V. M. Tatevskii

1957

SovietRxiv

Abstract

Full Text

V. M. Tatevskii

CHEMICAL STRUCTURE AND PHYSICOCHEMICAL PROPERTIES OF HYDROCARBONS*

NEW REGULARITIES AND METHODS OF CALCULATION

(Presented by Academician A. A. Balandin, 17 XI 1956)

In preceding works ($^{1-5}$) we showed that a number of physicochemical properties of paraffin hydrocarbons (alkanes) $C_{nH_{2n+2}}$—molecular volume, molecular refraction, heat of formation, heat of combustion, heat of vaporization, etc.—can be described by the equation**:

$$P = \sum_{i \le j = 1}^{4} n_{ij} P_{ij}, \tag{1}$$

where P is the physicochemical property under consideration per mole of substance (or its mean value per molecule), n_{ij} is the number of C_i—C_j bonds in the molecule, P_{ij} is the value of the given physicochemical property attributable to N_0 C_i—C_j bonds (or to one C_i—C_j bond), and i, j are indices denoting the primary, secondary, tertiary, or quaternary character of the carbon atoms in the C_i—C_j bond. It was also shown (^{3}) that equation (1) can be represented in the form

$$P = 2P_{12} + (n-3)P_{22} + \sum_{i,j<1}^{4} n_{ij} G_{ij}, \tag{2}$$

where $G_{12} = G_{22} = 0$, and the remaining G_{ij} are related to P_{ij} by the equations

$$G_{13} = P_{13} - \frac{2}{3}P_{12} - \frac{1}{3}P_{22}; \qquad G_{24} = P_{24} + \frac{1}{2}P_{12} - \frac{3}{2}P_{22}$$

$$G_{14} = P_{14} - \frac{1}{2}P_{12} - \frac{1}{2}P_{22}; \qquad G_{33} = P_{33} + \frac{2}{3}P_{12} - \frac{5}{3}P_{22}$$

$$G_{23} = P_{23} + \frac{1}{3}P_{12} - \frac{4}{3}P_{22}; \qquad G_{34} = P_{34} + \frac{5}{6}P_{12} - \frac{11}{6}P_{22}$$

$$G_{44} = P_{44} - P_{12} - 2P_{22}$$

Equations (1) and (2) are valid for any branched or normal alkanes. In particular, for normal alkanes we have from (1) or (2):

$$P_{\text{norm}} = 2P_{12} - 3P_{22} + nP_{22} \tag{3}$$

It was shown (^{3}) that all alkanes can be divided into groups in such a way that, independently of the number of carbon atoms of the alkanes falling into a given group—

therefore, for alkanes of a given (for example, the m-th) group, the condition will be approximately fulfilled:

$$\Delta^{(m)} = \sum_{i<j=1}^{4} n_{ij}^{(m)} G_{ij} \simeq \text{const.} \tag{4}$$

From (2) through (4) it then follows that, for alkanes of the m-th group,

$$P_n^{(m)} = 2P_{12} - 3P_{22} + \Delta^{(m)} + nP_{22}, \tag{5}$$

where n is the number of C atoms in the alkane, while the remaining quantities on the right-hand side of the equation are constants. Consequently, in each group of alkanes the physicochemical property P under consideration depends linearly on the number of carbon atoms in the alkanes of the group. Consequently, the members of each group exhibit homologous properties similar to those of the members of the series of normal alkanes. It also follows from (5) that the straight lines described by equation (5) for different groups must be parallel and differ only by a constant displacement along the P axis. Analysis of numerical data on molecular volumes, heats of formation, refractions, heats of vaporization, and vapor elasticities shows that these predictions of the theory are well confirmed by experimental data for a number of physicochemical properties of alkanes.

It is obvious that the regularities represented by equation (5) can be successfully used to calculate a number of physicochemical properties of higher alkanes from the physicochemical properties of lower alkanes. Indeed, if the values of P are known for two alkanes of the m-th group, then the coefficients of straight line (5) are determined, and the values of P for all the other alkanes of the same group (with other values of n) can be calculated from (5). Since the values of

---

* The work contains part of the results reported by the author at the Lomonosov Readings at Moscow State University in April 1956.

** The notation in this article differs slightly from that of the preceding works; the correspondence is easily established by comparing them.

P_{12} and P_{22} can be determined from the values of the corresponding physicochemical properties of normal alkanes, and $\Delta^{(m)}$ from the value of the same physicochemical property of one alkane of the m-th group, then, for calculating a given physicochemical property of all alkanes of the selected group, data on the physicochemical properties of normal alkanes and the experimental value of the property P for only one alkane of the same group can be used. It is obvious that the possibilities for calculating the physicochemical properties of higher alkanes afforded by equation (5) considerably extend and supplement the previously known calculation methods.

As was shown earlier (3), for all other classes of hydrocarbons containing alkyl radicals, the equation for calculating the physicochemical property P can be represented in the form:

$$P = C + \sum_{i,<j=1}^{4} n_{ij} P_{ij}, \tag{6}$$

where C is a quantity constant for a given structural nucleus (naphthenic rings, benzene nucleus, nucleus with double bonds, etc.), to which alkyl radicals are attached, and for the character of its substitution (the number and order of the substituting alkyl radicals in the nucleus), while $\Sigma n_{ij} P_{ij}$ refers to the substituting alkyl radicals. It is easy to see that hydrocarbons with a given nucleus ($C = \text{const}$) can be divided into groups according to the character of the substituting alkyl radicals in such a way that, for each group (for example, the m-th), it is possible to transform equation (6) into the form:

$$P_n^{(m)} = C^{(m)} + \Sigma n_{ij}^{(m)} G_{ij} + n P_{22}, \tag{7}$$

where, for the given group:

$$C^{(m)} \simeq \text{const}$$

$$\Sigma n_{ij}^{(m)} G_{ij} = \Delta^{(m)} \simeq \text{const}. \tag{8}$$

Then equation (6) will be reduced to the form:

$$P_n^{(m)} = C^{(m)} + \Delta^{(m)} + n P_{22}, \tag{9}$$

where all quantities, except n, are constant for the given group, and everything said above with respect to alkanes will also be valid with respect to hydrocarbons of other classes containing alkyl radicals.

Analysis of the available data on molecular volumes, heats of formation, refractions, and certain other properties of hydrocarbons of various classes shows that the experimental data for hydrocarbons of various classes confirm these predictions of the theory, if one considers those groups of hydrocarbons into which they can be divided on the basis of equation (9) and the previously derived equation (3) for a series of their physicochemical properties.

For such physicochemical properties as density or boiling point (which do not obey equations (1)–(9)), the method of using (5) or (9) may be as follows. For density we have:

$$d = \frac{M}{V},$$

where M is the molecular weight, V is the molecular volume. Since for hydrocarbons of a given m-th group both M and V obey linear equations of the type (5) or (9),

$$M^{(m)} = a^{(m)} + b \cdot n$$

$$V^{(m)} = g^{(m)} + h \cdot n,$$

where n is the number of C atoms in the hydrocarbon of the m-th group, the density of hydrocarbons of the m-th group will be expressed by a fractional linear function of n.

$$d_n^{(m)} = \frac{a^{(m)} + b \cdot n}{g^{(m)} + h \cdot n}.$$

On the basis of an analysis of the dependence of the heat of vaporization and vapor elasticity on temperature for hydrocarbons of the m-th group, it can be shown that the boiling point of hydrocarbons of the m-th group at a given pressure can likewise, in a first approximation, be expressed by a fractional-linear function of n.

Moscow State University
named after M. V. Lomonosov

Received
5 XI 1956

CITED LITERATURE

1. V. M. Tatevskii, DAN, **75**, No. 6, 819 (1950).
2. V. M. Tatevskii, ZhFKh, **25**, No. 2, 241 (1951).

3. V. M. Tatevskii, *Chemical Structure of Hydrocarbons and Regularities in Their Physicochemical Properties*, 1953.

4. V. M. Tatevskii, *Scientific Notes of Moscow University*, issue 174 (inorganic and physical chemistry), 235 (1955).

5. V. M. Tatevskii, DAN, **109**, No. 1, 131 (1956).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.