PART II

Computation of Hydrocarbon Formation from the Data of Gas Analyses.

A. Three basic assumptions in all computations of gas analyses

When investigating all computations from gas analyses in a continuous catalytic hydrogenation of carbon monoxide, and for any course of synthesis of this kind, three general assumptions can be made, which may be always assumed to be known:

First assumption (for all participants of reactions):

"the sum of all substances entering a reaction is equal to the sum of all converted or resulting materials".

Second assumption (for each individual gas constituent):

"In the case of gaseous materials which enter a reaction, or are formed, the sum of materials in the gas in the intake or outlet is equal to the sum of the amounts consumed or formed, and the undecomposed part".

Third assumption (for nitrogen only):

"The amount of nitrogen present in the entering gas is neither increased nor reduced during the conversion".

These three rules furnish us the foundation for all mathematical derivations and for any testing for the results.

B. Algebraic Expression of the Three Assumptions:

1. The two basic stoichiometric equations and their solution.

According to the first assumption, all amounts of materials entering the reaction space must exactly equal the amounts of materials leaving that space. We may disregard the high melting point paraffin deposited upon the catalysts, because its amount does not markedly affect the results of gas analyses, and because the computations are valid for a continuous synthesis in a state of equilibrium. When only or almost only hydrocarbons are formed, the reaction participants which come under consideration are either known individually (e.g. n-butane, i-butane, n-butene, i-butene)

or at least the class to which they belong (C_{H_n}). We may
therefore denote as equal the amounts of materials entering and
leaving the space, as follows:

$$a\ CO + b\ H_2 = c_n\ CH_{n_m} + d\ CO_2 + e\ H_2O$$

This equation is called below the "first basic stoichiometric
equation". The values a, b, c and d in that equation represent
the amounts of carbon monoxide and hydrogen consumed in that space,
or the amounts of carbon dioxide, hydrocarbons and water formed
in that space (v explanation of symbols). They are used in all
computations and are called below the "intermediate values".

We can derive a number of stoichiometric steps from the
above equation, because the expressions of the sums of the three
elements carbon, oxygen, and hydrogen are always equal:

For carbon: $a = c_n + d$

For oxygen: $a = 2d + e$

For hydrogen: $2b = n_m \cdot c_m + 2e$

Simple algebraic transformations of these three equations
permit a general solution of the first fundamental stoichiometric
equation in the collection of formulas.

The expression $c_m\ CH_{n_m}$ includes simultaneously all the hydrocarbons
formed. The gas analysis permits, however, to determine separately
the methane formed, and this expression can be broken up into the
volume of the higher hydrocarbons formed (exclusive of methane)

c^+ CH_n, and the volume of the methane formed c CH_4. Introducing
these expressions into the first basic stoichiometric equation
gives us

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

We call this equation the "second basic stoichiometric equation"
For sums of the three elements we can derive the three following
equations:

For carbon: $a = c^+ + c + d$

For oxygen: $a = 2b + e$

For hydrogen: $2b = n \cdot c^+ + 4c + 2e$

Algebraic transformation of these three equations gives us
a general solution of the second basic stoichiometric equation,
found in the collection of formulas. Not all of the numerous
solutions have equally great practical worth. The maximum accuracy
is obtained if the greatest possible number of experimental data
(a, b, c and d) are included. The experimentally not readily
determinable volume of the steam formed, e, should not be represented.
This explains the selection of the six solutions found.

These solutions are remarkable in many respects. They show
in the first place in what way the volume c^+, which is in most cases
required in the synthesis of higher hydrocarbons, depends on the
values obtained in gas analysis for a, b, c and d, as well as from n.
These equations form therefore the basis for all computations for
yield.

We also see that in addition to n, only three of the four known values a, b, c and d are required for the computation of c^+. For this reason, c^+, as well as the yield can be computed in four different but equally valuable ways.

The solution for d is of particular significance. This equation contains the four intermediate values a, b, c and d in addition to n, which gives us in a simple and convenient form the first expressions of numerical relationships between these values. This equation can be frequently used in derivations by always permitting the expression of any of the four values a, b, c and d in terms of the three others, as well as because of the relationship contained in it between n and the residual volume R.

2. Computation of intermediate values.

The second assumption states that for gaseous materials consumed, the amounts entering are equal to the sum of the amounts consumed and those not converted.

We may express the amount for carbon monoxide as follows:

Entering CO = consumed + unconverted CO.

The amount of the unconverted carbon monoxide is obtained from analysis and from the amount of the residual gas, as R. CO'. We get therefore:

CO = a + R . CO', or a = CO - R . CO'

We obtain similarly for the other three intermediate values:

$$b = H_2 - n \cdot H_2'$$

$$c = n \cdot CH_4' - CH_4$$

$$d = n \cdot CO_2' - CO_2$$

The algebraic expression for the first assumption leads to the mathematical relationship between the four magnitudes, a, b, c and d, and of n, while the expression for the second assumption brings us on the one hand to the relationship between the four intermediate values and the results of gas analysis, as well as from the residual volume. It will be shown that, leaving aside the yet to be discussed and not sufficiently dependable proportion of nitrogen, we exhaust here all the possibilities to basic fundamental relationships exclusively on the data of gas analysis. All future computations of this kind are therefore referred to the already given algebraic expressions for the first and second assumptions.

3. Computation of the Residual Volume from the Nitrogen Content:

The third assumption states that the amount of nitrogen present in the reacting gas is not affected by the conversion, and remains unaltered in the gas leaving the reaction space. This leads us to the method of computation of the residual volume from the nitrogen content, used since the beginning of work on gasoline synthesis.

The amount of nitrogen in the gas inlet as well as outlet stays in the same proportion to the total amount of gas as the percentage of N_2 found analytically is to 100. If we set the gas

intake = to 1, the residual gas volume can be computed

$$\frac{Gas\ intake}{Amount\ of\ nitrogen} = \frac{1}{Amount\ of\ nitrogen} = \frac{100}{N_2}$$

$$\frac{Gas\ outlet}{Amount\ of\ nitrogen} = \frac{R}{Amount\ of\ nitrogen} = \frac{100}{N_2'}$$

$$R_2 = \frac{N_2}{N_2'}$$

The third assumption leads us therefore to an additional basic relationship. Its practical importance is however but limited, because experience has shown that the values for R so obtained are connected with an uncontrollable, variable and in most cases not insignificant error. The reason for it is the fact that the analytical values for nitrogen are not obtained by direct nitrogen determinations, but by a difference. A relatively small volume of nitrogen carries therefore the sum of the errors of the determinations of all of the other gas constituents. Experience has also shown that errors are also introduced when R is determined from the N_2 values found in two gas samples taken at the same time, but which for some reasons, do not exactly belong together.

4. The n-R equation:

The second basic stoichiometric equation gives the following expression for the solution for d:

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

Were we to introduce into this expression the intermediate values

derived from the second assumption, we will get, after making

corresponding transformations:

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

Let us set:

$$p = (CO_2 + CO + CH_4) \qquad q = 2/(2CO_2 + CO) - (H_2 + 2CH_4)/$$

$$p' = (CO_2{}' + CO' + CH_4{}') \qquad q' = 2/(2CO_2{}' + CO') - (H_2{}' + 2CH_4{}')/$$

Using these abbreviations, the above equation can be solved for n

and for R:

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

These last identical equations will be called below the "n-R equation".

In addition to n and R, they contain only the data obtained from

gas analyses on the composition of the intake and outlet gases.

This equation permits the calculation of a numerical relationship

between n and R from each pair of gas analyses.

The n-R equation has been derived without the use of any

supplementary assumptions, and it satisfies therefore strictly the

first and the second assumptions.

"n_m - R equation" can be derived in an entirely analogous way

from the first basic stoichiometric equation. This then is applicable

when methane is not treated specifically, and when all hydrocarbons

including methane are entered into the computations together.

In these expressions the subscript m is added to all of the corresponding

abbreviations used above.   It follows then:

$$p_m = CO_2 + CO$$

$$q_m = 2(2CO_2 + CO - H_2)$$

$$p^0_m = CO_2' + CO^3$$

$$q^0_m = 2(2CO_2^0 + CO^0 - H_2^0)$$

$$n_m = \frac{q^0_m - R - C_m}{p_m - p^0_m \cdot R}$$

$$R = \frac{C_m + p_m \cdot n_m}{q^0_m + p^0_m \cdot n_m}$$

Recalculation of n to n_m and the reverse can be done as follows:

The equation for hydrogen: $q_m \cdot n_m = c^+ \cdot n + 4c$

The equation for carbon: $c_m = c^+ + c$

with which we get: $n = \dfrac{c^+ \cdot n + 4c}{c^+ + c}$

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

5. Applicability and Range of Validity of the Relationship Between the Auxiliary and Intermediate values.

The calculation of the actual factors requires numerical values for the magnitudes a, c and d, as we shall see below. If the residual volume could be in any way determined with sufficient accuracy, these numerical values could be readily determined from the equations for intermediate values derived from the second assumption. Unfortunately such is not the case. This fact offers the most important difficulty of all computations from gas analyses.

It has already been mentioned that the residual gas volume is not sufficiently accurately found from the so called nitrogen

determinations. The same applies also to direct measurements of residual volume, in particular when synthesis is conducted at an increased pressure.

There is a third possibility, and as far as is known today also the last one, of calculating R from the n - R equation. This would require however a knowledge of the numerical value for n. If neither R or n are known, there exists, as far as is known today, no possibility of obtaining these magnitudes entirely from results of gas analysis while strictly adhering to the first and second assumptions. This will require the use of a method of determination of a still different kind. We may find n from the analysis of the products formed, as has been described in greater detail below. If n obtained in this way is introduced into the n - R equation, value designated later as R_6 is obtained.

If we use assumed, only approximately correct values for n in the n - R equation we can still obtain acceptable approximation value for R (R_5, R_7), using only the results from gas analysis, and retaining the first and second assumptions. The latter claims that the factors calculated from these R values are in fact applicable for hydrocarbons of the composition CH_n. This is by no means the case when using the R values obtained by direct measurements (R_1, R_2), or from nitrogen (R_3, R_4). We will find for instance that these factors are valid for the formation of such hydrocarbons, in which the H : C ratio differs considerably from the correct average composition, e.g. $CH_{0.5}$ or CH_7.

The deciding advantage of the R values calculated from the n - R equation lies in this certainty of the relationship of the factors found for the formation of hydrocarbons from the accurately known average compositions CH_n.

We may mention the following for further consideration of the nature of the n - R equation. If pairs of values for n - R from different pairs of gas analyses are plotted, a curve is obtained starting from the 0 point. The curvature is such as to make it appear as if the coordinates of the apex of the curvature are the n and R values obtained from the corresponding gas analyses. However, such an exceptional point can be determined neither from differences, nor graphically. The non existence of such an exceptional point may be shown in the following way.

All relations between the intermediate values and the factors calculated with the use of n and R have the analytical form of a straight line, or an almost straight line. This can only be possible however if the n - R equation is applicable not only to a single course of synthesis, but for any number of them.

If whole numbers 1 to 9 be substituted for n in the n - R equation obtained from any kind of course of synthesis, and the corresponding values for R are calculated, nine pairs of values for n - R are obtained. Every pair of these values gives correct factors for a corresponding course of synthesis. Stoichiometrically there is nothing in the way of an actual occurance of these nine different

syntheses. This applies, however, not only to the whole number n

values used in the example, but also to all the fractional numbers,

and therefore for any n value, or for any pairs of n - R.

We may state it differently as follows: a pair of gas analyses

of an intake and outlet gases need not only be derived from some

single course of synthesis, but may be applicable simultaneously

for any number of different synthesis, with a definite n - R pair

of values belonging to every course of synthesis.

We may add the following particulars to the numerical example

of the range of validity of the n - R equation. In this example

always the same end gas composition is assumed from the entering

water gas, using for instance the following different requirements:

1. Acetylene or benzol (CH_1) is formed in addition to methane

   with residual gas volume of 47.3 percent and a yield of

   121.1/g/cbm.

2. With a residual gas volume of 61.7 percent and a yield of

   85.7/g/cbm in addition to methane only pure olefine

   hydrocarbons (CH_2) are formed.

3. With a residual gas volume of 68.9 percent and a yield of

   68.2/g/cbm only ethane (CH_3) is formed in addition to methane.

4. With a residual gas volume there is always 52.8/g/cbm

   formed in addition to the methane obtained in the other

   case of synthesis, taking the place of any other hydrocarbons.

5. For a residual gas volume of 81.5 percent and a yield

of 37.6/6/cbm there are formed in addition to methane

only hydrocarbons of the hypothetical composition CH_9.

<u>Range of validity of the n - R equation for a pair of</u>

<u>gas analyses.</u>

1. <u>Composition of the gases</u> CO_2 CO H_2 CH_4

           Intake   6.0   38.3   50.0   0.0

           Outlet   38.0   3.9   42.0   7.6

2. The n - R equation

    $p = 44.3$ $p' = 49.5$ $q = 0.6$ $q' = 45.4$

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

3. Auxiliary values:

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 =	12.0	17.4	20.1	21.7	22.8	24.0	24.9

4. Factors:

U =	75.4	68.0	64.3	61.0	60.6	58.9	57.6
M_V =	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	58.2	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. Remarks:

a). It has been assumed in all cases that hydrocarbons for
     which the yield has been calculated do not remain as a
     gas in the residual gas.

b). The agreement of the A values can only be obtained when
     the proper number of decimals has been used (calculating
     machine).

c). For $n = 4$, $A_2 = 0 : 0$

The values in the preceeding experiment show the variations of
the yield with n. It can be made still clearer by introducing into
the same example values for n and A which frequently occur during
the synthesis of higher hydrocarbons.

$n = 2.0$ 2.1 2.2 2.3 2.4 2.5
$A = 85.7$ 83.2 80.8 78.9 77.2 75.4

When n is changed by only 0.1, the yield will be changed by 2.5 g.

A determination of n to within 0.1 must under present conditions
be considered at least difficult. The most important task in this
field consists in developing means and ways for a more accurate and
if possible a simple evaluation of n, as well as occasionally to
find satisfactory approximation values for the individual different
syntheses. The value of n for the cobalt synthesis under normal
pressure is probably between 2.15 and 2.20, according to our present
knowledge.

It answers no purpose trying to calculate yields with a greater
accuracy than that with which the ratio of hydrogen to carbon in
the hydrocarbons formed or in the residual volumes can be at any
time determined.

We are in addition ignorant of the molecular volumes of most
of the higher hydrocarbons, which introduces additional uncertainity
in our computations of yield, as will be explained below, so that
our present information on yields should be rounded up to whole
numbers, and not give an impression of greater accuracy than
we can reach.

The agreements in yields we may observe in the numerical
example is found by computation with the values of n and R belonging
to each other. Were the latter not the case, the yields obtained
by the use of different formulas would deviate the more from each
other, the farther R is removed from the corresponding n value.
The locus for all yields obtained from the same formula and with
a given n is always a straight line. All these lines of yield
intersect in one point. In this particular point n and R meet
the requirements of the n - R equation for a corresponding pair
of gas analyses. (v drawing)

Relation between Yield and Residual Volume
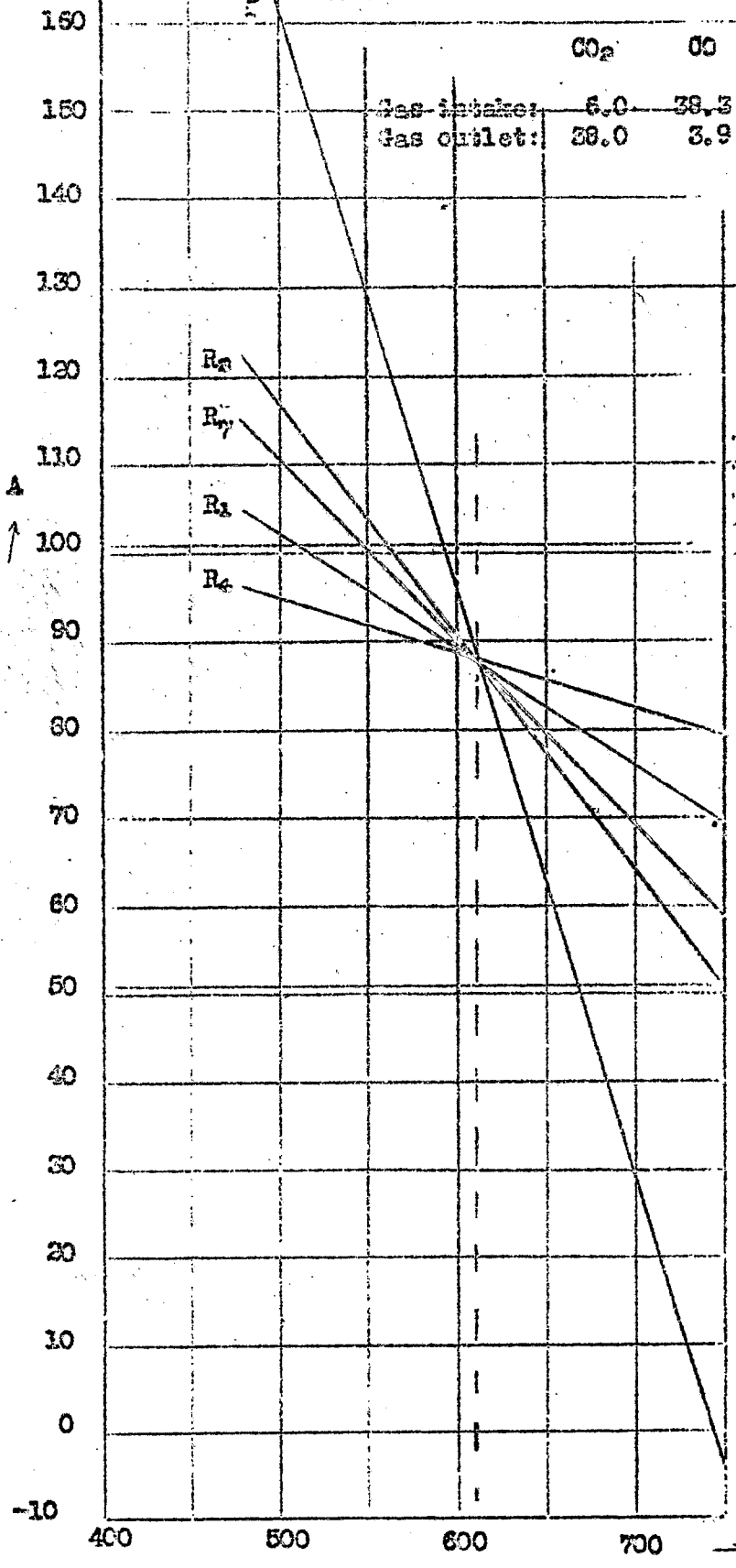
	CO_2	CO	H_2	CH_4
Gas-intake:	6.0	38.3	50.0	0.0
Gas outlet:	58.0	3.9	42.0	7.6

(n ~ R equation, U.p

Yields for n = 2

R =	0.5	0.617	0.75
A_1 =	104.5	85.7	65.0
A_2 =	122.0	85.7	45.0
A_3 =	175.3	85.7	~14.9
A_5 =	95.7	85.7	74.7
A_7 =	114.5	85.7	53.5

C. Calculation of characteristic numbers:

1. Conversion and Consumption Ratio

When the residual volume is obtained in either way, the intermediate values a, b, c and d can be readily calculated using the equations derived from the second assumption. A knowledge of numerical values of a and b give directly the conversion and consumption, using the following formulas:

$$U = \frac{a + b}{J} \cdot 10^2 \qquad\qquad X = \frac{b}{a}$$

We have already mentioned that U gives the consumption of carbon monoxide and hydrogen in percent of the (CO + H$_2$) content of the intake gas.

2. Formation of methane

a). Computation of the pure methane content in the end gas.

Gas analysis furnishes two numerical values for the calculation of the methane formation, first in parts by volume of methane + any higher saturated hydrocarbons present (represented by the symbols CH$_4$ or CH$_4$') and in the second part from the average C-value of these mixtures of hydrocarbons (designated as Z). There is no uniform method for the application of Z to calculations.

In operations, CH$_4$' may be multiplied by Z. This gives the volume of the total carbon present in the "methane" hydrocarbons, for a possible indication of an excess of materials.

Z must however be used in the accurate computations of the characteristic numbers in order to find the pure methane contents. It can be shown that these two data can be obtained from gas analyses only as an approximation.

Let m be the contents of pure methane in $CH_4{}'$

Kw is the higher hydrocarbon contents in $CH_4{}'$

then $CH_4{}' = m + Kw$

We may further call z the average C-number of the higher hydrocarbons present in $CH_4{}'$. We can then give the following equation for carbon:

$$Z \cdot CH_4{}' = 1 \cdot m + z \cdot Kw$$

combining these two equations we get:

$$m = CH_4{}' \frac{Z - z}{1 - z}$$

We may now set $m = \beta \cdot CH_4{}'$, and after multiplying the numerator and denominator with - 1, because z is always greater than Z, we get for the factor β : $\beta = \frac{z - Z}{z - 1}$

This equation shows that z as well as Z must be known for an accurate determination of the pure methane content in $CH_4{}'$. We cannot however determine z from the combined data of the two gas analyses, and can only experimentally by a fractional distillation analysis.

It has been suggested to divide $CH_4{}'$ by Z to obtain a value for pure methane largely from the two data of the gas analysis.

If this method of calculation is to give correct results we
must have:

$$\frac{1}{z} = f \ , \ \text{or} \ \frac{1}{z} = \frac{Z - z}{z - 1}$$

Transforming this expression we get

$$z = \frac{1 - z^2}{1 - z} = 1 + Z$$

This equation states that dividing Z by the C-number for
calculating the pure methane will give correct values only in the
special cases, where z, i.e. the carbon number of the hydrocarbons
higher than methane is larger by exactly 1 than the total C-number
Z found by combustion. In most cases we do not know whether this
requirement is fulfilled, nor does one know when it is fulfilled.
In many cases a.g. when the C-number, Z, is large(say 1.5)division
yields entirely impossible figures for pure methane. We cannot
therefore see a sufficiently useful method in the division of
Z by C.

W-450

NUMERICAL VALUES FOR β

n \	2.1	2.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0
	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0.0
2	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0.0
3	95	9	85	8	-75	-7	65	6	55	0.5
4	966	934	90	866	834	8	-766	-734	-7	68
5	-975	95	925	9	-875	85	835	8	-775	-75
6	98	96	941	92	9	83	86	84	82	80
7	983	967	95	933	916	9	883	867	85	833

Factor β for the Computation of Pure CH_4
(Connection with the two C-numbers z and Z)
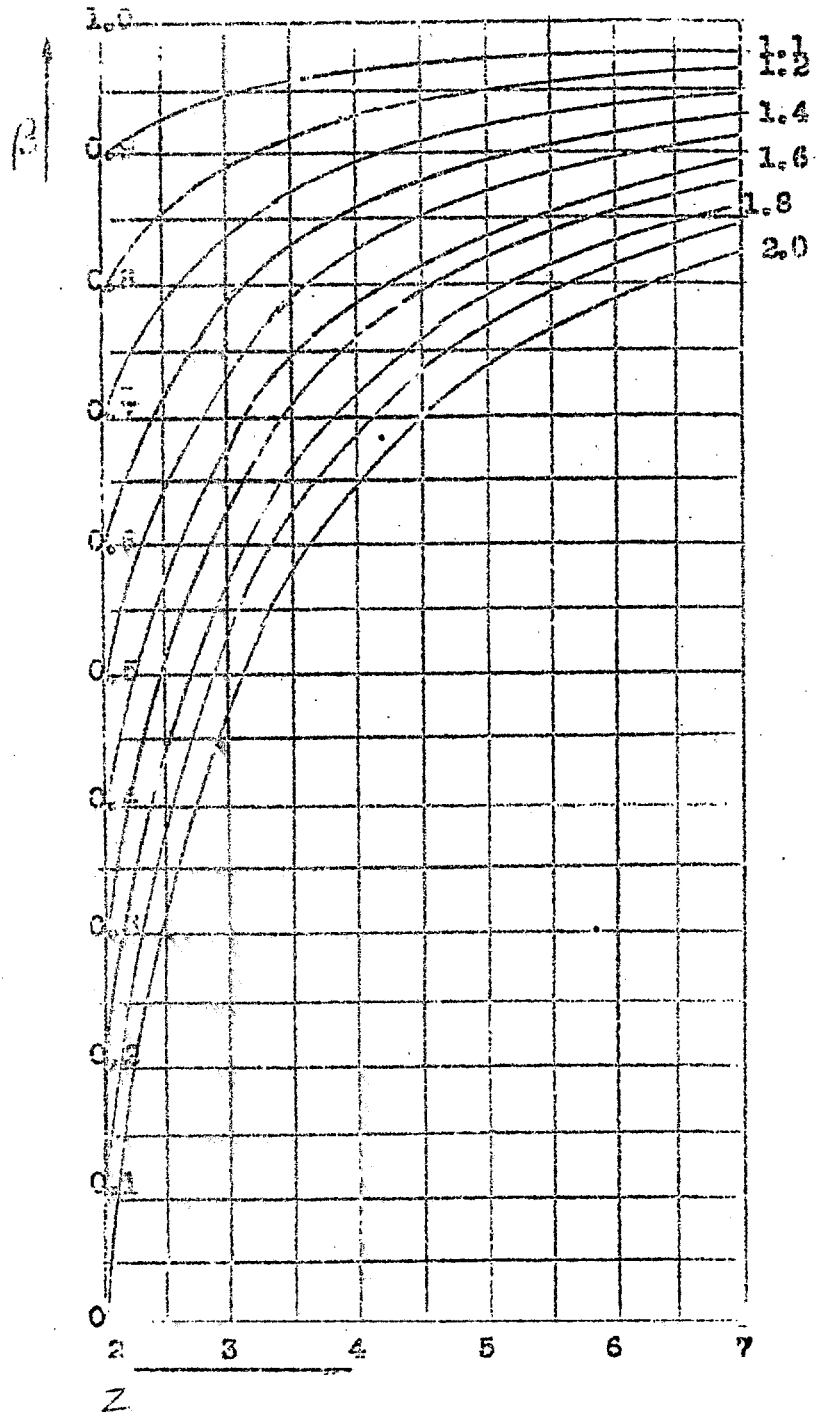
b). <u>Approximate values for the factor β</u>

β can be computed in cases of practical importance
by substituting numerical values for z and Z in the equation for the
factor β. Results of this calculation are presented in the numerical
table and the sheet of curves.

We have to distinguish between the end gases before and after
the recovery of the condensible hydrocarbons (r.c.hc.), e.g. by
adsorption with activated charcoal. Before the r.c.hc. there is
a relatively small amount of C_2, with much C_3, C_4, and still
higher hydrocarbons. The average value of the C-number Z is 1.5
to 1.7.

Back of the r.c.hc, with a single absorption by the activated
charcoal, methane contains practically only ethane, with possibly
some propane, and the Z-value varies between 1.0 and 1.2. If
larger C-number than 1.2 is found behind the activated charcoal,
it is best to discard the samples and find the reason for it.

The practical need of the existence of β is limited therefore
by two bounded regions. Were we to make the usually correct
assumption that when ethane alone is present Z behind the r.c.hc.
varies between 1.0 and 1.2, the numerical table and the sheet of
curves would give us the following values for β.

For $Z = 1.0, \beta = 0.9$ For $Z = 1.2, \beta = 0.8$

For the other range, i.e. when methane as determined by
combustion in front of the r.c.hc. is in large scale operations
mostly around 2 percent larger than behind the activated charcoal.
With an average methane content before the activated charcoal
treatment of 15 percent, we get $\beta = 0.867$. The corresponding
C-number Z varies in most cases between 1.5 and 1.7, and a z -
value of around 5 will be obtained from the sheet of curves.
If we accept temporarily a value of z = 5 before the r.c.hc. until
more dependable figures are obtained, we could calculate the
amount of pure methane for following approximate values for β:

Sample taken

z	Before r.c.hc.	After r.c.hc.	$\frac{1}{z}$
z	5	2	-
Z = 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

The last column contains for comparison the values for β
obtained by dividing Z by the C-number. One can readily see
that differences are not great with low C-numbers, but are very
large with high numbers.

An examination of the approximation values found, shows the
values of β always fluctuate between 1.0 and 0.8. The interval

inside of which any possible errors may exist would amount to not more than 20 percent of the "methane" values found by combustion.

Computations below of the effects upon the calculation yield of errors resulting from any possible inaccuracies in the value of β are shown below:

Composition of gas	CO	H_2	CH_4	Z	N_2
Intake	37.8	49.1	0.2	—	6.1
Outlet	30.1	29.3	5.1	—	12.0

Factors: U = 65.5 percent   Mv = 16.75 percent   A = 98.4/g/cbm

Changes of Mv with A and b:

b	Mv	Difference	A	Difference
1.00	16.75		98.4	
		0.92		1.1
0.95	15.83		99.5	
		0.92		1.1
0.90	14.91		100.6	
		0.91		1.2
0.85	14.00		101.8	
		0.90		1.0
0.80	13.10		102.8	

A change of b by 0.05 in the example taken results in a change of the calculated yield by not over 1 percent, although the formation of methane is relatively high, being 17 percent.

Summarizing the results of the different computations, we find that the following approximation rule can be used in the calculation of pure methane.

a). For the C-numbers Z 1.0 to 1.05 β = 1.0

 "   "   "   "   " 1.05 " 1.15 β = 0.9

b). For all C values Z over 1.15 β = 0.85

c). Gas samples taken back of r.c.hc. with the C-numbers Z exceeding 1.2 have not been considered.

When these rules are followed, β does not differ by more than
0.05 from the true values. The error in calculation of yield is
probably no greater than about 1 percent. The rule is applicable
if the higher hydrocarbons are removed with activated charcoal or
by low cooling. When scrubbing oil is used the proportions may
be different.

Ritter, Fischer and Stock (Krupp - Treibestoff - Werke)
determine the amount of pure methane in the end gas before the
r.c.hc. by preparing a so called artificial end gas for analytical
purposes by treating a partial stream with activated charcoal under
specified conditions. This gas contains only all of ethene in addition
to methane and produces with a greater regularities C-numbers 1.05-
1.06. In this case β is = to 0.99.

It has already been pointed out that the computations of the
characteristic numbers must always be made with pure methane i.e.
when Z is greater than 1.05, in which case CH_4' must in accordance
with the above be multiplied by β . β has however been omitted in
the formulas for the case of simplicity, i.e. CH_4' should always be
replaced by $CH_4' . \beta$.

C. Determination of the Formation of Methane:

Mv gives the percentage of the total decomposed ($CH + H_2$)
used up in the formation of methane. The first basic stoichiometric
equation gives for $n_m = 4$ as a solution for $c = 1/4 (a + b)$, or

a + b = 4c. The formation of methane will therefore always

require a quadruple volume of (CO + H_2). Our above definition of

the concept requires that:

$$\frac{K_T}{100} = \frac{4c}{a + b} \qquad\qquad M_V = \frac{4c}{a + b} \cdot 10^2$$

We get for Mco directly: $Mco = \frac{6}{a} \cdot 10^2$

These two factors can be converted into each other by:

$$M_V = Mco \cdot \frac{4}{1 \cdot X}$$

3. Yield of higher hydrocarbons:

Four equations could be derived from the second stoichiometric

equation; on the strength of these equations c^+ could be calculated

in four different ways from any three of the intermediate values

a, b, c and d. c^+ is the volume of the higher hydrocarbons formed,

and therefore the yield. It is customary to express the yield in

g, and c^+ must be re-calculated to weight by the multiplication

with the fraction (12 + n) divided by the molecular volume.

The question now arises what value to use for the molecular

volume of the higher hydrocarbons. Experimental determinations

are available only for the lower compounds up to octane. Up to

pentane the values are below 22.41, for heptane and octane they

are above. It is, however, impossible in this case to give any

approximate values. The average molecular volume of the hydrocarbons

formed remains as yet undetermined. It may be less than 22.41

(for ideal gases) but can also be above that figure.

One must further bear in mind that the molecular volumes of carbon monoxide and hydrogen also differ from the ideal value (carbon monoxide 22.40, hydrogen 22.43) and it appears therefore to be best to make calculations with the approximation value of 22.4. At any case one should bear in mind that we have here an additional unavoidable source of errors, and an additional reason for the but limited accuracy of the figures calculated.

The yield by weight is obtained from the product $c^+ \cdot \frac{12 + n}{22.4}$. The yield must be further referred to 1 cbm of the gas introduced, and the value so obtained must therefore be multiplied by 10. We obtain in this way the following four formulas for the calculation of the yield.

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

$$A_2 = \frac{12 + n}{22.4} (a - c - d) \cdot 10 \quad\quad\quad = h_2 (a - c - d)$$

$$A_3 = \frac{12 + n}{22.4} \cdot \frac{2}{4 - n} \cdot (3a - b - 4d) \cdot 10 \quad = h_3 (3a - b - 4d)$$

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

The fractions in front of the parenthesis depend only on n, but not on any gas analytical data, and recur in all computations. We can therefore simplify computations by replacing these fractions as well as the factor 10 by the factors h_1, h_2, h_3 and h_4 and obtain then the four expressions for the computations of the yield at the right. The collection of formulas contains numerical values occurring in normal hydrocarbon synthesis for h_1 to h_4.

In the equation for A_1 the methane term, namely $- 4c$ can also be expressed by the two characteristic numbers for the methane formation, Mv and Mco, and the term (a + b) by transformation U and the ideal gas content in the entering gas, J. We get then:

$$A_5 = h_1 \ (a + b) \ (100 - Mv) \ . \ 10^{-2} \quad = h' \ . \ J \ . \ U \ . \ (100 - Mv) \ . \ 10^{-2}$$

$$A_6 = h_1 \ . \ (a + b) \ (1 - \frac{Mco}{25(1 + X)}) \ . \ 10^{-2} = h' \ . \ J \ . \ U \ (1 - \frac{Mco}{25(1 + X)}) \ . \ 10^{-2}$$

Other transformations of A_1 or the three other A equations could be made in a similar way. The derived six formulas for A are equivalent to each other, and if no errors in computation are made, they all give the same numerical values.

The proportion of carbon monoxide and hydrogen in the intake gas which is completely consumed under the given consumption conditions, X, must be known for the determination of the maximum theoretical yield. This proportion J_X is obtained as follows: When the intake gas contains more hydrogen than J_X we may use

$$J_X = 30 \ (1 + X)$$

When the intake gas contains more carbon monoxide than is present in J_X, from $J_X = H_2 \ . \ \frac{1 + X}{X}$

The maximum yield is not usually given for the total conversion, but for a smaller conversion. When e.g. U = 90 percent, computations are made from:

$A_{max.}$ 90 = h_1 J_x . 90 (100 - Mv) . 10^{-4}

n is always found in the formulas for yield derived above.
n can be expressed by R and the gas analytical data by using the
n - R equation.   Substituting for n $n = \dfrac{q^1 \cdot R = g}{p - p^1 \cdot R}$

into the four formulas from A_1 to A_4, we get after the proper
transformations the same new expression for A from all four yield
formulas, which no longer contains n, and has instead all of the
four intermediate values a, b, c and d:

A_7 = 0.893 /(5a + b - 4) (2c + d)/.

This equation should be the most convenient for practical
use.   When sufficient number of decimals is used (calculating machine)
the same numerical values for a are obtained as from A_1 to A_4.

The formulas for yields derived above give the amounts of all
the higher hydrocarbons **without** methane.   The formula necessary
for the computation of the combined hydrocarbons including methane
can be derived in two ways: we can carry out a similar derivation
from the first basic stoichiometric equation as for the first.   And
we can also set the methane member (c) in the formulas A_1 - A_7 equal
to zero.   It has already been mentioned in the section on the n - R
equation, an index m is added on to all abbreviations when methane
enters together with all the other hydrocarbons into the computations.
We get in that case:

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

$$A_{3m} = \frac{10\ (12 + n_m)}{22.4}\ (a - d) \qquad\qquad = h_3\ (a - d)$$

$$A_{6m} = \frac{20\ (12 + n_m)}{22.4\ (4 + n_m)}\ (b + d) \qquad\qquad = h_6\ (b + d)$$

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

The factors h_1, h_3 and h_6 have the same numerical values as in A_1 to A_6.