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CALCULATIONS OF YIELDS IN THE MODERN STATE  
OF THE SYNTHESIS OF HIGHER HYDROCARBONS

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A. Introduction and Explanation of Symbols.

A new method of computation for expressing yields of higher hydrocarbons during the synthesis has been developed in Schwarzheide during the state laboratory (Reichsamt tests). Explanations have been given of this method of computation, but no description in which the method of computation is so completely explained that any

person could apply it, without any additional oral explanations. Experience has shown that the understanding in this field offers certain difficulties, and we will therefore first describe the State Laboratory method of computation (Reichsamts-rechenweise, RARW) before a comparison of this method with the new formulas developed in the meantime.

We have converted the State Laboratory notations into our abbreviated method of expression introduced by us with this new method of computations, so as to permit comparison of these different methods of computation. The abbreviations used have been explained in the article (Bureau of Mines translation T - 420). In addition to the symbols there, used new symbols have been added.

1. For amounts: volume of oxygen formed which is chemically combined in the oxygen-containing products, ( $1/2 O_2$ ).
2. As a superscript: a symbol designating values valid for the deduction of oxygen:  $n^\circ$  - average value for the H : C ratio in the CH part of the products formed, omitting methane, by deducting oxygen from the oxygen-containing compounds.

$n_m^\circ$ : same as before, but including methane.

$Aco^\circ$ : yield from the basic molar computations, briefly called "CO yield".

$Ai^\circ$ : yield calculated from the limiting yield computation for the ideal gas, briefly called "ideal gas yield".

B. The CO Yield:

1.  $100 - \text{contraction} = \text{residual volume } R$ .
2. The amounts of carbon monoxide and carbon dioxide  $R \bullet \text{CO}^g$ ,  $R \bullet \text{CO}_2^g$  are calculated as products from residual volume and from the percentage in the end gas.
3. The amounts formed or consumed are found by subtracting those products from the amounts entering:

$$a = \text{CO} - R \bullet \text{CO}^g \qquad d = R \bullet \text{CO}_2^g - \text{CO}_2$$

4. Subtracting the value of the carbon dioxide formed from the carbon monoxide used up, gives us the volume of the hydrocarbons formed  $\text{CH}_{nm}$  (including methane):

$$o_m = a - d$$

5. The parts by volume of CH must be multiplied by the molecular weight, i.e. 22.4 to convert them into grams. The molecular weight of  $\text{CH}_{nm}$  is called the basic molar constant.

$$A^{\circ}\text{CO} = \frac{\text{basic molar constant}}{22.4} \bullet (a - d) = \frac{12 + nm^{\circ}}{22.4} (a - d)$$

C. The Ideal Gas Yield:

1. As described under B - 1 to B - 3, the consumption of carbon monoxide and hydrogen are found from

$$a = \text{CO} - R \bullet \text{CO}^g \qquad b = \text{H}_2 - R \bullet \text{H}_2^g$$

2. The consumption ratio is found by division:  $X = \frac{b}{a}$
3. Computations are made of how much of the  $(\text{CO} + \text{H}_2)$  in the entering gas can be consumed with a given consumption ratio and with perfect conversion (ideal gas).

$$J_X = \text{CO} (1 + X) \text{ with an excess of hydrogen over } \text{H}_2 \text{ in } J_X.$$

4. With a complete conversion of 1 normal obm of ideal gas, the limiting yield would be reached with a complete conversion. It is calculated from the analyses of the liquid and gaseous products, with each individual class of substances participating in the sum in proportion found by fractionation.
5. The conversion of CO<sub>2</sub> is calculated by dividing the consumed carbon monoxide by that introduced:  $U_{CO} = \frac{a}{CO}$
6. The hydrocarbon yield CH<sub>nm</sub> amounts therefore to:  $A^{\circ}i = \text{limiting yield} \cdot \text{amount of ideal gas} \cdot \text{CO conversion} = \text{limiting yield} \cdot CO \left(\frac{1+b}{a}\right) \cdot \frac{a}{CO} = \text{limiting yield} \cdot (a+b)$

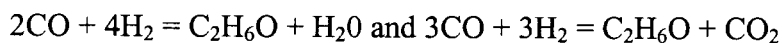
#### D. Limiting Yield and Basic Mol Constant:

The following considerations explain the concept "limiting yield". The formula for yield containing the limiting yield is  $A^{\circ}i = \text{limiting yield} \cdot (a+b)$ . This yield must be equal to the yield obtained from the third basic stoichiometric equation (see appendix)

$$\text{therefore limiting yield} = \frac{a+b+c}{a+b} \cdot h_1 \cdot 100$$

$c = 0$  when only pure hydrocarbons are formed. The limiting yield in that case is equal to  $h_1$ .

Model calculations give the same results. Ethanol, e.g., can be obtained according to the equations:



The limiting yield from one nobm ( $\text{CO} + \text{H}_2$ ) requires therefore:

for the formation of ethanol and for the removal of oxygen 223 g  $\text{C}_2\text{H}_6$

for the formation of ethane 192 g  $\text{C}_2\text{H}_6$

The H : C ratio in ethanol with the elimination of oxygen  $n^\circ = 3.0$ . We get therefore for  $h_1$ :

$$h_1 = \frac{20(12 + n^\circ)}{22.4(4 + n^\circ)} = 1.92$$

The limiting yield for pure hydrocarbon formation has therefore the same numerical value as  $h_1$ . With oxygenated compounds the limiting value is the greater, the less ( $\text{CO} + \text{H}_2$ ) have been used up.

$$\text{Limiting value} = \frac{(\text{CO} + \text{H}_2) - \text{Consumption for CH as hydrocarbons}}{(\text{CO} + \text{H}_2) - \text{Consumption for CH in oxygenated compounds}} \cdot h_1$$

$$\text{For ethanol: the limiting value} = \frac{7}{6} h_1 = \frac{7}{6} \cdot 192 = 223\text{g}$$

The basic molar constant for ethanol is equal to  $12 + n^\circ_m$ , or  $12 + 3.0 = 15.0$

### E. The Basic Stoichiometric Relationships:

According to RARW, the total yield is composed of the part of CH calculated as  $\text{Aco}^\circ$  or  $\text{Ai}^\circ$  and of the oxygen contained in the products. Accordingly oxygen must be represented in the basic stoichiometric relationships if R is to represent accurately the whole of the processes. When computations are made with a withdrawal of oxygen, the second basic stoichiometric equation must be extended by the term  $\text{oO}$ . This will give us the following equation which might be designated as the third basic stoichiometric equation.



This equation is used as a basis by RARW. Its algebraic evaluation can be found in the appendix.

It will be found that the calculation for the CO yield or the ideal gas yield have been made by the RARW using the same formulas as can be derived from the above basic stoichiometric equations for  $A_2^o$  or  $A_1^o$ . There exists as purely formal difference in that the introduction of the limiting value eliminates the oxygen term from the expression in paranthesis and reappears in the limiting yield.

RARW

$$A_{CO}^o = \frac{12 + n_m^o}{22.4} \cdot (a - d)$$

$$A_i^o = \text{limiting yield} \cdot (a + b)$$

$$= \frac{a + b + c}{a + b} \cdot h_1(a + b)$$

III basic stoichiometric equation

$$A_2^o = \frac{12 + n_m^o}{22.4} \cdot (a - d) = h_2(a - d)$$

$$A_i^o = h_1(a + b + c)$$

#### F. The Analytical Contraction:

The yields calculated by the RARW as  $A_{CO}^o$  and  $A_i^o$  were not usually in agreement. An agreement of the two yields has been found to be obtained by introducing one other contraction into the computations, and then such an agreement would exist only for one certain definite contraction. This is called the “analytical contraction” and must be found by testing. To do this the inlet and outlet amounts of gas originally found by measurement are changed in such a direction that subsequent computations would give

the same numerical values to the two yields. This is then considered correct.

This empirical method of computations is based on the n - R equation, as can be seen from the derivation of our new formulas. The two formulas for yields used by RARW,

$$A_{CO}^{\circ} = \frac{\text{basic molar constant}}{22.4} \bullet (a - d) \quad A_i^{\circ} = \text{limiting yield} \bullet (a + b)$$

also contained the values n, or  $n^{\circ}_m$ , and also naturally the corresponding R. The two yields differ from each other the more, the further R is removed from the value belonging to the  $n^{\circ}_m$  of the corresponding n - R equation. If n and R for the corresponding pair of gas analyses fulfill the requirements of the n - R equation, the two yields will be in agreement.

These relationships are valid not only for the two methods of computation of yields used by the RARW, but also for three other formulas of yield of different kinds ( $A_3$ ,  $A_a$ ,  $A_7$ ). Two of these, ( $A_a$  and  $A_3$ ) give appreciably greater deviations from each other than the two yields formerly obtained by the RARW. It would therefore be better to use these two new formulas in the combination with the testing. This however was not done.

The n - R equation permits the calculation from the residual volumes ( $R_6$ ,  $R_7$ ) and the corresponding n the analytical contraction for every pair of gas analyses. We have

therefore:

$$\text{analytical contraction} = 100 - R_6 \text{ (or } R_7\text{)}$$

G. Breaking Down the Oxygenated Compounds into the CH Part and Water or Oxygen

The RARW have come to the decision to break down the oxygenated compounds for calculation, treating the oxygen separately and not the water. Dr. Pichler has given as reason for it that in this way only CH yield term will contain hydrogen, which is not the case when water is separated. However, aside from this purely formal advantage, the other method of calculation with the separation of water is more convenient.

When oxygen is deducted, the yield may be calculated as  $O_{co}^{\circ}$  and also as  $A_i^{\circ}$  using the limiting yields, without directly using any term for oxygen. This, as so far known, exhausts the possibilities. All other expressions derived from the third basic stoichiometric equation contain the term of  $oO$ , and it can be used in computations if analysis fails to give the oxygen content of the products formed.

Against this we are also in a condition to eliminate the term for water when water is deducted, and then the formulas contain only the intermediate values  $a, b, c$  and  $d$ , obtained by gas analysis, in addition to  $R$  and  $n$ . In this way numerous formulas for yield, carbon dioxide formation,  $H : C$  ratio, the  $n - R$  relationship can be derived permitting the use of other data from gas analyses in addition to  $n$ . In this way the



formulas become generally applicable and correct even when oxygenated compounds are formed by not tested for, and can therefore not be included into the computations.

It is therefore to be recommended that in the future not oxygen but water be deducted from the oxygenated compounds in the evaluation of results.

For an easier understanding we will show the most important results obtained by the two methods of computation. The numerical examples apply to the formation of ethanol.

	CH part of the oxygenated products obtained by deducting of:	
	Water	Oxygen
Yields CH part Oxygen part Total yield	A = ... g C <sub>2</sub> H <sub>6</sub> Y = ... g of water A <sub>11</sub> = (A + Y) g C <sub>2</sub> H <sub>6</sub> O	A° = ... g C <sub>2</sub> H <sub>6</sub> ... g of oxygen ... C <sub>2</sub> H <sub>6</sub> O
H : C ratio Cal. for hydrocarbons formed  without methane including “	n = 2.0 n <sub>m</sub> -	° = 3.0 n <sub>m</sub> <sup>°</sup> -
Basic mol constant	12 + n = 14	12 + n° = 15
Limiting yield	$h_1 = \frac{2(12 + n)}{22.4(n + 4)}$ = 203.3 g C <sub>2</sub> H <sub>4</sub>	$\frac{a + b + c}{a + b} \cdot h_1$ = $\frac{a + b + c}{a + b} \cdot \frac{2(12 + n^\circ)}{22.4 \cdot (n^\circ + 4)}$ = $\frac{7}{6} \cdot 192 = 223 \text{ g C}_2\text{H}_6$

#### H. Use of Abbreviations in Formulas:

The advantages of deducting water instead of oxygen from oxygenated compounds can only be gained when using mathematically convenient abbreviations for the mathematical treatment. This therefore is to be recommended in the evaluation of subsequent experiments. A number of advantages of methodics will thereby be gained.

It becomes no longer necessary to obtain two constants for the calculation of the higher hydrocarbon yield, namely the basic mol constant and the limiting yield, but only the H : C ratio  $n$ . Yield will no longer have to be calculated twice (CO yield, ideal gas yield) and the use of a single formula becomes sufficient. The computations themselves become simplified.

Nor does it become any longer necessary to find the analytical contraction by probing, and calculations of  $R_6$  and  $R_7$  can be made from the  $n - R$  equation. The errors of calculations can be found in a simpler way over  $d_2$ ,  $n$ , or over  $A_1$ ,  $A_2$ ,  $A_3$ , and  $A_4$ . A deciding advantage is furthermore to be found in permitting to tell the true or approximately true value by testing for the accuracy of the basic data by way of comparison of the  $n$  values (from analysis of products or from experience), while by the RARW method of juxtaposition of the different contractions only relatively differences are obtained without indicating the correct value.

Finally the whole method of computation becomes clearer and easier to examine,

which permits the avoidance of errors of deduction. One can see how readily such errors of deduction are formed e.g. from the fact that up to March of this year the yield was calculated by the RARW with an erroneous term for the formation of methane: yield without methane = limiting yield  $(a + b) \cdot \left(1 - \frac{c}{a - d}\right)$  instead of the correct expression:

yield without methane = limiting yield  $(a + b - 4c)$ .

A method of computation from set formulas offers the additional advantage of permitting even technically untrained personnel to be instructed with no oral advice.

/S/ Roelin.

Oberhausen-Holteln

August 1944

CALCULATION OF YIELDS BY USING THE CHEMICALLY COMBINED OXYGEN AS SUCH.

1. The third basic stoichiometric equation



2. Equations for the sum of the three elements

$$\text{For carbon} \quad a = c^+ + c + d$$

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

$$\text{For hydrogen} \quad 2b = n^\circ \cdot c^+ + 4c + 2e$$

3. Solutions:

$$c_2^+ = \frac{2}{n^\circ + 4} (a + b - 4c + c)$$

$$c_2^+ = \frac{2}{4 - n^\circ} (3a - b - 4d - o)$$

$$c_2^+ = a - c - d$$

$$c_4^+ = \frac{2}{n^\circ + 2} (b - 3c + d + o)$$

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

4. Formulas for yields:

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

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

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

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

5. For the computations of yields, including methane:

$$n^\circ = n_m^\circ, \quad c = \text{zero.}$$