Původní práce

THE MULTIVARIANT SYSTEM OF OXIDES AND PREDICTION OF THEIR PARTIAL PROPERTIES IN OXIDE GLASSES

Part II

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A discussion is presented of the relationships between properties (geometric properties, bonding properties, those related to thermal vibrations, those due to stress formation, those related to diffusion phenomena) exhibing common group features.

An element in oxide glasses has its own specific partial properties and its own glass-forming ability; according to these characteristics the elements have been divided into seven classes distinctly distinguishable in the block arrangement of the periodic system.

The V-phenomenon constitutes a basis for a correlation model of the partial properties of glasses derived from the general properties of the atoms. Multiple linear and quadratic regression was applied in the study of the respective correlations. The results allow to predict the properties of oxides in oxide glasses.

6. Prediction of the relationship between properties

The course of partial properties in the V-phenomenon permits to study the relations between the properties and to classify them into groups exhibing a number of common features.

If two properties exhibit the V-phenomenon, they are related and a dependence can be found between them.

Study of these relationships, a field so far neglected in the chemistry of glass, is necessary for building up a system of constituents in oxide glasses because an effect imparted by an element and related to various properties of oxide glasses is not controlled monotonously in a certain standard manner. A number of properties stand apart from the helotism of the V-phenomenon pattern.

Knowledge of the features of the related properties in the groups allows to predict which general relation an element will exhibit with respect to a certain property.

Knowledge of the related properties in glass is likewise significant from the point of view of technological practice because on the basis of one known property one can estimate the effect of another property indirectly with a certain degree of probability.

The properties can be classified into the following two main groups:

I. Geometrical properties in which the V-phenomenon is not significant: specific volume, refractive index, permittivity, molar refraction. These properties depend on the spatial geometry of mass particles, their mutual positions and packing. Thermal history, separation into immiscible phases and the effect of combined ions (eci) have little effect on those properties which are generally not affected by influences related to transport and vibrations of mass particles.

II. Bonding properties in which the V-phenomenon is significant: thermal expansion of elasticity modulus, specific resistivity, thermal conductivity, heat capacity, viscosity, surface tension, and partially chemical durability; these properties depend in particular on the type and strength of chemical bonds and on the type of structural units in Stanworth's sense (polyions, oxo-anions, cations).

Within the two groups there exist mutual correlations. For instance, in group I there holds the Hopkinson's empirical equation:

$$\varepsilon/d = 2.2\tag{24}$$

and the Maxwell's equation:

$$n^2 = \varepsilon \tag{25}$$

where n is the refractive index for long wave lengths.

In group II one can point out for example the Babcock's relation for η and ρ (above t_g)

$$\eta = a\varrho^b. \tag{26}$$

The properties in group II are divided into the following sub-groups: IIa — the properties related to thermal vibrations (thermal expansion, thermal conductivity, heat capacity) depend strongly on z/a^2 , less on R_i . The effect of separation and that of the eci effect is less marked than in the case of properties IIb.

IIb — the properties determined by stress in glass structure

(i) evident in the bulk of the glass: viscosity, modulus of elesticity, electric conductivity — depends strongly on e_V or z/a^2 , less on R_i .

(ii) evident at the surface only (resistance to chemical effects, melting temperature of oxides, scratch hardness and microhardness) — depends on e_V or on z/a^2 , and very strongly on R_i .

Both microhardness and viscosity of glass are proportional to polarisability of mass particles and thus also to molar refraction of glass (Fayet [54]).

The more a property requires a change in geometry, i.e. plastic deformation, the larger the effect of polarisability both above and below t_q .

Polarisability is an outstanding and technologically significant characteristic in the chemistry of oxide glasses and should not be neglected in the prediction of the effects of elements. The oxides of elements (e.g. K, Pb) the mass particles of which exhibit a high polarisability (a high deformability and a high ionic refraction R_i) have low melting points, reduce viscosity, tend to volatilize from the melt, reduce markedly surface tension, scratch hardness and glass hygoscopicity. Oxides of polarisable elements exhibit a higher partial refractive index and a higher permittivity.

There is a satisfactory correlation between the properties within the subgroups (e.g. $E \times \eta$ [55]).

Finally it is possible to establish a special subgroup for those properties which are related to diffusion phenomena, such as chemical durability and crystallization phenomena.

It was found that while most of the properties not related to diffusion

phenomena are controlled by simple additivity expressed by the linear regression equation

$$A = a + \Sigma b_i m_i \tag{27}$$

the properties related to diffusion phenomena are more complex and require an additive description by means of an equation containing quadratic and multiplicative terms

$$A = a + \sum b_1 m_i + \sum b_2 m_i^2 + \sum b_3 m_i m_j.$$
(28)

This quadratic equation indicates that in the case of diffusion phenomena the elements influence themselves mutually, enter into interactions and the dependence of the properties on composition is nonlinear. In these cases the effect of an oxide cannot be expressed by partial molar factor F_A .

It should be stressed that the participation of oxides in the structure of oxide glasses does not proceed, within the V-phenomenon, identically with the course of partial properties A, so that the share of electropositive elements n the formation of glass must be studied separately.

7. The V-phenomenon and the participation of oxides in the constitution of glass

The participation of oxides in the constitution of glass is called here ad hoc their glass-forming ability for reasons of brevity. When applying the Stanworth's model of building units (cations, oxo-anions, polyions) we may define the glass-forming ability as the way in which the units are incorporated into the polymer network and how they participate in its structure. In this manner the glass-forming ability is distinguished from the network-forming ability, which concerns only the elements capable of forming directly the polymer network.

The V-phenomenon has been explained by us on the basis of two principles: by the Magnus bonding energy U_M and by the chemical bond specified by the mixed-bond index β .

With the V-phenomenon, U_M affects more the partial properties, β affects more the glass-forming ability. The two principles cannot be interchanged nor completely superimposed.

The glass-forming ability of an element in the glass network is related to the bond strength inside the atom in the molecule by which the electron is bound to the nucleus, the bond strength being expressed quantitatively by electronegativity X. The smaller the mass particle, the smaller the internuclear distance a, and the larger the difference between the electronegativity of the electropositive element and the electronegativity of oxygen ΔX , the more stable the structure of the oxo-anionic groups supporting the formation of glassy structure. Formation of a polymer network is therefore determined by the formation of polyions and oxo-anions and bound to positive values of U_M . Another precondition, however, is a high electronegativity X, a prevalence of covalency over ionicity, and a low value of the mixed-bond index β .

A very fitting example of the double uninterchangeable effect of U_M and β is the behaviour of Zn(II), Be(II) and Mg(II).

 U_M of zinc has a negative value (--6,9) and in accordance with it by its partial properties zinc lies along branch I of the V-phenomenon together with the light metals (IA) and (IIA) of the periodic system. In agreement with its negative U_M , zinc behaves as a modifier.

Its $\beta \sim 1$ and high electronegativity X (1.5), however, rank it among the intermediary elements. According to $\psi = 0.532$ its guiding coordination number y = 6. However, in orthosilicate Zn_2SiO_4 zinc has y = 4. Contrary to the case of Ca_2SiO_4 the former orthosilicate is also known in vitreous state, although its NSi no longer meets the requirements for a continuous lattice of SiO₄ tetrahedrons and although the deformability of its mass particle $(R_i = 9.7)$ is low and does not contribute to the formation of the vitreous state. As indicated by density and IR spectral measurements, the glasses contain both co-ordination forms of Zn side by side although there is still considerable disagreement as regards Zn(II) in oxide glasses. The high electronegativity X and $\beta = 1$ shift Zn(II) towards branch II elements as regards its glass-forming ability.

The U_M of Be(II) amounts to +0.8. Its small effective radius $r_i(0.27)$, its low value of ψ 0.25, y = 4, $\beta = 1$ and a high electronegativity X (1.5) are the reasons why Be(II) is disaligned from branch I of the V-phenomenon towards the network-forming elements and predetermine its active role in the polymer network.

Similarly, Mg(II) is capable of existing in glass with two co-ordination numbers, namely y = 6 and y = 4. The y = 6 corresponds to a negative $U_M(-1.5)$, y = 4 corresponds to a positive U_M (+0.8). Its value of $\psi = 0.625$ ranks it among the modifiers, while the positive U_M implies a slight possibility of active participation in the network.

As to their glass-forming ability oxides can be divided into the following groups:

Group I: The modifying elements of the 1st order (MOD I). The group comprises light s- and d_0 -metals lying in vertical columns IA and IIA of the Periodic system. In the V-phenomenon they are located along branch I. The group includes alkali metals and alkaline earths and is identical with the historical group of modifiers. The atomic characteristics are as follows: U_M negative, X lower than 1, ionicity prevails over covalency, the bonds are non-directional, the deformability low. The elements are structurally passive, merely equalizing the unsaturated bonds in the polymer network.

Group II. The modifying elements of 2nd order (MOD II). These include the s-elements Zn(IIB), Cd(IIB), and the heavy element Pb with 18 electrons in the outer shell. The U_M is negative and ranks these elements with respect to their effects on properties among the modifiers, this being expressed by their positions in close proximity to branch I of the V-phenomenon. However, their electronegativities X are higher than with group I (1.5) and $\beta = 1$ ranks them simultaneously among the intermediary elements as regards their glass-forming ability as defined above. The bonds are mildly directional. The deformability R_i is low with the exception of Pb(II).

Group III: Pseudomodifiers (the modifying elements of 3rd order) (MOD III). The transition *d*-elements, namely rare earths (Sc, Y, La) and lanthanoids from column IIIB lie at the connecting line of V- phenomenon having an approximately identical slope as the modifiers of 1st and 2nd orders. The difference from modifiers of 2nd order lies in the U_M values which although negative, have small values close to zero. As compared to group I the electronegativity is higher than 1, $\beta < 1$. The group represents a transition to intermediary elements; however, by their partial properties in glass the elements are closer to modifiers. Group IV: The structurally active elements (INTM). They are delimitated by the mixed-bond index $\beta = 1$. The elements are roughly identical with the historical group of intermediary elements. The elements in question are Be (IIA), Al (IIIA), Ga (IIIA), In (IIIA), Zr (IVB) and Hf (IVB). The U_M is positive, the elements lie at the boundary between branches I and II of the V-phenomenon. In glass, y is 4, with the exception of In, Zr and Hf where y is equal to 6. The degree of ionicity and covalency is equalized in free oxides. The bonds are directional. All the elements of this group are capable to form components of the polymer network. When y = 4, they are able to substitute isomorphously (SiO₄). Both Zr (IV) and Hf (IV) separate readily as a result of incompatibility of their polyhedrons with silicon tetrahedrons.

Group V: Conditionally network-forming elements (CNVF). The group comprises ,heavy' elements Hg (II), Tl (I, III), Pb (II, IV), Bi (III). With higher oxidation numbers the U_M is positive, with the lower ones it its negative. Pb (II) acts in glass as modifier of order. The high electronegativities $x \sim 1.5$ and the low β (between 0.5 and 1) indicate to oriented bonds and to possible polymeration in the glass network on the condition that even a minor amount (approx. 5%] of element (Si, Ta, Nb) with high bond strength is present. Mercury cannot exist in silicate glasses in its oxide bond owing to the low sublimation temperature of its metal vapours.

Group VI: Imperfectly network-forming elements (INWF). The *d*-elements, acid in nature, Ti (IVB), Sn (IVA), Nb (VB), Ta (VB), V (VB), Mo (VIB), W (VIB) lie mostly along branch II of the V-phenomenon. The positive U_M is indicative of the formation of oxo-anions. $\beta < 1$ implies directional bonds. The small internuclear distance a (1.3) indicates that their oxides are capable to exist in vitreous state (monooxide glasses) but only after very rapid quenching of the melt.

Group VII: Network-forming elements (NWF). The elements of the group are characteristic by their co-ordination number y = 4. The *p*-elements (B, Si, P, and Ge) with 8 electrons in the outer shell are distributed along the step-like line in the region beyond the boundary of the post-transition elemets (Fig. 6). Ge with its 18 electrons at the left-hand side of the step-shaped boundary represents a transition between the post-transitional elements and the network-forming ones, and exhibits y = 4, and exceptionally also y = 6.

B (III) has an exceptional position in the group. In glass it forms structural units with y = 3 and y = 4. These co-ordination units, however, are not distributed throughout the glass statistically, but form higher structural units (chains, rings, spatial formations). These higher structural units depend on the composition of glass (on the ratio to alkali metals, on the amount of Al_2O_3) and are reorganized with increasing temperature below the transformation interval. That is why B_2O_3 changes its partial properties F_A within a very wide range in relation to glass composition and temperature, so that its F_A cannot be fixed accurately in the V-phenomenon.

Classification into the historical groups of network-forming, intermediary and modifying elements has thus ceased to be empirical only and has been given a quantitatively formulated framework.

The suggested groups are comprehensively illustrated and the V-phenomenon supplemented by the schematic diagram in Fig. 4 which shows the relationship of U_M and β .

Modifiers of the order I, II and III lie along three special connecting lines A, B, C differing in the oxidation number.

The structurally active intermediary elements lie along the horizontal line D.

Several interesting configurations can be observed along branch II of the V-phenomenon:

The conditionally glass-forming elements lie along the common line E.

The imperfectly network-forming elements with oxidation number IV are situated along line F.

The imperfectly network-forming elements with oxidation number V are placed along line G.

Elements with oxidation number VI lie along line H.

Line I joins network-forming elements having the co-ordination number y = 4 and/or the oxidation number z = 4. Boron lies apart from this line, this bearing out its exceptional position among the network-forming elements.

This is evidence for the assertion that for the formation of a three-dimensional continuous network of silicate glasses the number 4 is significant both in z or in y or jointly (Volf [¹¹]).

In the U_M vs. β schematic diagram the elements lie at the main connecting lines characterized by their oxidation numbers, which bears out the significance of the oxidation number for the system of structural components of oxide glasses.

Apart from the main z-lines (A, B, C, D, F, G, H) there are differentiated auxiliary connecting lines (E, I) characterized rather more by the co-cordination number y = 4. They have opposite slopes. Also in this schematic diagram the V-phenomenon exhibits a variety in slopes of the connecting lines.

8. The topology of elements in the Periodic system

The effects of elements in oxide glasses are projected through the periodicity of characteristics of atoms into the Periodic system which is shown here in two new forms, namely (a) in the form of a long block table (Fig. 6), and (b) in a diagram of dimensionless quantities (Fig. 7).

In the periods designated by the main quantum number n the light metals comprise columns IA and IIA, namely the s-elements (n = 2 and 3) and the d_0 -elements with unoccupied orbit d_0 (n = 4 to 6). The effect of d_0 -elements in oxide glasses differs from that of the s-elements. Thus the factors for n_D in the triade K(I)—Rb(I)—Cs(I) do not lie along one z-line common to elements with oxidation number (I), but along a line having a slope reverse to that of the Na(I)—Li(I) connecting line. Also in other properties the d_0 -elements differ from the s-elements and in the V-phenomenon form either independent clusters or lie along z-line differing in its slope more or less from the z-line of s-elements (e.g. in the case of surface tension). Be(II) and Mg (II) likewise differ from the triade Ca(II)—Sr(II)—Ba(II) along a separate branch.

However, even the triades of elements having n = 4, 5, 6 do not lie on a common z-line, but they exhibit a marked inflexion in the position of molar factors F_A ; elements with n = 4 differ from those with n = 5 and n = 6. The horizontal triade Fe—Co—Ni has therefore little in common with the neighbouring triade Ru—Rh—Pd (n = 5) and Os—Ir—Pt (n = 6). In its properties in glass Ti(IV) differs from Zr(IV), although in a number of glasses both elements are present side by side. The F_A factors of d_0 -elements, e.g. those of



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Ca—Sr—Ba also do not lie along a common z-line but along the inflected line Ca—Sr—Ba.

The F_A factors of the triade of pseudomodifiers of *d*-elements Sc---Y---La (IIIB) constitute a transition between the partial properties of the d_0 -elements of the *A*-subgroups (Ca---Sr---Ba) and the transient *d*-elements of the *B*-subgroups, as indicated by the similarity of optical properties of the respective oxides in silicate glasses.

The palladium and platinum elements form thermolabile oxides and exist in glass as pyrosols of metallic particles.

The transition elements IB (Cu, Ag, Au) and the IIB (Zn—Cd—Hg) have 18-electrons in the outer shell, and are similar in glass to post-transition elements III, IV, V and VI below the step-shaped line; in glass these elements should be preferably regarded as a separate group with 18 electrons.

Elements IIIA to VA (B, Si, P, As, n = 2 to 4) belong to network formers. The elements adjacent to the step-shaped line, i.e. Al, Ge, Sb can participate in the network.

The post-transition elements are characterized by an inert pair of electrons typical in particular for the "heavy" elements Hg, Tl, Pb and Bi and exist in glasses with two oxidation numbers z and (z - 2). Towards the lower n (from below upwards) the effect of the inert pair of electrons rapidly diminishes (Al, Ga, Ge show one z only). Elements with the inert pair are metallophillic.

The higher the oxidation number (z = 3) the more expressive the effect of differences in electron configuration (*p*-elements, *d*-elements, elements with 18-electron shell) between the molar factors F_A of oxides of isovalent elements with identical oxidation number as compared to elements with low oxidation number. For instance, elements Si (IV), Sn (IV), Ti (IV), Zr (IV) lie along the z-line exhibiting a greater dispersion than would be expected, as can be seen from the position of their dissociation energies e_V versus z/a^2 (Fig. 1a).

In what way is the V-phenomenon projected into the Periodic system?

The modifiers of the lst order, s-elements and d_0 -elements aligned along branch I of the V-phenomenon and having negative U_M , $\beta > 1$, X > 1, fill columns IA and IIA.

Be (II) and Mg (II) lie apart from branch (I) in the direction of branch (II) towards elements B (III) and Al (III).

The pseudomodifiers situated close to branch (I) and having z = III, $U_M \sim 0, \beta > 1$ and X < 1, fill column IIIB.

The intermediary elements having $\beta = 1$ exhibit alternating y = 4 or y = 6 and lie scattered in IIA (Be), IVB (Ti, Zr) and III (A, I Ga, In).

The elements in VB (Nb, Ta) and VIB (Mo, W) imply by their tendency to the network-forming ability. However, their oxides exist in vitreous state only when rapidly quenched from melt; they belong into the group of imperfect network-forming elements.

Elements VIB to IB constitute a break in the Periodic system. Elements having n = 4 exist in glasses with lower oxidation numbers only than would correspond to the oxidation number of their vertical columns. Elements of n = 5 and n = 6 are present in oxide glasses mostly in metallic form, producing oxides only under a great excess of bound oxygen, e.g. in P₂O₅ glasses.

Elements IB in glass are related to the group of platinum and paladium metals and have a similar tendency to form pyrosols in glasses (ruby glass).

Modifiers in IIB and those of 2nd order differ from modifiers of the 1st order

in that the negative U_M ranks them among modifiers, and $\beta = 1$ among the intermediary elements.

The elements situated to the right of the second stepshaped line are non-metals.

The *d*-elements VIIB to IB constitute a central group dividing the Periodic table into two sections, the left-hand one (IA, IIA, IIIA to VIB) and then right-hand one (IIB, IIIA to VIIA). In each of two sections in the direction to the right the ionicity increases and the covalency decreases together with the tendency to network-forming ability. However, the left-hand section is generally more ionic in character, the right-hand one being more covalent. As a result of this the network-forming ability in the left-hand section never attains the degree of proper network-forming elements (including only imperfect network-formers); on the other hand, the right-hand section does not contain modifiers of the lst order.

The modifiers of the lst order (Na, Ca) and the proper networkformers (Si, P) are present solely in groups A, having 8 electrons in the outer shell.

The periodic relationship of the main characteristics of atoms can be demonstrated in an interesting way in a diagram of dimensionless quantities r_i/r_0 and z_0/z_i , i.e. radius and charge of an electropositive element and that of oxygen.

These dimensionless characteristics have been suggested by Plumat [3] for the mapping of elements with respect to their glass-forming ability. The adapted Plumat principle was applied in the present study for investigating the relations between r_i , z, β , U_M , X and the electron configuration.

In the diagram in Fig. 7 elements of the same oxidation number lie along connecting lines. The diagram is divided by skew lines demarcating fields I to IV (a, b). The top field (a) and the bottom one (b) are separated by line GH passing in neighbourhood of elements Cu—Cd—Sc—Ti—V, that is of d-elements having n = 4.

The position of this dividing line is defined by the equation

$$r_i = 0.1 z + 1 \tag{29}$$

The AB line separates the modifying s and d_0 -elements aligned along branch (I) of the V-phenomenon.

The CD line separates the network-forming elements lying on branch (II) of the V-phenomenon.

The Ti—As boundary separates the right hand networkformers from the imperfect networkformers.

Field IIb encloses modifiers of the 3rd order, which are situated close to branch (I) of the V-phenomenon.

Field IIIa comprises structurally active (intermediary) elements.

Field IIIb contains structurally active elements with higher ionisation energies.

Field IVb encloses elements with imperfect network-forming ability, field IVa networkformers.

Electronegativities X increase in the direction from the left to the right. Elements with $\beta = 1$ are designated by black rings.

As(V) lies at the very boundary of the GH dividing line lowest in the field of networkformers. Its co-ordination number in oxide glasses is not 4; however, the oxygens are distributed around the central mass particle so that they



Fig. 7. Clasification of elements according to dimensionless quantities r_0/r_i and z_i/z_0 .

form an outer tetrahedron. The high positive UM (+11.7) and the low β (0.53) provide evidence, together with the two dimensionless quantities, for the polymeration and network-forming ability of this oxide.

9. Mathematical model of partial properties F_A derived from atoms and prediction of the properties of oxides in oxide glases

When using the assumptions that

a) the partial properties of electropositive elements in oxide bonds depend on the characteristics of atoms,

b) the characteristics of atoms are not subject to substantial changes in oxide glasses,

c) interactions occur only rarely in the case of simple (three-up to four-component glasses) insofar as they do not contain two isovalent elements at the same time,

d) with glasses of identical acidobasicity and of identical degree of networkforming ($N_{\rm Si} = 0.400$), the co-ordination number y is not subject to changes, one can attempt to correlate the partial properties of oxides in glass and the characteristics of atoms of electropositive elements bound to oxygen.

In this way it is possible to obtain theoretical F_A values using the regression method, and to facilitate distinguishing the properties of Ist and the IInd group (art. 6).

The following characteristics were chosen for the correlation:

- oxidation number z, as it significantly affects the positions of elements in the diagram of U_M vs. β (Fig. 4),
- internuclear distance a: The partial properties are related to the bonding energy between M and \bullet . The bonding energy is considered to be a sum of the attractive and repulsive forces between mass particles of opposite sings. Both forces are to a certain degree proportional to the inverse values of internuclear distance a;
- deformability R_i which determines the adaptability of the electropositive element to its immediate environment;
- bond strength I expressed indirectly by potentials z/a^2 , U_M , e_V .

	α K ⁻¹ (×10 ⁻⁶) Appen		λ (N . m ⁻¹ . K ⁻¹) (×10 ⁻⁴) GanFuSi		
	I	II	I	ÎI	
C	+1.5811	+1.2111	-110.1108	-22.3616	
<i>b</i> ₁	-0.4160	0.3524	+2.9196	-6.3660	
b_2	—0 . 0 347	-0.4133	-31.1195	+14.6117	
b3	-0.0025	+0.0425	-0.3352	-0.1078	
b4	-0.5153	+0.3973		+2.2094	
bs	+0.0532	+0.0130	+2.4646	+1.9086	
b_6	+0.000	-0.0033	+0.1048	+0.2187	
\mathbb{R}^2	0.999	0.9661	0.9771	1.0000	
Sxy	0.006	0.034	1.296	0	

	Table V	a			
Regression	coefficents	for	equation	(30)	

Table V lists the regression coefficients b_i determined by linear multiple regression:

$$F_A = C + b_1 z + b_2 a + b_3 R_i + b_4 (z/a^2) + b_5 U_M + b_6 e_V .$$
(30)

	E (MPa) (×10¹) Gan-FuSi		$\lambda [N \cdot m^{-1}] (\times 10^{-5})$ Dietzel		
	I	II	I	II	
$C \\ b_1 \\ b_2 \\ b_3 \\ b_4 \\ b_5 \\ b_6$	$\begin{array}{r} +3407.6081 \\748.4099 \\395.9616 \\6.4655 \\189.0172 \\ +133.7846 \\ +18.0579 \end{array}$	$\begin{array}{r}+75189.5618\\-16423.9669\\+26875.7895\\+1996.6557\\+2470.4756\\+1686.0464\\-40.7251\end{array}$	$\begin{array}{r} -6326.0973 \\ +1869.6106 \\ +938.2047 \\ -54.9837 \\ +50.6918 \\ -250.9433 \\ -2.4175 \end{array}$	$-11628.0922 \\ -1.8560 \\ +6123.4541 \\ -140.9726 \\ +1695.1241 \\ +0.0466 \\ +8.6235$	
R ² S _{xy}	0.9850 79.453	1.0000 0	0.9992 21.966	1.0000 0	

Table VbRegression coefficients for equation (30)

For each property the regression coefficients are listed separately for each branch of the V-phenomenon. Table V shows the determination coefficient R^2 and specifies the standard error of estimate S_{xy} . The calculation was carried out on the Computer 327 computer.

The values allow to formulate the following conclusions:

1. Along branch (I) of the V-phenomenon in all the properties regression coefficient z surpasses coefficient a; along branch (II) a surpasses z.

2. In the case of surface tension and modulus of elasticity, i.e. in properties of IIb associated with stress, the effect of R_i is always more marked in branch (II). With thermal expansion and thermal conductivity as properties of IIa depending on thermal oscillation of mass particles the effect of R_i is smaller. 3. Among the bonding energy potentials, the Magnus energy U_M merely supplements the electrostatic field strength z/a^2 .

4. The determination coefficient R^2 exceeds 0.93 and in 9 out of 14 cases (65 %) it is closely equal to unity.

The equations given provide a more exact picture of the V-phenomenon. The coefficient $R^2 = 1$ proves that a) there is a good agreement between the partial properties of oxides in glass and the complex of characteristics of the respective atoms, b) that the six selected characteristics are satisfactory for a description of the relationships.

The general relations between the F_A of oxides and the characteristics of atoms are so far unknown. In the present stage when the approach is based mostly on phenomenology, the application to mathematical statistics is fully justified.

In addition to linear regression, interesting relations are provided by quadratic regression between F_A as a dependent variable and the independent variables z/a^2 (or e_V) and R_i . The determination coefficient R^2 close to unity indicates that the partial properties can be predicted with a considerable probability on the basis of bonding strength and ionic refraction. The relationships are listed in Table VI according to the equation

	λ [W . m ⁻¹ . K ⁻¹] (×10 ⁻⁷) Gan FuSi		E [MPa] (×10¹) Gan FuSi		γ [N · m ⁻¹] (×10 ⁻⁵) Dietzel	
	I	II	I	II	I	II
C	-4.745	+8.392	+585.768	+2133.104		-17.484
<i>b</i> ₁	-0.474	+0.362	-83.875	+1063.378	+4011.861	+1466.754
b2	+0.348	-0.003	-+14.858	-132.038	-7.218	+14.245
b_3	0.006	-0.002	+1.194	-36.020	-3890.366	-580.476
b_4	+0.001	-0.004	+1.213	+4.377	-37.705	-63.902
b_5	-0.002	+0.004	-0.099	-0.443	+0.835	+1.029
R2	0.929	0.999	0.865	1.000	0.099	1.000
X_1	ev	ev	ev	e _v	$z a^2$	$z a^2$
X_2	R_i	R_i	Ri	R_i	\dot{R}_i	Ri

Table VI Regression coefficients for equation (31)

$$F_A = C + b_1 X_1 + b_2 X_2 + b_3 X_1^2 + b_4 X_1 X_2 + b_5 X_2^2$$
(31)

where X_1 is either e_V or z/a^2 , and X_2 is R_i .

They provide evidence for the relation between partial properties of oxides in glass on bond strength and ionic refraction, which depends on the volume of mass particles.

The properties of group I do not exhibit the V-phenomenon; however, they can be related to volume V_i taken up by mass particles of electropositive elements and their oxygen envelope on the oxide

$$V_{i} = \left(N_{L} \frac{4}{3}\pi\right) \left[(m_{M}r_{i})^{3} + (n_{0}r_{0})^{3}\right]$$
(32)

as suggested by Mackenzie (27). The first member m on the right-hand side of the equation is a constant.

Elements having the same oxidation number lie along the same z-lines; however, no mathematical relation has so far been established for the positions of the lines (Fig. 8, 9).

The suggested mathematical model is regarded as the first hopeful step. The model has the advantage of allowing to predict, with a certain degree of probability, the properties even of inconventional oxides on which there is so far little knowledge in connection with glass systems.

On the basis of the V-phenomenon, the confrontation with various models of glass can be considered as a part of general inorganic chemistry.

CONCLUSION

1. The system of partial properties of oxides in oxide glasses, in particular silicate ones, and its mathematical model can be derived from the characteristics of atoms bound to oxygen.

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2. Molar factors F_A which express the partial effect of 1 mol % of an oxide on a property of glass, when ranked according to the electrostatic field strength z/a^2 of the oxides, are arranged along two crossing branches (the V-phenomenon).

3. The V-phenomenon is a general phenomenon which holds for instance in the case of thermochemical data in inorganic chemistry.



Fig. 8. Correlation of molar factors for permittivity (after Appen) and the volume of co-ordination groups $M - O_y = V_i$.



Fig. 9. Correlation of molar factors for the refractive index after Appen and the volume of co-ordination groups $M - O_y = V_i$.

4. It does not hold for the properties related to geometrical arrangement of mass particles in oxide glasses (permittivity, specific volume, refractive index).

5. The arrangement of the factors along the two branches of the V-phenomenon is governed by the Magnus bonding energy U_M determining the tendency of elements to form oxo-anions, and by the mixed-bond index of ioniccovalent bonds.

6. The V-phenomenon allows to derive a multivariant model of oxide glasses.

7. The V-phenomenon allows to specify partial properties F_A in correlation with the characteristics of the atoms by means of multiple regression.

8. The F_A factors hold only for glasses having a continuous three-dimensional network. Below Si/O 0.333 (e.g. in "invert" glasses) the sequence of factors of oxides changes.

9. The correlation can be used as a basis for prediction of properties of oxides in glasses.

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MULTIVARIANTNÍ SYSTÉM OXIDŮ A PREDIKCE JEJICH DÍLČÍCH VLASTNOSTÍ V OXIDOVÝCH SKLECH (ČAST II)

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V druhé části práce je diskutována příbuznost vlastností (vlastnosti geometrické, vlastnosti vazebné, související s tepelnými vibracemi, určované vznikem napětí, vlastnosti spojené s difúzními jevy) majících společné skupinové znaky.

Prvek v oxidových sklech se projevuje jinak ve svých vlastnostech, jinak co do sklotvornosti. Podle indexu smíšenosti iontokovalentních vazeb a Magnusovy vazebné energie byly prvky rozděleny co do sklotvornosti do 7 tříd: 1. prvky modifikující I. řádu, 2. prvky modifikující II. řádu, 3. prvky modifikující III. řádu, 4. prvky struk-turně aktivní, 5. prvky podmíněně sítotvorné, 6. prvky nedokonale sítotvorné, 7. prvky sítotvorné. Toto rozdělení souhlasí s umístěním prvků v blokové úpravě Periodické soustavy i ve schématu podle bezrozměrných veličin r_0/r_i a z_i/z_0 .

V-fenomén tvoří předpoklad pro korelační model dílčích vlastností oxidů ve sklech odvozený z obecných vlastností atomů. Ke studiu korelací bylo užito vícenásobné regrese (lineární a kvadratické). Výsledky umožňují predikci vlastností oxidů v oxidových sklech.

- Obr. 6. Blokový tvar Periodické soustavy s rozmístěním prvků modifikujících, intermediárních a sítotvorných.
- Obr. 7. Rozdělení prvků podle bezrozměrných veličin $r_0/r_i a z_i | z_0$. Obr. 8. Korelace molárních faktorů pro permitivitu podle Appena a objemu koordinač-ních skupin $M O_y = V_i$.
- Obr. 9. Korelace molárních faktorů pro index lomu podle Appena a objem u koordinačnich skupin $M - O_{y} = V_{i}$.

МНОГОВАРИАНТНАЯ СИСТЕМА ОКСИДОВ И ПРЕДИКАЦИЯ ИХ ЧАСТИЧНЫХ СВОЙСТВ В ОКИСНЫХ СТЕКЛАХ (ЧАСТЬ ІІ)

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Во второй части работы рассматривается сродство свойств (геометрические свойства, свойства связи, связанные с термическими вибрациями, определяемые образованием напряжения, свойства, связанные с явлениями диффузии), имеющих общие групповые знаки.

Элемент в оксидных стеклах проявляет свои свойства подругому, чем по отношению к стеклообразованию. Согласно показателю смешанности ионоковалентных связей и энергии свизи Магнуссна подразделяют элементы в зависимости от стеклообразования на 7 классов: 1. элементы модифицирующие І порядка, 2. элементы модифицирующиє II порядка, 3. элементы модифицирующие III порядка, 4. структурно активные элементы 5. условно структурирующие элементы, 6. песовершенно структурирующие элементы

7. структурирующие элементы. Эта классификация находится в согласии с размещением элементов в блочной обработке Перподпческой системы и в схеме по безразмерным величинам r_0/r_i и z_i/z_0 .

V-феномен образует предположение для корреляционной модели частичных свойств оксидов в стеклах, выведенное из общих свойств атомов. Для исследования корреляций пользовались многократной регрессией (иппейной и квадратической). На основании полученных результатов можно предсказать свойства оксидов в оксидных стеклах.

Рис.6. Блочная форма Периодической системы с размещением модифицирующих, интермедиальных и структурирующих элементос.

- Рис. 7. Подразделение элементов согласно безразмерным величинам ro/ri и zi/zo.
- Рис. 9. Корреляция колярных факторов для пермитивности (согласно Аппену) а объема координационных групп $M O_y = V_i$. Рис. 9. Корреляция молярных факторов для показателя преломления (согласно Аппену) а объема координационных групп $M O_y = V_i$.