Vaporization features of oxide systems studied by high-temperature mass spectrometry

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Abstract

Vaporization processes of the binary phosphate, borate, silicate and zirconate systems, obtained by the Knudsen effusion mass spectrometric method are summarized according to the position of oxide-modifiers in the periodic table of the atoms. The polymerization and association processes as a result of vaporization of borate and phosphate systems are predominant. The association and the dissociation of the oxide components during vaporization are the characteristic of silicate systems. In the zirconate systems studied mainly the dissociative vaporization processes of oxides at high temperatures were mentioned. The main factors for the prediction of the relative volatility of the binary systems are considered. © 1997 Elsevier Science B.V.

1. Introduction

Vaporization processes of oxide systems have an important role in the various fields of nuclear engineering. The variety of the vapour species with different volatilities, identified over oxide systems, is one of the reasons that narrows their use at high temperatures, especially during the immobilization of radioactive wastes in matrices. The advantages of the application of the high temperature mass spectrometric method to study vaporization processes of nuclear materials were considered in detail by Gilles [1]. Available information on the vaporization processes and thermodynamic properties of binary oxide systems, obtained by this method, was summarized recently in [2].

2. Experimental

The main value of the high-temperature mass spectrometric Knudsen effusion method is the opportunity to obtain simultaneously information on the composition of the vapour and the partial pressures of vapour species over

the system studied as well as the thermodynamic properties of the system (activities and chemical potentials of components, the Gibbs energies of the system and the partial and integral enthalpies of mixing) [1,2]. The vapour composition over the binary phosphate, borate, silicate and zirconate systems, identified using this method during last twenty years [2], are summarized and grouped according to the number of outer valence electrons of an oxide modifier, Table 1. This consideration was carried out at high temperatures, when the partial pressures of the vapour species are in the ranges $10^{-9}-10^{-4}$ bar. A comparison of the available thermodynamic properties obtained in the binary oxide systems was made in Ref. [2].

3. Results and discussion

The polymerization and the association are predominant processes during vaporization of phosphate and borate systems. Vaporization processes with the association and the dissociation of oxide components are the characteristics of silicate systems. In the vapour over all zirconate systems studied, mainly the dissociative processes of individual oxides were identified. 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, SiO_2

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Table 1

Vapour species over pseudobinary phosphate, borate, silicate and zirconate systems obtained by high-temperature mass spectrometric methods [2] and summarized according to the position of oxide modifier in the periodic table. Second quantum numbers of atoms of oxide-modifier participated in the chemical bonds of the gaseous molecules are also indicated in the first column

Periods (2–7) of the periodic table	Groups of the atoms classified according to the number of outer valence electrons (I–VII) in the periodic table					
	I	II	III	IV	V	VI, VII
2s, 2p	Li_2O-P_2O_5; $LiPO_2$, $LiPO_3$; Li_2O-B_2O_3; $LiBO$, $LiBO_2$, B_2O_3, $(LiBO_2)_2$, $(LiBO_2)_3$; Li_2O-SiO_2; Li_2SiO_3, LiO, Li_2O, SiO, Li, O_2; Li_2O-ZrO_2; LiO, Li_2O, LiO_2	BeO-B_2O_3; BeB_2O_4,B_2O_3	B_2O_3-P_2O_5; BPO_4, BPO_3; B_2O_3; B_2O_3			
3s, 3p	Na_2O-P_2O_5; $NaPO_3$,$Na_2P_2O_6$, PO, $NaPO_2$,PO_2, P_2O_5, O_2; Na_2O-B_2O_3; $NaBO_2$,$(NaBO_2)_3$, $(NaBO_2)_2$, B_2O_3; Na_2O-SiO_2; Na_2O_2	MgO-P_2O_5; $MgPO_2$, P_4O_{10}, PO_2, PO; MgO-B_2O_3; $MgBO_2$, Mg, MgB_2O_4, B_2O_3; MgO-SiO_2; Mg, SiO	Al_2O_3-B_2O_3; $AlBO_2$, $AlBO$, B_2O_3; Al_2O_3-SiO_2; Al, O_2, $AlSiO$, SiO, SiO_2	SiO_2-P_2O_5; P_4O_{10}, P_4O_6, PO_2, O_2; SiO_2-B_2O_3; B_2O_3, $SiBO$, SiO, SiO_2, O_2; SiO_2; SiO, SiO_2, O_2	P_2O_5; P_4O_{10}; P_2O_5-B_2O_3; BPO_4, BPO_3; P_2O_5-SiO_2; P_4O_{10}, P_4O_6, PO_2, O_2	
4s(3d), 4p(3d), 4d	K_2O-P_2O_5; KPO_3, KPO_2; CuO-P_2O_5; $CuPO_2$; K_2O-B_2O_3; KBO_2, $(KBO_2)_2$, $(KBO_2)_3$, B_2O_3; K_2O-SiO_2; K, O_2, $KSiO$	CaO-P_2O_5; $CaPO_2$, P_4O_{10}, PO_2, PO; ZnO-P_2O_5; Zn, ZnO, P_4O_{10}, O_2; CaO-B_2O_3; $CaBO_2$, CaB_2O_4, B_2O_3; ZnO-B_2O_3; Zn, ZnO, B_2O_3, O_2, BO, B_2O_2, BO_2; CaO-SiO_2; $CaSiO$, Ca_2SiO_3, SiO_2, SiO, Ca, O_2; CaO-ZrO_2; Ca, O_2, ZrO, ZrO_2		GeO_2-P_2O_5; $GePO_3$, P_4O_{10}, PO_2, GeO, O_2; GeO_2-B_2O_3; B_2O_3, GeO, O_2; GeO_2-SiO_2; GeO, O_2		Cr_2O_3-P_2O_5; $CrPO_2$; MnO-SiO_2; Mn, MnO, SiO, SiO_2

Valence shell							
5s(4d), 5p(4d), 5d	Rb_2O–P_2O_5; $RbPO_3$, $RbPO_2$; Ag_2O–P_2O_5; $AgPO_2$, $AgPO_3$, Rb_2O–B_2O_3; $RbBO_2$, $(RbBO_2)_2$, B_2O_3	SrO–P_2O_5; $SrPO_2$	SrO–B_2O_3; $SrBO_2$, Sr, BO, BO_2, B_2O_2, B_2O_3; SrO–SiO_2: $SrSiO$, SrO, Sr, SiO, O_2; SrO–ZrO_2: Sr, SrO, O, ZrO, ZrO_2	In_2O_3–B_2O_3; $InBO_2$; Y_2O_3–ZrO_2: YO, ZrO_2, ZrO, O	SnO–P_2O_5; $SnPO_2$; SnO–B_2O_3; $SnBO_2$; ZrO_2: ZrO_2, ZrO, O	Sc_2O_3–ZrO_2: ScO, Sc, O, ZrO_2, ZrO	MoO_3–B_2O_3; $BMoO_4$
6s(4d, 4f,5p, 5d), 6p(4f)	Cs_2O–P_2O_5; $CsPO_3$, $CsPO_2$; Cs_2O–B_2O_3; $CsBO_2$, $(CsBO_2)_2$, B_2O_3; Au_2O_3–B_2O_3; $AuBO$; Cs_2O–SiO_2: Cs, O_2, ($CsSiO_3$?)	BaO–P_2O_5; $BaPO_2$	BaO–B_2O_3; $BaBO_2$, Ba, BO, BO_2, B_2O_2, B_2O_3, BaB_2O_4; BaO–SiO_2: $BaSiO_3$ (?), O_2, Ba, BaO, SiO; BaO–ZrO_2: BaO, Ba, O	Eu_2O_3–P_2O_5: $EuPO_3$, $EuPO_2$; Tl_2O_3–P_2O_5: $TlPO_2$; Nd_2O_3–B_2O_3; $NdBO_2$; La_2O_3–SiO_2: SiO, O_2, LaO, La; Gd_2O_3–ZrO_2: GdO, Gd, O, ZrO, ZrO_2; Ho_2O_3–ZrO_2: HoO, Ho, O, ZrO, ZrO_2	PbO–P_2O_5; $PbPO_3$, $Pb(PO_3)_2$; PbO–B_2O_3; $PbBO_2$, Pb_2BO_3, B_2O_2, Pb_3BO_4, PbB_4O_6, BO_2, $Pb_2B_2O_5$, Pb, PbO, Pb_2O_2, O_2, BO, B_2O_3; PbO–SiO_2: PbO, Pb_2O_2; HfO_2–ZrO_2: ZrO, HfO, HfO_2, ZrO_2, O; PbO–ZrO_2: Pb, O_2	Bi_2O_3–P_2O_5; $BiPO_3$, $Bi(PO_3)_2$; Bi_2O_3–B_2O_3; $BiBO_2$, Bi_2BO_4, Bi_3BO_6, Bi_4O_6, $BiBO_3$ (?), Bi_3O_4, Bi_2O_3, Bi_2O_2, Bi_2O, BiO, Bi, Bi_2, O_2	WO_3–B_2O_3; BWO_4
7s (5f,6d)				UO_2–ZrO_2: UO_3, UO_2, UO, ZrO_2, ZrO, O			

and ZrO_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, SiO_2 and ZrO_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 the acid–base concept [2]: values of the differences of electron potentials, forming oxides; enthalpy of formation of the oxide modifier; the lattice energy of the oxide modifier per mole of O^{-2} at 298 K; the energies of the M–O–X bond (X = P, B, Si, Zr). The associated gaseous molecules were found over binary phosphate, borate and silicate systems with the same relative volatility of the individual oxides and the differences of the electron potentials, forming oxides in the binary systems, more than 0.8 eV/pm. Taking into consideration the observed regularities of the vaporization of oxide systems, the existence of the associated gaseous molecules might be expected and discussed over the $FeO–B_2O_3$, $SrO–B_2O_3$ and $BaO–SiO_2$, $FeO–SiO_2$ systems. 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 phosphorous 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 system 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 systems.

Despite the complex vapour composition over the oxide systems, the order of their relative volatility at constant temperatures is in agreement with the main regularities, observed earlier for the other types of inorganic compounds: the increase of the relative volatility of the systems from the first to the sixth period and its decrease from the first to the sixth group of the periodic table.

References

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