

Part IV

Application 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. n 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 any greater assurance or dependability. The same applies according to our experience also to the precision determination of nitrogen. One may therefore occasionally eliminate the determination of R_1 , R_2 (by measurements), or R_3 and R_4 (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 N_2 . Finding of n from the products will be more complicated, but will have to be carried out for the greatest accuracy of calculation of factors of new syntheses from an unfamiliar course of operations.

After R has been calculated, the calculation of the intermediate values a, b, c and d , and then the factors U, Mv, X and A will offer no difficulties. Mutually corresponding values of n and R will have to be used for the calculation of yields A_1 to A_6 .

2. Testing the Results.

a). Testing the basis.

A judgement of dependability of the basic assumption becomes relatively easy by an application of the newly developed relationships. To do 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 (Schwarzheide 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.

We should what follows proceed on this score. It is possible to calculate the yield using R_1 to R_3 on one side, A_7 on the other, without at all using the value a 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.

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

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

Calculating the n and R values which belong together from the $n - R$ formula always gives 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 values (R_1 to R_3), 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 hydrocarbon of the composition $(H_{2.15})$. The difference calculated in this way shall be designated with d'' .

$d'' = d_1 - d_2$ (calculated with the experimental R_1 to R_3 and $n = 2.15 \pm 0.15$), is equal to (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_2 , calculated from the so called nitrogen content, becomes smaller. R_2 becomes in both cases considerably smaller, and as a result d'' will be negative. With $R_2 = 0.782$ 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 93.2 - 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 92.8 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.

a). 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^i , CO^i , H_2^i , and CH_4^i .

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 β , 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.

R_1, R_2 from measurements: $R_0, R_2 = \frac{N_2}{N_2^0}$ Z β

$R_2 = \frac{200 + 300\beta - (H_2 + CH_4)}{200 + 300\beta - (H_2 + CH_4 \cdot \beta)}$	1.0 - 1.05	1.0
	1.05 - 1.15	0.9
	Over 1.15	0.85

$g = CO_2 + CO + CH_4$

$g^0 = CO_2^0 + CO^0 + CH_4^0 \cdot \beta$ $U = \frac{a+b}{j} \cdot 10^2$ $x = \frac{b}{a}$

$g = 2 / (200 + CO) - (H_2 + 2CH_4) /$

$g^0 = 2 / (CO_2^0 + CO^0) - (H_2^0 + 2CH_4^0 \cdot \beta) /$ $M = \frac{4c}{a+b} \cdot 10^2$

$\frac{R_0}{R_2} = \frac{p \cdot n + a}{p^0 \cdot n + q^0}$ $n = \frac{q^0 R - a}{p - p^0 R}$

$a = CO - R \cdot CO^0$ $c = R \cdot CH_4^0 \cdot \beta - CH_4$ $A_{\beta} = 0.893 / (5a + b - 4(2c + d))$

$b = H_2 - R \cdot H_2^0$ $d_1 = R \cdot CO_2^0 - CO_2$

$d_2 = \frac{1(a-b) + 2(a-b) + 4c}{n+4}$

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

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: ROW									
R ₂	0.670	0.699	0.663	0.661	0.386	0.666	0.707	0.720	
R ₃	=	0.637	0.637	0.517	0.565	0.627	0.675	-	
R ₆	0.697	0.708	0.697	0.672	0.707	0.682	0.723	0.748	
n _m from Brabag	2.37	2.33	2.375	2.375	2.375	2.37	2.365	2.365	
n _m from R ₂	2.17	2.20	2.22	2.26	2.24	2.25	2.14	2.01	
Works: Lurgi									
R ₂	0.609	0.628	0.594	0.605	0.605	0.591	0.609		
R ₃	0.537	0.568	0.587	0.550	0.515	0.490	0.614		
R ₆	0.620	0.635	0.605	0.620	0.625	0.615	0.627		
n _m from Brabag	2.14	2.08	2.08	2.08	2.22	2.36	2.36		
n _m from R ₂	2.23	2.08	2.06	2.08	2.13	2.23	2.27		
Works: Rhpr.									
R ₂	0.603	0.588	0.593	0.603	0.611	0.622	0.623	0.634	0.640
R ₃	0.563	0.558	0.523	0.598	0.530	0.566	0.488	0.695	0.583
R ₆	0.623	0.598	0.615	0.625	0.630	0.640	0.638	0.653	0.655
n _m from Brabag	2.41	2.36	2.38	2.40	2.42	2.43	2.45	2.45	2.47
n _m from R ₂	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 ₂	0.626	0.656	0.619	0.622	0.328		0.640		
R ₃	=	0.708	0.549	0.662	0.595		0.610		
R ₆	0.647	0.662	0.513	0.638	0.642		0.660		
n _m from Brabag	2.19	2.16	2.16	2.19	2.23		2.20		
n _m from R ₂	2.13	2.15	2.77	2.12	2.05		2.15		
Works: KWI.									
R ₂	0.575	0.580	0.570	0.567	0.570	0.570	0.602	0.700	
R ₃	-	-	0.662	0.550	0.538	0.623	0.540	0.630	
R ₆	0.539	0.597	0.590	0.583	0.591	0.538	0.632	0.730	
n _m from Brabag	2.41	2.38	2.38	2.38	2.41	2.43	2.46	2.46	
n _m from R ₂	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 $Q = 208(100 - M_V) \cdot 10^{-6}$

