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Definition of Hydrogen Deficiency for Hydrocarbons with Functional Groups

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Petroleum and other fossil hydrocarbon resources (coal, shale, etc.) are the most complex mixtures generated by nature. They contain thousands to millions of different molecules. To characterize petroleum and its fractions down to the molecular level, mass spectrometry, with the highest sensitivity achievable among the analytical instruments (down to nanogram or femtomole levels of a single component), has been an indispensable tool used in the hydrocarbon resource communities, particularly in the petroleum industry. However, in recent publications of petroleum mass spectrometry, use of the z number as expressed by $C_nH_{2n+z}X$, where X denotes functional groups or heteroatoms, would result in some confusion for expressing hydrogen deficiency in hydrocarbon backbone structures, especially for molecules containing carbon functional groups.[1,2]

Except for the light ends with boiling points equal to or below that of naphtha, it is impossible to differentiate and quantify individual isomers. The components are therefore conveniently grouped into compound classes and types with continuously increasing carbon numbers. The composition of petroleum and its fractions is represented by compound type and carbon number distributions. The backbone between adjacent carbon numbers in the same compound type is a methylene group, CH_2. This provides the basis for the Kendrick mass scale that converts the mass of ^{12}C to be exactly 12 to the mass of a methylene unit, $^{12}CH_2$, to be exactly 14 to differentiate compound types based on the mass defect.[3] Because the masses in the series of a given compound type differ by multiple CH_2 units, the mass defect would be identical for the whole compound type series regardless of the carbon number when using the Kendrick mass scale.[3,4]

The z series, that is $C_nH_{2n+z}X$, where n is the number of carbon atoms and X denotes functional groups or heteroatoms, is used to represent the compound type.[4−6] The differences in the carbon number in the same type are due to the different degrees (numbers) of substitution by methyl or alkyl groups. The deviation of hydrocarbon backbone structures from multiple methylene units is denoted as hydrogen deficiency. For example, alkanes have two extra hydrogen atoms compared to multiple methylene units and are therefore represented as a $z = +2$ series. Cycloalkanes with one saturated ring, like mono-olefins, have no extra or less hydrogen atoms compared to the multiple methylene units; therefore, they are denoted as $z = 0$ series (no hydrogen deficiency). Benzenes with a general formulas of C_nH_{2n-6} are called $z = -6$ series. This z-series system can also be applied to compounds containing heteroatoms, such as sulfur, nitrogen, and oxygen (except for carbon-containing functional groups, such as carbonyl and cyano compounds; see below). The number of double bonds and cyclic rings, i.e., double-bond equivalent (DBE), can be calculated from the z number by a formula of $DBE = -(z-2)/2$ for non-nitrogen containing compounds. Because the DBE number is always positive and the hydrogen deficiency numbers are mostly negative, except for paraffins (alkanes), mono-olefins, and monocycloparaffins, the conversion between the z number and DBE always involves a sign change except for paraffins.

For nitrogen-containing compounds, the z numbers need to be adjusted to account for the valence of 3 for nitrogen, one less than that of carbon. For example, carbazoles that have a structure similar to dibenzofurans and dibenzothiophenes ($z = -16$ series) with a N−H group to replace the O or S atom are in the $z = -15$ series, although all of these compound series have the same DBE of 9. The DBE for the nitrogen-containing compounds is therefore $-(z - y - 2)/2$, where y is the number of nitrogen atoms. Similarly, amines have z numbers of one more than that of corresponding alcohols, ethers, and their sulfur analogues; thus, alkyl amines are in the $z = +3$ series, compared to alcohols and mercaptans in the $z = +2$ series. The DBE of all of these compounds is 0, indicating a saturated hydrocarbon backbone structure with no hydrogen deficiency. The compound series of odd z numbers indicates the presence of an odd number of nitrogen atoms in the molecules. However, the DBE system yields the same results for sulfur-, oxygen-, and nitrogen-containing compounds with similar structures. These can represent the pros and cons of using z and DBE systems for hydrogen deficiency.

The system of expressing hydrogen deficiency by z-number works well for hydrocarbons containing non-carbon-containing functional groups, such as alcohols, ethers, mercaptans, sulfides, amines, furans, thiophenes, and carbazoles. The same system is equally applicable to sulfonic acid, sulfonates, and sulfates, although they contain double bonds between heteroatoms.

The confusion of using the z-number system to represent hydrogen deficiency in the hydrocarbon backbone arises when the molecules contain carbon-containing functional groups: ketones, aldehydes, acids, esters, amides, and nitriles. Except for ketones that can simply discount the carbon atom in the carbonyl group, the z number of other series is calculated by replacing the functional group by a hydrogen atom. Therefore, the z number of the acetone hydrocarbon backbone, $CH_3(CO)CH_3$, is +2, using a formula of C_2H_6 that

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Table 1

compound	structure	molecular formula	*z* number	DBE	hydrogen deficiency in the hydrocarbon backbone
acetone	$CH_3(CO)CH_3$	C_3H_6O	0	1	0
propionaldehyde	C_2H_5CHO	C_3H_6O	0	1	0
cyclohexanoic acid	$C_6H_{11}COOH$	$C_7H_{12}O_2$	−2	2	1
acetonitrile	CH_3CN	C_2H_3N	−1	2	0
acetamide	$CH_3(CO)NH_2$	C_2H_5N	+1	1	0
methane sulfonic acid	CH_3SO_3H	CH_4SO_3	+2	0	0

is the same as that used for propionaldehyde, C_2H_5CHO. The DBE is therefore $-(2 - 2)/2 = 0$, indicating a saturated structure with no hydrogen deficiency in the hydrocarbon backbone. Similarly, one-ring naphthenic acids with formulas of $C_nH_{2n-1}COOH$ should have a *z* number of 0 with a DBE of $-(0 - 2)/2 = 1$ to indicate only one cyclic saturated ring in the hydrocarbon backbone structure.

If the double bond in carbonyl and the triple bond in cyano groups are taken into account as "hydrogen deficiency" of carbon atoms and not just for the hydrocarbon backbone, both DBE and *z*-number systems would yield consistent results as reported in the literature.[1,2] Then, ketones and aldehydes have DBE of 1, and one-ring naphthenic acids have $z = -2$ from the formulas of $C_{(n+1)}H_{2(n+1)-2}O_2$ (or $C_{n'}H_{2n'-2}O_2$). Double bonds on heteroatoms, such as sulfonates, sulfates, and nitrates, on the other hand, will not be taken into account as hydrogen deficiency.

The *z*-number system was originally designed for expressing hydrogen deficiency as an elucidation of the total number of double bonds and cyclic rings in the hydrocarbon backbone of the molecule. Recent publications of *z*-number expression that is exchangeable with DBE include double and triple bonds in carbon-containing functional groups that do not contain hydrogen atoms, as mentioned above. However, if the functional group(s) in the molecule are unknown, the calculated *z* number and DBE from the molecular formula can only be considered as equivalent "hydrogen deficiency", with an understanding of possible inclusion of carbon-containing functional group(s) having double and/or triple bonds. If the functional group(s) are known, the number of carbon-containing functional groups (for example, 1 for each carbonyl group and 2 for each cyano group) should be added to the calculated *z* number or deducted from the calculated DBE to account for the total number of double bonds and cyclic rings, i.e., hydrogen deficiency, of the hydrocarbon backbone. For compounds containing non-carbon functional groups, the calculated *z* number and DBE would truly represent the hydrogen deficiency of the hydrocarbon backbone. A few examples are shown in Table 1 for illustrations.

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