Analysis of Disproportionation of Q^n Structons in the Simulation of the Structure of Melts in the Na$_2$O–SiO$_2$ System

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Abstract—A new version of the STRUCTON-1.2 computer program (2009) has been presented. The program combines the algorithm for calculating real distributions of Q^n structons in binary silicate melts (with allowance made for their disproportionation) and the statistical simulation of molecular-mass distributions of polymerized ions at different temperatures. This model has been used to perform test calculations for two melts in the Na$_2$O–SiO$_2$ system (Na$_6$Si$_2$O$_7$, Na$_6$Si$_3$O$_9$). The results of the calculations have made it possible to trace variations in the set and concentrations of chain and ring silicon–oxygen complexes with a decrease in the temperature in the order: stochastic molecular-mass distribution ⟶ molecular-mass distribution at $T = 2000$ K ⟶ molecular-mass distribution at the liquidus temperature. The main result of these calculations is that the dominant species of silicon–oxygen anions at the liquidus temperatures (in contrast to the stochastic distributions) exactly correspond to the stoichiometry of the initial melts: the Si$_2$O$_7^{6-}$ chain anions and (Si$_n$O$_{3n}$)$^{3n-}$ ring complexes are dominant in the Na$_6$Si$_2$O$_7$ and Na$_6$Si$_3$O$_9$ melts, respectively. It has been established that, with a decrease in the temperature, the average size of polymer complexes varies weakly in the Na$_6$Si$_2$O$_7$ melt but increases by a factor of approximately 1.5 in the metasilicate system.

Key words: silicate melts, structural simulation, disproportionation of Q^n particles, molecular-mass distribution, Na$_2$O–SiO$_2$ system

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INTRODUCTION

Results of experimental investigations [1–4], theoretical analysis [5–9], statistical modeling, and molecular dynamics simulation [10–13] have demonstrated that the structure of silicate melts is formed by discrete silicon–oxygen anions and their complexes of the general formula (Si$_i$O$_{3i + 1 - j}$)$^{2(i + 1 - j)-}$, where i is the size of an anion and j is the number of self-closures of terminal oxygen bonds inside a particle. Since formal constraints on the sizes of these complexes are absent, the structural state of a silicate liquid can be represented as a complex ion–polymer solution in which the average negative charge of an ensemble of low-polymer anions (SiO$_4^{4-}$, Si$_2$O$_7^{6-}$, Si$_3$O$_9^{6-}$, etc.) and larger polymerized particles is compensated for by a positive charge of metal modifier cations. These concepts underlie the polymer approach, which has been developed from the mid-1960s and for which the main problem consists in calculating molecular-mass distri-

butions that characterize the relative proportions of silicate particles with low and high degrees of polymerization as a function of the total composition [14–18]. The known molecular-mass distributions allow one to develop thermodynamic models of polymer melts that are consistent with the experimental data on the activity of oxide components in molten silicates and make it possible to predict physicochemical properties of silicate liquids at high values of the parameters P and T [6, 9].

In our previous work [19], a new statistical model was proposed for calculating molecular-mass distributions of anions in binary and ternary systems MeO–Me$_2$O–SiO$_2$ from a known distribution of Q^n structons, i.e., silicon–oxygen tetrahedra with different numbers of bridging bonds ($0 \le n \le 4$, Q^0 is a SiO$_4^{4-}$ ion). This model was implemented in the form of the STRUCTON computer program, which uses the Monte Carlo method and allows one to evaluate the probability of formation
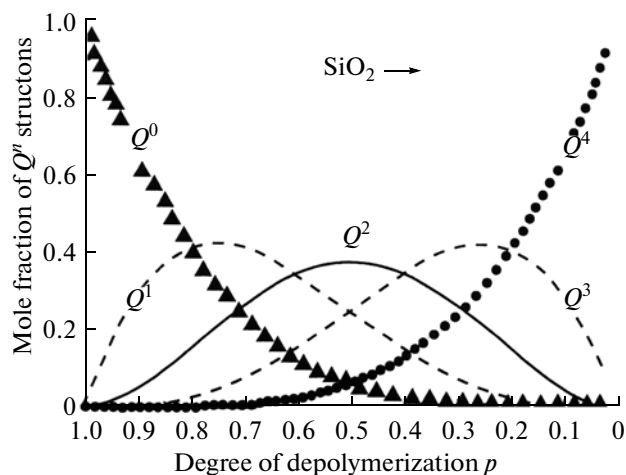
Fig. 1. Stochastic distribution of Q^n structons as a function of the degree of depolymerization p of the silicon−oxygen matrix. Calculations were performed using Eqs. (1) in the approximation of equal reactivities of nonbridging Si−O bonds.

(concentration) of silicate complexes from a specified distribution of Q^n structons. The solution to the problem of the calculation of molecular-mass distributions made it possible to systematically simulate polyanion ensembles involving linear−branched, ring, and various spatial structures as a function of the degree of polymerization (or depolymerization) of the melt [20]. The estimates obtained are based on the ideal (stochastic) distribution of Q^n structons, which follows from the combinatorial expressions [7, 21]

$$X_0 = p^4, \quad X_1 = 4p^3(1-p), \quad X_2 = 6p^2(1-p)^2, \\ X_3 = 4p(1-p)^3, \quad X_4 = (1-p)^4, \tag{1}$$
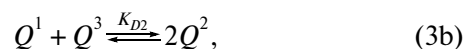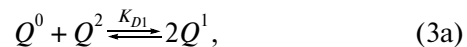
where X_n is the concentration (fraction) of Q^n structons and the degree of depolymerization of the melt p corresponds to the weighted-mean fraction of nonbridging bonds in the silicon−oxygen matrix [6, 18], which can be expressed through the relative concentrations of Q particles

$$p = X_0 + 0.75X_1 + 0.5X_2 + 0.25X_3. \tag{2}$$

The character of the relation between the parameters p and X_n (expressions (1), (2)) manifests itself in a symmetric distribution of Q_n structons on a polymerization scale and mirror relationships for the Q^0−Q^4 and Q^1−Q^3 species (Fig. 1). The results of the calculations in the range of degrees of depolymerization $0.52 \le p \le 0.98$ demonstrated that, under the assumption of the same reactivity of Si−O⁻ terminal bonds, size-limited and stable sets of polymer complexes are formed in silicate melts, and the average number of sets varies from 153 at $p = 0.52$ to 3 (SiO_4^{4-}, $Si_2O_7^{6-}$, $Si_3O_{10}^{8-}$) at

$p = 0.98$. In this case, we succeeded in parametrization of the dependence of the average size of an ensemble of silicon−oxygen anions on the structural properties of the ion−polymer solution [20].

As follows from the results of investigations using Raman scattering and nuclear magnetic resonance (NMR) spectroscopy at different temperatures, the real distributions of Q^n structons in silicate melts never coincide with the ideal distribution (1). This is a consequence of the occurrence of three disproportionation reactions [22−24]

$$Q^0 + Q^2 \xrightleftharpoons{K_{D1}} 2Q^1, \tag{3a}$$

$$Q^1 + Q^3 \xrightleftharpoons{K_{D2}} 2Q^2, \tag{3b}$$

$$Q^2 + Q^4 \xrightleftharpoons{K_{D3}} 2Q^3. \tag{3c}$$

The integrated result of these reactions is an increase in the concentration of tetrahedra of the Q^1, Q^2, and Q^3 type due to the decrease in the concentration of the Q^0 and Q^4 species. Therefore, the changeover from the model of anionic complexes corresponding to the ideal stochastic distribution of Q^n structons (1) to more realistic evaluation of molecular-mass distributions of polymer particles requires a consistent inclusion of the reactions of disproportionation of Q^n structons with different numbers of bridging bonds (3a)−(3c). In the case of the positive solution to this problem and calculations of deviations of the expected distributions of Q^n structons from the stochastic distribution, the corrected evaluations of X_n can be used as input information for the performance of the statistical modeling of the molecular-mass distributions with the use of the STRUCTON computer program [19]. This opens up possibilities for a systematic analysis of the evolution of the proportions of silicon−oxygen anions as a function of the quantity p and the temperature and, in prospects, for the reconstructions of dominant silicon−oxygen species along the liquidus curves in silicate systems. This paper reports on the approach to the solution of the above problems for the Na_2O−SiO_2 binary system as an example and some preliminary results that are a development of the model proposed in our earlier works [19, 20].

ALGORITHM FOR INCLUDING THE DISPROPORTIONATION REACTIONS

Let us consider reactions (3a)−(3c). The equilibrium constants for these reactions are written in the form

$$K_{Dn} = \frac{X_n^2}{[X_{n-1}][X_{n+1}]}, \quad n = 1, 2, 3. \tag{4}$$

A combination of three Eqs. (4) with Eq. (2) and the obvious identity

$$X_0 + X_1 + X_2 + X_3 + X_4 = 1 \qquad (5)$$

allows us to derive the closed system of five equations with respect to five unknowns X_n ($n = 0, 1, …, 4$). The solution to the nonlinear system of equations (2), (4), and (5) makes it possible to obtain the sought distribution of Q^n structons for a specified parameter p when the constants K_{Dn} are known.

The temperature dependence of the equilibrium constants of the disproportionation reactions can be described by the relationship

$$K_{Dn}(T) = s_n \exp(-H_n/RT), \quad n = 1, 2, 3, \qquad (6)$$

where s_n are the entropy factors and H_n are the enthalpies of the corresponding reactions (3a)–(3c).
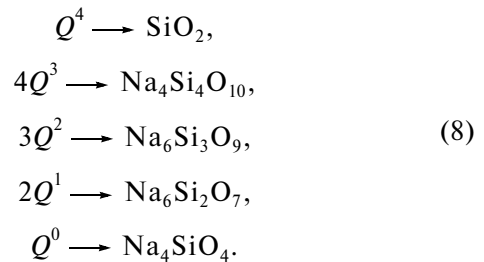
Our developed model based on the Monte Carlo method [19, 20] provides a maximum of the configurational entropy. In this case, the entropy factors do not depend on the temperature, because, in the limit of infinitely high temperatures, the disproportionation constants (6) do not depend on the enthalpies of reactions (3a)–(3c) and are determined by the ideal stochastic distribution of Q^n structons (1). Substitution of expressions (1) into relationship (6), gives the following formulas for s_n:

$$s_1 = s_3 = K_{D1}(\infty) = K_{D3}(\infty) = 8/3,$$
$$s_2 = K_{D1}(\infty) = 9/4. \qquad (7)$$

In terms of the model under consideration, we also assume that the enthalpies of the disproportionation reactions in relationship (6) do not depend on the temperature. This approximation has been widely used in the simulation of silicate systems (see, for example, [24–26]) in addition to other models in which the temperature dependence of the entropy factor and the enthalpy of disproportionation reactions is taken into account [27–29].

The constants of the disproportionation reactions are either determined from Raman and NMR spectroscopic data or calculated from thermodynamic data. Unfortunately, the direct use of NMR spectroscopy in the $Me_2O–SiO_2$ (Me = Li, K, Na) systems for melts at high temperatures faces technical problems and becomes almost impossible. Raman spectroscopy ensures the reliable determination of the disproportionation constant only for K_{D3} [28, 30], even though, in recent years, some progress in the determination of the constants K_{D1} and K_{D2} with the use of the Raman spectroscopy has been achieved using the simulation of the high-frequency spectral range with allowance made for the second coordination sphere of silicon atoms [29].

Consistent information on the set of constants K_{Dn} for silicate melts can be obtained using the calculations based on thermodynamic databases. In order to evaluate the constants of the disproportionation reactions in the $Na_2O–SiO_2$ system, we used the FACT thermodynamic base [31], as was previously done in [27–29, 32]. According to the data from the FACT database, the free energies of formation of Q^n structons can be determined from the free energies of formation of silica and four sodium silicates that can be constructed from Q^n structons in the framework of the model of associated solutions and under the assumption of quasicrystallinity of the corresponding solutions [27, 28, 32]:

$$Q^4 \longrightarrow SiO_2,$$
$$4Q^3 \longrightarrow Na_4Si_4O_{10},$$
$$3Q^2 \longrightarrow Na_6Si_3O_9, \qquad (8)$$
$$2Q^1 \longrightarrow Na_6Si_2O_7,$$
$$Q^0 \longrightarrow Na_4SiO_4.$$

The free energies of formation found for the structons from Eqs. (8) were used to calculate the enthalpies of the disproportionation reactions (4) with due regard for expressions (6) and (7). For the $Na_2O–SiO_2$ system, the enthalpies of reactions (4) thus obtained are as follows:

$$H_1 = 27.17 \text{ kJ/mol}; \quad H_2 = 32.23 \text{ kJ/mol};$$
$$H_3 = 20.75 \text{ kJ/mol}. \qquad (9)$$

Substitution of the determined enthalpies of the reactions (9) and the entropy factors (7) into Eqs. (6) allows us to calculate the equilibrium constants for all three disproportionation reactions as a function of the temperature. Then, by substituting the calculated constants K_{Dn} into Eqs. (4) and solving the nonlinear system of equations (2), (4), and (5) for a specified composition, we can find the distribution of Q^n structons at temperatures from the liquidus to an infinite temperature (corresponding to the stochastic distribution).

Figure 2 shows the calculated distribution of Q^n structons for the $Na_2O–SiO_2$ system at a temperature of 1200°C as a function of the degree of depolymerization of the melt p. On the whole, this distribution agrees with the calculations performed in [27, 33, 34], which were also carried out with the use of the FACT thermodynamic database [31] but are characterized by some differences in the formulation of the system of equations for the calculations of the structon concentrations. The positions of the peaks in the distribution of Q^n structons in our calculations coincide with the corresponding positions of the peaks in [27, 33, 34]. The observed quantitative differences in the distribu-
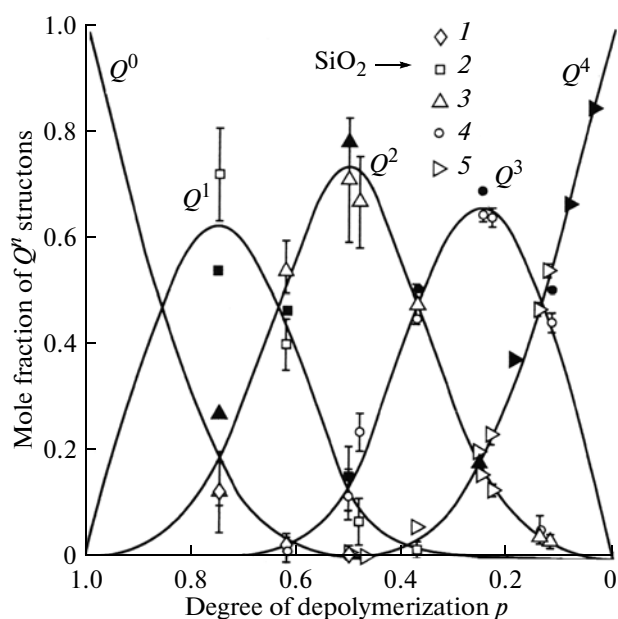
Fig. 2. Dependence of the distribution of Q^n structons on the degree of depolymerization of the melt at a temperature of 1200 K. Calculations were based on the data taken from the FACT thermodynamic database [31]. Open and closed symbols indicate the results of the calculations performed in [33, 34], respectively: (*1*) Q^0, (*2*) Q^1, (*3*) Q^2, (*4*) Q^3, and (*5*) Q^4.

tions of Q^n structons, including the height of the peaks, can also be associated with the fact that the temperature dependences of the entropy factor and the enthalpy of reactions were took into account in [27, 33]. The main difference of the calculated distributions from the stochastic distribution (Fig. 1) is an approximately twofold increase in the maximum of the concentration of Q^2 structons for the metasilicate (Na$_2$SiO$_3$ or Na$_6$Si$_3$O$_9$, $p \sim 0.5$ (see below)) melt and an increase in the maxima of the Q^1 and Q^3 species by a factor of ~1.5. The symmetrical location of the Q^1 and Q^3 maxima is retained but their "mirror behavior" is violated. A larger value of the enthalpy term for reaction (3a) ($H_1 = 27.17$ kJ/mol) as compared to reaction (3c) ($H_3 = 20.75$ kJ/mol) results in the fact that the relative maximum of the distribution of Q^1 structons appears to be systematically lower than the Q^3 maximum.

These relationships are retained at higher temperatures (Fig. 3). However, with an increase in the temperature, the peaks corresponding to different Q^n structons level off, their height decreases, and they are broadened. As was noted above, in the limit of high temperatures, the distribution of Q^n structons tends to the ideal stochastic distribution (Fig. 1).
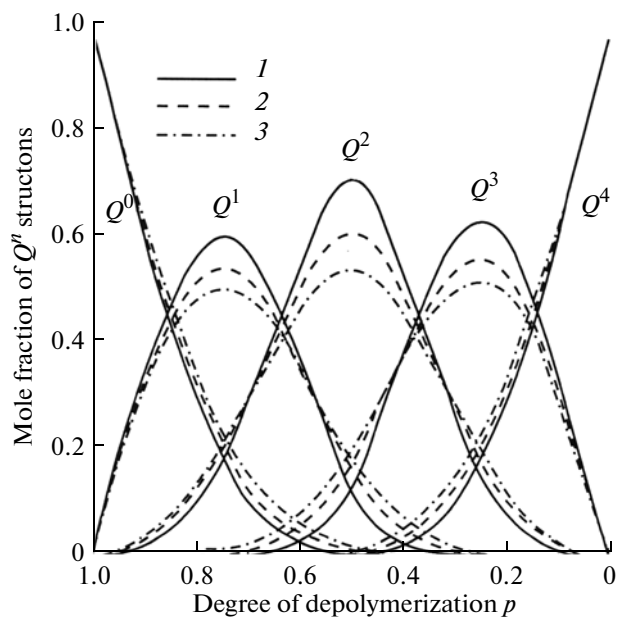
Fig. 3. Change in the distribution of Q^n structons as a function of the temperature. $T =$ (*1*) 1200, (*2*) 1800, and (*3*) 3000°C.

SIMULATION OF THE MOLECULAR-MASS DISTRIBUTIONS OF SILICON–OXYGEN ANIONS AS A FUNCTION OF THE TEMPERATURE

In order to evaluate the molecular-mass distributions of silicate melts with allowance made for the disproportionation reactions, the module for the calculations of the constants of the disproportionation reactions K_{Dn} at a specified temperature with the use of formulas (6) and (7), the enthalpies of reactions (9), and the solution to the system of equations (2), (4), and (5) was added to the initial STRUCTON computer program [19, 20]. The algorithm for solving this system of equations consisted in reducing the system to the fourth-order equation with one unknown $r = X_1/X_0$ and its solution by the simplest half-division method in the range $0-10^{20}$. The relative error in the determination of the unknown r did not exceed 10^{-9}, and all calculations were performed with a double accuracy. The flow chart of the STRUCTON computer program (version 1.2, 2009) is shown in Fig. 4.

By using this code, we performed the test calculations for two compositions in the Na$_2$O–SiO$_2$ system that correspond to two degrees of depolymerization of the melt ($p = 0.75$ and 0.51, Fig. 5) and represent variations in the molecular-mass distributions as a function of the temperature (Tables 1, 2). The polymer theory predicts that, for binary melts richer in SiO$_2$ as
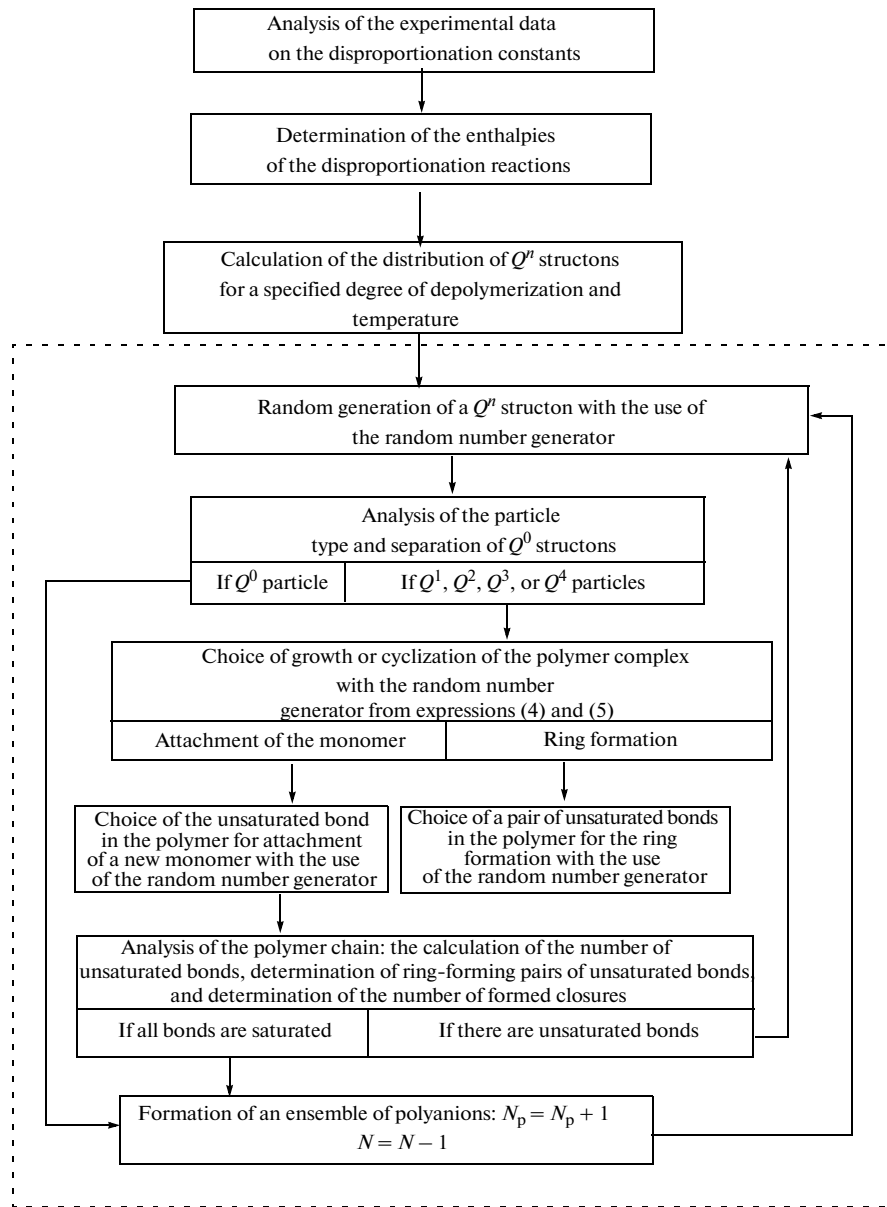
Fig. 4. Schematic flow chart of the program. The dashed line separates the blocks corresponding to the STRUCTON computer program [19].

compared to the orthosilicate ($N_{SiO_2} \geq 0.333$, composition N2S in Fig. 5), the degree of depolymerization and the composition are related by the simple expression [35]

$$p = (1 - N_{SiO_2} - N_{O^{2-}})/2N_{SiO_2}, \qquad (10)$$

where N_{SiO_2} is the mole fraction of silica and $N_{O^{2-}}$ is the number of "free oxygen" ions per mole of the melt. In the case of strongly depolymerized alkali silicate melts for which the polymerization constant according to [36] does not exceed 10^{-3} [37] and, hence, the

number of O^{2-} ions in this SiO_2 concentration range is negligible, the following approximation works well:

$$p \approx 0.5\left(\frac{1}{N_{SiO_2}} - 1\right). \qquad (11)$$

Therefore, the chosen values of p are close to two stoichiometric compositions $Na_6Si_2O_7$ (40.0 mol % SiO_2 at $p = 0.75$) and $Na_6Si_3O_9$ (49.5 mol % SiO_2 at $p = 0.51$). A small deviation to the range of melts with a higher basicity for the second composition as compared to the sodium metasilicate is associated with the difficulties of the simulation of molecular-mass distributions under conditions of the equality of the num-
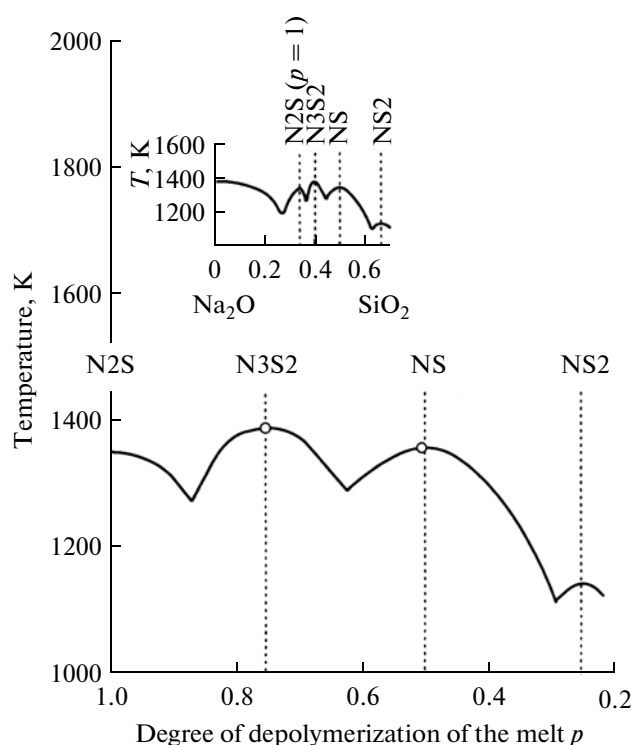
Fig. 5. Phase diagram of the $Na_2O–SiO_2$ system as a function of the silica content (inset at the top) and the degree of depolymerization of the melt. Circles indicate the melts for which the molecular-mass distributions were calculated as a function of the temperature (Tables 1, 2). Designations: N2S is Na_4SiO_4 ($2Na_2O \cdot SiO_2$), N3S2 is $Na_6SiO_2O_7$, NS is Na_2SiO_3 (or N3S3 is $Na_6Si_3O_9$), NS2 is $Na_2Si_2O_5$, and S is SiO_2.

bers of bridging and nonbridging bonds at $p = 0.5$ when the methods of the statistical simulation predict the beginning of an unlimited increase in silicon–oxygen complexes and the formation of particles with a high degree of polymerization $(Si_iO_{3i + 1 -j})^{2(i + 1 - j)-}$ [20].[1]

For both compositions, the calculations were carried out at two temperatures, i.e., 2000 K and the liquidus temperature that is equal to 1397 K for the disilicate melt ($p = 0.75$) and 1363 K for the metasilicate melt ($p = 0.51$). For comparison, the molecular-mass distributions that represent the stochastic distributions of Q^n structons are listed in Tables 1 and 2. A comparative analysis of these data leads to the following inferences.

As a result of the disproportionation of Q^n structons, the model concentration of SiO_4^{4-} ions at the liquidus temperature decreases (as compared to the stochastic molecular-mass distribution) by a factor of

approximately 1.5 for the $Na_6Si_2O_7$ melt and a factor of ~20 for the $Na_6Si_3O_9$ melt.

For both compositions, a decrease in the temperature leads to an increase in the number of chain species; in this case, for sodium disilicate at the liquidus temperature, $Si_2O_7^{6-}$ particles begin to dominate in the melt, which corresponds to the stoichiometry of this compound.

In the case of the more acidic sodium metasilicate at the liquidus temperature, ring particles of the general formula $(Si_nO_{3n})^{3n-}$ beginning with $(Si_3O_9)^{6-}$ ($n \geq 3$) are dominant in the melt. Their composition also corresponds to the stoichiometry of the initial melt.

With a decrease in the temperature, the average size of polymer complexes remains constant for the $Na_6Si_2O_7$ melt but increases by a factor of approximately 1.5 for the metasilicate system. It should be noted that the number of species of polymer particles is several tens (11–28) in the former case and varies insignificantly from 130 to 140 in the latter case.

CONCLUSIONS

Thus, a new algorithm has been proposed for simulating the temperature-dependent distributions of Q^n

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[1] In some calculations based on the STRUCTON computer program with the use of 10^4 initial Q^n structons at $p = 0.50$, we obtained polymer particles containing from 500 to ~1000 silicon atoms.

Table 1. Characteristics of polyanion ensembles representing stochastic and temperature-dependent distributions of Q^n structons for 40 mol % SiO_2 in the melt ($p = 0.75$)

Fraction of structon		Stochastic distribution	T, K	
			2000	1397
Q^0		0.3164	0.2149	0.1859
Q^1		0.4219	0.5750	0.6297
Q^2		0.2109	0.2054	0.1829
Q^3		0.0469	0.0047	0.0015
Q^4		0.0039	0 (~10^{-5})	0 (~10^{-6})
Anion concentration, mol %				
Monomer	SiO_4^{4-}	61.21 ± 0.51	42.87 ± 0.42	36.76 ± 0.43
Linear and branched chains ($j = 0$)	$Si_2O_7^{6-}$	15.03 ± 0.49	30.91 ± 0.52	37.89 ± 0.54
	$Si_3O_{10}^{8-}$	9.10 ± 0.30	15.93 ± 0.38	17.15 ± 0.44
	$Si_4O_{13}^{10-}$	5.42 ± 0.21	6.56 ± 0.40	5.72 ± 0.27
	Total	36.18 ± 0.58	56.49 ± 0.36	62.85 ± 0.49
Planar and branched ring complexes ($j = 1$)	$Si_3O_9^{6-}$	0.57 ± 0.13	0.43 ± 0.06	0.30 ± 0.07
	$Si_4O_{12}^{8-}$	0.65 ± 0.15	0.15 ± 0.06	0.06 ± 0.02
	$Si_5O_{15}^{10-}$	0.46 ± 0.09	0.05 ± 0.03	0.02 ± 0.02
	Total	2.50 ± 0.14	0.64 ± 0.07	0.39 ± 0.08
Simple three-dimensional complexes ($j = 2$)	$Si_4O_{11}^{6-}$	0.02 ± 0.02	–	–
	$Si_5O_{14}^{8-}$	0.02 ± 0.03	–	–
	$Si_6O_{17}^{10-}$	0.02 ± 0.01	–	–
	Total	0.09 ± 0.02	–	–
The other high-polymer anions ($j \geq 3$)		0.02 ± 0.05	0.00	0.00
Total of anions		100.00	100.00	100.00
Anion species		28 ± 1	13 ± 1	11 ± 1
Average anion size		1.95 ± 0.01	1.98 ± 0.01	1.99 ± 0.01

Note: The temperature $T = 1397$ K corresponds to the liquidus temperature of the sodium disilicate $Na_6Si_2O_7$. Average values were obtained from the results of ten calculations for the initial systems containing 10^4 Q^n structons, the standard deviations correspond to ±1σ, and j is the number of bridging oxygen atoms in the particle.

structons. This algorithm has been employed to modify the STRUCTON computer program (version 1.3, 2009), which allows one to calculate the molecular-mass distributions of polymer anions in silicate melts at different temperatures. This model has been used to perform test calculations for two compositions in the $Na_2O–SiO_2$ system ($Na_6Si_2O_7$, $Na_6Si_3O_9$). The results of the calculations have made it possible to trace variations in the set and concentrations of chain and ring silicon–oxygen complexes with a decrease in the temperature in the order: stochastic molecular-mass distribution $\longrightarrow$

molecular-mass distribution at $T = 2000$ K $\longrightarrow$ molecular-mass distribution at the liquidus temperature. The main result of these calculations is that the dominant species of silicon anions at the liquidus temperatures (in contrast to the stochastic distributions) exactly correspond to the stoichiometry of the initial melts: the $Si_2O_7^{6-}$ chains anions and $(Si_nO_{3n})^{3n-}$ ring complexes are dominant in the $Na_6Si_2O_7$ and $Na_6Si_3O_9$ melts, respectively.

This is not a trivial or predicted result, because the STRUCTON program does not include any special

Table 2. Characteristics of polyanion ensembles representing stochastic and temperature-dependent distributions of Q^n structons for 49.5 mol % SiO_2 in the melt ($p = 0.51$)

Fraction of structon		Stochastic distribution	T, K	
			2000	1363
Q^0		0.0677	0.0069	0.0022
Q^1		0.2600	0.1836	0.1411
Q^2		0.3747	0.6559	0.7522
Q^3		0.2400	0.1499	0.1037
Q^4		0.0576	0.0037	0.0009
Anion concentration, mol %				
Monomer	SiO_4^{4-}	55.85 ± 1.46	7.76 ± 0.52	2.74 ± 0.33
Linear and branched chains ($j = 0$)	$Si_2O_7^{6-}$	12.10 ± 0.70	8.68 ± 1.24	5.16 ± 0.68
	$Si_3O_{10}^{8-}$	5.20 ± 0.70	6.91 ± 1.15	5.02 ± 0.74
	$Si_4O_{13}^{10-}$	3.30 ± 0.12	5.71 ± 0.53	4.34 ± 0.47
	Total	26.32 ± 1.13	44.16 ± 1.50	39.56 ± 1.50
Planar and branched ring complexes ($j = 1$)	$Si_3O_9^{6-}$	0.31 ± 0.10	5.29 ± 0.84	8.69 ± 0.75
	$Si_4O_{12}^{8-}$	0.82 ± 0.25	3.85 ± 0.87	6.18 ± 0.60
	$Si_5O_{15}^{10-}$	0.70 ± 0.29	2.91 ± 0.38	4.00 ± 0.60
	Total	6.87 ± 0.51	33.21 ± 1.75	46.13 ± 1.59
Simple three-dimensional complexes ($j = 2$)	$Si_4O_{11}^{6-}$	–	0.11 ± 0.12	0.09 ± 0.07
	$Si_5O_{14}^{8-}$	0.21 ± 0.14	0.14 ± 0.14	0.07 ± 0.07
	$Si_6O_{17}^{10-}$	–	0.22 ± 0.18	0.12 ± 0.09
	Total	2.89 ± 0.12	9.40 ± 0.15	8.50 ± 0.10
The other high-polymer anions ($j \geq 3$)		8.07 ± 0.90	5.47 ± 0.75	3.07 ± 0.08
Total of anions		100.00	100.00	100.00
Anion species		137 ± 8	140 ± 4	130 ± 4
Average anion size		8.10 ± 0.31	11.97 ± 0.56	11.51 ± 0.49

Note: The temperature $T = 1363$ K corresponds to the liquidus temperature of the sodium metasilicate Na_2SiO_3. Average values were obtained from the results of ten calculations for the initial systems containing 10^4 Q^n structons, the standard deviations correspond to ±1σ, and j is the number of bridging oxygen atoms in the particle.

constraints on the formation of silicon−oxygen complexes,[2] and the molecular-mass distributions calculated at high temperatures in the given composition range are characterized by the dominance of SiO_4^{4-} monomers over other particles. Here, it is appropriate to recall that, in the study of polymer properties of sil-

icate melts, Esin [6] noted that there should appear relative maxima of concentrations of small-sized particles $(Si_iO_{3i + 1 - j})^{2(i + 1 - j)-}$ that, on the composition scale, should coincide with points of stoichiometric compounds, which usually coincide with maxima in the liquidus curves. However, by using the pure stochastic models of the distribution of silicon−oxygen anions, he failed to reveal reliable maxima for $Si_2O_7^{6-}$ dimers, $(Si_nO_{3n})^{3n-}$ ring species, and other complexes with respect to SiO_4^{4-} ions. It is evident that the results

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[2] Except that two arbitrarily chosen Q^n structons can be linked together only by one bridging bond. This constraint is equivalent to the fact that the silicate tetrahedra cannot be shared by edges or faces and the silicon−oxygen bonds cannot be formed through the vertices of the tetrahedra.

of our calculations with due regard for the reactions of disproportionation of Q^n structons in the melt confirm this prediction (Tables 1, 2). A more detailed analysis of the molecular-mass distributions for silicon−oxygen anions along the liquidus in the Na_2O-SiO_2 system is given in our earlier work [35].

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