

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_3 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 CH_2O ,

CH_2O , 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_1 to A_7 . 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:	$(CH)_e = C_n H_{2n} + 2O - H_2O = C_n H_{2n}$
For esters:	$(CH)_e = C_n H_{2n} O_2 - 2H_2O = C_n H_{2n} - 4$
For acids:	$(CH)_e = C_n H_{2n} O_2 - 2H_2O = C_n H_{2n} - 4$
For aldehydes and ketones:	$(CH)_{ald} = C_n H_{2n} O - H_2O = C_n H_{2n} - 2$
For olefines:	(Olef) = $C_n H_{2n}$
For paraffins:	(Par) = $C_n H_{2n} + 2$

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}
alcohols by	$\frac{2n}{n}$	= 2

The formula for the determination of n is therefore:

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

The calculation of the chemically bound water (= Wⁿ) 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 EZ. This fraction contains therefore,

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

One mol ester produces two moles water (= 36.032 g). The water content of these $\frac{g \cdot \text{EZ} \cdot M_e}{56,000}$ g of ester is therefore $W_e'' = \frac{36.032}{M_e} \cdot \frac{g \cdot \text{EZ} \cdot M_e}{56,000} = g \cdot \text{EZ} \cdot 0.6434 \cdot 10^{-3} \text{ g.}$

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

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

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 compound). The formula for the (CH) portion of the ester becomes then $(\text{CH})_e = g \cdot \text{EZ} \cdot k_e$.

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)

$$\text{Therefore, } Y = \frac{\sum (W'')}{M^3}.$$