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ANION DISTRIBUTION IN MELTED SILICATES

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16. Abstract

In approximate method for calculating the distribution of ions dispersed throughout the structure of Me_nO - SiO_2. Qualitatively explained series of regularities found by chromatography.

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The assumption that the distribution of silicates represents a polyanionic /2110* fluid, first stated in [1] but not in [2], as accepted in [3]. The approximate method for calculation [4] published by us [5] for the entire range of structures and the equations found for the distribution of ions is

$$Si_{i}O_{3i+i-c}^{-2(i+i-c)} \qquad \text{for} \quad i_m = 2c + 1. \tag{1}$$

Table 1 presents the concentrations of various ions, mols ($100N_{i,c}$), heat of fusion $\Delta H/Q$ of oxides and NeO activity, calculated according to the equations, equal to $N_{O^{2-}}$ when $i_m = 2c+1$. Data for $N_{SiO_2} \geqslant 0.67$ are missing, as in assumption (1) even $(Si_2O_5^{2-})_n$ ions are realized only for infinitely large values.

Table 1.

N_{SiO_2}	k	$[O^{2-}]$	$[SiO_4^{4-}]$	$[Si_2O_7^{6-}]$	$[Si_3O_{10}^{8-}]$	$[Si_4O_{13}^{8-}]$	$[Si_5O_{12}^{8-}]$	$[Si_6O_{14}^{8-}]$	$\sum_{c=2} N_{i,c} \cdot 100$	ΔH
0,33	0	0	100	0	0	0	0	0	0	2[illegible]
0,33	1	79	16	3	0,6	8	0,2	0,002	0,05	[illegible]
0,40	0	0	55	21	8	5,5	2,1	0,5	1	1[illegible]
0,40	1	48	19,7	8,1	3,3	6,9	2,8	2,4	6,5	1[illegible]
0,50	0	0	25	12,5	6,2	12,5	6,2	6,2	25	1[illegible]
0,50	1	33	15	6,7	3	9	4	5,4	24	0,9[illegible]
0,61	0	0	6,6	2,6	1	5,9	2,3	5,2	78	0,6[illegible]
0,61	1	9,4	2,8	0,8	0,2	2,7	0,8	2,6	80	0,5[illegible]

*Note: Commas indicate decimal points.

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If the shape of the anions is close to spherical, and the arrangement of tetrahedrons similar to cristobalite, then we obtain [6] a function difficult for the summation of orders $c = i_m + 1 - 1.7 i_m^{2/3}$. (2)

Simplifying (1) in the direction of (2) for less complicated anions, and assuming [6]

$$i_m = c + 1 \tag{3}$$

coming much closer for large values of c. In the last case the equations uniting $N_{O^{2-}}$ and $N_{1,4}$ with N_{SiO_2} and $\Delta H/Q$, we get the form*

$$1 - N_0 = \frac{N_{1,4}}{(1-x)(1-y_1)}, \tag{4}$$

$$N_{SiO_2} = \frac{N_{1,4} - x^3}{N_0(1-x)^2(1-y_1)^2 + 2(N_{1,4} - x^3) + N_{1,4}(1-x)(1-y_1) - x^2(1-x)}, \tag{5}$$

$$\Delta H = Q\left[1 + \frac{(1-x)(N_{1,4} - 2x^3)}{N_{1,4} - x^3}\right]. \tag{6}$$

*See [5] for designations.

where

$$y_1 = k^2 N_{1,1} / N_0^2. \tag{7}$$

The values calculated according to these $N_{i,c}$, mol%, and $\Delta H/Q$ at $i_m = c + 1$ are shown in Table 2. In addition when k = 0 for all substances with SiO_2, except that $N_{SiO_2} = 0.33$, we have anions of varied complexity (see Tables 1 and 2). This is conditioned by the process of the reaction [4]

$$2Si_iO_{3i+1-c}^{2(i+1-c)-} = Si_{i-1}O_{3i-2-c}^{2(i-c)-} + Si_{i+1}O_{3i+3-c}^{2(i+2-c)-}, \tag{8}$$

in which the O^{2-} ion is missing. Their constants of equilibrium in the concept of the approximation are equal to unity.

The results of the calculations are correlated with chromatographic data for aqueous solutions of sodium silicate [7]. In melts of the latter substance the constant $k = 10^{-3}$ [8], i.e., it is small. In agreement with the test, the content of ions SiO_4^{4-}, $Si_2O_7^{6-}$, and $Si_3O_{10}^{8-}$ ions increases monotonously, and the polystructure ($\sum_{c=2} N_{i,c}$) decreases* with an increase in the Na:Si ratio (up to three), while the concentrations of $Si_4O_{12}^{8-}$ go through a maximum near the composition of metasilicate. /2111

Table 2.

N_{SiO_2}	k	$[O^{2-}]$	$[SiO_4^{4-}]$	$[Si_2O_7^{6-}]$	$[Si_3O_{10}^{8-}]$	$[Si_4O_9^{6-}]$	$[Si_4O_{12}^{8-}]$	$[Si_7O_{19}^{10-}]$	$\sum_{c=2} N_{i,c} \cdot 100$	$\Delta H/Q$
0,40	0	0	59	17,7	5,3	2,7	0,8	0,03	2	1,5
0,40	1	60	16	4	1	1,9	0,5	0,04	7	1,11
0,50	0	0	30,4	11,9	4,6	5,9	2,3	0,29	25	1
0,50	1	50,7	14,8	4,3	1,2	2,5	0,7	0,1	16	0,91
0,61	0	0	18	6,5	2,3	4,7	1,7	0,62	52	0,62
0,61	1	37,5	10,9	3,2	0,9	2,4	0,7	0,2	39	0,51
0,67	0	0	15	5	1,7	3,9	1,3	0,8	60	0,5
0,67	1	29	7,2	1,8	0,4	1,6	0,4	0,3	51	0,29
0,80	0	0	6,9	1,7	0,4	1,6	0,4	0,32	83	0,25
0,80	1	25,9	6	1,4	0,3	1,2	0,3	0,21	60	0,21

*Note: Commas indicate decimal points.

Table 3.

Na:Si	$[SiO_2]$, M.	SiO_4^{4-}		$Si_2O_7^{6-}$		$Si_3O_{10}^{8-}$		$Si_4O_{12}^{8-}$	
		Experimental	Computed	Experimental	Computed	Experimental	Computed	Experimental	Computed
4 : 1	0,1	69,5	100	7	0	—	0	—	0
2 : 1	1	25,7	12,5	12,0	12,5	6,9	9,3	10,0	12,4
2 : 1	1	25,7	11,4	12,0	9	6,9	5,2	10,0	3,5
1.02 : 1	1	12,7	3,1	6,4	2,1	4,8	1,1	8,0	1,1
0.6 : 1	—	4,8	0,6	1,6	0,3	0,6	0,1	1,2	0,14

*Note: Commas indicate decimal points.

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Observed parallel with this are the extremes of $N_{i,c}$ and for other ions. Qualitative agreement in computations for melts with data for solutions is hardly possible in respect to the small concentrations of silicate in water. Comparison of the Si content, at.%, in silicates, calculated at k = 0 with the results given in Table 3 ($\%Si = 100iN_{i,c}/\Sigma iN_{i,c}$ $i_m = 2c + 1$ and $i_m = c + 1$).

The well-known qualitative agreement of calculations with chromotography occurs with cobalt [9] and lead [3] slag, where the constants k are sufficiently large (2.6 and 0.196).

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*For $i_m = 2c + 1$ magnitude $\sum_{c=2} N_{i,c} = \frac{x^3}{1 - x} \frac{y}{1 - y}$, and for $i_m = c + 1$ value $\Sigma N_{i,c} = \frac{x^2}{1 - x} \frac{y_1}{1 - y_1}$.

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