THE Cs-U-O PHASE DIAGRAM AND ITS APPLICATION TO URANIUM-PLUTONIUM OXIDE FAST REACTOR FUEL PINS

by

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TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>1</td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. CESIUM-URANIUM-OXYGEN PH. SE DIAGRAM</td>
<td>6</td>
</tr>
<tr>
<td>A. Estimation of Thermodynamic Properties of Cesium Uranates</td>
<td>6</td>
</tr>
<tr>
<td>B. Experimental Studies of the Reaction of Cesium with UO_{2+x}</td>
<td>8</td>
</tr>
<tr>
<td>C. Calculation of Phase Equilibria</td>
<td>14</td>
</tr>
<tr>
<td>D. Accuracy of Calculated Phase Equilibria</td>
<td>20</td>
</tr>
<tr>
<td>III. APPLICATION TO URANIUM-PLUTONIUM OXIDE FUEL PINS</td>
<td>22</td>
</tr>
<tr>
<td>IV. SUMMARY AND CONCLUSIONS</td>
<td>23</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>23</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>24</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

<table>
<thead>
<tr>
<th>No.</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Graphical Method of Estimation of Free Energies and Enthalpies of Formation of Cesium Uranates</td>
<td>7</td>
</tr>
<tr>
<td>2.</td>
<td>Selected Portions of the Cesium-Uranium-Oxygen Phase Diagram Showing Tie Lines to UO$_{2+X}$; Isothermal Sections from 873 to 1273 K</td>
<td>15</td>
</tr>
<tr>
<td>3.</td>
<td>Selected Portions of the Cesium-Uranium-Oxygen Phase Diagram; Isothermal Sections from 873 to 1273 K</td>
<td>16</td>
</tr>
<tr>
<td>4.</td>
<td>Cesium Equilibrium Pressure over Two-Phase Regions in Cs-U-O Phase Diagram</td>
<td>18</td>
</tr>
</tbody>
</table>

LIST OF TABLES

<table>
<thead>
<tr>
<th>No.</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Literature Information on the Cesium-Uranium Oxygen System</td>
<td>3</td>
</tr>
<tr>
<td>2.</td>
<td>Thermodynamic Properties of Cesium Uranates</td>
<td>8</td>
</tr>
<tr>
<td>3.</td>
<td>Summary of Experimental Results for Reaction of Cesium with Uranium Oxide</td>
<td>10</td>
</tr>
<tr>
<td>4.</td>
<td>X-Ray Data for Several Cesium Uranates</td>
<td>11</td>
</tr>
<tr>
<td>5.</td>
<td>Complete X-ray Diffraction Data for Experiment 5</td>
<td>13</td>
</tr>
<tr>
<td>6.</td>
<td>Calculated Oxygen Potentials and Cesium Pressures at Selected Temperatures in Three-Phase Regions of the Cs-U-O Phase Diagram</td>
<td>20</td>
</tr>
</tbody>
</table>
ABSTRACT

Portions of the cesium-uranium-oxygen system have been investigated between 873 and 1273 K and a phase diagram has been constructed using our data and the data of other workers in the field. Thermodynamic and kinetic data have been used to examine the reactions that occur in fast-reactor fuel pins between fission-product cesium and the uranium oxide blanket. It was concluded that at the low oxygen potentials existing at the interface between the uranium-plutonium mixed-oxide and the uranium oxide blanket, $\text{Cs}_2\text{UO}_4$ is the only Cs-U-O compound expected to be formed in the uranium oxide blanket.

I. INTRODUCTION

In uranium-plutonium mixed-oxide fast-reactor fuel pins, fission-product cesium has been observed to migrate axially, and high localized concentrations have been observed at the interface of the mixed-oxide fuel and the uranium oxide axial blanket.$^{1-13}$ These high concentrations of cesium have been associated with a "two-phase" region, which presumably is uranium oxide and a (mixture of) ternary Cs-U-O compound(s).$^4,5,8,10,13$ Moreover, cladding deformation$^1,12,13$ and cladding breach$^7,8,10$ adjacent to the fuel-blanket interface have been observed; these conditions of deformation and breaching could be explained by the formation of a low-density Cs-U-O compound. Gas-flow restrictions in prototypical gas-cooled fast-reactor fuel pins,$^{14}$ which can deleteriously affect the pressure equalization system of the fuel pin,$^{15,16}$ have also been attributed to the formation of a Cs-U-O compound. With the formation of a low-density Cs-U-O compound, an increase in volume occurs, the extent of which will depend on the composition of the compound because there are large differences in the molar volumes of Cs-U-O compounds: 86, 130, and 213 cm$^3$ for $\text{Cs}_2\text{UO}_4$,$^{17}$ $\text{Cs}_2\text{U}_2\text{O}_7$,$^{17}$ and $\text{Cs}_3\text{U}_4\text{O}_{12}$,$^{18}$ respectively. (In comparison, the molar volume of $\text{UO}_2$ is 24.6 cm$^3$.$^{18}$) The Cs-U-O compound or compounds present at the interface between fuel and blanket have not been determined in irradiated mixed-oxide fuel pins, and a literature survey of phase equilibria in the Cs-U-O system yielded incomplete and even conflicting data as to the cesium uranate(s) that might be expected to form. Therefore, phase studies of the Cs-U-O system were undertaken in the areas in which published data are in conflict in an effort to establish a consistent phase diagram for the Cs-U-O system and to define the composition of the cesium uranate(s) formed at the fuel-blanket interface in irradiated mixed-oxide fuel. Thermodynamic and analytical data derived at ANL, as well as literature data, were used in the construction of the diagram.
In uranium oxide-blanketed mixed-oxide fuel, two factors important to the formation of cesium uranate(s) at the fuel-blanket interface are temperature and oxygen potential. These factors are sufficiently well known to allow the results of out-of-pile experiments to be related with some degree of confidence to in-pile fuel behavior. Studies at ANL have indicated that the oxygen potential depends on the deviation from stoichiometry of uranium oxide (x in UO_{2+x}), as well as on temperature, which, near the fuel-blanket interface, ranges upward from 873 K. The stoichiometry of the blanket pellets may vary from stoichiometric uranium dioxide to UO_{2.01} or higher, depending on the extent of oxidation of the initially stoichiometric pellets during storage prior to loading the fuel pin. Stoichiometric uranium dioxide has an O/U atom ratio of exactly two and an oxygen potential of -640 kJ/mol at 873 K and -248 kJ/mol at 1273 K. The cesium pressure (or activity) at the fuel-blanket interface has not been experimentally determined. Consequently, out-of-pile experiments relevant to the formation of a Cs-U-O phase in the uranium oxide blanket of irradiated uranium-plutonium mixed-oxide fuel pins must include temperatures of 873 K and higher, oxygen potentials more negative than -210 kJ/mol, and cesium pressures (activities) up to and including that of liquid cesium.

Table 1 is a condensation of information on the Cs-U-O system found in the literature. The following are highlights from the table. (1) Efremova et al., Cordfunke et al., and van Egmond heated mixtures of Cs_2CO_3 and UO_3 in air and obtained compounds whose compositions varied from Cs_2UO_4 to Cs_2U_1_5O_4_6. However, none of the Cs-U-O compounds formed had a uranium valence of five, and only three compounds, Cs_2U_0_1_2, Cs_2U_6O_1_8 and Cs_2U_9O_2_7, had a net uranium valence of less than 6. (2) The compounds obtained by these three groups of researchers and by Spitzyn et al. were found to decompose to Cs_2U_0_1_2 when heated in air at temperatures above 1173 K. (3) At oxygen pressures less than 10^{-5} Pa, Cordfunke reported that only the Cs_2U_0_1_2-UO_2 phase region was stable above 873 K (and concluded that Cs_2U_0_1_2 was the compound of interest in mixed-oxide fuel rods). (4) Venker, Aitken, Adamson, and Aubert found that the hexavalent cesium uranates, Cs_2UO_4 or Cs_2U_2O_7, were stable at temperatures above 873 K in equilibrium with gaseous cesium and urania, in contrast to Cordfunke’s findings. (5) Efremova et al., van Egmond, and Rudorff et al. reported that pentavalent uranates, Cs_1.3UO_3 or Cs_0.5+2UO_3 (x = 0-0.5), exist in equilibrium with liquid cesium and UO_2.40. This is in conflict with the findings of Efremova et al., Cordfunke et al., van Egmond, and Rudorff et al. who found no pentavalent cesium uranate, CsUO_3, even though such compounds as NaUO_3, KUO_3, and RbUO_3 have been reported.

Efremova et al. reported that after heat treatment at 873 K in air of various mixtures of Cs_2CO_3 and UO_3, the ternary compounds Cs_2U_0_4, Cs_2U_2O_7, Cs_2U_6O_1_0, Cs_2U_9O_1_3, and Cs_2U_9O_1_9 were identified by X-ray diffraction analysis. A cesium analog of ternary uranium(V) oxides such as NaUO_3 or Na_3UO_4 was not reported. After heating various mixtures of Cs_2CO_3 and UO_3 in air at 873 K, Cordfunke et al. and van Egmond identified distinct X-ray patterns for Cs_2UO_4, α- and β-Cs_2U_2O_7, Cs_4U_5O_1_7, α-, β- and γ-Cs_2U_9O_1_2, Cs_2U_0_1_3, Cs_2U_0_1_5, Cs_2U_6O_1_8, Cs_2U_7O_2_2, Cs_2U_9O_2_7, and Cs_2U_1_5O_4_6. Of these, Cs_2U_0_1_2, Cs_2U_6O_1_8, and Cs_2U_9O_2_7 have a net uranium valence less than 6+. The compound CsUO_3 was not observed; under similar conditions, KUO_3 and RbUO_3 were observed. Cordfunke et al. presented their observation in the form of a pseudo-binary phase diagram at P_0_2 = 2 x 10^4 Pa over the temperature range 300-1500 K.
<table>
<thead>
<tr>
<th>Reactant(s)</th>
<th>Products</th>
<th>Experimental Conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cs}_2\text{CO}_3 + \text{UO}_3$</td>
<td>$\text{Cs}_2\text{U}_2\text{O}_7$, $\text{Cs}_2\text{U}<em>3\text{O}</em>{10}$, $\text{Cs}_2\text{U}<em>4\text{O}</em>{13}$, $\text{Cs}_2\text{U}<em>6\text{O}</em>{19}$</td>
<td>heated in air at 873 K</td>
<td>Efremova et al. (Ref. 22)</td>
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<tr>
<td>$\text{Cs}_2\text{CO}_3 + \text{UO}_3$</td>
<td>$\text{Cs}_2\text{U}_2\text{O}_7$ (α and β), $\text{Cs}_4\text{U}<em>5\text{O}</em>{17}$, $\text{Cs}_2\text{U}<em>4\text{O}</em>{12}$ (α, β, and γ), $\text{Cs}_2\text{U}<em>6\text{O}</em>{13}$, $\text{Cs}_2\text{U}<em>5\text{O}</em>{16}$, $\text{Cs}_2\text{U}<em>6\text{O}</em>{18}$, $\text{Cs}_2\text{U}<em>7\text{O}</em>{22}$, $\text{Cs}<em>2\text{U}<em>9\text{O}</em>{27}$, $\text{Cs}<em>2\text{U}</em>{15}\text{O}</em>{46}$</td>
<td>heated in air at 873 K</td>
<td>Cordfunke et al. (Ref. 17) and van Egmond (Refs. 18, 29-31)</td>
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<td>$\text{Cs}_2\text{UO}_4$, $\text{Cs}_2\text{U}_2\text{O}_7$</td>
<td>$\text{Cs}_2\text{U}<em>4\text{O}</em>{12}$</td>
<td>heated in air, $T &gt; 1323$ K</td>
<td>Cordfunke et al. (Ref. 17)</td>
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<td>$\text{Cs}_2\text{UO}_4$, $\text{Cs}_2\text{U}_2\text{O}_7$</td>
<td>$\text{Cs}_2\text{U}<em>4\text{O}</em>{12}$</td>
<td>heated in air, $T &gt; 1273$ K</td>
<td>Spitzyn et al. (Ref. 26, 27)</td>
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<td>$\text{Cs}_2\text{U}_2\text{O}_7$</td>
<td>$\text{Cs}_2\text{U}<em>4\text{O}</em>{12}$</td>
<td>heated in air for 6 hr at 1473 K</td>
<td>Spitzyn et al. (Ref. 27)</td>
</tr>
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<td>$\text{Cs}_2\text{U}_2\text{O}_7$</td>
<td>$\text{Cs}_2\text{U}<em>4\text{O}</em>{12}$</td>
<td>heated in air for 6 hr at 1273 K</td>
<td>Spitzyn et al. (Ref. 27)</td>
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<tr>
<td>$\text{Cs}_2\text{U}_2\text{O}_7$</td>
<td>$\text{Cs}_2\text{U}<em>4\text{O}</em>{12}$</td>
<td>$P_{\text{O}_2} &lt; 10^{-5}$ Pa $T &gt; 873$ K</td>
<td>Cordfunke (Ref. 33)</td>
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<td>$\text{Cs}_2\text{UO}_4$, $\text{Cs}_2\text{U}_2\text{O}_7$</td>
<td>$\text{Cs}_2\text{U}<em>4\text{O}</em>{12}$</td>
<td>$P_{\text{O}_2} &lt; 10^{-5}$ Pa $T &gt; 873$ K</td>
<td>Cordfunke (Ref. 33)</td>
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<tr>
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<td>$\text{Cs}_2\text{UO}_4$ or $\text{Cs}_2\text{U}_2\text{O}_7$</td>
<td>heated for 340 hr at 973 K in stainless steel capsule</td>
<td>Venker et al. (Ref. 34)</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Reactant(s)</th>
<th>Products</th>
<th>Experimental Conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs(g) + UO$_2$.00 (±0.05)</td>
<td>Cs$_2$UO$_4$ + stoichiometric urania</td>
<td>1023 K (in Mo capsule for 100 hr in a thermal gradient)</td>
<td>Aitken et al. (Ref. 37)</td>
</tr>
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<td>Cs(g)$^b$ + UO$_3$</td>
<td>Cs$_2$UO$_4$ + stoichiometric urania</td>
<td>heated in Mo capsule for 100 hr at 1123 K</td>
<td>Adamson et al. (Ref. 37,38)</td>
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<tr>
<td>Cs$_2$O + UO$_2$</td>
<td>Cs$_2$U$_2$O$_7$ (2 experiments)</td>
<td>heated in stainless steel capsule for:</td>
<td>Aubert et al. (Ref. 36)</td>
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<td>a) 1500 hr at 1073 K</td>
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<td></td>
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<td>b) 1000 hr at 1273 K</td>
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<tr>
<td>Cs$_2$O + UO$_2$.05</td>
<td>Cs$_2$U$_2$O$_7$ (4 experiments)</td>
<td>heated in stainless steel capsule for:</td>
<td>Aubert et al. (Ref. 36)</td>
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<td>a) 2000 hr at 973 K</td>
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<td>b) 1500 hr at 1073 K</td>
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<td>c) 1000 hr at 1173 K</td>
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<td>d) 1000 hr at 1273 K</td>
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<td>U$_3$O$_8$ + Cs$_x$O$_y$ + Cs(t)</td>
<td>Cs$_{1.3}$UO$_3$ [in equilibrium with UO$_2$.00 + Cs(t)]</td>
<td>heated in Ni capsule for 100 hr at 1073 K</td>
<td>Aitken et al. (Refs. 37, 39)</td>
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<td>(x = 2.5 ± 0.5)</td>
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<tr>
<td>Cs(t) + Cs$_2$UO$_4$</td>
<td>Cs$_{1.3}$UO$_3$ + Cs(t)</td>
<td>heated in Ni capsule for 113 hr at 1000 K</td>
<td>Aitken et al. (Ref. 37,39)</td>
</tr>
<tr>
<td>Cs(t) + Cs$_2$UO$_4$ + UO$_2$.00</td>
<td>Cs$_{0.5}$ + xUO$_3$ + Cs(t) + UO$_2$.00 (x = 0 - 0.5)</td>
<td>emf cell at 873 K</td>
<td>Adamson et al. (Ref. 41)</td>
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</tbody>
</table>

$^a$Cesium pressure = 1.35 x 10$^5$ Pa.

$^b$Cesium pressure = 2.5 x 10$^3$ Pa.
At temperatures above 1323 K, Cordfunke et al.\textsuperscript{17} reported that Cs\textsubscript{2}UO\textsubscript{4} is the only stable cesium uranate formed in air. Rudorff et al.\textsuperscript{24,25} confirmed that CsUO\textsubscript{3} does not form in the Cs-U-O system when Cs\textsubscript{2}UO\textsubscript{4} and UO\textsubscript{2} are heated at temperatures above 873 K in a sealed quartz tube. Under similar conditions, ternary uranium oxides with the composition MUO\textsubscript{3} (where M = Li, Na, K, and Rb) were formed from the reaction of M\textsubscript{2}UO\textsubscript{4} with UO\textsubscript{2}.\textsuperscript{24,25}

Spitzyn et al.\textsuperscript{26,27} reported that Cs\textsubscript{2}UO\textsubscript{4} was stable when heated in air for up to 6 hr at 1173 K, but that it decomposed into a different Cs-U-O phase when heated in air at 1273 K or higher temperatures for 6 hr.\textsuperscript{26} The same Cs-U-O decomposition product was observed by X-ray diffraction when several other cesium uranates were heated in air for 6 hr at different temperatures: Cs\textsubscript{2}U\textsubscript{2}O\textsubscript{7} heated at 1173 K; Cs\textsubscript{2}U\textsubscript{3}O\textsubscript{10}, at 1273 K; Cs\textsubscript{2}U\textsubscript{4}O\textsubscript{13}, at 1273 K; and Cs\textsubscript{2}U\textsubscript{6}O\textsubscript{19}, at 1273 K. Aitken et al.\textsuperscript{36} and Cordfunke et al.\textsuperscript{17} identified this decomposition product as being Cs\textsubscript{2}UO\textsubscript{12} (with a net uranium valence of less than 6+) however, the two groups reported different X-ray patterns for the compound.

Cordfunke\textsuperscript{33} reported that at oxygen pressures less than 10\textsuperscript{-5} Pa, only the Cs\textsubscript{3}U\textsubscript{4}O\textsubscript{12}-UO\textsubscript{2} phase region was stable above 873 K. All cesium uranates reported by Cordfunke et al.\textsuperscript{17} and van Egmond\textsuperscript{18,28-31} decomposed to Cs\textsubscript{2}UO\textsubscript{4} + UO\textsubscript{2} after one week at temperatures above 873 K. Cordfunke concluded that Cs\textsubscript{2}UO\textsubscript{4} was the compound of interest in mixed-oxide fuel rods.

Hexavalent cesium uranates have been reported at temperatures above 873 K and low oxygen potentials. In a 340-hr simulation study at 973 K and using a stainless steel capsule, Venker et al.\textsuperscript{34} identified Cs\textsubscript{2}UO\textsubscript{4} or Cs\textsubscript{2}U\textsubscript{2}O\textsubscript{7} by X-ray diffraction analysis as the product of the reaction of gaseous cesium (1.3 x 10\textsuperscript{5} Pa) with UO\textsubscript{2}.\textsuperscript{1} The oxygen potential\textsuperscript{26} of UO\textsubscript{2}.\textsuperscript{1} at 973 K is -215 kJ/mol. The oxygen potential in the stainless steel capsule was probably somewhat more negative due to reaction of oxygen (from UO\textsubscript{2}.\textsuperscript{1}) with the reaction vessel.\textsuperscript{35} Aitken et al.\textsuperscript{37} identified Cs\textsubscript{2}UO\textsubscript{4} and stoichiometric urania by X-ray diffraction analysis as the product of the reaction of gaseous cesium with urania pellets (initial O/U = 2.00 ± 0.00) held in a Mo capsule for 100 hr in a temperature gradient of 1323 to 823 K. In this experiment, Cs\textsubscript{2}UO\textsubscript{4} was observed at a position corresponding to 1023 K in the thermal gradient. Adamson et al.\textsuperscript{37,38} identified Cs\textsubscript{2}UO\textsubscript{4} and stoichiometric urania by X-ray diffraction analysis as the product of the reaction of gaseous cesium (2.5 x 10\textsuperscript{3} Pa) with UO\textsubscript{3} powder at 1123 K (100 hr) in a Mo capsule. In simulation studies in stainless steel capsules, Aubert et al.\textsuperscript{36} identified Cs\textsubscript{2}U\textsubscript{2}O\textsubscript{7} by X-ray diffraction analysis as the product of the reaction of Cs\textsubscript{2}O with UO\textsubscript{2}.\textsuperscript{0.00} at 1073 K (1500 hr) and at 1273 K (1000 hr). The diuranate, Cs\textsubscript{2}U\textsubscript{2}O\textsubscript{7}, was also identified by X-ray diffraction analysis as the product of the reaction of Cs\textsubscript{2}O with UO\textsubscript{2}.\textsuperscript{0.05} in a stainless steel capsule at 973 K (2000 hr), 1073 K (1500 hr), 1173 K (1000 hr), and 1273 K (1000 hr).

Out-of-pile experiments have also been performed with liquid cesium. Aitken et al.\textsuperscript{37,39} reported experiments conducted in nickel capsules in which a ternary uranium(V) oxide, Cs\textsubscript{1.3}UO\textsubscript{3}, was in equilibrium with UO\textsubscript{2}.\textsuperscript{0.00} and liquid cesium at 1073 K (100 hr). The starting materials\textsuperscript{40} in this experiment were powdered U\textsubscript{3}O\textsubscript{8} (1.2 g), Cs\textsubscript{2}O\textsubscript{x} (0.836 g; x = 2.5 ± 0.5), and Cs (5 g). In addition, Cs\textsubscript{1.3}UO\textsubscript{3} was formed by the reaction of Cs\textsubscript{2}UO\textsubscript{4} with liquid cesium in a nickel capsule at 1000 K (113 hr).\textsuperscript{37,39} The compound Cs\textsubscript{1.3}UO\textsubscript{3} was identified by chemical analysis and by a unique X-ray pattern.\textsuperscript{40} The reported X-ray pattern for Cs\textsubscript{1.3}UO\textsubscript{3} does not match the powder pattern for Cs\textsubscript{2}UO\textsubscript{4} (Ref. 17), Cs\textsubscript{2}U\textsubscript{2}O\textsubscript{7} (Ref. 17) or
Adamson et al.\textsuperscript{41} reported results obtained with an emf cell loaded with liquid cesium (5 g), Cs\textsubscript{2}UO\textsubscript{4} (5 g), and stoichiometric urania (10 g). At 873 K, the initial output corresponded closely to the oxygen potential for the equilibrium:

\[
\text{Cs}_{2}UO_{4} + \text{Cs}_{2}O \rightleftharpoons \text{Cs}_{2}UO_{2}O_{7}
\]

The emf increased slowly for the next 20 hr and reached a plateau value corresponding to an oxygen potential that was 21 kJ/mol more negative than the equilibrium oxygen potential for Eq. 1. This behavior was interpreted to "constitute strong independent evidence that Cs\textsubscript{2}UO\textsubscript{4} is converted to one or more stable Cs fuel compounds (Cs\textsubscript{0.5}xUO\textsubscript{3}; x = 0–0.5) in the presence of liquid cesium."

This review of the literature clearly indicates that some of the findings are in conflict with one another. This conflict centers about the stability of the cesium uranates formed and the conditions required for their formation. Of special interest with regard to the formation of a low-density compound at the fuel-blanket interface in uranium-oxide-blanketed mixed-oxide fuel is the identification of the cesium uranate compound or compounds that exist in equilibrium with liquid cesium and urania.

II. CESIUM-URANIUM-OXYGEN PHASE DIAGRAM

A. Estimation of Thermodynamic Properties of Cesium Uranates

To serve as a basis for the Cs-U-O phase diagram, thermodynamic functions for the cesium uranates were estimated from the measured values of the enthalpies of formation of Cs\textsubscript{2}UO\textsubscript{4}, Cs\textsubscript{2}UO\textsubscript{2}O\textsubscript{7}, Cs\textsubscript{2}O, and UO\textsubscript{3} and the measured entropy of Cs\textsubscript{2}UO\textsubscript{4}, Cs\textsubscript{2}O and UO\textsubscript{3} shown in Table 2. Also given in this table are enthalpy and entropy data for the reactants of the compounds listed therein. A graph was constructed (see Fig. 1) by plotting the free energy of formation of the cesium uranates from Cs\textsubscript{2}O and UO\textsubscript{3} per mole of oxides (i.e., moles Cs\textsubscript{2}O plus moles UO\textsubscript{3}) vs. the mole fraction of Cs\textsubscript{2}O in the compound. The graph was drawn starting with the experimental data for the compounds Cs\textsubscript{2}UO\textsubscript{4} and Cs\textsubscript{2}UO\textsubscript{2}O\textsubscript{7}, which may be written as Cs\textsubscript{2}O•UO\textsubscript{3} and Cs\textsubscript{2}O•2UO\textsubscript{3}, respectively. The value of the free energy for the next compound, Cs\textsubscript{4}U\textsubscript{5}O\textsubscript{17}, was chosen so that it was about 3.2 kJ/mol less negative than that obtained by a linear extrapolation using the values for Cs\textsubscript{2}UO\textsubscript{4} and Cs\textsubscript{2}UO\textsubscript{2}O\textsubscript{7}. This choice, although arbitrary in magnitude, makes the compound Cs\textsubscript{2}UO\textsubscript{2}O\textsubscript{7} stable with respect to decomposition into Cs\textsubscript{2}UO\textsubscript{4} and Cs\textsubscript{4}U\textsubscript{5}O\textsubscript{17}; that is, the reaction 3Cs\textsubscript{2}UO\textsubscript{2}O\textsubscript{7} = Cs\textsubscript{4}U\textsubscript{5}O\textsubscript{17} + Cs\textsubscript{4}U\textsubscript{5}O\textsubscript{17} has a positive value for the standard free-energy change. In a similar way, free-energy values were estimated for the next compound, Cs\textsubscript{2}U\textsubscript{3}O\textsubscript{13}, and for all other reported polyuranates formed by the combination of Cs\textsubscript{2}O and UO\textsubscript{3}.

A similar procedure was used to estimate the enthalpies of formation. Note that the \(\Delta G_f\) scale in Fig. 1 is set 20 kJ higher than the \(\Delta H_f\) scale. For Cs\textsubscript{2}UO\textsubscript{4}, the \(\Delta H_f\) value in Fig. 1 is actually only 3.8 kJ more negative than the \(\Delta G_f\) value. From the estimated values for the free energies and enthalpies of formation, the entropies of formation were computed. From the entropy of formation, the value of the absolute entropy for each compound was computed. The thermodynamic quantities for the compound Cs\textsubscript{2}U\textsubscript{3}O\textsubscript{12}, which may also be written as Cs\textsubscript{2}O•UO\textsubscript{3}•3UO\textsubscript{3}, were estimated from the values for Cs\textsubscript{2}U\textsubscript{3}O\textsubscript{13} by
Fig. 1. Graphical Method of Estimation of Free Energies and Enthalpies of Formation of Cesium Uranates.
Table 2. Thermodynamic Properties of Cesium Uranates

<table>
<thead>
<tr>
<th>Compound</th>
<th>$-\Delta H_f^{298}$ b (kJ/mol)</th>
<th>$-\Delta S_f^{298}$ (J/mol·deg)</th>
<th>$S_f^{298}$ (J/mol·deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs$_2$UO$_4$</td>
<td>1922 ± 1.24$^{2,43}$</td>
<td>441$^{c,d}$</td>
<td>220 ± 0.4$^{44}$</td>
</tr>
<tr>
<td>Cs$_2$U$_2$O$_7$</td>
<td>3205 ± 2.1$^{43,45}$</td>
<td>656</td>
<td>332</td>
</tr>
<tr>
<td>Cs$_4$U$_5$O$_7$</td>
<td>7670</td>
<td>1560</td>
<td>777</td>
</tr>
<tr>
<td>Cs$_2$U$_4$O$_2$</td>
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<td>1090</td>
<td>514</td>
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<tr>
<td>Cs$_2$U$<em>4$O$</em>{12}$</td>
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<td>1170</td>
<td>536</td>
</tr>
<tr>
<td>Cs$_2$U$<em>5$O$</em>{16}$</td>
<td>6950</td>
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<td>636</td>
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<tr>
<td>Cs$_2$U$<em>7$O$</em>{22}$</td>
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<td>987</td>
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<tr>
<td>Cs$<em>2$U$</em>{15}$O$_{46}$</td>
<td>19280</td>
<td>4010</td>
<td>1630</td>
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</table>

*a Estimated values unless otherwise noted.

b Enthalpies of formation, $\Delta H_f^{298}$ (J/mol): Cs$_2$O(c), -346.0 ± 1.2 (Ref. 46); UO$_2$(c), -1085 ± 0.8 (Ref. 47); γ-UO$_3$(c), -1228 ± 4 (Ref. 48); U$_4$O$_5$(c), -4510 (Ref. 49); U$_3$O$_7$(c), -3574 (Ref. 49).

c Standard entropies, $S_f^{298}$ (J mol$^{-1}$ deg$^{-1}$): Cs$_2$O(c), 147 ± 0.4 (Ref. 50); UO$_2$(c), 77.0 ± 0.02 (Ref. 19); γ-UO$_3$(c) 98.7 ± 0.4 (Ref. 49); U(c), 50.3 ± 0.2 (Ref. 51); O$_2$(g), 205.0 ± 0.04 (Ref. 51); Cs(c), 85.1 ± 0.4 (Ref. 51); U$_4$O$_9$, 336 ± 0.4 (Ref. 49); U$_3$O$_7$, 282 ± 0.4 (Ref. 49).

d Additional data: $\Delta G_f^{(Cs, g)} = 71,000 - 75.3$ T J/mol (Ref. 52).

assuming that (1) the enthalpies of formation differ by the difference between the enthalpies of formation of UO$_3$ and UO$_2$ and (2) that the absolute entropy was less by the difference in entropies between UO$_3$ and UO$_2$. The values for Cs$_2$U$_6$O$_{18}$ and Cs$_2$U$_8$O$_{27}$ were estimated in a similar manner from the thermodynamic quantities for Cs$_2$U$_6$O$_{19}$ and Cs$_2$U$_8$O$_{28}$, respectively.

B. Experimental Studies of the Reaction of Cesium with UO$_{2+x}$

Because of the diversity of opinion represented by the available literature, a program was initiated to define the phase equilibria relevant to the cesium-urania system. Our investigations included both isothermal capsule experiments and experiments with a thermogravimetric analysis (TGA) apparatus. The experiments involved exposure of hyperstoichiometric urania (O/U = 2.0 to 2.2) to either liquid or gaseous cesium and identification of the products by X-ray diffraction analysis. The product in these experiments was an orange powder that appeared to be homogeneous on visual inspection and X-ray diffraction analysis. All operations that involved the handling of cesium and the loading of X-ray capillaries were performed in a helium atmosphere.
In the experiments with liquid cesium, nickel capsules (7.9-mm ID, and 7 cm long) were loaded with approximately 2.5 g of powdered uranium oxide and 1.5 g of cesium and welded closed. During heat treatment over the temperature range from 873 to 1273 K, the capsule was positioned in such a way that only liquid cesium was in contact with the uranium oxide. At the end of the heat treatment, the capsule was quickly quenched (15 s) and the excess cesium removed by vacuum distillation at 573 K.

To study the reaction of gaseous cesium with uranium oxide, a Type 304 stainless steel capsule (2.5-cm ID, and 18 cm long) was loaded with a nickel tray containing 1.5 g of powdered uranium oxide and a separate nickel tray containing 5 g of cesium and welded closed. During heat treatment, the capsule was positioned so that only gaseous cesium contacted the uranium oxide. The gaseous cesium pressure was calculated from the temperature (600 K) at the coolest portion of the capsule, one end of which was maintained in a temperature gradient. The tray containing uranium oxide was in an isothermal zone at 1073 K.

In the TGA apparatus, powdered uranium oxide was exposed to gaseous cesium in a helium gas stream which had a 2 Pa H₂O impurity level and an oxygen potential of -364 kJ/mol at 1073 K maintained by an Fe/FeO buffer. The oxygen potential of the gas stream was measured with a calibrated emf cell having a sensor of yttria-stabilized zirconia.

The experimental conditions and the results of our experiments are summarized in Table 3. The normal cesium uranate, Cs₂UO₄, and "stoichiometric" uranium dioxide (a = 5.470 x 10⁻¹⁰ m) were identified by X-ray diffraction analysis in all cases. The X-ray data are shown in Tables 4 and 5 in the form of experimental d values which may be compared to similar literature data in Table 4 for UO₂, Cs₂UO₄, Cs₂U₂O₇ and Cs₂U₄O₁₂. The relative intensities (I/I₀) of the strongest lines in the X-ray diffraction pattern of UO₂, Cs₂UO₄, Cs₂U₂O₇ and Cs₂U₄O₁₂ are listed to show that the lines which we observed experimentally correspond to the most intense X-ray diffraction lines of Cs₂UO₄. In the TGA experiments, the kinetics of the reaction of gaseous cesium with powdered UO₂+x indicated that the reaction proceeded as shown in Eq. 2:

\[ x\text{Cs(g)} + \text{UO}_2+x + \frac{2-x}{2} \text{UO}_2 + \frac{x}{2} \text{Cs}_2\text{UO}_4 \]  

(2)

All the excess oxygen in the urania (x in UO₂+x) was consumed by reaction 2 in the first seven hours, whereupon the reaction ceased.

Our results clearly show that a hexavalent cesium uranate, Cs₂UO₄, is the Cs-U-O phase in equilibrium with liquid cesium and urania in the temperature range from 873 to 1273 K. This conflicts with the results of Aitken et al. 37,39,40 and Adamson41 who reported that Cs-U-O compounds with a net uranium valence of less than 6, Cs₁.₃UO₃ or Cs₀.₅+xUO₃ (x = 0–0.5), existed in equilibrium with liquid cesium and urania in the temperature range from 873 to 1073 K. Our results are consistent with the results of Efremova,22 Rudorff et al.,24,25 Cordfunke et al.,17 and van Egmond18,29-31 in that the pentavalent uranate, CsUO₃, does not exist in the Cs-U-O system. Moreover, our results clearly show that a hexavalent cesium uranate, Cs₂UO₄, can exist in equilibrium with gaseous cesium and urania at 1073 K. Our result is supported by the results
Table 3. Summary of Experimental Results for Reaction of Cesium with Uranium Oxide.

<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>Type of Experiment</th>
<th>Cesium Oxide Pressure, Pa</th>
<th>Uranium Oxide Temp., K</th>
<th>Initial O/U Atom Ratio of Uranium Oxide</th>
<th>Time at Temp., hr</th>
<th>Product Phases Identified By X-ray Diffraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni capsule</td>
<td>a</td>
<td>873</td>
<td>2.004</td>
<td>161</td>
<td>Cs₂UO₄ + stoichiometric uranium dioxide</td>
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<td>Ni capsule</td>
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*Uranium oxide sample in contact with liquid cesium.*
Table 4. X-Ray Data for Several Cesium Uranates

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<tr>
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<td>( \alpha-\text{Cs}_2\text{U}<em>4\text{O}</em>{12} ) (Ref. 18)</td>
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<td>( \gamma-\text{Cs}_2\text{U}<em>4\text{O}</em>{12} ) (Ref. 18)</td>
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(Cont'd)
Table 4. (Con’t)

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<th>(d, \AA)</th>
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<th>Experimental (d) Values(^a)</th>
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<tr>
<td>(\text{UO}_2) (Ref. 53)</td>
<td>(\text{Ce}_2\text{U}<em>6\text{O}</em>{12}) (Ref. 17)</td>
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\(^a\)In addition to urania lines.

\(^b\)See Table 2 for experimental conditions.

\(^c\)X-ray film number.
Table 5. Complete X-Ray Diffraction Data for Experiment 5

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<tr>
<th>$\text{Cs}_2\text{UO}_4$ d Values (Ref. 17)</th>
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aSee Table 2 for experimental conditions.
bCoincide with $\text{UO}_2$ lines.
of Aubert et al.,36 Venker et al.,34 Aitken et al.,37 and Adamson et al.,38 who showed that Cs$_2$U$_2$O$_7$ (973 to 1273 K), Cs$_2$UO$_4$/Cs$_2$U$_2$O$_7$ (973 K), Cs$_2$UO$_4$ (1073 K), and Cs$_2$UO$_9$ (1123 K), respectively, exist in equilibrium with gaseous cesium and urania. However, our result is in conflict with the finding of Cordfunke33 that only Cs$_2$UO$_{1+2}$ (with a net uranium valency of less than 6) exists in equilibrium with gaseous cesium and urania at temperatures above 873 K.

The experimental results and the thermodynamic data on cesium uranates obtained in this laboratory and the experimental data of Venker et al.,34 Aubert et al.,36 Cordfunke et al.,17,33 van Egmond,18,29-31 Aitken et al.,37 and Adamson et al.,38 were used to construct the phase diagrams shown in Figs. 2 and 3. Specifically, our results and the data of Venker et al.,34 Aitken et al.,37 and Adamson et al.,38 were used to construct the Cs$_2$UO$_4$-UO$_{2+x}$ tie line. The data of Aubert et al.,36 was used to construct the Cs$_2$U$_2$O$_7$-UO$_{2+x}$ tie line. The Cs$_2$U$_4$O$_{12}$-UO$_{2+x}$ tie line and remaining tie lines in Fig. 3 were based on the results of Cordfunke et al.,17,33 and van Egmond.18,29-31

Figures 2 and 3 represent isothermal sections over the temperature range from 873 to 1273 K. The Cs-UO$_{2+x}$ and Cs-Cs$_2$UO$_4$ tie lines exist only below 950 K. The Cs$_2$UO$_4$-UO$_{2+x}$, Cs$_2$U$_2$O$_7$-UO$_{2+x}$, and Cs$_2$U$_4$O$_{12}$-UO$_{2+x}$ tie lines exist over the range from 873 to 1273 K. The widths of these two-phase regions vary with temperature. Phase regions containing cesium uranates with a higher U/Cs atom ratio than that of Cs$_2$UO$_{1+2}$ may not exist over the entire temperature range from 873 to 1273 K. Uranium trioxide, UO$_3$, exists only below 930 K.48 At temperatures above 873 K, Cs$_2$U$_4$O$_{13}$ and Cs$_2$U$_5$O$_{16}$ form a solid solution.17,29

There are three key features related to Figs. 2 and 3. Firstly, the experimental data of Cordfunke et al.17 clearly establish a Cs$_2$U$_4$O$_{12}$-U$_3$O$_8$ tie line. The Cs$_2$U$_4$O$_{12}$-U$_3$O$_8$ tie line is consistent with the thermodynamic properties shown in Table 2. The existence of a Cs$_2$U$_4$O$_{12}$-U$_3$O$_8$ tie line indicates that there can be no tie line between UO$_{2+x}$ and a cesium uranate with a higher U/Cs atom ratio than that of Cs$_2$UO$_{1+2}$. Secondly, only three of the ten ternary cesium-uranium-oxygen compounds (Cs$_2$UO$_4$, Cs$_2$U$_2$O$_7$, Cs$_2$U$_4$O$_{12}$) exist in equilibrium with UO$_{2+x}$. Consequently, the cesium uranate which forms at the fuel-blanket interface (where UO$_{2+x}$ is always present in excess) must be either Cs$_2$UO$_4$, Cs$_2$U$_2$O$_7$, or Cs$_2$U$_4$O$_{12}$. Thirdly, Cs$_2$UO$_4$ is the compound which exists in equilibrium with liquid cesium and urania. Consequently, cesium analogs (which have not been observed to date) of pentavalent uranates such as Na$_2$UO$_3$,54 and Na$_3$UO$_4$23,54 do not exist in equilibrium with UO$_{2+x}$. If either of these cesium analogs existed in the temperature range 873 to 1273 K, it would exist in equilibrium with liquid cesium and urania.

C. Calculation of Phase Equilibria

By application of the phase rule, it can be shown that in the three-phase regions shown in Figs. 2 and 3 (e.g., Cs$_2$UO$_4$-Cs$_2$U$_2$O$_7$-UO$_2$ ), there is one degree of freedom; therefore, setting the temperature fixes the cesium partial pressure and the oxygen partial pressure of the system. On the other hand, along the two-phase tie lines (e.g., the Cs$_2$UO$_4$-UO$_{2+x}$ tie line), there are two degrees of freedom; therefore, at a set temperature, the cesium partial pressure depends on the oxygen partial pressure of the system. The dependency of the cesium partial pressure on the oxygen partial pressure at Cs-U-O compositions falling on the two-phase tie lines can be calculated from the
Fig. 2. Selected Portions of the Cesium-Uranium-Oxygen Phase Diagram Showing Tie Lines to UO$_{2+x}$; Isothermal Sections from 873 to 1273 K. (The solid area shows the extent of the two-phase region at 873 K. The Cs-UO$_{2+x}$ and Cs-Cs$_2$UO$_4$ tie lines exist only below 950 K.)
Fig. 3. Selected Portions of the Cesium-Uranium-Oxygen Phase Diagram; Isothermal Sections from 873 to 1273 K. (The solid areas show the width of two-phase regions at 1273 K. The compound UO$_3$ exists only below 930 K. The Cs-UO$_{2+x}$ and Cs-Cs$_2$UO$_4$ tie lines exist only below 950 K. Phase regions containing cesium uranates with a higher U/Cs atom ratio than Cs$_2$U$_4$O$_{12}$ may not exist over the entire temperature range; see text. SS = Cs$_2$U$_4$O$_{13}$-Cs$_2$U$_5$O$_{16}$ solid solution.)
measured thermodynamic properties of the phases present. The fixed cesium partial pressure and the fixed oxygen partial pressure in the three-phase regions can be calculated in a similar manner.

Consider the equilibrium

$$2\text{Cs}(g) + \text{UO}_2(c) + \text{O}_2(g) \not\equiv \text{Cs}_2\text{UO}_4(c) \quad (3)$$

which exists along the Cs$_2$UO$_4$-UO$_{2+x}$ tie line. The corresponding free energy relationship may be written as follows:

$$\Delta G_f^o(\text{Cs}_2\text{UO}_4,c) - 2\Delta G_f^o(\text{Cs},g) - 2RT \ln P_{\text{Cs}} - \Delta G_f^o(\text{UO}_2,c) - RT \ln P_{\text{O}_2} = 0 \quad (4)$$

The cesium pressure and the oxygen potential ($\Delta \tilde{G}_o^o = RT \ln P_{\text{O}_2}$) are related by

$$\ln P_{\text{Cs}} = \left[\Delta G_f^o(\text{Cs}_2\text{UO}_4,c) - 2\Delta G_f^o(\text{Cs},g) - \Delta G_f^o(\text{UO}_2,c) - \Delta \tilde{G}_o^o\right]/2RT \quad (5)$$

Similar expressions can be derived to relate the cesium pressure and the oxygen potential on the Cs$_2$U$_2$O$_7$-UO$_2$+$+x$ tie line and on the Cs$_2$U$_4$O$_{12}$-UO$_2$+$+x$ tie line. The calculated cesium pressures are shown in Fig. 4; these are based on the thermodynamic data from Table 2, with the assumption that $\Delta H_f^o$ and $\Delta S_f^o$ are independent of temperature. This approach is valid for Cs$_2$UO$_4$, on the basis of the known high-temperature thermodynamic properties of this compound. The effect on the thermodynamic properties of the $\alpha + \beta$ phase transition$^{17}$ of Cs$_2$U$_2$O$_7$ at 573 K and the $\alpha + \beta$ and $\beta + \gamma$ phase transitions$^{33}$ of Cs$_2$U$_4$O$_{12}$ at 898 and 968 K, respectively, is assumed to be small and has been neglected. This assumption has been shown to be valid in other ternary oxide systems.$^{52}$

Another assumption in the calculation of the cesium pressures shown in Fig. 4 is that the solubility of cesium in urania or in the cesium uranates does not significantly affect the thermodynamic properties shown in Table 2. This assumption appears to be valid. The measured$^{56}$ solubility of cesium in a (U,Pu)O$_2$ matrix is less than 1 ppm. A similar solubility of cesium in UO$_{2+x}$ would not affect the equilibrium oxygen pressure over the UO$_{2+x}$ even if the deviations from Raoult's law were large.

The estimated thermodynamic values for Cs$_2$U$_4$O$_{12}$ shown in Table 2 are used in this paper instead of values derived from Cordfunke's emf measurements.$^{33}$ The data of Venker et al.$^{34}$ Auburn et al.$^{36}$ Aitken et al.$^{37}$ Adamson et al.$^{38}$ and this work showing that Cs$_2$UO$_4$ and Cs$_2$U$_2$O$_7$ exist in equilibrium with UO$_{2+x}$ above 873 K demonstrate the inadequacy of Cordfunke's emf measurements$^{33}$ in obtaining the thermodynamic properties of Cs$_2$U$_4$O$_{12}$. According to Cordfunke's emf data, with an oxygen potential that is more negative than -170 kJ/mol, Cs$_2$U$_4$O$_{12}$ is the only possible cesium uranate in equilibrium with UO$_{2+x}$ in the temperature range of Cordfunke's experiments, 974-1024 K.

In Fig. 4, consider the 1273 K values. At lower oxygen potentials ($\Delta \tilde{G}_o^o$ more negative than -230 kJ/mol), the Cs$_2$UO$_4$-UO$_{2+x}$ region has the lowest equilibrium cesium pressure and is thus the only stable two-phase region at these oxygen potentials. Solid lines and solid symbols in Fig. 4 indicate the stable two-phase regions at each oxygen potential. Dashed lines and open symbols indicate the calculated equilibrium cesium pressure even though the corresponding two-phase region does not exist at that oxygen potential. As
Fig. 4. Cesium Equilibrium Pressure over Two-Phase Regions in Cs-U-O Phase Diagram. (Solid lines and solid symbols indicate the stable phases at each oxygen potential and the range of stability for each of the two-phase regions considered. Dashed lines and open symbols indicate the calculated cesium equilibrium pressure, even though the corresponding two-phase region does not exist at that oxygen potential. The gray area corresponds to oxygen potentials more negative than the oxygen potential of $\mathrm{UO}_2.002$.)
As the oxygen potential over the Cs$_2$U$_2$O$_{7-}$-UO$_2^{+x}$ region becomes more positive, the cesium equilibrium pressure decreases. At a unique oxygen potential (-225 kJ/mol at 1273 K), the cesium pressure over the Cs$_2$U$_2$O$_{7-}$-UO$_2^{+x}$ region is the same as the cesium pressure over the Cs$_2$U$_2$O$_7$-UO$_2^{+x}$ region [log $P_{Cs}$ (Pa) = -0.5]. This point is the intersection of the lines labeled Cs$_2$U$_2$O$_4$-UO$_2^{+x}$ and Cs$_2$U$_2$O$_7$-UO$_2^{+x}$ and represents the oxygen potential and cesium pressure of the Cs$_2$U$_2$O$_4$-Cs$_2$U$_2$O$_7$-UO$_2^{+x}$ region at 1273 K. At oxygen potentials slightly more positive than -225 kJ, the Cs$_2$U$_2$O$_7$-UO$_2^{+x}$ region has the lowest cesium equilibrium pressure. The Cs$_2$U$_2$O$_7$-UO$_2^{+x}$ region is thus the only stable two-phase region at these oxygen potentials.

As the oxygen potential over the Cs$_2$U$_2$O$_{7-}$-UO$_2^{+x}$ region becomes more positive, the cesium equilibrium pressure decreases. At a unique oxygen potential (-202 kJ/mol at 1273 K), the cesium pressure over the Cs$_2$U$_2$O$_{7-}$-UO$_2^{+x}$ region is the same as the cesium pressure over the Cs$_2$U$_4$O$_{12-}$-UO$_2^{+x}$ region [log $P_{Cs}$ (Pa) = -1.2]. This point is the intersection of the lines labeled Cs$_2$U$_2$O$_7$-UO$_2^{+x}$ and Cs$_2$U$_4$O$_{12-}$-UO$_2^{+x}$ and is the oxygen potential and cesium pressure of the Cs$_2$U$_2$O$_7$-Cs$_2$U$_4$O$_{12-}$-UO$_2^{+x}$ region at 1273 K. At oxygen potentials more positive than -202 kJ/mol, the Cs$_2$U$_4$O$_{12-}$-UO$_2^{+x}$ region has the lowest cesium equilibrium pressure. The Cs$_2$U$_4$O$_{12-}$-UO$_2^{+x}$ region is thus the only stable two-phase region at these oxygen potentials.

The three stable two-phase regions in Fig. 4 (Cs$_2$UO$_4$-UO$_2^{+x}$, Cs$_2$U$_2$O$_7$-UO$_2^{+x}$, and Cs$_2$U$_4$O$_{17}$-UO$_2^{+x}$) are shown as tie lines in the Cs-U-O phase diagrams in Figs. 2 and 3. The other tie lines in Fig. 3 can be constructed in a similar manner from the thermodynamic data in Table 2. The absence of possible tie lines can also be inferred from thermodynamic considerations. For example, no Cs$_4$U$_5$O$_{27}$-UO$_2^{+x}$ tie line exists because thermodynamic calculations show that there is no stable Cs$_4$U$_5$O$_{27}$-UO$_2^{+x}$ region (i.e., the calculated cesium equilibrium pressure over the hypothetical Cs$_4$U$_5$O$_{27}$-UO$_2^{+x}$ region is not the lowest cesium equilibrium pressure for any oxygen potential or temperature shown in Fig. 4).

In a fashion similar to the foregoing, the oxygen potentials and cesium pressures over the three-phase regions shown in Figs. 2 and 3 may be obtained. For example, the oxygen potential of the Cs$_2$UO$_4$-Cs$_2$U$_2$O$_7$-UO$_2^{+x}$ region may be calculated from the thermodynamic relationship associated with the equilibrium

$$\text{Cs}_2\text{UO}_4(c) + \text{UO}_2(c) + \frac{1}{2} \text{O}_2(g) \nrightarrow \text{Cs}_2\text{U}_2\text{O}_7(c)$$  \hspace{1cm} (6)

The oxygen potentials and cesium pressures over selected three-phase regions shown in Figs. 2 and 3 are given in Table 6; these were derived using the data from Table 2. As shown in Table 6, the oxygen potential of the Cs$_2$UO$_4$-Cs$_2$U$_2$O$_7$-UO$_2^{+x}$ region at 1273 K corresponds to UO$_2.03$. Therefore, the thermodynamic relationship associated with the equilibrium

$$\text{Cs}_2\text{UO}_4(c) + \text{UO}_{2+x}(c) + \frac{1-x}{2} \text{O}_2(g) = \text{Cs}_2\text{U}_2\text{O}_7(c)$$  \hspace{1cm} (7)

and the thermodynamic data$^{49}$ for UO$_{2+x}$ (instead of UO$_2$) should be used. However, the data in Table 6 have not been corrected for the deviations in stoichiometry of urania because these corrections are less than $\pm$ kJ/mol, which is within the uncertainty of the estimated thermodynamic values for cesium uranates.
Table 6. Calculated Oxygen Potentials (kJ/mol) and Cesium Pressures (Pa) at Selected Temperatures in Three-Phase Regions of the Cs-U-O Phase Diagram

<table>
<thead>
<tr>
<th>Region</th>
<th>873 K</th>
<th>1073 K</th>
<th>1273 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-log P_Cs</td>
<td>-ΔG_02</td>
<td>-log P_Cs</td>
</tr>
<tr>
<td>Cs(α) + Cs_2UO_4 + UO_2+X</td>
<td>-</td>
<td>633</td>
<td>-</td>
</tr>
<tr>
<td>Cs_2UO_4 + Cs_2U_2O_7 + UO_2+X</td>
<td>5.9</td>
<td>280</td>
<td>2.7</td>
</tr>
<tr>
<td>Cs_2U_2O_7 + Cs_2U_4O_12 + UO_2+X</td>
<td>6.7</td>
<td>261</td>
<td>2.8</td>
</tr>
<tr>
<td>Cs_2U_4O_12 + U_4O_3 + UO_2+X (a)</td>
<td>9.4</td>
<td>217</td>
<td>5.6</td>
</tr>
<tr>
<td>Cs_2U_4O_14 + U_4O_9 + U_3O_8 (a)</td>
<td>11.4</td>
<td>176</td>
<td>7.3</td>
</tr>
<tr>
<td>Cs_2U_4O_12 + Cs_2U_6O_18 + U_3O_8</td>
<td>11.5</td>
<td>175</td>
<td>7.7</td>
</tr>
<tr>
<td>Cs_2U_4O_18 + Cs_2U_9O_27 + U_3O_8</td>
<td>12.4</td>
<td>147</td>
<td>8.0</td>
</tr>
<tr>
<td>Cs_2U_5O_27 + Cs_2U_7O_22 + U_3O_8</td>
<td>15.7</td>
<td>72^b</td>
<td>9.4</td>
</tr>
<tr>
<td>Cs_2U_7O_22 + Cs_2U_15O_46 + U_3O_8</td>
<td>15.2</td>
<td>82^b</td>
<td>10.5</td>
</tr>
</tbody>
</table>

^a The oxygen potential in this three-phase region is the oxygen potential of the U_3O_8-γ-UO_2+X or U_4O_9-U_3O_8-γ two-phase region (Ref. 49), assuming no effect from cesium solubility. The oxygen potential is independent of the estimated thermodynamic properties of Cs_2U_4O_12; the cesium pressure depends on the estimated thermodynamic properties of Cs_2U_4O_12 in these three-phase regions.

^b Not a stable three-phase region at this temperature. The stable three-phase region at 873 K is Cs_2U_5O_27-Cs_2U_15O_46-U_3O_8, with ΔG_02 = -81 kJ/mol and log P_Cs = -15.3.

D. Accuracy of Calculated Phase Equilibria

The data in Table 6 are in accord with the experimental phase diagram. At a given temperature, the oxygen potential becomes more positive and the cesium pressure decreases going from top to bottom in the table. Furthermore, the estimated thermodynamic data predict the observed tie lines^3^ between U_3O_8 and Cs_2U_4O_12, Cs_2U_6O_18, Cs_2U_9O_27 and Cs_2U_7O_22 and the absence of a tie line between U_3O_8 and Cs_2U_5O_16 and between U_3O_8 and Cs_2U_4O_13. However, the set of thermodynamic data that predicts the observed tie lines to U_3O_8 is not unique and a slightly altered set would result in the same ordering of the oxygen potentials and predictions of tie lines. Therefore, while it appears that the estimated thermodynamic data in Table 2 are qualitatively correct, the quantitative accuracy of the data in Table 2 is uncertain and requires further experimentation.
In view of the lack of high-temperature thermodynamic measurements on most cesium uranates, the validity of the data in Table 6 is naturally subject to question. The data for the Cs(1) + Cs2UO4 + UO2+x region have the least uncertainty because reliable high-temperature thermodynamic data are available for Cs2UO4 and UO2. The data for the Cs2UO4-Cs2U2O7-UO2+x region were calculated using enthalpy measurements (at 298 K) and estimated entropy data for Cs2U2O7. An uncertainty of ±8 J/mol-deg in the entropy estimate becomes an uncertainty of ±8 kJ/mol in the calculated oxygen potential of the Cs2U2O7-Cs2UO4-UO2+x region. The uncertainty in the calculated oxygen potential of the three-phase regions which lie below the Cs2UO4-Cs2U2O7-UO2+x region in Table 6 is greater than ±8 kJ/mol and increases going down the table owing to the increasing uncertainty in the extrapolation technique shown in Fig. 1.

A lower limit for the oxygen potential in the three-phase regions containing cesium uranates with U/Cs atom ratios higher than that of Cs2U2O7 can be established within an uncertainty of ±8 kJ/mol because of the following considerations. The lower limit is given by the intersection of the solid lines labeled Cs2UO4-UO2+x and Cs2U2O7-UO2+x in Fig. 4. (The evidence for the existence of these two-phase regions has been previously discussed.) Consequently, in Fig. 4, lines corresponding to stable cesium uranates with a U/Cs atom ratio higher than Cs2U2O7 can intersect the Cs2U2O7-UO2+x line only at oxygen potentials more positive than that at the intersection of the Cs2U2O7-UO2+x line and the Cs2UO4-UO2+x line. The lower limit for the oxygen potential of three-phase regions containing cesium uranates with U/Cs atom ratios higher than that of Cs2U2O7 is therefore the oxygen potential of the Cs2UO4-Cs2U2O7-UO2+x field.

The phase equilibria shown in Figs. 2 and 3 and Table 6 may also be inaccurate in that all ten cesium uranates are shown to exist in the temperature range from 873 to 1273 K. The results of this study, as well as those of Aubert et al. and Cordfunke, show that the Cs2UO4-UO2+x, Cs2U2O7-UO2+x, and Cs2U4O12-UO2+x regions exist in the stated temperature range. In Fig. 3, regions containing U3O8 may not exist over the entire range of 873-1273 K. Cordfunke's pseudo-binary Cs-U-O phase diagram at Po2 = 2 x 10⁴ Pa shows that the transitions Cs2U15O46-U3O8 + Cs2U9O27-U3O8 + Cs2U4O12-U3O8 occur with increasing temperature. Cordfunke concludes that the Cs2U4O12-U3O8 region is the only stable two-phase region containing U3O8 at high temperatures. In contrast to Cordfunke's conclusion, we assert that all of these two-phase regions may exist at the highest temperature reached. As shown in Fig. 4, at Po2 = 2 x 10⁻⁷ Pa, the stable two-phase regions are Cs2U4O12-UO2+x at 873 K (-195 kJ/mol); Cs2U2O7-UO2+x at 1073 K (-240 kJ/mol); and Cs2UO4-UO2+x at 1273 K (-285 kJ/mol). Experimentally, at a fixed Po2 of 2 x 10⁻⁷ Pa, the transitions Cs2U4O12-UO2+x + Cs2U2O7-UO2+x + Cs2UO4-UO2+x would be observed during a temperature increase from 873 K to 1273 K. A similar ordering of the temperature and oxygen potential conditions for stable two-phase regions containing U3O8 may account for Cordfunke's observations. Consequently, in Fig. 3, phase regions containing U3O8 are shown to be unaffected by temperature in the range 873 to 1273 K because there are neither experimental thermodynamic data nor experimental phase data at a sufficient number of oxygen potentials to warrant our doing otherwise.
III. APPLICATION TO URANIUM–PLUTONIUM OXIDE FUEL PINS

The range of oxygen potentials of the urania blanket pellets prior to irradiation is shown as the gray area in Fig. 4. As shown in Table 6 and Fig. 4, at 1273 K, an oxygen potential more positive than -225 kJ/mol (corresponding to UO₂₋₀.₀₃²⁰) is required to form any cesium uranate other than Cs₂UO₄. Similarly, at 1073 K, an oxygen potential more positive than -251 kJ/mol (corresponding to UO₂₋₀.₀₁²⁰) is required to form any cesium uranate other than Cs₂UO₄. These high oxygen potentials are not likely to be encountered at the fuel-blanket interface for uranium oxide blanket pellets that are initially near stoichiometric composition. At 873 K, an oxygen potential more positive than -280 kJ/mol (corresponding to UO₂₋₀.₀₀₂²⁰) would be required to form a cesium uranate other than Cs₂UO₄. The accuracy of the determination⁵⁸,⁵⁹ of the O/U ratio in the uranium oxide blanket pellets is ±0.002. Thus UO₂₋₀.₀₀₂ blanket pellets might be loaded into a fuel pin in place of the specified stoichiometric uranium dioxide. When a fuel pin is brought to power, oxygen is expected to migrate across the fuel-blanket interface from the blanket to the fuel.⁶⁰ (The more negative oxygen potential encountered in going from the blanket to the fuel is the driving force for this solid-state diffusion of oxygen.) A small migration of oxygen is sufficient to substantially lower the oxygen potential of the blanket pellet. For example, the oxygen potential of UO₂₋₀.₀₀₁ is -290 kJ/mol at 873 K.²⁰ The oxygen potential of the uranium oxide at the fuel-blanket interface is further lowered by the consumption of oxygen in forming any cesium uranate. The solid-state diffusion of oxygen from the blanket to the fuel and the consumption of oxygen in forming any cesium uranate are expected to lower the oxygen potential of the blanket pellet to the point where Cs₂UO₄ is the only stable cesium uranate (even with the ±8 kJ uncertainty in the oxygen potential of the Cs₂UO₄-Cs₂U₂O₇-UO₂ₓ+ₓ region). No evidence was found in our kinetic studies to indicate kinetic constraints on Cs₂UO₄ formation. Therefore, we conclude that the normal cesium uranate, Cs₂UO₄, is the only Cs–U–O compound expected to be formed at temperatures of 873 K or higher in the uranium oxide blanket at the interface between the mixed-oxide fuel and the blanket in irradiated fast reactor fuel pins.

This conclusion differs from Cordfunke's⁶³ because our studies were directed toward more negative oxygen potentials. Cordfunke's experiments were performed at a much higher oxygen potential (pₒ₂ ≥ 10⁻⁵ Pa) than encountered in the fuel pins. As shown in Figs. 3 and 4 and Table 6, we concur with Cordfunke that the Cs₂U₄O₁₂–UO₂+ₓ two-phase region is stable at higher oxygen potentials. The stability of the Cs₂U₄O₁₂–UO₂+ₓ region over a wide range of oxygen potentials (-261 to -217 kJ/mol at 873 K, as shown in Table 6, for example) explains why Cordfunke observed Cs₂U₄O₁₂–UO₂+ₓ in experiments at pₒ₂ ≥ 10⁻⁵ Pa with widely varying initial Cs–U–O compositions.

In addition, the conclusion in our work that Cs₂UO₄ is the only Cs–U–O compound that forms in the uranium oxide blanket at the fuel-blanket interface differs from the findings of Cordfunke⁶³ because in our work the stabilities of regions containing UO₂+ₓ were compared. These comparisons were made because the UO₂+ₓ phase is always present at the fuel-blanket interface. At pₒ₂ ≤ 10⁻⁵ Pa, Cordfunke concluded that Cs₂U₄O₁₂, not Cs₂UO₄ or Cs₂U₂O₇, would form by observing the decomposition sequence Cs₂UO₄ → Cs₂U₂O₇ → Cs₂U₄O₁₂ → UO₂. Only Cs₂U₄O₁₂ existed in a two-phase region with UO₂+ₓ. Cordfunke thus compared relative stabilities along the Cs₂UO₄–Cs₂U₂O₇, Cs₂U₂O₇–Cs₂U₄O₁₂ and Cs₂U₄O₁₂–UO₂+ₓ
two-phase regions (see tie lines in Fig. 3). We have compared the stabilities in the Cs$_2$UO$_4$-UO$_2$+$\delta$, Cs$_2$U$_2$O$_7$-UO$_2$+$\delta$ and Cs$_2$U$_4$O$_{12}$-UO$_2$+$\delta$ two-phase regions (Fig. 4).

IV. SUMMARY AND CONCLUSIONS

Cladding deformation adjacent to the interface of the uranium oxide blanket and the uranium-plutonium mixed-oxide fuel in fast-reactor fuel pins has been attributed to the formation of a low density Cs-U-O compound. Because of the large differences in molar volumes of the cesium uranates, the identity of the Cs-U-O compound is important in determining the volume increase. The Cs-U-O system was investigated in phase regions containing liquid cesium for which published data were conflicting. Thermodynamic data on the cesium uranates were estimated and used, along with data from the literature, to construct a cesium-uranium-oxygen phase diagram which is consistent with most of the experimental phase data. Thermodynamic and kinetic data have been used to show that, at the low oxygen potentials existing at the interface between the uranium oxide blanket and the uranium-plutonium mixed-oxide fuel, Cs$_2$UO$_4$ is the only Cs-U-O compound likely to be formed in the blanket.

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61. The free energy values of Cs$_2$U$_6$O$_{19}$ and Cs$_2$U$_9$O$_{28}$ were chosen so that these compounds were unstable with respect to decomposition. Cordfunke et al.\textsuperscript{17} and van Egmond\textsuperscript{18,29-31} did not report a stable cesium uranate of the formula Cs$_2$U$_6$O$_{19}$. Cordfunke et al.\textsuperscript{17} and van Egmond\textsuperscript{18,29-31} assigned a chemical formula to an X-ray pattern after determining the unit cell from a Fourier analysis of the X-ray data. Efremova et al.\textsuperscript{22} probably erred in assigning the formula Cs$_2$U$_6$O$_{19}$ to an X-ray pattern based on chemical analysis. This error is not surprising because of the small differences in chemical composition of the cesium uranates. Efremova et al.,\textsuperscript{22} Cordfunke et al.\textsuperscript{17} and van Egmond\textsuperscript{18,29-31} agree that Cs$_2$U$_9$O$_{28}$ is not a stable cesium uranate.