be used in making calculations, unless the oxygen content has been determined in the analysis of the products.

On the other hand, when water is eliminated, the corresponding term also disappears and the formula contains, besides R and n, only the intermediate variables, a, b, c, and d, obtained by gas analysis. In this way, numerous formulas for the yield, the formation of carbon dioxide, the H:C ratio, the n-R relation, etc., may be derived, using only n and the values obtained by gas analysis. Thus, these formulas are capable of general application and are valid even for cases where oxygenated compounds form, but are not analysed and consequently cannot be introduced into the calculations.

In evaluating further experimental data, it is therefore advisable, to proceed by eliminating water from the oxygenated compounds, rather than oxygen alone as heretofore.

As an illustration, the most important values of the two methods are listed for comparison. The numerical examples are taken from the formation of ethanol.

	CH Fraction of the Oxygen Compound Obtained by Elimination of	
	Water	Oxygen
Yield:		
CH fraction	$A = \ldots$ g C_2H_4	$A^o = \ldots$ g C_2H_6
O fraction	$Y = \ldots$ g water	$\ldots$ g O
Total yield	$A_{11} = A + Y_g$ C_2H_6O	$\ldots$ g C_2H_6O
H:C ratio, calc. for the hydrocarbons formed:		
without methane	$n = 2.0$	$n^o = 3.0$
with methane	$n_m = \ldots$	$n_m^o \ldots$
Fundamental molar constant	$12+n = 14$	$12+n^o = 15$
Limiting yield	$h_1 = \dfrac{2(12+n)}{22.4\ (n+4)}$ $= 208.3$ g C_2H_4	$\dfrac{a+b+2}{a+b}\ h_1$ $= \dfrac{a+b+2}{a+b}\ \dfrac{2(12+n^o)}{22.4\ (n^o+4)}$ $= \dfrac{7}{6}x192 = 223$ g C_2H_6

USE OF ABBREVIATIONS IN FORMULAS

Elimination of water, rather than of oxygen, from oxygenated compounds, offers an advantage only when taken in conjunction with abbreviations used as a shortcut in mathematical operations. Therefore, this is also recommended in evaluating future experimental data. A number of advantages are then obtained.

In determing the hydrocarbon yield, a single constant, the H:C ratio n, now replaces two constants, the fundamental water constant and the limiting yield. The yield no longer need be calculated twice (CO yield, ideal gas); a single formula now suffices.

APPENDIX

Calculation of the Yield with Introduction of Chemically Bound Oxygen as Such

1. Third fundamental stoichiometric equation:

$$a\ CO + b\ H_2 = c_1^+ CH_nO + c\ CH_4 + d\ CO_2 + e\ H_2O + o\ O$$
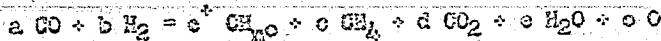
2. Summation equations for the three elements:

for carbon: $a = c_1^+ + c + d$

for oxygen: $a = 2d + e + o$

for hydrogen: $2b = n^o c_1^+ + 4c + 2e$

3. Solution

$$c_1^+ = \frac{2}{n^o+4}(a+b-4c+o) \qquad\qquad c_3^+ = \frac{2}{4-n^o}(3a-b-4d-o)$$

$$c_2^+ = (a-c-d) \qquad\qquad c_4^+ = \frac{2}{n^o+2}(b-3c+d+o)$$

$$d = \frac{n^o(a-e)+2(a+2c-b-o)}{n^o+4}$$

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Yield formulas:

$$A_1^o = \frac{12 \cdot n^c}{22.4} \cdot \frac{2}{n^o + 4} (a+b-4c+o)10 = h_1 (a+b+4c+o)$$

$$A_2^o = \frac{12+n^c}{22.4} (a-c-d)10 \qquad\qquad = h_2 (a-c-d)$$

$$A_3^o = \frac{12+n^o}{22.4} \cdot \frac{2}{4-n^c} (3a-b-4d-o)10 = h (3a-b-4d-o)$$

$$A_4^o = \frac{12+n^o}{22.4} \cdot \frac{2}{n^o+2} (b-3c+d+o)10 = h_4 (b-3c+d+o)$$

5. Inclusion of methane in the yield gives:

$$n^o = n_m^o \text{ and } c = o.$$

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