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CALCULATION OF YIELD FOR HIGHER HYDROCARBONS

BASED ON RECENT METHODS

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SUMMARY

The methods for the calculation of the yield and related properties, discussed in the preceding paper (Ib-3), are developed further and compared by RARW (Reichsamtversuchen Angewandte Rechenweise. Trans., Methods of calculation employed in experimental work carried out under the direction of the Reich).

INTRODUCTION AND EXPLANATION OF SYMBOLS

Experiments undertaken under the auspices of the Reich at Schwarzheide have led to a new method for calculating the yield obtained in the synthesis of higher hydrocarbons. Examples of this procedure have already been given (see preceding paper, Ib-3), but to date there has been no description of the method detailed enough to enable an outsider to use it without additional instructions. Experience has shown that an agreement on this subject presents certain difficulties. In order to compare the method used in government research (RARW = Reichsamtversuchen angewante Rechenweise) with the formulas that have been derived more recently. A description of RARW is given below.

To facilitate comparison between the two methods, RARW has expressed the abbreviated terms which were introduced in our own procedure. An explanation of the abbreviations used is given in the preceding paper (Ib-3). In addition, the following new symbols have been included:

o (1) as a coefficient: volumes of oxygen formed ($\frac{1}{2}$ O_2) present in chemical combination in the oxygenated products.

(2) as a superscript: indicates the value after deduction of oxygen.

n^o Average value for H:C ratio in the CH-portion of the products (not including methane) after deduction of oxygen from the oxygenated compounds.

n^o_m As above, but with methane included in the products.

A^{o}_{co} Yield according to the fundamental molar calculation designated as "CO yield".

A^{o}_{i} Yield according to the calculation of the limiting yield for an ideal gas, designated as "ideal gas yield".

THE CO YIELD

1. 100 – contraction = residual volume, R.

2. The final amounts of carbon monoxide and dioxide are given as the product of the residual volume times the content (percent) in the exit gas:

$$R(CO'),\ R(CO_2')$$

3. The amounts formed or reacted are given as the difference between the amounts in the product and the initial amounts:

$$a = CO - R(CO') \qquad d = R(CO_2') - CO_2$$

4. The volume of reacted carbon monoxide minus the volume of carbon dioxide formed gives the volume of hydrocarbons formed $CH^{o}_{n_m}$ (incl. methane):

$$c_m = a - d$$

5. Multiplication by the "molecular weight:22.4" gives the volumes of CH-products in grams. The molecular weight of $CH^{o}_{n_m}$ is known as the fundamental molar constant:

$$A^{o}_{co} = \frac{\text{fundamental molar constant}}{22.4}(a-d) = \frac{12 + n^{c}_{m}}{22.4}(a-d)$$

IDEAL GAS YIELD

1. Reacted carbon monoxide and hydrogen are determined as described in previous section, Nos. 1-3:

$$a = CO - R(CO') \qquad b = H_2 - RH'_2.$$

2. Dividing, we obtain the usage ratio:

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

3. For a given usage ratio the amount of $CO + H_2$ gas present in an ideal inlet gas that would undergo complete conversion is calculated, thus:

$$J_X = CO\ (1+x), \text{ for an excess of } H_2 \text{ over the H in } J_X.$$

4. The limiting yield is the possible yield, given complete conversion, for a m^3 of ideal gas measured under normal conditions. This yield is calculated from the analysis for fluid products (liquid and gas), each class of substance contributing to the total sum.

5. The CO conversion is obtained by dividing the reacted carbon monoxide by the carbon monoxide initially present:

$$U_{co} = \frac{a}{CO}$$

6. The yield in hydrocarbons CH_nO_m may then be written:

$$\overset{o}{Ai} = \text{limiting yield x amount of ideal gas x CO conversion}$$
$$= \text{limiting yield } \left[CO\left(1+\frac{b}{a}\right)\right]\frac{a}{CO}$$
$$= \text{limiting yield } (a+b)$$

LIMITING YIELD AND FUNDAMENTAL MOLAR CONSTANT

The following considerations may be useful in clarifying the concept of "limiting yield". The yield formula, which contains the limiting yield, reads as follows:

$$\overset{o}{Ai} = \text{limiting yield } (a+b)$$

This yield must be the same as the yield obtained from the third fundamental stoichiometric equation (see appendix).

Therefore:

$$\text{Limiting yield } (a+b) = h_1(a+b+c)$$

From which:

$$\text{Limiting yield} = \frac{a+b+c}{a+b}\ (h_1)(100).$$

When hydrocarbons above are formed, c equals zero and the limiting yield equals h_1.

Sample calculations lead to the same result. The formation of ethanol, for example, may be expressed in two ways:

$$2\ CO + 4\ H_2 = C_2H_6O + H_2O$$

or

$$3\ CO + 3\ H_2 = C_2H_6O + CO_2$$

In both cases 6 volumes $(CO + H_2)$ give one volume C_2H_6 as ethanol. When ethane forms, however, 1 volume C_2H_6 requires 7 volumes $(CO+H_2)$:

$$2\ CO + 5\ H_2 = C_2H_6 + 2\ H_2O$$

or

$$4\ CO + 3\ H_2 = C_2H_6 + 2\ CO_2$$

The limiting yield for 1 m^3 $CO + H_2$ under standard conditions is therefore:

Formation of ethanol and deduction of oxygen: 223 g C_2H_6
Formation of ethane: 192 g C_2H_6

For ethanol, after deduction of oxygen, the H:C ratio is given by $n^o = 3.0$. It follows that:

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

Thus, when hydrocarbons alone form, the limiting yield is equal to h_1. When oxygenated compounds form, the limiting yield is in inverse proportion to the amount of $CO + H_2$ that reacts.

$$\text{Limiting yield} = \frac{(CO + H_2) - \text{Amount reacting to give CH as hydrocarbons}}{(CO + H_2) - \text{Amount reacting to give oxygenated compounds}} \cdot h_1$$

For the example of ethanol:

$$\text{Limiting yield} = \frac{7}{6}\, h_1 = \frac{7}{6} \cdot 192 = 223\ g$$

The fundamental molar constant is given by $12 + n^o_H$ and for ethanol equals 12 + 3.0 or 15.0.

THE FUNDAMENTAL STOICHIOMETRIC RELATIONS

According to [illegible], the total yield is composed of $\mathring{A}_{co}$ or $\mathring{A}_{i}$ calculated for the CH-fraction and of the oxygen contained in the products.

Consequently, this oxygen must also appear in the fundamental stoichiometric relation, if this relation is to give a true picture of the total reaction. When oxygen is deducted, the second fundamental stoichiometric equation must, therefore, be extended to include the term oO. The following equation, known as the third stoichiometric equation, is then obtained:

$$a\,CO + b\,H_2 = c^+\,CH_nO + c\,CH_4 + d\,CO_2 + e\,H_2O + o\,O.$$

This equation is the basis for RARW. Its algebraic interpretation will be found in the appendix.

It can be shown that the RARW calculations for the CO and ideal gas yields call upon the same formulae as those derived from the above fundamental stoichiometric equation for $\overset{o}{A}_2$ or $\overset{o}{A}_1$. A purely formal difference is occasioned by the introduction of the limiting yield which takes the oxygen term out of the expression in parentheses and places it in the limiting yield:

RARW

$$\overset{o}{A}co = \frac{12 + \overset{o}{n}_m}{22.4}\,(a-d)$$

$$\overset{o}{A}i = \text{limiting yield } (a+b) = \frac{a+b+o}{a+b}\,h_1\,(a+b)$$

Third Fundamental Stoichiometric Equation

$$\overset{o}{A}_2 = \frac{12 + \overset{o}{n}_m}{22.4}\,(a-d) = h_2\,(a-d)$$

$$\overset{o}{A}i = h_1\,(a+b+o)$$

THE ANALYSIS CONTRACTION

The yields calculated by RARW for $\overset{o}{A}co$ and $\overset{o}{A}i$ do not in general agree. It was observed that the two yields are brought into agreement when another contraction is substituted in the calculation. Moreover, such an agreement exists for only one specific contraction. This contraction is known as the "analysis contraction" and must be determined empirically. For this purpose, the amounts of inlet and outlet gas obtained by measurement are altered in such a way that the ensuing calculation gives the same value for both yields. This value is then taken as the correct one.

As will be seen from the derivation of our new formulas, the n-R equation constitutes the basis for this empirical method of calculation. Both the yield formulas used by RARW:

$$\overset{o}{A}co = \frac{\text{fundamental molar constant}}{22.4}\,(a-d) \qquad \overset{o}{A}i = \text{limiting yield } (a+b)$$

implicitly contain the n or n_m^o value, and consequently the value for R. The difference between the two yields increases, as R differs from the value which, according to the n-R equation, corresponds to the given n_m^o. When n and R satisfy the n-R equation for a given set of gas analyses, the two yields coincide.

These relations hold not only for the two yield calculations already used by RARW, but also for three other different yield formulae (A_3, A_4, A_7). Two of these formulas (A_4 and A_7) show an even greater discrepancy than the yields already obtained by RARW. If the problem were still in the experimental stage it would, therefore, be advisable to consider these two new formulas. However, this is not the case.

Given n, the n-R equation offers a means of determining the appropriate residual volume (R_6, R_7) for every set of gas analyses and thus of calculating the analysis contraction. Therefore:

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

SEPARATION OF OXYGENATED COMPOUNDS INTO THE CH-RADICAL AND WATER OR OXYGEN

For the purpose of calculation, RARW has chosen to break down the oxygenated compounds by elimination of oxygen as such, rather than as water. The reason for this, as explained by Dr. Pichler, is that the CH yield then contains all the hydrogen, which is not the case when water is eliminated. Except for this rather theoretical advantage, the other method, which proceeds by eliminating water, is the more convenient.

When oxygen is eliminated, the yield is expressed as A_{co}^o, and, by means of the limiting yield, as Ai, without necessitating the introduction of an explicit term for oxygen. However, as far as we now know, the method offers no other advantages. All other expressions, derived from the third fundamental stoichiometric equation, contain the cO term. Hence, they cannot be used in making calculations, unless the oxygen content has been determined in the analysis of the products.

On the other hand, when water is eliminated, the corresponding term also disappears and the formula contains, besides R and n, only the intermediate variables, a, b, c, and d, obtained by gas analysis. In this way, numerous formulas for the yield, the formation of carbon dioxide, the H:C ratio, the n-R relation, etc., may be derived, using only n and the values obtained by gas analysis. Thus, these formulas are capable of general application and are valid even for cases where oxygenated compounds form, but are not analysed and consequently cannot be introduced into the calculations.

In evaluating further experimental data, it is therefore advisable to proceed by eliminating water from the oxygenated compounds, rather than oxygen alone as heretofore.

As an illustration, the most important values of the two methods are listed for comparison. The numerical examples are taken from the formation of ethanol.

	CH Fraction of the Oxygen Compound Obtained by Elimination of	
	Water	Oxygen
Yield:		
CH fraction	$A = \ldots$ g C_2H_4	$A^o = \ldots$ g C_2H_5
O fraction	$Y = \ldots$ g water	$\ldots$ g O
Total yield	$A_{11} = A + Y_g$ C_2H_6O	$\ldots$ g C_2H_6O
H:C ratio, calc. for the hydrocarbons formed:		
without methane	$n = 2.0$	$n^o = 3.0$
with methane	$n_m = -$	$n_m^o -$
Fundamental molar constant	$12+n = 14$	$12+n^o = 15$
Limiting yield	$h_1 = \frac{2(12+n)}{22.4\ (n+4)}$	$\frac{a+b+c}{a+b} h_1$
	$= 203.3$ g C_2H_4	$= \frac{a+b+c}{a+b} \frac{2(12+n^o)}{22.4\ (n^o+4)}$
		$= \frac{7}{6} \times 192 = 223$ g C_2H_5

USE OF ABBREVIATIONS IN FORMULAS

Elimination of water, rather than of oxygen, from oxygenated compounds, offers an advantage only when taken in conjunction with abbreviations used as a shortcut in mathematical operations. Therefore, this is also recommended in evaluating future experimental data. A number of advantages are then obtained.

In determing the hydrocarbon yield, a single constant, the H:C ratio n, now replaces two constants, the fundamental water constant and the limiting yield. The yield no longer need be calculated twice (CO yield, ideal gas); a single formula now suffices.

APPENDIX

<u>Calculation of the Yield with Introduction of Chemically Bound Oxygen as Such</u>

1. Third fundamental stoichiometric equation:

$$a\,CO + b\,H_2 = c^{+}\,CH_{n^o} + c\,CH_4 + d\,CO_2 + e\,H_2O + o\,O$$

2. Summation equations for the three elements:

for carbon: $a = c^{+} + c + d$

for oxygen: $a = 2d + e + o$

for hydrogen: $2b = n^o\,c^{+} + 4c + 2e$

3. Solution

$$c_1^{+} = \frac{2}{n^o+4}\,(a+b-4c+o) \qquad c_3^{+} = \frac{2}{4-n^o}\,(3a-b-4d-o)$$

$$c_2^{+} = (a-c-d) \qquad c_4^{+} = \frac{2}{n^o+2}\,(b-3c+d+o)$$

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

Yield formulas:

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

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

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

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

5. Inclusion of methane in the yield gives:

$$n^o = n_m^o \text{ and } c = o.$$

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