The Distribution of Structural Entities at Sub-Nanometric Scale in the Na_2O-SiO_2 System

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The structure of vitreous oxide systems can be evaluated at different structural levels, depending on the desired degree of complexity. At the first level, at the sub-nanometric scale, glasses from the Na_2O – SiO_2 consist of a structure comprised of structural entities $Q \equiv Si(O_b)_n(O_{nb})_{4-n}$, where O_b represents a bridged oxygen atom and O_{nb} non-bridged oxygen atom, ($n = 0 \div 4$). Herein, a thermodynamical model is presented which estimates the distribution of Q_n structural entities for glasses of different chemical compositions having practical interest. The obtained results were compared with experimental MAS-NMR data.

Keywords: entity distribution, Na_2O – SiO_2 vitreous system

The study of the chemical equilibrium in vitrogenous oxide melts has been approached by a number of researchers [1], who attempted to define the structure of silica melts using the approach of different theories based on experimental results.

Several researchers put forward a number of computational models for the distribution of structural entities, in order to evaluate certain properties and compare them with experimental data. Some models propose the existence of a distribution of silicate, borate or phosphate polymers and the corresponding mathematical computational model. Other models take into account the acid-base interactions between the components of the corresponding melts and allow the estimation of the distribution of structural entities based on that assumption.

Some of the most well known models for silicate melts are those proposed by different researchers [2-10].

Furthermore, the modern MAS-NMR method does not offer only qualitative information regarding the entities of the glass, but also quantitative information. These are referring to the degree in which different structural entities (most often tetrahedral ones) intervene in the structure of the glass.

Oxide vitreous systems present a hierarchic structure. Depending on the structural level considered, various structural entities characteristic for a given glass are found, as follows:

- atomic level: the types of atoms from the basic structure;
- basic polyhaedra level: the type of basic polyhaedra, their type of linking, angles between bonds, interatomic distances;
- the polymer level (aggregate level, cluster level, etc.) comprising of several polyhaedra linked together, taking intro account the type of linking, the angles between bonds, interatomic distances, the size and distribution of different structural entities;
- the structural level based on the separation of microphases;
- the surface structural level.

Theoretic basis

At the sub-nanometric scale, glasses from the Na_2O – SiO_2 consist of a structure consisting of structural entities $Q \equiv Si(O_b)_n(O_{nb})_{4-n}$, where O_b represents a bridged oxygen atom and O_{nb} non-bridged oxygen atom, ($n = 0 \div 4$). These structural entities, having a size smaller than 1 nm, are in thermodynamic equilibrium, determined by an equilibrium constant and by temperature.

The chemical equilibrium from silica melts as an acid-base interaction [9]. Thus, it is considered that SiO_2 is an acid, and the modifier oxide is a base in the Lewis terminology. Therefore, the Si-O-Si group is an electron acceptor (Lewis acid) and O^{2-} is an electron donor (Lewis base), and the reaction between SiO_2 and M_2O is an acid-base reaction.

The model is interesting, as it allows the calculation of the structural entity distribution on the basis of acid-base interactions, on the equilibrium constants [9].

According to this model, several reactions are possible, which, in turn, may be considered a combination of four partial basic reactions:

$$\begin{aligned} Q_4O_{1/2} + 1/2 \cdot O^{2-} &\Leftrightarrow Q_3 & \Delta G_1^0 &= -RT\ln K_1 \\ Q_3O_{1/2} + 1/2 \cdot O^{2-} &\Leftrightarrow Q_2 & \Delta G_2^0 &= -RT\ln K_2 \\ Q_2O_{1/2} + 1/2 \cdot O^{2-} &\Leftrightarrow Q_1 & \Delta G_3^0 &= -RT\ln K_3 \\ Q_1O_{1/2} + 1/2 \cdot O^{2-} &\Leftrightarrow Q_0 & \Delta G_4^0 &= -RT\ln K_4 \end{aligned} \quad (1)$$

where K_i are the opposite equilibrium constants, ΔG_i^o are Gibbs free energy of reaction, R - general gas constant and T - temperature in K degrees..

According to Stevels rule, which states that $O_{np} = 2R-4$ and $O_p = 8 - 2R$, where R=O/Si (according to the molar fraction of glass), the Q_4 ... Q_0 species characterize the following chemical compounds in the Na_2O – SiO_2 system: SiO_2; $Na_2O{\cdot}2SiO_2$; $Na_2O{\cdot}SiO_2$; $3Na_2O{\cdot}2SiO_2$; $2Na_2O{\cdot}SiO_2$.

The constants K_1, K_2, K_3 and K_4 are the equilibrium constants for the theoretical reactions and the real reactions presented in table 1.

Results and discussion

The computation of the structural entity distribution in the Na_2O – SiO_2 vitreous systems implies the knowledge of the constants K_i. For the computation of these constants, the Gibbs free energy must be known which, in standard state, ΔG^0_i, is calculated from the values of the free standard energy of the reactants and reaction products [11-15].

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Table 1
EQUILIBRIUM CONSTANTS IN SILICA-ALKALI SYSTEMS

Nr	Theoretical reaction	Real reaction	Gibbs free energy
1.	$Q_4\ O_{1/2} + 1/2\ O^{2-} \Leftrightarrow Q_3$	$2SiO_2 + Na_2O \Leftrightarrow Na_2O{\cdot}2SiO_2$	$\Delta G^0_1 = - RT \ln K_1$
2.	$Q_3\ O_{1/2} + 1/2\ O^{2-} \Leftrightarrow Q_2$	$SiO_2 + Na_2O \Leftrightarrow Na_2O{\cdot}SiO_2$	$\Delta G^0_2 = - RT \ln K_2$
3.	$Q_2\ O_{1/2} + 1/2\ O^{2-} \Leftrightarrow Q_1$	$2SiO_2 + 3Na_2O \Leftrightarrow 3Na_2O{\cdot}2SiO_2$	$\Delta G^0_3 = - RT \ln K_3$
4.	$Q_1\ O_{1/2} + 1/2\ O^{2-} \Leftrightarrow Q_0$	$SiO_2 + 2Na_2O \Leftrightarrow 2Na_2O{\cdot}SiO_2$	$\Delta G^0_4 = - RT \ln K_4$

In the Na_2CO_3 - SiO_2 system, the following reactions for the formation of different silicates were considered:

$$2Na_2CO_3 + SiO_2 = Na_4SiO_4 + 2CO_2 \quad (2)$$

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2 \quad (3)$$

$$Na_2CO_3 + 2SiO_2 = Na_2Si_2O_5 + CO_2 \quad (4)$$

$$Na_2CO_3 + 3SiO_2 = Na_2Si_3O_7 + CO_2 \quad (5)$$

The carbonate dissociation reaction is:

$$Na_2CO_3 = Na_2O + CO_2 \quad (6)$$

On the basis of the presented reactions, the $\Delta G^0 = f(T)$ graphs were made, out of which ΔG^0 is deduced for the existing silicates at the temperatures of 1400K, 1500 K, 1600 K and 1800 K. The data were taken from [16,17]. The obtained results are presented in table 2.

It can be observed that, by using table 2, the values of K_i can be calculated for various temperatures, not only for certain silicates. Thus, in the cases where thermodynamical data for the standard Gibbs free energy of formation for certain compounds was unavailable, the following functional relation was used [12-15]:

$$\lg K_i = f(pB) \quad (7)$$

where pB represents the basicity percentage of the compound resulting from a reaction from table 1.

To this purpose, the basicity percentage was calculated for all the compounds for which the $\lg K_i = f(pB)$ correlation was made, and from this, the values $\lg K_i$ (according to the calculated pB) corresponding to the compounds for which no data is available on ΔG^0.

The analytic method of mathematical regression was used, and the values for $\lg K_i$ at different temperatures were obtained. Afterwards, the values of K_i for all the desired silica-alkaline compounds at the given temperatures are calculated. The obtained results are presented in table 3.

It may be considered that in the Na_2O - SiO_2 binary system, as a result of the reactions taking place with the formation of different types of compounds, the SiO_2 oxide is neutralized stepwise by the alkali ions. One may observe from table 3 that the values of the calculated constants decrease with the saturation of the SiO_4 tetrahedron with alkali oxide (from right to left in the table; it must be noted that $K'_i = 1/K_i$).

Dron suggests the use of the ratio methods, in which the constants are compared to the first of them [9]. The results are presented in table 4.

Table 2
VALUES OF ΔG^0 IN THE Na SILICATES AS A FUNCTION OF TEMPERATURE

T [K]	ΔG^0 [kJ/mol] for the compounds:				
	Na_4SiO_4	Na_2SiO_3	$Na_2Si_2O_5$	$Na_2Si_3O_7$	$Na_2Si_4O_9$
1800	-167.47	-182.71	-247.40	-270.22	----
1600	-132.55	-150.01	-209.34	-230.27	----
1500	-111.62	-136.07	-188.41	-205.82	----
1400	-94.20	-122.09	-170.95	-188.41	----

Table 3
VALUES $K'_i = 1/K_i$ FOR THE ALKALINE SILICATES AT DIFFERENT TEMPERATURES

T [K]	N_2S	N_3S_2	NS	NS_2	NS_3	NS_4
1800	$1.38 \cdot 10^{-5}$	$8.02 \cdot 10^{-6}$	$5.02 \cdot 10^{-6}$	$6.68 \cdot 10^{-8}$	$1.45 \cdot 10^{-8}$	$9.00 \cdot 10^{-9}$
1600	$4.73 \cdot 10^{-5}$	$2.70 \cdot 10^{-5}$	$1.27 \cdot 10^{-5}$	$1.47 \cdot 10^{-7}$	$3.06 \cdot 10^{-8}$	$1.60 \cdot 10^{-8}$
1500	$1.30 \cdot 10^{-4}$	$5.60 \cdot 10^{-5}$	$1.83 \cdot 10^{-5}$	$2.77 \cdot 10^{-7}$	$6.86 \cdot 10^{-8}$	$2.70 \cdot 10^{-8}$
1400	$3.07 \cdot 10^{-4}$	$1.09 \cdot 10^{-4}$	$2.80 \cdot 10^{-5}$	$4.22 \cdot 10^{-7}$	$9.43 \cdot 10^{-8}$	$3.60 \cdot 10^{-8}$

(The notations used: $N = Na_2O$, $S = SiO_2$).

Table 4
VALUES FOR THE CONSTANTS $K_1 \div K_4$, IN THE Na_2O-SiO_2 SYSTEM, AS A FUNCTION OF TEMPERATURE.

T [K]	RS_2 (K_1)	RS (K_2)	R_3S_2 (K_3)	R_2S (K_4)
1500	1	66.1	202.2	469.3
1600	1	86.4	183.7	321.8
1800	1	75.1	120.1	206.6

Knowing the values of the determined reaction, K_1 ... K_4, the non-linear system of 6 equations with 6 variables is solved using specialized software. The distribution of the structural entities Q_0...Q_4 are obtained for the Na_2O-SiO_2 system, at the three temperatures T_1 = 1500 K, T_2 = 1600 K and T_3 = 1800 K.

The distribution of the structural entities Q_n as a function of molar fraction of Na_2O at the three given temperatures is presented in figures 1, 2 and 3.

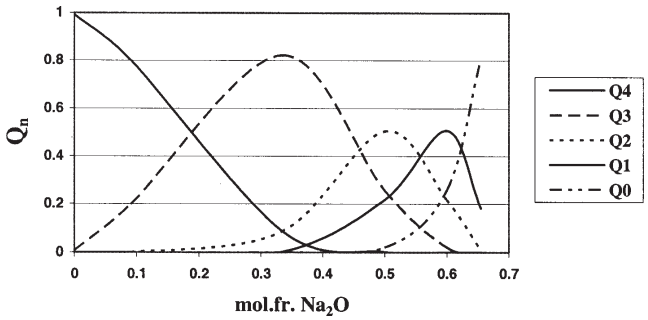

Fig. 1. The distribution of the structural entities Q_n as a function of molar fraction of Na_2O, at 1500K

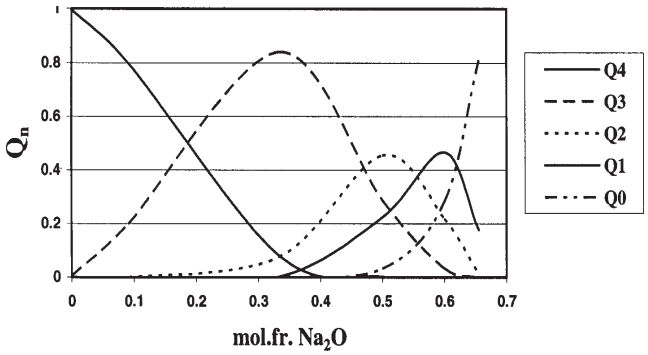

Fig. 2. The distribution of the structural entities Q_n as a function of molar fraction of Na_2O, at 1600K

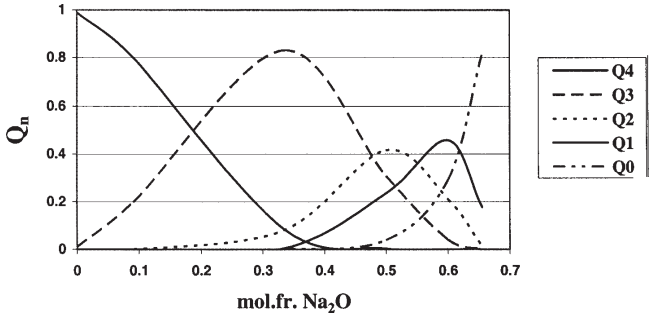

Fig. 3. The distribution of the structural entities Q_n as a function of molar fraction of Na_2O, at 1800K

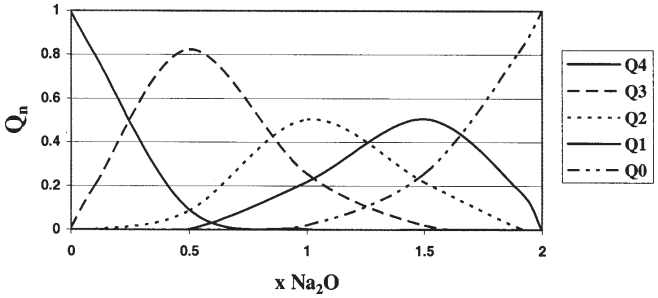

Fig. 4. The distribution of the structural entities Q_n as a function of x Na_2O, at 1500K

Also, the structural entity distributions as a function of the rate of neutralization x (x = 0 ÷ 1,9) were calculated. In figures 4, 5 and 6 are presented the correlations $Q_n = f(x)$.

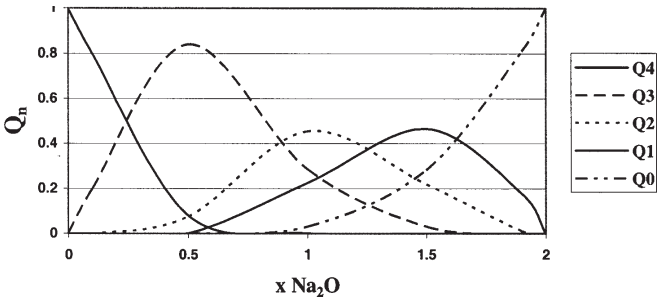

Fig. 5. The distribution of the structural entities Q_n as a function of x Na_2O, at 1600K

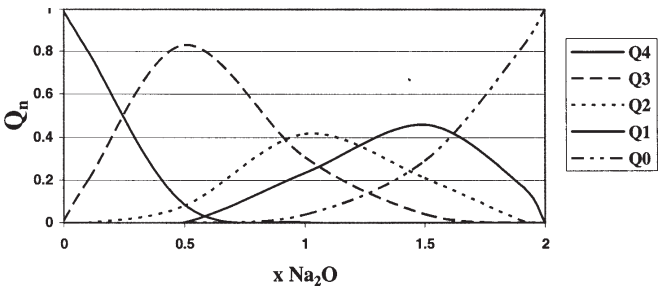

Fig. 6. The distribution of the structural entities Q_n as a function of x Na_2O, at 1800K

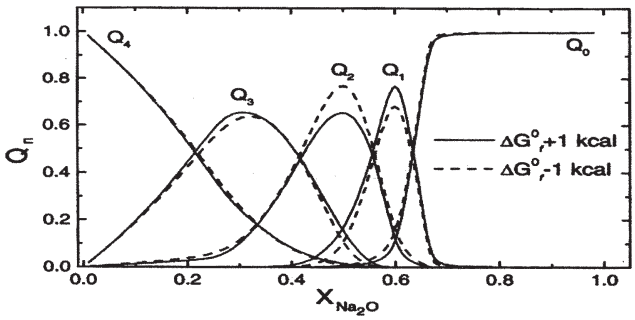

Fig. 7. The variation of structural entities distribution Q_n in the Na_2O-SiO_2 system, calculated by modifing the experimental values of $\Delta^f G^0$ at 1200°C by ±4.18 kJ/mol [18]

On the basis of the obtained results it may be concluded that the temperature does not significantly influence the structure entity distributions for a constant composition. As expected (according to Stevels), maximum percentages are obtained for Q_1 and Q_2, with no significant influence from temperature. An explanation for this phenomenon may be that the chemical equilibrium in melt is stable at a temperature T < 1500 K, at which point no processes of significant magnitude can influence greatly the structural distribution.

The results obtained are similar to those from literature.

Thus, it was calculated the structural entity distribution Q_n at 1200°C, from the experimental values of $\Delta^f G^0$, varying with ±4.18 kJ/mol [18]. The results are presented in figure 7.

The results presented in this paper are in good agreement with those presented in literature. A good correlation may be observed between the calculated results from Figure 1 and the experimental ones from figure 7.

Also, the data obtained are very similar to the data on structural entities distribution measured by MAS-NMR method (**M**agic **A**ngle **S**pin). In the Na_2O - SiO_2 system it was shown by a series of researchers [19-21] that, except for the case of very high concentrations of Na_2O or SiO_2, always exist at least three types of tetrahedral species. Selected experimental data is presented in table 5.

Table 5
DISTRIBUTION OF THE ENTITIES Q_n DETERMINED FOR THE Na_2O - SiO_2 SYSTEM

% mol Na_2O	Authors ↓	Entities Q_n [%] →	Q_0	Q_1	Q_2	Q_3
20	Malkawa & Co. [19]		50	47	3	0
25			38	61	1	0
33			11	79	10	0
36.4			7	76	17	0
20	Emerson & Co.[20]		54	40	6	0
33			7.5	85	7.5	0
25	Stebbins.[21]		45.2	44.1	10.7	0
33			31	44.6	20.2	4.2

It may observed that for the same compositions, various authors obtained different results, as the species distribution Q_n is influenced, besides the chemical composition, also by thermal and melting history.

It may be observed that the species distributions Q_n determined by experimental means are in good agreement to those presented herein.

Conclusions

In the Na_2O–SiO_2 vitreous system, K_p constants were calculated on the basis of thermodynamical data, and the structural entity concentrations $Q_v \equiv Si(O_p)_n(O_{np})_{4-n}$, (n = 0 ÷ 4) were calculated for three temperatures: 1500 K, 1600 K and 1800 K.

The structural entity Q_n curves were calculated as a function of R_2O molar fraction and of the rate of neutralization x.

As thermal equilibrium was obtained at a temperature T<1500 K, temperature variations above that value have little effect on the structural entity distribution.

The obtained results are in very good agreement with the data presented by other authors. This is proof that the starting hypotheses, as well as the methodology used, generate distribution very close in values to those determined experimentally.

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