CALCULATION OF GAS CONSUMPTION AND SYNTHESIS

COURSE IN THE HYDROGENATION OF CARBON MONOXIDE

BY DR. OTTO ROELEN

SUMMARY

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

INTRODUCTION

Introduction to the Mathematical Procedure

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

In the present paper, we shall attempt to develop the principles of a mathematical treatment of gas consumption in the hydrogenation of carbon monoxide. Starting from the fundamental quantitative relationships between reactants and products, equations whose manipulation offers no difficulty are easily derived.

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

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

Discussion of the Notation[*]

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

The Residual Volume, R

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

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

Description of Characteristic Variables

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

---

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

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

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

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

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

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

Characteristic Variables for CO + H_2 Conversion

A graphic representation of the characteristic variables is shown in figure 8.

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

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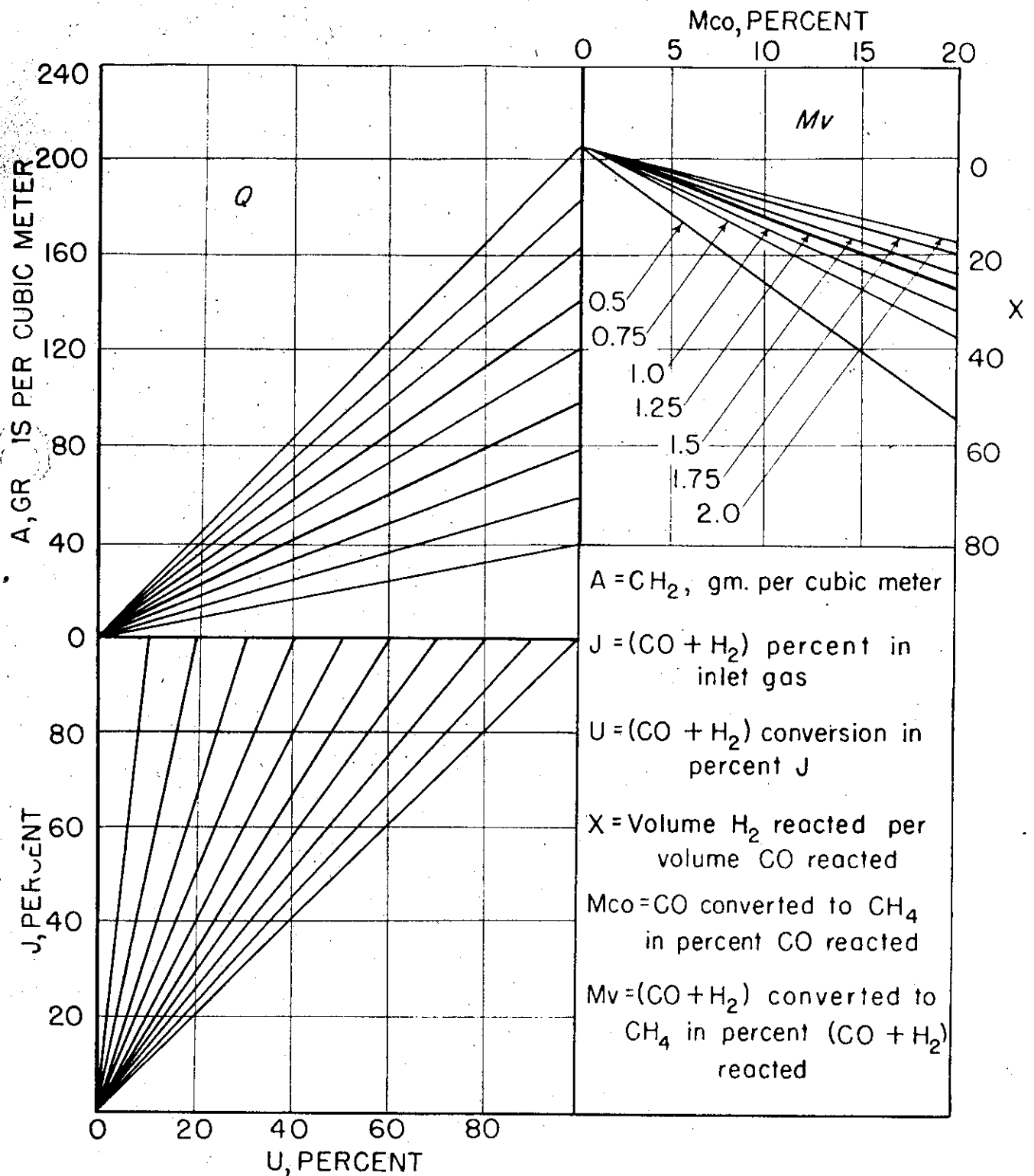
Figure 8. Graphic representation of characteristic variables.
(for n = 2.0)

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

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

In the following discussion the term conversion refers exclusively to the CO+H$_2$ conversion and is represented by the symbol, U. Values for the CO conversion, as well as for the H$_2$ conversion, may be omitted as these are evident from the H$_2$:CO usage ratio. The symbol Uco for the CO conversion may be used as intermediate value in certain calculations.

What has been said of conversion is also true for the amount of methane formed. In the following pages, the formation of methane designated as Mv is indicated solely by the CO+H$_2$ consumption. These Mv values are always susceptible to direct comparison no matter how widely the syntheses and catalysts differ.

Explanation of Selection of Symbols

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

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

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

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

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

(e) No symbols are given for concepts still in current use, but which became obsolete in the light of the present study, for example, the degree of liquefaction, the H$_2$ conversion, etc.

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

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

1. Gases

> (a) Synthesis gas.
> (b) Total CO_2 content.
> (c) The CO_2 knocked out for a given conversion.

2. Conversion

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

3. Products

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

Allowing for the various combinations of the different
fundamentals above enumerated, there are three methods of expressing the
yields herein discussed. In general, these different quantities are
easily expressed in terms of one another. The yields, therefore, from
any given set of data in most instances, for a given conversion, and
in most cases does not greatly differ. The scope of the present
discussion, for our purposes, with a limited use of yields is however
for a simple case only, but as far in place of higher conversions
(including methane) per mole refer to 1 cubic gram, these are largely
oxygenated per mole feed stock.

Third rule (for nitrogen only):

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

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

Algebraic Interpretation of the Three Rules

The Two Fundamental Stoichiometric Equations and Their Solution

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

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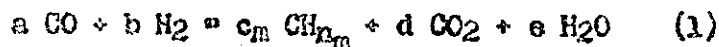
This equation will be known as the "first fundamental stoichiometric equation". The values, a, b, c, d, and e, represent the volumes of carbon monoxide and hydrogen reacted and the volumes of hydrocarbons, carbon dioxide, and water formed, and will be referred to as the "intermediate variables".

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

Summation equation for carbon: $a = c_m + d$
Summation equation for oxygen: $a = 2d + e$
Summation equation for hydrogen: $2b = n_m\ c_m + 2e$
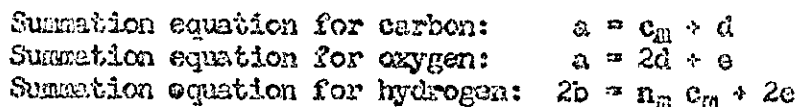
From these three equations general solutions of equation (1) are derived by simple algebra.

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

$$a\ CO + b\ H_2 = c^+\ CH_n + c\ CH_4 + d\ CO_2 + e\ H_2O \qquad (2)$$
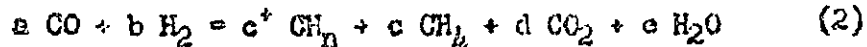
This equation is known as the "second fundamental stoichiometric equation".

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

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

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

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

Calculation of the Intermediate Variables

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

Inlet CO = reacted + unreacted CO

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

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

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

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

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

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

38

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

Calculation of the Residual Volume from the Nitrogen Content

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

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

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

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

$$R = \frac{N_2}{N_2'} \qquad (7)$$

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

The n-R Equation

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

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

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

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

Let:

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

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

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

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

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

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

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

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

$$p'_m = CO'_2 + CO' \qquad\qquad q'_m = 2(2CO'_2 + CO' - H'_2)$$

$$n_m = \frac{q'_m R - q_m}{p_m - p'_m R} \qquad\qquad R = \frac{q_m + p_m n_m}{q'_m + p'_m n_m}$$

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

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

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

This gives:

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

or:

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

<u>Application and Validity of the Correlation</u>

<u>Between Characteristic and Intermediate Variables</u>

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

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

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

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

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

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

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

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

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

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

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

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

(3) For a residual volume of 68.9% and a yield of 68.2 g/m^3, provided that aside from methane only ethane (C_2H_6) forms.

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

(5) For a residual volume of 81.5% and a yield of 37.6 g/m^3, provided that aside from methane only hydrocarbons of the hypothetical composition CH_9 form.

Table 10

Range of Validity of the n-R Equation for a

Set of Gas Analyses

1. **Gas Analyses**

	CO_2	CO	H_2	CH_4
Inlet, volume percent	6.0	38.3	50.0	0
Outlet, volume percent	38.0	3.9	42.0	7.6

2. **The n-R Equation**

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

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

3. Intermediate Variables

$n =$	1	2	3	4	5	7	9
$R =$	0.473	0.617	0.689	0.730	0.753	0.780	0.815
$a =$	36.5	35.9	35.6	35.4	35.3	35.2	35.1
$b =$	30.1	24.1	21.1	19.3	18.2	16.8	15.8
$c =$	3.6	4.7	5.2	5.5	5.8	6.0	6.2
$d_1 =$	12.0	17.4	20.1	21.7	22.8	24.0	24.9
$d_2 =$	12	17.4	20.1	21.7	22.8	24.0	24.9

4. Characteristic Variables

$U =$	75.4	68.0	64.3	61.0	60.6	58.9	57.6
$Mv =$	21.6	31.5	36.6	40.2	43.4	46.2	48.7
$X =$	0.65	0.67	0.595	0.545	0.516	0.475	0.450
$A_1 =$	121.1	85.7	68.2	58.2	51.3	43.1	37.6
$A_2 =$	121.1	85.7	68.2	58.2	51.3	43.1	37.6
$A_3 =$	121.1	85.7	68.2	--	51.3	43.1	37.6
$A_4 =$	121.1	85.7	68.2	58.2	51.3	43.1	37.6
$A_5 =$	121.1	85.7	68.2	58.2	51.3	43.1	37.6
$A_6 =$	121.1	85.7	68.2	58.2	51.3	43.1	37.6

5. Notes

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

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

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

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

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

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

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

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

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

The agreement in the yields occurs only when corresponding n and R values are used. When this is not the case, the differences in the yields obtained by means of the various formulas increase as R differs increasingly from the value which corresponds to the given n value. The geometrical locus of all yields calculated from one and the same formula for a given n may be considered a family of straight lines (figure 9). All these yield lines intersect at a point for which n and R satisfy the conditions of equation (6) for that particular set of gas analyses.

Calculation of Characteristic Variables

Conversion and Usage Ratio

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

$$U = \frac{a + b}{y} 10^2 \qquad (10) \qquad x = \frac{b}{a} \qquad (11)$$

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

Formation of Methane

Calculation of the Pure Methane in the Outlet Gas

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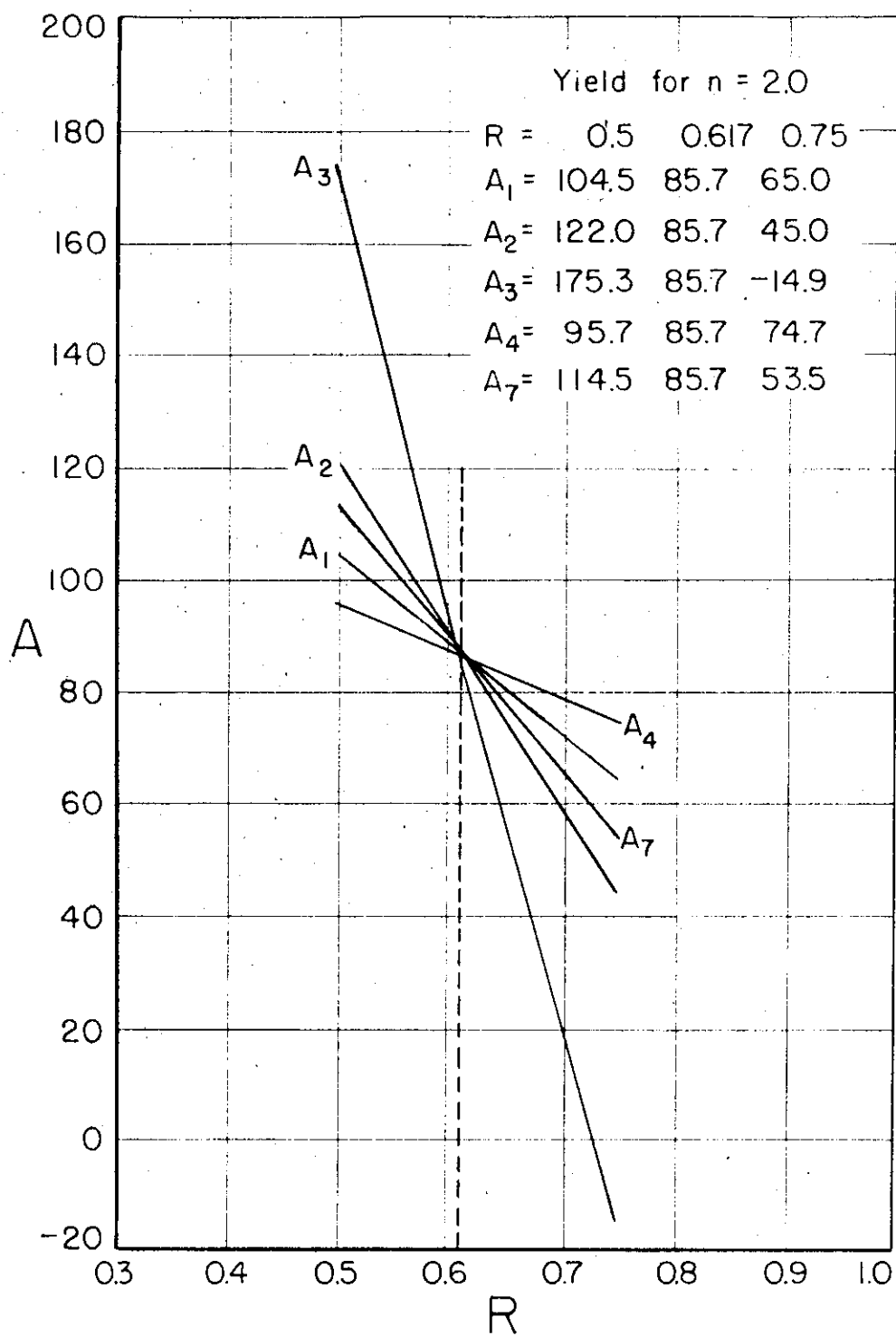
Figure 9.—The yields as functions of the residual volume.

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

L-269
2-18-47

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

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

Let m = pure methane content in CH_4^0

Kw = higher hydrocarbon content in CH_4^0

Then:

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

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

$$Z(CH_4^0) = 1 \, m + z \, Kw \qquad (13)$$

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

Combining (12) and (13) we obtain:

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

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

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

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

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

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

Transforming, we obtain:

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

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

Approximate Values for the β factor

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

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

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

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

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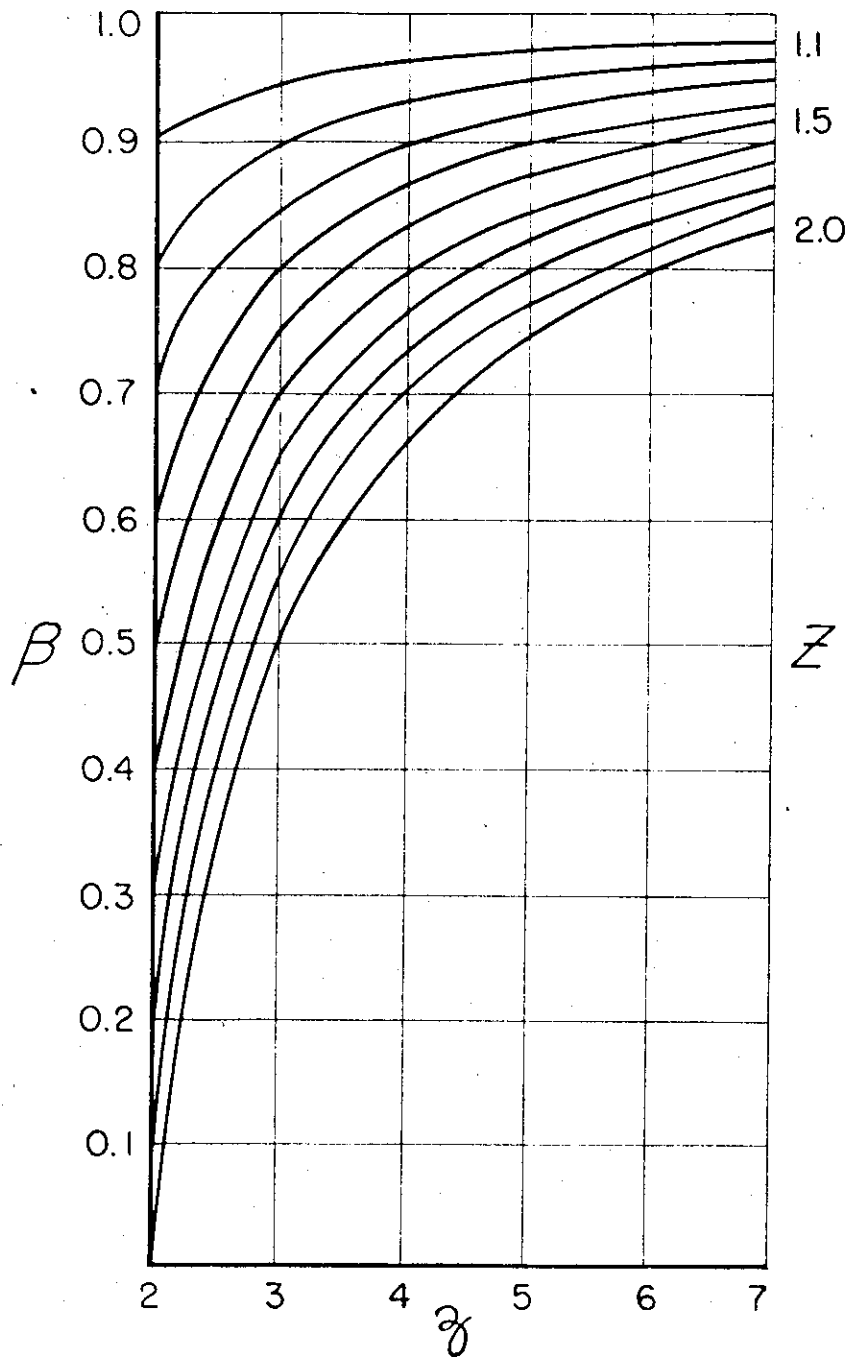
Figure 10. — The β factor for the calculation of pure methane. (as a function of the two C-numbers, γ and Z)

As for the other case, that of gas samples taken before adsorption, we know from industrial practice that the "methane" content determined by combustion is generally about 2% higher before than after adsorption. For an average "methane" content of 15% before adsorption, we obtain $\beta = 0.867$. Since the corresponding carbon number Z generally lies between 1.5 and 1.7 the value of z as determined from figure 2 must be about 5. For want of more reliable data, we may let z equal 5 for gas samples before removal of condensable hydrocarbons. The following approximate values may then be calculated for methane:

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

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

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

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

Gas composition:	CO	H_2	CH_4	Z	N_2
Inlet, volume percent	37.8	49.2	0.2	--	6.3
Outlet, volume percent	30.1	29.3	5.1	--	12.0

Characteristic variables: U = 65.5%   Nv = 16.75%   A = 98.4 g/m^3

Changes in Nv and A with β:

β	Nv	Diff.	A	Diff.
1.00	15.75		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	

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

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

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

(b) For Z > 1.15 β = 0.85

(c) Gas samples whose Z value is greater than 1.4 after adsorption are discarded.

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

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

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

Calculation of Methane Formation

Mv represents that percent of the total $CO + H_2$ gas mixture converted which enters into the formation of methane. From equation (1) as solved for $c = \frac{1}{4}(a + b)$ or $(a + b) = 4c$ we obtain $n_3 = 4$.

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

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

For Mco we may write:

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

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

$$Mv = Mco \frac{4}{1 + X} \qquad (19)$$

Yield of Higher Hydrocarbons

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

The equations derived above for the yield always contain n as one of the terms. Using equation (8), n may be expressed in terms of R and the gas analysis data. Substituting $\frac{O' R - Q}{p - p' R}$ for n, in any equations (20-23), we obtain for all four equations an identical new expression for A_7 in which n no longer appears but is replaced by the four intermediate variables a, b, c, and d.

$$A_7 = 0.893\left[5a + b - 4\,(2c + d)\right] \qquad (28)$$

This equation appears to be the most convenient for practical purposes when sufficient decimal places are retained (calculating machine). Numerical values are obtained which are identical with those for A_2 – A_4.

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

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

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

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

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

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

DETERMINATION OF HYDROGEN-CARBON RATIO AND OF

OXYGENATED COMPOUNDS IN THE PRODUCTS

Reasons for Extending the Evaluations

Equation (6) offers one means of calculating the relation between n and R. However, when gas analysis data alone are used, there exists no reliable methods for deciding which of a given number of n-R pairs applies to the particular synthesis run under consideration.

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

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

The quantitative analysis of the products formed has as still another purpose the determination of the total yield. The formulas derived above for the yield apply only to the formation of pure hydrocarbons, but do not take into account the possible formation of oxygenated groups. The yields calculated by h_1 to h_7 are, therefore, too low

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

Calculation of Oxygenated Groups from Gas Analysis Data

We know from experience, that the oxygenated by-products of the synthesis are composed largely of saturated alcohols. Therefore, it would seem possible to determine their amount from gas analysis data in such a way that a term similar to that for methane could be introduced into equation (2) and the equation solved for this term, for example, CH_2O, CH_3O, etc. However, no valid algebraic expression has been obtained in this way. Both sides of the equation cancel out or the expression is equal to zero. In consequence, the idea of calculating oxygenated groups by this method must be discarded.

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

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

Chemical Investigation of the Products Formed

Combustion

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

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

---

*/ Meyer, H., Analyse und Konstitutionsermittlung, 1938, p. 116.

Precise Fractional Distillation and Chemical Analysis

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

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

Three stoichiometric representations are possible for the oxygenated compounds:

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

The first case is not directly accessible to calculation since it cannot be reduced to equations (1) and (2). The second case cannot be used in calculations as it stands. Sample calculations for this case show that other yield formulas would have to be devised, taking into account any chemically bound carbon dioxide. The third formula may be used directly since the term for water (w) was always omitted in deriving the formulas for yield. Consequently, we are free to consider whatever portion we wish as chemically bound.

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

To calculate n from the products, the amounts which make up each individual fraction are multiplied by the corresponding n and the sum of all the values thus obtained is divided by the total weight of the product. Methane is neglected, according to the definition of n. This n appears directly or indirectly in all the formulas for the yield from A_1 to A_7. Since the derivation of these formulas is such that they express only the yield in hydrocarbons, it becomes necessary, when determining the oxygenated compounds present in the products, to deduct one molecule of water for each molecule of oxygen. One molecule of water, therefore, is deducted per molecule of alcohol, aldehyde, or ketone, and two molecules of water per molecule of acid or ester. The hydrocarbon fraction (HC) used in calculating n may then be expressed as follows:

For alcohols:
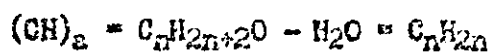
$$(CH)_a = C_nH_{2n+2}O - H_2O = C_nH_{2n}$$

For esters:

$$(CH)_o = C_nH_{2n}O_2 - 2H_2O = C_nH_{2n-4}$$

For acids:

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

For aldehydes and ketones:

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

For olefins:

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

For paraffins:

$$(Par.) = C_nH_{2n+2}$$
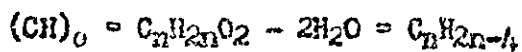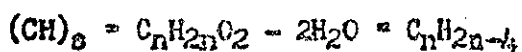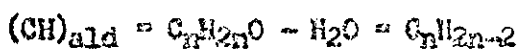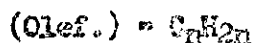
These hydrocarbons residues are now multiplied by the appropriate n value:

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

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

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

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

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

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

The formula for n therefore reads:

$$n = \frac{2\left[\sum(\text{olef.})\right]+\sum\left[n_p(\text{Par.})\right]+2\left[\sum(\text{CH})_a\right]+\sum\left[n_e(\text{CH})_e\right]+\sum\left[n_g(\text{CH})_g\right]+\sum\left[n_{\text{ald.}}2(\text{CH})_{\text{ald.}}\right]}{\sum(\text{Olef.})+\sum(\text{Par.})+\sum(\text{CH})_a+\sum(\text{CH})_e+\sum(\text{CH})_g+\sum(\text{CH})_{\text{ald.}}} \quad (29)$$

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

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

$$W_e'' = \frac{36.032 \; g \; EZ \; M_e}{M_e \; 56000} = g(EZ)(0.6434)(10^{-3}) \text{ grams} \quad (30)$$

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

$$\text{Grams ester} - W_e'' = \frac{g(EZ)M_e}{56000} - \frac{g(EZ)36.032}{56000} = g(EZ)\frac{M_e - 36.032}{56000} \quad (31)$$

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

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

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

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

$$Y = \frac{\sum(W'')}{m^3} \quad (33)$$

APPLICATION OF THE FORMULAS DERIVED

Evaluation of Gas Analysis and Synthesis Data

General Course of Calculations

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

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

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

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

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

Checking the Results

Check on the Experimental Data

The newly established relations offer a rather simple means of judging the accuracy of the experimental data. For this purpose values for k and n, obtained by different methods, are compared. The examples shown in table 12 will serve as illustrations.

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

A series of careful pilot stage experiments (Reinheitsversuche Schwerznoide) involving a variety of completely different synthetic procedures, consistently gave values for n ranging between 2.0 and 2.3. For the present, n = 2.15 ± 0.15 may, therefore, be considered a reliable approximate value. If the calculated n values (using k values obtained by measurement or from E_2) differ appreciably from the approximate values determined above, corresponding inaccuracies must be sought in the experimental data.

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

59

Table 13

Examples of Calculations of Syntheses Runs

No.	1		2			3		4	
Source	Lab.		R.-A.-Res. 1/			Lab.		Industry	
Catalyst	Cobalt		Iron			Cobalt		Cobalt	
Pressure	Normal		10 Atmos.			Normal		Normal	
Gas Analyses									
CO_2	5.2	31.2	0.0	12.2	11.22 2/	5.0	30.0	14.4	41.9
Olefins	0	0	0.0	1.0	1.0	0.0	2.6	--	0.5
CO	28.6	5.2	39.2	26.8	27.1	28.1	2.7	26.8	12.4
H_2	59.0	21.7	48.4	37.7	38.13	59.8	20.1	53.6	18.6
CH_4	0.2	32.9	3.7	7.9	7.99	0.2	18.9	0.4	11.9
C_2	--	--	--	1.14	--	--	1.77	--	1.06
N_2	6.9	28.8	8.6	14.4	14.56	6.9	25.6	4.9	14.6
Residual R_1	0.231		--		--	0.205		--	
Volumes R_2	--		0.603		0.608	--		--	
R_3	0.239		0.593		0.591	0.269		0.336	
R_7	0.221		0.605		0.642	0.222		0.364	
N from R_1	2.22		--		--	2.08		--	
" " R_2	--		2.145		1.914	--		--	
" " R_3	2.27		2.115		1.854	2.47		1.79	
N for R_7	2.15		2.150		2.150	2.35		2.150	
Cal. from R_1 d_1	2.01		--		--	3.15		--	
" " R_1 d_2	2.02		--		--	3.15		--	
Cal. from R_2 d_1	--		7.39		6.77	--		--	
" " R_2 d_2	--		7.36		6.77	--		--	
" " R_2 d_3	--		-0.02		-0.595	--		--	
Cal. from R_3 d_1	2.27		7.30		6.63	3.07		-0.32	
" " R_3 d_2	2.26		7.30		6.63	3.07		-0.32	
" " R_3 d_3	+0.45		-0.087		-0.782	-1.04		-1.16	
Cal. from R_7 d_1	1.70		7.38		7.20	1.65		0.85	
" " R_7 d_2	1.70		7.38		7.20	1.65		0.85	

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

Table 13 (Continued)

Examples of Calculations of Syntheses Runs

Yield						
Cal. with	A_7					
	R_1	143.5	—	—	146.5	—
" "	R_2	—	95.2	96.0	—	—
" "	R_3	141.4	96.2	98.9	130.3	120.6
" "	R_7	145.9	94.8	86.4	142.3	113.0
Conversion U						
Cal. with	R_1	92.90	—	—	94.7	—
" "	R_2	—	55.6	55.1	—	—
" "	R_3	92.70	56.0	56.0	93.1	86.90
" "	R_7	93.20	55.5	52.3	94.3	85.95
Methane for-						
mation, Mv						
Cal. with R_1		13.68	—	—	14.84	—
" " R_2		—	4.85	5.31	—	—
" " R_3		14.25	4.48	4.49	20.30	18.33
" " R_7		12.99	4.94	8.05	16.30	20.50

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

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

Check on the Formation of Carbon Dioxide

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

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

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

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

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

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

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

Example 2, table 13, offers almost perfect experimental data and consequently d'' is very small (~0.02). The third column of this example shows that changes occur when the carbon dioxide content of the outlet gas is reduced by 1%, for example, 12.2% to 11.22%, and the analysis recalculated on the basis of 100%. If we assume that this decrease in the carbon dioxide content occurs when the gas sample is taken, the measured residual volume R_2 remains unchanged whereas the residual volume R_3 determined from the nitrogen content decreases. In both cases, n decreases considerably and d'' becomes negative. At the same time, the value $d'' = 0.782$ for R_3, is of the same order of magnitude as the decrease of carbon dioxide in the gas analysis (~1.0%).

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

The method used in checking the formation of carbon dioxide could also be applied to the three other intermediate variables a, b, and c. However, there are certain distinctions. New fundamental relations cannot be established since only the equation already used for d_2 is available as a term of comparison. Moreover, for carbon monoxide, hydrogen, and methane the formation or breaking of chemical bonds cannot be assumed as readily as for carbon dioxide.

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

Compensation of Errors

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

Knowing d'', the correct composition of the outlet gas, may be determined and values of the characteristic variables calculated in the usual manner. If, however, only the yield is desired, it may be calculated directly from the inaccurate analytical values for the outlet gas, by substituting $(d - d'')$ in the yield formulas in place d_1 and letting $n = 2.15$.

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

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

Location of Errors in the Calculations

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

Moreover, the value for n in

$$n = 2\frac{(b + 2d) - (a + 2c)}{a - (c + d)} \qquad (26)$$

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

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

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

Use of Work Sheets

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

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

Calculations for the Prediction of the Course of a Synthesis

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

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

Uniform Use of Symbols

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

(1) Choice and accurate definition of symbols.

(2) Specification of abbreviations used.

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

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

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

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

Ruhrchemie Aktiengesellschaft
Oberhausen-Holten
July, 1944

Table 11

Sample Worksheet

Date			Time				E
					CO_2		
Amount Sy.-Gas m^3			Amount outlet gas m^3		Unsaturates		
	R	n	a.		O_2		
					CO		
1			b.		H_2		
2			a + b.		J		
3			c.		CH_4		
4			d_1"		Z		
6			d_2"		N_2		
7			d_{11}"		N_2-F		

$$\beta =$$
$$p =$$
$$p' =$$

Tot. Prod. C-Z Fract.	Amount in G. .g	Olefins Percent	Amount in G.	Amount in G. g-[Olef. +CH+W"]	Paraffins n_p	n_p-Par.	OH-Z	Alcohols W_a'' g-OH-Z 3.217·10^{-4}	$K_a \cdot 10^3$
1					4.000				0.250
2					3.000				0.500
3					2.667				0.751
4					2.500				1.001
5					2.400				1.251
6					2.333				1.627
7					2.286				2.127
8					2.250				2.628
9					2.222				3.003
10					2.200				3.379
11/12					2.174				4.255
13/14					2.148				6.257
15/16					2.129				0.500
17/18					2.114				
19/27					2.087				
>27					2.057				
Σ...	Σ(Olef)				$\Sigma(n_p \cdot Par)$		$\Sigma(W_a'')$		$\Sigma(OH)_a$

	A(')				

Characteristic Variables   Yields per m³

$U = \quad \%$ A_1

$M_v = \quad \%$ $A_{11} \dfrac{G}{E}$

$X =$ $A_{11} A_2 + Y$

$2(\text{Olef.}) = \ldots\ldots\ldots\ g \quad \xi(O$

$\xi\lceil n_p\cdot\text{Par} = \ldots\ldots\ldots\ g \quad \xi(P$

$2\lceil\xi(CH_a) = \ldots\ldots\ldots\ g \quad \xi(CH$

$\xi\lceil n_e(CH)_e = \ldots\ldots\ g \quad \xi(CH$

$\xi\lceil n_1(CH)_4 = \ldots\ldots\ g \quad \xi(CH$

$\xi\lceil n_e(CH)_{ald} = \ldots\ldots\ g \quad \xi(CH$

numerator $\ldots\ldots\ g \quad$ denominator

$\beta\text{-}CH_4' =$

$\dfrac{q}{\xi'} =$

$(CH)_a$		W_e'' in G_o	Esters				
$g\text{-}OH\text{-}Z\text{-}K_a$	$E\text{-}Z$	$g\text{-}E\text{-}Z$ $6.434\text{-}10^{-4}$	$K_e\cdot 10^3$	$(CH)_e$ $g\text{-}EZ\text{-}K_e$	N_e	$N_e(CH)$	
			0.679		0.667		
			0.929		1.000		
			1.179		1.200		
			1.430		1.333		
			1.680		1.429		
			1.930		1.500		
			2.431		1.600		
			2.931		1.667		
			3.432		1.714		
			3.682		1.733		
			4.683		1.790		
			7.437		1.867		
			0.000		0.000		
		$\xi(W_e'')$		$\xi(CH)_e$	$\xi(n_c\cdot(CH) =$		

Characteristic Variables	Yields per m^3	Without Met
		Actual Conversion
		Syn. Gas CO + H$_2$

$U = \quad \%$

$M_v = \quad \%$

$X =$

A_z

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

$A_{11} = A_z + Y$

$2 \ (\text{Olef.}) = \ldots\ldots\ldots \ g$	$(\text{Olef.}) = \ldots\ldots\ldots \ g$
$n_p \cdot \text{Par} = \ldots\ldots\ldots \ g$	$(\text{Par.}) = \ldots\ldots \ g$
$2 \ (\text{CH})_a = \ldots\ldots\ldots \ g$	$(\text{CH})_a \ldots\ldots\ldots \ g$
$n_e \cdot (\text{CH})_e = \ldots\ldots\ldots \ g$	$(\text{CH})_e \ldots\ldots\ldots \ g$
$n_1 \cdot (\text{CH})_4 = \ldots\ldots\ldots \ g$	$(\text{CH})_4 \ldots\ldots\ldots \ g$
$n_{ald.} (\text{CH})_{ald.} = \ldots\ldots \ g$	$(\text{CH})_{ald.} \ldots\ldots \ g$
numerator $\ldots\ldots\ldots \ g$	denominator $\ldots\ldots \ g$

ESTERS

E-Z	W_e in G. g x E-Z 6.434×10^{-4}	$K_e \times 10^3$	(CH)$_e$ g x EZ x Ke	N_e	$N_e \times$ (CH)$_e$	N-Z	W''_a in G. g x NZ 6.434×10^{-4}	A $K_a \times 10^{-}$
		0.679		0.667				—
		0.929		1.000				—
		1.179		1.200				
		1.430		1.333				0.179
		1.680		1.429				0.429
		1.930		1.500				0.679
		2.431		1.600				1.305
		2.931		1.667				1.681
		3.432		1.714				2.181
		3.682		1.733				2.681
		4.683		1.790				3.193
		7.437		1.867				4.685
		0.000		0.000				7.687
								0.000
$\sum (W''_e)$		$\sum (\text{CH})_e$		$\sum (n_e(\text{CH})_e]$		$\sum (n''_s)$		$\sum (\text{CH})_s$

67

ane | | | With Methane | | | | |

| % Conversion | | | Actual Conversion | | | % Conversion | |
| Syn. Gas | CO + H₂ | | Syn. Gas | CO + H₂ | | Syn. Gas. | CO + H₂ |

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

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

$W_a'' = \ldots\ldots\ldots$ g

$W_e'' = \ldots\ldots\ldots$ g

$W_s'' = \ldots\ldots\ldots$ g

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

$W'' = \ldots\ldots\ldots$ g

$Y = \dfrac{W''}{E} \ldots\ldots\ldots$ g/m³

CIDS | | | | | ALDEHYDES AND KETONES | | | |

| | $(CH)_s$ | | | | W_{ald}'' in G. | | $(CH)_{ald}$ | |
g NZ K_a	N_s	$N_s \times (CH)_s$	CO-Z	g CO-Z 6.434-10	$K_{ald}10^3$	g CO-Z K_{ald}	n_{ald}	$n_{ald}(CH)_{ald}$
	–					1.179		1.200
	–					1.931		1.500
	-2.000					2.431		1.600
	0.000					2.931		1.667
	0.667					3.432		1.714
	1.111					3.932		1.750
	1.333					4.689		1.790
	1.500					5.936		1.833
	1.600					6.936		1.857
	1.687					7.936		1.875
	1.778					11.439		1.913
	1.867					17.950		1.944
	0.000					0.000		0.000
			$\Sigma(W_{ald}'')$		$\Sigma(CH)_{ald}=$			$n_{ald}:$ $\Sigma[CH]_{ald}$

Table 15

List of Formulas for the Evaluation of Gas Analysis Data from

the Hydrogenation of Carbon Monoxide

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

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

$p = CO_2 + CO + CH_4$

$p' = CO_2' + CO' + CH_4'.B$

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

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

R_6, $R_7 = \dfrac{R.n + q}{p'.n + q'}$ $n = \dfrac{q'.R - q}{p - p'.R}$

$a = CO - R.CO'$ $c = R.CH_4'.B - CH_4$

$b = H_2 - R.H_2'$ $c_1 = R.CO_2' - CO_2$

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

R	B
1.0 – 1.05	1.0
1.05 – 1.15	0.9
Über 1.15	0.85

$U = \dfrac{a + c}{3}.5 \cdot 10^4$ $z = \dfrac{b}{a}$

$W = \dfrac{4c}{a + b}.10^3$

$A_7 = 0.693\left[3a + c - 4(2c_1 + d)\right]$

$n = 2.\dfrac{(b + 2d) - (c_1 + 2c)}{a - (c_1 + c)}$