



Thermodynamic study of the vaporization of Cs_2UO_4 by high temperature mass spectrometry

Jintao Huang^a, Michio Yamawaki^{a,*}, Kenji Yamaguchi^a, Futaba Ono^a, Masaru Yasumoto^b,
Hiroshi Sakurai^c, Jun Sugimoto^d

^aGraduate School of Quantum Engineering and Systems Science, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

^bResearch Center for Nuclear Science and Technology, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

^cNippon Nuclear Fuel Development Co., Ltd., 2163 Narita-cho, Oarai-machi, Higashi-Ibaraki-gun, Ibaraki-ken 311-13, Japan

^dDepartment of Reactor Safety Research, Japan Atomic Energy Research Institute, 2-4 Shirakata-shirane, Tokai-mura, Naka-gun, Ibaraki-ken 319-11, Japan

Abstract

With regard to the behavior of high radioactivity fission products in the case of accidents, the thermochemical behavior of Cs_2UO_4 at high temperature is not completely known. A study of the vaporization of Cs_2UO_4 was carried out from 873 to 1373 K using the Knudsen effusion mass spectrometric method. To simulate some LWR accident atmospheres, a $\text{D}_2/\text{D}_2\text{O}$ environment was established by introducing $\text{D}_2(\text{g})$ and/or $\text{D}_2\text{O}(\text{g})$ gas into the Knudsen cell, separately or as a mixed gas. Thus, the influence of the input of $\text{D}_2/\text{D}_2\text{O}$ on the vaporization of Cs_2UO_4 was investigated quantitatively. © 1998 Elsevier Science S.A.

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1. Introduction

As cesium is one of the most important fission products with high radioactivity, its compounds with uranium, cesium uranates, have been studied rather intensively for a long period [1–14]. In 1983, for example, the thermal stability of cesium monouranate, Cs_2UO_4 , was studied using the thermogravimetric method [15]. It was reported that traces of moisture tend to reduce the decomposition temperature of Cs_2UO_4 . Further, in a water vapor atmosphere, $\text{Cs}_2\text{U}_2\text{O}_7$ was found to be the product. Later, in 1985, a mass spectrometric study was carried out on the vaporization of Cs_2UO_4 [16]. According to this report, Cs_2UO_4 decomposes to $\text{Cs}_2\text{U}_4\text{O}_{12}$ and cesium vapor above 1223 K. There is still inconsistency with respect to our knowledge of the thermal stability of Cs_2UO_4 .

This study attempts to use a Knudsen effusion mass spectrometer equipped with a gas inlet system to investigate the vaporization behavior of Cs_2UO_4 quantitatively, both in vacuum and in gaseous atmosphere, water vapor or hydrogen. To simulate severe accident conditions, different

atmospheres that might occur in the case of broken fuel pins of light water reactors were established by introducing the appropriate gases. Thus, the possible vaporization behavior of Cs_2UO_4 was evaluated, especially under reducing atmosphere.

2. Experimental

2.1. Sample preparation

For the preparation of Cs_2UO_4 , a similar process to that reported in Ref. [18] was carried out. The reaction for the formation of Cs_2UO_4 is



The main product was confirmed as Cs_2UO_4 by X-ray diffraction identification, although trace amounts of uranium oxides such as UO_3 or U_2O_5 were also identified. The total impurities in each starting material, UO_3 and CsCO_3 , were about 30 ppm. It is estimated that Cs_2UO_4 obtained from these materials contains less than 100 ppm impurities in total. Since Cs_2UO_4 is highly hygroscopic, a

*Corresponding author. Tel.: +81 3 3812 2111, extn. 7422; fax: +81 3 5684 0229; e-mail: yamawaki@q.t.u-tokyo.ac.jp

dry glove box is essential during all the handling and transfer processes. All storage and transportation of the samples were carried out either in Ar atmosphere or in high vacuum.

2.2. Mass spectrometry with a mixture gas inlet system

The HT-12-90 high temperature mass spectrometer equipped with a gas inlet system used in this study has been described previously [18]. A Knudsen cell made of Pt and a sample holder made of Pt were used for this experiment. The authors have improved their gas inlet system and have made it possible to introduce a mixture of gases into the Knudsen cell. By adding a mixture of $D_2(g) + O_2(g)$ at different ratios, a water vapor environment with a different oxygen potential can be established inside the Knudsen cell. In this way, the atmosphere can be controlled better than by simply adding only $D_2(g)$ or only $D_2O(g)$. We did not choose a combination of $D_2(g) + D_2O(g)$ since it was not possible to maintain the inlet amount of $D_2O(g)$ at a stable value. The amounts of inlet gases were controlled by their initial pressures in the respective reservoirs.

To obtain the absolute pressures of the vapor species, the proportional factor, K , of the mass spectrometric system was obtained from the mass conservation of Ar consumed, i.e. taking the Ar flow rate at the input end of the gas supply equal to that observed at the other end, the orifice. The ionization efficiency curve (IEC) of Cs^+ was found to be very close to a simple ionization curve. Since Cs^+ is the dominant ion under all conditions, the influence of any possible fragmentation processes on the Cs^+ intensity could be neglected. For Cs^+ and $CsOD^+$, a 20 eV electron impact energy was used; 30 eV was employed for D_2O^+ , O_2^+ and CsO^+ .

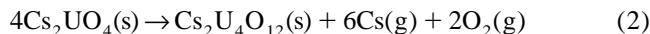
3. Results

3.1. Vaporization behavior of Cs_2UO_4 in vacuum

It was found that the ion intensity of Cs^+ decreased with time. For example, it took about 1 h to reach a stable intensity at 1373 K. This behavior is similar to that

reported in an earlier study on the Cs–U–O system [17]. This study suggested the influence of moisture picked up by the sample surface, which caused a change in the thermodynamic activity of the sample. Therefore, a 24 h or longer annealing process at around 700 K was used to reduce this effect before starting the experimental runs. Thus, all the measurements were made after the Cs^+ intensity became stable. The ions Cs^+ , O_2^+ and UO_2^+ were found in decreasing order of their intensities. Cs^+ was the dominant ion, the intensity of which was about three orders of magnitude higher than that of CsO^+ . The pressure–temperature dependence of each vapor species was determined (Table 1). Since oxygen also originated from the vacuum chamber as well as the Knudsen cell, the actual oxygen partial pressure originating from the inside of the Knudsen cell was difficult to estimate.

After the mass spectrometric experiment, the sample was first examined with the naked eye. We could see that the color of the upper part of the tested sample had changed to black from the original orange color of Cs_2UO_4 . X-ray diffraction phase identification showed that $Cs_2U_4O_{12}$ and UO_2 were responsible for the black coloration. This result is a little different from the earlier mass spectrometric study of Cs_2UO_4 by Bose et al., who found only $Cs_2U_4O_{12}$ [16]. Therefore, the following decomposition reaction was assumed



Comparing the present results with those of Bose et al., it can be seen that the main vapor species are the same. In both laboratories, $Cs(g)$ was found to be the dominant vapor species over Cs_2UO_4 , but the values of the slopes of the $Cs(g)$ pressure curves were different. Bose et al. obtained $4.1 \times 10^4 \text{ K}^{-1}$, while our value is $3.3 \times 10^4 \text{ K}^{-1}$. No further thermodynamic analysis was made due to the lack of accurate values of oxygen potentials.

3.2. Vaporization of Cs_2UO_4 under different simulated environments

Three experimental conditions were established by introducing certain amounts of $D_2(g)$ and/or $O_2(g)$, for

Table 1

Pressure–temperature relationship of the main vapor species over Cs_2UO_4 in the form $\ln P/Pa = a + b/T$ under different environmental conditions

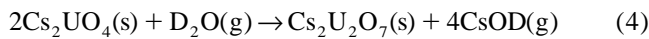
Environmental conditions	Cs(g)	CsOD(g)	$D_2O(g)$	$O_2(g)^a$
In vacuum	$a = 25.81 \pm 0.30$ $b = -33\,102 \pm 379$			$a = 42.54 \pm 2.62$ $b = -59\,070 \pm 3520$
D_2 inlet	$a = 15.43 \pm 0.10$ $b = -18\,430 \pm 118$	$a = 8.03 \pm 0.35$ $b = -12\,809 \pm 450$	$a = -8.48 \pm 0.63$ $b = 11\,483 \pm 809$	
$D_2 + O_2$ inlet ($D_2/O_2 = 2:1$)	$a = 21.22 \pm 0.17$ $b = -26\,591 \pm 216$	$a = 10.36 \pm 0.51$ $b = -16\,105 \pm 648$	$a = -8.47 \pm 0.28$ $b = 11\,632 \pm 326$	$a = 27.59 \pm 1.80$ $b = -40\,105 \pm 2417$
$D_2 + O_2$ inlet ($D_2/O_2 = 1:2$)	$a = 28.91 \pm 0.87$ $b = -37\,894 \pm 1163$	$a = 13.52 \pm 3.16$ $b = -21\,798 \pm 3990$	$a = -9.41 \pm 2.18$ $b = 9827 \pm 2903$	$a = 13.15 \pm 1.43$ $b = -18\,680 \pm 1920$

^aOxygen pressures given here are relative data and can be used to compare each experimental condition.

example $D_2(g)+O_2(g)$ with 2:1 or 1:2 input ratio as well as only $D_2(g)$. When deuterium–oxygen mixture gases were introduced, gases such as Cs, CsOD, O_2 , D_2O , CsO and UO_2 were detected as the vapor species. The pressure of D_2 was lower than the detection limit. Fig. 1 shows the experimental results when the input mole ratio of $D_2(g)$ to $O_2(g)$ was set at 2:1, which is equivalent to adding $D_2O(g)$ directly. The vaporization pattern was almost the same as a separate experiment introducing only $D_2O(g)$. After increasing the oxygen content in the $D_2(g)+O_2(g)$ mixture gas, the partial vapor pressures of the vapor species changed significantly. This is because the oxygen potential plays a large role in determining the equilibrium vapor composition.

When $D_2(g)$ was introduced, the observed vapor species were Cs, CsOD, D_2O and UO_2 . The pressure of $D_2(g)$ was still too low to be detected. The pressure–temperature relationships of the main vapor species are shown in Table 1. It was found that the Cs pressure over Cs_2UO_4 increased compared to the case in vacuum where the specimen was placed in a Pt cell.

In the above environments, the formation of $Cs_2U_2O_7(s)$ was identified by X-ray diffraction analysis, therefore the following reaction is assumed



At the average temperature of the experimental range, 1300 K, the enthalpy change of the above reaction can be calculated from the corresponding slope listed in Table 1.

For the three kinds of inlet gas conditions

$$\begin{aligned} \sum \Delta_r H^\circ(1300 \text{ K}) \\ = 364.5 \pm 13.5 \text{ kJ mol}^{-1} \quad (\text{in the case of the mixture inlet, } D_2/O_2 \\ = 2:1) \end{aligned}$$

$$\begin{aligned} \sum \Delta_r H^\circ(1300 \text{ K}) \\ = 444.2 \pm 90.5 \text{ kJ mol}^{-1} \quad (\text{in the case of the mixture inlet, } D_2/O_2 \\ = 1:2) \end{aligned}$$

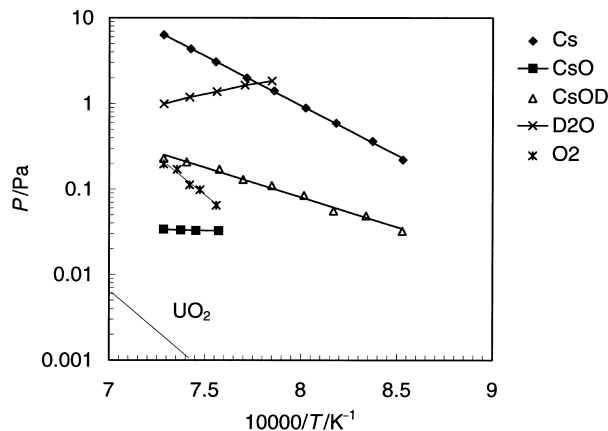


Fig. 1. Vapor pressures of Cs_2UO_4 with $D_2(g)+O_2(g)$ admission.

$$\begin{aligned} \sum \Delta_r H^\circ(1300 \text{ K}) \\ = 308.5 \pm 14.2 \text{ kJ mol}^{-1} \quad (\text{in the case of } D_2 \text{ inlet}) \end{aligned}$$

$$\sum \Delta_r H^\circ(\text{average}) = 372.4 \pm 47.9 \text{ kJ mol}^{-1}$$

The theoretical enthalpy change of the above reaction calculated from Cordfunke's reference was $\sum \Delta_r H^\circ(1300 \text{ K}) = 366.2 \text{ kJ mol}^{-1}$. The difference between the theoretical value and the experimental result was about 1.7%.

4. Discussion

In different environments, P_{Cs} changed significantly, which demonstrates the effect of different environmental conditions. A comparison was made and the effect of environment on the change in the Cs(g) pressure is shown in Fig. 2. The pressure of Cs increased when either D_2 or D_2O was introduced into the Knudsen cell compared with the case of the Pt cell. Especially in the case of D_2 inlet in which the oxygen potential was low, the Cs pressure at 1073 K was about 10 times higher than that over Cs_2UO_4 in vacuum. This result not only confirms that the Cs partial pressure over Cs_2UO_4 increases in a reducing atmosphere, but also gives the extent of the change at different water vapor pressures. This will be helpful in analyzing the probability of release of radioactive Cs(g) in the case of a severe accident occurring in water cooled reactors. This result is different from the vaporization behavior of Ba(g) and Sr(g) from their solid uranates such as $BaUO_3$ and $SrUO_3$ in a water vapor or hydrogen environment [19], where all the main vapor pressures over the uranates decreased with admission of either water vapor or hydrogen.

We note here that Bharadwaj et al. found $Cs_2U_2O_7(s)$ as the only decomposition product of Cs_2UO_4 in a water vapor environment, where P_{H_2O} was either 2.77, 9.21 or

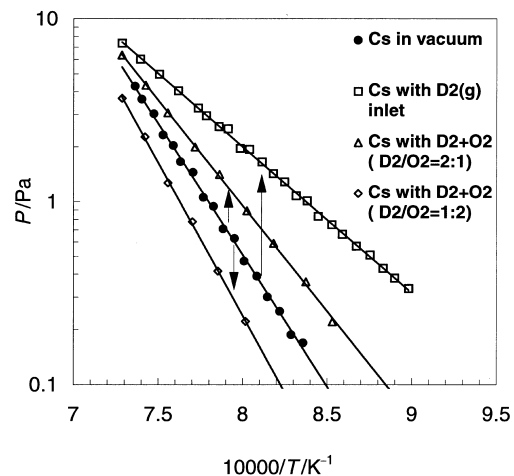


Fig. 2. Comparison of Cs pressure over Cs_2UO_4 under different conditions.

17.5 Torr [15]. In the final product after the present mass spectrometric experiment, however, only a small amount of $\text{Cs}_2\text{U}_2\text{O}_7(\text{s})$ was detected by X-ray diffraction analysis. This would be due to the low pressure of $\text{D}_2\text{O}(\text{g})$ in this case where only about 0.1–1 Pa $\text{D}_2\text{O}(\text{g})$ was established inside the Knudsen cell. Thus, decomposition reaction (4) would not be completed. Because of the existence of hydrogen or water vapor, CsOD did appear but its partial pressure was lower than that of $\text{Cs}(\text{g})$ under the present experimental conditions. The partial vapor pressure of cesium remains the highest over all other Cs-containing vapor species.

5. Conclusion

The vaporization behavior of Cs_2UO_4 was investigated either in vacuum or in gaseous environments at high temperatures up to 1373 K. In vacuum, $\text{Cs}(\text{g})$ was found to be the dominant vapor species over the compound. Two phases of $\text{Cs}_2\text{U}_4\text{O}_{12}$ and UO_2 were found as the final products after vaporization in the mass spectrometer. In a $\text{D}_2(\text{g})$ or $\text{D}_2\text{O}(\text{g})$ environment, Cs , CsOD , O_2 , D_2O and CsO were detected as the vapor species over the compound. Some $\text{Cs}_2\text{U}_2\text{O}_7$ was detected together with $\text{Cs}_2\text{U}_4\text{O}_{12}$ and UO_2 by X-ray diffraction analysis after water vapor or hydrogen was introduced into the Knudsen cell. Thermodynamic calculation for the decomposition reaction agreed with the mass spectrometric results. It is noted that a $\text{D}_2(\text{g})$ or $\text{D}_2\text{O}(\text{g})$ environment tends to increase the partial vapor pressure of cesium over Cs_2UO_4 . The change in the Cs pressure appears to be determined by the oxygen potential and temperature. The $\text{Cs}(\text{g})$ pressure was observed to be about one order of magnitude higher in

a $\text{D}_2(\text{g})$ environment, where the oxygen pressure is low, than in an oxidizing atmosphere.

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