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Mass spectrometric thermodynamic studies of oxide systems and materials

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Progress in methods of synthesis of advanced materials as well as utilization of such materials at high temperatures requires information on the vaporization processes and thermodynamic properties of oxide systems. The optimal experimental method for these purposes is high-temperature mass spectrometry. This review summarizes and classifies experimental results obtained in mass spectrometric studies of the high-temperature thermodynamic properties of oxide systems and materials carried out in the last two decades. Published data on the vaporization processes and thermodynamic properties of oxide materials for high-temperature technologies are discussed from the standpoint of acid – base concept and model approaches including statistical thermodynamic methods.
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I. Introduction

Advanced materials based on oxide systems exhibit a wide variety of physicochemical properties including electrical, magnetic, dielectric, piezoelectric, semiconductor, superconducting, thermal, mechanical, optical, photoelectrochemical, catalytic ones, *etc*. Progress in key fields of modern science and technology, namely, space industry, aviation industry, power engineering, instrumentation, telecommunications, electronics, metallurgy, energy saving and environmental science is to a great extent determined by novel oxide materials which are often synthesized and utilized at high temperatures. However, the influence of high temperatures on the oxide materials usually causes selective vaporization of their components as well as interaction with the environment. As a rule, this leads to changes in the chemical composition and, consequently, originally specified physicochemical properties of the materials.

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The condensed phase – vapour equilibria in these systems can be studied by a unique method of high-temperature chemistry, *viz*., high-temperature mass spectrometry. It allows one not only to carry out mass spectrometric analysis of the composition of vapour, but also to determine the thermodynamic properties of components in both the vapour and condensed phases.[1, 2] Although the pioneering publications by Ionov,[3] Inghram and Drowart[4] were reported more than six decades ago, the number of experimental high-temperature mass spectrometry studies continuously increases. According to a comprehensive bibliographic review by Miller and Armatys,[5] a total of 362 high-temperature mass spectrometry studies on various inorganic systems and materials were published by investigators from forty-five research laboratories between 1990 and 2010. However, the review by Miller and Armatys[5] does not cover a variety of publications reported by researchers from the Russian Federation; therefore, the total number of experimental studies in the title field is actually much larger.

Experimental results obtained by high-temperature mass spectrometric studies of oxide systems and refractory oxide ceramics, ceramic nuclear fuel, single-crystalline oxide materials, slags and glasses were comprehensively addressed earlier in monographs.[6, 7]

This review has been written (i) to analyze the most important recent methodological studies in high-temperature mass spectrometry, which determine the prospects for the development of the experimental method in the coming decades and (ii) to discuss the results of research into the vaporization processes and thermodynamic proper-

ties of oxide systems and materials that were reported since the 1994 monograph.[7] It should be noted that mass spectrometric studies of the vaporization processes and thermodynamic properties of individual oxides, as well as gaseous salts of oxygen-containing acids will be left out of consideration because these problems were analyzed in monographs [8,9] and reviews,[10–12] respectively.

Publications that appeared between 1990 and 2010 include remarkable and valuable reviews on high-temperature mass spectrometry,[5,13–26] as well as monographs [27,28] and original communications concerning the results of mass spectrometric studies of the vaporization processes and thermodynamic properties of oxide systems and materials.[29–37] This review covers the basic concepts and conclusions drawn in these studies and original publications in the title field. Unlike the authors of the studies mentioned above, we will (i) dwell on the research articles reported by Russian investigators and (ii) systematically analyze the results of mass spectrometric thermodynamic studies on oxide systems and materials from the standpoint of application fields.

II. Specific features of high-temperature mass spectrometric experiment: new approaches and solutions

Mass spectrometric thermodynamic studies belong to the key investigation lines in high-temperature chemistry of materials. This was shown with certainty in an IUPAC Technical Report [15] whose authors not only comprehensively treated fundamental aspects of the promising avenue of scientific research called high-temperature chemistry of materials, but also listed the fundamental publications that allow one to make familiar with its distinctive features.

As shown in monographs [1,2,6–9] and reviews,[4,5,14–16,26] unique position of high-temperature mass spectrometry is due to a great potential of the method which combines the classical Knudsen effusion method needed to determine the partial pressures with mass spectrometric analysis of the composition of vapour over the system or substance being studied. Mass spectrometric thermodynamic studies can be carried out at temperatures of up to 3000 K and more and allow one not only to identify the composition of vapour over the system under study, but also to determine a complete set of thermodynamic properties of both individual compounds and multicomponent systems. It should be emphasized that among experimental methods of high-temperature chemistry such as EMF method, high-temperature solution calorimetry and heterogeneous equilibria, at present high-temperature mass spectrometry is the sole approach which makes it possible to obtain reliable thermodynamic data on the properties of binary and multicomponent systems and materials at temperatures above 1800 K.

The IUPAC Technical Report [14] prepared by the leading researchers in this field, *viz*., Drowart, Chatillon, Hastie and Bonnell, is a key publication devoted to comprehensive treatment of modern theoretical and experimental foundations of high-temperature mass spectrometry. It presents a detailed analysis of various mass spectrometry techniques and errors in the determination of the partial pressures and thermodynamic properties of inorganic compounds. Particular attention is given to instrumental and physicochemical factors responsible for the accuracy of the method, including:

— the design of the Knudsen effusion cell;
— the mode of heating this device;
— the measurement of temperature;
— the mode of forming the molecular beam;
— the orientation of the molecular beam relative to the ion source of the mass spectrometer;
— the type of mass analyzer;
— the ion current detector of the molecular forms of vapour;
— the purity of the samples under investigation;
— the possible modification of the activities of components as a result of their interactions with the effusion cell material or with other substances introduced into the system;
— the degree of establishment of mutual equilibrium between the condensed phase and the gaseous phase in the Knudsen effusion cell; and
— the changes in the phase relationships in the system under study in the course of the experiment.

Considerable attention was given [14] to a very important and still unsolved problem in high-temperature mass spectrometry, namely, theoretical substantiation of calculations and experimental determination of the ionization cross-sections of molecular forms of vapour. The authors of Ref. 14 systematized scarce data on the ionization cross-sections of atoms and molecules. Table 1 presents the experimental values of the relative ionization cross-sections of a number of oxide molecules taken from Ref. 14; these data may appear to be useful in determining the partial pressures of molecular forms of vapour over oxide systems. Among the recently used theoretical approaches to calculations of the ionization cross-sections of atoms and molecules, mention should be made of a semiempirical method by Deutsch *et al*.[38] It was used to calculate the dependences of the ionization cross-sections on the electron impact energy for the following oxide molecules: AlO, Al_2O, WO, WO_2, WO_3,[39] and B_2O_3.[36]

The review [14] was completed by formulation of key problems in mass spectrometric thermodynamic studies, which remain topical at present:

— reproducibility of vapour sampling procedure for mass spectrometric analysis;

Table 1. Relative ionization cross-sections (σ_i) of some oxide molecules.[14]

Compound		Electron impact energy /eV	$\sigma_{AB^+}/\sigma_{A^+}$ (see [a])
AB	A		
ZrO_2	ZrO	11	0.16
UO_2	UO	20	0.32
UO_3	UO_2	70	0.33
SO_2	Ar	30	0.50
Ga_2O	O_2	35	6.9
As_4O_6	Ar	30	20.77
W_2O_6	Ag	50	2.4
W_3O_9	W_2O_6	50	1.25

[a] The ionization cross-section ratio of AB^+ and A^+ ions produced upon ionization of molecular species AB and A, respectively.

— ionization processes and reliability of mass spectrometric analysis of the chemical composition of vapour;

— correctness of using the partial pressures of corresponding molecular forms of vapour instead of the intensities of ion currents in the mass spectra of vapour in those cases where information on the absolute or relative ionization cross-sections of atoms and molecules is needed.

The potential of mass spectrometry in analyzing the composition and determining the thermodynamic properties of inorganic high-temperature vapours was illustrated by Hilpert,[13] who compared Knudsen effusion mass spectrometry, transpiration mass spectrometry and laser-induced vaporization mass spectrometry (Fig. 1). Unique features of these methods were discussed in the literature, in particular, monograph.[7] In transpiration mass spectrometry, the upper bound of the measured pressures can be increased to 0.1 MPa compared to the corresponding value for the classical Knudsen effusion mass spectrometry, while laser-induced vaporization mass spectrometry allows the upper bound of the temperature range under study to be increased to 6000 K.[13] Using the advantages of laser-induced vaporization mass spectrometry, Hastie *et al.*[18,19] determined the temperature dependence of the partial pressures of molecular forms of vapour over alumina, yttria, hafnia and a $ZrO_2-Y_2O_3$ sample up to a temperature of 5000 K. This method was also used[21] to determine the partial pressures of molecular forms of vapour over UO_2 at 2930 and 3040 K on a setup whose design (see Electronic Supplement, Fig. 1)† is analogous to that proposed in Refs 18 and 19.

A continuation of experimental mass spectrometry studies at atmospheric pressure using a high-pressure sampling mass spectrometer[40] can be exemplified by the investigation of the reaction of silica with water vapour.

Blasing and Muller used molecular beam mass spectrometry coupled with high-temperature gas inlet system to study the gas phase in the case of gasification and combustion of various coals.[41,42] The influence of the partial pressure of oxygen and the chemical composition of coal on the specific features of vaporization of sodium, potassium, sulfur and chlorine species in the course of thermal conversion at 1673 K was illustrated.

Among the mass spectrometric methods of investigation of the vaporization processes and thermodynamic properties of inorganic systems and materials (see above), Knudsen effusion mass spectrometry still occupies a leading position. We will dwell on new theoretical and methodological approaches implemented recently.

The advantages and specific features of high-temperature mass spectrometry, as applied to the determination of the thermodynamic properties of metals and alloys, were analyzed in a handbook by Copland and Jacobson,[16] who proposed an original and clear form of representation of the scheme of a Knudsen effusion mass spectrometer with a magnetic sector mass analyzer for high-temperature experiments (Fig. 2). It should be noted that the most efficient ionization of the molecular species effusing from the Knudsen cell and the lowest extent of contamination of the ion source is usually achieved at 90° geometry of the molecular beam and ion beam.

† For Electronic Supplement, see www.iopscience.iop.org/0036-021X.

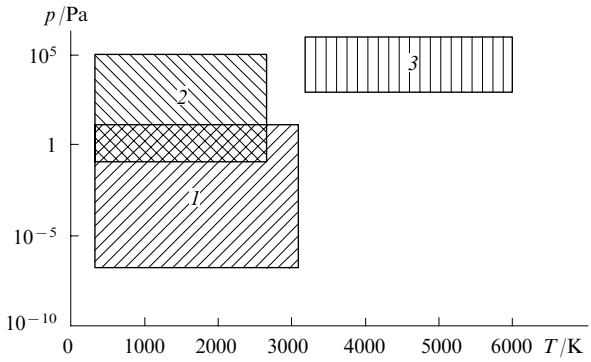


Figure 1. Temperature ranges and pressure ranges measured by methods of high-temperature mass spectrometry.[13]
Knudsen effusion mass spectrometry (*1*), transpiration mass spectrometry (*2*) and laser-induced vaporization mass spectrometry (*3*).

Studies[43–47] were continued by Knudsen effusion mass spectrometry. Chatillon and Heyrman[43] investigated conditions for controlled gas flow introduction into the Knudsen cell and analyzed surface reactivity taking gasification of coal with oxygen as an example. The thermodynamic properties of YbH, YbO and YbOH molecules in the gaseous phase were determined[44–46] using a similar controlled-pressure gas inlet system and different-type mass spectrometers, *viz.*, Nuclide12-90-HT and Nuclide HT-7. New intermetallic bonds and molecules were investigated[47] by Knudsen effusion mass spectrometry using a double effusion cell assembly to feed the vapour of a more volatile metal, in particular, lead. A simplified scheme of the assembly and its photograph are presented in Fig. 3.

Knudsen effusion mass spectrometry was used in elaborating experimental procedures for vaporization studies of organic compounds of low volatilily[48] and organometallic compounds.[49] It should be noted that a reactor designed to analyze organometallic compounds[49] comprises an evaporation cell and a cracking cell, being similar to a two-compartment reactor proposed by Gusarov and Gorokhov,[50] and differs from the latter only in the system of baffles in the cracking cell.

Kudin *et al.*[51] are successors to national traditions of research into ion-molecule equilibria involving neutral molecular species as well as positively and negatively charged ions present in the vapour phase using a Knudsen effusion cell as an ion-molecular beam source and a combined ion source of an automated mass spectrometer[52] (note that the phenomena in question were also considered in monographs[1,2,6,7]). This allows one to study both charged and neutral molecular species present in the vapour under thermoionic emission and electron impact conditions, respectively. A new approach was proposed[51] to determine the partial pressures of ions in saturated vapours over inorganic materials; vaporization of NaBr was studied using mass spectrometric approach and quantum chemical calculations.

The advantages of Knudsen effusion mass spectrometry as an additional experimental method for K–Ar dating of rocks on the surface of Mars and other planets using a double isotope dilution technique were illustrated in a study by Farley *et al.*[53]

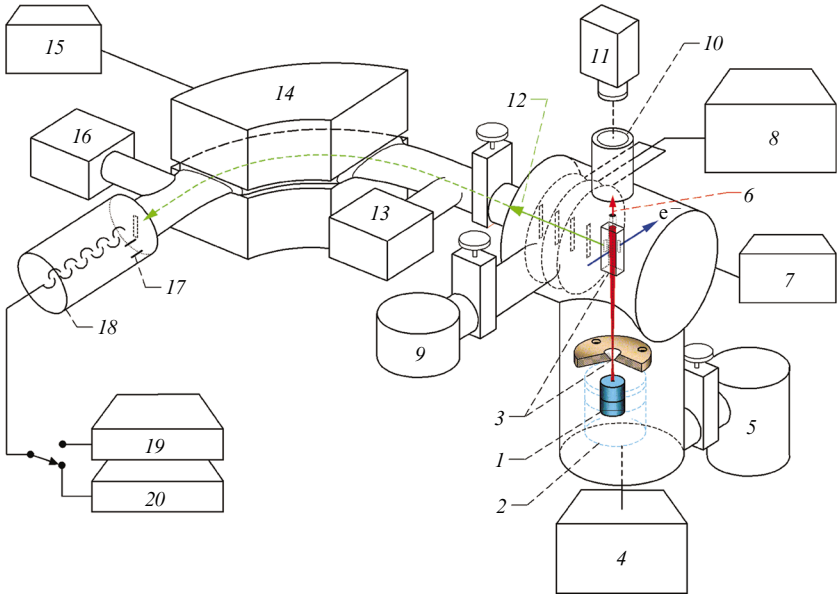


Figure 2. Knudsen effusion mass spectrometer with a magnetic sector mass analyzer.[16]
Knudsen effusion cell (*1*); tungsten heater and tantalum heat shields (*2*); molecular beam-defining apertures (*3*); low-voltage power supply for heater (*4*); turbomolecular pump (500 litre s^{-1}) (*5*); molecular beam (*6*); emission regulator (*7*); high-voltage power supply (*8*); turbomolecular pump (240 litre s^{-1}) (*9*); view port (*10*); video camera (*11*); ion beam (*12*); ion pump (50 litre s^{-1}) (*13*); magnet (*14*); magnet power supply (*15*); ion pump (50 litre s^{-1}) (*16*); movable Faraday cup (*17*); 20-dynode electron multiplier (*18*), ion counter (*19*); and electrometer (*20*).

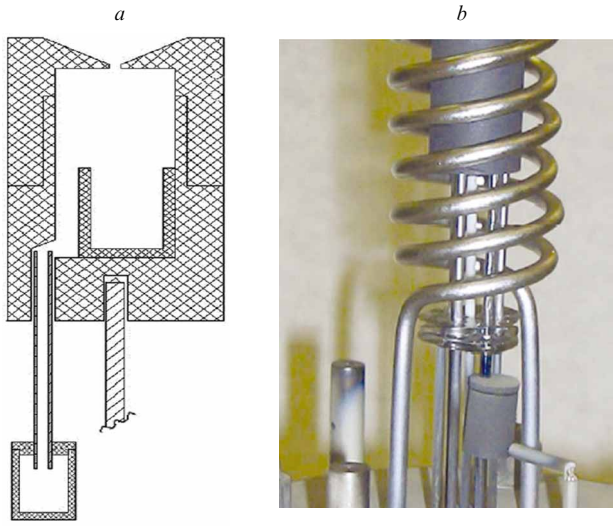


Figure 3. A simplified scheme of the double effusion cell assembly to feed the vapour of the more volatile metal (Pb) from the lower cell to the upper cell in studies of molecular species of PbE vapours (E = Si, Ge, Sn) (*a*) and a photograph of the assembly (*b*).[47]

Kobertz *et al.*[23,54] investigated the thermodynamic properties of aluminium nitride under equilibrium vaporization conditions by Knudsen effusion mass spectrometry and in the kinetic regime using a skimmer-coupled mass spectrometer with a thermal analysis system (NETZSCH GmbH, STA409 C) at $T > 1273$ K and compared the results obtained. It was found that the methods give complementary information in studies of high-temperature synthesis and operating conditions of materials. Metallic materials were studied on macro- and nano-scale by Broz *et al.*,[55] who combined Knudsen effusion technique and thermal analysis using a NETZSCH STA409 CD-QMS 403/5 system equipped with a quadrupole mass analyzer. The results of determination[55] of the activity of silver in the Ag–Pd system at 1510 K appeared to be consistent with published data.

The possibility to extend the temperature range suitable for Knudsen effusion mass spectrometry studies was considered.[25,56] The authors cited were the first to design and practically implement a laser heated Knudsen cell system for high-temperature experiments ($T > 3273$ K). Figure 4 presents a schematic of this system and the appearance of the Knudsen effusion cell with laser heated furnace.

High cost and the lack of commercially available static mass spectrometers with magnetic sector mass analyzers, which usually have better parameters for high-temperature mass spectrometric thermodynamic studies, gave an impetus to the design of systems with cheaper quadrupole mass spectrometers coupled with single- or multicell vaporizers. At present, researchers from Sweden,[57,58] Finland,[59–62] Japan,[63,64] France,[65,66] and India[67] use such systems to investigate the thermodynamic properties of inorganic compounds and materials at high temperatures. The absence of such studies carried out by researchers from the Russian Federation in this list is not surprising because a mass spectrometer for high-temperature thermodynamic studies of substances of low volatility (MS 1301 instrument equipped with double-cell vaporizers)[1] was designed at the Special Design Bureau of Analytical Instrumentation, USSR Academy of Sciences, as long ago as the 1970s and commercially produced since then. These modified instru-

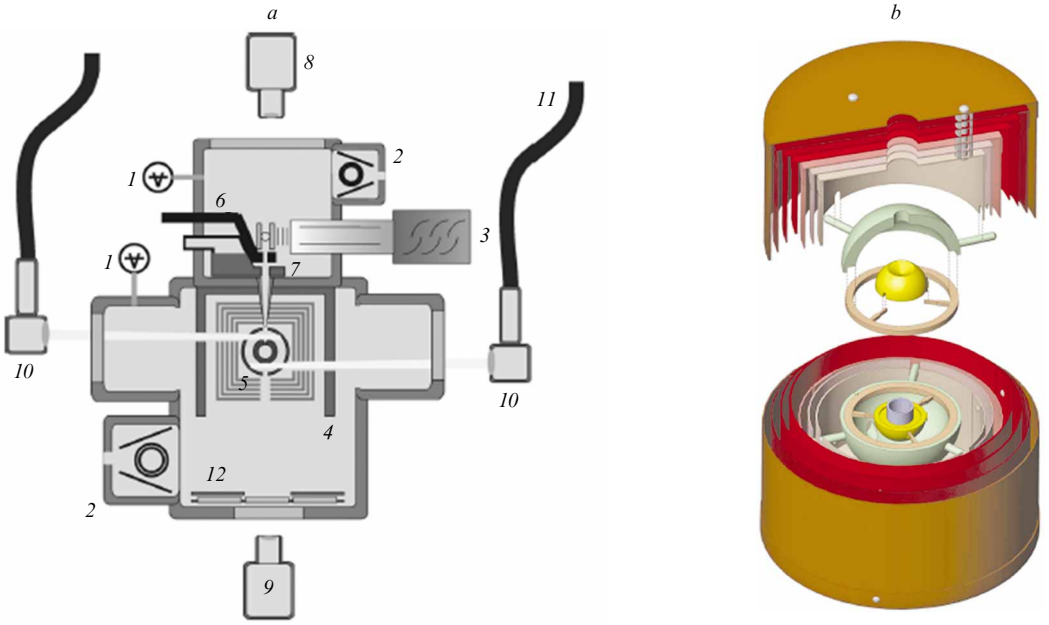


Figure 4. A schematic of laser heated Knudsen cell system (*a*) and the appearance of the ensemble *5* (*b*).[25, 56]
Vacuum gauges (*1*); turbomolecular pump (*2*); quadrupole mass spectrometer (*3*); furnace water cooling system (*4*); Knudsen effusion cell with laser heated furnace (*5*); chopper (*6*); liquid N_2 cold trap (*7*); video control camera (*8*); pyrometer (*9*); laser focusing optics (*10*); laser light guide (*11*); and protective revolving windows (*12*).

ments are still in operation in domestic research laboratories.

In the last decade, a variety of high-temperature double-cell and multicell vaporizers for mass spectrometric investigations were designed. Among them, mention may be made of the modified vaporizers for both magnetic sector [16, 68] and quadrupole mass spectrometers (see Electronic Supplement, Fig. 2).

It should be emphasized that progress in the design and production of multicell high-temperature vaporizers for differential mass spectrometric studies would be impossible without fundamental publications by Chatillon (they are surveyed in Refs 6, 7, and 14). The development of methodological and theoretical approaches in this field were continued by Chatillon and co-workers,[20, 69] in particular, in the design of an original mechanical device for effusion cell positioning in a multicell vaporizer with an accuracy of 0.01 mm (see Electronic Supplement, Fig. 3). The appropriateness of using differential mass spectrometry was demonstrated taking kinetic studies and the determination of the evaporation coefficients of molecular species in vapours over, *e.g.*, silica and alumina.[24, 70]

Heyrman *et al.*[71] critically analyzed thermodynamic data for the La–O and Y–O systems obtained by methods of high-temperature chemistry including Knudsen effusion mass spectrometry and proposed an original method of investigation of congruent vaporization in these systems. Also, the possibility of calculating changes in the refractive index of glasses in the $B_2O_3–SiO_2$ system caused by selective evaporation of boron oxide at 1588 K was demonstrated [72] using the method of complete isothermal evaporation [2] and high-temperature mass spectrometry.

Concluding this Section, it should be noted that recent high-temperature mass spectrometry studies mainly use well-known methods for the determination of the thermodynamic functions of mixing in inorganic systems and materials, namely:[1, 2, 6, 7]

— differential mass spectrometry (a comparison of ion currents);

— the 'oligomer–monomer' method;

— the Neckel–Wagner method; and

— the Belton–Fruehan method.

Great potential of the Belton–Fruehan method in the activity studies of components of binary and multicomponent oxide systems was demonstrated in a review [30] concerned with systematization of corresponding thermodynamic data in order to check their reliability compared to the data obtained using other mass spectrometry techniques (differential mass spectrometry, 'oligomer–monomer' method) as well as by the EMF and heterogeneous equilibria methods.

III. Vaporization processes and thermodynamic properties of oxide systems and materials

III.1. High-refractory oxide ceramics based on zirconia, hafnia and rare-earth element oxides

Unique potential of high-temperature mass spectrometry in studies of vaporization processes and thermodynamic properties of oxide systems can be best demonstrated in relation to high-refractory oxide ceramics based on zirconia, hafnia and rare-earth element oxides. This ceramics is characterized by low volatilily as well as high thermal and chemical stability and thus has a variety of technological applications from the formation of high-temperature protective coatings to the design of refractory and optical materials.[6, 7]

The composition of the gaseous phase over the samples of recently studied systems $Al_2O_3–Dy_2O_3$,[73, 74] $Nd_2O_3–HfO_2$,[75, 76] $Gd_2O_3–HfO_2$,[76] $Yb_2O_3–ZrO_2$,[77] $Y_2O_3–SiO_2$ [78] and $Lu_2O_3–ZrO_2$ (see Ref. 79) corresponds

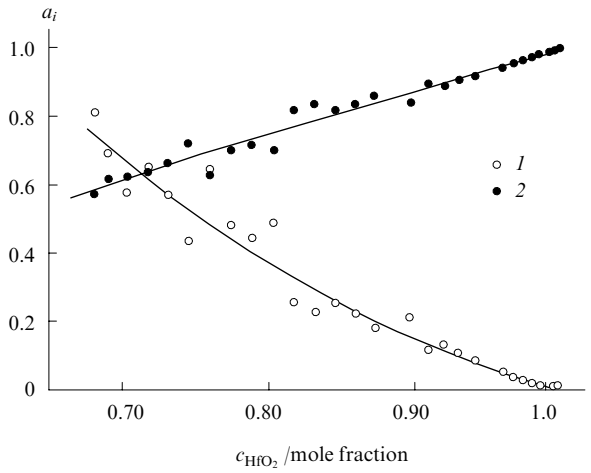


Figure 5. Activities of components in the $Nd_2O_3-HfO_2$ system plotted *vs.* content of HfO_2; $T = 2300$ K.[75,76]
Activity of Nd_2O_3 ($\times 100$) (*1*) and activity of HfO_2 (*2*).

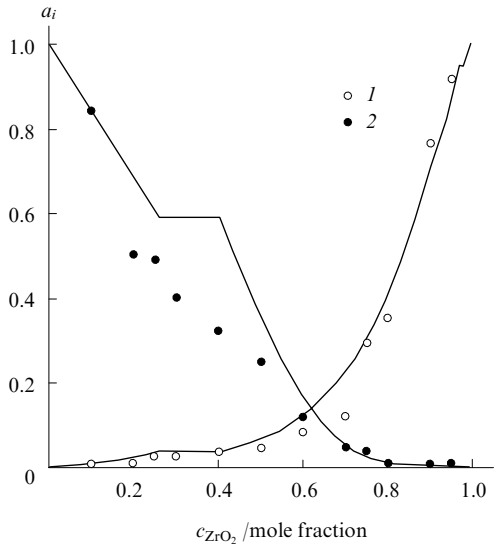


Figure 6. Activities of components in the $Yb_2O_3-ZrO_2$ system plotted *vs.* content of ZrO_2; $T = 2400$ K.[77]
Activity of ZrO_2 (*1*) and activity of Yb_2O_3 (*2*). Open circles and full circles denote the experimental data obtained by Knudsen effusion mass spectrometry, curves denote the results of CALPHAD-based calculations.

to vaporization of corresponding individual oxides.[8,9] The activities of components of these systems were determined by differential mass spectrometry using corresponding individual oxides as reference samples. The systems in question are characterized by negative deviations from ideality, except the $Y_2O_3-SiO_2$ system[78] studied at lower temperatures (below 2020 K). The concentration dependences of activities (a_i) of components in two systems, $Nd_2O_3-HfO_2$ ($T = 2300$ K) and $Yb_2O_3-ZrO_2$ ($T = 2400$ K), are shown in Figs 5 and 6, respectively. It should be noted that correctness of the activity values of the components in the $Yb_2O_3-ZrO_2$ system[77] was confirmed by the results of CALPHAD calculations of these parameters using the available data on the phase equilibria in this system (see Fig. 6).

III.2. Oxide materials for nuclear power engineering

Progress in nuclear power engineering, enhancement of the efficiency of nuclear reactors with extension of the operating temperature range and an increase in the number of systems under study impose more stringent requirements on the safety, as well as on the accuracy and reliability of experimental data on the vaporization processes and thermodynamic properties of oxide systems and materials used in various technological cycles. Following a tradition,[6,7] we will consider recent important results of mass spectrometric thermodynamic studies of the vaporization of nuclear fuel components, fission products and lithium-containing compounds (in connection with problems in the design of thermonuclear reactors).

Taking into account a paramount importance of the systems considered in this Section, we will also dwell on the results obtained in studies of individual oxides as components of nuclear fuel. Mass spectrometric studies of vaporization processes in uranium oxides were carried out[25,80–83] using a facility designed[80] to feed an adjustable oxygen flux into an effusion cell heated to a temperature of 1900 K. This made it possible to investigate the oxidation and vaporization of fresh and irradiated nuclear fuel and to determine the vaporization rates and the equilibrium pressure of UO_{2+x} vapour at specified partial pressures of oxygen. Vaporization of fission products of UO_2 (oxidized to U_3O_8) was studied in a wide temperature range.[81,82] The ratio of molecular species, UO_2 and UO_3, in the vapour over solid and molten stoichiometric uranium dioxide in the temperature range 2800–3400 K was determined for the first time in a single experiment.[83] A study[84] of sublimation of plutonium dioxide led to identification of a molecular species PuO_3; however, the existence of PuO_3 was not confirmed in a more recent study on vaporization in the Pu–O system under equilibrium conditions.[85] Vaporization of americium oxide[86] and neptunium oxide[87] was studied. It was found that at $O:Np \ll 1.9$, the total vapour pressure over the samples of reduced NpO_2, dilute neptunium oxide in americium dioxide and dilute neptunium oxide in a mixture of americium oxide and plutonium oxide increases as the O : Np ratio decreases.[87]

The activities of components in the UO_2-ZrO_2 system were determined by differential mass spectrometry under vaporization from tungsten cells in the temperature ranges 2200–2650 K[88] and 2000–2500 K.[89] Reasonable agreement between the results of determination of the activity of UO_2 in this system at 2205 K obtained independently by researchers from two different laboratories[88,89] is demonstrated in Fig. 7. It should be noted that at 2205 K, the UO_2-ZrO_2 system exhibits positive deviations from the ideal behaviour, which indicate a trend towards immiscibility. As temperature increases to 2498 K, these deviations become much smaller. In Fig. 8, the chemical potential of ZrO_2 in the

$$UO_2-ZrO_2,\ HfO_2-ZrO_2,\ Y_2O_3-ZrO_2,\ Lu_2O_3-ZrO_2$$

systems is plotted *vs.* ZrO_2 content ($T = 2700$ K).[88] These plots are indicative of strengthening of chemical interaction in the specified order in accordance with the acid-base concept (see monograph[7]).

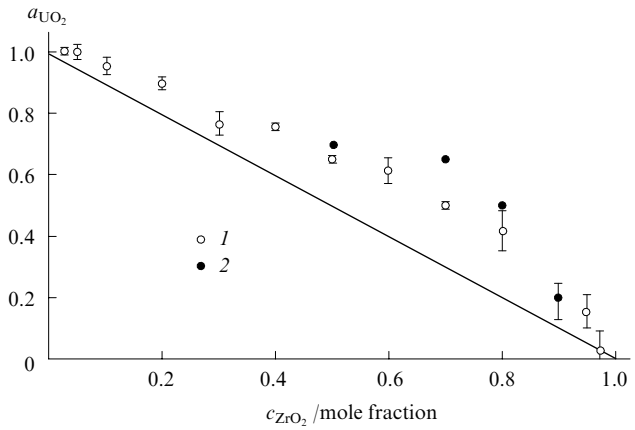


Figure 7. Activity of UO_2 in the UO_2-ZrO_2 system plotted *vs.* content of ZrO_2; $T = 2205$ K; experimental data obtained independently in different research laboratories.
Data taken from Ref. 89 (*1*) and Ref. 88 (*2*); the straight line is the plot for ideal solution.

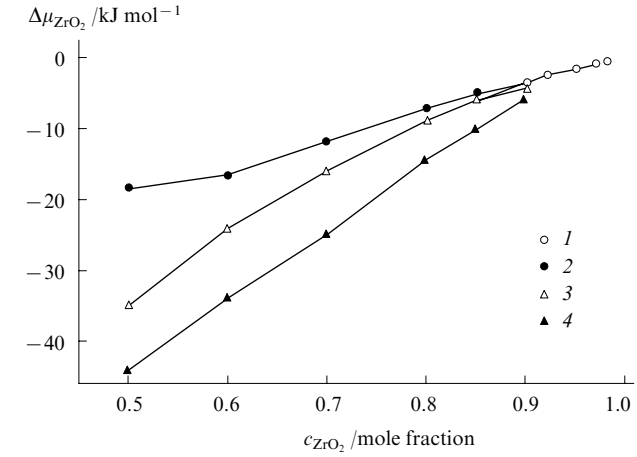


Figure 8. Chemical potential ($\Delta\mu$) of ZrO_2 in the UO_2-ZrO_2 (*1*), HfO_2-ZrO_2 (*2*), $Y_2O_3-ZrO_2$ (*3*) and $Lu_2O_3-ZrO_2$ (*4*) systems plotted *vs.* ZrO_2 content; $T = 2700$ K.[88]

The partial pressures of O, U, La, LaO, UO, UO_2 and UO_3 species over solid solutions in the $La_2O_3-UO_2$ system were determined under vaporization conditions.[90] It was found that the total pressure of La-containing species over the $La_2O_3-UO_2$ solid solutions obeys the Henry law as the La content in the condensed phase changes from 1 at.% to 5 at.% at 2393 K. Unfortunately, the error in the determination of experimental values[90] was not specified. A study[91] on vaporization of $(U, Dy)O_2$ samples containing less than 14.9 mass % of dysprosium at 2500 K showed that the total pressure of dysprosium species is an order of magnitude lower than that of uranium species. The partial pressures of UO_3, UO_2, PuO_2, PuO, Pu and UO vapour species over samples of the Pu–U–O system at 2300 K determined by Knudsen effusion mass spectrometry appeared to be equal to those obtained by CALPHAD approach.[92] The partial vapour pressures of molecular species over a $(Pu_{0.756}Am_{0.244})O_{2-x}$ sample in the temperature range 2000–2300 K were determined.[93] The results obtained were used to describe the phase diagram of the Pu–Am–O system using thermodynamic data for the Pu–Am and Am–O binary systems obtained from CALPHAD calculations.

Vaporization of actinide and lanthanide oxides accompanying vaporization of high burn-up commercial nuclear UO_2 fuel at temperatures below 2750 K was studied.[94] In the case in point, the fuel contained relatively high concentrations of neptunium, plutonium, americium, curium, lanthanum, cerium, neodymium, samarium, europium and gadolinium oxides. The total vapour pressure of molecular species over each oxide component of the fuel was shown to correlate with the atomic fraction of the corresponding actinide or lanthanide, which was, for example:

Element	^{237}Np	^{239}Pu	^{243}Am	^{244}Cm
Atomic fraction	0.001349	0.006913	0.001187	0.001162

Release of fission products from very high burn-up nuclear fuel at temperatures to 2750 K and corresponding microstructure changes were investigated.[95] The vapour contained both more volatile molecules containing rubidium, iodine, tellurium, caesium, as well as less volatile species containing barium and strontium. The thermal stability and high-temperature behaviour of advanced nuclear fuels at temperatures up to 2700 K was studied by Knudsen effusion mass spectrometry.[96] Recent researches in this field were reviewed by Colle *et al.*[25]

Sodium is used as a coolant in nuclear reactors; therefore, studies of the vaporization processes and thermodynamic properties of sodium oxide compounds are of great importance. The temperature dependence of the partial pressure of sodium species over the coexisting phase field $NaUO_3-Na_2U_2O_7-Na_2UO_4$ was measured by Knudsen effusion mass spectrometry in the temperature range 1117–1193 K. This allowed the Gibbs energy of formation of $NaUO_3$ in the condensed phase to be determined.[97] The enthalpy of formation of α-Na_2NpO_4 evaporated from a tungsten cell at temperatures below 2700 K was estimated in a recent mass spectrometric study of this compound.[98]

Yamawaki and co-workers[99–103] reported a series of publications devoted to the vaporization processes and thermodynamic properties of fission products of nuclear fuel. They studied the vaporization thermodynamics of two compounds, $BaUO_3$ (Ref. 99) and $SrUO_3$,[100] as well as their behaviour in various gaseous atmospheres simulating accident conditions,[101] at temperatures to 1920 K. The vaporization behaviour of $SrPuO_3$ and Cs_2UO_4 was also studied (see Refs 102 and 103, respectively). Having measured the temperature dependences of the partial pressures of molecular species over two-phase mixtures in the $ZrO_2-BaZrO_3$ and $BaZrO_3-Ba_2ZrO_4$ concentration ranges at temperatures below 2085 K, the standard enthalpy of formation of $BaZrO_3$ was determined.[104] The vaporization behaviour, thermodynamic properties and phase relationships in the Mn–Te–O system are discussed in detail.[26, 105, 106]

Knowledge of thermochemical properties of lithium-containing compounds (Li_4SiO_4, Li_2ZrO_3, Li_2TiO_3, $LiAlO_2$) is necessary for the design of new types of thermonuclear reactors. These properties were determined using Knudsen effusion mass spectrometry and considered by Yamawaki and co-workers.[107–111] Reliability of the experimental values of the thermodynamic properties of lithium

aluminates in the Li–Al–O system, identified by high-temperature mass spectrometry, was confirmed [112] by the results of the EMF method and differential scanning calorimetry studies of these properties.

III.3. Oxide materials for novel types of fuel cells

The design of new-generation solid-oxide fuel cells is a topical problem in modern high-temperature chemistry of materials.[113] Taking vaporization of $LaCrO_3$ in various gaseous atmospheres as an example, Hilpert *et al.*[114] gave convincing proofs that the degradation of electrical properties of solid-oxide fuel cells is, in particular, due to selective vaporization of components of interconnect materials, *e.g.*, chromium.

Systematic Knudsen effusion mass spectrometry studies of the vaporization processes and thermodynamic properties of perovskites and systems based on them were reported.[115–123] At present, Miller ans Matraszek [124] and Markus and co-workers [125] continued research in the field. Vaporization of $LaCrO_3$ from iridated tungsten cells in the temperature range 1887–2333 K results in Cr, CrO, CrO_2 and LaO as major forms of molecular species;[115] the temperature dependences of the activity of chromium oxide in the Cr-depleted $LaCrO_3-Cr_2O_3$ system and the thermodynamic properties of lanthanum chromate were determined. The thermodynamic functions of mixing as well as vaporization of $La_{1-x}Ca_xCrO_{3-\delta}$ and $La_{1-x}Sr_xCrO_{3-\delta}$ were respectively studied in the temperature range 1950–2050 K [116] and at 2000 K.[117]

Molecular species O_2, Ga, GaO, Ga_2O and LaO were identified in the vapour over the $La_2O_3-Ga_2O_3$ system in the temperature range 1494–1937 K and their partial vapour pressures were determined.[118] This made it possible to calculate the thermodynamic functions of mixing in the system in hand. Similar studies were combined with investigations of cation diffusion in a quasi-quaternary system $La_2O_3-Ga_2O_3-SrO-MgO$ in the temperature range 1600–1900 K [119, 120] and in the ternary system $MgO-Cr_2O_3-La_2O_3$.[121] The dependence of the activity of gallium oxide on the content of magnesium oxide in the ternary phase of perovskite $LaGa_{1-y}Mg_yO_{3-y/2}$ at 1700 K is presented in Fig. 9. A study of $MnO-Y_2O_3-ZrO_2$ solid solutions at 1700 K using the methods described above revealed large positive deviations from ideal behaviour of the activities of MnO.[122] Mass spectrometric thermodynamic studies of the solid solutions $LaGa_{1-x}Al_xO_3$, where $0 \leqslant x \leqslant 1$, $La_{0.9}Sr_{0.1}Ga_{0.8-x}Al_xMg_{0.2}O_{2.85}$, where $x = 0.1$, 0.2, 0.3 (see Ref. 123), and $SrCe_{0.95}Yb_{0.05}O_3$ (see Ref. 124) at 1800 K revealed that these systems are candidates for solid-oxide fuel cell materials. These results are complementary to those obtained in the studies of chromium vaporization from steels covered with spinel-based coatings.[125]

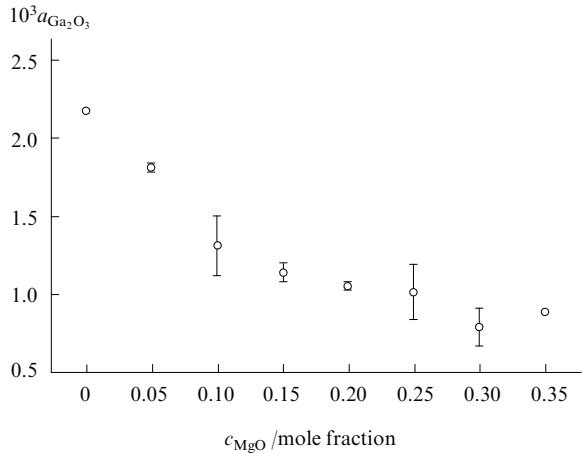


Figure 9. Activity of gallium oxide in the ternary phase of perovskite $LaGa_{1-y}Mg_yO_{3-y/2}$ plotted *vs.* MgO content; $T = 1700$ K.[119, 120]

Kudin and co-workers [126, 127] studied thermoionic emission from solid electrolytes and identified neutral and ionic species in the vapours over lithium vanadium bronze $Li_{0.2}VO_{2.6}$ (Ref. 126) and over solid electrolytes ($Li_4TiP_2O_9$ and $Na_4TiP_2O_9$) [127] by Knudsen effusion mass spectrometry following the procedure considered in Refs 51 and 52.

III.4. Oxide films, semiconductors and sensor materials

Oxide materials exhibit a variety of complementary physicochemical properties (see Introduction). This can be best illustrated taking binary and multicomponent oxide systems as examples; they will be considered in the text below. Investigation of the vaporization processes, thermodynamic properties and phase equilibria involving the gaseous phase is immediately related to the design and synthesis of materials possessing high-temperature superconductivity ($BaO-Y_2O_3$,[128] Pb-doped Bi–Sr–Ca–Cu–O,[129] as well as Tl–Ba–Ca–Cu–O,[130] $SrO-TiO_2$ [131]) unique optical ($TiO_2-Sc_2O_3-Lu_2O_3$,[132] $TiO_2-Nb_2O_5$,[133] $Bi_2O_3-SnO_2$ [134]), semiconductor (SnO_2-WO_3,[135] $ZnO-SnO_2$ [136]), piezoelectric ($K_{0.5}Bi_{0.5}TiO_3$,[137] $Bi_2O_3-Fe_2O_3$,[138] $Na_2O-Nb_2O_5$ [139]), ferroelectric ($PbO-ZrO_2-TiO_2$,[140] $PbTiO_3$ [141]), magnetic ($PbO-V_2O_5$,[142] $La_2O_3-SrO-CoO$ [143, 144] and $SrO-Mn_2O_3-Al_2O_3-Sb_2O_5$ [145]) as well as sensor ($Bi_2O_3-SnO_2$,[134] SnO_2-WO_3,[135] $ZnO-SnO_2$,[136] $Bi_2O_3-Fe_2O_3$,[138] $PbTiO_3$ [141]) properties.

Consider the results of recent Knudsen effusion mass spectrometric studies of these systems.

Vaporization of $BaO-Y_2O_3$ samples from platinum effusion cells in the temperature range 1550–1850 K affords BaO and Ba_2O_2 as major molecular species and small amounts of barium and oxygen species.[128] After determination of the partial pressures of these molecular species, the activities of components in the system under study and the thermodynamic properties of BaY_2O_4 and $Ba_3Y_4O_9$ were found.[128] A joint high-temperature mass spectrometry, DTA and TGA study of the vaporization of a sample containing $Bi_{1.9}Pb_{0.35}Sr_{2.0}Ca_{2.2}Cu_{3.0}O_{10.2}$ was reported by Wahlbeck *et al.*,[129] who determined the mass loss and the partial vapour pressure of bismuth species in the temperature interval 898–1015 K; the activity of bismuth in the $Bi_2Sr_2Ca_2Cu_3O_y$ sample was found to be 0.073 at 800 K. The mass loss of thallium oxide evaporated from $Tl_2Ba_2Ca_2Cu_3O_{10}$ was determined by the classical Knudsen method at 773 K.[130] The authors of a high-temperature differential mass spectrometric study of samples in the $SrO-SrTiO_3$ system at 1923 K determined the activity values of SrO and analyzed discrepancies between them and the phase equilibria in this system.[131]

Semenov *et al.*[132] studied the composition of vapour and determined the partial pressures of molecular species (TiO, TiO_2, LuO, ScO) for more than forty samples of the

$TiO_2-Sc_2O_3-Lu_2O_3$ system (including binary systems) at 2400 K. Although the system exhibits negative deviations from the ideal behaviour, no molecular associates were identified in the gaseous phase over the samples. The major molecular species identified in the vapour over the $TiO_2-Nb_2O_5$ system at 2200 K included TiO_2, TiO and NbO_2; the concentration dependences of their partial vapour pressures also confirmed negative deviations from ideality.[133] Alikhanyan and co-workers[134] studied the $Bi_2O_3-SnO_2$ system in the temperature range 1000–1270 K by Knudsen cell mass spectrometry, differential thermal analysis and powder X-ray diffraction under vaporization from platinum cells, determined the partial vapour pressures of Bi, BiO, Bi_2O_3, Bi_4O_6, O_2, SnO species and activities of components and constructed projections of the phase diagram of this system in the pressure–temperature and temperature–composition coordinates.

Molecular associates $SnWO_4$, Sn_2WO_5 and SnW_2O_7 were identified for the first time[135] in the vapour over the $SnO-WO_3$ system in addition to O_2, W_3O_9 and W_4O_{12} molecular species in the temperature interval 1250–1400 K. Only Zn, SnO and O_2 were identified in the vapour over samples of the $ZnO-SnO_2$ system (evaporation from quartz effusion cells was studied at temperatures between 1360 and 1460 K).[136] The partial vapour pressures of molecular species and the activities of components were also determined and a projection of the phase diagram of the $ZnO-SnO_2$ system at 1450 K was constructed in the pressure–composition coordinates. A study[137] on thermal decomposition of $K_{0.5}Bi_{0.5}TiO_3$ ceramics in the temperature range 1113–1213 K revealed only products of dissociative vaporization of potassium oxide and bismuth oxide, *i.e.*, K, Bi, BiO, in the vapour over the solid sample. The mass loss of the potassium and bismuth components shifts the starting composition to the three-phase region of the $K_2O-Bi_2O_3-TiO_2$ system.

Alikhanyan and co-workers[138] determined the partial pressures of Bi, Bi_2, BiO, Bi_2O_3, Bi_4O_6 and O_2 vapour species as well as the thermodynamic functions of mixing in the $Bi_2O_3-Fe_2O_3$ system at 1050–1100 K and recommended that the optimum temperature of solid-phase synthesis of bismuth ferrites be nearly 993 K. Determination of the temperature dependence of the activities of sodium oxide in the two-phase regions of the $Na_2O-Nb_2O_5$ system in the temperature range 1073–1473 K under vaporization from molybdenum cells[139] allowed one to calculate the integrated thermodynamic functions of formation in this system. The activities of Na_2O and Nb_2O_5 in the two-phase regions of the $Na_2O-Nb_2O_5$ system at 1000 K are presented in Fig. 10. An analysis of the thermodynamic properties of this system revealed stability of $NaNb_3O_8$ towards decomposition at $T < 950$ K.[139]

Selective vaporization of molecular species of lead oxide (mainly Pb, PbO and Pb_2O_2) was observed in a study of vaporization in the $PbO-ZrO_2-TiO_2$,[140] $PbTiO_3$ (Ref. 141) and $PbO-V_2O_5$ (Ref. 142) systems at temperatures below 1150 K. This made it possible to determine the activity of lead oxide in these systems; the results obtained corresponded to negative deviations from ideality. Lopatin *et al.*[142] raised the temperature to 1350 K, identified the molecular species V_2O_{10} and PbV_2O_6 in the vapour over samples of the $PbO-V_2O_5$ system and determined their partial pressures. Vaporization studies of the LaO–SrO–CoO system[143, 144] in the temperature range 1600–2087 K

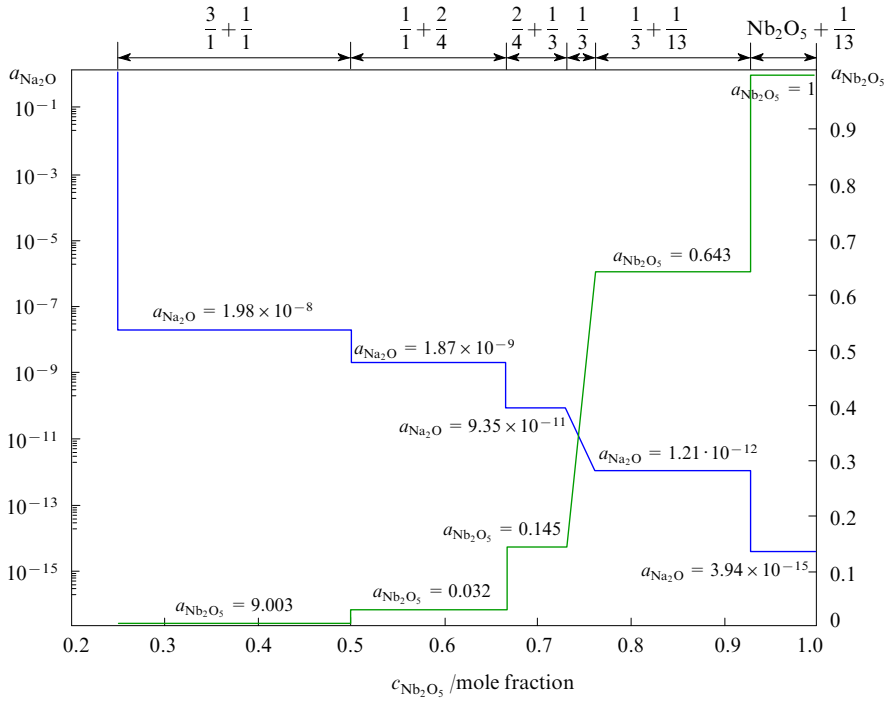


Figure 10. Activities of Na_2O and Nb_2O_5 in two-phase regions of the $Na_2O-Nb_2O_5$ system at 1000 K.[139]

Top: existence ranges of two stoichiometric phases. For instance, $\frac{3}{1}+\frac{1}{1}$ denotes the existence of $3\,Na_2O-Nb_2O_5$ and $Na_2O-Nb_2O_5$.

resulted in determination of the partial vapour pressures of cobalt species and the activity of cobalt oxide; the deviations from ideal behaviour in this system were shown to change their sign from positive to negative as the temperature increased and the content of cobalt oxide in the condensed phase decreased. Selective vaporization of molecular species Sb, Sb_2 and SbO as products of dissociative vaporization of antimony oxide from samples in the $SrO-Mn_2O_3-Al_2O_3-Sb_2O_5$ system at 1200 K was observed.[145] Heating to 1950 K led to the appearance of strontium and aluminium species, as well as AlO and Al_2O, in the vapour; this indicated the vaporization of corresponding oxides in the system under study.[145]

III.5. Metallurgical slags ‡

A review by Zaitsev and Shakhpazov[146] is devoted to progress in modern theory of metallurgical slags using the results obtained by high-temperature mass spectrometry. Adaptation of Knudsen mass spectrometry to studies of slags formed in binary systems containing Na_2O, K_2O, MnO, MgO and SiO_2 was considered in the monograph[28] and in the review[31] taking systems $(Na_2O, K_2O)-Al_2O_3-SiO_2$, $(Na_2O, K_2O)-SiO_2$, $(Na_2O, K_2O)-2SiO_2$, $Na_2O-Cs_2O-SiO_2$ and BaO–SrO as examples.

Zaitsev and Mogutnov[147] continued a research into vaporization processes and thermodynamic properties of the calcium silicate system during generation of volatile niobium and molybdenum suboxides produced in high-temperature reactions between the cell material (Nb or Mo) and samples under study. This approach allows one not only to study equilibria involving volatile products, but also to determine the activities of components in the system in hand by two independent methods. The results of previous mass spectrometric investigations of the CaO–SiO_2 system can be found in the monograph.[7] The thermodynamic functions of mixing in the calcium aluminate system in the temperature range 1833–2033 K were determined by Shultz and co-workers[148–150] and demonstrate negative deviations of this system from ideal behaviour.

There is considerable literature on the vaporization processes and thermodynamic properties of the Al_2O_3–SiO_2 system.[7, 27, 151–165] The emphasis was placed on experimental determination of the thermodynamic properties of mullite and on refinement of the phase diagram of the $Al_2O_3-SiO_2$ system. Vaporization processes in this system were studied and the partial vapour pressures of molecular species over the system were determined in a wide temperature range. Vaporization processes in $3Al_2O_3\cdot 2SiO_2$ were studied[151, 152] and the activities of components and the Gibbs energies of formation at 1833 and 1933 K were obtained. They match the values found earlier to an accuracy of 10%.[7, 9] The activities of Al_2O_3 and SiO_2 were determined for the mullite–Al_2O_3 concentration range in the temperature interval from 1400 to 1800 K.[153] Since the partial vapour pressures of molecular species in this temperature interval are low, the thermodynamic properties were determined following a procedure based on the formation of volatile products in the Knudsen cell. The activity of SiO_2 in the region of two-phase equilibrium between mullite and alumina in the $Al_2O_3-SiO_2$ system was shown to be 0.54–0.56.

The concentration dependence of the activity of SiO_2 under vaporization in the $Al_2O_3-SiO_2$ system containing from 40 mol.% to 90 mol.% of silica from a double single-temperature tungsten cell at 2150 K was measured. Small negative deviations from ideal behaviour observed at low concentrations of Al_2O_3 changed their sign as the content of alumina exceeded 10 mol.%. The advantages of yet another two studies[154, 155] include agreement (i) between the experimentally determined activities of SiO_2 and results of calculations using the polymeric model in combination with the Temkin and Lumsden approaches and (ii) between the results of modelling of the phase diagram of the $Al_2O_3-SiO_2$ system and published data on phase equilibria in this system.

In a continuation of mass spectrometric investigations of the thermodynamic properties of and phase equilibria in the $Al_2O_3-SiO_2$ system,[156–163] the activity values of SiO_2 in this system at 2220, 2300 and 2400 K were obtained[156, 157, 160] using the Belton–Fruehan method while the activity of Al_2O_3 was calculated using the Gibbs–Duhem equation. The activity of SiO_2 at 2200 K exhibits negative deviations from ideal behaviour in the concentration range from 0 mol.% to 60 mol% of SiO_2 and positive deviations in the concentration range from 60 mol.% to 100 mol% of SiO_2; the deviations decrease with increasing temperature (see figures in Ref. 156). At 2400 K, negative deviations of the activity of Al_2O_3 from ideal behaviour in $Al_2O_3-SiO_2$ melts were observed; the deviations changed the sign as the temperature decreased.

Thus, in spite of considerable research on the thermodynamic properties of the $Al_2O_3-SiO_2$ system at high temperatures, the results obtained in Refs 151–155 and 156–163 are rather contradictory. Therefore, the activities of components of the $Al_2O_3-SiO_2$ system were determined by high-temperature mass spectrometry in the temperature range 1850–1950 K under vaporization from molybdenum and tungsten cells.[164, 165] It was found that in the presence of molybdenum or tungsten, silica is partially reduced, the partial pressure of SiO increases while the partial pressure of oxygen decreases owing to formation of molybdenum or tungsten oxides. For the same reason, the relative content of SiO_2 in the vapour in the presence of the reducing agent decreases. Alumina is reduced to a small extent in the presence of molybdenum or tungsten and the partial pressures of Al, AlO and Al_2O species in the vapour increase only slightly. Probably, this can be due to the fact that alumina is reduced to a smaller extent than silica in the presence of molybdenum or tungsten. Low content of molybdenum or tungsten oxides in the vapour can be explained by decreasing the thermal stability of gaseous oxides in the series MO_3-MO_2-MO (M = Mo, W) with increasing temperature. The activity values of SiO_2 in the $Al_2O_3-SiO_2$ system determined in Refs 164 and 165 are in

‡ Division of the oxide systems to be considered from this point on into metallurgical slags and glass-forming systems is to some extent conditional. Therefore, the results of physicochemical characterization of certain oxide systems could be discussed either here or in the subsequent Sections. Note that this Section concerns glass-forming oxide systems including $CaO-TiO_2-SiO_2$, $BaO-TiO_2-SiO_2$, $ZnO-P_2O_5$, $SnO-ZnO-P_2O_5$, $Na_2O-ZnO-P_2O_5$ and $Al_2O_3-P_2O_5$. However, the vaporization processes and thermodynamic properties of these systems are considered here because

— the first two systems are compared with the calcium luminosilicate system (basic component of slags) and

— information on the behaviour of phosphate systems is scarce and it seems appropriate to discuss it within the same single chapter.

good agreement with published data [154, 155] and with the phase diagram of this system. Also, heating of samples in the $Al_2O_3-SiO_2$ system to 1900–2000 K was shown to lead to fast removal of silica from the condensed phase, which thus becomes alumina-enriched.

The vaporization processes and thermodynamic functions of mixing in one of the most important slag-forming system $CaO-Al_2O_3-SiO_2$, determined by mass spectrometry at 1833–2033 K, were discussed for the first time in the monograph [7] and then considered in more detail in another study.[166] More recently, studies by Zaitsev *et al.*[167–169] were performed and continued by Stolyarova *et al.*[170] It should be noted that the vapour composition over melts in the calcium-aluminosilicate system by and large matched that of molecular species identified previously over individual calcium oxide, alumina and silica.[8, 9] However, the gaseous phase over samples in this system contained not only these molecular species, but also calcium silicate and calcium aluminate.[166] The thermodynamic functions of mixing in the $CaO-Al_2O_3-SiO_2$ system [166–170] unambiguously indicate negative deviations from the ideal behaviour. Undoubtful advantages of Refs 167–169 include a wide concentration range of experimental studies of this system and the phase equilibria calculations for a wide temperature range (see Fig. 4 in the Electronic Supplement). It should be noted that correspondence between the calculated phase equilibria and commonly accepted published data points not ony to correctness of the model chosen,[169] but also to reliability of the methodological approach to the determination of the thermodynamic functions of mixing in the oxide systems when studying equilibria involving volatile products. The results of modelling [33, 171, 172] of the thermodynamic properties of glass-forming melts in the $CaO-Al_2O_3-SiO_2$ system using the generalized lattice theory of associated solutions [6, 7] will be considered below.

The composition of vapour over samples of the $MgO-SiO_2$ system is analogous to that of the vapours over corresponding individual oxides [8, 9] in the temperature range 1571–1890 K.[173–175] In addition to the determination of the thermodynamic functions of mixing, phase equilibria in the $MgO-SiO_2$ system were modelled [175] using the approach mentioned above (for detail, see monograph [28]). Mention was made that the thermodynamic behaviour of the $MgO-SiO_2$ system is characterized by negative deviations from ideality.[173–175]

Vaporization in the $MgO-Al_2O_3-SiO_2$ system in the temperature range 1623–2523 K occurs similarly to the vaporization of corresponding individual oxides (Refs 8 and 9).[172, 176–178] Shornikov and Archakov [176] determined the activities of components in melts of this system in the temperature range 1623–2523 K by the Belton–Fruehan method from the ion current ratios of SiO^+, Mg^+ and Al^+ produced upon ionization of corresponding molecular species in the vapour. Since these values differed by more than two orders of magnitude, the use of the Belton–Fruehan equation to obtain reliable values of the activities of components seems to be incorrect. Therefore, yet another series of studies on the determination of the thermodynamic functions of mixing in the $MgO-Al_2O_3-SiO_2$ system was reported.[172, 177, 178] The activities of components in this system found by differential mass spectrometry were compared with the results of modelling using the Gay–Kapoor–Frohberg approach [177, 178] and the isothermal cross-sections of the phase diagram at 1770, 1820 and 1890 K were obtained. Reasonable agreement between experimental and calculated activities of components and the phase equilibria in the $MgO-Al_2O_3-SiO_2$ system confirmed mutual consistence of information retrieved from the thermodynamic database [179] and the data used in calculations. It was shown that the thermodynamic functions of mixing for melts of the system in question at 1890 K can also be calculated using the generalized lattice theory of associated solutions.[172]

The vaporization and thermodynamic properties of diopside ($CaO \cdot MgO \cdot 2\,SiO_2$) in the temperature range 1550–1870 K were studied.[180, 181] It was found that the total vapour pressure over the following samples in isothermal conditions increases in the series [180, 181]

$$CaO \cdot MgO \cdot 2\,SiO_2 < Al_2O_3 \cdot 2\,SiO_2 < CaO \cdot Al_2O_3 \cdot 2\,SiO_2 < < CaO \cdot 2\,SiO_2 < MgO \cdot 2\,SiO_2$$

Zaitsev *et al.* [147, 182] used differential mass spectrometry during vaporization from molybdenum and niobium cells in the temperature range 1369–1817 K in order to determine the activities of components and the Gibbs energies of formation of compounds in the $MnO-SiO_2$ system. Using these values and assuming the existence of polymeric complexes $MnO \cdot SiO_2$, $MnO \cdot 2\,SiO_2$ and SiO_2 in melts, phase equilibria in this system were modelled using the theory of associated solutions.

The composition of the vapour and the activities of components in melts of the $CaO-TiO_2-SiO_2$ system under vaporization from molybdenum [183] and tungsten [184] cells were determined in the temperature range 1800–2200 K.[33, 171, 172, 183, 184] Main types of molecular species in the vapour over the melts studied include vaporization products of individual oxides that form the system. A comparison of the activity values of silica in the $CaO-TiO_2-SiO_2$ melts with those of silica in the $CaO-SiO_2$ melts suggests that

— replacement of CaO by TiO_2 in slags of relatively high basicity causes an abrupt increase in the activity of SiO_2; and

— in the more acid slags, the addition of titania to the $CaO-SiO_2$ melts has little effect on the activity of silica.[183]

The molecular species identified by differential mass spectrometry in the gaseous phase over melts in the $BaO-TiO_2-SiO_2$ system under evaporation from molybdenum effusion cells in the temperature range 1800–2150 K include SiO, Ba, BaO, TiO, TiO_2, MoO_3, MoO_2, $BaMoO_3$, $BaMoO_4$ and $BaTiO_3$.[185] It was found that if the system contains from 10 mol.% to 50 mol.% of SiO_2 at a BaO : TiO_2 mole fraction ratio of unity, the activities of silica and barium oxide demonstrate positive and negative deviations from ideal behaviour, respectively.

Figure 11 *a* presents the concentration dependences of the activity of silica in melts of the $CaO-Al_2O_3-SiO_2$, $CaO-TiO_2-SiO_2$ and $BaO-TiO_2-SiO_2$ systems determined using experimental data and from calculations using the generalized lattice theory of associated solutions.[33, 171, 172] This made it possible to calculate the relative numbers of chemical bonds formed in these melts taking into account the second coordination sphere (see Fig. 11 *b*) and to illustrate a correlation between positive deviations from ideality in the $CaO-TiO_2-SiO_2$ and $BaO-TiO_2-SiO_2$ melts and preferred formation of Si–O–Si, Si–O–Ti and Ti–O–Ti bonds as compared to negative

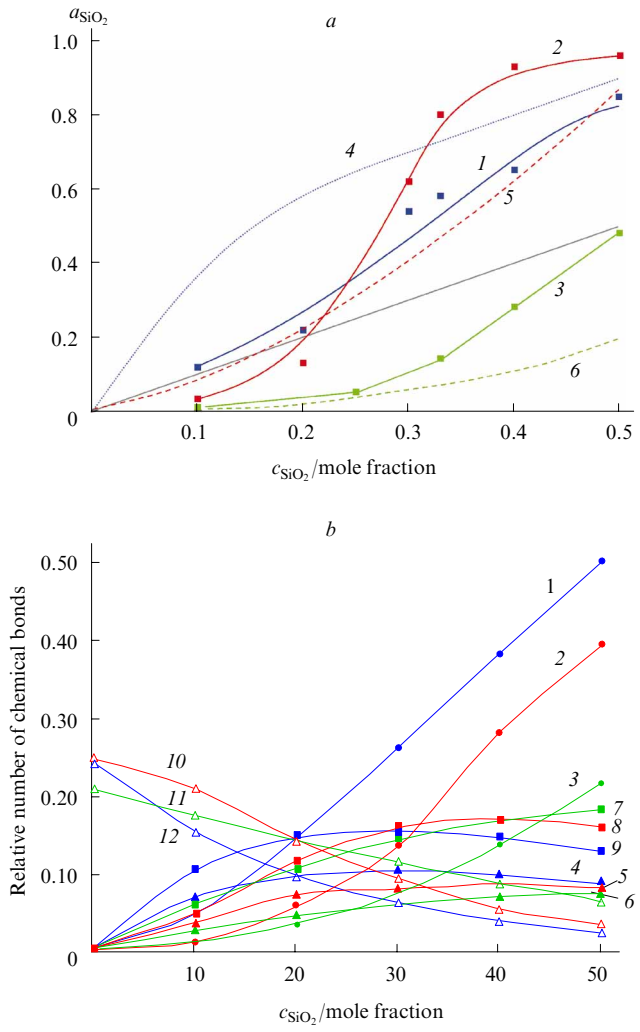


Figure 11. Activity of silica (*a*) and the relative number of chemical bonds (*b*) plotted *vs.* SiO_2 content in melts.[33, 171, 172]
(*a*) Systems $CaO-Al_2O_3-SiO_2$ (*1*, *4*), $CaO-TiO_2-SiO_2$ (*2*, *5*) and $BaO-TiO_2-SiO_2$ (*3*, *6*); the $CaO:Al_2O_3$, $CaO:TiO_2$ and $BaO:TiO_2$ mole fraction ratios are equal to unity, $T = 1900-1980$ K; coloured squares and correspondingly coloured solid curves (*1*–*3*) denote experimental values obtained by high-temperature mass spectrometry; dashed curves (*4*–*6*) denote the results of calculations using the generalized lattice theory of associated solutions; the straight lines corresponds to hypothetical ideal behaviour of the melt.
(*b*) $CaO-Al_2O_3-SiO_2$ melts: Si–O–Si (*1*), Al–O–Si (*2*), Ca–O–Si (*3*) and Ca–O–Al (*4*) bonds; $CaO-TiO_2-SiO_2$ melts: Si–O–Si (*5*), Ti–O–Si (*6*), Ca–O–Si (*7*), Ca–O–Ti (*8*) bonds; $BaO-TiO_2-SiO_2$ melts: Si–O–Si (*9*), Ti–O–Si (*10*), Ba–O–Si (*11*) and Ba–O–Ti (*12*) bonds; $CaO:Al_2O_3$, $CaO:TiO_2$ and $BaO:TiO_2$ mole fraction ratios are equal to unity, $T = 1900-1980$ K; calculated using the generalized lattice theory of associated solutions.

deviations from ideality in the $CaO-Al_2O_3-SiO_2$ melts and preferred formation of Ca–O–Si and Ca–O–Al bonds.

Although phosphate systems are of paramount importance in studies of dephosphorization in ferrous metallurgy, steel industry and in production of glass ceramic materials, vaporization processes in them have been investigated only recently in a few studies including the $CaO-P_2O_5-SiO_2$,[186] $ZnO-P_2O_5$,[187] $SnO-ZnO-P_2O_5$,[188] $Na_2O-ZnO-P_2O_5$,[189] $CaO-P_2O_5$,[190, 191] and $Al_2O_3-P_2O_5$ systems.[64, 192] In the temperature range 1260–1900 K, main types of molecular species in the gaseous phase over the $CaO-P_2O_5-SiO_2$ system represent vaporization products of phosphorus oxide.[186] Lopatin found [186] that the addition of silica to calcium metaphosphate, calcium polyphosphate and calcium diphosphate leads to a decrease in the partial pressures of dissociation products of phosphorus oxide and to an increase in the partial pressure in the case of calcium orthophosphate. Shilov and co-workers [187] determined the partial vapour pressures of Zn, P_2, PO, PO_2, P_2O_4 and oxygen in the temperature range from 940 to 1340 K and calculated the activities of components, enthalpies and entropies of mixing in the $ZnO-P_2O_5$ system using the ion current comparison method and the Belton–Fruehan equation. In addition to the molecular species mentioned above identified in the gaseous phase over the $ZnO-P_2O_5$ system, Shilov *et al.*[188] also identified Sn, SnO, $SnPO_2$ and $SnPO_3$ in the gaseous phase over the $SnO-ZnO-P_2O_5$ system in the temperature interval 900–1850 K under vaporization from platinum cells. The results of determination of the activities of components and the Gibbs energies in the isothermal cross-section of the phase diagram of the $Zn_2P_2O_7-Sn_2P_2O_7$ system at 1300 K indicated large negative deviations of these parameters from ideality. Shornikov and Archakov [189] studied vaporization of components in the $Na_2O-ZnO-P_2O_5$ system by mass spectrometry and reported a similar high-temperature behaviour. The thermodynamic properties of calcium phosphates in the $CaO-P_2O_5$ system were determined under vaporization of PO, P_2 and PO_2 using a double Knudsen cell in the temperature range 1373–1623 K.[190, 191] A similar approach was used by Nagai *et al.*[64, 192] to determine the Gibbs energy of formation of aluminium phosphate at in the temperature range from 1473 to 1573 K.

Vaporization processes in multicomponent slag-forming systems containing chromium oxide were investigated and the activities of components were determined.[193, 194] Alikhanyan and co-workers [193] studied vaporization in the $MgO-Al_2O_3-SiO_2-CrO_x$ system with the molar ratio $MgO:Al_2O_3 = 2$ (iridated molybdenum effusion cells, $T = 1873$ and 1973 K) and succeeded to plot the iso-activity lines for CrO and Cr_2O_3. A differential mass spectrometry study of vaporization in the $CaO-MgO-Al_2O_3-Cr_2O_3-FeO-SiO_2$ system (twenty samples, tungsten effusion cells, $1850 < T < 2750$ K) allowed the temperature dependences of the activity of Cr_2O_3 to be determined.[194] In that study the activities of chromium oxide were experimentally measured in the heating mode where full vaporization of iron species occurred; therefore, it is more correct to interpret the activities of Cr_2O_3 thus obtained as characteristics of the compositions of the condensed phase of the $CaO-MgO-Al_2O_3-Cr_2O_3-SiO_2$ system.

A study of vaporization processes in the $V_2O_3-CaO-MgO-Al_2O_3-SiO_2$ system (fourteen slag samples, tungsten effusion cells) in the temperature range from 1875 to 2100 K revealed VO_2, VO, O, WO_3 and WO_2 molecular species as major components of the gaseous phase.[195] It was found that the activities of V_2O_3 determined by differential mass spectrometry depend on the basicity of the slag and exhibit positive deviations from ideality at 1900 K, being nearly equal to the ideal values at 2100 K.

III.6. Glasses and glass-forming melts

The results of research into vaporization processes in model glasses and glass-forming melts are necessary to design various oxide materials with specified physicochemical properties, *e.g.*, multicomponent glasses, pyroceramics, films and coatings.[6,7,23,29,33,35] Specific features of the high-temperature behaviour of glasses and glass-forming melts studied by Knudsen effusion mass spectrometry were considered in detail in two monographs [6,7] and a number of more recent reviews [29,32,33,35] (see §). In this Section we will briefly outline the results of mass spectrometric studies of oxide glass-forming systems, namely, binary silicate and borate ones, and ternary borosilicate glasses, multicomponent glasses as well as glass-forming melts.

Vaporization processes and thermodynamic properties of binary silicate systems Na_2O-SiO_2,[28,196,197] K_2O-SiO_2,[28,198,199] $SrO-SiO_2$,[200,201] $BaO-SiO_2$,[202–204] $Bi_2O_3-SiO_2$,[205,206] as well as the K_2O-GeO_2 system[207] were studied by Knudsen effusion mass spectrometry (Table 2).

Taking the sodium silicate system as an example, Zaitsev *et al.*[28,196,197] provided convincing proofs of correctness of their procedure for generating equilibria in the effusion cell using reduction reactions resulting in volatile suboxides, namely, numerical values of the thermodynamic properties of this system agree with numerous data obtained earlier (see pp. 224–231 in monograph [7]). The advantages of the studies by Zaitsev *et al.*[28,196–199] include calculations of the phase diagrams of the sodium silicate and potassium silicate systems using the model of associated solutions assuming the existence of associates and polymeric complexes in melts. The results of modelling [28,196–199] are in reasonable agreement with experimental data on the phase equilibria in these systems; also, the immiscibility region was calculated for the Na_2O-SiO_2 system.[28,197]

It should be noted that information on the vaporization processes and thermodynamic properties of the K_2O-SiO_2,[28,198,199] $SrO-SiO_2$,[200,201] $BaO-SiO_2$[202–204] and $Bi_2O_3-SiO_2$[205,206] systems presented in Table 2 was obtained in these high-temperature mass spectrometric studies for the first time. Molecular species identified in the gaseous phase over the systems in question mainly corresponded to vaporization of individual oxides except the $SrO-SiO_2$ system [200,201] where two associates, $SrSiO_2$ and $SrSiO_3$, were identified in the gaseous phase. An analysis of the thermodynamic functions of mixing in the binary silicate systems characterized in Table 2 revealed negative deviations from ideal values in the temperature ranges studied. As earlier,[171,172] the thermodynamic properties of glass-forming melts in the $BaO-SiO_2$ [202–204] and $Bi_2O_3-SiO_2$ [205,206] systems as well as structure–property correlations were determined [202,203,206] using the generalized lattice theory of associated solutions. Specific features of this theory, as applied to describe and simulate glass-forming melts, are well documented (see pp. 227–235 in monograph [6] and pp. 307–315 in monograph [7]). This approach represents an extension of the Guggenheim model for regular solutions to systems containing molecules of different size, the interaction energy being dependent on the mutual orientation of molecules.

§ Unfortunately, a large number of these studies was not included in the review by Miller and Armatys.[5]

A detailed mass spectrometric study of the vaporization processes and thermodynamic properties of melts in the K_2O-GeO_2 system in the temperature range from 950 to 1550 K was carried out for the first time by Shornikov,[207] who found that the negative deviations from ideal behaviour of melts in the Na_2O-SiO_2, Na_2O-GeO_2, K_2O-SiO_2 and K_2O-GeO_2 systems at 1473 K differ insignificantly (within the measurement accuracy).

The composition of the gaseous phase and thermodynamic properties of binary borate systems $Na_2O-B_2O_3$,[208,209] $Rb_2O-B_2O_3$,[210] $Cs_2O-B_2O_3$,[211] $MgO-B_2O_3$,[212] $CaO-B_2O_3$,[58,213] $SrO-B_2O_3$,[214] $BaO-B_2O_3$[214] and $Al_2O_3-B_2O_3$[215,216] are presented in Table 2. According to the acid-base concept of vaporization of oxide systems, the presence of metaborates in vapours over these systems is not unexpected (see pages 320–333 in monograph [7] and a review [217] where the results of studies on the thermodynamic properties of gaseous metaborates were considered in detail). Unfortunately, the composition of the vapour over sodium metaborate was identified [208] ignoring the available identification [209] of the mass spectrum of the vapour over sodium metaborate using a single-temperature double effusion cell.

Nagai *et al.*[216] studied the $Al_2O_3-B_2O_3$ system by differential mass spectrometry and refined the available [215] temperature dependence of the Gibbs energy of formation of $Al_{18}B_4O_{13}$ (Fig. 12). Modelling of the thermodynamic properties of melts in the $Cs_2O-B_2O_3$,[211] $MgO-B_2O_3$,[212] and $CaO-B_2O_3$ [213] systems using the generalized lattice theory of associated solutions revealed preferred formation of M–O–B bonds in the condensed phases of these systems compared to the M–O–Si bonds (M = Cs, Mg, Ca). It was also shown that considerable deviations of the thermodynamic properties of the borate melts studied from ideality are to a great extent due to the formation of M–O–B bonds.

Reviews [29,31] are devoted to detailed consideration of the key results of systematic investigations of glasses and melts in ternary borosilicate systems $Na_2O-B_2O_3-SiO_2$, $Rb_2O-B_2O_3-SiO_2$, $Cs_2O-B_2O_3-SiO_2$, $MgO-B_2O_3-SiO_2$, $CaO-B_2O_3-SiO_2$, $SrO-B_2O_3-SiO_2$, $BaO-B_2O_3-SiO_2$ and $PbO-B_2O_3-SiO_2$ (see Table 2). The composition of vapours over glasses and melts in these systems is identical to that of the gaseous phase over corresponding binary systems. A feature of the thermodynamic behaviour of glasses and melts in these systems consists in negative deviations from ideal behaviour. Correctness of application of the generalized lattice model of associated solutions in order to describe the glass-forming systems containing two glass-forming oxides and one oxide modifier was repeatedly demonstrated taking calculations of the thermodynamic properties of melts in these ternary borosilicate systems as examples. It should be noted that information on the structure of borosilicate melts obtained within the framework of this model agrees with the results of structural studies of corresponding glasses and melts by small-angle and wide-angle X-ray scattering.[232–235]

Multicomponent borosilicate glasses are used in various fields of modern materials science, in particular, for disposal of intermediate-level activity waste.[236,237] The regularities of vaporization of multicomponent borosilicate glasses [29,238] can be explained with certainty using the principles of the acid–base concept which also allows one to compare the relative volatilities of the borosilicate glasses

Table 2. Results of Knudsen effusion mass spectrometry studies of vaporization processes and thermodynamic properties of oxide glass-forming systems.

System	T/K	Effusion cell material	Composition of vapour	Thermodynamic properties	Note	Ref.
			Binary silicate systems			
Na_2O-SiO_2	942 – 1719	Nb, Ta, Mo, Ni	Na, Na_2O, NaO, NaO_2, TaO, TaO_2, NbO, NbO_2, MoO, MoO_2, MoO_3, NiO	Activities of components, Gibbs energies of formation of sodium silicates	Obtained using the model of associated solutions assuming the existence of associates and polymeric complexes in melts. The results obtained agree with published data (negative deviations from ideality). The phase diagram of the system was calculated	28, 196, 197
K_2O-SiO_2	1057 – 1730	Nb, Ta, Mo, Ni	K, K_2O, KO, KO_2, TaO, TaO_2, NbO, NbO_2, MoO, MoO_2, MoO_3, NiO	Activities of components, enthalpies, entropies, Gibbs energies of formation	The same	28, 198, 199
$SrO-SiO_2$	1600 – 2300	Mo	SiO, SrO, Sr, $SrSiO_2$, $SrSiO_3$, MoO_2, MoO_3, $SrMoO_3$, $SrMoO_4$	Activities of components, Gibbs energies of formation in the system	Negative deviations from ideality	200, 201
$BaO-SiO_2$	1840 – 1970	Mo	SiO, BaO, Ba, MoO_2, MoO_3, $BaMoO_3$, $BaMoO_4$	The same	Calculated using the generalized lattice theory of associated solutions. Negative deviations of the thermodynamic properties from ideality	202 – 204
$Bi_2O_3-SiO_2$	1000	Mo + Ir	Bi	"	The same	205, 206
			Binary borate systems			
$NaBO_2$	1060 – 1185	Pt	$NaBO_2$, $(NaBO_2)_2$	Partial pressures, enthalpy of sublimation and enthalpy of formation of sodium metaborate	–	208, 209
$Rb_2O-B_2O_3$	950 – 1350	Mo	$RbBO_2$, $(RbBO_2)_2$	Activities of components, Gibbs energies of formation in the system	Large negative deviations of the thermodynamic properties from ideality	210
$Cs_2O-B_2O_3$	1020	Mo	$CsBO_2$, $(CsBO_2)_2$	The same	The same	211
$MgO-B_2O_3$	1640	Mo	B_2O_3, $MgBO_2$, MgB_2O_4	"	"	212
$CaO-B_2O_3$	1900	W	B_2O_3, CaB_2O_4	Activity of boron oxide in the system	"	58
$CaO-B_2O_3$	1575 – 1650	Mo	B_2O_3, CaB_2O_4	Activities of components, Gibbs energies of formation in the system	"	213
	2000	Mo	$CaBO_2$, CaO, BO, Ca, O_2	The same	"	213
$SrO-B_2O_3$	1840 – 1970	Mo	B_2O_3, SrB_2O_4	"	"	214
$BaO-B_2O_3$	1840 – 1970	Mo	B_2O_3, BaB_2O_4	"	"	214

Table 2 (continued).

System	T/K	Effusion cell material	Composition of vapour	Thermodynamic properties	Note	Ref.
			Binary borate systems			
$Al_2O_3-B_2O_3$	1248–1850	Mo	B_2O_3	Activity of boron oxide in the system	Correlation between the thermodynamic properties of the system and its phase diagram	215
	1373–1423	Mo	B_2O_3	The same	Negative deviations of the thermodynamic properties from ideality	216
			Ternary borosilicate systems			
$Na_2O-B_2O_3-SiO_2$	1300–1350	–	$NaBO_2$, $(NaBO_2)_2$, B_2O_3	Partial vapour pressures of molecular species and activities of components in the system	–	217–220
$Rb_2O-B_2O_3-SiO_2$	1000 1300	– –	$RbBO_2$, $(RbBO_2)_2$ $RbBO_2$, $(RbBO_2)_2$, B_2O_3	Activities of components, Gibbs energies of formation in the system	–	221
$Cs_2O-B_2O_3-SiO_2$	873–1073 1350	–	$CsBO_2$, $(CsBO_2)_2$ $CsBO_2$, $(CsBO_2)_2$, B_2O_3	The same	–	172, 222–225
$MgO-B_2O_3-SiO_2$	1550–1800	Mo	B_2O_3, SiO, MgB_2O_4, MoO_2, MoO_3	"	–	226
$CaO-B_2O_3-SiO_2$	1800	Mo	B_2O_3, SiO, CaB_2O_4, MoO_2, MoO_3	"	–	227, 228
$SrO-B_2O_3-SiO_2$	1720–1800	Mo	B_2O_3, SiO, SrB_2O_4, MoO_2, MoO_3	"	–	228, 229
$BaO-B_2O_3-SiO_2$	1650–1730	Mo	B_2O_3, SiO, BaB_2O_4, MoO_2, MoO_3	"	–	228, 230
$PbO-B_2O_3-SiO_2$	1100	SiO_2	PbO, Pb, O_2	Activities of components, Gibbs energies of formation in the system. Mass loss of the samples	–	231

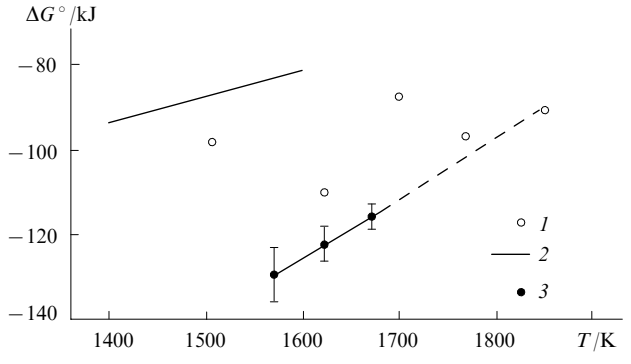


Figure 12. Gibbs energy of formation of $Al_{18}B_4O_{13}$ in the $Al_2O_3-B_2O_3$ system plotted *vs.* temperature.[216]
Data taken from P E Blackburn, A Buchler, J L Stauffer *J. Phys. Chem.* **70** 2469 (1966) (*1*), Ref. 215 (*2*) and Ref. 216 (*3*).

and melts. Table 3 presents the results of high-temperature mass spectrometric studies of the composition of vapours over multicomponent borosilicate glasses that are used in different countries for immobilization of radioactive wastes.[29] Also, it was found that the partial pressure of caesium metaborate and the total vapour pressure depends on the melt basicity of the multicomponent glass (Fig. 13).

Summing up, mention may be made that Knudsen effusion mass spectrometry can be used to analyze gas evolution upon heat treatment in the course of sol–gel synthesis of glasses and glass–ceramic materials. For instance, the molecular species identified in the gaseous phase in a vaporization study of a sol–gel mixture of magnesium oxide, alumina, silica and lithium oxide at 1273 K include H_2O, CO_2, NO, NO_2 and $LiNO_2$.[239]

III.7. High-temperature processes in the formation of rocks, production of cement clinker and gasification of coal

Concluding our consideration of the vaporization processes and thermodynamic properties of oxide systems and materials, we will dwell on a great potential of Knudsen effusion

Table 3. The content of oxides in the glasses used in different countries for radioactive waste disposal and the composition of the gaseous phase over the glasses, as identified by Knudsen effusion mass spectrometry.[29]

Content of oxides (mass %)									Composition of the gaseous phase at 1270 K
SiO_2	Al_2O_3	B_2O_3	Na_2O	CaO	Li_2O	Cs_2O	Fe_2O_3	other	
R7T7 glass (France)									
45.5	4.9	14.0	9.9	4.0	2.0	1.4	2.9	15.4	$CsBO_2$, $NaBO_2$, $LiBO_2$
Glass from South Korea									
45.3	4.9	14.0	9.8	4.0	2.0	1.4	2.9	15.7	$CsBO_2$, $NaBO_2$, $LiBO_2$
P0798 glass (Japan)									
46.6	5.0	14.2	10.0	3.0	3.0	0.8	2.0	15.4	$CsBO_2$, $NaBO_2$, $LiBO_2$
GC-12/9B glass (PR China)									
46.2	4.2	13.4	9.1	2.5	3.4	–	5.2	16.0	$NaBO_2$, $LiBO_2$, KBO_2
Type-A glass (Russian Federation)									
40.7	1.7	15.1	12.5	15.6	–	2.1	1.7	10.6	$CsBO_2$, $NaBO_2$, KBO_2
Type-B glass (Russian Federation)									
43.0	2.8	20.5	16.4	11.6	–	1.8	3.9	–	$CsBO_2$, $NaBO_2$, Na

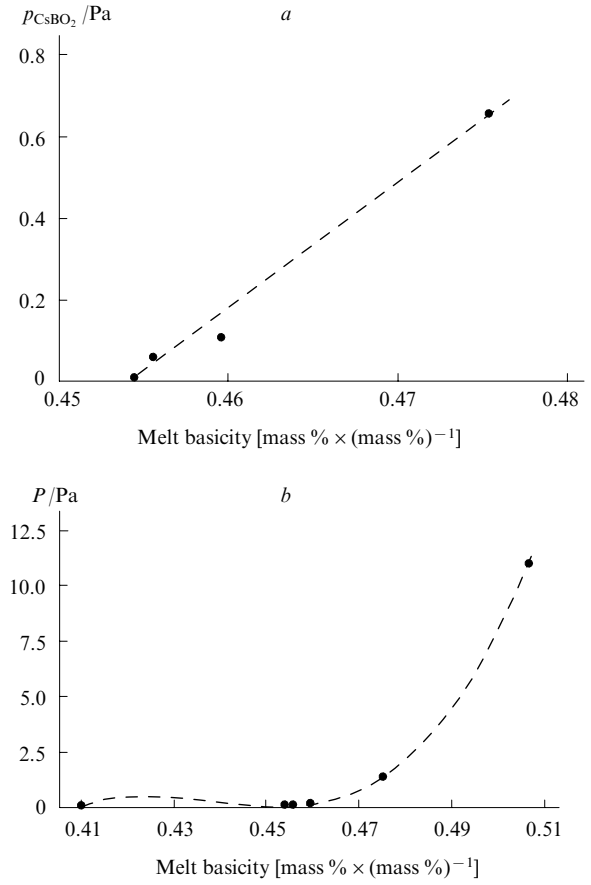


Figure 13. Partial vapour pressure of caesium metaborate (*a*) and total vapour pressure (*b*) plotted *vs.* basicity of multicomponent borosilicate glasses used for radioactive waste disposal.
The basicity was determined as the ratio of the total concentration of metal oxides to the total concentration of the acid oxides listed in Table 3.

mass spectrometry in solving applied problems. Relevant examples are provided by the results obtained in studies of high-temperature processes that accompany the formation of rocks, production of cement clinker and gasification of coal.

Inextricable connection between the conditions for the formation of rocks and minerals and the vaporization and condensation processes, whose interpretation requires thermodynamic information, has been repeatedly discussed (see, in particular, pages 254–263 in monograph [6]).

The vaporization processes and activities of potassium oxide and sodium oxide were studied by Knudsen effusion mass spectrometry in the temperature range from 1173 to 1373 K taking synthetic roedderite $(K, Na)_2Mg_5[Si_{12}O_{30}]$ (a total of eighteen samples) as an example.[240] The influence of the redox conditions on the vaporization processes in melts of the multicomponent system $CaO-MgO-FeO-Al_2O_3-SiO_2$ in the temperature range 1700–2600 K was considered by Shornikov.[241]

To solve the problem of production of high-quality cement clinker, Armatys *et al.*[242] determined for the first time the activities of components in the sodium sulfate–potassium sulfate and potassium sulfate–calcium sulfate [243] systems using the Belton–Fruehan and Neckel–Wagner methods by Knudsen effusion mass spectrometry (platinum effusion cells, $1100 < T < 1400$ K). A new molecule, $NaKSO_4$, was identified in the gaseous phase over these systems an addition to the molecular species corresponding to vaporization of sodium sulfate, potassium sulfate, potassium oxide, sodium oxide and sulfur oxide.[242]

Release of potassium, chlorine and sulfur molecular species during combustion of coal was studied by Hilpert and co-workers.[244] A thermodynamic concept of removal of alkali impurities at 1673 K during the coal combustion combined cycle was developed using the results of determination of the activities of alkali metal oxides by Knudsen effusion mass spectrometry in ash slags containing SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O and P_2O_5, which

were obtained in the absence and in the presence of an aluminosilicate sorbent.[245]

IV. Conclusion

Considering the List of Critical Technologies for the Russian Federation, our analysis of experimental data on the vaporization processes and thermodynamic properties of oxide systems and materials demonstrates that many problems cannot be solved without using the results of experimental research carried out by Knudsen effusion mass spectrometry. These technologies are of great social, economic and military value and include, in particular, the following:

— nuclear power engineering, nuclear fuel cycle technologies, as well as safety of nuclear waste and spent nuclear fuel;

— environmental monitoring and forecasting, prevention and elimination of environmental pollution;

— technologies of new and renewable energy sources including hydrogen power engineering;

— processing and utilizing technogenic substances and waste;

— engineering of structural nanomaterials;

— engineering of functional nanomaterials;

— engineering of composite materials and ceramics;

— engineering of crystalline materials;

— new-generation aerospace and transport engineering;

— engineering of electronic components including stability against space factors;

— creating power-saving transportation systems as well as energy distribution and consumption systems;

— production of energy efficient vehicles; and

— energy-efficient lighting devices.

Based on the aforesaid, a continuation of research activity and progress in Knudsen effusion mass spectrometry in the Russian Federation is of priority importance from the standpoint of design and production of new-generation domestic experimental equipment and improvement of basic physicochemical methods for investigation of the high-temperature behaviour of oxide materials.

At present, topical problems in modern mass spectrometric studies of the thermodynamic properties of oxide systems and materials include the following.

1. Elucidation of regularities in the vaporization of oxide systems and materials at high temperatures (as shown above, they can be explained using, *e.g.*, the acid–base concept).

2. Prediction of the relative volatility of oxide systems and materials used in various high-temperature technologies including combination with other classes of chemical compounds.

3. Prediction of the thermodynamic properties of oxide materials using statistical-thermodynamic approaches in order to establish correlations between their physicochemical properties and structure, as was demonstrated above taking modelling of the thermodynamic properties of glass-forming melts using the generalized lattice theory of associated solutions as an example.

4. The development of a national database of thermodynamic properties of oxide systems and models in order to predict the physicochemical properties of oxide materials including the composition of vapour, thermodynamic properties, viscosity and other parameters, as well as to construct the phase diagrams. It should be noted that a number of thermodynamic databases and model kits are available and widely used abroad (see, *e.g.*, pp. 152–161 in a monograph [246]). Also, it seems appropriate that Russian researchers continue to calculate the phase equilibria in oxide systems similarly to the studies reported by Zaitsev *et al.*[247, 248]

Summing up, although the history of mass spectrometric studies of the thermodynamic properties of oxide systems and materials covers nearly six decades, research into high-temperature processes continuously opens new prospects for solving fundamental and applied problems in modern materials science.

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