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 UO_3 gas over fluorite structure UO_{2+x} and U_3O_8 at 1573 and 1773 K. The results are compared to calculations from models and databases in the open literature. This study gives clarity to the thermochemical data for UO_3 gas and validates the mass loss transpiration method using thermogravimetry for determining equilibrium vapor pressures of non-stoichiometric oxides.

Keywords: UO_{2+x} , UO_3 , uranium, urania, volatilization, oxygen potential, phase equilibrium

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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 $\text{UO}_{2\pm x}$. At high temperatures and large values of x , $\text{UO}_{2\pm x}$ volatilizes as UO_3 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 $\text{UO}_{2\pm x}$ forming both UO_3 and $\text{UO}_2(\text{OH})_2$ vapors. Knowledge of the thermochemistry of UO_3 and H_2O facilitate determining equilibrium $\text{UO}_2(\text{OH})_2$ pressures for $\text{UO}_{2\pm x}$ in steam from experimentation [2] and allow for a better understanding of fuel response to severe accident conditions. While the behavior of H_2O is well understood from a computational thermodynamic standpoint, Olander [1] reviewed several studies[3; 4; 5] that gave conflicting calculated UO_3 vapor pressures (p_{UO_3}) over U_3O_8 . Further, a literature survey revealed no studies reporting equilibrium p_{UO_3} for fluorite structure $\text{UO}_{2\pm x}$. Since U is a heavy atom, this facilitates characterizing vaporization of $\text{UO}_{2\pm x}$ by mass loss determinations. Furthermore, $\text{UO}_{2\pm x}$ 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 $\text{UO}_{2\pm x}$ 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 Eqn. 1:

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

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; 8; 9], have shown that thermogravimetry can be used to determine p_i given knowledge of the 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 1623 K for 12 hours to sinter and fix the stoichiometry to $\text{UO}_{2.000\pm0.002}$. Calculated phase diagrams for the U-O binary are presented in Fig. 1.

A Netzsch STA 449 F1 Jupiter® was used for the thermogravimetric analysis. A simplified sketch of the apparatus is shown in Fig. 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 combining 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 Figs. 3 and 4. The partial pressure of UO_3 gas was computed with Eqn. 3 below:

$$p_{\text{UO}_3} = \left(\frac{\dot{m}/mw_U}{v + \dot{m}/mw_U} \right) \times p_{\text{sys}} \quad 3$$

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 meters 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:

$$p_{sys} = \left(1 - h \times 2.25577 \times 10^{-5}\right)^{5.25588} atm \quad 4$$

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 Eqn. 3 must be used. Since the integral (reacting) system can be considered U-O-H, the $UO_2(OH)_2$ 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 $UO_2(OH)_2$ has been documented to be well within experimental error and undetectable by the transpiration technique at similar conditions [2]. From Eqn.17 in [1], the following relation can be derived:

$$p_{UO_2(OH)_2} = K_{oxy} p_{UO_3} p_{H_2O} \quad 5$$

where $p_{UO_2(OH)_2}$ is the partial pressure of $UO_2(OH)_2$ and K_{oxy} is the equilibrium constant for the reaction:

Olander reported K_{oxy} decreases from 0.19 to 0.010 from 1500 K to 2000 K in [1]. In this study, the p_{H_2O} was never higher than 1.6×10^{-2} atm. This means $p_{UO_2(OH)_2}$ must be about 3 orders of magnitude or more lower than p_{UO_3} under the conditions investigated here.

Figs. 3 and 4 show constant p_{UO_3} and linear mass loss versus v that intersects the origin for flows between 35 and 50 ml/min; therefore, any value falling in between these two limits satisfies the requirements for the transpiration technique [6] in this case. A setting of 42.5 ml/min was selected for use in the remainder of the runs since that flow best represented the average UO_3 pressures for the plateau region. These measurement were made at $\log p_{O_2}/atm = -2$ and -1.7 at both 1573 and 1773 K.

3. Results

The experimentally determined p_{UO_3} with temperature and p_{O_2} in equilibrium with UO_{2+x} and $UO_{2+x} - U_3O_8$ are given in Table 1. The uncertainty in the $\log p_{O_2}/atm$ settings were determined by estimating the propagation of independent random errors [13] from the gas compositions and flow settings from Table 2. The microbalance drift can be as high as ± 10 $\mu g/hr$ yielding p_{UO_3} to an accuracy of 4.03×10^{-7} atm. The uncertainty in the temperature reading is estimated to be ± 0.05 K based on calibration of the thermocouple using melting points for the 5 different metal standards listed in Table 3.

4. Discussion

The reaction that forms $UO_3(g)$ from UO_{2+x} is given as:

where the UO_2^{ss} compound is a constituent of the overall UO_{2+x} hyperstoichiometric solution phase.

Applying the law of mass action yields

$$p_{UO_3} = K_{eq} a_{UO_2} \sqrt{p_{O_2} / p_{O_2}^\circ} \times p_{UO_3}^\circ \quad 8$$

where a_{UO_2} is the activity of UO_2^{ss} . The equilibrium constant, K_{eq} , can be represented as:

$$K_{eq} = e^{-\left(\frac{^\circ G_{UO_3(g)} - ^\circ G_{UO_2} - 1/2 ^\circ G_{O_2}}{RT} \right)} \quad 9$$

where R is the ideal gas constant and T is temperature.

In Fig. 5, the results from this study, along with one from [2], are plotted against calculated p_{UO_3} as a function of p_{O_2} from four different sources. The two relations, the Lindemer and Besmann [14] and Blackburn [3] models, describing the activity of UO_2 in UO_{2+x} with p_{O_2} along with the thermodynamic data used to compute the curves labeled Blackburn [3], Ozrin [5], and AECL [4] are well described in [1]. The Calphad (Calculation of Phase Diagrams) plot, based on the

assessment of the U-O system after Guéneau et al. [12], best reproduces the experimentally observed behavior. In [12], the Gibbs energy functions for $\text{UO}_3(\text{g})$, O_2 , and stoichiometric UO_2 come from the works of Konings et al. [15], the SGTE database [16], and Guéneau et al. [12] respectively. The compound energy formalism (CEF) sublattice model developed in [12] was used to determine the activity of UO_2 as a function of p_{O_2} .

As pointed out in [1], K_{eq} is the cause of the differences in the curves given in Fig. 5. Fig. 6 compares the a_{UO_2} versus p_{O_2} for the three different models evaluated in this work and shows good agreement between them. In fact, when an identical K_{eq} is used in Eqn. 8, nearly identical computed p_{UO_3} values are obtained regardless of which a_{UO_2} to p_{O_2} relation is operative. Olander [1] reviewed the available thermodynamic data and recommended K_{eq} based on transpiration measurements of $\text{UO}_3(\text{g})$ over U_3O_8 determined by Kirkorkian [2]. Fig. 7 shows that the Calphad and Kirkorkian et al. [2] K_{eq} plots with temperature are in very good agreement.

5. Conclusions

This work adds p_{UO_3} measurements in equilibrium with fluorite structure UO_{2+x} to those characterizing it over U_3O_8 [2; 10; 17] and illustrates the usefulness of the transpiration coupled TGA technique for determining equilibrium vapor pressures of nonstoichiometric oxides. The experimental results from this work give more certainty to the Gibbs energy of reaction for Eqn. 7 from either [12; 15; 16] and [2], which are practically equivalent, and can be combined with an appropriate model for UO_{2+x} , like those from [3; 12; 14], for a thermodynamic description of the equilibrium vapors over UO_{2+x} . This facilitates experimentally characterizing $\text{UO}_2(\text{OH})_2$ formation from UO_{2+x} reaction with pressurized water or steam and aids in better understanding fuel behavior under severe accident conditions.

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References

- [1] D. Olander, J. Nucl. Mater. 270 (1999) 187-193.
- [2] O. Krikorian, B. Ebbinghaus, M.G. Adamson, A.S. Fontes Jr, D. Fleming, Experimental studies and thermodynamic modelling of volatilities of uranium, plutonium, and americium from their oxides and from their oxides interacted with ash, Lawrence Livermore National Lab., CA (United States), 1993.
- [3] P. Blackburn, J. Nucl. Mater. 46 (1973) 244-252.
- [4] B. Lewis, B. Corse, W. Thompson, M. Kaye, F. Iglesias, P. Elder, R. Dickson, Z. Liu, J. Nucl. Mater. 252 (1998) 235-256.
- [5] V. Ozrin, Nuclear Safety Institute of the Russian Academy of Sciences NSI-SARR-43-96 (1996).
- [6] U. Merten, W. Bell, The Characterization of High-Temperature Vapors. in: J.L. Margrave, (Ed.), Wiley, New York, 1967.
- [7] M. Ali, R. Mishra, A.S. Kerkar, S.R. Bharadwaj, D. Das, J. Nucl. Mater. 301 (2002) 183-186.
- [8] R. Pankajavalli, S. Anthonysamy, K. Ananthasivan, P.V. Rao, J. Nucl. Mater. 362 (2007) 128-131.
- [9] R. Viswanathan, T.L. Narasimhan, S. Nalini, The Journal of Physical Chemistry B 113 (2009) 8362-8368.
- [10] R. Ackermann, R. Thorn, C. Alexander, M. Tetenbaum, The Journal of Physical Chemistry 64 (1960) 350-355.
- [11] D.R. Olander, Fundamental aspects of nuclear reactor fuel elements, California Univ., Berkeley (USA). Dept. of Nuclear Engineering, 1976.
- [12] C. Guéneau, N. Dupin, B. Sundman, C. Martial, J.C. Dumas, S. Gosse, S. Chatain, F. De Bruycker, D. Manara, R.J.M. Konings, J. Nucl. Mater. 419 (2011) 145-167.
- [13] J.R. Taylor, An introduction to error analysis: the study of uncertainties in physical measurements, University science books, 1997.
- [14] T.B. Lindemer, T.M. Besmann, J. Nucl. Mater. 130 (1985) 473-488.
- [15] R.J. Konings, O. Beneš, J. Phys. Chem. Ref. Data 39 (2010) 043102.
- [16] SGTE Substances Database Version 2.
- [17] S. Dharwadkar, S. Tripathi, M. Karkhanavala, M. Chandrasekharaiah, Thermodynamic properties of gaseous uranium hydroxide, Symposium on the thermodynamics of nuclear materials, International Atomic Energy Agency, Vienna (Austria), 1975, pp. 455-465.

Table 1. Experimental p_{UO_3} pressures with standard uncertainty $u(p_{\text{UO}_3})$ over single phase UO_{2+x} or U_3O_8 as a function of temperature, T , and p_{O_2} with standard uncertainty $u(p_{\text{O}_2})$.^{a,b}

T/K	$p_{\text{O}_2}/\text{atm}$	$u(p_{\text{O}_2})/\text{atm}$	$p_{\text{UO}_3}/\text{atm}$	$u(p_{\text{UO}_3})/\text{atm}$	Phases present (calc.)
1573	1.00×10^{-3}	2.37×10^{-4}	3.78×10^{-6}	4.03×10^{-7}	UO_{2+x}
1573	1.00×10^{-2}	1.83×10^{-4}	9.12×10^{-6}	4.03×10^{-7}	U_3O_8
1573	2.00×10^{-2}	2.00×10^{-4}	1.18×10^{-5}	4.03×10^{-7}	U_3O_8
1773	1.00×10^{-3}	2.37×10^{-4}	3.47×10^{-5}	4.03×10^{-7}	UO_{2+x}
1773	1.00×10^{-2}	1.83×10^{-4}	1.10×10^{-4}	4.03×10^{-7}	UO_{2+x}
1773	2.00×10^{-2}	2.00×10^{-4}	1.44×10^{-4}	4.03×10^{-7}	UO_{2+x}

^aStandard uncertainties u are $u(T) = 0.05 \text{ K}$ and $u(P_{\text{sys}}) = 0.03 \text{ atm}$.

^b1 atm = 101,325 Pa

Table 2. Sources of experimental uncertainty.

Source	Manufacturer	Uncertainty
Ar-2.00% O ₂ composition	Air Liquide	±1% of reported composition
Ar-4.01% H ₂ composition	Air Liquide	±2% of reported composition
Mixed gas flow rate	EnviroNics	±0.5% of the flow
Thermocouple	Netzsch	±0.05 K

Table 3. Reported purity of standards provided by Netzsch Instruments used for the TGA thermocouple calibration.

Material	Purity (%)
Ni	99.99
Al	99.999
Zn	99.999
Au	99.999
Ag	99.99

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7