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UNITED STATES  
DEPARTMENT OF THE INTERIOR  
BUREAU OF MINES  
OFFICE OF SYNTHETIC LIQUID FUEL  
LOUISIANA, MISSOURI

TOM Reel No. 49, Frames 470 - 523

T - 420

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Nov. 13, 1947

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July 1944

~~CALCULATIONS OF GAS UTILIZATION AND THE COURSE OF SYNTHESIS~~  
DURING THE HYDROGENATION OF CARBON MONOXIDE

by Otto Roelen

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Part I.Introduction

## 1. Introduction to the mathematical method of treatment:

Computations have been made for decades to determine the course of the synthesis and the yield from the analysis of gases of the hydrogenation of carbon monoxide. Such computations are carried out daily in many places. This is done today nearly as laboriously as some twenty years ago at the beginning of the work on gasoline synthesis, repeating the general derivations more or less completely for each individual computation. The great advantages derived from changing over to a strictly mathematical form with a simultaneous use of the corresponding abbreviations have not as yet been gained.

An attempt has been made in the following pages to show the basis of a mathematical treatment of the computations of the gas utilization during the hydrogenation of carbon monoxide. We started here from the basic relationships between the amounts of raw materials and of the resulting products. These fundamental relationships lead readily to convenient formulas which can be applied algebraically to any additional computations. This results in a comprehensive collection of formulas which include the whole field.

The application of these formulas eliminates sources of errors in application, shortens considerably the computations and actually permits to evaluate rapidly and accurately the gas analyses and to

test the results. A uniform use of such formulas would facilitate a comparison of synthesis data obtained at the different works.

Moreover, quantitative relationships between the participants of reactions become readily recognizable; such relationships could neither be found nor used without the use of a mathematical method of treatment. Finally the accuracy of such computations can be tested now better than formerly, i.e. finding what are sources of error and to what extent they affect this accuracy.

## 2. Selection of auxiliary figures and characteristic numbers:

The development accomplished in the course of years has not resulted in the introduction of uniform abbreviations nor in any agreement about the characteristic numbers to be used. We shall therefore give below a detailed explanation of the symbols, with an attempt to limit the use of factors to only a few.

### a). The residual volume $R$

The term "contraction" is a habit acquired in the initial stages of experimental investigations. At that time, contraction was a factor which was particularly readily determined in laboratory tests at a normal pressure, and was capable of leading to numerous conclusions. With cobalt catalysts, conversion is practically directly proportional to the contraction. However, contraction is merely an illustration of the process, but cannot be used directly in computations.

One cannot directly use the numerical value of contraction in calculating the conversion. The numerical value of the residual value is here preferable. The latter is determined experimentally, and the contraction is calculated from it. It will necessitate going backwards in subsequent computations, and have the two values add up to 100, which makes it simpler and more useful to limit one-self to the concept of the residual volume.

We may therefore eliminate the use of the concept "contraction" and its numerical value in judging the course of the synthesis and base our computations on the residual volume only. Substitution of the expression for the actual volume of the residual gas for the concept of contraction as an expression for the change of volume will simplify discussions. We shall use below the abbreviation R for the concept "residual volume". We introduce no symbol for contraction in our list of symbols.

b). The Characteristic Numbers Proper

The expressions for yield are the most important figures to characterize the course of synthesis. To judge the course of the synthesis computations of gas utilization are expected therefore either to show the yield expected or else to permit arriving at conclusions why the maximum yield has not been obtained.

Considerations of causes which might affect the maximum yield brings us the following:

1. Insufficient conversion,
2. Formation of methane instead of higher hydrocarbons,
3. Consumption of CO and H<sub>2</sub> in some other ratio, than expected,
4. Deposition of carbon,

Other stoichiometric transformations which will affect the gas utilization are not known. Deposition of carbon is either unavoidable or else would soon bring an end to the synthesis, and we may therefore leave it out of consideration here. There remain only the processes 1 to 3 which should enable us to find an adequate characterization of the course of synthesis. Such is indeed the case.

The conversion formation of methane and consumption proportions can be always computed for the theoretical calculations of the yield and the exposition below is limited to the computation of the following four values:

Conversion U

Methane formation M

Consumption proportion X

Yield A

c). Relation Between the Factors and the (CO + H<sub>2</sub>) Conversion.

Synthesis such as with cobalt and nickel, proceeds either

entirely or almost entirely with the formation of water, and the yield of higher hydrocarbons is proportional to the consumption of carbon monoxide in the simple and rigid ratio of 1 CO to 1 CH<sub>2</sub>. For this reason, computations of conversion and yield have become commonly based on the consumption of carbon monoxide. As a result attempts have been repeatedly made to prove the excess of the amounts of gas introduced by means of a carbon balance, which is also calculated from the consumption of carbon monoxide.

However, with iron catalysts carbon dioxide is formed in considerable and very variable amounts, and as a result computations of carbon monoxide conversion no longer offer any advantages. It becomes simpler and clearer to judge conditions from the conversion of (CO + H<sub>2</sub>). This method of computations offers the important advantage over the use of the CO conversion, in that the (CO + H<sub>2</sub>) conversions can be compared with each other even when synthesis takes place in different consumption proportion.

For this reason, whenever conversion is discussed below, the (CO + H<sub>2</sub>) conversion will be meant and designated by the abbreviation U. The values of the CO conversion can be dispensed with, as well as of the H<sub>2</sub> conversion. Their values are definitely established from the ratio of consumption of H<sub>2</sub> : CO. In the list of symbols an abbreviation of U<sub>CO</sub> is used for the CO conversion to be used

only for any possible intermediate computations.

What has been said about conversion applies also to the formation of methane. The methane formation will be given below entirely by the corresponding ( $\text{CO}+\text{H}_2$ ) consumption, and abbreviated to Mv. These Mv values are comparable for the most varied syntheses and catalysts, while the Mco values are not.

### 3. Explanation of symbols:

The number of the necessary abbreviations have been found to be so great that a careful selection had to be made to come inside the capacity of the usual typewriter. A total of some ninety different concepts require symbols.

For some of the abbreviations the commonly used symbols may be used, but not for the most of them. We have made the following rule when selecting our symbols:

- A). Symbols already in use have been retained as far as possible.
- B). As an aid to memory new symbols have been selected to agree with the concept.
- C). With many similar symbols, the simplest form has been selected for the most commonly used case.
- D). All symbols must be clearly distinguishable, and be capable of being written on the usual typewriter.
- E). No abbreviations have been given to concepts which are in use, but may be considered superfluous from the results from this investigation. There are for instance no abbreviations for the degree of liquefaction, for the  $\text{H}_2$  conversion, etc.



In cases when for the sake of clarity an addition to a symbol becomes necessary to one already in existence, the writing is facilitated by not placing the index letters below the line, but adding small letters to the existing symbol, e.g. by writing Uco instead of U<sub>co</sub>.

A summary of all of the abbreviations used will be found in the explanation of symbols at the end of the article. Abbreviations used in this article are a first attempt in this line. No claims are made to include all of the symbols required in the laboratories and in large scale operations. This is particularly not the case for abbreviation used for yields.

Yields can be expressed in numerous ways depending on the nature of the gas or gas constituent converted, as well as on the nature of conversion, and may be used for expressing the products formed, as well as for the method of computations in use: —

1. Kind of gas

- a). Synthesis gas,
- b). Total (CO + H<sub>2</sub>) content,
- c). The proportion of (CO + H<sub>2</sub>) which may be consumed from a given consumption proportion,

2. Conversion

- a). Actual conversion,
- b). The practically possible conversion, e.g. 90 percent,
- c). Complete conversion, 100 percent,

### Z. Products

- a). All hydrocarbons formed, including methane,
- b). Hydrocarbons formed, without methane,
- c). Hydrocarbons formed without methane, ethane, ethylene,
- d). a - c, with the addition however of oxygenated products or of oxygen-containing chemical groups.

There may be numerous combinations between the enumerated cases, and there are therefore numerous ways of expressing yields. These different expressions can however be more or less simply converted one into another. Their selection is therefore not a subject of a mathematical derivation, but a convention, and is not therefore the real object of the present work. We will limit ourselves here in all computations of yields to the simplest and most profitable cases, namely to gases of higher hydrocarbons without methane/cbm of synthesis gas, occasionally including also the oxygen-containing groups.

### 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 ( $C_n H_m$ ). We may therefore denote as equal the amounts of materials entering and leaving the space, as follows:



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:

$$\text{For carbon: } a = c_n + d$$

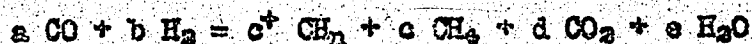
$$\text{For oxygen: } a = 2d + e$$

$$\text{For hydrogen: } 2b = n_m \cdot c_n + 2e$$

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

The expression  $c_n C_n H_m$  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)

$c^+$   $\text{CH}_2$ , and the volume of the methane formed  $c$   $\text{CH}_4$ . Introducing these expressions into the first basic stoichiometric equation gives us



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:  $2b = n + c^+ + 4c + 2e$

Algebraic transformations 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:

$$\text{Entering CO} = \text{consumed} + \text{unconverted CO.}$$

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

$$CO = a + R \cdot CO', \text{ or } a = CO - R \cdot CO'$$

We obtain similarly for the other three intermediate values:

$$b = H_2 - R \cdot H_2^1$$

$$c = R \cdot CH_4^1 - CH_4$$

$$d = R \cdot CO_2^1 - CO_2$$

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

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

$$\frac{\text{Gas outlet}}{\text{Amount of nitrogen}} = \frac{R}{\text{Amount of nitrogen}} = \frac{100}{N_2^t}$$

$$R_2 = \frac{N_2}{N_2^t}$$

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:

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



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:

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

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

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

$$n = \frac{q' - R - q}{p - p' \cdot R} \quad R \text{ or } H_y = \frac{p \cdot n + q}{p' \cdot n + q'}$$

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<sub>m</sub> - 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:

$$P_m = CO_2 + CO$$

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

$$P'_m = CO_2' + CO'$$

$$Q'_m = 2(2CO_2' + CO' - H_2')$$

$$n_m = \frac{Q'_m - R - Q_m}{P_m - P'_m - R}$$

$$R = \frac{Q_m + P_m \cdot n_m}{Q'_m + P'_m \cdot n_m}$$

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

The equation for hydrogen:  $c_m \cdot n_m = c' \cdot n + 4c$

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

with which we get:  $n = \frac{c' \cdot n_m + 4c}{c' + c}$

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

##### 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 occurrence 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 olefins 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/g/cbm there are formed in addition to methane only hydrocarbons of the hypothetical composition  $CH_n$ .
- Range of validity of the n - R equation for a pair of gas analyses.

1. <u>Composition of the gases</u>	$CO_2$	$CO$	$H_2$	$CH_4$
Intake	6.0	38.3	50.0	0.0
Outlet	39.0	3.9	42.0	7.6

2. The n - R equation

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

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

3. Auxiliary values:

n =	1	2	3	4	5	7	9
R =	0.473	0.617	0.689	0.720	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 <sub>v</sub> =	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 <sub>1</sub> =	121.1	85.7	68.2	58.2	51.3	43.1	37.6
A <sub>2</sub> =	121.1	85.7	68.2	58.2	51.3	43.1	37.6
A <sub>3</sub> =	121.1	85.7	68.2	58.2	51.3	43.1	37.6
A <sub>4</sub> =	121.1	85.7	68.2	58.2	51.3	43.1	37.6
A <sub>5</sub> =	121.1	85.7	68.2	58.2	51.3	43.1	37.6
A <sub>6</sub> =	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  $n = 4$ ,  $A_3 = 0 : 0$

The values in the preceding 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	76.4

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 uncertainty 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)



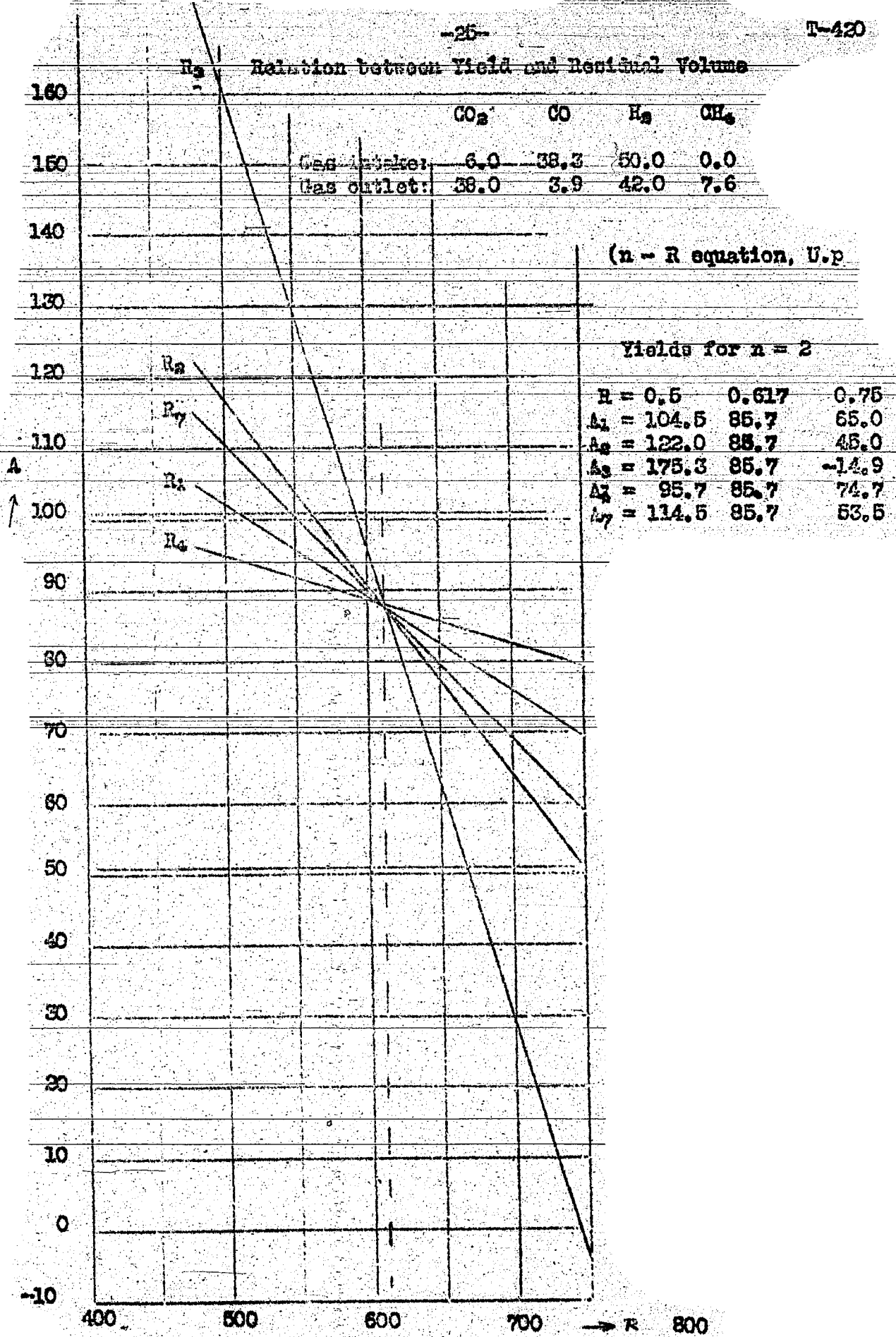
$H_2$  Relation between Yield and Residual Volume

	$CO_2$	CO	$H_2$	$CH_4$
Gas inlet:	6.0	38.3	50.0	0.0
Gas outlet:	38.0	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
$A_4 = 95.7$	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:

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

We have already mentioned that U gives the consumption of carbon monoxide and hydrogen in percent of the (CO + H<sub>2</sub>) 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<sub>4</sub> or CH<sub>4</sub><sup>1</sup>) 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<sub>4</sub><sup>1</sup> 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  $CH_4^1$

$K_w$  is the higher hydrocarbon contents in  $CH_4^1$

then  $CH_4^1 = m + Kw$

We may further call  $z$  the average C-number of the higher hydrocarbons present in  $CH_4^1$ . We can then give the following equation for carbon:

$$Z \cdot CH_4^1 = 1 \cdot m + z \cdot Kw$$

combining these two equations we get:

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

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

This equation shows that  $z$  as well as  $Z$  must be known for an accurate determination of the pure methane content in  $CH_4^1$ . 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  $CH_4^1$  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:

$$\frac{1}{Z} = f, \text{ or } \frac{1}{Z} = \frac{Z-2}{Z-1}$$

Transforming this expression we get

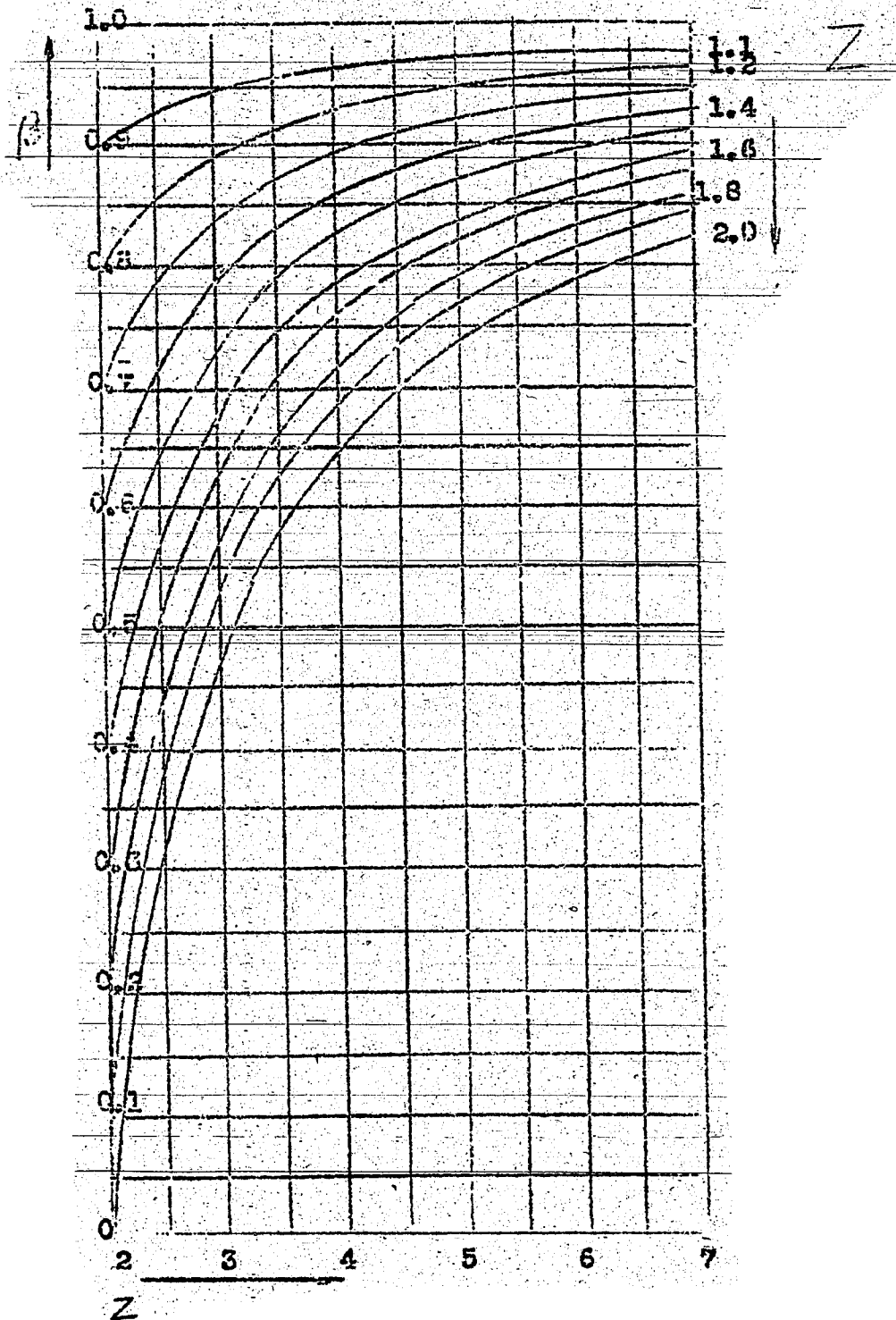
$$z = \frac{1-Z^2}{1-Z} = 1+Z$$

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 e.g. when the C-number, Z, is large (say 1.6) division yields entirely impossible figures for pure methane. We cannot therefore see a sufficiently useful method in the division of Z by C.

NUMERICAL VALUES FOR  $\beta$

	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0
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	808	834	8	766	734	7	68
5	975	95	925	9	875	85	825	8	775	75
6	98	96	941	92	9	88	86	84	82	80
7	983	967	95	933	916	9	883	867	85	833

Factor  $f$  for the Computation of Pure  $CH_4$   
 (Connection with the two G-numbers  $z$  and  $Z$ )



b). Approximate values for the factor  $\beta$

$\beta$  can be computed in cases of practical importance by substituting numerical values for  $z$  and  $Z$  in the equation for the factor  $\beta$ . 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.h.c.), e.g. by adsorption with activated charcoal. Before the r.c.h.c. 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.h.c. 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  $\beta$  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.h.c. varies between 1.0 and 1.2, the numerical table and the sheet of curves would give us the following values for  $\beta$ .

For  $Z = 1.1, \beta = 0.9$       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.h.c. 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.h.c. until more dependable figures are obtained, we could calculate the amount of pure methane for following approximate values for  $\beta$ :

		Sample taken		
		Before r.c.h.c.	After r.c.h.c.	$\frac{1}{z}$
	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  $\beta$  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  $\beta$  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  $\beta$  are shown below:

Composition of gas	CO	H <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub>	Na
Intake	37.8	49.1	0.8	-	0.1
Outlet	30.1	29.8	5.1	-	12.0

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

Changes of Kv with A and b:

b	Kv	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		1.1
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  $\beta = 1.0$   
 " " " " " 1.05 " 1.15  $\beta = 0.8$

b). For all C values Z over 1.25  $\beta = 0.85$

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

When these rules are followed,  $\beta$  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 - Treibstoff - Werke)

determine the amount of pure methane in the end gas before the r.c.h.c. 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 ethane in addition to methane and produces with a greater regularities C-numbers 1.05-1.06. In this case  $\beta$  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  $CH_4^1$  must in accordance with the above be multiplied by  $\beta$ .  $\beta$  has however been omitted in the formulas for the case of simplicity, i.e.  $CH_4^1$  should always be replaced by  $CH_4^1 \cdot \beta$ .

C. Determination of the Formation of Methane:

$M_1$  gives the percentage of the total decomposed ( $CH_4 + H_2$ ) 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;

$$\frac{Mv}{100} = \frac{4c}{a + b}$$

$$Mv = \frac{4c}{a + b} \cdot 10^2$$

We get for  $Mco$  directly:

$$Mco = \frac{6}{a} \cdot 10^2$$

These two factors can be converted into each other by:

$$Mv = Mco \cdot \frac{4}{1-x}$$

### 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.

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

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

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

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

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:

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

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

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

$$J_X = CO (1 + X)$$

When the intake gas contains more carbon monoxide than is present

$$\text{in } J_X, \text{ from } J_X = H_2 \cdot \frac{1 + X}{X}$$

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:

$$A_{\text{max. 90}} = h_2 J_x \cdot 90 (100 - 14v) \cdot 10^{-4}$$

$n$  is always found in the formulas for yield derived above.  $n$  can be expressed by  $R$  and the gas analytical data by using the

$$n - R \text{ equation. Substituting for } n \quad n = \frac{d^1 - R - c}{p - p' \cdot R}$$

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:

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

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

$$A_{3m} = \frac{20(12 + n_m)}{22.4(2 + n_m)} (b + d) = h_3 (b + d)$$

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

The factors  $h_1$ ,  $h_2$  and  $h_3$  have the same numerical values as in  $A_1$  to  $A_3$ .

### Part III

#### Determination of the Hydrogen - Carbon Monoxide Ratios and the Oxygen-Containing Groups in the Products.

##### A. Reasons for Extending the Evaluations.

The  $n - R$  equation permits the calculation of the relationship between  $n$  and  $R$ . However, with no additional gas analytical data no certain conclusions can be drawn which one of the many possible  $n - R$  pairs would be applicable to the course of synthesis investigated.

A sufficiently accurate evaluation of the residual volume is difficult from either direct measurements or from the determination of nitrogen. Moreover,  $R$  must be redetermined for each gas analysis and for each course of synthesis, and the numerical values may vary between wide limits. It is therefore impossible to determine beforehand the analytical data and to apply them.

When it comes to  $n$ , conditions are entirely different.  $n$  is characteristic for every course of synthesis, and remains more or less constant during its whole course. In addition, the numerical values vary only within narrow limits, and as a result, when these values have been determined, they may be used more or less frequently as approximation average values. Useful analytical values for  $n$  can be obtained from an analytical investigation of the products formed.

An evaluation of the results of analysis is also important for other reasons, namely to find the total yield, because the so-far developed formulas for yields include only the formation of pure hydrocarbons, without taking into consideration any oxygen-containing compounds which may have formed. Yields calculated by formulas  $A_1$  to  $A_7$  are therefore too low by failing to include the hydroxyl and carboxyl groups. Our first efforts will be directed towards the determination to what extent the oxygen-containing groups can be found from the results of gas analyses.

#### B. The Calculation of the Oxygen-Containing Groups from Results of Gas Analyses.

Experience has shown that most of the oxygenated compounds formed together with the hydrocarbons consist of saturated alcohols. One might consider their determination from results of gas analyses by the introduction of some corresponding member (such as  $\text{CH}_2\text{O}$ ,



$\text{CH}_3\text{O}$ , or similar) into the second basic stoichiometric equation, as has been done for methane. No attempts in this direction have so far resulted in useful algebraic expressions. The two sides of the equations cancel each other, or else the expressions become equal to zero. The determination of oxygen-containing compounds becomes therefore impossible by this method.

The reason for it is obvious. Considered purely stoichiometrically, alcohols may be considered composed of one molecule of an olefin and one of water. It is impossible to tell without additional experimental data in what proportion water leaves the reaction space as such, or in the combined form.

The division of the component groups of materials by the introduction of special members into the basic stoichiometric equations is successful for methane, because the latter can be determined separately by the methods of gas analysis. On the other hand, water can not at all be determined by the methods of gas analysis, and is very difficult to determine in other ways.

### C. Chemical Investigation of the Products Formed:

#### 1. Combustion.

The combustion analysis of the liquid products permits to determine directly the H : C ratio, and therefore n, and information will then be furnished about any possible oxygen content. However, no sufficient experience is as yet available for the purpose.

Work on this subject is at present in progress.

How to carry out such combustions is generally known, and we merely have to remind here, that combustion must be adjusted to the boiling ranges of the different fractions. Heavy oils may be burned in boats, possibly with the addition of kieselguhr. Low boiling fractions are best handled by the Dennstadt method (H. Meyer, *Analyse und Konstitutionsermittlung*, 1938, p. 118).

### 2. Precision Distillation and Chemical Analysis.

The oxygen-containing groups and the H : C ratio can also be determined by a precision fractionating separation, determining the amounts and chemical composition of the different fractions. This method is very complicated, but gives also a good insight into the composition of the fractions formed.

A large amount of calculations will be required for the evaluation of the results. This can be materially simplified by the use of suitable abbreviations, by a preliminary computation of the frequently recurring mathematical operations and by the use of suitable forms. Such a form is here offered.

We may imagine the oxygenated compounds to be formed stoichiometrically in three ways:

1. Hydrocarbon residue + oxygen
2. Hydrocarbon residue + carbon dioxide
3. Hydrocarbon residue + water.

The first path can not be used directly, because it cannot be related to the two basic stoichiometric equations. Neither can the second path be used directly. Sample calculations show, that different yield formulas would have to be used for these cases, with attention to any carbon dioxide in chemical combination.

The third path may be used directly, because the term for water (e) was always eliminated in the derivation of formulas for yield. We are therefore at liberty to assume any amount of the water as chemically bound.

An explanation of the use of the form is as follows:

When calculating n from the products of reaction, the amounts of the constituents of the individual fractions were multiplied by their corresponding value for n, and the sum of all the values so obtained was divided by the total weight of the product.

Methane is left here out of consideration, in accordance with the conception of the term n. This n is contained directly or indirectly in all the yield formulas from A<sub>1</sub> to A<sub>7</sub>. Because of their derivation, these formulas give only the yields of the hydrocarbon compounds, and we must therefore deduct 1 molecule of water for each atom of oxygen for each oxygen-containing compound in the products: one molecule of water for the aldehydes, alcohols and ketones, two molecules of water from the esters and acids. The proportion of hydrocarbons (abbreviated to (CH)) required for the calculation of n can then be expressed by the following formulas:

For alcohols:	$(CH)_2 = C_nH_{2n} + 2O - H_2O = C_nH_{2n}$
For esters:	$(CH)_e = C_nH_{2n}O_2 - 2H_2O = C_nH_{2n} - 4$
For acids:	$(CH)_a = C_nH_{2n}O_2 - 2H_2O = C_nH_{2n} - 4$
For aldehydes and ketones:	$(CH)_{ald} = C_nH_{2n}O - H_2O = C_nH_{2n} - 2$
For olefines:	(Olef) = $C_nH_{2n}$
For paraffins:	(Par) = $C_nH_{2n+2}$

These hydrocarbon residues must therefore be always multiplied by their corresponding n values:

For olefines by	$\frac{2n}{n}$	= 2
For paraffins by	$\frac{2n+2}{n}$	= $\frac{n}{p}$
For esters by	$\frac{2n-4}{n}$	= $n_e$
For acids by	$\frac{2n-4}{n}$	= $n_a$
For aldehydes and ketones by	$\frac{2n-2}{n}$	= $n_{ald}$
For alcohols by	$\frac{2n}{n}$	= 2

The formula for the determination of n is therefore:

$$n = \frac{2\Sigma(\text{olef}) + \Sigma(\text{paraff}) + 2\Sigma(CH)_2 + \Sigma n_e(CH)_e + \Sigma n_a(CH)_a + \Sigma n_{ald}(CH)_{ald}}{\Sigma(\text{olef}) + \Sigma(\text{par}) + \Sigma(CH)_2 + \Sigma(CH)_e + \Sigma(CH)_a + \Sigma(CH)_{ald}}$$

The calculation of the chemically bound water (= W<sup>u</sup>) as well as the part (CH) of the oxygenated compounds is done as shown below. The calculation of these values is essentially the same in all oxygen-containing products, and it will be illustrated on one single example.

Some one fraction of the products investigated weighs g gram, and its esterification number is SE. This fraction contains therefore,

$$\frac{g \cdot EZ}{\text{theor. EZ}} = \frac{g \cdot EZ \cdot M_e}{56,000} \text{ g ester } (M_e = \text{mol. wt. of the esters}).$$

One mol ester produces two moles water (= 36.032 g). The water

$$\text{content of these } \frac{g \cdot EZ \cdot M_e}{56,000} \text{ g of ester is therefore } W_e'' =$$

$$= \frac{36.032 \cdot g \cdot EZ \cdot M_e}{M_e \cdot 56,000} = g \cdot EZ \cdot 0.6434 \cdot 10^{-3} \text{ g.}$$

There remains therefore for the (CH) part of this ester:

$$g \cdot \text{ester} - W_e'' = \frac{g \cdot EZ \cdot M_e}{56,000} - \frac{g \cdot EZ \cdot 36.032}{56,000} = g \cdot EZ \left( \frac{M_e - 36.032}{56,000} \right).$$

The expression inside the brackets has been designated by  $k_e$  and can be calculated beforehand for all the fractions (also for any other oxygenated compounds). The formula for the (CH) portion of the ester becomes then  $(CH)_e = g \cdot EZ \cdot k_e$ .

The amount of paraffins per fraction is obtained by subtraction of olefins from  $g$  as well as of all the (CH) portions and all the  $(W'')$  portions. We get therefore:

$$(\text{par}) = g / (\sum (\text{Olef}) + \sum (\text{CH}) + \sum (W'')) /.$$

The total yield is obtained by the addition to the total  $A_1$  to  $A_7$  yields of (CH) also that of the chemically bound water. This amount  $Y$  is obtained from the sum of all the  $(W'')$  divided by the amount of the synthesis gas intake during the time interval when measurements were made (and reduced to normal conditions)

$$\text{Therefore, } Y = \frac{\sum (W'')}{m^0}.$$

Part IVApplication of the Formulas Derived.A. Evaluation from Gas Analyses and the Syntheses Data.1. General Course of Calculations

The evaluation of analyses with the formulas derived can be done in a variety of ways, depending on the available experimental material. One may try, e.g. to obtain useful data for the residual volume from direct measurements or by calculation of the so-called nitrogen content. The worth of such a value can be determined by substituting it into the  $n - R$  equation for the corresponding pair of gas analyses. It must then lie within the limits of values found correct by experience, e.g. in normal hydrocarbon synthesis as performed at present, between 2.0 and 2.5. If this is not correct, there must be some errors either in the gas analyses or in the calculations.

If the errors are in the analyses they can not be eliminated or bypassed. In that case one would have to calculate factors known to be incorrect and adjust the calculations. If the error is assumed in the residual volume, it is possible to obtain approximately correct factors by calculation from the available analyses, by assuming  $n$  to be known from experience and calculating from the  $n - R$  equation.

Finding the residual volume by measurements or by way of nitrogen and testing it requires more labor of calculation than the calculation

with an  $n$  known to be approximately correct and therefore used; moreover, if the assumption is correct, the same or practically the same numerical results are obtained; and it does not always offer, moreover, a greater accuracy or dependability. The same applies accordingly to our experience also to the precision determination of nitrogen. One can therefore occasionally eliminate the determination of  $R_1$ ,  $R_2$  (by measurements), or  $R_2$  and  $R_3$  (from  $N_2$  results) except as check for the basic assumptions. The load on the laboratories will be reduced by the elimination of the precision determination of  $N_2$ .

When sufficient data are furnished by analyses of the products, they can be used for the calculation of  $n$ , and from that of  $R_3$ . Finding of  $n$  for the products will be more complicated, but will have to be done in order for the greatest accuracy of calculation of factors of  $n$  from those from an unfamiliar course of operations.

After  $n$  has been calculated, the calculation of the intermediate values  $a, b, c$  and then the factors  $U, W, X$  and  $A$  will offer no difficulties. Actually corresponding values of  $n$  and  $R$  will have to be used for the calculation of yields  $A_1$  to  $A_3$ .

## 2. Checking the results.

### a) Control the basis.

A judgment of dependability of the basic assumption becomes relatively easy by an application of the newly developed relationships. For this, one has to compare values for  $n$  and  $R$ ,

obtained in different ways. This will be shown here on a few examples.

Examples 1 and 2 show the possible accuracy of the basis. Particularly careful work is required for it. Examples 3 and 4 show less accurate basis, as it frequently occurs. Some errors are contained in them. The question is, how to judge these errors.

In a series of semi-technical determinations made with great care (Schwarzhelde State office (Reichsamt)) gave values for  $n$  for a number of entirely different syntheses always varying between 2 and about 2.3. We may therefore assume  $n = 2.15 \pm 0.15$  as a safe approximation. When values for  $n$  corresponding to any  $R$  values obtained by direct measurements or from  $N_2$  differ from the above  $n$  values by a smaller or greater amount, there must be some corresponding inaccuracies in the basis. These conclusions must be drawn if no fundamental errors exist in the above derivations.

It must be assumed that the numerical material amassed over a long or a short time interval permits telling where to look for the causes of these deviations in the  $R$  and  $n$  values, which may be in measurements of the amounts of gas, or else in some place in the gas analysis. When such a proof can not be obtained, one may assume some of the fundamental assumptions to be more dependable, than some others, e.g. that the measurements of amounts of gas are more dependable than the gas analysis, or vice versa. It is however never possible to tell at once from the larger deviations in the  $n$  and  $R$  values, that the characteristic numbers and yields obtained from such fundamental data are of only correspondingly limited accuracy.



Examples for Calculating the Course of Synthesis.

Example No.	1.		2.			3.		4.	
Origin	Laboratory		State Lab. Tests			Laboratory		Operations	
Catalysts	Cobalt		Iron			Cobalt		Cobalt	
Pressure	Normal		10 atm.			Normal		Normal	
Gas Analyses				Normal	-1%CO <sub>2</sub>				
CO <sub>2</sub>	5.2	31.2	0.0	12.2	11.22	5.0	30.0	14.4	41.9
Hydrocarbons	0.0	0.0	0.0	1.0	1.01	0.0	2.6	-	0.5
CO	29.6	5.2	39.2	28.8	27.1	28.1	2.7	26.8	12.4
H <sub>2</sub>	59.0	21.7	16.4	27.7	32.13	52.9	20.1	52.6	18.6
CH <sub>4</sub>	0.2	12.9	3.7	7.9	7.99	0.2	18.9	0.4	11.9
C-Number	-	-	-	1.14	-	-	1.77	-	1.06
H <sub>2</sub>	6.2	23.9	6.6	14.4	14.56	6.9	25.6	4.9	14.6
Residual H <sub>1</sub>	0.221	-	-	-	-	0.225	-	-	-
Volumes H <sub>2</sub>	-	-	0.603	0.603	0.603	-	-	-	-
H <sub>2</sub>	0.229	-	0.586	0.591	0.591	0.229	-	0.336	-
H <sub>2</sub>	0.221	-	0.606	0.642	0.642	0.222	-	0.364	-
n from H <sub>1</sub>	2.22	-	-	-	-	2.02	-	-	-
" " H <sub>2</sub>	-	-	2.142	1.914	1.914	-	-	-	-
" " H <sub>3</sub>	2.22	-	2.215	1.854	1.854	2.47	-	1.79	-
n to H <sub>7</sub>	2.15	-	2.150	2.150	2.150	2.15	-	2.150	-
Calculated R <sub>1</sub> d <sub>1</sub>	2.01	-	-	-	-	1.13	-	-	-
with R <sub>2</sub> d <sub>2</sub>	2.01	-	-	-	-	1.13	-	-	-
" " R <sub>3</sub> d <sub>3</sub>	-	-	7.30	6.77	6.77	-	-	-	-
" " R <sub>3</sub> d <sub>3</sub>	-	-	7.30	6.77	6.77	-	-	-	-
" " R <sub>3</sub> d"	-	-	-0.07	-0.595	-0.595	-	-	-	-
" " R <sub>3</sub> d <sub>1</sub>	2.22	-	7.30	6.62	6.62	2.07	-	-0.32	-
" " R <sub>3</sub> d <sub>2</sub>	2.22	-	7.30	6.63	6.63	2.07	-	-0.32	-
" " R <sub>3</sub> d"	+0.45	-	-0.077	-0.782	-0.782	+1.04	-	-1.16	-
" " R <sub>7</sub> d <sub>1</sub>	1.70	-	7.30	7.20	7.20	1.65	-	0.85	-
" " R <sub>7</sub> d <sub>2</sub>	1.70	-	7.30	7.20	7.20	1.65	-	0.85	-
Yield A <sub>7</sub>	-	-	-	-	-	-	-	-	-
Cal. with R <sub>1</sub>	143.5	-	-	-	-	143.5	-	-	-
" " R <sub>2</sub>	-	-	95.2	96.0	96.0	-	-	-	-
" " R <sub>3</sub>	141.4	-	96.1	98.9	98.9	132.3	-	120.6	-
" " R <sub>7</sub>	145.9	-	94.3	86.4	86.4	142.3	-	113.0	-
Conversion U	-	-	-	-	-	-	-	-	-
Cal. with R <sub>1</sub>	92.90	-	-	-	-	91.7	-	-	-
" " R <sub>2</sub>	-	-	55.6	55.1	55.1	-	-	-	-
" " R <sub>3</sub>	92.70	-	56.0	56.0	56.0	92.1	-	86.90	-
" " R <sub>7</sub>	93.25	-	55.5	52.5	52.5	92.3	-	85.95	-
Methane Formation M <sub>v</sub>	-	-	-	-	-	-	-	-	-
Cal. with R <sub>1</sub>	13.68	-	-	-	-	14.84	-	-	-
" " R <sub>2</sub>	-	-	4.25	5.31	5.31	-	-	-	-
" " R <sub>3</sub>	14.35	-	4.40	4.49	4.49	20.50	-	18.33	-
" " R <sub>7</sub>	12.99	-	4.24	3.05	3.05	16.30	-	20.50	-

Nor should what follows mislead on this score. It is possible to calculate the yield using  $R_1$  to  $R_6$  on one side,  $A_7$  on the other, without at all using the value  $n$  in the calculations. A superficial consideration may lead us to conclude that difficulties can be overcome by using such calculations, based on the relationship between the yield and the H : C ratio in the products formed. The derivation of  $A_7$  proves however definitely, that this is not the case.

b). Proof of the formation of carbon dioxide.

The amount of carbon dioxide formed can be calculated from two different formulas.

$$d_1 = R \cdot CO_2^i - CO_2$$

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

Calculating the  $n$  and  $R$  values which belong together from the  $n - R$  formula always gives such exact agreement, that it can be used for the checking of the calculations.

When we calculate  $d_1$  and the intermediate values  $a$ ,  $b$  and  $c$  with the experimentally found  $R$  values ( $R_1$  to  $R_6$ ), and if we substitute into the equation for  $d_2$  an approximation value known to be correct for the hydrocarbon synthesis, e.g. 2.15, we will find  $d_1$  either greater or smaller than that which will be expected for the formation of hydrocarbons of the composition  $CH_{2.15}$ . The difference calculated in this way shall be designated with  $d''$ .

$d'' = d_1 - d_2$  (calculated with the experimental  $R_1$  to  $R_6$  and  $n = 2.15 \pm 0.15$ ), is equal to 0 when the basis of the normal

hydrocarbon synthesis is accurate within the limits of errors.

$d''$  is positive or negative if carbon dioxide is set free or enters into combinations in other processes than the formation of hydrocarbons  $CH_{2.15}$  (including the conversion).

A lower or higher carbon dioxide content in the outlet gas may readily be deducted from erroneous gas analysis, e.g. when the sealing liquid contains or absorbs carbon dioxide. We will show on one example what numerical effects this can have on the computations.

The example No. 2 in the preceding section has an almost error free basis, and  $d''$  is also correspondingly close to 0 (-0.02). The third column of this example shows changes produced when the carbon dioxide is arbitrarily reduced by about 1 percent (i.e. from 12.2 to 11.22 percent), and the gas analysis recalculated to 100 percent. Let us assume that this reduction in the carbon dioxide content was obtained during the sampling of the gas, so that the measurement of the residual volume  $R_2$  remains unchanged, while the residual volume  $R_3$ , calculated from the so called nitrogen content, becomes smaller.  $n$  becomes in both cases considerably smaller, and as a result  $d''$  will be negative. With  $R_2 = 0.732$  the order of magnitude of  $d_2$  will become numerically as large as the reduction of carbon dioxide in the gas analysis (-1.0 percent).

The carbon dioxide formation can therefore be proven by the computation of  $d''$  and helps in that way to the judging of the

numerical basis by permitting us to recognize whether it differs from that to be expected from the formation of hydrocarbons, and in what direction. Of course the assumption is made here that any contained error is actually in the carbon dioxide value, and that the gas analytical determination of the remaining three gas constituents is accurate.

We could use this same proof for the formation of the three other intermediate values a, b and c as for carbon dioxide formation. There are however some differences. No fundamental new relationships could be found, because only one equation is available for comparison purposes, namely the one for  $d''$  which has been used. Nor can we assume to the same extent the combination with, or the setting free of, carbon monoxide, hydrogen and methane, as we can for carbon dioxide.

Computations of  $d''$  permit us to follow not only sources of errors, but other processes as well, which would change the carbon dioxide in the outlet gas, as e.g. the absorption or liberation of carbon dioxide by the catalysts mass. This can be observed e.g. during the starting of catalysts mass saturated with carbon dioxide.

c. Cancellation of errors:

Calculations of  $d''$  gives us the deviations of the wrong from the correct gas analysis, assuming that the error in the gas analysis is only found for carbon dioxide. The direction and extent of such errors are known and it is possible to eliminate this error by corresponding corrections.

Knowledge of  $d''$  permits us the calculation of the correct composition of the end gas which can be used in the familiar way for the calculation of the characteristic numbers. However, if merely the yield is required, it can be determined correctly from erroneous end gas analyses by using  $d - d''$  in the formula for yield instead of  $d$ , and making the computations with  $n = 2.15$ .

We can get results for yield in example 2 with the excellent agreement of  $96.2 = 96.5$  g from the inaccurate analysis in the example 2, compared with 96.5 g with the correct gas analysis, while if the errors are not equalized the yield will be found to be 99 g with the corresponding  $n$ , and when calculated for  $n = 2.15$  the yield will vary between 93.8 and 117.5 g.

Fundamentally the same method of computation can be carried out not only for carbon dioxide, but also for carbon monoxide, hydrogen and methane. There is always however a prerequisite that a possible error would be found in only one of these gases, and that it be known which one is in error. Such assumptions are generally not fulfilled. This is the reason why this method of equalizing errors cannot be used always at will. Work in this direction has however not yet been concluded.

d). Testing for the error of computations:

It has already been mentioned that  $d_1$  is always =  $d_2$  within the limits of errors. This agreement can be used as a test for errors of computation.

Also,  $n$  calculated from  $n = 2 \cdot \frac{(b + 2d) - (a + 2c)}{a - (c + d)}$  must equal the  $n$  values which correspond to that particular  $R$  in the  $n - R$  equation with which  $a, b, c$  and  $d$  have been calculated.

The errors of computation can be tested also by calculating the yield not from a single formula, but from several. The values obtained with error-free computations (computing machine) must agree. This, and the degree of accuracy with which  $d_1$  and  $d_2$  and the different "A" values agree with each other, can be seen from the numerical example used above to prove the applicability of the  $n - R$  equation, and which illustrates the agreement for the whole range between  $n = 1$  and  $n = 9$ .

When the value for  $n = 2.0$  has been used in calculations, the composition of the end gas can be calculated backwards from the formulas given in the collection of formulas for  $CO_2$ ,  $CO$ ,  $H_2$ , and  $CH_4$ .

### 3. The use of Blank Forms

The use of blank forms has been found advantageous in practice in the course of calculations. This kind of blanks is shown. There is in addition a copy of a small collection of formulas added in which only formulas in practical use are summarized.

Experience has shown that when such blank forms are used, technically untrained help can be depended upon to calculate from the gas analyses the four characteristic numbers in around five

minutes after only a short training.

B. Preliminary Computations about the Course of the Synthesis.

Without going into details, it will become immediately apparent that the use of the derived formulas will result in important simplifications in the preliminary calculations of the course of the synthesis, e.g. in the laying out of the new installations. We have no assignments to do in that line, and this mere mention should suffice.

Diagram in the appendix show graphically the connection between the four characteristic numbers for the simple case when  $n = 2.0$ . This enables one always to calculate the fourth figure when the remaining three are given.

C. Uniform Use of Abbreviations and Characteristic Numbers:

In spite of the detailed treatment for decades of the hydrogenation of carbon monoxide, and in spite also of the voluminous exchanges of experience participated in by numerous concerns on the computations of the gas utilization, neither the definitions of the concepts, nor the abbreviations and the characteristics have been uniformly used. Such an agreement in the following fields would be desirable because of the resulting advantages, e.g. in:

1. The selection of characteristic numbers and their exact definition.
2. Fixing the abbreviations to be used.
3. Discussion of the most dependable values, for  $n$  and  $\rho$ , as well as an agreement on the average values.

4. Discussions of the relationships of oxygen-containing products in the yield, and a unification of corresponding methods of operation and courses of computations.
5. Setting up of generally useful rules for the equalization of errors.

A small collection of formulas for the evaluation of gas analyses in the hydrogenation of carbon monoxide.

$H_2, R_2$  from measurements:  $R_2, H_2 = \frac{H_2}{R_2} \cdot \beta$  %

$H_2 = \frac{2CO + 3CO_2 - (H_2 + CH_4)}{2CO + 3CO_2 - (H_2 + CH_4 \cdot \beta)}$	1.0 - 1.05	1.0
	1.05 - 1.15	0.9
	Over 1.15	0.85

$$p = CO_2 + CO + CH_4$$

$$p' = CO_2' + CO' + CH_4' \cdot \beta \quad U = \frac{a+b}{j} \cdot 10^2 \quad x = \frac{b}{a}$$

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

$$q' = 2/(CO_2' + CO') - (H_2' + 2CH_4' \cdot \beta) / \quad Mv = \frac{4c}{a+b} \cdot 10^2$$

$$R_6 = R_7 = \frac{p \cdot R + q}{p' \cdot n + q'} \quad n = \frac{aR - q}{p - p'R}$$

$$a = CO - R \cdot CO' \quad c = R \cdot CH_4' \cdot \beta - CH_4 \quad A_7 = 0.893 / 5a + b - 4(2c + d) /$$

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

$$d_2 = \frac{n(a - c) + 2(a - b) + 4c}{n + 4} \quad n = 3 \cdot \frac{(b + 2d) - (a + 2c)}{a - (c + d)}$$



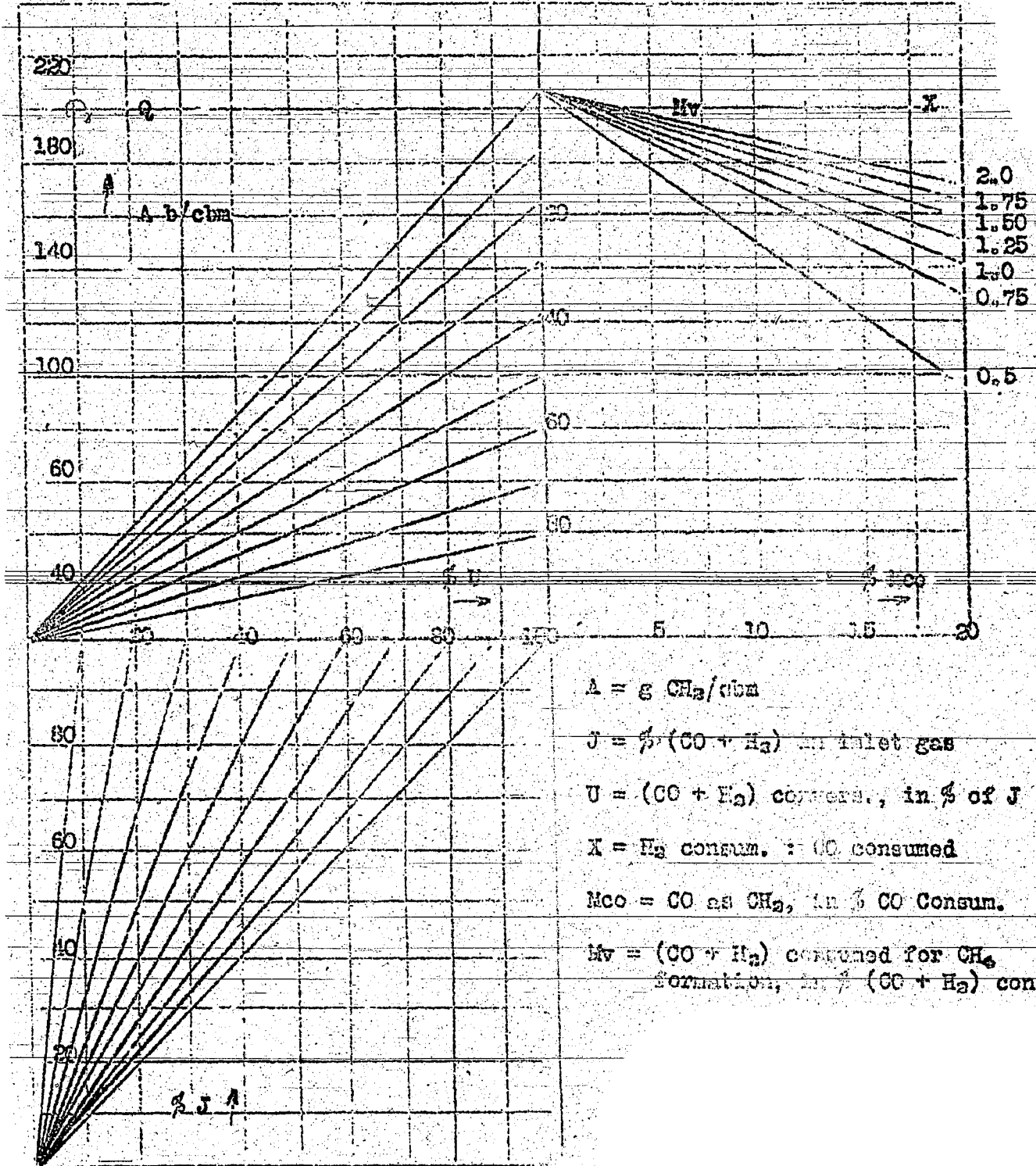
Testing the Basis for the Evaluation of the National Laboratory  
Experiments by Comparison by the n and R values.

Evaluation No.	Total	1	2	3	4	5	6	7	8
Works: RCH									
R <sub>2</sub>	0.670	0.699	0.668	0.661	0.686	0.656	0.707	0.720	
R <sub>3</sub>	-	0.687	0.637	0.517	0.555	0.627	0.675	-	
R <sub>6</sub>	0.697	0.708	0.697	0.672	0.707	0.682	0.723	0.748	
n <sub>m</sub> from Brabag	2.37	2.33	2.375	2.375	2.375	2.37	2.365	2.365	
n <sub>m</sub> from R <sub>2</sub>	2.17	2.20	2.22	2.25	2.24	2.25	2.14	2.01	
Works: Lurgi									
R <sub>2</sub>	0.609	0.628	0.594	0.605	0.605	0.591	0.609		
R <sub>3</sub>	0.537	0.568	0.567	0.550	0.515	0.490	0.614		
R <sub>6</sub>	0.620	0.635	0.605	0.620	0.625	0.615	0.627		
n <sub>m</sub> from Brabag	2.14	2.08	2.08	2.09	2.22	2.36	2.36		
n <sub>m</sub> from R <sub>2</sub>	2.23	2.08	2.08	2.08	2.13	2.28	2.27		
Works: Rhpr.									
R <sub>2</sub>	0.603	0.598	0.598	0.603	0.611	0.622	0.623	0.634	0.640
R <sub>3</sub>	0.566	0.558	0.528	0.588	0.530	0.566	0.498	0.695	0.593
R <sub>6</sub>	0.622	0.598	0.615	0.625	0.630	0.640	0.638	0.653	0.655
n <sub>m</sub> from Brabag	2.41	2.36	2.38	2.40	2.42	2.43	2.45	2.45	2.47
n <sub>m</sub> from R <sub>2</sub>	2.35	2.29	2.31	2.33	2.32	2.39	2.38	2.38	2.43
Evaluation No.	Total	1	2	3	4	5	6	7	
Works: Brabag									
R <sub>2</sub>	0.626	0.655	0.619	0.623	0.628		0.640		
R <sub>3</sub>	-	0.708	0.549	0.662	0.595		0.610		
R <sub>6</sub>	0.647	0.662	0.518	0.638	0.642		0.650		
n <sub>m</sub> from Brabag	2.19	2.16	2.16	2.19	2.23		2.20		
n <sub>m</sub> from R <sub>2</sub>	2.13	2.15	3.77	2.12	2.05		2.15		
Works: KWI.									
R <sub>2</sub>	0.575	0.580	0.570	0.567	0.570	0.570	0.602	0.700	
R <sub>3</sub>	-	-	0.662	0.550	0.538	0.623	0.540	0.630	
R <sub>6</sub>	0.589	0.597	0.590	0.588	0.591	0.588	0.632	0.730	
n <sub>m</sub> from Brabag	2.41	2.38	2.38	2.38	2.41	2.43	2.46	2.46	
n <sub>m</sub> from R <sub>2</sub>	2.39	2.28	2.27	2.29	2.29	2.37	2.38	2.36	

Graphic Determination of Characteristics  
(for  $n = 2.0$ )

I  $Q = 208 \left(1 - \frac{M_{CO}}{25(1+X)}\right) \cdot 10^{-4}$   
(from equations for  $A_6$ )

II  $Q = 208(100 - M_V) \cdot 10^{-6}$



$A = g \text{ CH}_2/\text{cbm}$

$J = \% (\text{CO} + \text{H}_2) \text{ in inlet gas}$

$U = (\text{CO} + \text{H}_2) \text{ convers., in \% of } J$

$X = \text{H}_2 \text{ consum.} : \text{CO consumed}$

$M_{CO} = \text{CO as CH}_2, \text{ in \% CO Consum.}$

$M_V = (\text{CO} + \text{H}_2) \text{ consumed for CH}_2 \text{ formation, in \% (CO + H}_2) \text{ cons.}$

Explanation of Symbols for the Computation of Gas Utilization

During the Hydrogenation of Carbon Monoxide.

I. Volumes

$CO_2, CO, H_2, CH_4, N_2$ , -- percent of the corresponding gas in the synthesis gas intake

$CO_2', CO', H_2', CH_4', N_2'$  -- percent of these gases in outlet gas.

$J, J'$ , -- percent of  $(CO + H_2)$  in the intake or outlet gases.

$J_x$  -- proportion of  $(CO + H_2)$  in synthesis gas which would be completely consumed with a given  $X$ , in percent of synthesis gas.

$$p = (CO_2 + CO + CH_4)$$

$$p' = (CO_2' + CO' + CH_4')$$

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

$$q' = 2/(2CO_2' + CO') - (H_2' + 2CH_4')/$$

$R$  -- residual volumes of the outlet reaction outlet gases from one volume of synthesis gas

$R_1$  -- measured residual volume

$R_2$  -- measured residual volume recalculated to normal conditions

$R_3$  -- residual volume calculated from  $N_2$  and  $N_2'$

$R_4$  -- residual volume calculated from precision determinations of  $N_2$

$R_5$  -- residual volume calculated from gas analyses for  $n = 2.0$

$R_6$  -- residual volume calculated from gas analyses with the value for  $n$  found from the analyses of the products.

$R_7$  -- residual volume calculated from gas analysis and an assumed value for  $n$ .

a - carbon monoxide consumed

b - hydrogen consumed

c - methane formed

c<sup>+</sup> - higher hydrocarbons formed, without methane

c<sub>m</sub> - total hydrocarbons formed, including methane

d - carbon dioxide formed

e - water formed

d<sub>1</sub>, e<sub>1</sub> - volumes of carbon dioxide or water found as such

d<sub>2</sub>, e<sub>2</sub> - volumes of carbon dioxide or steam calculated for the formation of pure hydrocarbons

' symbol for proportion of substances chemically or physically bound, or set free.

d'' carbon dioxide liberated or combined.

a, b, c, d and e: volumes of the corresponding gases used up or formed per unit volume of the intake synthesis gas, or in computations with the numerical results of gas analysis per hundred volumes of the intake synthesis gas.

E: cubic meters of synthesis gas intake during the time interval measured, calculated to normal state.

II Characteristic Numbers

U: (CO + H<sub>2</sub>) Conversion, in percent of J.

Uco: CO conversion in percent of CO.

Mv: (CO + H<sub>2</sub>) consumption for the formation of CH<sub>4</sub>, in total percent of (CO + H<sub>2</sub>).

Mco: CO as CH<sub>4</sub>, in percent of the CO consumed.

X: Ratio of hydrogen consumed: carbon monoxide consumed.

A: Yields, in g/cbm of synthesis gas.

$A_1 - A_9$  yields of hydrocarbons  $CH_n$ , without methane and without oxygen containing products.

$A_{10}$  yield including oxygen-containing products, but without methans, calculated from experimental data.

$A_{11}$  yield including oxygenated products, calculated from  $A_1$  to  $A_9$  with respect to oxygen containing groups.

$A_{max}$  90 maximum theoretically possible yield of higher hydrocarbons without methane with given X and  $M_V$  and with 90 percent ( $CO + H_2$ ) conversion.

$A_{11}$  as before but including methane.

### III Dimensionless Factors

n: average value for the atomic proportion hydrogen: carbon.

n: for the total higher hydrocarbons formed without methane for  $\sigma^+$ .

$n_{11}$ : for the total hydrocarbons formed including methane, for  $C_m$ .

$n_p$ : for the saturated paraffin hydrocarbons.

$n_e$ : for the CH part, from (ester - 2 mol water).

$n_{ald}$ : for the CH part, from (aldehyde - 1 mol water).

$n_a$ : for the CH part, from (acid - 3 mols water).

C-number: Average C values of the fraction of hydrocarbons passing over in the boiling range of the hydrocarbon fraction.

Z: the average C-number found in the gas analysis for  $CH_4$ .

z: average C number of the hydrocarbons in  $CH_4$  exclusive of pure methane.

$\beta$ : factor for pure methane in  $CH_4$ .

h: factor for recalculating yield from volumes,  $CH_4$  into grams.

k: factors for the calculation of  $\beta$  from the products, indexes the same as for z.

#### IV. Abbreviations for the Evaluation of Analyses of Liquid Products.

G: total weight of the products formed, without methane.

g: the weight of a fraction distilling in the distillation range of  
1. C-number.

(olef) - the amount of olefines in grams, in one fraction.

(par) - grams of paraffin hydrocarbons, in one fraction.

(OH) - grams of OH portion of the oxygen containing compounds of a  
fraction; indexes and computations as with n.

CH. Z, EZ, NZ, CO. Z - data from the determination of chemical  
groups for alcohols, esters, acids, and  
aldehydes.

W": grams of chemically bound water in a fraction, indexes as in n.

Y: amount of chemically combined water in the oxygen containing  
compounds/cfm of synthesis gas.

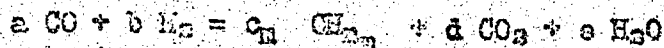
#### Collection of Formulas for the Computation of Gas Utilization in the Hydrogenation of Carbon Monoxide.

##### I. Generally Applicable Equations

(for any Values of n)

##### A. Basic Stoichiometric relationships:

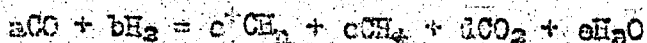
##### 1. The first basic stoichiometric relationships:



Solutions for the first basic equation:

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

##### 2. The second basic stoichiometric equation:



Solutions for the second basic equation:

$$c^+_{-2} = \frac{2}{n+4} (a+b-4c) \quad c^+_{-3} = a-c-d \quad c^+_{-4} = \frac{2}{4-n} (3a-b-4d)$$

$$c^+_{-6} = \frac{2}{n+2} (b+d-3c) \quad d_2 = \frac{n(a-c) + 2(a-b) + 4c}{n+4}$$

$$e = \frac{n(2c-a) + 4b - 3c}{n+4}$$

### B. Intermediate values:

$$a = CO - R \cdot CO^+ \quad b = H_2 - R \cdot H_2^+ \quad c = R \cdot CH_4^+ - CH_4$$

$$d_1 = R \cdot CO_2^+ - CO_2 \quad e + b = J - R \cdot J^+ = J \cdot U \cdot 10^{-2}$$

### C. Calculation of n and R:

$$1. R_3 = \frac{N_2}{N_2^+}$$

2. The n - R equations for the first basic stoichiometric equation.

$$1. p_m = CO_2 + CO$$

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

$$p^+_{-m} = CO_2^+ + CO^+$$

$$q^+_{-m} = 2(2CO_2^+ + CO^+ - H_2^+)$$

$$n = \frac{q^+_{-m} \cdot R - q_m}{p_m - p^+_{-m} \cdot R}$$

$$R = \frac{3q + p_m \cdot n_m}{q^+_{-m} + p^+_{-m} \cdot n_m}$$

3. The n - R equation from the second basic stoichiometric equation:

$$p = (CO_2 + CH_4 + CO)$$

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

$$p^+ = CO_2^+ + CH_4^+ + CO^+$$

$$q^+ = 2/(2CO_2^+ + CO^+) - (H_2^+ + 2CH_4^+)/$$

$$n = \frac{q^+ \cdot R - q}{p - p^+ \cdot R}$$

$$R_6 \text{ or } R_7 = \frac{p \cdot n + q}{p^+ \cdot n + q^+}$$

4. n from the intermediate values

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

5. Recalculating n into n\_m:

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

D. Calculation of the Characteristic Numbers:

## 1. Conversion and ratio of consumption

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

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

## 2. Methane formation

$$Mv = \frac{4c}{a+b} \cdot 10^2 \quad Mco = \frac{2}{a} \cdot 10^2 \quad Mv = Mco \frac{4}{1+X}$$

$$= \frac{2-z}{z-1} \quad \text{for } z = Z+1, \quad \beta = \frac{1}{Z}$$

E. Calculations of Yields:

## 1. Higher hydrocarbon yields without methane:

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

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

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

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

$$A_5 = h_1 \cdot (a+b) (100 - Mv) \cdot 10^{-2}$$

$$A_6 = h_1 (a+b) \left(1 - \frac{Mco}{25(1+X)}\right) \cdot 10^{-2}$$

$$A_7 = 0.393 / 5a + b - 4(2c + d)$$

Maximum theoretical yield:

$$J_X = CO (1 + X), \quad \text{when } H_2 \text{ in entering gas in excess over } H_2 \text{ in } J_X$$

$$J_X = H_2 \left(\frac{1+X}{X}\right), \quad \text{when } CO \text{ in entering gas in excess over } CO \text{ in } J_X$$



$$A_{\max 90} = h_1 \cdot J_X \cdot 90 (100 - Mv) \cdot 10^{-4}$$

3. Hydrocarbon yield including methane:

$$A_{2m} = \frac{20 (12 + n_m)}{22.4 (4 + n_m)} (a + b) = h_1 (a + b)$$

$$A_{3m} = \frac{10 (12 + n_m)}{22.4} (a - d) = h_2 (a - d)$$

$$A_{5m} = \frac{20 (12 + n_m)}{22.4 (2 + n_m)} (b + d) = h_3 (b + d)$$

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

4. Numerical values for the factor h:

n or n <sub>m</sub>	h <sub>1</sub>	h <sub>2</sub>	h <sub>3</sub>	h <sub>4</sub>
2.0	2.083	6.250	6.250	3.125
2.05	2.074	6.272	6.433	3.097
2.10	2.064	6.295	6.649	3.071
2.15	2.054	6.316	6.879	3.044
2.20	2.045	6.339	7.044	3.019
2.25	2.036	6.361	7.270	2.994
2.30	2.027	6.383	7.511	2.969
2.35	2.018	6.406	7.765	2.946
2.40	2.009	6.428	8.036	2.922

5. Yield of total products (higher hydrocarbons and oxygen-containing products, without methane).

$$A_{10} = \frac{G}{M} \quad A_{11} = A_1 \text{ (or } A_2 \text{ to } A_7) + Y$$

II. Testing the Formation of Carbon Monoxide:

d'' = d<sub>1</sub> - d'', calculated with R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> or R<sub>4</sub>, and with n = 2.15 (± 0.15).

### II Approximation Equations for $n = 2.0$

1. Solutions for the first basic stoichiometric equation.

$$c_m = \frac{1}{3}(a + b) \quad d = \frac{1}{3}(2a - b) \quad e = \frac{1}{3}(2b - a)$$

2. Solutions for the second basic stoichiometric equation.

$$c^* = \frac{1}{3}(a + b - 4c) \quad d = \frac{1}{3}(2a - b + c) \quad e = \frac{1}{3}(2b - a - 2c)$$

3. Residual volumes.

$$R = \frac{200 + 300a - (H_2 + CH_4)}{200' + 300a' - (H_2' + CH_4')}$$

$$R = \frac{100 - (400a + 300)}{100 - (400a' + 300')}$$

$$R = \frac{300 - (CO + 4H_2 + 4CH_4)}{300 - (CO' + 4H_2' + 4CH_4')}$$

4. Composition of end gas.

$$CO_2' = \frac{1}{R} \left( CO_2 + \frac{4(2 - X) + \frac{Mv}{100}(1 + X)}{36 - 4 \left[ \frac{4(2 - X) + \frac{Mv}{100}(1 + X)}{100} \right]} \right) (100 - 100R)$$

$$CO' = \frac{1}{R} \left( CO - \frac{5(100 - 100R)}{(1 + 4X) - \frac{Mv}{100}(1 + X)} \right)$$

$$H_2' = \frac{1}{R} \left( H_2 - \frac{3X(100 - 100R)}{(1 + 4X) - \frac{Mv}{100}(1 + X)} \right)$$

$$CH_4' = \frac{1}{R} \left( CH_4 + \frac{3 \cdot \frac{Mv}{100}(1 + X)(100 - 100R)}{4(1 + 4X) - \frac{Mv}{100}(1 + X)} \right)$$