

THE RELATIONSHIP BETWEEN INDEX OF HYDROGEN DEFICIENCY AND MOLECULAR MASS FOR HYDROCARBONS. APPLICATION IN SOLVING OF SOME ORGANIC CHEMISTRY PROBLEMS

CHEREJI-MACH I.Z., MĂRGINEANU D., NAUMESCU A.

ABSTRACT. In this paper we examine the possibilities to determine with mathematical methods, implying the *limits* and the *Index of Hydrogen Deficiency (IHD)* [1], the molecular formulas for hydrocarbons, having minimum available primary data, that is the carbon percentage % C. In this way we establish the class of hydrocarbons including the studied substance.

The proposed method proves to be a rapid solution to solve this type of Organic Chemistry problems.

I: Preliminary Considerations; Calculation Methods

At present, a prominent tendency towards approaching chemistry from mathematical perspectives has become increasingly manifest. The present paper gives prominence to this spirit aiming at the transposition in mathematical language of some chemical notions, with reference to the composition and structure of the molecules of organic substances.

Examining the possibilities to determine *the molecular formulas for hydrocarbons, having the carbon percentage*, the paper aims at the systematization and delimitations of the values range within which the new calculation methods can be applied.

We start from the premise that minimum information is provided, namely, the carbon percentage (% C) of the hydrocarbon whose identity must be determined.

The following mathematical considerations are established, in order to appeal only to carbon percentage with no other auxiliary data in the process of solving the problems:

By using the *Index of Hydrogen Deficiency (IHD)* and the mathematical notion of *limit*, we tried to determine a variation law of the carbon percentage within the homologous series for different classes of hydrocarbons.

First of all, we will try to establish certain regularities in the variation of carbon percentage for different classes of hydrocarbons, calculating the following types of limits:

$$\lim_{n \rightarrow \infty} \frac{\% C}{100}$$

Taking into account that:

$$\% C = \frac{mC}{M} \cdot 100 = \frac{\% C}{100} = \frac{mC}{M}$$

where M = the molecular mass of the hydrocarbon,
 m_C = the carbon atoms mass.

The limit becomes:
$$\lim_{n \rightarrow \infty} \frac{\% C}{100} = \lim_{n \rightarrow \infty} \frac{mC}{M}$$

For $IHD = 0$, ALKANES (C_nH_{2n+2}), $n \in [1, \infty)$:

$$\frac{12n}{14n+2} \Big|_{n=1} = 0,75, \quad \lim_{n \rightarrow \infty} \frac{12n}{14n+2} = \frac{6}{7} \quad 0,857143.$$

For $IHD = 1$, ALKENES, CYCLOALKANES, (C_nH_{2n}), $n \in [2, \infty)$:

$$\frac{12n}{14n} \Big|_{n=2} = \frac{6}{7} \quad 0,857143, \quad \lim_{n \rightarrow \infty} \frac{12n}{14n} = \frac{6}{7} \quad 0,857143.$$

Constant sequence; the value does not depend on "n".

For $IHD = 2$, ALKYNES (C_nH_{2n-2}), $n \in [2, \infty)$:

$$\frac{12n}{14n-2} \Big|_{n=2} = \frac{12}{13} \quad 0,923, \quad \lim_{n \rightarrow \infty} \frac{12n}{14n-2} = \frac{6}{7} \quad 0,857143;$$

DIENES, CYCLOALKENES (C_nH_{2n-2}), $n \in [3, \infty)$:

$$\frac{12n}{14n-2} \Big|_{n=3} = 0,9, \quad \lim_{n \rightarrow \infty} \frac{12n}{14n-2} = \frac{6}{7}$$

For $IHD = 3$, compounds with formula C_nH_{2n-4} , $n \in [4, \infty)$:

$$\frac{12n}{14n-4} \Big|_{n=4} = \frac{12}{13} \quad 0,923, \quad \lim_{n \rightarrow \infty} \frac{12n}{14n-4} = \frac{6}{7} \quad 0,857143.$$

For $IHD = 4$, DIYNES (C_nH_{2n-6}), $n \in [4, \infty)$:

$$\frac{12n}{14n-6} \Big|_{n=4} = \frac{24}{25} = 0,96, \quad \lim_{n \rightarrow \infty} \frac{12n}{14n-6} = \frac{6}{7} \quad 0,857143;$$

MONONUCLEAR ARENES (C_nH_{2n-6}), $n \in [6, \infty)$:

$$\frac{12n}{14n-6} \Big|_{n=6} = \frac{12}{13} \quad 0,923, \quad \lim_{n \rightarrow \infty} \frac{12n}{14n-6} = \frac{6}{7} \quad 0,857143.$$

For $IHD = 5$, compounds with formula C_nH_{2n-8} , $n \in [6, \infty)$:

$$\frac{12n}{14n-8} \Big|_{n=6} = \frac{18}{19} \quad 0,9473, \quad \lim_{n \rightarrow \infty} \frac{12n}{14n-8} = \frac{6}{7} \quad 0,857143$$

and so on.

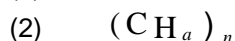
From the above data it results:

- In the case of alkanes, the carbon percentage ranges from 75% to $\approx 85,7143\%$; the carbon minimum percentage corresponds to methane and the carbon percentage tends towards the limit value of $85,7143\%$, asymptotically along with the increase of the carbon atoms number in the molecule.

- In the case of the other hydrocarbon classes with the Index of Hydrogen Deficiency of $IHD > 1$, the carbon percentage decreases simultaneously with the increase of the carbon atoms number in the molecule, manifesting an asymptotic tendency towards the limit value of $85,7143\%$.

In order to find a more accurate correlation among the number of carbon atoms, the Index of Hydrogen Deficiency and the carbon percentage, we will resort to the following argumentation:

Let us take a random hydrocarbon, whose molecular formula can be put down in two ways:



where n = the number of carbon atoms in the molecule;

IHD = the Index of Hydrogen Deficiency (sites of unsaturation);

a = the average number of hydrogen atoms belonging to a carbon atom of the substance under question.

The following mathematical restrictions are, obviously, required:

$$n \in \{ 1, 2, \dots, \infty \}; IHD \in \{ 0, 1, 2, \dots \}; a \in \{ 0, 1, 2, 3, 4 \}$$

Identifying the number of hydrogen atoms in formula (1) with the number of hydrogen atoms in formula (2), the following can be obtained:

$$2n + 2 - 2 \cdot IHD = a \cdot n$$

where IHD is expressed:

$$(3) \quad IHD = \frac{n \cdot (2 - a)}{2} + 1$$

On the other hand, taking into account the definition of a (= the average number of hydrogen atoms belonging to a carbon atom for the substance under question) and denoting by p the carbon percentage expressed as decimal fraction

0, the following relation can be written down:

$$(4) \quad a = \frac{12 \cdot (1 - p)}{p}$$

Replacing the relation (4) by (3) the following expression can be obtained at the end:

$$(5) \quad IHD = \frac{(7p - 6) \cdot n}{p} + 1$$

which can be simplified to:

$$(6) \quad IHD = A \cdot n + 1$$

$$\text{where } A = \frac{(7p - 6)}{p}$$

In order to check out and discuss the solutions of the expression (5), the following table has been drawn up, in which the second column represents the carbon percentage (p) calculated for hydrocarbons with known molecular formulas; further on, the results of the calculations with relation (6) noted in the last column, should be compared with the first column content (the molecular formulas of the hydrocarbons under question) to put into evidence the efficiency and possible limits of the calculation method proposed hereby.

The molecular formula of the hydrocarbon	p	A	Conclusions calculated n values IHD values
CH ₄	0,7500	- 1,00	only for $n = 1 \Rightarrow$ IHD = 0
C ₂ H ₆	0,8000	- 0,5000	only for $n = 2 \Rightarrow$ IHD = 0
C ₃ H ₈	0,8181	- 0,3340	only for $n = 3 \Rightarrow$ IHD = 0
C ₄ H ₁₀	0,8275	- 0,2507	only for $n = 4 \Rightarrow$ IHD = 0
C ₅ H ₁₂	0,8333	- 0,2002	only for $n = 5 \Rightarrow$ IHD = 0
C ₆ H ₁₄	0,8372	- 0,1667	only for $n = 6 \Rightarrow$ IHD = 0
C ₇ H ₁₆	0,8400	- 0,1428	only for $n = 7 \Rightarrow$ IHD = 0
C ₈ H ₁₈	0,8421	- 0,1250	only for $n = 8 \Rightarrow$ IHD = 0
C ₉ H ₂₀	0,8437	- 0,1115	only for $n = 9 \Rightarrow$ IHD = 0
C ₁₀ H ₂₂	0,8450	- 0,1006	only for $n = 10 \Rightarrow$ IHD = 0
C ₂₅ H ₅₂	0,8522	- 0,0406	only for $n = 25 \Rightarrow$ IHD = 0
C ₅₀ H ₁₀₂	0,8547	- 0,0200	only for $n = 50 \Rightarrow$ IHD = 0
C ₇₅ H ₁₅₂	0,8555	- 0,0134	only for $n = 75 \Rightarrow$ IHD = 0
C ₁₀₀ H ₂₀₂	0,8559	- 0,0101	only for $n = 100 \Rightarrow$ IHD = 0
C _n H _{2n}	0,8571	0	for any $n \Rightarrow$ IHD = 1
C ₂ H ₂	0,923	0,499	for $n = 2 \Rightarrow$ IHD = 2 for $n = 4 \Rightarrow$ IHD = 3 for $n = 6 \Rightarrow$ IHD = 4 for $n = 8 \Rightarrow$ IHD = 5
C ₃ H ₄	0,900	0,333	for $n = 3 \Rightarrow$ IHD = 2 for $n = 6 \Rightarrow$ IHD = 3 for $n = 9 \Rightarrow$ IHD = 4 for $n = 12 \Rightarrow$ IHD = 5
C ₄ H ₆	0,888	0,243	for $n = 4 \Rightarrow$ IHD = 2 for $n = 8 \Rightarrow$ IHD = 3 for $n = 12 \Rightarrow$ IHD = 4 for $n = 16 \Rightarrow$ IHD = 5
C ₅ H ₈	0,882	0,199	for $n = 5 \Rightarrow$ IHD = 2 for $n = 10 \Rightarrow$ IHD = 3 for $n = 15 \Rightarrow$ IHD = 4

The molecular formula of the hydrocarbon	p	A	Conclusions calculated n values IHD values
C_6H_{10}	0,878	0,166	for $n = 6 \Rightarrow IHD = 2$ for $n = 12 \Rightarrow IHD = 3$ for $n = 18 \Rightarrow IHD = 4$

II: Discussion and Conclusions:

II.1. Analyzing the previously reported data, a series of conclusions on the method efficiency and also on the manner of approaching the problem can be drawn.

Thus, it can be found that simply indicating, determining or calculating the carbon percentage, important information about the hydrocarbons class including the studied substance can be obtained, namely:

$p < \frac{6}{7}$ 0,857143, the hydrocarbon is certain to be an alkane;

$p = \frac{6}{7}$ 0,857143, the hydrocarbon is certain to be an alkene or a cycloalkane;

$p > \frac{6}{7}$ 0,857143, the hydrocarbon has $IHD > 1$.

The table shows that we can determine the molecular formula of alkanes directly from % C (p) with no supplementary information, as relation (5) admits unique solution in the case of alkanes. This finding seems extremely important.

Mention should be made that the p values for the two consecutive homologues show a tendency to become ever closer along with the increase of n values. Nevertheless, the calculations have revealed that, at the accuracy of p values given in textbooks and reference materials of two decimals, the molecular formulas for alkanes up to C_{75} - C_{80} can be determined univocally. The unique solution of relation (5) for alkanes lies in the fact that the term A is negative and as a result, there is only one n value satisfying all the supplementary requirements simultaneously ($n \in \mathbb{N}^*$, $N E \in \mathbb{N}$).

In the case $p = \frac{6}{7}$ 0,857143 it is determined that $A = 0$ and consequently,

relation (5) can give no information at all about n ; irrespective of n value, relation (5) has the solution $IHD = 1$. there must be other ways to find the molecular formula of the hydrocarbon on the basis of further data provided by the problem. Relation (5) verifies both the gross and molecular formulas of alkenes and cycloalkanes.

If $p > \frac{6}{7}$ 0,857143, the term A becomes positive and consequently,

relation (5) admits of an infinity of solutions for IHD , these representing multiples of the solution with minimum n . A distinct value IHD corresponds to each n , so we can conclude that the hydrocarbons are part of classes of different substances. However, only the gross formula of the compound has been determined; further data from the text are required to determine the molecular formula of the hydrocarbon. As the

correlation between n and IHD is already known, relation (1), it seems much easier to write down the structural formulas, especially if the general expression of the hydrocarbon formula proposed by P. Budrugaec [2] is taken into account:

$$C_n H_{2n+2-2d-4t-2c}$$

where: d , t , c represent the number of double bonds, triple bonds, and cycles (rings) present in the molecule of the studied organic compound respectively.

II.2. The method under proposal facilitates the solving of this type of Organic Chemistry problems included in text books for the Xth and XIIth grades [3], [4].

It must be taken into account that a number of mathematical operations - particularly the division operations - is considerably reduced, contributing in this way to a greater accuracy of the results. It has been noticed that the majority of errors in the solving of numerical problems are caused by *division* because, almost every time, a certain number of decimals is ignored, which ultimately leads to erroneous results.

The Index of Hydrogen Deficiency (IHD) notion [1] is remarkably efficient not only in problems solving but also in the systematization of the theoretical material, particularly when it comes to structure or isomery; that is the reason why special attention has been paid to this notion in the process of searching the most various correlations with other parameters characterizing the organic molecule.

At first sight, the newly proposed method of calculation is adequate only for *alkanes* and less efficient for *alkenes*, *cycloalkanes* and hydrocarbons with $IHD > 1$.

Nevertheless, taking into account the supplementary information provided by the proposed method even in the cases named before, we are convinced that *the implementation of the proposed method in solving the problems referring to structure determination of hydrocarbons is entirely justified.*

REFERENCES

1. Stanley H. Pine, *Organic Chemistry*, fifth edition, Mc.GRAW-HILL BOOK COMPANY, New York, U.S.A., 1990, pp. 19-21.
2. Budrugaec P., *CHEMISTRY problems*, Ed. Academy, Bucharest, Romania, 1986, pp. 122.
3. Albu C.D., Petrescu O., Cosma I., *CHEMISTRY, textbook for Xth grade*, E.D.P., R.A., Bucharest, Romania, 1994, pp. 12, 13, 19, 30.
4. Albu C.D., Ionescu I., Ilie Șt., *CHEMISTRY, textbook for XIIth grade*, E.D.P., R.A., Bucharest, Romania, 1994, pp. 28, 29, 83.