ASSOCIATED-SOLUTION APPROACH TO DESCRIPTION OF STRUCTURE AND PROPERTIES OF MOLTEN SLAGS.

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Abstract.

An associated-solution model of liquid slags and silicates, based on Prigogine's theory, has been developed. The available experimental information suggested that the liquid solution consist of non-associated molecules, associative ($2CaO \bullet Al_2O_3$, $CaO \bullet SiO_2$, $3/2CaF_2 \bullet 1/2Ca_3P_2$, $2CaO \bullet Al_2O_3 \bullet SiO_2$, $CaO \bullet Al_2O_3 \bullet 2SiO_2$, *etc*) and polymer species. The latter include SiO_2 networks and SiO_2 networks connected with associates. A set of equations for calculation of the mixing Gibbs energies and the components' activities was derived under the simplest assumption that the equilibrium constant of addition of a SiO_2 molecule to any silicon-oxygen structure depends on neither its size nor its configuration. Besides formation of associative and polymer complexes these equations take into account interaction between associated-solution species and differences in their size. The model free parameters were calculated by means of an optimising procedure from the vast data files on the activities of all components in the following melts: CaF_2-CaO, CaO-Al_2O_3, CaF_2-CaO-Al_2O_3, CaO-SiO_2, CaF_2-CaO-SiO_2 , MnO-SiO_2 ,CaO-Al_2O_3-SiO_2 ,CaF_2-CaO-Al_2O_3-SiO_2, CaF_2-CaO-Ca_3P_2, CaF_2- Ca_3P_2, Na_2O-SiO_2, K_2O-SiO_2, obtained in recent years. It is proved that the model describes the experimental data adequately. Evidences of correctness of the model were obtained by calculation of phase diagrams, by consideration of the liquid to glass transition, by treatment of experimental data on the structure and viscosity.

Introduction.

Thermodynamic modelling of liquid metallurgical slags and silicate melts is a challenging task. The key problem is connected with adequate representation of SiO_2 polymerisation reaction. The majority of the available models [1-10] are founded on the widely spread ionic-solution concept which considers the polymerisation as the following process:

$$SiO_4^{4-} + Si_xO_{3x+1}^{(2x+2)-} = Si_{x+1}O_{3x+4}^{2(x+2)-} + O^{2-}$$

Advantages and disadvantages of these models were discussed in reviews [11,12]. For our purposes it is important that they do not approximate adequately the thermodynamic properties of liquid oxide mixtures at $x(SiO_2) > 0.3 - 0.4$. Besides the O^{2-} ion has never been detected experimentally [12]. Pelton, Blander *et al.* [13-16] treated molten oxide mixtures with the help of the quasichemical theory of Guggenheim as short-range ordered liquids. In the modified quasichemical approach they considered the distribution of only cations on the cationic quasi-lattice assuming, that the concentration dependencies of enthalpy and non-configuration entropy, connected with the ordering process, could be approximated by polynomials of up to seventh degree. In this way a mathematical formalism was developed which allowed thermodynamic description of some binary and ternary systems. Hoch's model [17] is founded on the assumption that molecules of the components of different nature form in molten silicates complexes of various composition, their binding Gibbs energies being expressed by exponential functions. The model of Bottinga *et al.* [12] makes no explicit assumptions about the structure of liquid silicates, but implies that some ionic and/or molecular species are present in the melt that correspond to the known crystalline compounds of the system. The equilibrium distribution of these units has to be obtained by minimising the Gibbs energy of the melt under the constraint of a fixed bulk composition. Partial molar enthalpies and entropies of mixing for the solution species Bottinga *et al.* expressed by the van Laar formula for regular solutions and the Flory-Huggins equation, respectively. Though the models [12,17] seem rather empirical they emphasise importance of considering complexes other than silicon-oxygen polymer ones. The importance of the heteromolecular complexes was further emphasised by Shakhmatkin and M.M.Shults [18] and Kozhina [19] who assumed that the Na_2O-SiO_2 and K_2O-SiO_2 melts are associated solutions, where all sodium or potassium molecules are bonded in the following species: $Na_2O \bullet SiO_2$ and $Na_2O \bullet 2SiO_2$, or $K_2O \bullet SiO_2$, $K_2O \bullet 2SiO_2$ and $K_2O \bullet 4SiO_2$. As a result qualitative agreement with experiment was obtained. Several "structureless" models have been proposed in which significant part of thermodynamic parameters was assessed with the help of the phase diagrams. Berman and Brown [20] used polynomial representation of the excess Gibbs energy. Gaye and Welfringer [21] developed a statistical thermodynamic model based on description of the liquid in terms of cells composed of an oxygen anion surrounded by two cations and on approximation of the concentration functions of the energetic parameters by linear equations. Mikhailov [22] described the thermodynamic characteristics of molten oxide

mixtures in terms of the sub-regular ionic solutions, approximating the co-ordination number of cations by a second degree polynomial. Hallstedt *et al.* [23] briefly outlined an ionic model which in essence is "structureless" too because formation of silicon-oxygen anions more complex than SiO_4^{-4} was neglected. Metallurgical slags are usually contain non-oxide components such as CaF_2 that is added in order to obtain the required physical and chemical properties and products of refining reactions (CaS, Ca_3P_2). However neither of the above models was ever applied to molten mixtures of compound of different nature.

Substantial thermodynamic studies of slag systems of various natures and complexities were carried out in recent years by Knudsen effusion mass spectrometry combined with generation in the effusion cell of reactions, producing volatile substances [24-34]. This technique is described in details in paper by Zaitsev, presented at this conference. Representative files of experimental data, containing several hundred to several thousand values of activity of all components in wide temperature and concentration ranges, were obtained for melts of various nature and complexities: Na_2O-SiO_2, K_2O-SiO_2, MnO-SiO_2, Al_2O_3-CaO, CaO-SiO_2 , Al_2O_3-SiO_2, CaF_2-Al_2O_3-CaO, CaF_2-CaO-SiO_2, CaO-Al_2O_3-SiO_2, CaF_2-CaO-Al_2O_3-SiO_2, CaF_2- Ca_3P_2, CaF_2-CaO-Ca_3P_2. These results allowed a new approach to description of properties and structure of liquid metallurgical slags and silicates.

Basic concepts.

One of the fundamental results of the listed studies is that the entropy of liquid slags observed in experiment is substantially lower than the configuration entropy that follows from the ionic concept of slag structure (Table I). It can be seen that the entropy is even lower than the values expected in case, if the melts were ideal molecular solutions. These facts mean that the real number of particles in the molten slags and silicates is well below that of ions and even somewhat below the number of molecules.

Our approach to modelling of molten silicates is based on the fact that they belong to the systems with strong interparticle interaction between the majority of the components. It is known [36,37] that in liquid solutions of this type systems association, or compound formation, or chemical short-range ordering occur. It results in formation of molecular complexes (associates, compounds), which are in dynamic equilibrium with molecules of components. This idea is practically identical to the central assumption of Prigogine's associated-solution theory [38]. It is obvious that association will naturally lead to a decrease in the number of particles in solution, thus offering strong possibilities for explanation of the experimental values of the mixing entropy. If the potential possibilities of a qualitative

treatment of polymerisation reactions [39,40] are taken into account it seems reasonable to use the associated solution theory as a foundation for development of a thermodynamic model of liquid slags and silicate.

The associated-solution model of liquid slags.

The associated-solution theory starts from assumption that molecular complexes, or associates are of fixed stoichiometry and behave like independent particles. The complexes are in dynamic equilibrium with the non-associated molecules (monomer species), which can be described by the mass action law. This means that the equilibrium constant of the same reaction of association does not depend on the composition of the mixture where it occurs. The associated solution species are bonded by weak molecular forces and are distributed statistically.

In accordance with this it was supposed that molten slags (silicates) consist of monomer molecules, heteromolecular associative complexes (CAS_2, N_2S, KS_2, C_2A, MS, *etc*.) and polymer species. The latter include SiO_2 networks of various configurations and size (S_w , $2 \le w \le \infty$) and SiO_2 networks connected with some associates, for example with the AS (AS_y, $2 \le y \le \infty$), NS_2 or CAS_2 (NS_z, CAS_z , $3 \le z \le \infty$) associates. From here onward Fl designates CaF_2 ; C, CaO; A, Al_2O_3 ; M, MnO; N, Na_2O ; K, K_2O and S, SiO_2 . In constructing an associated-solution model it was also taken into account that the thermodynamic description of a multicomponent system such as CaF_2-CaO-Al_2O_3-SiO_2 should include descriptions of all simpler constituents. Thus, in accordance with the associated-solution theory [38] the Gibbs energy of formation of the solution can be defined as

$$\Delta_f G = \sum_i n(\mathrm{i})\Delta_f G_m^o(\mathrm{i}) + RT\{\sum_{J_1} n(\mathrm{J}_1)\ln[x(\mathrm{J}_1)] + \sum_i n(\mathrm{i})\ln[x(\mathrm{i})]\} - \sum_{w=2}^{\infty} n^o(\mathrm{S_W})\Delta_f G_m^o(\mathrm{S_W})$$
$$- RT\sum_{w=2}^{\infty} n^o(\mathrm{S_W})\ln[x^o(\mathrm{S_W})] + \Delta_f G^E , \qquad (1)$$

where i designates any associative or polymer species ; J_1 designates any non-associated molecule; $\Delta_f G_m^o(\mathrm{i}) = -RT\ln K(\mathrm{i}) = \Delta_f H_m^o(\mathrm{i}) - T\Delta_f S_m^o(\mathrm{i})$ are the molar Gibbs energies of formation of an associative or polymer complex i, K(i) being the equilibrium constant of the corresponding reaction of association or polymerisation; n(i), x(i) $n(J_1)$, $x(J_1)$ are amounts of substance and mole fractions of the associative solution species; n^o (S_w) and x^o (S_w) are amounts of substance and mole fractions of polymerised silica particles in pure liquid SiO_2 ; $\Delta_f G^E$ is the excess Gibbs energy change caused by interaction between the associated solution

species and by the differences between the volumes of the non-associated, associated and polymerised species. The suggestion first proposed in [41] was used to express the excess part of the mixing Gibbs energy. For the most complicated melt CaF_2-CaO-Al_2O_3-SiO_2 $\Delta_f G^E$ term had the following form:

$$\Delta_f G^E = \sum_{p,q,r,v} \frac{L_{p,q,r,v}[n(Fl)]^p[n(C)]^q[n(A)]^r[n(S)]^v}{[n(Fl)+n(C)+n(A)+n(S)]^{(p+q+r+v-1)}} \qquad (2)$$

Here n (Fl), n (C), n (A) and n(S) are amounts of substance of the components and $L_{p,q,r,v}$ are temperature dependent parameters. The conventional procedure of deriving partial thermodynamic functions from integral ones transforms the last expression into equations for calculation of activity coefficients. For example,

$$\begin{aligned}\ln\gamma(C) = &\sum_{p,q,r,v} \frac{L_{p,q,r,v}}{RT} q[x(Fl)]^p[x(C)]^{q-1}[x(A)]^r[x(S)]^v \\ &- \sum_{p,q,r,v} \frac{L_{p,q,r,v}}{RT}(p+q+r+v-1)\times[x(Fl)]^p[x(C)]^q[x(A)]^r[x(S)]^v\end{aligned} \qquad (3)$$

This type equations make it possible to express the equilibrium constants of the complex formation reactions in terms of the concentrations of the associated-solution species, *i.e.* in the form characteristic to the ideal associated-solution model. This last result allows us to find concentrations of the monomer species in associated solution by solving the system of the equations connecting the mole fractions of the components with those of the associated-solution species. For example, for a ternary solution, A-B-C, these equations can be written in the following form:

$$\begin{aligned}x(A_1) &= x(A) - \sum_i\sum_j\sum_k K(A_iB_jC_k)\times x^i(A_1)\times x^j(B_1)\times x^k(C_1)\times[i - x(A)\times(i+j+k-1)], \\ x(B_1) &= x(B) - \sum_i\sum_j\sum_k K(A_iB_jC_k)\times x^i(A_1)\times x^j(B_1)\times x^k(C_1)\times[j - x(B)\times(i+j+k-1)], \\ x(C_1) &= x(C) - \sum_i\sum_j\sum_k K(A_iB_jC_k)\times x^i(A_1)\times x^j(B_1)\times x^k(C_1)\times[k - x(C)\times(i+j+k-1)].\end{aligned} \qquad (4)$$

The components′ activities are to be determined as:

$$\begin{aligned}a(A) &= \gamma(A)x(A_1) \quad a(C) = \gamma(C)x(C_1) \\ a(Fl) &= \gamma(Fl)x(Fl_1) \quad a(S) = \gamma(S)x(S_1)/x^o(S_1)\ etc\end{aligned} \qquad (5)$$

where $x^o(S_1)$ is concentration of the monomer species S_1 in pure liquid SiO_2. As a first approximation in treatment of the SiO_2 polymerisation reaction it was suggested that the equilibrium constant of the addition of an SiO_2 molecule to any oxygen-silicon network S_w,

AS_y at y>1, NS_z at z>2, CAS_z at z>2, depends on neither the size nor the configuration of the complex and is equal to the equilibrium constant , K_P, of the reaction $S_1+S_1=S_2$. In more details the model was discussed elsewhere [29-31,42].

Determination of the model parameters.

In order to determine the number of types of associated complexes and their compositions, the available information on the nature of interparticle interaction in the studied systems, on equilibrium phase diagrams, on concentration functions of some structure-sensitive physical and chemical properties of melts such as viscosity, electric conductivity , on composition of vapour over melts have been analysed. Thermodynamics of solid compounds as well as the composition behaviour of the alpha functions, calculated from the data [26-32], were also taken into account. In some cases the choice of associates was confirmed by independent structural data. For example, the MS and M_2S complexes in the MnO-SiO_2 liquid solutions were discovered in the research of X-ray scattering from the surface of fused samples [43,44]. While considering three and four component melts, it was assumed that all associates inherent in the simpler constituent systems exist in the more complex solution. After preliminary considerations the whole files of the experimental data [25-34], were subjected to an optimisation procedure. This consisted in varying the model parameters and a least-square regression minimising the deviations between experimental and calculated activities. In application to the three and four component systems the optimisation procedure was two-stage. At the first stage all parameters of these solutions were assumed to be arbitrary. As a consequence, in all cases the thermodynamic function of the binary associates and the coefficients characterising the binary excess functions were found to coincide, within experimental error, with those obtained from the data for the simpler and similar melts. The same was observed while analysing the SiO_2 polymerisation process. Some examples of the coincidence are given in Table II. For this reason, at the second stage of optimisation of the experimental data for the three and four component systems the discussed values were taken to be equal to those obtained earlier for the simpler or similar melts and only new parameters were varied. This , however, did not lead to their significant change as compared with the first stage. The least-square regression procedure revealed that the experimental data on the activities of the components in the liquid slags and silicates listed in Tables III and IV can be described by the suggested model with a precision not worse than the experimental one (1-3%). In complete agreement with the laws of chemical equilibria, the thermodynamic

characteristics of the same association reaction do not depend on the composition of liquid solutions. The same is true about the $_{p,q,r,v}$ coefficients.

Discussion of the model.

The least-square regression procedure revealed that the experimental data on the activities of the components in the liquid solution listed in Tables III and IV can be described by the suggested model with a precision not worse than the experimental one (1-3%). In complete agreement with the laws of chemical equilibria, the thermodynamic characteristics of the same association reaction do not depend on the composition of liquid slags and silicates. The same is true about the $_{p,q,r,v}$ values. The correctness of the model is illustrated by Tables V where the calculated component activities in the CaF_2-CaO-Al_2O_3-SiO_2 melt, which is most important for metallurgy, are compared with the experimental data. One can see that the differences between the two-type values do not exceed the experimental error.

It should be emphasised that the agreement between the thermodynamic characteristics of the polymerisation reaction obtained from the experimental data for 7 different silicate systems of various complexity is a considerable advantage of the present model. This feature contrasts with the models based on the ionic solution concept according to which enthalpy and entropy of the same reaction usually alter in going from one system to another (see, for example, [2-4,10,11]). Furthermore, the associated-solution approach describes adequately liquid alkali silicates while the ionic-solution concept has failed, although these melts seem to be almost ideal ionic solutions [45-48]. Comparison of the values in Tables III and IV for binary silicates allows the following conclusions.

- The gains in both the Gibbs energy and enthalpy of the heteromolecular association are the highest in the case of the K_2O-SiO_2 melt and reduce progressively in the order: K_2O-SiO_2 > Na_2O-SiO_2 > CaO-SiO_2 > MnO-SiO_2 > Al_2O_3-SiO_2.
- The excess Gibbs energy term has a common form for all binary systems, however its parameters significantly differ and decrease in magnitude in the same order reaching zero in the case of Al_2O_3-SiO_2, which makes this melt the ideal associated solution.
- Stability of the equimolecular complex with respect to the associate of the orthosilicate composition decreases in the same order.
- Stability of the disilicate complex with respect to metasilicate one grows in going from the Na_2O-SiO_2 to the K_2O-SiO_2 melt.

These features are in complete agreement with the acidic-basic nature of the heteromolecular interaction in the studied molten silicates and favours the generality of the model.

Further evidence of correctness of the associated-solution model of the molten slags and silicates was obtained by calculation of the $CaO-Al_2O_3$, $CaF_2-CaO-Al_2O_3$ [49], $CaO-SiO_2$, $CaF_2-CaO-SiO_2$ [50], $MnO-SiO_2$ [29], $Al_2O_3-SiO_2$ [51], $CaO-Al_2O_3-SiO_2$ [31,51], Na_2O-SiO_2 [33,34], K_2O-SiO_2 [34] phase diagrams which included extrapolation of the components activities to unstudied temperature and concentration ranges. No thermodynamic data , derived from phase equilibria , were used in these computations. On the whole, agreement with independent experimental data for the phase diagrams was quite good.

It is of interest to apply the present model of molten slags and silicates for treatment of the results of structure studies aimed at revealing silicon-oxygen complexes of various types. Ref. [52] provides an example of this type investigations. Its authors studied the structure of sodium-silicate glasses in the concentration range of 20 to 56 mol. % Na_2O, using nuclear magnetic resonance spectroscopy and ^{29}Si isotope. Samples were prepared by smelting of the components at 1540 K for 3 hours with subsequent quenching in water or liquid nitrogen. From two to four peaks, distinct or overlapping, were observed in the NMR spectra, each corresponding to silicon-oxygen complexes with one (Q_1), two (Q_2), three (Q_3) or four (Q_4) bridging O atoms. According to the associated-solution model, some of the structure species of the Na_2O-SiO_2 melt, such as NS_2, S_w ($2 \leq w \leq \infty$) and NS_z ($3 \leq z \leq \infty$), should contain different number bridging O. Relative concentrations of the above complexes as a function of sodium oxide mole fraction were computed, using the thermodynamic parameters of the polymerisation and association reactions (Tables III). The calculations were carried out for three temperatures: 1540 K, from which the samples were quenched in ref. [52]; 773 K, which is in the glass-transition region, and 1173, which approximately averages between the above two. The results of the calculation, as one can see from Fig.1, are in agreement with data [52].

Glass transition.

The evidence presented above has unambiguously shown that the associated-solution approach to modelling of liquid slags allows adequate approximation of the thermodynamic properties in wide temperature and concentration ranges and, as a consequence, allows good description of phase equilibria. Thus, there is good reason to believe that the concept is realistic and depicts the actual structure of molten slags and silicates. If this is the case, the associated-solution model should make possible extrapolation of the thermodynamic functions of liquid phase into the temperature region of large supercooling and treatment of

liquid→glass transition. Refs [53-55] support to some extent this suggestion because according to them association leads to a change in relative stability of crystalline, liquid and glassy states; to growth in both viscosity and the activation energy of viscous flow; to a decrease in the driving force and the rate of crystallisation.

The system Na_2O-SiO_2, studied rather thoroughly in crystalline, liquid and glassy states, was chosen to consider possibilities of the present model in treatment of liquid→glass transition. It is convenient to begin with analysis of the heat capacity of molten sodium silicates because this function, being the second derivative of the Gibbs energy with temperature, is the most difficult for description when the model parameters are determined from the data on components' activities, like in our case. Concentration dependencies of the heat capacity of the Na_2O-SiO_2 melt at 800 and 1373 K, calculated with the help of the model under discussion and the data of Tables III and IV, are given in Fig.2 in comparison with the available information [57-70]. One can see that the calculation results differ from the experimental data by 1-2 % , which certainly is within the experimental errors. Note almost complete coincidence of the C_P values calculated at 800 K, which lies in the glass-transition region, with the heat capacity of supercooled liquid [57,58] measured immediately after it was formed from glass. Fig.2 also shows that the difference between C_P of the melt at 800 and 1373 K is rather low. This agrees with the findings reported in refs. [57,58,63,66,67,71], according to which the heat capacity of molten sodium silicate, within the experimental errors, is independent on temperature. Enthalpies of sodium meta- and disilicates in glassy, ΔH(g, 298.15-T_g), and liquid, ΔH(l, T_g- T_m), states in the temperature ranges from 298.15 K to the glass-transition point, T_g, and from T_g to the melting point, T_m, as well as the enthalpies of the crystals→glass transformations at standard temperature, $\Delta_v H$(298,15), are given in Table VI in comparison with information available in literature. Calculations were carried out using the present associated solution model, parameters of Tables III and IV, heat capacities of crystalline and glassy phases from [57-59,67]. Suggestion [76] about equality of the heat capacities of the crystalline and glassy phases were also used in calculations. According to refs [57,58] the transition of liquid to glass was supposed to be a second-order phase transformation, occurring at 706 and 750 K for meta- and disilicates correspondingly. The melting enthalpies of the above silicates were found from data [33]. As is obvious from Table VI, there is good agreement between the results of the calculation and independent experimental and reference data. This means that the model under discussion allows prediction of thermodynamic behaviour of slags and silicates both in the state of supercooled

liquid and in glassy state. This conclusion was further confirmed experimentally while studying the CaO-Al_2O_3-SiO_2 system [77].

Investigating the triangle gehlenite ($2CaO{\cdot}Al_2O_3{\cdot}SiO_2$) - anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$) - wollastonite (pseudowollastonite) ($CaO{\cdot}SiO_2$) we were fortunate to perform experiments with samples in two metastable states: glass with precipitations of Al_2O_3 and supercooled liquid. Samples of the first type were mixed with calcium fluoride and carefully ground to powder. The mole fraction of CaF_2 in the mixture was around 0.03. Then the powder was placed into the effusion cell and heated to the temperature range where the glass did not transform to liquid. CaF_2 evaporated and reacted with aluminium and silicon oxides, producing gaseous species. Although quite a narrow temperature range was accessible for these experiments, it was possible to measure the vapour pressure of AlF_3, CaF_2 and SiF_4. The pressure of the calcium fluoride coincided with the partial pressure of pure CaF_2, so that no CaF_2 dissolved in the glassy aluminosilicate. The pressures of aluminium and silicon fluorides did not allow [31,35] computation of the activity of all three components in the CaO-Al_2O_3–SiO_2 glass without an additional condition. As the studied samples contained the Al_2O_3 precipitates, it was supposed that (Al_2O_3) was equal to unity. The following Gibbs energies (J $mole^{-1}$) of the glassy aluminosilicate (x(CaO)=0.440 and x(Al_2O_3)=0.128) were obtained in these experiments:

T, K	1133	1140	1152	1165	1178
Exp.	-37630	-37700	-37655	-37590	-37645
Calc.	-37520	-37550	-37600	-37650	-37710

The last row here contains values found by calculation by means of the association-solution model and data of Tables III and IV under assumption that liquid transforms to glass at the isoentropic point and that heat capacities of glass and the equilibrium mixture of crystalline phases are equal.

Samples for investigation of the supercooled liquid were smelted from the glassy specimens and CaF_2. The mole fraction of CaF_2 was in the range of 0.014 to 0.03. The measurements were possible in the very narrow range of 1191 to 1214 K. At lower temperatures the pressures were beyond the sensitivity of the method and at higher ones the melt rapidly crystallized. The following vapour pressures ($p{\times}10^5$, Pa) were obtained in an experiment with the supercooled aluminosilicate melt of x(CaF_2) = 0.014, x(CaO) = 0.434 and x(Al_2O_3) = 0.126 at 1202 K:

Species	CaF_2	AlF_3	SiF_4
Experiment	1.04	1.71	4.35
Calculation	1.09	1.58	4.62

The last row here contains values found by calculation by means of the association-solution model and data of Tables III and IV. It is quite clear that the experiments with metastable samples provide an unambiguous support for validity of the model under considerarion.

There is one more property important for understanding liquid→glass transition. This is viscosity and its connection with the thermodynamic characteristics was expressed as [78,79]

$$\ln(\eta) = A + B/(TS^{conf.}), \qquad (5)$$

where A and B are constants and $S^{conf.}$ is the configuration entropy of liquid. The latter is equal to

$$S^{conf.}(T) = S^{conf.}(T_g) + \int_{T_g}^{T} \left(C_P^{conf.}/T\right) dT. \qquad (6)$$

Here $C_p^{conf.}$ is the configuration heat capacity of liquid and $S^{conf}(T_g)$ - the configuration entropy of liquid at the glass-transition temperature T_g, frozen-in during its transforming into glass. The former can be found as the difference between heat capacities of supercooled liquid and glass. For calculation of the configuration entropy the following equation was proposed [78,79]:

$$S^{conf.} = \Delta_m S + \int_0^{T_m} \left(C_p(\mathrm{c})/\mathrm{T}\right) dT - \int_0^{T_g} \left(C_p(\mathrm{g})/\mathrm{T}\right) dT - \int_{T_g}^{T_m} \left(C_p(\mathrm{l})/\mathrm{T}\right) dT, \qquad (7)$$

where C_P(c), C_P(g) and C_P(l) – heat capacities of crystals, glass and liquid.

$Na_2O{\cdot}2SiO_2$ and $Na_2O{\cdot}3SiO_2$ were chosen for analysing temperature behaviour of viscosity because for these compositions there are sufficient experimental information, found in independent experiments [80-85]. The T_g temperatures were accepted equal to 714 и 742 K found in viscosity measurement [79,82] for di- and trisilicates, correspondingly. Heat capacity of $Na_2O{\cdot}2SiO_2$ in crystalline and glassy states was taken from refs [59,67]. For this composition calculations resulted in $S^{conf.}$ = 27,57 J mole^{-1} K^{-1} and $C_p^{conf.}$ = 46,7 J mole^{-1} K^{-1}. These quantities allowed adequate description of temperature function of viscosity according to equation (5) with the following values of parameters: A= – 0,884 ± 0,038 and B=271430 ± 1420 (Fig.3).

There is no crystalline compound of trisilicate composition in the Na_2O-SiO_2 system and besides the heat capacity of $3Na_2O{\cdot}8SiO_2$, which is closest in composition to trisilicate,

is unknown. For this reason the thermodynamic functions of the equilibrium mixture of solid disilicate with quartz, formed from the liquid of trisilicate composition at the temperature of the $3Na_2O{\cdot}8SiO_2$ peritectoid transformation, were used in viscosity analysis. They were found from data [33,59,69]. Heat capacity of glassy $Na_2O{\cdot}3SiO_2$ was taken from ref. [69]. The calculations resulted in $S^{conf.}$ = 27,67 J mole^{-1} K^{-1} and $C_p^{conf.}$ = J mole^{-1} K^{-1} and optimal approximation of viscosity data were attained at A = -1,034 ± 0,027, B = 282830 ± 1060 (Fig.3). Fig. 3 clearly demonstrates that the association-solution approach describes rather well the non-Arrhenius temperature dependencies of sodium silicates viscosity in wide range from metallurgical temperatures to the glass-transition point.

Conclusions.

A new approach to thermodynamic modelling of liquid metallurgical slags has been developed. It is based on the ideas of the association-solution theory, and considers formation silicon-oxygen polymer networks and complexes between different components. The least-square regression procedure confirmed that the model describes the experimental data on the activities of the components in molten slag and silicates with a precision not worse than the experimental one (1 - 3 %). In complete agreement with the laws of chemical equilibria the thermodynamic characteristics of the same association reaction do not depend on the composition of liquid slags. Together with thermodynamic data on crystalline phases the model gives an accurate description of phase diagrams. It allows reliable extrapolation of the thermodynamic functions of molten silicates into the temperature range of liquid to glass transition and quantitative treatment of experimental data on the structure and viscosity.

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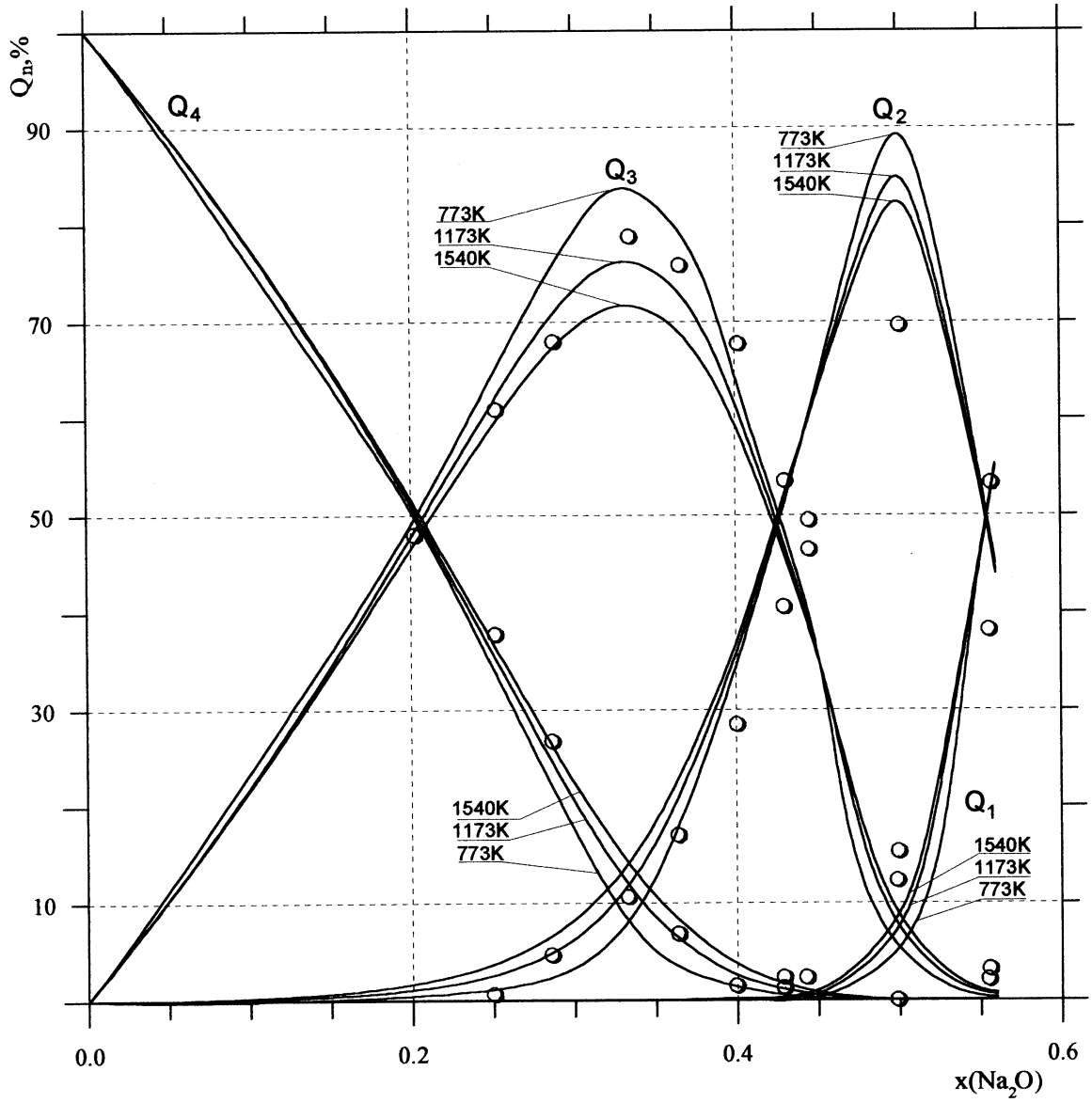

Figure 1. Relative concentrations of silicon-oxygen complexes with one (Q_1), two (Q_2), three (Q_3) or four (Q_4) bridging O atoms. Points – experimental data [52], lines – results of the calculation.

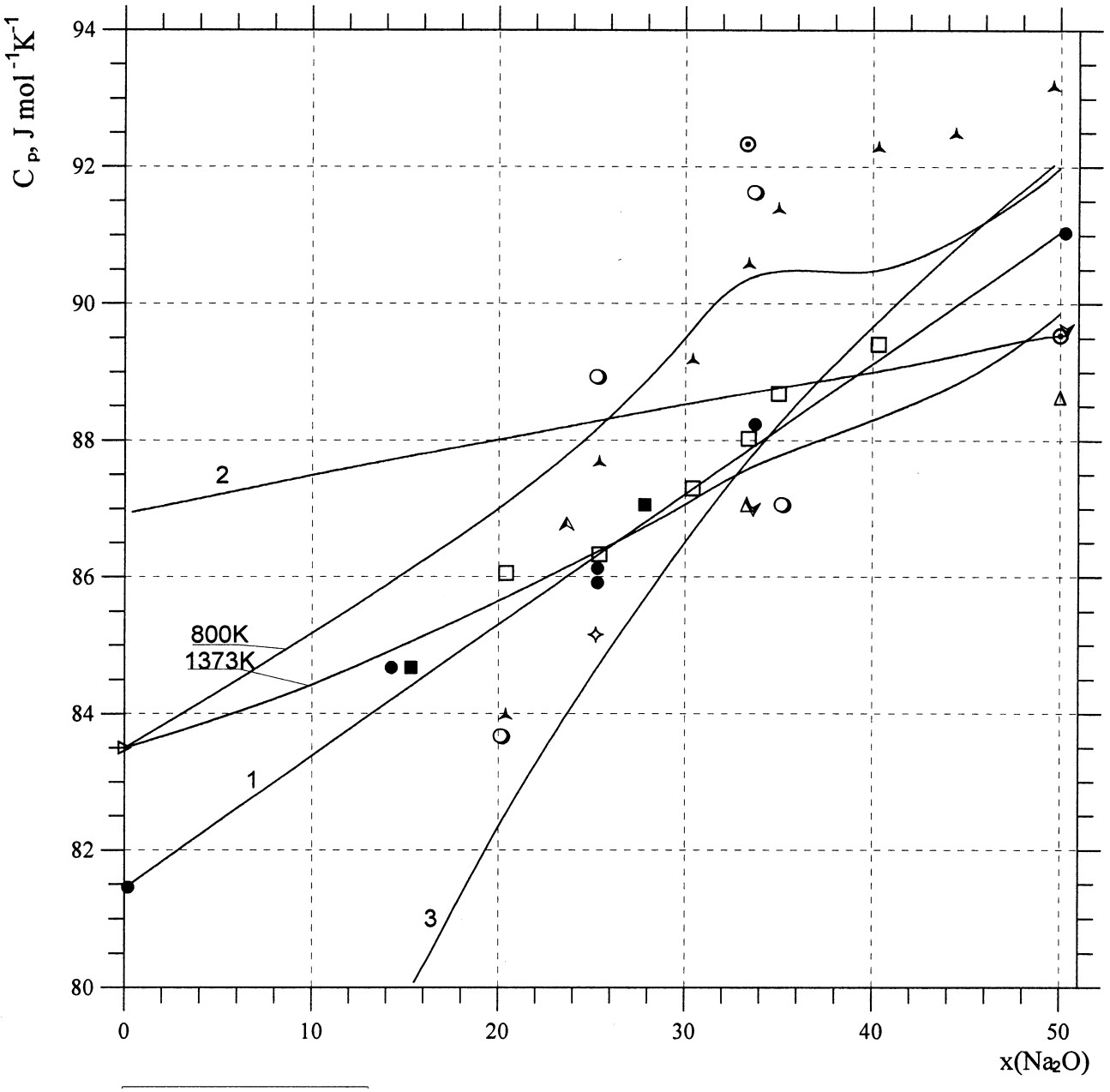

Figure 2. Heat capacity of the Na_2O-SiO_2 melts: lines for 1373 and 800 K – results of present calculations; 1 – [68]; 2 – [64]; 3 – [65]; ⅄ - [57,58]; ■ - [67]; - [66]; ✧ - [63]; ● - [68]; ⅄ - [60]; ⅄ - [61]; ⊙ - [59]; ▷ - [69]; Δ - [70]; ❍ - [62].

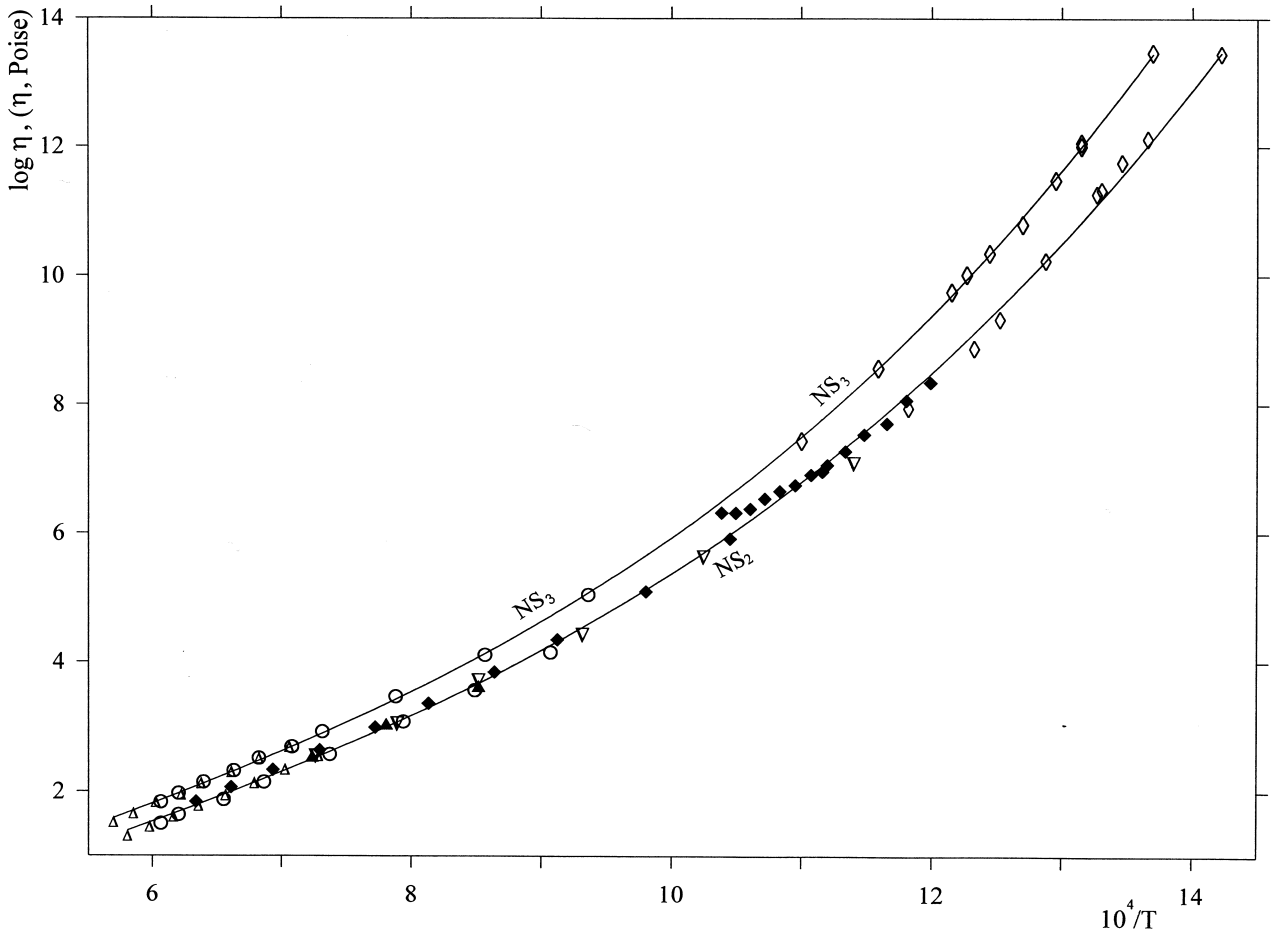

Figure 3. Temperature dependencies of viscosity of the $Na_2O{\cdot}2SiO_2$ and $Na_2O{\cdot}3SiO_2$ melts: lines - present calculations; ○ - [80]; ∇ - [81]; ◊- [82]; ▲ - [83]; Δ - [84]; ◆ - [85].

Table I. Comparison of experimentally obtained entropies of formation of CaF_2-Al_2O_3-CaO melts with the values calculated by means of the models of perfect molecular (p.m.s) and ionic (p.i.s) solutions. T=1723 K.

Composition		Entropy, J mol^{-1} K^{-1}			Composition		Entropy, J mol^{-1} K^{-1}		
$x(CaF_2)$	$x(Al_2O_3)$	exp.	p.m.s.	p.i.s.	$x(CaF_2)$	$x(Al_2O_3)$	exp.	p.m.s.	p.i.s.
0.15	0.25	6.1	7.8	13.5	0.45	0.15	5.5	8.4	15.6
0.2	0.25	6.2	8.3	14.7	0.45	0.25	6.2	8.9	18.2
0.25	0.25	6.3	8.6	15.7	0.45	0.35	7.2	8.7	19.9
0.3	0.2	6.0	8.6	15.5	0.5	0.1	5.1	7.8	13.9
0.3	0.3	6.8	9.1	17.3	0.5	0.2	5.6	8.6	17.3
0.35	0.2	5.9	8.7	16.1	0.5	0.35	6.9	8.3	20.4
0.35	0.35	7.4	9.1	18.7	0.6	0.005	4.4	5.8	8.1
0.4	0.15	5.6	8.4	15.3	0.65	0.005	4.3	6.6	11.0
0.4	0.25	6.2	9.0	17.7	0.8	0.002	3.5	4.7	7.3
0.4	0.35	7.3	9.0	19.4	0.975	0.0125	0.9	1.1	2.9

Table II. Comparison of the thermodynamic characteristics of some associates found as a result of optimising the experimental data for the CaF_2-CaO-Al_2O_3-SiO_2 melt with the values obtained from the data for binary solutions.

Asso-ciate	Δ_f , J mol^{-1}, found data for		Asso-ciate	Δ_f , J mol^{-1}, found data for	
	the four-component system	binary systems		the four-component system	binary systems
CS	-139000-0.6T	-138700-0.8T	S_k	-93000+27.3T	-92600+27.2T CaO-SiO_2
CA	-65200-8.30T	-65300-8.24T			-92750+27.4T K_2O-SiO_2
					-92370+27.1T Na_2O-SiO_2

Table III. Gibbs energies of formation of associative and polymerised species in molten slags and silicates.

Melts	Associate	Δ_f , J mol^{-1}
CaO-Al_2O_3, CaF_2-CaO-Al_2O_3, CaO-Al_2O_3-SiO_2, CaF_2-CaO-Al_2O_3-SiO_2	CA	-65270-8.2T
	C_2A	-111820+2.4T
MnO-SiO_2	MS	-76860-2.9T
	M_2S	-126990+12.4T
CaO-SiO_2, CaF_2-CaO-SiO_2, CaO-Al_2O_3-SiO_2, CaF_2-CaO-Al_2O_3-SiO_2	CS	-138680-0.8T
	C_2S	-270410+41.3T
Al_2O_3-SiO_2, CaO-Al_2O_3-SiO_2 , CaF_2-CaO-Al_2O_3-SiO_2	AS	-21240
MnO-SiO_2, CaO-SiO_2, CaF_2-CaO-SiO_2, CaO-Al_2O_3-SiO_2, CaF_2-CaO-Al_2O_3-SiO_2, Na_2O-SiO_2 , K_2O-SiO_2	SiO_2 networks	-92580+27.2T
CaO-Al_2O_3-SiO_2 , CaF_2-CaO-Al_2O_3-SiO_2	CAS	-207800+155.7T
	CAS_2	-330110+43.6T
	C_2AS	-246520-13.0T
Na_2O-SiO_2	N_2S	-520600+81.3T
	NS	-322800+32.5T
	NS_2	-433200+55.5T
K_2O-SiO_2	K_2S	-634000+89.3T
	KS	-386200+61.9T
	KS_2	-492000+54.7T
CaF_2-Ca_3P_2, CaF_2-Ca_3P_2-CaO	Ca_2PF	-37930+11.1T
	Ca_3PF_3	-80690+18.6T

Table IV . Excess Gibbs energy parameters.

Melts	$_{p,q,r,v}$, J	Melts	$_{p,q,r,v}$, J
$CaO-SiO_2$, $CaF_2-CaO-SiO_2$, $CaO-Al_2O_3-SiO_2$, $CaF_2-CaO-Al_2O_3-SiO_2$	$_{1,1}=$ $_{0,1,1}=$ $_{1,0,1}=$ $_{0,1,0,1}=$ -1070+11.9T $_{2,2}=$ $_{0,2,2}=$ $_{2,0,2}=$ $_{0,2,0,2}=$ -121900	$CaO-Al_2O_3-SiO_2$, $CaF_2-CaO-Al_2O_3-SiO_2$	$_{1,1,1}=$ $_{0,1,1,1}=$-149180
CaF_2-CaO, $CaF_2-CaO-Al_2O_3$, $CaF_2-CaO-SiO_2$, $CaF_2-CaO-Al_2O_3-SiO_2$	$_{1,1}=$ $_{1,1,0}=$ $_{1,1,0}=$ $_{1,1,0,0}=$ RT(3.84-0.00108T) $_{2,2}=$ $_{2,2,0}=$ $_{2,2,0}=$ $_{2,2,0,0}=$ RT(-11.87+0.00472T)	$MnO-SiO_2$	$_{1,1}$=-28150+32.7T $_{2,2}$=-60070
CaF_2-SiO_2, $CaF_2-CaO-SiO_2$, $CaF_2-CaO-Al_2O_3-SiO_2$	$_{1,1}=$ $_{1,0,1}=$ $_{1,0,0,1}$=5390 $_{2,2}=$ $_{2,0,2}=$ $_{2,0,0,2}=$ 90590-49.77T	Na_2O-SiO_2	$_{1,1}$=-24920 $_{2,2}$=-119000
$CaF_2-Al_2O_3$, $CaF_2-CaO-Al_2O_3$, $CaF_2-CaO-Al_2O_3-SiO_2$	$_{1,1}=$ $_{1,0,1}=$ $_{1,0,1,0}=$ RT(-5.53+0.00185T) $_{2,1}=$ $_{2,0,1}=$ $_{2,0,1,0}=$ RT(8.338-0.00251T)	K_2O-SiO_2	$_{1,1}$ = -31300+20.0T $_{2,2}$ = -139000+62.0T

Table V. Comparison of experimentally obtained activities of the components in CaF_2-CaO-Al_2O_3-SiO_2 melts chosen at random with the activities calculated by means of the suggested model (reference states are pure liquid components).

Mole fractions			T K	a(CaO)		a(SiO_2)		a(CaF_2)		a(Al_2O_3)	
SiO_2	CaF_2	Al_2O_3		exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.
0.076	0.479	0.223	1702	5.68×10^{-3}	5.73×10^{-3}	1.91×10^{-3}	1.88×10^{-3}	0.939	0.943	6.95×10^{-2}	6.91×10^{-2}
0.253	0.251	0.178	1706	2.86×10^{-3}	2.84×10^{-3}	4.87×10^{-2}	4.93×10^{-2}	0.511	0.505	4.24×10^{-2}	4.17×10^{-2}
0.335	0.252	0.051	1354	4.67×10^{-4}	4.59×10^{-4}	0.201	0.198	0.543	0.547	1.24×10^{-3}	1.23×10^{-3}
0.079	0.303	0.276	1719	1.97×10^{-2}	1.96×10^{-2}	5.84×10^{-4}	5.91×10^{-4}	0.644	0.638	4.85×10^{-2}	4.79×10^{-2}
0.174	0.255	0.176	1584	1.86×10^{-2}	1.89×10^{-2}	1.54×10^{-3}	1.57×10^{-3}	0.546	0.546	0.171	0.169
0.131	0.199	0.272	1744	2.22×10^{-2}	2.19×10^{-2}	1.45×10^{-3}	1.47×10^{-3}	0.402	0.402	4.84×10^{-2}	4.92×10^{-2}
0.383	0.102	0.107	1585	2.00×10^{-3}	1.97×10^{-3}	0.147	0.146	0.195	0.192	9.08×10^{-3}	9.12×10^{-3}
0.401	0.054	0.125	1729	2.96×10^{-3}	3.02×10^{-3}	0.162	0.165	9.21×10^{-2}	9.12×10^{-2}	1.52×10^{-2}	1.53×10^{-2}
0.426	0.053	0.078	1644	2.21×10^{-3}	2.18×10^{-3}	0.209	0.209	9.69×10^{-2}	9.76×10^{-2}	6.04×10^{-3}	6.13×10^{-3}
0.454	0.059	0.177	1751	1.13×10^{-3}	1.14×10^{-3}	0.330	0.325	9.54×10^{-2}	9.68×10^{-2}	2.86×10^{-2}	2.84×10^{-2}
0.324	0.103	0.212	1773	2.78×10^{-3}	2.81×10^{-3}	9.54×10^{-2}	9.57×10^{-2}	0.175	0.175	6.06×10^{-2}	6.12×10^{-2}
0.256	0.210	0.143	1673	6.60×10^{-3}	6.55×10^{-3}	2.46×10^{-2}	2.48×10^{-2}	0.427	0.426	1.90×10^{-2}	1.91×10^{-2}

Table VI. Enthalpies of sodium meta- and disilicates in glassy and liquid states and the enthalpy of the crystals→glass transformation at standard temperature.

Silicate	Source	T_g,K	$\Delta_v H$(298,15), kJ mole^{-1}	ΔH(g, 298.15-T_g), kJ mole^{-1}	ΔH(l, T_g- T_m), kJ mole^{-1}
$Na_2O{\cdot}SiO_2$	present	706	41,8*	55,1*	120,1*
			36,8**	55,1**	120,1**
			37,4***	54,7***	120,1***
	57	706	32,2	55,1	122,3
	70	900	50,55	86,9	81,9
	72	660	35,6 ±2,9	49,5	127,7
	62		36,2		
	74		36,0		
$Na_2O{\cdot}2SiO_2$	present	750	35,9*	88,3*	107,4*
			29,8**	88,3**	107,4**
			32,5***	91,7***	107,4***
	57		29,1±2,4	88,3	107,9
	73		22,0	84,0	111,1
	72		28,0±2,2		
	75		36,8±0,4		
	62		30,9		
	74		32,7		

* - C_P of the $Na_2O{\cdot}SiO_2$ и $Na_2O{\cdot}2SiO_2$ crystalline phases are taken from [59];

** - C_P of the $Na_2O{\cdot}SiO_2$ и $Na_2O{\cdot}2SiO_2$ crystalline phases are taken from [57,58];

*** – C_P of crystalline and glassy phases are assumed equal, above T_g C_P of the $Na_2O{\cdot}SiO_2$ и $Na_2O{\cdot}2SiO_2$ crystalline phases are taken from [57,58] and [59], correspondingly.