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Figure 1

Figure 1: Figure 1

Abstract

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SELF-DIFFUSION OF ALKALI IONS IN SILICATE MELTS

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The results of measurements of transport numbers in acidic silicate melts ([1–3]) show that in three-component melts containing two cations, there is a mutual influence of the cations on their relative mobility. The cause of this mutual influence may be the dependence of the strength of the bond of a cation with the silicon-oxygen anion on the strength of the bond of the second cation with this anion, caused by the mutual polarization of oxygen by both cations.

Another factor responsible for this mutual influence is the change in the degree of looseness of the structure when cations of different size are combined in pairs. It was noted ([1]) that the relative role of these two factors in melts of this kind depends on the difference in the coordination numbers of the pair of cations. As this difference increases, the role of the factor associated with the degree of looseness of the structure (the "geometrical" factor) increases, which leads to a decrease in the relative mobility of the cation of larger size; as this difference decreases, the role of the bond-strength factor increases, raising the relative mobility of the cation of larger size.

Fig. 1. Dependence of $\lg D_{Na^+}$ on $\frac{1}{T}$:
1 –melt $Na_2O \cdot 2SiO_2$;
2 –melt $Na_2O \cdot Li_2O \cdot 4SiO_2$;
3 –melt $Na_2O \cdot K_2O \cdot 4SiO_2$;
4 –melt $Na_2O \cdot CaO \cdot 4SiO_2$.

It is of interest to trace how, for different pair combinations of cations, not only the relative but also the absolute mobility changes. For this purpose, the present work presents the results of measuring the self-diffusion coefficients of potassium and sodium cations in the following silicate melts:

$Na_2O \cdot 2SiO_2$, $Na_2O \cdot Li_2O \cdot 4SiO_2$, $Na_2O \cdot K_2O \cdot 4SiO_2$, $K_2O \cdot 2SiO_2$, $K_2O \cdot Li_2O \cdot 4SiO_2$, $Na_2O \cdot MgO \cdot 4SiO_2$, $Na_2O \cdot CaO \cdot 4SiO_2$, $Na_2O \cdot SrO \cdot 4SiO_2$, $Na_2O \cdot BaO \cdot 4SiO_2$, $K_2O \cdot MgO \cdot 4SiO_2$, $K_2O \cdot CaO \cdot 4SiO_2$, $K_2O \cdot SrO \cdot 4SiO_2$, $K_2O \cdot BaO \cdot 4SiO_2$.

For the measurements we used the procedure described by us in detail in work ([4]). Radioactive isotopes Na^{24} and K^{42} were employed.

The measurements were carried out in the temperature range 850–1210°C for melts containing only alkali-metal cations, and 1100–1300° for melts containing alkali and alkaline-earth metal cations. The experiments showed that the temperature dependence of the self-diffusion coefficients

diffusion of cations is well described by the equation $D = D_0 e^{-E/RT}$, where E is the activation energy, as is seen from Fig. 1, in which, by way of example, the straight lines $\lg D_{Na} = f\left(\frac{1}{T}\right)$ are presented. In all cases the measurement error does not exceed 10%, and only in the case of the melt $K_2O \cdot CaO \cdot 4SiO_2$ was this error larger ($\approx 20\%$); therefore, in this melt a considerably larger number of measurements was carried out.

The results of the measurements are presented in Table 1, which gives D_0 and E, as well as the values of the self-diffusion coefficients at $t = 1200°$, for which the transport numbers were determined.

Table 1

Chemical composition	Diffusing cation	Radius of the second cation, Å	$D_{1200°}$, cm^2/sec	D_0, cm^2/sec	E, cal/mol	ΔF^*, cal/mol	ΔH^*, cal/mol	ΔS^*, cal/mol·deg
$Na_2O \cdot 2SiO_2$	Na^+	—	$3,2 \cdot 10^{-5}$	$1,8 \cdot 10^{-3}$	11900	23700	9000	−10
$Na_2O \cdot Li_2O \cdot 4SiO_2$	Na^+	0,60	$2,9 \cdot 10^{-5}$	$2,8 \cdot 10^{-3}$	13400	24000	10500	−9,2
$Na_2O \cdot K_2O \cdot 4SiO_2$	Na^+	1,33	$2,6 \cdot 10^{-5}$	$6,3 \cdot 10^{-3}$	16100	24200	13200	−7,5
$Na_2O \cdot BaO \cdot 4SiO_2$	Na^+	1,35	$1,6 \cdot 10^{-5}$	2,3	34800	25700	31900	4,2
$Na_2O \cdot SrO \cdot 4SiO_2$	Na^+	1,13	$1,5 \cdot 10^{-5}$	$1,1 \cdot 10^{-1}$	26200	25900	23300	−1,8
$Na_2O \cdot CaO \cdot 4SiO_2$	Na^+	0,99	$1,3 \cdot 10^{-5}$	$1,2 \cdot 10^{-2}$	19900	26300	17000	−6,3
$Na_2O \cdot MgO \cdot 4SiO_2$	Na^+	0,65	$1,4 \cdot 10^{-5}$	$1,6 \cdot 10^{-2}$	20500	26000	17600	−5,7

Chemical composition	Diffusing cation	Radius of the second cation, Å	D_{1200°, cm^2/sec	D_0, cm^2/sec	E, cal/mol	ΔF^*, cal/mol	ΔH^*, cal/mol	ΔS^*, cal/mol·deg
$K_2O \cdot 2SiO_2$	K^+	—	$2,7 \cdot 10^{-5}$	$8,7 \cdot 10^{-4}$	10200	25400	7700	−12
$K_2O \cdot Li_2O \cdot 4SiO_2$	K^+	0,60	$1,7 \cdot 10^{-5}$	$8,7 \cdot 10^{-3}$	18200	26300	15300	−7,5
$K_2O \cdot Na_2O \cdot 4SiO_2$	K^+	0,95	$2,3 \cdot 10^{-5}$	$5 \cdot 10^{-3}$	15800	25600	12900	−8,6
$K_2O \cdot BaO \cdot 4SiO_2$	K^+	1,35	$8,9 \cdot 10^{-6}$	56	45900	28300	43000	10
$K_2O \cdot SrO \cdot 4SiO_2$	K^+	1,13	$6,8 \cdot 10^{-6}$	$4,8 \cdot 10^{-1}$	32700	29000	29800	0,51
$K_2O \cdot CaO \cdot 4SiO_2$	K^+	0,99	$6,6 \cdot 10^{-6}$	$1,7 \cdot 10^{-1}$	29800	29300	26900	−1,6
$K_2O \cdot MgO \cdot 4SiO_2$	K^+	0,65	$5,2 \cdot 10^{-6}$	$9,3 \cdot 10^{-3}$	21900	29800	19000	−7,3

In work (4) the equivalence of the mechanisms of diffusion and electrical conductivity in the melt $Na_2O \cdot 2SiO_2$ was shown. If this is also true for three-component melts, then the ratio of the self-diffusion coefficients in these melts should be equal to the ratio of the transport numbers. The transport numbers of the sodium ion at 1200° in the melts $Na_2O \cdot K_2O \cdot 4SiO_2$ and $Na_2O \cdot CaO \cdot 4SiO_2$, calculated from the self-diffusion coefficients (for the latter melt the self-diffusion coefficient of the Ca^{++} ion was measured at 1200°), are respectively 0.53 and 0.75, while those measured directly are 0.52 and 0.70; i.e., in three-component melts as well the mechanisms are the same. On this basis, from the mobility of one of the cations, using the data on transport numbers, one may judge the mobility of the other cation.

It follows from the results presented in Table 1 that the self-diffusion coefficient in melts containing cations only of alkali metals is larger than in melts containing cations of alkali and alkaline-earth metals. The activation energy in the first group is smaller than in the second. The latter circumstance is a consequence of the fact that divalent cations of alkaline-earth metals form bridges between silicon–oxygen anionic complexes and thereby compact the structure of the melt. In the first group of melts, on passing from binary to ternary melts the self-diffusion coefficient decreases, while the activation energy increases.

On passing from the melt $Na_2O \cdot 2SiO_2$ to the melt $Na_2O \cdot Li_2O \cdot 4SiO_2$, despite the weakening of the Na–O bond, the mobility of the sodium ion decreases as a result of the action of the "geometrical factor."

Replacement in the ternary melt of lithium oxide by potassium oxide leads to

an even greater lowering of the mobility of the sodium ion, since in this case not only the "geometrical" factor but also the bond-strength factor acts in the direction of reducing this mobility.

In the series of melts $K_2O \cdot 2SiO_2$, $K_2O \cdot Na_2O \cdot 4SiO_2$, and $K_2O \cdot Li_2O \cdot 4SiO_2$, compaction of the structure proves to be predominant, and therefore the self-diffusion coefficient of the potassium ion decreases.

In the second group of melts, containing alkaline-earth metal ions, in the series of melts $K_2O{\cdot}BaO{\cdot}4SiO_2$, $K_2O{\cdot}SrO{\cdot}4SiO_2$, $K_2O{\cdot}CaO{\cdot}4SiO_2$, and $K_2O{\cdot}MgO{\cdot}4SiO_2$, the self-diffusion coefficient of the potassium cation decreases, while the transport number of the potassium ion increases. In this series, the structure becomes compacted and the strength of the bond between the potassium ion and the anions decreases, while the bond strength of the alkaline-earth cations with the anions increases. Compaction of the structure reduces the mobility both of the potassium ion and of the alkaline-earth metal ions, but the mobility of the latter decreases to a greater extent as a result of the strengthening of their bond with the anions. For this reason, the transport number of the potassium ion in this series increases despite the decrease in the self-diffusion coefficient.

In sodium-containing melts of the second group, the self-diffusion coefficient of the sodium ion changes only slightly. At the same time, the data on transport numbers indicate that the relative mobility of the sodium ion in this group of melts decreases on going from the melt $Na_2O \cdot MgO \cdot 4SiO_2$ to the melt $Na_2O \cdot CaO \cdot 4SiO_2$, owing to an increase in bond strength caused by the greater force of the magnesium cation as compared with the calcium cation. On going from the melt $Na_2O \cdot CaO \cdot 4SiO_2$ to the melt $Na_2O \cdot SrO \cdot 4SiO_2$ and further to $Na_2O \cdot BaO \cdot 4SiO_2$, the transport number of the sodium ion increases as a result of compaction of the structure, which retards the motion of the alkaline-earth metal ions to a greater degree the larger their size.

Comparison of the data in Table 1 with the results for transport numbers makes it possible to conclude that the increase in the relative mobility of the sodium ion in the series $Na_2O \cdot CaO \cdot 4SiO_2$, $Na_2O \cdot SrO \cdot 4SiO_2$, and $Na_2O \cdot BaO \cdot 4SiO_2$ is due to the decrease in mobility of the alkaline-earth metal ions under the influence of the "geometrical" factor. It is of interest to consider the results obtained by using the theory of absolute reaction rates.

According to this theory ([5]),

$$D = \lambda^2 \frac{kT}{h} e^{\frac{\Delta S^*}{R}} e^{-\frac{\Delta H^*}{RT}} = \lambda^2 \frac{kT}{h} e^{-\frac{\Delta F^*}{RT}}, \tag{1}$$

where λ is the distance between two equilibrium positions of the diffusing particle, k is Boltzmann' s constant, h is Planck' s constant, T is the absolute temperature, R is the gas constant, ΔH^* is the heat of activation of the diffusion process, ΔS^* is the entropy of this process, and ΔF^* is the free energy of activation.

To calculate λ, the structural models considered in work ([6]) were used. For melts with sodium oxide, $\lambda = 5.75$ Å, and with potassium oxide, 6.67 Å.

Table 1 gives the values of ΔF^*, ΔH^*, and ΔS^* at 1200°, calculated from equation (1), for sodium and potassium ions. The values of $\Delta F^*_{1200^\circ}$ vary from melt to melt in accordance with the change in D_{1200°.

The quantity ΔS^* is the difference between the entropies of the transition state (S_{trans}) and the ground state (S_{ground}) of the diffusing particle. The entropy in each of the mentioned states will increase with decreasing bond strength and with increasing looseness of the structure. It may be assumed that the influence of these factors on going from one melt to another will affect the ground state to a greater extent, since in the transition state there are fewer degrees of freedom and this state should differ to a lesser degree for different melts.

Consequently, bearing in mind that $\Delta S^* = S_{\text{trans}} - S_{\text{ground}}$, an increase in bond strength decreases S_{ground} and increases ΔS^*; loosening of the structure increases S_{ground} and decreases ΔS^*.

Let us consider the change in the quantities ΔH^* and ΔS^* in the first group of melts. In the series $K_2O \cdot 2SiO_2$, $K_2O \cdot Na_2O \cdot 4SiO_2$, and $K_2O \cdot Li_2O \cdot 4SiO_2$, the influence of the "geometric" factor leads to an increase in ΔH^*. In the same series, the quantity ΔS^* increases (becomes less negative) owing to the influence of the same "geometric" factor (densification of the structure—decrease in S_{bas}).

On going from the melt $Na_2O \cdot 2SiO_2$ to the melt $Na_2O \cdot Li_2O \cdot 4SiO_2$, despite the decrease in bond strength due to densification of the structure, both ΔH^* and ΔS^* increase (decrease in S_{bas}). When Li_2O is replaced by K_2O, further densification of the structure occurs and, in addition, the bond is strengthened, as a result of which a further increase in ΔH^* and ΔS^* is observed.

In the second group of melts (melts containing alkaline-earth-metal ions), ΔH^* and ΔS^* appreciably exceed those for the melts of the first group. This circumstance reflects the denser structure of these melts, caused by the presence of divalent cations that play the role of bridges between anions. In the series of melts $Na_2O \cdot BaO \cdot 4SiO_2$, $Na_2O \cdot SrO \cdot 4SiO_2$, and $Na_2O \cdot CaO \cdot 4SiO_2$, the structure becomes looser and the bond strength decreases, which causes a decrease in ΔH^* and ΔS^*. On going from the melt $Na_2O \cdot CaO \cdot 4SiO_2$ to the melt $Na_2O \cdot MgO \cdot 4SiO_2$, along with a further decrease in bond strength, the role of the "geometric" factor increases. The action of this factor proves to be predominant, and therefore ΔH^* and ΔS^* increase somewhat. In the series of melts $K_2O \cdot BaO \cdot 4SiO_2$, $K_2O \cdot SrO \cdot 4SiO_2$, $K_2O \cdot CaO \cdot 4SiO_2$, $K_2O \cdot MgO \cdot 4SiO_2$, the strength of the bonds of the potassium ion with anions decreases and the role of the "geometric" factor increases. In this group the bond strength plays the greater role, as a result of which ΔH^* and ΔS^* decrease.

It is interesting to note that, for all the melts investigated, an increase in ΔH^* is accompanied by a simultaneous increase in ΔS^*. According to the compensation rule (7), an increase in the activation energy is accompanied by an increase in

D_0. From the standpoint of the considerations set forth above, the fulfillment of this general rule as applied to cation diffusion in the melts studied becomes understandable. The factors of bond strength and the "geometric" factor thus influence ΔH^* and ΔS^* in such a way that E and D_0 change in the same direction.

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Note: Figure translations are in progress. See original paper for figures.