



Characterization of urania vaporization with transpiration coupled thermogravimetry [☆]



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ABSTRACT

Transpiration measurements are very useful for determining equilibrium vapor pressures of materials. However, the traditional technique involves condensing the volatiles entrained in a carrier gas outside of the hot measurement zone. One potential problem is deposition en route to a cooled collector. Thermogravimetric analysis (TGA) can be used to measure in situ mass loss due to vaporization and therefore obviate the need to analyze the entire gas train due to premature plating of vapor species. Therefore, a transpiration coupled TGA technique was used to determine equilibrium pressures of UO₃ gas over fluorite structure UO_{2+x} and U₃O₈ at $T = (1573 \text{ and } 1773) \text{ K}$. The results are compared to calculations from models and databases in the open literature. This study gives clarity to the thermochemical data for UO₃ gas and validates the mass loss transpiration method using thermogravimetry for determining equilibrium vapor pressures of non-stoichiometric oxides.

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1. Introduction

Urania is used as a conventional light water reactor (LWR) nuclear fuel and is a non-stoichiometric oxide represented by the formula UO_{2+x}. At high temperatures and large values of x , UO_{2+x} volatilizes as UO₃ gas. This phenomenon is important for understanding conventional LWR (light water reactor) fuel behavior under severe accident scenarios as pointed out by Olander [1]. A breach of cladding allows pressurized water or steam to contact and oxidize UO_{2+x} forming both UO₃ and UO₂(OH)₂ vapors. Knowledge of the thermochemistry of UO₃ and H₂O facilitate determining equilibrium UO₂(OH)₂ pressures for UO_{2+x} in steam from experimentation [2] and allow for a better understanding of fuel response to severe accident conditions. While the behavior of H₂O is well understood from a computational thermodynamic standpoint, Olander [1] reviewed several studies [3–5] that gave conflicting

calculated UO₃ vapor pressures (p_{UO_3}) over U₃O₈. Further, a literature survey revealed no studies reporting equilibrium p_{UO_3} for fluorite structure UO_{2+x}. Since U is a heavy atom, this facilitates characterizing vaporization of UO_{2+x} by mass loss determinations. Furthermore, UO_{2+x} is non-stoichiometric with the value of x depending critically on the system oxygen partial pressure (p_{O_2}). Therefore, the aim of this effort is to clarify the equilibrium p_{UO_3} over UO_{2+x} with temperature and p_{O_2} by using a transpiration coupled thermogravimetric analysis (TGA) technique.

2. Experimental procedure

Merton and Bell provide an excellent and detailed description of the transpiration method in [6]. In brief, an equilibrium concentration of vapors over a sample is established and entrained in a carrier gas that is then transported to a cold trap. The composition of the resulting condensate is analyzed and the mass (m_i) and equilibrium partial pressures (p_i) of each species i can be determined using equation (1):

$$p_i = \left(\frac{m_i/mw_i}{v \cdot t + m_i/mw_i} \right) \cdot p_{\text{sys}}, \quad (1)$$

where v is the carrier gas molar flow rate, mw_i is the molecular weight of i , t is time, and p_{sys} is the system pressure.

Several studies, for example [7–9], have shown that thermogravimetry can be used to determine p_i given knowledge of the

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major molecular components of the equilibrium vapor and a sufficiently high p_i to effect measurable weight loss. Evidence suggests that UO_3 and O_2 are the dominant gas phase species over UO_{2+x} at large x and high temperatures in the (U + O) system [1,2,10,11].

These experiments were conducted for either UO_{2+x} fluorite structure solutions or $\delta\text{-U}_3\text{O}_8$. Which phase was present was calculated by minimizing the Gibbs energy of the system under the conditions of the measurement using the Calphad assessment of the (U + O) binary from [12]. The starting material was Areva UO_{2+x} powder (>99.85 mass% uranium oxide) pressed into a cylindrical pellet about 3 mm in diameter and 5 mm in height. The specimen was conditioned in Ar-4\%H_2 at $T = 1623\text{ K}$ for 12 h to sinter and fix the stoichiometry to $\text{UO}_{2.000\pm 0.002}$. Calculated phase diagrams for the (U + O) binary are presented in figure 1.

A Netzsch STA 449 F1 Jupiter[®] was used for the thermogravimetric analysis. A simplified sketch of the apparatus is shown in figure 2. The ID of the carrier gas inlet tubing was 1.753 mm while that of the outlet is 4.57 mm. These small openings provided enough constriction to limit diffusion out of the reaction chamber, a necessary requirement for a transpiration apparatus [6]. A sample of UO_{2+x} weighing ~350 mg was placed on a flat alumina plate. Oxygen pressures were fixed with an EnviroNics[®] Series 2000 Multi-Component Gas Mixer by combing Ar-4\%H_2 and Ar-2\%O_2 feed streams in appropriate ratios determined from an equilibrium calculation of the following reaction:



The sensitivity of the microbalance used in this work is $\pm 0.002\ \mu\text{g}$. Thus, urania begins to volatilize noticeably, from the gravimetric standpoint of this study, at temperatures around 1500 K and $p_{\text{O}_2} > 10^{-6}\text{ atm}$ (1 atm = 101,325 Pa).

The experimental procedure used was as follows. The sample was heated to temperature under an Ar-4\%H_2 flow to maintain the oxygen stoichiometry of 2. Argon-4% H_2 and Ar-2\%O_2 combinations were then set to achieve a $\log p_{\text{O}_2}/\text{atm} = -3$ and the steady state rate of weight loss was recorded for carrier gas flows between 200 and 35 ml/min at standard temperature and pressure (STP) at both 1573 and 1773 K. This was done in order to determine proper conditions that sufficiently minimized surface reaction kinetics and diffusion limitations. The results of these two series of preliminary runs are shown in figures 3 and 4. The partial pressure of UO_3 gas was computed with equation (3) below:

$$p_{\text{UO}_3} = \left(\frac{\dot{m}/mw_{\text{U}}}{\dot{V} + \dot{m}/mw_{\text{U}}} \right) \cdot p_{\text{sys}}, \quad (3)$$

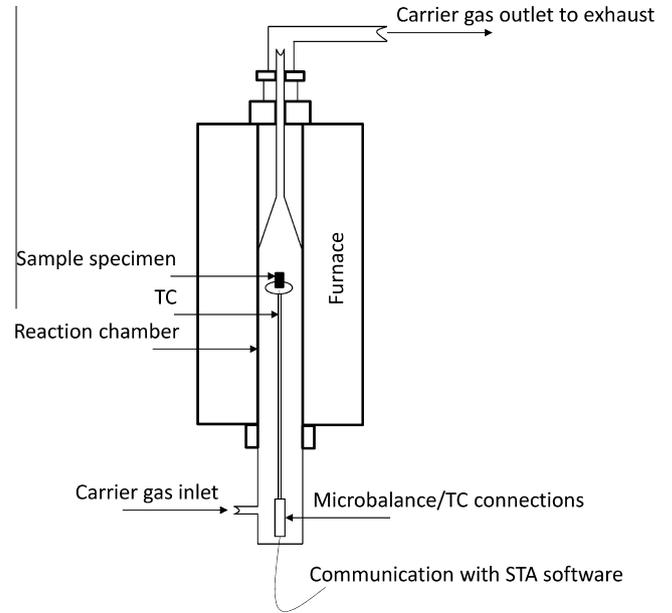


FIGURE 2. Simplified diagram of the simultaneous thermal analyzer (STA) used in this study.

where \dot{m} is rate of mass loss of the UO_{2+x} sample and mw_{U} is the molecular weight of U. The measurements were conducted at an elevation, h , of about 260 m above sea level and the laboratory was kept at a nearly constant 298 K temperature; therefore, p_{sys} was assumed to be constant at 0.97 atm estimated from the following relation:

$$p_{\text{sys}} = \left(1 - h \cdot 2.25577 \cdot 10^{-5} \right)^{5.25588} \text{ atm}. \quad (6)$$

While UO_3 is volatilizing, the oxygen bound to U in the UO_3 molecule is replaced in the solid UO_{2+x} phase since the atmosphere is continuously purged with one of a fixed p_{O_2} . This means the net \dot{m} is equivalent to U loss only and therefore equation (3) must be used. Since the integral (reacting) system can be considered (U + O + H), the $\text{UO}_2(\text{OH})_2$ oxyhydroxide species will only form in very small relative concentrations due to the low partial pressure of water vapor and high temperature of the measurements [1]. The mass loss from $\text{UO}_2(\text{OH})_2$ has been documented to be well within experimental error and undetectable by the transpiration technique

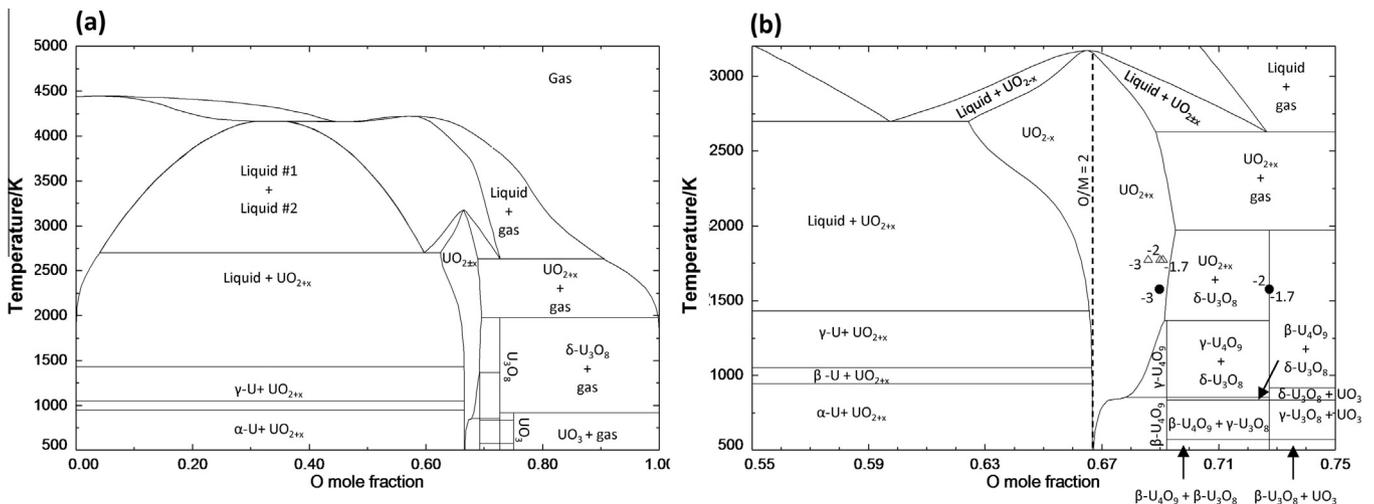


FIGURE 1. (a) Phase diagram of the integral (U + O) binary system calculated using the Calphad assessment of Guéneau *et al.* (b) Section in the vicinity of the UO_{2+x} solution. The symbols show the calculated compositions and the corresponding $\log p_{\text{O}_2}$ in atm for the transpiration measurements from this work.

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