

HIGH TEMPERATURE MASS SPECTROMETRIC STUDY OF OXIDE MELTS

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Vaporization processes and thermodynamic properties of oxide melts have the great importance in various fields of high temperature technologies. Comparison of available thermodynamic properties of binary borate, silicate, germanate and phosphate melts studied by high temperature mass spectrometric method is carried out from the point of view of acid-base concept. Reliability of the data obtained by this method illustrated by the comparison with the values found using the various mass spectrometric approaches and by the various methods of high temperature chemistry such as EMF, high temperature solution calorimetry and exchange equilibria in slags.

It was shown that the deviations from the ideality of the chemical potentials of P_2O_5 , B_2O_3 , SiO_2 and GeO_2 as function of the content of oxide-modifier in the series of binary systems are in the agreement with the variety of vaporization processes such as dissociation, association and polymerization.

Introduction

The progress in advanced fields of technology, e.g. metallurgy, power engineering, rocket engineering, jet aircraft, instrument making, as well as laser, electronic and communication engineering, demands the development and use of new superhard, high-melting, heat-resistant materials with given properties. Oxide materials are very valuable from this point of view. They are characterized by a great variety of physical and chemical properties which are indispensable in any branch of modern manufacture. Knowledge of high temperature behaviour including vaporization processes and thermodynamic properties of oxide melts is one of the steps in the solution of the task considered. The influence of the vapour temperature on the properties of materials in various industrial processes may be more thoroughly taken into account if one considers phase equilibria among all the phases, both the condensed and gaseous ones. This is important for the production and use of high-temperature coatings, composites, glasses and ceramics.

Modern technologies operate nowadays with data bases of models and thermodynamic data of oxide melts which allowed to calculate the properties of multicomponent melts and new materials. Results of the experimental studies of these properties are one of the criteria of such calculations. One of the powerful methods of studies of vaporization processes and thermodynamic properties at high temperatures is the high temperature Knudsen effusion method. This method allows to identify the composition of the gaseous phase and to obtain thermodynamic properties of components in the vapour and condensed phases (1).

The purpose of this review is to summarize and to discuss experimental data on vaporization processes and thermodynamic properties of the binary oxide systems, obtained using this method.

Vaporization processes of the binary oxide melts

As follows from Table 1 owing to the high temperature mass spectrometric studies a lot of experimental information was obtained on vaporization processes of binary oxide melts.

In the last two decades mass spectrometry has taken a leading place in the investigation of the vaporization of oxide melts started by the work of Preston and Turner (65). One of the first studies in this field, anticipating the possibility of using high-temperature mass spectrometry to study glasses and even oxide systems in general, was work investigating the volatility of glaze components using spectrograph (66). As early as 1940, Harrison et al. (66) determined the temperatures of vaporization of boron (723 K), lead (1023 K) and chromium (1273 K) from glazes containing oxides of potassium, sodium, calcium, lead, zinc, aluminium, silicon, boron and chromium. It was also shown that the volatility of B_2O_3 is higher than that of PbO when glazes with a high content of calcium and small content of boric and lead oxides vaporize.

The questions of obtaining and the application of oxide melts at high temperatures are closely connected with the studies of vaporization processes. However the results of earlier publications, where these processes were studied without mass spectrometric analysis of vapour phase, are very contradictory. For example, data on partial pressures of vapour species in the $Na_2O-B_2O_3$ system are significantly different in the publications carried out by the dynamic method with nitrogen leak-in (67), by the Knudsen effusion method (68) and by the method based on the velocity of vaporization (69). Attention will be given at this point only to the vaporization process for the composition of melt containing $Na_2O \cdot 2B_2O_3$.

Determining mass losses in the course of sodium diborate vaporization at 1423-1673 K, the conclusion was arrived at (67) that the vapour contained 51.6 mass % of Na_2O and 48.4

mass % of B_2O_3 . The vapour pressure was determined assuming that, during vaporization, 30.1 mass % of Na_2O and 69.9 mass % of $Na_2O \cdot 2B_2O_3$ pass to the gaseous phase. This conclusion has been questioned (68), since the vapour composition can be represented only in accordance with the composition of the condensed phase, in which sodium and boron oxides are in the ratio 30.8 mass % of Na_2O and 69.2 mass % of B_2O_3 . On the basis of determining the vapour chemical composition and of measurement of the $Na_2O \cdot 2B_2O_3$ volatility Solomin (69) showed that, at 1473 K, the extent to which sodium diborate decomposes is not very great, while at 1673 K the vapour contains 30 % of $NaBO_2$. Authors (70) measured the mass losses during vaporization the melt containing $Na_2O \cdot 2B_2O_3$ at 1673 K and suggested that this compound vaporizes with decomposition on B_2O_3 and $NaBO_2$. At the same time, Kolykov (71), using the results of the chemical analysis of the condensate collected during the vaporization of a number of glasses of the Na_2O - B_2O_3 system, established that the composition of the condensate (and, consequently, of the vapour) changed with a change of temperature. The validity of the assumption about $Na_2O \cdot 2B_2O_3$ vaporization at 1673 K, with the subsequent decomposition into B_2O_3 and $NaBO_2$ (stated when measuring mass losses (68)), as well as the conclusions of Ref. (69), have been confirmed when studying the Na_2O - B_2O_3 system by the mass spectrometric technique (25-27, 34).

In the Na_2O - SiO_2 system disagreement of the results obtained by the Knudsen effusion method (72) and by the determination of vapour pressure using the weight of condensate (65) were mentioned.

Thus, the main reason of the disagreements mentioned is in the general reason for all mentioned experimental approaches (67-72) the absence of the reliable information on the composition of the vapour phase over the melts in the Na_2O - B_2O_3 and Na_2O - SiO_2 systems. As mentioned above one of the advantages of the high temperature mass spectrometric method is the opportunity to identify the content of the gaseous phase.

Piacente and Matousek (4) were the first who applied this experimental approach to study oxide melt containing $Na_2O \cdot 2SiO_2$. These results confirmed data in Ref. (72) and illustrated disagreement with the results obtained in Ref. (65).

Vaporization processes of the individual oxides, salts and complex oxide systems have been discussed in the following monographs (73-75). In the present study we shall consider the features of vaporization of the silicate, germanate, borate and phosphate melts. The absence of some experimental data will not allow to have the general theory of the prediction the composition of vapour over oxide melts. However the question on the regularities of oxide melts vaporization has the practical and theoretical importance. The solution of this question first of all is closely connected with the changes of content in the vapour phase over the individual oxides as a function of temperature (73).

Results of mass spectrometric studies of vaporization processes of silicate (2-23, 43, 60, 61), table 2, and germanate (5, 20, 24-33), table 3, melts illustrates the same vapour species over the melts as over the individual oxides.

Alkaline silicate melts vaporizes in general as individual oxides with the dissociation on alkaline metal and oxygen with the corresponded residual in the condensed phase. As in the Na_2O - GeO_2 system it seems that the similar behaviour can be expected during vaporization of the other alkaline germanate systems with the presence in the gaseous phase alkaline metal, oxygen and germanium monoxide. However the level of association in vapour during vaporization of silicate and germanate melts becomes lower compared with the individual oxides in the order of the following systems Bi_2O_3 - GeO_2 , Sb_2O_3 - GeO_2 , PbO - SiO_2 . For example, in Ref. (33) it was shown, that the ratio of the partial pressures of the main vapour species (p_i) in the Bi_2O_3 - GeO_2 at 1100 K was $p_{Bi} : p_{O_2} : p_{Bi_4O_6} : p_{Bi_2O_3} = 1 : 0.3 : 0.1 : 0.05 : 0.02$. But when the mole fraction of Bi_2O_3 was decreased the content of multiatomic molecules was also decreased and

was found on the level of the sensitivity of mass spectrometer. Comparison of the vapour composition over the melts of individual PbO and of the PbO-SiO₂ (21, 73) illustrated that the level of polymerization of PbO was decreased from four to two. In the gaseous phase over the MgO-SiO₂ system the tendency to dissociation of SiO₂ was increased compared with the individual oxide with the formation of SiO and O₂ (12-14). The formation of the gaseous compounds in vapour over germanate and silicate melts as follows from the results (2-33,60,61) was not typical.

However for the formation of the new vapour species the ratio of the volatility of the individual oxides was one of the main factors. In the cases, when these values were closed to each other the identification new vapour species was possible such as in the systems SrO-B₂O₃-SiO₂ the SrSiO vapour species were found (43), in the CaO-SiO₂ - CaSiO₃ (15) and in the BaO-GeO₂ - BaGeO₂ (28). From the one hand it may be the exception to the rule, but from the other hand together with the information on the existence of the following vapour species such as KSiO (76), Li₂SiO₃ (2,3,74), AlSiO (61,77) allows to suggest the existence more complex vapour molecules over silicate and germanate melts particularly at the temperatures higher than 1600 K.

The main feature of the vaporization of borate melts was the transition to the gaseous phase of associates as the monomers and the dimers, table 4. The formation of the new vapour species was found in the alkaline borate systems (1, 25-27, 34) as well as in the Bi₂O₃-B₂O₃ and PbO-B₂O₃ systems: Bi₂BO₄, Bi₃BO₆, BiBO₃, Pb_nO_n•BO and Pb_nO_n•B₂O₃ (n=1-5) (49,50). Data on the vaporization processes of alkalineborates were in the good agreement but the same information on the alkali earths borates was contradictory. Composition of vapour over the MO-B₂O₃ (M= Be, Mg, Ca, Sr, Ba) systems was the function of chemical nature of oxide modifier and the ratio of mole fractions of MO: B₂O₃ (35-47). It should be mentioned that the vaporization of B₂O₃ was the characteristic of the vaporization of all borates studied. However, the presence in the gaseous phase over the BeO-B₂O₃ only M(BO₂)₂ molecule, its dissociation in the vapour over the MgO-B₂O₃ and BaO-B₂O₃ systems with the formation of the MBO₂ and M vapour species and the absence of such molecule over the SrO-B₂O₃ system had no explanation nowadays and was not discussed. In this connection the influence of the temperature on the equilibrium constant of the gaseous phase reaction which can be lead to the changes of the composition of vapour over the MO-B₂O₃ (M=Be, Mg, Ca, Sr, Ba) should be mentioned.

There were the few mass spectrometric studies on the vaporization processes of phosphate melts (1, 51-59, 64), table 5. In vapour over phosphate melts the gaseous species corresponded to the vaporization of the individual oxides, new associates (NaPO₃, NaPO₂, CaPO₂, BaPO₂, GePO₃) and PO, PO₂ were identified. Detail review on the vaporization processes of phosphate melts was presented in Ref. (54).

Thermodynamic properties of oxide melts

Despite the fact that vaporization processes of oxide melts have been studied by the high temperature mass spectrometric method in detail for the series of oxide melts, table 1, the complete set of thermodynamic functions was obtained only for some of them. So in this review only publications where partial vapour pressures (p_i), enthalpy vaporization of components

($\Delta H_{v,i}$), activities (a_i), coefficients of activities (f_i) and chemical potentials of components ($\Delta \mu_i$), Gibbs energies (ΔG) as well as integral enthalpy (ΔH) and partial enthalpies of formation (ΔH_i) have been obtained should be mentioned.

Silicate systems. Silicate melts and glasses, known since the fifteenth century BC in ancient Egypt, account for 90 % of commercial production to date. It is not surprising, therefore, that the study of the $\text{Na}_2\text{O-SiO}_2$ system, on which they are based, has been undertaken by the Knudsen mass spectrometric effusion technique by many authors (4-9), table 2. In addition to the practical importance of this system, interest in it as a model system has been stimulated by a large number of studies in which thermodynamic functions have been determined by various methods of high temperature chemistry (78-83) including the e.m.f. method, the gas solubility (or chemical equilibrium) method, by optical absorption and by high temperature calorimetry. This allowed (4-9) confirmation of the correctness of the results of the application of the Knudsen mass spectrometric effusion technique as a whole to the $\text{Na}_2\text{O-SiO}_2$ system and an extension of its use for the investigation of more complex glass-forming systems. However partial molar enthalpies of mixing of Na_2O were obtained by the flow method (79) were determined with the relative error more than 40 % and did not allow to find the reliable values of integral enthalpies of formation of sodium silicate melts. In spite of the discrepancy of the values of vaporization enthalpy of Na_2O at 1200-1720 K one can observe a general tendency for a decrease of the values with an increase in the Na_2O concentration. Altemose and Tong think that the results obtained by them (5) for the concentration range of the $\text{Na}_2\text{O-SiO}_2$ system lower than 4 mass % Na_2O are not completely reliable, because no equilibrium was established in the effusion cell, due to the appreciable depletion of the surface owing to sodium vaporization. The lower values of determining sodium vaporization enthalpies by the transpiration method (79) are considered (7) to have been obtained because of the presence of water vapour in the flow of the carrier gas. Nevertheless, it is necessary to underline the undoubted merit of this work (79) which made it possible to determine the Na partial pressures, $\Delta H_{v,T}(\text{Na}_2\text{O})$ and Na_2O activities at atmospheric pressure. The decrease of Na_2O activity with decrease of temperature from 1873 to 1273 K (6) is consistent with the previously calculated data (84).

Concentration dependencies of the K_2O activity in the $\text{K}_2\text{O-SiO}_2$ melts containing 11.9-43.9 mass % of potassium oxide at 1300-1800 K were calculated in (10) using the data on partial vapour pressures of potassium and oxygen.

Activities of components in the binary silicate melts containing MgO (12-14), CaO (15), Mn (22) and FeO (23) were obtained in publications mentioned. Agreement of the data found with the results of the experimental studies of these systems by the e.m.f. method and the other methods of the high temperature chemistry confirmed the reliability of the values obtained (85-96).

The positive deviations from the ideality at 1473 K have been shown in the $\text{B}_2\text{O}_3\text{-SiO}_2$ system and the negative deviations have been observed at the temperature 1588 K (18,19). Hilpert (17) believed that the positive deviations from the ideality were connected with the existence in this system the immiscibility gap (97) confirmed by high temperature calorimetry method (98,99). However, as have been convincingly shown in (100), immiscibility gap in the $\text{B}_2\text{O}_3\text{-SiO}_2$ system was absent and the data (98,99) could not be compared with the values obtained in (17) because they obtained at 1223 K for the solid phase but not to the melt.

Negative deviations from ideality have also been noted in the $\text{Al}_2\text{O}_3\text{-SiO}_2$ system (22,23,60,61) at the temperatures 1873, 1973, 2073 K. Authors (23) have been analysed the data on the SiO_2 activity measured in this system on the samples melted at 1900, 2100 and 2500 K. They mentioned that the reliable data could be obtained using samples melted at 2500 K. In the compositions of melts of the system close to that of pure SiO_2 it has been noted that, following a decrease of temperature, equilibrium establishes very slowly (12 hours at 1873 K). This is characteristic of glass-forming melts having a high viscosity.

The same feature have been mentioned in the $\text{GeO}_2\text{-SiO}_2$ system (20) where the positive deviations from the ideality have been observed.

Germanate systems. As in the $\text{GeO}_2\text{-SiO}_2$ system (20), thermodynamic functions of melts have been obtained by high temperature mass spectrometric method in the following systems $\text{Na}_2\text{O-GeO}_2$ (24,27), $\text{B}_2\text{O}_3\text{-GeO}_2$ (25-27,29-31) and $\text{GeO}_2\text{-P}_2\text{O}_5$ (56,57) systems, table 3. However the reliability of these data have been confirmed by the results of the e.m.f. and high temperature calorimetry methods only in the $\text{Na}_2\text{O-GeO}_2$ system (24,101,102). Data on thermodynamic properties of the $\text{B}_2\text{O}_3\text{-GeO}_2$ system (25-27,29-31) have been used in Ref. (103) for the calculation of the phase diagram of this system. The correlation of the GeO_2 and P_2O_5 activities with the phase diagram of the $\text{GeO}_2\text{-P}_2\text{O}_5$ system have been illustrated in Refs. (56,57).

Borate systems. Thermodynamic properties of borate melts have been studied by high temperature mass spectrometric method in the following systems $\text{Na}_2\text{O-B}_2\text{O}_3$ (34), $\text{BeO-B}_2\text{O}_3$ (35), $\text{CaO-B}_2\text{O}_3$ (38), $\text{BaO-B}_2\text{O}_3$ (47), $\text{ZnO-B}_2\text{O}_3$ (48), $\text{PbO-B}_2\text{O}_3$ (49) and $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ (34), table 4.

The NaBO_2 and B_2O_3 activities, the chemical potentials of components, partial molar enthalpy of B_2O_3 and excess integral thermodynamic functions as a function of concentration in the $\text{Na}_2\text{O-B}_2\text{O}_3$ system have been obtained (34) at temperature range 1248-1373 K. Agreement with the data obtained by the e.m.f. method in this system (104) have been shown. The main feature of the study of the $\text{BeO-B}_2\text{O}_3$ was the illustration of the correlation of the B_2O_3 activities found in this system with the phase diagram (35). In Ref. (38) it was found that the activities of components in the $\text{CaO-B}_2\text{O}_3$ system were in agreement with the values calculated by Richardson from the phase diagram (105) and obtained by the method of exchange equilibrium in slags (106). Rather complicated composition of vapour mentioned during vaporization of the $\text{BaO-B}_2\text{O}_3$ and $\text{SrO-B}_2\text{O}_3$ systems (39-46) made difficult the determination of thermodynamic functions of mixing in these systems. Activities of B_2O_3 have been obtained only in the $\text{BaO-B}_2\text{O}_3$ system in Ref. (47). Experimental values of activities of components obtained by high temperature mass spectrometric method have confirmed the existence of immiscibility gaps in the $\text{ZnO-B}_2\text{O}_3$ and $\text{B}_2\text{O}_3\text{-B}_2\text{O}_3$ systems (48,50). Agreement of the values of PbO activities obtained by the e.m.f. (107,108) and high temperature mass spectrometric methods has been illustrated in the $\text{PbO-B}_2\text{O}_3$ system at 1273 K.

Phosphate systems. Reliable identification of the composition of the gaseous phase is one of the feature of the reliability of determination of thermodynamic functions in the phosphate systems, table 5. It was shown (51) that the composition of vapour was significantly different in the $\text{Na}_2\text{O-P}_2\text{O}_5$ system, when the mole fraction of P_2O_5 changed from 0.5 to 0.3 mole fractions. Correlation of thermodynamic functions with the phase diagram has been illustrated in the $\text{ZnO-P}_2\text{O}_5$ system (55). These results were confirmed later in Ref. (38). The accuracy of the determination of activities in the $\text{PbO-P}_2\text{O}_5$ system was checked by the data obtained using the Gibbs-Duhem equation (58,59).

Reliability of thermodynamic functions in oxide melts

In view of the fact that the experimental data obtained may be used in further calculations, it is necessary to indicate the main points which allow one to draw a conclusion as to the reliability of the values of thermodynamic functions of oxide melts found by the high temperature mass spectrometric technique.

The first of these is the necessity of considering the correlation of the values obtained with the results found by means of various techniques of determining thermodynamic functions within the framework of mass spectrometric method (the comparison method, the dimer-

monomer method, the Belton-Fruehan method (115), all of which are described in Ref. 1), table 6. Such comparisons have been made for the investigation of thermodynamic properties of melts in the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ (25-27, 34), $\text{Na}_2\text{O}-\text{GeO}_2$ (24-27), $\text{B}_2\text{O}_3-\text{GeO}_2$ (25-27, 29-31) and $\text{B}_2\text{O}_3-\text{SiO}_2$ (17-19). Similar comparisons have been made in the literature for the $\text{K}_2\text{O}-\text{SiO}_2$ (7,10), $\text{PbO}-\text{SiO}_2$ (21), $\text{CaO}-\text{SiO}_2$ (15), $\text{FeO}-\text{SiO}_2$ (23), $\text{MgO}-\text{SiO}_2$ (12-14), $\text{MnO}-\text{SiO}_2$ (22) and $\text{PbO}-\text{B}_2\text{O}_3$ (49) systems.

The second of these points is the comparison of the values obtained by high temperature mass spectrometry with those found by various techniques of high temperature chemistry: by the electromotive force method, by high-temperature calorimetry of solutions, and by exchange equilibria, as is done, for instance, for $\text{Na}_2\text{O}-\text{SiO}_2$ melts (4-8, 79-83), table 6. Examples of correlation of thermodynamic functions in the oxide systems studied by various methods of high temperature chemistry are presented in table 6 for some binary oxide melts. For the consideration of their agreement approach suggested by Rudny (118) may be used. However, it should be underlined, that in Ref. (116) it was mentioned that the reason for the disagreement between the data obtained by the tensimetric method and the e.m.f. method was the determination of activity in the volume of the melt in the first case and in the surface in the second.

In the case when experimental values of partial thermodynamic functions of the components in the systems under study were available, the verification of intercorrelation of these values was carried out by the Gibbs-Duhem equation. This may be considered as the third important point for checking the reliability of the experimental data obtained.

It was also shown that the values obtained of the thermodynamic properties of the melts in question meet the criteria of phase stability relative to the continuous nature of its change of state (119,120). In particular, for the activity values of germanium dioxide in $\text{B}_2\text{O}_3-\text{GeO}_2$ melts (25-27, 29-31) these criteria are satisfied. In spite of the increased partial pressure of GeO vapour over melts of the $\text{GeO}_2-\text{P}_2\text{O}_5$ system compared to the value over pure GeO_2 , this does not contradict the criterion of phase stability (56,57,64). Thus, this criterion ought to be taken into consideration from the point of view of the reliability of the experimental data obtained.

The question of the agreement of experimental values of thermodynamic properties in oxide systems with the corresponding isothermal cross-sections of phase diagrams should also be taken into account for the verification of the results of the research done. Thus, in the range of nonvariant equilibrium of the $\text{CaO}-\text{SiO}_2$ system at mole fractions $\text{CaO} > 0.65$ one observes constant values of activities of CaO and SiO_2 at 1933 K (15).

Regularities of oxide system vaporization

The characteristic features of vaporization processes of components of oxide systems are presented in tables 2-5.

In the vapour over silicate, germanate, borate and phosphate melts, in addition to polymerization such as in borate melts, one can observe association of components, which has resulted in the identification of new compounds in the gaseous phase. This may be due to various factors, one of them being the interaction of oxides in melts or vapour. As a result of the publications considered in tables 2-5, it has been shown that, under isothermal conditions, the changes of chemical potentials of components and the Gibbs energies in the melts under investigation correspond to the decrease of bond energies between atoms of mixed type which form in these systems. Such changes are mainly accounted for by interactions of an acid-base nature.

The relative volatility and the character of the vaporization processes of the binary oxide systems are in agreement with the decrease of the relative volatility of individual oxides of P_2O_5 , B_2O_3 , GeO_2 and SiO_2 . More complicated associated vapour species in oxide systems are observed as a result of the increase of the atom masses oxide-modifiers in the rows of the periodic table. This fact is connected with the participation of d- and f-electrons in the chemical bonds and the penetration of s-electrons under the cover of the 3d-, 4d-, 4f- and 5d-electrons. The deviations from ideality of the P_2O_5 , B_2O_3 , GeO_2 and SiO_2 chemical potentials as a function of the content of oxide modifiers in the series of binary systems are in agreement with the variety of vaporization processes of their components, such as dissociation, association and polymerization. The following parameters were taken into account to understand the vaporization character of the binary oxide systems from the point of view of acid-base concept (37,121,122): values of the differences of electron potentials, forming oxides; enthalpy of formation of oxide-modifier; the lattice energy of oxide modifier per mole of O^{2-} at 298 K; the energies of the M-O-X bond (X= P, B, Ge, Si). The associated vapour species over binary borate and silicate systems were observed as a result of the decrease of the lattice energy of the oxides; the increase of the enthalpy of formation of the individual oxides and the negligible changes in the values of the M-O-B and M-O-Si bond energies compared with the same values in the individual oxides (B_2O_3 and SiO_2) in the periods of the periodic table. In the case of the phosphate systems the energy of the M-O-P bond is lower than the value of the energy of the P-O-P bond in phosphorus oxide. This might be one of the reasons why the quantity of the associated vapour species over phosphate systems is predominant compared with the relative quantity of the polymerized species over borate systems. The increase of the volatility in the binary systems in the rows of the periodic table and the predominance of the dissociative forms in vapour are connected with the increase of the lattice energy of the individual oxides, the decrease of the enthalpy of formation of the individual oxides and the decrease of the differences of the electron potentials of oxides forming binary oxide melts.

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Table1. Binary oxide systems studied by high temperature mass spectrometric (publications where systems studied have to be found in the corresponding cross-sections)

Oxides	SiO ₂	GeO ₂	B ₂ O ₃	P ₂ O ₅
Li ₂ O	(2,3)		(1)	(1)
Na ₂ O	(4-9)	(24-27)	(25-27,34)	(51)
K ₂ O	(7,10)		(1)	(1)
Cs ₂ O	(11)		(1)	(1)
BeO			(35)	(52-54)
MgO	(12-14)		(36)	(52-54)
CaO	(15)		(37,38)	(52-54)
SrO	(43)		(39-43)	(52-54)
BaO	(16)	(28)	(44-47)	(52-54)
ZnO			(48)	(55)
B ₂ O ₃	(17-19)	(25-27,29-31)		(1)
SiO ₂		(5,20)	(17-19)	(64)
GeO ₂	(5,20)		(25-27,29-31)	(56,57,64)
PbO	(21)		(49)	(58,59)
Sb ₂ O ₃		(32)		
Bi ₂ O ₃		(33)	(50)	
MnO	(22)			
FeO	(23)			(58,59)
Al ₂ O ₃	(22,23,60,61)		(62,63)	(1)

Table 2.
Composition of vapour and thermodynamic properties of silicate melts studied by high temperature mass spectrometric method

System	Temperature, K	Material of the effusion cell	Composition of vapour	Thermodynamic functions studied	Reference
1	2	3	4	5	6
$\text{Na}_2\text{O} \times 2 \text{SiO}_2$	1278-1553	Mo, MgO, Re, Ta	Na, O_2	p_i , $\Delta H_{v,i}$	(4)
$\text{Na}_2\text{O} - \text{SiO}_2$	1163-1923	Mo	Na, O_2	$\Delta H_{v,i}$, ΔH_r	(5)
$\text{Na}_2\text{O} - \text{SiO}_2$	1373-1623	Pt	Na, O_2	p_i , $\Delta H_{v,i}$, a_i , f_i	(6)
$\text{Na}_2\text{O} \times 4 \text{SiO}_2$	1351-1540	C	Na, O_2	p_i , $\Delta H_{v,i}$	(7)
$\text{Na}_2\text{O} - \text{SiO}_2$	1205-1423	Mo	Na, O_2	p_i , $\Delta H_{v,i}$, $\Delta \mu_i$, ΔG , ΔH	(8)
$\text{Na}_2\text{O} - \text{SiO}_2$	1300-1500	Pt	Na, O_2	p_{O_2} , $a_{\text{Na}_2\text{O}}$	(9)
$\text{K}_2\text{O} \times 4 \text{SiO}_2$	1333-1538	C	K, O_2	p_i , $\Delta H_{v,i}$, a_i	(7)
$\text{K}_2\text{O} - \text{SiO}_2$	1300-1800	Pt	K, O_2	p_i , $\Delta H_{v,i}$, a_i	(10)
$\text{Cs}_2\text{O} - \text{SiO}_2$	900-1100	Mo	Cs, O_2	p_i	(11)

1	2	3	4	5	6
MgO - SiO ₂	1873 1973	Pt-Rh Pt-Ir	SiO, Mg	a _i	(12-14)
CaO - SiO ₂	1933-2133	W	Ca, CaO, SiO, SiO ₂ , O, CaSiO ₃ , (WO ₃ , WO ₂)	p _i , ΔG , a _i	(15)
BaO - SiO ₂			Ba, SiO, BaO		(16)
B ₂ O ₃ - SiO ₂	1390-1590	Pt Mo	B ₂ O ₃	a _i p _i , ΔH _{v,i} ,, Δμ _i , ΔG, ΔH, ΔH _i	(17) (18,19)
Al ₂ O ₃ - SiO ₂	1873-2073 1833-1933	Mo Mo	SiO, SiO ₂ (MoO ₂ , MoO ₃) SiO, SiO ₂ , Al, AlO, Al ₂ O, O	a _i p _i , ΔG , a _i	(22,23) (61)
GeO ₂ - SiO ₂	1373-1453 1170-1514 1800-2000	Pt Al ₂ O ₃	GeO, O ₂ GeO, O ₂ GeO, O ₂ , SiO, SiO ₂	p _i , a _i , ΔH _{v,i} ,, Δμ _i , ΔG, ΔH, ΔH _i ΔH _{v,i} ,	(20) (5)
PbO - SiO ₂	1173	Pt, ZrO ₂	PbO, Pb ₂ O ₂	a _i	(21)
MnO - SiO ₂	1673-1723	Mo	Mn, MnO, SiO,	a _i	(22)

			SiO ₂ (MoO ₃ , MoO ₂)		
1	2	3	4	5	6
FeO - SiO ₂	1673	Mo	Fe, FeO, SiO, SiO ₂ , MoO ₃ , MoO ₂	a _i	(23)

Table 3.

Composition of vapour and thermodynamic properties of germanate melts studied by high temperature mass spectrometric method

System	Temperature, K	Material of the effusion cell	Composition of vapour	Thermodynamic functions studied	Reference
1	2	3	4	5	6
Na ₂ O - GeO ₂	1390-1590	Pt	Na, GeO, O ₂	a_i p_i , $\Delta H_{v,i}$, $\Delta \mu_i$, ΔG , ΔH , ΔH_i	(24-27)
BaO - GeO ₂	1670-1788	Mo	BaGeO ₂ , BaO, GeO	p_i , ΔH_r	(28)
B ₂ O ₃ - GeO ₂	1390-1490	Pt	B ₂ O ₃ , GeO, O ₂	p_i , $\Delta H_{v,i}$, $\Delta \mu_i$, ΔG , ΔH , ΔH_i , ΔH_i	(25-27, 29-31)
GeO ₂ - SiO ₂	1373-1453	Pt	GeO, O ₂	p_i , a_i , $\Delta H_{v,i}$, $\Delta \mu_i$, ΔG , ΔH , ΔH_i , ΔH_i	(20)
	1170-1514	Al ₂ O ₃	GeO, O ₂		(5)
	1800-2000		GeO, O ₂ , SiO, SiO ₂		
P ₂ O ₅ - GeO ₂	1423	Pt	GeO, O ₂ , GePO ₃ , PO ₂ , P ₄ O ₁₀	p_i , a_i , $\Delta \mu_i$, ΔG	(56,57)
Bi ₂ O ₃ - GeO ₂	1090-1260	Pt	GeO, O ₂ , Bi, BiO, Bi ₄ O ₆ , Bi ₂	p_i	(33)

1	2	3	4	5	6
$\text{Sb}_2\text{O}_3 - \text{GeO}_2$	650-740 950-1150	Ta, W	$\text{Sb}_4\text{O}_6, \text{Sb}_3\text{O}_3, \text{Sb}_2\text{O}_4$, Sb_2O_2 $\text{Sb}_4\text{O}_6, \text{Sb}_3\text{O}_3, \text{Sb}_2\text{O}_4$, $\text{Sb}_2\text{O}_2, \text{GeO}, \text{O}_2$	$\text{p}_{\text{Sb}_4\text{O}_6}$	(32)

Table 4.

Composition of vapour and thermodynamic properties of borate melts studied by the high temperature mass spectrometric method

System (x_i - mole fraction of B_2O_3)	Temperature, K	Material of the effusion cell	Composition of vapour	Thermodynamic functions studied	Reference
1	2	3	4	5	6
$Na_2O - B_2O_3$	1248 1373	Pt	$NaBO_2$, $(NaBO_2)_2$ $NaBO_2$, $(NaBO_2)_2$, B_2O_3	p_i , a_i , $\Delta H_{v,i}$, $\Delta \mu_i$, ΔG , ΔH , ΔH_i	(25-27,34)
$BeO - B_2O_3$ $0 \leq x_i \leq 1$	1180-1563	Pt, Ni	$(BeBO_2)_2$, B_2O_3	p_i , a_i , $\Delta H_{f,i}$	(35)
$MgO - B_2O_3$, $x_i = 0.06$	1600-2000	W	$MgBO_2$, $(MgBO_2)_2$, B_2O_3 , Mg	p_i , $\Delta H_{v,i}$	(36)
$SrO - B_2O_3$, $x_i = 0.33; 0.50; 0.67$	1300-1442	Pt	$SrBO_2$, $(SrBO_2)_2$, B_2O_3 , Sr, B_2O_2	p_i , $\Delta H_{v,i}$	(39-43)
$BaO - B_2O_3$, $1 < x_i < 0.5$ $x_i = 0.25$	1473 1434-1630	Pt Pt	$BaBO_2$, $(BaBO_2)_2$, B_2O_3 $BaBO_2$, Ba, B_2O_2 , B_2O_3 , BO	p_i , a_i p_i , $\Delta H_{v,i}$	(44,47) (45,46)
$ZnO - B_2O_3$	1250-1484	Pt	B_2O_2 , B_2O_3 , BO, O_2 ,	p_i , a_i , $\Delta H_{v,i}$	(48)

			BO ₂ , ZnO, Zn		
1	2	3	4	5	6
B ₂ O ₃ - Al ₂ O ₃	1248-1850	Mo	B ₂ O ₃	p _i , a _i , ΔH _{v,i}	(62,63)
B ₂ O ₃ - GeO ₂	1390-1490	Pt	B ₂ O ₃ , GeO, O ₂	p _i , ΔH _{v,i} , a _i , Δμ _i , ΔG, ΔH	(25-27, 29-31)
B ₂ O ₃ - SiO ₂	1390-1590	Pt Mo	B ₂ O ₃	p _i , ΔH _{v,i} , a _i , Δμ _i , ΔG, ΔH	(17-19)
PbO - B ₂ O ₃	1050-1482	Pt	Pb, O ₂ , PbO, Pb ₂ O ₂ ,B ₂ O ₃ , PbBO ₂ , Pb ₂ BO ₃ , BO ₂ , Pb ₃ BO ₄ , PbB ₄ O ₆ , Pb ₂ B ₂ O ₅	p _i , Δ H _{v,i} , a _i , f _i	(49)
Bi ₂ O ₃ - B ₂ O ₃	1120-1310	Pt	Bi ₄ O ₆ , Bi ₃ O ₄ , Bi ₂ O ₃ , Bi ₂ O ₂ ,Bi ₂ O, Bi ₂ , BiO, Bi, O ₂ , BiBO ₂ , Bi ₂ BO ₄ , Bi ₃ BO ₆ (BiBO ₃)	ΔH _{f,i} , a _i , Δμ _i , ΔG,	(50)

Table 5.
Composition of vapour and thermodynamic functions studied by the high temperature mass spectrometric method

System	Temperature, K	Material of the effusion cell	Composition of vapour	Thermodynamic functions studied	Reference
1	2	3	4	5	6
Na ₂ O - P ₂ O ₅	1200-1400	Pt	NaPO ₃ , Na, O ₂ , NaPO ₂ , PO ₂	p _i , a _i	(51)
MO -P ₂ O ₅ (M=Be,Mg,Ca, Sr, Ba)	1800-2000	W	P ₄ O ₁₀ , PO ₂ , PO, MPO ₂ (M=Ca, Sr, Ba)	p _i	(52-54)
ZnO - P ₂ O ₅	940-1340	Mo	Zn, O ₂ , PO,P ₂ , PO ₂ (Zn ₂ P ₂ O ₆)	p _i , a _i , ΔG, ΔH	(55) (38)
GeO - P ₂ O ₅	1423	Pt	GeO, O ₂ , GePO ₃ , PO ₂ , P ₄ O ₁₀	p _i , a _i , ΔG	(56,57,64)
PbO - P ₂ O ₅	1573	Fe (Pd)	PbO, PO, PO ₂	a _i	(58,59)
Fe _t O - P ₂ O ₅ , 2/3 <t< 1	1643	Fe	PO, PO ₂ , P ₂ , Fe	p _i , a _i	(58,59)

Table 6.
Examples of correlation of thermodynamic functions in the oxide systems studied by various methods of high temperature chemistry

System studied	Reference	Mass spectrometric method of the determination of thermodynamic properties	Correlation with the results obtained by the other methods
1	2	3	4
Na ₂ O-SiO ₂	(4-8)	Comparison method	the e.m.f. method (78,80,81), high temperature calorimetry (83), transpiration method (79), exchange equilibrium (82), ion-molecular equilibrium (9)
K ₂ O-SiO ₂	(7,10)	Comparison method	high temperature calorimetry (10)
CaO-SiO ₂	(15)	Comparison method, the Belton-Fruehan method	the e.m.f. method (109,110), the Knudsen method (111), exchange equilibrium (85,94,95,112-114)
PbO-SiO ₂	(21)	Dimer-monomer method	the e.m.f. method (88-90)
FeO-SiO ₂	(23)	Comparison method	the e.m.f. method (91,92)
MgO-SiO ₂	(12-14)	Approach similar to the Belton-Fruehan method	the e.m.f. method (85-87)
MnO-SiO ₂	(22)	Comparison method	the e.m.f. method (91)

1	2	3	4
$\text{Na}_2\text{O}-\text{B}_2\text{O}_3$	(25-27,34)	Comparison method, the Belton-Fruehan method, dimer- monomer method	the e.m.f. method (104)
$\tilde{\text{Na}}\text{O}-\text{B}_2\text{O}_3$	(37,38)	Comparison method	exchange equilibrium (106)
$\text{PbO}-\text{B}_2\text{O}_3$	(49)	The Belton-Fruehan method, dimer- monomer method	the e.m.f. method (107,108)
$\text{Na}_2\text{O}-\text{GeO}_2$	(24-27)	Comparison method, the Belton-Fruehan method	the e.m.f. method (101), high temperature calorimetry (102)