Physico-chemical principles of universal methodology of controlling structure and properties of metallic and nonmetallic materials

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Abstract. Physico-chemical principles of universal methodology of controlling a structure and properties of metallic and nonmetallic, primarily organic and inorganic, substances and materials are examined. The aim of the methodology developed is to determine the relationships between chemical composition, as well as type of bond between elements of electronic-nuclear chemical microstructure, on nano-, meso- and macrostructural levels of the structure and characteristic properties of materials. Special emphasis is put on analysis of the effect of covalent, metallic and ionic components of chemical bond on the structure and properties of substances and materials within one system.

Introduction

Metals and nonmetals (based on organic and inorganic substances) are the basic types of materials that are used in mechanical engineering. At the same time, ‘mixed’ types of materials, which combine advantages of metals and nonmetals, are increasingly used. Nowadays materials are considered to be characterised by a multilevel structural organisation (e.g., micro-, meso- and macrostructure). Therefore, it is important to determine the effects of a substance's chemical composition and bond type between elements of the electronic-nuclear microstructure on both the chemical structure (molecular or nonmolecular – metallic) and nano-, meso- and macrostructural levels of the structure, which determine characteristic mechanical and physico-chemical properties of materials [1]. Since the transition from typical metals to nonmetals is gradual, it is important to assess quantitatively the ratio of covalent, metallic and ionic components of chemical bond upon elemental composition change [2].
1. electronic-nuclear microstructure \((1a)\) is common for both metallic and nonmetallic materials, as any material is formed by chemical elements (atomic cores) linked together by chemical bonds;

2. differences in structure of subsequent levels (and, consequently, properties) are determined by the character of chemical bond (primarily covalent, metallic or ionic); these differences appear at molecular-, nano-sublevels and then at meso- and macrolevels.

Thus, elemental composition and chemical bond type are basic factors that determine both a structure and properties of metals and polymers. For example, Periodic Law envisages the need to take into account the effect of chemical composition on properties of chemical substances. However, it is clear that this effect is not direct. Composition and nature of elements determine a chemical bond type, while the latter determines chemical, physical and mechanical properties of substances and materials. This is why in physical chemistry attempts are made to assess quantitatively the impact of chemical bond type on structure of substances, e.g. by using electronegativity \([3, 4]\).

According to classical chemical views there are three main extreme types of chemical bond: covalent, ionic and metallic chemical bonds. It is also known that in most substances chemical bonds can be considered as intermediate (mixed) ones in terms of their type. For example, G. Sproul pointed out \([3]\) that “interatomic bonding is often characterized by one of three bonding models: ionic, covalent, or metallic… Many compounds can be reasonably categorized as one of these three types, although it is generally recognized that most heteroatomic bonds exhibit a mixture of these ideal bond types”.

The concept of chemical bond as a combination of three components (covalent, metallic and ionic) in binary heteronuclear compounds or the two components (covalent and metallic) in homonuclear (“elementary”) substances may only look rather simple. Major problem here is to develop a model that would be applicable to a great variety of chemical compounds. Such model of a chemical bond would have to summarise all other more specific models, neglecting specific features and including what these models have in common. As a result, due to its generalising character such model of chemical bond might look rather simplistic at first glance.

Thus, developing an approach, which would take into account three components of chemical interaction is not an easy (due to the huge amount of chemical substances) but, under certain conditions, realistic task. Therefore, it is reasonable to start from the so called “elementary” (homonuclear) substances and binary (heteronuclear) compounds, which are basic types of chemical substances and attractive modelling objects due to minimal variability in terms of chemical composition. The latter facilitates comprehensive assessment of chemical bond change upon variation of chemical composition within approaches adopted in physical chemistry.

When describing a chemical bond as a combination of the two or three extreme types mere acknowledgment of metallic component of chemical bond is itself often a controversial issue, especially when it comes to substances that do not exhibit metallic properties. Concise, yet comprehensive review of “a hard life” of metallic bond and especially the metallic component of chemical bond in nonmetallic substances and materials is given in \([5]\). G. Lewis was the first to show the applicability of “electronic gas” model to a chemical bond and for the first time proposed considering the third (in addition to covalent and ionic) type of chemical interaction – metallic \([6]\), as well as suggested mixed types of chemical bond. Later L. Pauling noted the possibility of mixed-type bonds and the need to take into account metallic component \([7]\). L. Pauling also stressed common nature of covalent and metallic bonds, as well as an essential distinction of the latter from the covalent bond – additional freedom of movement for electrons \([5]\). However, L. Pauling did not suggest ways of calculating the metallic character of chemical bond, assessing only its ionic character.

The need to take into account metallic component of chemical bond was highlighted later by other authors who suggested various ways of assessing it (as well as covalent and ionic components) \([8-13]\). It was also reported that metallic character determines specific properties of substances and materials \([14, 15]\). A number of researchers suggested estimating covalent character as electronegativity average and ionic character as electronegativity difference \([3, 4, 16, 17]\). This allowed constructing semi-quantitative van Arkel-Ketelaar triangles of bonding; at these triangles' vertices the substances with typical covalent, metallic and ionic bond types are located (for example, F2, Cs and CsF, respectively \([14, 15, 17]\). In these triangles the authors identify areas where ionic, metallic and covalent (molecular
and network) structures exist. However, the authors do not indicate ways of assessing the metallic character of chemical bond.

In 1991 authors of the present paper suggested method of assessing covalent character $C_C$ and metallic character $C_M$ of a homonuclear bond by using electronegativity $X$ and the first ionization energy assuming $C_C = 100\%$ for fluorine-fluorine bond. Later (in 1992) an attempt was made to systematise chemical bonds by bond type and assess the effect of bond type on structure and properties in the form of “Chemical triangle of chemical composition, nature of chemical bond, structure and properties of chemical compounds and polymers” whose vertices were formed by extreme covalent, metallic and ionic bonds [2].

In 2005, a method of assessing components (CC, CM and ionic character CI) of heteronuclear bonds was developed [2]. The calculation algorithm is as follows:

$$X_{AV} = \frac{(X_{E1} + X_{E2})}{2}, \quad (1)$$

$$C_{C1} = 25.3 \times X_{AV}, \% \quad (2)$$

$$C_{M1} = 100 - 25.3 \times X_{AV}, \% \quad (3)$$

$$C_{II} = 1 - \exp(-0.18 \times \Delta X^2), \quad (4)$$

$$C_C = C_C(1 + C_{II}), \% \quad (5)$$

$$C_M = C_M(1 + C_{II}), \% \quad (6)$$

$$C_I = C_I \times 100/(1 + C_{II}), \% \quad (7)$$

where $X_{E1}$ and $X_{E2}$ – electronegativity values of two elements; $\Delta X$ – electronegativity difference for elements $E_1$ and $E_2$; $X_{AV}$ – average electronegativity; $C_{C1}$, $C_{M1}$ and $C_{II}$ – intermediate values of covalent, metallic and ionic character, respectively.

One can see that the above formulae allow assessing all three components of heteronuclear interaction, including $C_M$. It is also clear that formulae (1) – (7) are not specific to heteronuclear bonds and can be applied to homonuclear bonds too. In this case $C_{II} = 0 \%$ and formulae (1) – (7) are effectively reduced to formulae (2) and (3).

In the present paper the mechanism of any chemical bond formation is envisaged as overlapping of electron shells of at least two individual atoms; this leads to emergence of shared electrons (SE) that bond chemical elements [1, 2]. SE are termed 'valence electrons' in predominantly covalent bonds (in line with valence bond theory). This is accompanied by restructuring of electron shells of individual atoms and transformation of the latter into chemical elements in the form of nuclei or atomic cores (figure 1).

Similar to other researchers, but using formulae (1)-(7), the authors of the present paper placed at a triangle's vertices the three extreme types of chemical bond (figure 2) while mixed homo- and heteronuclear bonds and compounds formed by these bonds are located at the sides and the area of this “Chemical triangle” (CT). Values of covalent character ($C_C$) for some homo- and heteronuclear bonds are given in brackets at the left and the right sides of CT (or more precisely on the axes parallel to the sides of CT). The left side of CT represents homonuclear compounds of $s$-, $p$-, $d$- and $f$-elements (I) as well as respective basic metallic and nonmetallic (low-, oligo-, highmolecular compounds and polymer solids, e.g. diamond) substances. Heteronuclear chemical bonds are characterised by three components and therefore occupy the area of CT (e.g. $\text{Mg}_3\text{Sb}_2$, figure 2). However, for convenient presentation of various binary heteronuclear chemical compounds (like oxides, nitrides, carbides, etc.) they are located within the CT on additional dotted axes parallel to the right side of CT (figure 2). Chemical bonds cannot be found at the bottom and right sides of CT, as well as at M and I vertices (this is why these sides are shown as dotted lines) due to the fact that $C_C$ cannot be 0.
Figure 1. Representation of possible localisation - delocalisation of SE: along the X axis - metallic (M) and along the Y axis - ionic (I) components of homo- (E'-E') and heteronuclear (E'-E'') chemical interaction. Point C is characterized by 100% covalent character - extreme localisation of SE along Y-axis.

Figure 2. “Chemical triangle”, which represents intermediate bond types and basic homo- and heteronuclear chemical compounds (ChC). Figures in parentheses indicate C_c of some chemical bonds.
When considering the information given in figure 1 and figure 2, one can see that the ratio of chemical bonds' components has an effect on structure of chemical compounds (low- or high-molecular, nonmolecular metallic or ionic, amorphous or crystalline, etc.). For example, when \( C_C > C_M \) (for homonuclear substances) or \( C_C > C_M + C_I \) (for heteronuclear compounds) molecular compounds are formed. If \( C_C < C_M \) (for homonuclear substances) or \( C_C < C_M + C_I \) (for heteronuclear compounds) chemical elements form nonmolecular metallic or ionic substances.

The closer to vertex C and the farther from vertices' M and I of CT, the higher the likelihood of formation of substances with lower density, electrical and thermal conductivity, as well as those that are less prone to crystallisation. Closer to the centre of CT and vertices M and I mainly solid, prone to crystallisation, multinuclear metallic, covalent and ionic compounds (such as iron, silicon oxide, sodium oxide, etc.) are formed. It is of great interest to study the effect of chemical bond location within this system, which is determined by components of chemical bond, on elements' ability to form various high molecular structures (figure 2, area between IIb' and IIb), on components of intermolecular interaction, as well as on chemical and supramolecular physical structure of polymers, their mechanical and physico-chemical properties. Solids used in mechanical engineering (steel, cast iron, alloys, intermetallic substances like \( \text{Mg}_2\text{Sb}_2 \), etc.) are located at the bottom part of CT (figure 2, area between Ic and IIc). Polymer materials are located near vertex C (figure 2, area between Ib and IIb). Closer to vertex C substances exist in the gaseous state due to prevailing covalent component of chemical bond.

3. Conclusion
Development of innovative approaches and even new paradigms in material science in light of the above discussion appears to be quite promising in perfecting the technology of materials for mechanical engineering.

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