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Původní práce

OXYGEN ANOMALIES OF OXIDE GLASSES

Part I

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Alkaline binary and ternary systems exhibit an anomalous dependence of properties on composition, which varies with the individual network formers as well as with modificators. Most attention has so far been given to borate anomalies. The present paper is concerned with the study of chemical dependence of anomalies, using a comparative method on borate glasses (Part I), on silicate, alkali-aluminosilicate and phosphate glasses (Part II), and on germanate and tellurate glasses (Part III). A list of symbols employed in all the parts is enclosed to Part I. The phenomenological model has been studied within the entire range of the vitreous state in terms of the volume characteristics, of invariant points of phase equilibria, of thermochemical characteristics, and in particular in connection with boundaries of cross-linking. With the exception of the effect of combined isovalent ions a change in the „state" of oxygens has been found as the common feature of all the anomalies.

The borate anomalies are spread all over the range of the vitreous state. However, they are concentrated above all at the relative standard compositions, in particular at that of pentaborate. The pentaborate ratio, which exhibits a minimum of thermal expansion, a minimum of tan δ, a minimum of activation energy of viscous flow, and a maximum of activation energy of the diffusion processes (chemical resistance) is considered to be related to the change from the ionic bond of oxygen atoms to a covalent one. In the transition between the two structures there appears the contact effect as the change in ionic vibration and that of Mie's indexes m and n, and the subsequent change in properties.

INTRODUCTION. THE METHOD

The anomalies of thermal expansion of alkali-borate glasses were first pointed out by Gooding and Turner in 1934 [40] although they had already been mentioned earlier in the studies by Grenet [63] and Samsoen [64]. The anomalies have not so far been satisfactorily explained. A survey of the theoretical concepts suggested so far has been treated in detail by Němec [1], Fanderlik [2] and Vogel [3].

We have found that the borate anomaly is not unique and that similar anomalies occur also in other binary and ternary systems with respect to various properties.

This finding has motivated a complex study and new evaluation of anomalies and their causes, aimed at their phenomenological chemical models. In this case, a chemical model is understood to be a summary description of phenomena related to chemical dependence of their properties. In a phenomenological chemical model one seeks the relations between the changes of properties and the changes in chemical composition, the change from a cross-linked structure to a chain-linked one, the invariant points of phase equilibria, the thermochemical characteristics, the types of bonds, the changes in the coordination number, and the volume characteristics, with minimum respect to the structural points of view.

The low-component (in particular binary) systems lie for the most part beyond the boundaries of technical application. However, study of their anomalies is useful as they

a) affect to various degrees also the multicomponent glasses,

b) delimitate and render more precise the application of additivity in the interpolation of properties from a given composition,

c) are instructive in the chemistry of glass, as a relatively young field of science, from the point of view of interdependence of properties.

The simple linear additive equation introduced by Winkelmann and Schott

$$A = f(c) = \Sigma g_i x_i \tag{1}$$

simplifies glasses as a mixture of oxides. Interpolation of properties from composition according to equation (1) assumes an ideal linear relationship between property A and composition c.

Deviations from an ideal linear course are here designated summarily as anomalies. Comparative study of anomalies in various systems indicates that in spite of their diversity, they have the common feature of involving a change in the "state" of oxygen atoms.

The properties will be divided into the following three groups:

(i) The properties depending on geometrical arrangement and tightness of mass particles. In a simplified way they will be called here geometrical properties. They include density, refractive index, permittivity, and the secondary properties such as Poisson's ratio, elasticity moduli, microhardness;

(ii) The properties showing a chemical dependence of activation energy.*) For the sake of simplicity they are summarized here under the term activated properties. They include diffusion phenomena, viscosity, electrical conductivity, chemical resistance;

(iii) The properties specified in relation with vibration of particles (thermal expansion, dielectric losses).

It has been proved advantageous to study relationships between the positions of anomalies in the system and the invariant points of its phase equilibria. It should be borne in mind that phase diagrams concern equilibrium states, while glasses are thermodynamically unequilibrial systems. The relationships between changes in properties in connection with phase diagrams have already been pointed out by Kurnakov [4], Demkina [5], Winter [6], and more recently by Babcock [7]. A glass corresponding by its composition to a compound in the diagram of phase equilibria has the lowest entropy, while in the eutectic the entropy is the highest. At the boundaries of primary phases or at the points of contact between two chemically differing regions the glass has therefore the greatest miscibility between the two adjacent phase fields.**) The invariant points in the phase diagrams serve as suitable tools for precisioning topologically anomalous changes in properties (their extreme values, maxima, minima, deflections) in terms of composition.

The co-ordination number y is usually changed together with the ratio of oxides of uni- or bivalent metals to the sum of network-forming and intermediate element

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*) The chemical dependence is understood here as a dependence on chemical composition of glass, similarly to the temperature dependence, which is a dependence on temperature, and the like.

**) The term „miscibility" (ability of mixing) has been explained from the standpoint of thermodynamics by Denbigh (4, cf. paragraph 1.17).

oxides. The change in co-ordination number from $y = 4$ to $y = 6$ is revealed by increased ionicity and by a change in geometrical properties. However, insofar as the change of co-ordination number has not been proved experimentally (e.g. by the NMR method) the changes in properties should be related to the change in y with utmost caution only.

It has been found expedient to follow not only the course of chemical dependence of property A but also its activation energy E_A, because activation energy responds sensitively to the change in the "state."

The change in entropy ΔS_A then indicates the degree of disarrangement and that of miscibility.

E_A and ΔS_A were calculated from the following formulas:

— activation energy related to electrical conductivity [9]

$$E_a = 19.4 \frac{B}{T} \qquad [\mathrm{J\,.\,mole^{-1}}] \tag{2}$$

where B is the term in the Arrhenius equation

$$\log \varrho = A + \frac{B}{T} \tag{3}$$

— activation energy of viscous flow [10]

$$E_\eta = 2.303 R \frac{BT}{T - T_0} \qquad [\mathrm{J\,.\,mole^{-1}}] \tag{4}$$

— change in entropy of viscous flow [10]

$$\Delta S_\eta = 2.303 R \frac{BT}{(T - T_0)^2} \qquad (\mathrm{J\,.\,mole^{-1}}]. \tag{5}$$

The volume characteristics [11] then will be used for studying

(1) molar volume V_{M} defined by the equation

$$V_{\mathrm{M}} = \overline{W}_{\mathrm{g}}/d \qquad [\mathrm{cm^3\,.\,mole^{-1}}] \tag{6}$$

where $\overline{W}_{\mathrm{g}}$ is the mean molecular weight of glass

$$\overline{W}_{\mathrm{g}} = \Sigma\, W_i f_i, \tag{7}$$

(2) unit volume V_1 related to 1 gramatom of oxygen (cm³/gramatom O)

$$V_1 = \frac{\overline{W}_{\mathrm{g}}}{(n_{\mathrm{O}})_i \mathrm{O}_i f_i} \tag{8}$$

The unit volume shows whether the entering cation M contracts the structure or distracts it. Its reciprocal value

$$\overline{N}_{\mathrm{O}} = \frac{1}{V_1} \tag{8a}$$

expresses the density of spatial arrangement of oxygen atoms. Ray [12] has pointed out the existence of a relationship between V_1 [or $\overline{N}_{\mathrm{O}}$] and the course of some properties.

(3) Molar refractivity R_M [cm³] describes the relationship between d, n_D and V_M and the changes in its course indicate in some cases the changes in the constitution of glasses (in optical spatial arrangement).

(4) Total refractivity of oxygens R_O [cm³] is a measure of the mean size of oxygen mass particles in the occupied glass space. It is given by the relation

$$R_O = \frac{R_M - \Sigma\,(m_M)_i f_i R_i}{\Sigma (n_O)_i f_i}. \tag{9}$$

The values of ionic refractivity R_i have been taken over from the study by Bacanov [13].

The change in R_O in terms of composition may also indicate a region of changes in glass constitution.

According to Gladstone and Dale [14] the relationship between density and refractive index is specified by the values of atom refractivity R_a after Young and Finn [15]; they are a measure of the deformability of ions.

The degree of cross-linking is of considerable significance for the study of anomalies. Its value is specified by

(a) the ratio of atoms (gramatoms) of electropositive element M to all the oxygen atoms (gramatoms) present in the glass. It is calculated from the formula suggested by Blau [16]:

$$N_M = M : O = \frac{\dfrac{(m_M)\,p_M}{W_M}}{\Sigma\dfrac{(n_O)\,p_M}{W_M}} = \frac{(m_M)\,m_i}{\Sigma\,(n_O)\,m_i}; \tag{10}$$

(b) the number of bridging oxygens Y and non-bridging oxygens X in the polyhedron according to Stevels [17], [18], (19);

(c) the degree of cross-linking v_n after Kühne [20]:

$$v_n = \frac{\left[\dfrac{\Sigma\,(F_i(m_M)_i\,m_i}{\Sigma\,m_i(m_M)_i}\right]\mathrm{NWF} + \mathrm{NWD}}{\left[\dfrac{\Sigma\,(F_i(m_M)_i\,m_i)}{\Sigma\,m_i(m_M)_i}\right]\mathrm{MOD}}\;\frac{\Sigma\,(O^{2-})_{\mathrm{MOD}}}{\sum\limits_{n}^{x}[(O^{2-})_{\mathrm{NWF+NWD}} + (O^{2-})_{\mathrm{MOD}}]}$$

where F_i is the bond strength (z/a^2 or U_M or e_v or X) of oxide i [21],

m_i is the mole % of oxide i,

$(m_M)_i$ is the number of atoms M in i-th oxide M_mO_n.

The anomalies in the system Na_2O—B_2O_3 have been studied most extensively, and for this reason they will serve as a basis of comparison for other systems.

The main efforts in the study of anomalies, in particular borate ones, have been recently concentrated rather more at the use of modern physical methods and at the effect of melting process than at the investigation of changes in properties in terms of compositions.

The studies provided the following main findings:

(i) B(III) co-exists in the glass in two coordination numbers $y = 3$ and $y = 4$ as structural units (BO_3) and (BO_4).

(ii) The (BO_4) tetrahedra are formed continuously with increasing M_2O content up to 30—40 mole % M_2O.

(iii) The anomalous changes are suppressed by melting in vacuo while the extreme values of changes in properties are completely eliminated [22].

However, the studies in question have not provided explanation of the borate anomaly. None the less, they should be taken into account in the construction of the chemical model.

Anomalies arise distinctly in binary systems and less distinctly in ternary systems. The anomalous changes in the course of properties in terms of composition are suppressed by introduction of further components. Anomalies have been found only in systems containing, apart from the oxide of a network-forming or an intermediate element, also oxides of univalent and bivalent elements acting as oxygen donors. Anomalies do not arise in binary systems composed solely of oxides of network forming elements.

The calculations carried out in the present study were based on the system of data tabellated by Mazurin [23].

THE ANOMALIES IN BORATE GLASSES

a) Description of the chemical dependence of anomalies in various properties

In the case of alkali borates the anomalies have been studied within a comparatively wide range of properties, so that more detailed information is available than that on the anomalies in other binary systems.

Binary systems of alkaline borates are suitable for the study of anomalies owing to the wide range of vitreous state including the regions of cross-linking and chain-linking.

The upper glass forming limit in the systems Na_2O—B_2O_3 and K_2O—B_2O_3 is 38 mole % and 34 mole % respectively [24], [25] in the E_1 eutectic region (1 : 1/1 : 2).

Anomalies are exhibited by borates of all alkali metals as well as of elements with formal valency I such as Ag, Tl, and some elements with valency II such as Ba, Pb.

The following points should be elucidated before a chemical model of borate anomalies can be constructed:

1. the difference in the effects of cations on anomalies,
2. the part played by the two co-existing coordination numbers of boron in anomalies,
3. the effect of melting in vacuo,
4. localization (topology) of anomalous changes in terms of composition,
5. the causes of inversions in properties.

The analysis will be concerned simultaneously with the systems Na_2O—B_2O_3 and K_2O—B_2O_3 for which adequate amounts of tabellated data are available.

In spite of the identical formal valency, Na(I) and K(I) show the following differences:

(a) in coordination number y

$$y(\mathrm{Na}) = 6,\ (8),$$
$$y(\mathrm{K}) = (6),\ 8;$$

(b) in the value of effective radius r_i

$$r_i[{}^{(6)}\mathrm{Na}^{\mathrm{I}}] = 0.102\ \mathrm{nm}, \qquad r_i[{}^{(6)}\mathrm{K}^{\mathrm{I}}] = 0.138\ \mathrm{nm},$$
$$r_i[{}^{(8)}\mathrm{Na}^{\mathrm{I}}] = 0.110\ \mathrm{nm}, \qquad r_i[{}^{(8)}\mathrm{K}^{\mathrm{I}}] = 0.151\ \mathrm{nm};$$

c) in deformability

ionic refractivity [13]	$R_i[\mathrm{Na^I}] = 0.47$,
	$R_i[\mathrm{K^I}] = 2.24$,
atomic refractivity [15]	$R_a[\mathrm{Na^I}] = 4.75$,
	$R_a[\mathrm{K^I}] = 8.25$;

(d) in electron structure: $\mathrm{Na^I}$ is an s-element of the short period, $\mathrm{K^I}$ is an sd_0-element of the long period (with unoccupied d-orbit);

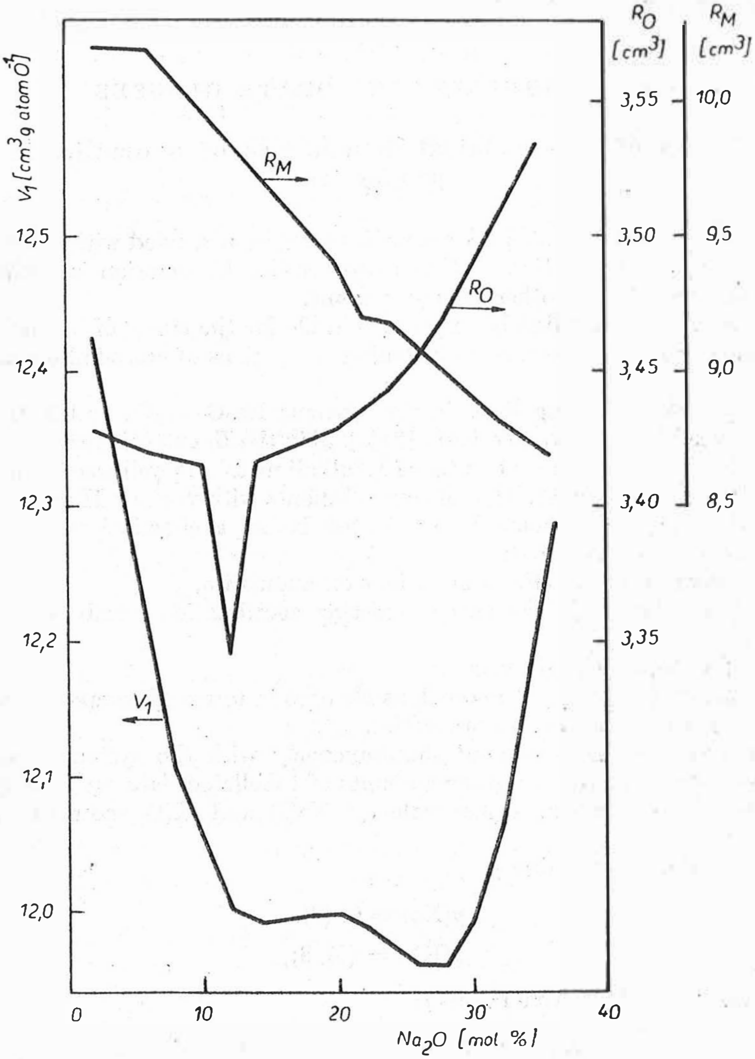


Fig. 1. Volume characteristics (V_1, R_M, R_O) *in the system* $\mathrm{Na_2O{-}B_2O_3}$.

(e) Both elements in the system M_2O—B_2O_3 differ in the phase equilibria diagrams as well as in the number and positions of invariant points (Table I and II).

The best known anomaly of borate systems is that of thermal expansion. With increasing Na_2O content the α decreases up to 16.7 mole % Na_2O, and then increases with further increase in Na_2O content (Figs. 4, 5). However, this anomaly is not unique.

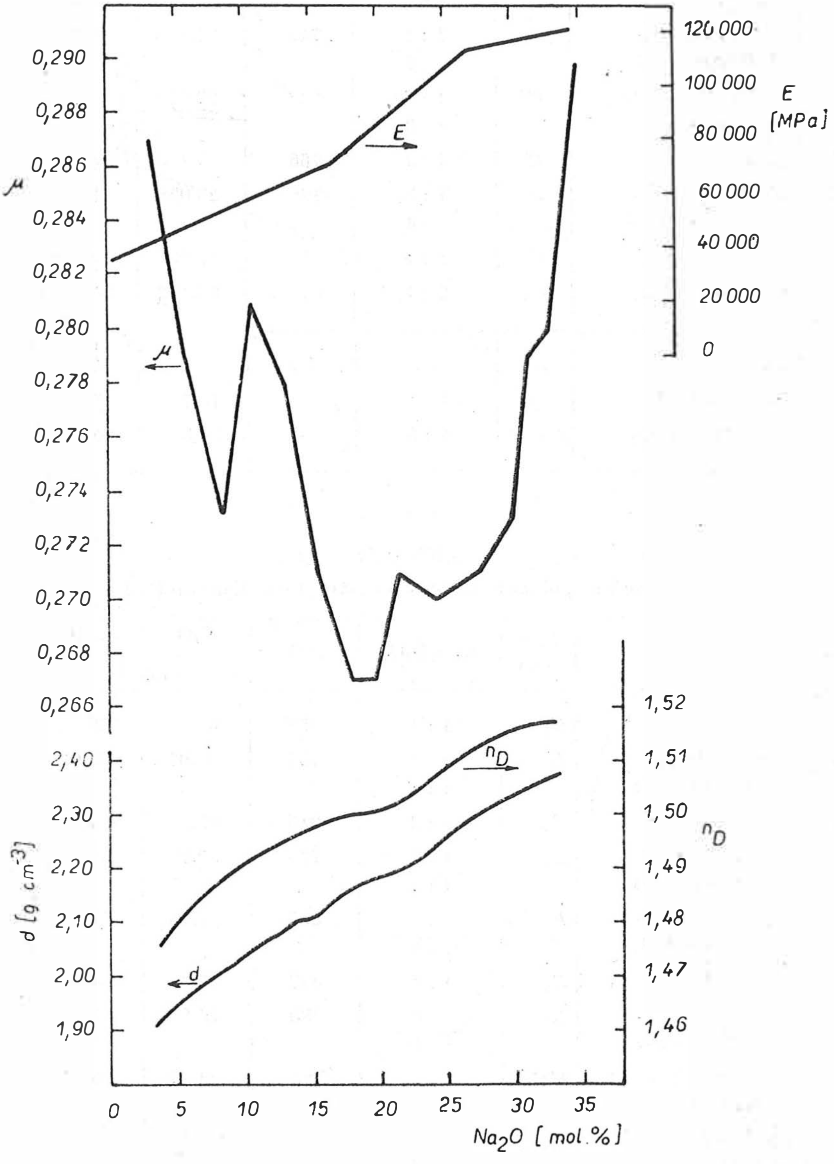


Fig. 2. Geometrical properties in the system Na_2O—B_2O_3; *d* [37], n_D [37], μ [42], *E* [50].

Table I

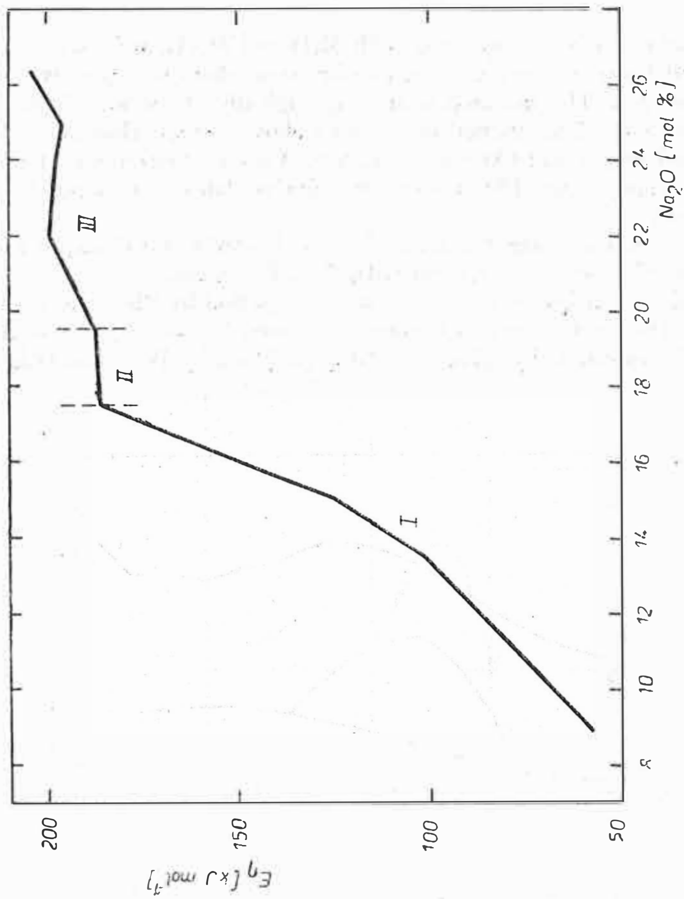
Invariant points in the $Na_2O—B_2O_3$ phase diagram [72]

No.	Phase		Na_2O/B_2O_3	t °C	Na_2O	B_2O_3	N_B
					mole %		
1	$Na_2O . B_2O_3$	C_1	1 : 1	966	49.902	50.098	0.500
2	$Na_2O . 2 B_2O_3$	C_2	1 : 2	742,5	33.540	66.460	0.571
3	$Na_2O . B_2O_3 +$ $+ Na_2O . 2 B_2O_3$	E_1	$\frac{1:1}{1:2}$	740	34.476	65.524	0.567
4	$Na_2O . 2 B_2O_3 +$ $+ Na_2O . 3 B_2O_3$	E_2	$\frac{1:2}{1:3}$	722	29.772	70.228	0.584
5	$Na_2O . 3 B_2O_3$	R	1 : 3	766	25.123	74.877	0.590
6	$Na_2O . 3 B_2O_3 +$ $+ Na_2O . 4 B_2O_3$	P	$\frac{1:3}{1:4}$	766	26.078	73.922	0.596
7	$Na_2O . 4 B_2O_3$	C_3	1 : 4	816	19.995	80.005	0.615
8	$2 Na_2O . B_2O_3$	C_4	2 : 1	625	66.632	33.368	0.400
I	—	—	—	—	5	95	0.655
II	$Na_2O . 5 B_2O_3$	—	1 : 5	—	16.7	83.3	0.624
III	$2 Na_2O . 5 B_2O_3$	—	2 : 5	—	26.3	73.7	0.595

Table II

Invariant points in the $K_2O—B_2O_3$ phase diagram [73]

No.	Phase	Process	K_2O/B_2O_3	t °C	K_2O	B_2O_3	N_B
					mole %		
1	$K_2O . B_2O_3$	C_1	1 : 1	950	50	50	
2	$K_2O . B_2O_3 +$ $+ K_2O . 2 B_2O_3$	E_1	$\frac{1:1}{1:2}$	787	37.97	60.03	0.554
3	$K_2O . 2 B_2O_3$	C_2	1 : 2	815	33.3	66.7	0.571
4	$K_2O . 2 B_2O_3 +$ $+ K_2O . 3 B_2O_3$	E_2	$\frac{1:2}{1:3}$	770	30.73	69.27	0.581
5	$K_2O . 2 B_2O_3 +$ $+ K_2O . 4 B_2O_3$	K_1	$\frac{1:2}{1:4}$	825	27.14	72.86	0.593
6	$K_2O . 4 B_2O_3$	C_3	1 : 4	857	15.6	84.4	0.628
7	$K_2O . 4 B_2O_3 +$ $+ K_2O . 5 B_2O_3$	K_2	$\frac{1:4}{1:5}$	780	16.67	83.33	0.625
8	$K_2O . 2 B_2O_3 +$ $+ K_2O . 4 B_2O_3$	ME	$\frac{1:2}{1:4}$	752	29.82	70.18	0.584
9	$\alpha K_2O.5 B_2O_3 +$ $+ K_2O . 4 B_2O_3$	MKC	$\frac{1:5}{1:4}$	760	—	—	—



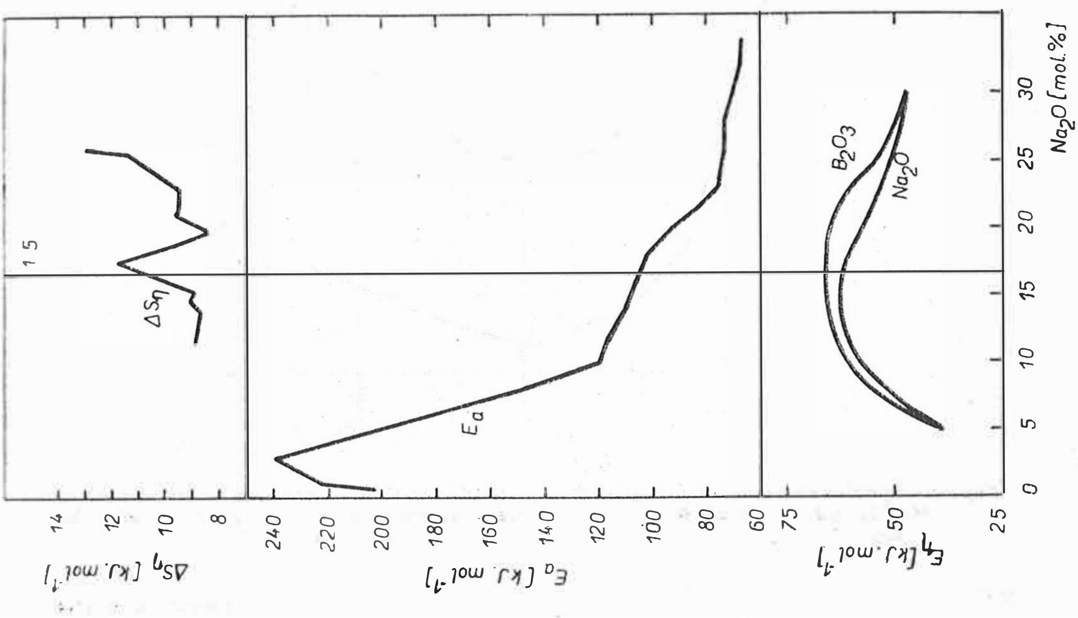


Fig. 3. Activated properties in the system Na_2O—B_2O_3; *a)* E_h *[55],* E_a *[according to 52],* ΔS_η *[according to 80]; b)* E_η *[according to 80].*

All the properties of borate systems with M(I) and M(II), with the exception of specific heat and thermal conductivity, exhibit anomalous non-additive courses of chemical dependence. The anomalies are topologically dispersed throughout the range of vitreous state. The anomalous changes show a shape that is characteristic for the individual properties: (A) a sharp inverse V-shape (maximum or minimum), a) narrow or b) widely open, (B) positive or negative deflection shape U a) shallow or b) outstanding.

Borate anomalies are related in literature to the twin coordinating number of boron and to co-existence of (BO_3) and (BO_4) building units.

The two possible co-ordination numbers were found first by Biscoe and Warren [26] by *X*-ray diffraction and their conclusions have been borne out by the method of nuclear magnetic resonance by Silver and Bray [27] and by Bray and O'Keefe [28].

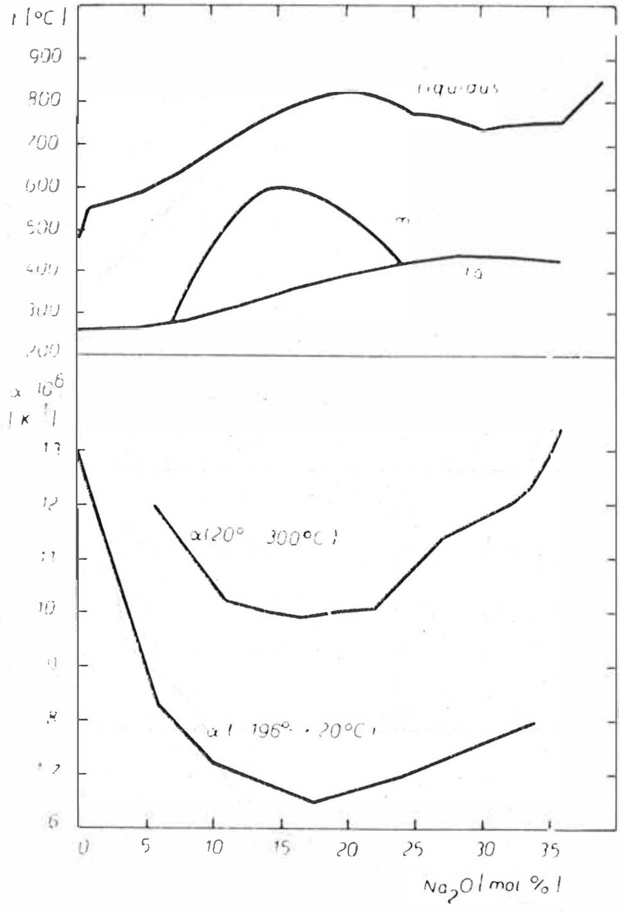


Fig. 4. Properties in the system $Na_2O—B_2O_3$; *thermal expansion coefficient α, a) 20—300 °C (65), b) — 196 to 20 °C [66]; the course of transformation temperature* t_g; *m.i. = metastable immiscibility [68].*

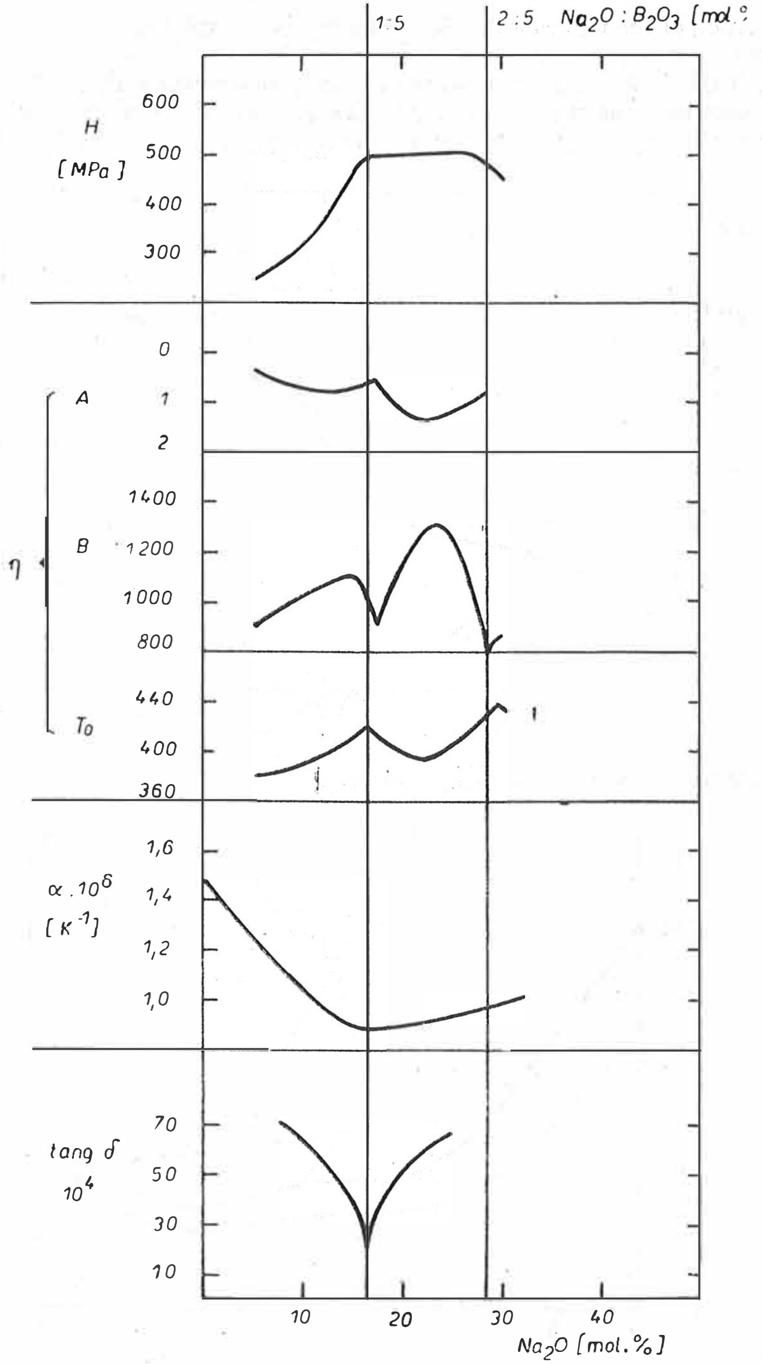


Fig. 5. Properties in the system Na_2O—B_2O_3 *in regions of relative compositions II and III (1 : 5 and 2 : 5 respectively); H — microhardness [22], [60]; A, B,* T_0 *— constants in the Vogel-Fulcher-Tamann's equation [80],* α *[40]; tan* δ *[62].*

The formation of the two coordination units has been explained by Krogh-Moe [29] as follows:

Atom *B*(III) in its base state has the electron configuration $1^2[K]2s^2 2p^1[L]$. One of the *s* electrons in the outer orbit may be excited into state *p*, so that three electron couples may be formed by combining with three oxygens producing (BO_3). However,

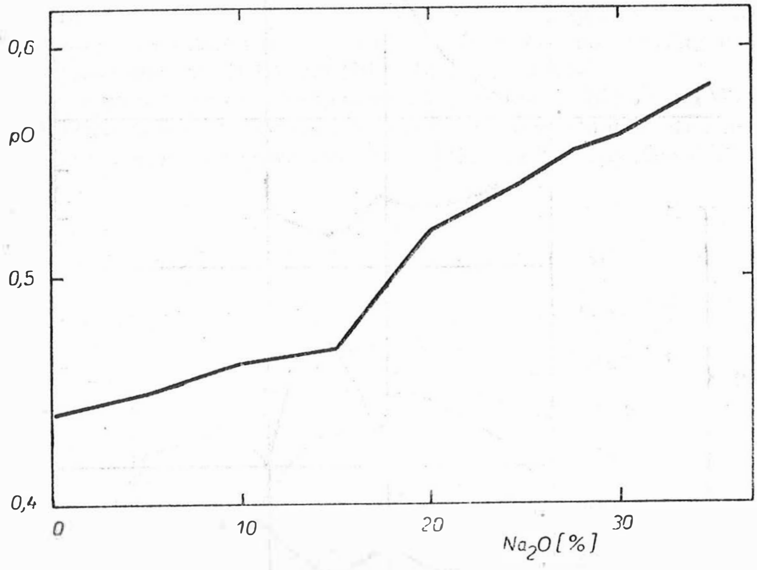


***Fig. 6.** Acidobasicity in the system* $Na_2O—B_2O_3$ [58].

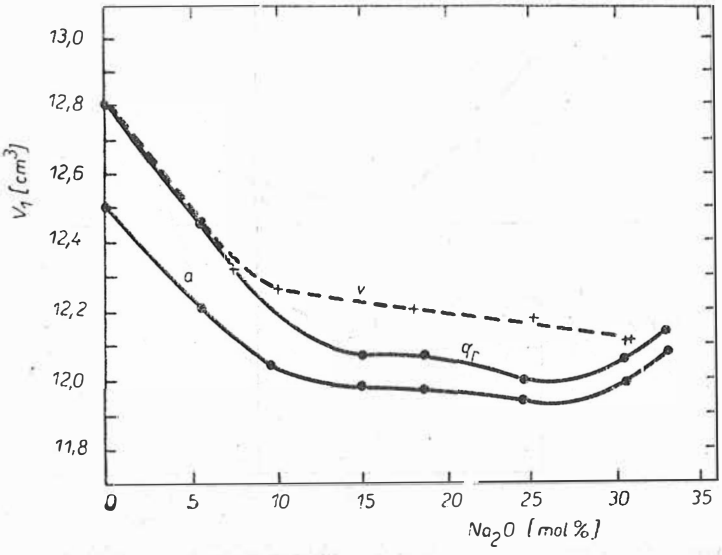


***Fig. 7.** V_1 in the system* $Na_2O—B_2O_3$ [22] *in samples (a) annealed, (q) quenched; (v) quenched from vacuum-melted glass.*

the $B(\mathrm{III})$ atom may accept still another couple of electrons into the remaining free p orbit. This produces the (BO_4) unit with an additional negative charge.

The studies yielded the finding that the (BO_4) building units multiply in borate glasses gradually with increasing content of monovalent alkaline oxides roughly up to 33 mole % M_2O according to the curve described by the Beekenkamp equation [30]

$$[BO_4] = \frac{\dfrac{x}{(1-x)}}{1 + \exp\,(11.5\,x - 4.8)} \tag{12}$$

where x is the molar fraction of alkali metal oxide.

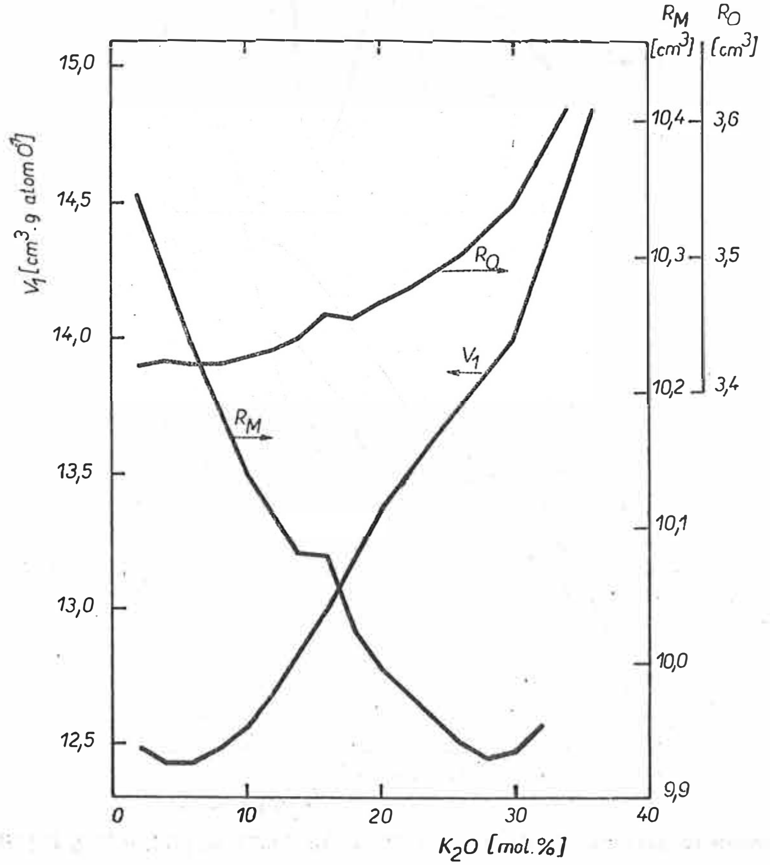


Fig. 8. Volume characteristics in the system K_2O—B_2O_3 (V_1, R_M, R_O).

The base building units, triangular planar pyramids (BO_3) and tetrahedra (BO_4), are not distributed statistically throughout the borate glass matrix, being aggregated in defined groups, chain-linked or cross linked formations [31], [32].

The anomalous changes take place:

a) in the region of invariant points of phase equilibria;

b) by introducing alkali metal ions into energetically variously advantageous points in the glass constitution, which has its effect on the course of volume characteristics;

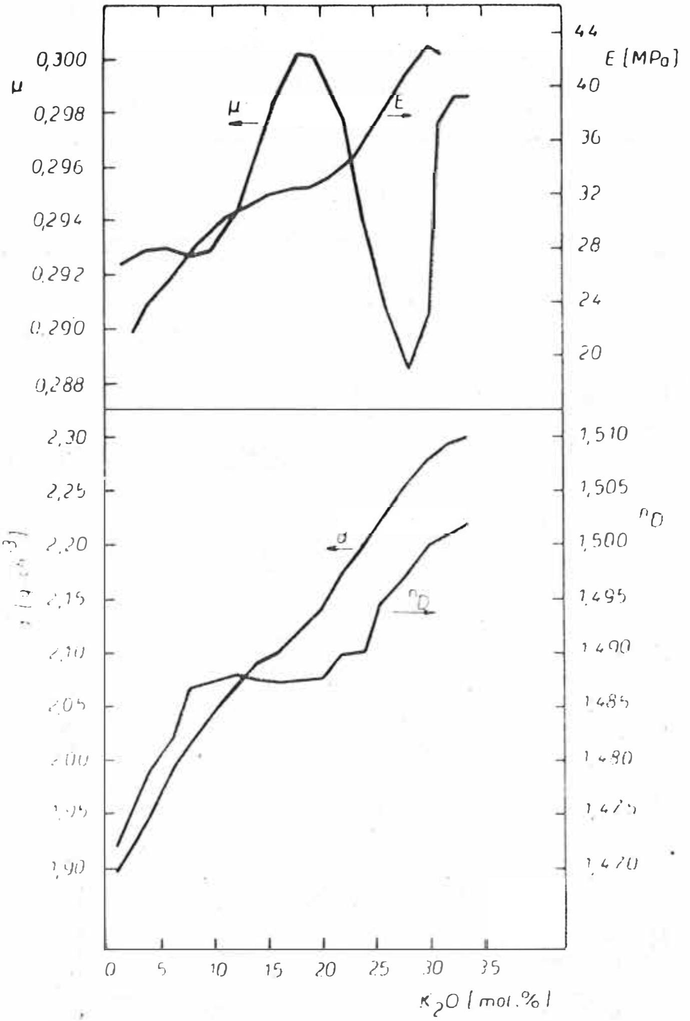


Fig. 9. Geometrical properties in the system $K_2O—B_2O_3$: *d [37]*, n_D *[37]*, *μ [79]*, *E [49]*.

c) most distinctly in the regions of three relative points, e.g. in the system $Na_2O—B_2O_3$ at relative compositions at I. 5, II. 16.7, III. 26.26 mole % Na_2O.*)

The invariant points of phase equilibria in the systems $Na_2O—B_2O_3$ and $K_2O—B_2O_3$ are listed in Tables I and II.

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*) „Reference or relative composition" is defined here as a compound of definit chemical composition, to which the change in properties is referred (or related).

The maximum volatilization in both systems is exhibited by compound 1 : 2 [33].

In the system $Na_2O—B_2O_3$ the maximum viscosity corresponds to coumpounds 1 : 3 and 1 : 4 [34]. Eipeltauer and Schaden [80] found extreme values of the constants in the VFT equation for triborate and tetraborate, namely a maximum for constant B and a minimum for constants A and T_0 (Fig. 5). The water-extraction minimum lies at the 1 : 3 compound.

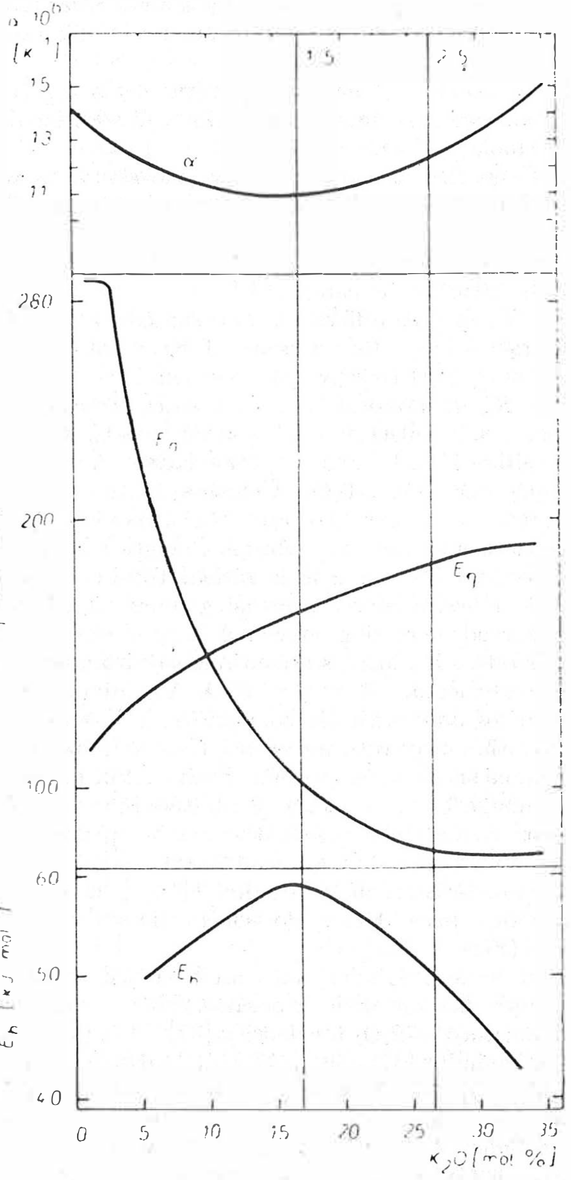

Fig. 10. Activation energies in the system $K_2O—B_2O_3$: E_h *[55]*, E_a *[53]*, E_η *[86]*; α *[12]*.

The maximum of viscous flow activation energy (Fig. 3b) and that of the chemical resistance activation energy (Fig. 3a) is situated at the composition corresponding to compounds 1 : 3 and 1 : 4; this is in an agreement with the findings by Kurnakov [4] and Demkina [5] that the highest bond strength occurs in the regions of compounds in the phase equilibrium diagrams.

In contrast to that of viscosity, the course of activation energy of electrical conductivity does not exhibit any extreme changes in the system $Na_2O—B_2O_3$ (Fig. 3a).

In the system $K_2O—B_2O_3$, extreme viscosity characteristics have been established at the compound 1 : 2 [36]. The volume characteristics likewise show anomalous courses (Figs. 1, 8).

The course of V_M decreases continuously with increasing Na(I) content while in the case of K(I) the course is similar but exhibits an additional distinct deflection between 30 and 32 mole % K_2O.

In Na-borates, V_1 at first decreases steeply (the structure contracts), between 12 and 28 mole % Na_2O there is a calm zone containing two shallow flat minima at 14 to 16 mole % and 26 to 28 mole % Na_2O respectively, that is approximately at points of relative compositions II. and III. Above 28 mole % Na_2O, the V_1 shows a sharp increase (the structure expands).

In K-borates, the V_1 shows a different course similar to that of V_1 in the systems $Na_2O—SiO_2$ and $Na_2O—GeO_2$. Introduction of K(I) brings about a merely brief decrease up to 4 mole % K_2O (relative composition I).

Molar refractivity R_M in Na-borates and K-borates decreases with incrasing M_2O content; with K-borates, a deflection arising at 28 mole % K_2O is similar to that of V_M (relative composition III). Because R_M for relative compositions I and II in the systems $Na_2O—B_2O_3$ and $K_2O—B_2O_3$ decreases continuously, this is taken as evidence that no profound geometrical reconstructions take place, that the optical filling up of space does not show any abrupt changes leading to extreme values, and so that only the „state" of oxygens is varied. Total refractivity of oxygens R_O in Na-borates shows at first a curved decreasing course and from 12 mole % Na_2O upwards a mildly curved increasing course. A local sharp peak arises at 12 mole % Na_2O. With K-borates, R_O increases continuously from the beginning, showing merely a slight disturbance at 16 mole % K_2O. A minimum of the mean size of oxygens therefore arises only with Na-borates. With K-borates the mean size of oxygens increases continuously with increasing K_2O content.

The course of volume characteristics differs from that of properties and activation energies in that, although being not linearly additive in some instances, it does not exhibit any distinct extreme changes that could be qualified as inversions. The transitions of volume characteristics are continuous.

To the volume characteristics there are linked up the geometrical properties: density, refractive index, permittivity, Poisson's ratio and the Young's modulus of elasticity in tension (Figs. 2, 9).

Both density and refractive index have an S-shaped course with two shallow peaks which are more distinct with K-borates. The results obtained by various authors in the system $Na_2O—B_2O_3$ for density [37], [38], [39], [40], [41], [42], [43], [44], [45] and refractive index [37], [39], [41], [43], [46] and in the system $K_2O—B_2O_3$ for density [37], [38], [45], [47], [48], [49] and refractive index [37], [46], [48] are in a quite satisfactory agreement. At temperatures above t_g the peaks and densities are shifted towards higher M_2O contents. Permittivity has not so far been measured. The Poisson's ration μ [42] shows a more varied course than d and n_D, showing 2 minima and 1 peak with Na-borates at (—) 10, (+) 18 and (—) 25 mole % Na_2O

and with K-borates at (—) 10, (+) 18 and (—) 28 mole % K_2O. Modulus of elasticity in tension was measured in the system Na_2O—B_2O_3 by Fanderlik [50], in the system K_2O—B_2O_3 by Nemilov [51]. In both systems the course is rather monotounous showing a slight S-shaped curving free from extremes (Figs. 2, 9). In the case of activated properties the courses of chemical dependence for Na-and K-borates are similar.

With all the glasses in the systems M_2O—B_2O_3 the course of log ϱ is roughly parallel. At first, log ϱ decreases steeply towards 5 mole % M_2O (relative composition II), then decreases slowly towards 26 mole % M_2O (relative composition region III). Activation energy E_a was calculated for Na-borates using the values by Schukarev and Mjuller [52]. E_a exhibits a peak at 4 mole % Na_2O (relative composition I), attains a calm course beyond 26 mole % (relative composition III) and shows no changes further on. An almost parallel course is further exhibited by the curve of activation energy E_a for K-borates, which has been calculated from the values of log ϱ according to Markin and Mjuller [53]; however, the curve has no initial maximum. The standstill section is attained at 23 mole % K_2O. No local changes in resistivity occur at relative composition II.

The course of viscosity curves for all the systems M_2O—B_2O_3 is almost parallel with the initial minimum between 5 to 10 mole % M_2O in the region of relative composition I while a maximum occurs at around 20 mole % M_2O [54].

In the system Na_2O—B_2O_3, the chemical resistance to water [55] expressed by total extraction loss, is of U-shape with minimum extraction loss at 25 mole % Na_2O. Its activation energy shows a single maximum at 17 mole % Na_2O, that is at relative composition II [55]. A similar course has been established in the system K_2O—B_2O_3 with a minimum extraction loss at about 20 mole % and with an activation energy maximum at 16 mole % K_2O. The maximum separation into immiscible phases lies at relative composition II [56], [57] (Fig. 4).

The basicity as measured by Duffy and Ingram [58] shows a marked steeper increase between relative composition II and 20 mole % Na_2O (Fig. 6). The basicity was not measured in the system K_2O—B_2O_3.

As regards the position of anomalies, it should be stressed that not all the anomalies are located precisely at the points corresponding to relative compositions, their position being somewhat shifted. Appen [59] pointed out that in such cases the shift may be due to traces of certain structures corresponding to local composition in the glassy constitution. The extreme values of the changes, if the course is flat, are likewise difficult to ascribe precisely to a certain composition. Moreover, determination of a change in property in terms of change in composition was carried out in series and larger composition intervals then would be required just in the neighbourhood of relative points. The author has attempted to locate more accurately the extreme points by approximating the values by means of multiple polynomials and to determine the extreme values mathematically; however, the procedure has also not provided more satisfactory results. This is why use is made here of so-called relative points which are supporting compositions (corresponding to certain stoichiometric compounds) towards which the anomalies converge. Anomalies of different properties need not coincide by their extreme values with all the relative points (I, II, III). The extreme values of chemical dependence of the property and of the respective activation energy likewise need not always coincide (e.g. in the case of chemical resistance). This can be easily understood because the various properties depend to various degrees not only on structure given by the geometry of spatial layout of particles or their groups, but also on whether the respective property depends more on the nucleus or on the electron envelope of the atom, on the degree relaxation effects are involved, etc.

The most distinct anomalies are those pertaining to relative compositions II and III. The changes in properties occur here in the following three forms:

(A) as bends (with microhardness);

(B) as sharp, narrow, locally limited, fast disappearing extremes (with tan δ, with constants of VFT-equation (A, B, T_0) and with the change in the entropy of viscous flow ΔS_η, and likewise with activation energy of chemical resistance);

(C) as widely open extremes (the minimum of thermal expansion coefficient).

The various shapes imply that various mechanisms are involved so that they should be dealt with separately.

The chemical dependence of microhardness H exhibits two changes on annealed samples in the system $Na_2O—B_2O_3$. Tomlinson [60] found a sharp V-minimum at 4 mole % Na_2O (i.e. at relative composition I), Everstein [22] reported a bend at relative composition II at 18 mole % Na_2O. Then follows the smooth part of the curve terminated by an inflection at 30 mole % N_2O. The bend at 18 mole % Na_2O corresponds to inflection of t_g, which is in agreement with the observation by Douglas [61] according to which the hardness of glass is related to viscosity.

A marked narrow sharp V-shaped minimum is exhibited by dielectric losses in the system Na_2O-B_2O_3 [Stevels 62]. Electrical conductivity does not show any parallel extreme. Dielectric losses have not been measured in the system $K_2O—B_2O_3$.

The chemical dependence of the coefficient of thermal expansion α converges continuously towards relative composition II (Figs. 4, 10) as pointed out by a number of authors for Na-borates [40], [63], [64], [65], [66] as well as for K-borates [48], [67]. On introduction of M_2O, α first decreases to a minimum at 17 mole % M_2O (relative composition II) and only then increases similarly to the case of commercial silicate glasses. The anomaly of thermal expansion disappears in the transformation interval region. At very low temperatures in the range of —196° to +20 °C Uhlmann and Shaw [68] found that the chemical dependence of α has the shape of a very wide *U* with one side branch decreasing and the other increasing, but free of any distinct convergency towards relative composition II. Thermal expansion of glasses melted in vacuo has not been measured.

It should be stressed that the anomaly of thermal expansion is not an exclusive property of alkali borates. It also arises with phosphate glasses, in invert silicate glasses, germanate glasses and tellurate glasses. This anomaly disappears when other oxides are introduced into binary glasses. The fact that there is no co-existence of coordination numbers in the binary systems where the thermal expansion anomaly has been established (invert glasses, phosphate glasses, tellurate glasses), contrary to the borates, allows to assume that the thermal expansion anomaly is not generally related to the twin coordination number and that another chemical model of these anomalous phenomena has to be seeked. It is assumed that the proved twin co-ordination of boron provides conditions for a wider variety of combinations of (BO_3) and (BO_4) units in various borate groups which are considered to have the nature of compounds. These ,,compounds" in the polymer structure of borate glasses differ mutually in oxygen bonds, acidobasicity, the freedom of vibration of mass particles, the freedom of alkali metal ion transport and in spatial arrangement of the structural units, while, on the other hand, the chemical dependence of the given characteristics in borate glasses remains similar to, if not identical with that in borate compounds, so that it is possible to seek a topological relationship of anomalies with the diagrams of phase equilibria, with relative composition, with known borates; when taking into account the similarity or diversity of the chemical relationships of borate anomalies with those of the systems, it should be possible to construct a phenomenological chemical model on the basis of chemical topology.

b) The relation of anomalies to the chemistry of alkali borates

It appears advantageous to simplify the problems by specifying the relative points of anomalies by correlating them to chemical compounds (with the exception of relative composition I), namely to pentaborates:

pentaborate 1 : 5
dipentaborate 2 : 5.

One of the possible approaches to the explanation of borate anomalies is seen to be based on the chemical nature of pentaborates of alkali metals and their hydrates.

Lithium pentaborate 1 : 5 is known as anhydride [69] and constitutes a phase in the system $Li_2O—B_2O_3$.

Sodium pentaborates 1 : 5 and 2 : 5 have not been established by Morey and Merwin [70] as independent phases. Milman and Bouaziz [71], however, have established the existence of incongruently melting $Na_2O . 5\,B_2O_3$ in the subsystem $Na_2O . 4\,B_2O_3—B_2O_3$ and the existence of incongruently melting $2\,Na_2O . 5\,B_2O_3$ in the subsystem $Na_2O . B_2O_3—Na_2O . 4\,B_2O_3$.

Sodium pentaborate 1 : 5 is not known in anhydrous state. Its decahydrate $Na_2O . 5\,B_2O_3 . 10\,H_2O$ however, is formed spontaneously from a mixture of borax with boric acid [31]. The extremes in the course of the chemical dependences of properties in the system $Na_2O—B_2O_3$ are proportional to the content of H_2O in vitreous borates. On the other hand, the extremes are suppressed and eventually completely eliminated by melting in vacuo (Fig. 7).

Anhydrous sodium dipentaborate 2 : 5 is not known. Its composition is close to the eutectic E_2 [1 : 2/1 : 3] [72] and it is difficult to decide which extreme values of Na-borates in relative composition III should be attributed to the compound or rather to the eutectic. The proximity of pentaborate 2 : 5 composition to that of eutectic E_2 is illustrated in Table I.

Three modifications of anhydrous potasium pentaborate 1 : 5 are known. The α and β forms melt incongruently above 760 °C [31] while only the γ-modification is metastable at all temperatures. $K_2O . 5\,B_2O_3$ forms a stable poorly soluble octohydrate. The anhydride is comprised as a phase in the system $K_2O—B_2O_3$ [73].

Potasium dipentaborate 2 : 5 is known in the form of pentahydrate only. Anhydride is neither a separate phase nor a separate compound [73].

As crystalline pentaborate hydrates give up their water molecules gradually and with unequal ease, Atterberg [74] assumed that the molecule of pentaborate, e.g. $NaB_5O_8 . 5\,H_2O$ should be more correctly described by the chemical formula $NaH_4B_5O_{10} . 3\,H_2O$. According to this assumption, four hydrogens should be directly built into the molecule as bound to oxygen.

When speaking about the pentaborate ratio 1 : 5 or 2 : 5, on does not consider pentaborate as a stoichiometric molecule, but as a condition for the formation of a polyanionic stable polymer.

The conditions under which borate polyanions arise are known from the chemistry of borates. At relative composition II boroxol groups composed of $(BO_3)_n$ prevail in borate glass. The (BO_4) units improve the stability of borates, but only under certain conditions:

1. The ratio of ${}^{(4)}B$ to the total number of B(III) must be equivalent to the ratio of the anion charge to the total number of boron atoms and has to be expressed by integers. The pentaborate ratio $Na_2O : B_2O_3$ is therefore converted to the ratio ${}^{(4)}B : \Sigma\, B$(III).

2. Stability of the borate polymer is increased only when the ratio of ${}^{(4)}B$ to $\Sigma\, B$(III) is expressed by a small integer (1 or 2). This is why only two relative compositions arise, namely II and III.

3. If the ratio ${}^{(4)}B : \Sigma\, B$(III) does not comply with the two previous conditions, no stable polyanion can be formed. The anomalies concentrated at relative compositions II and III fade away in both directions.

4. Hydrogen bonds have to be present if a stable polyanion is to be formed under the conditions mentioned above. Formation of the polyanion is facilitated by the presence of OH-groups.

Compounds containing hydrogen bound to oxygen are known to show a strong tendency to association. Preparation of anhydrous glasses of the system Na_2O—B_2O_3 by melting without evacuation is extremely difficult if not impossible. They are usually melted from a mixture of H_3BO_3 with $Na_2B_4O_7$. Sodium tetraborate keeps 2 moles of H_2O even at melting temperatures under normal pressure [31].

It is assumed that the pentaborate ratio arises in the presence of bonds with hydrogen bridges as an associated component e.g. from tetraborate and boric oxide.

The conception of additive formation of pentaborate from tetraborate and B_2O_3 is further substantiated by Raman's spectra, by means of which Konijnendijk [32] determined tetraborate groups in glasses remelted in vacuo situated before relative composition II. The shortage of hydrogen bonds arising during melting in vacuo does not allow formation of the stable polyanion.

Polymeration changes continuously the constitution of vacuum-melted borate glasses, the vitreous state is not impaired, the constitution is continuously strengthened, so that no local anomalous extremes in the course of properties arise. Moreover, vacuum melting brings about introduction of the (BO_4) polar groups, the structure becomes more „ionic", as indicated by the increase in basicity [58], and the type of oxygen bonds, which will be dealt with below, is also subject to continuous changes free from any extremes.

Association is probably likewise of significance in the formation other alkali borates, as relative point II in the system K_2O—B_2O_3 also lies at the 1 : 5 ratio.

This hypothesis of topological identity of relative compositions, suggested by the present author, is in agreement with the conception of structural groups proposed by Konijnendijk [32] and Zachariasen [75]. In a pentaborate group one polar (BO_4) tetrahedron is surrounded by four planar (BO_3) ones.

The resulting two rings (I) and (II) lie in mutually perpendicular planes [75]. (BO_4) plays the part of the central ion. The structural group has 4 unsaturated bonds and represents a "composite tetrahedron" capable of spatial networkforming. This structural group constitutes a nucleus even for dipentaborate with 5 unsaturated oxygens, which contains two (BO_4) tetrahedra (Fig. 11). Both structural formulae of pentaborates are of course only hypothetical, being far more complex in the presence of OH-groups.

Both relative pentaborate compositons (II) and (III) divide the system Na_2O—B_2O_3 into the following three sections:

(I) According to our conception, roughly up to 10—12 mole % Na_2O, Na(I) occupy preferentially energetically advantageous positions in borate glass composed of boroxole groups $(BO_3)_n$. The boundary of 10—12 mole % Na_2O is demarcated by terminating contraction and terminating steep decrease of V_1. Monotonous course of V_1 in vacuum-melted glasses likewise begins at this boundary (Fig. 7). This is also where the phase separation starts. The constitution of borate glasses comprises their cyclic chains up to relative composition II, corresponding stoichiometrically to pentaborate, in the presence of hydrogen bridges which are a necessary factor for the formation of the polyion.

(II) Between relative compositions II and III, i.e. between pentaborate and dipentaborate, Na(I) acts mainly as an oxygen donor. Basicity increases, and the structure is abruptly transformed from a chain-linked into a spatially cross-linked one.

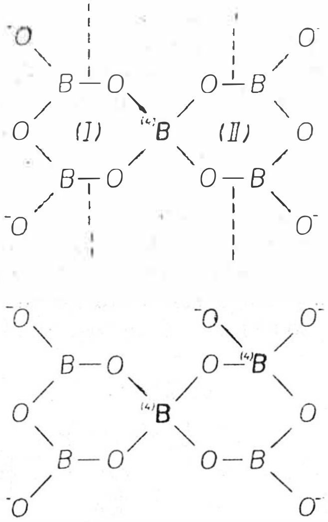

Fig. 11. The structure of the pentaborate entity 1 : 5 and 2 : 5 according to [32] and [75].

(III) Beyond the third relative point there occurs an extended band of changes between 22 and 28 mole % Na_2O. Mass particles of Na(I) are linked to the lattice similarly to the silicate lattice. Electrical conductivity does not undergo any further changes. The formation of (BO_4) tetrahedra decreases strongly between about 33 and 40 mole % Na_2O. Within this third region the structure of Na-borate glasses is similar to that of sodium tetrasilicate by its three-dimensional cross-linking in the presence of non-bridging oxygens.

Although the conception of the nature of structures in the respective three regions cannot be proved by direct measurement, indirect evidence is provided by the course of chemical dependence of some properties.

The fact that the division of the system $Na_2O—B_2O_3$ into three sections can be demonstrated visually on optical absorption in the presence of CoO, CuO and Mn_2O_3, has so far been disregarded. With all these ionically colouring oxides the colouring is markedly intensified above 16.7 mole % Na_2O. In the case of glasses coloured with cobalt oxide, the colouring passes with increasing Na_2O content from pink through violet to intensive blue colour. Below relative composition II of pentaborate the absorption is centered in an asymmetrical band at 550 nm with a secondary peak at 520 nm and a very faint band at 1200 and 1500 nm. Beyond the 1 : 5 pentaborate the absorptive intensity increases significantly, the 1200 nm band disappears, those at 550 and 1500 nm are shifted and split into three distinct peaks. At about 30 mole % Na_2O the absorption begins to resemble by its course that of CoO in silicate glasses. The changes in absorption were studied and explained by Brodie [76], verified by Aglan and Moore [77] and by Bamford [78]. A similar course of absorption has also been established in the system Na_2O—P_2O_5.

Division of the system Na_2O—B_2O_3 into three sections has further been borne out by acidobasicity according to Duffy and Ingram [58]. In sections (I) and (III) the course proceeds almost parallel with increasing Na_2O content, while region II exhibits a steep increase in basicity.

The division of the system Na_2O—B_2O_3 into three sections by two relative points is finally very well demonstrated by the course of viscosity as shown in the interesting study by Kaiura and Toguri [79]. Using the values by Eipeltauer and Schaden [80] the present author calculated the activation energy E_η (Fig. 3b). In region (I) the activation energy rises steeply and continuously. Section (II) is characterized by a static course between 17 and 20 mole % Na_2O. In section (III) the activation energy again rises mildly showing a maximum at 22 mole % Na_2O in the region of compound C_3 1 : 4.

Uhlman and Shaw [68] and Kaiura and Toguri [79] pointed out the interesting relation between t_0 (in equation VFT) and t_g (both in °C) in the given three regions. Above relative point II (about 17 mole % Na_2O) both t_0 and t_g exhibit close values up to relative point III. At lower Na_2O concentration (in region I) the t_0 values are much lower than those of t_g, and vice versa in region III, as indicated by Table III.

Table III

Values of t_0, t_g and Δt

Na_2O mole %	t_0 °C	t_g °C	Δt °C	Region
0	—273	250	—523	I
5.45	—93	271	—364	
10.2	+155	304	—149	
17.2	+397	374	+23	II
21.9	+451	413	+38	
27.1	+453	430	+23	
33.3	+513	433	+80	III

c) The mechanism of anomalies of borate glasses

Relative point I, which has not so far been dealt with, lies between 4 and 6 mole % Na_2O in region I. A sharp minimum of microhardness H [60] and a maximum of log ϱ [39] lie in its proximity. A similar anomaly is encountered also in other binary systems at the onset of entry of a modifying (Na, Zn) or intermediary element (Al, Ti), e.g. into a silicate network; this anomaly will be treated in more detail in the discussion in part III.

An analogy of the inverse change in properties at the relative compositions, in particular in the case of the 1 : 5 pentaborate, occurs in the isoelectric point.

The isoelectric point is the designation of pH in solutions containing identical concentrations of ions with positive and negative charges in an amphoterous electrolyte. In the isoelectric point the share of non-dissociated ampholyte attains a maximum and the proportion of ampholyte split into ions is at a minimum.

The isoelectric point is a significant physico-chemical characteristic. A number of transport properties (viscosity, diffusion, electrical conductivity) attain minimum values at the isoelectric point.

In borate glasses (as well as in other systems showing anomalies of the same type) a similar situation occurs at the boundary contact of two structures: chain-linked and cross-linked. According to our conception, oxygens of different „states" are in contact at this boundary.

Having followed the position of elements with prevailing ionicity and those with prevailing covalency in the M—O bonds along two different branches of the V-phenomenon [21], [81] the present author tried to seek the cause of anomalies in changes of the bond as indicated by the inverse changes in properties.

In free state, an oxygen atom has the electron configuration $1s^2 2s^2 2p^4$. The stable electron structure of the nearest rare gas neon $1s^2 2s^2 2p^6$ can be achieved in various ways (cf. e.g. 82):

(a) by accepting two electrons which yields oxidic anion O^{2-}. The oxygen is then bound by an electrostatic ionic bond. This is the case of some oxides and glasses with a three-dimensional, co-ordinated spatially linked network, insofar as the glasses contain modifying elements of very low electronegativity, requiring a very low energy for their ionisation. The resulting bond is

$$\mathrm{M} - {}^{io}\mathrm{O}^{io} - \mathrm{B}.$$

(b) In a non-coordinated chain-linked mono-or bidimensional structure, oxygen is bound to the M atom by a simple covalent bond and in a stable octet structure of a rare gas shows one excess negative formal charge, $\mathrm{M—O^-}$. This formally negative charge is equalized by the same formal charge in B(III) so that an electrically neutral molecule is formed ($\mathrm{M—{}^{co}O^{co}—B^{III}}$).

Our explanation of the inversion of properties is based on the conversion of the oxygen bond from the ionic form to the covalent one, so that the oxide, with respect to its responses, quantified by the partial molecular additive factor g_i, is transferred from its position along branch (I) of the V-phenomenon onto branch (II), along which elements with prevailing M—O covalent bond are situated.

Insofar as there exists a continuous spatial network, glass (below t_g) represents a structurally ionic solution where „the solvent" is the glass network with ionically built-in modifying elements.

However, as soon as the spatial network turnes into linear or cyclic chains, the polymer ceases to act as solvent and mass particles of alkali metals and alkaline earths elements acquire a „covalent" bond with oxygen. In the spatial network, Na^+ act as ions in a solidified solution, in a chain-linked constitution the Na^I exist in covalent bonds with oxygen as in molecules.

Correctness of this hypothesis, which is based on the knowledge of two possible oxygen bonds in general inoragnic chemistry, is borne out by the fact that inversions and anomalous changes occur even in other instances at the boundary between crosslinked and chain-linked glassy constitution, e.g. in the system $Na_2O—SiO_2$ (transition to invert glasses) and in the system $Na_2O—P_2O_5$, as shown below.

In Weyl's words [83], the relative composition II glass passes from the region corresponding to Bernal's liquid into that corresponding to the Frenkel's type liquid. At relative point II the properties show various effects.

The course of tan δ is similar to that of the isoelectric point. There is a sharp deep minimum (Fig. 5) disappearing rapidly in both directions. Dielectric losses are usually related to enharmonic vibrations. At the point of relative composition there arises a great change in the entropy of viscous flow ΔS_η. This can be explained by the assumption that at this point, and at this point only, there is present the same amount of oxygen O^{II-} belonging to the chain-linking region and of oxygens O^{2-} belonging to the cross-linking one. Oxygens of both bond types increase the enharmonicity. The minimum of tan δ therefore represents the contact effect at this point.

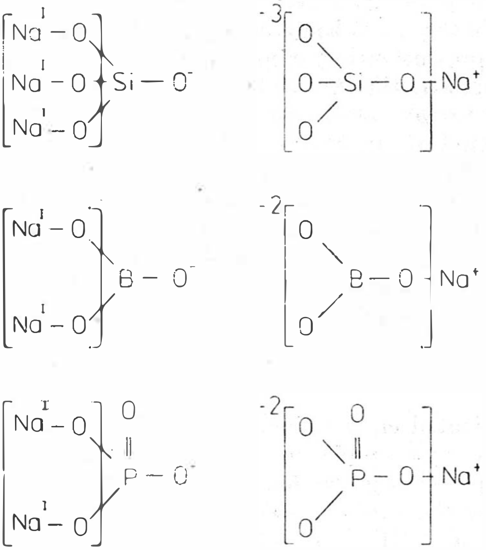

Fig. 12. „Covalent" and „ionic" M—O bond in structural units with central elements Si, B *and* P.

The viscosity characteristics show extremes in both relative points. At relative point II, activation energy E_η exhibits a smooth course, while the change of entropy ΔS_η has a maximum. If a high entropy is regarded as a measure of increased miscibility this thermodynamical conception is in agreement with the change in activation energy. In contrast to this, activation energy attains a maximum at the 1 : 4 compound, where the degree of arrangement is the highest.

The thermal expansion coefficient α has a quite different course. It converges from the side of chain-linking as well as from the cross-linking one towards relative composition II forming a rounded minimum in the range of pentaborate, where both branches are widely open. This fact allows to assume that the mechanism involved differs markedly from the previous contact effect. An explanation can be found in Mie's equation relating α to the Grüneisen's constant [81].

In regions II and III, Na^+ is bound ionically, electrostatically to O^{2-}. If in the region I Na^+ is not bound to O^{2-} but to O^{II-}, the Coulombic attractive and repulsive forces cease to be effective, and the coefficients m and n in the Mie's equation converge towards zero value.

In region II and III there holds the Mie's designation

$$\frac{m + n + 3}{6} = \gamma = \frac{\varkappa 3\alpha V}{c_p} \tag{13}$$

where γ is the Grüneisen's constant. Both c_p and V_M do not show any abrupt changes with changing composition.

In region I, as a result of $m \rightarrow n \rightarrow$ zero, the lefthand expression, and thus also the Grüneisen's constant γ, converge towards the value of 3/6, i.e. 0.5, so that the term on the right-hand side must also decrease, proportionally with the cubic expansion coefficient involved.

Beyond relative point II the „state" of oxygens changes, ionic bonds arise, and α increases with increasing Na_2● content.

A minimum thermal expansion coefficient may arise generally as a result of the following three reasons:

(a) at the contact of two different (incompatible) structures, a chain-linked and a cross-linked one,

(b) in the region of separation into immiscible phases,

(c) when groups with a non-polar bond are present together with those with a polar one.

With borate glasses the given three causes are superposed and mutually supplemented. With other systems, the α-anomaly may have only one cause.

Local disarrangement of oxygens is probably responsible for slowed-down diffusion and reduced extraction losses. However, the Na(I) particles as donors of oxygen required for the formation of (B●$_4$) remain free since the donor-acceptor relation results in weaker bonds only, if M(I) is bound via a non-bridging oxygen (85). In its part of oxygen donor, Na(I) retains in region II the ability of transmitting current, so that no marked anomalies in electrical conductivity arise at relative point II. Electrical conductivity increases continuously without showing any extremes.

SUMMARY

The phenomenological chemical model of borate anomalies may therefore be described as follows:

In the absence of ●H-groups polymeration in the systems M_2O—B_2O_3 proceeds uniformly without exhibiting any extreme changes of properties.

A pulse is necessary to bring about distinct anomalous changes in the chemical dependence of properties. Such a (chemical) pulse is provided by hydrogen bonds.

(3) B^{III}as acceptor obtains one oxygen from the coordinating envolope of oxygens from Na(I) which acts as a donor. (B●$_4$) units are also formed apart from the planar (B●$_3$) units.

Up to 16.7 mole % Na_2● (up to relative composition II), B_2●$_3$ forms cyclic boroxol groups (B●$_3$)$_n$. Their stability is increased by (B●$_4$). The sharing of oxygens between (B●$_3$) and (B●$_4$) results in their joining, which promotes polymeration. The condition for the formation of a stable polyanion (a conception taken over from the knowledge of borates) is that the ratio of $^{(4)}B$ to all the B(III) atoms should be expressed by a simple ratio of integers and that strengthening occurs only when the "molecule" contains only small amounts of (B●$_4$) (1 or 2). Stability of the polyion is promoted by hydrogen bonds. If the ratio of $^{(4)}B$ to Σ B(III) is not expressed by simple integers (between ratios 1 : 5 and 2 : 5), the stable polyanion is not formed. This is why the anomalies are bound to a narrow composition range around the relative points.

At the point of the pentaborate ratio, there occur simultaneously two polymeric, bond-incompatible structures, the chain-linked structure and the cross-linked one. The two incompatible structures are probably the cause of phase separation which attains a maximum at the 1 : 5 ratio.

At a 1 : 5 ratio the change in entropy increases and a higher miscibility occurs. The contact effect is similar to the isoelectric one.

The change of properties at the boundaries of two structures in the direction opposite to that of the cross-linked structure is expained by a change in the oxygen bond from its ionic type to the covalent one.

The further polar units of (BO_4) arising beyond the 1 : 5 ratio only increase the ionic nature of the polymer. Beyond the 2 : 5 ratio the constitution of alkali borate glasses is similar to that in the system Na_2O—SiO_2.

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List of Symbols

A	property; constant in the Arrhenius—type equation
B	constant in Arrhenius-type equation
c	composition
c_p	specific heat under constant pressure $[J \,.\, g^{-1} K^{-1}]$
C	a compound as invariant point in phase diagram
d	density $[g \,.\, cm^{-3}]$
ΣD	summary capability of a system as oxygen donor
e_v	dissociating energy (related to 1 mole volume) $[J \,.\, m^{-3}]$
E	eutectic; modulus of elasticity in tension
E_a	activation energy related to electrical conductivity $[J \,.\, mole^{-1}]$
E_A	activation energy related to property A $[J \,.\, mole^{-1}]$
E_h	activation energy related to chemical resistance $[J \,.\, mole^{-1}]$
E_η	activation energy related to viscosity $[J \,.\, mole^{-1}]$
f_i	partial molar fraction of oxide i; $\Sigma f_i = 1$
F_i	bond strength in the M_i — O bond
g_i	partial additive molar factor
H	microhardness [MPa]
K	congruently melting composition (in phase diagram)
m	Mie's index of attractive forces
m_i	content of i-th oxide, in mole %
$(m_M)_i$	the number of atoms of electropositive element in i-th oxide M_mO_n
M	electropositive element
${}^{(y)}M^{z}$	electropositive element with formal valency z and coordination number y
MD	modification transformation
ME	congruently melting metastable eutectic
MKC	metastable congruent melt
MOD	modifying element
n	Mie's index of repulsive forces
n_D	refractive index
$(n_O)_i$	the number of oxygen atoms in i-th oxide
$\bar{N}_O$	volume characteristic-density of oxygen atoms contained $[O \,.\, cm^{-3}]$
NWF	network-forming element
NWD	network dwelling (intermediate) element
N_M	Huggins' symbol for the M/O ratio
${}^{-}O$	non-bridging oxygen
${}^{+}O$	bridging oxygen
${}^{io}O$	oxygen with ionic bond
${}^{co}O$	oxygen with covalent bond
O^{2-}	ionically bound oxygen
O^{II-}	atomary bound oxygen
p_M	amount of oxide M_mO_n in % by wt.
P	peritectic
r_i	effective ion radius $[10^{-10}\, m]$
R	gas constant; invariant decomposition point
R_M	molar refractivity $[cm^3]$
R_a	atomic refractivity
R_i	ionic refractivity
R_O	total refractivity of oxygens $[cm^3]$

ΔS_η	change in entropy of viscous flow
t	temperature in °C
t_0	constant in the VFT equation (in °C)
T	temperature in K
T_0	constant in equation VFT (in K)
U_M	Magnus's lattice energy
v_n	Kühne's degree of cross-linking
V_M	volume characteristic — molar volume [$cm^3 . mole^{-1}$]
V_1	volume characteristic — volume related to 1 gramatom of oxygen [cm^3/gram atom O^{2-}]
W_i, W_M	molecular weight of i-th oxide of electropositive element M
W_g	mean molecular weight of glass
x_i	content of i-th oxide in glass
X	electronegativity; Stevels's symbol for number of non-bridging oxygens in the polyhedron
y	coordination number
Y	Stevels's symbol for the number of bridging oxygens in the polyhedron
z	charge; formal valency
z/a^2	strength of electrostatic field
α	thermal expansion coefficient [10^{-6} K^{-1}]
γ	surface tension [10^{-3} N . m^{-1}]
γ	Grüneisen's constant
ε	permittivity
ψ	ratio of oxides
$\varkappa$	compressibility
ϱ	resistivity [Ω . cm]

indexes i, j designate i-th or j-th oxide

KYSLÍKOVÉ ANOMÁLIE OXIDOVÝCH SKEL I

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Alkalické binární a ternární systémy jeví anomální závislosti vlastností na složení, a to různé u jednotlivých síťotvorných prvků i u různých modifikátorů. Nejvíce jsou dosud prostudovány anomálie boritanové. Cílem práce je studium chemické závislosti anomálií srovnávací metodou u skel boritanových (část I), u skel křemičitanových, alkalicko-hlinito-křemičitých a fosforečnanových (část II), a posléze u skel germaničitanových a telluričitanových (část III). Symboly ke všem částem jsou zařazeny za část I. Fenomenologický model je studován v celém rozsahu skelného stavu k objemovým charakteristikám, k invariantním bodům fázových rovnováh, k termochemickým charakteristikám, a zvláště k hranici trojrozměrného zesítění. S výjimkou efektu kombinovaných iontů byla u všech anomálií nalezena jako společný znak změna „stavu“ kyslíků.

Boritanové anomálie jsou rozloženy v celém rozsahu skelného stavu. Soustřeďují se však hlavně ke vztažným složením, zejména k pentaboritanu. Pentaboritanový poměr, ve kterém leží minimum teplotní roztažnosti, minimum tang δ, minimum aktivační energie viskozního toku a maximum aktivační energie difúzních pochodů (chemické odolnosti), je spatřován ve vztahu ke změně iontové vazby kyslíků na kovalentní. Na přechodu mezi oběma strukturami se projeví jako stykový efekt změna vibrací iontů a změna Mie-ových indexů m a n a návazná inverze vlastností.

Fenomenologický chemický model boritanových anomálií můžeme popsat takto:

Za nepřítomnosti OH-skupin probíhá polymerizace v systémech M_2O—B_2O_3 plynule bez extrémních změn vlastností.

Aby došlo k výrazným anomálním změnám v chemické závislosti vlastností, je třeba impulsu. Tímto (chemickým) impulsem jsou vodíkové vazby.

$^{(3)}B^{III}$ jako akceptor získává jeden kyslík z koordinační slupky kyslíků od Na(I), který působí jako donor. Vedle plošných jednotek (BO_3) vznikají také jednotky (BO_4).

B_2O_3 do 16,7 mol. % Na_2O (do II. vztažného složení) tvoří cyklické boroxolové skupiny $(BO_3)_n$. (BO_4) zvyšuje jejich stabilitu. Sdílením kyslíků mezi (BO_3) a (BO_4) dochází k jejich spojování, což podporuje polymerizaci. Aby vznikl stabilní polyaniont (představa, kterou přijímáme ze znalosti boritanů), je nutné, že poměr $^{(4)}B$ ke všem atomům B(III) musí být vyjádřen jednoduchým poměrem celých čísel a že ke zpevnění dochází jen při malém množství (BO_4) v „molekule“ (1 nebo 2). Stabilitu polyiontu podporují vodíkové vazby. Není-li poměr $^{(4)}B : \Sigma\, B$(III) vyjádřen jednoduchými celými čísly (mezi poměrem 1 : 5 a 2 : 5), ke tvorbě stabilního polyaniontu nedochází. Proto jsou anomálie vázány na úzké rozpětí složení kolem vztažných bodů.

V místě pentaboritanového poměru se stýkají dvě polymerní, vazebně nekompatibilní struktury, zřetězená a prostorově zesítěná. Obě nekompatibilní struktury jsou patrně příčinou fázové separace, která při poměru 1 : 5 dosahuje maxima.

Při poměru 1 : 5 se zvyšuje změna entropie, dochází k vyšší směsitelnosti. Stykový efekt se podobá izoelektrickému efektu.

Změna vlastností na hranici dvou struktur opačným směrem než u struktury zesítěné je vysvětlitelná tím, že se mění vazba kyslíku z iontové na kovalentní.

Nad poměrem 1 : 5 další vznikající polární jednotky (BO_4) zvyšují pouze iontovou povahu polymeru.

Nad poměrem 2 : 5 se podobá stavba alkalickoboritanových skel stavbě skel v systému $Na_2O—SiO_2$.

Obr. 1. Objemové charakteristiky (V_1, R_M, R_O) *v systému* $Na_2O—B_2O_3$.
Obr. 2. Geometrické vlastnosti v systému $Na_2O—B_2O_3$; d [37], n_D [37], μ [42], E [50].
Obr. 3. Aktivované vlastnosti v systému $Na_2O—B_2O_3$; *a*) E_h [55], E_a [*podle 52*], ΔS_η [*podle 80*]; *b*) E_η [*podle 80*].
Obr. 4. Vlastnosti v systému $Na_2O—B_2O_3$; *koeficient teplotní roztažnosti* α; *a*) 20—300 °C (65), *b*) *—196 až 20 °C* [*66*]; *průběh transformační teploty* t_g; *m. i. = metastabilní immiscibilita* [*98*].
Obr. 5. Vlastnosti v systému $Na_2O—B_2O_3$ *v oblasti II a III vztažného složení 1 : 5 a 2 : 5; H — mikrotvrdost* [*22*], [*60*]; A, B, T_0 *— konstanty ve Vogel-Fulcher-Tammannově rovnici* [*80*], α [*40*]; *tang* δ [*62*].
Obr. 6. Acidobasicita v systému $Na_2O—B_2O_3$ [58].
Obr. 7. V_1 *v systému* $Na_2O—B_2O_3$ [22] *u vzorků* (*a*) *chlazených*, (*q*) *prudce ochlazených* (*v*) *prudce ochlazených z taveniny tavené vakuově.*
Obr. 8. Objemové charakteristiky v systému $K_2O—B_2O_3$ (V_1, R_M, R_O).
Obr. 9. Geometrické vlastnosti v systému $K_2O—B_2O_3$; d [*37*], n_D [*37*], μ [*49*], E [*49*].
Obr. 10. Aktivované vlastnosti v systému $K_2O—B_2O_3$: E_h [55], E_a [*53*], E_η [*86*], α [*12*].
Obr. 11. Struktura pentaboritanové entity 1 : 5 a 2 : 5 podle [*32*] *a* [*75*].
Obr. 12. „Kovalentní“ a „iontová“ vazba M—O v strukturních jednotkách s centrálním prvkem Si, B *a* P.

КИСЛОРОДНЫЕ АНОМАЛИИ ОКСИДНЫХ СТЕКОЛ

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Щелочные бинарные и тернарные системы проявляют аномальные зависимости от состава, отличающиеся у отдельных структурирующих элементов и у разных модификаторов. До сих пор наиболее подробно изучены боратные аномалии. Целью предлагаемой работы является исследование химической зависимости аномалий с помощью сопоставительного метода у боратных стекол (часть I), у силикатных, щелочноалюмосиликатных и фосфатных стекол (часть II), и у германатных и теллуранатных стекол (часть III). Символы и ссылки ко всем частям приводятся в конце первой части. Феноменологическая модель исследуется в полном диапазоне стекловидного состояния в отношении к объемным характеристикам, к инвариантным точкам фазовых равновесий, к термохимическим характеристикам, а именно к пределам трехразмерного структурирования. За исключением эффекта комбинированных ионов у всех аномалий было установлено в качестве общего признака изменение ,,состояния" кислородов.

Борные аномалии расположены в полном диапазоне стекловидного состояния. Однако они сосредоточиваются главным образом к относительным составам, именно к пентаборату. Пентаборатное отношение, в котором лежит минимум температурного расширения, минимум tang δ, минимум энергии активации пластического течения и максимум энергии активации процессов диффузии (химической устойчивости), заключается в отношении к изменению ионной связи кислородов в ковалентную связь. На переходе между обеими структурами проявляется в качестве контактного эффекта изменение вибраций ионов и изменение показателей m и n с последовательной инверсией свойств. Следовательно, феноменологическую химическую модель боратных аномалий можно описать следующим образом:

В отсутствии OH-групп полимеризация в системах M_2O—B_2O_3 проходит непрерывно, без экстремальных изменений свойств. Для резких аномальных изменений в химической зависимости свойств нужен импульс. Таким (химическим) импульсом служат водородные связи.

Рис. 1. Характеристики объема (V_1, R_M, R_O) *в системе* Na_2O—B_2O_3.

Рис. 2. Геометрические свойства в системе Na_2O—B_2O_3; d [*37*], n_D [*37*], μ [*42*], E [*50*].

Рис. 3. Активированные свойства в системе Na_2O—B_2O_3: a) E_h [*55*], E_a [*согласно 52*], ΔS_η [*согласно 80*]; E_η [*согласно 80*].

Рис. 4. Свойства в системе Na_2O—B_2O_3; *коэффициент температурного расширения a) 20—300 °C* [*65*], *b) —196—20 °C* [*66*]; *ход температуры превращения* t_g; *м. и. = метастабильная иммисциобильность* [*68*].

Рис. 5. Свойства в системе Na_2O—B_2O_3: *в области* II *и* III *относительного состава 1 : 5 и 2 : 5; H — микротвердость* [*22*], [*60*]; *A, B,* T_0 — *константы в уравнении Фогел—Фульхер—Таманна* [*80*], α [*40*]; tang δ [*62*].

Рис. 6. Кислото-основность в системе Na_2O—B_2O_3 [*58*].

Рис. 7. V_1 *в системе* Na_2O—B_2O_3 [*22*] *у проб* (*a*) *охлаждаемых*, (q) *резко охлаждаемых*; (*v*) *резко охлаждаемых из расплава, полученного во вакууме.*

Рис. 8. Характеристики объема в системе K_2O—B_2O_3 (V_1, $\bar{R}_M$, R_O).

Рис. 9. Геометрические свойства в системе K_2O—B_2O_3: d [*37*], n_D [*37*], μ [*49*], E [*49*].

Рис. 10. Активированные свойства в системе K_2O—B_2O_3: E_h [*55*], E_a [*53*], E_η [*86*], α [*12*].

Рис. 11. Структура пентаборатной энтиты 1 : 5 и 2 : 5 согласно [*32*] *и* [*75*].

Рис. 12. «Ковалентная» и «ионная» связь M-O в структуральных единицах с центральным элементом Si, B. P.