Formation and Properties of Strontium Uranates

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The formation and nonstoichiometry of strontium uranates, especially those with the Sr/U atom ratio around unity, were examined by means of thermogravimetry and X-ray diffraction. The reaction of $SrCO_3$ with U_3O_8 in air, where Sr/U=1, produced the stoichiometric β-$SrUO_4$, which had an orthorhombic structure. The reactions in vacuum and in hydrogen yielded the products of the composition $SrUO_{3.563}$ and $SrUO_{3.175}$, respectively. On the other hand, the reduction of β-$SrUO_4$ in vacuum and in hydrogen gave $SrUO_{3.48}$ and $SrUO_{3.65}$, respectively. Stoichiometric $SrUO_3$ was prepared by the reaction of SrO with UO_2. The reduction product of β-$SrUO_4$, $SrUO_{4-x}$, was oxidized in air below 500 °C to α-$SrUO_4$ which was rhombohedral. During the phase transition to β-$SrUO_4$, α-$SrUO_4$ exhibited anomalous behavior; that is, α-$SrUO_4$ was first reduced and then reoxidized to nearly the initial composition with the formation of β-$SrUO_4$. Of the uranates with Sr/U$\neq$1, the formations of SrU_4O_{13}, SrU_2O_7, and Sr_2UO_5 were examined; the single phase SrU_2O_7 was not obtained. Thermograms for their reduction, followed by the oxidation of the resultants, suggest the existence of the compounds SrU_4O_{11} and $SrU_2O_{6.0-6.6}$. No uranates containing only U(IV) were obtained by hydrogen reduction of the uranates containing U(VI) formed in air at high temperatures.

It is widely known that so-called uranates[1] are formed by the reaction of uranium oxides with alkali or alkaline earth oxides, carbonates, nitrates, chlorides, *etc.* There have been many reports concerning the preparation, properties, and crystal structures of these uranates. However, the literature data on their composition and crystal structure often seem to be incomplete or conflicting. Interest in these uranates, which are possibly produced in the reactions of the matrix oxide with the alkali and alkaline earth metals as fission products in nuclear fuel, has given the stimulus to investigate systematically the compound systems.

Strontium uranates can be, according to Keller,[2] classified into the following three groups of compounds: $SrUO_3$,[3,4] Sr_2UO_4(?),[3] and Sr_3UO_5[5,6] in the system SrO–UO_2 containing uranium in tetravalent state; SrU_2O_6[5,7,8] in the system SrO–U_2O_5 containing U(V); and SrU_4O_{13},[6,9] SrU_2O_7(?),[5,6,10] $Sr_2U_3O_{11}$,[6] (α and β) $SrUO_4$,[6,9,11–17] Sr_2UO_5,[4,6,9,16–19] and Sr_3UO_6[3,6,15,20–22] in the system SrO–UO_3 containing U(VI). However, the physical and chemical properties as well as the phase relations of these strontium uranates have not been well investigated. In the present paper, we examine the formation, reactivity, and nonstoichiometry of the uranates; our interst was centered on the compounds with the Sr/U atom ratio around unity as determined by means of thermogravimetry.

Experimental

Materials. Strontium carbonate, $SrCO_3$, uranium dioxide, UO_2, and triuranium octoxide, U_3O_8, were used as starting materials. $SrCO_3$ was prepared by adding strontium nitrate aqueous solution into ammonium carbonate ammoniacal solution, similar to the procedure for producing the precipitated calcium carbonate.[23] U_3O_8 was prepared by heating ammonium diuranate in air at 900 °C for one day. UO_2 was obtained by reducing U_3O_8 at 1000 °C in a stream of hydrogen for 10 h.

Almost all reactions were performed with samples in the form of pressed pellets. The compounds of $SrCO_3$ and UO_2 or U_3O_8 were thoroughly mixed in an agate mortar and compacted at 3 ton/cm² into cylindrical pellets of 10 mm in diameter and of about 2 mm in thickness. The weight of each pellet was usually about 800 mg.

Apparatus and Procedures. The experimental apparatus for thermogravimetry was similar to that described in an earlier paper, where the equilibrium nitrogen pressure was measured in the UN–U_2N_3 system.[24] It consists of a Cahn RH-type automatic electrobalance, a Kanthal resistance furnace, a pressure measurement system, and vacuum pumps. The balance was adjusted so as to have a maximum weight change of 500 mg, and a sensitivity of 0.01 mg. A fused quartz crucible, 20 mm in height and 18 mm in outer diameter, was suspended from the balance, and then a quartz tube of 26 mm in inner diameter was connected to the vessel containing the balance. After being connected, the system was evacuated to 1×10^{-5} mmHg or below.

The temperature of the specimen was measured by means of a Pt/Pt+13%Rh thermocouple placed close to the crucible inside the reaction tube. Most of the experiments were made at the heating rate of 2 °C/min unless otherwise specified.

X-Ray Analysis. The samples were finely ground and loaded into capillaries, and then vacuum-sealed. The X-ray powder photographs were obtained with a Nerelco 114.6 mm camera using the nickel-filtered Cu$K\alpha$ radiation.

Results and Discussion

Reaction of $SrCO_3$ with U_3O_8 (Sr/U=1). Strontium monouranate, $SrUO_4$, is known to be dimorphic: one is rhombohedral[11] and the other is orthorhombic.[13,20] They are conventionally named α- and β-$SrUO_4$ respectively. The reaction of $SrCO_3$ with U_3O_8 in air, where the Sr/U atom ratio is unity, yielded yellow colored β-$SrUO_4$. The equiatomic mixture was heated in air from room temperature to 1100 °C, and then it was kept at 1100 °C for 3 h. A typical thermogravimetric curve is shown in Fig. 1, together with the results obtained in other atmospheres, and also with the decomposition curve of $SrCO_3$. The weight loss of $SrCO_3$ due to decomposition should be 29.1%, but in this figure it was normalized to the $SrCO_3$+1/3U_3O_8 mixture for the sake of convenience, where the value was to be 10.27%. This was attained at 1100 °C. As seen in the figure, the reaction of $SrCO_3$ with U_3O_8 in air began at 470 °C and then it proceeded stepwise. When the thermogravimetric curve of the reaction is compared with the decomposition curve of $SrCO_3$, it may be deduced that the first step is the reaction

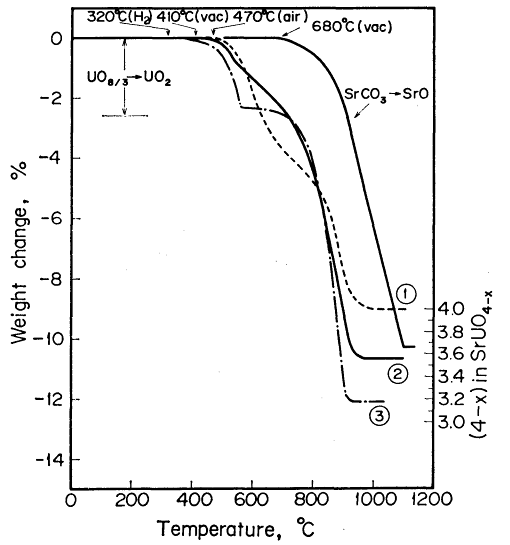

Fig. 1. Thermograms for the reaction of $SrCO_3$ with U_3O_8 in various atmospheres: ① in air; ② in vacuum; ③ in hydrogen; heating rate, 2 °C/min.

of $SrCO_3$ with U_3O_8, and that the second is the reaction of the decomposition product of $SrCO_3$ with U_3O_8. The X-ray pattern of the product was identical with that of the β-$SrUO_4$, which is orthorhombic and isomorphous with $BaUO_4$ with space group Pbcm, $z=4$.[13,17] The composition of the product was $SrUO_{3.997}$. Therefore, the overall weight change consists of weight loss due to the thermal decomposition of $SrCO_3$ plus weight gain due to oxidation in forming the uranate. The average valency of uranium in the compound is seen to increase from +5.33 to +5.99 during the reaction.

In vacuum, the reaction occurred at 410 °C and finished at about 950 °C. The composition of the product was $SrUO_{3.563}$ under the condition that the sample was heated to 1100 °C and then kept at that temperature for 1 h. Because the formal valency of uranium in this compound is +5.13, the U_3O_8 is regarded as losing a part of the combined oxygen. In a strict sense, the oxygen content varies as functions of oxygen pressure, temperature, and holding time; the number of oxygen atoms per formula can be changed in the range between 3.55 and 3.65 at 1100—900 °C in vacuum. According to X-ray analysis, the crystal was rhombohedral with space group $R\bar{3}m$, $z=1$, which is isomorphous with $CaUO_4$.[11] Although the structure of oxygen deficient $SrUO_{4-x}$ is basically the same as that of the α-$SrUO_4$, it has vacant O(II) sites due to nonstoichiometry.[25] The product was dark green.

In a hydrogen atmosphere, the reaction of $SrCO_3$ with U_3O_8 started at 320 °C. The reaction obviously proceeded stepwise, as seen in Fig. 1. The first is the reduction of U_3O_8 to UO_2 in the reaction mixture, because the same curve is obtained when U_3O_8 is reduced to UO_2 in hydrogen. The second step proceeds at temperatures above 700 °C, and probably corresponds to the reaction of $SrCO_3$ with UO_2. The overall composition of the product heated to 1000 °C was $SrUO_{3.175}$. The product was dark gray. No stoichiometric $SrUO_3$

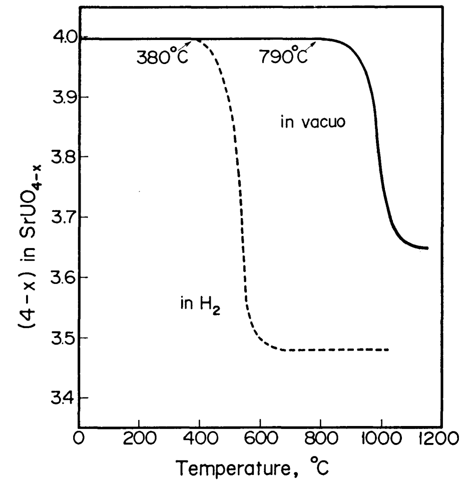

Fig. 2. Thermograms for reduction of β-$SrUO_4$ in vacuum and in hydrogen atmosphere: heating rate, 2 °C/min.

was obtained by the reaction under the following conditions: maximum temperature, 1000 °C; holding time at 1000 °C, 1 h; atmosphere, hydrogen; and heating rate, 2 °C/min. The bulk composition of the products obtained under the conditions was $SrUO_{3.18-3.20}$.

The products, obtained by the reactions in vacuum or in hydrogen, gradually took up oxygen into the crystal even at room temperature when exposed to air, and the color changed from dark green or dark gray to red over 3 months. According to X-ray analysis, the red product was rhombohedral with nearly the same lattice parameters as those of the stoichiometric α-$SrUO_4$.[26]

Reaction of $SrCO_3$ with UO_2 ($Sr/U=1$). Behavior of the reaction in a vacuum was similar to that of the second step of the reaction of $SrCO_3$ with U_3O_8 in a hydrogen atmosphere. The reaction began at about 580 °C and finished at 950 °C. The composition of the product heated to 1100 °C was $SrUO_{3.21}$; the stoichiometric $SrUO_3$ was not obtained.

Reduction of β-$SrUO_4$. Thermograms of β-$SrUO_4$ heated in vacuum and in a hydrogen atmosphere are in Fig. 2. When the reaction was performed in a vacuum of 10^{-6} mmHg, the dissociation began at 790 °C and continued at a slow rate even at 1100 °C. The composition of the product kept at 1100 °C for 3 h was $SrUO_{3.65}$; its oxygen amount was slightly larger than that obtained by the reaction of $SrCO_3$ and U_3O_8 in vacuum, *i.e.* $SrUO_{3.56}$. As already mentioned, the oxygen content of the product is not only a function of temperature and of oxygen pressure, but tends to decrease with time at temperatures as high as 1100 °C. If the sample is heated for a longer time, the oxygen content must be smaller than that in $SrUO_{3.65}$. The equilibrium oxygen pressure over $SrUO_{4-x}$ at the given temperatures has not been measured.

The reduction in hydrogen began at 380 °C and finished at about 650 °C. The composition of the product heated to 1000 °C and kept at that temperature for 1 h was $SrUO_{3.48}$. Its oxygen content was much larger than that obtained by the reaction of $SrCO_3$ with U_3O_8 in hydrogen, *i.e.* $SrUO_{3.18}$. It was very dif-

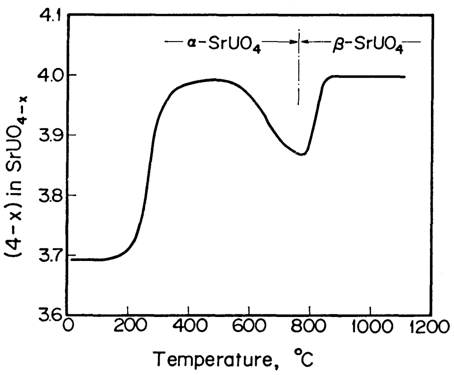

Fig. 3. Thermogram for oxidation of α-$SrUO_{4-x}$ in air: sample weight, 0.86476 g; heating rate, 2 °C/min.

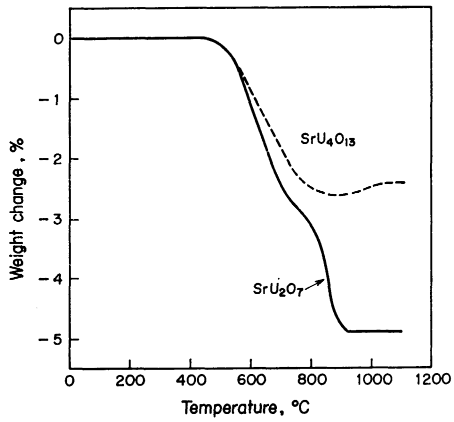

Fig. 4. Thermograms for formation of SrU_4O_{13} and SrU_2O_7 by the reaction of $SrCO_3$ with U_3O_8 in air at a heating rate of 2 °C/min.

ficult to get a lower oxygen content than that for $SrUO_{3.48}$, even if β-$SrUO_4$ was heated in a hydrogen atmosphere at 1000 °C for more than 3 h.

Preparation of $SrUO_3$. As already mentioned, the attempts to prepare $SrUO_3$ in a hydrogen atmosphere at temperatures below 1000 °C by the reaction of $SrCO_3$ with U_3O_8 and by the reduction of $SrUO_4$ were unsuccessful. Thus, as a next step, an equimolar mixture of SrO and UO_2 was heated in a vacuum at 1100 °C for 3 h. The product had the composition $SrUO_{3.04}$ and was yellowish-brown. When the compound was heated in air at a rate of 2 °C/min, it ignited at about 60 °C and changed into yellow β-$SrUO_4$, passing through a red-heated state for a short time of about 10 min.

In another experiment, an equimolar mixture of SrO and UO_2 was heated in a vacuum at 1650 °C for 5 h by using a tantalum-resistor high temperature vacuum furnace. For comparison, in one further experiment β-$SrUO_4$ was reduced in a hydrogen stream at 1500 °C for 3 h by using a high frequency-induced furnace. Both the products had the composition $SrUO_3$ and their X-ray diffraction lines were in the same pattern. However, these patterns were not consistent with the reported data, which have been assigned to the orthorhombic perovskite structure.[2] The structure analysis of $SrUO_{3.00}$ by X-ray and neutron diffraction will be reported elsewhere.

Oxidation of α-$SrUO_{4-x}$. The nonstoichiometric $SrUO_{4-x}$, which was prepared by the reaction of $SrCO_3$ with U_3O_8 or by the reduction of $SrUO_4$ in a vacuum or in hydrogen, had the rhombohedral structure. Here this uranate is designated as α-$SrUO_{4-x}$. Although the compound is oxidized at a very slow rate in air even at room temperature, the oxidation is accelerated by heating. Figure 3 shows a thermogram for the oxidation of α-$SrUO_{4-x}$ in air, where the initial composition of the sample is $SrUO_{3.688}$. As seen in Fig. 3, the α-$SrUO_{3.688}$ began to be oxidized at about 150 °C, and attained to its maximum oxygen content, $SrUO_{3.991}$, around 500 °C. This oxidation process is not reversible. Above 500 °C the compound with the composition $SrUO_{3.991}$ began to lose its oxygen. The weight loss continued till 770 °C, at which the minimum oxygen content, $SrUO_{3.867}$, was observed. The compound was still in the α phase region, and if it was cooled from 770 °C, the oxygen content again increased on the same line with that of the heating process up to the maximum point at 500 °C, and the oxygen content remained unchanged on further cooling of the temperature. On the other hand, if the sample was heated above the temperature giving the minimum oxygen content, the α phase transformed into the β phase, along with oxidation. The transition was finished at 870 °C. The product was a mixture of α-$SrUO_4$ and β-$SrUO_4$ at temperatures between 770 and 870 °C. The oxidation process in this region was not reversible.

The temperature and the composition at the minimum point varied with oxygen pressure and heating rate. When α-$SrUO_{4-x}$ was heated in oxygen at different pressures, the composition and the transition temperature were as follows: $SrUO_{3.867}$ at 770 °C in air (160 mmHg O_2), $SrUO_{3.839}$ at 790 °C in 50 mmHg O_2, and $SrUO_{3.805}$ at 800 °C in 10 mmHg O_2.[26] When the heating rate of the sample was varied from 2 to 5 °C/min, the composition at the minimum point in air was changed from $SrUO_{3.867}$ at 770 °C to $SrUO_{3.838}$ at 800 °C.

The weight loss of α-$SrUO_4$ at temperatures from 500 to 770 °C in air is due to oxygen nonstoichiometry, because the weight loss is enhanced with temperature and also with decreasing oxygen pressure. Therefore, the minimum point of oxygen content in Fig. 3 seems to have resulted from the competitive reactions between the weight loss due to the reduction of the α-$SrUO_4$ and the weight gain due to the formation of the β-$SrUO_4$.

Formation of Strontium Uranates with $Sr/U<1$. Strontium uranates SrU_4O_{13} and SrU_2O_7 were prepared by the reactions between $SrCO_3$ and U_3O_8 in air. Figure 4 shows thermograms for the formation of these compounds. The shape of the curves for the formation of SrU_4O_{13} is different from that for SrU_2O_7. In the case of SrU_4O_{13}, the minimum oxygen content appeared at about 900 °C. The shape of the curve and the initiation temperature of the reaction for SrU_2O_7 were similar to those obtained by the reaction of the equiatomic mixture of $SrCO_3$ and U_3O_8. The reactions proceeded stepwise. The compositions of the products were $SrU_4O_{12.741}$ for Sr : U=1 : 4 and $SrU_2O_{6.933}$ for Sr : U=1 : 2. They were not in the stoichiometric compositions.

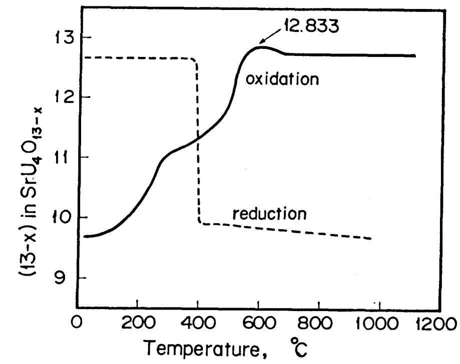

Fig. 5. Thermograms for reduction of SrU_4O_{13} in hydrogen and for oxidation of the resultant uranate in air at a heating rate of 2 °C/min.

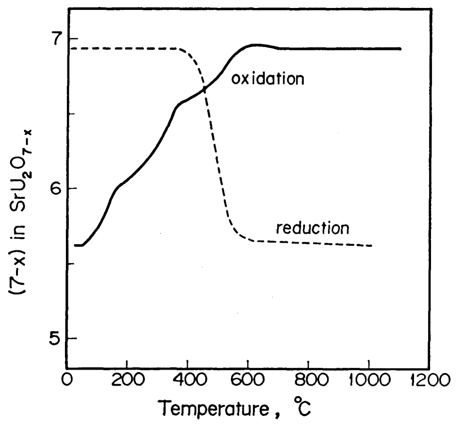

Fig. 6. Thermograms for reduction of SrU_2O_7 in hydrogen and for oxidation of the resultant uranate in air at a heating rate of 2 °C/min.

The SrU_4O_{13} obtained here was reduced in a hydrogen atmosphere by heating from room temperature to 1000 °C. The result is shown in Fig. 5. As seen in the figure, the composition was changed from $SrU_4O_{12.741}$ to $SrU_4O_{9.658}$ by reduction. The latter was found to be a mixture of UO_2 and α-$SrUO_{4-x}$. When the resultant product was oxidized in air to 1100 °C, the thermogram showed a bend near the composition SrU_4O_{11}. The existence of the compound SrU_4O_{11} has not been reported so far, and we did not examine further whether there was a compound or not at this composition. The compound SrU_4O_{13} has been prepared by using the reaction of $Sr(NO_3)_2$ with U_3O_8.[6] Cordfunke and Loopstra[6] have pointed out that it shows nonstoichiometry; $SrU_4O_{12.8}$. Our results were in good agreement with theirs.

Figure 6 shows thermograms of the reduction of the compound with Sr : U=1 : 2, followed by the oxidation of the product obtained in the reduction process. The compound obtained in air showed a nearly stoichiometric bulk composition $SrU_2O_{6.933}$, but it was seen not to be a single phase compound from the X-ray pattern, as Cordfunke and Loopstra[6] stated. When heated in a hydrogen atmosphere, it was reduced to $SrU_2O_{5.572}$. Next, the resultant product was oxidized by heating in air. As shown in the thermogram in Fig. 6, the curve bends near the compositions of $SrU_2O_{6.0}$ and $SrU_2O_{6.6}$.

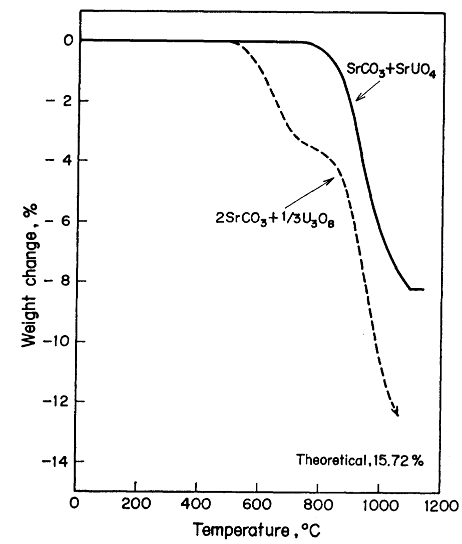

Fig. 7. Thermograms for formation of Sr_2UO_5 by the reaction of $SrCO_3$ with U_3O_8 and by the reaction of $SrCO_3$ with $SrUO_4$ in air at a heating rate of 2 °C/min.

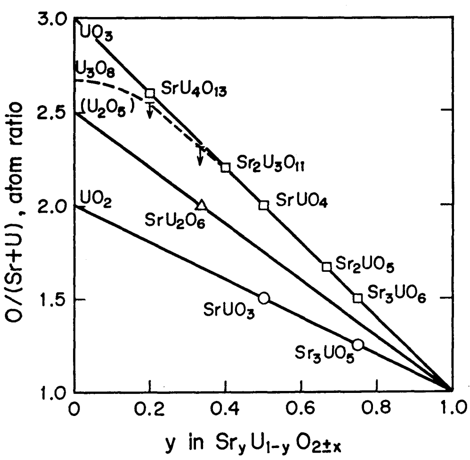

Fig. 8. Summary for compounds in the system Sr–U–O.

According to Hoekstra and Katz,[5] there exists a nonstoichiometric compound $SrU_2O_{6\pm x}$ with CaF_2-type f.c.c. structure. The anomalies in our curve may be interpreted to correlate with the lower and the upper limits of this nonstoichiometric $SrU_2O_{6\pm x}$.

Formation of Sr_2UO_5. For preparing the compound Sr_2UO_5, the reaction of $SrCO_3$ with U_3O_8 was first examined. A thermogram for this reaction is shown in Fig. 7. The shape of the curve was similar to that observed in the formation reaction of the other uranates mentioned above, for example $SrUO_4$. The theoretical weight loss of this reaction was 15.72%, but the reaction did not finish when the sample was heated to 1060 °C and kept at that temperature for 3 h. Next, the reaction of $SrCO_3$ with $SrUO_4$ was studied as a way to obtain Sr_2UO_5. Its thermogram is also shown in Fig. 7. The reaction started at about 750 °C and finished at 1100 °C. The product was the stoichiometric Sr_2UO_5, which was pale yellow. To prepare Sr_3UO_6, a mixture of $SrCO_3$ with $SrUO_4$ was heated under the same conditions as in the formation of Sr_2UO_5, but the reaction did not terminate. It seems that the chemical reactivity in the formation reaction of the uranates tends to be lowered as the content of strontium increases.

Reduction of Sr_2UO_5 by hydrogen at 1000 °C did not yield Sr_2UO_4, but the product with the composition of $Sr_2UO_{4.618}$. When heated in air, the reduction product was again oxidized in a manner similar to the case where the α-$SrUO_{4-x}$ was oxidized in air. From the curve, it could not be distinguished whether the reduction product is a new compound or a mixture containing α-$SrUO_{4-x}$.

Summary for Strontium Uranates. All of the strontium uranates are shown in Fig. 8. In the system SrO–UO_3, five uranates are known. The valence state of uranium in the uranates formed in air is nearly or exactly +6. This value is higher than +5.33 of uranium in U_3O_8, which is the most stable compound in the uranium–oxygen system in air. However, the compound SrU_4O_{13} is not stoichiometric, the valence state of uranium being +5.87. The dashed line in Fig. 8 shows the bulk composition when a mixture of $SrCO_3$ and U_3O_8 is heated in air. In the system SrO–U_2O_5, there is only one compound SrU_2O_6 which shows a rather wide range of oxygen nonstoichiometry. Although it was reported that the uranate has the homogeneity range between 5.95 and 6.4 in the number of oxygen atoms per formula,[5] there is another report in which the SrU_2O_6 is described to be a mixture of CaF_2-type f.c.c. uranate, $Sr_yU_{1-y}O_{2\pm x}$, and a solid solution containing β-$SrUO_4$.[10] Our results show that the nonstoichiometry range is 6.0 to 6.6 in air. In the system SrO–UO_2, two uranates are known. When reduced in hydrogen at 1000 °C, U_3O_8 is readily converted into the stoichiometric UO_2. However, strontium uranates containing U(VI) are not reduced to the uranates containing U(IV) under the same condition; *i.e.* $SrU_4O_{9.69}$ for SrU_4O_{13}, $SrU_2O_{5.57}$ for SrU_2O_7, and $SrUO_{3.48}$ for $SrUO_4$. In addition to this, when exposed to air at room temperature, these uranates, which are prepared by vacuum or hydrogen reduction, are gradually oxidized by accommodating oxygen into the crystal, whereas UO_2 is scarcely oxidized. The uranates containing U(IV) can be produced only by the reactions of SrO with UO_2.

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