21
9/12/78
252XTLS

MASTER

Chemical Thermodynamics of the System Cs-U-Zr-H-I-O in the LWR Fuel-Clad Gap

Theodore M. Besmann
Terrence B. Lindemer

OAK RIDGE NATIONAL LABORATORY
OPERATED BY UNION CARBIDE CORPORATION · FOR THE DEPARTMENT OF ENERGY

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
Price: Printed Copy ~~\$4.50~~ ^{4.00}; Microfiche \$3.00

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, contractors, subcontractors, or their employees, makes any warranty, express or implied, nor assumes any legal liability or responsibility for any third party's use or the results of such use of any information, apparatus, product or process disclosed in this report, nor represents that its use by such third party would not infringe privately owned rights.

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

CHEMICAL THERMODYNAMICS OF THE SYSTEM Cs-U-Zr-H-I-O

IN THE LWR FUEL-CLAD GAP

Theodore M. Besmann
Terrence B. Lindemer

Submitted for publication in Nuclear Technology

Date Published - January 1978

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
DEPARTMENT OF ENERGY

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
INTRODUCTION	2
IN-REACTOR CONDITIONS	3
FUEL ROD CONTAINING STEAM	10
FUEL ROD CONTAINING 50% STEAM--50% AIR	12
CONCLUSIONS	14
APPENDIX A: CALCULATED EQUILIBRIUM PARTIAL PRESSURES (MPa)	17
REFERENCES	19

CHEMICAL THERMODYNAMICS OF THE SYSTEM Cs-U-Zr-H-I-O
IN THE LWR FUEL-CLAD GAP*

Theodore M. Besmann
Terrence B. Lindemer

Chemical Technology Division
Oak Ridge National Laboratory

ABSTRACT

Equilibrium thermodynamic calculations were performed on the Cs-U-Zr-H-I-O system that is assumed to exist in the fuel-clad gap of light water reactor fuel under in-reactor, steam, and 50% steam--50% air conditions. The in-reactor oxygen potential is assumed to be controlled by UO_{2+x} rather than $\text{Zr} + \text{ZrO}_2$. Thus, the important condensed phases present are UO_{2+x} , Cs_2UO_4 , and CsI , and the major gaseous species are Cs , CsI , and Cs_2I_2 . The presence of steam does not alter the species present, although CsOH also becomes a major gaseous species. In a 50% steam--50% air mixture, the condensed phases U_3O_8 or UO_3 , $\text{Cs}_2\text{U}_{15}\text{O}_{46}$, and ZrI_3 or liquid ZrI_2 are present at equilibrium, and the gaseous species ZrI_2 , ZrI_3 , and ZrI_4 have large partial pressures.

* Research sponsored by the Department of Energy under contract with Union Carbide Corporation.

INTRODUCTION

In light water reactor (LWR) fuel, the chemical species present at the fuel-clad interface (fuel-clad gap) will influence the chemical interactions with the Zircaloy clad and the escape of fission products from a defected fuel element. X-ray fluorescence of irradiated fuel revealed the major elements in the fuel-clad gap to be uranium, zirconium, and cesium along with smaller amounts of iodine and tellurium (1). Oxygen is not detectable by this technique, but is probably present. The yields in a thermal neutron flux for ^{133}Cs plus ^{137}Cs are 13.0% and 13.7%, those for ^{127}I plus ^{129}I are 0.89% and 2.00%, and those for ^{128}Te plus ^{130}Te are 1.81% and 3.38% for ^{235}U and ^{239}Pu fissioning, respectively. The yield for yttrium and all the rare-earths (RE) is $\approx 55\%$ (2).

Contact and bonding, via a reaction zone, frequently occur between the clad and the fuel pellets. Cubicciotti et al. (1), using a scanning electron microscope (SEM) with an X-ray detector, and Bazin et al. (3), using an electron microprobe analyzer, determined that the zone lies between a zirconium oxide layer (on the inner surface of the clad) and the fuel. The elements seen in this region are uranium, zirconium, and cesium, all presumably as oxide phases. The only cases in which cesium was not associated with large amounts of uranium occurred when cesium was found with iodine or chlorine, probably as a halide.

Romeo and Wolff (4) observed an interaction layer at the zirconium oxide-uranium oxide interface in areas of fuel-clad bonding. Electron microprobe analysis revealed virtually no uranium in the layer, although zirconium and cesium were found. Cesium deposits were particularly evident near pellet cracks and at pellet-pellet interfaces.

Romeo and Wolff (4) believe that cesium transports to the clad as elemental liquid or vapor, whereas we postulate that cesium exists as a halide (primarily the iodide). The halides are volatile compounds whose migration can be driven by the temperature gradient between fuel and clad. This explanation may reconcile the observations.

For the purposes of the present work, it was assumed that cesium is always associated with urania and/or iodine. Equilibrium thermodynamic calculations have been performed for three different fuel conditions: typical in-reactor operation of an intact fuel element, exposure to steam, and exposure to a 50% steam--50% air mixture. The latter two environments appear to be typical for hypothetical cask failure during shipping of spent fuel, although the exact steam-air mixture case is generally indicative of the system in an air and steam environment.

IN-REACTOR CONDITIONS

In an oxide fuel, the chemical potential of oxygen, μ_{O_2} , is a fundamental parameter that defines many of the equilibrium chemical species. The μ_{O_2} , called the oxygen potential, is $RT \ln (p_{O_2}/p_{O_2}^o)$, in which R is the gas constant ($J \text{ mol}^{-1} K^{-1}$); T is the temperature (K); p_{O_2} is the oxygen partial pressure (MPa); and $p_{O_2}^o$ is the oxygen pressure in the standard state, 0.101 MPa (1.00 atm). The standard free energy at a temperature, ΔG_T^o , for each equilibrium was calculated from the sufficiently accurate approximation $\Delta G_T^o = \Delta H_{298}^o - T \Delta S_{298}^o$ (5). In this instance, ΔH_{298}^o and ΔS_{298}^o are the differences in the enthalpies and entropies of formation of the products and reactants at 298 K. All thermodynamic data used are listed in Table I.

Cubicciotti et al. (1) have compared the oxidation rates of Zircaloy-clad fuel (clad inner surface) with those for zirconium in a pure oxygen atmosphere. They note that the rates appear comparable and conclude that the oxidation is kinetically limited by processes occurring at or below the clad surface. Further, the determination of μ_{O_2} from EMF-probe measurements taken over a radial cross section of highly irradiated LWR fuels (11.4 and 18.9 Gwd/t) gave $-555 \leq \mu_{O_2} \leq -450$ kJ/mol at 1023 K (6). One measurement is included in which the probe contacted both clad and fuel. These μ_{O_2} values are much more positive than those for the $\langle \text{Zr} \rangle + \langle \text{ZrO}_2 \rangle^a$ equilibrium. Consequently, the oxygen potential at the pellet-clad interface can be assumed to be controlled by the fuel and not by the $\langle \text{Zr} \rangle + \langle \text{ZrO}_2 \rangle$ equilibrium.

The behavior of tellurium is difficult to define because there is no available thermodynamic information for the element in the multicomponent system found in a fuel rod. The μ_{O_2} values of the fuel-clad system are below those for the $\langle \text{Te} \rangle + \langle \text{TeO}_2 \rangle$ equilibrium, μ_{O_2} (J/mol) $\approx -322,000 + 176 T$; therefore, tellurium would not be present as an oxide. The presence of cesium tellurides has been proposed (1), but no thermodynamic information is available either for these compounds or for their analogs in the system of tellurium-selenium-alkali metals. Zirconium tellurides exist, but have not been detected in the fuel-clad system. No further consideration will be given to the chemistry of tellurium, and its small concentration prevents it from greatly influencing the more major components.

^aThe following notation is used: $\langle \rangle$ pure element or compound in the solid state, $\{ \}$ liquid state, $()$ gaseous state.

Equilibrium thermodynamic calculations were thus performed for the system Cs-U-Zr-I-O.

Cubicciotti et al. (1) have calculated an oxygen balance for Zircaloy-clad irradiated urania fuel. Their balance indicates that sufficient oxygen is liberated to yield $\langle \text{UO}_{2+x} \rangle + \langle \text{Cs}_2\text{U}_2\text{O}_7 \rangle$ or higher oxygen-containing cesium uranates. Their assumptions for the oxygen balance in the system U-Y-RE-O in which yttrium and RE are assumed to be present as Y_2O_3 and RE_2O_3 are apparently in error. Instead, the system should be considered as an extensive CaF_2 -type solid solution, and several authors have reported that $\text{O}/(\text{U} + \text{Y} + \text{RE}) \geq 2$ at the μ_{O_2} values and RE concentrations of interest here (7-9). Applying this result to the remainder of the oxygen balance calculation of Cubicciotti et al. yields only sufficient oxygen for the formation of $\langle \text{Cs}_2\text{UO}_4 \rangle$.

The large excess of cesium over iodine guarantees that, although $\langle \text{CsI} \rangle$ may form, either elemental cesium or $\langle \text{Cs}_2\text{UO}_4 \rangle$ will be present with $\langle \text{UO}_{2+x} \rangle$. Calculations were performed using the data listed in Table I and Blackburn's (10) model for oxygen potentials in $\langle \text{UO}_{2+x} \rangle$. It was discovered that the use of thermodynamic values for stoichiometric $\langle \text{UO}_2 \rangle$, in cases where the hyperstoichiometric phase is stable, yielded insignificantly different results and, thus, the values for $\langle \text{UO}_2 \rangle$ are used throughout. The μ_{O_2} -temperature conditions necessary for the existence of these phases are shown in Fig. 1. When $\langle \text{Cs}_2\text{UO}_4 \rangle$ is stable, the pressure of (Cs), p_{Cs} , is defined at a given μ_{O_2} and temperature by the equilibrium $\langle \text{Cs}_2\text{UO}_4 \rangle \rightleftharpoons \langle \text{UO}_2 \rangle + 2(\text{Cs}) + (\text{O}_2)$. Once p_{Cs} is defined, then the partial pressures of other gaseous species are readily calculated. Isobars for (Cs) and (Cs_2O) in the presence of $\langle \text{Cs}_2\text{UO}_4 \rangle$ and $\langle \text{UO}_{2+x} \rangle$ are shown in

Table I. Thermodynamic Data

	Enthalpy of Formation (298 K)	Entropy of Formation (298 K)	
	ΔH_f° , 298 K (kJ/mol)	ΔS_f° , 298 K (J mol ⁻¹ K ⁻¹)	Reference
<UO ₂ >	-1085	-178.2 ^a	(11)
<U ₃ O ₈ >	-3574	-688.0	(12)
< γ -UO ₃ >	-1230	-259.2	(12)
<ZrI ₃ >	-397.5	-8.58	(13)
{ZrI ₂ }	-234.2	31.1	(13)
<CsI>	-351	-21.1	(14)
<Cs ₂ UO ₄ >	-1922	-411	(15)
<Cs ₂ U ₂ O ₇ >	-3205	-656.5	(15)
<Cs ₂ U ₁₅ O ₄₆ >	-19280	-4013	(15)
<TeO ₂ >	-323	-176	(16)
<ZrO ₂ >	-1098	-194	(13)
<ZrH ₂ >	-169	-13.5	(17)
(Cs)	76.65	90.46	(13)
(Cs ₂)	106	113.7	(13)
(CsO)	628	67.8	(13)
(Cs ₂ O)	-92	45.2	(13)
(CsH)	116.5	64.69	(14)
(CsOH)	-259	1.71	(18)
(H ₂ O)	-241.8	-44.39	(13)
(I)	106.8	122.7	(13)
(I ₂)	62.44	144.5	(13)
(HI)	26	83.18	(13)
(CsI)	-157	132	(14)
(Cs ₂ I ₂)	-461	143	(14)
(ZrI)	591	179	(13)
(ZrI ₂)	-66.6	190	(13)
(ZrI ₃)	-222	185	(13)
(ZrI ₄)	-355	176	(13)

^aDerived from $S_{298\text{ K}}^\circ$ <UO₂> = 77.03 J Mol⁻¹ K⁻¹ (19), $S_{298\text{ K}}^\circ$ <U> = 50.2 J mol⁻¹ K⁻¹ (20), and $S_{298\text{ K}}^\circ$ (O₂) = 205.00 J mol⁻¹ K⁻¹ (21).

Fig. 1. Oxygen potential versus temperature for the two-phase region $\langle UO_{2+x} \rangle + \langle Cs_2UO_4 \rangle$ with isobars for (Cs) and (Cs₂O).

Fig. 1. Only (Cs) is calculated to have a significant pressure, and even then, only at low μ_{O_2} values and higher temperatures. The (Cs) isobars for the $\langle Cs_2UO_4 \rangle + \langle UO_{2+x} \rangle + \{Cs\}$ equilibrium are, of course, consistent with p_{Cs} over elemental cesium. The species (Cs_2) and (CsO) were calculated to have negligible partial pressures. Equations for all significant species partial pressures are listed in Appendix A.

The subsystems involving iodine were calculated next. The species $\langle CsI \rangle$ was assumed to be present and the partial pressures of (CsI) and (Cs_2I_2) are independent of μ_{O_2} ; results of the calculations are shown in Fig. 2 as a function of temperature. The partial pressure relationships for (I) and (I_2) over the $\langle CsI \rangle + \langle UO_{2+x} \rangle + \langle Cs_2UO_4 \rangle$ system were derived from the equilibria $\langle CsI \rangle \rightleftharpoons (Cs) + 0.5(I_2)$ or (I) and are given in Appendix A. Here p_{Cs} over $\langle Cs_2UO_4 \rangle$ is defined at given μ_{O_2} and temperature values. The condensed-phase zirconium iodides were found to be unstable with respect to $\langle CsI \rangle$ under these conditions. Assuming the gas-phase iodine can contact zirconium metal, the pressures of (ZrI_2) , (ZrI_3) , and (ZrI_4) can be found from $\langle Zr \rangle + y(I_2) \rightleftharpoons (ZrI_{2y})$, where p_{I_2} is fixed by $\langle CsI \rangle$. The relationships for the Zr-I pressures are also given in Appendix A.

The iodine and zirconium iodide pressures are greatest at the maximum oxygen potential. In the presence of $\langle UO_{2+x} \rangle$ the maximum is at the $\langle UO_{2+x} \rangle + \langle U_4O_9 \rangle$ boundary, and the I and Zr-I pressures are shown in Fig. 2. The (I) and (I_2) pressures are very low, which indicates that the $\langle CsI \rangle$ must indeed be stable. The computed pressures of Zr-I species were found to decrease rapidly with μ_{O_2} and in the μ_{O_2} range for irradiated fuel determined by Adamson et al. (6), the pressures are considerably less

Fig. 2. Logarithm of pressure versus reciprocal temperature for (CsI) , (Cs_2I_2) and for (I) , (I_2) , (ZrI_2) , (ZrI_3) , and (ZrI_4) at μ_{O_2} fixed by the equilibrium between $\langle \text{UO}_{2+x} \rangle$ and $\langle \text{U}_4\text{O}_9 \rangle$.

than those for the cesium iodides. The species (ZrI) was found to have a negligible pressure under all conditions investigated.

FUEL ROD CONTAINING STEAM

Considered next is the fuel-clad system during exposure to (H₂O). It can be demonstrated that <UO_{2+x}> is stable under these conditions and does not oxidize to form other phases. The oxygen potential for equilibrium between <UO_{2+x}> and <U₄O₉> is defined as μ_{O_2} (J/mol) = -324,000 + 150.0 T; for <UO_{2+x}> to undergo a phase change to <U₄O₉>, the oxygen potential must exceed this boundary. The oxygen potential controlled by steam is fixed by its ratio (p_{H₂O}/p_{H₂}), where μ_{O_2} (J/mol) = -483,000 + 88.78 T + 38.29 log (p_{H₂O}/p_{H₂}). For μ_{O_2} to exceed the <UO_{2+x}> + <U₄O₉> equilibrium and therefore allow the formation of <U₄O₉>, it is calculated that (p_{H₂O}/p_{H₂}) ≥ 10⁵ for T ≤ 1200 K. When <UO_{2+x}> is oxidized by (H₂O), however, (H₂) is liberated, thus decreasing the (p_{H₂O}/p_{H₂}) ratio. Since it takes a very small fraction of (H₂) to cause the ratio to fall below the (p_{H₂O}/p_{H₂}) ≥ 10⁵ limit for oxidation, the reaction ceases for a finite supply of (H₂O) when a very small p_{H₂} is generated. The practical consequence of this result is that fuel exposed to (H₂O) would apparently not undergo a phase change with resultant restructuring, thereby limiting the release of fission products.

Partial pressures of (CsOH), (CsH), and (HI) over <UO_{2+x}> + <Cs₂UO₄> were calculated at p_{H₂O} + p_{H₂} = 0.101 MPa (1.00 atm) and T ≤ 1200 K. The pressures of (HI) are always negligible. Under all conditions the pressure of (CsOH) is several orders of magnitude greater than that for (CsH) (Fig. 3). At oxygen potentials of ~-450 kJ/mol, the equilibrium pressure of (CsOH) is calculated to become independent of μ_{O_2} . The phases <UO_{2+x}>, <Cs₂UO₄>,

Fig. 3. Oxygen potential versus temperature for the two-phase region $\langle UO_{2+x} \rangle + \langle Cs_2UO_4 \rangle$, in $p_{H_2O} + p_{H_2} = 0.101$ MPa, with isobars for $(CsOH)$ and (CsH) .

and $\langle \text{CsI} \rangle$ are still stable under these conditions, and the partial pressures described in the previous section exist in this system. The phase $\langle \text{ZrH}_2 \rangle$ was computed not to be stable in the fuel element, although some hydrogen may dissolve in the clad.

FUEL ROD CONTAINING 50% STEAM--50% AIR

In the case where the fuel-clad gap contains 50% steam--50% air at 0.101 MPa total pressure, the oxygen potential is controlled by the oxygen pressure in the steam-air mixture, $\mu_{\text{O}_2} = -19.14 T$ (J/mol). Under these conditions the condensed phases, at equilibrium, containing cesium and uranium are $\langle \text{Cs}_2\text{U}_{15}\text{O}_{46} \rangle$ and either $\langle \text{UO}_3 \rangle$ for $T \leq 1130$ K or $\langle \text{U}_3\text{O}_8 \rangle$ for $T \geq 1130$ K. The transition temperature for the uranium oxides is calculated from their thermodynamic values and μ_{O_2} .

At the high oxygen potentials in the steam-air mixture $\langle \text{CsI} \rangle$ is no longer stable. The phases $\langle \text{ZrI}_3 \rangle$ or $\{ \text{ZrI}_2 \}$ may, however, form in the presence of $\langle \text{Zr} \rangle$, and their equilibrium with $\langle \text{Zr} \rangle$ controls the iodine and iodide pressures (Fig. 4). The phase $\langle \text{ZrI}_3 \rangle$ is the equilibrium stable phase at $T \leq 758$ K and $\{ \text{ZrI}_2 \}$ is the stable phase at $T \geq 758$ K. The changes in slope of the zirconium iodide pressures are due to this phase transition. The (ZrI_2) , (ZrI_3) , and (ZrI_4) species are seen to be the overwhelmingly dominant iodine-containing gases, although (ZrI) was calculated to have a negligible pressure. Should mass transport or chemical kinetic processes prevent $\langle \text{ZrI}_3 \rangle$ or $\{ \text{ZrI}_2 \}$ from forming, iodine would be present as the element and its pressure would simply be the result of the vaporization of the inventory. The only cesium-containing species with significant partial pressures are (CsOH) and (CsI) , which are also

Fig. 4. Logarithm of pressure versus reciprocal temperature for (ZrI_2) , (ZrI_3) , (ZrI_4) , (I) , (I_2) , (CsI) , (Cs_2I_2) , and $(CsOH)$ in 50% steam--50% air at a total pressure of 0.101 MPa.

plotted in Fig. 4. Note that the changes in slope of these species are due to $\langle \text{UO}_3 \rangle$ transforming to $\langle \text{U}_3\text{O}_8 \rangle$ above 1130 K. The phase $\langle \text{ZrH}_2 \rangle$ is again predicted not to form.

CONCLUSIONS

1. The oxygen potential in the fuel-clad gap of irradiated LWR fuel appears to be controlled by the phase $\langle \text{UO}_{2+x} \rangle$. At low oxygen potentials, which correspond to low burnup, the (Cs) pressure is high and the species is apparently the dominant source of gaseous cesium. At high burnups and therefore higher oxygen potentials, the (Cs) pressure falls well below that for (CsI) and (Cs_2I_2) , and these iodides apparently become the major sources of gas-phase cesium and iodine. Should gas-phase iodine equilibrate with the clad, (ZrI_2) , (ZrI_3) , and (ZrI_4) may also form but are not likely to become major species.

2. In the presence of steam at 0.101 MPa the urania fuel is not expected to oxidize and undergo a phase change to $\langle \text{U}_3\text{O}_8 \rangle$. Release of fission products can, therefore, still be considered to be limited. The equilibrium pressure of (CsOH) is significant and, due to the decrease in (Cs) pressure with increasing oxygen potential, becomes the dominant cesium-bearing gas-phase species at higher oxygen potentials. The iodine and iodide pressures remain as described for the in-reactor case.

3. A 50% steam--50% air environment at 0.101 MPa fixes a high oxygen potential such that the phases $\langle \text{UO}_3 \rangle$ or $\langle \text{U}_3\text{O}_8 \rangle$, $\langle \text{Cs}_2\text{U}_{15}\text{O}_{46} \rangle$, and $\langle \text{ZrI}_3 \rangle$ or $\{\text{ZrI}_2\}$ are stable. The major gaseous species are (ZrI_2) , (ZrI_3) , and (ZrI_4) , which have very high pressures. Should $\langle \text{ZrI}_3 \rangle$ or $\{\text{ZrI}_2\}$ not form due to mass transport or chemical kinetic processes, the iodine pressures

would simply be those due to the inventory of elemental iodine. The major cesium-containing species are (CsOH) and (CsI), although their equilibrium pressures are low ($<10^6$ MPa at 1200 K).

ACKNOWLEDGMENTS

The authors would like to thank Edward C. Beahm of the Oak Ridge National Laboratory for his helpful comments and suggestions and Betty C. Drake and Vivian A. Jacobs for assistance with manuscript preparation.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

APPENDIX A: CALCULATED EQUILIBRIUM PARTIAL PRESSURES (MPa)

$$[\theta = p_{O_2} \text{ (MPa)}/0.101]$$

1. Intact Fuel Rod in the $\langle UO_2 \rangle + \langle Cs_2UO_4 \rangle$ Phase Field

$$\log p_{Cs} = 10.7 - \frac{25800}{T} - 0.5 \log \theta$$

$$\log p_{Cs_2O} = 13.5 - \frac{38900}{T} - 0.5 \log \theta$$

$$\log p_I = -\frac{2050}{T} + 0.5 \log \theta$$

$$\log p_{I_2} = -3.40 + \frac{3800}{T} + \log \theta$$

$$\log p_{CsI} = 7.00 - \frac{10100}{T}$$

$$\log p_{Cs_2I_2} = 8.65 - \frac{12600}{T}$$

$$\log p_{ZrI_2} = -8.6 + \frac{13800}{T} + \log \theta$$

$$\log p_{ZrI_3} = -17.6 + \frac{27100}{T} + 1.5 \log \theta$$

$$\log p_{ZrI_4} = -26.8 + \frac{39200}{T} + 2 \log \theta$$

2. Fuel Rod Containing Steam at $\sigma = (p_{H_2} + p_{H_2})/0.101$

$$\log p_{CsOH} = 5.16 - \frac{8320}{T} + 0.5 \log \left[\frac{\sigma}{\sigma + \theta^{1/2} \exp(-5.33 + \frac{29000}{T})} \right]$$

$$\log p_{CsH} = 8.46 - \frac{28000}{T} - 0.5 \log \theta +$$

$$0.5 \log \left[\frac{\sigma}{\sigma + \theta^{1/2} \exp(-5.33 + \frac{29000}{T})} \right]$$

3. Fuel Rod Containing 50% Steam--50% Air at a Total Pressure of 0.101 MPa

$$\log p_I = 5.05 - \frac{12500}{T}$$

$$\log p_{I_2} = 6.85 - \frac{17100}{T}$$

($T \leq 758$ K)

$$\log p_{ZrI_2} = 9.22 - \frac{10400}{T}$$

$$\log p_{ZrI_3} = 9.11 - \frac{9170}{T}$$

$$\log p_{ZrI_4} = 8.79 - \frac{9140}{T}$$

($T \geq 758$ K)

$$\log p_{ZrI_2} = 7.30 - \frac{8750}{T}$$

$$\log p_{ZrI_3} = 6.23 - \frac{6750}{T}$$

$$\log p_{ZrI_4} = 4.94 - \frac{5920}{T}$$

($T \leq 1130$ K)

$$\log p_{CsI} = 9.61 - \frac{20900}{T}$$

$$\log p_{Cs_2I_2} = 13.9 - \frac{34200}{T}$$

$$\log p_{CsOH} = 3.44 - \frac{15100}{T}$$

($T \geq 1130$ K)

$$\log p_{CsI} = 22.5 - \frac{35300}{T}$$

$$\log p_{Cs_2I_2} = 39.6 - \frac{63000}{T}$$

$$\log p_{CsOH} = 16.3 - \frac{29500}{T}$$

REFERENCES

1. D. CUBICCIOTTI, J. E. SANECKI, R. B. STRAIN, S. GREENBERG, L. A. NEIMARK, and C. E. JOHNSON, "The Nature of Fission Product Deposits Inside Light-Water-Reactor Fuel Rods," Stanford Research Institute, Menlo Park, California (1976).
2. M. E. MEEK and B. F. RIDER, "Compilation of Fission Product Yields," NEDO-12154-1, General Electric Corporation, Vallecitos Nuclear Center (1974).
3. J. BAZIN, J. JOUAN, and N. VIGNESOULT, "Behavior and Physico-Chemical State of Fission Products in Fuel Elements for Pressurized Water Reactors," NRC-TR-1, U.S. Nuclear Regulatory Commission, Washington (1976) and Paris Bull. Inform. Sci. Tech. 196, 55 (1974).
4. G. ROMEO and U. E. WOLFF, "Bonding Between UO_2 Fuel and Zircaloy-2 Cladding," Trans. Am. Nucl. Soc. 26, 213 (1977).
5. O. KUBASCHEWSKI, E. L. EVANS, and C. B. ALCOCK, Metallurgical Thermochemistry, Pergamon Press, New York (1967).
6. M. G. ADAMSON, E. A. AITKEN, S. K. EVANS, and J. H. DAVIES, "Oxygen Distribution and Its Measurement in Irradiated Oxide Fuels," Proc. Symp. Thermodynamics of Nuclear Materials 1974, Vienna, Oct. 21-25, 1974, I, 59, International Atomic Energy Agency, Vienna (1975).
7. E. STADLBAUER, U. WICHMANN, U. LOTT, and C. KELLER, "Thermodynamics and Phase Relationships of the Ternary Lanthanum-Uranium-Oxygen System," J. Solid State Chem. 10, 341 (1974).
8. K. HAGEMARK and M. BROLI, "Equilibrium Oxygen Pressures Over Solid Solutions of Urania-Yttria and Urania-Lanthana at 1100° to 1400°C," J. Am. Ceram. Soc. 50, 563 (1967).

9. J. F. WADIER, "Phase Diagram and Thermodynamic Properties of the Uranium-Neodymium-Oxygen System," CEA-R-4507, Centres d'Etudes Nucleaires de Fontenay-aux-Roses (1973).
10. P. E. BLACKBURN, "Oxygen Pressures Over Fast Breeder Reactor Fuel. (1). A Model for UO_{2+x} ," J. Nucl. Mater. 46, 244 (1973).
11. H. L. SCHICK, Thermodynamics of Certain Refractory Compounds, II, p. 93, Academic Press, New York (1966).
12. Tables of Thermodynamic Data, Tech. Rept. Ser. No. 38, International Atomic Energy Agency, Vienna (1964).
13. D. R. STULL and H. PROPHET, Project Directors, JANAF Thermochemical Tables, 2nd ed., NSRDS-NBS 37, Supt. of Documents, Washington (1971).
14. R. C. FEBER, "Thermodynamic Data for Selected Gas Impurities in the Primary Coolant of High-Temperature Gas-Cooled Reactors," LA-NUREG-6634, Los Alamos Scientific Laboratory (1977).
15. D. C. FEE, I. JOHNSON, S. A. DAVIS, G. E. STAHL, W. A. SHINN, and C. E. JOHNSON, "Formation of Cs-U-O at the Fuel-Blanket Interface in Mixed-Oxide Fuel Pins," ANL 76-126, Argonne National Laboratory (1977).
16. D. D. WAGMAN, W. H. EVANS, V. B. PARKER, I. HALOW, S. M. BAILEY, and R. H. SCHUMM, "Selected Values of Chemical Thermodynamic Properties. Tables for the First Thirty-Four Elements in the Standard Order or Arrangement," NBS Tech. Note 270-3, Supt. of Documents, Washington (1968).
17. D. D. WAGMAN, W. H. EVANS, V. B. PARKER, I. HALOW, S. M. BAILEY, R. H. SCHUMM, and K. L. CHURNEY, "Selected Values of Chemical Thermodynamic Properties. Tables for Elements 54 Through 61 in the Standard Order of Arrangement," NBS Tech. Note 270-5, Supt. of Documents, Washington (1971).

18. M. W. CHASE, J. L. CURNUTT, A. T. HU, H. PROPHET, A. N. SYVERUD, and L. C. WALKER, JANAF Thermochemical Tables, 1974 Supplement, Phys. Chem. Ref. Data 3(2), 418 (1974).
19. E. A. FISCHER, P. R. KINSMAN, and R. W. OHSE, "Critical Assessment of Equation of State Data for UO_2 ," J. Nucl. Mater. 59, 125 (1976).
20. F. L. OETTING, M. H. RAND, and R. J. ACKERMAN, The Chemical Thermodynamics of Actinide Elements and Compounds. Part 1, The Actinide Elements, International Atomic Energy Agency, Vienna (1976).
21. R. HULTGREN, P. D. DESAI, D. T. HAWKINS, M. GLEISER, K. K. KELLY, and D. D. WAGMAN, Selected Values of the Thermodynamic Properties of the Elements, American Society for Metals, Metals Park, Ohio (1973).

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

INTERNAL DISTRIBUTION

1. C. F. Baes	56. W. J. McDowell
2. E. C. Beahm	57. R. P. Milford
3-33. T. M. Besmann	58. G. W. Parker
34. J. Braunstein	59. H. Postma
35. K. B. Brown	60. J. H. Shaffer
36. J. Brynestad	61. Martha Stewart
37. D. O. Campbell	62. I. L. Thomas
38. S. Cantor	63. D. B. Trauger
39. C. F. Coleman	64. V. C. A. Vaughen
40. J. L. Collins	65. R. P. Wichner
41. J. T. Dabbs	66. R. G. Wymer
42. D. E. Ferguson	67-68. Central Research Library
43. L. M. Ferris	69. Document Reference Section
44. W. R. Grimes	70. Laboratory Records, ORNL-RC
45. O. L. Keller	71-80. Laboratory Records
46. W. J. Lackey	81. ORNL Patent Office
47. J. M. Leitnaker	82. C. H. Ice, consultant
48. T. B. Lindemer	83. E. L. Gaden, Jr., consultant
49. R. A. Lorenz	84. L. E. Swabb, Jr., consultant
50. J. C. Mailen	85. K. D. Timmerhaus, consultant
51-55. A. P. Malinauskas	86. G. R. Choppin, consultant

EXTERNAL DISTRIBUTION

87. Dr. R. P. Epple, Office of Material Sciences, Division of Basic Energy Sciences, U.S. Department of Energy, Washington, D.C. 20555
88. Research and Technical Support Division, DOE-ORO, P. O. Box E, Oak Ridge, TN 37830
- 89-115. Technical Information Center, Oak Ridge, TN 37830
116. W. Chubb, Westinghouse Electric Corp., Monroeville, PA 15146
117. R. DiSalvo, U.S. Nuclear Regulatory Commission, Division of Reactor Safety Research, Fuel Behavior Branch, 1130 SS, Washington, DC 20555
118. J. A. Dearien, Aerojet Nuclear Co., Systems Safety Research Division, Idaho Falls, ID 83401
119. P. E. MacDonald, Aerojet Nuclear Co., Systems Safety Research Division, Idaho Falls, ID 83401
120. L. Baker, Argonne National Laboratory, Argonne, IL 60439
121. M. Blander, Argonne National Laboratory, Argonne, IL 60439
122. T. F. Kassner, Argonne National Laboratory, Argonne, IL 60439
123. L. R. Kelman, Argonne National Laboratory, Argonne, IL 60439
124. R. W. Weeks, Argonne National Laboratory, Argonne, IL 60439
125. R. S. Denning, Battelle Memorial Institute, 505 King Avenue, Columbus, OH 43201

126. R. Ritzman, Battelle Memorial Institute, 505 King Avenue,
Columbus, OH 43201
127. C. R. Hann, Battelle Pacific Northwest Laboratory, P. O. Box 999,
Richland, WA 99352
128. J. T. A. Roberts, Electric Power Research Institute, 3412 Hilview
Avenue, Palo Alto, CA 94304
129. F. A. Kulacki, Ohio State University, Columbus, OH 43210
130. B. I. Spinrad, Oregon State University, Corvallis, OR 97331