Investigation of vaporization behavior of hyper-stoichiometric uranium dioxide by Knudsen effusion mass spectrometry

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Abstract

The determination of partial pressures of $UO_3(g)$ and $O_2(g)$ over $UO_{2+x}(s)$ as function of the O/U ratio was attempted at 1473, 1673, 1773 and 1873 K under the condition of the decreasing O/U ratio of the condensed phase by Knudsen effusion mass spectrometry. From these vapor pressures the Gibbs free energy of formation of $UO_3(g)$, $\Delta G_f^0(UO_3,g)$, was also evaluated. The partial pressures of $O_2(g)$ over $UO_{2+x}(s)$ obtained in this study almost agreed with the experimental data reported in the past as well as the values derived from the empirical equation given by Nakamura and Fujino. Further, it was found that the values of $\Delta G_f^0(UO_3,g)$ obtained in this study were in good agreement with the recommended values.
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1. Introduction

From the view point of evaluating release behavior of volatile radio nuclides in core disruptive accidents it is essential to know the vaporization behavior of hyper-stoichiometric uranium dioxide, $UO_{2+x}(s)$. The vaporization behavior of uranium-bearing volatile vapor species, or, $UO_3(g)$, are inconsistent among several literature sources [1], where the discrepancies are two orders of magnitude at 1500 K and one order of magnitude at 2000 K. Our previous paper concerning the mass-spectrometric study of $UO_{2+x}(s)$ co-loaded with MgO(s) says the values of the Gibbs free energy of formation of $UO_3(g)$, $\Delta G_f^0(UO_3,g)$, is a little higher than the recommended values given by Olander [1]. Hashiz-

ume et al., however, inferred from their experimental results concerning the volatilization of urania in steam that this recommended value underestimated the $UO_3(g)$ vapor pressure [2]. This suggestion contradicts our former result [3]. In our previous study MgO(s) was used as an oxygen supplier to avoid the reduction of stoichiometry of $UO_{2+x}(s)$ under the vacuum condition and the detected ionic currents of UO_3^+ and Mg^+ ultimately became constant at constant temperatures. But the sample of $UO_2(s)$ put on the sample of MgO(s) might reduce the surface area of the sample of MgO(s) and cover its intrinsic vaporization behavior since the reduction of the vaporization area makes the vapor pressures inside a Knudsen cell smaller than the equilibrium pressures [4]. Further, the uncertainties of the values of $\Delta G_f^0(MgO,s)$ influence the values of $\Delta G_f^0(UO_3,g)$ since the reference data of $\Delta G_f^0(MgO,s)$ are utilized in the evaluation of $\Delta G_f^0(UO_3,g)$. So to overcome this problem the mass-spectrometric measurements of pure $UO_{2+x}(s)$ are carried out and $\Delta G_f^0(UO_3,g)$ is evaluated from the measured partial pressures of $UO_3(g)$ and $O_2(g)$ over

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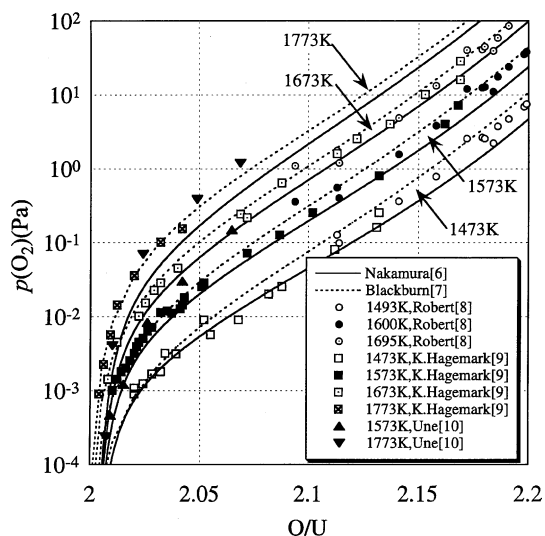*E-mail address:* kuni@popsvr.tokai.jaeri.go.jp (K. Nakajima).

Fig. 1. Comparison of oxygen partial pressures over UO_{2+x} at higher temperatures reported in the past.

UO_{2+x}(s) again. However, the following problems are anticipated to occur in this method. The O/U ratio of the condensed phase decreases with time due to the preferential loss of oxygen from an orifice of Knudsen cell and the ion currents of UO_3^+ and O_2^+ change with the decrease of the O/U ratio. Then, it could not be judged from the detected ion currents behavior of vapor species whether the equilibrium between the gas phase and the condensed phase holds. Fortunately, many studies concerning the oxygen potentials of UO_{2+x}(s) have been conducted since the late 1950s [5] and the estimated values derived from the empirical equations given by Nakamura and Fujino [6] and Blackburn [7] are in good agreement with the experimental data reported in the past [8–10] as shown in Fig. 1. So, if the partial pressures of O_2(g) evaluated in this study agree with these reported values the method used in this study, which is described later, is expected to be effective. Therefore, the purpose of this study is to make sure that this method is applicable to the measurement of the vapor pressures over UO_{2+x}(s) having extensive hyper-stoichiometric composition besides seeing if the previous result of $\Delta G_f^0(UO_3,g)$ is appropriate.

2. Experimental

2.1. Sample

The powder sample of UO_2(s) used in this study is supplied by Spencer Chemical, USA and its impurity levels are listed in Table 1 in our previous paper [3]. Hyper-stoichiometric uranium dioxides, UO_{2+x}(s), for

test specimens were prepared by heating U_3O_8(s) put in a Knudsen cell under a vacuum condition. At first, U_3O_8(s) was prepared by heating UO_2(s) at 873 K in air. Then, it was weighed out about 230 mg and put into a Pt Knudsen cell with an orifice of 0.5 mm $\varnothing$ in diameter. The samples having the O/U ratios of 2.12 and 2.10 were prepared by heating U_3O_8(s) in the Knudsen cell for 4 and 4.5 h in vacuum, respectively. The O/U ratio was determined by measuring the weight increase after ignition at 873 K in air to U_3O_8(s). The weight change was measured in accuracy of about ±0.05 mg, which corresponded to a change of ±0.005 in the oxygen-to-uranium ratio.

2.2. Mass-spectrometric measurement

Mass-spectrometric measurements combined with a Knudsen cell were carried out at the prescribed temperatures of 1673, 1773 or 1873 K. A quadrupole mass spectrometer (MEXM-1200 ABB EXTREL, USA) was used in this study. Knudsen cell was made of iridium and its orifice diameter is 1.0 mm $\varnothing$. The detailed description of this apparatus has been reported in the previous paper [11]. Mass-spectrometric measurements were conducted by heating the powder samples having the weight of 200 mg. The samples of the O/U ratio of 2.12 were used in the mass-spectrometric measurements at 1673 and 1773 K. On the other hand, the samples of the O/U ratio of 2.10 were used in the mass-spectrometric measurements at 1773 and 1873 K. The vapor species of UO_3(g) and O_2(g) were identified and ionized at 70 eV, where the ion currents of UO_3^+ become the maximum [3]. Moving a shutter allowed us to distinguish O_2(g) vapor species effusing through an orifice from those of background. The ion currents of UO_3^+ and O_2^+ were measured at the prescribed temperature until the vapor species of O_2(g) effusing through the orifice could not be distinguished from those of background. Lowest temperature was restricted to the ability of mass balance in measuring the loss of amount of the vapor species effusing from the Knudsen cell. Highest temperature was restricted to the validity of molecular flow in the orifice of Knudsen cell [12].

2.3. Determination of the absolute vapor pressures from their ion currents

The determination of the absolute vapor pressure from its ion current was carried out by the modified integral method [13]. This method requires the total losses of amounts of the vapor species and the ion currents of the vapor species at any time during the mass-spectrometric measurement. The total losses of amounts of UO_3(g) and O_2(g) during the measurement were evaluated from the changes of the weight and the O/U

ratio of the sample before and after the mass-spectrometric measurement. The total losses of weights of $UO_3(g)$ and $O_2(g)$ effusing from the orifice, or, $\Delta W(UO_3)$ and $\Delta W(O_2)$, are obtained by solving the following simultaneous equations:

$$W_1(O)/M(O)/W_1(U)/M(U) = \rho_1, \qquad (1)$$

$$W_2(O)/M(O)/W_2(U)/M(U) = \rho_2, \qquad (2)$$

$$W_1(O) + W_1(U) = W_1(\text{sample}), \qquad (3)$$

$$W_2(O) + W_2(U) = W_2(\text{sample}), \qquad (4)$$

where W is the weight, M the mass number and ρ the O/U ratio. Subscripts of 1 and 2 mean the states before and after the mass-spectrometric measurement, respectively. Since unknown factors, $W_1(O)$, $W_1(U)$, $W_2(O)$ and $W_2(U)$, can be obtained from the above equations, $\Delta W(UO_3)$ and $\Delta W(O_2)$ are calculated by the following equations:

$$\Delta W(UO_3) = (W_1(U) - W_2(U))M(UO_3)/M(U), \qquad (5)$$

$$\Delta W(O_2) = W_1(\text{sample}) - W_2(\text{sample}) - \Delta W(UO_3). \qquad (6)$$

Consequently, the partial pressures of $UO_3(g)$ and $O_2(g)$ can be evaluated in the modified integral method [13] from the measured ion currents of UO_3^+, I_{UO_3}, and O_2^+, I_{O_2}, by using the following equations:

$$p_{UO_3}(T,t) = \frac{\Delta W(UO_3)}{\Delta t \cdot s \cdot L} \sqrt{\frac{2\pi \cdot R \cdot T}{M(UO_3)}} \frac{\int_{t_1}^{t_2} I_{UO_3}(t')\sqrt{T_{t'}}\,dt'}{\int_0^{t_{\text{end}}} I_{UO_3}(t')\sqrt{T_{t'}}\,dt'}, \qquad (7)$$

$$p_{O_2}(T,t) = \frac{\Delta W(O_2)}{\Delta t \cdot s \cdot L} \sqrt{\frac{2\pi \cdot R \cdot T}{M(O_2)}} \frac{\int_{t_1}^{t_2} I_{O_2}(t')\sqrt{T_{t'}}\,dt'}{\int_0^{t_{\text{end}}} I_{O_2}(t')\sqrt{T_{t'}}\,dt'}, \qquad (8)$$

where T is the average sample temperature in the time interval of $\Delta t = t_2 - t_1$, t the middle of time in this time interval, $T_{t'}$ the sample temperature at time t'. In this study the mass-spectrometric measurement was carried out by holding the temperature at 1473 K at first in order to identify the vapor species of $UO_3(g)$ and $O_2(g)$ effusing from the Knudsen cell and not by heating directly up to the prescribed temperature. Further, it seems that the sample temperatures at the turning points are changed stepwise in the whole temperature profile of the mass-spectrometric measurement since it takes only a few minutes to attain the prescribed temperatures. So the above equations are simplified to the following equations:

$$p_{UO_3}(T,t) \cong \frac{\Delta W(UO_3)}{s \cdot L} \sqrt{\frac{2\pi \cdot R \cdot T}{M(UO_3)}}$$
$$\times \frac{I_{UO_3}(t) \cdot \sqrt{T}}{\sqrt{1473} \cdot \int_{t'=0}^{t_i} I_{UO_3}(t')\,dt' + \sqrt{T} \cdot \int_{t'=t_i}^{t_{\text{end}}} I_{UO_3}(t')\,dt'}, \qquad (9)$$

$$p_{O_2}(T,t) \cong \frac{\Delta W(O_2)}{s \cdot L} \sqrt{\frac{2\pi \cdot R \cdot T}{M(O_2)}}$$
$$\times \frac{I_{O_2}(t)\sqrt{T}}{\sqrt{1473} \cdot \int_{t'=0}^{t_i} I_{O_2}(t')\,dt' + \sqrt{T} \cdot \int_{t'=t_i}^{t_{\text{end}}} I_{O_2}(t')\,dt'}, \qquad (10)$$

where t_i is the time when the temperature changes from 1473 K to the prescribed temperature. In the above equations $\int_{t_1}^{t_2} I(t)\sqrt{T_{t'}}\,dt'$ is approximated to be $I(t)\sqrt{T}\Delta t$ by converging Δt to zero. Strictly speaking, the isotopic abundant ratios of the vapor species effusing through an orifice are different from those in the gas phase inside a Knudsen cell because the number of collision of the vapor species per unit of time per unit of area is proportional to the reciprocal square root of their mass. But this difference is considered to be negligible. So the vapor species effusing through an orifice are assumed to have the same abundant ratios as those in the gas phase within a Knudsen cell. The above equations are also applied to the determination of the vapor pressures at 1473 K by substituting 1473 for T in their numerators.

In this study, the mass-spectrometric measurement of silver was also conducted in order to know the unknown factor $s \cdot L$ of the Knudsen cell which was evaluated from the following equation:

$$s \cdot L(T_k) \cong \frac{\Delta W(Ag)}{p_{Ag}^{\text{ref}}(T_k)} \sqrt{\frac{2\pi \cdot R \cdot T_k}{M(Ag)}} \frac{I_{Ag}(t)\sqrt{T_k}}{\sum_j \sqrt{T_j} \cdot \int_{t'=t_j}^{t'=t_{j+1}} I_{Ag}(t')\,dt'}, \qquad (11)$$

where p_{Ag}^{ref} is the reference data [14] and t_j is the time when the temperature changes to T_j. This equation is simplified in the same method mentioned above. Then, the unknown factor $s \cdot L$ was determined by averaging the values of $s \cdot L(T_k)$ obtained at temperature T_k.

2.4. Evaluation of the O/U ratio of the condensed phase during the mass-spectrometric measurement

If the partial pressures of $UO_3(g)$ and $O_2(g)$ are known, the O/U ratio of the condensed phase during the mass-spectrometric measurement could be evaluated from Graham's law of effusion, or, the following relations:

$$z_U(T,t) = \frac{p_{UO_3}(T,t) \cdot s \cdot L \cdot N_A}{\sqrt{2\pi \cdot R \cdot T \cdot M(UO_3)}}, \qquad (12)$$

$$z_O(T,t) = \left(2 \frac{p_{O_2}(T,t)}{\sqrt{M(O_2)}} + 3 \frac{p_{UO_3}(T,t)}{\sqrt{M(UO_3)}} \right) \cdot \frac{s \cdot L \cdot N_A}{\sqrt{2\pi \cdot R \cdot T}},$$

(13)

where z is the number of atoms effusing through an orifice of Knudsen cell per unit of time. Precisely, the time dependence of the O/U ratio, $\rho(T,t)$, is determined from the following equation:

$$\rho(T,t) = \frac{\frac{W_1(O)}{M(O)} \cdot N_A - \int_0^{t_i} z_O(1473,t) \, dt' - \int_{t_i}^t z_O(T,t) \, dt'}{\frac{W_1(U)}{M(U)} \cdot N_A - \int_0^{t_i} z_U(1473,t) \, dt' - \int_{t_i}^t z_U(T,t) \, dt'}.$$

(14)

3. Results and discussion

3.1. Time dependence of the ion currents of UO_3^+ and O_2^+

Fig. 2 shows the time dependence of the ion currents of (a) UO_3^+ and (b) O_2^+ observed in the mass-spectrometric measurement at 1673 K. This figure also shows the ion currents of UO_3^+ and O_2^+ observed in the case of closed shutter, or the background ion currents. As shown in this figure, the background ion currents of $O_2(g)$ in the beginning of the measurement are so high that the contribution of these ion currents to the observed ion currents cannot be disregarded. So the background ion currents of O_2^+ are regarded as those indicated with the dotted lines in this figure which are obtained by connecting linearly 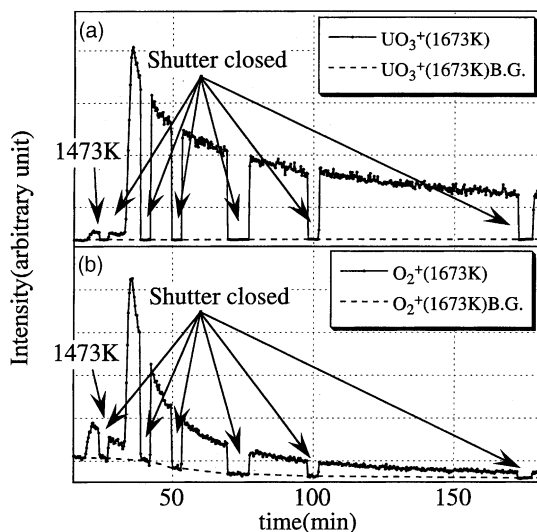between these background ionic currents. Further, Fig. 3 shows the time dependence of the ion currents of (a) UO_3^+ and (b) O_2^+ at
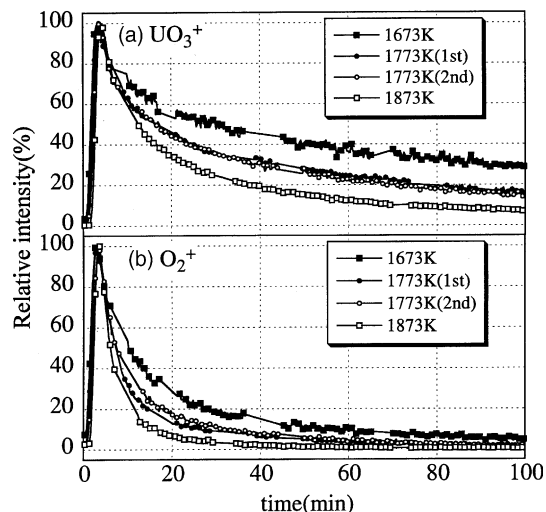

Fig. 3. Comparison of the ion currents of (a) UO_3^+ and (b) O_2^+ at 1673, 1773 and 1873 K.

1673, 1773 and 1873 K obtained by subtracting the background ion currents from the observed ion currents and normalized in such a way that the maximum ion currents are equal to be 100. As shown in this figure the ion currents of UO_3^+ and O_2^+ rapidly change at the turning points of temperature where the temperature changes stepwise from 1473 K to the prescribed temperature and, regardless of the prescribed temperature, these ion currents reach their maximum only a few minutes later. The mass-spectrometric measurements at 1773 K were carried out two times to make sure of the reproducibility of the experimental data. Although the sample compositions are slightly different, the similar time dependence of both the ion currents was observed. It is also found that both the ion currents of UO_3^+ and O_2^+ are decreasing faster with increasing temperatures and that the ion currents of O_2^+ are decreasing faster than those of UO_3^+.

3.2. Vapor pressures of $UO_3(g)$ and $O_2(g)$ over $UO_{2+x}(s)$

The determined vapor pressures of $UO_3(g)$ and $O_2(g)$ at 1673, 1773 (1st), 1773 (2nd) and 1873 K are plotted in Fig. 4(a)–(d), respectively. These figures also include the apparent vapor pressures at the temperatures increasing from 1473 K to the prescribed temperature besides those at 1473 K. Furthermore, the experimental and estimated data reported in the past [2,3,6,7] are indicated for comparison. As shown in Fig. 4(b) and (c), the vapor pressures over $UO_{2+x}(s)$ at $0.02 < x < 0.09$ at 1773 K are in good agreement. Then, the absolute vapor pressures determined in this study are considered to be reproducible. Furthermore, it is found that the determined
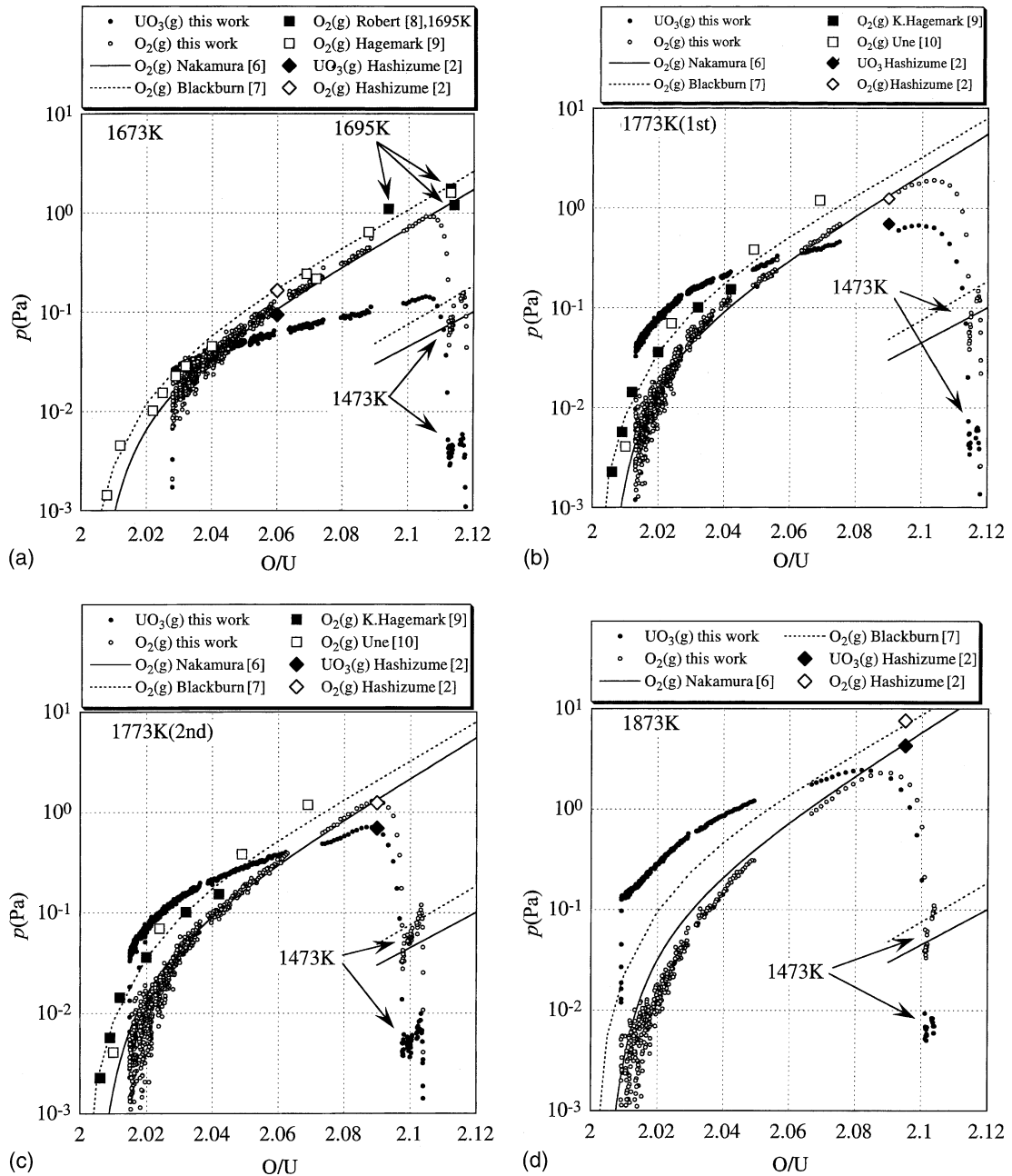

Fig. 2. Time dependence of the ion currents of (a) UO_3^+ and (b) O_2^+ at 1673 K.

Fig. 4. Vapor pressures of $UO_3(g)$ and $O_2(g)$ over UO_{2+x} at (a) 1673 K, (b) 1773 K (1st), (c) 1773 K (2nd), (d) 1873 K.

$O_2(g)$ pressures almost agree with the experimental values reported in the past and the values derived from the empirical equation given by Nakamura and Fujino. On the other hand, it seems that the determined $UO_3(g)$ vapor pressures are also in good agreement with the recommended value given by Olander, which are indicated in the table in Hashizume's paper [2]. In addition, it is found that the appreciable deviations of the O/U

ratio from the starting composition have already occurred at 1473 K.

3.3. The activity of $UO_2(s)$ in $UO_{2+x}(s)$

According to Olander, $UO_{2+x}(s)$ is represented as a binary solution of stoichiometric $UO_2(s)$ and neutral atomic oxygen and the activity of $UO_2(s)$ in $UO_{2+x}(s)$,

$a(UO_2)$, is evaluated from the $O_2(g)$ pressure by the following equation utilizing the Gibbs–Duhem equation:

$$\ln a_{UO_2}(x, T) = -\frac{1}{2}\int_0^x x' \frac{d\ln p_{O_2}(x', T)}{dx'}\,dx'. \tag{15}$$

Then, all the data of $O_2(g)$ partial pressures over $UO_{2+x}(s)$ ranging up to the stoichiometric $UO_2(s)$ are required for the calculation of $a(UO_2)$ in $UO_{2+x}(s)$. As shown in Fig. 4, the determined $O_2(g)$ pressures almost agree with the values derived from Nakamura's equation. However, the range of application of Nakamura's equation cannot extend to the stoichiometric $UO_2(s)$. Fortunately, the uncertainties in the oxygen potential do not greatly affect the UO_2 activity [1] and the $O_2(g)$

pressures derived from Blackburn's model are not largely deviated from our data as shown in Fig. 4. Then, the UO_2 activities based on Blackburn's model were used in the evaluation of $\Delta G_f^0(UO_3,g)$ and expressed by the following equations:

$$\ln a_{UO_2}(x) = -x + 2\ln(1 + x/2) + \ln(1 - x) - 36x^3. \tag{16}$$

3.4. The Gibbs free energy of formation of $UO_3(g)$

$\Delta G_f^0(UO_3,g)$ in this study is evaluated from the following reaction:
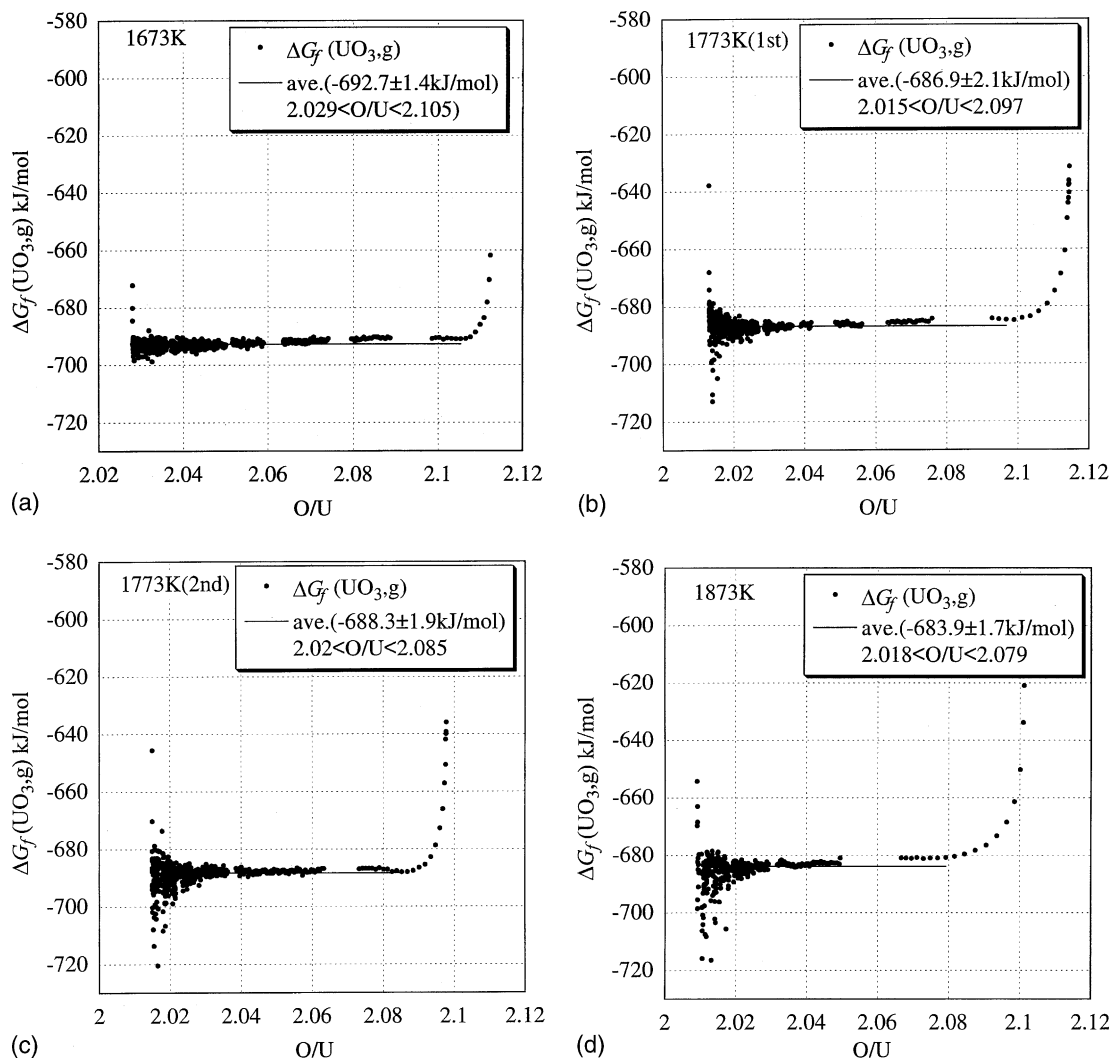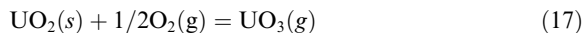
$$UO_2(s) + 1/2 O_2(g) = UO_3(g) \tag{17}$$

Fig. 5. Standard Gibbs free energy of formation of $UO_3(g)$ at (a) 1673 K, (b) 1773 K (1st), (c) 1773 K (2nd), (d) 1873 K plotted as function of the O/U ratio.

and calculated from the following equation utilizing $\Delta G_f^0(UO_2,s)$ given by Cordfunke and Konings [15]:

$$\Delta G_f^0(UO_3,g) = -RT\ln[p(UO_3)/p(O_2)^{1/2} \cdot a(UO_2)] + \Delta G_f^0(UO_2,s). \quad (18)$$

The results at 1673, 1773 (1st), 1773 (2nd) and 1873 K are plotted as function of the O/U ratio in Fig. 5(a)–(d), respectively. Fig. 6 also indicates the results evaluated from the vapor pressures of $UO_3(g)$ and $O_2(g)$ at 1473 K, which are obtained from all the mass-spectrometric measurements in this study. As shown in these figures, there exists the range for each run where the values of $\Delta G_f^0(UO_3,g)$ seem to be almost independent of the O/U ratio. Therefore, it is considered that the equilibrium between the gas phase and the solid phase is nearly realized in the Knudsen cell at this range.

In Fig. 7 the temperature dependence of the averaged values of $\Delta G_f^0(UO_3,g)$ indicated in Figs. 5 and 6 are shown, together with the reference data [1,15–18]. This figure also includes the values of $\Delta G_f^0(UO_3,g)$ reported in our previous paper [3]. The values of $\Delta G_f^0(UO_3,g)$ obtained in this study almost agree with the recommended value given by Olander. But our previous data are a little higher than the recommended values [1]. As one of the reasons of this difference, the vapor pressures over MgO(s) inside a Knudsen cell or the measured vapor pressures might be different from the equilibrium pressures [4]. Normally the samples used in a Knudsen effusion experiment are prepared to have large vaporization areas and on such conditions the measured vapor pressures become nearly equal to the equilibrium pressures. In the cases that vaporization areas and vapor-
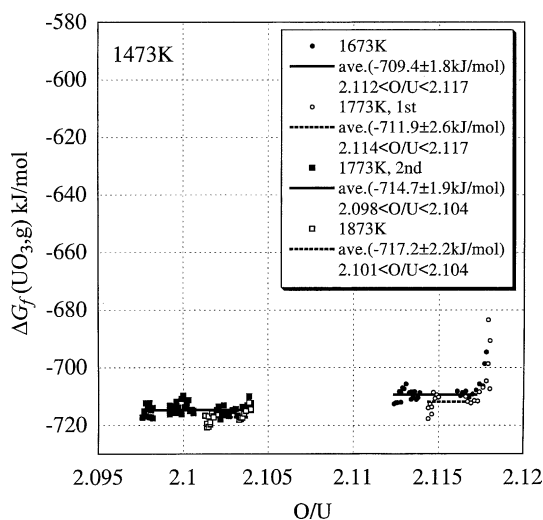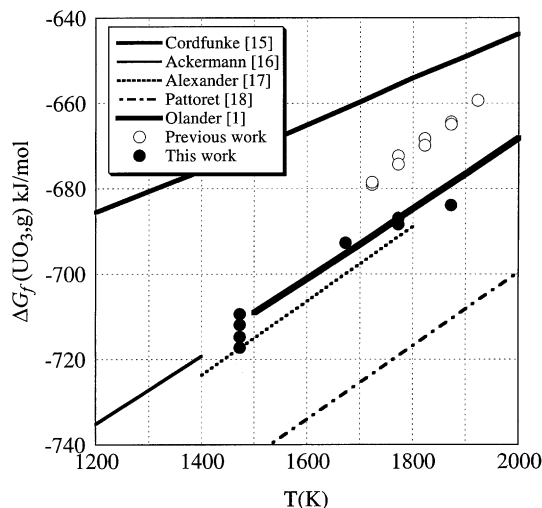

Fig. 7. Comparison of standard Gibbs free energy of formation of $UO_3(g)$.

ization coefficients are small, however, the vapor pressures inside a Knudsen cell become smaller than the equilibrium pressures due to the loss of the vaporizing atoms and/or molecules effused through an orifice of Knudsen cell. The vaporization area of the MgO(s) sample in the previous study might become small since the $UO_2(s)$ sample put on the MgO(s) sample reduced the surface area of the MgO(s) sample. Further, the vaporization coefficients of Mg(g) for MgO(s) are reported to be less than 0.2 at temperatures higher than 1700 K [4]. So the vapor pressures of Mg(g) in the Knudsen cell might become smaller than the equilibrium pressures on the previous experiment condition. Then, the vapor pressures of $O_2(g)$ could also become smaller than the equilibrium pressures since MgO(s) congruently vaporizes at temperatures higher than the boiling point of magnesium metal. The vapor pressures of $O_2(g)$ reported in our previous paper are evaluated by utilizing the reference data of $\Delta G_f^0(MgO,s)$, assuming that the equilibrium pressures over MgO(s) hold in a Knudsen cell. Therefore, these $O_2(g)$ pressures might be overestimated. In other words, our values of $\Delta G_f^0(UO_3,g)$ reported in the past could move to the lower values based on Eq. (18) since $a(UO_2)$ is not sensitive to the change of $p(O_2)$. Consequently, the values of $\Delta G_f^0(UO_3,g)$ in this study are considered to be more reliable since they are more directly evaluated without the aids of the oxygen supplier and the reference data of $\Delta G_f^0(MgO,s)$.

On the other hand, the averaged value of $\Delta G_f^0(UO_3,g)$ obtained at 1473 K becomes lower as the prescribed temperature of the mass-spectrometric experiment is higher as indicated in Fig. 6. Furthermore, Fig. 7 shows that the values of $\Delta G_f^0(UO_3,g)$ in this study tend to become low with the prescribed temperature increased

Fig. 6. Standard Gibbs free energy of formation of $UO_3(g)$ evaluated from the vapor pressures of $UO_3(g)$ and $O_2(g)$ at 1473 K plotted as function of the O/U ratio.

although the temperature dependence of $\Delta G_f^0(UO_3,g)$ for each run is similar with that of the recommend value. This tendency might be caused by the existence of the O(g) vapor species. Based on the thermodynamic consideration, the partial pressure of O(g) is close to that of $O_2(g)$ in cases where the temperature is higher and the partial pressure of $O_2(g)$ is lower. So the partial pressures of $UO_3(g)$ and $O_2(g)$ were recalculated in such a case. When the loss of weight of O(g) is expressed as $\Delta W(O)$ Eq. (6) can be modified by the following equation:

$$\Delta W(O_2) + \Delta W(O) = W_1(sample) - W_2(sample) \\ - \Delta W(UO_3). \quad (19)$$

Since another unknown factor increases, the following reaction is utilized to know $\Delta W(O_2)$, which is required in the calculation of $p(O_2)$:

$$1/2 O_2(g) = O(g).$$
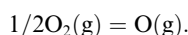
This equilibrium constant, K, can be expressed as the following equation:

$$K = \frac{p_O}{\sqrt{p_{O_2}}}. \quad (20)$$

It should be noted that the unit of the pressure in the above equation is Pa. In this study this equilibrium constant is derived from the values of $\Delta G_f^0(O,g)$ given by Cordfunke and Konings [15]. Based on the kinetic theory of gases, $\Delta W(O)$ can be expressed as the follow equation:

$$\Delta W(O) = \int_0^{t_{end}} p_O(T,t) \cdot s \cdot L \cdot \sqrt{\frac{M(O)}{2\pi \cdot R \cdot T}} dt. \quad (21)$$

According to Eq. (10), $p(O_2)$ can be simplified as the following equation:

$$p_{O_2}(T,t) \cong C \cdot \Delta W(O_2) \cdot I_{O_2}(t) \cdot T, \quad (22)$$

where C is the constant which is independent of temperature T and time t. From Eqs. (19)–(21) $\Delta W(O)$ can be simplified as follows:

$$\Delta W(O) = \int_0^{t_{end}} K(T) \sqrt{p_{O_2}(T,t)} \cdot s \cdot L \cdot \sqrt{\frac{M(O)}{2\pi \cdot R \cdot T}} dt \\ \cong C' \sqrt{\Delta W(O_2)} \int_0^{t_{end}} K(T) \sqrt{I_{O_2}(t)} dt \\ \cong C' \sqrt{\Delta W(O_2)} \left(K(1473) \int_0^{t_i} \sqrt{I_{O_2}(t)} dt \right. \\ \left. + K(T) \int_{t_i}^{t_{end}} \sqrt{I_{O_2}(t)} dt \right), \quad (23)$$

where C' is the constant regardless of temperature T and time t. This equation is substituted into Eq. (18) and $\Delta W(O_2)$ can be evaluated. As for the change of the O/U
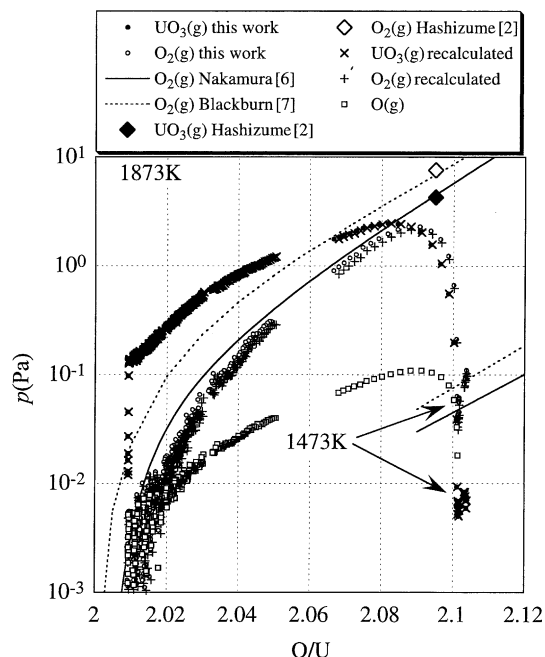

Fig. 8. Vapor pressures of $UO_3(g)$, $O_2(g)$ and $O(g)$ over UO_{2+x} at 1873 K.

ratio of the condensed phase, Eq. (13) is modified by the following equation:

$$z_O(T,t) = \left(\frac{p_O(T,t)}{\sqrt{M(O)}} + 2 \frac{p_{O_2}(T,t)}{\sqrt{M(O_2)}} + 3 \frac{p_{UO_3}(T,t)}{\sqrt{M(UO_3)}} \right) \\ \cdot \frac{s \cdot L \cdot N_A}{\sqrt{2\pi \cdot R \cdot T}}. \quad (24)$$

The recalculated values of $p(UO_3)$, $p(O_2)$ and $p(O)$ at 1873 K in this manner are plotted as function of the O/U ratio in Fig. 8. For comparison this figure also includes the results indicated in Fig. 4(d). As shown in this figure, these two results almost agree each other although the $O_2(g)$ pressures are a little bit lower. Further, the difference of the values of $\Delta G_f^0(UO_3,g)$ derived from these results was found to be less than 1 kJ/mol. Therefore, it was concluded that the existence of the O(g) vapor species negligibly affect the evaluation of $\Delta G_f^0(UO_3,g)$ in this study.

Although the values of $\Delta G_f^0(UO_3,g)$ in this study are lower than expected from their temperature dependences, the values of $\Delta G_f^0(UO_3,g)$ in this study agree with the recommended value within the experimental error. Therefore it is considered that this recommended value is reliable.

4. Summary

In this study the mass-spectrometric measurement of pure $UO_{2+x}(s)$ are carried out at 1473, 1673, 1773 and

1873 K under the condition of the decreasing O/U ratio of the condensed phase with time by Knudsen effusion mass spectrometry. It was found that the partial pressures of $O_2(g)$ over $UO_{2+x}(s)$ obtained in this study almost agreed with the experimental data reported in the past as well as the values derived from the empirical equation given by Nakamura and Fujino. Further, it was found that the values of $\Delta G_f^0(UO_3,g)$ obtained in this study were in good agreement with the recommended values given by Olander. Therefore, it is considered that this recommended value is reliable.

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