

Volume changes caused by alkali ions in borate, germanate and silicate glasses and their relation to cation mobility

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It can be shown that volume changes in silicate, borate and germanate glasses can be simply described by the ionic volumes of the corresponding cation addition, if these changes are related to the total number of oxygen atoms. Changes in the volume per mole oxygen are also caused by a varying coordination number as in the case of borate and germanate glasses. Molar volumes defined this way obey simple superposition rules for binary and ternary glasses. In addition, the volume per oxygen atom (or mole), a measure of the average distance of oxygen atoms, provides a quantity which is closely related to the diffusion of gas atoms and alkali ions. Thus a decreasing (increasing) volume per mole oxygen gives rise to a decrease (increase) of the diffusion coefficient of cations or gas atoms. Examples will be presented where this relation is fulfilled qualitatively or quantitatively even. For the quantitative description of diffusion the volume changes caused by external hydrostatic pressure and their known effect on diffusion will be used, in order to model the effect of volume changes caused by a changing composition.

1. Introduction

During a recent treatment of ionic diffusion and the mixed alkali effect [1 and 2], it was shown that the molar volume of silicate glasses defined as the ratio of sample volume and number of oxygen moles can be used to explain the decrease in the diffusion coefficient of the larger cation, if this is successively replaced with a smaller cation. This was qualitatively and quantitatively described by a concomitant decrease in the volume per mole oxygen V_O and the average distance of oxygen atoms, respectively. This distance is the inverse cube root of V_O . As oxygen atoms are network-forming atoms and as their radius is much larger than the one of other network formers like boron, silicon and even germanium, one may comprehend that the oxygen packing density determines the mesh size of the amorphous network of the glass. On the other hand, it appears to be reasonable that diffusion of quasi interstitial particles like ions and helium atoms is affected by the mesh size. Quasi interstitial diffusion is used in this context for particles jumping into neighboring sites which are mostly empty.

The treatment of V_O was presented in no detail in [1 and 2] and no evidence was provided for the simple superposition rule used for the ternary glasses. Because the concept of describing the network of an oxidic glass via V_O has not been used so far to the author's knowledge, it will be described in more detail in this paper. It

will be also shown that Vegard's Law is not fulfilled for binary silicate glasses and that by the use of V_O it can be replaced by a similar simple rule. Furthermore V_O will be calculated for a much larger variety of glasses including borate and germanate glasses and mixed borate-silicate ones, where the coordination number of oxygen around either boron and germanium changes during the addition of alkali oxides. In addition, the changes in V_O will be compared with changes in helium diffusivity and alkali ion mobility in a variety of glasses.

2. Binary silicate glasses containing alkali and alkali earth additions

The mass density of binary silicate glasses of the type $(A_2O)_x-(SiO_2)_{1-x}$ (A being an alkaline metal) and $(EO)_x-(SiO_2)_{1-x}$ (E being an alkaline earth metal), as compiled in the Handbook of Glass Data by Mazurin and Streltsina [3], was used, in order to calculate V_O at room temperature. By dividing with the number of moles of oxygen, the sum of bridging and nonbridging oxygen atoms were taken into account. According to its definition the volume V_O is given by the following trivial equations:

for alkali oxides

$$V_O = \frac{x M(A_2O) + (1-x) M(SiO_2)}{\gamma (2-x)} \quad (1)$$

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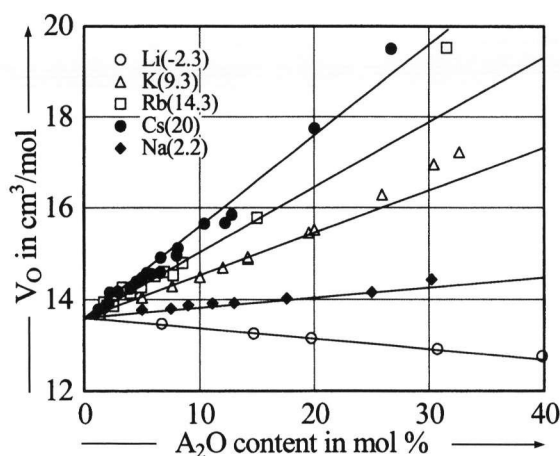


Figure 1. Volume per mole oxygen V_O in silicate glasses with additions of alkaline metal oxides. Results are evaluated from measured densities [4] and the slope of the straight lines is given in brackets in units of cm^3/mol .

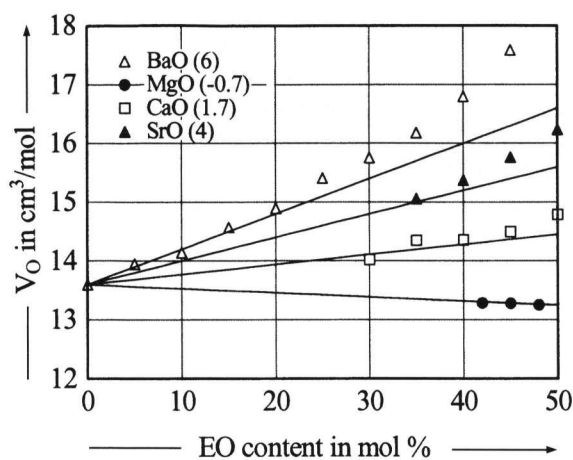


Figure 2. Volume per mole oxygen V_O in silicate glasses with additions of alkaline earth metal oxides. Results are evaluated from measured densities [5] and the slope of the straight lines is given in brackets in units of cm^3/mol .

and for alkali earth oxides

$$V_O = \frac{x M(\text{EO}) + (1-x) M(\text{SiO}_2)}{\gamma(2-x)}, \quad (2)$$

where in the denominator both the $2-2x$ bridging plus the x nonbridging moles of oxygen, i.e. its sum $2-x$, were taken into account. M is the molecular weight of the compound following in brackets and γ is the mass density of the glass. Unfortunately, the term partial molar volume of oxygen was used for V_O in previous publications, although this quantity is very well defined as the derivative of volume with respect to the amount of oxygen atoms.

The results for V_O as calculated via equations (1) and (2) and data from [4] and [5] are presented in figures 1 and 2.

The volume per mole oxygen V_O changes with concentration mostly linearly as described by the straight lines intercepting the ordinate at the value for vitreous quartz. Therefore, V_O can be expressed by the following equation:

$$V_O = 13.6 + V_A x, \quad (3)$$

where $13.6 \text{ cm}^3/\text{mol}$ is the value of pure SiO_2 and x is the mole fraction of A_2O and EO , respectively. Thus V_A as given in the insets of figures 1 and 2 and in table 1 has the meaning of a partial molar volume of the oxide with 2A^+ and E^{2+} , respectively. These values are compared in figure 3 with the ionic volume V_i of A or E . A straight line can be drawn through the data points for the alkali ions according to the following relation:

$$V_A = -3.2 + 2V_i. \quad (4)$$

The corresponding relation for the alkali earth oxides is

$$V_A = V_i - 0.5. \quad (5)$$

The volume expansion is proportional to the volume of the cations. For alkali ions the proportionality factor of 2 is in agreement with the definition of V_A being the volume change for one mole of A_2O and two moles of A^+ , respectively. For alkaline earth cations the factor is 1 in agreement with the composition of the oxide EO . However, with the exception of barium data from [1] were available for large concentrations of EO only, where the dependence on concentration appears to be stronger. Thus the description of the alkali earth data by equation (5) is less reliable.

In order to test the validity of Vegard's Law, the molar volume of the alkali glasses was calculated via equations (1) and (2) without the factor $(2-x)$ in the denominator and plotted in figure 4 versus the content of alkali oxide. Vegard's Law predicts the following relationship to be obeyed:

$$V(\text{glass}) = x V(\text{A}_2\text{O}) + (1-x) V(\text{SiO}_2), \quad (6)$$

where V is the molar volume of the material in brackets. In agreement with equation (6) the data points in figure 4 can be described by straight lines with an intercept corresponding to $V(\text{SiO}_2)$, however the slopes are smaller when compared with equation (6) as shown in table 2.

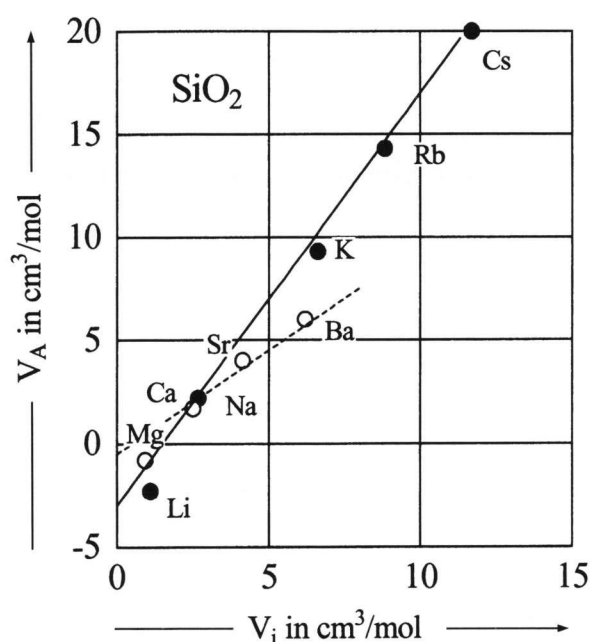
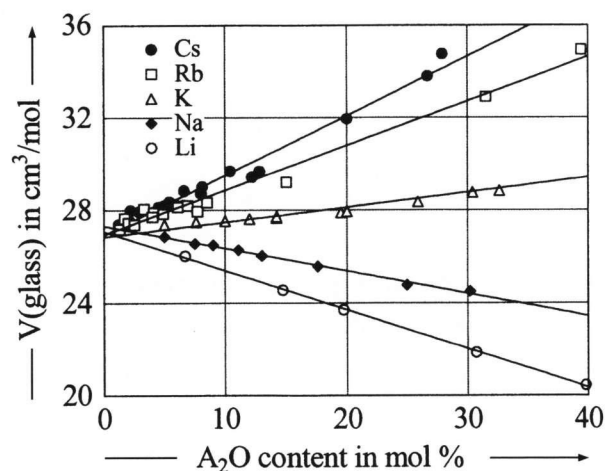
3. Binary borate and germanate glasses containing alkali additions

Values of V_O were calculated according to its definition from density data [6] by the following equations (see equations (1) and (2))

$$V_O = \frac{x M(\text{A}_2\text{O}) + (1-x) M(\text{B}_2\text{O}_3)}{\gamma(3-2x)} \quad (7)$$

Table 1. Ionic radii of alkali and alkali earth ions, r_i for a coordination number of 6, corresponding ion volume V_i [1] and slope of the straight lines shown in figures 1 and 2

	alkali ion					alkali earth ion			
	A ⁺		R ⁺			E ²⁺			
	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Mg ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺
r_i in nm	0.076	0.102	0.138	0.152	0.167	0.072	0.100	0.118	0.135
V_i in cm ³ /mol	1.1	2.67	6.6	8.8	11.7	0.94	2.5	4.1	6.2
V_A in cm ³ /mol	-2.3	2.2	9.3	14.3	20	-0.7	1.7	4	6

Figure 3. Partial molar volume V_A as defined in the text versus volume of the ions A calculated from their ionic radii for a coordination number of 6 and valence +1 for the alkaline (closed circles) and 2+ for the alkaline earth metals (open circles). The lines have slope 2 (solid) and 1 (dashed), respectively.Figure 4. Molar volume of silicate glasses $V(\text{glass})$ as a function of the alkali concentration.

and

$$V_O \equiv \frac{x M(A_2O) + (1-x) M(GeO_2)}{\gamma(2-x)} \quad (8)$$

V_O values obtained this way are presented in figures 5 and 6. In comparison with the silicate glasses, V_O decreases with increasing x at low values of x and for the smaller alkali ions in both types of glasses.

In borate and germanate glasses the coordination number of boron or germanium is changed during the addition of alkaline oxides [7]. Besides GeO_4 resembling the SiO_4 tetrahedral coordination there is also GeO_6 coordination of oxygen atoms. The number of the new units increases with increasing alkaline content reaching a maximum between 10 to 20 mol% A_2O in agreement with the volume decrease visible in figure 4. For boron, BO_3 units are replaced successively with BO_4 ones. By assuming that the formation of GeO_6 and BO_4 units and the corresponding contribution V_{co} to V_O is independent of the type of alkaline ion, we can write

$$V_O = V_{co}(x) + V_A x \quad (9)$$

In agreement with this assumption a master curve for all alkali oxides could be constructed, which represents V_{co} by using the values compiled in table 3 for V_A . With some deviations visible for the germanate glasses, the master curves can be approximated by exponential decay functions:

$$V_{co}(\text{borate}) \equiv 11.7 + 0.8 \exp\left(-\frac{x}{0.08}\right) \quad (10)$$

and

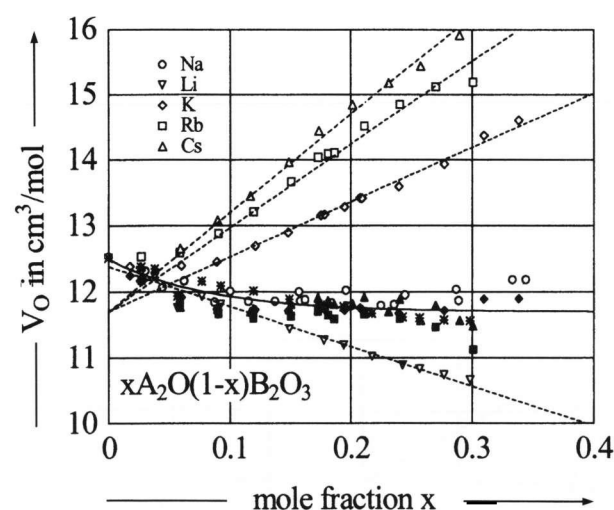
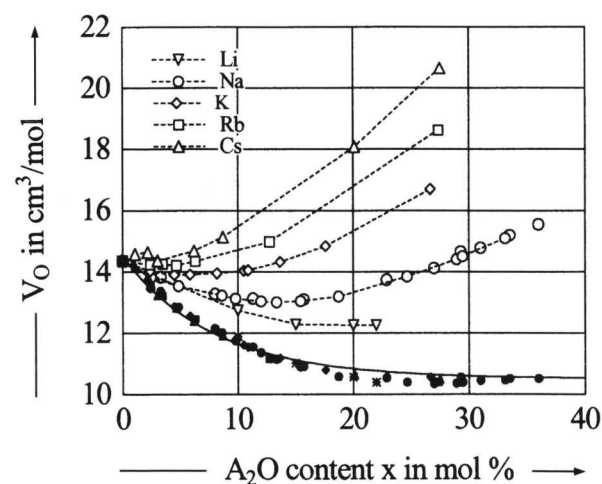
$$V_{co}(\text{germanate}) \equiv 10.5 + 4 \exp\left(-\frac{x}{0.08}\right) \quad (11)$$

As shown in figure 7 the values of V_A can be related to the volume of the alkali ions. The same behavior was observed for silicate glasses (see equation (4) and figure 4). The straight lines in figure 7 correspond to the following relationships

$$V_A(\text{borate}) = -5.5 + 2V_i \quad (12)$$

Table 2. Various quantities of alkali oxides and the slopes of the straight lines shown in figure 4 as well as the expected ones according to equation (6)

	Li ₂ O	Na ₂ O	K ₂ O	Rb ₂ O	Cs ₂ O
density in g/cm ³	2.013	2.27	2.32	3.72	4.25
molar weight in g/mol	29.9	62	94.2	186.9	281.8
molar volume in cm ³ /mol	14.9	27.3	40.6	50.3	66.3
slope $\{V(A_2O) - V(SiO_2)\}$	-12.3	0	13.4	23.1	39.1
according to equation (6) in cm ³ /mol					
slope of the straight lines in figure 4 in cm ³ /mol	-16.8	-9.7	6.4	19.3	25.8


 Figure 5. Volume per mole oxygen V_O in alkali borate glasses (open symbols). The dashed straight lines fit the behavior at high alkali contents. Closed data points represent $V_O = V_A x$ with V_A values as compiled in table 3. The solid line approximates the behavior of the closed symbols according to the function given in equation (10).

 Figure 6. Volume per mole oxygen V_O in alkali germanate glasses (open symbols). The dashed lines connect data points. Closed data points represent $V_O = V_A x$ with V_A values as compiled in table 3. The solid line approximates the behavior of the closed symbols according to the function given in equation (11).

and

$$V_A(\text{germanate}) = 10 + 2V_i \quad (13)$$

Table 3. Volume change caused by alkali oxides in germanate and borate glasses after subtraction of the volume shrinkage caused by a changing coordination number (see text)

	Li ₂ O	Na ₂ O	K ₂ O	Rb ₂ O	Cs ₂ O
$V_A(\text{GeO}_2)$ in cm ³ /mol	8.5	14	23	34	37
$V_A(\text{B}_2\text{O}_3)$ in cm ³ /mol	-3	0	8	12.3	15

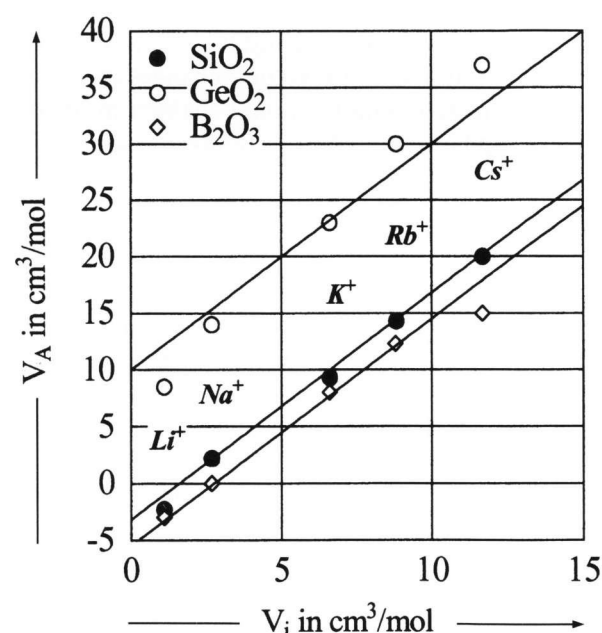


Figure 7. Partial molar volume of alkaline oxides for silicate, borate and germanate glasses as defined by equations (3 and 9) plotted versus the corresponding ionic volume of cations. The straight lines represent equations (4, 12 and 13).

As in silicate glasses the volume change caused by the alkaline ions is equivalent to the ionic volume of the cations.

4. Ternary glasses containing two alkali ions

For ternary glasses of the formulae $(A_yR_{1-y}O)_x(\text{SiO}_2)_{1-x}$, $(A_yR_{1-y}O)_x(\text{GeO}_2)_{1-x}$ and $(A_yR_{1-y}O)_x(\text{B}_2\text{O}_3)_{1-x}$, the volume per mole oxygen V_O is calculated via equations (1, 2, 7 and 8) where $M(A_2O)$ has to be replaced with the aver-

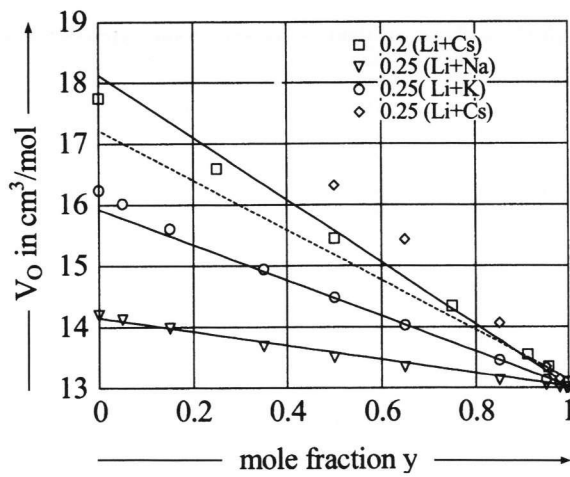


Figure 8. Volume per mole oxygen V_O in mixed lithium silicate glasses as a function of the mole fraction $y = \text{Li}_2\text{O}/(\text{Li}_2\text{O} + \text{A}_2\text{O})$ [9]. The straight lines are calculated according to equation (14) whereas the dashed line corresponds to $x = 0.2$.

age value $y M(\text{A}_2\text{O}) + [1 - y]M(\text{R}_2\text{O})$. In these glasses the contribution of the two alkalis A and R to V_O is in a good approximation additive, i.e. the volume changes are equivalent to the corresponding fractional changes in binary glasses. This can be expressed by the following equation:

$$\begin{aligned} V_O &= V_O^0 + xy V_A + x(1 - y) V_R \\ &= V_O(x\text{R}_2\text{O}) - yx(V_R - V_A), \end{aligned} \quad (14)$$

where V_O^0 is the volume per mole oxygen for the network-forming glass, i.e. $13.6 \text{ cm}^3/\text{mol}$ for SiO_2 , or $V_{\text{co}}(x)$ for borate and germanate glasses, x is the total alkaline content as a mole fraction of the two alkaline oxides ($\text{A}_2\text{O} + \text{R}_2\text{O}$), V_A and V_R are the molar volumes in the binary glasses as compiled in tables 1 and 3, y is the mole fraction of the alkaline oxide containing A, i.e. $y = \text{A}_2\text{O}/(\text{R}_2\text{O} + \text{A}_2\text{O})$, and $V_O(x\text{A}_2\text{O})$ is the volume per mole oxygen for the binary glass containing A_2O with a content x . For A being the smaller cation, V_O decreases with increasing y . By splitting V_O^0 into two parts, $y V_O^0$ and $(1 - y) V_O^0$, equation (14) can be rewritten as

$$V_O = y V_O(x\text{A}_2\text{O}) + (1 - y) V_O(x\text{R}_2\text{O}) \quad (15)$$

which corresponds to the mean value of the two binary oxides.

In figures 8 to 11 experimental results from density measurements [6 and 8] were used to calculate V_O and to plot it versus y . The straight lines represent equation (14) with values for V_A and V_R taken from binary glasses and equation (15), respectively, where the straight lines are connecting the values of the two binaries. The agreement between the predictions of equation (14) or (15) and experimental findings is good with the exception of caesium in a silicate glass where larger positive deviations occur. Deviations occurring for a mixed sodium-rubidium borate glass will be discussed later.

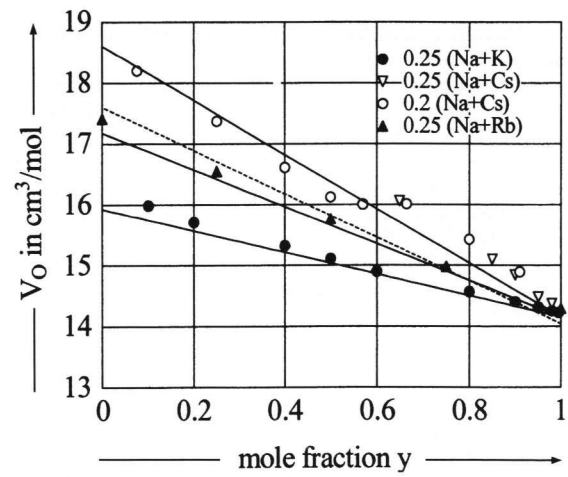


Figure 9. Volume per mole oxygen V_O in sodium silicate glasses as a function of the mole fraction $y = \text{Na}_2\text{O}/(\text{Na}_2\text{O} + \text{A}_2\text{O})$ [9]. The straight lines are calculated according to equation (14) whereas the dashed line corresponds to $x = 0.2$.

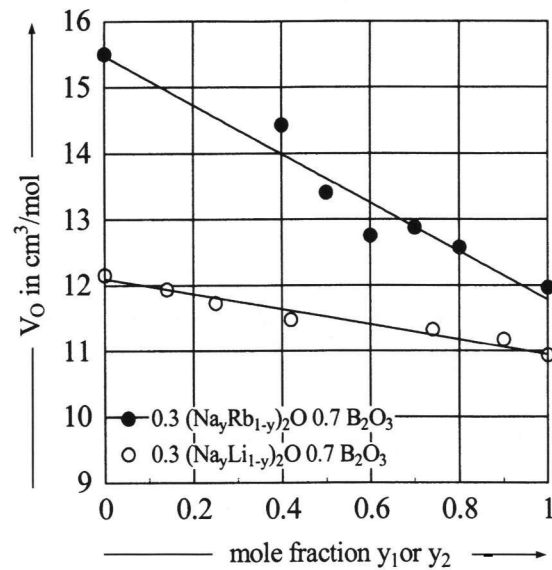


Figure 10. Volume per mole oxygen V_O in sodium borate glasses as a function of the mole fraction $y_1 = \text{Na}/(\text{Rb} + \text{Na})$ and $y_2 = \text{Li}/(\text{Li} + \text{Na})$ [10].

5. Diffusion and its relation to V_O

A compilation of results on the diffusion and conductivity in glasses is provided in [9]. In order to avoid any effects of a changing charge density on diffusion, we will compare results only, if they correspond to the same total alkali content, i.e. $x = \text{constant}$. Then changes of V_O are caused mainly by replacing a smaller cation by a larger one or vice versa. For the special case of mixed borate/silicate glasses, the network-forming species is substituted, which gives rise to changes of V_O as well. According to its definition relative changes in V_O are equivalent to relative changes in the total volume for $x = \text{constant}$, i.e.

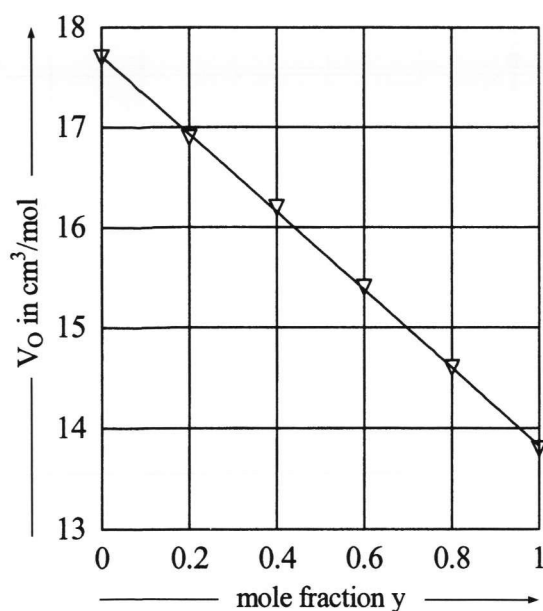


Figure 11. Volume per mole oxygen V_O in Na/Rb germanate glass as a function of the mole fraction $y = \text{Na}/(\text{Na}+\text{Rb})$ [9].

$$\frac{\delta V_O}{V_O} = \frac{\delta V}{V}. \quad (16)$$

It is assumed that compositional changes lead to homogeneous changes of the average O=O distance and V_O , respectively, and that equivalent homogeneous changes are caused by a change of the external hydrostatic pressure, δp . This gives rise to the following equivalence

$$\delta p = K \frac{\delta V}{V} = K \frac{\delta V_O}{V_O}, \quad (17)$$

where K is the bulk modulus. The effect of hydrostatic pressure on the diffusion coefficient is described by an activation volume V^* according to its definition:

$$D \equiv D(0) \exp\left(\frac{\delta p V^*}{k_B T}\right), \quad (18)$$

where $D(0)$ is the diffusion coefficient for $\delta p = 0$, and k_B and T have the usual meaning. Note that for the use of equation (18) and the following ones, the use of SI units is recommended, i.e. the common unit cm^3/mol for molar volumes should be replaced with m^3/mol . Inserting equation (17) into equation (18) yields.

$$\frac{\delta \ln D}{\delta V_O} \equiv \frac{\ln D - \ln D(0)}{\delta V_O} = \frac{K V^*}{k_B T V_O}. \quad (19)$$

Integration yields

$$k_B T \ln D \equiv C + K V^* \ln V_O, \quad (20)$$

where C is a constant.

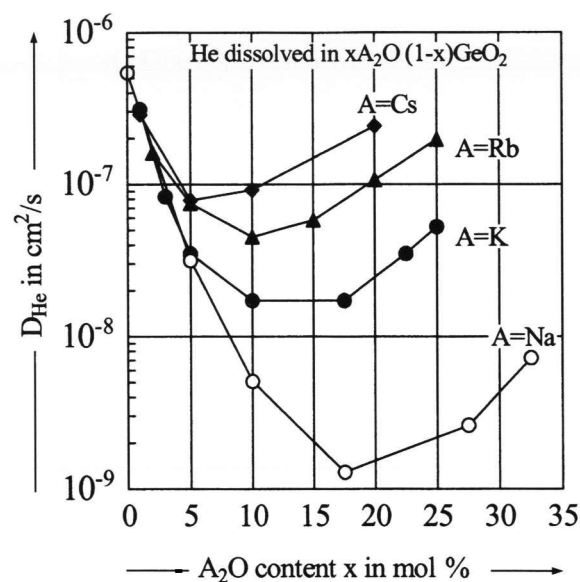


Figure 12. Diffusion coefficient of helium at 250°C in various germanate glasses [11] as a function of the alkali content x .

5.1 Diffusion of helium

In germanate glasses changes in V_O are the largest and, therefore, we expect large effects on the diffusion coefficient as well. Diffusion coefficients of helium at 250°C [11] are plotted in figure 12 as a function of the alkali content. Comparing figure 12 with figure 6 qualitatively reveals the expected correlation as discussed in the previous paragraph. D increases (decreases) monotonously with increasing (decreasing) V_O . In order to compare quantitatively, we have to eliminate effects on D stemming from a changing charge density, i.e. cation concentration. Therefore D -values were taken at a constant composition x from the data points or from connecting lines in figure 12 and presented in figure 13 versus the corresponding value of V_O in a double logarithmic plot. Then the slope of the isocompositional lines should be given by $K V^*/(k_B T)$ according to equation (20). In the range of V_O between 13 and 16 cm^3/mol , the slope $d \lg D/d \lg V_O$ is about 19 and independent of x . Using a value of $K = 23.9$ GPa [12 and 13] gives an activation volume for helium of $V^* \approx 3.5$ cm^3/mol , which is about 50% of the volume of the helium atom using a Van der Waals radius of 0.14 nm. This is a reasonable figure because the activation volume is the difference between the volume expansion caused by the helium atom between the saddle point and the equilibrium position. Deviations from the linear relation between $\ln D$ and $\ln V_O$ occur at larger values of V_O . They may be caused by a breakdown of the linear relation between pressure and volume change, i.e. equation (17).

5.2 Diffusion in mixed alkali glasses

Equation (20) can be also used for mixed glasses. If a larger cation is replaced by a smaller one, V_O decreases

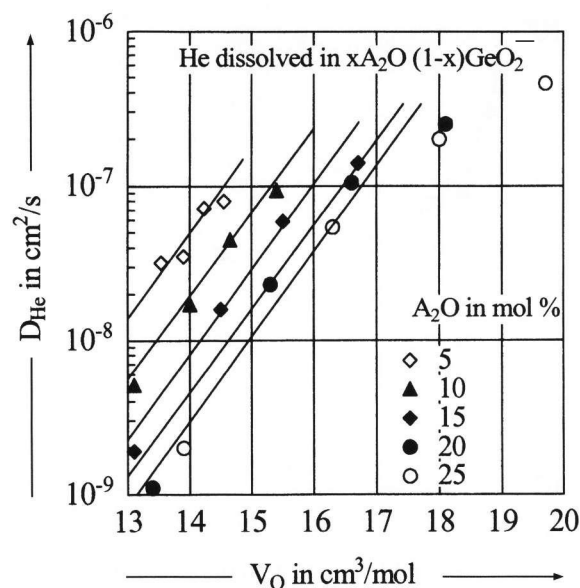


Figure 13. Double logarithmic plot of helium diffusion coefficients at the given composition x according to the data points or the connecting lines in figure 12 versus V_O as obtained from figure 1.

as shown in section 4 and, therefore, on the basis of equation (20) the diffusion coefficient of the cations should decrease. Under these circumstances the larger cation R is the majority component which determines d.c. conductivity and, therefore, its reduced mobility gives rise to the corresponding decrease in conductivity. This is one part of the mixed alkali effect as discussed in [1]. For the case of the alkali ions in silicate glasses, the activation volumes were known and the bulk modulus was treated as a fitting parameter in [1] yielding good agreement with experimental values of K . Replacing a smaller cation with a larger one should lead to an increase of the mobility of the smaller one according to equation (19). It was argued in [1 and 2] that this effect is overcompensated by a preferential occupancy of low-energy sites by smaller cations. In the present study we will give two more examples of the mixed alkali effect in borate and germanate glasses.

In figure 14 the conductivity σ of two mixed borate glasses is compared with the one of the corresponding mixed silicate glasses. For low values of $y = A/(A+R)$ with A being either sodium or lithium and R being potassium, the conductivity is determined by the majority cation K. Then σ is proportional to D_R and the behavior of $\ln \sigma$ is given by equations (12, 13, 14 and 20) as

$$k_B T \ln \sigma = C' + K V_R^* \ln [V_O(xR_2O) - 2y x (V_{iR} - V_{iA})], \quad (21)$$

where C' is a constant containing the proportionality constant between conductivity and diffusivity, and V_{iR} and V_{iA} are the volumes of the corresponding cations. Because the second term in brackets in the last equation

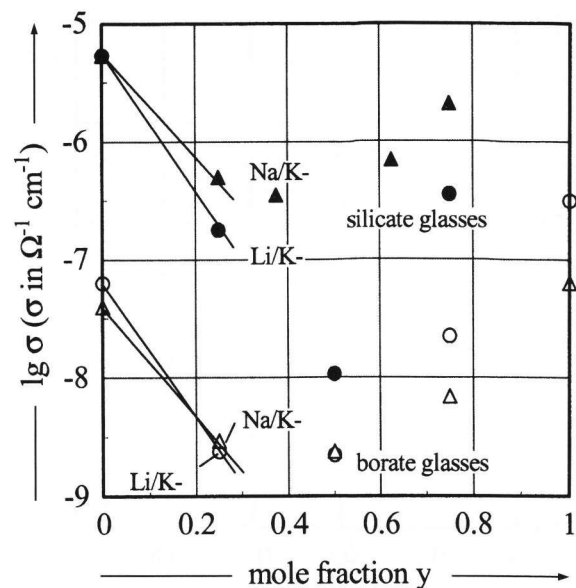


Figure 14. Conductivity σ at 300°C in mixed Li/K and Na/K borate glasses [14] versus $y = A/(A+R)$ in comparison with corresponding values for silicate glasses [15]. The straight lines are connecting the first two data points at small y and the slope of the lines is compiled in table 4.

is small when compared with the first one, we can use a series expansion of the logarithm

$$k_B T \ln D = C + K V_R^* \ln [V_O(xR_2O)] - \frac{2K V_R^* y x (V_{iR} - V_{iA})}{V_O(xR_2O)}. \quad (22)$$

This linear relation between $\ln \sigma$ and y has been used in [1] to explain the mixed alkali effect in silicate glasses and it is used in figures 14 and 15 to present experimental data for borate and germanate glasses. By comparing the slopes at $y \rightarrow 0$ of the borate glasses with those of the corresponding silicate glasses, we obtain similar values for Li/K- and Na/K-mixed glasses. This is in agreement with the prediction of equation (22), because the quantities determining the slope (last term on the right hand side of equation (22)) are about the same for silicate and borate glasses as shown in table 4. However, the experimental slopes in the borate and germanate mixed glasses are larger by about a factor of two than the calculated ones. This again is consistent with the findings for the silicate glasses [1]. The discrepancy may be due to either a) a bulk modulus being smaller at measuring temperature than the room temperature value used for the calculation or b) a systematic error due to the approximations used during the derivation of equation (22). Nevertheless, the systematic deviation between experimental and theoretical values is the same for silicate, borate and germanate mixed glasses.

For the mixed germanate glass shown in figure 15, diffusivities have been measured as well. In accordance with the silicate glasses, the diffusivity of the larger cation R decreases steadily for $y \rightarrow 1$, whereas the smaller

Table 4. Molar volume per mole oxygen V_O (xR_2O) for the binary glass with an alkali content of x as taken from figures 1, 5 and 6. Bulk modulus K at room temperature for $y = 0$ [3], activation volume V_R^* was approximated as in [1] to be V_i . R is the larger cation, i.e. either sodium, potassium or rubidium. The slope is calculated from equation (22) or taken from figures 14 and 15 at $y \rightarrow 0$. The value of the experimental slope of the germanate glass was determined from the conductivity data, whereas the one in brackets is from the diffusivity of rubidium (slopes are for $\lg \rho$ versus x plots).

glass	K in GPa	$V_R^* \approx V_i$ in cm^3/mol	x	$V_O(xR_2O)$ in cm^3/mol	$V_{iR} = V_{iA}$ in cm^3/mol	theoretical slope	experimental slope
Li/K borate	27.4	6.6	0.2	13.36	5.5	2.7	5.7
Li/K silicate	31.7	6.6	0.2	15.45	5.5	3.1	5.9
Na/K borate	27.4	6.6	0.2	13.36	3.9	1.9	4.5
Na/K silicate	31.7	6.6	0.2	15.45	3.9	2.3	4.1
Na/Rb germanate	ca. 38	8.8	0.25	18.0	6.1	5.2	8.7 (9.2)

Table 5. Coefficients of the polynomial function $a_0 + a_1z + a_2z^2 + a_3z^3 + a_4z^4 + a_5z^5$ (z in mol%) for different alkali contents x

x	a_0	a_1	a_2	a_3	a_4	a_5
0.1	13.79	-0.137	$6.4 \cdot 10^{-3}$	$-1.4 \cdot 10^{-4}$	$1.4 \cdot 10^{-6}$	$-5.13 \cdot 10^{-9}$
0.2	14.04	-0.151	$4.4 \cdot 10^{-3}$	$-6.14 \cdot 10^{-5}$	$4.12 \cdot 10^{-7}$	$-1.09 \cdot 10^{-9}$
0.3	14.3	-0.0954	$1.65 \cdot 10^{-3}$	$-1.74 \cdot 10^{-5}$	$1.31 \cdot 10^{-7}$	$5 \cdot 10^{-10}$

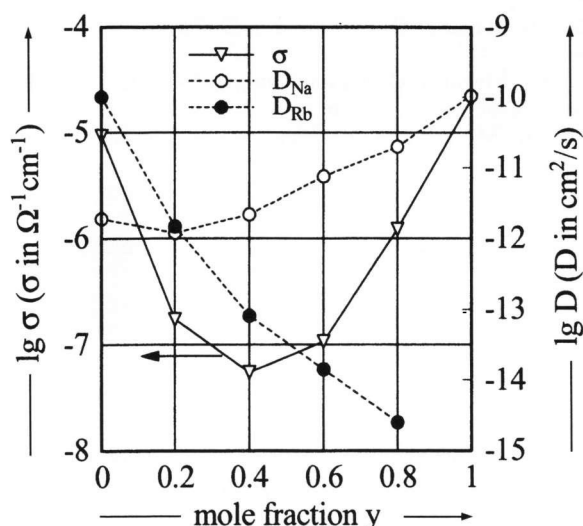


Figure 15. Conductivity and diffusivities at 300°C in mixed Na/Rb germanate glasses [16] with $y = \text{Na}/(\text{Na} + \text{Rb})$. The lines are connecting data points and the slope of the first segment at $y \rightarrow 0$ is compiled in table 4 as an experimental value.

one is rather independent of y at $y \rightarrow 0$. The first effect is in agreement with equation (20) and the last effect is due to a decreasing site energy distribution (see [2]).

An exception from this general trend in mixed oxide glasses appeared to be the Na/Rb-borate one [10] as shown in figure 16. The diffusion coefficient of rubidium is not decreasing steadily with increasing y , and the volume V_O does not depend linearly upon y . But both are related because D shows a maximum at about $y = 0.6$ where V_O exhibits a local minimum, which is in accordance with the correlation discussed in this paper. Why this exceptional behavior of V_O is observed remains unclear.

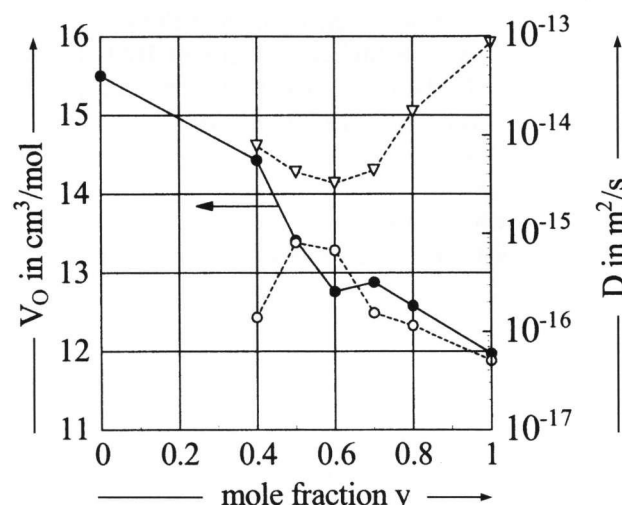


Figure 16. Diffusion coefficient of sodium (open triangles) and rubidium (open circles) at 400°C and volume per mole oxygen V_O in $0.3(\text{Na}_y\text{Rb}_{1-y})_2\text{O} \cdot 0.7\text{B}_2\text{O}_3$ [10] versus $y = \text{Na}/(\text{Na} + \text{Rb})$.

5.3 Sodium diffusion in borate/silicate glasses

In the following we will discuss the mobility of sodium ions in ternary sodium silicate/borate glasses of the composition $(\text{Na}_2\text{O})_x(\text{B}_2\text{O}_3)_z(\text{SiO}_2)_{1-x-z}$. Experimental data of the diffusion coefficient and of V_O are presented in figure 17. According to equation (19) the following equation should be obeyed

$$\frac{d \ln D}{dz} = \frac{K V^*}{k_B T V_O} \frac{d V_O}{dz} \quad (23)$$

If we use the ionic volume of sodium ($= 2.7 \text{ cm}^3/\text{mol}$ [1]) for V^* , $V_O = 14.1 \text{ cm}^3/\text{mol}$, and the slopes of the straight lines in figure 17 as values for the derivatives, the last equation yields a value of $K = 31 \text{ GPa}$, which is

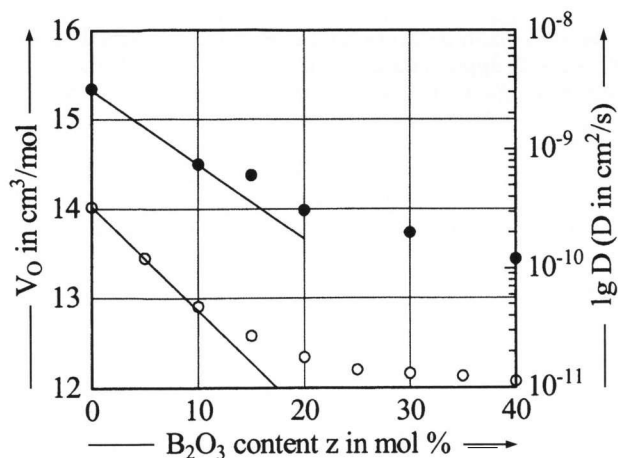


Figure 17. Diffusivity D_{Na} at 380°C (closed circles) [18] and volume per mole oxygen V_{O} (open circles) [19] in an $(\text{Na}_2\text{O})_{0.2}(\text{B}_2\text{O}_3)_z(\text{SiO}_2)_{0.8-z}$ glass. The linear decrease for small B_2O_3 contents is in agreement with the prediction of equation (23) (see text).

in very good agreement with the experimental value of 35 GPa [17]. Deviation from the linear behavior occurs for both quantities V_{O} and $\lg D$ at the same alkali content z as seen in figure 17, which maybe considered as an additional piece of evidence for the validity of equation (23). However, at higher contents of B_2O_3 the interpretation of the data is more complicated, because the physically relevant concentration of ions is changing. As physically relevant we consider the ratio of number of ions and number of network-forming elements (silicon and boron), which changes despite the constant molar fraction of Na_2O . This will be discussed in the appendix.

6. Conclusions

Relating the volume of oxidic glasses to the packing density of oxygen atoms or its reciprocal quantity, the volume per mole oxygen V_{O} provides a simple quantity which reveals the effect of modifier ions as well as the effect of changing coordination numbers around the glass-forming atoms, like boron and germanium. Relative changes in the volume per oxygen atom caused by modifier ions scale with their ionic volume, and V_{O} saturates with an increasing coordination of boron and germanium. All these volume changes are significant for diffusion, as demonstrated for ionic diffusion and diffusion of helium atoms.

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8. Appendix

In order to separate the effect of V_{O} on the alkali mobility, the cation concentration was kept constant for all the examples discussed so far. This was achieved by considering binary glasses and mixed alkali glasses with the same alkali content and one network-forming element only. However, in a ternary glass of the composition $(\text{Na}_2\text{O})_x(\text{B}_2\text{O}_3)_z(\text{SiO}_2)_{1-x-z}$, the ratio of cations per network-forming elements (boron and silicon) changes with z despite the constant mole fraction of the alkali oxide, x . For the extreme cases of a pure borate glass this ratio is half as much as for the pure silicate glass. The ratio of cations per network-forming element is given for the intermediate cases by

$$r = \frac{x}{1-x+z} \quad (24)$$

The ratio r will be called effective alkali content in the following, because it is a measure of the spatial density of both cations and anions and, therefore, it is the appropriate quantity to describe the Coulomb interaction between them. Thus changes in the conductivity of a borate/silicate glass caused by varying z are due to both changing r and changing V_{O} . According to equation (20) we can express this dependence by

$$\ln \sigma = -\ln \varrho = C(r) + \frac{K V^* \ln V_{\text{O}}}{k_{\text{B}} T} \quad (25)$$

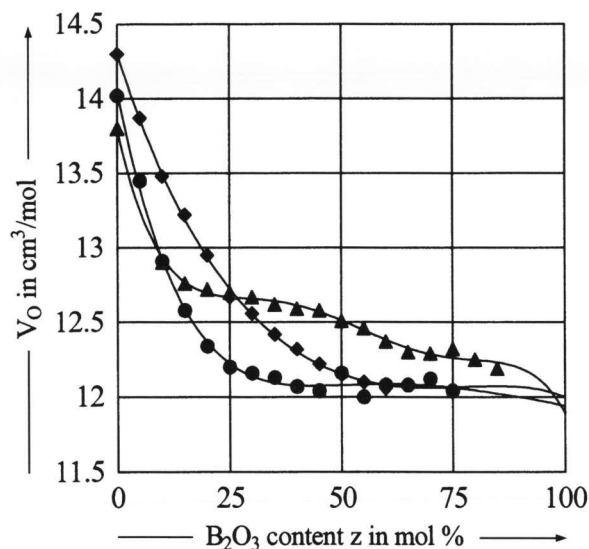


Figure 18. Volume per mole oxygen V_O calculated from density data [19] for the ternary glass $(\text{Na}_2\text{O})_x(\text{B}_2\text{O}_3)_z(\text{SiO}_2)_{1-x-z}$ as a function of z and for $x = 0.1$ (triangles), 0.2 (circles) and 0.3 (diamonds). The solid lines are polynomial fits $V_O = \sum a_i z^i$ with the coefficients a_i given in table 5.

where the proportionality between D and σ was assumed and ϱ is the resistivity. If we assume further on, that K , V^* and the function $C(r)$ do not depend on z , we can compare predictions of equation (25) with experimental values of the resistivity according to the procedure given in the following. First experimental data on the density of the glasses were transformed into V_O . For the sodium borate/silicate glasses corresponding results are shown in figure 18. Then $C(r)$ is calculated for $z = 0$, i.e. for the pure silicate glasses. The corresponding data are taken from [20] and plotted versus $r = x/(1-x)$ in figure 19. In the same figure it is shown that the data can be approximated by the following relation

$$\lg \varrho = 7.42 - 4r + 10.5 \exp(-22.5r) \quad \text{for } z = 0. \quad (26)$$

Inserting the last equation in equation (25) yields

$$\lg \varrho = -7.42 + \frac{4x}{1-x+z} - 10.5 \exp\left(\frac{-2.25x}{1-x+z}\right) + \frac{K V^*}{k_B T} (\lg V_O - \lg V_O^0). \quad (27)$$

Changes in V_O as a function of z are calculated from density data [19] and plotted in figure 18. They are approximated by polynomial functions of 5th order with coefficients given in table 5. Thus equation (27) can be used to calculate $\lg \varrho$ as a function of z . Results of these calculations are included in figure 20. The calculated behavior shows the right trends but there are remarkable deviations especially at higher boron contents. These discrepancies may be a result of fitting $C(r)$ to $z = 0$, i.e. the silicate glass, instead of fitting it to the results for $z = 1$, i.e. the borate glass.

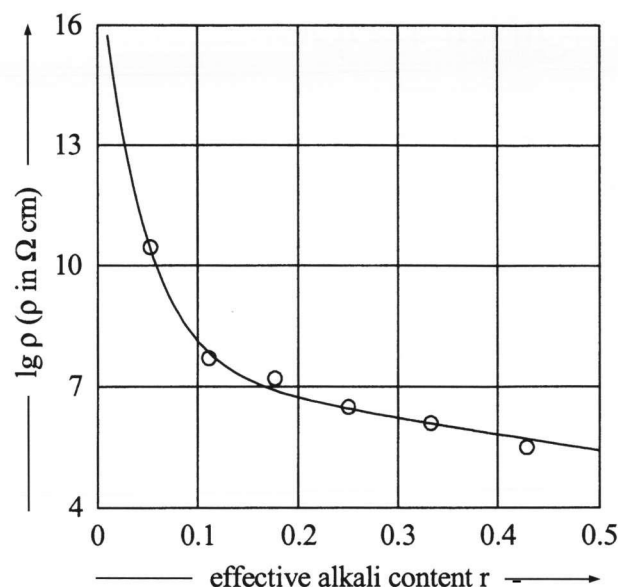


Figure 19. Resistivity of a sodium silicate glass at 150°C as a function of $r = x/(1-x)$ [20] (compare equation (24)). The solid line corresponds to the function $\lg \varrho = 7.42 - 4r + \exp(-22.5r)$ which was chosen more or less arbitrarily, in order to describe the decrease of $\lg \varrho$ with increasing r .

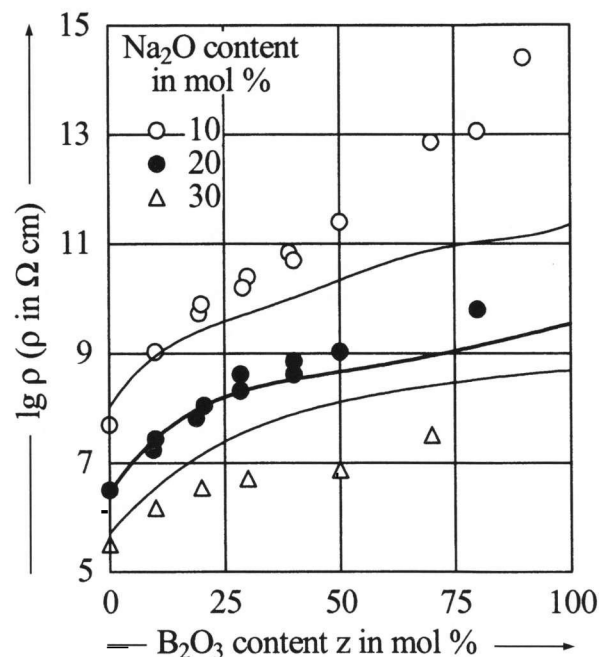


Figure 20. Resistivity of a ternary silicate-borate glass $(\text{Na}_2\text{O})_x(\text{B}_2\text{O}_3)_z(\text{SiO}_2)_{1-x-z}$ at 150°C as a function of z . The solid lines are calculated without a fitting parameter as described in the text.

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