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Morphological Classification of Chemical Structural Units

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A new classification of chemical structural units (csu), based on their elemental chemical transformations, is presented. It origins from a new uniform numerical definitions of acids, bases, oxidators and reductors and a new numerical approach to the periodic chart of elements. According to these assumptions csu and their combinations are distributed in a multi-dimensional classification space. Much attention has been paid to prove experimentally that the virtual classification steps present the real steps of chemical reactions of csu. Thermal decomposition stages as well as syntheses of salts in solid state were investigated. Applications of classification presented in research and didactics have been discussed.

Key words: compounds classification, atomic cores periodic system, chemical structural unit, acid-base theory, elementary reactions

To my wife Hanna

Contents

List of symbols

n – number of electron shells in an atomic core

q – atomic core charge

l – number of valence subshells at atomic core

n_c, q_c, l_c – n, q, l of the coordination center

n_z, q_z – n, q of the ligand

e_v – number of valence electrons

e_z – number of elementary charges introduced by ligands

$\bar{e}_v$ – mean value of e_v

$\bar{e}_z$ – mean value of e_z

G_{ox} – oxidation state
G_{ac} – acidation state

red – reducer
ox – oxidizer

ac – acid
bas – base

redac – coupled reducer and acid
oxbas – coupled oxidizer and base

1. Introduction

The Periodic System of elements developed by Mendeleev seemed to have solved the problems of classification in chemistry and, since it had been formulated, no considerable attention was paid to the systematics of chemical compounds, as may be evidenced by only a limited number of publications, not exceeding hundred items. It is worth to distinguish here the classification of chemical compounds based on their quantitative composition, in the form of Gibbs triangle, with no relation to the periodic system of elements [1]. Arrangement of hydrocarbons into homologous series is also unrelated to the Periodic Table. This old method of the classification has found its generalization in a uniform system presented by Jurkiewicz as late as in 1950s [2]. Classifications of chemical compounds, based on the periodic table of elements, are generally known. In systems of this type chemical compounds, mostly those composed of two elements are attributed to individual fields of the periodic table [3]. The periodic table of elements was also used for grouping various sequences of compounds with similar structures [4]. The morphological classification, subject of this review paper, is concerned with other objects, classified according to quite different principles. Chemical compounds represent a set, which is much too differentiated to be classified on general principles. The classical chemical approach: atoms - molecule of a chemical compound – has been replaced in the morphological classification by the system: atomic cores – Chemical Structural Unit (csu) – molecular or macroscopic system of the chemical compound. Chemical structural units are the basic components of all sets referred to as chemical compounds and can be described by definite numbers, connected with their elementary transformations and numbers expressed their elemental composition. This approach leads to the original and uniform morphological classification of structures and chemical transformations of csu and their derivatives presented in this review.

The morphological classification has been directly inspired by the method of ordering the inorganic compounds according to oxidation numbers, developed in 1930s by T. Miłobędzki [3] and widely applied in the lectures on inorganic chemistry.

The parameters of the morphological classification, taking into account the elemental composition and the elementary transformations of csu, are derived from the Periodic System of Atomic Cores and from the uniform definition of acids, bases, oxidizers and reducers (both developed especially for this classification) [9,13].

2. The periodic system of atomic cores

The morphological classification of molecules and molecular ions has been based on the atomic core concept, which is a positively charged part of an atom, free of any valence electrons on the s, sp, dsp, and fdsp sub-shells. The atomic core can be univocally identified by means of the following three numbers: number of electron shells “n”, which can change from 0 to 6, according to the possibility of filling the core electron shells K, L, M, N, O, P; number corresponding to the electric charge of the atomic core “q” in elementary units (this charge assumes 1+ and 2+ in the block s, from 1+ or 2+ to 8+ in the block sp, from 1+ or 3+ up to 11+ in the block dsp, and from 1+ to 16+ in the block fdsp); number of virtual valence sub-shells, “l”, which can change from 1 to 4, conforming to the number of valence subshells s, sp, dsp, fdsp [8,9,13].

These numbers create a 3-dimensional classification system of atomic cores, which can be represented as plane tables (Fig. 1) for the four blocks (s, sp, dsp, and fdsp) of the elements. Representations with integrated s, sp, and dsp (Fig. 2) or fully integrated blocks (Fig. 3), the closest to the primary Mendeleev’s version, are also employed. Replacement of the atomic number, characterizing a chemical element, by three appropriately defined numbers is reasonable from the classificational viewpoint, since it enables to formulate sub-sets of a system by setting the values of successive parameters n, q, and l. Setting a value of one of these parameters enables to define: a period of elemental cores, if n = const; a group of elemental cores, if q = const; a block of elemental cores, if l = const.

Setting two parameters enables to define: sub-periods of elemental cores, if n = const and l = const; sub-groups of elemental cores, if q = const and l = const; inner sub-groups in periods if n = const and q = const.

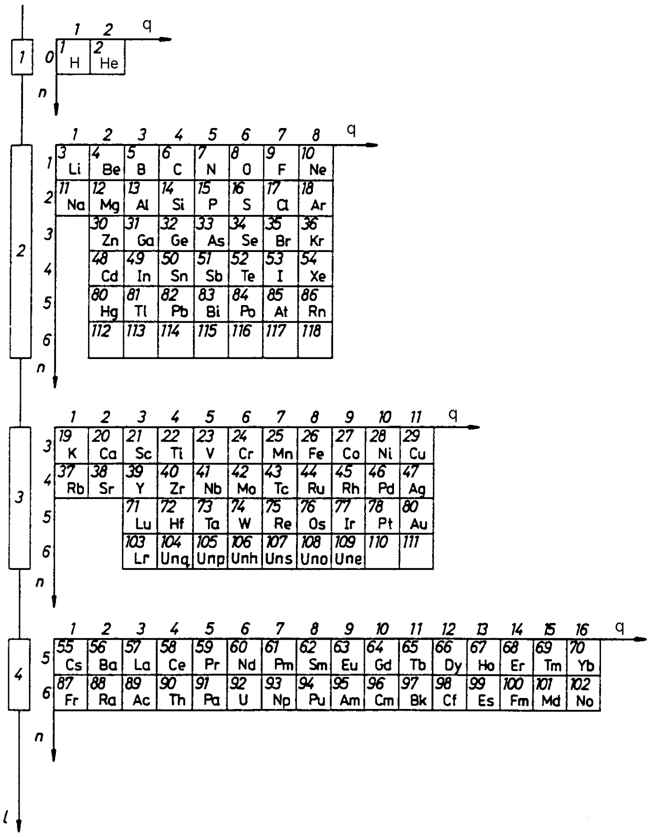
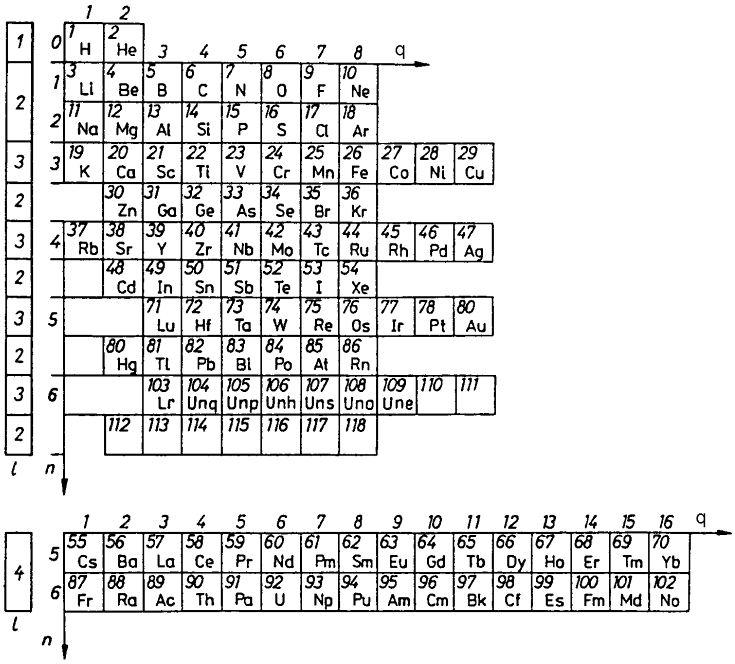


Figure 1. Block-shaped periodic system of atomic cores of chemical elements.

The inner subgroups of elements, which are defined like sub-periods and sub-groups, have not been distinguished formerly because of their scarcity, resulting from the limited number of the admissible values of "l". As late as for n = 3, an inner sub-group of two elements may be formed, *e.g.* Mn^{7+} and Br^{7+}. For n = 5 such a sub-group may consist of 3 elements, *e.g.* Ce^{4+}, Hf^{4+}, and Pb^{4+}.

The various modifications of the periodical system arise from different ways of representing the three-dimensional classification system on a plane. The classification of elemental cores in the aspect of properties of their valence shells and assignment to groups, periods and blocks is most simply represented by the block version (Fig. 1) and two integrated versions (Fig. 2 and Fig. 3). The "long" version of the periodical system is less consistent in this respect.

The classification of atomic cores, while retaining the natural succession of elements, has a number of peculiarities with regard to the classical periodic system: the number of each period is reduced by one, thus leading to the appearance of period zero (H^+ and He^{2+}); extended numbering of groups conforming to the core charge (from 1+ to 16+); identical core structure within each sub-period while the core charge increases; the role of the noble gases atoms as standards of stable structures has been accepted by the cores: Li^+, Na^+, K^+, Rb^+, Cs^+, and Fr^+ – besides, the following standard cores: Zn^{2+}, Cd^{2+}, Hg^{2+}, Uub^{2+}, and, consequently, Lu^{3+} and Lr^{3+} have appeared (Fig. 3); existence of four blocks of the elements: s, sp, dsp, and fdsp (Fig. 1); different assignment of the group I and II elements to the blocks (Fig. 3) (Li^+, Na^+ - block sp; K^+, Rb^+ - block dsp; Cs^+, Fr^+ – block fdsp; Ca^{2+}, Sr^{2+} – block dsp; Ba^{2+}, Ra^{2+} – block fdsp); dif-



l	n	1	2	3	4	5	6	7	8	q		
1	0	1 H	2 He									
2	1	3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne			
	2	11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar			
3	3	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu
2			30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr			
3	4	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag
2			48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe			
3	5			71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	80 Au
2			80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn			
3	6			103 Lr	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	110	111
2			112	113	114	115	116	117	118			

l	n	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	q
4	5	55 Cs	56 Ba	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	
	6	87 Fr	88 Ra	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	

Figure 2. Periodic system of atomic cores with integrated s, sp, and dsp blocks.

n		*l*	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*	*15*	*16* q
0	–	*s*	*1* H	*2* He														
1	K^2	*sp*	*3* Li	*4* Be	*5* B	*6* C	*7* N	*8* O	*9* F	*10* Ne								
2	K^2L^8	*sp*	*11* Na	*12* Mg	*13* Al	*14* Si	*15* P	*16* S	*17* Cl	*18* Ar								
3	$K^2L^8M^8$	*dsp*	*19* K	*20* Ca	*21* Sc	*22* Ti	*23* V	*24* Cr	*25* Mn	*26* Fe	*27* Co	*28* Ni	*29* Cu					
	$K^2L^8M^{18}$	*sp*		*30* Zn	*31* Ga	*32* Ge	*33* As	*34* Se	*35* Br	*36* Kr								
4	$K^2L^8M^{18}N^8$	*dsp*	*37* Rb	*38* Sr	*39* Y	*40* Zr	*41* Nb	*42* Mo	*43* Tc	*44* Ru	*45* Rh	*46* Pd	*47* Ag					
	$K^2L^8M^{18}N^{18}$	*sp*		*48* Cd	*49* In	*50* Sn	*51* Sb	*52* Te	*53* I	*54* Xe								
5	$K^2L^8M^{18}N^{18}O^8$	*fdsp*	*55* Cs	*56* Ba	*57* La	*58* Ce	*59* Pr	*60* Nd	*61* Pm	*62* Sm	*63* Eu	*64* Gd	*65* Tb	*66* Dy	*67* Ho	*68* Er	*69* Tm	*70* Yb
	$K^2L^8M^{18}N^{32}O^8$	*dsp*			*71* Lu	*72* Hf	*73* Ta	*74* W	*75* Re	*76* Os	*77* Ir	*78* Pt	*79* Au					
	$K^2L^8M^{18}N^{32}O^{18}$	*sp*		*80* Hg	*81* Tl	*82* Pb	*83* Bi	*84* Po	*85* At	*86* Rn								
6	$K^2L^8M^{18}N^{32}O^{18}P^8$	*fdsp*	*87* Fr	*88* Ra	*89* Ac	*90* Th	*91* Pa	*92* U	*93* Np	*94* Pu	*95* Am	*96* Cm	*97* Bk	*98* Cf	*99* Es	*100* Fm	*101* Md	*102* No
	$K^2L^8M^{18}N^{32}O^{32}P^8$	*dsp*			*103* Lr	*104* Rf	*105* Db	*106* Sg	*107* Bh	*108* Hs	*109* Mt	*110* Uun	*111* Uuu					
	$K^2L^8M^{18}N^{32}O^{32}P^{18}$	*sp*		*112* Uub	*113* Uut	*114* Uuq	*115* Uup	*116* Uuh	*117* Uus	*118* Uuo								

▤ *l* = 1 (*s*)
☐ *l* = 2 (*sp*)
▥ *l* = 3 (*dsp*)
▨ *l* = 4 (*fdsp*)

Figure 3. Integrated periodic system of atomic cores of chemical elements.

ferent compositions of the groups II sp and III dsp (Fig. 3). Since Zn, Cd, Hg and Uub belong to the block sp, the sub-group II sp comprises Be^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Uub^{2+}. Similary, since Lu and Lr are in the block dsp, the sub-group III dsp consists of Sc^{3+}, Y^{3+}, Lu^{3+} i Lr^{3+}.

Basing the concept of a chemical element on the concept of an atomic core seems to give a possibility to resolve a number of formal and real problems connected with the concept of chemical element as being a collection of electrically neutral atoms [13]:

- The concept of "electropositivity" loses its simple physical sense in the core-based conception of chemical element. The interaction between the electrically charged atomic cores and the valence electrons is considered only in terms of electronegativity, which may be generally defined as the energy of binding first electron on the valence sub-shell of the atomic core. The quantitative description of electronegativity is therefore directly related with respective ionisation energies of atoms (with opposite sign).
- In such a concept the periodic system of elements, being a classification of isolated atomic cores, provides a basis for classification of structurally formulated fragments of molecules and molecular ions, in which it is possible to distinguish atomic cores, being the coordination centres and their environment, formed by valence electrons and ligands. Conforming to the generally accepted principle, the quality of the central core depicted by the numbers n_c, q_c, and l_c, determines the classificational assignment of the structure to the compounds of the given element, hence, also to a definite field in the periodic system, specified in terms of these numbers.

3. Chemical structural units (csu)

In the atomic conception of the chemical element the atoms bear not only the quality features of the element, but also, to a certain degree, the structural features, connected with the orientation of hybridised orbitals of the valence electrons. In the atomic core conception of the element, accepted as the basis of the morphological classification, the chemical elemental features have been separated from the structural features. The chemical features are represented by the spherical atomic cores, having no orientation properties, whereas the structural features appear as fully developed in the chemical structural units. Such units are elementary structures with single-core coordination centre enveloped by the valence electron shells, along with the covalently bound simple anionic ligands, as well as hydrogen cations inserted among the free valence electron pairs at either the coordination centre or the ligands [9,13].

The chemical structural units (csu) can exist as either uncharged molecules of chemical compounds, as ions in salt systems, or as fragments of multicentre molecules and molecular ions. It is possible to distinguish: atomic cores as chemical structural units (csu) – Na^+, Sc^{3+}; csu with valence electrons – Xe^0, S^{2-}, Sb^{3+}, Fe^{2+}, Sm^{3+}; homoligand csu – SF_6^0, PO_4^{3-}, TlO^+, MnO_4^-, SN_2^0; electron-ligand csu – CO^0 , CN^-,

SO_3^{2-}, SbO^+, MnO_4^{2-}, AmO_2^{2+}; csu with H^+ cations at the coordination centre – NH_3^0, HPO_3^{2-}; csu with H^+ cations at the ligands – $Si(OH)_4^0$, $H_3PO_4^0$; heteroligand csu – $HOSO_2F^0$, $SOCl_2^0$.

The definition of chemical structural units in multicentre systems is somewhat arbitrary. In order to single out monocentric components in a multicentre molecule or an ion, it is necessary to perform such a section of bonds, which would not result in arising of properties, that do not exist in the primary molecule. As the homolytic division leads to free radicals with unpaired electrons, which are a source of properties not existing in the initial structure, heterolytic splitting of multicentre systems has been accepted. As a result, chemical structural units with valence electron pairs and dielectron vacancies have been singled out. The fragmentation of multicentre molecules can be unique in some cases and may proceed in two or more ways in other cases. The heterolytic splitting can lead, therefore, to one or several kinds of csu:

$$S_3O_9^0 \mid 3SO_3^0 \qquad\qquad S_3O_{10}^{2-} \mid 2SO_3^0 + SO_4^{2-}$$

or it may be performed in different ways:

$$\begin{array}{ll} S_2O_3^{2-} \mid SO_3^0 + S^{2-} \qquad & P_4O_{10}^0 \mid 3PO_3^- + PO^{3+} \\ \qquad\ \ \mid SO_3^{2-} + S^0 & \qquad\ \ \mid 2PO_3^- + 2PO_2^+ \\ & \qquad\ \ \mid PO_4^{3-} + 3PO_2^+ \end{array}$$

Investigation of the mechanism of thermal decomposition of chemical compounds seems to indicate that structurally complex multicentre molecules are in specific equilibrium with all distinguishable components of their structure [11,13,14]. Such heterolytic fragments can appear where this equilibrium is disturbed by external conditions. Many csu, revealed as a result of fragmentation of complex molecules, can also exist as independent species either as chemical molecules or as ionic components in salt systems. Many such fragments do not occur as independent species, because of their limited stability. The morphological classification of chemical structural units deals with the elementary structures and their transformations, which consist in the changes of electron and ligand environment of the coordination centres. Such transformations are the elementary processes of oxidation-reduction or acid-base reactions.

4. Uniform numerical definition of acids-bases and oxidizers-reducers

4.1. Previous definitions: Contrary to the acid-base processes, the redox reactions are more carefully and univocally defined as the processes, in which the electric charge is transferred in the form of valence electrons. In their definition use has been made of a numerical parameter, namely oxidation state, which for about 70 years serves as the basis for classification of simple inorganic compounds and is recommended by IUPAC in the terminology of such compounds. On the other hand, the concepts of acids and bases, as well as the acid-base reactions, are defined in different ways, and the defining concepts may be divided into three groups [6]:

a) Definitions based on the structure of compounds in solutions. Such definitions permit to define an acid and a base before an eventual acid-base reaction, here referred to as the neutralization reaction. The fundamental Arrhenius' definition has been extended by German and Cady to the form of the solvent definition.

b) Definitions relating the concepts of acids and bases to definite reactions of transferring the electric charge in the form of ions. Such definitions have been based on the mechanism of the acid-base reactions. The basic definition is here the Broensted definition and the numerous, mainly anionic extensions made *e.g.* by Lux and Flood.

c) Definitions connected with the structural effects of acid-base reactions, leading to formation of a covalent bond (definitions that seem to be based on the structure of products of the acid-base reactions under consideration). These definitions have been formulated by Lewis and extended by Pearson, distinguishing acidic and basic parts of the compounds.

4.2. Numerical description of chemical structural units (csu) [6,8,9,13]: The common and uniform treatment of all the charge-transfer reactions has been based on the classical definition of the redox reactions and of the definition of acids and bases, proposed by Lux and Flood and derived from the Broensted concept. The charge transfer processes, that form the basis of these assumptions, have been limited to the transfer of electrons, monopositive hydrogen cores and simple anionic ligands such as F^-, OH^-, NH_2^-, O^{2-}, NH^{2-}, N^{3-}.

The transformations of chemical compounds, expressed in numerical terms as changes in their numerical descriptions, such as the oxidation states in the redox reactions, are of fundamental importance in the classification proposed. Hence, on deriving a uniform definition of transformations associated with charge transfer, it seems advisable to base oneself on the oxidation state and on its acid-base analogue. However, a detailed analysis shows, that the oxidation state, so deeply seated in chemistry, is not a reasonable magnitude. It does not consider the charge transfer processes from the point of view of the system concerned, since the loss of electrons is associated with an increase of the oxidation state and gaining electrons decrease the oxidation state. Moreover, within the sp block of elements analogous structures of csu may appear at various oxidation states (see Fig. 4a). It seems rational to utilise the number of free valence electrons e_v of the given atomic core, connected with the oxidation number G_{ox} by the relation: $G_{ox} = q - e_v$, where q is the core charge. The number e_v decreases as electrons are splitted off and it increased when electrons are attached onto the valence shells. Analogous structures of csu in the sp block of elements appear at identical values of e_v (Fig. 4b). On accepting e_v to be a parameter, which changes in the electron transfer reactions, we can derive a definition for its equivalent in the ion transfer processes: this is the e_z number, which corresponds to the electric charge (in

G_{ox}	- 3	- 2	- 1	0
	$\lvert\overline{\underline{\mathrm{N}}}\rvert^{3-}$	$\lvert\overline{\underline{\mathrm{O}}}\rvert^{2-}$	$\lvert\overline{\underline{\mathrm{F}}}\rvert^{1-}$	$\lvert\overline{\underline{\mathrm{Ne}}}\rvert^{0}$

G_{ox}	+ 5	+ 6	+ 7
	PO_4^{3-}	SO_4^{2-}	ClO_4^{1-}

(a)

G_{ox}	+ 7	+ 6	+ 5	+ 4	+ 3	+ 2	+ 1
7	ClO_4^{1-}	$Cl_2O_6^{0}$	ClO_3^{1-}	$Cl_2O_4^{0}$	ClO_2^{1-}		
6		SO_4^{2-}	$S_2O_6^{2-}$	SO_3^{2-}	$S_2O_4^{2-}$	SO_2^{2-}	
5			PO_4^{3-}	$P_2O_6^{4-}$	(PO_3^{3-})	$P_2O_4^{4-}$	PO_2^{3-}

q_c

$e_v = 8$

$\lvert\overline{\underline{\mathrm{N}}}\rvert^{3-}$	$\lvert\overline{\underline{\mathrm{O}}}\rvert^{2-}$	$\lvert\overline{\underline{\mathrm{F}}}\rvert^{1-}$	$\lvert\overline{\underline{\mathrm{Ne}}}\rvert^{0}$

$e_v = 0$

PO_4^{3-}	SO_4^{2-}	ClO_4^{1-}

(b)

	0	1	2	3	e_v
7	ClO_4^{1-}	$Cl_2O_6^{0}$	ClO_3^{1-}	$Cl_2O_4^{0}$	
6	SO_4^{2-}	$S_2O_6^{2-}$	SO_3^{2-}	$S_2O_4^{2-}$	
5	PO_4^{3-}	$P_2O_6^{4-}$	(PO_3^{3-})	$P_2O_4^{4-}$	

q_c

Figure 4. Oxidation state G_{ox} and e_v number as classification parameters of csu.

elementary units of charge), brought to the coordination centre by the ligands and which increases with increasing the number of the ligands attached to the centre. In the case of negatively charged species, enveloping the central core in the csu, both e_v and e_z assume positive values, whereas hydrogen cations penetrating the valence electron pairs, do not alter the e_v and are carriers of negative values of e_z. The principle of using the numerical description of csu by e_v and e_z of the coordination centre may be illustrated by the following examples:

$${}^{e_z}_{e_v} \quad {}^{0}_{8}\mathrm{F}^-,\ {}^{0}_{8}\mathrm{O}^{2-},\ {}^{-1}_{8}\mathrm{OH}^-,\ {}^{8}_{0}\mathrm{SO}_4^{2-},\ {}^{6}_{2}\mathrm{SO}_3^{2-},\ {}^{5}_{2}\mathrm{HSO}_3^-,\ {}^{7}_{0}\mathrm{SO}_3\mathrm{F}^-$$

In the case of a heteroligand csu, it is possible to distinguish, within the total e_z value, the partial contributions $e_z^{'}$, $e_z^{''}$ ... brought in by the individual ligands, as in the following example:

$$\begin{smallmatrix}e_z\\ e_v\end{smallmatrix}\quad {}^{6}_{0}\mathrm{HSO_3F}^{0}\quad e_{zF}=1\quad e_{zO}=6\quad e_{zH}=-1$$

As might be expected from the definition, the e_v and e_z numbers do not distinguish isomers and tautomers in particular. The e_z values of individual tautomers, having identical e_v values, are identical, as may be seen in the following example:

$${}^{5}_{2}\mathrm{HSO_3^-}\quad \text{or}\quad {}^{5}_{2}\mathrm{SO_2OH^-}$$

Irrespective of the position of hydrogen cations, relative to the valence electrons of the coordination centre, their presence in the structure generates the same e_z. Hence, the change of e_z in a reaction of hydrogen cation transfer does not depend on the position of hydrogen cations in the starting materials or the products of reaction. The valence structures of the ligands can also be described in terms of the numbers e_{zl} and e_{vl}. Simple ligands formed *e.g.* by the elements of the 1st period having n = 1 can be described as follows:

$$\begin{array}{llll}
\begin{smallmatrix}e_z\\ e_v\end{smallmatrix} & {}^{0}_{8}\mathrm{N}^{3-} & {}^{0}_{8}\mathrm{O}^{2-} & {}^{0}_{8}\mathrm{F}^{-}\\
 & & {}^{-1}_{8}\mathrm{NH}^{2-} & {}^{-1}_{8}\mathrm{OH}^{-}\\
 & & & {}^{-2}_{8}\mathrm{NH_2^-}
\end{array}$$

The e_z and e_v numbers provide a basis for a general and uniform definition of elementary acid-base and redox reactions. This definition consists in defining the following notions: red – reducer, featured by e_v decrease, donor of electrons; ox – oxidiser, featured by e_v increase, acceptor of electrons; bas – base, featured by e_z decrease, donor of negatively charged ligands or acceptor of H^+ cations; ac – acid, featured by e_z increase, acceptor of negatively charged ligands or donor of H^+ cations.

4.3. Monofunctional transformations of chemical structural units [8,13]: When considering various reactions in terms of the changes in e_z and e_v of the coordination centre of the csu transformed, we can distinguish a group of redox processes associated with transfer of electrons, in which e_v changes with no change in e_z, as in the following example:
$\begin{smallmatrix}e_z\\ e_v\end{smallmatrix}\ 2\,{}^{0}_{5}\mathrm{Fe}^{3+} + {}^{0}_{2}\mathrm{Sn}^{2+} \rightarrow 2\,{}^{0}_{6}\mathrm{Fe}^{2+} + {}^{0}_{0}\mathrm{Sn}^{4+}$ and acid-base processes with ionic ligand transfer, in which e_z changes with no change in e_v of the coordination centre, *e.g.*:

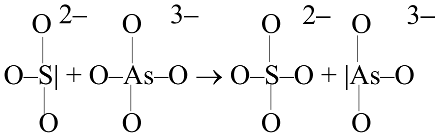
$$\begin{smallmatrix}e_z\\ e_v\end{smallmatrix}\ {}^{6}_{2}\mathrm{SO_3^{2-}} + {}^{4}_{0}\mathrm{SiO_2^0} \rightarrow {}^{4}_{2}\mathrm{SO_2^0} + {}^{6}_{0}\mathrm{SiO_3^{2-}};\quad \begin{smallmatrix}e_z\\ e_v\end{smallmatrix}\ {}^{-3}_{8}\mathrm{NH_3^0} + {}^{-1}_{8}\mathrm{HCl}^{0} \rightarrow {}^{-4}_{8}\mathrm{NH_4^+} + {}^{0}_{8}\mathrm{Cl}^{-}$$

The reactants in the redox process are: a reducer (red) – a donor of electrons which is transformed in the reaction into an oxidizer (ox), described by a decreased value of e_V: ${}^{z}_{v}\mathrm{red} \rightarrow {}^{z}_{v\text{-}n}\mathrm{ox} + \mathrm{ne}^{-}$, *e.g.* $2\,{}^{0}_{8}\mathrm{I}^{-} \rightarrow {}^{0}_{7}\mathrm{I}^{0}_{2} + 2\mathrm{e}$; an oxidizer (ox) – an acceptor of electrons which is transformed, in the reaction, into a reducer (red) described by an increased value of e_V: ${}^{z}_{v}\mathrm{ox} + \mathrm{me}^{-} \rightarrow {}^{z}_{v+m}\mathrm{red}$, *e.g.* ${}^{0}_{5}\mathrm{Fe}^{3+} + 1\mathrm{e}^{-} \rightarrow {}^{0}_{6}\mathrm{Fe}^{2+}$. The red-ox process is a reaction of an oxidizer with a reducer, where an electron transfer gives rise to a new reducer and a new oxidizer: $\mathrm{m}\,{}^{z}_{v}\mathrm{red}_{1} + \mathrm{n}\,{}^{z}_{v}\mathrm{ox}_{2} \rightarrow \mathrm{m}\,{}^{z}_{v\text{-}n}\mathrm{ox}_{1} + \mathrm{n}\,{}^{z}_{v+m}\mathrm{red}_{2}$, where n×m is the number of electrons transferred from the reducer to the oxidizer, *e.g.* $2\,{}^{0}_{8}\mathrm{I}^{-} + 2\,{}^{0}_{5}\mathrm{Fe}^{3+} \rightarrow {}^{0}_{7}\mathrm{I}^{0}_{2} + 2\,{}^{0}_{6}\mathrm{Fe}^{2+}$.

In an analogous manner the following are the reactants in the ac-bas process: a base (bas) – a donor of negative charges brought in the form of simple anions or an acceptor hydrogen cations which is transformed, in the reaction, into an acid (ac) described with a decreased value of e_Z: ${}^{z}_{v}\mathrm{bas}(+\mathrm{nH}^{+}) \rightarrow {}^{z-n}_{v}\mathrm{ac} + \mathrm{nA}^{-}$, (where nA^{-} is the number of negative charges transferred in the form of anions) *e.g.* ${}^{6}_{2}\mathrm{SO}^{2-}_{3} \rightarrow {}^{4}_{2}\mathrm{SO}^{0}_{2} + \mathrm{O}^{-2}$, ${}^{-3}_{8}\mathrm{NH}^{0}_{3} + \mathrm{H}^{+} \rightarrow {}^{-4}_{8}\mathrm{NH}^{+}_{4}$; an acid (ac) – an acceptor of negative charges transferred in the form of simple anions or a donor of hydrogen cations which, in the reaction, is transformed into a base (bas), described by an increased value of e_Z: ${}^{z}_{v}\mathrm{ac} + \mathrm{mA}^{-} \rightarrow {}^{z+m}_{v}\mathrm{bas}(+\mathrm{mH}^{+})$, *e.g.* ${}^{4}_{0}\mathrm{SiO}^{0}_{2} + \mathrm{O}^{2-} \rightarrow {}^{6}_{0}\mathrm{SiO}^{2-}_{3}$, ${}^{-1}_{8}\mathrm{HCl} \rightarrow {}^{0}_{8}\mathrm{Cl}^{-} + \mathrm{H}^{+}$

The acid-base process is a reaction proceeding between a base and an acid, which leads to the formation of a new acid and a new base, as a result of transfer of anionic ligands or hydrogen cations: $\mathrm{m}\,{}^{z}_{v}\mathrm{bas}_{1} + \mathrm{n}\,{}^{z}_{v}\mathrm{ac}_{2} \rightarrow \mathrm{m}\,{}^{z-n}_{v}\mathrm{ac}_{1} + \mathrm{n}\,{}^{z+m}_{v}\mathrm{bas}_{2}$; *e.g.* ${}^{6}_{2}\mathrm{SO}^{2-}_{3} + {}^{4}_{0}\mathrm{SiO}^{0}_{2} \rightarrow {}^{4}_{2}\mathrm{SO}^{0}_{2} + {}^{6}_{0}\mathrm{SiO}^{2-}_{3}$, ${}^{-3}_{8}\mathrm{NH}^{0}_{3} + {}^{-1}_{8}\mathrm{HCl} \rightarrow {}^{-4}_{8}\mathrm{NH}^{+}_{4} + {}^{0}_{8}\mathrm{Cl}^{-}$.

4.4. Bifunctional transformations of chemical structural units [8,9]: Besides the processes that proceed with the change of only e_V or e_Z, there are processes in which both of these numbers change, thus indicating the simultaneous occurrence of both red-ox and ac-bas transformations. The nature of such a process depends on the structure of the valence shells of the given coordination centre. The course of reaction is different in case of species with the sp block central cores, in which free valence electrons e_V are bound along with anionic ligands within one and the same valence shell, than in species with the dsp block central cores, where the e_V electrons are bound in the d subshell of a shell n, as well as a number of ligands bound mainly in the sp subshell of the next electron shell (n + 1). Within the chemical structural units formed by the sp block central core, where both electrons and ligands are bound with the coordination centre on the same valence orbitals, the possibility of attachment of a ligand or an electron pair depends on the existence of electron vacancy in the sp shells of the centre. Such a vacancy can be formed by the action of an oxidizer, which withdraws electrons, or of an acid, which withdraws anionic ligands, and that can then be filled with other structural elements by the action of a base – donor of anionic ligands, or a reducer – donor of electrons. Under such a situation, a particular importance is given to bifunctional reagents, which are capable of acting *e.g.* as electron acceptors (ox) and, at the same time, as donors of anionic ligands (bas). Such reagents provoke a red-ac transformation of a partner, which loses electrons but accepts simple anions at the same time. An example of such a situation is observed in the action of arsenate(V) on sulphate(III): ${}^{6}_{2}SO_3^{2-} + {}^{8}_{0}AsO_4^{3-} \rightarrow {}^{8}_{0}SO_4^{2-} + {}^{6}_{2}AsO_3^{3-}$, where the condition of $e_z + e_v$ = const is observed and the electric charge of the reacting species remains unchanged. The elementary nature of such a transformation is a result of a specific coupling of the events of oxidation-reduction (change in e_v) and acid-base transformation (change in e_z) where, in consequence, the appearance of a new oxide ligand at the coordination centre is accompanied by elimination of an equivalent pair of electrons, and inversely, elimination of an oxide ligand is accompanied by the appearance of an electron pair at the coordination centre. Formally, it can be regarded as a transfer of an oxygen atom.



It is worth to mention that free oxygen, for simplicity taken as an oxygen atom, is a bifunctional reagent, since it is, at the same time, an oxidizer, an acceptor of electron pair and a donor of an oxide anion: $O^0 + 2e^- \rightarrow O^{2-}$. Similarly free hydrogen, for simplicity taken as hydrogen atom, exhibits a dual action, since in many reactions it is, at the same time, a reducer, an electron donor, and an acid – donor of hydrogen cation formed: $H^0 \rightarrow H^+ + e^-$.

For these reasons the general definition distinguishes, in addition to the oxidation-reduction and acid-base reactions, also a group of reactions in which both these processes proceed at the same time and are coupled with each other. The coupled redac-oxbas process proceeds in the following systems of reagents. A reducer coupled with an acid (redac) is a donor of electrons and acceptor of anions of equivalent electric charge, or a donor of electrons and equivalent number of hydrogen cations, which is transformed in the reaction into an oxidizer coupled with a base (oxbas). The product is described with e_v smaller and e_z higher than those of the starting species, with the condition of $e_z + e_v$ = const:

${}^{z}_{v}\text{redac} + nA^- \rightarrow m\,{}^{z+n}_{v-n}\text{oxbas} + ne^-(+nH^+)$, *e.g.* ${}^{6}_{2}SO_3^{2-} + O^{2-} \rightarrow {}^{8}_{0}SO_4^{2-} + 2e^-$,

${}^{-2}_{6}CH_3OH \rightarrow {}^{0}_{4}CH_2O + 2e^- + 2H^+$, which is formally univocal with the following notation:

${}^{z}_{v}\text{redac} + nA^0 \rightarrow {}^{z+n}_{v-n}\text{oxbas}(+nH^0)$, *e.g.* ${}^{6}_{2}SO_3^{2-} + O^0 \rightarrow {}^{8}_{0}SO_4^{2-}$,

${}^{-2}_{6}CH_3OH \rightarrow {}^{0}_{4}CH_2O + 2H^0$. An oxidizer coupled with a base (oxbas) is an acceptor of electrons and donor of anions of equivalent charge or acceptor of electrons and an equal number of protons, which is transformed in the reaction into a reducer coupled with an acid (redac), described with a smaller value of e_z and a higher value of e_v, but with observation of the conditions $e_z + e_v$ = const:

${}^{z}_{v}\mathrm{oxbas} + \mathrm{me}^{-}(+\mathrm{mH}^{+}) \rightarrow {}^{z-m}_{v+m}\mathrm{redac} + \mathrm{mA}^{-}$, *e.g.* ${}^{8}_{0}\mathrm{AsO}_4^{3-} + 2\mathrm{e}^{-} \rightarrow {}^{6}_{2}\mathrm{AsO}_3^{3-} + \mathrm{O}^{2-}$, ${}^{1}_{4}\mathrm{HNO} + 2\mathrm{e}^{-} + 2\mathrm{H}^{+} \rightarrow {}^{-1}_{6}\mathrm{H}_3\mathrm{NO}$, which is formally univocal with the following notation: ${}^{z}_{v}\mathrm{oxbas} + (+\mathrm{mH}^{0}) \rightarrow {}^{z-m}_{v+m}\mathrm{redac} + \mathrm{mA}^{0}$, *e.g.* ${}^{8}_{0}\mathrm{AsO}_4^{3-} \rightarrow {}^{6}_{2}\mathrm{AsO}_3^{3-} + \mathrm{O}^{0}$,

${}^{1}_{4}\mathrm{HNO} + 2\mathrm{H}^{0} \rightarrow {}^{-1}_{6}\mathrm{H}_2\mathrm{NOH}$. The coupled reaction redac-oxbas is a reaction proceeding between a coupled reducer redac and a coupled oxidizer oxbas. The transfer of ionic ligands and electrons (transfer of atoms concerned) results in formation of a new coupled oxidizer (oxbas) and a new coupled reducer (redac): $\mathrm{m}\,{}^{z}_{v}\mathrm{redac}_1 + \mathrm{n}\,{}^{z}_{v}\mathrm{oxbas}_2 \rightarrow \mathrm{m}\,{}^{z+n}_{n-n}\mathrm{oxbas}_1 + \mathrm{n}\,{}^{z-m}_{v-m}\mathrm{redac}_2$, *e.g.*

${}^{6}_{2}\mathrm{SO}_3^{2-} + {}^{8}_{0}\mathrm{AsO}_4^{3-} \rightarrow {}^{8}_{0}\mathrm{SO}_4^{2-} + {}^{6}_{2}\mathrm{AsO}_3^{3-}$, ${}^{-2}_{6}\mathrm{CH}_3\mathrm{OH} + {}^{1}_{4}\mathrm{HNO} \rightarrow {}^{0}_{4}\mathrm{CH}_2\mathrm{O} + {}^{-1}_{6}\mathrm{H}_3\mathrm{NO}$.

4.5. Disproportionation and synproportionation reactions [9,11]: The disproportionation reactions, in which a molecule splits into two parts described with different values of either e_z, e_v or a coupled system $e_z + e_v$ and their opposite synproportionation reactions, present a peculiar case of reactions within the uniform definition of acids, bases, oxidizers and reducers:

$$
\begin{array}{lll}
{}^{z}_{v}\mathrm{redox} \;\substack{\mathrm{dis}\rightarrow\\ \leftarrow\mathrm{syn}}\; {}^{z}_{v-n}\mathrm{ox} + {}^{z}_{v+n}\mathrm{red}, & \textit{e.g.} & {}^{0}_{7}\mathrm{S}_2^{2-} \;\substack{\mathrm{dis}\rightarrow\\ \leftarrow\mathrm{syn}}\; {}^{0}_{6}\mathrm{S}^{0} + {}^{0}_{8}\mathrm{S}^{2-} \\
{}^{z}_{v}\mathrm{acbas} \;\substack{\mathrm{dis}\rightarrow\\ \leftarrow\mathrm{syn}}\; {}^{z+n}_{v}\mathrm{bas} + {}^{z-n}_{v}\mathrm{ac}, & \textit{e.g.} & {}^{0}_{7}\mathrm{S}_2\mathrm{O}_7^{2-} \;\substack{\mathrm{dis}\rightarrow\\ \leftarrow\mathrm{syn}}\; {}^{8}_{0}\mathrm{SO}_4^{2-} + {}^{6}_{0}\mathrm{SO}_3, \\
 & & 2\,{}^{-1}_{8}\mathrm{OH}^{-} \;\substack{\mathrm{dis}\rightarrow\\ \leftarrow\mathrm{syn}}\; {}^{0}_{8}\mathrm{O}^{2-} + {}^{-2}_{8}\mathrm{H}_2\mathrm{O}, \\
2\,{}^{z}_{v}\mathrm{redac-oxbas} \;\substack{\mathrm{dis}\rightarrow\\ \leftarrow\mathrm{syn}}\; {}^{z+n}_{v-n}\mathrm{oxbas} + {}^{z-n}_{v+n}\mathrm{redac}, & \textit{e.g.} & 2\,{}^{4}_{4}\mathrm{ClO}_2^{-} \;\substack{\mathrm{dis}\rightarrow\\ \leftarrow\mathrm{syn}}\; {}^{8}_{0}\mathrm{ClO}_4^{-} + {}^{0}_{8}\mathrm{Cl}^{-}
\end{array}
$$

Besides the symmetrical acts, also asymmetrical reactions are encountered, such as *e.g.* $4\,{}^{6}_{2}\mathrm{ClO}_3 \;\substack{\mathrm{dis}\rightarrow\\ \leftarrow\mathrm{syn}}\; 3\,{}^{8}_{0}\mathrm{ClO}_4^{-} + {}^{0}_{8}\mathrm{Cl}^{-}$.

4.6. Transformations of multicentre species [9,11,12,13]: The general, uniform definition of oxidizers-reducers and acids-bases covers transformations of various multicentre species, built up from chemical structural units. The values of e_z i e_v of structural units are replaced by mean values of $\bar{e}_z$ and $\bar{e}_v$ of central cores of the multicentre species. The $\bar{e}_z$ number is a sum of charges of simple ligands, divided by the number of central cores. By analogy, $\bar{e}_v$ is the number of valence electrons remained at the central cores (along with the centre-binding electrons) shared by one core in the coordination centre. The values of $\bar{e}_z$ and $\bar{e}_v$ are integers, which remain constant in cases where the species is composed of one type of simple structural units, as *e.g.* ${}^{e_z}_{e_v}$ ${}^{0}_{6}\mathrm{S}^{0}$, ${}^{0}_{6}\mathrm{S}_6^{0}$, ${}^{0}_{6}\mathrm{S}_7^{0}$, ${}^{0}_{6}\mathrm{S}_8^{0}$, ${}^{0}_{6}\mathrm{S}_9^{0}$ ... (nS^{0}). In cases, where the species consist of different structural units, their $\bar{e}_z$ and $\bar{e}_v$ are variable fractional numbers. An important case is presented by molecules composed of two different structural units, if the share of one of them increases infinitely, as *e.g.*: ${}^{e_z}_{e_v}$ ${}^{8}_{0}\mathrm{SO}_4^{2-}$, ${}^{7}_{0}\mathrm{S}_2\mathrm{O}_7^{2-}$, ${}^{6.66}_{0}\mathrm{S}_3\mathrm{O}_{10}^{2-}$, ${}^{6.5}_{0}\mathrm{S}_4\mathrm{O}_{13}^{2-}$, ${}^{6.4}_{0}\mathrm{S}_5\mathrm{O}_{16}^{2-} \ldots ({}^{8}_{0}\mathrm{SO}_4^{2-} \cdot \mathrm{n}\,{}^{6}_{0}\mathrm{SO}_3^{0})$. In this case $\bar{e}_z$ decrease from the initial value 8 and, as n increases, they tend to the limit value of 6, which is the value of e_z of the csu SO_3^{0}.

In the uniform definition of acids-bases and oxidizers-reducers also the changes in mean values of $\bar{e}_z$ and $\bar{e}_v$ account for the acts of either ac-bas or red-ox type. In equations of the reactions multicentre species are represented as sets of csu described by integral values of e_z and e_v, thus enabling to derive the equations of the partial reactions: ${}^{6.5}_{0}S_4O_{13}^{2-} + O^{2-} \rightarrow {}^{6.66}_{0}S_3O_{10}^{2-} + {}^{8}_{0}SO_4^{2-}$, which can be represented in terms of csu as: $({}^{8}_{0}SO_4^{2-} \cdot 3\,{}^{6}_{0}SO_3^{0}) + O^{2-} \rightarrow ({}^{8}_{0}SO_4^{2-} \cdot 2\,{}^{6}_{0}SO_3^{0}) + {}^{8}_{0}SO_4^{2-}$ and by analogy: ${}^{\;\;0}_{6.5}S_4^{2-} + 2e^- \rightarrow {}^{\;\;0}_{6.66}S_3^{2-} + {}^{0}_{8}S^{2-}$, which can be represented in terms of csu as: $({}^{0}_{8}S^{2-} \cdot 3\,{}^{0}_{6}S^{0}) + 2e^- \rightarrow ({}^{0}_{8}S^{2-} \cdot 2\,{}^{0}_{6}S^{0}) + {}^{0}_{8}S^{2-}$.

5. Principles of morphological classification of chemical structural units (csu)

The classification of chemical structural units, both those existing as independent fragments of chemical structures and those occurring as fragments of multicentre molecules and ions is based on their numerical description, which consists of:

- numerical representation of elemental composition of the csu (ΣE) in terms of the parameters of tridimensional periodic system of atomic cores, *i.e.* number of core electron shells n, core charge q, and number of valence sub-shells l. This values enable to classify the csu, according to the component elements,
- numerical treatment of the area of chemical transformations (ΣT), which is the electron and ligand sheath of the coordination centre, in terms of the e_z and e_v numbers, that determine the elementary transformations of the red-ox and ac-bas type. For ΣE = const, it gives classification systems of structures related by the elementary transformations and being the essential object of the morphological classification.

5.1. Chemical elements in the morphological classification: The chemical composition of csu, *i.e.* the kind of element of the coordination centre and the kinds of the ligand elements, treated in numerical terms, leads to the conventional and generally accepted principles of classification of chemical compounds in terms of parameters of the periodical system of elements. The element, which is the csu coordination centre, determines the membership of the csu in the family of compounds of this element, as shown in Table 1.

Table 1.

csu	H^-	H_3PO_3	CN_2^{2-}	VOF_2	Pm^{3+}
central core	H^+	P^{5+}	C^{4+}	V^{5+}	Pm^{7+}
n_c	0	2	1	3	5
q_c	1	5	4	5	7
l_c	1	2	2	3	4
membership in the family of csu	csu of hydrogen	csu of phosphorus	csu of carbon	csu of vanadium	csu of promethium

Two numbers, n_z and q_z, describe the membership of csu in the sub-set of molecules of the given element, both in the case of hydrogen and the anionic ligand, which is always based on an element of the sp block as shown in Table 2.

Table 2.

csu	NH_4^+	CN^-	SF_6	BNO^{2-}		HSO_3F			CuS_2^{2-}
central core	N^{5+}	C^{4+}	S^{6+}	B^{3+}		S^{6+}			Cu^{11+}
n_c	1	1	2	1		2			3
q_c	5	4	6	3		6			11
l_c	2	2	2	2		2			3
ligands	H^+	N^{3-}	F^-	N^{3-}	O^{2-}	H^+	F^-	O^{2-}	S^{2-}
n_z	0	1	1	1	1	0	1	1	2
q_z	1	5	7	5	6	1	7	6	6
membership in subset of csu	Nitrogen - H^+	Carbon - N^{3-}	Sulphur - F^-	Boron - O^{2-}; N^{3-}		Sulphur - H^+; F^-; O^{2-}			Copper - S^{2-}

The numerical description of elemental composition of the csu with the trielemental ligands environment (that are, up to now, the limit of our knowledge in this respect), is confined to nine numbers. Three of them: n_c q_c and l_c are concerned with the coordination centre and the remaining six: n'_z q'_z, n''_z $q''_z$and n'''_z q'''_zdescribe the ligand-forming elements.

In the case of homoligand molecules, the numerical description is limited to five parameters: n_c q_c l_c n_z q_z. If we vary only one of the numbers, describing the elemental composition of the csu, we obtain one-dimensional classification systems, derived from corresponding cross-sections of the periodic system. The following series of csu may be the examples presented in Table 3.

Table 3.

Group in the periodic system (Mendeleev's series)	n_c	H_2O 1	H_2S 2	H_2Se 3	H_2Te 4	H_2Po 5
Period in the periodic system (Langmuir's series)	q_c	AlO_4^{5-} 3	SiO_4^{4-} 4	PO_4^{3-} 5	SO_4^{2-} 6	ClO_4^- 7
Intra-periodic group	l_c	PbO_2 2	HfO_2 3	CeO_2 4		
Ligand group	n_z	PF_3 1	PCl_3 2	PBr_3 3	PI_3 4	
Ligand period	q_z	BN_2^{3-} 5	BO_2^- 6	BF_2^+ 7		

$l_c = 2$

n_c	4	5	6	7	8	q_c
2		(PO_3^{3-})	SO_3^{2-}	ClO_3^{1-}		
3	GeO_3^{4-}	AsO_3^{3-}	SeO_3^{2-}	BrO_3^{1-}		
4	SnO_3^{4-}	SbO_3^{3-}	TeO_3^{2-}	IO_3^{1-}	XeO_3^{0}	
5		BiO_3^{3-}	PoO_3^{2-}	AtO_3^{1-}	(RnO_3^{0})	

n_z	5	6	7	q_z
1	AsN_2^{1-}	AsO_3^{1-}	AsF_6^{1-}	
2	AsP_2^{1-}	AsS_3^{1-}	$AsCl_6^{1-}$	
3		$AsSe_3^{1-}$	$AsBr_6^{1-}$	
4			AsI_6^{1-}	

$l_z = 2$

$n_c = 3$

l_c	4	5	6	7	8	q_c
3	TiO_4^{4-}	VO_4^{3-}	CrO_4^{2-}	MnO_4^{1-}		
2	GeO_4^{4-}	AsO_4^{3-}	SeO_4^{2-}	BrO_4^{1-}	RuO_4^{0}	

n_c	2	3	4	l_c
1	CO_2^{0}			
2	SiO_2^{0}			
3	GeO_2^{0}	TiO_2^{0}		
4	SnO_2^{0}	ZrO_2^{0}		
5	PbO_2^{0}	HfO_2^{0}	CeO_2^{0}	

$q_c = 4$

Figure 5. Examples of two-parameter classifications of csu according to the type of elements involved: q_c, n_c, l_c – parameters describing the central core element; q_z, l_z – parameters describing the ligand.

If we take, as variables, two numbers used for describing the chemical composition of homoligand molecules, we can also distinguish two cases: the variables are either the number describing the central cores or those describing the ligands. Here we obtain tabular classification systems derived from corresponding fragments of the periodic system (Fig. 5).

5.2. Chemical reactions and the morphological classification: If the numbers describing the central core element are constant, we can single out sets of csu transformable in elementary acts of red-ox and ac-bas reactions, which are the object of the essential part of morphological classification. Thus, assuming $n_c = 2$, $q_c = 6$, $l_c = 2$, $n_z = 1$, and $q_z = 6$ we define the set of oxygen-containing csu of sulphur, interconnected by elementary transformations. Further classification of thus isolated sets of csu is based on the numbers e_z and e_v, which describe the ligand and electron environment of their central cores. The changes in this environment result from elementary acts of ac-bas and red-ox processes, that consist in binding or elimination of electric charges either as valence electrons or ligands. The negative charge of the ligands is secured, owing to the high electronegativity of the ligand-forming element, which is higher than that of the coordination centre. Figure 6 shows a number of ligands, in the system q_c *vs.* n_c

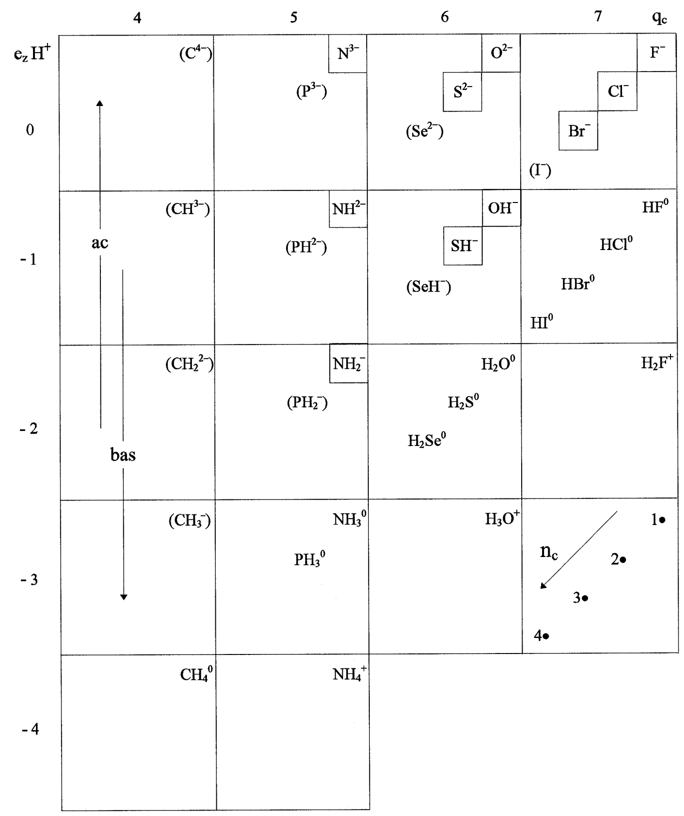


Figure 6. Classification of hydrogen ligands in the system q_c *vs.* $e_z\,H^+$ with the n_c axis split into diagonals of corresponding fields.

and e_{zH+}. The ligands, that belong to this family, are transformed in the ac-bas reactions, involving hydrogen cations, at q_c = const and n_c = const. The ligands based on strongly negative elements, occurring usually in csu of both sp and dsp block elements, have been marked with checks. The weakly bounded ligands of elements of lower electronegativity, occurring primarily at centres formed by the dsp elements, have been put in parentheses.

The e_z and e_v numbers, which assume only integral values in csu, determine the fundamental classification lattice, which is conveniently represented in the form of a table. The individual fields are inter-related by the elementary transformations: ac-bas (e_v = const), red-ox (e_z = const), and redac-oxbas ($e_z + e_v$ = const), as shown in Fig. 7. This dynamic classification network enables to outlay the homoligand csu of all elements. In csu of the sp block elements the valence electrons e_v and the ligands e_z are bound within the same valence shell of the coordination centre, which enables to reduce the $e_z - e_v$ table to a right triangle, in which the hypotenuse joins the position $e_v = 8$ with e_z = max. Such a limitation does not exist for simple csu of the dsp block elements, since in this case the number of covalently bound simple ligands, mainly within the sp orbitals of the coordination centre is, to a considerable degree, inde-

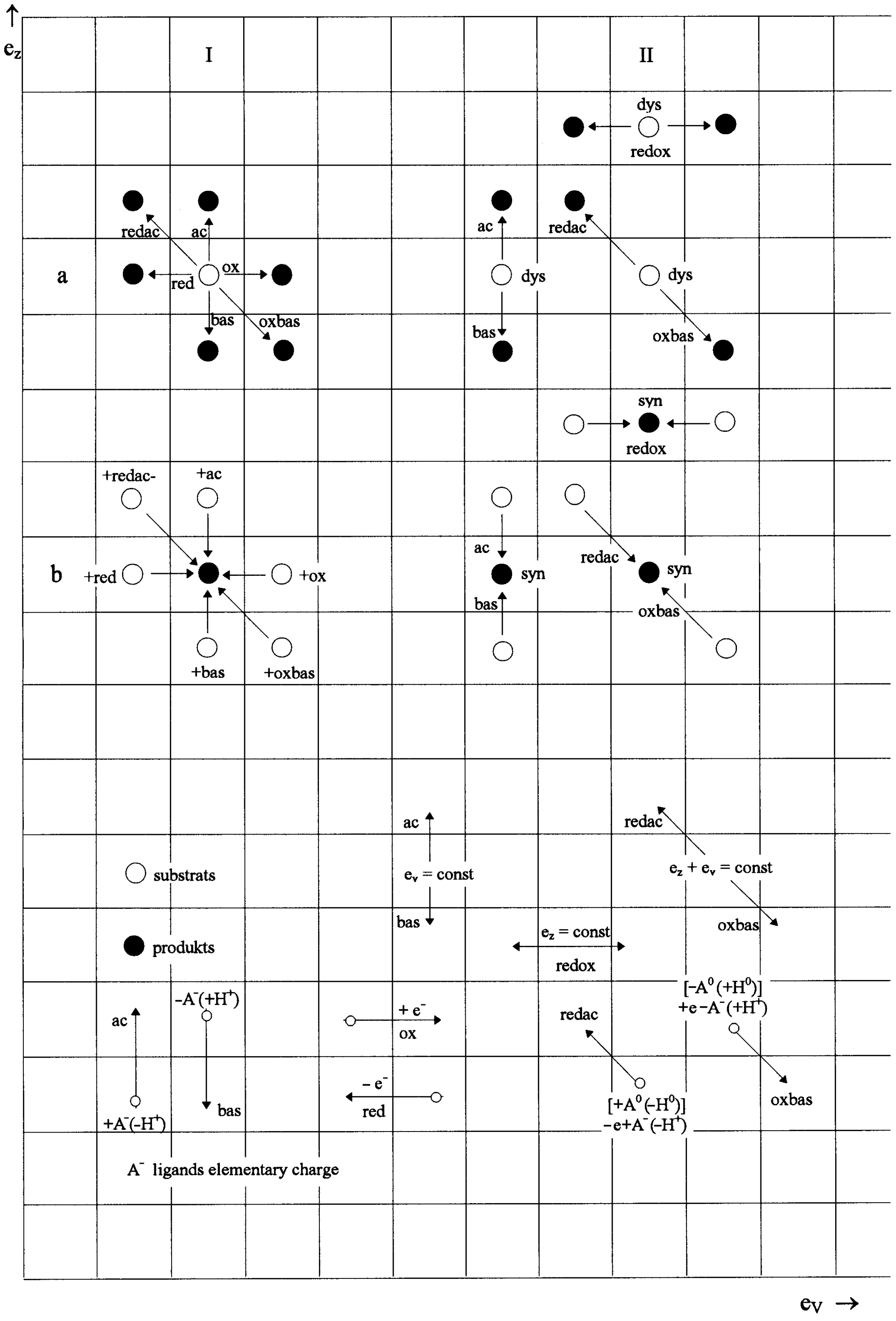
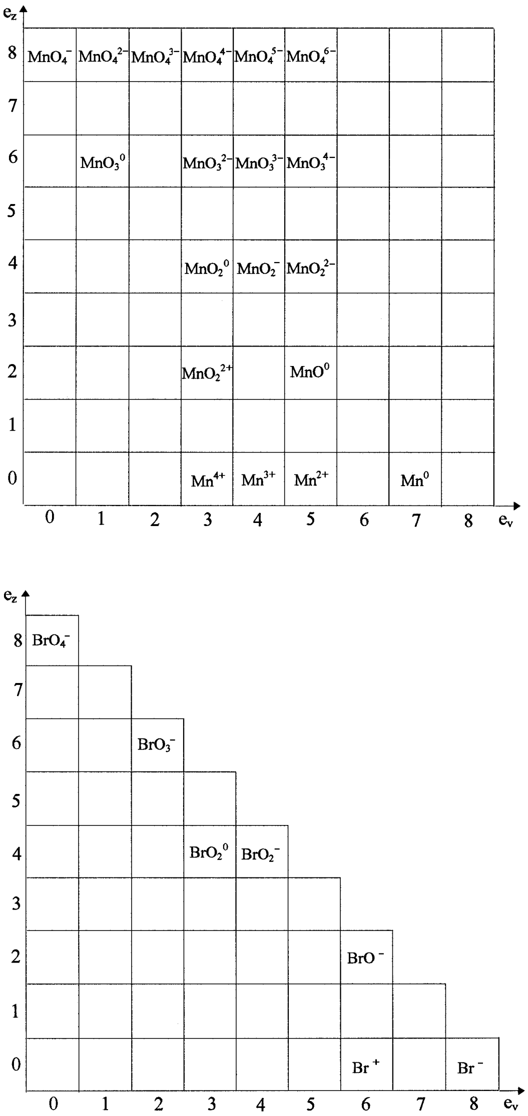


Figure 7. Transformations of chemical structural units in the classification system e_Z *vs.* e_V: a – chemical properties of csu, b – csu preparation method, I – unidirectional transformations, II – dis- and synproportionation reactions.

pendent of the number of valence electrons e_v localised in the d orbitals of the central core, as shown in Fig. 8 as an example of classification of oxygen-containing csu of manganese and bromine. Depending on the charge of the ligands, resulting from the assignment of electrons to them conforming to the direction of polarization, csu appear only in the fields that fulfil the condition $e_z = n \cdot k$ (where k is the charge of the ligand) and, in the case of elements of the sp block, central cores have been described by even numbers of e_v electrons. As an example, the classification of simple csu of phosphorus with H^+, F^-, O^{2-}, and N^{3-} in the e_z *vs.* e_v and q_z coordinates is shown in Fig. 9. Chemical structural units bearing identical charge, which results from the bal-



e_z \ e_v	0	1	2	3	4	5	6	7	8
8	MnO_4^-	MnO_4^{2-}	MnO_4^{3-}	MnO_4^{4-}	MnO_4^{5-}	MnO_4^{6-}			
7									
6		MnO_3^0		MnO_3^{2-}	MnO_3^{3-}	MnO_3^{4-}			
5									
4				MnO_2^0	MnO_2^-	MnO_2^{2-}			
3									
2				MnO_2^{2+}		MnO^0			
1									
0				Mn^{4+}	Mn^{3+}	Mn^{2+}		Mn^0	

e_z \ e_v	0	1	2	3	4	5	6	7	8
8	BrO_4^-								
7									
6			BrO_3^-						
5									
4				BrO_2^0	BrO_2^-				
3									
2							BrO^-		
1									
0							Br^+		Br^-

Figure 8. Oxy – csu of a dsp element (Mn) and of a sp element (Br) in the e_z – e_v classification.

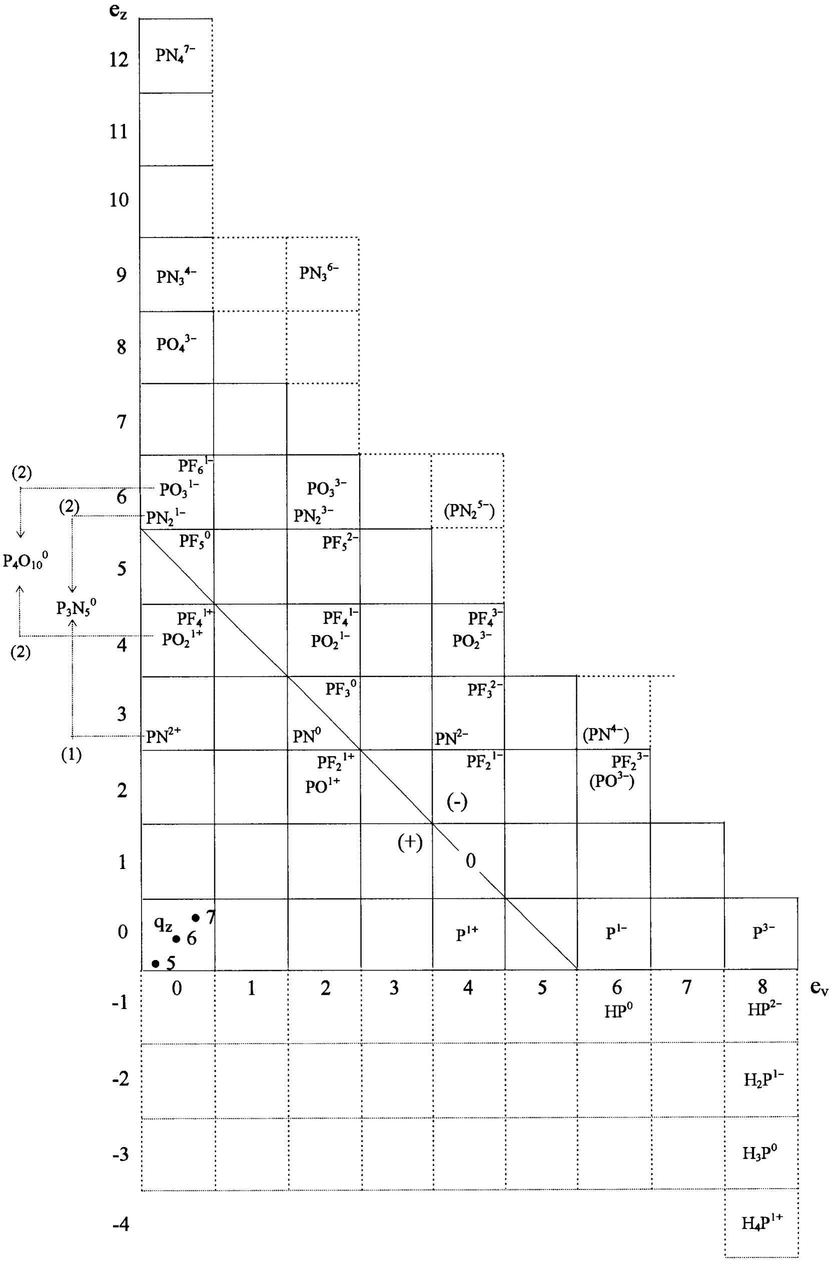


Figure 9. Phosphorus csu with F^-, O^{2-}, N^{3-}, and H^+ ligands in the $e_z - e_v$ and q_z classification systems.

ance of charge of the central core q_c and charge of ligands e_z and valence electrons e_v are disposed, in the $e_z - e_v$ system, on the hypotenuses that fulfil the condition $e_z + e_v =$ const. Electrically neutral csu are disposed on the hypotenuse of $e_z + e_v = q_c$, and the electrically charged csu occur on successive hypotenuses differing by 1 and determined by the condition $e_z + e_v > q_c$ (negatively charged csu) or $e_z + e_v < q_c$ (positively charged csu).

For the classificational considerations on simple heteroligand csu the $e_z - e_v$ system can be extended by the use of fractional values of $e'_z, e''_z, e'''_z, \ldots$, describing the contributions of individual ligands, under the general condition of $e_z = e'_z + e''_z + e'''_z$. From the viewpoint of classification the primary parameter is here total e_z supplemented by fractional values of e'_z. Figure 10 shows a classification system for the diheteroligand hydroxy csu of sulphur with the e_{zH} axis disposed on the hypotenuse of the particular fields e_z and e_v. The e_{zH} value does not determine the position of hydrogen, but merely indicates its presence. Also other e_z values do not distinguish isomeric structures. Figure 11 shows the classifications of triheteroligand csu of sulphur, in which the e_{zF} and $e_{zH'}$ axes determine the secondary tables inscribed in the $e_z - e_v$ fields. The values of e_{zO} arise from the values of total e_z and e_{zF}, as well as e_{zH}, $e_{zO} = e_z - (e_{zF} + e_{zH})$. Such a triheteroligand system is, until today, the limiting case of existing heterogeneous ligands at the coordination centre of csu. Since the classification system of elementary transformations in the four-axis system of $e'_z\, e''_z, e'''_z\; e_v$ is not very clear, it is preferred

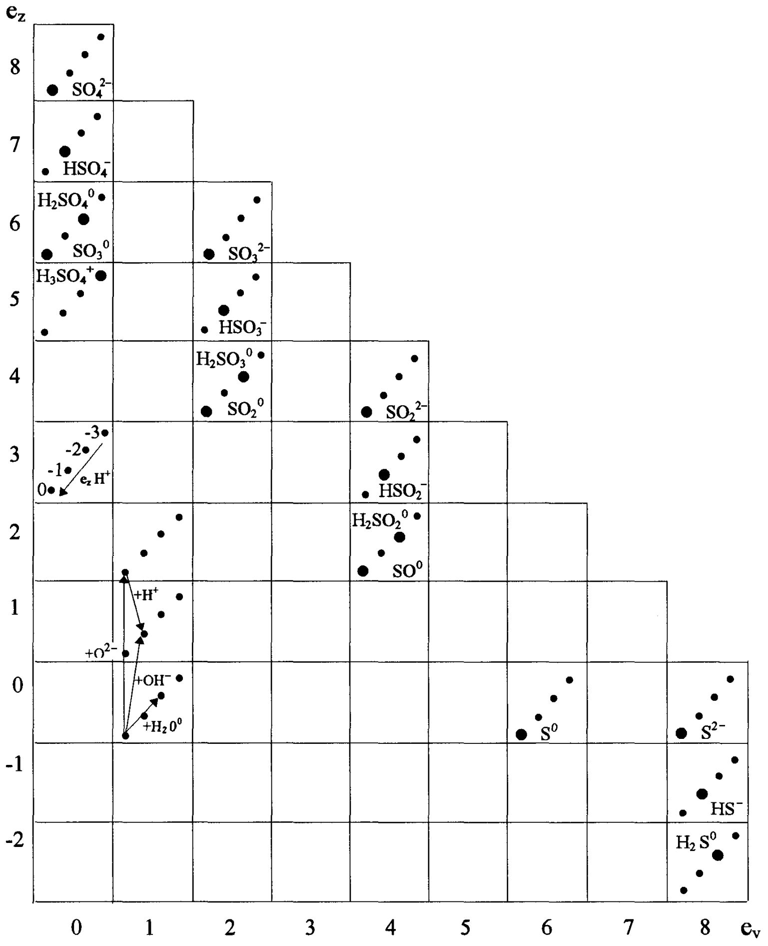


Figure 10. Oxy-hydrogen csu of sulphur in $e_z - e_v$ and e_{zH+} classification systems.

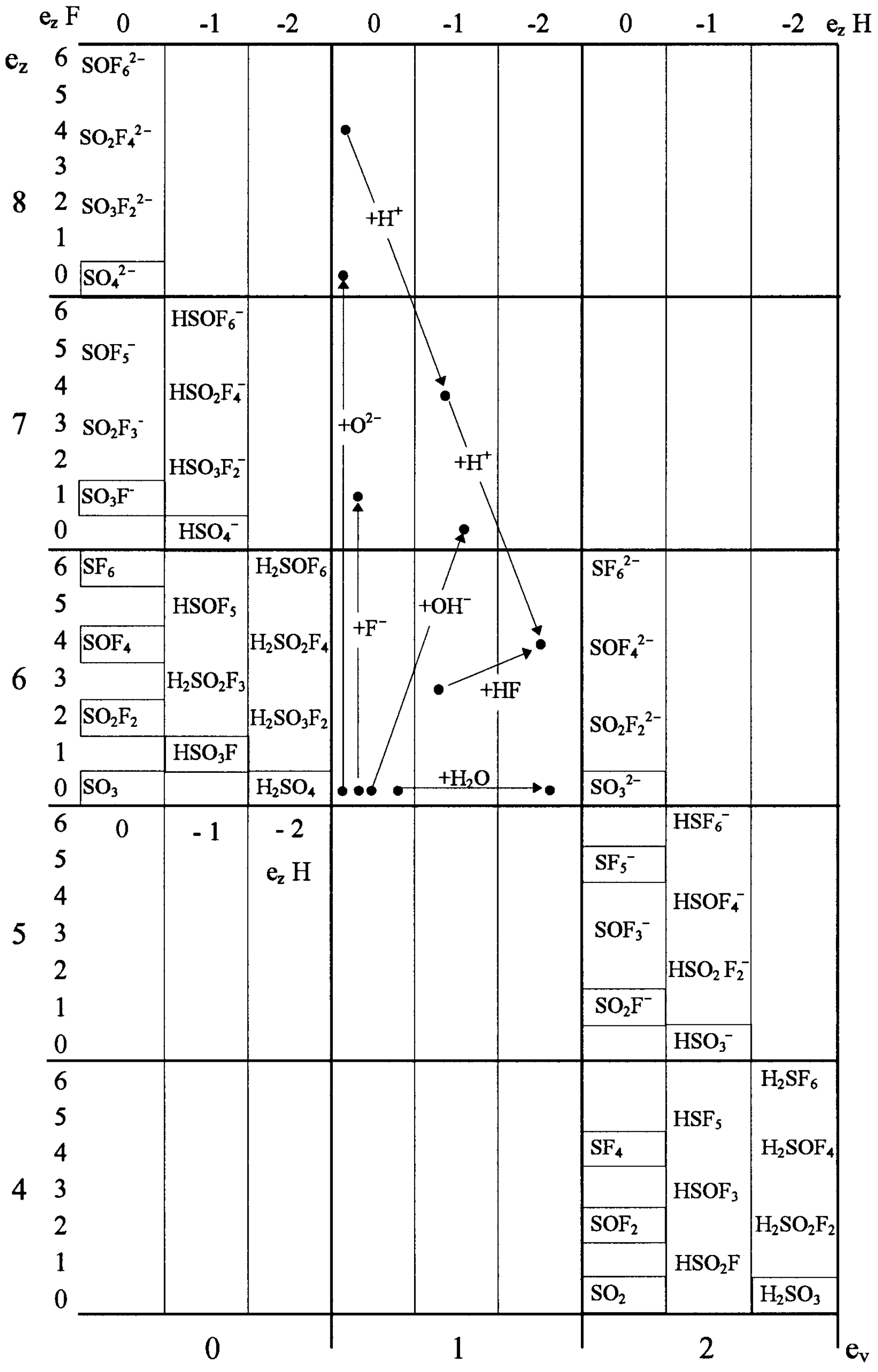


Figure 11. Oxy-fluo-hydrogen csu of sulphur in the $e_z - e_v$ and $e_{zF} - e_{zH}$ classification systems. Known csu in frames.

to use in such cases the system of e'_z e''_z... with neglecting the e_v and assuming e_v = const (frequently, e_v = 0). Figure 12 shows the classification of diheteroligand oxy-fluoride csu of sulphur in the system $e_{zO} - e_{zF}$ and $e_v = 0$, and Figure 13 presents the classification of analogous triheteroligand csu with hydrogen in the system e_{zO} e_{zF} e_{zH} and $e_v = 0$, in which the hydrogen cations are localised at the oxide ligands as OH^-. The known csu have been pointed.

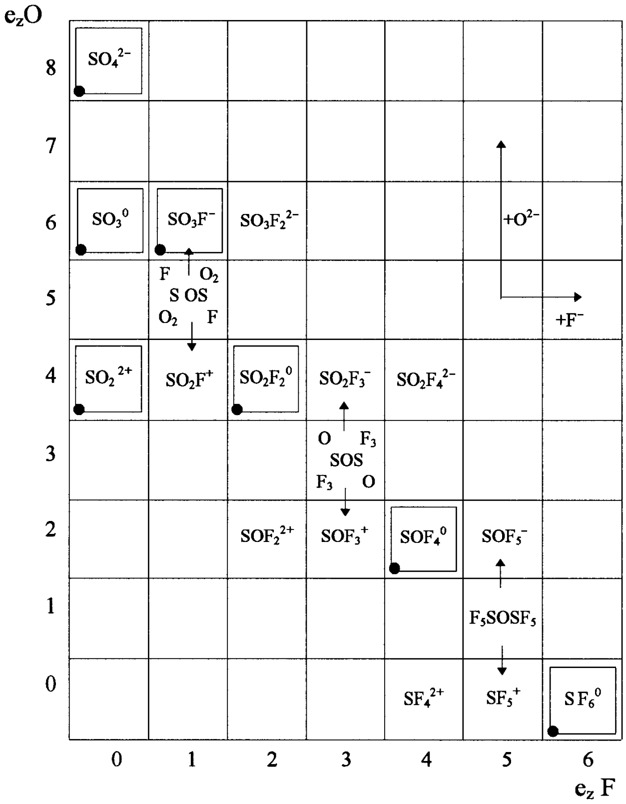


Figure 12. Oxy-fluorine csu of sulphur in the $e_{zO} - e_{zF}$ classification system. Known csu in frames.

Further extension of the $e_z - e_v$ system, enabling to classify oligomers derived from csu, is connected with their description in terms of mean $\bar{e}_z$ and $\bar{e}_v$ values and with the number of central cores in the oligomer ”n” as the classification parameters. Bicentric and multicentre species described by integral values of $\bar{e}_z$ and $\bar{e}_v$ can be comprised together with csu in the primary classification system $e_z - e_v$, as shown in the example of oxygen-containing species of sulphur (Fig. 14). In addition to the e_z and e_v numbers, the table shows also the oxidation state as $G_{ox} = q_c - e_v$ and a symmetrical acid-base value expressed as $G_{ac} = q_c - e_z$.

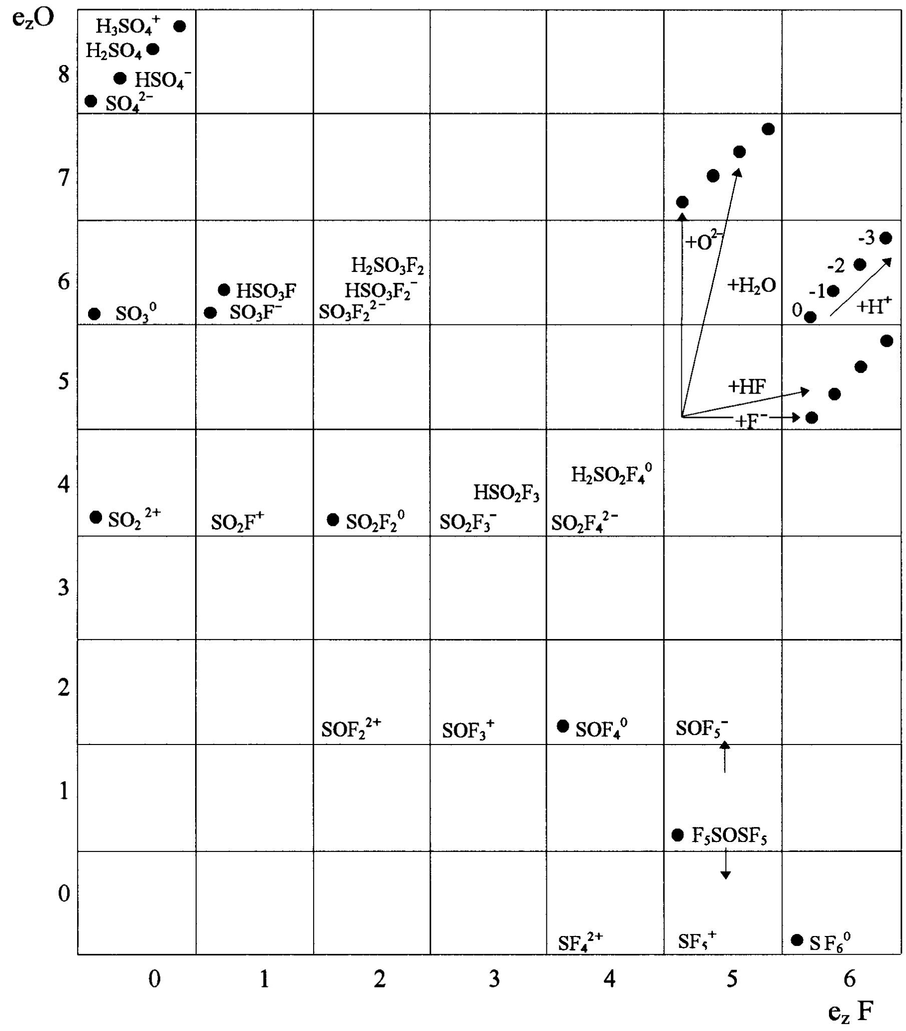


Figure 13. Oxy-fluo-hydrogen csu of sulphur in the $e_{zO} - e_{zF}$ and e_{zH} classification systems.

In the case of fractional values of $\bar{e}_z$ and $\bar{e}_v$, the system is extended by the number of central cores "n". Among the multicentre csu better known until today are only those csu, in which only electron ($e_z = 0$) or ligand ($e_v = 0$) homogeneous environment of the coordination centre exists. The classification of such systems can be presented on a plane, as shown for the example of the extended classification of oxygen-containing species of sulphur in Fig. 15 in point system. In the series of $S^{2-}{\cdot}mS^0$ and $SO_4^{2-} \cdot mSO_3^0$ the numbers $\bar{e}_z$ and $\bar{e}_v$ assume fractional values convergent to $e_v = 6$ and $e_z = 6$, respectively. The identity of the numbers e_v and e_z for corresponding "n" in either series conforms with the known Fajans rule concerning the equivalence of electron pairs and oxide ligands.

G_{ac}	e_z									
-2	8	SO_4^{2-}								
-1	7	$S_2O_7^{2-}$								
0	6	$(SO_3)_n^0$	$S_2O_6^{2-}$	SO_3^{2-}						
+1	5			$S_2O_5^{2-}$						
+2	4	SO_2^{2+}		SO_2^0	$S_2O_4^{2-}$	SO_2^{2-}				
+3	3					$S_2O_3^{2-}$				
+4	2			SO^{2+}		SO^0	$(S_2O_2^{2-})$	SO^{2-}		
+5	1							(S_2O^{2-})		
+6	0					(S^{2+})		S_n^0	S_2^{2-}	S^{2-}
	e_v	0	1	2	3	4	5	6	7	8
	G_{ox}	+6	+5	+4	+3	+2	+1	0	-1	-2

Figure 14. Oxygen-containing csu of sulphur and their multicentre derivatives described by integral values of e_z and e_v in the $e_z - e_v$ classification system, with indication of oxidation state of the central core G_{ox} and its acid-base equivalent G_{ac}.

The parameters of the morphological classification of oligomers also do not distinguish isomeric modifications. Isomerism does not occur among homoligand csu. Among heteroligand csu isomerism is limited to geometric modifications and tautomerism. In bicentric and higher csu oligomers structural isomerism may occur and the morphological classification may be applied only to definite series of structures, *e.g.* unbranched chains.

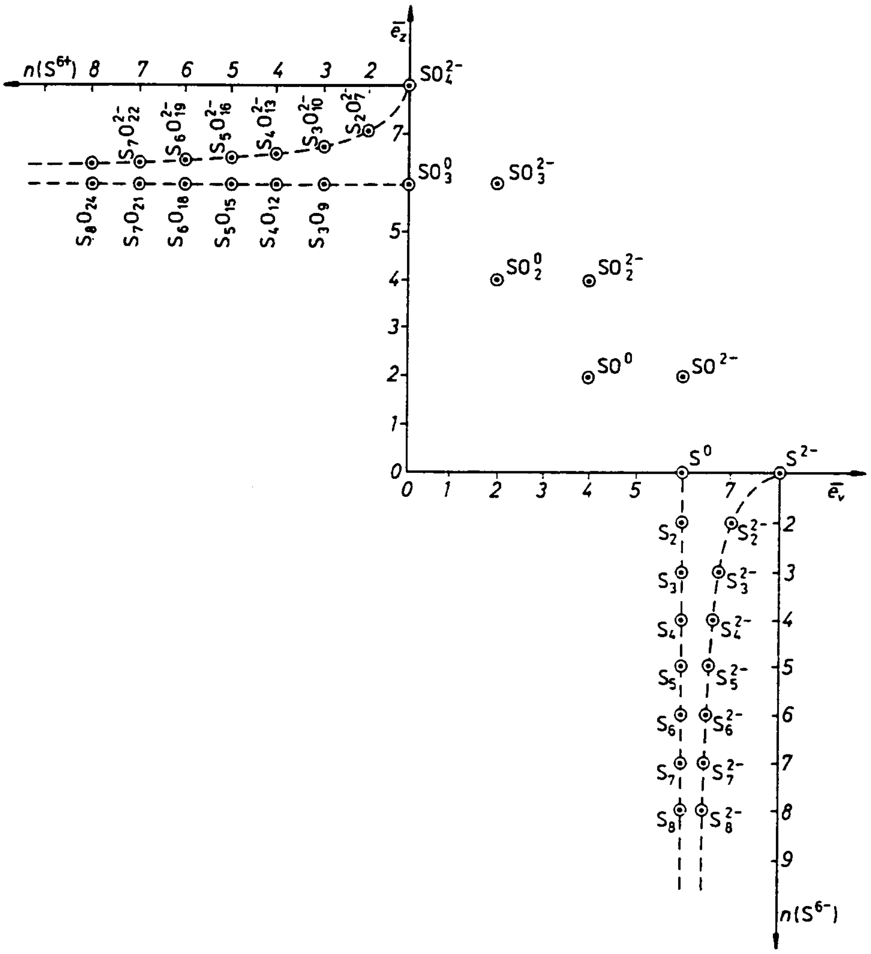


Figure 15. Chemical structural units, multicentre oxygen-containing species of sulphur, and its homoelemental species in point-form classification system in coordinates of mean values of $\bar{e}_z - \bar{e}_v$ and number of central cores n.

6. Bonds and geometry of chemical structural units

Elimination of the classificational barrier between molecules of chemical compounds and ions, resulting from the concept of chemical structural units, which can normally bear a balance electric charge, the value of which only in some special cases may be zero, enables the molecules and the ions to be treated as equivalent from the classificational viewpoint. Such an approach extends markedly the area of structural considerations within the frames of morphological classification. Similarly, taking into account of hydrogen-less molecule skeletons extends the area of comparing the structure of csu and the observed regularities in this respect.

As an example, Fig. 16 shows the classification of csu and bicentric species of oxo hydrides of carbon and their skeletons denoted by S [6,8,11,18]. The parameters of $e_z = e_{zO} + e_{zH}$ and e_v determine five morphological series of csu of definite morphological difference D.

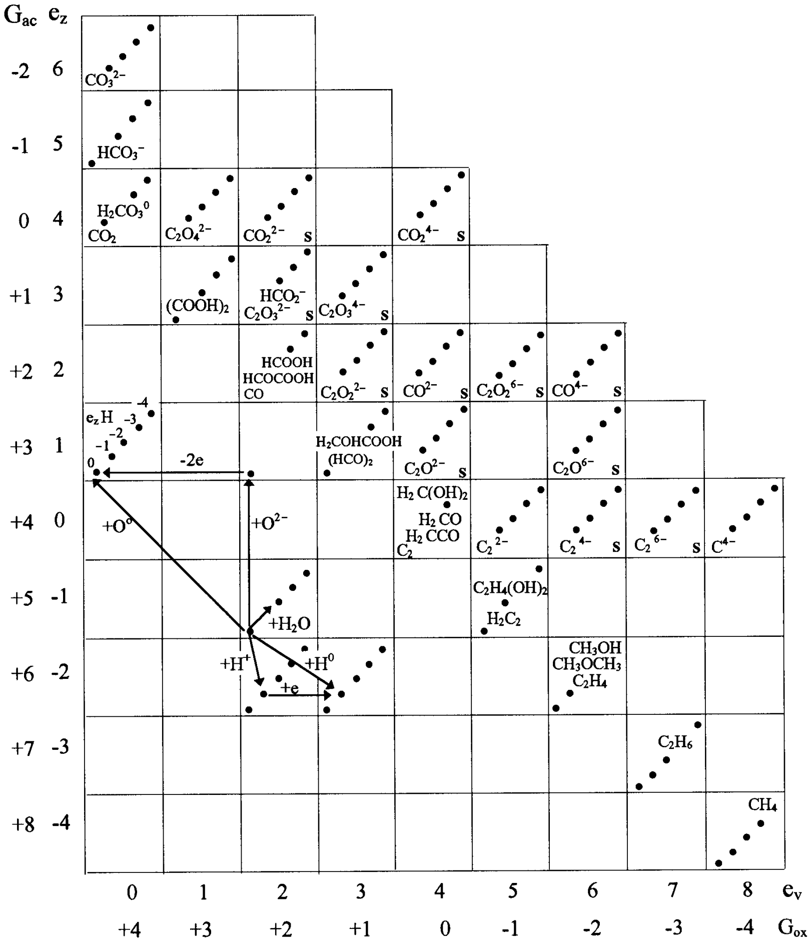


Figure 16. Oxy-hydrogen csu of carbon along with the bicentric species and skeletons “S” in the system $e_z - e_v$ and e_{zH}.

Thus, for $e_{zH} = 0$ we have (skeletons included):

1. e_z = const, *e.g.*: $e_z = 2$ ${}^2_2CO^0$, $({}^2_3CO^{1-})_2$, ${}^2_4CO^{2-}$, $({}^2_5CO^{3-})_2$, ${}^2_6CO^{4-}$; $D_m = e$

2. e_v = const, *e.g.*: $e_v = 6$ ${}^0_6C_2^{4-}$, ${}^1_6C_2O^{6-}$, ${}^2_6CO^{4-}$; $D_m = O^{2-}$

3. $e_z + e_v$ = const, *e.g.*: $e_z + e_v = 5$ ${}^0_5C_2^{2-}$, ${}^1_4C_2O^{2-}$, ${}^2_3C_2O_2^{2-}$, ${}^3_2C_2O_3^{2-}$, ${}^4_1C_2O_4^{2-}$; $D_m = O^0$

and for e_v = const we have:

4. e_{zO} = const, *e.g.*: $e_{zO} = 6$ ${}^6_0CO_3^{2-}$, ${}^5_0HCO_3^{1-}$, ${}^4_0H_2CO_3^0$; $D_m = H^+$

5. $e_Z = \text{const}$, *e.g.*: $e_Z = 0 \ ^{e_{ZH}} \ ^{0}_{4}C_2, \ ^{-1}_{4}H_2C_2O, \ ^{-2}_{4}H_2CO, \ (^{-3}_{4}H_6C_2O_3), \ ^{-4}_{4}H_4CO_2; D_m = H_2O$

(the csu given in parentheses are unknown)

The elements of similar electronegativity, belonging to one and the same period of the sp block in the Mendeleev's system, form csu of analogous electron-ligand structure. Individual fields of the $e_Z - e_V$ classification of successive sp elements accommodate identical structures, which differ only in interatomic distances, electric charge, and stability responsible for the existence or non-existence of the csu. Fig. 17 shows the electronic structure of csu and bicentric oxygen species (including skeletons) of carbon and nitrogen [6,8,11,18]. Besides to analogous structures of csu of the two elements, differing only in electric charge, we can see the absence of nitrogen structures corresponding to skeletons of dimethyl ether (NON^{4-}), ethylene glycol ($ONNO^{4-}$), unstable methylene glycol (ONO^{3-}), and the simplest hydroxy acid ($ONNO_2^{2-}$).

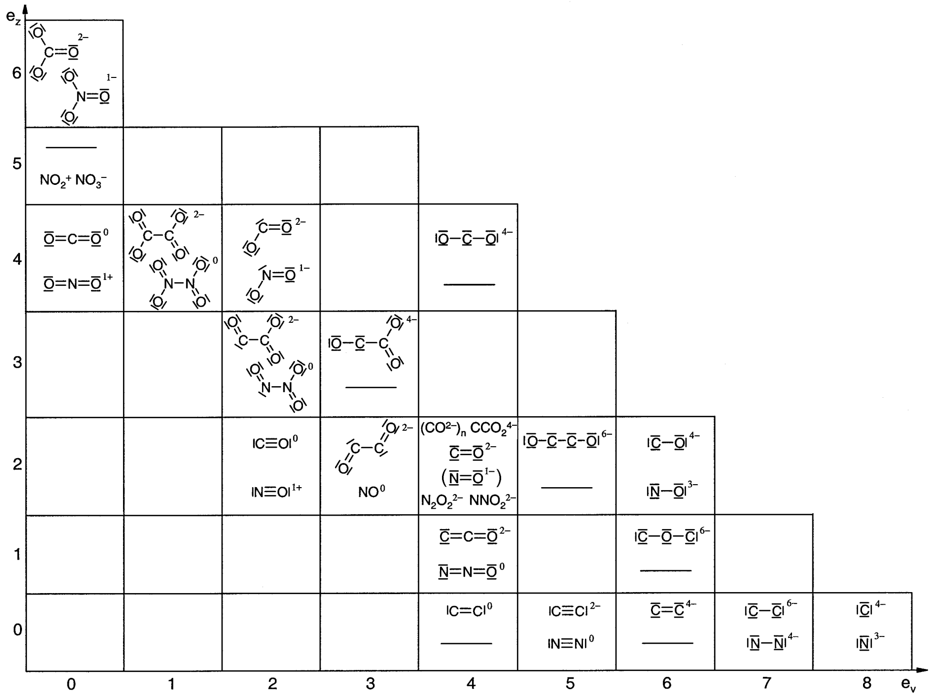


Figure 17. Electronic schemes of oxy-hydrogen csu of carbon and nitrogen, along with their bicentric species, in the $e_Z - e_V$ classification system.

In the line of $e_Z + e_V = 5$ the monomeric structures such as NO_2^0, $NO_2^0 + NO^0$ and NO^0 appear in addition to bicentric oxygen-containing anions and skeletons of carbon and their uncharged nitrogen analogues. The analogy is not so close between the skeletons and csu of nitrogen and carbon, described with the numbers: $e_Z = 2$ $e_V = 4$. Unlike the structurally identical csu $^{6}_{0}CO_3^{2-}$ and $^{6}_{0}NO_3^{-}$, as well as $^{4}_{2}CO_2^{2-}$ and $^{4}_{2}NO_2^{-}$, the line of $e_z + e_v = 6$ is not limiting here. The ${}^{2}_{4}\mathrm{AO}$ species of carbon and nitrogen exhibit a vacancy, which is filled in a dimeric system. The nitrate(I) anion may be an example of such a dimer, whereas formaldehyde, which is a monomer, is endowed with multimer-forming capability. Besides, both of the two elements form identical structures, CCO_2^{4-} and NNO_2^{2-} at $e_z = 2$ and $e_v = 4$. In the group of carbon analogues of oxygen-containing nitrogen csu only nitrogen pentoxide has no carbon analogue, apparently because of the lack of electric charge in CO_2.

Besides the stoichiometric composition and electronic structure, the use of the $e_z - e_v$ lattice is essential for the morphological classification of the geometric structures. Let us consider it, using the example of oxygen-containing csu and skeletons of the sp block elements of the second period (Na – Ar). The Fajans rule of structural equivalence of electron pairs and oxide ligands shows the general difference in structure of oxygen-containing compounds, as compared with fluorine- and nitrogen-containing compounds. It points also to the elements, in which the maximum coordination number with respect to oxide anions (or $e_{z\,\mathrm{O}\,\max}$) at $e_v = 0$ is equal to the maximum number of pairs of valence electrons (or $e_{v\,\max}$) at $e_z = 0$, as being undisturbed from the classificational viewpoint. Among the oxygen-containing sp block elements of the second and third periods, forming mostly covalent bonds, this symmetry is observed in the elements, in which max. e_z for O^{2-} is 8 and also max e_v is 8.

In the 1st period (Li – Ne) the classificational asymmetry in the system of structures of oxygen-containing csu is due to the bond and packing conditions, which generally limits the e_z values to $e_z = 6$ at $e_v = 0$, and to $e_z = 4$ at $e_v = 2$ (Fig. 16), while retaining e_v max. = 8 and condition $(e_z + e_v)_{\max.} = 8$ for csu with $e_v > 2$. In the 4th period (Cd – Xe) it is possible, for $e_v = 0$, to pack six oxide ligands (TeO_6^{6-}, IO_6^{5-}, XeO_6^{4-}) up to attain $e_z = 12$. Nevertheless, the problem of limiting both $e_z + e_v$ and e_v to 8 seems to be unresolved, since we know the skeleton ${}^{8}_{2}\mathrm{XeO}_4^{2-}$, and the iodide anion I^- seems to have a coordination vacancy, which might be responsible for the formation of polyiodide anions.

The classification of geometric structures of oxygen-containing csu of the sp block elements of the 2nd period is shown in Fig. 18 [11]. The increased share of ionic bond, observed in oxygen compounds of aluminium, magnesium and sodium, results in an increase of the coordination number with respect to oxide anion, owing to which the compounds with coordination number 4 are accompanied by those with coordination number 6.

Disregarding the systems with prevalently ionic bond we can state, that monocentric csu and oxygen-containing skeletons with a complete ligand-electron environment are disposed in the line $e_z + e_v = 8$. Any deficit in this environment, described by the condition $e_z + e_v < 8$, is compensated in the 1st period by the formation of multiple bonds, whereas in the 2nd and 3rd periods there is a complication of structures, which consists in joining of csu to retain the tetrahedral ligand and valence electron environment of the coordination centres.

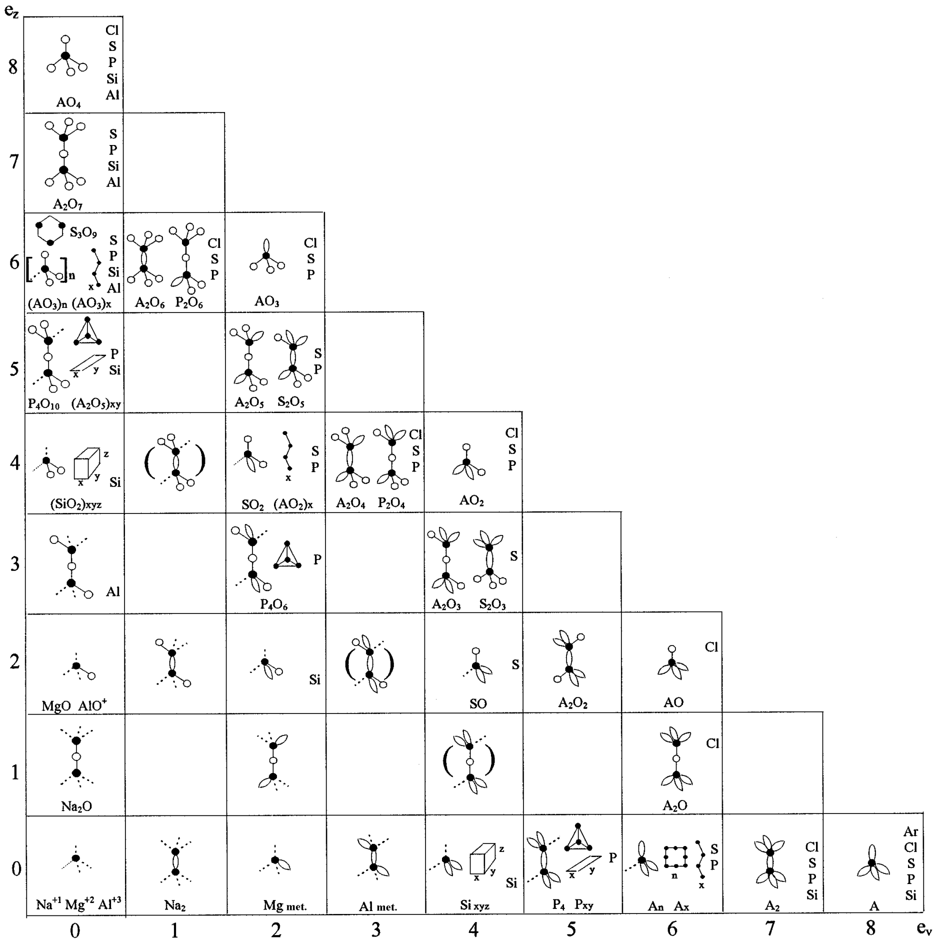


Figure 18. Geometrical structures of csu of the sp elements of period II and their derivative multicentre structures, according to Gontarz [11].

The csu of identical ligand-electron deficit, described by identical values of $e_Z + e_V = \text{const}$, have similar outlay of ligand and valence electron pairs. In the classification lattice they are disposed on successive hypotenuses, described by the condition $e_Z + e_V = \text{const.}$, as shown in Fig. 18. With increasing structural deficit, which is manifested by the decrease of the sum of $e_Z + e_V$, the structures of csu change in a regular manner, tending toward higher degrees of complication. The series of the structures observed begins with complete coordination structures with $e_Z + e_V = 8$, such as ${}^8_0AO_4 \ldots {}^0_8|\overline{\underline{A}}|$, through bicentric systems of $e_Z + e_V = 7$, also having complete coordination ${}^7_0O_3AO\,A\,O_3 \ldots\ldots {}^0_7|\overline{\underline{A}} - \overline{\underline{A}}|$, to structures with 2-electron coordination vacancy having $e_Z + e_V = 6$, ${}^6_0AO_3 \ldots {}^0_6|\overline{\underline{A}}$, which can exist either as oligomeric n-centre rings: $({}^6_0AO_3)_n \ldots.({}^0_6|\overline{\underline{A}})_n$, or as linear polymers $({}^6_0AO_3)_x \ldots.({}^0_6|\overline{\underline{A}})_x$ (disregarding, for considerable values of x, the end fragments ${}^8_0AO_4 \ldots. {}^0_8|\overline{\underline{A}}|$, in polymolecules $({}^6_0AO_3)_x \cdot {}^8_0AO_4 \ldots.({}^0_6|\overline{\underline{A}})_x \cdot {}^0_8|\overline{\underline{A}}|$.

A further increase of the structural deficit ($e_z + e_v = 5$) leads to the formation of bicentric species of the type: ${}^{5}_{0}O_2AO\,AO_2 \ldots {}^{0}_{5}\underline{\overline{A}} - \underline{\overline{A}}$ with two electron-pair vacancies, having five oxide ligands interchangeable with valence electron pairs. Such csu are components of cage oligomers: ${}^{5}_{0}A_4O_{10} \ldots\ldots {}^{0}_{5}A_4$ or laminar polymers $({}^{5}_{0}A_2O_5)_{xy} \ldots\ldots ({}^{0}_{5}A_2)_{xy}$.

At last, for $e_z + e_v = 4$ we have csu with two coordination vacancies and two oxide ligands interchangeable with valence electron pairs: ${}^{4}_{0}AO_2 \ldots {}^{0}_{4}\underline{\overline{A}}$, which can exist only as elements of tridimensional polymers: $({}^{4}_{0}AO_2)_{xyz} \ldots ({}^{0}_{4}\underline{\overline{A}})_{xyz}$; solid SiO_2 and diamond are examples of such structures. Monocentric csu with two coordination vacancies can play the role of bridges, both inside ring structures (Fig. 19a) and in cross-linking linear molecules into band- and layer- structures (Fig. 19b,c).

Chemical structural units with three vacancies can be distinguished as elements of basket or cage structures (Fig. 20).

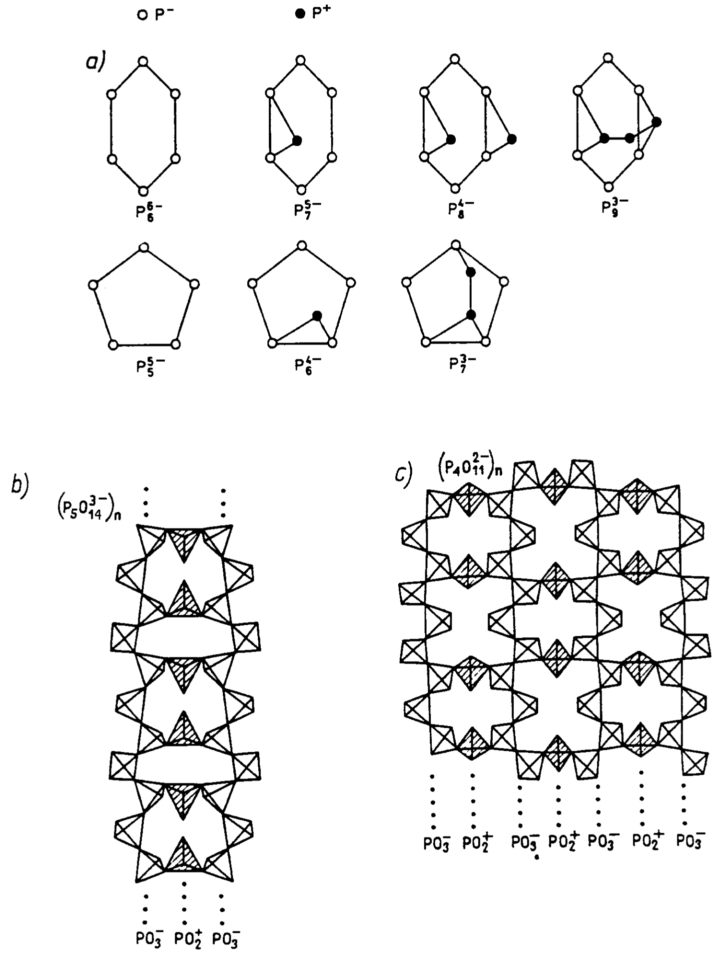


Figure 19. Chemical structural units with two electron-pair vacancies as intra-ring bridges (a), cross-linking bridges in band structures (b), and as layer-forming elements (c).

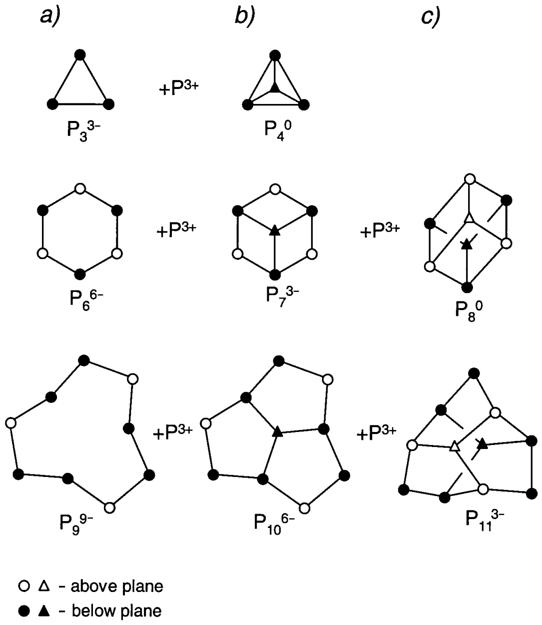


Figure 20. Chemical structural units with three electron-pair vacancies as binding elements in formation of basket- (b) and cage-shaped (c) species from ring structures (a).

Chemical structural units with coordination vacancies occur also as repeated structural elements in homologue series of oligomeric molecules. The ring-shaped homologues described by integral values of e_z and e_v and linear homologues described by fractional values of e_z or e_v are classified in systems of either constant e_z and e_v and variable number of central cores "n", variable e_z and e_v = const. Or variable e_v, e_z = const. and variable "n", as shown in Fig. 15. Assuming the starting element in the homologue series as G and the homologue increment as D_h, we can give the general formula of the series as $G(D_h)_n$. Figure 21 shows homologous series of silicates (b) with variable e_z and n and $e_v = 0$, and skeletons of saturated hydrocarbons (c) with variable e_v and n and $e_z = 0$, as well as their geometrically identical structures composed of tetrahedrons (a). The curves traced through successive members of the homologue series tend, with increasing values of "n", asymptotically to the values of e_z or e_v of the homologue increment D_h [9,11,12].

A characteristic difference appears in the classification of structures of simple csu formed by the dsp block elements [17,27,28]. This difference results from the valence electrons located on the d orbitals, where they cannot play the role of pseudoligands and are geometrically inert. A classificational consequence of this fact is manifested by the distribution of analogous structures in the $e_z - e_v$ system, which are in some range significantly independent from e_v number as shown in Fig. 22 for the oxygen csu of chromium [17]. The csu structure is, to some extend, effected by the balance charge of valence electrons d and atom core ($q_c - e_v = G_{ox}$), as in the case of csu on G_{ox} = 4+ and 3+.

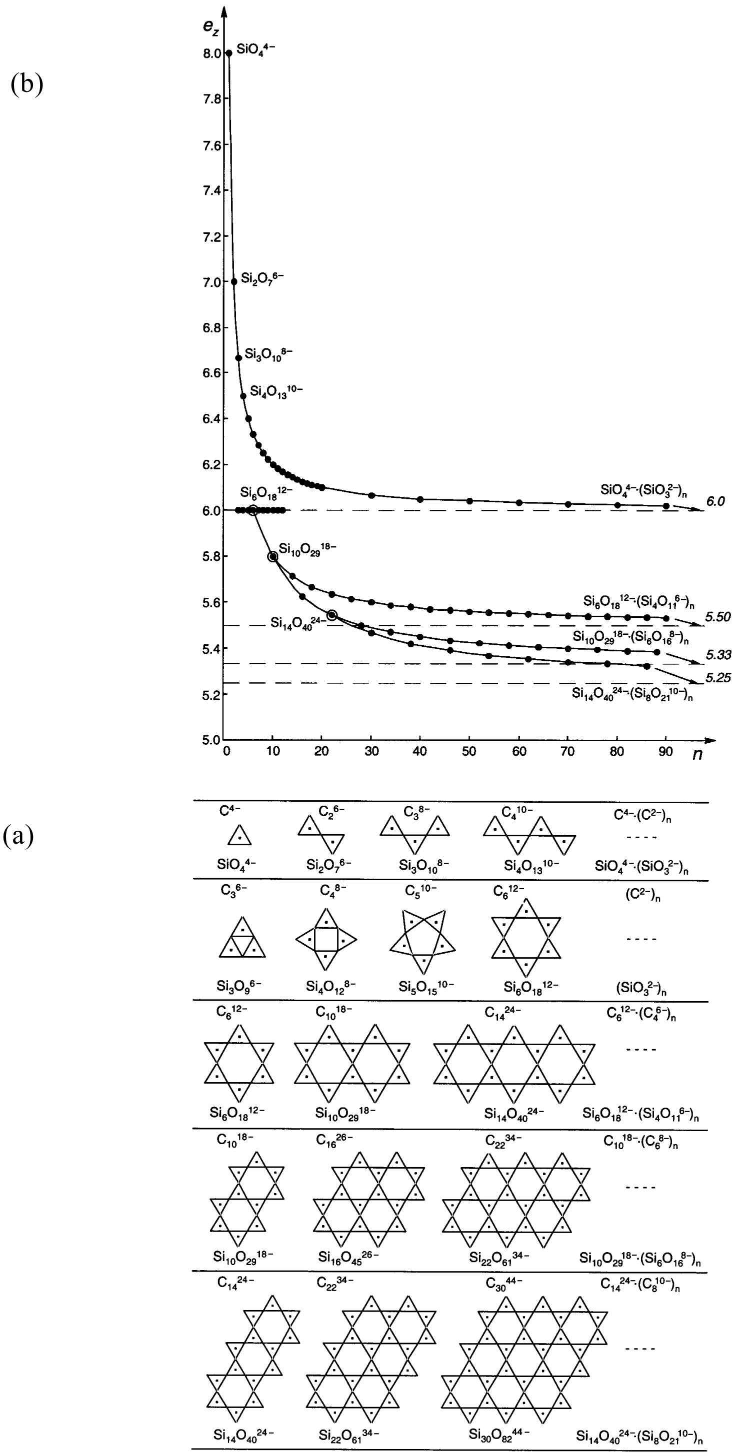


Figure 21. Structures of oxy-silicate anions and saturated hydrocarbon skeletons (a) and their homologous series (b) and (c) in the e_Z (e_V) n classification system.

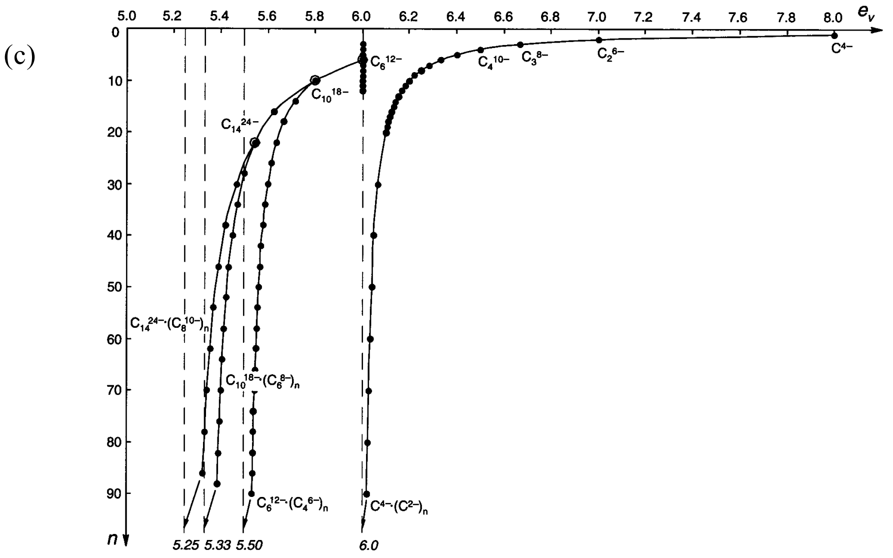


Figure 21. (continued)

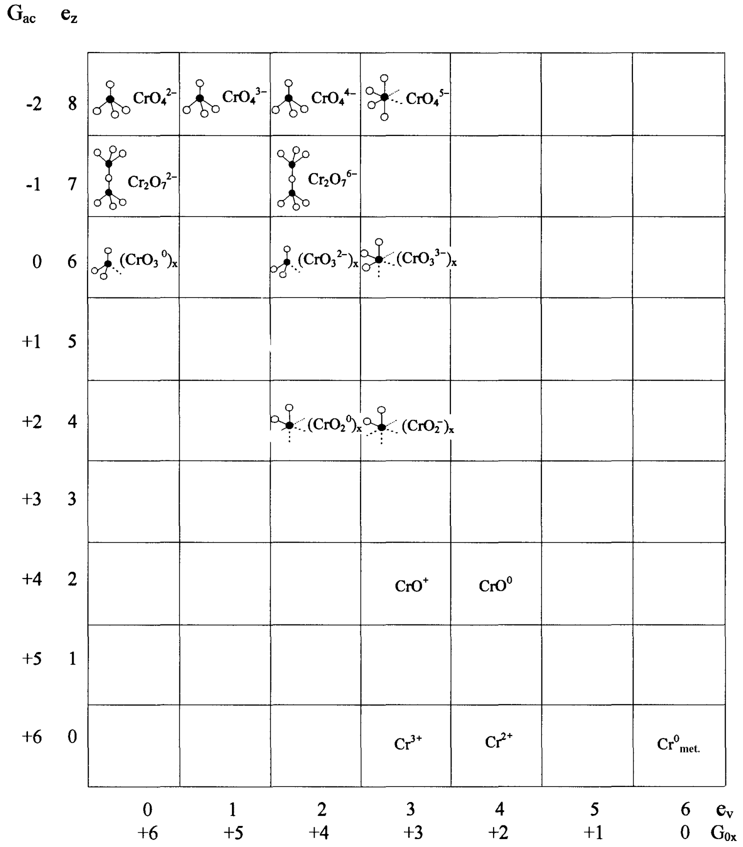


Figure 22. Geometrical structures of oxygen-containing csu of a dsp-block element (Cr) in the $e_z - e_v$ classification system.

7. Chemical transformations of csu in the morphological classification

7.1. Transformations of csu in the system $e_z - e_v$: In the morphological classification of chemical transformations the csu are disposed according to their values of e_z and e_v. Such a classification makes it possible to demonstrate elementary transformations, as leading to csu that occupy the closest positions in the classificational environment. Within the domain of oxygen-containing csu such transformations consist in the transfer of either an oxide ligand O^{2-} (ac-bas), of an electron pair (red-ox), or of an oxygen atom (redac-oxbas). A set of such elementary transformations constitutes a stage mechanism of more complex processes. Experimental validity of the elementary virtual transformations as steps of real reactions is here a fundamental problem.

A very valuable contribution in this respect has been brought by Z. Gontarz *et al.* owing to his investigations on thermal decomposition of salts of oxy-acids of sp and dsp block elements [13,17,18,23,25,26]. The results of these studies enable us to formulate some rules, which are important for implementation of the classification principles for interpretation of experimental results:

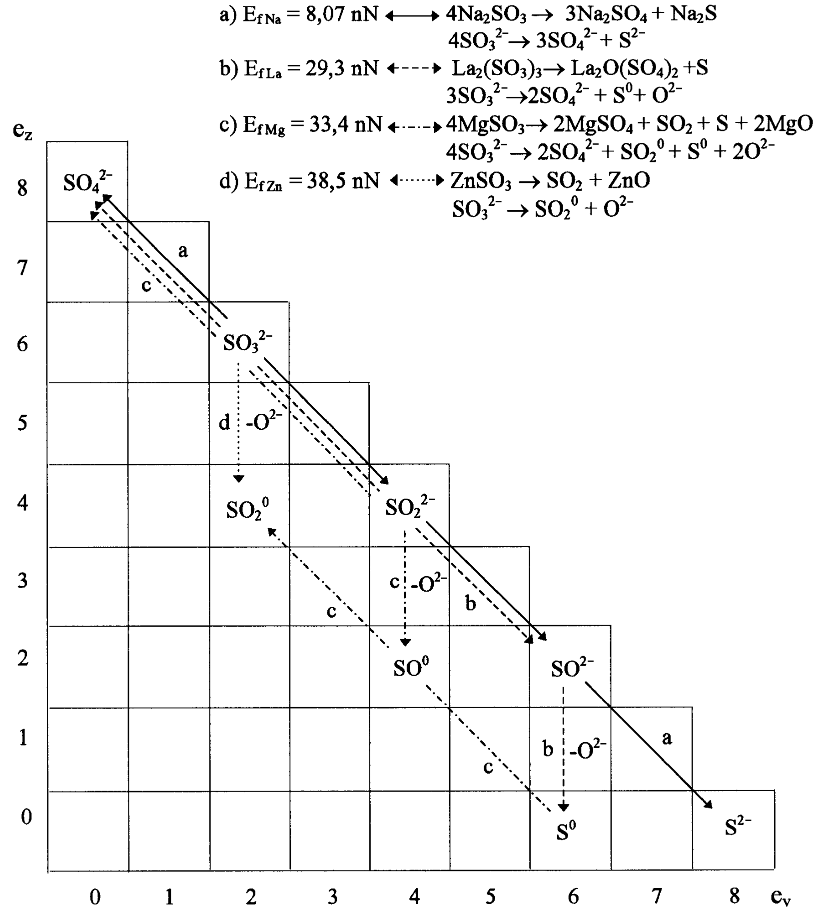
- The reactions of thermal decomposition of salts of oxyacids are effected in the system of two homogeneously interpenetrating reagents, cations and anions; the anion is the main substrate of the process and the simple cationic counterion either enters the reaction at some stages of the process or remains inert.
- Simple, single-core cations, bearing no valence electrons, can play the role of acids – acceptors of anion (e.g. oxide) ligands. The acidic properties of the cations are in a satisfactory correlation with the electronegativity force (E_f), postulated in our former works as the energy of binding the first electron by a cation (respective ionization energy taken with opposite sign) divided by its radius, calculated for six-coordinated csu. The values of E_f have been collected in Table 4 [14].
- Comparison of thermal decompositions of oxyacid salts of the sp block elements shows that the increase of the number of valence electrons e_v in csu leads to an increase of its basic (anion-donor) properties and the increase of charge e_z, brought in by the anionic ligands increases the reducing (electron-donor) properties. The observed effects are in agreement with the assumption of coulombic repulsion between the charges of the e_v shell and those of the e_z shell in the environment of the core of csu under consideration.

Basing on these presumptions Z. Gontarz [13,18] has proved for the examples of thermal decomposition of sulphates(IV), the experimental reality of the virtual steps of elementary reactions, resulting from the disposition of the oxygen-containing sulphur csu in the $e_z - e_v$ classification (Fig. 23). The thermal decomposition of a sulphate(IV), having a cation of small electronegativity force such as sodium (E_f = 8.07 nN), is a process of redac-oxbas disproportionation, not disturbed by the reaction with the counterion:

$4\,{}^{6}_{2}SO_3^{2-} \rightarrow 3\,{}^{8}_{0}SO_4^{2-} + {}^{0}_{8}S^{2-}$ (Fig. 23a), proceeding through the virtual elementary stages along the line $e_z + e_v = 8$: ${}^{6}_{2}SO_3^{2-} \rightarrow {}^{4}_{4}SO_2^{2-} \rightarrow {}^{6}_{2}SO^{2-} \rightarrow {}^{0}_{8}S^{2-}$ (Fig. 23a).

Table 4. Electronegativity force of cations, nN.

sp	Li$^+$	11.67									
	Na$^+$	8.07	Mg^{2+}	33.4	Al.$^{3+}$	85.9					
			Zn^{2+}	38.5	Ga^{3+}	79.3					
			Cd^{2+}	28.4	In^{3+}	56.1					
			Hg^{2+}	29.3	Tl^{3+}	51.2					
dsp	K$^+$	5.04	Ca^{2+}	19.0	Sc^{3+}	53.2					
	Rb$^+$	4.17	Sr^{2+}	15.6	Y^{3+}	36.4					
					Lu^{3+}	39.0					
fdsp	Cs$^+$	–	Ba^{2+}	11.7	La^{3+}	29.3	Ce^{3+} 32.5	Pr^{3+} 34.7	Nd^{3+} 36.0	Sm^{3+} –	Eu^{3+} 42.2



a) $E_{fNa} = 8{,}07$ nN ⟷ $4Na_2SO_3 \rightarrow 3Na_2SO_4 + Na_2S$
$4SO_3^{2-} \rightarrow 3SO_4^{2-} + S^{2-}$
b) $E_{fLa} = 29{,}3$ nN ←---→ $La_2(SO_3)_3 \rightarrow La_2O(SO_4)_2 + S$
$3SO_3^{2-} \rightarrow 2SO_4^{2-} + S^0 + O^{2-}$
c) $E_{fMg} = 33{,}4$ nN ←·-·→ $4MgSO_3 \rightarrow 2MgSO_4 + SO_2 + S + 2MgO$
$4SO_3^{2-} \rightarrow 2SO_4^{2-} + SO_2^0 + S^0 + 2O^{2-}$
d) $E_{fZn} = 38{,}5$ nN ←······→ $ZnSO_3 \rightarrow SO_2 + ZnO$
$SO_3^{2-} \rightarrow SO_2^0 + O^{2-}$

Figure 23. Experimental reality of the virtual steps of thermal decomposition of sulphates(IV) with cationic counterions of different electronegativity force according to Gontarz [11].

Increasing e_v the basic properties of the intermediate products increase with respect to the initial ${}^{6}_{2}SO_3^{2-}$ and the cationic counterions of higher electronegativity can bind oxide ligands, until the final product of the decomposition (the sulphide anion) has been attained. The real existence of the virtual elementary stage in the form of ${}^{6}_{2}SO^{2-}$ anion is confirmed by the thermal decomposition of lanthanum salt ($E_f = 29.3$ nN): $3\,{}^{6}_{2}SO_3^{2-} \rightarrow 2\,{}^{8}_{0}SO_4^{2-} + {}^{0}_{6}S^{0} + O^{2}$ (LaO^{+}), (Fig. 23b). The real existence of the virtual elementary stage ${}^{4}_{4}SO_2^{2-}$ is confirmed by the thermal decomposition of magnesium salt ($E_f = 33.4$ nN): $4\,{}^{6}_{2}SO_3^{2-} \rightarrow 2\,{}^{8}_{0}SO_4^{2-} + {}^{4}_{2}SO_2^{0} + {}^{0}_{6}S^{0} + O^{2-}$, where SO_2 and S are remainders of the unstable SO (Fig. 23c). Finally, cationic counterions of considerable electronegativity can inhibit the disproportionation by binding oxide ligands directly from the initial SO_3^{2-} anion. Such a case is observed in the decomposition of a zinc salt ($E_f = 38.5$ nN): ${}^{6}_{2}SO_3^{2-} \rightarrow {}^{4}_{2}SO_2^{0} + O^{2-}$ Fig. 23d).

The stage mechanisms presented above for the thermal decomposition of sulfate(IV) are in accordance with the course of oxidation of sulfide (Fig. 24). Only the sulfides with inert counterions of small electronegativity force, *e.g.* sodium ($E_f = 8.07$ nN) are converted into sulfate(VI) under the action of oxygen: ${}^{0}_{8}S^{2-} + 2O_2^{0} \rightarrow {}^{8}_{0}SO_4^{2-}$ (Fig. 24a). In other sulfides, having counterions of higher electronegativity force

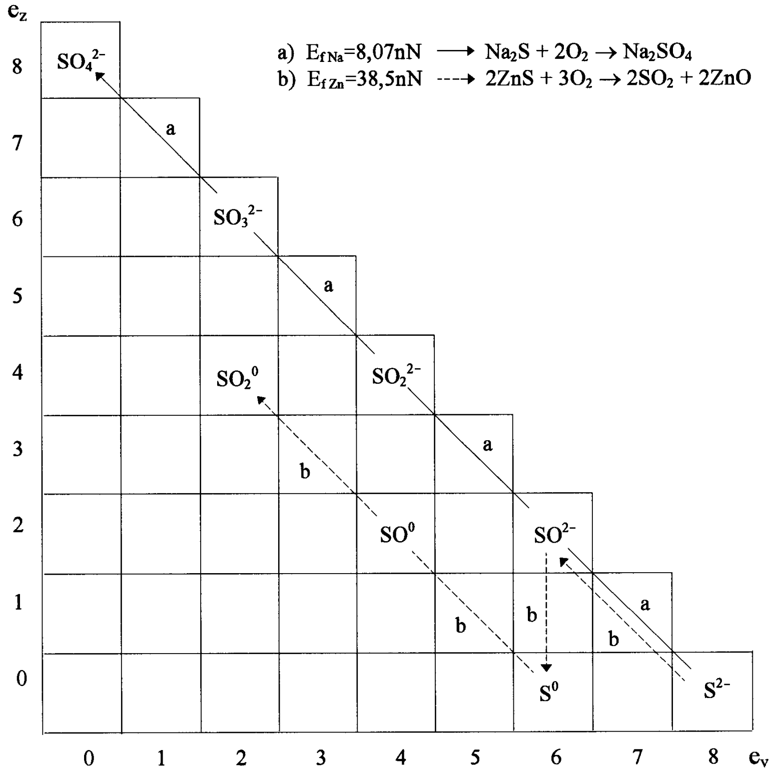


Figure 24. Sulphide oxidation steps in relation to electronegativity force of cationic counterions according to Gontarz [11].

(*e.g.* Zn^{2+}) an insuperable barrier in the line $e_z + e_v = 8$ is the most basic anion SO^{2-}, which loses readily the oxide ligand to the benefit of the cation, thus, shifting further oxidation to the line $e_z + e_v = 6$: ${}^{0}_{8}S^{2-} + 1.5O_2^0 \rightarrow {}^{4}_{2}SO_2^0 + O^{2-}$ (*e.g.* ZnO) (Fig. 24b). The SO^{2-} anion exists only at the moment of binding valence electrons of S^{2-} by oxygen, and the oxide anion formed is then bound immediately by the cation.

7.2. Transformations of bicentric species in the system $e_z - e_v$ [11,13,18,20]: The experimental feasibility of the elementary stages of virtual transformation of bicentric sulphur species, situated on the line $e_z + e_v = 7$, has been confirmed in the studies carried out by Z. Gontarz, concerning thermal decomposition of the salts with inert cations of low E_f values. The first stage of the process consists usually in splitting the anion into two monocentric csu to be disposed on the lines of $e_z + e_v = 8$ (complete coordination) and $e_z + e_v = 6$ (csu with coordination vacancy), which are then transformed conforming their donor-acceptor properties (Fig. 25). The bicentric anion ${}^{7}_{0}S_2O_7^{2-}$ undergoes thermal decomposition with formation of ${}^{8}_{0}SO_4^{2-}$ and ${}^{6}_{0}SO_3$ (Fig. 25a).

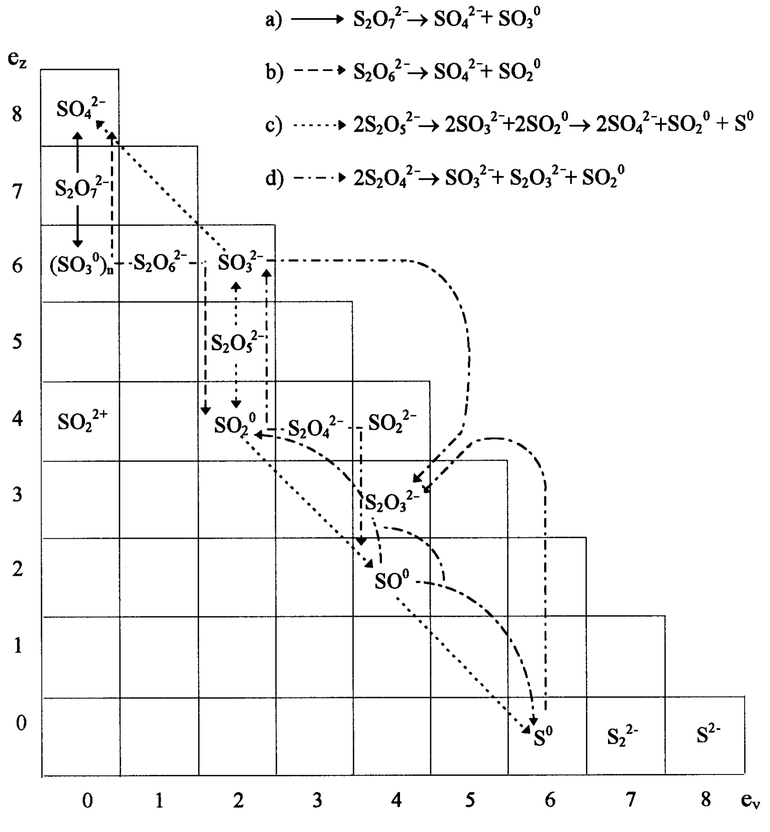


Figure 25. Reaction steps in thermal decomposition of disulphates with inert cationic counterions according to Gontarz [11].

The bisulfate(V) anion ${}^{6}_{1}S_2O_6^{2-}$ decomposes, on heating, to ${}^{8}_{0}SO_4^{2-}$ and ${}^{4}_{2}SO_2$. Addition of a base (donor of oxide anions) inhibits the basic branch of the subsequent stage of the reaction leading to SO_4^{2-} and SO_3^{2-}. This fact may be accounted for the existence of the following elementary stages: ${}^{6}_{1}S_2O_6^{2-} \rightarrow {}^{6}_{2}SO_3^{2-} + {}^{6}_{0}SO_3^{0}$ and ${}^{6}_{2}SO_3^{2-} + {}^{6}_{0}SO_3^{0} \rightarrow {}^{4}_{2}SO_2 + {}^{8}_{0}SO_4^{2-}$ (Fig. 25b).

The bisulfate (IV) $S_2O_5^{2-}$, while heated below 380°C gives, in the elementary process the sulfate(IV) SO_3^{2-} anion and sulphur dioxide SO_2. On heating above 380°C, the decomposition of bisulfate (IV) yields sulfate and sulphur, along with sulphur dioxide, formed in reactions of SO_3^{2-} with SO_2^{0}, since sulphur dioxide is a stronger electron acceptor. The first step, proceeding at definite temperature interval, is followed by further virtual steps with high probability of real existence (Fig. 25c):
$2\,{}^{5}_{2}S_2O_5^{2-} \rightarrow 2\,{}^{6}_{2}SO_3^{2-} + 2\,{}^{4}_{2}SO_2^{0}$; ${}^{6}_{2}SO_3^{2-} + {}^{4}_{2}SO_2^{0} \rightarrow {}^{8}_{0}SO_4^{2-} + {}^{2}_{4}SO^{0}$; ${}^{6}_{2}SO_3^{2-} + {}^{2}_{4}SO^{0} \rightarrow$
$\rightarrow {}^{8}_{0}SO_4^{2-} + {}^{0}_{6}S^{0}$.

The virtual steps of thermal decomposition of bisulfate(III) with anions $S_2O_4^{2-}$, as found from the classification, have been justified by the above described real steps of thermal decomposition of other salts having bicentric oxide anions ($S_2O_7^{2-}$, $S_2O_6^{2-}$, $S_2O_5^{2-}$) and leading to products that are identical with those found experimentally in the decomposition of salts with anion $S_2O_4^{2-}$ and inert cationic counterions (Fig. 25c), such as:

$$2\,{}^{4}_{3}S_2O_4^{2-} \rightarrow {}^{6}_{2}SO_3^{2-} + {}^{4}_{3}S_2O_3^{2-} + {}^{4}_{2}SO_2$$

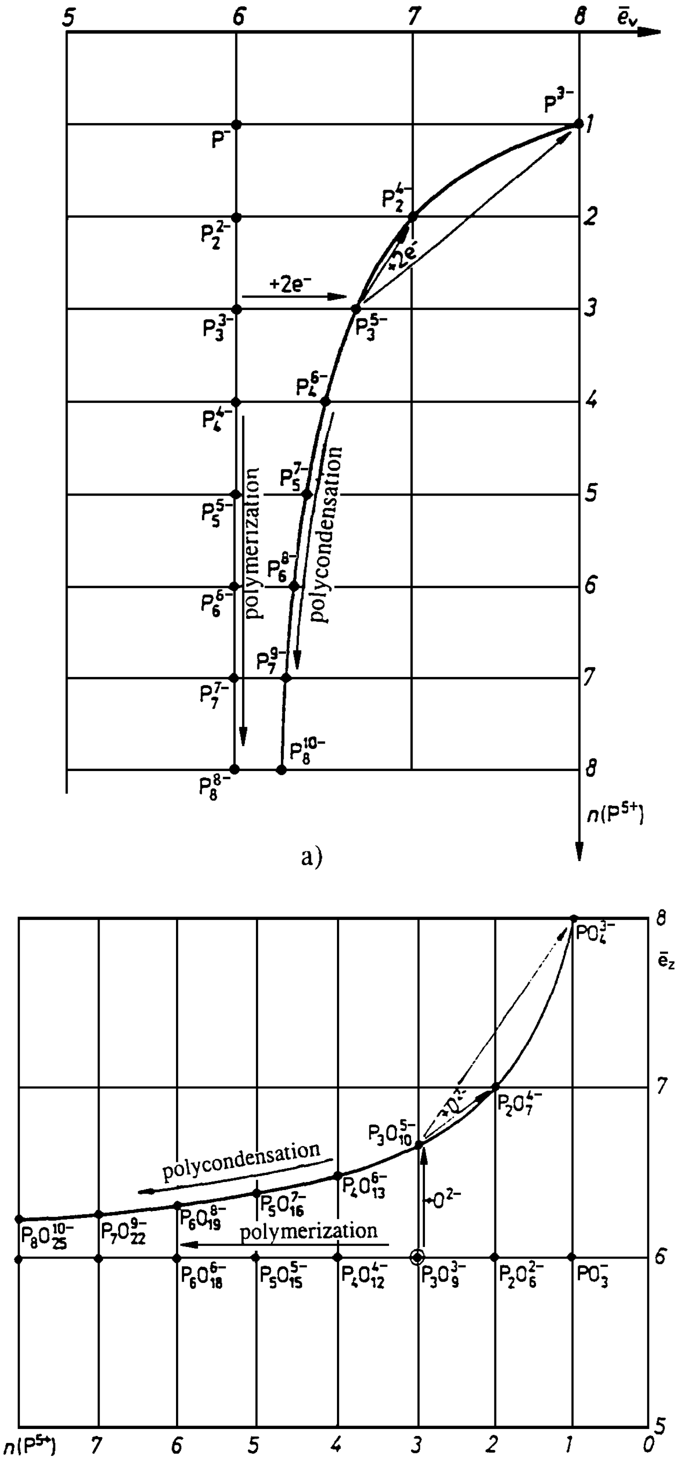
and which seams to result from virtual elementary steps (Fig. 25d):

$$2\,{}^{4}_{3}S_2O_4^{2-} \rightarrow (2\,{}^{4}_{4}SO_2^{2-} + 2\,{}^{4}_{2}SO_2^{0}) \rightarrow 2\,{}^{6}_{2}SO_3^{2-} + 2\,{}^{2}_{4}SO^{0} \rightarrow {}^{6}_{2}SO_3^{2-} + {}^{3}_{4}S_2O_3^{2-} + {}^{4}_{2}SO_2^{0},$$

recognized in the decomposition of salts with other oxy-anions of sulphur.

The concordance of the virtual elementary steps with the real process of thermal decomposition of oxy-anions in salts formed by the sp block elements has been investigated in extensive studies performed by Z. Gontarz on the effect of cationic counterions on thermal decomposition of salts having anions of the type ${}^{6}_{2}AO_3^{n-}$ of various sp elements, as well as in his studies on thermal decomposition of salts of oxy-acids of the dsp block elements.

7.3. Transformations of multicentre species in the morphological classification [12,18]: Unlike the classification of simple csu in the $e_V - e_Z$ system, such simple relationships between the structure and elementary chemical reactions do not occur in the classification of multicentre species in the system of mean $\bar{e}_V$ or $\bar{e}_Z$ and number of central cores "n". The transformations of multicentre species are secondary in nature, as compared with the transformations of the component csu. The changes in the mean $\bar{e}_V$ and $\bar{e}_Z$ values are the consequence of respective changes in the e_V and e_Z values of a csu in an elementary act, effected in one of the component csu. The change in the electron or ligand environment of a component csu, expressed in a respective change of $\bar{e}_V$ or $\bar{e}_Z$, results in a reconstruction of the multicentre species and formation of a new spe-



a)

b)

Figure 26. Transformations of ligand-less ($e_z = 0$) and only oxygen containing ($e_v = 0$) phosphorus multicenter species in the $\bar{e}_z$ ($\bar{e}_v$) – $n(P^{5+})$ classification system.

cies, which is described by other values of $\bar{e}_V$ or $\bar{e}_Z$. Thus, for example, in a ring-shaped species ${}^{6}_{0}P_3O_9^{3-}$, consisting of three identical csu ${}^{6}_{0}PO_3^{-}$, an action of a base (donor of oxide ligands) causes, that one of the component csu in the ring fills the coordination vacancy by attachment of an oxide anion. As a result, the ring is broken and a linear ${}^{6.67}_{0}P_3O_{10}^{5-}$ is formed. The composition of this ion, with unchanged "n", may be represented as $[{}^{8}_{0}PO_4^{3-} \cdot 2\,{}^{6}_{0}PO_3^{-}]$. In the $\bar{e}_Z - n$ classification this reaction is a transition to a neighbouring classification position at n = const. (Fig. 26a). An analogous transformation within ring-shaped phosphide species, provoked by electron donors (reducers) is shown in Fig. 26b. A similar scheme is observed in transformation of other ring-shaped species, classified in the line $e_Z = 6$ or $e_V = 6$, which form corresponding linear species having identical number of central cores "n". Filling a coordination vacancy in a csu, being a link in a chain structure, results in a separation of a full coordinated csu with shortening the chain by one unit:

$${}^{6.67}_{0}P_3O_{10}^{5-}\,({}^{8}_{0}PO_4^{3-} \cdot 2\,{}^{6}_{0}PO_3^{-}) + O^{2-} \rightarrow {}^{8}_{0}PO_4^{3-} + {}^{7}_{0}P_2O_7^{4-}\,({}^{8}_{0}PO_4^{3-} \cdot {}^{6}_{0}PO_3^{-})$$

as shown in the $\bar{e}_Z - n$ classification system in Fig. 26a, and an analogous shortening of a phosphide chain, owing to an action of a reducer, is shown in Fig. 26b.

Classification of multicentre species in the system $\bar{e}_Z$ ($\bar{e}_V$) – n represents univocally the steps of transformation of oligomers, provoked by donors of anionic ligands or electrons. These transformations end by csu of complete coordination environment, described by either $e_Z = 8$, $e_V = 0$ or $e_Z = 0$ $e_V = 8$. Reverse processes, resulting in the action of acceptors of anionic ligands or electrons on csu of full coordination shell, can proceed in many classification variants.

8. Scope of application of the morphological classification of csu

The morphological classification is an open system, which can be precised in view of some specific applications and which provides a possibility of extensive correlations in the range of structures and reactions of simple csu and their complexes. It is the first attempt in chemistry to systematize the chemical compounds as structures that are intercorrelated by elementary transformations. Such an approach creates new possibilities of application of the classification. The scope of problems, dealt with in terms of the morphological classification of simple chemical structural units, is presented in our publications [5–28], where we show both the versatility and limitations of the classification.

8.1. The morphological classification in research: The importance of the morphological classification in chemical research is a result of the real nature of virtual elementary transformations predicted in the $e_Z - e_V$ system as occurring as single steps of real chemical reactions. Owing to this property, the $e_Z - e_V$ lattice becomes a matrix for donor-acceptor transformations of simple csu as independent components of macroscopic chemical structures or of complex molecules. Z. Gontarz [22] has used the e_Z – e_V matrix for the correlation of experimental data in determining the elementary steps of transformation of anions in salts of oxy-acids, both in the solid state and as melts. From his extensive studies in this domain an example, concerning the possibility of existing of highly-coordinated iodate(V) as a step in thermal decomposition of meta-iodate(V), has been quoted here (Fig. 27). The classification of oxyiodate csu in the $e_Z - e_V$ lattice involves the problem of the range of applicability of Fajans rule of structural equivalence of electron pairs and oxide ligands, which concerns in this case the possibility of existing of csu with $e_Z + e_V = 10$ and $e_Z + e_V = 12$ for $e_V > 0$. In the series meta ($e_Z + e_V = 8$) iodate oxyanions the increase of e_V is accompanied by a decrease of their anion-acceptor properties (ac) with a simultaneous increase of anion-donor properties (bas). In this respect the generally known meso- ($e_Z = 10$) and ortho- ($e_Z = 12$) iodates(VII) with $e_V = 0$ represent a limiting case of the highest stability. Similarly, the increase of e_Z causes the decrease of electron acceptor properties (ox).

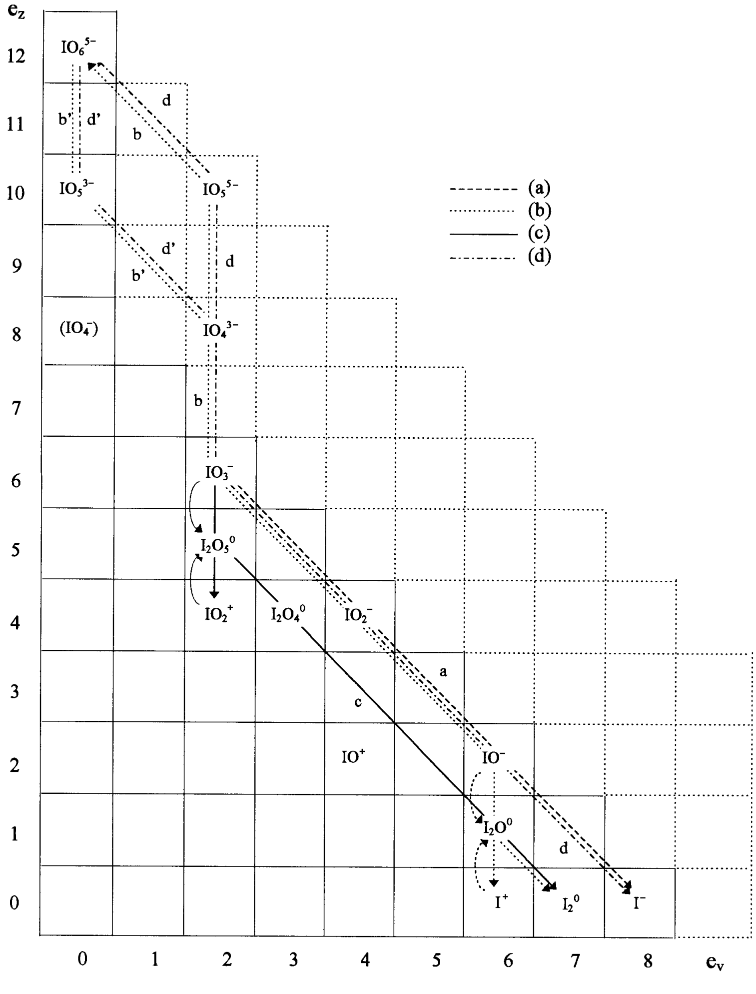


Figure 27. Classificational analysis of the effect of cationic counterions on thermal decomposition of iodate(V) according to Gontarz [22].

The metaiodate (V) ($e_Z = 6$) are stronger acceptors of valence electrons e_V, owing to a lower value of e_Z, as the yet not obtained meso ($e_Z = 8$) and ortoiodate (V) $e_Z = 10$. For this reason it is not possible to find iodates(V) of higher coordination degree in the products of reaction of metaiodate(V) with donors of oxide anions. The meso and orthoiodates (V) formed in the first step of a base action on metaiodate (V) are immediately oxidized by the meta substrate to orthoiodate(VII): $4\mathrm{NaIO_3} + 6\mathrm{Na_2O} \rightarrow 3\mathrm{Na_5IO_6} + \mathrm{NaI}$ (Fig. 27d). The knowledge of regularities in the variability of ac-bas and red-ox properties of csu in the morphological classification system $e_z - e_v$ is an important element for the correlation of the virtual steps with the positions of starting materials and products of thermal decomposition of iodates(V) having various cationic counterions. It enables also to propose step mechanisms of decomposition of such compounds, conforming the experimental results. The products of thermal decomposition of metaiodate(V) differ, depending on the electronegativity force E_f of the cationic counterion involved, since it determines the anion-acceptor properties (ac) of the cation. According to Gontarz's observations, three different cases can be encountered. Thermal decomposition of potassium salt ($E_f = 5.4$ nN) proceeds according to equation: $2\,{}^{6}_{2}\mathrm{JO}_3^- \rightarrow 2\,{}^{0}_{8}\mathrm{I}^- + 3\mathrm{O}_2^0$. The iodate anion is unable to bind the oxygen released in the decomposition occurring at 500°C to form iodate(VII).

The products of thermal decomposition of magnesium salt ($E_f = 33.4$ nN) are shown in the following balance equation: $10\,{}^{6}_{2}\mathrm{JO}_3^- \rightarrow 2\,{}^{12}_{0}\mathrm{IO}_6^{5-} + 4\,{}^{0}_{7}\mathrm{I}_2^0 + 9\mathrm{O}_2^0$. The electronegativity force of magnesium cation is only sufficient to bind the oxide ligand from the least basic csu occurring on the pathway of decomposition iodate(V), namely from ${}^{2}_{6}\mathrm{IO}^-$. Magnesium oxide, formed along with free iodine I_2^0, has a lower binding force to the oxide anion than ${}^{6}_{2}\mathrm{IO}_3^-$. This fact enables the formation of iodates(V) with a higher coordination: ${}^{8}_{2}\mathrm{IO}_4^{3-}$ then ${}^{10}_{2}\mathrm{IO}_5^{5-}$ as steps in the decomposition of magnesium metaiodate(V). The increasing number of oxide ligands with the same number of electrons $e_v = 2$, results in an increase of electron-donor properties (red). As a consequence, the higher coordinated iodate(V) acts as a reducer on the meta-iodate(V) in a specific process of disproportionation, which leads to a formation of ortho-iodate(VII) and iodine (Fig. 27b).

Thermal decomposition of aluminum iodate(V) ($E_f = 85.9$ nN) gives the products shown in the following equation: $4\,{}^{6}_{2}\mathrm{IO}_3^- \rightarrow {}^{0}_{7}\mathrm{I}_2^0 + 2\mathrm{O}^2 + 5\mathrm{O}_2^0$. The strongly acidic aluminum cation binds the oxide ligands directly from the starting ${}^{6}_{2}\mathrm{IO}_3^-$ to form IO_2^+, which syn-proportionates with the meta-iodate(V) anion and gives the iodine(V) oxide, which decomposes to free iodine. The oxide ligands bound firmly in aluminum oxide do not give secondary reaction with ${}^{6}_{2}\mathrm{IO}_3^-$ (Fig. 27c). Basing on these reactions Gontarz has proposed also a step mechanism of decomposition of iodate(V) with inert cationic counterion in the presence of an external donor of oxide anions (Fig. 27d).

In the studies of oxy-nitrogen csu of silicon S. Podsiadło used the $e_{zO} - e_{zN}$ matrix of silicon for $e_v = 0$ (Fig. 28) [10,16,21]. Only one, from the more than six possible csu of this kind, has been found in literature assuming, that the coordination number of silicon does not exceed 6 (SiON^-, Fig. 28). The existence of three further csu (SiNO_2^{3-}, SiNO_3^{5-} and $\mathrm{SiN_2O}_2^{6-}$) has been proved in a solid-state synthesis based on the classificational preassumptions. The products of this reaction have been identified by the X-ray phase analysis, as well as the products of their thermal decomposition. So *e.g.* $SiN_2O_2^{6-}$ was obtained both in the action of lithium nitride on silicon dioxide, and in reaction of lithium oxide with lithium nitrosilicate:

$SiO_2 + 2N^{3-} \rightarrow SiN_2O_2^{6-}$, *e.g.* $SiO_2 + 2Li_3N \rightarrow Li_6SiN_2O_2$ (Fig. 28c);
$SiN_2^{2-} + 2O^{2-} \rightarrow SiN_2O_2^{6-}$, *e.g.* $Li_2SiN_2 + 2Li_2O \rightarrow Li_6SiN_2O_2$ (Fig. 28c′).

The use of X-ray phase analysis has enabled to confirm the identity of both the products obtained by different methods. The thermogravimetric analysis has also confirmed the identity of their thermal decompositions, which result in formation of corresponding homoligand products in appropriate proportions (in this case 1:1). $2SiN_2O_2^{6-} \rightarrow SiO_4^{4-} + SiN_4^{8-}$, *e.g.* $2Li_6SiN_2O_2 \rightarrow Li_4SiO_4 + Li_8SiN_4$ (Fig. 28z). The existence of csu $SiNO_2^{3-}$ (Fig. 28 a,a′,x) and $SiNO_3^{5-}$ – (Fig. 28 b,b′,y) has been shown by the same methods.

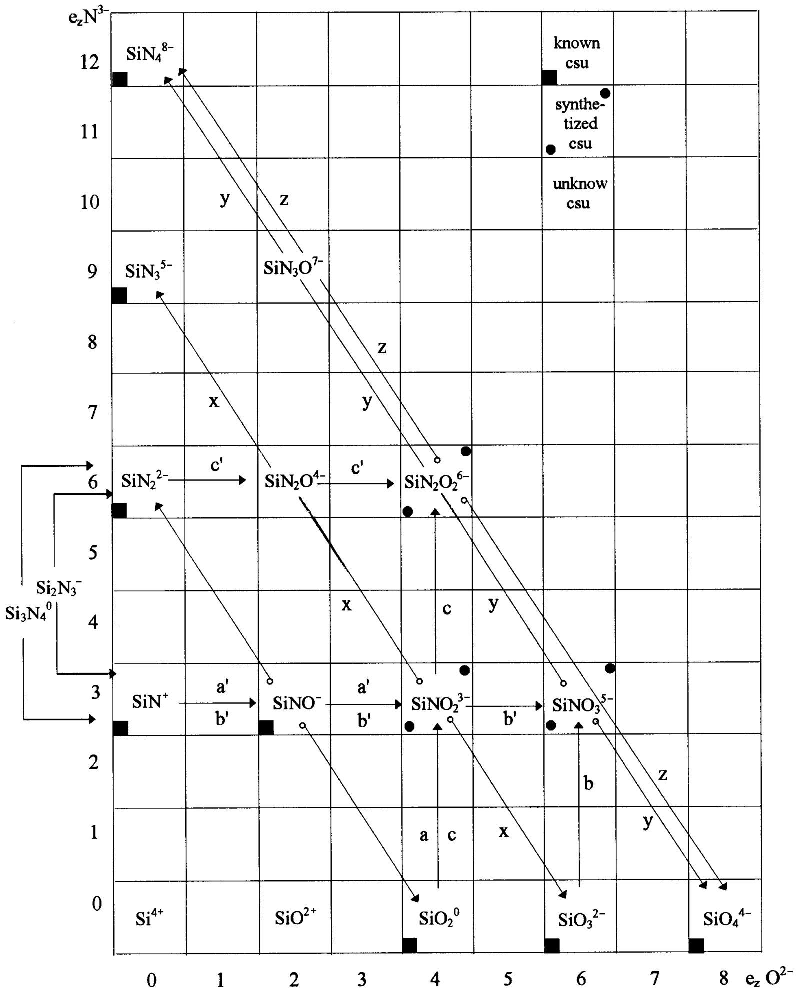


Figure 28. Synthesis of oxynitride silicates in the e_{zO2-} – e_{zN3-} classification system according to Podsiadło [10].

8.2. The morphological classification in didactics: After a period of increasing questioning the necessity of knowledge of chemical compounds acquired by students, particularly strong in the fifties and sixties of the 20th century, the importance of the properties and transformations of a large variety of chemical compounds in chemical education has been finally accepted in the late seventies. An expression of this state is the generally acknowledged crucial work ”Chemistry of the Elements” by N.N. Greenwood and A. Ernshaw, edited by Pergamon Press in 1985. However, from the methodic viewpoint, the book brings no novelty, as compared with its predecessors, *i.e.* the “Lehrbuch der Anorganischen Chemie” by H. Remy, published by Akad. Verl. Ges. in 1948. The authors of both these books devoted to the descriptive chemistry, do not transcend the periodical system of elements, as far as ordering of the matter is concerned.

The science of chemical compounds, referred to as the descriptive chemistry, presents much difficulty to both the students and the teachers, because of its encyclopedic character. A logical base for the treatment of such an enormous set as that of millions of chemical compounds, should be provided by comprehensive classification systems. The morphological classification, being an extension of the periodic system to the range of chemical structural units and their compounds, provides a step ahead in this direction. By its pointing to the analogies and regularities in the structure and properties of csu, as well as to correlations between the facts observed, the morphological classification makes the descriptive chemistry a logically ordered branch of science, with a considerable share of specific deduction and broad possibilities of generalization. The students can acquire the descriptive material with less of their memory engaged to the benefit of associating the facts. A detailed presentation of lectures based on the morphological classification has been given in our manuals [5,6] and didactic monographs [7–12].

8.3. Nomenclature aspects of the morphological classification: Besides the number e_v, which is directly connected with the oxidation state as the nomenclature parameter, the morphological classification involves the parameter e_z which, along with e_v, gives more possibility for the alphanumerical nomenclature of chemical structural units and their combinations, as shown in the following examples:

${}^{12}_{0}IO_6^{5-}$	..... oxo12-iodate 0	${}^{7}_{0}SO_3F^{-}$	..... oxo 6-fluo 1-sulphate 0
${}^{8}_{0}IO_4^{-}$	..... oxo 8-iodate 0	${}^{6}_{0}S_3O_9^{0}$	3 cyclo-sulphur 0-oxide 6
${}^{6}_{2}IO_3^{-}$	..... oxo 6-iodate 2	$S_4O_{10}^{2-}$	..... chain -3 oxo 6- oxo 8-sulphate 0
${}^{5}_{2}I_2O_5^{0}$	biiod 2-oxyd 5	$(AsO_2^{-})_n$	..... catena-oxo 4-arsenate 2
${}^{4}_{2}IO_2^{+}$	oxo 4-iodyl 2		

9. Final remarks

The morphological classification is based on an unconventional, but more up-to-date system of elementary chemical structural concepts. These comprise the chemical elements as sets of positively charged atomic cores which form, along with valence electrons, chemical structural units (csu) of negative, zero, or positive balance charge. The csu are taken as the essential components of macroscopic systems of chemical compounds, either directly or in the form of their various bounded complexes. The change in the fundamental concepts results in changes of the secondary concepts and definitions leading to unconventional chemical reasoning, which is easy to accept by beginners but difficult to apply by people used to the traditional system. This difficulty is, however, rewarded by the possibility of morphological classification of chemical structures and their transformations, which was impossible to achieve in the traditional system of fundamental chemical notions. It is the first attempt in chemistry to systematize the chemical compounds as structures that are intercorrelated by elementary transformations. Such an approach creates new possibilities of application of this classification. Much attention has been paid to prove experimentally that the classification steps are the real stages of chemical reactions of csu. The morphological classification deals with csu in a broad variety of structural situations and events. It results from the description of csu by numbers of e_z and e_v and the description of multicenter species by mean values of $\bar{e}_z$ and $\bar{e}_v$. The applicability of such classification is, however, limited. In chemical compounds of more complicated systems of component csu, as in organic compounds with heteroatom functional groups, both the $e_z - e_v$ numbers and the mean values of $\bar{e}_z$ and $\bar{e}_v$ lose their classificational significance and may be used reasonably only for the n-hydrocarbon part (or of another type isomer) and, separately, for the functional groups. Similar situations occur in the domain of organometallic complexes, where the classification may concern only either the coordination centre or particular ligands, with no possibility of their common treatment. As much as in the domain of csu the morphological classification can serve as an extension of the periodic system of elements to the area of structures and transformations of the classified species.

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