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Investigation of vaporization thermodynamics of $SrUO_3$ by means of mass spectrometry

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Abstract

The vaporization properties of $SrUO_3$ have been studied for the first time by means of Knudsen effusion mass spectrometry over a temperature range of 1534 to 1917 K. The sample used was a mixture of $SrUO_3$ and 23 wt% UO_2. The main vapor species over the mixture were Sr(g), UO_2(g) and SrO(g) in decreasing order of their partial pressures. The standard enthalpy of formation of $SrUO_3$ was evaluated by using the second law and the third law treatments, in which estimated values of $H°(T) - H°(298.15)$ and gef(T) were employed on account of absence of published data. The standard enthalpies of the formation of $SrMO_3$ with pseudo-cubic perovskite structure, where M stands for metallic cations with the valence of four, were also discussed based on the relationship between the ionic radii of M^{4+} of the compounds and their enthalpy values. © 1997 Elsevier Science B.V.

1. Introduction

In order to understand thermodynamic behaviors of perovskite compounds ABO_3, where A stands for barium and strontium while B represents uranium, plutonium, zirconium, molybdenum and rare-earth elements, a lot of research works have been done [1–3]. As one kind of likely fission product compounds, their properties are essential to interpret phenomena in high burnup uranium based fuels. For strontium monouranates, early studies on the chemical and thermodynamic properties of the α-$SrUO_4$ phase with a rhombohedral cell as well as that of the β-$SrUO_4$ phase with an orthorhombic cell were made by Cordfunke and Loopstra [4]. They found that $SrUO_{3.3}$ could be produced by reduction of $SrUO_4$. In 1993, Takahashi et al. studied the thermodynamic properties of $SrUO_{4-x}$ $(0 \leq x \leq 0.5)$ by using the solution calorimetric method [5]. However, the data of $SrUO_3$ are still in need. In the present study, the vaporization properties of $SrUO_3$ have been investigated for the first time in a high temperature range of 1534–1917 K by using the Knudsen effusion mass spectrometric method.

2. Experimental

The sample was prepared by means of hydrogen reduction of $SrUO_4$, similar to the preparation of $BaUO_3$ [6]. A mixture of $SrUO_3$ and UO_2 was employed for the mass spectrometric study, since it was not easy to prepare single phase $SrUO_3$. The amount of UO_2 in the mixture was determined as 23 wt% by X-ray powder diffraction analysis. The sample prepared was found to possess an orthorhombic crystal structure with lattice parameters of $a = 0.610794$ nm, $b = 0.859360$ nm and $c = 0.618218$ nm, which were very close to the data given in Ref. [7].

A modified Nuclide 12-90-HT type magnetic focusing 90° sector instrument was used for the research, which had been described previously [8]. A tungsten Knudsen cell

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with an effusion orifice of 0.5 mm in diameter was employed in this measurement. The test material was put in a container cup of platinum, which was then installed inside the Knudsen cell. A Pt/Pt–Rh thermocouple was welded to the bottom of the Knudsen cell to determine the temperature. By using silver as a standard reference material, the vapor pressure and temperature were calibrated. The mixture of $SrUO_3 + UO_2$ stored in argon was loaded into the Knudsen cell and then to the mass spectrometer in the atmosphere of air. During this procedure the sample was exposed to air for about 15–30 min. Before each vapor pressure measurement run, the sample was annealed in vacuum at 500–700°C for 24 h in order to remove the surface contaminants.

After the mass spectrometric measurement, the sample was examined again by means of X-ray diffraction analysis. It was found that the lattice parameters had slightly varied to $a = 0.611177$ nm, $b = 0.850198$ nm and $c = 0.618590$ nm. Although the change in the cell volume was as small as 0.9%, the oxygen content in strontium monouranate was estimated to have changed to $SrUO_{3.1}$ during the mass spectrometric measurement, which was very close to that found in $BaUO_3$ [6].

3. Results

3.1. Ionization efficiency curves

First, the ionization efficiency curves of Sr^+ and SrO^+ were measured. It was found that the appearance potentials of SrO^+ and Sr^+ were about 6.0 and 5.7 eV, respectively, which are close to the literature values [9]. Only simple ionization was found to occur for Sr(g) and SrO(g) up to 30 eV in the impact electron energy. Since no evidence of fragmentation was observed, the impact electron energy was set to 22 eV so as to obtain higher ion intensities.

The ionization cross-sections of molecules were calculated by using the equation: $\sigma_M = 0.75 \Sigma \sigma_A$ [10], where σ_A is the atomic cross-section of each constituent atom given by Mann [11].

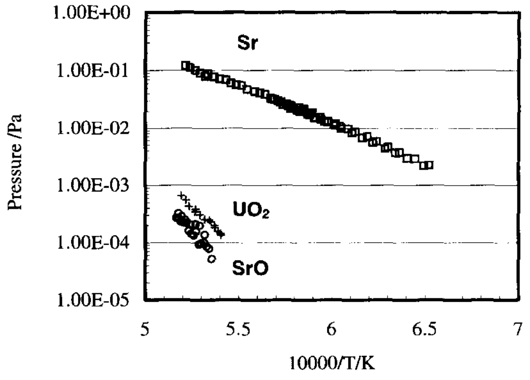

Fig. 1. Partial pressures over $SrUO_3 + UO_2$.

Table 1
Estimation of $H°(T) - H°(298.15)$ and gef(T) of $SrUO_3$

Temp. (K)	$H°(T) - H°(298.15)$ (J/mol)	$-(G°(T) - H°(298.15))/T$ (J/mol K)
1500	164798	245.266
1600	179771	252.437
1700	194832	259.317
1800	209707	265.925
1900	224298	272.266
2000	238629	278.355

3.2. Vaporization characteristics

The main vapor species detected were Sr(g), UO_2(g) and SrO(g) in the decreasing order of vapor pressure. Accordingly, the following reactions were assumed to occur in the Knudsen cell:

$$SrUO_3(s) = Sr(g) + 0.5O_2(g) + UO_2(s), \tag{1}$$

$$Sr(g) + 0.5O_2(g) = SrO(g), \tag{2}$$

$$UO_2(s) = UO_2(g). \tag{3}$$

The absolute partial vapor pressures of the vapor species obtained over the mixture of $SrUO_3 + UO_2$ are plotted in Fig. 1. The temperature dependence equations are expressed as below:

$$\ln P_{Sr}/Pa = 14.08 - 30\,868/T/K, \tag{4}$$

$$\ln P_{UO_2}/Pa = 28.40 - 68\,891/T/K, \tag{5}$$

$$\ln P_{SrO}/Pa = 32.20 - 77\,890/T/K. \tag{6}$$

Therefore, thermodynamic calculation can be made by

Table 2
$\Delta_f H°(298.15)$ of $SrUO_3$ from the 3rd law treatment

No.	Temp. (K)	$\Delta_f H°$ (kJ/mol)	No.	Temp. (K)	$\Delta_f H°$ (kJ/mol)
1	1867.0	−1696.84	12	1897.2	−1693.08
2	1871.7	−1700.87	13	907.3	−1696.29
3	1876.4	−1700.96	14	1910.6	−1701.71
4	1879.6	−1694.50	15	1915.4	−1698.07
5	1881.4	−1700.09	16	1917.3	−1696.59
6	1886.8	−1702.10	17	1921.1	−1699.50
7	1888.9	−1695.75	18	1924.8	−1696.53
8	1891.1	−1697.73	19	1925.9	−1700.44
9	1896.0	−1697.44	20	1932.1	−1696.69
10	1900.9	−1701.36	21	1934.9	−1700.78
11	1905.6	−1702.21	22	1929.8	−1699.71

Average: $\Delta_f H°(298.15) = -1698.6 \pm 2.2$ kJ/mol the second law treatment and the third law treatment shown as the following equations:

By the 2nd law treatment: $\Delta_r H°(T)$

$$= \Delta_r H°(298.15) + \Delta\{H°(T) - H°(298.15)\}, \quad (7)$$

By the 3rd law treatment:

$$\Delta_r H°(298.15) = \Delta_r G°(T) + T\Delta\text{gef}(T). \quad (8)$$

3.3. Thermodynamic evaluation

In order to calculate the standard enthalpy of formation of $SrUO_3$ the enthalpy increment $H°(T) - H°(298.15)$ and the Gibbs energy function gef(T) of $SrUO_3$ are to be known. Unfortunately, however, there were few literature data to be utilized for this purpose so that some values have been estimated as listed in Table 1. Those estimated values were employed to obtain the final results. It was assumed that the difference between the values of $H°(T) - H°(298.15)$ of a complex oxide $SrUO_3$ and the sum of those of the constituent oxides is almost the same as that of $SrZrO_3$. This is because both the complex oxides possess almost the same crystal structure and fairly close melting points (2700 K for $SrUO_3$ and 3023 K for $SrZrO_3$). Our assumption can also be supported by the fact that perovskite compounds, $SrZrO_3$ and $SrCeO_3$, showed very close values of heat capacity as reported by Saha et al. [12]. The same rule was assumed to apply for gef(T), too. So the values of $H°(T) - H°(298.15)$ and gef(T) were calculated as the sum of those of SrO(s) and UO_2(s) plus the difference between that of $SrZrO_3$(s) and the sum of those of SrO(s) and ZrO_2(s), respectively. All the other necessary thermodynamic data of Sr(g), SrO(g), SrO(s), O_2(g), UO_2(s), ZrO_2(s) and $SrZrO_3$(s) were taken from Cordfunke and Konings [13].

From the second law treatment, the value of $\Delta_f H°(298.15)$ of $SrUO_3$ was evaluated as -1785 ± 60 kJ/mol by using the estimated $H°(T) - H°(298.15)$ values of $SrUO_3$. On the other hand, the third law treatment for each data point gave an averaged value of -1698.6 ± 21.9 kJ/mol based on the estimated gef(T) values, such as shown in Table 2. The errors of estimation of $H°(T) - H°(298.15)$ and gef(T) were evaluated to be less than 3%. In this sense, the 5% difference in these two standard enthalpies of formation values obtained from the second law and third law treatments is acceptable.

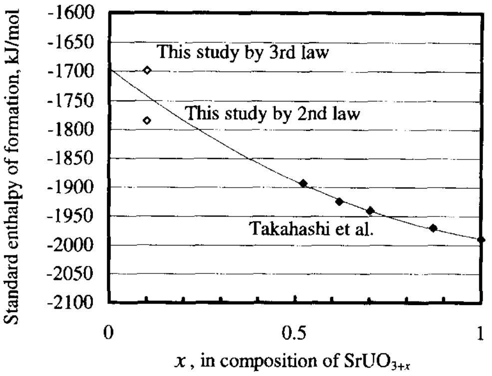

Fig. 2. Standard enthalpies of formation of $SrUO_{3+x}$.

4. Discussion

For comparison, our results were expressed graphically, together with the available data of $\Delta_f H°(298.15)$ of α-$SrUO_{4-y}$ $(0 \leq y \leq 0.5)$ in Ref. [5], in Fig. 2. Thus, for the wider range of x in $SrUO_x$ $(3 \leq x \leq 4)$, a curve-fitting was made by combining those literature data with our results obtained by the 2nd law and 3rd law treatments as follows:

$$\Delta_f H°(SrUO_{3+x}, \text{kJ/mol})$$

$$= -1695.55 - 480.81x + 187.92x^2. \quad (9)$$

Since there exist other $SrMO_3$ type compounds, it is of significance to estimate the standard enthalpies of formation $\Delta_f H°(298.15)$ for them as done for $BaMO_3$ [3,6,14].

Table 3
Comparison of estimated values of $\Delta_f H°(SrMO_3)$

Compounds $SrMO_3$	Experimental $\Delta_f H°(SrMO_3)$ (kJ/mol)	Ionic radii of M^{4+} R (10^{-1} nm) [15]	Estimated from Eq. (8) (kJ/mol)
$SrTiO_3$	−1671 [16]	0.605	−1657
$SrMoO_3$		0.650	−1280
$SrHfO_3$	−1784 [16]	0.71	−1781
$SrZrO_3$	−1767 [16]	0.72	−1765
$SrTbO_3$		0.76	−1618
$SrPrO_3$		0.85	−1562
$SrPuO_3$		0.86	−1666
$SrCeO_3$		0.87	−1696
$SrUO_3$	−1698.6 [a]	0.89	−1684
$SrThO_3$		0.94	−1807

[a] This study by the 3rd law treatment.

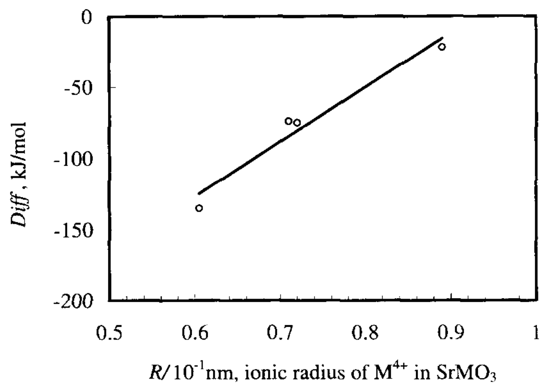

Fig. 3. Relationship between the ionic radius of M^{4+} and Diff.

The crystal structure of $SrMO_3$ was considered as pseudo-cubic perovskite structure although orthorhombic crystal form may be taken in some of the cases. A similar treatment was carried out as we had done for $BaMO_3$ [6]. In other words, the difference between $\Delta_f H°(SrMO_3)$ and $\Delta_f H°(SrO) + \Delta_f H°(MO_2)$ was considered to be related to the radius R of ion M^{4+} as shown in Fig. 3. The following equation expresses this relationship:

$$\begin{aligned}\mathrm{Diff} &= \Delta_f H°(SrMO_3) - \{\Delta_f H°(SrO) + \Delta_f H°(MO_2)\} \\ &= 372.07 \times R - 348.78. \qquad (10)\end{aligned}$$

By using this equation the values of standard enthalpy of formation were estimated and summarized together with some experimental data in Table 3. Although there are relatively few experimental values for $\Delta_f H°(SrMO_3)$ to be used for evaluation, the errors of estimation of this treatment in $SrMO_3$ compounds are expected to be within ± 20 kJ/mol, which is the same with those in $BaMO_3$ series because of the similarity of strontium and barium. An exception would be for the cases of $SrMoO_3$ and $SrPrO_3$ since both of them had relatively large errors brought about by this treatment.

5. Conclusion

The main vapor species over $SrUO_3 + UO_2$ were Sr(g), UO_2(g) and SrO(g) in the decreasing order of vapor pressure. The temperature dependencies of their partial pressures were obtained in the temperature range of 1534–1917 K. The values of standard enthalpy of formation of $SrUO_{3.1}$ as treated by the second law and the third law were -1785 ± 60 and -1698.6 ± 21.9 kJ/mol, respectively. The 5% difference between these two values is acceptable since the error was estimated to be within 3% in the values of either $H°(T) - H°(298.15)$ or gef(T)) of $SrUO_3$. The values obtained from the second law and third law treatment are consistent with the published data of $SrUO_{4-x}$ $(0 \leq x \leq 0.5)$ if the oxygen content x was extrapolated toward the lower value direction. The values of the standard enthalpies of formation of $SrMO_3$ type compounds were also evaluated and compared with one another.

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