Application of the Belton-Fruehan mass spectrometric method to study thermodynamic properties of oxide melts

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ABSTRACT

Thermodynamic properties of oxide systems studied by the Belton-Fruehan mass spectrometric method are considered. The reliability of the component activities, the Gibbs energies, the partial and integral enthalpies of components obtained in the frame of this approach in oxide melts , is confirmed by the comparison with the data found by the various methods of high temperature chemistry.

1. INTRODUCTION

The Knudsen effusion mass spectrometric method is widely used nowadays for the determination of thermodynamic functions and for the investigation of the vaporization processes of the inorganic materials and melts at high temperatures. One of the reason for that is the new method, that was suggested by Belton and Fruehan [1] to study thermodynamic properties of binary and multicomponent systems in the frame of high temperature mass spectrometric approach.

2. EXPERIMENTS

The main feature of the Belton-Fruehan method, which is characteristic of high temperature mass spectrometry, is the measurement of ratios of ion currents (I_i and I_j) arising during ionization of not less than two gas-phase components (i, j) in the system under study. The determination of the activity of i-component i (a_i) in the binary system, for example, can be carried out according to the following equation:

$$ln\, a_i = - \int x_j \, d\, ln\, (I_i / I_j), \qquad (1)$$

where x_i is mole fraction of i-component.

Since the study of thermodynamic properties of the $CoO-FeO-SiO_2$ [2], $Na_2SiO_3 - K_2SiO_3$, $Na_2Si_2O_5 - K_2Si_2O_5$ [3], $CaO-(K_2O + Na_2O)-SiO_2$ systems by Belton et al. in 1973-1977, a lot of thermodynamic information was obtained based on this method such as activities of components and coefficients of component activities (γ_i), the chemical potentials of components ($\Delta \mu_i$), the Gibbs energies of the system (ΔG), the partial and integral enthalpies of formation (ΔH_i, ΔH) as well as the partial and integral entropies of formation (ΔS_i, ΔS).

Information on thermodynamic properties obtained using the Belton-Fruehan method in the various fields of high temperature chemistry is summarized in Table I. This method was used by many groups of investigators to study

the main compositions of metallurgical slags: $Cu_2O-K_2O-SiO_2$, $Cu_2O-Na_2O-SiO_2$, $CaO-SiO_2$, $CaO-Al_2O_3-SiO_2$, $FeO-MgO-SiO_2$;

glass-forming oxide systems: $Na_2O-B_2O_3$, Na_2O-GeO_2, $Na_2O-B_2O_3-GeO_2$, $ZnO-PbO-B_2O_3$, $GeO_2-P_2O_5$, $RbBO_2-CsBO_2$;

the systems containing natural minerals: $NaAlSi_3O_8-KAlSi_3O_8$, $NaAlSi_2O_6-KAlSi_2O_6$, $(Na,K)AlSi_4O_{10}-(Na,K)Al_2Si_5O_{12}$ and $NaAlSiO_4-KAlSiO_4-SiO_2$;

highly refractory ceramics systems: $ZrO_2-Lu_2O_3$, $ZrO_2-Y_2O_3$, $HfO_2-Y_2O_3$, $ZrO_2-Hf_2O_3$.

3. RESULTS

The agreement between the results of the determination of the activities of components and enthalpies of formation in oxide systems obtained by the mass spectrometric Belton-Fruehan and by the 'dimer-monomer' and comparison methods, as well as by the EMF technique, by the high temperature calorimetric method, by the measuring sulphide capacities and heterogenious equilibria in slags, has been illustrated for the series of oxide systems, Table II. Comparison of the results obtained by these methods in the Na_2O-GeO_2 and $CaO-SiO_2$ systems, as an example, is shown in Figs. 1 and 2. The disagreement between the GeO_2 and CaO activities , found by the various experimental approaches, including the Belton-Fruehan method, is within the accepted accuracy level.

As can be seen from Table I, vaporization of oxide systems, in addition to the processes of polymerization and dissociation, is also accompanied by the association of vapour molecular forms. That is the reason why, the main advantages of this method Eqn. (1), the use of ratios of ion currents values (I_i / I_j) can disappear because of the necessity of raising I_i or I_j to a power, in accordance with the stoichiometry of the vaporization reaction. Semenikhin et al. [21] suggested different variants of using the Belton-Fruehan method when studying quasi-ternary oxide systems vaporizing with dissociation of components in the gaseous phase. They carried out the series of transformations of Eqn. (1) taking into account the complicated vapour composition of the system, which permitted this disadvantage to be overcome. Sidorov and Korobov [47] considered a general

Table I Thermodynamic properties of oxide systems studied by the Belton-Fruehan mass spectrometric method (to be continued on the next page)

Oxide system studied	Tempera-ture, K	Vapour species	Thermo-dynamic functions obtained	Reference, year, authors
$CoO{\cdot}0.5SiO_2$-$0.5FeO{\cdot}SiO_2$	1723	Co, Fe, O_2	a_i	[2] 1973, Belton et al.
Na_2SiO_3-K_2SiO_3	1373	Na, K, O_2	a_i , Δ G	[3] 1974, Belton et al.
$Na_2Si_2O_5$-$K_2Si_2O_5$	1373	Na, K, O_2	a_i , Δ G	[3] 1974, Belton et al.
CaO-(K_2O + Na_2O)-SiO_2	1373	Na, K, O_2	a_i , ΔG^E	[4] 1977, Choudary et al.
Cu_2O-K_2O-SiO_2	1373	Cu, K, O_2	a_i	[5] 1986, Kowalska et al.
Cu_2O-Na_2O-SiO_2	1373	Cu, Na, O_2	a_i	[6] 1988, Kowalska et al.
CaO-SiO_2	1933-2133	Ca, CaO, SiO, SiO_2, O, $CaSiO_3$	a_i , Δ G	[7] 1991, Stolyarova et al.
CaO-Al_2O_3-SiO_2	1833-2033	Ca, CaO, SiO, SiO_2, O, $CaSiO_3$, Al, AlO	a_i , Δ G	[8-10] 1991, Stolyarova et al.
FeO-MgO-SiO_2	1820-1980	Fe, Mg, SiO, O_2	a_i	[11] 1992, Plante et al.
$LiReO_4$-$CsReO_4$	833	$LiReO_4$, $CsReO_4$, $Li_2Re_2O_8$, $Cs_2Re_2O_4$, $LiCsRe_2O_8$	a_i, γ_i	[12] 1979, Lukas et al.
$KReO_4$-$RbReO_4$	855	$KReO_4$, $RbReO_4$, $K_2Re_2O_8$, $Rb_2Re_2O_8$, $KRbRe_2O_8$	a_i, γ_i	[13] 1979, Lukas et al.
Na_2O-B_2O_3	1248-1373	$NaBO_2$, $Na_2B_2O_4$, B_2O_3	a_i , Δ G, Δ H_i	[14] 1979, Shultz et al.
Na_2O-GeO_2	1390-1590	Na , GeO, O_2	a_i , Δ G, Δ H_i	[15] 1979, Shultz et al.
Na_2O-B_2O_3-GeO_2	1273-1373	Na , GeO, O_2 , $NaBO_2$, $Na_2B_2O_4$, B_2O_3	a_i , Δ G	[16-19] 1979,1980, Shultz et al.
PbO-B_2O_3	1050-1482	Pb, O_2 , PbO, Pb_2O_2, BO_2, B_2O_3, $PbBO_2$, Pb_2BO_3, Pb_3BO_4, PbB_4O_6, $Pb_2B_2O_5$	a_i	[20] 1987, Semenikhin et al.
ZnO-B_2O_3	1250-1484	Zn, O_2, ZnO, B_2O_3, B_2O_2, BO_2	a_i, Δ H_i	[21] 1987, Semenikhin et al.
ZnO-PbO-B_2O_3	1200-1430	Pb, O_2 , PbO, Pb_2O_2, BO_2, B_2O_3, $PbBO_2$, Pb_2BO_3, Pb_3BO_4, PbB_4O_6, $Pb_2B_2O_5$, Zn, ZnO, B_2O_2	a_i, γ_i	[21] 1987, Semenikhin et al.
GeO_2 - P_2O_5	1423	GeO, P_4O_{10}, O_2 , PO_2, $GePO_3$	a_i , Δ G	[22] 1990, Stolyarova et al.
$RbBO_2$ - $CsBO_2$	764-978	$RbBO_2$, $CsBO_2$, $Rb_2B_2O_4$, $RbCsB_2O_4$	a_i, γ_i , Δ G , Δ μ	[23,24] 1992, Kato et al.
$NaAlSi_3O_8$-$KAlSi_3O_8$	1150-1880	Na, K, O_2	a_i, Δ G , Δ H	[25] 1982, Rammensee et al. [26] 1985, Frazer et al. [27] 1983, Roges et al.

$NaAlSi_2O_6$-$KAlSi_2O_6$	1450	Na, K, O_2	a_i	[28] 1982, Frazer et al.
$(Na,K)AlSi_4O_{10}$-$(Na,K)Al_2Si_3O_{12}$	1450-1850	Na, K, O_2	a_i	[29] 1985, Frazer et al.
$NaAlSiO_4$-$KAlSiO_4$-SiO_2	1920	Na, K, O_2	a_i, ΔG, ΔH, ΔS	[30] 1987, Rammensee et al. [31] 1987, Frazer et al.
ZrO_2-Y_2O_3	2773	ZrO_2, ZrO, O,YO, Y	a_i	[32] 1981, Belov et al.
ZrO_2-Lu_2O_3	2700	ZrO_2, ZrO, O, LuO, Lu	a_i	[32] 1981, Belov et al.
HfO_2-Y_2O_3	2843	HfO_2, HfO, O,YO, Y	a_i	[33] 1980, Belov et al.
ZrO_2-Hf_2O_3	2773	ZrO_2, ZrO, O, HfO, HfO_2	a_i	[33] 1980, Belov et al.

Table II Agreement between thermodynamic properties of oxide systems obtained by the Belton-Fruehan mass spectrometric method and the data found by the other methods of high temperature chemistry

Oxide system studied by the Belton-Fruehan method	Refe-rence	Experimental method (approach) used for the comparison of thermodynamic functions	Thermo-dynamic functions	Refe-rence
CaO-SiO_2	7	EMF method By measuring of the sulphide capacities in slags	a_i	34 35
CaO-Al_2O_3-SiO_2	8-10	EMF method Studies of heterogenious equilibria in slags By measuring of the sulphide capacities in slags	a_i, ΔG	34 36, 37 38
FeO-MgO-SiO_2	11	Exchange equilibria in slags	a_i	39,40
Na_2O-B_2O_3	14	Mass spectrometric method: - dimer-monomer; - comparison method; EMF method High temperature calorimetry	a_i, ΔG, ΔH_i	14 41 42
Na_2O-GeO_2	15	Mass spectrometric method: - comparison method; EMF method High temperature calorimetry	a_i, ΔG,ΔH_i	15, 43 44
Na_2O-B_2O_3-GeO_2	16-19	Mass spectrometric method: - dimer-monomer; - comparison method;	a_i, ΔG	17,18
PbO-B_2O_3	20	Mass spectrometric method: - dimer-monomer; EMF method	a_i	20 45,46
$NaAlSi_3O_8$-$KAlSi_3O_8$	25,26	High temperature calorimetry	ΔH	27
HfO_2-Y_2O_3	33	Mass spectrometric method using the equilibrium constant of the gaseous reaction	a_i	33
ZrO_2-Hf_2O_3	33	Mass spectrometric method using the equilibrium constant of the gaseous reaction	a_i	33

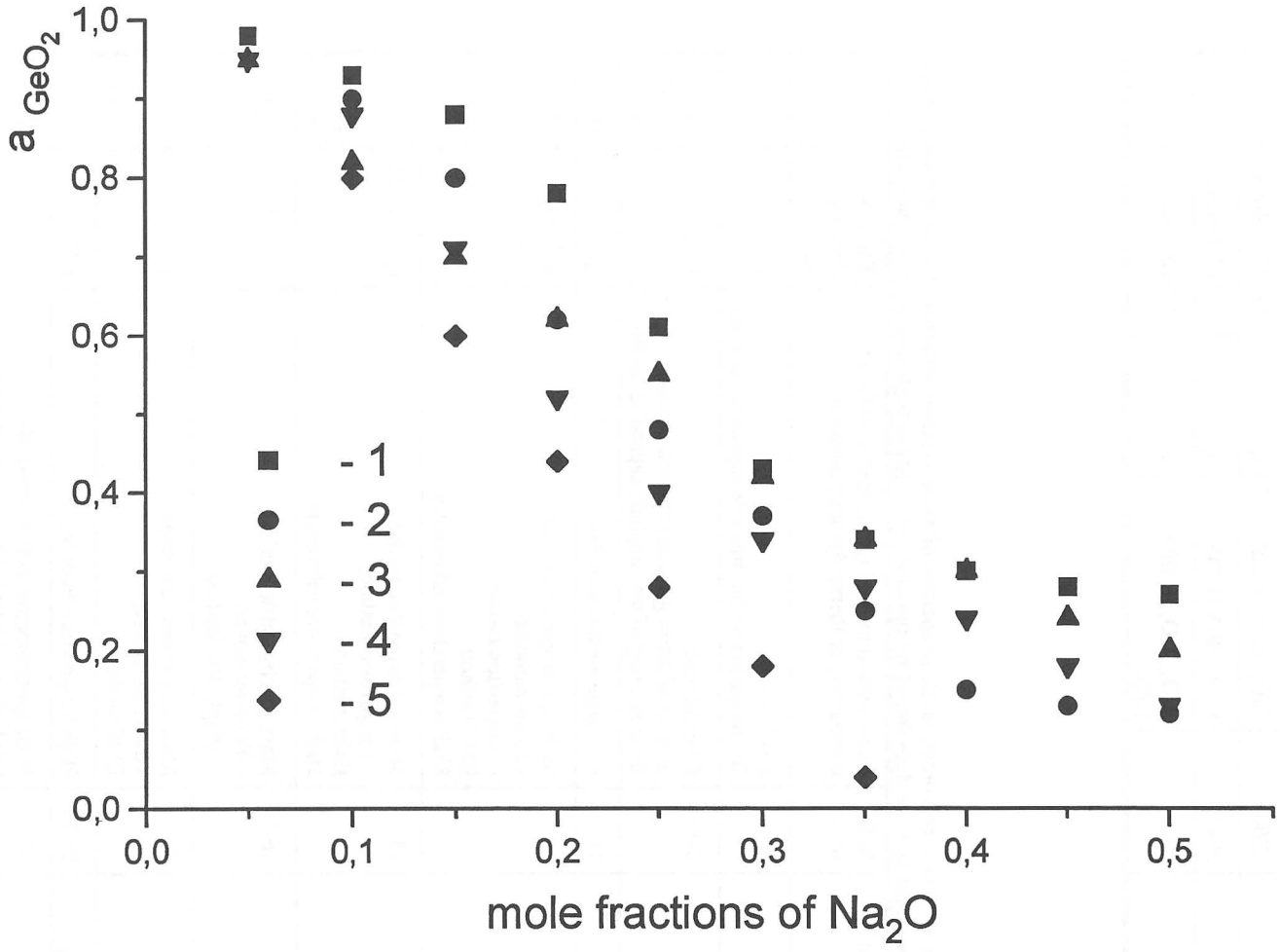

Fig. 1. The GeO_2 activities as a function of the concentration in the Na_2O-GeO_2 system, obtained in the temperature range 1450-1550 K by : 1- mass spectrometric method of comparing of the ion currents[15] ; 2- the Belton-Fruehan mass spectrometric method [15]; 3- the EMF method [15] ; 4- calculated using the Gibbs-Duhem equation from the Na_2O activities [15] ; 5- the EMF method [43] .

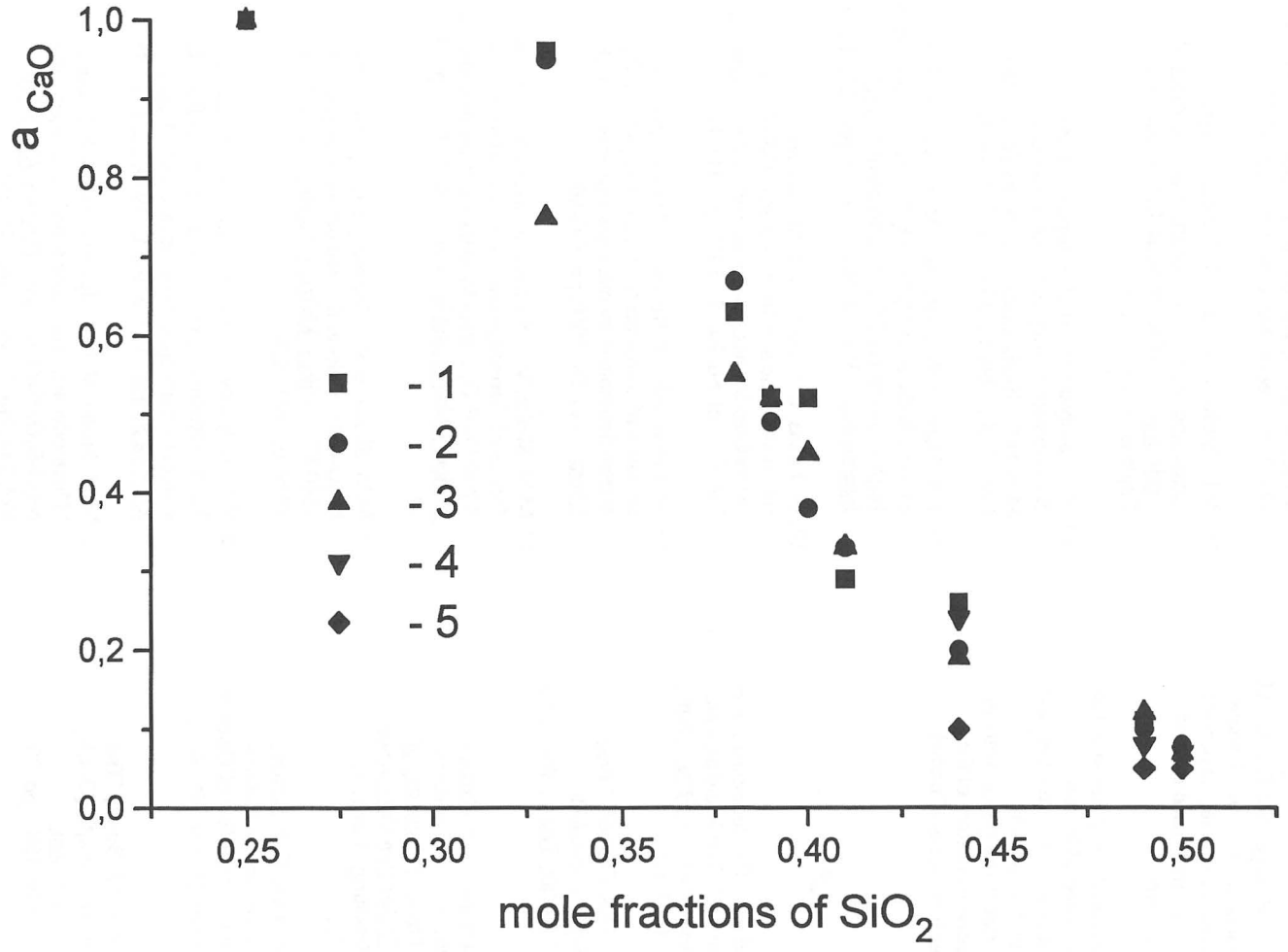

Fig. 2. The CaO activities as a function of the concentration in the CaO-SiO_2 system, obtained in the temperature range 1873-1933 K by : 1- mass spectrometric method of comparing of the ion currents[7] ; 2- calculated using the Gibbs-Duhem equation from the SiO_2 activities [7] ; 3- the Belton-Fruehan mass spectrometric method [7]; 4- the EMF method [34] ; 5- measuring of sulphide capacities in slags [35].

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