Since the time of discovery of noncovalency bonds the energy of the hydrogen bond in water remains the reliably measured value. Yet quite a number of versatile organic compounds have been synthesized; certain success is attained in the field of structural studies, in measuring intramolecular bonds energies, in carbohydrates, nucleic acids, and proteins chemistry, and in the development of the chemistry of organoelemental compounds. The lack in the scientific publications of the information on the energy of hydrogen bonds and specific intermolecular interactions between the simplest organic compounds (methane, ethane, ethylene, methyl ether, and formic acid) provides special difficulties in their investigation. This impedes the progress in the development of the theoretical concepts of the solution chemistry, in the establishment of correspondence between the structure and energy in various classes of organic compounds, the understanding of the solvates structure, and the specific features of interspecies interaction. Even more difficulties exist in the development in the field of solution chemistry of an independent supramolecular chemistry, the chemistry of intermolecular bonds corresponding to the association between two or more chemical species of large size. A vigorous development is observed in the physical chemistry of organoelemental compounds serving as a certain bridge connecting the inorganic and organic chemistry where frequently appear concepts contradicting the current notions existing in these fields, but which are key points for creating hypotheses, new ideas, and developing of theories inadequate to the existing ones. Let us mention here the statement of Sidgewick that the molecules with the electronic configuration of a noble gas are incapable of association, whereas our investigation established the existence in the vapor of dimers of carbonyl compounds of the elements from the subgroup of chromium, iron, and nickel.

In the physical chemistry of organic compounds and their solutions is firmly established and successfully developed the concept of the correspondence between the structure and the energy, determined by the investigation of molecular structures, of the condensed states, and of the distribution of electrons and charges on the atoms in the molecule, and by measuring the thermodynamic properties. One of the
advantages of the thermodynamic methods consists in the successful application of the notion of the bond vacancies even at the lack of the sufficient information on the molecular structure and the distribution of the charge on the functional groups of the molecule. The discovery of the nature of the hydrogen bonds and specific intermolecular interactions, establishment of new previously unknown types, and their energies makes it possible to solve practical problems; in particular, it opens further opportunities in the development of the chemistry of biologically important substances and in the understanding of the empirical correlations between the thermodynamical properties and molecular parameters measured by various methods.

The key problem elaborated in the monograph is the concept that a carbon atom in the four-valency state not only is capable but actually forms the fifth coordination in the intermolecular interactions with an energy comparable with the energy of the hydrogen bond in water. The unique feature of the behavior of the carbon atom with an essentially unshared 2s^2(c)-electron pair is its ability to act as a donor or an acceptor depending on the properties of the element participating in the interaction, to take part in the formation of solvate structure, and in the formation of specific interaction. These qualities are also inherent to molecules of amino acids, carbohydrates, and proteins.

We do not plan to consider comprehensively in this monograph all the problems of hydrogen bonds and the specificity of intermolecular interaction involving the pentacoordinate carbon atom, in all classes of organic and organoelemental compounds. We limit the scope of the discussion to the principal organic compounds: ethers, ketones, alcohols, carboxylic acids, and hydrocarbons, which always stimulated the appearance of new hypotheses and development of theories, essentially necessary for all classes of organic, organoelemental compounds, hydrocarbons, amino acids, and peptides. The information on fundamental aspects of this monograph may be obtained from its table of contents. At the same time the special importance of the theory of the hydrogen bonds and of specific intermolecular interaction, in substantiation of their types and energy determination, should be stressed. The refining of the current concepts in the field of hydrogen bonds and specific interactions in liquid and crystalline organic compounds, solutions of nonelectrolytes, of the theoretical regularities are necessary for the understanding of phenomena in organic and complex biologic systems and for further purposeful development of the key problems of the specific interactions and hydrogen bonds in the biologically important substances.

The critical analysis of the total scope of thermochemical and thermodynamic properties of alkyl derivatives of elements of the II–VI main groups established in the investigations of the author inevitably infringes on the views regarding the classical model of the sp^3-hybridized valence orbitals of the carbon atom whose attraction prevented the doubts in its imperfection (Chap. 1). As a result of this analysis the phenomenon of the reverse dative bond between the carbon atoms of the alkyl chain and the contacting central atom of the molecule was substantiated and also the capability of the terminal methyl groups to participate in the specific intermolecular interactions revealing the pentacoordinated state. These fundamental statements led to the founded rejection of the model of the sp^3-hybridized
carbon atom based on the quantum-chemical calculations of the methyl derivatives of the elements of subgroups of boron and tin, and methyl compounds of nitrogen and oxygen, additionally confirming the capability of a pentacoordinate carbon to take part in the formation of the specific interaction. The implementation of these concepts into the theoretical footing of organic and inorganic chemists may be somewhat inertial due to the unconventional ideas and the approach to the theory of the hydrogen bonds and specific interaction. But the fact that here are compiled the self-consistent energies of the hydrogen bonds of various types and specific intermolecular interactions adequately reflecting their nature, the data, which are highly necessary for the specialists, gives a hope that they will be gratefully acknowledged.

The scientific idea of the reverse dative bond in organoelemental compounds with a hydrocarbon group confirmed with the quantum-chemical calculations in its development underlies the new concepts on the nature of the bonds in the alkyls of nontransition elements and in organic compounds with a heteroatom. This idea ensures the understanding of the chemistry of liquid solvents and liquid and solid nonelectrolytes (Chap. 2). The results of thermodynamic calculation are attractive for they provide an unambiguous solution of the problem of measuring the energy of the hydrogen bonds and the specific intermolecular interactions whose quantitative value remained unknown and even unestimated approximately. The growing number of carbon atoms in the alkyl chain results in more stable specific interactions formed by the terminal methyl group of the propyl fragment (Chap. 3). This fact is due to the weakening of the influence of the reverse dative bond on the terminal methyl group with the growing number of carbon atoms in the alkyl chain. From the large number of the established rules of the energy changes in the specific interactions of the saturated and unsaturated cyclic ethers and organic cyclic oxides, we report one among them regarding the regular decrease in the energy of low-stability hydrogen bonds between the hydrogen atoms of the CH₂ groups and the oxygen atom of the oxides with the growing number of the methylene groups in the molecular ring.

The alternative character of the theory and the necessity of its further development prompted the elaboration of the principles of proving various types of hydrogen bonds and specific intermolecular interactions and the procedures of thermodynamic calculation of their energies based on the enthalpies of vaporization that were suitable for all classes of organic compounds. These principles are reported in Chap. 3 and are elaborated in the successive chapters.

In Chap. 4, thermodynamic analysis is performed of the structural and thermodynamic characteristics of liquid and solid symmetric and unsymmetrical ketones with saturated and unsaturated alkyl chains, cyclic ketones, diketones, and oxyketones. As a result the self-consistent energy values were obtained for the specific intermolecular interactions and the H-bonds of low stability formed by the oxyketones. An important attention is paid to the new conception in the theory of the structure and stabilization of the molecules of ketones, alcohols, to the extrastabilizing effect of the isostructural methyl groups ensuring their reduced values of the enthalpy characteristics in the vaporization processes and the equal contribution
into the enthalpy characteristic of the vaporization of four CH₂ groups with contiguous methyl groups. This principle is valid for various classes of organic compounds and reflects the analogy of the structural fragments at the number of CH₂ groups exceeding eight in ketones, alcohols, and obviously in more complex organic substances with the heteroatoms in the molecules and in the complex biological systems. A special attention is paid to the thermodynamic investigation of saturated and unsaturated ketones with a large number of carbon atoms and isostructural methyl groups.

In Chap. 5, various types of hydrogen bonds and specific intermolecular interaction were substantiated and their nature was revealed in liquid and solid monohydric and polyhydric alcohols with saturated and unsaturated chains, with the open and cyclic structure and isostructural alkyl groups. Theoretical problems are discussed and the regularities in the stability series of bonds are substantiated. The results obtained impelled to carry out thermodynamic investigation of isostructural and acetylene alcohols, and their solutions with polyatomic saturated and unsaturated ketones. The findings obtained confirmed the developed concept of the stabilizing effect of the isostructural methyl group.

In Chaps. 6 and 7, the theory of the hydrogen bond finds further development and are extended the theoretical notions and rules to liquid and solid aldehydes, esters, and carboxylic acids. The performed thermodynamic analysis of the enthalpy and structural entropy characteristics of vaporization of carboxylic acids associated in vapor resulted in valid energy values of various types of hydrogen bonds and specific intermolecular interactions of saturated and unsaturated mono- and dibasic acids, acids with an isostructural methyl group, hydroxycarboxylic acids, methoxy- and ethoxycarboxylic acids, peroxycarboxylic acids, and cyclic carboxylic acids. The established array of valid self-consistent energies of various types of hydrogen bonds and specific intermolecular interactions is illustrated by the regular series of their stabilization.

Chapter 8 illustrates the application of the developed theory of specific interactions to alkanes and alkenes and the established regularities of the specific interactions existing in their condensed state.

In writing the book the author tried to reveal the depth of the analyzed problem and to provide its clear description remembering that “formulas are not the essence of the theory, and a real theoretician uses them sparingly expressing with words all that is possible to express in words” (L. Boltzmann). The author is deeply grateful to Professor Josef Barthel (Regensburg University, Editor-in-Chief of the Journal of Molecular Liquids) for his suggestion and demand of the author to write a monograph basing on the theme of the article submitted to the Journal of Molecular Liquids. The ideas reported in this article underlie the development of the thermodynamic theory of the hydrogen bond and the specific interactions originating from the pentacoordinated carbon atom.

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