



Thermodynamic properties of the $\text{UO}_2\text{--ZrO}_2$ system studied by the isothermal mass spectrometric vaporization method

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Abstract

The Knudsen effusion high-temperature mass spectrometric method was used to study the vaporization processes and thermodynamic properties of the $\text{UO}_2\text{--ZrO}_2$ system in the temperature range 2200–2650 K. The work was carried out with the MS 1301 mass spectrometer developed for studies of physico-chemical properties of inorganic substances at high temperatures. Vaporization of the solid solutions containing 0.02–0.45 mol fractions of UO_2 was done using tungsten cells. The vaporization processes and the chemical potentials of ZrO_2 in the $\text{UO}_2\text{--ZrO}_2$ system and in the $\text{Y}_2\text{O}_3\text{--ZrO}_2$, $\text{Lu}_2\text{O}_3\text{--ZrO}_2$ and $\text{HfO}_2\text{--ZrO}_2$ systems, available in the literature, were discussed from the point of view of the acid–base concept. © 1997 Elsevier Science B.V.

1. Introduction

The $\text{UO}_2\text{--ZrO}_2$ system is one of the most important systems in the consideration of the chemical constitution of irradiated nuclear fuels [1] and in the simulation of the release of radionuclides with concrete during severe reactor accidents [2]. Available data on the phase diagram of the $\text{UO}_2\text{--ZrO}_2$ system were summarized by Paschoal et al. [3]. Additional experimental results were presented at 1973 K confirming that in the pseudobinary $\text{UO}_2\text{--ZrO}_2$ system, cubic (U, Zr) O_2 and tetragonal (Zr, U) O_2 are separated by a broad two-phase region [3]. The complete phase diagram of the $\text{UO}_2\text{--ZrO}_2$ system was also recently calculated based on an optimized thermodynamic data set in the frame of the CALPHAD approach [4]. It was shown, that a regular solution model is applied to all phases available in the system [4].

The vaporization of three samples of this system, con-

taining 0.15, 0.30 and 0.50 mol fractions of UO_2 , was studied by the high-temperature mass spectrometric method by Belov et al. [5] at 2400 K. It was found, that the partial pressures of UO_2 were a quantity directly proportional to the mol fraction of UO_2 in the solid solutions at 2400 K. The features of vaporization processes and thermodynamic properties of the individual oxides UO_2 and ZrO_2 were studied in detail in Refs. [6–9].

The Knudsen effusion high temperature mass spectrometric method was used to study the vaporization processes and thermodynamic properties of the samples containing 0.02–0.45 mol fractions of UO_2 in the $\text{UO}_2\text{--ZrO}_2$ system in the temperature range 2200–2650 K.

2. Experimental

Samples for the investigations were prepared from sintered pellets by crushing. The pellets were obtained by granulation, pelleting, sintering and annealing of UO_2 and ZrO_2 powders. The specific surface of the powders were about 3.00 and 30.00 m^2/g , respectively. The size of the initial particles of powders was less than 100 μm . Sintering of the pellets, containing 0.22 and 0.45 mol fractions

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of UO_2 , was performed at 1923 K during 2 h in a metallic furnace with tungsten heater in Ar-H_2 atmosphere. The evaluated partial pressure of oxygen at the sintering temperature was about 10^{-11} bar. Then the samples were annealed at 2423 K during 3 h. The particle size of the components of the system studied was higher than 20 μm for UO_2 and ZrO_2 . The chemical composition of the samples obtained was confirmed by X-ray diffraction and spectrochemical analysis.

This study was carried out with the MS 1301 magnetic mass spectrometer, designed for Knudsen effusion high-temperature mass spectrometric studies of low volatile inorganic substances and manufactured by the Institute of Analytical Instrument-making of the USSR Academy of Sciences, Leningrad. The mass resolution ($k_{0,1}$) of the MS 1301 mass spectrometer on the level of 10% intensities of the lines is 600. Experiments were carried out at the ionization energy 70 eV. The sensitivity of the installation determined using the vapor pressure of gold as a standard was not less than 10^{-9} bar. Vaporization was done using tungsten effusion cells. The temperature was measured by the optical pyrometer EOP-66 with the vanishing glow lamp filament according to the traditional approach [10]. This pyrometer was developed and produced at Kharkov Optical Plant, Ukraine.

3. Results and discussion

The relative ion current intensities of the ion species (mass spectra of the vapor) corresponding to the vaporization of UO_2 and ZrO_2 and of the samples studied are

given in Table 1. The main vaporization processes over the individual UO_2 and ZrO_2 are also presented in the table. The agreement between the mass spectra of vapor over the initial compositions studied and over individual urania and zirconia allowed to suggest the same vaporization processes in the $\text{UO}_2\text{-ZrO}_2$ system as over pure oxides, see reactions (1) to (5) in Table 1. These results are in agreement with the composition of vapor over the $\text{UO}_2\text{-ZrO}_2$ system identified earlier by Belov et al. [5].

Partial pressures of UO_2 and ZrO_2 vapor were obtained further by the ion current comparison method [10]. Partial pressures of the gaseous species UO_2 and ZrO_2 over individual urania and zirconia were in agreement with the data in Refs. [5,7,11] and were used as standards. The complete isothermal vaporization method [10] was also used for the calculation of the partial pressures of the UO_2 and ZrO_2 vapor species. Fig. 1 illustrates one of the vaporization isotherms obtained during the vaporization of the $\text{UO}_2\text{-ZrO}_2$ sample, containing 0.45 UO_2 . The vaporization temperature from 40 to 240 min was 2498 K, from 241 to 500 min was 2643 K. The changes in the composition of the sample are also indicated in Fig. 1.

The ZrO_2 and UO_2 activities (a_{ZrO_2} , a_{UO_2}) were calculated as a result of comparison between the vapor pressures of ZrO_2 and UO_2 over the $\text{UO}_2\text{-ZrO}_2$ system (p_{ZrO_2} , p_{UO_2}) and over the individual oxides ZrO_2 and UO_2 ($p_{\text{ZrO}_2}^0$, $p_{\text{UO}_2}^0$):

$$a_{\text{ZrO}_2} = p_{\text{ZrO}_2} / p_{\text{ZrO}_2}^0, \quad (1)$$

$$a_{\text{UO}_2} = p_{\text{UO}_2} / p_{\text{UO}_2}^0, \quad (2)$$

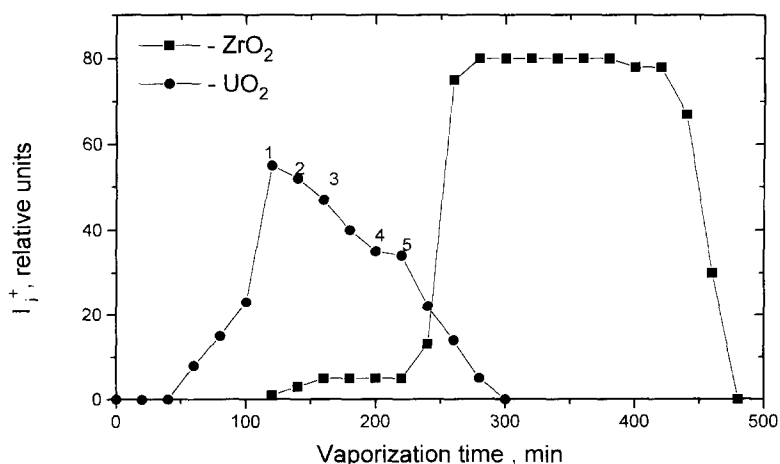


Fig. 1. Vaporization isotherm of the UO_2 (—●—) and ZrO_2 (—■—) vapor species as a function of the vaporization time of the $0.45\text{UO}_2\text{-}0.55\text{ZrO}_2$ sample. The vaporization temperatures were 2498 K from 40 to 240 min, and 2643 K from 241 to 500 min. The numbers over the vaporization isotherm correspond to the changes in the composition of the condensed phase, calculated according to the complete isothermal vaporization method [10]: 1 – 0.43; 2 – 0.35; 3 – 0.20; 4 – 0.08; 5 – 0.015 mol fractions of UO_2 .

Table 1
Ion species in the mass spectra of vapor and vaporization processes over UO_2 , ZrO_2 and the UO_2 - ZrO_2 system

Composition of condensed phase studied	Temperature (K)	Ionization energy (eV)	Ion species in the mass spectra of vapor (relative units)		Vaporization process ^a	Refs.
			$\text{UO}_3^+:\text{UO}_2^+:\text{UO}^+:\text{U}^+$	$\text{ZrO}_2^+:\text{ZrO}^+:\text{Zr}^+$		
$\text{UO}_{1.97 \pm 0.10}$	2300–2450	70	0.01:1:0.35:0.20		$[\text{UO}_3] = (\text{UO}_3)$ (1) $[\text{UO}_2] = (\text{UO}_2)$ (2) $[\text{UO}_2] = (\text{UO}) + (\text{O})$ (3)	[5]
$\text{UO}_{2.1 \pm 0.1}$ ZrO_{2-x}	2200–2650 2625	10–12	(-) ^b ; 1:(0.02–0.03):(-) ^b			Present study
		70	0.003:1:(0.38 ± 0.03):(0.49 ± 0.03)	1:3.14:0.64	$[\text{ZrO}_2] = (\text{ZrO}_2)$ (4) $[\text{ZrO}_2] = (\text{ZrO}) + (\text{O})$ (5)	[7]
ZrO_{2-x} 0.45 UO_2 -0.55 ZrO_2 (mol fractions)	2490–2630 2610	70	1:(3.9 ± 0.2):(0.8 ± 0.1)			Present study
		70	(< 0.003):1:(0.41 ± 0.02):(0.47 ± 0.02)	1:(3.7 ± 0.1):(0.75 ± 0.04)	$[\text{UO}_3] = (\text{UO}_3)$ (1)	Present study
0.22 UO_2 -0.78 ZrO_2 (mol fractions)	2610	70	(< 0.003):1:(0.40 ± 0.02):(0.48 ± 0.02)	1:(3.8 ± 0.1):(0.79 ± 0.04)	$[\text{UO}_2] = (\text{UO}_2)$ (2) $[\text{UO}_2] = (\text{UO}) + (\text{O})$ (3) $[\text{ZrO}_2] = (\text{ZrO}_2)$ (4) $[\text{ZrO}_2] = (\text{ZrO}) + (\text{O})$ (5) $[\text{UO}_3] = (\text{UO}_3)$ (1)	Present study
					$[\text{UO}_2] = (\text{UO}_2)$ (2) $[\text{UO}_2] = (\text{UO}) + (\text{O})$ (3) $[\text{ZrO}_2] = (\text{ZrO}_2)$ (4) $[\text{ZrO}_2] = (\text{ZrO}) + (\text{O})$ (5)	

^a Formulae enclosed in round brackets correspond to species in the gas phase, while those in square brackets refer to the condensed phase.

^b Information on the identification of UO_3^+ and U^+ ions at an ionization energy 10–12 eV is absent in the paper [5].

according to the vaporization processes (2) and (4) in Table 1.

Changes of the deviations from the ideal behavior of the $\text{UO}_2\text{-ZrO}_2$ system were shown as far as the temperature increases from 2200 K to 2650 K, see Fig. 2a and b. These changes can be considered as a result of attaining the thermodynamic equilibrium of the solid solutions in the $\text{UO}_2\text{-ZrO}_2$ system in the form of the cubic $(\text{U, Zr})\text{O}_2$ phase from 2200 K to 2650 K according to the phase diagram [3]. Fig. 3 illustrates the chemical potential of ZrO_2 as a function of the ZrO_2 content in the following systems: $\text{UO}_2\text{-ZrO}_2$, $\text{Y}_2\text{O}_3\text{-ZrO}_2$, $\text{Lu}_2\text{O}_3\text{-ZrO}_2$, $\text{HfO}_2\text{-ZrO}_2$. The decrease of the deviations from the ideality and the relative volatility of these systems are in agreement

with the position of the oxide modifier in the periodic table and the increase of the chemical interactions according to the acid–base concept [10].

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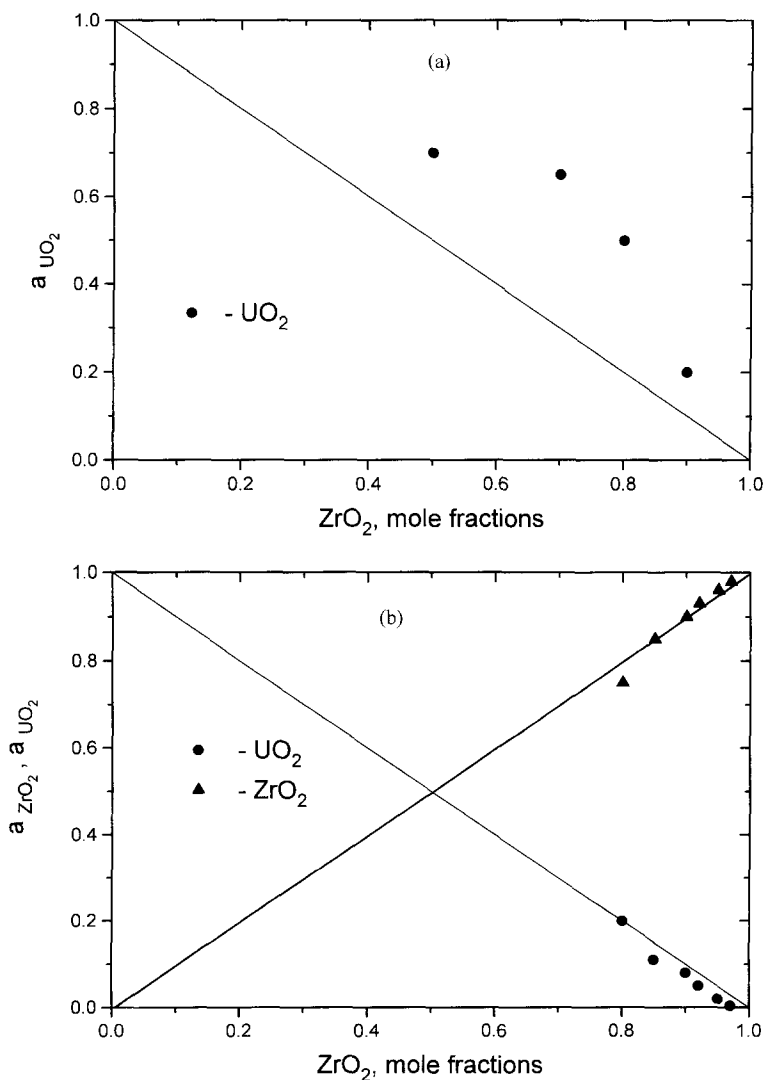


Fig. 2. UO_2 (\bullet) and ZrO_2 (\blacktriangle) activities in the $\text{UO}_2\text{-ZrO}_2$ system at 2203 K (a) and at 2498 K (b). The lines corresponding to ideal behavior are added.

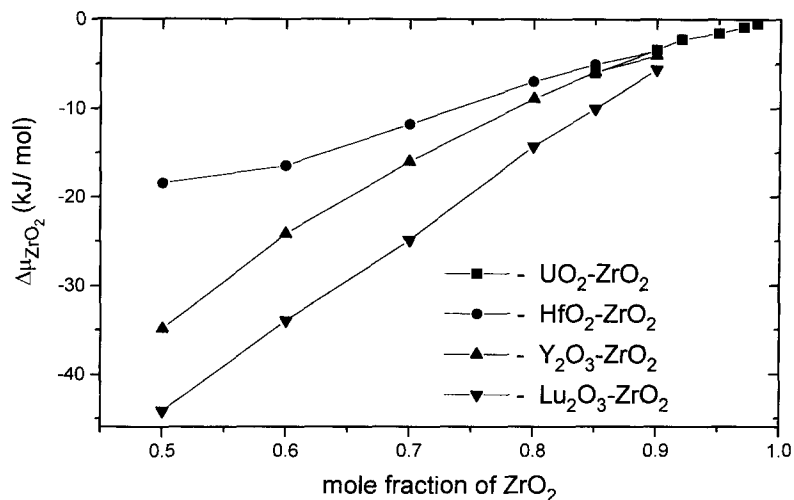


Fig. 3. Chemical potential of ZrO₂ as a function of the ZrO₂ content in: the UO₂-ZrO₂ system (1), obtained in the present study at 2498 K, and in the HfO₂-ZrO₂ (2), Y₂O₃-ZrO₂ (3), Lu₂O₃-ZrO₂ (4) systems at 2700 K investigated in Ref. [12].

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