

THERMODYNAMIC PROPERTIES OF SODIUM-CONTAINING GLASSFORMING OXIDE MELTS

ELENA L. KOZHINA, MIKHAIL M. SHULTZ

*Institute of Silicate Chemistry of the Russian Academy of Sciences,
Odoevskogo, 24-2, St.-Petersburg 199155, Russia
E-mail: konakov@isc1.nw.ru*

Submitted May 3, 1999; accepted November 30, 1999.

Electro-motive force investigation of $\text{Na}_2\text{O-R}_a\text{O}_b$ ($R = \text{P, Si, B, Ge}$) and $\text{Na}_2\text{O-Q}_2\text{O}_3\text{-SiO}_2$ ($Q = \text{B, Al}$), as well as $\text{Na}_2\text{O-ZnO-P}_2\text{O}_5$ melts is carried out over a glassforming range. Temperature range under study varies within the limits 800 - 1400 K depending on the system under consideration. A complete set of thermodynamic properties, both partial and integral, is calculated being referred to the corresponding properties of the pure oxides. The results are discussed in terms of acid-base interaction in melt. Chemical structure of the melts is simulated from the ideal associated mixture model. On this basis an account for "germanate" and "borate anomalies" is proposed.

INTRODUCTION

During last several years we have been performing a systematic thermodynamic investigation of a great variety of slag and glassforming melts. We have summarised valuable experimental information about electrochemical processes and thermodynamic properties of alkali-borate, -silicate, -germanate, -phosphate, -borosilicate and -alumosilicate melts. The comprehensive thermodynamic and acid-base information is very important both in theoretical and practical terms. The interpretation of results in terms of the acid-base interaction theory allows describing such an important aspect of properties and structure of melts, as chemical properties, association phenomena, polymerisation and oxidation-reduction equilibrium. Reliable information is reached from the experiments by electro-motive (EMF) technique over the temperature range 800 - 1400 K:

- a complete set of the thermodynamic properties, both partial and integral, for the melt of the following systems: $\text{M}_2\text{O-SiO}_2$ ($M = \text{Li, Na, K, Cs}$) [1 - 4], $\text{M}_2\text{O-GeO}_2$ ($M = \text{Li, Na, K}$) [5, 6], $\text{M}_2\text{O-B}_2\text{O}_3$ ($M = \text{Li, Na, Cs}$) [7, 8], $\text{M}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ ($M = \text{Li, Na, Cs}$) [4, 9], $\text{M}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ ($M = \text{Li, Na}$) [9], $\text{Na}_2\text{O-P}_2\text{O}_5$ [10].
- identification of the devitrification phenomena and an evaluation of the immiscibility gaps for the metastable oxide melts,
- identification of the melt crystallisation raising and evaluation of the crystal phase amount.

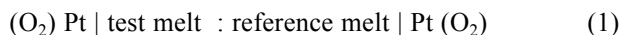
On practical term these results contribute a lot to an extension of the Thermodynamic Data Bank. Moreover, the results discussed in terms of acid-base interaction conception enable us to develop the theory of melt mixture structure. On the other hand these data allow us to evaluate conditions of glass, ceramic and

glass-ceramic manufacture from raw materials for the construction of buildings. GeO_2 - and P_2O_5 -containing glasses seem to be very promising to develop new materials using for non-linear optic, computers, fibers and waveguides.

The aim of this paper is to collate the results of the thermodynamic study of $\text{Na}_2\text{O-R}_a\text{O}_b$ ($R = \text{Si, Ge, B, P}$) [2, 5, 7, 10], $\text{Na}_2\text{O-Q}_2\text{O}_3\text{-SiO}_2$ ($Q = \text{B, Al}$) [9] as well as $\text{Na}_2\text{O-ZnO-P}_2\text{O}_5$ melts.

EXPERIMENTAL PART

To accomplish this task we have carried out the experiments by the electro-motive force (EMF) technique over the glass-forming range. The temperature varied over a range 1100-1450 K. For P_2O_5 -containing systems the range was 850-1200 K. An unconventional variant of a concentration galvanic cell with transference has been worked out when using two air platinum electrodes which are dipped into the crucible containing the melt. The measuring electrode is a platinum wire, the reference one is the platinum wire with a drop of a reference glass.



Pre-crystallized glass of the composition 31.95 Na_2O ·16.82 Al_2O_3 ·51.23 SiO_2 (mole %) has been used as a reference system for all the experiments.

Taking into account the reversibility of the platinum electrode with respect to oxygen according to the reaction



and the conductivity due to the only alkali cation, the EMF values of the cell is related to the activity of Na_2O as follows:

$$\Delta E = RT/2F (\ln a_{\text{Na}_2\text{O}}' - \ln a_{\text{Na}_2\text{O}}'') = -1/2F (\mu_{\text{Na}_2\text{O}}' - \mu_{\text{Na}_2\text{O}}'') \quad (3)$$

where $a_{\text{Na}_2\text{O}}'$ and $a_{\text{Na}_2\text{O}}''$ are the activity of Na_2O in respectively test and reference compositions. Relative partial properties of sodium oxide have been calculated from the temperature dependencies of the EMF values. Using the Gibbs-Duhem's equation a complete set of the thermodynamic partial properties of a glass-forming oxide has been calculated as well. The next step is the estimation of the potential of the melt formation. When studying ternary melts of $\text{Na}_2\text{O}-\text{Q}_2\text{O}_3-\text{SiO}_2$ ($\text{Q}=\text{B}; \text{Al}$), the Darken's approach [11] to integration the Gibbs-Duhem's equation was used to calculate the partial properties of glassforming oxides as well as the potential of the melt formation.

The samples were prepared in a platinum crucible from the following raw materials: Na_2CO_3 , SiO_2 (chemically pure grade), H_3BO_3 , GeO_2 and $\text{Al}(\text{OH})_3$ (very pure grade). The syntheses were performed at temperature 200 °C above the liquidus temperature for 3 - 4 h when stirring the samples.

Samples of the system $\text{Na}_2\text{O}-\text{ZnO}-\text{P}_2\text{O}_5$ containing 38 and 52 mol.% of P_2O_5 ($X_{\text{P}_2\text{O}_5} = 0.38; 0.52$) have been prepared at 1300 K in quartz crucibles from the following starting materials: $\text{Na}_4\text{P}_2\text{O}_7$, Na_2CO_3 and ZnO (all of the pure-for-analysis grade). Electro-motive force investigation of the melts of these samples has been carried out at temperatures 850 - 1200 K. The study has been performed using the cells with and without transference, which we developed before to study binary melts $\text{Na}_2\text{O}-\text{P}_2\text{O}_5$ [10] and $\text{ZnO}-\text{P}_2\text{O}_5$ [12]. Galvanic cell with transference of the type (1) was employed to measure the thermodynamic activity of the alkaline oxide. The reproducibility of the EMF values measured in the series of 8-10 parallel experiments was ± 10 mV.

To measure the activity of ZnO , a construction of the galvanic cell without transference was developed using the electrode reversible to Zn^{2+} ions in the melts:



The reproducibility of measurements of the EMF values of the cell (4) is ± 20 mV. To check the reliability of the experimental results, the latter have been compared with that, obtained using the galvanic cell with transference similar to the cell (1), but using $0.42 \text{ ZnO} \cdot 0.58 \text{ SiO}_2$ melt as a reference. The results are in good agreement within the limits of the experimental error [12]. Partial functions of Na_2O are obtained from the temperature dependencies of the EMF values of the cell (1). The calculation procedure is presented in [1 - 3], where we pioneered the reference of these functions to the corresponding properties of the pure oxides. The values of $\Delta\mu_{\text{Na}_2\text{O}}$ are defined with the accuracy $\pm 1.7 \text{ kJ mol}^{-1}$. The partial thermodynamic data of ZnO have been obtained using the cell (2) and normalized to the corresponding properties of pure oxide with the help of the data presented in [8]. To

calculate the partial properties of P_2O_5 we used the Gibbs-Duhem equation for the ternary system, when $X_{\text{P}_2\text{O}_5}$, temperature and pressure are constant. Taking into account the law of mass balance, we performed integration by parts. Then the free Gibbs energy of $\text{Na}_2\text{O}-\text{ZnO}-\text{P}_2\text{O}_5$ melts formation over the joints with $X_{\text{P}_2\text{O}_5} = 0.38, 0.52$ have been calculated at 1073 and 1173 K.

An unconventional way to normalize these thermodynamic data to the corresponding properties of pure oxides was developed, while the common way is the only comparison to a reference melt [13 - 17]. The first step of normalising the data for $\text{Na}_2\text{O}-\text{SiO}_2$ and $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ melts to pure oxides was the calculation of partial properties of Na_2O related to the reference electrode. Then we have used the limit equations for partial thermodynamic functions of a component, when its amount approaches zero. We normalised $\Delta\mu_{\text{SiO}_2}$, for example, to pure SiO_2 by parallel shifting the concentration dependence to 0 when X_{SiO_2} tends to 1. Next, thermodynamic potentials of sodium metasilicate and sodium metaborate formation have been used [18] to estimate the $\Delta\mu_{\text{Na}_2\text{O}}$ value related to pure Na_2O for the composition $0.5 \text{ Na}_2\text{O} \cdot 0.5 \text{ SiO}_2$. This estimation enables the calculation of chemical potential of Na_2O referred to pure Na_2O over the composition range. Thermodynamic properties of other compound in Na_2O -containing melts not available in the literature were calculated by transformation the data obtained to the pure oxides according to formula cited in [5,10]. The accuracy of the chemical potentials, partial entropies and enthalpies of the components determined was $\pm 2.5 \text{ kJ mol}^{-1}$, $\pm 5.3 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\pm 8.0 \text{ kJ mol}^{-1}$, respectively.

RESULTS AND DISCUSSION

Figures 1 - 3 compare the chemical potentials and partial entropies values for various melts. The curves represent data calculated from the experiments and then

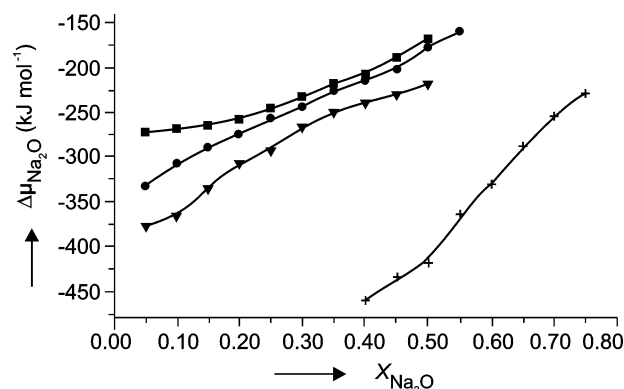


Figure 1. Chemical potentials of Na_2O in various oxide melts at 1300 K.

■ - $\text{Na}_2\text{O} - \text{SiO}_2$, ● - $\text{Na}_2\text{O} - \text{GeO}_2$, ▼ - $\text{Na}_2\text{O} - \text{B}_2\text{O}_3$, ✚ - $\text{Na}_2\text{O} - \text{P}_2\text{O}_5$ (1073K)

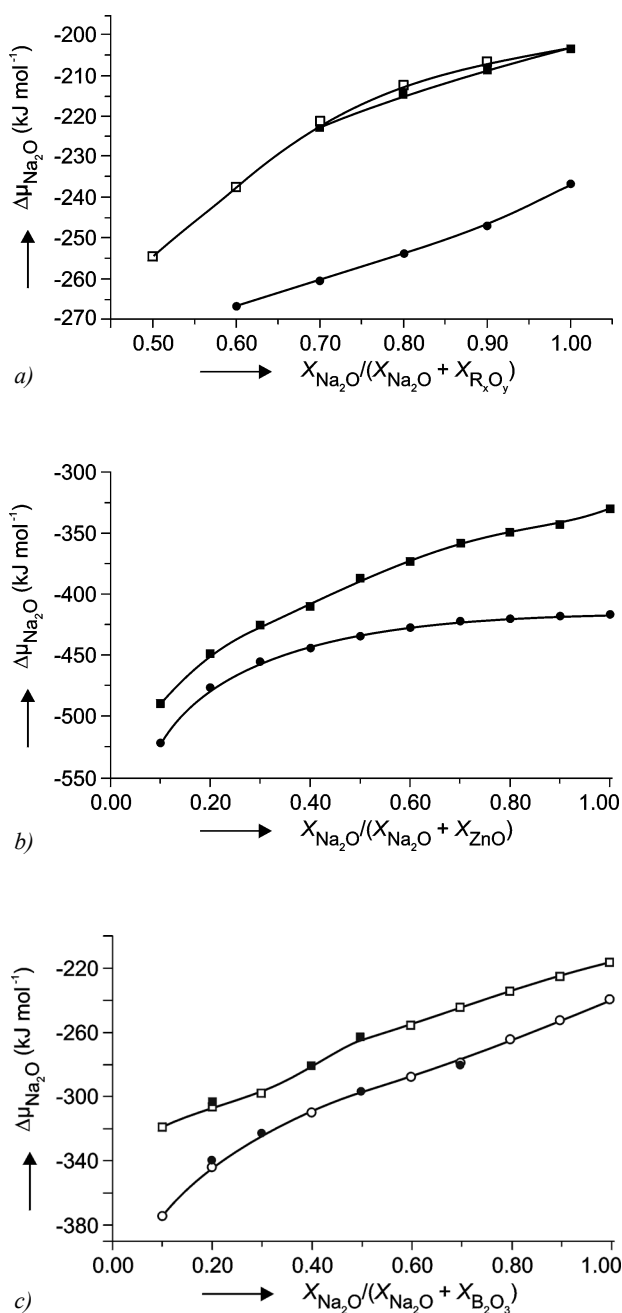


Figure 2. Chemical potential of Na₂O in various ternary melts referring to pure Na₂O. $T = 1300$ K.

a) Na₂O-Al₂O₃-SiO₂, □ - our data, $X_{SiO_2} = 0.6$, ■ - literary data [16], ● - our data, $X_{SiO_2} = 0.7$; b) Na₂O-ZnO-P₂O₅, ● - $X_{P_2O_5} = 0.38$, ■ - 0.52; c) Na₂O-B₂O₃-SiO₂, □ - our data, $X_{B_2O_3} = 0.40$ ○ - our data, $X_{B_2O_3} = 0.60$ ■ - literary data [17] $X_{B_2O_3} = 0.40$, ● - literary data [17], $X_{B_2O_3} = 0.60$

normalized by referring to pure Na₂O using the above procedure. Experimental errors are not indicated on the diagrams because they are negligible within the limits of the chemical potential values. Circles in figures 2 - 3 correspond to the studied compositions, those ones in

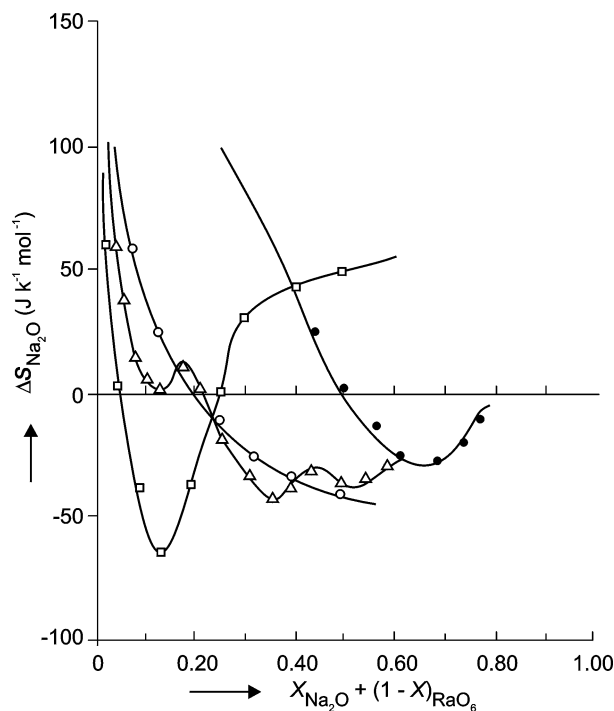


Figure 3. Partial molar entropy of Na₂O in referring to pure Na₂O.

○ - Si, 1300 K, □ - B, 1300 K, △ - Ge, 1300 K, ● - P, 1073 K

figure 1 include intermediate computed data as well. The Gibbs free energy and enthalpy of the melt formation values are summarized in table 1.

We correlated our measurements with the results obtained by [13 - 17]. Good agreement is noted between our normalised data and that of [13 - 17], which we have recalculated to refer them to pure Na₂O according a schema proposed by us [1 - 5]. The data of the Na₂O-SiO₂ and Na₂O-B₂O₃ melts [2, 7], which have served as a reference system in [13 - 17], have been taken into account.

It is established that the formation of the all above melts from its mother oxides is accompanied by a considerable negative deviation from the ideal behaviour of Gibbs free energies and enthalpies. Table 1 compares Gibbs free energies and enthalpies when various sodium-containing oxide melts are formed at 1300 K. For the sodium-phosphate melts these data are evaluated at 1073 K. This gives evidence for a strong chemical interaction between Na₂O and above acid oxides, which being considerably different in their chemical nature follows the patterns similar to acid-base interaction. This negative deviation is found to increase in order: sodium - silicates < germanates < aluminosilicates < borosilicates < borates < phosphates. This is due to the strong chemical interaction between initial oxides resulting in the formation of salt-like groupings, which constitute the melt. These groupings are most likely similar in their stoichiometry and thermal effects of formation and to some extent in

Table 1. ΔG_f and ΔH_f of the sodium-containing melts at 1300 K (kJ mol⁻¹)

$X_{\text{Na}_2\text{O}}$	Na ₂ O - SiO ₂		Na ₂ O - B ₂ O ₃		Na ₂ O - GeO ₂		Na ₂ O - P ₂ O ₅ (1073 K)	
	ΔG_f	ΔH_f	ΔG_f	ΔH_f	ΔG_f	ΔH_f	ΔG_f	ΔH_f
0.1	-26.8	-18.4	-36.4	-38.9	-33.5	-27.6		
0.2	-53.6	-43.1	-67.4	-76.2	-61.8	-55.7		
0.3	-78.7	-73.3	-94.0	-98.8	-86.0	-81.6		
0.4	-98.6	-99.2	-116.0	-110.1	-105.9	-107.2	-224.0	-186.7
0.5	-113.7	-120.6	-134.0	-113.9	-120.7	-129.8	-258.5	-224.4
0.6					-127.8	-137.3	-278.8	-254.1
0.7							-285.2	-272.3

structure to those of the crystalline compounds available in the system according to the phase diagram. The experimental data show that sodium oxide is almost entirely bound into compound even at high temperature (800 - 1400 K). For example, in the sodium metagermanate melt the Na₂O activity is found to be less than 10⁻⁸, and in sodium metaphosphate melt this value does not exceed 10⁻²¹. So, chemical structure of the melts is suggested to be determined by the equilibrium coexistence of the compounds which formation is most relevant in the melt at a given composition. These are the reasons for choosing the ideal associated mixture model to simulate the thermodynamic properties and chemical structure of above melts. On the basis of extensive results accumulated in our earlier studies [1 - 10, 19] we have concluded that this model provides rather adequate description of the thermodynamic behaviour of the systems formed by components which are different in their nature, remaining simple in computation without the adjustable parameters. According to the assumption made in this model, there are domains with the structures similar to that of some compound. So, the melt can be considered as an ideal mixture of these domains. The melt chemical structure exists due to the equilibrium of various compounds, available in the system at the given composition. It is determined by equilibrium constants of the reaction of compound formation from the initial oxides. We have applied to each of such reactions in all above melts both the mass action law and equations of material balance for the given composition of the melts. It yields to the system of equations for each oxide melt, which solution permitted the calculation of "the true molar fractions" of reaction participants using the data on the equilibrium constants. For each compound a range of existence and maximal content within the limits of the range are estimated. Computer simulated data correspond well to that calculated from NMR and Raman spectroscopy data [20]. That confirms the relevancy of the model to describe adequately melt chemical structure and thermodynamic properties. Figure 4 shows the abundance of various compounds at given composition in the Na₂O-ZnO-P₂O₅ and Na₂O-GeO₂ melts. We have modelled using this data the

chemical potential values of Na₂O and established the limits giving a good agreement between the experimental and simulated data.

Equilibrium shifted to sodium borates formation is observed between sodium borate and sodium silicate structural units in Na₂O-B₂O₃-SiO₂ melts. This is due to more negative values of ΔG_f for sodium borate compounds than for sodium silicate ones. Taking into consideration the differences in Na₂O chemical potential and Gibbs free energy values for silicate and borate subnetwork (figure 2, table 1), one may propose that the first step of the process is the sodium tetraborate grouping's formation. Di- and metaborates as well as di- and metasilicates are formed when Na₂O content increases. By contrast, in Na₂O-Al₂O₃-SiO₂ melts the equilibrium between sodium aluminates and sodium silicates is dramatically shifted to the formation of latter ones. The decrease in chemical potential values when Al₂O₃ substitutes SiO₂ (figure 2) results from the equilibrium shift of the reaction occurring in the melt towards the formation of more stable compound. In a given composition range it is a ternary compound Na₂O·Al₂O₃·nSiO₂.

As for Na₂O-ZnO-P₂O₅ system, thermodynamic regularities follow their distinct patterns. Formally the sodium-zinc-phosphate melts results from interaction of an oxide with strong basic properties (Na₂O), an oxide with strong acidic properties (P₂O₅) as well as amphoteric oxide (ZnO). One would expect that the thermodynamic behaviour of this melt follows the same patterns as the melts of Na₂O-Al₂O₃-SiO₂ system which components are of a similar chemical nature. Namely, Na₂O is strong basic oxide, SiO₂ is acidic one and Al₂O₃ is known to have amphoteric properties.

From the results obtained it follows that sodium-zinc-phosphate melts are formed with quite considerable exothermic effects. Their Gibbs energies and enthalpies of formation demonstrate negative deviations from the ideal behavior as it is evident from the table 1. This gives evidence of the chemical interaction between the oxides Na₂O, ZnO and P₂O₅ resulting in the formation of salt-like groupings in the melt. The deviations become more pronounced as P₂O₅ content decreases. However, the equilibrium constants of zinc phosphates formation are noticeably smaller

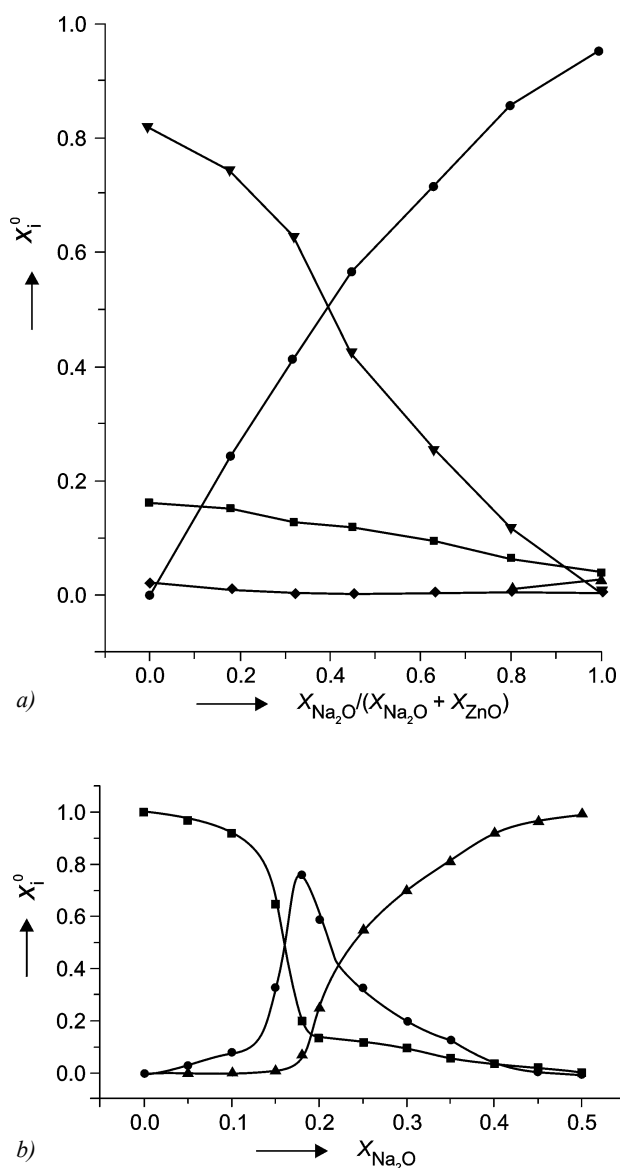


Figure 4. Simulation of the chemical structure of $\{x\text{Na}_2\text{O} + (0.62-x)\text{ZnO} + 0.38\text{P}_2\text{O}_5\}$ and $\{x\text{Na}_2\text{O} + (1-x)\text{GeO}_2\}$ melts. Curves correspond to mole fractions of the following compounds: a) - $\{x\text{Na}_2\text{O} + (0.62-x)\text{ZnO} + 0.38\text{P}_2\text{O}_5\}$ at 1073 K, \blacksquare - P_2O_5 , \bullet - $\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$, \blacktriangle - $2\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$, \blacktriangledown - $\text{ZnO} \cdot \text{P}_2\text{O}_5$, \blacklozenge - $2\text{ZnO} \cdot \text{P}_2\text{O}_5$; b) - $\{x\text{Na}_2\text{O} + (1-x)\text{GeO}_2\}$ at 1273 K, \blacksquare - GeO_2 , \bullet - $2\text{Na}_2\text{O} \cdot 9\text{GeO}_2$, \blacktriangle - $\text{Na}_2\text{O} \cdot \text{GeO}_2$

than those of formation of alkali ortho-, pyro- and metaphosphates. This is in agreement with acid-base properties of the components of zinc phosphate and alkali phosphate systems. It has been found experimentally that the chemical interaction of the components of oxide melts increases in the series $\text{ZnO} \cdot \text{P}_2\text{O}_5 < \text{Na}_2\text{O} \cdot \text{ZnO} \cdot \text{P}_2\text{O}_5 < \text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$. It can be noted, that negative deviations from additive behavior of ΔG_f both from the joint with $X_{\text{P}_2\text{O}_5} = 0.38$ and with $X_{\text{P}_2\text{O}_5} = 0.52$ is not so considerable. It is due to the

formation of a number of ternary compounds in the melts according to the phase diagram of $\text{Na}_2\text{O} \cdot \text{ZnO} \cdot \text{P}_2\text{O}_5$ system. Rather low values of the deviations from additivity result from that it is hardly probable that the ternary compound formation appreciably affects the chemical structure of the melts. Hence, the formation of binary sodium- and zinc phosphates formation mentioned above may be the determining factor in the chemical structure and thermodynamic properties of the melts. Taking into consideration the differences in Na_2O and ZnO chemical potential values one may propose, that the first step of the process is sodium phosphate grouping's formation.

We can note that the formation of ternary compounds is of the high importance in the $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ melts. The formation of the relevant binary compounds in the other above ternary systems runs concurrently and dominates the process of the ternary compound occurrence. Suggestion can be made; it is necessary that the structure of various glassforming oxides would be similar to promote the ternary compound formation in the melt. An example of the $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ melts gives evidence for this.

Numerous structural studies have been carried out in order to elucidate the causes of the "borate and germanate anomalies". They are manifested by extreme in concentration dependencies of various parameters: density, viscosity, refractive index. These phenomena are usually accounted for the variation in the coordination number with regard to oxygen like $\text{B}^3 \rightarrow \text{B}^4$; $\text{Ge}^4 \rightarrow \text{Ge}^6$. As for thermodynamic properties, complicated character of the entropies concentration dependencies is noted for binary sodium oxide systems, as can be seen in figure 3. We have attempted to account for this non-monotone behaviour by the change in relative content of compounds, available in the melts. As can be seen in figure 4, the chemical structure of sodium zinc phosphate melt changes with Na_2O content increase. It varies from the chains of PO_4 tetrahedra in pure P_2O_5 to metaphosphates (tetrahedra with one non-bridging oxygen atoms) and then to pyro- and orthophosphates (two and three non-bridging oxygen, respectively). The contributions from different compounds to the chemical constituents of partial and integral entropies are in accordance with the above structural changes in melts. We have derived in [5] an equation for the partial entropy of the components ($\Delta S_{\text{M}_2\text{O}}$), where the number of moles of arisen compounds (n_i), the entropies of their formation from oxides (ΔS_{n}^0) and the mole fraction as well as the number of moles of both the resultant compounds and unreacted oxides (X_j^0, n_j) are involved.

$$\Delta S_{\text{M}_2\text{O}} = [\Delta S_{\text{n}}^0 (n_i + X_{\text{RaOb}} \frac{dn_i}{dX_{\text{M}_2\text{O}}})] - R \{ \sum [X_j^0 (n_j + X_{\text{RaOb}} \frac{dn_j}{dX_{\text{M}_2\text{O}}})] \} \quad (5)$$

From the figure 4 it follows that the structure of the melt in the low-alkali region corresponds predominantly to the solution of the first compound formed in the system under consideration in the glass-forming oxide. In

sodium-borate and -germanate melts the occurrence of the compounds, in which the co-ordination numbers of boron and germanium atoms vary as follows: $B^3 \rightarrow B^4$, $Ge^4 \rightarrow Ge^6$ is established. These compounds ($Na_2O \cdot 4B_2O_3$, $2Na_2O \cdot 9GeO_2$) are formed just over low-alkali region of both systems. They provide a considerable negative contribution to the partial entropies of alkali oxides ($\Delta S_{r1}^0 < 0$), while the positive contribution of configuration entropy runs concurrently for the both systems. In the low alkali region, where the number of such groupings is large and the derivative dn_j / dX_{M_2O} increases, this results in the sharp decrease in the partial entropy of Na_2O . The increase in the amount of the second compound ($Na_2O \cdot 2B_2O_3$ or $Na_2O \cdot GeO_2$) with the rise of the alkali content leads to an increase in the corresponding contribution to the partial entropy, which is positive due to the ΔS_{r2}^0 values. This fact accounts for availability of minima on the dependencies $\Delta S(Na_2O)$ vs. X_{Na_2O} .

Such consideration of the reasons for the germanate and borate anomalies is consistent with any structural interpretations mentioned above. Without pretending an accurate description of the melt structure as a geometric arrangement of atoms, we attempted to explain the non-monotony behaviour of the melt dependencies on their composition in the context of chemical processes, which proceed in the system. A sharp difference in the thermodynamic properties of the compounds that are formed in the low- and high-alkali regions is undoubtedly associated with their structural distinctions. We hope that they will be described subsequently in more detail using structurally sensitive techniques.

The same idea outlines the consideration of the chemical potential values dependencies in figure 1. Bends of the curves falling out the limits of error are observed. These data present evidence for a concentration fluctuation. There is no reason to relate this to miscibility gap. They are most probably due to the change in chemical structure of the melts. The behaviour of the simulated chemical potential is determined by the formation of compounds, or precise by the ratio of their equilibrium constants for the reaction formation. The model results in the smoothen dependence $\Delta\mu_{Na_2O} = f(X_{Na_2O})$ in the region where a given compound just arises. But it becomes steeper, so the derivative $d\mu_i / dX_i$ sharply increases, when the greatest amount of the given compound is reached.

CONCLUSION

The EMF study of sodium-containing glassforming oxide melts is carried out for silicate, borate, germanate, phosphate and zinc-phosphate systems. The temperature range under study is 1100 – 1450 K, for P_2O_5 -containing systems – 850 – 1200 K. The set of partial properties of the components, as well as Gibbs free energy values of the melt formation are obtained, being normalized to pure oxides. At the formation of melts a significant negative deviation from the ideal

behavior of these thermodynamic properties is observed. This negative deviation is found to increase in order: sodium-silicates < germanates < aluminosilicates < borosilicates < borates < phosphates. This is due to the strong chemical interaction between initial oxides resulting in the formation of salt-like groupings, which constitute the melt. The chemical interaction of the components of oxide melts is found to increase in the series: $ZnO \cdot P_2O_5 < Na_2O \cdot ZnO \cdot P_2O_5 < Na_2O \cdot P_2O_5$. A computer simulation of the chemical structure are made from the ideal association mixture model. Based on this modeling, reasons of germanate and borate “anomalies” are suggested.

References

1. Kozhina E.L., Shakhmatkin B.A., Shultz M.M.: Vestnik Leningr. State Univ. Ser. I, 55 (1986).
2. Shakhmatkin B.A., Shultz M.M.: Fizika i Khimiya Stekla 6, 129 (1980). (in Russian)
3. Kozhina E.L.: Fizika i Khimiya Stekla 16, 679 (1990). (in Russian)
4. Kozhina E.L., Shultz M.M.: XVIII International Congress on Glass. San Francisco, California, USA. July 5-10, 1998. Proceedings on CD. Abstract: ICG XVIII Meeting Guide, AB 89.
5. Kozhina E.L., Shultz M.M.: Glass Physics and Chemistry, 21, 186 (1995).
6. Kozhina E.L., Bessedina S.V., Konakov V.G., Shultz M.M.: Glass Physics and Chemistry, 25, 401 (1999).
7. Shakhmatkin B.A., Shultz M.M.: Fizika i Khimiya Stekla (in Russian) 8, 270 (1982).
8. Kozhina E.L., Shultz M.M.: Glass Physics and Chemistry, 22, 338 (1996).
9. Shultz M.M., Kozhina E.L., Shakhmatkin B.A.: Fizika i Khimiya Stekla 15, 500 (1989). (in Russian)
10. Kozhina E.L., Shultz M.M.: J.Chem.Thermodynamics 29, 797 (1997).
11. Darken L.S.: J.Amer. Ceram. Soc. 72, 2909 (1950).
12. Konakov V.G., Shultz M.M., Shakhmatkin B.A.: J.Chem.Thermodynamics 29, 785 (1997).
13. Itoh H., Sasahira A., Maekawa T., Yokokawa T.: J.Chem.Soc., Faraday Trans. 80, 473 (1984).
14. Yokokawa T., Kohsaka S. J.Chem.Eng.Data, 24, 167 (1979).
15. Yokokawa T., Tamura M., Sato S., Niwa K. Phys.Chem. Glasses, 15, 113 (1974).
16. Itoh H., Yokokawa T.: Trans. Japan Inst. Metals 25, 879 (1984).
17. Asai K., Yokokawa T.: Trans. Japan Inst. Metals 23, 571 (1982).
18. Barin I., Knacke O.: *Thermochemical properties of inorganic substances*. 921 p. Springer-Verlag, Berlin-Heidelberg-New York. 1973.
19. Shultz M.M.: Trans.Indian Ceramic Soc. 46, 95 (1987).
20. Martin S.W. Eur.J.Solid.State Inorg.Chem. 28, 163 (1991).

Submitted in English by the authors.

TERMODYNAMICKÉ VLASTNOSTI TAVENIN
OXIDU SODNÉHO A SKLOTVORNÝCH OXIDŮ

ELENA L. KOZHINA, MIKHAIL M. SHULTZ

Institute of Silicate Chemistry
of the Russian Academy of Sciences,
Odoevskogo, 24-2, St.-Petersburg 199155, Russia

Taveniny $\text{Na}_2\text{O}-\text{R}_a\text{O}_b$ ($\text{R} = \text{P}, \text{Si}, \text{B}, \text{Ge}$), $\text{Na}_2\text{O}-\text{Q}_2\text{O}_3-\text{SiO}_2$ ($\text{Q} = \text{B}, \text{Al}$), a $\text{Na}_2\text{O}-\text{ZnO}-\text{P}_2\text{O}_5$ byly

zkoumány metodou EMF v teplotním rozmezí 800 - 1400 K. Byla vypočtena kompletní sada parciálních a integrálních termodynamických vlastností tavenin vztažených k vlastnostem čistých oxidů. Výsledky jsou diskutovány z pohledu acido-bazických interakcí v tavenině. Chemická struktura tavenin je simulována modelem ideálního míchání. Na tomto základě byl navržen popis germanicitých a boritých anomálií.

AN INTRODUCTION
TO THE MECHANICS OF FLUIDS

By C. Truesdell and K.R. Rajagopal.

Birkhäuser, Boston / Basel / Berlin 2000.
296 pages, hardcover, price 148.00 DM.
ISBN 3-7643-4014-2 and 0-8176-4014-2.

<http://www.birkhauser.ch> or <http://www.birkhauser.com>

When writing this review it came to my knowledge that Clifford Ambrose Truesdell (1919 - 2000) has died. Comparable with Einstein, Heisenberg, Feynman and a few others he was without doubt one of the most eminent scientists of the twentieth century. Unfortunately - or should I say fortunately? - he was active in a field less en vogue than relativity and quantum mechanics: continuum thermomechanics. He initiated the renaissance of classical continuum mechanics (rational mechanics) in the second half of the 20th century, extended rational science to include thermodynamics and laid the foundations of rational mixture theory. He founded two scientific journals, which range among the best in the world, the "Archive of Rational Mechanics and Analysis" and the "Archive of the History of Exact Sciences", wrote and edited innumerable books, many of which have now become classics of science (e.g. The Classical Field Theories (1960, with R. Toupin), The Non-Linear Field Theories of Mechanics (1965, with W. Noll), Rational Thermodynamics (1969)). Apart from his editorial work in Flüge's "Handbook of Physics", one of the leading compendia of physics in the 20th century, he cooperated also in one of the most important scientific editions of mankind, Euler's "Opera Omnia" (edited from 1911, up to now 76 volumes published, all still available at the Birkhäuser editorial!). This last Truesdell book was written in cooperation with a famous young professor, belonging to the second generation of the influential Truesdell school, K.R. Rajagopal (now at Texas A&M University), member of the advisory editorial board of Birkhäuser's series "Modeling and Simulation in Science, Engineering and Technology" (series editor N. Bellomo), in which the book has been published. Rajagopal has presented some of his ideas as well as his overwhelming didactic skills at the Fourth Winter School "Mathematical Theory in Fluid Mechanics" at Paseky (Czech Republic), 3-9 December 1995, where I had the opportunity to attend his lectures. His book "Mechanics of Mixtures" (together with L. Tao) has also

been reviewed in this journal (*Ceramics-Silikáty 2 / 1997*).

The present book is divided into eleven chapters:

1. Bodies, configurations and motions,
2. Kinematics and basic laws,
3. Constitutive equations, reduced constitutive equations, and internal constraints,
4. Simple fluids,
5. Flows of incompressible fluids in general,
6. Some flows of particular nonlinear fluids,
7. Some flows of fluids of grade two,
8. Navier-Stokes fluids,
9. Incompressible Euler fluids,
10. Compressible Euler fluids,
11. Singular surfaces and waves.

The title "An Introduction to the Mechanics of Fluids" sounds very unpretentious. In fact, this advanced monograph presents one of the best new views on the subject for those who like relative simplicity and certain abstractness combined with mathematical rigor and elegance. It needs no comment that all details in this book are carefully worked out and to a large degree based on original work and lifelong experience. The topics range from Euler fluids to memory fluids, and the framework is general enough to treat other nonlinear fluids than those explicitly mentioned. Agreeable is the fact that models of fluids of second and third order, which can be useful in experimental work, are presented in great extent due to Rajagopal's expert knowledge in this field. The book should be useful for graduates and researchers not only in applied mathematics and mechanical engineering but also in advanced materials science and technology. For those without sufficient mathematical training Truesdell's book "A First Course in Rational Continuum Mechanics" (1991) can be warmly recommended as an introduction. As far as I know, based on this "First Course" Truesdell planned to write one book on hydrodynamics and one on elasticity. With the present book, "An Introduction to the Mechanics of Fluids", the first plan is fulfilled and each public scientific library as well as all hydrodynamics hand libraries should own this timeless book. The second will remain a promise never to be realized. Doubtlessly everyone who decides to buy this book can be sure to have bought a classic of science and the heritage of an outstanding scientist.

Willi Pabst
ICT Prague